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Syntheses and Crystal Structures of Intramolecularly Stabilized Organo Aluminum, Gallium, and Indium Compounds Containing the *C,P*-Chelating *o*-Carboranylphosphino Ligand [*o*-$C_2B_{10}H_{10}(CH_2PMe_2)$-*C,P*]$^-$ (Cab^{C,P}). X-ray Structure of Pentacoordinated Group 13 Metal Complexes (Cab^{C,P})$_2$MX (M = Ga, In; X = Cl)

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The new phosphino-*o*-carborane ligand HCab^P (**1**; Cab^P = *closo*-1-[(dimethylphosphino)methyl]-1,2-dicarbaborane) with substitution at the carbon and phosphorus atoms was used for the synthesis of the *C,P*-chelated bis(phosphino-*o*-carborane) group 13 metal complexes (Cab^{C,P})$_2$MX (**4**). Reaction of LiCab^{C,P} (**2**; LiCab^{C,P} = *closo*-1-[(dimethylphosphino)methyl]-2-lithio-*o*-carborane) with MX_3 (M = Al, Ga, In; X = Cl, Br) in a 1:1 molar ratio produced the tetracoordinated metallacyclic compound (Cab^{C,P})MX_2 (**3**), in which the metal atom was stabilized via intramolecular *C,P*-coordination. The corresponding bis-chelate complexes, (Cab^{C,P})$_2$MX (**4**), were synthesized by reacting **3** with an additional *C,P*-chelate ligand **2**. Complexes **4** were also formed upon reaction of **2** with MX_3 in a 2:1 molar ratio. The ^{1}H and ^{13}C NMR spectra of **4** revealed that intramolecular M−P coordination occurs in solution, resulting in the formation of pentacoordinated complexes (Cab^{C,P})$_2$MX (**4**). The trigonal bipyramidal (*tbp*) coordination of the metal center was confirmed by single-crystal X-ray determination of the complexes (Cab^{C,P})$_2$GaCl (**4b**) and (Cab^{C,P})$_2$InCl (**4c**). Similar intramolecularly base-stabilized gallanes, (Cab^{C,P})GaMe$_2$ (**5b**) and (Cab^{C,P})$_2$GaMe (**6b**), which were tetra- and pentacoordinated, respectively, were synthesized from the reaction of **3b** and **4b** with LiMe or MeMgBr. The Lewis acid **3b** added the base PMe_3 to yield the pentacoordinated adduct (Cab^{C,P})$GaCl_2$·PMe_3 (**7b**). The ^{1}H and ^{13}C NMR spectra revealed that intramolecular Ga−P coordination occurs in solution, resulting in a pentacoordinated structure.

Introduction

Motivated by an interest in the coordination behavior of organometallic compounds containing the bidentate ligand 2-[(dimethylamino)methyl]phenyl, [*o*-(Me_2NCH_2)-C_6H_4],[1] we began a systematic study of the use of phosphino-*o*-carborane molecules as supporting ligands for group 13 metal complexes. In the related amino-*o*-carboranyl ligand system HCab^N [HCab^N = *closo*-1-{(dimethylamino)methyl}-1,2-dicarbaborane], tetracoordinated complexes of type (Cab^{C,N})GaX$_2$ (X = Cl or Me) have been successfully isolated and structurally characterized.[2] However, due to the unstable nature of organogallanes, a pentacoordinated geometry has not been established using the amino-*o*-carboranyl ligand system. To stabilize the Lewis acidic metal center as well as the higher coordination geometry by the *o*-carboranyl ligand backbone, in the present work we have used a PMe_2 tether instead of a NMe_2 sidearm. Indeed, by introducing the PMe_2 sidearm, a series of pentacoordinated group 13 metal complexes were produced in high yields. These newly formed pentacoordinated gallium species showed enhanced stability, which in turn explained the balanced electronic and steric effects derived from using the phosphine-tethered *o*-carboranyl ligand system.

In this study, group 13 organometallic complexes of bis-*C,P*-chelates (Cab^{C,P})$_2$MX (**4**) (M = Al, Ga, In; X = Cl, Br), in which the metal centers may be regarded as having pentacoordination as a result of intramolecular M−P coordination, have been prepared and structurally characterized. In addition, the tetracoordinated gallium complex **3b** was further tested for its reaction with PMe_3, which allowed the synthesis of an intramolecularly stabilized pentacoordinated gallium complex. To the best of our knowledge, this is the first report of a *C,P*-chelating *o*-carboranylphosphine being intramolecularly coordinated to a group 13 metal atom, thereby improving the stability of the pentacoordinated metal center. Here we report the detailed synthesis and complete characterization of a series of organometallic

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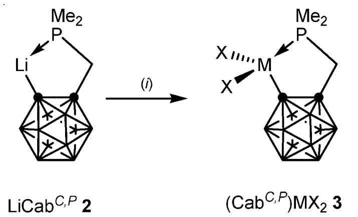
group 13 compounds containing the potentially bidentate phosphino-*o*-carboranyl ligand. The crystallographic and spectroscopic characteristics of these complexes reveal strong coordination effects of the phosphorus donor in the phosphino-*o*-carboranyl ligand system.

Results and Discussion

We recently prepared gallium complexes of the type $(\mathrm{Cab}^{C,N})\mathrm{GaX}_2$ (X = Cl or Me),[2] which involve the *C,N*-chelate amino-*o*-carboranyl ligand system. We observed that in this ligand system, as the incoming metal becomes bigger, the probability of forming the desired intramolecularly stabilized *C,N*-chelate amino-*o*-carboranyl decreases unless specific electronic factors intervene. Thus, in the present work we incorporated a strong donor sidearm such as the dimethylphosphino group onto the *o*-carboranyl ligand backbone in order to increase the stability of the corresponding Lewis acidic metal center. Such variations of the sidearm donor atoms have the potential to enable rational modifications that can be tuned to stabilize desired structural characteristics such as bis-chelates. In this respect, we investigated the synthesis of intramolecularly coordinated group 13 metal complexes bearing a phosphine donor unit, which we conjectured would stabilize the desired Lewis acidic metal moiety. In this study, we were able to demonstrate the suitability of the unique *C,P*-chelate phosphino-*o*-carboranyl ligand system to stabilize our desired pentacoordinated group 13 metal complexes.

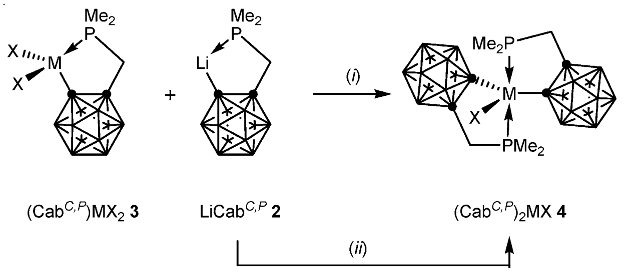
Preparation of Tetracoordinated Group 13 Metal Complexes. The new bidentate ligand *closo*-1-[(dimethylphosphino)methyl]-1,2-dicarbaborane (HCab^{P}) (**1**) was prepared by applying a standard procedure to phosphinomethyl-*o*-carborane.[3] The intramolecularly stabilized tetracoordinated mono(*C,P*-chelate) complexes, $(\mathrm{Cab}^{C,P})\mathrm{MX}_2$ (M = Al, Ga, In; X = Cl, Br) (**3**), were synthesized in toluene from the appropriate metal reagents MX_3 and the lithium compound $\mathrm{LiCab}^{C,P}$ (**2**). The $(\mathrm{Cab}^{C,P})\mathrm{MX}_2$ system is stabilized by the formation of a five-membered chelate ring. Compounds **3** were purified by low-temperature recrystallization in toluene. Satisfactory elemental analyses were obtained for compounds **3**, and the ^{1}H and ^{13}C NMR spectral data were consistent with the presence of the bidentate (phosphinomethyl)-*o*-carboranyl ligand. Compounds **3** in solution were deduced to have C_s symmetry from the ^{1}H NMR spectra, which contained a singlet peak corresponding to the protons in PMe_2 and a singlet peak corresponding to the protons in the PCH_2 group. The signals for both the PMe_2 and PCH_2 functional groups in **3** were at lower field than for ligand **1**, consistent with coordination of the phosphine sidearm and formation of a stable five-membered *C,P*-chelate ring.

Scheme 1. Synthesis of Mono(phosphino-*o*-carboranyl) Group 13 Metal Compounds[a]



[a] Legend: (*i*) MX_3 (M = Al, Ga, In; X = Cl, Br), toluene, −78 °C.

Scheme 2. Synthesis of Bis(phosphino-*o*-carboranyl) Group 13 Metal Compounds[a]



[a] Legend: (*i*) toluene, −78 °C; (*ii*) 1/2 MX_3 (M = Al **a**, Ga **b**, In **c**; X = Cl, Br), toluene, −78 °C.

Preparation of Pentacoordinated Group 13 Metal Complexes. The bis(*C,P*-chelate) complexes $(\mathrm{Cab}^{C,P})_2$-MCl (**4**) were obtained by reacting **3** with an additional lithium reagent $\mathrm{LiCab}^{C,P}$ (**2**). Alternatively, bis(*C,P*-chelate) (**4**) can be obtained via direct metalation with the ligand **2**. Thus, the reaction of 2 equiv of **2** with MX_3 afforded a series of bis-chelates $(\mathrm{Cab}^{C,P})_2\mathrm{MX}$ (M = Al **a**, Ga **b**, In **c**; X = Cl, Br) (**4**) in 52−73% yield (Scheme 2). The driving force for this reaction is the formation of the intramolecular P→M coordination in **4**. The stabilization of **4** is due to the formation of a five-membered chelate ring. Compounds **4** were moderately stable in air and showed only slow decomposition when in contact

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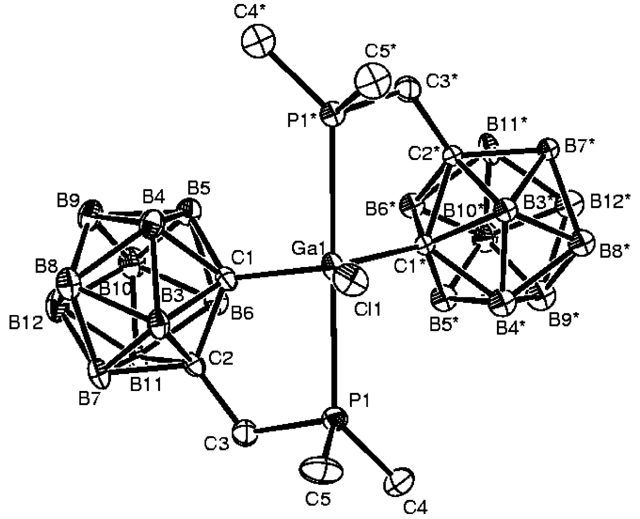

Figure 1. Molecular structure of **4b** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms and solvent have been omitted for clarity.

with moisture. Compounds **4** were purified by low-temperature recrystallization in toluene (colorless crystals, mp 220−222 °C). Satisfactory elemental analyses were obtained for compounds **4**, and the ^{1}H and ^{13}C NMR spectral data were consistent with the presence of the bidentate phosphinomethyl-*o*-carboranyl ligand **1** (see Experimental Section).

Indeed, the ^{1}H NMR spectrum consists of two singlets from the PMe_2 resonances (at δ 1.92 and 2.20 ppm) and an AB pattern for the PCH_2 protons [at δ 2.28 and 3.52 (J_{gem} = 10 Hz)]. This result demonstrates that, under these conditions, the PMe_2 and PCH_2 hydrogen atoms are diastereotopic and are consistent with the coordination of at least one PMe_2 ligand to the gallium atom. Furthermore, the appearance of the diastereotopic PMe_2 proton signals at lower field relative to the chemical shift of these protons in the free ligand $HCab^P$(**1**) also provides evidence of M−P coordination. This observation is consistent with similar findings for the general intramolecularly coordinated metal complexes of the $HCab^N$ ligand system.[2,4] Furthermore, the observation in the ^{1}H NMR spectrum of only one set of lines for the PMe_2 and PCH_2 protons for the two *o*-carboranylphosphine groups of the compound suggests the presence of only molecules in the *trans* conformation in solution. If the *cis* isomer had been present, two sets of lines of equal intensity, one for each type of proton, would have been expected. Since only one pattern is observed for the two *o*-carboranylphosphine groups, compound **4** will most likely have the stereochemistry shown in Scheme 2.

X-ray structural determinations of compounds **4b** and **4c** authenticated the expected trigonal bipyramid geometries illustrated in Figures 1 and 2, wherein the P donors occupy the axial coordination site. The overall geometry is similar to that found in the diarylamino complexes L_2MCl (L = $PhCH_2NMe_2$; M = Al, Ga, In).[5] Thus, the gallium or indium metal atom has a distorted trigonal bipyramid geometry with the two phosphorus donor atoms in the axial positions and two carbon atoms of the *o*-carboranyl unit and the chloride ligand in the equatorial plane. The P_2C_2MCl (M = Ga, In) portion of both **4b** and **4c** approaches an ideal trigonal bipyramidal geometry, with a P−M−P bond angle of 175.0(2)° for Ga and 176.6(1)° for In and a Cl−M−P bond angle of 87.5(9)° for Ga and 88.3(5)° for In. Angular distortions of the trigonal bipyramids arise from the geometric constraints associated with the bite angle of the bidentate ligands [P−M−C angle of 83.5(4)° for Ga and 81.2(2)° for In] in the presence of the nearly linear P−M−P bond angle. The Ga−P and In−P bond distances of 2.650(3) and 2.732(2) Å are substantially longer than the corresponding normal values for Ga−P (~2.4 Å) and In−P (~2.6 Å) single bonds.[6,7] It has been noted that the apical bonds in trigonal bipyramid complexes are generally weaker than those in the equatorial plane.[8] This type of trigonal bipyramidal structure has been observed for $Al[o\text{-}(Ph_2PCH_2)C_6H_4]_3$, in which the central aluminum metal atom is coordinated to three carbon atoms in the equatorial plane and two of the three phosphino functions in axial positions.[9]

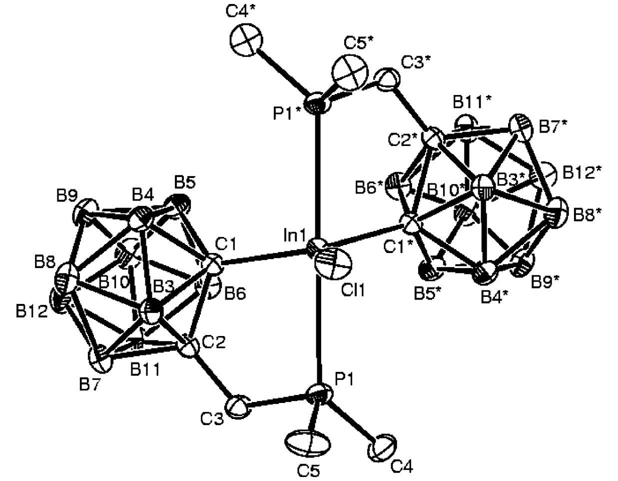

Figure 2. Molecular structure of **4c** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms and solvent have been omitted for clarity.

Ideal Geometries Optimized by Density Functional Theory (DFT) Calculations of Pentacoordinated Group 13 Metal Complexes. To examine the stabilizing influence of the chelating phosphino-*o*-carboranyl ligand on **4**, we performed a series of density functional calculations on the model complexes **4b** and

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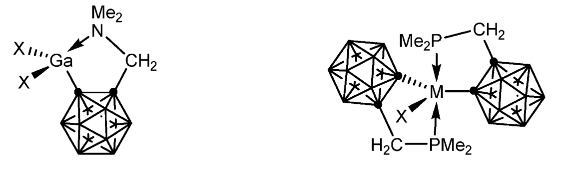
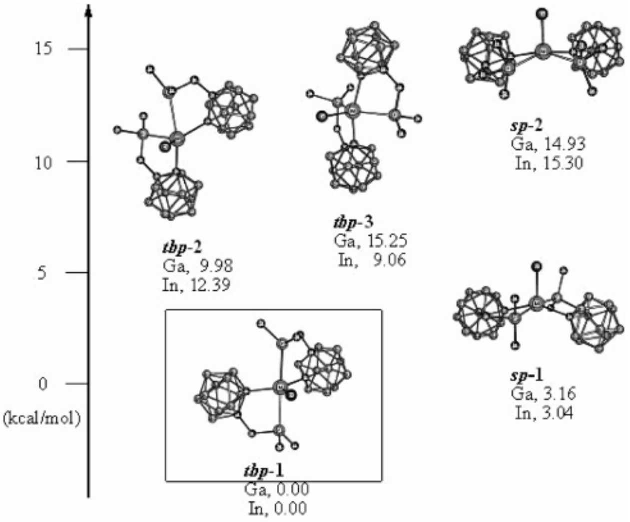
Chart 1. Stable Geometries Derived from the Use of Ancillary Ligand Systems ($\mathrm{Cab}^{C,N}$ and $\mathrm{Cab}^{C,P}$)



Stable tetra-coordinated $(\mathrm{Cab}^{C,N})\mathrm{GaX}_2$ Stable penta-cordinated $(\mathrm{Cab}^{C,P})_2\mathrm{MX}$

Chart 2. Optimized Geometry of Pentacoordinated Gallium and Indium Complexes



4c, the optimized structures of which are shown in Chart 2. The coordination sphere of the metal center included the two carbon and two phosphorus atoms of the two *C,P*-chelating *o*-carboranyl phosphine anions and was completed by one chloride ligand. This pentacoordinate geometry has five possible geometrical isomers, belonging to either the trigonal bipyramidal (*tbp*) or square pyramidal (*sp*) subgroups. Among these *tbp* and *sp* subgroups, an additional three and two geometrical isomers, respectively, would be possible depending on the site preference of the carbon and phosphorus atoms of the *C,P*-chelating ligand. Therefore, the structures of each of the bis-chelates **4b** and **4c**, shown in Chart 2, were optimized using the Amsterdam Density Functional (ADF) program, and the results are shown in the Supporting Information. The structural analysis of **4b** and **4c** revealed that the optimal geometry is the *tbp*-1 geometry shown in Chart 2, which has two phosphine donors in axial positions. A possible explanation for why this geometry is favored would be that the small and hard carbon donor atom prefers an equatorial position (sp^2 hybrid orbital), whereas the large and soft phosphorus donor atom prefers an axial position (dp hybrid orbital). As can be seen in Table 4, this combination gives the shortest bond distance for each donor atom, indicating the strongest interaction between the ligand and the metal. These calculations confirmed that the structures of **4b** and **4c** fit quite neatly with the *tbp* geometry of the model complexes $(\mathrm{Cab}^{C,P})_2\mathrm{MCl}$ (M = Ga **4b**, In **4c**). The main structural features of the calculated structures of **4b** and **4c**, including the most significant geometrical parameters, are in good agreement with those determined by X-ray crystallographic methods (see Supporting Information).

Reactivity of Tetra- and Pentacoordinated Gallium Complexes. When compounds $(\mathrm{Cab}^{C,P})\mathrm{GaX}_2$ (**3b**) and $(\mathrm{Cab}^{C,P})_2\mathrm{GaX}$ (**4b**) were reacted with 1 or 2 equiv of MeLi or MeMgBr reagent, the corresponding mono- and dimethylated compounds $(\mathrm{Cab}^{C,P})\mathrm{GaMe}_2$ (**5b**) and $(\mathrm{Cab}^{C,P})_2\mathrm{GaMe}$ (**6b**) were obtained. According to Scheme 3, chlorine ions of compounds **3b** and **4b** can be selectively replaced by methyl ligands to give the crystalline compounds **5b** and **6b**, respectively. The molecular structure of **5b** (Figure 3) has been determined by X-ray diffraction analysis and confirmed to be the intramolecularly stabilized tetracoordinated organogallane species. The structure of **5b**, which has a short Ga−P bond (2.438(1) Å), is similar to the amino-tethered analogous compound $(\mathrm{Cab}^{C,N})\mathrm{GaMe}_2$.[2] The ^{1}H NMR spectra of this product were consistent with the proposed structure.

To determine whether the gallium compounds **3b** and **4b**, which are tetra- and pentacoordinated, respectively, still exhibit Lewis acidity, the reactions of **3b** and **4b** with PMe_3 were investigated. While complex **3b** added the base PMe_3 to yield the pentacoordinated adduct $(\mathrm{Cab}^{C,P})\mathrm{GaCl}_2\cdot\mathrm{PMe}_3$ (**7b**), the anticipated hexacoordinated complex derived from **4b** was not obtained. The adduct **7b** was stable to dissociation at room temperature and thus was fully characterized by elemental analysis, high-resolution mass spectral analysis, and NMR spectroscopy. The C_s symmetry of **7b** in solution is derived from the ^{1}H, ^{31}P, and ^{13}C NMR spectra. The ^{1}H NMR spectra have signals consistent with compound **7b**: a singlet for the unique PMe_2 proton, a singlet for the PCH_2 group, and a singlet attributable to the added PMe_3. The signals for both PMe_2 and PCH_2 in adduct **7b** are at lower field than for compound **3b**, which is consistent with a *tbp* geometry with the two donor atoms in the axial positions and a fast envelope inversion.

Much effort has been devoted to incorporating an additional *C,P*-chelate ligand to achieve tris-chelate metal complexes such as $(\mathrm{Cab}^{C,P})_3\mathrm{M}$. However hexacoordinated stable complexes cannot be obtained due to steric constraints associated with the bulky *o*-carboranyl unit. Here we have provided the first report of intramolecularly coordinated group 13 metal complexes containing the *o*-carboranyl *C,P*-chelating ligand system. A combination of X-ray crystallographic and spectroscopic studies and DFT calculations confirmed the nature of these compounds. The X-ray crystallographic study of complexes **4b** and **4c** provided the first structural data on the pentacoordinated *tbp* structures derived from the *o*-carboranylphosphine ligand system. Additionally, the present results indicate that the internal coordination of the phosphorus atom of the *o*-carboranyl ligand to the metal center significantly influences not only the stability of the starting compounds but also the products obtained when a base is added to the metal compounds. This may result from stabilization of the metal−carbon bond by the chelate effect, the electronic properties of the metal center, and the strength of the metal−phosphorus bond. Thus, application of the *C,P*-chelating

Table 1. X-ray Crystallographic Data and Processing Parameters for Compounds 4b·C_7H_8, 4C·C_7H_8, and 5b

	4b·C_7H_8	**4c**·C_7H_8	**5b**
formula	$B_{20}C_{17}H_{36}P_2ClGa$	$B_{20}C_{17}H_{36}P_2ClIn$	$B_{10}C_7H_{24}PGa$
fw	623.76	668.86	317.05
cryst class	monoclinic	monoclinic	monoclinic
space group	*P*2/*a*	*P*2/*c*	*P*2(1)/*n*
Z	4	4	4
cell constants			
a, Å	12.935(1)	13.241(1)	7.8914(7)
b, Å	12.918(1)	12.989(1)	14.853(1)
c, Å	10.5524(8)	10.5305(6)	14.578 (1)
α, deg			
β, deg	107.961(8)	108.062(6)	102.357(2)
γ, deg			
V, $Å^3$	1677.3(2)	1721.8(3)	1669.1(3)
μ, mm^{-1}	1.007	0.869	1.719
cryst size, mm	0.334 × 0.227 × 0.125	0.34 × 0.124 × 0.078	0.227 × 0.117 × 0.089
D_{calcd}, g/cm^3	1.235	1.290	1.262
F(000)	632	668	648
radiation	Mo Kα ($\lambda = 0.7107$), $T = 293(2)$ K		
θ range, deg	1.58 to 25.97	1.57 to 25.97	1.98 to 28.31
h, *k*, *l* collected	$0 \le h \le 15$, $0 \le k \le 15$, $-13 \le l \le 12$	$-16 \le h \le 15$, $-4 \le k \le 16$, $-5 \le l \le 12$	$-10 \le h \le 10$, $-19 \le k \le 19$, $-19 \le l \le 19$
no. of rflns measd	3474	3614	16 912
no. of unique rflns	3290	3382	4145
no. of rflns used in refinement ($I > 2\sigma(I)$)	1602	2646	2246
no. of params	181	181	186
$R_1{}^a$ ($I > 2\sigma(I)$)	0.0642	0.0515	0.0507
$wR_2{}^b$ (all data)	0.1867	0.1547	0.1684
GOF	0.675	1.009	1.029

[a] $R_1 = \sum||F_o| - |F_c||$ (based on reflections with $F_o{}^2 > 2\sigma F^2$). [b] $wR_2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o{}^2) + (0.095P)^2]$; $P = [\max(F_o{}^2, 0) + 2F_c{}^2]/3$ (also with $F_o{}^2 > 2\sigma F^2$).

Table 2. Selected Interatomic Distances (Å) for Compounds 4b·C_7H_8, 4c·C_7H_8, and 5b

4b·C_7H_8									
Ga(1)−C(1)	2.006(7)	Ga(1)−Cl(1)	2.221(3)	Ga(1)−P(1)	2.651(2)	C(1)−C(2)	1.686(9)	C(2)−C(3)	1.526(9)
P(1)−C(3)	1.834(7)	P(1)−C(4)	1.832(8)						
4c·C_7H_8									
In(1)−C(1)	2.194(5)	In(1)−Cl(1)	2.410(2)	In(1)−P(1)	2.733(1)	C(1)−C(2)	1.696(7)	C(2)−C(3)	1.529(7)
P(1)−C(3)	1.828(5)	P(1)−C(4)	1.822(6)						
5b									
Ga(1)−C(6)	2.015(4)	Ga(1)−C(7)	1.999(4)	Ga(1)−P(1)	2.438(1)	Ga(1)−C(1)	2.053(4)	C(2)−C(3)	1.533(6)
P(1)−C(3)	1.833(5)								

Table 3. Selected Interatomic Angles (deg) for Compounds 4b·C_7H_8, 4c·C_7H_8, and 5b

4b·C_7H_8							
C(1)−Ga(1)−P(1)	83.6(2)	C(2)−C(1)−Ga	120.6(4)	C(2)−C(3)−P(1)	114.5(5)	C(3)−P(1)−Ga(1)	100.5(2)
C(5)−P(1)−C(3)	103.5(4)	C(5)−P(1)−Ga(1)	112.4(3)	Cl(1)−Ga(1)−P(1)	87.60(5)	Cl(1)−Ga(1)−P(1)*	87.60(5)
C(1)* −Ga(1)−P(1)*	83.6(2)						
4c·C_7H_8							
C(1)−In(1)−P(1)	81.3(1)	C(2)−C(1)−In(1)	119.0(3)	C(2)−C(3)−P(1)	117.6(4)	C(3)−P(1)−In(1)	101.0(2)
C(5)−P(1)−C(3)	105.8(3)	C(5)−P(1)−In(1)	111.9(2)	Cl(1)−In(1)−P(1)	88.37(3)	Cl(1)−In(1)−P(1)*	88.37(3)
C(1)* −In(1)−P(1)*	81.3(1)						
5b							
C(7)−Ga(1)−C(1)	112.0(2)	C(6)−Ga(1)−C(1)	112.4(2)	C(2)−C(1)−Ga(1)	117.8(3)	C(3)−C(2)−C(1)	117.7(4)
C(2)−C(3)−P(1)	114.6(3)	C(5)−P(1)−C(3)	104.6(3)	C(3)−P(1)−Ga(1)	103.3(1)	C(5)−P(1)−C(4)	104.8(3)
C(4)−P(1)−Ga(1)	116.4(2)	C(7)−Ga(1)−C(6)	123.8(2)				

phosphino-*o*-carboranyl ligand allowed the synthesis of stable bis-chelate group 13 metal(III) compounds.

Experimental Section

General Procedures. All manipulations were performed under a dry, oxygen-free, nitrogen or argon atmosphere using standard Schlenk techniques or in a Vacuum Atmospheres HE-493 drybox. Toluene and hexane were dried and distilled from sodium benzophenone. ^1H, ^{13}C, ^{31}P, and ^{27}Al NMR spectra were recorded on a Varian Mercury 300BB spectrometer operating at 300.1, 75.4, 101.3, and 78.2 MHz, respectively. All proton and carbon chemical shifts were measured relative to internal residual benzene from the lock solvent (99.5% C_6D_6) and then referenced to Me_4Si (0.00 ppm). All ^{31}P and ^{27}Al chemical shifts were measured relative to external 1 M H_3PO_4 and 1 M $[Al(OH_2)_6]^{3+}$. IR spectra were recorded on a Biorad FTS-165 spectrophotometer. High- and low-resolution mass spectra were obtained on a VG Micromass 7070H mass spectrometer. Elemental analyses were performed on a Carlo Erba Instruments CHNS-O EA1108 analyzer. All melting points were uncorrected. The following starting materials were prepared according to literature procedures: Decaborane and propargyl bromide were purchased from the Callery Chemical Co. and Aldrich, respectively, and used without further purification. $HCab^P$ **1** ($HCab^P$ = *closo*-1-dimethylphosphinomethyl-*o*-carborane)[3] was prepared by the literature method. The starting materials MX_3 ($AlBr_3$, $GaCl_3$, $InCl_3$) and PMe_2Cl

Table 4. Relative Energies and Important Structure Parameters of the Optimized Geometries for Pentacoordinated Complexes (Cab^{C,P})$_2$MCl (M = Ga 4b, In 4c)

metal		*tbp*-1	*tbp*-2	*tbp*-3	*sp*-1	*sp*-2
Ga	relative energy (kcal/mol)	0	9.98	15.25	3.16	14.93
	M−C (Å)	2.05_{eq}	2.04_{eq} 2.06_{ax}	2.14_{ax}	2.08	2.06
	M−P (Å)	2.67_{ax}	2.46_{eq} 3.48_{ax}	2.69_{eq}	2.72	3.05
In	relative energy (kcal/mol)	0	12.39	9.06	3.04	15.30
	M−C (Å)	2.25_{eq}	2.25_{eq} 2.28_{ax}	2.30_{ax}	2.27	2.28
	M−P (Å)	2.79_{ax}	2.71_{eq} 3.11_{ax}	2.83_{eq}	2.83	2.93

were purchased from Strem Chemicals and sublimed or distilled under dynamic vacuum prior to each use. All other chemicals, including *n*-BuLi, MeLi, and MeMgBr, were purchased from Aldrich.

Synthesis of Cab^{C,P}AlBr$_2$ (3a). To a stirred solution of HCab^P **1a** (0.65 g, 3.0 mmol) in 20 mL of hexane, which was cooled to −10 °C, was added 2.5 M *n*-BuLi (1.4 mL, 3.6 mmol) via a syringe. A suspension of AlBr$_3$ (0.80 g, 3.0 mmol) in 10 mL of toluene was slowly added to the resulting white suspension of the lithium salt of **2** at −78 °C. The reaction temperature was maintained at −78 °C for 1 h, following which the reaction mixture was warmed slowly to room temperature. After being stirred for an additional 12 h, the reaction mixture was filtered. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of toluene and then recrystallized from this solution by cooling to −20 °C. Cab^{C,P}AlBr$_2$ (**3a**) was isolated from the reaction solution in 47% yield (0.57 g, 1.4 mmol) as colorless crystals. Exact mass calcd for $^{12}C_5{}^{1}H_{18}{}^{10}B_{10}{}^{27}Al_1{}^{80}Br_2{}^{31}P_1$ 404.0259, found 404.0271. Anal. Calcd: C, 14.86; H, 4.49. Found: C, 14.79; H, 5.31. Mp = 150−151 °C. IR (KBr pellet, cm^{-1}): ν(C−H) 3177w, 2989w, 2914w, ν(B−H) 2594s. ^{1}H NMR (300.00 MHz, C$_6$D$_6$): δ 0.76 (d, 3H, $^2J_{P-H}$ = 5.4 Hz, P*Me*$_2$), 0.81 (d, 3H, $^2J_{P-H}$ = 5.7 Hz, P*Me*$_2$), 1.24 (d, 2H, $^2J_{P-H}$ = 15.0 Hz, PC*H*$_2$). ^{13}C{^{1}H} NMR (75.44 MHz, C$_6$D$_6$): δ 4.69 ($^1J_{P-C}$ = 52.1 Hz, P*Me*$_2$), 21.53. ^{27}Al NMR (78.17 MHz, C$_6$D$_6$): δ 146.01. ^{13}C{^{1}H} NMR (121.44 MHz, C$_6$D$_6$): δ −40.78.

Synthesis of Cab^{C,P}GaCl$_2$ (3b). The same method as described for **3a** but with GaCl$_3$ (0.53 g, 3.0 mmol) instead of AlBr$_3$ produced **3b** (77%, 0.83 g, 2.3 mmol) as a colorless crystalline solid. Exact mass calcd for $^{12}C_5{}^{1}H_{18}{}^{10}B_{10}{}^{70}Ga_1{}^{35}Cl_2{}^{31}P_1$ 358.0709, found 358.0718. Anal. Calcd: C, 16.78; H, 5.07. Found: C, 16.75; H, 4.99. Mp = 270−272 °C. IR (KBr pellet, cm^{-1}): ν(C−H) 3428w, 2993w, 2966w, ν(B−H) 2585s. ^{1}H NMR (300.00 MHz, C$_6$D$_6$): δ 0.23 (d, 6H, $^2J_{P-H}$ = 15.9 Hz, P*Me*$_2$), 1.49 (d, 2H, $^2J_{P-H}$ = 17.1 Hz, PC*H*$_2$) ^{13}C{^{1}H} NMR (75.44 MHz, C$_6$D$_6$): δ 7.44 ($^1J_{P-C}$ = 28.0 Hz, P*Me*$_2$), 33.17. ^{13}C{^{1}H} NMR (121.44 MHz, C$_6$D$_6$): δ −25.11.

Synthesis of Cab^{C,P}InCl$_2$ (3c). The procedure was analogous to that described for **3a** but using InCl$_3$ (0.66 g, 3.0 mmol) instead of AlBr$_3$ to give **3c** (53%, 0.64 g, 1.6 mmol) as colorless crystals. Exact mass calcd for $^{12}C_5{}^{1}H_{18}{}^{10}B_{10}{}^{115}In_1{}^{35}Cl_2{}^{31}P_1$ 404.0492, found 404.0504. Anal. Calcd: C, 14.90; H, 4.50. Found: C, 14.58; H, 4.61. Mp = 208−210 °C. IR (KBr pellet, cm^{-1}): ν(C−H) 3471w, 2963w, 2913w, ν(B−H) 2582s. ^{1}H NMR (300.00 MHz, C$_6$D$_6$): δ 0.60 (d, 6H, $^2J_{P-H}$ = 8.4 Hz, P*Me*$_2$), 1.62 (d, 2H, $^2J_{P-H}$ = 10.8 Hz, PC*H*$_2$). ^{13}C{^{1}H} NMR (75.44 MHz, C$_6$D$_6$): δ 12.3 ($^1J_{P-C}$ = 31.7 Hz, P*Me*$_2$), 39.1. ^{31}P{^{1}H} NMR (121.44 MHz, C$_6$D$_6$): δ −30.44.

Synthesis of (Cab^{C,P})$_2$AlBr (4a). To a stirred solution of Cab^{C,P}AlBr$_2$ **3a** (0.40 g, 1.0 mmol) in 20 mL of toluene at −78 °C was added a suspension of LiCab^{C,P} **2** (0.22 g, 1.0 mmol) in 20 mL of toluene. The reaction temperature was maintained at −78 °C for 1 h, following which the reaction mixture was warmed slowly to room temperature. After being stirred for an additional 12 h, the reaction mixture was filtered. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of toluene and then recrystallized from this solution by cooling to −20 °C. (Cab^{C,P})$_2$AlBr **4a** was isolated from the reaction solution in 45% yield (0.24 g, 0.45 mmol) as colorless crystals. Exact mass calcd for $^{12}C_{10}{}^{1}H_{36}{}^{10}B_{20}{}^{27}Al_1{}^{80}Br_1{}^{31}P_2$ 544.3152, found 544.3173. Anal. Calcd: C, 22.18; H, 6.70. Found: C, 22.01; H, 7.41. Mp = 164−166 °C. IR (KBr pellet, cm^{-1}): ν(C−H) 3354w, 3051w, 2926w, ν(B−H) 2593s. ^{1}H NMR (300.00 MHz, C$_6$D$_6$): δ 0.63 (d, 6H, $^2J_{P-H}$ = 6.9 Hz, P*Me*$_2$), 0.67 (d, 6H, $^2J_{P-H}$ = 6.9 Hz, P*Me*$_2$), 1.42 (d, 2H, $^2J_{P-H}$ = 15.0 Hz, PC*H*$_2$), 1.73 (d, 2H, $^2J_{P-H}$ = 15.0 Hz, PC*H*$_2$). ^{13}C{^{1}H} NMR (75.44 MHz, C$_6$D$_6$): δ 11.80 ($^1J_{P-C}$ = 21.3 Hz, P*Me*$_2$), 14.41 ($^1J_{P-C}$ = 21.7 Hz, P*Me*$_2$), 33.29, 33.55. ^{27}Al NMR (78.17 MHz, C$_6$D$_6$): δ 79.77. ^{13}C{^{1}H} NMR (121.44 MHz, C$_6$D$_6$): δ −44.80.

Synthesis of (Cab^{C,P})$_2$GaCl (4b). Using a method similar to that described for **4a** but using Cab^{C,P}GaCl$_2$ **3b** (0.36 g, 1.0 mmol) instead of **3a**, compound **4b** was obtained in 68% (0.37 g, 0.68 mmol) yield as colorless crystals. Exact mass calcd for $^{12}C_{10}{}^{1}H_{36}{}^{10}B_{20}{}^{70}Ga_1{}^{35}Cl_1{}^{31}P_2$ 542.3098, found 542.3113. Anal. Calcd: C, 22.25; H, 6.72. Found: C, 22.21; H, 6.77. Mp = 181.9 °C (dec). IR (KBr pellet, cm^{-1}): ν(C−H) 3054w, 2989w, 2920w, ν(B−H) 2582s. ^{1}H NMR (300.00 MHz, C$_6$D$_6$): δ 0.64 (d, 6H, $^2J_{P-H}$ = 3.0 Hz, P*Me*$_2$), 0.65 (d, 6H, $^2J_{P-H}$ = 3.0 Hz, P*Me*$_2$), 1.54 (d, 2H, $^2J_{P-H}$ = 16.8 Hz, PC*H*$_2$), 1.72 (d, 2H, $^2J_{P-H}$ = 16.8 Hz, PC*H*$_2$). ^{13}C{^{1}H} NMR (754.4 MHz, C$_6$D$_6$): δ 12.10 ($^1J_{P-C}$ = 22.6 Hz, P*Me*$_2$), 14.95 ($^1J_{P-C}$ = 22.6 Hz, P*Me*$_2$), 33.36, 33.46. ^{13}C{^{1}H} NMR (121.44 MHz, C$_6$D$_6$): δ −37.75.

Synthesis of (Cab^{C,P})$_2$InCl (4c). The method was similar to that described for **4a** but using Cab^{C,P}InCl$_2$ **3c** (0.40 g, 1.0 mmol) instead of **3a** to yield **4c** (65%, 0.38 g, 0.65 mmol) as colorless crystals. Exact mass calcd for $^{12}C_{10}{}^{1}H_{36}{}^{10}B_{20}{}^{115}In_1{}^{35}Cl_1{}^{31}P_2$ 588.2881, found 588.2899. Anal. Calcd: C, 20.54; H, 6.20. Found: C, 20.57; H, 6.30. Mp = 296.1 °C (dec). IR (KBr pellet, cm^{-1}): ν(C−H) 3020w, 2963w, 2923w, ν(B−H) 2581s. ^{1}H NMR (300.00 MHz, C$_6$D$_6$): δ 0.57 (d, 6H, $^2J_{P-H}$ = 6.3 Hz, P*Me*$_2$), 0.63 (d, 6H, $^2J_{P-H}$ = 6.0 Hz, P*Me*$_2$), 1.61 (d, 2H, $^2J_{P-H}$ = 10.8 Hz, PC*H*$_2$), 1.71 (d, 2H, $^2J_{P-H}$ = 10.8 Hz, PC*H*$_2$). ^{13}C{^{1}H} NMR (75.44 MHz, C$_6$D$_6$): δ 10.60 ($^1J_{P-C}$ = 18.1 Hz, P*Me*$_2$), 13.18 ($^1J_{P-C}$ = 18.1 Hz, P*Me*$_2$), 34.53, 34.69. ^{13}C{^{1}H} NMR (121.44 MHz, C$_6$D$_6$): δ −35.62.

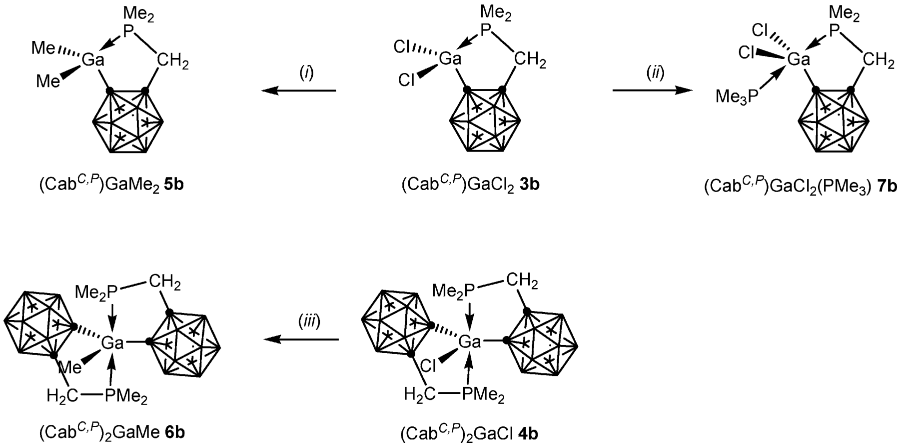
Alternate Procedure for the Preparation of (Cab^{C,P})$_2$AlBr (4a). To a stirred solution of HCab^P **1a** (0.44 g, 2.0 mmol) in 20 mL of hexane, cooled to −10 °C, was added 2.5 M *n*-BuLi (0.8 mL, 2.0 mmol) via a syringe. A suspension of AlBr$_3$ (0.27 g, 1.0 mmol) in 5 mL of toluene was then added to the resulting white suspension at −78 °C. The reaction temperature was maintained at −78 °C for 1 h, following which the reaction mixture was warmed slowly to room temperature. After stirring for an additional 12 h, the reaction mixture was filtered. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of toluene and then recrystallized from this solution by cooling to −20 °C. (Cab^{C,P})$_2$AlBr **4a** was isolated from the reaction solution in 52% yield (0.28 g, 0.52 mmol).

Alternate Procedure for the Preparation of (Cab^{C,P})$_2$GaCl (4b). The method was similar to the alternate procedure for **4a** but using GaCl$_3$ (0.18 g, 1.0 mmol) instead of AlBr$_3$ to yield **4b** (73%, 0.39 g, 0.73 mmol).

Alternate Procedure for the Preparation of (Cab^{C,P})$_2$InCl (4c). The method was similar to the alternate procedure for **4a** but using InCl$_3$ (0.22 g, 1.0 mmol) instead of AlBr$_3$ to yield **4c** (68%, 0.39 g, 0.68 mmol).

Reaction of Cab^{C,P}GaCl$_2$ (3b) with MeLi. To a stirred solution of Cab^{C,P}GaCl$_2$ (**3b**) (0.36 g, 1.0 mmol) in 20 mL of toluene was added 1.4 M MeLi (1.57 mL, 2.2 mmol) via a syringe at −78 °C. The reaction temperature was maintained at −78 °C for 1 h, following which the reaction mixture was warmed slowly to room temperature. After being stirred for

Scheme 3. Reactivity of Tetra- and Pentacoordinated Gallium Complexes[a]



[a] Legend: (*i*) MeLi, toluene, −78 °C; (*ii*) PMe_3, toluene, 25 °C; (*iii*) MeMgBr, toluene, −78 °C.

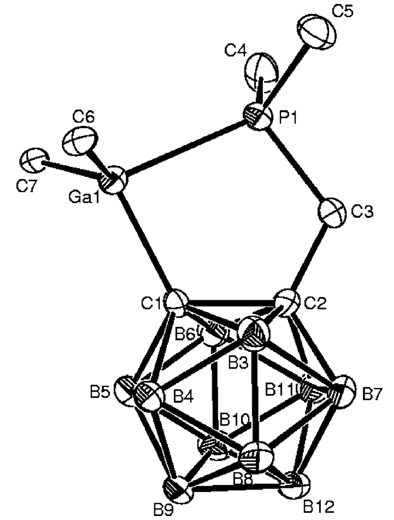


Figure 3. Molecular structure of **5b** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms have been omitted for clarity.

an additional 1 h, the reaction mixture was filtered. The solvent was removed under vacuum, and the resulting residue was taken up in a minimum of toluene and then recrystallized from this solution by cooling to −20 °C. $Cab^{C,P}GaMe_2$ (**5b**) was isolated from the reaction solution in 77% yield (0.24 g, 0.77 mmol) as colorless crystals. Exact mass calcd for $^{12}C_7{}^1H_{24}{}^{10}B_{10}{}^{70}Ga_1{}^{31}P_1$ 318.1802, found 318.1811. Anal. Calcd: C, 26.52; H, 7.63. Found: C, 26.47; H, 7.49. Mp = 208 °C (dec). IR (KBr pellet, cm^{-1}): ν(C−H) 2996w, 2994w, 2967w, 2917w, 2915w, ν(B−H) 2585s. ^1H NMR (300.00 MHz, C_6D_6): δ −0.15 (d, 3H, $^3J_{P-H} = 11.1$ Hz, Ga*Me*$_2$), 0.16 (d, 3H, $^3J_{P-H} = 11.1$ Hz, Ga*Me*$_2$), 0.49 (d, 3H, $^2J_{P-H} = 5.4$ Hz, P*Me*$_2$), 0.65 (d, 3H, $^2J_{P-H} = 5.4$ Hz, P*Me*$_2$), 1.68 (d, 2H, $^2J_{P-H} = 14.4$ Hz, PC*H*$_2$). $^{13}C\{^1H\}$ NMR (75.44 MHz, C_6D_6): δ −19.25 (Ga*Me*$_2$), −19.20 (Ga*Me*$_2$), 9.12 ($^1J_{P-C} = 26.4$ Hz, P*Me*$_2$), 33.47. $^{13}C\{^1H\}$ NMR (121.44 MHz, C_6D_6): δ −43.76.

Reaction of $(Cab^{C,P})_2GaCl$ (4b) with MeMgBr. The method was similar to that described for **5b** but using **4b** (0.54 g, 1.0 mmol) and MeMgBr (0.33 mL, 1.0 mmol, 3.0 M solution in Et_2O) instead of **3b** and MeLi to yield $(Cab^{C,P})_2GaMe$ (**6b**) (62%, 0.32 g, 0.62 mmol) as colorless crystals. Exact mass calcd for $^{12}C_{11}H_{39}{}^{10}B_{20}{}^{70}Ga_1{}^{31}P_2$ 522.3644, found 522.3659. Anal. Calcd: C, 25.44; H, 7.57. Found: C, 25.63; H, 8.02. Mp = 195 °C (dec). IR (KBr pellet, cm^{-1}): ν(C−H) 3054m, 3022w, 2990w, 2951w, 2921w, ν(B−H) 2582s. ^1H NMR (300.00 MHz, C_6D_6): δ −0.21 (t, 3H, $3^J{}_{P-H} = 6.0$ Hz, Ga*Me*), 0.38 (s, 6H, P*Me*$_2$), 0.62 (s, 6H, P*Me*$_2$), 1.66 (d, 2H, $^2J_{P-H} = 6.9$ Hz, PC*H*$_2$), 1.70 (d, 2H, $^2J_{P-H} = 6.9$ Hz, PC*H*$_2$). $^{13}C\{^1H\}$ NMR (75.44 MHz, C_6D_6): δ −3.45 (Ga*Me*), 14.16 ($^1J_{P-C} = 24.9$ Hz, P*Me*$_2$), 36.33, 38.05. $^{13}C\{^1H\}$ NMR (121.44 MHz, C_6D_6): δ −40.63.

Reaction of $Cab^{C,P}GaCl_2$ (3b) with PMe_3. A solution of **3b** (0.36 g, 1.0 mmol) and trimethylphosphine (0.10 mL, 1.0 mmol) in toluene (10 mL) was stirred for 6 h at room temperature and subsequently evaporated to dryness. Crystallization from toluene (5 mL) at −20 °C gave the pure crystalline product $(Cab^{C,P})GaCl_2{\cdot}P\mathit{Me}_3$ (**7b**) (81%, 0.35 g, 0.81 mmol). Exact mass calcd for $^{12}C_8{}^1H_{27}{}^{10}B_{10}{}^{35}Cl_2{}^{70}Ga_1{}^{31}P_2$ 434.1151, found 434.1163. Anal. Calcd: C, 22.14 H, 6.27. Found: C, 22.08; H, 6.42. Mp = 215−216 °C. IR (KBr pellet, cm^{-1}): ν(C−H) 3456w, 2994w, 2967w, 2918w, 2850w, ν(B−H) 2584s. ^1H NMR (300.00 MHz, C_6D_6): δ 0.25 (d, 9H, $^2J_{P-H} = 15.9$ Hz, P*Me*$_3$), 0.67 (d, 3H, $^2J_{P-H} = 8.7$ Hz, P*Me*$_2$), 0.75 (d, 3H, $^2J_{P-H} = 8.4$ Hz, P*Me*$_2$), 1.52 (d, 2H, $^2J_{P-H} = 16.5$ Hz, PC*H*$_2$). $^{13}C\{^1H\}$ NMR (75.44 MHz, C_6D_6): δ 2.19 ($^1J_{P-C} = 18.6$ Hz, P*Me*$_3$), 9.44 ($^1J_{P-C} = 23.6$ Hz, P*Me*$_2$), 35.05. $^{13}C\{^1H\}$ NMR (121.44 MHz, C_6D_6): δ −19.86, −5.01.

X-ray Crystallography. Details of the crystal data and a summary of the intensity data collection parameters for **4b**, **4c**, and **5b** are listed in Table 1. Crystals of **4b**, **4c**, and **5b** were grown from toluene solutions stored at −20 °C. In each case a suitable crystal was mounted in thin-walled glass capillaries and transferred to the goniometer of a Bruker SMART 1000 CCD area detector system, where it was cooled to −60 °C for the duration of the experiment. Initial unit cell parameters were obtained from SMART10 software. Data integration, correction for Lorentz and polarization effects, and final cell refinement were performed using SAINTPLUS.11 The data were further corrected for absorption using SABABS.[12] The initial structure solutions were obtained by the direct methods routine in SHELXTL.[13] Subsequent refinement cycles (based on F^2) and Fourier synthesis revealed the positions of all non-hydrogen atoms. These atoms were refined using anisotropic displacement tensors. All hydrogen atoms were added in calculated positions for the final refinement cycle.

Computational Details. Stationary points on the potential energy surface were calculated using the Amsterdam Density Functional (ADF) program, developed by Baerends et al.[14,15]

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(10) *SMART V5.05 Software for the CCD Dector System*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

(11) *SAINTPLUS, V5.00 Software for the CCD Dector System*; Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1998.

(12) *SADABS*. Program for absorption correction using SMART CCD based on the method of: Blessing, R. H. *Acta Crystallogr.* **1995**, *A51*, 33.

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and vectorized by Ravenek.[16] The numerical integration scheme applied for the calculations was developed by de Velde et al.[17,18] The geometry optimization procedure was based on the method of Versluis and Ziegler.[19] The electronic configurations of the molecular systems were described by double-ζ STO basis sets with polarization functions for the H, B, and C atoms, while triple-ζ Slater-type basis sets were employed for the P, Cl, Ga, and In atoms.[20,21] The 1s electrons of B and C, the 1s-2p electrons of P and Cl, the 1s-3p electrons of Ga, and the 1s-4p electrons of In were treated as frozen cores. A set of auxiliary[22] s, p, d, f, and g STO functions, centered on all nuclei, was used in order to fit the molecular density and the Coulomb and exchange potentials in each SCF cycle. Energy differences were calculated by augmenting the local exchange–correlation potential of Vosko et al.[23] with Becke's[24] nonlocal exchange corrections and Perdew's[25] nonlocal correlation corrections (BP86). Geometries were optimized including nonlocal corrections at this level of theory. First-order Pauli scalar relativistic corrections[26,27] were added variationally to the total energy for all systems. In view of the fact that all systems investigated in this work show a large HOMO–LUMO gap, a spin-restricted formalism was used for all calculations. No symmetry constraints were used.

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Supporting Information Available: Crystallographic data (excluding structure factors) for the structures **4b**, **4c**, and **5b** reported in this paper and listings giving optimized geometries of the crucial structures (**4b** and **4c**) reported (Cartesian coordinates, in Å). This material is available free of charge via the Internet at http://pubs.acs.org.

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