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[(dcpe)Pt(ECp*)$_2$] (E = Al, Ga): Synthesis, Structure, and Bonding Situation of the First Aluminum(I) and Gallium(I) Complexes of Phosphine-Substituted Transition Metal Centers

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Herein we describe the first phosphine-substituted transition metal complexes with terminal coordinated Cp*E ligands (E = Al, Ga; Cp* = pentamethylcyclopentadienyl). The reaction of [(dcpe)Pt(H)(CH$_2$*t*-Bu)] (dcpe = bis(dicyclohexylphosphino)ethane) with Cp*E yields the tetrahedrally coordinated complexes [(dcpe)Pt(AlCp*)$_2$] (**1**) and [(dcpe)Pt(GaCp*)$_2$] (**2**), respectively. Quantum-chemical DFT calculations on the model complexes [(dhpe)Pt(AlCp)$_2$] (**1M**) and [(dhpe)Pt(GaCp)$_2$] (**2M**; dhpe = diphosphinoethane) verify rather weak Pt−E bonds for both complexes. A comparison with the complexes [M(ER)$_4$] and [(CO)$_n$M−ER] shows that Cp*E represents a moderate σ-donor/π-acceptor and that the bond strength is strongly influenced by the ancillary ligands at the transition metal center; in particular, (CO)$_n$M fragments give more polar bonds than phosphine-substituted metal centers such as L$_2$Pt.

Introduction

Low-coordinated organometallic fragments ER of the group 13 elements (B to In) exhibiting the formal oxidation state +1 are of special interest as new ligands in transition metal complexes L$_n$M−E^{I}R (e.g., R = Cp*, C(SiMe$_3$)$_3$, Si(*t*-Bu)$_3$, 2,6-disubstituted aryl groups).[1] The numerous studies concerning this subject are limited to a large extent to the coordination of E^{I}R species to transition metal carbonyl fragments (CO)$_n$M. Only a few remarkable exceptions have to be emphasized, including the complexes synthesized by Schnöckel ([(CpNi)$_2$(μ_2-AlCp*)$_2$]),[2] Uhl ([Ni{EC(SiMe$_3$)$_3$}$_4$] (E = Ga, In)),[3] and Jutzi ([Ni(GaCp*)$_4$], [Cp*(Cp*Ga)$_2$Fe(GaCl$_2$)(THF)]).[4] The influence of ligands other than CO at the transition metal center M, e.g. regarding the stability of the M−E bond, is clearly a valid target for further investigations. Taking on this synthetic challenge and continuing our earlier work on low-valent earth metal compounds,[5] we have set out to prepare and investigate the first Al(I) and Ga(I) complexes of phosphine-substituted transition metal centers.

Results and Discussion

In 1990 we already found that the complex [(dcpe)Pt(H)(CH$_2$*t*-Bu)], first described by Whitesides et al.,[6] is not only suitable for oxidative additions of C−H bonds, as was known before, but also for insertions into E−C bonds (E = Al, Ga, In) to yield complexes with a Pt−E bond such as [(dcpe)Pt(ER$_2$)(R)] (E = Al, Ga; R = CH$_2$*t*-Bu and E = In; R = CH$_2$SiMe$_3$). The Pt/Ga and Pt/In compounds have been investigated by X-ray analysis, whereas the corresponding Pt−Al compound was identified spectroscopically by NMR, but could not be isolated yet.[7] As an intermediate in this kind of reaction, a reactive 14-valence-electron species of the formula [(dcpe)Pt] has been postulated, which is able to undergo oxidative additions or further ligand coor-

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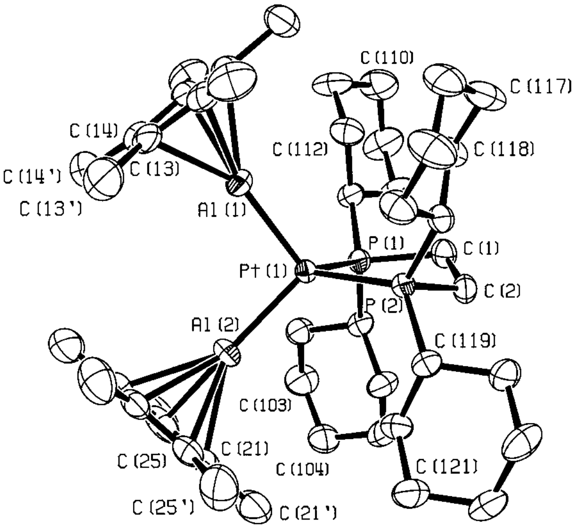
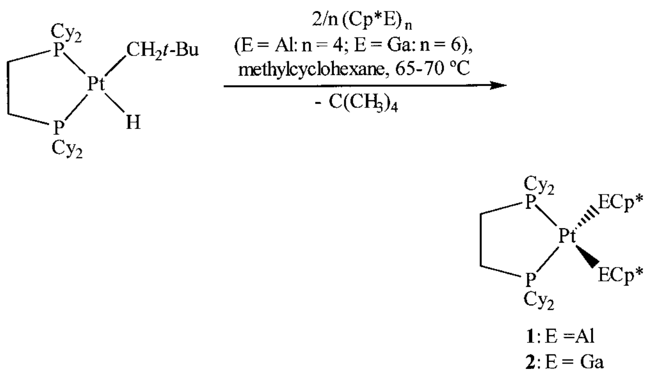


Figure 1. Molecular structure of [(dcpe)Pt(AlCp*)$_2$] (**1A**) with thermal ellipsoids at 50% probability.

Scheme 1



dination.[7] Our earlier work refers to the first possibility. We now want to present some examples of the second possibility, where the [(dcpe)Pt] fragment is trapped by coordination of the new ligands ER.

Synthesis of the Complexes [(dcpe)Pt(ECp*)$_2$]. The new complexes [(dcpe)Pt(ECp*)$_2$] (E = Al (**1**), Ga (**2**)) are formed quantitatively according to Scheme 1 (as determined on the basis of in situ NMR spectroscopy) and can be precipitated by slow evaporation of a toluene solution of **1** or by cooling a solution of complex **2** in pentane in the form of yellow crystals (about 45−50% practical yield of the analytically pure compounds).

The ^{31}P NMR spectra of the reaction solutions confirm the selective formation of **1** and **2**, respectively, and the complete disappearance of the platinum starting compound [(dcpe)Pt(H)(CH$_2$*t*-Bu)]. To the best of our knowledge complex **1** represents the only example of a fully structurally characterized organometallic compound including a direct unsupported Pt−Al bond.

Structure. According to the single-crystal structure analysis, each of the complexes **1** and **2** shows two independent molecules **A** and **B** (enantiomers) in the unit cell, which differ only slightly in their structural features; therefore, we restrict the discussion of the structures to the molecules **1A** and **2A**, respectively (Figures 1 and 2). Crystallographic parameters and data collection and refinement details are given in Table 1. The complexes [(dcpe)Pt(ECp*)$_2$] (E = Al (**1**), Ga (**2**)) crystallize in the monoclinic space group $P2_1/c$ ($Z = 8$).

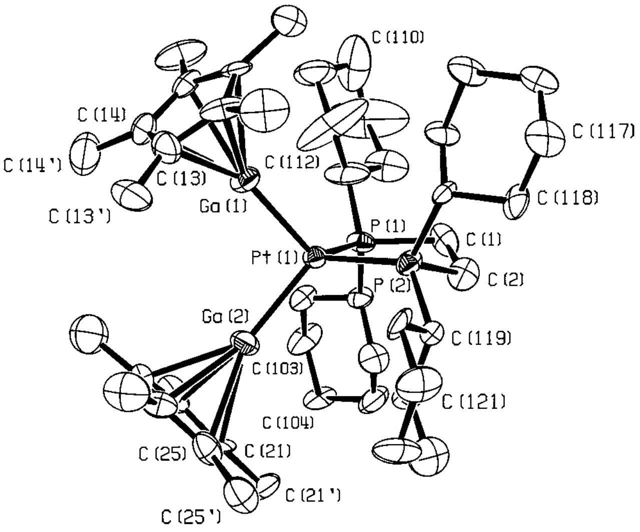


Figure 2. Molecular structure of [(dcpe)Pt(GaCp*)$_2$] (**2A**) with thermal ellipsoids at 50% probability.

Table 1. Crystallographic Data for [(dcpe)Pt(AlCp*)$_2$] (1) and [(dcpe)Pt(GaCp*)$_2$] (2)

	1	2
fw	942.08	1027.56
empirical formula	$C_{46}H_{78}Al_2P_2Pt$	$C_{46}H_{78}Ga_2P_2Pt$
cryst color, habit	yellow, rhombic	
cryst size, mm^3	0.40 × 0.35 × 0.30	0.60 × 0.36 × 0.20
temp, K	203(0)	193(2)
wavelength, Å	0.710 73, Mo Kα (graphite monochromator)	
cryst syst, space group	monoclinic, $P2_1/c$	
unit cell dimens		
a, Å	12.225(9)	12.260(3)
b, Å	19.123(14)	18.970(5)
c, Å	40.55(3)	40.507(11)
α, deg	90	90
β, deg	93.889(14)	93.813(13)
γ, deg	90	90
V, Å^3	9458(12)	9400(4)
Z	8	8
density (calcd), Mg/m^3	1.323	1.452
θ range for data collecn, deg	1.85−25.01	2.00−23.74
no. of rflns collected	46 988	12 894
no. of indep rflns	16 426 (R_{int} = 0.0640)	12 390 (R_{int} = 0.0564)
abs cor	semiempirical from ψ-scans	
final R_F ($I > 2\sigma(I)$)	R1 = 0.0452, wR2 = 0.0897	R1 = 0.0731, wR2 = 0.1220
R_{wF^2} (all data)	R1 = 0.0560, wR2 = 0.0936	R1 = 0.1558, wR2 = 0.1526
no. of params	909	939
largest diff peak and hole, e Å^{-3}	2.126 and −1.816	1.510 and −1.194
diffractometer used	Bruker-axs-SMART	Siemens P4
programs used	SHELXS-86, SHELXL-97	
structure refinement	full-matrix least squares on F^2	

The platinum center of both compounds **1A** and **2A** is, as expected, coordinated in a nearly tetrahedral mode by the chelate ligand dcpe and the two η^5-Cp*E units (idealized C_{2h} symmetry of the ensemble P(1)P(2)Pt(1)-E(1)E(2)), following the d^{10} configuration on the Pt^0 center as well as steric requirements, similar to the situation in phosphine complexes such as Pt(PEt$_3$)$_4$.[8a] These facts are in accordance with the value of 112°

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determined for the cone angle of Cp*Ga, which corresponds with the values determined for phosphine ligands such as PF_3 (104°) and PMe_3 (118°).[8b] The Pt−P distances as well as the Pt−H and Pt−Ga distances within each molecule of **1** and **2**, respectively, are almost identical within the accuracy of the measurement.

Exhibiting values of 2.327(2) and 2.335(2) Å, the Pt−Al distances in **1A** are distinctly shortened in comparison to the value of the shortest Pt−Al distance known for binary alloys of 2.52 Å.[9] An estimation of the Pt−Al distances by means of the sum of the covalent radii results in values from 2.71 to 2.77 Å. For the Al(1)−Pt(1)−Al(2) angle and the P(1)−Pt(1)−P(2) angle values of 97.37(8) and 90.38(7)° can be observed, which are narrowed compared to the typical tetrahedral angle. In addition, with respect to the tetrameric solid-state structure of $(AlCp^*)_4$ with Al−Al distances of 2.767(5)−2.773(4) Å,[10a] a long, clearly nonbonding Al(1)−Al(2) distance of 3.558 Å is found for molecule **1A**. In relation to the situation within the free ligand (gas phase: monomer, 2.015 Å)[10a,b] the distance $Cp^*_{centroid}$−Al is representative for the polarity of the M−E bond in bimetallic complexes including this ligand.[11] As expected, the average value of 1.967 Å found for **1A** is close to this limit and differs distinctly from the shortened $Cp^*_{centroid}$−Al distances of 1.819−1.776 Å in metal carbonyl complexes such as $[(CO)_5Cr{-}AlCp^*]$[11] and $[(CO)_4Fe{-}AlCp^*]$.[5] The latter is a consequence of the acceptor capability of the CO ligands at the transition metal center. The fragments $(CO)_nM$ favor a significantly polarized $M^{\delta-}{-}E^{\delta+}$ bond and a shortened (thus more polar) Cp*−E σ-bond[12] (for a discussion of ionic vs covalent contributions in main-group CpE compounds, see ref 12b). It is worth noting that a recent energy decomposition analysis of the $[(CO)_4Fe{-}ECp^*]$ (E = B−Tl) bonds has shown that the bonding interactions are caused by about 50% electrostatic attraction and by about 50% covalent interactions for E = Al−Tl. The Fe−B bond of $[(CO)_4Fe{-}BCp^*]$ exhibits a larger ionic character (62%) than those of the heavier group 13 complexes.[13]

The ^{27}Al NMR spectrum of **1** shows a broad signal with a chemical shift of −114.5 ppm, whereas the signals of $[(CO)_5Cr{-}AlCp^*]$[11] and $[(CO)_4Fe{-}AlCp^*]$[5] are observed at −26.1 and 0.4 ppm, respectively. The values reported for the Al(I) starting compound Cp*Al range from −80.7 ppm for the tetrameric species to −149 ppm for the monomeric unit,[10b] but the cation $Cp^*_2Al^+$, which is probably the most appropriate Al(III) compound for comparison to the Al(I) species Cp*Al, shows a chemical shift of −115.2 ppm.[10c] However, one should note that there are many different and sometimes subtle factors that influence the chemical shift within ^{27}Al NMR spectra, such that the use of chemical shift values to assign a relative oxidation state to Al is not meaningful, particularly when it is bonded to different transition metals with different coordination spheres.[14]

The bonding situation in **2** is analogous to the situation in **1**. The Pt−Ga distances in molecule **2A** (2.355(2)−2.367(2) Å) are clearly shortened in comparison with the Pt−Ga distance of 2.438(1) Å within the complex $[(dcpe)Pt\{Ga(CH_2t\text{-}Bu)_2\}(CH_2t\text{-}Bu)]$ (the only comparable example).[7a] An estimation of the Pt−Ga distances by means of the sum of the covalent radii results in values from 2.59 to 2.65 Å.[7a] In binary intermetallic phases the shortest Pt−Ga distance has been determined to a value of 2.45 Å.[15] Furthermore, the short Pt−Ga bonds and the small Ga(1)−Pt(1)−Ga(2) angle of 97.07(7)° cause a shortened nonbonding Ga(1)−Ga(2) distance of 3.538 Å, compared to the hexameric solid-state structure of $(GaCp^*)_6$ with longer Ga−Ga distances of 4.073(2)−4.173(3) Å.[10b] The $Cp^*_{centroid}$−Ga distances of 2.017 and 2.058 Å found for **2A** are close to the value for the free ligand (gas phase: monomer, 2.081 Å)[10b] and again differ distinctly from the $Cp^*_{centroid}$−Ga distances of 1.910−1.863 Å in metal carbonyl complexes with a highly polar character such as $[(CO)_5Cr{-}GaCp^*]$ and $[(CO)_4Fe{-}GaCp^*]$.[4,8b]

Theoretical Studies on Model Complexes. The structures of the model complexes $[(dhpe)Pt(ECp)_2]$ (E = Al (**1M**) and E = Ga (**2M**)) have been optimized at the DFT level of theory (Figure 3).[16] The comparison of the calculated and experimental bond lengths and angles shows that the structural data of **1M** and **2M** are in good agreement with the observed values of **1** and **2** (Table 2). The use of Cp instead of Cp* explains the somewhat longer E−C distances of the model compounds.[5]

Interestingly low values were obtained for the net charge transfer of the two CpE ligands to the Pt fragment (0.14 e for **1M** and 0.03 e for **2M**) (NBO method,[20] Table 3). This is a consequence of two opposing effects: the σ(Pt←E) donation (0.33 e for each Pt−Al bond and 0.19 e for each Pt−Ga bond) and the π(Pt→E) back-donation (0.29 e for one Pt−Al bond and 0.22 e for one Pt−Ga bond). Accordingly, the CpGa ligand in **2M** is a moderate π-acceptor. In contrast to that, the NBO analysis of the hypothetical homoleptic complexes $Pt(AlCH_3)_4$ and $Pt(GaCH_3)_4$ gave significantly stronger π(Pt→E) back-donation of 0.56 e (E = Al) and

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[16] In **1M** and **2M** Cp* has been replaced by Cp and the cyclohexyl substituents have been replaced by hydrogen atoms. The DFT calculations were performed with the gradient-corrected exchange functional of Becke[17a] and the correlation functional of Perdew[17b] (BP86). The Ahlrichs SVP basis was used throughout.[18a] This basis set contains a quasi-relativistic pseudopotential for Pt[18b] with a (7s6p5d) valence basis set in a [211111/411/41] contraction especially optimized for the Ahlrichs SVP basis.[18c] Geometry optimizations were carried out using the RI approximation as implemented in the Turbomole program package.[19a] NBO analysis was carried out using Gaussian98.[19b] All stationary points were characterized as minima by full calculation of the Hessian matrix.

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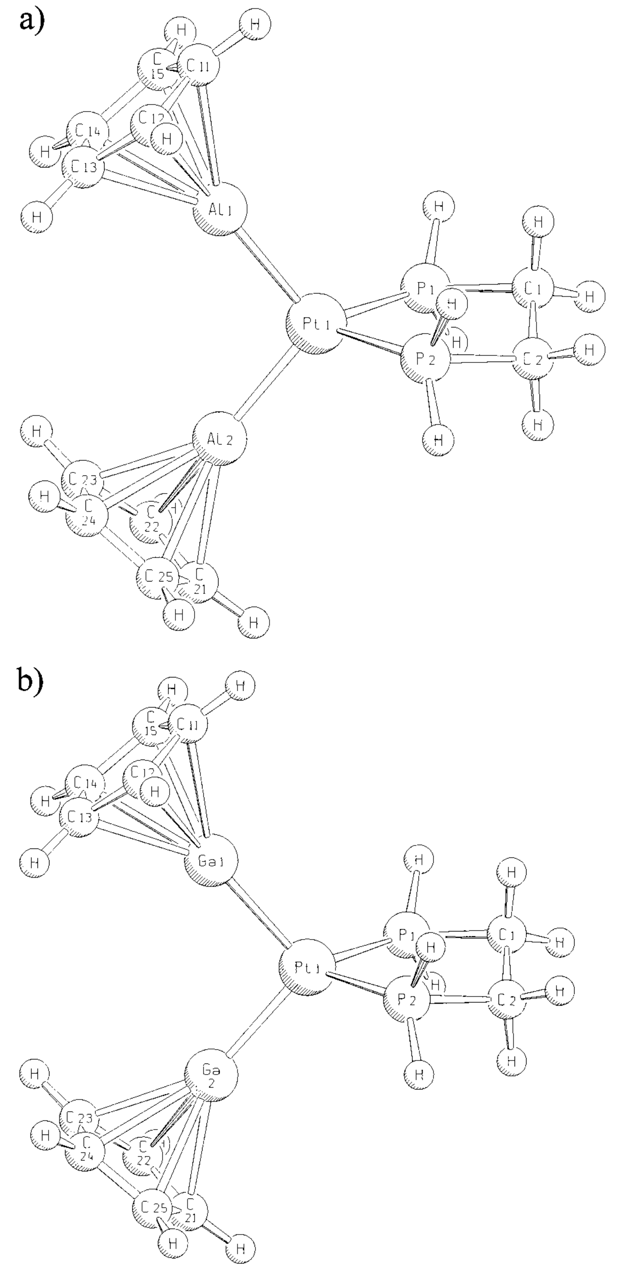

Figure 3. Calculated structures of (a) **1M** and (b) **2M**, optimized by DFT methods.

0.50 e (E = Ga) and even larger values for the charge transfer $\sigma(\mathrm{Pt} \leftarrow \mathrm{E})$ of 0.73 e (E = Al) and 0.65 e (E = Ga).[21] The M→ER π-back-donation is strongly influenced by the organic group R.[22]

The Pt−E bonds in the model complexes **1M** and **2M** are less polarized ($q(\mathrm{Pt}) = -0.28$ and $q(\mathrm{Al}) = +0.68$ in **1M**; $q(\mathrm{Pt}) = -0.21$ and $q(\mathrm{Ga}) = +0.59$ in **2M**) than in the comparable model complexes $\mathrm{Pt(EMe)_4}$ (E = Al, $q(\mathrm{Pt}) = -0.69$ and $q(\mathrm{Al}) = +0.77$; E = Ga, $q(\mathrm{Pt}) = -0.58$ and $q(\mathrm{Ga}) = +0.69$).[21] According to that, the calculated Pt−E dissociation energies for **1M** with $D_e = 29.6$ kcal/mol and for **2M** with $D_e = 18.3$ kcal/mol are distinctly lower compared to those for $\mathrm{Pt(AlCH_3)_4}$ ($D_e = 62.8$ kcal/mol) and $\mathrm{Pt(GaCH_3)_4}$ ($D_e = 48.9$ kcal/mol).[21] In this context the effect of the CO ligands can be clearly demonstrated, also. In complexes of the type $\mathrm{(CO)_nM{-}ER}$ the bonds exhibit an even greater polar character ($q(\mathrm{Fe}) = -0.57$, $q(\mathrm{Al}) = +1.21$)[5] and therefore are stronger than in **1M** and **2M** ($D_e[\mathrm{CpAl{-}Fe(CO)_4}] = 53.1$ kcal/mol, $D_e[\mathrm{(H_3Si)_2NGa{-}W(CO)_5}] = 36.7$ kcal/mol, $D_e[\mathrm{(H_3Si)_2NAl{-}W(CO)_5}] = 44.4$ kcal/mol).[21] As a consequence of all investigations[5,21,23−25] the M−ER bond is decisively influenced by the polarity $\mathrm{M}^{\delta-}{-}\mathrm{E}^{\delta+}$, but the distances M−E are not a suitable measure for the bond order and strength of these compounds.[25] The covalent bond orders $P(\mathrm{Pt{-}E})$ are 0.52 (**1M**) and 0.42 (**2M**), corresponding to approximately half a single bond, as is the case for $\mathrm{Pt(ECH_3)_4}$ with $P(\mathrm{Pt{-}Al}) = P(\mathrm{Pt{-}Ga}) = 0.49$.[21] It is interesting to note that the significantly larger donation and back-donation in compounds $\mathrm{Pt(ECH_3)_4}$ does not lead to a higher bond order, which means that the increase in the charge exchange enhances the Coulombic interactions more than the covalent interactions.

The comparatively weak Pt−E bonds of **1M** and **2M** are the result of the low acceptor property of the [(dcpe)-Pt] fragment and moderate σ-donor/π-acceptor capability of the Al and Ga centers, due to the Cp ligand. Thus, the still unknown homoleptic complexes of the type $[\mathrm{Pt(ECp^*)}_n]$ should be more labile than their alkyl relatives $[\mathrm{Pt(ER)}_n]$. The present work shows that two factors are important for the bonding situation in transition metal group 13 metal compounds: the ligands L at the transition metal center as well as the groups R at the group 13 metal.[26] They determine the bonding situation in the complexes $[\mathrm{L}_n\mathrm{M(ER)}_m]$ and permit the variation of the charge distribution and the bond strength over an unusually wide range. The strongest influence can be assigned to the π-acidic carbonyl ligands, which effectively compete with the ER ligands in the corresponding compounds of the type $[\mathrm{(CO)}_n\mathrm{M{-}ER}]$. Even the idea of a reduction of M through coordination of ECp* as has been proposed for this series of compounds leading to a formulation of the oxidation state +3 for E.[10b] However, this seems to be questionable: at least it is not of relevance in the present case.

Experimental Section

General Comments. All manipulations were carried out under a purified argon atmosphere using standard vacuum

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[25] The partial charges alone are not sufficient for an estimation of the strength of the charge interactions. The three-dimensional distribution of the electron density, which is strongly influenced by the valence configurations of the bonding partners, plays an important role in the bonding region, also.

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for 1, 1M, 2, and 2M

	[(dcpe)Pt(AlCp*)$_2$] (**1**)	[(dhpe)Pt(AlCp)$_2$] (**1M**)		[(dcpe)Pt(GaCp*)$_2$] (**2**)	[(dhpe)Pt(GaCp)$_2$] (**2M**)
Pt(1)−Al(1)	2.327(2)	2.358	Pt(1)−Ga(1)	2.355(2)	2.439
Pt(1)−Al(2)	2.335(2)	2.358	Pt(1)−Ga(2)	2.367(2)	2.439
Al(1)−Al(2)	3.502	3.659	Ga(1)−Ga(2)	3.538	3.680
Pt(1)−P(1)	2.2915(19)	2.353	Pt(1)−P(1)	2.251(4)	2.326
Pt(1)−P(2)	2.2938(18)	2.353	Pt(1)−P(2)	2.256(5)	2.326
Al(1)−C(11)	2.313(6)	2.367	Ga(1)−C(11)	2.39(2)	2.445
Al(1)−C(12)	2.288(6)	2.356	Ga(1)−C(12)	2.33(2)	2.446
Al(1)−C(13)	2.284(6)	2.343	Ga(1)−C(13)	2.29(2)	2.442
Al(1)−C(14)	2.302(7)	2.345	Ga(1)−C(14)	2.37(2)	2.442
Al(1)−C(15)	2.322(6)	2.360	Ga(1)−C(15)	2.38(2)	2.444
Al(2)−C(21)	2.306(7)	2.367	Ga(2)−C(21)	2.40(2)	2.445
Al(2)−C(22)	2.291(6)	2.356	Ga(2)−C(22)	2.36(2)	2.446
Al(2)−C(23)	2.310(6)	2.343	Ga(2)−C(23)	2.32(2)	2.442
Al(2)−C(24)	2.332(6)	2.345	Ga(2)−C(24)	2.37(2)	2.442
Al(2)−C(25)	2.334(7)	2.360	Ga(2)−C(25)	2.44(2)	2.444
Cp*$_{\text{centroid}}$−Al(1)	1.958	2.028	Cp*$_{\text{centroid}}$−Ga(1)	2.017	2.122
Cp*$_{\text{centroid}}$−Al(2)	1.975	2.028	Cp*$_{\text{centroid}}$−Ga(2)	2.058	2.122
Pt(2)−Al(3)	2.326(2)		Pt(2)−Ga(3)	2.382(2)	
Pt(2)−Al(4)	2.317(2)		Pt(2)−Ga(4)	2.371(2)	
Al(3)−Al(4)	3.558		Ga(3)−Ga(4)	3.510	
Pt(2)−P(3)	2.279(2)		Pt(2)−P(3)	2.266(4)	
Pt(2)−P(4)	2.2796(19)		Pt(2)−P(4)	2.264(5)	
Al(3)−C(31)	2.317(7)		Ga(3)−C(31)	2.42(2)	
Al(4)−C(41)	2.312(6)		Ga(4)−C(41)	2.36(2)	
Cp*$_{\text{centroid}}$−Al(3)	1.981		Cp*$_{\text{centroid}}$−Ga(3)	2.067	
Cp*$_{\text{centroid}}$−Al(4)	1.952		Cp*$_{\text{centroid}}$−Ga(4)	2.033	
Al(1)−Pt(1)−Al(2)	97.37(8)	103.2	Ga(1)−Pt(1)−Ga(2)	97.07(7)	99.9
P(1)−Pt(1)−P(2)	90.38(7)	88.8	P(1)−Pt(1)−P(2)	92.2(2)	90.5
P(1)−Pt(1)−Al(1)	115.27(6)	116.0	P(1)−Pt(1)−Ga(1)	119.06(13)	116.8
P(2)−Pt(1)−Al(2)	117.50(7)	116.0	P(2)−Pt(1)−Ga(2)	118.35(13)	116.8
P(1)−Pt(1)−Al(2)	119.40(7)	116.7	P(1)−Pt(1)−Ga(2)	117.58(12)	117.2
P(2)−Pt(1)−Al(1)	118.76(6)	116.7	P(2)−Pt(1)−Ga(1)	114.31(13)	117.2
C(2)−C(1)−P(1)	114.1(4)	111.6	C(2)−C(1)−P(1)	112.7(12)	111.9
C(1)−C(2)−P(2)	114.0(4)	111.6	C(1)−C(2)−P(2)	114.3(12)	111.9
C(1)−P(1)−Pt(1)	105.2(2)	105.9	C(1)−P(1)−Pt(1)	104.5(5)	104.7
C(2)−P(2)−Pt(1)	105.23(19)	105.9	C(2)−P(2)−Pt(1)	103.3(6)	104.7
Al(3)−Pt(2)−Al(4)	100.02(7)		Ga(3)−Pt(2)−Ga(4)	95.21(7)	
P(3)−Pt(2)−P(4)	90.63(6)		P(3)−Pt(2)−P(4)	92.3(2)	

Table 3. NBO Analysis of [(dhpe)Pt(ECp)$_2$] (E = Al, Ga) at BP86/SVP[a]

E	q[(dhpe)Pt]	q(Pt)	q(E)	q(Cp)	p$_x$(E)[b]	p$_y$(E)[b]	p$_z$(E)	Δq(E)[d]	Δq_π(E)[d]	Δq_σ(E)[d]	Δq(Cp)[d]	P(Pt−E)
Al	−0.14	−0.28	0.68	−0.61	0.28	0.27	0.29	+0.04	−0.29	+0.33	+0.03	0.52
Ga	−0.03	−0.21	0.59	−0.58	0.25	0.27	0.23	−0.03	−0.22	+0.19	+0.04	0.42
Al			0.65[c]	−0.65[c]	0.13[c]	0.13[c]	0.21[c]					
Ga			0.62[c]	−0.62[c]	0.15[c]	0.15[c]	0.15[c]					

[a] Partial charges q, p orbital populations, difference of the p populations, charges of the complexes and the free ligand Δq, Wiberg bond index P. [b] p(π) AO of E. [c] Values for the free ligand ECp; calculated in the geometry of the complexes. [d] Negative values represent a higher electronic charge, and positive values represent a lower electronic charge in the complex relative to the free ligand.

techniques. The solvents were distilled over standard drying agents and stored over molecular sieves prior to use. [(dcpe)Pt(H)(CH$_2$$t$-Bu)],[6] (GaCp*)$_6$,[8b] and (AlCp*)$_4$[27] were prepared according to literature methods. The decomposition point determinations were performed in a sealed glass capillary using a Büchi SMP-20 melting point apparatus. Elemental analyses were performed by the Microanalytical Laboratory of the Ruhr-Universität Bochum. The NMR spectra were recorded in benzene-d_6 at 298 K using a Bruker Avance DPX 250 spectrometer (^{1}H, 250.1 MHz; ^{13}C, 62.9 MHz; ^{31}P, 101.3 MHz; ^{27}Al, 65.2 MHz). Chemical shifts are reported in ppm and were referenced to the solvent resonances as internal standards and [Al(H$_2$O)$_6$]$^{3+}$ and orthophosphoric acid as external standards, respectively. IR data were collected using a Perkin-Elmer 1720 X-FT spectrometer. The samples were measured as KBr pellets.

Preparation of [(dcpe)Pt(AlCp*)$_2$] (1). An amount of 100 mg (0.145 mmol) of [(dcpe)Pt(H)(CH$_2$$t$-Bu)] and 47 mg (0.073 mmol) of (AlCp*)$_4$ were suspended in 0.5 mL of methylcyclohexane. After the sample was heated for 4 h at 65 °C in an evacuated and sealed NMR tube, the reaction was complete according to the ^{31}P NMR spectrum and all volatile components were removed in vacuo, whereby the raw product could be obtained in quantitative yield. The resulting yellowish solid was washed several times with a small amount of pentane and recrystallized by slow evaporation of a solution of **1** in toluene. Yield of crystalline product: 63 mg (46%). Dec pt: 108 °C. ^{1}H NMR: δ 2.21 (s, 30 H, 2 Cp*), 2.02−0.97 (m, 48 H, Cy$_2$P(CH$_2$)$_2$-PCy$_2$). ^{13}C NMR: δ 113.4, 35.8, 33.18, 30.29, 29.3, 28.0, 27.3, 27.0, 26.8, 23.3, 11.5. ^{31}P NMR: δ 52.5 (s with Pt satellites, $^1J_{\text{P−Pt}} = 3482$ Hz). ^{27}Al NMR (C$_6$D$_6$): δ −114.5. IR (KBr): 2919 (s), 2842 (s), 1443 (s), 1371 (m), 1257 (s), 1171 (w), 1095 (s), 1014 (s), 847 (m), 800 (m), 733 (m), 700 (m), 638 (w), 523 (w), 448 (m) cm^{-1}. Anal. Calcd for C$_{46}$H$_{78}$Al$_2$P$_2$Pt: C, 58.65; H, 8.34. Found: C, 58.93; H, 8.59.

Preparation of [(dcpe)Pt(GaCp*)$_2$] (2). An amount of 100 mg (0.145 mmol) of [(dcpe)Pt(H)(CH$_2$$t$-Bu)] and 59 mg (0.048 mmol) of (GaCp*)$_6$ were suspended in 0.5 mL of methylcyclohexane. After the sample was heated for 20 min at 70 °C in

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[27] Schulz, S.; Roesky, H. W.; Koch, H. J.; Sheldrick, G. M.; Stalke, D.; Kuhn, A. *Angew. Chem.* **1993**, *105*, 1828−1830; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1729−1731.

an evacuated and sealed NMR tube, the reaction was complete according to the ^{31}P NMR spectrum and all volatile components were removed in vacuo, whereby the raw product could be obtained in quantitave yield. The resulting yellowish solid was washed several times with a small amount of pentane and recrystallized by cooling slowly a solution of **1** in 5 mL of hot pentane to −35 °C. Yield of the crystalline product: 75 mg (50%). Dec pt: 104 °C. ^1H NMR (C_6D_6): δ 2.37 (s, 30 H, 2 Cp*), 1.95−0.99 (m, 48 H, $Cy_2P(CH_2)_2PCy_2$). ^{13}C NMR (C_6D_6): 113.1, 38.3. 34.5, 30.2, 29.2, 28.0, 27.9, 27.1, 22.9, 11.1. ^{31}P NMR (C_6D_6): δ 53.6 (s with Pt satellites, $^1J_{P-Pt} = 4625$ Hz). IR (KBr): 2911 (s), 1446 (s), 1380 (m), 1262 (m), 1168 (w), 1102 (s), 1005 (s),887 (w) 849 (m), 799 (m), 736 (m), 642 (m), 526 (m), 457 (w) cm^{-1}. Anal. Calcd for $C_{46}H_{78}Ga_2P_2Pt$: C, 53.77; H, 7.65. Found: C, 53.42; H, 7.71.

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Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond lengths and angles for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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