Coordination Chemistry of Pentahalocyclopentadienyls☆

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The coordination chemistry of perhalocyclopentadienyl ligands, first developed in the early 1970's as a part of a research program directed towards the synthesis of oxidation-resistant fuel additives, has been revived in the last ten years. This renewed interest stems from the discovery that the coordinated cyclopentadienyl ligand allows multiple functionalizations. Thus, the high versatility of this important class of ligands can be broadened even further, which may be important with regard to industrial applications of metallocenes.

1. Introduction

Soon after the discovery of ferrocene, its high thermal stability and excellent solubility in a wide range of organic solvents led to a search for possible applications. One part of this applied research was directed towards fuel additives, and many patents in this field have since been published.[1] However, its relatively easy oxidation, leading via ferrocenium species ultimately to the deposition of Fe(III) oxides, severely restricted its practical use. Therefore, a search for substituted ferrocenes with higher oxidative stability was started, and one approach was the persubstitution with halogens, particularly fluorine or chlorine. While a synthesis of perchloroferrocene was successfully developed in the Air Force Materials Laboratories by Hedberg and Rosenberg in the early 1970's,[2] the quest for perfluoroferrocene is still going on.[3] Nevertheless, besides perchloroferrocene, a more "academic" research towards other perhalometallocenes continued first in the 1970's and has been intensified in the last decade. More than 25 perhalogenated cyclopentadienyl complexes, listed in Table 1, have been prepared and studied.

2. Synthesis of Perhalometallocenes

The traditional approach to the synthesis of metallocenes is the metathesis reaction of the appropriately substituted lithium, sodium or thallium cyclopentadienide with a transition metal halide. For this purpose, of course, the alkali metal or Tl(I) cyclopentadienide has to be prepared first. LiC_5Cl_5 was first reported in 1955,[4] but isolation was only achieved in 1972, with Tl^+ or large ammonium or phosphonium cations.[5] All these salts proved to be very unstable, and decomposed quickly above −15°C to intensely coloured "tars". The only transition metal derivatives that could be prepared from them were σ-complexes of mercury $(C_5Cl_5)HgR$.[6] More than ten years later, a synthesis of the $(C_5F_5)^-$ anion was developed by Seppelt *et al.*, but although some of these salts seemed to be more stable than their perchloro counterparts, they turned out to be totally unreactive towards transition metal halides.[7] No reports of a successful preparation of $(C_5Br_5)^-$ or $(C_5I_5)^-$ salts have appeared, and they are most likely too unstable to survive the conditions needed for a halide metathesis reaction. Since the standard method could not be applied for the

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Table 1. Known pentahalocyclopentadienyl complexes $(C_5X_5)ML_n$

M L_n	F	Cl	Br	I
$V(CO)_4$		**1a**	**1b**	
$Mn(CO)_3$ [a]		**2a**	**2b**	**2c**
$Mn(CO)_2PR_3$		**3**		
$Fe(C_5H_5)$		**4**		
$Fe(C_5X_5)$ [a]		**5a**	**5b**	**5c**
$Fe(CO)_2C_3F_7$		**6a**[b]	**6b**[b]	
$Ru(C_5H_5)$	**7**			
$Ru(C_5X_5)$ [a]		**8a**	**8b**	**8c**
$Ru(C_5Me_5)$ [a]	**9a**	**9b**	**9c**	**9d**
$Os(C_5X_5)$		**10a**	**10b**	**10c**
$Rh(COD)$		**11a**	**11b**	
$Rh(CO)_2$		**12**		

[a] Also mixed halide derivatives known. – [b] (C_5Cl_4I) or (C_5Br_4I) ligands only.

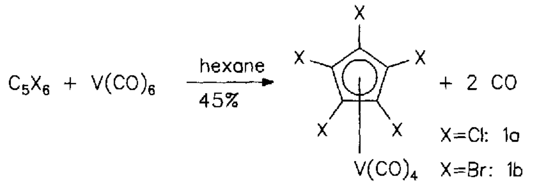
synthesis of perhalocyclopentadienyl complexes, several rather more sophisticated strategies had to be developed.[8–51]

2.1. Reaction of Hexahalocyclopentadienes C_5X_6 with Metal Carbonyls

The first successful reaction of this type was the photoinduced reaction of perchlorocyclopentadiene with dimanganesedecacarbonyl[19] (eq. 1). The σ-C_5Cl_5 complex obtained by this route can be transformed thermally[12] or photochemically[28] to pentachlorocymantrene $(C_5Cl_5)Mn(CO)_3$ (**2a**).

$$Mn_2(CO)_{10} + C_5Cl_6 \xrightarrow[h\nu]{C_6H_{12}} \begin{array}{ll} (OC)_5Mn-(\sigma C_5Cl_5) & 21\% \\ + (OC)_5MnCl & \\ + C_{10}Cl_{10} & \end{array} \qquad (1)$$

The only other report of a successful synthesis by this method deals with the preparation of the vanadium complexes **1a,b** from $V(CO)_6$ and C_5X_6. Here, the π-complexes are obtained directly (eq. 2).



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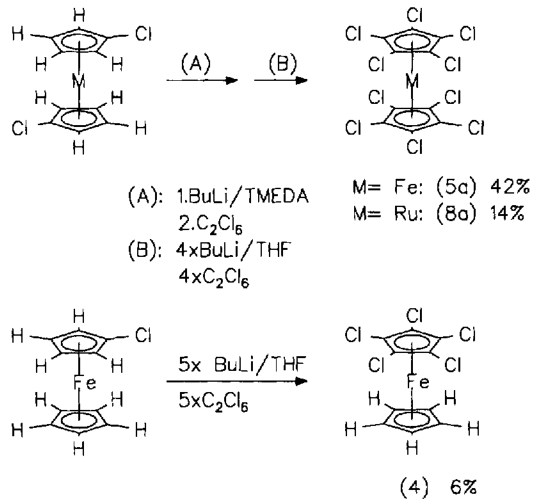
2.2. Halogenation of Lithiated Metallocenes

The first successful synthesis of a perhalometallocene was performed by this method. Starting from 1,1′-dichloroferrocene, stepwise alternating treatment with butyllithium and hexachloroethane led ultimately to decachloroferrocene.[2] Similarly, perchlororuthenocene **8a** can be obtained from 1,1′-dichlororuthenocene, and pentachloroferrocene **4** from monochloroferrocene[11][55] (eq.3).



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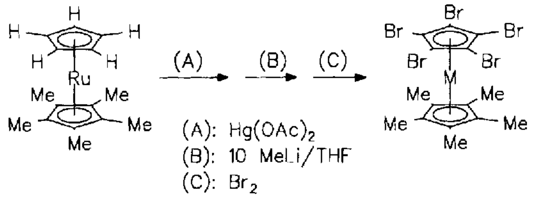
It should be mentioned that a sequence starting with mercuriation of pentamethylruthenocene, followed by treatment with an excess of MeLi and then with excess bromine produces the pentabromocyclopentadienyl compound **9c**[41] (eq. 4). Mixed perhalocyclopentadienyl complexes could be obtained by a sequence of lithium-halogen exchange reactions on **2b** or **5a**, followed by iodination with I_2 (see also Section 4.2.3.).[11a][52]



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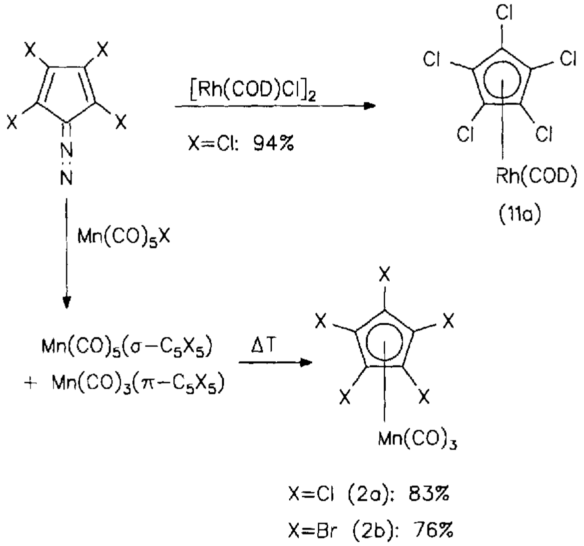
2.3. Carbene Insertion into Metal–Halogen Bonds

This method was developed by Reimer and Shaver in 1974, and was first used for the synthesis of pentachlorocyclopentadienyl derivatives of rhodium and manganese[12] (eq. 5).



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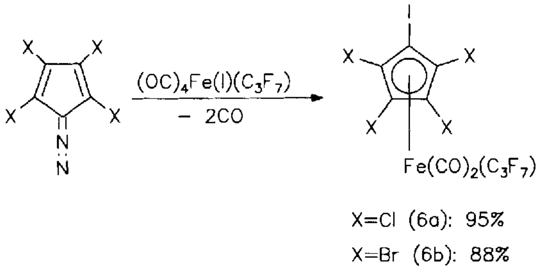
Herrmann and Huber extended this procedure to tetrabromodiazocyclopentadiene, which gave with $Mn(CO)_5Br$ perbromocymantrene **2b**.[17] Furthermore, the mixed halide derivatives $(C_5Cl_4Br)Mn(CO)_3$ (**2a′**) and $(C_5Br_4I)Mn(CO)_3$

(**2b'**) could be obtained by treating $C_5Cl_4N_2$ with $Mn(CO)_5Br$ and $C_5Br_4N_2$ with $Mn(CO)_5I$, respectively.[12][17]

Using the same strategy in the reaction with $Fe(CO)_4(C_3F_7)I$, Herrmann also succeeded in preparing the "mixed" perhalocyclopentadienyl complexes $(C_5X_4I)Fe(CO)_2(C_3F_7)$, X = Cl, Br (eq.6).[18]



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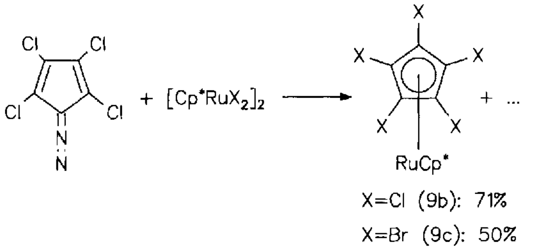
In an appendix to the original paper by Reimer and Shaver, it was stated that the method was examined for several halide complexes, but despite an obvious reaction no definite products could be isolated. This observation apparently deterred other researchers from pursuing further investigations, and it was only ten years later that a paper by Gassman and Winter described another application involving the successful synthesis of pentachloro-pentamethyl-ruthenocene **9b** (eq. 7).[23] Only recently, our group in Munich discovered that pentabromo-pentamethyl-ruthenocene **9c** and pentabromocyclopentadienyl-cyclooctadiene-rhodium **11b** can also be obtained in a similar manner.[53]



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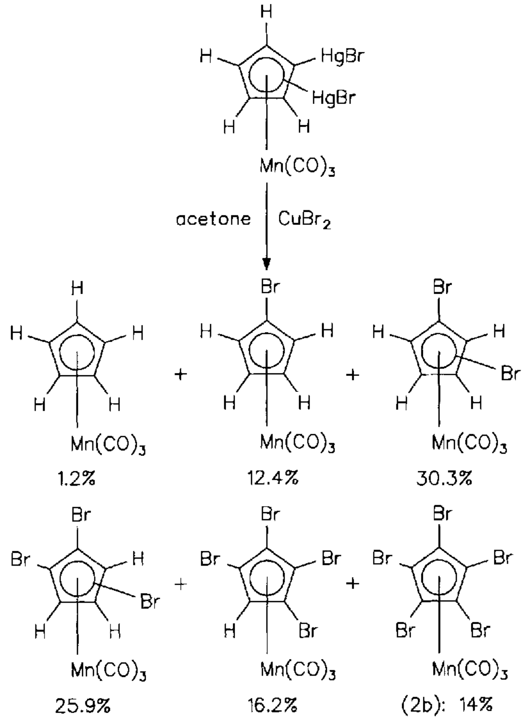
As can be seen from these equations, only the rhodium complexes simply insert the cyclopentadienylidene carbene. The carbonyl complexes lose two molecules of CO, either immediately or after heating. The ruthenium system also involves a reduction step from Ru(III) to Ru(II), which is either achieved by treatment with excess diazo compound or by the addition of Zn powder as a reductant.

2.4. Permercuriation of Metallocenes Followed by Electrophilic Halogenation

This method has produced by far the greatest number of perhalometallocenes, and remains the only method by which pentaiodocyclopentadienyl complexes can be produced.

It was first discovered by Nefedov as a side reaction when he treated bis(bromomercuri)cymantrene with $CuBr_2$ and obtained a mixture of all possible bromocymantrenes, with a 14% yield of pentabromocymantrene **2b**[10] (eq. 8). Two papers by Boev and Dombrovskii described the permercuriation of ferrocene and several monosubstituted derivatives with $Hg(OOCCF_3)_2$, followed by treatment with KI_3 or KBr_3 to give $(C_5I_4R)Fe(C_5I_5)$ and $(C_5Br_4R)Fe(C_5Br_5)$, respectively.[15][16]



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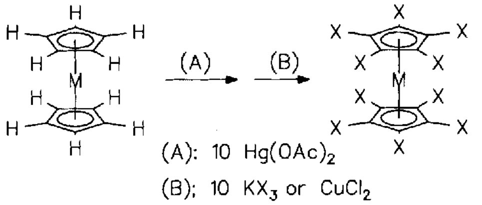
The compounds were, however, poorly characterized. Repetitions of these experiments by *Deacon et al.*[54] and by our group[55][56] verified by mass spectroscopy and other methods, that the iodinated product consists mainly of heptaiodoferrocene, with small amounts of $(FeC_{10}I_8H_2)$, $(FeC_{10}I_9H)$ and $(FeC_{10}I_9HgI)$, together with other Hg-containing species. The postulated **5c** was **not detected**.

A series of permercuriations of metallocenes with $Hg(OAc)_2$, followed by treatment with $CuCl_2$, KBr_3 or KI_3 was reported by Winter *et al.* Thus, the three decahaloferrocenes **5a**–**c**,[43] -ruthenocenes **8a**–**c**[37][43] and -osmocenes **10a**–**c**[49] can be obtained. From pentamethylruthenocene, the pentahalopentamethylruthenocenes **9b**–**d**[33][43] have also been prepared (eq. 9).

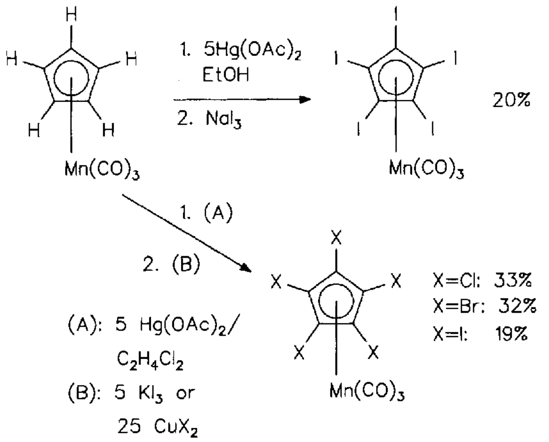


(9)

X \ M	Fe	Ru	Os	RuCp*
Cl	26%	64%	36%	58%
Br	57%	41%	40% *	30%
I	64%	34%	51%	52%

* $CuBr_2$ instead of KBr_3

Permercuriation of cymantrene, followed by treatment with $CuCl_2$, $CuBr_2$, KI_3[39] or NaI_3[38] produces the corresponding pentahalocymantrenes **2a–c** (eq. 10). In our hands, however, it turned out that only reactions carried out on the relatively small scales reported in the literature give products of sufficient purity. Attempts to scale-up the reactions by a factor of ten invariably led to a mixture of nearly all the possible halocymantrenes, similar to the results reported in the original paper by Nefedov.



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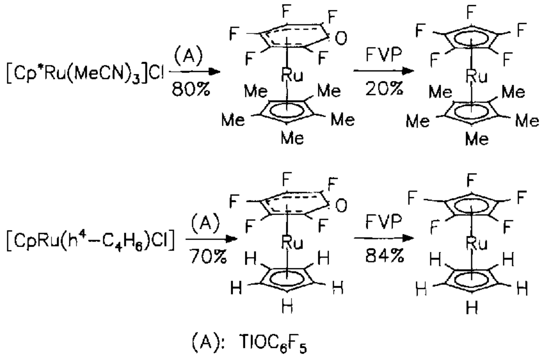
2.5. Miscellaneous Methods

All the methods mentioned so far were unsuccessful in producing fluorinated metallocenes. The only successful approach was reported by Hughes' group in 1992/4, which used a very unusual strategy. Flash vacuum pyrolysis of $(C_5Me_5)Ru(C_6F_5O)$ at 750°C/10^{-4} Torr or of $(C_5H_5)Ru(C_6F_5O)$ at 640°C/10^{-4} Torr led to the formation of the pentafluororuthenocenes **9a** and **7a**, respectively[31][40] (eq. 11).



(11)

The extremely high temperatures needed for this technique most likely preclude any further applications, since only ruthenocenes are known to possess such high thermal stabilities. However, the methods for the preparation of the other pentahalocyclopentadienyl complexes cannot be employed for all systems either. The mercuriation method fails in cases where Hg^{2+} acts as an oxidant towards the unsubstituted metallocene. The reasons for the failure of the diazo method in several instances are not yet clear, but in those systems where it works, it gives by far the highest yields.

3. Properties of Perhalometallocenes

As stated in the introduction, the search for ferrocene derivatives with high stabilities towards oxidation was the starting point for the research on perhalometallocenes. Perchloroferrocene certainly fulfilled this criterion, since it is "unaffected by heating either with concentrated nitric or concentrated sulfuric acid at 100°C for 10 min." and also remains intact after "stirring a carbon tetrachloride solution with cold concentrated nitric acid for 29 h".[2] To the best of our knowledge, no other experiments of this type have been reported for the other perhalocyclopentadienyl complexes, as generally, perchloroferrocene is the most extensively studied compound of all perhalometallocenes. Pentachloroferrocene **4** and pentachloropentamethylruthenocene **9b** have also been examined with regard to many of their physical properties, while most of the other compounds have merely been characterized by their IR-, NMR- and mass spectra.

3.1. Thermal Stability

The rhodium complexes **11a,b** are "somewhat thermally unstable and turn black after several days",[12] while **12** "proved to be very unstable and all attempts to isolate it have failed".[21] They also seem to be light sensitive, which is also true for the two vanadium compounds **1a,b**. Other pentahalocyclopentadienyl complexes are rather stable (Table 2), with decachlororuthenocene **8a** being the most stable of all (360–5°C dec.). Those compounds that melt without decomposition have apparently not been tested for their thermal decomposition temperatures, so the figures in Table 2 do not necessarily allow the compounds to be arranged in a sequence of increasing thermal stability. A systematic study of the effects of increasing chlorine substitution on ferrocene also showed a decreasing trend in the thermal stabilities. However, it could not be decided whether this trend was due to poorer donor abilities of the perhalocyclopentadienyl ligands or to steric effects caused by interactions of chlorine substituents on different rings in eclipsed conformations.[11b]

Table 2. Thermal stabilities [a]

1a	80° D	**4**	150° D	**7**	?	**9c**	270° D
1b	108° D	**5a**	245° D	**8a**	360–5° D	**9d**	190° D
2a	83–85° M	**5b**	210° D	**8b**	>300° M	**10a**	225° S
2b	117° M	**5c**	136 M	**8c**	240–60° D	**10b**	244° D
2c	141° D	**6a**	61° M	**9a**	?	**10c**	295° D
3	?	**6b**	95–100° S	**9b**	>300° M	**11a**	92–4° D

[a] D: decomposition; M: melting point; S: sublimation temp.

3.2. Redox Properties

As stated above, decachloroferrocene shows an extremely high resistance towards decomposition by oxidizing acids. The general redox properties of **4**, **5a**, **9a** and **9b** have been studied by cyclic voltammetry (CV),[23][24][34][35][48] while the Ru complexes have also been subjected to Fourier-transform ion-cyclotron mass spectrometry.[32][35] All complexes undergo irreversible two-electron oxidations under standard

CV conditions, most probably due to reaction of the metallocenium cations with the anion of the supporting electrolyte. However, by using faster scan rates and/or NBu_4^+ $[B(C_6H_3(CF_3)_2)_4]^-$ as the electrolyte, reversible one-electron oxidation potentials could be determined (Table 3).

Table 3. Reversible oxidation potentials of perhalometallocenes

	4	**5a**	**9a**	**9b**	**FeCp$_2$**	**RuCp$_2$**
E_f or E°′ [V] [a]	1.246	0.774	1.07	0.94	0.00	0.44
ΔG_i ° [eV]			170.8	165.4		164.6

[a] Vs. ferrocene/ferrocenium couple.

The iron complexes undergo a series of irreversible two-electron reductions, which lead to loss of the chlorine substituents.

The FT-IC mass spectra of **9a** and **9b** allowed the determination of the free energies of ionization in the gas phase, ΔG_i (Table 3).

Ionization potentials for a series of chlorinated ferrocenes were also determined by mass spectrometry.[29] A value of 7.9 eV was obtained for **5a**, compared to 6.9 eV for ferrocene and 5.8 eV for decamethylferrocene. Similar results were obtained from a UPS study of a series of twenty substituted ferrocene derivatives.[24]

All these measurements confirm the qualitative observation that perhalometallocenes are quite oxidation resistant.

3.3. Crystal Structure Determinations

The solid-state structures of the pentafluorocyclopentadienyl complex **7**[40], the pentachlorocyclopentadienyl complexes **8a**,[9] **9b**,[23] **10a**,[49] **11a**,[13] the perbromo derivatives **1b**,[26] **8b**,[37] **11b**[53] and the pentaiodocyclopentadienyl derivatives **2c**[39] and **9d**[33] have been reported. Quite interestingly, there is no structure report for a ferrocene derivative. **5a** was found to decompose under X-ray irradiation. Crystals of **4** could be measured, but the structure could not be solved due to severe disorder problems.[22] Similar disorder problems also prevented solution of the structure of **9a**.[31]

In essence, in all the structures there is only minor variation in the C−C bond lengths of the coordinated pentahalocyclopentadienyl rings, with the notable exception of the two rhodium complexes. These show the rather unusual $\eta^1+\eta^4$-coordination mode, corresponding to a diene-yl structure with two short and three long bonds in the cyclopentadienyl ring.

Quite interesting is a comparison of the metal-ring centroid distances in the five Ru complexes (Table 4).

The distances of the two cyclopentadienyl rings show only small variations; the symmetrically substituted ruthenocenes have their rings slightly more separated than the unsymmetrical ones, and in the halogenated derivatives the rings are closer to one another. However, the halogen substituents are significantly shifted away from the metal, out of the ring plane, so that unfavourable halogen-halogen contacts are avoided.

Table 4. Structural data for penta- and decahaloruthenocenes (Cp^xRuCp'[a]

	7	**9b**	**9d**	**8a**	**8b**	**RuCp$_2$**	**RuCp*$_2$**
D (Cp^x-Cp')[Å] [b]	3.563	3.599	3.588	3.598	3.61	3.632	3.616
D (Cp^x-Ru)	1.716	1.783	1.785	1.80	1.805	1.816	1.808
D ($Cp'-Ru$)	1.847	1.816	1.803				

[a] $Cp^x = C_5X_5$, $Cp' = C_5R_5$ with R = H, Me, X. – [b] This distance is approximated by the sum of the two Ru−Cp distances

The three unsymmetrical metallocenes also show an asymmetry in their metal-ring distances, which increases with the electronegativity of the halogen, with the metal invariably being closer to the halogenated ring. Clearly, the better electron donors C_5H_5 and C_5Me_5 "push" the metal closer to the electron deficient pentahalocyclopentadienyl ring. This leads to the conclusion that backbonding from the metal to the empty ligand orbitals becomes an important factor in the perhalometallocenes, in contrast to the "normal" electron-rich metallocenes.

Although no crystal structure determination is available, a detailed IR-spectroscopic investigation by Phillips *et al.*[22] enabled an estimation to be made of the relative bond strengths in the ferrocene system. In this study, the stretching force constants for the metal-ring vibrations were calculated. They are 263 Nm^{-1} for ferrocene, 356 Nm^{-1} for decamethylferrocene, 384 Nm^{-1} for **5a**, and 391 Nm^{-1} for the $Fe-C_5Cl_5$ vibration and 258 Nm^{-1} for the $Fe-C_5H_5$ vibration in **4**. These values show that in comparison with the parent compound, strengthening of the metal-ring bond can also be achieved by persubstitution with an electron-donating substituent as well as with electronegative substituents. Comparison of the unsymmetrical **4** with its symmetrical counterparts shows a decrease of the bond strength to the C_5H_5 ring and an increase for the perchloro ligand, which parallels the X-ray structural results for the Ru complexes mentioned above.

This experimental result seems contradictory to *ab initio* coreless MO calculations for **5a**, which predict elongation of the iron-cyclopentadienyl bond as a result of polysubstitution with Cl.[20]

3.4. Spectroscopic Properties

3.4.1. IR Spectra: A detailed IR spectroscopic study of chlorinated ferrocenes was mentioned in the preceding section. IR spectra of most of the other perhalometallocenes have been measured, but have not been interpreted in detail. The υ(CO) stretching vibrations in metal carbonyls are a good indication of the electronic situation at the metal. All the carbonyl-pentahalocyclopentadienyl complexes (**1a,b**, **2a−c**, **3**, **6a,b**, **12**) show a hypsochromic shift of 20−40 cm^{-1} for υ(CO) in comparison to their parent compounds (Table 5).

Table 5. Comparison of υ(CO) frequencies of pentahalogenocyclopentadienyl complexes $M(CO)_n(C_5X_5)$ with their parent compounds

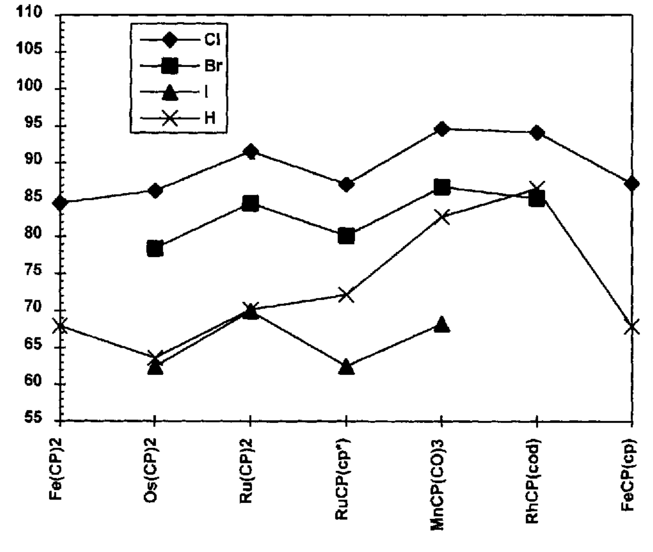
X	$V(CO)_4$	$Mn(CO)_3$	$Fe(CO)_2C_3F_7$	$Rh(CO)_2$
Cl	2046; 1982; 1963	2048; 1982	2062; 2023 [a]	2096s; 2082vs; 2028vs
Br	2043; 1979; 1963	2045; 1963	2058; 2020 [a]	
H	2030; 1954; 1933	2028; 1947	2020; 1990	2051vs; 1987vs

[a] C_5X_4I ligand.

Thus, it is quite obvious that the halogen inductively removes electron density from the metal, reducing its capacity for back donation to the carbonyl ligands.

3.4.2. NMR and NQR Spectra: ^{13}C-NMR data have been reported for most of the pentahalogenocyclopentadienyl complexes. The chemical shifts for the cyclopentadienyl ligand mainly depend on the attached halogen, with a minor contribution from the coordinated metal fragment. Compared to hydrogen, iodine acts as a shielding substituent, while the other halogens have a deshielding effect, which increases with increasing electronegativity. Thus, for pentaiodocyclopentadienyl complexes, the observed shift varies from ca. 62–70 ppm, while the corresponding ranges for the other perhalogenated cyclopentadienyl systems are 78–87 ppm (Br), 84–95 ppm (Cl) and 103–110 ppm (F). A graphical representation of the variation of chemical shifts is presented in Figure 1.

Figure 1. ^{13}C-NMR chemical shifts for pentahalocyclopentadienyl ligands C_5X_5[a]



[a] CP = (C_5X_5); cp = (C_5H_5); cp* = (C_5Me_5).

As can be seen from this graphical representation, the chemical shifts for the ring carbons vary in a similar manner for the three halogens Cl, Br and I, which means that the variation in electronic and steric influence on going from one halogen to another is roughly the same for all metallocenes studied.

The ^{51}V-NMR data of **1a,b** show a strong deshielding effect of more than 500 ppm by the halogens when compared with the parent compound $(C_5H_5)V(CO)_4$, indicating a rather low electron density at the metal.[26]

^{55}Mn-NQR spectra were studied for **2a**,[25][50] and showed a relatively large value for the quadrupole coupling constant e^2Qq_{zz} of 78.922 MHz. This indicates that the charge separation between the manganese atom and the cyclopentadienyl ring increases when hydrogen is substituted by chlorine, since $(C_5H_5)Mn(CO)_3$ has a quadrupole coupling constant of only 65.5 MHz.

^{35}Cl-NQR spectra have been measured for **2a**[12][25] and **11a**[12] and show very complex features. However, this was interpreted as an indication of the presence of two crystallographically independent molecules in the unit cell, and not as an electronic effect. From the small size of signal splitting it was deduced that all the chlorines are chemically equivalent.

3.4.3. Mass Spectra: High- and low-resolution mass spectra have been obtained for most of the perhalogenated cyclopentadienyl compounds (except for **9d**, **11a,b** and **12**). However, only in a few cases was a thorough analysis of the fragmentation behaviour carried out.

1a either successively loses all its carbonyl ligands to give the fragments $\{VC_5Cl_5(CO)_n\}$ and $\{VC_5Cl_4(CO)_n\}$ for n = 0–4 or (C_5Cl_5) from $\{VC_5Cl_5(CO)_m\}$ for m = 0–2. Successive loss of three chlorines from $V(C_5Cl_5)$ or of all chlorines from (C_5Cl_5) occurs subsequently. **1b** behaves similarly, except that the fragmentation series $\{VC_5Br_4(CO)_n\}$ is absent.[26]

Two detailed mass spectrometric investigations of several chloroferrocenes have been published.[8][29] For **5a**, the molecular ion is the most intense peak. Loss of (Cl_5C_5) to give $\{FeC_5Cl_5\}$ predominates over cleavage of $FeCl_2$ to give a $\{C_{10}Cl_8\}$ fragment. Further fragmentations correspond to successive loss of the Cl substituents from C_5Cl_5, and there seem to be no other iron-containing species besides Fe^+. This indicates that the $\{FeC_5Cl_5\}$ fragment is quite stable.

In pentachloroferrocene **4**, the molecular peak is again the most intense one. Fragmentation occurs either via loss of HCl or $FeCl_2$. There seem to be no other iron-containing fragments.[1][29]

The mass spectra of the two pentafluorocyclopentadienyl complexes **7** and **9a** show interesting differences. While the former has a base peak of (RuC_5H_5), corresponding to loss of the C_5F_5 ring, with other fragments derived from the parent ion by loss of HF and also of the C_5H_5 ligand, the latter shows no peak due to the loss of the perfluorinated ligand, but a prominent peak due to the (RuC_5F_5) fragment.[40]

A special mass spectroscopic technique, FT-ICR-MS, was mentioned above. It can be used to determine equilibrium constants for the gas-phase ionization, and was applied for **9a,b**. From these measurements, a new parameter scale (γ) for substituent effects in cyclopentadienyl complexes was developed. Based on pre-defined values of 0.0 for C_5H_5 and of −1.0 for C_5Me_5, γ-values of +1.06 for **9b** and 1.5 for **9a** were obtained.[32][35] The similar values for C_5F_5 and C_5Cl_5 indicate that electronically there is not much difference between these ligands {compare the γ-value of +3 estimated for the [$C_5(CF_3)_4H$] ligand!}.[35]

3.4.4. Miscellaneous Spectroscopic Investigations: The XPS spectrum of **9b** was recorded, and showed roughly the same Ru($3d_{5/2}$) binding energies for this chlorinated complex and ruthenocene itself. This shows that, "inductively, the pentachlorocyclopentadienyl ligand is a balance for the pentamethylcyclopentadienyl ligand".[23]

Electric dipole moments, the electronic polarizability distribution and the dielectric relaxation time have been studied for **4** and **5a**.[30][46][47] Examination of the mean magnetic susceptibility of **4** showed a strong dependence of this parameter on the solvent used (253 $JT^{-2}mol^{-1}$ in C_6D_6, and 160 $JT^{-2}mol^{-1}$ in CCl_4), indicating that chlorinated solvents decompose this compound, and the size of the C_6D_6 value highlights the important contribution that the electron-rich chlorine substituents make to this molar susceptibility.[42]

The ^{57}Fe Mössbauer spectrum of **5a** has been recorded. It shows a quite normal isomer shift (ca. 0.53 mm/sec), but an unusually large quadrupole splitting (2.75 mm/sec; compared to 2.4 mm/sec for ferrocene).[14] This was explained by a proximity effect of the chlorine substituents on the e_{2g} orbitals of iron, leading to an elongation of the iron-cyclopentadienyl ring distance.[14][20]

3.4.5. Solubility: Most of the perhalocyclopentadienyl complexes show good to excellent solubilities in chlorinated solvents. The only exceptions are the pentaiodocyclopentadienyl complexes **5c**, **8c** and **10c**, with the latter two being soluble only in DMSO and the former being completely insoluble in all organic solvents. On the other hand, the vanadium and manganese derivatives even exhibit excellent solubilities in non-polar solvents such as hexane or benzene.

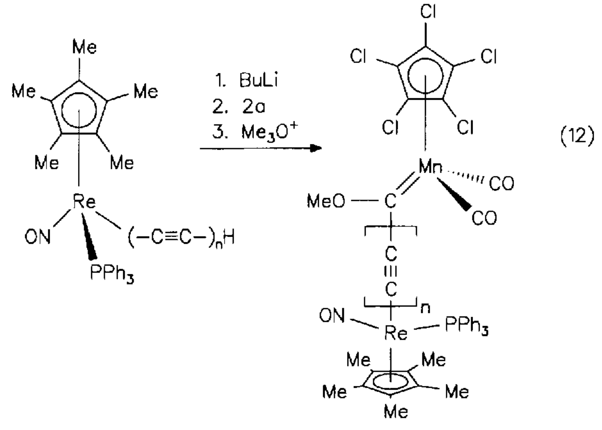
4. Reactions and Applications of Pentahalocyclopentadienyl Complexes

4.1. Reactions at the Non-Cyclopentadienyl-Ligand-Metal Fragment

The photochemistry of **2a** was explored by Young and Wrighton.[27] Irradiation of this compound in methylcyclohexane glass at 95 K leads to clean loss of one CO ligand to give (C_5Cl_5)Mn(CO)$_2$, as was shown by FT-IR spectroscopy. Warming this glass in the dark to 298 K regenerates the starting material quantitatively. If the irradiation is performed in the presence of PPh_3 at 298 K, the monosubstitution product **3** can be isolated in 46% yield. Similarly, irradiation of **2a** in neat Et_3SiH at 298 K leads to oxidative addition of Si−H to give (C_5Cl_5)Mn(CO)$_2$(SiEt$_3$)(H). This result contradicts an earlier statement that "irradiation of solutions of (**2a**) in either the presence or the absence of an additional ligand resulted in rapid and extensive decomposition".[12] A possible explanation for the latter observation might be the presence of the σ-C_5Cl_5 precursor, which was shown by another study of the Wrighton group to lose the C_5Cl_5 radical upon irradiation at temperatures > 200 K with the formation of $Mn(CO)_5Cl$ + $C_{10}Cl_{10}$ + "unidentified products".[28]

A monophosphine-substituted complex analogous to **3** is accessible by refluxing a benzene solution of **2a** with PEt_3.[12]

Nucleophilic addition of the lithioethynyl- or lithiobutadiynyl-rhenium complexes Cp*Re(NO)(PPh$_3$)(C≡C)$_n$−Li to **2a**, followed by addition of $(Me_3O)^+BF_4^-$ yields the Fischer-type carbene complexes (C_5Cl_5)Mn(CO)$_2$[=C-(OMe)C_{2n}Re(NO)(PPh$_3$)Cp*], which in turn give after treatment with BF_3 the dimetallacumulenes (C_5Cl_5)-(OC)$_2$Mn−(C_{2n+1})−Re(NO)(PPh$_3$)Cp*[45] (eq. 12).



(12)

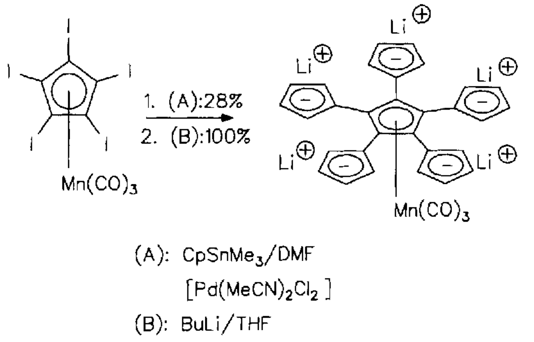
Treatment of a solution of the rhodium complex **11a** with a mixture of CO and H_2 leads to hydrogenation of the diolefin ligand and to formation of the dicarbonyl **12**. This compound can be isolated by removing the solvent with a rapid stream of CO gas, but replacing the CO atmosphere by an inert gas leads to decomposition to a material of unknown composition within a few days.[57]

4.2. Reactions at the Pentahalocyclopentadienyl Ligand

4.2.1. Nucleophilic Substitution of Halide: This type of reaction has only been reported for decachloroferrocene **5a**. Refluxing **5a** with 25 equivalents of NaOMe in methanol for 18 h gave a mixture of 72% (C_5Cl_5)Fe(C_5Cl_4OMe) and 28% (C_5Cl_4OMe)$_2$Fe. Similarly, refluxing with ca. 17 equivalents of NaOEt in ethanol for 58 days (!) gave a mixture of mono-, di-, tri- and tetraethoxy-substituted derivatives. An attempted nucleophilic substitution by treatment with excess CsF in sulfolane at 100°C for 24 h resulted in no reaction.[11]

4.2.2. Coupling of Pentaiodocyclopentadienyl Complexes with Alkynylstannanes: Stille coupling of (C_5I_5)Mn(CO)$_3$ (**2c**) with 1-trimethylstannylpropyne in DMF with $PdCl_2(MeCN)_2$ as catalyst was reported to give [C_5(C≡CMe)$_5$]Mn(CO)$_3$ in 38% yield.[38] Applying a similar procedure to substituted 1-trimethylstannylbutadiynes with $Pd_2dba_3(AsPh_3)_4$ gave the corresponding pentakis(butadiynyl)cyclopentadienyl derivatives in 5−11% yield.[44]

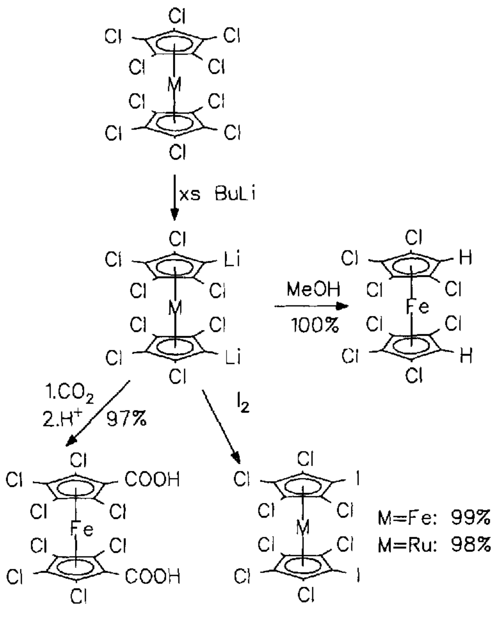
Reaction of **2c** with trimethylstannyl-cyclopentadiene at 90°C in DMF with 30% $PdCl_2(MeCN)_2$ as catalyst gave pentacyclopentadienyl-cymantrene [$C_5(C_5H_5)_5$] Mn(CO)$_3$ in 28% yield, which could be lithiated with five equivalents of butyllithium in 100% yield to give the pentalithiated derivative[51] (eq. 13).



(13)

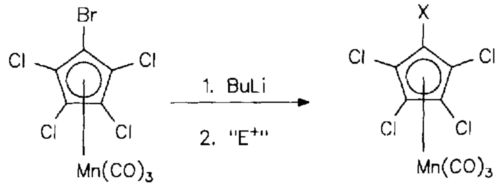
Attempts to use this Pd-catalyzed coupling with other pentahalocyclopentadienyl complexes have so far been unsuccessful.[38][57]

4.2.3. Halogen-Metal Exchange Reactions with Organolithium Compounds: The first report of this type of reaction applied to perhalometallocenes came from Hedberg and Rosenberg. Treatment of **5a** with an excess of *n*-BuLi in THF between −196°C and −40°C, followed by hydrolysis with water gave a 100% yield of $(C_5Cl_4H)_2Fe$. Addition of *n*-BuLi to an ethereal solution of **5a** at −70°C, followed by treatment with iodine or excess dry ice gave near-quantitative yields of $(C_5Cl_4I)_2Fe$ or $(C_5Cl_4COOH)_2Fe$. A similar reaction with decachlororuthenocene (**8a**) and iodine as the electrophile gave a 98% yield of $(C_5Cl_4I)_2Ru$[11] (eq. 14).



(14)

Our group in Munich started to investigate the halogen-lithium exchange reaction of $(C_5Cl_4Br)Mn(CO)_3$ (**2a'**) approximately 10 years ago. Addition of *n*-BuLi to a hexane solution of **2a'** resulted in precipitation of a highly pyrophoric compound, presumably $(C_5Cl_4Li)Mn(CO)_3$. A solution of this compound in Et_2O, prepared either from the isolated precipitate or formed *in situ* from **2a'** and BuLi in Et_2O, gave after treatment with a series of electrophiles a large number of functional derivatives of **2a**, $(C_5Cl_4E)Mn(CO)_3$ (eq. 15)



(15)

The substituents introduced by this procedure include: H, Me, SiR_3, CO_2H, SR,[58] $SnMe_3$, PPh_2, SePh, CHO,[59] $Mn(CO)_5$, $AuPPh_3$,[60] $(TiCp_2)_{0.5}$, MCp_2Cl (M = Ti, Zr, Hf),[61] N_3, and N_2R[62].

Some of these functional tetrachlorocymantrenes can be transformed into further derivatives. Thus, the carboxylate function can be transformed into $CONH_2$, CN, NCO, NH_2[59] or into a succinimidyl ester function[36]. The thio- and seleno ether derivatives can undergo further lithium-halogen exchange, affording symmetrical and unsymmetrical cymantrenyl polychalcogeno ethers.[63][64][65][66][67]

A mechanistic study of the metal-halogen exchange reaction showed that treatment of **2a'** with a tenfold excess of *n*-BuLi in THF, followed by hydrolysis with MeOH led to > 98% conversion to $(C_5Cl_3H_2)Mn(CO)_3$[68]. Applying this strategy to other electrophiles allowed the isolation of several difunctional derivatives $(C_5Cl_3E_2)Mn(CO)_3$ with E = $AuPPh_3$,[69] PR_2, SiR_3, CHO, CR_2OH, COR.[70]

When pentabromocymantrene **2b** is treated with one or two equivalents of *n*-BuLi followed by the electrophiles $SiMe_2RCl$ (R = H, Me, Cl), the corresponding mono- or bis-silyl derivatives can be obtained in high yield. The $SiMe_3$ derivative can be treated with one more equivalent of *n*-BuLi and $SiMe_3OSO_2CF_3$ to give the tris-silylcyclopentadienyl complex $[C_5Br_2(SiMe_3)_3]Mn(CO)_3$, while with the $SiMe_2H$ substituent the pentakis-silyl derivative $[C_5(SiMe_2H)_5]Mn(CO)_3$ can be obtained.[71][72]Starting from these dimethylsilyl complexes further silyl functionalization can be achieved to give all members of the series $[C_5(SiMe_2R)_{5-n}Br_n]Mn(CO)_3$ for R = Me[72][73], Cl[74] or F[75].

A mechanistic study showed that by treatment with excess *n*-butyllithium followed by MeOH as the electrophile, all five bromines can be substituted by H[68]. With I_2 as the electrophile, also using a large excess of *n*-BuLi, only a mixture of the bis- and tris-iodo derivatives is obtained (see above[52]).

Although we performed most of our studies with the manganese systems **2a'** and **2b**, we also found that other pentahalocyclopentadienyl complexes undergo the halogen-metal exchange reaction and can be further functionalized. Thus, the rhodium complex **11a** can be transformed to tetrachlorocyclopentadienyl complexes $(C_5Cl_4E)Rh(COD)$ with E = SR,[64] H, Me, SiR_3, $SnMe_3$ or COOLi.[59] Pentachloroferrocene **4** gives with *n*-BuLi and MeSSMe as the electrophile acceptable yields of the mono-, bis- and tris-thioethers $[C_5Cl_n(SMe)_{5-n}]FeCp$, but further introduction of a fourth and a fifth thioether function was only possible in trace amounts.[67] Pentabromopentamethylruthenocene also reacts with *n*-butyllithium, but temperatures of 0°C and higher are required and complex product mixtures are obtained. With *tert*-butyllithium, however, halogen-metal exchange occurs even at −78°C, and multiple substitution of bromine is possible. However, a strong dependence on the electrophile is observed: with MeSSMe only two SMe groups can be introduced, and with $SiMe_2HCl$ only three $SiMe_2H$ groups, irrespective of the degree of excess of the lithium reagent. Only with MeOH is complete substitution of all the bromines possible.[76]

As is readily apparent from these last paragraphs, the halogen-metal exchange reaction is strongly dependent on many reaction parameters, i.e. the nature of the metal and the halogen, as well as on the organolithium reagent, temperature, solvent, stoichiometry and concentration.[68][77][78]

4.3. Application of Pentahalocyclopentadienyl Complexes

Despite the original underlying reasons for studying this class of compounds, no "real" applications have emerged to date. There have been only two studies devoted to possible uses of these compounds.

The first of them examined the usefulness of the rhodium compound **11a** as a catalyst for the cyclotrimerization of acetylenes. It turned out that for the trimerization of the acceptor-substituted DMAD, **11a** was slower than its Cp or Cp* counterparts, while with the donor substituted 3-hexyne, **11a** was found to be the best catalyst; with tolane only a conversion of less than 1% was attained.[21]

The other study used **2a'**, after transformation to the carboxylic acid, as a metal carbonyl label for oligonucleotide analysis by FT-IR spectroscopy. Here, its oxidative and hydrolytic stability was exploited to good effect, as this is essential during polyacrylamide gel electrophoresis.[36]

5. Conclusion

Studies of perhalogenated cyclopentadienyl systems have shown that there are many ways of constructing multiply-functionalized metallocenes from them, which are not accessible by other methods or which are only accessible in substantially lower yields. Although there is still no preparative method that gives high yields, no undesirable environmentally harmful side products and that works equally well for all metals, the perhalocyclopentadienyl ligands open up more possibilities for fine-tuning of the properties of metallocenes, which have been developed as a class of compounds from a laboratory curiosity to an industrial chemical during the last decade.

First of all I want to express my gratitude to Professor *Wolfgang Beck*, who has supported this research in numerous ways. Therefore, this article is also dedicated to him on the occasion of his 65th birthday. I also want to thank my co-workers who have performed most of the laboratory work that has generated the results presented herein: Mrs. *Doris Steiner*, Dr. *Adrian Blum*, Dr. *Julian Hofmann*, Dr. *Werner Kempinger*, Dr. *Uwe Birk*, Dipl.-Chem. *Roland Teuber*, Dr. *Susanna Schubert*, Dipl.-Chem. *Sabine Soheili*, Dipl.-Chem. *Tilmann Kießling*, Dipl.-Chem. *Achim Basken*, Dipl.-Chem. *Markus Lang* and Dipl.-Chem. *Cornelia Stramm*.

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☆ This article is dedicated to Professor *Wolfgang Beck* on the occasion of his 65th birthday.

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