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Coordination Chemistry of $Ga(C_5Me_4Ph)$: Novel Homoleptic d^{10} Cluster Complexes of Palladium†

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The synthesis and characterization of the novel sterically encumbered Ga(I) ligand $GaCp^{*Ph}$ (1b) ($Cp^{*Ph} = C_5Me_4Ph$) is presented. $GaCp^{*Ph}$ reacts with the Pd(0) source $Pd_2(dvds)_3$ (dvds = tetramethyldivinyldisiloxane) to give the trinuclear cluster $[Pd_3(GaCp^{*Ph})(\mu^2\text{-}GaCp^{*Ph})(\mu^3\text{-}GaCp^{*Ph})_2(dvds)]$ (**2a**). **2a** is the first example of a Ga(I)-containing cluster with a potentially labile olefinic ligand. It was found that **2a** is an intermediate in the formation of the dinuclear cluster $[Pd_2(GaCp^{*Ph})_2(\mu^2\text{-}GaCp^{*Ph})_3]$ (**2b**), which is formed on reaction of **2a** with $GaCp^{*Ph}$. Both clusters were found to be labile toward GaCp*, AlCp*, or phosphines, giving substitution products in all cases.

Introduction

Since the discovery of the low-valent group 13 element compounds AlCp*[1] and GaCp*[2,3] and the development of convenient laboratory syntheses,[4,5] their coordination chemistry has been studied in some detail.[6] Especially the d^{10} metal centers Ni, Pd, and Pt have been studied intensively, with the main focus being the mononuclear complexes of the type $[M(ECp^*)_4]$.[7−10] Beyond the investigation of the structural and bonding situation involving the M-ECp* moiety, we have demonstrated more recently that coordinatively unsaturated fragmenents such as $[Ni(AlCp^*)_3]$ exhibit interesting reactivity and are able to activate the sp^2 C−H bonds of benzene and Si−H bonds of organosilanes. The instability of $[M(AlCp^*)_5]$ (M = Fe, Ru) has been discussed as a consequence of sp^3 C−H activation of the methyl groups of Cp* at the electrophilic aluminum centers of the intermediate $[M(AlCp^*)_n]$ ($n < 5$) to yield stable isomers of the parent $[M(AlCp^*)_5]$ with two and even three activated CH_3 groups and H-bridged M−Al bonds.[11] Last but not least, we should mention the most unusual rearrangement of $[Cp(CH_3)_2RhGaCp^*]$ into the zwitterionic complex $[CpRh\{\eta^5\text{-}C_5H_4(Ga(CH_3)_3)\}]$, which involves C−C bond cleavage at the electrophilic Ga center.[12,13] These findings point to the unique potential of the electrophilic main-group metal ligands ECp* in typical organometallic reactions, e.g., bond activation of small molecules. Depending on a delicate choice of precursors and reaction conditions, one can form not only monomeric systems such as $[M(ECp^*)_n]$ but also oligonuclear homoleptic cluster compounds $[M_a(ECp^*)_b]$ (M = Ni, Pd, Pt) showing fluxional behavior and an increased reactivity toward ligand substitution as compared to their mononuclear congeners.[14,15] Key questions of the chemistry of those oligonuclear compounds include: What ranges of M, E, a, and b of such compounds are accessible in preparative yields? Will it be possible to derive even giant clusters $[M_a(ECp^*)_b]$ with $a > b \gg 1$, e.g., a core cluster of M_a stabilized by a shell of

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surface-bound ECp* ligands, similar to Schnöckel's metalloid aluminum cluster [$Al_{50}Cp^*_{12}$][16] but with a core of transition-metal atoms? Will it be possible to tune the oligonuclear clusters [$M_a(ECp^*)_b$] toward interesting bond activation and coupling reactions?

A general concept to systematically address the above questions is based on a variation of the cone angle of the low-valent group 13 ligands ER (R = organic moiety). Sterically demanding ligands ER should be able to stabilize low-coordinated transition-metal fragments and thus allow the study of their reactivity toward small molecules in more detail. Furthermore, the M/E ratio of cluster compounds [$M_a(ER)_b$] is likely to change in favor of the transition metal M and, thus, is thought to allow the formation of compounds with larger cluster cores M_a. Consequently, we have recently started to study the coordination chemistry of the bulky gallium(I) bisimidinate Ga(DDP) {DDP = 2-(2,6-diisopropylphenyl)amino-4-[(2,6-diisopropylphenyl)imino]-2-pentene}[17] in comparison to that of GaCp*.[18] It has been shown that Ga(DDP) is a suitable ligand for a variety of transition metals, e.g., we communicated some novel Au−Ga complexes in this journal. Low-coordinated transition-metal centers (Ni, Pd, Pt, Rh) and mononuclear sructures are a common feature of all complexes of Ga(DDP) that we have isolated and studied so far and on which subject we will report in detail elsewhere soon.[19] However, the reactivity and coordination properties of Ga(DDP) are rather different from those of GaCp*. The electronic properties of the sp^2-hybridized Ga(DDP) are determined by the weak Ga−N π-bonding and charge donation to the Ga center. Thus, one remarkable difference is the reactivity of the oxidized species $Ga(DDP)Cl_2$, which is much less Lewis acidic than its counterpart $GaCp^*Cl_2$, having a large effect on the insertion chemistry of the ligands in transition-metal halogenides.

Fine-tuning the steric situation at the group 13 ligand ER without changing the electronic situation of the M−E bond too much appears to be crucial for the goal of the synthesis of clusters [$M_a(ER)_b$]. We were thus led to introduce substituted Cp* groups: C_5Me_4R' (R′ = Ph, *t*-Bu, $SiMe_3$, etc.), in particular $C_5Me_4R' = Cp^{*Ph}$ (R′ = Ph). Recently, we reported on the synthesis and characterization of the novel Al(I) compound $AlCp^{*Ph}$ ($Cp^{*Ph} = C_5Me_4Ph$), which has been shown to react with d^{10} M(0) sources such as $M(COD)_2$ (M = Ni, Pt; COD = 1,5-cyclooctadiene).[20] Indeed, monomers of the type [$M(AlCp^{*Ph})_4$] could be neither spectroscopically observed nor isolated. Herein, we now present our studies on the coordination chemistry of $GaCp^{*Ph}$ as a sterically slightly more demanding derivative of the GaCp* ligand family. In particular, the formation of mononuclear compounds [$M(ER)_4$] was found to be suppressed by the introduction of a phenyl group in the place of a methyl group. In fact, $GaCp^{*Ph}$ shows a rich cluster chemistry as demonstrated by the first isolated and structurally characterized cluster [$M_3(ECp^{*Ph})_4(dvds)$] (dvds = tetramethyldivinyldisiloxane) with potentially labile olefinic co-ligands.

Results and Discussion

Preparation and Characterization of $GaCp^{*Ph}$ (1b). The preparation of $GaCp^{*Ph}$ (**1b**) was carried out analogously to the published procedure for GaCp*.[21] GaI ("Green's GaI") is synthesized in situ from gallium and iodine in benzene by ultrasonic sonification, giving "GaI" as a pale green solid.[22] Subsequent addition of the potassium salt of tetramethylphenyl cyclopentadiene (**1a**) gives a slightly yellow solution and a light gray precipitate. After filtration and removal of the solvent in vacuo, **1b** is obtained as a pure orange liquid by vacuum distillation of the oily crude residue (10^{-2} Torr, 120 °C) in reproducible yields of around 60% based on gallium.

The ^1H NMR spectrum of **1b** in C_6D_6 at room temperature exhibits two singlet resonances at 1.93 and 2.00 ppm for the chemically inequivalent CH_3 groups, as well as a multiplet for the aromatic C_6H_5 protons. The ^{13}C NMR spectrum measured under the same conditions expectedly gives rise to two sets of signals for the C_5Me_4 moiety (10.0 and 10.7 and 126.3, 114.1, and 114.4 ppm) and four signals for the C_6H_5 group (128.1, 128.5, 131.4, and 136.7 ppm).

Reaction of [$Pd_2(dvds)_3$] with $GaCp^{*Ph}$. As previously reported, the reaction of [$Pd_2(dvds)_3$] with excess of GaCp* (dvds = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane) is very sensitive to the reaction conditions. At low temperatures of −30 °C in hexane, the dinuclear compound [$Pd_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3$] is quantitatively obtained, whereas reaction at room temperature in toluene leads to the trinuclear cluster [$Pd_3(GaCp^*)_8$] in high yields.[15] In contrast, the reaction of [$Pd_2(dvds)_3$] with an excess of the phenyl derivative $GaCp^{*Ph}$ in hexane at −30 °C gives a mixture of the Pd_2Ga_5 complex [$Pd_2(GaCp^{*Ph})_2(\mu^2\text{-}GaCp^{*Ph})_3$] (**2b**) and the novel trinuclear Pd_3Ga_4 complex [$Pd_3(GaCp^{*Ph})(\mu^2\text{-}GaCp^{*Ph})(\mu^3\text{-}GaCp^{*Ph})_2(dvds)$] (**2a**). The two compounds crystallize from the reaction mixture (hexane) as yellow (**2b**) and orange (**2a**) single crystals. Interestingly, changing the stoichiometry of the reactants did not alter the composition of the product mixture. However, variation of the reaction time led to a variation of the product ratio, with **2a** being more abundant at shorter reaction times of typically a few minutes. In addition, as **2a** and **2b** exhibit different ratios M/E (3:4 for **2a** and 2:5 for **2b**), it is reasonable to assume that **2a** represents an intermediate on the path to the formation of **2b**. Indeed, it is possible to synthesize **2a** quantitatively from [$Pd_2(dvds)_3$] and the *exact* stoichiometric amount of $GaCp^{*Ph}$ in the presence of an *excess* of dvds in hexane at room temperature according to Scheme 1. The dinuclear complex **2b** can then be prepared quantitatively upon reaction of **2a** with excess of $GaCp^{*Ph}$. It should be pointed out here that

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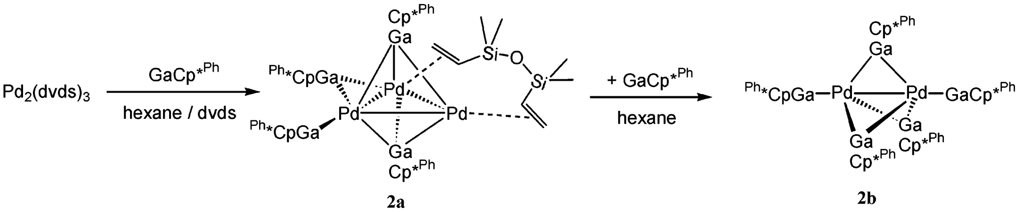
Scheme 1. Reaction of [Pd_2(dvds)$_3$] with GaCp*^{Ph}



2a or a related structure with a Pd_3 triangle bridged by GaCp* units, e.g., [Pd_3(GaCp*)$_n$] (n = 5, 6, etc.), has never been observed in such reactions. However, in the case of AlCp*, we isolated the related cluster [Pd_3(AlCp*)$_6$].[15] Compound **2b** proved to be stable in the presence of excess GaCp*^{Ph} under all conditions with respect to the formation of [Pd(GaCp*^{Ph})$_4$].

Both title complexes **2a** and **2b** are weakly soluble in *n*-hexane but dissolve well in aromatic hydrocarbons such as benzene or toluene. They are highly air-sensitive, but stable at room temperature in the solid state when stored under an inert gas atmosphere. The ^1H NMR spectrum of **2a** at room temperature in C_6D_6 shows six singlets [δ (ppm) = 2.12 (s, 6H), 2.09 (s, 12H), 2.06 (s, 6H), 1.95, (s, 6H), 1.94 (s, 12H), 1.90 (s, 6H)], i.e., two resonances for the methyl ligands of each chemically inequivalent GaCp*^{Ph} ligand, which points to three different Cp*^{Ph}Ga ligands in a ratio of 1:1:2. Furthermore, a complex multiplet at 4.60−4.10 ppm (6H) reveals the presence of one coordinated dvds ligand. The ^1H NMR spectrum of **2b** at room temperature in C_6D_6 exhibits only two signals for the methyl groups of the GaCp*^{Ph} at 1.98 ppm (30H) and 1.90 ppm (30H) and a multiplet for the phenyl group at 7.50−7.19 ppm (25H). Thus, in contrast to **2a**, complex **2b** is fluxional in solution, as has also been described for the parent cluster [Pd_2(GaCp*)$_5$]. The fluxional process of this latter complex involves the exchange of the terminal and bridging ligands and has been recently studied in more detail.[15] We suggest that the situation is quite similar for **2b**. As monitored by ^1H NMR spectroscopy, heating a solution of the Pd_3Ga_4 cluster **2a** in benzene leads to decomposition, giving the spectroscopically clean Pd_2Ga_5 cluster **2b**. Precipitation of a black solid indicates the formation of palladium metal in the course of this remarkably selective thermolysis reaction. Because of this thermal decomposition reaction, no assignable ^{13}C NMR spectrum of **2a** could be obtained. Despite several attempts, also no correct elemental analysis of **2a** could be obtained. However, the X-ray crystal structure together with the ^1H NMR spectrum is certainly sufficient to confirm the molecular structure of **2a** in the solid state and in solution.

The molecular structures of **2a** and **2b** were finally elucidated by X-ray crystallography. Complex **2a** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of **2a** is depicted in Figure 1 and consists of a triangular Pd_3 core coordinated by two axial μ^3-bridging and two equatorial Cp*^{Ph}Ga ligands (one terminal and one μ^2-bridging). Additionally, one dvds ligand occupies the vacant equatorial coordination sites of two palladium centers.

The Pd−Pd distances vary in the range between 2.591(1) and 2.841(1) Å, because of their rather different coordination environments: Pd(1) is coordinated by one terminal, one μ^2-, and two μ^3-bridging Cp*^{Ph}Ga ligands, and Pd(2) is coordinated by one μ^2- and two μ^3-bridging Cp*^{Ph}Ga ligands, and additionally by one alkene double bond of the dvds moiety, whereas Pd(3) is coordinated by only two μ^3-bridging Cp*^{Ph}Ga ligands and the second double bond of the dvds ligand. The Pd(1)−Pd(2) bond (2.591(1) Å) is the shortest, obviously because of the presence of an edge-bridging GaCp*^{Ph} ligand. In contrast, the Pd(2)−Pd(3) bond, at 2.841(1) Å, is rather long but still considerably shorter than that in the related triangular cluster [Pd_3(AlCp*)$_6$],[15] which is presumably a result of the bridging dvds ligand. However, the distance of 2.841(1) Å is close to the Pd−Pd separation in the linear trinuclear complex [Pd_3(GaCp*)$_8$] [2.843(5) Å], which is regarded as bonding, whereas the longest Pd−Pd distance in [Pd_3(AlCp*)$_6$] (3.619(2) Å) must be regarded as nonbonding.[15] The rather symmetric triangular structure of the cluster core is also reflected by the bond angles for the Pd_3 core in **2a**, which are all very similar and lie between 54.94(2)° and 63.85(2)°. As expected, the Pd−Ga distance for the terminal ligand is the shortest (2.367(1) Å), while all other Pd−Ga distances vary between 2.490(1) and 2.657(1) Å. No obvious correlation between the bridging modes and the Pd−Ga distances is observed.

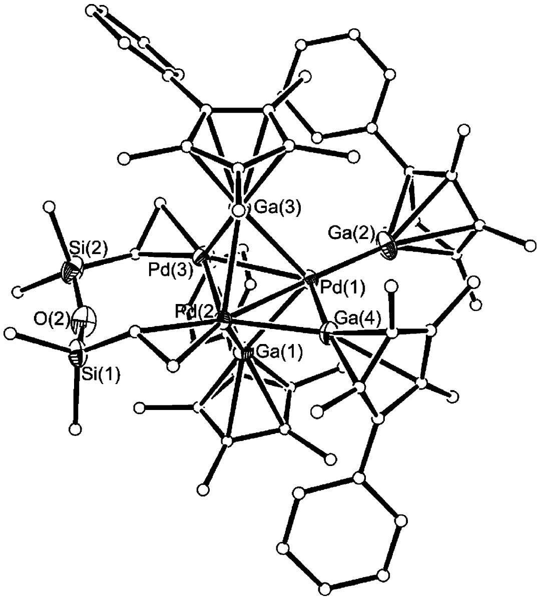


Figure 1. Molecular structure of [Pd_3(GaCp*^{Ph})(μ^2-GaCp*^{Ph})(μ^3-GaCp*^{Ph})$_2$-(dvds)] (**2a**) in the solid state (ORTEP drawing; 50% level of probability for the metal atoms; carbon atoms displayed as spheres for clarity). Selected bond lengths (Å): Pd(1)−Pd(2) 2.591(1), Pd(2)−Pd(3) 2.841(1), Pd(1)−Pd(3) 2.774(1), Pd(1)−Ga(1) 2.566(1), Pd(1)−Ga(2) 2.367(1), Pd(1)−Ga(3) 2.530(1), Pd(1)−Ga(4) 2.464(1), Pd(2)−Ga(1) 2.591(1), Pd(2)−Ga(3) 2.657(1), Pd(2)−Ga(4) 2.549(1), Pd(3)−Ga(1) 2.490(1), Pd(3)−Ga(3) 2.456(1).

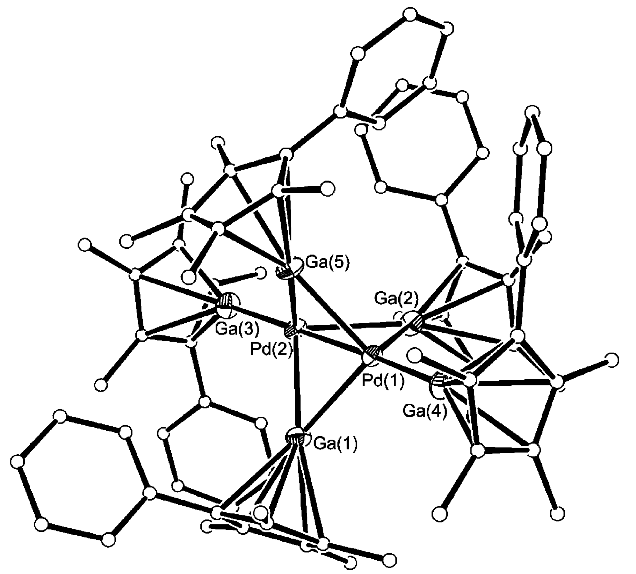


Figure 2. Molecular structure of $[Pd_2(GaCp^{*Ph})_2(\mu^2\text{-}GaCp^{*Ph})_3]$ (**2b**) in the solid state (ORTEP drawing; 50% level of probability for the metal atoms; carbon atoms displayed as spheres for clarity). Selected bond lengths (Å): Pd(1)−Pd(2) 2.572(10), Pd(1)−Ga(4) 2.336(13), Pd(1)−Ga(1) 2.479(1), Pd(1)−Ga(2) 2.467(1), Pd(1)−Ga(5) 2.465(1), Pd(2)−Ga(3) 2.338(1), Pd(2)−Ga(1) 2.468(1), Pd(2)−Ga(2) 2.493(1), Pd(2)−Ga(5) 2.491(1).

The C=C double bonds of the coordinated diene moiety in **2a** are very slightly elongated (mean = 1.38 Å) compared to uncoordinated C=C bonds (1.34 Å), indicating only a weak π-back-bonding from the Pd(0) center to the alkene ligands. Virtually the same situation was described in the complex $[Pd(PMe_3)(\eta^2,\eta^2\text{-}C_6H_{10}O)]$.[23] It should be mentioned that the free ligand $GaCp^{*Ph}$ (**1b**) has not been characterized by an X-ray crystal structure analysis so far, and a discussion of the Ga−C bond lengths of its complexes **2a** and **2b** is therefore difficult.

Complex **2b** crystallizes in the triclinic space group $P\bar{1}$ and is almost isostructural with $[Pd_2(GaCp^*)_5]$, exhibiting only small deviations in the geometrical parameters because of the presence of the phenyl groups.[15] The molecular structure of **2b** is shown in Figure 2 and consists of a central unit of two palladium atoms with a rather short Pd−Pd bond of 2.572(1) Å, compared to 2.609(1) Å in $[Pd_2(GaCp^*)_5]$. The Pd_2 unit of **2b** is surrounded by two terminal and three bridging $Cp^{*Ph}Ga$ ligands. The terminal Pd−Ga bond distances in **2b** of 2.336(1) and 2.338(1) Å are somewhat shorter than those in $[Pd_2(GaCp^*)_5]$ (2.358(1) and 2.362(1) Å). The bridging Cp*Ga units have values in the range of 2.465(1)−2.493(1) Å. The average values for the Ga−$Cp^{*Ph}_{Centr.}$ distance are, at 1.998 Å for the terminal and 2.023 Å for the bridging $GaCp^{*Ph}$ ligands, only slightly shorter than the average values in $[Pd_2(GaCp^*)_5]$ (1.999 Å for the terminal and 2.048 Å for the bridging ligands).

Reactions of $Ni(COD)_2$ with $GaCp^{*Ph}$. Recall that activation reactions at low-coordinated, reactive fragments $[Ni(AlCp^*)_n]$ ($n < 4$) are possible.[24] Thus, treatment of $[Ni(COD)_2]$ with AlCp* in hexane leads to the formation of $[Ni(AlCp^*)_4]$, but in benzene, C−H activation of the solvent is observed, giving $[Ni(AlCp^*)_3\{AlCp^*(Ph)\}(H)]$. In contrast, the reaction of $[Ni(COD)_2]$ with GaCp* yields only $[Ni(GaCp^*)_4]$ regardless of which solvent is used. Particularly, in the gallium case, bond activation reactions were not observed. A possible explanation for this result involves the solubility of the ligands: That is, AlCp* is only poorly soluble in organic solvents, and its concentration is very low throughout the whole reaction. Hence, intermediates $[Ni(AlCp^*)_n]$ ($n < 4$) are more likely to be generated. In contrast, GaCp* is highly soluble, and thus, reactive intermediates are not formed or are very short-lived. In the hope that the increased steric bulk of $GaCp^{*Ph}$ might favor the formation of low-coordinated intermediates of the kind $[Ni(GaCp^{*Ph})_3]$, we treated $[Ni(COD)_2]$ with $GaCp^{*Ph}$. Reaction of $[Ni(COD)_2]$ with $GaCp^{*Ph}$ in hexane resulted in a brown solution, from which only $[Ni(COD)_2]$ could be reisolated, however. Also, in the presence of phosphines or other co-reactants (such as benzene or organosilanes), defined reactions to yield new products were not observed. Recently, we reported on similar observations in the reaction of $[Ni(COD)_2]$ with $AlCp^{*Ph}$, which lead to unidentifiable product mixtures under all conditions. The reason for the apparent inertness of $[Ni(COD)_2]$ with respect to the phenyl-substituted ligand $GaCp^{*Ph}$ in terms of isolable products probably lies in the fact that the steric demand of $GaCp^{*Ph}$ does not allow the coordination of four ligands to one metal center, and thus, the substitution of the four olefinic ligands in $[Ni(COD)_2]$ becomes thermodynamically unfavorable. In other words, COD effectively competes with $GaCp^{*Ph}$, leading to the thermodynamic product upon crystallization: $[Ni(COD)]_2$. Investigations of the substitution chemistry of potentially more reactive Ni(0) sources such as the labile [Ni(CDT)] (CDT = *t*,*t*,*t*-1,5,9-cyclododecatriene) and even $[Ni(C_2H_4)_3]$ featuring less-competing alkene ligands is the subject of current research.

Ligand-Exchange Reactions at 2a and 2b. As recently shown, electronically and sterically unsaturated complexes $[M_a(GaCp^*)_b]$ react with a wide variety of ligands to yield substitution products. Thus, substitution of coordinated GaCp* in $[M_2(GaCp^*)_5]$ by AlCp*, PPh_3, CO, or isonitriles (*t*-BuNC) is favorable, as in all reactions, partial or full ligand exchange was observed. It was shown that π-acceptor ligands prefer a terminal position in the dinuclear products, whereas remaining GaCp* ligands are found in bridging positions. In addition, AlCp* substitutes GaCp* preferring the bridging position, as shown by the compound $[(Cp^*Ga)Pd(\mu^2\text{-}AlCp^*)_3\text{-}Pd(GaCp^*)]$.[15] Scheme 2 provides an overview of ligand-substitution reactions of complex **2a**. Treatment of **2a** with AlCp* in toluene leads to quantitative substitution of $GaCp^{*Ph}$ and dvds and the formation of the trinuclear complex $[Pd_3(AlCp^*)_6]$. After gentle heating of a mixture of the two starting materials in toluene, immediate precipitation of dark red microcrystals is observed, which are identified by NMR spectroscopic analysis as the known cluster $[Pd_3(AlCp^*)_6]$. Similarly, treatment of **2a** with stoichiometric GaCp* in toluene at room temperature leads to

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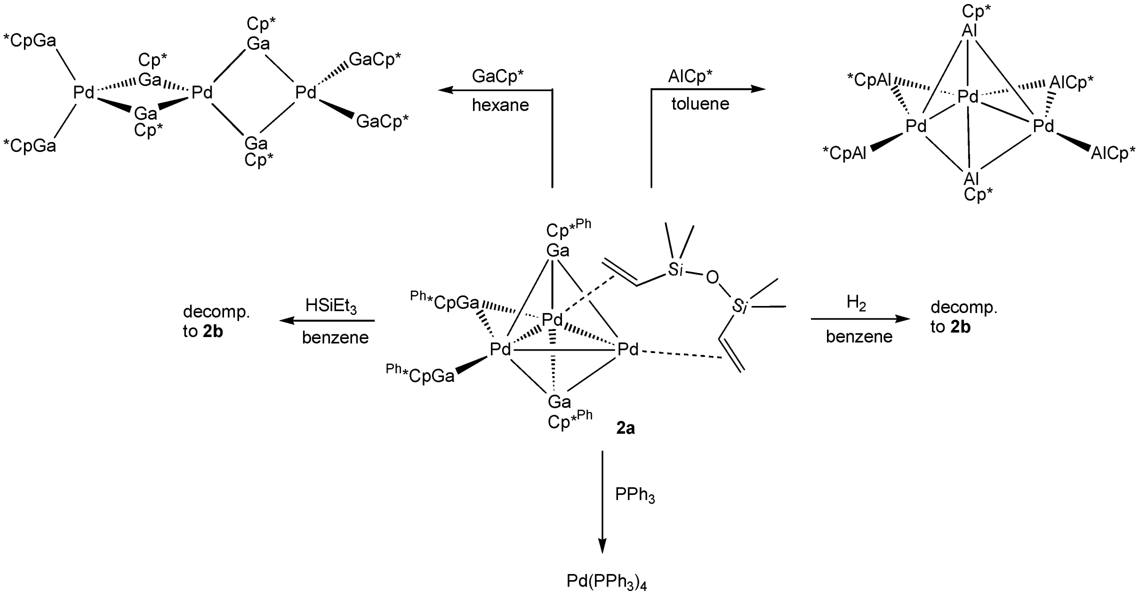
Scheme 2. Ligand-Exchange Reactions of $Pd_3(dvds)(GaCp^{*Ph})_4$



the formation of the known linear Pd_3Ga_8 cluster $[Pd_3(GaCp^*)_8]$ as shown by ^1H NMR spectroscopy.[15]

The reaction of **2a** with excess of PPh_3 in C_6D_6 at room temperature leads to a mixture of $GaCp^{*Ph}$ and PPh_3-containing species, as indicated by ^1H and ^{31}P NMR spectroscopy. However, isolation and identification of pure products were not successful. Heating the solution to 80 °C even for a short time leads to the loss of all $GaCp^{*Ph}$ ligands and formation of the homoleptic phosphine complex $[Pd(PPh_3)_4]$. Variation of the amount of PPh_3 in this reaction does also not lead to defined mixed-ligand cluster complexes. Apparently, the choice of the phospine ligand plays an important role. **2a** does not undergo selective activation reactions with $HSiEt_3$ or H_2. Instead, the formation of **2b** was observed in both reactions.

As indicated by ^1H NMR spectroscopy, substitution of the $GaCp^{*Ph}$ ligand in **2b** with AlCp* and GaCp* yields the compound $[Pd_2(ECp^*)_5]$ (E = Al, Ga).

Conclusions and Outlook

In this article, we have presented the preparation and characterization of new d^{10} cluster complexes of palladium using the novel compound $GaCp^{*Ph}$ as a stabilizing ligand. The higher cone angle of $GaCp^{*Ph}$ compared to GaCp* does indeed inhibit the coordination of four ligands to one transition-metal center; thus, di- and trinuclear cluster complexes are the preferred products. The novel trinuclear Pd_3Ga_4 cluster **2a** was isolated and characterized as an intermediate in the formation of the dinuclear Pd_2Ga_5 cluster **2b**. Compound **2a** is the first example of a trinuclear Pd/Ga cluster coordinated by a potentially substitution-labile olefinic ligand. However, all attempts to selectively substitute only these olefinic groups by other ligands such as ECp* (E = Al, Ga), PPh_3, H_2, or $HSiEt_3$ lead either to full substitution of all of the $GaCp^{*Ph}$ ligands or to a thermal decomposition of **2a** giving **2b**. $Ni(COD)_2$ proved to be inert toward $GaCp^{*Ph}$, as the substitution of four olefinic ligands by three $GaCp^{*Ph}$ ligands is obviously unfavorable in the case of Ni(0). Taking all of the results above together, it is clear that the concept of slightly increasing the steric bulk of ECp*-type ligands, the title ligand $GaCp^{*Ph}$ being an example, holds promise for further success in line with the goal of the synthesis of transition-metal-rich oligonuclear clusters of the type $[M_a(ER)_b]$. A delicate balance of ligand properties, transition-metal precursors, and reaction conditions appears to be important for the synthetic success. Exactly this complex situation seems to offer rich opportunities for unusual further discoveries in this chemistry.

Experimental Section

All manipulations were carried out in an atmosphere of purified argon using standard Schlenk and glovebox techniques. Hexane, toluene, THF, and Et_2O were dried using an mBraun Solvent Purification System; all other solvents were dried by distillation over standard drying agents. The final H_2O content in all solvents used was checked by Karl Fischer titration and did not exceed 5 ppm. $[C_5Me_4PhH]$,[25] $[Pd_2(dvds)_3]$,[26] AlCp*,[27] and GaCp*[21] were prepared according to recent literature methods. Elemental analyses were performed by the Microanalytical Laboratory of the Ruhr-Universität Bochum. Melting or decomposition points were determined thermogravimetrically on a Seiko EXSTAR 6300S11 TG/DTA instrument. NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer (^1H, 250.1 MHz; ^{13}C, 62.9 MHz) in C_6D_6 at 298 K unless otherwise stated. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards.

The crystal structures of **2a** and **2b** were measured on an Oxford Excalibur 2 diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97 and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.

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Table 1. Crystallographic Data for Compounds **2a** and **2b**

	2a	**2b**
empirical formula	$C_{68}H_{86}Ga_4OPd_3Si_2$	$C_{75}H_{85}Ga_5Pd_2$
M_r (g mol^{-1})	1573.63	1547.95
temperature (K)	104(2)	105(2)
wavelength (Å)	0.71073	0.71073
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a (Å)	12.546(3)	12.139(2)
b (Å)	13.577(4)	13.509(4)
c (Å)	20.051(5)	22.7429(19)
α (deg)	97.25(2)	103.958(15)
β (deg)	96.51(2)	92.333(12)
γ (deg)	101.04(2)	108.32(2)
V (Å^3)	3292.2(15)	3408.3(12)
Z	2	2
ρ_{calc} (g cm^{-3})	1.587	1.508
μ (mm^{-1})	2.489	2.502
$F(000)$	1584	1564
2θ range (deg)	2.88−25.05	2.97−25.17
index ranges	$-10 \leq h \leq 14$, $-16 \leq k \leq 16$, $-23 \leq l \leq 23$	$-12 \leq h \leq 14$, $-16 \leq k \leq 16$, $-27 \leq l \leq 23$
reflections, collected	25856	23341
reflections, unique	11608 ($R_{int} = 0.0444$)	12035 ($R_{int} = 0.0440$)
GOF on F^2	0.929	0.962
final R indices [$I > 2s(I)$]	R1 = 0.0456 wR2 = 0.0727	R1 = 0.0549 wR2 = 0.1459
R indices (all data)	R1 = 0.0727 wR2 = 0.1085	R1 = 0.0793 wR2 = 0.1591

The relatively high residual electron-density peaks in the refined crystal structure of **2a** (1.726 and −0.956) are located rather far from the metal centers and can thus not be explained by absorption effects; yet no meaningful model for a disorder in the ligand sphere was found. The presence of solvent molecules can also be excluded. Two Cp*^{Ph} rings in the crystal structure of **2b** were strongly disordered (Ga1 and Ga3), which could not be modeled in the refinement. Therefore, some ring carbon atoms of the Cp*^{Ph} ligands show rather large anistropic parameters and could only be refined isotropically. Comparably high residual electron-density peaks (2.407 and −1.290) are also explained by this disorder. However, the disorders of both structures **2a** and **2b** are not relevant for the structural issues discussed in this article. Supplementary crystallographic data for both **2a** and **2b** have been deposited with the Cambridge Crystallographic Data Centre. These data can be obtain free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, U.K.; fax (+44)1223-336-033; e-mail: deposit@ccdc.cam.uk).

[K(C_5Me_4Ph)] (1a). [C_5HMe_4Ph] (27.54 g, 0.139 mol) was added to a suspension of KH (5 g, 0.125 mol) in THF (200 mL). The suspension was allowed to stir for 15 h at room temperature. The white precipitate was collected by filtration and washed with THF (3 × 20 mL) and dried in vacuo for 15 h. Yield: 28.3 g (96%).

[GaCp*^{Ph}] (1b). GaI was prepared in situ from Ga (3.54 g, 0.051 mol) and I_2 (6.46 g, 0.051 mol) in benzene (40 mL) by ultrasonic irradiation according to the literature method, giving a green solid. To the suspension was added K(C_5Me_4Ph) (12.0 g, 0.051 mol). The mixture was allowed to stir for 48 h. The resulting gray solid was removed by filtration and washed with toluene (3 × 20 mL). The solvent was removed in vacuo. The residue was distilled under vacuum at 125 °C, giving GaCp*^{Ph} in 59% yield as orange liquid.

^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ (ppm) = 7.27 (m, 5H), 2.00 (s, 6H), 1.93 (s, 6H). ^{13}C NMR (C_6D_6, 62.9 MHz, 25 °C): 136.7, 131.4, 128.5, 128.1, 126.3, 114, 114.1, 10.7, 10.0.

[Pd$_3$(dvds)(GaCp*^{Ph})(μ^2-GaCp*^{Ph})(μ^3-GaCp*^{Ph})$_2$] (2a). A solution of [Pd$_2$(dvds)$_3$] (500 mg, 1.295 mmol) and dvds (402 mg, 2.159 mmol) in hexane (5 mL) was cooled to −30 °C and treated with [GaCp*^{Ph}] (461 mg, 1.727 mmol). The resulting orange solution was slowly warmed to room temperature, whereupon an orange precipitate was formed. The mixture was cooled to −30 °C. The product was isolated by means of cannulation, washed twice with small amounts of hexane, and dried in vacuo. Yield: 491 mg (72%).

^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ (ppm) = 7.27 (m, 20H), 4.21 (m, 6H), 2.12 (s, 6H), 2.09 (s, 12H), 2.06 (s, 6H), 1.95 (s, 6H) 1.94 (s, 12H), 1.90 (s, 6H), 0.17 (s, 3H), 0.16 (s, 3H), 0.11 (s, 3H), 0.02 (s, 3H).

[Pd$_2$(GaCp*)$_2$(μ^2-GaCp*)$_3$] (2b). A suspension of **2a** (125 mg, 0.079 mmol) in hexane (15 mL) was treated with [GaCp*^{Ph}] (74 mg, 0.277 mmol). The mixture was stirred for 30 min until the color of the precipitate turned from orange to yellow. The mixture was cooled to 0 °C. The product was isolated by means of cannulation, washed twice with small amounts of hexane, and dried in vacuo. Yield:140 mg (76%).

^{1}H NMR (C_6D_6, 250 MHz, 25 °C): δ (ppm) 7.50−7.19 (m, 25H), 1.98 (s, 30H), 1.90 (s, 30H). ^{13}C NMR (C_6D_6, 62.9 MHz, 60 °C): 136.6, 131.5, 128.2, 126.4, 122.5, 114.4, 11.6, 10.8. Anal. Calcd for $C_{75}H_{85}Ga_5Pd_2$: C, 58.19; H, 5.53. Found: C, 57.62, H, 6.18.

Substitution Experiments with 2a and 2b. In a typical experiment, **2a** or **2b** (50 mg) was dissolved in toluene (1 mL). After the respective reactant had been added, the reaction mixture was stirred for several minutes at 60 °C. Small impurities were filtered off by extraction with toluene, and the solvent was removed in vacuo to yield the products as colored powders. All analytical data for these products were in accordance with the published data (Table 1).

Supporting Information Available: X-ray crystallographic data in CIF format for compounds **2a** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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