Transition Metal Chemistry of Low Valent Group 13 Organyls

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The coordination of low-valent group 13 organyls E^IR [E = Al, Ga, In; R = Cp*, $C(SiMe_3)_3$] to transition metals has attracted increasing interest over the past decade. Complexes and cluster compounds of these new ligands with a number of transition metals have been isolated and characterised. The E^IR moiety is formally isolobal with CO and PR_3 (R = alkyl, Cp*) or carbenes (R = chelating group) with varying σ-donor and π-acceptor properties depending on the organic group R as well as the group 13 metal E. In this review, different ways of forming M–E bonds such as substitution reactions of labile ligands or insertion of E^IR into transition metal halide bonds are described. Furthermore, the reactivity of homoleptic complexes $M_a(E^IR)_b$ is discussed, outlining the use of these new complex types in bond activation reactions.

1. Introduction

Since the pioneering discovery by H. Schnöckel in 1989 that the low valent group 13 metals Al^I and Ga^I can be stabilised by coordination of Cp*[1−3] and the subsequent development of convenient synthetic procedures for AlCp* [4,5]and GaCp*[6,7] by H. Roesky and P. Jutzi, much work has been devoted to the coordination of these compounds to transition metal centres.[8,9]

The E^IR fragment is isolobal with CO and PR_3, i.e. it exhibits σ-donation as well as π-accepting properties. The extent of σ-donation and π-acceptance is, of course, dependent on the nature of the metals, but also to a large extent

Roland A. Fischer (far right), born in 1961 in Rosenheim, Germany, studied chemistry at the Technische Universität München (1981−1986). In 1989 he received his doctorate for his work on alkyne complexes of rhenium under the guidance of W. A. Herrmann. After a postdoctoral fellowship at the University of California at Los Angeles with H. D. Kaesz (1989−1990), he returned to the Technische Universität München and completed his habilitation in 1995 on the coordination chemistry of aluminium, gallium and indium at transition metals and on the use of these complexes as MOCVD sources for intermetallic phases. From 1996 to 1997 he was Professor of Inorganic Chemistry at the Ruprecht-Karls-University Heidelberg and in 1998 he moved to the Ruhr-Universität Bochum. His research interests deal with various aspects of organometallic and materials chemistry with some emphasis on precursor chemistry for MOCVD. His scientific work has been honoured among others with the Heinz-Meier-Leibnitz award from the Bundesministerium für Bildung und Forschung (Federal Ministry for Education and Science) (1993), a Karl-Winnacker scholarship (1995) and the award of the Alfried-Krupp-von-Bohlen-und-Halbach Foundation (1996).

Christian Gemel (centre) was born in 1971 in Vienna, Austria. From 1990−1996 he studied Chemistry at the Technical University of Vienna, receiving his Doctorate in 1997 for his work on organoruthenium chemistry in the group of Karl Kirchner. After postdoctoral visits to Kenneth G. Caulton, Indiana University (1998) and Klaus Richard Poerschke, MPI Mülheim (2000−2001), he joined the group of Prof. Roland Fischer in 2002. He became a permanent research staff member in 2004.

Tobias Steinke (far left), born in 1974 in Bochum, Germany trained as a teacher of chemistry from 1995−2000. In 2001 he started to work on his PhD under the guidance of Prof. Fischer on the coordination chemistry of ECp to transition metals. His doctoral work has been awarded with the Wolfgang-Seel-Preis.*

Mirza Cokoja (centre left) was born in 1979, Oberhausen, Germany and studied chemistry at the Ruhr University Bochum from 1998−2003. He received his Diploma in 2003 for his work on the insertion reactions of ECp into Ru−Cl Bonds.*

Andreas Kempter (centre right) was born in 1978, Sigmaringen, Germany and studied chemistry at the Ruhr University Bochum from 1999−2004. He received his Diploma in 2004 for his work on the coordination chemistry of sterically encumbered low valent group 13 metals.

MICROREVIEWS: This feature introduces the readers to the author's research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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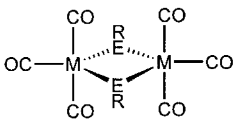
on the organic group R. For R = Cp*, for example, the vacant p-orbitals of the group 13 metal are partially populated by the π-donor orbitals of the Cp* groups thus diminishing the π-acceptor properties of the ligand. In fact, the contribution of the σ-donation has been calculated to be very large, resulting in the highest contribution of the bond energy being the electrostatic attraction between the partially positive group 13 metal and the partially negative transition metal, following the order Al > Ga > In.[10]

In contrast to the chemistry of transition metal borylene complexes which has been recently reviewed by H. Braunschweig,[11−13] the free ligands E^IR are stable and isolable. This facilitates access to their transition metal complexes since classic organometallic synthetic approaches can be applied. Substitution of labile ligands by E^IR is the most general route of forming transition metal-group 13 element bonds. Homoleptic as well as heteroleptic complexes $[M_a(E^IR)_bL_c]$ are accessible from a wide range of transition metal complexes such as carbonyl, olefin or phosphane complexes. The ease of oxidation of E^IR provides less common synthetic pathways. Thus, E^IR can act as in situ reducing agents towards higher oxidation state transition metal complexes $[L_nMX_n]$, giving either insertion products if the oxidised group 13 metal remains coordinated to the transition metal centre or low oxidation state complexes $[M_a(E^IR)_b]$ by cleavage of X_2ER.

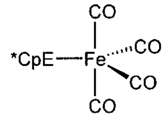
In this review we wish to highlight recent developments in this particular field from a mainly synthetic point of view. Fundamental bonding and general structural issues have been intensively discussed in the literature previously.[10,14−17] However, interest in E^IR has somewhat diminished during the last few years most likely because the chemistry of these new species has been considered to be quite unexciting. In contrast, our recent results which focus particularly on the transition metal chemistry of AlCp*, GaCp* and InCp* have revealed the unexpected potential of these compounds in classic organometallic and cluster chemistry. Herein we hope to convince the reader that these "exotic" ligands and related compounds hold much promise for the future.

2. Carbonyl Complexes $M_a(CO)_b(ER)_c$

Since the first isolation of E^IR, investigations of their properties as ligand towards transition metals have mostly involved metal carbonyl fragments. In particular, the reaction of E^IR with homoleptic transition metal carbonyls has been studied in detail. Hence, the complexes $[Mn_2(CO)_8\{\mu^2\text{-}[InC(SiMe_3)_3]\}_2]$,[18] $[Co_2(CO)_6(\mu^2\text{-}ECp^*)_2]$ (**1a**: E = Al,[19] **1b**: Ga[6]) or $[Ni_4(\mu^2\text{-}GaCp^*)_4(CO)_6]$[6] were obtained by treatment of the homoleptic metal carbonyl clusters with E^IR. The compounds $[Cr(CO)_5(ECp^*)]$ (E = Al,[20] Ga,[6] In[21]), $[(GaCp^*)_2Mo(CO)_4]$,[22] $[Fe_2(CO)_6\{\mu^2\text{-}In[C(SiMe_3)_3]\}_2]$ (**2**)[23] and $[Fe(CO)_4(GaCp^*)]$ (**3a**)[6] were obtained by substitution of chelating olefin ligands such as cyclooctene, norbornadiene, cyclooctatetraene and cycloheptatriene, respectively. Some carbonyl complexes, such as $[Fe(CO)_4(AlCp^*)]$ (**3b**),[24] are also available by salt metathesis from carbonylmetallates and $E^{III}RX_2$.[25−27]

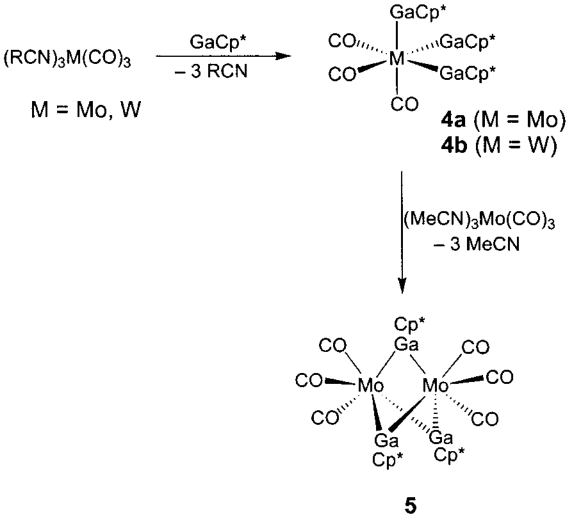


1a (M = Co, ER = AlCp*)
1b (M = Co, ER = GaCp*)
2 (M = Fe, ER = $InC(SiMe_3)_3$)



3a (E = Ga)
3b (E = Al)

A recent example of ligand substitution on metal carbonyl fragments is the reaction of $[fac\text{-}(RCN)_3M(CO)_3]$ (R = Me, M = Mo; R = Et, M = W) with GaCp* giving the monomeric compounds $[fac\text{-}(GaCp^*)_3M(CO)_3]$ (**4a**: M = Mo, **4b**: W).[28] It was shown that compound **4a** can act as a building block for the synthesis of dinuclear complexes affording $[Mo_2(CO)_6\{\mu^2\text{-}(GaCp^*)\}_3]$ (**5**) upon reaction with $[fac\text{-}(MeCN)_3Mo(CO)_3]$ (Scheme 1).

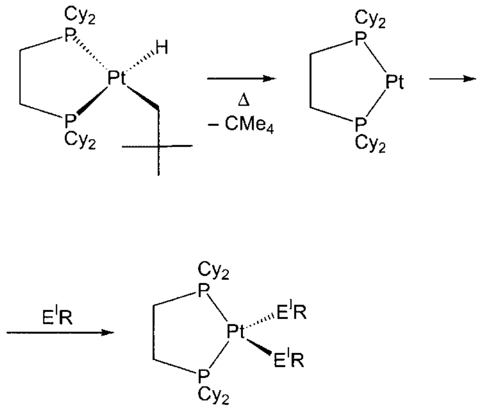


Scheme 1. Synthesis of $[Mo_2(CO)_6\{\mu^2\text{-}(GaCp^*)\}_3]$ (**5**)

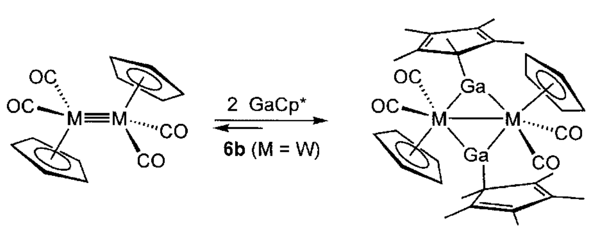
In contrast to the well explored substitution reactions of ECp*, the addition to coordinatively unsaturated centres is only known for the in situ formed $[(dcpe)_2Pt]$ complex [dcpe = bis(dicyclohexylphosphanyl)ethane] leading to $[(dcpe)_2Pt(E^IR)_2]$.[29,30] The unsaturated 14 VE fragment $[(dcpe)_2Pt]$ is thermally formed from $[(dcpe)_2PtH(neopentyl)]$ and trapped in the presence of E^IR ligands (Scheme 2).

An unsaturated carbonyl system which has been studied in more detail is the reaction of GaCp* with the multiple bonded dimeric complexes $[CpM(CO)_2]_2$ (M = Mo, W). Reaction with GaCp* yields the addition products $[Cp(CO)_2M(\mu\text{-}GaCp^*)]_2$ (**6a**: M = Mo, **6b**: M = W) (Scheme 3).[28]

An unusual feature of **6a** and **6b** is the η^1-coordination mode of the Cp* moieties bound to the bridging Ga atoms, presumably a consequence of the steric overcrowding in the



Scheme 2. Trapping of the unsaturated fragment [(dcpe)$_2$Pt] with E^{I}R



6a (M = Mo)
6b (M = W)

Scheme 3. Synthesis of [Cp(CO)$_2$M(μ-GaCp*)]$_2$ (**6a**: M = Mo, **6b**: M = W)

molecules. The GaCp* coordination in the tungsten complex is surprisingly weak and shows a temperature dependent association/dissociation equilibrium.

3. Homoleptic Complexes of the Type [M$_a$(ECp*)$_b$] (M = Ni, Pd, Pt)

3.1 Monomeric Complexes [M(ECp*)$_4$]

The COD ligands in [Pt(COD)$_2$] and [Ni(COD)$_2$] (COD = 1,5-cyclooctadiene) can be readily replaced by ECp* or E[C(SiMe$_3$)$_3$] yielding monomeric complexes of the type [M(E^{I}R)$_4$] (M = Pt, Ni; R = Cp*; Figure 1).[22,31,32] Analogous Pd compounds can be obtained by treatment of [Pd(tmeda)(CH$_3$)$_2$] with ECp*. In contrast to the reaction of [Pd(tmeda)(CH$_3$)$_2$] (tmeda = *N,N,N′,N′*-tetramethylethylenediamine) with PR$_3$ giving Pd(PR$_3$)$_n$ which usually proceeds via a ligand-assisted reductive elimination of ethane, the reaction with ECp* includes a methyl group migration and reduction of the palladium centre by ECp*.[33]

All complexes [M(E^{I}R)$_4$] are kinetically inert, indicating the high bond energy of the ECp* to transition metal linkage. Substitution reactions with PR$_3$ or CO do not take place and a coalescence of [M(E^{I}R)$_4$] and the free E^{I}R is not observed in the NMR spectra. Also, the synthesis of heteroleptic complexes [M(ECp*)$_n$(E′Cp*)$_m$] ($n + m = 4$) is not possible by ligand substitution. Interestingly, in the series [M(ECp*)$_4$] (M = Ni, Pd, Pt and E = Al, Ga, In), only [Pt(InCp*)$_4$] seems to be thermally unstable, decomposing at temperatures above −30 °C. This indicates weaker σ-donor properties of InCp* compared with InC(SiMe$_3$)$_3$, AlCp* or GaCp*.

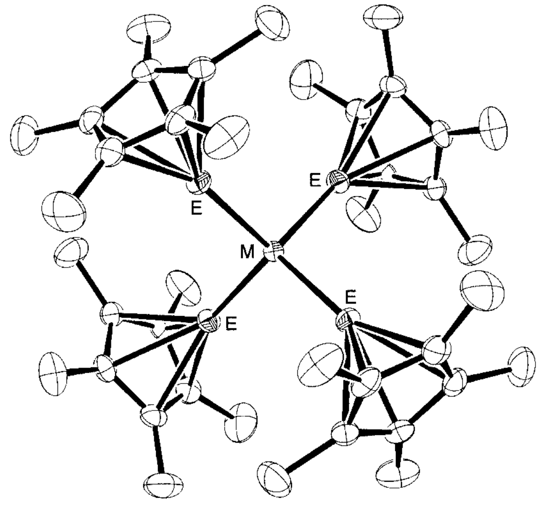


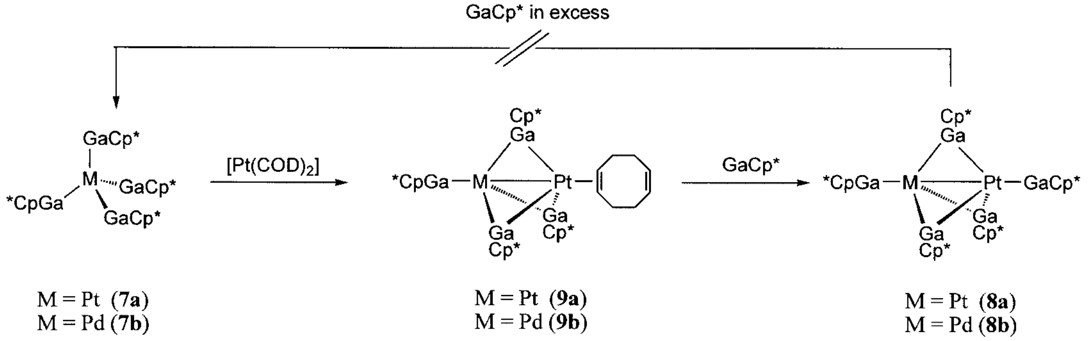
Figure 1. Monomeric Clusters [M(ECp*)$_4$]

3.2 Cluster Complexes [M$_2$(ECp*)$_5$] and [M$_3$(ECp*)$_8$]

Compared with the above examples, neutral homoleptic cluster compounds of the type [M$_a$(ECp*)$_b$] (M = Pd, Pt; b > a > 1) represent quite a novel and more promising field in the coordination chemistry of E^{I}R (E = Al, Ga, In). Recent studies concerning the synthesis of cluster compounds have been focused on the coordination of E^{I}R to transition metal carbonyl fragments [(CO)$_n$M$_a$]. Constitution and structural characteristics of new GaCp*-substituted Ni$_4$ [6] and Rh$_6$ carbonyl clusters[34] or [{(CpNi)(μ$_2$-AlCp*)}$_2$][35] are directly related to classical transition metal carbonyl cluster structures. In contrast, the novel homoleptic series [M$_a$(ECp*)$_b$] has no direct structural analogue in classical carbonyl or phosphane cluster chemistry, although recently the coordination chemistry of PR$_3$ has been extended to include a bridging mode.[36] These complexes exhibiting bridging and terminal E^{I}R ligands are still rare in comparison with other M−E complexes. In principle, access to [M$_a$(ECp*)$_b$] proceeds via two different reaction pathways: (i) by building block synthesis and (ii) via direct methods. In both cases, E^{I}R reacts with a transition metal complex bearing labile ligands (e.g. olefins) with full substitution of the ligands, the nature of the products being determined mainly by kinetic factors.

3.2.1 Building Block Synthesis of Homoleptic Clusters [MPt(GaCp*)$_5$]

The monomeric compounds [M(GaCp*)$_4$] (**7a**: M = Pt, **7b**: M = Pd; Figure 1) can serve as building blocks for the synthesis of the dinuclear cluster complexes [MPt(GaCp*)$_5$] (**8a**: M = Pt, **8b**: M = Pd) with terminal and bridging GaCp* ligands (Scheme 4). The reaction of [Pt(COD)$_2$]



Scheme 4. Building block synthesis of clusters $M_a(ECp^*)_b$

with an equimolar amount of $[M(GaCp^*)_4]$ and subsequent addition of GaCp* yields $[Pt_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$ (**8a**) and the analogous "trimetallic" heterodinuclear compound $[PtPd(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$ (**8b**).

It has been shown that the $[M(GaCp^*)_4]$ species form reactive yet isolable dinuclear associates with $[Pt(COD)_2]$. Based on variable temperature NMR spectroscopic data these intermediates were identified as $[Pt_2(GaCp^*)(\mu^2\text{-}GaCp^*)_3(\eta^2\text{-}COD)]$ (**9a**) and $[PtPd(GaCp^*)(\mu^2\text{-}GaCp^*)_3(\eta^2\text{-}COD)]$ (**9b**).[33]

3.2.2 Direct Synthesis of Homoleptic Clusters $[M_a(ECp^*)_b]$

The reaction of ECp* with transition metal complexes having olefin ligands generally leads to a full substitution of the olefins by ECp*. However, in most cases the ratio of the reactants does not directly determine the composition of the products. Instead, the formation of mono-, di- or trinuclear products is influenced by kinetic factors, i.e. by the reaction temperature, the nature of the transition metal-olefin complex or simply the solubilities of the starting materials and products.

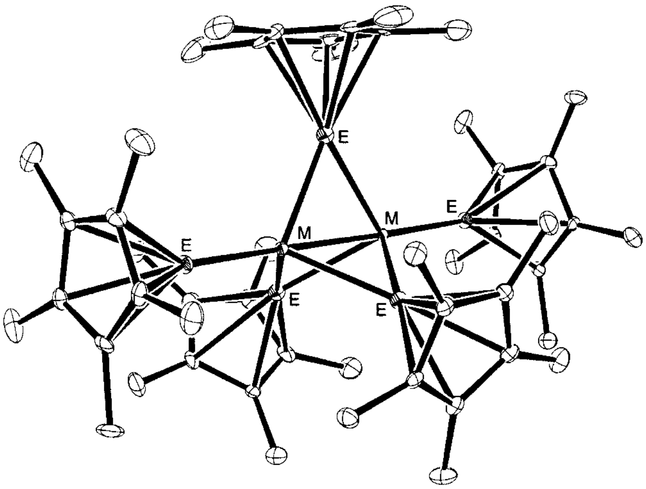
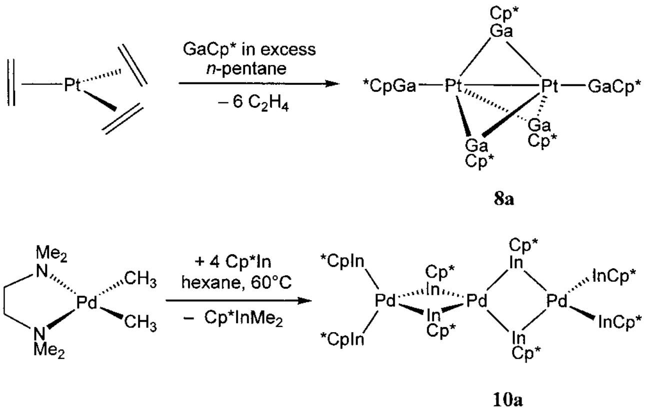


Figure 2. Dimeric clusters $[M_2(ECp^*)_5]$

The first direct synthesis of a homoleptic cluster complex was reported in 2000 (Scheme 5). $[Pt_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$ (**8a**) is quantitatively formed from the reaction of $[Pt(C_2H_4)_3]$ with an excess of GaCp* and could be isolated in analytically pure form in high yields.[37]



Scheme 5. Synthesis of $[Pt_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$ (**8a**) and $[Pd_3(InCp^*)_4(\mu^2\text{-}InCp^*)_4]$ (**10a**)

The monomeric complex $[Pt(GaCp^*)_4]$ (**7a**) which is quantitatively formed in the reaction of $[Pt(COD)_2]$ with GaCp* was not observed in this reaction. It was shown

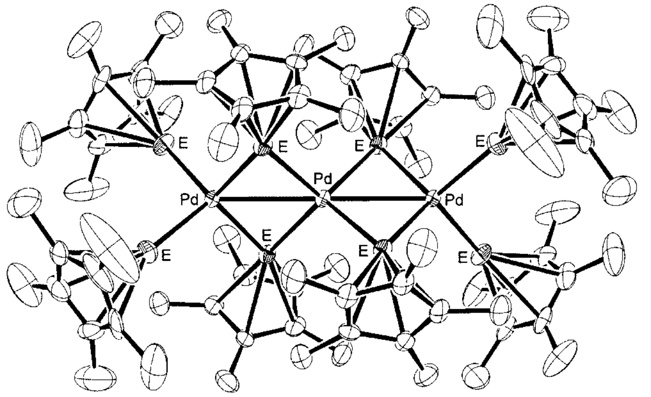
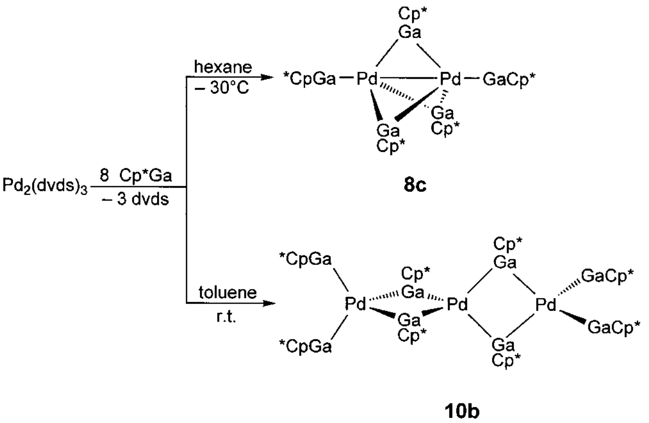


Figure 3. Trimeric clusters $[Pd_3(ECp^*)_8]$

later that [$Pt_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3$] (**8a**) is also kinetically stable in the presence of free GaCp* and does not react to give [$Pt(GaCp^*)_4$] (**7a**).[33]

When [$(tmeda)Pd(CH_3)_2$] is treated with an excess of InCp*, the trinuclear complex [$Pd_3(InCp^*)_4(\mu^2\text{-}InCp^*)_4$] (**10a**) is quantitatively formed. Complex **10a** is also kinetically inert and does not react to give mononuclear [$Pd(InCp^*)_4$] in the presence of InCp*.[38]

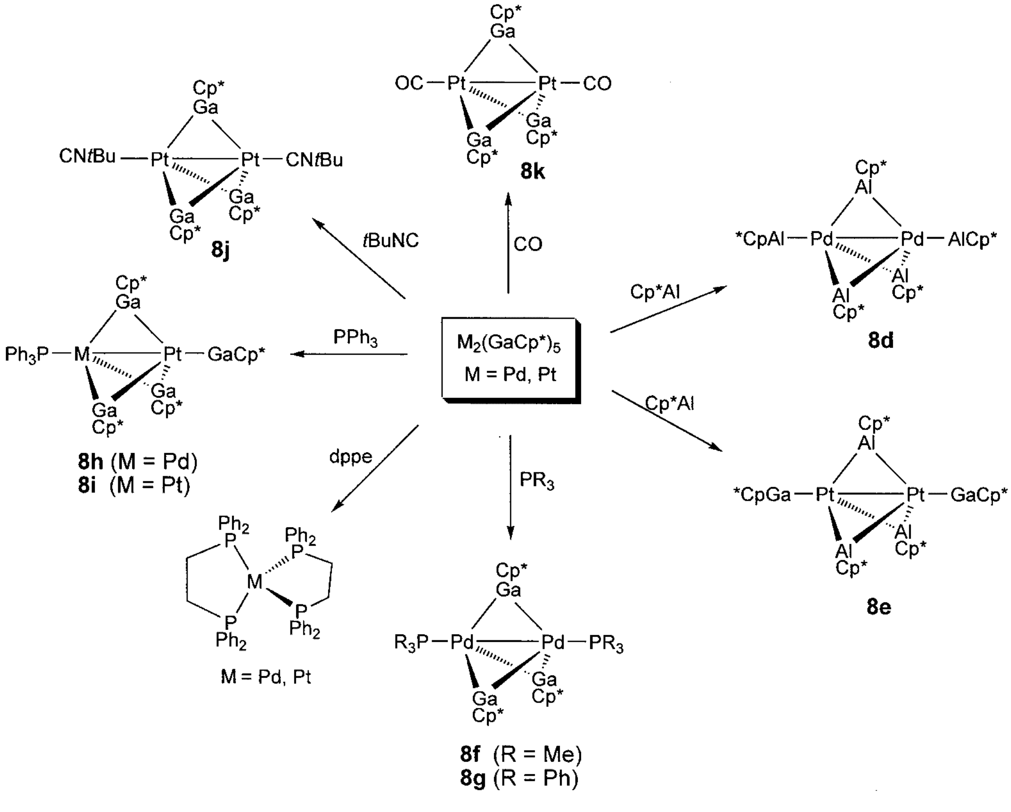
A good illustrative example of the subtle kinetic control of cluster formation is the reaction of [$Pd_2(dvds)_3$] with GaCp* (dvds = 1,3 divinyl-1,1,3,3-tetramethyldisiloxane). Depending on the reaction conditions, two different homoleptic clusters are formed. At −30 °C in hexane the reaction yields the dinuclear compound [$Pd_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3$] (**8c**) in quantitative yields. Only trace amounts (< 3%) of the monomeric compound [$Pd(GaCp^*)_4$] (**7b**) are observed. The reaction in toluene at room temperature yields the trinuclear complex [$Pd_3(GaCp^*)_4(\mu^2\text{-}GaCp^*)_4$] (**10b**) in high yield, while the dimeric species **8c** is formed in only very small amounts (< 2%) under these conditions (Scheme 6).



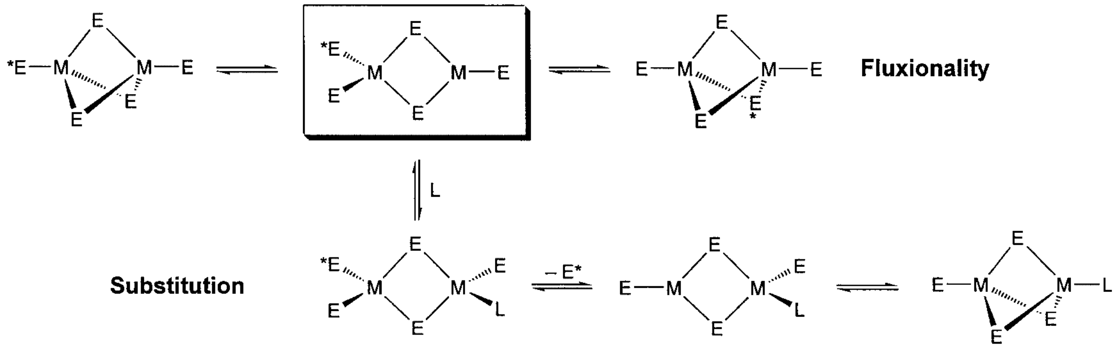
Scheme 6. Synthesis of [$Pd_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3$] (**8c**) and [$Pd_3(GaCp^*)_4(\mu^2\text{-}GaCp^*)_4$] (**10b**)

3.2.3 Reactivity of Homoleptic Cluster Complexes [$M_a(ECp^*)_b$] (M = Pd, Pt)

While the syntheses and structural chemistry of M−E complexes and their use as precursors to new materials have attracted widespread interest, remarkably little is still known about their general chemical reactivity. The coordinate M−E bond in such complexes is relatively polar and strong when E = Al, Ga[16] and the steric demand of the E^{I}R ligands is rather large.[22] Thus, neither dissociative nor associative reactions are very likely to occur at the central metal. Hence, the organometallic chemistry of such compounds would appear to be rather unfruitful. Indeed, the electronically and sterically saturated monomeric complexes [$M(ECp^*)_4$] turn out to be completely kinetically inert.[39] In sharp contrast, however, the related unsaturated cluster complexes [$M_a(ER)_b$] ($b > a > 1$) react with a selection of ligands (Cp*Al, CO, phosphanes, isocyanides) to give new di- and trinuclear substitution products (Scheme 7).[40]



Scheme 7. Reactivity of [$M_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3$]



On the basis of quantum chemical calculations by Frenking, the substitution of GaCp* or InCp* by AlCp* in homoleptic complexes is a thermodynamically favourable reaction.[16] Indeed, treatment of [M_2(GaCp*)$_2$(μ^2-GaCp*)$_3$] with AlCp* quantitatively yields the "trimetallic" compound [Pt_2(GaCp*)$_2$(μ^2-AlCp*)$_3$] (**8e**) or the fully substituted dinuclear complex [Pd_2(AlCp*)$_2$(μ^2-AlCp*)$_3$] (**8d**).

The reaction of [M_2(GaCp*)$_2$(μ^2-GaCp*)$_3$] with PPh_3 quantitatively yields the mono- or disubstituted complexes [MPt(GaCp*)(PPh_3)(μ^2-GaCp*)$_3$] (**8h**: M = Pd, **8i**: M = Pt) and [Pd_2(PPh_3)$_2$(μ^2-GaCp*)$_3$] (**8g**). Whereas the substitution reactions at Pd centres giving **8f** and **8g** readily occur at room temperature, the substitution of GaCp* by PPh_3 in the related Pt_2Ga_5 complex **8a** requires both a longer reaction time and a higher temperature (90 °C). In the case of the "trimetallic" compound **8b**, the substitution can only be observed at the Pd centre, leaving the Pt-GaCp* bond unchanged. This is in good agreement with the fluxionality of [M_2(E^IR)$_5$] in solution (vide infra). Whereas ligands attached to a palladium centre usually show fast exchange between the terminal and bridging positions, such processes are slower on platinum centres. A dissociative mechanism of the bridging ligands forming unsaturated metal centres as intermediates is assumed for the substitution reactions as well as for the fluxional processes of [M_2(E^IR)$_5$].

Generally, heteroleptic monomeric complexes of the type [M(GaCp*)$_{4-x}$(L)$_x$] ($x = 1-4$) are not accessible via substitution reactions. However, when the chelating diphosphane ligand dppe [dppe = bis(diphenylphosphanylethane)] is added to [M_2(GaCp*)$_2$(μ^2-GaCp*)$_3$], all Cp*Ga units are substituted and the monomeric complexes [M(dppe)$_2$] (M = Pd, Pt) are formed quantitatively. The reaction of [Pt_2(GaCp*)$_2$(μ^2-GaCp*)$_3$] (**8a**) with the strong π-acceptors CN*t*Bu or CO gives the disubstitution products [Pt_2(CN*t*Bu)$_2$(μ^2-GaCp*)$_3$] (**8j**) and [Pt_2(CO)$_2$(μ^2-GaCp*)$_3$] (**8k**), respectively, with the GaCp* ligands preferring the bridging positions.

In contrast to the substitution reactions of [M_2(GaCp*)$_2$(μ^2-GaCp*)$_3$] complexes, where the cluster core is always retained, the reaction of the trinuclear compound [Pd_3(InCp*)$_8$] (**10a**) with PPh_3 or dppe leads to a rearrangement of the linear Pd_3 core to give the triangular Pd_3 clusters [Pd_3(InCp*)$_3$(PPh_3)$_3$] (**10c**) and [Pd_3(InCp*)$_3$(dppe)$_2$] (**10d**) (Scheme 8).

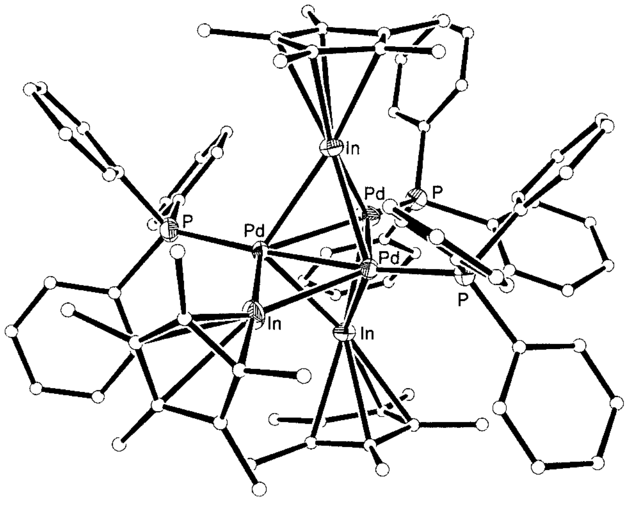
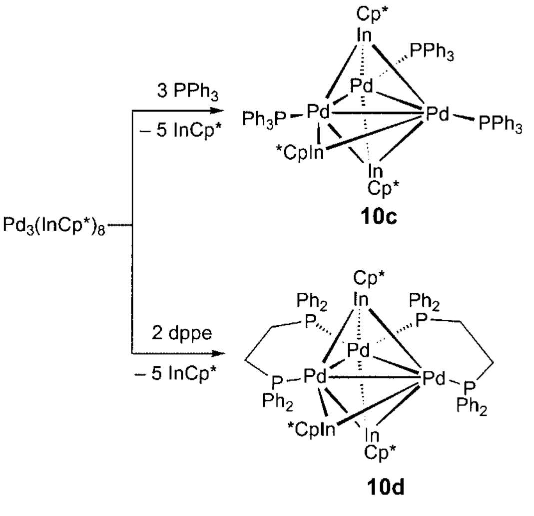


Figure 4. Triangular cluster **10c**

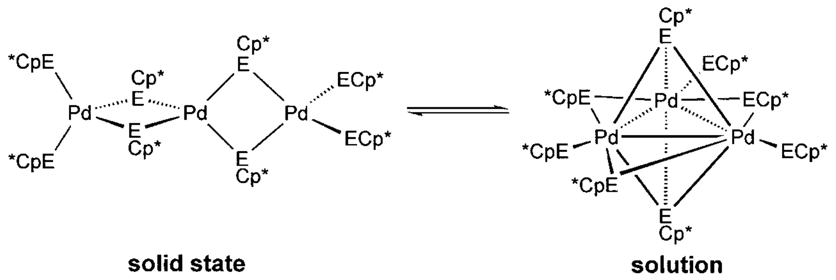


Scheme 8. Synthesis of [Pd_3(InCp*)$_3$(PPh_3)$_3$] (**10c**) and [Pd_3(InCp*)$_3$(dppe)$_2$] (**10d**)

In both complexes two InCp* units cap both faces of a Pd triangle resulting in a trigonal bipyramidal geometry. The third InCp* ligand is found in a μ^2-coordination mode parallel to the Pd_3 plane. Additionally, each Pd centre is coordinated by one or two terminal phosphane ligands.

3.2.4 Solution Structures and NMR Spectroscopy

Whereas [Pt_2(GaCp*)$_2$(μ^2-GaCp*)$_3$] (**8a**) exhibits a static NMR spectrum at room temperature, i.e. two well dis-



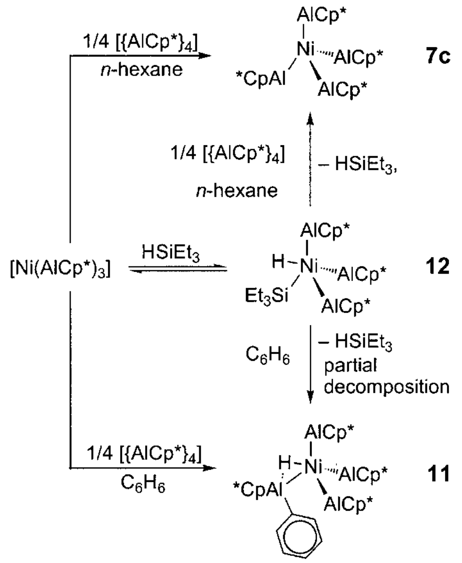
tinguishable signal sets (singlets) for the bridging and the terminal GaCp* ligands, the corresponding palladium cluster $[Pd_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$ (**8c**) is dynamic in solution and gives rise to only one Cp* signal set. The ^1H NMR spectrum of $[PtPd(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$ (**8b**) at room temperature shows two resonances with an integral ratio of 1:4. Clearly the fluxional process involves only the Pd centre of the dimeric structure, leaving the terminal Pt bound GaCp* unchanged. With regards to the dependence on the group 13 metal, it was found that the fluxional process in $[Pd_2(AlCp^*)_2(\mu^2\text{-}AlCp^*)_3]$ (**8d**) is slower than in $[Pd_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$ (**8c**). These results are in very good agreement with the calculated bond energies in $[M\{E(CH_3)\}_4]$ (M = Ni, Pd, Pt; E = B − Tl) by Frenking.[16] For the transition metal the order Ni ≈ Pt > Pd can be observed, while for the group 13 elements the trend is B > Al > Ga ≈ In > Tl.

The ^1H NMR spectrum of $[Pd_3(GaCp^*)_4(\mu^2\text{-}GaCp^*)_4]$ (**10b**) at room temperature exhibits two resonances with an integral ratio of 1:3, whereas $[Pd_3(InCp^*)_4(\mu^2\text{-}InCp^*)_4]$ (**10a**) shows this signal splitting only at −80 °C. The reason for the unusual ratio of 1:3 is still uncertain and is not in agreement with the solid-state structure. A dissociation of the trinuclear component into two $[Pd(ECp^*)_3]$ fragments and one $[Pd(ECp^*)_2]$ (E = Ga, In) unit cannot be excluded. However, the addition of an excess of InCp* does not yield the saturated mononuclear species $[Pd(InCp^*)_4]$. The reactivity of these cluster complexes with phosphanes (PPh_3 or dppe) suggests that the nuclearity is sustained in solution (vide supra). Thus a triangular structure of **10a** and **10b** similar to the triangular phosphane clusters **10c** and **10d** in solution has been suggested. The structure bears two axial and six equatorial ligands. The equatorial ligands (terminal as well as bridging) are presumed to be fluxional in solution, giving a coalesced signal corresponding to six ligands.

3.3 Bond Activation Reactions by $M(ECp^*)_n$

The donor acceptor bond in $[L_nM{\leftarrow}ECp^*]$ has been calculated to be rather polar in the case of E = Al and Ga. The electron density of the transition metal centre on coordination should therefore increase considerably.[10,16,17,24,31,41] This is an intrinsically interesting feature especially from the point of view of classical bond activation reactions being relevant in organometallic chemistry (H_2, C−H, Si−H, B−H, etc.). Whereas CO, phosphanes or NHCs (nitrogen heterocyclic carbenes) are widely used as supporting and directing ligands for reactivity and selectivity in organometallic chemistry, almost nothing is known about the corresponding potential of E^IR ligands.

The reaction of $[Ni(COD)_2]$ with four equivalents of AlCp* in benzene does not yield the expected complex $[Ni(AlCp^*)_4]$ (**7c**) but instead gives $[NiH(AlCp^*)_3(AlCp^*Ph)]$ (**11**) in almost quantitative yields (Scheme 9).[39]



Scheme 9. Synthesis of **7c**, **11** and **12**

As shown by NMR spectroscopy, the C_6H_6 in **11** is not exchanged by C_6D_6, showing the kinetic inertness of complex **11**. It is assumed that the activation of benzene, which does not occur in the case of $[Ni(CO)_n]$, $[Ni(PR_3)_n]$ or other d^{10} Ni complexes, takes place on a reactive, low-coordinate fragment $[Ni(AlCp^*)_n]$ ($n < 4$) giving an intermediate of the type $[(AlCp^*)_nNi(H)(C_6H_5)]$. The reactive fragment $[Ni(AlCp^*)_n]$ is not formed from $[Ni(AlCp^*)_4]$ (**7c**) by a dissociative process but, rather, is an intermediate in the course of the formation of kinetically inert **7c** and is apparently trapped in the presence of suitable reaction partners prior to the formation of **11**. The subsequent migration of the phenyl group to an AlCp* ligand, accompanied by oxidation of the aluminium and formation of a strong Al−C bond, as well as the coordination of a fourth equivalent of AlCp* contribute to the driving force of the whole activation reaction.

Similarly, in the presence of $HSiEt_3$ (Scheme 9), the formation of the hydrosilyl complex $[Ni(AlCp^*)_3(H)(SiEt_3)]$ (**12**) can be observed. In contrast to **11**, the hydride may be found in a terminal and not in a bridging position, showing the electron deficient nature of the Al^{III} centre in **11**. Compound **12** selectively reacts with C_6H_6 giving **11** via cleavage of $HSiEt_3$, indicating that $[Ni(AlCp^*)_3]$ is the probable relevant intermediate for the C−H activation of benzene.

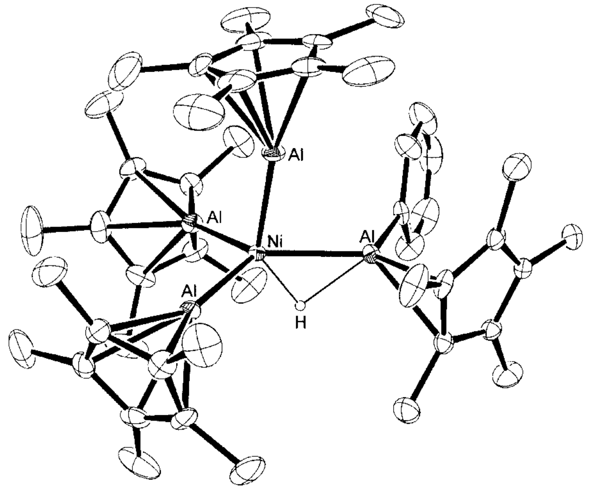


Figure 5. $[NiH(AlCp^*)_3(AlCp^*Ph)]$ (**11**)

Another example of C−H bond activation was found in the reaction of $[(\eta^6\text{-}C_6H_5CH_3)Fe(\eta^4\text{-}C_4H_8)]$ with AlCp* giving a product with the empirical formula $[Fe(AlCp^*)_5]$ (**13**).[42] The solid-state structure of **13** indeed exhibits a central iron atom in a distorted trigonal bipyramidal coordination environment. However, two C−H bonds of two Cp* ring methyl groups are attached to adjacent AlCp* ligands, giving an unusual $Cp^*Al{-}CH_2(C_5Me_4)Al{-}CH_2(C_5Me_4)Al$ chelating system (Figure 6). The hydrides occupy a bridging position between the Fe and Al centres. It is noteworthy that the Fe^0 source is inert in the presence of Cp*Ga or Cp*In, accentuating again the role of Cp*Al as a suitable ligand for bond activation reactions.

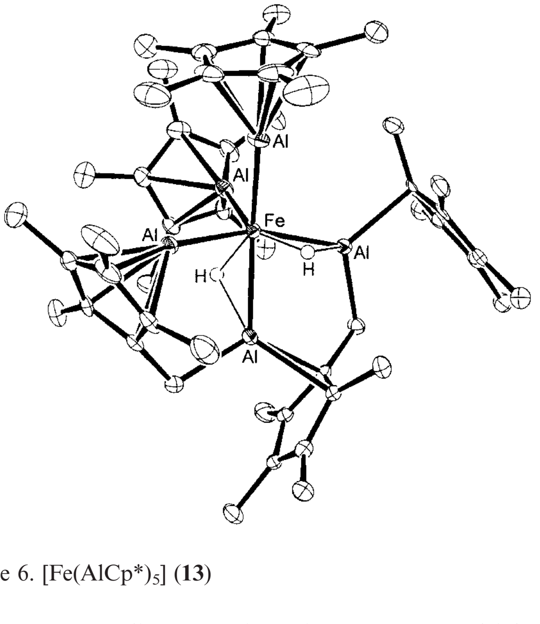
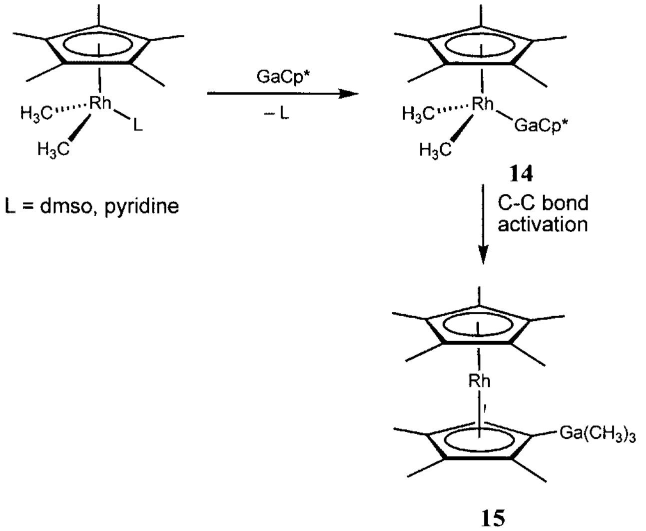


Figure 6. $[Fe(AlCp^*)_5]$ (**13**)

However, bond activations are not only restricted to Cp*Al, as shown by the reaction of $[Cp^*Rh(CH_3)_2L]$ (L = dimethyl sulfoxide, pyridine) with GaCp* (Scheme 10). In the first step of this reaction sequence, the ligand L is substituted by GaCp* giving $[Cp^*Rh(GaCp^*)(CH_3)_2]$ (**14**). This is isostructural with the starting complex. Complex **14** is thermally unstable and slowly reacts further in solution at room temperature to give the zwitterionic rhodium species $[Cp^*Rh\{(\eta^5\text{-}C_5Me_4)Ga(CH_3)_3\}]$ (**15**).[43]



Scheme 10. Reaction of $[Cp^*Rh(CH_3)_2L]$ (L = dmso, pyridine) with GaCp*

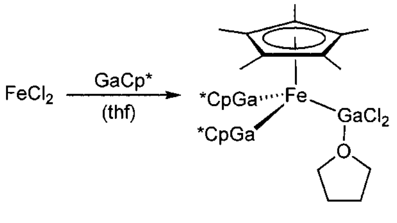
The mechanism of this reaction sequence is still uncertain. However, the driving force presumably includes the migration of the methyl groups to ECp* (E = Al, Ga) accompanied by oxidation of the group 13 metal centre and the formation of a strong E−C bond. This is a rather general point in the reactions of M−C bonds with ECp* and is very similar to the classical alkyl migration to transition metal bonded electrophilic π-ligands such as CO and olefins.

4. Insertion Reactions of ECp* into Metal−Halide and Metal−Metal Bonds

Insertion reactions of E^IX (X = halide) have been known for a long time and date back to the studies of Graham, Chatt and Hsieh more than 30 years ago. In particular, the insertion of InX (X = Cl, Br) has been the focus of much research. In the 1960s, Graham et al. reported insertions of InBr into the metal−metal bonds of $[Co_2(CO)_8]$ and $[Mn_2(CO)_{10}]$ which they assumed to give $[(\mu^2\text{-}Br)_2\text{-}In\{Co(CO)_4\}_2]_2$ and $[BrInMn(CO)_5]_2$, respectively.[44−47] Later, Chatt et al. studied the insertion of InCl into the Pt−Cl bond of [*trans*-$Pt(Cl)(SiPh_3)\{PMe_2(Ph)\}_2$] and claimed that the product was [*trans*-Pt($InCl_2$)($SiPh_3$)(PMe_2Ph)$_2$].[48] A. T. T. Hsieh reported a number products from the insertion of InX into metal-metal and metal-halide bonds of carbonyl and carbonyl free complexes of tungsten, molybdenum, manganese, iron, mercury and the metals of the cobalt triad.[49−52] Hsieh also investigated the behaviour of InCl towards Ph_3PAuCl, suggesting the formation of $Ph_3PAuInCl_2$.[53] Due to the insolubility of the products, however, the structural proposals were solely based on infrared spectroscopy, elemental analyses and comparisons of the melting points.

The actual complexity of these reactions was first shown by H. Schmidbaur[54] who isolated gold/indium clusters from a reaction analogous to that of Hsieh.[53] Treatment of (PPh_3)AuCl with InCl in THF yielded the In^{II} dimer [In_2Cl_4(THF)$_4$], whereas addition of a chelating ligand such as dppe led to the cluster [(dppe)$_2Au_3In_3Cl_6$(THF)$_6$]. A slight change in the stoichiometry gave the ionic cluster [(dppe)$_2$Au]$^+$[(dppe)$_2Au_3In_3Br_7$(THF)]$^-$.[55] The reaction of InBr with [CpNi(Br)(PR_3)] (R = Me, Ph) typically yields ionic [CpNi(PR_3)$_2$]$^+$[$InBr_4$]$^-$ "*ate*" complexes,[56,57] while only special conditions such as the presence of strong Lewis-bases (e.g. $Ph_3P=O$, quinuclidine) suppress this reaction so that Ni−In bonded compounds can be isolated.

These examples clearly show that insertion reactions of E^IX are extremely sensitive to the reaction conditions and that many possible reaction pathways have to be considered. The access to E^IR species with enhanced solubility and their ability to stabilise intermediates stimulated a reexamination of these classic insertion reactions. Jutzi reported on the insertion of GaCp* into the Fe−Cl bonds of $FeCl_2$ giving [Cp*Fe(GaCp*)$_2$($GaCl_2$·thf)] (**16**) and revealing the potential of E^IR as reducing and Cp*-transfer reagents together with the capacity to behave as stabilising "spectators" (Scheme 11).[58]



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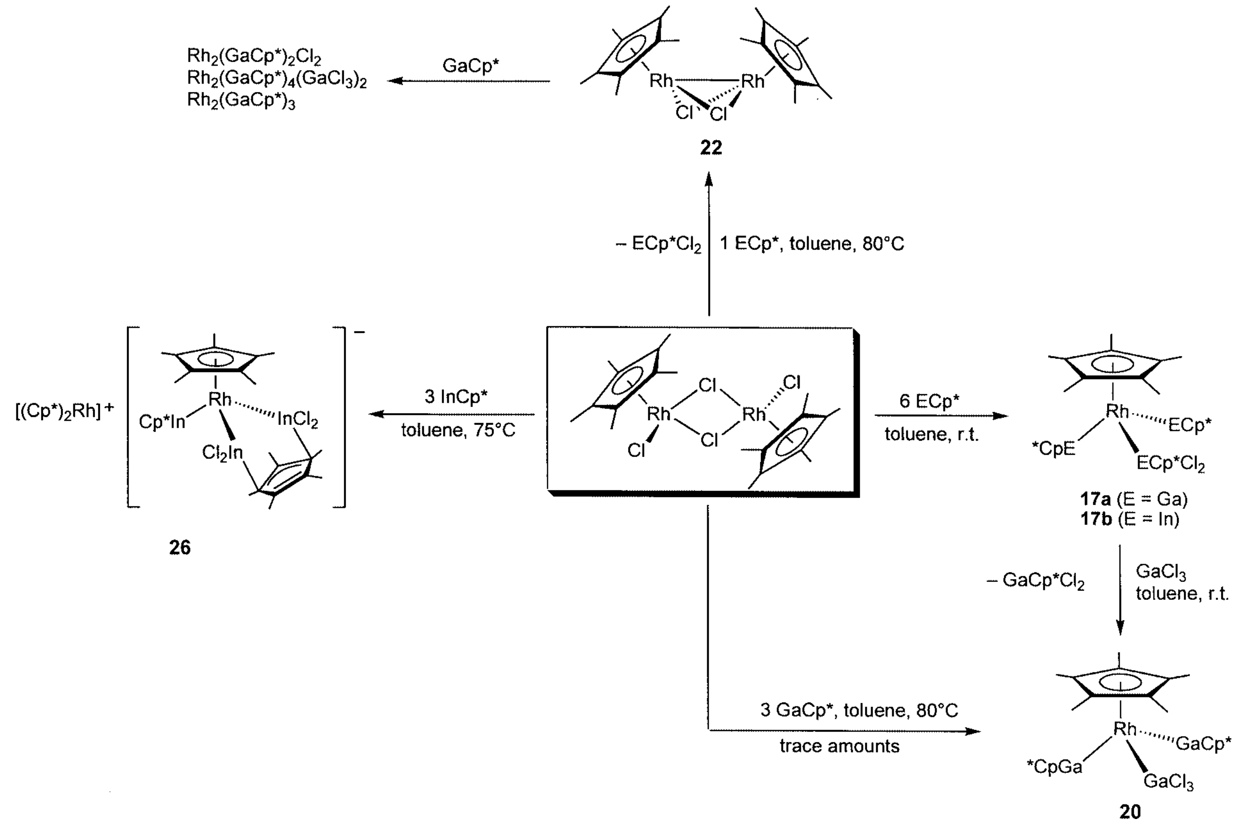
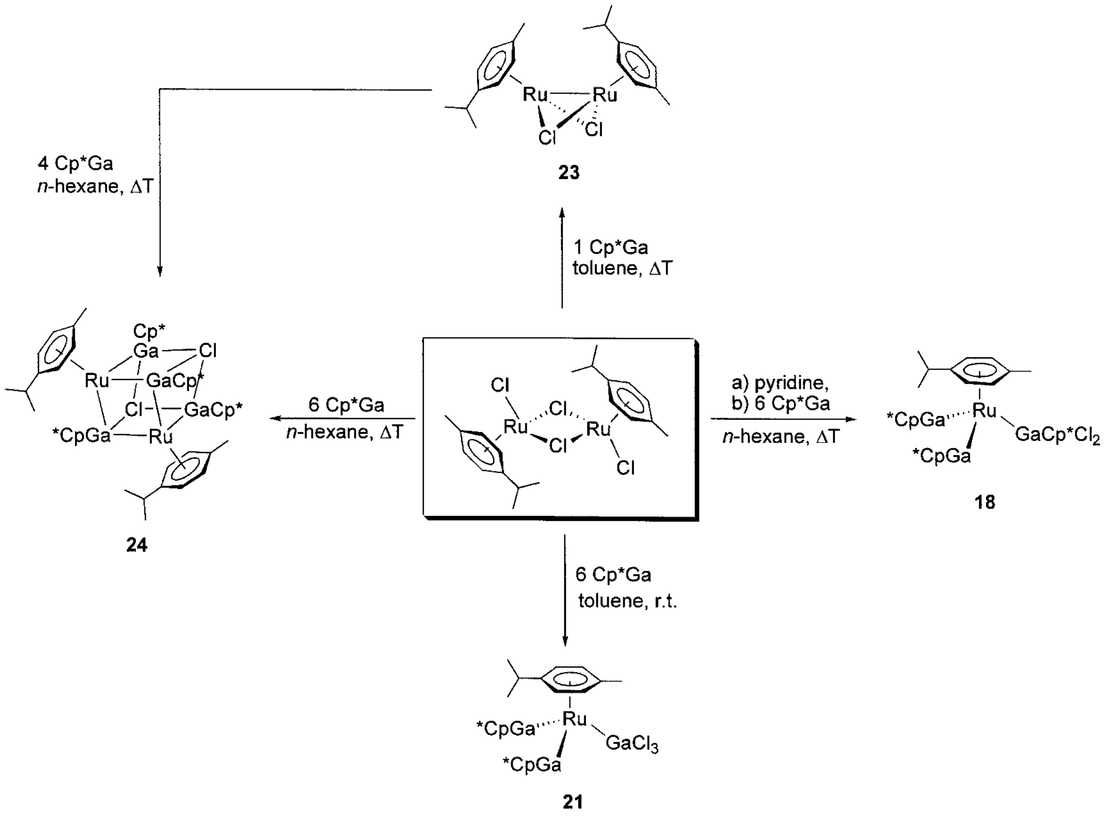
Scheme 11. Reaction of $FeCl_2$ with GaCp*

4.2 Rhodium- and Ruthenium−ECp* Coordination Compounds and Clusters

In general, depending on stoichiometry as well as reaction conditions, a variety of insertion products may be formed from the reactions of ECp* (E = Ga, In) and the isolobal d^6 complexes [{Cp*$RhCl_2$}$_2$][59,60] or [{(*p*-cymene)$RuCl_2$}$_2$][61] (Scheme 12 and 13). The reaction of [{RhCp*Cl_2}$_2$] with six equivalents of E^IR in toluene



Scheme 12. Reactions of ECp* with [{Cp*$RhCl_2$}$_2$]



Scheme 13. Reactions of GaCp* with [{(*p*-cymene)RuCl$_2$}$_2$]

at room temperature leads to simple, monomeric insertion products [RhCp*(ECp*)$_3$Cl$_2$] (**17a**: E = Ga, **17b**: E = In). The analogous ruthenium complex [(*p*-cymene)Ru(GaCp*)$_3$Cl$_2$] (**18**) can be obtained from the reaction of GaCp* with [{(*p*-cymene)RuCl$_2$}$_2$] only by prior treatment of the dimeric starting complex with pyridine. The formation of the intermediate monomer [(*p*-cymene)RuCl$_2$(pyridine)] is followed by insertion of GaCp* into the Ru−Cl bonds and substitution of pyridine by GaCp*. If dmso is used instead of pyridine, the substitution can be suppressed yielding [(*p*-cymene)Ru(GaCp*)$_2$(Cl)$_2$(DMSO)] (**19**). However, in contrast to the isolobal Rh complex, only GaCp* gave defined reaction products, whereas InCp* yielded intractable product mixtures under all conditions tested.

The compound [Cp*Rh(GaCp*)$_3$Cl$_2$] (**17a**) reacts readily in the presence of Lewis acids. When **17a** is treated with one equivalent of GaCl$_3$ in toluene, the Lewis acid-base adduct [Cp*Rh(GaCp*)$_2$(GaCl$_3$)] (**20**) is immediately formed. Complex **20** is also formed as a side product in the thermal decomposition of complex **17a**, showing the lability of the Cp*−Ga bond. In the case of the Ru(*p*-cymene) fragment, the corresponding complex [(*p*-cymene)Ru(GaCp*)$_2$(GaCl$_3$)] (**21**) can be isolated in the stoichiometrically quantitative yield of 67% ("quantitative" is based on the amount of chlorine in the starting material) if [{(*p*-cymene)RuCl$_2$}$_2$] is treated directly with GaCp* in the absence of pyridine. Clearly the dimeric structure starting material is retained in some of the reaction intermediates, facilitating the Cp*−Cl exchange between two Ga centres.

Changing the stoichiometric ratio of the reactants or the reaction conditions leads to new structural types for the insertion products. The reaction of [{RhCp*Cl$_2$}$_2$] with only one equivalent of ECp* gives the Rh^{II} dimer [{RhCp*Cl}$_2$] (**22**) which is also accessible from the reaction of the precursor with Na/Hg[62,63] or elemental gallium.[64] The analogous Ru^{I}−Ru^{I} complex [{(*p*-cymene)RuCl}$_2$] (**23**), which has not been reported in literature before, can be obtained by treatment of [{(*p*-cymene)RuCl$_2$}$_2$] with one equivalent of GaCp* in toluene. Several attempts to use classic reducing agents (Li, K, C$_8$K, sodium naphthalide) for this reduction failed, resulting only in the uncontrolled formation of Ru metal.

Further reaction of **23** with four equivalents of GaCp* gives the dimeric cage compound **24** in very good yields. The cube-like cage core consists of two Ru(*p*-cymene), four GaCp* ligands and two μ^3-bridging chlorine atoms. Complex **24** can also be prepared by direct treatment of GaCp* with [{(*p*-cymene)RuCl$_2$}$_2$], albeit in very low yields.

Several products can be obtained from the reaction of [{Cp*RhCl}$_2$] with ECp*. However, the molecular structures of these products are not clear yet. The homoleptic cluster complex [(RhCp*)$_2$(GaCp*)$_3$] (**25**) could be isolated as a thermal decomposition product of one of these insertion products.

The reaction of [{Cp*RhCl$_2$}$_2$] with only three equivalents of InCp* (instead of six as in the synthesis of **17b**) leads to the salt [Cp*$_2$Rh][Cp*Rh(InCp*){In$_2$Cl$_4$(μ^2-Cp*)}] (**26**). The molecular structure of the anionic part exhibits a distorted tetrahedral RhIn$_3$ core. The striking feature of the anion is the Cp* ring bridging two indium centres. The C$_5$ ring takes an almost parallel arrangement to the Cl−In−Cl planes with deviations smaller than 10°. Complex **26** is the first example of an intramolecular bridging Cp* ring. The only structural analogies are the solid-state structures of Et$_2$GaCp and EtGaCp$_2$, consisting of linear polymers with intermolecular bridging C$_5$H$_5$ ligands.[65]

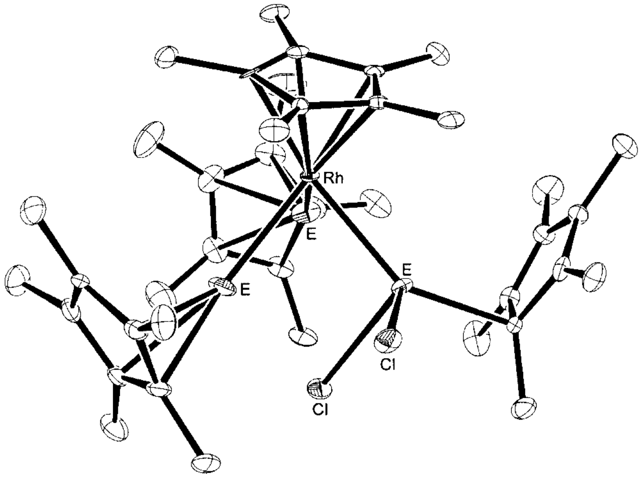


Figure 7. [Cp*Rh(ECp*)$_3$Cl$_2$] (**17a**: E = Ga, **17b**: E = In)

4.2.1 Solution Structures and NMR Spectroscopy

The monomeric insertion products **17a** and **17b** as well as **18** can be regarded as acid-base adducts between Cp*ECl$_2$ and the basic d^8 transition metal centres in [Cp*Rh(ECp*)$_2$] and [(*p*-cymene)Ru(ECp*)$_2$], respectively. However, the NMR spectroscopic data are not consistent with simple acid-base adducts. Instead, in all these complexes the three ECp* ligands are equivalent on the NMR time scale down to −80 °C. Clearly a fast exchange of the chlorides between all group 13 atoms takes place, resulting in three coalesced ECp* ligands. A similar fluxional process was observed in the acid-base adducts of GaCp* and GaCp*X$_2$ (X = Cl, Br). In this case, coalescence of the Cp* rings at −80 °C in [D$_8$]toluene was observed.[66] DFT calculations on the systems R$_3$E−ER and their isomers R$_2$E−ER$_2$ revealed that the difference in energy between these two forms is strongly dependent on both the groups R as well as the group 13 metal E. The adducts Cl$_3$B−GaH and Cl$_3$B−InH for example, exhibit bridging chlorines in the energetic minimum.[67]

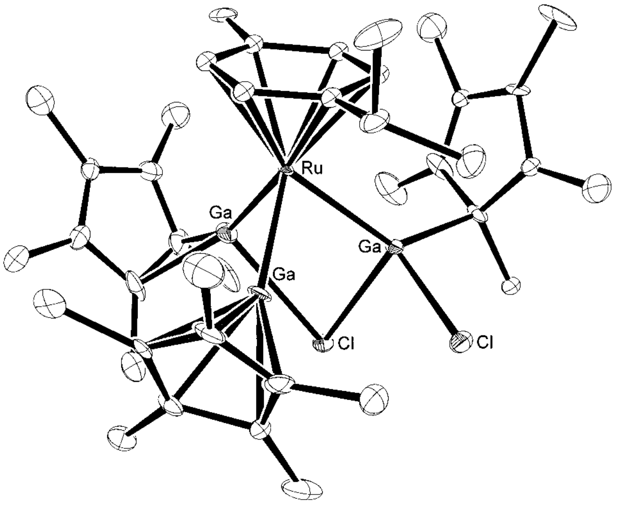


Figure 8. [(*p*-cymene)Ru(GaCp*)$_3$Cl$_2$] (**18**)

Additionally, in solution, a fast Cp* exchange of the InCp* units in the anionic part of complex **26** can be assumed. The NMR spectra show three signal sets for the Cp* groups in a ratio of 2:2:1. Also, complex **26** does not show any decoalescence even at −80 °C.

4.2.2 Solid State Structures

The molecular structures of [RhCp*(ECp*)$_3$Cl$_2$] (**17a**, **17b**) and [(*p*-cymene)Ru(GaCp*)$_3$Cl$_2$] (**18**) exhibit cage-like motifs with E−Cl−E bridges. Generally, only one of the chlorine atoms is found in a bridging position, while the second chlorine is terminally coordinated. The strong difference in hapticity of the Cp* rings is a common feature of these structures. The Cp* ring on the ECl$_2$ unit is σ-bonded, while the Cp* group in the ECp* ligand showing no chloride interactions is clearly η^5-bonded. The bridging chloride atom exhibits some ground state *cis* effect on the coordination of the Cp* on the ECl unit which shows a "nonclassical" hapticity best described as η^3 or η^2. The free p-electron pairs at the Cl atoms effectively compete with the π-density at the Cp* for the empty p-orbitals on the group 13 metal centre. Therefore, the fluxional process in solution is reflected in the solid-state structures which can be re-

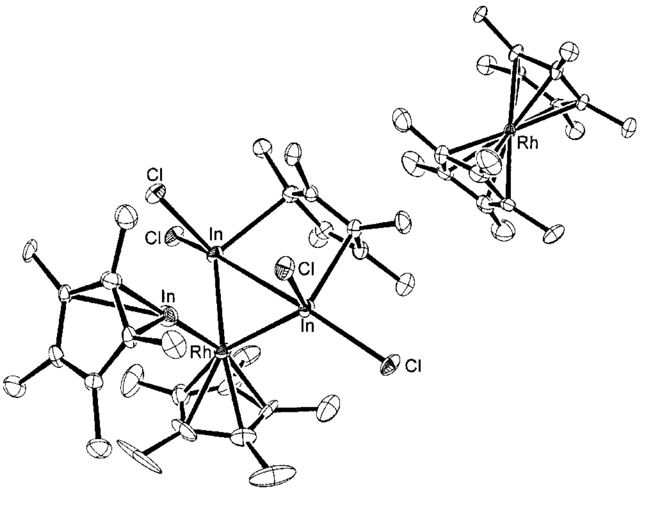


Figure 9. [Cp*$_2$Rh][Cp*Rh(InCp*){In$_2$Cl$_4$(μ^2-Cp*}] (**26**)

garded as trapped "intermediates" of a chlorine exchange between two ECp* centres.

In contrast, the $GaCl_3$ complexes $[Cp^*Rh(GaCp^*)_2(GaCl_3)]$ (**20**) and [(*p*-cymene)$Ru(GaCp^*)_2(GaCl_3)$] (**21**) are simple acid-base adducts without Ga−Cl−GaCp* interactions. Consequently, all Cp* units in both complexes are η^5-bonded to the Gallium centres.

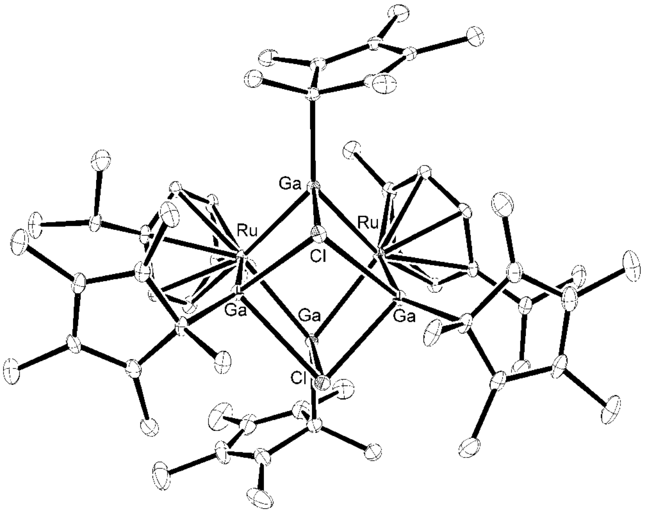


Figure 10. [Ru(*p*-cymene)$(GaCp^*)_2Cl]_2$ (**24**)

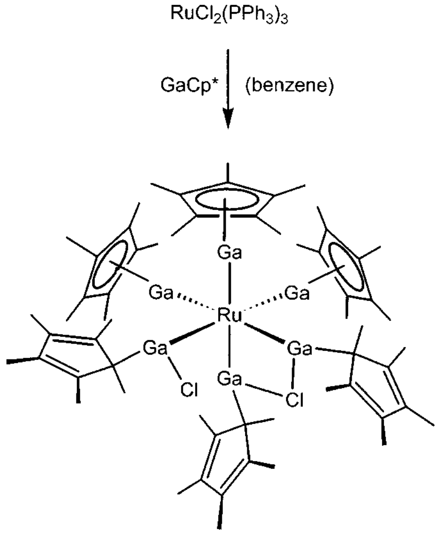
4.3 Reaction of ECp* with other Ruthenium Complexes

In contrast to [{(*p*-cymene)$RuCl_2\}_2$], $[\{Cp^*RuCl\}_4]$ reacts both with GaCp* and InCp* to give the monomeric "piano-stool" complexes $[Cp^*Ru(ECp^*)_3Cl]$ [E = Ga (**27a**), In (**27b**)] (Scheme 14).

In solution, all three ECp* ligands of **27a** and **27b** are equivalent on the NMR time scale down to −80 °C, due to a fast exchange of the chlorides between the three group 13 metals. In the solid state the chloride is either terminally coordinated to gallium (**27a**) or bridging two indium atoms (**27b**). As in complexes **17a**, **17b** and **18**, the influence of the chlorine coordination on the hapticity of adjacent Cp* ligands can be observed.

The reaction of ECp* with $[Cp^*RuCl]_4$ can be described as redox-neutral. The neutral *p*-cymene ligand is a stronger π-acceptor in comparison with the anionic Cp* ligand and thus has a more polarised bond to ruthenium. This situation leads to an increased electron density on all metal centres. Indeed, the chloride of compound **27a** can be easily removed by treatment with $NaBPh_4$, giving the cationic complex $[Cp^*Ru(GaCp^*)_3]^+[BPh_4]^-$ (**27c**). In contrast, **17a**, **17b** or **18** do not show any reaction with $NaBPh_4$. Notably, the cation **27c** can also be obtained by treatment of $[\{RuCp^*Cl_2\}_2]$ with GaCp*, thus having $[Cp^*GaCl_3]^-$ as the counterion instead of $[BPh_4]^-$.

The reaction of GaCp* with $[(Ph_3P)_3RuCl_2]$ leads to a complete substitution of the PPh_3 ligands and insertion of GaCp* into the ruthenium-halide bonds (Scheme 15). The product is the octahedral homoleptic complex $[Ru(GaCp^*)_6Cl_2]$ (**28**) which exhibits fluxional chloride ligands and coalescence of all GaCp* moieties.



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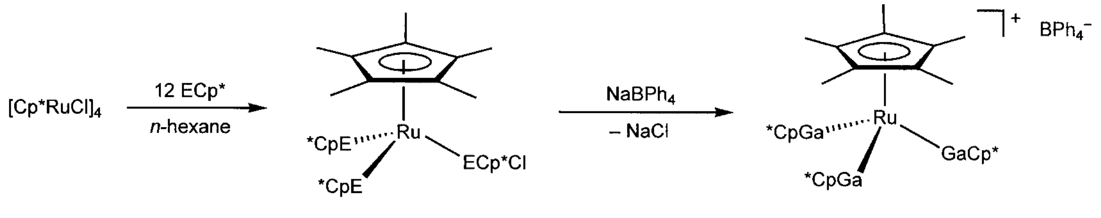
Scheme 15. Reaction of GaCp* with $[(Ph_3P)_3RuCl_2]$

5. Coordination Chemistry of Sterically Bulky Ligands

While the coordination chemistry of ECp* is a well explored field, sterically encumbered low-valent group 13 ligands such as E^ITrip {E = Al, Ga, In; Trip = Bis[2,5-(2,4,6-$iPr_3C_6H_3$)phenyl]},[14,15,68−73] E^ITp [E = Al, Ga, In; Tp = Tris(pyrazoyl)hydroborato][74−82] or E^I(DDP) (E = Al, Ga; DDP = 2-Diisopropylphenylamino-4-diisopropylphenylimino-2-pentene[83−88] have been little used as li-



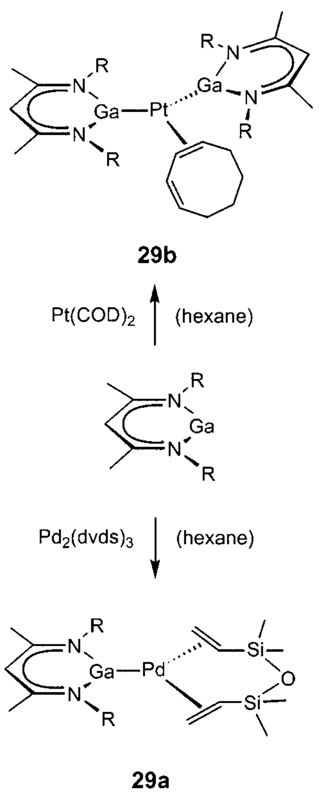
27a (E = Ga)
27b (E = In)

27c

Scheme 14. Synthesis of $[Cp^*Ru(E^ICp^*)_3Cl]$

gands in transition metal chemistry. The iron carbonyl complexes $[(CO)_4Fe-E^IR]$ (E = Ga; R = DDP, Trip, Tp; E = In, R = Tp)[14,89–91] and the tungsten complex $[(CO)_5W-In^ITp]$[91] are the only such complexes reported so far. The difference in the steric demand as well as in the electronic properties of these ligands compared with ECp* points to a different coordination chemistry. As an example for this class of bulky ligands, the coordination chemistry of Ga(DDP) has recently been studied in more detail.[92]

The reactions of ML_n (M = Ni, Pd, Pt; L = olefin) with GaCp* lead to a full substitution of the olefinic ligands and give homoleptic monomeric, di- or trimeric clusters in all cases (vide supra). However, according to Scheme 16, the reaction of $[Pd_2(dvds)_3]$ with Ga(DDP) does not lead to complete substitution but, rather, gives the monosubstituted complex [{(DDP)Ga}Pd(dvds)] (**29a**). Similarly, the reaction of $[Pt(COD)_2]$ with Ga(DDP) leads to the disubstituted complex $[(1,3\text{-}COD)Pt\{Ga(DDP)\}_2]$ (**29b**). Clearly, complete substitution of the olefins is prevented by the high steric demand of Ga(DDP).



Scheme 16. Reactions of Ga(DDP) with $[Pd_2(dvds)_3]$ and $[Pt(COD)_2]$

In contrast to $[M(ECp^*)_4]$ complexes, which are kinetically inert, the electronically unsaturated complexes **29a** and **29b** are substitutionally labile and form dimeric, Ga(DDP) bridged complexes on reaction with CO.

Ga(DDP) shows similar reducing abilities to GaCp*. However, the steric demand of the organic group as well as the reduced Lewis acidity of the gallium centre somehow limits the kinetic access to halide transfer reactions. A reaction mixture of $[\{Cp^*RhCl_2\}_2]$ and Ga(DDP) shows oxidised gallium species but the highly reactive Rh^I-products are not stable under these conditions and nonspecific decomposition is observed.

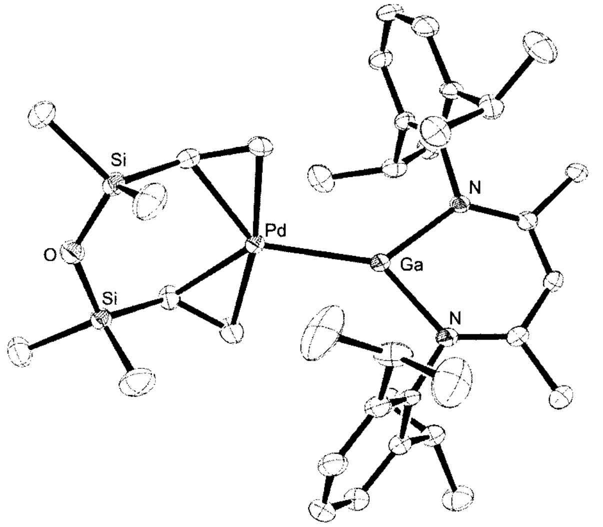
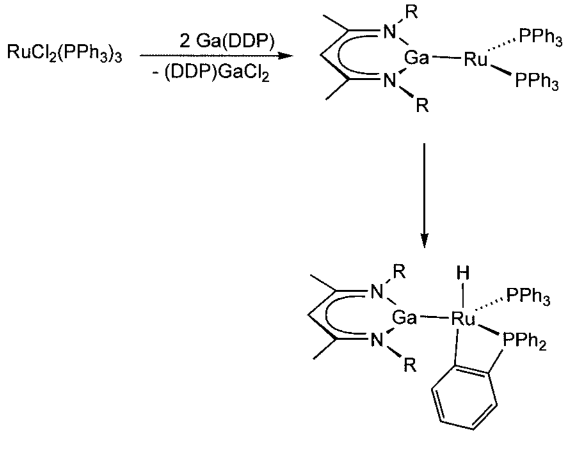


Figure 11. [{(DDP)Ga}Pd(dvds)] (**29a**)

A representative example of the difference between Ga(DDP) and GaCp* is their reactivity towards $[(Ph_3P)_3RuCl_2]$. Whereas GaCp* causes complete substitution of the Ph_3P ligands and the insertion of GaCp* into the ruthenium-halide bonds with the conservation of the oxidation state of Ru^{II} (vide supra), Ga(DDP) leads to a selective reduction of Ru^{II} to Ru^0. A free Ga^{III}-species was detected by ^1H NMR spectroscopy which, in contrast to Cp^*GaCl_2, is not acidic and does not stabilise the Ru^0 centre. Instead, the highly reactive Ru^0 is stabilised by orthometallation of one of the phenyl-rings by reoxidation of the ruthenium centre (Scheme 17). Similar orthometallation reactions are known to take place in the reactions of $[(PPh_3)_3RuCl_2]$ with other reducing agents such as potassium naphthalide.[93,94]



Scheme 17. Reaction of $[(PPh_3)_3RuCl_2]$ with Ga(DDP)

In contrast, reactions of Ga(DDP) with transition metal halides in the oxidation state +I do not give Ga(DDP)Cl_2 but, rather, lead to insertion of Ga(DDP) into the transition metal halide bond.

The Rh^I-compound [$(Ph_3P)_3RhCl$] reacts with Ga(DDP) to give the monomeric complex [$(PPh_3)_2RhCl$\{Ga(DDP)\}] (**30**) (Figure 12). However, the chloride can be found in a bridging position between the gallium and the rhodium centre. This is the first example of a halide-bridged transition-metal group 13 metal complex reported so far. Interestingly, the Lewis acidic properties of coordinated Ga(DDP) are not sufficiently strong to cause a complete migration of the chlorine atom.

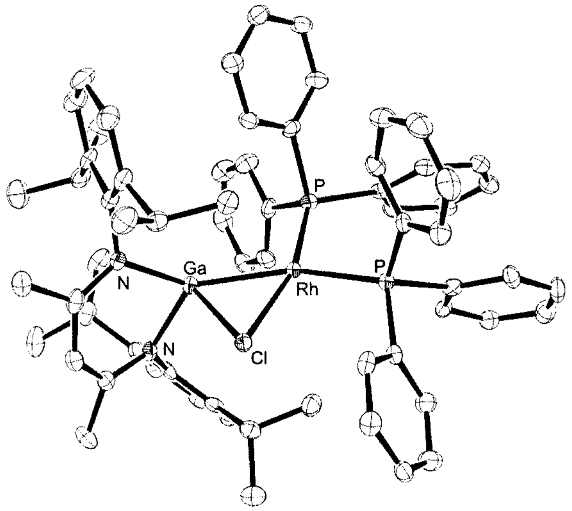
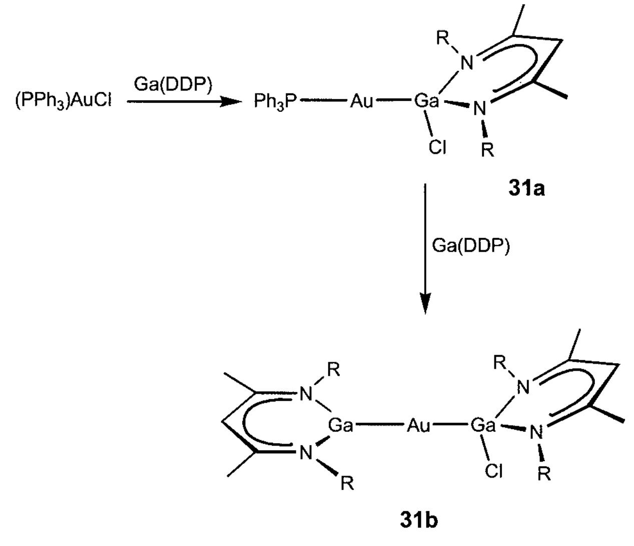


Figure 12. [$(PPh_3)_2RhCl$\{Ga(DDP)\}] (**30**)

Whereas the reaction of [$(PPh_3)AuCl$] with GaCp* leads to unselective decomposition, the reaction with Ga(DDP) yields the complexes [$(Ph_3P)Au$\{Ga(DDP)\}Cl] (**31a**) and [\{(DDP)Ga\}Au\{Ga(DDP)\}Cl] (**31b**) (Scheme 18). In these compounds, an insertion of a Ga(DDP) into a gold−halide bond with full migration of the chloride is observed.



Scheme 18. Reaction of [$(PPh_3)AuCl$] with Ga(DDP)

6. Summary and Outlook

Since their discovery, the low valent group 13 organyls GaCp* and AlCp* have attracted much attention as ligands towards transition metals. They are formally isolobal with CO, phosphanes and NHCs but in contrast, their bonds to transition metals have been calculated to be very polar, the strongest contribution being the coulombic attraction between the metals. Early research concentrated on transition metal carbonyl fragments in order to elucidate the general properties of this new class of ligand. However, recent research is focussing on more reactive transition metal fragments, without competing strong π-acceptor ligands such as CO. The strong polarity of the metal−metal bond is quite interesting in the context of organometallic chemistry. In particular, for bond activation reactions the high increase in electron density of transition metal centres by E^IR is potentially useful or, qualitatively speaking, it should facilitate oxidative addition reactions. In particular, the reactivity of the unsaturated fragments [$M(E^IR)_n$] is not understood and will necessitate further research. In addition, the chemistry of sterically demanding ligands E^IR with R = DDP, Tp^R or similar substituents holds much promise for the discovery of novel and unusual reactions. Based on the above examples we speculate that these exotic "metallic" ligands E^IR may well be very useful in a classical sense as ancillary ligands in organometallic chemistry. However, it should be mentioned here that the title compounds [$M_a(ECp^*)_b$] may also be regarded as the basic building blocks of Schnöckels elaborate cluster [$Al_{38}(AlCp^*)_{12}$][95] showing that ECp*, in general, seems to be a suitable stabilising ligand for large metal clusters. The use of [$M_a(E^IR)_b$] as building blocks for the synthesis of larger transition metal ECp* clusters as well as molecular precursors for intermetallic M/E nanoparticles seems worthy of exploration.

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