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Group 13−Group 13 Donor−Acceptor Complexes

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Group 13−group 13 donor−acceptor complexes Cp*M−Al(t-Bu)$_3$ (M = Al **1**, Ga **2**, In **3**) and Cp*M−Ga(t-Bu)$_3$ (M = Al **4**, Ga **5**, In **6**) were obtained from reactions between [Cp*M]$_x$ (M = Al, x = 4; Ga, In, x = 6) and M(t-Bu)$_3$ (M = Al, Ga). **3**, **4**, and **6** represent the first compounds containing dative In(I)−Al(III), Al(I)−Ga(III), and In(I)−Ga(III) bonds. **1**−**6** were characterized by elemental analyses, mass and multinuclear NMR spectroscopy (^{1}H, ^{13}C), and single-crystal X-ray analysis (except for **5**).

Introduction

Group 13 metal organic compounds containing metal−metal bonds have attracted considerable attention within the last two decades. Univalent compounds with the metal centers in the formal oxidation state I (e.g., [Cp*M]$_x$ (M = Al, Ga, In)) and divalent compounds (oxidation state II; e.g., [Tms$_2$CHM]$_2$ (M = Al, Ga, In)) have been synthesized and their reactivity has been studied in detail.[1] Alanediyls RAl and their heavier congeners RM (M = Ga, In) were found to exhibit a strong Lewis basicity. Their electronic ground state is singlet with the singlet−triplet energy gap increasing with increasing atomic number, as was previously observed for carbenes. In addition, the Lewis basicity of group 13 diyls was found to increase with increasing π-donor capability of the organic substituent R.[2] Consequently, strong π-donor ligands such as amido (NR$_2$) groups and the Cp* substituent enhance the stability of group 13−transition metal (TM) complexes RM−TML$_n$,[3] which have been synthesized and structurally characterized in large numbers,[4] and group 13−group 13 donor−acceptor complexes of the type RM−M′R′$_3$.[5] In addition, the nature of the metal−metal bond within these complexes was investigated in detail by computational calculations.[6] Homoleptic group 13−group 13 complexes can also be described as valence isomers of the corresponding divalent compounds R$_2$M−MR$_2$.[7] For instance, DFT calculations indicate that H$_2$Al−AlH$_2$ is more stable than the corresponding valence isomer HAl−AlH$_3$ by 9.17 kcal/mol, whereas Cp*Al−AlH$_3$ is more stable than the dialane Cp*(H)-Al−AlH$_2$ by 10.79 kcal/mol.[8] Even though Cp*Al−AlH$_3$ is unknown, to date, several homonuclear Cp*M−MR$_3$[9] and heteronuclear complexes Cp*M−M′R$_3$ (M, M′ = B, Al, Ga, In),[10] most of them containing the strong Lewis acids B(C$_6$F$_5$)$_3$ and Al(C$_6$F$_5$)$_3$, have been synthesized and structurally characterized in the last decade.[11]

To compare the relative Lewis basicity of group 13 diyls Cp*M (M = Al, Ga), the deviation of the BC$_3$ skeleton in Cp*M−B(C$_6$F$_5$)$_3$ complexes from planarity was investigated. As was expected, Cp*Al was found to be slightly more Lewis basic than Cp*Ga.[12] Much more surprising, these data suggested Cp*Al to be almost as strong a base as PPh$_3$. We have prepared and structurally characterized a large number of group 13−group 15 Lewis acid−base adducts of the type R$_3$E−MR′$_3$ (E = N, P, As, Sb, Bi; M = Al, Ga) during the last decade. Consequently, we became interested in comparing such adducts with group 13−group 13 complexes RM−M′R′$_3$ in order to estimate the Lewis basicity of Cp*M compared to group 15 triorganyls ER$_3$. The Lewis acids t-Bu$_3$M (M = Al, Ga) were chosen because their structural parameters are known,[13] and several Lewis base adducts R$_3$E−Al(t-Bu)$_3$ and R$_3$E−Ga(t-Bu)$_3$ (E = P, As, Sb, Bi) have been synthesized and structurally characterized previously in our group.[14] To date, M(t-Bu)$_3$ adducts of group 13 diyls are almost unknown except for

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(1) For review articles see, for example: (a) Dohmeier, C.; Loos, D.; Schnöckel, H. *Angew. Chem., Int. Ed.* **1996**, *35*, 129. (b) Linti, G.; Schnöckel, H. *Coord. Chem. Rev.* **2000**, *206*, 285. (c) Uhl, W. *Naturwissenschaften* **2004**, *91*, 305. (d) Uhl, W. *Rev. Inorg. Chem.* **1998**, *18*, 239. (e) Uhl, W. *Coord. Chem. Rev.* **1997**, *163*, 1. (f) Uhl, W. *Adv. Organomet. Chem.* **2004**, *51*, 53.

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(3) Frenking, G. *J. Organomet. Chem.* **2001**, *635*, 9.

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(7) In addition, some univalent group 13 diyls containing β-diketiminato or sterically extremely demanding terphenyl substituents have been synthesized. Their Lewis basicity was found to be even higher than that of Cp*-substituted diyls (ref 5).

(8) Gorden, J. D.; MacDonald, C. L. B.; Cowley, A. H. *J. Chem. Soc., Chem. Commun.* **2001**, 75. Detailed computational investigations on the role of the substituents on the relative stability of the two isomeric forms are given in ref 2. The relative stability of different isomers of Al$_2$H$_4$ was also investigated by Lammertsma et al.: Lammertsma, K.; Güner, O. F.; Drewes, R. M.; Reed, A. E.; Schleyer, P. v. R. *Inorg. Chem.* **1989**, *28*, 313.

(9) Cp*Al−Al(C$_6$F$_5$)$_3$ (ref 8); Cp*Ga−Ga(t-Bu)$_3$ (ref 15); Cp*Ga−Ga(Cp*)X$_2$ (X = Cl, I) (ref 15).

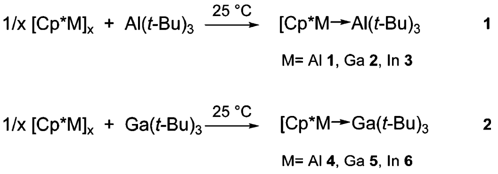
(10) Cp*Al−B(C$_6$F$_5$)$_3$ (ref 16); Cp*Ga−B(C$_6$F$_5$)$_3$ (refs 15, 17). Cp*Ga−Al(C$_6$F$_5$)$_3$: Gordon, J. D.; MacDonald, C. L. B.; Cowley, A. H. *Main Group Chem.* **2005**, *4*, 33.

(11) In addition, several B(C$_6$F$_5$)$_3$ complexes of β-diketiminato- and terphenyl-substituted diyls have been structurally characterized (for details see ref 5).

(12) The basicity of analogously substituted Lewis bases typically decreases upon descending a group in the periodic table.

10.1021/om0606946 CCC: $33.50

Scheme 1. Synthesis of 1−6



Cp*Ga−Ga(t-Bu)$_3$, which was prepared by Jutzi et al.[15] However, no X-ray crystallographic data are available for this compound.

Results and Discussion

Equimolar amounts of [Cp*M]$_x$ dissolved in toluene (M = Al) and pentane (M = Ga, In), respectively, and M(t-Bu)$_3$ (M = Al, Ga) react at ambient temperature with subsequent formation of the donor−acceptor complexes Cp*M−Al(t-Bu)$_3$ (M = Al **1**, Ga **2**, In **3**) and Cp*M−Ga(t-Bu)$_3$ (M = Al **4**, Ga **5**, In **6**). **1**−**6** were obtained after storage at −30 °C in high yields as colorless crystalline solids. The ^{1}H NMR spectra of **1**−**6** each show two singlets due to the Cp* substituent and the t-Bu groups. The resonances of the Cp* substituent (δ 1.65 **1**, 1.77 **2**, 1.98 **3**, 1.67 **4**, 1.79 **5**, 2.03 **6**) are shifted to higher field compared to those of uncomplexed Cp*M, as was previously observed for Cp*M−B(C$_6$F$_5$)$_3$ (M = Al,[16] Ga[15,17]) whereas those of the t-Bu groups are shifted to lower field.[18] The different chemical shift ranges observed in the ^{1}H NMR spectra for the t-Bu groups in **1**−**6** reflect the different Lewis basicities of the group 13 diyls. In both adduct groups, the *biggest downfield shift* was observed for complexes containing the *strongest* Lewis base Cp*Al. Comparable findings have been previously reported for group 13−group 15 adducts [R$_2$(H)N−AlMe$_3$,[19] R$_3$N−InMe$_3$,[20] R$_3$P−MMe$_3$ (M = Al[21], Ga[22]), R$_3$Sb−M(R′)$_3$ (M = Al,[23] Ga[24])]. In contrast, the downfield shift in R$_3$Sb−M(t-Bu)$_3$ adducts (R = Me, Et, i-Pr, t-Bu) was found to decrease with increasing Lewis basicity of the stibine R$_3$Sb,[25] most likely resulting from repulsive interactions between the sterically demanding organic ligands.

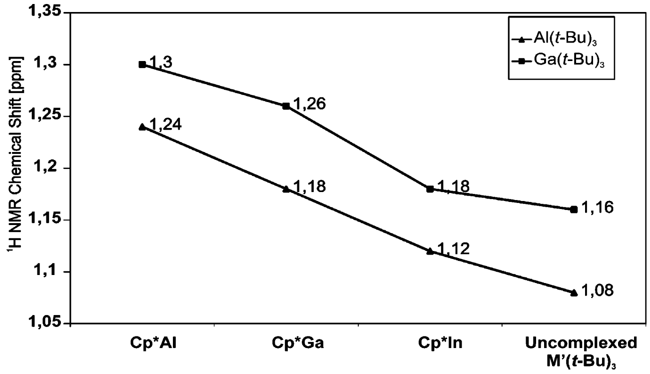


Figure 1. ^{1}H NMR chemical shift (t-Bu group) of group 13−group 13 donor−acceptor complexes Cp*M−M′(t-Bu)$_3$ (M = Al, Ga, In; M′ = Al, Ga) and uncomplexed M′(t-Bu)$_3$.

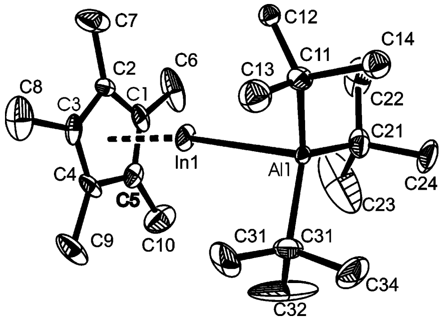


Figure 2. Molecular structure and atom-numbering scheme of **3**. Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity. Only the major part of the disordered t-Bu group is shown.

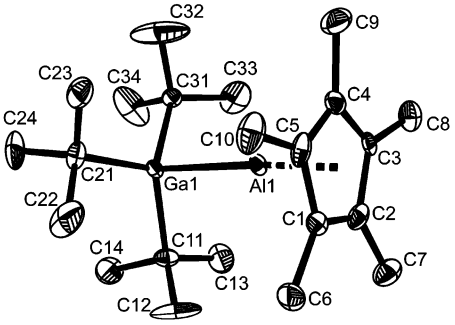


Figure 3. Molecular structure and atom-numbering scheme of **4**. Thermal ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

The solid-state structures of compounds **1**−**4** and **6** were determined by single-crystal X-ray diffraction. Suitable crystals were obtained from solutions in toluene (**1**, **4**) and pentane (**2**, **3**, **6**), respectively, after storage at −30 °C for 24 h.

1−**4** and **6** are isostructural and crystallize in the monoclinic space group $P2_1/c$ (No. 14). The intermetallic Al−Al (2.689(2) Å, **1**) and Ga−Al bond distances (2.629(2) Å, **2**) are significantly elongated compared to those in Cp*M−Al(C$_6$F$_5$)$_3$ (M = Al 2.591(2) Å;[8] Ga 2.515(11) Å[10]), the only structurally characterized RM−AlR′$_3$ donor−acceptor complexes (M = Al, Ga) to date. The bond elongation clearly reflects the different electronic (Lewis acidity: Al(C$_6$F$_5$)$_3$ > Al(t-Bu)$_3$) and steric influences (steric demand: Al(t-Bu)$_3$ > Al(C$_6$F$_5$)$_3$) of the organic substituents of the Lewis acid AlR$_3$ within these two donor−acceptor complexes. The Ga(I)−Al bond distance in **2** is significantly shorter than the Al(I)−Al distance in **1**, as was observed for Cp*M−Al(C$_6$F$_5$)$_3$ (M = Al, Ga), resulting from different

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[13] t-Bu$_3$M (M = Al, Ga) were structurally characterized by single-crystal X-ray analysis: (a) Woski, M.; Mitzel, N. W. *Z. Naturforsch.* **2004**, *59b*, 269. (b) Cowley, A. R.; Downs, A. J.; Marhant, S.; Macrae, V. A.; Taylor, R. A. *Organometallics* **2005**, *24*, 5702. (c) Kuczkowski, A.; Schulz, S.; Nieger, M. *Appl. Organomet. Chem.* **2004**, *18*, 244. In addition, the molecular structure of t-Bu$_3$Al was determined by electron diffraction [(d) Rankin, D. W. H. Personal communication] and calculated by density functional theory (B3LYP/SDD) [(e) Kuczkowski, A.; Schulz, S.; Nieger, M.; Schreiner, P. R. *Organometallics* **2002**, *21*, 1408].

[14] See the following and references therein: (a) Schulz, S. In *Structure and Bonding*, Vol. 103: *Group 13 Chemistry I: Fundamental New Developments*; Roesky, H. W., Atwood, D. A., Eds.; 2002; p 117. (b) Schulz, S. *Adv. Organomet. Chem.* **2003**, *49*, S. 225.

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Table 1. Crystallographic Details for 1, 2, 3, 4, and 6

	1	**2**	**3**	**4**	**6**
empirical formula	$C_{22}H_{42}Al_2$	$C_{22}H_{42}AlGa$	$C_{22}H_{42}AlIn$	$C_{22}H_{42}AlGa$	$C_{22}H_{42}InGa$
molecular mass	360.5	403.3	448.4	403.3	491.1
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a [Å]	14.3246(3)	14.240(6)	14.140(4)	14.309(4)	14.179(6)
b [Å]	10.0441(2)	9.951(4)	10.496(3)	9.947(3)	10.519(4)
c [Å]	16.7107(4)	16.567(7)	16.579(4)	16.646(5)	16.601(7)
β [deg]	91.807(2)	91.545(11)	90.629(5)	91.432(7)	90.153(6)
V [Å^3]	2403.1(1)	2346.7(17)	2460.5(10)	2368.6(11)	2476.2(17)
Z	4	4	4	4	4
T [K]	123(2)	120(2)	120(2)	120(2)	120(2)
radiation (λ [Å])	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ [mm^{-1}]	0.123	1.212	0.998	1.200	2.021
D_{calcd} [g cm^{-3}]	0.996	1.141	1.210	1.131	1.317
$2\theta_{max}$ [deg]	50	56	56	56	56
cryst dimens [mm]	0.50 × 0.35 × 0.15	0.46 × 0.35 × 0.32	0.42 × 0.40 × 0.40	0.22 × 0.20 × 0.17	0.40 × 0.38 × 0.35
no. of reflns	14 993	16 407	18 483	22 851	19 086
no. of unique reflns	4217	5690	5962	5638	6003
R_{merg}	0.0332	0.0805	0.0855	0.1732	0.0993
no. of params refined/restraints	222/0	221/0	216/0	223/0	216/0
$R_1{}^a$	0.0743	0.1074	0.1017	0.0901	0.0970
$wR_2{}^b$	0.1952	0.2959	0.2508	0.1692	0.2739
goodness of fit^c	1.135	0.972	1.124	1.002	1.086
final max./min. $\Delta\rho$ [e Å^{-3}]	0.866/−0.378	1.336/−0.932	1.930/−1.160	1.171/−0.712	1.189/−1.619

^{a} $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$ (for $I > 2\sigma(I)$). ^{b} $wR_2 = \{\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]\}^{1/2}$. ^{c} Goodness of fit $= \{\sum[w(|F_o{}^2| - |F_c{}^2|)^2]/(N_{observns} - N_{params})\}^{1/2}$.

Table 2. Selected Bond Lengths [Å] and Angles [deg] of Cp*M−M′(*t*-Bu)$_3$ 1, 2, 3, 4, and 6

	1	**2**	**3**
	M = M′ = Al	M = Ga, M′ = Al	M = In, M′ = Al
M−M′	2.689(2)	2.629(2)	2.843(2)
ϕ(M−C$_{Cp*}$)	2.218	2.253	2.480
M−Cp*$_{centr}$	1.858	1.913	2.173
M′−C$_{t-Bu}$	2.031(3)	1.974(9)	1.989(8)
M′−C$_{t-Bu}$	2.031(3)	1.984(8)	1.998(10)
M′−C$_{t-Bu}$	2.035(3)	2.027(9)	2.067(11)
ϕ(M′−C$_{t-Bu}$)	2.032	1.995	2.018
Cp*$_{centr}$−M−M′	175.0	174.2	170.0
C$_{t-Bu}$−M′−C$_{t-Bu}$	116.4(2)	116.2(4)	117.2(5)
C$_{t-Bu}$−M′−C$_{t-Bu}$	116.0(2)	117.4(4)	117.5(4)
C$_{t-Bu}$−M′−C$_{t-Bu}$	115.9(2)	117.8(4)	118.4(5)
$\sum$(C$_{t-Bu}$−M′−C$_{t-Bu}$)	348.3	351.4	353.1

	4	**6**
	M = Al, M′ = Ga	M = In, M′ = Ga
M−M′	2.620(2)	2.845(2)
ϕ(M−C$_{Cp*}$)	2.194	2.492
M−Cp*$_{centr}$	1.861	2.187
M′−C$_{t-Bu}$	2.022(6)	1.991(11)
M′−C$_{t-Bu}$	2.019(6)	2.018(9)
M′−C$_{t-Bu}$	2.060(6)	2.052(14)
ϕ(M′−C$_{t-Bu}$)	2.034	2.020
Cp*$_{centr}$−M−M′	175.5	170.3
C$_{t-Bu}$−M′−C$_{t-Bu}$	115.4(3)	117.0(5)
C$_{t-Bu}$−M′−C$_{t-Bu}$	116.8(3)	118.5(6)
C$_{t-Bu}$−M′−C$_{t-Bu}$	116.3(3)	118.4(5)
$\sum$(C$_{t-Bu}$−M′−C$_{t-Bu}$)	348.5	353.9

electrostatic repulsion between the group 13 metal atoms.[26] In addition, the Al−Ga bond length in **4** (2.620(2) Å) is also shorter than that in **1** (2.689(2) Å). This finding, which is somehow unexpected since analogously substituted group 13/15 adducts of the type $R_3E{-}MR'_3$ (M = Al, Ga; E = N−Bi) typically show shorter Al−E than Ga−E bond distances, cannot be explained by repulsive interactions between the organic substituents (Cp*, *t*-Bu) because both the Al−C$_{Cp*}$ (2.218 Å, **1**; 2.194 Å, **4**) and the M′−C$_{t-Bu}$ bond lengths (2.032 Å, **1**; 2.034 Å, **4**) are almost equal. Most likely, the stronger electropositive character of the metal atom in Al(*t*-Bu)$_3$ compared to Ga(*t*-Bu)$_3$ leads to a stronger repulsive electrostatic interaction with the strong electropositive Cp*Al. Unfortunately, **4** represents the only structurally characterized complex with an Al(I) donor and Ga(III) acceptor to date, consequently allowing no comparisons with other complexes of the desired type. The In−Al and In−Ga bond distances as observed for **3** (2.843(2) Å) and **6** (2.845(2) Å) are the longest of both adduct groups, as was expected due to the increased atomic radius of In compared to those of Al and Ga, respectively. Since **3** and **6** also represent the first compounds with dative In−Al and In−Ga bonds, their structural parameters cannot be compared in detail with others.

Table 3. Selected Bond Lengths [Å] of Group 13 Diyls [Cp*M]$_x$ (M = Al, Ga, In)

	[Cp*Al]$_4$	Cp*Al	[Cp*Ga]$_6$	Cp*Ga	[Cp*In]$_6$	[Cp*In]
ref	36	37^a	38	39^a	40	40^a
ϕ(M−C$_{Cp*}$)	2.344	2.388	2.400	2.405	2.592	2.592
M−Cp*$_{centr}$	2.015	2.063	2.081	2.081	2.302	2.288

^{a} As determined by electron diffraction (gas phase).

Each Cp* substituent in **1**−**4** and **6** adopts an η^5-binding mode to the group 13 metal, as was indicated by the ^{1}H and ^{13}C NMR spectra. The smallest variations within the M−C$_{Cp*}$ bond lengths were observed for **1** (0.015 Å) and **4** (0.020 Å), whereas much larger variations were found for **2** (0.032 Å), **3** (0.048 Å), and **6** (0.043 Å). The average M−C$_{Cp*}$ bond lengths (2.218 Å, **1**; 2.253 Å, **2**; 2.480 Å, **3**; 2.194 Å, **4**; 2.492 Å, **6**) and M−Cp*$_{centr}$ distances (1.858 Å, **1**; 1.913 Å, **2**; 2.173 Å, **3**; 1.861 Å, **4**; 2.187 Å, **6**) are longer than those in Cp*Al−Al(C$_6$F$_5$)$_3$ (Al−C$_{Cp*}$ 2.178 Å; Al−Cp*$_{centr}$ 1.810 Å)[8] and Cp*Ga−Al(C$_6$F$_5$)$_3$ (Ga−C$_{Cp*}$ 2.226 Å; Ga−Cp*$_{centr}$ 1.810 Å)[10] but significantly shorter compared to uncomplexed group 13 diyls Cp*M (Table 3). Heteronuclear Cp*Al−BR$_3$ complexes also show shorter Al−C bond lengths, ranging from 2.15 to 2.18 Å.[16,27] The shortening of the M−C$_{Cp*}$ bonds results from the transformation of the

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[25] The Lewis basicity increases with increasing steric demand of the organic ligand R.

[26] Upon complexation, the positive charge at the metal atom M(I) increases, with M = Al showing a larger positive charge compared to M = Ga (see ref 2a).

[27] Romero, P. E.; Piers, W. E.; Decker, S. A.; Chau, D.; Woo, T. K.; Parvez, M. *Organometallics* **2003**, *22*, 1266.

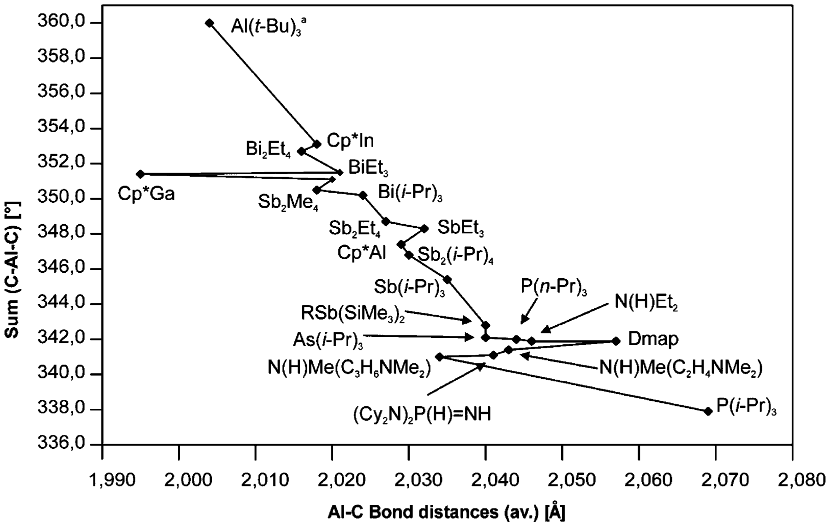

Figure 4. Structural parameters of *t*-Bu$_3$Al adducts.

partially antibonding *electron lone pair* of the diyl Cp*M into a donor−acceptor bond upon coordination to M(*t*-Bu)$_3$ and the development of positive (donor center) and negative charges (acceptor center) at the group 13 metals.[2a] The Cp*$_{\text{centr}}$−M−M moieties in **1**−**4** and **6** deviate slightly from linearity (175.0°, **1**; 174.2°, **2**; 170.0°, **3**; 175.5°, **4**; 170.3°, **6**), as was previously observed for comparable complexes Cp*Al−M(C$_6$F$_5$)$_3$ (M = B 172.9°; Al 170.1°)) and Cp*Ga−M(C$_6$F$_5$)$_3$ (M = B 176.9°; Al 170.6°), respectively.

It was of particular interest to compare the relative Lewis basicities of group 13 diyls Cp*M with simple Lewis bases such as group 15 organics ER$_3$ (E = N−Bi). According to a simple model as described by Haaland et al.,[28] the coordination geometry of the group 13 Lewis acid changes from trigonal planar (uncomplexed form) to distorted tetrahedral upon adduct formation. Consequently, the sum of the C−Al−C bond angles decreases from 360° to lower values. Simultaneously, the average Al−C bond length increases. The stronger the Lewis acid−base interaction, the more pronounced the deviation from planarity, leading to smaller C−Al−C bond angles and the Al−C bond length increase. Figure 4 shows average Al−C bond lengths and the sum of the C−Al−C bond angles of group 15−Al(*t*-Bu)$_3$ adducts as determined by single-crystal X-ray diffraction.[29]

The structural parameters of the Al(*t*-Bu)$_3$ group reveal a strong relationship between the deviation from planarity and the strength of the Lewis base. Amines and phosphines for instance show significantly smaller C−Al−C bond angles than stibines and bismuthines. In addition, the Al−C bond length of the adducts is generally elongated compared to that of pure Al(*t*-Bu$_3$) except for Cp*Ga−Al(*t*-Bu)$_3$, **2**. According to these structural parameters, the Lewis basicity of group 13 diyls Cp*M is comparable to that of trialkylstibines and -bismuthines ER$_3$ and tetraalkyldistibines and -dibismuthines E$_2$R$_4$ (E = Sb, Bi), respectively. The basicities of group 13 diyls steadily decrease with increasing atomic number of the central group 13 metal (Lewis basicity: Cp*Al > Cp*Ga > Cp*In), as was observed for group 13 diyl−B(C$_6$F$_5$)$_3$ adducts.[5] The adduct Cp*In−Al(*t*-Bu)$_3$, **3**, shows the smallest deviation from planarity (∑C−Al−C 353.3°), indicating Cp*In to be the weakest Lewis base. Comparable findings have been made for the corresponding Ga(*t*-Bu)$_3$ adducts. Cp*In−Ga(*t*-Bu)$_3$, **6**, shows the smallest deviation (∑C−Al−C 353.9°) from planarity observed so far.

Conclusions

Group 13 diyls Cp*M (M = Al, Ga, In) readily undergo Lewis acid−base reactions with M′(*t*-Bu)$_3$ (M′ = Al, Ga) with subsequent formation of the adducts Cp*M−M′(*t*-Bu)$_3$. A comparison of the structural parameters of the M′(*t*-Bu)$_3$ fragment in these complexes (M−C, ∑C−M−C) shows that the Lewis basicity of Cp*M steadily decreases with increasing atomic number of the group 13 element. In addition, the Lewis base strength of Cp*M was found to be comparable to that of triorganostibines and -bismuthines ER$_3$ (E = Sb, Bi).

Experimental Section

General Procedures. All manipulations were performed in a glovebox under an N$_2$ atmosphere or with standard Schlenk techniques. Solvents were dried over sodium/potassium and degassed prior to use. [Cp*Al]$_4$,[30] [Cp*Ga]$_6$,[31] [Cp*In]$_6$,[40] Al(*t*-Bu)$_3$,[32] and Ga(*t*-Bu)$_3$[33] were prepared according to literature methods. A Bruker Avance 300 spectrometer was used for NMR spectroscopy.

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^{1}H and ^{13}C{^{1}H} NMR spectra were referenced to internal C_6D_5H (^{1}H: $\delta = 7.154$; ^{13}C: $\delta = 128.0$). Mass spectra (EI) were recorded on a Finnigan MAT 8230 spectrometer. Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the Elementaranalyse Labor of the University of Paderborn. Yields are given for the pure products.

General Synthesis of [Cp*Al−M(*t*-Bu)$_3$] (M = Al, Ga). One millimole of M(*t*-Bu)$_3$ was added at ambient temperature to a solution of 1 mmol of Cp*Al (0.16 g) in 10 mL of toluene and stirred for 12 h. Clear yellow solutions were formed, which were concentrated to 5 mL and stored at −30 °C. Colorless crystals of **1** and **4** were formed within 48 h.

General Synthesis of [Cp*Ga−M(*t*-Bu)$_3$] and [Cp*In−M(*t*-Bu)$_3$] (M = Al, Ga). One millimole of M(*t*-Bu)$_3$ was added at ambient temperature to a solution of 1 mmol of Cp*M (monomeric unit) in 3 mL of pentane. The resulting colorless solutions were stored at −30 °C. Colorless crystals of **2**, **3**, and **6** were formed within 12 h.

[Cp*Al−Al(*t*-Bu)$_3$], 1. Yield: 0.31 g (85%). Mp: 172 °C. Anal. $C_{22}H_{42}Al_2$ (360.6 g/mol): found (calcd): H, 11.59 (11.74); C, 73.04 (73.27). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.24 (s, 27H, C*CH*$_3$), 1.64 (s, 15H, Cp*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 9.2 (C$_5$*Me*$_5$), 18.2 (*C*CH$_3$), 33.3 (C*C*H$_3$), 114.5 (*C*$_5$Me$_5$). EI-MS (70 eV, 100 °C): *m*/*z* (%) 198 (5) [Al(*t*-Bu)$_3$]$^+$, 162 (20) [Cp*Al]$^+$, 141 (45) [Al(*t*-Bu)$_2$]$^+$, 135 (35) [Cp*]$^+$, 57 (100) [*t*-Bu]$^+$.

[Cp*Ga−Al(*t*-Bu)$_3$], 2. Yield: 0.37 g (92%). Mp: 181 °C. Anal. $C_{22}H_{42}AlGa$ (403.4 g/mol): found (calcd): H, 10.34 (10.49); C, 65.34 (65.50). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.19 (s, 27H, C*CH*$_3$), 1.77 (s, 15H, Cp*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 9.4 (C$_5$*Me*$_5$), 32.5 (C*C*H$_3$), 114.0 (*C*$_5$Me$_5$). EI-MS (70 eV, 70 °C): *m*/*z* (%) 204 (5) [Cp*Ga]$^+$, 198 (10) [Al(*t*-Bu)$_3$]$^+$, 141 (55) [Al(*t*-Bu)$_2$]$^+$, 135 (45) [Cp*]$^+$, 69 (45) [Ga]$^+$, 57 (100) [*t*-Bu]$^+$.

[Cp*In−Al(*t*-Bu)$_3$], 3. Yield: 0.40 g (89%). Mp: 118 °C. Anal. $C_{22}H_{42}AlIn$ (448.4 g/mol): found (calcd): H, 9.41 (9.44); C, 58.86 (58.93). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.12 (s, 27H, C*CH*$_3$), 1.98 (s, 15H, C$_5$Me$_5$). ^{13}C NMR (300 MHz, C_6D_6, 25 °C): δ 10.0 (C$_5$*Me*$_5$), 22.6 (*C*CH$_3$), 31.2 (C*C*H$_3$), 113.8 (*C*$_5$Me$_5$). EI-MS (70 eV, 50 °C): *m*/*z* (%) 250 (55) [Cp*In]$^+$, 198 (10) [Al(*t*-Bu)$_3$]$^+$, 141 (30) [Al(*t*-Bu)$_2$]$^+$, 135 (10) [Cp*]$^+$, 115 (80) [In]$^+$, 84 (5) [Al(*t*-Bu)]$^+$, 57 (100) [*t*-Bu]$^+$.

[Cp*Al−Ga(*t*-Bu)$_3$], 4. Yield: 0.38 g (95%). Mp: 218 °C. Anal. $C_{22}H_{42}AlGa$ (403.4 g/mol): found (calcd): H, 10.41 (10.49); C, 65.41 (65.50). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.30 (s, 27H, C*CH*$_3$), 1.67 (s, 15H, C$_5$Me$_5$). ^{13}C NMR (300 MHz, C_6D_6, 25 °C): δ 9.1 (C$_5$*Me*$_5$), 25.6 (*C*CH$_3$), 33.9 (C*C*H$_3$), 114.3 (*C*$_5$Me$_5$). EI-MS (70 eV, 90 °C): *m*/*z* (%) 183 (60) [Ga(*t*-Bu)$_2$]$^+$, 162 (15) [Cp*Al]$^+$, 135 (65) [Cp*]$^+$, 127 (15) [Ga(*t*-Bu)]$^+$, 69 (35) [Ga]$^+$, 57 (100) [*t*-Bu]$^+$.

[Cp*Ga−Ga(*t*-Bu)$_3$], 5. Analytical results were analogous to those described by Jutzi et al.[15] Yield: 0.42 g (94%). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.26 (s, 27H, *t*-Bu,), 1.79 (s, 15H, Cp*). ^{13}C NMR (75 MHz, C_6D_6, 25 °C): δ 9.5 (C$_5$*Me*$_5$), 27.6 (*t*-Bu), 33.0 (*t*-Bu), 113.9 (*C*$_5$Me$_5$).

[Cp*In−Ga(*t*-Bu)$_3$], 6. Yield: 0.43 g (87%). Mp: 91 °C. Anal. $C_{22}H_{42}GaIn$ (491.1 g/mol): found (calcd): H, 8.53 (8.62); C, 53.68 (53.81). ^{1}H NMR (300 MHz, C_6D_6, 25 °C): δ 1.18 (s, 27H, C*CH*$_3$), 2.03 (s, 15H, C$_5$Me$_5$). ^{13}C NMR (300 MHz, C_6D_6, 25 °C): δ 10.3 (C$_5$*Me*$_5$), 22.6 (*C*CH$_3$), 31.0 (C*C*H$_3$), 113.5 (*C*$_5$Me$_5$). EI-MS (70 eV, 50 °C): *m*/*z* (%) 250 (65) [Cp*In]$^+$, 183 (100) [Ga(*t*-Bu)$_2$]$^+$, 135 (15) [Cp*]$^+$, 127 (35) [Ga(*t*-Bu)]$^+$, 115 (95) [In]$^+$, 69 (45) [Ga]$^+$, 57 (20) [*t*-Bu]$^+$.

X-ray Structure Solution and Refinement. Crystallographic data for **1**, **2**, **3**, **4**, and **6** are summarized in Table 1; bond lengths and angles, in Table 2. Figures 2 and 3 show ORTEP diagrams of the solid-state structures of **3** and **4**. Data for **1** were collected on a Nonius Kappa-CCD diffractometer; all other, with a Bruker-AXS SMART APEX CCD. The structures were solved by direct methods (SHELXS-97)[34] and refined by full-matrix least-squares on F^2 (SHELXL-97).[35] Empirical absorption corrections were applied for **2**, **3**, **4**, and **6**. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined by a riding model. All structures suffer to a certain extent from disordered *t*-Bu groups (rotation along M−C axis), as is indicated by large anisotropic displacement parameters. For **2**, **3**, and **6** the disorder could be treated with a split model for the methyl-C atoms (site occupation factors 0.73/0.27(1) for **2**, 0.59/0.41(2) for **3**, and 0.61/0.39(2) for **6**, respectively). The crystallographic data of **1**, **2**, **3**, **4**, and **6** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-604178 (**1**), CCDC-612869 (**2**), CCDC-612870 (**3**), CCDC-612871 (**4**), and CCDC-612872 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam-ak.uk).

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Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates for **1**, **2**, **3**, **4**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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