Inorg. Chem. **2006**, *45*, 3133–3138

Inorganic Chemistry

Article

Insertion of the Ga(I) Bis-imidinate Ga(DDP) into the Metal Halogen Bonds of Rh(I) Complexes. How Electrophilic Are Coordinated Ga(DDP) Fragments?†

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Received December 22, 2005

The reactivity of Ga(DDP) (DDP = 2-((2,6-diisopropylphenyl)amino-4-((2,6-diisopropylphenyl)imino)-2-pentene) towards the rhodium–chloride bonds of [RhCl(PPh$_3$)$_3$] and [RhCl(COE)$_2$]$_2$ (COE = cyclooctene) is investigated. Reaction of the first complex leads to [(Ph$_3$P)$_2$Rh{Ga(DDP)}(μ-Cl)] (**1**), exhibiting a chloride bridging the gallium and the rhodium atoms, whereas the second complex leads to a full insertion of the Ga(DDP) ligand into the Rh–Cl bond giving [(COE)(benzene)Rh{(DDP)GaCl}] (**2**) on coordination of the solvent C_6H_6. Compounds **1** und **2** readily react with the halide abstracting reagent Tl[BAr^F] (BAr^F = B[3,5-(CF$_3$)$_2$C$_6$H$_3$]$_4$), yet the products could not be isolated and characterized because of their lability. The Au(I) complex [{(DDP)Ga}Au{Ga(DDP)}Cl] reacts with Na[BAr^F] giving the linear, symmetric cationic complex [{(DDP)Ga·THF}$_2$Au][BAr^F] (**3**·2THF), exhibiting two THF molecules coordinated to the Ga(DDP) moieties.

Introduction

Low-valent group 13 element organyls of the general type ECp* (E = Al, Ga) have been widely used as ligands for various transition metal centers.[1−4] Their σ-donor capability is rather strong, leading to a Lewis acidic group 13 metal coordinated to an electron-rich transition metal in the complexes.[5,6] These intermetallic compounds have been shown to undergo classical organometallic reactions such as C−H, Si−H, or C−C bond activations in which the group 13 metal usually plays a crucial role being not only a spectator ligand but actively taking part as a reaction partner.[7,8] Thus, GaCp* readily inserts into the metal−halogen bonds of [RhCp*Cl$_2$]$_2$ and [Rh(*p*-cymene)Cl$_2$]$_2$ forming cagelike complexes with terminal Ga−Cl bonds and Ga−Cl−Ga bridges.[9−11] Furthermore, a C−C bond rupture process is taking place in the reaction of RhCp*(L)(CH$_3$)$_2$ with GaCp* giving the zwitterion RhCp*(C$_5$Me$_4$GaMe$_3$). The C−C bond activation was shown to topologically take place at the gallium instead of the rhodium center.[12,13] In the course of these reactivity studies of reactive transition metal fragments with E^{I}R compounds we became interested in sterically more encumbered ligands to stabilize coordinatively unsaturated transition metal centers. Among numerous known bulky Ga(I) compounds, P. P. Power's bis-imidinate Ga(DDP) is a very prominent and well-studied example.[14−16] Recently, we reported on the reaction of Ga(DDP) with AuCl(PPh$_3$), giving the linear insertion products [(PPh)Au{GaCl(DDP)}]

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† Organo group 13 complexes of transition metals [XLII]; communication [XLI], see ref 32.

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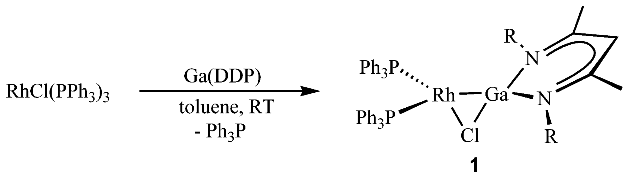
10.1021/ic0521731 CCC: $33.50

Scheme 1. Insertion of Ga(DDP) into the Rh−Cl Bond of $[RhCl(PPh_3)_3]$



and [{(DDP)Ga}Au{Ga(DDP)}Cl].[17] Ga(DDP) is by far more bulky than GaCp*. However, its electronic features are also distinctly different from the Cp* congener. The Ga^I center in Ga(DDP) is isolobal to NHCs, the vacant p orbital not being stabilized by additional π-electrons (as in the case of GaCp*, which is stabilized by the strong π-donor Cp*)[14,16] which leads to an increase of the electrophilicity of the gallium center on coordination to transition metals. On the other side, the oxidized species $Ga(DDP)X_2$ is less acidic than its counterpart $GaCp^*Cl_2$, leading to a different behavior of the ligands toward transition metal halogenides and alkyls.[18] In this paper, we wish to report on insertion reactions of Ga(DDP) into the metal−halogen bonds of rhodium(I) complexes, as well as the creation of a cationic transition metal Au(I)−Ga(DDP) complex by abstraction of a chloride ion.

Results and Discussion

Insertion Reaction of Ga(DDP) into Rh−Cl Bonds. The reaction of $[(Ph_3P)_3RhCl]$ with 1 equiv of Ga(DDP) in toluene at room temperature gives a bright-red solution. After removal of the solvent in vacuo and recrystallization of the residue from a 3:1 mixture of hexane/THF at −30 °C, air-sensitive red rhombohedric crystals of $[(Ph_3P)_2Rh\{Ga(DDP)\}(\mu\text{-}Cl)]$ (**1**) are obtained in yields of around 60% (Scheme 1). The complex dissolves well in aprotic organic solvents and is stable at room temperature when stored in an inert gas atmosphere.

The ^1H NMR spectrum shows one set of signals for the DDP ligand, with a reduced (C_s) symmetry (e.g., two signals for the ^{i}Pr−CH protons). This indicates the transfer of the chloride from the rhodium to the gallium center in the course of the reaction, as also found in the complexes [{(DDP)Ga}Au{Ga(DDP)Cl}] and $[(Ph_3P)Au\{Ga(DDP)Cl\}]$.[17] The $^iPr-CH_3$ groups show four distinct doublet-signals at 2.00, 1.16, 1.00, and 0.61 ppm (each d, 6H). The PPh_3 moieties give rise to a multiplet at 6.63−7.61 ppm, the total integral indicating two PPh_3 groups (i.e., the loss of one PPh_3 ligand in the course of the reaction). The unusual high-field shift of one of the CH_3 groups of the DDP ligand (2.00 ppm, d, 6H) can be best explained by an anisotropic interaction with a phenyl group of a PPh_3 moiety. The ^{31}P NMR shows two doublets of doublets at 53.1 and 41.5 ppm, pointing to an asymmetric coordination environment with respect to the two phosphine atoms. The ^{13}C NMR spectrum shows the typical sets of signals for coordinated Ga(DDP) and Ph_3P ligands, respectively.

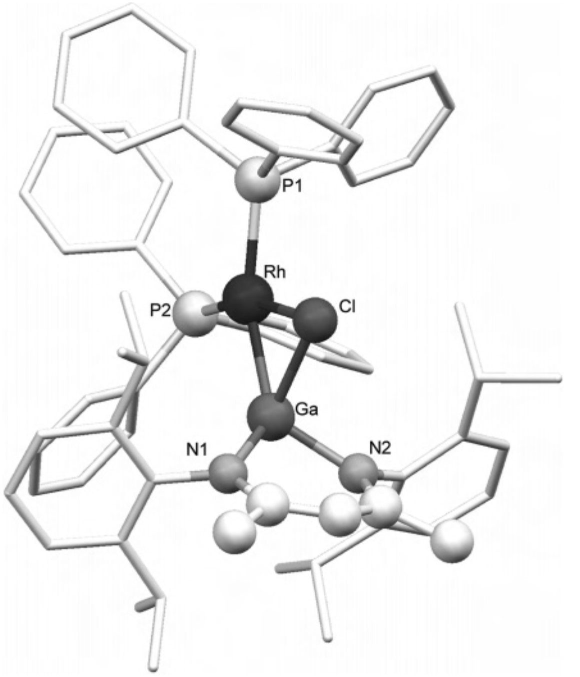


Figure 1. Molecular structure of **1**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Rh−Ga = 2.3870(6), Ga−Cl = 2.4853(11), Rh−Cl = 2.4515(11), Rh−P1 = 2.3062(11), Rh−P2 = 2.1927(12), Ga−N1 = 1.996(3), Ga−N2 = 1.989(3), Ga−Rh−Cl = 61.80(3), P1−Rh−P2 = 103.24(4), P2−Rh−Ga = 101.33(3), P1−Rh−Cl = 93.35(4), Rh−Ga−Cl = 60.38(3), N1−Ga−N2 = 93.05(13).

Compound **1** crystallizes in the monoclinic space group $P2_1/c$. The molecular structure (Figure 1) consists of a central Rh atom in a distorted square planar coordination geometry, surrounded by two Ph_3P units and the {Ga(DDP)Cl} moiety (angular sum of P−Rh−P, P−Rh−Ga, Ga−Rh−Cl, and Cl−Rh−P is 359.7°).

The Rh−Ga bond distance (2.3870(6) Å) is similar to the ones found in $[Cp^*Rh(GaCp^*)_3Cl_2]$ (2.35−2.45 Å) or the "all-hydrocarbon" complex $[(Cp^*Rh)_2(GaCp^*)_3]$ (2.387−2.405 Å).[9]

The most interesting feature of this structure is the chlorine-bridged Rh−Ga bond giving a triangular arrangement of the atoms with similar Rh−Cl and Ga−Cl bond distances (Rh−Ga = 2.3870(6), 2.4853(11) Å; Rh−Cl = 2.4515(11) Å). Obviously, the steric demand of the ligands forbids the formation of a stable 16VE RhL_4 complex leading to a more electrophilic 14VE RhL_3 center. Thus, two electrophilic metal centers are competing for the electrons of the basic chloride ligand, therefore "forcing" the chlorine as a 4VE donor into the bridging position. The Ga−Cl bond length is significantly longer than those in $(DDP)GaCl_2$ (2.22 Å)[18] or the related gold compounds [{(DDP)Ga}Au{Ga(DDP)}Cl] and $[(Ph_3P)Au\{Ga(DDP)Cl\}]$ (Ga−Cl = 2.28−2.29 Å),[17] but it is comparable to the one in $[Cp^*Rh(GaCp^*)_3Cl_2]$ (2.438 Å)[9] or the bond length for bridging chlorides (Ga−Cl−Ga motifs) found in the cluster compound $[\{(Cp''Rh)_2(\mu\text{-}Ga)\}_2(\mu^4,\eta^2\text{-}Ga_2Cl_3)_2]$ (Ga−Cl = 2.445(2) Å and 2.363(2) Å).[19] In contrast, the Rh−Cl distance remains nearly

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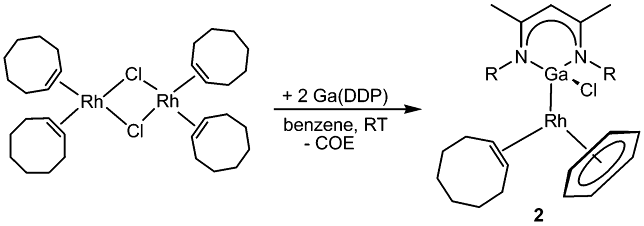
Scheme 2. Reaction of [Rh (COE)$_2$Cl]$_2$ with Ga(DDP)



unchanged, compared to the parent compound (Ph$_3$P)$_3$RhCl (2.416 Å),[20] indicating the strong Lewis acidity of the hypothetical 14VE [Rh(PPh$_3$)$_2${Ga(DDP)Cl}] complex. To the best of our knowledge compound **1** represents the first example of a halide-bridged transition metal−group 13 metal bond. Hence, compound **1** can be regarded as a "frozen intermediate" of an insertion reaction of GaDDP into a Rh−Cl bond.

According to Scheme 2, reaction of the Rh(I) precursor [Rh(COE)$_2$Cl]$_2$ (COE = cyclooctene) with Ga(DDP) leads to the replacement of one olefin by the Ga(I) ligand, full migration of the chloride to the gallium center, and coordination of the solvent C_6H_6 forming [(COE)(η^6-benzene)Rh{(DDP)GaCl}] (**2**). It should be noted that the reaction in absence of C_6H_6 did not give defined products. Recrystallization of the raw product from hexane gives **2** as a deep green solid in a 60% yield.

The ^{1}H NMR spectrum in C_6D_6 at room temperature shows the expected signal set for a (DDP)GaCl moiety with two distinct septets for the ^{i}Pr−CH groups and four distinct doublets for the ^{i}Pr−CH$_3$ groups, respectively. The COE signals are found at 2.83 (2H), 1.89 (2H), 1.41 (4H), 1.20 (4H), and 1.00 ppm (2H). Interestingly, in C_6D_6 no signal for coordinated C_6H_6 could be detected; instead, a singlet for free C_6H_6 at 7.15 ppm integrating to about six protons is found. Obviously, an exchange between coordinated C_6H_6 and the deuterated solvent C_6D_6 takes place. In accordance with this, the ^{13}C NMR spectrum of **2** in C_6D_6 shows a triplet signal in the range of a coordinated C_6D_6 ligand (97.4 ppm). Such arene exchange reactions are also known for other Rh^I compounds (e.g., in [(Rh(η-ArH)(η-C$_8$H$_{14}$){SnCl(NR$_2$)$_2$}] (ArH = PhMe, C$_6$H$_3$Me$_3$-1,3,5, or C$_6$Me$_6$)[21] and [(Rh(η-Arene)(P(OPh)$_3$)$_2$]ClO$_4$ (ArH = PhMe, C$_6$H$_3$Me$_3$-1,3,5, or C$_6$H$_6$)).[22] However, the ^{1}H NMR spectrum of **2** in THF-d_8 shows a sharp singlet signal at 5.65 ppm, assignable to a coordinated C_6H_6 molecule.

Crystals suitable for X-ray analysis could be obtained by slow evaporation of the solvent of a saturated benzene-solution. Compound **2** crystallizes in the triclinic space group $P\bar{1}$. The molecular structure (Figure 2) can be described as a half-sandwich complex with a two-legged piano-stool coordination sphere consisting of an η^2-coordinated cyclooctene ligand and a {(DDP)GaCl} moiety. The covalent Ga−Cl interaction is reflected by the only slightly distorted tetrahedral environment of the gallium center (angular sum of the N1−N2−Ga−Rh plane is 345°). The Rh−Ga−Cl bond angle of 112° is also in accordance with a complete migration of the chlorine atom from the rhodium to the gallium center in the course of the reaction. The Ga−Cl bond distance (2.32 Å) is only slightly longer than those in the gold compounds [{(DDP)Ga}Au{Ga(DDP)Cl}] and [(Ph$_3$P)Au{Ga(DDP)Cl}] (Ga−Cl = 2.28−2.29 Å).[17] The Rh−Ga distance (2.40 Å) is longer than in **1**, but it is in the same range as that found in the GaCp* compounds [Cp*Rh(GaCp*)$_2$(GaCl$_3$)] (Rh−Ga = 2.34−2.41 Å) or the dimeric complex [(Cp*Rh)$_2$(GaCp*)$_3$] (Rh−Ga = 2.38−2.41 Å).[9] Interestingly, the Rh−C$_{\text{olefin}}$ bond distances (Rh−C$_{\text{coe}}$ = 2.113(4) and 2.141(4) Å) are significantly shorter than those in the dimeric compound [RhCp*(C$_2$H$_4$)(μ^2-GaCp*)]$_2$ (Rh−C$_{\text{ethylene}}$ = 2.24−2.29 Å), pointing to a higher degree of π-back-bonding in **2**.[9]

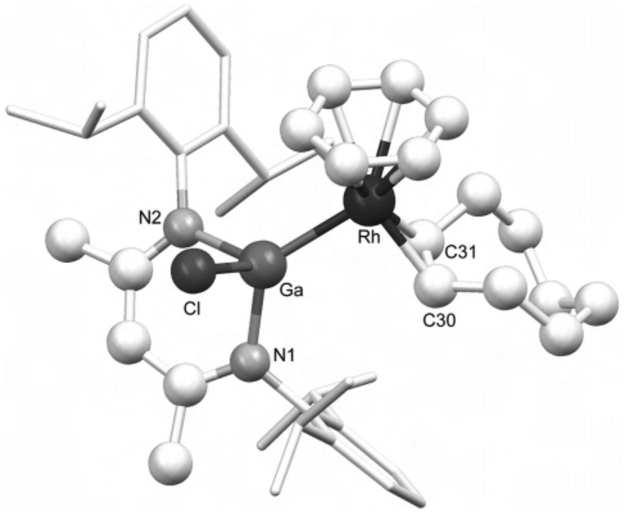


Figure 2. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (deg): Rh−Ga = 2.4037(8), Ga−Cl = 2.321(2), Ga−N1 = 2.018(3), Ga−N2 = 1.974(3), Rh−C30 = 2.141(4), Rh−C31 = 2.113(4), Rh−Ga−Cl = 112.08(4), N1−Ga−N2 = 93.12(12), N1−Ga−Rh = 122.84(9), N2−Ga−Rh = 129.12(9).

Chloride Abstraction from 1 and 2, Cationic Ga(DDP) Complexes. In several attempts to abstract the chlorine atoms of both compounds **1** and **2** by TlBAr^F (BAr^F = tetra-((3,5-bis-triflourmethyl)phenyl)borate) to produce [(coe)Rh(C$_6$H$_6$){Ga(DDP)}]$^+$ or [(Ph$_3$P)$_2$Rh{Ga(DDP)}]$^+$ did not lead to products stable enough to be isolable, at least so far in our hands. However, both compounds **1** and **2** were found to readily react with TlBAr^F, as indicated by a significant change in the ^{1}H NMR spectra and the formation of TlCl. In the spectra of both compounds, the characteristic splitting of the ^{i}Pr−CH-signal of the {(DDP)GaCl} moiety disappears, indicating the formation of a C_{2v} symmetric (i.e., halogen-free) Ga(DDP) moiety. In addition, the reaction products were found to be soluble only in polar solvents such as THF or fluorobenzene, which is in agreement with an ionic nature of the products. Unfortunately, no crystals suitable for X-ray analysis of either compound could yet be obtained. The resulting species could also not be spectroscopically characterized in more detail since all attempts to purify the obviously very labile products failed and resulted in decomposition.

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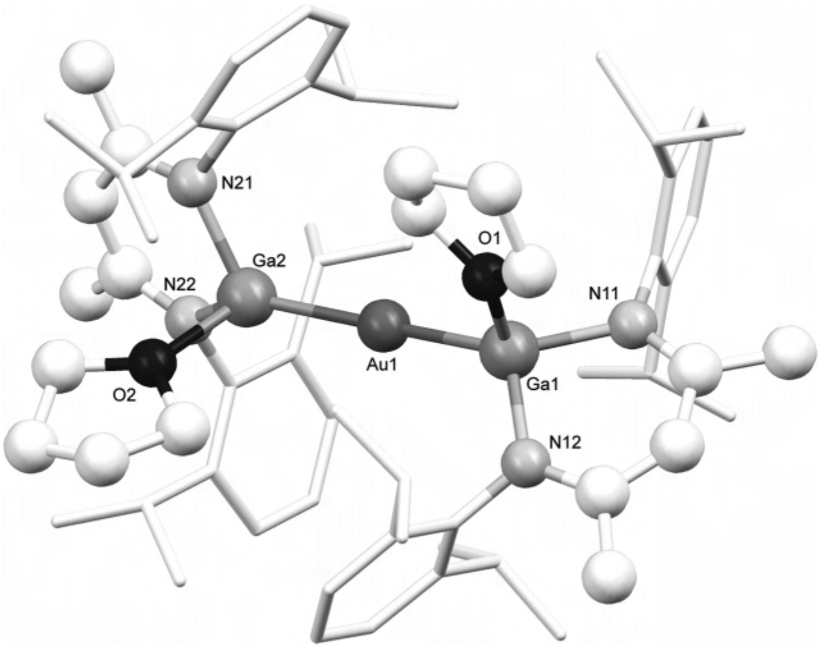
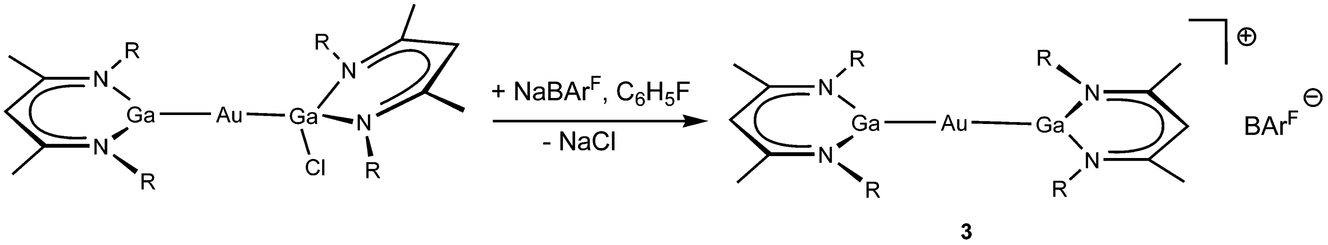


Figure 3. Molecular structure of **3**·2THF. Hydrogen atoms and the BAr^F anion are omitted for clarity. Selected bond length (Å) and angles (deg): Au1−Ga1 = 2.393, Au1−Ga2 = 2.391, Ga1−N11 = 1.956, Ga1−N12 = 1.948, Ga1−O1 = 2.178, Ga2−N21 = 1.986, Ga2−N22 = 1.958, Ga2−O2 = 2.151, Ga1−Au1−Ga2 = 170.93, Au1−Ga1−O1 = 105.09, N11−Ga1−N12 = 95.38, N11−Ga1−Au1 = 134.85, N12−Ga1−Au1 = 119.61, Au1−Ga2−O2 = 105.6, N21−Ga2−N22 = 95.50, N21−Ga2−Au1 = 118.59, N22−Ga2−Au1 =137.68.

Scheme 3. Reaction of [{(DDP)Ga}Au{ClGa(DDP)}] with $NaBAr^F$



To prove the concept, we selected the related Au(I) compound [{(DDP)Ga}Au{Ga(DDP)}Cl][17] which was treated in the same manner with $NaBAr^F$ in THF solution. Halide abstraction from the coordinated {ClGa(DDP)} moiety occurred as discussed above for the Rh congeners, and the cationic compound [{(DDP)Ga·THF}$_2$Au][BAr^F] (**3**·2THF) was obtained. The ^1H NMR spectrum in THF-d_8 shows only one C_{2v} symmetric signal set for both coordinated Ga(DDP) ligands, as well as signals for the [BAr^F] anion, in a ratio of 2:1. The ^{13}C NMR spectrum is in total agreement with this result. The spectroscopic features of the coordinated Ga(DDP) ligand of **3**·2THF match the observation in the case of the instable cationic Rh complexes.

Crystals of **3**·2THF, suitable for X-ray analysis, were obtained by slow diffusion of hexane into a saturated THF solution at room temperature. The molecular structure (Figure 3) of the cation consists of a central gold atom almost linearly coordinated by two Ga(DDP) ligands (Ga1−Au−Ga2 = 170.89°). Both Ga−Au distances are equal (Ga−Au = 2.392 Å) and are slightly shorter than the distances found for the parent compound [{(DDP)Ga}Au{Ga(DDP)}Cl] (2.41 Å),[17] but they are longer than the distances found for the equatorial GaCp* units in the trimeric cluster [$Au_3(\mu\text{-}GaI_2)(Cp^*Ga)_5$] (Au−Ga = 2.384 and 2.377 Å).[23] A very interesting feature of the solid-state structure of **3**·2THF is the weak coordination of THF to each of the gallium centers giving [(DDP)-Ga(THF)] moieties. This is in agreement with an "electrophilization" of the Ga(I) center of Ga(DDP) when coordinated to a transition metal center, since such adducts are unknown for free Ga(DDP). It should be noted, that a similar observation was recently reported on the adduct (DDP)Al−B(C_6F_5)$_3$ showing intramolecular Al−F interactions in the solid state.[24] However, the Ga−O distances (2.14−2.17Å) are significantly longer than in the Ga(III)−THF adduct [(THF)$GaCl_3$] (1.91 Å).[25] Similarly elongated Ga−O bond lengths are, for example, known for hypervalent trigonal-pyramidal or octahedral gallium complexes for axially coordinated THF ligands (e.g., $GaX_3(THF)_2$ Ga−O = 2.11 (X = Cl)[26] and 2.14 Å (X = Br)[27]), as well as for other Ga(III) complexes with weakly acidic gallium centers. The THF-free compound [{(DDP)Ga}$_2$Au][BAr^F] (**3**) cannot be synthesized analogously to its THF adduct by a simple one-pot reaction in the absence of THF using a noncoordi-

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nating solvent (e.g., C_6H_5F). Instead, the well-known cation $[(Ph_3P)_2Au]^{+}$[28] is formed in high yields. However, treatment of pure [{(DDP)Ga}Au{ClGa(DDP)}] with Na[BAr^F] in flourbenzene gives **3** in high yields (Scheme 3). Crystals of **3** suitable for X-ray analysis can also be obtained by crystallization in the absence of THF, indeed showing an undistorted, linear $[Au\{(GaDDP)\}_2]$ moiety as the cation. However, the overall structural quality was poor because of the twinning of the crystals, and thus a depiction of this structure is not included herein.

Conclusions

The rhodium complexes, $[RhCl(PPh_3)_3]$ and $[RhCl(COE)_2]_2$, readily react with Ga(DDP) giving the insertion products $[(Ph_3P)_2Rh\{Ga(DDP)\}(\mu\text{-}Cl)]$ (**1**) and [(COE)(η^6-benzene)Rh{(DDP)GaCl}] (**2**), respectively. Compound **1** exhibits a chloride bridging the gallium and the rhodium atom, which is explained by the steric bulk of the DDP ligand not allowing the coordination of additional ligands. The very electrophilic rhodium center in the hypothetical 14VE complex $[(Ph_3P)_2Rh\{GaCl(DDP)\}]$ effectively competes with the electrophilic Ga(I) center of the Ga(DDP) ligand for the electrons of the chloride, finally leading to a Rh−Cl−Ga bridge. In contrast, a full migration of the chloride from the rhodium to the gallium center is observed on reaction of $[RhCl(COE)_2]_2$ giving [(COE)(η^6-benzene)Rh{(DDP)GaCl}] (**2**) on coordination of the solvent C_6H_6.

Abstraction of the chloride from both **1** or **2** does not give isolable products. However, reaction of the halide-abstracting reagent Na[BAr^F] with the Au(I) complex [{(DDP)Ga}Au{ClGa(DDP)}] leads to the linear, symmetric cationic complex $[\{(DDP)Ga\}_2Au][BAr^F]$ (**3**). The rather strong electrophilicity of the coordinated gallium center in cation **3** becomes visible by crystallization of the product from a saturated solution in THF, leading to a molecular structure of **3**·2THF showing THF molecules axially coordinated to each gallium center.

Experimental Section

All manipulations were carried out in an atmosphere of purified argon using standard Schlenk and glovebox techniques. Hexane and THF were dried using an mBraun Solvent Purification System; benzene and fluorbenzene 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. $[(COE)_2RhCl]_2$,[29] $[(Ph_3P)_3RhCl]$,[20] $[(Ph_3P)AuCl]$,[30] Na[BAr^F],[31] Ga(DDP),[14] and [{(DDP)Ga}Au{ClGa(DDP)}][17] were prepared according to literature methods. Elemental analyses were performed by the Microanalytical Laboratory of the Ruhr-Universität Bochum. NMR spectra were recorded on a Bruker Avance DPX-250 spectrometer (^{1}H, 250.1 MHz; ^{13}C, 62.9 MHz) in C_6D_6 or THF-d_8 at 298 K. Chemical shifts are given relative to TMS and were referenced to the solvent resonances as internal standards.

The crystals of **1**, **2**, and **3**·2THF were measured on a 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.

$[(Ph_3P)_2Rh\{Ga(DDP)\}\mu\text{-}Cl]$ (1). $[(Ph_3P)_3RhCl]$ (300 mg, 0.33 mmol) and Ga(DDP) (237 mg, 0.49 mmol) in 10 mL of toluene were stirred at room temperature overnight. The solvent was removed in vacuo. The red solid was recrystallized from 10 mL of hexane/3 mL of THF at −30 °C to yield deep red crystals (235 mg, 63%). ^{1}H NMR (C_6D_6, RT): δ 7.15 (ar, 36H), 5.06 (s, 1H, C*H*), 3.99 (sept. 2H, C*H*(CH$_3$)$_2$), 2.93 (sept. 2H, C*H*(CH$_3$)$_2$), 2.00 (d, 6H, CH(C*H*$_3$)$_2$), 1.52 (s, 6H, C*H*$_3$), 1.16 (d, 6H, CH(C*H*$_3$)$_2$), 1.00 (d, 6H, CH(C*H*$_3$)$_2$), 0.61 (d, 6H, CH(C*H*$_3$)$_2$). ^{13}C NMR (C_6D_6, RT): δ 168.82 (CN), 146.91 (ar), 144.25 (ar), 143.59 (ar), 136.39 (ar), 135.93 (ar), 135.73 (ar), 134.70 (ar), 134.51 (ar), 128.83 (ar), 127.64 (ar), 127.48 (ar), 127.29 (ar), 127.14 (ar), 125.34 (ar), 124.42 (ar), 100.23 (γ-C), 29.80 (*C*H(CH$_3$)$_2$), 29.07 (*C*H(CH$_3$)$_2$), 28.31 (CH(*C*H$_3$)$_2$), 24.73(CH(*C*H$_3$)$_2$), 24.60 (CH(*C*H$_3$)$_2$), 24.54(CH(*C*H$_3$)$_2$), 24.15 (C*Me*). ^{31}P NMR (C_6D_6, RT): δ 53.1 (dd). 41.5 (dd). Anal. Calcd (found) for $RhGaN_2P_2C_{65}H_{71}Cl$: C, 67.03 (67.87); H, 6.16 (6.22); N, 2.53 (2.44).

Rh(COE)(C_6H_6)(μ-ClGa(DDP)) (2). $[(COE)_2RhCl)]_2$ (100 mg, 0.14 mmol) and Ga(DDP) (136 mg, 0.28 mmol) in 5 mL of benzene were stirred at room temperature overnight. The solvent was removed in vacuo. Recrystallization of the deep green solid out of hexane at −30 °C gave deep green crystals in a 60% yield (135 mg). ^{1}H NMR (C_6D_6, RT): δ 7.08−7.24 (ar, 12H), 5.12 (s, 1H, C*H*), 4.08 (m, 2H, C*H*CH$_3$), 3.36 (m, 2H, C*H*CH$_3$), 2.83 (d, 2H, cyclooctene), 1.89 (d, 2H, cyclooctene), 1.69 (d, 6H, CHC*H*$_3$), 1.68 (s, 6H, CC*H*$_3$), 1.44 (d, 6H, CHC*H*$_3$), 1.41 (m, 4H, cyclooctene), 1.25 (d, 6H, CHC*H*$_3$), 1.20 (m, 4H, cyclooctene), 1.09 (d, 6H, CHC*H*$_3$), 1.00 (m, 2H, cyclooctene). ^{13}C NMR (C_6D_6, RT): δ 166.9 (*C*N), 146.1 (ar), 144.9 (ar), 143.4 (ar), 128.1 (ar), 127.9 (ar), 126.8 (ar), 125.4 (ar), 123.4 (ar), 98.9 (γ-*C*), 97.4 (t, coord. *C*$_6$D$_6$), 57.0 (d, C═C, $J_{C-Rh} = 14.6$ Hz), 35.3 (br, cyclooctene), 32.6 (br, cyclooctene), 29.8, 29.7, 28.0, 27.9, 26.6 (br, cyclooctene), 26.4, 26.3, 25.1, 25.0, 24.9, 24.8, 24.4, 24.3, 23.5, 23.4. ^{1}H NMR (THF-*d*$_8$, RT): δ 7.14−7.30 (ar, 6H), 5.65 (s, 6H, C_6H_6), 5.19 (s, 1H, C*H*), 3.80 (m, 2H, C*H*CH3), 3.28 (m, 2H, C*H*CH3), 2.67 (d, 2H, cyclooctene), 1.83 (d, 2H, cyclooctene), 1.76 (s, 6H, CC*H*$_3$), 1.43 (d, 6H, CHC*H*$_3$), 1.41 (d, 6H, CHC*H*$_3$), 1.22 (d + m, 12H, CHC*H*$_3$ + cyclooctene), 1.03 (d + m, 10H, CHC*H*$_3$ + cyclooctene). ^{13}C NMR (THF-*d*$_8$, RT): δ 167.4 (*C*N), 146.5 (ar), 145.5 (ar), 144.2 (ar), 129.1 (ar), 127.3 (ar), 125.7 (ar), 124.1 (ar), 99.2 (γ-*C*), 98.7 (d, C_6H_6, $J_{C-Rh} = 2.14$ Hz), 57.6 (d, C=*C*, $J_{C-Rh} = 14.54$ Hz), 35.7, 32.9, 30.4, 28.3, 27.6, 27.1, 26.5, 25.2, 25.1, 24.6, 23.8. Anal. Calcd (found) for RhGa $N_2C_{43}H_{61}Cl$: C, 63.44 (63.44); H, 7.55 (7.58); N, 3.44 (3.46).

$[\{(DDP)Ga\}_2Au][BAr^F]$ (3). [{(DDP)Ga}Au{ClGa(DDP)}] (90 mg, 0.075 mmol) and Na(BArF) (80 mg, 0.09 mmol) in 3 mL of C_6H_5F were stirred at room temperature for 1 h. The white precipitate of NaCl was filtered off, and the solvent of the resulting yellow solution was removed in vacuo. The remaining colorless solid was washed twice with hexane and dried in vacuo. Yield: 145 mg (95%). ^{1}H NMR (C_6H_5F/C6D6, RT): δ 8.36 (br, 8H, BArF), 7.65 (s, 4H, BArF), 7.34−6.34 (ar, 12H), 5.26 (s, 2H, C*H*), 2.50 (m, 8H, C*H*CH$_3$), 1.61 (s, 12H, CC*H*$_3$), 1.09 (d, 24H, CHC*H*$_3$), 0.85 (d, 24H, CHC*H*$_3$). ^{13}C NMR: Because of the large ^{13}C NMR signals for the solvent, no satisfying ^{13}C NMR spectrum of this sample could be recorded.

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[{(DDP)Ga·THF}$_2$Au][BAr^F] (3·2THF). The reaction was performed in a manner similar to that described above using 47 mg of [(Ph$_3$P)AuCl)] (0.1 mmol), 100 mg Ga(DDP) (0.2 mmol), 90 mg Na(BArF) (0.1 mmol), and THF. Yield: 150 mg (73%). Crystals, suitable for X-ray analysis, were obtained by slow diffusion of hexane into a saturated THF solution of **3**·2THF at room temperature. ^{1}H NMR (THF-d_8, RT): δ 7.79 (m, 8H, BArF), 7.57 (s, 4H, BArF), 7.11−7.24 (ar, 12H), 5.36 (s, 2H, C*H*), 2.79 (m, 8H, C*H*CH$_3$), 1.79 (s, 12H, CC*H*$_3$), 1.11 (d, 24H, CHC*H*$_3$), 0.95 (d, 24H, CHC*H*$_3$). ^{13}C NMR (THF-d_8, RT): δ 168.8 (*C*N), 162.8 (q, BArF-ar), 144.3 (ar), 141.5 (ar), 135.6 (ar), 130.2 (q, BArF-ar), 129.7 (q, BArF-ar), 128.0 (ar), 125.5 (q, $J_{C-F} = 272$ Hz, BArF-*C*F$_3$), 125.0 (ar), 118.2 (BArF-ar), 99.7 (γ-*C*), 29.2 (*C*HCH$_3$), 24.4 (CH*C*H$_3$), 24.1 (C*Me*). ^{1}H NMR (10:1 C$_6$H$_5$F/C$_6$D$_6$, RT): δ 8.25 (m, 8H, BArF), 7.55 (s, 4H, BArF), 7.11−7.24 (ar, overlaid by C$_6$H$_5$F), 5.17 (s, 2H, C*H*), 3.43 (m, 8H, THF), 2.43 (m, 8H, C*H*CH$_3$), 1.53 (s, 12H, CC*H*$_3$), 1.44 (m, 8H, THF), 1.02 (d, 24H, CHC*H*$_3$), 0.77 (d, 24H, CHC*H*$_3$). Anal. Calcd (found) for AuGa$_2$N$_4$BO$_2$C$_{98}$H$_{110}$F$_{24}$: C, 54.01 (53.81); H, 5.09 (5.24); N, 2.57 (2.85).

Supporting Information Available: Crystallographic data files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0521731