

DSM Science & Technology Awards 2005

Name	Tobias Steinke
University	Ruhr-University Bochum (D)
Department	Department of Organometallics & Materials Chemistry
PhD Supervisor	Prof. Dr. R. A. Fischer

Contributions to Coordination Chemistry of low valent Aluminium, Gallium and Indium Organyls $E^I Cp^*$ to Transition Metal Centers

Tobias Steinke

Anorganische Chemie II, Organometallics and Materials Chemistry, Ruhr-Universität
Bochum, Universitätsstrasse 150, 44780, Bochum, Germany

Introduction

The surge in the interest in the coordination chemistry of aluminum, gallium, and indium at transition metals is attributed to impulses that have only recently become effective and which originate from two different motivations. One stems from the understanding that organometallic compounds are potential precursors for applications in the field of new materials, and the other from the resurgence of the chemistry of low-valent Group 13 organyls $E^I R$ ($E = Al, Ga, In$; $R =$ sterically demanding organic groups such as Cp^* , $C(SiMe_3)_3$), which is currently expanded to the coordination chemistry at d-block metals, giving access to new types of bimetallic complexes $[(L_n M)_a(ER)_b]$ ($M =$ transition metal; $E = Al, Ga, In$) and clusters.¹

However, recent studies concerning the synthesis of M-E complexes and clusters have been mainly focused on the coordination of $E^I R$ to transition metal carbonyl fragments $[(CO)_n M_a]^1$, while the reactivity of these complexes was only insufficiently investigated. Constitution and structural characteristics of $[M_a(CO)_n(ER)_b]$ are directly related to classical transition metal carbonyl cluster structures. In contrast, only a few examples of homoleptic complexes $[M(ER)_4]$ ($M = Pt, Ni, E = Ga, In$) were known.¹ Particularly, the first synthesis of the dinuclear cluster compound $[Pt_2(GaCp^*)_2(\mu_2-GaCp^*)_3]^2$ has demonstrated the coordinative potential of the ligands $E^I R$, which exceeds significantly the coordination chemistry of CO or phosphanes.

In the course of this work the synthesis, structural characterization and reactivity of novel homoleptic cluster compounds $[M_a(ECp^*)_b]$ was investigated. These results are the basis for technological applications, which are currently within the scope of further investigations.³ For example, this impact is expressed in the synthesis of nanocolloids (CuAl, PtGa₂), metal organic incs, or the collaboration with NANOSOLAR for the preparation of solar cells (Cu/Ga, Cu/In).

Results

1. Insertion reactions of E^IR into rhodium halide bonds

Depending on stoichiometry and reaction conditions, the insertion of E^IR into the rhodium chlorine bonds of $[\{\text{Cp}^*\text{RhCl}_n\}_2]$ ($n = 1, 2$) yields a variety of insertion products, emphasizing the prospects as well as the complexity of these reaction type. Treatment of $[\{\text{Cp}^*\text{RhCl}_2\}_2]$ with an excess of E^IR yields the complexes $[\text{Cp}^*\text{Rh}(\text{E}^{\text{I}}\text{R})_3\text{Cl}_2]$ ($\text{E} = \text{Ga}, \text{R} = \text{Cp}^* \mathbf{1a}$; $\text{E} = \text{In}, \text{R} = \text{Cp}^* \mathbf{1b}$; $\text{E} = \text{In}, \text{R} = \text{C}(\text{SiMe}_3)_3 \mathbf{2}$), exhibiting cage-like intermetallic RhE_3 centers with E–Cl–E bridges.⁴ The reaction with 3 equivalents of GaCp^* yields the Lewis acid–base adduct $[\text{Cp}^*\text{Rh}(\text{GaCp}^*)_2(\text{GaCl}_3)]$ ($\mathbf{3}$) in trace amounts. By using three equivalents of InCp^* , the novel complex $[\text{Cp}^*_2\text{Rh}]^+ [\text{Cp}^*\text{Rh}(\text{InCp}^*)\{\text{In}_2\text{Cl}_4(\eta^2\text{-Cp}^*)\}]^-$ ($\mathbf{4}$) was isolated. The anion shows an intermetallic RhIn_3 center with an intramolecular bridging Cp^* ring. The reduction of $[\{\text{Cp}^*\text{RhCl}_2\}_2]$ to the Rh^{II} dimer $[\{\text{Cp}^*\text{RhCl}\}_2]$ is observed, when only one equivalent of ECp^* is used. The reaction of $[\{\text{Cp}^*\text{RhCl}\}_2]$ with 6 equivalents of GaCp^* yields dimeric Rh/Ga complexes with the empirical formulae $[(\text{Cp}^*\text{Rh})_2(\text{GaCp}^*)_2\text{Cl}_2]$ ($\mathbf{5}$) and $[(\text{Cp}^*\text{Rh})_2(\text{GaCp}^*)_4(\text{GaCl}_3)]$ ($\mathbf{6}$), respectively. As a thermal decomposition product of $\mathbf{5}$ the all hydrocarbon cluster complex $[(\text{RhCp}^*)_2(\mu_2\text{-GaCp}^*)_2(\mu_3\text{-GaCp}^*)]$ ($\mathbf{7}$) is isolated.⁵

2. Homoleptic complexes of the type $[\text{M}_a(\text{E}^{\text{I}}\text{Cp}^*)_b]$ ($\text{M} = \text{Ni}, \text{Pd}, \text{Pt}$)

The access to homoleptic compounds $[\text{M}_a(\text{ECp}^*)_b]$ proceeds via two different reaction pathways: (i) by building block synthesis and (ii) via direct methods. In both cases, E^IR 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.

2.1. Monomeric complexes $[\text{M}(\text{E}^{\text{I}}\text{Cp}^*)_4]$

The existing class of monomeric, homoleptic compounds $[\text{M}(\text{E}^{\text{I}}\text{R})_4]$ ($\text{M} = \text{Ni}, \text{Pt}$; $\text{E} = \text{Ga}, \text{In}, \text{R} = \text{Cp}^*, \text{C}(\text{SiMe}_3)_3$) has been extended with five novel members. The cod ligands in $[\text{M}(\text{cod})_2]$ ($\text{M} = \text{Ni}, \text{Pt}$) are readily replaced by ECp^* ($\text{E} = \text{Al}, \text{Ga}$) yielding the complexes $[\text{Pt}(\text{GaCp}^*)_4]$ ($\mathbf{8a}$) and $[\text{Ni}(\text{AlCp}^*)_4]$ ($\mathbf{8b}$). Analogous Pd compounds $[\text{Pd}(\text{E}^{\text{I}}\text{R})_4]$ can be obtained by treatment of $[\text{Pd}(\text{tmeda})(\text{X})_2]$ ($\text{X} = \text{CH}_3, \text{Cl}$; $\text{tmeda} = \text{N}, \text{N}, \text{N}', \text{N}'\text{-tetramethylethylenediamine}$) with ECp^* ($\text{E} = \text{Al}, \text{Ga}$) or $\text{In}(\text{C}(\text{SiMe}_3)_3)$, respectively.⁶ In contrast to the reaction of $[\text{Pd}(\text{tmeda})(\text{CH}_3)_2]$ with PR_3 , the reaction

with $E^I R$ includes a methyl group or chlorine migration and reduction of the palladium center by $E^I R$ giving the side products $E^{III} R X_2$. Unlike the insertion reactions described above, the low basicity of the d^{10} Pd center permits the complete cleavage of the acidic species $E^{III} R X_2$. The classical reaction mechanisms of CO containing complexes, that is, insertion into M-C(alkyl) bonds and reductive elimination, can evidently be transferred to $E^I R$.⁷ Noteworthy, all complexes $[M(E^I R)_4]$ are kinetically inert, indicating the high bond energy of ECp^* to transition metal linkage.

2.2. Cluster complexes $M_a(E^I Cp^*)_b$

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 $E^I R$ ($E = Al, Ga, In$). The reaction of $[Pt(cod)_2]$ with an equimolar amount of $[M(GaCp^*)_4]$ (**8a**: $M = Pt$, **8c**: $M = Pd$) and subsequent addition of $GaCp^*$ yields $[Pt_2(GaCp^*)_2(\mu_2-GaCp^*)_3]$ (**9a**) and the trimetallic complex $[PtPd(GaCp^*)_2(\mu_2-GaCp^*)_3]$ (**9b**). It has been shown that $[M(GaCp^*)_4]$ form reactive yet isolable dinuclear associates with $[Pt(cod)_2]$. These intermediates were identified as $[MPt(GaCp^*)(\mu_2-GaCp^*)_3(\eta^2-cod)]$ ($M = Pt$ **10a**, Pd **10b**).⁶

An efficient starting compound for the synthesis of di- and trinuclear cluster compounds $[Pd_a(E^I R)_b]$ was shown to be $[Pd_2(dvds)_3]$ ($dvds = 1,3$ divinyl-1,1,3,3-tetramethyldisiloxane). Depending on the reaction conditions and reactants the formation of $[Pd_2(GaCp^*)_2(\mu_2-GaCp^*)_3]$ (**9c**), $[Pd_3(AlCp^*)_4(\mu_2-AlCp^*)_4]$ ($E = In$ **11a**, $E = Ga$ **11b**) and $[Pd_3(AlCp^*)_2(\mu_2-AlCp^*)_2(\mu_3-AlCp^*)_2]$ (**12**) is observed. These clusters have no direct structural analogs in carbonyl or phosphane chemistry. The formation of these clusters is determined by kinetic factors, and clusters with different nuclearity are not interconvertible to each other by addition of free ligand. Obviously, the stronger σ -donor $AlCp^*$ is capable to stabilize more effectively the coordinatively unsaturated metal centers, resulting in a smaller M/E ratio of 3:6, while $GaCp^*$ or $InCp^*$ prefer linear structures with a M/E ratio of 3:8.^{7,8}

2.3. Fluxionality and Reactivity of $M_a(E^I Cp^*)_b$

The fluxionality of $[M_2(ECp^*)_5]$ and $[Pd_3(ECp^*)_8]$ and the reactivity towards ligand substitution was studied in some detail.⁷ A qualitative relationship between rates of fluxional processes and ligand substitution reactions was established, resulting in mechanistic suggestions for both. The qualitative trend for the relative rates of the

ligand exchange processes is in good agreement with the calculated M-E bond energies in the monomeric compounds $[M\{E(CH_3)\}_4]$ ($M = Ni, Pd, Pt; E = B-Tl$), which have the order $Ni \approx Pt > Pd$ for the transition metals, while for the Group 13 elements the trend $B > Al > Ga \approx In > Tl$ is found.⁹ The NMR spectroscopic analysis of $[Pd_3(ECp^*)_8]$ leads to a better understanding of the molecular structures of $[Pd_3(ECp^*)_8]$ in solution, which have a triangular rather than a linear arrangement of the transition-metal centers as found in the solid state.

While the electronically and sterically saturated monomeric complexes $[M(ECp^*)_4]$ turn out to be completely kinetically inert (*vide supra*), the related unsaturated cluster complexes $[M_a(ECp^*)_b]$ ($b > a > 1$) react with a selection of ligands (Cp^*Al , CO, phosphanes, isocyanides) to give novel di- and trinuclear substitution products. The π -acceptors CO, *t*-BuNC and PPh_3 were found in terminal positions of the dinuclear clusters, whereas the remaining ECp^* prefer the bridging positions. Interestingly, $AlCp^*$ favors the bridging position in direct competition with $GaCp^*$ in the case of $[Pt_2(GaCp^*)_2(\mu_2-AlCp^*)_3]$ (**9d**). This may be due to the stronger σ -donor properties of $AlCp^*$. In general, the $AlCp^*$ -containing dinuclear clusters $[Pt_2(GaCp^*)_2(\mu_2-AlCp^*)_3]$ (**9d**) and $[Pd_2(AlCp^*)_2(\mu_2-AlCp^*)_3]$ (**9e**) do not undergo further substitution reactions with phosphanes, confirming the higher bond strength of M-Al in the first place.⁸

In contrast to the substitution reactions of $[M_2(ECp^*)_5]$, where the cluster core is always retained, the reaction of the trinuclear compound $[Pd_3(InCp^*)_8]$ (**11a**) with PPh_3 or dppe (dppe = bis(diphenylphosphino)ethane) leads to a rearrangement of the linear Pd_3 core to give the triangular Pd_3 clusters $[Pd_3(\mu_2-InCp^*)(\mu_3-InCp^*)_2(PPh_3)_3]$ (**13a**) and $[Pd_3(\mu_2-InCp^*)(\mu_3-InCp^*)_2(dppe)_2]$ (**13b**).⁸

3. Bond activations

Whereas CO and phosphanes are widely used as supporting and directing ligands for reactivity and selectivity in organometallic chemistry, a corresponding potential of the $E^I R$ ligands has not yet been described. In the course of this work this potential has been indicated by an aromatic CH and SiH bond activation on a Ni^0 center as well as a two-fold and three-fold aliphatic CH bond activation in the synthesis of $[Fe(AlCp^*)_5]$.

The reaction of $[Ni(cod)_2]$ with $AlCp^*$ in hexane yields the compound $[Ni(AlCp^*)_3(HAlPhCp^*)]$ (**14**). The oxidative addition of benzene, which is taking place

on the reactive, low-coordinate fragment $[\text{Ni}(\text{AlCp}^*)_3]$ is the first example of an aromatic C-H bond activation on a Ni d^{10} center and points to a general route for the generation of reactive, undercoordinated fragments of the type $[\text{M}(\text{ER})_n]$, which are not available by other synthetic routes. The reactive Intermediate $[\text{Ni}(\text{AlCp}^*)_3]$ can be trapped by reaction of $[\text{Ni}(\text{cod})_2]$ with AlCp^* in HSiEt_3 , giving the complex $[\text{NiH}(\text{AlCp}^*)_3(\text{SiEt}_3)]$ (**15**). Interestingly, the oxidative addition of silane is reversible. The thermal activation of **15** in presence of ligand L such as ECp^* (E = Al, Ga) or PPh_3 yields heteroleptic products of the type $[\text{Ni}(\text{AlCp}^*)_3\text{L}]$, which are not available by direct substitution of E^1R in $[\text{M}(\text{E}^1\text{R})_4]$.¹⁰

While numerous reports on CO-substituted complexes of the type $[\text{M}(\text{CO})_m\text{-(E}^1\text{R})_n]$ ($n = 1-3$)¹¹ exist, the question what is the limit for the coordination number n in the general, homoleptic case $[\text{M}(\text{E}^1\text{R})_n]$, is still unanswered: is $n = 5$ possible, perhaps also $n = 6$, or even more? A first insight is gained through the reactions of the Fe^0 precursor $[(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{Fe}(\eta^4\text{-C}_4\text{H}_8)]$ with excess of AlCp^* , leading to two different CH activated isomers of $[\text{Fe}(\text{AlCp}^*)_5]$ (**15**). The X-ray analysis confirms the CH activation of two and three methyl groups of two and three different Cp^* rings. The methylene moieties are attached to the adjacent Al atoms and the hydrides are localized in a bridging position between the central Fe atom and the Al centers. Quantum mechanical calculations by Frenking et al. show a very good agreement between the structural parameters of the optimized and the experimentally determined structures. Amazingly, a hypothetical structure $[\text{Fe}(\text{AlCp}^*)_5]$ with five Fe-Al bonds and intact Cp^* -ligands without bridging H atoms does not represent an energetic minimum. It can be assumed, that low coordinated intermediates $[\text{Fe}(\text{AlCp}^*)_n]$ ($n < 5$) on the pathway leading to the activated isomers of $[\text{Fe}(\text{AlCp}^*)_5]$, respectively, are responsible for the presumably intramolecular CH activation reactions. However, the mechanism and the role of the metal atoms during the formation of these isomers is still uncertain. Hence, a deeper experimental and theoretical insight is required.¹²

Perspectives for Advanced Materials

The results of this basic research are essential for a deeper understanding of the possible reactivity patterns of E^IR to transition metal centers and can be regarded as the basis for further applications in advanced materials. Only last year Schnöckel et al. have synthesized the giant cluster [Al₃₈(AlCp*)₁₂], showing that E^IR is a suitable ligand for stabilizing naked metal clusters.¹³ Yet, the synthesis of intermetallic nanoparticles of the type M_xE_y is much more sophisticated. Combinations of Al, Ga, and In with d-block metals are a classical subject of metallurgy and inorganic solid state chemistry with different application for catalytic investigations (Ni/Al, Cu/Al), magnetic or other materials properties. Recent studies were mainly focused on the synthesis of noble metal colloids by using classical aqueous reductive methods. However, these reaction conditions are not tolerated by electropositive metals like Al or Ga.

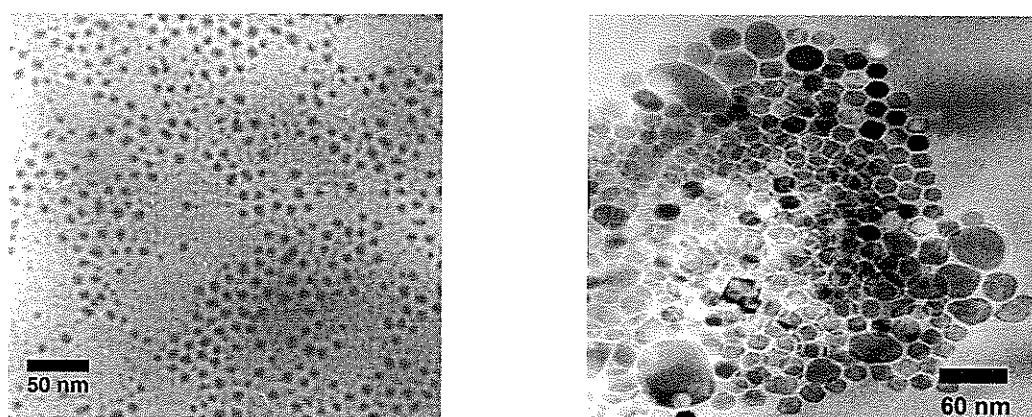


Figure 1. TEM image of PtGa₂ (left) and Cu_xGa_y (right) nanoparticles

Primary experiments in nonaqueous media have shown that the homoleptic cluster compounds [M₂(E^ICp*)₅] are suitable precursors for the synthesis of intermetallic nanoparticles. For example, the thermolysis of a solution of [Pt₂(GaCp*)₅] at 150°C under H₂ pressure results in selective cleavage of the Cp* shell as Cp*H and the formation of PtGa₂ nanoparticles with a surprisingly narrow size distribution of about 10 nm (Figure 1).³ Further precursors such as [Ni(AlCp*)₄] and [Fe(AlCp*)₅] are currently under investigation. Another synthetic route to intermetallic nanoparticles M_xE_y involves the co-decomposition of a transition metal precursor in the presence E^IR. For instance, the reaction of [Cu(OCH(Me)CH₂NMe₂)₂] with GaCp* and HDA or treatment of [CpCuPMe₃] with AlCp* under H₂ pressure results in the formation of mixed copper nanoalloys Cu_xE_y (E = Al, Ga).³

References

- [1] For recent reviews see: a) C. Gemel, T. Steinke, M. Cokoja, A. Kempter, R. A. Fischer, *Eur. J. Inorg. Chem.* **2004**, 4161-4176; b) R. A. Fischer, J. Weiß, *Angew. Chem. Int. Ed.* **1999**, *38*, 2830-2850.
- [2] D. Weiß, M. Winter, R. A. Fischer, C. Yu, K. Wichmann, G. Frenking, *Chem. Commun.* **2000**, 2495-2496.
- [3] M. Cokoja, Ph.D. thesis **2005**, Ruhr-Universität Bochum.
- [4] T. Steinke, C. Gemel, M. Cokoja, M. Winter, R. A. Fischer, *Chem. Commun.* **2003**, 1066-1067.
- [5] T. Steinke, C. Gemel, M. Winter, R. A. Fischer, *Dalton Trans.* **2005**, 55-62.
- [6] C. Gemel, T. Steinke, D. Weiß, M. Cokoja, M. Winter, R. A. Fischer, *Organometallics* **2003**, *22*, 2705-2710.
- [7] T. Steinke, C. Gemel, M. Winter, R. A. Fischer, *Angew. Chem. Int. Ed.* **2002**, *41*, 4761-4763.
- [8] T. Steinke, C. Gemel, M. Winter, R. A. Fischer, *Chem. Eur. J.* **2005**, *11*, 1636-1646.
- [9] a) J. Uddin, C. Boehme, G. Frenking, *Organometallics* **2000**, *19*, 571-582; J. Uddin, G. Frenking, *J. Am Chem. Soc.* **2001**, *123*, 1683-1693.
- [10] T. Steinke, C. Gemel, M. Cokoja, M. Winter, R. A. Fischer, *Angew. Chem. Int. Ed.* **2004**, *43*, 2299-2302.
- [11] For example see: M. Cokoja, T. Steinke, C. Gemel, M. Winter, R. A. Fischer, **2003**, *684*, 277-286.
- [12] T. Steinke, M. Cokoja, C. Gemel, A. Kempter, A. Krapp, G. Frenking, U. Zenneck, R. A. Fischer, *Angew. Chem. Int. Ed.* **2005**, *44*, in press.
- [13] J. Vollet, J. R. Hartwig, H. Schnöckel, *Angew. Chem. Int. Ed.* **2004**, *41*, 3186-3189.