J. Am. Chem. Soc. 1981, 103, 6367–6372

spread. Some ^{1}H spectra were recorded with a JEOL C 60 HL spectrometer with JNM-VT temperature unit; the technique has been described earlier.[34] Temperatures at thermal equilibrium were measured before and after an experiment with a Lauda R 42 resistance thermometer, the sensor being positioned in an NMR tube filled with solvent only.

Experimental signal shifts, δ^{exptl}, were determined relative to solvent signals; for $\delta(^{13}\mathrm{C})$ we took the data of ref 35, for protons: benzene δ 7.3, toluene $\delta(\mathrm{CH_3})$ 2.3, THF $\delta(\mathrm{CH_2}\text{-}\beta)$ 1.9. Calculation of δ^{exptl} relative to isostructural diamagnetic molecules gave the isotropic shifts of Table II with negative shifts to low field. All isotropic shifts were referenced to 298 K either by temperature-dependent measurements (^{1}H for **5** and **10**) or on the basis of the Curie law. Errors due to deviations from Curie behavior are believed to be small. An approximation was necessary for diamagnetic reference signals. Appropriate molecules would be $(\mathrm{C_5H_5})_2\mathrm{Re{-}R}$.[36] However, their NMR data are not complete. On the other hand, $\delta(^1\mathrm{H})$ for $(\mathrm{C_5H_5})_2\mathrm{Re{-}R}$ are similar to those of $(\mathrm{C_5H_5})_2\mathrm{Fe}$. We therefore used $\delta(\mathrm{C_5H_5})$ 4.1 and for protons of the peralkylated cyclopentadienyls $\delta(\alpha\text{-}1)$ 2.1, $\delta(\alpha\text{-}2{-}5)$ 1.6, and $\delta(\beta)$ 0.9.[37] Mean values of δ 1.0 were taken for aliphatic protons in positions 1′ to 4′, δ 7.3 for phenylprotons, and δ 2.3 for $\mathrm{CH_3}$ in mesitylene. Since ^{13}C data for diamagnetic molecules of the type $(\mathrm{C_5H_5})_2\mathrm{M{-}R}$ do not appear to exist, we tentatively used ferrocene (δ 67.8) and benzene (δ 128.0) as mean values for all phenyl carbons and TMS for the $\mathrm{Si(CH_3)_3}$ group; for introduced errors cf. ref 7. The accuracy of δ^{exptl} (^{1}H) depended on the shift range: $\delta < 50$, ± 0.1; $\delta < 300$, ±1; $\delta > 300$, ±5; all δ^{exptl} (^{13}C), ±1.

MO Calculations. Extended Hückel type calculations were carried out according to ref [40]. The following parameters, adapted from the X-ray results on **11**,[9,15] were used for the model calculations on **1**, **5**, and **6**: $\mathrm{Cp_2V}$ fragment (C_s symmetry), C–C in Cp = 1.42 Å, C–H = 1.08 Å, V–Cp(center) = 1.975 Å, ∠Cp(center)–V–Cp(center) = 150°; phenyl, C–C = 1.40 Å, C–H = 1.08 Å. Compound **5**: V–C1′ = 2.03 Å. Compound **6**: V–C1′ = 2.03 Å, C1′–C2′ = 1.234 Å, C2′–ipso–C = 1.447 Å. Compound **1**: V–C1′ = 2.0 Å, C1′–H1′ = 1.09 Å, tetrahedral symmetry at C1′.

The atomic parameters for vanadium are[41]

orbital	H_{ii}, eV	ζ_1[a]	ζ_2[a]
4s	−9.17	1.60	
4p	−5.46	1.60	
3d	−10.48	4.75 (0.4558)	1.50 (0.7516)

[a] Slater exponents; the coefficients of the double-ξ-3d functions are given in parentheses.

The parameters for C and H are standard values,[40] and a modified Wolfsberg–Helmholz formula[42] was used.

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Supplementary Material Available: Listing of experimental ^{13}C and ^{1}H NMR shifts (1 page). Ordering information is given on any current masthead page.

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Synthesis of [1.1]Ferrocenophanes via 1,1′-Bis(6-fulvenyl)ferrocene

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Abstract: An efficient and practical synthesis of [1.1]ferrocenophane is described. The sequence of reactions starts with 1,1′-dilithioferrocene, which is added to 6-dimethylaminofulvene, producing, after hydrolysis, the previously unknown 1,1′-bis(6-fulvenyl)ferrocene in better than 80% yield. Other procedures for the preparation of the compound are also given. The fulvene is reduced with lithium tri(*sec*-butyl)borohydride in THF to the 1,1′-bis(cyclopentadienylmethyl)ferrocene dianion, from which the [1.1]ferrocenophane is obtained by reaction with ferrous chloride in THF in average yield of 35 to 45% after purification. Thus, the ferrocenophane is available for the first time through a satisfactory preparative method in large enough quantities to investigate its chemistry. From the intermediates used in this synthesis, substituted ferrocenophanes can also be obtained.

The compound [1.1]ferrocenophane (**1**), in which two ferrocenes are linked together by two bridging methylene groups, shows several very unusual properties, which are based on the relative proximity of the two metallocenes and a high degree of rotational flexibility around the bridging methylene groups. Dissolution of **1** in aqueous acidic media appears to produce hydrogen[4] and the dication of **1**. It is believed that initial protonation at the iron atoms is followed by rapid elimination of hydrogen, a process which is facilitated by the proximity of the hydrogens in an appropriate conformation as well as the possibility of **1** forming a stable dication. Nothing is known about this dication of **1**, except that it can be reduced quantitatively to the neutral species. This reversibility, however, makes **1** an interesting candidate for the modification of semiconductor surfaces in solar energy systems for the production of hydrogen from water.[5] Oxidation of **1** leads to a monocation[6,7] of the mixed-valence type, which was claimed[6] to be in equilibrium with an average valence species. The dimethyl derivative **2** of [1.1]ferrocenophane has been oxidized to a mono- and a dication.[6] The diamagnetism of the dication was taken as evidence for a strong intramolecular interaction, supposedly due to the proximity of the ferrocenes rather than a coupling through the saturated bridges. However, there also exists a possibility that

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(1) IBM Postdoctoral Fellow, 1979–1980.

(2) IBM Postdoctoral Fellow, 1972–1973.

(3) NATO Postdoctoral Fellow, 1979–1980.

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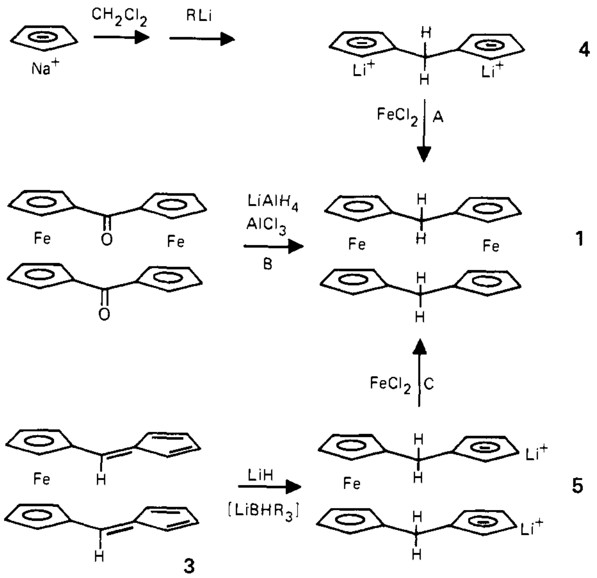
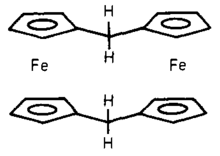
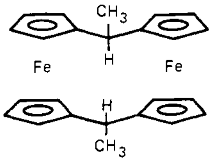
Scheme I. Preparative Methods for [1,1]Ferrocenophane



the material obtained by the two-electron oxidization is not the dication at all.[8] [1.1]Ferrocenophane (**1**) is a very useful starting material for the synthesis of more complex metallocenophanes,[9] for the preparation of the corresponding cis-fixed ferrocenyl methyl carbonium ion,[10] and, as very recent observations in this laboratory have shown, of the bridge carbanion, which is stabilized by an intramolecular C–H–C hydrogen bond.[11]

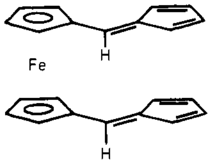


1



2

Up to this time, it has been impossible to investigate any of these phenomena and reactions in detail, because there existed only two very unsatisfactory preparative methods for **1**. In this paper, we now report a quite satisfactory synthesis of **1**, which allows us to prepare this compound on a larger scale and with relative ease. The synthesis makes use of the previously unknown 1,1′-bis(6-fulvenyl)ferrocene (**3**) as the key intermediate, which itself can be obtained by either one of two very simple procedures in high yield. The bisfulvene **3** not only is a precursor for **1**, but also serves as a convenient intermediate in the synthesis of the substituted ferrocenophane **2** and analogous species. It also has made it possible for us to prepare mixed metal metallocenophanes.[12] Some aspects of this work have been published in preliminary communications.[13,14]



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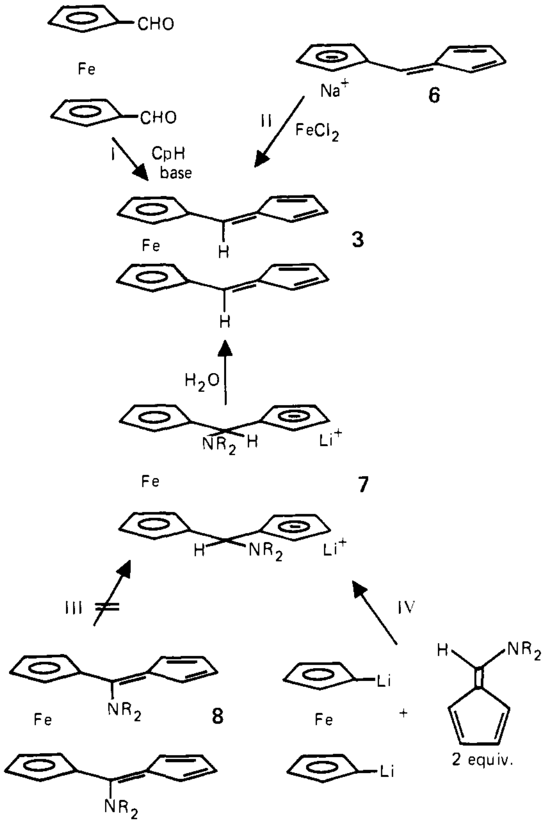
Scheme II. Synthesis of 1,1′-Bis(6-fulvenyl)ferrocene



Synthetic Routes to [1.1]Ferrocenophane

There exist three different synthetic approaches to [1.1]-ferrocenophane, which are outlined in Scheme I. The first one (route A), using the bis(cyclopentadienyl)methane dianion **4** and ferrous chloride was described[15] already in 1969. This reaction produces mainly oligomeric materials, the yield of **1** being only 1.8%. The second method of preparation (route B) is the reduction[16,17] of the corresponding diketone, which itself is available only by a poorly reproducible and low-yield double Friedel–Crafts reaction of chlorocarbonylferrocene with itself[18] or of a mixture of ferrocene and 1,1′-bis(chlorocarbonyl)ferrocene.[19] The third alternative (route C), using the bisfulvene **3** as an intermediate, promises to be much more reasonable, since one of the two ferrocenes of **1** already exists and only the cyclization through the formation of the second ferrocene is required. Unfortunately, the only published attempt[17] to prepare 1,1′-bis(6-fulvenyl)ferrocene (**3**) was inadequate, leading to an impure red oil, which polymerized during purification attempts. Substituted derivatives of **3** are known and have been used in the synthesis of substituted ferrocenophanes as, for example, **2**, but the reduction of the analogues of **3** by $LiAlH_4$ to the dianion corresponding to **5**, followed by the reaction with ferrous chloride, only produce the substituted ferrocenophanes in "modest" yield.[20]

We considered it to be a hopeless and uninteresting task to attempt an improvement of route A, since even a doubling or tripling of the yield would only give us a few percent of **1**. Likewise, route B has very little appeal, so that, in a relative sense,

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(8) Loss of a proton from the dication of [1.1]ferrocenophane to produce the diamagnetic α-ferrocenyl carbonium is a distinct possibility. This and related reactions are currently under investigation in this laboratory.

(9) The synthesis of multinuclear metallocenes derived from **1** will be described in a separate publication.

(10) Mueller-Westerhoff, U. T.; Nazzal, A.; Prössdorf, W.; Mayerle, J. J.; Collins, R. L., submitted for publication.

(11) Mueller-Westerhoff, U. T.; Nazzal, A.; Prössdorf, W., submitted for publication.

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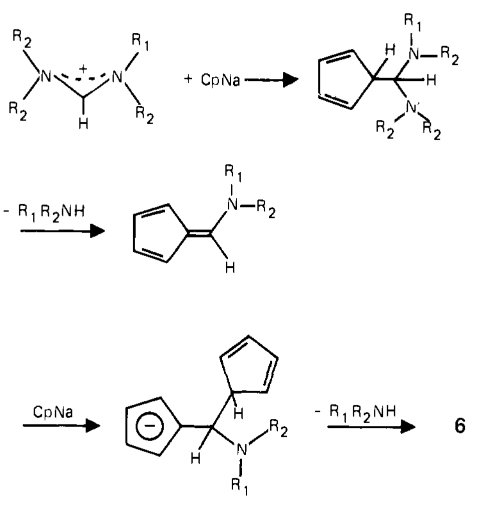
Scheme III. The Formation of 6 from Formamidinium Salts and CpNa



route C appeared to be the most promising one. This pathway has indeed some advantages. First of all, the bis(fulvenyl)ferrocene 3, contrary to what is described in the literature,[17] is a well-defined crystalline material of mp 112 °C. Secondly, its reduction to the dianion 5 can be effected rather cleanly. Finally, the side product in the reaction of 5 with ferrous chloride are only the even-numbered oligomers of 1, which are known[15] to be much less soluble than 1 or the "trimer" [1.1.1]ferrocenophane, so that the isolation and purification of 1 becomes much easier.

For the reasons outlined above, the synthesis of [1.1]-ferrocenophane, reported here, had to have two subgoals: first, a reliable and efficient synthesis of 1,1′-bis(6-fulvenyl)ferrocene (3) and, this done, the conversion of 3 to 5 and 1 in more than "modest" yield.

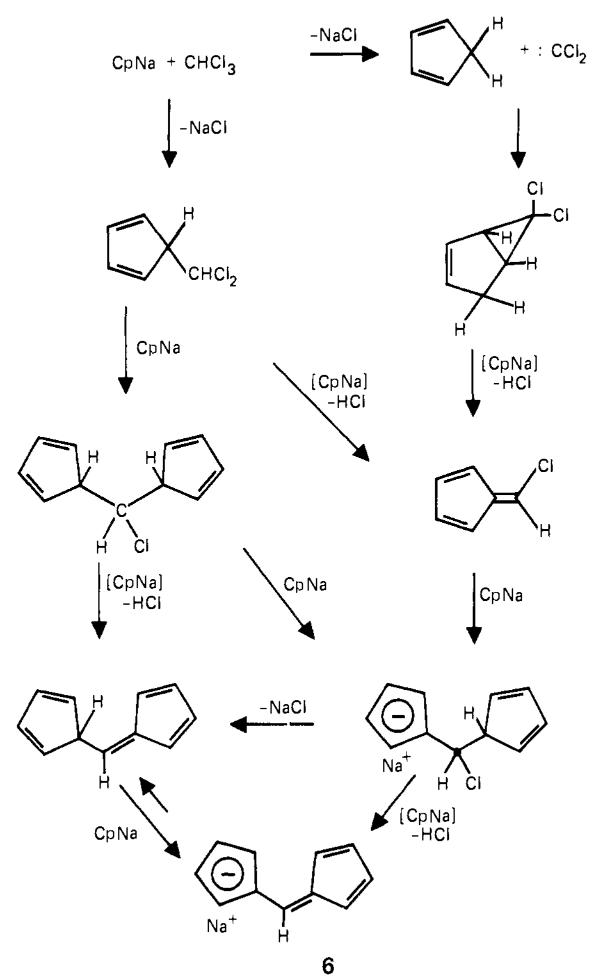
Results

Synthesis of 1,1′-Bis(6-fulvenyl)ferrocene. The several possible routes to bis(fulvenyl)ferrocene 3, regardless of their individual merit, are listed in Scheme II. They either start from a substituted ferrocene or one must first prepare the fulvenyl cyclopentadiene ligand by one of several methods and then react this ligand with $FeCl_2$ to give 3. The various possibilities are discussed one by one in the following.

Bis(fulvenyl)ferrocene from 1,1′-Ferrocenedicarboxaldehyde (Route I). The reaction of 1,1′-ferrocenedicarboxaldehyde and cyclopentadiene in the presence of a base was described[17] as being unsuccessful; the oily product obtained was characterized only by its infrared spectrum. We have made only a few attempts to repeat this reaction, because it is known[6,20] that even 1,1′-diacetyl- and 1,1′-dibenzoylferrocene produce the much more stable substituted bis(fulvenyl)ferrocenes only in widely varying yields under similar reaction conditions. Indeed, we found that this method is unsatisfactory.

Bis(fulvenyl)ferrocene from Sodium Fulvenylcyclopentadienide (Route II). A more logical and more generally applicable approach would be the reaction of the fulvenylcyclopentadienide anion 6 with ferrous chloride. This is indeed the reaction by which we first obtained the pure bis(fulvenyl)ferrocene 3 as a crystalline material. The ligand anion 6 had been first observed spectroscopically in 1969 by Jutz and Amschler,[21] but had never been isolated. It is formed[21] in the reaction of sodium cyclopentadienide and substituted formamidinium salts, but, in our hands, this reaction never went to completion, leaving unreacted sodium cyclopentadienide in the reaction mixture. For this reason, the product of the subsequent reaction with ferrous chloride is a mixture of ferrocene, the known[22] mono(fulvenyl)ferrocene and 3, which can be separated only by column chromatography. This severely limits the quantities to be prepared on a practical scale. With the obvious but not proven assumption that a N,N-disubstituted 6-aminofulvene would be an intermediate in the reaction of cyclopentadienide with formamidinum salts (Scheme III), we attempted to improve the formation of 6 by reacting 6-dimethylaminofulvene with sodium cyclopentadienide in refluxing THF. This reaction, which can be conveniently followed by UV–vis spectroscopy of samples taken at intervals, is exceedingly slow. After heating the mixture to reflux, the evolution of dimethylamine can be observed and the absorption maximum of 6 at 458 nm can be seen to grow stronger, but even after 10 days of reflux, the 320-nm absorption of the starting fulvene is still present, indicating an approximately 70% conversion to 6. Addition of pyridine as an auxiliary base does not accelerate the reaction significantly, but the presence of crown ethers drastically shifts the equilibrium toward 6. After 10 h of reflux, the reaction is essentially complete, as judged by the ratio of the 320- and 458-nm absorptions. To assure completion, we allow the reaction to continue over night. By addition of ferrous chloride, 3 was formed in yields of up to 90% with the product being contaminated to only a minor degree by ferrocene and mono(fulvenyl)ferrocene. This method therefore constitutes the first useful synthesis of 3.

Scheme IV. The Formation of 6 from $CHCl_3$ and CpNa



Since sodium cyclopentadienide is known[23] to react with dichloromethane to give di(cyclopentadienyl)methane, it appeared to be plausible that the reaction between chloroform and cyclopentadienide should be an alternate route to fulvenylcyclopentadienide 6, as outlined in Scheme IV. The formation of 6-chlorofulvene as well as of chlorobenzene in the heterogeneous reaction of cyclopentadiene and chloroform in pentane in the

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presence of potassium *tert*-butoxide has been reported.[24] Although a direct comparison between this reaction and the homogeneous reaction in THF of sodium cyclopentadienide and chloroform is inappropriate, some conclusions about the reaction mechanism can be drawn, which pertain to both reactions. In both cases, intermediates formed by either carbene addition or nucleophilic substitution can be involved. The reaction in THF is independent of the mode of addition of the reactants, contrary to what was observed[23] for the reaction of sodium cyclopentadienide with methyl chloroacetate. Upon addition of a small amount of CpNa to a 200-fold excess of chloroform in THF at 0 °C, the absorption maximum of **6** at 458 nm appears immediately. No other absorption above 330 nm was observed, excluding the presence of significant amounts of chlorofulvene, which has a strong peak at 371 nm. The reaction is, however, more complex than the immediate formation of **6** would indicate. Using a CpNa to $CHCl_3$ ratio of 4:1 suggested by the idealized equation

$$4CpNa + CHCl_3 \rightarrow \mathbf{6} + 3NaCl + 2CpH$$

an acid–base equilibrium between **6** and cyclopentadiene is established which makes the clean formation of **3** quite unlikely. In fact, **3** was produced in 19% yield together with large amounts of ferrocene and monofulvenylferrocene. Reducing the CpNa to $CHCl_3$ ratio to 1:1 eliminated the formation of these by-products almost completely, but only a 13% yield of **3** was obtained. Because of its simplicity, this reaction can be used as a reasonable preparative method for **3**, in spite of the low yield.

From 1,1′-Bis(6-dimethylaminofulvenyl)ferrocene (Route III). The reductive elimination of dimethylamine from 6-dimethylamino fulvene by $LiAlH_4$ in ether is known to lead to the unsubstituted fulvene.[25] The analogous reduction of 1,1′-bis(6-dimethylaminofulvenyl)ferrocene (**8**), the synthesis of which we had reported earlier,[26] via the dianion **7** would be an alternate route to **3** in which the product could not be contaminated by ferrocene and mono(fulvenyl)ferrocene, as had been the case in the above reactions. This reduction, however, cannot be realized owing to the bifunctional nature of this bisfulvene. A complex mixture of reduced species is obtained instead. This can be understood if one realizes that the reduction of dimethylaminofulvene to fulvene is successful only if the intermediate anion can precipitate from solution and thus escape further reduction. In THF instead of ether as solvent, this reduction leads to methylcyclopentadienide anion as the sole product, presumably by transfer of amine to the hydridoaluminate and further reduction of the resulting fulvene. Since the reduction of the bis(dimethylaminofulvenyl)ferrocene **8** has to be carried out in a solvent such as THF in order to allow the reduction to continue to the dianion, this also leads to double reduction of one or both fulvene halves. That this is the reason for the failure of this reduction to the dianion **7** can be seen from the fact that the mono(dimethylaminofulvenyl)ferrocene can be reduced quantitatively by $LiAlH_4$ in ether to its anion which upon hydrolysis leads to the mono(fulvenyl)ferrocene. The use of other reducing agents does not improve the conversion of **8** to the bis(fulvenyl)ferrocene **3**. Lithium trialkylborohydrides do not react at all with **8**. Sodium and potassium hydride do react in a slow and ill-defined fashion, but almost no **3** can be isolated after addition of water. Because of the known problems of $LiAlH_4$ reactions in the preparation of [1.1]ferroceneophane, the complete reduction of **8** to **5** and conversion of **5** to **1** with $FeCl_2$ are not practical routes either.

From 1,1′-Dilithioferrocene and 6-Dimethylaminofulvene (Route IV). For the synthesis of **3**, the double addition of dilithioferrocene to 6-dimethylaminofulvene is the method of our choice. It consists of the addition of a THF solution of 2 equiv of the fulvene to a hexane suspension of 1,1′-dilithioferrocene as its TMEDA complex to produce a yellow-brown solution of the dianion **7** as its dilithium salt. This dianion, upon addition of water, immediately loses dimethylamine to produce deep blood-red solutions of the bis(fulvenyl)ferrocene **3**, which can be isolated in yields between 85 and 95% of the recrystallized, pure product. Aside from producing **3** in high yields, the advantages of this method are that both components to be used can be obtained easily from commercially available starting materials. Thus, 1,1′-dilithioferrocene can be conveniently prepared from ferrocene.[27] We have also found that 6-dimethylaminofulvene can be prepared just as efficiently from commercial cyclopentadienyllithium as from the more reactive cyclopentadienylsodium, which was used in the published synthesis.[28]

Synthesis of [1.1]Ferrocenophane 1 from 1,1-Bis(6-fulvenyl)ferrocene (3). The reaction of substituted difulvenyl ferrocenes with $LiAlH_4$, followed by addition of $FeCl_2$, has been reported[20] to produce the 1,12-disubstituted [1.1]ferrocenophanes in "modest" yields. We have initially carried out the reduction of the parent difulvenylferrocene **3** according to this procedure and found ourselves greatly frustrated by the low yields of **1**, which typically were around 5% and in some rare instances near 10%. The reduction of **3** with complex metal hydrides can be followed by the change in color of the reaction mixture. The fulvene dissolves with intensively deep blood-red color, while the resulting dianion **5** is yellow. Analysis of the reduction product by TLC, with hydrolysis occurring as a spot is placed on the plate, revealed that only one product had been formed. The reduction step, therefore, clearly was not the problem, so that the low yields of **1** were due to the second step, the addition of $FeCl_2$ to the solution of the dianion. A deep brown or black color of this solution was usually observed, which we attribute to metallic iron. Since $LiAlH_4$ acts solely as a source of LiH in this reaction, the AlH_3 formed in the addition of $LiAlH_4$ to the fulvene may complex the resulting cyclopentadienide and, in the following addition of $FeCl_2$, reduce the $FeCl_2$ to metallic iron before it can react to form the ferrocenophane. Attempts to precipitate and isolate the dianion **7** did not result in improved yields of **1**, presumably because the AlH_3 is tightly bound to the dianion. A crucial and supposedly generally applicable improvement is brought about by using lithium trialkylborohydrides as the source of LiH in the addition reaction. The addition of $LiBHR_3$ to the fulvene occurs smoothly and the only by-product is a trialkylborane, known to be sufficiently inert so as not to interfere with the subsequent reaction with transition metal salts. The only problem may arise from the decomposition of **1** in the presence of air and trialkylborane in THF solution. This may lead to severe reductions in yield, unless the proper workup procedures as specified in the experimental sections are adhered to.

We first used triethylborohydride and found it to lead to a considerable but not reproducible increase in yield, which varied from 15 to 50%. An investigation into the causes for this erratic behavior revealed that the reaction of **3** with $LiBHEt_3$ sometimes, but not always, produces two reduction products in about equal proportions, which can be detected by TLC but which we did not identify. Upon reaction with $FeCl_2$, a good yield of **1** was usually evident by TLC analysis of the reaction mixture, but much of the product was lost on workup, in spite of the fact that **1** is quite stable in solution and especially in the solid, once it is purified. We have linked this variation in yield to the quality of different batches of the commercial hydride.

A drastic improvement was evident when lithium tri-*sec*-butylborohydride was used as the reducing agent. In this case, only one reduction product was obtained consistently and the subsequent reaction with ferrous chloride produced **1** in good yield. We have in this way obtained **1** reproducibly in yields of 35 to 45% as golden-yellow crystals. This reaction can be carried out on a large enough scale to allow the preparation of **1** in over 5-g batches.

Pure [1.1]ferrocenophane (**1**) is infinitely stable in the solid state and stable in solution as long as air is excluded. In solution, oxidation to the mono- and diketone occurs rapidly. The oxidation by MnO_2 has already been reported[20] to occur with great ease.

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We have used this oxidation as a means to quantitatively convert **1** to the diketone. Ironically, for lack of a better method, this diketone was previously employed[16,17] as a source for **1**. For us, it has become a valuable intermediate in the synthesis of [1.1]-ferrocenophane derivatives.

Many physical properties of **1** have already been described in the literature.[32] Of significance is the NMR spectrum, which has been reported to show only one singlet for the four bridging methylene group protons at 3.55 ppm in $CDCl_3$ and 3.47 ppm in CS_2 solution and two multiplets for the ferrocene protons in the α and β positions. We have investigated the temperature dependence of this spectrum (at 100 and 360 MHz) in order to arrive at an estimate for the barrier to the syn–syn exchange, which renders to exo and endo protons equivalent in the NMR time scale. The room-temperature spectrum at 100 MHz in CS_2–CD_2Cl_2 (1:1) showed the sharp singlet ($W_{1/2} = 3$ Hz) at 3.44 ppm and the triplets ($J < 2$ Hz) at 4.02 and 4.22 ppm. Lowering the temperature to −70 °C leads to some broadening of the signals at 3.44 and 4.22 ppm, while the 4.02-ppm signal remained sharp. At −100 °C, all signals became broad, possibly owing to the increased viscosity of the solvent, but still no separation of exo and endo signals for the methyl groups was observed. The 360-MHz spectrum of **1** in CS_2 was taken down to −80 °C, at which temperature only a modest broadening (with the full width at half-height increasing from 1.5 to 2.0 Hz) but no coalescence of the CH_2 group signal was observed. Since neither experiment allowed the determination of the chemical shift difference $\Delta\delta$ between the exo and endo protons, the magnitude of the activation barrier remains unknown. It is evident, however, that it must be unusually small.

1,12-Dimethyl[1.1]ferrocenophane (2) from 3. This compound has been previously prepared in very low yield from 1,1′-bis(6-methyl-6-fulvenyl)ferrocene via reduction with $LiAlH_4$ and reaction of the resulting dianion with $FeCl_2$.[20] The problems of the use of $LiAlH_4$ in such reactions have been discussed above in the conversion of **3** to **1**. They can be completely avoided, if **3** is used as the starting material. Addition of 2 equiv of methyllithium in THF solution proceeds cleanly to give the ligand dianion, reaction of which with $FeCl_2$ in THF leads to **2** in yields of up to 75%. A mixture of the exo–exo and exo–endo isomers is formed. Isomer separation can be achieved by fractional crystallization from hexane, since the exo–exo isomer is much less soluble. Single crystals of this isomer were obtained already by Watts[17] and an X-ray structure has been determined, confirming the syn conformation of [1.1]ferrocenophanes.[29]

Surprisingly, the ratio of exo–exo to exo–endo isomers obtained in the two syntheses of **2** is very different. While in the earlier work an approximate 6:1 ratio of exo–exo to exo–endo was estimated,[17] our synthesis produced these isomers in a ratio of 1:2. It is clear that the stereochemistry of the product is determined in the addition of either lithium hydride or methyllithium to the bisfulvenes, and not in the subsequent reaction with ferrous chloride. In spite of several attempts to analyze this situation, we have no good arguments to explain the predominance of one or the other isomer.

The exo–endo isomer, which was not isolated in the previous work,[17] melts much lower than the exo–exo **2** (108–109 vs. 184–185 °C). Its surprisingly high solubility indicates much greater flexibility, connected with the rotational syn–syn interconversion, which is degenerate in this isomer and appears to have a low barrier. In the exo–exo isomer, however, this syn–syn interconversion corresponds to an exo–exo to endo–endo exchange. For reasons of steric repulsion, this exchange cannot be completed, so that this isomer can only rotate from the exo–exo conformation to just beyond the half-way point of the syn–syn interconversion and then must return to the starting conformation. These considerations are confirmed by the NMR spectra of these two compounds. The α and α' protons in the exo–exo isomer are inequivalent and the NMR spectrum shows one of them as a separate peak at 4.54 ppm while the other coincides with both β protons to form a multiplet at 4.10 ppm. On the other hand, in the NMR spectrum of the exo–endo isomer the ferrocene protons appear as four sharp multiplets of equal intensity, indicating rapid and degenerate exchange, analogous to the unsubstituted [1.1]ferrocenophane, whereby, however, the α and α' as well as the β and β' protons are magnetically nonequivalent.

Summary

Up to this time, it has been impossible to investigate in detail many of the very interesting physical and chemical properties of [1.1]ferrocenophane, simply because the methods for its preparation were so poor. The synthesis described in detail in the present paper constitutes an important new route not only to [1.1]-ferrocenophane itself, but also provides efficient access to a variety of substituted metallocenophanes.

Experimental Section

All reactions were carried out under positive pressure of nitrogen or argon in multineck flasks closed with oil-filled bubblers. Solvents were best commercial grade and were used without purification, except for THF, which was distilled from $LiAlH_4$. The complex $FeCl_2$–2THF was prepared as described earlier.[30,31] Sodium cyclopentadienide solution in THF was prepared[28] on a large scale (5 L of a 2.5 to 3 M solution) and kept under argon in a dispenser storage vessel. The 360-MHz NMR spectra were obtained from the NMR Facility of the University of California at Davis. The other NMR spectra were recorded on a Varian HA 100 instrument. Melting points were determined on a Kofler hot stage and are uncorrected. Electronic spectra were recorded on a Cary 17 spectrometer. Elemental analyses were obtained from Childers Laboratories or Berkeley Analytical Laboratory.

1,1′-Bis(6-fulvenyl)ferrocene (3) via Sodium 6-Cyclopentadienylfulvene (6). 1. From *N*,*N*′-Dimethyl-*N*,*N*′-diphenylformamidinium Perchlorate and Sodium Cyclopentadienide. To a suspension of 6.5 g (20 mmol) of the formamidinium perchlorate in 100 mL of dry THF was added 40 mmol (21 mL of a 1.9 M solution) of sodium cyclopentadienide in THF. The mixture was refluxed for 12 h, after which time 5 g of $FeCl_2$–2THF, suspended in 100 mL of THF, was added all at once. After 3 h of stirring at room temperature, the red-brown mixture was poured into water and extracted with hexane until the extracts became pale red. The hexane solution was washed twice with water, dried over Na_2SO_4, and reduced in volume to about 50 mL. The resulting mixture was chromatographed on Al_2O_3 Basic III with hexane. There bands developed, of which the first contained 50 mg of ferrocene, the second 500 mg of mono(fulvenyl)ferrocene, and the third 1.1 g (33% yield) of bis(fulvenyl)ferrocene **3**. This ratio indicates that 22.6% of the sodium cyclopentadienide was unreacted, but only a total of 48.3% of the starting sodium cyclopentadienide is accounted for in the total product.

2. From 6-Dimethylaminofulvene and Sodium Cyclopentadienide. In a 1000-mL three-necked flask, 24.2 g (0.2 mol) of 6-dimethylaminofulvene was dissolved in 100 mL of THF, and 85 mL of a 2.35 M solution (0.2 mol) of sodium cyclopentadienide in THF was added. The mixture was refluxed for 2 days, after which time the evolution of dimethylamine has slowed down considerably and the UV–vis spectrum of a sample showed the absorption of the fulvenylcyclopentadienide anion at 458 nm to be much stronger than the 6-dimethylaminofulvene band at 320 nm. To this solution, 25 g of $FeCl_2$–2THF was added all at once; the mixture was allowed to cool and evaporated on a rotary evaporator. The residue was separated by chromatography as in section 1, giving ferrocene (2.0 g), monofulvenylferrocene (2.4 g), and bis(fulvenyl)ferrocene (4.3 g, 13%).

3. From Dimethylaminofulvene and CpNa with 18-Crown-6. A mixture of 6.05 g of 6-dimethylaminofulvene (0.05 mol) in 300 mL of THF, 0.8 g (0.005 mol) of 18-crown-6, and 18.5 mL (0.05 mol) of a 2.75 M solution of sodium cyclopentadienide in THF was refluxed for 24 h while a slow stream of argon was passed over the surface of the boiling solution. After 10 g (0.037 mol) of $FeCl_2$–2THF (50% excess) was added all at once, the red solution was stirred at room temperature for 1 h and then poured into ice water, yielding 8.4 g of a red solid, consisting mostly of bis(fulvenyl)ferrocene (**3**). For purification, the solid was dissolved in ether, filtered through a short column of SiO_2, and evaporated. The red

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[31] Herzog, S.; Gustav, K.; Krueger, E.; Oberender, Hh.; Schuster, R. *Z. Chem.* **1963**, *3*, 428.

[32] Gmelin, "Handbuch der Anorganischen Chemie", Vol 41, Part A, p 149.

crystals (7.9 g, 94% yield) are sufficiently pure for most subsequent reactions. Recrystallization form hexane at −60 °C affords **3** in analytical purity.

4. From Sodium Cyclopentadienide and Chloroform. To 11.9 g (0.1 mol) of chloroform in 250 mL of THF as added 140 mL (0.4 mol) of a 2.9 M solution of sodium cyclopentadienide in THF. The mixture was stirred overnight. A suspension of 30 g of $FeCl_2$–2THF in 100 mL of THF was added and the mixture stirred for 1 h, poured into water, and extracted with methylene chloride. The solution was dried, evaporated, and chromatographed as above to give 6.8 g of ferrocene, 4.5 g of mono(fulvenyl)ferrocene, and 3.2 g (19% yield) of bis(fulvenyl)ferrocene.

In the above reaction between CpNa and $CHCl_3$, the UV-vis spectrum showed that the first drop of CpNa already produced the anion **6** (absorption at 458 nm). This suggested a reaction produce **3** without ferrocene and mono(fulvenyl)ferrocene, if the ratio of CpNa and $CHCl_3$ would be reduced. The following describes this reaction using a 1:1 ratio.

To 11.9 g of chloroform in 250 mL of THF was added 35 mL (0.1 mol) of a 2.9 M CpNa solution in THF. After the mixture was stirred for 16 h at room temp., 15 g $FeCl_2$–2THF was added. The TLC analysis of the reaction product showed that almost no ferrocene or mono(fulvenyl)ferrocene was present. The mixture was poured into water, extracted with methylene chloride, dried, and evaporated as above. Filtration over a short column of Al_2O_3 Basic III with hexane as eluent gave 1.1 g of pure bis(fulvenyl)ferrocene. The yield is 13% based on sodium cyclopentadienide.

1,1′Bis(6-fulvenyl)ferrocene (3) from 1,1′-Dilithioferrocene and 6-Dimethylaminofulvene. In a 1-L three-necked flask, the 1,1′-dilithioferrocene–TMEDA complex was prepared according to the literature procedure[27] from 45 g of ferrocene, 99 mL of TMEDA, and 390 mL of 1.6 M *n*-butyllithium. The hexane solvent was removed through a fritted filter stick and the solid washed twice with degassed, dry hexane. To this solid, suspended in 500 mL of dry hexane, a solution of 45 g of 6-dimethylaminofulvene (0.37 mol) in 500 mL of dry THF was added all at once and the resulting yellow solution stirred for 30 min. After slow addition of 50 mL of water, the mixture was poured into a 2-L separatory funnel containing 800 mL of ether and extracted with water until the aqueous phase was neutral. The ether layer was dried over sodium sulfate and evaporated. In most runs, the product was pure enough by TLC and NMR at this stage that the crystals left after evaporation of the ether solution could be isolated by slurrying up with methanol and filtration. Alternatively, one recrystallization from hexane at −60 °C led to the pure product. The total yield was 50–55 g (80 to 88%) of pure product.

Properties of 1,1′Bis(6-fulvenyl)ferrocene (3). Compound **3** forms deep-red, almost black crystals of mp 112 °C, which are very soluble in all nonpolar solvents and less soluble in polar solvents. Solutions of **3** have an intense blood-red color. In hexane solutions, **3** shows electronic transitions at 495 nm (ϵ 3120), 412 (sh, 4100), 343 (22 700), and 303 (23 350). The ^1H NMR spectrum in $CDCl_3$ consists of two multiplets of 4 H each ($J < 2$ Hz) for the ferrocene protons at 4.43 and 4.60 ppm, fulvene multiplets at 6.16 and 6.43 ppm of 2 H each, a four-proton multiplet at 6.54 ppm and a singlet for the two exocyclic protons at 6.77 ppm. Anal. Calc for $C_{22}H_{18}Fe$: C, 78.13; H, 5.36. Found C, 78.06; H 5.40. The mass spectrum of **3** shows the parent ion peak at *m/e* 338 with over three times the intensity than the next strong peak at *m/e* 141 (fulvenylcyclopentadienide). All other peaks ($M - C_5H_5$, $M - C_6H_5$, etc.) are considerably weaker. As is to be expected for a fulvene substituted by a weak donor group, **3** shows a considerable tendency to polymerize, even in the solid state. It can, however, be kept unchanged for several weeks in the refrigerator. In reactions of **3** with transition metal carbonyls, only polymers of **3** were obtained.

[1.1]Ferrocenophane (1) from 3. Solid **3** (10 g, 0.03 mol) was placed in a nitrogen-flushed three-necked 1-L flask. After addition of 60 mL of 1 M L-Selectride in THF, the mixture was stirred and warmed to 50 °C until the red color of fulvenylferrocene had disappeared. To the resulting yellow suspension of the dianion **5**, 500 mL of dry, degassed hexane was added; the mixture was stirred for a few minutes and allowed to settle. The solvent was removed through a fritted filter stick and discarded. This washing was repeated twice. The residue was then dissolved in 500 mL of dry THF. To this solution, a suspension of 8.2 g of $FeCl_2$–2THF was added during 1 h. The mixture was stirred for an additional hour, after which time the solvent was removed by distillation at reduced pressure and under nitrogen. The residue was stirred with 250 mL of methanol for 30 mins, while an inert atmosphere was maintained, then filtered and washed with methanol and once with 10 mL of cold ether. The product thus obtained contained **1** and oligomers and polymers. This mixture was extracted with several portions (total about 300 mL) of hot CCl_4 and the volume of the combined extracts was reduced to 50 mL. A chromatography column, dimensions 8 × 80 cm, having a fritted disk with stopcock at the outlet, was prepared by the following simplified degassing procedure. A nitrogen line was attached to the outlet of the column, CCl_4 added to three-fourths the height of the column, and a rapid nitrogen flow maintained while Al_2O_3 Basic III was gradually added. The nitrogen flow was stopped, the aluminum oxide allowed to settle and the nitrogen line attached to the top of the column. The CCl_4 solution prepared above, which contains some solid, was then added to the column and elution with CCl_4 allowed to go as rapidly as the column allowed. The first fraction eluted from the column was collected; the rest, containing the even-numbered oligomers, was discarded. Evaporation of the first zone produced the golden yellow leaflets of **3**, which were suspended in a small amount of cold hexane and filtered. The yield was 3.5 to 5.4 g (30–46%).

The highest yield was consistently obtained with the following modified procedure, which approximates the high dilution technique and replaces the direct addition of ferrous chloride to the THF solution of **5**. This procedure requires more solvent and more time, so that there is a tradeoff between cost and yield. A 2-L three-necked flask with nitrogen bubbler, a 500-mL pressure equalized addition funnel, and a rubber septum was charged with 1000 mL of dry THF. The $FeCl_2$ was added to the addition funnel containing 300 mL of THF and kept in suspension by a continuous stream of dry nitrogen passed through a glass pipet to the bottom of the addition funnel. While the solution of **5** was slowly transferred dropwise and continuously through a wide bore stainless steel needle entering the reaction flask through the rubber septum, the $FeCl_2$ suspension was added at approximately the same rate. Workup was as described above.

1,12-Dimethyl[1.1]ferrocenophane (2) from 3. To a solution of 10.0 g (29.6 mmol) of **3** in 400 mL of absolute THF was added 43 mL of a 1.4 M solution (60 mmol) of CH_3Li in ether, whereby the originally deep red solution turned to yellow. This solution was transferred gradually through a stainless steel tubing to a 2000-mL flask containing 500 mL of THF, while simultaneously a suspension of 8.1 g of $FeCl_2$–2THF in 400 mL of THF was added at approximately the same rate. After 30 min stirring at room temperature, 3 mL of water as gradually added and the solution vacuum evaporated. The residue was extracted with CCl_4 and chromatographed with CCl_4 on silica gel. The first fraction contained **2** as a mixture of exo–exo and exo–endo isomers. A minor amount of the tetramer was isolated from the second fraction. The yield of **2** was 8.9 g (71%). Recrystallization from hexane yielded approximately 3 g of the exo–exo isomer of mp 184–85 °C (lit.[17] 185–86 °C). Evaporation of the solvent produced nearly pure exo–endo isomer. One recrystallization from hexane afforded the pure compound of mp 108–109 °C.

The NMR spectra of the two isomers have been discussed in the Results section. The full data are given below for $CDCl_3$ solutions. **exo–exo 2**: methyl signals at 1.15 ppm (6 H, doublet, $J = 7.5$ Hz), bridge methine protons quartet at 3.72 ppm (2 H, $J = 7.5$ Hz) and two multiplets at 4.10 (12 H) and 4.54 ppm (4 H) for the ferrocene protons, in qualitative agreement with the reported[17] spectrum. **exo–endo 2**: doublet (6 H, $J = 7.0$ Hz) at 1.25 ppm, quartet (2 H, $J = 7.0$ Hz) at 3.56 ppm, two multiplets of 8 H each at 4.11 and 4.20 ppm.

The tetramer was characterized by its mass spectrum (main peaks at *m/e* 848 and 424 with only minor other peaks at lower mass) and its NMR spectrum, which shows a major doublet at 1.45 ppm and a minor doublet at 1.66 ppm for the methyl groups, the methine quartet at 3.66 ppm, and an only modestly broadened singlet for all ferrocene protons. The fact that all ferrocene protons are equivalent in the tetramer may be connected to the complex rotational processes in this large but flexible cyclic system.

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