

Review
Ferrocenophanes with all carbon bridges

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Abstract

The most prevalent organometallic analogs of cyclophanes are the ferrocenophanes, in which the two cyclopentadienyl (Cp) groups of ferrocene are joined by an atomic or a molecular bridge. This review describes the synthesis and study of ferrocenophanes that possess exclusively carbon-based bridges. The use of this class of ferrocenophane in the design and development of new organometallic materials is emphasized. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Ferrocene; Ferrocenophane; Organometallic; Polymers

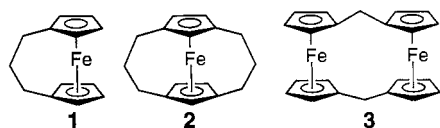
1. Introduction

Since its discovery in the early 1950s, ferrocene has attracted the attention of scientists worldwide [1]. Remarkably, this ‘new type of organo-iron compound’ was found to be aromatic, highly stable, and soluble in most common organic solvents. The X-ray crystal structure of ferrocene revealed an iron metal sandwiched by two cyclopentadienyl (Cp) ligands, which lie in parallel planes [2,3]. The Cp ligands are bonded covalently to the iron center; however, they rotate freely with respect to each other and slightly prefer the staggered conformation (ring twist angle = 36°) [4]. While ferrocene is diamagnetic, the lone pairs on the metal center permit it to act as a weak base [5–10]. In the presence of strong non-oxidizing acids, for example, the metal center undergoes protonation and subsequent rapid isotopic exchange with the ten protons of the Cp rings. Other reviews provide comprehensive descriptions of the properties and reactivities of ferrocene and its derivatives [11,12].

Soon after the discovery that ferrocene could easily be functionalized [13–15], interest in the preparation of bridged ferrocenes (ferrocenophanes) began. Ferrocenophanes are ring systems in which the two Cp groups of ferrocene are joined by an atomic or a molecular bridge. Scientists have synthesized a wide variety of ferrocenophanes with numerous modes of ring attachment [16,17]. Some bridges contain from two to more than ten contiguous carbon atoms, while others contain heteroatomic atoms, such as phosphorus, sulfur, silicon, and germanium [18–25]. In addition to mono-bridged systems, multi-bridged ferrocenophanes containing as many as five bridges on one ferrocene have been prepared [26–29]. Macromolecules containing more than one bridging ferrocene nucleus have also been synthesized [30–46]. The incorporation of various types of bridges has given rise to questions regarding the structural integrity of ferrocenophanes and the influence that the bridges can have on the chemistry of these molecules. Depending on the size and chemical makeup, for example, bridging ultimately limits the relative motion of the rings. If the bridge cannot accommodate the natural Cp–Cp’ separation of ferrocene, then the rings are forced to tilt away from planarity, influencing both the conformation as well as the chemistry of the ferrocenophanes.

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The nomenclature of ferrocenophanes is derived from the system proposed by Smith [47] and Vögtle et al. [48] for naming bridged organic aromatic cyclophanes and metallocenophanes. All bridged ferrocenes are referred to as ‘ferrocenophanes’. Ferrocenophanes can then be divided into two different classes. The first class is comprised of derivatives in which one ferrocene nucleus is connected by one or more bridges between the Cp rings. These ferrocenes are denoted as $[m][n][o][p][q]$ ferrocenophanes, where the number in the square brackets represents the length of the bridge. Using the above convention, [3]ferrocenophane **1** contains a single three-carbon bridge, and [3][3]ferrocenophane **2** contains two three-carbon bridges. Ferrocenophanes can further be described by denoting the location of these bridges on each of the Cp rings, as in [3](1,1′)[3](3,3′)ferrocenophane **2**. This nomenclature indicates that the bridges are located on C-1 and C-3 of both Cp rings.



The second class of ferrocenophanes is composed of derivatives in which two or more ferrocene nuclei are connected by one or more bridges. These structures are named $[m.n.o.p. . .]$ ferrocenophanes; the numbers in the square brackets represent the length of the bridge joining the two nuclei, and the number of ferrocene nuclei can be derived from the number of different bridges. Thus, using this convention, [1.1]ferrocenophane **3** is a binuclear structure with two bridges joining the two ferrocene moieties. These species can be further described by denoting the placement of the bridges on the ring, as in [1.1](1,1′′;1′,1′′′)ferrocenophane **3**.

Ferrocenophanes have drawn interest for a variety of reasons [49,50]. Many of the desirable characteristics of the parent ferrocene are retained in the ferrocenophanes, leading to useful applications for the bridged structures. First, ferrocene and many of its derivatives are highly thermally stable, withstanding temperatures as high as 500°C [51]. Second, unlike many organometallic compounds, ferrocene is stable in air. Consequently, ferrocene-based materials can be used in a wide variety of applications without fear of degradation. Third, ferrocene and its derivatives can reversibly undergo single electron oxidation to give stable, deep green ferrocenium radical cations. This feature makes ferrocenyl systems particularly attractive electrochemical agents for use in chemical sensing and other technologies [52]. Fourth, the π -electrons of both Cp rings of ferrocene are delocalized through the d-electrons of the transition metal, thereby providing a

conjugated organometallic system that can be used as the basis for the construction of new types of stable optoelectronic materials [53–55].

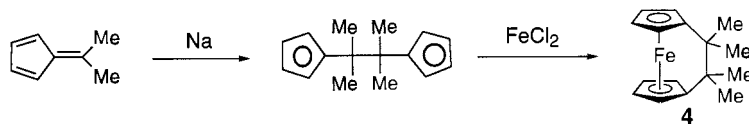
Due to these attractive features, ferrocenes and ferrocenophanes have found use as building blocks for metal-based polymers [49,56–60]. Polymers with metals incorporated in the backbone are of particular interest due to potential interactions between the metal centers. This type of ‘electronic communication’ might manifest itself either as through-bond effects, through-space effects, or perhaps a combination of both. The cooperativity can be used to influence redox processes and other reactions at the metal centers. To this end, strained [1]ferrocenophanes and [2]ferrocenophanes have been used as monomers in thermal ring opening polymerizations to give polymers with transition metals in the backbone [49,57–60]. While these polymers are stable toward oxygen and elevated temperatures [59], they appear to lack the necessary conjugation required for electron delocalization through the backbone [49].

An alternative strategy utilized by our research group involves the ring opening metathesis polymerization (ROMP) of unsaturated ferrocenophanes [60]. The driving force for this method of polymerization is the relief of ring strain in the monomer [61,62]. This approach is particularly attractive for generating conjugated polymers because the unsaturation in the monomer is retained in the resulting polymer. Consequently, the goal of achieving conjugation through the backbone of the polymer chain can be realized. Furthermore, since ROMP catalysts can tolerate a wide range of functional groups [63], it should be possible to utilize specifically designed ferrocenophanes to yield conjugated organometallic polymers with tailored electronic properties.

Indeed, there have been many different classes of ferrocenophanes reported in the past 30 years, and several reviews have documented these discoveries [16,17]. Due, however, to the recent developments outlined above, we feel that a review of carbon-rich ferrocenophanes is timely. Consequently, this review will be restricted to the synthesis and structure of ferrocenophanes having all carbon bridges.

2. [1]Ferrocenophanes

To our knowledge, no examples of [1]ferrocenophanes bridged by a single carbon atom have been reported. A single carbon bridge would substantially distort the Cp rings from planarity, forcing the ferrocenyl moiety into an unstable puckered conformation. There are, however, numerous examples of [1]ferrocenophanes bridged by single heteroatoms, such as oxygen, sulfur, silicon, and germanium [20–24]. Apparently, the relatively large atomic radii of these atoms

Scheme 1. Synthesis of 1,1,2,2-tetramethyl[2]ferrocenophane **4** from 6,6-dimethylfulvene.

affords less tilting of the Cp rings and thus greater stability than in the case of a single carbon bridge.

3. [2]Ferrocenophanes

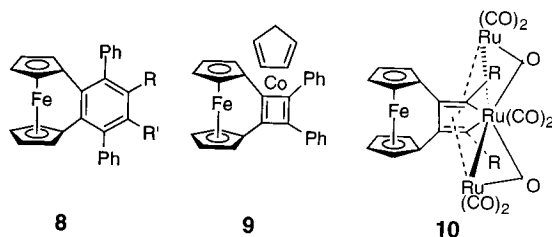
Due to the relatively short length of C–C bonds, ferrocenophanes bridged by two carbon atoms, [2]ferrocenophanes, would also be expected to experience substantial strain. Indeed, these species are strained; their synthesis is, however, well-documented [64–71]. The first example of these compounds, 1,1,2,2-tetramethyl[2]ferrocenophane, was produced in low yield from the reaction of 6,6-dimethylfulvene with sodium to give the dianion salt, which was treated with ferrous chloride to give the desired product (Scheme 1) [64]. The yield of **4** was significantly improved by McGlinchey et al. using the direct co-condensation of 6,6-dimethylfulvene and iron vapor [67].

Analysis of [2]ferrocenophanes by $^1\text{H-NMR}$ spectroscopy can be used to probe the degree of tilt of the Cp rings [66,72]. Analysis by X-ray crystallography, however, provides a more concrete description. The single crystal X-ray structure of 1,1,2,2-tetramethyl[2]ferrocenophane **4**, for example, revealed a ring twist angle of 26° and ring tilt angle of 23° [73]. The distance between carbon 1 of Cp 1 and carbon 1' of Cp 1' was found to be 2.70 Å, whereas the distance between the centers of the Cp and Cp' groups of ferrocene is approximately 3.32 Å. These data provide strong evidence that [2]ferrocenophanes bridged by two saturated carbon atoms are highly strained.

Unsaturated analogs have also been synthesized, and their structure and reactivity have been compared with the saturated versions. Tilley and co-workers, for example, synthesized *ansa*-(vinylene)[2]ferrocenophane **6** in moderate yield from the McMurry coupling of 1,1'-ferrocenedicarbaldehyde **5** [71]. The single crystal X-ray structure reveals a bent geometry with a ring tilt angle of 23° , which is comparable with that of the unsaturated analog. The CH=CH–C angle was found to be 117.8° and the CH=CH distance 1.32 Å, which are surprisingly close to the ideal values for alkenes. This highly strained molecule was targeted as a monomer for ROMP to give poly(ferrocenylenevinylene) **7** (Scheme 2). The polymerization of **6** using a molybdenum-based ROMP initiator [74] yields insoluble poly(ferrocenylenevinylene) **7**. Unfortunately, the poor solubility of **7** prevented its complete characterization [71].

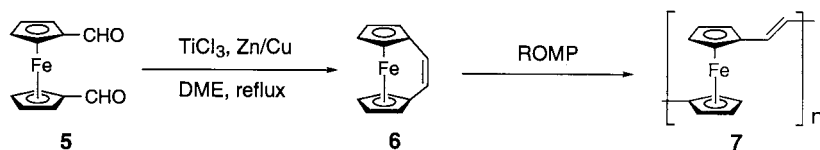
Scheme 2 illustrates the concept that the incorporation of unsaturated carbon bridges into ferrocenophanes can be used as a strategy to produce fully conjugated organometallic polymers. As with other macromolecules of this type [75,76], however, poor solubility has hindered the preparation and characterization of high molecular weight species. Consequently, the problems associated with solubility must be solved before useful, processable materials can be prepared.

Other interesting unsaturated [2]ferrocenophanes include derivatives of (tetraphenyl-phenylene)-[2]ferrocenophane **8** ($R = R' = \text{Ph}$), and π -cyclopentadienyl (ferrocenylcyclobutadiene) cobalt **9**, which were synthesized by Yasufuku et al. [68,69]. Treatment of 1,1'-bis(phenylethynyl)ferrocene with $\text{Ru}_3(\text{CO})_{12}$ under reflux in benzene afforded the ruthenium [2]ferrocenophane complex **10** [70]. This molecule was generated during efforts to explore the reaction of acetylenes with transition metal complexes.



Compound **8** ($R = R' = \text{Ph}$) exhibits a ring twist angle of 29° and a ring tilt angle of 24° [68]. The distance between carbon 1 of Cp 1 and carbon 1' of Cp 1' was found to be 2.73 Å, which is comparable with that of the saturated analog **4**. In the ruthenium [2]ferrocenophane complex **10** [70], the plane of the ruthenacyclopentadiene is nearly perpendicular to the Cp rings, and the ring tilt angle of 22° is only slightly smaller than that reported for **4** and **8**. As a whole, the single crystal X-ray data for [2]ferrocenophanes indicate that these molecules are highly strained; thus, appropriately designed derivatives represent good candidates for ROMP.

Due to their rigid conformation and substantial ring strain, [2]ferrocenophanes exhibit markedly different reactivities when compared with ferrocenophanes having longer, more flexible bridges. For example, Watts et al. demonstrated that the Lewis basicity of ferrocenyl derivatives increases with increasing distortion of the Cp rings from planarity [6]. Indeed, the [2]ferrocenophanes can be protonated more readily



Scheme 2. Synthesis of poly(ferrocenylenevinylene) **7** from 1,1'-ferrocenedicarbaldehyde **5**.

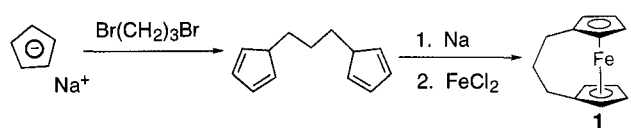
than less distorted derivatives whose Cp rings are more parallel. Other differences in reactivity include Friedel–Crafts acetylation, which is substantially more difficult with [2]ferrocenophanes than with [3]-, [4]-, and [5]ferrocenophane analogs [77]. The presence of longer flexible heteroannular bridges, which do not disturb the Cp rings from planarity, appears to have little effect on the overall reactivity of the ferrocenophanes when compared to their non-bridged analogs [66]. These studies highlight the influence of structure/composition on the chemistry and reactivity of ferrocenophanes.

4. [3]Ferrocenophanes

Due to their structural flexibility and the multitude of available synthetic pathways, [3]ferrocenophanes have been the most widely studied of the carbon-bridged ferrocenophanes. The known structures vary all the way from mono-bridged to tetra-bridged; only the per-bridged [3][3][3][3][3]ferrocenophanes have yet to be prepared. In the late 1950s, Lüttringhaus and Kullick synthesized the saturated [3]ferrocenophane **1**. The reaction of sodium cyclopentadienide with 1,3-dibromopropane gave the bis-cyclopentadienyl hydrocarbon, which was then doubly deprotonated and treated with ferrous chloride (Scheme 3) [78].

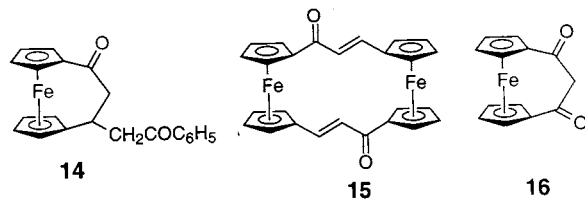
The saturated [3]ferrocenophane-1-one **12** ($n = 2$) was synthesized by Rinehart and co-workers via the heteroannular cyclization of β -ferrocenylpropionic acid **11** ($n = 2$) using polyphosphoric acid as the dehydrating agent (Scheme 4) [65,79,80]. This reaction, however, suffered from low yields and the formation of the undesired homonuclear side product **13**. While the homonuclear side products **13** exhibit an interesting geometry, their chemistry at the metal center is similar to that of unbridged analogs. The similarity likely arises from the absence of ring tilt in these derivatives.

Other internal addition reactions have been used to prepare [3]ferrocenophanes [81]. For example, the reaction of 1-acetyl-1'-(3-oxo-3-phenyl-1-propenyl)ferrocene with potassium hydroxide in boiling ethanol gives two



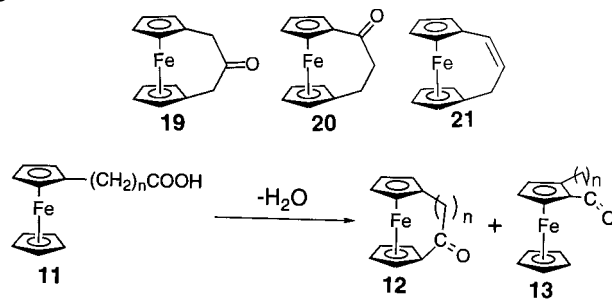
Scheme 3. Two-step synthesis of [3]ferrocenophane **1**.

products: the internal Michael addition affords 1-oxo-3-phenacyl[3](1,1')ferrocenophane **14**, and the retro-Claisen–Schmidt reaction forms the dinuclear 1,14-dioxo[3.3](1,1')ferrocenophane-2,15-diene **15** [81]. In other examples, the internal Claisen condensation of methyl-1'-acylferrocenecarboxylate gives [3]ferrocenophane-1,3-dione **16** [82]. The latter species has been used to form a variety of derivatives with substituents attached to the 1 and 3 positions of the bridge.

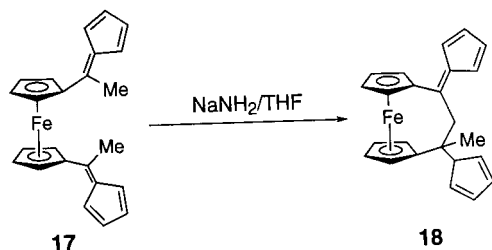


The [3]ferrocenophane **18**, which is derived from the base-catalyzed heteroannular cyclization of the bisfulvene **17** (Scheme 5) [33], provides yet another structural motif for three-carbon bridged ferrocenophanes. Stereochemical constraints imposed by the bridge substituents prevent the fulvene group from attaining coplanarity with the Cp ring. The lack of conjugation is supported by the hypsochromic shift and reduced intensity of the absorption maximum of **18** when compared with similar non-bridged ferrocenes [33].

Starting from the bridged ketones [3]ferrocenophane-1-one **20** and [3]ferrocenophane-2-one **19**, a wide variety of [3]ferrocenophanes can be produced. For example, the partially unsaturated [3]ferrocenophan-1-ene **21** can be readily obtained from both **19** and **20**. It seems tenable that compound **21** possesses sufficient strain to undergo ROMP (vide infra). The resultant homoconjugated polymers would thus provide an important basis of comparison for studies of fully conjugated versions such as **7**.



Scheme 4. Synthesis of [3]ferrocenophan-1-one **12** by dehydrative coupling.

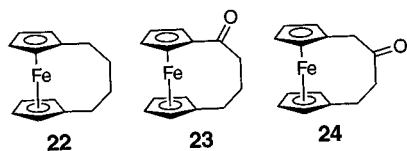


Scheme 5. Synthesis of **18** via the base-catalyzed heteroannular cyclization of **17**.

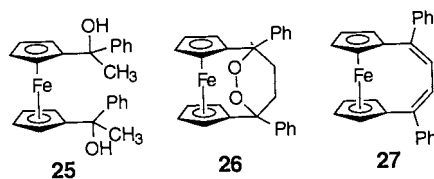
In the single crystal X-ray structure of **20**, the Cp rings are slightly staggered with a ring twist angle of 11.8° and a ring tilt angle of 8.8° [83]. The distance between carbon 1 of Cp 1 and carbon 1' of Cp 1' was found to be 3.10 Å. This distance is larger than that observed for the two carbon-bridged ferrocenophanes **4** and **8**, but remarkably similar to the distance between the Cp and Cp' carbons of ferrocene itself (3.32 Å) [2,4]. These observations indicate that the [3]ferrocenophanes possess less ring tilt strain than the [2]ferrocenophanes. For compound **21**, however, there is probably sufficient bond angle strain about the olefin moiety to promote the ring opening metathesis polymerization.

5. [4]Ferrocenophanes

As with the three-carbon bridged ferrocenophanes, there are abundant synthetic routes for the preparation of four-carbon bridged analogs. Synthesis of the saturated [4]ferrocenophane **22** provides an illustrative example. The most direct path involves treatment of 1,4-dibromobutane with sodium cyclopentadienide; the product is then doubly deprotonated and treated with iron dichloride as in Scheme 3 [78]. An alternative route involves the co-condensation of [2.4]hepta-4,6-diene with iron to give **22** as one of four different isomers [84]. Yet another pathway involves the diazomethane-promoted ring expansion of **20** to give two isomers, [4]ferrocenophane-1-one **23** and [4]ferrocenophane-2-one **24** [85]. Reduction of either **23** or **24** should readily yield **22**.



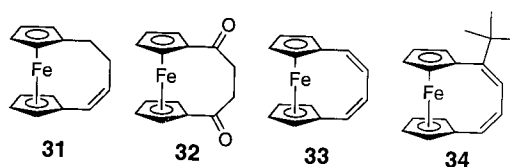
Exposure of 1,1'-bis(α -hydroxy- α -phenylethyl)ferrocene **25** to acidic media affords a mixture of insoluble crystalline **26** and soluble **27** [86]. Compound **26** can also be generated by the oxidative cyclization of 1,1'-bis(1-phenylvinyl)ferrocene with molecular oxygen in the presence of Lewis acids [87].

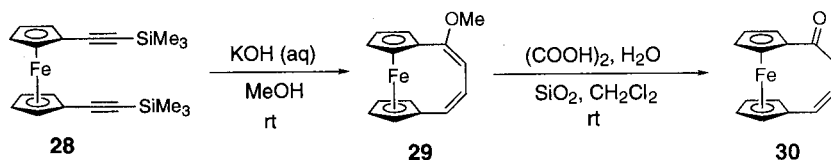


Callstrom et al. have synthesized [4]ferrocenophanes having mono-olefinic and di-olefinic bridges using a cyclization reaction [88,89]. The base-catalyzed heteroannular cyclization of 1,1'-bis((trimethylsilyl)ethynyl)ferrocene **28** affords the fully conjugated 1,1'-(1-methoxy-1,3-butadienylene)ferrocene **29** (Scheme 6). Subsequent hydrolysis gives the 1,1'-(4-oxo-1-butenylene)ferrocene **30** in good yield (e.g. 76%).

Studies of **29** by X-ray crystallography reveal that considerable strain is afforded by the presence of the unsaturated bridge. Ring twist angles of 36 and 43° as well as ring tilt angles of 7 and 11° were measured for the two independent molecules found in the unit cell for **29**. The ring tilt angles are comparable to those of **20**; however, the additional length afforded by the four-carbon bridge permits the molecule to adopt a staggered conformation similar to that of ferrocene (36°) [4].

Reduction of **30** using $\text{LiAlH}_4/\text{AlCl}_3$ in refluxing diethyl ether can be used to deoxygenate the ring to give the mono-unsaturated 1,1'-(1-butenylene)ferrocene **31** in high yield (e.g. 83%). In addition to **27** and **29**, other highly unsaturated butadiene-bridged ferrocenophanes are also available. One synthesis starts with [4]ferrocenophane-1,4-dione **32**, which can be prepared in relatively good yield (e.g. 55%) by intramolecular coupling of commercially available 1,1'-diacetylferrocene [90]. The diketone **32** serves as a useful synthetic intermediate due to facile derivation of the 1 and 4 positions of the bridge. For example, reduction to the diol and subsequent dehydration gives the fully unsaturated [4]ferrocenophane-1,3-butadiene **33** [91]. Compound **33** can also be prepared by other methods [88,89]. A comparison of the single crystal X-ray structures of **32** and **33** reveals the influence of incorporating exocyclic versus endocyclic double bonds onto the bridge [91]. The bridges for both molecules impose similar twist angles of 43.6° (for **32**) and 44.0° (for **33**), and similar ring tilt angles of 10.2° (for **32**) and 6.7° (for **33**). However, the angles of the bridge sp^2 centers of **33** are distorted ca. 10° from ideal, whereas the bridge angles of **32** more closely resemble 120° of sp^2 centers. This comparison suggests additional strain in **33**, which would make this molecule a good candidate for ROMP.



Scheme 6. Synthesis of **30** via the acid-catalyzed hydrolysis of **29**.

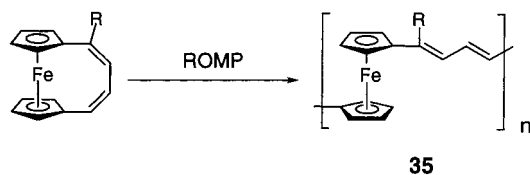
As with unsaturated **6**, [4]ferrocenophanes **29** and **33** represent attractive candidates for the generation of conjugated organometallic polymers via ROMP (Scheme 7). Although [4]ferrocenophane-1,3-butadiene **33** is less strained than **6**, the ring tilt strain along with the bond angle strain described above was believed to be sufficient to drive the polymerization [76]. Indeed, the ROMP of **29** and **33** proved to be facile [76]; however, the resultant oligomers/polymers produced from **29** were likely hydrolytically unstable [88,89], and those produced from **33** were poorly soluble [76].

Subsequently, [4]ferrocenophane-1-*tert*-butyl-1,3-butadiene **34** was targeted in an effort to overcome the limitations arising from the poor solubilities [60]. The molecule was prepared in two steps from **30**. The single crystal X-ray structure of **34** revealed unusually small ring twist and ring tilt angles (2° and ca. 0° , respectively). Substantial bond angle strain in the bridge, however, appeared to be manifested in the olefinic moieties as a deviation from 120° for the sp^2 centers (i.e. the bond angles in the bridge ranged from 126° to 137°).

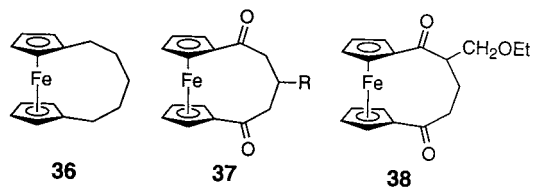
As illustrated in Scheme 7, compound **34** was polymerized using a tungsten-based ROMP initiator [92] to give high molecular weight polymers ($M_w > 300\,000$) that were soluble in common organic solvents. The polymers were also observed to be air stable and thermally stable. Analysis of the polymers by UV–vis spectroscopy revealed a bathochromic shift of the absorption maxima, indicating a moderate degree of conjugation along the backbone. These results warrant further study of these new soluble conjugated organometallic polymers.

6. [5]Ferrocenophanes

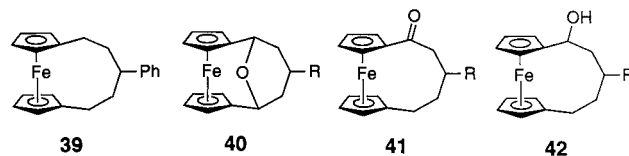
While the readily accessible [3]ferrocenophanes and [4]ferrocenophanes have been studied exhaustively, a

Scheme 7. Polymerization of [4]ferrocenophane-1,3-butadiene derivative to afford polymer **35**.

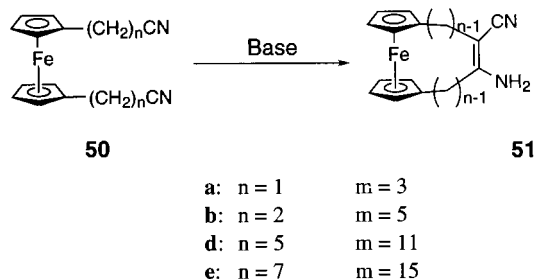
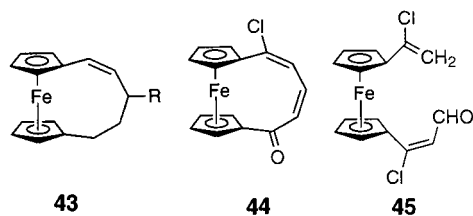
number of interesting [5]ferrocenophanes based on the parent **36** have also been prepared [16,93]. Many [5]ferrocenophanes can be derived from 3-phenyl[5]ferrocenophane-1,5-dione (**37**; R = Ph) and 2-ethoxymethyl-[5]ferrocenophane-1,5-dione **38** [93].



Complete reduction, for example, of **37** (R = Ph) using lithium aluminum hydride (LAH) with $AlCl_3$ gives the 3-phenyl[5]ferrocenophane **39**. Partial reduction of **37** affords the diol derivative, and acidic alumina-catalyzed dehydration of this intermediate gives the ether analog **40**. Oxidation of **40** with manganese dioxide yields the monoketone **41**, which can then be reduced by LAH to produce the alcohol derivative **42**. An alternative route to the [5]ferrocenophanes involves the diazomethane-promoted ring enlargement of α -oxo-[4]ferrocenophanes **23** to give α -oxo-[5]ferrocenophanes **41** (R = H) [85].



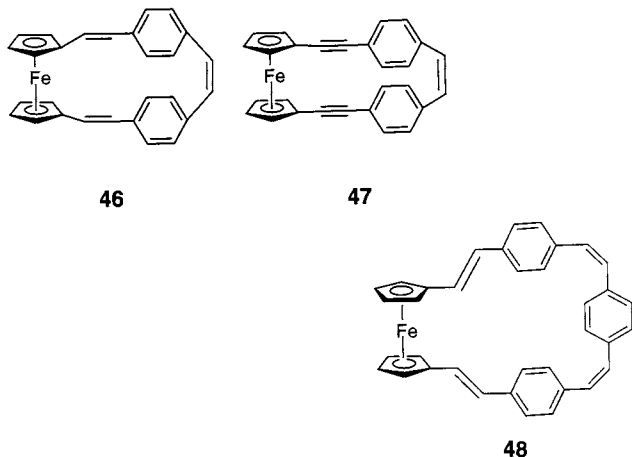
Partially unsaturated [5]ferrocenophanes are also available. Dehydration, for example, of **42** under acidic conditions yields the unsaturated [5]ferrocenophane-1-ene **43** (R = H). Furthermore, the [5]ferrocenophane-1-chloro-2,4-diene-1-one **44** can be generated from the α,β -unsaturated aldehyde **45** [94]. The UV–vis spectrum of **45** and other [5]ferrocenophanes having the potential for extended conjugation exhibit bathochromic shifts in their absorption maxima when compared with those of fully saturated analogs. These studies might be interpreted to indicate that a lengthening of the bridges of ferrocenophanes to five or more carbon atoms introduces sufficient flexibility to permit overlap between the Cp π electrons and the π clouds of adjacent exocyclic and endocyclic double bonds [72].



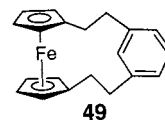
Scheme 8. Synthesis of $[m]$ ferrocenophanes **51** ($m = 3, 5, 11, 15$) by cyclization of dinitriles.

7. $[m]$ Ferrocenophanes ($m > 5$)

Ferrocenophanes with bridges containing more than five carbon atoms can also be prepared. One interesting class of these molecules contains a series of organic cyclophanes that bridge the Cp rings of ferrocene. Kasahara and co-workers synthesized a number of examples that possess transannular π -electron interactions across the bridge [95–99]. The compounds [2]paracyclo[2]paracyclo[2]ferrocenophane-1,9,17-triene **46** and [2]paracyclo[2]paracyclo[2]-ferrocenophane-9-en-1,17-diyne **47**, for example, were derived from the intramolecular titanium-induced reductive coupling of dialdehydes [95]. As with the conjugated systems described above, these molecules exhibit a bathochromic shift in their absorption maxima compared with their less conjugated starting materials. Tanner and Wennerström prepared various isomers of [2]paracyclo[2]paracyclo[2]paracyclo[2]ferrocenophane-1,9,17,25-tetraene **48** using one-pot multiple Wittig reactions [99].



Another interesting class of $[m]$ ferrocenophanes that also contain an aromatic ring in the bridge is illustrated by the unconjugated [2]metacyclo[2]ferrocenophane **49** [100]. The single crystal X-ray structure of this molecule reveals substantial strain as indicated by a ring twist angle of approximately 0° and a ring tilt angle of 9° . The UV–vis spectra show that these molecules lack the extended conjugation found in **46–48**.



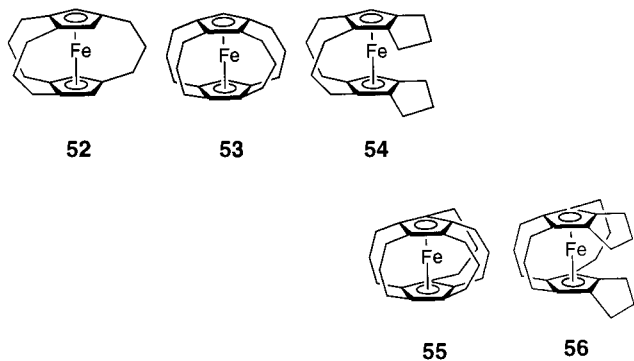
Nesmeyanov developed a general route to macrocyclic bridged $[m]$ ferrocenophanes of type **51** [101]. Base-catalyzed cyclization of 1,1'-bis(ω -cyanoalkyl)-ferrocenes ($\text{Fc}[(\text{CH}_2)_n\text{CN}]_2$, $n = 1, 2, 5$ or 7 ; Fc = ferrocene) **50** gave low yields of the alicyclic compounds (Scheme 8) [101]. The larger $[m]$ ferrocenophanes ($m \geq 5$) were targeted in an effort to examine the influence of long bridges upon the conformation of ferrocenophanes. As expected, the ferrocenophanes having bridges composed of five or more carbon atoms exhibited substantially less strain than those having shorter bridges. In fact, comparison with unbridged ferrocenes revealed no detectable strain in the larger molecules.

8. $[m]''$ Ferrocenophanes

Multiply-bridged monoferrocenes are yet another class of ferrocenophane. Due to the fact that the metal centers are more or less encapsulated in a carbon cage, studies of the chemical and structural properties of these molecules have drawn widespread interest [26–29]. The added bridges tend to shorten the Cp–Cp' distances and increase the electron density of the metal center [102]. In early studies of the mono-bridged **20** [83], the single crystal X-ray structure indicated the presence of strain in the molecule. Consequently, the potential for introducing additional bridges into the ferrocenophanes were less than encouraging. The report, however, of the synthesis of [3][3](1,1';3,3')ferrocenophane **2** [103] brought about renewed enthusiasm. The single crystal X-ray structure of **2** revealed a distortion in the distances between the Cp rings: the average C-2–C-2' distance is 3.01 Å, the C-1–C-1' and C-3–C-3' distances are 3.09 Å, and the C-4–C-4' and C-5–C-5' distances are 3.36 Å [103]. The average of these values (3.18 Å) is smaller than that of ferrocene itself (3.32 Å). This observation suggests that the second trimethylene

bridge shortens the Fe–Cp distance, thereby adding strain to the molecule.

Despite the strain associated with the incorporation of trimethylene bridges, various [3]ferrocenophanes having two, three and four bridges have been reported [104–108]. The single crystal X-ray structure of [3][3][3]ferrocenophane **52**, for example, showed the Cp rings to be eclipsed and the average distance between them to be 3.15 Å, which is shorter than that for ferrocene [109]. The observed ring tilt angle of 2.4° is smaller than that observed for the two-bridge analog **2** (9°) [103]. This comparison shows that the even placement of multiple bridges about the molecule decreases the ring tilt angle.

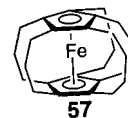


The incorporation of more than three trimethylene bridges has proven to be a formidable task. For example, the attempted synthesis of [3][3][3][3]ferrocenophane **53** by acetylation yielded instead the di-bridged ferrocenophane **54** [110]. Similarly, the attempted synthesis of [3][3][3][3][3]ferrocenophane **55** yielded instead the tri-bridged ferrocenophane **56** [111]. The structure of **54** was confirmed by single crystal X-ray crystallography [110]. In this structure, the Cp rings are nearly eclipsed and the ring tilt angle is 11.1°; the planar distances between the carbon atoms of the two Cp rings ranged from a maximum of 3.46 Å to a minimum of 3.03 Å. Similarly, the single crystal X-ray structure of **56** shows the two Cp rings in an eclipsed conformation with a ring tilt angle of 12.5° [111].

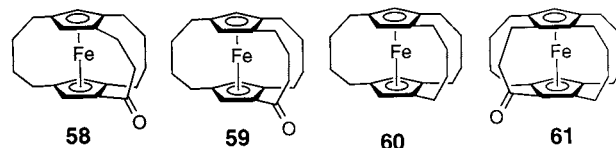
Given that [3]ferrocenophane **1** appears to exhibit more strain than [4]ferrocenophanes **22**, Hisatome et al. proposed that the use of four-carbon rather than three-carbon bridges might afford some relief of strain, and thus facilitate the syntheses of more highly bridged derivatives [108]. Indeed, soon after the synthesis of the di- and tri-bridged ferrocenophanes, the synthesis of more highly bridged species was demonstrated using this strategy [26,27,29].

Compound **57** represents, to our knowledge, the only example of a ferrocenophane having four trimethylene bridges (note that the fifth bridge consists of a tetramethylene unit) [28]. This molecule was targeted as a precursor to the pertrimethylene-bridged ferroceno-

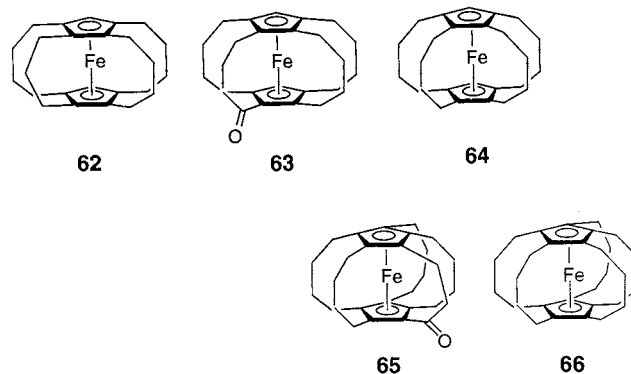
phane **55**. Attempts to effect the ring contraction, however, appear to have been futile. Despite these efforts and others [85,111], the synthesis of the penta-bridged [3]ferrocenophane **55** has thus far eluded chemists. The strain associated with the incorporation of multiple three-carbon bridges is likely responsible for the lack of success.



Another strategy targeting the synthesis of highly bridged ferrocenophanes involved the following set of reactions [26,27,29,112,113]. Treatment of [4][4]- α -oxo[3]ferrocenophane **58** with diazomethane in the presence of $\text{BF}_3 \cdot \text{OEt}_2$ afforded the bridged [4][4]- α -oxo[4]ferrocenophane **59**. Compound **59** was then reduced with LAH to give [4][4][4]ferrocenophane **60**. Formylation followed by a series of reactions afforded [4][4][4]- α -oxo[3]ferrocenophane **61** in relatively good yield.



Reduction of **61** with LAH generated the completely saturated [4][4][4][3]ferrocenophane **62**. A second bridge-enlargement involving **63** afforded [4][4][4]- α -oxo[4]ferrocenophane **63** [26]. The ketone **63** was then reduced with LAH to give [4][4][4][4]ferrocenophane **64**. Cyclization of the propionic acid derivatives of [4][4][4][4]ferrocenophanes affords the per-bridged [4][4][4][4]- α -oxo[3]ferrocenophane **65** [26,29]. The per-bridged ferrocenophane **66** was finally realized by Hisatome and co-workers in the mid-1980s [27,29].



As expected, the single crystal X-ray structure of [4][4][4][3]ferrocenophane **62** showed the Cp rings to be eclipsed [112]. The distance between the centers of the Cp and Cp' groups (3.235 Å), however, was surprisingly

similar to that found in ferrocene itself (3.32 Å). This comparison suggests only moderate ring tilt strain in **62**. The single crystal X-ray structure of the symmetrically bridged [4][4][4][4]ferrocenophane **66** provided similar results: the Cp rings are eclipsed and the ring tilt angle is approximately 0°. The distance between the centers of the Cp and Cp' groups was measured to be 3.244 Å, which is essentially indistinguishable from that found for **62** [29].

These studies summarize the effects of incorporating multiple bridges into the ferrocenophane network. While the incorporation of bridges consisting of three carbons or less substantially influences the structure and reactivity of ferrocenophanes, the incorporation of longer, more flexible bridges leads to behavior more characteristic of unbridged ferrocenyl species.

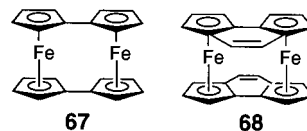
9. Multinuclear ferrocenophanes

Multinuclear ferrocenophanes exhibit a variety of interesting characteristics, such as metal basicity [5–10], intramolecular C–H···C hydrogen bonds [114], and electrical conductivity [49]. Much of the interest in these systems stems from the potential interactions between the metal centers, which might give rise to unique physical and chemical phenomena. Even though the metal atoms in these systems do not lie in intimate contact, electronic communication between the metals is possible via through-bond and/or through-space processes. The nature of the connecting bridges will undoubtedly affect the properties of the molecular or polymeric species.

10. [0.0]Ferrocenophanes

The most simple multinuclear ferrocenophane, [0.0]ferrocenophane **67**, has been prepared using a variety of strategies [30,34,41,115]. Hedberg and Rosenberg, for example, employed a modified Ullman coupling reaction by mixing 1,1'-diiodoferrocene with a large excess of copper bronze at elevated temperatures [41]. The product **67** was precipitated into hexanes and recrystallized from benzene. The resultant orange crystals possessed limited solubility in common organic solvents, and was stable to 300°C. Rausch and co-workers synthesized **67** via the pyrolysis of polymercury ferrocenes [42]. Both strategies produced the dinuclear ferrocenophane in low yields (< 20%). Mueller-Westerhoff et al. provided an improved method by directly reacting dihydrofulvalene and fulvalene dianion with ferrous chloride in THF; the yields of **67** ranged from 18 to 22% [34]. The single crystal X-ray structure of **67** revealed two undistorted ferrocenes with coplanar Cp groups [115]. A related ferrocenophane is the phenyl-

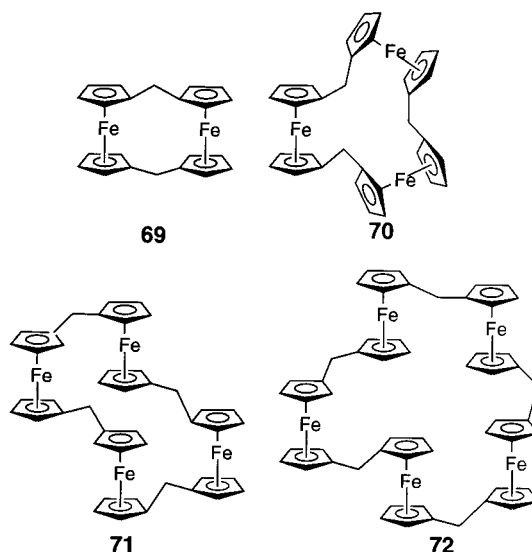
bridged bis(indacenyliron) **68**. This bimetallic species was synthesized in 10% yield by the reaction of dilithium indacene with ferrous chloride [30]. Molecule **68** exists as a mixture of *syn* and *anti* isomers, where the bridging ethylene moieties lie on the same or opposite faces of ferrocenophane, respectively.



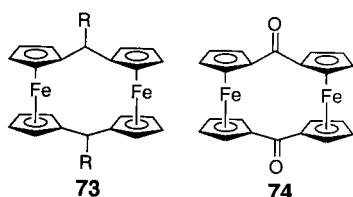
Compound **67** undergoes facile oxidation of a single ferrocenyl moiety to yield a stable radical cation as part of a mixed valent molecule [116]. Furthermore, oxidation of **67** with tetracyanobenzoquinodimethane (TCNQ) forms ionic charge transfer complexes that exhibit anisotropic electrical conductivities (e.g. 10 Ω⁻¹ cm⁻¹) [34]. The bulk conductivities were measured at room temperature on compressed disks of **67**. These data provide further support for the promising use of ferrocenyl species in the construction of optoelectronic materials.

11. [1ⁿ]Ferrocenophanes

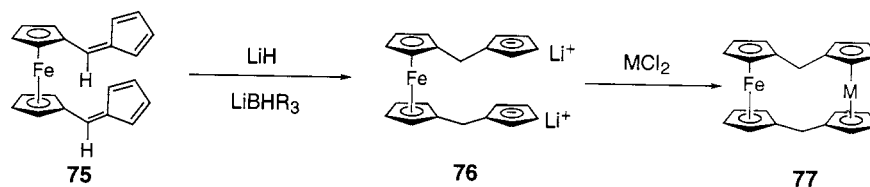
Macromolecular ferrocenophanes can be prepared by connecting the ferrocenyl moieties with carbon bridges of varying lengths. Katz and co-workers, for example, prepared the [1ⁿ]ferrocenophanes (*n* = 2–5; **69**–**72**) via the reaction of bis(cyclopentadienyl)methane dianion with ferrous chloride [30,31]. While all four species are produced simultaneously and in significant amounts (e.g. 10–40%), their separation is extremely difficult. The nomenclature here can be illustrated using **69** and **72** as examples: [1.1]ferrocenophane and [1.1.1.1]ferrocenophane, respectively.



Substituted [1.1]ferrocenophanes such as **73** are also available [32,33]. These molecules are structurally interesting because the two bridges can either adopt the *cis* or *trans* conformation. The single X-ray crystal structure of [1.1]ferrocenophane **73** ($R = \text{CH}_3$) shows the compound in the *cis* conformation with the methyl groups in the *exo* position. The ring twist angle is 22.4° and the ring tilt angle is 2.7° [117]. These values suggest that the single carbon bridge affords sufficient flexibility for the Cp rings to rotate to their energetically favored staggered conformation. Initially, it was believed that the *trans* conformer would be rigid and sterically disfavored by the repulsive forces of the inner α -protons [114]. Successful synthesis of the *anti* conformer was, however, confirmed by single X-ray crystal diffraction of *exo,exo,anti*-1,12-dimethyl[1.1]ferrocenophane [118]. The ring twist angle of 18° is similar to that for the *cis* conformer. One of the ferrocenes in the *trans* conformer is, however, severely ring tilted by 23° . Similarly, the diketone **74** can be prepared by an intramolecular Friedel–Crafts cyclization of 1,1'-bis-(chlorocarbonyl)ferrocene [32,33]. This reaction is, however, poorly reproducible and low-yielding.



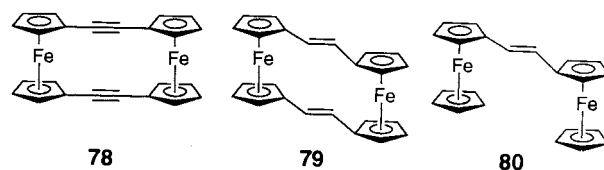
Other routes to [1.1]ferrocenophanes involve the reduction of 1,1'-bis(6-fulvenyl)ferrocene [33,119] **75** to give the dianion **76** (Scheme 9) [35]. Subsequent addition of ferrous chloride gives **77** ($M = \text{Fe}$) in relatively good yield (30–46%). Mixed [1.1]metallofenophanes **77** ($M = \text{Ru}$) can also be synthesized by this pathway [36]. These molecules are of particular interest due to the different redox properties of the two metals. For example, [1.1]ferrocenophane **69** possesses two quasi-reversible one-electron oxidations [120]. However, electrochemical investigations of the [1.1]metallofenophane of iron and ruthenium **77** ($M = \text{Ru}$) show a one-electron quasi-reversible oxidation associated with ferrocene and a two-electron irreversible oxidation associated with ruthenocene.



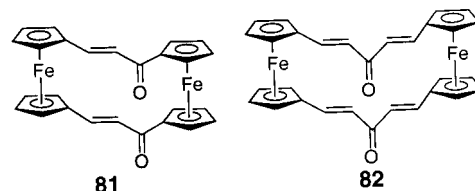
Scheme 9. Syntheses of [1.1]metallofenophanes **77** ($M = \text{Fe}$ or Ru).

12. [m^n]Ferrocenophane

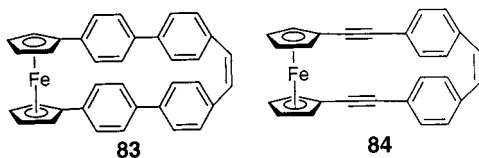
Multinuclear ferrocenophanes bridged by longer than a single carbon atom are known [38,39,43]. These species are referred to as [m^n]ferrocenophanes, where m represents the length of the bridge and n is the number of ferrocene nuclei. Unsaturated bridges between two ferrocene nuclei are particularly interesting due to the potential for facile electronic communication. Many species of this type have been prepared. For example, [2.2]ferrocenophane-1,13-diyne **78** was synthesized in one step via the copper-catalyzed coupling of 1-ethynyl-1'-iodoferrocene [43]. This compound has limited solubility and a high melting point, which are characteristic of compounds with high symmetry and rigidity. The rigid [2.2]ferrocenophane-1,13-diene **79** was prepared by the reductive coupling of 1,1'-dicarbonyl ferrocene using low valent titanium reagents [38]. The insolubility of both of these compounds hindered their analysis. The UV–vis spectrum of **79** showed a bathochromic shift and an increase in the intensity of the absorption maxima when compared with that of the singly-connected derivative **80**, which suggests extended conjugation in the former [38].



Base-catalyzed condensation reactions yielded [3.3]ferrocenophane-1,15-diene-3,14-dione **81** and [5.5]ferrocenophane-1,4,16,19-tetraene-3,18-dione **82** [39,40]. The IR and NMR spectra of **81** indicate that the olefinic bonds are *trans*. Furthermore, the UV–vis spectra of **81** and **82** reveal bathochromic shifts and increased absorption intensities associated with extended π -conjugation.



Ferrocenophanes with extended transannular π -electronic interactions through cyclophane bridges have also been prepared and analyzed. The syntheses of [0]biphenyl[2]bi-phenyl[0]ferrocenophan-13-ene [97] **83** and [2]paracyclo [2]paracyclo[2]ferrocenophan-9-ene-1,17-diyne [98] **84**, for example, were carried out via reductive coupling of carbonyl groups using low valent titanium reagents. These rigid molecules were targeted for use as π -stacked electronic materials. If the poor solubilities can be remedied, this species should make excellent candidates for ROMP-derived conjugated organometallic polymers.



13. Summary

As this review illustrates, advances in the chemistry of carbon-bridged ferrocenophanes have been many despite their relatively brief history. The fundamental properties of these species, when coupled with the synthetic tools currently available, provide a promising outlook for the use of carbon-bridged ferrocenophanes as building blocks for new materials.

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