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Cp* Chemistry of main-group elements†

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In the chemistry of main-group elements the pentamethylcyclopentadienyl (Cp*) group represents a very important substituent. Owing to its quite variable bonding modes, ranging from mainly ionic to mainly covalent and from η^5 *via* $\eta^{2/3}$ to η^1, an effective adjustment to the electronic situation at the respective element centre is feasible. Furthermore, the steric requirements of the σ- or π-bound Cp* group enable the kinetic stabilization of otherwise highly reactive species. Covalent Cp*–element bonds are comparatively weak, consequently allowing fast sigmatropic and haptotropic rearrangement processes. A further consequence is that the Cp* radical as well as the Cp*$^-$ anion are potential leaving groups. This phenomenon forms the basis of a rich faceted substitution and elimination chemistry. As proof of this statement, several examples from phosphorus, silicon, and gallium chemistry are presented.

1 Introduction

During the last fifty years cyclopentadienyl (Cp) ligands have played a very important role in the organometallic chemistry of s-, p-, d-, and f-block elements. Their versatile application is based on the highly variable Cp–element interaction and on the fact that several kinds of substituents and functionalities can readily be introduced to the C_5 perimeter, thus allowing many variations in structure and chemistry. The Cp chemistry of the main-group elements (s- and p-block elements) has experienced great progress especially during the last two decades, so that the main principles of structure, bonding, and reactivity are well understood.[1–5] This article concentrates on a Cp ligand which has been used extensively in our and in other groups and which turned out to be of great value in the chemistry of main-group elements for many purposes, namely the pentamethylcyclopentadienyl (Cp*) ligand. Basic concepts of structure and bonding in relevant compounds as well as characteristic reactivity patterns will be described, demonstrating that the Cp* ligand is a real "star" in this part of chemistry.

2 Bonding and structure

Main-group elements interact with the Cp* ligand in a variety of fashions which are specified structurally in terms of the position of the element with respect to the pentagonal cylinder defined by the C_5 perimeter (see Fig. 1). When the element resides inside the cylinder the bonding situation is referred to as a π interaction with hapticities from η^1 to η^5. A σ interaction is inferable from an outside position; this situation is connected with changes in C–C bond lengths and angles and in the hybridization towards sp^3 of the element-bound carbon centre. The range of electronegativities harboured by the main-group element fragments is responsible for variable Cp*–El interactions from predominantly ionic to predominantly covalent, with many borderline bonding situations.

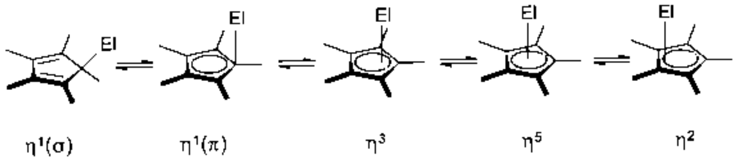
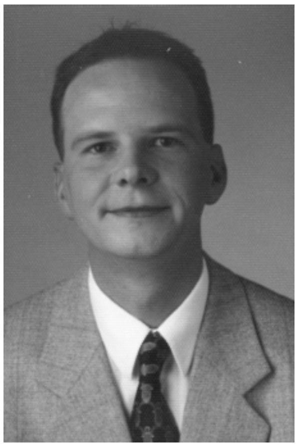


Fig. 1 Structural alternatives for Cp*–element compounds.

Peter Jutzi



Guido Reumann

Prof. Dr. Peter Jutzi studied chemistry at the Technical University of Munich and received his Ph.D. degree in 1965 under the supervision of Prof. Dr. M. Schmidt at the University of Marburg. After his habilitation at the University of Würzburg in 1971 he was appointed associate professor in 1974. In 1979 he moved as a full professor of Inoganic Chemistry to the University of Bielefeld. His scientific interest is the field of experimental organometallic chemistry. Current topics of research are: cyclopentadienyl chemistry of s-, p-, and d-block elements; nanostructured materials from CVD processes; multiferrocenyl systems as electron transfer reagents; functionalized silasesquioxanes and metallasilasesquioxanes; higher-coordinated silicon compounds.

Dr. Guido Reumann was born in Wiedenbrück, Germany in 1967. He studied chemistry at the University of Bielefeld and received his diploma in 1995. He earned his PhD degree under the supervision of Prof. Dr. Peter Jutzi in 1999. His research interest is centered around the reactivity of Cp substituted monovalent Group 13 compounds.

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† Dedicated to Prof. Dr. Dr. h.c. Max Schmidt on the occasion of his 75th birthday.

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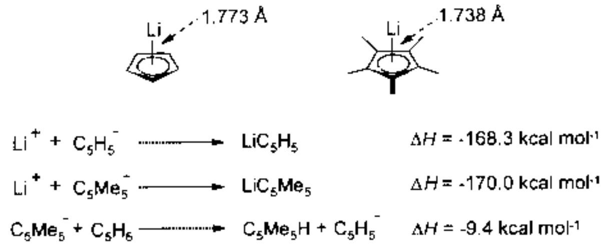
2.1 Predominantly ionic Cp* compounds

Electrostatic interactions dominate the bonding between Cp* fragments and electropositive elements like alkali metals and heavier alkaline-earth metals and lead to the presence of highly ionic species; the contribution of covalent bonding in such compounds is in the range of only a few percent.[6] Compared with the parent cyclopentadienide anion, the pentamethylcyclopentadienide anion is the better nucleophile; *ab initio* calculations show that the electron-releasing methyl groups destabilize the Cp anion, as documented by the isodesmic reaction involving proton transfer (see Scheme 1).[7] Alkyl substitution results in slightly stronger Li–Cp* bonding, as shown by the shorter Li–Cp(centroid) distance and by the slightly higher heterolytic association energy (see Scheme 1).[7]



Scheme 1 Comparison of the Cp^- and the Cp^{*-} anion.

Solid-state and gas-phase structures are determined by π interaction between the respective cation and an η^5-coordinated Cp* anion. Solid-state structures of some alkali metal pentamethylcyclopentadienides are schematically represented in Fig. 2. The supersandwich structure of LiCp* (a) with bridging lithium cations and bridging η^5-Cp^{*-} anions was found by X-ray powder diffraction studies only recently.[8] On the basis of a structural relationship between Cp and Cp* compounds, a bent-supersandwich structure of type (b) with interstrand contacts, caused by additional electrostatic interactions between the cation and σ-electron density in methyl groups of the Cp^{*-} anion, can be predicted for the heavier alkali metal pentamethylcyclopentadienides. Interstrand contacts are avoided by pyridine coordination in the supersandwich structure of KCp*·2py.[9] A half-sandwich structure with an η^5-Cp* ligand is observed for KCp*·18-crown-6;[10] here, the crown ether molecule fills the coordination sphere at the K^+ centre.

In the solid-state structure of the metallocene $BaCp^*_2$ the optimization of electrostatic interactions leads to a bent-sandwich structure with intermolecular barium–methyl group contacts, as shown in a perspective view in Fig. 3 (ball and stick model).[11] Interestingly, bending of the Cp* ligands is also observed in the gas-phase structures of the calcium, strontium, and barium metallocenes. Arguments for this phenomenon include the operation of attractive van der Waals forces between the rings and induced polarization of the metal centre by the ligands; the energy benefits associated with bending are very small (2–4 kJ mol^{-1}).[12]

The optimization of electrostatic interactions in alkali metal and in alkaline earth metal cyclopentadienides might lead to very surprising and complicated structures. An impressive example is the ion pair $[Cs_2Cp^*(18\text{-crown-}6)_2]^+$ $[Cs_4Cp_3Cp^*_2(18\text{-crown-}6)_2]^-$·2THF.[13] In the cation an inverse-sandwich structure (Cs–Cp*–Cs) is present with the two Cs^+ cations additionally coordinated by 18-crown-6. In the anion the central unit is built by an anionic Cp–Cs–Cp–Cs–Cp fragment, which can be regarded as part of a bent CsCp-supersandwich structure, and in which the two Cs^+ cations are additionally coordinated by a Cp*Cs(18-crown-6) unit. All Cp* groups are in bridging positions, and two of the three Cp groups reside in terminal positions. The structure of this compound is presented in Fig. 4 (THF molecules are omitted).

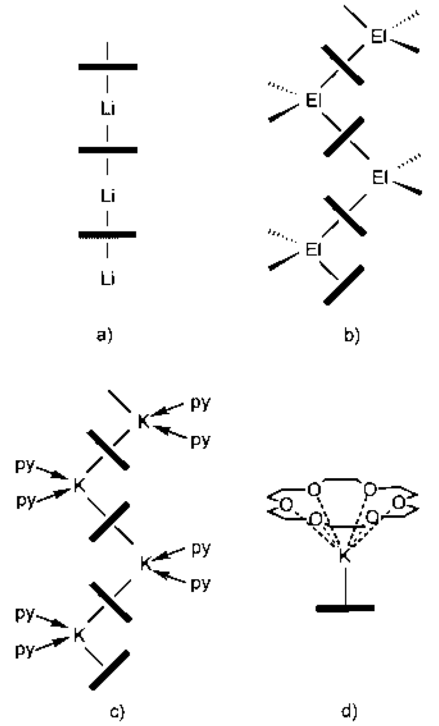


Fig. 2 Schematic structures of alkali metal pentamethylcyclopentadienides.

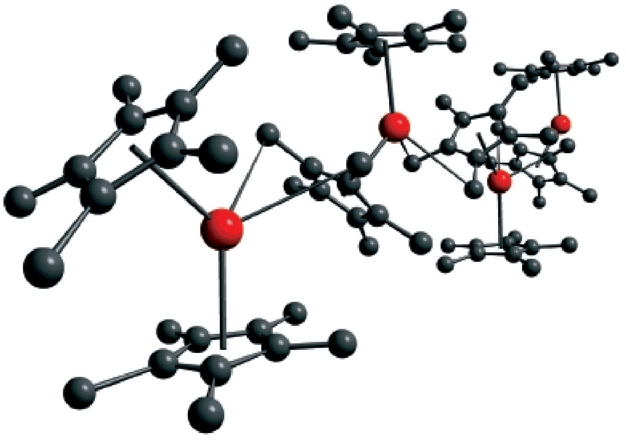


Fig. 3 Solid-state structure of $BaCp^*_2$ (ball and stick model).

2.2 Predominantly covalent Cp* compounds

In all other main-group element compounds the El–Cp* bonding is regarded as predominantly covalent; some "borderline" situations are discussed later. The covalent character is caused by the comparatively higher electrophilicity of the corresponding element cation. According to the alternatives presented in Fig. 1, σ and π structures have to be discussed.

2.2.1 σ-Cp* structures. Fluxionality based on 1,5-sigmatropic rearrangements is characteristic for most of the covalent σ-Cp* compounds of the main-group elements.[1] The degenerate process is described in Fig. 5. The dynamic behaviour of Cp*El compounds has been investigated in detail mainly by DNMR studies and by theoretical calculations. Ground-state and transition-state energies are strongly influenced by the respective element and by the further element-bound substituents. At a rough guess, the dynamic behaviour can be correlated with the ease for El–Cp* bond splitting, *i.e.* with the leaving-group character (see below) of the respective Cp* group.

In combination with many main-group elements, the Cp* substituent can be regarded as very bulky and thus as suitable for kinetic stabilization of unusual bonding situations. Some

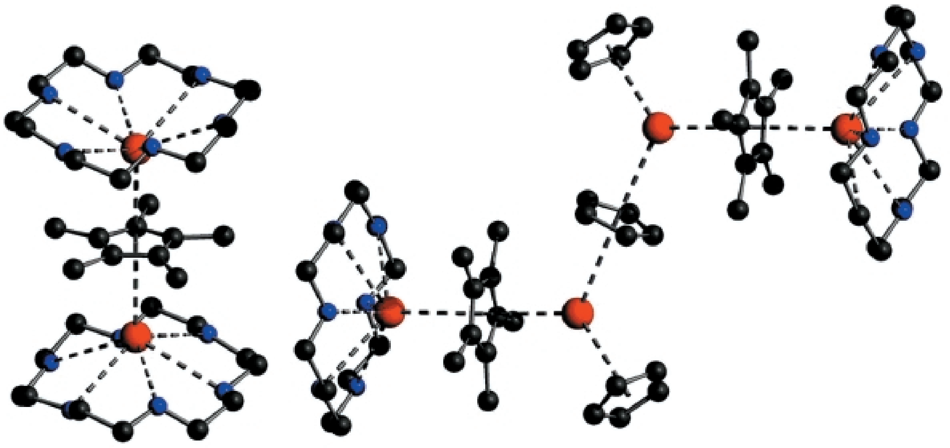


Fig. 4 Structure of $[Cs_2Cp^*(18\text{-crown-}6)_2]^+[Cs_4Cp_3Cp^*_2(18\text{-crown-}6)_2]^-$.

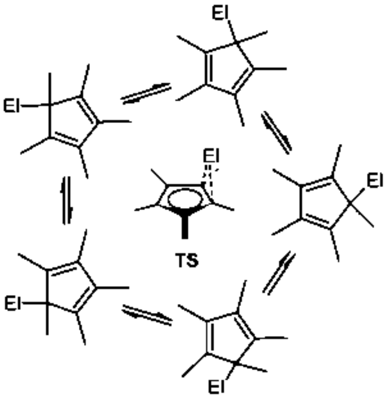
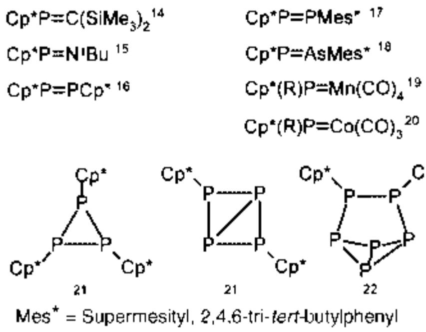


Fig. 5 Degenerate sigmatropic rearrangements in Cp*El compounds.



Scheme 2 Kinetically stabilized Cp*–phosphorus compounds.

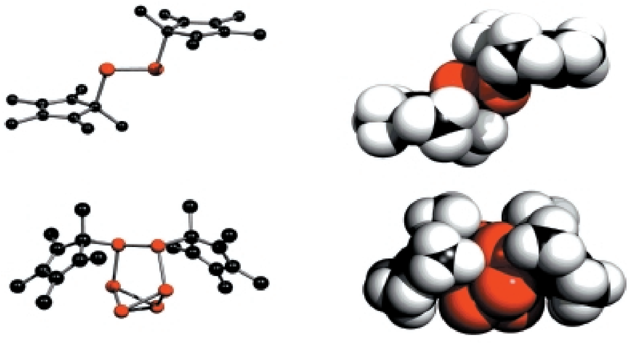


Fig. 6 Molecular structure of $Cp^*_2P_2$ and of $Cp^*_2P_6$ (ball and stick model and space filling model).

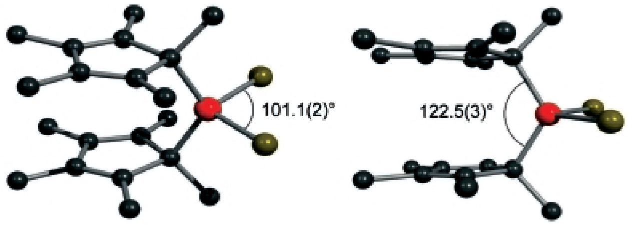


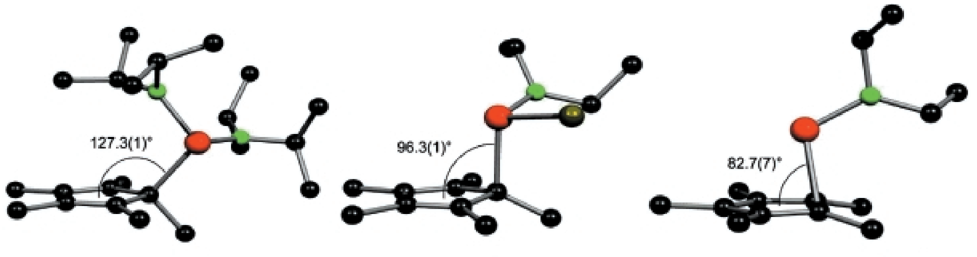
Fig. 7 Molecular structure of $Cp^*_2SiCl_2$.

representative examples from phosphorus chemistry are collected in Scheme 2. Stable compounds containing (p–p)π [14–18] or (p–d)π bonds [19,20] can be prepared as well as compounds with strained ring systems.[21,22] In Fig. 6 two such species, $Cp^*_2P_2$ and $Cp^*_2P_6$, are presented in the form of their ball and stick and of their space filling models; the steric protection of the P_n-units is clearly demonstrated.

Further examples for kinetic stabilization stem from the chemistry of silicon. In general, organosilanetriols easily condense to oligomeric or polymeric organosiloxanes; however, the silanetriol $Cp^*Si(OH)_3$ is stable towards condensation and can be crystallized in the form of the hemihydrate $Cp^*Si(OH)_3\cdot 0.5\ H_2O$.[23] The corresponding solid-state structure reveals that $Cp^*Si(OH)_3$ and water molecules are hydrogen-bound to form a multilayer arrangement with the Cp* groups forming the hydrophobic outer sheets and the silanetriol groups together with the water molecules forming the hydrophilic inner sheets. The molecular structure of $Cp^*_2SiCl_2$ depicted in Fig. 7 demonstrates the space requirement of the Cp* groups by the large C(Cp*)–Si–C(Cp*) angle of 122° and by the small Cl–Si–Cl angle of 101°. As a result of steric congestion, this compound is rather stable against nucleophilic attack.[24] Similar distortions are observed also in other compounds containing two Cp* substituents as for example in Cp^*_2BF [25] and in Cp^*_2S.[26]

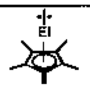
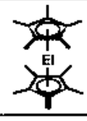
Structures with σ-bound Cp* groups are found in all Cp* species of Group 16 and 17 elements. We have reported on several Cp* compounds of electronegative elements; the organic halides Cp*Cl, Cp*Br, and Cp*I are of special interest for the synthetic chemist, because they react with metal carbonyls and with the main-group metals Mg, Sn, Sb, and Bi under oxidative addition.[27]

2.2.2 π-Cp* structures. Synthesis, structure, and bonding of complexes with covalent π-Cp–El units has been described in detail in recent reviews, including information about Cp* complexes.[2–5] Therefore, only some qualitative features of structure and bonding are presented here. To a first approximation, electron-counting and the octet rule may be used as instruments for a classification of half-sandwich and of sandwich complexes. In each class, the relevant El fragments are isolobal and isoelectronic; this criterion allows the search for novel members in that series. Four classes of Cp*El complexes are described in Scheme 3.[2,3] In the η^5-Cp* half-sandwich complexes of type I the El fragment interacts with five π electrons from the Cp* unit to generate an electron-octet situation at the respective element



$Cp^*As(N^iPr_2)_2$ $Cp^*As(Cl)(NEt_2)$ $Cp^*As(NEt_2)^+$

Fig. 8 Structures of Cp* arsenic compounds.

type		η	isolobal / isoelectronic El fragments
I		5	RBe RB^+ RC^{2+} Al Ga In Tl Ge^+ Sn^+ Pb^+
II		2 / 3	R_2Al R_2C^+ RGe RSn RPb RP^+ RAs^+ $D\rightarrow Ge^+$ $D\rightarrow Sn^+$
III		5	Mg Al^+
IV		2 / 3	Si Ge Sn Pb SiH^+ P^+ As^+ Sb^+

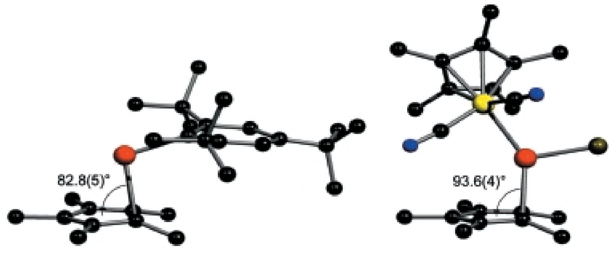
Scheme 3 Classification of covalent π-Cp*El complexes.

centre. Such complexes are regarded as *nido*-clusters following the concept of Wade, Williams, and Rudolph.[28] In the $\eta^{2,3}$- Cp* complexes of type II only three π electrons are necessary for El–Cp* interaction; as a result, comparatively weaker El–Cp* bonding is observed. Analogously, electron counting can explain the bonding in the sandwich complexes of type III and IV. A much better understanding of the actual electronic situation is based on modern theoretical calculations.[2] It is important to note that the structural information about complexes of type II and IV relies on crystal structure data. In solution, these compounds are highly fluxional due to fast haptotropic rearrangements, even at low temperatures. One of the most interesting aspects in this class of compounds concerns the possibility to stabilize elements in their low oxidation states. Prominent examples stem from aluminium (Cp*Al),[29] gallium (Cp*Ga)[30] and silicon (Cp^*_2Si)[31] chemistry.

2.3 Borderline situations in bonding and structure

Solid-state structure determinations as well as high level calculations have shown the difficulty to predict structure and bonding in certain families of Cp*El compounds. No clear-cut differentiation between (a) predominant ionic or covalent bonding, (b) σ or π structures, and (c) several hapticities (η^1, $\eta^{2,3}$, or η^5) is possible, as demonstrated by some typical examples.

Ab initio calculations in the Group 14 metallocene series have shown that the atomic charge of Pb in Cp_2Pb (not in Cp^*_2Pb) is 1.10; *i.e.* the bonding is between ionic and covalent.[32] Fig. 8 shows the solid-state structures of three Cp* arsenic compounds with quite different bonding situations within the Cp*As unit: $\eta^1(\sigma)$ in $Cp^*As(N^iPr_2)_2$, $\eta^1(\pi)$ in $Cp^*As(Cl)(NEt_2)$, and $\eta^2(\pi)$ in $Cp^*As(NEt_2)^+$.[33] The $\eta^1(\pi)$ bonding is unexpected. Fig. 9 depicts two Cp* compounds of type II (Scheme 3) with the predictable $\eta^2(\pi)$ interaction. The geometry within the Cp*Ge unit in the complex Cp*GeMes* is expected (angle 82.8(5)°),[34] but that within the Cp*Ga unit in the complex $Cp^*Ga(Cl)(Fe(CO)_2Cp^*)$ is unexpected (angle 93.6(4)°).[35] All compounds from Figs. 8 and 9 are highly fluxional in solution, *i.e.* shallow potential surfaces around the equilibrium geometries are observed. In Scheme 4 a class of Cp*El compounds is described where the electron count obviously does not help correctly to predict the structure. Though all El fragments are isolobal and isoelectronic, some compounds prefer a π and others a σ structure. In such compounds the different structures depicted in Fig. 1 once more represent low minima on a rather shallow energy surface.



Cp*GeMes* $Cp^*Ga(Cl)(Fe(CO)_2Cp^*)$

Fig. 9 Different η^2 constellations in Cp*El compounds.

El	Cl(R)Al $AsCl_2$ $SbCl_2$	CR_3 SiR_3 GeR_3 SnR_3 NR_2 PR_2 AsR_2 SbR_2

Scheme 4 $\eta^{2,3}(\pi)$ *versus* $\eta^1(\sigma)$ bonding in Cp*El compounds.

2.4 The Cp* group as "electron-buffer" substituent

The flexibility in bonding as described in sections 2.1–2.3 enables the Cp* group ideally to adjust to the electronic situation at the respective central atom. This phenomenon can be nicely documented in a series of solid-state structures of transition-metal complexes with Cp*Ga as a terminal σ-donor ligand, which are presented in Fig. 10 together with the structure of the uncomplexed Cp*Ga and with information about the respective Cp*(centroid)–Ga distances.[30,36,37] The shortest Cp*(centroid)–Ga distance is observed in the complex $Cp^*GaFe(CO)_4$;[36] a short distance correlates with an increased electron donation from the π system to compensate the electron deficiency at the gallium centre caused by strong electron donation from gallium to iron. The bonding in $Cp^*GaFe(CO)_4$ has recently been analysed and contrasted with that in $PhGaFe(CO)_4$.[38] In the nickel complex $(Cp^*Ga)_4Ni$[37] the Cp*-(centroid)–Ga distance is similar to that in the uncomplexed Cp*Ga molecule due to weak electron donation from gallium to nickel. A rather short Cp*(centroid)–Ga distance (1.916 Å) is also found in the complex $Cp^*Ga\rightarrow Ga(Cp^*)I_2$, indicating strong electron donation from Ga^I to Ga^{III}.[39] As a result of these and other investigations, the Cp* group in Cp*–El compounds can be regarded as an effective "electron buffer".

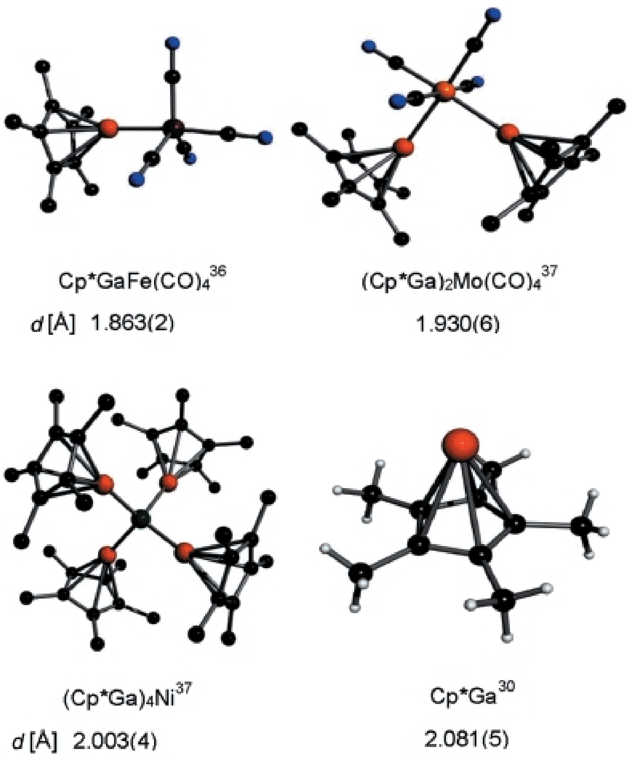


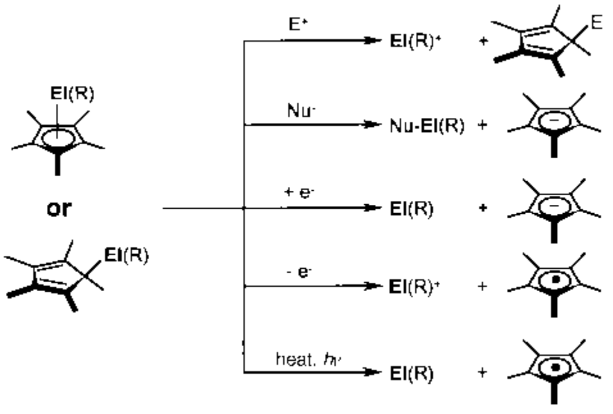
Fig. 10 Cp*Ga as a terminal σ-donor ligand (*d* = Cp*(centroid)–Ga).

3 Reactivity with regard to the Cp* group

For the synthetic chemist, Cp* compounds of main-group elements are well established Cp* transfer agents in metathesis-type reactions. Owing to the quite different polarity of the respective Cp*–El bond, tuning of the Cp* nucleophilicity and thus adapting to the special requirements is easily accomplished. The following listing contains the most often used Cp* transfer agents with decreasing nucleophilicity of the Cp* anion fragment: KCp*, NaCp*, LiCp*, $MgCp*_2$, TlCp*, Me_3SnCp*, and Me_3SiCp*.

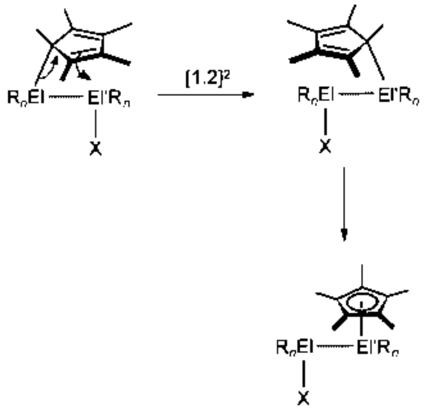
The intrinsic Cp*–El reactivity is interesting not only from the aspect of Cp* transfer capability, but also concerning the chemistry of the respective main-group element itself. In this context it is important to remember that on the one hand the Cp* group is suitable for kinetic and/or thermodynamic stabilization (see section 1) and that on the other hand it behaves as a potential leaving group. The $Cp*^-$ anion as well as the Cp* radical[40] are rather stable entities and thus easily eliminated under certain conditions. In the following, we will concentrate on this important aspect of Cp*–El chemistry.

As summarized in Scheme 5, σ- or π- Cp*–El compounds can react with electrophiles, with nucleophiles, with electron-transfer agents as well as under thermal or photochemical activation. In the reaction with electrophiles E^+ a $Cp*^-$ anion is formally transferred to give the neutral Cp*–E and the cationic $El(R)^+$ species. In the reaction with nucleophiles Nu^-, substitution of the $Cp*^-$ anion takes place and the compound NuEl(R) is formed. In a single-electron reduction process, $Cp*^-$ anion elimination results in the formation of a reduced El(R) species. In a single-electron oxidation process the Cp* radical is eliminated, and a cationic $El(R)^+$ species is formed; the Cp* radical dimerizes to $(Cp*)_2$ or reacts under hydrogen transfer to give Cp*H and tetramethylfulvene (TMF).[40] Under thermal or photochemical activation, elimination of the Cp* radical takes place, leaving a highly reactive El(R) fragment which is subject to further reactions.



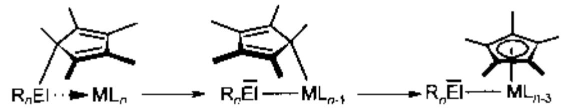
Scheme 5 Reactivities of Cp*–El bonds.

Another reaction sequence based on the leaving-group character of the Cp* substituent in covalent El–Cp* compounds is described in Scheme 6: whereas a Cp* unit migrates to a neighbouring element centre, a substituent from that element migrates back to the former Cp*-substituted centre. A concerted process of this type corresponds to a "dyotropic rearrangement";[41] due to the lack of mechanistic studies, the processes in question are described as $[1,2]^2$ migrations.[42]



Scheme 6 $[1,2]^2$ migration including the Cp* group.

A further Cp* migration process is presented in Scheme 7. In a $Cp*El(R)_n$ molecule coordinated to a transition metal the Cp* substituent can migrate to a vacant coordination site at the metal centre. The Cp*–M σ bond thus formed can rearrange to a π bond with elimination of two ligands L. During this process a coordinative El→M bond is transformed to a covalent El–M bond.

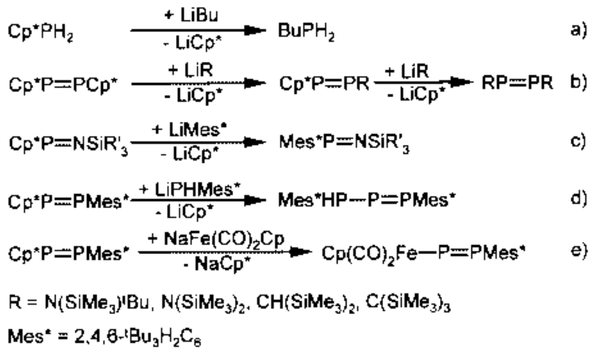


Scheme 7 [1,2] Cp* migration.

Finally, another important Cp* property in Cp*–El compounds merits attention: during a reaction sequence a π-bound Cp* ligand can easily rearrange to a σ-bound one and *vice versa*, thus allowing important electronic and steric changes at the relevant El centre. All phenomena described here make Cp* a highly versatile non-spectator ligand or substituent. In the following sections, examples from gallium, silicon, and phosphorus chemistry will be presented to verify this statement.

3.1 Cp* Phosphorus chemistry

Several examples of facile heterolytic Cp*–P bond cleavage with the formation of alkali metal pentamethylcyclopentadienides as the driving force are collected in Scheme 8. The nucleophilic substitution of $Cp*^-$ in pentamethylcyclopentadienylphosphane with butyllithium leads to the formation of



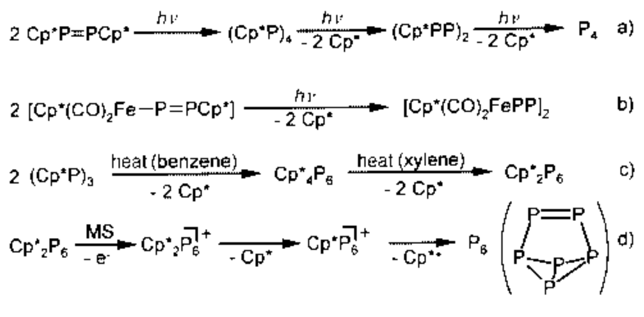
Scheme 8 Heterolytic Cp*–P bond cleavage.

butylphosphane (eqn. a).[43] Next, it is possible to perform substitution reactions at phosphorus atoms involved in (p–p)π double bonds (eqns. b–d). Stepwise Cp^{*-} substitution is feasible in the reaction of the diphosphene Cp*P=PCp* with different C- and N-nucleophiles (eqn. b);[16] similarly, the Cp* substituent in iminophosphanes can be exchanged against the supermesityl (Mes*) group (eqn. c).[44] The reaction of the diphosphene Cp*P=PMes* with lithium supermesitylphosphide leads to a phosphino-substituted diphosphene (eqn. d), which can be deprotonated to give a triphosphaallyl anion.[45] Finally, the $Cp(OC)_2Fe$ group can be introduced into the above diphosphene by reaction with the corresponding sodium ferrate (eqn. e).[46]

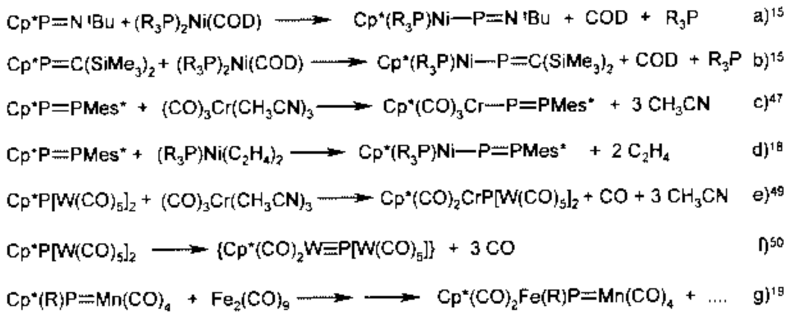
Cp* transfer from phosphorus to a transition metal under simultaneous formation of a covalent phosphorus–transition metal bond is the notable feature of the reactions collected in Scheme 9. The presence of weakly bound σ or π ligands at the transition metal is a prerequisite in these rearrangement processes. The eqns. (a)–(d) describe reactions of Cp*-substituted double-bond systems with zerovalent nickel or chromium complexes, which result in the introduction of a metallo-substituent at the phosphorus atom of the respective P=X double bond.[15,18,47] The eqns. (e)–(g) inform about the reactions of other types of Cp*–phosphorus compounds with transition-metal complexes. An alternative synthetic route to a transition-metal complex containing a planar η^3-P unit[48] is presented in eqn. (e); in the reaction of the phosphinidene complex $Cp^*P[W(CO)_5]_2$ with a zerovalent chromium complex, Cp* transfer from phosphorus to chromium is observed.[49] Thermal treatment of the above phosphinidene complex leads, with Cp* transfer and CO extrusion, to a metal-stabilized phosphido complex containing a tungsten–phosphorus triple bond (eqn. f); this highly reactive intermediate, if not trapped, dimerizes to yield a W_2P_2-tetrahedral cluster compound.[50] Finally, a Cp* migration process starting from a σ^3,λ^4-phosphanediyl complex is described in eqn. (g); in a multistep reaction with $Fe_2(CO)_9$ the ferriophosphanediyl complex $Cp^*(OC)_2Fe(R)P{=}Mn(CO)_4$ is an important intermediate.[19]

Cp* migration combined with Cp*, CH_3CN, and CO elimination is the important feature in the reactions described in Scheme 10. Transition-metal complexes with naked terminal or bridging P_x ligands are formed in the reactions of the cyclic polyphosphanes $(Cp^*P)_3$ and $Cp^*_4P_6$ with complexes of the type $(OC)_3M(CH_3CN)_3$ with M = Cr, Mo, or W. Thus, an alternative access to this class of compounds[51] has been found. In eqns. (a) and (b) the synthesis of complexes with terminal η^3-P_3 units is described.[52] A mixture of P_x complexes is formed in the reaction of $Cp^*_4P_6$ with the molybdenum complex $(OC)_3Mo(CH_3CN)_3$, as presented in eqn. (c); the formation of the hexaphosphabenzene complex $[(Cp^*Mo)_2(\mu\text{-}\eta^6\text{-}P_6)]$ merits special attention.[52]

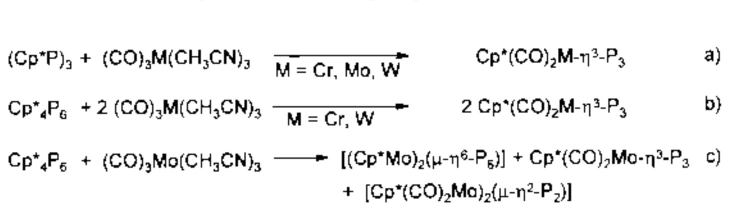
Homolytic Cp*–P bond cleavage and concomitant Cp* loss is the common important feature in the reactions described in Scheme 11. Photolysis of the diphosphene Cp*P=PCp* leads to the corresponding dimer, and with elimination of two Cp* radicals to the butterfly species $(Cp^*PP)_2$, which easily eliminates two further Cp* radicals to give elemental phosphorus P_4 (eqn. a).[53] Similarly, the ferrio-substituted diphosphene $Cp^*(OC)_2FeP{=}PCp^*$ yields the corresponding butterfly species (eqn. b).[47] A surprising reaction sequence has been observed in the thermal treatment of the cyclotriphosphane $(Cp^*P)_3$ (eqn. c): boiling in benzene leads to the formation of the bicyclohexaphosphane $Cp^*_4P_6$, which on boiling in xylene is transformed to the tricyclohexaphosphane $Cp^*_2P_6$ (see section 2.2.1, Fig. 6).[16]



Scheme 11 Homolytic Cp*–P bond cleavage.



Scheme 9 Cp* migration from phosphorus to a transition metal.



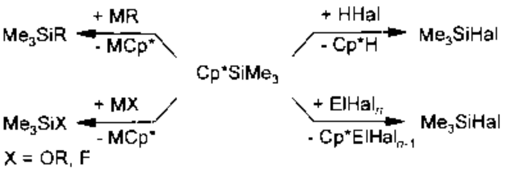
Scheme 10 Cp* migration from phosphorus to a transition metal and Cp* elimination.

Very recent mass-spectrometric studies have shown that Cp* loss in this compound leads to formation of the novel phosphorus allotrope P_6.[54]

3.2 Cp* Silicon chemistry

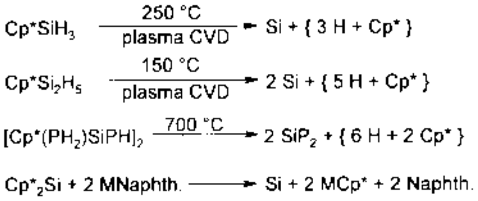
The chemistry of cyclopentadienyl silicon compounds has been described in detail in a recent review, including Cp* silicon compounds.[55] The interested reader is referred to this article. Here we concentrate on the presentation of some typical examples concerning selective heterolytic and homolytic Cp*–Si bond cleavage, Cp* migration in a $[1,2]^2$-type process, and (π-Cp*Si)–(σ-Cp*Si) rearrangement.

The heterolytic Cp*–Si bond cleavage is described in a more general fashion in Scheme 12.



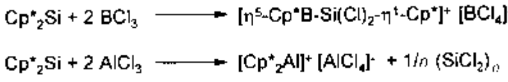
Scheme 12 Heterolytic Cp*–Si bond cleavage.

Examples for homolytic Cp*–Si bond cleavage are collected in Scheme 13. The silanes Cp^*SiH_3 and $Cp^*Si_2H_5$, which compared to SiH_4 and to Si_2H_6 are easily to handle due to the protecting effect of the Cp* group, have been applied in the Metalorganic Chemical Vapour Deposition (MOCVD) process for the preparation of thin silicon-containing films.[56] Under plasma conditions these precursor molecules decompose selectively at rather low temperatures; this property allows the preparation of multilayers with smooth interfaces.[57] The clean thermal decomposition of the phosphinosilane $[Cp^*(PH_2)SiPH]_2$ leads to the formation of the silicon phosphide SiP_2.[58] The last example for homolytic Cp*–Si bond splitting stems from the solution chemistry of decamethylsilicocene (Cp^*_2Si): reduction to elemental silicon is observed in the reaction with alkali metal naphthalenides. This competing cleavage reaction lowers the yield in the preparation of Cp^*_2Si (by reduction of $Cp^*_2SiCl_2$ with alkali metal naphthalenides).[59]



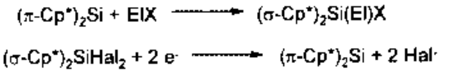
Scheme 13 Homolytic Cp*–Si bond cleavage.

Cp* migration in form of a $[1,2]^2$-rearrangement process is observed in the chemistry of Cp^*_2Si. Two surprising results of such rearrangements are presented in Scheme 14. In the reaction of Cp^*_2Si with BCl_3 one of the two Cp* ligands is bound to the boron atom in the final product. In the analogous reaction with $AlCl_3$ both Cp* ligands have migrated to the aluminum atom in the product $[Cp^*_2Al]^+$ $[AlCl_4]^-$.[60]



Scheme 14 Cp* migrations in silicon chemistry.

Not a Cp*–Si bond cleavage in the true sense of the word, but a π-Cp*Si–σ-Cp*Si rearrangement is often observed in the chemistry of Cp^*_2Si.[55] The flexible bonding mode in this compound allows reactions which can easily be understood by the assumption of a transient σ-Cp* substituted silylene. In oxidative addition reactions a π–σ rearrangement takes place; *vice versa*, a σ–π rearrangement is observed in reductive elimination reactions, as shown in the examples given in Scheme 15.



Scheme 15 π(Cp*) ↔ σ(Cp*) rearrangements in silicon chemistry.

3.3 Cp* Gallium chemistry

The characteristic features of Cp* gallium chemistry resemble those of Cp* silicon chemistry. Typical examples for heterolytic and homolytic Cp*–Ga bond cleavage, for Cp* migration as well as for π–σ rearrangements, are collected in Scheme 16. Interestingly, heterolytic Cp*–Ga bond splitting is preferred over ^{i}Pr–Ga bond splitting in the reaction of $^iPr_2GaCp^*$ with diethylamine (eqn. a).[61] Similarly, Cp*–Ga bond cleavage is preferred over Cl–Ga bond cleavage in the reaction of the ferriogallane $Cp^*(CO)_2FeGa(Cl)Cp^*$ with ^{i}PrOH (eqn. b).[35] Homolytic Cp*–Ga bond splitting is observed in the reaction of Cp*Ga with the diazabutadiene ^{t}BuNCHCHN^{t}Bu, whereby the radical $(^tBuNCHCHN^tBu)_2Ga$ is formed (eqn. c).[62] Surprisingly, Cp*Ga decomposes to elemental gallium under MOCVD conditions only at temperatures higher than 600 °C (eqn. d).[36] Cp* migration from gallium to iron and chlorine migration from iron to gallium are the key steps in the reaction of Cp*Ga with $FeCl_2$ in THF as solvent, whereby the iron complex $Cp^*Fe(Cp^*Ga)_2GaCl_2{\cdot}THF$ is formed (eqn. e).[35] Two examples for a π–σ rearrangement of the Cp* group in Cp*Ga are described in equations (f) and (g); both reactions correspond to oxidative additions (Ga^I to Ga^{III}).[63]

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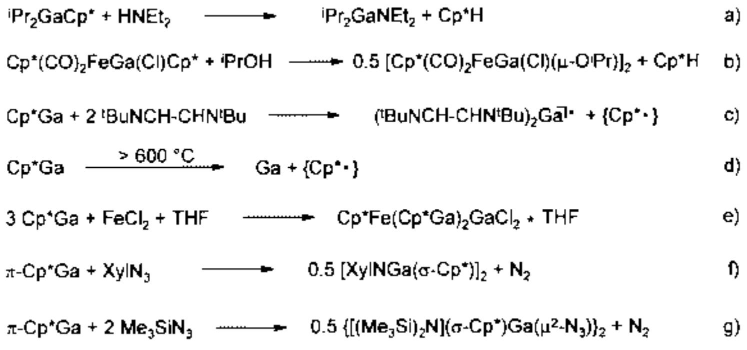

Scheme 16 Reactivity of the Cp*–Ga bond.

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