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Metal–Metal Interactions in Linked Metallocenes

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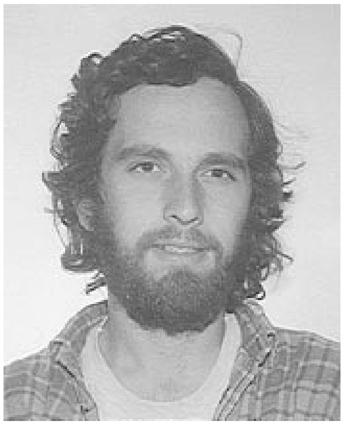
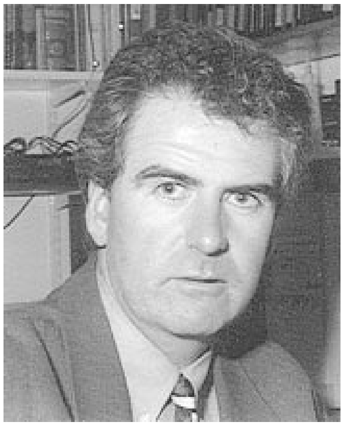
1. Introduction

Since ferrocene was first obtained as the product of attempts to synthesize fulvalene by the coupling of cyclopentadienylmagnesium bromide over iron(III) chloride,[1] a great deal of research effort has been expended on the study of bis(η^5-cyclopentadienyl)-metal complexes. One of the rich areas of metallocene study has been that of linked metallocenes;



Stephen Barlow was born in Hampshire, England, in 1970. He received his B.A. from the University of Oxford in 1992, having done undergraduate research in Dr. O'Hare's group on structural aspects of organometallic intercalation chemistry. His D.Phil. research, which was concerned with the synthesis and properties of various linked metallocene systems, was also carried out under the supervision of Dr. O'Hare at Oxford. He is now engaged in postdoctoral work in materials chemistry with Dr. S. R. Marder at the California Institute of Technology.



Dermot O'Hare was born and educated in Newry, Co Down, N. Ireland. He received his B.A. in 1982 at Balliol College, Oxford, and subsequently remained there to carry out his D.Phil. under the supervision of Professor M. L. H. Green FRS. In 1985 he was awarded a Royal Commission of 1851 Research Fellowship. In 1986–87 he spent one year at the CR&D Laboratories of E.I. duPont de Nemours in Wilmington, DE, working with Professor J. S. Miller. He is currently a University Lecturer in Inorganic Chemistry and a Septcentenary Fellow of Balliol College, Oxford. He has published research articles on a wide range of topics from synthetic molecular organometallic chemistry to time-resolved, in situ synchrotron X-ray diffraction. In 1993 he co-authored with Professor D. W. Bruce the book entitled *Inorganic Materials*, which has just appeared as a 2nd edition. In 1996 he was awarded the Royal Society of Chemistry's Sir Edward Frankland Fellowship.

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organic modifications to cyclopentadienyl-type ligands and to metallocenes themselves have permitted the construction of a range of molecules comprising more than one metallocene unit. Much of the interest in these species has been concerned with the nature of interactions between metal centers. A number of potential applications for metallocene systems with intermetallic interactions may be envisaged. For example, doping of appropriately linked metallocene polymers may lead to interesting low-dimensional conductors. In a partially oxidized poly(ferrocenylene) one would expect, by analogy with various monooxidized biferrocenes (section 3.1), distinct Fe^{II} and Fe^{III} sites between which electron transfer can take place leading to semiconductivity through a hopping mechanism; this has been supported by calculations.[2] Indeed several studies have focused on the oxidation products of poly(ferrocenylene).[3,4] Hypothetical polymers in which fused-ring ligands alternate with metal atoms have been described by Burdett[5] (with the ligand being naphthalene) and by Manríquez and Román[6] (pentalene, *s*-indacene); extrapolating from the properties of small molecule analogues (*vide infra*), such polymers should give access to much more strongly delocalized conductors than poly(ferrocenylene). Metallocene polymers based on helicene ligands have been proposed by Katz as potential "chiral conductors of electricity".[7,8] The advantages of molecular and polymer-based ferromagnetic materials have been reviewed elsewhere.[9−11] Such a magnet might be possible on the basis of an extended structure composed of linked metallocenes. There are examples of linked metallocenes with significant antiferromagnetic interactions between metal centers;[12,13] appropriate design of the linking groups to maximize the superexchange, combined with the use of two alternating metals with different spins, could lead to a ferrimagnet. Molecular materials which undergo a spin-crossover are another area of current interest where magnetic phenomena are important;[14] an example of a double-spin crossover has been found in the metallocene-like triple-decker $\{Cp^*CrP_5CrCp^*\}^+X^-$ ($X = PF_6$, SbF_6)[15] and one can speculate that other examples might be found by extending the chemistry of fused-ring bridged binuclear metallocenes, which have triple-decker-like orbital schemes,[16,17] to metals other than Fe, Co, and Ni. Several studies have centered on the use of binuclear metallocenes for third-order nonlinear optical properties.[18] Other species for second-order properties could be imagined where the interaction between a metallocene donor and a metallocenium acceptor is important.

This paper reviews the various classes of linked metallocenes which have been synthesized (covering the literature up to early 1996), emphasizing those systems in which metal−metal interactions have been studied. For example, little mention is made of poly(vinylferrocene) and none of ferrocenyl siloxanes, as the metal centers in these systems behave essentially independently of one another. "Metallocene" is taken to mean a molecular unit where a transition metal is sandwiched between two cyclopentadienyl-type ligands and bears no ancillary ligands. Thus, related species such as bis(arene)metal complexes and cyclopentadienyl metal carbonyl complexes are only mentioned when their properties make an interesting contrast to those of metallocenes, or when no analogously bridged metallocene species has yet been studied. Tris(cyclopentadienyl)dimetal species such as $(Cp_3Ni_2)^+$ are excluded. Figure 1 shows how different types of linked metallocene have been divided up between the sections of this review. In section 2 we briefly survey the various methods by which intermetallic interactions have been observed in systems based on linked metallocenes. In section 1.1 we briefly describe aspects of the nomenclature of metallocenes and metallocenophanes, to help those unfamiliar with the termninology better understand the structures described in later sections.

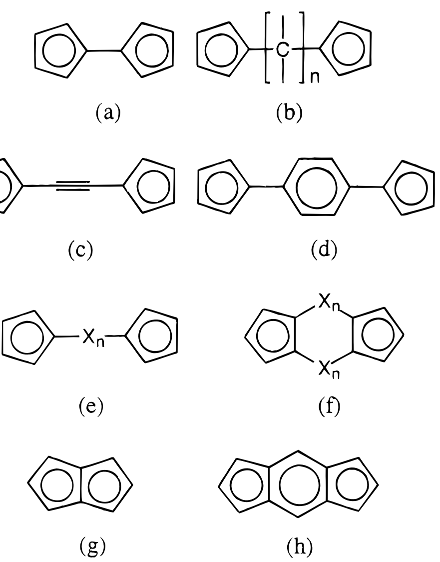


Figure 1. Examples of different types of linked cyclopentadienyl systems: (a) fulvalene, (b−d) carbon-bridged nonfused ring systems, (e and f) heteroatom-bridged systems (X represents an appropriately substituted noncarbon atom), and (g and h) fused-ring ligands.

1.1. A Note on Metallocene Nomenclature

The positions at which a metallocene may be substituted are numbered 1 to 5 on one cyclopentadienyl ring and then 1′ to 5′ on the second ring. In the case of bimetallocenes (Figure 2a), which are discussed in section 3.1, two different systems of numbering are in use. The system we have followed here treats the molecule as two metallocenes: one of these has rings numbered 1 to 5 and 1′ to 5′ while the other has rings numbered 1″ to 5″ and 1‴ to 5‴ and the two are joined by a bond between the 1 and 1″ positions. Thus the unprimed and doubly primed positions refer to the central fulvalene ligand, while the singly and triply primed positions are those on the terminal rings. If two metallocenes are joined 1 to 1″ *and* 1′ to 1‴ then we have what is referred to as either a bimetallocenylene, a bis(fulvalene)dimetal complex, or a [0.0]metallocenophane (Figure 5a). [1.1]-Metallocenophanes (Figure 10c; Figure 15c) have a single atom bridge linking 1 to 1″ and another linking 1′ to 1‴; they are also known as $[1^2]$metallocenophanes. In general a $[n^m]$metallocene is a ring formed by *m* metallocenylenes and m bridges, each *n* atoms long. An example of a $[1^4]$metallocenophane (or a [1.1.1.1]metallocenophane) is shown in Figure 10d. A [*n*]metallocenophane (i.e. $m = 1$) is a single metallocene where a bridge of *n* atoms links the 1 and 1′ positions, tying the two rings together. An example of [3]metallocenophane is shown in Figure 17.

2. Studying Interactions between Metallocenes

Much of the interest in the construction of molecules comprised of more than one metallocene unit has focused on phenomena associated with interactions between the metal centers. Various types of metal–metal interaction and the techniques used to study them are summarized below. The discussion, and the examples chosen, are somewhat biased in favor of iron species; this simply reflects how most oligometallocene chemistry has focused on iron. The reasons for this are the ease of organic functionalization of ferrocene, the chemical stability of ferrocene and ferrocenium species, and the diamagnetism of neutral ferrocenes (thus enabling characterization by NMR). Since much of this section is concerned with techniques as applied to mixed-valence species, we begin by briefly introducing the concept of mixed-valence species.

2.1. Mixed-Valence Species

When one electron is removed from a molecule with two (or more) metallocene centers, for example biferrocene (i.e. $Fv(FeCp)_2$) or $Pn(CoCp^*)_2$ (Fv = fulvalene; Pn = pentalene), two extreme situations may be envisaged: either a mixed-valence cation with distinct localized M^{II} and M^{III} sites, or a completely delocalized cation with two equivalent metals, each in oxidation state 2.5+. These extremes correspond to classes I and IIIA respectively in Robin and Day's classification of mixed-valence species.[19] Class I compounds show no metal–metal electronic interactions; their properties are the sum of those of the component metallocene and metallocenium units. Class IIIA compounds feature strong metal–metal interactions; the properties of the component species are replaced by those of a new delocalized species. Between these two extremes lies a wide range of intermediate cases with many gradations of metal–metal interactions (class II). The position of mixed-valence species on this scale has been probed by a number of techniques, with varying time scales, which are discussed in some of the following sections.

2.2. Electrochemistry

Electrochemical techniques (commonly cyclic voltammetry[20–22] and, formerly, polarography) have been among the most widely used tools to investigate metal–metal interactions in metallocene systems. The popularity of electrochemistry techniques is due to a number of factors: they are applicable to any soluble redox active metallocene system (whereas Mössbauer is ony applicable to iron compounds, ESR to paramagnetic systems with suitable relaxation times, etc.), one can use the most chemically stable member of a redox series, whereas use of other techniques may require isolation of oxidized or reduced species, which may be chemically very sensitive, and the equipment and the experiment are relatively simple.

In a molecule with *n* completely noninteracting equivalent redox centers, it can be shown that, in an electrochemical experiment, one should observe a separation, ΔE, of $(RT/F)\ln 2^n$ between the first and last redox events.[23] This means that for a molecule, X, with two redox centers, a separation of approximately 36 mV should be expected at 20 °C. (It can also be shown that for a polymer composed of noninteracting redox centers, such as poly(vinylferrocene), where *n* is very large, the distribution of *n* redox events results in an electrochemical response with exactly the same form as a mononuclear species.[23]) However, 36 mV is a rather smaller separation than that typically resolvable in routine electrochemical experiments. Larger, measurable separations are indicative of some sort of interaction between the two sites. Increased separation reflects an increased comproportionation constant, *K*, for the reaction:

$$X + X^{2+} \overset{K}{\rightleftharpoons} 2X^{+}$$

i.e. an increased stabilization of the mixed-valence species. Factors contributing to this stabilization include both electrostatic and electronic effects. The importance of electrostatics has been demonstrated by Sutton, Sutton, and Taube for $[(NH_3)_5Ru(4,4'\text{-bipyridyl})Ru(NH_3)_5]^{5+}$; they measured the comproportionation constant by redox titration of the intervalent charge-transfer band of the mixed-valence species (an alternative method to measure *K* and more sensitive than electrochemistry). Evaluation of the electronic contribution by Hush analysis of the charge-transfer band (*vide infra*) led to the conclusion that electrostatic effects accounted for most of the observed stabilization energy of the mixed-valent compound.[24] The electrostatic contribution means that electrochemical interactions between metal centers may be observed in the absence of any *electronic* interactions, i.e. in class I systems, as well as class II and III systems. However, the electronic contribution to ΔE also means that large electrochemical interactions are characteristic of electronically interacting species. Thus, electrochemistry may be used as a screening technique to look for species which may show more interesting interactions.

In metallocene systems too it has been found that ΔE depends upon the separation between the metal centers and the degree of conjugation in the bridge linking the two metallocenes. Thus, for example, in the polymer $[Fe(C_5H_3Me)_2(CH_2)_2]_n$, which is probably class I, relatively long nonconjugated bridges lead to a rather small ΔE of approximately 60 mV, presumably electrostatically dominated, in dichloromethane.[25] $Pn(FeCp^*)_2$, which may be regarded as two ferrocenes fused together, each sharing one side of a cyclopentadienyl ring, and thus representing a system with strong electronic interactions betwen metal centers, has an extremely large ΔE of 1030 mV (in the same solvent).[17] Care should be taken when comparing ΔE data from different sources as the dielectric constant of the solvent used has a significant effect on the electrostatic contributions to ΔE; thus, separations of 900 and 710 mV between the two oxidations of Pn-

$(CoCp^*)_2$ are found in dichloromethane and THF respectively.[17]

2.3. X-ray Crystallography

Metallocenes and their corresponding metallocenium ions generally have different M−C bond lengths; for example decamethylferrocene has an average Fe−C bond length of 2.050 Å,[26,27] whereas average values ranging from 2.086 to 2.096 Å have been found in various salts of the decamethylferrocenium ion.[28] The long time scale (hours to days) of data acquisition for an X-ray diffraction experiment means that if distinct metallocene and metallocenium environments are observed the system is valence trapped in the solid state at the temperature of the diffraction experiment. Electron transfer between the metallocene centers on a time scale comparable with that of the experiment will lead to the observation of M−C bond lengths which are the average of those for the metallocene and metallocenium ion. For example, the structure of $[Fv\{Fe(C_5H_4I)\}_2]^+I_3^-$ at 295 K features two equivalent iron centers with average Fe−C bond lengths of 2.070 and 2.073 Å for the chlorocyclopentadienyl and fulvalene ligands respectively, whereas $([Fv\{Fe(C_5H_4)\}_2]^+)_2I_8^{2-}$ has two distinct iron environments, one corresponding to a ferrocenium center with average Fe−C_5H_4Cl and Fe−Fv bond lengths of 2.09 and 2.08 Å, respectively, and the other with average bond lengths of 2.05 and 2.02 Å.[29] A possible complication is that of crystallographic disorder between metallocene and metallocenium sites, leading to apparent detrapping; however, analysis of thermal parameters has been used to circumvent this problem in some cases, for example, in interpreting the structure of $\{Fv(FeCp)_2\}^+I_3^-$.[30,31]

2.4. ^{57}Fe Mössbauer Spectroscopy

^{57}Fe Mössbauer spectroscopy has found many applications in the study of a wide range of iron-containing systems in the solid state.[32] A typical ^{57}Fe Mössbauer spectrum shows two peaks; the energy by which the center of the spectrum is shifted from that of iron foil is the "isomer shift", δ, and the separation between the two peaks is the "quadrupolar splitting", ΔE_q. The isomer shift depends upon the difference in the electron density at the nucleus in the ground and excited states and upon the relative nuclear radii of the two states. The quadrupolar splitting arises because the Mössbauer excited state is characterized by a nuclear spin (I) of $^3/_2$, so transitions are observed from the ground state ($I = {}^1/_2$) to $m_I = \pm{}^3/_2$ and to $m_I = \pm{}^1/_2$ states. The size of ΔE_q depends upon the changes in the quadrupolar moment of the nucleus occurring between the ground and excited state and upon the changes in the electric field gradient at the nucleus. Ferrocene and the ferrocenium ion have readily distinguishable ^{57}Fe Mössbauer spectra; although they both have very similar isomer shifts, ferrocene typically shows a quadrupolar splitting of 2.42 mm s^{-1}, whereas ferrocenium salts show values in the range 0−0.1 mm s^{-1}. For a mixed-valence species in which the electron transfer rate between the metals is much slower than *ca.* 10^7 s^{-1} superimposed ferrocene and ferrocenium signals are observed, whereas a "Mössbauer-detrapped" species, for which the intramolecular electron transfer rate is much faster than *ca.* 10^7 s^{-1}, shows a single signal with a quadrupole splitting intermediate between typical ferrocene and ferrocenium values. For example, the ^{57}Fe Mössbauer spectrum of $[Fv\{Fe(C_5H_4I)\}_2]^+I_3^-$ at 4.2 K shows a single doublet, characterized by $\delta = 0.51$ mm s^{-1} and $\Delta E_q = 1.44$ mm s^{-1}, indicating a rate of electron-transfer in excess of 10^7 s^{-1}.[29] In contrast, $([Fv\{Fe(C_5H_4Cl)\}_2]^+)_2I_8^{2-}$ shows a trapped spectrum comprising two overlapping doublets with $\delta = 0.45$ mm s^{-1}, $\Delta E_q = 2.14$ mm s^{-1} and $\delta = 0.51$ mm s^{-1}, $\Delta E_q = 0.52$ mm s^{-1}.[29] In both these cases, very similar spectra are observed at 300 K. Intermediate cases are also observed in which low-temperature spectra correspond to a "trapped" situation (i.e. distinct Fe^{II}/Fe^{III} environments), but where increasing detrapping (i.e. averaging towards the "$Fe^{2.5+}$" situation) is seen as the temperature is increased. Examples with this behavior include the triiodide and IBr_2^- salts of biferrocene.[30,31] As discussed further in section 3.1, due to solid-state effects whereby the electron-transfer process is coupled to phonon modes of the crystal, the transition from trapped to detrapped states in mixed-valence ferrocene systems does *not* pass through an intermediate broadened régime; thus one cannot extract electron-transfer rates from coalescence temperatures in the manner analogous to the extracting of rate information from variable-temperature NMR data. An obvious limitation of ^{57}Fe Mössbauer spectroscopy is that only iron-containing systems may be studied.

2.5. ESR Spectroscopy

An ideal situation for the study of electronic interactions between metal centers by electron-spin resonance (ESR or EPR) occurs where the paramagnetic species involved have nondegenerate ground states, and there are suitable nuclei to which hyperfine coupling can be observed. These conditions are met in bis(arene)vanadium chemistry, where the ground state is $^2A_{1g}$ and ^{51}V is 99.75% abundant with $I = {}^7/_2$. Chromium contains 9.50% ^{53}Cr, also with $I = {}^7/_2$ (the other naturally occuring isotopes have $I = 0$), so ^{53}Cr satellites may be used to investigate detrapping between metal centers in bis(arene)chromium cation species. Hyperfine coupling to protons has also been used to obtain similar information in these species. Unfortunately, many paramagnetic metallocene or metallocenium species have degenerate ground states. This requires the use of low temperatures, often employing liquid helium, to obtain ESR spectra. Thus, any information given by such ESR refers either to the solid or to frozen solutions, not to fluid solutions, and data will only be available for a restricted temperature range. In some cases hyperfine coupling can still be resolved. For example, hyperfine coupling to ^{59}Co (100%, $I = {}^7/_2$) may be observed in dilute samples of cobaltocenes at low temperatures. The 15-line spectrum of the bis(fulvalene)dicobalt monocation therefore indicates that this species is detrapped on the ESR time scale.[33,34]

The broad anisotropic spectra of the ferrocenium ion, arising from a $^2E_{2g}$ ground state,[35] and the lack of a suitable metal isotope, precludes examination of hyperfine coupling patterns to examine detrapping in mixed-valence ferrocene/ferrocenium systems. However, the anisotropy of the spectra may be used to advantage, since distortion of the environment of an iron atom from axial symmetry significantly reduces the **g** anisotropy of the spectrum. Species exhibiting detrapping on the ESR time scale, corresponding to rates of intramolecular electron transfer of greater than *ca.* 10^9-10^{10} s^{-1}, have different electronic states with much lower **g** anisotropies than analogous trapped species. Thus, the pentaiodide of bis(fulvalene)diiron $\{(Fv_2Fe_2)^+I_5^-\}$, which is shown to be completely delocalized by IR spectroscopy, has a **g** anisotropy, $\Delta g = g_{\|} - g_{\perp}$, in the solid state of 0.41.[36] However, $([Fv\{Fe(C_5H_4Cl)\}_2]^+)_2I_8^{2-}$, trapped on the Mössbauer time scale, so inevitably also trapped on the ESR time scale, has $\Delta g = 1.40$ (solid state).[29] ESR spectra may also be observable at higher temperatures for ESR detrapped species (and in some cases, such as that of $\{(Cp^*Fe)_2(s\text{-indacene})\}^+BF_4^-$, at room temperature[17]); often liquid helium temperatures are employed for the observation of "normal" ferrocenium spectra.

2.6. Magnetic Measurements

Two situations of applicability for magnetic measurements may be distinguished: that of mixed-valence ferrocene/ferrocenium species and that where a molecule comprises more than one paramagnetic center. In both cases one measures the magnetic susceptibilty of a solid sample over as wide a temperature range as possible, typically employing a Faraday balance or a SQUID magnetometer. The possibility of both intra- and intermolecular interactions may complicate the interpretation of solid state data; this was the case in an attempt to compare intramolecular interactions in two isomers of $\{Cp^*Ni(C_5H_4)\}_2C_6H_4$.[37]

In the first case the **g** tensors found for ESR detrapped species result in lower averaged **g** values, $\langle g\rangle$, and thus lead to lower values of the effective magnetic moment ($\mu^2 = \langle g\rangle^2(S(S + 1))\mu_B$). Thus, for example $\{s\text{-Ic}(FeCp^*)_2\}^+BF_4^-$ (*s*-Ic = *s*-indacene) has an effective magnetic moment of 1.91 μ_B,[17] whereas decamethylferrocenium pentacyanopropenide is a more "normal" ferrocenium salt with a moment of 2.99 μ_B.[28]

In the case of a molecule with more than one paramagnetic metallocene center there are possibilities for intramolecular ferro- or antiferromagnetic interactions between the spins. Significant intramolecular antiferromagnetic interactions, manifested in the reduction of the effective magnetic moment as the temperature is decreased, have been found in some metallocene systems. For example, CpNiLCrLNiCp (where L represents the ligand shown in Figure 16a) has a high-temperature magnetic moment of 4.85 μ_B, consistent with three noninteracting $S = 1$ centers (for which would expect $\mu_{eff} = 4.90$ μ_B according to $\mu_{eff}^2 = \sum g^2(S(S + 1))$, but as the temperature is lowered this moment drops more and more, reaching 2.58 μ_B at 1.9 K.[13] The diamagnetism of the bis(fulvalene)diiron dication[38] may be regarded as an extreme example of intramolecular antiferromagnetic coupling.

Information about magnetic interactions may also be obtained using NMR methods (*vide infra*).

2.7. NMR Spectroscopy

Variable-temperature NMR has been used to study the rates of exchange processes. In the simplest case one can observe the temperature at which coalesence between the signals from two exchanging species coalesce and calculate the rate of exchange at that temperature from $\tau = 2^{0.5}\pi^{-1}\delta_\nu^{-1}$, where δ_ν is the difference in the frequencies of the two species and τ is the reciprocal of the rate of exchange.[39] Watanabe *et al.* have studied species $\{CpRu^{II}FvRu^{IV}XCp\}^+$ (X = halide), where electron exchange between metal centers is accompanied by transfer of the halide ligand, and where both metal centers are diamagnetic.[40] In this system, coalescence corresponds to the situation where the resonances due to the Ru^{II} and Ru^{IV} ends of the molecule are no longer distinguishable. For $\{CpRu^{II}FvRu^{IV}BrCp\}^+PF_6^-$ in acetone-d_6, τ was calculated to be 1.8×10^{-3} s at the coalescence temperature of 228 K, while the free energy barrier for the electron/ligand exchange process was found to be 43.4 kJ mol^{-1}. Unfortunately in the case of a mixed-valence metallocene/metallocenium system without ancillary ligands at least one of the two species involved will be paramagnetic, which leads to unusual chemical shifts and often very broad lines. Thus, such techniques have not been widely applied to mixed-valence-linked metallocenes. However, NMR line broadening studies have been used to study electron exchange in MCp_2/MCp_2^+ (M = Fe, Co, Ni) mixtures in solution, and the technique should be applicable to mixed-valence-linked metallocene systems. Observation of the broadening and shifting of the resonances due to the neutral and cationic species, one or both of which are paramagnetic, as a function of temperature allowed the determination of the rate constants for the second-order electron exchange reactions between metallocene and metallocenium ions.[41−44]

NMR spectroscopy of paramagnetic species can, however, be used to advantage. The Evans' method allows one to determine the effective magnetic moment of a paramagnetic species in solution.[45] Typically the NMR tube contains a known quantity of the compound of interest plus a standard, often tetramethylsilane. Within the tube is a sealed capillary containing only solvent and the standard. The difference in chemical shifts between the standard in contact with the paramagnetic spcies and that in the capillary allows the calculation of the magnetic moment. An obvious advantage over the use of solid-state magnetic measurements is that possible complications from intermolecular interactions are eliminated. A disadvantage is the limits imposed on the temperature range available for study by the boiling and freezing points of the solvent. Köhler and coworkers have made extensive use of the NMR spectra of the paramagnetic species themselves. For example, they found the paramagnetic shift (defined as the difference in chemical shifts between the paramgnetic species and its diamagnetic iron analogue) of chromocene at 298 K to be −324 ppm, whereas the spectrum of bis(fulvalene)dichromium was approximately seven times less shifted.[46] These data were interpreted in terms of a diamagnetic ground state for the dichromium compound with a thermally accessible paramagnetic excited state. Another study focused on the decamethylbimetallocenes, $Fv(MCp^*)_2$; the paramgnetic shifts for $Fv(VCp^*)_2$ varied linearly with reciprocal temperature, thus indicating Curie behavior, whereas the dinickel analogue showed temperature-dependent behavior characteristic of strong antiferromagnetic behavior.[12]

2.8. Infrared Spectroscopy

Delocalization on the infrared time scale (10^{-11}–10^{-12} s) is regarded as synonymous with complete delocalization. “IR localized” species show bands characteristic of separate metallocene and metallocenium units, whereas delocalized species lack these bands, but have new bands corresponding to the averaged valence “$(\text{metallocene})^{0.5+}$” unit. In the case of ferrocene-based systems the most useful feature appears to be a band assigned to a perpendicular C−H bending mode. In KBr, this band is found at 815 cm^{-1} for ferrocene and at 851 cm^{-1} for ferrocenium triiodide. An example of an IR delocalized system, $\{[2.2]\text{ferrocenophane-1,13-diyne}\}^+I_3^-\cdot 0.75I_2$, shows a single band at 830 cm^{-1},[34] while an example of a IR localized species, $[Fv\{Fe(C_5H_4I)\}_2]^+I_3^-$, has bands at 822 and 849 cm^{-1}.[29] Wood and Strauss have pointed out some of the difficulties associated with extracting rate information about exchange processes from IR data.[47]

2.9. Photoelectron Spectroscopy

Photoelectron spectroscopy is a useful technique for the monitoring of rapidly oscillating electron density, with a time scale of *ca.* 10^{-17} s. X-ray photoelectron spectroscopy (XPS, also known as electron spectroscopy for chemical analysis: ESCA), which gives information about the core electronic levels of an atom, has been used to study partially oxidized linked ferrocenes. Thus, biferrocenium salts show two $^2P_{3/2}$ core ionizations, one characteristic of ferrocene and the other of ferrocenium, indicating an Fe^{II}/Fe^{III} situation,[48] whereas the monocation of bis(fulvalene)diiron shows only one $^2P_{3/2}$ ionization, corresponding to neither that of ferrocene nor of ferrocenium and indicating an average valence system.[49]

2.10. Electronic Spectroscopy

Mixed-valence compounds often exhibit strong absorptions in the near-infrared (near-IR) region of the electromagnetic spectrum: these absorptions are assigned to intervalence electron transfer. Thus, in a metallocene system the near-IR transition corresponds to electron transfer from the M^{II}/M^{III} configuration to a vibrational excited state of the M^{III}/M^{II} configuration. Hush has developed a theoretical treatment of such systems.[50a] In Hush's model, the energy of the intervalence transition is dependent upon the the differing geometries and bond lengths in the two “donor” and “acceptor” halves of the molecule, and is relatively insensitive to the degree of delocalization in the ground state and the separation between donor and acceptor. Coupled with assumptions about the forms of the potential wells involved, one can estimate the barrier for thermal electron transfer; the rate of electron transfer is given by

$$k_{\mathrm{th}} = (kT/h)e^{h\nu/4RT}$$

where k_{th} is the rate constant for thermal electron transfer and ν is the frequency of the transition in Hertz. The strength of the intervalence band, however, is also dependent on the distance between the donor and acceptor and upon the interaction between them. Thus

$$\alpha^2 = (4.5 \times 10^{-4})\epsilon_{\max}\Delta_{1/2}/\nu r^2$$

where $\epsilon_{\max}$, $\Delta_{1/2}$, and ν are respectively the maximum extinction coefficient, width at half height (in frequency units), and frequency of the intervalence band. r is the adiabatic charge-transfer distance. Cases where the distinction between this parameter and the geometric donor−acceptor separation have been overlooked may account for at least some of the apparent quantitative failings of Hush theory, as has been discussed recently by Cave and Newton[50b] and by Karki and Hupp.[50c] The interaction parameter, α, is defined by

$$\psi_{\mathrm{g}} = (1 - \alpha^2)^{0.5}\Phi_{\mathrm{i}} + \alpha\Phi_{\mathrm{j}}$$

where ψ_{g} is the ground state wave function and Φ_{i} and Φ_{j} are wave functions for donor and acceptor components, respectively. The possibility of estimating α is an important feature of near-IR measurements; this is a purely electronic parameter, whereas electron-transfer rates as estimated by, say, Mössbauer spectroscopy are also dependent by Frank−Condon effects. Criteria have been suggested whereby systems can be assigned to one of Robin and Day's classes based on α.[19,51] However, the assumptions of Hush theory are only valid when systems are weakly interacting. Problems with applying Hush theory to more strongly interacting species have been encountered in a number of studies; for example, disparities between ESR results and Hush analysis have been found for copper hemocyanins.[52] Attempts to compare the near-IR absorptions of the biferrocene and bis(fulvalene)diiron monocations have met with same problems. In acetonitrile the biferrocene monocation shows an absorption at 1900 nm, from which Hush theory predicts a rate constant for electron transfer of 1.3×10^{10} s^{-1}; the interaction parameter was estimated to be *ca.* 0.09.[51] For the bis(fulvalene)diiron monocation, however, the absorption is centered at 1550 nm in the same solvent so Hush predicts a *slower* rate of electron transfer.[38] This is in conflict with ESR, Mössbauer, and IR results which suggests faster electron transfer in bis(fulvalene)diiron. The interaction parameter is calculated at *ca.* 0.2, which although greater than in the biferrocene monocation, still corresponds to trapped valencies, again inconsistent with other spectroscopic evidence. In fact, it should be realized that in delocalized systems the “intervalence” charge transfer band can no longer be considered as transfer from one metal center to the other as the electron is now shared equally between the two metals. The model

Hush originally described involved two harmonic potential wells lying side by side and crossing. In the delocalized extreme, there will be a *single* ground-state potential well lying beneath an excited-state well. The transition now represents transfer of an electron from one delocalized orbital to another.[36]

More meaningful use of Hush theory is exemplified by a recent study of bis(ferrocenyl) polyenes, Fc-$(CH{=}CH)_n$Fc, where coupling energies, determined by Hush analysis, were found to vary from 0.061 to 0.022 eV as n varied from 1 to 6.[53] A variant treatment developed by Piepho, Krausz, and Schatz[54] (and hence often referred to as PKS theory) has also been applied to analyze mixed-valence metallocene near-IR absorptions.

Intervalent charge-transfer bands may be observed in both σ- and π-bridged systems. In the former case, through-space mechanisms are generally believed to be responsible: near-IR bands are usually only observed in species sufficiently flexible to allow the two metal centers into close proximity. In π-bridged systems near-IR bands are much more widely observed, even when the metals are well separated, suggesting through-bond mechanisms are also important.

3. Fulvalene Systems

3.1. Bimetallocenes

Bimetallocenes, $Fv(MCp)_2$, also known as bimetallocenyl complexes or bis(cyclopentadienylmetal)-fulvalene complexes, comprise two metallocenes linked by a single bond; in general most bimetallocenes and their salts have been found to have the two metals coordinated to opposite faces of a more or less planar bridging fulvalene ligand, as shown in Figure 2a. The vast majority of studies of bimetallocenes has been concerned with electron transfer in monooxidized biferrocene and its various derivatives. Biferrocene was first prepared in very low yield by pyrolysis of Fc_2Hg over palladium black.[55] The Ullmann coupling of haloferrocenes by copper, discovered by Rausch,[56,57] has been the basis of most subsequent syntheses of biferrocenes. Related reactions are the coupling of lithioferrocene or ferrocenyl Grignards by a variety of reagents.[58−60]

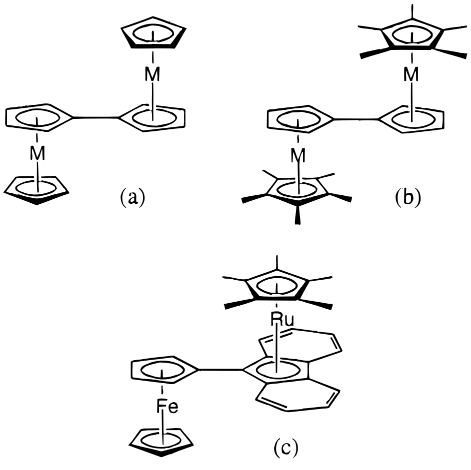


Figure 2. Some bimetallocenes.

More recently more general routes have been devised which also allow the formation of non-iron bimetallocenes; the reaction of the dilithium or dithallium derivative of fulvalene with a suitable Cp*-(metal) half-sandwich source, or with a mixture of a metal(II) salt and a source of $(Cp^*)^-$, has allowed formation of a series of decamethylbimetallocenes $\{Fv(MCp^*)_2\}^{n+}$ (Figure 2b) ($n = 0$, M = V,[12] Fe,[12,61] Co,[12] and Ni;[12] $n = 1$, M = Fe;[61,62] $n = 2$, M = Fe,[61,62] Co,[12,61] Rh[61]). Several other species have been obtained by more exotic and specialized routes; for example, a series of steps from fluoren-9-one and lithioferrocene led to the pentamethyl Fe−Ru dibenzobimetallocene species shown in Figure 2c,[63] the reaction of the fulvalene dianion with $(CpNi)^+$ gave binickelocene,[64] Fv(FeCp)(NiCp) was obtained by reaction of $FcC_5H_4^-$ (which could also be written as $CpFeFv^-$) with $(CpNi)^+$,[65] while $\{Fv(FeCp)(RhCp)\}^+$ was obtained as a side product in the preparation of various termetallocenes (*vide infra*).[66]

In general biferrocenium salts are class II: they are trapped on the IR and XPS[48] time scales and show intervalent charge transfer bands in solution. However, salts may be Mössbauer and ESR trapped or detrapped or may undergo a transition from a trapped to a detrapped state at some transition temperature, T_c. Biferrocene itself shows two oxidations separated by 330 mV in acetonitrile.[67] Little variation is observed between the values of ΔE for various biferrocene derivatives, indicating very similar levels of metal−metal interaction in the isolated monocations. Similarly, analysis of solution near-IR absorptions of monocationic species by Hush theory shows little variation between different species. Thus, differences in Mössbauer and ESR behavior between different salts must be attributed to solid state effects: factors so far identified as influencing the degree of detrapping include the identity of the counterion, the relative orientation of the counterion and the cation, the symmetry of the cation, the crystallinity of the salt, the planarity of the fulvalene bridging ligand and the tilting of the rings of the ferrocene units.

Mössbauer spectra of biferrocenium salts which undergo a trapped−detrapped transition give valuable insight into the mechanism of the transition. In the intermediate régime spectra are not broadened, as one would expect if one were simply observing a gradual increase of the rate of intramolecular electron transfer with increasing temperature. Instead the intermediate spectra are a superimposition of the trapped Fe^{II}/Fe^{III} spectrum and the detrapped $Fe^{2.5}$ spectrum; the lines have similar profiles to those seen in the respective extreme spectra. It has, therefore, been concluded that a phase transition takes place over the temperature range of the intermediate spectral régime. In the low-temperature and high-temperature phases electron transfer is respectively much slower and faster than 10^7 s^{-1}. In the intermediate spectral régime domains of both phases are present within a crystal. The presence of a distinct transition is also indicated by DSC measurements on $\{Fv(FeCp)_2\}^+I_3^-$ which show an endothermic peak centered at *ca.* 330 K;[68] Mössbauer spectra show a

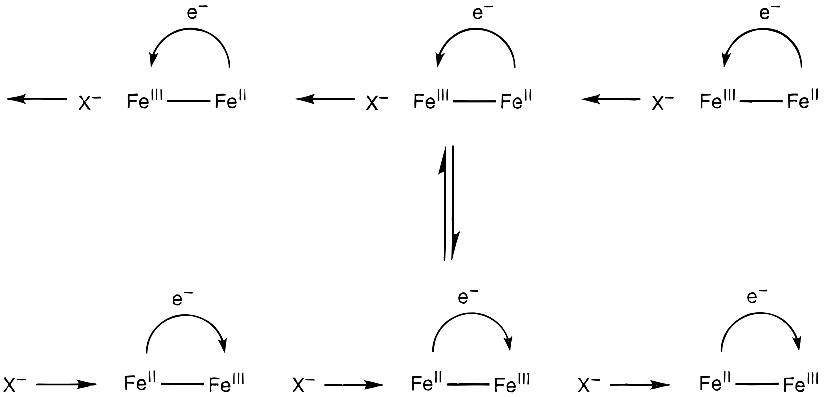


Figure 3. Schematic representation of electron transfer coupled with counterion oscillation in a Mössbauer-delocalized biferrocenium salt.

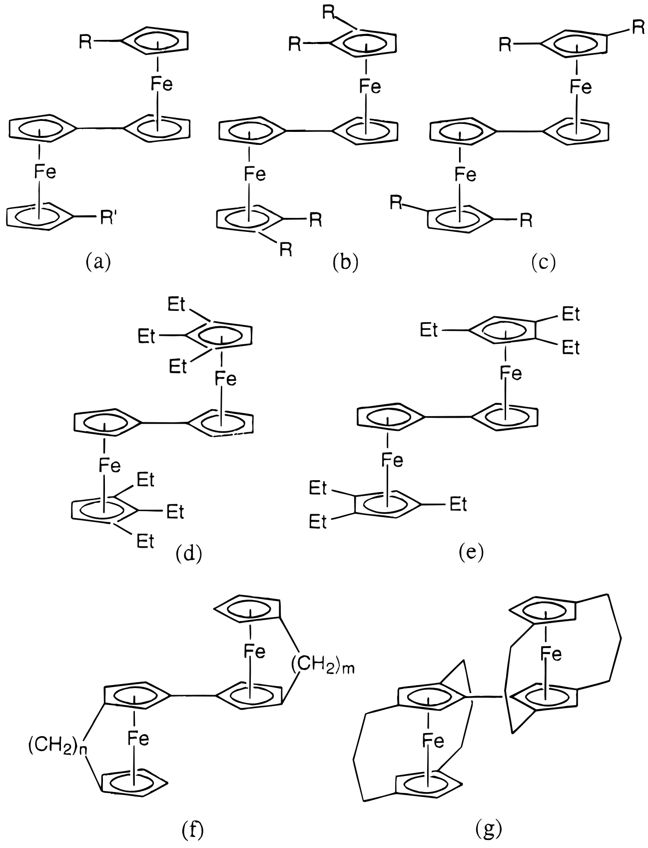


Figure 4. Some substituted biferrocene systems in which electron transfer has been studied.

trapped spectrum at 300 K,[36] but a single $Fe^{2.5}$ doublet above *ca.* 350 K.[30,31]

The effects of varying the counterion have been illustrated in a number of studies. Thus biferrocenium triiodide becomes Mössbauer detrapped above *ca.* 350 K, whereas the IBr_2^- salt becomes fully Mössbauer detrapped above 200 K.[30,31] Although the crystal structure of $\{Fv(FeCp)_2\}^+I_3^-$ at 296 K shows an apparently centrosymmetric cation, analysis of the thermal parameters suggested static disorder between trapped Fe^{II} and Fe^{III} sites, consistent with the Mössbauer results. This difference may be understood if one considers that in a localized Fe^{II}/Fe^{III} structure electrostatics will cause the anion to approach the Fe^{III} center more closely. When electron transfer takes place the anion will have to move as it will now be closest to an Fe^{II} center. Thus one can envisage a cooperative phase transition whereby phonons involving anions jumping between alternative lattice sites are excited simultaneously with the onset of intracation electron transfer, as depicted schematically in Figure 3. A theoretical treatment enumerating the various factors which may affect such a transition has been described.[69] In a triiodide anion the anion oscillation will involve interconversion between the configurations $I{-}I\cdots I^-$ and $I^-\cdots I{-}I$. Since IBr_2^- is lighter than I_3^-, a phonon mode involving the former anion will, given the same crystal structure, be of lower energy, thus allowing the excitation of the mode to occur at lower temperature.

Another example of anion dependent behavior is provided by the salts of monooxidized 1′,1‴-diethylbiferrocene (Figure 4a, $R = R' = Et$): the triiodide, dibromoiodide, picrate, and hexafluorophosphate are respectively detrapped above 275 K, partially detrapped at the decomposition temperature of 290 K, trapped up to at least 300 K, and detrapped above 280 K.[70] Interestingly, replacement of I_3^- by IBr_2^- in this case leads to *increased* detrapping temperatures, T_c. The same trend is observed in the corresponding salts of 1′,1‴-dibromobiferrocene (Figure 4a, $R = R' = Br$) and 1′,1‴-diiodobiferrocene (Figure 4a, $R = R' = I$).[71] In these cases the effect responsible is believed to be interactions between the anion and the substituent of the cation; evidence for these interactions is provided by the crystal structures of $[Fv\{Fe(C_5H_4Et)\}_2]^+I_3^-$[72] and $[Fv\{Fe(C_5H_4I)\}_2]^+I_3^-$.[29] These interactions will have to be overcome in order to excite the anion oscillation phonon mode and are expected to be stronger in the IBr_2^- salts. Replacement of triiodide by $CuBr_2^-$ or $FeCl_4^-$ also leads to increased values of T_c in $[Fv\{Fe(C_5H_4I)\}_2]^+$ salts,[73] while replacement of triiodide with $(TCNQ)_2^-$ {TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane} in salts of monooxidized 1′,1‴-di-*n*-propylbiferrocene (Figure 4a, $R = R' = {}^nPr$) leads to a large reduction in T_c.[74] Differences have also been observed between the triiodide, hexafluorophosphate, and hexafluoroantimonate of the 1′,1‴-dibenzylbiferrocene monocation (Figure 4a, $R = R' = CH_2Ph$).[75,76]

A demonstration of the variation of T_c with crystal structure is provided by $[Fv\{Fe(C_5H_4CH_2Ph)\}_2]^+I_3^-$. Both triclinic and monoclinic polymorphs may be obtained and presumably differ in the relative orientation of anion and cation; the latter is detrapped down to 25 K (the coldest temperature measured), whereas the former is trapped up to at least 300 K.[77] Another contrast is provided by the iodine oxidation products of the series Fv{Fe(C_5H_4X)}$_2$ where X = Cl, Br, or I.[29,78] The 1′,1‴-dichlorobiferrocenium salt is Mössbauer trapped up to at least 340 K, whereas the diiodo and dibromo analogues are detrapped even at 4.2 K on the Mössbauer and ESR time scales (although not on the IR time scale). Whereas the crystal structure of the diiodo compound shows equivalent iron atoms and triiodide anions situated symmetrically between neighboring cations, that of the dichloro species features distinct ferrocene and ferrocenium sites and an octaiodide dianion ($I^-\cdots I—I\cdots I—I\cdots I—I\cdots I^-$).[29] The ferrocene and ferrocenium units have very different orientations with respect to the anion. Thus, they cannot be readily interconverted via a relatively low-energy phonon mode.

The importance of the relative orientation of anion and cation is further illustrated by comparison between the triiodides of 1′,2′,3′,1‴,2‴,3‴-hexaethylbiferrocene (Figure 4d) and 1′,2′,4′,1‴,2‴,4‴-hexaethylbiferrocene (Figure 4e) for which values of T_c are 170 and >300 K, respectively.[79] Examination of the crystal structures[79] shows that ring tilt and planarity of the fulvalene ligand (factors which are believed to be important in determining T_c—*vide infra*) are comparable, but while in the first case the triiodide anion is perpendicular to the fulvalene ligand, and hence parallel to the electron transfer pathway, in the second compound the triiodide and fulvalane are aligned parallel to one another. Thus the electron transfer/anion charge oscillation phonon mode is excited at lower energy in the former compound. The same comparison may be made between the triiodides of 1′,1‴-di(*p*-bromobenzyl)biferrocene (Figure 4a, R = R′ = *p*-$BrC_6H_4CH_2$, I_3^-, and fulvalene parallel, T_c = 200 K) and 1′,1‴-di(*o*-iodobenzyl)biferrocene (Figure 4a, R = R′ = *o*-IC_6H_4-CH_2, perpendicular T_c < 77 K).[80]

It is unsurprising that if the two ferrocene units of a biferrocenium salt have greatly differing substituents, such as in the triiodide of 1′-acetylbiferrocene (Figure 4a, R = $COCH_3$, R′ = H), trapped behavior is enforced.[70] The two ferrocene centers are highly inequivalent and the cationic charge will reside on the most electron-rich ferrocene center (in this case the nonacetylated ferrocene). One would not only expect reduced solid-state electron-transfer rates in such species, but also reduced rates in solution, as estimated from near-IR data; however, no solution data have yet been reported. The magnitude of this non-zero zero-point energy difference in unsymmetrically substituted biferrocenes can be related to the increased values of the separation between oxidation potentials, ΔE, relative to those for symmetrically substituted compounds. More surprising is the observation of Mössbauer trapping in the triiodide of 1′-ethyl-1‴-*n*-propylbiferrocene (Figure 4a, R = Et, R′ = ^{n}Pr),[70] whereas the 1′,1‴-diethyl[31,74] and di-*n*-propyl[31] salts become detrapped above 275 and 245 K, respectively. One would expect the two ferrocene units in the 1′-ethyl-1‴-*n*-propylbiferrocene to be very similar electronically, an expectation confirmed by electrochemical measurements.[70] It has been suggested that a very small non-zero zero-point energy difference, too small to be detected electrochemically, is sufficient to account for the difference in Mössbauer behavior.[70] Alternatively solid-state effects arising from large differences in the orientations of the counterion with respect to the two inequivalent ferrocenes may be responsible; unfortunately the crystal structure has not been reported.

Several pronounced effects of sample crystallinity on the Mössbauer behavior of ferrocenium salts have been reported; less crystalline material is more prone to show trapped behavior, presumably as a result of the effects of defects on the propagation of the charge oscillation phonons. Notably, grinding of the triclinic polymorph of [Fv{Fe($C_5H_4CH_2Ph$)}$_2$]$^+I_3^-$, although having little effect on its powder diffraction pattern, results in the appearance of some trapped Mössbauer signals at room temperature, whereas the original material is detrapped at least as low as 25 K.[77]

Distortion of the two cyclopentadienyl rings of the bridging fulvalene ligand from planarity in the crystal structures of the triiodide of multiply-bridged species such as that shown in Figure 4g is believed to account for its fully Mössbauer trapped behavior.[81,82]

The introduction of interannular bridges into biferrocene derivatives may lead to tilting of the cyclopentadienyl rings, both in solution and the solid state. Dong *et al.* have suggested ring tilt will lead to increased mixing of the ferrocene HOMO with the orbitals of the bridging ligand, and thus to increased metal–metal interaction in the bridged species. Thus, the molecules represented by Figure 4f (for $n = m = 3$; $n = 3$, $m = 4$; $n = m = 4$) show larger ΔE values than biferrocene under the same conditions.[83] Similarly, the triiodide of the $n = m = 3$ member is ESR and Mössbauer detrapped at least as low as 77 K, whereas that of the $n = m = 5$ species, which would be expected to have a much lower ring tilt, is Mössbauer trapped at 300 K.[84] Moreover, various other biferrocenium species without interannular bridges, and so presumably with more-or-less parallel rings in solution, show significant ring tilts in the solid state. These ring tilts are solid-state effects, determined by weak nonbonded interactions between the substituents of the cyclopentadienyl rings and the triiodide counterions. In a recent paper Dong *et al.* compared the crystallographically determined ring tilts and detrapping temperatures for the triiodides of biferrocene and several disubstituted (Figure 4a, R = Et, ^{n}Pr, I) and tetrasubstituted (Figure 4b, R = *n*-propyl, CH_2Ph; Figure 4c, R = Et, ^{n}Pr, CH_2Ph) derivatives.[85] In all of these salts the triiodide ion and fulvalene ligand are oriented perpendicular to one another. Compounds where other factors expected to affect the detrapping were present, such as different anion orientation or strong van der Waals interactions, were excluded from the comparison. A relationship was established whereby increased ring tilt led to a decrease in the detrapping temperature: the two extreme cases are biferrocenium itself, which has a ring tilt of 0.3° and becomes completely detrapped above *ca.* 365 K and the diiodo compound, where the ring tilt is 15.6° and detrapping occurs right down to 4.2 K.

The rate of intervalent electron transfer in the mixed-valence bicobaltocene cation, as estimated by Hush theory, has been found to be faster than in the analogous iron species.[86]

Comparison of the solution ^{1}H NMR spectra of Fv(VCp*)$_2$ and Fv(CoCp*)$_2$ with those of the parent metallocenes have been used to infer that these two compounds behave as two vanadocenes (two $S = {}^3/_2$ centers) and two cobaltocenes (two $S = {}^1/_2$ centers), respectively, with very little magnetic interaction between the two metal centers.[12] However, differences between the spectra of Fv(NiCp*)$_2$ and nickelocene have been used to infer substantial antiferromagnetic coupling in the former species.[12] Both diamagnetism[64] and paramagnetism with antiferromagnetic interactions[12] have been claimed for the unsubstituted binickelocene, Fv(NiCp)$_2$.

The neutral, monocationic, and dicationic forms of all the decamethylbimetallocenes so far studied, apart from the divanadium species, can be reversibly interconverted electrochemically. Separations between the two redox potentials for Fv(MCp*)$_2$ are reported to be 375 (EtCN)[12] or 240 mV (THF)[61] for M = Fe, 430 (EtCN)[12] or 400 mV (DMF)[61] for M = Co, 120 mV (DMF)[61] for M = Rh and 190 mV (EtCN)[12] for M = Ni. Reduction to mono- and dianions and oxidation to tri- and tetracations have also been observed for dicobalt[12,61] and dinickel[12] species, respectively. The relatively low value of ΔE for the dirhodium species was taken to be indicative of ligand valence bond rearrangement during reduction of the 37-electron monocation to a structure with a C=C bond on the fulvalene bridge, and η^4-diene coordination to Cp*Rh, thus facilitating an 18-electron configuration for each rhodium atom in the neutral species.[61] Similar behavior has been reported for species such as (biphenyl){Cr(CO)$_3$}$_2$,[87,88] {(biphenyl)(FeCp*)$_2$}$^{2+}$,[89,90] and {(dihydrophenanthrene)(FeCp*)$_2$}$^{2+}$;[91,92] two-electron reduction of these species is accompanied by rearrangement of the bridging ligand from η^6:η^6-coordination to an η^5:η^5-bicyclohexadienylidene structure in the second electron transfer.

3.2. Bis(fulvalene)dimetal Complexes

A second class of fulvalene-bridged metal compounds comprises the bis(fulvalene)dimetal complexes, Fv$_2$M$_2$ (Figure 5a). Alternative nomenclatures refer to these species as bis(fulvalenemetal) complexes, bimetallocenylenes, [0.0]metallocenophanes or, rather confusingly, 1,1′-bimetallocenes. The most general preparation of these materials is the reaction of the fulvalene dianion with an appropriate metal(II) source: in this way Fv$_2$M$_2$ complexes have been obtained for M = V,[33,93] Cr,[33,46] Fe,[38,94] Co,[34,95] Ni,[96] and Mo.[97] The last example is particularly interesting as the only claimed example of an isolable monomeric molybdenocene is the poorly characterized Mo(C$_5$Ph$_5$)$_2$.[98,99] The diiron compound has also been obtained by a variety of other routes: the coupling of 1,1′-diiodoferrocene with copper,[100] pyrolysis of poly[Fe(C$_5$H$_4$)$_2$Hg],[101] and coupling of 1,1′-dilithioferrocene with [CuI(P^{n}Bu$_3$)]$_4$.[60] More recently

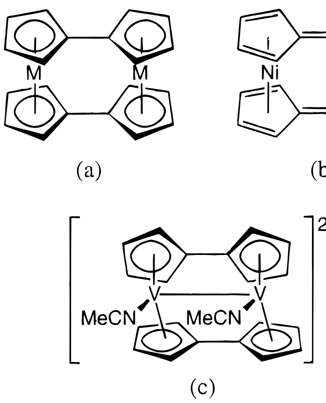


Figure 5. Bis(fulvalene)dimetal complexes showing (a) the generalized structure, (b) a resonance form for Fv$_2$Ni$_2$, and (c) the product obtained by oxidation of Fv$_2$V$_2$ in acetonitrile.

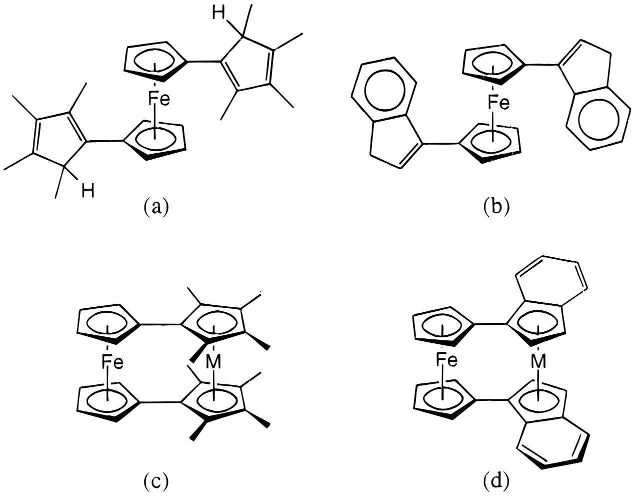


Figure 6. Ligands and unsymmetrical bis(fulvalene)dimetal complexes synthesized by Scott *et al.*; M = Fe, ZrCl$_2$ and, for d only, ThCl$_2$.

Scott *et al.* have used the reaction of 1,1′-dilithioferrocene with 2,3,4,5-tetramethylcyclopent-2-enone or indan-1-one to yield the species shown in Figure 6, parts a and b, respectively; deprotonation and reaction with iron(II) chloride or zirconium(IV) chloride gave the bimetallics in Figure 6, parts c and d.[102] More recently the Fe/ThCl$_2$ bimetallic has also been reported.[103] Plenio has performed analogous chemistry using 3,4-dimethylcyclopent-2-enone, but the reaction of Fe(C$_5$H$_4$C$_5$H$_2$Me$_2$Li)$_2$ with iron(II) chloride was reported to give polymeric species rather than the substituted bis(fulvalene)diiron compound.[104] Kelly and Meghani have prepared bis(1,1′-biindenyl)diiron and bis(1,1′-bitetrahydroindenyl)diiron.[105]

The bis(fulvalene)diiron system shows quite different properties to biferrocene. The first oxidation of bis(fulvalene)diiron occurs at considerably more negative potential (−280 mV relative to ferrocenium/ferrocene in acetonitrile) than that of biferrocene (−100 mV), indicating that some factor leads to greater stabilization of the cation in the former case.[67] The first and second oxidations of bis(fulvalene)diiron are separated by 590 mV, while ΔE for biferrocene is 330 mV. A variety of salts of the monocation of Fv$_2$Fe$_2$ have been studied by ^{57}Fe Mössbauer,[38,49,106] ESR,[36,38,67] XPS,[38,49] and IR spectroscopies;[34,36] in each case the monocation has been found to be completely detrapped on the time scale of the techniques employed. A feature, which has been shown to be composed of two bands,[94] resembling the intervalence transfer band observed in other mixed-valence species is present in the near-IR spectra of $(Fv_2Fe_2)^+$ salts. Origins for these bands have been discussed in terms of transitions between ground bonding and excited antibonding states.[107] If one interprets the near-IR spectrum of the bis(fulvalene)diiron cation in terms of Hush's model, i.e. in terms of electron transfer from one distinguishable Fe^{II} site to an Fe^{III} site, one finds that the rate of electron transfer in this species is predicted to be slower than in the biferrocene monocation, which is not even Mössbauer detrapped (although the latter measurement is in the solid rather than solution).[38,49,94,106] This points to the inappropriateness of Hush theory to strongly coupled systems. The crystal structure of the picrate of monooxidized Fv_2Fe_2 has been determined[108] and shows that the two iron atoms are 0.34 Å closer than in the unoxidized parent compound in which, in contrast to early suggestions of a distorted geometry based on ^{1}H NMR data,[100] essentially "normal" ferrocene geometry is found, with an Fe−Fe separation of 3.98 Å.[109] Magnetic susceptibility measurements have shown the picrate to have a magnetic moment close to the spin-only value (e.g. 1.88[49] and 1.72 μ_B[38] according to two separate studies by Cowan *et al.*); this is consistent with the low **g** anisotropy observed in the ESR spectra of $(Fv_2Fe_2)^+$ salts. In contrast to dicationic biferrocene salts, salts of dioxidized bis(fulvalene)diiron are diamagnetic.[38,67,110] However, no structural data are available to indicate whether a direct Fe−Fe bond accounts for this diamagnetism or if strong superexchange interactions via the ligands must be invoked.

Although the diamagnetism of Fv_2Fe_2, $(Fv_2Fe_2)^{2+}$, $(Fv_2Co_2)^{2+}$, and Fv_2Mo_2 seems well established (an 18-electron diamagnetic configuration can be envisaged for the molybdenum complex, similar to that shown for the dinickel species in Figure 5b, but in which the quadruple Mo−Mo bond of the molybdenum(II) acetate starting material is retained), some controversy has taken place about the magnetism of the other bis(fulvalene)dimetal complexes. Smart and co-workers believe the neutral and dicationic divanadium,[33,93] dichromium,[33] and dinickel complexes,[96] as well as the neutral dicobalt species,[96] to be diamagnetic on the basis of susceptibility measurements, whereas Köhler *et al.* have reported paramagnetically shifted solution ^{1}H NMR data for the neutral divanadium, dichromium, and dinickel complexes.[46] Theoretical studies have not clarified the situation.[111,112] This apparent contradiction may well arise from the difficulty in purifying these highly insoluble materials; the solubility of Fv_2Fe_2 in cold benzene is reported to be only 200 mg L^{-1}.[100] Indeed, Smart has pointed out the possibility of obtaining variable amounts of bimetallocenes as impurities since residual NaCp may be present in the reaction mixture used to generate the fulvalene dianion.[96] The monocation of the divanadium species has a rather low magnetic moment, which may indicate intermolecular antiferromagnetic interactions; its ESR spectrum shows hyperfine coupling to only one vanadium center, indicating trapping on the ESR time scale.[33] Fv_2V_2 can be converted to $\{Fv_2V_2(MeCN)_2\}^{2+}$ (Figure 5c), as well as to solvent-free diamagnetic $(Fv_2V_2)^{2+}$; the former compound has two unpaired electrons and a single V−V bond.[33] Polarography of an acetonitrile solution of the dicobalt dication showed two reversible reductions separated by 880 mV,[95] somewhat larger than the separation between the two oxidations of the diiron complex in the same solvent. This larger separation may be due to the greater ligand character of the frontier orbitals of cobaltocene (e_1*) relative to those of ferrocene (e_2). Essentially the same reason has been suggested to explain why electron exchange is faster between cobaltocene and cobaltocenium than between ferrocene and ferrocenium.[43] INDO calculations sugest that ligand-mediated superexchange should be more efficient in cobaltocene than ferrocene systems.[113] $(Fv_2Co_2)^+$ has been shown to be IR[34] and ESR detrapped;[33,34] a 15-line ESR spectrum is seen, indicative of coupling to two $I = {}^7/_2$ cobalt nuclei. The crystal structure of Fv_2Ni_2 has been determined; unlike that of the diiron analogue, significant bond length alternation is seen; one can envisage a substantial contribution from the resonance form shown in Figure 5b which features bis(η^4-butadiene)nickel(0) units.[112] The magnetic moment of $(Fv_2Ni_2)^+$, both in solution and the solid state, is consistent with the presence of one unpaired electron.[96] Doubt is cast on the origin of near-IR absorptions in bis(fulvalene)dimetal complexes by the observation of such bands in both neutral and dicationic dinickel complexes, as well as in the monocation.[96]

Recently several heterobimetallic species, Fv_2MM' $\{M = Fe, M' = Co; M = Ru, M' = Ni\}$ have been studied.[65,114−116] The iron−nickel species was obtained by reaction of $Fe(C_5H_4C_5H_4Li)_2$ with $Ni(NH_3)_6Cl_2$ and was found to be diamagnetic.[65] The most interesting result is the paramagnetism of $(Fv_2FeCo)^+PF_6^-$,[114−116] the structure of which is very similar to that of $(Fv_2Fe_2)^+PF_6^-$.[115] The magnetic moment was found to be 2.37 μ_B at 295 K and 1.03 μ_B at 77 K, suggesting the simple view of this cation as comprising a cobaltocenium ion and a ferrocene unit to be naïve.

In addition to interest in their intramolecular interactions, bis(fulvalene)dimetal complexes have also attracted attention as components of salts with relatively large and anisotropic electrical conductivities.[117] The size and shape of the bis(fulvalene)dimetal species appears to lead to favorable stacking of planar acceptor anions such as TCNQ (TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane). For example, a pressed pellet of $(Fv_2Co_2)(TCNQ)_3$ has a conductivity of $3 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$; this conductivity may be related to the stacks of partially reduced TCNQ molecules in the crystal structure.[118,119]

3.3. Higher Fulvalene-Based Metallocene Oligomers

Besides the bimetallic species described above, a number of higher nuclearity fulvalene-based metallocene species have been reported. The first preparations of such species led to mixtures of oligo- or poly(ferrocenylene), $H[(C_5H_4)Fe(C_5H_4)]_nH$, with vary-

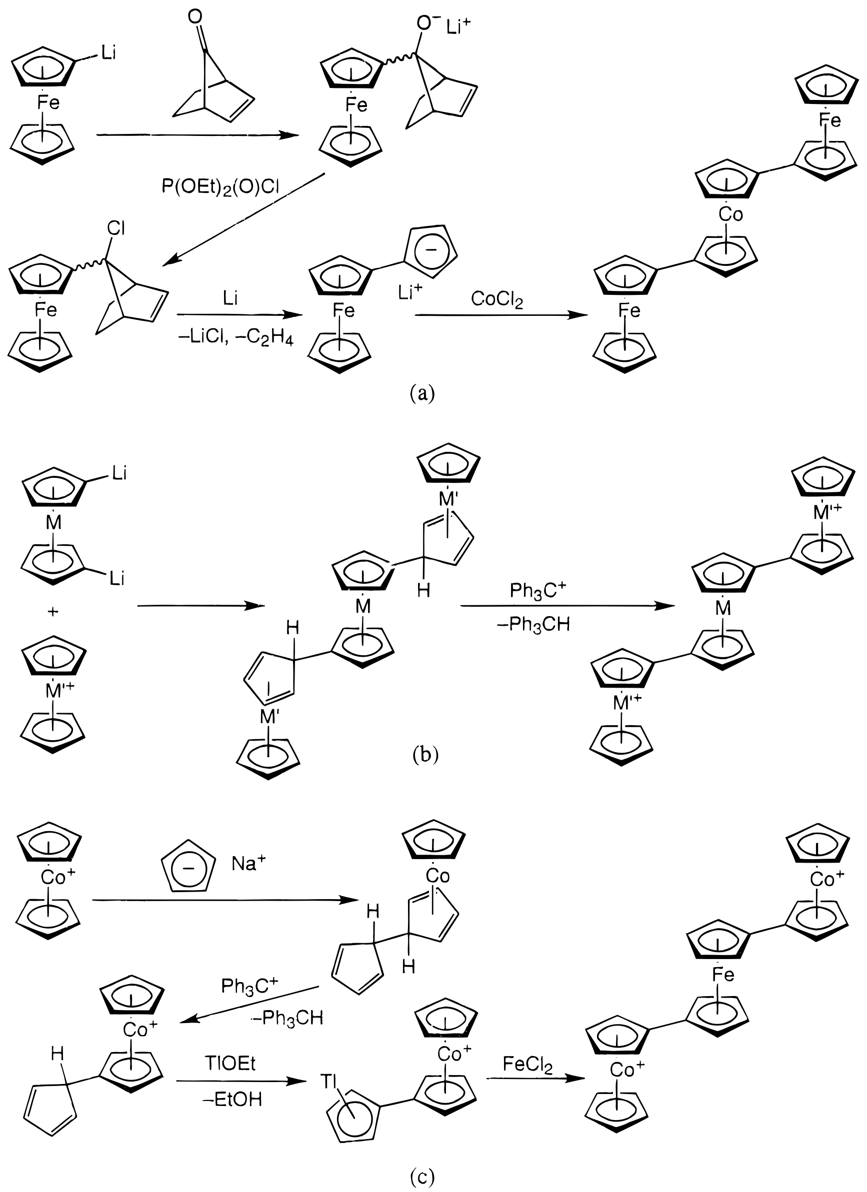


Figure 7. Three alternative syntheses of termetallocenes devised by Schottenberger and co-workers; in b, M = Fe, M′ = Co, Rh; M = Ru, M′ = Co; M = Os, M′ = Co.

ing chain lengths; more recently more selective routes have been designed. Korshak and co-workers reported that di-*tert*-butyl peroxide-induced polymerization of ferrocene to poly(ferrocenylene).[120−122] Later reinvestigation of this reaction showed that the product also contained varying amounts of CH_2 and CH_2OCH_2 linkages, presumably arising from side-reactions with the peroxide, in addition to direct ferrocene−ferrocene bonds.[123,124] Terferrocene, $(FcC_5H_4)_2Fe$, was first isolated in 14% yield (along with 57% biferrocene) from a mixed Ullmann reaction between bromoferrocene and 1,1′-dibromoferrocene.[125] Higher oligomers comprising as many as six ferrocenes were chromatographically separated from the reaction product of a cobalt(II) chloride induced coupling of lithioferrocene;[126] species with up to five ferrocenes were separated from another mixed Ullmann reaction.[127] The reaction of 1,1′-dihaloferrocenes with magnesium is reported to give crystalline poly(ferrocenylene) with molecular masses up to *ca.* 4600 (i.e. *ca.* 25 ferrocene units).[128]

A number of selective syntheses of homo- and heterotermetallocenes have been described by Schottenberger, Schwarzhans, and co-workers; Figure 7 shows three strategies. Figure 7a shows the synthesis of a termetallocene with metal sequence Fe−Co−Fe.[129] An analogous strategy starting with 1,1′-dilithioferrocene has been used to obtain $Fe(FvLi)_2$, the reaction of which with $CpNi^+$ gave the Ni−Fe−Ni species.[65] The strategy shown in Figure 7b has been used to obtain metal sequences Co−Fe−Co, Rh−Fe−Rh, Co−Ru−Co, and Co−Os−Co.[66,130,131] The Co−Fe−Rh termetallocene was obtained from the route in Figure 7b, using lithioferrocene and a mixture of cobaltocenium and rhodocenium hexafluorophosphates; the products were separated by preparative HPLC.[66] The route in Figure 7c provides an alternative route to the Co−Fe−Co system and potentially offers a route to Co−M−Co metal systems where M is not restricted to Fe, Ru, and Os.[129] The crystal structure of the hexafluorophosphate salt of the Co−Ru−Co dicationic termetallocene has been determined. The cation has an unusual conformation in which the fulvalene bridges are almost planar and the two cobaltocenium substituents of the ruthenocene are almost eclipsed, thus stacking the two cobaltocenium units above one another.[131]

The pentanuclear species shown in Figure 8a was obtained as a dication by a route analogous to that in Figure 7b, but using the bis(fulvalene)diiron monocation in place of cobaltocenium or rhodocenium.[131]

Plenio has obtained the substituted termetallocene in Figure 8b from reaction of lithioferrocene with 3,4-dimethylpent-2-enone, followed by lithiation to give a ferrocene-substituted cyclopentadienide, and reaction with iron(II) chloride; attempts to produce analogous species using ferrocene-functionalized indenide species were unsuccessful.[104]

The properties of the higher nuclearity fulvalene complexes have received relatively little attention. The conductivity of various oxidized derivatives of low molecular mass poly(ferrocenylene), along with that of other oxidized polymeric ferrocene compounds, was measured by Cowan *et al.*; however, the materials were otherwise poorly characterized and the polymers probably contained some CH_2 and CH_2OCH_2 bridges.[3] Oxidation of purer material (obtained from 1,1′-dihaloferrocenes and magnesium) with TCNQ led to materials with conductivities as high as $1.4 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$. These were Mössbauer trapped at 78 K, but detrapped at room temperature.[4] The neutral compounds have also been studied by UV PES.[132]

Terferrocene has been shown to undergo three one-electron oxidations, separated by 240 and 370 mV.[133] The rather large separation between the first two oxidations suggests (by comparison with other termetallocenes—*vide infra*) that the central ferrocene undergoes oxidation first. A plausible sequence of oxidations accounting for the relatively large separation of all three waves would be:

$$\mathrm{Fe{-}Fe{-}Fe} \rightleftharpoons \mathrm{Fe{-}Fe^{+}{-}Fe} \rightleftharpoons \mathrm{Fe^{+}{-}Fe{-}Fe^{+}} \rightleftharpoons \mathrm{Fe^{+}{-}Fe^{+}{-}Fe^{+}}$$

Quaterferrocene, $H[(C_5H_4)Fe(C_5H_4)]_4H$, shows four oxidations separated by 200, 250, and 280 mV.[133] Interestingly, the first oxidation potential of such species decreases with increasing oligomerization: thus, relative to ferrocene, biferrocene, terferrocene, and quaterferrocene have first oxidation potentials of −90, −180, and −240 mV, respectively.[133] This result implies that the metallocene substituents of an oxidized metallocene stabilize the cation by donating electron density. In the same study near-IR absorptions were observed for partially oxidized ter- and quaterferrocene. The electrochemistry of various heterotrimetallic species has been studied by Schottenberger and co-workers.[131] The Fe−Co−Fe species shows, as one would expect, oxidation of the cobaltocene at much lower potential than oxidation of the two ferrocenes. The two ferrocene oxidations are separated by only 120 mV, indicating rather weak interactions between the distant metal centers. The Co−M−Co (M = Fe, Ru, Os) species show weak Co−Co interactions; in each case the cobaltocenium/cobalt couples are observed at potentials separated by less than 100 mV. In the Ni−Fe−Ni species any separation there might be between oxidation of the two nickelocene moieties could not be resolved. The cyclic voltammogram of the pentametallic in Figure 8a also shows three oxidations in a 2:1:2 ratio corresponding to removal of one electron from each bis(fulvalene)diiron unit, followed by oxidation of the bridging ferrocene at intermediate potential and removal of the second pair of bis(fulvalene)diiron electrons at higher potential.[131]

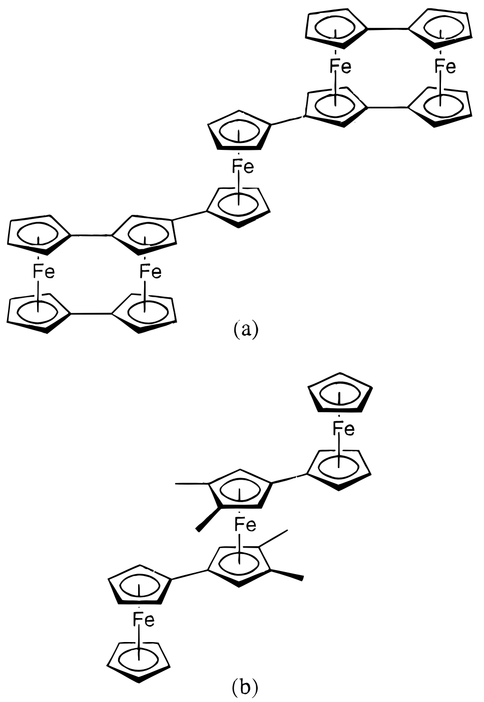


Figure 8. (a) Pentanuclear and (b) trinuclear fulvalene-linked species.

3.4. Some Related Systems

Metal−metal interactions in several other systems closely related to the bimetallocene and bis(fulvalene)dimetal complexes have been studied. Bis(benzenechromium)biphenyl and bis(biphenyl)dichromium provide an interesting comparison with the isoelectronic ferrocene species, $Fv(FeCp)_2$ and Fv_2Fe_2. ESR spectra of fluid solutions of the monocation of (biphenyl){Cr(benzene)}$_2$ revealed hyperfine coupling to all the ligand protons, indicating detrapping on the ESR time scale; solution spectra of $\{(biphenyl)_2Cr_2\}^+$ were inexplicably broad and hyperfine coupling could not be resolved. However, ESR spectra of rigid glasses indicated trapped behavior for both monocations; the mobility of the counterion was suggested to be an important factor.[134] The ESR spectra of the dications of both species were consistent with $S = 1$ configurations ([(biphenyl){Cr(benzene)}$_2$]$^{2+}$ had previously been suggested to be a diradical from ESR evidence;[135] however, this confusion arose from the adventitious presence of the monocation in a sample of the dication).[134] In the case of ([(biphenyl){Cr(benzene)}$_2$]$^{2+}$, the zero-field splitting parameter in the ESR spectra suggest the two rings of the central biphenyl ligand are twisted with a dihedral angle of *ca.* 60°, whereas in the crystal structure of [(biphenyl){Cr(benzene)}$_2$ the biphenyl is planar.[136] (biphenyl){V(benzene)}$_2$ has also been shown to be a triplet by ESR spectroscopy.[137] The paramagnetism of $\{(\text{biphenyl})_2\text{Cr}_2\}^{2+}$ may be contrasted with the diamagnetism of $(\text{Fv}_2\text{Fe}_2)^{2+}$; important factors determining the different behavior may include the greater M−M separation in the former species and the differing electronic configurations of bis(arene)chromium and ferrocenium cations ($e_2{}^4a_1{}^1$ and $a_1{}^2e_2{}^3$ configurations for the respective frontier orbitals[138]).

Two classes of (η^5-cyclopentadienyl)(η^6-arene)iron analogues of biferrocene have been studied; these differ in whether the two cyclopentadienyl or the two arene rings are linked and were first described by Morrison, Ho and Hendrickson.[139] Remarkably the $\text{Fe}^{\text{I}}/\text{Fe}^{\text{II}}$ monocation in the salt $[\text{Fv}\{\text{Fe}(\text{C}_6\text{Me}_6)\}_2]^+\text{BF}_4{}^-$ is not only detrapped on the Mössbauer time scale, but also on the IR time scale;[140] this contrasts to the salts of $\{\text{Fv}(\text{FeCp*})_2\}^+$ which are IR trapped. It is proposed that the differences arise from the different molecular orbitals involved; the partially occupied $e_1{}^*$ HOMO of an Fe^{I} species has more ligand character than the partially occupied e_2 orbital of a ferrocenium ion, thus facilitating stronger superexchange interactions in the former case.[140]

Other related systems in which metal−metal interactions have been studied include biphenyl- and fulvalene-linked metallacarboranes,[141−143] (biphenyl)$\{\text{Cr(CO)}_3\}_2$,[87,88] (biphenyl)$\{\text{Cr(CO)}_2\text{PR}_3\}_2$,[144] (biphenyl)$\{\text{Cr(CO)}_2\}_2(\mu\text{-dppm})$,[144] (biphenyl)$\{\text{Cr(CO)}_2\}_2(\mu\text{-P}_2\text{Me}_4)$,[145] $\text{Fv}\{\text{Mn(CO)}_2\}_2(\mu\text{-dppm})$,[146] $[\text{Fv}\{\text{Fe(dppm)PMe}_3\}_2]^{2+}$,[147] $[\text{Fv}\{\text{Fe(dppe)PMe}_3\}_2]^{2+}$ [147] (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$; dppe = $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$), and $\text{Fv}\{\text{Co(cod)}\}_2$[148] (cod = 1,4-cyclooctadiene).

4. Metallocenes Linked by Carbon Bridges (Excluding Fused-Ring Systems)

4.1. Metallocenes Linked by Saturated Carbon Bridges

A large number of such molecules have been synthesized and several have been studied with respect to metal−metal interactions. Compared to bimetallocenes, linked species with a single carbon bridge show substantially weaker metal−metal interactions. Thus, whereas the two oxidations of biferrocene in acetonitrile are separated by 330 mV, those of diferrocenylmethane, Fc_2CH_2, are separated by only 170 mV.[67]

Higher nuclearity single carbon-bridged species include trimetallics, which were first synthesized as long ago as 1961, when $(\text{FcCHPhC}_5\text{H}_4)_2\text{Fe}$ and the $\{(\text{FcCHPhC}_5\text{H}_4)_2\text{Co}\}^+$ cation were prepared by the addition of 6-ferrocenylfulvene to phenyllithium, followed by the addition of anhydrous iron(II) chloride and cobalt(II) chloride (with an acidic workup in air), respectively.[149] In 1962 the reaction of 6-ferrocenylfulvene and lithium aluminum hydride, followed by addition of iron(II) chloride, to afford the CH_2 bridged species $(\text{FcCH}_2\text{C}_5\text{H}_4)_2\text{Fe}$ was reported.[150] The same species was later isolated by Neuse, Quo, and Howells from a mixture of products arising from the reaction of [(*N*,*N*-dimethylamino)methyl]ferrocene and ferrocene in the presence of zinc chloride and hydrochloric acid.[151] Barr, Lentzner, and Watts also synthesized $(\text{FcCH}_2\text{C}_5\text{H}_4)_2\text{Fe}$, by reduction of the diketone $(\text{FcCOC}_5\text{H}_4)_2\text{Fe}$ with lithium aluminum hydride in the presence of aluminum chloride. The diketone itself was one of many products isolated from the reaction of 1,1′-bis(chlorocarbonyl)ferrocene, ferrocene, and aluminum chloride.[152] However, only recently have metal−metal interactions in such species been studied; we recently synthesized $(\text{FcCMe}_2\text{C}_5\text{H}_4)_2\text{Fe}$ (Figure 9a) from the reaction of $\text{FcCMe}_2\text{C}_5\text{H}_4\text{Li}$ (from 6-ferrocenyl-6-methylfulvene and methyllithium) and $\text{FeCl}_2\cdot1.5\text{THF}$.[153] Cyclic voltammetry in dichloromethane reveals three oxidations separated by 140 and 200 mV. This behavior is qualitatively similar to that for terferrocene (*vide supra*), consistent with an analogous sequence of electron transfers. One would certainly expect the central ferrocene unit would be the first to be oxidized as it bears two, rather than one, electron-donating alkyl substituent. The lower ΔE values than those for terferrocene reflect the longer bridge between metallocene units. The triply oxidized derivative, $\{(\text{FcCMe}_2\text{C}_5\text{H}_4)_2\text{Fe}\}^{3+}(\text{CF}_3\text{SO}_3{}^-)_3$, has also been prepared; variable-temperature magnetic susceptibility measurements indicate no significant magnetic interactions between the $S = {}^1/_2$ ferrocenium centers.[153] The crystal structures of $(\text{FcCMe}_2\text{C}_5\text{H}_4)_2\text{Fe}$ and $\{(\text{FcCMe}_2\text{C}_5\text{H}_4)_2\text{Fe}\}^{3+}(\text{CF}_3\text{SO}_3{}^-)_3$[153] also make interesting comparisons[154] with that of $(\text{FcSiMe}_2\text{C}_5\text{H}_4)_2\text{Fe}$ (*vide infra*).

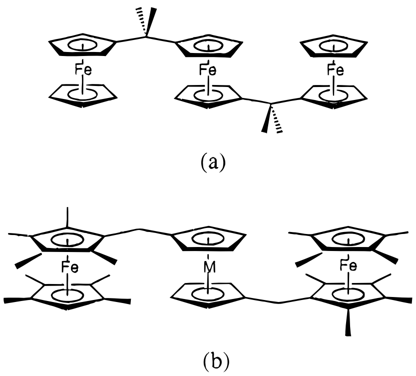
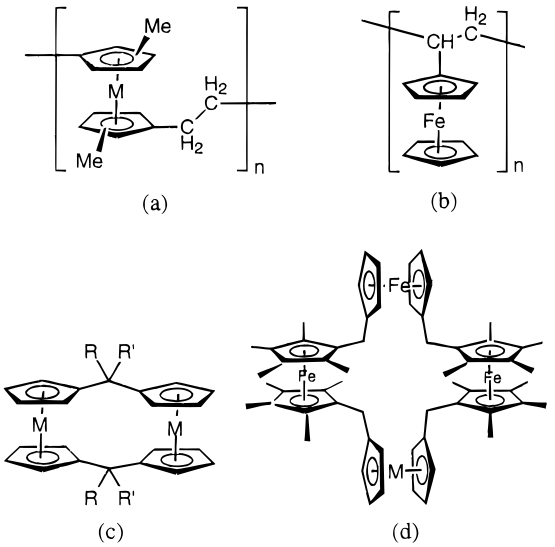


Figure 9. Trimetallics with saturated carbon bridges derived (a) from 6-methyl-6-ferrocenylfulvalene and (b) from 6-(2,3,4,5,1′,2′,3′,4′-octamethylferrocen-1-yl)fulvalene (M = Fe, Co, Cr).

The reaction of 6-(2,3,4,5,1′,2′,3′,4′-octamethylferrocen-1-yl)fulvene and lithium aluminum hydride has been used to obtain analogous trimetallic species with heavily methylated end groups.[153] $(\text{Fc}''\text{CH}_2\text{C}_5\text{H}_4)_2\text{M}$ (Figure 9b) (Fc″ = 2,3,4,5,1′,2′,3′,4′-octamethylferrocen-1-yl; M = Fe, Co, Cr), and a variety of partially and fully oxidized derivatives have been synthesized, affording a variety of sequences of metal centers with spins of 0, ${}^1/_2$, 1, or ${}^3/_2$. Two examples have been structurally characterized.[153,155] Magnetic susceptibility studies revealed no evidence for any intramolecular magnetic interactions in any of the salts. The cyclic voltammogram of the diiron cobalt compound makes an interesting comparison with the fulvalene Fe−Co−Fe species, $(\text{FcC}_5\text{H}_4)_2\text{Co}$, discussed previously. Whereas a separation of 120 mV was reported between the two ferrocene oxidations of the fulvalene compound, no such separation was resolvable for the CH_2-bridged species, reflecting the effect of the longer more insulating bridge.



(a) (b)
(c) (d)

Figure 10. Some metallocene systems with saturated carbon bridges: (a) polymer synthesized by thermal ring opening of a [2]metallocenophane, (b) poly(vinylferrocene), (c) a generalized [1.1]metallocenophane, and (d) a [1^4]metallocenophane.

Longer saturated bridges lead to almost unresolvable separations between oxidations. Thus, no separation was detected between the two oxidations of $FcCH_2CH_2Fc$ in acetonitrile,[67] although a value of 80 mV has been reported for $Fc(CMe_2)_2Fc$ in dichloromethane.[156] Interestingly, the dicobalt analogue of the latter compound, which was obtained by the reaction of $CpCo(\eta^2\text{-}C_2H_4)_2$ with 6,6-dimethylfulvene, has a rather large ΔE of 200 mV, albeit in a different solvent (dimethoxyethane).[156] The electrochemistry of the high molecular weight polymers $[M(C_5H_3Me)_2(CH_2)_2]_n$ (M = Fe, Ru) (Figure 10a), prepared by thermal ring opening of [2]metallocenophanes,[157,158] has also been studied: whereas the ruthenocene polymer, like ruthenocene itself, shows irreversible redox behavior,[158] the iron polymer shows two reversible waves, with $\Delta E = ca.$ 60 mV, corresponding to initial oxidation of alternate iron centers, followed by oxidation of the intervening ferrocenes.[25,159] One of the materials arising from tetracyanoethylene oxidation of the iron polymers shows significant antiferromagnetic interactions, but these may well be between paramagnetic anions and cations, rather than reflecting metal–metal interactions.[159] These species are interesting as examples of high molecular weight polymers with transition metals in the main chain. Other examples of polymers with alternating hydrocarbon and ferrocene sections are known, but are generally of low molecular weight and have not been investigated electrochemically; early examples included species with alternating ferrocenylene and CH_2 units prepared by condensation reactions of $FcCH_2NMe_2$[160] and $FcCH_2OH$.[161] Recently, thermal ring-opening reactions of the [2]metallocenophanes 3,4′-$M(C_5H_3{}^tBu)_2(CMe_2)_2$[162] (M = Fe, Fe^+, Co, Co^+) have led to low molecular weight oligomers comprised of hydrocarbon segments alternating with ferrocene, ferrocenium, cobaltocene, or cobaltocenium units.[163] Poly(vinylferrocene) (Figure 10b), in which the ferrocenyl groups do not form part of the polymer chain, has three saturated carbon atoms between each metallocene; a single oxidation wave is observed, indicating negligible metal–metal interactions in this system.[23,164]

In general, stronger electrochemical metal–metal interactions occur when two linkages are made between two metallocenes and the metals are brought into closer proximity: this effect is general and may also be seen by comparing biferrocene and bis(fulvalene)diiron or singly and doubly acetylene-bridged species. Thus, the series of [1.1]ferrocenophanes represented by Figure 10c (M = Fe) with R = R′ = H, with R = Me, R′ = H, and with R = R′ = Me showed ΔE values in 90% aqueous ethanol of 190, 200, and 300 mV, respectively, whereas, under the same conditions, a value of 100 mV was found for Fc_2CHMe.[165] Unusually, whereas ruthenocene shows an irreversible two-electron oxidation (at 420 mV *vs* ferrocenium/ferrocene in benzonitrile), [1.1]ruthenocenophane (Figure 10c, M = Ru, R = R′ = H) shows a *reversible* two electron oxidation at −120 mV *vs* ferrocenium/ferrocene in benzonitrile.[166a] A diamagnetic dication can be obtained by chemical oxidation; however, the ^1H NMR spectrum does not appear to be consistent with either a symmetric Ru–Ru-bonded species or with a Ru^{II}/Ru^{IV} species.[166a] A crystal structure indicated a Ru–Ru-bonded species, the unusual conformation of which explained the NMR data.[166b]

In general near-IR intervalence absorptions are not observed in the monooxidized derivatives of ferrocenes with insulating hydrocarbon bridges. Thus, $(Fc_2CH_2)^+$ shows no near-IR band[167] and it is now accepted, after some controversy, that [1.1]ferrocenophane monocations do not exhibit a band assignable to intervalence transfer.[168,169] However, $(Fc_3CH)^+$, in which the ferrocenes are presumably constrained to be rather closer to one another than the ferrocenes in the low energy conformations of $(Fc_2CH_2)^+$, does show an intervalence band.[167] Thus, most linked metallocenes with saturated carbon bridges belong to class I in Robin and Day's classification; the only interactions detected are at the electrochemical level and can be attributed to electrostatic and inductive effects. However, some confusion was caused by early papers describing studies on salts of [1.1]ferrocenophanes (Figure 10c, also known as [1^2]metallocenophanes). Most remarkably it was reported that the $DDQH^-$ (DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone) salt of the 1,13-dimethyl[1.1]ferrocenophane (Figure 10c, M = Fe, R = Me, R′ = H) dication was diamagnetic[36] and showed unusual Mössbauer spectra.[36,170] Later reinvestigations[168,169] of the 1,13-dimethyl[1.1]ferrocenophane system showed that the monocation belonged to class I: it was found to be ESR and Mössbauer trapped and showed no near-IR band. The magnetic moment was also consistent with an ESR-trapped structure and the crystal structure of the triiodide showed distinct Fe^{II} and Fe^{III} sites. The dication was shown by ESR spectroscopy to be paramagnetic, with small magnetic exchange interactions between metal centers. The diamagnetic dication previously observed was probably a carbocation arising through hydride abstraction from the bridging atom, $(C_5H_4C^+MeC_5H_4)_2Fe_2$, rather than a ferrocenium species. Such carbocations have since been shown to be particularly stable.[117,171,172]

Several other aspects of [1.1]ferrocenophane chemistry have attracted interest. The conformational flexibility of [1.1]ferrocenophane itself has been studied by variable-temperature NMR spectroscopy,[117,173] X-ray crystallography,[174,175] and molecular mechanics models.[176] Crystal structures of no fewer than three isomers of $[(C_5H_4)_2CHMe]_2Fe_2$ have been reported.[177−180] Reaction of [1.1]ferrocenophanes and *n*-butyllithium leads to removal of a proton from one of the ferrocenophane's bridges; the resulting carbanions are unusually stable and have been studied by NMR,[181−183] theoretically[184] and crystallographically.[185] [1.1]Ferrocenophanes have also attracted attention as hydrogen generation catalysts; protonation of these species in strong acids is followed by loss of dihydrogen to leave diferrocenium salts, which can then be reduced back to the parent species, for example, by tin.[186−189]

The [1^n]metallocenophanes with $n > 2$ have also been studied; these comprise *n* metallocenes arranged in a ring; an example of a [1^4]metallocenophane is shown in Figure 10d. The nomenclature of *n* metallocenophanes has been diuscussed by Mueller-Westerhoff.[117] The first examples of such molecules was the series of [1^n]ferrocenophanes $[(C_5H_4)_2CH_2]_nFe_n$; the [1^2], [1^3], [1^4], and [1^5] species, in an approximate ratio of 1:2:3:4, were isolated in *ca.* 18% overall yield from the reaction of $(LiC_5H_4)_2CH_2$ with anhydrous iron(II) chloride.[190] An alternative strategy has been used by Mueller-Westerfhoff's group; the reaction of 1,1′-bis(cyclopentadienylmethyl)ferrocene or 1,1′-bis(cyclopentadienylmethyl)ruthenocene dianions with metal halides yields [1^n]-metallocenophanes with even *n* only. Thus, the reaction of the bis(cyclopentadienylmethyl)ferrocene dianion with $FeCl_2{\cdot}1.5THF$ gave, with careful control of the reaction conditions, a 40% yield of [1^2]ferrocenophane and a 2.1% yield of [1^4]ferrocenophane.[191] $[(C_5H_4)_2CH_2]_4Ru_4$,[192] $[(C_5H_4)_2CH_2]_4Ru_2Fe_2$,[192] and $\{[(C_5H_4)_2CH_2]_4Fe_2Co_2\}^{2+}(PF_6^-)_2$[117] have been obtained in analogous reactions. The disordered crystal structure of the diiron−dicobalt dicationic species has, however, been described briefly in a review.[117] We have recently described another route to [1^4]metallocenophanes: a trimetallocene functionalized at each terminal ferrocene with a cyclopentadienyl group gives [1^n]metallocenophanes where *n* is a multiple of four. We have isolated the triiron cobalt species shown in Figure 10d (M = Co) and its tetrairon analogue (Figure 10d, M = Fe).[193] Despite the potentially interesting metal−metal interactions possible in [1^n]metallocenophanes, few studies in these areas have been carried out. The electrochemistry of our tetrairon species (Figure 10d, M = Fe) shows two waves corresponding to successive oxidation of methylated and nonmethylated metallocenes. The oxidation of the unmethylated metallocenes occurs at slightly higher potential than ferrocene itself (+40 mV *vs* ferrocenium/ferrocene), despite bearing two alkyl bridges, reflecting the proximity of the two methylated ferrocenium cations.

A second method of inducing somewhat larger metal−metal interactions than those in singly bridged species, at least at the electrochemical level, has been demonstrated by Köhler and co-workers who have designed a ligand in which two cyclopentadiene groups are held at a fixed angle (*ca.* 120° between the planes of the two rings) by a rigid insulating bridge.[194] Deprotonation of this ligand, followed by reaction with sodium cyclopentadienide and iron(II) chloride, afforded the three iron complexes shown in Figure 11.[195] The crystal structures of the two bimetallic species have been determined; the intramolecular iron−iron distances are 6.11 and 5.34 Å for the *syn*,*syn* (Figure 11a) and *syn*,*anti* (Figure 11b) isomers, respectively. In both cases the bridges and the ferrocenes are somewhat distorted from their idealized geometries; these distortions lead to greater iron−iron distances than one might otherwise expect. Presumably the rigidity of the bridges will lead to similar metal−metal distances in solution; however, ΔE values of 160 and 140 mV (in THF; 200 and 195 mV in propionitrile) are found for the *syn*,*syn* and *syn*,*anti* isomers, respectively, i.e. greater interactions are observed in the species with the larger Fe−Fe separation. It is possible that the relative orientation of the two metallocene units is important. Different degrees of delocalization or superexchange in the two species has also been suggested. The trimetallic species (Figure 11c) shows three waves in THF separated by 190 and 100 mV. This behavior is qualitatively similar to that of terferrocene, of $(FcCMe_2C_5H_4)_2Fe$ (Figure 9a) and of the face-to-face naphthalene trimetallic discussed below; presumably a similar sequence of oxidations occurs. One would certainly expect the central ferrocene to be oxidized first as it bears four, rather than two, electron-donating alkyl substituents.

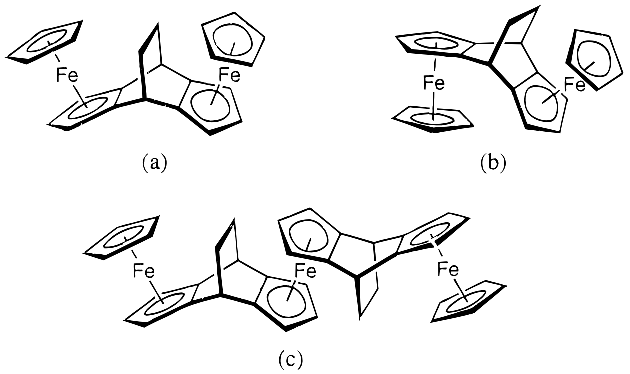


Figure 11. Rigidly bridged ferrocenes prepared by Köhler and co-workers.

Another type of linked metallocene system with rigid insulating bridges is the cobaltocenium species produced by protonation of (1,3,5,7-tetra-*tert*-butyl-*s*-indacene)$(CoCp)_2$; this chemistry is discussed further in the section on fused-ring metallocenes.[196,197]

4.2. Metallocenes Linked by Unsaturated Carbon Bridges

Ferrocenes linked by olefinic bridges show slightly larger metal−metal interactions than those with analogous saturated bridges. Thus, whereas only one two electron oxidation wave was observed in acetonitrile in a polarographic study of $FcCH_2CH_2Fc$,[67] the *cis* and *trans* isomers of $(C_5H_4Et)Fe(C_5H_4CMe{=}CMeC_5H_4)Fe(C_5H_4Et)$ each show two one-electron

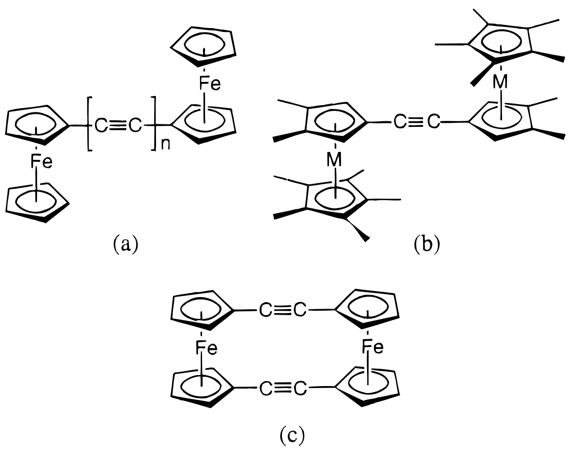


Figure 12. Some acetylene-bridged metallocenes.

oxidation waves in the same solvent, separated by 150 mV[198] (ΔE for *trans*-FcCH=CHFc is reported to be 120 mV in dichloromethane[199]). The monooxidized olefin-bridged species also show near-IR absorptions (although interpretation of such bands is complicated by interconversion of the *cis* and *trans* isomers of the monocations),[198] as do monooxidized FcCH=CHFc and FcCPh=CPhFc (as isomeric mixtures),[167] whereas observation of intervalent charge transfer is very rare in compounds with saturated carbon bridges. The series of polyene-bridged bimetallics $\mathrm{Fc(CH{=}CH)}_n\mathrm{Fc}$ ($n = 1-6$, all *trans*) has recently been studied. The compounds were synthesized by Wittig methodolgies. Peak separations of 170, 129, and *ca.* 100 mV were observed in dichloromethane for $n = 1$, 2, and 3 species respectively; separations were not resolved in the longer species. The coupling energy was estimated by Hush analysis of the monooxidized species to decrease from 0.061 to 0.022 eV as n increased from 1 to 6.[53] Recently polymers, albeit of low molecular weight, with alternating ferrocene and olefin units have been described, although no studies on the metal−metal interactions in these materials have yet been reported. Species of formula Ac-$[(\mathrm{C_5H_4})\mathrm{Fe}(\mathrm{C_5H_4})\mathrm{CMe{=}CMe}]_n(\mathrm{C_5H_4})\mathrm{Fe}(\mathrm{C_5H_4})\mathrm{Ac}$ (Ac = acetyl) were obtained by the titanium-promoted self-condensation of 1,1′-diacetylferrocene.[200] Another type of olefin-bridged species is represented by $\{\mathrm{FcC}(=\mathrm{CH_2})\mathrm{C_5H_4}\}_2\mathrm{Fe}$; in dichloromethane three oxidation waves are observed, separated by 260 and 120 mV. The magnitudes of these separations are close to those found for $(\mathrm{FcCMe_2C_5H_4})_2\mathrm{Fe}$ (*vide supra*), but in this case the separation between the first two oxidations is the largest, whereas for the $\mathrm{CMe_2}$-bridged compound this is the smaller separation.[153]

The alkene bridged ruthenocenes *trans*-$\mathrm{Cp^*Ru(C_5H_4\text{-}CH{=}CHC_5H_4)RuCp^*}$ and *trans*-$\mathrm{CpRu(C_5Me_4CH{=}CHC_5Me_4)RuCp}$ undergo a two-electron oxidation accompanied by a valence bond rearrangement to give species with bridging η^6:η^6-pentafulvadiene ligands.[201]

Several acetylene-bridged metallocene systems have been reported; examples are shown in Figure 12. Many preparations of such species rely on coupling reactions of substituted ferrocenes. For example, the molecule in Figure 12a with $n = 1$ was obtained by the reaction of FcC≡CCu and FcI.[202] The analogous reaction of 1,1′-diiodoferrocene with FcC≡CCu gave the trimetallic $(\mathrm{FcC{\equiv}CC_5H_4})_2\mathrm{Fe}$,[202] which had previously been synthesized by a rather more elaborate route.[203] The species shown in Figure 12c, [2.2]ferrocenophane-1,13-diyne, was obtained from self-coupling of the cuprous salt of 1-ethynyl-1′-iodoferrocene (which was prepared in a rather complex series of steps).[204] The species in Figure 12b were obtained by a different strategy: reaction of a preformed acetylene-bridged dicyclopentadienyl ligand with a metal half-sandwich synthon. This strategy may, in principle, be extended to a wide range of metals. Indeed, both the diiron and dinickel complexes have been prepared.[205] The third order nonlinear optical properties of acetylene-bridged ferrocenes have attracted attention; a recent example synthesized (by a coupling reaction) for such purposes is the species represented by Figure 12a where $n = 4$.[206]

At the electrochemical level acetylene bridges appear to lead to similar metal−metal interactions to those found in C=C-bridged systems, these being somewhat larger than those found in systems with saturated bridges with equivalent numbers of carbon atoms in the bridge. Thus, the two oxidations of diferrocenylacetylene (Figure 12a, $n = 1$) are separated by 130 mV in dichloromethane.[207] In the same solvent values of 160 and 265 mV were found for the species in Figure 12b with M = Fe and Ni, respectively.[205] The larger separation for the nickel species may reflect the greater ligand character of the frontier orbitals of a nickelocene ($\mathrm{e_1}^*$ *vs* $\mathrm{e_2}$ in ferrocene). For 1,4-diferrocenylbutadiyne (Figure 12a, $n = 2$) the increased bridge length leads to a poorly resolved ΔE of *ca.* 100 mV,[207] while for [2.2]ferrocenophane-1,13-diyne (Figure 12c) ΔE is 355 mV.[207]

The structures of 1,4-diferrocenylbutadiyne[206] and the methylated acetylene-bridged nickel complex (Figure 12b, M = Ni) have been determined:[205] whereas the diiron species has normal ferrocene geometry, the structure of the nickel compound shows evidence for some contribution from a resonance form with η^4-coordination of the bridged ligand. Nonetheless, a solution magnetic moment determination suggested four unpaired electrons for the nickel compound.[205]

The monocation of diferrocenylacetylene shows a near-IR absorption assigned to intervalence electron transfer.[207,208] Unfortunately its ESR spectra are complicated by the presence of equilibrium amounts of the dication (due to the low comproportionation constant attested to by the low value of ΔE).[207] The triiodide is Mössbauer trapped.[34,208] The dication shows unusual ESR spectra and temperature-dependent magnetic susceptibility (the effective magnetic moment per iron falls from 2.52 μ_B at 286 K to 1.39 μ_B at 5 K), which have been attributed to weak intramolecular antiferromagnetic exchange interactions.[34] Near-IR transitions were also observed for the electrochemically generated monocation of diferrocenylbutadiyne.[207] However, the behavior of the [2.2]ferrocenophane-1,13-diyne monocation is reminiscent of that of bis(fulvalene)diiron: the cation is detrapped on Mössbauer,[34,208] ESR[207] (a rhombic spectrum characterized by $g = 1.88$, 1.98, and 2.57 is reported for an electrochemically generated sample,

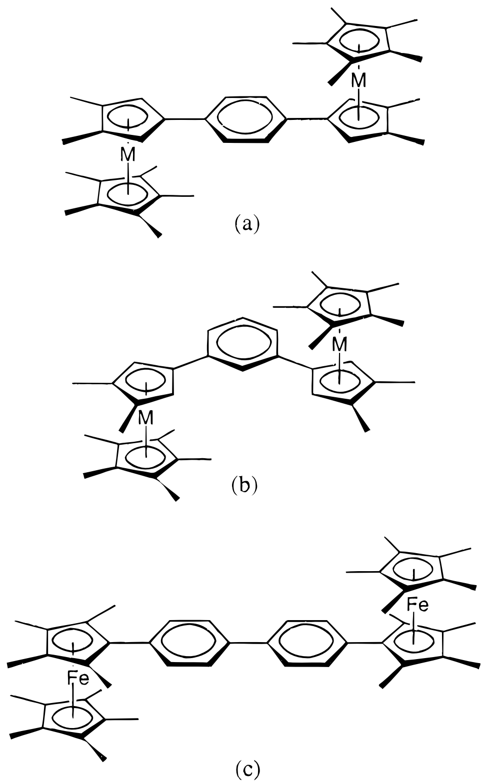


Figure 13. Some phenylene-bridged metallocenes.

while **g** values of 1.87, 2.00, and 2.27 are reported for bis(fulvalene)diiron picrate[38]), and IR time scales.[34] Since there is too large a separation between the metals in this cation to allow direct metal–metal interaction, its delocalized behavior is attributed to ligand-mediated effects. No data have yet been reported for the dication.

Examples of phenylene-bridged metallocenes in which metal–metal interactions have been studied are shown in Figure 13; in general the synthesis of these species involves the reaction of a phenylene-bridged cyclopentadienyl ligand with an appropriate metal half-sandwich source. The electrochemistry of $\{Cp^*Fe(C_5H_2Me_2)\}_2$-*p*-C_6H_4 (Figure 13a, M = Fe), $\{Cp^*Fe(C_5Me_4)\}_2$-*p*-C_6H_4, and the biphenylene-bridged species in Figure 13c and its analogue in which the terminal Cp* rings are replaced with Cp rings was compared in a study by Bunel *et al.*[209] The first two compounds showed two reversible oxidations separated by *ca.* 120 mV, whereas in the biphenylene-bridged species no separation was resolvable. In another study the *m*-phenylene-bridged diiron species (Figure 13b, M = Fe) was shown to show a separation of 60 mV.[37] Similar comparisons of the *para* and *meta* dinickel complexes (Figure 13, parts a and b, respectively, M = Ni) again reveal stronger interactions in the *para* case despite the increased metal–metal distance, although no distinctions between first and second oxidations were discernible in the dicobalt species.[37] Another example with a bridge containing olefinic and phenylene sections, $FcCH{=}CHC_6H_4$-$CH{=}CHFc$, has been studied electrochemically; the length of the bridge meant no separation was resolvable between the oxidation potentials of the two ferrocenes.[67] This type of compound has also attracted interest as third-order nonlinear optical materials, for a recent example see the work of König *et al.*[210] Species such as 1,8-diferrocenylnaphthalene are related to the phenylene bridged species. However, whereas X-ray crystallography shows the cyclopentadienyl and phenylene units of the bridging ligand to be essentially coplanar in the dinickel species with the molecular structure shown in Figure 13b,[37] the metallocenes are forced out of conjugation in the naphthalene-bridged complexes and metal–metal interactions are believed to take place between the cyclopentadienyl π-orbitals of neighboring metallocenes.[211] Thus, these species are classed as face-to-face metallocenes (*vide infra*).

The magnetic susceptibility of the phenylene-bridged metallocenes of Figure 13a,b has also been studied: as expected the neutral diiron species and the dicobalt dications are diamagnetic.[37] The behavior of the isoelectronic neutral dicobalt species and dinickel dications is consistent with an antiferromagnetic ground state and a thermally populated excited state with either two independent $S = {}^1/_2$ centers or an $S = 1$ configuration. In any case the antiferromagnetic coupling is stronger in the *para* species (effective magnetic moments at 300 K of 2.49 and 2.15 μ_B for the *para* and *meta* isomers respectively). The neutral dinickel species also appear to feature some intramolecular antiferromagnetic interactions, although *inter*molecular interactions are a complicating factor.

Another interesting class of linked metallocene system with an unsaturated bridge is that where the bridge is a carbenium ion. The diferrocenylmethyl cation, $(FcCHFc)^+$, was first reported in 1959,[212] but only recently have there been any studies on the metal–metal interactions in such species. In addition to studying the electrochemistry of the known species $(FcCHFc)^+$ and $\{Fc(CH)_3Fc\}^+$, Tolbert and co-workers have synthesized a series $Fc(CH{=}CH)_m$-$CH_2(CH{=}CH)_mFc$, where $m = 1$, 2, and 3, and converted these to the corresponding polymethine cation bridged species $\{Fc(CH)_nFc\}^+$, where $n = 5$, 9, and 13, respectively, by treatment with trityl tetrafluoroborate.[213] Remarkably, all these species were all found to exhibit electrochemical peak separation; ΔE values of 330, 180, 140, 70, and 40 mV were found for the $n = 1$, 3, 5, 9, and 13 cations, respectively. This type of bridge evidently promotes much stronger metal–metal interaction than a simple olefinic bridge; the polymethine cation species with up to five atom bridges show peak separation greater than or comparable to $FcCH{=}CHFc$ in the same solvent. The synthesis of other interesting carbocation-linked species has been recently described by Schottenberger and co-workers.[214]

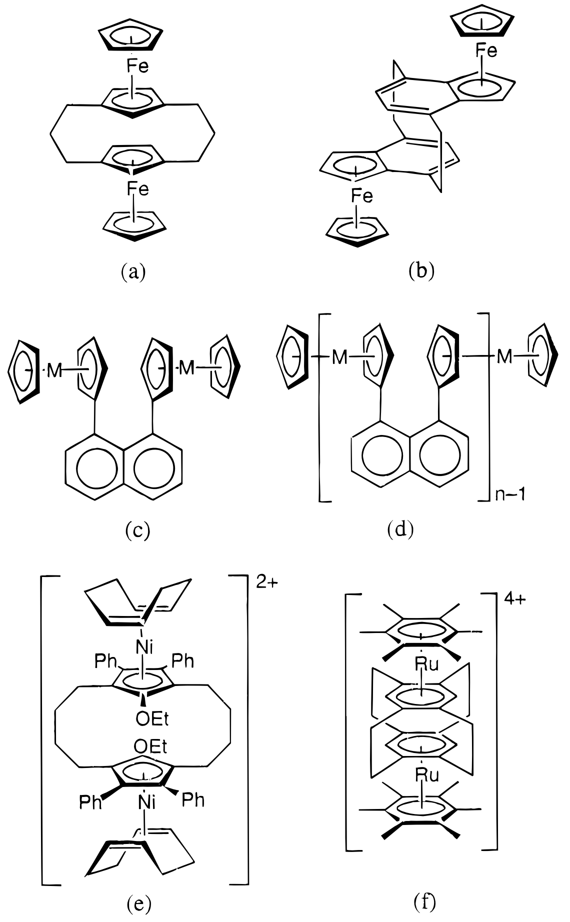
Also formally belonging to the class of linked metallocenes with unsaturated carbon bridges are many ketone-bridged ferrocenes. Despite the abundance of these species, very few of these species have been investigated with respect to metal–metal interactions. However, it is worth noting that the monocation of diferrocenylketone, $Fc_2C{=}O$, shows a near-IR intervalence transition for which through-bond contributions are believed to be important.[167]

4.3. Face-to-Face Metallocenes

Several systems have been designed where the interactions between metallocenes takes place through the cyclopentadienyl ring of one metallocene being stacked above that of another metallocene. For example, transannular interactions between the π-electrons of the two ferrocenes of the compound in Figure 14a are believed to be responsible for the differences between its UV/vis spectrum and those of unbridged model compounds.[215] Hopf and Dannheim have reported the bridged indenyl compound in Figure 14b, as well as a related trimetallic specie.[216]

Rosenblum and co-workers have studied the naphthalene-bridged systems in Figure 14c,d. The diiron compound (Figure 14c, M = Fe), which was synthesized by the palladium-catalyzed coupling of FcZnCl and 1,8-diiodonaphthalene, undergoes two reversible oxidations separated by 195 mV in dichloromethane (or by 150 mV in acetonitrile).[217] Interestingly the first oxidation takes place at considerably lower potential than that of either ferrocene or 1-ferrocenylnaphthalene (-158 mV relative to the 1-ferrocenylnaphthalene couple in dichloromethane). The monocation, which shows a near-IR intervalent transition in solution, is trapped on the IR time scale;[217] this is consistent with a structure determination of the tetrafluoroborate salt, which reveals distinct ferrocene and ferrocenium sites.[211] The bimetallic ruthenium species has also been formed in an analogous reaction of $CpRu(C_5H_4ZnCl)$.[211]

Low molecular weight oligomers ($M_w = 6000$, $M_n = 3600$) were obtained by the palladium-catalyzed condensation of $Fe(C_5H_4ZnCl)_2$ or $Ru(C_5H_4ZnCl)_2$ with 1,8-diiodonaphthalene[218] and are shown in Figure 14d (some material with different end groups was also obtained). Some of the species were separated chromatographically; the cyclic voltammogram of the triiron species in dichloromethane shows three well-separated waves ($\Delta E = 165$ and 131 mV). This behavior is similar to that of several other trimetallics (*vide supra*) and may indicate an analogous sequence of oxidations. The first oxidation also occurs at significantly lower potential than the bimetallic species (-252 mV relative to 1-ferrocenylnaphthalene), indicating some delocalization of charge in the partially oxidized species, either via interaction of the cofacial π-orbitals of adjacent metallocenes, or via the naphthalene bridges. The latter possibility seems somewhat unlikely, as the ferrocenes are twisted out of conjugation with the naphthalene π-system.



(a) (b)

(c) (d)

(e) (f)

Figure 14. Some face-to-face metallocenes and related compounds.

More recently another route to naphthalene-bridged face-to-face metallocene polymers (Figure 14d) has been developed; both polymers with only ferrocenes and polymers with alternating ferrocene and nickelocene units have been obtained. Use of long-chain alkyl substituents to solubilize the growing polymer chains has allowed the synthesis of high molecular mass species ($M_n = 14\,363$, $M_w = 18\,398$).[219]

Metal−metal interactions have been studied in several other non-metallocene face-to-face linked sandwich compounds. The face-to-face linked CpNi(cod) (cod = 1,5-cyclooctadiene) species in Figure 14e shows two reversible one-electron reductions separated by 240 mV;[220] this is a rather large separation for a compound with such long insulating bridges and thus illustrates the interactions possible when organometallic sandwich complexes are held in a face-to face stacked arrangement. An analogously bridged Cp*Co(η^4-cyclopentadieneone) complex shows two reversible oxidations with $\Delta E = 150$ mV.[220] Gleiter *et al.* have studied a series of compounds where two CpCo(butadiene) units are linked by four $(CH)_n$ (n = 3, 5, 7) bridges between the two butadiene moieties. In all cases discernable separation of oxidation waves was observed; for the $n = 3$ member the separation was as large as 445 mV in dichloromethane.[221] In the bis(areneruthenium)cyclophane species in Figure 14f two reversible two-electron reductions were found, each corresponding to reduction of one ruthenium center and shift from η^6:η^6- to η^6:η^4-coordination, separated by 533 mV.[222,223] Another related system is that of ([2_3]paracyclophane){$Cr(CO)_3$}$_3$ where weak interannular interactions have been studied by ^1H NMR, IR, and UV spectroscopies.[224]

5. Metallocenes Linked through Heteroatoms

5.1. Metallocenes Linked by Silicon Bridges

A wide range of silicon-bridged metallocenes has been synthesized; representative examples are shown in Figure 15. The intermetallic interactions in many of these molecules have been studied by electrochemistry; a few examples have also been studied by other techniques.

Dement'ev *et al.* have elegantly shown that metal−metal interaction decreases with increasing bridge length in the series of silicon-bridged bimetallics, Fc_2-

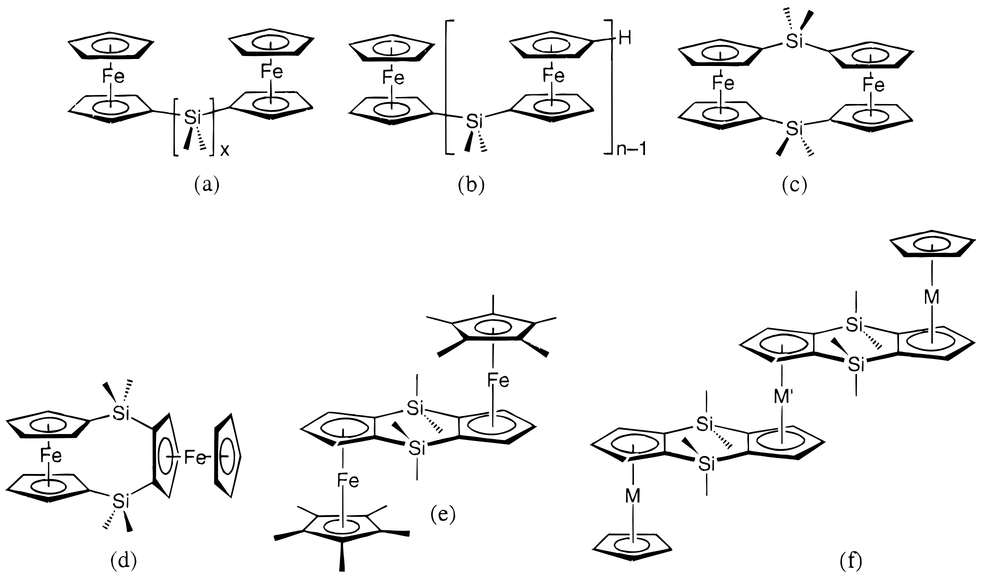


Figure 15. Selected linked metallocenes with $SiMe_2$ bridges.

$(SiMe_2)_x$, shown in Figure 15a (these were prepared by reaction of FcLi with $Cl(SiMe_2)_xCl$).[225] Cyclic voltammetry in dichloromethane showed ΔE values of 150, 110, 80, and 0 mV for the $x = 1$, 2, 3, and 6 members of the series, respectively. Significantly, for a given value of x, ΔE is greater for the Si species than for its carbon-bridged analogue (*vide supra*), despite the longer metal−metal distances brought about by the greater length of C−Si and Si−Si bonds. These data indicate that there is at least some through-bond, as well as through-space, contribution to the metal−metal interactions in silicon-bridged species. A related linked species is the ferrocenyl substituted [1]ferrocenophane, $Fe(C_5H_4)_2SiMeFc$,[226,227] for which two reversible oxidations have been observed.[226] Although metal−metal interactions have not been studied in $[Fe(C_5H_4)_2]_2Si$, in which two [1]ferrocenophanes share the same bridging atom,[228] interesting results might be anticipated by comparison with those for related bis(arene)vanadium species. Molecules studied by Elschenbroich and coworkers comprise two bis(arene)vanadium analogues of [1]silaferrocenophanes in which either the two silicons are linked by a direct bond[229] or form opposite corners of a disilacyclobutane.[230] In both types of compound 15-line ESR spectra are observed, indicating the electron exchange coupling constant to be much greater than the ^{51}V hyperfine coupling constant.

Rulkens *et al.* have studied the electrochemistry of the oligomers in the series $Fc(SiMe_2C_5H_4FeC_5H_4)_{n-1}H$ (Figure 15b) with $n = 2-8$.[231] The oligomers were prepared by the reaction of lithioferrocene with the strained ferrocenophane $Fe(C_5H_4)_2SiMe_2$, followed by a hydrolytic workup, and could be separated by column chromatography. Similar oligomeric materials have also been prepared from dilithioferrocene and dialkyldichlorosilanes.[232] For the $n = 2$ member, which is of course the same as the $x = 1$ member of the series in Figure 15a, two one-electron oxidation waves were observed, separated by 150 mV in 1:1 CH_2Cl_2/MeCN, consistent with the results of Bocarsly *et al.*[233] and of Dement'ev *et al.*[225] For the trimeric ($n = 3$) species two waves were observed in a 2:1 ratio, separated by 260 mV. These data were interpreted as indicative of oxidation of the two terminal ferrocenes at the same potential, as they are too far apart to interact with one another, followed by oxidation of the central ferrocene. The increased value of ΔE in the trimetallic species relative to that in the bimetallic reflects the fact that the third electron must be removed adjacent to *two* cations, whereas in the $n = 2$ compound there is only one neighboring cation, making withdrawal of the second electron more difficult. The $n = 4$ member has waves in the ratio 2:1:1, again consistent with the oxidation of two well-separated ferrocenes, followed by oxidation of the intervening species at higher potential. The $n = 8$ member has waves in the ratio 4:1:3 with separations of 140 and 100 mV. The $n = 3$ member was also synthesized more rationally by Pannell *et al.* and slightly different electrochemical results reported; three waves were observed in dichloromethane.[226] It is possible that this is because the change of solvent leads to a subtle change in the balance between initial oxidation of the two terminal ferrocenes or of the one central ferrocene. More recently the mixed iron−ruthenium−iron compound, $(FcSiMe_2C_5H_4)_2Ru$, has also been synthesized.[234]

The electrochemical behavior observed for the $n = 8$ member of the series in Figure 15b approaches that of high molecular weight poly$[Fe(C_5H_4)_2SiMe_2]$ (i.e. a member of the series with very large n), where two waves are observed separated by 210 mV (in dichloromethane).[25] The crystal structures of members of the series have also served as models for understanding the preferred conformations of the polymers.[154,226,231,235,236] Manners has recently published several surveys where detailed coverage of the synthesis and properties of these polymers (which have, despite some ambiguity been dubbed, poly(ferrocenylsilanes)), and those of related polymers, may be found.[237−240] A wide range of such high molecular weight polymers, poly$[Fe(C_5H_4)_2SiRR']$, has been obtained by thermal,[226,227,241−246] anionic,[231,247,248] γ-radiation-initiated,[249] and noble metal complex-catalyzed[246,250,251] ring-opening polymerization of strained

[1]ferrocenophanes, $Fe(C_5H_4)_2SiRR'$. Polymers have also been prepared where the cyclopentadienyl rings bear trimethylsilyl groups[252] or various numbers of methyl groups.[253] The thermal ring-opening reaction is believed to occur by a mechanism involving heterolytic C–Si cleavage.[254] The variety of polymers that have been obtained exhibit a wide range in their solubility, rheological, and electrochemical properties. Thus, poly[$Fe(C_5H_4)_2SiPh_2$] and poly[$Fe(C_5Me_4)_2SiMe_2$] are insoluble in all organic solvents tried,[227,241,253] whereas poly[$Fe(C_5H_4)_2SiMe_2$] is readily soluble in common solvents such as benzene, THF, and dichloromethane.[241,243] Glass transition temperatures in the series poly[$Fe(C_5H_4)_2SiR_2$] have been found to decrease with increasing length of the organic side chain, R.[243] In general two oxidation waves are observed for these materials (three[227] or four[226] in poly[$Fe(C_5H_4)_2SiFcMe$], which also has pendant ferrocenyl side groups); these can be attributed to oxidation at alternating metal centers, followed by oxidation of the intermediate iron centers. The separation between the two oxidation waves, ΔE, has been found to be dependent on the nature of the substituents at silicon.[25,227,242] For example, ΔE values of 210, 270, 290, and 290 mV have been measured for poly[$Fe(C_5H_4)_2SiMe_2$], poly[$Fe(C_5H_4)_2SiEt_2$], poly[$Fe(C_5H_4)_2Si^nBu_2$], and poly[$Fe(C_5H_4)_2Si(n\text{-hexyl})_2$], respectively; alternative steric and electronic arguments to explain this trend have been proposed.[25] The bis(arene)chromium complex, $Cr(C_6H_5)_2SiMe_2$, is related to strained [1]ferrocenophanes and has been converted to analogous polymers via thermal copolymerization with $Fe(C_5H_4)_2SiMe_2$ and via anionically initiated polymerization.[255] However, no studies relating to the metal–metal interactions in these polymers have been reported.

Doped samples of poly(ferrocenylsilanes) have been found to be trapped on the Mössbauer time scale and to show low electrical conductivities.[256] However, Hmyene *et al.* have claimed that low molecular mass oligo(ferrocenylsilanes) undergo reaction with tetracyanoethylene to give ferromagnetic materials of composition $[Fe(C_5H_4)_2SiR_2]_n(TCNE)_n$ (R = Me, *n*-hexyl) containing Fe^{II} and Fe^{III} sites which are Mössbauer trapped at low temperature but detrapped at room temperature.[257] Mössbauer detrapping is very surprising in these systems given the relatively low level of electrochemical metal–metal interaction observed in these $SiMe_2$-bridged ferrocenes. We have investigated the reactions of the high molecular weight polymers, $[Fe(C_5H_4)_2SiMe_2]_n$, $[Fe(C_5H_4)_2Si^nBu_2]_n$, $[Fe(C_5H_3Me)_2SiMe_2]_n$, $[Fe(C_5H_4)(C_5Me_4)SiMe_2]_n$, and $[Fe(C_5Me_4)_2SiMe_2]_n$, and the small molecule model $(FcSiMe_2C_5H_4)_2Fe$ with TCNE; only the ring-methylated compounds underwent reaction. Magnetic studies of the oxidation product of $[Fe(C_5Me_4)_2SiMe_2]_n$ gave no evidence for magnetic interactions, either cation–cation or cation–anion.[253]

The $SiMe_2$-bridged [1.1]ferrocenophane shown in Figure 15c has recently been reported independently by three different groups.[258–260] It has been prepared by two routes: from the reaction of $SiMe_2(C_5H_4Li)_2$ and iron(II) chloride[258,260] and from reaction of $Fe(C_5H_4SiMe_2C_5H_4Li)_2$ (prepared from $Fe(C_5H_4SiMe_2Cl)_2$) and iron(II) chloride.[259] The latter methodology has also permitted synthesis of the mixed iron–ruthenium [1.1]metallocenophane, using $RuCl_2(Me_2SO)_4$ in place of iron(II) chloride.[234] The electrochemistry of the diiron species shows two reversible oxidations separated by 250 mV (in CH_2Cl_2).[259] Unfortunately studies on analogous carbon-bridged [1.1]ferrocenophanes employ different solvents so cannot be compared directly; however, both carbon and silicon-bridged [1.1]ferrocenophanes do show greater values of ΔE than the corresponding singly bridged species Fc_2XR_2.

The unusual molecule shown in Figure 15d was obtained as a minor pyrolysis product of poly[$Fe(C_5H_4)SiMe_2$].[261,262] Despite having a longer iron–iron distance than that in the [1.1]ferrocenophane in Figure 15c, the separation between the two ferrocene oxidations was found to be very similar.[263]

The molecule $(C_5H_4)_2(SiMe_2)_2$,[264–267] hereafter referred to as LH_2, in which two cyclopentadiene rings are linked by two $SiMe_2$ bridges from adjacent positions on the rings, has been used in the synthesis of a number of organometallics including metallocenes, two examples of which are shown in Figure 15e,f. A number of bimetallic complexes of L (which is shown in Figure 16a) have been synthesized by Siemeling, Jutzi, and co-workers from Li_2L or H_2L.[268] $Me_3SnLSnMe_3$ (η^1-coordination) and Cp*FeLFeCp* were both formed exclusively as the *trans* isomer in which the metal fragments are coordinated to opposite faces of the ligand (the iron species is shown in Figure 15e). However, Cp*RuLRuCp* and $(CO)_2CoLCo(CO)_2$ were formed in *cis*:*trans* ratios of 3:7 and 2:1, respectively. Interestingly, these two compounds were synthesized from tetrameric and dimeric metal sources, respectively; this may give some kinetic preference for formation of the *cis* isomers. The reaction product of LH_2 and iron pentacarbonyl is formed solely with a *cis* arrangement of the iron fragments, allowing an Fe–Fe bond, as found in $[CpFe(CO)_2]_2$. Royo and co-workers have also reported $LMCl_2$ (M = Ti, Zr, Hf),[269] *trans*-$L(TiCl_3)_2$,[269] both *cis* and *trans* isomers of $L\{Mo(CO)_3X\}_2$ (X = H, Cl)[270] and a number of other molybdenum and tungsten carbonyl species.[271]

Metal–metal interactions in the Cp*FeLFeCp* system shown in Figure 15e have been studied by a variety of techniques.[272] Cyclic voltammetry in dichloromethane showed a ΔE of 272 mV, slightly greater than that for the silicon-bridged [1.1]ferrocenophane despite the greater iron–iron separation in Cp*FeLFeCp*. No intervalence charge transfer band was observed in the near-IR spectrum of the salt $\{Cp^*FeLFeCp^*\}^+PF_6^-$. The monocationic salt was also studied by Mössbauer and ESR spectroscopies; the results were consistent with trapped Fe^{II} and Fe^{III} sites in the salt.

Reaction of Li_2L with Cp^TFeCl (Cp^T = 1,2,4-*tris*-(trimethylsilyl)cyclopentadienyl) gave a mixture of the bimetallic and trimetallic species $Cp^TFeLFeCp^T$ and $Cp^TFeLFeLFeCp^T$ as well as higher oligomers (only *trans* isomers detected).[273] Other trimetallic complexes were obtained via $(LH)_2Fe$, mainly as the *trans*–*trans* isomers, but with some *cis*–*trans* material: Cp*FeLFeLFeCp* and $(CO)_2CoLFeLCo(CO)_2$.[273]

Bimetallic and trimetallic compounds of the form CpMLMCp and CpMLM′LMCp (Figure 15f), have been constructed and studied by Köhler's group, the trimetallics either via CpMLLi or $M(LLi)_2$. The dichromium, diiron, dicobalt, and dinickel species[274−276] were studied as were the following hetero- and homotrimetallics: M = Fe, M′ = V, Cr, Fe, and Co; M = Co, M′ = Cr; M = Ni, M′ = Cr, Fe, Co, Ni.[13,274,277,278] The complexes were studied by cyclic voltammetry in propionitrile; in many cases low temperatures (*ca.* −25 °C) were employed to obtain maximum resolution of the more subtle features of the voltammograms. The dimeric species[274−276] show greater ΔE values than the singly bridged relation Fc_2SiMe_2[225,233] or the related species with rigid carbon bridges in Figure 11c;[195] this behavior parallels that found for Cp*FeLFeCp*.[272] For example, the dichromium species exhibits two one-electron oxidations separated by 215 mV and two one-electron reductions separated by 325 mV.[274−276] In the case of the triiron complex[274] three waves are observed; the first two oxidations are barely resolved (ΔE = 60 mV) and together correspond to formation of a terminal−terminal dication, whereas the third oxidation is separated from the first by 310 mV. This situation is qualitatively similar to that observed for $(FcSiMe_2C_5H_4)_2Fe$[226,231] (*vide supra*); the slightly larger ΔE may be due to the different solvents used in the two cases. The trinickel complex exhibits two waves in a 2:1 ratio separated by 270 mV; any distinction there may be between the first two oxidations could not be resolved in this case.[278] The heterotrimetallic species show two waves in a 2:1 or 1:2 ratio.[13,278] In some cases the two-electron wave is resolvable into two one-electron events; it corresponds to the oxidations of the terminal metallocenes (which occur at very similar potentials, owing to the large separation between the two metal centers) whereas the one-electron oxidation is that of the central metallocene. Whether the two- or one-electron wave is observed at the lower potential depends upon the redox activity of the parent metallocene units. In some cases additional oxidations and/or reductions were observed.[13,278]

Most of the linked metallocenes reported by Köhler's group contain at least one paramagnetic metallocene building block: for vanadocene units $S = {}^3/_2$, for chromocene and nickelocene $S = 1$, and for cobaltocene $S = {}^1/_2$. ^1H and ^{13}C NMR spectroscopies were used to study the delocalization of spin density in some of the paramagnetic species. CpMLMCp (M = Cr, Co, Ni) and CpNiLM′LCp (M = V, Cr, Ni) were also studied by magnetic susceptibility measurements; in each case significant decreases in the effective magnetic moment were detected at low temperatures and were interpreted in terms of intramolecular antiferromagnetic exchange interactions.[13,275,276,278]

In most cases Köhler's group's trimetallics were obtained as solely the *trans*−*trans* isomers, as shown in Figure 15f. This is unsurprising as the crystal structures of $LLi_2{\cdot}2TMEDA$[279] and CpFeLLi·TMEDA[277] (TMEDA = *N,N,N′,N′*-tetramethylethylenediamine) show the metals in a *trans* disposition relative to one another. However, in a few reactions some *cis* products were obtained.

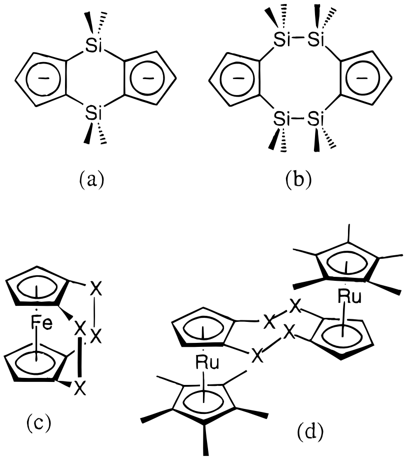


Figure 16. Structures a and b are the ligands with double silicon bridges between two cyclopentadienyl rings referred to in the text as L and L′, respectively. Structures c and d show two complexes of the L′ ligand, $SiMe_2$ being represented by X for clarity.

The analogue of LH_2 with Si_2Me_4 bridges rather than $SiMe_2$ (Figure 16b), hereafter $L'H_2$, is closely related to the LH_2 ligand, but has Si_2Me_4 bridges between the two rings. However, the more flexible nature of the longer bridging system increasingly favors formation of [2]1,1′[2]2,2′-metallocenophanes relative to that of oligomers, e.g. $Fe\{C_5H_3(SiMe_2)_2\}_2$, L′Fe (Figure 16c), is formed from Li_2L and Cp*Fe(acac).[280] However, Cp*RuL′RuCp* (Figure 16d) has been characterized.[280]

5.2. Metallocenes Linked by Germanium, Tin, and Lead Bridges

These compounds are much scarcer than C- or Si-bridged species. GeR_2-bridged [1]ferrocenophanes (R = Me, Et, Ph) have been found to undergo thermal[281−284] and noble metal-catalyzed[251,284] ring-opening polymerization in an analogous manner to SiRR′-bridged [1]ferrocenophanes. The cyclic voltammogram of the $GeMe_2$-bridged polymer in dichloromethane shows two oxidations separated by 200 mV; this is similar to the ΔE of 210 mV observed for the $SiMe_2$ polymer.[25]

Low molecular weight SnR_2-bridged ferrocene polymers, analogous to poly(ferrocenylsilanes), have been obtained from the reaction of dilithioferrocene and R_2SnCl_2; depending on the reaction conditions soluble[285] (shown to have a degree of polymerization of *ca.* 13) or insoluble[286,287] products may be obtained. A soluble Sn^nBu_2-bridged example has been studied by cyclic voltammetry and found to have two oxidations separated by 240 mV, whereas for the Si^nBu_2-bridged polymeric species, ΔE was found to be 290 mV.[25] This result shows Fe−Fe separation plays an important rôle in determining the size of ΔE; if through-bond effects alone were responsible one would expect a *greater* separation in the tin-bridged case where more overlap is possible between the bridging atom's d-orbitals and the cyclopentadienyl π-orbitals.

The preparation of insoluble material assumed to be poly$[Fe(C_5H_4)_2SnR_2]$ (R = Me, ^{n}Bu) was found to be accompanied by the formation of very small quantities of [1.1]ferrocenophanes, $[(C_5H_4)_2SnR_2]_2Fe_2$.[286,287] The structure of the *n*-butyl-substituted species was determined by X-ray crystallography; metal–metal interactions in this system have subsequently been studied by Dong *et al.*[288] Polarographic measurements on a dichloromethane solution of 1,1,12,12-tetra-*n*-butyl[1.1]stannaferrocenophane showed two reversible oxidations separated by 200 mV. Attempts to synthesize $\{[(C_5H_4)_2Sn^nBu_2]_2Fe_2\}^+I_3^-$ by oxidation of the neutral species with iodine in dichloromethane led to cleavage of a Sn–C bond and formation of the *endo–endo* dibutyl isomer of $[(C_5H_4)_2Sn^nBuI]_2Fe_2$, the structure of which was crystallographically determined. The monocation of $[(C_5H_4)_2Sn^nBu_2]_2Fe_2$ was generated in solution by comproportionation of neutral and dioxidized species; a band at 1700 nm, assigned to intervalence charge transfer, was observed in the near-IR spectrum. No such band is observed in analogous carbon bridged [1.1]ferrocenophanes.[117] Since the carbon species presumably have a shorter iron–iron separation than the tin species (this has been shown crystallographically for the corresponding neutral molecules, but not for the monocations) it seems that a through-bond interaction contributes to the intervalence transition here. Overlap between Sn d-orbitals and the cyclopentadienyl π-orbitals was proposed by the authors as the most likely mechanism to allow this process. An interesting reaction of tin-bridged ferrocenes was reported by Nesmeyanov *et al.*; oxidation of Fc_2SnCl_2 with chlorine or bromine afforded the zwitterionic species $Fc_2SnCl_2X_2$ ($X = Cl, Br$), with two ferrocenium units and a six-coordinate $\{\text{stannate(IV)}\}^{2-}$.[289]

The lead-bridged species Fc_2PbPh_2, $(FcPbPh_2C_5H_4)Fe(C_5H_4PbPh_3)$, and $[(C_5H_4)_2PbPh_2]_2Fe_2$ have been studied by cyclic voltammetry in dichloromethane and found to have ΔE values of 165, 136, and 279 mV, respectively.[290] Notably, the lead-bridged [1.1]ferrocenophane shows greater Fe–Fe interactions than Sn^nBu_2-,[288] $SiMe_2$-,[259] or CRR′-bridged[165] [1.1]ferrocenophanes. One would expect some contribution to the differences in ΔE will be made by the different substituents on the group IVb atom, as well as by the identity of the bridging atom itself. Unfortunately, however, other directly analogous group IVb-linked metallocenes are not available for direct comparison, so preventing identification of the important factor in this case.

5.3. Linked Metallocenes with Other Heteroatom Bridges

The reaction of lithioferrocene with BF_3 or $^nBu_3B$ was found to give a mixture of BFc_3 and $Li^+(BFc_4)^-$.[291] The latter compound is readily oxidized by molecular oxygen to the zwitterionic species BFc_4, the crystal structure of which reveals one ferrocenium and three ferrocene units around the boron atom. Four reversible redox processes were observed in dichloromethane (ΔE values of 270, 200, and 120 mV as increasing numbers of ferrocenes are oxidized); this reflects the close proximity of all four iron centers. Weaker electrochemical interactions (estimated at *ca.* 70 mV) were observed in DME for the oxidations of $BMes_3\{Cr(CO)_3\}_2$ and $BMes_3\{Cr(CO)_3\}_3$ (Mes = 2,4,6-trimethylphen-1-yl).[292] Near-IR bands assigned to intervalence charge transfer were observed for both BFc_4 and the electrochemically generated $(BFc_4)^+$ cation.[290]

The monocation of FcN=NFc exhibits a near-IR intervalence charge-transfer band. A through-bond mechanism, via the π-orbitals of the N=N bond is assumed to be operative, as for species such as FcCH=CHFc (*vide supra*).[167]

A number of oligomeric and polymeric phosphorus(III) and phosphorus(V) species have been prepared. Low molecular mass $H[Fe(C_5H_4)_2P(X)Ph]_nOH$ ($X = O, S$) were first prepared in 1967 by an aluminum chloride-catalyzed condensation of ferrocene and $PhPCl_2$, followed by oxidation with hydrogen peroxide,[293] and by the $ZnCl_2$-catalyzed condensation of ferrocene and $PhP(X)Cl_2$ ($X = O, S$).[294] Phosphorus-bridged [1]ferrocenophanes have also been found to undergo anionic[295] or thermal[296] ring-opening oligomerization and polymerization reaction like their silicon-bridged analogues. Polymers with both phosphorus(III)[295,296] (e.g. poly$[Fe(C_5H_4)_2PPh]$ and phosphorus(V)[296] (e.g. poly$[Fe(C_5H_3SiMe_3)_2P(S)Ph]$) bridges have been synthesized. Two waves separated by 190 mV are observed in the cyclic voltammogram of poly$[Fe(C_5H_3{}^nBu)(C_5H_4)PPh]$; ΔE values between 160 and 290 mV are found for poly$[Fe(C_5H_4)_2SiRR']$ species under the same conditions.[25,227]

The near-IR spectra of monooxidized derivatives of several phosphorus-bridged species have been recorded by Delgado-Pena *et al.*[167] Whereas no intervalence charge-transfer bands were observed in solutions of $(Fc_3P)^+$ and $(PhFc_2P)^+$, the corresponding phosphine oxide cations $\{Fc_3P(O)\}^+$ and $\{PhFc_2P(O)\}^+$ exhibited intense near-IR absorptions. These results were taken to indicate through-bond contributions to the charge transfer are important in this system and operate via the π-orbital of the phosphine oxide species.

Diferrocenyl sulfide (Fc_2S) has been synthesized in a number of ways;[297–299] the most selective preparation employs the reaction of lithioferrocene and bis(phenylsulfonyl) sulfide and was reported by O'Connor-Salazar and Cowan.[299] These authors also studied the electrochemistry of Fc_2S and observed two oxidations separated by 290 mV (in CH_2Cl_2); this is a much greater separation than that observed for similar carbon- and silicon-bridged species and approaches that observed for the unbridged biferrocene (330 mV in CH_2Cl_2[225]). The monocation of Fc_2S was generated electrochemically; no intervalence transition was detected.

Rauchfuss and co-workers have discovered an interesting phosphine-induced polymerization reaction of trithiaferrocenophanes (Figure 17); the driving force for the reaction is formation of a P=S bond.[300–302] The resulting polymer is insoluble when trithiaferrocenophane itself is used, but use of *n*- and *tert*-butyl substitution of the cyclopentadienyl rings has permitted synthesis of soluble products which GPC shows have high molecular masses. (For example, the average degree of polymerization for poly$[Fe(C_5H_3{}^nBu)(C_5H_4)S_2]$ is 160.) An interesting property of these polymers is their ability to be reductively depolymerized and oxidatively repolymerized as shown

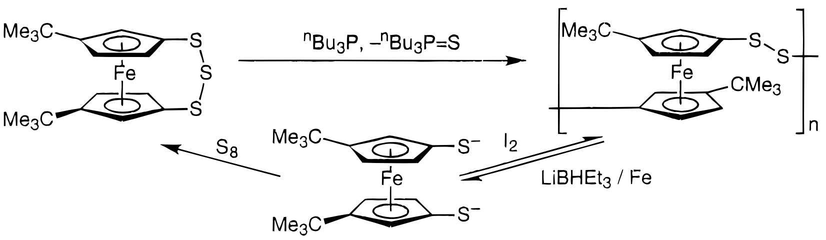


Figure 17. Desulfurization polymerization of a trithiaferrocenophane and reversible cleavage of the polymer.

in Figure 17. Cyclic voltammetry shows two waves, consistent with oxidation of alternate iron sites, as found for poly(ferrocenylsilanes), poly(ferrocenylgermanes), and poly(ferrocenylphosphines). The separations between the two waves are 319 mV in CH_2Cl_2 for poly[Fe($C_5H_3{}^nBu$)(C_5H_4)S_2][300,302] and *ca.* 290 mV in CH_2Cl_2 for poly[2-Fe($C_5H_3{}^tBu$)(C_5H_4)S_2] and for poly[2,3′-Fe($C_5H_3{}^tBu$)$_2S_2$].[301] These values are similar to those for Fc_2S; the effect of the longer bridge is evidently balanced by the fact that the second oxidation involves making a cation next to *two* other cations in the polymer, rather than one in diferrocenyl sulfide. The related desulfurization of ferrocenophanes with two S_3 bridges was found to give giant networks; again butyl groups were used to solubilize the materials.[303]

Other S- and SS-bridged ferrocenes have been obtained by Heberhold *et al.*;[304] dilithioferrocene and FcSSFc gave ($FcSC_5H_4$)$_2$Fe; reaction of RLi (R = ^{n}Bu, Ph, Fc) and trithiaferrocenophane, followed by aerial oxidation, afforded (RSC_5H_4)Fe(C_5H_4)SS-(C_5H_4)Fe(C_5H_4SR), while the AIBN-initiated reaction of FcSH and norbornadiene yielded oligomers R[S(C_5H_4)Fe(C_5H_4)S]$_n$R (R = nortricyclyl or 5-*exo*-norborn-2-enyl). Recently SS-, SeSe-, and TeTe-bridged ferrocene systems have been used as chiral ligands for rhodium and iridium hydrosilylation catalysts.[305] Recently Manners' group reported that Fe(C_5H_4)$_2$S could be synthesized and thermally converted to an insoluble material assumed to be poly-[Fe(C_5H_4)$_2$S].[306] None of these species has yet been investigated with respect to metal–metal interactions, although interesting properties are anticipated by analogy with those of the species described above; a soluble derivative of poly[Fe(C_5H_4)$_2$S] might be expected to show a very large ΔE.

Fc_2Se has been prepared by the reaction of Fc_2Hg and $SeCl_2$[307] and by the reaction of FcHgCl and FcSeCN.[308] FcSeSeFc has been obtained from FcHgCl and Cu(SeCN)$_2$.[308] Both compounds have been studied electrochemically (in acetonitrile) and found to have two oxidation waves separated by 220 and 140 mV, respectively.[308] These separations may be compared with those of 170 and 0 mV found in the solvent for Fc_2CH_2 and $FcCH_2CH_2Fc$, respectively.[67] Unfortunately direct comparison with the sulfur-bridged species is hampered by the different solvents employed in the different electrochemical studies; however, it does appear that somewhat weaker electrochemical interactions are present in the selenium complexes. The monocations of both selenium-bridged species were generated electrochemically by Shu *et al.* and showed no intervalence band in the near-IR spectrum.[308] Kramer *et al.* have prepared the salt $(Fc_2Se)^+I_3^-\cdot I_2\cdot 0.5CH_2Cl_2$ and reported its crystal structure, which shows distinct ferrocene and ferrocenium sites.[309] They also observed no intervalence transfer band in solution (in accordance with the results of Shu *et al.* for the same cation) and found the salt was trapped on both Mössbauer and IR time scales. The effective magnetic moment was also found to be normal for a ferrocenium salt. The absence of near-IR absorptions in $(Fc_2S)^+$ and $(Fc_2Se)^+$ may be contrasted with the case of BFc_4, where a band is present. One would expect through-bond intervalence transfer to be favored with the more polarizable S and Se; however, the boron compound has closer ferrocene and ferrocenium units. Thus, a principally through-space mechanism appears to be operating in this type of system. Other chalcogen-bridged species, ($FcXC_5H_4$)$_2$Fe, have been prepared from dilithioferrocene and FcXXFc (X = Se, Te).[304]

Recently Rauchfuss and co-workers have reported low molecular weight poly[Fe($C_5H_3{}^nBu$)(C_5H_4)Se_2], prepared from a Se_3-bridged ferrocenophane in an analogous fashion to the S_2-bridged polymers described above.[302] Cyclic voltammetry (ΔE = 285 mV in CH_2Cl_2) reveals similar metal–metal interactions than those in the S_2-bridged analogues.

Diferrocenylmercury, Fc_2Hg, which was first prepared by the reduction of FcHgCl with sodium,[310] has been shown to have only one oxidation wave, indicating essentially no metal–metal interaction.[67] The reaction of Fe(C_5H_4HgCl)$_2$ with sodium iodide or sodium thiosulfate gives material formulated as poly-[Fe(C_5H_4)$_2$Hg]; this material may contain cyclic species.[311]

6. Metallocenes Linked through Delocalized Fused Rings

6.1. The Pentalene and Indacene Ligand Systems

Pentalene (Pn), *s*-indacene (*s*-Ic), and *as*-indacene (*as*-Ic) (collectively represented as L″) are the hydrocarbons shown in Figure 18, respectively. The neutral unsubstituted species are highly unstable, and although substitution of the rings has allowed the preparation of stabilized derivatives such as 1,3,5-tri-*tert*-butylpentalene[312] and 1,3,5,7-tetra-*tert*-butyl-*s*-indacene,[313] no *as*-indacenes have yet been reported. Organometallic chemistry has usually circumvented pentalene and the indacenes themselves, but involved deprotonation of dihydropentalene and dihydroindacenes, $L''H_2$, to yield $L''H^-$ or L''^{2-} species. As well as the various linked metallocene complexes in the following sections, some interesting other organometallic compounds have been prepared. Manganese tricarbonyl derivatives of both 2,7-dimethyl-*as*-in-

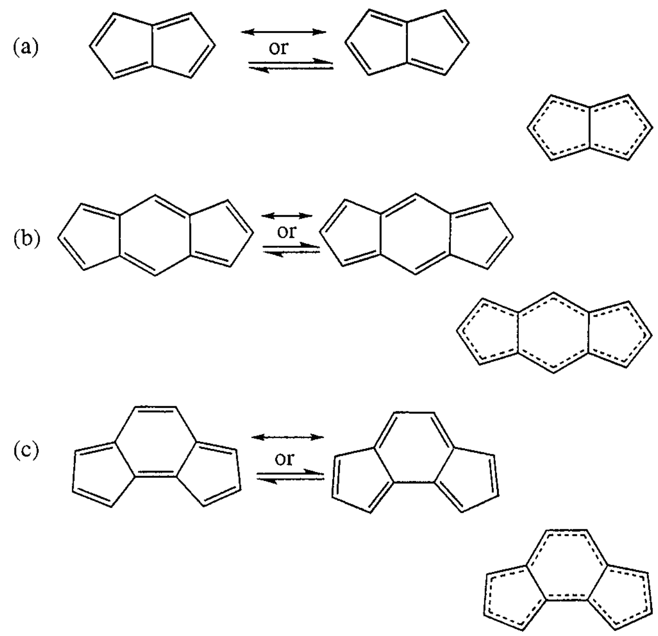


Figure 18. Cyclopentadienyl fused ring systems: (a) pentalene (Pn), (b) *s*-indacene (*s*-Ic), and (c) *as*-indacene (*as*-Ic).

dacene (*as*-Ic′) and *s*-indacene have been prepared; while *s*-Ic$\{Mn(CO)_3\}_2$ is formed solely as the *trans* isomer,[314] with the metal atoms complexed to opposite faces of the ligand system, *as*-Ic′$\{Mn(CO)_3\}_2$ is formed as a mixture of *cis* (minor) and *trans* (major) isomers.[315] The structure of the *cis* isomer has been determined by X-ray crystallography and features an indacene ring system significantly distorted from planarity due to steric repulsion between the two $Mn(CO)_3$ moieties.[315] *as*-Ic′$\{Mo(CO)_3Me\}_2$ is formed exclusively as the *trans* isomer.[315] Remarkably, another carbonyl derivative, *s*-Ic″$\{Fe(CO)_3\}_2$ (Figure 22a) {Ic″ = 1,3,5,7-tetra-*tert*-butyl-*s*-indacene}, is formed as solely the *cis* isomer.[196,197] This complex was formed directly from the reaction of 12 π-electron 1,3,5,7-tetra-*tert*-butyl-*s*-indacene (which, unlike other indacenes and pentalenes, is stable at room temperature) and $Fe_2(CO)_9$, rather than via deprotonation of a dihydroindacene. The crystal structure reveals a rather peculiar bonding mode; each iron can be considered as having distorted η^5-coordination.

6.2. Sandwich Compounds with Two Pentalene or Indacene Ligands

The first organometallic pentalene derivative, bis(hydropentalene)iron (Figure 19a), was reported in 1963;[316] it was synthesized in good yield by the reaction of lithiohydropentalene and iron(II) chloride. It was also shown that the complex could be further deprotonated once or twice with *tert*-butyllithium, opening up possibilities for the construction of pentalene-based oligomers which were not exploited until 1993 (*vide infra*). The reaction of dilithiopentalene with iron(II) chloride did not, however, afford bis(pentalene)diiron (Figure 19b, M = Fe) but a molecule comprising one iron atom and two pentalene molecules.[317] The two alternative structures shown in Figure 19, parts c and d, have been proposed and are consistent with NMR data for the complex; the crystal structure showed the structure in Figure 19d to be correct.[318] However, the reaction of cobalt(II) chloride,[317] nickelocene, or $NiCl_2{\cdot}DME$[319] with dilithiopentalene produced low yields of bis(pentalene)dimetal complexes (Figure 19b, M = Co, Ni). Both the cobalt and nickel species are diamagnetic. Unfortunately the structures have not been crystallographically determined so the geometric and electronic structures of these complexes are not clear. For example, an η^3-allyl-η^5-cyclopentadienyl coordination at each nickel atom, whereby each metal of bis(pentalene)dinickel could attain an 18-electron configuration, would be highly strained, requiring a very short Ni–Ni distance. Distortion of the ligand from planarity and/or displacement of the metal atoms away from one another (as noted in certain bis(benzene)dipalladium complexes[320]) have been suggested.[319] Interestingly, oxidation of bis(pentalene)dicobalt with H_2O_2 results in loss of a cobalt atom and formation of a cobaltocenium ion, which spectral data suggest is isostructral with the isoelectronic iron complex represented by Figure 19c.[317]

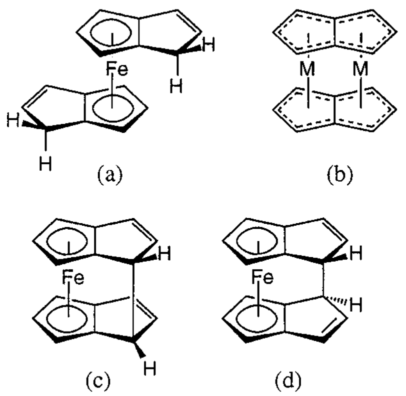


Figure 19. Pentalene complexes: (a) one of the two isomers of bis(hydropentalene)iron, (b) a bis(pentalene)dimetal complex, and (c and d) possible structures for the product of the reaction of dilithiopentalene and iron(II) chloride; (d) is that confirmed by the crystal structure.

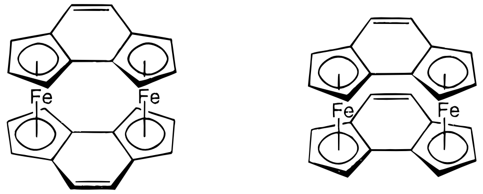


Figure 20. The two isomers of bis(*as*-indacene)diiron.

The first indacene complex to be reported was bis(*as*-indacene)diiron, prepared from dilithio-*as*-indacene and iron(II) chloride.[321,322] NMR and crystallographic studies have been used to infer that the complex exists as a mixture of the isomers shown in Figure 20.[323] Bis(*as*-indacene)dicobalt[324] and bis(*as*-indacene)dinickel[325] have also been claimed; it is stated that the former species is paramagnetic, in contrast to bis(pentalene)dicobalt and bis(fulvalene)dicobalt (*vide supra*).

6.3. Multidecker Pentalene and Indacene Complexes

The three compounds $Pn(MCp^*)_2$ (M = Fe, Co, Ni, see Figure 21a) were synthesized by the reaction of

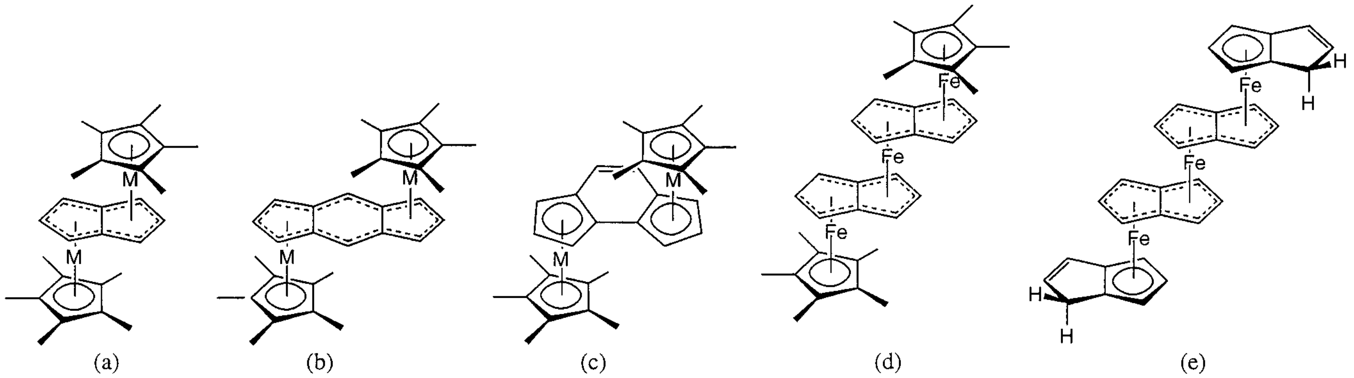


Figure 21. Bimetallic complexes of (a) pentalene, (b) *s*-indacene, and (c) *as*-indacene, and (d and e) trimetallic pentalene multideckers.

dilithiopentalene and Cp*M(acac); the crystal structures of the iron and cobalt species, as well as that of $\{Pn(FeCp^*)_2\}^+BF_4^-$, have since been reported.[16,17] Subsequently the ruthenium analogue has been made from dilithiopentalene and $(Cp^*RuCl)_4$; the mixed-metal species Cp*FePnCoCp* and Cp*FePnRuCp* have been made by the reaction of lithiohydropentalene with Cp*Fe(acac), followed by lithiation and reaction with $(Cp^*RuCl)_4$ or Cp*Co(acac). Most of these species have also been converted to both their mono- and dicationic oxidized derivatives.[17]

It should be realized that these fused ring molecules cannot be regarded as simply two metallocenes like those in previous sections of this article; the number of bonding electrons in the $Pn(FeCp^*)_2$ is

$$\begin{array}{lr} \text{for the Cp* groups} & 2 \times 5 = 10 \\ \text{for the Fe atoms} & 2 \times 8 = 16 \\ \text{for the pentalene} & \underline{= 8} + \\ & \underline{= 34} \end{array}$$

Thus, there are only 17 electrons per iron atom demonstrating this is *not* merely a ferrocene derivative. In fact a molecular orbital scheme derived from extended Hückel calculations is more akin to that for Cp_3M_2 triple-decker complexes. All four neutral $Pn(MCp^*)_2$ complexes are diamagnetic, as are $\{Pn(CoCp^*)_2\}^{2+}$ and $\{Pn(NiCp^*)_2\}^{2+}$. The diiron dication, however, appears to have two unpaired electrons.[17]

The triple-decker-like nature of these complexes, where the two metals have orbitals overlapping with common ligand orbitals, is reflected in the extremely large separations between the first and second oxidation potentials: 1030, 900, and 860 mV for Fe, Co, and Ni complexes respectively in dichloromethane. $\{Pn(FeCp^*)_2\}^+BF_4^-$ and $\{Cp^*FePnRuCp^*\}^+BF_4^-$ are both detrapped down to 1.5 K on the Mössbauer time scale (10^{-7} s).[17,326,327] The mixed-metal case is particularly unusual, illustrating the high degree of metal–metal interaction possible in fused ring systems. $\{Cp^*FePnCoCp^*\}^+BF_4^-$, shows a ferrocene-like Mössbauer spectrum;[17] this is simply a consequence of the fact that the molecular orbitals of this cation will be more or less the same, with the same populations, as the neutral diiron complex.

A series of indacene complexes $Ic(MCp^*)_2$ (Ic = *s*- or *as*-indacene, M = Fe, Co, Ni, Figure 21b,c) has been prepared from reaction of the appropriate dilithioindacene and Cp*M(acac).[17] In most cases the mono- and dioxidized derivatives have also been prepared. Representative examples from this family of compounds have been characterized by X-ray crystallography: invariably the metal atoms are coordinated to opposite faces of the fused-ring system. Another *as*-indacene iron complex was reported in 1980: *as*-$Ic(FeCp)_2$ was prepared in 3% yield by the reaction of iron(II) chloride with a mixture of dilithio-*as*-indacene and LiCp.[328] It has also been structurally characterized.[329] We have discovered an alternative route to analogous compounds; treatment of 1,3,5,7-tetra-*tert*-butyl-*s*-indacene (*s*-Ic″) with $CpCo(C_2H_4)_2$ yields *s*-Ic″$(CoCp)_2$, remarkably as a mixture of *cis* (major) and *trans* (minor) isomers (Figure 22b), although unfortunately we have been unable to separate the isomers.[196,197] Another possible route to *cis*-indacene derivatives might be to block one face of the ligand by complexation of a $Cr(CO)_3$ unit to the six-membered ring of a dihydroindacene before doubly deprotonating and reacting with a "CpM^+" synthon; one could envisage both "CpM" units complexing to the opposite face of the ligand from the chromium moiety, which could be removed at a later stage. We have recently synthesized $(\eta^6\text{-}Ic^*H_2)Cr(CO)_3$ (Ic^*H_2 = 1,5-dihydro-1,2,3,4,5,6,7,8-octamethyl-*s*-indacene)[330,331] and determined its structure.[332]

A study by Manríquez *et al.*,[17] employing an extensive arsenal of physical techniques, shows that the *s*-indacene ligand enables much stronger interactions between the metal centers than the *as*-indacene. For example, *s*-$Ic(CoCp^*)_2$ and the isoelectronic $\{s\text{-}Ic(NiCp^*)_2\}^{2+}$ are diamagnetic, whereas *as*-$Ic(CoCp^*)_2$ has a slightly higher magnetic moment than one would expect from two noninteracting $S = {}^1/_2$ centers. In the *s*-indacene case one cannot regard the molecule as antiferromagnetically coupled cobaltocenes: this simplified picture would require one to leave two unpaired electrons on the bridging carbons. In fact the situation is much more akin to that of a pentalene complex (*vide supra*) or a triple decker, with the orbitals of the two metal atoms overlapping with the same π-orbitals of the ligand. However, in the *as*-indacene case a "normal" relatively localized structure comprising two cobaltocenes and a C=C double bond on the bridge can be envisaged. The enhanced air sensitivity of the *s*-$Ic(FeCp^*)_2$ relative to *as*-$Ic(FeCp^*)_2$[333] again indicates

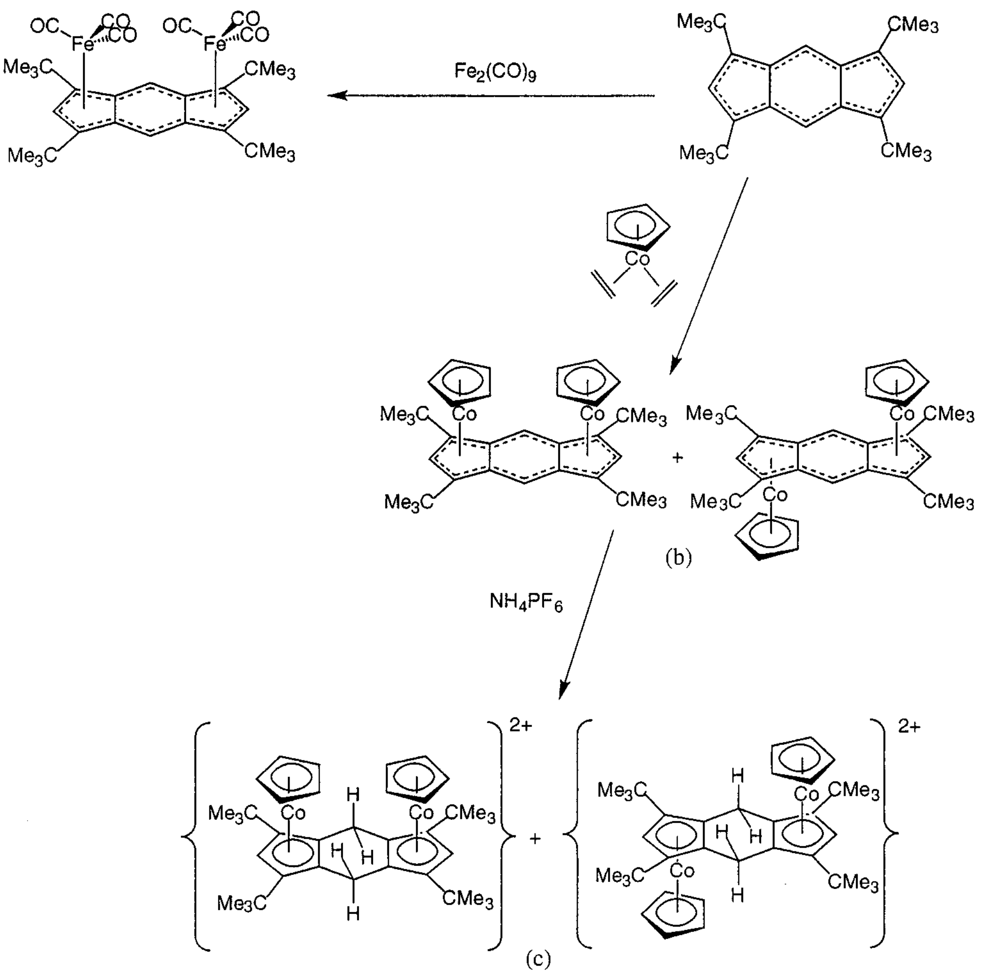


Figure 22. Some organometallic chemistry of 1,3,5,7-tetra-*tert*-butyl-*s*-indacene (Ic″).

that the former compound cannot be regarded merely as "two ferrocenes with a bridge".

Surprisingly, and in contrast to Pn(NiCp*)$_2$ (*vide supra*), both *as*-Ic(NiCp*)$_2$ and *s*-Ic(NiCp*)$_2$ are paramagnetic, despite the fact the crystal structure of the latter shows the indacene has essentially η^3-coordination to the nickel, an arrangement that would be expected to lead to a low-spin 18-electron configuration for each nickel. Both the dicationic diiron complexes are also paramagnetic.

Other evidence for the greater metal–metal interactions in *s*-indacene complexes comes from electrochemical measurements. The separation, ΔE, between oxidation to the mono- and dications are 480 and 460 mV for *as*-Ic(FeCp*)$_2$ and *as*-Ic(CoCp*)$_2$, respectively, whereas under comparable conditions the analogous *s*-indacene complexes have ΔE values of 820 and 810 mV (and for the pentalene species 1030 and 900 mV). However, the Ni indacene complexes both show similar separations (550 and 570 mV for *as*- and *s*-Ic, respectively) consistent with a picture of the indacene behaving as two allyl moieties and a benzene ring in each case.

Interestingly the cyclic voltammogram of *s*-Ic″(CoCp)$_2$ (dominated by the major *cis* isomer) in dichloromethane shows two waves separated by 820 mV;[196,197] i.e. a very similar ΔE to that observed for *trans*-*s*-Ic(CoCp*)$_2$. An attempt to chemically oxidize *s*-Ic″(CoCp)$_2$ using ammonium hexafluorophosphate lead instead to protonation, as shown in Figure 22c.[196,197] The resulting species, with cobaltocenium ions linked with rigid insulating bridges, are members of the nonfused ring carbon-linked class discussed above and warrant further study.

{*s*-Ic(FeCp*)$_2$}$^+$BF$_4^-$ has been studied by Mössbauer spectroscopy;[17,326,327] completely detrapped behavior is observed, even as low as 1.5 K. Its ESR spectrum, like that of {Pn(FeCp*)$_2$}$^+$BF$_4^-$, is relatively isotropic for a ferrocenium-type system ($\Delta g = 0.35$). Although no IR data are reported for these species (indeed suitable bands for distinguishing localized *vs* delocalized behavior have yet to be identified), it seems likely that they are completely delocalized. In contrast, the analogous *as*-indacene-diiron tetrafluoroborate salt is localized on the Mössbauer time scale, with incipient detrapping only detectable at room temperature,[17,333] and shows a more ferrocenium-like ESR spectrum ($\Delta g = 1.52$).[17] {*as*-Ic(FeCp*)$_2$}$^+$TCNE$^-$ {TCNE = tetracyanoethylene} has also been found to be trapped at low temperatures, but increasingly detrapped as the temperature is raised.[333] This type of anion-dependent behavior is reminiscent of that found in biferrocenium systems. {*as*-Ic(FeCp)$_2$}$^+$I$_3^-$ has also been investigated by Mössbauer spectroscopy;[334,335] detrapping is observed with valence averaging occurring as the temperature is raised from 100 to 300 K. It seems likely that both Cp and Cp* cations have similar levels of intrinsic metal–metal interaction (ΔE for the Cp complex is reported to be 410 mV[334] and for the Cp* compound 480 mV[17]), and the differences between the salts are due to counterion effects. “Intervalence” near-IR absorptions have been reported for the pentalene and indacene bimetallic monocations, but analyses of such strongly coupled systems in terms of Hush theory is clearly inappropriate.

By analogy with the behavior of the bimetallic pentalene and indacene systems described above, the synthesis of oligomeric or polymeric materials consisting of alternating metal atoms and fused-ring ligands is expected to offer a range of interesting delocalized properties. Strategies for the rational stepwise construction of such compounds have been outlined by Manríquez and Román.[6] However, synthetic progress toward such a goal has been hampered by escalating insolubility with increasing oligomerization; the trimetallic species in Figure 21d,e, derived from bis(hydropentalene)iron, have been reported,[336] the molecule in Figure 21e, which could, in principle, function as a building block for higher oligomers, has a solubility in boiling toluene of only *ca*. 400 mg L^{-1}.[336] Clearly, further progress will require a readily available fused-ring ligand with solubilizing substituents. To this end we have recently begun investigating the organometallic chemistry of such ligands. Tetra-*tert*-butyl-*s*-indacene[313] is a potential component of soluble fused-ring oligomers and polymers; bimetallic compounds which we have made as a part of such as study have already been mentioned. We have also developed a large-scale synthesis for 1,5-dihydro-1,2,3,4,5,6,7,8-octamethyl-*s*-indacene (*s*-Ic*H$_2$);[330,331] this is cheap and straightforward compared to preexisting routes to various dihydro-*as*-[314,321,322,337,338] and *s*-indacene systems[313,314,339−342] and to dihydropentalene,[343] so may lead to an expansion of the field of fused-ring chemistry. The ligand system is also very electron rich, as can be seen by comparison of the properties of two singly metalated derivatives, (*s*-Ic*H)Mn(CO)$_3$ and {(*s*-Ic*H)RhCp*}$^+$SbF$_6^-$,[330,331] with those of their unmethylated analogues.[314 344]

6.4. Trindene Complexes

Another class of fused-ring system, closely related to the indacenes is trindene, shown in Figure 23a, and hereafter abbreviated to TdH$_3$. Figure 23b,c show alternative valence bond representations of triply deprotonated trindene, Td^{3-}; it can be seen to be related to the fulvalene and *as*-indacene dianions.

The synthesis of trindene[345] is somewhat tedious and not amenable to performing on a large scale; this, coupled with the poor solubility of trindene complexes, may explain the scarcity of organometallic trindene chemistry. Metallocenes based on the trindene system have so far been limited to (TdH)$_2$Fe$_2$ and possibly Td$_2$Fe$_3$ (in minuscule amounts); these compounds were synthesized by the reaction of TdHLi$_2$ and TdLi$_3$, respectively, with iron(II) chloride.[345] No data pertaining to potential metal−metal interactions in these compounds have been reported, but Td$_2$Fe$_3$ would be anticipated to show very strong metal−metal interactions, by analogy with Td{Rh(cod)}$_3$ (*vide infra*) and with bis(fulvalene)diiron. The trication of this complex may exhibit magnetic frustration if the three unpaired electrons couple antiferromagnetically like those in (Fv$_2$Fe$_2$)$^{2+}$.

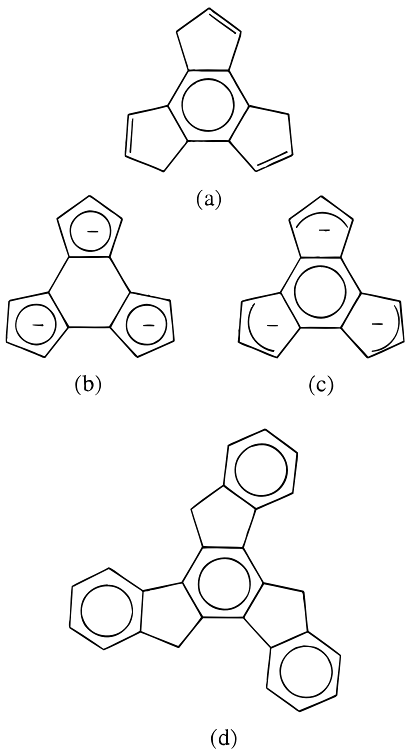


Figure 23. (a) Trindene, TdH$_3$, (b and c) alternative representations of the Td^{3-} anion, and (d) truxene.

A number of trimetallic non-metallocene trindene complexes of the type Td[M]$_3$ [[M] = Re(CO)$_3$,[346,347] Mn(CO)$_3$,[347] Rh(cod) [cod = 1,5-cyclooctadiene],[348] Rh(CO)$_2$[348]] have been synthesized and some have been studied electrochemically.[349] An interesting feature of trindene is that the coordination of three metal fragments forces two of the metals into close proximity. The structure of Td{Re(CO)$_3$}$_3$ has been determined;[347] the metals show η^5-coordination to the ligand and, as in the case of *cis*(*as*-indacene){Mn(CO)$_3$}$_2$,[315] steric repulsion between neighboring metals results in distortion of the ring system from planarity. Another consequence of this close proximity is observed in the cyclic voltammogram of Td{Rh(cod)}$_3$;[349] in dichloromethane the first and second oxidations are separated by 170 mV, presumably since two Rh units on opposite sides of the ring system are involved. However, the removal of a third electron requires the creation of a metal cation of the same side of the ring system as another oxidized metal; this results in a much larger separation of 490 mV between the second and third oxidation waves.

A related ring system is truxene (Figure 23d); the Mn(CO)$_3$ and Re(CO)$_3$ complexes are even less soluble than their trindene analogues and thus very hard to purify.[350]

6.5. Helicene-Bridged Complexes

Katz *et al.* have been interested in the construction of organometallic polymers based upon fused ring systems, although some of their efforts have been frustrated by the formation of dimeric species rather than polymers (for example the reaction of dilithio-*as*-indacene with iron(II) chloride was hoped to give a polymer but actually gave bis(*as*-indacene)di-

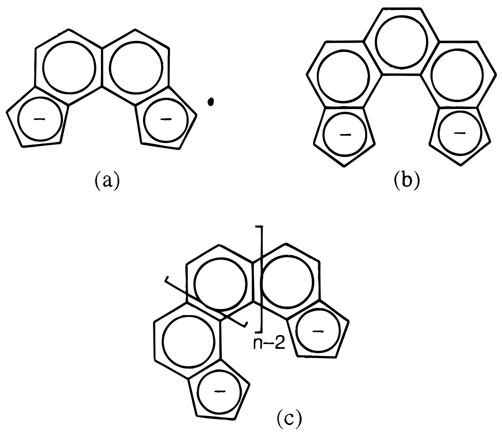


Figure 24. Some helicene hydrocarbons.

iron).[321,322] Such polymers are expected to exhibit high electronic delocalization by analogy with the properties of molecular fused-ring organometallics (*vide supra*).[6] Thus, mixed-valence derivatives of such polymers could show high electrical conductivity; Katz's group has recently investigated the possibility of synthesizing a chiral conductor of electricity based on helicene ligands. These are related to the indacene ligands but have a number (n) of benzenoid rings between the two terminal cyclopentadienyl functionalities. Bis(ligand)dimetal complexes of the two ligands shown in Figure 24, parts a and b, were made in preliminary studies, although characterization of the neutral diiron species was complicated by their very low solubilities and the dicationic dicobalt derivative of the ligand in Figure 24a could only be obtained in very low yields.[351]

The ligand shown in Figure 24c with $n = 5$, where two cyclopentadienyl rings are linked through five fused benzenoid rings, permitted the synthesis of an interesting helical ferrocene where the ligand takes the form of a helix thus placing one cyclopentadienyl ring above the other, allowing coordination of an iron atom.[352] This species and the analogous cobaltocenium species were also obtained optically pure.[353] The reaction of the deprotonated helicene[351] represented by Figure 24c ($n = 7$) with $CoBr_2$·DME followed by oxidation gave short-chain cobaltocenium oligomers, $\{(\mathrm{helicene})_{x+1}\mathrm{Co}_x\}^{x+}$, with protonated end groups.[7] These oligomers were also obtained in optically pure form.[8] Electrochemical reduction of the oligomers on platinum yielded a conductive film.[8] The reaction of the dilithiated seven-benzene helicene (Figure 24c, $n = 7$) with $(\mathrm{Cp^*CoCl})_2$ gave, after oxidation, $\{(\mathrm{helicene})(\mathrm{CoCp^*})_2\}^{2+}$.[354] Solution electrochemical measurements on this species show two reversible reductions in acetonitrile with a separation of 130 mV; this is a much closer separation than is found in analogous $\mathrm{Ic(CoCp^*)_2}$ complexes (albeit in a different solvent) and presumably reflects the less efficient communication between the metals possible through the many rings of the helicene bridge. ESR showed the unpaired electron of the monocationic species to be localized on one cobalt center.[354] The neutral species was found to be a diradical[354] like *as*-$\mathrm{Ic(CoCp^*)_2}$ but unlike *s*-$\mathrm{Ic(CoCp^*)_2}$, which is diamagnetic.[17]

7. Summary

Metal–metal interactions have been studied in a large number of different bridged metallocene systems. Metal–metal interactions are manifested in a number of ways and to greatly varying extents: in some systems the only small electrochemical effects are detected, while in others complete delocalization between metal centers occurs. Both through-space and through-bond effects are important in the transmission of these metal–metal interactions.

Generally stronger metal–metal interactions are favored in systems with closer metal–metal approaches and where metallocenes are held in specific rigid conformations with respect to one another. Metal–metal communication through unsaturated carbon bridges occurs more efficiently than through saturated bridges. Elements from the second and lower rows of the periodic table also allow stronger interactions than comparable carbon bridges. Only small differences between compounds with second, third, fourth, and lower row bridges are observed, presumably owing to compromise between opposing through-bond and through-space effects. The strongest metal–metal interactions of all are observed in pentalene-bridged systems, which essentially consist of two or more metallocenes fused together.

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