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Reviews

α-Metallocenylmethylium Ions and Isoelectronic Fulvene Complexes of d^6 to d^9 Metals. Structural Considerations[§]

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This review collects the structural features of those metallocene derivatives in which a carbenium ion center is connected adjacent to a cyclopentadienyl ring η-bound to a transition metal. In the first part we briefly summarize the investigations and observations that led to the structure of the α-ferrocenylmethylium ion. This part is followed by examples of metallocenylmethylium ions and metallocenyldimethylium dications of the iron triad, the isoelectronic ferrocenylboranes, fulvenechromium tricarbonyl complexes, α-cymantrenylcarbenium ions, and [cyclopentadienyl-cyclobutadienecobalt] methylium ions. In all cases we notice a bending of the α-carbenium ion center toward the metal. The bending angle is largest for fulvenechromium tricarbonyl and the ruthenocenyl- and osmocenylmethylium ions.

1. Introduction

The discovery of ferrocene in 1951/1952[1,2] and the assignment of its structure as a sandwich complex[3,4] with two cyclopentadienyl rings led to the emergence of the new area of metallocene chemistry. Shortly afterward it was recognized that ferrocene closely resembles aromatic π-systems in terms of reactivity; for example, it readily undergoes electrophilic substitution reactions under mild conditions. The analogy in behavior to aromatic hydrocarbons, e.g., *benzene*, is also reflected in the name *ferrocene*, which was proposed by Woodward et al.[3b] At the end of the 1950s and the beginning of the 1960s, when various substitution products were available, there were several reports in the literature that suggested that a carbenium ion center adjacent to the ferrocenyl moiety is considerably stabilized. For example, ferrocenylcarbinols could be transformed to ethers under mild conditions,[5] and ferrocenylmethylcarbinol was easily dehydrated to vinylferrocene.[6] The reverse reaction, the addition of weak acids to vinylferrocene, was also observed.[7] Due to these results, chemists took a closer look at the α-ferrocenylmethylium cation. We will summarize these results in the following. Since the literature on this topic has been covered on several occasions,[8] especially by Watts in 1979 and 1988,[9] we will focus on the most recent developments, especially structural aspects and only briefly review the key achievements before 1990. As indicated in the title, we exclude in our review the fulvene and allyldiene complexes of the "early" transition metals. This strongly expanding area would go beyond the scope of this review.

Table 1. Comparison of Relative Rates of the Solvolysis of α-Metallocenylcarbinyl Acetates in 80% Acetone/Water at 30 °C

compd	rel rate
trityl acetate (**1**)	0.15
methylferrocenylcarbinyl acetate (**2**)	1.00
methylruthenocenylcarbinyl acetate (**3**)	1.34
methylosmocenylcarbinyl acetate (**4**)	5.37

2. The Structure of the Ferrocenylmethylium Ion

Important for the discussion of the structure of the ferrocenylmethylium cation were solvolysis experiments and stereochemical investigations. A comparison of the solvolysis rates of the metallocenylcarbinyl acetates **2**−**4** listed in Table 1 with trityl acetate (**1**) demonstrated that metallocenes of the iron group are very effective in stabilizing a positive charge in the position adjacent to the metallocenyl groups.[10] The results parallel those obtained for the addition of CH_3CO_2H to the vinyl metallocenes.[7] In connection with the data reported in Table 1

[§] Dedicated to Prof. Dr. Roald Hoffmann on the occasion of his 70th birthday.

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(1) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039−1040.,

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(8) (a) Rosenblum, M.; Abbate, F. W. *Adv. Chem. Ser.* **1967**, *62*, 532−548. (b) Cais, M. *Organomet. Chem. Rev.* **1966**, *1*, 435−454. (c) Kerber, R. C.; Ehntholt, D. J. *Synthesis* **1970**, 449−465.

(9) (a) Watts, W. E. *J. Organomet. Chem.* **1979**, *7*, 399−459. (b) Watts, W. E. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: London, 1988; Vol. 8, pp 1013−1071.

(10) (a) Richards, J. H.; Hill, E. A. *J. Am. Chem. Soc.* **1959**, *81*, 3484−3485. (b) Hill, E. A.; Richards, J. H. *J. Am. Chem. Soc.* **1961**, *83*, 3840−3846.

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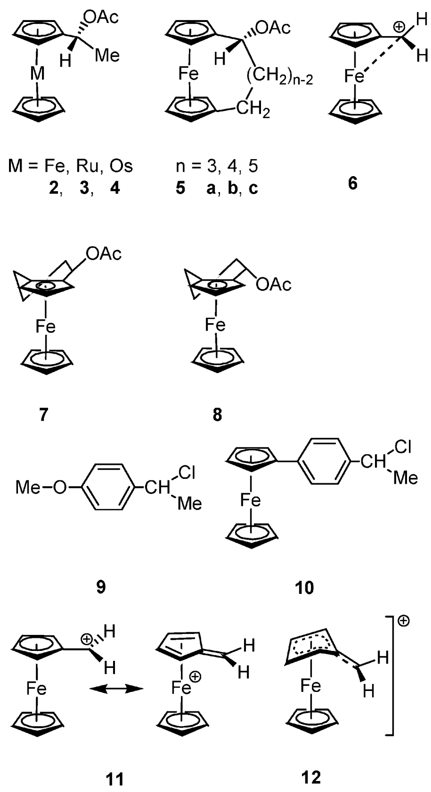
Chart 1



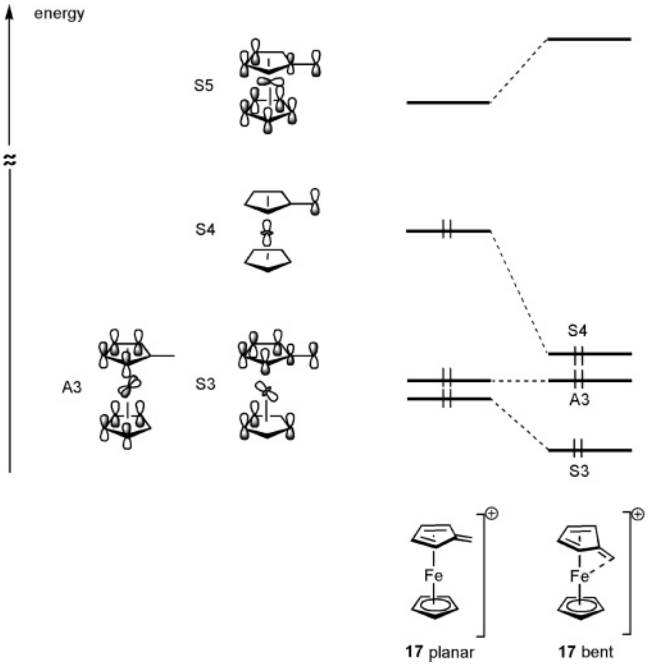
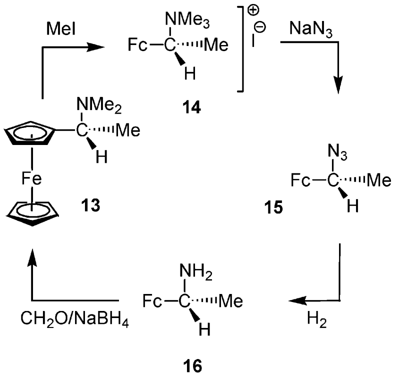


Figure 1. Correlation diagram between the frontier orbitals of a planar (left) and bent α-ferrocenylmethylium ion. The letters S and A stand for symmetric and antisymmetric with respect to the plane of symmetry.

Scheme 1



it is of interest that α-acetoxy-1,1′-trimethyleneferrocene (**5a**)[10a] solvolyzes more slowly by a factor of 29 than **2**. These results led to the proposal that the carbenium center is stabilized by the iron center as shown in **6** (Chart 1).[10b]

It was argued that by shifting the fulvene part of the molecule relative to the CpFe moiety a somewhat more stable structure might arise due to a better overlap of all carbon centers of the fulvene ring with the metal. The solvolysis experiments by Richards and Hill[10] were augmented by experiments carried out by Trifan and Bacskai.[11] They studied the solvolysis of the *exo*- and *endo*-α-acetoxy-1,2-tetramethyleneferrocenes **7** and **8** (Chart 1) in 80% acetone/water at 30 °C. The data show a large difference between the *endo* (rel rate 1) and the *exo* (rel rate 2240) species. These results support the idea of a metal participation, which is possible only in the transition state for the solvolysis of **7**. Further support for this view stems from the activation parameters, which show only similar $\Delta S^{\ddagger}$ values (**7**, −12.0 eu; **8**, −11.0 eu) and a difference of 5 kcal/mol for $\Delta H^{\ddagger}$ in favor of **7**.[11] Further evidence for an intermediate cation with an interaction between the iron atom and the *exo*-carbon (C6) (see Figure 2) was given by the observation that the hydrolysis of optically pure *β*-ferrocenylpropyl tosylate proceeds with retention of configuration.[11]

The hypothesis of a metal−C6 interaction in the intermediate cation was challenged by Traylor et al.[12] They suggested that the intermediate species is stabilized by resonance effects within the fulvene system. Their arguments were based on the observation that the relative solvolysis rate of **9** is greater by a factor of only 2.5 than that of **10** (Chart 1). It was concluded that σ^{+}_{para} of the ferrocenyl group (−0.71) is very close to σ^{+}_{para} of the methoxy group (−0.78), and thus the contribution of the Fe···C6 interaction should be small. As a result, structure **11** was proposed for the α-ferrocenylmethylium ion.

The interpretation by Traylor et al. was scrutinized critically by Cais,[13] who in turn favored a metal−C interaction and pointed out a further alternative to **6** by bending the fulvene ring at the C2 and C5 positions, which leads to **12**.

All structures proposed suggested stereoselectivity for the nucleophilic substitution of α-ferrocenylalkyl derivatives. This topic, first raised by Trifan and Bacskai,[11] was dealt with by Ugi et al.,[14] who prepared optically pure **13** and carried out the cycle **13**−**14**−**15**−**16**−**13** (Scheme 1). All reactions proceeded with essentially complete retention of configuration.

In 1971 the geometry of the α-ferrocenylmethylium ion was partially optimized by Gleiter and Seeger[15] using a modified extended Hückel method. It was found that C6 of the fulvene

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[12] (a) Ware, J. C.; Traylor, T. G. *Tetrahedron Lett.* **1965**, 1295−1302. (b) Tidwell, T. T.; Traylor, T. G. *J. Am. Chem. Soc.* **1966**, *88*, 3442−3444. (c) Traylor, T. G.; Ware, J. C, *J. Am. Chem. Soc.* **1967**, *89*, 2304−2316.

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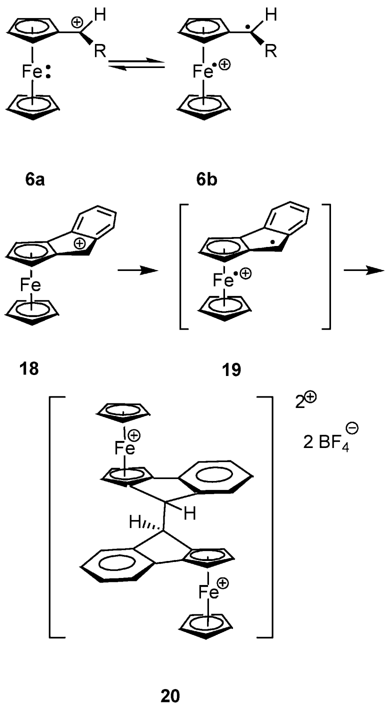
Scheme 2



ring was strongly bent toward the iron atom (**17**, Figure 1). According to extended Hückel calculations the approach of C6 toward the iron center leads to a stabilization of the highest occupied molecular orbitals, S_3 and S_4, which are symmetric with respect to the symmetry plane of the parent ferrocenylmethylium ion (Figure 1). The lowest unoccupied molecular orbital (S_5) is destabilized. As a result of the bending of C6, the total energy is lowered and the reduced Mulliken overlap population between Fe and C6 is increased to the same extent as for the other Fe−C bonds. On the basis of these calculations it was also pointed out that a structure with a planar fulvene ligand should have a small HOMO−LUMO gap, which might favor a triplet ground state. The question of having an equilibrium between a closed shell (e.g., **6a**) and a biradical structure (e.g., **6b**) for the ferrocenylmethylium ion (Scheme 2) was first raised by Rinehart et al.[16] to explain the formation of diferrocenylethane upon treatment of ferrocenylmethylcarbinol with sulfuric acid.

This topic was further pursued by Cais et al.[17] when he tried to generate the cation **18**, which underwent spontaneous dimerization to form the paramagnetic dication **20** (Scheme 2).[17a] In the following years the assumed diradicals could be trapped by nitrosobenzene,[17b] and the resulting products were characterized by ESR spectroscopy and chemical transformation to ferrocenyl-containing anilines.

Similar behavior was reported by Rybinskaya et al.,[18] who observed that the α-nonamethylferrocenylmethylium cation undergoes dimerization when stored in the solid state or solution. By use of nonamethylferrocenylmethylium ions substituted by bulky groups at the carbenium ion centers to prevent dimerization it was shown by ^{1}H NMR spectroscopy that in solution there were diamagnetic and paramagnetic species present. It was found that the population of the triplet state increased as a function of the electron-withdrawing ability of the aryl substituent R in **6a**/**6b** (C_6F_5 > α-$C_{10}H_7$ > C_6H_5).

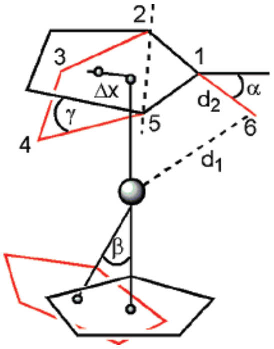


Figure 2. Definition of the structural parameters α, β, γ, d_1, d_2, and Δx and the enumeration of the center of the fulvene moiety used to characterize the geometry.

Table 2. Most Relevant Geometrical Parameters of 21−24 as Derived by X-ray Investigations[a]

compd	α [deg]	β [deg]	γ [deg]	Δx [Å]	d_1 [Å]	d_2 [Å]
21	6.8	2.1	−0.6	0.075	2.957	1.444
22	24.0	4.9	−1.7	0.038	2.686	1.421
	12.8	2.9	1.6	0.076	2.869	1.387
23	21.1	8.4	−0.4	0.081	2.715	1.417
24	22.7	1.5	1.3	0.167	2.567	1.370

[a] For the meaning of α, β, γ, Δx, d_1, and d_2 see Figure 2.

X-ray diffraction studies on single crystals of the tetrafluoroborates of ferrocenyldiphenylcyclopropenium- (**21**),[19] α,α′-diferrocenylmethylium- (**22**),[20] and ferrocenyldiphenylmethylium ions (**23**)[21] as well as nonamethylferrocenylmethylium ion (**24**) tetra[3,5-bis(trifluoromethyl)]phenylborate[22] confirm the bending of the C6 atom of the fulvene ring toward the iron atom. To characterize the most relevant geometrical data, we use the parameters α, β, γ, Δx, d_1, and d_2 as defined in Figure 2. In Table 2 these data are listed. It is seen that the parameters α and d_1 vary considerably.

In **21** the positive charge of the carbenium center is delocalized in the cyclopropenylium ring. This delocalization results in a bending angle α = 6.8° with an Fe···C6 distance of 2.96 Å. In **22**−**24** an increase of the angle α and a reduction of the Fe···C6 (d_1) distance is encountered. Also d_2, the C1−C6 bond length, is slightly reduced when d_1 is diminished. As discussed above, these geometrical changes were rationalized on the basis of quantum chemical calculations.[15]

3. Thermodynamic and Spectroscopic Studies on Ferrocenylmethylium Ions

These properties have been summarized by Watts;[9a] therefore we confine ourselves to give only a short survey. The $\mathrm{p}K_\mathrm{R}^+$ values for the systems such as the ones shown in Scheme 3 have been reported. The systems include substituents at the C6 carbon atom at the fulvene ring as well as at the C_4H_4 part. Most $\mathrm{p}K_\mathrm{R}^+$ values obtained differ by ≤±2. Compared to the benzyl cation (about −25) and triphenylmethyl cation (−66) this indicates a strong stabilization by the Fe group.

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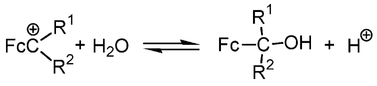
Scheme 3



R^1 = H, Me, Me, Ph, Ph
R^2 = H, H, Me, H, Ph

NMR spectroscopic studies of ferrocenylcarbocations were extensively used in structural, conformational, kinetic, and mechanistic studies.[9] Here we would like to mention only those conclusions that can be drawn from the ^{13}C NMR data and the results concerning the energy barrier to rotation around the *exo* double bond (C1−C6 bond) of the fulvene part.

The results obtained from ^{13}C NMR investigations[23a] reveal that the magnitude for the $^1J_{CH}$ values for C6 ranges from 158 to 169 Hz. This value points to a sp^2 hybridization at this carbon atom. All of the ^{13}C resonances of the ferrocenyl skeleton in the cation appear downfield shifted compared to the corresponding resonances of the alcohol precursors. The strongest shift is observed for the signals of the C6 carbon. The variation of the $\Delta\delta$ values for C6 shows that the concentration of positive charge at this center increases in the order primary > secondary > tertiary.

The energy barrier of rotation around the C5−C6 bond was determined by means of ^{1}H NMR spectroscopy.[20b] The activation energies (E_a) range between 16.5 and 24.0 kcal/mol.

It is interesting to note that the hydrolysis of the [*n*]-ferrocenophan-1-yl acetates **5a**−**c** (Chart 1) revealed[24] that the rate increases from **5a** ($n = 3$) to **5c** and **5b** ($n = 4$). The slower rate for **5a** was ascribed to the fact that the shorter bridge prevents full conjugation of the ferrocene moiety and the developing positive charge. Recent structural investigations and DFT calculations[25] on **25a**−**c** (Chart 2) revealed a strong influence of the substituent R on the bending angle. The angle α varied from 13.7° (**25b**) to 30.5° (**25c**) to 42.8° (**25a**).

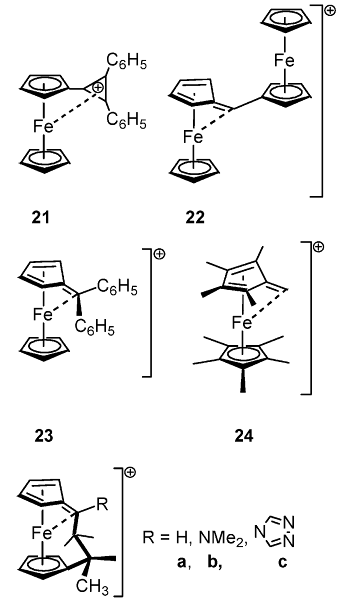
Related to the ferrocenylcarbenium ions discussed so far are the ferrocenyl (Fc)-, nonamethylferrocenyl (Fc*)-, and ruthenocenyl (Rc)-terminated allylium salts **26**−**31** (Chart 3).[26] These cations were available from formylmetallocenes (**32**, Mc = Fc, Fc$^+$, Rc), which were first transformed into the (2-bromovinyl)-metallocenes **33** via a Wittig reaction (Scheme 4). Bromine−lithium exchange followed by reaction with another equivalent of formylmetallocene afforded the alcohol **34**. The desired cations **26**−**31** were obtained by treatment of **34** with the appropriate acids (cf. Chart 3).

The solid-state structures of the symmetrically substituted salts of **26b**, **27b**, and **30b** as well as the unsymmetrical species **28a**, **29b**, and **31a** were investigated.[26] The bending angles α between the C6 atom of the fulvene fragment vary for **26**−**28** between 1.0° and 14.5°. They are larger for **29**−**31** (see below).

4. Congeners of the Iron Group

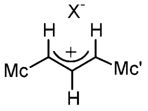
The solvolysis experiments of Richards and Hill[10] summarized in Table 1 as well as the addition reactions of acetic acid to vinylmetallocenes[7] of the iron group suggested that ruthenocenyl- and osmocenylmethylium ions should be more stable than the iron congener. This suggestion was verified by the isolation and characterization of several cations.

Chart 2

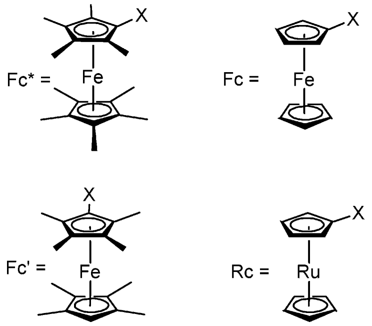


21 **22** **23** **24** **25**

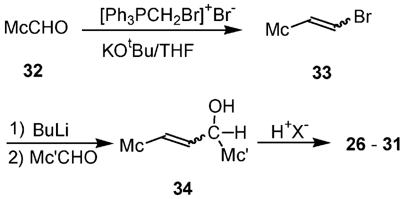
Chart 3



Mc	Mc'	BF_4^-	PF_6^-
Fc	Fc	**26a**	**26b**
Fc*	Fc*	**27a**	**27b**
Fc	Fc*	**28a**	**28b**
Fc	Rc	**29a**	**29b**
Rc	Rc	**30a**	**30b**
Rc	Fc'	**31a**	



Scheme 4



The parent ruthenocenylmethylium ion **35** was prepared from ruthenocenylmethanol and acids, such as HPF_6, HBF_4, or the Lewis acid $(C_6H_5)_3C^+PF^-{}_6$, under mild conditions.[27] In contrast to the ferrocene analogues, the cation **35** is stable under nitrogen in the solid state and in dichloromethane solution.

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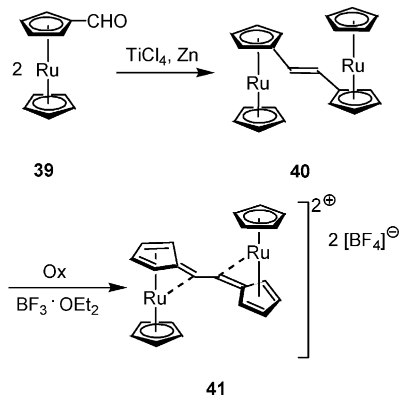
Table 3. Most Relevant Geometrical Parameters of 35−38 as Derived by X-ray Investigations[a]

compd	α [deg]	*β* [deg]	*γ* [deg]	Δ*x* [Å]	*d*$_1$ [Å]	*d*$_2$ [Å]
35	39.9	5.1	3.0	0.224	2.272	1.404
36	38.2	5.5	2.8	0.264	2.270	1.401
37	40.8	6.9	1.6	0.231	2.244	1.426
38	33.9	7.0	2.9	0.209	2.407	1.400

[a] For the meaning of α, *β*, *γ*, Δ*x*, *d*$_1$, and *d*$_2$ see Figure 2.

Scheme 5



Determination of the crystal structure of **35** with the anion $CF_3SO_3^-$ or tetrakis[3,5-bis(trifluoromethyl)phenyl]borate ($BarF^-$) turned out to be complicated due to disorder. Nevertheless, it is clear that the CH_2 group is coordinated to the metal, causing a large value for α (42.6°). The Ru⋯CH_2 bond lengths range from 2.25(1) to 2.40(1) Å for disordered structures. The value for α in the case of the nondisordered cation **35** is 39.9° (see Table 3).

The X-ray structure of the nonamethyl(ruthenocenyl)methylium ion (**36**) shows a Ru⋯CH_2 distance of 2.270 Å and the bending angle α is 38.2°.[28] A comparison with the nonamethyl(osmocenyl)methylium ion (**37**) reveals an Os⋯CH_2 distance of 2.444 Å and a bending angle α of 40.8°.[29]

A more complex species in which a η^5-cyclopentadienyl-η^6-fulvene ruthenium(II) cation is incorporated in a larger system is **38**, in which a ruthenocenyl and ferrocenyl system compete for the cationic center.[30] The Ru⋯CH distance was found to be 2.407(6) Å. The distance between the formal carbenium ion center and the iron atom is 3.155(5) Å. The bending angle α of the CH moiety was measured to be 33.9°. The length of the C5−C6 bond was reported to be 1.40 Å.

These data, especially the comparison between the nonamethyl(metallocenyl)methylium ions **24** (see Table 2) and **36** and **37** (see Table 3), reveal an increase of the bending angle α between the fulvene moiety and the metal in the order Os > Ru ≫ Fe, indicating a stronger metal−C6 interaction for the heavier metals.

A starting point for a new group of complexes containing the CpRu(fulvene) fragment was formylruthenocene (**39**) (Scheme 5). By treatment of **39** with $TiCl_4$/Zn in THF the anticipated 1,2-bis(ruthenocenyl)ethylene (**40**) resulted.[31] Cyclic voltammograms showed an irreversible two-electron oxidation wave at significantly lower potential than that of ruthenocene. A 2-fold electrochemical oxidation with *p*-benzoquinone in the presence of $BF_3 \cdot O(C_2H_5)_2$ resulted in the formation of the stable dication **41**.[31] In an analogous manner the dications **42** and **43** were prepared[31] and investigated (Chart 5). X-ray investigations[31] carried out on single crystals of the dications revealed short distances between the metal atoms and the former olefinic carbons (2.571(4) and 2.474(4) Å, respectively), which corresponds to bending angles α of about 40°.

Chart 4

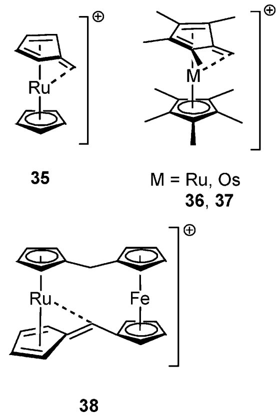
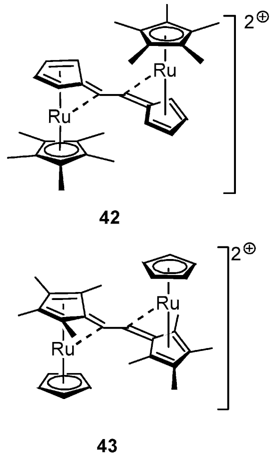


Chart 5



Closely related systems to **41−43** were generated from ruthenocene-terminated butadienes (e.g., **44**) and hexatrienes (Chart 6), which were readily available from a Wittig reaction of 3-ruthenocenyl-2-propenals with ruthenocenylmethylphosphonium salts or by treatment of the propenals with $TiCl_4$/Zn, respectively.[32,33] Cyclic voltammetry of these complexes revealed reversible two-electron redox processes. The oxidation potentials for the ruthenocene-terminated oligoenes decreased with growing number of −HC═CH− units as follows: Rc−CH═CH−Rc +0.09 V, Rc−$(CH{=}CH)_2$−Rc −0.06 V, and Rc−$(CH{=}CH)_3$−Rc −0.07 V (Rc = ruthenocenyl). The two-electron oxidation of the bis(ruthenocenyl)butadienes **44a−c**[33] with 2 equiv of *p*-benzoquinone/$BF_3 \cdot OEt_2$ at 0 °C afforded the dicationic complexes **45a−c**. The same holds for the bis(ruthenocenyl)hexatrienes. NMR spectroscopic investigations reveal a *trans* configuration of the central double bond in

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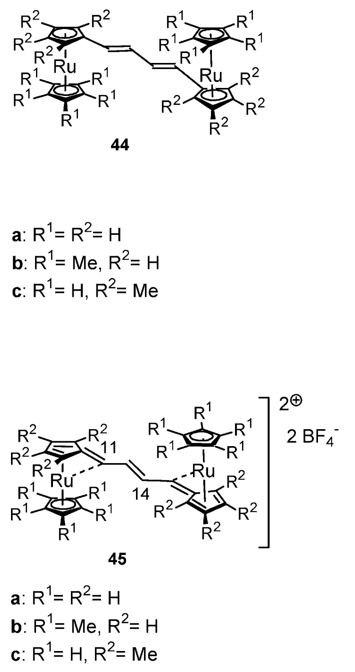
(32) Sato, M.; Kudo, A.; Kawata, Y.; Saitoh, H. *Chem. Commun.* **1996**, 25−26.

(33) Sato, M.; Nagata, T.; Tanemura, A.; Fujihara, T.; Kumakura, S.; Unoura, K. *Chem.−Eur. J.* **2004**, *10*, 2166−2178.

Chart 6



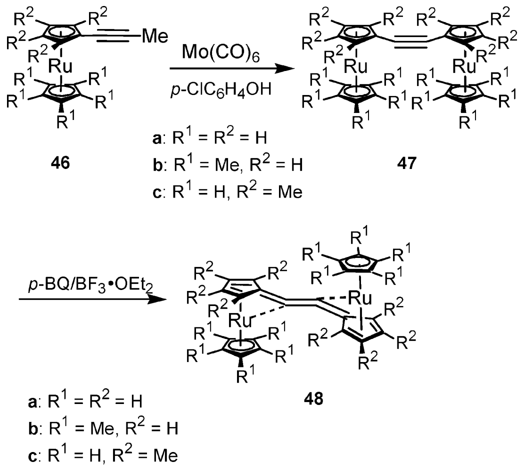
44

a: $R^1 = R^2 = H$
b: $R^1 = Me$, $R^2 = H$
c: $R^1 = H$, $R^2 = Me$

45

a: $R^1 = R^2 = H$
b: $R^1 = Me$, $R^2 = H$
c: $R^1 = H$, $R^2 = Me$

Scheme 6



46 **47** **48**

a: $R^1 = R^2 = H$
b: $R^1 = Me$, $R^2 = H$
c: $R^1 = H$, $R^2 = Me$

solution. The [Ru(C_5H_5)] moieties adopt in solution the *syn* and *anti* configuration. X-ray data from **45a** in which a *syn*−*trans* configuration was found to reveal the following distances between ruthenium atoms Ru1 and Ru2 and the α-C atoms C11 and C14: Ru1−C11 = 2.354(6) Å and Ru2−C14 = 2.358(7) Å. The bending angles α were 36.2° and 36.9° and the lengths of the *exo*-double bonds 1.407(10) and 1.409(11) Å, respectively.

The 1,2-bis(ruthenocenyl)ethynes **47a**−**c** (Scheme 6) were available from **46a**−**c** by a metathesis reaction with $Mo(CO)_6$/*p*-ClC_6H_4-OH as catalyst.[34] Oxidation of **47a**−**c** with *p*-benzoquinone [(*p*-BQ)/BF_3•OEt_2] gave the stable dications **48a**−**c**. The ^{13}C NMR signals for the carbon atoms of the bridging chain in **48a**−**c** appear at $\delta = 77.7$ ppm (**48a**), $\delta = 80.1$ ppm (**48b**), and $\delta = 76.3$ ppm (**48c**), suggesting the presence of a bis(1,4-butadienediyl)butatriene bridge for the central part. This view was confirmed by X-ray data of **48c**,[34b] which show that the bridging ligand is coordinated in the η^6-mode and an *anti* configuration is adopted by the two (η-C_5H_5)Ru groups. The Ru−C6 distance was found to be 2.178(3) Å, somewhat shorter than in **48b** (av 2.410 Å)[34a] and **35** (2.272(4) Å).[27] The bending angle is α = 32.7°. This value is smaller than that recorded for **36** (38.2°), **35** (39.9°), and **48b** (41.3°).[34b] The length of the exocyclic double bond of **48c**, d_1, is 1.409(4) Å, which compares well to other Ru−fulvene complexes such as **35**, **36**, and **48b**. The length of the central double bond of **48c** was reported to be 1.262 Å. This value is identical to that in **48b**. In Figure 3 we present the molecular structure of **48c**.[34b] It shows the *anti* configuration for the (η-C_5H_5)Ru groups and a coordination of the C6 atoms to Ru.

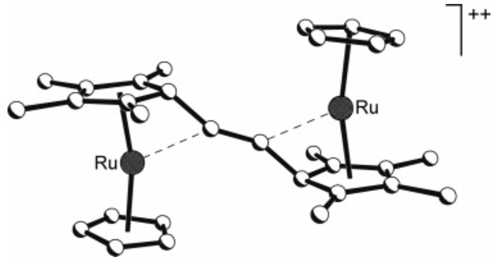
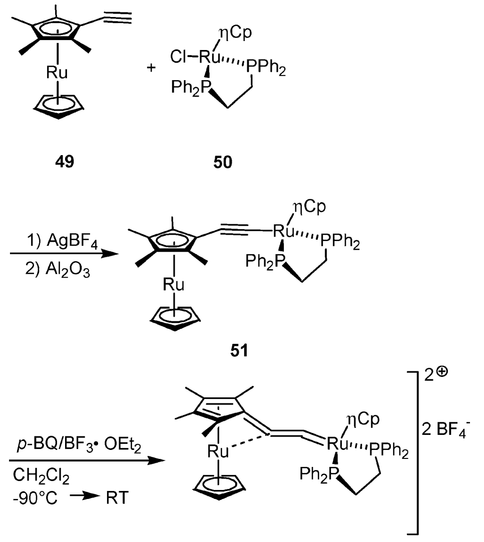


Figure 3. Molecular structure of **48c**.[34b] The hydrogen atoms are omitted for the sake of clarity.

Scheme 7



49 **50**

51

52

Scheme 7 shows a synthetic protocol in which 1-ethynyl-2,3,4,5-tetramethylruthenocene (**49**) was reacted with RuCl$\mathbf{P}_2$L ($\mathbf{P}_2$ = dppe, L = ηC_5H_5), **50**, leading to the complex **51** with two metal centers.[35] Two-electron oxidation of the latter yielded the dications **52**. The ^1H NMR spectrum of **52** and related species showed that the protons of the η-C_5H_5 ring of the ruthenocenyl moiety are shifted by 1.2 to 1.5 ppm to lower field as compared to the neutral species (e.g., **51**). Also the proton signals for the η-C_5H_5 ligand coordinated to the Ru atom with the dppe ligand show a similar low-field shift. These results suggest that the positive charges are delocalized on both Ru centers.[35] X-ray data of **52** reveal a Ru−C6 bond length of 2.281(9) Å, a value that is close to that reported for **45** (2.272(4) Å).[27] The angle α for **52** is reported to be 40.4(10)°.[35]

5. Metallocenyl Dications of the Iron Triad and Ferrocenylboranes

The first ferrocenyl dication was reported in 1967. It was generated from the corresponding diol, **53**, in FSO_3H-SbF_5

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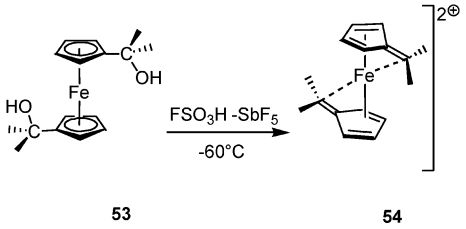
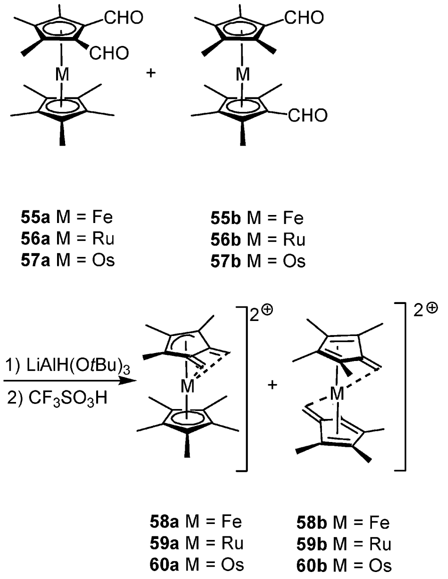
Scheme 8



Scheme 9

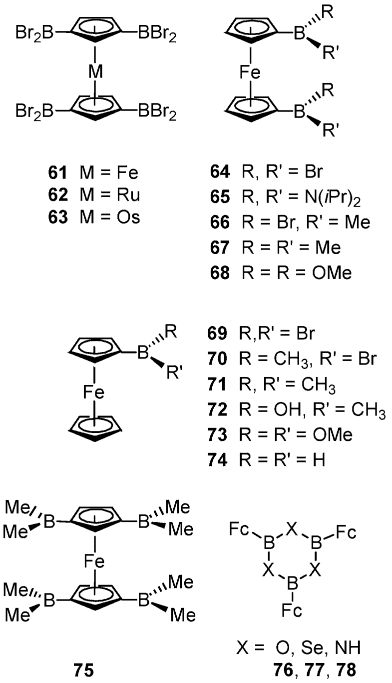


(Scheme 8).[36] The existence of **54** in solution was confirmed by ^{1}H NMR spectroscopy. The singlet due to the methyl protons (−3.20 ppm) is close to that found for related carbenium ions.

The higher stability of the ruthenocenyl- and osmocenylmethylium ions was the motivation to generate the dications **58**−**60**.[37] The starting points for the syntheses of these dications were the corresponding decamethylmetallocenes. These were partially oxidized by $BaMnO_4$ to yield the expected monoaldehydes as major product and, as minor components, the dialdehydes **55a**−**57a** and **55b**−**57b**, respectively (Scheme 9). In this mixture (1,2-dialdehyde (**a**) + 1,1′-dialdehyde (**b**)) the 1,2-isomers (**a**) dominate. After separation the dialdehydes were reduced to the diols, which were then converted to the respective dications **58**−**60**. Evidence for the existence of the dications is provided by the fact that the proton signals for the 1,1′-dications and the 1,2-dications are strongly shifted toward lower field in comparison with the monocation signals. The AB quadruplets of the protons of the CH_2 protons in the 1,1′-dications **58b**−**60b** and the signals of the α- and *β*-methyl groups of the rings are in accord with the proposed structures (Scheme 9). Furthermore, the AB quadruplets of the CH_2 groups indicate that the *gauche* conformation of **58b**−**60b** is predominant in solution. This result is in accord with results of extended Hückel calculations.

The mono- and dications of the iron triad metallocenes suggested a possible stabilization of the corresponding boranes. In 1976 Siebert and co-workers raised the question whether the BX_2 moiety is also bent toward the metal in ferrocenylhaloboranes.[38] This question was answered in 1995[39,40] and 1996[41] on the basis of structural investigations on the tetrakis(dibromoboryl)metallocenes **61**−**63** (Chart 7) and various 1,1-bis(boryl)ferrocenes (**64**, **65**), and dibromoborylferrocene (**69**), to which further derivatives[42] such as **66**−**68**, **70**−**73**, and **75**−**78** were added (Chart 7).

Chart 7



Structural investigations by means of the X-ray technique carried out for the series **61**−**63** revealed a bending of the BBr_2 groups toward the metal, which is displayed by values for α = 1.5°, 6.9° (**61**), 7.4°, 12.2° (**62**), and 6.7°, 12.6° (**63**). The cyclopentadienyl rings in **61**−**63** show a conformation between a staggered and eclipsed situation. For **64** a bending angle α of 10.2° was encountered for the BBr_2 moieties, whereas the B[N(*i*Pr)$_2$]$_2$ groups in **65** are coplanar to the cyclopentadienyl rings. This result shows that a strong electrophilic center is necessary for a modest Fe···B interaction.

The strongest bending was found for **69** with α = 18.3°, where only one electrophilic center is interacting with the metal.[42] It is interesting to note that also for the trimers **76**−**78** with donor atoms in the ring a bending between 5° and 10° was found. The bending of the BH_2 group in **74** was calculated[42] to be 26.5° using the DFT method. A Bader analysis of the electron density topology of **74** reveals no direct iron−boron bonding. Strongly delocalized orbital interactions have been identified. They involve the boron p-orbital, C_{ipso} of the adjacent cyclopentadienyl ring, d-orbitals of the iron atom, and a through-space interaction with the second cyclopentadienyl ring. The

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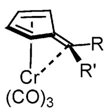
Chart 8



79a R = R' = H
79b R = R' = C_6H_5
79c R = R' = SCH_3
79d R = R' = cyclopropyl
79e R = R' = S-CH_2-CH_2-S
79f R = H, R' = $N(CH_3)_2$
79g R = R = R' = S-CH=CH-S

Table 4. Most Relevant Geometrical Parameters of the Fulvene−Cr(CO)₃ Complexes 79a−g as Derived by X-ray Investigations[a]

compd	α [deg]	Δ*x* [Å]	γ [deg]	d_1 [Å]	d_2 [Å]
79a	34.4(21)[b]	0.22(5)[b]	0.5(24)[b]	2.35(2)[b]	1.36(2)[b]
79b	28.4	0.19(1)	1.5	2.55(1)	1.45(1)
79c	27.1	0.19	2.0	2.556(6)	1.390(1)
79d	23.9	0.20	2.8	2.627(4)	1.404(5)
79e	19.1	0.11	0.3	2.775 (4)	1.397(6)
79f	12.2	0.07	−1.1	2.966(7)	1.404(10)
79g	7.9	0.03	2.1	3.045(5)	1.397(7)

[a] For the meaning of α, Δ*x*, γ, d_1, and d_2 see Figure 2. [b] Average values taken from five independent molecules.

structural data are augmented by electrochemical studies and Mössbauer spectra on **67**, **71**, and **75**.

6. (η^6-Fulvene)chromium Tricarbonyl Complexes and Congeners

The first η^6-fulvene complex that was studied by means of X-ray analysis was $[(\eta^6\text{-}C_5H_4C(C_6H_5)_2)]Cr(CO_3)$ (**79b**) (Chart 8).[43] This complex was prepared from chromium hexacarbonyl and 6,6-diphenylfulvene by heating.[44] A more efficient procedure was used in the reaction between the appropriate fulvene and $(CH_3CN)_3Cr(CO)_3$ in THF or pentane.[45] The structure of **79b** confirmed the strong bending of C6 that was predicted for the α-ferrocenylmethylium ion **17**. The neutral complex **79b** shows an inclination of the C1−C6 bond by α = 28.4° with respect to the planar five-membered ring (Table 4). The C1−C6 bond length was found to be 1.45 Å, and the Cr−C6 bond 2.55 Å. The strong bending of the C1···C6 bond is in line with extended Hückel calculations reported for **79a**.[46] With the help of Figure 4 it is demonstrated that C6 of the fulvene ligand of **79a** is strongly bent toward the metal atom. To rationalize this, a schematic drawing of the highest occupied molecular orbital as obtained from extended Hückel calculations is shown in Figure 4b.[46] The bending of C6 causes a bonding interaction between C6 and the Cr-centered e_s-orbital.[46]

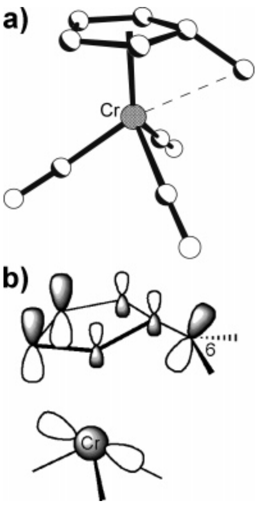
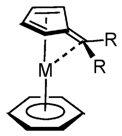
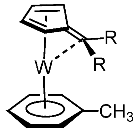


Figure 4. (a) Molecular structure of **79a**.[45c] The hydrogen atoms are omitted for the sake of clarity. (b) Schematic drawing of the highest occupied molecular orbital, e_s, of **79a**.

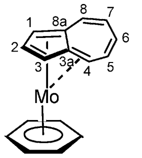
Chart 9



R = CH_3, C_6H_5
M = Mo **80a**, **80b**
M = W **81a**, **81b**



R = CH_3, C_6H_5
82a, **82b**



83

A study of the structures of various fulvene−Cr(CO)₃ complexes substituted at C6 (**79b**−**g**, Chart 8)[45] revealed a strong bending for the unsubstituted fulvene ligand (**79a**) and only a small inclination for **79g**, where a fully conjugated 6π-system is connected to the C6 atom of the fulvene ligand. Paralleling this reduction of α is a decrease in the Δ*x* value (Table 4).

In line with these results are those obtained from ^{13}C NMR studies.[45a] The difference Δ of the chemical shift between C6 of the free fulvene ligand and the corresponding Cr(CO)₃ complex, $\Delta = \delta_{\text{ligand}} - \delta_{\text{complex}}$, of **79a**−**g** varies from 49.7 ppm for **79a** to −1.4 ppm for **79g**. The difference Δ correlates linearly with the Cr−C6 distance (d_1), indicating that the structures in solution and in the solid state of **79** are very close.

Isoelectronic species were obtained when bis(η-benzene)-molybdenum and tungsten were treated with 6,6-dimethyl- and 6,6-diphenylfulvene, respectively.[47] The resulting red to purple complexes **80a**, **80b**, **81a**, and **81b** are listed in Chart 9. By treatment of bis(η-toluene)tungsten with 6,6-dimethyl- and 6,6-diphenylfulvene the complexes **82a** and **82b** resulted. For four of them (**80a**, **80b**, **82a**, **82b**) detailed geometrical parameters are available. The most relevant data are given in Table 5.[47] As anticipated, the C6 center of the fulvene moiety is considerably bent (α) toward the metal. On the basis of extended Hückel calculations on the parent system $Mo(\eta^6\text{-}C_6H_6)(\eta^6\text{-}C_5H_4CH_2)$ (**80c**) this bending was explained by a strong interaction between

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(46) Albright, T. A.; Hoffmann, R.; Hofmann, P. *Chem. Ber.* **1978**, *111*, 1591−1602.

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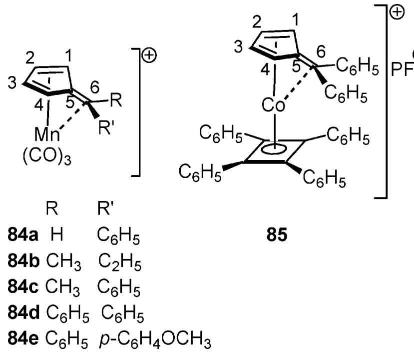
Table 5. Most Relevant Structural Data of the Fulvene Complexes 80a, 80b, 81a, and 81b[a]

compd	α [deg]	Δ*x* [Å]	*γ* [deg]	*d*₁ [Å]	*d*₂ [Å]
80a	35.0	0.37	6.2	2.31(2)	1.42(2)
80b	34.4	0.32	4.9	2.375(3)	1.437(4)
81a	33.8	0.29	4.0	2.39(3)	1.45(3)
81b	35.3	0.32	4.9	2.33(1)	1.44(2)

[a] For the meaning of α, Δ*x*, *γ*, d_1, and d_2 see Figure 2.

Chart 10



the metal 4d-orbitals and the π*-orbitals of fulvene.[47] It is interesting to note that in the azulene complex [$(C_{10}H_8)(C_6H_6)$Mo] **83** the C3a−C4 bond is strongly bent (α = 33°) toward the metal center.[48a] In the $Cr(CO)_3$ complex of 4,6,8-trimethylazulene, however, there is no evidence for an interaction between the Cr center and C4 or C8 of the azulene ring, respectively.[48b]

In connection with the calculations on **79a**[46] and **80c**[47] there are others, using the DFT methology, on related systems containing benzylic cations and anions stabilized by chromium tricarbonyl complexation[49] In the case of these cations the stabilization was traced back to a direct interaction of the metal center with the *exo*-CH_2 carbon centers.[49]

7. Carbenium Centers Stabilized by Mn and Co

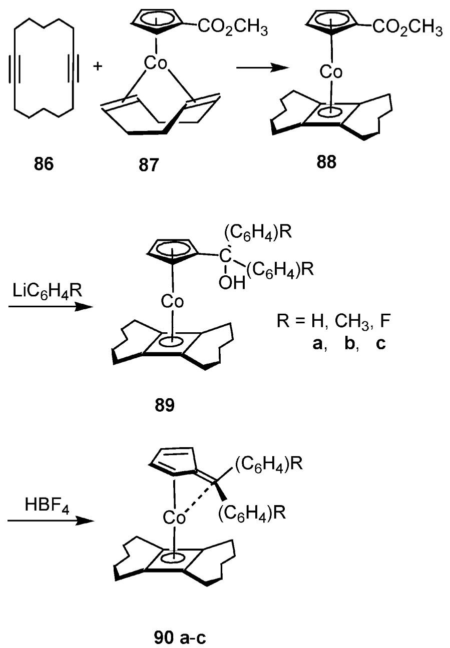
The α-cymantrenylmethylium ions **84a**−**e** were generated in solution by treating the corresponding carbinols with concentrated sulfuric acid (Chart 10).[50] The ^{13}C NMR spectra showed a downfield shift (δ = 144−201 ppm) for the carbenium center C6 as compared to the corresponding α-substituted ferrocenylmethylium ions (δ = 116−161 ppm). This indicates a decrease of electron density at C6 for the cymantrenyl systems with respect to the ferrocenyl species. The geometrical parameters of **84d** as a blue tetrakis[3,5-(trifluoromethyl)phenyl] borate are available from X-ray diffraction studies of single crystals.[51] The most relevant geometrical parameters of **84d** are collected in Table 6. We notice only a small bending angle, α = 7.7°, consistent with a long Mn···C6 bond of 3.05 Å. Quantum chemical calculations (B3LYP) on the parent cation with a planar fulvene ring and an inclined exomethylene carbon atom show a considerable stabilization for the bent structure. The bending goes along with an elongation of the C1−C6 bond from 1.36 Å to 1.38 Å due to an electron transfer from the metal to the fulvene moiety.[51]

Table 6. Most Relevant Structural Data of the Complexes 84d and 90b[a]

compd	α [deg]	Δ*x* [Å]	*γ* [deg]	*d*₁ [Å]	*d*₂ [Å]
84d	7.7	0.02	−1.6	3.045(4)	1.413(5)
90b	9.5[b]	0.02[b]	−1.5[b]	2.989(6)[b]	1.414(6)[b]

[a] For the meaning of α, Δ*x*, *γ*, d_1, and d_2 see Figure 2. [b] Average values taken from two independent molecules.

Scheme 10



Seyferth and Merola generated in 1978 [η^5-cyclopentadien-1-yl-η^4-tetraphenylcyclobutadienecobalt]diphenylmethylium hexafluorophosphate (**85**) and showed by means of ^{13}C NMR spectroscopy that the C6 carbon atom is deshielded compared to the carbinol by $\Delta\delta$(C6) = 135.4 ppm. This shift is indicative for transition-metal-stabilized tertiary carbenium ions.[52]

A cobalt-stabilized carbenium ion, which allowed the growing of single crystals, was obtained by the reaction sequence shown in Scheme 10. From 1,8-cyclododecadiyne **86** and the cobalt complex **87** it was possible to obtain **88**, from which the carbinols **89a**−**c** could be synthesized. Treatment of the carbinols with HBF_4 in ether affords the tetrafluoroborates of the violet carbocations **90a**−**c**.[53] Investigation of single crystals of **90b** using the X-ray technique shows a bending of the C6 atom by α = 9.5° toward the metal and a pronounced bond alternation in the fulvene ligand (cf. Table 6). The interaction between C6 and the metal in **90b** is further substantiated by comparison of the ^{13}C NMR chemical shift of **90b** with that of **89b** ($\Delta\delta$ = −65 ppm). This points to a weaker interaction between metal and fulvene C6 carbon in **90** as compared to the corresponding ferrocene derivatives. Restricted HF ab initio calculations on **23** and the $[Co(C_4H_4(C_5H_4CPh_2)]^+$ complex reveal that the natural charge at the cobalt center is larger than that at the iron center.[53]

A species in which two cations with Co···C interactions are tied close together is shown in **91** (Chart 11). The spectroscopic properties of **91** are close to those reported for **90**.[54] The dication **91a** is a good candidate for an interaction involving both

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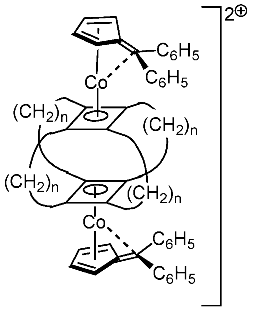
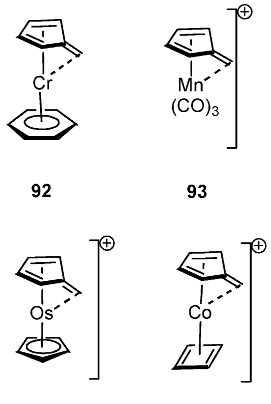
Chart 11



91a n = 3
91b n = 5

Chart 12



92 **93**

94 **95**

metallocene units. This is brought about by the short bridges, which force both units into close proximity.[55]

8. Theoretical Investigations

The understanding of the structural behavior of α-metallocenylmethylium ions of d^6 and d^9 transition metals was aided by quantum chemical calculations. At the beginning the method used was an extended Hückel version.[15,37,46,47] Later on HF-SCF ab initio calculations[53] and the DFT methodology[49,51] were applied. A comparison between the experimentally determined structural parameters and those derived by theoretical methods was difficult in those cases where bulky substituents at the C6 center of the fulvene ligand or at the other ring make a bending of the C6 center to the metal less favored.

For a better comparison of the fulvene complexes we optimized all the geometrical parameters of the parent systems **17**, **35**, **79a**, and **92**−**95** with respect to the total energy at the B3LYP/LANL2DZ level of theory.[56,57] In Table 7 we list the most relevant geometrical parameters together with the net charge q at the C6 center. Approximately linear relationships for the computed Wiberg bond order between C(6) and the metal and the values for the angle α as well as the charge q at C(6) are encountered.[58]

Table 7. Most Relevant Geometrical Parameters and Charges (q) at C(6) Derived from DFT Calculations on 17, 35, 79a, and 92−95[a]

compd	α [deg]	Δx [Å]	γ [deg]	d_1 [Å]	d_2 [Å]	q (C6)
79a	28.3	0.19	0.4	2.49	1.41	−0.35
92	34.1	0.33	3.8	2.33	1.42	−0.40
93	21.8	0.24	2.2	2.67	1.39	−0.22
17	31.7	0.32	3.9	2.43	1.39	−0.25
35	32.9	0.28	2.5	2.44	1.41	−0.30
94	37.7	0.26	2.6	2.36	1.43	−0.35
95	20.6	0.19	0.4	2.68	1.38	−0.23

[a] For the meaning of α, Δx, γ, d_1, and d_2 see Figure 2.

9. Concluding Remarks

The past 20 years have witnessed a considerable growth of metallocenylmethylium ions and fulvene complexes, respectively, of d^6 to d^9 metals. This development was realized in all four groups: In the sixth group the fulvene−$Cr(CO)_3$ complexes were augmented by fulvene $M(C_6H_6)$ complexes with M = Mo and W. In the seventh group the first derivative of a cymantrenylmethylium ion was isolated and structurally investigated. In the iron triad the metallocenylmethylium ions of ruthenium and osmium proved to be stable species whose structural parameters were recorded. Furthermore the allylium salts that were terminated with ferrocenyl and/or ruthenocenyl fragments extended the variety of species. The dications of (pentafulvadiene)diruthenium complexes and bis(cyclopentadienylidene)-cumulene diruthenium complexes provide new classes of stable dications stabilized by metal−carbon interactions. Finally in the ninth group a cobaltocenyldiphenylmethylium ion stabilized by a cyclobutadiene moiety was investigated. This summary shows that in groups 7 and 9 there clearly is a call for action. This will very likely provide more stable samples.

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