$[M(GaCp^*)_4]$ (M = Pd, Pt) as Building Blocks for Dimeric Homoleptic Cluster Compounds of the Type $[MPt(GaCp^*)_5]$

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The monomeric homoleptic Pt(0) complex $[Pt(GaCp^*)_4]$ (**1**) has been synthesized by reaction of $[Pt(COD)_2]$ with GaCp* in hexane. The monomeric homoleptic Pd(0) complexes $[Pd(GaCp^*)_4]$ (**2**) and $[Pd\{InC(SiMe_3)_3\}_4]$ (**3**) are accessible by reaction of $[Pd(tmeda)(CH_3)_2]$ with GaCp* and $[InC(SiMe_3)_3]$, respectively. These reactions were shown to proceed via methyl group transfer from palladium to indium or gallium, respectively. Complexes **1** and **2** can be used as building blocks for the synthesis of dinuclear cluster compounds. Thus, reaction of $[Pt(COD)_2]$ with **1** or **2** and subsequent addition of GaCp* yields $[Pt_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$ (**4a**) and $[PtPd(GaCp^*)(\mu^2\text{-}GaCp^*)_3]$ (**5a**). Intermediates of this dimerization reactions, i.e., $[Pt_2(GaCp^*)(\mu^2\text{-}GaCp^*)_3(\eta^2\text{-}COD)]$ (**4b**) and $[PtPd(GaCp^*)(\mu^2\text{-}GaCp^*)_3(\eta^2\text{-}COD)]$ (**5b**), were isolated and characterized by means of variable-temperature NMR spectroscopy.

Introduction

Coordination of low-valent group 13 metal compounds E^IR (E = Al, Ga, In; R = Cp*, $C(SiMe_3)_3$) to transition metal fragments gives access to a wide variety of intermetallic complexes $[(L_nM)_a(ER)_b]$ (a < b).[1] A common pathway for the formation of M−E bonds is the replacement of labile ligands by E^IR. Thus, the COD ligands in $[Pt(COD)_2]$ and $[Ni(COD)_2]$ are readily replaced by GaCp*, $GaC(SiMe_3)_3$, or $InC(SiMe_3)_3$, yielding monomeric complexes of the type $[M(ER)_4]$ (M = Pt, Ni).[2] The access to cluster compounds having E^IR as ligands is however far more sophisticated. Recent investigations on this subject have focused on the coordination of E^IR species to transition metal carbonyl fragments $[M_a(CO)_b]$.[3] But, the incoming σ-donor E^IR stabilizes the remaining M−CO bonds in the products and thus intrinsically limits the full substitution of CO versus E^IR. Only a few exceptions are known, i.e., cluster complexes that contain no strong π-acceptor ligands. These "*all hydrocarbon*" species are limited to $[(CpNi)_2(\mu^2\text{-}AlCp^*)_2]$[4] synthesisized by Schnöckel in 1994 and $[Pt_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$[5] and $[Pd_3(InCp^*)_4(\mu^2\text{-}InCp^*)_4]$[6] synthesized by us in 1999 and 2002. In this context we were interested in studying in detail more general pathways to homoleptic cluster compounds $[M_a(E^IR)_b]$ by using the monomeric species $[M(ER)_4]$ as building blocks.

Results and Discussion

1. Monomeric $M(ER)_4$ Complexes. Recently we reported on the synthesis and characterization of $[Pt_2(GaCp^*)_2(\mu^2\text{-}GaCp^*)_3]$[5] (**4a**) as the first homoleptic platinum complex with terminal and bridging GaCp* ligands. It is quantitatively formed in the reaction of $[Pt(C_2H_4)_3]$ with excess GaCp* and could be isolated in analytically pure form in high yields. This was a rather surprising result, as we actually expected to obtain $[Pt(GaCp^*)_4]$ in analogy with the known reaction of $[Pt(COD)_2]$ with $InC(SiMe_3)_3$, giving $[Pt\{InC(SiMe_3)_3\}_4]$.[2b] However, this observation encouraged us to study the reactivity of GaCp* toward other Pt(0) precursors in more detail.

The reaction of $[Pt(COD)_2]$, as an alternative Pt(0) precursor with respect to $[Pt(C_2H_4)_3]$, with an excess of GaCp* in hexane at −80 °C, leads exclusively to the full substitution of the COD ligands by GaCp*, now surprisingly giving the monomeric homoleptic complex $[Pt(GaCp^*)_4]$ (**1**) as pale orange crystals in a yield of 88% (Scheme 1).

Complex **1** is very air sensitive, both in solution and in the solid state, but stable over several weeks at room

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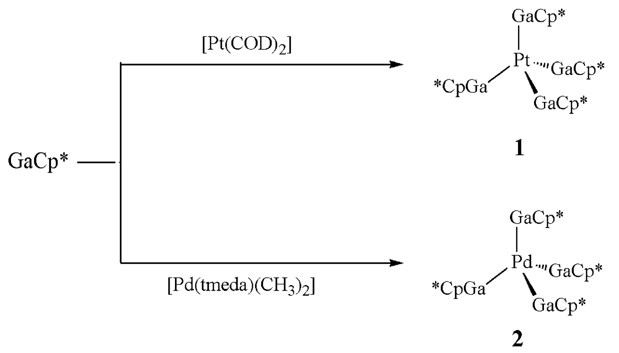
Table 1. Crystallographic Data for Compounds 1 and 2

	1	**2**
empirical formula	$C_{40}H_{60}Ga_4Pt$	$C_{40}H_{60}Ga_4Pd$
molecular weight	1014.85	926.16
temperature (K)	213(2)	213(2)
wavelength Mo Kα (Å)	0.71073	0.71073
cryst size (mm)	0.35 × 0.35 × 0.25	0.44 × 0.32 × 0.20
cryst syst	tetragonal	tetragonal
space group	$I\bar{4}$	$I\bar{4}$
a (Å)	12.1466(12)	12.1107(16)
b (Å)	12.1466(12)	12.1107(16)
c (Å)	15.095(3)	15.192(4)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
V (Å^3)	2227.2(6)	2228.2(7)
Z	2	2
δ_{calc} (g cm^{-3})	1.513	1.380
μ (mm^{-1})	5.540	2.806
F(000)	1004	940
θ range for data collection (deg)	2.70−25.04	2.15−29.99
index ranges	$-14 \leq h \leq 13$, $-14 \leq k \leq 7$, $-11 \leq l \leq 17$	$-17 \leq h \leq 11$, $-17 \leq k \leq 13$, $-21 \leq l \leq 18$
no. of reflns collected	2841	2137
no. of unique reflns	1872 [$R_{int} = 0.0323$]	1911 [$R_{int} = 0.0333$]
no. of reflns obsd	1760 $F_o > 4\sigma(F_o)$	1556 $F_o > 4\sigma(F_o)$
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	1872/0/102	1911/0/107
abs corr	empirical	empirical
max. and min. transmn	1.000 and 0.7272	1.000 and 0.571
goodness-of-fit on F^2	0.856	1.024
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0286$ $wR_2 = 0.0628$	$R_1 = 0.0388$ $wR_2 = 0.0824$
R indices (all data)	$R_1 = 0.0320$ $wR_2 = 0.0675$	$R_1 = 0.0541$ $wR_2 = 0.0899$
largest diff peak and hole (e Å^{-3})	0.717 and −0.772	0.390 and −0.395

Scheme 1



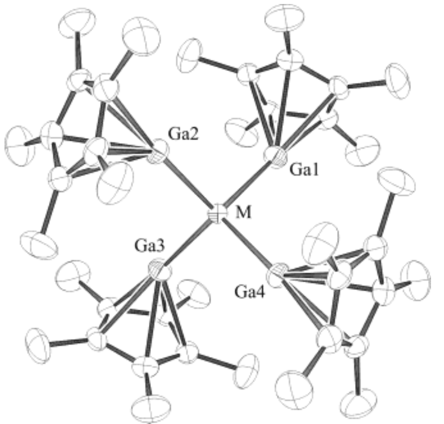


Figure 1. Molecular structure of **1** (M = Pt) and **2** (M = Pd), with thermal ellipsoids at 50% probability. Selected bond lengths (Å) and angles (deg) for **1**: Pt(1)−Ga(1) = 2.335(2), Ga(1)−C(1) = 2.333(10), Ga(1)−C(2) = 2.355(10), Ga(1)−C(3) = 2.334(10), Ga(1)−C(4) = 2.320(10), Ga(1)−C(5) = 2.331(10), Cp*$_{centroid}$−Ga(1) = 2.007, Ga(1)−Pt−Ga(2) = 1.0940(6), Cp*$_{centroid}$−Ga(1)−Pt(1) = 160.7. Selected bond lengths (Å) and angles (deg) for **2**: Pd(1)−Ga(1) = 2.3668(7), Ga(1)−C(1) = 2.343(6), Ga(1)−C(2) = 2.332(6), Ga(1)−C(3) = 2.349(6), Ga(1)−C(4) = 2.372(6), Ga(1)−C(5) = 2.336(6), Cp*$_{centroid}$−Ga(1) = 2.019, Ga(1)−Pd−Ga(2) = 109.421(19), Cp*$_{centroid}$−Ga(1)−Pd(1) = 155.5.

temperature when it is stored under an inert gas atmosphere. It readily dissolves in nonpolar organic solvents such as benzene or hexane. The NMR spectrum of **1** is rather simple, as expected for a highly symmetric homoleptic compound with η^5-coordination of the Cp* rings. The ^{1}H NMR in C_6D_6 exhibits only one singlet for the Cp* methyl protons at 1.89 ppm. This relatively low value with respect to the free ligand (δ 1.92) is possibly an effect of the anisotropic magnetic field of the aromatic Cp* units. As the molecular structure in the solid state reveals, the Cp*$_{centroid}$−Ga−Pt angle is not linear, and it is thus likely that the CH_3 groups of the Cp* units pass the anisotropic magnetic field of an adjacent Cp* unit on rotation of the Ga−Cp*$_{centroid}$ bond in solution, shifting in total the coalesced signal upfield. The ^{13}C NMR in the same solvent gives rise to two resonances at 113.0 and 10.7 ppm, representing the ring carbon atoms and the methyl groups of the Cp* ligands, respectively. Suitable crystals of **1** could be obtained by stepwise cooling of a concentrated solution in hexane to a final temperature of −80 °C. Important crystallographic data are summarized in Table 1; the molecular structure of **1** is depicted in Figure 1. Compound **1** crystallizes in the tetragonal space group $I\bar{4}$ ($Z = 2$) and is isostructural to [Ni(GaCp*)$_4$].[2d] The platinum atom is tetrahedrally coordinated by four gallium atoms with a Ga−Pt−Ga angle of 109.40(6)° and a Pt−Ga distance of 2.335(2) Å. The Cp* units are nearly symmetrically bonded to the Ga centers with a Ga$-$Cp*$_{centroid}$ distance of 2.007 Å, being close to the free ligand of 2.081 Å (gas phase, monomer).[7] However, a substantial deviation from linearity is observed for the Cp*$_{centroid}$$-Ga-$Pt angles (160.7°), as reported earlier for [Ni(GaCp*)$_4$].[2d] Finally it should be noted that the highly symmetric solid state structure is in good agreement with the symmetric solution structure observed by NMR spectroscopy as mentioned above.

As for palladium, [Pd(tmeda)(CH$_3$)$_2$] was selected as the source for Pd(0), since Pd olefin complexes are generally far more reactive and difficult to handle with respect to Pt(0) olefin compounds, e.g., [Pd(COD)$_2$] readily decomposes to Pd metal in the solid state below room temperature.[8] [Pd(GaCp*)$_4$] (**2**) is quantitatively formed in the reaction of [Pd(tmeda)(CH$_3$)$_2$] with *exactly 5* equiv of GaCp* in hexane solution at room temperature (Scheme 1). Crystallization from hexane at -60 °C gives **2** as air-sensitive pale yellow crystals in a good yield of 80%. The complex dissolves well in nonpolar organic solvents and is stable at room temperature when stored under an inert gas atmosphere. The NMR spectra of **2** are very similar to those of compound **1**, the ^{1}H NMR in C$_6$D$_6$ shows one resonance at 1.95 ppm, and the ^{13}C spectrum shows two resonances at 113.3 and 10.5 ppm, respectively. Suitable crystals for X-ray analysis could be obtained from hexane. Important crystallographic data are summarized in Table 1, and the molecular structure is shown in Figure 1. The complex crystallizes in the tetragonal space group $I\bar{4}$ ($Z = 2$) and is isostructural to **1**. The Pd atom is tetrahedrally surrounded by four Ga atoms with a Ga$-$Pd$-$Ga angle of 109.421(19)° and a Pd$-$Ga distance of 2.3668(7) Å. Again, the Cp* units are nearly symmetrically bonded to the Ga atoms with a Ga$-$Cp*$_{centroid}$ distance of 2.019 Å, and a deviation from linearity is observed for the Cp*$_{centroid}$$-Ga-$Pd angles (155.5°).

[Pd(tmeda)(CH$_3$)$_2$] is known to react with phosphines PR$_3$, giving [Pd(PR$_3$)$_n$] ($n = 2-4$).[9] This reaction was shown to proceed via ethane elimination and subsequent substitution of the tmeda ligand by PR$_3$. The amount of PR$_3$ used in this reaction directly determines the composition of the products [Pd(PR$_3$)$_n$]. However, using 4 instead of 5 equiv of GaCp* in the preparation of **2** results in a somewhat lower yield (<50%) together with a second product, which could not be identified. Monitoring the reaction by ^{1}H NMR spectroscopy in C$_6$D$_6$ reveals that only a very small amount of ethane is formed. Instead, a new singlet assignable to six protons appears at -0.15 ppm (^{13}C, δ -7.8), a chemical shift typical for Ga$-$CH$_3$ groups. From this observation we conclude that the fate of the Pd methyl groups is a transfer to GaCp* forming [GaCp*(CH$_3$)$_2$] as a byproduct rather than the reductive elimination of ethane.

The reaction of [Pd(tmeda)(CH$_3$)$_2$] with 5 equiv of InC(SiMe$_3$)$_3$ in hexane solution at 60 °C leads to the formation of the homoleptic complex [Pd{InC(SiMe$_3$)$_3$}$_4$] (**3**) (Scheme 1). Dark red-brown microcrystals of product **3** were isolated by recrystallization from cyclopentane in a yield of 65%.

Compound **3** is very moisture and air sensitive, but stable over several weeks at room temperature under an inert gas atmosphere. It readily dissolves in nonpolar organic solvents such as hexane or toluene. Elemental analysis of **3** is in good agreement with the formula [Pd{InC(SiMe$_3$)$_3$}$_4$]. The ^{1}H NMR in C$_6$D$_6$ exhibits only one singlet for the SiMe$_3$ groups at 0.42 ppm. The signal of the α-carbon atom in the ^{13}C NMR spectrum is found at 64.7 ppm. This value is very similar to those of [Ni{(InC(SiMe$_3$)$_3$}$_4$] (δ 61.6)[2a] and [Pt{(InC(SiMe$_3$)$_3$}$_4$] (δ 60.2)[2b] and lies between the free ligand [{InC(SiMe$_3$)$_3$}$_4$] (δ 73.0)[10] and the shift usual for indium(III) compounds (δ < 30.0).[11] Interestingly, this shift seems to be less dependent on the transition metal than on the coordination mode of the ligand. Thus, the signals for bridging InC(SiMe$_3$)$_3$ groups in transition metal complexes are usually found in the range 48$-$52 ppm.[12]

Analogously to the reaction of [Pd(tmeda)(CH$_3$)$_2$] with GaCp* (vide supra), a transfer of the methyl groups from the Pd to InC(SiMe$_3$)$_3$ is observed. [Me$_2$InC(SiMe$_3$)$_3$] was identified in the ^{1}H NMR in C$_6$D$_6$ due to a singlet at 0.13 ppm for the methyl groups (6H) and a singlet for the SiMe$_3$ groups at 0.24 ppm (27H), respectively. These values are in good agreement with the literature data reported for this compound.[13]

Compound **3** crystallizes in the cubic space group $Fd3m$.[14] The high degree of rotational disorder of the SiMe$_3$ groups and the high symmetry of the crystal caused problems in the structure refinement, and the obtained data will thus not be presented here in detail. Similar problems were observed in [Pt{InC(SiMe$_3$)$_3$}$_4$], and a good structural analysis could not be obtained.[2b] However, the presence of a palladium center tetrahedrally surrounded by four InC(SiMe$_3$)$_3$ ligands could be unequivocally refined, confirming the monomeric structure of [Pd{InC(SiMe$_3$)$_3$}$_4$], as already suggested by ^{1}H and ^{13}C NMR data. All data for the partial XRD refinement are given in the Supporting Information.

2. Cluster Compounds. Reaction of **1** with an equimolar amount of [Pt(COD)$_2$] in toluene at room temperature and subsequent addition of 1 equiv of GaCp* yields [Pt$_2$(GaCp*)$_2$(μ^2-GaCp*)$_3$] (**4a**) in 93% yield (Scheme 2). All analytical data are in good agreement with the data earlier reported for this compound.[5] Interestingly, when **4a** is treated with an excess of GaCp*, only trace amounts of **1** can be detected even after 1 day at room temperature (Scheme 2). Additionally, no exchange of free to coordinated ligand can be observed on the NMR time scale. This is in good agreement with the observation that [Pt(C$_2$H$_4$)$_3$] reacts even with a large excess of GaCp* to give quantitatively

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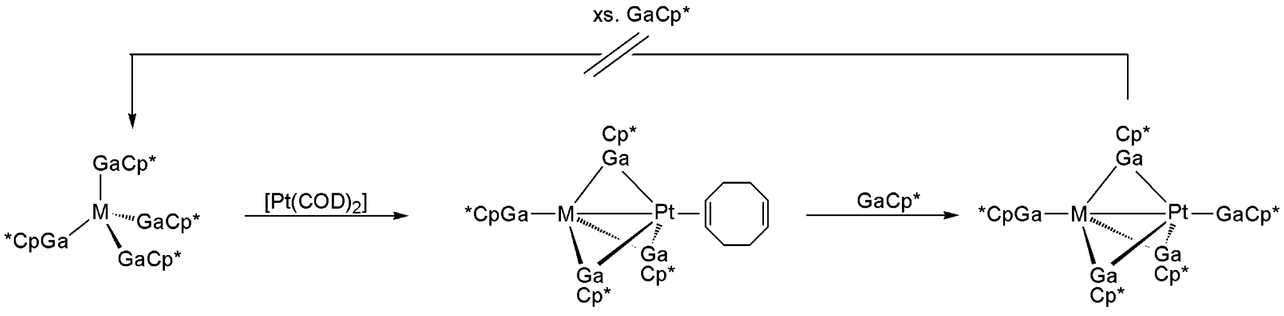
Scheme 2



M = Pt (**1**)
M = Pd (**2**)

M = Pt (**4b**)
M = Pd (**5b**)

M = Pt (**4a**)
M = Pd (**5a**)

4a instead of **1**. Most likely kinetic factors determine the exlusive formation of **4a**, which is then stable also in the presence of free GaCp*.

Analogously, treatment of [Pt(COD)$_2$] with **2** instead of **1** and subsequent addition of 1 equiv of GaCp* yields the novel "trimetallic" compound [PdPt(GaCp*)$_2$(μ^2-GaCp*)$_3$] (**5a**). Complex **5a** can be crystallized from Et$_2$O in a yield of 56%. It is stable at room temperature and dissolves readily in nonprotic organic solvents. Surprisingly the ^{1}H NMR spectrum of **5a** in C$_6$D$_6$ at room temperature shows only two resonances at 2.06 and 1.94 ppm with an integral ratio of 1:4. Accordingly, the ^{13}C spectrum shows four signals at 114.1, 113.1, 11.5, and 10.4 ppm, respectively. This is not consistent with a static spectrum of a nonsymmetric structure having three equivalent bridging GaCp* ligands and two nonequivalent terminal GaCp* ligands. Thus, NMR spectra at low temperature were recorded. At −30 °C the signal at 1.94 ppm in the ^{1}H NMR considerably broadens, indicating a fluxional process exchanging the three bridging and one of the terminal GaCp* ligands. At −80 °C the ^{1}H NMR spectrum is still exhibiting a very broad signal between 2.4 and 1.8 ppm without decoalescence. However, the ^{13}C NMR spectrum at this temperature shows decoalescence of the larger signals at 113.1 and 11.5 ppm into two signals each at 12.3/10.7 and 112.8/114.0 ppm, respectively, with an approximate integral ratio of 3:1 (toluene-d_8). Taking into account that [Pt$_2$(GaCp*)$_5$] shows a perfectly static spectrum at room temperature and below,[5] it is reasonable to assume that the fluxional process is working only at the Pd center of the dimeric structure, leaving the terminal Pt-bound GaCp* unchanged. Unfortunately it was not possible to obtain crystals of **5a** suitable for X-ray analysis. Several crystallization experiments from different solvents yielded strongly disordered crystals which showed only weak reflections. However, in addition to the low-temperature ^{13}C spectrum, also elemental analysis is in very good agreement with a formula of [PtPd(GaCp*)$_5$], and on the basis of the known structure of [Pt$_2$(GaCp*)$_5$] a central PdPt core coordinated by three bridging and two terminal Cp*Ga ligands is suggested.

The order of mixing the three reagents in the preparation of **5a** is crucial for the success of this synthesis. Thus, [Pt(COD)$_2$] and **2** must be allowed to react sufficiently before GaCp* is added in order to yield **5a**. If GaCp* is added too early, substantial amounts of **1** can be detected among other products. This is also true for the preparation of **4a**, but to a somewhat lower degree. It is reasonable to assume that the preparation of **4a** and **5a** proceeds via intermediates of the type [MPt(GaCp*)$_4$(COD)] (M = Pt, Pd). Monitoring these reactions by ^{1}H NMR spectroscopy (C$_6$D$_6$) shows a mixture of complexes in both cases. Besides free cyclooctadiene, several peaks for coordinated GaCp* and coordinated COD ligands can be observed. No peaks assignable to the starting materials are detectable. However, performing these reactions in hexane instead of C$_6$D$_6$ allows the isolation of one of these intermediates. Mixing [Pt(COD)$_2$] with **1** or **2**, respectively, in hexane at room temperature yields pale yellow precipitates (**4b** and **5b**, Scheme 2), which were isolated from the orange solutions by means of cannulation, washed with hexane, and dried in vacuo. Both products are formed in low yields and are thermally very labile. Thus, characterization was only possible by ^{1}H and ^{13}C NMR spectroscopy, which were recorded immediately from freshly prepared samples.

The ^{1}H NMR spectrum of **4b** in C$_6$D$_6$ shows two singlets for the Cp* methyl protons at 2.03 and 1.99 ppm with an integral ratio of 1:3, pointing to a dimeric structure with one terminal and three bridging GaCp* ligands similar to the structure of compound **4a**. Additionally, resonances assignable to an η^2-bound COD ligand are observed. Two broad multiplets (2H each) at 4.67 and 3.00 ppm represent the uncoordinated and the coordinated double bond, respectively, and a broad multiplet (8H) at 2.15 ppm can be assigned to the aliphatic ring protons of the COD ligand. The ^{13}C spectrum in C$_6$D$_6$ is also consistent with a structure of the type [(GaCp*)Pt(μ^2-GaCp*)$_3$Pt(η^2-COD)]. The GaCp* ligands give rise to four peaks at 114.5 (5C), 113.2 (15C), 11.6 (15C), and 10.6 ppm (5C), respectively. The resonance of the olefinic carbons of the COD ligands are found at 129.5 (uncoordinated) and 69.9 ppm (coordinated), respectively. No signals for the aliphatic carbons of the COD ligand could be detected. However, when the ^{13}C spectrum is recorded at −80 °C (toluene-d_8), two new peaks at 27.8 and 24.3 ppm are observed, assignable to the aliphatic carbons of the COD ligand. However, at this temperature, the signals for both olefinic carbons cannot be detected. Taking into account that all ^{1}H resonances of the COD ligand are considerably broadened, two parallel fluxional processes are reasonable: The first one, with a decoalescence above room temperature, exchanges the coordinated and the uncoordinated double bonds of the COD ligand. At −80 °C a second fluxional process becomes important, which leads to broadened, i.e., nondetectable, signals for both olefinic carbons. This process obviously suspends the symmetry of each double bond (i.e., four instead of two olefinic COD signals are expected in the fully decoalesced spectrum). The rotation of the olefinic ligand around the Pt−olefin bond axis seems to be a reasonable mechanism for this fluxional process.

The ^{1}H spectrum for **5b** in C_6D_6 is very similar to that of **4b**. The GaCp* ligands give rise to two singlets at 2.05 (15H) and 2.02 ppm (45H), and the COD ligand shows broad signals at 4.83 (2H), 2.97 (2H), and 2.10 ppm (8H). In the ^{13}C spectrum in C_6D_6 the GaCp* ligands show resonances at 114.3 (5C), 113.4 (15C), 11.0 (15C), and 10.4 ppm (5C). The only detectable signal for the COD ligand can be found at 64.9 ppm, representing the coordinated double bond. The signal for the uncoordinated double bond is obviously covered by the solvent peaks of either C_6D_6 or toluene-d_8. Again, recording the spectrum at −80 °C reveals the signals for the aliphatic COD carbons at 26.2 and 24.3 ppm, and the signal at 64.9 ppm can no longer be observed.

Compounds **4b** and **5b** are thermally unstable and decompose in solution at room temperature completely after several hours. The main products of this decomposition are, as shown by NMR spectroscopy, **4a** and **5a**, respectively, accompanied by free COD.

Summary

The reported synthesis and characterization of the homoleptic monomeric compounds of the type $[M(E^IR)_4]$ (M = Pd, Pt; E = Ga, In; R = Cp*, $C(SiMe_3)_3$) now completes the homologous series of [M(GaCp*)$_4$] and $[M\{InC(SiMe_3)_3\}_4]$ complexes (M = Ni, Pd, Pt). The main aspect of this work however is the use of these compounds as building blocks for novel dimeric homoleptic complexes of the type [MPt(GaCp*)$_5$] (M = Pt, Pd) (**4a**, **4b**), which have no direct structural congener in classical carbonyl cluster chemistry. The formation of these dinuclear products upon combining [M(GaCp*)$_4$] with a suitable M(0) source and additional GaCp* is strongly dependent on the order of mixing the three reagents. It was shown that the monomeric complexes **1** and **2** form reactive, yet isolable dinuclear intermediates on reaction with $[Pt(COD)_2]$. Variable-temperature ^{1}H and ^{13}C NMR data revealed that the intermediates are dimeric clusters with a Pt_2 and a PtPd core, respectively, bearing four GaCp* ligands and still one η^2-coordinated COD ligand. These results show that also the choice of the M(0) precursor is very important for the success of the cluster synthesis.

As a particular useful precursor for Pd(0) in this chemistry, $[Pd(tmeda)(CH_3)_2]$ was found, which was shown to be smoothly reduced by 1 equiv of E^IR via a methyl group transfer from palladium to the group 13 metal center.

Experimental Section

General Data. All manipulations were carried out in an atmosphere of purified argon using standard Schlenk and glovebox techniques. The solvents were distilled over standard drying agents and stored over molecular sieves prior to use. $[Pt(COD)_2]$,[15] $[Pd(tmeda)(CH_3)_2]$,[9a] GaCp*,[16] and $InC(SiMe_3)_3$[10] were prepared according to 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 (^{1}H, 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 structure of compound **1** was measured on a SMART CCD1000 diffractometer, and the structure of **2** was measured on a Siemens P4 four-circle goniometer. The structures were solved by direct methods using SHELXS-97[17] and refined against F^2 on all data by full-matrix least-squares with SHELXL-97.[18]

[Pt(GaCp*)$_4$] (1). $[Pt(COD)_2]$ (0.412 g, 1.000 mmol) in hexane (5 mL) was cooled to −80 °C and treated with a solution of GaCp* (0.922 g, 4.500 mmol) in hexane (2 mL). The resulting yellow solution was slowly warmed to room temperature, whereupon the color turned darker and an orange precipitate was formed. The precipitate was dissolved by warming the solution to 50 °C and the product crystallized by slow cooling to −80 °C. The crystals were isolated by means of cannulation, washed twice with a small amount of cold hexane, and dried in vacuo. Yield: 0.891 g, orange crystals (88%). Anal. Calcd for $C_{40}H_{60}Ga_4Pt$: C, 47.34; H, 5.96. Found: C, 46.97; H, 6.07. ^{1}H NMR: δ 1.89 (s, 60H). $^{13}C\{^1H\}$ NMR: δ 113.0 (t, $J_{PtC} = 7.2$ Hz), 10.7.

[Pd(GaCp*)$_4$] (2). $[Pd(tmeda)(CH_3)_2]$ (0.183 g, 0.7226 mmol) in hexane (5 mL) was cooled to −80 °C and treated with a solution of GaCp* (0.740 g, 3.613 mmol) in hexane (2 mL). The resulting yellow solution was warmed to room temperature and stirred for 10 min, whereupon a pale yellow precipitate formed. The crystallization of the product was completed by slow cooling to −60 °C. The crystals were isolated by means of cannulation, washed twice with a small amount of cold hexane, and dried in vacuo. Yield: 0.536 g, pale yellow crystals (80%), dec 85 °C. Anal. Calcd for $C_{40}H_{60}Ga_4Pd$: C, 51.87; H, 6.53. Found: C, 51,73; H, 6.65. ^{1}H NMR: δ 1.95 (s, 60H). $^{13}C\{^1H\}$ NMR: δ 113.3, 10.5.

$[Pd\{InC(SiMe_3)_3\}_4]$ (3). $[Pd(tmeda)(CH_3)_2]$ (0.100 g, 0.396 mmol) in hexane (3 mL) was treated with a suspension of $InC(SiMe_3)_3$ (0.686 g, 1.980 mmol) in hexane (10 mL). The mixture was heated to 60 °C for 1 h, whereupon a dark solution formed. After filtration and removing the solvent in vacuo, the dark red precipitate was recrystallized from cyclopentane by cooling to −30 °C. Yield: 0.384 g, red-brown crystals (65%), dec 152 °C. Anal. Calcd for $C_{40}H_{108}Si_{12}In_4Pd$: C, 32.20; H, 7.30. Found: C, 31.44, H, 7.35. ^{1}H NMR: δ 0.42 (s, 108H). $^{13}C\{^1H\}$ NMR: δ 64.7 (InC), 6.6. ($SiMe_3$).

[Pt$_2$(GaCp*)$_2$(μ^2-GaCp*)$_3$] (4a). $[Pt(COD)_2]$ (0.090 g, 0.217 mmol) and **1** (0.220 g, 0.217 mmol) were dissolved in toluene (5 mL) and stirred for 5 min at room temperature. GaCp* (0.044 g, 0.217 mmol) was then added, whereupon the color of the solution turned dark red. After removal of all volatiles in vacuo, the residue was dried in vacuo. Yield: 0.284 g (93%). All analytical data were in good agreement with the data reported.[5]

[Pt$_2$(GaCp*)(μ^2-GaCp*)$_3$(η^2-COD)] (4b). $[Pt(COD)_2]$ and **1** in a molar ratio of 1:1 were dissolved in hexane (5 mL) and stirred for 5 min at room temperature, whereupon a yellow precipitate formed. The yellow solid was isolated by means of cannulation, washed with a small amount of hexane at room temperature, and dried in vacuo. The product was dissolved in C_6D_6, and NMR experiments were performed immediately.

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[14] The $C(SiMe_3)_3$ groups are rotationally disordered, and six positions are observed for the three Si atoms with occupancy factor 0.5.

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^{1}H NMR: δ 4.67 (m, 2H), 3.00 (m, 2H), 2.20 (m, 8H), 2.04 (s, 15H), 1.99 (s, 45H). ^{13}C{^{1}H} NMR: δ 129.5, 114.5, 113.2, 69.9, 11.6, 10.6.

[PtPd(GaCp*)$_2$(μ^2-GaCp*)$_3$] (5a). [Pt(COD)$_2$] (0.064 g, 0.156 mmol) and **2** (0.144 g, 0.156 mmol) were dissolved in toluene (5 mL) and stirred for 5 min at room temperature. GaCp* (0.032 g, 0.156 mmol) was then added, whereupon the color of the solution turned dark red. After removal of all volatiles in vacuo, the residue was redissolved in diethyl ether (3 mL) and the product crystallized by slow cooling to −80 °C. Yield: 0.115 g (56%), dec 90 °C. Anal. Calcd for $C_{50}H_{75}Ga_5PdPt$: C, 45.28; H, 5.70. Found: C, 45.15; H, 5.82. ^{1}H NMR: δ 2.06 (s, 15H), 1.94 (s, 60H). ^{13}C{^{1}H} NMR: δ 114.1, 113.1, 11.5, 10.4.

[PtPd(GaCp*)(μ^2-GaCp*)$_3$(η^2-COD)] (5b). This compound was prepared analogously to **4b** using **2** instead of **1**. The product was dissolved in C_6D_6, and NMR experiments were performed immediately. ^{1}H NMR: δ 4.83 (m, 2H), 2.97 (m, 2H), 2.10 (m, 8H), 2.05 (s, 15H), 2.02 (s, 45H). ^{13}C{^{1}H} NMR: δ 114.3, 113.4, 64.9, 11.05, 10.4.

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Supporting Information Available: Listings of atomic coordinates, bond distances and angles, dihedral angles, and anisotropic thermal parameters for compounds **1** and **2** as well as details for the structural analysis and refinement of **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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