

New Types of Group 4 and 13 Metal Complexes Stabilized by Homo- or Hetero-Donor Functionalized Dicarbollide Ligands: Syntheses, Characterizations, and Structural Studies of $[\{\eta^5-C_2B_9H_9(D)\}-(\eta^1-NMe_2CH_2)]M(NMe_2)_2$ (D = CH₂NMe₂, PPh₂; M = Ti, Zr) and $[(\eta^1-D)(\eta^1-NMe_2CH_2)C_2B_9H_{10}]MMe_2$ (D = CH₂NMe₂, PPh₂; M = Al, Ga)

Jong-Dae Lee,*,[†] Ha-Yeon Kim,[†] Won-Sik Han,[‡] and Sang Ook Kang*,[‡]

[†]Department of Chemistry, Chosun University, Gwangju 501-759, Korea, and [‡]Department of Advanced Materials Chemistry, Sejong Campus, Korea University, Chungnam 339-700, Korea

Received March 14, 2010

A series of group 4 and 13 metal complexes coordinated to either a homo- or hetero-donor and a dicarbollyl ligand derived from N,N'- or P,N-chelated ligands were synthesized and characterized. Two homo- and hetero-donor tethered ligands of the type 7,8-(Me₂NCH₂)(µ-H)(Me₂NCH₂)-7,8-C₂B₉H₁₀ (Dcab^{NN}H, 3) and 7-PPh₂-8-Me₂NHCH₂-7,8-C₂B₉H₁₀ (Dcab^{PN}H, 6) were prepared using the standard deborination methods from $1,2-(NMe_2CH_2)_2-1,2-C_2B_{10}H_{10}$ (2) and $1-PPh_2-2-Me_2NCH_2-1,2-C_2B_{10}H_{10}$ (2) and (2) $C_2B_{10}H_{10}$ (5), respectively. Subsequent reactions of 3 with $M(NMe_2)_4$ (M = Ti, Zr) produced single nitrogen donors involving π,σ -dicarbollides of the type [{ η^5 -C₂B₉H₉(CH₂NMe₂)}(η^1 -NMe₂CH₂)]M- $(NMe_2)_2$ (M = Ti (4), Zr (5)). Structurally similar nitrogen donor stabilized π,σ -dicarbollides of the type $[\{\eta^5 - C_2 B_9 H_9 (PPh_2)\}(\eta^1 - NMe_2 CH_2)]M(NMe_2)_2 (M = Ti(7), Zr(8))$ were produced from the reaction of 6 with $M(NMe_2)_4$ (M = Ti, Zr). When group 13 metals were attempted with dissimilar ligands, 3 and 6, σ , σ -type complexes were formed with the engagement of two tethered donors at the dicarbollide ligand in an exo-polyhedral manner irrespective of the dissimilar donor properties, nitrogen or phosphine. As a result, a series of group 13 metal complexes bearing ligands **3** and **6**, $[(\eta^1 - NMe_2CH_2)_2C_2B_9H_{10}]MMe_2$ (M = A1 (11), Ga (12)) and $[(\eta^{1}-PPh_{2})(\eta^{1}-NMe_{2}CH_{2})C_{2}B_{9}H_{10}]MMe_{2} (M = A1 (13), Ga (14))$, were prepared by reacting **3** and **6** with trimethylaluminum (TMA) and trimethylgallium (TMG), respectively. New types of π,σ - and σ,σ -coordination were established by extensive structural studies of each metal complex comprising N,N'- or P,N-chelated dicarbollide: 7, 9, 10, 11, 13, and 14.

Introduction

The preparation of new types of π , σ -coordination complexes with various donor groups is currently of interest in both academia and industry because of the remarkable activity for the copolymerization of ethylene with α -olefins.¹⁻³ The concept " π , σ -coordination" came from a unique ligand layout designed from the array of two dissimilar coordinating functionalities: π -cyclopentadienide and σ -amide.⁴⁻⁶ One such reference is a titanium complex of the type [(η^5 -Me₄C₅)Me₂Si-(η^1 -*t*-BuN)]TiCl₂, which represents a characteristic π , σ -bonding interaction at the titanium metal center.

- (1) Siemeling, U. Chem. Rev. 2000, 100, 1495.
- (2) Butenschön, H. Chem. Rev. 2000, 100, 1527.

In the search for new types of ligand systems capable of π,σ coordination, the dicarbollyl moiety appears to be a suitable candidate as a π -bonding group instead of the cyclopentadienyl ligand (Cp). The dicarbollide dianion, $(C_2B_9H_{11})^{2-}$, is a versatile ligand that is an isolobal inorganic analogue of the Cp^- ion. The preparation of π,σ -coordination complexes with this dicarbollyl functionality is a challenging project, because the incorporation of a dicarbollyl fragment into the ligand framework will create new metal/charge combinations. The formal replacement of the monoanionic Cp⁻ ligand in $[CpM^{III}]^{2+}$ with the isolobal, dianionic $(C_2B_9H_{11})^{2-}$ ligand to give a $[(C_2B_9H_{11})M^{III}]^+$ fragment reduces the overall charge by one unit but leaves the gross structural and metal frontier orbital properties unchanged. Furthermore, secondary metal/ ligand interactions with σ -coordination appeared to play an important role in improving the capability of π -bonding in a dicarbollide unit. It should be noted that the weaker ionic character of the pendant neutral amino group enhances the metal's π -binding capability with the dicarbollyl ligand through η^5 coordination.

As part of our ongoing efforts to induce π , σ -bonding, a wide variety of pendant donors have been incorporated to

^{*}To whom correspondence should be addressed. Tel: +82-41-860-1334. Fax: +82-41-867-5396. E-mail: sangok@korea.ac.kr.

⁽³⁾ Li, X.; Nishiura, M.; Hu, L.; Mori, K.; Hou, Z. J. Am. Chem. Soc. 2009, 131, 13870.

⁽⁴⁾ Bunel, E. E.; Burger, B. J.; Bercaw, J. E. J. Am. Chem. Soc. 1988, 110, 976.

⁽⁵⁾ Shapiro, P. J.; Bunel, E. E.; Schaefer, P. J.; Bercaw, J. E. Organometallics 1990, 9, 867.

⁽⁶⁾ Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. J. Am. Chem. Soc. **1994**, 116, 4623.



Figure 1. Single side arm enhancing the metal's π -bonding capability.





the parent dicarbollyl compounds.⁷⁻¹⁰ Recently, chelating dicarbollide ligands with a nitrogen donor were investigated in the context of the production of π,σ -group 4 metal complexes.^{11–15} In such ligand systems, the amine or amide donors were found to be the most effective ancillary functionalities to form π,σ -bonds with group 4 metals. Moreover, we recently reported the preparation of π,σ -type group 13 metal complexes,^{16,17} in which the amine donor was a key ingredient that induced the primary π -interaction with dicarbollide, as shown in Figure 1. As an extension of this work, two donor groups with homo and hetero functionalities were engaged to the dicarbollide to determine the scope of π, σ -coordination with transition and main-group metals. Similar to monofunctionalized group 4 metal dicarbollides, difunctionalized dicarbollyl ligand systems with N, N'(3) and N,P (6) tethers formed the expected π,σ -group 4 metal complexes, whereas group 13 metals completed their tetrahedral geometry with σ,σ -bonding with the disubstituted donors. Therefore, π,σ - and σ,σ -type coordination was demonstrated in the structures of 7, 9, and 10 and 11, 13, and 14, respectively.

Results and Discussion

Scheme 1 summarizes the syntheses of group 4 metal complexes of the zwitterionic dicarbollyl ligand, abbreviated as

- (7) Hosmane, N. S.; Maguire, J. A.; Yinghuai, Z. Main Group Chem. 2006. 5. 251.
- (8) Yinghuai, Z.; Yulin, Z.; Carpenter, K.; Maguire, J. A.; Hosmane, N. S. J. Organomet. Chem. 2005, 690, 2802.
- (9) Wang, H.; Shen, H.; Chan, H.-S.; Xie, Z. Organometallics 2008, 27, 3964.
- (10) Shen, H.; Chan, H.-S.; Xie, Z. Organometallics 2007, 26, 2694.
- (11) Lee, J.-D.; Lee, Y.-J.; Son, K.-C.; Cheong, M.; Ko, J.; Kang, S. O. *Organometallics* **2007**, *26*, 3374.
- (12) Lee, J.-D.; Lee, Y.-J.; Son, K.-C.; Han, W.-S.; Cheong, M.; Ko, J.; Kang, S. O. J. Organomet. Chem. 2007, 692, 5403.

(13) Gao, M.; Tang, Y.; Xie, M.; Qian, C.; Xie, Z. Organometallics 2006, 25, 2578

- (14) Xie, Z. Coord. Chem. Rev. 2006, 250, 259.
 (15) Lee, Y.-J.; Lee, J.-D.; Ko, J.; Kim, S.-H.; Kang, S. O. Chem. Commun. 2003, 1364.
- (16) Lee, J.-D.; Kim, S.-K.; Kim, T.-J.; Han, W.-S.; Lee, Y.-J.; Yoo, D.-H.; Cheong, M.; Ko, J.; Kang, S. O. J. Am. Chem. Soc. 2008, 130,
- 9904
- (17) Son, K.-C.; Lee, Y.-J.; Cheong, M.; Ko, J.; Kang, S. O. J. Am. Chem. Soc. 2006, 128, 12086.



Figure 2. Molecular structure of 3 with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity, except for H100 and H101 atoms.

Dcab^{NN}H (3). Treatment of *o*-carborane (1), 1,2-C₂B₁₀H₁₂, with 2 equiv of *n*-BuLi and then Eschenmoser's salt, $H_2C=$ $NMe_2^+I^-$, afforded 1,2-(Me_2NCH_2)_2-1,2-C_2B_{10}H_{10} (2) in excellent yield. The complete conversion of 2 into 7,8-(Me₂- NCH_2)(μ -H)(Me₂NCH₂)-7,8-C₂B₉H₁₀ (3) was then achieved by heating in neat methanol. The ¹H NMR spectrum of 3showed a singlet pattern for methyl protons of the NMe₂ group at δ 2.69. However, the methylene protons of the NCH₂ group are diastereotopic, each giving rise to an AB spin pattern (δ 3.07, 3.53). A single-crystal X-ray structural determination of 3 revealed the formula of the salt to be the zwitterionic form of 3 with a NMe₂ unit linked to the HNMe₂ cation by an $N \cdots H - N$ hydrogen bond (Figure 2).

As shown in Scheme 1, reaction of 3 with 1 equiv of $M(NMe_2)_4$ (M = Ti, Zr) in toluene gave the expected π,σ -coordination products $[\{\eta^5-C_2B_9H_9(CH_2NMe_2)\}(\eta^1-NMe_2)]$ $(CH_2)M(NMe_2)_2$ (M = Ti (7), Zr (8)) in 84 and 78% yield, respectively.

Compounds 7 and 8 were characterized by ¹H, ¹¹B, and ¹³C NMR spectroscopy and elemental analyses. The

Table 1. Comparison of th	e NMR Spectroscopic	Data for 3, 6, and 7–14
---------------------------	---------------------	-------------------------

	¹ H NMR (δ)				¹³ C NMR (δ)			
compd	CH_2	NMe ₂	M-NMe ₂	M-Me	CH_2	NMe ₂	M-NMe ₂	M- <i>Me</i>
3 ^{<i>a</i>}	3.07, 3.53	2.69			65.0	43.4		
6 ^{<i>a</i>}	2.99, 3.42	2.66			64.2	42.6		
7^{b}	2.93, 4.12	2.64, 2.88	3.48, 3.66		69.6	52.3	47.2, 52.6	
	3.56 (free)	2.33 (free)			64.4 (free)	47.8 (free)		
8 ^b	2.94, 4.10	2.64, 2.86	3.45, 3.58		68.2	51.4	48.1, 53.0	
	3.55 (free)	2.31 (free)	,		64.1 (free)	47.5 (free)	ŕ	
9 ^b	2.93, 4.13	2.72, 2.94	3.46, 3.63		69.5	52.1	47.2, 52.3	
10 ^b	2.88, 4.09	2.68, 2.91	3.40, 3.58		68.7	51.9	48.0, 52.8	
11 ^c	2.34, 2.51	1.54	,	-0.19, -0.22	71.5	56.8	ŕ	-8.70, -8.71
12 ^c	2.40, 2.54	1.62		0.58, 0.60	71.8	57.1		1.48, 1.49
13 ^c	2.38, 3.03	1.61		-0.21, -0.49	71.8	57.2		-7.47, -9.51
14 ^c	2.41, 3.11	1.66		0.56, 0.84	71.3	56.8		1.51, 2.97

 a (CD₃)₂SO was used as the solvent, and the chemical shifts are reported relative to the residual H of the solvent. b C₆D₆ was used as the solvent, and the chemical shifts are reported relative to the residual H of the solvent. c CD₃C₆D₅ was used as the solvent, and the chemical shifts are reported relative to the residual H of the solvent.

deprotonation of 3 was evident from the disappearance of the bridge hydrogen atoms of B-H-B and N-H-N (¹H NMR, δ –2.05 and 3.49). As shown in Table 1, the ¹H NMR spectra of 7 and 8 showed two singlets (δ 3.48, 3.66 for 7 and δ 3.45, 3.58 for 8) corresponding to the methyl protons of each M-NMe₂ due to the asymmetric group 4 metal center. The coordination of the nitrogen atom of one of the side arms to the central metal atom was evident from the downfield shift of methyl protons in the ¹H NMR spectrum. The methylene protons of the CH_2 group in 7 and 8 were diastereotopic, each giving rise to an AB pattern and a broad singlet for the noncoordinated NCH_2 unit. In comparison with the parent ligand 3, the downfield shift was apparent for the methylene protons of NCH_2 and methyl protons of NMe_2 in the side arms of 7 and 8, appearing at δ 2.93, 4.12 and 2.64, 2.88 for 7 and δ 2.94, 4.10 and 2.64, 2.86 for 8, respectively. These shifts are consistent with the findings for other intramolecularly coordinated group 4 metal complexes containing methylene spacers, such as (Dcab^N) M(NMe₂)₂, (M = Ti, Zr).¹⁸ Their ¹³C NMR spectra were consistent with the results derived from the ¹H NMR spectrum. The ¹¹B NMR spectrum showed a similar splitting pattern for the asymmetric η^5 -dicarbollyl metal complexes. The solid-state IR spectra of 7 and 8 revealed a characteristic B-H absorption at approximately 2522 cm^{-1} .

A single-crystal X-ray structural determination confirmed 7 to be a monomeric π,σ -coordination complex, in which the Ti atom is π -bound to a pentagonal C₂B₃ bonding face, σ -bound to two terminal NMe₂ ligands, and coordinated by the nitrogen atom of one of the side arms in a stable pianostool structure (Figure 3). Table 2 gives the crystallographic data for 7. Table 3 and the Supporting Information give the selected bond lengths and angles. The molecule is a $Ti(NMe_2)_2$ unit that is bonded to a η^5 -dicarbollyl ligand. The dimethylamino fragment coordinates to the titanium in the remaining basal site of the overall three-legged pianostool conformation, giving a five-membered ring. As shown in Table 3, the central Ti atom is coordinated pseudotetrahedrally to a pair of NMe₂ ligands (Ti-N(1)/N(2) =1.889(4)/1.901(4) A), the NMe₂ side arm, and the C₂B₃ plane of the dicarbollyl ligand. The observation of a Ti-N(3)distance of 2.240(3) Å, which is consistent with a $Ti-N(sp^3)$



Figure 3. Molecular structure of 7 with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

single bond $([\eta^2 - (C_6H_5CH_2)_2C_2B_9H_9]Ti(NEt_2)_2(NHEt_2),$ 2.225(2) $Å^{19}$) confirms that the N atom is coordinated to the metal in a strain-free manner. The central Ti atom is η^5 coordinated to the dicarbollide ligand with Ti-cage atom distances ranging from 2.344(5) to 2.534(4) A with an average value of 2.432 A, indicating a highly asymmetric bonding mode. The titanium atom is centered approximately over the ring, giving rise to a $Ti(1)-C_2B_3$ face (centroid) distance of 1.964 Å. Such slip distortion may be due to intramolecular interactions between Ti and the nitrogen atom of the side arm. The corresponding C_2B_3 (centroid)-C(1)-C(3) angle is 146.7°. The endocyclic C(1)-C(3)-N(3)bond angle is $107.0(3)^\circ$, which departs from the tetrahedral sp³-C value. The π,σ -type coordination character in a series of related compounds is probably best characterized by the C_2B_3 (centroid)-Ti-N(side arm) angle (α angle in Table 3), which responds sensitively to steric and electronic geometry changes. In 7, this angle is 97.6°. We recently communicated

⁽¹⁸⁾ Lee, J.-D.; Lee, Y.-J.; Son, K.-C.; Cheong, M.; Ko, J.; Kang, S. O. *Organometallics* **2007**, *26*, 3374.

⁽¹⁹⁾ Kwong, W.-C.; Chan, H. -S.; Tang, Y.; Xie, Z. Organometallics 2004, 23, 4301.

	3	6 · (CH ₃) ₂ CO	7	9.CH ₃ C ₆ H ₅	10	$11 \cdot CH_3C_6H_5$	13	14
formula formula wt cryst syst Z, space group a/Å b/Å c/Å b/A c/Å b/A c/Å b/A c/A b/A c/A b/A c/A b/A c/A b/A b/A c/A b/A b/A c/A b/A b/A c/A b/A b/A c/A b/A b/A c/A b/A b/A c/A b/A b/A c/A b/A d/A	$\begin{array}{c} C_8 B_9 H_{27} N_2 \\ 248.61 \\ monoclinic \\ 4, P21/m \\ 8.387(5) \\ 17.688(8) \\ 17.688(8) \\ 17.688(8) \\ 17.688(8) \\ 17.688(8) \\ 10.664(9) \\ 15.64(2) \\ 0.053 \\ 0.4 \times 0.5 \times 0.5 \\ 3308/3061 \\ 0.053 \\ 0.0663, 0.1862 \\ 0.1159, 0.2070 \end{array}$	$\begin{array}{c} C_{20}H_{3,5}B_{9}NOP\\ 433.75\\ monoclinic\\ 4, P2_{1}/c\\ 13.612(7)\\ 9.983(7)\\ 2.983(7)\\ 2.942.7(3)\\ 0.117\\ 0.107\\ 0.1032\\ 0.1032\\ 0.1032\\ 0.0972, 0.2129\\ 0.1956, 0.2508\\ \end{array}$	$\begin{array}{c} C_{12}B_{9}H_{37}N_{4}Ti\\ 382.65\\ monoclinic\\ 4, P2_{1}/m\\ 9.203(1)\\ 15.714(2)\\ 14.790(2)\\ 14.790(2)\\ 2137.0(5)\\ 0.404\\ 0.10\times0.22\times0.34\\ 0.100\times0.22\times0.34\\ 11.211/3982\\ 0.00740, 0.1422\\ 0.0740, 0.1422\\ 0.01617, 0.1710\\ \end{array}$	$\begin{array}{c} C_{24,50}H_{43}B_9N_3PTi\\ 555.78\\ monoclinic\\ 4, P2_{1}/c\\ 20.912(2)\\ 8.186(9)\\ 17.829(2)\\ 3051.3(6)\\ 0.354\\ 0.304\\ 0.30575, 0.20\\ 21093/7562\\ 0.0883\\ 0.0575, 0.1316\\ 0.0575, 0.1316\\ 0.1509, 0.1721\\ \end{array}$	$\begin{array}{c} C_{21}H_{39}B_{9}N_{3}PZr\\ 552.72\\monoclinic\\ 4, P2_{1}/c\\ 9.675(5)\\ 15.611(9)\\ 15.611(9)\\ 19.168(9)\\ 2800(3)\\ 0.466\\ 0.32\times0.28\times0.15\\ 27040/6931\\ 0.3123\\ 0.3123\\ 0.0813, 0.1793\\ 0.2403, 0.2382\\ \end{array}$	$\begin{array}{c} C_{17}H_{38}AlB_9N_2\\ 394.76\\ \text{orthorhombic}\\ 4,\ P2_12_1\\ 9.728(8)\\ 13.140(1)\\ 19.147(2)\\ 2447.4(4)\\ 0.08\\ 0.30\times 0.15\times 0.10\\ 24426/6140\\ 0.0946\\ 0.0937,\ 0.2094\\ 0.06357,\ 0.2094\\ 0.1645,\ 0.2656\end{array}$	$\begin{array}{c} C_{19}H_{33}AlB_9NP\\ 430.70\\ triclinic\\ 2, P\overline{1}\\ 9.589(1)\\ 11.284(1)\\ 11.284(1)\\ 11.284(1)\\ 13.809(2)\\ 1430.6(3)\\ 0.134\\ 0.28\times0.21\times0.15\\ 0.355\\ 0.0355\\ 0.0355\\ 0.0673, 0.1620\\ 0.0459, 0.1859\\ 0.1459, 0.1859\\ \end{array}$	$\begin{array}{c} C_{19}B_9H_{34}GaNP\\ 474.18\\ triclinic\\ 2, P\overline{1}\\ 9.595(6)\\ 11.269(7)\\ 11.269(7)\\ 11.269(7)\\ 11.28(2)\\ 1.028\\ 0.28\times 0.22\times 0.10\\ 1.028\\ 0.28\times 0.22\times 0.10\\ 1.028\\ 0.0179\\ 0.0179\\ 0.0678, 0.1670\end{array}$
$^{a}R_{1} = \sum F_{0} - F_{c} $ (based	on reflections with .	$F_{0}^{2} > 2\sigma F^{2}$), $^{p}wR_{2} = 1$	$\left[\sum \left[w(F_{o}^{2}-F_{c}^{2})^{2}\right]/\sum \left[w(F_{o}^{2}-F_{c}^{2})^{2}\right]\right]$	$\left[n_{0}^{2} \right]^{2} \left[1^{1/2}; w = 1 \right] \left[\sigma^{2} (F_{0}^{2})^{2} \right]$	$(0.095P)^{2}; P = [m]$	$ax(F_{o}^{2}, 0)+2F_{c}^{2}]/3$ (also	$0 \text{ with } F_0^2 > 20F^2$	

syntheses and structural studies of the zwitterionic dicarbollylamino ligand 3 and the corresponding titanium metal complex 7.15

P.N-functionalized dicarbollyl systems were studied as an extension of ligand variation. The new type of 7-PPh₂-8-Me₂N(H)CH₂-7,8-C₂B₉H₁₀ ligand, abbreviated as Dcab^{PN}H (6), was prepared by applying a standard deborination procedure¹¹ to 1-PPh₂-2-Me₂NCH₂-1,2-C₂B₁₀H₁₀ (5) (Scheme 2).

In this procedure, the reaction of 5 with 3 equiv of KOH in ethanol at 78 °C and subsequent protonation with phosphoric acid led to the formation of the deborinated zwitterionic compound 6. The characteristic asymmetric pattern in the ¹¹B NMR spectrum in the range from δ -8.4 to -34.6 and the presence of an absorption peak at δ -2.48 in the ¹H NMR spectrum indicate a B-H-B interaction on the C_2B_3 open face. Similar to the case for 3, the ¹H NMR spectrum of 6 showed an AB spin pattern for the methylene protons at δ 2.99 and 3.42 for the NCH₂ unit and a singlet for the methyl protons at δ 2.66 for the NMe₂ unit. Figure 4 shows the ORTEP diagram of 6. It is clearly a zwitterionic structure, in which the N atom is bonded to two methyl groups and one hydrogen atom.

As shown in Scheme 2, reaction of 6 with $M(NMe_2)_4$ in toluene gave π, σ -type group 4 metal complexes of the type $[\{\eta^5 - C_2 B_9 H_9 (PPh_2)\}(\eta^1 - NMe_2 CH_2)]M(NMe_2)_2 (M = Ti(9),$ Zr(10) in good yield (87% for 9, 65% for 10). The ¹H NMR spectrum was similar to that of the parent ligand 6, except for the B-H-B and N-H proton resonances centered at δ -2.48 and 8.08, respectively. The ¹H NMR spectra of **9** and 10 revealed a pair of singlets for the methyl protons of the $M-NMe_2$ group due to the asymmetric metal center, centered at δ 3.46, 3.63 (9) and δ 3.40, 3.58 (10), respectively. The methylene protons of the NCH_2 unit in 9 and 10 were diastereotopic, each giving rise to an AB spin pattern. In comparison with the parent ligand 6, the downfield shift was apparent for the methylene protons of NCH_2 and methyl protons of NMe₂ in the side arms of **9** and **10**, appearing at δ 2.93, 4.13 and 2.72, 2.94 for **9** and δ 2.88, 4.09 and 2.68, 2.91 for 10, respectively. Their ¹³C NMR spectra are consistent with the ¹H NMR data. The ¹¹B NMR spectra exhibited splitting patterns similar to those for asymmetric η^2 -dicarbollyl metal complexes. The solid-state IR spectra of 9 and 10 showed characteristic B-H absorptions at approximately 2521 cm^{-1} .

An X-ray structural analysis of 9 showed that the Ti atom exhibited π,σ -type coordination with difunctional dicarbollide, having a π -bonding mode with the C₂B₃ open cage and a σ -bonding mode with the NMe₂ side arm (Figure 5). Table 2 gives the crystallographic data for 9. Table 3 and the Supporting Information give selected bond lengths and angles. The structure of 9 is similar to that of 7, except for the presence of an uncoordinated phosphine tether. The Ti-N(2)/N(3) distances are 1.910(3)/1.889(3) Å, and the Ti-N(1) distance is 2.276(3) Å. The central Ti atom is η^5 -coordinated to the dicarbollide ligand, where Ti-cage atom distances range from 2.394(4) to 2.484(3) Å with an average value of 2.437 Å, indicating a highly asymmetric bonding mode. The C_2B_3 (centroid)-Ti-N(side arm) angle of 9 is 97.6°.

As shown in Figure 6, the structure of zirconium complex 10 reveals it to be isomorphous and isostructural with 9. The central Zr atom is π -bound to the C₂B₃ ligand with a C₂B₃-(centroid)–Zr distance of 2.112 Å. The Zr-N(1) distance of 2.377(6) Å confirms that the N-donor atom is coordinated to the metal in a strain-free manner and is consistent with a

Table 3. Compilation of the Characteristic Structural Parameters of 7, 9 · CH₃C₆H₅, 10, 11 · CH₃C₆H₅, 13, and 14^a

	7 (M = Ti)	$9 \cdot \mathrm{CH}_3\mathrm{C}_6\mathrm{H}_5(\mathrm{M}=\mathrm{Ti})$	$10(\mathrm{M}=\mathrm{Zr})$	$11 \cdot \mathrm{CH}_3\mathrm{C}_6\mathrm{H}_5(\mathrm{M}=\mathrm{Al})$	13 (M = Al)	$14(\mathrm{M}=\mathrm{Ga})$
М-С7	2.406(4)	2.399(3)	2.534(7)			
M-C8	2.534(4)	2.484(3)	2.580(8)			
M-B9	2.458(5)	2.462(4)	2.592(1)			
M-B10	2.418(5)	2.444(4)	2.557(9)			
M-B11	2.344(5)	2.394(4)	2.512(9)			
M-Cent	1.964	1.966	2.112			
M-N/C(ligand)	1.889(4), 1.901(4)	1.910(3), 1.889(3)	2.040(7), 2.016(7)	1.939(5), 1.944(5)	1.939(4), 1.937(4)	1.964(3), 1.959(4)
M-N(side arm)	2.240(3)	2.276(3)	2.377(6)	1.985(4), 1.988(4)	2.475(1), 2.019(3)	2.446(7), 2.096(2)
Cent $-M-N$ (α angle)	97.6	97.6	93.6			
N(P)-M-N				105.5(1)	97.7(9)	97.0(6)

^a Distances are given in angstroms and angles in degrees.

Scheme 2. Synthesis of 6 and the π,σ -Type Group 4 Metal Complexes 9 and 10



Figure 4. Molecular structure of $6 \cdot (CH_3)_2 CO$ with thermal ellipsoids drawn at the 30% level. Hydrogen atoms and solvent molecules are omitted for clarity, except for H100 and H101 atoms.

 $Zr-N(sp^3)$ single bond.^{20,21} As shown in Table 3, all other bond distances and angles around the Zr and the N atoms were similar to those found in **9**.

Previously, we reported the use of monofunctionalized dicarbollyl ligand systems to prepare π,σ -coordinated group 13 metal complexes.^{16,17} In comparison with previous results derived from the monofunctional group, diffunctional dicarbollides proceeded with a different metal coordination mode: an σ,σ -fashion. The initial interaction of group 13 metals with the first donor tether brought the metal into a favorable position to form a tetrahedral geometry by interacting with

the second donor tether. Due to the availability of the extra donor site, a π -interaction with remote dicarbollide was not foreseeable. Such exo-polyhedral bis-donor interactions stabilized the group 13 metal center with a uninegative dicarbollide, as evidenced by the bridge hydrogen on the open face of the C₂B₃ pentagon. Formally, **11**, **13**, and **14** are charge-balanced between anionic (DcabH)⁻ and cationic [Me₂Al(D)(NMe₂-

CH₂)]⁺ (D = Me₂NCH₂, PPh₂) units. As shown in Scheme 3, reaction of **3** or **6** with 1 equiv of MMe₃ (M = Al, Ga) produced the exo-polyhedral σ , σ -type complexes **11–14** in good yield (91–74%).

Treatment of **3** with 1 equiv of MMe₃ (M = Al, Ga) in toluene under reflux for 12 h gave the σ , σ -type complexes in good to high yield, [(η^1 -NMe₂CH₂)₂C₂B₉H₁₀]MMe₂ (M = Al (11), 91%; M = Ga (12), 71%). As shown in Table 1, the ¹H NMR spectra of 11 and 12 show two M-*Me* peaks at δ -0.19, -0.22 (11) and δ 0.58, 0.60 (12) and a bridging hydrogen of the C₂B₃ cage at δ -2.14 (11) and δ -2.17 (12), indicating that only one methyl group on MMe₃ had been removed. Disappearance of the N···H-N proton and

⁽²⁰⁾ Carpenetti, D. W.; Kloppenburg, L.; Kupec, J. T.; Petersen, J. L. Organometallics 1996, 15, 1572.

⁽²¹⁾ Bowen, D. E.; Jordan, R. F.; Rogers, R. D. Organometallics 1995, 14, 3630.



Figure 6. Molecular structure of 10 with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity.

Scheme 3. Synthesis of the σ,σ-Type Dicarbollyl Group 13 Metal Complexes 11–14



the upfield shift of methyl protons in the NMe₂ side arm indicated the presence of two dative σ -bonds of N \rightarrow M \leftarrow N. Furthermore, σ , σ -bonded structures were proposed on the basis of the observation of a diastereotopic splitting pattern of the methylene protons of NCH₂ and two separate methyl resonances for the coordinated nitrogen functionality of NMe₂. The ²⁷Al NMR chemical shift of **11** (δ +154) confirms that the central aluminum atom is a four-coordinated compound.²²

Single-crystal X-ray structural studies authenticated the σ,σ -type interactions at the aluminum metal center (Figure 7 for 11). Table 2 gives the crystallographic data for 11. Table 3 and the Supporting Information give selected bond lengths and angles. The seven-membered chelate ring was formed by the ligand bound to AlMe₂. This species is believed to be a kinetically stabilized complex, in which there is an initial σ -electronic interaction of the aluminum atom with the amine side arm and concomitant η^{1} -type coordination with the neighboring second amine side arm. The central aluminum atom in 11 is coordinated to a pair of methyl ligands and two nitrogen atoms of the side arm in a σ -bonding manner. The Al-C bond lengths (1.939(5) and 1.944(5) Å) are shorter than the corresponding Al–C σ -bond, [Me₂Al(NH₂^{*t*}Bu)₂]I, (1.960(8) and 1.929(9) Å).²³ The Al-N(1)/N(2) bond lengths of the NMe₂ side arm (1.985(4)/1.988(4) Å) are shorter than for the corresponding four-coordinated cationic Al compound $[Me_2Al(NH_2^{t}Bu)_2]I$, (1.988(7) and 1.996(6) Å).²³ The shorter Al-N distances reflect the positive charge on Al in 11. The chelate bite angle N-Al-N in 11 is 105.5(1)°. This



Figure 7. Molecular structure of $11 \cdot CH_3C_6H_5$ with thermal ellipsoids drawn at the 30% level. Hydrogen atoms and solvent molecules are omitted for clarity, except for the H101 atom.

angle is larger than $[Me_2Al(NH_2'Bu)_2]I$ (98.2(3)°).²³ Indeed, this value is similar to that for the distorted triangular Al compound reported elsewhere.²⁴

A similar protocol was applied to the preparation of $[(\eta^1 - PPh_2)(\eta^1 - NMe_2CH_2)C_2B_9H_{10}]MMe_2 (M = Al (13), Ga (14)), as shown in Scheme 3. The addition of MMe_3 (M = Al, Ga) to the toluene solution of$ **6** $resulted in the formation of <math>\sigma,\sigma$ -bonded group 13 metal complexes as observed in 11. As shown in Table 1, compounds 13 and 14 exhibit characteristic shifts and splitting patterns of M-*Me*, NCH₂, NMe₂, and PPh₂ units. The ²⁷Al NMR chemical shift of 13 (δ +150) confirms that the central aluminum atom is a four-coordinated compound.²²

Single-crystal X-ray structural studies of 13 confirmed the σ,σ -coordination between the Al atom and the PPh₂ and NMe₂ side arm (Figure 8). Table 2 gives the crystallographic data for 13. Table 3 and the Supporting Information give selected bond lengths and angles. The six-membered chelate ring was formed by the ligand bound to AlMe₂. The Al-P/N bond lengths of 13 are 2.475(1)/2.019(3) Å, respectively. The Al-P bond distance confirmed that the P-donor atom is coordinated to the metal in a strain-free manner and the bond distance is consistent with a four-coordinated Al-P single bond.²⁵ The chelate bite angle P–Al–N of 97.7(9)° is significantly smaller than that in the corresponding fourcoordinated cationic Al compound $[\eta^2(O,P)-(2-PPh_2-4-Me 6^{-1}Bu-C_6H_2O]_2Al^+$ (120.0(3)°),²⁵ reflecting the electronic and size effects of P,N-donor atoms with differing P,Odonors.

Compound 14 was also produced from the same synthetic protocol (Scheme 3). Similar to the case for 13, the ¹H NMR spectral pattern for the NCH₂, NMe₂, Ga–Me, and PPh₂ units were observed in 14. The X-ray crystal structure of 14 (Figure 9) showed that the Al atom essentially adopts an σ , σ -bonding posture with the NMe₂ groups. Similar to 13, the Ga–P bond length (2.446(7) Å) is in the range of a typical

⁽²²⁾ Benn, R.; Janssen, E.; Lehmkuhl, H.; Rufihska, A. J. Organomet. Chem. **1987**, 333, 155.

⁽²³⁾ Atwood, D.; Jegier, J. Inorg. Chem. 1996, 35, 4277.

⁽²⁴⁾ Radzewich, C. E.; Guzei, I. A.; Jordan, R. F. J. Am. Chem. Soc. **1999**, *121*, 8673.

⁽²⁵⁾ Haddad, M.; Laghzaoui, M.; Welter, R.; Dagorne, S. Organometallics 2009, 28, 4584.



Figure 8. Molecular structure of **13** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity, except for the H101 atom.



Figure 9. Molecular structure of **14** with thermal ellipsoids drawn at the 30% level. Hydrogen atoms are omitted for clarity, except for the H101 atom.

Ga-P single bond^{26,27} in a four-coordinated tetrahedral geometry. The P-Ga-N bite angle of **14** is 97.0(6)°, which is similar to **13**.

Conclusions

Apparently similar electrophilic early-transition and main-group metals were examined for the formation of new types of coordination compounds consisting of a N, N'- and P,N-donor unit tethered to a dicarbollyl ligand.

Group 4 metals (Ti and Zr) preferred π,σ -coordination with the involvement of a dicarbollyl ligand and one of the donor groups in the N,N'- and P,N-functionalized units, whereas group 13 metals (Al and Ga) completed their four-coordination only with tethered donors through both nitrogen atoms and a nitrogen and phosphine combination in a σ,σ -coordination manner. This study shows that the two side arm donors dictate the formation of σ,σ -coordination with group 13 metals. Therefore, a monotethering strategy is desirable for forming π,σ -type coordination with group 13 metals.

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. THF was freshly distilled over potassium benzophenone. Toluene, n-hexane, and n-pentane were dried and distilled over sodium benzophenone. Dichloromethane and hexane were dried and distilled over CaH₂. The ¹H, ¹¹B, ¹³C, ³¹P, and ²⁷Al NMR spectra were recorded on a Varian Mercury 300 spectrometer operating at 300.1, 96.3, 75.4, 121.4, and 78.2 MHz, respectively. All ¹¹B chemical shifts were referenced to BF_3 . $O(C_2H_5)_2$, with a negative sign indicating an upfield shift. 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 tetramethylsilane (Me₄Si). The IR spectra were recorded on a Biorad FTS-165 spectrophotometer. Elemental analyses were performed with a Carlo Erba Instruments CHNS-O EA1108 analyzer. All melting points were uncorrected. o-Carborane was purchased from Katchem and used as received. All other reagents were obtained from commercial suppliers (Aldrich and TCI) and used as received.

Preparation of $[closo-1,2-(CH_2NMe_2)_2-1,2-C_2B_{10}H_{10}]$ (2). n-BuLi (2.5 M, 4.4 mL) was added to a stirred solution of o-carborane 1 (0.72 g, 5 mmol) in toluene (100 mL) via a syringe through a serum cap at 0 °C. The resulting white suspension was stirred at 25 °C for 10 min and placed in an ice bath. When the toluene solution was cold, Eschenmoser's salt, CH2=NMe2+I-(2.03 g, 11.1 mmol), was added to the lithio-o-carborane. The reaction temperature was maintained at 0 °C for 1 h. The reaction mixture was then warmed slowly to room temperature. After it was stirred for an additional 12 h under reflux, the reaction mixture was filtered and dried in vacuo to give a white crystalline powder. The resulting residue was taken up in a minimum of *n*-pentane and recrystallized from solution by cooling to -5 °C to afford 2 as colorless crystals. Yield: 86% (1.1 g, 4.3 mmol). Mp: 87 °C. Anal. Calcd for C₈H₂₆B₁₀N₂: C, 37.18; H, 10.14; N, 10.84. Found: C, 37.30; H, 10.12; N, 10.80. IR spectrum (KBr pellet, cm⁻¹): ν (B–H) 2640, 2580, ν (C–H) 3001, 2829, 2781. ¹H NMR (300 MHz, CDCl₃): δ 2.32 (s, 12H, NMe₂), 3.11 (s, 4H, NCH₂). ¹³C NMR (75.4 MHz, CDCl₃): δ 46.7 (NMe₂), 62.6 (NCH₂). ¹¹B NMR (96.3 MHz, CDCl₃): $\delta - 3.9$ (4B), -10.8 (6B).

Preparation of [*nido*-7,8-(NMe₂CH₂)₂-7,8-C₂B₉H₁₀] (3). Compound 2 (0.78 g, 3.0 mmol) was dissolved in degassed methanol (20 mL) and heated under reflux under N₂ for 12 h. Methanol was removed under reduced pressure, and the residue was washed with Et₂O (10 mL × 3). The volatiles were removed under vacuum to provide the final crude product. The product was purified by recrystallization from ethanol in 95% yield (0.95 g, 3.8 mmol). Mp: 294 °C dec. Anal. Calcd for C₈H₂₇B₉N₂: C, 38.65; H, 10.95; N, 11.25. Found: C, 38.52; H, 10.98; N, 11.30. IR spectrum (KBr pellet, cm⁻¹): ν (B–H) 2515, ν (C–H) 3025, 2989, 2963. ¹¹B NMR (96.3 MHz, acetone-*d*₆): δ -7.5 (2B), -10.8 (1B), -13.4 (1B), -15.5 (1B), -19.5 (2B), -33.1 (1B), -35.8 (1B).

Preparation of $[closo-1-PPh_2-2-CH_2NMe_2-1,2-C_2B_{10}H_{10}]$ (5). *n*-BuLi (2.5 M, 1.3 mL, 3.3 mmol) was added to a stirred

⁽²⁶⁾ Vălean, A. M.; Gómez-Ruiz, S.; Lönnecke, P.; Silaghi-Dumitrescu, I.; Silaghi-Dumitrescu, L.; Hey-Hawkins, E. *Inorg. Chem.* **2008**, *47*, 11284.

⁽²⁷⁾ Lee, J.-D.; Ko, J.; Cheong, M.; Kang, S. O. Organometallics 2005, 24, 5845.

solution of 1-PPh₂-o-carborane 4 (1.64 g, 5.0 mmol) in toluene (100 mL) via a syringe through a serum cap at 0 °C. The resulting white suspension was stirred at 25 °C for 10 min and placed in an ice bath. When the toluene solution was cold, Eschenmoser's salt, $CH_2 = NMe_2^+I^-$ (1.02 g, 5.5 mmol), was added to the 1-lithio-2-PPh₂-o-carborane. The reaction temperature was maintained at 0 °C for 1 h. The reaction mixture was then warmed slowly to room temperature. After it was stirred for an additional 12 h under reflux, the reaction mixture was filtered and dried in vacuo to give a white crystalline powder. The resulting residue was taken up in a minimum of *n*-pentane and recrystallized from this solution by cooling to -5 °C to afford 5 as colorless crystalline solids. Yield: 81% (1.56 g, 4.05 mmol). Mp: 86 °C. Anal. Calcd for C17H28B10NP: C, 52.97; H, 7.32; N, 3.63. Found: C, 53.01; H, 7.28; N, 3.60. IR spectrum (KBr pellet, cm⁻¹): v(B-H) 2638, 2584, v(C-H) 2988, 2780. ¹H NMR (300 MHz, CDCl₃): δ 2.32 (s, 6H, NMe₂), 3.13 (s, 2H, NCH₂), 7.28–7.34 (m, 10H, PPh₂). ¹³C NMR (75.4 MHz, CDCl₃): δ 47.2 (NMe₂), 63.1 (NCH₂), 125.7 (PPh₂), 128.4 (PPh₂), 134.6 (PPh₂). ¹¹B NMR (96.3 MHz, CDCl₃): δ -4.5 (2B), -6.2 (1B), -9.7 (2B), -11.2 (3B), -12.5 (2B). ³¹P NMR (121.4 MHz, CDCl_3): $\delta - 11.8 (PPh_2)$.

Preparation of [*nido*-7-PPh₂-8-CH₂NMe₂-7,8-C₂B₉H₁₀] (6). Compound 5 (1.16 g, 3.0 mmol) and KOH (0.22 g, 4.0 mmol) were dissolved in degassed ethanol (20 mL) and then heated under reflux in N2 for 12 h. Ethanol was removed under reduced pressure, and the residue was suspended in benzene (60 mL). Azeotropic distillation was then performed to remove the H₂O and ethanol, and the remaining white solid was dried overnight under vacuum. The solid was mixed with benzene (30 mL) under N₂ to form a slurry, and H₃PO₄ was then added. The resulting two-phase mixture was stirred vigorously for 15 h. The volatiles were removed by rotary evaporation under reduced pressure, and the residue was washed with H₂O to yield an off-white solid. The product was purified by recrystallization from acetone to yield 6 as colorless crystals. Yield: 94% (1.06 g, 2.8 mmol). Mp: 268 °C dec. Anal. Calcd for C₁₇H₂₉B₉NP: C, 54.35; H, 7.78; N, 3.73. Found: C, 54.31; H, 7.73; N, 3.70. IR spectrum (KBr pellet, cm⁻¹): v(B–H) 2517, v(C–H) 3020, 2982, 2887. ¹¹B NMR (96.3 MHz, acetone- d_6): $\delta - 8.4$ (2B), -11.3 (1B), -13.7 (1B), -18.6 (1B), -19.2 (2B), -31.8 (1B), -34.6 (1B). 31 P NMR (121.4 MHz, acetone- d_6): $\delta - 21.7 (PPh_2)$.

Preparation of $[(\eta^5-C_2B_9H_9CH_2NMe_2)(\eta^1-NMe_2CH_2)]$ Ti-(NMe₂)₂ (7). Over a period of 30 min, a 20 mL toluene solution of Ti(NMe₂)₄ (0.45 g, 2.0 mmol) was added to a stirred solution of 3 (0.50 g, 2.0 mmol) in toluene (20 mL) at 0 °C. Subsequently, the cold bath was removed and the solution was stirred at room temperature for 36 h. The solvent was removed in vacuo, and the residue was purified by recrystallization with a CH₂Cl₂/toluene mixture at -30 °C. Yield: 84% (0.64 g, 1.68 mmol). Mp: 131 °C dec. Anal. Calcd for C₁₂H₃₇B₉N₄Ti: C, 37.67; H, 9.75; N, 14.64. Found: C, 37.74; H, 9.77; N, 14.69. IR (KBr, pellet, cm⁻¹): ν(B-H) 2521, ν(C-H) 2989, 2964, 2855. ¹¹B NMR (96.3 MHz, C₆D₆): δ -4.5 (1B), -6.8 (1B), -7.2 (2B), -10.6 (1B), -15.9 (1B), -31.8 (2B), -34.7 (1B).

Compound 8. A procedure analogous to that used to prepare 7 was employed, but instead with the zwitterion **3** (0.50 g, 2.0 mmol) and Zr(NMe₂)₄ (0.54 g, 2.0 mmol). Yield: 78% (0.66 g, 1.56 mmol). Mp: 138 °C dec. Anal. Calcd for $C_{12}H_{37}B_9N_4Zr$: C, 33.84; H, 8.75; N, 13.15. Found: C, 33.86; H, 8.80; N, 13.26. IR spectrum (KBr pellet, cm⁻¹): ν (B–H) 2523, ν (C–H) 2994, 2950, 2880. ¹¹B NMR (96.3 MHz, C₆D₆): δ –5.1 (2B), -8.6 (1B), -10.4 (1B), -18.4 (3B), -32.1 (1B), -35.3 (1B).

Compound 9. A procedure analogous to that used to prepare 7 was employed, but instead with the zwitterions **6** (0.75 g, 2.0 mmol) and Ti(NMe₂)₄ (0.45 g, 2.0 mmol). Yield: 87% (0.88 g, 1.74 mmol). Mp: 133 °C dec. Anal. Calcd for C₂₁B₉H₃₉N₃PTi: C, 49.49; H, 7.71; N, 8.24. Found: C, 49.53; H, 7.68; N, 8.29. IR spectrum (KBr pellet, cm⁻¹): ν (B–H) 2520, ν (C–H) 3002, 2978, 2951. ¹¹B NMR (96.3 MHz, C₆D₆): δ –3.7 (1B), -7.9 (1B), -11.7 (2B), -17.2 (2B), -31.8 (1B), -34.3 (2B). ³¹P NMR (121.4 MHz, C_6D_6): $\delta -27.4$ (*P*Ph₂).

Compound 10. A procedure analogous to that used to prepare 7 was employed, but instead with the zwitterion **6** (0.75 g, 2.0 mmol) and Zr(NMe₂)₄ (0.72 g, 2.0 mmol). Yield: 65% (0.72 g, 1.3 mmol). Mp: 128 °C dec. Anal. Calcd for C₂₁B₉H₃₉N₃PZr: C, 45.61; H, 7.11; N, 7.60. Found: C, 45.58; H, 7.14; N, 7.63. IR spectrum (KBr pellet, cm⁻¹): ν (B–H) 2522, ν (C–H) 2984, 2955, 2948. ¹¹B NMR (96.3 MHz, C₆D₆): δ –4.6 (1B), –7.1 (2B), –11.6 (1B), –19.4 (3B), –33.7 (1B), –36.8 (1B). ³¹P NMR (121.4 MHz, C₆D₆): δ –26.8 (*P*Ph₂).

Preparation of $[(\eta^1-NMe_2CH_2)_2C_2B_9H_{10}]AlMe_2$ (11). A 5 mL portion of a toluene solution of AlMe₃ (0.14 g, 2.0 mmol) was added to 20 mL of a stirred toluene solution containing 3 (0.50 g, 2.0 mmol) by cannula at -78 °C. Subsequently, the dry ice/acetone bath was removed and the solution was heated under reflux in N₂ for 12 h. The formation of 3 was demonstrated by ¹H NMR spectroscopy. The volatiles were removed under vacuum, and the residue was purified by recrystallization with a toluene at -15 °C. Yield: 91% (0.55 g, 1.82 mmol). Mp: 135 °C dec. Anal. Calcd for C₁₀B₉H₃₂AlN₂: C, 39.42; H, 10.59; N, 9.20. Found: C, 39.18; H, 10.54; N, 9.27. IR spectrum (KBr pellet, cm⁻¹): ν (B–H) 2518, ν (C–H) 3105, 2993, 2951. ¹¹B NMR (96.3 MHz, CD₃C₆D₅): δ –8.4 (2B), –10.2 (1B), –18.6 (1B), –20.8 (3B), –30.8 (1B), –33.7 (1B).

Compound 12. A procedure analogous to that used to prepare **11** was employed, but instead with the zwitterion **3** (0.50 g, 2.0 mmol) and GaMe₃ (0.23 g, 2.0 mmol). Yield: 71% (0.49 g, 1.42 mmol). Mp: 130 °C dec. Anal. Calcd for C₁₀B₉H₃₂GaN₂: C, 34.57; H, 9.28; N, 8.06. Found: C, 34.60; H, 9.33; N, 8.00. IR spectrum (KBr pellet, cm⁻¹): ν (B–H) 2518, ν (C–H) 2994, 2972. ¹¹B NMR (96.3 MHz, CD₃C₆D₅): δ –7.8 (2B), –10.7 (1B), –15.5 (2B), –19.4 (2B), –32.8 (1B), –35.7 (1B).

Compound 13. A procedure analogous to that used to prepare **11** was employed, but instead with the zwitterion **6** (0.75 g, 2.0 mmol) and AlMe₃ (0.14 g, 2.0 mmol). Yield: 80% (0.69 g, 1.6 mmol). Mp: 125 °C dec. Anal. Calcd for C₁₉B₉H₃₄AlNP: C, 52.86; H, 7.94; N, 3.24. Found: C, 52.81; H, 8.00; N, 3.21. IR spectrum (KBr pellet, cm⁻¹): ν (B–H) 2520, ν (C–H) 3100, 2986, 2980. ¹¹B NMR (96.3 MHz, CD₃C₆D₅): δ –8.5 (1B), –11.4 (1B), –18.6 (3B), –20.4 (2B), –32.4 (1B), –36.1 (1B). ³¹P NMR (121.4 MHz, CD₃C₆D₅): δ –38.7 (*P*Ph₂).

Compound 14. A procedure analogous to that used to prepare **11** was employed, but instead with the zwitterion **6** (0.75 g, 2.0 mmol) and GaMe₃ (0.23 g, 2.0 mmol). Yield: 74% (0.70 g, 1.48 mmol). Mp: 122 °C dec. Anal. Calcd for C₁₉B₉H₃₄GaNP: C, 48.10; H, 7.22; N, 2.95. Found: C, 48.06; H, 7.17; N, 2.98. IR spectrum (KBr pellet, cm⁻¹): ν (B–H) 2519, ν (C–H) 3104, 2988, 2961. ¹¹B NMR (96.3 MHz, CD₃C₆D₅): δ –7.7 (2B), –12.8 (1B), –17.5 (3B), –19.7 (1B), –30.4 (1B), –35.3 (1B). ³¹P NMR (121.4 MHz, CD₃C₆D₅): δ –35.8 (PPh₂).

Crystal Structure Determination. Crystals of 3, 6-11, 13, and 14 were obtained from toluene at -15 °C, sealed in glass capillaries under argon, and mounted on the diffractometer. A preliminary examination and data collection were performed using a Bruker SMART CCD detector system single-crystal X-ray diffractometer equipped with a sealed-tube X-ray source $(40 \text{ kV} \times 50 \text{ mA})$ using graphite-monochromated Mo K α radiation ($\lambda = 0.7107$ Å). Preliminary unit cell constants were determined with a set of 45 narrow-frame (0.3° in ω) scans. The double-pass method of scanning was used to exclude noise. The collected frames were integrated using an orientation matrix determined from the narrow-frame scans. The SMART software package was used for data collection, and SAINT was used for frame integration.²⁸ The final cell constants were determined by a global refinement of the xyz centroids of reflections harvested from the entire data set. Structure solution

⁽²⁸⁾ *SMART and SAINT*; Bruker Analytical X-ray Division, Madison, WI, 2002.

and refinement were carried out using the SHELXTL-PLUS software package. $^{\rm 29}$

Acknowledgment. This study was supported by a National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2010-0018456). We also thank the support from WCU and BK-21 programs.

Supporting Information Available: Text giving additional details of the syntheses, and tables and CIF files giving crystallographic data for **3**, **6**, **7**, **9**, **10**, **11**, **13**, and **14**. This material is available free of charge via the Internet at http:// pubs.acs.org.

⁽²⁹⁾ Sheldrick, G. M. *SHELXTL-PLUS Software Package*; Bruker Analytical X-ray Division, Madison, WI, 2002.