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Open-Shell Organometallics as a Bridge between Werner-Type and Low-Valent Organometallic Complexes. The Effect of the Spin State on the Stability, Reactivity, and Structure

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Contents

I. Abbreviations

Cp	cyclopentadienyl
Cp*	pentamethylcyclopentadienyl
Cy	cyclohexyl
dippe	bis(diisopropylphosphino)ethane
dmCh	6,6-dimethylcyclohexadienyl
DME	dimethoxyethane
dmp	*N*,*N*′-dimethylpiperazine
dmpe	1,2-bis(dimethylphosphino)ethane
dmpm	1,2-bis(dimethylphosphino)methane
DPE	*o*,*o*′-$C_6H_4OC_6H_4$ (Li_2DPE = *o*,*o*′-dilithium diphenyl ether)
dppm	1,2-bis(diphenylphosphino)methane
dppe	1,2-bis(diphenylphosphino)ethane
Fc	ferrocene
Mes	mesityl
Nor	bicyclo[2.2.1]hept-1-yl (norborn-1-yl)
Np	neopentyl
OEP	2,3,7,8,12,13,17,18-octaethylporphyrinato (2−)
Pdl	2,4-pentadienyl
Pdl′	2,4-dimethyl-2,4-pentadienyl
PPN	bis(triphenylphosphine)iminium
py	pyridine
pz	pyrazine
TCNE	tetracyanoethylene
tmeda	*N*,*N*,*N*′,*N*′-tetramethylethylenediamine
THF	tetrahydrofuran
THT	tetrahydrothiophene
tmtaa	tetramethyldibenzotetraaza[14]annulene
Tol	tolyl
$Tp^{(R,R')}$	hydrotris(3-R-5-R′-pyrazolyl)borato
TPP	5,10,15,20-tetraphenylporphyrinato (2−)
trimpsi	$Me_3CSi(CH_2PMe_2)_3$
Xyl	xylyl

II. Introduction

Since the beginning of the systematic development of transition metal organometallic chemistry, which

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Rinaldo Poli was born in Barga, Italy, in 1956. After his graduation cum laude at the University of Pisa in 1981 he obtained a fellowship from the Scuola Normale Superiore in Pisa, where he completed his Ph.D. in Chemistry in 1985 under the supervision of Fausto Calderazzo. During this time, he also carried out research in Geoffrey Wilkinson's laboratory at the Imperial College of Science and Technology, London (August 1983 through July 1984). He then joined the Laboratory for Molecular Structure and Bonding at Texas A&M as a research associate with Al Cotton. In 1987, he became Assistant Professor at the University of Maryland, being promoted to Associate Professor in 1992 and to Professor in 1995. Since 1996, he is Professeur de Chimie at the Université de Bourgogne, at Dijon. He was the recepient of the Camille and Henry Dreyfus New Faculty Award (1987), the NSF Presidential Young Investigator Award (1990), an Exxon Education Foundation Award (1991), an Alfred P. Sloan Research Fellowship (1992–94), and the Medaglia Nasini (1992). He was Visiting Professor at the Technische Universität München (1993–94) on a Humboldt fellowship, and at the Tokyo Metropolitan University (1995). His research interests encompass a wide variety of topics in coordination chemistry (of Werner type, organometallic, and clusters), ranging from thermodynamics to kinetics, mechanism, catalysis, magnetic phenomena, electrochemistry, molecular and electronic structure, and bonding.

can be attributed to the discovery and development of the metallocenes by Wilkinson and Fischer,[1] the field has been and is still dominated by compounds that follow the so-called effective atomic number (EAN) rule, also more familiarly termed the 18-electron rule. In this respect, these complexes are not akin to traditional coordination compounds (i.e. complexes like those pioneered by Alfred Werner), thus the two fields of transition metal organometallic chemistry and classical coordination chemistry have developed independently. There is, however, a growing number of organometallic systems, especially for the light (first row, or 3d) transition metals, that are stable with less than 18 valence shell electrons and whose structural and magnetic properties are reminiscent of Werner-type complexes. We prefer to use the term "Werner-type complexes" or "Werner-type coordination compounds" rather than "classical coordination compounds" because the field of low-valent organometallic complexes can also be considered as classical in many respects.

Clearly, 18-electron organometallics and Werner-type complexes are the two extremes of a more general picture and the open-shell organometallic compounds (the subject of this review) represent the "gray area" between these two extremes. The chemistry of these compounds has remained comparatively little explored, the main reasons being perhaps the greater technical difficulty associated with the handling of these compounds (instability toward air, moisture, and thermal conditions) with respect to the Werner-type complexes, and the less effective use of spectroscopic tools of characterization relative to the diamagnetic, low-valent organometallics. Low-valent organometallics have been extensively investigated in relation to their potential involvement in catalytic processes such as olefin hydrogenation, hydroformylation, and polymerization, the field being for quite some time influenced by the idea that only species with 18 or 16 electrons in the valence shell could be involved as catalytic intermediates or transition states.[2] More recently, however, organometallic radicals (i.e. species with a spin doublet ground state and typically 17 or 19 valence electrons) have been recognized as intermediates in a number of catalytic processes.[3–7] Species with more than one unpaired electron have also been shown to be active catalysts, for instance $[Cp^*Cr(CH_3)(THF)_2]^+$ and oxide-supported Cp_2Cr and $(Pdl)_2Cr$ for ethylene polymerization.[8,9]

The purpose of this review is to present both an overview of the current knowledge in this area and a framework in which the chemical behavior of these systems may be placed, bridging the gap between the two fields of coordination chemistry represented by Werner-type complexes at one extreme and low-valent organometallics at the other. Particular attention will be devoted to the effects of spin state changes, as these do not appear to be widely appreciated by the organometallic community. To this purpose, the review will deal only with those electronically unsaturated compounds with the potential to exist in more than one spin state, therefore it excludes d^0 and d^{10} system (which can only adopt a $S = 0$ ground state) as well as d^1 and d^9 systems (which can only adopt a $S = {}^1/_2$ ground state). It is pertinent to mention that the stability, reactivity, and structure of organic open-shell systems, such as carbenes, nitrenes, and nitrinium ions, markedly depend on their ground-state electronic configuration (e.g. singlet vs triplet). Therefore, differences between singlet and triplet ground states for 16-electron organometallics (isolobal with the 6-electron organic systems) may be expected. Analogously, the behavior of 15-electron organometallics is anticipated to parallel that of 5-electron organics such as carbyne.

Concerning the type of carbon-based ligands covered by this review, both 2-electron L-type ligands (e.g. CO, olefins) and X-type ligands (alkyl, aryls), as well as multielectron systems (e.g. allyl, Cp, arene, etc.) will be considered. The now commonly used X and L ligand classification[10] will be employed throughout this review. The symbol R will be used to indicate both alkyl and aryl groups. Also considered will be special cases of non-carbon-based ligands (e.g. H, PR_3) when they are found in nonorganometallic compounds with properties similar to their organometallic analogues (e.g. compounds that are organometallic "in spirit").[11]

The general sections of the review (sections III–VII) discuss the theoretical framework for open-shell organometallic complexes and implications on their stability and structure and on the thermodynamics and kinetics of their reactions and precede a systematic review (section VIII) organized by metal electron count (d^2 through d^8). In spite of the ambiguity that exists in some cases for the assignment of a formal oxidation state to metal centers in organometallic systems (e.g. an alkene complex of a d^n center vs a metallacyclopropane complex of a d^{n+2} center), we cannot find a better way to organize this material and take full responsibility for inappropriate assignments. Each d^n section is organized in subsections by descending electron count. Each of these describes σ-complexes first, followed by complexes with open π-ligands, half-sandwich complexes, and finally sandwich systems and their ligand adducts. Derivatives with open pentadienyl ligands will be covered together with the corresponding cyclopentadienyl derivatives. Each of these sub-subsections is organized by increasing group number and in descending order within each group (e.g. V, Nb, Ta). Section VIII is not meant to be a comprehensive review of all organometallic compounds known with the characteristics mentioned above. It is hoped, however, that all general classes of compounds by nature of metal, electronic configuration, number of valence electrons, and spin state are covered. Good sources of specific references to the original literature are the *Comprehensive Organometallic Chemistry* series.[12,13] A number of excellent reviews on σ-hydrocarbyl compounds are also available,[14−16] as well as a relatively recent review on open metallocenes and related compounds containing the pentadienyl ligand system.[17]

Relevant studies that have appeared between the submission and the revision of this manuscript have been incorporated into the text, rather than placed in a separate appendix. The review covers work that has appeared prior to approximately May 1996.

III. At the Interface between Werner Chemistry and Low-Valent Organometallic Chemistry

III.1. The Two Extremes

It is useful to first briefly recall the main characteristics of coordination compounds of either type, i.e. low-valent, 18-electron organometallic compounds on one side and Werner-type compounds on the other. Essentially, the bonding models that most successfully rationalize the structural and physical properties at the two extremes involve covalent bonding (molecular orbital theory) for organometallic compounds and ionic bonding (crystal field theory) for Werner-type compounds. Obviously, the actual bonding situation lies somewhere in between the two extremes. Indeed, the failure of the purely ionic model to explain some features of Werner-type compounds (e.g. the spectrochemical series) is at least qualitatively corrected by invoking a covalent contribution to the metal−ligand bonding (ligand field theory).

For a generic ML$_n$ organometallic complex, strong covalent bonding with the n ligands generates a set of n M−L bonding orbitals (σ) and, correspondingly, a set of n M−L antibonding orbitals (σ*) at very high energy (see Figure 1). The remaining $(9 - n)$ metal valence-shell orbitals are stabilized by back-bonding to the π-acidic ligands that are ubiquitous for these complexes (e.g. CO, olefins, arenes, Cp, carbenes, etc.). Thus, maximum stability results when all nine valence-shell orbitals are doubly occupied to give rise to a closed-shell 18-electron configuration. Since the HOMO−LUMO gap is large, these systems have no alternative choice but to adopt a spin-paired (diamagnetic) configuration. There are, however, just as for the simplistic crystal field description of Werner-type complexes, properties and trends that cannot be easily rationalized on the basis of a purely covalent model, as detailed in the next section.

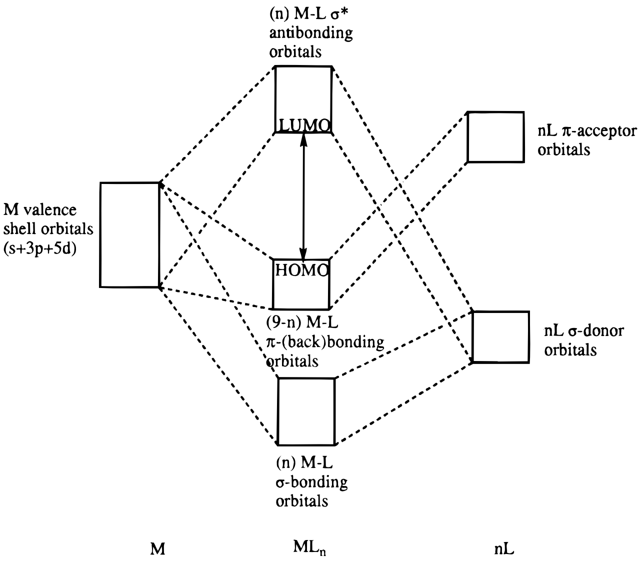
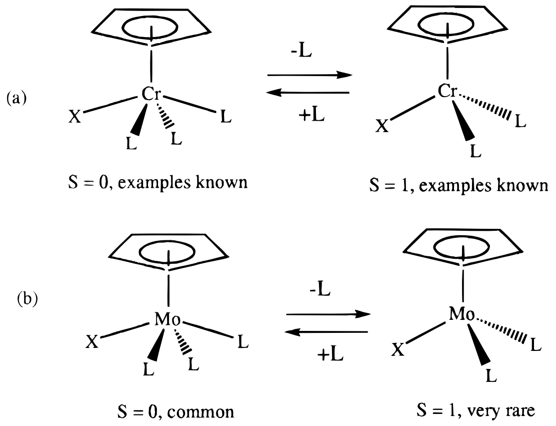


Figure 1. A generic MO correlation diagram for a low-valent, 18-electron organometallic.

III.2. Examples of Organometallics Violating the 18-Electron Rule—Some Trends

Intermediate oxidation state group 6 complexes provide interesting examples for our discussion. Half-sandwich Cr(II) complexes exist as 18-electron CpCrXL$_3$ (especially with strongly π-acidic ligands such as CO), but also as 16-electron, spin triplet CpCrXL$_2$ complexes [with weaker π-acidic L ligands, for instance Cp*Cr(CH$_3$)(dmpe)].[9] The hypothetical equilibrium shown in Scheme 1a is thus shifted to either side depending on the electronic nature of the ligands. Chromocene is also a spin triplet 16-electron derivative, but it reacts with CO to afford saturated Cp$_2$Cr(CO).[18] These 16-electron complexes can be considered analogous to octahedral, low-spin (t$_{2g}$^{4}) Cr(II) Werner-type complexes of type CrX$_2$L$_4$, as the Cp ligand is isoelectronic with a XL$_2$ ligand system. As a matter of fact, most octahedral Cr(II) Werner-type

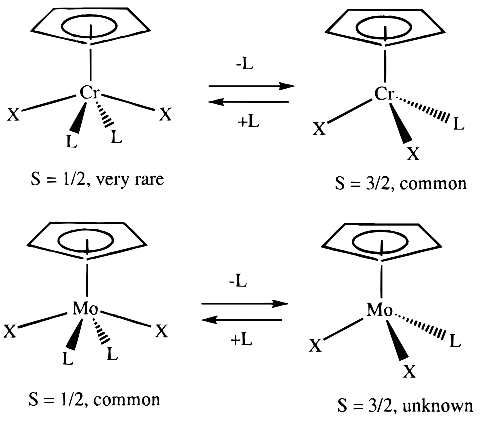
Scheme 1



complexes are high spin ($t_{2g}^3e_g^1$), but this is the consequence of the Werner-type ligands being weaker field ligands with respect to tertiary phosphines and cyclopentadienyl ligands. It is extremely rare, in complexes with organometallic ligands, that electrons occupy M−L σ^*-orbitals (a few exceptions will be pointed out later). On going from chromium to its heavier congener molybdenum, on the other hand, the vast majority of organometallic Mo(II) derivatives are electronically saturated, 18-electron $CpMoXL_3$ or Cp_2MoL systems, whereas many Werner-type complexes of Mo(II) are 16-electron, spin triplet (i.e. low-spin t_{2g}^4) octahedral complexes, for instance $MoX_2(PMe_3)_4$ (X = halogen).[19] The first example of an organometallic 16-electron, spin triplet Mo(II) complex, $Cp^*MoCl(PMe_3)_2$, has only recently been synthesized in our laboratory.[20] The hypothetical equilibrium of Scheme 1b is in most cases shifted to the left.

Upon increasing the oxidation state by one unit, Cr(III) affords no organometallic complex where the 18-electron configuration is reached, the vast majority of chromium(III) organometallics being 15-electron, pseudooctahedral systems with a spin quartet ground state and analogous to Werner-type (t_{2g}^3) complexes, for instance $[CrR(H_2O)_5]^{2+}$ or $Cp^*CrMe_2(PMe_3)$.[21,22] A rare example of a 17-electron $CpCrX_2L_2$ system is $CpCr(\eta^3\text{-}C_3H_5)_2$ (the π-bonded allyl ligand is isoelectronic with a XL ligand system), which is nevertheless unstable at room temperature.[23,24] Other examples of 17-electron Cr(III) complexes are available from work in our laboratory (see section VIII.2.1.3). Thus, the hypothetical equilibrium in Scheme 2a lies predominantly to the right. On the other hand, Mo(III) forms an extensive series of mononuclear 17-electron $CpMoCl_2L_2$ compounds.[25] However, no mononuclear 15-electron $CpMoXL_2$ analogous to CpCr(III) systems has been obtained to date[26,27] (e.g. the equilibrium in Scheme 2b lies on the left hand side), in spite of the prevalence of this electron count for octahedral Mo(III) Werner-type complexes. In fact, MoX_3L_3 Werner-type complexes never add an additional ligand to afford a 17-electron adduct (the sole exception being made for the strong field (and highly nephelauxetic) cyanide ligand, which affords the "organometallic" $[Mo(CN)_7]^{4-}$ complex[28]).

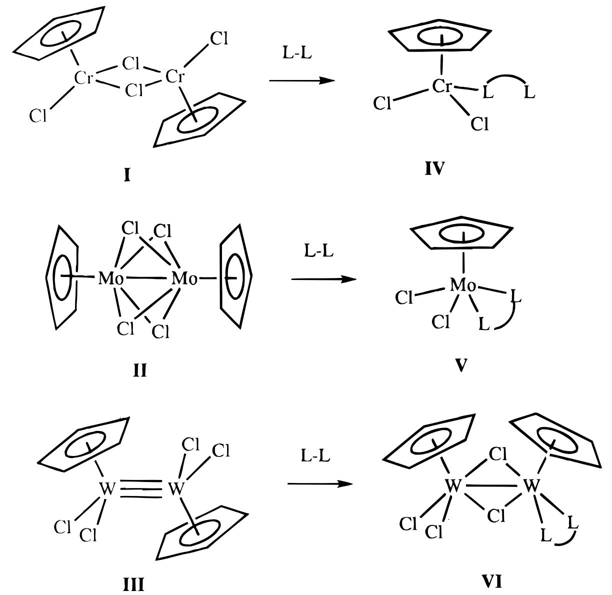
Scheme 2



Upon increasing the oxidation state even higher to IV, the 18-electron configuration is still achieved for half-sandwich Mo organometallics with π-acidic ligands, such as $CpMoX_3(CO)_2$,[29,30] and $CpMoCl_3[P(OCH_2)_3CEt]_2$,[31] although also 16-electron, spin triplet, pseudo-7-coordinate complexes $CpMoCl_3L$ are quite stable.[32] Half-sandwich W(IV) compounds, on the other hand, have only been so far obtained as diamagnetic 18-electron compounds.

The most striking example of the different behavior of metals within the same group in middle-valent organometallics is perhaps provided by the $[CpMCl_2]_2$ complexes of Cr, Mo, and W. The structures of the starting complexes and the products of their reactions with bidentate diphosphine ligands are illustrated in Scheme 3. Chromium compound **I** has two antiferromagnetically coupled 15-electron metal centers, each with a spin quartet ground state,[33] and the addition of bidentate ligands affords 15-electron, dangling phosphine products **IV** that retain the spin quartet electronic configuration.[34] Molybdenum compound **II** has an 18-electron tetrachloro-bridged structure with a metal-metal bond and adds bidentate ligands to afford mononuclear 17-electron **V**.[25] Finally, tungsten compound **III** contains a metal−metal triple bond (although for particular cyclopentadienyl derivatives, a structure analogous to **II** is adopted instead);[35] ligand addition only provides an electronically saturated adduct **VI** that retains its dinuclear nature and a single metal−metal bond.[36]

Scheme 3



The emerging trend is that the 18-electron rule is more strictly obeyed by metals of the lower rows, this being often accomplished by the formation of strong metal−metal bonds that competes efficiently with the formation of metal−ligand bonds (the strength of metal−metal bonds increases upon descending a group of transition metals). Metal−metal bonding plays an important role for heavy metals not only with carbon-based ligands, but also with Werner-type ligands. A bridge could be established here between Werner chemistry and cluster chemistry, but this topic is outside the focus of this review; we are only concerned here with bridging Werner chemistry and low-valent organometallic chemistry.

The trends shown above for group 6 metals can also be seen in other groups. For instance, the coordination number for group 5 M(III) Werner-type complexes is not greater than 6 (14-electron, S = 1) for all metals (V, Nb, and Ta),[37] but V(III) forms a large number of 16-electron (S = 1) systems of type $CpVX_2L_2$[38] or Cp_2VX and a very limited number of 18-electron Cp_2VXL, whereas Nb(III) and Ta(III) form few 16-electron, S = 1 $CpMX_2L_2$, no unambiguous example of stable mononuclear Cp_2MX, and a large number of 18-electron $CpMX_2L_3$ and Cp_2MXL (see section VIII.1.1.2). A saturated complex is also obtained with the cyano ligand, $[Nb(CN)_8]^{5-}$.[39]

To summarize what has been presented so far, electronically unsaturated, open-shell configurations tend to be more common for higher oxidation state systems and for lighter (3d) transition metals. These electronically unsaturated organometallic systems tend to parallel classical Werner-type complexes in terms of their coordination geometry and spin state, especially for 3d metals. Softer, carbon-based ligands increases the tendency to achieve a more saturated configuration with respect to the harder ligands typical of Werner chemistry.

III.3. Factors Responsible for the Stability Trends

III.3.1. π-Donor Ligands

There are several factors that can be held responsible for the stability trends illustrated above. For instance, raising the formal oxidation state of the metal often involves the introduction of ligands such as halides or isoelectronic analogues (e.g. alkoxides, alkylthiolates, etc.) that have lone pairs available for additional π-donation to the metal center. These ligands can better stabilize electronically unsaturated configurations through this π-bonding mechanism. Caulton has recently published a review article emphasizing the importance of this bonding picture (termed "π-stabilized unsaturation") in organometallic chemistry.[40] One of the many manifestations of this phenomenon, for instance, is the relative stability of several 16-electron halide-containing complexes such as $OsH_2Cl_2L_2$,[41] IrH_2ClL_2,[42] and RuH_3IL_2.[43] The corresponding unsaturated hydride complexes are unknown, while their corresponding 18-electron ligand adducts, e.g. MH_4L_3 (M = Ru, Os) and IrH_3L_3, are stable compounds. This effect is certainly important, yet electronically unsaturated compounds lacking π-donating ligands, for instance the 15-electron $CpCrMe_2(PMe_3)$ and the 16-electron $CpVMe_2(PMe_3)_2$, are also quite stable.

III.3.2. Metal–Ligand Bond Strength

It is generally known that the strength of the metal−ligand bond for any given ligand increases upon descending a group of transition metals.[44] Therefore, the tendency of a heavier metal to reach a more saturated configuration may be greater simply because of the greater energy associated with the formation of metal−ligand bonds. This factor may play a role in determining the greater stability of more saturated systems for the heavier metals, e.g. the cases presented in Schemes 1 and 2, or the 18-electron Cp_2MoL vs the 16-electron Cp_2Cr, or the 18-electron $CpNbCl_2(PMe_3)_3$ vs the 16-electron $CpVCl_2(PMe_3)_2$.

The greater bond strength for 4d and 5d metals relative to 3d metals is in agreement with the greater tendency of systems with these metals to reach a more saturated configuration. However, bond formation, even for 3d metals, should always provide a stabilizing factor (see section V for additional considerations on the bond strength). Consequently, the reluctance of a 3d metal system to form an additional M−L bond when electronically possible must be the result of other competing factors that raise the energy of the system by a greater amount than it would be lowered by the M−L bond formation.

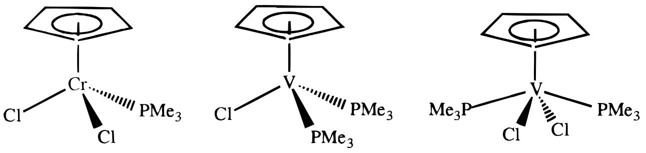
III.3.3. Steric Effects

When a new ligand adds to the coordination sphere, interligand repulsions become more important, thus steric effects compete against the formation of new metal−ligand bonds. Extremely bulky ligands have been successfully used for the stabilization of complexes with extremely low coordination numbers, for instance $Mn[C(SiMe_3)_3]_2$.[45] $CpMoX_2L_2$ (Scheme 2) may achieve a greater electron count with respect to Werner-type MoX_3L_3 complexes because the Cp ligand (an XL_2-type ligand) occupies a smaller space than the combination of one X and two L monodentate ligands. Undoubtedly, steric effects play a fundamental role in determining ground-state coordination geometries and stabilities as shown perhaps most effectively by the applications of the concept of ligand cone angle.[46]

The size of the metal may be also an important factor. Metal atoms of the 3d series have a smaller covalent radius than the corresponding 4d and 5d atoms and the length of metal−ligand bonds is correspondingly shorter for the 3d metals. Therefore, there is a greater repulsive interaction between the ligands in a 3d metal complex than in the corresponding complexes of the heavier congeners. In this respect, the reason for $CpCrX_2L$ not to add another L ligand could be attributed to the smaller size of Cr^{3+} with respect to Mo^{3+}.

The combination of metal size (3d < 4d ≈ 5d) and metal−ligand bond strength (3d < 4d < 5d) seems particularly effective at rationalizing the trends described in section III.2. After all, similar arguments rationalize other differences between 3d and heavier congeners in lower valent chemistry. The typical example of this trend is the stability of dinuclear $[CpM(CO)_3]_2$ (M = Mo, W) and Cp* analogues, whereas $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_3]_2$ are in equilibrium with an appreciable amount of the mononuclear 17-electron radical in solution (the equilibrium favors the mononuclear radical to a greater extent for the bulkier Cp* system)[5] and $(\eta^5\text{-}C_5Ph_5)Cr(CO)_3$ exists only as the mononuclear radical even in the solid state.[47] The strength of metal−metal bonds, just as the strength of metal−ligand bonds, increases down a group of transition metals.[44] However, other observations cannot be fully rationalized on the basis of steric effects and metal−ligand bond strengths only. Consider, for instance, the series of compounds shown in Scheme 4. Coordination of an additional PMe_3 ligand to **VII** to afford a

Scheme 4



15-electron, S = 3/2 15-electron, S = 3/2 16-electron, S = 1

VII **VIII** **IX**

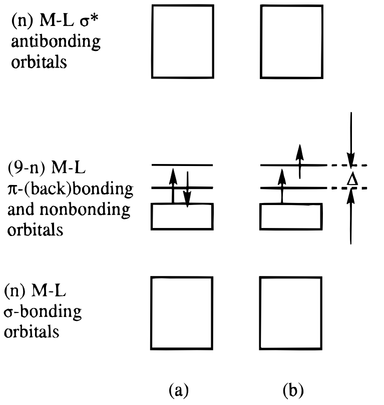


Figure 2. A generic MO diagram for a 16-electron compound: (a) low spin (S = 0); and (b) high spin (S = 1).

17-electron compound does not occur. Indeed, CpCr(III) systems rather establish dissociation equilibria with 13-electron, pseudo-5-coordinate $CpCrX_2$ or $[CpCrXL]^+$ structures, as shown by EPR spectroscopic studies.[48] Neither can **VIII** add a molecule of PMe_3, although V^{2+} has a larger size than Cr^{3+}. Pseudo-7-coordinate, 17-electron complexes of types $CpVXL_3$, $[CpVX_2L_2]^-$, or $CpCrX_2L_2$ are very rare (see section VIII.2.1.2). Both the Cr^{3+} and V^{2+} systems are stable as 15-electron complexes with a spin quartet ground state, electronically analogous to Werner-type octahedral d^3 complexes. However, V^{3+} in compound **IX** is able to bind four monodentate ligands in addition to the Cp ring to form 16-electron complexes with a spin triplet ground state, in spite of the smaller size of V^{3+} with respect to V^{2+}. Fourteen-Electron $CpVX_2L$-type complexes are available only with encumbering X and L ligands, see section VIII.1.2.2. Analogues of **IX** are also stable with bulkier phosphines than PMe_3, e.g. $CpVCl_2(PEt_3)_2$.[38] This comparison strongly suggests that compounds **VII** and **VIII** have the steric ability to bind an additional ligand and to raise their electron count by two units. Alkyl analogues of the compounds in Scheme 4 are also known,[22,49] indicating that the stabilization by π-donation is not a determining factor.

The determining factor that allows a rationalization of the differences outlined above, as well as a host of other observations, has to do with pairing energy. The role pairing energy plays in organometallic chemistry is identical to the role it plays in Werner chemistry.

III.3.4. Spin State

When we approach crystal field theory, we learn that the choice of spin state in a complex of a given geometry is determined, in simple terms, by the comparison between an orbital energy difference (e.g. Δ_0 in octahedral complexes) and the pairing energy (PE).[50] In simplistic terms, pairing energy is the energetic cost of pairing up two electrons in the same orbital (see section IV for a more detailed analysis of the pairing energy). Whenever a certain number of electrons is distributed among two or more orbitals whose energy difference is comparable to the pairing energy, different electronic configurations differing by the spin state can be adopted (e.g., for the case of the familiar $t_{2g}-e_g$ splitting in octahedral complexes, this happens for electronic configurations d^4 through d^7). For complexes with very strong field ligands such as CO, large orbital energy gaps result, thereby favoring 18-electron configurations and a spin-paired ground state. A 17-electron compound will have only one electron in the HOMO, but the HOMO−LUMO gap is still greater than PE, thus only the electronic configuration with one unpaired electron is experimentally observed in most cases (exceptions occur, see later). If the complex has an electronic configuration with 16-electrons or less, however, the situation becomes more interesting. For a 16-electron complex, if we had all the electrons paired in the lowest eight valence shell orbitals, a complex with a relatively small HOMO−LUMO gap (Δ) would result (Figure 2a). This will be the preferred configuration when Δ > PE. There is, however, the possibility that Δ is lower than PE, in which case the high-spin configuration in Figure 2b becomes the ground state. This situation is analogous (isolobal) with that of singlet and triplet carbenes. Both organometallic 16-electron systems and organic carbenes (and also nitrenes, nitrinium ions, etc.) are two electrons short of the closed-shell configuration. A change of spin-state costs energy, thus the occurrence of a spin state change during an organometallic reaction must be taken into account to rationalize the overall enthalpic picture, such as for the cases discussed in sections III.2 (e.g. Schemes 2 and 3) and III.3.3. As early as 1974, Calderazzo *et al.* measured a low bond dissociation energy for the V−CO bond in $Cp_2VI(CO)$ and realized that “spin pairing has to take place upon carbonylation”.[81] Only a year later, Wong and Brintzinger analogously rationalized the lower stability of the $Cp_2Cr(CO)$ compound toward CO dissociation relative to the Mo and W analogues, by writing: “one is led to the conclusion that a higher spin pairing energy for chromium and/or a higher resistance of the chromium sandwich against the required structural distortion might contribute to the decreased stability of the chromocene carbonyl complex”.[18] In an adjoining paper, Brintzinger *et al.* substantiate the relevance of spin pairing energies by using a theoretical model.[51] In spite of this early work, the importance of electron pairing in organometallic stability and reactivity has remained essentially unappreciated.

It is easy to see, in general, for which electronic configurations a spin-state change is possible. Leaving aside for a moment the possibility that electrons may occupy the higher energy, M−L σ*-orbitals, the possible electronic configurations and relative spin states are summarized in Figure 3. The configura-

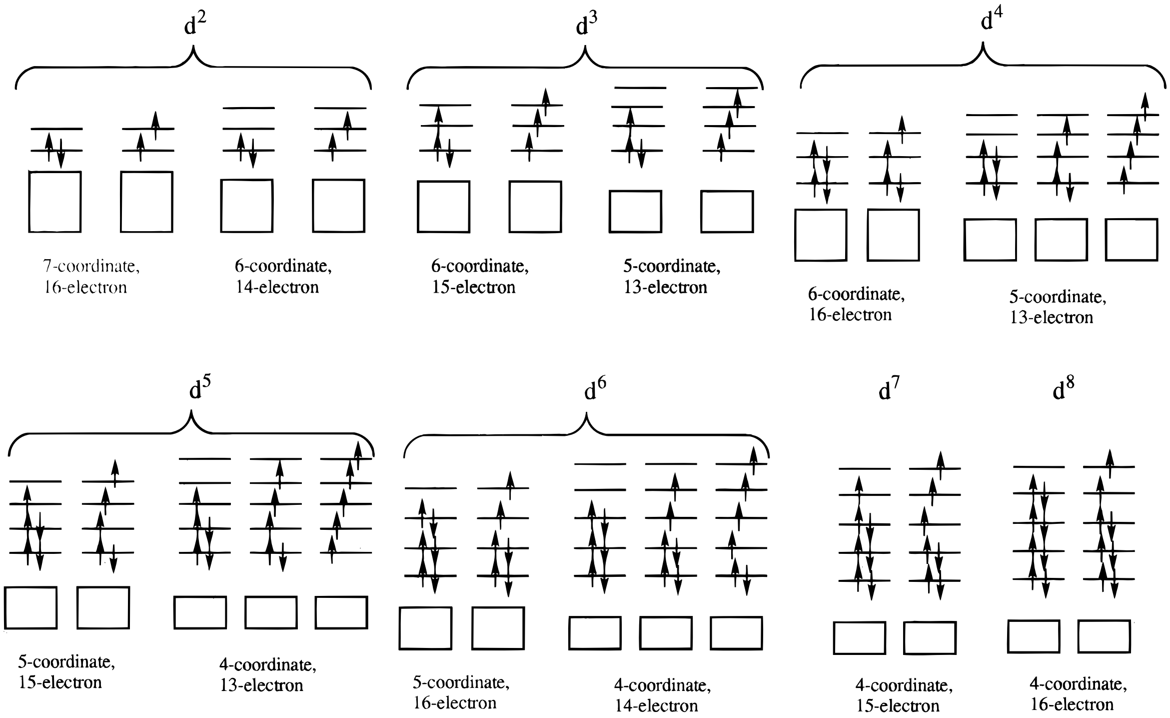


Figure 3. Open-shell configurations that allow variability of the spin state (no occupation of M−L σ*-orbitals).

tions shown are restricted to coordination numbers equal to or greater than four (electron counts equal to or greater than 13), and do not take into account the possibility of orbital degeneracy in cases of higher symmetry.

The most commonly encountered open-shell organometallics have an electron count of 16, less frequently of 15, and even less frequently of lower values, especially for 4d and 5d elements; coordination numbers lower than four are rare. Isolated examples of compounds with coordination numbers 3 and 2 have, however, been reported with extremely bulky ligands, e.g. $[Mn(Mes)_3]^-$ and $Mn\{C(SiMe_3)_3\}_2$.[45,52] Complexes with coordination numbers lower than four make use of only s- and p-type orbitals to receive the ligand electrons, and have one or more empty p-type orbitals at substantially higher energy than the electronically populated d-block. These empty, high-energy p orbitals, therefore, do not play a role in determining the electronic configuration and the spin state. The possible electronic structures of lower-coordinate systems that are not reported in Figure 3 (e.g. 4-coordinate d^2, d^3, or d^4) are easily derived from higher coordinate configurations. Essentially, for any given d^n configuration, a decrease of coordination number by one unit removes one orbital (and two electrons) from the low-energy manifold of M−L σ-orbitals and replaces it with one empty, metal-based orbital in the frontier region. Thus, the possible electronic configurations and spin states are identical with those of the higher coordination number systems. This is explicitly illustrated in Figure 3 for the d^2 configuration upon going from the 7-coordinate, 16-electron count to a 6-coordinate, 14-electron count and for the d^3 configuration upon going from 6-coordinate, 15-electron to 5-coordinate, 13-electron.

For d^8 systems in a 4-coordinate environment, the square-planar configuration is usually favored for organometallic compounds. Under those circumstances, the empty orbital ($d_{x^2-y^2}$) has a much higher energy with respect to the HOMO (high Δ), always leading to a diamagnetic ground state. If the nature of the ligands is such as to impose a different geometry (e.g. for Cp and hydrotris(pyrazolyl)borate derivatives), then a lower Δ results, making it possible to obtain high-spin complexes, as shown in section VIII.7.2. For complexes of d^9 and d^{10} configurations, even when coordinative unsaturation leads to electron counts of less than 17 (e.g. $CH_3Au(PPh_3)_3$), the empty orbitals are s−p hybrids at much higher energy with respect to the electronically populated d orbitals, always leading to the lowest possible spin state ($S = {}^1/_2$ for d^9; $S = 0$ for d^{10}).

IV. Orbital Splitting and Pairing Energy

IV.1. Introduction

The consideration of the energy difference between two states of different spin as being due to the mere difference between an orbital splitting (Δ) and a pairing energy (PE) is conceptually useful, but not rigorously correct. First, this argument is based on the independence of the single-electron orbital energies on the orbital occupation (Koopman's theorem), whereas the actual orbital occupation influences the average potential experienced by each individual electron. In a SCF-HF calculation, quite significant changes of orbital energies can occur upon electronic redistribution to a different configuration. Secondly, summarizing the electron−electron repulsion into a single term (PE) is an oversimplification. For a situation of two electrons in two nondegenerate orbitals (orbitals $n + 1$ and $n + 2$, following n doubly occupied orbitals) such as the 16-electron case illustrated in Figure 2, the singlet−triplet gap under Koopman's theorem can be calculated from the SCF-

HF results as[53]

$$E_S - E_T = (\epsilon_{n+1} - \epsilon_{n+2}) + J_{n+1,n+1} - J_{n+1,n+2} + K_{n+1,n+2} \quad (1)$$

where the $(\epsilon_{n+1} - \epsilon_{n+2})$ term is the orbital energy difference $(-\Delta)$, and the other terms describe the pairing energy. The J terms are Coulomb integrals and represent electron−electron repulsions (the n+1,n+1 term relates to the singlet state where the n+1 orbital is doubly occupied, and the n+1,n+2 term relates to the triplet state) and the K term represents the exchange interaction when orbitals n+1 and n+2 are singly occupied and is a contribution from the triplet state. Thus, we see that the pairing energy has a Coulombic contribution, $(PE)_{coul}$, and an exchange contribution, $(PE)_{ex}$. The detailed expression of $(PE)_{coul}$ and $(PE)_{ex}$ in terms of coulomb and exchange integrals depends on the electronic configurations that are being compared, because the total energy for each individual state has one J term per each pair of electrons independent of their spin, and one K term per each pair of electrons *of the same spin*. For instance, for the 15-electron, d^3 system (quartet vs doublet spin, see Figure 3, with variability of electronic occupation in the orbitals n+1, n+2, and n+3), the expression becomes

$$E_D - E_Q = (\epsilon_{n+1} - \epsilon_{n+3}) + J_{n+1,n+1} - J_{n+1,n+3} + K_{n+1,n+3} + K_{n+2,n+3} \quad (2)$$

The $J_{n+1,n+1}$ term is the greater J integral because it relates to the repulsion between two electrons in the same orbital. As a consequence, $(PE)_{coul}$ will be positive, as is $(PE)_{ex}$. The substantial difference between eqs 1 and 2 is that the first one has only one K term, whereas the second one has two.

The situation can be further complicated by the availability of a multitude of different states when two or more orbitals at close energy can provide an electron for promotion to a higher energy orbital and generation of a higher spin state. This is exemplified by the 16-electron, d^4 system (Figure 3) when the n+1 and n+2 orbitals are degenerate, as in linear Cp_2M (M = Cr, Mo, W).[51] The two degenerate orbitals are termed δ, because they engage in metal−Cp δ-bonding, and this is the reason for their slight stabilization with respect to the next orbital (σ), which is essentially nonbonding. The remaining two d orbitals are raised in energy by the π-interaction with the Cp rings and become part of the high-energy antibonding manifold. A calculation of single-electron orbital energies at the extended Huckel (EHMO) level, augmented by the evaluation of the electron-electron repulsion energies in terms of Racah repulsion parameters A, B, and C, gives the following six electronic states, corresponding to the electronic configurations in parentheses: $^1\Sigma^+$ (δ^4), $^1\Delta$ and $^3\Delta$ ($\delta^3\sigma^1$), $^1\Sigma^+$, $^1\Gamma$, and $^3\Sigma^-$ ($\delta^2\sigma^2$). Depending on the energy difference between the one-electron δ- and σ-orbitals, $\Delta E(\sigma-\delta)$, the lowest energy electronic state can be either $^1\Sigma^+$ (δ^4) at high ΔE, $^3\Delta$ ($\delta^3\sigma^1$) at intermediate ΔE, or even $^3\Sigma^-$ ($\delta^2\sigma^2$) at low ΔE (see Figure 4). This happens because the $^3\Sigma^-$ term has a lower electron repulsion energy than the $^3\Delta$ term by $8B$. For chromocene, at the calculated value of $\Delta E(\sigma-\delta)$ = 7200 cm^{-1}, the $^3\Delta$ ($\delta^3\sigma^1$) term is the ground state, but the $^3\Sigma^-$ ($\delta^2\sigma^2$) term lies only a few thousand wave numbers above $^3\Delta$. The picture for molybdenocene is very similar to that of chromocene, although the B and C values for Mo (440 and 1990 cm^{-1}) are much smaller than those of Cr (710 and 2790), as expected from the greater diffuseness of the Mo 4d orbitals with respect to the Cr 3d orbitals.[51]

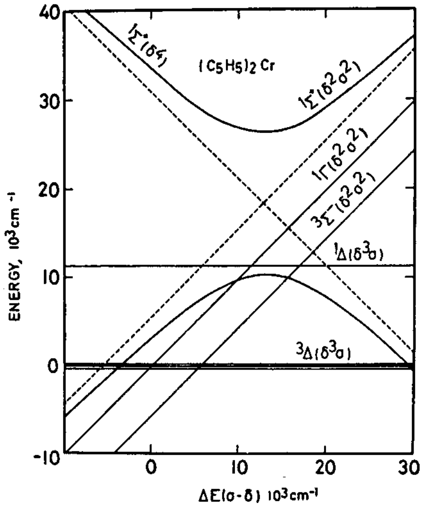


Figure 4. Term energies as a function of the difference in orbital energies for the d^4, d^3s^1, and d^2s^2 configurations of chromocene assuming $D_{\infty h}$ symmetry. (Reprinted from ref 51. Copyright 1975 American Chemical Society).

IV.2. Factors Affecting the Magnitude of Δ and (PE)

The orbital splitting is affected by the geometry of the complex, as mentioned above for the d^8 4-coordinate complexes. In many cases, the molecular geometry does not determine, but rather, *is determined by* the choice of spin state, as will be discussed in section VII. Given a particular geometry, the orbital splitting can be tuned by the nature of the ligands, both in terms of σ- and π-effects. The most direct influence of σ-bonding, however, is on the energy of the antibonding orbitals, which are very rarely occupied for open-shell organometallics. The essentially metal-based orbitals where all the action is (Figure 3) are directly affected by π-bonding. Ligand-to-metal π-donation raises the energy of these orbitals, whereas metal-to-ligand π-(back) donation lowers it. The effect of each of the above mechanisms or the combination of them on Δ has to be examined case by case, for it depends on the molecular geometry and symmetry, on the number of π-acceptors and π-donors, whether they are single-sided or double-sided π-ligands, etc. As an illustrative example, consider the difference between spin singlet $Cp^*Mo(PPh_2)(PMe_3)_2$ and spin triplet $Cp^*MoCl(PMe_3)_2$, both pseudo-6-coordinate d^4 complexes. The orbital separation Δ in the phosphido compound is certainly larger than for the chloro analogue because the phosphido ligand is a single-sided π-donor and thus raises the energy of only one metal orbital (the LUMO), favoring spin pairing, see Figure 5. Chloride, on the other hand, is a double-sided π-donor (and a weaker one at that), thus two metal orbitals

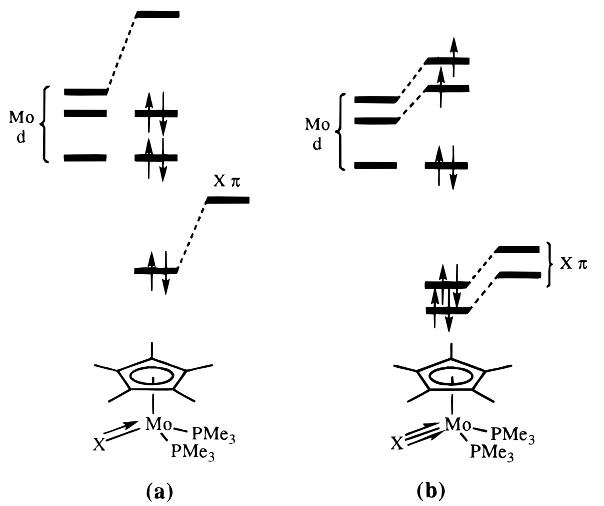


Figure 5. Qualitative π-interaction diagram between the lone pairs of (a) the single-sided π-donor PPh_2 group and (b) the double-sided π-donor Cl, with the 16-electron $Cp^*MoX(PMe_3)_2$ fragment.

are engaged to give rise to a small Δ and two independent two-center−three-electron π-interactions.[20]

The orbital splitting Δ is also affected by the nature of the metal. If the two orbitals under consideration have different spatial and bonding relationships with the ligands (e.g. for the octahedral geometry, the t_{2g} set is nonbonding with the maximum probability away from the ligands, whereas the e_g set is antibonding with the maximum probability located along the metal−ligand axes), Δ increases upon descending a group of transition elements (3d < 4d < 5d).[50] If the two orbitals have similar characteristics (which is the common situation for open-shell organometallics), the metal effect is less predictable. For the above-mentioned chromo- and molybdenocene pair, the calculated Δ gap is greater for the lighter metal.[51]

As mentioned above, the Coulombic component of the pairing energy will be smaller when the metal orbitals are more expanded.[50] A greater principal quantum number, a lower oxidation state, less electronegative ligands and the presence of negative charges on the complex are all factors that are expected to decrease $(PE)_{coul}$. The term nephelauxetic effect is employed to describe the expansion of the orbitals of the free ion upon addition of the ligands. Conversely, a smaller principal quantum number, a greater oxidation state, more electronegative ligands and the presence of positive charges on the complex are all factors that will increase $(PE)_{coul}$. Thus, other factors being equal, the pairing energy will increase in the order 5d < 4d < 3d,[54] or with an increase in oxidation state, or with an increase of the electronegativity of the coordination sphere. Thus, the higher tendency to adopt a higher spin configuration will exist for 3d metals in higher oxidation states and with electron-withdrawing ligands, whereas 5d metals in low oxidation states and with electron-releasing ligands are more likely to adopt a low-spin configuration.

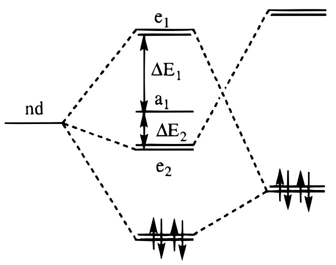


Figure 6. Significant MO correlation diagram for a sandwich compound (labels based on D_n symmetry).

Table 1. Effective One-Electron 3d Splittings (Refer to Figure 6) and Ground-State Configurations for Sandwich Compounds[57]

compound	ΔE_1, cm^{-1}	ΔE_2, cm^{-1}	ground state (calcd)
$(C_6H_6)_2V$	17 100	17 900	$^2A_1(e_2{}^4a_1{}^1)$
$Cp(C_7H_7)V$	13 600	21 500	$^2A_1$
$Cp(C_6H_6)Cr$	18 300	13 400	$^2A_1$
$[(C_6H_6)_2Cr]^+$	20 100	16 600	$^2A_1$
$[Cp(C_7H_7)Cr]^+$	20 000	19 000	$^2A_1$
Cp_2Mn	24 300	5 000	$^6A_1(e_2{}^2a_1{}^1e_1{}^2)$
$[Cp(C_6H_6)Mn]^+$	21 400	9 900	$^2A_1$ or $^2E_2$
$[Cp_2Fe]^+$	28 800	2 100	$^2E_2(e_2{}^3a_1{}^2)$

The exchange component of the pairing energy is, as seen above, a function of one or more exchange integrals *K*. The numeric values of these integrals are in general proportional to the numerical values of the corresponding Coulombic integrals, thus the greater $(PE)_{coul}$ is, the greater $(PE)_{ex}$. In addition, the number of unpaired electrons, or more precisely the number of electron pairs with the same spin, in both high-spin and low-spin configurations is very important in determining the magnitude of $(PE)_{ex}$. As already shown above, $(PE)_{ex}$ has one *K* term for the transition between the $S = 0$ and $S = 1$ states in 16-electron d^2 systems, and two *K* terms for the transition between $S = 1/2$ and $S = 3/2$ in 15-electron d^3 systems. There is, therefore, a greater contribution of $(PE)_{ex}$ toward the stabilization of configurations with a larger number of unpaired electrons. This is probably the main reason for manganocene to adopt a spin sextet ground state. The exchange component of the pairing energy is so important in this case, e.g. $(PE)_{ex}$ has six *K* terms, as to overcome the expense of promoting two electrons in the π-type Mn−Cp antibonding orbitals. Although the occupation of antibonding orbitals (for instance e_g^* in octahedral geometry) is common in Werner chemistry with weak field ligands, this is only a very rare occurrence for organometallic compounds. Indeed, many other sandwich complexes that are isoelectronic with manganocene have a spin doublet ground state.[55] Calculations on a series of 17-electron sandwich compounds have revealed the importance of orbital interactions (see MO diagram of Figure 6).[56] The e_1 orbitals (d_{xz},d_{yz}) are raised by the ligand π-interaction, whereas the e_2 orbitals (d_{xy},$d_{x^2-y^2}$) are stabilized by the δ-interaction. The one-electron calculations show, as one would predict, that the ΔE_1 separation increases as the energy of the ring-based orbitals increases (e.g. in the order $(C_7H_7)^+$ < arene < Cp^-) and as the energy of the metal d orbital decreases (Ti > V > Cr > Mn > Fe). Concurrently, the ΔE_2 separation decreases.[57] The calculated values for several systems are shown in Table 1. The photoelectron spectra of the metallocenes and decamethylmetallocenes with various electronic configuration are in good agreement with a ligand field treatment of the electronic structure elaborated on the diagram in Figure 6, including limited configuration interaction.[58]

IV.3. Occupation of Metal–Ligand σ-Type Antibonding Orbitals

Although the occupation of antibonding orbitals (for instance e_g* in octahedral symmetry) is common in Werner-type complexes with weak field ligands, this is only a very rare occurrence for organometallic compounds because of the stronger covalent nature of the M−L bonds and the consequent energetic destabilization of the orbitals in question. One case where antibonding orbitals are occupied (the 17-electron manganocene) has already been mentioned above. Compounds with a 19-electron configuration, e.g. cobaltocene or CpFe(η^6-C_6H_6), can also be considered members of this class unless the 19th electron is mostly localized on the ligand system.

A few isolated cases of organometallic 18-electron complexes have also been determined to be paramagnetic. One class of such derivatives consists of the d^6, pseudooctahedral Mn(I) complexes (ring)Mn(CO)$_2$L (ring = Cp, η-C_5H_4Me, or Cp*; L = py, py-3-CN, py-4-COCH$_3$, pz, $^1/_2$pz, TCNE, 1/4TCNE, or $^1/_2$dppe), which exhibit temperature-dependent magnetic moments in agreement with a diamagnetic ground state and thermal population of the other components of the $^5T_{2g}$ state under zero-field splitting.[59] The same phenomenon is observed for the isoelectronic Cr(0) complex (η-C_6H_6)Cr(CO)$_2$(py).[59] For the manganese series, the room temperature magnetic moment was found to correlate with the basicity of the ligand according to the equation $\mu_{\mathrm{eff}}(300\ \mathrm{K}, \mu_B) = 7.42 - 2.76\mathrm{p}K_{\mathrm{BH^+}}$.[59] A more recent example, which is isoelectronic with the above complexes, is the half-sandwich cationic d^6 Fe(II) complex [Cp*Fe(dppe)(Me$_2$CO)]$^+$. The end-on coordination of acetone in this complex was verified crystallographically.[60] The measured magnetic moment corresponds to two unpaired electrons, both in the solid state in the 77−300 K range and in solution at room temperature, indicating a S = 1 ground state. This is unusual because either a diamagnetic or a high spin (S = 2) state is expected for a pseudooctahedral compound.[60] In addition, NMR data indicate diamagnetism for the related [CpFe(dppe)(Me$_2$CO)]$^+$ complex.

The occupation of M−L σ*-orbitals in the ground state or the easy accessibility of low-lying magnetic states can be attributed to the presence of weak ligands and/or to high pairing energies and is likely to occur only for metals of the 3d row, for which ligand field splittings are smaller than for metals of the 4d and 5d series. More examples of systems of this type will probably be discovered in the future. However, they clearly represent only exceptions to the general rule which places valence electrons only in M−L σ-bonding or nonbonding orbitals for organometallic compounds.

IV.4. More Trends

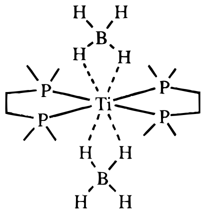
We can find numerous literature examples that can be rationalized on the basis of the above spin-pairing arguments. For instance, removal of a CO ligand from Fe(CO)$_5$ produces the reactive 16-electron Fe(CO)$_4$ intermediate that has long been known to adopt a spin triplet ground state.[61−63] Notably, this is a low-oxidation state system in which the pairing energy is expected to be low, but it is also a system of a 3d metal. On the other hand, calculations indicate that the corresponding Ru(CO)$_4$ and Os(CO)$_4$ adopt a spin singlet ground state.[64] Experimental studies aimed at determining the spin state for these reactive transients do not seem to have been undertaken. However, studies of chemical reactivity are in agreement with a spin triplet for Fe(CO)$_4$ and singlet for Ru(CO)$_4$ (see section VI).[65] The same spin state difference is calculated for the unstable 16-electron d^8 transients CpCo(CO) (spin triplet)[66] vs CpRh(CO) (spin singlet).[67] The CpIr(CO) complex is calculated to be either a spin singlet or spin triplet ground state depending upon the level of sophistication.[66,67]

There are several additional cases of isoelectronic and isostructural complexes within the same group of metals in which the lighter representative has a greater number of unpaired electrons than the heavier element. Examples of this type are compounds CpM(η^3-allyl)$_2$ (S = 1 for M = V and S = 0 for M = Ta, see section VIII.1.1.2), the tetrahedral homoleptic MR$_4$ and MAr$_4$ (S = $^3/_2$ for Mn and $^1/_2$ for Re, see section VIII.2.3), and the 5-coordinate, *tbp* group 5 aryl complexes (S = 2 for MnMesBr$_2$(PMe$_3$)$_2$ and S = 0 for RePh$_3$(PEt$_2$Ph)$_2$, see section VIII.3.2).

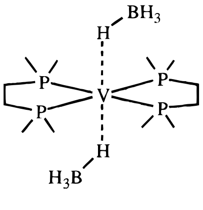
An interesting comparison is that between the spin triplet [Cp*MoCl$_4$]$^-$ complex[68] and the isoelectronic and isostructural spin singlet Cp*ReCl$_4$ (although a low-lying spin triplet state is probably thermally populated, see section VIII.1.1.2).[69] Given that the higher oxidation state of Re(V) should favor higher pairing energies, the trend can be attributed to the more diffuse 5d orbitals in the rhenium case. This allows the prediction of spin triplet and singlet ground states for the yet unknown Cp*TcCl$_4$ and [Cp*WCl$_4$]$^-$ complexes, respectively, because the pairing energy in Tc(V) should be greater, and that of W(IV) smaller, than those of either Mo(IV) or Re(V).

The 6-coordinate, 14-electron *trans*-TiX$_2$(dmpe)$_2$ system leads to a paramagnetic (S = 1) ground state for X = Cl (as one would predict from the t_{2g}^2 configuration for the pseudooctahedral geometry) but to a diamagnetic one for X = CH$_3$.[70] One rationalization that was initially advanced invoked a greater amount of Ti-to-P back-bonding in the dimethyl derivative, substantially splitting the pseudo-t_{2g} set into a lower-energy d_{xy} orbital and a higher-energy (d_{xz},d_{yz}) degenerate set. However, calculations at various levels of sophistication on the model systems TiX$_2$(PH$_3$)$_4$ and TiX$_2$(Be)$_4$ have indicated that the orbital separation (Δ) is in fact smaller for the dimethyl complex, but a substantially smaller electron-electron repulsion in the dimethyl compound [$(\mathrm{PE})_{\mathrm{Me}} \ll (\mathrm{PE})_{\mathrm{Cl}}$] allows the two electrons to remain paired in the lower energy orbital.[53]

Another interesting comparison is that of the tetrahydroborato complexes M(BH$_4$)$_2$(dmpe)$_2$ (M = Ti, V). For d^2 Ti(II), the two BH$_4^-$ ligands bind in a η^2-fashion (**X**), whereas for d^3 V(II), they adopt a less usual η^1-coordination mode (**XI**).[71] If the interaction between the η^2-BH_4 group and the titanium center were strongly covalent, each BH_4 group should engage two metal orbitals, resulting in a diamagnetic "18-electron" structure, while the paramagnetism of the molecule ($\mu_{eff} = 2.6\ \mu_B$) and the long Ti···H distances (2.04(2) and 2.09(2) Å) show that the interaction can be regarded as largely ionic. The vanadium compound has, as expected, three unpaired electrons, the η^1 configuration being presumably enforced by the slightly smaller size of V^{2+} with respect to Ti^{2+}.[71] Spin pairing by an η^2-BH_4 group, on the other hand, is observed in $CpV(\eta^2\text{-}BH_4)(dmpe)$ ($S = {}^1/_2$),[49,72] whereas all other $CpVXL_2$ compounds have a $S = {}^3/_2$ ground state (see section VIII.2.1.2).



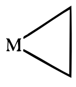
IX



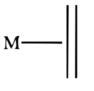
X

An isoelectronic series of 16-electron, d^2 systems is represented by the Zr(II) complexes $(arene)ZrCl_2(PMe_3)_2$ (e.g. arene = toluene),[73] the Nb(III) complexes $(ring)NbCl_2L_2$,[74] and the Mo(IV) complex $[Cp^*MoCl_2(PMe_3)_2]^+$.[75] The Zr(II) complexes are diamagnetic, that of Mo(IV) is paramagnetic, whereas those of Nb(III) have a ground state that delicately depends on the nature of the ligands: $Cp^*NbCl_2(PMe_3)_2$ is paramagnetic, $CpNbCl_2(dppe)$ is diamagnetic, and $(\eta^5\text{-}C_5H_4Me)NbCl_2(PEt_3)_2$ shows a spin equilibrium between a spin singlet ground state and a triplet excited state at $E = 2.2(1)$ kcal/mol.[76] Although one might argue for slight differences in orbital separation for the various cases, the trend is also consistent with a pairing energy increase along the series, as expected from the increase of formal oxidation state from Zr(II) to Nb(III) to Mo(IV). Similarly, the 16-electron $[(C_6H_3Bu^t{}_3\text{-}1,3,5)_2M]^{n+}$ complex is diamagnetic for M = Zr (n = 0), but has two unpaired electrons for M = Nb (n = 1),[77] whereas the 15-electron compounds $Y(arene)_2$ (arene = 1,3,5-$C_6H_3Bu^t{}_3$) and Cp_2V have $S = {}^1/_2$ and $S = {}^3/_2$ ground states, respectively (see section VIII.2.1.4).

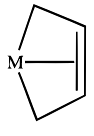
Other general trends that emerge from the body of data assembled in section VIII of this review are as follows. Olefins and dienes are always better at enforcing low-spin configurations, in view of their better π-accepting capability, than phosphine ligands. Back-bonding to alkenes or polyolefins, especially in early transition metal systems, is so pronounced that the compounds are often more properly described as higher oxidation state metallarings, e.g. **XII** rather than **XIII**, **XIV** rather than **XV**, etc., as unambiguously shown in many cases by X-ray crystallography (specific examples will be pointed out in section VIII).



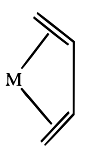
XII



XIII



XIV



XV

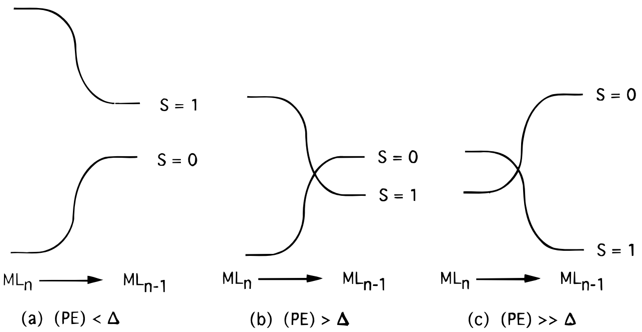


Figure 7. Reaction coordinate for the dissociation of a ligand from an organometallic 18-electron compound when the coordinatively unsaturated intermediate has (a) a singlet ground state or (b) a triplet ground state. Part c represents the case of a 16-electron complex that is thermodynamically more stable than its 18-electron ligand adduct.

Phosphine ligands, however, are better at pairing the electrons than N-donor ligands or alkyl and aryl ligands. Examples here are the 4-coordinate $FeAr_2L_2$ (S = 1 for L = PR_3; S = 2 for L_2 = bipy) and $[FeAr_4]^{2-}$ (S = 2). Open pentadienyl ligands favor electron pairing over the corresponding cyclic ligands: $Ti(Pdl)_2$ is diamagnetic whereas $Cp^*{}_2Ti$ is paramagnetic (section VIII.1.2.4); $V(Pdl)_2$ and Cp_2V have a spin doublet and spin quartet configuration, respectively (section VIII.2.1.3).

V. The Influence of a Spin Change on the Thermodynamics of Organometallic Reactions

The point of focus here is that for a given d^n configuration, states of different spin have different energy, therefore a spin-state change during an organometallic reaction that involves an open-shell system as a starting material, product, and/or intermediate is a factor that will affect the thermodynamics and/or the kinetics of the reaction. We shall focus in this section on the thermodynamic aspect and address the kinetic one in the section that follows. For instance, the energy profile along a ligand dissociation reaction from an 18-electron complex, if the ground state of the 16-electron product is a singlet, will look like Figure 7a, the energy difference between reactant and product being, by definition, the bond dissociation energy of the bond being broken. If stabilizing effects in the intermediate by weak interactions with the solvent, by ligand π-donation, or by reduction of steric repulsions can be neglected, this is also a measure of the "intrinsic bond strength" which may be extrapolated to other systems of similar nature. The high spin state for the unsaturated product correlates energetically with a much higher energy excited state of the starting material, having one electron in a metal-based frontier orbital and one in a high energy M−L antibonding orbital. On the other hand, a spin triplet ground state for the 16-electron product leads to a situation as shown in Figure 7 part b or c. In these cases, the product is *energetically stabilized* by the spin-state change, the stabilization being greater the greater the difference [(PE) − Δ]. When the [(PE) − Δ] difference becomes sufficiently large (Figure 7c), unsaturated compounds can even become more stable

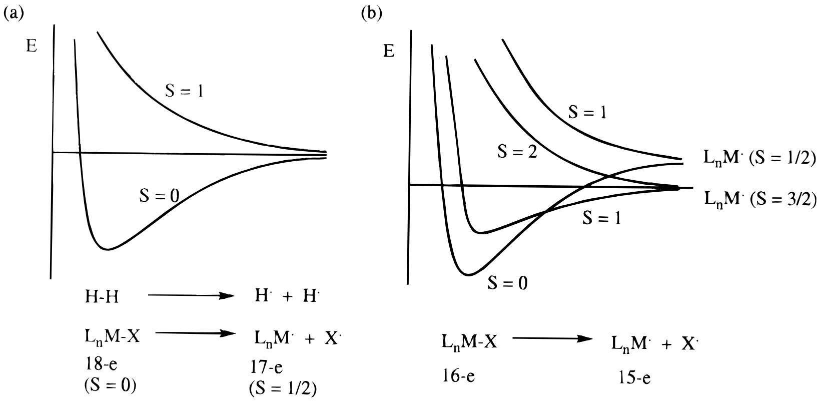


Figure 8. Two possible reaction coordinates for the homolytic rupture of a σ-bond.

than their saturated adducts. As discussed in the previous section, this effect is expected to be most important for 3d systems and least important for 5d systems.

Similar energy profiles can be drawn for reductive elimination reactions, migratory insertions, or any other type of organometallic process that relates an 18-electron reagent with a 16-electron product, the energy difference between starting material and product being related in those cases to a proper combination of bond dissociation energies for bonds being broken and formed during the process.

Processes relating 17-electron and 15-electron systems experience the same phenomenon illustrated above for 18/16-electron pairs, since 17-electron compounds are in general spin doublets and 15-electron compounds may adopt spin doublet or quartet configurations (see Figure 3). The reaction coordinates in Figure 7 are therefore valid also for ligand dissociation/association reactions (and also reductive elimination/oxidative addition, insertion/elimination, etc.) that relate 17- and 15-electron systems or any pair of open-shell systems from Figure 3 where the possibility of a spin change exists.

As mentioned above, there are several other factors that can provide stabilization to coordinatively unsaturated intermediates in organometallic reactions, namely weak interactions with donor solvent molecules (even such weak donors as noble gases!)[78] or counterions,[79] intra- or intermolecular agostic interactions[80] and the participation of lone pairs from potential π-donors that are present in the coordination sphere (see section III.3.1). In addition, a steric effect can also influence the relative energy of an unsaturated reaction intermediate with respect to the saturated starting complex by destabilizing the more saturated, more crowded system (section III.3.2). In general, it will be difficult to sort out the contribution of each of these factors. There are situations, however, where the stabilizing effect of keeping a higher number of unpaired electrons in an electronically less saturated configuration is of dramatic importance, as shown in section VIII. A perusal of that section will show, at least at the qualitative level, how the consideration of the expected energetic changes upon a change of the spin state helps rationalize an enormous number of observations.

The relative energy of an unsaturated system M plus the dissociated ligand L at infinite distance with respect to M−L is defined as the *metal−ligand bond dissociation energy*. Experimentally, such a parameter can be obtained by thermochemical methods or, in case of a reversible process, by equilibrium measurements. For the purpose of this review, we define as an “operational bond strength” the energy difference between ML_n and (ML_{n-1} + L) systems *along the same spin surface*. This corresponds to the energy change during the dissociation process (bond dissociation energy) only if the ground states of the two complexes have the same spin (e.g. Figure 7a). This bond strength is still modulated by solvent and counterion interactions, π-donor ligands and steric effects. In case of a reaction that involves a spin-state change (Figure 7, part b or c), this bond strength cannot be measured directly from equilibrium data or thermochemical cycles; its value can only be obtained or estimated by theoretical calculations or from the knowledge of the experimental bond dissociation energy and the energy involved in the spin state change [(PE) − Δ].

The situation depicted in Figure 7 concerns the rupture of a M−L bond, that is, the two bonding electrons remain together on L after the bond is broken. Breaking a M−X bond involves separation of the two electrons and a change of electron count and spin state for the metal complex, but the overall spin state for the $M^\bullet + X^\bullet$ system will, in fact, remain the same unless there is a subsequent electronic redistribution in $M^\bullet$. The situation is analogous to breaking the H_2 bond (S = 0) to afford two H atoms (S = $^1/_2$), see Figure 8a. Therefore, there is no energetic effect related to a spin state change, for instance, in the large number of homolytic scission processes leading from a saturated (18-electron) organometallic to a 17-electron (S = $^1/_2$) radical. An effect is present, for instance, for the processes depicted in Figure 8b, where a 16-electron L_nM-X complex (S = 0 ground state) would lead to a 15-electron L_nM product with a S = $^3/_2$ ground state. Whereas no unambiguous example of this kind has apparently been described as yet, it is not unlikely that one might be found in the future, since the energetic stabilization of the higher spin state by the pairing energy (exchange component) increases with the number of unpaired electrons.

There are several experimental determinations of bond dissociation energies for systems involving a change of the spin state, mostly relating saturated 18-electron species with paramagnetic (spin triplet)

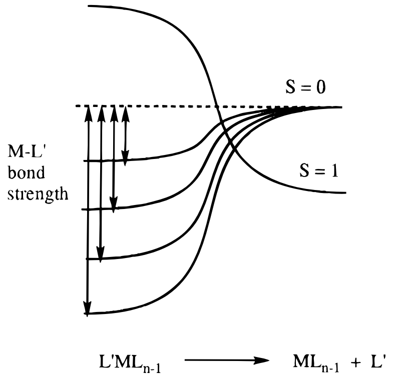


Figure 9. Influence of the bond strength on the reaction coordinate for the ligand addition/dissociation equilibrium involving a spin triplet 16-electron complex.

16-electron species. The first such determination was probably that of Calderazzo *et al.* of 13.1(10) kcal/mol for the V−CO bond in $Cp_2VI(CO)$.[81] The authors proposed spin pairing to be the factor determining the unusually low dissociation enthalpy. A year later, Brintzinger *et al.* used the same argument to justify the low dissociation enthalpy of 18.8(5) kcal/mol for the Cr−CO bond in $Cp_2Cr(CO)$.[18] More recently, the related Cr−CO BDE in $(\eta^5\text{-}C_5H_4Me)_2Cr-CO$ was measured as 16.1(8) kcal/mol.[82] Brintzinger was also probably the first to report theoretical calculations (extended Huckel with empirical electron pairing energies from Racah parameters) on open-shell organometallics,[51] leading to the proposal that the low value of D_{M-CO} in $Cp_2Cr(CO)$ with respect to $Cp_2Mo(CO)$ and $Cp_2W(CO)$ can been attributed to a much greater spin-pairing energy in the chromium case. This is in spite of the fact that all Cp_2M (M = Cr, Mo, W) molecules have a spin triplet ground state.

Recently, Theopold *et al.* have reported a low Co−CO bond dissociation energy for compound $Tp^{Pr^i,Me}Co(CO)_2$, which is in equilibrium with the stable 16-electron (S = 1) $Tp^{Pr^i,Me}Co(CO)$ (ΔH = 12.9(2) kcal/mol), and attribute this low value *solely* to the steric encumbrance of the tris(pyrazolyl)borate ligand.[83] A steric effect certainly appears reasonable for the encumbered $Tp^{Pr^i,Me}$ ligand, but a contribution from the spin-pairing energy, little as it may be, must also be present. It would be interesting to calculate the singlet−triplet gap for geometry optimized 16-electron TpCo(CO) models.

As is evident from Figure 9, the ability of a spin triplet 16-electron species to form a spin singlet adduct depends on the strength of the M−L interaction. The reaction of many spin triplet 16-electron complexes with CO is quantitative, whereas the same complexes do not react with N_2 or the reactions lead to equilibrium situations (these two reagents are isosteric). This is the case of compounds $Cp^*MoCl(PMe_3)_2$,[20] $[Cp^*Fe(dippe)L]^+$,[84] and $Tp^{Pr^i,Me}Co(CO)$.[83] Matrix isolation studies show the formation of weak 18-electron L_nM-L' adducts (L′ = rare gas, e.g. Kr or Xe, or hydrocarbon, e.g. CH_4) for spin singlet $M(CO)_5$ (M = Cr, Mo, W),[85] $CpM(CO)_3$ (M = V, Nb, Ta)[86] $M(CO)_4$ (M = Ru, Os),[62] and CpM(CO) (M = Rh, Ir),[87] but not for spin triplet $Fe(CO)_4$,[88] CpCo(CO),[89] or Cp_2M (M = Mo, W).[90]

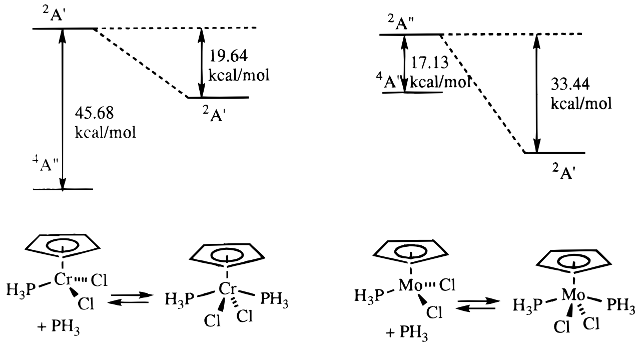


Figure 10. Total energies of the MP2 geometry-optimized $CpMCl_2(PH_3)$ ($^4A''$ or $^2A'$) + PH_3 vs $^2A'$ $CpMCl_2(PH_3)_2$ (M = Cr or Mo).

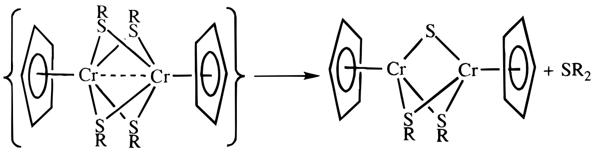
A sophisticated calculation on reaction 3 (M = Ti, V, Cr)[91] has shown that the ground state for the MH_2 system is always high spin ($^3B_1$, $^4B_2$, and $^5B_2$, respectively) with an increasing gap to a more spin-paired state along the series (32.6 kcal/mol to $^1A_1$ for Ti, 39.9 kcal/mol to $^2A_1$ for V, and 58.6 kcal/mol to $^3B_2$ for Cr). The interaction with H_2 to produce $MH_2{\cdot}H_2$ is calculated to take place without a spin-state change, in spite of a stronger interaction with H_2 for the lower-spin states. However, the Ti system goes further to the classical TiH_4 species with spin pairing to ^1A, whereas the same transformation is endoergic for the V and Cr systems.

$$MH_2 + H_2 \rightarrow MH_2{\cdot}H_2 \rightarrow MH_4 \qquad (3)$$

Calculations of the BDE for the Fe−CO bond in $Fe(CO)_5$ at various levels of sophistication based on the density functional method have yielded 45−47 kcal/mol for the dissociation to the excited singlet state, and values correspondingly lower by 1.8 kcal for the dissociation to the spin triplet ground state.[54] Calculations on more complex systems are being carried out in our laboratory, featuring geometry optimization at the MP2 level. Our first case study is the system shown in Scheme 2, the results being shown in Figure 10.

The calculated ground state for the 15-electron system is the spin quartet for both cases (no experimental verification is yet available for the unknown Mo system). The spin quartet−doublet gap is greater for the chromium system, which can mostly be attributed to a reduced pairing energy for the Mo complex (e.g. $J_{n+1,n+1}$ = 347.5 kcal/mol for Mo and 522.0 kcal/mol for Cr). The change in orbital splitting ($\Delta = \epsilon_{n+3} - \epsilon_{n+1}$ = 10.0 kcal/mol for Mo and 8.7 kcal/mol for Cr) does not play a major role in this case. The bond strength is greater for Mo (33.44 kcal/mol) than for Cr (19.64 kcal/mol). The overall effect is to favor the 17-electron structure for the Mo system and the 15-electron structure for the Cr system, as experimentally observed. No significant Cl−M π-bonding is shown by the calculations, and steric effects are minimized by the use of the small PH_3 ligand.[92] Calculations of this type on more open-shell organometallic reactions will provide much needed insights into this area of chemistry.

The same arguments can be used to explain the structural difference between $[CpMCl_2]_2$ for Cr and Mo (see Scheme 3), as well as some intriguing reactivity differences between Cr and Mo complexes having the same structure. For instance, whereas $CpMo(\mu\text{-}SR)_4MoCp$ complexes (isoelectronic and isostructural with **II**) form a well-established series of stable compounds,[93] corresponding Cr compounds have not been unambiguously characterized,[94−96] and they have been assigned trinuclear structures.[97] Reactions that should produce compounds of such stoichiometry lead instead, under forcing conditions, to the sulfido-bridged $CpCr(\mu\text{-}S)(\mu\text{-}SR)_2CrCp$,[95,98] showing that the hypothetical $[CpCr(SR)_2]_n$ product evolves by S−C bond breaking and elimination of SR_2, see eq 4. In these dimeric Cr(III) products, the two $S = {}^3/_2$ Cr(III) centers are strongly antiferromagnetically coupled.[97] The greater stability of Cr(III) in a lower coordination environment and in a higher spin state might force the observed rearrangement, whereas no analogous reaction has ever been reported for the corresponding Mo(III) dimers.



(4)

The stability of 15-electron $S = {}^3/_2$ $CpCrX_2L$ and $CpVXL_2$ compounds and their reluctance to coordinate an additional L ligand, whereas analogous 16-electron $CpVX_2L_2$ are stable (see section III.3.3), can be reconciled with the necessary spin pairing upon addition of L to the 15-electron Cr(III) complex and the absence of a spin state change upon addition of L to the 14-electron V(III) complex. A literature discussion that may need slight revision concerns the difference in structure and stability between Cp_2MR derivatives of Ti, V, and Nb.[99] It was argued that the difference between the atomic radii (Ti, 1.32 Å; V, 1.22 Å; and Nb, 1.34 Å) is solely responsible for several observations, for instance the η^3-configuration of R = allyl for Ti and Nb, whereas the V derivative adopts a η^1-configuration. Analogously, whereas several Cp_2TiR readily add N_2, the corresponding Cp_2VR complexes do not. However, it is also evident that there is no spin change for d^1 Ti(III) upon rearrangement of an η^1-allyl (15-electron) derivative to η^3 (17-electron) or upon addition of N_2. On the other hand, spin pairing must occur during the same transformations for the group 5 M(III) metals (16-electron to 18-electron). The tradeoff of a smaller pairing energy and a greater bond strength, as for the Cr/Mo comparison illustrated above, will favor the rearrangement for Nb but not for V. In strong support of this idea, 17-electron V(III) derivatives have been obtained with more strongly bonding, albeit sterically more encumbering, ligands, e.g. $[Cp_2V(CO)L]^+$ (L = CO, PEt_3, PBu^n_3) and $[Cp_2VL_2]^+$ (L = CNCy or L_2 = dppe).[100] A similar argument can rationalize the chelating nature of the $o\text{-}C_6H_4CH_2NMe_2$ ligand in Cp_2TiR and its monodentate nature in paramagnetic ($\mu_{eff} = 2.6\ \mu_B$) Cp_2VR,[101] and also the mononuclear structure of Cp_2VCl as compared with the dinuclear, di-μ-chloro-bridged structure of $[Cp_2MCl]$ (M = Sc, Ti).[102] Fieselmann and Stucky note that if a spin pairing occurred to allow dimerization of Cp_2VCl, then the repulsion between the $1a_1$ metal orbital (which contains the two metal electrons) and the bridging Cl lone pairs would energetically destabilize the structure.[102] Although this effect would certainly contribute to disfavoring dimerization of Cp_2VCl, the *energetic effect* of pairing the electrons is also expected to play a role.

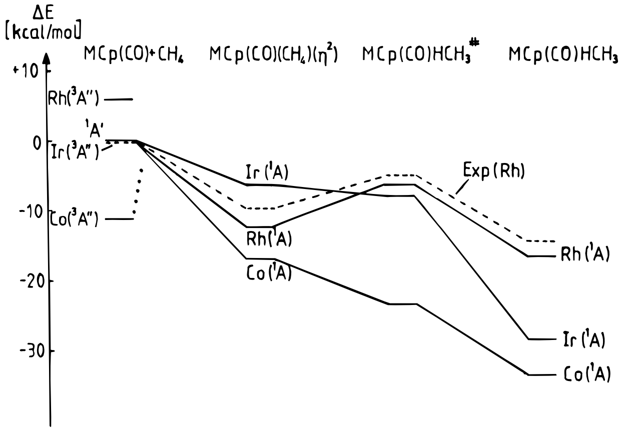
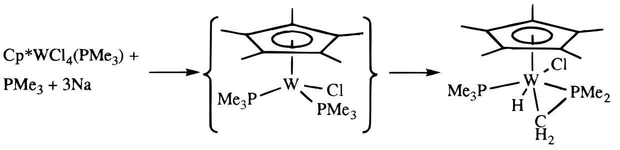


Figure 11. Theoretical investigation of the reaction between CpM(CO) and CH_4 (M = Co, Rh, Ir). (Reprinted from ref 66. Copyright 1996 American Chemical Society.)

The effect of the spin state on the energetic picture is reversed for the case of the oxidative addition reaction. Taking as an example a 16-electron L_nM complex that reacts with X−Y to afford an 18-electron $L_nM(X)(Y)$ product, the ideal removal of the X and Y radicals leaves the metal with two unpaired electrons (triplet state). If the 16-electron material is a ground-state singlet, therefore, a greater energetic cost is involved in the formation of the M−X and M−Y bonds. Calculations carried out by Siegbahn explain in this manner the lower thermodynamic gain for the oxidative addition of CH_4 to CpRh(CO) with respect to CpIr(CO), since the spin triplet starting complex is less stable by 5.9 kcal/mol for Rh and more stable by 0.3 kcal/mol for Ir (see Figure 11).[66] The overall enthalpic picture should, however, be also dependent on the strength of the M−X and M−Y bonds.

The bond strengths may play a role in the different outcomes observed for the reactions between $Cp^*MCl_4(PMe_3)$ (M = Mo, W), PMe_3, and Na. For M = Mo, the product is the stable 16-electron $Cp^*MoCl(PMe_3)_2$ with a spin triplet configuration,[20] whereas for M = W the product involving formal PMe_3 metalation of an analogous $Cp^*WCl(PMe_3)_2$ intermediate is obtained (eq 5).[103] The spin state of the presumed 16-electron tungsten intermediate is not known but, in case it were a spin singlet, the greater energetic cost associated with the "unpairing" of the electrons would be counterbalanced by the formation of stronger W−C and W−H bonds. Oxidative addition reactions are in most instances thermodynamically more favored for the heavier 5d elements.[104]



(5)

VI. The Influence of a Spin Change on the Kinetics of Organometallic Reactions

We need to be concerned here with the spin crossover in a reaction that relates two complexes, a starting complex and a product, that differ in spin state such as the case illustrated in Figure 7, part b or c. The analysis of this phenomenon follows the general treatment of radiationless adiabatic transitions.[105,106] The rate of the reaction is affected by two parameters: one is a classical Arrhenius activation energy, i.e. the energy necessary for bringing the geometry of the activated complex to a configuration where intersystem crossing can occur. This is a situation where the two spin states have an identical geometry (Franck–Condon principle) and similar energy. The second parameter is the so-called prohibition factor which determines the transition probability and can be treated as a purely entropic contribution to the activation free energy. Spin–orbit interactions are the main cause for the breakdown of the selection rule that forbids intersystem crossing. Therefore, the greater the spin–orbit coupling is, the greater the probability that the spin change occurs at or near the crossover point of the two different energy surfaces. Spin–orbit coupling increases with the principal quantum number: it is relatively small for light main group elements such as carbon, resulting in a high level of diabaticity in organic systems, but it is much greater for transition metal complexes, especially those of the 4d and 5d series. It is therefore expected that the transition probability will be high (e.g. the reactions are highy adiabatic) for transition metal complexes.

It has been and it continues to be argued whether a "spin block" exists for organometallic reactions involving a spin-state change, experimental studies in this area being rather scarse. It is unlikely, on the basis of the above arguments and the measured high rates of intersystem crossing for transition metal complexes,[106,107] that the transition probability at the crossover point contributes much in slowing down organometallic reactions involving a spin-state change. There may be, however, a certain additional Arrhenius barrier related to the need to achieve a suitable geometry for the spin flip to occur. In principle, the exothermic reaction of ligand addition to a spin triplet 16-electron complex to afford a diamagnetic 18-electron compound (whose reaction coordinate is the reverse of the path illustrated in Figure 7b) has a spin-related barrier that does not exist in the corresponding reaction where the ligand adds to a diamagnetic 16-electron complex (reverse of the path in Figure 7a). Obviously, even for the latter case, a certain barrier may be present because of the internal reorganization of the unsaturated complex and the entering ligand, as well as solvation changes for both species. These effects can be very important, especially for sterically crowded systems, and will also affect the barrier of reactions involving a spin-state change.

The assessment of the amount of the activation energy that can be attributed to the spin change, therefore, is a difficult exercise, unless rate data are available for two comparable systems, only one of which involves the spin-state change. A situation of this type has been described for the addition of CO to the 16-electron derivatives $M(CO)_4$ (M = Fe, Ru, Os) in the gas phase. All reactions show second order kinetics but the addition to $Fe(CO)_4$ is about 3 orders of magnitude slower ($k = 5.2 \pm 1.2 \times 10^{-14}$ cm^3 $molecule^{-1}$ s^{-1})[108] than the addition to the other two complexes, in agreement with the spin triplet ground state of the former and the spin singlet ground state of the other two. The rates of these latter additions ($k = 2.8 \pm 0.8 \times 10^{-11}$ for $Ru(CO)_4$[65] and $5.5 \pm 0.6 \times 10^{-11}$ for $Os(CO)_4$,[65] both in the units of cm^3 $molecule^{-1}$ s^{-1}) are essentially diffusion limited, consistent with the inexpensive internal rearrangements for these relatively uncrowded systems and the absence of solvation effects. Of interest is also the comparison of two reactions of the same metal system with the same substrate in two different spin states (e.g. singlet vs triplet dioxygen). The reaction of the Vaska-type $IrX(CO)(PPh_3)_2$ (X = F, Cl, Br) complexes with singlet or triplet oxygen afford the same peroxo complex $IrX(CO)(PPh_3)_2(O_2)$, but the former reaction is ~10 orders of magnitude faster than the latter.[109]

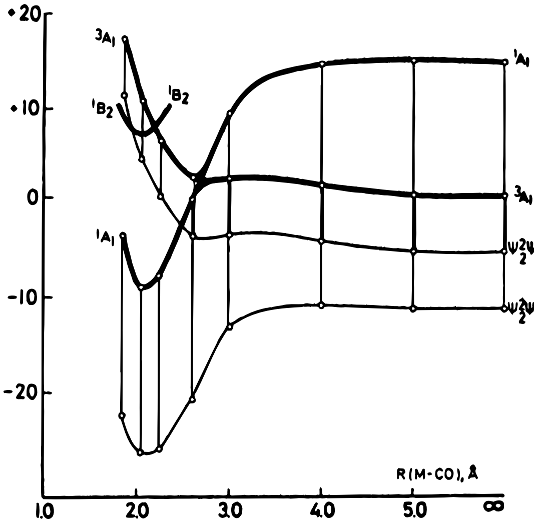


Figure 12. Correlation diagram for the addition of CO to Cp_2Mo. Thin lines are one-electron energies calculated by EHMO and vertical lines are electron repulsion energies calculated by use of Racah parameters. Solid lines are the resulting energies for singlet and triplet states. Energies are in 10^3 cm^{-1}. (Reprinted from ref 51. Copyright 1975 American Chemical Society.)

The reaction coordinate for the CO addition to Cp_2Mo, with CO approaching the metal end-on along the bond axis toward its equilibrium position while the angle between the two rings is steadily increased, has been calculated by approximate methods (see Figure 12).[51] The calculations indicate a comparatively small activation barrier (5.7 kcal/mol), because the initial triplet ground state $^3A_1$ does not become appreciably repulsive until the Mo–C distance has decreased below 2.5 Å, where the singlet state is already strongly binding with respect to the reactants. This result is consistent with the efficiency of CO as a trapping agent for free molybdenocene and tungstenocene species arising as intermediates in a number of reaction systems.[90] The situation is apparently similar for the CO addition to Cp_2Cr, since the reaction proceeds virtually instantaneously even at −78 °C in petroleum ether solution.[18] Quite different, instead, is the reaction coordinate for

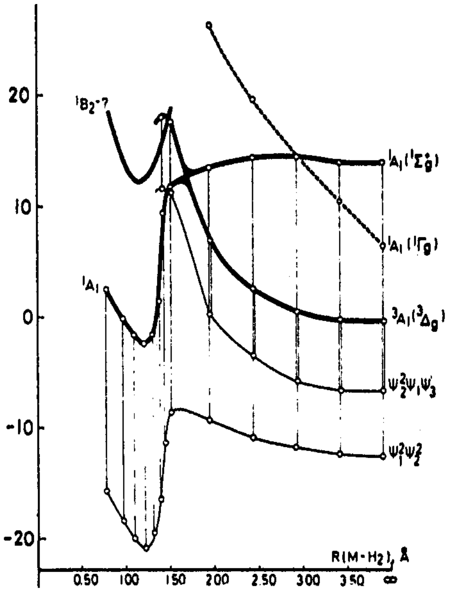


Figure 13. Formation of Cp_2MoH_2 by approach of an H_2 molecule to Cp_2Mo. Details as in Figure 12. (Reprinted from ref 51. Copyright 1975 American Chemical Society.)

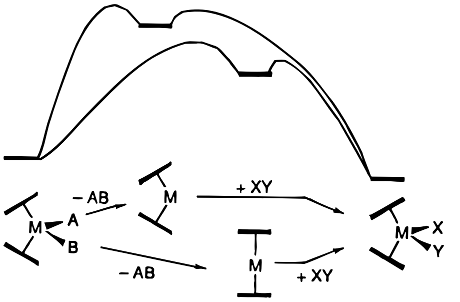


Figure 14. Proposed energetics for the reaction pathways for reductive elimination of AB from *ansa*- and non-*ansa* bent metallocenes. (Reprinted from ref 110. Copyright 1995 Royal Society of Chemistry.)

oxidative addition of H_2 to Cp_2Mo (see Figure 13).[51] In this case, the calculated activation energy is essentially equal to the singlet−triplet gap. According to these calculations, therefore, there is no substantial "spin block" to the addition of CO to molybdenocene, but there is a significant one to the oxidative addition of H_2. Indeed, molybdenocene is not efficiently trapped by H_2,[90] although the oxidative addition product Cp_2MoH_2 is a known stable compound.

In this regard, it is interesting to observe that the *ansa*-molybdenocene dihydride affords, upon photolytic H_2 elimination (which is less facile than for Cp_2MoH_2), an intermediate which is capable of oxidatively adding the C−H bond of benzene. The greater stability of the *ansa* derivative with respect to reductive elimination has been rationalized on the basis of the inability of the 16-electron system to adopt the electronically preferred parallel ring structure, which would raise the activation energy (see Figure 14).[110] The spin state of such an *ansa* intermediate is not known, but we observe here that the reactivity difference in the follow-up oxidative addition reaction might well be explained by a reduced (or absent) spin-crossing barrier in the *ansa* system.

A similar situation is found for CO and CH_4 addition to spin triplet CpCo(CO): the CO addition proceeds very rapidly to afford the 18-electron $CpCo(CO)_2$, but no tendency for the CH_4 oxidative addition is experimentally observed,[89] contrary to the corresponding systems of Rh and Ir. Theoretical calculations[66] predict in fact a greater thermodynamic gain associated with the formation of $CpM(CO)(H)(CH_3)$ for M = Co with respect to M = Rh or Ir (stable CpCo(CO)(H)(R) compounds, however, have not yet been reported). Thus, the lack of reactivity toward CH_4 would seem consistent with a large barrier for the spin-crossover reaction. Still according to the calculations,[66] the energy separation between geometry-optimized singlet and triplet CpCo(CO) species is 11.2 kcal/mol, but the vertical excitation energy (same geometry for both states) should be substantially higher, since the molecular geometry changes substantially upon changing the spin state. In addition, it is deemed unlikely that the interaction with the methane molecule significantly brings down this crossing point, because the singlet and triplet states for the $CpCo(CO)(CH_4)$ complex are equally different in geometry ($Co-CH_4$ distance of 2.40 and 3.71 Å, respectively), with a vertical excitation energy of 23.9 kcal/mol at the triplet minimum and 31.4 kcal/mol at the singlet minimum. For the CO addition reaction, on the other hand, it is found that even the triplet state has an appreciable binding energy for CO, and that the Co−CO bond distances for the two states are quite similar, thus spin triplet CpCo(CO) can interact with CO following a path that is attractive all the way.[66]

Certain reactions that involve π-stabilized unsaturated complexes may be slow because the stabilizing lone pair needs to be "pushed back" onto the ligand in order to allow the coordination of the incoming ligand. This may be the reason, for instance, for the slow H_2 oxidative addition to the π-stabilized (diamagnetic) 16-electron $WCl_2(PMe_2Ph)_4$ to afford 18-electron $WH_2Cl_2(PMe_2Ph)_4$.[111] This factor, however, cannot play a role in the slow H_2 oxidative addition to paramagnetic ($S = 1$) $[(Me_3SiNCH_2CH_2)_3N]WH$ reported recently by Schrock, because the amide−metal π interactions occur in the plane perpendicular to the metal orbitals that are utilized for the interaction with the incoming H_2 substrate. A spin−change related barrier has tentatively been invoked for this reaction.[112]

The reaction coordinate for the oxidative addition of H_2 to $FeCH_2^+$ (having a $^4B_2$ ground state), ultimately leading to Fe^+ (^6D, s^1d^6) + CH_4 without an energy minimum for a $Fe(CH_3)(H)^+$ intermediate, has been calculated at the MR-SDCI-CASSCF level and is reported in Figure 15. In this case, the highest activation barrier is for the oxidative addition of H_2 after formation of a molecular H_2 complex along the quartet spin surface, whereas the subsequent spin change to the $Fe(CH_4)^+$ complex ($^6A''$ ground state) proceeds along an ever descending energy curve.[113]

Other examples of kinetic studies for reactions involving a spin-state change are the additions of CO, N_2, or PMe_3 to the spin triplet $Cp^*MoCl(PMe_3)_2$, recently carried out in our laboratory.[20] Whereas CO adds very rapidly ($k = 22 \pm 2$ M^{-1} s^{-1} at 25 °C, ΔH^*

Table 2. Rates of CO vs N_2 Addition to 16-Electron Complexes

complex	S	solvent/T, °C	k_2, M^{-1} s^{-1} (CO added)	k_2, M^{-1} s^{-1} (N_2 added)	ref
$CpV(CO)_3$	0?	heptane/25	1.3×10^8	1.5×10^8	86
$CpNb(CO)_3$	0?	heptane/25	7.6×10^6	4.9×10^6	86
$CpTa(CO)_3$	0?	heptane/25	5.0×10^6	2.9×10^6	86
$CpW(CH_3)(CO)_2$	0?	heptane/room temperature	$2.0(2) \times 10^7$	$4.7(5) \times 10^6$	115
$Cp^*MoCl(PMe_3)_2$	1	THF/room temperature	$2.2(2) \times 10^1$	$1.47(7) \times 10^{-2}$	114

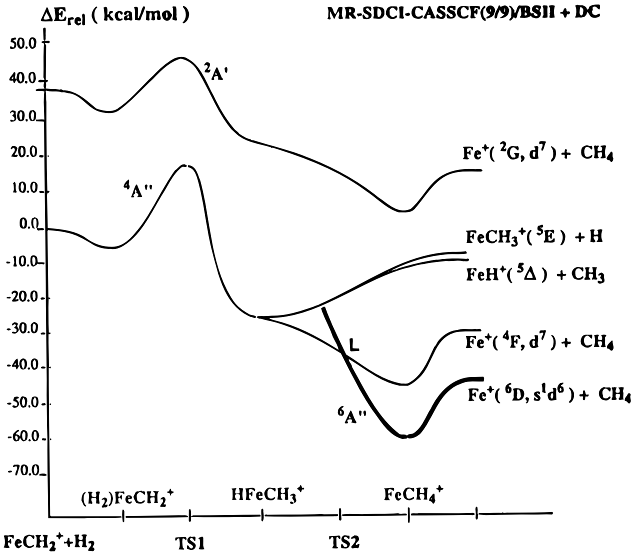
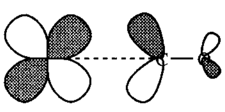


Figure 15. The potential energy profile of reaction $FeCH_2^+ + H_2$. (Reprinted from ref 113. Copyright 1994 American Chemical Society.)

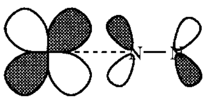
$= 5.0 \pm 0.3$ kcal/mol), the *isosteric and isolobal* N_2 ligand adds several orders of magnitude more slowly ($k = (1.47 \pm 0.07) \times 10^{-2}$ M^{-1} s^{-1} at 298 K, $\Delta H^* = 14.0 \pm 1.0$ kcal/mol).[114] This difference in rate could be attributed to the spin change occurring much earlier along the reaction coordinate in the case of the CO addition, consistent with the greater diffuseness of the CO orbitals (e.g. compare **XVI** with **XVII** for the σ-donor interaction and **XVIII** with **XIX** for the π-acceptor interaction). In other words, even at a relatively long Mo−CO distance, the spin singlet state is already substantially bonded whereas the triplet state is not yet significantly repulsive. On the other hand, the poorer ligand N_2 needs to approach the metal to a much closer distance, where the triplet state begins to be significantly repulsive, to cause the spin flip to occur.[114]

XVI

XVII



XVIII



XIX

The large contribution of the spin-state change to the activation barrier of these addition reactions is also consistent with the generally much more similar rates of CO and N_2 additions to other (presumably diamagnetic) 16-electron intermediates, such as $CpM(CO)_3$ (M = V, Nb, Ta) and $CpW(CH_3)(CO)_2$ (see Table 2).[86,115] The spin states of these $CpM(CO)_3$ compounds should be 1 if these would adopt a C_{3v}-symmetric structure. However, IR work in low-temperature matrices indicate a C_s structure,[86] even for the lighter V complex for which a spin triplet configuration is predicted to provide the greatest stabilization. The faster rates of CO and N_2 addition for $CpV(CO)_3$ vs its heavier congeners is in fact evidence *against* a spin-state change during the reaction. The reason for this difference may be the formation of more stable $CpM(CO)_3 \cdots Solv$ intermediates for the Nb and Ta systems, which would slow down the reaction with CO or N_2.

Table 3. Rates of CO Addition to (η^5-Ring)$_2$V in Toluene at 25 °C[117]

complex	k_2, $M^{-1}s^{-1}$	rel rate	S
Cp^*_2V	1.42 ± 0.01	1	$^3/_2$
Cp(pd′)V[a]	34 ± 5	24	$^1/_2$
$(pd)_2V$[b]	42 ± 5	30	$^1/_2$
Cp_2V	91 ± 5	64	$^3/_2$

[a] pd′ = η^5-2,4-dimethylpentadienyl. [b] pd = η^5-pentadienyl.

The addition of PMe_3 to $Cp^*MoCl(PMe_3)_2$ is much slower than the addition of N_2 and proceeds only to an equilibrium position in which the 16-electron species is the prevalent one.[20] Since the Mo−L bond strength is likely to be in the order CO > PMe_3 > N_2, the additional barrier for the PMe_3 addition has probably a steric origin.

The ability of CO to induce electron pairing in its addition to electronically unsaturated, high-spin systems is also documented in other cases: when the S = 1 Cp^*_2VH and Cp^*_2VMe systems are treated with CO at room temperature, an immediate addition occurs to afford diamagnetic $Cp^*_2VH(CO)$ and $Cp^*_2V(COMe)(CO)$, respectively. On the other hand, the oxidative addition of H_2 to Cp^*_2VMe (ultimately leading to Cp^*_2VH and CH_4) proceeds more slowly (12 days at 375 psi).[116] The CO additions to closed, half-open, and open vanadocenes proceed at comparable rates (see Table 3), irrespective of the spin state of the starting material, in accord with little or no spin-change-related barrier for these additions.[117]

A stable isoelectronic analogue of CpCo(CO) is the hydrotris(pyrazolyl)borate complex $Tp^{Pr^i,Me}Co(CO)$. This is also a spin triplet compound and adds CO to afford the diamagnetic adduct with a rate constant $k = 3(1) \times 10^9$ M^{-1} s^{-1} at 224 K, i.e. close to the diffusion limit.[83] A dinitrogen adduct of formula $Tp^{Pr^i,Me}Co(CO)(N_2)$ does not form. A spin triplet system that is capable of adding both CO and N_2 is $[CpFe(dippe)]^+$, but no rate data are provided for either reaction.[84] It was only shown, by ^1H-NMR investigation of the equilibrium between the 16-electron complex and its 18-electron N_2 adduct, that these two species are in the slow exchange regime at room temperature. The measurement of the rates of CO and N_2 addition to these and/or other spin triplet 16-electron systems, as well as theoretical calculations of the reaction coordinate, would be desirable to better define the influence of metal−ligand bonding on the nature of the transition state and on the amount of spin change-related activation energy.

For an *endothermic reaction*, the activation enthalpy must obviously be at least as large as the enthalpy of the reaction. A spin change may introduce an extra barrier (e.g. see Figure 7b). However, a comparison between parts b and a in Figure 7 shows that the spin change introduces a *thermodynamic stabilization of the transition state* with respect to the situation of no spin-state change, and *ultimately may accelerate the reaction*. This has been a point of confusion in the literature, in that a spin change is usually, albeit not always correctly, taken to mean a *slower* process. The first time that such an argument has apparently been presented concerns the nature of the 16-electron intermediate during the CO insertion reaction in $Cp_2TaR(CO)$ to form $Cp_2Ta(COR)$.[118] Since calculations have shown that C_{2v}-symmetric Cp_2MX compounds have an energy diagram in which the two highest occupied orbitals are nearly degenerate,[119] then "the ground state for the d^2 configuration should be a triplet". In such a situation, "spin multiplicities should be correlated along the reaction coordinate; so a singlet starting material should form a singlet product; but in those special cases the latter would be an electronically excited state of the product. This should result in an increased activation energy, and such paths should therefore be slow." [118] In reality, if the intermediate were a spin triplet, the activation barrier may be *smaller* than for a spin singlet intermediate if crossing of the two spin energy surfaces occurs below the energy of the excited spin singlet intermediate, given the expected high-spin change probability for a metal such as tantalum. In addition, a $Cp_2Ta(COR)$ system could be bent (e.g. the acyl group could reside on the wedge plane in a lateral position rather than at the center) and, even if at the center, the expected low pairing energy for d^2 Ta(III) may lead to a ground-state singlet. Magnetic circular dichroism experiments on the photochemically generated Cp_2TaH complex have not allowed a conclusive determination of the ground state for this 16-electron transient.[90] Another d^2 system of this type is $[Cp_2WCH_2CH_3]^+$, which forms by insertion from a $[Cp_2W(CH_3)({=}CH_2)]^+$ intermediate, and further evolves to the isolated $[Cp_2WH(C_2H_4)]^+$ or to $[Cp_2WEt(PMe_2Ph)]^+$ when the reaction is carried out in the presence of PMe_2Ph.[120]

Along similar lines, Bergman *et al.* were puzzled by the "especially facile" dissociative phosphine exchange reaction on $CpCo(PPh_3)_2$.[121] Since the 16-electron $CpCo(PR_3)$ intermediate is predicted to have a spin triplet configuration in the most symmetric linear geometry (see section VII), it was proposed that either "its electronic configuration does not destabilize it appreciably" or that "the substitution reaction avoids the linear intermediate".[121] The efficient CO dissociation from $CpCo(CO)_2$ was also taken by Rest *et al.* to indicate a bent, spin singlet geometry for the 16-electron CpCo(CO) photoproduct, "thus avoiding spin-imposed high activation energies of formation".[87] These considerations have been reiterated in later contributions, even by theoreticians.[122] In fact, a spin triplet intermediate would be energetically *stabilized* and its formation can be kinetically accelerated if the curve crossing (Figure 7b) occurs at a sufficiently low energy, not only avoiding a paradox, but in fact providing a plausible rationalization of the above mentioned experimental observations. As mentioned above, recent calculations indeed suggest that CpCo(CO), although bent, has a spin triplet ground state.[66] The isolobal and stable 16-electron $Tp^{Pr^i,Me}Co(CO)$ compound also has a bent geometry and a *spin triplet* ground state, and forms *extremely rapidly* by CO dissociation from $Tp^{Pr^i,Me}Co(CO)_2$.[83]

Basolo *et al.* comment on the unusually slow CO substitution on $Fe(CO)_5$ with respect to $Ru(CO)_5$ and $Os(CO)_5$, and attribute it to the spin triplet configuration of $Fe(CO)_4$.[123] However, the fact that triplet $Fe(CO)_4$ is energetically more stable than singlet $Fe(CO)_4$ means that the spin-state change is likely to accelerate the bond breaking process. A slow reaction could be in agreement with a small probability of intersystem crossing or with the two spin surfaces crossing at a much higher energy than that of spin singlet $Fe(CO)_4$. However, the first possibility seems unlikely given the fast rates of intersystem crossing measured in general for coordination compounds,[106,124] whereas the second possibility is excluded by the observed fast recombination of spin triplet $Fe(CO)_4$ and CO.[108] It is an experimental fact that CO dissociation from $Fe(CO)_5$ is unusually slow,[123] but the spin change is unlikely to be the reason. The reason appears to be instead an inherently stronger Fe−CO bond with respect to the Ru−CO and Os−CO bonds, as shown both experimentally (BDE = 42 kcal/mol for Fe−CO by pulsed laser pyrolysis)[125] and by theoretical calculations.[54] This is contrary to the conventional view that M−L bond strengths increase upon descending a group of transition metals.[44]

We have recently reported that the 17-electron $CpMoCl_2(PR_3)_2$ system exchanges phosphine ligands extremely rapidly following a dissociative path via a 15-electron intermediate, this behavior departing from that typical of lower-valent 17-electron organometallics (e.g. $V(CO)_6$),[126] which on the other hand exchange ligands rapidly via 19-electron associative intermediates. We proposed, probably for the first time, that a spin-state change from doublet to quartet in reaching the hypothetical dissociative intermediate could be largely responsible for this mechanistic variation.[127] More recent calculations (see Figure 10) show that, indeed, the hypothetical 15-electron intermediate would have a spin quartet ground state which is substantially stabilized energetically by the spin-state change.

The β-H elimination reaction from coordinatively unsaturated alkyl compounds is known to be a facile reaction and this is likely the main reason for the thermal instability of transition metal complexes with β-H-containing alkyl ligands. The decomposition of these materials can be suppressed or slowed down in a number of ways.[128] A necessary requirement for the elimination is the availability of an *empty* metal orbital to initiate the interaction with the β-C−H bond of the alkyl ligand. For high spin, open-shell alkyl compounds that have all the valence-shell orbitals occupied by at least one electron (e.g. the $S = 1$ 16-electron d^2 systems, or the $S = {}^3/_2$ 15-electron d^3 systems, etc., see Figure 3) this requirement is obviously not fulfilled, unless promotion to a higher-energy, lower-spin state, or ligand dissociation occurs, both of which require extra-activation. This is the reason for the relative stability of alkylpentaaquochromium(III) complexes, $[CrR(H_2O)_5]^{2+}$. These materials decompose in most instances, in fact, by Cr−R bond homolysis rather than via β-H elimination.[21] An example of β-H elimination from a Cr(III) alkyl has been recently described for the thermal decomposition of $MeC(CH_2PMe_2)_3CrCl(n\text{-}Bu)_2$ (20−30% decomposition over 3.5 h at room temperature; very rapid decomposition upon mild heating). Under all conditions, butane, 1-butene, and *cis*- and *trans*-2-butene are found as decomposition product. The presence of internal olefins, as well as the absence of octane suggests that the decomposition does not produce butyl radicals, but rather proceeds through β-H elimination/reductive elimination steps. The decomposition path illustrated in Scheme 5, involving dissociation of an arm of the tripodal ligand, has been suggested.[129] The strong trans effect of the alkyl groups possibly favors this pathway, whereas for $[CrR(H_2O)_5]^{2+}$ a similar path would only be possible if a H_2O ligand trans to another H_2O (and cis to the R group) would dissociate. However, an alternative possibility to be considered is a spin-state change to afford 17-electron alkene−hydride intermediates without phosphine dissociation. Other stable β-H-containing open-shell alkyl derivatives involve tetrahedral manganese(II) and square-planar chromium(II) centers (see sections VIII.4.2 and VIII.3.3, respectively).

Scheme 5

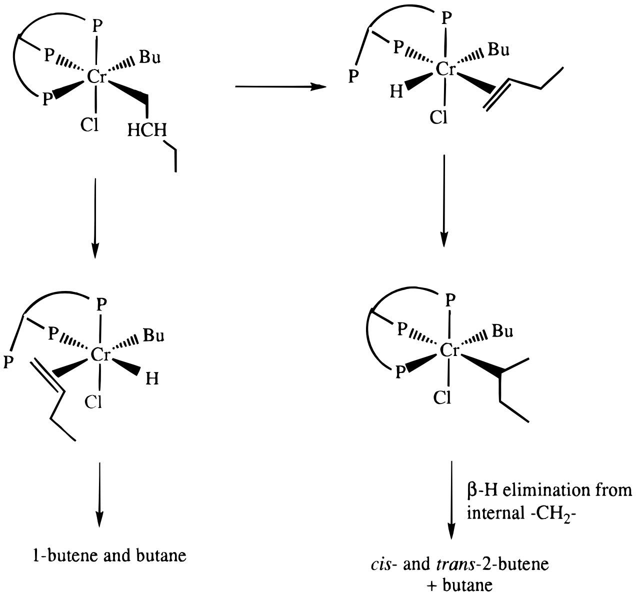


Table 4. MP2-Optimized Bond Distances (Å) and Angles (deg) for Singlet and Triplet States of CpM(CO)[a]

metal	S	M−Z[a]	M−CO	Z−M−CO[b]
Co	1	1.96 (1.93)	1.83 (1.80)	146.4 (139.8)
	0	1.75 (1.75)	1.73 (1.75)	136.0 (137.6)
Rh	1	2.08 (2.09)	1.91 (1.90)	135.7 (136.0)
	0	1.99 (2.03)	1.83 (1.85)	133.3 (136.0)
Ir	1	2.06 (2.07)	1.85 (1.85)	135.7 (138.2)
	0	1.99 (2.01)	1.83 (1.83)	137.2 (140.3)

[a] Values in parentheses are the corresponding optimized parameters at the B3LYP level.[66] [b] Z is the Cp ring centroid.

VII. The Influence of the Spin State on the Structure of Organometallic Compounds

A change of spin state can affect the molecular structure in terms of bond lengths, angular distortions, and even overall molecular geometry. It is well known from Werner chemistry that bond distances are quite sensitive to the spin state. Those cases, however, systematically involve electronic structures that differ by one or more electrons being transferred from M−L σ^*-orbitals to essentially metal-based nonbonding orbitals (e.g. high- vs low-spin octahedral d^4−d^7 complexes). In most examples of open-shell organometallics, the electronic redistribution involves orbitals of similar type, these having M−L π (for π-acidic ligands) or π^* (for π-basic ligands), but not σ^*-contributions, thus smaller changes in metal−ligand bond lengths are expected. An exception is the 5-coordinate alkyl- or aryliron(III) porphyrin system, which exists in the spin states $S = {}^1/_2$ and ${}^5/_2$ depending on the nature of the organic groups and porphyrin base (see section VIII.4.1).[130,131] A structure determination, however, has apparently been reported only for a low-spin complex, [phenyl(*meso*-tetraphenylporphyrinato)iron(III)].[132]

There is a limited number of open-shell organometallics for which theoretical geometry optimizations have been carried out for more than one spin state. The “axial” and “equatorial” Fe−(CO) distances for the geometry-optimized $^3B_2$ ground state and $^1A_1$ excited state of $Fe(CO)_4$ are hardly different both at the modified coupled pair functional (MCPF)[133] and nonlocal density functional (NL-SCF)[54] levels. MP2 or B3LYP geometry-optimized CpM(CO) (M = Co, Rh, Ir) fragments show a slight contraction of all bond lengths upon going from the triplet to the singlet state (see Table 4).[66] This has been explained in theoretical terms by a poor mixing between singly occupied and doubly occupied orbitals resulting in a poorer ability of higher spin systems to form hybrid orbitals that are more suitable for bonding.[66] Alternatively, the trend could also be explained by an electronic distribution which is better suited for M−Cp and M−CO back-bonding interactions in the lower spin state. Similarly, MP2 geometry-optimized 15-electron $CpMCl_2(PH_3)$ (M = Cr, Mo) and 16-electron $CpMoCl(PH_3)_2$ show a slight shortening of all bonds upon going from the higher to the lower spin state (see Table 5).[92,114]

The only system whose structure has been experimentally determined in two different spin states

Table 5. Structural Differences in MP2 Geometry-Optimized Spin Doublet and Quartet $CpMoCl_2(PH_3)$[92] and between Spin Singlet and Triplet $CpMoCl(PH_3)_2$[114] Compounds

	$CpMoCl_2(PH_3)$		$CpMoCl(PH_3)_2$	
parameter	$S = ^3/_2$	$S = ^1/_2$	$S = 1$	$S = 0$
M−C (Cp)[a], Å	2.438	2.414	2.363	2.356
M−Cl, Å	2.479	2.465	2.499	2.464
M−P, Å	2.659	2.607	2.561	2.496
Cl−M−Cl, deg	100.77	116.72		
Cl−M−P, deg	85.07	83.00	88.96	93.41
P−M−P, deg			94.56	83.77

Table 6. Bond Lengths (Å) and Angles (deg) for *all-trans*-$WCl_2(OAr)_2L_2$[315]

parameter	Ar = *p*-Tol, L = $PMePh_2$ (S = 0)	Ar = 2,6-$Ph_2C_6H_3$, L = PMe_2Ph (S = 1)
W−O	1.848(5), 1.840(5)	1.966(4)
W−Cl	2.471(2), 2.440(2)	2.354(2)
W−P	2.526(3), 2.534(3)	2.551(2)
W−O−C	166.3(6), 171.7(5)	140.0(4)

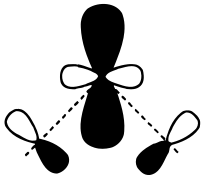
appears to be $(\eta^5\text{-}C_5H_4Me)_2Mn$.[134] In this system, however, the higher spin state involves occupation of metal−ligand σ*-orbitals. There is a significant elongation of the Mn−C bonds on going from the minor $^2E_2'$ form (2.14 Å) to the more abundant $^6A_1'$ form (2.433(8) Å).[134] For other systems, we can compare experimental results on similar compounds where the spin-state change is induced by a change of part of the coordination sphere, and probe bond length changes in the remainder of the molecule. For $TiX_2(dmpe)_2$, the average Ti−P distance is 2.515[8] Å for the spin singlet bis(phenoxide) derivative[70] and 2.514[8] Å (by X-ray) or 2.52[1] Å (by neutron) for the spin singlet dimethyl derivative,[135] but it is significantly longer (in the range 2.586(5)−2.626(1) Å) in the spin triplet dichloride analogue.[136] Both the decreased electronegativity of the Me group and the push−pull interaction which is possible in the phenoxide compound may be responsible for the Ti−P bond shortening via an increase of Ti−P π-backbonding. Selected distances for two related *all-trans*-$WCl_2(OR)_2L_2$ compounds are shown in Table 6. No major difference is observed for the W−P distances, whereas the W−O distances are much shorter (and the W−Cl distances correspondingly longer) for the diamagnetic compound. This phenomenon has been attributed to a stronger W−O π bonding in the O-*p*-tolyl compound, as also probed by the wider W−O−C angle in the spin singlet compound.

Angular deformations are also expected, especially when π-interactions are present, because the π-donor ligands tend to rearrange in order to maximize the π-interaction with the empty orbital(s), whereas the π-acceptors tend to maximize the π-interaction with the filled orbital(s). This effect is evident, for instance, in 16-electron four-legged piano stool structures of type $(ring)MX_2L_2$, where X = halide and L = phosphine. The angles X−M−X and L−M−L, in particular the former, can be correlated with the spin state, as shown in Table 7. The reason for this effect is the stronger π-overlap of the halogen lone pairs with the empty d_{z^2} orbital in the spin singlet structure, which favors a X−M−X closing toward the ideal 90° angle of the d_{z^2} nodal cone, see **XX**.[137] In turn, this bending causes a rehybridization of the σ orbitals which pushes the two L ligands to larger L−M−L angles.[138] The anomalously small L−M−L angle in $[Cp^*MoCl_2(PMe_2Ph)_2]^+$ (Table 7) can be attributed to $Cp^*{-}PMe_2Ph$ steric repulsions.

Table 7. Angular Parameters (deg) in Spin Singlet and Triplet 16-Electron Four-Legged Piano Stool Compounds of Type *trans*-$(ring)MX_2L_2$

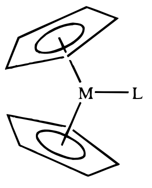
compound	S	X−M−X	L−M−L	ref
$(\eta^6\text{-toluene})ZrCl_2(PMe_3)_2$	0	109.40(9)	141.14(8)	73
$(\eta^6\text{-}C_7H_8)ZrCl_2(PMe_3)_2$[a]	0	99.7(1)	140.4(1)	189
$(\eta^6\text{-}C_7H_7SiMe_3)ZrI_2(PMe_3)_2$[b]	0	104.17(2)	139.44(5)	187
$(\eta^5\text{-}C_5H_4Me)NbCl_2(PEt_3)_2$	0	114.38(7)	148.96(7)	76
$CpVCl_2(PMe_3)_2$	1	126.1(0)	132.6(0)	38
$[CpMoCl_2(PMe_3)_2]^+$	1	123.0(1)	133.5(1)	218
$[Cp^*MoCl_2(PMe_2Ph)_2]^+$	1	138.23(9)	116.80(8)	26

[a] C_7H_8 = cycloheptatriene. [b] $C_7H_7SiMe_3$ = (trimethylsilyl)-cycloheptatriene.

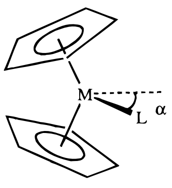


XX

The 16-electron d^2 Cp_2ML case is shown by extended Huckel calculations to have an energy minimum at α = 0 (see **XXI**) for the S =1 configuration and at α > 0 (**XXII**) for the S = 0 configuration.[119] Whereas this prediction is amply verified for spin triplet molecules (see section VIII.1.1.3), there is no example as yet of a structurally characterized mononuclear spin singlet compound. The rearrangement to the spin-paired configuration and the consequent angular deformation makes the coordination of another donor a very favorable process, as experimentally observed. A few structure determinations have been reported for the related (but structurally and electronically different) diamagnetic open metallocene adducts, $M(Pdl)_2L$ (M = Ti, Zr, Hf; L = CO, PR_3) (section VIII.1.1.3).



XXI



XXII

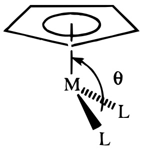
Half-sandwich $(ring)ML_2$ systems having a 16-electron configuration may be either bent (**XXIII**) or planar (**XXIV**). Calculations at the extended Huckel level have shown a bent minimum for the spin singlet $CpMn(CO)_2$ transient (θ = 160°). This would allow a retention of configuration for ligand substitutions on optically active $CpML_1L_2L_3$ systems.[139] The planar structure, however, seems to be preferred by spin triplet complexes, such as $[(\eta^5\text{-pentadienyl})Fe(PEt_3)_2]^+$ and $[Cp^*Fe(dppe)]^+$.[140,141] The planar structure is also preferred for spin singlet complexes when a

Table 8. Geometries and Relative Energies of Singlet and Triplet States for CpM(CO) Systems (M = Co, Rh, Ir) at the MP2 Level (Data are from Ref 66)

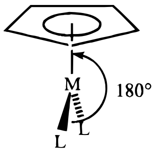
metal	state	α[a]	Δ*E*(S−T)[b]
Co	$^1A'$	136.0	−11.2
	$^3A''$	146.4	
Rh	$^1A'$	133.3	5.9
	$^3A''$	135.7	
Ir	$^1A'$	137.2	−0.3
	$^3A''$	135.7	

[a] Refer to **XXVI**. [b] Singlet to triplet excitation energy in kcal/mol, from PCI-80 calculations.

π-donor is present in the coordination sphere. This is the case for all compounds of type CpRuXL (see section VIII.5.1.2).[142,143] The planar structure is calculated to be the energy minimum for $CpRuI(PH_3)$, $CpRu(OH)(PH_3)$, and $[CpRuH_2]^-$, while $[CpRu(CO)_2]^+$ shows an energy minimum for a bent structure with $\theta = 160°$, like $CpMn(CO)_2$, all these being spin singlet species.[139,143]

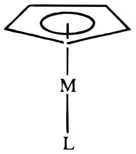


XXIII

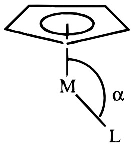


XXIV

A linear structure for CpML (**XXV**) would give, by symmetry, a spin triplet ground state for a 16-electron configuration (d^8 system). However, for high pairing energy systems, a bent structure (**XXVI**) can also result in a triplet ground state. Empirical MO calculations at the extended Hückel level show that the total energy for spin singlet systems decreases upon bending, especially when the L ligand is a good σ-donor and/or a good π-acceptor. The calculated energy gain is 16.5 kcal/mol for CpCo(CO) ($\alpha = 122°$) and 17.5 kcal/mol for CpRh(CO) ($\alpha = 122°$).[122] Other calculations confirm that the rhodium species should have a bent geometry and a spin singlet ground state, but also predict a bent structure and *spin triplet* ground state for CpCo(CO) (see Table 8).[66,67] It seems conceivable that an unsaturated Co complex of this type could be stabilized and isolated by using a very large phosphine ligand, allowing a determination of its structure and magnetic properties. Thus, to date, a linear "one-legged piano stool" structure as in **XXV** has not been experimentally observed nor calculated for any 16-electron complex, whereas it is known for the 18-electron counterparts.



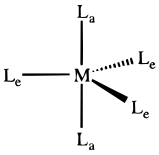
XXV



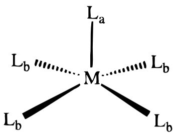
XXVI

For complexes without extended π-systems, 6-coordination is dominated by the ubiquitous octahedral geometry, independent of the electron count and spin state. Distortions of this structure are typically related to Jahn−Teller effects and to π-effects, as is experienced by diamagnetic d^4 complexes of Mo(II) and other metals.[144] Whereas structures of $S = 1$ (σ-organo)molybdenum(II) have not been reported as yet, the octahedral structure of spin triplet $CrMe_2(dmpe)_2$ is relatively undistorted.[136]

Five-coordinate complexes are known with both the trigonal-bipyramidal (*tbp*, **XXVII**) and the square-pyramidal (*sp*, **XXVIII**) structure. There seems to be no specific geometrical preference for any particular electronic configuration. The geometric constraints of the ligands appear to often determine the molecular geometry. For instance, d^3 $CrPh_3L_2$ complexes are *tbp*, but porphyrin complexes Cr(TTP)R are *sp* (see section VIII.2.2.1). Ligands that are particularly good at enforcing a *sp* geometry are, besides the porphyrins, the Shiff bases and other similar macrocyclic rigid ligands, whereas a good ligand for enforcing a *tbp* geometry is the triamidoamine, $[N(CH_2CH_2NR)_2]^{3-}$ and isoelectronic analogues. In other cases, the reason for the choice of geometry is not obvious. Consider for instance the d^2 *tbp* $[N(CH_2CH_2NEt_2)_2]VPh_2$ [145] and *sp* V(Mes)-$[CyNC(Mes)NCy]_2$,[146] both being $S = 1$ systems, see section VIII.1.3. The different bite of the chelating ligands in the two cases might play an important role. Another interesting case is seen for d^4 Mn(III) complexes, the *sp* [147]*spiro*-$[Mn(C_4H_8)_2(py)]^-$ and the *tbp*[148] $MnMesBr_2(PMe_3)_2$, both with four unpaired electrons. A change of spin state also does not appear to affect the choice of molecular structure as dramatically as found for the 4-coordinate geometry (*vide infra*); for instance, both $MnMesBr_2(PMe_3)_2$ ($S = 2$)[148] and the isoelectronic $ReAr_3(PEt_2Ph)_2$ ($S = 0$)[149] are *tbp*, see section VIII.3.2.3. Complexes with a d^6 configuration are all diamagnetic. The Fe(II), Ru(II), and Os(II) complexes always adopt a *sp* geometry, whereas complexes of the group 9 metals, especially Rh(III) and Ir(III), have been found in both *sp* and *tbp* geometries. The choice of structure type appears to depend on the nature of the X ligands, compounds of type MR_2XL_2 (R = π-neutral ligand such as alryl, acyl, or H; X = π-donor ligand such as Cl) being usually trigonal bipyramidal with an acute angle (e.g. < 90°) between the two M−R bonds and those of type MRX_2L_2 being usually square pyramidal. A theoretical study shows that the square-pyramidal structure is favored by the presence of a strong σ-donor and/or π-acceptor ligand *trans* to the vacant octahedral site, whereas the *tbp* structure is favored by the presence of a σ-acceptor and/or π-donor ligand trans to the acute angle.[150,151]



XXVII



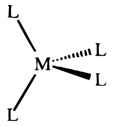
XXVIII

For 4-coordinate complexes, the geometries observed are the tetrahedral (**XXIX**), the square planar (**XXX**), a D_{2d} distorted square planar (**XXXI**), where the angle α is close to 180°, and a more distorted C_{2v}

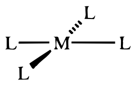
Table 9. Structural Preferences for 4-Coordinate Organometallic Compounds According to d^n Configuration

d^n configuration	geometry	spin state	known systems
d^2	tetrahedral	1	V(III), Cr(IV), Mo(IV), W(IV)
d^3	tetrahedral	$^{3}/_{2}$	Cr(III), Mn(IV)
	tetrahedral	$^{1}/_{2}$	Re(IV), Os(V)
d^4	square planar	2	Cr(II)
	XXXI	2	Cr(II), Mn(III)
	XXXII	2	Cr(II) in Tp$^{Bu^t}$CrEt
	tetrahedral	0	Ti(0), Fe(IV), Ru(IV), Os(IV), Co(V)
d^5	tetrahedral	$^{5}/_{2}$	Mn(II), Fe(III) (?)
	tetrahedral	$^{1}/_{2}$	Co(IV), Ir(IV)
d^6	tetrahedral	2	Fe(II) [FeR_4^{2-}, FeR_2L_2 (L = N-donor)], Co(III)
	square planar	1	Fe(II) [FeR_2L_2 (L = P-donor)]
d^7	tetrahedral	$^{3}/_{2}$	Co(II) [CoR_4^{2-}, CoR_2L_2 (L = N-donor)]
	square planar	$^{1}/_{2}$	Co(II) [CoR_2L_2 (L = P-donor)], Rh(II), Ir(II), Pt(III)
d^8	**XXXII**	1	Fe(0) [$Fe(CO)_4$]
	XXXII	0	Ru(0) [$Ru(CO)_n(PR_3)_{4-n}$; $n = 4, 2$]
	square planar	0	Ru(0) [$Ru(PR_3)_4$], Os(0), Co(I), Rh(I), Ir(I), Ni(II), Pd(II), Pt(II), Au(III)

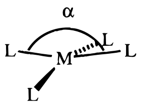
geometry which is best described as a trigonal bipyramid with a vacant equatorial position (**XXXII**).



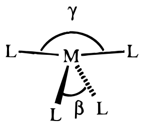
XXIX



XXX



XXXI



XXXII

As a result of the vacancy, the axial ligands typically relax somewhat away from the remaining equatorial ligands, so that the γ angle is less than 180°. A trigonal bipyramid with a vacant axial position is also possible in principle and claimed for reactive d^8 intermediates, but never observed for stable compounds. The choice of molecular geometry depends delicately on the number of electrons and on their distribution in the metal orbitals (i.e. the spin state), together with electron−electron repulsions and steric effects. In Werner chemistry, we are familiar with the d^8 case: the tetrahedral geometry is adopted by spin triplet complexes (e.g., $[NiF_4]^{2-}$) and the square-planar geometry is adopted by spin singlet complexes [e.g., $NiCl_2(PMe_3)_2$, and all derivatives of Pd(II), Pt(II), Au(III), Rh(I), and Ir(I)]. Most organometallic complexes of d^8 metals, in the absence of geometrical constraints (e.g. tripodal ligands, see above), also chose the square-planar, low-spin arrangement. However, dichotomies are found for other electron counts, as shown by Table 9. Some situations parallel those found for analogous Werner-type complexes, but alkyl and aryl ligands are better able to enforce low-spin configurations that are not found in Werner chemistry.

For the tetrahedral geometry, the electrons in the t_2 orbitals will on the average be closer to and feel greater repulsion from the M−L bonding electrons. For the square-planar geometry, on the other hand, all orbitals are farther away from the M−L bonding electrons with respect to the tetrahedral arrangement, except for the $d_{x^2-y^2}$ orbital which has strong M−L σ*-character. Thus, the less sterically encumbered tetrahedral geometry is preferred for d^2 and even d^3 in spite of one electron being in a t_2 orbital (only for high spin complexes). However, for d^4, an $e^2t_2^2$ configuration becomes unfavorable and the sterically more encumbered square-planar geometry (but with reduced unpaired electron-bonding electron repulsions) becomes the preferred geometry for high-spin compounds (e.g. Cr(II)). Systems with smaller pairing energies enforce a low-spin configuration, which allows the structure to relax back to tetrahedral. The Mn(III) systems are somewhat unusual in that they adopt the D_{2d} distorted square-planar geometry, perhaps because of steric repulsions since the ionic radius is small. Some Cr(II) complexes with bulky ligands are also significantly distorted from the ideal square-planar geometry and adopt the D_{2d} geometry, whereas compound Tp$^{Bu^t}$CrEt, interestingly, adopts structure **XXXII** because of the geometric constraint of the Tp$^{Bu^t}$ ligand instead of the tetrahedral geometry.[152]

For high spin (S = $^{5}/_{2}$) d^5 systems, the square-planar geometry is unfavorable because one electron would be forced in the antibonding $d_{x^2-y^2}$ orbital, thus the tetrahedral geometry is again adopted. On the basis of sole unpaired electron-bonding electron repulsion arguments, one would expect a square-planar geometry with S = $^{3}/_{2}$; however, the S = $^{5}/_{2}$ configuration is further stabilized by a large electron-pairing contribution, especially $(PE)_{ex}$ (containing in this case 4 K terms for the quartet−sextet gap). Systems with d^6 and d^7 configurations are most interesting because both tetrahedral and square-planar geometries are adopted by the same ion, e.g. Fe(II) and Co(II), respectively, depending on the nature of the ligands. With ligands that favor higher pairing energies, the ion is found with the highest possible spin (quintet for d^6, quartet for d^7) in a tetrahedral geometry (in the alternative square-planar geometry, the antibonding $d_{x^2-y^2}$ orbital would be populated). With those ligands that favor lower pairing energies or for the heavier, lower pairing energy 4d and 5d ions, a lower-spin configuration (triplet for d^6, doublet for d^7) is adopted in a square-planar geometry. This is true irrespective of the ligands steric bulk.

A special word for the d^8 configuration is warranted. The overwhelming preference is, of course, for the square-planar geometry with an empty $d_{x^2-y^2}$ orbital. However, there are exceptions to this rule. $Fe(CO)_4$ is a rare case of a spin triplet organometallic

d^8 complex. Given the unfavorable occupation of the $d_{x^2-y^2}$ orbital in a square-planar geometry, the structure distorts asymmetrically to give a geometry of type of **XXXII** ($\beta = 120°$; $\gamma = 145°$).[88] The structure of the excited-state spin singlet has been predicted to be square planar, but calculations at various levels indicate a structure very close to that of the spin triplet ground state.[54,133] An analogous structure has been calculated for spin singlet $Ru(CO)_4$.[54,64] This geometry has been recently experimentally observed for the isoelectronic, spin singlet $Ru(CO)_2(PBu^t{}_2Me)_2$ ($\beta = 133.3(4)°$; $\gamma = 165.56(8)°$), and is well reproduced by calculations on the model compound $Ru(CO)_2(PH_3)_2$.[153] The reason for the different geometries of Ru(0) and Rh(I) 4-coordinate compounds is traced to the energies of the d orbitals. For the lower oxidation state Ru(0) complex, stronger M−L π-back-bonding favors the distortion from the planar geometry. Stronger π-acceptor ligands are also predicted to favor a nonplanar structure.[153,154] Indeed, $Ru(R_2PCH_2CH_2PR_2)_2$ transients seem to be square planar, like the isoelectronic $[Rh(R_2PCH_2CH_2PR_2)_2]^+$.[155] On the other hand, compound $RhCl(CO)(PBu^t{}_3)_2$ represents a unique case of a Rh(I) compound with a nonplanar structure,[156] the distortion being similar to that observed for the $Ru(CO)_2(PBu^t{}_2Me)_2$ compound. Both electronic and steric arguments have been advanced to rationalize the geometry of this molecule.[156] In the tris(pyrazolyl)borate Co(I) TpCo(CO) derivatives, another rare example of high-spin d^8 system, the tripodal nature of the tridentate ligand enforces a structure of type **XXXII**, similar to that of $Fe(CO)_4$. This is reproduced rather well by DFT calculations.[157] A tetrahedral geometry, on the other hand, is observed for Co(II) derivatives, TpCoX,[158] and for Co(0) derivatives, e.g. $[TpCo(CO)]^-$.[157]

VIII. Survey of Open-Shell Organometallics

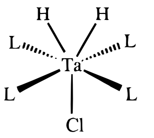
VIII.1. d^2 Systems

VIII.1.1. 16-Electron Systems

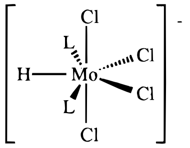
VIII.1.1.1. σ-Complexes. Systems of this type with π-neutral ligands are rare, possibly because of steric crowding in the coordination sphere and strong reducing properties for the early transition metal systems (e.g. Zr(II), Hf(II), Nb(III), etc.). The steric crowding is relieved in part for compounds with multiply bonded ligands (e.g. oxo, imido, nitrido) or for the half-sandwich and sandwich compounds, the latter ones being discussed in later sections.

Ta(III) forms the class of diamagnetic hydrido complexes TaH_2ClL_4 (L = PMe_3 or L_2 = dmpe), **XXXIII**, and $[TaH_2Cl(PMe_3)_3]_2(\mu\text{-}N_2)$.[159] Compound $TaCl(C_2H_4)(PMe_3)_4$ has not been structurally characterized but, given the high π-basicity of Ta, is likely to be best described as a tantala(III)cyclopropane derivative.[160] The diamagnetic Ta(III) alkylidene complex $TaCl(CHCMe_3)(PMe_3)_4$ also belongs to this class.[161]

Compounds $[PHR_3][MoHX_4(PR_3)_2]$ (X = Cl, Br; R = Et, Bu^n), **XXXIV**, can formally be considered as d^2 complexes. The $[MoHCl_4(PBu^n{}_3)_2]^-$ ion has a pentagonal-bipyramidal structure with axial chloride ligands and has two unpaired electrons.[162]

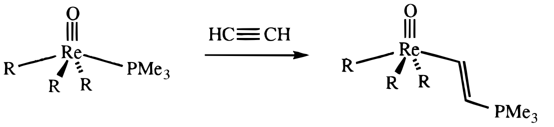


XXXIII



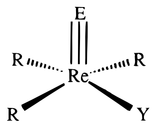
XXXIV

For rhenium(V), oxo compounds $[ReOR_4]^-$ and $ReOR_3L$,[163−166] as well as imido compounds $[Re(NR')R_4]^-$ and $Re(NR')R_3L$[167] (**XXXV**) and related nitrido compounds $Re(N)R_2L_2$,[168,169] are members of this class once the oxo or imido group is thought of as contributing six electrons via formation of a Re−O or Re−N triple (σ+2π) bond. All these compounds are square pyramidal with the multiply bonded main group atom in the apical position and diamagnetic, with the “metal lone pair” residing in the d_{xy} orbital. Formally saturated compounds are known with chelating ligands and small phosphines, e.g. $ReOX_2Me(bipy)$ (X = Cl, CH_3, CH_2SiMe_3, Np) and $ReOClMe_2(PMe_2R)_2$ (R = Me, Ph).[166,170] The addition of alkynes to $ReOR_3(PMe_3)$ affords the product of apparent insertion into the Re−P bond, see eq 6.[171]



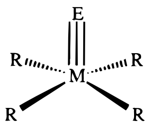
(6)

Ruthenium(VI) and osmium(VI) complexes that are isoelectronic and isostructural with the above-mentioned Re(V) compounds, e.g. $M(O)R_4$,[172−174] $[M(N)R_4]^-$,[175−177] and $M(NR')R_4$[178] (**XXXVI**) as well as mixed-ligand derivatives such as $[M(N)R_2X_2]^-$ (M = Ru, Os; X = Cl, OR', SCN, ReO_4 or X_2 = SCH_2CH_2S, SO_4, CO_3, WS_4, CrO_4),[176,177,179−182] have been described. All these compounds are diamagnetic. While the $[Os(N)R_4]^-$ complexes are inert to CO, the neutral complexes $Os(O)R_4$ and $Os(NMe)R_4$ are reductively carbonylated to $Os(CO)_5$, R_2CO, and CO_2 or MeNCO through the preliminary formation of an 18-electron CO adduct, and the methylimido reacts with $CNBu^t$ to afford the insertion product, $Os(NMe)(CH_2SiMe_3)_3[C(NBu^t)CH_2SiMe_3]$, but none coordinates simple σ-donors such as PMe_3, PPh_3, py, or MeCN.[183] The small methyl group, however, allows the achievement of a saturated configuration in the series of uncharged compounds $Os(N)Me_3L_2$ (e.g. L = THF or L_2 = tmeda).[175] In spite of the low-spin configuration and the available open coordination site, the ethyl compound $Os(O)Et_4$ is an isolable compound, albeit thermally much more sensitive than the corresponding $Os(O)Me_4$ derivative. However, the decomposition process generates extensive amounts of *n*-butane in addition to ethane and ethylene, indicating that radical-type alkyl−osmium bond cleavage also plays a role in the decomposition in addition to the expected β-H elimination process.[174]



(E = O, NR';
Y = L, R⁻)

XXXV



(M = Ru, Os;
E = O, N⁻, NR')

XXXVI

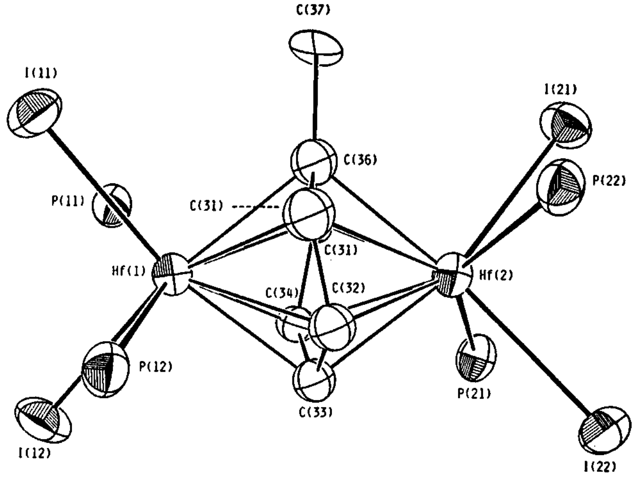
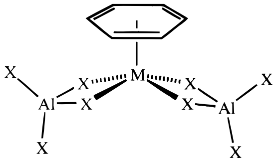


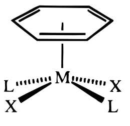
Figure 16. Side view of compound $Hf_2I_4(PMe_2Ph)_4(\mu\text{-}\eta^6{:}\eta^6\text{-toluene})$. The phosphine substituents are omitted. (Reprinted from ref 186. Copyright 1991 American Chemical Society.)

VIII.1.1.2. Half-Sandwich Complexes. A few arene compounds of group 4 M(II) metals with tetrahaloaluminate ligands with general structure $(\eta^6\text{-arene})M[(\mu\text{-}X)_2AlX_2]_2$ (M = Ti, Zr, Hf; X = Cl, Br, I), **XXXVII**, have been described.[184,185] These are all diamagnetic, even for the lighter Ti for which the pairing energy should be higher. The titanium compounds $[(arene)Ti(AlX_4)_2]$ (X = Br, I) react with CO to give dicarbonyl products formulated as salts of 16-electron cations, $[(arene)Ti(CO)_2(AlX_4)]^+AlX_4^-$, rather than as electronically saturated products.[185]

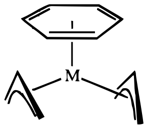
Cotton *et al.* have described an interesting dinuclear complex where two $HfI_2(PMe_3)_2$ moieties bind the opposite faces of an arene ring (see Figure 16). The electronic structure of this material involves sharing, by the two metals, of the arene electrons, while both metals can independently engage with the two arene "δ-type" acceptor orbitals, resulting in a spin-paired ground state.[186] Analogous compounds with only one $MX_2(PR_3)_2$ (X = halogen) unit bound to one face of the arene ligand, **XXXVIII** (arene = toluene; M = Zr, Hf; X = Cl, I; L = PMe_3), have also been reported, as well as related cycloheptatriene complexes.[73,187–189] These are all diamagnetic compounds. Other systems, also diamagnetic, are the bis-allyl compounds **XXXIX** (M = Zr, Hf; arene = benzene, toluene).[190]



XXXVII

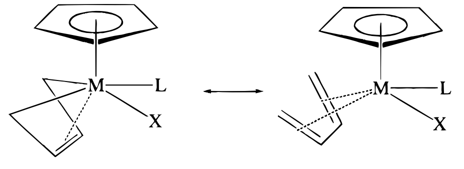


XXXVIII



XXXIX

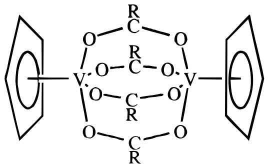
All the known 16-electron cyclopentadienyl systems of group 4 metals contain diene ligands, e.g. Cp*M(diene)ClL (M = Zr, Hf; L = THF, py, PR_3, etc.)[191] and CpM(diene)(allyl) (M = Ti, Zr, Hf; diene = butadiene; allyl = 1-methylallyl),[192,193] and structural work indicates that the terminal carbons are closer to the metal center than the internal ones. This can be viewed as an extreme case of metal-to-butadiene back-bonding, i.e. the orbital where the two highest electrons reside has more carbon than metal character, and the electronic configuration at the metal is formally d^0 (e.g. **XL** rather than **XLI**). Stable compounds with less π-acidic ligands have not been described. Reactive intermediates of this type may be involved, for instance, in the ethylene dimerization reaction catalyzed by $CpZrMe(dmpe)_2$[194] and in the disproportionation reaction of 1,3-cyclohexadiene to benzene and cyclohexene catalyzed by $(\eta^5\text{-cyclohexadienyl})Zr(H)(dmpe)_2$.[195]



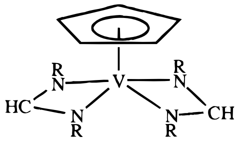
XL XLI

Group 5 metals (V, Nb, Ta) form an extensive series of four-legged piano stool $(ring)MX_2L_2$ complexes. Whereas all the above group 4 complexes are diamagnetic, the group 5 derivatives (oxidation state III) are always paramagnetic (S = 1) for V, and the spin state depends on the nature of the coordination sphere for Nb and Ta.

Razuvaev *et al.* reported in 1974 the formation of $CpV(O_2CR)_2$ compounds from the interaction of vanadocene and carboxylic acids.[196] These materials were later found to be dinuclear, carboxylato-bridged compounds (**XLII**).[197,198] However, the absence of a metal–metal bonding interaction is consistent with a 16-electron configuration around each vanadium center. Carbamates have an analogous tetrabridged dinuclear structure.[199] These dinuclear systems show reduced magnetic moments (1.4–1.8 μ_B per V atom) because of antiferromagnetic coupling between the two spin triplet metal centers.[199,200] Dinuclear tetrathiolato-bridged compounds, $[CpV(\mu\text{-}SR)_2]_2$, also have antiferromagnetically coupled S = 1 metal centers. A mononuclear system is obtained from Cp_2V and formamidine (**XLIII**).[201] An analogous mononuclear structure has been proposed for paramagnetic (μ_{eff} = 2.76 μ_B) CpV(tmtaa).[202]



XLII

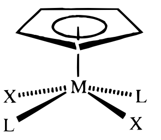


XLIII

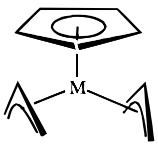
Stable group 5 $CpMX_2L_2$ compounds (**XLIV**) are an interesting class of molecules from the magnetic point of view. For vanadium,[38,72,203,204] dihalide as well as dialkyl and mixed halide–allyl complexes have been reported, and these are always paramagnetic. For Nb, only dihalide derivatives are known.[74,205] The room temperature contact-shifted NMR properties reported for $Cp^*NbCl_2(PMe_3)_2$, $Cp^*NbCl_2(PMe_2Ph)_2$ and $Cp^*NbCl_2(dppe)$ have led to the proposal of a spin triplet ground state.[74] We have more recently shown by variable-temperature NMR that $Cp^*NbCl_2(PMe_3)_2$

is indeed a Curie–Weiss spin triplet paramagnet, but the related complex $Cp'NbCl_2(PEt_3)_2$ has a diamagnetic ground state and spin singlet–triplet gap of ~800 cm^{-1}, whereas $CpNbCl_2(dppe)$ is diamagnetic.[76] Few tantalum derivatives are known. Interestingly, whereas $Cp^*TaCl_2(PMe_3)_2$ is paramagnetic ($\mu_{eff} = 2.1\ \mu_B$),[206] the corresponding derivative $Cp^*TaMe_2(bipy)$ has been described as a diamagnetic compound.[207] A lower than expected magnetic moment for $Cp^*TaCl_2(PMe_3)_2$ may be caused by an equilibrium with a diamagnetic, presumably dimeric $\{Cp^*TaCl_2(PMe_3)\}$, or by a spin equilibrium for the 16-electron species.[206] A diamagnetic $CpTaCl_2(PMe_2Ph)$ compound, also described as a dimer, has been described.[208] The difference in spin state between $Cp^*TaCl_2(PMe_3)_2$ and $Cp^*TaMe_2(bipy)$ is likely caused by the change from the halides to the less electronegative alkyl ligands with a resulting decrease of pairing energy, since the change from the phosphine ligands to the N-donor ligand usually causes the opposite effect (see section IV.3). No examples in this class with N-donor ligands for V(III) or Nb(III) appear to be known.

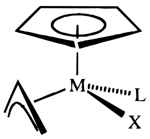
Cp bis-allyl compounds (**XLV**) are also well represented and all paramagnetic for V,[209,210] whereas the only representative for a heavier metal, $Cp^*Ta(\eta^3\text{-}PhC_3H_4)_2$, is diamagnetic.[211] Mixed-ligand $CpM(\eta^3\text{-allyl})XL$ (**XLVI**) are also known, but only for V(III).[72,209,212] A particular case, formed by coupling of a diphenylacetylene and a butadiene ligand on V(I), is shown in eq 7.[213] Other allyl derivatives are also formed by coupling reactions between coordinated diene ligands on 16-electron V(I) and olefins or dienes.[209]



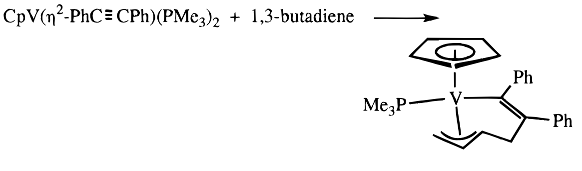
XLIV



XLV



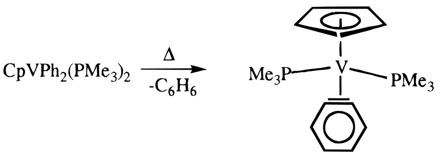
XLVI



(7)

Compounds of type $CpMX_2(\eta^4\text{-diene})$ have been described for Nb and Ta,[214] all being diamagnetic, but like for Group 4 $CpMXL(\eta^4\text{-diene})$ systems, structural work indicates that they are more correctly formulated as but-2-ene-1,4-diyl derivatives of M(V). A similar picture is also valid for $CpNbCl_2(alkyne)$ complexes.[215]

There are no reports of simple ligand additions to the 16-electron vanadium(III) complexes to form stable 18-electron adducts. For instance, replacement of a 2-electron chloride ligand with a 4-electron allyl ligand in $CpVClMe(PMe_3)_2$ affords the 16-electron, S = 1 compound $CpV(\eta^3\text{-}C_3H_5)Me(PMe_3)$ with expulsion of one molecule of PMe_3.[72] Certain reactions may involve an initial ligand addition. The CO addition to $CpVR_2(PMe_3)_2$ (R = Me, Ph) to produce RCOR and the 18-electron $CpV(CO)_2(PMe_3)_2$ could in principle involve preliminary CO addition with spin pairing, or PMe_3 dissociation.[49] The reaction between $CpV(\eta^3\text{-allyl})_2$ complexes with CO induces coupling of the two allyl functions and formation of $CpV(CO)_4$.[209,210] It is likely that the first step of this reaction is CO addition to form a $CpV(allyl)_2(CO)$ intermediate, although this step may be preceded by rearrangement of one of the two allyl ligands to η^1. The PMe_3 exchange on $CpVMe_2(PMe_3)_2$ is described as a slow reaction, and the ligand scrambling between $CpVMe_2(PMe_3)_2$ and $CpVCl_2(PMe_3)_2$ goes to completion in ~12 h at 25 °C.[49] Both these reactions could occur via preliminary PMe_3 dissociation or could be associative with a spin-state change. A related situation occurs for the β-H elimination process in β-H-containing $CpVR_2(PMe_3)_2$ compounds. For instance, reaction of $CpVMeCl(PMe_3)_2$ with Bu^nLi yields the stable V(I) 1-butene complex $CpV(\eta^2\text{-}CH_2{=}CHEt)(PMe_3)_2$.[203] The β-H elimination process on the presumed $CpVMeBu^n(PMe_3)_2$ intermediate could occur after preliminary PMe_3 dissociation or Cp ring slippage, or else must involve spin pairing. The same applies to the elimination of benzene from $CpVPh_2(PMe_3)_2$ to afford a benzyne complex, see eq 8.[204] The latter compound is considered as a high-spin d^2 V(III) benzometallacyclopropene with the benzyne regarded as a 2-electron ligand and differs from diamagnetic $CpV(PMe_3)_2(alkyne)$ complexes, where the alkyne acts as a 4-electron donor (see section VIII.3.1.3).

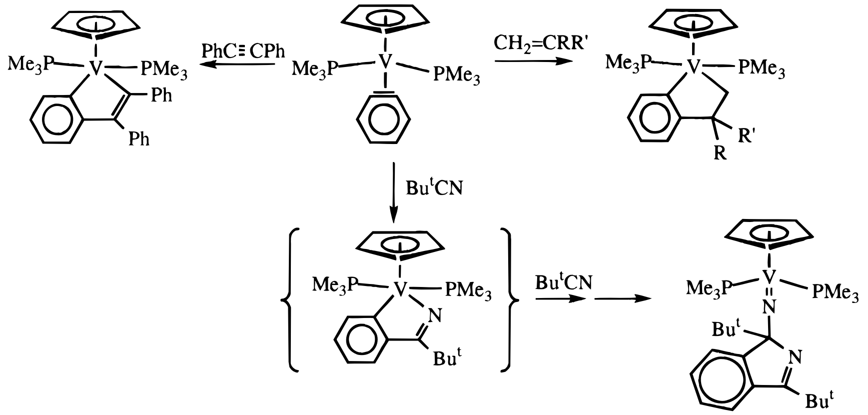


(8)

The addition of H_2 to $CpVMe_2(PMe_3)_2$ to generate CH_4 and a black, uncharacterized solid, is suppressed by the presence of free PMe_3, strongly indicating that at least in this case the reaction proceeds via predissociation of PMe_3.[72] Other evidence for a dissociative mechanism is the isolation of 14-electron and 12-electron dialkyl compounds by the use of bulkier alkyl groups (see sections VIII.1.2.3 and VIII.1.3). The benzyne compound product of eq 8 inserts alkynes, alkenes, and nitriles, to afford metallacycles (see Scheme 6). These reactions are most probably preceded by phosphine dissociation, thereby avoiding electron pairing, as indicated by the decrease of the rate of reaction by the addition of extra PMe_3 in some cases.

It appears that the energy required to pair two electrons for this V(III) system and to overcome the steric resistance of the coordination sphere is rather high. However, an exception to this rule is found for the alkylidene complexes $CpV(CHCMe_3)L_2$ (L = PMe_3 or L_2 = dmpe), where the carbene ligand has distinct nucleophilic character (i.e. X_2 type rather than L type). These compounds are diamagnetic, possibly because one of the two metal orbitals available for the two metal electrons is engaged in an agostic interaction with the alkylidene hydrogen, as unambiguously shown by the X-ray structure of the dmpe

Scheme 6



derivative (Figure 17), leaving the other orbital to hold the last two electrons.

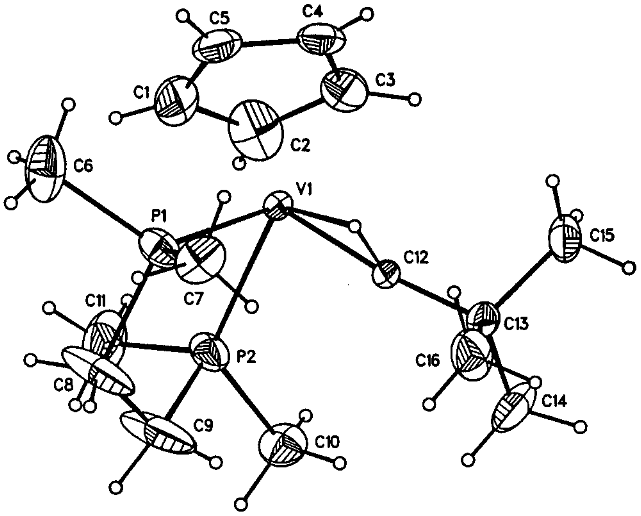
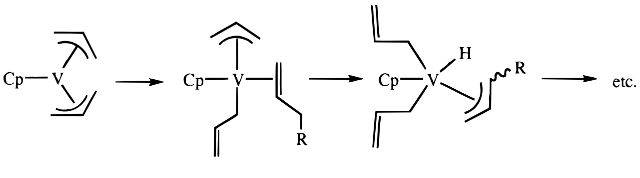


Figure 17. Molecular structure of $CpV(CHCMe_3)(dmpe)$. (Reprinted from ref 203. Copyright 1993 American Chemical Society.)

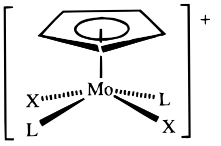
A reaction that also seems to involve electron pairing is the $CpV(\eta^3\text{-allyl})_2$-catalyzed olefin isomerization. Initial coordination of the olefin can involve preliminary η^3-to-η^1 rearrangement of one allyl ligand, but the 1−3 hydrogen shift must then take place via C−H oxidative addition to form a 16-electron (η^3-allyl)hydrido intermediate (Scheme 7) of formally d^0 V(V).[210] Consistent with this view, the related $CpTi(\eta^3\text{-allyl})_2$ complex is not a catalyst for this reaction.

Scheme 7

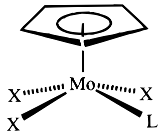


For S = 1 half-sandwich complexes of niobium, ligand addition seems more facile, provided the steric requirements of both the coordination sphere and the entering ligand allow the addition. For instance, although the reduction of Cp^*NbCl_4 with sodium in the presence of phosphines affords only 16-electron $Cp^*NbCl_2(PR_3)_2$ derivatives,[74,205] the corresponding reduction of $CpMCl_4$ (M = Nb, Ta) gives instead the 18-electron $CpMCl_2(PMe_3)_3$.[216] These are described as very labile complexes, one or more PMe_3 being readily displaced by other ligands, and these exchange reactions no doubt involve PMe_3 dissociation to afford a $CpMCl_2(PMe_3)_2$ intermediate. The sterically less demanding isonitrile ligands can afford 18-electron Cp*Nb(III) compounds, e.g. $Cp^*NbCl_2(CNXyl)_3$.[217] Compound $Cp^*Ta(\eta^3\text{-}PhC_3H_4)_2$ reacts with CO, but this reaction does not stop at the level of the presumed adduct, but rather continues with additional CO coordination and reductive coupling of the two allyl groups to afford 1,6-diphenyl-1,5-hexadiene and $Cp^*Ta(CO)_4$.[211]

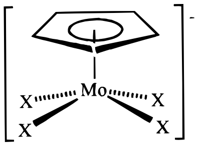
There are no half-sandwich compounds of Cr(IV). Mo(IV) complexes are always spin triplet (except for the tetrathiolato anions $[CpMo(SR)_4]^-$ or when other strong π-donor ligands are present), whereas W(IV) compounds exist only when stabilized by π-donor thiolato ligands and are always diamagnetic. The chemistry of Mo(IV) complexes of type $[(ring)MoX_2L_2]^+$, $(ring)MoX_3L$, and $[(ring)MoX_4]^-$ (**XLVII**, **XLVIII**, and **IL**) with X = halide has been recently developed in our own laboratory.[32,68,75,218−220] These complexes are always paramagnetic. The cationic and neutral complexes are able to coordinate an additional ligand to afford diamagnetic 18-electron complexes when the steric requirements are not too stringent. For instance, while $Cp^*MoCl_3(PMe_3)$ does not coordinate additional PMe_3, both $CpMoCl_3L$ (L = PMe_3, PMe_2Ph) complexes afford the corresponding $CpMoCl_3L_2$ in the presence of excess phosphine.[32,75] Complex $[CpMoCl_2(PMe_3)_2]^+$ adds Cl^- to afford $CpMoCl_3(PMe_3)_2$, whereas $[CpMoI_2(PMe_3)_2]^+I^-$ is a stable salt.[75] The iodide for chloride substitution on $[CpMoX_2(PMe_3)_2]^+$ is extremely rapid in comparison with the analogous substitution on the neutral $CpMoX_2(PMe_3)_2$; this is the reason for the electron transfer (oxidative) chain-catalyzed $CpMoX_2(PMe_3)_2/X'^-$ exchange, which is apparently the only reported example of such catalysis where the even-electron system is faster than the odd-electron one for orga-



XLVII



XLVIII

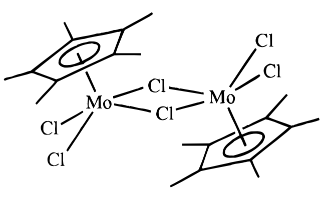


IL

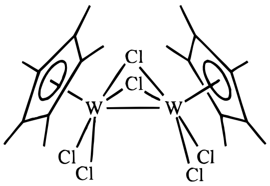
nometallic systems.[75] Complex $[CpMoCl_2(dppe)]^+$, obtained by Cl^- abstraction from $CpMoCl_3(dppe)$ with $AgBF_4$, was not magnetically characterized, but is also likely to adopt a spin triplet configuration.[221]

Although $Cp^*MoCl_3(PMe_3)$ is paramagnetic, the related $Cp^*MoHCl(PPh_2)(PMe_3)$ has a spin singlet ground state, certainly the result of the stronger π interaction of the phosphido ligand.[103] Whereas the tetrahalocomplexes $[Cp^*MoX_4]^-$ (X = Cl, Br, I) are all paramagnetic,[68,219,220] the related tetrathiolato derivatives $[CpM(SR)_4]^-$ (M = Mo, W) are diamagnetic.[222-224] Other analogous 16-electron anionic complexes are the $[Cp^*Mo\{S(CH_2)_nS\}_2]^-$ ($n = 2, 3$).[225] Complexes $[CpW(EC_6F_5)_4]^-$ (E = S, Se) are effectively saturated through π-donation and are diamagnetic, as well as $CpW(EC_6F_5)_3(CO)$ (E = S, Se).[222,226]

The dinuclear $[Cp^*MoX_3]_2$ (X = Cl, Br, I) compounds adopt the *anti* geometry illustrated in **L** with antiferromagnetic coupling between the two S = 1 metal centers and no direct metal−metal bond.[68,219] The corresponding W compounds, on the other hand, appear to be diamagnetic and are likely to have the alternative *syn* geometry illustrated in **LI**.[227] The reason for this difference may lie in the greater strength of the metal−metal bonds for W.

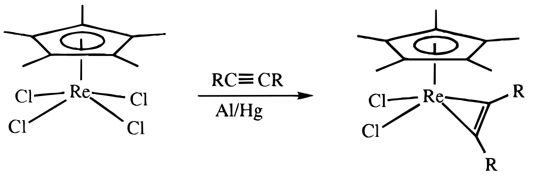


L



LI

The only examples in this class for group 7 metals are rhenium compounds. Cp^*ReCl_4 is described as a paramagnetic compound on the basis of the failure to observe a ^{13}C-NMR spectrum, but detailed magnetic studies have not been reported. Its unshifted ^1H-NMR resonance at 2.22 ppm (CD_2Cl_2, 0 °C), however, indicates a spin singlet ground state.[69] Mixed chloro−alkyl complexes $Cp^*ReCl_nR_{4-n}$, on the other hand, have an unclear trend of magnetic properties. The ^1H-NMR resonance of Cp^*ReCl_3Me is found at +36.5 at +50 °C and at +13.5 at −50 °C;[228] in spite of the large contact shift, a greater shift at a greater temperature is a signature of a singlet ground state. Compound $Cp^*ReCl_2Me_2$, however, is reported as diamagnetic, whereas $Cp^*ReClMe_3$ and Cp^*ReMe_4 are paramagnetic.[229,230] Cp^*ReMe_4 is assigned a triplet ground state and the NMR spectrum is described as temperature dependent, but the temperature dependence of the chemical shift is not described in detail.[229] Both $Cp^*ReCl_nMe_{4-n}$ complexes (n = 4, 3) readily add PMe_3 to afford the saturated $Cp^*ReCl_nMe_{4-n}(PMe_3)$ adducts with pseudooctahedral geometries.[228,231] $Cp^*ReEtCl_3$ cannot be isolated, because it spontaneously eliminates ethylene and ethane to afford metal−metal-bonded $[Cp^*ReCl_3]_2$.[232] Compounds Cp^*ReCl_2O and $Cp^*ReCl_2(NR)$ and dialkyl derivatives are also formally 16-electron,[69,233] but strong π-donation from the oxo or imido ligand affords effectively saturated, diamagnetic compounds.[234] The reduction of Cp^*ReCl_4 in the presence of alkynes affords the derivatives **LII** (eq 9), also to be considered as 16-electron rhenacyclopropene derivatives of Re(V). These and corresponding dialkyl derivatives are diamagnetic. These compounds can further insert unsaturated organic molecules under acid-catalyzed conditions to afford electronically saturated derivatives.[235,236]

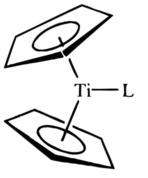


(9)

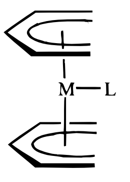
LII

VIII.1.1.3. Sandwich Derivatives. Complexes of type $(ring)_2Ti(L)$ (**LIII**) have been described. When L is an olefin, there is a question whether the compounds should be described as d^2 ML or d^0 MX_2. For instance, the structure of diamagnetic $Cp^*_2Ti(C_2H_4)$ exhibits a certain degree of metallacyclopropane character (C−C = 1.438(5) Å),[237] For the paramagnetic ($\mu_{eff} = 2.18 \pm 0.01$ μ_B per Ti) dinitrogen adduct $Cp^*_2Ti(\mu\text{-}N_2)TiCp^*_2$,[238] the d^2 configuration seems appropriate. At lower temperature, additional N_2 adds to the system to produce an unstable $[Cp^*_2Ti(N_2)]_2(\mu\text{-}N_2)$.[238] An elusive bis(dinitrogen) adduct, $Cp^*_2Ti(N_2)_2$, has also been described, although its observed paramagnetism is not consistent with the 18-electron configuration of the proposed formulation.[239] These systems undergo facile reactions with a variety of substrates, e.g. CO, isocyanides, olefins, and also H_2.[237] While PPh_3 only affords the 16-electron, diamagnetic $Cp_2Ti(PPh_3)$,[240] the smaller PMe_3 ligand only affords an 18-electron bis-adduct, $Cp_2Ti(PMe_3)_2$, although this product can release one PMe_3 ligand under very mild conditions in a variety of reactions.[241]

Bis(pentadienyl)titanium (“open titanocene”) derivatives (**LIV**) are similar to the metallocene derivatives but the greater steric demands of the Pdl ligands with respect to the Cp ligand allows the isolation of diamagnetic monoadducts with ligands, such as CO, PF_3, and a variety of phosphines and phosphites,[242-247] which form only bis-adducts of titanocene. No tendency of these compounds to reach a saturated configuration has been observed, even with CO, presumably for steric reasons. Sixteen-electron adducts with CO, phosphines and phosphites have also been decribed for “half-open” titanocenes, e.g. compounds with one pentadienyl and one cyclopentadienyl ligand (**LV**).[248-250] These derivatives are also diamagnetic. The CO adduct establishes an equilibrium with the 18-electron bis-adduct, $Cp(Pdl)Ti(CO)_2$.[249] It has been shown that the open penta-

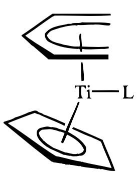


LIII



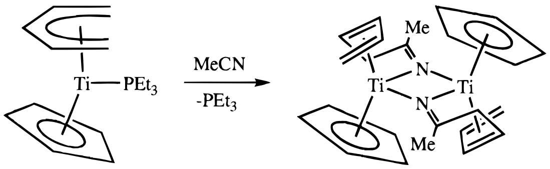
(M = Ti, Zr, Hf)

LIV



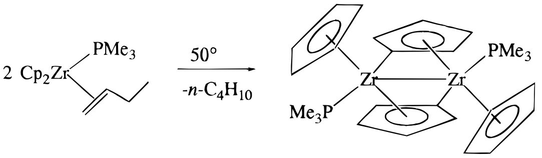
LV

dienyl ligand is at one time more reactive and more strongly metal bound relative to the cyclopentadienyl ligand: although the Pdl ligand establishes a tighter bonding interaction with Ti in Cp(Pdl)Ti(PEt$_3$) relative to Cp, the reaction with MeCN affords a coupling product as shown in eq 10.[248,249]



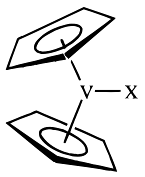
(10)

Ligand adducts of zirconocene and permethylzirconocene are in general saturated complexes of type (ring)$_2$ZrL$_2$.[241,251] No stable 16-electron Cp$_2$ZrL or Cp*$_2$ZrL compound has been described, such complexes being however proposed as intermediates in a variety of reactions.[252−254] Thermally induced olefin dissociation from Cp$_2$Zr(PMe$_3$)(1-butene) yields a dinuclear product of intermolecular C−H oxidative addition (see eq 11).[255] The dinuclear complex [Cp*Zr(N$_2$)]$_2$(μ-N$_2$) reversibly releases N$_2$ to afford "Cp*$_2$Zr", without the observation of a 16-electron intermediate.[256] In line with the known greater steric demand of open pentadienyl ligands, however, open zirconocenes form stable, diamagnetic 16-electron monoadducts, (η^5-2,4-C$_7$H$_{11}$)$_2$ZrL and (η^5-C$_5$H$_7$)$_2$ZrL (L = tertiary phosphine). These derivatives are, however, quite labile and relatively bulky phosphine ligands are readily replaced by smaller phosphines or phosphites.[257,258] Bis-adducts with an 18-electron configuration are isolated only for L = CO or chelating diphosphine ligands, e.g. dmpe. Diamagnetic, 16-electron monophosphine adducts of open hafnocene have also been reported.[257]



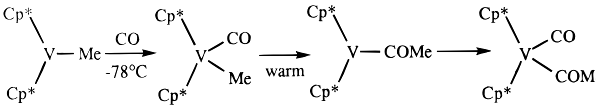
(11)

Cp$_2$VX (**LVI**) derivatives have been extensively investigated and are all spin triplet systems, except for X = N(SiMe$_3$)$_2$;[259] in this case, the strong π-donating properties of the ligand could be responsible for the electron pairing. The first derivatives were described by de Liefde Meijer for X = halide.[260] Other derivatives have X = alkyl, aryl, alkylthiolate, trialkylstannyl, etc.[96,101,102,116,259,261−274] Initial claims as to the diamagnetism of some of these compounds[259,268] have subsequently been proven incorrect.[273] The π-donating properties of the thiolato ligand are still insufficient to cause spin pairing, as compounds Cp$_2$V(SR) (R = Me, Et, Ph) are also paramagnetic.[263] The use of sterically encumbering alkyls (e.g. Pr^i, Bu^t)[264] or allyls (e.g. 3-methyl-2-butenyl, 2-*tert*-butylallyl)[275] leads only to reduction to Cp$_2$V. It is notable that even the allyl derivatives, with the potential of giving saturated (therefore diamagnetic) products, still afford complexes with two unpaired electrons with a presumably η^1-bonded allyl ligand.[275] The same is true for the tris-cyclopentadienyl compound.[275]



LVI

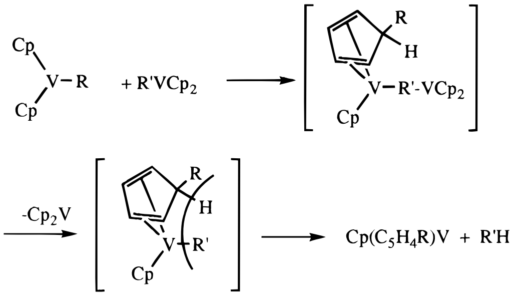
The simple alkyl, alkenyl, and alkynyl derivatives thermally decompose presumably by homolytic dissociation of the V−R bond,[273,276] while the analogous compounds with peralkylated Cp rings are more stable and melt without decomposition. The greater thermal stability of Cp$_2$V(CH$_2$C$_6$H$_4$-*o*-NMe$_2$) and Cp$_2$V(C$_6$H$_4$-*o*-CH$_2$NMe$_2$)[101,277] with respect to Cp$_2$VR was attributed to chelation by the dimethylamino function,[269,277] but the measured magnetic moment of 2.6 μ_B for both compounds militates against the formation of an electronically saturated product. A structure determination on these complexes has not been carried out, and analogous genuine 16-electron Cp$_2$VR complexes do not show a tendency to bind hard (O- or N-based) ligands to afford 18-electron adducts. The relatively high thermal stability of Cp$_2$VR compounds with β-H containing alkyl groups (e.g. Et, Pr^n, Bu^n, etc.)[264] can be understood on the basis of the necessary and unfavorable electron pairing in order to accomplish the β-H elimination process. This lack of reactivity does not seem to be determined by thermodynamics, because in the related Cp* system the hydride derivative Cp*$_2$VH has been prepared and shown not to react with C$_2$H$_4$, even under high pressures.[116] Carbon monoxide, however, does add to the same hydride derivative to afford a stable 18-electron Cp*$_2$VH(CO) adduct, providing a rare example of an electron pairing reaction for this class of (ring)$_2$VX compounds.[116] The same electron pairing occurs during the H/D exchange process for the Cp*$_2$VH compound when exposed to D$_2$[116] and during the addition of CO to Cp*$_2$VMe, but the latter reaction continues with CO insertion and further coordination as shown in eq 12, each intermediate being detected by ^{1}H-NMR or IR spectroscopy.[116] CO addition to Cp$_2$V(η^1-C$_3$H$_5$), on the other hand, induces migration of the allyl ligand to a Cp carbon, to generate CpV[η^4-C$_5$H$_5$(C$_3$H$_5$)](CO)$_2$.[278] CO also adds to Cp$_2$VI and to Cp$_2$V(SR) (R = Me, Ph), although in these cases only an equilibrium is established with the respective diamagnetic adducts;[81] the CO addition to Cp*$_2$VX (X = I, CN, SAr) is equally reversible.[279] (Ind)$_2$VI, on the other hand, does not absorb CO unless in the presence of NaBPh$_4$, in which case [(Ind)$_2$V(CO)$_2$]$^+$ is obtained.[280] Analogously, [Cp$_2$V(CO)$_2$]$^+$,[81,263] [Cp*$_2$V(CO)$_2$]$^+$,[279] and [Cp*$_2$V(CNBu^t)$_2$]$^+$ derivatives are obtained under appropriate conditions from the corresponding 16-electron precursors.[279]



$$\mathrm{Cp^*_2V{-}Me} \xrightarrow[-78^\circ\mathrm{C}]{\mathrm{CO}} \mathrm{Cp^*_2V(CO)(Me)} \xrightarrow{\text{warm}} \mathrm{Cp^*_2V{-}COMe} \longrightarrow \mathrm{Cp^*_2V(CO)(COMe)} \qquad (12)$$

The thermal decomposition of Cp$_2$VAr in the solid state gives ArH, Cp$_2$V, and Cp(C$_5$H$_4$R)V according the proposed mechanism shown in Scheme 8. Labeling

Scheme 8



cross-over experiments using C_6H_5 and C_6D_5 derivatives indicate that the hydrogen abstraction from Cp is intermolecular, whereas the arylation of the Cp ring is intramolecular. This result also excludes homolytic dissociation of the V−Ar bond with production of aryl radicals as a mechanistic pathway.[267]

An EHMO calculation on Cp_2VPh indicates that the two metal-based orbitals are very close in energy (0.2 eV), and this was taken to indicate that the high-spin situation is preferred, but no estimates of pairing energy were provided. The calculation, however, accurately predicts that the benzene plane in Cp_2VPh coincides with the Cp_2V wedge plane (for steric reasons), whereas the same plane in Cp_2VCCPh will be perpendicular to the Cp_2V wedge plane (for electronic reasons). Electronically, a perpendicular orientation should always be preferred because of the π-interaction between the benzene π-system and the highest energy metal orbital.[273]

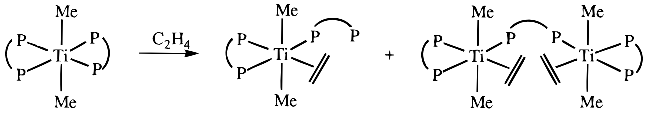
The 16-electron cationic $[Cp_2VL]^+$ derivatives with L = acetone or pyridine, again with two unpaired electrons, are obtained by treatment of Cp_2VCl with aqueous $NaBPh_4$ in the presence of the appropriate ligand.[100] When stronger ligands are present, however, these systems afford diamagnetic, 18-electron $[Cp_2VL_2]^+$ products (e.g. L = CO, CNCy, $PHPh_2$, or L_2 = dppe).[100,281]

Several Cp_2MX (M = Nb, Ta; X = π-donor ligand) molecules, either with unsubstituted[282−285] or substituted[286−289] Cp rings have been reported. Although several of these derivatives have been claimed as mononuclear, no molecular weight determination has apparently been reported to establish the nuclearity. All these compounds are diamagnetic and many react readily with neutral donors to form Cp_2MXL derivatives. The lack of a reaction between Cp_2NbBr and CO or PMe_2Ph (whereas Cp_2NbBrL products are readily obtained by reduction of Cp_2NbBr_2 in the presence of L) points to a dinuclear, bromo-bridged formulation for this derivative.[284] Electrochemical reductions of Cp_2NbCl_2 under a variety of conditions have been suggested to proceed via the 16-electron Cp_2NbCl species,[290,291] whereas the polarographic and cyclic voltammetric reduction of $(\eta^5\text{-}C_5H_4SiMe_3)_2NbCl_2$ in the absence of trapping ligands gives indication for the dimerization of an intermediate unstable $(\eta^5\text{-}C_5H_4SiMe_3)_2NbCl$[292] and, finally, the reduction of $[\eta^5\text{-}C_5H_3(SiMe_3)_2]_2NbCl_2$ is said to produce a stable 16-electron $[\eta^5\text{-}C_5H_3(SiMe_3)_2]_2NbCl$.[293] When X is a π-neutral ligand, Cp_2MX (M = Nb, Ta) complexes are at best available in small concentrations in equilibrium with electronically saturated isomers derived from C−H oxidative addition processes, for instance $Cp^*_2Ta(CH_3)$ with $Cp^*_2TaH(CH_2)$,[294] $Cp^*_2Ta(CH{=}CH_2)$ with $Cp^*_2TaH(C{=}CH_2)$,[294] and Cp^*_2TaPh with $Cp^*_2TaH(\eta^2\text{-}C_6H_4)$.[295] The "$Cp_2Ta(CH_3)$" species, obtained in situ by irradiation of $Cp_2Ta(CH_3)(C_2H_4)$ or by thermolysis of $Cp_2Ta(CH_3)(PMe_3)$, abstracts heteroatoms from oxiranes, thiiranes, and aziridines to give $Cp_2Ta({=}E)(CH_3)$ (E = O, S, NR).[296] Cp_2NbH and the tantalum analogue are the probable intermediates in the thermal decomposition of Cp_2MH_3 to the dimeric "metallocenes" and in a number of other reactions.[297−299] The previously proposed intermediacy of a 16-electron Cp_2NbPr^i complex in the intramolecular hydride/methylene and hydride/methyl H scrambling process for $Cp_2Nb(H)(CH_2{=}CHMe)$ has been questioned in favor of saturated agostic intermediates. However, the slower exchange between the two inequivalent Cp rings must still proceed via a 16-electron intermediate.[300]

No 16-electron group 6 metallocene derivatives of d^2 M(IV) have been isolated, but the intermediacy of $[Cp_2WH]^+$ and $[Cp_2WR]^+$ in chemical transformations has been proposed.[120,301] If Cr(IV) derivatives of type $[(ring)_2CrX]^+$ (and perhaps also Mo(IV) analogues) could be isolated, they would likely adopt a spin triplet ground state.

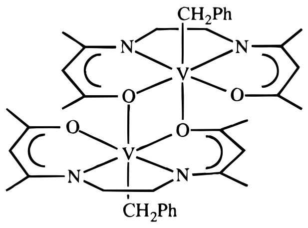
VIII.1.2. 14-Electron Systems

VIII.1.2.1. σ-Complexes. The Ti(II) complex *trans*-$TiMe_2(dmpe)_2$, recently described by Girolami,[135] is diamagnetic unlike the similar $TiX_2(dmpe)_2$ (X = Cl, BH_4) compounds. The reason for this difference is likely related to the lower pairing energy in the more covalent alkyl complex (see also section IV).[53] This compound reacts at low temperature with excess ethylene to afford a mixture of two compounds, as shown in eq 13, which are themselves diamagnetic 14-electron Ti(II) materials and which become active catalysts for the selective dimerization of ethylene to 1-butene upon warming above −40 °C.[302] No analogous Zr(II) or Hf(II) compounds appear to have been described.



(13)

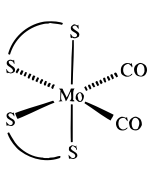
Few (σ-organo)vanadium(III) complexes have been described, many of them only assumed to be 6-coordinate without structural confirmation. An example is $Li_3[V(DPE)_3]{\cdot}6THF$, with two unpaired electrons (μ_{eff} = 2.89 μ_B).[303] Other less thoroughly characterized examples are $2PhCH_2V(acac)_2{\cdot}Mg(acac)_2$, $3PhCH_2V(acac)_2{\cdot}Al(acac)_2$, $RV(acac)_2{\cdot}THF$, and a variety of mixed benzyl−chloro complexes.[304,305] The Schiff base complex **LVII** is a dimer in the solid state and



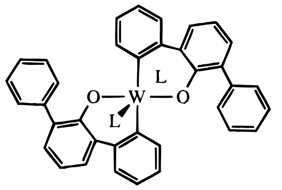
LVII

a 5-coordinate monomer in solution. The solid-state magnetic moments of this complex (2.40 μ_B) and of the methyl analogue (2.16 μ_B) indicate antiferromagnetic coupling between the two S = 1 metal centers.[306] No analogous Nb(III) or Ta(III) 6-coordinate compounds are known.

For group 6 metals, Cr(IV) has only been found in 4-coordinate derivatives (see section VIII.1.4). Six-coordinate Mo(IV) and W(IV) are common in Werner chemistry, these having a spin triplet (t_{2g}^2) ground state, and a few organometallic analogues have been described. Carbonyl derivatives of Mo(IV) are stabilized by dithiolate ligands, e.g. $Mo('S_2')_2(CO)_2$ ($'S_2'^{2-}$ = substituted 1,2-benzenedithiolate(2−)), **LVIII**. These compounds are diamagnetic.[307] The porphyrin complex Mo(TPP)(Ph)(Cl) was investigated crystallographically but not magnetically.[308] A poorly characterized $Li_2WPh_6 \cdot 3Et_2O$ is described as a black, pyrophoric, diamagnetic powder.[309] On the other hand, the more stable $LiW(C_6F_5)_5 \cdot 2Et_2O$ has a magnetic moment of 2.70 μ_B at room temperature. On the basis of the variable-temperature magnetic study, a relatively low spin−orbit coupling constant of 100 cm^{-1} is calculated, from which a distorted octahedral $[W(C_6F_5)_5(Et_2O)]^-$ geometry is proposed for the complex.[310] Incompletely characterized $W(CH_2Ph)_4(bipy)$ and $Li_2W(CH_2Ph)_6 \cdot nEt_2O$ materials have also been described.[311] Compounds $W(OC_6H_3Ph\text{-}C_6H_4)_2L_2$ (L = PMe_2Ph, $PMePh_2$) (**LIX**) are diamagnetic and readily add small molecules,[312] whereas the substitution of the phosphine ligands with N-donor ligands (e.g. py, bipy, phen), produces compounds with a thermally populated triplet state, for which the singlet−triplet gap has been quantitatively determined by variable-temperature ^1H-NMR spectroscopy.[313] A varying degree of π-accepting capability for the aromatic N-donor ligands is responsible for the gap variation along the series. Analogous Werner-type $WCl_2(OR)_2L_2$ complexes can similarly be either diamagnetic or paramagnetic.[314−316]

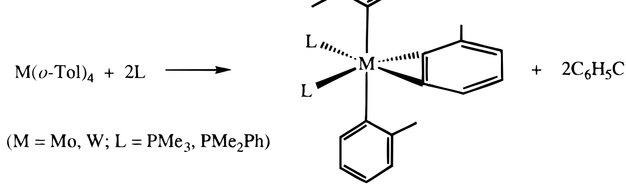


LVIII



LIX

Other compounds that may be considered to belong to this class are the "η^2-aryne" compounds (**LX**) obtained by phosphine-induced *ortho*-hydrogen elimination from $M(o\text{-}Tol)_4$ (eq 14). Their structural characterization points to their more proper description as metallacyclopropene derivatives of M(IV), and their NMR properties indicate diamagnetism.[317] The isoelectronic $[Re(o\text{-}Tol)_2(\eta^2\text{-}2\text{-}MeC_6H_3)(L)_2]^+$ cations have also been described.[318]



LX

(14)

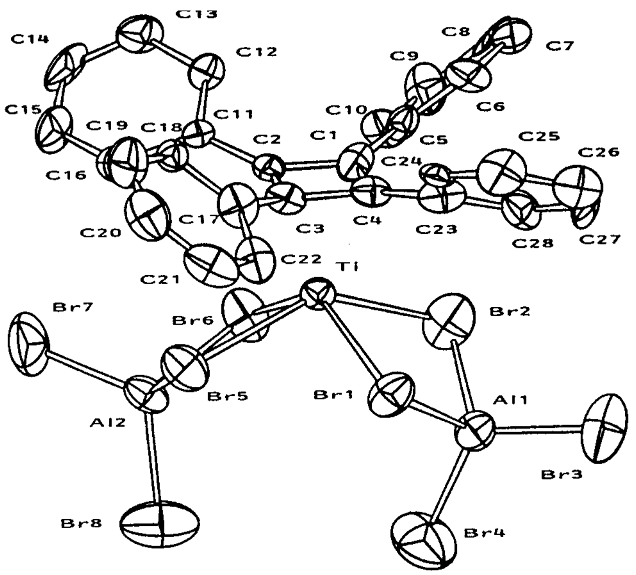
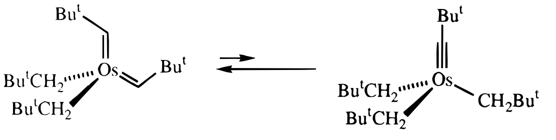


Figure 18. Molecular structure of $(\eta^4\text{-}C_4Ph_4)Ti[(\mu\text{-}Br)_2AlBr_2]_2$. (Reprinted from ref 321. Copyright 1989 VCH Verlagsgesellshaft.)

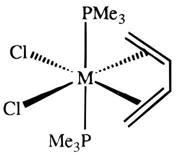
Finally, a class of diamagnetic bis-alkylidene Os(VI) complexes, $Os(=CHR)_2(CH_2R)_2$ (**LXI**), has been recently developed. These are isostructural with previously known $OsO_2(CH_2R)_2$ species but, unlike the latter, are not stabilized by additional π-donation. Interestingly, these compounds do not rearrange to the isomeric trialkylalkylidyne species which would be isostructural with known d^0 W(VI) complexes. However, the rearrangement to the trialkyl−alkylidyne isomer is believed to be a necessary step during the H scrambling process which equalizes all the α-protons on the NMR time scale (eq 15).[319]



LXI

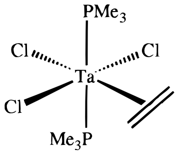
(15)

VIII.1.2.2. π-Complexes. The diamagnetic $MCl_2(PMe_3)_2(\eta^4\text{-diene})$ (M = Zr, Hf; diene = 2,3-dimethyl-1,3-butadiene, 1,3-cyclohexadiene) compounds **LXII** may be considered members of this class.[73,190] However, the structure determination of $HfCl_2(PMe_3)_2(\eta^4\text{-}CH_2{=}CMe{-}CMe{=}CH_2)$ indicates that there is a strong contribution in the diene-metal bonding of the σ^2,π-metallacyclopentene resonance form, thus the compound seems more properly described as 7-coordinate Hf(IV).[188] The same argument may be applied to compounds $TaCl_3(PMe_3)_2(C_2H_4)$ (**LXIII**)[160] and $Tp^{Me,Me}NbCl_2(RC{\equiv}CR)$ (**LXIV**)[320] as well as to the cyclobutadiene compound of titanium, $(\eta^4\text{-}C_4Ph_4)Ti[(\mu\text{-}Br)_2AlBr_2]_2$ (see Figure 18), which is a stable model of the intermediate in the cyclotrimerization of alkynes to Dewar-benzene catalyzed by (arene)$Ti(AlX_4)_2$ or by the zirconium analogue.[321]

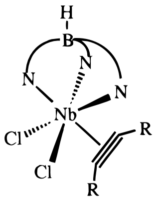


(M = Zr, Hf)

LXII

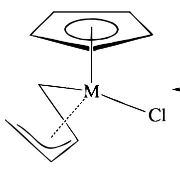


LXIII

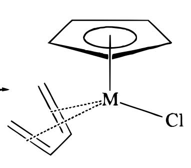


LXIV

VIII.1.2.3. Half-Sandwich Compounds. Complexes Cp*MCl(diene) have been described for M = Ti, Zr, and Hf, including the crystallographically characterized Cp*HfCl(2,3-$Me_2C_4H_4$), whose pattern of C−C and Hf−C distances is more in accord with a Hf(IV) d^0 complex containing an alkyl−allyl ligand (**LXV**) than with a diene Hf(II) complex (**LXVI**).[191,322] All these derivatives are diamagnetic. The zirconium and hafnium, but not the titanium derivatives, readily add neutral 2-electron donors to afford 16-electron adducts.



LXV

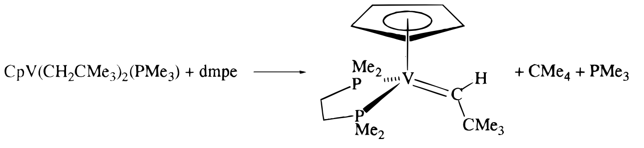


LXVI

A peculiar class of Ta(III) arene derivatives, of general formula (η^6-C_6R_6)Ta(OR′)$_n$$X_{3-n}$ and (η^6-1,3,5-$C_6Bu^t{}_3H_3$)Ta(OR′)$_2$X (n = 1, 2; X = Cl, Br, H, R, Ar), originates from alkyne cyclotrimerization reactions at reduced tantalum centers.[323−328] These compounds are diamagnetic and show extensive back-bonding to the arene ligand, such that the complexes are probably better described as tantala(V)norbornadiene derivatives, e.g. **LXVII**. The π-donation from the alkoxide ligands is probably essential for stabilizing this low-coordination environment for tantalum.

The reaction of CpVCl_2(PMe_3)$_2$ with MCH_2R (R = Ph, M = MgBr; R = Bu^t, M = Li; R = CMe_2Ph, M = MgCl) affords CpV(CH_2R)$_2$(PMe_3) (**LXVIII**) with elimination of PMe_3.[203,210] Evidently, the steric bulk of these alkyl groups prevents the second phosphine from remaining coordinated to the metal, whereas smaller alkyl groups lead to 16-electron systems without phosphine dissociation (see section VIII.1.1.2). These derivatives are paramagnetic (by ^{1}H-NMR) and thermolabile. The neopentyl compound affords an alkylidene derivative in the presence of dmpe through a process of α-H elimination (eq 16), whereas the neophyl compound undergoes orthometalation at the phenyl ring (δ-elimination; eq 17).[203] These reactions do not require spin pairing, because the metal has an empty orbital available to accept the hydride ligand and form the presumed 16-electron S = 1 intermediates.

Compounds Cp*TaMe_2(η-C_2H_4) and Cp*TaMe(PPh_2)(η-C_2H_4) may formally be considered 14-electron Ta(III) compounds. However, by analogy with the Cp*TaMe_2(η-diene) complex discussed in section VIII.1.1.2, strong back-bonding to the olefin allows these compound to be more properly described as Ta(V), d^0 complexes with tantalacyclopropane rings.[103] The phosphido derivative probably also displays a strong Ta−P π-interaction.



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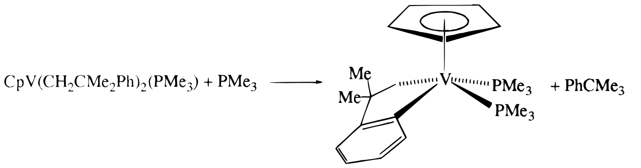
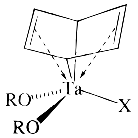
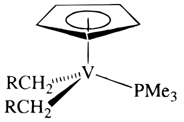


(17)

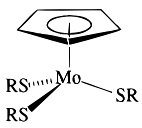
Compounds Cp*Mo(SBu^t)$_3$ (**LXIX**)[329] and [η^5:σ-$C_5H_4SiMe_2NPh$]Mo(NMe_2)$_2$ (**LXX**)[330] probably find the origins of their stability and diamagnetism in the steric hindrance of the ligands and Mo−S π-bonding.



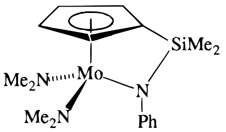
LXVII



LXVIII

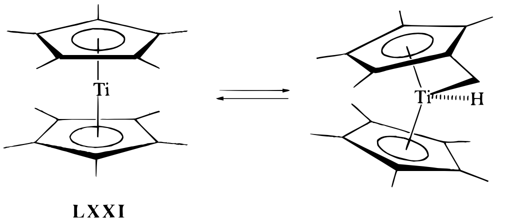


LXIX



LXX

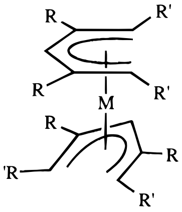
VIII.1.2.4. Metallocene Derivatives. Titanocene is an unstable molecule which has probably never been observed as such.[251] Initial reports of this compound as the product of the reaction of $TiCl_2$ with CpNa, or Cp_2TiMe_2 and H_2, or by reduction of Cp_2TiCl_2, were later proven to correspond to the isomeric dimer $Cp_2(\mu$-η^5:η^5-$C_5H_4C_5H_4)Ti_2(\mu$-$H)_2$.[331,332] A more reactive form obtained by decomposition of $[Cp_2TiH]_n$ was later proven to correspond to $Cp_3(C_5H_4)Ti_2$.[333,334] The corresponding Cp* analogue **LXXI** is a thermally sensitive but isolable compound, for which a tautomeric equilibrium between yellow spin triplet Cp*$_2$Ti and green spin singlet Cp*(η^6-$C_5Me_4CH_2$)TiH has been established by ^{1}H-NMR, see eq 18.[239] This compound reversibly adds N_2 to form various types of dinitrogen adducts, H_2 to form Cp*$_2TiH_2$, and CO to form Cp*$_2$Ti(CO)$_2$.[239,240] The analogous bis(pentadienyl)titanium complexes (“open titanocenes”, **LXXII**), on the other hand, are stable diamagnetic compounds.[335−338] These readily add small molecules (e.g. CO, PF_3, small phosphines and phosphites, but not N_2) to give equally diamagnetic 16-electron



(18)

LXXI

monoadducts.[242,243] Zirconocene and hafnocene, like



(M = Ti, Zr)

LXXII

titanocene, are not stable compounds, reactions that are supposed to produce such materials inevitably leading to C−H oxidative addition products.[251] Permethylzirconocene, like permethyltitanocene (eq 18), is presumed to exist in equilibrium with Cp*(η^6-$C_5Me_4CH_2$)ZrH,[239] A stable open zirconocene has been isolated when using the bulky 1,5-bis(trimethylsilyl)pentadienyl ligand, $[1,5\text{-}(Me_3Si)_2C_5H_5]_2Zr$.[338]

Vanadicinium cations, $[Cp_2V]^+$,[100] $[Cp^*_2V]^+$[279] and $[(C_5Me_4Et)_2V]^+$,[339] cannot be isolated without an additional donor ligand, probably because of the availability of an empty orbital on the metal center and the limited steric requirement of these cyclopentadienyl rings.

VIII.1.3. 12-Electron Systems

Five-coordinate complexes of V(III) are more common than 6-coordinate analogues. Well characterized examples are V(Mes)[CyNC(Mes)NCy]$_2$,[146] V(acacen)X (acacen = N,N′-ethylenebis(acetylacetone iminate; X = Ph, Mes),[306] and V(tmtaa)X (tmtaa = dibenzotetramethyltetraaza[14]annulene; X = Me, Bz, Ph, Mes),[202,340] all of type **LXXIII**, and $[N(CH_2CH_2Y)_2]VX_2$ (Y = NEt_2, PEt_2, PMe_2; X = Me, Ph)[145,341,342] of type **LXXIV**. $VXCl_2{\cdot}2THF$ (X = 2,4-$Me_2C_6H_4$, Mes, C_6Me_5) compounds are also described, although structural details are not given.[343] All these V(III) compounds have two unpaired electrons. The reaction between $HfCl_4$, LiEt, and tmeda affords the structurally characterized $[Li(tmeda)]_2[Hf(C_2H_4)Et_4]$ see (Figure 19). Although this has been described as an alkyl−alkene complex of Hf(II), the long C−C distance of 1.49(6) Å in the “ethylene” moiety and the lithium interactions with both C atoms of such moiety make the alternative description as a hafna(IV)-cyclopropane compound more reasonable.[302]

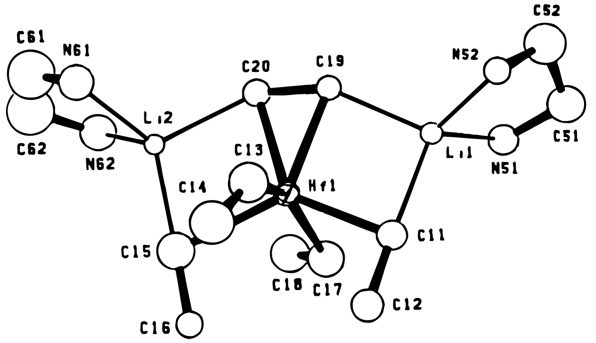
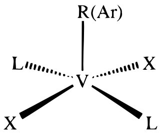
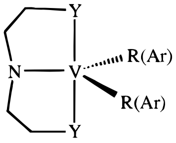


Figure 19. Molecular structure of $[Li(tmeda)]_2[Hf(C_2H_4)Et_4]$. (Reprinted from ref 302. Copyright 1993 American Chemical Society.)

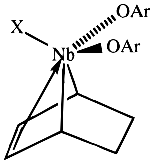


LXXIII



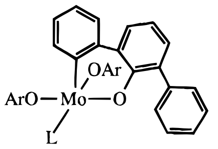
LXXIV

The reduction of $MCl_2(OAr)_3$ (M = Nb, Ta; Ar = 2,6-$Pr^i{}_2C_6H_3$) with sodium amalgam in the presence of either 1,3- or 1,4-cyclohexadiene yields the diamagnetic complexes $M(OAr)_3(\eta^4\text{-}C_6H_8)$ and $M(OAr)_2Cl(\eta^4\text{-}C_6H_8)$. The significant OAr-to-M π-donation (M−O−C angles > 150°) enhances M-to-diene backbonding, and these compounds are more properly described as M(V) derivatives as in **LXXV**.[344] The involvement of open-shell M(III), d^2 intermediates, however, is assured during the hydrogenation and disproportionation of cyclohexadiene which is catalyzed by these compounds. Five-coordinate, square pyramidal $Mo(OC_6H_3PhC_4H_4)(OC_6H_3Ph_2\text{-}2,6)_2L$ (L = $NHMe_2$, py), see **LXXVI**, show broad EPR resonances (a rare occurrence for Mo(IV) systems), but a magnetic moment has not been reported.[345]



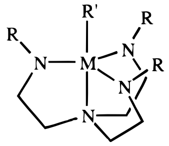
(X = Cl, OAr)

LXXV



LXXVI

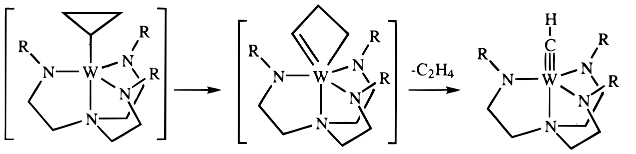
A recently developed class of Mo(IV) and W(IV) alkyls and aryls (and even hydrides) is that containing the triamidoamine ligand $[N(CH_2CH_2NR)]^{3-}$, adopting a distorted trigonal-bipyramidal structure, see **LXXVII**. These derivatives are effectively 16-electron compounds in view of the π-donation from two out of three symmetry adapted linear combinations of the amido lone pairs to the metal d_{xy} and $d_{x^2-y^2}$ orbitals. All isolated compounds are paramagnetic, since the two metal electrons occupy degenerate d_{xz} and d_{yz} orbitals. The Mo compounds are quite stable, whereas only few W analogues can be isolated (e.g. the Me, Ph and H derivatives), the others undergoing facile α-H elimination processes (e.g. see equations 19−22).[346−348] These processes involve a spin change from triplet to singlet, thus the greater reluctance of Mo to undergo these reactions may be related to greater stability or inertness of the spin triplet open-shell system.



LXXVII

The diamagnetic alkyne complexes $[MX_4(RC{\equiv}CR)]_2$ (M = Mo, W) and $ReX_5(RC{\equiv}CR)$ are presumably stabilized by the metal π-alkyne interaction.[349]

For half-sandwich complexes, the use of R groups that are bulkier than neopentyl or neophyl in the reaction of MR with $CpVCl_2(PMe_3)_2$, for instance $Y(SiMe_3)_2$ (Y = CH, N), leads to the release of both



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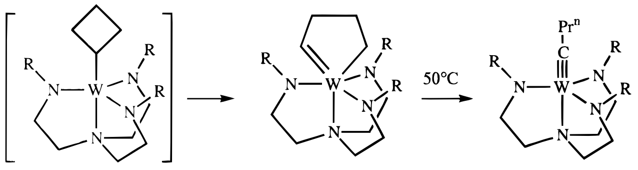

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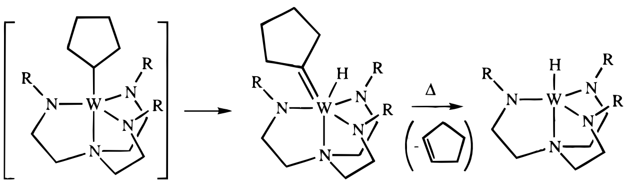

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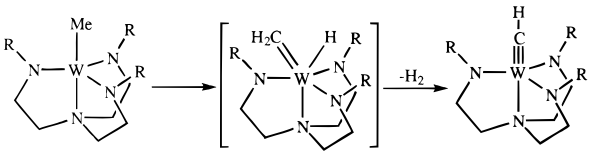
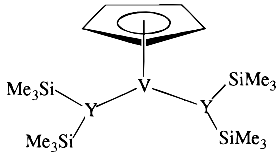


(22)

PMe$_3$ molecules and formation of the paramagnetic (by ^{1}H-NMR) CpV[X(SiMe$_3$)$_2$]$_2$ (**LXXVIII**).[203] Whereas the amido (Y = N) ligands can provide additional electron density through N lone pair π-donation, the alkyl derivative (Y = CH) is a genuine 12-electron system. Complex CpV(CH$_2$Ph)$_2$ was reported as the product of alkylation of CpVCl$_2$(PEt$_3$)$_2$ with PhCH$_2$MgBr and the IR characterization points to η^1 rather than η^3 coordination of the benzyl ligand.[210] However, in view of the existence of CpV(η^3-allyl)$_2$ and the relatively small steric encumberance of the benzyl group (at least compared with CH(SiMe$_3$)$_2$), it is hard to imagine that a 12-electron CpV(η^1-CH$_2$Ph)$_2$ would not have any tendency to retain at least one PEt$_3$ ligand. The transient {Cp*VMe$_2$}, formed from Cp*CpVMe and MeLi, dimerized spontaneously to the metal–metal bonded [CpV(μ-Me)$_2$]$_2$.[274]

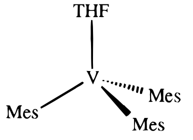


LXXVIII

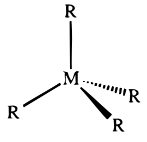
VIII.1.4. 10-Electron Systems

Four-coordinate d^2 systems can only be sterically stabilized by very bulky ligands. A variety of VAr$_3$L (Ar = Mes, 2,6-Me$_2$C$_6$H$_3$; L = THF, py, bipy) compounds, with a spin triplet ground state, have been reported.[350−352] The tetrahedral coordination geometry of VMes$_3$(THF) (**LXXIX**) was later established by crystallographic methods,[146,353] and the [VMes$_4$]$^-$ complex was assigned a distorted tetrahedral coordination on the basis of a spectroscopic investigation.[354] The availability of empty orbitals on the V(III) center makes it possible to easily add unsaturated reagents to this compound (e.g. CO, CO$_2$, RNC, RNCO, RNCNR), ultimately inserting into the V−Mes bonds.[146] There are apparently no derivatives of this type for Nb and Ta.

Stable tetrahedral CrR$_4$ compounds, **LXXX**, have been reported with R = CH$_2$SiMe$_3$,[355,356] Nor,[357] 1-Cam,[357] Bu^t,[358] Np,[359] CH$_2$CMe$_2$Ph,[359] CH$_2$CPh$_3$,[359] Mes,[360] *o*-Tol,[317] and cyclohexyl,[361] while others (R = Me, Pr^i, *s*-Bu, *n*-Bu, 3-pentyl, cyclohexylmethyl), although not isolated, have been characterized in solution by EPR spectra.[358] All these compounds have a ground-state triplet.[362] Liquid-phase EPR studies show an observable single $\Delta m = 1$ resonance even at room temperature, indicating that D and E must be very small and that the ligand field must be very nearly tetrahedral. At −196 °C a second, weaker transition corresponding to the "forbidden" $\Delta m = 2$ transition is also observed. The lines are somewhat broader for the bulkier systems (R = CH$_2$CEt$_3$, CH$_2$CMe$_2$Ph), consistent with some distortion of the tetrahedral symmetry in these cases.[363] A subsequent single-crystal EPR study on Cr(Nor)$_4$ shows the molecule to have an isotropic g factor for $\Delta m = 1$ and no $\Delta m = 2$ and double-quantum transitions, but the spectrum is rendered more complex in glasses of various organic solvents, consistent with the adoption of several conformations.[364]



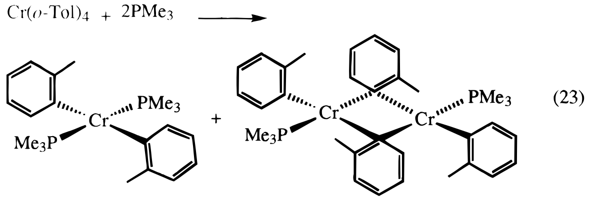
LXXIX



(M = Cr, Mo, W)

LXXX

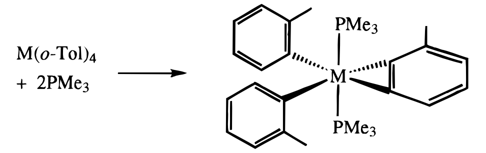
Steric protection has a lot to do with the thermal stability of these derivatives, as CrMe$_4$ starts decomposing above −78 °C, Cr(Bu^n)$_4$ and Cr(CH$_2$Cy)$_4$ are stable for several hours at 0 °C in solution, whereas Cr(Nor)$_4$ has a half-life of 7.6 h at 250 °C. Notably, the most stable compounds of this class do not have β-H atoms that could easily eliminate, but compounds with β-H atoms are also reasonably stable. For instance, Cr(Bu^t)$_4$ decomposes in heptane at 70 °C with a half life of 4.5 min and an activation energy of 29 ± 3 kcal/mol, to afford isobutane and isobutylene in a 6.5/1 ratio.[358] The CrR$_4$ compounds are reported to be unusually inert toward addition reactions of a variety of reagents. For instance, the (trimethylsilyl)methyl derivative does not react with water, amines, phosphines, CS$_2$, alkenes, phenylacetylene, succinimide, Ph$_3$C$^+$, and CO at 100 °C and 200 psi.[356] It reacts, however, with dioxygens and it is attacked by concentrated HCl and H$_2$SO$_4$, whereas the sterically more crowded norbornyl derivative also resists attack by these latter reagents. The nature of the chromium product in these decomposition reactions has not been the subject of extensive interest. The tertiary phosphine addition to Cr(*o*-Tol)$_4$ induces reductive elimination of bitolyl and formation of Cr(*o*-Tol)$_2$(PMe$_3$)$_2$ (major) and [Cr(*o*-Tol)(μ-*o*-Tol)(PMe$_3$)]$_2$ (minor) (eq 23).[317]



(23)

Analogous MoR_4 compounds are fewer in number, those with R = Mes,[365] Nor,[366] and o-Tol,[367] having been described. An initial report of $Mo(CH_2SiMe_3)_4$[355] was later found to be incorrect, the material being in fact the metal−metal-bonded Mo(III) species, $Mo_2(CH_2SiMe_3)_6$.[356] $MoMes_4$ can be oxidized to the stable Mo(V), cation, $[MoMes_4]^+$.[368] As for the chromium analogues described above, a cubic **g** tensor allows the observation or a room temperature EPR absorption for the spin triplet tetrahedral structures. However, UPS and XPS characterization of $MoMes_4$ gives evidence for a static splitting related to a D_{2d} distortion.[369]

Even fewer are the homoleptic tetraalkyl or tetraaryls of W(IV). A W(IV) compound described as $W(CH_2Ph)_4$ has been described as a diamagnetic, air and moisture-sensitive substance with a thermal decomposition pattern analogous to those of $Ti(CH_2Ph)_4$ and $Zr(CH_2Ph)_4$. The structure of this material is unknown but it probably involves W-arene π-interactions. Its reaction with bipy affords $W(CH_2Ph)_4(bipy)$.[311] The o-tolyl and 2,5-xylyl derivatives, on the other hand, are paramagnetic ($\mu_{eff} = 2.9\ \mu_B$) and are therefore probably tetrahedral.[317] The M(o-Tol)$_4$ (M = Mo, W) derivatives do not afford stable ligand adducts, but rather react with tertiary phosphines to induce *ortho*-hydrogen elimination with formation of aryne complexes (eq 24).[317]



(24)

VIII.1.5. Lower-Coordination Systems

Homoleptic Ti(II) alkyl and aryl complexes, e.g. TiR_2 (R = Ph,[370−372] CH_2Ph,[372,373] CH_2SiMe_3[374]), and the mixed compound $PhTi(CH_2Ph)$[375] have been described. No structural studies for these derivatives have been reported. The solubility properties led the authors to propose an oligomeric nature for these materials, and the low magnetic moments (e.g. 0.59 and 0.83 μ_B for $TiPh_2$ and $TiBz_2$, respectively) are consistent with this view.[372,373] The compounds dissolve in excess LiR, with possible formation of $[TiR_{2+n}]^{n-}$ complexes,[374] and react with other neutral donors (e.g. ethers, NH_3, and other N-donor ligands) to form adducts.[370−372,375]

V(III) forms the homoleptic compound VR_3 with the sterically very demanding $CH(SiMe_3)_2$ ligand.[376]

VIII.2. d^3 Systems

VIII.2.1. 15-Electron Systems

VIII.2.1.1. σ-Complexes. The organometallic chemistry of 6-coordinate (σ-organo)vanadium(II) is little explored, with few well-defined and fully characterized compounds being reported. The homoleptic V(II) aryl compound $[VPh_2{\cdot}(LiPh)_4{\cdot}3.5Et_2O]$ ($\mu_{eff} = 3.85\ \mu_B$) was reported by Kurras in 1960[377,378] and an X-ray structure for the similarly formulated $[Li(Et_2O)]_4[VPh_6]$ complex with a fairly regular octahedral coordination around V(II) has more recently been determined (see Figure 20).[379]

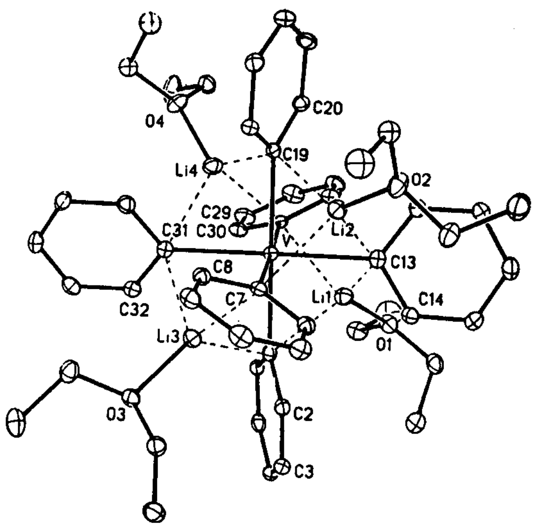
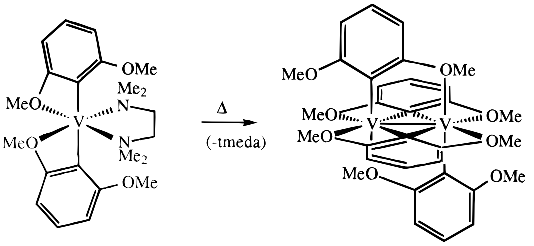


Figure 20. Molecular structure of $[Li(Et_2O)]_4[VPh_6]$. (Reprinted from ref 379. Copyright 1988 American Chemical Society.)

Three unpaired electrons are also measured for $VMe_2(dmpe)_2$[136] and for $V[2,6\text{-}(CH_3O)_2C_6H_3]_2(tmeda)$.[380] The latter compound loses tmeda upon heating to affod dinuclear, metal−metal-bonded, $V_2[2,6\text{-}(CH_3O)_2C_6H_3]_4$ (see eq 25). The related product of transmetalation obtained from $VCl_2(tmeda)_2$ and $(o\text{-}Me_2NCH_2)C_6H_4Li$ activates dinitrogen and produces $\{[(o\text{-}Me_2NCH_2)C_6H_4]_2V(py)\}_2(\mu\text{-}N_2)$ (eq 26), whose magnetic properties ($\mu_{eff} = 3.47\ \mu_B$ per V atom) and crystallographic characterization [N−N = 1.228(4) Å] indicate that the bridging N_2 ligand has not undergone a significant extent of reduction.[381] Addition of more pyridine to the latter complex affords $(o\text{-}Me_2NCH_2C_6H_4)_2Vpy_2$, also with three unpaired electrons.[382] $VCl_3(THF)_3$ reacts with and is partially reduced by



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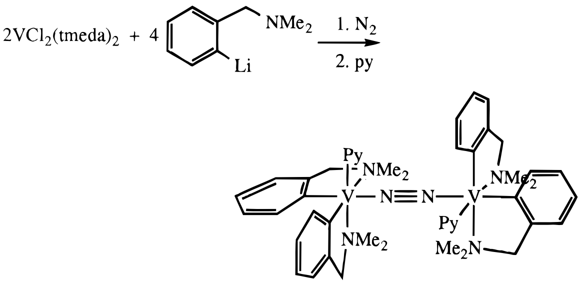


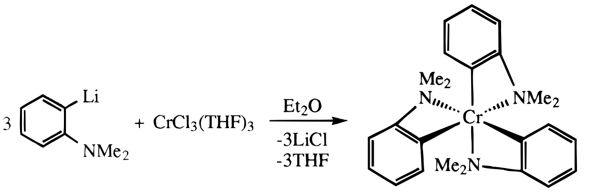
(26)

Table 10. Crystallographically Characterized Alkylchromium(III) Complexes

compound	stereochemistry	ref
$\{Cr[(\mu\text{-}CH_3)_2Li(dioxane)_{2/2}]_3\}_\infty$		762
$[Li(Et_2O)]_3[CrPh_6]$		379
$Cr(p\text{-}CH_3C_6H_4)Cl_2(THF)_3$	*mer*	763,764
$Cr(CHCl_2)(acac)_2(py)$	*trans*	765
$Cr(CH_2Cl)(acac)_2(py)$	*trans*	765
$CrPh_3(THF)_3$	*fac*	766
$[Cr(C_6H_4\text{-}o\text{-}OMe)_2(bipy)_2]I\cdot H_2O$	*cis*	767,768
$[CrPh_2(bipy)_2]I$	*cis*	769
$[Cr(CH_2SiMe_3)_2(bipy)_2]I$	*cis*	770
$Cr(C_6H_4\text{-}o\text{-}CH_2NMe_2)_3$	*fac*	771
$Cr(C_6H_4\text{-}o\text{-}NMe_2)_3$	*fac*	572
$[Bu^tSi(CH_2PMe_2)_3]CrMe_3$	*fac*	411
$[Bu^tSi(CH_2PMe_2)_3]CrBu^n{}_3$	*fac*	411
$[MeC(CH_2PMe_2)_3]CrBu^n{}_2Cl$	*fac*	129
$Cr(C_3F_7)(Me_2NCS_2)_2py$	*cis*	390
$Cr(CH_2Ph)_3(1,3,5\text{-}(CyN)_3C_3H_6)$	*fac*	772

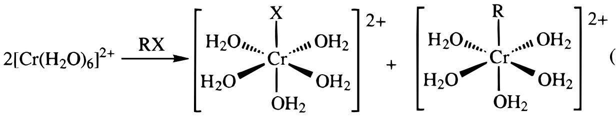
alkynyllithium reagents, yielding the structurally characterized octahedral $[Li(tmeda)(\mu\text{-}C{\equiv}CPh)_2]_2V(tmeda)$ and $V(C{\equiv}CR)_2(tmeda)_2$ ($R = Ph, Bu^t$) complexes.[383] The magnetic properties of these derivatives have not been investigated, except for a mention of noninformative ^{1}H-NMR spectra.[383] No Nb and Ta analogues appear to be known.

In contrast with the little developed chemistry of (σ-organo)vanadium(II), a large variety of alkylated versions of octahedral Cr(III) Werner-type complexes have been reported and very extensively investigated. A number of older and more detailed reviews on this chemistry are available.[21,384−386] Homoleptic $[CrR_6]^{3-}$ complexes, as well as mixed complexes of types $[CrR_5L]^{2-}$, CrR_3L_3, $CrR_nCl_{3-n}L_3$, $[CrR_2L_4]^+$, and $[CrRL_5]^{2+}$ have been prepared by various methods. In case the R group contains donating functions (e.g. 2-(dimethylamino)phenyl, see eq 27)[269,387] unsolvated neutral complexes are also formed.



(27)

The monoalkylpentaaquochromium(III) derivatives, $[CrR(H_2O)_5]^{2+}$, have been the subject of extensive investigations. The first examples ($R = CH_2Ph$, $CHCl_2$) were obtained by Anet and Leblanc by oxidative addition of alkyl halides to aqueous Cr^{2+} (eq 28),[388,389] but a large variety of such derivatives have later been obtained by this and other methods.[21] None of these aquo complexes has been isolated in crystalline form from water solution.



(28)

A number of structure determinations has been reported for alkylchromium(III) complexes (see Table 10). All of the compounds show the expected octahedral geometry around Cr(III), and all of those investigated magnetically are invariably found to adopt a $S = {}^3/_2$ ground state, which is also evidenced in other cases by broad, paramagnetically shifted NMR resonances.[390−392] A representative structure of $Bu^tSi(CH_2PMe_2)_3CrMe_3$ is shown in Figure 21. The structural data also show a significant *trans* influence of the alkyl groups, which is consistent with the accelerated rate of *trans* substitution. An acceleration factor of up to 10^5 for $[CrR(H_2O)_5]^{2+}$ is observed when compared with $[CrX(H_2O)_5]^{2+}$ (X = Cl, I, SCN) and up to almost 10^9 when compared with $[Cr(H_2O)_6]^{3+}$.[21]

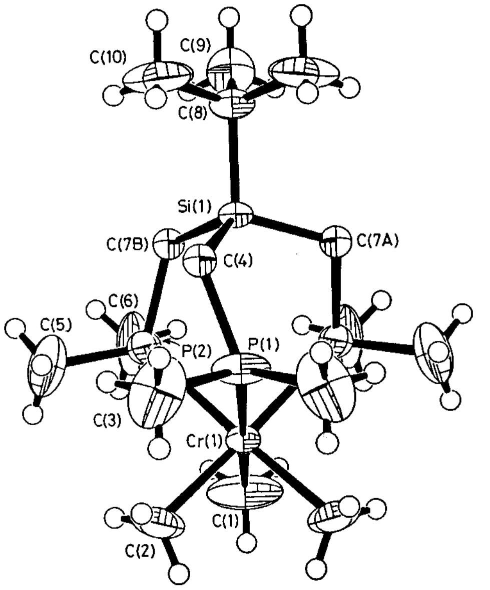


Figure 21. ORTEP drawing of $Bu^tSi(CH_2PMe_2)_3CrMe_3$. (Reprinted from ref 411. Copyright 1987 Royal Society of Chemistry.)

These organochromium(III) derivatives undergo thermal Cr−R bond homolysis and heterolytic cleavage with electrophilic reagents such as acids, dihalogens, and mercuric chloride.[393−400] Particular attention has been devoted to the aquation reaction of $[CrR(H_2O)_5]^{2+}$, which involves, in certain cases, an homolytic Cr−R dissociation equilibrium.[21]

The oxidation of the alkylpentaaquochromium(III) complexes by outer-sphere reagents (e.g. NO^+, $Ru(bipy)_3{}^{3+}$, ^2E $Cr(bipy)_3{}^{3+}$, $Ni(H_2O)_2(cyclam)^{3+}$) is believed to afford a short-lived RCr^{3+} intermediate, which subsequently decomposes by homolysis (R = alkyl, benzyl) or by intramolecular electron transfer (R = alkoxyalkyl).[401−404] The observed dependence of the rate constant on the nature of the alkyl group has led to the proposal that the transition state is significantly dissociated, $[Cr\cdots R^{3+}]^*$, and therefore strongly influenced by the stability of the radicals produced.[404] NO^+, however, can also react as an eletrophilic reagent toward complexes with $R = CH_2Ar$.[401,405] More details on these and other reactions of alkylpentaaquochromium(III) complexes can be found in the excellent review by Espenson.[21]

Other reactivity patterns of the organochromium(III) compounds, however, indicate that the R group can also engage in classical β-H elimination chemistry. This particular reaction is not observed for simple $[CrR(H_2O)_5]^{2+}$ complexes, perhaps because of the high instability of $[CrH(H_2O)_5]^{2+}$,[406,407] in apparent agreement with the facile β-X elimination from $[Cr(CH_2CH_2X)(H_2O)_5]^{2+}$ (eq 29).[408−410]

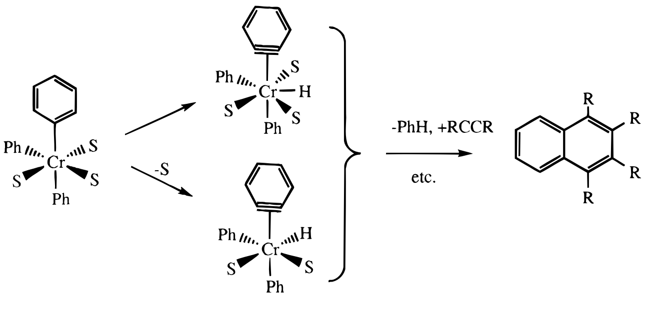
$$\{[Cr(CH_2CH_2X)(H_2O)_5]^{2+}\} \rightarrow [CrX(H_2O)_5]^{2+} + C_2H_4 \quad (29)$$

Polyalkyl complexes engage more easily in β-H elimination processes, supposedly because one alkyl ligand accelerates ligand dissociation in the corresponding trans position, which is however cis with respect to another alkyl, and the latter can then easily β-H eliminate. This is another presumed reason for the greater stability of β-H containing $[CrR(H_2O)_5]^{2+}$ complexes, since the only labile H_2O ligand is that *trans* to the alkyl. This observation implies a dissociative mechanism with formation of a 13-electron intermediate. The alternative path of elimination *without* ligand dissociation would require spin pairing in order to reach the required 17-electron configuration for the hydride−olefin intermediate. No evidence has apparently ever been presented for the formation of 7-coordinate σ-complexes of organochromium(III), nor for the involvement of such structures as associative intermediates of ligand exchange reactions.

The use of capping ligand, e.g. $Bu^tSi(CH_2PMe_2)_3$ and $MeC(CH_2PMe_2)_3$ allows the isolation of stable compounds even with β-H containing alkyl ligands such as Bu^n.[129,411] The thermal decomposition of $MeC(CH_2PMe_2)_3CrClBu^n{}_2$, indicating reversible β-H elimination/insertion steps, has been discussed above in section VI (Scheme 5).[129] The lack of facile β-H elimination in these octahedral Cr(III) derivatives is one important feature that makes them efficient catalysts for ethylene polymerization.[411]

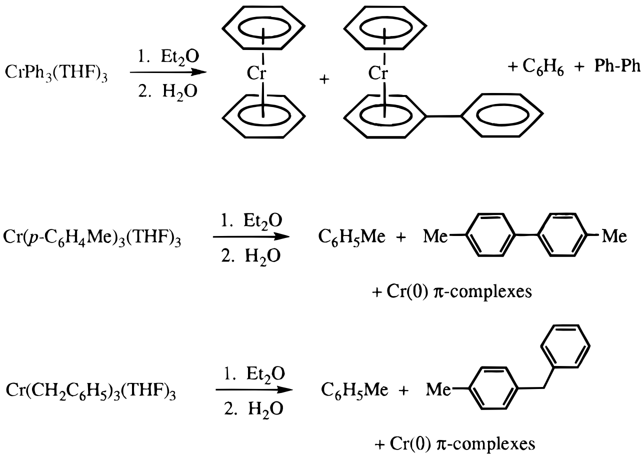
The reaction of triphenylchromium with 2-butyne or diphenylacetylene induces formation of the cyclotrimerization products (i.e. hexamethyl- and hexaphenylbenzene, respectively) but also tetrasubstituted cyclic products (e.g. 1,2,3,4-tetramethyl- or tetraphenylnaphthalene) where two molecules of the acetylene combine with a benzene ring.[412−414] The latter products are explained by the sequence illustrated in Scheme 9, where β-C−H activation of one of the phenyl ligands to form a benzyne intermediate is proposed. Analogously, trivinylchromium and 2-butyne or diphenylacetylene gives 1,2,3,4-tetramethyl- or tetraphenylbenzene.[415] Similar β-H eliminations of simple alkyl ligands to form olefins and even α-H elimination from CH_3 to form carbene need to be invoked to rationalize the formation of products such as 1,2,3,4-tetraphenylbenzene from $CrEt_3(L)_3$ and 1,2,3,4-tetraphenylcyclopentadiene from $CrMe_3(L)_3$ in their respective reactions with diphenylacetylene.[416]

Scheme 9

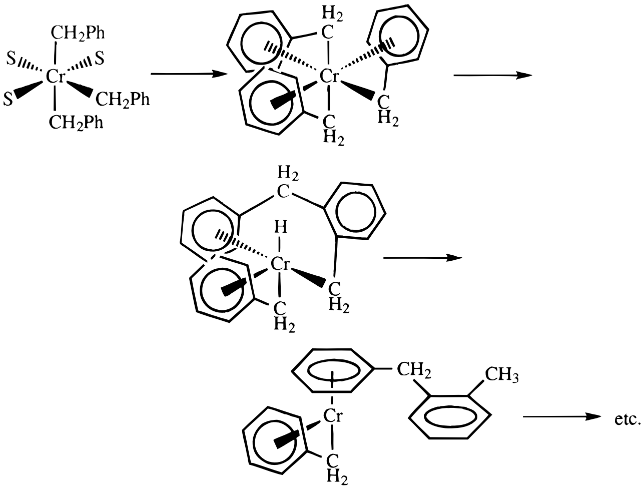


Triaryl- and tribenzylchromium(III) derivatives undergo an unusual rearrangement reaction to π-arene complexes when exposed to oxygen-free diethyl ether at room temperature. The rearrangement produces an uncharacterized black intermediate, which affords $[(\pi\text{-arene})_2Cr]$ complexes upon anaerobic hydrolytic treatment (Scheme 10).[417−421] This reaction appears to involve preliminary dissociation of THF in the ether solvent,[422] and an intermediate described as $CrPh_3{\cdot}2THF$ has been isolated and characterized (μ_{eff} = 3.97 μ_B).[423] The biaryl ligand derives from a radical-type coupling process as shown by *para*-coupling for the *p*-tolyl derivative,[420] whereas the benzyl derivative undergoes *ortho*-coupling through metalation chemistry (Scheme 11).[419,424] The use of D_2O has shown that undeuterated, monodeuterated, and polydeuterated compounds are formed, indicating the occurrence of processes of fast H/D exchange.[385,424]

Scheme 10



Scheme 11



Contrary to the large number of octahedral organochromium(III) complexes, analogous Mo(III) derivatives are extremely rare. Two examples are $Li_3Mo(Ar)_6{\cdot}3Et_2O$ (Ar = Ph, *p*-Tol), which show the expected three unpaired electrons for an octahedral geometry.[425,426]

Compounds $MnMe_4L_2$ (L_2 = dmpe or $(PMe_3)_2$) are the remarkable disproportionation products of alkylation (methyl derivatives of Mn(II) being also ob-

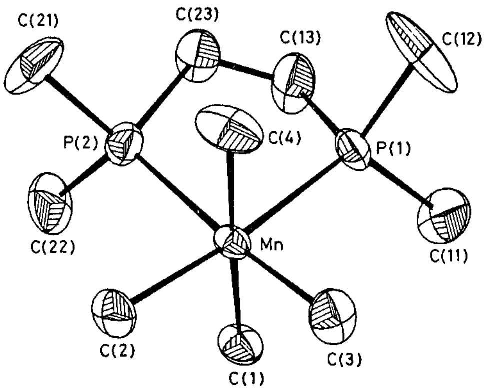


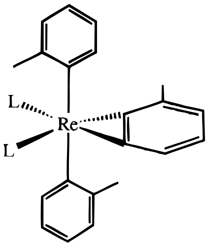
Figure 22. Molecular structure of $MnMe_4(dmpe)$. (Reprinted from ref 427. Copyright 1983 Royal Society of Chemistry.)

tained) of $Mn(acac)_3$ in the presence of the suitable ligand. Their magnetic moments and EPR properties are fully consistent with the expected $t_{2g}{}^3$ configuration for the crystallographically confirmed (for the dmpe complex) octahedral coordination geometry (see Figure 22).[427] The same geometry and magnetic properties are also found for the product of further alkylation, $[Li(tmeda)]_2[MnMe_6]$, which gives irreversible conproportionation when interacted with a Mn(II) alkyl complex (eq 30).[428]

$$[Li(tmeda)]_2[MnMe_6] + [Li(tmeda)]_2[MnMe_4] \rightarrow 2[Li(tmeda)]_2[MnMe_5] \quad (30)$$

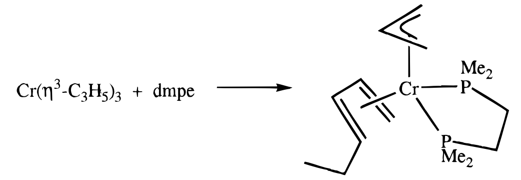
The reaction of $[Li(tmeda)]_2[MnMe_6]$ with $RC{\equiv}CR$ affords *cis*-$RMeC{=}CMeR$. If the mechanism involves alkyne activation by initial coordination, a spin-pairing process must take place. No rate data have been reported for this reaction.[429]

The "η^2-aryne" complexes $ReTol_2(\eta^2\text{-}C_6H_3Me)L_2$ (L = PMe_3, PMe_2Ph), **LXXXI**, like the analogous Mo and W compounds (section VIII.1.2.1), are best described as metallacyclopropene derivatives of the +IV metal, and have only one unpaired electron.[318]



LXXXI

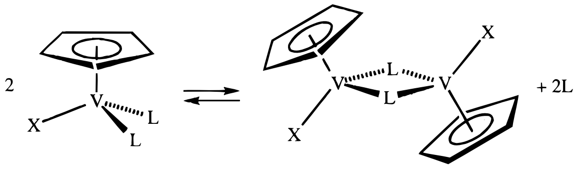
VIII.2.1.2. π-Complexes. The homoleptic allyl compound $Cr(\eta^3\text{-}C_3H_5)_3$ has long been known as a mononuclear 15-electron compound with a spin quartet ground state ($\mu_{eff} = 3.78\ \mu_B$),[430] but its coordination chemistry has not been extensively explored. Carbon monoxide adds and induces a reductive coupling of the allyl ligands to form $Cr(CO)_6$. The addition of phosphine ligands generates insoluble and thermally sensitive $Cr(C_3H_5)_3(PR_3)$ products that have resisted further characterization. A simple addition process would involve a difficult (for Cr^{3+})[92] spin-pairing process. The reaction with the bidentate phosphine dmpe, on the other hand, affords a crystallographically characterized 17-electron Cr(I) product (see eq 31), which results again from the reductive coupling of allyl ligands.[431]



(31)

The rhenium(IV) alkyne complexes $ReX_4(RC{\equiv}CR)L$ have one unpaired electron.[432] The parent $[ReX_4(RC{\equiv}CR)]_2$ compounds are di(μ-halo) dimers without metal−metal bonds[349,433] and show antiferromagnetic coupling between the two $S = {}^1/_2$ metal centers.[432] The alkyne ligand in these complexes is readily displaced by other ligands (e.g. dppe, THF).[432,434]

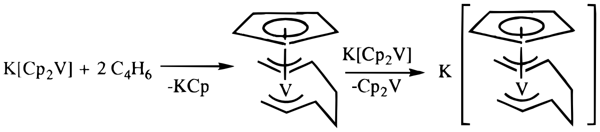
VIII.2.1.3. Half-Sandwich Compounds. A few half-sandwich compounds of V(II) have been reported, most of these being of the $CpVXL_2$ type (**LXXXII**), where X = halide, aryl, or alkyl, including those susceptible to β-H elimination processes.[49,72,435,436] All magnetically investigated compounds show three unpaired electrons and a variable-temperature study for CpVCl(dmpe) indicates Curie−Weiss behavior. The reduction of $CpVX_2(PR_3)_2$ complexes with aluminum or zinc does not afford $CpVX(PR_3)_2$, but rather dimeric, halide-bridged $[CpVX(PR_3)]_2$ (**LXXXIII**) because the acidic AlX_3 or ZnX_2 byproducts are good scavengers of the phosphine ligands (see eq 32). These dimers have again 15-electron V(II) centers in a three-legged piano stool geometry and no metal−metal bond, as demonstrated by the X-ray structure of $[CpVCl(PEt_3)]_2$.[437] A variable-temperature magnetic study indicates antiferromagnetic coupling between two $S = {}^3/_2$ centers, with $J = -109\ cm^{-1}$ and **g** = 2.00.[437] A similar dinuclear structure is probably adopted by the compounds described as $[CpVX(THF)]$ (X = Cl, I).[212,435]



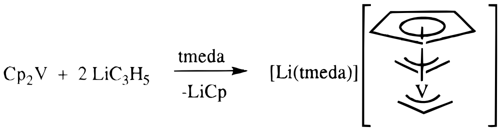
(32)

LXXXII **LXXXIII**

The halide bridges of these dimeric complexes are easily opened (e.g. by excess phosphine, see eq 32),[436] but stable 17-electron V(II) complexes (which would necessarily have a $S = {}^1/_2$ ground state), are not easily formed. For instance, the reaction of $[CpVCl(PEt_3)]_2$ with CO is slow and does not produce a stable V(II)−carbonyl adduct, but rather a mixture of $CpV(CO)_4$, $CpV(CO)_3(PEt_3)$, and yet other uncharacterized products.[436] However, exchange of the halide ligand in CpVCl(dmpe) with tetrahydroborate affords $CpV(\eta^2\text{-}BH_4)(dmpe)$, having two hydrogen bridges between V and B. This product has only one unpaired electron ($\mu_{eff} = 1.6\ \mu_B$ at 25 °C) and a sharp EPR spectrum at room temperature.[49,72] Although each V−H−B moiety formally establishes an electron-deficient three-center−two-electron interaction, the BH_4 ligand nevertheless engages two metal orbitals, leaving only two residual metal orbitals for holding the three metal electrons and therefore forcing the spin pairing.[72] Another example of a 17-electron complex is $[CpVH(dmpe)]_2(\mu\text{-dmpe})$. The corresponding 15-electron "CpVH(dmpe)" does not exist; rather, a stable diamagnetic dimer, $[CpV(\mu\text{-H})(dmpe)]_2$, is known.[438] Presumably 17-electron adducts of CpVH(dmpe) are formed more easily than for CpVR(dmpe) (R = alkyl) for steric reasons. Other derivatives that have been described as having a 17-electron configuration are bis(allyl) complexes (see eq 33 and 34).[209] However, the products were only described as paramagnetic and a magnetic moment was not reported to substantiate the structural claim.



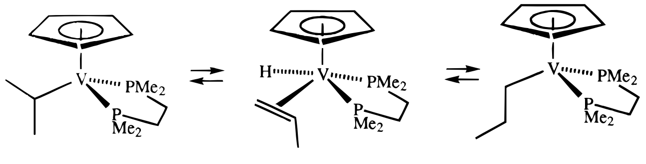
(33)



(34)

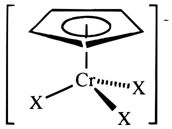
The formation of spin-paired ($S = {}^1/_2$), 17-electron intermediates seems probable in a number of reactions. A remarkable one is the alkylation of CpVCl(dmpe) with *isopropyl* Grignard, to afford the *n-propyl* derivative.[72] The classical sequence of β-H elimination and reverse insertion, through a 17-electron hydride−olefin complex (see Scheme 12), would explain the rearrangement. Alternatives to this spin-pairing mechanism, of course, are the dissociation of one arm of the phosphine ligand or a Cp ring slippage. Normally, unsaturated metal alkyl complexes thermodynamically favor the products of β-H elimination, but the opposite preference exists for this system. The normal alkyl may be thermodynamically favored over the branched alkyl for steric reasons, similar to Schwartz's hydrozirconation reagent.[439] The observation of this rearrangement reaction has led Teuben, Caulton, *et al.* to discover that this system is an active catalyst for the hydrogenation and isomerization of olefins.[72] The authors further postulate that the catalytic activity of a 14-electron CpTiR(dmpe) system should be improved with respect to the V(II) system, since no spin pairing would be necessary. This hypothesis has not been tested, because such 14-electron Ti(II) derivatives have not yet been described. The hydrogenolysis of $CpVPr^n(dmpe)$ consumes 1 equiv of H_2 rather slowly producing 1 equiv of propane and the diamagnetic complex $[CpV(\mu\text{-H})(dmpe)]_2$.[438] Again, although several mechanistic possibilities exist, an initial oxidative addition of H_2 would require an unfavorable spin pairing. The dimeric compound $[CpVCl(PEt_3)]_2$ oligomerizes acetylene to benzene and propyne to 1,2,4-, 1,3,5-, *but also* 1,2,3 trimethylbenzene, suggesting a complex mechanism of oligomerization.[436]

Scheme 12

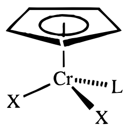


While 15-electron ($S = {}^3/_2$) half-sandwich vanadium(II) complexes are common and analogous 17-electron ($S = {}^1/_2$) systems are an exception, the 17-electron configuration is common for half-sandwich Nb(II) compounds, for instance $(\eta^6\text{-arene})Nb(AlX_4)_2$[440] and $(\eta^6\text{-}C_7H_8)NbCl_2(PMe_3)_2$,[441] and no 15-electron system appears to be known for organometallic Nb(II). Paramagnetic tantalum(II) derivatives do not appear to have been reported.

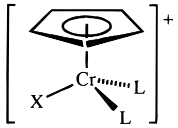
The half-sandwich, three-legged piano stool Cr(III) compounds of generic formula $[CpCrX_3]^-$, $CpCrX_2L$, $[CpCrXL_2]^+$, and $[CpCrL_3]^{2+}$ form an extensive and well-studied class of compounds (**LXXXIV**−**LXXXVII**). The first examples were reported by Fischer in 1963,[442] but these materials have more recently attracted much attention from other researchers, especially in view of their ability to model the catalytic activity of chromium-based Phillips ethylene polymerization catalysts.[9,443,444] Like the isoelectronic octahedral (σ-organo)chromium complexes discussed in section VIII.2.1.1, these materials invariably show a spin quartet ground state, even when they are completely surrounded by organic ligands, e.g. $[CpCr(CH_2Ph)_3]^-$.[445] Their short electronic relaxation times make them amenable to ^1H-NMR investigations,[22] whereas the compounds do not show EPR spectra at room temperature. Frozen solution EPR spectra can be observed for $CpCrMeCl(PMe_3)$ and for the Cp* analogue only upon cooling to 77 K, whereas the spectrum of antiferromagnetically coupled $[CpCrMe(\mu\text{-Cl})]_2$ can also be observed in isotropic solutions at 205 K.[48]



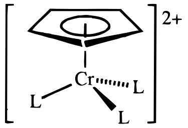
LXXXIV



LXXXV



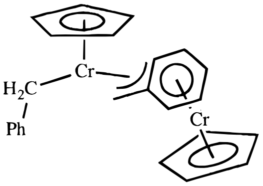
LXXXVI



LXXXVII

The aquo complex $[CpCr(H_2O)_3]^{2+}$ has limited stability in water, slowly losing C_5H_6 to afford $[Cr(H_2O)_6]^{3+}$,[446] whereas the Cp* analogue is stable in water.[447] The rate of water exchange on $[CpCr(H_2O)_3]^{2+}$ was found to be quite rapid.[446]

The cationic $[Cp^*CrMe(THF)_2]^+BPh_4^-$ compound has been proven an efficient catalyst for ethylene polymerization and persuasive evidence has been provided that the dissociation of one THF ligand precedes ethylene coordination.[9] Coordination of the olefin without THF dissociation would involve an energetically unfavorable electron pairing. The equilibrium constant of THF dissociation (eq 35) has been estimated independently by ^{1}H-NMR integration and by measurement of the THF retardation effect on the rates of ethylene polymerization, consistently giving values of ~1 × 10^{-3} M.[9] Other Cr(III) systems that



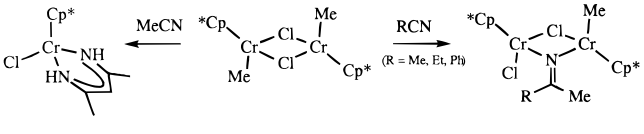
LXXXVIII

can easily provide an open coordination site on a 13-electron Cr(III) species are also active ethylene polymerization catalysts, for instance the unusual mixed-valence Cr(I)/Cr(III) complex Cp*Cr(η^1-Bz)(μ-η^3:η^6-Bz)CrCp* (**LXXXVIII**).[448]

$$[\mathrm{Cp^*CrMe(THF)_2}]^+ \rightleftarrows [\mathrm{Cp^*CrMe(THF)}]^+ + \mathrm{THF} \tag{35}$$

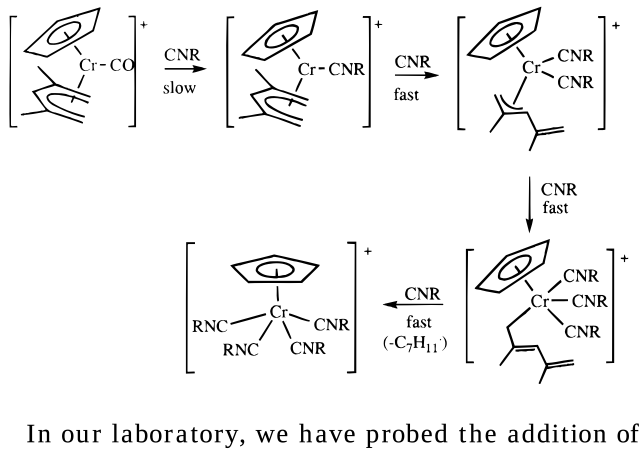
The insertion of an acetonitrile ligand into a Cr–Me bond in a presumed Cp*CrClMe(RCN) intermediate obtained by RCN addition to [Cp*Cr(μ-Cl)Me]$_2$ ultimately leads to dinuclear ketimino-bridged or mononuclear β-diketimino complexes (see Scheme 13).[449] No ligand dissociation nor spin pairing are needed for this reaction.

Scheme 13



The addition of neutral ligands to three-legged piano stool Cr(III) complexes would involve an unfavorable spin pairing and is therefore a difficult reaction. A stable 17-electron Cr(III) complex is [CpCr(Pdl′)(CO)]$^+$ (see section VIII.2.1.3). Its reaction with isocyanides to ultimately afford the 18-electron [CpCr(CNR)$_4$]$^+$ product has been proposed to proceed via half-sandwich 17-electron intermediates (see Scheme 14).[450]

Scheme 14



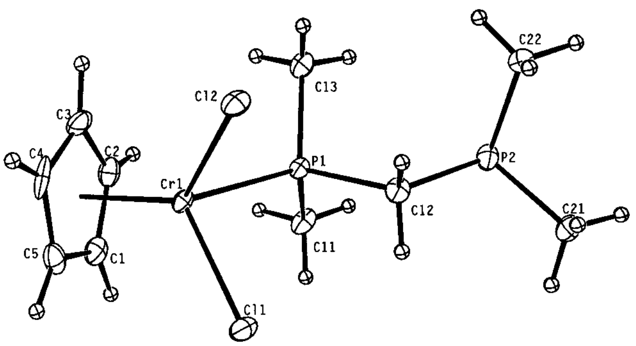


Figure 23. Molecular structure of compound CpCrCl$_2$(dmpm). (Unpublished result from this laboratory.[34])

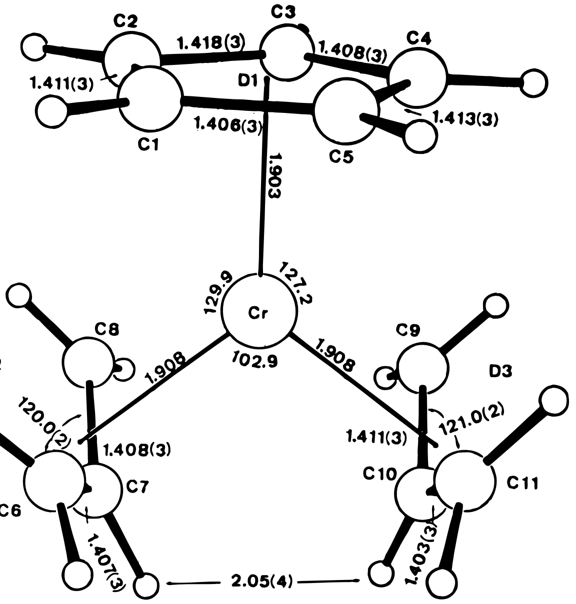


Figure 24. Molecular structure of compound CpCr(η^3-C$_3$H$_5$)$_2$. (Reprinted from ref 23. Copyright 1986 American Chemical Society.)

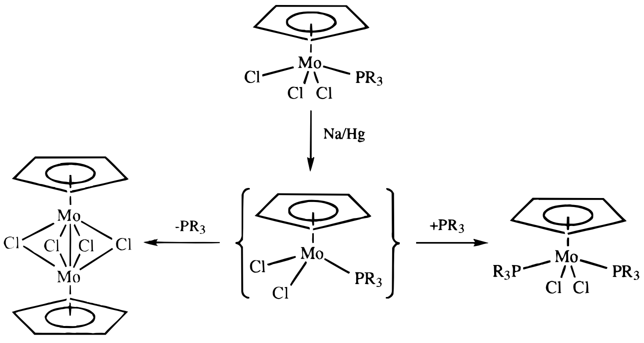
In our laboratory, we have probed the addition of bidentate ligands (dmpm, dmpe, dppe) to [CpCrCl$_2$]$_2$ to see whether a 17-electron structure could be enforced by the chelate effect. However, only 15-electron structures with dangling phosphine were obtained both in the solid state (Figure 23) and in solution (paramagnetically shifted ^{1}H-NMR resonances, no EPR spectrum), and the same is true for the subsequent products of alkylation, CpCrMe$_2$(L–L), that are devoid of additional π-stabilization.[34] Theopold *et al.* have shown that the reaction of Cp*Cr(Bz)$_2$L (L = THF or py) with the bidentate ligand bipy leads to spontaneous reduction to Cp*Cr(Bz)bipy with elimination of a benzyl radical.[445] CpCrMe$_2$(dmpe), on the other hand, is stable at the THF reflux temperature.[34] This difference is probably due to the formation of a more stable benzyl radical and to the more severe steric pressure in the Cp* system.

Theoretical calculations have shown that the model compound CpCrX$_2$(PH$_3$) and free PH$_3$ at infinite distance are more stable than the hypothetical 17-electron adduct, CpCrX$_2$(PH$_3$)$_2$ (see section V),[92] because the cost of pairing the electrons is greater than the energy gained by forming the new Cr–PH$_3$ bond. Besides the above-mentioned [CpCr(Pdl′)(CO)]$^+$, another reported 17-electron Cr(III) complexes (albeit stable only below 0 °C) is CpCr(η^3-C$_3$H$_5$)$_2$ (Figure 24).[24] It is to be noted that these 17-

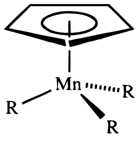
electron derivatives have only soft and π-acidic carbon-based ligands, thus presumably lowering significantly the electron pairing energy of Cr(III). With this idea in mind, we have probed the chemistry of half-sandwich Cr(III) cyanide compounds and have found that $[CpCr(CN)_3]^-$ reacts in solution with excess CN^- to afford equilibrium mixtures of the corresponding 17-electron tetracyano complexes, whose spin doublet configuration is shown by EPR spectroscopy.[451] The same methods suggest the presence of 17-electron $CpCr(CN)_2L_2$ structures in solution for L_2 = chelating diphosphine (e.g. dmpe) or L = small monodenate phosphine ligands (e.g. PMe_3, PMe_2Ph).[451]

No organometallic, 15-electron half-sandwich Mo(III) complex similar to the above Cr(III) systems has been reported to date, whereas 17-electron $CpMoX_2L_2$, $[CpMoXL_3]^+$, and $[CpMoL_4]^{2+}$ provide an extensive series of stable systems.[25] The phosphine exchange reaction on $CpMoCl_2(PR_3)_2$ occurs via a dissociative 15-electron $CpMoCl_2(PR_3)$ intermediate, and we have proposed that a spin state change to $S = {}^3/_2$ might contribute to favor this pathway with respect to the more typical (for organometallic radicals) associative exchange.[127] MP2 and DFT calculations confirm a spin quartet ground state for $CpMoCl_2(PH_3)$ (see section V).[92] In our laboratory, we have devoted a considerable effort toward the stabilization and isolation of one such complex. The use of bulky phosphine ligands is fruitless because of the thermodynamic sink of the metal−metal-bonded $[CpMo(\mu\text{-}Cl)_2]_2$, thus either ligand dissociation or ligand disproportionation occurs (see Scheme 15), depending on the ligand cone angle.[26] In order to suppress this thermodynamic sink, charged $[CpMoCl(PR_3)_2]^+$ species have been targeted. The thermal decarbonylation of $[(ring)MoClL_2(CO)]^+$ (ring = Cp, L_2 = dppe; ring = Cp*, L_2 = dppe or L = PMe_3), however, shows that the presumably formed $[(ring)MoClL_2]^+$ intermediate is extremely acidic and abstracts F^- from the PF_6^- counterion.[27] The use of more innocent anions may allow the isolation of this species.

Scheme 15

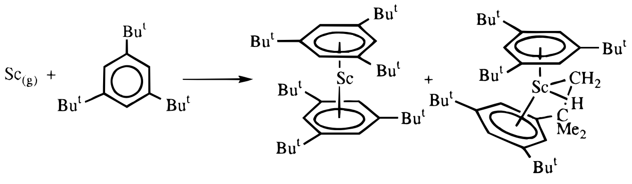


For group 7 metals, a series of $CpMnR_3$ complexes (**LXXXIX**; R = Me, Et, Pr, Bu, Bu^i) has been described.[452−454] No magnetic studies appear to have been reported for these materials, but given the properties of the isoelectronic V(II) and Cr(III) compounds described above, it seems obvious that such compounds should have a spin quartet ground state. In support of this idea, all of them, even those for which a β-elimination is possible, are rather thermally stable (up to > 175°).[452]



LXXXIX

VIII.2.1.4. Sandwich Compounds. Sc(0), Y(0), La(0), and Lu(0) bis-arene compounds (e.g. **XC**) all have one upaired electron in a d orbital.[455,456] These compounds are stable only with extremely bulky arene ligands, e.g. 1,3,5-$C_6H_3Bu^t_3$. No ligand additions to these compounds have been reported, but the reaction of Sc atoms with 1,3,5-$C_6H_3Bu^t_3$ yields also a Sc(II) product in addition to the Sc(0) bis-arene complex, which may derive from direct intramolecular C−H oxidative addition of the latter (see eq 36).[455]



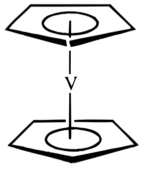
XC (36)

Vanadocene (**XCI**) and a number of derivatives with substituted Cp rings, including the bis(indenyl) compound, have three unpaired electrons[267,280,457,458] and relatively sharp, paramagnetically shifted resonances in the ^1H- and ^{13}C-NMR spectra.[273,459,460] However, the energy of the excited state doublet configuration must not be too far away. Indeed, the similar open metallocene derivative $(Pdl')_2V$, the half-open $Cp(Pdl^\#)V$ ($Pdl^\#$ = 1,5-bis(trimethylsilyl)-2,4-pentadienyl), and $(dmCh)_2V$ show a doublet ground state configuration.[336,461−464] Theoretical calculations at the SCF-DV-Xα level reproduce the experimental ground states for Cp_2V and Pdl_2V.[465] A spin change occurs for the facile addition of neutral 2-electron donors to Cp_2V to afford spin doublet 17-electron Cp_2VL adducts (e.g. L = CO, CS_2, CH_2O, bipy, or electron-deficient olefins and alkynes such as diethyl fumarate or maleate).[81,100,466,467] $Cp^*{}_2V(CO)$[279] is in equilibrium with $Cp^*{}_2V$ + CO at low P_{CO}.[117] π-Backbonding must be important in the V−L interaction, because electron-donating ligands such as phosphines, pyridine, and electron-richer olefins do not bind to the Cp system. However, phosphine adducts of the sterically more crowded $(Pdl)_2V$[242,244] as well as half-open $Cp(Pdl^\#)V$[463,468] are known. The little importance of steric bulk for these ligand addition reactions is also indicated by the ability of the corresponding d^2 $[Cp_2V]^+$ system to reach an 18-electron configuration in $[Cp_2VL_2]^+$, even for the rather bulky L_2 = dppe. Further addition of CO to afford 19-electron $(ring)_2V(CO)_2$ intermediates in associative ligand exchange reactions has been shown, whereas bis(pentadienyl) derivatives exchange CO predominantly via a dissociative 15-electron intermediate.[469] Bis(indenyl)vanadium[470] adds two CO ligands to afford a ring-slipped $(Ind)_2V(CO)_2$ adduct.[471] The addition of isocyanides to Cp^*_2V yields a product of C−N bond breaking, $Cp^*_2V(CN)(CNR)$ ($R = Bu^t$, Cy).[279]

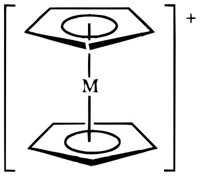
While the ligand addition to Cp_2V is straightforward, oxidative addition of RX (e.g. alkyl halides, HCl, HSR, $HSnR_3$, etc.) does not produce the expected V(IV) Cp_2VRX derivatives, but rather the V(III) Cp_2VX compounds.[96,260,272] The only expection to this rule was found when R = Me.[472] The reaction, however, is proposed to take place via an initial oxidative addition.[260,472] Intermediates interpreted as the oxidative addition products have also been observed in other cases.[116,273,281] Treatment with $HSiCl_3$ produces the V(IV) derivative $Cp_2V(SiCl_3)_2$.[473] Stable products of simple oxidative addition to Cp_2V, besides the above-mentioned $Cp_2V(CH_3)Cl$, are obtained with PhSSPh, i.e. $Cp_2V(SPh)_2$.[474] When the oxidative addition of RSSR is carried out with a deficiency of the disulfide, the only product obtained is $Cp_2V(SR)$ (R = Ph, Me, Et). An independent study shows that $Cp_2V(SR)_2$ and Cp_2V conproportionate rapidly to $Cp_2V(SR)$.[263] The oxidation potential is critical for this oxidative addition reactions: while Cp_2V reacts with I_2 to afford only Cp_2VI, the more easily oxidizable Cp^*_2V yields Cp^*_2VI or $Cp^*_2VI_2$, depending on the amount of I_2 used.[279]

Contrary to vanadocene, niobocene, and tantalocene are not stable systems, dimerizing with oxidative addition of a Cp C−H bond.[297,475,476] The sharp EPR spectrum assigned to niobocene, as obtained at low temperature by H atom abstraction from Cp_2NbH_3 followed by spontaneous H_2 reductive elimination[477] or by sodium naphthalenide reduction of Cp_2NbCl_2,[478] is consistent with a spin doublet ground state for this species. Oxidative additions to Cp_2Nb yield the expected $Cp_2Nb(X)_2$ products (e.g. X = halogen, SR).[476,478]

Isoelectronic with vanadocene are chromicinium cations (**XCII**). Few derivatives of this type have been described. These are stable only when sterically protected, e.g. $Cp^*_2Cr^+$, and always have a spin quartet ground state.[339,479] The half-open Cp(Pdl′)-Cr^+ complex is the proposed intermediate of the dissociative CO exchange on $Cp(Pdl')Cr(CO)^+$.[450]



XCI



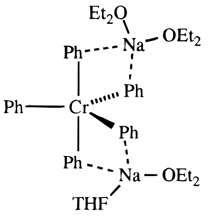
(M = Cr, Mo)

XCII

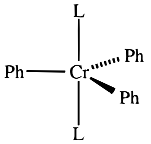
A single and remarkable example of a molybdenicinium cation, e.g. $[(C_5Ph_5)_2Mo]^+$ in a salt with the Br_3^- counterion, is known, its stability (decomposes at 200−220 °C) being presumably due in large part to steric protection. A certain amount of spin-pairing stabilization toward ligand addition, however, is indicated by its magnetic moment of 3.5 μ_B[480]

VIII.2.2. 13-Electron Systems

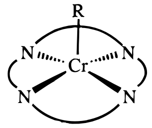
VIII.2.2.1. σ-Complexes. Compound $CrAr_3{\cdot}LiAr{\cdot}Et_2O$ (Ar = o-C_6H_4OMe), with a magnetic moment of 3.89 μ_B, has been described but the structure has not been determined.[481] Assuming that the ether molecule is coordinated and the aryl groups are all bonded only via the carbon atom, the compound would be 5-coordinate with a 13-electron count. Similarly, compound $Na_2CrPh_5(Et_2O)_3$ ($\mu_{eff} = 3.66\ \mu_B$) and the lithium analogue are most likely pentacoordinated.[482,483] The crystal structure of $[Na(Et_2O)_2][Na(Et_2O)(THF)][CrPh_5]$ shows a distorted pentagonal-bipyramidal geometry, as shown in **XCIII**.[484] Similar compounds are $CrPh_3{\cdot}2THF$ ($\mu_{eff} = 3.97\ \mu_B$)[423] and $CrPh_3(PPh_2R)_2$ (R = Et, Bu) ($\mu_{eff} = 3.89\ \mu_B$), presumably also trigonal bipyramidal (**XCIV**).[485] These react promptly with THF to form more stable 6-coordinate complexes. The porphyrin compounds Cr(TTP)R (**XCV**; R = Ph, p-$C_6H_4Bu^t$, CH_2SiMe_3) also have a spin quartet ground state.[486]



XCIII



XCIV

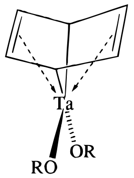


XCV

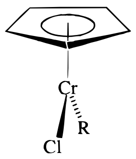
VIII.2.2.2. π-Complexes. Rhenium(IV) alkoxides form stable adducts with alkyne, $ReX_4(RC{\equiv}CR)$, with a single unpaired electron.[487] Analogous halide compounds are dimeric[433] and easily form ligand adducts, e.g. $ReCl_4(Pr^nC{\equiv}CPr^n)(POCl_3)$.[432]

VIII.2.2.3. Half-Sandwich Complexes. The reduction of $(\eta^6$-$C_6R_6)Ta(OR')_2Cl$ (R = Me, Et; OR′ = 2,6-diisopropylphenoxide) with excess Na/Hg provides the monomeric Ta(II) complexes $(\eta^6$-$C_6R_6)Ta(OR')_2$ that are characterized by a $S = {}^1/_2$ ground state ($\mu_{eff} = 2.14\ \mu_B$ for the C_6Et_6 compound).[326,488] A structure determination shows a two-legged piano stool geometry with a severely distorted arene ring (**XCVI**), much like what is observed for the Ta(III) precursor (see section VIII.1.2.3).

EPR investigations have shown that a sterically driven monomer−dimer equilibrium exists for the $[(ring)CrXR]_2$ class of compounds (ring = Cp, Cp*, X = Cl, Br; R = Me, Et, CH_2SiMe_3). Whereas the dimers have a halide-bridged structure with antiferromagnetically coupled 15-electron Cr(III) metals and terminal R ligands (analogous to **I**), the monomers have a 13-electron configuration and a $S = {}^1/_2$ ground state.[48] The stabilities of these compounds and, especially, their ground states, seem remarkable in view of the relatively small steric demand of the ligands (e.g. for Cp*CrMeCl) and the high pairing energies associated with Cr(III). It has been suggested that significant Cr(III)−Cl π-bonding in a planar two-legged piano stool structure (**XCVII**) may be important in stabilizing these complexes.[48] None of the above compounds has been isolated in the solid state. On the other hand, a 13-electron dialkyl complex, $Cp^*Cr(CH_2SiMe_3)_2$, has been reported.[445] An analogous $\{Cp^*Cr(CH_2Ph)_2\}_n$ has not been crystallographically characterized, but the reduced magnetic moment ($\mu_{eff} = 3.0\ \mu_B$ per Cr at room temperature) is consistent with antiferromagnetic coupling in a dinuclear structure.[445]



XCVI



XCVII

VIII.2.3. 11-Electron Systems

Alkyl and aryl compounds of Cr(III) obtained by alkylation of $CrCl_3(THF)_3$ adopt the coordination number 4 when the steric bulk prevents further coordination of solvent molecules. Trimesitylchromium(III) ($\mu_{eff} = 3.74\ \mu_B$) has been described as $CrMes_3(THF)$, **XCVIII**, and a molecular weight study in solution even suggests further dissociation of THF to give unsolvated $CrMes_3$.[489] The reaction of $CrMes_3$(THF) with isocyanides and isocyanates proceeds easily to insertion products.[490] Tetraalkyl and -aryl anions (**IC**) are also known. The tetrahedral $[Cr(CH_2EMe_3)_4]^-$ (E = Si, C) are rapidly oxidized by oxygen or electrochemically at a potential greater than −1.28 V (E = Si) or −1.65 V (E = C) vs SCE to the corresponding neutral Cr(IV) species. The latter, in turn, can be reduced back to the Cr(III) anion with amalgamated sodium or electrolytically. An analogous behavior has been reported for $[CrMes_4]^-$.[354] The optical spectrum, EPR spectrum, and magnetic properties agree with a ground state having three unpaired electrons ($^4T_1$).[354,356] Molybdenum systems of type $[MoR_4]^-$ appear to exist, but their structure and magnetic properties have not been determined.[366,367]

For group 7 metals, both manganese(IV) and rhenium(IV) tetraalkyls and -aryls (**C**) are known. Compound $Mn(Nor)_4$, obtained from $MnCl_2$ and norbornyllithium,[357] has properties completely analogous to those of the above mentioned anionic Cr(III) complexes (e.g. $\mu = 3.78\ \mu_B$).[357] The air oxidation of $Mn(CH_2R)_2$ (R = $SiMe_3$, CMe_2Ph, Bu^t) in the presence of excess $Mg(CH_2R)_2$ affords green solutions whose EPR properties are consistent with the presence of unstable $Mn(CH_2R)_4$, but the latter compounds could not be isolated.[427,491] The homoleptic Re(*o*-Tol)$_4$ compound is isostructural with $Mn(Nor)_4$ (tetrahedral), but adopts a low-spin configuration ($e^3t_2^0$; $\mu_{eff} = 1.31\ \mu_B$).[492] Its reaction with tertiary phosphines proceeds similarly to that of the Mo and W counterparts (see eq 14), to afford the *ortho*-metalated product Re(*o*-Tol)$_2$(η^2-2-MeC_6H_3)L_2 (L = PMe_3, PMe_2Ph).[318]

Reversible oxidation of M(*o*-Tol)$_4$ (M = Ru, Os) affords the corresponding cations, but only the osmium complex [Os(*o*-Tol)$_4$]$^+$ (**CI**) has been isolated as a stable species. This tetrahedral compound has a single unpaired electron like the isoelectronic Re(IV) system and reacts instantaneously with THF to afford the parent Os(IV) neutral complex, whereas it is stable in CH_2Cl_2.[367]

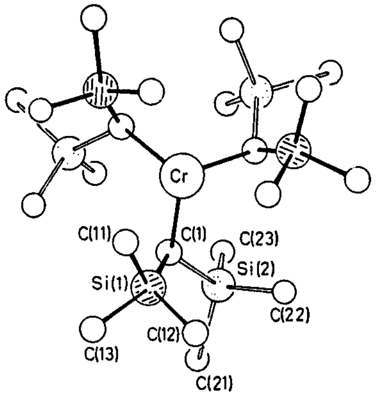
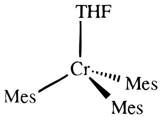
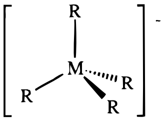


Figure 25. Molecular structure of $Cr[CH(SiMe_3)_2]_3$. (Reprinted from ref 376. Copyright 1978 Royal Society of Chemistry.)

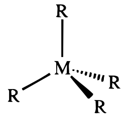


XCVIII



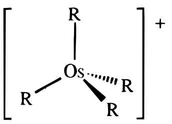
(M = Cr, Mo)

IC



(M = Mn, Re)

C



CI

VIII.2.4. Lower Coordinate Systems

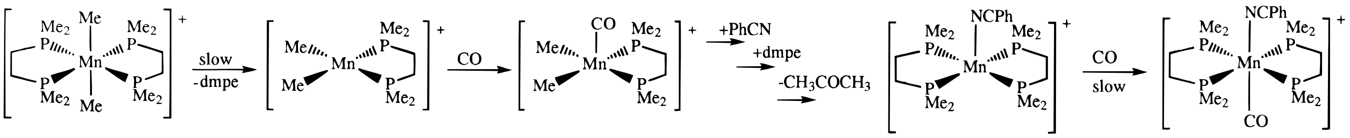
Three-coordinate CrR_3 compounds have been reported only with very encumbering alkyl groups. The first such compound reported was with R = 2,2,3-trimethylbicyclo[2.2.1]hept-1-yl (4-camphyl), obtained by the interaction of $CrCl_3(THF)_3$ with 4-camphyllithium.[357] It is notable that with the slightly less crowded 2,3,3 analogue (1-camphyl), the tetraalkyl-Cr(IV) system is obtained by the same procedure (see section VIII.1.4). Subsequently, Barker and Lappert described a similar compound with R = $CH(SiMe_3)_2$, whose X-ray structure shows a perfect trigonal-planar geometry (see Figure 25). This compound does not react with 2-electron neutral donors (e.g. amines, py, CO_2) but reacts with radical sources (e.g. NO and Ph_3CCl, the latter with formation of free trityl radical).[376,493] Both CrR_3 compounds have a spin quartet ground state.

VIII.3. d^4 Systems

VIII.3.1. 16-Electron Systems

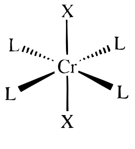
VIII.3.1.1. σ-Complexes. A few octahedral (σ-organo)chromium(II) compounds of type CrX_2L_4 (**CII**), e.g. $CrMe_2(dmpe)_2$[136] and $CrPh_2(bipy)_2$,[494] have been reported, all showing a spin triplet ground state, whereas corresponding coordination compounds, e.g. $CrCl_2(dmpe)_2$, adopt a high-spin ($t_{2g}^3e_g^1$) configuration. Compound $(2\text{-}CH_3OC_6H_4)_2Cr(bipy)$ ($\mu_{eff} = 2.58\ \mu_B$) is most likely 6-coordinate with chelating anisyl

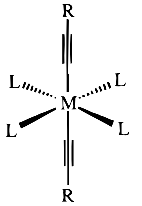
Scheme 16



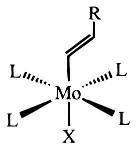
ligands,[495] but 5-coordination is also a possibility. Four-coordinate CrR_2L_2 complexes always adopt a spin quintet ground state (see section VIII.3.3). Bonding of the neutral ligands in these compounds, therefore, is sufficiently strong to more than compensate for the unfavorable pairing of two electrons upon going from the spin quintet to the spin triplet configuration. This effect is likely the most important factor making lower coordinate, spin quintet (σ-organo)chromium(II) complexes more common than the spin triplet, 16-electron type.

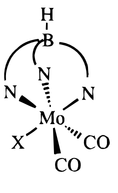
A number of compounds initially formulated as octahedral W(II) organometallics have later been reformulated as compounds in other oxidation states. Among these, $Li_4MPh_6{\cdot}4Et_2O$ (M = Mo, W)[496] have later been shown to contain *o*-phenylene units.[15] The thermal or photochemical reaction of WMe_6 with PMe_3 was initially reported to afford $WMe_2(PMe_3)_4$,[497] but this compound was later reformulated as $WMe(\equiv CMe)(PMe_3)_4$.[498] A compound of formula $MoH_2(dppe)_2$ has been destribed,[499] but the amount of hydrogen in the compound is not confirmed spectroscopically. More soluble derivatives have been shown to be tetrahydride compounds instead, $MoH_4(R_2PCH_2CH_2PR_2)_2$ (R = *m*-tolyl or *p*-tolyl).[500] On the other hand, $M(C\equiv CR)_2L_4$ (M = Mo, W),[501] **CIII**, and $MoX(CH{=}CHR)L_4$ (L = PR_3 or L_2 = $R_2PCH_2CH_2PR_2$),[502] **CIV**, seem to be genuine d^4 complexes. All these compounds exhibit a *trans* geometry and are diamagnetic, whereas corresponding dihalide complexes, MoX_2L_4, have two unpaired electrons. Compound $W(C\equiv CPh)_2(dppe)_2$ does not readily oxidatively add H_2, although $WH_2(C\equiv CPh)_2(dppe)_2$ is a stable compound.[501] Carbonyl complexes $MX_2(CO)_2L_2$ (e.g. halogen or alkoxide or thiolate; L = py, PR_3, $P(OR)_3$, etc.) are also known for both Mo and W, e.g. $W(SPh)_2(CO)_2(phen)$.[503] These are all stabilized by ligand π-interactions, which induce substantial distortions of the octahedral geometry,[144] and are all diamagnetic. Analogous derivatives, also diamagnetic, are the tris(pyrazolyl)borate compounds $Tp^{Me,Me}Mo(EAr)(CO)_2$ (E = S, Se),[504] **CV**, but the corresponding $Tp^{Me,Me}MoX(CO)_2$ (X = Cl, Br, I) derivatives have a spin triplet ground state[505] and represent rare cases of spin triplet carbonyl complexes for any transition metal.


CII


(M = Mo, W)

CIII

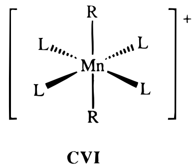

CIV

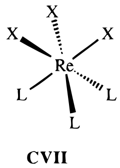

CV

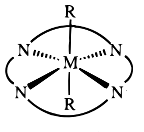
Octahedral Mn(III) complexes, **CVI**, are quite rare. One such example is $[MnMe_2(dmpe)_2]^+$,[506] with a low-spin (t_{2g}^4) configuration analogous to the isoelectronic $CrMe_2(dmpe)_2$. This compound reacts with CO to afford the products illustrated in Scheme 16. An initial CO addition to afford an 18-electron $[MnMe_2(dmpe)_2(CO)]^+$, followed by CO migratory insertion, reductive elimination of acetone, and coordination of CO and nitrile would seem the most logical route to the products. However, the CO addition step would require an unfavorable electron pairing process and, indeed, the reaction requires forcing conditions. A considerable retardation effect by added dmpe seems to indicate a preliminary decoordination of the phosphine ligand, which would produce a 4-coordinate intermediate analogous to known square-planar, spin quintet complexes (see section VIII.3.3). The purple intermediate $[Mn(NCPh)(dmpe)_2]^+$ has been isolated but not fully characterized.[506] Other recent examples are the alkynyl complexes $[Mn(C\equiv CR)(dmpe)_2]^+$, also characterized by a S = 1 ground state.[507] The class of homoleptic isocyanide complexes $[Mn(CNR)_6]^{3+}$ have been generated electrochemically but not isolated.[508]

Unusual 16-electron Re(III) compounds, **CVII**, are $ReI_3(CO)_3$[509] and $ReCl_3(CNBu^t)(PPh_3)_2$.[510] NMR spectroscopy indicates diamagnetism for the isocyanide complex, whereas a variable-temperature magnetic study for $ReI_3(CO)_3$ indicates a spin−orbit triplet (μ_{eff} = 3.59 μ_B at 298K) and a substantial TIP, characteristic of the 5d t_{2g}^4 configuration.[509]

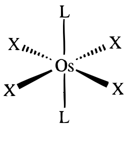
No stable Fe(IV) organometallic has ever been described; a study by Kochi *et al.* shows[511] that a transient $[FeR_2(bipy)_2]^{2+}$, obtained by double oxidation of the neutral Fe(II) precursor, eliminates R−R intramolecularly with high selectivity. No spectroscopic properties could be gathered on the Fe(IV) transient and its electronic ground state is therefore unknown; however, a reductive elimination reaction of R−R has no orbital requirements and should proceed equally rapidly independent of the compound spin state. Ru(IV) and Os(IV) compounds of type MR_2(porphyrin), **CVIII**, are stable and diamagnetic.[512,513] A 16-electron, presumably octahedral, $OsH_4(PR_3)_2$ transient is obtained by phosphine photodissociation from $OsH_4(PR_3)_3$.[514] The related $OsMe_4(PPh_3)_2$ and $Os(CH_2SiMe_3)Cl_3(PMe_3)_2$, **CIX**, however, are described as stable diamagnetic compounds.[172]


CVI


CVII

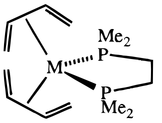

(M = Ru, Os)

CVIII


CIX

VIII.3.1.2. π-Complexes. The 6-coordinate Ti(0) and Zr(0) butadiene complexes $M(\eta^4\text{-butadiene})_2(dmpe)$ (M = Ti,[515] Zr[516,517]), **CX**, have been described. Both these complexes are diamagnetic, but only the

Zr complex is able to form saturated compounds by adding an additional 2-electron donor, probably for steric reasons.[517] Thus, CO, PMe_3, and dmpe add

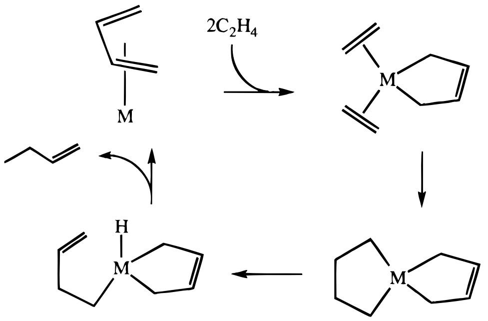


(M = Ti, Zr)

CX

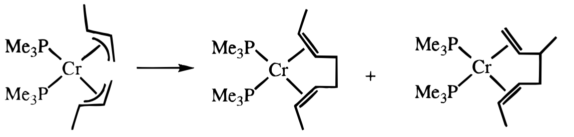
reversibly to the Zr compound but do no add to the Ti compound under mild conditions. At high pressure, CO slowly adds to Ti(η^4-butadiene)$_2$(dmpe) to yield $[Ti(CO)_3(dmpe)_{3/2}]_n$.[518] H_2 rapidly adds to the Zr complex to produce butane, while no reaction occurs with the Ti complex.[515] However, both complexes catalyze the dimerization of small olefins by a proposed mechanism that involves olefin coordination to a metallacyclopentene intermediate (Scheme 17). The diamagnetism of these molecules could be enforced, among other things, by extensive π-backbonding to the butadiene ligand, to formally afford a d^0 metallacyclopentene moiety. A similar derivative for group 5 is the Ta compound $TaCl(PMe_3)_4(C_2H_4)$, formally to be considered a 7-coordinate complex of Ta(III) (see section VIII.1.1.1).[160]

Scheme 17



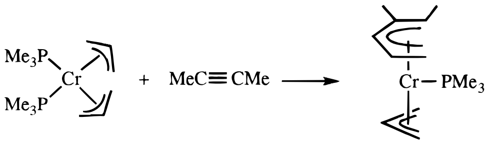
Chromium(II) π-allyl complexes, e.g. Cr(η^3-allyl)$_2$-$(PR_3)_2$ and Cr(η^3-allyl)$_2(R_2PCH_2CH_2PR_2)_2$, e.g. **CXI**, are rather thermally labile, being stable only at subfreezing temperatures.[519] They easily undergo an oxidative coupling of the two allyl ligands to afford poorly characterized products described as 14-electron (!!!) Cr(0) compounds (eq 37), the magnetic properties of which have not been determined, and insert alkynes and dienes to afford 16-electron, paramagnetic dienyl-allyl Cr(II) products (eqs 38 and 39).[519] It is remarkable that the second double bond does not interact with the metal in the crystallographically characterized product of reaction 39 to form a diamagnetic 18-electron structure.

Diallylmolybdenum(II) analogues of the above chromium species have not been described, but a related compound is the 16-electron hydridoallyl complex, MoH(η^3-CH_2CMeCH_2)(η^2-dppe)(η^1-dppe) (**CXII**).[520] This compound is remarkable in many respects: it does not reach a saturated configuration by coordination of its own dangling phosphine; it is not stabilized by additional π-bonding since none of its ligands have additional lone pairs; it is not stabilized by pairing energy since it is diamagnetic. An equilibrium of this species with the 18-electron trimethylenemethane isomer (see eq 40) has been proposed on the basis of NMR studies, the 16-electron and 18-electron species being present at room temperature and −80 °C, respectively.[520]

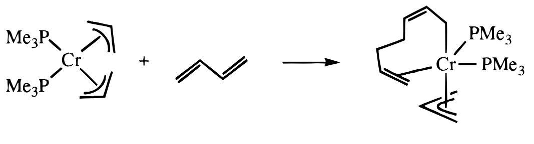


(37)

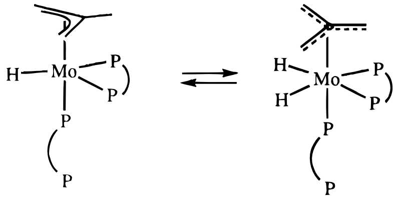
CXI



(38)



(39)



(40)

CXII

Stable 16-electron organotungsten(II) compounds do not appear to exist, but a π-alkene intermediate seems to be formed during the oxygen abstraction reaction by $WCl_2(PMePh_2)_4$ from allyl alcohols.[521]

VIII.3.1.3. Half-Sandwich Compounds. If the cycloheptatrienyl ligand is treated as a cationic 6-electron π-ligand, the group 4 (η^7-C_7H_7)MXL_2 compounds, **CXIII** are formally systems of d^4 M(0). Systems of this type are known for both Ti,[522,523] and Zr,[524] with X being a halogen and L = PR_3, or L_2 = $R_2PCH_2CH_2PR_2$, DME, THF, $R_2NCH_2CH_2NR_2$, and all are diamagnetic. Neither the Ti nor the Zr compounds have any tendency to add an additional 2-electron donor to afford 18-electron compounds, possibly for steric reasons (the C_7H_7 has a cone angle as large as Cp*), but rather engage in ligand dissociation equilibria, to afford diamagnetic dimers of formula $[(C_7H_7)ML(\mu\text{-}X)]_2$ (M = Ti, Zr).[522,525] Thermally stable alkyl derivatives are also known for Ti, e.g. $(C_7H_7)TiR(dmpe)$ (R = Me, Et) can be sublimed at 150 °C, demonstrating that a π-donor ligand is not necessary to stabilize the electronic unsaturation and that these compounds do not easily undergo β-H elimination chemistry.[522]

An unusual half-sandwich, arene complex of Ti(0) is compound (η^6-$C_{10}H_8$)Ti(trimpsi), whose structure is shown in Figure 26. Contrary to the related bis(arene)titanium(0) systems which are discussed in the following section, this compound is described as paramagnetic, but a magnetic moment to substantiate the presumed spin triplet ground state has not

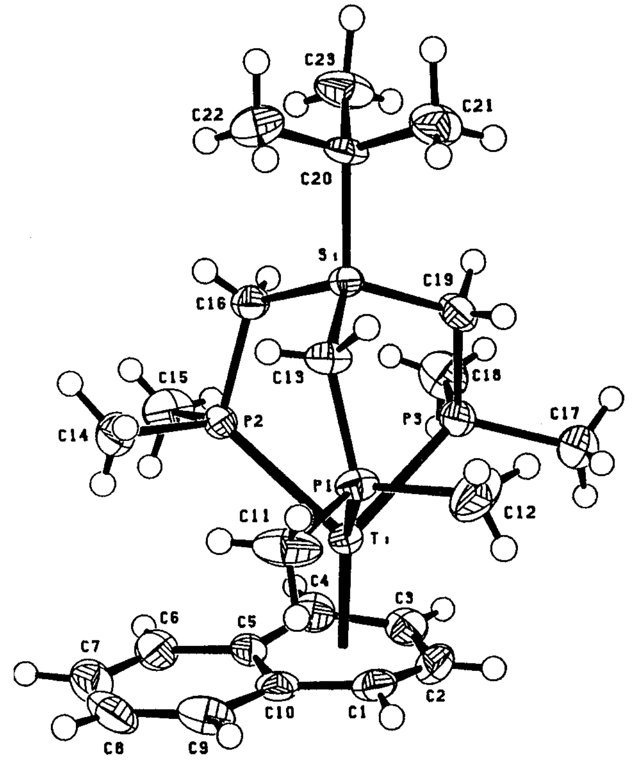
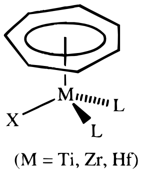
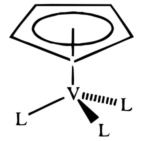


Figure 26. Molecular structure of (η^6-$C_{10}H_8$)Ti(trimpsi). (Reprinted from ref 526. Copyright 1988 VCH Verlagsgesellshaft.)

been reported.[526] Treatment with CO rapidly yields the 18-electron (trimpsi)Ti(CO)$_4$.



CXIII



CXIV

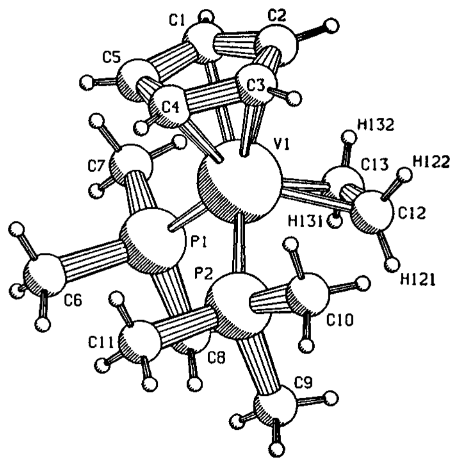
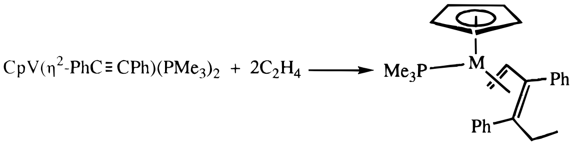


Figure 27. Crystal structure of CpV(η^2-C_2H_4)(PMe_3)$_2$. (Reprinted from ref 213. Copyright 1990 American Chemical Society.)

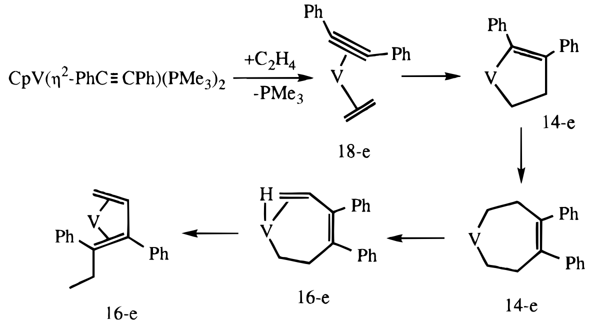
Extremely reactive (ring)VL$_3$ (ring = Cp, Cp*; L = CO) intermediates, **CXIV**, have been generated at low temperature by matrix isolation techniques and studied by IR spectroscopy. Their magnetic properties are unknown,[86] but their reactivity and IR properties are more consistent with a spin singlet ground state (see section VI). Complexes of this type where L is an organic π-ligand (olefin, diene) and/or phosphines, on the other hand, are sufficiently stable to be isolated.[203,209,213,527] These compounds are paramagnetic (by NMR), therefore presumably having a S = 1 ground state. A crystal structure of CpV(η^2-C_2H_4)(PMe_3)$_2$ (Figure 27) indicates a very small amount of π-back-donation into the π^* ethylene orbitals, therefore the compound is best described as a V(I)−ethylene complex rather than a V(III) metallacyclopropane complex.[213] Ligand addition proceeds only with replacement of ethylene, to either form other paramagnetic 16-electron complexes (e.g. CpV(bipy)(PMe_3)) or diamagnetic 18-electron complexes (CpV(CO)$_2$(PMe_3)$_2$ and CpV(η^2-PhC≡CPh)(PMe_3)$_2$, the latter one by virtue of a 4-electron $\sigma + \pi$ donation from the alkyne). Oxidative addition of PhSSPh affords [CpV(μ-SPh)$_2$]$_2$.[527] The alkyne derivative is also quite reactive, but contrary to the ethylene derivative (*vide supra*) it is a source of the 16-electron CpV(η^2-PhC≡CPh)(PMe_3) fragment by dissociation of PMe_3.

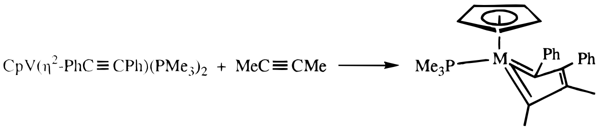
An unusual way to obtain diene complexes is shown in eq 41, featuring a linear 1:2 cotrimerization of diphenylacetylene with ethylene. The proposed mechanism of the reaction involves fundamental coupling and β-H elimination/insertion processes (see Scheme 18).[213] The unsaturated intermediates of this scheme could also be stabilized by PMe_3 coordination and/or donation from the additional double bond in the ligand itself. The condensation between the alkyne complex CpV(η^2-PhC≡CPh)(PMe_3)$_2$ and another molecule of alkyne, on the other hand, ultimately affords a bent metallacyclopenta-1,3,5-triene (see eq 42),[213,528] which is diamagnetic by virtue of the interaction with the C2-C3 double bond, bringing the electron count to 18.



(41)

Scheme 18



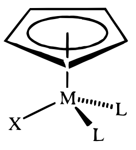


(42)

The reactive intermediates CpM(CO)$_3$ (M = Nb, Ta) are made the same way as their V analogue (*vide supra*) and, like the latter, react rapidly with 2-electron donor ligands such as N$_2$, H$_2$, and CO (see section VI).[86] Contrary to vanadium, however, other unsaturated systems with larger L ligands have not been reported.

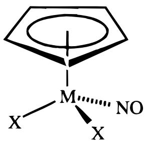
Half-sandwich Cr(II) complexes have been less developed than the above mentioned V(I) complexes. Examples of this class of compounds are CpCrMe(dmpe) and Cp*CrBz(bipy) (**CXV**).[9,445] These compounds have received attention because they could in principle be models for the chromium-catalyzed ethylene polymerization process. However, detailed studies have demonstrated that half-sandwich Cr(III) rather than Cr(II) species acts as a catalyst. All that the 16-electron compounds seem to be able to do is to oligomerize ethylene to short chain olefins.[9] This indicates that ethylene is able to bind to the metal (possibly with spin pairing, if no predissociation of another ligand takes place) and insert into the Cr–alkyl bond, but the subsequent β-H elimination process is much more favorable for Cr(II) with respect to Cr(III). Other recent examples of this class are Cp[(Ph$_2$PCH$_2$SiMe$_2$)$_2$N]Cr[529] and Cr(Pdl′)X(dmpe) (X = Cl, Me), all these also having a S = 1 ground state.[530] Stable 18-electron complexes, on the other hand, are CpCr(SePh)(CO)$_3$[531] and [CpCr(CNBu^t)$_4$]$^+$.[450] Evidently, the introduction of stronger π-acids favors coordination of an additional ligand through either reduction of the pairing energy and/or increase of the orbital gap for the unsaturated system.

Another class of half-sandwich, formally Cr(II), complexes corresponds to the formula CpCr(NO)X$_2$, **CXVI**. Only two derivatives of this kind, CpCr(NO)I(NPh$_2$) and Cp*Cr(NO)(OPr^i)$_2$, seem to be stable,[532,533] in contrast with the many corresponding derivatives of Mo and W (*vide infra*). The diamagnetism (reported only for the dialkoxide complex) can be ascribed to strong X to Cr π-donation. Compounds with X = Cl, Br, and I have been generated by one-electron oxidation of the stable 17-electron [CpCr(NO)X$_2$]$^-$, but immediately decompose by NO elimination.[534] The decomposition has been ascribed to the presumed spin triplet configuration of these derivatives, which removes one electron from a Cr–NO π bonding orbital thereby weaking the Cr–NO interaction. This reaction represents a rare case of facile NO dissociation from a transition metal.



(M = Cr, Mo)

CXV



(X = Cr, Mo, W)

CXVI

Whereas there are literally hundreds of half-sandwich 18-electron complexes of Mo(II) and W(II), related complexes with a 16-electron configuration are very rare, and most have only been observed as short-life intermediates in chemical reactions, these having a high tendency to reach again a saturated configuration via coordinative or oxidative addition reactions. For instance, the CpMX(CO)$_2$ (M = Mo, W; X = Cl, CH$_3$) fragments are obtained by photolytic CO ejection from CpMX(CO)$_3$, but the primary photoproduct rapidly reacts with N$_2$, C$_2$H$_4$, CO, and other substrates to afford saturated adducts.[115,535,536] The magnetic properties of these intermediates are not known. Rare examples of stable 16-electron complexes are based on the general formula (ring)MXL$_2$ where ring is Cp or substituted derivative, L is CO or phosphine, and X is an efficient π-donor group such as a phosphido or arsenido ligand.[103,537–539] Consequently, all these complexes are effectively electronically saturated and diamagnetic. Nevertheless, some of them readily add ligands to form 18-electron adducts. (The sterically crowded and electron-rich Cp*Mo(PPh$_2$)(PMe$_3$)$_2$ does not add CO.)

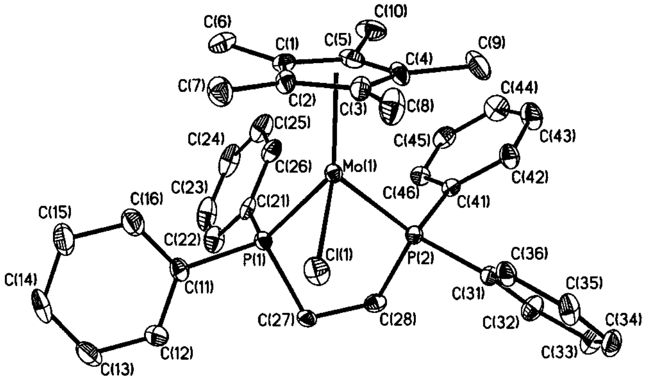


Figure 28. Crystal structure of Cp*MoCl(dppe). (Unpublished results from this laboratory.)

The analogous Cp*MoClL$_2$ (L = tertiary phosphine) compounds recently prepared in our laboratory,[20] on the other hand, have a spin triplet configuration. The structure of Cp*MoCl(dppe) is shown in Figure 28. However, they still readily add ligands to afford saturated derivatives. For instance, Cp*MoCl(PMe$_3$)$_2$ adds CO and N$_2$ (the former ~10^3 times faster than the latter, see section VI) to afford the corresponding Cp*MoCl(PMe$_3$)$_2$L adducts and oxidatively adds H$_2$ to afford Cp*MoCl(H)$_2$(PMe$_3$)$_2$. Equilibrium studies (eq 43) provide a binding energy of $\Delta H = 22.8 \pm 2.1$

$$\mathrm{Cp^*MoCl(PMe_3)_2 + N_2 \rightarrow Cp^*MoCl(PMe_3)_2 + N_2} \quad (43)$$

kcal/mol for the Mo–N$_2$ bond, but the bond strength (according to our definition in section IV) is greater, because part of the energy spent in breaking the Mo–N$_2$ bond is regained as a result of the spin-state change. Calculations at the MP2 level on the CpMoCl(PH$_3$)$_2$ model system are shown in Figure 29 and agree well with the experimental observations.

Compound Cp*MoCl(dppe) adds CO but not N$_2$. Since the configuration of the four-legged piano stool Cp*MoCl(dppe)(L) product is forced to be *cis* with the new L ligand *trans* to the stronger *trans*-labilizing phosphorus donor, the Mo–L binding energy might be smaller, and the weaker N$_2$ ligand might not be sufficient to regain the cost of pairing the two electrons. Analogous tungsten complexes have not been reported.

A peculiar class of 16-electron Mo(II) and W(II) derivatives are the nitrosyl complexes CpM(NO)X$_2$ (X = halogen, SR, alkyl, aryl),[540–543] **CXVI**, all these being diamagnetic compounds. The stability of these

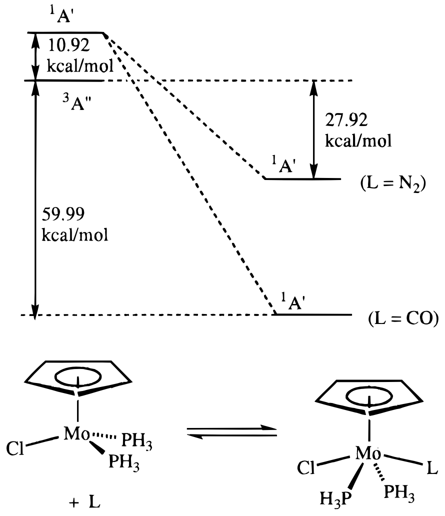
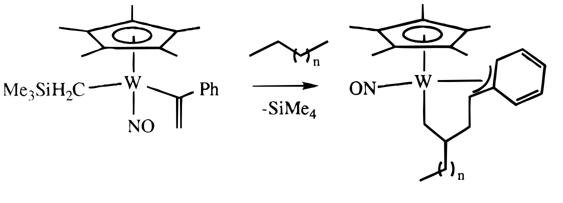


Figure 29. Geometry-optimized MP2 energies for the $CpMoCl(PH_3)_2 + L \rightleftarrows CpMoCl(PH_3)_2L$ (L = CO, N_2) system.

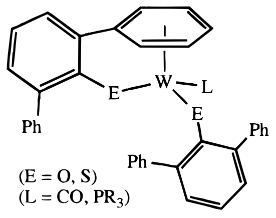
derivatives toward loss of NO, in contrast with the chromium analogues discussed above, may indeed be related to the spin singlet state which retains the maximum number of electrons in the M−NO π-bonding orbitals. An alkyl hydride complex, Cp*W(NO)(CH_2SiMe_3)H, has also been reported.[544] These compounds have linear M−N−O moieties, therefore justifying their formal consideration as NO^+ complexes of d^4 metals. Since the above list includes compounds devoid of ligand lone pairs, the diamagnetism is not related to a π-stabilization. Calculations on the CpMo(NO)Me_2 model compound indicate a significant HOMO−LUMO gap because of the strong Mo−NO back-bonding and a metal-localized LUMO[545] and agree with the experimentally facile addition of Lewis bases to achieve a saturated 18-electron configuration. For instance, CpW(NO)R_2 adds PMe_3, but not sterically more demanding phosphines or weaker bases such as N_2, CO_2, or C_2H_4.[541,543] Furthermore, whereas Cp*W(NO)I_2 is a monomer both in the solid state and in solution,[542] the analogous $[Cp^*Mo(NO)X_2]_2$ (X = Cl, Br, I) are halide-bridged dimers, at least in the solid state. An unusual reaction is the facile alkane C−H activation by Cp*W(NO)(CH_2SiMe_3)(CPh=CH_2) to afford an 18-electron η^3-benzyl derivative, as shown in eq 44.[546]



(44)

The orthometalation of PPh_3 upon reaction with Cp*W(NO)(CH_2SiMe_3)H also affords an 18-electron product, i.e. Cp*W(NO)($PPh_2C_6H_4$)(H).[544] Another unusual reaction is the isomerization of CpW(NO)Ar_2 to CpW(NAr)(O)Ar, which is promoted by water. The use of $H_2{}^{18}O$ does not lead to incorporation of ^{18}O.[547]

Another class of half-sandwich W(II) complexes with a 16-electron configuration is the arene bis(alkoxo) and bis(thiolato) complexes studied by Rothwell (see **CXVII**).[312,548] These compounds are diamagnetic and do not add another molecule of ligand (e.g. the compound with dppm has a dangling phosphine). Steric factors have been invoked to explain this lack of reactivity, although strong π-donation from the alkoxide or thiolate lone pairs may also serve to stabilize the molecule.

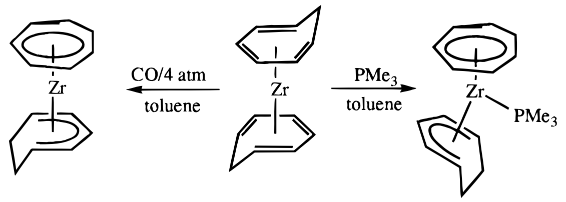


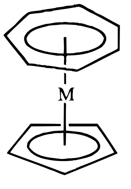
CXVII

No stable half sandwich 16-electron complex with Mn(III) or Re(III) appears to have been reported. Saturated Mn(III) compounds are known, e.g. CpMn(H)($SiHPh_2$)(dmpe).[549]

VIII.3.1.4. Sandwich Compounds. The (cycloheptatrienyl)(cyclopentadienyl)M derivatives, **CXVIII**, and indenyl analogues have been described for M = Zr and Hf.[189] These can be formally considered as complexes of d^4 M(0) when conventionally considering the cycloheptatrienyl as a 6-electron cationic ligand. Other Group 4 M(0) complexes in this class are (η^6-arene)$_2$M (M = Ti, Zr, Hf)[550,551] (**CXIX**) and (η^6-cycloheptatriene)$_2$M for M = Ti, Zr[524,525] (**CXX**). These derivatives are all diamagnetic. Curiously, the (η^6-cycloheptatriene)$_2$Zr compound undergoes the isomerization reaction in Scheme 19 upon exposure to CO under pressure without formation of a CO adduct, whereas addition of PMe_3 forms the corresponding 18-electron adduct of the rearrangement product.[524] Bis(arene) compounds of Zr and Hf are known only with sterically encumbering ligands. Tertiary phosphine adducts of systems with smaller rings can be obtained directly by cocondensation of the arene, the phosphine, and metal vapors.[552,553] Oxidative addition of $Me_3SnSnMe_3$ to $(C_6H_5Me)_2M(PMe_3)$ to afford $(C_6H_5Me)_2M(SnMe_3)_2$ (M = Zr, Hf) is supposed to proceed through the 16-electron bisarene derivatives.[554]

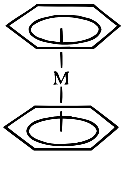
Scheme 19





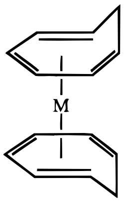
M = Zr, Hf

CXVIII



M = Ti, Zr, Hf

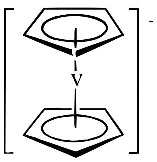
CXIX

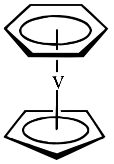


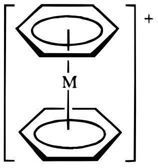
M = Ti, Zr

CXX

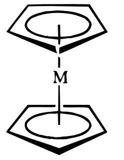
Vanadocene can be reduced by interaction with potassium to afford K[Cp_2V] (**CXXI**), whose magnetic properties have not been reported, although the compound is described as paramagnetic, therefore presumably having a spin triplet configuration.[209] This electron-rich metallocene system easily reacts with neutral ligands with loss of one of the Cp rings, e.g. forming $CpV(CO)_4$ upon adding CO.[209,435] Vanadium(I) also forms the classes of Cp(η^6-arene)V[209,274,555] (**CXXII**) and [(η^6-arene)$_2$V]$^+$ (**CXXIII**) derivatives,[185,556–559] both systems being paramagnetic with two unpaired electrons. Whereas [(η^6-arene)$_2$V]$^+$, obtained by 1-electron oxidation of the bis(arene) V(0) complex, is stable, the corresponding oxidation of (η^6-arene)$_2$Nb by $Fc^+BAr_4^-$ gives extremely reactive [(η^6-arene)$_2$Nb][BAr_4] products that promptly give ligand adducts with CO, acetylenes, and THF.[185,560,561] The magnetic properties of these salts have not been reported. Corresponding Ta(I) compounds do not exist.


CXXI


CXXII

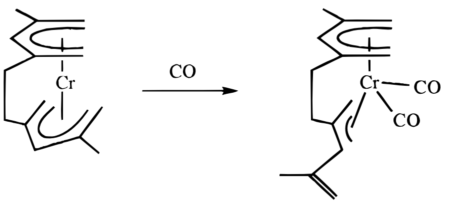

(M = V, Nb)

CXXIII


(M = Cr, Mo, W)

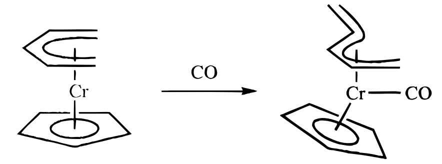
CXXIV

Chromocene and ring-substituted derivatives, **CXXIV**, show a spin triplet ground state[457,458] and observable, paramagnetically shifted ^{1}H- and ^{13}C-NMR resonances.[339,459,460] In spite of the large pairing energy expected for these systems, CO adds rapidly and irreversibly to chromocene to form $Cp_2Cr(CO)$, which however has a rather weak Cr–CO bond.[18] "Open chromocenes", also spin triplet systems,[336,337,461,462,530,562] show no reactivity toward CO, but the strain introduced by linking together the two pentadienyl units via an ethylene bridge induces CO binding to afford an 18-electron diamagnetic dicarbonyl adduct where one ring has slipped to a η^3 configuration (eq 45), and even reversible binding of alkylphosphines and alkyl phosphites to form labile monoadducts.[464] Other reactions of open chromocenes are with isocyanides and chelating diphosphines, these proceding beyond simple coordination, inducing reductive elimination of the two dienyl ligands and formation of Cr(0) products, e.g. $Cr(dmpe)_3$ or $Cr(CNR)_6$.[530] CO and isonitriles bind strongly also to *ansa*-chromocene systems, the carbonyl ligand remaining coordinated even upon 1-electron oxidation.[563] The forced bending of the two η^5-ligands of Cp_2Cr from a coplanar arrangement is calculated to provide an extra thermodynamic help to the addition reaction, part of which is steric and part electronic because of raising of frontier orbital energies.[82] How the triplet–singlet gap is modified by the bending process was not a point of this investigation.



(45)

The mixed (pentadienyl)(cyclopentadienyl)chromium ("half-open chromocene") also forms a strong bond to CO, which is accompanied by a rearrangement of the Pdl ligand from the U-shape to the S-shape (eq 46) and a spin change from triplet to singlet.[463,564] The CO exchange reaction in Cp(Pdl)Cr(CO) is dissociative, with ΔH^* in the 20–26 kcal/mol range depending on the substituents on the Pdl ligand.[463] This activation enthalpy is higher than some M–CO dissociation energies for first row diamagnetic M–CO compounds that lead to a spin triplet upon CO dissociation (see section V), suggesting that the dissociation may lead to a spin singlet S–Pdl intermediate which subsequently rearranges to the U–Pdl isomer with a spin triplet ground state. The measured ΔS^* values, however, have been interpreted by a concomitant S-to-U rearrangement and CO dissociation.

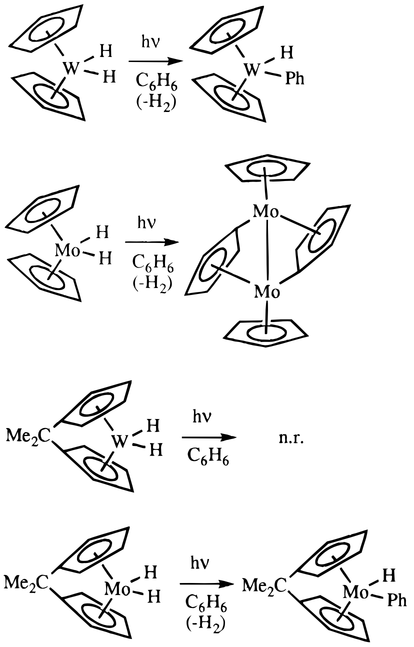


(46)

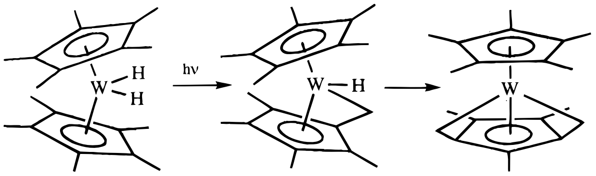
Isoelectronic with chromocene are also [Cp(η^6-arene)Cr]$^+$ complexes, **CXXV**, recently obtained by 1-electron oxidation of the 17-electron neutral analogues.[55] Magnetic susceptibilities were not measured for these thermally labile materials, but their ^{1}H-NMR spectroscopic properties are consistent with a S = 1 ($^3E_2$) ground state.[55]

Contrary to chromocene, molybdenocene and tungstenocene cannot be isolated and can only be produced as very reactive intermediates, e.g. by photolysis of the carbonyl adducts or Cp_2MH_2. They have, however, been trapped and observed in argon matrices as spin triplet (by magnetic circular dicroism) unsolvated compounds.[90,298,565,566] In the absence of trapping reagents, both Cp_2M (M = Mo, W) intermediates activate the Cp C-H bond of a second molecule, to afford the dinuclear [CpM(μ-η^1:η^5-C_5H_4)(μ-H)]$_2$ (M = Mo, W) compounds.[90] Both molybdenocene and tungstenocene are efficiently trapped by CO. Cp_2Mo is also efficiently trapped by alkenes and alkynes, but not by C–H bonds in saturated hydrocarbons, whereas Cp_2W reacts readily with H_2 and Ar–H bonds to afford Cp_2WH_2 or $Cp_2W(Ar)(H)$ products.[565–569] When the two Cp groups are tied together and distorted from the coplanar arrangement by an *ansa*-bridge, the chemistry dramatically changes (see Scheme 20). The *ansa*-bridged Mo system (less accessible) is sufficiently reactive to insert into aromatic C–H bonds, whereas the W system can no longer be generated by reductive elimination of H_2 from the dihydride (or CH_4 from the hydride methyl) (see also section VI).[110]

Scheme 20

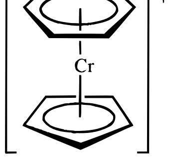


The steric protection of Cp* does not appear to be sufficient to stabilize these unsaturated systems, as photolyis of Cp^*WH_2 does not afford decamethyltungtocene but rather a product of double ring activation (see eq 47).[570] Molybdenum, however, forms a stable 16-electron derivative with the sterically more encumbering pentaphenylcyclopentadienyl ring, $(C_5Ph_5)_2Mo$, whose magnetic moment is consistent with the presence of two unpaired electrons.[480]

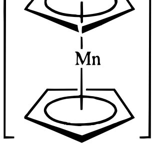


(47)

The oxidation of manganocene is irreversible, but the corresponding oxidation of Cp^*_2Mn gives stable $[Cp^*_2Mn]^+$ salts, **CXXVI**, with a spin triplet ($^3E_{2g}$, $e_{2g}{}^3a_{1g}{}^1$) ground state,[479] which have been extensively studied for their properties as molecular magnetic materials.[571]



CXXV

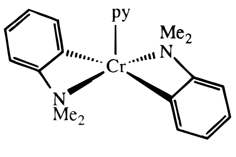


CXXVI

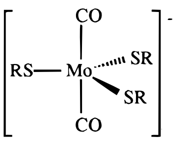
VIII.3.2. 14-Electron Systems

The structurally characterized $Cr(C_6H_4\text{-}o\text{-}NMe_2)_2(py)$ complex **CXXVII** has two unpaired electrons.[572] The diamagnetic, trigonal-bipyramidal $[Mo(SR)_3(CO)_2]^-$ complexes **CXXVIII** owe their stability to the steric protection by the bulky R groups (e.g. 2,4,6-$C_6H_2Pr^i{}_3$) and to Mo−S π-bonding. They readily bind one additional CO ligand to form 16-electron complexes.[573]

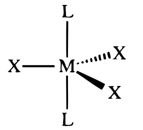
A 5-coordinate geometry, **CXXIX**, and four unpaired electrons have been established for the crystallographically characterized trigonal-bipyramidal $MnMesBr_2(PMe_3)_2$[148] and $MnMe[o\text{-}C_6H_4(CH_2)_nNMe_2]_2$ ($n = 2, 3$),[574] whereas the structure determined for spiro-$[Mn(C_4H_8)_2(py)]^-$ and proposed for the analogous $[Li(tmeda)]_2[MnMe_5]$ (the first one also a spin quintet compound; the second one not magnetically characterized) is square pyramidal, **CXXX**.[147,428,575]



CXXVII

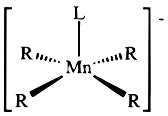


CXXVIII



(M = Mn, Tc, Re)

CXXIX



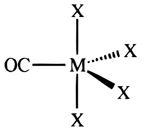
CXXX

The equilibrium between 5-coordinate $[MnMe_5]^{2-}$ and 4-coordinate $[MnMe_4]^-$ (eq 48) is solvent dependent.[428]

$$[Li(tmeda)]_2[MnMe_5] \rightleftarrows [Li(tmeda)_2][MnMe_4] + LiMe \quad (48)$$

Technetium(III) compounds with sterically hindered arylthiolato ligands, $Tc(SR)_3L_2$ (L = CO, isocyanide) or with the bulky "umbrella" ligand tris(*o*-thiophenyl)phosphine), $[P(o\text{-}C_6H_4S)_3]Tc(CNR')$ are trigonal-bipyramidal, diamagnetic compounds (**CXXIX**).[576−578] The π-donation from the equatorial thiolato ligands can provide four additional electrons, making these molecules effectively saturated. The $[P(o\text{-}C_6H_4S)_3]Tc(CNR')$ complexes can add a second isocyanide ligand to afford a 16-electron adduct, which is on the other paramagnetic.[576]

The Re(III) compounds $ReAr_3(PEt_2Ph)_2$ (Ar = Ph, *p*-Tol) also show a trigonal-bipyramidal structure (**CXXIX**) but, contrary to the Mn(III) analogues, are diamagnetic.[149,579] It is rather remarkable that, in spite of the absence of strong π-stabilization, ligand additions to these low-coordinate Re complexes have not been reported and that the compounds apparently do not dimerize to metal−metal-bonded species. Ru(IV) and Os(IV) also form diamagnetic, trigonal-bipyramidal complexes of formula $M(EAr)_4(CO)$ (E = S, Se), **CXXXI**, these being presumably stabilized sterically and by E−M π-bonding.[580]



(M = Ru, Os)

CXXXI

Table 11. Structurally Characterized 4-Coordinate σ-Organochromium(II) Complexes

compound	preparation	μ_{eff}, μ_B	α,[a] deg	ref
$CrNp_2$(dippe)	$[CrCl_2(dippe)]_2 + MgNp_2$	4.7	28.4	584
$Cr(CH_2SiMe_3)_2$(dippe)	$[CrCl_2(dippe)]_2 + Mg(CH_2SiMe_3)_2$	4.7	15.8	584
$CrMes_2(THF)_2$	$CrCl_2(THF)_2$ + 2 MesLi	4.69	27.6(6)	583
$CrMes_2$(bipy)	$CrMes_2(THF)_2$ + bipy	4.86	31.5(3)	583
$CrMes_2(PMe_3)_2$	$CrCl_2(PMe_3)_2 + MgMes_2$	4.9	0	584
$[Li(THF)]_2[CrMes_4]$	$CrCl_2(THF)_2$ + 4 MesLi	4.69	0	583
$[Li(THF)_2]_2[CrPh_4]$	$CrCl_2(THF)_2$ + 4 PhLi	4.73	0	583
$[Li(tmeda)]_2[CrMe_4]$	$[Li(THF)]_4[Cr_2Me_8]$ + tmeda	4.98	0	588
$[(Ph_2PCH_2SiMe_2)_2N]CrR$ ($R = CH_3$, CH_2Ph)	$[\{(Ph_2PCH_2SiMe_2)_2N\}CrCl]_2$ + MR (M = Li, Na, K)	5.1	0	529

[a] Dihedral angle between CrX_2 and CrL_2 planes. This angle is 0° for a square-planar geometry, and 90° for a tetrahedral geometry.

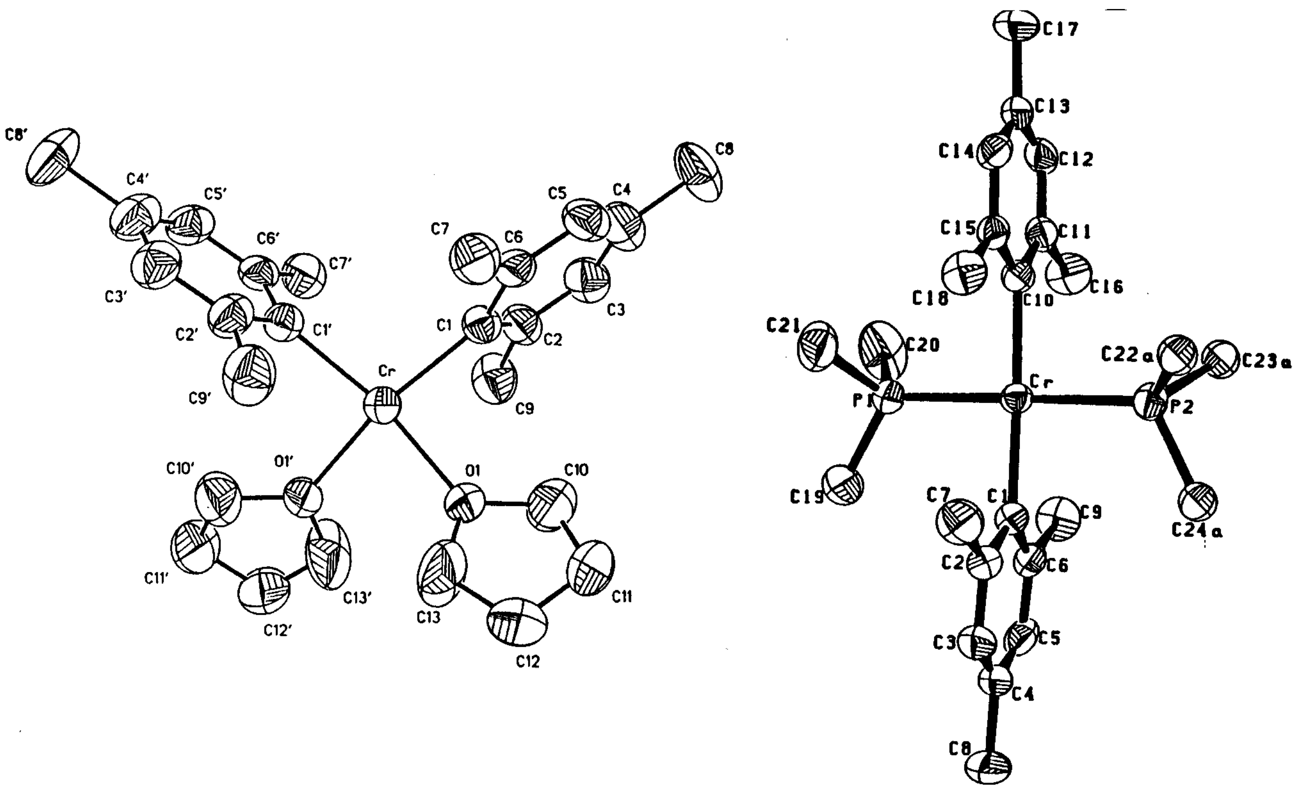
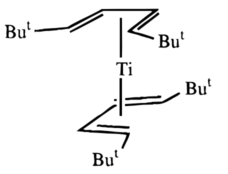


Figure 30. Crystal structures of $CrMes_2(THF)_2$ (left) and $CrMes_2(PMe_3)_2$ (right). (Reprinted from refs 583 and 584, respectively. (Copyright 1990 Elsevier and 1988 American Chemical Society.)

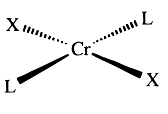
VIII.3.3. 12-Electron Systems

Diamagnetic Ti(η^4-diene)$_2$ compounds, **CXXXII**, have been obtained with sterically encumbered diene ligands by metal vapor methods. The relative disposition of the two diene ligands is suggested by NMR spectroscopy, which also indicates a high barrier to rotation.[581] Thus, the compound can be viewed as adopting a pseudotetrahedral coordination geometry.

Four-coordinate Cr(II) compounds, **CXXXIII**, are fairly common. The preferred structure for mononuclear complexes appears to be square planar rather than tetrahedral, although tetrahedrally distorted structures are observed for sterically crowded systems (see Table 11). Compounds $CrMes_2$·3THF and $CrMes_2$·bipy·THF were originally described as 5-coordinate complexes on the basis of the difficult THF loss (>60 °C under high vacuum),[582] but a later X-ray investigation has shown 4-coordinate geometries for both.[583] Their magnetic moments (four unpaired electrons) are also typical of 4-coordinate Cr(II), whereas a triplet ground state has been reported for 5-coordinate Cr(II) complexes (see section VIII.3.2). Curiously, the $CrMes_2(THF)_2$ adopts a tetrahedrally distorted cis structure,[583] whereas the sterically more encumbering $CrMes_2(PMe_3)_2$ is undistorted trans square planar (see Figure 30).[584] The preference of these compounds for the square-planar geometry find its rationale in the less severe d electron-bonding pair repulsion with respect to the alternative tetrahedral geometry, much like the case of the d^8 systems in a strong ligand field (see section VII). The stability of these systems can be related to the unavailability of any empty orbitals for attack by external bases (the only empty orbital is directed toward the positions occupied by the four ligands). Compound [(Ph_2PCH_2-

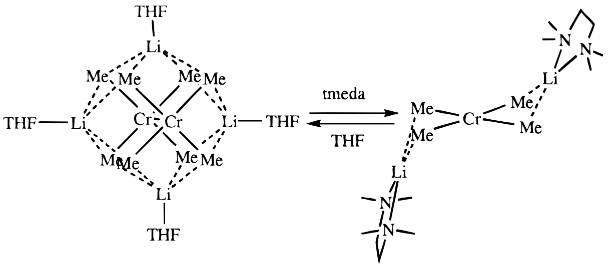


CXXXII



CXXXIII

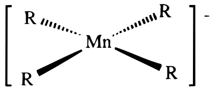
$SiMe_2)_2N]CrCH_2Ph$ shows an acute $Cr-CH_2-Ph$ angle, suggesting an interaction between the Ph group and the metal atom.[529] Lower magnetic moments with respect to four unpaired electrons are indicative of dimerization with formation of "quadruply bonded" Cr_2L_8-type systems. Examples of this kind are provided by the homoleptic $[Li(THF)]_4[Cr_2Me_8]$ (**CXXXIV**) and by other similar derivatives originally reported by Krausse *et al.*,[585,586] whose low magnetic moment of 0.57 μ_B indicates the formation of metal–metal bonds and/or strong antiferromagnetic coupling between the two metals. The nuclearity control appears to be very delicate; for instance, $Li_2CrPh_4 \cdot 4THF$ is monomeric ($\mu_{eff} = 4.73\ \mu_B$).[587] In addition, the nuclearity of the tetramethylchromate(II) complex is controlled by the mere modification of the coordination sphere on the Li counterion, e.g. see $[Li(tmeda)]_2[CrMe_4]$ (**CXXXV**). The transformation of the dinuclear into the mononuclear species is reversible (eq 49).[588]



(49)

CXXXIV CXXXV

Early reports of Cr(II) compounds, e.g. $LiCrAr_3 \cdot Et_2O$ (Ar = p-$C_6H_4NMe_2$) and $MCrPh_3 \cdot 1.5Et_2O$ (M = Li, Na), with low magnetic moments (0.3–0.8 μ_B) and no structural details,[395,481] can probably be best interpreted in terms of dinuclear structures. No corresponding 4-coordinate compounds of Mo(II) or W(II) appear to be known, apparently because of the facile coordination of additional ligands or dimerization to quadruply bonded clusters, e.g. $[Mo_2Me_8]^{4-}$ and $Mo_2Me_4(PMe_3)_4$.[589]



CXXXVI

There are few reports of 4-coordinate (σ-organo)manganese(III), all anionic $[MnR_4]^-$, **CXXXVI**. One of these is $Li[Mn(DPE)_2] \cdot 2THF$, although the low magnetic moment of 2.95 μ_B indicates the probable association into a dinuclear structure.[303] The crystal structure of $[MnMe_4]^-$ is most interesting because it shows a slight tetrahedral distortion of the expected square-planar geometry (see section VII) for a d^4 metal ion (see Figure 31).[428] The dihedral angle between the two *cis*-C–Mn–C planes (α in Table 11) is 26.2°. The reluctance of this anion to dimerize to a hypothetical quadruply bonded $[Mn_2Me_8]^{2-}$ dimer, which would be isoelectronic with the known $[Cr_2Me_8]^{4-}$ dimer, has been attributed to steric crowding due to the smaller size of the Mn(III) center (which is responsible for the tetrahedral distortion mentioned above), the greater contraction of the d orbitals which disfavors metal–metal bonding, and the Li–Mn ion separation caused by the presence of the strongly chelating tmeda ligands.[428] The same coordination geometry and magnetic properties are also found for the isoelectronic $[MnOMe_3]^{2-}$ ion, which is a rare example of an oxo–alkyl complex for a transition metal of the 3d series,[590] and are also likely to be adopted by the incompletely characterized *spiro*-$[Mn(C_4H_8)_2]^-$ anion.[147]

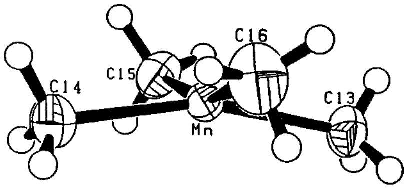


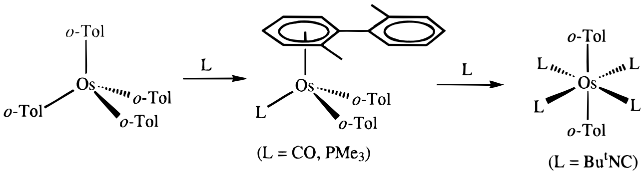
Figure 31. Crystal structure of the $[MnMe_4]^-$ anion in $[Li(tmeda)_2][MnMe_4]$. (Reprinted from ref 428. Copyright 1991 American Chemical Society.)

The tetraaryl rhenium(III) derivative $[Re(o\text{-}Tol)_4]^-$ appears to exist in solution but attempts to isolate it have failed.[367] This and other isoelectronic Re(III) compounds are likely to be found tetrahedral and diamagnetic.

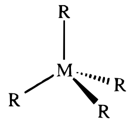
As for isoelectronic 4-coordinate Fe(IV), the only reported compound is $Fe(Nor)_4$, obtained from $FeCl_3 \cdot OEt_2$ and 1-norbornyllithium.[357] The compound is remarkable in that it is perfectly diamagnetic, therefore the ligand field of the alkyl groups is sufficiently high to cause spin pairing into the $e^4t_2{}^0$ configuration of the presumed tetrahedral geometry, **CXXXVII**. In comparison with the d^3 analogues $Mn(Nor)_4$ and $[Cr(CH_2SiMe_3)_4]^-$, which adopt the high-spin configuration $e^2t_2{}^1$, the d^4 Fe(IV) and Co(V) compounds would be expected to gain more by adopting the high-spin configuration in view of more favorable Coulombic and exchange components of the pairing energy. On the other hand, the more electronegative higher oxidation state metals presumably lead to a greater covalency for the M–R bonds, pushing the energy of the t_2 set higher. Therefore, the effect of Δ wins in this case over the effect of (PE).

Isoelectronic and isostructural with $Fe(Nor)_4$ are also tetraalkyl and tetraaryl compounds of ruthenium and osmium,[16,361,492] **CXXXVII**, all of which are diamagnetic compounds. Whereas tetra-*o*-tolyl derivatives of molybdenum, tungsten, and rhenium undergo orthometalation reactions upon tratement with Lewis bases, $Os(o\text{-}Tol)_4$ undegoes reductive coupling upon interaction with L (see Scheme 21).[591]

Scheme 21

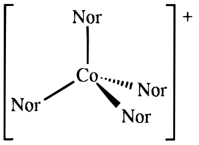


The diamagnetic and presumably tetrahedral $[Co(Nor)_4]^+$ ion, **CXXXVIII**, is obtained by reversible oxidation of the parent Co(IV) complex.[592,593] Four-coordinate complexes of Rh(V) and Ir(V) are apparently unknown but, should one be made, it would undoubtedly be diamagnetic.



(M = Fe, Ru, Os)

CXXXVII



CXXXVIII

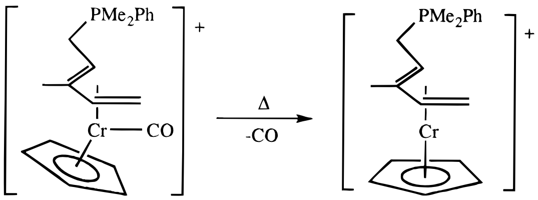
VIII.3.4. Lower Coordination Systems

A compound described as Cr(Mes)$_2$ was reported by Tsutsui and Zeiss in 1960 from the interaction of CrCl$_2$ and MesMgBr,[594] whereas seven years later, the same reaction was reported by Stolze and Hähle to produce CrMes$_2$(THF), with four unpaired electrons.[582] This compound transforms 2-butyne to hexamethylbenzene, much as triarylchromium derivatives do.[594] A similar compound, CrAr$_2$ (Ar = *o*-C$_6$H$_4$OMe) described later by Hein and Tille, is believed to possess a dimeric structure on the basis of the low observed magnetic moment (0.54 μ_B).[481] A poorly characterized WNor$_2$ (μ_{eff} = 0.64 μ_B) has also been described.[595]

VIII.4. d^5 Systems

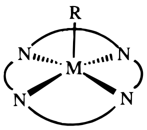
VIII.4.1. 15-Electron Systems

Thermal decarbonylation of the 17-electron Cr(I) species [Cp*(η^4-CH$_2$CHC(Me)CHCH$_2$PMe$_2$Ph)Cr(CO)]$^+$ affords the 15-electron [Cp*(η^4-CH$_2$CHC(Me)CHCH$_2$-PMe$_2$Ph)Cr]$^+$ complex, which has however not been isolated (eq 50). The kinetic analysis yields ΔH^* = 23.0 kcal/mol.[450] While (σ-organo)manganese(II) compounds prefer the 4-coordinate, tetrahedral geometry (see section VIII.4.2), half-sandwich Mn(II) complexes all have a 17-electron configuration, either as mononuclear CpMnXL$_2$ or as dihalo-bridged dinuclear [CpMn(μ-X)L]$_2$ derivatives. These derivatives, like the parent manganocene system, adopt a high-spin configuration (S = $^5/_2$) in which the M−L σ*-orbitals are occupied (a rare ocurrence for organometallic systems, see section III.3.4).[596,597]



(50)

Five-coordinate (σ-organo)iron(III) are well represented in the extensively investigated class of alkyl and arylporphyrinato complexes, which adopt a square-pyramidal structure with the organic ligand occupying the apical position, **CXXXIX**.[130−132,598−602] These compounds are generally low-spin (S = $^1/_2$), but can also adopt a high spin (S = $^5/_2$) ground state in conjunction with electron-withdrawing (e.g. perfluorinated) organic ligand and/or basic porphyrins,[130,131] and cases of a spin equilibrium have also been reported.[598] The high-spin situation involves occupation of M−L σ*-orbitals. No solvent coordination to these system has been observed; however, the spin state is found to be solvent dependent at low temperature.[598]

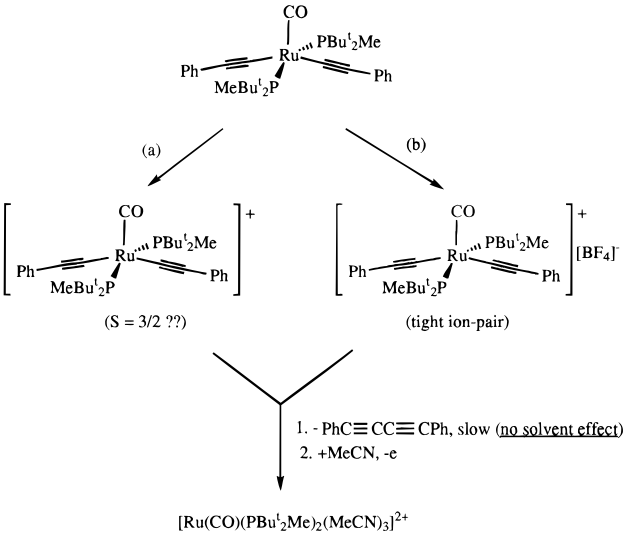


(M =Fe, Ru)

CXXXIX

Porphyrin derivatives of Ru(III), e.g. Ru(TPP)Ph and Ru(OEP)Ph, **CXXXIX**, assumed to have a S = $^1/_2$ ground state are also known.[513,603,604] Other examples of 5-coordinate Ru(III) complexes are the unstable [Ru(C$_2$Ph)(R)(CO)(PBu$^t_2$Me)$_2$]$^+$ (R = C≡CPh or CH=CHPh), obtained by 1-electron oxidation of the corresponding 16-electron Ru(II) complexes.[605] The oxidation potentials for the Ru(II)/Ru(III) processes are practically identical in MeCN and CH$_2$-Cl$_2$, hinting to the possibility that MeCN *does not* coordinate the Ru(III) center in the oxidation product. In addition, the Ru(III) ions decompose by a strictly intramolecular reductive elimination of PhC$_2$R, the rate and activation parameters of which are again independent of whether MeCN or CH$_2$Cl$_2$ is used as solvent. The attempted rationalization of this behavior invokes close ion pairing between the Ru(III) cationic species and the BF$_4^-$ counterion,[605] which would also prevent the formation of a formally 13-electron [Ru(CO)(PBu$^t_2$Me)$_2$]$^+$ species (Scheme 22, path b). Although the 15-electron species appears relatively stable on the cyclic voltammetric time scale, attempts at generating this species by controlled chemical oxidation only produced complex organometallic product mixtures. The structure and magnetic properties of the [Ru(C$_2$Ph)(R)(CO)(PBu$^t_2$-Me)$_2$]$^+$ complexes are therefore unknown. A possibility that has not been considered is that such species might adopt a S = $^3/_2$ ground state, which would be favored by greater pairing energies in this system with respect to the Ru(II) precursors. This possibility (Scheme 22, path a) would account for the lack of MeCN coordination to the system, assuming that the

Scheme 22



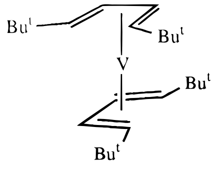
energy gained by the formation of the Ru−MeCN bond is less than the spin change-related energy loss (e.g., a situation analogous to that of Figure 7c, the two energy surfaces corresponding to $S = {}^3/_2$ and $S = {}^1/_2$).

Five-coordinate Co(IV) complexes of type RCo(chel)$^+$ could be obtained by 1-electron oxidation of 5-coordinate Co(III) precursors, but present evidence only supports the formation of 17-electron ligand adducts, RCo(chel)(L)$^+$, in the presence of a donor solvent.[606−608]

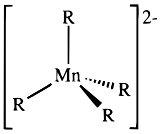
VIII.4.2. 13-Electron Systems

The formation of V(diene)$_2$ complexes **CXL** with the sterically demanding 1,4-di-*t*-butylbutadiene by the metal vapor method has been communicated.[581] The compound has been characterized by EPR spectroscopy (sharp octet at $g = 1.957$, $A_V = 76.1$ G), but the magnetic moment is not reported. The structure assignment is based on the analogy with the diamagnetic Ti species.

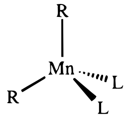
Four-coordinate (σ-organo)manganese(II) complexes have been extensively covered in a recent review.[597] Dinegative $[MnR_4]^{2-}$ (R = Me, Et, Bu^n, CH$_2$SiMe$_3$, CH$_2$CH$_2$Bu^t; R$_2$ = DPE)[303,429,491,609] (**CXLI**), neutral MnR$_2$L$_2$ (L = PR$_3$, dmpe, tmeda)[491,610−614] (**CXLII**), and monopositive complexes (e.g. MesMn(OEt$_2$)$_3$]$^+$)[615] (**CXLIII**) have been described. These all adopt a tetrahedral geometry with a high-spin ($e^2t_2^3$) configuration ($\mu_{eff} = 5.5−5.8\ \mu_B$) and characteristic EPR spectra. A ligand dissociation equilibrium has been established in a few cases, leading to dimeric, alkyl-bridged complexes, e.g. [Mn(μ-R)(R)(PMe$_3$)]$_2$ (see eq 51) or Mn$_2$(μ-R)$_2$R$_2$(μ-dmpe).[611,612]



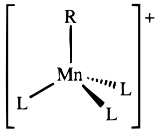
CXL



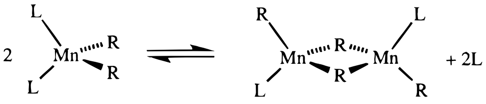
CXLI



CXLII



CXLIII



(51)

The phosphine-containing compounds are thermally quite stable, in spite of their low coordination number. This stability can be at least in part understood in view of the high-spin configuration which leaves no empty orbitals available for attack by external nucleophiles. This holds true even for those compounds with β-hydrogen-containing alkyl ligands. The high activation energy for ligand coordination or β-elimination processes may be attributed to the necessary spin-state change before any of these reactions may take place. For instance, Mn(CH$_2$Ph)$_2$(dmpe) can be induced to thermolyze in decalin at 160° in the presence of excess dmpe, giving a product whose EPR spectrum is characteristic of an octahedral, $S = {}^1/_2$ Mn(II) compound, presumably via a C−H oxidative addition with formation of Mn(IV) metallacycles, followed by the reductive elimination of toluene.[611] The higher thermal lability of ether-coordinated dialkylmanganese(II) compounds[616] suggests, in fact, that the β-elimination is preceded by ligand dissociation to 11-electron, 3-coordinated MnR$_2$L intermediates.

Ligand addition reactions to afford 5-coordinate, 15-electron Mn(II) products have not been reported; only chelating diphosphine ligands seem to be able to afford higher coordination numbers for Mn(II), in which case 17-electron ($S = {}^1/_2$) octahedral compounds are obtained, e.g. Mn[*o*-(CH$_2$)$_2$C$_6$H$_4$](dmpe)$_2$[611] or MnMe$_2$(dmpe)$_2$.[136] However, although the aryl ligand C$_6$H$_4$-*o*-CH$_2$NMe$_2$ forms a mononuclear 4-coordinate complex, the isomeric alkyl ligand CH$_2$-*o*-C$_6$H$_4$NMe$_2$ affords a dinuclear alkyl-bridged compound, as confirmed by the X-ray analysis and the low magnetic moment.[617] It is interesting to note that while MnBu$^t{}_2$(dmpe) does not undergo β-elimination, attempts to obtain the corresponding diethyl compound afforded MnH(C$_2$H$_4$)(dmpe)$_2$.[612] This suggests that the smaller steric hindrance of Et allows the formation of spin doublet MnEt$_2$(dmpe)$_2$, at which point the β-elimination may more easily take place. This process, however, would presumably require partial dissociation to a 5-coordinate MnEt$_2$(dmpe)(η^1-dmpe), because the 6-coordinate ($S = {}^1/_2$) would still have no available low-energy empty orbitals (the metal-based e$_g$* orbitals are destabilized and of unsuitable geometry).

The organometallic chemistry of 4-coordinate Mn(II) is not limited to alkyl derivatives. Neutral derivatives with the same stoichiometry as **CXLII** are also known when the 1-electron ligands are inorganic (e.g. halides) and the L ligands are carbon-based, e.g. olefins, isocyanides, and CO. The interaction between the presumably dinuclear[618] [MnX$_2$L] (X = Cl, Br, L; L = tertiary phosphine) complexes and alkenes affords presumably mononuclear 1:1 adducts, MnX$_2$L(alkene), the binding ability varying in the order Cl > Br ≫ I and PR$_3$ > PPhR$_2$ > PPh$_3$.[619] No stable adducts could be isolated for alkene = C$_2$H$_4$, whereas a stable adduct was isolated for C$_2$(CN)$_4$. However, this involves binding through a cyano lone pair and electron transfer to afford a Mn(III)−TCNE$^{\bullet-}$ product, rather than through the C=C π-density.[620] Reversible coordination is also observed with CO,[621] while Bu^{t}NC affords a stable adduct with $\mu_{eff} = 5.2\ \mu_B$.[622]

Apparently, there has been no report of four-coordinate Fe(III) complexes, in spite of the stability of Werner-type analogues such as tetrahedral $S = {}^5/_2$ [FeCl$_4$]$^-$. The reluctance of the latter to add additional ligands is possibly related to the pairing energy stabilization. Apparently, the combination of the greater covalency of the organic ligands (decreasing the pairing energy) and their reducing power, makes it less likely for this ion to attain sufficient stability in this configuration. Fe(III) organometallics are most often found as 5- or 6-coordinate systems.

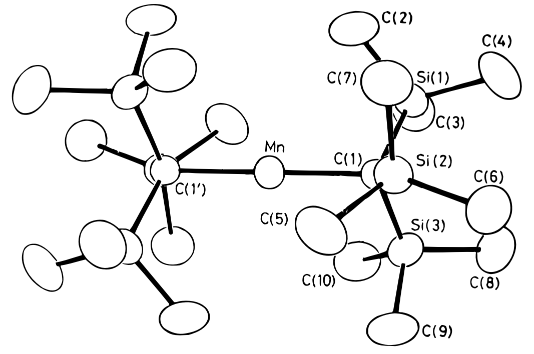
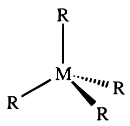


Figure 32. X-ray molecular structure of Mn[C(SiMe$_3$)$_3$]$_2$. (Reprinted from ref 45. Copyright 1985 Royal Society of Chemistry.)

The only reported 4-coordinate Co(IV) compounds appears to be Co(Nor)$_4$ **CXLIV**.[357] Contrary to the isoelectronic and isostructural Mn(II) systems described above, this system has a $S = {}^1/_2$ ($e^4t_2^1$) configuration, as shown by magnetic susceptibility measurements[357,592] and by the observation of relatively sharp room temperature EPR spectra (relatively long spin−lattice relaxation time).[623] Together with Fe(Nor)$_4$ discussed in section VIII.3.3, this is a rare example of a low-spin tetrahedral complex for a 3d metal. The proposed tetrahedral structure has more recently been confirmed by a crystallographic study.[624] The sharpness of the EPR lines further argues in favor of a tetragonal elongation of the tetrahedral crystal field (which splits the singly occupied t_2 set into an upper e set and a lower b_2 orbital) leading to a ^2B ground state with a significant energy separation between b_2 and e. In case of a ^2E ground state (tetragonal compression), a much shorter relaxation time would be expected.[623]

A single example of a 4-coordinate Ir(IV) organometallic has been recently reported, i.e. IrMes$_4$ which exhibits a distorted tetrahedral structure with a low spin configuration, as shown by EPR spectroscopy,[625] whereas no analogous derivative appears to be reported for Rh(IV).



(M = Co, Ir)

CXLIV

VIII.4.3. Lower Coordination Systems

Only Mn(II) species seem to be known for this class. The structure of homoleptic dialkylmanganese compounds is controlled by the steric bulk of the alkyl or aryl group. A mononuclear, 2-coordinate compound is formed by the sterically demanding (Me$_3$Si)$_3$C (see Figure 32).[45] When the steric bulk is gradually decreased, larger and larger oligomers are obtained, each pair of metal atoms being linked by two bridging organic groups via three-center−two-electron interactions. Thus, the neophyl compound is a dimer,[491] the mesityl a trimer,[626] the neopentyl a tetramer,[491] and the (trimethylsilyl)methyl a polymer.[491] The bis(neopentyl) compound is dinuclear in the gas phase, as shown by an electron diffraction study.[627] The Mn(CH$_3$)$_2$ and MnPh$_2$ compounds have also been described as polymeric,[628,629] but later studies question this formulation, as an attempt to reproduce these results gave products containing variable amounts of halides and/or magnesium.[491] In the dinuclear bis(neophyl) compound (Figure 33), the formally 3-coordinate manganese atom attempts to increase its coordination number by interacting with one double bond in the phenyl ring of the bridging neophyl group (Mn−C ~2.7 Å). Also, the *ortho*-hydrogen atom of the phenyl group is close to the manganese atom, and heating *in vacuo* at 80−100 °C induces elimination of *tert*-butylbenzene, presumably following initial orthometalation at this C−H bond.[491]

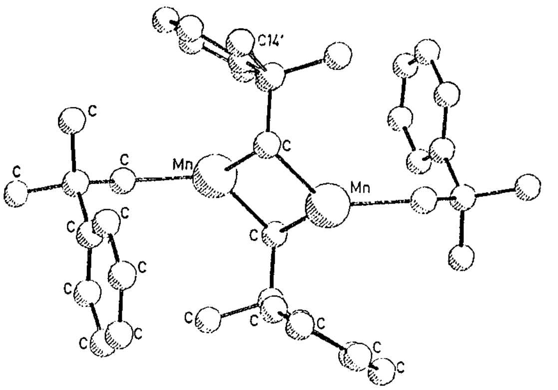


Figure 33. X-ray molecular structure of Mn$_2$(CH$_2$CPhMe$_2$)$_2$(μ-CH$_2$CPhMe$_2$)$_2$. (Reprinted from ref 491. Copyright 1976 Royal Society of Chemistry.)

The crystallographically characterized Mn[CH(SiMe$_3$)$_2$]$_2$(THF) is mononuclear.[614] Compound MnPh$_2$(PCy$_3$), on the other hand, is probably dinuclear given its magnetic moment of 2.73 μ_B,[630] as are other compounds described in section VIII.4.2. The reaction of this compound with CH$_2$=CHCH$_2$X giving allylbenzene could conceivably occur via either insertion of the double bond into the Mn−Ph bond, followed by β-X elimination, or by an oxidative addition/reductive elimination sequence. The latter, however, seems less likely given that spin pairing would be necessary. In agreement with this idea is the lack of reactivity of PhCH$_2$X.[630] Insertion into the Mn−R bond of this and other Mn(II) alkyl and aryl compounds has also been observed for CO$_2$, aldehydes, ketones, esters, CS$_2$, and SO$_2$.[631] In addition, diarylmanganese(II) compounds cyclotrimerize alkynes to arenes in noncoordinating solvents.[629]

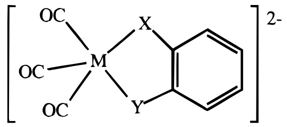
Poorly characterized materials initially described as Li[MnR$_3$] (R = Me, Et, Bu^n, Ph, *p*-CH$_3$C$_6$H$_4$, *p*-CH$_3$OC$_6$H$_4$) [632] have later been questioned in favor of an alternative formulation based on the 4-coordinate [MnR$_4$]$^{2-}$ complexes.[491] However, genuine LiMnR$_3$ complexes have subsequently been structurally characterized as the dimeric [Mn$_2$(μ-Ph)$_2$Ph$_4$]$^{2-}$ and the monomeric [Mn(Mes)$_3$]$^-$ ($\mu_{eff} = 5.9\ \mu_B$).[52,633] Magnetic susceptibility and/or EPR studies indicate five unpaired electrons for all the mononuclear species and antiferromagnetic interactions between the high spin ($S = {}^5/_2$) Mn(II) centers for all oligonuclear materials.

Coordination of neutral ligands to these compounds is generally facile, the products being 4-coordinate, tetrahedral complexes (section VIII.4.2). The addition of isocyanates to some of these materials is also a facile reaction, but proceeds further to products of insertion into the Mn−R bonds.[490]

VIII.5. d^6 Systems

VIII.5.1. 16-Electron Systems

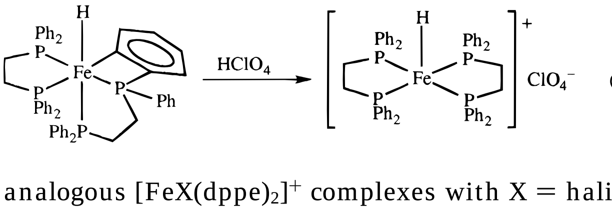
VIII.5.1.1. σ-Complexes. The $M(CO)_5$ fragments (M = Cr, Mo, W) have been studied in the gas phase and found to add CO at essentially diffusion limited rates and the rare gas Xe at only slightly slower rates, consistent with a singlet ground state for all fragments.[85,634] The same fragments are shown to interact with matrix molecules such as CH_4 and noble gases at low temperatures.[635] The bond dissociation energies for the M−Xe interaction is in the narrow $(8.0 - 9.0) \pm 1.0$ kcal/mol for the three metals.[85] Equally diamagnetic are the thermally stable agostic $Cr(CO)_3(PCy_3)_2$[636,637] and Mo and W analogues. e.g. $Mo(CO)(Bu^i_2PCH_2CH_2PBu^i_2)_2$.[638] Unlike the analogous complexes of Mo and W, $Cr(CO)_3(PCy_3)_2$ reacts only with difficulty with N_2 or H_2 either at low temperature or under pressure. The stable 5-coordinate $[M(CO)_3X_2]^{2-}$ (M = Cr, Mo, W) complexes are effectively saturated via M−X π-bonding. Examples include cathecholato complexes as well as others where X_2 is doubly deprotonated 2-aminophenol or 1,2-diaminobenzene, see **CXLV**.[639,640]



(M = Cr, Mo, W; X, Y = O, NH)

CXLV

Five-coordinated (σ-organo)iron(II) complexes are less common than 4-coordinate ones (section VIII.5.2). A rare example is provided by $FeMe_2(PPh_3)_3$, whose thermal decomposition above −10 °C has prevented a thorough characterization.[641] Another peculiar example is the cationic hydrido complex $[FeH(dppe)_2]^+$, isolated as a BPh_4 or ClO_4 salt by simple ion metathesis of $FeHCl(dppe)_2$, or by proton addition to the orthometalated complex shown in eq 52.[642,643] This compound is diamagnetic, whereas



(52)

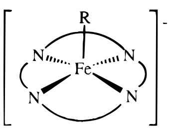
analogous $[FeX(dppe)_2]^+$ complexes with X = halide are paramagnetic, and easily adds a number of neutral ligands, such as CO, N_2, acetone, NH_3, MeCN, and H_2, the latter giving one of the first nonclassical hydride complexes, $[FeH(H_2)(dppe)_2]^+$, although not initially recognized as such.[642] Analogous preparation and properties have been described for $[FeH(pp_3)]^+$ ($pp_3 = P(CH_2CH_2PPh_2)_3$).[644]

The reduction of (TPP)FeEt has led to diamagnetic $[(TPP)FeEt]^-$ **CXLVI** which is reoxidized by dioxygen to the parent Fe(III) compound.[599] The diamagnetism of this system contrasts with the S = 2 analogous porphyrin complexes of iron(II) with axial halide, alkoxide, or acetate. This phenomenon can be attributed to the lower electronegativity of the alkyl group (which lowers the pairing energy), or the lack of π-donor orbitals on the alkyl (which reduces the orbital gap), or both. Analogous σ-alkyl- and alkynylphthalocyanine derivatives of iron(II) are also diamagnetic.[645,646] Diamagnetic carbeneiron(II) porphyrin complexes **CXLVII** have also been reported.[601,603,647] The structurally characterized, paramagnetic ($\mu_{eff} = 4.45\ \mu_B$) $Fe\{(CPhSiMe_3)C_5H_4N\text{-}2\}Cl(tmeda)$ adopts a distorted structure closer to the tbp than to the sp, with one N atom of the tmeda ligand and the pyridyl N atom occupying the pseudo-axial positions.[648]

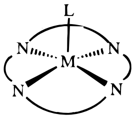
An extensive class of (σ-organo)ruthenium(II) and -osmium(II) complexes with a 16-electron configuration exist, these all adopting a square-pyramidal geometry **CXLVIII**. On going from Fe(II) to Ru(II) and Os(II), we no longer find the adoption of the high spin state and all compounds are diamagnetic. All are energetically stabilized by π-donor ligands, even such weak π-donor ligands as acetylides.[649] If these π-donor ligands are replaced with strictly π-neutral ligands (e.g. alkyls or hydrides), electronically saturated compounds are inevitably obtained. For instance, although compounds $MRX(CO)(PR'_3)_2$ (M = Ru, Os; R = halide, H, alkyl, aryl, silyl, stannyl, etc.) are stable with a variety of π-donating X groups,[650−659] compound $RuH_2(CO)(PBu^t_2Me)_2$ is not an isolable compound and readily binds bases as poor as H_2.[649] The 16-electron complexes with π-donor ligands, however, also have a tendency to bind an additional donor ligand (e.g. acetonitrile) and form saturated species,[605,649] and the X-ray structure of Ru(*p*-Tol)Cl(CO)$(PPh_3)_2$ shows evidence of agostic interactions.[654] Stable 16-electron Os(II) compounds are much less common than the Ru(II) analogues. The Os(II) transient $OsH_2(PR_3)_3$ is obtained from H_2 photodissociation from $OsH_4(PR_3)_3$.[514]

Among the compounds of type **CXLVIII** are also the alkylidene complexes of general formula $MCl_2(=CHR')(PR_3)_2$ (M = Ru, Os), the alkylidene ligand occupying the apical position. The ruthenium compounds are efficient catalysts for the ring-opening metathesis polymerization of cyclic olefins in aqueous media.[660−664] Diamagnetic, 16-electron porphyrin derivatives Ru(porphyrin)L (porphyrin = TPP, OEP; L = C_2H_4, alkylidene) as well as osmium analogues are also known.[512,647,665] These derivatives do not appear to have tendency to add an additional axial ligand, although 18-electron $M(porphyrin)L_2$ (L = CO, THF, py) derivatives are known.

For group 9 metals, 5-coordinate Co(III) alkyl complexes **CIL** are important intermediates in the biological functions of vitamin B_{12}. Model compounds have been isolated and structurally characterized,[666,667] e.g. see Figure 34. These compounds are shown by NMR spectroscopy to be diamagnetic.

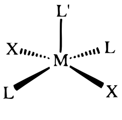


CXLVI



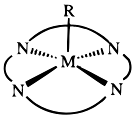
(M = Fe, Ru, Os)

CXLVII



(M = Ru, Os)

CXLVIII



(M = Co, Rh)

CIL

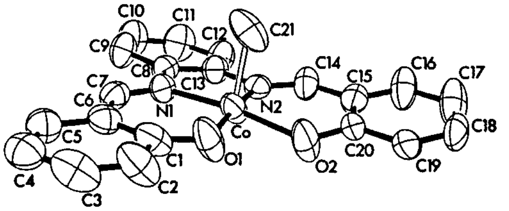
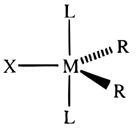
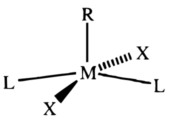


Figure 34. X-ray structure of Co(saloph)CH_3. (Reprinted from ref 667. Copyright 1985 American Chemical Society.)

Examples of 16-electron Rh(III) and Ir(III) compounds are known with either the trigonal-bipyramidal **CL** or with the square-pyramidal **CLI** geometry; see also section VII.[668−674] All these compounds are diamagnetic. The square-pyramidal structure is enforced by the ligand geometry in the RhR(porphyrin) complexes.[603] Compound $RhPhCl_2(PPh_3)_2$ shows an agostic interaction of one of the *o*-phenyl hydrogens, to give an effective octahedral geometry,[675] whereas other compounds do not. The bent geometry of the apical NO ligand shows that this is a 1-electron donor in the square-pyramidal compound $IrMes_2(NO)(PMe_3)_2$.[676]



CL

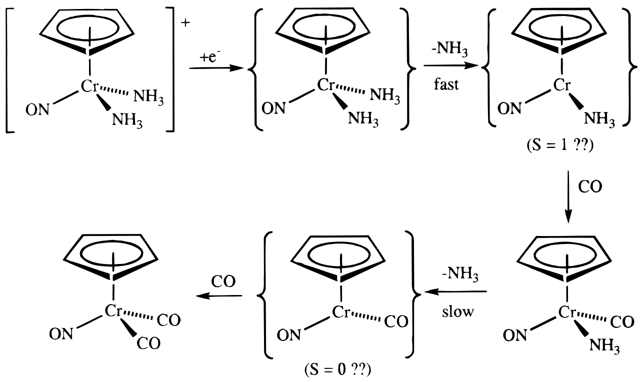


CLI

VIII.5.1.2. Half-Sandwich Compounds.

No half-sandwich Cr(0) complex with a 16-electron configuration has been isolated. It has been shown that $[CpCr(NO)(NH_3)_2]^+$, a stable 17-electron compound, is reduced irreversibly by Zn or Mg under a CO atmosphere to $CpCr(NO)(CO)_2$.[677] When using Mg, an intermediate of proposed composition $CpCr(NO)(CO)(NH_3)$ is rapidly obtained, which proceeds to the dicarbonyl only with difficulty. Since $[CpCr(NO)(NH_3)_2]^+$ is unreactive toward CO, the hypothesis is that the first NH_3/CO substitution proceeds very rapidly after formation of $CpCr(NO)(NH_3)_2$ by reduction.[534] The reason for the much faster first substitution may be related to the possible energetic stabilization of a 16-electron {CpCr(NO)(NH_3)} intermediate if this adopts a spin triplet ground state (see Scheme 23). The stronger CO ligand might, on the other hand, enforce a spin singlet configuration for the 16-electron CpCr(NO)(CO) intermediate, thus rendering the second substitution slower. Other dissociative substitutions supposedly generating the CpCr(NO)(CO) fragment, e.g. from $CpCr(NO)(CO)_2$, are rather slow. Half-sandwich Mn(I) derivatives are common and are quite stable as 18-electron complexes. Dissociation of a ligand (typically a CO) yield reactive intermediates such as $CpMn(CO)_2$, presumably having a bent structure (**XXIII**),[678] but none has so far been isolated.

Scheme 23



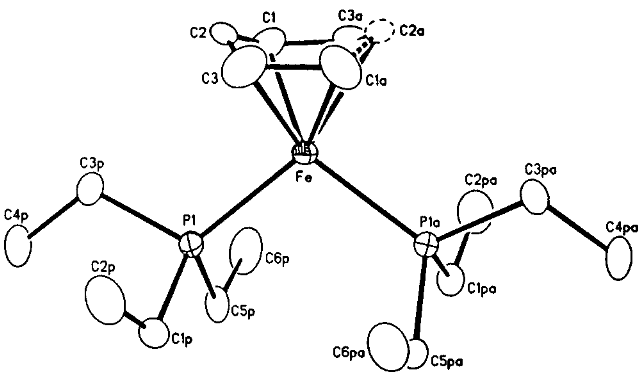
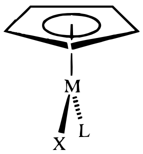


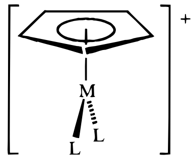
Figure 35. ORTEP drawing of the cation $[(\eta^5\text{-pentadienyl})Fe(PEt_3)_2]^+$. The pentadienyl ligand exhibits a 2-fold rotation disorder. (Reprinted from ref 140. Copyright 1990 American Chemical Society.)

$CpFe(CO)_2X$ ("Fp"X) derivatives constitute a very extensive class of compounds, invariably having an 18-electron configuration. The photolysis of $CpFeCl(CO)_2$ in a low-temperature inert matrix affords the unstable CpFeCl(CO) intermediate, which binds CO again upon annealing above 60 K, and the corresponding CpRuCl(CO) fragment shows similar reactivity.[535] Noncarbonyl containing complexes, however, are also widely known, for instance $CpFeClL_2$ (L = isocyanide, monodentate phosphine or L_2 = bidentate phosphine) and Cp* analogues,[679−682] and paramagnetic (S = 1) 5-coordinate derivatives based on these systems, **CLII** and **CLIII**, are stable.[84,141,683] The structure of the related $[(\eta^5\text{-Pdl})Fe(PEt_3)_2]^+$ is shown in Figure 35.[140] No additional PEt_3 or other large phosphines (cone angle > 130°) will bind to this complex. On the other hand, PMe_3, $P(OMe)_3$, and the capping phosphine $MeC(CH_2PMe_2)_3$ replace the PEt_3 ligands completely to afford 18-electron $[(\eta^5\text{-Pdl})FeL_3]^+$ products, whereas CO or Bu^{t}NC afford the addition products $[(\eta^5\text{-Pdl})Fe(PEt_3)_2L]^+$.[140]



(M = Fe, Ru)

CLII



(M = Fe, Ru)

CLIII

Steric protection is important for these systems, as demonstrated by the fact that treatment of CpFeCl(dippe) with $Na[BPh_4]$ in MeOH affords the stable 16-electron $[CpFe(dippe)]^+$ complex,[84] whereas the analogous treatment of $Cp^*FeCl(PMe_3)_2$ with KPF_6 in MeOH affords only $[Cp^*Fe(PMe_3)_3]^+$, presumably by a ligand disproportionation process.[681] $[CpFe(dippe)]^+$ engages in an equilibrium with the 18-electron dinitrogen adduct (eq 53), whereas the corresponding Cp* derivative shows no tendency to

$$[\mathrm{CpFe(dippe)}]^+ + \mathrm{N_2} \rightleftarrows [\mathrm{CpFe(dippe)(N_2)}]^+ \quad (53)$$

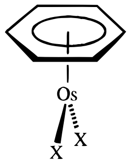
add N_2, although it does add CO, MeCN, or $CNBu^t$ to afford the corresponding saturated $[Cp^*Fe(dippe)L]^+$ complexes. Resonances for both the paramagnetic 16-electron Cp complex and for the diamagnetic dinitrogen adduct are seen in the ^{1}H-NMR spectrum, indicating a relatively slow association/dissociation process. The thermodynamic parameters of eq 53 are $\Delta H° = 18.2 \pm 0.5$ kJ mol and $\Delta S° = 68 \pm 2$ J mol^{-1} K^{-1}.[84] The actual "strength" of the Fe$-$N$_2$ bond (according to our definition in section IV) is greater, because part of the energy spent in breaking the Fe$-$N$_2$ bond is regained as a result of the spin-state change. The structurally characterized $[Cp^*Fe(dppe)]^+$ complex is likewise in equilibrium with the saturated complexes $[Cp^*Fe(dppe)(H_2O)]^+$ and $Cp^*Fe(dppe)(OSO_2CF_3)$, as indicated by solution magnetic susceptibility studies.[141] A variety of solvent adducts of formula $[CpFe(dppe)(solvent)]^+$ have been generated in situ, even with solvent = CH_2Cl_2 or $CHCl_3$ but no magnetic or NMR data have been reported, thus it is not clear whether the solvent is effectively coordinated or not.[684]

Compound $Cp^*Fe(acac)(PMe_3)$ shows a temperature-dependent, paramagnetically shifted ^{1}H-NMR spectrum. It therefore seems likely that this compound has a 16-electron, spin triplet configuration with a monodentate acac ligand or is in equilibrium with a paramagnetic product of phosphine dissociation. Substitution of PMe_3 with CO affords a diamagnetic $Cp^*Fe(acac)(CO)$ derivative.[681] The thermal instability reported for the sterically crowded $Cp^*Fe(CH_3)(PMe_3)_2$ might well be related to phosphine dissociation with formation of a spin triplet 16-electron product, whereas the analogous $Cp^*Fe(CH_3)[P(OMe)_3]_2$ and $Cp^*Fe(CH_3)(dppe)$ are thermally stable.[680] Given that $P(OMe)_3$ is more encumbering than PMe_3,[243,246] this difference is probably a result of electronic effects which may include a greater electron pairing stabilization of the spin triplet $Cp^*Fe(CH_3)(L)$ when L is the less π-acidic PMe_3 ligand.

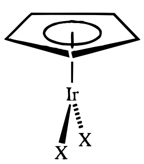
(ring)RuCl(PR_3) systems are the dissociative intermediates in phosphine exchange reactions on the saturated (ring)RuCl$(PR_3)_2$.[685] Stable derivatives of this type (**CLII** and **CLIII**) are isolated when sterically demanding tertiary phosphine ligands and π-donating X ligands are utilized. Examples of these are $Cp^*RuCl(PR_3)$,[658,686,687] $Cp^*Ru(OR)(PR_3)$,[688] and $Cp^*Ru(NR_2)(PR_3)$.[689] The presence of π-donating ligand, however, is not absolutely necessary, as demonstrated by the existence of $[Cp^*Ru(dppe)]^+$ and $[CpRu(dcpe)]^+$.[690−692] Although these cationic complexes are obtained in potentially coordinating solvents such as THF with the potentially coordinating $CF_3SO_3^-$ counterion, the NMR properties indicate a symmetric C_{2v} structure as in **XXIV**.[690] However, sterically unprotected systems such as the hydrido complexes Cp^*RuHL are not stable and undergo spontaneous ligand coordination to Cp^*RuHL_2, or oxidative addition (e.g. to Cp^*RuH_3L).[687,693] The same reactions easily take place also for the systems with π-donor ligands.[686,688,689,692,694]

Rare examples of Os(II) compounds that belong to this class are the (η^6-arene)OsX_2 species **CLIV**, X being a strongly π-donating group such as an amide, alkoxide, or thiolate.[695,696] As a consequence, these derivatives are diamagnetic and adopt a planar structure (see section VII).

Group 9 M(III) half-sandwich complexes with a 16-electron configuration are in general nonisolable, reactive intermediates, even for the relatively high pairing energy Co(III) system. For instance, the dissociative phosphine exchange reaction in $CpCoMe_2(PPh_3)$ produces the supposed intermediate $CpCoMe_2$,[697] but this species has not been isolated, nor detected spectroscopically, and its spin state is therefore unknown. The same intermediate is also proposed for the reactions of $CpCoMe_2(PPh_3)$ with diphenylacetylene and with ethylene.[697] A few isolable 16-electron complexes of this type, **CLV**, have been reported for iridium, e.g. Cp*Ir(η^2-*N*,*O*-amino acid) complexes.[698,699] These are stabilized by π-donation from the N and O donors, adopt a planar structure, and are diamagnetic. The addition of phosphines, unhindered amines, or CO immediately generates saturated adducts.



CLIV



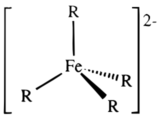
CLV

VIII.5.2. 14-Electron Systems

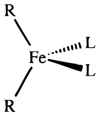
A few 4-coordinate complexes of Fe(II), **CLVI**−**CLIX**, are known. In the presence of strong field ligands such as alkyls or aryls, Fe(II) may take up additional small ligands to afford octahedral, electronically saturated, diamagnetic derivatives, e.g. $FeMe_2(PMe_3)_4$[700] and $FeR_2(bipy)_2$.[701] Otherwise, 4-coordinate derivatives are stable. Compound $Li_2[Fe(DPE)_2]\cdot5THF$ has four unpaired electrons ($\mu_{\mathrm{eff}} = 4.54$ μ_B) and is thus unlikely to be an octahedral complex with two coordinated THF molecules.[303] Similarly, $Li_2[FePh_4](dioxane)_{2.5}$ is reported to have $\mu_{\mathrm{eff}} = 5.27$ μ_B,[702] and a normal high-spin moment is reported for $FeMes_2L_2$ (L_2 = bipy or L = other N-donor).[703,704] Structure determinations for $[Li(OEt_2)]_2[FeNapht_4]$,[705,706] $Fe[C(SiMe_3)_2C_5H_5N\text{-}2]_2$,[707] and $FeBz_2(dippe)$[708] show a distorted tetrahedral coordination geometry. Other high-spin complexes are $Fe(CPh{=}CPhMes)_2L_2$ (L = THF or L_2 = bipy) and $Fe(CPh{=}CPh{-}CPh{=}CPhMes)_2$ (presumably also tetraherally coordinated via the ligand double bonds), all obtained by adding tolane to $FeMes_2$.[709] Certain bis(phosphine) adducts of FeR_2 and $FeAr_2$, however, have lower moments (3.2−3.6 μ_B),[710,711] consistent with only two unpaired electrons, and they are likey to adopt a square planar structure (e.g. $Fe(C_6F_5)_2(PEt_2Ph)_2$ is isomorphous with square-planar $Co(C_6F_5)_2(PEt_2Ph)_2$).[712] Bis-nitrile complexes also show reduced magnetic moments, consistent with a square-planar structure.[704] Bulkier aryl groups (e.g. Mes) provide greater steric protection and higher thermal stability.[711] This T_d to D_{4h} rearrangement is not sterically driven, since some square-planar complex (e.g. $FeMes_2(PEt_2Ph)_2$) have more encumbering ligands than many tetrahedral complexes (see also section

VII). The recently reported Fe{C(SiMe$_3$)$_2$C$_5$H$_4$N-2}$_2$ is unusual because it adopts a butterfly-distorted structure with a large [160.4(3)°] angle between the two carbon donors and a much smaller [116.3(2) Å] angle between the two pyridyl N donors.[648] A more regular tetrahedral geometry may result in too severe steric interaction between the SiMe$_3$ groups on adjacent carbon donors. This compound has four unpaired electrons.[648] The iron centers in the less sterically hindered [Fe{CH(Si^{t}BuMe$_2$)C$_5$H$_4$N-2}$_2$]$_2$ have a coordination geometry closer to tetrahedral. In this latter compound, the two S = 2 metal centers are antiferromagnetically coupled.[648] The poorly characterized Li$_2$[Fe{2,6-(CH$_3$O)$_2$C$_6$H$_3$}$_4$]·LiBr·4THF is reported to have a moment of 3.84 μ_B.[713]

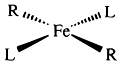
Anionic, tetrahedral [CoR$_4$]$^-$ complexes **CLIX** can only be stabilized by bulky ligands, the favored coordination numbers for this ion being otherwise 5 or 6. [Co(Nor)$_4$]$^-$ is obtained by reduction of the neutral Co(IV) compound, and adopts a low spin (e^{4}t$_2$^{2}; S = 1) configuration.[592,593]



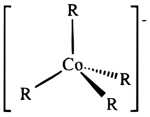
CLVI



CLVII



CLVIII



CLIX

VIII.5.3. Lower-Coordinate Systems

The reaction between FeCl$_2$ and MesMgBr affords a compound described as FeMes$_2$·0.2THF.[703,711] The dinuclear [FeMes(μ-Mes)]$_2$ structure with a short (2.614(3) Å) Fe–Fe contact[714] is consistent with the anomalous magnetic moment of 2.69 μ_B, due to antiferromagnetic coupling. This material reacts with Bu^{t}NC by insertion to afford the dinuclear iminoacyl derivative Fe$_2${η^2-C(Mes)NBu^t}$_2$(μ-C(Mes)-NBu^t)$_2$, which also shows Fe–Fe antiferromagnetic coupling.[715] The reaction of Fe$_2$Mes$_4$ with PCy$_3$ affords the 3-coordinate FeMes$_2$(PCy$_3$) complex with four unpaired electrons (μ_{eff} = 5.56 μ_B), whereas the bis-phosphine adducts described in the previous section have only two unpaired electrons.[711] Other bulky donors, e.g. 2,6-lutidine, also add to FeMes$_2$ to afford 3-coordinate products whose magnetic moments invariably show four unpaired electrons.[704] Similar magnetic moments have also been observed for LiFeMe$_3$·4diox and Mg[FeMes$_3$]$_2$(THF)$_{5.75}$, but structural details for these compounds are not known.[711] RhMes$_3$ is a mononuclear diamagnetic compound with a pyramidal RhC$_3$ fragment, showing close contacts between the metal atom and one methyl hydrogen from each mesityl group, to afford what can be described as a distorted *fac*-octahedral RhC$_3$H$_3$ geometry (see Figure 36). NMR work, however, does not support the existence of agostic interactions.[716]

VIII.6. d^7 Systems

VIII.6.1. 15-Electron Systems

VIII.6.1.1. σ-Complexes. A most unusual system in this class is the Mn(0) compound [K(THF)$_x$]$_2$[Mn-(C$_2$H$_4$)$_2$(C$_4$H$_8$)], obtained by potassium reduction of CpMn(η^6-biphenyl), although the ethylene cation contacts and the long ethylene C–C distances (1.444 and 1.417 Å) in the structurally characterized [Na-{(Me$_2$NCH$_2$CH$_2$)$_2$NMe}]$^+$ analogue (see Figure 37) make an oxidation state assignment to this compound somewhat ambiguous. A magnetic moment for this compound has not been reported.[147]

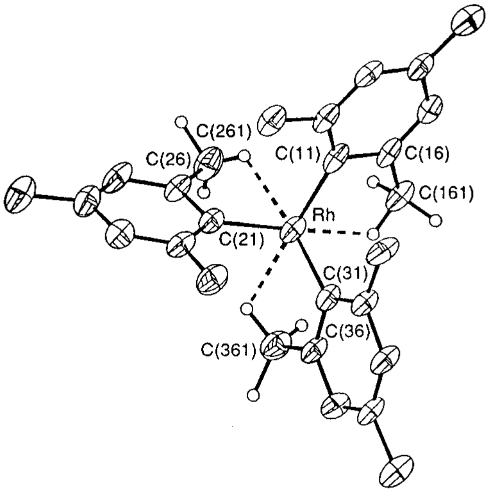


Figure 36. X-ray molecular structure of RhMes$_3$. (Reprinted from ref 716. Copyright 1990 Royal Society of Chemistry.)

There are several tetrahedral derivatives of cobalt(II), for the most part tetraalkylcobaltate dianions, see **CLX**.[158,303,610,702,712,713,717] The structure of [Li-(tmeda)]$_2$[Co(CH$_2$SiMe$_3$)$_4$] features a linear edge-shared "tritetrahedron", with two alkyl ligands bridging the central Co(II) center with each of the two lateral Li(I) centers (see Figure 38).[718] Although the alkylate anions are easily formed, the isolation of neutral derivatives of the type CoR$_2$L$_2$ is reported as a rather delicate process involving, even in successful cases, extensive decomposition to black solids. However, Co(CH$_2$R)$_2$(tmeda) complexes (R = CMe$_3$, SiMe$_3$) were isolated and crystallographically determined to have a mononuclear tetrahedral geometry, **CLXI**. These compounds have a S = $^3/_2$ ground state, as indicated by their characteristic blue color, magnetic susceptibility, and EPR spectroscopic properties.[718] Compounds containing phosphines, however, are yellow and are described as square-planar compounds with a *trans* relative geometry, **CLXII**, on the basis of very small dipole moments and magnetic moments in the 2.3–2.7 μ_B region.[712] This geometry is confirmed by single-crystal X-ray methods for CoMes$_2$(PEt$_2$Ph)$_2$.[719] Although these moments are a little high for the low-spin, S = $^1/_2$ configuration, other square-planar coordination compounds of Co(II) also have high magnetic moments, apparently because of a large orbital contribution.

A rare example of 4-coordinate Rh(II) alkyl complex is Rh(C$_6$H$_2$Pr^i$_3$-2,4,6)$_2$(THT)$_2$, possessing a square-planar geometry and a spin doublet ground state,[720] which is expected on the basis of the structure (high energy d$_{x^2-y^2}$ orbital) and the lower pairing energy for Rh(II) with respect to Co(II). Analogous compounds of Ir(II), e.g. IrMes$_2$L$_2$ (L = SEt$_2$, PMe$_3$, py, 4-NC$_5$H$_4$Bu^t) are also square planar with one unpaired electron.[676]

No stable 4-coordinate Ni(III) complexes have been reported, although L$_2$NiArR$^{+\bullet}$ intermediates have

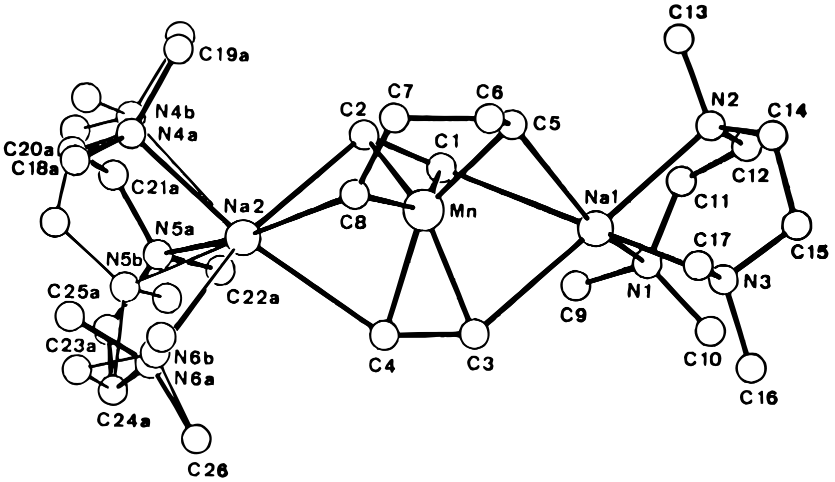


Figure 37. X-ray structure of $[Na(pmdeta)]_2[Mn(C_4H_8)(C_2H_4)_2]$. (Reprinted from ref 147. Copyright 1992 Elsevier.)

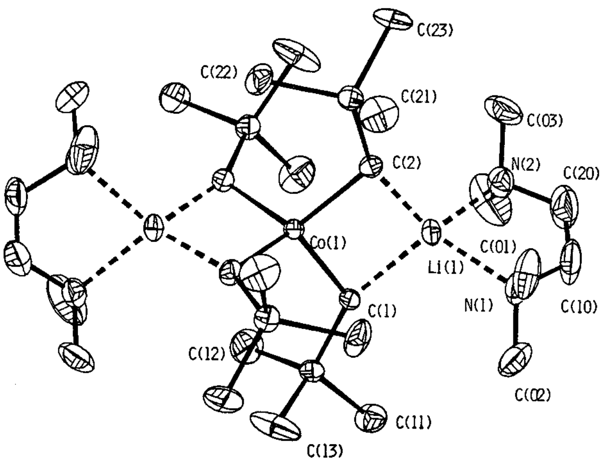
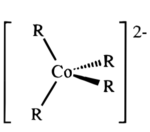
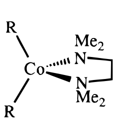


Figure 38. X-ray structure of compound $[Li(tmeda)]_2[Co(CH_2SiMe_3)_4]$. (Reprinted from ref 718. Copyright 1990 Pergamon Press.)

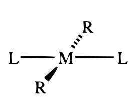
been implicated in the Ni(II)-catalyzed cross-coupling reaction between ArBr and RLi or RMgBr.[721,722] A square-planar geometry is observed for the stable Pt(III) anion, $[Pt(C_6Cl_5)_4]^-$, **CLXIII**.[723]



CLX

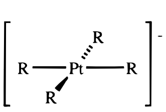


CLXI



(M = Co, Rh, Ir)

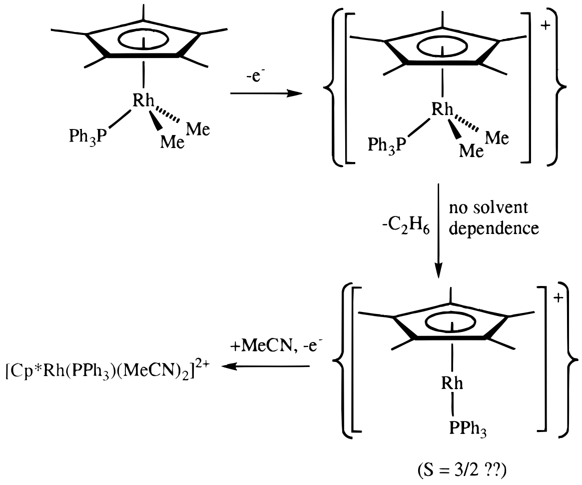
CLXII



CLXIII

VIII.6.1.2. Half-Sandwich Compounds. Fifteen-electron complexes of Rh(II) with the half-sandwich geometry (one-legged piano stool) have been invoked as high-energy reaction intermediates. The reductive elimination of ethane from $Cp^*Rh(CH_3)_2(PPh_3)$ is induced by 1-electron oxidation to the corresponding Rh(IV) 17-electron cation.[724] Normally, organometallic processes involving ligand dissociation or reductive elimination from a 17-electron system are mediated by solvent coordination, thereby forming a 19-electron adduct and avoiding the formation of a highly unsaturated intermediate. However, no significant solvent dependence has been observed for the rate of this particular reaction (in MeCN, acetone, THF, CH_2Cl_2), indicating the nonintervention of 19-electron species and the formation of a 15-electron $[Cp^*Rh(PPh_3)]^+$ intermediate (see Scheme 24). Subsequently, this species coordinates MeCN and is oxidized further to $[Cp^*Rh(PPh_3)(MeCN)_2]^{2+}$, or reacts with $Cp^*Rh(CH_3)_3(PPh_3)$ in CH_2Cl_2 to afford $Cp^*Rh(CH_3)(X)(PPh_3)$ ($X = CH_2Cl_2$ or PF_6^-).[724] The lower energy pathway through a 15-electron species rather than through a presumed facile MeCN coordination to a 19-electron species was left without a satisfactory interpretation. In light of the considerations presented in the early part of this review, it is tempting to propose that a significant kinetic boost to the direct reductive elimination process from $[Cp^*Rh(CH_3)_2(PPh_3)]^+$ may be provided by a spin-state change to a quartet ground state for the unsaturated 15-electron product of elimination.

Scheme 24



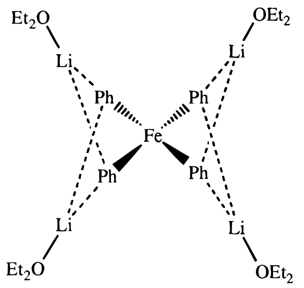
VIII.6.2. Lower Coordination Systems

Co(II) forms also lower coordination compounds when surrounded with very bulky ligands. For instance, although the already relatively bulky (trimethylsilyl)methyl ligand forms the 4-coordinate homoleptic $[CoR_4]^{2-}$ complex (see previous section), the sterically more emcumbering mesityl ligand is only able to reach coordination number three in the homoleptic $[CoMes_3]^-$.[633] The physical and spectroscopic properties are identical for Li and PPN salts, indicating merely electrostatic interactions between the $[Co(Mes)_3]^-$ fragment and the lithium counterion. Variable-temperature magnetic susceptibility and ^1H-NMR studies indicate Curie behavior, and the measured effective magnetic moment of 3.8 μ_B at 300 K is consistent with a $S = {}^3/_2$ ground state, corresponding to a $(z^2)^2(xz,yz)^3(xy,x^2-y^2)^2$ occupation of the metal d orbitals in the supposed trigonal planar coordination environment.[725] Such a trigonal planar arrangement has been shown by X-ray crystallography for the related compound $[Li(tmeda)_2][CoCl\{CH(SiMe_3)_2\}_2]$.[718] Magnetic susceptibility measurements for the latter compound have not been reported, but the EPR spectrum is interpreted as being consistent with a $S = {}^1/_2$ ground state with the unpaired electron in the d_{xy} orbital, the x axis pointing along the Co−Cl direction.[718] A neutral dimesitylcobalt(II) compound has also been described by Zeiss and Tsutsui in 1961, who also found that this system catalyzes the cyclotrimerization of 2-butyne to hexamethylbenzene.[629]

VIII.7. d^8 Systems

VIII.7.1. 16-Electron Systems

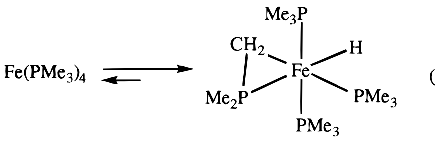
VIII.7.1.1. Square Planar Geometries and Distortions Thereof. A most remarkable compound of this type is the phenyllithium complex of iron(0), $[Li(Et_2O)]_4[FePh_4]$, whose planar rectangular structure (see **CLXIV**) suggests some degree of ligand−ligand interactions. The magnetic properties of this complex, which is able to activate dinitrogen, do not appear to have been established.[726]



CLXIV

$Fe(CO)_4$, $Ru(CO)_4$, and $Os(CO)_4$ are only unstable reaction intermediates. They have, however, been experimentally investigated in low-temperature matrices[88] and in the gas phase.[65,108,727] Calculations have shown a spin triplet ground state for the iron species,[61] whereas the Ru and Os analogues are diamagnetic.[67]

Phosphine-substituted analogues have also been found to be, in many cases, unstable reaction intermediates.[155] Compound $Fe(PMe_3)_4$ exists in solution in equilibrium with the C−H oxidative addition product (eq 54) and is described as paramagnetic.[728,729]

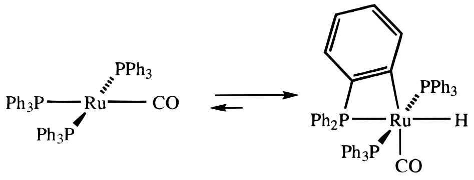


(54)

Compounds $M(dmpe)_2$ (M = Fe, Ru) are intermediates in the reductive elimination/oxidative addition of arenes from $M(dmpe)_2(H)(Ar)$ (eq 55). The process

$$M(dmpe)_2(H)(C_{10}H_7) + ArH \rightleftarrows M(dmpe)_2(H)(Ar) + C_{10}H_8 \quad (55)$$

is more facile in the series Os < Ru < Fe.[730] A reactive $Ru(CO)(PPh_3)_3$ is believed to be in equilibrium with its orthometalated isomeric form (eq 56).[731]



(56)

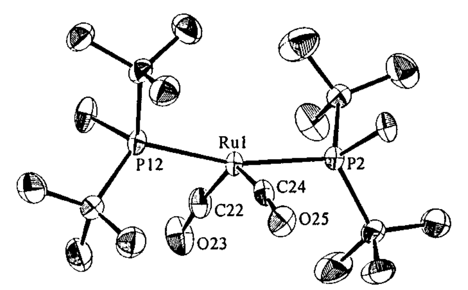
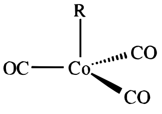


Figure 39. ORTEP drawing of $Ru(CO)_2(PBu^t{}_2Me)_2$. (Reprinted from ref 153. Copyright 1995 American Chemical Society.)

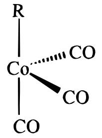
$Ru(dmpe)_2$ and $Ru(CO)_2(PMe_3)_2$ have been isolated and investigated in low-temperature matrices.[732−734] Although there is considerable evidence that $Ru(dmpe)_2$ is square planar, the $Ru(CO)_2(PMe_3)_2$ fragment has been proposed to form weak solvent adducts $Ru(CO)_2(PMe_3)_2{\cdots}S$ with a trigonal-bipyramidal structure and a OC−M−CO angle of at least 130°.[734] On the other hand, the sterically more uncumbered $Ru(CO)_2(PBu^t{}_2Me)_2$ is sufficiently stable to be isolated and is shown by X-ray crystallography (see Figure 39) to be unsolvated.[153] The compound has a spin singlet ground state and a very different structure than the typical square-planar configuration observed for isoelectronic d^8 systems (e.g. $Rh(CO)_2(PR_3)_2{}^+$) with four monodentate ligands, this being close to a trigonal bipyramid to which one equatorial ligand has been removed (see **XXXII**). It reacts very rapidly with H_2 and MeNC to give 18-electron adducts, but does not react with MeCN.[153] Compounds $OsCl(NO)L_2$ (L = $PPr^i{}_3$, $PPr^i{}_2Ph$) are rare examples of isolatable 16-electron Os(0) complexes. They are diamagnetic and an X-ray structure for the $PPr^i{}_3$ complex shows a square-planar geometry.[735] Other diamagnetic Ru(0) and Os(0) square planar complexes are the reactive $[M(porphyrin)]^{2-}$.[512,665]

Many experimental and theoretical studies have addressed the stability and structure of $CoR(CO)_3$ intermediates deriving from the CO dissociation of $CoR(CO)_4$ (R = H, CH_3). Isomeric structures based on the trigonal bipyramid with a vacancy in either an axial, **CLXV**, or equatorial, **CLXVI**, position have been proposed and both are calculated as diamagnetic and more stable than the quasi-tetrahedral spin triplet alternative.[736−739] These intermediates bind CO, N_2, H_2, and Ar to afford saturated species.

Compound $CoMe(PPh_3)_3$ has moderate thermal stability and weakly interacts with dinitrogen, whereas the corresponding hydride complex can only be isolated as the dinitrogen adduct, $CoH(N_2)(PPh_3)_3$.[740] Structure and magnetic properties for these compounds do not seem to be available. Compound $CoEt(PMe_3)_3$ is the intermediate in the H scrambling process which equilibrates hydrido and C_2H_4 protons in $CoH(C_2H_4)(PMe_3)_3$.[741]



CLXV



CLXVI

Hydrotris(pyrazolyl)borates allow the stabilization and isolation of $Tp^{R,R'}CoL$ molecules (L = CO, C_2H_4, $^1/_2N_2$), typically having sterically protecting groups at the 3 position of the pyrazole rings (e.g. $Tp^{R,R'} = Tp^{Pr^i,Me}$).[157,742] These compounds are all paramagnetic with a spin triplet ground state. Rather than adopting the expected tetrahedral geometry, the ligands arrange themselves in a pseudo-C_{2v} fashion (e.g. **XXXII**, see section VII).

Contrary to the TpCo(CO) systems, the corresponding Rh and Ir species are only highly reactive intermediates which insert, like the corresponding Cp systems (see next section), into unactivated C−H bonds.[743,744] There seems to be, therefore, a perfect parallel between the chemical reactivity of 16-electron Cp and Tp derivatives of the group 8 metals. However, recent flash photolysis studies on $Tp^{Me,Me}Rh(CO)_2$ indicate the formation of at least three intermediates before the ultimate formation of the C−H insertion product, $Tp^{Me,Me}Rh(CO)(H)(R)$.[745] It is possible that one of these intermediates is a spin triplet $Tp^{Me,Me}Rh(CO)$, analogous to the isolated Co counterparts described above.

All stable four-coordinate compounds of Rh(I) and Ir(I) are unavoidably square planar and diamagnetic, as well as all compounds of Ni(II), Pd(II), and Pt(II) containing metal−carbon bonds. It would be interesting to see whether derivatives of type TpNi(R) could be isolated, if so measure their spin state, and see whether they would adopt a tetrahedral structure such as Werner-type Ni(II) complexes or a distorted C_{2v}-type structure like the isoelectronic TpCo(CO).

VIII.7.1.2. Half-Sandwich and Analogous Systems. The Cp ligand, like the hydrotris(pyrazolyl)borate ligand, is able to enforce a nonsquare planar geometry for late transition metal d^8 complexes. The proposed formation of a reactive CpCo(CO) intermediate on photolysis of $CpCo(CO)_2$ was first advanced by Lee and Brintzinger,[746] later discounted by Rest *et al.* in favor of a dinuclear $[CpCo(CO)]_2$,[87,747] and more recently reinforced by Bergman *et al.*, who found evidence that CpCo(CO) and Cp*Co(CO) do not bind Kr, Xe, or cyclohexane, whereas they bind CO rather easily to afford the dicarbonyl derivatives, and the parent dicarbonyl to form $(ring)_2Co_2(CO)_3$ (Ring = Cp or Cp*).[89] CpCoL complexes with L = tertiary phosphine also seem to be formed as dissociative intermediates in the reaction of $CpCo(PMe_3)_2$ with $(ring)Mn(CO)_3$ (ring = Cp or Cp′), to afford the dinuclear mixed-metal compounds $(ring)Mn(CO)(\mu\text{-}CO)_2Co(PMe_3)Co$,[748] and in the exchange reactions of $CpCoL_2$,[121] whereas $CpCo(CO)_2$ exchanges the CO ligands by an associative mechanism involving a ring slippage.[749] In contrast with the Co systems, CpML intermediates and Cp* analogues of Rh and Ir (L = CO, PR_3) are quite reactive and are able to form adducts with inert gases (e.g. Kr, Xe) and to insert intermolecularly into aromatic and aliphatic C−H bonds.[78,87,750−754] The same reactivity is also shown by the isoelectronic (η^6-arene)OsL system.[755]

VIII.7.2. Lower Coordination Systems

The remarkable $Li_3[Fe(Napht)_3]\cdot nEt_2O$ is described as a diamagnetic compound which is capable of coordinating and reducing dinitrogen.[756] No structural information is available on this material.

A 3-coordinate Co(I) complex, $CoMe(PPh_3)_2$, was described as the product of the reaction between $Co(acac)_3$, PPh_3, and $Me_2Al(OEt)$ in a 1/2/2 ratio. The magnetic properties of this material have not been reported. Upon dissolution in THF or toluene at room temperature, the compound releases methane but this decomposition is suppressed by the presence of excess PPh_3.[641] Three-coordinate $RhCl(PR_3)_2$ species are supposed intermediates in the photochemical alkane carbonylation and dehydrogenation reactions catalyzed by $RhCl(PMe_3)_2(CO)$.[757−759] Three-coordinate Pt(II) complexes appear to be viable intermediates of ligand exchange and isomerization reactions of square-planar complexes, e.g. *cis*-$Pt(PEt_3)_2(R)X$ (R = alkyl or aryl) and *cis*-PtR_2L_2 (R = CH_3 or Ph; L = sulfoxide or thioether).[760]

The homoleptic nickel aryl complexes $NiMes_2$[594] and $Ni(C_6F_5)_5$[761] have been described, but neither species has been isolated from solution and their structure and magnetic properties are unknown.

IX. Conclusion and Outlook

The energetic effect of a spin-state change must be part of the arsenal of considerations (which includes steric effects, solvent and counterion interactions, metal−ligand bond strengths, π-stabilization, etc.) that help organometallic chemists rationalize trends in stability, reactivity, and structure. In particular, an open-shell organometallic compound with more than one unpaired electron may owe its failure to react with particular nucleophiles to the greater cost of pairing the electrons with respect to the energy gain associated with the formation of more metal-ligand bonds. Also, activation barriers for organometallic reactions in which a higher spin, less saturated intermediate is generated are affected by the spin-pairing stabilization. The understanding of how various parameters (e.g. nature of the metal and ligands, coordination geometries and distortions thereof imposed by ligand constraints, etc.) affect these thermodynamic stabilizations and reaction barriers will undoubtedly help develop more efficient catalysts and more selective reactions. The magnitude of the spin pairing-related stabilization (e.g. the energy gap between different spin states for an open-shell system) is a difficult parameter to measure experimentally. Significant advances in this field will be achieved by a synergistic use of theory and experiments.

X. Acknowledgments

I thank all the authors whose work is referenced in this review for their contribution to this area of chemistry. Particularly illuminating for the formation of the ideas expressed in the first part of this review article have been some of the results reported by Hans H. Brintzinger, Fausto Calderazzo, Kenneth G. Caulton, Sandro Gambarotta, Gregory S. Girolami, Michael B. Hall, Peter Legzdins, Jan H. Teuben, Klaus H. Theopold, and Geoffrey Wilkinson. My own modest contribution to this area was made possible by funding from the Camille and Henry Dreyfus Foundation, the Alfred P. Sloan Foundation, the Exxon Education Foundation, and the National Science Foundation, which I gratefully acknowledge.

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