Gallium Ligands

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Substituent-Free Gallium by Hydrogenolysis of Coordinated GaCp*: Synthesis and Structure of Highly Fluxional $[Ru_2(Ga)(GaCp^*)_7(H)_3]$ **

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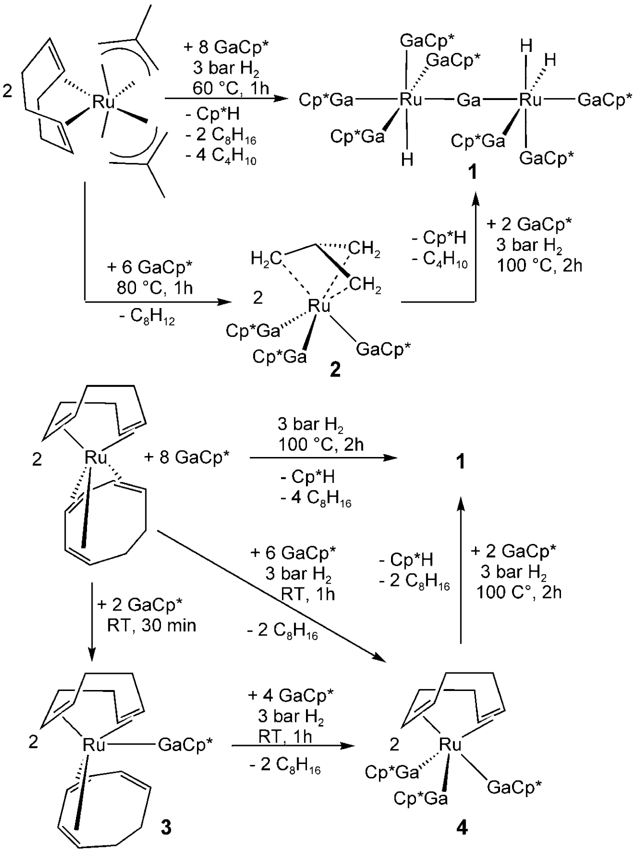
Monovalent organo Group 13 metal compounds ER (E = Al, Ga, In; R = bulky substituent: e.g. alkyl, aryl, C_5Me_5 (Cp*), amides, β-diketiminate, amidinates, guanidinates) behave as very potent σ-donor ligands in coordination chemistry.[1] A more recent highlight is $[\eta^5\text{-}\{(Me_3Si)C_5H_4\}_3U(AlCp^*)]$ containing the first unsupported actinide–aluminum bond.[2] Much work has been done elucidating the bonding properties of similar d/f-block compounds of the general formula $[L_aM_b(ER)_c]$.[3] But far less information has been gathered on the reaction chemistry and associated potential applications of this class of compounds. The homoleptic compounds $[M_a(ECp^*)_b]$ are particularly interesting because of the flexible binding properties of the Cp* at the Group 13 metal atom.[4] The soft chemical synthesis of M/E Hume–Rothery phases using all-hydrocarbon ligand $[ML_n]$ and ECp_n^* as precursors ($n = 1$, E = Al, Ga; $n = 2$, E = Zn; M = Cu, Ni)[5,6] and the recent discovery of $[Mo(ZnMe)_9(ZnCp^*)_3]$ and $[\{Mo(CO)_4\}_4(Zn)_6(\mu\text{-}ZnCp^*)_4]$,[7] resulting from the reactions of $[Mo(GaCp^*)_n(CO)_{6-n}]$ with $ZnMe_2$, illustrate novel prospects for a targeted approach to intermetallic nanomaterials based on molecular Group 13/transition-metal complexes.[8]

In this context, splitting the Cp* group from coordinated ECp* ligands to initiate M/E cluster growth is a particularly important aspect. We reported on the selective protolysis of coordinated GaCp* by $[H(OEt_2)_2]BAr^F$ ($BAr^F = B[\{C_6H_3(CF_3)_2\}_4]$), to give for example, $[Pt_2H(Ga)(GaCp^*)_7]^{2+}$ from $[Pt(GaCp^*)_4]$.[9] Likewise $[(Cp^*Ga)_4Rh(GaMe)]^+$ results from $[(Cp^*Ga)_4Rh\{Ga(Me)(\eta^1\text{-}Cp^*)\}]$ by elimination of Cp*H.[10] Selective oxidative cleavage of Cp* to yield fulvalene species is also possible: treatment of $[Pt(GaCp^*)_4]$ with $[Cp_2Fe]BAr^F$ (Cp = C_5H_5) leads to the trinuclear cluster $[Pt_3(Ga)(GaCp^*)_6]^+$.[11] However, the cited soft chemical synthesis of M/E materials[5,6] is based on the co-hydrogenolysis of $[ML_n]$ and ECp* and is not likely to involve charged species.[5] In addition, pure GaCp* is quite inert against H_2 in solution or in the gas phase,[5c] which suggests GaCp* coordination compounds as intermediates in the M/E materials formation.

With the aim of characterizing early intermediates of such reactions we selected the hydrogenolysis of $[Ru(\eta^4\text{-cod})(\eta^3\text{-}C_4H_7)_2]$ (cod = cyclooctadiene, $\eta^3\text{-}C_4H_7$ = 2-methylallyl) in the presence GaCp* as our test case (Scheme 1). From this reaction the title compound $[(GaCp^*)_4(H)Ru(\mu\text{-}Ga)Ru(H)_2(GaCp^*)_3]$ (**1**) was isolated in 78%, with Cp*H, cyclooctane, and isobutane as by-products (identified by NMR spectroscopy). The treatment of $[Ru(\eta^4\text{-cod})(\eta^3\text{-}C_4H_7)_2]$ with three molar equivalents GaCp* in the absence of H_2 selectively gives $[Ru(GaCp^*)_3(tmm)]$ (**2**; tmm = $C(CH_2)_3^{2-}$). Accordingly, hydrogenolysis of **2** in the presence of GaCp* again affords **1**, Cp*H, and isobutane. Similarly, $[Ru(\eta^4\text{-cod})(\eta^6\text{-cot})]$ (cot = cyclooctatetraene) can be used as the ruthenium



Scheme 1. Reaction pathways in the synthesis of compound **1**.

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source in the synthesis of **1**, yet the yield is distinctly lower and the intermediate products [Ru(GaCp*)(η^4-cod)(η^4-cot)] (**3**) and [Ru(GaCp*)$_3$(η^4-cod)] (**4**) are formed. Reaction of **4** with one molar equivalent of GaCp* under a hydrogen atmosphere leads to **1** under cleavage of Cp*H and cyclooctane.

Single crystals of **1**, suitable for X-ray diffraction studies, were obtained by slowly cooling a saturated toluene solution of **1** to −30 °C for several days. Important crystallographic data are compiled in the Supporting Information and the molecular structure in the solid state is shown in Figure 1.

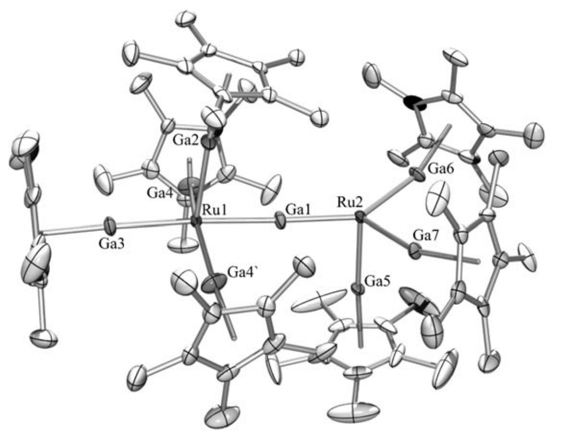


Figure 1. Molecular structure of **1**. The thermal ellipsoids are set at 50% probability (the hydrogen atoms of the Cp* ligands have been omitted for clarity). The hydride ligands at the ruthenium center could not be refined. See Supporting Information for selected bond lengths and angles.

Compound **1** crystallizes in the monoclinic space group *C*2*m*. The hydrido ligands could not be located in the course of the refinement. However, from the ^{1}H NMR spectroscopy data discussed below we conclude that three hydride ligands are distributed over the Ru centers in solution. The structural parameters of the Ru and Ga centers in the solid state, in particular the Ga-Ru-Ga bond angles of the Ru-GaCp* units, suggest that each ruthenium atom is in fact hexacoordinate resulting in two different octahedral Ru fragments {(GaCp*)$_4$(H)Ru(μ-Ga)} and {(GaCp*)$_3$(H)$_2$Ru(μ-Ga)}, respectively. As shown in Figure 1, one coordination site appears to be free at Ru1 and two sites are free at Ru2.

The two Ru fragments are connected by a substituent-free, "naked" Ga atom with an almost perfectly linear arrangement (Ru1-Ga1-Ru2 178.0(1)°). At this point we refer to our recent work on related electron-rich ruthenium-polyhydride complexes and clusters which contain AlCp* and GaCp* ligands, but in which no substituent-free Al or Ga atoms are found. The formation of E−H species by the insertion of ECp* into the Ru−H bond was not observed in those cases.[14] The Ru−Ga1 bonds of **1** are 2.322(1) (to Ru2) and 2.387(1) Å (to Ru1) whereas the Ru−GaCp* bond lengths average to 2.365 Å (2.313(1)–2.440(1) Å). These data are quite comparable to the Ru−Ga distances in related Ru−GaCp* complexes and clusters.[14,15] Following usual electron-counting rules, **1** can be viewed as being formally composed of the unsaturated neutral 16 electron fragment {(GaCp*)$_3$(H)$_2$Ru^{II}} and the saturated neutral 18 electron fragment {(GaCp*)$_4$(H)Ru^0(Ga)} (the H ligands are counted as two-electron donating H$^-$ and the naked Ga ligand is counted as zero electron donating Ga$^+$). The linear arrangement Ru-Ga-Ru of **1** can be explained by the strong σ- and π-accepting abilities of the substituent-free Ga$^+$, as demonstrated by DFT calculations on [(GaCp*)$_4$PtGa]$^+$ and [Pt$_2$H(Ga)(GaCp*)$_7$]$^{2+}$.[9] Note, that the Pt dimer [Pt$_2$H(Ga)(GaCp*)$_7$]$^{2+}$ is isoelectronic to **1** (a total of 34 valence electrons for both M$_2$Ga$_8$ core structures).

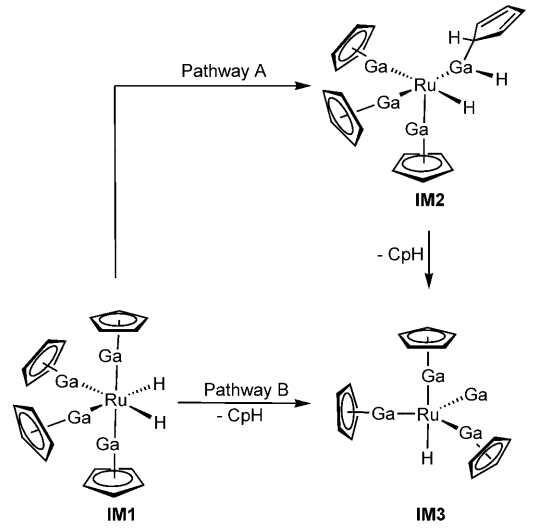
The ^{1}H NMR spectrum of **1** in C$_6$D$_6$ recorded at room temperature reveals only two sharp signals at $\delta = 1.91$ and −15.51 ppm with an intensity ratio of close to 105:3 representing seven chemically equivalent GaCp* ligands as well as three chemically equivalent and, based on their chemical shifts, unambiguously ruthenium-located hydride ligands, respectively. The ^{1}H NMR shifts of the hydrides as well as of the GaCp* groups are in agreement with shifts of ruthenium complexes of these ligands.[14,15] Accordingly, the ^{13}C NMR spectrum shows only two signals at $\delta = 117.2$ and $\delta = 10.4$ ppm.

The origin of the highly symmetric or fluxional nature of **1** in solution is puzzling. A chemically meaningful static structure of such a high symmetry for a Ru$_2$Ga core structure surrounded by seven GaCp* and three hydride ligands is not conceivable. However, the ^{1}H NMR spectrum remains totally unchanged down to −100 °C (the experimental limit for low-temperature NMR spectroscopy with our set up). Clearly what occurs is an extremely fast fluxional process, in which all the GaCp* and hydride ligands exchange over both Ru and the bridging Ga metal centers! What would such a fast fluxional process look like? Let us first consider dissociation/association processes. Thus, reversible dissociation of H$_2$, GaCp*, and/or Cp*H, respectively, have to be taken into account as possible ligand-exchange pathways. However all three processes can be ruled out experimentally: High-temperature NMR studies of pure, isolated **1** in the presence of excess H$_2$ (3 bar), GaCp*, or Cp*H, do not show coalescence with the free ligands up to 80 °C. Furthermore, at elevated temperatures no H/D exchange can be detected in the presence of D$_2$ (3 bar) or Cp*D. The transversal relaxation time T_1 of more than 600 ms clearly excludes the presence of a nonclassical dihydrogen ligand in **1**.[16] These experiments certainly rule out intermolecular pathways. But, a reasonable intramolecular process could not be modeled by means of DFT calculations. Several pathways have been considered (see Supporting Information for details), but in all cases the calculated transition states were way too high in energy to explain such a fast process. For example, we considered the symmetric intermediate [(GaCp)$_3$(H)Ru(μ-GaH)(μ-GaCp)Ru(H)(GaCp)$_3$] (**2^{Cp}**), which may be formed by migration of one hydride ligand to the bridging gallium atom and a concomitant relocation of one GaCp* ligand to a bridging position between the two adjacent ruthenium centers. This species is very similar in energy to [(GaCp)$_4$(H)Ru(μ-Ga)Ru(H)$_2$(GaCp)$_3$] (**1^{Cp}**) (−1.6 kcal mol^{-1}). However, the transition state for such a movement is calculated to be +38.2 kcal mol^{-1} which rules out this process to be part of a fast equilibrium. Comparison of the IR spectra under different conditions (solution in cyclopentane, KBr pellet, nujol dispersion) unequivocally confirms the presence of terminal rather than bridging ruthenium-bound hydride ligands in solution, which excludes symmetric [Ru(μ-H)$_3$Ru] complexes as intermediates. Note that there are examples of oligohydride complexes showing a hydride-exchange rate that is faster than the NMR time scale.[16b]

What is the key message of the synthesis of **1**, beyond its remarkable solution and solid-state structure? First, the hydrogenation of GaCp*-containing transition-metal complexes has never been investigated in detail, although it has recently been shown that hydrogenolysis of such complexes under somewhat extremer conditions leads to M/Ga alloy nanoparticles.[5,6] [Ru(η^4-cod)(η^6-cot)] itself is a very suitable precursor for very small and high-purity Ru nanoparticles.[12,13] Indeed, treatment of [Ru(η^4-cod)(GaCp*)$_3$] with 3 bar H$_2$ in mesitylene at 150 °C for seven days results in the formation of RuGa and RuGa$_2$ nanoparticles and co-hydrogenolysis of [Ru(η^4-cod)(η^3-C$_4$H$_7$)$_2$] and GaCp* in a molar ratio of 1:2 leads to RuGa$_2$ and Ru nanoparticles (Supporting Information).[17] Accordingly, **1** can be considered as an intermediate in such an alloy formation process: that is, **1** represents an early molecular step towards Ru/Ga nanoparticles during a wet chemical synthesis. Therefore, it is interesting to take a closer look to the hydrogenolyis mechanism of coordinated GaCp* releasing Cp*H as observed in case of **1**.

Synthesis of **1** from [Ru(η^4-cod)(η^3-C$_4$H$_7$)$_2$] under D$_2$ atmosphere in C$_6$D$_6$ leads to only 30 % deuterium incorporation at the hydride positions of **1**, whereas using [Ru(η^4-cod)(η^6-cot)] as the starting material yields almost complete deuteration (> 90 %). Fast scrambling of deuterides into the {Ru(tmm)} group, which involves thermodynamically comparatively stable {Ru(2-methylallyl)} intermediates, is a reasonable explanation for this difference. When C$_6$H$_6$ is used as the solvent, in both cases significantly less deuterium ends up in the product, suggesting H/D exchange with the solvent at an early stage of the reaction. Notably, **1** is kinetically inert. Neither H/D exchange with C$_6$D$_6$, D$_2$, or Cp*D, nor ligand exchange reactions in the presence of free GaCp* or Cp*H were observed.

We investigated potential mechanistic pathways of the formation of **1** by means of DFT calculations on the B3LYP[18]/LanL2DZ[19] level of theory using GaCp instead of GaCp* as the ligand.[20] As isobutane, cyclooctane, and Cp*H were spectroscopically determined as the only carbon-containing side products in the synthesis of **1**, and because the hydrogenation of coordinated olefins is usually a very fast process, we chose [Ru(GaCp)$_4$(H)$_2$] (**IM1**) as the likely first key intermediate before the loss of CpH. In principal, two different pathways for CpH elimination from **IM1** are feasible (Scheme 2). Pathway A represents a two-step mechanism starting with a hydride transfer from the ruthenium to a gallium atom giving [Ru(GaCp)$_3$(H){GaH(C$_5$H$_5$)}] (**IM2**). Subsequent CpH elimination from the [GaH(C$_5$H$_5$)] ligand leads to another likely key intermediate of this reaction, that is, [Ru(GaCp)$_3$(H)(Ga)] (**IM3**) featuring a terminally bound gallium atom. In pathway B, **IM3** is directly formed from **IM1** by concerted CpH elimination from the two metal centers without prior hydride transfer. Dimerization of intermediates formed by association/dissociation equilibria of GaCp from **IM3** and **IM1** finally lead to [(GaCp)$_4$(H)Ru(μ-Ga)Ru(H)$_2$-(GaCp)$_3$] (**1^{Cp}**) (see the Supporting Information).



Scheme 2. Key intermediates in the synthesis of **1^{Cp}** which have been substantiated by DFT calculations.

The key issues raised in the modeling of this reaction sequence by DFT are thus: 1) the energy of the transition states of hydride transfer and CpH eliminations along pathways A and B and 2) the energy balance of GaCp association/dissociation from **IM1** and **IM3**. For pathway A the intermediate **IM2** as well as the respective transition state for the CpH elimination, namely **TS1** could be localized on the potential-energy surface. Intermediate **IM2** is energetically less favorable than **IM1** by 22.2 kcal mol^{-1} which points to the loss of aromatization energy of a GaCp ring. The transition state **TS2** for the CpH elimination in pathway A is energetically very unfavorable being 51.0 kcal mol^{-1} above **IM2** (73.2 kcal mol^{-1} above **IM1**). However, the pentacoordinate [Ru(GaCp)$_3$(H)(Ga)] (**IM3**) is surprisingly energetically favorable and the formation of **IM3** from **IM1** is calculated to be endergonic by only 7.6 kcal mol^{-1}.

For pathway B, the transition state of the direct CpH elimination from the two metal centers (**TS3**) is 35.5 kcal mol^{-1} above **IM1**. This is a remarkably low activation barrier compared to **TS2** (pathway A), but still high enough to be in good agreement with the observation, that the synthesis of **1** occurs only under relatively forcing reaction conditions (60 °C, 3 bar H$_2$). The cost in energy is partially a result of a change in the coordination mode of the GaCp ring, shifting from η^5 in **IM2** to η^3 in **TS3**. Notably, the main process in the reaction is the migration of the Cp group towards the hydride ligand. Finally, the association of free GaCp to **IM3** leading to octahedral [Ru(GaCp)$_4$(H)(Ga)] is exergonic by only 2.5 kcal mol^{-1}, whereas dissociation of GaCp from **IM1** giving [Ru-(GaCp)$_3$(H)$_2$] costs 17.9 kcal mol^{-1}. Theses results point to the presence of parallel GaCp association/dissociation equilibria in solution. The required intermediates for the formation of **1^{Cp}**, that is, [Ru(GaCp)$_4$(H)(Ga)] and [Ru(GaCp)$_3$(H)$_2$], are energetically available. The final dimerization of these two fragments is very exergonic, releasing 37.0 kcal mol^{-1}. Unfortunately, the proposed key intermediate [Ru(GaCp*)$_4$(H)$_2$] (i.e. **IM1**, Scheme 2) could not be isolated nor spectroscopically detected on monitoring the reaction of Scheme 1 in situ in a pressurized NMR tube. However, we recently reported on the synthesis, structure, and reactivity of the closely related complex [Ru(GaCp*)$_2$(PCy$_3$)$_2$(H)$_2$][14a] which may support our assumption of an **IM1**-like intermediate on the way to **1**.

We conclude that the observed selective hydrogenolytic removal of a Cp* ligand from coordinated GaCp* leading to the well defined neutral complex [(GaCp*)$_4$(H)Ru(μ-Ga)Ru(H)$_2$(GaCp*)$_3$] (**1**) featuring a bridging "naked" Ga ligand[21] suggests a general applicability of this "deprotection" method within the series of [L$_a$M$_b$(ECp*)$_c$] compounds.[4] We emphasize the important feature of this hydrogenolysis that is common to the protolytic[9,11] and the oxidative cleavage[12] of Cp*, namely that M–Ga complexes or clusters of higher nuclearity are formed featuring substituent-free Ga centers in bridging positions as well as M–H bonds. Our result highlights the potential of Cp* as a removable protecting group, a property that is in contrast to those of the other typical substituents R being used for the stabilization of low-valent Group 13 compounds, in particular the N,N chelating bisketoiminates and related species.[1a,f–i] We think that an in depth understanding of this chemistry is the key for the development of a very controlled molecular-building-block synthetic route to both M–E clusters, that correspond to Hume–Rothery-type intermetallic phases, and to alloy nanomaterials.

Experimental Section

Details of the preparation as well as structure determination of **1** are given in the Supporting Information. CCDC-707429 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre www.ccdc.cam.ac.uk/data_request/cif.

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