

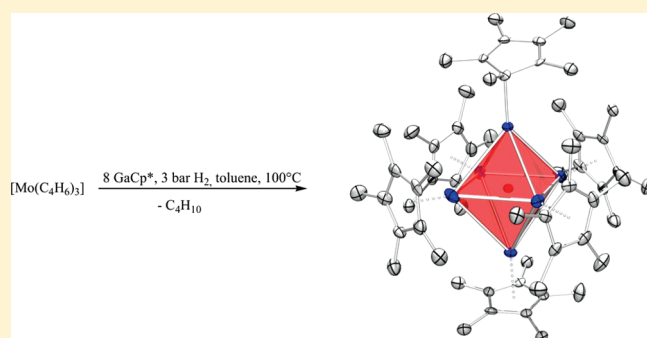
Homoleptic Hexa and Penta Gallylene Coordinated Complexes of Molybdenum and Rhodium[†]

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Supporting Information

ABSTRACT: The reactions of molybdenum(0) and rhodium(I) olefin containing starting materials with the carbenoid group 13 metal ligand GaR (R = Cp*, DDP; Cp* = pentamethylcyclopentadienyl, DDP = HC(CMeNC₆H₃-2,6-ⁱPr₂)₂) were investigated and compared. Treatment of [Mo(η^4 -butadiene)₃] with GaCp* under hydrogen atmosphere at 100 °C yields the homoleptic, hexa coordinated, and sterically crowded complex [Mo(GaCp*)₆] (1) in good yields $\geq 50\%$. Compound 1 exhibits an unusual and high coordinated octahedral [MoGa₆] core. Similarly, [Rh(GaCp*)₅][CF₃SO₃] (2) and [Rh(GaCp*)₅][BAR^F] (3) (BAR^F = B{C₆H₃(CF₃)₂}₄) are prepared by the reaction of GaCp* with the rhodium(I) compound [Rh(coe)₂(CF₃SO₃)₂] (coe = cyclooctene) and subsequent anion exchange in case of 3. Compound 2 features a trigonal bipyramidal [RhGa₅] unit. In contrast, reaction of excess Ga(DDP) with [Rh(coe)₂(CF₃SO₃)₂] does not result in a high coordinated homoleptic complex but instead yields [(coe)(toluene)Rh{Ga(DDP)}(CF₃SO₃)] (4). The common feature of 2 and 4 in the solid state structure is the presence of short CF₃SO₂O...Ga contacts involving the GaCp* or rather the Ga(DDP) ligand. Compounds 1, 2, and 4 have been fully characterized by single crystal X-ray diffraction, variable temperature ¹H and ¹³C NMR spectroscopy, IR spectroscopy, mass spectrometry, as well as elemental analysis.



INTRODUCTION

Low valent group 13 metal ER species (E = Al, Ga, In; R = bulky, mono anionic substituents; i.e., Cp* = pentamethylcyclopentadienyl; alkyl, aryl, dialkylamide, β -diketiminato, guanidinate, amidinate, or halide) have emerged as interesting carbenoid ligands in coordination chemistry exhibiting metal-atom ligands.^{1–9} Comparison of the ligand properties of GaCp* and Ga(DDP) is quite representative for the whole family of ER ligands. The steric and electronic situations differ characteristically in both cases. While in GaCp* the sp hybridized Ga(I) center is coordinated by the rather flexible, comparably soft Cp* group, showing facile haptotropic shifts, in Ga(DDP) on the contrary, the sp² hybridized Ga(I) is stabilized by a coordinatively rigid, and electronically hard β -diketiminato. In general, ER ligands are more or less isolobal to CO, PR₃, and *N*-heterocyclic carbenes, that is, they exhibit very strong covalent σ -donation as well as typically weak π -accepting properties and substantial electrostatic (ionic) contributions to the overall bonding interaction.^{10,11} While in GaCp* the two vacant p-orbitals are quite populated by the π -donating Cp* group, this effect is less pronounced in case of Ga(DDP), creating a more Lewis acidic gallium center. In both cases, however, the (residual) Lewis acidity at the gallium is usually increased on coordination of the gallium to a transition metal center.

Important synthetic procedures for the preparation of transition metal complexes of ER (R = bulky organic group) include ligand substitution reactions at [L_nM] using ER compounds as reagents. Many binary carbonyls (L = CO) give substitution products on reaction with ER under liberation of CO, for example, [Fe₂(CO)₉] or [Co₂(CO)₈].¹² In particular, GaCp* reacts with heteroleptic olefin containing carbonyl complexes, for instance [(nbd)Mo(CO)₄] or [(cht)Fe(CO)₃] (nbd = 2, 5-norbornadiene, cht = cycloheptatriene), to give [(GaCp*)₂-Mo(CO)₄] and [Fe₂(GaCp*)₃(CO)₆], respectively.¹² However, the successive substitution of CO (or other strong acceptor ligands) is limited by the coordination of GaCp*. The strong σ -donor abilities of GaCp* increase the overall electron density of the transition metal on coordination and thus lead to stronger π -back bonding of the remaining CO ligands, which then cannot be substituted anymore. Therefore, homoleptic GaCp* containing complexes can only be obtained by substitution of labile and very weak π -acceptor ligands such as ethene or acetonitrile. The same situation is observed for other ER ligands. Thus, [Ni(GaCp*)₄],¹³ the analogue to [Ni(CO)₄], is readily available from [Ni(cod)₂] (cod = 1,5-cyclooctadiene) and likewise [M(GaCp*)₄]¹⁴

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(M = Pd, Pt) can be prepared from [Pt(cod)₂] and [Pd(tmeda)(CH₃)₂] (tmeda = tetramethylethylenediamine).

The particular bifunctional feature of the ER ligands in contrast to their isolobal C or P ligator analogues mentioned above is the combination of reduction (insertion) and coordination properties which is nicely shown by the synthesis of [Pd(GaCp*)₄] from [Pd(CH₃)₂(tmeda)] and 5 equiv of GaCp* with [Cp*Ga(CH₃)₂] as the stoichiometric byproduct. The iso-electronic cationic congeners [M(GaCp*)₄]⁺ (M = Cu, Ag) could also be obtained by such type of reactions.¹⁵ Also, oligonuclear complexes [Pd₃(AlCp*)₆],¹⁶ [PdM(GaCp*)₅] (M = Pd, Pt),^{14,16} [Pd₃(InCp*)₈],^{14,16} and group 11 metal dimers [Cu₂(GaCp*)(μ-GaCp*)₃Ga(CF₃SO₃)₃]¹⁷ and [M₂(GaCp*)₃(μ-GaCp*)₂][CF₃SO₃]₂^{15,17} (M = Cu, Ag) have been isolated under optimized conditions and reaction stoichiometries with the right choices of the transition metal precursors.

Despite the wealth of work done to coordinate ER to metal centers across the periodic table, and particularly in contrast to the d¹⁰ metal complexes [M(ER)₄], corresponding to [M(CO)₄], the homoleptic, mononuclear complexes [M(ER)_n] (n > 4), which should be analogues to the classic penta- or hexacarbonyl complexes, [M(GaCp*)₅] (Fe, Ru, Os) and [M(GaCp*)₆] (M = Cr, Mo, W), have not been reported, so far.^{18–21} In all known cases, olefins could not be fully substituted from [M(olefin)_x] or [M(olefin)_x(PR₃)_y] starting materials and heteroleptic products [L_nM(GaCp*)_m] (L = olefin, PR₃) were isolated instead.²² In fact, no homoleptic complexes of the general formula [M_a(ER)_b] have been reported for coordination numbers greater than four. However, we like to note two exceptions at this point of the introduction. First, the complexes [M(AlCp*)₅] (M = Fe, Ru) exhibit penta coordinated [MAI₅] cores, but the actual structures are C–H activated isomers.²³ Second, the cation [Rh(GaCp*)₄(GaCH₃)]⁺ has been described and represents a formal analogue to [Rh(CO)₅]⁺. However, this complex with a [RhGa₅] core is not fully homoleptic, and the synthesis is quite special.²⁴ Nevertheless, these examples demonstrate, that *homoleptic*, closed shell 18 electron complexes [M(ER)_n] with n > 4 are a valid target, at least for R = Cp*.

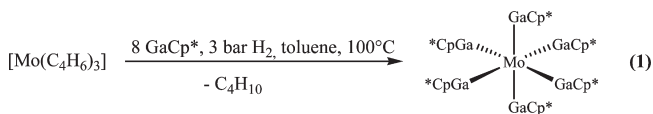
We have already communicated the complex [Mo(GaCp*)₆] (1) as the crucial starting material for the synthesis of the unprecedented zinc-rich compound [Mo(ZnCp*)₃(ZnCH₃)₉].²⁵ Below we like to highlight and discuss the synthesis, structural and spectroscopic properties of [Mo(GaCp*)₆] in detail on its own right, as it represents the important and still only example of a homoleptic, *hexa* gallylene coordinated transition metal complex. In addition, we will report the related *penta* gallylene coordinated [Rh(GaCp*)₅]⁺ and its characterization as the second fully homoleptic example of the targeted family of transition metal complexes [M(ER)_n] (n > 4). The compounds will be put into the context of the different reaction behavior and ligand properties of GaCp* and Ga(DDP).

RESULTS AND DISCUSSION

Reaction of [Mo(η⁴-butadiene)₃] with excess GaCp* in toluene under 3 bar hydrogen atmosphere at 100 °C yields [Mo(GaCp*)₆] (1) in reproducible yields around 50% as an orange powder with *n*-butane as the byproduct (Scheme 1).²⁵

Single crystals of 1 being suitable for X-ray diffraction studies can be obtained by heating up a saturated mesitylene solution and slowly cooling it to –30 °C over several days. The result of the structure solution and refinement is shown in Figure 1.

Scheme 1. Synthesis of Compound 1



Complex 1 crystallizes in the triclinic space group *P* $\bar{1}$. Most interestingly, the molybdenum center of the metal core [MoGa₆] is surrounded by six GaCp* ligands in an almost perfect octahedral fashion as determined by the continuous shape measure *S*_Q(*P*) = 0.195 (Figure 1).^{26,27} Only small deviations from the perfect octahedral coordination environment can be observed with respect to the bond angles. For a more detailed structural description of 1 see the Supporting Information of our previous communication.²⁵ Achieving such a high coordination number around the transition metal center is only possible because of asymmetrically coordinated Cp* units to the gallium centers and therefore haptotropic shifts resulting in coordination modes from η¹-(Ga4) to η⁵-(Ga1, Ga2, Ga3, Ga5, Ga6). Beside, the shortened Mo–Ga bond distances in 1 compared to [*fac*-(Cp*Ga)₃Mo(CO)₃]²⁸ and [*cis*-Mo(Cp*Ga)₂(CO)₄]¹³ the average η⁵-Cp*_{centroid}–Ga distance (2.069 Å) is somewhat shortened compared to the free ligand (2.081 Å; monomer in the gas phase).²⁹ This shortening is an indirect measure for the polarity of the Mo–Ga bond, an indication for the strong σ-donor property of the Cp*Ga fragment and a measure of the increased electrophilicity at the Ga center upon coordination to Mo.

The ¹H NMR (one signal at 1.96 ppm) as well as the routine ¹³C{¹H} NMR spectrum of pure 1 in C₆D₆ at room temperature reveal the expected signals for the Cp* unit.²⁵ Noteworthy, the high fluctuation of the Cp* groups around the six gallium atoms in the ligand sphere is still present even at –78 °C (low temperature ¹H NMR measurements in d₈-toluene). The absorptions in the FTIR spectrum of 1 assigned to the Cp* group at 2943, 2877 as well as 2829 cm^{–1} are in the typical range and are quite comparable with Cp* absorptions in the first homoleptic GaCp* containing compound [Ni(GaCp*)₄] (2958, 2906, and 2855 cm^{–1}).¹³ The ν(Mo–Ga) vibrations are expected in the near IR region (below 200 cm^{–1}) and were outside the range of measurement. At this point we like to highlight an important breakthrough in the mass spectrometric characterization of metal-rich molecules. Quite a number of attempts to obtain meaningful mass spectrometric data on compounds [M_a(ECp*)_b] using standard techniques for sample transfer and ionization failed. However, by using liquid injection field desorption ionization mass spectrometry (LIFDI-MS) and a special configuration of the ionization chamber gave excellent results. In the ideal case, this method allows the identification of the molecular ion peak [M]^{•+} of such compounds. Herein, the molecular ion peak [M]^{•+} of 1 at *m/z* = 1326 as well as one fragment signal at *m/z* = 1190 for [M – Cp*]^{•+}, could be nicely detected (see Supporting Information).

Our related investigations on the coordination chemistry of GaCp* and Ga(DDP) toward d⁶ metal centers, however, gave no equally satisfying preparative or spectroscopic results similar to 1. For instance, use of bulky Ga(DDP) instead of GaCp* according to Scheme 1 does not lead to any specific product formation like partial substitution of butadiene and coordination of Ga(DDP) toward the Mo center. The analogous reaction of [W(η⁴-butadiene)₃] failed too, and no pure products could be isolated.

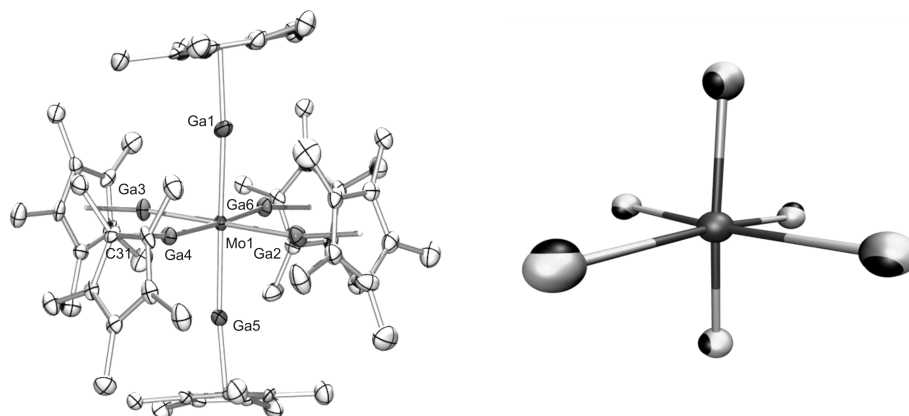
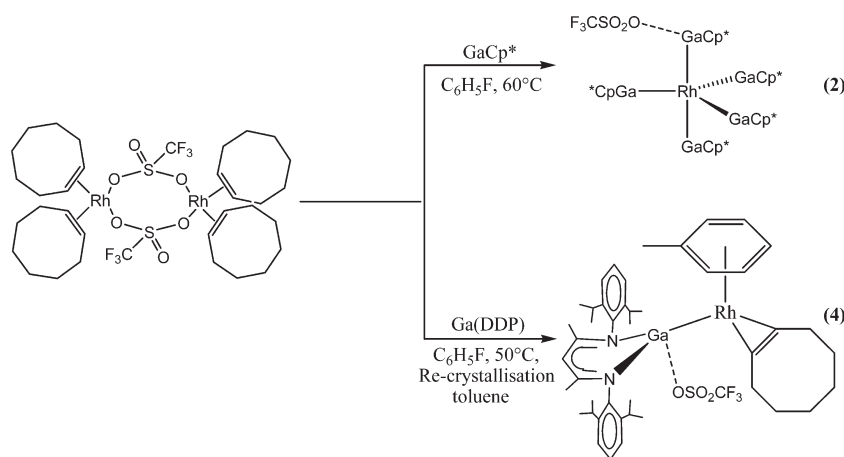


Figure 1. Molecular structure of $[\text{Mo}(\text{GaCp}^*)_6]$ (**1**) in the solid state as determined by single crystal X-ray diffraction (left) and superimposition of the ideal (black) and experimental (gray) polyhedra (right). The displacement ellipsoids are shown at 50% probability level, hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mo1–Ga4 2.384(1), Mo1–Ga1 2.458(1), Mo1–Ga5 2.474(1), Mo1–Ga3 2.476(1), Mo1–Ga6 2.485(1), Mo1–Ga2 2.493(1), Ga4–C31 2.088(4), Ga1–Cp*_{centroid} 2.127, Ga2–Cp*_{centroid} 2.091, Ga3–Cp*_{centroid} 2.040, Ga5–Cp*_{centroid} 2.057, Ga6–Cp*_{centroid} 2.024, Ga4–Mo1–Ga1 87.92(2), Ga4–Mo1–Ga5 88.77(2), Ga4–Mo1–Ga3 85.12(2), Ga1–Mo1–Ga5 175.22(3), Ga4–Mo1–Ga6 174.35(3), Ga3–Mo1–Ga2 176.39(3), Ga1–Mo1–Ga3 90.39(2), Ga5–Mo1–Ga3 92.77(2), Ga1–Mo1–Ga6 91.15(2), Ga5–Mo1–Ga6 92.49(2), C31–Ga4–Mo1 168.01(12), Ga3–Mo1–Ga6 89.31(2), Ga4–Mo1–Ga2 91.32(2), Mo–Ga1–Cp*_{centroid} 175.21, Mo–Ga2–Cp*_{centroid} 167.42, Mo–Ga3–Cp*_{centroid} 170.30, Mo–Ga5–Cp*_{centroid} 167.36, Mo–Ga6–Cp*_{centroid} 166.04.

Scheme 2. Synthesis of Compounds 2 and 4



This difference is explained by the much stronger bonded butadiene in the tungsten case which has been first described by Gausing and Wilke who carried out substitution reactions of CO and cot (cot = cyclooctatetraene) using $[\text{M}(\eta^4\text{-butadiene})_3]$ ($\text{M} = \text{Mo}, \text{W}$).³⁰ Herein, variation of the reaction conditions using higher hydrogen or high temperatures give any substitution of the olefin from the tungsten metal. Furthermore, the chromium homologue of **1** was targeted by the reaction of $[\text{Cr}(\text{C}_{10}\text{H}_8)_2]$ ³¹ with GaCp^* . However, no reasonable product formation was seen in several NMR spectroscopic experiments under a wide variety of reaction conditions. Consequently, a different synthetic approach has to be developed to yield the Cr and W homologues of **1**, at least by using much more substitution labile starting Cr and W compounds.

Accordingly and on the basis of the existence of the high coordinated complexes **1** and $[\text{Rh}(\text{GaCp}^*)_4(\text{GaCH}_3)][\text{BAr}^F]$, we then targeted the isolation of the corresponding, fully homoleptic cation $[\text{Rh}(\text{GaCp}^*)_5]^+$ stabilized in the form of an appropriate salt. As shown in Scheme 2, treatment of the

rhodium(I) dimer $[\text{Rh}(\text{coe})_2(\text{CF}_3\text{SO}_3)]_2$ with stoichiometric amounts of 10 equiv of GaCp^* in fluorobenzene at 60 °C results in the formation of $[\text{Rh}(\text{GaCp}^*)_5][\text{CF}_3\text{SO}_3]$ (**2**) in very good yields $\geq 80\%$.

Compound **2** dissolves well in polar solvents like fluorobenzene, dichloromethane, or tetrahydrofuran (thf) and is stable for several weeks when stored under an inert gas atmosphere at -30 °C. As expected, the ^1H NMR spectrum of **2** in CD_2Cl_2 shows one signal at 1.91 ppm for the equivalent ring protons of the GaCp^* ligand, again indicating fluxional processes. First, a fast exchange of the CF_3SO_3 group between the Ga centers has to be taken into account and second, the exchange of equatorial and axial positions in the $[\text{RhGa}_5]$ core (as it is quite typical for penta coordinated species). Likewise for **1**, the fluctuation of the Cp^* groups can be observed up to -78 °C determined by low temperature ^1H NMR measurements. The routine $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum illustrates no unusual features and gives rise to two signals at 11.09 (GaC_5Me_5) and 117.21 (GaC_5Me_5) ppm. Note that the carbon atom of the CF_3SO_3 group was not detected

in the ^{13}C NMR spectrum under the standard measurement conditions. The ^{19}F NMR spectrum shows one signal in the expected range at -78.7 ppm. In contrast to compound **1**, the molecular peak of **2** could not be detected by LIFDI mass spectrometry, rather facile loss of $\{(\text{Cp}^*)_2\text{Ga}(\text{CF}_3\text{SO}_3)\}$ occurs and results in the detection of the fragment $[\text{M} - \{(\text{Cp}^*)_2\text{Ga}(\text{CF}_3\text{SO}_3)\}]^+$ ($m/z = 788$). This observation of the species $[\text{Rh}(\text{GaCp}^*)_3(\text{Ga})]^+$ under mass spectrometric conditions, however, agrees nicely with the fluctuating behavior of **1** and **2** and the known ligand property of naked Ga^+ together with the leaving group properties of the neutral gallium(III) molecule $(\text{Cp}^*)_2\text{Ga}(\text{CF}_3\text{SO}_3)$.³² Furthermore, the rhodocenium cation $[\text{RhCp}^*_2]^+$ ($m/z = 373$) was detected in the mass spectrum as a characteristic fragmentation and rearrangement product of **2**. FTIR spectroscopic results of **2** display the expected absorptions for the Cp^* groups at 2938, 2885, and 2834 cm^{-1} comparable to $[\text{Mo}(\text{GaCp}^*)_6]$ as well as $[\text{Ni}(\text{GaCp}^*)_4]$. IR spectroscopy is a popular but often ambiguous method to distinguish between (contact) ion pair and covalent bonding modes of the triflate anion acting as a weak nucleophile. Herein, the characteristic absorption of ionic existing CF_3SO_3^- is near 1280 cm^{-1} and is shifted to higher wave numbers around 1380 cm^{-1} for more covalent character.³³ The IR spectrum of **2** shows a strong signal at 1219 cm^{-1} and weak absorptions at 1295 and 1373 cm^{-1} which could confirm a more ionic than covalent situation in compound **2**. Deep red needles of **2** suitable for X-ray measurements were obtained by slow diffusion of *n*-hexane into a saturated fluorobenzene solution at room temperature over several days. Compound **2** crystallizes in the triclinic space group $P\bar{1}$. The coordination geometry can be best described as a distorted trigonal bipyramid (Figure 2). Caused by steric overcrowding, the trigonal bipyramidal coordination geometry of the $[\text{RhGa}_5]$ core is strongly distorted. A similar, yet distinctly weaker distortion has also been found in $[\text{Rh}(\text{GaCp}^*)_4(\text{GaCH}_3\text{Cp}^*)]$ and $[\text{Rh}(\text{GaCp}^*)_4(\text{GaCH}_3)][\text{BAR}^F]$ ($\text{BAR}^F = \text{B}\{\text{C}_6\text{H}_3(\text{CF}_3)_2\}_4$).²⁴ The deviation from the ideal trigonal bipyramid is reflected in the Ga5-Rh1-Ga2 angle ($154.297(18)^\circ$) with a pronounced deviation from linearity. The equatorial angles also strongly deviate from the ideal 120° angles and have values of $106.604(16)^\circ$ (Ga4-Rh1-Ga3), $143.643(17)^\circ$ (Ga1-Rh1-Ga3) and $109.655(16)^\circ$ (Ga1-Rh1-Ga4). The angles between equatorial and axial ligands (ideally 90°) show values between $79.725(15)^\circ$ (Ga1-Rh1-Ga2) and $100.423(16)^\circ$ (Ga5-Rh1-Ga4). The Rh-Ga distances (average $2.3572\text{ \AA}$) are significantly elongated with respect to the average Rh-Ga distance in $[\text{Rh}(\text{GaCp}^*)_4(\text{GaCH}_3)][\text{BAR}^F]$ ²⁴ ($\text{O} 2.2957\text{ \AA}$) but comparable to other Rh-GaCp* compounds, which show Rh-Ga distances between $2.3292(15)\text{ \AA}$ in $[\text{Cp}^*\text{Rh}(\text{GaCp}^*)(\text{CH}_3)_2]$ ³⁴ and an average value of $2.408\text{ \AA}$ for $[\{\text{Rh}(\eta^2, \eta^2\text{-nbd})(\text{PCy}_3)(\text{GaCp}^*)_2\}\{\text{BAR}^F\}]$ ²² ($\text{nbd} = 2,5\text{-norbornadiene}$). With exception of the Cp^* group coordinated to Ga1, all Cp^* ligands are η^5 coordinated to the gallium atoms with an average bond distance of $1.991\text{ \AA}$, comparable with free GaCp^* ($2.081(5)\text{ \AA}$, monomer in the gas phase).²⁹ This value for Ga-Cp^* centroid of **2** clearly reflects the enhanced electrophilic character of the coordinated Ga centers as compared with **1**.^{25,29} The η^1 coordination mode of the Cp^* moiety of Ga1 (Ga1-C5 bond distance $2.055(3)\text{ \AA}$) is obviously a result of steric overcrowding at Rh and the presence of a weak donor-acceptor interaction between Ga1 and the CF_3SO_3^- anion. The Ga1-O1 distance of $2.079(2)\text{ \AA}$ is well comparable to the Ga-O distances in the $\text{RGa-OSO}_2\text{-CF}_3$ fragments ($\text{R} = \text{organic substituent}$) of, for example,

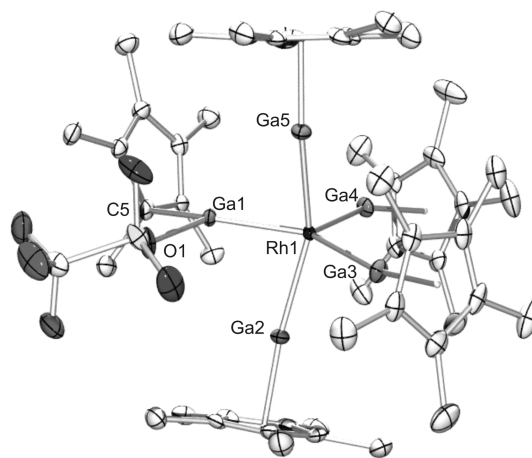
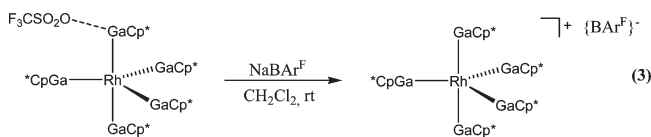


Figure 2. Molecular structure of **2** in the solid state as determined by single crystal X-ray diffraction; displacement ellipsoids are shown at 50% probability level, hydrogen atoms are omitted for clarity. Selected interatomic distances ($\text{\AA}$) and angles ($^\circ$): Rh1-Ga1 $2.3326(4)$, Rh1-Ga2 $2.3393(4)$, Rh1-Ga3 $2.3799(4)$, Rh1-Ga4 $2.3800(4)$, Rh1-Ga5 $2.3542(4)$, $\text{Ga2-Cp}^*\text{centroid}$ 1.963 , $\text{Ga3-Cp}^*\text{centroid}$ 1.996 , $\text{Ga4-Cp}^*\text{centroid}$ 2.039 , $\text{Ga5-Cp}^*\text{centroid}$ 1.964 , Ga1-C5 $2.055(3)$, Ga1-O1 $2.079(2)$, $\text{Rh1-Ga2-Cp}^*\text{centroid}$ 171.87 , $\text{Rh1-Ga3-Cp}^*\text{centroid}$ 166.79 , $\text{Rh1-Ga4-Cp}^*\text{centroid}$ 161.73 , $\text{Rh1-Ga5-Cp}^*\text{centroid}$ 156.29 , O1-Ga1-Rh1 $115.94(7)$, O1-Ga1-C5 $92.74(12)$, C5-Ga1-Rh1 $148.82(10)$, Ga5-Rh1-Ga2 $154.297(18)$, Ga4-Rh1-Ga3 $106.604(16)$, Ga2-Rh1-Ga3 $89.454(16)$, Ga5-Rh1-Ga4 $100.423(16)$, Ga1-Rh1-Ga3 $143.643(17)$, Ga1-Rh1-Ga4 $109.655(16)$, Ga1-Rh1-Ga5 $83.584(15)$, Ga1-Rh1-Ga2 $79.725(15)$.

Scheme 3. Synthesis of Compound 3



$[\text{Ga}(\text{thf})_4\text{H}(\text{CF}_3\text{SO}_3)_2][\text{Ga}(\text{thf})_2(\text{CF}_3\text{SO}_3)_4]$ ³⁵ ($\text{thf} = \text{tetrahydrofuran}$, $\text{Ga-O} = 1.947(9)\text{--}1.988(9)\text{ \AA}$), $[\{2,6\text{-(Me}_2\text{NCH}_2)_2\text{-C}_6\text{H}_3\}\text{Ga}(\text{CF}_3\text{SO}_3)_2\text{H}][\text{CF}_3\text{SO}_3]$ ³⁶ ($\text{Ga-O} = 1.939(8)\text{--}1.962(9)\text{ \AA}$), $[\{(\text{CF}_3\text{SO}_3)\text{Bi}(\text{GaDDP})_2\}]$ ³⁷ ($\text{Ga-O} = 2.027(1)\text{ \AA}$) or $[(\text{TTP})\text{Ga}(\text{CF}_3\text{SO}_3)\cdot\text{C}_7\text{H}_8]$ ³⁸ ($\text{TTP} = \text{tetraphenylporphyrin}$, $\text{Ga-O} = 1.963\text{ \AA}$). It should be mentioned that coordination of the anion at Lewis acidic gallium centers is not observed in the compound $[\text{Rh}(\text{GaCp}^*)_4(\text{GaCH}_3)][\text{BAR}^F]$ because of the much weaker nucleophilic character of the BAR^F anion. We were thus led to treat compound **2** with a slight excess NaBAR^F in CH_2Cl_2 at room temperature which results in the formation of $[\text{Rh}(\text{GaCp}^*)_3]\text{-}[\text{BAR}^F]$ (**3**) as a microcrystalline orange powder which is stable under inert atmosphere at -30°C for several weeks (Scheme 3).

Surprisingly, once compound **3** is isolated in pure solid form, it is very labile when dissolved again in common polar solvents like CH_2Cl_2 and thf . The first signs of decomposition are detected during NMR measurements within 2 h resulting in elimination of Cp^*H and a series of further not assigned broad peaks in the Cp^* area. The initial deep red solution slowly turns yellow, and some metallic precipitate is observed. Even at low temperatures around -30°C , crystallization of the pure compound **3** was not successful and always gives rise to a yellow oil and metal deposition in the Schlenk flask. However, quick preparation of fresh solutions in

CD_2Cl_2 and immediate NMR measurements showed very dominant signals in the ^1H NMR spectrum at 1.91 ppm (s, 75H) for the Cp^* groups as well as broad signals at 7.65 (br, 4H) and 7.72 (br, 8H) ppm for the BAR^{F} anion. Low temperature ^1H NMR measurements gave results very similar to compounds **1** and **2**. Thus, splitting of the initial one Cp^* signal is not observed at -78°C , as it is the case for **1** and **2**. The ^{19}F NMR spectrum shows one sharp signal at -62.9 ppm for the CF_3 groups. ^{11}B NMR measurement displays one peak at -6.6 ppm in the expected range. As discussed above, decomposition of **3** takes place in solution after a few minutes. The ^{13}C NMR measurement has been done only with a minimum number of scans to obtain signals for the pure product. Herein, peaks at 11.12 (GaC_5Me_5) and 117.45 (GaC_5Me_5) ppm for the GaCp^* ligand as well as signals for the BAR^{F} anion at 117.88 (s, para CH), 125.03 (q, $-\text{CF}_3$, $J = 272.3$ Hz), 128.99 (s, ipso to the CF_3 units) and 135.23 ppm (s, ortho CH) were detected. The signal for the carbon atom ipso to boron could not be observed because of low scan number measurement as suggested above and also reported in the literature for different BAR^{F} containing structures in the past.³⁹ Unfortunately, the LIFDI mass spectrum did neither display the molecular ion peak $[\text{M}]^{+}$ nor the characteristic fragment $[\text{Rh}(\text{GaCp}^*)_3(\text{Ga})]^+$ as this was seen for **2**, but rather the rhodocenium cation $[\text{RhCp}^*_2]^+$ ($m/z = 373$) as the dominant peak. FTIR absorptions of **3** were detected at 2956, 2895, and 2836 cm^{-1} characteristic for the Cp^* units as well as one strong peak at 1264 cm^{-1} for the C–F vibration. This distinctly different behavior of **2** and **3** with respect to stability of the $[\text{Rh}(\text{GaCp}^*)_5]^+$ unit in solution and the Cp^* transfer to Rh in case of **2** and **3** in the course of redox reactions, that is, $\text{Rh}(\text{I}) \rightarrow \text{Rh}(\text{III})$ and $\text{Ga}(\text{I}) \rightarrow \text{Ga}(\text{0})$, is quite puzzling and may need further investigation based on density functional theory. Also note, that the closely related cation $[\text{Rh}(\text{GaCp}^*)_4(\text{GaCH}_3)]^+$ is perfectly stable as BAR^{F} salt in solution.

The differences in the reaction behavior of low valent gallium compounds GaR can be nicely illustrated on the basis of the rhodium(I) precursor used in the preparation of compound **2**. In contrast to the formation of compound **2** by using GaCp^* as ligand, the reaction of $\text{Ga}(\text{DDP})$ with $[\text{Rh}(\text{coe})_2(\text{CF}_3\text{SO}_3)]_2$ in fluorobenzene at 50°C and recrystallization from a saturated toluene solution leads to the formation of the mono gallylene complex $[(\text{coe})(\text{toluene})\text{Rh}(\text{GaDDP})(\text{CF}_3\text{SO}_3)]$ (**4**) (Scheme 2). At this point, we like to highlight that the different choices of the stoichiometric ratios of the reactants are based on different reaction pathways in comparison to the less bulky GaCp^* known from several publications over the past years.^{17,40} The reaction with $\text{Ga}(\text{DDP})$ involves three steps, that is, replacement of one coe ligand accompanied by an insertion reaction of gallium into the $\text{Rh}-\text{O}$ bond as well as coordination of one toluene molecule during the crystallization process. Notably, a quite similar reaction of $\text{Ga}(\text{DDP})$ with $[\text{Rh}(\text{coe})_2\text{Cl}]_2$ was observed leading to $[(\text{coe})(\text{benzene})\text{Rh}(\text{GaDDP})(\text{Cl})]$.⁴¹ The ^1H NMR spectrum of **4** in C_6D_6 shows signals for one coordinated coe at 2.79 (m, 2H) ppm and 0.92–1.48 ppm (m, 12H) at which the latter signals overlap with signals of the DDP moiety (24H, $\text{CH}(\text{CH}_3)_2$). The DDP unit gives rise to four further signals at 1.69 (s, 6H, CH_3), 3.48 (m, 4H, $\text{CH}(\text{CH}_3)_2$), 5.20 (s, 1H, $\gamma\text{-CH}$) as well as 6.99–7.15 (m, 6H, aryl). In addition the signals for a coordinated toluene are found at 2.10 (s, 3H) and within the multiplet at 6.99–7.15 ppm overlapping with the DDP unit. The ^{13}C NMR as well as the ^{19}F NMR spectrum do not show any unusual features. Pure yellow crystals of **4** can be obtained by

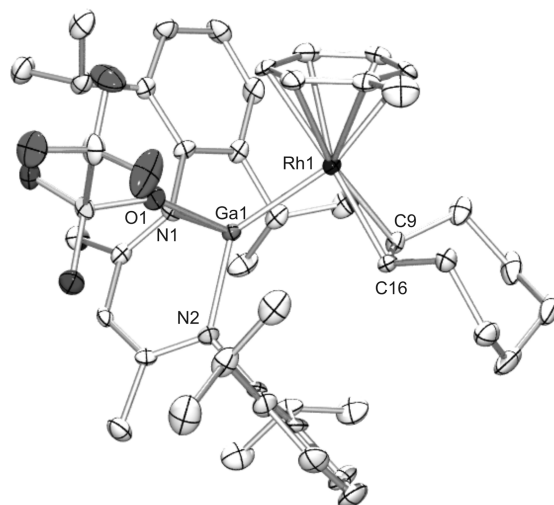


Figure 3. Molecular structure of **4** in the solid state as determined by single crystal X-ray diffraction; displacement ellipsoids are shown at 50% probability level, hydrogen atoms are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Rh1–Ga1 2.3696(6), Ga1–O1 2.113(3), Ga1–N1 1.957(4), Ga1–N2 1.999(3), Rh1–C9 2.125(4), Rh1–C16 2.136(4), C9–C16 1.409(6), N1–Ga1–N2 94.87(14), N1–Ga1–Rh1 133.39(11), N2–Ga1–Rh1 124.55(10), O1–Ga1–Rh1 107.00(8), N1–Ga1–O1 95.28(14), N2–Ga1–O1 90.37(13).

recrystallization from a saturated toluene solution at -30°C . Complex **4** crystallizes in the monoclinic space group $P2_1/n$. The coordination environment of the Rhodium atom in **4** as determined by single crystal X-ray diffraction can be best described as a piano stool configuration (Figure 3). The N1–N2–Ga1–Rh1 plane is nearly trigonal planar with an angular sum of 352.81° . The Rh1–Ga1 bond distance (2.3696(6) Å) is comparable with Rh–Ga distances in other Rh–Ga complexes, that is, $[\text{Rh}(\text{PPh}_3)_2\mu\text{-Cl}(\text{Ga}(\text{DDP}))]$ ⁴¹ (2.3870(6) Å), $[(\text{coe})(\text{benzene})\text{Rh}(\text{GaDDP})\text{Cl}]$ ⁴¹ (2.4037(8) Å), $[\text{Rh}(\eta^2, \eta^2\text{-cod})(\text{GaCp}^*)_3][\text{BAR}^{\text{F}}]$ ²² (cod = 1,5-cyclooctadiene) (O 2.379 Å) or $[\text{Rh}(\text{cod})(\text{IMes})\{\text{Ga}\{[\text{N}(\text{Ar})\text{C}(\text{H})_2]\}_2\}]$ ⁴² (IMes = $:\text{C}\{\text{N}(\text{C}_6\text{H}_2\text{Me}_3-2,4,6)\text{-CH}_2\}$, Ar = $\text{C}_6\text{H}_3\text{Pr}_2-2,6$) (2.4259(6) Å). The Ga1–O1 distance (2.113(3) Å) is slightly longer than in compound **2** but lies well in the range of gallium–oxygen distances in $\text{RGa-OSO}_2\text{CF}_3$ fragments (R = organic substituent) of the structures discussed above (vide supra).

CONCLUSIONS

The reactions of olefin containing d^6 and d^9 metal starting materials with GaR ligands (R = Cp^* and DDP) lead to a full substitution of the olefin ligands in the case of GaCp^* to yield the steric crowded transition metal complexes $[\text{Mo}(\text{GaCp}^*)_6]$ (**1**), $[\text{Rh}(\text{GaCp}^*)_5][\text{CF}_3\text{SO}_3]$ (**2**), and $[\text{Rh}(\text{GaCp}^*)_5][\text{BAR}^{\text{F}}]$ (**3**). While $[\text{Mo}(\eta^4\text{-butadiene})_3]$ is sufficiently reactive only under H_2 atmosphere and higher temperatures, the reaction of $[\text{Rh}(\text{coe})_2(\text{CF}_3\text{SO}_3)]_2$ with GaCp^* takes place under mild conditions without hydrogen. All three compounds **1**–**3** represent proof of principle to obtain homoleptic, highly gallylene coordinated congeners of the classic transition metal carbonyl complexes $[\text{M}(\text{CO})_n]$ for coordination numbers $n > 4$, despite of the steric bulk of Cp^* as the substituent at the gallium center. The fluxional behavior and the facile haptotropic shift of the Cp^* ligand reduces the strain of the otherwise steric overcrowded

situation in case of rigid substituents. However, redox-reactions and Cp* transfer may limit the stability of the complexes $[M(\text{GaCp}^*)_n]$ as it is the case of compound **3**. In sharp contrast to the versatile, soft coordinating properties of GaCp*, the reaction of Ga(DDP) with $[\text{Rh}(\text{coe})_2(\text{CF}_3\text{SO}_3)]_2$ does not lead to a homoleptic complex with an all-Ga coordination sphere around the Rh center, rather the heteroleptic mono gallium complex $[(\text{coe})(\text{toluene})\text{Rh}(\text{GaDDP})(\text{CF}_3\text{SO}_3)]$ (**4**) was isolated. This is certainly due to the rigidity of the DDP ligand and the much increased steric bulk and concave ligand shape.³ In addition, the overall positive charge at the species $[\text{Rh}(\text{GaCp}^*)_5]^+$ and $[(\text{coe})(\text{toluene})\text{Rh}(\text{GaDDP})]^+$ contributes to the more electrophilic nature of the coordinated Ga centers which undergo Lewis acid–base adduct formation with the counterion triflate as weak nucleophile. Similar observations have been made in reactions of GaCp* and Ga(DDP) toward $[\text{Cu}(\text{CF}_3\text{SO}_3)_2]$. These results nicely show the importance of electronic and steric properties of the two different Ga(I) ligands which effect their reactivity toward substitution labile transition metal complexes, not only leading to different products but also allowing for different reaction pathways.

EXPERIMENTAL SECTION

General Remarks. All manipulations were carried out in an atmosphere of purified argon using standard Schlenk and glovebox techniques. Hexane and toluene were dried using an mBraun Solvent Purification System. Fluorobenzene and mesitylene were dried by alumina column under dry atmosphere. The final H₂O content in all solvents used was checked by Karl Fischer-Titration and did not exceed 5 ppm. $[\text{Rh}(\text{coe})_2(\text{CF}_3\text{SO}_3)]_2$,⁴³ $[\text{Mo}(\eta^4\text{-butadiene})_3]$,³⁰ GaCp*,^{12,44} Ga(DDP),⁴⁵ and NaBAR^F were prepared according to literature methods. Elemental analyses were performed by the Microanalytical Laboratory of the University of Bochum. NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer (¹H, 250.1 MHz; ¹³C, 62.9 MHz; ¹⁹F, 235.3 MHz; ¹¹B, 80.3 MHz) in C₆D₆ and CD₂Cl₂ at 298 K unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards. The X-ray diffraction intensities were collected on an Oxford Xcalibur2 diffractometer with a Sapphire2 CCD. The crystal structures were solved by direct methods using SHELXS-97 and refined with SHELXL-97.⁴⁷ The crystals were coated with a perfluoropolyether, picked up with a glass fiber, and immediately mounted in the cooled nitrogen stream of the diffractometer. CCDC 679006 (**1**), 819987 (**2**), and 819988 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. FT-IR spectra were measured in an ATR setup with a Bruker Alpha FTIR spectrometer under inert atmosphere in a glovebox. Mass spectrometry was measured with a Jeol AccuTOF GCv; Ionization method: liquid injection field desorption ionization (LIFDI; special ionization cell obtained from Linden CMS GmbH, Leeste, Germany; <http://www.linden-cms.de>), solvents: toluene (**1** and **4**), CH₂Cl₂ (**2**), and thf (**3**).

Syntheses. $[\text{Mo}(\text{GaCp}^*)_6]$ (**1**). A sample of freshly prepared $[\text{Mo}(\eta^4\text{-C}_4\text{H}_6)_3]$ (0.300 g, 1.162 mmol) was introduced into a Fischer–Porter bottle and then dissolved in toluene (12 mL). After addition of GaCp* (1.666 g, 8.129 mmol) the reaction mixture was pressurized to 3 bar dihydrogen. The orange solution was warmed to 100 °C, whereupon a red microcrystalline precipitate was formed. After stirring for further 16 h at 80 °C the reaction mixture was transferred into a Schlenk tube. The red crystals were isolated by means of a cannula, washed with a small amount of *n*-hexane, and dried in vacuo. Recrystallization from mesitylene gave well formed dark red needle-shaped

single crystals. Yield: 0.785 g (51%). Anal. Calcd. for C₆₀H₉₀Ga₆Mo₁: C, 54.36; H, 6.84. Found: C, 53.86; H, 6.24. ¹H NMR $\delta_{\text{H}}(\text{C}_6\text{D}_6)$, 1.96 (s, 90H, C₅Me₅). ¹H NMR $\delta_{\text{H}}(\text{d}_8\text{-toluene})$, 1.95 (s, 90H, C₅Me₅). ¹H NMR $\delta_{\text{H}}(\text{d}_8\text{-thf})$, 1.99 (s, 90H, C₅Me₅). ¹³C{¹H} NMR $\delta_{\text{C}\{\text{H}\}}(\text{C}_6\text{D}_6)$, 117.11 (C₅Me₅), 11.91 (C₅Me₅). IR (ATR, cm^{−1}): 2943 (w), 2877 (m), 2829 (m), 2700 (w), 1478 (w), 1413 (m), 1363 (m), 1285 (w), 1011 (w), 934 (w), 789 (w), 723 (w), 639 (w), 587 (w), 414 (s). MS (LIFDI, toluene): *m/z* 1326 [M]⁺, 1190 [M − Cp*]⁺.

$[\text{Rh}(\text{GaCp}^*)_5][\text{CF}_3\text{SO}_3]$ (**2**). To a solution of $[\text{Rh}(\text{coe})_2(\text{CF}_3\text{SO}_3)]_2$ (0.200 g, 0.212 mmol) in fluorobenzene (5 mL) GaCp* (0.443 g, 2.162 mmol) was added. The reaction mixture was heated at 60 °C for 1 h, then the solvent was reduced in vacuo, the residue washed with *n*-hexane and dried in vacuo to give a red-purple solid. Recrystallization of the crude product by slow diffusion of *n*-hexane into a solution of **2** in fluorobenzene gave deep red single crystals. Yield: 0.435 g (81%). Anal. Calcd. for C₅₁H₇₅F₃S₁O₃Rh₁Ga₅: C, 48.11; H, 5.94; S, 2.51. Found: C, 47.73; H, 5.83; S, 2.43. ¹H NMR $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$, 1.91 (s, 75H, C₅Me₅). ¹H NMR $\delta_{\text{H}}(\text{d}_8\text{-thf})$, 1.90 (s, 75H, C₅Me₅). ¹H NMR $\delta_{\text{H}}(\text{d}_8\text{-thf})$, 1.89 (s, 75H, C₅Me₅). ¹³C{¹H} NMR $\delta_{\text{C}\{\text{H}\}}(\text{CD}_2\text{Cl}_2)$, 117.21 (C₅Me₅), 11.09 (C₅Me₅). ¹⁹F{¹H} NMR $\delta(\text{CD}_2\text{Cl}_2)$, −78.7 (s, SO₃SF₃). IR (ATR, cm^{−1}): 2938 (w), 2885 (w), 2834 (w), 1580 (w), 1482 (w), 1409 (w), 1373 (w), 1285 (w), 1219 (s), 1179 (m), 1112 (m), 973 (s), 792 (w), 748 (w), 705 (w), 679 (w), 524 (w), 582 (w), 513 (w), 461 (w), 413 (w). MS (LIFDI, CH₂Cl₂): *m/z* 788 [M − {(Cp*)₂Ga(CF₃SO₃)}]⁺, 373 [RhCp*₂]⁺.

$[\text{Rh}(\text{GaCp}^*)_5][\text{BAR}^{\text{F}}]$ (**3**). To a solution of **2** (0.120 g, 0.094 mmol) in CH₂Cl₂ (5 mL) NaBAR^F (0.105 g, 0.109 mmol) was added, and a further 5 mL of CH₂Cl₂ was added. The reaction mixture was stirred at room temperature for 45 min and filtered to remove the generated colorless NaOTf. The solution was concentrated approximately to 4 mL, and *n*-hexane (12 mL) added which results in the precipitation of an orange powder. The powder was isolated, the residue washed with *n*-hexane and dried in vacuo to give a slightly orange solid. Yield: 0.184 g (94%). Anal. Calcd. for C₈₈H₉₆F₂₄Rh₁Ga₅: C, 49.47; H, 4.40. Found: C, 47.40; H, 4.36 (for deviation of C value see explanation in the main text). ¹H NMR $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$, 1.91 (s, 75H, C₅Me₅), 7.56 (br, 4H, BAR^F), 7.72 (br, 8H, BAR^F). ¹H NMR $\delta_{\text{H}}(\text{CD}_2\text{Cl}_2)$, 1.83 (s, 75H, C₅Me₅), 7.53 (br, 4H, BAR^F), 7.72 (br, 8H, BAR^F). ¹³C{¹H} NMR $\delta_{\text{C}\{\text{H}\}}(\text{CD}_2\text{Cl}_2)$, 135.23 ppm (s, ortho CH, BAR^F), 128.99 (s, ipso to the CF₃ units, BAR^F), 125.03 (q, −CF₃, *J* = 272.3 Hz, BAR^F), 117.88 (s, para CH, BAR^F), 117.21 (C₅Me₅), 11.09 (C₅Me₅). ¹⁹F{¹H} NMR $\delta(\text{CD}_2\text{Cl}_2)$, −62.9 (s, CF₃). ¹¹B{¹H} NMR $\delta(\text{CD}_2\text{Cl}_2)$, −6.6 (s, BAR^F). IR (ATR, cm^{−1}): 2956 (w), 2895 (w), 2836 (w), 1597 (w), 1411 (w), 1375 (w), 1341 (m), 1264 (s), 1152 (w), 1114 (s), 939 (w), 878 (w), 831 (w), 792 (w), 738 (w), 707 (w), 676 (w), 663 (w), 585 (w), 444 (w). MS (LIFDI, THF): *m/z* 373 [RhCp*₂]⁺.

$[(\text{coe})(\text{toluene})\text{Rh}(\text{GaDDP})(\text{CF}_3\text{SO}_3)]$ (**4**). $[\text{Rh}(\text{coe})_2(\text{CF}_3\text{SO}_3)]_2$ (0.150 g, 0.159 mmol) and Ga(DDP) (0.162 g, 0.334 mmol) in fluorobenzene (5 mL) were stirred at 50 °C for 2 h. The solvent was reduced in vacuo, the residue washed with *n*-hexane and dried in vacuo to give a yellow solid. Recrystallization of the crude product by cooling a saturated toluene solution of **3** to −30 °C gave yellow single crystals. Yield: 0.145 g (98%). Anal. Calcd. for C₄₅H₆₃F₃S₁O₃N₂Rh₁Ga: C, 57.40; H, 6.74; N, 2.97; S, 3.41. Found: C, 58.12; H, 6.32; N, 3.22; S, 3.32. ¹H NMR $\delta_{\text{H}}(\text{C}_6\text{D}_6)$, 6.99–7.15 (m, 11H, aryl DDP and C₆H₅CH₃), 5.20 (s, 1H, γ-CH), 3.48 (m, 4H, CH(Me)₂), 2.79 (m, 2H, COE), 2.10 (s, 3H, C₆H₅CH₃), 1.69 (s, 6H, CH₃ groups, DDP), 1.48–0.92 (m, 36H, CH(Me)₂ and COE). ¹³C{¹H} NMR $\delta_{\text{C}\{\text{H}\}}(\text{C}_6\text{D}_6)$, 168.60 (CN), 143.35 (ar), 137.90 (C1, toluene), 129.30 (CH 2,6; toluene) 127.39 (CH 3,5; toluene), 126.97 (ar), 125.66 (CH 4; toluene), 124.43 (ar), 100.62 (γ-C), 57.16 (d, C=C, *J*_{Rh–C} = 14.1 Hz), 34.90 (coe), 32.40 (coe), 26.46, 25.27 (coe), 24.40, 21.48 (CH₃, toluene) (Note: not all carbon signals of the DDP unit could be observed because of low scan number measurement). ¹⁹F{¹H} NMR $\delta(\text{C}_6\text{D}_6)$, −77.1 (s, SO₃CF₃).

IR (ATR, cm^{-1}): 2934 (w), 2902 (w), 2841 (w), 2820 (w), 2020 (w), 1540 (w), 1502 (w), 1449 (w), 1424 (w), 1377 (m), 1349 (w), 1333 (w), 1296 (w), 1276 (w), 1245 (w), 1222 (m), 1191 (m), 1156 (m), 1089 (w), 1047 (w), 1003 (m), 930 (w), 896 (w), 873 (w), 852 (w), 827 (w), 789 (w), 773 (w), 753 (w), 718 (w), 701 (w), 686 (w), 621 (m), 576 (w), 562 (w), 538 (w), 514 (w), 502 (w), 458 (w), 434 (w). MS (LIFDI, toluene): m/z 940 $[\text{M}]^+$, 830 $[\text{M} - \text{coe}]^+$, 791 $[\text{M} - \text{CF}_3\text{SO}_3]^+$.

■ ASSOCIATED CONTENT

S Supporting Information. Crystallographic data in CIF format. Further details are given in Figures S1–S8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

[†]Organo group 13 complexes of transition metals LVIII; for communication LVII see ref 32.

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■ REFERENCES

- (1) Gemel, C.; Steinke, T.; Cokoja, M.; Kempter, A.; Fischer, R. A. *Eur. J. Inorg. Chem.* **2004**, 4161–4176.
- (2) Anderson, C. E.; Braunschweig, H.; Dewhurst, R. D. *Organometallics* **2008**, 27, 6381–6389.
- (3) Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, 111, 354–396.
- (4) Braunschweig, H.; Gruss, K.; Radacki, K. *Inorg. Chem.* **2008**, 47, 8595–8597.
- (5) Coombs, N. D.; Clegg, W.; Thompson, A. L.; Willock, D. J.; Aldridge, S. J. *Am. Chem. Soc.* **2008**, 130, 5449–5451.
- (6) Dohmeier, C.; Loos, D.; Schnoekel, H. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 129–49.
- (7) Kuchta, M. C.; Bonanno, J. B.; Parkin, G. J. *Am. Chem. Soc.* **1996**, 118, 10914–10915.
- (8) Linti, G.; Schnoekel, H. *Coord. Chem. Rev.* **2000**, 206–207, 285–319.
- (9) Roesky, P. W. *Dalton Trans.* **2009**, 1887–1893.
- (10) Uddin, J.; Frenking, G. *J. Am. Chem. Soc.* **2001**, 123, 1683–1693.
- (11) Uddin, J.; Boehme, C.; Frenking, G. *Organometallics* **2000**, 19, 571–582.
- (12) Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H.-G. *Organometallics* **1998**, 17, 1305–1314.
- (13) Jutzi, P.; Neumann, B.; Schebaum, L. O.; Stammler, A.; Stammler, H.-G. *Organometallics* **1999**, 18, 4462–4464.
- (14) Gemel, C.; Steinke, T.; Weiss, D.; Cokoja, M.; Winter, M.; Fischer, R. A. *Organometallics* **2003**, 22, 2705–2710.
- (15) Bollermann, T.; Puls, A.; Gemel, C.; Cadenbach, T.; Fischer, R. A. *Dalton Trans.* **2009**, 1372–1377.
- (16) Steinke, T.; Gemel, C.; Winter, M.; Fischer, R. A. *Chem.—Eur. J.* **2005**, 11, 1636–1646.
- (17) Bollermann, T.; Prabusankar, G.; Gemel, C.; Seidel, R. W.; Winter, M.; Fischer, R. A. *Chem.—Eur. J.* **2010**, 16, 8846–8853.
- (18) Lee, G. R.; Maher, J. M.; Cooper, N. J. *J. Am. Chem. Soc.* **1987**, 109, 2956–62.
- (19) Bernhardt, E.; Finze, M.; Willner, H.; Lehmann, C. W.; Aubke, F. *Angew. Chem., Int. Ed.* **2003**, 42, 2077–2079.
- (20) Bernhardt, E.; Finze, M.; Willner, H.; Lehmann, C. W.; Aubke, F. *Chem.—Eur. J.* **2006**, 12, 8276–8283.
- (21) Ricks, A. M.; Bakker, J. M.; Douberly, G. E.; Duncan, M. A. *J. Phys. Chem. A* **2009**, 113, 4701–4708.
- (22) Cadenbach, T.; Gemel, C.; Bollermann, T.; Fischer, R. A. *Inorg. Chem.* **2009**, 48, 5021–5026.
- (23) Steinke, T.; Cokoja, M.; Gemel, C.; Kempter, A.; Krapp, A.; Frenking, G.; Zenneck, U.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2005**, 44, 2943–2946.
- (24) Cadenbach, T.; Gemel, C.; Zacher, D.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2008**, 47, 3438–3441.
- (25) Cadenbach, T.; Bollermann, T.; Gemel, C.; Fernandez, I.; von Hopffgarten, M.; Frenking, G.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2008**, 47, 9150–9154.
- (26) Gausing, W.; Wilke, G. *Angew. Chem.* **1981**, 93, 201–2.
- (27) Pomije, M. K.; Kurth, C. J.; Ellis, J. E.; Barybin, M. V. *Organometallics* **1997**, 16, 3582–3587.
- (28) Drew, M. G. B. *Coord. Chem. Rev.* **1977**, 24, 179–275.
- (29) Cirera, J.; Ruiz, E.; Alvarez, S. *Organometallics* **2005**, 24, 1556–1562.
- (30) Cokoja, M.; Steinke, T.; Gemel, C.; Welzel, T.; Winter, M.; Merz, K.; Fischer, R. A. *J. Organomet. Chem.* **2003**, 684, 277–286.
- (31) Loos, D.; Baum, E.; Ecker, A.; Schnoekel, H.; Downs, A. J. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 860–862.
- (32) Buchin, B.; Gemel, C.; Cadenbach, T.; I. Fernández, I.; G. Frenking, G.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2006**, 45, 8097–8099.
- (33) Lawrance, G. A. *Chem. Rev.* **1986**, 86, 17–33.
- (34) Cadenbach, T.; Gemel, C.; Schmid, R.; Block, S.; Fischer, R. A. *Dalton Trans* **2004**, 3171–3172.
- (35) Linti, G.; Seifert, A. Z. *Inorg. Allg. Chem.* **2008**, 634, 1312–1320.
- (36) Cowley, A. H.; Gabbaie, F. P.; Atwood, D. A.; Carrano, C. J.; Mokry, L. M.; Bond, M. R. *J. Am. Chem. Soc.* **1994**, 116, 1559–60.
- (37) Prabusankar, G.; Gemel, C.; Parameswaran, P.; Flener, C.; Frenking, G.; Fischer, R. A. *Angew. Chem., Int. Ed.* **2009**, 48, 5526–5529.
- (38) DiPasquale, A. G.; Mayer, J. M. J. *Am. Chem. Soc.* **2008**, 130, 1812–1813.
- (39) Neumann, E.; Pfaltz, A. *Organometallics* **2005**, 24, 2008–2011.
- (40) Kempter, A.; Gemel, C.; Fischer, R. A. *Chem.—Eur. J.* **2007**, 13, 2990–3000.
- (41) Kempter, A.; Gemel, C.; Hardman, N. J.; Fischer, R. A. *Inorg. Chem.* **2006**, 45, 3133–3138.
- (42) Green, S. P.; Jones, C.; Mills, D. P.; Stasch, A. *Organometallics* **2007**, 26, 3424–3430.
- (43) Werner, H.; Bosch, M.; Schneider, M. E.; Hahn, C.; Kukla, F.; Manger, M.; Windmuller, B.; Weberndorfer, B.; Laubender, M. J. *Chem. Soc., Dalton Trans.* **1998**, 3549–3558.
- (44) Jutzi, P.; Schebaum, L. O. *J. Organomet. Chem.* **2002**, 654, 176–179.
- (45) Hardman, N. J.; Eichler, B. E.; Power, P. P. *Chem. Commun.* **2000**, 1991–1992.
- (46) Reger, D. L.; Wright, T. D.; Little, C. A.; Lamba, J. J. S.; Smith, M. D. *Inorg. Chem.* **2001**, 40, 3810–3814.
- (47) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, A64, 112–122.