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Crystal Structures of Tris(*tert*-butyl)boron, -aluminum, -gallium, and -indium: Nonplanarity of the AlC_3 Skeleton and Evidence of Inter- and Intramolecular "Agostic" or Hyperconjugative Interactions

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X-ray crystal structures determined at low temperatures (150−220 K) for the tris(*tert*-butyl) derivatives of boron, aluminum, gallium, and indium (M) reveal essentially monomeric molecular units throughout with consistently longer M−C bonds than in the corresponding monomeric trimethyl derivatives. Comparison of the three structures shows a significant strengthening of intermolecular M···β-CH_3 binding in the order M = B ∼ Ga < In < Al, resulting in a distinctly nonplanar MC_3 skeleton with the M atom displaced 0.25 Å above the plane of the quaternary C atoms in the case where M = Al. Tilting of the *tert*-butyl groups about the M−C bonds, which is concerted when M = B or Al, appears to reflect the influence of intramolecular hyperconjugation or "agostic" bonding.

Introduction

Recent studies of the structures of crystalline trimethyl derivatives MMe_3 of the group 13 elements M = B,[1] Al,[2] Ga,[1] In,[3] and Tl[1] highlight the role of methyl bridging. This may be symmetrical, as in the dimeric aluminum compound,[2] or unsymmetrical with markedly different primary and secondary metal−methyl interactions, as in the gallium, indium, and thallium compounds.[1,3] Only the boron compound has a crystal structure made up of layers in which the monomeric molecules interact only through weak van der Waals, or possibly electrostatic, interactions, with no intermolecular contacts shorter than the sum of the relevant van der Waals radii.[1] Increasing the bulk of the alkyl substituent reduces its capacity to coordinate to a second group 13 atom. Thus, tris(*tert*-butyl) derivatives, M^tBu_3, differ from their trimethyl counterparts in forming monomeric molecules which appear on the evidence of their physical and spectroscopic properties to interact only weakly with one another in the condensed phases.[4−6]

Replacing alkyl by aryl or other unsaturated organic ligands gives rise to new electronic and geometric options for secondary bonding. Triphenylaluminum follows the example of trimethylaluminum in forming crystals made up of dimeric $Ph_2Al(\mu\text{-}Ph)_2AlPh_2$ molecules with symmetrical phenyl bridges,[7] whereas the corresponding gallium and indium compounds are monomeric but with evidence of M···Ph intermolecular association that is weak for M = In and weaker still for M = Ga.[8] Increasing the bulk of the aryl group militates against bridging, and the corresponding trimesityl derivatives are all monomeric in the crystalline state[9−11] with central MC_3 units that are planar. Whereas the mesityl groups are all configured in the expected propeller-like fashion in the aluminum and gallium compounds,[9,10] they are inequivalent in the indium compound[11] with evidence of *intra*molecular interactions between the metal and *ortho*-methyl groups of the mesityl substituents suggested by In···C contacts of 3.30−3.36 Å, which are shorter than in trimethylindium.[3] Crystalline tribenzylaluminum is also noteworthy for displaying unusually strong interactions between the $Al(CH_2Ph)_3$ molecules involving the metal and an *ortho* CH function of the phenyl group, with the result that the metal is displaced 0.475 Å above the plane described by the three methylene C atoms.[12]

Here we are concerned with the tris(*tert*-butyl) derivatives, M^tBu_3, of boron (**1**), aluminum (**2**), gallium (**3**),

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and indium (**4**). Interest in these compounds stems not only from the steric and electronic implications of the *tert*-butyl groups but also from their volatility and susceptibility to alkene elimination, making them surrogate group 13 element hydrides and, hence, potential source materials in chemical vapor deposition of the metal or a derivative of the metal.[4–6,13,14] Our studies of the reactions of the compounds with various bases[15] have led to the growth of single crystals of **1**–**4** and determination of their structures. Hence the essentially monomeric molecular character of the compounds in the solid as well as the liquid and gas phases has been confirmed. However, intermolecular interactions assume increasing importance in the order B ∼ Ga < In < Al, and although the central MC_3 unit of the M^tBu_3 molecule is planar within the limits of experimental uncertainty in **1**, **3**, and **4**, the corresponding unit in **2** takes the form of a shallow pyramid. With relatively short intermolecular $M\cdots CH_3$ distances, **2** and **4** adopt pseudo-polymeric structures with the M^tBu_3 molecules linked through highly unsymmetrical $M-{}^tBu\cdots M$ bridges. In addition, the *tert*-butyl groups of the molecules in **1** and **2** are each tilted about the M–C axis. There are thus parallels with the structures of various organo derivatives of the alkali metals (M′), e.g., $[CH_3M']_n$,[13] $[(Me_3Si)_3SiM']_2$,[16] and $[(Me_3Si)_2(2\text{-}C_5H_4N)CLi]_2$,[17] which show the characteristics[18,19] of the so-called “agostic” CH···M bonding normally associated with organotransition-metal compounds.[20] While this manuscript was in preparation, Woski and Mitzel reported[21] on the crystal structure of the aluminum compound **2** and Uhl et al.[22] on that of the indium compound **4**, with results essentially concordant with those described here.

Experimental Section

Syntheses. Tris(*tert*-butyl)boron (**1**) was prepared by the reaction of tris(methoxy)boron with *tert*-butyllithium in *n*-pentane solution following the procedure outlined by Nöth and Taeger.[23] Tris(*tert*-butyl)aluminum (**2**), -gallium (**3**), and -indium (**4**) were prepared by the reaction of the appropriate trichloride with a stoichiometric amount of either *tert*-butyllithium in *n*-pentane solution (**2** and **3**) or *tert*-butylmagnesium chloride in Et_2O solution (**4**), the procedures being broadly as described previously.[6,24,25] All the reagents were from Aldrich. After removal of the solvent, the tris(*tert*-butyl) compound was isolated and purified by fractional condensation in vacuo (and in the dark in the case of photosensitive **4**[6]). The purity of each was checked by reference to the IR and/or Raman spectra and to the ^1H NMR spectra of toluene-d_8 solutions, which showed no significant changes at temperatures between 190 and 300 K.[4–6,23]

X-ray Crystallography. Crystals of **1**, **2**, and **3** were each grown in situ in a Pyrex capillary by laser-assisted zone refinement[26] at 210, 250, and 255 K, respectively; those of **4** were grown by slow sublimation in vacuo, and a selected crystal was mounted under perfluoropolyether oil on a glass fiber. X-ray diffraction data from Mo Kα radiation ($\lambda = 0.71073$ Å) were collected on a Bruker Smart Apex (**1**, **2**, and **3**) or an Enraf-Nonius Kappa (**4**) CCD diffractometer, the temperature of the crystal being controlled by an Oxford Cryosystems CRYOSTREAM device.[27] Details of the crystals, data collection, structure solution, and refinement are given in Table 1. Crystals of **1** at 210 K were hexagonal with a structure solved in the space group $P6_3/m$; the others were monoclinic with structures solved in the space group $P2_1/c$ or $P2/c$. Solutions were by direct methods (SHELXS-97[28a] for **1**, **2**, and **3** and SIR92[29a] for **4**), while refinement entailed the use of SHELXTL[28b] (**1**–**3**) or CRYSTALS[29b] (**4**).

The unit cell of **2**, with the dimensions listed in Table 1, may be transformed to a metrically hexagonal cell with the matrix (−1 0 −1/1 0 0/0 −1 0), but merging in any of the trigonal or hexagonal point groups yielded $R_{int} > 0.70$. An orthorhombic *C*-centered cell results from transformation with the matrix (0 0 −1/2 0 1/0 −1 0); merging in *mmm* in this setting gave $R_{int} = 0.11$, while an alternative orthorhombic cell had $R_{int} = 0.58$. The presence of only one set of glide absences, coupled to the slightly better merging statistics for $2/m$ symmetry, suggested that the crystal structure was really monoclinic but twinned. The structure was solved in $P2_1$, and the model changed to $P2_1/c$ after symmetry checking.[30] The twin law used was a 2-fold rotation about [001], described by the matrix (−1 0 −1/0 −1 0/0 0 1), which corresponds to a rotation about the *a* axis of the *C*-centered orthorhombic cell described above. During refinement the methyl groups were treated using the Sheldrick rotating rigid group model. There are two molecules of Al^tBu_3 in the asymmetric unit, and two of the ^tBu groups in one of these molecules are rotationally disordered about their Al–C vectors with an additional small displacement in the quaternary C position. All ^tBu groups were restrained to have similar 1,2 and 1,3 C···C distances and local 3-fold symmetry; “opposite” or closely situated C positions in the disordered ^tBu groups were constrained to have equal anisotropic displacement parameters. The final conventional

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Table 1. X-ray Crystallographic Details for M^{t}Bu$_3$ where M = B (1), Al (2), Ga (3), and In (4)

	B^{t}Bu$_3$ **1**	Al^{t}Bu$_3$ **2**	Ga^{t}Bu$_3$ **3**	In^{t}Bu$_3$ **4**
A. Crystal Data				
formula	$C_{12}H_{27}B$	$C_{12}H_{27}Al$	$C_{12}H_{27}Ga$	$C_{12}H_{27}In$
fw	182.15	198.32	241.06	286.17
T, K	210(2)	150(2)	220(2)	150(2)
cryst syst	hexagonal	monoclinic	monoclinic	monoclinic
space group	$P6_3/m$	$P2_1/c$	$P2/c$	$P2_1/c$
a, Å	8.5187(8)	17.762(3)	15.807(8)	14.6447(4)
b, Å	8.5187(8)	10.1219(17)	9.002(4)	9.2183(3)
c, Å	10.819(2)	17.929(3)	15.455(7)	10.9815(3)
β, deg		120.342(3)	100.086(10)	105.1466(14)
V, Å^3	679.93(15)	2781.9(10)	2165.2(18)	1431.0
Z	2^a	8	6^b	4
D_{calcd}, Mg m^{-3}	0.890	0.947	1.109	1.328
abs coeff, mm^{-1}	0.047	0.110	1.872	1.617
B. Data Collection, Solution, and Refinement				
cryst size, mm	4 × 0.50 × 0.50	1 × 0.38 × 0.38	1 × 0.50 × 0.50	0.10 × 0.14 × 0.14
θ range, deg	2.76–24.98	2.27–24.71	1.31–24.71	5.0–27.5
index ranges	$-9 \le h \le 10$	$-20 \le h \le 19$	$-18 \le h \le 18$	$-19 \le h \le 18$
	$-10 \le k \le 8$	$-11 \le k \le 11$	$-10 \le k \le 10$	$0 \le k \le 11$
	$-12 \le l \le 12$	$-21 \le l \le 19$	$-18 \le l \le 17$	$0 \le l \le 14$
no. of data collected/indep	4858/425	13 888/4709	8589/3627	15 163/3485
R_{int}	0.0561	0.0688	0.0456	0.036
abs correction	SADABS^c	SADABS^c	SADABS^c	SORTAV^d
T_{min}	0.649	0.436	0.428	0.80
T_{max}	1	1	0.801	0.85
no. of data/restraints/params	425/0/25	4709/562/285	3627/378/227	2459/0/118
R_1/data with $F > 4\sigma(F)$	0.0713/265	0.0561/3128	0.0549/1707	0.0312/2459
wR_2 (F^2 and all data)	0.2353	0.1496	0.1549	0.0364
goodness-of-fit on F^2	1.074	1.002	0.955	0.9989
largest diff peak/hole, e Å^{-3}	0.17/−0.13	0.44/−0.32	0.43/−0.81	0.71/−0.88

[a] The molecule lies on a crystallographic −6 site. [b] One molecule lies on a crystallographic 2-fold axis. [c] Sheldrick, G. M. *SADABS*; University of Göttingen: Germany, 2002. [d] Blessing, R. H. *Acta Crystallogr., Sect. A* **1995**, *51*, 33.

R-factor [based on F and 3128 data with $F > 4\sigma(F)$] was 0.056; wR_2 (based on all 4709 data to a resolution of 0.85 Å) was 0.150 for 285 parameters and 562 restraints. Final difference map extrema were +0.44 and −0.32 e Å^{-3}. A refinement carried out with the AlC_3 skeletons tightly restrained (restraint SE ±0.01) to be planar increased the conventional R-factor from 0.056 to 0.134.

No similar problems of twinning were encountered with a crystal of **3** at 220 K, but all the ^{t}Bu groups in the two independent molecules are rotationally disordered about the Ga−C bonds; similarity restraints were applied as for **2**. In this case $R_1 = 0.055$ [based on F and 1707 data with $F > 4\sigma(F)$] and $wR_2 = 0.160$ (based on F^2 and all 3627 data to a resolution of 0.85 Å). Final difference map extrema were +0.43 and −0.80 e Å^{-3}. An attempt to collect data at 120 K failed, possibly because of a phase change or disintegration of the crystal.

Crystals of **1** at 210 K and of **4** at 150 K presented problems of neither twinning nor disorder. Refinement yielded $R_1 = 0.0713$ [based on F and 265 data with $F > 4\sigma(F)$] and $wR_2 = 0.2353$ (based on F^2 and all 425 data) for **1**. **4** was refined against F using 2459 data (out of 3485 unique data) with $F > 6\sigma(F)$; $R_1 = 0.0312$ and $wR = 0.0364$. Final difference map extrema were +0.17/−0.13 (**1**) and +0.71/−0.88 e Å^{-3} (**4**). Lowering the temperature of **1** caused a phase change between 210 and 170 K, but attempts to grow a crystal of the low-temperature phase at 150 K were inconclusive.

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 284558−284561 for compounds **1**, **2**, **3**, and **4**, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: 0044-(0)1223-336033; e-mail: deposit@ccdc.ac.uk or http://www.ccdc.cam.ac.uk).

Theoretical Methods. Density functional theory (DFT) calculations involving the BP method with TZVPP basis sets were carried out using the TURBOMOLE program suite.[31] Trial calculations have shown that this methodology reproduces satisfactorily the observed geometries and dimensions of known molecules of this kind.[32]

Results and Discussion

The vibrational spectra of tris(*tert*-butyl)boron, -aluminum, -gallium, and -indium (**1**−**4**), as reported previously[3,23] and confirmed by us, do not vary significantly from one phase to another, with nothing to suggest aggregation of the molecules or perturbation of the organic ligands. Likewise, the ^{1}H NMR spectra of solutions at temperatures between 190 and 300 K are also unremarkable.

The crystal structures also reveal essentially monomeric molecular units throughout, with the dimensions summarized in Table 2; the results for **2** and **4** are in line with those reported previously.[21,22] Thus, we note that crystalline **1** and **3** consist of isolated M^{t}Bu$_3$ molecules (M = B or Ga) exposed to no intermolecular contacts within the sums of the relevant van der Waals radii.[33] While not isostructural, **3** resembles crystalline BMe$_3$[1] in its topology,[34] with a molecular coordination number of 14 and a coordination environment akin to a distorted bcc arrangement. Molecules in **1** reside on a

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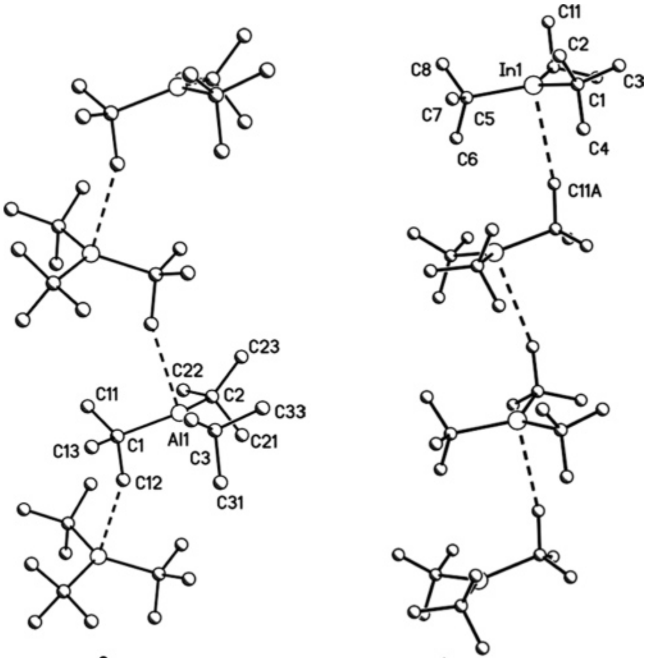
Table 2. Selected Interatomic Distances (Å) and Angles (deg) for the Tris(*tert*-butyl) Compounds 1−4

		2			
dimension[a]	**1**	molecule 1[b]	molecule 2[c]	**3**[d]	**4**
M−C	1.618(3), 1.618(3), 1.618(3)	2.012(4), 1.998(4), 2.007(4)	1.991(5)−2.015(5)	1.986(8)−2.020(7)	2.216(3), 2.225(3), 2.226(3)
$M-C_{mean}$	1.618	2.006	2.004	2.007	2.222
C−C	1.543(4), 1.543(4), 1.546(5)	1.537(4), 1.545(4), 1.546(4), 1.554(5), 1.529(5), 1.533(4), 1.538(5), 1.551(5), 1.524(5)	1.526(7)−1.548(6)	1.354(17)−1.593(16)	1.520(6), 1.513(6), 1.519(6), 1. 522(5), 1.518(5), 1.533(5), 1.515(5), 1.527(6), 1.527(6)
$C-C_{mean}$	1.544	1.540	1.538	1.49	1.522
C−M−C	120.0	119.04(18), 118.30(17), 118.03(15)	107.0(4)−128.4(5)	119.1(3)−120.6(3)	121.58(13), 121.26(13), 116.79(14)
∑C−M−C	360.0	355.37		360.0	359.63
C−C−M	108.7(2), 108.7(2), 120.6(2)	114.3(3), 105.0(3), 114.3(3), 114.2(3), 114.3(3), 105.9(3), 114.0(3), 104.9(3), 115.5(3)	104.8(4)−119.2(10)	99.0(15)−125.5(15)	109.0(3), 110.1(3), 111.1(3), 110.2(2), 111.7(2), 109.5(2), 111.0(2), 107.4(2), 112.1(3)
$C-C-M_{mean}$	120.6, 108.7	114.4, 105.3			110.2
intermolecular contacts					
Al1⋯C12	*e*	2.937(4)		*e*	
Al2⋯C41			2.967(4)		
In1⋯C11					3.467(5)
Al1⋯C12−C1		158.2(4)			
Al2⋯C41−C4			157.4(3)		
In1⋯C11−C9					162.9(3)

[a] M = B, Al, Ga, or In. For numbering of specific atoms see Figure 1. [b] Ordered molecule centered on Al1 (see text). [c] Disordered molecule centered on Al2 (see text). [d] Disordered molecules. [e] No intermolecular contacts shorter than the sums of the relevant van der Waals radii.



2 **4**

Figure 1. Comparison of the arrangement of the molecules and intermolecular interactions in crystalline $\mathrm{Al^tBu_3}$ (**2**) and $\mathrm{In^tBu_3}$ (**4**) both at 150 K.

crystallographic C_{3h} (-6) site; the molecular coordination number is 12, and the packing is topologically close to hcp.

Intermolecular Features. By contrast, and as illustrated in Figure 1, crystalline **2** and **4** display short intermolecular M⋯C contacts {Al⋯C 2.937(4) and 2.967(4) Å, In⋯C 3.467(5) Å; cf. 3.85, 4.13 Å for the sums of the contact radii[33]} which build up a pseudopolymer about a screw axis (**2**) or a glide plane (**4**). In neither these nor **1** and **3**, however, is there a statistically significant difference between the three M−C distances of each $\mathrm{M^tBu_3}$ molecule (M = B, Al, Ga, or In), by contrast with the properties of most of the analogous trimethyl derivatives in comparable circumstances.[1−3] At 1.618 (**1**), 2.006 (**2**), 2.008 (**3**), and 2.222 Å (**4**), the average M−C distances are 0.040−0.061 Å longer than in the corresponding gaseous $\mathrm{MMe_3}$ molecule.[35] A similar elongation, found with gaseous $\mathrm{ZnMe_2}$ and $\mathrm{Zn^tBu_2}$,[36] has been attributed on the evidence of quantum chemical calculations not to nonbonded interactions, but to the decreased polarity of the metal−carbon bond in the ^{t}Bu derivative. Crystal structures of adducts of **2** and **3** with phosphines, arsines, stibines, and bismuthines (L) reveal discrete $\mathrm{L{\cdot}M^tBu_3}$ molecules; as expected, the M−C distances are slightly longer than in the parent tris(*tert*-butyl) compounds (2.016−2.069 and 2.014−2.044 Å for M = Al and Ga, respectively[37]). The sum of the C−M−C angles in **1**, **3**, and **4** is 360.0°, 360.0°, and 359.6°, respectively, indicating a planar or near-planar $\mathrm{MC_3}$ skeleton, although the In atom in **4** is displaced by 0.08 Å from the plane of the quaternary C atoms toward the $\mathrm{CH_3}$ group of an adjacent $\mathrm{In^tBu_3}$

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molecule with which the relatively short In···C contact is established. In **2**, however, the C−M−C angles sum to 355.5° on average, and the Al atom lies 0.25 Å above the plane of the quaternary C atoms (the actual values being 0.251(2) Å for Al1 and 0.242(3) Å for Al2). The average C−Al−C angle of 118.0° is in fact not very different from that found in complexes of **2** with distibine and dibismuthine bases (117.0−117.6°[37]), where the weakness of the interaction perturbs the alane only so far as to give rise to an AlC_3 pyramid of shallow pitch. As refinement calculations with the central AlC_3 skeletons of the Al^{t}Bu$_3$ molecules tightly restrained to be planar led to a marked increase in R-factor, we have every reason to believe that the effect is real and not an artifact associated, for example, with the twinning of the crystals.

It is in **2** therefore that intermolecular forces are at their strongest and semifrustrated alkyl bridging is most clearly evident. The two Al^{t}Bu$_3$ molecules per asymmetric unit, **2-A** and **2-B** (based on Al1 and Al2, respectively), are linked together to form spirals about crystallographic 2_1 axes, with each spiral built of symmetry repeats of one crystallographically independent molecule only. The shortest intermolecular Al···C distances of 2.937(4) and 2.967(4) Å for molecules **2-A** and **2-B**, respectively, are to the methyl groups based on C12 (**2-A**) and C41 (**2-B**) (see Figure 1). The Al2···C41 interaction seems to hold the relevant ^{t}Bu group in place, while the other groups in molecule **2-B** are disordered. The Al···Me interaction gives the somewhat misleading appearance of being through a hydrogen atom, as one Al···H distance is in both cases much shorter (Al···H12A 2.41 Å, Al···H41A 2.42 Å, as against 3.35 Å for the sum of the contact radii[33]) than the other two (2.95−3.03 Å). No standard uncertainties can be assigned since the H atoms are in ideal positions, but in that these are consistent with difference maps (see Supporting Information), the estimated distances are judged to be reliable. It may be noted in this context that the angles at the bridging methyl carbon are 158.2(4)° (C1−C12···Al1) and 157.4(3)° (C4−C41···Al2); the corresponding angle for the short intermolecular contact in **4** is 162.9(3)°. The closest structural analogy to **2** is to be found in crystalline tribenzylaluminum, where unusually strong intermolecular interactions involving an *ortho* CH of the phenyl group [such that Al···C = 2.453(6) Å] cause the Al atom and coordinated methylene C atoms to form a pyramidal AlC_3 unit with the metal atom displaced 0.475 Å above the plane of the C atoms.[12]

Intramolecular Features. The orientation of the ^{t}Bu groups in the M^{t}Bu$_3$ molecules provides a second feature of note. In the boron compound **1** these groups are arranged in a concerted manner so that one β-carbon atom (C3, see Figure 2) of each lies more or less in the plane defined by the BC_3 core, so that the heavy-atom $B(CC_3)_3$ skeleton conforms to C_{3h} symmetry. At 120.6(2)° the B−C−C3 angle is arrestingly large compared with the corresponding angle of 108.7(2)° made by the β-carbon atoms that lie out of the BC_3 plane. The relatively high temperature of the crystal (210 K) caused the thermal motion of the ^{t}Bu groups to be quite large, making it impossible to place the hydrogen atoms in other than calculated positions. Although the canting of the ^{t}Bu groups in the BC_3 plane might be seen as the result of steric effects, the same cannot be said about the ^{t}Bu groups in the ordered Al^{t}Bu$_3$ molecule **2-A** in crystalline **2**, where the canting occurs in just the opposite sense. Here the Al−C−C bond angles show a consistent pattern for all three ^{t}Bu groups with one angle averaging 105.3°, significantly smaller than the other two, with average values of 114.4°. More than that, the effect is concerted in that the tight Al−C−C angles are made to methyl groups occupying the face of an AlC_3 pyramid that opposes the short Al···C secondary contacts, with the Al−C−C planes all nearly orthogonal to the plane formed by the three C_α atoms of the central AlC_3 skeleton. This disposition of the ^{t}Bu groups is presumably dictated by the intermolecular contacts since it does not obviously meet the optimization of intramolecular steric requirements. Hence the ^{t}Bu groups are all canted about the Al−C bonds so that one CH_3 group of each is drawn *toward* the 3-fold axis of the AlC_3 core.

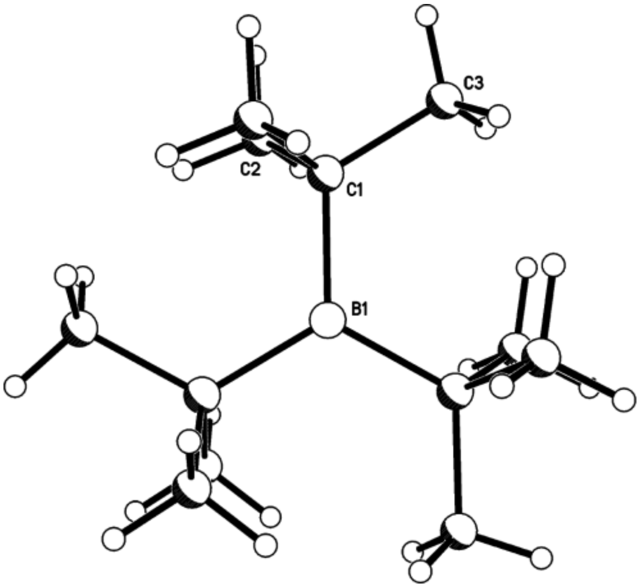

Figure 2. B^{t}Bu$_3$ molecules in crystalline **1** at 210 K showing the orientation of the ^{t}Bu groups. This view is oriented along the [001] direction.

Disorder prevents any similar trait from being detected in **3**. The In−C−C bond angles in **4** range from 107.4(2)° to 112.1(3)° with the disposition of the ^{t}Bu groups appearing to minimize steric interactions between them, although it is perhaps significant that the smallest angle is made by an In−C−C unit that is roughly orthogonal to the InC_3 skeleton. Such variations of M−C−C angle as may be observed do not appear to be matched, within the limits of experimental uncertainty, by any comparable variation in the C−C−C angles of the ^{t}Bu groups, which average to 106.1°, 107.4°, ca. 108°, and 108.7° in **1**, **2**, **3**, and **4**, respectively. Structural studies of other *tert*-butyl compounds reveal[38,39] a clear dependence of the C−C−C angle on the electronegativity of the atom to which the ^{t}Bu group is bound, with values ranging from 106.2° for the relatively carbanionic lithium derivative to 111.6° for the more

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(38) *Landölt-Börnstein Numerical Data and Functional Relationships in Science and Technology*; New Series, Group II; Springer: Berlin and Heidelberg, Vol. 7, 1976; Vol. 15, 1987; Vol. 21, 1992.

carbocationic chloro compound. The geometries observed for the organic groups in **1**−**4** are therefore generally in keeping with this pattern.

The tilting of the ^{t}Bu groups in the molecules of **1** results in shortest B···C$_\beta$ distances of 2.57 Å. Although this is appreciably shorter than the sum of the relevant contact radii (ca. 3.6 Å[33]), the disposition of the ^{t}Bu groups does not suggest significant secondary interaction. The ^{t}Bu groups in the Al^{t}Bu$_3$ molecules of **2-A** are oriented so as to give shortest Al···C$_\beta$ and Al···H−C$_\beta$ distances measuring no more than 2.82−2.85 and 2.92−2.98 Å, respectively. One C$_\beta$ atom of each ^{t}Bu group thus establishes a slightly closer contact with the Al atom than does the nearest CH$_3$ group of a *neighboring* molecule, even if the intramolecular Al···H distances are rather more attenuated than the shortest intermolecular ones. In both cases, however, the intramolecular distances fall well within the sums of the relevant van der Waals radii (3.85 and 3.35 Å[33]), and the Al···C$_\beta$ distance is only about 40% longer than the primary bond to the quaternary carbon atom. The behavior is similar in sense, if not in degree, to that of numerous alkyl-transition metal compounds normally described as exhibiting "β-agostic" behavior, e.g., EtTiCl$_3$(dmpe), where dmpe = Me$_2$PC$_2$H$_4$PMe$_2$.[20,40]

The systematic tilting of the ^{t}Bu groups in **1** and in the ordered Al^{t}Bu$_3$ molecules of **2** may simply be a consequence of intramolecular nonbonded repulsion between the ^{t}Bu groups in the first case and of the intermolecular forces operating in the second case. It is more likely, however, that hyperconjugation is at work. This would involve the vacant valence *n*p orbital of the tricoordinated group 13 atom and occupied orbitals of the C-CH$_3$ fragments. No different in principle from "agostic" bonding,[20] such hyperconjugation has been invoked to explain the abnormally large B−C−C angles (up to 120.2°) displayed by tricoordinated ethylboron compounds in which the B−C−C unit is more or less coplanar with the central CBX$_2$ skeleton.[41] At the same time, ab initio calculations (MP2/6-31G*) on the model compounds EtMH$_2$, where M = B or Al, suggest that the M−C−C angle is greater than tetrahedral when the empty *n*p orbital on M is perpendicular to the M−C−C plane, but less than tetrahedral when it lies in this plane (e.g., 118° vs 105° for EtBH$_2$).[41] In the event that the *n*p orbital on the central atom is occupied by a lone pair, the reverse pattern is predicted to arise.

To investigate whether *tert*-butyl follows the same behavior as an ethyl group and to check on the possible role of intermolecular forces, we have carried out DFT calculations (BP/TZVPP) on the model compounds ^{t}BuMH$_2$ for M = B, Al, or Ga, as well as M^{t}Bu$_3$ for M = B or Al. The results for the dihydrides confirm expectations based on the precedents set by the analogous ethyl derivatives[41] in that the M−C−C angle is calculated to be as follows for M = B, Al, and Ga, respectively: (a) 96.6°, 104.1°, and 105.8° when the vacant *n*p orbital lies in the M−C−C plane, and (b) 114.0°, 112.0°, and 112.2° when it is perpendicular to this plane (see Figure 3). In the case of ^{t}BuBH$_2$, the first conformer (with the vacant 2p orbital in the B−C−C plane) is calculated to be more stable than the second by 3.3 kJ mol^{-1}.

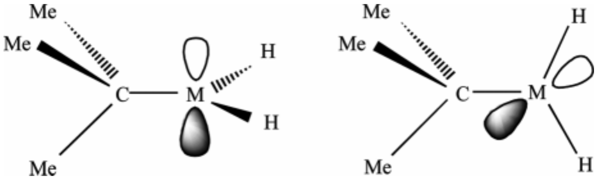

Figure 3. Alternative molecular geometries calculated for the model compounds ^{t}BuMH$_2$ (M = B, Al, or Ga).

For both B^{t}Bu$_3$ and Al^{t}Bu$_3$ the calculations reveal, as expected, molecules with planar MC$_3$ cores. The mean bond distances in the minimum-energy structure for each of the free molecules are estimated to be M−C = 1.641 and 2.038 Å and C−C = 1.555 and 1.542 Å for M = B and Al, respectively, in satisfactory agreement with the experimental findings, particularly when it is appreciated that crystallization results typically in shortening of polar bonds (such as M−C). This structure finds the ^{t}Bu groups oriented in no specific way with respect to the MC$_3$ plane but so as to be staggered with respect to one another. Even so, it is noteworthy that the M−C$_\alpha$−C$_\beta$ angle is smallest (101.8° and 104.4° for M = B and Al, respectively) when the plane it defines is more or less perpendicular to the MC$_3$ plane, and largest (120.5° and 118.2°) when the two planes are coincident, or nearly so. The orientation of the ^{t}Bu groups with respect to one another preferred in crystalline **1** at 210 K and **2-A** at 150 K must therefore be determined by the intermolecular forces, although the pattern of M−C$_\alpha$−C$_\beta$ bond angles is already apparent in the free molecules. The stabilization energy associated with the hyperconjugation, and the tilting of the ^{t}Bu groups which it favors, is only small, and in competition with the nonbonded repulsions between the groups, it leads to torsional barriers that are not out of the ordinary. That is certainly the impression given by the pronounced tendency toward rotational disorder of the ^{t}Bu groups (in **2**, **3**, and possibly the low-temperature phase of **1**, for example). Nevertheless, the tilting emphasizes once again that agostic behavior involves primarily not the hydrogen atoms but the carbon framework of C$_2$ and larger alkyl groups.[20,40,42]

We have also combed the Cambridge Structural Database[39] for X-ray data on neutral molecules containing *tert*-butyl groups linked to a tricoordinated B, Al, or Ga center. Although it is not easy to make due allowance for steric effects, competing delocalization (associated, for example, with the presence of a π-donor co-ligand), and intermolecular forces, the results illustrated in Figure 4 suggest that tilting of the *tert*-butyl group about the M−C axis is a general and hitherto largely unnoticed feature. The tris(*tert*-butyl) derivatives are noteworthy for providing the central group 13 atom

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[40] See, for example: Haaland, A.; Scherer, W.; Ruud, K.; McGrady, G. S.; Downs, A. J.; Swang, O. *J. Am. Chem. Soc.* **1998**, *120*, 3762. Scherer, W.; Hieringer, W.; Spiegler, M.; Sirsch, P.; McGrady, G. S.; Downs, A. J.; Haaland, A.; Pedersen, B. *J. Chem. Soc., Chem. Commun.* **1998**, 2471.

[41] Boese, R.; Bläser, D.; Niederprüm, N.; Nüsse, M.; Brett, W. A.; Schleyer, P. v. R.; Bühl, M.; Hommes, N. J. R. v. E. *Angew. Chem., Int. Ed.* **1992**, *31*, 314.

[42] Scherer, W.; Sirsch, P.; Shorokhov, D.; Tafipolsky, M.; McGrady, G. S.; Gullo, E. *Chem. Eur. J.* **2003**, *9*, 6057.

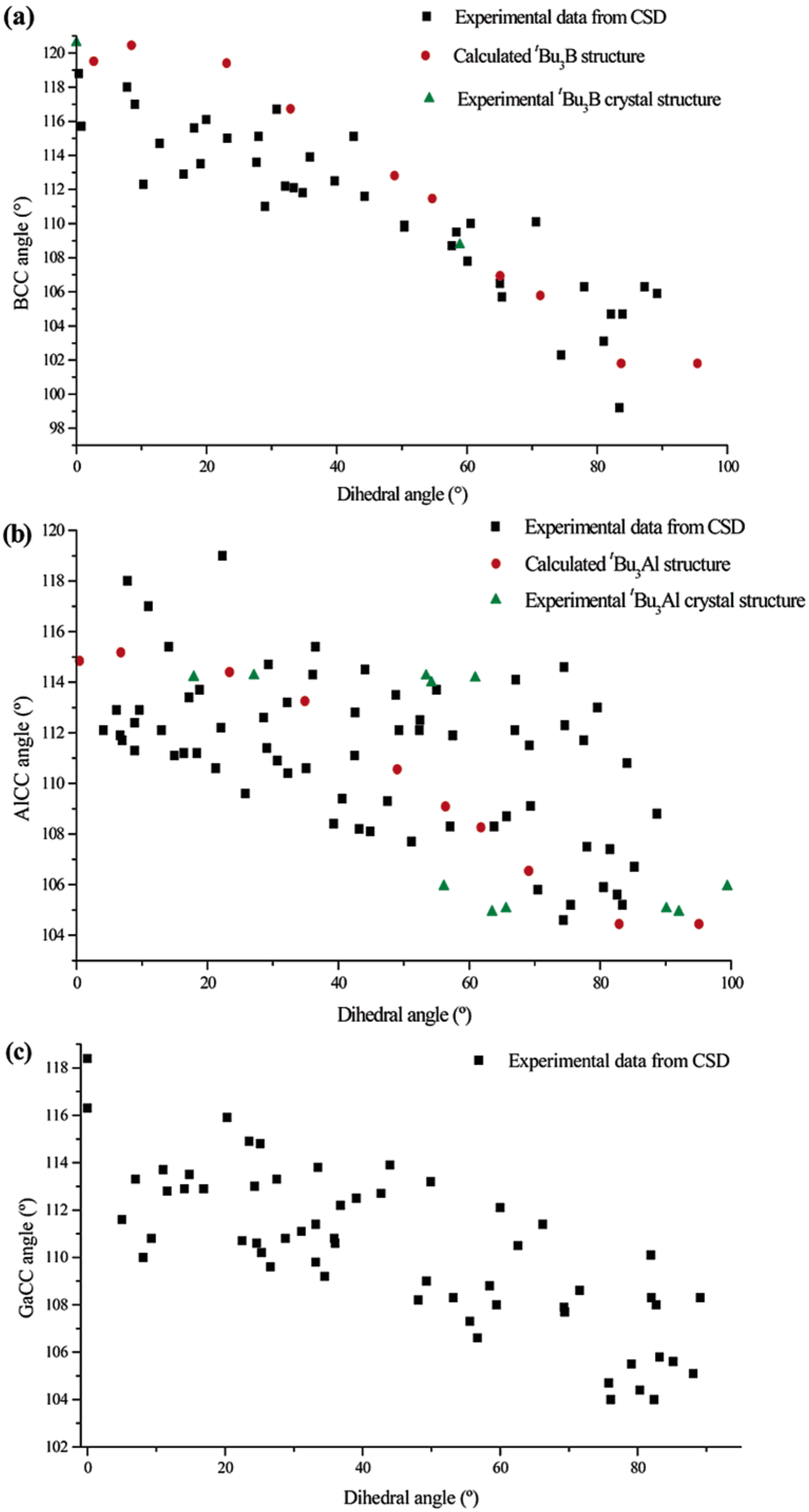

Figure 4. Correlation between the M−C−C angle and mean dihedral angle subtended by this unit with respect to the C_nMX_{3-n} plane for neutral tricoordinated molecules of the type ${}^{t}Bu_nMX_{3-n}$ (n = 1−3): (a) M = B; (b) M = Al; and (c) M = Ga.

with a tricoordinated environment in which there is minimal opportunity for π-type delocalization. With M = B, previous crystallographic studies of *tert*-butyl derivatives have extended to a number of compounds in which such delocalization is likely to be slight (thus excluding, for example, compounds in which boron is bound to nitrogen or oxygen), and here the tilting of the *tert*-butyl groups manifests itself quite clearly in the correlation between the B−C−C and dihedral X−B−C−C angles in compounds of the type $^t\mathrm{Bu}_n\mathrm{BX}_{3-n}$. Unfortunately, however, all the examples of tricoordinated Al and Ga compounds $^t\mathrm{Bu}_n\mathrm{MX}_{3-n}$ characterized hitherto include π-donor ligands (amide, aryloxide, alkenyl, etc.) attached to the metal atom, and this factor doubtless contributes to the much greater degree of scatter revealed in these two cases by the correlation between the M−C−C and dihedral X−M−C−C angles. Nevertheless, the sense of the tilting is still more or less as predicted by the calculations, with the M−C−C angle decreasing as the plane of the unit moves into alignment with the vacant np orbital on M and increasing as the plane and the orbital approach orthogonality. The respective minimum and maximum values for each element are as follows: B 99.2/118.8°, Al 104.6/119.0°, and Ga 104.0/118.4°.[39]

The In^{t}Bu$_3$ molecules in crystalline **4** show a relatively small variation in the In−C−C angles (107.4−112.1°), although the smallest value does indeed correspond to an In−C−C unit that is almost perpendicular to the plane of the three quaternary C atoms. Only one other crystalline *tert*-butylindium compound featuring a tricoordinated In atom has been characterized to date, viz., $^t\mathrm{Bu}_2\mathrm{InN(SiPh}_3)(2,6\text{-}^i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)$,[39] with In−C−C angles ranging from 117.4° to 106.3° and conforming roughly to the behavior of analogous Al and Ga compounds.

Whether tilting of the *tert*-butyl groups occurs in the opposite sense when the central atom carries an occupied np orbital is less easily assessed, as the character of the lone pair orbital changes with the switch from planar to pyramidal geometry. We note, however, that the gaseous molecules $^t\mathrm{BuNH}_2$,[43] ^{t}BuOR (R = H,[44] Me,[44,45] or ^{t}Bu [45]), $^t\mathrm{Bu}_2\mathrm{S}$,[46] and $^t\mathrm{Bu}_3\mathrm{PNH}$[47] are reported on the evidence of their electron diffraction patterns all to display structures in which the 3-fold axis of the *tert*-butyl group is tilted by 4−8° with respect to the C_α−X bond (X = N, O, S, or P). It has generally been assumed that this tilting is designed to minimize steric interactions, and the possibility that hyperconjugation may be a significant factor appears not to have been considered.

Conclusions

The differences between the M^{t}Bu$_3$ crystal structures we have determined clearly reflect secondary M−^{t}Bu···M forces that gain strength in the order M = B ∼ Ga < In < Al. This reflects a pattern of generally decreasing electronegativity of M (B 2.28, Ga 2.42, In 2.14, Al 1.71 on the Sanderson scale, for example[48]) and hence increasing polarity of the primary M−C bonds. Size is likely also to be a factor, however, in that the shorter contact distances favored by Al over In, for example, would incur substantial repulsions between ^{t}Bu groups in the molecules forming the contact were the AlC$_3$ cores constrained to be planar. At their strongest, the interactions cause structural perturbation akin to that widely identified with *intra*molecular agostic bonding.[20] However striking the change from a planar to a pyramidal MC$_3$ fragment may appear, the energy change associated with such a distortion is only small. For a tricoordinated group 13 molecule of this sort without the opportunity for significant π-type interactions, the relevant portion of the potential energy surface defining this motion has a shallow curvature, and this feature is accentuated by an increasing Coulombic contribution to the primary metal−ligand bonding. Recent analyses suggest that such Coulombic factors may override delocalized C−H···M bonding as a controlling influence in agostic interactions.[20,42] Central to all such phenomena is the electroneutrality principle and the enhancement of electron density at an electropositive center by whatever means its valence shell and environment permit. As with similar situations involving organo-transition-metal species, the secondary interactions involving M^{t}Bu$_3$ molecules may be seen to represent an early stage on the reaction coordinate that leads to isobutene elimination and the formation of $^t\mathrm{Bu}_2\mathrm{MH}$, very likely preceding isomerization of the coordinated butyl groups to which these compounds are known to be susceptible.[13]

Acknowledgment. We thank the EPSRC for research funding of the Oxford and Edinburgh groups, including the award of studentships (to S.M. and V.A.M.).

Supporting Information Available: Crystallographic information files (CIFs) for compounds **1**−**4** and thermal ellipsoid plots drawn at the 30% probability level. This material is available free of charge via the Internet at http://pubs.acs.org.

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