Chem. Rev. **1991**, *91*, 509−551

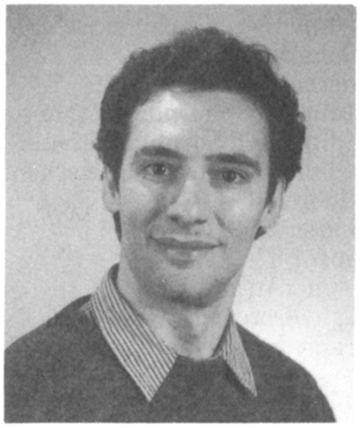
Monocyclopentadienyl Halide Complexes of the d- and f-Block Elements

RINALDO POLI

Contribution from the Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland 20742

Received January 22, 1991 (Revised Manuscript Received March 25, 1991)

Contents



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 laboratories at the Imperial College, London (August 1983 through July 1984), on a student exchange program. Poli then moved to the United States with a post-doctoral fellowship from Al Cotton at Texas A&M, and in 1987, he joined the faculty of the University of Maryland where he is currently Assistant Professor. He obtained the Giuseppe Stampacchia award from the University of Rome in 1983, the Distinguished New Faculty award from the Camille and Henry Dreyfus Foundation in 1987, the title of Dottore di Ricerca from the Italian Ministry of Education in 1988, and the Presidential Young Investigator award from the National Science Foundation in 1990. His research interests are primarily in the field of organometallic compounds with an odd-electron configuration and in coordination chemistry.

0009-2665/91/0791-0509$09.50/0 © 1991 American Chemical Society

I. Abbreviations

bipy	2,2′-bipyridine
COD	cyclooctadiene
COT	cyclooctatetraenediyl
Cp	η^5-cyclopentadienyl
Cp*	η^5-pentamethylcyclopentadienyl
Cy	cyclohexyl
DME	dimethoxyethane
dmpe	bis(dimethylphosphino)ethane
dppe	bis(diphenylphosphino)ethane
dppm	bis(diphenylphosphino)methane
Fl	η^5-fluorenyl
Ind	η^5-indenyl
Np	neopentyl
phen	*o,o′*-phenanthroline
THF	tetrahydrofuran
tmeda	tetramethylethylenediamine

II. Introduction

Complexes containing both cyclopentadienyl and halide ligands were prepared soon after the first report of ferrocene. Historically, the first systems to be developed were those containing more than one cyclopentadienyl ring. In the earliest review article on cyclopentadienyl metal compounds by Wilkinson and Cotton in 1959,[1] only $TiCp_2X_2$, $ZrCp_2X_2$, VCp_2X_2, MCp_2Br_3 (M = Nb, Ta), $MoCp_2Cl_2$, and UCp_3Cl were reported, although monocyclopentadienyl chemistry was already developed for low oxidation state carbonyl derivatives. By 1964, the list of bis-Cp compounds had been extended to Hf and several rare earth MCp_2Cl systems, while the first few mono-Cp systems started to appear, e.g. $CpTiX_3$, $CpTiCl_2$, $CpZrCl_3$, and $CpCrX_2$.[2] The chemistry of systems containing two cyclopentadienyl rings developed very rapidly while studies of monoring systems remained limited, until recently, to $CpTiCl_3$, $CpTiCl_2$, and Cp^*MX_2 (M = Rh, Ir), with sporadic reports on compounds of V, Nb, Ta, Cr, Mo, and Co.[3] A surge of activity in this area starting from the early 1980's is mainly due to the development of the Cp* systems.

Some of these materials have been shown to serve as catalysts or catalyst precursors for organic reactions (Ziegler–Natta polymerization of olefins,[4] olefin hydrogenation[5] including asymmetric hydrogenation,[6] isomerization,[7] and hydrosilylation,[8] disproportionation of acetaldehyde,[9] hydrogen transfer from methanol to organic substrates,[10] cocyclization of alkynes and nitriles to pyridines,[11] and others[12,13]) or have been shown to be useful in medicinal applications as tumor inhibitors.[14] Their major use, however, is as synthons for a wide variety of other cyclopentadienyl-substituted materials in either high or low oxidation states. As a notable example, the first system shown to be capable of intermolecular oxidative addition of C–H bonds in saturated hydrocarbons was derived from the $[Cp^*IrCl_2]_2$ precursor.[15] Although the chemistry of monocyclopentadienyl halide compounds and derivatives now extends to most metals of the d and f blocks, opportunities exist for further widening the scope of this chemistry. This review article, besides providing an overview of the current status in this field of research, will hopefully help investigators who are looking for new ground in this area.

Only compounds containing one cyclopentadienyl or substituted cyclopentadienyl ring (η^5-$C_5H_nR_{5-n}$), including those with fused aromatic rings (indenyl, fluorenyl, etc.) will be covered in this report. Some solvent stabilized forms of cyclopentadienyl metal halide complexes will also be reviewed. Complexes of heteroatom-containing rings that are isoelectronic with the cyclopentadienyl ring (e.g. $C_4H_4N^-$, $C_4H_4P^-$, etc.) are not included. This review article covers work published up to the end of 1990.

The most frequently encountered nonfused rings are Cp and Cp*, the monosubstituted C_5H_4R rings, and C_5Me_4Et. When addressing general classes of derivatives, the symbol C_5H_4R will indicate rings with either R = H (Cp) or R ≠ H; C_5Me_4R will indicate systems where R is either Me (Cp*) or others; C_5R_5 will indicate either Cp or Cp*, while the most general ring (Cp and Cp* included) will be indicated by the symbol (ring).

The chemistry of transition-metal halides containing open pentadienyl in place of cyclopentadienyl rings has not been explored, although transition-metal–pentadienyl chemistry is a mature field. The synthesis of these molecules typically involves the introduction of the pentadienyl ligand into precursors that already contain the desired additional ligands (eq 1, pd = η^5-C_5H_7 or substituted derivative).[16]

$$MX_nL_m + pd^- \rightarrow (pd)MX_{n-1}L_{m-2} + X^- + 2L \quad (1)$$

The review is organized with three general sections on the preparation, structure, and reactivity of these systems, followed by a specific review by group number where extensive reference to the original literature reports is given. Within each group, the elements are listed in increasing oxidation state. For each subsection of sections VI–XIV, the topics have been arranged in the following sequence: synthetic methods, adduct formation, hydrolysis, ligand substitution, and redox reactions.

III. Synthetic Methods

A. Transmetalation Reactions

The most general method for the preparation of monocyclopentadienyl metal halide compounds is the replacement of a halide by a cyclopentadienide ligand in the transition-metal halide of the desired oxidation state (eq 2). A variety of (ring)M′ reagents have been

$$(ring)M' + MX_n \rightarrow (ring)MX_{n-1} + [M'X] \quad (2)$$

used, the most typical ones being those with M′ = Li, Na, K, Tl, MgX, $^1/_2$Mg, and ER_3 (E = Sn, Si; R = Me, *n*-Bu).

The alkali metal cyclopentadienides seem most appropriate for the preparation of derivatives with a high ionic character, such as those of the lanthanides and actinides. Early transition-metal halides in their highest oxidation states react with difficulty with ionic Cp-delivering agents and reduction often ensues, while the best results seem to be obtained with Tl, SiR_3, or SnR_3 derivatives.

One problem associated with this strategy is the selectivity to the mono-ring product. This is especially important when the steric bulk is low and the (ring)-delivering agent is ionic, e.g. during the formation of Cp_2TiCl_2 from $TiCl_4$ and CpNa. Sometimes a careful control of the reaction conditions can direct the transmetalation reaction to the selective formation of the mono-(ring) product. For instance, the reaction of $HfCl_4$ with Cp*Li in high boiling point hydrocarbons (xylenes or mesitylene) proceeds to the bis-Cp* system, whereas the use of lower boiling point solvents such as toluene or THF results in the isolation of Cp*$HfCl_3$ in high yields even in the presence of excess Cp*Li.[572]

The product is usually recovered by sublimation of the residue, which is necessary in order to eliminate the inorganic byproduct. This procedure suffers serious limitations for thermally sensitive, low volatility materials such as those with unsubstituted Cp, e.g. $CpZrCl_3$.[562] Derivatives with more substituted rings, e.g. Cp*, tend to be more volatile and thermally more robust. The use of (ring)ER_3 (E = Si, Sn; R = Me, Bu) as ring-transfer agent avoids the sublimation problem as the R_3EX byproduct is soluble and/or volatile and can be easily eliminated. The formation of the strong E–X bond is the driving force of this reaction. A problem that has been noted occasionally with this procedure is partial polymerization of the (ring)ER_3 reagent.[19]

B. Metal Halide and Cyclopentadiene

In selected cases the transition-metal halide deprotonates the cyclopentadiene molecule and induces formation of the mono-ring metal halide product with elimination of HX (eq 3).

$$\text{(ring)H} + MX_n \rightarrow \text{(ring)}MX_{n-1} + HX \qquad (3)$$

This usually occurs for the late transition elements where the (ring)–M bond is highly covalent and presumably enjoying strong stabilization through δ backbonding. This strategy has proven most successful for the Cp* systems (e.g. Ru,[20,21] Rh,[22] Ir[22,23]), where the cyclopentadiene ring is stable toward Diels–Alder dimerization and can withstand long reflux times, but cases where the method has been successfully applied to the Cp system (e.g. Rh(III)[24] and Pd(II)[25]) have been reported.

C. From Cyclopentadienylmetal Oxides

Some high-valent systems that are difficult to obtain by direct transmetalation reactions have been conveniently obtained in two steps starting from mixed oxo–halide materials, to which the cyclopentadienyl ring can be more easily transferred, followed by hydrohalogenation (eq 4). A system that can be obtained following the procedure outlined in eq 4 parts a and b is $CpMoCl_4$.[26,27] The mixed oxo–halide–(ring) intermediate can also be obtained by an alternative route and then converted to the product by the procedure of eq 4b, as for $CpMoBr_4$.[28] Compounds having more than one O atom/M atom can also be utilized as starting materials.

$$\text{(ring)}M' + MOX_n \rightarrow \text{(ring)}MOX_{n-1}\ [M'X] \qquad (4a)$$

$$\text{(ring)}MOX_{n-1} + 2HX \rightarrow \text{(ring)}MX_{n-1} \qquad (4b)$$

Deoxygenating agents can be different than HX. For instance, Cp*ReO_3 and excess Me_3SiCl afford Cp*$ReCl_4$ in a process that also involves metal reduction.[29] Analogously, Cp*Re(O)(i-Pr)$_2$ and $CpTiCl_3$ give Cp*$ReCl_2$(i-Pr)$_2$ which further proceeds to [Cp*$ReCl_2$]$_2$.[30]

D. Oxidative Addition of 5-Halocyclopentadiene

Oxidative addition across the carbon–halogen bond of halocyclopentadiene systems can lead to the incorporation of both the cyclopentadienyl ring and the halide atom into the metal coordination sphere (eq 5).

$$\text{(ring)X} + ML_n \rightarrow \text{(ring)}MXL_{n-3} \qquad (5)$$

This method is anticipated to be most effective for basic transition metals for which the oxidative addition process is favorable. This method has so far only been applied to the preparation of [Cp*NiCl]$_2$ and [Cp*CoCl]$_2$ from the corresponding binary carbonyls.[31]

E. Reduction of Higher Valent Cyclopentadienyl Derivatives

The cyclopentadienyl ligand may be able to stabilize metal oxidation states for which stable binary halide precursors are not available or not reactive. In these cases, the desired (ring)–metal complexes are commonly obtained by redox reactions from the most easily prepared cyclopentadienyl metal halides. For early transition metals, the highest oxidation state system is usually the easiest to prepare by transmetalation reactions. For elements in the middle of the d series such as Mo, W, and Re, the highest oxidation state systems are still the most easily accessible ones, although by other methods. These can be reduced with the desired stoichiometric amount of reducing agent. Even for a few late transition metals, e.g. Ru and Rh, low-valent systems are accessible by reduction of the derivatives in their most common oxidation state (eq 6).

$$\text{(ring)}MX_n + m\text{[red]} \rightarrow \text{(ring)}MX_{n-m} + m\text{[red]–X} \qquad (6)$$

Systems prepared in this manner are $CpTiCl_2$,[32–35] (C_5Me_4R)TaX_2,[36,37] (ring)MCl_2 (M = Mo, W),[38–41] (C_5Me_4R)ReX_n (n = 2, 3),[42–44] Cp*RuCl,[45,46] and Cp*RhCl.[47,48] Reductants such as sodium, sodium amalgam, zinc, magnesium, and aluminum have been employed. Other reactants can occasionally result in reduction, for instance $[Et_3BH]^-$ reduces Cp*$RuCl_2$ to the monochloride,[46] SnR_4 reduces Cp*$ReCl_4$ to the trichloride,[42] and Li_3N reduces $CpTiCl_3$ to the monochloride.[49] The choice of reducing agent may be of importance in terms of both the desired extent of reduction and the tendency of the reduced transition-metal system to retain the halide ions in the coordination sphere. An example of the first type of problem is provided by the Cp*$ReCl_4$ system, which is reduced by $SnEt_4$ to [Cp*$ReCl_3$]$_2$[42] and by the stronger reductant aluminum to the corresponding Re(III) dimer, [Cp*$ReCl_2$]$_2$.[43] Examples of the second type of problem are the Ti(IV)/Ti(III) and Mo(V)/Mo(III) systems. Reduction of $CpTiCl_3$ with zinc produces $CpTiCl_2$,[32–34] whereas reduction with Cp_2Co generates the $[CpTiCl_3]^-$ ion.[50,51] Analogously, reduction of $CpMoCl_4$ with zinc generates $\{CpMoCl_2\}_n$,[40] whereas Na/Hg results in the formation of the $[Cp_2Mo_2Cl_5]^-$ ion.[41] Undoubtedly Zn^{2+} has a higher affinity than either Cp_2Co^+ or Na^+ for Cl^-. On the other hand, the neutral mixed-valence $Cp^*{}_2Ru_2Cl_3$ is obtained from the cobaltocene reduction of $[Cp^*RuCl_2]_2$.[52] In this case, the driving force to the neutral product may be the stronger metal–metal interaction in the pseudo-face-sharing bioctahedral product with respect to the hypothetical pseudo-edge-sharing $[Cp^*RuCl(\mu\text{-}Cl)]_2^-$.

F. Oxidation of Lower Valent Cyclopentadienyl Derivatives

Particular systems for middle to late transition elements in high oxidation state are conveniently prepared by oxidation of suitable lower valent precursors that already contain the cyclopentadienyl ring. These precursors can be of the $CpMX_n$ type themselves, in which case the oxidizing agent is usually elemental halogen (eq 7). Examples of this situation are provided by the

$$(\text{ring})MX_n + m/2X_2 \rightarrow (\text{ring})MX_{n+m} \qquad (7)$$

formation of $CpMoCl_3$ from $CpMoCl_2$ and $PhI{\cdot}Cl_2$[53] and that of Cp^*RuX_3 from Cp^*RuCl_2 and excess X_2 (X = Cl, Br, I).[54]

The $CpTiCl_3$ system can be obtained from the interaction of $CpTiCl_2$ with a chloride radical source. Although this procedure is in general less convenient than the direct transmetalation reaction discussed above, it may present some advantage in particular cases. For instance the sterically encumbered $[1,2,4\text{-}(Me_3Si)C_5H_2]Li$ does not cleanly react with $TiCl_4$, whereas it does so with $TiCl_3(THF)_3$ to produce $[1,2,4\text{-}(Me_3Si)C_5H_2]TiCl_2(THF)$, from which the corresponding trichloride can be obtained by interaction with HCl.[55]

Other synthetic procedures that involve oxidation utilize starting materials that contain other ligands, which are eliminated during the oxidation process (eq 8). Carbonyl derivatives are commonly used for this purpose. For instance, $CpV(CO)_4$ is oxidized to $CpVX_3$ by Cl_2 or Br_2[56] and to $CpVI_2$ by I_2.[57]

$$(\text{ring})ML_n + m[X] \rightarrow (\text{ring})MX_m + nL \qquad (8)$$

The oxidizing agent can be other than elemental halogen, for instance $CpVCl_3$ is also obtained by treating $CpV(CO)_4$ with $SOCl_2/CCl_4$.[58] $CpCrX_2$ and Cp^*CrX_2 systems have been obtained from $[CpCr(CO)_3]_2$ and $[Cp^*Cr(CO)_n]_2$ (n = 2, 3) by oxidation with X_2 or with the corresponding allyl halide.[59-61] PCl_5 is a very efficient chlorinating agent for $(\text{ring})M(CH_3)(CO)_3$ derivatives of the heavier group 6 metals (eq 9).[62,63]

$$(\text{ring})M(CH_3)(CO)_3 + \tfrac{5}{2}PCl_5 \rightarrow (\text{ring})MCl_4 + 3CO + \tfrac{5}{2}PCl_3 + MeCl \qquad (9)$$

G. From Bis(cyclopentadienyl) Precursors

One of the first methods utilized for the preparation of $CpTiCl_3$ is cleavage of a Cp–Ti bond in Cp_2TiCl_2 by a chlorine radical source.[64,65] This reaction is accelerated by UV light. This method has also been utilized for other selected systems, e.g. $CpMCl_3$ (M = Zr,[66,67] Hf[68]) and $CpVCl_3$[58] (eq 10). When Cl_2 is the halogenating agent, 1,2,3,4,5-pentachlorocyclopentane is the other product, whereas from Cp_2ZrCl_2 and Me_3CCl, isobutylene and CpH are formed.[67]

$$Cp_2MX_n + \text{excess } X^{\bullet} \rightarrow CpMX_{n+1} + \text{other products} \qquad (10)$$

It has been established that photolysis of $(C_5R_5)_2TiCl_2$ produces $(C_5R_5)TiCl_2$ and a C_5R_5 radical. In the absence of a halide source, the formation of $CpTiCl_2$ has been observed, whereas when the reaction is conducted in chlorocarbon solvents, clean and rapid conversion to $(C_5R_5)TiCl_3$ occurs.[69,70] Introduction of electron-withdrawing substituents on the rings of Cp_2TiX_2 (X = Cl, Br) does not change the photoreactivity of the system, i.e. rupture of a Ti–Cp bond is still observed. On the other hand, $Cp^*{}_2TiI_2$ is photodecomposed, in the presence of iodoform, to Cp^*TiI_3, whereas the analogous Cp and (C_5H_4R) systems undergo different photoprocesses that involve rupture of a Ti–I bond.[71] Cleavage of a Cr–(C_5R_5) in chromocene or decamethylchromocene [by CCl_4 for Cp_2Cr[60] and HX (X = Br, I) for $Cp^*{}_2Cr$[61]] is accompanied by metal oxidation to produce $(C_5R_5)CrX_2(THF)$.

Ligand redistribution from a bis-Cp derivative and the corresponding metal halide (eq 11) has also been employed in selected cases. This method appears most

$$(\text{ring})_2MX_n + MX_{n+2} \rightarrow 2(\text{ring})MX_{n+1} \qquad (11)$$

successful for systems where the (ring)–M bond is mostly ionic, i.e. for early d-block metals in high oxidation states [Ti(IV) being the only reported example], and for lanthanides and actinides. A variation on this theme which also involves valence conproportionation is the synthesis of $CpTiCl_2$ from $Cp_2Ti(CO)_2$ and $TiCl_4$.[72]

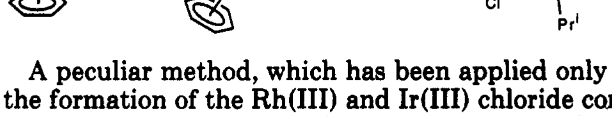
When the (ring)–M bond is ionic (for lanthanides), a (ring) ligand can also be cleaved off the bis-(ring) complex by the interaction with 1 equiv of HX (eq 12).

$$(\text{ring})_2MX + HX \rightarrow (\text{ring})MX_2 + (\text{ring})H \qquad (12)$$

H. Other Methods

$[Cp^*NbCl_2]_2$ has been produced by hydrogenolysis of $Cp^*NbMe_2Cl_2$.[73] No mention is made of the other product of the reaction, but since the corresponding tantalum system yields a stable $[Cp^*TaCl_2H]_2$ system, it is not unlikely that a similar course is taken by the niobium reaction and the Nb(IV) hydride dimer is unstable toward further reduction to the observed Nb(III) product with expulsion of a H_2 molecule. An analogous reductive elimination is that from the presumed $Cp^*ReCl_2(i\text{-}Pr)_2$ intermediate to form $[Cp^*ReCl_2]_2$.[30]

Addition of HCl to a fulvene system has been employed for the preparation of the molybdenum(III) compound $[(C_5H_4\text{-}i\text{-}Pr)MoCl_2]_2$,[74,75] see eq 13.



(13)

A peculiar method, which has been applied only to the formation of the Rh(III) and Ir(III) chloride compounds, involves a remarkable rearrangement of hexamethyl(Dewar benzene) with expulsion of two carbon

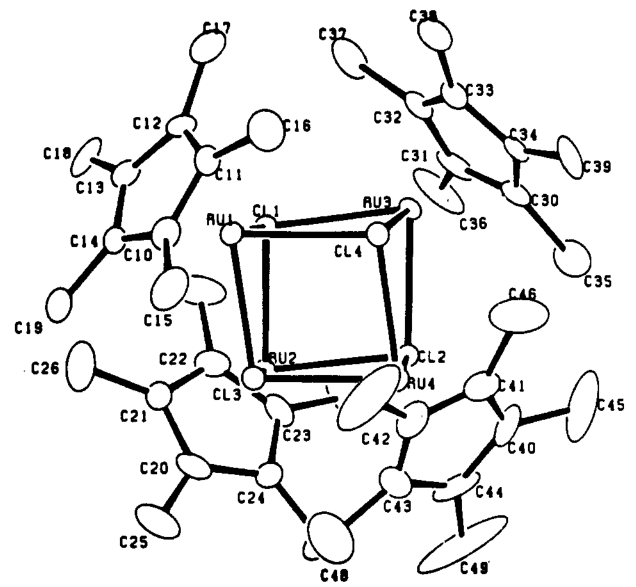
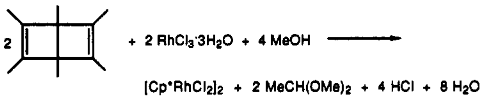


Figure 1. ORTEP drawing of $[Cp^*Ru(\mu_3\text{-}Cl)]_4$. Reproduced from ref 78; copyright 1990 American Chemical Society.

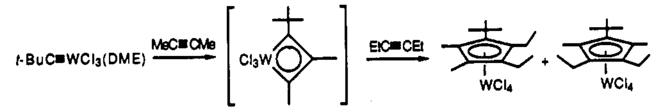
atoms[76] (see eq 14). The reaction is quantitative for the rhodium system, whereas only low yields are obtained for iridium.



(14)

Quantitative gas chromatography shows the formation of dimethylacetal in accord with the above stoichiometry for the rhodium reaction. It seems that the reaction proceeds through the intermediate $C_5Me_5(CHClMe)$, since this molecule forms from hexamethyl(Dewar benzene) and HCl and the reaction of this intermediate and either $RhCl_3{\cdot}3H_2O$ or the iridium analogue in methanol affords a very good yield of $[Cp^*MX_2]_2$ and dimethylacetal.

Another method that involves ring assembling on the metal center, this time a ring expansion, was discovered by Schrock and is to date limited to the formation of the W(V) system (eq 15).[77]



(15)

IV. Structure

A. CpMX Systems

Two structural types (I and II) are known for this class of compounds. Cp*RuCl assumes a tetranuclear, cubane-like structure (see Figure 1). The 18-electron configuration at the metal precludes any metal–metal bonding and the Ru–Cl bonds are quite labile, the cluster being easily broken up by donor ligands to generate mononuclear Cp^*RuClL_2 derivatives. The corresponding iodide derivative is presumed to have a similar structure.[78] It is interesting to note that the tetranuclear arrangement is preferred with respect to the hypothetical dinuclear arrangement of type II with a double Ru–Ru bond. A dinuclear structure, on the other hand, is observed for the bridged alkoxo compounds $[Cp^*Ru(\mu\text{-}OR)]_2$, but a theoretical analysis shows that the stabilization of the structure and its diamagnetism are due to RO-to-Ru π bonding rather than Ru–Ru bonding.[79] The structural change from I (Cl) to II (OR) is thus the result of the better π-donating properties of the alkoxide ligands. A tetranuclear structure of type I has been proposed for CpTiCl on the basis of mass spectral and ^{1}H NMR data.[35,49]

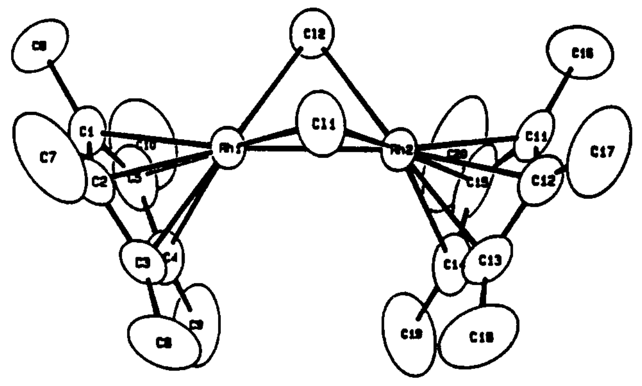
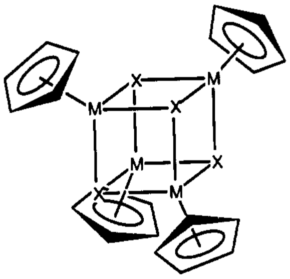
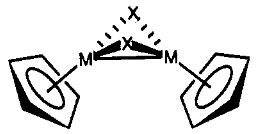


Figure 2. View of the $[Cp^*RhCl]_2$ molecule. Reproduced from ref 48; copyright 1990 American Chemical Society.



I



II

Structure II has been observed by X-ray methods for $[Cp^*CrCl]_2$[80] and $[Cp^*RhCl]_2$[48] (Figure 2), both containing a metal–metal interaction [Cr–Cr, 2.642 (2) Å; Rh–Rh, 2.617 (1) Å]. The bent arrangement observed for the central M_2Cl_2 core for both compounds may be related to the presence of the metal–metal interaction. The rhodium compound is diamagnetic, whereas the chromium complex shows small paramagnetic shifts in the NMR spectrum.

The Cp*CoX (X = Cl, Br, I) compounds are also dinuclear as shown by mass spectrometry, but their solid-state structure has not been determined. They probably have a structure of type II in analogy to the Cr and Rh systems mentioned above.[31] Solid CpCoCl has been investigated by variable-temperature magnetic susceptibility. The metal centers are strongly antiferromagnetically coupled ($J = -238$ cm^{-1}).[81] The 16-electron Cp*NiX (X = Br, I) fragments, on the other hand, can attain the 18-electron configuration upon dimerization without the need to establish a metal–metal interaction.[31] The structure of these compounds may be of type II without the metal–metal interaction, although there also exists the possibility of a planar $Ni_2(\mu\text{-}X)_2$ core. Given the preference of d^8 Ni(II) with strong field ligands for square-planar coordination, it is also possible that a η^3 coordination is adopted by the Cp* ligand, in analogy with other known $[NiX(\eta^3\text{-allyl})]_2$ complexes, but if this is the case, then a fluxional process is operative as shown by ^{1}H and ^{13}C NMR. No

TABLE I. Crystallographically Characterized $\{(\text{ring})MX_2\}_n$ Compounds

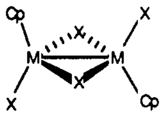
compound	type	M–M configuration[a]	M–M distance, Å	ref(s)
$[Cp^*VCl_2]_3$	VIII		ca. 3.2	85
$[(C_5Me_4Et)VBr_2]_2$	IV	$\sigma^2\delta^{*2}$	2.565 (1)	83, 85
$[Cp^*TaBr_2]_2$	IV	$\sigma^2\delta^{*2}$	2.748 (2)	36
$[CpCrCl_2]_2$	III		3.362 (1)	88
$[Cp^*CrCl_2]_2$	III		*b*	61
$[Cp^*CrBr_2]_2$	III		*b*	471
$[Cp^*CrI_2]_2$[c]	III		3.771 (3)	103
$[Cp^*Cr(\mu\text{-}I)(I_3)]_2$[c]	III		3.654 (3)	103
$[Cp^*Cu(\mu\text{-}X)I]_2$[d]	III		*b*	472
$[(C_5H_4\text{-}i\text{-}Pr)MoCl_2]_2$	IV	σ^2	2.607 (1)	74
$[Cp^*WCl_2]_2$	IV	σ^2	2.626 (1)	84
$[(C_5H_4\text{-}i\text{-}Pr)WCl_2]_2$	V	$\sigma^2\pi^4$	2.3678 (8)	38
$[(C_5H_4Et)ReCl_2]_2$	III	$(\sigma/\delta)^2\pi^2(\delta^*/\pi)^2(\delta/\pi^*)^2$	2.506 (1)	43
$[Cp^*RuCl_2]_2$	III	*e*	*b*	52
$[Cp^*RhCl_2]_2$	III		3.7191 (6)	*f*
$[Cp^*RhBr_2]_2$	III		3.854 (1)	569
$[Cp^*RhI_2]_2$	III		4.132 (0)	*g*
$[(C_5Me_4Et)RhI_2]_2$	III		4.033 (2)	*h*
$[Cp^*IrCl_2]_2$	III		3.769 (1)	*i*
$[Cp^*IrBr_2]_2$	III		3.902 (13)	571
$[Cp^*IrI_2]_2$	III		4.072 (1)	571

[a] See ref 83. [b] Value not reported. [c] In the $\{[Cp^*Cr(\mu\text{-}I)(I_3)]_2\cdot[Cp^*Cr(\mu\text{-}I)I]_2\}_n$ structure. [d] X = Cl/I, 1:1. In the $[Cp^*{}_2Cr(\mu\text{-}Cl)(\mu\text{-}I)I_2\cdot I_2]_n$ structure. [e] Although a net single bond might be expected, the compound is nonbonded and paramagnetic ($\mu_{eff} = 1.89$ μ_B per Ru center). [f] Churchill, M. R.; Julis, S. A.; Rotella, F. J. *Inorg. Chem.* **1977**, *16*, 1137. [g] Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1979**, *18*, 2918. [h] Nowell, I. W.; Fairhurst, G.; White, C. *Inorg. Chim. Acta* **1980**, *41*, 61. [i] Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1977**, *16*, 1488.

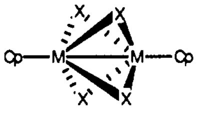
indenyl analogues appear to have been described. The analogous CpPdX species have only been briefly described. Solubility and IR spectroscopic properties indicate a dinuclear, halide-bridged structure and IR evidence is taken to suggest that the Cp ring does not adopt a η^5 binding mode.[25] The corresponding indenyl system, $[IndPdCl]_2$, has been shown by ^1H and ^{13}C NMR to adopt the η^3 coordination.[82]

B. $CpMX_2$ Systems

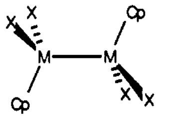
All known compounds of this class would have an electron count of less than 18 as mononuclear species. Therefore, they all dimerize and in doing so the metal centers increase their electron count through formation of halide bridges and/or metal–metal bonds. Some, however, do not reach the electronically saturated configuration and are stable as paramagnetic species. Four different structural types, illustrated in III–V and VIII, have been found. Table I reports all known crystallographically characterized compounds.



III



IV



V

The structural types III–V have been the subject of a recent theoretical investigation.[83] Calculations for the type V structure indicate that the metal-based interactions separate out into a $\sigma\pi\pi\delta\delta^*\pi^*\pi^*\sigma^*$ ordering, for a $\sigma^2\pi^4$ configuration consistent with a metal–metal triple bond for the tungsten compound. This electronic structure is similar to that described for $M_2(OR)_6$ molecules (M = Mo, W). The green color of the compound has been tentatively assigned to the $\pi \rightarrow \delta/\delta^*$ transitions, which is lower in energy than the analogous transition in $Mo_2(OR)_6$, presumably because the poor π-donor ability of Cl results in the δ/δ^* levels not being substantially destabilized by ligand-to-metal π donation. UPS data (1st ionization energy) for $[(C_5H_4\text{-}i\text{-}Pr)WCl_2]_2$ suggest that this compound is almost as electron rich as $W_2(O\text{-}t\text{-}Bu)_6$, and more electron rich than any dimolybdenum hexaalkoxide.[83]

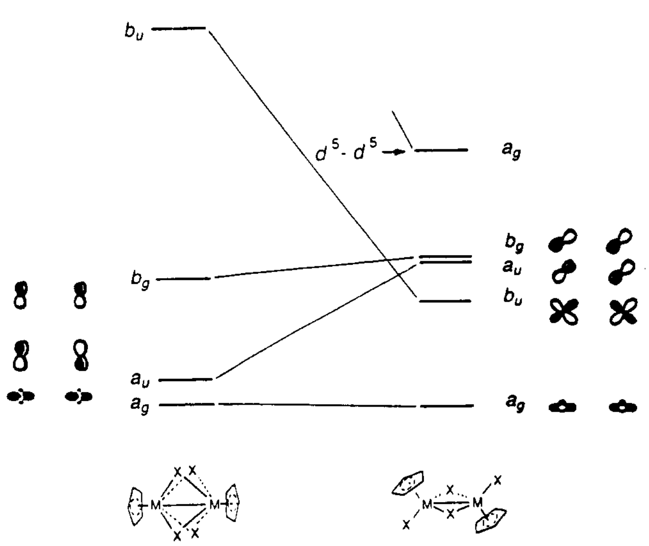


Figure 3. Correlation diagram for the opening of a $[CpM(\mu\text{-}X)_4MCp]$ dimer to a $[CpXM(\mu\text{-}X)_2MXCp]$ dimer. Reproduced from ref 83; copyright 1990 Royal Society of Chemistry.

For the type IV structure (C_{2h} symmetry), three low-energy metal-based orbitals σ (a_g), δ^* (a_u), and δ (b_g) can accommodate up to six metal electrons (see left-hand side of Figure 3). The reversal of the metal based δ and δ^* levels is due to the participation of the appropriate symmetry-adapted p atomic orbital combinations of the $(\mu\text{-}X)_4$ fragment. Whether the actual ordering in each particular case is $\delta < \delta^*$ or $\delta^* < \delta$ is consequential only for d^2–d^2 species (M = group 5 metal). For the Mo complex, six metal electrons fill the three orbitals for a formal single metal–metal bond.[83]

Type III structures have been found either with or without a direct metal–metal interaction. Calculations for the metal–metal bonded species based on the structural parameters for the rhenium dimer in Table I (C_{2h} symmetry) results in the four metal-based orbitals shown on the right hand side of Figure 3. The a_g is σ/δ in character, b_u is essentially pure π, while the nearly isoenergetic a_u and b_g orbitals are δ^*/π and δ/π^* hybrids. For the Re compound (d^4–d^4), a formal net metal–metal bond is anticipated.[83]

For the formation of a structure of type V, specific requirements of metal–metal overlap and d electron count must be met. For the d^2–d^2 Ta system, structure V would have a weaker M–M bonding and would be expected to be Jahn–Teller unstable. For Mo and Re the failure to form a type V structure can be ascribed to a diminished d–d overlap. In addition, for the Re case a small HOMO–LUMO (δ–δ^*) gap would favor second-order Jahn–Teller distortion to another geometry.[83]

In the Mo case, the d–d overlap has been increased by coordination of one additional Cl^- ion. The

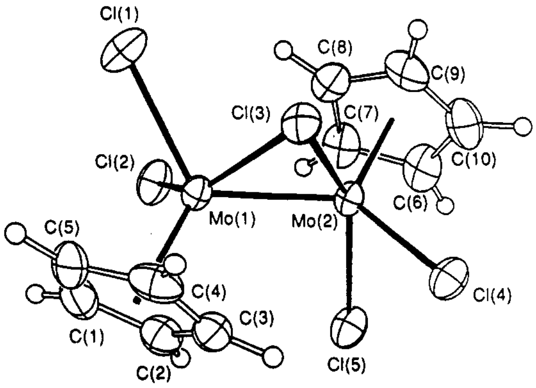
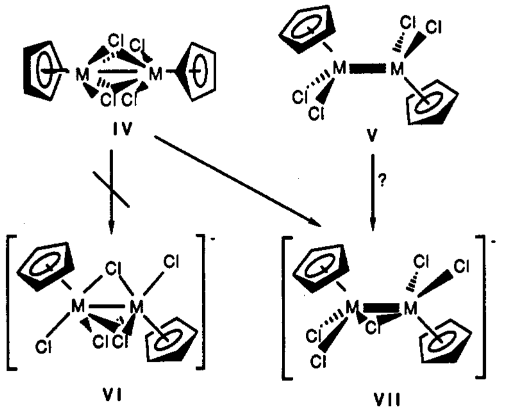


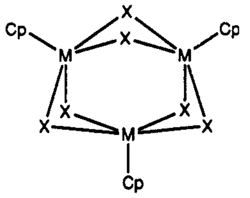
Figure 4. ORTEP view of the $[Cp_2Mo_2Cl_5]^-$ ion. Reproduced from ref 41; copyright 1990 Royal Society of Chemistry.

SCHEME I



$[Cp_2Mo_2Cl_5]^-$ ion, which is obtained from $\{CpMoCl_2\}_n$ and Cl^- (Scheme I), does not adopt structure VI which would be the expected one given structure IV for the neutral precursor (C_5H_4-*i*-Pr analogue). It rather adopts structure VII (see Figure 4), which can be viewed as the Lewis acid–base adduct between chloride and an isomeric "$Cp_2Mo_2Cl_4$" of structure V.[41] It is clear that there exists a very delicate balance between the optimization of metal–metal or metal–ligand bonding in the congeneric pair $[CpMX_2]_2$ (M = Mo or W). This is also shown by the structural change from $[(C_5H_4\text{-}i\text{-Pr})WCl_2]_2$ (type V)[38] to $[Cp^*WCl_2]_2$ in the compound containing interstitial (noncoordinated) $P_2(t\text{-Bu})_4$ (type IV).[84] It is also worth noting that $[(C_5H_4\text{-}i\text{-Pr})MoCl_2]_2$ was obtained as a pink solid by one synthetic route[74] and as a brown substance from another route.[39] The pink material converts into the brown one upon recrystallization. The brown compound has structure IV, whereas the identity of the pink material has not been established.

Whether a structure with two or four bridges is adopted depends on several factors. A type IV structure cannot accommodate, for geometrical reasons that are related to (μ-X)–(μ-X) repulsions, molecules that prefer a metal–metal nonbonded configuration, such as the dimers of Cr, Ru, or Rh. For metal–metal bonded complexes, the use of the correlation diagram in Figure 3 allows the prediction of little preference for either structure for d^1–d^1 dimers, although a type III structure would experience a larger HOMO–LUMO gap and lower interligand repulsions in the bridge system. The d^2–d^2 and d^3–d^3 electron counts favor a type IV structure, whereas a type III structure is predicted for a d^4–d^4 dimer.[83] The d^2–d^2 $[(C_5Me_4Et)VBr_2]_2$ and $[Cp^*TaBr_2]_2$ molecules and the d^3–d^3 $[(C_5H_4\text{-}i\text{-Pr})MoCl_2]_2$ molecule (Table I) have in fact a structure of type IV. $[Cp^*NbCl_2]_2$, originally proposed as having structure III,[73] is also likely to have structure IV. However, Cp^*VCl_2 does not adopt either of the structures discussed so far but rather a trinuclear structure with loose metal–metal distances (ca. 3.2 Å) as shown in VIII.[85]



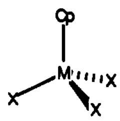
VIII

A number of derivatives in this class have been described as oligonuclear, mainly on the basis of their solubility. One such example is $CpTiX_2$ (X = Cl, Br), for which magnetic susceptibility measurements in the 100–300 K temperature range show Curie–Weiss behavior with a positive Weiss constant and no observable TIP (temperature-independent paramagnetism), indicating some kind of association.[33] NQR measurements seem to indicate only one type of chloride,[86,87] which would be consistent with a polymeric structure and against a dimeric compound of type III, although a dimer of type IV or a trimer of type VIII would not be excluded. $CpMoCl_2$ has also been indicated as an oligomeric substance.[40] In the case of Cp^*RuCl_2, a variable proportion of dinuclear and less soluble, oligonuclear species is obtained depending on the solvent used for the synthesis.[52] Osmometric determinations on $[Cp^*RhX_2]_2$ show these compounds to be dinuclear in solution, although the presence of higher oligomeric species has been suggested.[76]

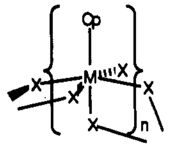
Dinuclear compounds of type III that *do not* show direct metal–metal bonds generally have some degree of antiferromagnetic coupling between the two metal centers. This is the case for $[CpCrCl_2]_2$, as shown by temperature-dependent ^1H NMR studies.[88] ^1H NMR also shows evidence for the existence of two isomers for compounds $[CpCrCl_2]_2$[88] and $[Cp^*CrI_2]_2$,[61] interpreted as III and the corresponding derivative with the two rings in a relative syn configuration.

C. $CpMX_3$ Systems

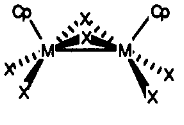
Compounds of this class have been found either as monomers, structure IX, as polymers, structure X, or as doubly bridged dimers, $[CpM(\mu\text{-}X)_2X_2]$, structures XI.



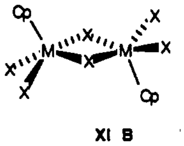
IX



X



XI A



XI B

TABLE II. Crystallographically Characterized $\{(ring)MX_3\}_n$ Compounds

compound	type	M-M distance, Å	ref
$CpTiCl_3$	IX		253, *a*
$(C_5Me_4Et)TiCl_3$	IX		234
$[CpTiCl_3]^-$	IX		51
$CpZrCl_3$	X		*a*
$(C_5H_4Me)VCl_3$	IX		89
$(C_5Me_4Et)VCl_3$	IX		403
$[(C_5H_4Me)VCl_3]^-$	IX		409
$CpVI_3$	IX		92
$[(C_5Me_4Et)TaBr_3]_2$	XIB	4.1230 (9)	37
$[CpCrCl_3]^-$	IX		*b*
$[(C_5Me_4Et)ReCl_3]_2$	XIA	3.074 (1)	43

[a] Engelhardt, L. M.; Papasergio, R. I.; Raston, C. L.; White, A. H. *Organometallics* 1984, *3*, 18. [b] Müller, B.; Krausse, J. *J. Organometal. Chem.* 1972, *44*, 141.

The reported crystal structures are listed in Table II. Structure IX is typical of complexes of the 1st row transition elements, which exhibit a number of unpaired electrons as expected given the d^n configuration in a pseudooctahedral ligand field (none for $CpTiCl_3$, one for $CpTiCl_3^-$ (by EPR)[50] and $CpVCl_3$,[56] two for $CpVCl_3^-$,[89] and three for the $CpCrCl_3^-$ ion[90]). The structure of $CpTiBr_3$ vapors has been shown to be of type IX by electron diffraction methods.[91] $CpVI_3$ has a structure of type IX with close [3.824 (4) Å] intermolecular I···I contacts in the solid state, whereas two distinct and yet undefined species, apparently in equilibrium with each other, are present in solution.[92]

Thd d^3–d^3 rhenium $[(C_5Me_4Et)ReCl_3]_2$ species assumes structure XIA. It may be argued that, for 2nd and 3rd row transition elements, the tendency to form metal–metal bond tends to favor the formation of cluster species. In the rhenium case, the electronic configuration requires the formation of a metal–metal single bond to attain the closed-shell configuration, and the observed metal–metal distance of 3.074 (1) Å and the diamagnetism seem consistent with this view.[30,43] On the other hand, the d^1–d^1 Ta (IV) system could also give rise to a single metal–metal bond interaction, but the observed structure for $[(C_5Me_4Et)TaBr_3]_2$ is of type XIB with no direct metal–metal bond and the molecule is paramagnetic with a magnetic moment corresponding to two unpaired electrons.[37]

Compounds of large ions that are void of d electrons (e.g. lanthanides, actinides, Zr, Hf, and to a certain extent also Ti) readily form bis-solvent adducts with a pseudooctahedral geometry, $CpMX_3L_2$, where one of the L ligands occupies a position trans to the Cp ring. The solvent-free $CpMX_3$ species may retain a similar coordination geometry around the metal center by forming infinite chains of halide-bridged units, as was found for the $CpZrCl_3$ compound (type X, see Figure 5). The difference between the $CpMCl_3$ (M = Ti, Zr) structures parallels exactly the difference between the tetrahedral and edge-sharing polyoctahedral MCl_4 structures (M = Ti, Zr, respectively). $CpZrCl_3$ and $CpHfCl_3$ are much less soluble than their Ti counterpart in noncoordinating solvents, consistent with their polynuclear nature. Cp^*ZrCl_3 and Cp^*HfCl_3 have likewise been assumed to be oligomeric in the solid state. Unlike the unsubstituted Cp analogues, however, they can be readily sublimed and He(I) and He(II) photoelectron spectra parallel that of the corresponding Ti species.[93] Thus, at least in the gas phase, they have a mononuclear structure of type IX.

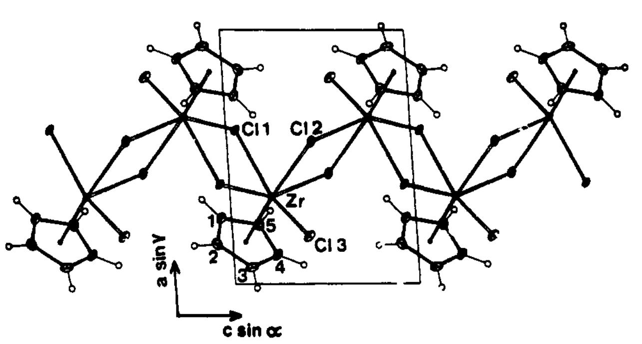


Figure 5. Structure of $CpZrCl_3$. Reproduced from ref *a*, Table II; copyright 1984 American Chemical Society.

TABLE III. Crystallographically Characterized $\{(ring)MX_4\}_n$ Compounds

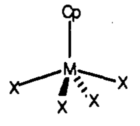
compound	type	M-M distance, Å	ref
$[Cp^*NbF_4]_2$	XIII	*a*	95
$[Cp^*TaF_4]_2$	XIII	*a*	95
Cp^*TaBr_4	XII		85
$(C_5H_4\text{-}i\text{-}Pr)WCl_4$	XII		85

[a] Not reported.

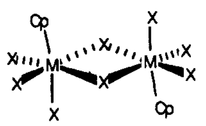
No structural details are available for the d^2 $CpMoCl_3$ system.[53] The d^4 Cp^*RuX_3 (X = Cl, Br, I) compounds have been described as oligomeric on the basis of their poor solubility in most organic solvents.[54] A dinuclear structure of type XI without a metal–metal bond would be expected to be stable on electron-counting grounds.

D. $CpMX_4$ Systems

Either mononuclear (type XII) or doubly bridged dinuclear (type XIII) structures have been found for this class of compounds (see Table III).



XII



XIII

The d^0 V(V) compounds are not known. Given the high oxidation power of the corresponding V(IV) $CpVX_3$ compounds,[89] the $CpVX_4$ compounds would probably not be stable, except perhaps for the fluoride. The corresponding $CpMX_4$ (M = Nb, Ta; X = F, Cl) compounds have been reported. Both Cp^*NbF_4[94] and Cp^*TaF_4[95] assume a dinuclear structure (XIII) in the solid state but they are mononuclear in solution as shown by ^1H and ^{19}F NMR and by their high solubility in common organic solvents. The niobium structure is further stabilized by solvate AsF_3 molecules which establish Lewis acid–base interactions with the terminal fluoride ligands, whereas there are no interactions between interstitial AsF_3 and the tantalum dimer. On the other hand, the Cp^*TaBr_4 compound crystallizes as a monomer of type XII.[85] Compounds $CpMCl_4$ (M = Nb, Ta) have been presumed to be dimeric.[96] They are soluble in CH_2Cl_2, from which they can be recrystallized.[97] However, they more readily dissolve in coordinating solvents, e.g. MeCN, PhCN, and $P(OMe)_3$, presumably because of the formation of the mononuclear $CpMCl_4L$ adducts. It is not to be excluded that, given the greater steric requirements of the Cp* group (with respect to Cp) and the chloride ligands (with respect to F), the Cp^*MCl_4 (M = Nb, Ta) molecules would also assume a mononuclear structure in analogy to the tetrabromide Nb compound. The Cp* systems are more readily soluble than their Cp counterparts in nonpolar media. The isoelectronic $Cp^*TaCl_3(SiMe_3)$[98] and $Cp^*TaCl_2(c\text{-}C_4H_8)$[99] complexes are mononuclear.

The d^1 Mo and W chloride and the Mo bromide compounds are known. A molecular weight study of $[C_5Me_4(t\text{-}Bu)]WCl_4$ by differential vapor pressure techniques in CH_2Cl_2 at 0 °C is consistent with a dinuclear formulation.[77a] However, $(C_5H_4\text{-}i\text{-}Pr)WCl_4$ is a four-legged piano-stool monomer of type XII in the solid state and the similarity of the low-energy IR spectra suggest that all $(C_5H_4R)MCl_4$ (M = Mo, W; R = H, Me, *i*-Pr) compounds have similar solid-state structures.[39,100] $CpMoCl_4$ is insoluble in CH_2Cl_2, whereas it slightly dissolves in THF and the resulting solution exhibits a sharp EPR signal that can be attributed to a mononuclear species, either with or without coordinated THF (a dinuclear d^1–d^1 species with either a metal–metal bond or a triplet ground state with a large zero-field splitting is expected to be EPR silent).[62] On the other hand, Cp^*MoCl_4 exhibits an absolutely identical EPR spectrum in CH_2Cl_2 and THF,[101] suggesting that Cp^*MoCl_4 is at least in a considerable proportion mononuclear in solution and probably not able to coordinate an additional THF molecule. Similar EPR properties have been found for Cp^*WCl_4.[63]

The d^2 Re chloride system has been described. Although no crystal structure on rhenium tetrahalide compounds is reported, the compound where one chloride has been replaced by a methyl group, $Cp^*ReMeCl_3$, shows a mononuclear four-legged piano-stool structure of type XII.[42] NMR data suggests that solutions of Cp^*ReX_4 (X = Cl, Br) contain at least two species, a paramagnetic monomer and a diamagnetic dimer.[102]

E. Other Systems

No pentahalide system, $CpMX_5$, has been reported to the best of our knowledge. On the basis of the known stability of the +6 oxidation state for certain metals, it is tempting to predict that compounds of this class may be made in the future. Particularly attractive appear to be the pentafluoride derivatives of tungsten, rhenium, and osmium. The unreported 18-electron $CpReF_6$, isoelectronic with the known Cp^*ReO_3, might also exist as a stable species.

The structure of the $[Cp_2Mo_2Cl_5]^-$ ion (Figure 4) is unique in having two metals linked by a formal triple bond (Mo–Mo = 2.413 (1) Å) and bridged by a single halide ligand. As discussed earlier, this molecule can be viewed as the formal Lewis acid–base adduct between the bridging chloride ion and a $Cp_2Mo_2Cl_4$ dimer with a structure of type V.[41]

The triply bridged $[Cp^*Cr(\mu\text{-}I)_3CrCp^*]^+$ cation has the structure shown in Figure 6 and metal–metal separations of 3.001 (5) and 3.012 (5) Å for the two independent ions in the salt with the remarkable I_{16}^{2-} dianion. This distance is shorter than those exhibited by the isoelectronic and structurally analogous $Cr_2X_9^{3-}$ species and therefore implies metal–metal bonding. The ^1H NMR resonance for the Cp* protons (δ −14) is much less paramagnetically shifted than that of $Cp^*_2Cr_2I_4$, but detailed magnetic studies have not been carried out.[103] Analogous triply bridged systems have been structurally characterized for cobalt, $[(C_5Me_4Et)_2Co_2(\mu\text{-}Cl)_3]^+$[104] and $[Cp^*_2Co_2(\mu\text{-}Cl)_3]^+$,[105] rhodium, $[Cp^*_2Rh_2(\mu\text{-}Cl)_3]^+$,[106] iridium, $[Cp^*_2Ir_2(\mu\text{-}Cl)_3]^+$,[107] and a similar triply bridged system, but with two additional terminal chloride per metal, is the $[Cp^*_2Cl_4Ta_2(\mu\text{-}Cl)_3]^+$ ion.[108,109] None of these systems exhibits a metal–metal interaction, because of the closed shell 18-electron configuration in the Co(III), Rh(III), and Ir(III) cases and because there are no d electrons available in the Ta(V) case.

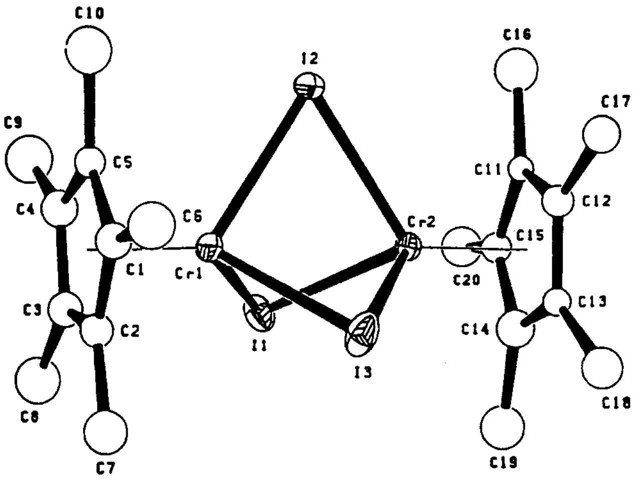


Figure 6. ORTEP view of the $[Cp^*Cr(\mu\text{-}I)_3CrCp^*]^+$ cation. Reproduced from ref 103; copyright 1990 American Chemical Society.

The mixed-halide tetranuclear $[Cp^*_4Cr_4(\mu\text{-}F)_5Cl_2]^+$ ion has a complex structure in which each Cr center maintain the favorable pseudooctahedral Cp^*CrX_3 configuration. Magnetic susceptibility measurements indicate strong antiferromagnetic coupling of the S = 3/2 ions via the fluoride bridges.[110]

V. Reactivity

A. Splitting of the Metal–Ring Bond

By and large, the role of the (ring) ligand is limited to the thermodynamic, kinetic, and steric stabilization of the complexes, and all the chemical reactivity is directed to the terminal or bridging halide ligands (exchange reactions) or to the metal center itself (addition or electron-transfer reactions). The ionic lanthanide systems react with protic substances to generate (ring)H and the lanthanide salt.[111] This reaction does not occur for any of the d-block elements. $CpTiCl_3$ is stable under continuous HCl bubbling, but the Cp ring is cleaved off by treatment with chlorine, to give $TiCl_4$ and 1,2,3,4,5-pentachlorocyclopentane.[65]

Splitting of the metal–(ring) bond for systems of the d-block elements has been observed only in rare occasions. $[Cp^*RuCl]_4$ is decomposed by excess pyridine in acetone to the $[Ru(py)_6]^{2+}$ ion.[45] Excess of PMe_3 in warm toluene leads to reduction of Cp^*ReCl_4 and formation of a mixture of $Cp^*ReCl_2(PMe_3)_2$ and $ReCl_3(PMe_3)_3$.[43] In analogous conditions, the interaction between $CpMoCl_2$ and excess PMe_3 produces $MoCl_2(PMe_3)_4$ and $Mo_2Cl_4(PMe_3)_4$ in addition to the simple addition product, $CpMoCl_2(PMe_3)_2$.[101] It seems that the Mo(II) complexes arise from thermal decomposition of the preformed Mo(III) Cp-containing species.[112] The role of phosphine coordination (especially when the phosphine is a strong base such as PMe_3) to promote metal reduction has also been observed for other systems such as Ru(III), albeit the reduction products retain the M–(ring) linkage in these cases (see section V.D.). The Rh(V) complex $Cp^*RhH_3(SiEt_3)$ reacts with PMe_3 to yield $HRh(PMe_3)_4$, Et_3SiH, and Cp*H, but the reaction of $[Cp^*RhCl_2]_2$ with excess PMe_3, even at 60°, does not yield products of scission of the Rh–Cp* bond. This difference has been related to the different stability of Cp*H with respect to Cp*Cl.[113]

B. Lewis Acidity and Addition Reactions

Lewis acidity is observed only for neutral or cationic species; anionic species do not coordinate neutral Lewis bases. For instance, the Cp^*LnX_2 (Ln = lanthanide) compounds are extremely acidic and it is difficult to obtain them free of coordinated solvent molecules, whereas the $[Cp^*LnX_3]^-$ ions, while still electronically unsaturated, do not show any tendency to coordinate extra neutral donors.

All neutral, mononuclear $CpMX_n$ fragments known where M is a transition element are electronically unsaturated. To achieve electronic saturation (18 electrons) one would have to employ a d^{10} ion such as Hg^{2+} (not a transition-metal ion!) for $n = 1$, a d^8 ion (Au^{3+}) for $n = 2$, d^6 Pt^{4+} for $n = 3$, d^4 Ir^{5+} for $n = 4$, d^2 Os^{6+} for $n = 5$, and d^0 Re^{7+} for $n = 6$. No such species has been described, except for the ill-characterized Cp^*PtBr_3, to which the ionic formulation $[Cp^*Pt(\mu\text{-}Br)_3PtCp^*]Br_3$ has been assigned.[114] These unsaturated fragments increase their electron count by either coordinating solvent molecules, by forming oligomeric or two- or three-dimensional polymeric structures with bridging halide ligands, or simply by accepting π-electron density from the terminal halide ligands in mononuclear systems. Formation of a dinuclear or oligonuclear structure may be supplemented by the formation of direct metal–metal bonding interactions. Thus, coordination of the Lewis base must disrupt the halide-to-metal π donation or the halide-bridging network and the metal–metal bonds if these are present. The Lewis acidity of these systems depends therefore on the strength of the metal-bridging halogen and metal–metal bonds for polynuclear systems and on the strength of the π component of the metal–halogen bond for mononuclear systems. These, in turn, depend on the nature of the halide but also on the electronic configuration of the system and on inductive effects of ring substituents transmitted through the cyclopentadienyl–metal bond. In addition, there has to be sufficient room around the metal center to allow coordination of the new ligand, thus the steric properties of ring substituents and the metal size are also of importance.

Replacement of Cp with Cp* or other alkyl-substituted rings reduces the Lewis acidity of the system due to both electronic and steric effects. The halogen lone-pair π donation argument is well illustrated by the following example. $CpTiF_3$ and $CpTiCl_3$ do not form stable adducts with THF, whereas the tribromide compound forms a stable mono-adduct, $CpTiBr_3(THF)$, and the triiodide analogue forms a stable bis-adduct, $CpTiI_3(THF)_2$.[115] Similarly, $CpTiCl_2(THF)$ starts to lose the coordinated THF at room temperature and complete removal occurs at 120 °C at a pressure of ca. 10^{-4} mmHg, whereas the analogous bromide system requires a higher temperature (ca. 150 °C) to achieve the same transformation and $CpTiI_2(THF)$ starts to decompose before all the THF can be removed.[33] Replacement of Cp with Cp* causes the THF loss in the Ti(III)-chloride system to occur readily at room temperature.[116] The difference between Cp and Cp* is also shown by the Zr(IV) chloride system: while $CpZrCl_3$ forms a bis-THF adduct, $CpZrCl_3(THF)_2$,[117] only a mono-adduct is obtained with the analogous Cp* derivative.[118]

For series of metals with the same d^n configuration, the Lewis acidity decreases upon moving toward the right [e.g. $CpLnX_2$ (Ln = lanthanide) > $Cp(Zr,Hf)X_3$ and $CpAcX_3$ (Ac = actinide) > $Cp(Nb,Ta)X_4$] as a combination of several factors, such as the increased number of ligands (steric argument) and the increased total electron count. For instance, the Cp^*LnX_2 systems bind three molecules of THF, $CpZrCl_3$ binds two THF molecules with the resulting $CpZrCl_3(THF)_2$ adduct exchanging rapidly the THF ligands in solution;[117] finally, the $CpMCl_4$ (M = Nb, Ta) molecules from only labile monoadducts with hard donor ligands.[119] The binding of THF by the lanthanide systems is quite strong and the solvent-free species are not always obtained by simple thermal decomposition under vacuum, although partial loss of one of the coordinated THF molecules is readily accomplished.[120] An effective method to remove completely THF from the coordination sphere has been described recently[121] by van der Heijden et al.: electrophilic attack at the coordinated THF of $Cp^*LaI_2(THF)_3$ by Me_3SiI leads to the formation of $Me_3SiO(CH_2)_4I$, which is too sterically hindered to coordinate to the lanthanum center, and produces solvent-free Cp^*LaI_2.

The Lewis acidity always increases upon descending a group of metals as a result of the increased size of the metal center and/or the decreased strength of the M–X π interaction. For instance, although $CpTiCl_3$ does not coordinate THF or DME, stable $CpMCl_3(THF)_2$[117,122] and $CpMCl_3(DME)$[19,67] (M = Zr, Hf) adducts have been reported. Although investigations to this effect have not been carried out, it is likely that the Lewis bases are more tightly bound to the hafnium system and that the zirconium species will be more active as a Lewis acid catalyst.[117]

The coordination of phosphines is always preferred with respect to that of hard donors such as ethers or amines, even for early transition metals. Phosphines may only suffer from steric effects. For instance, whereas $CpTiCl_3$ does not form adducts with THF or DME, it forms a stable 1:1 adduct with dmpe.[123] Ethers and amines are not usually able to add to late transition-metal systems and only soft donor ligands such as phosphines, sulfides, olefins, isocyanides, and CO will coordinate. No stable adduct of hard donors have been reported for metals past group 5. It is not clear whether coordination of THF to $(ring)MCl_4$ (M = Mo, W) can occur, although formation of an adduct for $CpMoCl_4$ might explain its higher solubility in THF with respect to CH_2Cl_2.

The coordination of phosphines seems also sufficiently favorable to allow strong metal–metal interactions to be broken. Examples of this situation are found for the addition to the singly bonded $[(ring)Mo(\mu\text{-}Cl)_2]_2$[40,74] and $[Cp^*ReCl_2(\mu\text{-}Cl)]_2$[43] molecules to form $(ring)MoCl_2L_2$ (L = monodentate phosphine or L_2 = chelating diphosphine) and $Cp^*ReCl_3(PMe_3)$, respectively; to the doubly bonded $[Cp^*ReCl(\mu\text{-}Cl)]_2$ to form $Cp^*ReCl_2(PMe_3)_2$;[44] and to the triply bonded $[(C_5H_4Me)WCl_2]_2$ to form $(C_5H_4Me)WCl_2(\mu\text{-}Cl)_2W(dmpe)(C_5H_4Me)$.[38]

C. Hydrolysis

The reactivity of cyclopentadienylmetal halides toward hydrolysis is regulated by the same considerations that govern the reaction with Lewis bases. In fact, water is a Lewis base (a hard one) and the first step of the hydrolysis reaction is likely to be coordination of the water molecule to the metal center. The reaction, however, proceeds further to eliminate one or more halide ligands as HX and replace them with terminal or bridging hydroxo or oxo ligands. Thus, there is an additional driving force with respect to simple Lewis base coordination which is given by the bond reorganization from O–H and M–X to M–O and H–X. This additional driving force makes the reaction with water possible also for metal systems that do not normally form adducts with hard Lewis bases, such as Cp^*MoCl_4[124] and Cp^*ReCl_4.[125,126] The hydrolysis of $\{Cp^*RuCl_n\}$ systems (*n* = 2, 3) has not been investigated, but the corresponding alcoholysis in the presence of a base proceeds to the stable alkoxide derivatives $[Cp^*Ru(\mu\text{-}OR)]_2$.[52] The reaction of $[Cp^*CoX_2]_2$ in water yields the product of simple ligand substitution, $[Cp^*Co\cdot aq]^{2+}$, at pH < 9,[127] thus behaving as a simple inorganic salt that ionizes in water. This trend is consistent with the reduced strength of M—OH and M═O bonds, with respect to M–halogen bonds, on going from the left to the right of the transition series.

The hydrolysis reaction is more difficult for the bulkier and more electron-rich Cp* systems and clean results can often be obtained only in the presence of a base such as an amine which provides an additional driving force by trapping HX. As an example, $CpTiCl_3$ is more moisture sensitive than Cp^*TiCl_3. The latter can be exposed to air for brief periods, even in solution, without decomposition. Hydrolysis eventually takes place, but the presence of a base is necessary to drive the reaction to completion.[128]

The requirement for the initial coordination of water is nicely shown by the zirconium system, which gives the crystallographically characterized diaquo adduct in the presence of 15-crown-5.[129] The crown ether serves to stabilize the coordinated water through hydrogen bonding and thus avoids attack at the Zr–Cl bonds. Without this extra stabilization, hydrolysis would probably take place. Although the hydrolytic behavior of $CpZrCl_3$ has not been reported, that of the corresponding Cp^*ZrCl_3 system has been well investigated[130,131] and the Cp system is expected to be at least as reactive as the Cp* system as discussed above.

D. Ligand Exchange Reactions

The halide ligands can be exchanged with a wide variety of anionic substrates. Certain neutral nucleophiles, when used in excess stoichiometry, are also able to displace the halide after having added as Lewis bases to the metal center. This is most typical for soft metal centers (late transition metals) and for soft, strong-field ligands, such as isocyanides and phosphines. The chelate effect makes this displacement possible also for conjugated organic π systems (dienes, arenes etc.) and for harder, strong-field ligands such as bipy and phen.[132,133]

Very polar donor solvents such as acetonitrile, acetone and the like are able to displace the chloride ions. These "ionization" processes are most favorable for the late transition-metal systems, where X-to-M π donation does not play a major role in the stabilization of the M–X bonds. For instance, $[Cp^*RuCl]_4$ gives[45,46] $[Cp^*Ru(solvent)_3]^+$ and, in the presence of Ag^+ salts, $[Cp^*MX_2]_2$ (M = Co,[134] Rh,[135–137] Ir[138,139]) gives $[(ring)M(solvent)_3]^{2+}$. These species are very useful synthetic intermediates for further substitution reactions. Partial ionization may also occur in solvents with a high dielectric constant but poor ligating properties (e.g. H_2O, MeOH, and $MeNO_2$), as for the case of $[Cp^*RuCl_2]_2$ which gives $[Cp^*Ru(\mu\text{-}Cl)_3RuCp^*]Cl$[52] and of $[Cp^*CoX_2]_2$ which gives $[Cp^*Co(\mu\text{-}X)_3CoCp^*]X$.[140] A similar reaction takes place for $[Cp^*RhCl_2]_2$ with the aid of $NaBPh_4$[141] and for $[Cp^*IrCl_2]_2$ with the aid of $AgClO_4$ or $TlBF_4$.[107]

Exchange reactions of halide ligands with other negatively charged nucleophiles have been accomplished by three major synthetic strategies. The direct interaction of the metal complex with the negatively charged nucleophile as an alkali metal or tetraalkylammonium salt, including alkyl- and aryllithium or Grignard reagents, is the one of widest applicability. By this route several mixed-ring bis(cyclopentadienyl) complexes of Sc, Ti, Zr, Hf, Nb, and W (see the sections dealing with the individual elements for references) have also been prepared. For particular nucleophiles, the use of the silver salts has proven effective to help drive the reaction. For instance the thermally unstable $CpTi(EF_6)_3$ (E = As, Sb) have been obtained by the low-temperature interaction between $CpTiCl_3$ and $Ag(EF_6)$.[142] The degree of substitution can sometimes be controlled by the stoichiometric ratio. For the alkylation reactions, the nature of the counterion or alkyl delivering agent can be of importance; dialkylzinc and tetraalkyltin reagents tend to give rise to a lower degree of substitution with respect to alkyllithium or Grignard reagents (e.g. see the Ta(V) system, section IX.I, and the Re(V) system, section XI.D).

A second synthetic method involves the use of the protonated nucleophile (e.g. carboxylic acid, alcohol, etc.) in the presence of a base, typically a tertiary amine, to provide the driving force by trapping the HX molecule which is formed during the exchange. There are a number of cases in which elimination of HX does not require the use of base, especially for the late transition-metal systems.

The third method consists in the utilization of a silylated derivative, typically Me_3Si–Nu, which replaces the halide ligand (most typically chloride) by eliminating the volatile Me_3SiX. This method parallels the synthesis of $(ring)MX_n$ systems from $(ring)SiMe_3$ and MX_{n+1} discussed in section III.A and is the only viable one for the introduction of nucleophiles that are not stable as free anions or as protonated species (e.g. the aryldiazenido ligand, Ar—N═N—) or that have a strong reducing power as free anions (e.g. LiN(Me)NMe$_2$ and CpTiCl$_3$[143]). In some instances, this methodology gives cleaner reactions and better results even if one of the other methods can be applied. For instance, Me$_3$Si–NHNR$_2$ reacts with CpTiCl$_3$ to give CpTiCl$_2$(NHNR$_2$) selectively, whereas when the free hydrazine is employed, this can further deprotonate the hydrazido(1–) ligand to afford dinuclear [μ-hydrazido(2–)] impurities.[144]

Several reactions that are initiated by a nucleophilic ligand exchange proceed to generate more complex products, for instance clusters are obtained when the nucleophile is a transition-metal carbonyl anion (e.g. see the reaction of [Cp*RhCl$_2$]$_2$ with the [Co(CO)$_4$]$^-$ ion[145] and with other carbonylmetalates[146,147]). Several examples where the (ring)M unit has been anchored, through formal ligand substitution processes, to polyoxometalates and boranes or carboranes have also been reported.

E. Redox Reactions

The simplest redox reactions are the reductions with various forms of sodium or other active metals and the oxidations with dihalogen. These reactions yield other cyclopentadienylmetal halide systems in different oxidation states and have already been discussed above (sections II.E and II.F). Other reductions that involve simple electron transfer (e.g. by cobaltocene) have also been discussed in section II.E.

Oxidation reactions of lower valent systems may also be accomplished by oxidizing agents other than dihalogens. For instance, CpTiCl$_2$ is oxidized to the derivatives of Ti(IV) by peroxides, disulfides, and ketones (section VII.B), and H$_2$ or alkynes oxidatively add to the W(III) dimer system described in section X.D. Oxidative addition of allyl chloride to [Cp*RuCl]$_4$ yields the mononuclear Ru(IV) derivative, Cp*Ru(η^3-C$_3$H$_5$)Cl$_2$.[78]

Coordination of strong field ligands such as CO, phosphines, or organic π systems makes the system much more susceptible to reduction, especially for the late transition metals. For instance, while the {Cp*RuCl$_2$}$_n$ system adds phosphines to form mononuclear, 17-electron Cp*RuCl$_2$(PR$_3$) derivatives in nonreducing solvents, in alcoholic solvents the Ru(II) complexes Cp*RuCl(PR$_3$)$_2$ are readily obtained. Similar reductions occur in the presence of arenes or dienes (see section XII.D). Certain nucleophiles are reducing agents themselves, for instance thioates giving disulfides, and while their use under mild conditions may result in simple substitution of the halide ligands, under more forcing conditions the metal will be reduced, as is the case for the Ru(III) system (see section XII.D). The reaction of the Rh(III) and Ir(III) systems with olefins under reducing conditions (alcohol solvent) to Cp*ML$_2$ (M = Rh, Ir) complexes requires the presence of base to trap the acid formed during the reaction (sections XIII.E and F).

The presence of particular ligands makes it possible to access particular oxidation states for which the parent (ring)MX$_n$ system has not been made or is not stable. This is particularly the case for early transition-metal systems. For instance Cp*ZrCl$_3$ is reduced in the presence of COT to give the Zr(III) product Cp*Zr(COT)[148] and the reduction of CpZrCl$_3$ in the presence of dmpe yields the Zr(II) derivative CpZrCl(dmpe)$_2$.[149] Neither (ring)ZrCl$_2$ nor (ring)ZrCl have been reported as stable compounds.

A more detailed account of the redox reactivity for each particular (ring)MX$_n$ system is provided in the sections that follow.

VI. Scandium and Yttrium

The Cp*ScCl$_2$ system has been reported only very recently, but no details about its preparation have been given. The (C$_5$Me$_4$CH$_2$C$_6$H$_4$-*m*-X)ScCl$_2$ (X = H, CH$_3$) analogues were prepared by interacting AlCl$_3$ with (C$_5$Me$_4$CH$_2$C$_6$H$_4$-*m*-X)Sc(acac)$_2$, the latter compound being in turn obtained from Sc(acac)$_3$ and (C$_5$Me$_4$CH$_2$C$_6$H$_4$-*m*-X)Li.[150] The sequential reaction of ScCl$_3$(THF)$_3$ with K$_2$COT and Cp*Na in either order yields the mixed sandwich compound Cp*Sc(COT), but a Cp*ScCl$_2$ intermediate was not isolated, nor described.[151] Treatment of YCl$_3$(THF)$_x$ with Cp*Li in a 1:1 ratio gives a complex mixture of various Cp*-containing products, as indicated by the NMR spectrum,[152] whereas the corresponding reaction on the La and Ce trichlorides gave well-defined, crystalline Cp*LnCl$_3$·Li(THF)$_2$ (see section VII.B). The preparation of a compound of stoichiometry CpYCl$_2$(THF)$_3$ has been claimed, although no details of its preparation and characterization were given. Its reaction with K$_2$COT gives the mixed sandwich compound CpY(COT)·THF.[153]

The reaction of Cp*ScCl$_2$ with (C$_5$Me$_4$R)Li (R = *n*-Pr, CH$_2$Ph) gives the mixed-ring scandocene chloride systems, Cp*(C$_5$Me$_4$R)ScCl, and the reaction of (C$_5$Me$_4$CH$_2$C$_6$H$_4$-*m*-X)ScCl$_2$ with (C$_5$Me$_4$CH$_2$C$_6$H$_4$-*m*-Y)Li analogously gives (C$_5$Me$_4$CH$_2$C$_6$H$_4$-*m*-X)(C$_5$Me$_4$CH$_2$C$_6$H$_4$-*m*-Y)ScCl (X = H, Y = CH$_3$; X = CH$_3$, Y = CF$_3$, NMe$_2$).[150]

VII. Lanthanides and Actinides

Since the large lanthanide and actinide ions have a pronounced tendency to form complexes with a high coordination number, mono-Cp halide derivatives are in most cases stable only with the sterically more demanding Cp* ligand, whereas several Cp$_2$MX and Cp*$_2$MX derivatives are known.[154]

A. Lanthanide(II)

The Sm(II) THF adduct, [Cp*Sm(μ-I)(THF)$_2$]$_2$, forms during the reaction between SmI$_2$ and Cp*$_2$Sm(THF)$_2$ or from the 1:1 interaction of SmI$_2$ and KCp*.[155] Cp*YbI$_2^-$ was obtained from Cp*$_2$Yb and LiI.[156] The 1:1 reaction of Cp*$_2$Yb(THF)$_2$ or Cp*$_2$Yb(OEt$_2$)$_2$ with Me$_3$SiX (X = Cl, Br) in benzene affords solvent-free Cp*YbX.[157] YbCl$_2$ and the equimolar amount of (C$_5$R$_5$)Na in THF or DME generate the corresponding (C$_5$R$_5$)YbClL$_2$ (L = THF or L$_2$ = DME). NMR properties are consistent with either a mononuclear or dinuclear, halide-bridged structure.[158]

B. Lanthanide(III)

The complexes [Cp*LnCl$_3$]$^-$ (Ln = La, Ce, Pr, Nd, Yb, Lu)[152,156,159–163] are generally obtained from the corresponding LnCl$_3$ or LnCl$_3$(THF)$_3$ and Cp*$^-$. The complex [Cp*YbI$_3$]$^-$ was obtained from metallic Yb or from $[Cp^*YbI_2]^-$ and Cp^*I.[156] These and other similar ions are also formed as intermediates during the one-pot preparation of other derivatives, for instance $[Li(tmeda)_2][Cp^*LnMe_3]$ or $[Li(tmeda)_2][Cp^*LnCl(t\text{-}Bu)_2]$ (Ln = Yb, Lu) from $LnCl_3$ and Cp^{*-} followed by methylation,[164,165] and $(CpGd)_5(\mu_2\text{-}OMe)_4(\mu_3\text{-}OMe)_4(\mu_5\text{-}O)$ or $Na_2(t\text{-}BuOGd)_4(\mu_3\text{-}O\text{-}t\text{-}Bu)_8(\mu_6\text{-}O)$ from $GdCl_3$ and CpNa followed by treatment with MeONa or t-BuOK, respectively.[166]

The THF-solvated neutral complexes $(ring)LnX_2(THF)_n$ (Ln = La, Ce, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu; X = Cl, Br, I; n = 2, 3, or 4)[111,120,167–170] have been prepared either from LnX_3 and 1 equiv of $(ring)^-$, by conproportionation of $(ring)_3Ln$ and LnX_3, or from $(ring)_2LnCl$ and 1 equiv of HCl. Complexes with n = 3 have been structurally characterized in the solid state for Ln = La, Ce, Er, and Yb.[120,171,172] Their geometry consists of a pseudooctahedral coordination environment with the η^5-Cp ring occupying one coordination position and the three THF molecules having a meridional arrangement with one THF trans to the Cp ring. Dissolution of these compounds in noncoordinating solvents or prolonged evacuation results in partial or complete loss of the coordinated THF. Solvent-free Cp^*YbX_2 (X = Cl, I) has been obtained by oxidative addition of alkyl or aryl halides to $Cp^*_2Yb\cdot OEt_2$ according to the stoichiometry presented in eq 16, as shown by ^1H NMR monitoring,[173,174] and also by the interaction between $Cp^*_2Yb(THF)_2$ and $TiCl_4$ (2 equiv) or $Cp^*_2YbCl(THF)$ and $TiCl_4$ in toluene. The byproduct of these reaction is Cp^*TiCl_3.[157] Solvent-free Cp^*LaI_2 has been obtained from the THF solvate by interaction with Me_3SiI (see section V.A).[121]

$$Cp^*_2Yb\cdot OEt_2 + (1 + a)RX \rightarrow (1 - a)Cp^*_2YbX + aCp^*YbX_2 + Et_2O + aCp^*R + 1.0\ (\text{total})\ [R\text{–}R,\ R\text{–}H,\ R(\text{–}H)] \quad (16)$$

Alkali metal salts of heptamethylindenyl (Hmi) react with the stoichiometric amount of $LnCl_2$ (Ln = La, Er, Nd) to afford products analyzing as $(Hmi)LnCl_2\cdot nTHF$ (La, n = 1; Er, n = 0.5; Nd, n = 0). NMR characterization of the La compound indicates a probable η^5 bonding of the indenyl group.[175] Other indenyl compounds of Pr, Nd, Sm, and Gd have also been described.[176]

A dinuclear, asymmetric, halide-bridged species, $CpSmCl(THF)_2(\mu\text{-}Cl)_2SmCl_2(THF)_3$, where only one of the two metals has a Cp ring has also been prepared and characterized by single-crystal X-ray methods.[177]

$CpLnX_2(THF)_n$ species are quite reactive and exchange ligands rapidly. For instance, Sm and Yb diiodides react with CpNa in THF to form Cp_2LnI complexes.[167] Replacement of chloride ligands in $[Li(THF)_2][Cp^*LnCl_3]$ by lipophilic bulky groups R occurs but the isolation of the $Cp^*LnR_2\cdot L_n$ products [R = CH_2SiMe_3, $CH(SiMe_3)_2$, $N(SiMe_3)_2$] is difficult. Redistribution reactions caused by the high mobility of the Cp* and R ligands can easily occur.[164,152] By this procedure, the isolation of the monoalkyl derivative $[LiL_2][Cp^*LuCH(SiMe_3)_2Cl_2]$ [L_2 = $(THF)_2$, TMEDA][161,162] has been recently reported. $Cp^*LaI_2(THF)_3$ reacts analogously to give the salt-free $Cp^*La[CH(SiMe_3)_2]_2(THF)$, whereas $\{Cp^*LaI_2\}_n$ gives salt- and solvent-free $Cp^*La[CH(SiMe_3)_2]_2$.[121,161] The mixed sandwich complexes CpLn(COT) (Ln = Sm, Ho, Er) and Cp*Ln(COT) (Ln = La, Ce) were obtained by treatment of the corresponding $CpLnCl_2(THF)_3$ or $[Li(THF)_2][Cp^*LnCl_3]$ with K_2COT.[153] A stable bisacetylide complex, $CpHo(CCPh)_2$, has been prepared by reaction of $CpHoCl_2(THF)_3$ and LiCCPh.[178]

C. Lanthanide(IV)

A remarkable compound described as $CpCeCl_3\cdot nTHF\cdot xHCl$ has been obtained by treating $CeCl_4\cdot nTHF\cdot xHCl$ with CpNa in THF at −40 °C.[179] Other syntheses from similar Ce(IV) precursors, however, yield Ce(III) products, $(C_5Me_4R)CeCl_2\cdot py$ or $Li[(C_5Me_4R)CeCl_3]\cdot 2py$.[170,180]

D. Actinide(IV)

UX_4 and 1 equiv of (ring)M (M = Tl, Li, or MgX) yield the solvated complex $(ring)UX_3L_2$ (X = Cl, Br; L = THF, L_2 = $MeOCH_2CH_2OMe$).[181–186] Similar derivatives can be prepared for thorium starting from $ThCl_4$ or $ThCl_4L_n$[186–188] and for neptunium starting from $NpCl_4$.[189] The THF ligands are fairly labile and can be replaced with a number of other hard donor ligands (e.g. Ph_3PO, $Ph_2(O)PCH_2CH_2P(O)Ph_2$, $Me_3CCONMe_2$, bipy, phen, etc.).[182,184,185] The crystal structure of $(C_5H_4Me)UCl_3(THF)_2$ shows a pseudooctahedral arrangement of the ligands with one of the THF molecules trans to the C_5H_4Me ring.[185] The structure of $CpUCl_3(Ph_3PO)_2$ has a similar arrangement of the ligands.[190] NMR investigations on $CpUCl_3(DME)$ shows that the two ends of the chelating DME ligand undergo rapid site exchange, whereas $(C_5H_4R)UCl_3(THF)_2$ (R = H, Me) exhibit broad, complex, temperature-dependent spectra suggestive of the presence of a number of species in dynamic equilibrium.[185] On the other hand, $Cp^*UCl_3(Ph_3PO)_2$ appears rigid on the NMR time scale with two inequivalent Ph_3PO ligands.[184]

The corresponding indenyl system, $IndUCl_3(THF)_2$, was prepared either by reaction of IndNa with UCl_4 or from Ind_3UCl and UCl_4 in the appropriate ratio. Exchange of THF with Ph_3PO produces the less soluble $IndUCl_3(THF)(Ph_3PO)$ and $IndUCl_3(Ph_3PO)_2$ adducts. The $IndUBr_3(THF)_2$, $IndUBr_3(THF)(Ph_3PO)$, $IndThCl_3(THF)_2$, and $IndThCl_3(THF)(Ph_3PO)$ compounds were prepared in an identical manner. The Ph_3PO adducts are sensitive toward disproportionation to Ind_3AnX and $AnX_4(Ph_3PO)_2$ (An = U, Th; X = Br, Cl), the Th complexes being more sensitive than the U analogues. The crystal structure of $IndUBr_3(THF)(Ph_3PO)$ shows the expected pseudooctahedral geometry with Ph_3PO trans to the η^5 indenyl system.[191,192]

The reaction of $CpUCl_3(THF)_2$ with $(C_5H_4Me)Tl$ (1 equiv) and CpTl (2 equiv) yielded, respectively, $(C_5H_4Me)_2CpUCl$ and "$Cp_2UCl_2\cdot THF$". Exchange of Cp ligands among different metal centers appears to be facile and the equilibrium of redistribution illustrated in eq 17 has been suggested.[182] Similar disproportionations are observed when starting from $(C_5Me_4Et)UCl_3(MeCONMe_2)_2$.[188] Reaction of $(C_5Me_4R)UCl_3(THF)_2$ (R = Me, Et) with cyclopentadienyl lithium or Grignard reagents gives a variety of mixed ring systems $Cp^1Cp^2UCl_2$ [Cp^1, Cp^2 = Cp*, C_5Me_4R (R = Me, Et), C_5H_4R (R = H, Me)]. NMR shows that these derivatives establish facile redistri-

$$2[Cp_3U]_2[UCl_6] + 6THF \rightleftharpoons 3CpUCl_3(THF)_2 + 3Cp_3UCl \quad (17)$$

TABLE IV. Known Group 4 Neutral Cyclopentadienyl Metal Halides

ox. state	X: F	X: Cl	X: Br	X: I
II		CpTiCl		
III		(ring)$TiCl_2$ $CpZrCl_2$ (?)		
IV	$CpTiF_3$ $(C_5H_4R)ZrF_3$ (?) $(C_5H_4R)HfF_3$ (?)	(ring)$TiCl_3$ (ring)$ZrCl_3$ (ring)$HfCl_3$	(ring)$TiBr_3$ $CpZrBr_3$	(ring)TiI_3 $CpZrI_3$

bution equilibria in solution (eq 18) and also generate variable amounts of Cp_3UCl and $CpUCl_3$ derivatives.[184]

$$\text{“}Cp^1UCl_3\text{”} + (Cp^2)^- \rightarrow Cp^1{}_2UCl_2 + Cp^1Cp^2UCl_2 + Cp^2{}_2UCl_2 \quad (18)$$

Reaction of $CpUCl_3(THF)_2$ with K[$HBpz_3$] yields the hydrotris(pyrazolyl)borato derivative, $CpUCl_2(HBpz_3)$,[181] whereas the corresponding thorium derivative does not yield an identifiable product. However, the $CpThX_2(HBpz_3)(L)_x$ (X = Cl, Br; L = $MeCONMe_2$, $Me_3CCONMe_2$; x = 1, 1.5) compounds was cleanly obtained from the corresponding amide complexes of $CpThX_3$.[193] The dihydrobis(pyrazolyl)borate uranium(IV) derivative, $CpUCl_2(H_2Bpz_2)$, has also been prepared from $CpUCl_3(THF)_2$.[193] $CpUCl_3(THF)_2$ reacts with the appropriate amount of Na(acac) to generate $CpUCl_{3-x}(acac)_x$ (x = 1, 2).[194]

Alkylation of $Cp^*AnCl_3(THF)_2$ with benzyllithium results in the tris-benzyl complex, $Cp^*An(CH_2Ph)_3$ (An = U, Th).[186] Alkylation of a THF solution of $CpUCl_3$ with 1 equiv of alkyllithium at −78 °C yields thermally unstable $CpUCl_2R$ (R = Me, Et, n-Bu). The high selectivity observed after reaction with carbonyl compounds proves formally the formation and relative low-temperature stability of the uranium alkyl complex.[195] The reaction of $CpUCl_3$ with O_2 has been investigated. It proceeds via an initial organometallic–O_2 complex, which then reacts intramolecularly or with cyclopentadiene formed by decomposition of the U compound.[196]

VIII. Titanium, Zirconium, and Hafnium

All the known monocyclopentadienyl halide complexes of group 4 metals are shown in Table IV.

A. Titanium(II)

Reduction of $CpTiCl_3$ with Li_3N in a 3:2 Ti/Li_3N molar proportion produces green $[CpTiCl]_4$ which is diamagnetic and shows only one type of Cp ^1H NMR resonance.[35,49] A compound of Ti(II) has also been detected during the stepwise electrochemical reduction of $CpTiCl_3$.[197]

B. Titanium(III)

Syntheses

The first member of this series, $CpTiCl_2$, was first prepared from Cp_2TiCl_2 and $(i\text{-}Bu)_2AlCl$[198] and suggested to have a dimeric or polymeric nature. Reduction of $CpTiX_3$ (X = Cl, Br, I) with Zn dust in THF at room temperature generates the $CpTiX_2(THF)$ compounds. These materials are thermally unstable and lose THF upon heating to yield $CpTiX_2$.[32-34] Another preparation method for the chloride compound is conproportionation between $TiCl_4$ and $Cp_2Ti(CO)_2$ in xylene. At room temperature, an immediate reaction takes place with complete loss of CO and formation of an intermediate green precipitate, to which the formulation $Cp_2Ti(\mu\text{-}Cl)_2TiCl_2$ has been assigned. After reflux, this derivative transforms into $CpTiCl_2$.[72] $Cp^*TiCl_2{\cdot}THF$ was obtained from Cp^*TiCl_3 by zinc reduction in THF.[116] More recently, $CpTiCl_2$ has also been obtained from $CpTiCl_3$ by reduction with Li_3N[35] or with $[Li\{\mu\text{-}P(SiMe_3)_2\}(THF)_2]_2$.[199] $[1,2,4\text{-}(SiMe_3)_3C_5H_2]TiCl_2(THF)$ has been obtained from $TiCl_3(THF)_3$ and $[1,2,4\text{-}(SiMe_3)_3C_5H_2]Li$.[55]

The $[Cp_2Co][(C_5H_4R)TiCl_3]$ salts are obtained by reduction of $(C_5H_4R)TiCl_3$ with Cp_2Co.[50,51,89] Contrary to an earlier report,[200] the [(ring)$TiCl_3$]$^-$ anions seem stable in solution.

Reactivity

$CpTiX_2$ forms bis-adducts, $CpTiX_2L_2$, with monodentate or bidentate (chelating) amines or phosphines, and with cyclohexylisocyanide.[34,72,201,202] Bis-adducts are also formed with alcohols and DME, whereas THF was originally reported to form only pseudotetrahedral monoadducts.[203] However, a structurally characterized form has more recently been shown to contain a mixture of mono- and bis-adducts $CpTiCl_2(THF)_n$ (n = 1, 2).[204] The $CpTiCl_2(PMe_3)_2$ and $CpTiCl_2(CN\text{-}2,6\text{-}C_6H_3Me_2)_2$ derivatives have also been prepared by reduction of $CpTiCl_3$ in the presence of the appropriate ligand, presumably through the intermediacy of $CpTiCl_2$ or its THF adduct.[205]

The chloride ligands can be abstracted with $NaBPh_4$ in a coordinating solvent, to give crystalline $[CpTi(solv)_5][BPh_4]_2$ (solv = MeCN, py).[206] They can be replaced by carboxylato groups to give $CpTi(O_2CR)_2$ by treating $CpTiCl_2$ either with RCO_2Na or with RCO_2H and amine,[207] and by dithiocarbamate groups to give $CpTi(S_2CNR_2)_2$ upon reaction with NaS_2CNR_2.[208] With hydrotripyrazolylborate, $CpTiCl(HBpz_3)$ is obtained.[209]

$CpTiCl_2$ does not form stable $CpTiR_2$ derivatives with RM (R = Me, Me_3SiCH_2; M = Li or MgCl),[202] and disproportionation products are obtained instead, but the bis-benzyl derivative, $CpTi(CH_2Ph)_2$, is stable.[116] Li-o-$C_6H_4CH_2NMe_2$ and $LiCH_2$-o-$C_6H_4NMe_2$ generate the stable mononuclear, four-legged piano-stool compounds $CpTi(C_6H_4CH_2NMe_2)_2$ and $CpTi(CH_2C_6H_4NMe_2)_2$.[210] An analogous derivative has presumably been obtained by interaction with 2 equiv of $LiCH_2PPh_2$, but attempts to isolate the material were unsuccessful.[211] $(C_5R_5)TiCl_2$ and 2 equiv of allyl Grignard afford the corresponding $(C_5R_5)Ti(C_3H_5)_2$ complex,[116] while with substituted allyl reagents, no stable Ti(III) product could be obtained. For example, 1-methylallyl yielded $CpTi(\eta^3\text{-}1\text{-}MeC_3H_4)(\eta^4\text{-}C_4H_6)$.[212] Interaction of Cp^*TiCl_2 with (enediyl)magnesium generates a paramagnetic species that is believed to be Cp^*Ti(diene) and which catalyzes a head-to-tail linear dimerization of isoprene and 2,3-dimethylbutadiene with high selectivity.[213] $CpTiCl_2$ and $Na_2C_2B_{10}H_{12}$ give a solution presumably containing the neutral $CpTi(C_2B_{10}H_{12})$ species. Reduction with zinc allows the isolation of $[CpTi(C_2B_{10}H_{12})]^-$ as the Et_4N^+ salt.[214]

$CpTiX_2$ is oxidized by aldehydes and ketones, R^1R^2CO, to give isomeric mixtures of the pinacolate complexes $CpCl_2TiOCR^1R^2CR^1R^2OTiCl_2Cp$[215] and it undergoes oxidative addition of compounds containing a S–S linkage or peroxides to give $CpTiCl_2(ER)$ (E = S, O) or $CpTiX_2(S_2CNR_2)$ products.[87,216] Oxidation also results upon interaction of $CpTiCl_2$ with diphenyldiazomethane to afford $[CpTiCl_2]_2(\mu\text{-}NN{=}CPh_2)$ which, upon warming, eliminates $CpTiCl_3$ to afford $[CpTiCl(\mu\text{-}\sigma{:}\eta\text{-}NNCPh_2)]_2$, or with azobenzene to yield $CpTiCl_3$ and $[CpTiCl]_2(\mu\text{-}PhNNPh)(\mu\text{-}NPh)$. The first step of the latter transformation is proposed to be the formation of an azo compound, $[CpTiCl(\mu\text{-}PhN{=}NPh)]_2$, on the basis of the formation of a stable derivative of such stoichiometry when azobenzene was replaced with benzo[*c*]cinnoline.[204,217] $CpTiCl_2$ also acts as deoxygenating agent toward nitrosobenzene to generate mainly azo- and azoxybenzene. The nature of the Ti product was not specified.[218]

$CpTiCl_2$ reacts with sources of chlorine radicals to give $CpTiCl_3$.[69,219] Mild oxidizing agents are also sufficient to cause this transformation, for instance HCl[55,220] or $PbCl_2$.[221] From the reaction with Cp*Li, followed by treatment with HCl, the mixed-ring systems $CpCp^*TiCl_2$ have been obtained.[222]

Treatment of $CpTiCl_2$, generated in situ by photolysis of Cp_2TiCl_2, with 1,2-diketones (biacetyl, substituted 1,2-benzoquinone) produces 4- or 5-coordinated Ti(IV) addition products with an unpaired electron on the ligand system.[70]

C. Zirconium(III) and Hafnium(III)

The reaction between $ZrCl_3$ and CpNa in THF at −20 °C has been reported. Both the frozen solution and the powder obtained after sublimation of the residue exhibit an EPR spectrum with a two-component g tensor which has been assigned to $CpZrCl_2$ on the basis of its similarity to the spectrum of $CpTiCl_2$. However, the compound could not be isolated in a pure state and purification attempts led only to Cp_2ZrCl_2.[223]

EPR and spin-trapping techniques show that the photolysis of substituted zirconocene and hafnocene dichloride complexes, $(C_5H_4R)_2MCl_2$ (M = Zr, Hf) proceeds with a mechanism identical with that of the corresponding titanocene dichloride complexes (see section VIII.D). That is, the primary photoprocess is homolytic cleavage of the $M\text{–}(C_5H_4R)$ bond. Contrary to the titanium case, however, the $(C_5H_4R)MCl_2$ zirconium and hafnium product are not stable.[224]

D. Titanium(IV)

The chemistry of $CpTiCl_3$ and similar compounds up to the late 1970's has been reviewed elsewhere.[225]

Syntheses

$CpTiCl_3$ is the first of the compounds covered by this review article to have been described in the literature and it has since been the most widely used. It was first prepared by Gorsich by two independent methods.[64,65,226] The first is the redistribution of $TiCl_4$ and Cp_2TiCl_2 either with or without solvent, although the use of a solvent and a slight excess of $TiCl_4$ are beneficial to the yield and the ease of product workup. The second method involves chlorination of Cp_2TiCl_2. Prolonged exposure of the mixture to chlorine results in cleavage of the second Cp ring with formation of $TiCl_4$. The corresponding bromination of Cp_2TiCl_2 gives $CpTiBrCl_2$.[64,65,226b] Slight variations of the same procedures, as well as their extension to substituted derivatives, have later been reported by other authors.[18,227–231] More recently, it has been found that Cp_2TiCl_2 gives $CpTiCl_3$ also by treatment with ClF. This process is thermodynamically more favored than the expected fluorination of the titanium center.[232] Irradiation of Cp_2TiBr_2 in chloroform is believed to generate $CpTiClBr_2$.[69]

Other methods that have been used for the preparation of $CpTiCl_3$ include treatment of $TiCl_4$ with Cp_2Mg[18,233] or CpNa, although the latter tends to proceed to the formation of the bis-Cp derivative.[228] $(C_5Me_4Et)TiCl_3$ and $[(MeO)_3Si(CH_2)_3C_5H_4]TiCl_3$ have been obtained from $TiCl_4$ and $(C_5Me_4Et)Li$[234] and $[(MeO)_3Si(CH_2)_3C_5H_4]Na$,[235] respectively. $[1,2,4\text{-}(SiMe_3)_3C_5H_2]Li$ and $TiCl_4$, however, fail to give any tractable material. The desired $[1,2,4\text{-}(SiMe_3)_3C_5H_2]TiCl_3$ compound was prepared by an indirect route from $[1,2,4\text{-}(SiMe_3)_3C_5H_2]TiCl_2(THF)$ and HCl.[55] The Cp_2Mg route also allows the preparation of the tribromide and triiodide systems from $TiBr_4$ or TiI_4.[233] A convenient method for preparing $CpTiBr_3$ from $CpTiCl_3$ and BBr_3 has been recently described.[236] Another method involves treatment of $CpTi(OR)_3$ with the appropriate CH_3COX (X = F, Cl, Br, I).[237,238] This method has also been applied to the synthesis of Cp^*TiI_3.[213] The patent literature described the formation of $CpTiCl_3$ from $CpTiCl(OBu)_2$ and chlorine.[239]

The best and most general synthetic method, however, appears to be the interaction of TiX_4 (X = Cl, Br, I) with the properly substituted (trimethylsilyl)- or (trimethylstannyl)cyclopentadiene. Compounds prepared in this manner are $(C_5R_5)TiX_3$ and $(C_5H_4R)TiX_3$ (X = Cl, Br, I) including exotic ones with R = $SiMe_3$, BCl_2, BBr_2, $B(OEt)_2$, $AsMe_2$, $SbMe_2$, $GeMe_3$, $SnMe_3$, $CH_2CH_2AsPh_2$, or $CH_2CH_2As(Ph)CH_2CH_2AsPh_2$.[4c,213,230,240–244]

Cp^*TiCl_3 was first serendipitously obtained by heating $TiCl_4$ with various butenes at 300 °C,[245a] and subsequently prepared from $TiCl_4$ and Cp*Li.[245b] It was also obtained as a byproduct during the synthesis of $Cp^*_2TiCl_2$ from $TiCl_3$ and Cp*Na followed by treatment with aqueous HCl.[246] A modification of this method that utilizes $TiCl_3(THF)_3$ and Cp*Li followed by oxidation with a HCl–ether–pentane solution gave a 70% yield of product.[220] The same general procedure has also been utilized for the preparation of $(C_5Me_4\text{-}i\text{-}Pr)TiCl_3$.[247]

Reactivity

Lewis Acidity. $CpTiCl_3$ has a reduced Lewis acid character with respect to $TiCl_4$, as evident from the apparent lack of reaction with py, PPh_3, SMe_2, or $AsMe_3$.[248,249] Adducts in a 1:1 ratio with bidentate ligands, $CpTiCl_3L_2$ [L_2 = bipy, phen, *o*-$C_6H_4(AsMe_2)_2$, dmpe, aprotic Schiff base] are stable. There is, however, no reaction with dppe, 2,5-dithiahexane, or DME.[67,123,240,249,250,251] THF adducts of $CpTiX_3$ (X = Br, I) are also known[115] (see also section V.A).

Hydrolysis and Other Oxygen Scavenging Reactions. Ti(IV) in $CpTiCl_3$ has a high affinity for oxygen ligands. It is readily hydrolyzed to $[CpTiCl_2]_2O$ with small amounts of water and to $[CpTiCl(\mu\text{-}O)]_4$ with larger amounts.[65,252-257] $[(C_5H_4Me)TiCl(\mu\text{-}O)]_4$ has been analogously prepared from $(C_5H_4Me)TiCl_3$.[258] The aqueous chemistry of $CpTiCl_3$ has been the subject of a recent review article.[259] $CpTiCl_3$ engages in an oxygen scrambling reaction with $Cp^*Re(O)R_2$ (R = Me, Et, *i*-Pr, CH_2CMe_3, CH_2Ph) or $Cp^*Re(O)(RCCR')$, resulting in the formation of $Cp^*ReCl_2R_2$[30,260] or $Cp^*ReCl_2(RCCR')$,[261] respectively, and, presumably, $[CpTiCl(O)]_4$. The rhenium dialkyl product cannot be obtained by the more logical alkylation of Cp^*ReCl_4. $Cp^*Re(O)(CH_2Ph)_2$ and $CpTiX_3$ (X = Cl, Br), on the other hand, produce the alkylidyne-bridged dimer, $[Cp^*ReX]_2(\mu\text{-}X)(\mu\text{-}CPh)$.[262] The redistribution reaction between $CpTiCl_3$ and $[CpTiOCl]_4$ affords $[CpTiCl_2]_2O$, whereas $CpTiCl_3$ and $CpTiCl(OCMe_2CMe_2O)$ produce $CpCl_2TiOCMe_2CMe_2OTiCl_2Cp$.[263] The $CpTiCl_3/LiAlH_4$ system is an effective reagent for deoxygenation of substituted 7-oxabicyclo[2.2.1]hepta-2,5-diene systems to the corresponding substituted benzenes.[264]

Cp^*TiCl_3 is stable with respect to moisture for brief periods both as a solid and in solution. Over longer periods decomposition occurs to generate mixtures of different products. In aqueous alkaline solutions, the formation of a yellow solid polymer compound of formula $[Cp^*TiO(OH)]_n$ ($n = 4$–6) has been reported, whereas partial hydrolysis leads to $(Cp^*TiClO)_n$.[245a] More recent work has shown that, in toluene, the base-assisted hydrolysis of Cp^*TiX_3 (X = Cl, Br, I) affords different products depending on the Ti/H_2O ratio and the nature of X: with a Ti/H_2O ratio of 2:1, the $[Cp^*TiX_2]_2(\mu\text{-}O)$ derivatives are obtained; when the Ti/H_2O molar ratio is lowered to 1:1, the $[Cp^*TiX(\mu\text{-}O)]_n$ derivatives (X = Cl, $n = 3$; X = Br, $n = 4$) are isolated. These reactions are faster in the order I < Br < Cl.[128] The adamantane-like $(Cp^*Ti)_4O_6$ molecule is obtained by using a 3/2 Ti/H_2O molar ratio in toluene, whereas hydrolysis in refluxing acetone yields only $[Cp^*TiCl(\mu\text{-}O)]_3$.[128,265,266] In the presence of NEt_3, the trichloride compound with the sterically hindered 1,2,4-$C_5H_2(SiMe_3)_3$ (Si_3Cp) ring yields the μ-oxo complex $[(Si_3Cp)TiCl_2]_2(\mu\text{-}O)$ with 0.5 equiv of water, the bis-μ-oxo complex $[(Si_3Cp)TiCl]_2(\mu\text{-}O)_2$ with 1 equiv, and the $[(Si_3Cp)Ti]_4(\mu\text{-}O)_6$ compound with an excess.[267]

Ligand Exchange. A general method for the replacement of halide ligands is interaction with a proton-containing substrate in the presence of a base, typically an amine. Products obtained in this way are the amido derivatives $CpTiCl_2(NHR)\cdot 4NH_2R$ (R = H, Me),[248] the thiolates $(C_5H_4R)TiCl_2(SR')$ and $CpTi(SPh)_3$,[268,269] the alcoholates or phenolates $(C_5R_5)TiCl_x(OR')_{3-x}$,[238,270-275] the Schiff base derivatives, $CpTiCl(SB)$,[276] the carboxilates $CpTi(O_2CR)Cl_2$ and $CpTi(O_2CR)_2Cl$,[277] the substituted acetylacetonato (acac) complexes $CpTiCl(acac)_2$,[278] and the hydrazido complexes $CpTiCl_2(NR^1NR^2R^3)$.[144] The tris-alkoxide compounds can be used for the preparation of other trihalide derivatives by the interaction with the appropriate AcX substrate; the direct exchange of chloride for other halide ions in $(ring)TiCl_3$ is a difficult reaction.[238,279] Mixed alkoxo–halide derivatives such as $CpTi(OMe)Cl_2$ have also been obtained from $(C_5H_4R)TiX_3$ and alcohol in the absence of base.[226a]

Certain negatively charged nucleophiles replace the chloride ligands directly. Products obtained by this route are $CpTi(NCS)_3$,[269] $CpTiCl_2(HBpz_3)$,[209] xanthates $CpTi(S_2COR)Cl_2$ and $CpTi(S_2COR)_2Cl$,[280] dithiocarbamato complexes $CpTi(S_2CNHR)Cl_2$ and $CpTi(S_2CNHR)_2Cl$,[281,282] $[CpTiCl(\mu\text{-}NNR_2)]_2$, $(CpTiCl_2)_2(\mu\text{-}RNNR)$,[283] $(C_5H_4R)TiCl_x(SR')_{3-x}$ ($x = 0, 1, 2$),[268] $CpTiCl(1,2\text{-}Se_2C_6H_4)$,[284] and $CpTiCl(MBP)$ [MBP = 2,2'-methylenebis(6-*tert*-butyl-4-methylphenolato) dianion].[285] With $(LiS)_2C_6H_3\text{-}4\text{-}CH_3$ in stoichiometric amount, $CpTiCl(S_2C_6H_3\text{-}4\text{-}CH_3)$ is obtained, whereas an excess gives $[CpTi(S_2C_6H_3\text{-}4\text{-}CH_3)_2]^-$.[286] $CpTiBr_3$ and 3 equiv of Na(SMe) or Li(SeMe) give the corresponding $CpTi(EMe)_3$ (E = S, Se), whereas the reaction with Na(TeMe) gives Te_2Me_2 as the only Te containing product.[236] The interaction with NH_4S_x in the presence of PPh_4Cl produces the $[CpTi(S_2)(S_5)]^-$ anion.[287] From $(C_5H_4Me)TiCl_3$ and Li_2S_2, a simple substitution product could not be isolated. However, subsequent exposure to molecular oxygen yields the clusters $(C_5H_4Me)_4Ti_4S_8O$ (major) and $(C_5H_4Me)_4Ti_4S_8O_2$ (minor).[288] $CpTiCl_3$ reacts with the lithiated triaminosilane $PhSi(NLiSiMe_3)_3$ at low temperature to form $CpTiCl[(NSiMe_3)_2Si(Ph)N(Li)SiMe_3]$.[289] With $NaCo(CO)_4$, the $CpTi[Co(CO)_4][OCCo_3(CO)_9]_2$ molecule has been obtained.[290]

Mixed-ring systems, $(ring^1)(ring^2)TiCl_2$, have been obtained from the interaction of $(ring^1)TiCl_3$ with various sources of $(ring^2)^-$.[6,238,247,291-308] In these reactions the cyclopentadienide anion can be functionalized with an olefinic group,[309,310] a chloride,[311] a carbomethoxy group,[312] or a phosphine moiety[313-315] or be covalently bound to a polymer support.[316] Heteronuclear complexes with bis(cyclopentadienyl)methane bridges, e.g. $(CO)_3Mn(\mu\text{-}C_5H_4\text{-}C_5H_4)TiCl_2Cp$, have also been prepared in this manner,[317] as well as pyrrolyl, $(ring)(\eta^5\text{-}C_4H_4N)TiCl_2$,[304,307,318] and phospholyl, $Cp(\eta^5\text{-}PC_4Me_4)TiCl_2$ and $Cp(\eta^5\text{-}3,4\text{-}PC_4H_2Me_2)TiCl_2$,[319] derivatives.

The trialkyl or triaryl derivatives $CpTiMe_3$ and Cp^*TiR_3 (R = Me, CH_2SiMe_3, Ph, C_6F_5, CH_2Ph) are obtained by treating the appropriate trichloride precursor with 3 equiv of lithium or Grignard reagents.[219,244,320-323] $[1,2,4\text{-}(SiMe_3)_3C_5H_2]TiMe_3$ has been prepared in the same manner.[55] By the use of only 2 equiv of alkyllithium or Grignard, the dialkyl derivatives Cp^*TiClR_2 have been prepared[323,324] while treatment with ZnR_2 (R = Me, Et), even in large excess, yields only $CpTiRCl_2$.[325] The latter derivative (R = Me) is also obtained, although less conveniently, by using 1 equiv of MeLi or MeMgCl.[324] The compounds $(C_5R_5)TiFc_xCl_{3-x}$ [Fc = ferrocenyl, $CpFe(\eta^5\text{-}C_5H_4)$; R = H, $x = 3$; R = Me, $x = 2$] are obtained from $(C_5R_5)TiCl_3$ and FcLi.[326] The reaction of Cp^*TiCl_3 with $[o\text{-}C_6H_4(CH_2)_2]Mg(THF)_2$ in a 2:3 molar ratio yields the dinuclear compound $\{Cp^*Ti[o\text{-}(CH_2)_2C_6H_4]\}_2\{\mu\text{-}[o\text{-}(CH_2)_2C_6H_4]\}$ whose structure has been determined.[323] In the presence of N_2, $CpTiCl_3$ reacts with excess PhLi to give, after hydrolysis, small amounts of aniline.[327]

$(C_5R_5)TiCl_3$ compounds react with 3 equiv of 1-methylallyl- or 2-butenylmagnesium bromide to give low yields of the allyl–butadiene complexes, $(C_5R_5)Ti(1\text{-}MeC_3H_4)(C_4H_6)$. The reaction probably proceeds through the tris-allyl complexes, which decompose with elimination of *trans*-2-butene.[212,220] Cp^*TiCl_3 and (2,3-dimethyl-2-butene-1,4-diyl)$Mg\cdot 2THF$ yield the corresponding $Cp^*TiCl(diene)$ in moderate yields where the diene presumably has a η^3,σ configuration.[328] Other $Cp^*TiX(diene)$ complexes have been analogously obtained from the reaction of Cp^*TiX_3 (X = Cl, Br, I) with (2-butene-1,4-diyl)magnesium and homologues or with 2 equiv of *i*-BuMgBr as reducing agent in the presence of the appropriate conjugated diene.[213,329] An analogous derivative, the mononuclear *o*-xylidene complex $Cp^*TiCl[o\text{-}(CH_2)_2C_6H_4]$, is obtained from Cp^*TiCl_3 and $[o\text{-}(CH_2)_2C_6H_4]Mg(THF)_2$ in toluene. When the latter reaction is conducted in THF, however, a different product is obtained, shown by X-ray crystallography to be $[Cp^*Ti(\mu\text{-}Cl)]_2[o\text{-}(CH_2)_2C_6H_4]$ where the exocyclic 1,3-diene system binds one titanium center and the endocyclic diene system binds the other one.[330]

Reaction with trimethylsilyl-substituted substrates also results in chloride replacement with elimination of Me_3SiCl. Derivatives obtained in this manner are $CpTiCl_2(N{=}NPh)$, $(C_5H_4R)TiCl_2(NPPh_3)$,[331] $CpTiCl_2(N_3)$,[332,333] $CpTiCl_2(NHR)$ which upon heating eliminates HCl and gives $[CpTiCl(\mu\text{-}NR)]_2$,[334,335] $CpTiCl_2(NR^1NR^2R^3)$,[143,144,281,336] $(CpTiCl_2)_2(\mu\text{-}MeNNMe)$,[283] $CpTiCl_2(N{=}P(Ph)_2CH_2PPh_2)$,[337] $CpTiCl_2(ONMe_2)$,[281] and $CpTiCl_2(N{=}PPh_2{-}N{=}S(O)Me_2)$.[338] On the other hand, $CpTiCl_3$ does not react with $(Me_3Si)_2NNHC(S)SMe$ to afford either mononuclear or bridged dinuclear derivative of the hydrazido(2−) ligand.[339] The reaction of $CpTiCl_3$ with $Me_3SiNHNHSiMe_3$ does not yield the expected $(CpTiCl_2)_2(\mu\text{-}NHNH)$, but rather $CpTiCl_2(THF)$ and N_2 plus NH_3. A completely analogous reaction occurs with $LiNHNH_2$.[340] Silylated quadridentate Schiff bases give derivatives of formula CpTiCl(SB).[341,342] Treatment of $CpTiCl_3$ with 2 equiv of $Se(SiMe_3)_2$ in THF affords the oxo-centered cluster $(CpTi)_4Se_7O$ containing a tetrahedral arrangement of CpTi units with one edge-bridging Se, two face-capping Se, and two face-capping Se_2 units.[343] On the other hand, the reaction of $(C_5H_4Me)TiCl_3$ with 2 equiv of $E(SiMe_3)_2$ is accompanied by partial metal reduction to generate the hexa-capped trigonal bipyramidal $[(C_5H_4Me)Ti]_5(\mu_3\text{-}E)_6$ (E = Se, Te) clusters.[344] Trimethylstannyl derivatives seem to operate in the same fashion and increase the selectivity of substitution when the ligand involved is very reactive. This is the case for the $CpTi(NSO)_3$ molecule, which can be assembled from $CpTiCl_3$ and Me_3SnNSO, whereas it does not form when K(NSO) is used.[345]

The replacement of chloride ligands can also be aided by the use of silver salt. Tris-carboxilate derivatives, $CpTi(O_2CR)_3$, have been prepared in this manner.[346] The interaction of $CpTiCl_3$ with 3 equiv of $AgEF_6$ (E = As, Sb) in liquid SO_2 affords deep red solutions of the corresponding $[CpTi^{3+}(EF_6)_3\cdot solv]$ species, which slowly decompose in solution at −50 °C and are nonexistent in the solid state. They can be regarded as Lewis acid (EF_5) adducts of $CpTiF_3$.[142] Dissolution of $CpTiCl_3$ in MeCN followed by treatment with $AgNO_3$ affords a solution of $[CpTi(MeCN)_n](NO_3)_3$ which, upon treatment with $(Bu_4N)_7SiW_9V_3O_{40}$, affords pure $(Bu_4N)_4[CpTi\cdot SiW_9V_3O_{40}]$ in which the CpTi moiety is solidly anchored on the surface of the polyoxometalate.[347] Analogous CpTi-containing polyoxometalates, $[n\text{-}Bu_4N]_4[CpTiPW_{11}O_{39}]$,[348] $[Me_3NH]_5[CpTiW_{11}SiO_{39}]\cdot H_2O$ and $[Me_3NH]_4K[CpTiMo_{11}SiO_{39}]\cdot H_2O$,[349] $K_7Na_2[(CpTiOH_2)_3W_{18}P_2O_{68}]\cdot 15H_2O$,[350] and $K_7[CpTiP_2W_{17}O_{61}]$[351] have been prepared from $CpTiCl_3$ and aqueous solutions of $[H_3PW_{11}O_{39}]^{4-}$, $W_{11}SiO_{39}{}^{8-}$, $Mo_{12}SiO_{40}{}^{4-}$, $HW_9PO_{34}{}^{8-}$, or $P_2W_{17}O_{61}{}^{10-}$, respectively.

Spontaneous HCl elimination occurs during the reaction of $CpTiCl_3$ with a number of protic substances in refluxing methylene chloride. Heterocyclic thioketones (Htk) form $CpTi(tk)_xCl_{3-x}$ products,[352–354] 2,6-diacetylpyridine dioxime (LH) gives $CpTiL_xCl_{3-x}$ (x = 1, 2),[521] and a number of Schiff bases HSB or H_2SB' give $CpTi(SB)Cl_2$, $CpTi(SB)_2Cl$, or $CpTi(SB')Cl$ derivatives.[250,251,356]

Ligand redistributions between $(ring)TiX_3$ (X = halogen) and $(ring)TiY_3$ (Y = alkoxide) to produce $(ring)TiX_nY_{3-n}$ are facile reactions.[275,357,358] A ligand redistribution reaction also occurs between Cp^*TiCl_3 and the ketene complex $Cp_2Ti(\eta^2\text{-}OCCH_2)$, to produce $Cp_2ClTiOC({=}CH_2)TiCl_2Cp^*$.[359] $CpTiCl_3$ ring opens 1,2-propylene oxide to form a $CpTi(OC_3H_6Cl)_3$ material in which the alkoxide groups are derived from ring opening at the α and β positions in a 73:27 relative proportion.[360]

Redox. Reduction of $CpTiCl_3$ with Zn dust affords the Ti(III) material, $CpTiCl_2$, isolated in 70% yield.[34] An alternative procedure using Li_3N as the reducing agent has been described. Further reduction using Li_3N in a higher proportion (3:2 Ti:Li_3N) produces diamagnetic $[CpTiCl]_4$. Yet higher proportions of Li_3N produce nitrogen-containing, incompletely characterized materials. The presence of phosphines does not change the course of these reactions.[35,49] Reduction of $CpTiCl_3$ to $CpTiCl_2(THF)$ has also been accomplished with the lithium compound $[Li\{\mu\text{-}P(SiMe_3)_2\}(THF)_2]_2$.[199] $CpTiCl_3$ can be reduced polarographically in DMF in three successive one-electron steps. The formation of the intermediate $CpTiCl_2$ and CpTiCl, and the [CpTi] final product were proposed. Analogous behavior was observed for Cp^*TiCl_3, the electron donation from the methyl groups shifting all three reduction potentials to more negative values.[197] The cyclic voltammogram of $(C_5H_4R)TiCl_3$ in CH_2Cl_2 shows a reversible reduction wave at −355 V vs Ag/AgCl (R = Me) and the chemical reduction by Cp_2Co yields the stable $[Cp_2Co][C_5H_4R)TiCl_3]$ salts.[50,51,89]

The interaction between $(ring)TiCl_3$ and Et_2AlCl has been investigated by EPR. Ti(III) species are formed in a two-step process. The first step has been interpreted as the formation of a Ti(IV) intermediate of the type $(ring)EtTi[(\mu\text{-}Cl)_2AlEt_2][(\mu\text{-}Cl)_2AlEtCl]$, which is followed by loss of an ethyl radical with reduction to Ti(III). In the presence of excess Et_2AlCl, a mixture of $(ring)TiAl_2Cl_{8-x}Et_x$ (x = 0–4) compounds is eventually obtained. Values of the rate constant for the reduction process decrease with increasing number of methyl groups on the cyclopentadienyl ring.[361] Similar EPR studies have been carried out on the interaction between $(C_5R_5)TiCl_3$ and methylaluminoxane, $(MeAlO)_n$. Both the Cp and the Cp* systems show the development of two different doublet resonances, assigned to aluminoxane-bound (through chloride and methyl bridges) CpTi–hydride species. In addition, the Cp* system develops a sextet signal over long reaction times, which is assigned to a $C_5Me_3(CH_2)_2Ti(H)Cl$ species. All these species exchange the spin-active hydrogen for deuterium by treatment with D_2.[362]

The interaction of $CpTiCl_3$ with $LiAlH_4$ has been studied calorimetrically and by EPR. Products with the following stoichiometry are formed in a sequential fashion upon increasing the Al:Ti ratio: $\{2CpTiCl_2 \cdot AlH_2Cl\}$, $CpTiCl(\mu\text{-}H)_2AlHCl$, $[Cp(Cl)TiH_2]_2Al_2H_3Cl$, and $CpTiCl(\mu\text{-}H)_2AlH_2$. With further excess of $LiAlH_4$ the exceedingly unstable $CpTi(AlH_4)_2$ is obtained.[363]

Other Ti(III) products are the $CpTiCl_2L_2$ complexes (L = PMe_3 or 2,6-$Me_2C_6H_3N$), obtained by reduction of $CpTiCl_3$ with magnesium in the presence of the appropriate L.[205] Curiously, no reduction occurs with sodium naphthalenide in the presence of dmpe, the product of this reaction being the Ti(IV) adduct, $CpTiCl_3$(dmpe).[123]

By reduction of $(C_5R_5)TiCl_3$ with Mg in the presence of cycloheptatriene, the $Cp^*Ti(\eta^7\text{-}C_7H_7)$ complex is obtained, while the analogous reduction in the presence of COT or direct interaction with K_2COT gives the paramagnetic $(C_5R_5)Ti(COT)$ derivatives.[148,364] Reaction with the sodium salt of the carborane dianion, $Na_2C_2B_{10}H_{12}$, presumably leads to the neutral Ti(III) mixed sandwich $CpTi(C_2B_{10}H_{12})$ compound. Subsequent reduction with zinc allows the isolation of $[CpTi(C_2B_{10}H_{12})]^-$ as the Et_4N^+ salt.[214]

$CpTiCl_3$ reacts with sodium naphthalenide at low temperature to generate an uncharacterized, thermally unstable intermediate that functions as weakly solvated monocyclopentadienyltitanate. Interaction of this with CO leads to the formation of salts of the $[CpTi(CO)_4]^-$ anion.[365] Identical procedures afford $[Cp^*Ti(CO)_4]^-$ from Cp^*TiCl_3.[366]

E. Zirconium(IV)[367]

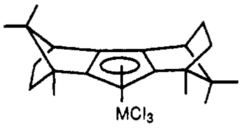
Synthesis

The most popular route for the preparation of $CpZrCl_3$ utilizes a radical-induced Zr–Cp bond cleavage in Cp_2ZrCl_2 and replacement with chlorine under photolytic conditions. Radical chlorine sources such as Me_3CCl and Cl_2 have been used.[66,67,368] This method is not a clean route to the substituted analogues.[117] The use of bromine leads to the formation of $CpZrBrCl_2$.[226b] The transmetalation reaction of CpNa and $ZrCl_4$, even at low temperature and with slow addition to an excess of the zirconium compound, leads to the formation of Cp_2ZrCl_2 as the major product.[67] However, polymer-attached lithium cyclopentadienide reacts with $ZrCl_4$ to produce polymer-bound $CpZrCl_3$.[369] The use of Cp_2Mg as Cp source has also been described[18] but the product decomposes during the necessary sublimation step.

Although the use of $CpSiMe_3$ as a Cp source in analogy to the preparation of $CpTiCl_3$ from $TiCl_4$ has been claimed to be a successful method for preparing $CpZrCl_3$,[4c] partial polymerization of the $CpSiMe_3$ was found to occur with concomitant formation of Cp_2ZrCl_2 as well as intractable side products. This difference of behavior has been attributed to the heterogeneous reaction conditions in the zirconium case. Attempts to utilize soluble complexes of the type $ZrCl_4(OR_2)_2$ gave no appreciable reaction. However, the bis-SMe_2 complex, $ZrCl_4(SMe_2)_2$, reacts rapidly leading to the formation of $CpZrCl_3(SMe_2)_2$ which could not be isolated due to the lability of the SMe_2 ligands but it could be transformed to the DME adduct in 69–74% yield.[19]

The use of thallium reagents and coordinating solvents leads to the satisfactory synthesis of solvent–adducts. $ZrCl_4(THF)_2$ and $(C_5H_4Me)Tl$ in toluene at 0 °C afford the $(C_5H_4Me)ZrCl_3(THF)_2$ derivative,[117] while $ZrCl_4$ and CpTl in DME at 0 °C afford $CpZrCl_3$(DME).[67] Other derivatives have also been obtained by this method.[370]

The Cp^*ZrCl_3 compound has been prepared from $ZrCl_4$ and Cp^*Li in a variety of solvents. This reaction does not seem to suffer the limitations found for the synthesis of the corresponding Cp system, in that a second Cp* ring does not easily bind the zirconium center and the product is obtained free from $Cp^*_2ZrCl_2$ impurities. Furthermore, the product does not decompose upon sublimation. When the solvent has donor properties, adducts are isolated from solution. Only weakly basic ether and bulky triethylamine could be completely removed by sublimation.[118,220,371] By the same method, the optically active system illustrated in XIV, which has proven effective in asymmetric Lewis acid catalysis, has also been prepared.[372] The use of Cp^*SiMe_3 simplifies the separation procedure, since the $SiMe_3Cl$ byproduct is easily removed under reduced pressure together with the reaction solvent.[243]



(M = Zr, Hf)

XIV

Bromide and iodide compounds have only been briefly described. $CpZrX_3$ (X = Br, I) have been prepared from the corresponding ZrX_4 and Cp_2Mg or, in low yield, from ZrX_3 and CpH vapors.[18] $(C_8H_{17}C_5H_4)ZrF_3$ has been reported in the patent literature.[226c]

Reactivity

Ligand Adducts. $CpZrCl_3$ is able to coordinate additional neutral hard ligands.[66,117,129] $CpZrCl_3(THF)_2$ exchanges rapidly the THF ligands in solution[117] and $CpZrCl_3$(DME) analogously exchanges the DME ligand, whereas the corresponding $CpTiCl_3$(tmeda) is stereochemically rigid at room temperature.[67] $CpZrCl_3(py)_2$ becomes rigid at −45 °C.[66] Cp^*ZrCl_3 also forms adducts with amines and ethers, but not with "softer" ligands such as PPh_3 or dppe.[118] The mono-adduct $Cp^*ZrCl_3(PMe_3)$ has been reported, although this has been prepared by a method other than the direct interaction between Cp^*ZrCl_3 and the phosphine.[373]

Hydrolysis. Base-assisted hydrolysis of Cp^*ZrCl_3 gives oxo-centered trinuclear complexes as opposed to titanium which forms complexes where oxygen bridges two metal atoms (vide supra). When an excess of water is used, the compound $(Cp^*ZrCl)_3(\mu_3\text{-}O)(\mu_3\text{-}OH)(\mu_2\text{-}OH)_3$ is isolated, whereas with a small amount of water the product is the corresponding molecule with the capping OH ligand replaced by a capping Cl ligand.[130,374] A product of an even earlier stage of hydrolysis, $(Cp^*ZrCl)_3(\mu\text{-}Cl)_4(\mu^3\text{-}O)$, has been obtained upon controlled hydrolysis with the stoichiometric amount of water, whereas the reaction with wet lithium hydroxide affords the dinuclear bis-hydroxide-bridged species, $[Cp^*ZrCl_2(H_2O)(\mu\text{-}OH)]_2$.[131] A bis-water adduct has been obtained by reacting $CpZrCl_3$ with 15-crown-5 in the presence of water. Presumably, the hydrogen bonding to the crown molecule stabilizes the coordinative mode and does not allow the hydrolytic reaction to take place.[129]

Ligand Exchange. The substitution chemistry of cyclopentadienyl zirconium trihalide derivatives has been much less investigated than that of the corresponding titanium systems, but the reactivity patterns so far reported are rather similar for the two metals. The reaction of $(C_5R_5)ZrCl_3$ or $IndZrCl_3$ with sources of substituted cyclopentadienyl or other similar anions (e.g. pyrrolyl) provides an entry into mixed-ring systems, $(C_5R_5)(ring)ZrCl_2$ and $Ind(ring)ZrCl_2$.[118,122,297,299,301,304,368,370,375–378] Metathesis of $Li_2[X(C_5H_4)_2]$ with 2 equiv of $CpZrCl_3{\cdot}2THF$ or Cp^*ZrCl_3 leads to the dinuclear mixed-ring complexes $[X(C_5H_4)_2][(C_5R_5)ZrCl_2]_2$ ($X = CH_2$, $SiMe_2$).[379]

$CpZrCl_3$ reacts with the stoichiometric amount of $(LiS)_2C_6H_3$-4-CH_3 to give $CpZrCl(S_2C_6H_3$-4-$CH_3)$ and with an excess of the same reagent to give the anion $[CpZr(S_2C_6H_3$-4-$CH_3)_2]^-$.[286] The reaction between Cp^*ZrCl_3 and 1 equiv of $(THF)_3LiE(SiMe_3)_3$ ($E = Si$, Ge) affords the corresponding $Cp^*ZrCl_2[E(SiMe_3)_3]$ derivatives.[380] $(C_5R_5)ZrCl_3$ and $R'_2NCS_2^-$ ($R' = Me$, Et) yield the 18-electron $Cp^*Zr(S_2CNR'_2)_3$ with a pentagonal-bipyramidal geometry.[381]

Spontaneous elimination of HCl occurs between $CpZrCl_3$ and indene to give the mixed-ring $CpIndZrCl_2$,[382] between $(C_5H_4R)ZrX_3$ and alcohols to give mixed halo–alkoxo derivatives,[226a] and between Cp^*ZrCl_3 and the polyhedral oligosilsesquioxane $(SiR)_7(\mu\text{-}O)_8(OH)_3$ to afford $Cp^*Zr(\mu\text{-}O)_3[(SiR)_7(\mu\text{-}O)_8]$.[383] The hydrazido derivative $CpZrCl_2(NMeNMe_2)$ has been prepared from $CpZrCl_3$ and $Me_3SiNMeNMe_2$.[144]

Cp^*ZrCl_3 can be alkylated by the appropriate amount of R_2Mg or RMgX to give $Cp^*ZrR_xCl_{3-x}$ (R = Me, Ph, $PhCH_2$, Np; x = 1, 2, or 3).[118,371] The crystalline $Cp^*ZrNpCl_2(PMe_3)$ derivative was obtained when carrying out the alkylation in the presence of PMe_3. $CpZrCl_3$ and aryllithium reagents (aryl = Ph, p-$C_6H_4CH_3$, and m-$C_6H_4CH_3$) yield the tris(aryl) derivatives, $CpZr(aryl)_3$, which easily form adducts with donor–solvent molecules.[66] $CpZrFc_3$ (Fc = ferrocenyl) has been analogously obtained by using FcLi.[326] With an excess of $Me_2N(CH_2)_3MgCl$, only the bis-substituted $Cp^*ZrCl[(CH_2)_3NMe_2]_2$ product is obtained. Conproportionation of this with Cp^*ZrCl_3 gives the monosubstituted material, $Cp^*ZrCl_2[(CH_2)_3NMe_2]$.[373]

Cp^*ZrCl_3 and 3 equiv of 2-butenylmagnesium bromide yield the allyl–butadiene complex $Cp^*Zr(\eta^3\text{-}C_4H_7)(\eta^4\text{-}C_4H_6)$,[220] whereas $CpZrCl_3$ and allyl Grignard afford unstable $CpZr(\eta^1\text{-allyl})(\eta^3\text{-allyl})_2$,[384–386] which undergoes ligand exchange with $CpZrCl_3$ to produce $CpZrCl_2(allyl)$.[386–388] Cp^*ZrCl_3 and substituted allylmagnesium bromide afford $Cp^*Zr(allyl)Br_2$ (allyl = 1,2,3- or 1,1,2-trimethylallyl) in low yields.[389]

Reduction of Cp^*ZrCl_3 with Na/Hg in THF in the presence of diene affords the 14-electron $Cp^*ZrCl(diene)$ derivatives (diene = 2-methyl-1,3-butadiene; 2,3-dimethyl-1,3-butadiene). Although this is formal reduction reaction, crystallographic evidence points to the high contribution of a η^3,σ resonance structure for the diene and a metal in the oxidation state IV. The corresponding compound with the unsubstituted butadiene was obtained by ligand exchange between Cp^*ZrCl_3 and $Cp^*Zr(\eta^4\text{-}C_4H_6)(\eta^3\text{-}C_4H_7)$.[328,390] The interaction of Cp^*ZrCl_3 with 1,6-heptadiene and 2 equiv of sodium, followed by bromination, cleanly and stereoselectively produces *cis*-1,2-bis(bromoethyl)cyclopentane. The reaction is presumed to proceed through zirconacyclopentane derivatives.[391]

Redox. Interest in the reduction chemistry of $(C_5R_5)ZrCl_3$ has developed only recently. The only derivative of Zr(III) appears to be $Cp^*Zr(COT)$, obtained from Cp^*ZrCl_3 and Mg in the presence of COT.[148] The analogous reaction with cycloheptatriene gives $Cp^*Zr(\eta^7\text{-}C_7H_7)$.[148] In the presence of dmpe and a catalytic amount of naphthalene, sodium reduces $CpZrCl_3$ to the Zr(II) complex $CpZrCl(dmpe)_2$, having a pseudooctahedral structure with the chloride ligand trans to the Cp ring.[149]

The interaction of $CpZrCl_3$ with methylaluminoxane, $(MeAlO)_n$, has been investigated by EPR. An initial color change without the appearance of EPR signals is attributed to the formation of Zr(IV) adducts with the aluminoxane. Following this, an EPR singlet is obtained for low Al:Zr ratios, attributed to a reduced, aluminum-bound, $CpZrCl_3^-$ moiety. At higher Al:Zr ratios, two EPR doublets are obtained indicative of two different Zr(III) hydride species. These are assigned to $Cp(H)Zr(\mu\text{-}Cl)_2$-aluminoxane and $Cp(H)Zr(\mu\text{-}Cl)(\mu\text{-}CH_3)$-aluminoxane groups in analogy to the corresponding titanium system.[362]

Low-temperature interaction of $(C_5R_5)ZrCl_3$ with $Na^+Napht^{\bullet-}$, followed by exposure to CO, gives $[(C_5R_5)Zr(CO)_4]^-$ in analogy to the titanium system.[365,366]

F. Hafnium(IV)

$CpHfCl_3$ has been prepared from $HfCl_4$ and Cp_2Mg and isolated as the bis-THF adduct in 25% yield.[122] This preparation suffers from the competitive formation of the bis-Cp derivative, but this is not an issue for the formation of polymer-bound $CpHfCl_3$ from lithiated cyclopentadiene copolymers and $HfCl_4$.[369] More recently, a 63% yield of the DME adduct, $CpHfCl_3(DME)$, has been obtained by starting from the bis-SMe_2 complex, $HfCl_4(SMe_2)_2$, and $CpSnBu_3$ in DME as solvent.[19] A 55:45 mixture of $CpHfCl_3$ and $HfCl_4$ has been obtained by chlorination of Cp_2HfCl_2 with Cl_2 gas in CCl_4.[68] Cp^*HfCl_3 is prepared similarly to the zirconium analogue, that is from $HfCl_4$ and Cp^*Li in a low boiling point solvent to avoid the formation of the bis-Cp^* system,[17,220] or by the use of the Cp^*SiMe_3 reagent (99% yield).[243] The system illustrated in XIV was prepared via $HfCl_4$ and the lithium reagent.[372] Reports of $(C_5H_4Et)HfF_3$ and $IndHfF_3$ have appeared in the patent literature.[226a,b]

Reactivity

Reactivity studies on cyclopentadienyl hafnium trihalides are even less common than those of the zirconium analogues. The mixed-ring $Cp^*CpHfCl_2$ has been obtained from Cp^*HfCl_3 and CpNa in analogy to the zirconium system,[303] and other mixed-ring systems have also been described.[122,150] Cp^*HfCl_3 has been alkylated with 3 equiv of $MeMgBr$[392] or FcLi[326] to afford Cp^*HfMe_3 and Cp^*HfFc_3 (Fc = ferrocenyl), respectively. Reaction of Cp^*HfCl_3 with either 1 equiv of or excess t-Bu_2P^- yields, respectively, $Cp^*HfCl_2(P\text{-}t\text{-}Bu_2)$ and $Cp^*HfCl(P\text{-}t\text{-}Bu_2)_2$,[393] and 1 equiv of 2-lithiopyridine yields $Cp^*HfCl_2(\eta^2\text{-}2\text{-}NC_5H_4)$.[394] $(THF)_3LiE$-

TABLE V. Known Group 5 Neutral Cyclopentadienyl Metal Halides[a]

ox. state	X: F	X: Cl	X: Br	X: I
II				[CpVI]
III		Cp^*VCl_2	$(C_5R_5)VBr_2$	$CpVI_2$
		$(C_5Me_4R)NbCl_2$		
		$(C_5Me_4R)TaCl_2$	$(C_5Me_4R)TaBr_2$	
IV		(ring)VCl_3	(ring)VBr_3	$CpVI_3$
		$(C_5H_4R)NbCl_3$ (?)	$CpNbBr_3$	
		Cp^*TaCl_3		
V	$(C_5R_5)NbF_4$	(ring)$NbCl_4$	$CpNbBr_4$ (?)	
	Cp^*TaF_5	(ring)$TaCl_4$	(ring)$TaBr_4$	

[a] Structures in brackets indicate solvent-stabilized species.

$(SiMe_3)_3$ (E = Si, Ge) (1 equiv) gives the corresponding $Cp^*HfCl_2[E(SiMe_3)_3]$ derivatives.[380]

Cp^*HfCl_3 and 3 equiv of 2-butenylmagnesium bromide, contrary to the analogous Ti and Zr systems, affords a stable tris-allyl compound, $Cp^*Hf(C_4H_7)_3$. On heating, the analogue of the Ti and Zr products, the allylbutadiene complex $Cp^*Hf(\eta^3\text{-}C_4H_7)(\eta^4\text{-}C_4H_6)$, is obtained.[220] $CpHf(C_3H_5)_3$ has been analogously prepared from $CpHfCl_3$ and allylmagnesium chloride.[68] Ligand redistribution between $(C_5R_5)HfCl_3$ (2 equiv) and the allyl complexes $(C_5R_5)Hf(allyl)_3$ (1 equiv) gives the corresponding $(C_5R_5)Hf(\eta^3\text{-allyl})Cl_2$ complexes.[68,395] Thermolysis of the 1-methylallyl Cp* complex affords Cp^*HfCl_3 together with the cluster $Cp^*{}_3Hf_3Cl_5(C_4H_4)$ and a mixture of butenes.[395] Cp^*HfCl_3 and Na/Hg in the presence of diene or ligand exchange between Cp^*HfCl_3 and $Cp^*Hf(\eta^3\text{-}C_4H_7)(\eta^4\text{-}C_4H_6)$ gives the Cp^*HfCl(diene) products in analogy with the zirconium system described above.[328,390]

The reaction of Cp^*HfCl_3 with Mg in the presence of cycloheptatriene gives the sandwich complex $Cp^*Hf(\eta^7\text{-}C_7H_7)$. The analogous reaction carried out in the presence of COT does not produce a paramagnetic Hf(III) product in analogy with the corresponding Ti and Zr systems (vide supra). The intermediate formation of $Cp^*HfCl(COT)$ has been observed after which the subsequent reduction step leads to a variety of products including the Hf(IV) hydride, $Cp^*HfH(COT)$.[148] While the reductive carbonylation of $(C_5R_5)ZrCl_3$ with sodium naphthalenide provides entry into the $(C_5R_5)Zr(CO)_4{}^-$ anions, the corresponding reduction of Cp^*HfCl_3 gives exceedingly unstable materials. Treatment of Cp^*HfCl_3 with Na^+Napht^- in the presence of dmpe at low temperature followed by atmospheric pressure carbonylation provides $Cp^*HfCl(CO)(dmpe)$.[396] Stabilization of both $[(C_5R_5)Hf(CO)_4]^-$ (R = H, Me) anions has been achieved by using potassium naphthalenide as the reducing agent and, for the Cp* compound, by adding the potassium ion complexant 15-crown-6 or cryptand-2.2.2 before carbonylation.[397]

IX. Vanadium, Niobium, and Tantalum

All the known monocyclopentadienyl halide complexes of group 5 metals are shown in Table V.

A. Vanadium(II)

The reaction of the triple-decker $(CpV)_2[\mu,\eta^6:\eta^6\text{-arene}]$ complexes (arene = benzene, mesitylene) with dichloroethane or iodine in THF gives $CpVX(THF)$ (X = Cl or I, respectively). Further treatment of $CpVI(THF)$ with I_2 gives $CpVI_2(THF)$. The reaction of $CpVCl(THF)$ with Cp^*Li gives the mixed vanadocene, $CpCp^*V$.[398]

B. Vanadium(III)

$CpVI_2$ has been prepared by direct iodination of $CpV(CO)_4$.[57] The THF adduct, $CpVI_2(THF)$, is formed by iodination of $(CpV)_2(\mu,\eta^6:\eta^6\text{-}C_6H_6)$ or $CpV(\eta^6\text{-}C_6H_5Pr)$.[398] The $CpVX_2$ (X = Cl, Br) species do not appear to be stable at room temperature. Only a brief report exists of a $CpVBr_2{\cdot}ZnBr_2{\cdot}3THF$ system obtained from $CpVBr_3$ and Zn at −20 °C.[58] The corresponding chloride has been reported as the product of a similar reaction from $CpVCl_3$ but it was not isolated.[399] The interaction between $VX_3(THF)_3$ (X = Cl, Br) and various Cp^- delivering agents produces in all cases an unstable purple solution. All attempts to isolate and identify the purple product led to disproportionation to Cp_2VX and $VX_3(THF)_3$. The product is probably not $CpVX_2(THF)_n$, since addition of small trialkylphosphines or other potential stabilizing ligands (dimethoxyethane, nitriles, pyridine, etc.) gave only the disproportionation products with no trace of mono-Cp complexes.[400] Stabilization can be achieved by an additional halide ion, as shown by the isolation of the stable $[Cp_2Fe]^+[CpVBr_3]^-$ and $[Cp_2Co]^+[(C_5H_4Me)VCl_3]$ salts by reduction of the V(IV) trihalide derivatives.[89,92]

The Cp* derivatives have a higher stability than their Cp counterparts. Both the bromide and chloride species, $[Cp^*VBr_2]_2$ and $[Cp^*VCl_2]_3$, have been prepared by sodium amalgam reduction of the corresponding trihalide or by interaction of $VX_3(THF)_3$ with Cp^*SnBu_3. These compounds cleanly react with X_2 to generate the trihalide Cp^*VX_3 (X = Cl, Br) complexes.[85]

The interaction between $CpVCl_2$ (generated in situ at −40 °C) and $CpCr(COT)$ in the presence of zinc results in the formation of the mixed-metal species $(Cp_2CrV)(\mu\text{-COT})$.[399]

C. Niobium(III)

$[Cp^*NbCl_2]_2$ is the product of hydrogenolysis of $Cp^*NbMe_2Cl_2$, whereas the corresponding tantalum starting material yields a different product, $[Cp^*TaHCl_2]_2$. The C_5Me_4Et analogue has also been prepared and cryoscopic measurements in benzene are in accord with the dimer formulation. The compound does not react with ethylene, while it reacts with 3-hexyne to give Cp^*NbCl_2(3-hexyne).[73]

D. Tantalum(III)

The $[(C_5Me_4R)TaX_2]_2$ (X = Cl, Br) compounds have been obtained by sodium amalgam reduction of the corresponding Ta(V) tetrahalides[36] or Ta(IV) trihalide dimers.[37] The reaction of these materials with halogenated hydrocarbons regenerates the Ta(V) precursors.

From $[Cp^*TaBr_2]_2$ and 2-butyne the adduct $Cp^*TaBr_2(MeCCMe)$ was obtained, and the reaction with PMe_3 results in a variety of products, including $(C_5Me_4R)TaX_3(PMe_3)$.[36] Internal olefines and dienes also yield adducts, such as $(C_5Me_4R)TaBr_2(CH_2{=}CHC_6H_4\text{-}p\text{-}Me)$ and $(C_5Me_4R)TaBr_2(\sigma^2,\eta^2\text{-}CH_2CH{=}$

$CHCH_2$), the latter being best considered as a Ta(V) derivative of but-2-en-1,4-diyl.[401]

These compounds display interesting E–H activation chemistry. H_2 oxidatively adds to generate $[(C_5Me_4R)TaCl_2]_2(\mu\text{-}H)_2$ from the chloride compounds and a mixture of $(C_5Me_4R)_2Ta_2(\mu\text{-}H)_xBr_{6-x}$ from the bromide compounds.[36] The C–H bond of C_2H_4 oxidatively adds across the metal–metal bond to generate the vinyl–hydride compounds $(C_5Me_4R)X_2Ta(\mu\text{-}H)(\mu\text{-}X)(\mu,\sigma{:}\pi\text{-}C_2H_3)TaX(C_5Me_4R)$ in good yields. An analogous product was obtained with propylene, 1-butene, and 1-pentene.[401] The reaction of $(C_5Me_5R)_2Ta_2X_4$ (X = Cl, Br) with 2 equiv of BH_4^- involves B–H bond breaking and formation of the unsymmetrical $B_2H_6^{2-}$ bridge in the $(C_5Me_4R)_2Ta_2(\mu\text{-}X)_2(B_2H_6)$ product. When 4 equiv of BH_4^- are used instead, the isolated compound is $(C_5Me_4R)_2Ta_2(B_2H_6)_2$.[402]

E. Vanadium(IV)

Syntheses

Fischer first reported $CpVX_3$ (X = Cl, Br) as the product of the interaction between $CpV(CO)_4$ and X_2.[56] This route has been more recently employed for the high yield synthesis of $(C_5Me_4R)VX_3$ (R = Me, Et; X = Cl, Br).[403,404] Other methods of preparation involve the interaction between VCl_4 and $CpSiMe_3$ in hydrocarbons[4c] or between $(ring)_2VCl_2$ and $SOCl_2$ or Cl_2[58,89,226b,405,406] or between $CpV(CO)_4$ and $SOCl_2$.[58] A very recent, convenient synthetic procedure for the Cp^*VX_3 (X = Cl, Br) materials is dihalogen oxidation of the corresponding dihalides.[85] $CpVBr_3$ has been recently reinvestigated, and the corresponding iodide, $CpVI_3$, has also been prepared from $CpV(CO)_4$ and I_2,[92] a reaction that had been previously reported to produce $CpVI_2$ (vide supra).

Reactivity

The adducts $CpVCl_3L_2$ (L_2 = dmpe, dppe) have been prepared in high yields from $CpVCl_3$, whereas the interaction with PMe_3 is accompanied by decomposition.[406] In the presence of hard donors such as THF or MeCN, $(C_5H_4Me)VCl_3$ undergoes ligand redistribution, giving $(C_5H_4Me)_2VCl_2$ and solvent adducts of VCl_4.[89]

$CpVCl_3$ and $CpVBr_3$ can be interconverted by interaction with excess Br_2 or Cl_2.[56] Reaction of $CpVCl_3$ with $Me_3SiNRNR_2$ ($NRNR_2$ = $NMeNMe_2$, $NPhNH_2$) gives the corresponding hydrazido(1–) complexes, $CpVCl_2(NRNR_2)$, and the analogous reaction with $Me_3SiNPPh_3$ gives the phosphineiminate complex, $CpVCl_2(NPPh_3)$.[406] Attempts to transform $CpVCl_3$ into σ-organo derivatives have failed.[58] *i*-PrMgBr acts as a reducing agent and, in the presence of cyclic olefins, mixed-sandwich compounds are obtained: 1,3-cyclohexadiene yields a nonseparable mixture containing Cp_2V, $V(C_6H_6)_2$, and $CpV(C_6H_6)$, while 1,3,5-cyclooctatriene gives a mixture of $CpV(C_8H_{10})$ and $CpV(C_8H_9)$, and cycloheptatriene yields $CpV(C_7H_7)$.[407]

Treatment of an equimolar mixture of $CpVCl_3$ and Cp_2VCl_2 with either Ag_2O or Ag_2CO_3 gives the structurally characterized $Cp_2ClV(\mu\text{-}O)VCl_2Cp$, whereas there is no reaction between Ag_2O or Ag_2CO_3 and either $CpVCl_3$ or Cp_2VCl_2 alone. Cp^*VCl_3 does not react with Ag_2CO_3 either.[408a]

Reaction of $(C_5H_4Me)VCl_3$ with moist air, KO_2, NO, or O_2/NaOH yields $(C_5H_4Me)VOCl_2$ and the corresponding air oxidation of $CpVBr_3$ gives $CpVOBr_2$.[56] The $(ring)VX_3$ molecules are among the most powerful neutral organometallic oxidizing agents. $(C_5H_4Me)VCl_3$ shows a reversible one-electron reduction wave at −0.055 V vs Cp_2Fe/Cp_2Fe^+, whereas the corresponding Ti compound is reduced at a much more negative potential. Chemical reduction was accomplished with Cp_2Co to afford the $[Cp_2Co][C_5H_4R)VCl_3]$ salt.[51,89] Interaction with the organic donor tetramethyltetrathiafulvalene (TmTTF) gave the charge-transfer complexes $[TmTTF]_x[(C_5H_4Me)VCl_3]$ (*x* = 1,2).[408b,409] Reduction processes for the $CpVX_3$ series occur at 460, 510, and 425 mV with respect to the Ag/AgCl reference for X = Cl, Br, and I, respectively. The bromide compound is able to oxidize ferrocene to afford the $[Cp_2Fe][CpVBr_3]$ salt.[92] In the presence of dppe, reduction of $CpVCl_3$ with Mg affords the complex CpVCl(dppe).[406]

F. Niobium(IV)

There exists only a brief report about the compound $CpNbBr_3$, which has been prepared by interaction of $NbBr_5$ and Cp_2Mg or $CpSnMe_3$. The corresponding reactions on $NbCl_5$ or TaX_5 (X = Cl, Br) give products of substitution without reduction.[97] Evidence for the existence of $(C_5H_4R)NbCl_3$ (R = H, Me, *t*-Bu) in solution of MeCN or THF has been obtained by EPR during the reduction of the corresponding tetrachloride compounds with Al or $SnCl_2$ and by subsequent derivation with $C_5H_4R'^-$ to form $(C_5H_4R)(C_5H_4R')NbCl_2$. The same solutions have also been obtained by interaction of $NbCl_4(MeCN)_3$ with $(C_5H_4R)SnBu_3$ but no crystalline products could be isolated.[410] $[CpNbCl_3]$ has been proposed as an intermediate during the reduction of $CpNbCl_4$ to $[CpNb(\mu\text{-}Cl)(diene)]$ by (2-butene-1,4-diyl)magnesium derivatives.[411] A copolymer-attached form of $CpNbCl_3$ has also been described. This is obtained by reacting $NbCl_5$ with a cyclopentadiene substituted copolymer which had been treated with excess MeLi. If the same copolymer is reduced with *n*-BuLi and then quenched with R_3SnCl, subsequent treatment with $NbCl_5$ results in the formation of polymer-attached $CpNbCl_4$ instead.[412,413] EPR measurements of polymer-attached $CpNbCl_3$ suggest a piano-stool structure with a local C_{3v} axis through the three chlorine atoms.[414]

G. Tantalum(IV)

Reduction of $(C_5Me_4R)TaX_4$ (X = Cl, Br) with 1 equiv of sodium amalgam in toluene affords dinuclar Ta(IV) species, $[(C_5Me_4R)TaX_3]_2$. These can be reduced further with sodium to the corresponding Ta(III) dimers described in section IX.D.[37] Cp^*TaCl_3 was first obtained by thermal decomposition of Cp^*TaCl_2(propylene) in C_6H_5Cl at 100 °C. The compound reacts with PMe_3 in toluene to produce mononuclear, paramagnetic $Cp^*TaCl_3(PMe_3)$.[415]

H. Niobium(V)

Syntheses

$CpNbCl_4$ was originally obtained in 90% yield from $CpNb(CO)(C_2Ph_2)_2$ and $SOCl_2$ in benzene, 1,2,3,4-tetraphenylbutadiene being a secondary product of this reaction. The $CpNb(CO)(C_2Ph_2)_2$ starting material was obtained from $CpNb(CO)_4$ and diphenylacetylene in pentane under UV irradiation.[416] A more convenient sybthesis involves the interaction of $NbCl_5$ with the *stoichiometric amount* of Cp_2Mg or $CpER_3$ (E = Sn, Si; R = Me, Bu). Substituted Cp analogues, including a polymer-attached $CpNbCl_4$ material, have been prepared similarly.[26,96,97,240,410,412,417–420] The choice of solvent appears to be most critical for this synthesis. For example, toluene affords the C_5H_4R derivatives in high yields for R = H, Me, *n*-Bu presumably because the product is little soluble and precipitates immediately. For R = *t*-Bu, the product is more soluble and side-reactions take place which reduce the yields of the monoring system; better results, however, are obtained when carrying out the reaction in heptane. Analogously, the reaction of $NbCl_5$ with 2 equiv of $(C_5H_4Me)SnBu_3$ in heptane gives exclusively the monoring system, whereas the $(C_5H_4Me)_2NbCl_2$ forms in high yields when the same reaction is conducted in toluene.[148] The yields of the bis-Cp derivatives can also be increased by using an excess of Bu_3SnCp reagent.[421] The use of the more common CpNa reagent produces intractable partially reduced mixtures.

A mixed bromo–chloro system, $FlNbBrCl_3$, has been reported as long ago as 1963 in a patent. It was obtained from Fl_2NbCl_3 and bromine.[226b] The patent literature also reports $CpNbBr_4$.[226c] The $(C_5R_5)NbF_4$ (R = H, Me) molecules have been prepared from the corresponding tetrachloride derivatives and AsF_3. Single crystals of the Cp* system obtained from AsF_3 contain the solvent molecule as well as HF and correspond to the formula $[Cp^*NbF_4(AsF_3)_2]_2 \cdot [Cp^*NbF_4(HF)AsF_3]_2$.[94]

Reactivity

Adducts. The Lewis acidity of $CpNbCl_4$ is evidenced by the formation of mono-adducts with neutral donors such as MeCN, PhCN, $P(OMe)_3$, or dppe.[96] The THF adduct has also been isolated and characterized.[422] Reaction with PMe_3 and PEt_3 in THF leads to labile phosphine adducts, which were not isolated.[423]

Hydrolysis. Hydrolysis of $(C_5H_4R)NbCl_4$ gives the corresponding $[(C_5H_4R)Nb(H_2O)Cl_3]_2(\mu\text{-}O)$ and/or $[(C_5H_4R)NbCl_2(\mu\text{-}Cl)]_2(\mu\text{-}O)$ depending on reaction conditions.[96,417,424–427] More diverse structures have been observed during the hydrolysis of the corresponding Cp* system. An equimolar amount of H_2O in the presence of amine yields mononuclear $Cp^*NbCl_3(OH)$, whereas 0.5 mol of water generates the μ-oxo dimer $[Cp^*NbCl_3]_2(\mu\text{-}O)$. Further hydrolysis of either of these materials generates $[Cp^*NbCl_2(OH)]_2(\mu\text{-}O)$ which, upon heating under vacuum, transforms into the trinuclear cluster $[Cp^*NbCl]_3(\mu_2\text{-}Cl)(\mu_2\text{-}O)_3(\mu_3\text{-}O)$.[418]

Alcoholysis of $(C_5H_4R)NbCl_4$ with catechol or substitution reactions with NaOPh yields $(C_5H_4R)NbCl_2(OPh)_2$ (R = H, $SiMe_3$) and $CpNbCl_2(O_2C_6H_4)$. For the reaction of the R = $SiMe_3$ system with catechol, preferential hydrolysis takes place and catechol reacts with the resulting (μ-O) dimer to give $[(C_5H_4SiMe_3)NbCl_2]_2(\mu\text{-}O)(\mu\text{-}O_2C_6H_4)$.[428]

Ligand Substitution. $CpNbCl_4$ reacts with $(i\text{-}PrO)_2P(S)(SH)$ in the presence of NEt_3 to generate $CpNbCl_3[S_2P(O\text{-}i\text{-}Pr)_2]$ in moderate yields.[429] The reaction of $CpNbCl_4$ with $(Me_3Si)_2NMe$ affords the mononuclear imido complex $CpNbCl_2(NMe)$,[430] whereas no reaction takes place with the similar $(Me_3Si)_2NNHC(S)SMe$ derivative.[339] The hydrazido(1−) complexes $CpNbCl_3(NRNR_2)$ ($NRNR_2$ = $NMeNMe_2$, $NPhNH_2$) have been prepared from $CpNbCl_4$ and $Li(NRNR_2)$.[406] The substitution reaction of Cp^*NbF_4 with lithium salts of β-diketone affords the chelate complexes $Cp^*NbF_3(RCOCHCOR)$ (R = Me, Ph).[431]

The reaction of Cp^*NbCl_4 with (2-butene-1,4-diyl)magnesium and analogous reagents generates the "butadiene" complexes Cp^*NbCl_2(diene) and Cp^*Nb(diene)$_2$, which have been described as complexes of Nb(V) with the diene in the 2-alkene-1,4-diyl form. The corresponding reaction on the Cp system affords the same Nb(V) materials when "diene" = 2,3-dimethylbutadiene, but a mixture of monodiene monomer and a reduced Nb(IV) product, $[CpNb(\mu\text{-}Cl)(\text{diene})]_2$, when "diene" = isoprene, and the pure reduced Nb(IV) dimer is obtained when "diene" = butadiene. The latter can also be obtained from Cp^*NbCl_4 by heterogeneous reduction with Mg in the presence of 1,3-butadiene. However, homogeneous reduction with *i*-PrMgBr or EtMgBr in the presence of 1,3-butadiene gives predominantly mononuclear $CpNbCl_2$(butadiene), and the homogeneous reaction of $CpNbCl_4$ with the THF soluble HMPT adducts, (2-butene-1,4-diyl)magnesium·$(HMPT)_2$ or (2-methyl-2-butene-1,4-diyl)magnesium·$(HMPT)_2$ gave in each case the corresponding pure Nb(V) diene monomer. This shows that the formation of the dinuclear Nb(IV) dimer is crucially dependent on the steric bulk of the diene along with the solubility of the reducing agent.[411,432]

The reaction of $CpNbCl_4$ with 4 equiv of 2,4-dimethylpentadienylpotassium, in an attempt to generate "half-open" niobiocene derivatives, affords $CpNb(\eta^8\text{-}C_{14}H_{22})$ where $C_{14}H_{22}$ = 1,4,7,9-tetramethyl-1,3,7,9-decatetraene, presumably through an initial metastable $[CpNb(2,4\text{-}C_7H_{11})_2]$ intermediate which undergoes an intramolecular coupling reaction. The product contains two "diene" units coordinated to the niobium center, one of which is in the s-cis and the other in the s-trans configuration.[433]

Redox. The Nb(V) systems have a higher propensity to be reduced with respect to their tantalum homologue (vide infra). $CpNbCl_4$ reacts with $CpSn(n\text{-}Bu)_3$ to afford the bis-Cp Nb(IV) complex, Cp_2NbCl_2.[434] From the reaction of $CpNbCl_4$ and $Se(SiMe_3)_2$, crystals of the reduced trinuclear compound $CpNb(Cl)(\mu\text{-}Se)(\mu\text{-}Se_2)(CpNb)(\mu\text{-}Se)_2Nb(Cl)Cp$ were isolated.[435]

Reduction of $(C_5H_4R)NbCl_4$ (R = H, Me, *t*-Bu) with either Al or $SnCl_2$ in MeCN or THF produces EPR-active solutions consistent with the presence of a single Nb(IV) product, attributed to a $(C_5H_4R)NbCl_3$ species, perhaps stabilized by solvent coordination. The products could not be isolated but the subsequent interaction with $C_5H_4R'^-$ produces homogeneous (R = R′) and mixed-ring $(C_5H_4R)(C_5H_4R')NbCl_2$ compounds, which were isolated in >60% yields.[410]

The interaction of $CpNbX_4$ with $EtAlCl_2$ in the presence of diphosphine results in metal reduction with formation of the 17-electron $CpNbX_3$(L–L) (L–L = dmpe, X = Cl;[436,437] L–L = dppe, X = Cl or Br[96,426,427]). Nb(IV) derivatives of formula $(C_5H_4R)NbCl_3L_2$ (L = PMe_3, PMe_2Ph; L_2 = dppe) have also been obtained by reduction of the Nb(V) precursor with sodium amalgam in the presence of the appropriate ligand.[417,438] In similar conditions or even with magnesium as a reductant, the Nb(I) species $CpNb(L_2)_2$ (L_2 = dmpe, dppe) have also been obtained.[406] When these reactions are carried out under a CO atmosphere, the Nb(III) $(C_5H_4R)NbCl_2(CO)L_2$ products are obtained instead.[119,417,423,438] Reduction with sodium amalgam or magnesium under carbon monoxide in the presence of dmpe yields $CpNb(CO)_2(dmpe)$;[406,436] whereas when the reduction is carried out under H_2, an incompletely characterized dihydride, $CpNbH_2(dmpe)$, is obtained.[406] On the other hand, reduction of $CpNbCl_4$ with zinc amalgam in CH_2Cl_2 in presence of various phosphines give only *monophosphine* adducts of Nb(IV), isolated as methylene chloride solvates, $CpNbCl_3L{\cdot}CH_2Cl_2$ (L = PMe_2Ph, $PMePh_2$).[119]

Reductive high-pressure carbonylation of $(C_5R_4Me)NbCl_4$ under forcing conditions either with zinc, or with sodium as reducing agent and Cu/Al mixture as halogen acceptor, provides an entry into the corresponding Nb(I) tetracarbonyl derivatives, $(C_5R_4Me)Nb(CO)_4$,[419,439] whereas reductive carbonylation of $CpNbCl_4$ with amalgamated aluminum at room temperature and atmospheric pressure gives $CpNbCl_2(CO)_3$[440] which has later been reformulated as $[CpNb(\mu\text{-}Cl)Cl(CO)_2]_2$.[441,442] Reduction of $(C_5H_4R)NbCl_4$ in the presence of diarylacetylenes gives the stable mononuclear Nb(III) products $(C_5H_4R)NbCl_2(ArCCAr)$,[441,442] whereas the analogous derivatives containing terminal acetylenes, e.g. phenylacetylene and 1-hexyne, decompose to generate a mixture of trisubstituted benzenes.[443] Reductive isocyanation of $CpNbCl_4$ with sodium amalgam and *tert*-butylisocyanide gives $[CpNb(CN\text{-}t\text{-}Bu)_4Cl]^+$, isolated as the $[NbCl_4O(THF)]^-$ salt. The source of the oxygen atom in the anion is unknown.[444]

I. Tantalum(V)

Syntheses

A convenient synthesis of $CpTaCl_4$ involves the interaction of $TaCl_5$ with $CpER_3$ (E = Sn, Si; R = Me, Bu) or with Cp_2Mg, analogous to the synthesis of the niobium counterparts described above.[26,96,97,240,420] Cp^*TaCl_4 can be prepared conveniently in an analogous fashion[419,420,445–447] and a polymer-bound $CpTaCl_4$ material has also been prepared in this manner.[412] In a recent modification of the procedure from $TaCl_5$ and $(C_5Me_4R)SnBu_3$ (R = Me, Et), $(C_5Me_4R)TaCl_4$ were prepared in 90–95% yields by use of CH_2Cl_2 as solvent and low-temperature crystallization.[448] The use of Cp*Li or Cp*Na gives a complex mixture of products. The Cp^*TaCl_4 compound had been first prepared from $Cp^*TaNpCl_3$ and HCl.[415]

Cp^*TaF_4 forms from the exothermic metathetical reaction of Cp^*TaCl_4 and AsF_3. It crystallizes as a dimer-containing solvating AsF_3, from which the AsF_3-free compound can be obtained upon prolonged heating in vacuum.[95] The compound $CpTaBr_4$ has also been reported. It is obtained by the interaction of $TaBr_5$ with Cp_2Mg or $CpSnMe_3$,[97] whereas the corresponding reaction on $NbBr_5$ gives reduction to the Nb(IV) product. The $(C_5Me_4R)TaBr_4$ compounds have also been mentioned without details of their preparation.[37]

The dinuclear cationic derivative $[Cp^*Cl_2Ta(\mu\text{-}Cl)_3TaCl_2Cp^*]^+$ has also been reported. It has been isolated as a byproduct with the $\{[TaCl_5(\mu\text{-}O)TaCl_3]_2(\mu\text{-}Cl)_2\}^{2-}$ counterion during the synthesis of Cp^*TaCl_4 from $TaCl_5$ and Cp^*SnBu_3, presumably due to adventitious contact with moisture.[108]

Reactivity

Adducts. Mono-adducts of Cp^*TaCl_4 with PMe_3, PMe_2Ph, and $P(OMe)_3$ have been prepared, whereas no reaction occurs with PPh_3. A 1:1 adduct is also obtained with monodentate dppe. All these phosphine adducts undergo rapid exchange with excess free ligand.[415,447] $CpTaCl_4$ forms a stable 1:1 adduct with trimethyl- and tricyclohexylphosphine but other phosphines form adducts that are too labile to be isolated. Other Lewis acid–base adducts that have been isolated include $[CpTaCl_4]_2(bipy)$ and $CpTaCl_4(DME)$.[119] An adduct of the Cp* system is also formed with methylenephosphoranes to give the neutral ylide derivatives $Cp^*TaCl_4(CH_2PRR'_2)$. The crystal structure of the compound with R = Me and R′ = Ph shows a pseudooctahedral geometry with the carbon-bound η^1-ylide trans to the Cp* ring.[449a] The 1:1 adduct of Cp^*TaF_4 and $HN{=}PPh_3$ has also been prepared and structurally characterized.[449b]

Hydrolysis. The hydrolysis of Cp^*TaCl_4 has been presumed to afford either $[Cp^*TaCl_2(OH)]_2O$ or $[Cp^*TaCl_3(H_2O)]_2O$ on the basis of IR data.[98] Further studies have shown that exposure of Cp^*TaCl_4 to the ambient atmosphere affords a 1:3 mixture of $[Cp^*TaCl_3]_2O$ and $[Cp^*TaCl_2(OH)]_2O$. Hydrolysis is faster in solution and a complex equilibrium mixture containing also a third compound, believed to be the mononuclear $Cp^*TaCl_3(OH)$, is obtained, with the ratio of these species being critically dependent on the amount of H_2O used. Excess H_2O gave the pure $[Cp^*TaCl_2(OH)]_2O$ species. All of these species can be reconverted to the tetrachloride compound by treatment with HCl.[450,451] The compound $\{[Cp^*TaCl_2]_2(\mu\text{-}Cl)_3\}_2\{[TaCl_5(\mu\text{-}O)TaCl_3]_2(\mu\text{-}Cl)_2\}$ is presumably another product of Cp^*TaCl_4 partial hydrolysis.[108] The oxo-bridged $[Cp^*TaCl_3]_2(\mu\text{-}O)$ dimer can also be obtained from Cp^*TaCl_4 and $(Me_3Si)_2O$, indicating the stronger Ta–O bond with respect to the Si–O bond.[452]

Ligand Substitution. The reaction between Cp^*TaCl_4 and anionic ylides $[RR'P(CH_2)_2]^-$ yields $Cp^*TaCl_3(CH_2)_2PRR'$ derivatives that are presumably an equilibrium mixture of monomers and dimers in solution. Analogous materials have also been obtained by using the $[Ph_2P(X)CH_2]^-$ (X = O, S) anions.[453] One chloride ligand has also been replaced with the OCH_2SiMe_3 group by condensation with the corresponding alcohol and elimination of HCl,[454] and with a $SiMe_3$ group by the use of the $Al(SiMe_3)_3{\cdot}OEt_2$ reagent, and the reaction with $LiOCH_2CO_2Et$ affords the pseudooctahedral $Cp^*TaCl_3(OCH_2CO_2Et)$.[98,455] *o*-Diphenols $4\text{-}R'C_6H_3(OH)_2$ replace two chlorides on the same tantalum center to afford $(C_5H_4R)TaCl_2(O_2C_6H_3R')$, whereas $Me_2C(p\text{-}C_6H_4OH)_2$ replaces one chloride on each of two tantalum centers to give the dinuclear $[(C_5H_4R)TaCl_3]_2[(OC_6H_4)_2CMe_2]$.[456] Cp^*TaF_4 reacts with lithium salts of para-substituted benzamidines to yield the complexes $Cp^*TaF_3[(Me_3SiN)_2C\text{-}p\text{-}C_6H_4R]$ (R = H, CF_3, NMe_2, Me, CN, OMe) and with lithium β-diketonates to yield $Cp^*TaF_3[OC(Ph)CHC(Ph)O]$. These reactions proceed under elimination of LiF.[457,458] Interaction between Cp^*TaCl_4 and $Me_2S(O){=}NPPh_2{=}NSiMe_3$ gives $Me_2S(O){=}NPPh_2{=}NTaCp^*Cl_3$,[338] whereas there is no reaction between $CpTaCl_4$ and $(Me_3Si)_2NNHC(S)SMe$.[339] The reaction between Cp^*TaCl_4 and Me_3SiOR (R = Me, Et) yields the corresponding $Cp^*TaCl_3(OR)$, which is stable with respect to elimination of RCl and formation of the $[Cp^*TiCl_2(\mu\text{-}O)]_2$ compound.[452] The interaction between Cp^*TaCl_4 and the equimolar amount of tris(trimethylstannyl)amine, $N(SnMe_3)_3$, gives the structurally characterized inorganic heterocycle $[Cp^*Ta(Cl)N]_3$ with alternating tantalum and nitrogen atoms in a benzene-like structure.[459] $(C_5Me_4R)Ta(SCH{=}CHS)_2$ and $Cp^*Ta(SCH_2CH_2S)_2$ derivatives have been obtained from the corresponding tetrachlorides and $Na_2S_2C_2H_2$ or $Na_2S_2C_2H_4$, respectively.[460] The reaction of Cp^*TaCl_4 with Li_2S_2 (1:2 molar ratio) affords an uncharacterized material, but a higher proportion (4 equiv) of Li_2S_2 gives good yields of $[Cp^*TaS_3Li_2(THF)_2]_2$, which can be described as a salt of the $[Cp^*TaS_3]^{2-}$ anion with three terminal sulfides.[461] Treatment of $CpTaCl_4$ with $S(SiMe_3)_2$ has resulted in the isolation of three products: $[Cp_8Ta_6S_{10}]^{2+}[TaSCl_5]^{2-}$ where the cation has a central edge-sharing bioctahedral $\{Ta_2S_{10}\}$ core bridged by the sulfide ligands to four $\{Cp_2Ta\}$ moieties, $Cp_3Ta_3S_7Cl_2$, and $Cp_4Ta_4S_{13}$, all having exclusively Ta(V) centers.[435]

Addition of methyllithium to Cp^*TaCl_4 results in the formation of the tetramethyl complex, Cp^*TaMe_4; whereas an analogous reaction with $(PhCH_2)MgCl$ produces the carbene complex $Cp^*Ta(CH_2Ph)_2(CHPh)$.[447] One chloride ligand of Cp^*TaCl_4 has been replaced by either $CH_2C_6H_4$-*p*-Me or CH_2CMe_3 by the use of the corresponding dialkylzinc to afford $(C_5Me_4R)TaCl_3(CH_2C_6H_4\text{-}p\text{-}Me)$.[448] The reaction of $(C_5R_5)TaCl_4$ with (2-butene-1,4-diyl)magnesium and its higher analogues provides a general route to the mono-, bis-, and mixed-diene complexes $(C_5R_5)TaCl_2$(diene), (C_5R_5)Ta(diene)$_2$, and (C_5R_5)Ta(diene)(diene′) containing Ta(V)–metallacyclopentane structures.[432b,446,462] $CpTaCl_4$ and pentadienyl anions give the Cp_2Ta(pentadienyl) compounds (pentadienyl = 2,3-C_7H_{11}, 2,4-C_7H_{11}) where the pentadienyl shows localized Ta–alkyl and Ta–olefin coordination.[433]

Redox. Treatment of $CpTaCl_4$ with $EtAlCl_2$ in toluene followed by the addition of ethanol precipitates Cp_2TaCl_2.[96,426] Direct access to the latter compound in high yields from $CpTaCl_4$ can also be achieved by the interaction with 3 equiv of $CpSnBu_3$.[463] Reduction of $(C_5R_5)TaCl_4$ in THF yields a variety of products depending on the ring, amount of reducing agent, solvent, and other conditions. One reducing equivalent of Mg and 1 equiv of PMe_3 in THF yield paramagnetic $(C_5R_5)TaCl_3(PMe_3)$ and, under the same conditions, the Cp system and dmpe form $CpTaCl_3$(dmpe) presumed to have a pseudooctahedral geometry with the diphosphine in a chelating mode.[445,464] Two reducing equivalents of Mg in THF or sodium sand in toluene and excess PMe_3 yield $(C_5R_5)TaCl_2(PMe_3)_n$ (*n* = 3 for Cp and 2 for Cp*).[438,442,464,465] On the other hand, reduction of the Cp* system with metallic sodium in PMe_3 as solvent yields the product of double C–H activation of coordinated PMe_3, $Cp^*TaH_2(\eta^2\text{-}CHPMe_2)(PMe_3)$.[466] A similar reduction but this time in THF as solvent yields yet another product, the double ring-metalated compound $[C_5Me_3(CH_2)_2]Ta(H)_2(PMe_3)_2$.[467] In the presence of CO, reduction by $Al/HgCl_2$ yields the Ta(III) complex $Cp^*TaCl_2(CO)_2(THF)$ in high yields,[468] whereas $CpTaCl_4$ and Mg under CO and in the presence of phosphine yield complexes of the type $CpTaCl_2(CO)L_2$ (L = PMe_3, PEt_3, PMe_2Ph, PPh_3)[119] and, with amalgamated aluminum under CO, the formation of $CpTaCl_2(CO)_3$ has been reported.[440] Other authors, under the same conditions, have obtained $[CpTa(\mu\text{-}Cl)Cl(CO)_2]_2$ instead.[441,442]

TABLE VI. Group 6 Neutral Cyclopentadienyl Metal Halides

ox. state	X: Cl	Br	I
II	Cp^*CrCl		
III	$(C_5R_5)CrCl_2$ (ring)$MoCl_2$ (ring)WCl_2	$(C_5R_5)CrBr_2$ $(C_5H_4R)MoBr_2$	$(C_5R_5)CrI_2$
IV	$CpMoCl_3$ $(C_5R_4R')WCl_3$ (?)		
V	(ring)$MoCl_4$ (ring)WCl_4	$(C_5H_4R)MoBr_4$	

The $[(C_5Me_4R)TaX_2]_2$ (X = Cl, Br) compounds have been obtained by sodium amalgam reduction of the corresponding tetrahalide compounds[36] in an inert solvent. This reduction proceeds through the isolable dimeric Ta(IV) systems $[(C_5Me_4R)TaX_3]_2$.[37]

Reductive high-pressure carbonylation of $(C_5R_4Me)TaCl_4$ (R = H, Me) with zinc affords the respective Ta(I) tetracarbonyls, $(C_5R_4Me)Ta(CO)_4$.[419] More recently, it has been found that ligated PMe_3 facilitates the preparation of $Cp^*Ta(CO)_4$ under mild conditions and in reasonable yields: Cp^*TaCl_4 and 4 equiv of amalgamated Na in THF under 1.5 atm CO and in the presence of 1 equiv of PMe_3 affords $Cp^*Ta(CO)_4$ in 47% yield.[465] Reaction of $CpTaCl_4$ with Na as the reducing agent, followed by treatment with mesityl oxide, results in the formation of $CpTaCl_2(Me_2C{=}CHC(O)Me)$.[469]

X. Chromium, Molybdenum, and Tungsten

All the known monocyclopentadienyl halide complexes of group 6 metals are shown in Table VI.

A. Chromium(II)

$[Cp^*CrCl]_2$ was first obtained from the interaction of $[Cp^*CrCl_2]_2$ and aluminum hydride reagents and has since been made more rationally by reacting anhydrous $CrCl_2$ with Cp*Li.[80]

B. Chromium(III)

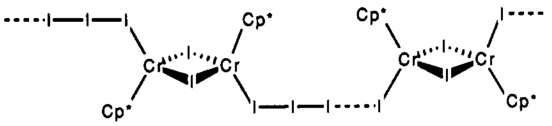
$CpCrX_2$ (X = Cl, Br, I) derivatives were first reported by Fischer et al. in 1963. The Br and I systems were obtained from $[CpCr(CO)_3]_2$ and the corresponding allyl halide in hexane, whereas there is no reaction with allyl chloride. The chloride system was obtained by expulsion of THF at 80 °C under vacuum from the adduct, $CpCrCl_2$(THF), which is obtained from Cp_2Cr and CCl_4 in THF through the intermediacy of $[Cp_2Cr][CpCrCl_3]$.[60]

A more recent investigation by paramagnetic NMR shows that $[Cp_2Cr]^+[CpCrCl_3]^-$ is transformed to *trans*-$Cp_2Cr_2Cl_4$ on heating and to a mixture of *cis*/*trans*-$Cp_2Cr_2Cl_4$ on standing in chloroform.[88]

Only very recently have the Cp* analogues been reported. $CrCl_3(THF)_3$ and Cp*Li produce $Cp^*CrCl_2(THF)$. Alternatively, the reactions of decamethylchromocene with HX in THF generate the corresponding $Cp^*CrX_2(THF)$ (X = Br, I), through the intermediacy of Cp^*_2CrX and $[Cp^*_2Cr][Cp^*CrX_3]$, which can be isolated for X = I. From all these THF adducts, the solvent-free $[Cp^*CrX_2]_2$ can be obtained upon warming. The iodide compound can also be obtained from $[Cp^*Cr(CO)_3]_2$ and I_2.[61] $[Cp^*CrCl_2]_2$ has also been obtained from the reaction of $Cp^*CrI(CO)_3$ and allyl chloride.[59]

A compound of formula "Cp^*CrBr_3" has been reported. Its structure can be interpreted as $\{[Cp^*CrBr(\mu\text{-}Br)]_2 \cdot Br_2\}_n$, which therefore indicates that the hypothetical Cr(IV) Cp^*CrBr_3 would be more oxidizing than free bromine.[470] The dimer $[Cp^*CrBr_2]_2$, free from extra bromine, has also been obtained from $[Cp^*Cr(CO)_3]_2$ and excess bromine in CH_2Cl_2, followed by extraction with THF. This compound activates molecular oxygen to form Cp^*CrOBr_2.[471]

The reaction of $[Cp^*Cr(CO)_2]_2$ with excess I_2 results in the formation of a material whose empirical formula corresponds to Cp^*CrI_3. Its solid-state structure consists of the copolymer $\{[Cp^*CrI(\mu\text{-}I)]_2 \cdot [Cp^*Cr(I_3)(\mu\text{-}I)]_2\}_n$ (XV).[103]



XV

The reaction of "Cp^*CrI_3" with excess Zn/Hg forms Cp^*CrI_2. This material exhibits only a single ^1H NMR resonance at δ −68 in $CDCl_3$[103] in contrast to the same compound obtained directly from $[Cp^*Cr(CO)_3]_2$ and I_2.[61] Unlike $Cp^*_2Cr_2Br_4$, the iodide compound does not react cleanly with O_2.[103] Treatment of "Cp^*CrI_3" with excess I_2 affords another remarkable polyiodide structure, corresponding to the empirical formula $Cp^*_2Cr_2I_{11}$. On the basis of an X-ray analysis this complex is formulated as $[Cp^*_2Cr_2(\mu\text{-}I)_3]^+{}_2[I_{16}]^{2-}$. The formation of this compound, thus, can be viewed as abstraction of I^- from $Cp^*_2Cr_2(\mu\text{-}I)_2I_2$ by the large excess of I_2 (eq 19). Ag^+ is also effective in this I^- abstraction reaction. The

$$2Cp^*_2Cr_2(\mu\text{-}I)_2I_2 + 7I_2 \rightarrow 2Cp^*_2Cr_2(\mu\text{-}I)_3^+ + I_{16}^{2-} \tag{19}$$

structure of the $[Cp^*_2Cr_2(\mu\text{-}I)_3]^+$ cation is illustrated in Figure 6.

A mixed halide compound containing a polyiodide chain, $[Cp^*CrCl_{1/2}I_{3/2}] \cdot I_2$ has been obtained by diiodine oxidation of $[Cp^*CrCl(CH_3)]_2$. The compound is isostructural with $[Cp^*IrI_2]_2 \cdot I_2$ (vide infra) and its structure is similar to that shown above for Cp^*CrI_3 (XV) except that I_2 molecules are symmetrically disposed between $[Cp^*Cr(\mu\text{-}X)I]_2$ units where the bridging X positions are occupied randomly by Cl and I with a probability of 50:50.[472] Another mixed halide compound, $[Cp^*_4Cr_4(\mu\text{-}F)_5Cl_2]^+PF_6^-$, has been reported.[110]

Reaction of Cp_2Cr with CCl_4[60] or $CHCl_3$[88] affords the salt $[Cp_2Cr]^+[CpCrCl_3]^-$. $[CpCrX_3]^-$ (X = Cl, Br) ions have also been obtained by interaction of chromocene with the corresponding HX,[60] direct interaction of $CrCl_3$ and CpLi in THF,[90] and interaction of $Li^+CpCr(pyrr)_3^-$ with triethylamine or pyridine hydrochloride.[473] The $[(C_5H_4Me)_4Cr_4S_4]^+[(C_5H_4Me)CrBr_3]^-$ salt has also been described.[474]

All the $(C_5R_5)CrX_2$ derivatives react readily with neutral ligands to afford the adducts $(C_5R_5)CrX_2L$ (L = py, THF, PPh_3, PMe_3, PEt_3).[60,475] $[CpCrCl_2]_2$ reacts with allylmagnesium chloride to afford the mononuclear $CpCr(\eta^3\text{-}C_3H_5)_2$,[476] while the $[Cp^*CrR(\mu\text{-}Cl)]_2$ dimers have been obtained by treating $[Cp^*CrCl_2]_2$ with 2 equiv of RLi (R = Me, Et, Ph) or $PhCH_2MgCl$.[477] $[CpCrCl_3]Li(THF)_2(Diox)$ has been transformed to $[CpCrMe_3]Li(Diox)_2$ and $[CpCrPh_3]Li(Et_2O)$.[90]

C. Molybdenum(III)

$[(C_5H_4\text{-}i\text{-}Pr)MoCl_2]_2$ has been prepared from the arene–fulvene complex $Mo(\eta^5{:}\eta^1\text{-}C_5H_4\text{-}\mu\text{-}CMe_2)(\eta^6\text{-}C_6H_6)$ and HCl.[74,75] This compound, as well as other $[(C_5H_4R)MoCl_2]_2$ derivatives and $[(C_5H_4\text{-}i\text{-}Pr)MoBr_2]_2$, has also been prepared by reduction from $(C_5H_4R)MoX_4$ in analogy to the tungsten derivatives of identical stoichiometry (vide infra).[39] The corresponding insoluble Cp derivative has been obtained by reduction of $CpMoCl_4$ with Zn powder,[40,41] whereas the reduction with sodium amalgam gives a soluble species, presumed to be the sodium salt of the $[Cp_2Mo_2Cl_5]^-$ anion. The PPN^+ salt of the latter anion has been obtained from $CpMoCl_2$ and PPN^+Cl^- and characterized crystallographically (see Figure 4).[41]

Reaction between $(C_5H_4R)MoCl_2$ and a variety of monodentate or bidentate phosphines gives the 17-electron derivatives $(ring)MoCl_2L_2$ (R = H, L = PMe_3, PEt_3, PMe_2Ph, $PMePh_2$, PPh_3, L_2 = dppe;[40,62,478] R = *i*-Pr, L = PMe_3, PMe_2Ph, L_2 = $i\text{-}Pr_2PCH_2CH_2\text{-}i\text{-}Pr$[74,75]). Interaction with dmpe does not afford the expected 17-electron dmpe-substituted product but rather $[(C_5H_4\text{-}i\text{-}Pr)Mo(dmpe)_2][PF_6]$ or $[(C_5H_4\text{-}i\text{-}Pr)MoH(dmpe)_2][PF_6]_2$, depending on workup.[74] The formation of the transient $CpMoCl_2(dmpe)$ species from $CpMoCl_2$ has been observed by EPR.[479]

D. Tungsten(III)

$(C_5H_4R)_2W_2X_4$ complexes have been prepared by sodium amalgam reduction of the corresponding $(C_5H_4R)WX_4$ (R = Me, *i*-Pr; X = Cl, Br).[38,39] The $Cp^*_2W_2Cl_4$ compound has been obtained from the reduction of Cp^*WCl_4 by $P(t\text{-}Bu)_2^-$.[84] The low-temperature reaction between $[CpW(CO)_2(\mu\text{-}H)]_2$ and HCl affords, as a small yield byproduct, a blue carbonyl-free compound, which has been interpreted as $[CpWCl_2]_2$.[480] Both the unbridged, triply bonded $[(C_5H_4R)WCl_2]_2$ and the quadruply bridged $[Cp^*WCl_2]_2$ are green.

$[(C_5H_4Me)WCl_2]_2$ reacts with dmpe to give the 1:1 adduct $(C_5H_4Me)WCl_2(\mu\text{-}Cl)_2W(C_5H_4Me)(dmpe)$, contrary to the Mo analogue which yields mononuclear products, while addition of H_2 to the *i*-Pr analogue gives $[(C_5H_4\text{-}i\text{-}Pr)_2WCl_2(\mu\text{-}H)]_2$ containing a W–W double bond.[38]

Reaction of $[(C_5H_4R)WCl_2]_2$ with excess but-2-yne gives the flyover bridge compounds *cis*-$[(C_5H_4R)WCl_2]_2(\mu\text{-}C_4Me_4)$, which undergo thermal rearrangement in solution or in the solid state to the isomeric trans species. Reaction of the *i*-Pr substituted dimer with 1 equiv of R′CCR′ (R′ = $SiMe_3$, Et) affords the mono-adducts $[(C_5H_4\text{-}i\text{-}Pr)WCl(\mu\text{-}Cl)]_2(\mu\text{-}C_2R'_2)$.[481]

E. Molybdenum(IV)

$IndMoCl_3$ has been described in the patent literature.[226b] The $[CpMoCl_4]^-$ complex, as the PPh_3-*t*-Bu salt, was reported as the major product of the interaction between $CpMo(CO)_2(\eta^2\text{-}N{=}C\text{-}t\text{-}Bu_2)$ and PPh_3 in refluxing CCl_4.[482] Although the $CpMoCl_3L_2$ (L_2 = dmpe, dppe) compounds are known,[479,483] the neutral $CpMoCl_3$ systems has been prepared only very recently. It forms by oxidation of $CpMoCl_2$ with the stoichiometric amount of $PhI{\cdot}Cl_2$ in CH_2Cl_2 or by reduction of $CpMoCl_4$ with $TiCl_3$ or by conproportionation of equimolar amounts of $CpMoCl_2$ and $CpMoCl_4$. Its reaction with dmpe or dppe gives the known 1:1 adducts and the cage phosphite $P(OCH_2)_3CEt$ gives a bis-adduct, whose structure has been determined, but a similar adduct is not obtained with PMe_3.[53]

F. Tungsten(IV)

No stable derivatives of this class have been reported. $(C_5R_4\text{-}t\text{-}Bu)WCl_3$ (R = Me, Et) has been implicated as a possible intermediate during the reaction of $W(C\text{-}t\text{-}Bu)(DME)Cl_3$ with $RC{\equiv}CR$, ultimately leading to the disproportionation products $(C_5R_4\text{-}t\text{-}Bu)WCl_4$ and $(C_5R_4\text{-}t\text{-}Bu)W(RC{\equiv}CR)Cl_2$. Attempts to synthesize this material by reducing $(C_5R_4\text{-}t\text{-}Bu)WCl_4$ with sodium amalgam yield only products of two-electron reduction.[77] However, a stable bis(phosphine) adduct, $CpWCl_3(PMe_3)_2$, has been recently prepared.[484]

G. Molybdenum(V)

Syntheses

$CpMoCl_4$ was originally formed from $CpMoOCl_2$ and HCl as a method for the purification of the oxo–dichloride compound; treatment of $CpMoCl_4$ with moist air regenerates pure $CpMoOCl_2$. $CpMoCl_4$ was also obtained by reaction of HCl with $CpMoO_2Cl$, $[CpMoO_2]O$, or $[CpMoO_2]_2$.[27] An improved method with extension to the (C_5H_4Me) system uses the in situ generation of $(C_5H_4R)MoOCl_2$ from $[MoOCl_3]_n$ and $(C_5H_4R)Tl$.[26] The preparation of $(CH_3COC_5H_4)MoCl_4$ has been reported in the patent literature.[226c] The Cp* system has been conveniently prepared in high yields from $Cp^*Mo(CH_3)(CO)_3$ (which is easily available from $Cp^*Mo(CO)_3^-$) and PCl_5.[63] Attempts to prepare Cp^*MCl_4 (M = Mo, W) directly from MCl_x (x = 5 or 6) and a mild Cp* source such as Cp^*SnBu_3 have failed. The adaptation of this method also provides a convenient alternative for the preparation of the (C_5H_4R) (R = H, Me, *i*-Pr) system in three steps from $Mo(CO)_6$.[39,62]

$CpMoBr_4$ has been prepared by the interaction of $CpMoOBr_2$ with gaseous HBr. The starting material, which can be obtained from $Cp_2Mo_2(CO)_6$ in boiling bromoform in air, can be replaced with other oxobromo or oxo complexes, although less satisfactory results are obtained in these cases.[28] $(C_5H_4Me)MoBr_4$ has been recently prepared from $[(C_5H_4Me)Mo(CO)_3]_2$ and PBr_5.[39]

Reactions

Chloride ions do not add to Cp^*MoCl_4 to give a stable $Cp^*MoCl_5^-$ complex, but PMe_3 gives a stable $Cp^*MoCl_4(PMe_3)$ adduct.[63] On the other hand, decomposition to uncharacterized materials occurs when PMe_3 interacts with $CpMoCl_4$.[101]

Cp^*MoCl_4 can be converted in good yields to the corresponding tetramethyl derivative, Cp^*MoMe_4, by addition as a solid to a dilute solution of the Grignard reagent in THF. Addition of the Grignard to the Mo compound results in reduction of the metal instead.[485]

$(C_5H_5R)MoCl_4$ (R = H, Me) can be converted to $(C_5H_4R)MoOCl_2$ with propylene oxide; whereas slow hydrolysis in water gives $[(C_5H_4R)Mo(\mu\text{-}O)]_2$.[26] The hydrolysis of the Cp* analogue with 1.5 equiv of H_2O gives a solid which has been formulated as $[Cp^*MoCl_2(OH)]_2O$ on the basis of elemental analysis and by analogy of the hydrolysis of Cp^*TaCl_4 (vide supra). In the presence of oxidizing agents (Na_2MoO_4, Na_2WO_4, or $NaVO_3$), however, $[Cp^*MoO_2]_2O$ is obtained, whereas oxidation with Na_2WO_4 in anhydrous THF gives $[Cp^*MoOCl]_2O$.[124] $CpMoBr_4$, like the analogous tetrachloride, is moisture sensitive. Water vapor transforms it to $CpMoOBr_2$, whereas with excess water the tetranuclear oxo derivative $[CpMoO_2]_4$ is obtained.[28]

$CpMoCl_4$ can be reduced to $CpMoCl_2$ by Zn in THF,[40] whereas sodium amalgam generates the $[Cp_2Mo_2Cl_5]^-$ ion.[41] Reduction of $(C_5H_4R)MoX_4$ with sodium amalgam affords $[(C_5H_4R)MoX_2]_2$ (R = Me, *i*-Pr; X = Cl, Br).[39]

H. Tungsten(V)

Syntheses

The first compound of this class to be reported was $(C_5R_4\text{-}t\text{-}Bu)WCl_4$ (R = Me, Et), obtained from $W(C\text{-}t\text{-}Bu)(DME)Cl_3$ and excess of 2-butyne or 3-hexyne, respectively. Treatment of $(C_5R_4\text{-}t\text{-}Bu)W(alkyne)Cl_2$ with excess Cl_2 in pentane also affords $(C_5R_4\text{-}t\text{-}Bu)WCl_4$ in high yields.[77] The sequential addition of 2-butyne and 3-hexyne to $W(CCMe_3)Cl_3(DME)$ generates $(C_5Me_2Et_2\text{-}t\text{-}Bu)WCl_4$, which is shown to be a mixture of two different isomers after derivatization with Np_2Zn.[77b] Later, Cp^*WCl_4 was prepared conveniently on a large scale by adding $Cp^*WMe(CO)_3$ to PCl_5.[63,486] $[WCl_4]_2(\mu\text{-}\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ was obtained from $[WOCl_3]_2(\mu\text{-}\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ and PCl_5.[436] $(C_5H_4R)WCl_4$ (R = H, Me, *i*-Pr) complexes were similarly prepared, and $(C_5H_4\text{-}i\text{-}Pr)WBr_4$ has been obtained from $(C_5H_4\text{-}i\text{-}Pr)WMe(CO)_3$ and PBr_5.[39]

Reactions

Cp^*WCl_4 reacts with PMe_3 to give a stable $Cp^*WCl_4(PMe_3)$ adduct, whereas no reaction takes place with PPh_3.[63,486] Analogously, $[WCl_4]_2(\mu\text{-}\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ affords the crystallographically characterized $[WCl_4(PMe_3)]_2(\mu\text{-}\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$ compound.[487] Cp^*WCl_4 also reacts with Et_4NCl to form a stable $Et_4N[Cp^*WCl_5]$ salt.[63]

Addition of a large excess of $LiAlH_4$ ($LiAlD_4$) to Cp^*WCl_4 in Et_2O or THF followed by workup in methanol (methanol-d^1) yields $[Cp^*WH_4]_2$ ($[Cp^*WD_4]_2$). The first step of this reaction involves reduction to $[Cp^*WCl_2]_2$. By analogous methods the

TABLE VII. Group 7 Neutral Cyclopentadienyl Metal Halides[a]

ox. state	X: Cl	X: Br	X: I
II	[(C_5H_4R)MnCl]	[(C_5H_4R)MnBr]	[(C_5H_4R)MnI]
III	(C_5Me_4R)$ReCl_2$	Cp*$ReBr_2$	
IV	(C_5Me_4R)$ReCl_3$		Cp*ReI_3
V	(C_5Me_4R)$ReCl_4$	Cp*$ReBr_4$	

[a] Structures in brackets indicate solvent-stabilized species.

C_5Me_4R (R = Et, *n*-Pr, *t*-Bu) and C_5Et_4R (R = Et, *t*-Bu) tetrahydride complexes have also been prepared from the corresponding tetrachlorides, as well as the compound $[WH_4]_2(\eta^5,\eta^5\text{-}Et_4C_5CH_2CH_2C_5Et_4)$.[488] Treatment of ($C_5Me_4R$)$WCl_4$ with MeMgCl at room temperature (R = Me) or with MeLi at −78 °C (R = *t*-Bu) yields (C_5Me_4R)WMe_4.[486,489] (C_5Me_4-*t*-Bu)WCl_4 and $ZnMe_2$ yield paramagnetic (C_5Me_4-*t*-Bu)WCl_2Me_2, whereas ($C_5Me_2R_2$-*t*-Bu)WCl_4 and Np_2Zn afford the neopentylidyne complex ($C_5Me_2R_2$-*t*-Bu)W($CCMe_3$)Cl_2 (R = Me, Et) with formal oxidation from W(V) to W(VI).[77b,489] Ligand redistribution between Cp*WCl_4 and Cp*WMe_4 in a 1:3 ratio presumably generates the Cp*$WClMe_3$ species which has not been isolated but rather reacted directly with Na/Hg under N_2 to yield [Cp*WMe_3]$_2$(μ-N_2).[490]

Reduction of (C_5H_4R)WX_4 with 2 equiv of amalgamated sodium affords (C_5H_4R)WX_2 (X = Cl, Br).[38,39] Reduction of Cp*WCl_4(PMe_3) with Mg affords an uncharacterized red crystalline material which, upon interaction with (C_5Me_4R)Li (R = Me, *n*-Pr), produces the corresponding Cp*(C_5Me_4R)WCl_2 compound in modest yields.[491] The reaction of Cp*WCl_4 with LiP-*t*-Bu_2 results in reduction of the metal to the [Cp*WCl_2]$_2$ compound, which cocrystallizes with P_2(*t*-Bu)$_4$, whereas the analogous reaction with LiPHPh gives small yields of Cp*WCl_4(PH_2Ph). The source of PH_2Ph is presumably abstraction of a proton from the solvent (THF) or from a disproportionation of LiPHPh.[84]

XI. Manganese, Technetium, and Rhenium

The chemistry of (ring)ReX_n systems has started to develop after the discovery of Cp*ReO_3. Recent accounts of this research are available.[102,492–496] All the known monocyclopentadienyl halide complexes of group 7 metals are shown in Table VII.

A. Manganese(II)

"(C_5H_4Me)MnCl" was first described as an intermediate during the synthesis of CpMn(C_6H_6) from $MnCl_2$ and CpNa in THF, followed by treatment with PhMgBr, but it was not isolated.[497] The THF stabilized complexes [(C_5H_4Me)MnX(THF)]$_2$ (X = Cl, Br, I) were isolated after reaction of either (C_5H_4Me)$_2$Mn or (C_5H_4Me)Na with MnX_2 in the proper stoichiometric ratio in THF. Reaction of these materials with PEt_3 yields the corresponding [(C_5H_4Me)MnX(PEt_3)]$_2$ complexes. [(C_5H_4Me)MnI(THF)]$_2$ and PMe_3 produce (C_5H_4Me)MnI(PMe_3)$_2$.[498] Anhydrous $MnCl_2$ reacts, after treatment with an equimolar amount of tmeda, with CpNa to yield the tmeda stabilized Cp derivative of Mn(II), CpMnCl(tmeda). Attempts to obtain the base-free CpMnCl by heating in a high vacuum resulted in the sublimation of Cp_2Mn(tmeda) instead.[499]

B. Rhenium(III)

[(C_5Me_4R)$ReCl_2$]$_2$ (R = Me, Et) is obtained from (C_5Me_4R)$ReCl_4$ by reduction with activated (by $HgCl_2$) aluminum.[43,44] [Cp*$ReCl_2$]$_2$ also forms from the chlorination of Cp*Re(O)(*i*-Pr)$_2$ by Cp$TiCl_3$, presumably through the intermediacy of Cp*$ReCl_2$(*i*-Pr)$_2$.[30] The bromide compound Cp*$ReBr_2$ has been obtained by reduction of Cp*Re(O)Br_2 with AlH(*i*-Bu)$_2$[495] or of Cp*$ReBr_4$ with Al/$HgCl_2$ or $SnBu_4$.[43]

[Cp*$ReCl_2$]$_2$ reacts with chlorine in CCl_4 at low temperature to yield [Cp*$ReCl_3$]$_2$, whereas at higher temperature the Re(V) species, Cp*$ReCl_4$, is obtained. It reacts with PMe_3 to afford the mononuclear bis-adduct, Cp*$ReCl_2$(PMe_3)$_2$.[43,44]

C. Rhenium(IV)

[Cp*$ReCl_3$]$_2$ has been obtained from Cp*$ReCl_4$ and SnR_4 (R = Et, *n*-Bu) or by reduction of the same precursor with activated aluminum.[42–44] Its dinuclear constitution has been inferred from its diamagnetism and from an X-ray analysis on [(C_5Me_4Et)$ReCl_2$(μ-Cl)]$_2$, which was obtained by the analogous reduction of (C_5Me_4Et)$ReCl_4$.[43] [Cp*$ReCl_3$]$_2$ has also been obtained from Cp*Re(O)Et_2 and Cp$TiCl_3$.[30] The corresponding iodide species, [Cp*ReI_3]$_2$, is obtained from Cp*ReH_6 by thermal treatment with I_2 or photochemical reaction with MeI.[500]

[Cp*$ReCl_3$]$_2$ reacts with PMe_3 to form the mononuclear paramagnetic Cp*$ReCl_3$(PMe_3) complex.[42,43] Reduction of [(C_5Me_5R)$ReCl_3$]$_2$ with amalgamated aluminum affords the Re(III) dimers, [(C_5Me_4R)$ReCl_2$]$_2$, whereas oxidation with Cl_2 in CCl_4 gives the corresponding Re(V) tetrachloride compounds.[43,44] [Cp*$ReCl_3$]$_2$ reacts with 2-butyne to yield products of disproportionation, the allylidene Re(V) complex Cp*$ReCl_2$(σ,η^3-C(CH_3)C(Cl)CH_2) and the Re(III) alkyne complex Cp*$ReCl_2$(MeCCMe).[43,501]

D. Rhenium(V)

Cp*$ReCl_4$ has been obtained from Cp*ReO_3 and excess Me_3SiCl. This water- and air-sensitive compound reacts with H_2O_2 to reform the trioxo species.[29]

The interaction of Cp*Re(CO)$_3$ with either Br_2 or pyridinium hydrobromide perbromide gives, besides the expected mixture of *cis*/*trans*-Cp*$ReBr_2$(CO)$_2$, a carbonyl-free green material that has been tentatively formulated as Cp*$ReBr_4$. This is also obtained from direct oxidation of Cp*$ReBr_2$(CO)$_2$.[502] Cp*$ReBr_4$ has also been reported by Herrmann.[43]

Cp*$ReCl_4$ adds equimolar amounts of PMe_3 to form the pseudooctahedral Cp*$ReCl_4$(PMe_3) where the phosphine is located in a trans position relative to the Cp* ligand.[29] However, excess of PMe_3 in warm toluene leads to reduction and formation of a mixture of Cp*$ReCl_2$(PMe_3)$_2$ and $ReCl_3$(PMe_3)$_3$.[43] Hydrolysis of Cp*$ReCl_4$ with 1 equiv of H_2O generates the Cp*$ReOCl_2$ complex, whereas more extensive hydrolysis in the presence of base affords [Cp*ReO(μ-O)]$_2$.[125,126] Aminolysis with 3 equiv of RNH_2 gives the imine system, Cp*Re(=NR)Cl_2, plus 2 equiv of RNH_3Cl.[503] The methylimine complex can be obtained in better yields

TABLE VIII. Group 8 Neutral Cyclopentadienyl Metal Halides

ox. state	X: Cl	X: Br	X: I
II		Cp^*FeBr (?)	
	Cp^*RuCl		Cp^*RuI
II,III	$Cp^*_2Ru_2Cl_3$	$Cp^*_2Ru_2Br_3$	$Cp^*_2Ru_2I_3$
III	Cp^*RuCl_2	Cp^*RuBr_2	Cp^*RuI_2
IV	Cp^*RuCl_3	Cp^*RuBr_3	Cp^*RuI_3

from the interaction of Cp^*ReCl_4 and $CH_3N(SiMe_3)_2$.[504] The interaction between Cp^*ReCl_4 and xanthate or dithiocarbamate yields the compounds $Cp^*ReCl_3(S_2CR)$ (R = OCy, NEt_2).[505] In the presence of NEt_3, Cp^*ReCl_4 and toluene-3,4-dithiol or 2-aminothiophenol yield $Cp^*Re(3,4\text{-}S_2C_6H_3CH_3)_2$ or $Cp^*Re(2\text{-}SC_6H_4NH)_2$, respectively. With only 1 equiv of 2-aminothiophenol, $(C_5Me_4Et)ReCl_2(2\text{-}SC_6H_4NH)$ was isolated by starting from $(C_5Me_4Et)ReCl_4$.[506]

The alkylation of $(C_5Me_4R)ReCl_4$ (R = Me, Et) has been investigated. With 1 equiv of $SnMe_4$, the monomethyl derivatives, $(C_5Me_4R)ReCl_3(CH_3)$, are obtained. $SnEt_4$ or $Sn(n\text{-}Bu)_4$, on the other hand, leads to the reduced Re(IV) dimer $[Cp^*ReCl_2(\mu\text{-}Cl)]_2$, presumably through the intermediacy of the unstable Cp^*ReCl_3R (R = Et, *n*-Bu) which eliminate alkyl radicals, found as a mixture of alkane and alkene.[42] CH_3MgCl (4 equiv) yields $Cp^*Re(CH_3)_4$.[507]

Reaction of Cp^*ReCl_4 with 2-butyne, 3-hexyne, or 2-pentyne in the presence of $HgCl_2$-activated Al granules affords $Cp^*ReCl_2(R^1C{\equiv}CR^2)$ (R^1, R^2 = Me, Et) and minor amounts of $[Cp^*ReCl(R^1C{\equiv}CR^2)_2]^+AlCl_4^-$. When the same reduction procedure is carried out in the presence of a diene, the corresponding $Cp^*ReCl_2(diene)$ is obtained.[43,44,501,508]

Cp^*ReCl_4 reacts with $LiAlH_4$ in Et_2O at low temperature, followed by treatment with methanol, to afford a mixture of Cp^*ReH_6 and $[Cp^*ReH_3]_2$,[509] whereas reaction of $(C_5Me_4R)ReCl_4$ with $NaBH_4$ yields exceedingly sensitive materials which could not be isolated, but their subsequent interaction with CpNa followed by sublimation produces $(C_5Me_4R)CpReH$, presumably through the intermediacy of $Cp^*CpRe(BH_4)_x$.[510]

Stepwise dechlorination of Cp^*ReCl_4 can be accomplished with Al/$HgCl_2$. At 20 °C the $[Cp^*ReCl_3]_2$ compound is obtained, whereas at 60 °C further reduction to the Re(III) dimer, $[Cp^*ReCl_2]_2$, occurs.[42-44] Reduction of Cp^*ReBr_4 with either $SnBu_4$ or Al/$HgCl_2$ affords $[Cp^*ReBr_2]_2$.[43]

XII. Iron, Ruthenium, and Osmium

All the known monocyclopentadienyl halide complexes of group 8 metals are shown in Table VIII.

A. Iron

No stable derivatives of Fe(II) or Fe(III) of formula $CpFeX_n$ or $[CpFeX_{n+1}]^-$ (*n* = 1 or 2) appear to have been reported, although several derivatives containing additional neutral ligands are known. Kölle reported that the interaction of $FeBr_2{\cdot}DME$ with 1 equiv of Cp*Li at -80 °C generates an unstable {Cp*FeBr} intermediate. Upon warming, decomposition occurs with formation of decamethylferrocene. Upon subsequent treatment with 1 equiv of CpNa, a mixture of Cp^*_2Fe, Cp^*CpFe, and Cp_2Fe is produced, whereas treatment with CO at -80 °C results in the formation of $Cp^*FeBr(CO)_2$ in 59% yields.[511]

The compound $[HB(pz)_3FeCl_3]^-$ ($HB(pz)_3^-$ = hydrotripyrazolylborate) has been reported,[512] thus the pseudooctahedral $(ring)FeCl_3^-$ seems a reasonable synthetic target.

B. Ruthenium(II)

Syntheses

$[Cp^*RuCl]_4$ has been prepared by interaction of $[Cp^*Ru(OMe)]_2$ with Me_3SiCl[52,513] or more conveniently from the same precursor with LiCl in Et_2O[514] and also from Cp^*RuCl_2 and 1 equiv of Et_3BH^- or zinc in a variety of solvents.[45,46] The zinc reduction is also possible in methanol, however prolonged reduction in this solvent leads to a mixture of $[Cp^*RuCl]_4$ and $[Cp^*Ru(OMe)]_2$.[515] $[Cp^*RuI]_4$ is obtained by halide exchange from the corresponding chloride.[78]

Reactivity

The bridging Ru–Cl bonds of $[Cp^*RuX]_4$ are quite labile and donor ligands easily split the molecule into monomers. CO and PMe_3 react to give Cp^*RuL_2Cl in improved yields with respect to earlier procedures. Similar adducts with bipy, 1,5-COD, and a number of conjugated dienes have also been prepared. With ethylene, a reversible equilibrium is established with the $[Cp^*Ru(\eta^2\text{-}C_2H_4)Cl]_x$ compound.[78,513] With bulky phosphines [e.g. $P(i\text{-}Pr)_3$, PCy_3], the coordinatively unsaturated $Cp^*Ru(PR_3)Cl$ compounds are obtained.[20,79,516]

$[Cp^*RuCl]_4$ dissolves in MeCN to yield a solution of the $Cp^*Ru(MeCN)_3^+$ cation with Cl^- as the counterion from which the stable triflate salt can be isolated by addition of AgO_3SCF_3.[46,517] The solvated complex $[Cp^*Ru(Me_2CO)(H_2O)_2]^+PF_6^-$ has been obtained in acetone by the addition of KPF_6.[45] The chloride can be metathesized by addition of sodium iodide to generate $[Cp^*RuI]_4$[78] and by treatment with MeOH or addition of LiOR (R = Me, Et) to yield $[Cp^*Ru(OR)]_2$.[79,514] With the bulky alkoxide reagent LiO-$[2,6\text{-}(t\text{-}Bu)_2C_6H_3]$, the crystallographically characterized sandwich complex $Cp^*Ru[\eta^5\text{-}OC_6H_3(t\text{-}Bu)_2]$ is obtained where the substituted phenoxide ligand is stabilized in the oxocyclohexadienyl resonance form.[79]

The reaction with allyl chloride in THF instantaneously generates the Ru(IV) allyl complex $Cp^*Ru(\eta^3\text{-}C_3H_5)Cl_2$.[78] Reaction with aromatic compounds gives the corresponding $[Cp^*Ru(\eta\text{-}ring)]^+$ (ring = C_6H_6, 3-methylthiophene, 2,6- or 3,5-lutidine, furan, and pyridine). When pyridine is added in excess of 1 equiv and in acetone, the $[Ru(py)_6]^{2+}$ ion is obtained instead.[45] Reaction with C_6Me_6 in a melt or in hydrocarbon solution affords the $[Cp^*Ru(\eta^6\text{-}C_6Me_6)]^+$ cation, isolated as the PF_6^- salt.[52,513] This compound is difficult to prepare from other Cp^*Ru^{II} sources.

C. Ruthenium(II,III)

The mixed-valence compounds $Cp^*_2Ru_2(\mu\text{-}X)_3$ (X = Cl, Br, I) are obtained by interaction of the corresponding $[Cp^*RuX_2]_2$ with 1 equiv of cobaltocene. As the extent of reduction cannot be controlled entirely by the stoichiometry, complexes $[Cp^*RuX]_4$ being also formed, an easier route to the chloride complex was through conproportionation of $[Cp^*RuCl_2]_2$ with $[Cp^*RuCl]_4$. The mixed-valence complexes are paramagnetic compounds characterized by a broad ^1H NMR singlet and an axial EPR spectrum. The reaction of the chloro complex with a variety of donor ligands affords mixtures of Ru(II) and Ru(III) products.[52]

D. Ruthenium(III)

Syntheses

Cp^*RuCl_2 has been prepared by the reaction of $RuCl_3 \cdot H_2O$ with C_5Me_5H in refluxing methanol[20] or ethanol.[21] The materials obtained from methanol or 2-propanol have the same empirical formula but are generally less soluble in $CHCl_3$ or CH_2Cl_2 and are thought to be higher oligomers compared to the product obtained from ethanol.[21,52] A byproduct of this reaction is Cp^*_2Ru. Aging of the compound with loss of solubility was observed during storage at ambient temperature. Crystals grown from CH_2Cl_2 were shown by X-ray crystallography to be made up of dimers $[Cp^*RuCl(\mu\text{-}Cl)]_2$.[52] The corresponding bromo and iodo complexes are prepared by halide ion metathesis from the chloride system and are formulated as dimers according to osmometric molecular weight determinations and by analogy to the corresponding chloro complex.[52]

Reactivity

Ligand Addition/Substitution. ^1H NMR studies provide evidence for the equilibrium shown in eq 20 (S = solvent molecule):

$$2Cp^*RuX_2(S) \rightleftarrows [Cp^*RuX(\mu\text{-}X)]_2 \rightleftarrows [Cp^*_2Ru_2(\mu\text{-}X)_3]^+X^- \quad (20)$$

The monomeric species is the dominant one in donor solvents, e.g. acetonitrile. The ionic form seems to be present in polar ionizing solvents such as water (prior to hydrolysis) and MeOH, whereas the neutral dinuclear form exists in $CHCl_3$ and CH_2Cl_2. The equilibrium is locked into the ion form by oxidation of the mixed valence chloro complex $Cp^*_2Ru_2(\mu\text{-}Cl)_3$ with $[Cp_2Fe]^+PF_6^-$, to give the hexafluorophosphate salt.[52]

Cleavage reactions of $[Cp^*RuCl_2]_2$ to afford paramagnetic derivatives Cp^*RuCl_2L occur for L = py[52] and PR_3 (R = Me, Et, *i*-Pr, Ph, Cy; R_3 = $MePh_2$).[518,519]

One chloride can be replaced with a bidentate acac ligand in the NEt_3-assisted reaction of Cp^*RuCl_2 with Hacac.[52] Reaction with ArSH (Ar = Ph, *p*-C_6H_4Cl, *p*-C_6H_4Me) in CH_2Cl_2 gives the tris(thiolato)-bridged complexes $[Cp^*Ru(\mu\text{-}SAr)_3RuCp^*]^+Cl^-$ containing a Ru–Ru single bond (2.630 (1) Å). On the other hand, the analogous treatment with $PhCH_2SH$ results in the formation of the neutral complex $[Cp^*RuCl(SCH_2Ph)]_2$. Analogous $[Cp^*RuCl(SR)]_2$ derivatives have been prepared from $[Cp^*RuCl_2]_2$ and Me_3SiSR (R = Et, *i*-Pr, *t*-Bu).[520–522] Further treatment of the latter derivatives with excess SR^- or direct interaction of $[Cp^*RuCl_2]_2$ with excess SR^- leads to the paramagnetic, neutral $[Cp^*Ru(\mu\text{-}SR)_3RuCp^*]$ complexes and to RSSR.[523] The reaction of Cp^*RuCl_2 with $LiAlH_4$ generates the structurally characterized hydride species $[Cp^*Ru(\mu\text{-}H)_2]_2$ which contains a Ru–Ru triple bond.[524]

Redox. Reduction of Cp^*RuX_2 with Cp_2Co sequentially produces the mixed-valence $Cp^*_2Ru_2Cl_3$ complex and the Ru(II) compounds $[CpRuX]_4$, and treatment in ROH in the presence of base gives high yields of the Ru(II) alkoxides, $[Cp^*Ru(\mu\text{-}OR)]_2$ (R = Me, Et, *n*-Pr, *n*-Bu).[52,513]

The result of the reaction between Cp^*RuCl_2 and phosphine ligands described above depends critically on the nature and amount of the phosphine. As the basicity or donor properties of the phosphine increase it becomes more difficult to stabilize a Ru(III) paramagnetic complex and products of metal reduction are obtained instead.[20] When an excess of the bulky phosphines PCy_3 or $P(i\text{-}Pr)_3$ is used, coordinatively unsaturated, 16-electron $Cp^*RuCl(PR_3)$ complexes are obtained. The analogous $P(t\text{-}Bu)_3$ complex was obtained from Cp^*RuCl_2 and the phosphine in the presence of zinc.[518] In the case of the less basic PPh_3, the product of reduction, $Cp^*RuCl(PPh_3)_2$ can still be obtained, but only after prolonged reflux in ethanol.[525] Reduction to Ru(II) products also occurs with a variety of other ligands, such as 1,5-COD or norbornadiene,[21] or with benzene and $AgBF_4$ in EtOH, which yields the mixed-sandwich complex $[Cp^*Ru(\eta^6\text{-}C_6H_6)]^+BF_4^-$.[526] At the reflux temperature of MeOH, EtOH, or PrOH, and without Ag^+, analogous derivatives with benzene, toluene, mesitylene, phenol, and other functionalized aromatic rings have been prepared.[527,528] Modification of this procedure by using silver acetate and by applying ultrasound at the ethanol reflux temperature increased considerably the yields and allowed the preparation of a wider variety of arene derivatives, including binuclear $[(Cp^*Ru)_2(\eta^6,\eta^6\text{-arene})]^{2+}$ compounds where arene = polyarene (e.g. phenanthrene, triphenylene, biphenyl, etc.).[529] Reduction also occurs in the presence of Cp^- or substituted cyclopentadienyl reagents, giving high yield of the mixed-ring ruthenocenes, $Cp^*(ring)Ru$ (ring = Cp, Ind, Fl, C_5Cl_5, $C_5H_4COCH_3$).[530] Pentamethylruthenocene, Cp^*CpRu, has been conveniently prepared by reaction of Cp^*RuCl_2 with CpH in the presence of zinc dust[531] and an analogous reaction with 2,4-dimethyl-2,4-pentadiene gives the half-open ruthenocene $Cp^*Ru(\eta^5\text{-}C_5H_5Me_2)$.[532] The reaction with indenyllithium gives the sandwich compound Cp^*IndRu, which reacts further with $[Cp^*Ru(MeCN)_3]^+$ to give $[Cp^*Ru(\mu\text{-}\eta^5{:}\eta^6\text{-}Ind)RuCp^*]^+$.[533] Cp^*IndRu also form from Cp^*RuCl_2 and IndNa in THF.[534] When no coordinating ligand is present, the interaction with $AgBF_4$ in ethanol generates the cluster $[(Cp^*Ru)_3(\mu^2\text{-}Cl)_2(\mu^2\text{-}H)(\mu^3\text{-}CH)]^+BF_4^-$ in yields as high as 40%.[535]

The above reactions suggest that the Cp^*Ru^{III} moiety is stabilized mainly by donor ligands, and becomes a fairly strong oxidant when it bears acceptor ligands. This conclusion is substantiated by electroanalytical measurements.[536,537] The cyclic voltammetric behavior of $[Cp^*RuX_2]_2$ (X = Cl, Br, I) is complex and solvent-dependent and reflects the presence of the equilibria shown in eq 20. In methanol, two reversible one-electron reduction steps are observed, presumably to afford solvent stabilized dinuclear Cp^*RuX. More complex results are obtained in CH_2Cl_2 and THF, in which the Ru(II) product of reduction was found to be unstable. The first irreversible reduction is assigned to the two-electron reduction of neutral $[Cp^*RuX_2]_2$ followed by synproportionation with starting material to yield the mixed-valence $Cp^*_2Ru_2X_3$, and the second, partially reversible reduction involves the formation of

TABLE IX. Group 9 Neutral Cyclopentadienyl Metal Halides

ox. state	X: Cl	Br	I
II	Cp*CpCl Cp*RhCl	Cp*CoBr	Cp*CoI
II,III,III	$Cp*_2Co_3Cl_6$		
III	$(C_5Me_4R)CoCl_2$ $(C_5R_5)RhCl_2$ $Cp*IrCl_2$	$Cp*CoBr_2$ $(C_5R_5)RhBr_2$ $Cp*IrBr_2$	$(ring)CoI_2$ $(C_5R_5)RhI_2$ $(C_5R_5)IrI_2$

$[Cp*RuX]_2$ which subsequently decomposes. A more complex behavior is observed in the presence of excess Cl^-.[537]

Besides reduction, the $Cp*RuCl_2$ system is also susceptible to oxidation. Treatment with excess X_2 (X = Cl, Br, I) in dichloromethane affords the Ru(IV) derivatives $CpRuX_3$ in excellent yields. With only 1 equiv of I_2, the mixed trihalogeno complex $Cp*RuCl_2I$ was obtained.[54] Treatment with allyl chloride affords the oxidized $Cp*RuCl_2(\eta\text{-}C_3H_5)$ complex and $C_3H_4Cl_2$. The same product is obtained by using allyl alcohol, allyl acetate, allyl benzyl or phenyl ether, allylamine, or allyl phenyl sulfide with C–O, C–N, or C–S bond cleavage and oxidation of the alcohol solvent or the PhS function to disulfide. Allyl bromide gives a mixture of halogen exchange products.[52,538,539]

E. Ruthenium(IV)

The $Cp*RuX_3$ (X = Cl, Br, I) systems are obtained by oxidation of $Cp*RuCl_2$ with excess X_2. Most of the reactivity studies have been carried out on the bromide system. In CH_2Cl_2 as solvent, coordinative addition of selected two-electron donors occurs to afford the saturated Ru(IV) complexes $Cp*RuBr_3L$ (L = CO, PPh_3). On the other hand, reduction of the metal occurs in ethanol, which is transformed to acetaldehyde, with formation of the paramagnetic $Cp*RuBr_2L$ (L = PPh_3, py) complexes. With $NaBH_4$ in dry ethanol in the presence of PPh_3, the trihydride complex, $Cp*RuH_3(PPh_3)$ is formed.[54]

XIII. Cobalt, Rhodium, and Iridium

All the known monocyclopentadienyl halide complexes of group 9 metals are shown in Table IX.

A. Cobalt(II)

$CoCl_2$, $CoBr_2\cdot DME$, and CoI_2 react with Cp*Li in THF at low temperature to form $[Cp*CoX]_2$ in high yields. The chloride compound is more stable than the bromide, and the iodide compound cannot be isolated. Its formation is inferred by the oxidation of the pentane extract with I_2, which gives $Cp*CoI_2$.[81,140,540] $[Cp*CoCl]_2$ has also been conveniently prepared by treatment of $CoCl_2$ with $Cp*SnBu_3$.[541] An alternative preparation method is oxidative addition of 5-halo-1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (halo = chloro, bromo, iodo) to $Co_2(CO)_8$ in petroleum ether at low temperature.[31]

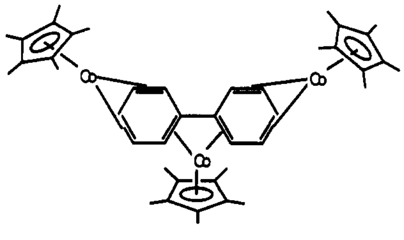
In solutions of coordinating solvents (S), an equilibrium with the 17-electron Cp*CoX(S) mononuclear species is established as shown by a combination of quantitative EPR and ^1H NMR studies (eq 21). The proportion of monomer increases with the coordinating power of the solvent.[81] Selected neutral donors split the molecule into paramagnetic monomers of formula Cp*CoXL (X = Cl, Br; L = py, PMe_3, PMe_2Ph).[81,542] Reaction with CO and with bidentate, chelating ligands (L = CO; L_2 = bipy, COD, 1,3-butadiene), however, leads to valence disproportionation to Co(I) and Co(III) products, e.g. $Cp*CoL_2$ and either $[Cp*CoX_2]_2$ or $Cp*CoX_2L$ or $[Cp*CoXL_2]^+X^-$ depending on the nature of X and L. When L = diphenylacetylene, the Co(I) product is Cp*Co(1,2,3,4-tetraphenylcyclobutadiene).[81,140,540]

$$[Cp*CoX]_2 + 2S \rightleftarrows 2Cp*CoX(S) \qquad (21)$$

Halide exchange with anionic ligands yields $[Cp*Co(\mu\text{-}Y)]_2$ (Y = SMe, OEt, NH_2), and $Cp*_2Co_2(\mu\text{-}X)(\mu\text{-}Y)$ (X = Cl, Br; Y = PPh_2, NMe_2). Reaction of $[Cp*CoCl]_2$ with $TlPF_6$ in propylene carbonate readily generates the solvated $Cp*Co^+$ ion. Without isolation, this has been converted to $[Cp*Co(\eta^6\text{-arene})]^+$ complexes where arene = $[2_n]$cyclophane.[22]

Reduction with Na/Hg in the presence of CO or ethylene yields $Cp*Co(CO)_2$ or $Cp*Co(C_2H_4)_2$, respectively.[540] Although the Cp*CoX compounds are extremely sensitive to oxygen, they are not as reducing as cobaltocene, which suggests that air oxidation may involve oxygen uptake rather than electron transfer. In THF, the chloride compound shows three oxidation waves in the cyclic voltammogram, assigned to two consecutive processes of the dimer and to the oxidation of the solvated monomer which is in equilibrium with it. In the presence of LiCl, the cylic voltammogram simplifies to leave only a single oxidation wave. This is assigned to oxidation of the chloride adduct, $[Cp*CoCl_2]^-$, which has been identified by EPR in frozen solution but not isolated. The product of oxidation of the latter is suggested to be $[Cp*Co(\mu\text{-}Cl)_3CoCp*]^+$.[81]

A peculiar reduction occurs during the interaction between $[Cp*CoCl]_2$ and PhLi, to produce the trinuclear Co(I) system illustrated in XVI, as suggested by NMR. The reaction is presumed to proceed through a "Cp*CoPh" intermediate which would undergo dinuclear reductive coupling of the phenyl groups to afford $[Cp*Co]_2(\mu\text{-}\eta^6\text{:}\eta^6\text{-Ph-Ph})$. The latter loses in part biphenyl and rearranges to the product in order to achieve an 18-electron count.[543]



XVI

From the low-temperature reaction of $[Cp*CoCl]_2$ with NO, the structurally characterized $(Cp*CoCl)_2(\mu\text{-}NO)(\mu\text{-}Cl)$ has been obtained in low yields.[541]

B. Rhodium(II)

Although the Rh(III) $[Cp*RhCl_2]_2$ system has been known for several years, only recently has its Na/Hg reduction to $[Cp*RhCl]_2$ been discovered.[47,48] No iridium analogue has been reported to date. The compound is reoxidized spontaneously to the Rh(III) precursor by CH_2Cl_2 or $CHCl_3$, and it reacts with molecular oxygen to afford a thermally sensitive material formulated as the asymmetric dimer $Cp^*Rh(\mu,\eta^1:\eta^2\text{-}O_2)(\mu\text{-}Cl)RhClCp^*$ and with nitrosobenzene to give the crystallographically characterized $Cp^*Rh(\mu,\eta^1:\eta^2\text{-}PhNO)(\mu\text{-}Cl)RhClCp^*$ compound.[48] Compounds $[(C_5H_4PPh_2)RhX]_2$ (X = Cl, I) have been prepared by treatment of $[(C_5H_4PPh_2)Rh(solvent)]^{2+}$ (solvent = CH_2Cl_2) with the corresponding halide. NMR work shows that the PPh_2 phosphorus is coordinated to the metal, and a metal–metal bonded dinuclear structure with terminal halide ligand and bridging $C_5H_4PPh_2$ groups has been proposed.[544]

C. Cobalt(II,III,III)

The compound $(C_5Me_4Et)_2Co_3Cl_6$ is one of the products of the reaction of $CoCl_2$ with $(C_5Me_4Et)SnMe_3$ followed by addition of Cl_2. Its structure is uncertain as an X-ray analysis has not been carried out. The compound has a low molar conductance in CH_2Cl_2. Treatment of this material with water or $CaCl_2{\cdot}H_2O$ in a chlorinated solvent (CH_2Cl_2, chlorobenzene) produces $[(C_5Me_4Et)CoCl_2]_2$ and, from the latter, the trinuclear mixed-valence species can be reobtained by prolonged treatment with warm chlorobenzene. Treatment with aqueous $FeCl_2/HCl$ in air gives $[(C_5Me_4Et)_2Co_2(\mu\text{-}Cl)_3]^+[FeCl_4]^-$, whereas treatment with aqueous NH_3 followed by PF_6^- produces $[(C_5Me_4Et)Co(NH_3)_3][PF_6]_2$. Treatment with $AlCl_2Et$ in benzene or toluene and then PF_6^- in water gives high yields of $[(C_5Me_4Et)Co(\eta^6\text{-}ring)][PF_6]_2$ (ring = C_6H_6, $C_6H_5CH_3$), whereas if the $AlCl_2Et$ treatment is conducted in cyclohexane followed by the addition of cyclohexa-1,3-diene and then aqueous PF_6^-, the $[(C_5Me_4Et)Co(\eta^5\text{-}C_6H_7)][PF_6]$ salt is formed.[545]

D. Cobalt(III)

$\{CpCoI_2\}_n$ has been prepared by thermal decarbonylation of the mononuclear carbonyl adduct, $CpCoI_2(CO)$, which is obtained by oxidative addition of I_2 to $CpCo(CO)_2$. The similar preparation of the corresponding bromide compound failed and only cobalticenium salts were obtained. For the chloride system, the $CpCoCl_2(CO)$ precursor could not be prepared.[546] The same strategy also led to the formation of Cp^*CoX_2.[546–548] The neutral iodide dimer containing a functionalized ring, $\{[C_5Me_4(CH_2CH_2CH{=}CH_2)]CoI_2\}_2$, is obtained from $[C_5Me_4(CH_2CH_2CH{=}CH_2)]Co(CO)_2$ and I_2, which generates the isolable diiodide monocarbonyl intermediate, followed by thermal decarbonylation either in the solid state or in solution of a high-boiling hydrocarbon. Intermolecular iodide bridge formation is preferred to intermolecular complexation of the double bond of the 3-butenyl side chain.[549,550] $\{CpCoI_2\}_n$ also forms from the reaction of $CpCo(\eta^4\text{-}C_5H_6)$ with I_2.[551]

The $[Cp^*CoX_2]_2$ (X = Cl, Br) dimers have also been obtained from the valence disproportionation of $[Cp^*CoX]_2$ with dienes.[140,540] Reaction of anhydrous $CoCl_2$ with $(C_5Me_4Et)SnMe_3$, followed by treatment with Cl_2 gas, affords the $[(C_5Me_4Et)CoCl_2]_2$ complex together with the trinuclear compound $(C_5Me_4Et)_2Co_3Cl_6$ described in the previous section. The two products can be interconverted (vide supra). The dinuclear formulation of the green Co(III) product is based on molecular weight determinations.[545] In weakly coordinating solvents such as THF, MeOH, or acetone, $CpCoI_2$ rapidly decomposes to produce, among other products, the cobalticenium ion, whereas the compound is quite stable in benzene and CH_2Cl_2. The corresponding Cp* compound is stable toward this decomposition pathway.[546]

In an attempt to synthesize Cp^*_2Co, it was found that the reaction of $[Co(NH_3)_6]Cl_2$ and Cp^*Li, followed by in situ oxidation with $FeCl_3$, produces $[Cp^*Co(\mu\text{-}Cl)_3CoCp^*]^+$. Salts of $[Cp^*Co(\mu\text{-}X)_3CoCp^*]^+$ (X = Cl, Br, I) can also be obtained by oxidation of the corresponding $[Cp^*CoX]_2$ with FeX_3 (X = Cl, Br) or I_2[140,540] and $[(C_5Me_4Et)_2Co_2(\mu\text{-}Cl)_3]^+$ was obtained from the trinuclear mixed-valence $(C_5Me_4Et)_2Co_3Cl_6$ and aqueous $FeCl_2/HCl/O_2$.[545]

A solvent-dependent equilibrium is established between the species $[Cp^*CoX_2]_2$ and $[Cp^*Co(\mu\text{-}X)_3CoCp^*]^+X^-$ (eq 21a); toluene favors the neutral compound, whereas the ionic form is present in nitromethane. In dichloromethane, a mixture of the two

$$[Cp^*CoX_2]_2 \rightleftarrows [Cp^*Co(\mu\text{-}X)_3CoCp^*]^+X^- \quad (21a)$$

forms is present with the relative amount of ionic form increasing in the order Cl < Br < I.[140] The $[Cp^*_2Co_2(\mu\text{-}Cl)_3]_2[Co_2Cl_6]$ salt was unexpectedly isolated from the reaction of $Na^+[Cp^*_2Co_2(\mu\text{-}CO)_2]^-$ with $GeMe_2Cl_2$.[105]

$CpCoI_2$ forms a mono-adduct with PPh_3 and with py.[546] Cp^*CoI_2 forms adducts with PPh_3, PMe_2Ph, $P(OPh)_3$, $AsPh_3$, and *t*-BuNC. An excess of the latter yields $[Cp^*CoI(CN\text{-}t\text{-}Bu)_2]I$.[134,552] Analogous adducts have been obtained from $[C_5Me_4(CH_2CH_2CH{=}CH_2)]CoI_2$.[550] Other $(C_5Me_4R)CoX_2L$ adducts form from $(C_5Me_4R)CoX_2$ and PPh_3, py (only Cl), or CO (only Br, I), whereas bipy, dppe, and PMe_2Ph give $[(C_5Me_4R)CoXL_2]^+X^-$.

The halide ligands can be replaced by basic solvents, especially if in the presence of Ag^+. In aqueous NH_3, the $[(C_5Me_4Et)Co(NH_3)_3]^{2+}$ ion is obtained.[140,545] The solvent adduct $[Cp^*Co(MeCN)_3][PF_6]_2$ has been obtained from Cp^*CoI_2 and $AgPF_6$ in acetonitrile, whereas a similar reaction in dimethyl sulphoxide leads to rupture of the Cp*–Co bond and formation of $[Co(OSMe_2)_6][PF_6]_2$. In acetone, on the other hand, the $[Cp^*Co(OCMe_2)_3][PF_6]_2$ product appears to undergo a rapid solvolysis of the PF_6^- anion to give a difluorophosphate complex which, contrary to the rhodium analogue, is unstable and decomposes to give several unidentified products.[134] $CpCo^{2+}$ species solvated by acetone, trifluoroacetic acid, or propylene carbonate have also been prepared by using $[CpCoI_2]_n$ and $AgBF_4$. These species are unstable and must be generated in the presence of a substrate; e.g., arenes such as $[2_n]$-cyclophane form $[CpCo(\eta^6\text{-}arene)]^{2+}$ complexes. Similar intermediates containing the Cp* ring have been obtained from $[Cp^*CoCl_2]_2$ and $AgBF_4$ in the same solvents.[22] Water spontaneously and completely converts the $[Cp^*CoX_2]_2$ (X = Cl, Br) complexes to solutions of the $[Cp^*Co{\cdot}aq]^{2+}$ cations. Spectroscopic and electrochemical data support the presence of mononuclear dications in acidic solution and dinuclear $[Cp^*Co(\mu\text{-}OH)_3CoCp^*]^+$ ions as the major species at Ph > 9. The latter has been isolated as the BPh_4^- salt.[127] KOH in isopropyl alcohol, on the other hand, converts $[Cp^*CoX_2]_2$ to $[Cp^*CoX]_2(\mu\text{-}H)(\mu\text{-}X)$ (X = Cl, Br, I).[548] The halide ligands in $[Cp^*CoX_2]_2$ (X = Cl, Br) can also be exchanged with arenes in the presence of $AlCl_3$ to afford the mixed-ring sandwich complexes $[Cp^*Co(\eta^6\text{-arene})]^{2+}$.[553] The reaction of $[Cp^*CoCl_2]_2$ with dimethylglyoxime ($dmgH_2$) gives $Cp^*Co(dmgH)Cl$.[554]

Reduction of $[(C_5Me_4Et)CoCl_2]_2$ or $[Cp^*CoI_2]_2$ with Na/Hg in the presence of excess olefin or diene gives $(C_5Me_4R)CoL_2$ (L = ethylene; L_2 = butadiene, COD).[545,547,555,556] Analogous reduction in the presence of propylene, followed by treatment with $P(OMe)_3$, results in the formation of $CpCo(C_2H_3CH_3)[P(OMe)_3]$.[557]

E. Rhodium(III)

Reviews covering both general and particular aspects of rhodium(III) as well as iridium(III) cyclopentadienyl–halide chemistry up to the early 1980's are available.[5d,558–560]

Syntheses

$[CpRhX_2]_n$ (X = Br, I) has been obtained by addition of the appropriate dihalogen to $CpRh(1\text{-}exo\text{-}C_6H_5C_5H_5)$.[561] The chloride compound has been obtained by reflux of $RhCl_3\cdot 3H_2O$ with freshly cracked CpH in methanol[76] and from $CpRhCl(\eta^3\text{-}C_3H_5)$ with HCl in MeOH.[562] Kasahara et al. reported that $CpRhI_2$ is also obtained by a remarkable ring contraction from $[RhCl(COD)]_2$ and I_2 in ether at 0 °C[563] but later attempts to repeat this procedure have not been successful.[76]

Reaction of the commercial $RhCl_3\cdot xH_2O$ with hexamethyl(Dewar benzene) in methanol at 65 °C gives a nearly quantitative yield of $[Cp^*RhCl_2]_2$.[564] An alternative preparative method is interaction of the same rhodium starting material with 1-(1-chloroethyl)-pentamethylcyclopentadiene.[76,565,566] This material can also be conveniently prepared from $RhCl_3\cdot xH_2O$ and Cp*H in methanol.[22] $[(C_5Me_4Et)RhCl_2]_2$ has been obtained from $RhCl_3\cdot xH_2O$ and C_5Me_4EtH,[567] and more recently the entire homologous series of $[(C_5Me_nH_{5-n})RhCl_2]_2$ (n = 0–5) has been made available through the interaction of hydrated $RhCl_3$ and the corresponding cyclopentadiene in warm methanol.[24]

$[Cp^*RhBr_2]_2$ has been prepared from $RhBr_3\cdot 2H_2O$ and hexamethyl(Dewar benzene) or by halide exchange from the corresponding chloride with NaBr in acetone or LiBr in MeOH.[568] Recrystallization from 1,2-dichloroethane resulted in partial halide exchange with chloride originating from the solvent.[569] A 55:45 mixture of $[Cp^*RhBr_2]_2$ and $[CpRhBr_2]_2$ is generated by oxidation of $CpRh(\eta^4\text{-pentamethylcyclopentadiene})$ with N-bromosuccinimide. An analogous mixture of the chlorides is obtained by treatment of the same precursor with Cl_2 or HCl.[570] The $[Cp^*RhI_2]_2$ compound has been prepared by halide exchange from the corresponding chloride.[76,564,565,571] It is also formed from the reaction of $Cp^*RhI(Ar)(CO)$ with MeI, which also gives ArCOMe,[572] and from $Cp^*RhMePh(CO)$ and PhI.[573]

Reactivity

Adducts and Substitution Reactions. $[Cp^*RhCl_2]_2$ has labile chloride ligands and has a tendency to become cationic with three bridging anionic ligands. For instance, it reacts with $NaBPh_4$ in MeOH to produce $[Cp^*Rh(\mu\text{-}Cl)_3RhCp^*]BPh_4$ and with $TlPF_6$ to give the PF_6^- salt. These reactions are reversible; treatment with a source of Cl^- regenerates the neutral precursor. With NaOH, $AgPF_6$, Ag_2O, or $AgNO_3$ in water, the $[Cp^*Rh(\mu\text{-}OH)_3RhCp^*]^+$ complex is obtained,[141,574,575] which in acidic solution gives the less well-characterized aquo cation, $[Cp^*Rh(aq)]^{2+}$.[47]

The halogen bridges are cleaved by a variety of monodentate (L) or bidentate (L_2) ligands to form mononuclear $(C_5R_5)RhX_2L$, $[(C_5R_5)RhXL_2]^+$, or $[(C_5R_5)RhL_3]^{2+}$ or binuclear $[(C_5R_5)RhX_2]_2(L\text{-}L)$ derivatives. This occurs with amines, pyridines,[76,561,564,565,576] bipy and phen,[132,133] hydrazines,[577] dimethylglyoxime,[554] isocyanides,[578–583] phosphines,[76,564,565,584–589] pyridazine,[590] and sulfur ligands.[135,591] Addition of Me_2AsSMe produces $Cp^*RhCl_2(Me_2AsSMe)$ where the monodentate ligand is coordinated through arsenic.[591b] With dimethyl sulfide, a compound of stoichiometry $[Cp^*RhCl_2]_2(SMe_2)$ containing a bridging thioether is obtained.[135] The macrocyclic 1,4,7,10,13,16-hexathiacyclooctadecane ligand forms the $[Cp^*{}_2Rh_2Cl_2(S_6C_{12}H_{24})]^{2+}$ cation where the two rhodium centers have terminal chlorides and are bridged by the macrocyclic ligand.[592] Cleavage of the bridging iodides in $[Cp^*RhI_2]_2$ by $P(OMe)_3$ is followed by Michaelis–Arbuzov type reactivity to generate $Cp^*RhI[P(OMe)_3][P(O)(OMe)_2]$ in acetone, or $\{Cp^*Rh[P(OMe)_3]_2[P(O)(OMe)_2]\}^+$ in methanol.[593]

Exchange of chloride with other halides occurs as mentioned above. Other exchange reactions with AgO_2CCH_3,[141] thiolates, $1,2\text{-}C_2(CN)_2S_2^{2-}$,[135] S_2CZ^- (Z = NR_2, Me, PR_2, OR),[135,594,595] N_3^-, NCO^-, SCN^-, NO_2^-, NO_3^-,[596] β-diketonates,[597] catechol,[598] N-alkyl-N-nitrosohydroxylamido ($RN(NO)O^-$),[599] and α-aminoacidates[600] to give $\{Cp^*RhX_2\}_n$, $[Cp^*RhX_3]^-$, Cp^*RhX_2L, or $Cp^*RhClXL$ type complexes have been described. The functionalized carboxylate $Ph_2PCH_2COO^-$ gives mononuclear $Cp^*RhCl(OCOCH_2PPh_2)$ where the new ligand is O and P bound to the metal center.[601] Diphenylphosphine sulfide, $Ph_2P(S)H$, in the presence of KOH, gives the unstable $Cp^*Rh(PSPh_2)_2$ which rearranges to the dithiophosphinate complex $Cp^*Rh(S_2PPh_2)(PSPh_2)$.[602,603] Elimination of Me_3SiCl during the reaction of $[Cp^*RhCl_2]_2$ with $(Me_3Si)_2S$ yields the cubane cluster $[Cp^*Rh(\mu_3\text{-}S)]_4$.[604] Hydrotripyrazolylborate and similar reactants give the $[Cp^*Rh(Ypz_3)][PF_6]_n$ products (Y = BH, Bpz, n = 1; Y = CH, n = 2).[605,606] The pyrazolate anions (from pzH and Et_3N) reacts with ring-unsubstituted $[CpRhCl_2]_2$ to form the bis-pyrazolate-bridged dimer, $[CpRhCl(\mu\text{-}pz)]_2$.[607] Related to the above exchange reactions is also the formation of the mixed-metal $Cp^*ClRh(\mu\text{-}SPPh_2)_2P(S_2CNEt_2)$ and $\{(\eta^6\text{-}C_6Me_6)Ru(\mu\text{-}Cl)[\mu\text{-}PO(OMe)_2]_2RhCp^*\}^+$ systems by interaction with $[Pt(S_2CNEt_2)(Ph_2PS)_2]^-$ and $\{(\eta^6\text{-}C_6Me_6)RuCl[PO(OMe)_2]_2\}^-$, respectively.[608,609]

Interaction between $[Cp^*RhCl_2]_2$ and Na_2MoO_4 in water affords the compound $[Cp^*RhMoO_4]_4$, whose structure shows a triple cubane framework consisting of two $Rh_2Mo_2O_8$ cores,[610] whereas $(PPh_4)_2WS_4$ gives the linear mixed-metal trimer, $[Cp^*RhCl(\mu\text{-}S)_2]_2W$.[611] Under slightly different conditions, the latter reagent gives another derivative, $[Cp^*RhW(O)(\mu\text{-}S_2)(\mu\text{-}S)_2]_2$.[612] With $NaVO_3$, the $(Cp^*Rh)_4V_6O_{19}$ molecule is assembled. This consists of an octahedral arrangement of vanadium atoms around a central oxygen atom, each vanadium being in turn surrounded by six oxygen atoms in an octahedral arrangement. The four Cp*Rh units cap alternate triangular face of the resulting "superoctahedron" for an overall T_d molecular symmetry.[613] The *cis*-$Nb_2W_4O_{19}^{4-}$ anion gives the rhodium-containing polyoxometalate $[Cp^*Rh(Nb_2W_4O_{19})]^{2-}$ as a mixture of two diastereomers.[614]

Interaction between $CpRhBr_2$ and $[CpM(CO)_n]^-$ (2 equiv; M = Ni, n = 1; M = Fe, n = 2; M = Mo, W, n = 3) yields the corresponding $Cp_3RhM_2(CO)_{2n}$ clusters.[147] $[Cp^*RhCl_2]_2$ and 2 equiv of the dianion $Fe_3(CO)_9(PPh)_2^{2-}$ give the mixed metal clusters $Cp^*RhFe_3(CO)_x(\mu_4\text{-}PPh)_2$ (x = 8, 9),[146] whereas with 4 equiv of $Co(CO)_4^-$ the cluster $Cp^*{}_2Rh_2Co_2(CO)_7$ is obtained.[145]

The *arachno*-thiaborane $[6\text{-}SB_9H_{12}]^-$ ion reacts with $[Cp^*RhCl_2]_2$ to form several products, one of which has been identified by X-ray crystallography as the pseudoicosahedral $(Cp^*Rh)_2(SB_9H_8Cl)$ with two Cp^*Rh fragments occupying two adjacent vertices of the polyhedral structure.[615] Chlorine transfer to a borane cluster also occurs during the reaction between $[Cp^*RhCl_2]_2$ with *arachno*-$B_{10}H_{12}$-6,9-$(PMe_2Ph)_2$, to give the eleven-vertex nido compound 7-$(Cp^*Rh)B_{10}H_{11}$-8-Cl-11-(PMe_2Ph) in low yield.[616,617] Other rhodaborane clusters obtained from $[Cp^*RhCl_2]_2$ and borane or carborane reagents are *closo*-[1-$(Cp^*Rh)B_{10}H_9$-2-X] (X = H, OMe),[617] *nido*-[6-$(Cp^*Rh)B_9H_{13}$],[618] $(Cp^*Rh)_2B_{17}H_{19}$,[619] *closo*-[2-Cp^*Rh-1,6-$C_2B_7H_9$],[620] *nido*-[5-$(Cp^*Rh)B_9H_{13}$],[621] *closo*-[3-Cp^*Rh-1,2-$C_2B_9H_{11}$],[622] and the mixed-metal isonido cluster compounds $Cp^*{}_2RhHIrB_9H_{10}$ and $Cp^*{}_2RhHIrB_9H_9Cl$.[623] The telluraborane *nido*-[7-$TeB_{10}H_{11}]^-$ gives *closo*-[2-(Cp^*Rh)-1-$TeB_{10}H_{10}$].[624] Some of these reactions generate several different byproducts while others are quite selective and afford products in high yields. The $[CpRhI_2]_n$ material reacts with Tl[3,1,2-$TlC_2B_9H_{11}$] to produce the rhodacarborane *closo*-3,1,2-$CpRhC_2B_9H_{11}$.[625]

$[Cp^*RhCl_2]_2$ reacts in alcohol solvent with CO in the presence of excess Et_3N to undergo ligand substitution followed by nucleophilic addition at the coordinated CO with production of $Cp^*Rh(CO)(COOR)_2$ (R = Me, Et).[626]

Formation of $[Cp^*Rh(solvent)_3][PF_6]_2$ (solvent = MeCN, Me_2SO, pyridine, acetone, CH_2Cl_2, MeOH, CS_2 or NH_3) complexes occurs by treating $[Cp^*RhCl_2]_2$ with $AgPF_6$ in the appropriate solvent.[135–137] These complexes are very useful intermediates; they interact with phosphines, phosphites, sulfides,[135,627] and thionitrosodimethylamine[628] to form $[Cp^*RhL_3]^{2+}$ complexes and/or other mixed-ligand derivatives, with the $P_3O_9{}^{3-}$ ion to form $[Cp^*Rh(P_3O_9)]^-$,[629] with $(Bu_4N)_9P_2W_{15}Nb_3O_{62}$ to form impure samples of $(Bu_4N)_7[Cp^*RhP_2W_{15}Nb_3O_{62}]$,[630] with CpM(COT) (M = Co, Rh) to form the asymmetric $[Cp^*Rh(COT)MCp]^{2+}$ systems,[631] and with a number of aromatic compounds to form mixed sandwich complexes $[Cp^*Rh(ring)]^{2+}$ (e.g. ring = arene, aniline, anisole, oxycyclohexadienyl, thiophenes).[137,632–636] When the aromatic system is indene or the like, the first $[Cp^*Rh(\eta^6\text{-polyene})]^{2+}$ product often rapidly loses a proton to afford a monocharged sandwich species, $[Cp^*Rh(\eta^5\text{-polyenyl})]^+$, where the condensed aromatic system binds the metal through a cyclopentadienyl ring.[637,638] $[Cp^*Rh(ring)]^{2+}$ complexes have also been obtained directly from $[Cp^*RhCl_2]_2$ by refluxing with the aromatic compound in trifluoroacetic acid.[639] The mixed-sandwich complex $Cp^*Rh(\eta^5\text{-}C_4H_4BN\text{-}i\text{-}Pr_2)$ has been obtained from $[Cp^*RhCl_2]_2$ and $Li_2[C_4H_4BN\text{-}i\text{-}Pr_2]$[640] and, similarly, $Cp^*Rh[\eta^6\text{-}C_4H_4B_2(NMe_2)_2]$ is obtained by using $Li_2[1,2\text{-}C_4H_4B_2(NMe_2)_2]$.[641]

The alkylation of $[Cp^*RhCl_2]_2$ is a particularly interesting reaction. Reaction with MeLi gives low yields of the Rh(IV) derivative *cis*-$[Cp^*RhMe(\mu\text{-}CH_2)]_2$, which converts to the corresponding trans isomer. The isomerization is catalyzed by Lewis acids.[642] The yields of the Rh(IV) bis-methylidene-bridged dimer can be increased to almost quantitative by adding excess acetone as oxidizing agent. Carrying out the Al_2Me_6 addition at low temperature generates an intermediate species originally interpreted as $Cp^*RhMe_2(\mu\text{-}Me)Al(Me)(\mu\text{-}Cl)_2AlMe_2$ and later reformulated as $[Cp^*RhMe_3]_2AlMe$, according to eq 22 (M = Rh).[643]

$$2[Cp^*MCl_2]_2 + 5Al_2Me_6 \rightarrow 2(Cp^*MMe_3)_2AlMe + 4Al_2Me_4Cl_2 \quad (22)$$

Addition of ligands to this species generates complexes of the type Cp^*RhMe_2L, whereas oxidation with air or, better, with a hydride acceptor such as acetone, results in smooth convertion into *cis*-$[Cp^*RhMe(\mu\text{-}CH_2)]_2$ which rapidly isomerizes to the trans compound.[644,645] In addition, a less understood reaction takes place when $[Cp^*RhCl_2]_2$ and Al_2Me_6 are mixed in very concentrated solution to give methane and the trinuclear di-μ_3-methylidyne complex $(Cp^*Rh)_3(\mu_3\text{-}CH)_2$.[646] Alkylation with Al_2Et_6, on the other hand, produced $Cp^*Rh(C_2H_4)_2$ as the major product in addition to small amounts of the 1-methylallyl complex $Cp^*RhCl(CH_2CHCHMe)$. This reaction differs dramatically from the analogous alkylation of $Cp^*RhCl_2(PMe_3)$, which gives the expected diethyl complex, $Cp^*RhEt_2(PMe_3)$.[647]

$[Cp^*RhCl_2]_2$ reacts with mono- or polyolefins in ethanol, usually in the presence of a base such as Na_2CO_3. Products are either of the $Cp^*RhCl(allyl)$, $[Cp^*Rh(\eta^5\text{-dienyl})]^+$, or $Cp^*Rh(diolefin)$ type with the implication of hydride intermediates. The latter are relevant to the activity of these materials as olefin hydrogenation catalysts.[570,648–651] In the absence of olefin, the $[Cp^*RhCl_2]_2$ compound reacts with alcohol and base to form the dinuclear hydride $(Cp^*RhCl)_2(\mu\text{-}H)(\mu\text{-}Cl)$. The same product is obtained when the Rh precursor is reacted with $NaBH_4$ or $LiAlH_4$ or H_2 in a basic medium.[5a,652]

Redox. A cyclic voltammetric investigation of $[Cp^*RhCl_2]_2$ in CH_2Cl_2 is consistent with the reactivity shown in Scheme II.[47]

Scheme II

$$[Cp^*RhCl_2]_2 \xrightleftharpoons{+e,\ -Cl^-} Cp^*Rh(\mu\text{-}Cl)_3RhCp^* \quad (23)$$

$$2Cp^*Rh(\mu\text{-}Cl)_3RhCp^* \rightarrow [Cp^*RhCl_2]_2 + [Cp^*RhCl]_2 \quad (24)$$

$$Cp^*Rh(\mu\text{-}Cl)_3RhCp^* \xrightarrow{+e,\ -Cl^-} [Cp^*RhCl]_2 \quad (25)$$

$$[Cp^*RhCl]_2 \xrightarrow{-2e,\ +2Cl^-} [Cp^*RhCl_2]_2 \quad (26)$$

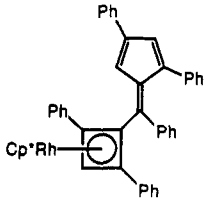
The valence disproportionation of eq 24 is slower in the presence of excess Cl^-, indicating chloride dissociation as the rate-determining step. In acetone, the cyclic voltammogram is only slightly different with respect to the voltammogram obtained in CH_2Cl_2. The difference is due to equilibrium 27, which is shifted to the right in the more ionizing acetone solvent. As a result, the oxidation wave due to process 28, which occurs at a more positive potential with respect to process 23, is more pronounced.

$$[Cp^*RhCl_2]_2 \rightleftarrows [Cp^*Rh(\mu\text{-}Cl)_3RhCp^*]^+ + Cl^- \quad (27)$$

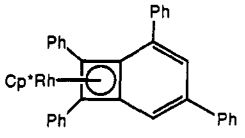
$$[Cp^*Rh(\mu\text{-}Cl)_3RhCp^*]^+ \xrightarrow{+e} Cp^*Rh(\mu\text{-}Cl)_3RhCp^* \quad (28)$$

The reduced complex $[Cp^*RhCl]_2$ has been obtained by chemical reduction of $[Cp^*RhCl_2]_2$ with Na/Hg[48] or with Cp_2Co.[47]

In analogy to the reaction with olefins, the reaction of $[Cp^*RhCl_2]_2$ with alkynes also requires base. Under these conditions, phenylacetylene gives two products, XVII and XVIII, both containing a coordinated cyclobutadiene functionality.[653]



XVII



XVIII

$[Cp^*RhCl_2]_2$ reacts with zinc under CO to produce $Cp^*Rh(CO)_2$,[654] with Na/Hg in the presence of a variety of phosphine or phosphite ligands to yield Cp^*RhL_2 complexes[587] and with $Ni(PF_3)_4$ to generate $Cp^*Rh(PF_3)_2$. In the latter reaction the nickel complex functions as both PF_3 source and dehalogenating agent.[655,656] Conproportionation of $[Cp^*RhCl_2]_2$ with $Cp^*Rh(PMe_2H)_2$ gives the Rh(II) dimer $[Cp^*Rh(\mu\text{-}PMe_2)]_2$.[588] In the reaction with methoxydivinylborane, cobaltocene acts as the reducing agent and chloride acceptor for $[Cp^*RhCl_2]_2$ to afford Cp_2CoCl and $Cp^*Rh[MeOB(CH{=}CH_2)_2]$.[657]

The reaction of $[Cp^*RhCl_2]_2$ with R_3SiH gives the Rh(V) dihydride compounds $Cp^*Rh(H)_2(SiR_3)_2$ (R_3 = Me_3, Et_3, Me_2Ph, $n\text{-}Bu_3$).[658-661] The analogous reaction with Ph_3SiH gives a mixture of $Cp^*RhH_2(SiPh_3)_2$ and $Cp^*RhH_2(SiPh_3)(SiPh_2Cl)$,[662] whereas that with $(EtO)_3SiH$ to generate $Cp^*Rh(H)_2[Si(OEt)_3]_2$ requires the presence of triethylamine.[663] The intermediate $Cp^*_2Rh_2HCl_3$ complex was detected in these reactions.

The possibility to stabilize Cp*Rh (and Ir) complexes in higher oxidation state by the use of dihalogen oxidation has been speculated. However, reaction of $[Cp^*MX_2]_2$ (M = Rh, Ir) with chlorine or bromine gave at best only unstable materials and $[Cp^*RhCl_2]_2$ does not react at all with chlorine. However, $[Cp^*RhI_2]_2$ reacts with 1 equiv of I_2 to give "Cp^*RhI_3" and with excess I_2 to give "Cp^*RhI_4". Spectroscopic data are consistent with these molecules as being dimers of Rh(III) with polyiodide chains as ligands, in analogy with the structurally characterized Ir analogues.[664]

F. Iridium(III)

Syntheses

$[Cr^*IrCl_2]_2$ has been prepared from $IrCl_3{\cdot}3H_2O$ and 1-(1-chloroethyl)pentamethylcyclopentadiene. The hexamethyl(Dewar benzene) route employed in the rhodium case (vide supra) also generates the desired products but in much lower yields.[76,665] More recently, this material has been conveniently prepared from $IrCl_3{\cdot}xH_2O$ and Cp*H in methanol.[22,23,666] $[(C_5Me_4Et)IrCl_2]_2$ was prepared in low yields from anhydrous $IrCl_3$ and $(Cr_5Me_4Et)Na$, whereas the direct reaction between $IrCl_3{\cdot}xH_2O$ and C_5Me_4EtH, contrary to the rhodium system, fails to give any of the expected product.[567]

Interaction of CpIr(COT) and an equimolar amount of I_2 in methylene chloride at room temperature affords insoluble brown $CpIrI_2$.[667] An analogous synthesis has been accomplished starting from CpIr(η^4-1,3-cyclohexadiene), obtained in situ from $[(\eta^4\text{-}C_6H_8)IrCl]_2$ and CpTl.[668] The Cp* analogue was obtained by halide metathesis from the corresponding chloride and NaI in acetone,[665] whereas $[Cp^*IrBr_2]_2$ was obtained from the chloride and LiBr in MeOH.[568]

"Cp^*IrI_3" and "Cp^*IrI_4" are prepared as described above for the Rh counterparts. The structure of the "triiodide" compound is almost identical with that illustrated above in XV for the Cp^*CrI_3 species, the only difference being the I_4^{2-} ligands that bridge different dinuclear units of Ir(III) are more symmetric ($I^-{\cdots}I_2{\cdots}I^-$ for the Ir compound as opposed to $I_3^-{\cdots}I^-$ for the Cr compound). The "tetraiodide" compound is also formulated as a Ir(III) species.[664]

Reactivity

The $[(C_5R_5)IrX_2]_2$ systems react with amines, pyridines, phosphines, sulfides, CO, and isocyanides to afford derivatives of the $(C_5R_5)IrX_2L$ type.[15,576,583,585,591b,665,667-669] Bipy, phen, and dppe give $[Cp^*IrCl(L\text{-}L)]^+$ cations.[13,133,670]

Exchange of the chloride ligands with other halides occurs readily, and other exchange reactions proceed in general similarly to those of the corresponding rhodium systems,[135-137,141,575,597,600,633,635,671] as do the reactions with olefins.[570,648-651,665] However, the reaction with 2 equiv of LiNH-*t*-Bu per Ir atom to afford the mononuclear imido complex Cp*IrN-*t*-Bu has not been reported for rhodium.[672] Reaction of $[Cp^*IrCl_2]_2$ with pyrazole and KOH yields a neutral $Cp^*Ir(pz)_2(Hpz)$ compound with three equivalent pyrazole ligands on the NMR time scale, whereas the similarly prepared analogue with 3,5-dimethylpyrazole shows two types of ligands in a 2:1 ratio.[673]

Attempts to obtain $[Cp^*_2Ir_2(\mu\text{-}Cl)_3]^+$ by treatment of $[Cp^*IrCl_2]_2$ with $NaBPh_4$ in MeOH in analogy with the rhodium system failed, but reaction with $AgClO_4$ or $TlBF_4$ in dichloromethane gives the corresponding salts $[Cp^*_2Ir_2(\mu\text{-}Cl)_3]X$ (X = ClO_4, BF_4). Addition of iodide to these salts generates $Cp^*_2Ir_2Cl_3I$ which is a mixture of isomers with the iodide in bridging or terminal positions, and treatment with $P(OMe)_3$ gives a mixture of $Cp^*IrCl_2[P(OMe)_3]$ and $[Cp^*IrCl\{P(OMe)_3\}_2]ClO_4$.[107] $[Cp^*Ir(\mu\text{-}Cl)_3IrCp^*]^+$ has also been obtained by treating $[Cp^*IrCl_2]_2$ with 48% aqueous HBF_4 in acetic anhydride/CH_2Cl_2.[639]

Interaction in water with Na_2MoO_4,[610] $(NH_4)_2WS_4$,[612] or $NaVO_3$[613] gives $[Cp^*IrMoO_4]_4$, $[Cp^*IrWO(\mu\text{-}S_2)(\mu\text{-}S)_2]_2$, or $(Cp^*Ir)_4V_6O_{19}$ in complete analogy with the rhodium system. From the *arachno*-$[B_9H_{14}]^-$ system, the *nido*-[6-$Cp^*IrB_9H_{13}$] product is obtained.[621] Reaction with TlB_3H_8, on the other hand, gives a mixture of 2-(Cp^*IrX)B_3H_8 (X = Cl, H) together with some Cp^*IrH_4. The hydride species undergoes a thermal rearrangement to 1-(Cp^*IrH)B_3H_8.[674]

The complex $[Cp^*Ir(acetone)_3]^{2+}$ is the main entry to mixed-sandwich complexes of the type $[Cp^*Ir(\eta^6\text{-ring})]^{2+}$ where ring = arene[138,139] or thiophene.[634,635,675,676] It also reacts with CpRh(COT) to produce the mixed-metal system $[Cp^*Ir(COT)RhCp]^{2+}$.[631] Mixed-sandwich complexes have also been obtained by refluxing $[Cp^*IrCl_2]_2$ with the arene in CF_3COOH as solvent.[639]

The reaction of $[Cp^*IrX_2]_2$ with either KOH or $NaBH_4$ in *i*-PrOH, or H_2 and NEt_3 in CH_2Cl_2 yield the $(Cp^*IrX)_2(\mu\text{-H})(\mu\text{-X})$ (X = Cl, Br, I) complexes in analogy with the rhodium system.[5a,568,652] However, extended treatment of $[Cp^*IrX_2]_2$ or $(Cp^*IrX)_2(\mu\text{-H})(\mu\text{-X})$ with 2-propanol and Et_3N or with H_2 in the presence of a base gives the bis-hydride complexes, $[Cp^*IrX(\mu\text{-H})]_2$, whereas the rhodium analogue forms only the mixed halo–hydrido-bridged system.[568] The reaction of $[Cp^*IrCl_2]_2$ with H_2 in a *i*-PrOH/acetone/H_2O mixture yields $[Cp^*Ir(\mu\text{-H})_3IrCp^*]^+$.[5a] This has been converted with Et_3BH^- to the Ir(V) hydride complex Cp^*IrH_4, which in turns reacts with CCl_4 to regenerate the dichloride parent system.[677] Other Ir(V) compounds, $Cp^*IrH_2Cl(SiEt_3)$ and $Cp^*IrH_2(SiEt_3)_2$, are obtained sequentially from $[Cp^*IrCl_2]_2$ and Et_3SiH. The presence of NEt_3 is beneficial in the second step of this sequence. An analogous oxidation is induced by Bu_3SnH, to give $Cp^*Ir(H)_2(SnBu_3)_2$.[661] The reaction with Ph_3SiH stops at the monosilyl product, $Cp^*IrH_2Cl(SiPh_3)$.[662,678]

$[Cp^*IrCl_2]_2$ reacts with Al_2Me_6 in pentane to initially form the $(Cp^*IrMe_3)_2AlMe$ derivative in analogy to the rhodium system (see eq 22 (M = Ir)).[643] However, subsequent oxidation by air gives the Ir(V) derivative Cp^*IrMe_4 in moderate yields. When acetone was added to this reaction mixture, the formation of products analogous to those obtained for rhodium, i.e. *cis*- and *trans*-$[Cp^*IrMe(\mu\text{-CH}_2)]_2$ is observed, although yields are lower. Other byproducts of this reaction are *cis*-$Cp^*MeIr(\mu\text{-CH}_2)_2IrClCp^*$ and the trinuclear $(Cp^*Ir)_3(\mu_3\text{-CH})_2$ cluster.[645,679,680] When $[Cp^*IrCl_2]_2$ and Al_2Me_6 are mixed in toluene or benzene followed by quenching with acetone, a mixture of *trans*-*m*- and *p*-tolyl-$Cp^*(CH_3C_6H_4)Ir(\mu\text{-CH}_2)_2IrMeCp^*$ complexes or the corresponding phenyl analogue forms in low yields, showing that oxidative addition of the solvent C–H bonds has occurred.[681] The alkylation with Al_2Et_6 proceeds in analogy to the rhodium system to form $Cp^*Ir(C_2H_4)_2$ and minor amounts of $Cp^*IrCl(CH_2CHCHMe)$.[647] The reaction of $[Cp^*IrCl_2]_2$ with allyl Grignard affords $Cp^*Ir(\eta^3\text{-C}_3H_5)Cl$.[682,683]

$Fe_3(CO)_{12}$ reduces $[Cp^*IrCl_2]_2$ to a mixture of $Cp^*Ir(CO)_2$ and $Cp^*IrFe_2(CO)_9$.[76,684] A better and higher yield procedure for the formation of the Ir dicarbonyl species is reduction of $[Cp^*IrCl_2]_2$ with Zn under a CO atmosphere.[23] $Ni(PF_3)_4$ gives a mixture of the reduced $Cp^*Ir(PF_3)_2$ system and an isomer of the latter which derives from oxidative addition of a P–F bond, $Cp^*IrF(PF_2)(PF_3)$.[655,656]

XIV. Nickel, Palladium, and Platinum

All the known monocyclopentadienyl halide complexes of group 10 metals are shown in Table X.

TABLE X. Group 10 Neutral Cyclopentadienyl Metal Halides

ox. state	X: Cl	X: Br	X: I
II	Cp^*NiCl $CpPdCl$	Cp^*NiBr $CpPdBr$	Cp^*NiI
IV		Cp^*PtBr_3 (?)	

A. Nickel(II)

Reaction of $NiX_2\cdot DME$ (X = Cl, Br) with Cp^*Li in THF at −10 °C yields thermolabile $[Cp^*NiX]_2$ compounds, characterized by mass spectrometry.[511] Oxidative addition of 5-halo-1,2,3,4,5-pentamethyl-1,3-cyclopentadiene (halo = bromo, iodo) to $Ni(CO)_4$ in THF produces $[Cp^*NiX]_2$ (X = Br, I). The iodo compound appears to be thermally more stable. A byproduct of this reaction is $Cp^*NiX(CO)$.[31] CpNiCl has been mentioned as the product of hydrochlorination of CpNiR. It has been trapped by PPh_3 to form the $CpNiCl(PPh_3)$ adduct, whereas it decomposes in the absence of phosphine at temperatures higher than −20 °C to give a mixture of nickelocene and an ill-characterized $CpNi_2Cl_3$ compound.[685]

$[Cp^*NiX]_2$ (X = Cl, Br) reacts with PPh_3 to yield $Cp^*NiX(PPh_3)$, with CpNa to yield Cp^*CpNi, with COD to yield $[Cp^*Ni(COD)]^+$, and with Na_2COT to yield $(Cp^*Ni)_2(COT)$.[511] The direct interaction of $NiCl_2$ with CpLi and then allylmagnesium chloride to generate $CpNi(\eta^3\text{-C}_3H_5)$ presumably proceeds through the intermediacy of CpNiCl.[686] Reaction of $[Cp^*NiBr]_2$ with $P(OMe)_3$ initially generates the $Cp^*NiBr[P(OMe)_3]$ adduct, followed by Michaelis–Arbuzov type reaction with extra $P(OMe)_3$ to give $Cp^*Ni[P(OMe)_3][P(O)(OMe)_2]$.[593]

B. Palladium and Platinum(II)

CpPdX (X = Cl, Br) have been obtained from the interaction of C_5H_6 and PdX_2 in water. The compounds are insoluble in common organic solvents but soluble in liquid ammonia, from which they can be recovered unchanged. They do not reacts with CpNa.[25] The corresponding indenyl system, $[IndPdCl]_2$, has been obtained from $PdCl_2$ and IndNa[687] or from Na_2PdCl_4 and indene in the presence of MeONa.[82] More recently, these as well as other η^3-allylpalladium chloride dimers have been prepared from the reaction of Na_2PdCl_4 and, e.g., $CpSiMe_3$ or $IndSiMe_3$.[688]

Analogous species of Pt do not appear to have been described. The reaction of $PtCl_2$ and CpNa produces the dinuclear Cp_4Pt_2 complex,[689] whereas, in the presence of CpH, MX_2 (M = Pd, Pt; X = Cl, Br) and CpNa give mixtures of Cp_4M_2 and $(CpM)_2(\mu\text{-CpH})$.[690] No intermediacy of CpMX species has been indicated in these reactions. A variety of adducts with two electron neutral donors, CpMXL, has been prepared directly from MX_2L_2 and a source of Cp^- or by other routes.[686,691–695]

C. Platinum(IV)

A Cp* bromo complex of Pt(IV) has been obtained in low yields from the reaction of $(C_5Me_5H)PtCl_2$ and excess Br_2 in $CHCl_3$. The compound has been formulated as $[Cp^*Pt(\mu\text{-Br})_3PtCp^*]Br_3$ but its characterization is made difficult by the poor solubility in all common solvents.[114] Mixed halo–alkyl derivatives $Cp^*PtMe_nBr_{3-n}$ (n = 1,2,3) have been reported recently. While Cp^*PtMe_3 and Cp^*PtMe_2Br were obtained from $Cp^*MgCl{\cdot}THF$ and, respectively, $PtMe_3I$ or $PtMe_2Br_2$, the $Cp^*PtMeBr_2$ derivative was obtained by bromination of Cp^*PtMe_2Br in which the formation of CH_3Br was also observed.[696] Prolonged exposure of $Cp^*PtMeBr_2$ to excess Br_2 gives a small amount of a highly insoluble brick red solid, which may be the same material obtained[114] by Taylor and Maitlis. The mixed methyl–chloro compound, Cp^*PtMe_2Cl, has also been reported.[697]

Acknowledgments. I would like to thank Prof. Thomas B. Rauchfuss for suggesting me to write this review article, and professors Malcolm L. H. Green, Louis Messerle, and Klaus H. Theopold, and Dr. Philip Mountford for the communication of results prior to publication. I thank the Camille and Henry Dreyfus Foundation (New Faculty Award), the Petroleum Research Fund, and the National Science Foundation (Presidential Yound Investigator Award) for support.

XV. References

(1) Wilkinson, G.; Cotton, F. A. *Prog. Inorg. Chem.* **1959**, *1*, 1.
(2) Birmingham, J. M. *Adv. Organometal. Chem.* **1964**, *2*, 365.
(3) Wilkinson, G.; Abel, E. W.; Stone, F. G. A. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982.
(4) (a) Gorsich, R. D. U.S. Patent 3,080,305, March 5, 1963; *Chem. Abstr.* **1963**, *59*, 3957c. (b) Gorsich, R. D. U.S. Patent 3,161,629, Dec 15, 1964; *Chem. Abstr.* **1965**, *62*, 6586f. (c) Krebs, K. W.; Engelhard, H.; Nischk, G. E. Ger. Offen. 1,959,322, July 29, 1971; *Chem. Abstr.* **1971**, *75*, 88768p. (d) Yu, G.; Chen, W.; Wang, Y. *Kexue Tongbao* **1983**, *28*, 408; *Chem. Abstr.* **1983**, *99*, 122968m. (e) Yu, G.; Chen, W.; Wang, Y. *Kexue Tongbao* **1984**, *29*, 421; *Chem. Abstr.* **1984**, *101*, 91491d. (f) Qian, H.; Yu, G.; Chen, W. *Gaofenzi Tongxun* **1984**, 226; *Chem. Abstr.* **1985**, *102*, 46291y. (g) Skupinski, W.; Walczuk, P. *Polimery* (*Warsaw*) **1986**, *31*, 393; *Chem. Abstr.* **1987**, *106*, 34327j. (h) Ishihara, N.; Kuramoto, M.; Oui, M. Eur. Pat. Appl. EP 210,615, 4 Feb 1987; *Chem. Abstr.* **1987**, *106*, 177084p. (i) Ishihara, N.; Kuramoto, M.; Oui, M. Eur. Pat. Appl. EP 224,097, 3 Jun 1987; *Chem. Abstr.* **1987**, *107*, 1766754r. (j) Ishihara, N.; Kuramoto, M.; Oui, M. *Macromolecules* **1988**, *21*, 3356. (k) Antberg, M.; Lueker, H.; Boehm, L. Eur. Pat. Appl. EP 293,815, 7 Dec 1988; *Chem. Abstr.* **1989**, *111*, 195585k. (l) Zambelli, A.; Oliva, L.; Pellecchia, C. *Macromolecules* **1989**, *22*, 2129. (m) Kuramoto, M.; Maezawa, H.; Hayashi, H. PCT Int. Appl. WO 89 02,901, 6 Apr 1989; *Chem. Abstr.* **1989**, *111*, 78818c. (n) Maezawa, H.; Tomotsu, N.; Kuramoto, M. Eur. Pat. Appl. EP 322,663, 5 Jul 1989; *Chem. Abstr.* **1989**, *111*, 233879u. (o) Maezawa, H.; Tomotsu, N. Jpn. Kokai Tokkyo Koho JP 01,240,503 [89,240,503], 26 Sept 1989; *Chem. Abstr.* **1990**, *112*, 140026u. (p) Ishihara, N.; Kuramoto, M. Eur. Pat. Appl. EP 322,731 5 Jul 1989; *Chem. Abstr.* **1989**, *111*, 233953p. (q) Schmidt, G. F.; Campbell, R. E., Jr. U.S. Patent 4,808,680, 28 Feb 1989; *Chem. Abstr.* **1989**, *111*, 78807y. (r) Chien, J. C. W.; Wang, B.-P. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 1539. (s) Chien, J. C. W.; Wang, B.-P. *J. Polym. Sci., Part A: Polym. Chem.* **1990**, *28*, 15.
(5) (a) White, C.; Oliver, A. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1973**, 1900. (b) Gill, D. S.; White, C.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 617. (c) Skupinski, W.; Cieslowska, I.; Malinowski, S. *J. Organometal. Chem.* **1979**, *182*, C33. (d) Maitlis, P. M. *Adv. Chem. Ser.* **1979**, *173*, 31. (e) Hamlin, J. E.; Hirai, K.; Gibson, V. C.; Maitlis, P. M. *J. Mol. Catal.* **1982**, *15*, 337. (f) Oro, L. A.; Campo, M.; Carmona, D. *J. Mol. Catal.* **1987**, *39*, 341.
(6) Cesarotti, E.; Ugo, R.; Vitiello, R. *J. Mol. Catal.* **1981**, *12*, 63.
(7) Schneider, W. U.S. Patent 3,535,396, 20 Oct 1970; *Chem. Abstr.* **1971**, *74*, 13549p.
(8) (a) Millan, A.; Towns, E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 673. (b) Millan, A.; Fernandez, M.-J.; Bentz, P.; Maitlis, P. M. *J. Mol. Catal.* **1984**, 89.
(9) Cook, J.; Hamlin, J. E.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2342.
(10) Smith, T. A.; Maitlis, P. M. *J. Organometal. Chem.* **1985**, *289*, 385.
(11) Cioni, P.; Diversi, P.; Ingrosso, G.; Lucherini, A.; Ronca, P. *J. Mol. Catal.* **1987**, *40*, 337.
(12) Mirabelli, M. G. L.; Sneddon, L. G. *J. Am. Chem. Soc.* **1988**, *110*, 449.
(13) Ziessel, R. *J. Chem. Soc., Chem. Commun.* **1988**, 16.
(14) Koepf-Maier, P.; Grabowski, S.; Koepf, H. *Eur. J. Med. Chem., Chim. Ther.* **1984**, *19*, 347; *Chem. Abstr.* **1984**, *101*, 222105f.
(15) Janowicz, A. H.; Bergman, R. G. *J. Am. Chem. Soc.* **1982**, *104*, 352.
(16) Ernst, R. D. *Chem. Rev.* **1988**, *88*, 1255.
(17) Roddick, D. M.; Fryzuk, M. D.; Seidler, P. F.; Hillhouse, G. L.; Bercaw, J. E. *Organometallics* **1985**, *4*, 97.
(18) Reid, A. F.; Wailes, P. C. *J. Organometal. Chem.* **1964**, *2*, 329.
(19) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426.
(20) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274.
(21) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161.
(22) Plitzko, K.-D.; Boekelheide, V. *Organometallics* **1988**, *7*, 1573.
(23) Ball, R. G.; Graham, W. A. G.; Heinekey, D. M.; Hoyano, J. K.; McMaster, A. D.; Mattson, B. M.; Michel, S. T. *Inorg. Chem.* **1990**, *29*, 2023.
(24) Lyatifov, I. R.; Dzhafarov, G. M.; Kurbanov, T. Kh. *J. Gen. Chem. USSR* **1989**, *59*, 1606.
(25) Smidt, J.; Jira, R. *Angew. Chem.* **1959**, *71*, 651.
(26) Bunker, M. J.; De Cian, A.; Green, M. L. H. *J. Chem. Soc., Chem. Commun.* **1977**, 59.
(27) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* **1964**, 1567.
(28) Cousins, M.; Green, M. L. H. *J. Chem. Soc.* (*A*), **1969**, 16.
(29) Herrmann, W. A.; Voss, E.; Küsthardt, U.; Herdtweck, E. *J. Organometal. Chem.* **1985**, *294*, C37.
(30) Herrmann, W. A.; Felixberger, J. K.; Anwander, R.; Herdtweck, E.; Kiprof, P.; Riede, J. *Organometallics* **1990**, *9*, 1434.
(31) Jutzi, P.; Mix, A. *Chem. Ber.* **1990**, *123*, 1043.
(32) Coutts, R. S. P.; Martin, R. L.; Wailes, P. C. *Aust. J. Chem.* **1971**, *24*, 1079.
(33) Coutts, R. S. P.; Martin, R. L.; Wailes, P. C. *Aust. J. Chem.* **1971**, *24*, 2533.
(34) Lucas, C. R.; Green, M. L. H. *Inorg. Synth.* **1976**, *16*, 237.
(35) Kilner, M.; Parkin, G.; Talbot, A. G. *J. Chem. Soc., Chem. Commun.* **1985**, 34.
(36) Ting, C.; Baenziger, N. C.; Messerle, L. *J. Chem. Soc., Chem. Commun.* **1988**, 1133.
(37) Ting, C.; Messerle, L. *Inorg. Chem.* **1989**, *28*, 173.
(38) Green, M. L. H.; Mountford, P. *J. Chem. Soc., Chem. Commun.* **1989**, 732.
(39) Green, M. L. H.; Hubert, J. D.; Mountford, P. *J. Chem. Soc., Dalton Trans.*, **1990**, 3793.
(40) Linck, R. L.; Owens, B. E.; Poli, R.; Rheingold, A. L. *Gazz. Chim. Ital.*, in press.
(41) Poli, R.; Rheingold, A. L. *J. Chem. Soc., Chem. Commun.* **1990**, 552.
(42) Herrmann, W. A.; Felixberger, J. K.; Herdtweck, E.; Schäfer, A.; Okuda, J. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 466.
(43) Herrmann, W. A.; Fischer, R. A.; Felixberger, J. K.; Paciello, R. A.; Kiprof, P.; Herdtweck, E. *Z. Naturforsch.* **1988**, *43b*, 1391.
(44) Herrmann, W. A.; Fischer, R. A.; Herdtweck, E. *J. Organometal. Chem.* **1987**, *329*, C1.
(45) Chaudret, B.; Jalon, F. A. *J. Chem. Soc., Chem. Commun.* **1988**, 711.
(46) Fagan, P. J.; Ward, M. D.; Calabrese, J. C. *J. Am. Chem. Soc.* **1989**, *111*, 1698.
(47) Kölle, U. *J. Electroanal. Chem.* **1990**, *292*, 217.
(48) Sharp, P. R.; Hoard, D. W.; Barnes, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 2024.
(49) Kilner, M.; Parkin, G. *J. Organometal. Chem.* **1986**, *302*, 181.
(50) Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1989**, 2453.
(51) Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J. *Polyhedron* **1989**, *8*, 1780.
(52) Kölle, U.; Kossakowski, J. *J. Organometal. Chem.* **1989**, *362*, 383.
(53) Poli, R.; Kelland, M. A., submitted for publication.
(54) Oshima, N.; Suzuki, H.; Moro-oka, Y.; Nagashima, H.; Itoh, K. *J. Organometal. Chem.* **1986**, *314*, C46.
(55) Okuda, J. *Chem. Ber.* **1990**, *123*, 87.
(56) Fischer, E. O.; Vigoureux, S.; Kuzel, P. *Chem. Ber.* **1960**, *93*, 701.
(57) King, R. B.; Hoff, C. D. *J. Organometal. Chem.* **1982**, *225*, 245.
(58) Thiele, K.-H.; Oswald, L. *Z. Anorg. Allg. Chem.* **1976**, *423*, 231.
(59) Davidson, J. L.; Vasapollo, G. *J. Organometal. Chem.* **1985**, *291*, 43.
(60) Fischer, E. O.; Ulm, K.; Kuzel, P. *Z. Anorg. Allg. Chem.* **1963**, *319*, 253.

(61) Köhler, F. H.; Lachmann, J.; Müller, G.; Zeh, H.; Brunner, H.; Pfauntsch, J.; Watcher, J. *J. Organometal. Chem.* **1989**, *365*, C15.
(62) Krueger, S. T.; Owens, B. E.; Poli, R. *Inorg. Chem.* **1990**, *29*, 2001.
(63) Murray, R. C.; Blum, L.; Liu, A. H.; Schrock, R. R. *Organometallics* **1985**, *4*, 953.
(64) Gorsich, R. D. *J. Am. Chem. Soc.* **1958**, *80*, 4744.
(65) Gorsich, R. D. *J. Am. Chem. Soc.* **1960**, *82*, 4211.
(66) Erker, G.; Berg, K.; Treschanke, L.; Engel, K. *Inorg. Chem.* **1982**, *21*, 1277.
(67) Wells, N. J.; Huffman, J. C.; Caulton, K. G. *J. Organometal. Chem.* **1981**, *213*, C17.
(68) Sontag, C.; Berke, H.; Sarter, C.; Erker, G. *Helv. Chim. Acta* **1989**, *72*, 1676.
(69) Harrigan, R. W.; Hammond, G. S.; Gray, H. B. *J. Organometal. Chem.* **1974**, *81*, 79.
(70) Brindley, P. B.; Davies, A. G.; Hawari, J. A.-A. *J. Organometal. Chem.* **1983**, *250*, 247.
(71) Bruce, M. R. M.; Sclafani, A.; Tyler, D. R. *Inorg. Chem.* **1986**, *25*, 2546.
(72) Floriani, C.; Fachinetti, G. *J. Chem. Soc., Dalton Trans.* **1973**, 1954.
(73) Belmonte, P. A.; Cloke, F. G. N.; Theopold, K. H.; Schrock, R. R. *Inorg. Chem.* **1984**, *23*, 2365.
(74) Grebenik, P. D.; Green, M. L. H.; Izquierdo, A.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Dalton Trans.* **1987**, 9.
(75) Green, M. L. H.; Izquierdo, A.; Martin-Polo, J. J.; Mtetwa, V. S. B.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1983**, 538.
(76) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Am. Chem. Soc.* **1969**, *91*, 5970.
(77) (a) Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808. (b) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574.
(78) Fagan, P. J.; Mahoney, W. S.; Calabrese, J. C.; Williams, I. D. *Organometallics* **1990**, *9*, 1843.
(79) Loren, S. D.; Campion, B. K.; Heyn, R. H.; Tilley, T. D.; Bursten, B. E.; Luth, K. W. *J. Am. Chem. Soc.* **1989**, *111*, 4712.
(80) Theopold, K. H., personal communication, December 1990.
(81) Kölle, U.; Fuss, B.; Belting, M.; Raabe, E. *Organometallics* **1986**, *5*, 980.
(82) Nakasuji, K.; Yamaguchi, M.; Murata, I.; Tatsumi, K.; Nakamura, A. *Organometallics* **1984**, *3*, 1257.
(83) Green, J. C.; Green, M. L. H.; Mountford, P.; Parkington, M. J. *J. Chem. Soc., Dalton Trans.* **1990**, 3407.
(84) Harlan, C. J.; Jones, R. A.; Koschmieder, S. U.; Nunn, C. M. *Polyhedron* **1990**, *9*, 669.
(85) Messerle, L., personal communication, November 1990.
(86) Scaife, D. E., 1974, quoted in ref 87.
(87) Coutts, R. S. P.; Wailes, P. C. *J. Organometal. Chem.* **1975**, *84*, 47.
(88) Köhler, F. H.; de Cao, R.; Ackermann, K.; Sedlmair, J. *Z. Naturforsch.* **1983**, *38B*, 1406.
(89) Morse, D. B.; Hendrickson, D. N.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 496.
(90) Arndt, P.; Kurras, E.; Otto, J. *Z. Chem.* **1983**, 443.
(91) Ronova, I. A.; Alekseev, N. V. *Dokl. Akad. Nauk SSSR* **1969**, *185*, 1303; *Chem. Abstr.* **1969**, *71*, 25439d.
(92) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1991**, *30*, 775.
(93) Terpstra, A.; Louwen, J. N.; Oskam, A.; Teuben, J. H. *J. Organometal. Chem.* **1984**, *260*, 207.
(94) Roesky, H. W.; Sotoodeh, M.; Xu, Y. M.; Schrumpf, F.; Noltemeyer, M. *Z. Anorg. Allg. Chem.* **1990**, *580*, 131.
(95) Roesky, H. W.; Schrumpf, F.; Noltemeyer, M. *J. Chem. Soc., Dalton Trans.* **1990**, 713.
(96) Bunker, M. J.; De Cian, A.; Green, M. L. H.; Moreau, J. J. E.; Siganporia, N. *J. Chem. Soc., Dalton Trans.* **1980**, 2155.
(97) Burt, R. J.; Chatt, J.; Leigh, G. J.; Teuben, J. H.; Westerhof, A. *J. Organometal. Chem.* **1977**, *129*, C33.
(98) Arnold, J.; Shina, D. N.; Tilley, T. D.; Arif, A. M. *Organometallics* **1986**, *5*, 2037.
(99) Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1980**, *19*, 3112.
(100) Green, M. L. H.; Mountford, P., personal communication, December 1990.
(101) Poli, R., unpublished observations.
(102) Herrmann, W. A.; Okuda, J. *J. Mol. Catal.* **1987**, *41*, 109.
(103) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1990**, *112*, 1860.
(104) Couldwell, C.; Husain, J. *Acta Crystallogr.* **1978**, *B34*, 2444.
(105) Olson, W. L.; Dahl, L. F. *Acta Crystallogr.* **1986**, *C42*, 541.
(106) Adrianov, V. G.; Lutsenko, Z. L.; Rubezhov, A. Z.; Struchkov, Yu. T. *Koord. Khim.* **1986**, *12*, 558.
(107) Valderrama, M.; Scotti, M.; Campos, P.; Sariego, R.; Peters, K.; von Schnering, H. G.; Werner, H. *New J. Chem.* **1988**, *12*, 633.
(108) Green, J. C.; Overton, C. P.; Prout, K.; Marin, J. M. *J. Organometal. Chem.* **1983**, *241*, C21.
(109) Marin, J. M.; Mtetwa, V. S. B.; Prout, K. *Acta Crystallogr.* **1985**, *C41*, 55.
(110) Thomas, B. J.; Mitchell, J. F.; Theopold, K. H.; Leary, J. A. *J. Organometal. Chem.* **1988**, *348*, 333.
(111) Manastyrskyj, S.; Maginn, R. E.; Dubeck, M. *Inorg. Chem.* **1963**, *2*, 904.
(112) Krueger, S. T.; Poli, R.; Rheingold, A. L.; Staley, D. L. *Inorg. Chem.* **1989**, *28*, 4599.
(113) Paneque, M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1989**, 105.
(114) Taylor, S. H.; Maitlis, P. M. *J. Organometal. Chem.* **1977**, *139*, 121.
(115) Nogina, O. V.; Uralets, I. A.; Drogunova, G. I.; Obezyuk, N. S. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1976**, 135.
(116) Nieman, J.; Pattiasina, J. W.; Teuben, J. H. *J. Organometal. Chem.* **1984**, *262*, 157.
(117) Erker, G.; Sarter, C.; Albrecht, M.; Dehnicke, S.; Krüger, C.; Raabe, E.; Schlund, R.; Benn, R.; Rufinska, A.; Mynott, R. *J. Organometal. Chem.* **1990**, *382*, 89.
(118) Wolczanski, P. T.; Bercaw, J. E. *Organometallics* **1982**, *1*, 793.
(119) Burt, R. J.; Leigh, G. J.; Hughes, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 793.
(120) Hazin, P. N.; Huffman, J. C.; Bruno, J. W. *Organometallics* **1987**, *6*, 23.
(121) van der Heijden, H.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 255.
(122) Renaut, P.; Tainturier, G.; Gautheron, B. *J. Organometal. Chem.* **1978**, *148*, 35.
(123) Hughes, D. L.; Leigh, G. J.; Walker, D. G. *J. Organometal. Chem.* **1988**, *355*, 113.
(124) Umakoshi, K.; Isobe, K. *J. Organometal. Chem.* **1990**, *395*, 47.
(125) Herrmann, W. A.; Flöel, M.; Kulpe, J.; Felixberger, J. K.; Herdtweck, E. *J. Organometal. Chem.* **1988**, *355*, 297.
(126) Herrmann, W. A.; Jung, K. A.; Herdtweck, E. *Chem. Ber.* **1989**, *122*, 2041.
(127) Kölle, U.; Fuss, B. *Chem. Ber.* **1984**, *117*, 753.
(128) Palacios, F.; Royo, P.; Serrano, R.; Balcázar, J. L.; Fonseca, I.; Florencio, F. *J. Organometal. Chem.* **1989**, *375*, 51.
(129) Erker, G.; Sarter, C.; Werner, S.; Krüger, C. *J. Organometal. Chem.* **1989**, *377*, C55.
(130) Babcock, L. M.; Day, V. W.; Klemperer, W. G. *Inorg. Chem.* **1989**, *28*, 806.
(131) Hidalgo, G.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Chem. Commun.* **1990**, 1118.
(132) Cosnier, S.; Deronzier, A.; Vlachopoulos, N. *J. Chem. Soc., Chem. Commun.* **1989**, 1259.
(133) Youinou, M.-T.; Ziessel, R. *J. Organometal. Chem.* **1989**, *363*, 197.
(134) Fairhurst, G.; White, C. *J. Chem. Soc., Dalton Trans.* **1979**, 1524.
(135) Russell, M. J. H.; White, C.; Yates, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 849.
(136) Thompson, S. J.; Bailey, P. M.; White, C.; Maitlis, P. M. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 1976.
(137) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1977**, 1654.
(138) Grundy, S. L.; Maitlis, P. M. *J. Organometal. Chem.* **1984**, *272*, 265.
(139) Grundy, S. L.; Smith, A. J.; Adams, H.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 1747.
(140) Kölle, U.; Fuss, B. *Chem. Ber.* **1984**, *117*, 743.
(141) Kang, J. W.; Maitlis, P. M. *J. Organometal. Chem.* **1971**, *30*, 127.
(142) Klapötke, T. *Inorg. Chim. Acta* **1988**, *150*, 165.
(143) Kiremire, E. M. R.; Leigh, G. J.; Dilworth, J. R.; Henderson, R. A. *Inorg. Chim. Acta* **1984**, *83*, L83.
(144) Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Dalton Trans.* **1986**, 385.
(145) Braunstein, P.; Lehner, H.; Matt, D.; Tiripicchio, A.; Tiripicchio Camellini, M. *Nouv. J. Chim.* **1985**, *9*, 597.
(146) Ohst, H. H.; Kochi, J. K. *Organometallics* **1986**, *5*, 1359.
(147) Walther, B.; Scheer, M.; Böttcher, H.-C.; Trunschke, A.; Ewald, H.; Gutschick, D.; Miessner, H.; Skupin, M.; Vorbeck, G. *Inorg. Chim. Acta* **1989**, *156*, 185.
(148) Blenkers, J.; Bruin, P.; Teuben, J. H. *J. Organometal. Chem.* **1985**, *297*, 61.
(149) Gambarotta, S.; Chiang, M. Y. *J. Chem. Soc., Chem. Commun.* **1987**, 698.
(150) Bulls, A. R.; Bercaw, J. E.; Manriquez, J. M.; Thompson, M. E. *Polyhedron* **1988**, *7*, 1409.
(151) Buin, P.; Booij, M.; Teuben, J. H.; Oskam, A. *J. Organometal. Chem.* **1988**, *350*, 17.
(152) Booij, M.; Kiers, N. H.; Heeres, H. J.; Teuben, J. H. *J. Organometal. Chem.* **1989**, *364*, 79.
(153) Jamerson, J. D.; Masino, A. P.; Takats, J. *J. Organometal. Chem.* **1974**, *65*, C33.
(154) Evans, W. J. *Adv. Organometal. Chem.* **1985**, *24*, 131.
(155) Evans, W. J.; Grate, J. W.; Choi, H. W.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 941.
(156) Watson, P. L. *J. Chem. Soc., Chem. Commun.* **1980**, 652.

(157) Yasuda, H.; Yamamoto, H.; Yokota, K.; Nakamura, A. *Chem. Lett.* **1989**, 1309.
(158) Swamy, S. J.; Schumann, H. *J. Organometal. Chem.* **1987**, *334*, 1.
(159) Albrecht, I.; Hahn, E.; Pickardt, J.; Schumann, H. *Inorg. Chim. Acta* **1985**, *110*, 145.
(160) Tilley, T. D.; Andersen, R. A. *Inorg. Chem.* **1981**, *20*, 3267.
(161) Schaverien, C. J.; van der Heijden, H.; Orpen, A. G. *Polyhedron* **1989**, *8*, 1850.
(162) van der Heijden, H.; Pasman, P.; de Boer, E. J. M.; Schaverien, C. J.; Orpen, A. G. *Organometallics* **1989**, *8*, 1459.
(163) Watson, P. L.; Whitney, J. F.; Harlow, R. L. *Inorg. Chem.* **1981**, *20*, 3271.
(164) Albrecht, I.; Schumann, H. *J. Organometal. Chem.* **1986**, *310*, C29.
(165) Schumann, H.; Albrecht, I.; Lauke, H.; Reier, F. W. *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, 1988; Vol. 4, pp 1–5.
(166) Schumann, H.; Kociok-Köhn, G.; Loebel, J. *Z. Anorg. Allg. Chem.* **1990**, *581*, 69.
(167) Namy, J. L.; Girard, P.; Kagan, H. B.; Caro, P. E. *Nouv. J. Chim.* **1981**, *5*, 479.
(168) Suleimanov, G. Z.; Kurbanov, T. K.; Nuriev, Y. A.; Rybakova, L. F.; Beletskaya, I. P. *Dokl. Akad. Nauk. SSSR* **1982**, *265*, 896; *Chem. Abstr.* **1983**, *98*, 34677q.
(169) Suleimanov. G. Z.; Nuriev, Y. A.; Syutkina, O. P.; Kurbanov T. K.; Beletskaya, I. P. *Bull Acad. Sci. USSR, Div. Chem. Sci.* **1982**, 1490.
(170) Zhou, P.; Tian, H.; Shen, Q. *Youji Huaxue* **1985**, 385; *Chem. Abstr.* **1986**, *104*, 224986e.
(171) Day, C. S.; Day, V. W.; Ernst, R. D.; Vollmer, S. H. *Organometallics* **1982**, *1*, 998.
(172) Deacon, G. B.; Fallon, G. D.; Wilkinson, D. L. *J. Organometal. Chem.* **1985**, *293*, 45.
(173) Finke, R. G.; Keenan, S. R.; Schiraldi, D. A.; Watson, P. L. *Organometallics* **1986**, *5*, 598.
(174) Finke, R. G.; Keenan, S. R.; Watson, P. L. *Organometallics* **1989**, *8*, 263.
(175) Tsutsui, M.; Chen, L.-B.; Bergreiter, D. E.; Miyamoto, T. K. *J. Am. Chem. Soc.* **1982**, *104*, 855.
(176) Chen, W.; Xiao, S.; Wang, Y.; Yu, G. *Kexue Tongbao* **1984**, *29*, 892; *Chem. Abstr.* **1985**, *102*, 7981d.
(177) Depaoli, G.; Zanonato, P.; Valle, G. *Inorg. Chim. Acta* **1990**, *170*, 109.
(178) Ely, N. M.; Tsutsui, M. *Inorg. Chem.* **1975**, *14*, 2680.
(179) Yu, G.; Chen, W.; Gong, D.; Tong, M.; Zheng, J. *Kexue Tongbao* **1985**, *30*, 1495; *Chem. Abstr.* **1986**, *105*, 42999z.
(180) Shen, Q.; Zhou, P.; Tian, H.; Li, S. *New Front. Rare Earth Sci. Appl., Proc. Int. Conf. Rare Earth Dev. Appl.* **1985**, *1*, 181; *Chem. Abstr.* **1987**, *106*, 33223k.
(181) Bagnall, K. W.; Edwards, J. *J. Organometal. Chem.* **1974**, *80*, C14.
(182) Bagnall, K. W.; Edwards, J.; Tempest, A. C. *J. Chem. Soc., Dalton Trans.* **1978**, 295.
(183) Doretti, L.; Zanella, P.; Faraglia, G.; Faleschini, S. *J. Organometal. Chem.* **1972**, *43*, 339.
(184) Dormond, A. *J. Organometal. Chem.* **1983**, *256*, 47.
(185) Ernst, R. D.; Kennelly, W. J.; Day, C. S.; Day, V. W.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 2656.
(186) Mintz, E. A.; Moloy, K. G.; Marks, T. J.; Day, V. W. *J. Am. Chem. Soc.* **1982**, *104*, 4692.
(187) Bagnall, K. W.; Beheshti, A.; Heatley, F. *J. Less-Common Met.* **1978**, *61*, 63.
(188) Bagnall, K. W.; Beheshti, A.; Heatley, F.; Tempest, A. C. *J. Less-Common Met.* **1979**, *64*, 267.
(189) Karraker, D. G.; Stone, J. A. *Inorg. Chem.* **1979**, *18*, 2205.
(190) Bombieri, G.; de Paoli, G.; Del Prà, A. *Inorg. Nucl. Chem. Lett.* **1978**, *14*, 359.
(191) Goffart, J.; Piret-Meunier, J.; Duyckaerts, G. *Inorg. Nucl. Chem. Lett.* **1980**, *16*, 233.
(192) Meunier-Piret, J.; Germain, G.; Declercq, J. P.; Van Meerssche, M. *Bull. Soc. Chim. Belg.* **1980**, *89*, 241.
(193) Bagnall, K. W.; Beheshti, A.; Edwards, J.; Heatley, F.; Tempest, A. C. *J. Chem. Soc., Dalton Trans.* **1979**, 1241.
(194) Bagnall, K. W.; Edwards, J.; Rickard, C. E. F.; Tempest, A. C. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1321.
(195) Dormond, A.; Aaliti, A.; Moïse, C. *J. Org. Chem.* **1988**, *53*, 1034.
(196) Leonov, M. R.; Il'yushenkova, V. A.; Fomin, V. M.; Il'yushenkova, N. V. *Radiokhimiya* **1988**, *30*, 324; *Chem. Abstr.* **1989**, *110*, 75694c.
(197) Gubin, S. P.; Smirnova, S. A. *J. Organometal. Chem.* **1969**, *20*, 229.
(198) Bartlett, P. D.; Seidel, B. *J. Am. Chem. Soc.* **1961**, *83*, 581.
(199) Blake, P. C.; Hey, E.; Lappert, M. F.; Atwood, J. L.; Zhang, H. *J. Organometal. Chem.* **1988**, *353*, 307.
(200) Symons, M. C. R.; Mishra, S. P. *J. Chem. Soc., Dalton Trans.* **1981**, 2258.
(201) Coutts, R. S. P.; Martin, R. L.; Wailes, P. C. *Aust. J. Chem.* **1972**, *25*, 1401.
(202) Green, M. L. H.; Lucas, C. R. *J. Organometal. Chem.* **1974**, *73*, 259.
(203) Coutts, R. S. P.; Martin, R. L.; Wailes, P. C. *Aust. J. Chem.* **1973**, *26*, 47.
(204) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Am. Chem. Soc.* **1983**, *105*, 7295.
(205) Razavi, A.; Mallin, D. T.; Day, R. O.; Rausch, M. D.; Alt, H. G. *J. Organometal. Chem.* **1987**, *333*, C48.
(206) Coutts, R. S. P. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 41.
(207) Coutts, R. S. P.; Martin, R. L.; Wailes, P. C. *Aust. J. Chem.* **1973**, *26*, 941.
(208) Coutts, R. S. P.; Wailes, P. C. *Aust. J. Chem.* **1974**, *27*, 2483.
(209) Manzer, L. E. *J. Organometal. Chem.* **1975**, *102*, 167.
(210) (a) Manzer, L. E.; Gearhart, R. C.; Guggenberger, L. J.; Whitney, J. F. *J. Chem. Soc., Chem. Commun.* **1976**, 942. (b) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068.
(211) Etienne, M.; Choukroun, R.; Basso-Bert, M.; Dahan, F.; Gervais, D. *Nouv. J. Chim.* **1984**, *8*, 531.
(212) Zwijnenburg, A.; Van Oven, H. O.; Groenenboom, C. J.; De Liefde Meijer, H. J. *J. Organometal. Chem.* **1975**, *94*, 23.
(213) Yamamoto, H.; Yasuda, H.; Tatsumi, K.; Lee, K.; Nakamura, A.; Chen, J.; Kai, Y.; Kasai, N. *Organometallics* **1989**, *8*, 105.
(214) Salentine, C. G.; Hawthorne, M. F. *J. Chem. Soc., Chem. Commun.* **1975**, 848.
(215) Coutts, R. S. P.; Wailes, P. C.; Martin, R. L. *J. Organometal. Chem.* **1973**, *50*, 145.
(216) Coutts, R. S. P.; Wailes, P. C. *J. Organometal. Chem.* **1974**, *73*, C5.
(217) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1982**, 1015.
(218) Fochi, G.; Floriani, C. *J. Chem. Soc., Dalton Trans.* **1984**, 2577.
(219) Razuvaev, G. A.; Latyaeva, V. N.; Vyshinskaya, L. I. *J. Gen. Chem. USSR* **1965**, *35*, 171.
(220) Blenkers, J.; De Liefde Meijer, H. J.; Teuben, J. H. *J. Organomet. Chem.* **1981**, *218*, 383.
(221) Luinstra, G. A.; Teuben, J. H. *J. Chem. Soc., Chem. Commun.* **1990**, 1470.
(222) Demerseman, B.; Mahé, R.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1984**, 1394.
(223) Samuel, E.; Guery, D.; Vedel, J.; Basile, F. *Organometallics* **1985**, *4*, 1073.
(224) Ji, H.; Xu, G.; Chen, S.; Liu, Y. *Bopuxue Zazhi* **1987**, *4*, 53; *Chem. Abstr.* **1988**, *108*, 112628r.
(225) Bottrill, M.; Gavens, P. D.; Kelland, J. W.; McMeeking, J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, 1982; Vol. 3, pp 331–433.
(226) (a) Gorsich, R. D. U.S. Patent 2,952,697, Sept 13, 1960; *Chem. Abstr.* **1961**, *55*, 14479b. (b) Gorsich, R. D. U.S. Patent 3,080,305, Mar 5, 1063 *Chem. Abstr.* **1963**, *59*, 3957c. (c) Gorsich, R. D. U.S. Patent 3,161,629, Dec 15, 1964; *Chem. Abstr.* **1965**, *62*, 6586f.
(227) Barkdoll, A. E.; Lorenz, J. C. U.S. Patent 3,038,915, June 12, 1962; *Chem. Abstr.* **1962**, *57*, 16655b.
(228) Brantley, J. C.; Morehouse, E. L.; Parts, L. U.S. Patent 3,306,919, Feb 28, 1967; *Chem. Abstr.* **1967**, *67*, 11592d.
(229) Chandra, K.; Sharma, R. K.; Kumar, N.; Garg, B. S. *Chem. Ind. (London)* **1980**, 288.
(230) Kauffmann, T.; Ennen, J.; Berghus, K. *Tetrahedron Lett.* **1984**, *25*, 1971.
(231) King, R. B. *Organometallic Syntheses*; Academic Press: New York, 1965; Vol. 1, p 78.
(232) Klapötke, T. *Polyhedron* **1989**, *8*, 311.
(233) Sloan, C. L.; Barber, W. A. *J. Am. Chem. Soc.* **1959**, *81*, 1364.
(234) Alcock, N. W.; Toogood, G. E.; Wallbridge, M. G. H. *Acta Crystallogr.* **1984**, *C40*, 598.
(235) Booth, B. L.; Ofunne, G. C.; Stacey, C.; Tait, P. J. T. *J. Organometal. Chem.* **1986**, *315*, 143.
(236) Klapötke, T.; Köpf, H.; Gowik, P. *J. Chem. Soc., Dalton Trans.* **1988**, 1529.
(237) Nesmeyanov, A. N.; Nogina, O. V.; Berlin, A. M. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1961**, 743.
(238) Nesmeyanov, A. N.; Nogina, O. V.; Dubovitskii, V. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1968**, 514.
(239) Kaufman, D. U.S. Patent 2,922,803, Jan 26, 1960; *Chem. Abstr.* **1960**, *54*, 10900f.
(240) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156.
(241) Jutzi, P.; Kuhn, M. *J. Organometal. Chem.* **1979**, *173*, 221.
(242) Jutzi, P.; Seufert, A. *J. Organometal. Chem.* **1979**, *169*, 373.
(243) Llinás, G. H.; Mena, M.; Palacios, F.; Royo, P.; Serrano, R. *J. Organometal. Chem.* **1988**, *340*, 37.
(244) Mena, M.; Pellinghelli, M. A.; Royo, P.; Serrano, R.; Tiripicchio, A. *J. Chem. Soc., Chem. Commun.* **1986**, 1118.
(245) (a) Röhl, H.; Lange, E.; Gössl, T.; Roth, G. *Angew. Chem., Int. Ed. Engl.* **1962**, *1*, 117. (b) King, R. B.; Bisnette, M. B. *J. Organometal. Chem.* **1967**, *8*, 287.
(246) Bercaw, J. E.; Marvich, R. H.; Bell, L. G.; Brintzinger, H. H. *J. Am. Chem. Soc.* **1972**, *94*, 1219.

(247) Mallin, D. T.; Rausch, M. D.; Mintz, E. A.; Rheingold, A. L. *J. Organometal. Chem.* **1990**, *381*, 35.
(248) Anagnostopoulos, A.; Nicholls, D. *J. Inorg. Nucl. Chem.* **1966**, *28*, 3047.
(249) Clark, R. J. H.; Stockwell, J. A.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1976**, 120.
(250) Pandey, O. P.; Sengupta, S. K.; Tripathi, S. C. *Synth. React. Inorg. Met.-Org. Chem.* **1983**, *13*, 867.
(251) Pandey, O. P.; Sengupta, S. K.; Tripathi, S. C. *Trans. Met. Chem.* **1983**, *8*, 362.
(252) Corradini, P.; Allegra, G. *J. Am. Chem. Soc.* **1959**, *81*, 5510.
(253) Porri, L.; Corradini, P.; Morero, D.; Allegra, G. *Chim. Ind. (Milan)* **1960**, *42*, 487.
(254) Saunders, L.; Spirer, L. *Polymer* **1965**, *6*, 635.
(255) Skapski, A. C.; Troughton, P. G. H.; Sutherland, H. H. *J. Chem. Soc., Chem. Commun.* **1968**, 1418.
(256) Skapski, A. C.; Troughton, P. G. H. *Acta Crystallogr.* **1970**, *B26*, 716.
(257) Thewalt, U.; Schomburg, D. *J. Organometal. Chem.* **1977**, *127*, 169.
(258) Petersen, J. L. *Inorg. Chem.* **1980**, *19*, 181.
(259) Döppert, K. *Naturwissenschaften* **1990**, *77*, 19.
(260) Felixberger, J. K.; Kiprof, P.; Herdtweck, E.; Herrmann, W. A.; Jacobi, R.; Gütlich, P. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 334.
(261) de Boer, E. J. M.; de With, J.; Orpen, A. G. *J. Am. Chem. Soc.* **1986**, *108*, 8271.
(262) Herrmann, W. A.; Kiprof, P.; Felixberger, J. K. *Chem. Ber.* **1990**, *123*, 1971.
(263) Marsella, J. A.; Moloy, K. G.; Caulton, K. G. *J. Organometal. Chem.* **1980**, *201*, 389.
(264) Wong, C. H.; Hung, C. W.; Wong, H. N. C. *J. Organometal. Chem.* **1988**, *342*, 9.
(265) Babcock, L. M.; Day, V. W.; Klemperer, W. G. *J. Chem. Soc., Chem. Commun.* **1987**, 858.
(266) Babcock, L. M.; Klemperer, W. G. *Inorg. Chem.* **1989**, *28*, 2003.
(267) Okuda, J. *J. Organometal. Chem.* **1990**, *397*, C37.
(268) Klapötke, T.; Laskowski, R.; Köpf, H. *Z. Naturforsch.* **1987**, *42b*, 777.
(269) Köpf, H.; Block, B. *Z. Naturforsch.* **1968**, *23b*, 1534.
(270) Bharara, P. C. *J. Organometal. Chem.* **1976**, *121*, 199.
(271) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009.
(272) Riediker M.; Duthaler, R. O. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 494.
(273) Skupinski, W.; Wasilewski, A. *J. Organometal. Chem.* **1981**, *220*, 39.
(274) Taube, R.; Knoth, P. *Z. Anorg. Allg. Chem.* **1990**, *581*, 89.
(275) Wade, S. R.; Wallbridge, M. G. H.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1982**, 271.
(276) Alyea, E. C.; Malek, A. *Inorg. Nucl. Chem. Lett.* **1977**, *13*, 587.
(277) Pandey, O. P.; Sengupta, S. K.; Tripathi, S. C. *Acta Chim. Hung.* **1984**, *116*, 29.
(278) Saxena, S.; Singh, Y. P.; Rai, A. K. *J. Organometal. Chem.* **1984**, *270*, 301.
(279) Nesmeyanov, A. N.; Nogina, O. V.; Drogunova, G. I.; Lokshin, B. V. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1973**, 386.
(280) Pandey, O. P.; Sengupta, S. K.; Tripathi, S. C. *Polyhedron* **1984**, *3*, 695.
(281) Hughes, D. L.; Jimenez-Tenorio, M.; Leigh, G. J.; Walker, D. G. *J. Chem. Soc., Dalton Trans.* **1989**, 2389.
(282) Pandey, O. P.; Sengupta, S. K.; Tripathi, S. C. *Monatsch. Chem.* **1985**, *116*, 431.
(283) Hughes, D. L.; Latham, I. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1986**, 393.
(284) Köpf, H.; Klapötke, T. *J. Organometal. Chem.* **1986**, *310*, 303.
(285) Floriani, C.; Corazza, F.; Lesueur, W.; Chiesi-Villa, A.; Guastini, C. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 66.
(286) Köpf, H.; Klapötke, T. *J. Organometal. Chem.* **1986**, *307*, 319.
(287) Müller, A.; Krickemeyer, E.; Sprafke, A.; Schladerbeck, N. H.; Bögge, H. *Chimia* **1988**, *42*, 68.
(288) Zank, G. A.; Jones, C. A.; Rauchfuss, T. B.; Rheingold, A. L. *Inorg. Chem.* **1986**, *25*, 1886.
(289) Brauer, D. J.; Bürger, H.; Liewald, G. R. *J. Organometal. Chem.* **1986**, *307*, 177.
(290) Schmid, G.; Stutte, B.; Boese, R. *Chem. Ber.* **1978**, *111*, 1239.
(291) Cesarotti, E.; Kagan, H. B.; Goddard, R.; Krüger, C. *J. Organometal. Chem.* **1978**, *162*, 297.
(292) Chen, S.; Li, J.; Wang, J. *Gaodeng Xuexiao Huaxue Xuebao* **1986**, *7*, 322; *Chem. Abstr.* **1987**, *107*, 59169t.
(293) Chen, S.; Li, J.; Wang, J. *Huaxue Xuebao* **1984**, *42*, 163; *Chem. Abstr.* **1984**, *101*, 55255w.
(294) Colletti, S. L.; Halterman, R. L. *Tetrahedron Lett.* **1989**, *30*, 3513.
(295) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 4228.
(296) Huang, Q.; Qian, Y.; Tang, Y. *J. Organometal. Chem.* **1989**, *368*, 277.
(297) Moriarty, K. J.; Rogers, R. D.; Paquette, L. A. *Organometallics* **1989**, *8*, 1512.
(298) Ott, K. C.; deBoer, E. J. M.; Grubbs, R. H. *Organometallics* **1984**, *3*, 223.
(299) Paquette, L. A.; Moriarty, K. J.; McKinney, J. A.; Rogers, R. D. *Organometallics* **1989**, *8*, 1707.
(300) Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Crocq, V. *Organometallics* **1988**, *7*, 1873.
(301) Paquette, L. A.; Moriarty, K. J.; Meunier, P.; Gautheron, B.; Sornay, C.; Rogers, R. D.; Rheingold, A. L. *Organometallics* **1989**, *8*, 2159.
(302) Qichen, H.; Yanlong, Q.; Youqi, T. *Trans. Met. Chem.* **1989**, *14*, 315.
(303) Rogers, R. D.; Benning, M. W.; Kurihara, L. K.; Moriarty, K. J.; Rausch, M. D. *J. Organometal. Chem.* **1985**, *293*, 51.
(304) Sharma, A. K.; Kaushik, N. K. *Acta Chim. Hungar.* **1984**, *116*, 361.
(305) Singh, J. J.; Singh, G.; Kumar, N.; Sharma, R. K.; Multani, R. K. *Ind. J. Chem.* **1982**, *21A*, 631.
(306) Singh, P.; Rausch, M. D.; Bitterowlf, T. E. *J. Organometal. Chem.* **1988**, *352*, 273.
(307) Sodhi, G. S.; Sharma, A. K.; Kaushik, N. K. *J. Organometal. Chem.* **1982**, *238*, 177.
(308) Spink, W. C.; Rausch, M. D. *J. Organometal. Chem.* **1986**, *308*, C1.
(309) Macomber, D. W.; Hart, W. P.; Rausch, M. D.; Priester, R. D.; Pittman, C. U., Jr. *J. Am. Chem. Soc.* **1982**, *104*, 884.
(310) Qian, Y.; Zhuang, J.; Xu, M.; Xu, W.; He, Y.; Li, B. *Wuji Huaxue* **1986**, *2*, 90; *Chem. Abstr.* **1988**, *108*, 75533h.
(311) Conway, B. G.; Rausch, M. D. *Organometallics* **1985**, *4*, 688.
(312) Rausch, M. D.; Lewison, J. F.; Hart, W. P. *J. Organometal. Chem.* **1988**, *358*, 161.
(313) Leblanc, J. C.; Moise, C.; Maisonnat, A.; Poilblanc, R.; Charrier, C.; Mathey, F. *J. Organometal. Chem.* **1982**, *231*, C43.
(314) Rausch, M. D.; Edwards, B. H.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1983**, *105*, 3882.
(315) Rausch, M. D.; Spink, W. C. *Synth. React. Inorg. Met.-Org. Chem.* **1989**, *19*, 1093.
(316) Verdet, L.; Stille, J. K. *Organometallics* **1982**, *1*, 380.
(317) Härter, P.; Boguth, G.; Herdtweck, E.; Riede, J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1008.
(318) Sodhi, G. S.; Sharma, A. K.; Kaushik, N. K. *Synth. React. Inorg. Met.-Org. Chem.* **1982**, *12*, 947.
(319) Nief, F.; Ricard, L.; Mathey, F. *Organometallics* **1989**, *8*, 1473.
(320) Blom, R.; Rypdal, K.; Mena, M.; Royo, P.; Serrano, R. *J. Organometal. Chem.* **1990**, *391*, 47.
(321) (a) Clauss, K.; Bestian, H. *Liebigs Ann. Chem.* **1962**, *654*, 8. (b) Razuvaev, G. A.; Latyaeva, V. N.; Vyshinskaya, L. I.; Kilyakova, G. A. *J. Gen. Chem. USSR* **1966**, *36*, 1496.
(322) Giannini, U.; Cesca, S. *Tetrahedron Lett.* **1960**, No. 14, 19.
(323) Mena, M.; Royo, P.; Serrano, R.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1989**, *8*, 476.
(324) Erskine, G. J.; Hunter, B. K.; McCowan, J. D. *Tetrahedron Lett.* **1985**, *26*, 1371.
(325) Erskine, G. J.; Hurst, G. J. B.; Weinberg, E. L.; Hunter, B. K.; McCowan, J. D. *J. Organometal. Chem.* **1984**, *267*, 265.
(326) Wedler, M.; Roesky, H. W.; Edelmann, F. T.; Behrens, U. *Z. Naturforsch.* **1988**, *43b*, 1461.
(327) Volpin, M. E.; Shur, V. B.; Kudryavtsev, R. V.; Prodayko, L. A. *J. Chem. Soc., Chem. Commun.* **1968**, 1038.
(328) Blenkers, J.; Hessen, B.; van Bolhuis, F.; Wagner, A. J.; Teuben, J. H. *Organometallics* **1987**, *6*, 459.
(329) Chen, J.; Kai, Y.; Kasai, N.; Yamamoto, Y.; Yasuda, H.; Nakamura, A. *Chem. Lett.* **1987**, 1545.
(330) Mena, M.; Royo, P.; Serrano, R.; Pellinghelli, M. A.; Tiripicchio, A. *Organometallics* **1988**, *7*, 258.
(331) Dilworth, J. R.; de Liefde Meijer, H. J.; Teuben, J. H. *J. Organometal. Chem.* **1978**, *159*, 47.
(332) Choukroun, R.; Gervais, D. *J. Chem. Soc., Dalton Trans.* **1980**, 1800.
(333) Choukroun, R.; Gervais, D.; Dilworth, J. R. *Trans. Met. Chem.* **1979**, *4*, 249.
(334) Jekel-Vroegop, C. T.; Teuben, J. H. *J. Organometal. Chem.* **1985**, *286*, 309.
(335) Vroegop, C. T.; Teuben, J. H.; van Bolhuis, F.; van der Linden, J. G. M. *J. Chem. Soc., Chem. Commun.* **1983**, 550.
(336) Dilworth, J. R.; Latham, I. A.; Leigh, G. J.; Huttner, G.; Jibril, I. *J. Chem. Soc., Chem. Commun.* **1983**, 1368.
(337) Katti, K. V.; Cavell, R. G. *Inorg. Chem.* **1989**, *28*, 413.
(338) Roesky, H. W.; Schrumpf, F.; Noltemeyer, M. *Z. Naturfrosch.* **1989**, *44b*, 35.
(339) Schrenk, V.; Mattes, R. *Z. Anorg. Allg. Chem.* **1988**, *566*, 71.
(340) Latham, I. A.; Leigh, G. J. *J. Chem. Soc., Dalton Trans.* **1986**, 399.
(341) Dey, K.; Koner, D.; Biswas, A. K.; Ray, S. *J. Chem. Soc., Dalton Trans.* **1982**, 911.

(342) Dey, K.; Ray, S.; Koner, D. *Proc. Indian Acad. Sci.: Chem. Sci.* **1983**, *92*, 257; *Chem. Abstr.* **1984**, *100*, 139251j.
(343) Maué, P. G.; Fenske, D. *Z. Naturforsch.* **1988**, *43b*, 1213.
(344) Fenske, D.; Grissinger, A. *Z. Naturforsch.* **1990**, *45b*, 1309.
(345) Plenio, H.; Roesky, H. W.; Edelmann, F. T.; Noltemeyer, M. *J. Chem. Soc., Dalton Trans.* **1989**, 1815.
(346) Razuvaev, G. A.; Latyaeva, V. N.; Lineva, A. N. *J. Gen. Chem. USSR* **1971**, *41*, 1560.
(347) Finke, R. G.; Rapko, B.; Domaille, P. J. *Organometallics* **1986**, *5*, 175.
(348) Ho, R. K. C.; Klemperer, W. G. *J. Am. Chem. Soc.* **1978**, *100*, 6772.
(349) Knoth, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 759.
(350) Knoth, W. H.; Domaille, P. J.; Farlee, R. D. *Organometallics* **1985**, *4*, 62.
(351) Keana, J. F. W.; Ogan, M. D.; Lü, Y.; Beer, M.; Varkey, J. *J. Am. Chem. Soc.* **1985**, *107*, 6714.
(352) Pandey, O. P. *Inorg. Chim. Acta* **1986**, *118*, 105.
(353) Pandey, O. P.; Sengupta, S. K.; Tripathi, S. C. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2395.
(354) Pandey, O. P.; Sengupta, S. K.; Tripathi, S. C. *Inorg. Chim. Acta* **1984**, *90*, 91.
(355) Pandey, O. P. *Ind. J. Chem.* **1987**, *26A*, 978.
(356) Kher, S.; Verma, V.; Kapoor, R. N. *Trans. Met. Chem.* **1983**, *8*, 163.
(357) Nesmeyanov, A. N.; Nogina, O. V.; Lazareva, N. A.; Dubovitskii, V. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1967**, 777.
(358) Nesmeyanov, A. N.; Nogina, O. V.; Lazareva, N. A.; Dubovitskii, V. A.; Lokshin, B. V. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1971**, 2354.
(359) Mackenzie, P. B.; Ott, K. C.; Grubbs, R. H. *Pure Appl. Chem.* **1984**, *56*, 59.
(360) Choukroun, R. *Inorg. Chim. Acta* **1981**, *58*, 121.
(361) Mach, K.; Varga, V.; Antropiusová, H.; Polácek, J. *J. Organometal. Chem.* **1987**, *333*, 205.
(362) Bueschges, U.; Chien, J. C. W. *J. Polym. Sci., Part A: Polym. Chem.* **1989**, *27*, 1525.
(363) Bulychev, B. M.; Tokareva, S. E.; Soloveichick, G. L.; Evdokimova, E. V. *J. Organometal. Chem.* **1979**, *179*, 263.
(364) Kool, L. B.; Rausch, M. D.; Rogers, R. D. *J. Organometal. Chem.* **1985**, *297*, 289.
(365) Kelsey, B. A.; Ellis, J. E. *J. Am. Chem. Soc.* **1986**, *108*, 1344.
(366) Kelsey, B. A.; Ellis, J. E. *J. Chem. Soc., Chem. Commun.* **1986**, 331.
(367) Some aspects of this chemistry have been recently reviewed: Erker, G. *J. Organometal. Chem.* **1990**, *400*, 185.
(368) Casey, C. P.; Nief, F. *Organometallics* **1985**, *4*, 1218.
(369) Chang, B.-H.; Grubbs, R. H.; Brubaker, C. H., Jr. *J. Organometal. Chem.* **1985**, *280*, 365.
(370) Sodhi, G. S.; Kaushik, N. K. *Bull. Soc. Chim. Fr.* **1982**, 45.
(371) Wengrovius, J. H.; Schrock, R. R. *J. Organometal. Chem.* **1981**, *205*, 319.
(372) Erker, G.; van der Zeijden, A. A. H. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 512.
(373) van den Hende, J. R.; Hessen, B.; Meetsma, A.; Teuben, J. H. *Organometallics* **1990**, *9*, 537.
(374) Babcock, L. M.; Day, V. W.; Klemperer, W. G. *J. Chem. Soc., Chem. Commun.* **1988**, 519.
(375) Paquette, L. A.; Moriarty, K. J.; Rogers, R. D. *Organometallics* **1989**, *8*, 1506.
(376) Schore, N. E. *J. Am. Chem. Soc.* **1979**, *101*, 7410.
(377) Sodhi, G. S.; Kumar, S.; Kaushik, N. K. *Acta Chim. Hungar.* **1983**, *114*, 329.
(378) Tueting, D. R.; Iyer, S. R.; Schore, N. E. *J. Organometal. Chem.* **1987**, *320*, 349.
(379) Reddy, K. P.; Petersen, J. L. *Organometallics* **1989**, *8*, 2107.
(380) Arnold, J.; Roddick, D. M.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Inorg. Chem.* **1988**, *27*, 3510.
(381) (a) Jain, V. K.; Garg, B. S.; Singh, R. P. *Aust. J. Chem.* **1977**, *30*, 2545. (b) Gau, H.-M.; Fay, R. C. *Inorg. Chem.* **1987**, *26*, 3701.
(382) Sodhi, G. S.; Kaushik, N. K. *Synth. React. Inorg. Met.-Org. Chem.* **1981**, *11*, 641.
(383) Feher, F. J. *J. Am. Chem. Soc.* **1986**, *108*, 3850.
(384) Berg, K.; Erker, G. *J. Organometal. Chem.* **1984**, *270*, C53.
(385) Erker, G.; Berg, K.; Angermund, K.; Krüger, C. *Organometallics* **1987**, *6*, 2620.
(386) Erker, G.; Berg, K.; Krüger, C.; Müller, G.; Angermund, K.; Benn, R.; Schroth, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 455.
(387) Erker, G.; Berg, K.; Benn, R.; Schroth, G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 625.
(388) Erker, G.; Berg, K.; Benn, R.; Schroth, G. *Chem. Ber.* **1985**, *118*, 1383.
(389) Larson, E. J.; Van Dort, P. C.; Dailey, J. S.; Lakanen, J. R.; Pederson, L. M.; Silver, M. E.; Huffman, J. C.; Russo, S. O. *Organometallics* **1987**, *6*, 2141.
(390) Blenkers, J.; De Liefde Meijer, H. J.; Teuben, J. H. *Organometallics* **1983**, *2*, 1483.
(391) Nugent, W. A.; Taber, D. F. *J. Am. Chem. Soc.* **1989**, *111*, 6435.
(392) Schock, L. E.; Marks, T. J. *J. Am. Chem. Soc.* **1988**, *110*, 7701.
(393) Roddick, D. M.; Santarsiero, B. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1985**, *107*, 4670.
(394) Arnold, J.; Woo, H.-G.; Tilley, T. D.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1988**, *7*, 2045.
(395) Hessen, B.; Spek, A. L.; Teuben, J. H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1058.
(396) Kelsey Stein, B.; Frerichs, S. R.; Ellis, J. E. *Organometallics* **1987**, 2017.
(397) Frerichs, S. R.; Ellis, J. E. *J. Organometal. Chem.* **1989**, *359*, C41.
(398) Duff, A. W.; Jonas, K.; Goddard, R.; Kraus, H.-J.; Krüger, C. *J. Am. Chem. Soc.* **1983**, *105*, 5479.
(399) Bachmann, B.; Hahn, F.; Heck, J.; Wünsch, M. *Organometallics* **1989**, *8*, 2523.
(400) Nieman, J.; Teuben, J. H.; Huffman, J. C.; Caulton, K. G. *J. Organomet. Chem.* **1983**, *255*, 193.
(401) Ting, C.; Messerle, L. *J. Am. Chem. Soc.* **1987**, *109*, 6506.
(402) Ting, C.; Messerle, L. *J. Am. Chem. Soc.* **1989**, *111*, 3449.
(403) Hammer, M. S.; Messerle, L. *Inorg. Chem.* **1990**, *29*, 1780.
(404) Herberhold, M.; Kremnitz, W.; Kuhnlein, M.; Ziegler, M. L.; Brunn, K. *Z. Naturforsch.* **1987**, *42B*, 1520.
(405) Bottomley, F.; Darkwa, J.; Sutin, L.; White, P. S. *Organometallics* **1986**, *5*, 2165.
(406) Jimenez-Tenorio, M.; Leigh, G. J. *Polyhedron* **1989**, *8*, 1784.
(407) Müller, J.; Goll, W. *J. Organometal. Chem.* **1974**, *71*, 257.
(408) (a) Bottomley, F.; Sutin, L.; White, P. S. *J. Organometal. Chem.* **1988**, *338*, 205. (b) Morse, D. B. *Chem. Mater.* **1990**, *2*, 33; *Chem. Abstr.* **1990**, *112*, 56182j.
(409) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1988**, *110*, 2646.
(410) Broussier, R.; Olivier, J. D.; Gautheron, B. *J. Organometal. Chem.* **1981**, *210*, 169.
(411) Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1988**, *110*, 5008.
(412) Chang, B.-H.; Lau, C.-P.; Grubbs, R. H.; Brubaker, C. H., Jr. *J. Organometal. Chem.* **1985**, *281*, 213.
(413) Lee, J. G.-S.; Brubaker, C. H., Jr. *J. Organometal. Chem.* **1977**, *135*, 333.
(414) Kilmer, N. H.; Brubacker, C. H., Jr. *Inorg. Chem.* **1979**, *18*, 3283.
(415) McLain, S. J.; Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 4558.
(416) Nesmeyanov, A. N.; Anisimov, K. N.; Kolobova, N. E.; Pasynskii, A. A. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1969**, 87.
(417) Andreu, A. M.; Jalón, F. A.; Otero, A.; Royo, P.; Manotti Lanfredi, A. M.; Tiripicchio, A. *J. Chem. Soc., Dalton Trans.* **1987**, 953.
(418) de la Mata, J.; Fandos, R.; Gómez, M.; Gómez-Sal, P.; Martinez-Carrera, S.; Royo, P. *Organometallics* **1990**, *9*, 2846.
(419) Herrmann, W. A.; Kalcher, W.; Biersack, H.; Bernal, I.; Creswick, M. *Chem. Ber.* **1981**, *114*, 3558.
(420) Yasuda, H.; Okamoto, T.; Nakamura, A. *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, 1988; Vol. 4, pp 20–23.
(421) Curtis, M. D.; Bell, L. G.; Butler, W. M. *Organometallics* **1985**, *4*, 701.
(422) Teuben, J. H., unpublished results, quoted in ref 119.
(423) Burt, R. J.; Leigh, G. J. *J. Organometal. Chem.* **1978**, *148*, C19.
(424) Andreu, A. M.; Jalón, F. A.; Otero, A. *J. Organometal. Chem.* **1988**, *353*, 185.
(425) Bottomley, F.; Keizer, P. N.; White, P. S.; Preston, K. F. *Organometallics* **1990**, *9*, 1916.
(426) Daran, J.-C.; Prout, K.; De Cian, A.; Green, M. L. H.; Siganporia, N. *J. Organometal. Chem.* **1977**, *136*, C4.
(427) Prout, K.; Daran, J.-C. *Acta Crystallogr.* **1979**, *B35*, 2882.
(428) Jalón, F. A.; Otero, A.; Royo, P.; Fernández, J. M.; Rosales, M. J.; Toscano, R. A. *J. Organometal. Chem.* **1987**, *331*, C1.
(429) Woodward, S.; Riaz, U.; Curtis, M. D.; Haggerty, B. S.; Rheingold, A. L. *Organometallics* **1990**, *9*, 2703.
(430) Gibson, V. C.; Williams, D. N.; Clegg, W.; Hockless, D. C. R. *Polyhedron* **1989**, *8*, 1819.
(431) Xu, Y.; Roesky, H. W.; Schrumpf, F.; Noltemeyer, M. *Z. Naturforsch.* **1990**, *45b*, 423.
(432) (a) Okamoto, T.; Yasuda, H.; Nakamura, A. *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, 1988; Vol. 4, pp 33–36. (b) Okamoto, T.; Yasuda, H.; Nakamura, A. *Organometallic Syntheses*; King, R. B., Eisch, J. J., Eds.; Elsevier: Amsterdam, 1988; Vol. 4, pp 37–40.
(433) Melendez, E.; Arif, A. M.; Rheingold, A. L.; Ernst, R. D. *J. Am. Chem. Soc.* **1988**, *110*, 8703.
(434) Green, M. L. H.; Josseaume, B. *J. Organometal. Chem.* **1980**, *193*, 339.

(435) Fenske, D.; Maué, P. G. *Z. Naturforsch.* **1989**, *44b*, 531.

(436) Bunker, M. J.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1981**, 85.

(437) Bunker M. J.; Green, M. L. H.; Couldwell, C.; Prout, K. *J. Organometal. Chem.* **1980**, *192*, C6.

(438) Alt, H. G.; Engelhardt, H. E. *Z. Naturforsch.* **1989**, *44b*, 367.

(439) Herrmann, W. A.; Biersack, H. *J. Organometal. Chem.* **1980**, *191*, 397.

(440) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Organometal. Chem.* **1980**, *186*, 237.

(441) Curtis, M. D.; Real, J. *Organometallics* **1985**, *4*, 940.

(442) Curtis, M. D.; Real, J.; Kwon, D. *Organometallics* **1989**, *8*, 1644.

(443) Williams, A. C.; Sheffels, P.; Sheenan, D.; Livinghouse, T. *Organometallics* **1989**, *8*, 1566.

(444) Aspinall, H. C.; Roberts, M. M.; Lippard, S. J. *Inorg. Chem.* **1984**, *23*, 1782.

(445) Gibson, V. C.; Bercaw, J. E.; Bruton, W. J., Jr.; Sanner, R. D. *Organometallics* **1986**, *5*, 976.

(446) Okamoto, T.; Yasuda, H.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *Organometallics* **1988**, *7*, 2266.

(447) Sanner, R. D.; Carter, S. T.; Bruton, W. J., Jr. *J. Organometal. Chem.* **1982**, *240*, 157.

(448) Meyer, T. Y.; Garner, L. R.; Baenziger, N. C.; Messerle, L. *Inorg. Chem.* **1990**, *29*, 4045.

(449) (a) Fandos, R.; Gómez, M.; Royo, P.; Garcia-Blanco, S.; Martinez-Carrera, S.; Sanz-Aparicio, J. *Organometallics* **1987**, *6*, 1581. (b) Schrumpf, F.; Roesky, H. W.; Noltemeyer, M. *Z. Naturforsch.* **1990**, *45b*, 1600.

(450) Jernakoff, P.; de Meric de Bellefon, C.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Nouv. J. Chem.* **1988**, *12*, 329.

(451) Jernakoff, P.; de Meric de Bellefon, C.; Geoffroy, G. L.; Rheingold, A. L.; Geib, S. J. *Organometallics* **1987**, *6*, 1362.

(452) Gibson, V. C.; Kee, T. P. *J. Chem. Soc., Chem. Commun.* **1989**, 656.

(453) Fandos, R.; Gómez, M.; Royo, P. *Organometallics* **1989**, *8*, 1604.

(454) Arnold, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 3318.

(455) Arnold, J.; Tilley, T. D. *J. Am. Chem. Soc.* **1985**, *107*, 6409.

(456) Gómez, M.; Royo, P.; Selas, J. M. *J. Organometal. Chem.* **1986**, *314*, 131.

(457) Roesky, H. W.; Schrumpf, F.; Noltemeyer, M. *Z. Naturforsch.* **1989**, *44b*, 1369.

(458) Schrumpf, F.; Roesky, H. W.; Subrahmanyan, T.; Noltemeyer, M. *Z. Anorg. Allg. Chem.* **1990**, *583*, 124.

(459) Plenio, H.; Roesky, H. W.; Noltemeyer, M.; Sheldrick, G. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1330.

(460) Tatsumi, K.; Takeda, J.; Sekiguchi, Y.; Kohsaka, M.; Nakamura, A. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 332.

(461) Tatsumi, K.; Inoue, Y.; Nakamura, A.; Cramer, R. E.; VanDoorne, W.; Gilje, J. W. *J. Am. Chem. Soc.* **1989**, *111*, 782.

(462) Yasuda, H.; Tatsumi, K.; Okamoto, T.; Mashima, K.; Lee, K.; Nakamura, A.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1985**, *107*, 2410.

(463) Green, M. L. H.; Moreau, J. E. *J. Organometal. Chem.* **1978**, *161*, C25.

(464) Gibson, V. C.; Kee, T. P.; Clegg, W. *J. Chem. Soc., Dalton Trans.* **1990**, 3199.

(465) Gibson, V. C.; Kee, T. P.; Clegg, W. *J. Organometal. Chem.* **1988**, *353*, C23.

(466) Kee, T. P.; Gibson, V. C.; Clegg, W. *J. Organometal. Chem.* **1987**, *325*, C14.

(467) Carter, S. T.; Clegg, W.; Gibson, V. C.; Kee, T. P.; Sanner, R. D. *Organometallics* **1989**, *8*, 253.

(468) Kwon, D.; Curtis, M. D. *Organometallics* **1990**, *9*, 1.

(469) Guggolz, E.; Ziegler, M. L.; Biersack, H.; Herrmann, W. A. *J. Organometal. Chem.* **1980**, *194*, 317.

(470) Morse, D. B., Ph.D. Thesis, University of Illinois, 1989.

(471) Morse, D. B.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1988**, *110*, 8234.

(472) Herrmann, W. A.; Thiel, W. R.; Herdtweck, E. *J. Organometal. Chem.* **1988**, *353*, 323.

(473) Tille, D. *Z. Naturforsch.* **1966**, *21b*, 1239.

(474) Pasynskii, A. A.; Eremenko, I. L.; Katugin, A. S.; Nefedov, S. E.; Gasanov, G. S.; Orazsakhatov, B.; Ellert, O. G.; Shklover, V. E.; Struchkov, Y. T. *Metalloorg. Khim.* **1988**, *1*, 172, *Chem. Abstr.* **1989**, *110*, 212997v.

(475) Grohmann, A.; Köhler, F. H.; Müller, G.; Zeh, H. *Chem. Ber.* **1989**, *122*, 897.

(476) Angermund, K.; Döhring, A.; Jolly, P. W.; Krüger, C.; Romão, C. C. *Organometallics* **1986**, *5*, 1268.

(477) Richeson, D. S.; Mitchell, J. F.; Theopold, K. H. *Organometallics* **1989**, *8*, 2570.

(478) Owens, B. E.; Poli, R., unpublished results.

(479) Owens, B. E.; Poli, R. *Inorg. Chim. Acta* **1991**, *179*, 229.

(480) Alt, H. G.; Frister, T.; Trapl, E. E.; Engelhardt, H. E. *J. Organometal. Chem.* **1989**, *362*, 125.

(481) Green, M. L. H.; Mountford, P. *Organometallics* **1990**, *9*, 886.

(482) Kilner, M.; Midcalf, C. *J. Chem. Soc. (A)* **1971**, 292.

(483) Stärker, K.; Curtis, M. D. *Inorg. Chem.* **1985**, *24*, 3006.

(484) Mountford, P., personal communication, December 1990.

(485) Schrock, R. R.; Kolodziej, R. M.; Liu, A. H.; Davis, W. M.; Vale, M. G. *J. Am. Chem. Soc.* **1990**, *112*, 4338.

(486) Liu, A. H.; Murray, R. C.; Dewan, J. C.; Santarsiero, B. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 4282.

(487) MacLaughlin, S. A.; Murray, R. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1985**, *4*, 796.

(488) Okuda, J.; Murray, R. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 1681.

(489) Holmes, S. J.; Schrock, R. R. *Organometallics* **1983**, *2*, 1463.

(490) O'Regan, M. B.; Liu, A. H.; Finch, W. C.; Schrock, R. R.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 4331.

(491) Parkin, G.; Bercaw, J. E. *Polyhedron* **1988**, *7*, 2053.

(492) Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1297.

(493) Herrmann, W. A. *Comments Inorg. Chem.* **1988**, *7*, 73.

(494) Herrmann, W. A. *J. Organometal. Chem.* **1990**, *382*, 1.

(495) Herrmann, W. A. *J. Organometal. Chem.* **1986**, *300*, 111.

(496) Herrmann, W. A.; Herdtweck, E.; Flöel, M.; Kulpe, J.; Küsthardt, U.; Okuda, J. *Polyhedron* **1987**, *6*, 1165.

(497) Coffield, T. H.; Sandel, V.; Closson, R. D. *J. Am. Chem. Soc.* **1957**, *79*, 5826.

(498) Köhler, F. H.; Hebendanz, N.; Thewalt, U.; Kanellakopulos, B.; Klenze, R. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 721.

(499) Heck, J.; Massa, W.; Weinig, P. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 722.

(500) Herrmann, W. A.; Theiler, H. G.; Herdtweck, E.; Kiprof, P. *J. Organometal. Chem.* **1989**, *367*, 291.

(501) Herrmann, W. A.; Fischer, R. A.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1263.

(502) Nunn, C. M.; Cowley, A. H.; Lee, S. W.; Richmond, M. G. *Inorg. Chem.* **1990**, *29*, 2105.

(503) Herrmann, W. A.; Weichselbaumer, G.; Paciello, R. A.; Fischer, R. A.; Herdtweck, E.; Okuda, J.; Marz, D. W. *Organometallics* **1990**, *9*, 489.

(504) Herrmann, W. A.; Marz, D. W.; Herdtweck, E. *J. Organometal. Chem.* **1990**, *394*, 285.

(505) Takacs, J.; Kiprof, P.; Weichselbaumer, G.; Herrmann, W. A. *Organometallics* **1989**, *8*, 2394.

(506) Takacs, J.; Kiprof, P.; Herrmann, W. A. *Polyhedron* **1990**, *9*, 2211.

(507) Flöel, M.; Herdtweck, E.; Wagner, W.; Kulpe, J.; Härter, P.; Herrmann, W. A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 787.

(508) Herrmann, W. A.; Fischer, R. A.; Herdtweck, E. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1509.

(509) Herrmann, W. A.; Okuda, J. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1092.

(510) Paciello, R. A.; Kiprof, P.; Herdtweck, E.; Herrmann, W. A. *Inorg. Chem.* **1989**, *28*, 2890.

(511) Kölle, U.; Fuss, B.; Khouzami, F.; Gersdorf, J. *J. Organometal. Chem.* **1985**, *290*, 77.

(512) Fukui, H.; Ito, M.; Moro-oka, Y.; Katajima, N. *Inorg. Chem.* **1990**, *29*, 2868.

(513) Kölle, U.; Kossakowski, J. *J. Chem. Soc., Chem. Commun.* **1988**, 549.

(514) Kölle, U.; Kang, B.-S.; Thewalt, U. *J. Organometal. Chem.* **1990**, *386*, 267.

(515) Canestrari, M.; Chaudret, B.; Dahan, F.; Huang, Y.-S.; Poilblanc, R.; Kim, T.-C.; Sanchez, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1179.

(516) Campion, B. K.; Heyn, R. H.; Tilley, D. T. *J. Chem. Soc., Chem. Comm.* **1988**, 278.

(517) Fagan, P. J.; Ward, M. D.; Caspar, J. V.; Calabrese, J. C.; Krusic, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 2981.

(518) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308.

(519) Suzuki, H.; Lee, D. H.; Oshima, N.; Moro-oka, Y. *Organometallics* **1987**, *6*, 1569.

(520) Dev, S.; Imagawa, K.; Mizobe, Y.; Cheng, G.; Wakatsuki, Y.; Yamazaki, H.; Hidai, M. *Organometallics* **1989**, *8*, 1232.

(521) Hidai, M.; Imagawa, K.; Cheng, G.; Mizobe, Y.; Wakatsuki, Y.; Yamazaki, H. *Chem. Lett.* **1986**, 1299.

(522) Tanase, T.; Imagawa, K.; Dev, S.; Mizobe, Y.; Yano, S.; Hidai, M. *New J. Chem.* **1988**, *12*, 697.

(523) Dev, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1990**, *29*, 4797.

(524) Suzuki, H.; Omori, H.; Lee, D. W.; Yoshida, Y.; Moro-oka, Y. *Organometallics* **1988**, *7*, 2243.

(525) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166.

(526) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Inorg. Chem.* **1986**, *25*, 3407.

(527) Kaganovich, V. S.; Kudinov, A. R.; Rybinskaya, M. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1986**, 456.

(528) Kaganovich, V. S.; Kudinov, A. R.; Rybinskaya, M. I. *Metalloorg. Khim.* **1990**, *3*, 70.

(529) Chávez, I.; Cisternas, A.; Otero, M.; Román, E.; Müller, U. *Z. Naturforsch.* **1990**, *45b*, 658.

(530) Gassman, P. G.; Winter, C. H. *J. Am. Chem. Soc.* **1988**, *110*, 6130.
(531) Kudinov, A. R.; Rybinskaya, M. I.; Struchkov, Y. T.; Yanovskii, A. I.; Petrovskii, P. V. *J. Organometal. Chem.* **1987**, *336*, 187.
(532) Kreindlin, A. Z.; Petrovskii, P. V.; Rybinskaya, M. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1987**, 1772.
(533) Kudinov, A. R.; Rybinskaya, M. I. *Metalloorg. Khim.* **1988**, *1*, 1429; *Chem. Abstr.* **1990**, *112*, 21110g.
(534) Crossley, N. S.; Green, J. C.; Nagy, A.; Stringer, G. *J. Chem. Soc., Dalton Trans.* **1989**, 2139.
(535) Kakigano, T.; Suzuki, H.; Igarashi, M.; Moro-oka, Y. *Organometallics* **1990**, *9*, 2192.
(536) Haga, M.; Sakamoto, H.; Suzuki, H. *J. Organometal. Chem.* **1989**, *377*, C77.
(537) Kölle, U.; Kossakowski, J. *Inorg. Chim. Acta* **1989**, *164*, 23.
(538) Nagashima, H.; Mukai, K.; Shiota, Y.; Ara, K.-I.; Itoh, K.; Suzuki, H.; Oshima, N.; Moro-oka, Y. *Organometallics* **1985**, *4*, 1314.
(539) Nagashima, H.; Mukai, K.; Shiota, Y.; Yamaguchi, K.; Ara, K.-I.; Fukahori, T.; Suzuki, H.; Akita, M.; Moro-oka, Y.; Itoh, K. *Organometallics* **1990**, *9*, 799.
(540) Kölle, U.; Khouzami, F.; Fuss, B. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 131.
(541) Strauss, R. C.; Keller, E.; Brintzinger, H. H. *J. Organometal. Chem.* **1988**, *340*, 249.
(542) Raabe, E.; Kölle, U. *J. Organometal. Chem.* **1985**, *279*, C29.
(543) Lehmkuhl, H.; Nehl, H.; Benn, R.; Mynott, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 646.
(544) He, X.; Maisonnat, A.; Dahan, F.; Poilblanc, R. *J. Chem. Soc., Chem. Commun.* **1990**, 670.
(545) Green, M. L. H.; Pardy, R. B. A. *J. Chem. Soc., Dalton Trans.* **1979**, 355.
(546) Roe, D. M.; Maitlis, P. M. *J. Chem. Soc. (A)* **1971**, 3173.
(547) Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1985**, *23*, 15.
(548) Macazaga, M. J.; Delgado, S.; Medina, R. M.; Masaguer, J. R. *J. Organometal. Chem.* **1984**, *277*, 423.
(549) Okuda, J.; Zimmermann, K. H. *Chem. Ber.* **1989**, *122*, 1645.
(550) Okuda, J.; Zimmermann, K. H. *Chem. Ber.* **1990**, *123*, 1641.
(551) Knizhnikov, V. A.; Shirokii, V. L.; Sutormin, A. B.; Novikova, M. G.; Maier, N. A.; Ol'dekop, Y. A. *Metalloorg. Khim.* **1989**, *2*, 1160; *Chem. Abstr.* **1990**, *112*, 235566j.
(552) Miller, E. J.; Landon, S. J.; Brill, T. B. *Organometallics* **1985**, *4*, 533.
(553) Kölle, U.; Fuss, B.; Rajasekharan, M. V.; Ramakrishna, B. L.; Ammeter, J. H.; Böhm, M. C. *J. Am. Chem. Soc.* **1984**, *106*, 4152.
(554) Kölle, U.; Raabe, E.; Krüger, C.; Rotzinger, F. P. *Chem. Ber.* **1987**, *120*, 979.
(555) Beevor, R. G.; Frith, S. A.; Spencer, J. L. *J. Organometal. Chem.* **1981**, *221*, C25.
(556) Olson, W. L.; Stacy, A. M.; Dahl, L. F. *J. Am. Chem. Soc.* **1986**, *108*, 7646.
(557) Brookhart, M.; Lincoln, D. M.; Volpe, A. F., Jr.; Schmidt, G. F. *Organometallics* **1989**, *8*, 1212.
(558) Hughes, R. P. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 5, pp 277–540.
(559) Leigh, G. J.; Richards, R. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 5, pp 541–628.
(560) (a) Maitlis, P. M. *Acc. Chem. Res.* **1978**, *11*, 301. (b) Maitlis, P. M. *Chem. Soc. Rev.* **1981**, *10*, 1.
(561) Angelici, R. J.; Fischer, E. O. *J. Am. Chem. Soc.* **1963**, *85*, 3733.
(562) Powell, J.; Shaw, B. L. *J. Chem. Soc. (A)* **1968**, 597.
(563) Kasahara, A.; Izumi, T.; Tanaka, K. *Bull. Chem. Soc. Japan* **1967**, *40*, 699.
(564) Kang, J. W.; Maitlis, P. M. *J. Am. Chem. Soc.* **1968**, *90*, 3259.
(565) Booth, B. L.; Haszeldine, R. N.; Hill, M. *J. Chem. Soc. (A)* **1969**, 1299.
(566) Kang, J. W.; Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1968**, 1304.
(567) Dooley, T.; Fairhurst, G.; Chalk, C. D.; Tabatabaian, K.; White, C. *Trans. Met. Chem.* **1978**, *3*, 299.
(568) Gill, D. S.; Maitlis, P. M. *J. Organometal. Chem.* **1975**, *87*, 359.
(569) Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1978**, *17*, 3011.
(570) Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc. (A)* **1970**, 2875.
(571) Churchill, M. R.; Julis, S. A. *Inorg. Chem.* **1979**, *18*, 1215.
(572) Fanizzi, F. P.; Sunley, G. J.; Maitlis, P. M. *J. Organometal. Chem.* **1987**, *330*, C31.
(573) Sunley, G. J.; Fanizzi, F. P.; Saez, I. M.; Maitlis, P. M. *J. Organometal. Chem.* **1987**, *330*, C27.
(574) Gould, R. O.; Jones, C. L.; Robertson, D. R.; Tocher, D. A.; Stephenson, T. A. *J. Organometal. Chem.* **1982**, *226*, 199.
(575) Nutton, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 1997.
(576) Puebla, M. P.; Sarasa, M. D. *Opt. Pura Apl.* **1987**, *20*, 201; *Chem. Abstr.* **1989**, *110*, 95511u.
(577) Rigby, W.; McCleverty, J. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 382.
(578) Faraone, F.; Marsala, V.; Tresoldi, G. *J. Organometal. Chem.* **1978**, *152*, 337.
(579) Hanson, A. W.; McAlees, A. J.; Taylor, A. *J. Chem. Soc., Perkin Trans. 1* **1985**, 441.
(580) Jones, W. D.; Duttweilwer, R. P., Jr.; Feher, F. J. *Inorg. Chem.* **1990**, *29*, 1505.
(581) Jones, W. D.; Feher, F. J. *Organometallics* **1983**, *2*, 686.
(582) McCleverty, J. A.; Williams, J. *Trans. Met. Chem.* **1978**, *3*, 201.
(583) Pill, T.; Polborn, K.; Beck, W. *Chem. Ber.* **1990**, *123*, 11.
(584) Baxter, S. M.; Ferguson, G. S.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4231.
(585) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1981**, 2003.
(586) Jones, W. D.; Feher, F. J. *Inorg. Chem.* **1984**, *23*, 2376.
(587) Klingert, B.; Werner, H. *Chem. Ber.* **1983**, *116*, 1450.
(588) Klingert, B.; Werner, H. *J. Organometal. Chem.* **1983**, *252*, C47.
(589) Werner, H.; Klingert, B.; Rheingold, A. L. *Organometallics* **1988**, *7*, 911.
(590) Oro, L. A.; Carmona, D.; Lahoz, F. J.; Puebla, M. P.; Esteban, M.; Foces-Foces, C.; Cano, F. H. *J. Chem. Soc., Dalton Trans.* **1986**, 2113.
(591) (a) Abel, E. W.; Beckett, M. A.; Ellis, D.; Orrell, K. G.; Sik, V.; Stephenson, D. *J. Chem. Res. (Synopses)* **1988**, 232. (b) Abel, E. W.; Beckett, M. A. *Polyhedron* **1987**, *6*, 1255.
(592) Bell, M. N.; Blake, A. J.; Schröder, M.; Stephenson, T. A. *J. Chem. Soc., Chem. Commun.* **1986**, 471.
(593) Valderrama, M.; Scotti, M.; Campos, P.; Werner, H.; Müller, G. *Chem. Ber.* **1990**, *123*, 1005.
(594) Cornock, M. C.; Robertson, D. R.; Stephenson, T. A.; Jones, C. L.; Milburn, G. H. W.; Sawyer, L. *J. Organometal. Chem.* **1977**, *135*, C50.
(595) Robertson, D. R.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1978**, 486.
(596) Rigby, W.; Bailey, P. M.; McCleverty, J. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 371.
(597) Rigby, W.; Lee, H.-B.; Bailey, P. M.; McCleverty, J. A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 387.
(598) Espinet, P.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 1542.
(599) Ahmed, M.; Edwards, A. J.; Jones, C. J.; McCleverty, J. A.; Rothin, A. S.; Tate, J. P. *J. Chem. Soc., Dalton Trans.* **1988**, 257.
(600) Krämer, R.; Polborn, K.; Wanjek, H.; Zahn, I.; Beck, W. *Chem. Ber.* **1990**, *123*, 767.
(601) Braunstein, P.; Matt, D.; Nobel, D.; Bouaoud, S.-E.; Grandjean, D. *J. Organometal. Chem.* **1986**, *301*, 401.
(602) Pinillos, M. T.; Jarauta, M. P.; Carmona, D.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *J. Organometal. Chem.* **1988**, *345*, C13.
(603) Pinillos, M. T.; Jarauta, M. P.; Carmona, D.; Oro, L. A.; Apreda, M. C.; Foces-Foces, C.; Cano, F. H. *J. Chem. Soc., Dalton Trans.* **1989**, 1987.
(604) Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1990**, *9*, 2875.
(605) O'Sullivan, D. J.; Lalor, F. J. *J. Organometal. Chem.* **1973**, *57*, C58.
(606) Restivo, R. J.; Ferguson, G.; O'Sullivan, D. J.; Lalor, F. J. *Inorg. Chem.* **1975**, *14*, 3046.
(607) Bailey, J. A.; Grundy, S. L.; Stobart, S. R. *Organometallics* **1990**, *9*, 536.
(608) Fotheringham, J. D.; Stephenson, T. A. *J. Organometal. Chem.* **1985**, *284*, C12.
(609) Kläui, W.; Buchholz, E. *Inorg. Chem.* **1988**, *27*, 3500.
(610) Hayashi, Y.; Toriumi, K.; Isobe, K. *J. Am. Chem. Soc.* **1988**, *110*, 3666.
(611) Howard, K. E.; Rauchfuss, T. B.; Wilson, S. R. *Inorg. Chem.* **1988**, *27*, 3561.
(612) Ozawa, Y.; Hayashi, Y.; Isobe, K. *Chem. Lett.* **1990**, 249.
(613) Hayashi, Y.; Ozawa, Y.; Isobe, K. *Chem. Lett.* **1989**, 425.
(614) Besecker, C. J.; Day, V. W.; Klemperer, W. G.; Thompson, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 4125.
(615) Ferguson, G.; Hawthorne, M. F.; Kaitner, B.; Lalor, F. J. *Acta Crystallogr.* **1984**, *C40*, 1707.
(616) Fontaine, X. L. R.; Fowkes, H.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1165.
(617) Fontaine, X. L. R.; Fowkes, H.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1987**, 2417.
(618) Fontaine, X. L. R.; Fowkes, H.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1986**, 547.

(619) Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; MacKinnon, P. I.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1986**, 1111.
(620) Bown, M.; Jelinek, T.; Stíbr, B.; Hermánek, S.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1988**, 974.
(621) Bown, M.; Fowkes, H.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; MacKinnon, P.; Nestor, K. *J. Chem. Soc., Dalton Trans.* **1988**, 2597.
(622) Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Nestor, K.; Thornton-Pett, M.; Hermánek, S.; Jelínek, T.; Stíbr, B. *J. Chem. Soc., Dalton Trans.* **1990**, 681.
(623) Nestor, K.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Chem. Commun.* **1989**, 455.
(624) Faridoon; McGrath, F. M.; Spalding, T. R.; Fontaine, X. L. R.; Kennedy, J. D.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1819.
(625) Hanusa, T. P.; Todd, L. J. *Polyhedron* **1985**, *4*, 2063.
(626) Burk, P. L.; Van Engen, D.; Campo, K. S. *Organometallics* **1984**, *3*, 493.
(627) Thompson, S. J.; White, C.; Maitlis, P. M. *J. Organometal. Chem.* **1977**, *136*, 87.
(628) Tresoldi, G.; Sergi, S.; Lo Schiavo, S.; Piraino, P. *J. Organometal. Chem.* **1987**, *328*, 387.
(629) Besecker, C. J.; Day, V. W.; Klemperer, W. G. *Organometallics* **1985**, *4*, 564.
(630) Edlund, D. J.; Saxton, R. J.; Lyon, D. K.; Finke, R. G. *Organometallics* **1988**, *7*, 1692.
(631) Bieri, J. H.; Egolf, T.; von Philipsborn, W.; Piantini, U.; Prewo, R.; Ruppli, U.; Salzer, A. *Organometallics* **1986**, *5*, 2413.
(632) El-Amouri, H.; Gruselle, M.; Jackson, P. A.; Jaouen, G.; Vaissermann, J. *Organometallics* **1990**, *9*, 2871.
(633) Espinet, P.; Bailey, P. M.; Downey, R. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1048.
(634) Huckett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686.
(635) Russell, M. J. H.; White, C.; Yates, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 857.
(636) Valderrama, M.; Scotti, M.; Prati, E. *Bol. Soc. Chil. Quim.* **1986**, *31*, 53; *Chem. Abstr.* **1987**, *106*, 176637j.
(637) Bickert, P.; Hafner, K. *Tetrahedron Lett.* **1982**, *23*, 2309.
(638) Bickert, P.; Hafner, K. *Coll. Czech. Chem. Commun.* **1988**, *53*, 2418.
(639) Rybinskaya, M. I.; Kudinov, A. R.; Kaganovich, V. S. *J. Organometal. Chem.* **1983**, *246*, 279.
(640) Herberich, G. E.; Ohst, H. *Chem. Ber.* **1985**, *118*, 4303.
(641) Herberich, G. E.; Hessner, B.; Hostalek, M. *J. Organometal. Chem.* **1988**, *355*, 473.
(642) Isobe, K.; Andrews, D. G.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc. Chem. Commun.* **1981**, 809.
(643) Vázquez de Miguel, A.; Gómez, M.; Isobe, K.; Taylor, B. F.; Mann, B. E.; Maitlis, P. M. *Organometallics* **1983**, *2*, 1724.
(644) Isobe, K.; Vázquez de Miguel, A.; Bailey, P. M.; Okeya, S.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1983**, 1441.
(645) Vázquez de Miguel, A.; Isobe, K.; Taylor, B. F.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1982**, 758.
(646) Vázquez de Miguel, A.; Isobe, K.; Bailey, P. M.; Meanwell, N. J.; Maitlis, P. M. *Organometallics* **1982**, *1*, 1604.
(647) Vázquez de Miguel, A.; Maitlis, P. M. *J. Organometal. Chem.* **1983**, *244*, C35.
(648) Bennett, M. A.; McMahon, I. J.; Pelling, S.; Robertson, G. B.; Wickramasinghe, W. A. *Organometallics* **1985**, *4*, 754.
(649) Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1969**, 1155.
(650) Moseley, K.; Maitlis, P. M. *J. Chem. Soc. (A)* **1970**, 2884.
(651) Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1969**, 1156.
(652) White, C.; Gill, D. S.; Kang, J. W.; Lee, H. B.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1971**, 734.
(653) Moreto, J.; Maruya, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1982**, 1341.
(654) Kang, J. W.; Maitlis, P. M. *J. Organometal. Chem.* **1971**, *26*, 393.
(655) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1971**, *93*, 5260.
(656) King, R. B.; Efraty, A. *J. Am. Chem. Soc.* **1972**, *94*, 3768.
(657) Herberich, G. E.; Pampaloni, G. *J. Organometal. Chem.* **1982**, *240*, 121.
(658) Fernandez, M.-J.; Bailey, P. M.; Bentz, P. O.; Ricci, J. S.; Koetzle, T. F.; Maitlis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 5458.
(659) Fernandez, M.-J.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1982**, 310.
(660) Ruiz, J.; Mann, B. E.; Spencer, C. M.; Taylor, B. F.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1987**, 1963.
(661) Ruiz, J.; Spencer, C. M.; Mann, B. E.; Taylor, B. F.; Maitlis, P. M. *J. Organometal. Chem.* **1987**, *325*, 253.
(662) Fernandez, M.-J.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 2063.
(663) Ruiz, J.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1986**, 862.
(664) Millan, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1982**, 73.
(665) Booth, B. L.; Haszeldine, R. N.; Hill, M. *J. Organometal. Chem.* **1969**, *16*, 491.
(666) White, C. W.; Yates, A.; Maitlis, P. M. *Inorg. Synth.*, volume in preparation, quoted in ref 23.
(667) Yamazaki, H. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 582.
(668) Bezrukova, A. A.; Khandkarova, V. S.; Andrianov, V. G.; Struchkov, Y. T.; Rubezhov, A. Z. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1987**, 1922.
(669) Gilbert, T. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3502.
(670) Glueck, D. S.; Bergman, R. G. *Organometallics* **1990**, *9*, 2862.
(671) White, C.; Thompson, S. J.; Maitlis, P. M. *J. Organometal. Chem.* **1977**, *127*, 415.
(672) Glueck, D. S.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2719.
(673) Carmona, D.; Oro, L. A.; Lamata, M. P.; Elguero, J.; Apreda, M. d. C.; Foces-Foces, C.; Cano, F. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1114.
(674) Nestor, K. Ph.D. Thesis, University of Leeds, 1989.
(675) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199.
(676) Huckett, S. C.; Angelici, R. J. *Organometallics* **1988**, *7*, 1491.
(677) Gilbert, T. M.; Bergman, R. G. *Organometallics* **1983**, *2*, 1458.
(678) Fernandez, M.-J.; Maitlis, P. M. *Organometallics* **1983**, *2*, 164.
(679) Isobe, K.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1981**, 808.
(680) Isobe, K.; Vázquez de Miguel, A.; Nutton, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1984**, 929.
(681) Isobe, K.; Vázquez de Miguel, A.; Maitlis, P. M. *J. Organometal. Chem.* **1983**, *250*, C25.
(682) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 3388.
(683) McGhee, W. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 4246.
(684) Guggolz, E.; Ziegler, M. L.; Kalcher, W.; Plank, J.; Riedel, D.; Herrmann, W. A. *Z. Naturforsch.* **1981**, *36b*, 1053.
(685) Lehmkuhl, H.; Naydowski, C.; Benn, R.; Rufińska, A.; Schroth, G.; Mynott, R.; Krüger, C. *Chem. Ber.* **1983**, *116*, 2447.
(686) McClellan, W. R.; Hoehn, H. H.; Cripps, H. N.; Muetterties, E. L.; Howk, B. W. *J. Am. Chem. Soc.* **1961**, *83*, 1601.
(687) Samuel, E.; Bigorgne, M. *J. Organometal. Chem.* **1969**, *19*, 9.
(688) Lin, S.; Boudjouk, P. *J. Chin. Chem. Soc. (Taipei)* **1989**, *36*, 35.
(689) Fischer, E. O.; Schuster-Woldan, H. *Chem. Ber.* **1967**, *100*, 705.
(690) Fischer, E. O.; Meyer, P.; Kreiter, C. G.; Müller, J. *Chem. Ber.* **1972**, *105*, 3014.
(691) Anderson, G. K. *Organometallics* **1986**, *5*, 1903.
(692) Clark, H. C.; Shaver, A. *Can. J. Chem.* **1976**, *54*, 2068.
(693) Cross, R. J.; McLennan, A. J. *J. Chem. Soc., Dalton Trans.* **1983**, 359.
(694) Cross, R. J.; Wardle, R. *J. Chem. Soc. (A)* **1971**, 2000.
(695) Werner, H.; Kraus, H.-J. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 948.
(696) Roth, S.; Ramamoorthy, V.; Sharp, P. R. *Inorg. Chem.* **1990**, *29*, 3345.
(697) Rockensüss, W.; Roesky, H. W.; Gilje, J. W.; Noltemeyer, M. *Eur. J. Solid State Inorg. Chem.* **1990**, *27*, 599.