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Maximum spin cyclopentadienyl complexes of 3d transition metals

H. Sitzmann *

FB Chemie der Universitat, Erwin-Schroedinger Strasse, 67663 Kaiserslautern, Germany

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Contents

Abbreviations: acac, acetylacetonate; dme, 1,2-dimethoxyethane; dmpe, 1,2-bis(dimethylphosphino)ethane; dppe, 1,2-bis(diphenylphosphino)ethane; Me, methyl; Mes, mesityl; thf, tetrahydrofuran; tmeda, 1,2-bis(dimethylamino)ethane; VE, valence electrons; μ_{eff}, effective magnetic moment; μ_B, Bohr magnetons.

* Tel.: + 49-631-2054399; Fax: + 49-631-2054676.
E-mail address: sitzmann@chemie.uni-kl.de (H. Sitzmann).

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Abstract

For decades maximum spin behavior of transition metal cyclopentadienyl complexes seemed to be limited to a small set of 3d central atoms in certain oxidation states such as V(II), V(III), Cr(III), Mn(II), and nickelocenes. The observation of four unpaired electrons for the Fe(II) central atoms of the tetraisopropylcyclopentadienyliron bromide dimer in 1996 erased such limitations. High spin behavior has then also been observed for chromocenes and nickel(II) half sandwich complexes. Many of these species are easily accessible, highly reactive and serve as versatile starting compounds for a broad range of follow-up products.

Keywords: Maximum spin; Cyclopentadienyl complexes; 3d Transition metals

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1. Introduction

1.1. About the scope of this article

Among all cyclopentadienyl complexes of the transition metals the paramagnetic species form a small subgroup, which consists almost exclusively of low spin complexes. While Poli in a recent review article gave a comprehensive treatment of paramagnetic organo complexes of the transition metals [1], the present article concentrates on paramagnetic complexes of the 3d transition metals with a maximum number of unpaired electrons and places emphasis on recent developments. In order to avoid extensive overlap with Ref. [1], the coverage of cyclopentadienyl-vanadium chemistry (which is mainly maximum spin chemistry for the V(II) and V(III) oxidation state) has been limited to a few recent results. A similar argument applies for complexes of Cr(III), which has been covered by Theopold [2] and later in Ref. [1]. Although Mn(II) has been found to exhibit maximum spin behavior almost half a century ago, the recent results have been arranged in a context with a selection of earlier results in this area. Zinc and copper are not relevant for this article and have not been included.

Although d^1 as well as d^9 complexes have no choice regarding the spin state and are therefore not subject of this article, a Sc(II) complex obtained recently has been included in the scandium chapter.

Important literature references are the Comprehensive Organometallic Chemistry volumes [3,4], whereas references [5] (can spin state change slow organometallic reactions?) and [6] (spin density distribution in transition metal complexes) provide additional insight into the topics under discussion. Very recently, theoretical models of exchange interactions in dimeric transition metal complexes have been reviewed [7].

1.2. General aspects of high spin behavior

If the nine valence orbitals of a transition metal interact with a set of ligands, the filled σ donor orbitals of the ligand set are lowered in energy, while an equal number of metal orbitals of suitable symmetry is shifted to higher energy to become strongly antibonding. Although these modified orbitals are now delocalized MOs with some ligand orbital character, they will be called metal orbitals, because they are derived mainly from the respective metal orbitals.

Since strong field ligands with strong π acceptor properties are not a likely component of maximum spin complexes, the remaining d orbitals of the metal may engage in some degree of back bonding, but in most cases they will be of non bonding or weakly antibonding character depending on the ligand properties. For a qualitative discussion of the main principles this set of metal d orbitals can be regarded as approximately non bonding.

In the vast majority of organometallic complexes strong covalency provides for a large energy gap between the strongly antibonding and the non bonding (or weakly antibonding) orbitals. This gap becomes larger as we descend from the 3d to the 4d and 5d series, because 4d and 5d transition metals form stronger bonds than their 3d congeners.

The ligand set of most 3d transition metal complexes provides four or more (but rarely more than seven) fully occupied donor orbitals interacting with an equal number of suitable metal orbitals and leaving an approximately non bonding set of five or less (but rarely less than two) d orbitals at the central atom (Fig. 1).

Therefore, we may distinguish between three different situations encountered in maximum spin complexes:

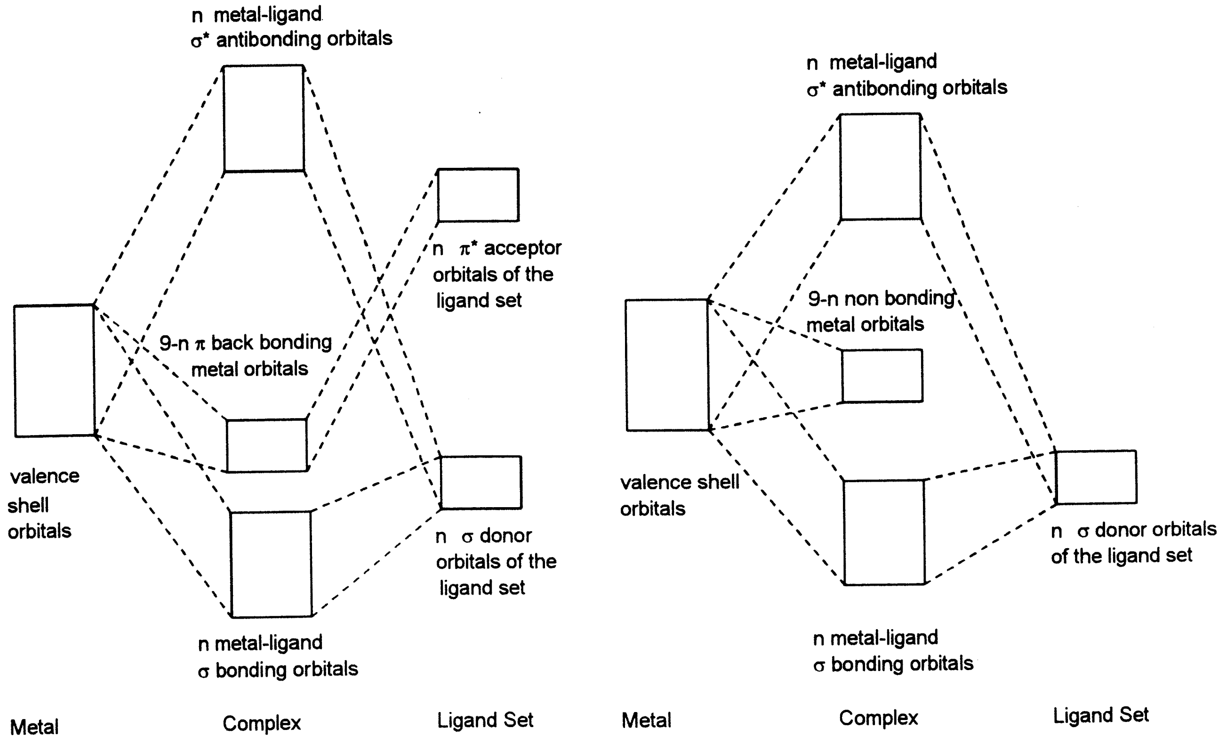


Fig. 1. Two MO diagrams for transition metal complexes. The diagram on the left illustrates the situation encountered in most organotransition metal complexes, where strong σ donation of the ligands into suitable metal orbitals is synergetically enhanced by strong π back donation from filled metal orbitals into empty ligand orbitals of π symmetry. This provides for a large energy gap between metal–ligand back bonding and metal–ligand antibonding orbitals of the complex. If π acceptor orbitals of the ligand set are missing or too high in energy, the diagram on the right side is valid, where metal–ligand back bonding is absent and the metal orbitals not engaged in ligand–metal σ interaction remain essentially non bonding. In this case the energy gap between these non bonding metal orbitals and the metal–ligand antibonding orbitals is relatively small. It can be even smaller, if filled π donor orbitals of the ligands are available to shift this non bonding set of metal orbitals to higher energy (not shown here).

1.3. Unpaired electrons in non bonding metal-centered orbitals only

If the number of d electrons left at the central atom is less than or equal to the number of approximately non bonding d orbitals, no spin pairing is observed for these d electrons in the 3d row. This feature is common to cyclopentadienyl complexes with a d^2 or d^3 configuration like Ti(II), V(III), or V(II), Cr(III). The phenylacetylide complex $[(C_5H_5)V(PMe_3)_2(C{\equiv}C{-}Ph)_2]$ [8] and the V(II) complex $[(C_5H_5)V(CH_3)(dppm)]$ [9] are shown as examples in Fig. 2.

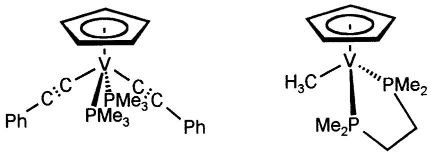


Fig. 2. Complexes with unpaired electrons in the non bonding orbitals only. In the bis(alkynyl)vanadium complex the ligand set provides seven filled donor orbitals shifting seven metal orbitals up in energy. The two remaining metal orbitals are singly occupied with the two d electrons of the V(III) central atom. The second example shows a V(II) methyl complex with a d^3 configuration and six electron pairs of the ligand set engaged in ligand–metal σ donation. The three remaining metal d orbitals hold three unpaired electrons.

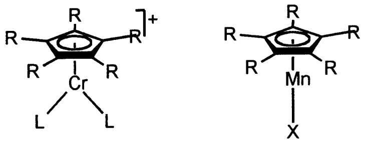


Fig. 3. Hypothetical complexes with four of five unpaired electrons in non bonding d orbitals. This figure shows two hypothetical examples for complexes, which can be predicted to exhibit maximum spin: if a cyclopentadienylchromium(II) complex possesses only two donor ligands without significant π acceptor properties in addition to the cyclopentadienyl ring, four non bonding d orbitals should contain four unpaired electrons. The manganese(II) central atom of the second example shown possesses five approximately non bonding d orbitals, which should contain five unpaired electrons. Both types of complexes are yet unknown and require sufficient steric bulk of both the cyclopentadienyl derivative and the additional ligand(s) in order to prevent dimerization.

If the coordination number is low enough, even cyclopentadienyl complexes with a d^4 or d^5 central atom could belong to this class of maximum spin complexes, although no example for such d^4 or d^5 cyclopentadienyl complexes is known yet (Fig. 3).

There are some 3d transition metal complexes such as $[(C_5Me_5)Ti(\eta^4\text{-}C_4H_6)(\eta^3\text{-}C_3H_5)]$ [10] or $[(C_5H_5)V(BH_4)(dmpe)]$ [11], which seem to be exceptions preferring spin pairing, although they should be maximum spin complexes (see Fig. 4 for explanation).

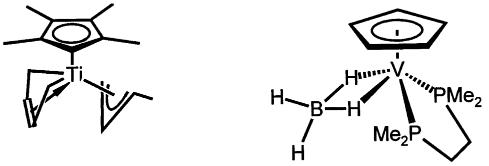


Fig. 4. Examples, which seem to contradict the principles outlined here. The diamagnetic butadiene complex $[(C_5Me_5)Ti(\eta^4\text{-}C_4H_6)(\eta^3\text{-}C_4H_7)]$ has 16 VE and may be regarded as a Ti(II) species with a d^2 configuration. In this case the ligand set donates seven electron pairs to the central ion and leaves two approximately non bonding d orbitals, which should contain two unpaired electrons in contrast to experimental observation. In fact, butadiene acts as a strong π acceptor, receives both electrons from the metal and forms a metallacyclopentene complex containing Ti(IV) with a d^0 configuration, which must be diamagnetic. Likewise, the V(II) complex $[(C_5H_5)V(BH_4)(dmpe)]$ has only one unpaired electron, although its d^3 electron configuration should give rise to a spin quartet with three unpaired electrons. The $\eta^2\text{-}BH_4^-$ anion occupies two metal orbitals, however, and therefore the ligand set leaves only two approximately non bonding metal d orbitals. The energy gap to the orbital next in energy is large enough to enforce spin pairing.

1.4. Unpaired electrons in non bonding and in antibonding metal-centered orbitals

If there are more d electrons than non bonding d orbitals available, the vast majority of organometallic complexes prefers spin pairing in contrast to traditional coordination compounds. Only for a very small number of organometallic complexes is the energy gap between strongly antibonding and approximately non bonding orbitals small enough to permit occupation of the antibonding d orbitals, although there are singly occupied non bonding molecular orbitals available. This situation is so unusual for organometallic complexes, that this type of maximum spin complexes is extremely rare. The most well-known exception, where this energy gap is too small to result in spin pairing, is manganocene. The reason for this unusual behavior must be associated with the half-filled d-shell of Mn^{2+} [12], where electron–electron repulsion and exchange interaction [13] favor a d^5 high spin configuration. As we shall see in the manganese section of this article, bonding in manganocene is no longer strongly covalent, but largely ionic, resulting in unusually long metal–carbon distances. Other exceptions are a few half sandwich complexes of manganese(II), very recently dimeric iron half sandwich complexes and certain chromocenes with four unpaired electrons with d^6 Fe(II) or d^4 Cr(II) central atoms have been observed; these will be discussed in the appropriate sections of this article.

1.5. Unpaired electrons in the antibonding set of metal-centered orbitals only

For the third type of maximum spin complexes the central atom holds enough d electrons to doubly occupy the approximately non bonding metal orbitals and to allow for single occupation of the strongly antibonding set of metal d orbitals. An example of this type is nickelocene (Fig. 5). This class of maximum spin complexes is naturally limited by the fact, that only d^9 complexes with five electron pairs from ligand–metal σ donation (19 VE), d^8 complexes with six (20 VE), and d^7 complexes with seven ligand electron pairs (21 VE) fulfil the numerical criteria. Most of such complexes one could imagine are likely to eliminate one two electron donor ligand or to rearrange to a lower hapticity of a multidentate ligand.

It is obvious now, that there are different strategies to design maximum spin complexes. If n d electrons are to be accomodated with parallel spin in singly occupied non bonding d orbitals, we have to provide n non bonding orbitals by restricting the number of electron pairs donated by the ligand set to $9 - n$. This situation is often encountered in d^2 and d^3 complexes and may be extended to d^4 and d^5 complexes with the aid of extremely bulky ligands.

Population of non bonding as well as antibonding metal orbitals with unpaired electrons is more difficult to achieve. Apart from manganese(II) complexes, this situation could be invoked recently for some chromocenes and for two halide-bridged cyclopentadienyliron(II) complexes. Possible ways to reduce the energy gap between antibonding and non bonding metal orbitals will be discussed in the chapters on chromocenes and iron(II) complexes of this article.

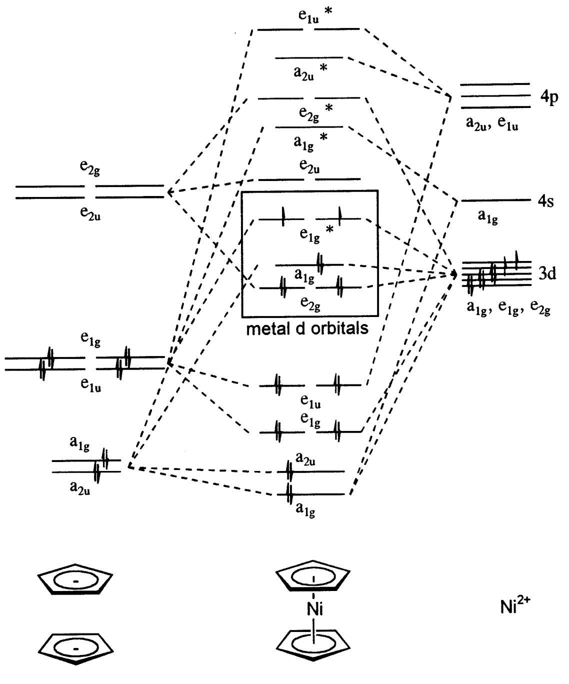


Fig. 5. MO digram for nickelocene. In nickelocene the two cyclopentadienyl anions donate six electron pairs to the central atom and shift six metal orbitals of suitable symmetry to high energy. The e_{2g} set (d_{xy} and $d_{x^2-y^2}$) and the a_{1g} MO (d_{z^2}) are approximately non bonding and fully occupied with six electrons, the remaining two d electrons populate the e^*_{1g} set (d_{xz} and d_{xz}) with parallel spin at high energy. The electron count amounts to 20 VE.

If the nonbonding set of orbitals is to be doubly occupied and the antibonding set of orbitals is intended to hold two unpaired electrons, the central atom needs a ligand set donating six electron pairs for M–L σ bonding to have two antibonding d orbitals and a d^8 electron configuration resulting in a VE count of 20. Apart from nickelocene the isoelectronic monoanion of cobaltocene [14], whose spin state has not yet been determined, is a likely candidate. Other examples for this type of maximum spin complex (e.g. d^6 or d^7 with seven electron pairs donated by the ligand set and a total of 20 or 21 VE) appear to be unknown. Elimination of a two electron donor ligand or hapticity changes are likely to follow the generation of such complexes.

Common to all three situations outlined above is, that the difference in energy between the lowest and highest of the singly occupied orbitals must not exceed the spin pairing energy.

2. Scandium complexes

Cyclopentadienyl complexes of scandium in oxidation states lower than Sc^{3+} are unknown. With closely related di- and triphosphacyclopentadienyl ligands novel scandium(I) and scandium(II) complexes have become accessible. By cocondensation of scandium vapor with RC≡P (R = CMe_3) the forest-green Sc(I) triple decker $[\{(\eta^5\text{-}P_3C_2R_2)Sc\}_2(\mu,\eta^6{:}\eta^6\text{-}P_3C_3R_3)]$ (**1**) [15] and the dark purple Sc(II) sandwich compound $[(\eta^5\text{-}P_2C_3R_3)_2Sc]$ (**2**) [16] (R = CMe_3) have been obtained (Fig. 6) as very air-sensitive, but thermally stable complexes, which could be sublimed at temperatures above 200°C.

In contrast to the planar middle deck the five-membered rings of **1** are puckered with C–Sc distances being shorter than P–Sc. **1** has a total valence electron count as low as 22 VE and possesses four unpaired electrons. The sandwich complex **2** shows a well resolved EPR spectrum at 120 K and a magnetic moment of 1.70μ_B at room temperature in solution.

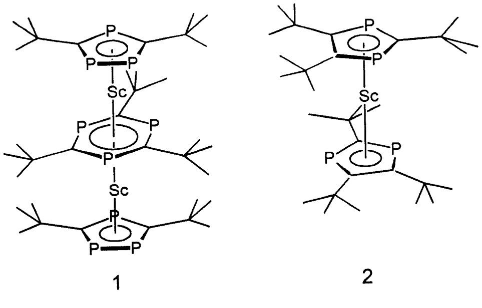


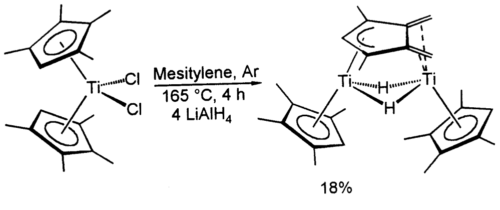
Fig. 6. Paramagnetic scandium complexes with di- or triphosphacyclopentadienide ligands. Complex **1** exhibits four unpaired electrons and with a total VE count of 22 marks the lower limit known for such triple decker complexes. The sandwich complex **2** is a unique example of a Sc(II) metallocene derivative.

3. Titanium complexes

If the MO diagram shown in Fig. 5 is applied to titanocene, the two d electrons of the Ti(II) central atom can be expected to occupy the doubly degenerate e_{2g} niveau resulting in a spin triplet configuration. The titanocene parent compound $[(C_5H_5)_2Ti]$ is extremely reactive [17] and has only been observed in neutralization–reionisation experiments in the mass spectrometer [18].

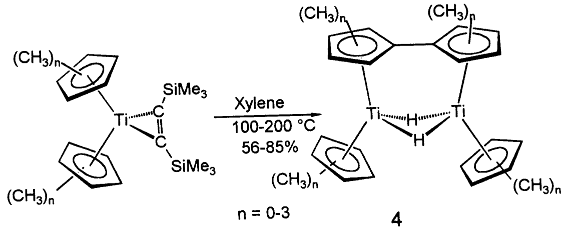
Attempted generation of more stable titanocene derivatives from precursors with methylated cyclopentadienyl ligands yielded a range of mono- and dinuclear products. Reduction of $[C_5Me_4H)_2TiCl_2]$ with $LiAlH_4$ at 165°C gave mixed-valent $[\{(C_5Me_4H)Ti(\mu\text{-}H)\}_2\{\mu,\eta^3:\eta^4\text{-}C_5Me_2H(CH_2)_2\}]$ (**3**) (Fig. 7) with Ti(II)/Ti(III) central atoms [19].

Thermal decomposition of bis(trimethylsilyl)acetylene complexes gives green Ti(III) fulvalene complexes of the type $[\{(C_5Me_nH_{5-n})Ti(\mu\text{-}H)\}_2(\mu,\eta^5:\eta^5\text{-}C_{10}Me_{2n}H_{8-2n})]$ (**4**) in high yield for $n = 0-3$ (Fig. 8). For $n = 4$ two regioisomers of the blue, diamagnetic compound $[(C_5Me_4H)Ti\{\eta^7\text{-}C_5Me_2H(CH_2)_2\}]$ (**5**) have been obtained [20] (Fig. 9). Either the low symmetry of **5** provides for a fairly large splitting even within the 'approximately non bonding' set of orbitals or (more likely) the butadiene subunit of the doubly metalated tetramethylcyclopentadienyl ligand has to be regarded as part of a metallacycle, which corresponds to a Ti(IV) complex comparable to the Ti(butadiene) complex shown in Fig. 4 [21][1].



3

Fig. 7. Instead of octamethyltitanocene the mixed-valent dinuclear titanium hydride **3** has been obtained by reduction of the dichloride precursor.



4

Fig. 8. Removal of an alkyne ligand results in formation of hydride-bridged Ti(III) fulvalene complexes with a variety of methylated cyclopentadienyl ligands carrying at least two ring protons.

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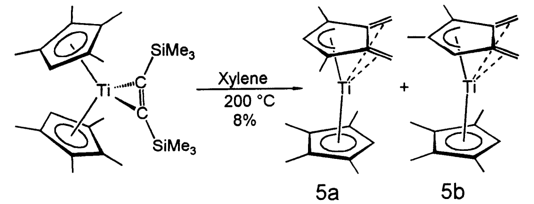
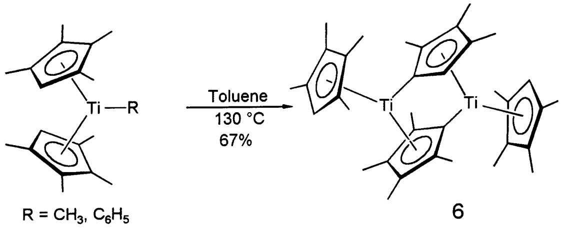
[1] In a formal sense the $C_5HMe_2(CH_2)_2$ ligand must then be regarded as a trianion, which may be compared to the interpretation of the C_7H_7 ligand as a 10π system and $[(C_5H_5)V(C_7H_7)]$ as a V(IV) complex.



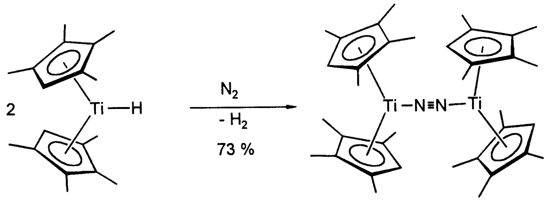
5a **5b**

Fig. 9. With tetramethylcyclopentadienyl ligands a similar procedure (cf. Fig. 8) gives the diamagnetic complexes **5a** and **5b** with 16 valence electrons shown.



6

Fig. 10. By methane or benzene elimination from Ti(III) precursors dinuclear complexes with bridging η^5:η^1-C_5Me_4 ligands can be generated.



7

Fig. 11. The Ti(III) hydride shown undergoes spontaneous reduction with formation of **7** when dinitrogen is admitted.

Thermal decomposition of $[(C_5Me_4H)_2TiCH_3]$ or $[(C_5Me_4H)_2TiPh]$ at 130°C yields green–brown, dinuclear $[\{(C_5Me_4H)Ti(\mu,\eta^5:\eta^1\text{-}C_5Me_4)\}_2]$ (**6**) (Fig. 10) [22]. The corresponding hydride $[(C_5Me_4H)_2TiH]$ can be converted to the blue-metallic, paramagnetic dinitrogen complex $[\{(C_5Me_4H)_2Ti\}_2(N_2)]$ (**7**) (Fig. 11), which has been crystallographically characterized.

This transformation is a rare example of reduction by admission of N_2 and presumably proceeds via disproportionation with subsequent reductive elimination of H_2 and formation of an equilibrium mixture containing octamethyltitanocene (**8**). **8** could be isolated as a waxy residue by nitrogen elimination from $[\{(C_5Me_4H)_2Ti\}_2(N_2)]$ (**7**) according to Fig. 12 [22].

Dinitrogen as excellent leaving group had also been utilized earlier, when decamethyltitanocene **9** was synthesized as the first isolable substituted titanocene by evaporation of solutions of the crystallographically characterized, paramagnetic precursor [{$(C_5Me_5)_2Ti$}(μ,η^1:η^1-N_2)] [23] as orange–yellow, crystalline material. The effective magnetic moment of decamethyltitanocene (**9**) is 2.60 BM at 298 K. In solution **9** establishes an equilibrium with its tautomer, the green hydride species **10** (Fig. 13). In the solid state or upon slow solvent removal from such equilibrium mixtures rearrangement of **10** to **9** occurs [24]. The Ti–C distance in **9** was predicted to be 2.33 Å [25].

Replacement of one methyl group of each C_5Me_5 ring with a *tert*-butyldimethylsilyl substituent allows the straightforward synthesis of the Ti(III) precursor [$(C_5Me_4SiMe_2R)_2TiCl$] (**11**) (R = CMe_3), which can be reduced by sodium amalgam to the silyl-substituted titanocene derivative (**12**) (R = CMe_3) (Fig. 14) in high yield as moderately air-sensitive dark red cubes, which melt above 195°C with decomposition. Like **9**, **12** possesses two unpaired electrons, the effective magnetic

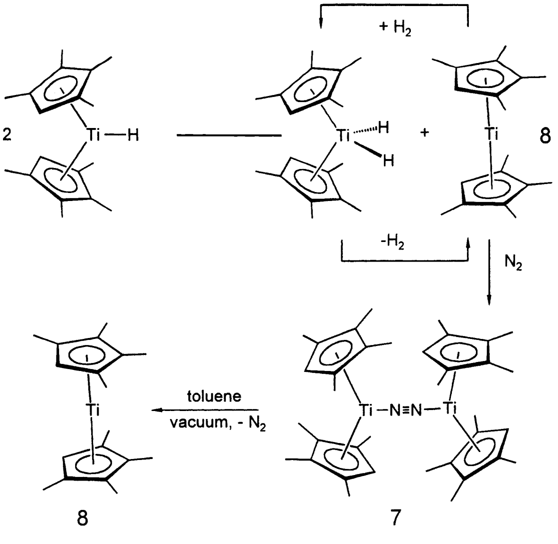


Fig. 12. An equilibrium mixture of octamethyltitanocene **8** with the corresponding mono- and dihydrides reacts with N_2 to form the dinuclear dinitrogen complex **7**, which eliminates N_2 and forms octamethyltitanocene under appropriate conditions.

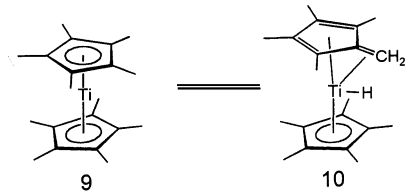
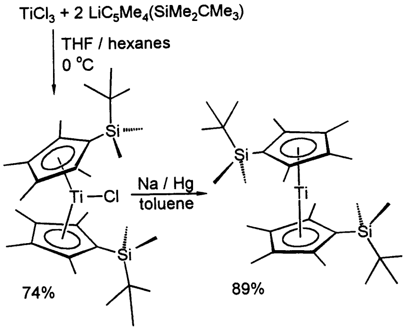


Fig. 13. The decamethyltitanocene **9** is a well-characterized titanocene with two unpaired electrons. It exists in an equilibrium with the fulvalene hydride complex **10**.



11 12

Fig. 14. bis(Dimethyl-*tert*-butylsilyl)octamethyltitanocene **12** is the first titanocene which could be crystallographically characterized. **12** also exhibits two unpaired electrons.

moment is 2.4 BM [26]. The crystal structure analysis of **12** shows a centrosymmetric molecule, which implies strictly parallel rings and a Cp_{cent}–Ti–Cp_{cent} angle of 180°. The ring normals are tilted away from the Cp_{cent}–Ti axis by 2.5° with the silyl substituted ring C atoms being closest to the central atom (C1–Ti = 2.315(3) Å). C3 and C4 show C–Ti distances of 2.39 and 2.38 Å. This interesting feature demonstrates, that steric arguments alone are not sufficient to explain the stability of **12**. DFT calculations indicate, that the silyl substituted ring carbon atom carries about twice the negative charge (0.38 e^-) attributed to the methyl substituted ring atoms (0.17 e^-), which can be explained by the charge stabilizing effect of α silyl groups [27]. The intra ring C–C bonds are longest for Si-substituted C1 (C1–C2 1.436(4) Å, C1–C5 1.440(4) Å) and shortest for C3–C4 on the opposite site of the ring (1.403(6) Å).

Bis(tetramethyl-trimethylsilylcyclopentadienyl)titanium (**13**) was subsequently prepared by bis(trimethylsilyl)acetylene elimination from $[(C_5Me_4SiMe_3)_2Ti(\eta^2\text{-}Me_3SiC{\equiv}CSiMe_3)]$ (**14**) at 70°C in vacuo or by repeated evaporation of hexane solutions of **14** at room temperature (Fig. 15) [28]. **13** forms brown–pink plates and dichroic solutions, which appear pale green in incident and red in transmitted light. No EPR signal, but broad NMR signals with temperature dependent chemical shifts as a consequence of a d^2 configuration with two unpaired electrons have been observed. The crystal structure shows a molecule on a center of symmetry with a crystallographic mirror plane passing through Ti, Si, the $SiMe_3$-substituted ring carbon, and one Si–CH_3 carbon atom. This implies a C_2 axis through Ti and perpendicular to the plane of symmetry as well as a perfectly staggered conformation and strictly parallel rings. The geometric features of titanocene **13** closely resemble **12** with its short Ti–$CSiMe_3$ bond, a similar intraring C–C distance pattern and an angle of 2.3° between the ring normal and the ring center-Ti axis. Even the silyl group displays a very similar conformation with one alkyl substituent (CMe_3 or CH_3) oriented away from the central atom and two methyl groups located between the ring plane and a parallel plane through the central atom.

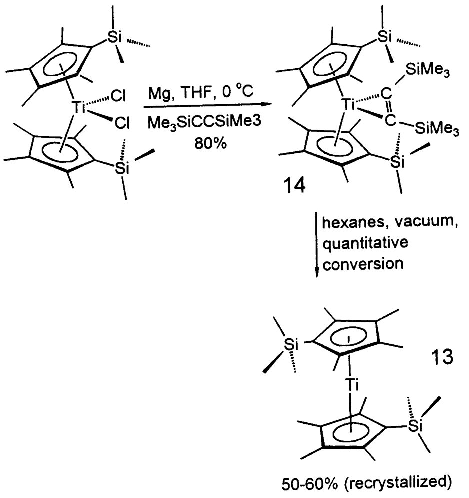
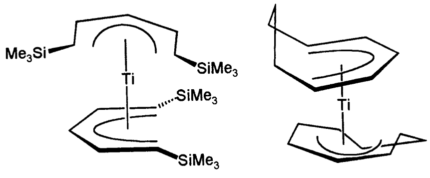


Fig. 15. Structure and magnetic properties of octamethyl-bis(trimethylsilyl) derivative **13** closely resemble those of **12**.



15 16

Fig. 16. The open titanocenes **15** and **16** are diamagnetic in contrast to the known bis(cyclopentadienyl)titanium complexes (see text for explanation).

Due to electronic and steric effects bis(pentadienyl)titanium(II) derivatives (open titanocenes) are surprisingly stable diamagnetic Ti(II) species [29]. Fig. 16 shows bis{bis(trimethylsilyl)pentadienyl}titanium(II) **15** and bis(cyclooctadienyl)titanium(II) (**16**), which have both been crystallographically characterized [29b,c]. Even the 'half-open' titanocene derivative $[(C_5H_5)Ti\{C_6H_2(SiMe_3)_5\text{-}1,2,4,5,6]$ with a silylated cyclohexadienyl ligand is diamagnetic [30]. An EH MO treatment of the parent compound $[(C_5H_5)Ti(C_5H_7)]$ is given in Ref. [31], where the $3d_{xy}$ niveau is shown to be the metal d orbital lowest in energy. The significant energy gap to the d orbital next in energy is explained by a strong δ-type back bonding interaction with the low-lying LUMO of the pentadienyl ligand (Fig. 17).

Compared to cyclopentadienyl rings, the open pentadienyl system is a stronger electron acceptor [29e] for geometric and electronic reasons:

1. With an open edge the area enclosed by five pentadienyl carbon atoms is much larger than the cyclopentadienyl ring. In order to form bonds to these wide-

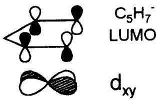
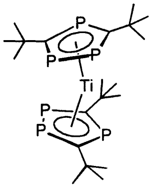


Fig. 17. The δ type back donation into the pentadienyl LUMO stabilizes the d_{xy} orbital and provides for an energy gap to the next MO large enough to enforce spin pairing in open titanocenes.



17

Fig. 18. The hexaphosphatitanocene **17** is also a diamagnetic low spin complex (see text for explanation).

spread carbon atoms the central atom has to move very close to the pentadienyl plane (1.64 Å), which increases the orbital overlap. As a side effect severe steric congestion and interligand contacts below the sum of van der Waals distances are observed. This steric effect is increased by relatively short Ti–C distances (2.27 Å for **15**; cf. 2.35 Å for **12**).

2. The pentadienyl LUMO is energetically low and well-suited for δ-type back bonding interaction with metal orbitals of matching symmetry. If the terminal carbon atoms of the pentadienyl ligand (cf. Fig. 17) approach each other, the LUMO is shifted to higher energy, because the corresponding orbital lobes are out of phase. Therefore, the cyclopentadienyl LUMO is much less suitable for interaction with the d_{xy} and $d_{x^2-y^2}$ orbitals [31] and weak δ-type back bonding is typical for cyclopentadienyl complexes [32].

Whereas the reagent $TiCl_2(THF)_n$, generated by reduction of $TiCl_4$ with magnesium in THF, is common in open titanocene synthesis [29a–d], it has not yet been used for titanocene preparation. Pure $TiCl_2(THF)_2$ has recently been isolated as a black solid by reduction of $TiCl_4$ with *n*-butyllithium [33].

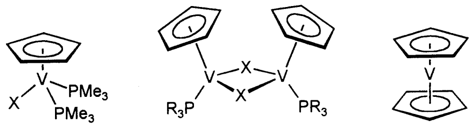
The dark red, sublimable hexaphospha–titanocene $[(R_2C_2P_3\text{-}1,2,4)_2Ti]$ (**17**) (R = CMe_3) has been synthesized by cocondensation of Ti vapor with RC≡P or reaction of RC≡P with $[(C_6H_5Me)_2Ti]$ at −78°C or by reaction of $TiCl_n$ ($n = 2$, 3) with $KR_2C_2P_3\text{-}1,2,4$ in boiling toluene [34] (Fig. 18).

17 is a diamagnetic low spin complex and crystallizes in the orthorhombic system. The individual molecules exhibit crystallographic C_2 symmetry and a bent geometry with an interplanar angle of 16°. As discussed before for open titanocenes, the relatively short centroid-metal distance of 1.94 Å (cf. 2.01 for **12**) arises from the larger ring perimeter and is presumably one reason for spin pairing (cf. the similar argumet regarding the open pentadienyl ligand in the preceding paragraph and the theoretical work on the triphosphacyclopentadienyl ligand in a recent publication on manganese complexes thereof [35]).

4. Vanadium complexes

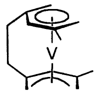
Vanadium in its +2 and +3 oxidation states usually displays maximum spin behavior in half sandwich complexes (e.g. the bis(trimethylphosphane) complex **18** [36]), dimeric complexes (e.g. the halide-bridged phosphane complexes **19** [37]) or vanadocenes (e. g. the parent compound **20**) [38]) (Fig. 19). Low spin complexes are not very common, examples are the tetrahydridoborate complex $[(C_5H_5)V(BH_4)$-(dmpe)] with two hydride ligands bridging the V and B atoms (see Fig. 4) or the open vanadocene **21** [39] (Fig. 20). For a comprehensive treatment the reader is referred to the review article of Poli [1]. Some recent results are being presented in the following paragraphs.

A crystal structure reinvestigation of the parent vanadocene $[(C_5H_5)_2V]$ (**20**) showed a centrosymmetric molecule with a vanadium-ring distance of 1.93 Å. The experimentally determined electron density (X–X method) at the vanadium central atom was 1.9 instead of 3.0 d electrons, which has been attributed to the covalent vanadium-ring interaction [40].



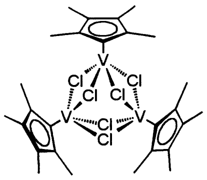
18 19 20

Fig. 19. Like complexes **18**–**20**, most vanadium(II) cyclopentadienyl complexes have three unpaired electrons.



21

Fig. 20. Some related vanadium(II) compounds exhibit low spin behavior with only one unpaired electron like the borohydride shown in Fig. 4 and the open vanadocene derivative **21** shown here. The reasons for spin pairing have been discussed for open titanocenes and in the introduction, respectively.



22

Fig. 21. Antiferromagnetic coupling causes complications in the trinuclear vanadium complex **22**.

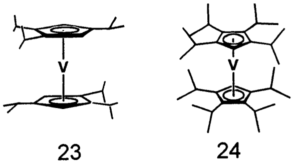


Fig. 22. Hexa- and octaisopropylvanadocene exhibit three unpaired electrons like the parent compound.

$[VCl_3(THF)_3]$ and $C_5Me_5SnBu_3$ give $[\{Cp^*VCl_2\}_3]$ (**22**), which shows a very unusual trimeric structure (Fig. 21) with six chloro bridges in pairwise arrangement, a room temperature magnetic moment of 2.78 BM and a complicated temperature dependency, which results from the problems coming up when three $S=1$ nuclei forming approximately an isosceles triangle try to establish antiferromagnetic coupling [41] (for background information see [42]).

Recently hexa- (**23**) and octaisopropylvanadocene (**24**) (Fig. 22) have been obtained as deep purple, crystalline solids. The magnetic properties of both compounds and the solid state structure of the hexaisopropyl derivative **23** closely resemble the parent vanadocene [43].

5. Chromium complexes

5.1. Chromium(IV) complexes

Tetrakis(1-norbornyl)chromium [44], and tetra(cyclohexyl)chromium [45] with two unpaired electrons have been reported, an overview on complexes with metal–carbon σ bonds has been given in lit. [46]. Paramagnetic cyclopentadienyl complexes of chromium(IV) appear to be unknown.

5.2. Chromium(III) complexes

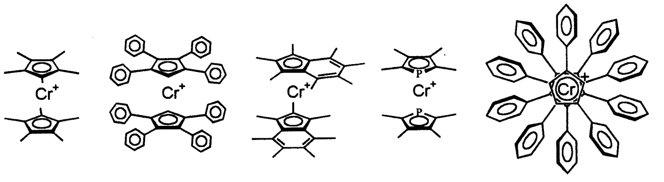
For cyclopentadienylchromium(III) compounds high spin behavior is well known and has been documented in a number of review articles [1,2]. With up to six electron pairs from ligand donation Cr(III) complexes are expected to possess three closely spaced d orbitals in the non bonding range suitable for accomodation of three unpaired electrons.

Chromium(III) cyclopentadienyl complexes with a spin quartet configuration have been known since 1955, when chromocenium tricarbonyl(cyclopentadienyl)chromate was obtained from chromocene and carbon monoxide [47]. The spin state of chromocenium cations is not changed by introduction of ring substituents as has been shown for green–yellow $[(C_5Me_5)_2Cr]^+PF_6^-$ (**25**) ($\mu_{eff}=3.73$ BM in the temperature range from 4.5 to 81 K, and 3.74 BM at 304 K in solution) [48], black $[(C_5HPh_4)_2Cr]^+PF_6^-$ (**26**) [49], the dark–red bis(heptamethylindenyl) derivative $[(C_9Me_7)_2Cr]^+PF_6^-$ (**27**) ($\mu_{eff}=3.47$ BM in the temperature range from 5 to 190 K) [50] as well as for the red diphosphachromocenium salt $[(Me_4C_4P)_2Cr]^+$ BPh_4^- (**28**) [51] (Fig. 23).

The salts **25**–**28** have been characterized by EPR-spectroscopy, for **27**, **21** and the dark red decaphenyl derivative $[(C_5Ph_5)_2Cr]^+BF_4^-$ (**29**) (Fig. 23) [52] a crystal structure analysis has been carried out. With an average Cr–C distance of 2.28 Å **29** displays the expected effect of steric crowding, compared to 2.21 Å for **27**. For $[(C_5Me_4Et)_2Cr]^+$ and for neutral diethyloctamethylchromocene as well as for other metallocenes and metallocenium cations $[(C_5Me_4Et)_2M]^{0/+}$ ($M = V$, Cr, Cr^+, Mn, Mn^+, Fe^+, Co, Ni^+) a comparative study of ^1H- and ^{13}C-NMR spectra has been carried out. The spectral window for the chromocenium derivative, for example, extends from 809 to -477 ppm (^{13}C-NMR) and is still smaller than that of the neutral vanadocene $[(C_5Me_4Et)_2V]$ with more than 1800 ppm spectral width. The data have been used to infer the sign of spin density in the cyclopentadienyl π orbitals [53].

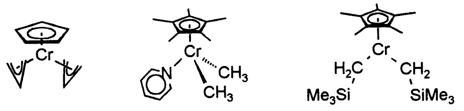
Although the majority of mononuclear chromium(III) species with one cyclopentadienyl ring are three-legged piano stool complexes with 15 VE and three unpaired electrons [54], examples with 13 or 17 VE are also known. The thermally labile allyl complex $[(C_5H_5)Cr(\eta^3\text{-}C_3H_5)_2]$ (**30**) [55] with 17 VE as well as the pyridine adduct $[(C_5Me_5)Cr(CH_3)_2(NC_5H_5)]$ (**31**) (15 VE) [56], and the trimethylsilylmethyl compound $[(C_5Me_5)Cr(CH_2SiMe_3)_2]$ (**32**) (13 VE) [57] are structurally characterized examples for this class of compounds (Fig. 24). The concentration-dependent dissociation of halide-bridged alkyl complexes $[\{(C_5H_5)CrMe(\mu\text{-}Cl)\}_2]$, $[\{(C_5Me_5)CrR(\mu\text{-}Cl)\}_2]$ (R = Me, Et, CH_2SiMe_3), and $[\{(C_5Me_5)CrMe(\mu\text{-}Br)\}_2]$ with formation of the corresponding monomers has been studied by EPR spectroscopy [58].

The dimeric dichloride $[\{(C_5H_5)Cr(\mu\text{-}Cl)Cl\}_2]$ (**33**) has been synthesized by heating $[(C_5H_5)_2Cr]^+$ $[(C_5H_5)CrCl_3]^-$ (**34**) and isolated as deep blue-green crystals by



25 26 27 28 29

Fig. 23. Chromocenium cations are isoelectronic with vanadocenes and exhibit three unpaired electrons like these.



30 31 32

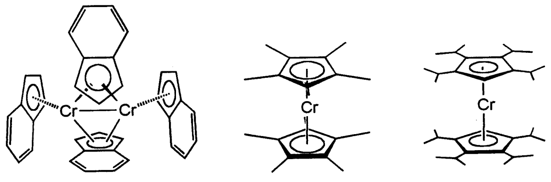
Fig. 24. Cyclopentadienylchromium(III) half sandwich complexes may have a formal valence electron count of 17 VE (**30**), 15 VE (**31**), or 13 VE (**32**).

sublimation [59]. $[\{(C_5Me_5)Cr(\mu\text{-}Cl)Cl\}_2]$ (**35**) [60], and $[\{(C_5Me_5)Cr(\mu\text{-}Br)Br\}_2]$ (**36**) [61] have also been investigated by X-ray diffraction.

The Cr···Cr distances of 3.29 Å for $[\{(C_5H_5)Cr(\mu\text{-}Cl)CH_3\}_2]$ (**37**) [62], 3.28 Å for $[\{(C_5Me_5)Cr(\mu\text{-}Cl)CH_3\}_2]$ (**38**) [63], and 2.61 Å for $[\{(C_5Me_5)Cr(\mu\text{-}CH_3)CH_3\}_2]$ (**39**) [56] reflect the degree of antiferromagnetic interaction, which has been found strongest for **39** resulting in an effective magnetic moment of 2.1 BM [56] (cf. 3.5 BM for **38** [64]). These halides are versatile starting materials, whose halide ligands can be replaced with alkyl groups or other substituents via nucleophilic substitution reactions. The methyl compounds with bridging chloride ligands are dark red, whereas the methyl-bridged compound **39** is brown.

5.3. Chromium(II) complexes

For more than 40 years high spin behavior has been completely unknown for chromocenes, which are usually dark red and contain a d^4 Cr(II) central atom with two unpaired electrons. Spin pairing with formation of a spin triplet state is to be expected on the basis of the metallocene MO diagram shown in Fig. 5. Open chromocenes also exhibit two unpaired electrons [29d]. Only bis(indenyl)chromium (**40**) is brown and diamagnetic, but did not receive much attention[2] until 1996, when its dimeric structure with two terminal η^5-indenyl and two bridging η^3-indenyl ligands and a Cr–Cr bond length of 2.18 Å (Fig. 25) was discovered [65].



40 S = 0 **41** S = 1 **42** S = 2

Fig. 25. The chromium (II) complexes **40**–**42** display variations of structure and spin state (see text).

One example for the common chromocenes with two unpaired electrons is decamethylchromocene (**41**), for which also in 1996 a crystal structure analysis consistent with the results of a CP-MAS-NMR investigation showed two independent molecules in the unit cell [66]. One year later octaisopropylchromocene (**42**) was shown to be the first chromocene exhibiting high spin behavior. It displays a continuous transition from a low spin configuration with $2.83\mu_B$ at 2 K to a high spin configuration with four unpaired electrons and an effective magnetic moment of $4.90\mu_B$ at 300 K [67]. In solution low spin behavior has been observed for **42** [68]. The strongly electron donating tetraalkylcyclopentadienyl ligands for steric reasons create an even stronger intramolecular repulsion, which ultimately leads to a

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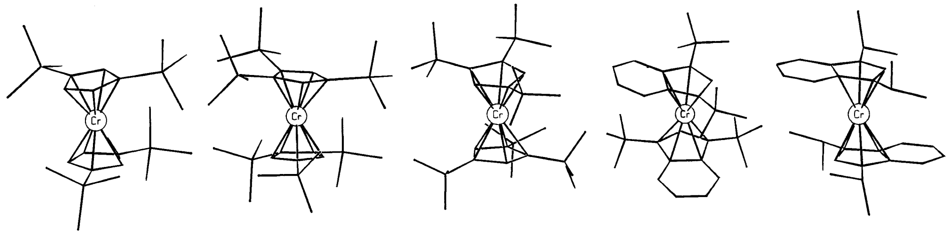
[2] Bis(indenyl)chromium is not mentioned in W. Abel, F.G.A. Stone, G. Wilkinson (Eds.), Comprehensive Organometallic Chemistry, Pergamon, Oxford, 1982, or Comprehensive Organometallic Chemistry II, Pergamon, Oxford 1995, for example.

weakening of the ligand field because of increased metal–carbon distances. In an attempt to investigate the influence of bulky substituents on chromocene EMe_3 groups have been introduced and 1,1′,3,3′-tetrakis(trimethylsilyl)chromocene $[\{(C_5H_3(SiMe_3)_2\text{-}1,3\}_2Cr]$ (**43**), 1,1′,2,2′,4,4′-hexakis(trimethylsilyl)chromocene $[\{(C_5H_2(SiMe_3)_3\text{-}1,2,4\}_2Cr]$ (**44**), hexa(*tert*-butyl)chromocene $[\{(C_5H_2(CMe_3)_3\text{-}1,2,4\}_2Cr]$ (**45**), and bis{1,3-di(*tert*-butyl)indenyl}chromium (**46**) [69] have been synthesized (Fig. 26). The first chromocene with high spin behavior also at low temperature was bis(1,3-diisopropylindenyl)chromium (**47**) [70]. In Table 1 structural parameters of these metallocenes are listed.

The silylated and alkylated cyclopentadienyl complexes **43**, **44** and **45** display the expected degree of steric congestion. The tetrakis(trimethylsilyl) derivative **43** is not distorted significantly, for the hexakis(trimethylsilyl) derivative **44** the steric bulk shows the typical effect of silyl group displacement out of the ring plane while the metal-ring distance is only moderately increased. Consequently **44** is a low spin chromocene with two unpaired electrons from 2 to 300 K [69]. Even the hexa(*tert*-butyl) derivative **45** is a low spin complex under the same conditions, although the six *tert*-butyl groups are sterically more demanding and increase the ring–Cr distance to an average value of 1.85 Å, which is larger than the 1.83 Å value observed for octaphenylchromocene [71]. In centrosymmetric hexaisopropylchromocene **48** [68] the alkyl groups are oriented just as shown for hexaisopropylvanadocene (**23**, Fig. 22). **48** shows no effects of steric strain in contrast to hexa(*tert*-butyl)chromocene **45**, which adopts an ecliptic conformation with two of the *tert*-butyl groups facing each other.

Strongly related to electronic factors is the high spin character of bis(1,3-dialkylindenyl)chromium complexes. There is no steric congestion detectable in bis(diisopropylindenyl)chromium **47**, which features four unpaired electrons and an effective magnetic moment of 4.4 ± 0.2 BM from 20 to 350 K [70] (structural data are compiled in Table 1).



$[\{C_5H_3(SiMe_3)_2\}_2Cr]$ $[\{C_5H_2(SiMe_3)_3\}_2Cr]$ $[\{C_5H_2(CMe_3)_3\}_2Cr]$ [{1,3-di(tert.-butyl)-indenyl}$_2$Cr] [{1,3-di(isopropyl)-indenyl}$_2$Cr]

43 44 45 46 47

Fig. 26. The chromocenes **43**–**47** have been structurally characterized recently. Remarkable is the pair of bis(1,3-dialkylindenyl)chromium complexes **46** and **47**, where the bulkier ligand creates the shorter Cr–C distances (see Table 1).

Table 1
Structural parameters of chromocenes with bulky cyclopentadienyl or indenyl ligands

Name	$[\{C_5H_3(SiMe_3)_2\}_2Cr]$	$[\{C_5H_2(SiMe_3)_3\}_2Cr]$	$[\{C_5H_2(CMe_3)_3\}_2Cr]$	$[\{C_9H_5(CMe_3)_2\}_2Cr]$	$[\{C_9H_5(CHMe_2)_2\}_2Cr]$
No.	**43**	**44** [a]	**45** [a]	**46**	**47**
Cr–ring plane (Å)	1.793	1.804; 1.802	1.847; 1.846	1.901; 1.901	1.982; 1.976
		1.811; 1.808	1.844; 1.846		
Deviation (Å) of α-E from ring plane (E = C, Si)	0.157 (Si1)	0.50, 0.27 Si 1/11	0.349/0.322 C11/A	0.165, 0.225 C11/61	0.083, 0.096 C11/61
	0.073 (Si2)	0.22, 0.43 Si 2/12	0.181/0.170 C21/A	0.263, 0.299 C31/81	0.072, 0.060 C31/81
		0.37, 0.37 Si 4/14	0.407/0.410 C41/A	0.095, 0.091 C41/91	0.008, 0.013 C41/91
		0.53, 0.53 Si 6/16	0..351/0.317 C61/A	0.082, 0.128 C51/10	0.040, 0.004 C51/10
		0.19, 0.46 Si 7/17	0.173/0.198 C71/A		
		0.32, 0.32 Si 9/19	0.368/0.449 C91/A		
Interplanar angle (°) between ring planes	10.0	6.2 (Cr1)	10.3 (Cr)	6.9	2.8
		7.4 (Cr2)	10.9 (CrA)		
Interplanar angle between five- and six-membered ring				4.5 (C1–C5)	(C1–C5)
	–	–	–	5.6 (C6–C10)	0.5 (C6–C10)

[a] Two independent molecules.

The ring–Cr distance of 1.97 Å is much larger than the distances found in low spin chromocenes including octaphenylchromocene [71], hexaisopropylchromocene [70], or bis(heptamethylindenyl)chromium [50]. Even the deep violet high spin chromocene **46** with two 1,3-di(*tert*-butyl)indenyl ligands does not reach this value despite its larger steric bulk. The couple **46** and **47** comprises a unique example where larger steric bulk in an electronically similar situation leads to a conformant change with a significant contraction of the metallocene core. With only one alkyl substitutent, as seen in bis(1-cyclohexylmethylindenyl)chromium **49**, a red–brown metallocene has been obtained [72], whose chromium–carbon distances fall into the range from 2.195(2) to 2.345(2) Å (av. 2.26 Å) [73]. This centrosymmetric molecule with only one primary alkyl substituent per indenyl ligand exhibits larger Cr–C distances than hexa(*tert*-butyl)chromocene (av. 2.22 Å) and a magnetic moment of $2.8\mu_B$. The unexpected behavior of bis(mono- or dialkylindenyl)chromium complexes is most likely a consequence of the electronic structure of the indenyl ligand. The energy difference between the singly occupied MO and the lowest d orbital of cobaltocene is almost twice as big as the energy difference between the two corresponding molecular orbitals of diindenylcobalt (2.1 vs. 1.1 eV by PES [74]), for example. The high spin character of these bis(1,3-dialkylindenyl)chromium complexes proves, that there must be a relatively small energy gap between the four d orbitals lowest in energy and suggests, that indenyl ligands and their derivatives may be interesting tools for evoking maximum spin behavior in complexes other than metallocenes as well.

Because the response of manganocenes to variations of the steric bulk of alkylcyclopentadienyl ligands is more subtle than that of chromocenes, this feature of bulky alkylcyclopentadienyl ligands will be discussed in more detail in the manganese section of this article.

5.4. Chromium(I) complexes

The maximum spin situation with five unpaired electrons has not yet been verified for chromium(I) cyclopentadienyl complexes. Stable 17 VE radicals such as $[(C_5Ph_5)Cr(CO)_3]^\bullet$ [75] and its substitution products $[(C_5Ph_5)Cr(CO)_2(PR_3)]^\bullet$ [76] have been isolated and characterized. A review article on organometallic 17 VE complexes with one unpaired electron is also available [77].

6. Manganese complexes

6.1. Manganese(V) complexes

By UV–vis irradiation of $[(C_5H_5)Mn(CO)_3]$ in an argon matrix containing O_2 a cyclopentadienyl complex of Mn(V) could be obtained, which has been characterized by means of IR spectroscopy and isotopic substitution as $[(C_5H_5)Mn(O)_2]$ [78]. Although the magnetic properties have not been investigated, this d^2 complex is likely to contain two unpaired electrons.

6.2. Manganese(IV) complexes

Tetrakis(1-norbornyl)manganese as the first organometallic complex of manganese(IV) has been prepared as early as 1972 and possesses three unpaired electrons [44]. Salts of the homoleptic hexamethylmangante(IV) dianion are also known to possess three unpaired electrons and have been fully characterized [79].

If manganocene is reacted with dimethylcadmium, at 80 K an intermediate could be observed by IR spectroscopy, which upon warming up decomposed with disproportionation and formation of $[(C_5H_5)MnMe_3]$ (**50**), Cd metal and organic byproducts. **50** forms amber crystals, which can be sublimed at room temperature and melt at 87°C. Derivatives with primary and secondary alkyl groups other than methyl are also known, magnetic properties have not been reported [80].

6.3. Manganese(III) complexes

Organomanganese(III) complexes like $[Li(tmeda)_2]^+[MnMe_4]^-$ [79] or $[(Mes)MnBr_2(PMe_3)_2]$ [81] possess four unpaired electrons, whereas known half sandwich complexes have 18 VE and are diamagnetic, e.g. $[(C_5H_5)MnH(SiHPh_2)(dmpe)]$ [82]. Very recently the thermally labile, paramagnetic 16 VE half sandwich cations $[(C_5H_4Me)Mn(dmpe)(-C{\equiv}CR]^+$ ($R = Ph, SiMe_3$) (**51**) of Mn(III) have been synthesized, whose NMR spectra suggest a low spin electron configuration with two unpaired electrons. In solution slow dimerization of the phenyl derivative to the diamagnetic dication $[(C_5H_4Me)(dmpe)Mn{\equiv}C{-}C(Ph){=}C(Ph){-}C{\equiv}Mn(dmpe)(C_5H_4Me)]^{2+}$ occurs [83].

The decamethylmanganocenium cation exhibits a low spin configuration with two unpaired electrons [84], which forms ferromagnetically ordered charge transfer complexes with the radical anions of TCNE or TCNQ [85]. An attempt to oxidize octaisopropylmanganocene to the octaisopropylmanganocenium cation with tetracyanoethylene resulted in metallocene cleavage [86].

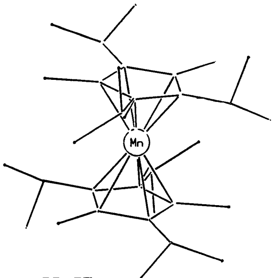
6.4. Manganese(II) complexes

Due to the strong electron-electron repulsion and the exchange interaction between the five unpaired 3d electrons of the Mn^{2+} ion, this cation has a marked tendency to remain in the $S = 5/2$ spin state in its cyclopentadienyl complexes. In the gas phase the parent manganocene (**52**) exhibits a high spin ground state in equilibrium with a small amount of the low spin isomer. The energy difference between the two spin states has been estimated at 2.1 kJ mol^{-1} [87] and is even smaller in 1,1′-dimethylmanganocene (**53**), which in the gas phase at 100°C forms a 62:38 equilibrium mixture of high spin and low spin isomer. This mixture could be structurally characterized by gas phase electron diffraction [88]. The ratio of inter ring distances for the two spin isomers of dimethylmanganocene is 1.191; the high spin isomer is stretched by almost 20% compared to the low spin isomer.

The sizable difference illustrates the strong effect of antibonding orbital population in the high spin isomer. The spin equilibrium found for the parent manganocene and its dimethyl derivative can be shifted to pure high spin behavior by introduction of just one trimethylsilyl substituent at each ring. The crystal structure of 1,1′-bis(trimethylsilyl)manganocene shows the absence of steric strain with trans oriented silyl substituents and leaves the electronic effect of the $SiMe_3$ groups as the sole explanation for exclusive high spin character [89]. Likewise, exclusive low spin behavior can be induced by introduction of eight [89] or ten [90] electron donating methyl groups. In decamethylferrocene two pentamethylcyclopentadienyl rings can be assembled easily at a distance of 3.31 Å [90] without much steric strain (free rotation on the nmr time scale for octa- and decamethylferrocene may be taken as an indication; even for octaisopropylferrocene cooling is necessary in order to observe separate signals for the rotamers [91]). The reason for pure low spin behavior of octa- (**54**) and decamethylmanganocene (**55**) is the stronger electron donor ability of the tetra- or pentamethylated cyclopentadienyl ring causing larger ligand field splitting. Bending of methyl groups out of the cyclopentadienyl ring plane directed away from the metal is to some extent a steric effect, but may at least in part also be a consequence of electron donation from filled cyclopentadienyl π orbitals in empty metal d orbitals and (albeit weak) back donation from filled metal d orbitals into empty cyclopentadienyl π^* orbitals, thereby inducing some pyramidalization of the ring carbon atom.

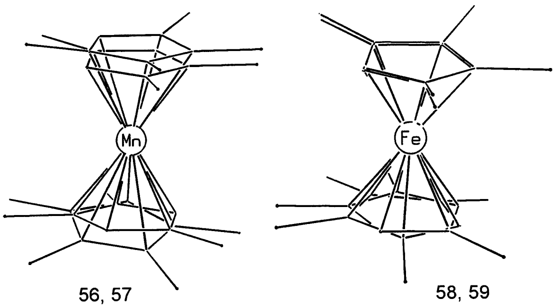
If we want to see significant steric effects, we need to employ alkyl groups larger than methyl. The crystal structures of the decaethylferrocenium cation [92] or even decabenzylferrocene [93] teach us, that primary alkyl groups are not well suited to exert a steric influence on metal–Cp interaction. They strongly tend to bend away from the metal and their steric bulk extends only into the space around the molecule. Tertiary butyl substituents inevitably extend towards the metal in a metallocene structure but they also need much space in the ring plane and therefore build up strong steric repulsion within the cyclopentadienyl ring plane itself. This disadvantage is avoided by secondary alkyl groups like isopropyl, which neatly orient themselves with one methyl up and one down if they are vicinally bound to the cyclopentadienyl ring. In octaisopropylmanganocene (**56**) the effect of eight isopropyl substituents results in pure high spin behavior even at 2 K with an effective magnetic moment of $5.87\mu_B$ [94] (Ref. [86] gives a value of $5.73\mu_B$), whereas hexaisopropylmanganocene (**57**) is predominantly a low spin species. It shows a gradual increase of the effective magnetic moment from $1.89\mu_B$ at 5 K to $3.25\mu_B$ at 348 K in the solid state [86]. Indeed 1,1′,2,2′,4,4′-hexaisopropylmanganocene **57** can be superimposed on decamethylmanganocene **55** without any significant difference in the MC_{10} core and even the six α C atoms of **57** are nearly congruent with the six methyl C atoms in the 1,1′,2,2′,4,4′ positions of decamethylmanganocene (Fig. 27).

Hexaisopropylmetallocenes in general have a conformation with two vicinal isopropyl groups oriented with methyl groups up and down while the isopropyl substituent in 4 position stretches both methyl groups away from the metal and therefore does not exert much steric strain. The two rings are related by a center of symmetry which brings two vicinal isopropyl groups of one ring on top of the flat lying isopropyl group of the other ring in order to avoid steric strain. For this



55, 57

Fig. 27. The MnC_{10} skeleton of decamethylmanganocene (**55**) is nearly identical with that of hexaisopropylmanganocene (**57**) and even the six α carbon atoms both molecules have in common show little deviation.



56, 57

58, 59

Fig. 28. The different behavior of ferrocene and manganocene under steric congestion is illustrated by superimposition of octa- (**56**) and hexaisopropylmanganocene (**57**) on the left side and hexa- (**58**) and octaisopropylferrocene (**59**) on the right side. The two manganocene derivatives show a dramatic difference in Mn–C bond length, whereas the impact of steric bulk on the iron sandwich is visible, but not comparable to the manganese example.

reason four isopropyl groups per five-membered ring are necessary as a minimum to see deviations from the behavior so well-known from C_5Me_5 derivatives. If, however, a 1,1′,2,2′,3,3′-hexaisopropylmanganocene can be synthesized, it should be significantly more congested than the 1,1′,2,2′,4,4′-isomer, because there is no conformation available, which completely avoids steric strain.

Fig. 28 shows a superimposition of octaisopropylmanganocene (**56**) and hexaisopropylmanganocene (**57**) and illustrates the dramatic effect caused by just one more isopropyl substituent on each five-membered ring. This kind of soft manganocene behavior can be related to the d^5 configuration of Mn^{2+} which in the high spin isomer achieves a maximum of favorable exchange interaction [95].

The high spin state of octaisopropylmanganocene can only be a result of the steric effect of eight isopropyl groups, because the electron donor ability of the tetraisopropylcyclopentadienyl ligand itself should not be smaller than that of tetramethyl- or triisopropylcyclopentadienyl. The crystal structure of octaisopropylmanganocene (cf. Fig. 28) shows a bent sandwich with Mn–C distances from 2.38–2.45 Å (average value 2.42 Å) [86], which is comparable to 2.42 Å in the high spin isomer of 1,1′-dimethylmanganocene [88] or 2.38 Å in the parent manganocene [96]. If branching of the alkyl substituents and a proper conformation force eight methyl groups between the two metallocene ring planes, the five-membered rings may either be sqeezed firmly together or move apart depending on the strength of the metal-ring bond.

For comparison a superimposition of the crystal structures of hexaisopropylferrocene (**58**) [97] and octaisopropylferrocene **59** has been included in Fig. 28. Although octaisopropylferrocene is severely crowded [91], the inter ring distance is only about 0.1 Å larger [98] than that found in the parent compound [99] or the decamethyl derivative [90] and is surpassed only slightly by the decaphenyl derivative [100].

A similar effect could be achieved in 1,1′,2,2′,4,4′-hexa(*tert*-butyl)manganocene (**60**) [94]. A range of decaalkylmanganocenes with increasing steric bulk including 1,1′-diisopropyl-octamethylmanganocene (**61**) [94], the two tetraisopropyl-hexamethylmanganocene isomers **62** [98] and **63** [101], hexaisopropyl-tetramethylmanganocene **64** as well as octaisopropylmanganocene and hexa(*tert*-butyl)-manganocene are shown in Fig. 29.

If the steric bulk is somewhere between decamethyl- and octaisopropylmanganocene, evidence for temperature dependent spin equilibria corresponding with a gradual spin transition from low spin at low temperature to high spin at high temperature has been observed [94,101] and the onset of such a spin transition has been reported for hexaisopropylmanganocene [86].

An interesting behavior has been found for 1,1′,2,2′,4,4′-hexaisopropyl-3,3′,5,5′-tetramethyl-manganocene (**64**) [94] (for a schematic drawing see Fig. 29), where the isopropyl group in four-position is prevented from aligning with the ring plane by its two methyl neighbours. Even without evidence from the crystal structures of two bismuth complexes carrying the same cyclopentadienyl ligand [102], the magnetic behavior of hexaisopropyltetramethylmanganocene **64** provides strong evidence for the indirect steric effect of two additional methyl groups. These do not force the two rings apart by themselves, but they help to move the 4-$CHMe_2$ group into a position more or less erected out of the ring plane. At 2 K the rings manage to come close enough to allow for a low spin configuration to occur. When the

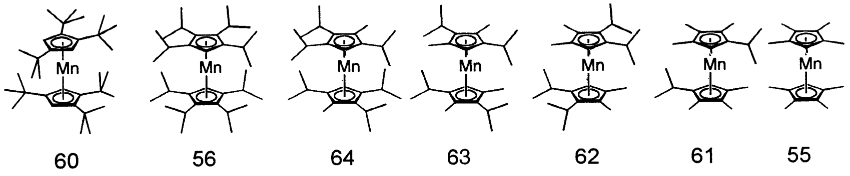


Fig. 29. Manganocenes with increasing steric bulk from right to left show a variation of their magnetic behavior ranging from pure low spin (right) to pure high spin behavior even at very low temperatures (left). The derivatives with intermediate bulk show spin transitions (see text).

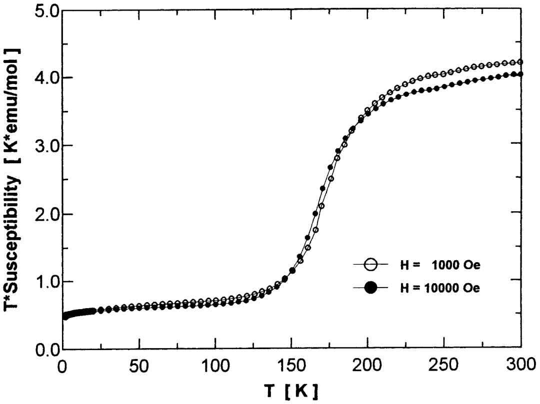
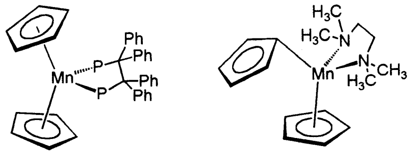


Fig. 30. The χT vs. T plot of the magnetic susceptibility data of hexaisopropyltetramethyl-manganocene **64** shows an abrupt spin transition with hysteresis at 167 K.



65 **66**

Fig. 31. Donor adducts of manganocene show very long Mn–C distances. Therefore the diphosphane chelate **65** should not be regarded as a 21 VE complex, but as an ionic compound. The tmeda adduct **66** shows almost equal C–C distances within the upper cyclopentadienyl ring, which is therefore not regarded as an η^1 cyclopentadienyl ligand, but rather as a loosely coordinated counterion.

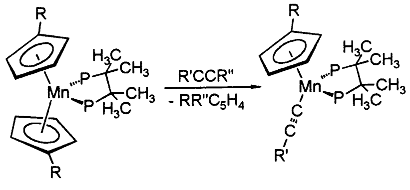
temperature is increased this situation changes abruptly at 167 K where a transition to high spin behavior with hysteresis can be observed [94] (Fig. 30).

Donor adducts of manganocene or dimethylmanganocene with phosphanes [103] or TMEDA [104] are colorless or light yellow high spin complexes (the same is true for high spin manganocenes, whereas low spin manganocenes are red or orange–red), which show long Mn–C distances not resembling covalent bonds, but being indicative of ionic character. The dppe adduct of manganocene (**65**) shows Mn–C distances up to 2.74 Å [103] and the η^1-C_5H_5 ring of [(η^5-C_5H_5)Mn(TMEDA)(η^1-C_5H_5)] (**66**) displays five equal C–C bond lengths [104] (Fig. 31).

The dmpe adducts of manganocene or 1,1′-dimethylmanganocene, [$(C_5H_4R)_2$-Mn($Me_2PCH_2CH_2PMe_2$)] (R = H (**67**), Me (**68**), both are high spin complexes) react with alkynes R′C≡CR″ (R′ = Ph, $SiMe_3$; R″ = H, $SnMe_3$) with elimination of C_5H_4RR'' to form half sandwich complexes [(C_5H_4R)Mn($Me_2PCH_2CH_2PMe_2$)-(C≡CR′)] (**69**), which display a low spin electron configuration [83], Fig. 32.

High spin half sandwich complexes of the type [{(C_5H_5)Mn(PR_3)(μ-Cl)}$_2$] (**70**) (Fig. 33) have been obtained from manganocene, $MnCl_2$, and the respective phosphane in high yields. They display antiferromagnetic coupling between the two manganese centers [105] and their ^{13}C-NMR signals appear in a wide spectral range from -500 to $+1500$ ppm [89]. With low spin manganocenes, e.g. $[(C_5Me_5)_2Mn]$ such half sandwich complexes could not be synthesized this way [89]. $MnCl_2$, TMEDA, and NaC_5H_5 gave $[(C_5H_5)Mn(TMEDA(Cl)]$ (**71**), which carries a synthetic potential as starting material for manganese half sandwich complexes [104]. Insoluble $[(C_5H_4Me)MnCl]_x$ (**72**) has been isolated as a colorless, presumably polymeric precipitate. Its magnetic properties have not been investigated [106].

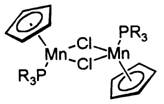
With open pentadienyl the structurally interesting complex $[(C_5H_5)Mn(\mu,\eta^5{:}\eta^2\text{-}2,4\text{-}C_7H_{11})Mn(C_5H_5)]$ (**73**, Fig. 34) containing both low spin and high spin manganese(II) could be synthesized in good yield by simply reacting manganese dichloride with a mixture of 2,4-dimethylpentadienide anion and cyclopentadienide in a 1:1:1 ratio, where half of the open pentadienide anion is consumed as a reducing reagent. The structure shows a dinuclear complex with a Mn–Mn bonding distance of 2.46 Å and distinguishes clearly one low spin manganese atom in a



67, 68 69

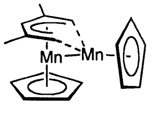
R = H, CH$_3$; R' = Ph, SiMe$_3$; R" = H, SnMe$_3$

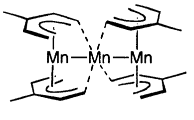
Fig. 32. Mn(II) half sandwich complexes **69** display a low spin configuration with one unpaired electron.



70

Fig. 33. The chloro-bridged dimer **70** is shown as an example for a class of high spin Mn(II) half sandwich complexes, which displays high spin behavior and has been investigated by ^{13}C- and ^{1}H-NMR spectroscopy.





73 74

Fig. 34. In both **73** and **74** the Mn atom(s) showing π-coordination to the open pentadienyl ligand can be regarded as the center of a diamagnetic anion with 18 VE coordinated to high spin Mn(II) with or without an additional cyclopentadienyl ligand.

half-open sandwich environment from a high spin manganese central atom in a half sandwich coordination geometry by short and long Mn–Cp distances in accordance with the effective magnetic moment of 5.84 BM [107]. Using only 2,4-dimethylpentadienide the trinuclear complex $[\{(\mu,\eta^5:\eta^1\text{-}2,4\text{-}C_7H_9)_2Mn\}_2Mn]$ (**74**, Fig. 34) could be synthesized with a high spin Mn(II) central atom coordinated by one terminal carbon atom of each of the four pentadienide ligands and connected to the two manganese atoms of the open sandwich moieties by Mn–Mn bonds of 2.52 Å [108].

In both complexes the open or half open manganocene units can be regarded as diamagnetic manganocene anions with 18 valence electrons bonded to either a $[Mn(C_5H_5)]^+$ cation or a Mn^{2+} cation with a high spin d^5 configuration [107].

6.5. Manganese(I) complexes

Some paramagnetic 18 VE cyclopentadienyl complexes are known for manganese, which belong to the $[(C_5R_5)Mn(CO)_2L]$ type with R = H, Me and nitrogen donors L including pyridine, pyrazine or tetracyanoethylene. These complexes possess a diamagnetic ground state with easily accessible magnetic states of integer spin [109].

The $[(C_5H_5)Mn(CO)_2]$ 16 VE fragment generated by UV irradiation of the tricarbonyl binds relatively strongly to hydrocarbons [110]. The relationship between singlet or triplet ground state and coordination of weakly coordinating ligands like saturated hydrocarbons or noble gases has been discussed, e.g. in Ref. [111].

7. Iron complexes

7.1. Iron(IV) complexes

In liquid sulfur dioxide with tetrabutylammonium hexafluorophosphate as supporting electrolyte decamethylferrocenium hexafluorophosphate shows a reversible oxidation wave at 1.34 V and could be oxidized by controlled potential coulometry at 1.6 V to a yellow–brown solution of the $[(C_5Me_5)_2Fe]^{2+}$ dication (**75**), which was stable for at least 4 h in solution at −30°C and could be isolated as a mixture with the supporting electrolyte. The magnetic susceptibility measured in solution corresponds to an effective magnetic moment of $2.73\mu_B$ and is consistent with the presence of two unpaired electrons. This is in accord with the electron configuration of most chromocenes. A maximum spin configuration with four unpaired electrons is not expected here, because the higher oxidation state tends to increase the ligand field splitting.

The unsubstituted dication $[(C_5H_5)_2Fe]^{2+}$ could be generated at an anodic potential of 1.79 V, but quickly decomposed in solution at −40°C [112][3].

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[3] The potentials given in this publication are referenced to the $[Fe(bpy)3]^{2+/3+}$ couple ($E° = 0.74$ V).

7.2. Iron(III) complexes

Ferrocenium cations are a vast class of paramagnetic complexes and invariably have one unpaired electron. We could expect a situation comparable to the isoelectronic Mn^{2+}, but there are no cyclopentadienyliron(III) complexes with five and not even with three unpaired electrons. Here also the higher oxidation state strengthens the ligand field effects. With the exception of the bis(heptamethylindenyl)iron cation with a $^2A_1$ ground state [113], these 17 VE species possess a $^2E_{2g}$ ground state.

7.3. Iron(II) complexes

Ferrocene and all its derivatives known so far are low spin complexes [114]. Neither electron withdrawing substituents nor weakening of the ligand field with bulky substituents (see Section 6.4) have yet been able to change its spin state. If the steric bulk of the cyclopentadienyl ligands exceeds that of the pentaphenyl derivative like the pentaisopropylcyclopentadienyl ring, no ferrocene is formed. Instead a redox reaction takes place:

$$FeCl_2 + 2NaC_5R_5 \underset{(R = CHMe_2)}{\rightarrow} Fe + 2NaCl + 2C_5R_5$$

We must assume, that two pentaisopropylcyclopentadienyl rings cannot both come close enough to the iron center to build up strong bonding interactions. In this situation the system does not yield a high spin metallocene like manganese, but the thermally stable pentaisopropylcyclopentadienyl radical [115].

If $[FeBr_2(DME)]$ is reacted with only one equivalent of tetra- or pentaisopropylcyclopentadienide, the orange–red cyclopentadienyl iron(II)halides $[(C_5R_4R')FeBr]_2$ (**76a**,**b**) without additional donor ligands can be isolated as stable compounds [116]. Attempts to prepare the C_5Me_5 derivative failed because of a ligand redistribution reaction, which gives decamethylferrocene and iron(II) halide [117]. The dimers **76** are the only known maximum spin cyclopentadienyl complexes of iron. They contain d^6 Fe(II) with four unpaired electrons, exhibit an effective magnetic moment of $5.15\mu_B$ (**76a**) and their stability results from effective blocking of the disproportionation pathway by introduction of four or five bulky ring substituents. The formal coordination number of the iron atom is five (Fig. 35) and the bromide bridges not only serve as weak field ligands, but also provide for ferromagnetic coupling to occur within the dimeric units (Fig. 36).

These dimers are very reactive and reversibly add donor ligands like tetrahydrofuran or acetonitrile (most probably without changing the spin state) and carbon monoxide irreversibly with spin pairing to yield the dicarbonyl halides $[(C_5R_4R')Fe(CO)_2Br]$ [$R = CHMe_2$, $R' = H$ (**77a**), $CHMe_2$ (**77b**)] [116]. The pentaisopropylcyclopentadienyl derivative **77b** upon reduction with cobaltocene or potassium metal gave the corresponding 17 VE Fe(I) species $[(C_5R_5)Fe(CO)_2]^\bullet$ (**78**) ($R = CHMe_2$). **78** is unique among the cyclopentadienyliron dicarbonyl radicals, because it does not dimerize in solution [116], cf. the pentaphenylcyclopentadienyl derivative [118].

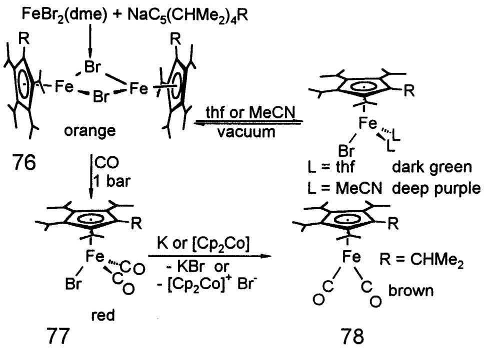


Fig. 35. The reversible reaction of the cyclopentadienyliron halide **76** with donor solvents and the irreversible addition of carbon monxide are shown above. Reduction of the dicarbonyl halide **77** gives the only known cyclopentadienyliron dicarbonyl radical which does not dimerize in solution (**78**).

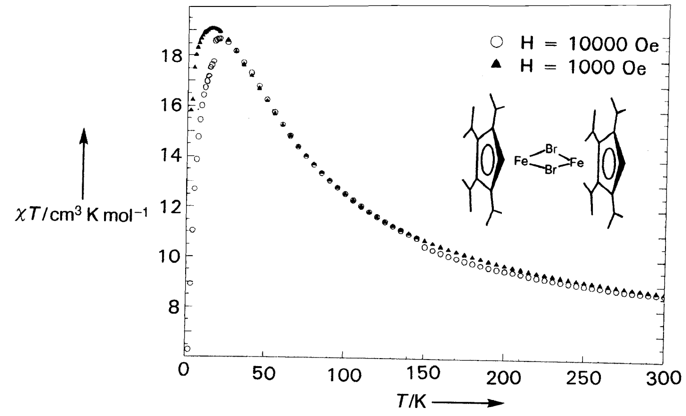
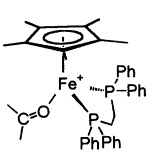


Fig. 36. The bromide-bridged complex **76** shows ferromagnetic coupling within the dimeric molecules. The maximum below 50 K corresponds to saturation effects, not to antiferromagnetic interaction. The χT vs. T plot has been reproduced with permission from WILEY-VCH (see Ref. [116]).



79

Fig. 37. The acetone complex shown here is a unique example of a cyclopentadienyliron(II) complex with two unpaired electrons, a paramagnetic 18 VE complex. For a d^6 configuration this represents an intermediate spin situation.

The $[(C_5Me_5)Fe(dppe)(acetone)]^+$ cation (**79**) (Fig. 37) possesses two unpaired electrons ($\mu_{eff} = 2.90\mu_B$ in the solid state) and is the only known example of an intermediate spin iron(II) compound with 18 valence electrons [119], one of only a few paramagnetic organometallic complexes with 18 valence electrons.

Oxidation of the orange, neutral 17 VE radical $[(C_5Me_5)Fe(dppe)]$ with ferrocenium hexafluorophosphate gave the orange 16 VE cation $[(C_5Me_5)Fe(dppe)]^+$, which exhibits an effective magnetic moment of $3.3\mu_B$ in solution corresponding to the presence of two unpaired electrons [120].

With the bulky diphosphane 1,2-bis(diisopropylphosphino)ethane (dippe) the diamagnetic end-on dinitrogen complex $[(C_5H_5)Fe(N_2)(dippe)]^+[BPh_4]^-$ has been obtained. In argon atmosphere loss of the N_2 ligand occurs with formation of the corresponding 16 VE cation $[(C_5H_5)Fe(dippe)]^+$, which is another intermediate spin Fe(II) complex with two unpaired electrons and a magnetic moment of 3.6 μ_B. The high value has been discussed in terms of a significant orbital contribution [121]. The pentamethylcyclopentadienyl derivative $[(C_5Me_5)Fe(dippe)]$ $[BPh_4]$ does not take up dinitrogen and displays an effective magnetic moment of $3.8\mu_B$ [121]. This example illustrates, how steric bulk can induce spin state changes in half sandwich complexes by supporting a low coordination number of the central atom.

The results of a theoretical investigation by DFT calculations on the diphosphane iron complexes mentioned above are in accord with the experimental results in most cases [122]. Only for the cationic acetone complex **79** and the corresponding triflate $[(C_5Me_5)Fe(dppe)(OSO_2CF_3)]$ [123] the calculations predict diamagnetic behavior instead of the experimentally observed paramagnetism [122].

Iron(II) compounds with two pyrazolylborate ligands can be low spin or high spin complexes or show spin crossover phenomena depending on the substituent pattern of the pyrazolyl rings employed or on the fourth substituent at the boron atom [124]. The pyrazolyl borates are being regarded as ligands with almost negligible ligand field strength [125].

7.4. Iron(I) complexes

There are no cyclopentadienyl complexes of d^7 Fe(I) with three unpaired electrons at the central atom. There are, however, stable 19 VE $[(C_5H_5)Fe(arene)]$ complexes with one unpaired electron available, if the arene is peralkylated [126–128]. The paramagnetic, dinuclear complex $[\{(C_5Me_5)Fe\}_2(\mu\text{-}CO)_3]$ with a total electron count of 32 VE has a doubly degenerate π^* HOMO consisting mainly of the d_{xy} and d_{xz} orbitals, which holds two unpaired electrons [129]. The stable 17 VE complex $[(C_5R_5)Fe(CO)_2]$ ($R = CHMe_2$) has been mentioned in the preceding chapter, the generation of related radicals with less bulky ring substituents by UV irradiation is well known and has been discussed in a recent review article [130].

8. Cobalt complexes

8.1. Cobalt(V) complexes

Cyclopentadienyl complexes of cobalt(V) are unknown. A rare example of an organometallic Co(V) complex is the diamagnetic cation $[CoR_4]^+$ (R = 1-norbornyl) [132].

8.2. Cobalt(IV) complexes

The cobaltocenium dication $[(C_5H_5)_2Co]^{2+}$ is accessible via reversible oxidation of the corresponding monocation in liquid sulfur dioxide by cyclic voltammetry [131]. Although its magnetic properties appear to be unknown, it is not a candidate for high spin behavior.

Tetrakis(1-norbornyl)cobalt has one unpaired electron [44] and is according to a crystal structure determination [132] an example for tetrahedral low spin complexes.

8.3. Cobalt(III) complexes

High spin cyclopentadienyl complexes of the d^6 cation Co^{3+} are unknown.

8.4. Cobalt(II) complexes

Whereas bis{tris(pyrazolyl)borates} of cobalt(II) are high spin complexes even at low temperatures [133], the search for a high spin cobaltocene with three unpaired electrons is still going on while all known cobaltocenes are spin doublets with an $e_{2g}^4 a_{1g}^2 e_{2g}^1$ configuration at the metal center. In attempts to induce a high spin configuration bulky cyclopentadienyl ligands were used to push the rings away from the central atom and lower the ligand field strength. Nevertheless, octaisopropylcobaltocene is still a low spin species [97], attempts to introduce even greater steric bulk (in a cobaltocenium ion) with tenfold isopropyl substitution have been unsuccessful [134] and since six trimethylsilyl substituents failed to cause high spin behavior of chromocene [69], the hexakis(trimethylsilyl) derivative [135] is most likely also a low spin complex, although it has not yet been subjected to magnetic measurements. Even the dimeric cyclopentadienylcobalt(II)halides are low spin complexes with one unpaired electron per Co^{2+} central atom, which exhibit antiferromagnetic intra-dimer coupling, as has been shown for $[\{(C_5Me_5)Co(\mu\text{-}Cl)\}_2]$ [136,137] and $[\{(C_5HR_4)Co(\mu\text{-}Cl)\}_2]$ (R = $CHMe_2$) [138]. For the bromo-bridged derivative $[\{(C_5H_2R_3\text{-}1,2,4)Co(\mu\text{-}Br)\}_2]$ (R = CMe_3) no magnetic susceptibility data have been reported [139]. Another attempt to combine two weak field ligands with a sterically demanding tetraisopropylcyclopentadienyl ring at a cobalt(II) central atom, the acetonitrile complex $[(C_5HR_4)Co(MeCN)_2]^+$ (R = $CHMe_2$) also yielded a low spin complex [138].

8.5. Cobalt(I) complexes

Sixteen VE complex fragments [CpCo(L)] can be generated by thermal or photochemical ligand dissociation and have been calculated to possess a triplet ground state (L = CO [140]; L = C_2H_4, PH_3 [141]). Although there is no cyclopentadienyl ligand bulky enough to admit only one CO ligand to the respective cyclopentadienylcobalt fragment, tris(pyrazolyl)borates can be tailored to fill that gap: With hydridotris{(3-isopropyl,5-methyl-pyrazolyl)borat} the triplet species [{HB(3-R,5-Me–pz)$_3$}Co(CO)] in the presence of carbon monoxide is in a ligand dissociation equilibrium with the diamagnetic dicarbonyl [{HB(3-R,5-Me–pz)$_3$}Co(CO)$_2$] for R = $CHMe_2$ [142].

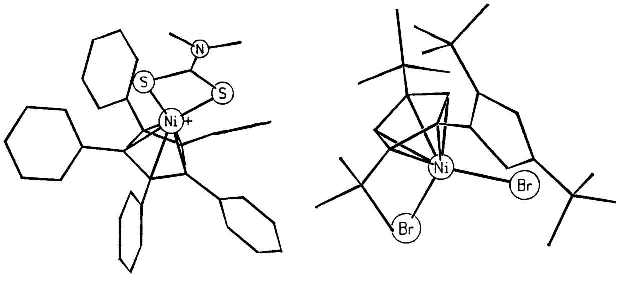
9. Nickel complexes

9.1. Nickel(IV) complexes

$[(C_5Me_5)_2Ni]^{2+}$ is a rare example of an isolable Ni(IV) cyclopentadienyl complex. As an 18 VE complex isoelectronic with ferrocene, it is diamagnetic [143]. High spin cyclopentadienyl complexes of Ni(IV) are unknown.

9.2. Nickel(III) complexes

Apart from a sizable class of nickelocenium cations [144], which are all low spin complexes with one unpaired electron, there are only very few mono(cyclopentadienyl) complexes of Ni(III). The first of these was the 17 VE $[(C_5Ph_5)Ni(S_2CNMe_2)]^+$ cation (**80**) obtained as the tetrafluoroborate salt by Kläui [145], followed by the neutral, monomeric cyclopentadienylnickel dibromide derivative **81** published by Jutzi [146]. The bulky ring ligand has been derived from tetra(*tert*-butyl)dihydrofulvalene and features one rare 2,4-di(*tert*-butyl)-1,3-cyclopentadien-1-yl substituent besides two *tert*-butyl groups (Fig. 38).



80

81

Fig. 38. The nickel(III) half sandwich complexes **80** and **81** shown here are both low spin complexes with one unpaired electron.

Again both of them turned out to be low spin complexes with an effective magnetic moment of $1.82\mu_B$ and $1.77\mu_B$, respectively.

9.3. Nickel(II) complexes

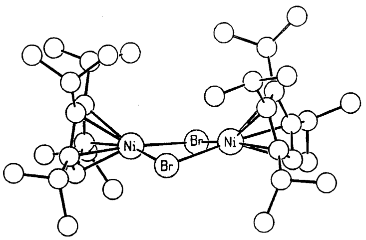
Nickelocene is a triplet molecule with a weak ferromagnetic interaction in the solid state [147]. Its substituted derivatives with two unpaired electrons also possess maximum spin for a d^8 configuration. Decaphenylnickelocene used to be the only exception and was long thought to be diamagnetic, because the weak paramagnetism was assumed to arise from a pentaphenylcyclopentadienyl radical impurity [148]. Structural alternatives like η^5- and η^3-coordination of the rings were recently argued against by a comparison of powder diffraction data from decaphenylnickelocene and -ferrocene, which turned out to be isostructural. The weak paramagnetism was explained by the significant diamagnetic contribution of the $C_{70}H_{50}$ ligand environment of the central atom [149]. It would be interesting to know how weak this paramagnetism is and how this value compares to the (still unknown) magnetic moment of the decaphenylferrocenium cation [150] and to the value of $2.75\mu_B$ for decaphenylmolybdenocene [151].

Less uniform are cyclopentadienylnickel(II) halides. The parent compound $[(C_5H_5)NiCl]$ disproportionates in solution above −20°C [152] and can be stabilized with an additional two electron donor ligand as diamagnetic 18 VE complexes [CpNi(L)Cl].

With relatively bulky cyclopentadienyl derivatives isolable dimers with bridging halide ligands are formed. $[(C_5Me_5)Ni(\mu\text{-}Br)]_2$ (**82a**) [153,154] gives well resolved ^1H- and ^{13}C-NMR spectra in the normal chemical shift range as does its diiodo derivative (**83b**) [154] and therefore is regarded as a diamagnetic compound. The silylated derivative $[(C_5H_2(SiMe_3)_3Ni(\mu\text{-}Cl)]_2$ (**84**) is a thermally sensitive oil, which was used for follow-up reactions [155]. Its magnetic properties have not been investigated. The pentaphenylcyclopentadienyl derivatives $[(C_5Ph_5)Ni(\mu\text{-}X)]_2$ (X = Cl, Br) (**85a**,**b**) [156] are told to be diamagnetic [157]. In contrast to all of these derivatives, the tetraisopropylcyclopentadienyl compound $[\{(C_5HR_4)Ni(\mu\text{-}Br)\}_2]$ (**86**) ($R = CHMe_2$) displays paramagnetic behavior in solution. In the solid state an effective magnetic moment of $2.61\mu_B$ corresponding to Ni^{2+} central atoms with two unpaired electrons and a weak antiparallel spin coupling ($\Theta = 1.90$ K) have been observed. The crystal structure shows a puckered four-membered Ni_2Br_2 ring with a non bonding Ni···Ni distance of 3.41 Å and unsymmetric bromo bridges [158] (Fig. 39).

Interestingly, the 18 valence electron cyclopentadienylnickel derivative $[(C_5Me_5)Ni(acac)]$ (acac = acetylacetonato) has a diamagnetic ground state and a low lying triplet excited state, which exhibits a low spin-high spin equilibrium with an equilibrium constant of 0.47 at 303 K [159].

The bromo bridges of **86** can be replaced with azido bridges with preservation of the paramagnetic nature of the dimeric complex. Reactions of **86** with Na_2S_2, Na_2Se_2, or Na_2Te_2 give the diamagnetic complexes **87a**–**c** with dichalcogenide bridges [160] (Fig. 40).



86

Fig. 39. The dimer **86** shows a puckered four-membered Ni_2Br_2 ring and a non bonding Ni···Ni distance, for details see text.

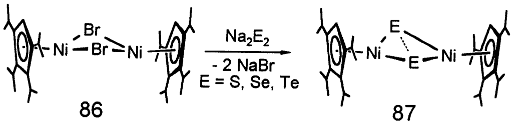


Fig. 40. **86** is highly reactive and can be converted to the diamagnetic dichalcogenides **87** easily.

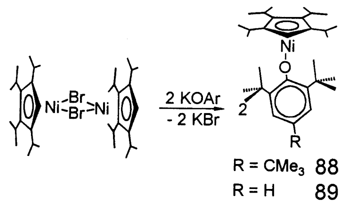
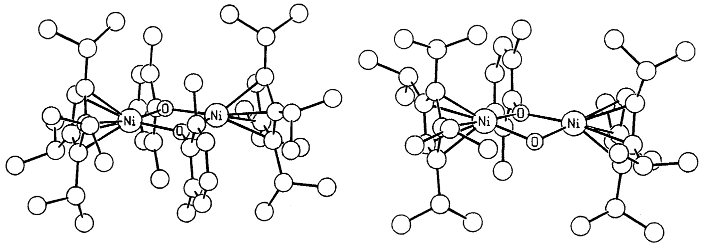


Fig. 41. With extremely bulky phenoxides the deep purple, monomeric cyclopentadienylnickelphenoxide derivatives **88** and **89** have been obtained from **86** as sublimable complexes.

If phenolate or carboxylate anions are introduced by reactions of **86** with the respective alkali salts, paramagnetic complexes are formed. With extremely bulky phenoxides paramagnetic, sublimable monomers have been obtained, namely the tri(*tert*-butyl)phenoxide $[\{(C_5HR_4)Ni\{\mu\text{-}OC_6H_2(CMe_3)_3\text{-}2,4,6\}_2]$ (**88**) and the di(*tert*-butyl)phenoxide $[\{(C_5HR_4)Ni\{\mu\text{-}OC_6H_3(CMe_3)_2\text{-}2,6\}_2]$ ($R = CHMe_2$) (**89**) [161] (Fig. 41). Dimeric $[\{(C_5HR_4)Ni(\mu\text{-}OC_6H_3Me_2\text{-}2,6)\}_2]$ ($R = CHMe_2$) (**90**) with bridging 2,6-dimethylphenoxide ligands as well as its partial hydrolysis product $[\{(C_5HR_4)Ni\}_2(\mu\text{-}OH)(\mu\text{-}OC_6H_3Me_2\text{-}2,6)]$ ($R = CHMe_2$) (**91**) have been characterized by X-ray diffraction [161] (Fig. 42). The dimeric phenoxides are orange, whereas the monomers exhibit a deep purple color.

9.4. Nickel(I) complexes

There are many paramagnetic complexes of Ni(I) like the crystallographically characterized bipyridine complex $[(C_5H_5)Ni(bipy)]$ [162]. These are out of the scope of this article, however, because there is only one spin state available for d^9 complexes.



90 **91**

Fig. 42. The orange dimer **90** was formed with 2,6-dimethylphenolate. Its partial hydrolysis product **91** could also be crystallographically characterized. Both complexes are paramagnetic like the monomers shown before.

10. Conclusions

With the ferromagnetically coupled high spin iron(II) dimer $[\{(C_5HR_4)Fe(\mu\text{-}Br)\}_2]$ ($R = CHMe_2$) in 1996 the first representative of a new generation of cyclopentadienyl complexes with maximum spin has been discovered. In addition to those 3d central atoms, whose tendency towards formation of high spin cyclopentadienyl complexes has been known for decades, maximum spin behavior has also been found for chromocenes and for half sandwich complexes of iron(II) and nickel(II) within the last few years. This new dimension of maximum spin cyclopentadienyl complex chemistry is mainly a consequence of the introduction of extremely bulky alkylcyclopentadienyl ligands like tetra- and pentaisopropyl- as well as tri(*tert*-butyl)cyclopentadienyl into metallocene and half sandwich chemistry of the 3d transition metals.

Now cobalt is the only remaining 3d transition metal from Ti to Ni, which does not exhibit more than one unpaired electron in any of its cyclopentadienyl complexes.

Due to a large ionic contribution to metal-cyclopentadienyl bonding high spin metallocenes are much more reactive than the corresponding low spin metallocenes, even if they carry bulky substituents. The same is true for high spin half sandwich compounds, which seem to offer a great, but almost unexplored potential as easily available starting compounds for the generation of a broad variety of mono(cyclopentadienyl) complexes.

Investigation of this synthetic potential as well as the search for new classes of high spin cyclopentadienyl complexes are both challenge and opportunity for further research.

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