Spin-Spin Coupling Constants $^1J(^{27}Al,^{13}C)$ and $^1J(^{13}C,^{11}B)$ in Comparable Organoaluminum and -boron Compounds. NMR Spectroscopy of Lithium Tetra(*tert*-butyl)alanate

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The ^{13}C, ^{27}Al and ^{11}B NMR spectra of tri(*tert*-butyl)alane, $AlBu^t_3$, and of the corresponding borane, BBu^t_3, respectively, were examined in order to determine the magnitude of the coupling constants $^1J(^{27}Al,^{13}C) = 94 \pm 5$ Hz and $^1J(^{13}C,^{11}B) = 52 \pm 2$ Hz by measurement of the line widths of the ^{13}C NMR signals and of the relaxation rates of the quadrupolar ^{27}Al and ^{11}B nuclei. This is the first example of $^1J(^{27}Al,^{13}C)$ determined for a monomeric trialkylalane. In addition, the coupling constants were calculated by DFT methods (B3LYP) using the 6-311+G(d,p) basis set. The ^1H, ^{13}C and ^{27}Al NMR spectra of lithium tetra(*tert*-butyl)alanate, $Li[AlBu^t_4]$, were measured under various conditions. Ion-pair separation in THF revealed the expected patterns for ^{27}Al-^{13}C spin-spin coupling across one and two bonds as well as for the three-bond ^{27}Al-^1H spin-spin coupling.

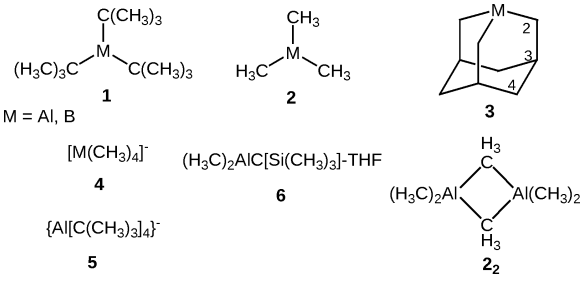
Key words: Trialkylaluminum, Trialkylboranes, Tetra(*tert*-butyl)alanate, ^{13}C, ^{11}B, ^{27}Al NMR, Coupling Constants, DFT Calculations

Introduction

The straightforward observation of resolved splitting of NMR signals of spin-1/2 nuclei of type A owing to indirect nuclear A-X spin-spin coupling [J(A,X)] with quadrupolar nuclei X is frequently hampered by rapid quadrupole-induced relaxation causing short relaxation times T^Q(X). Therefore, scalar relaxation of the second kind [1], T_2^{SC}(A), becomes efficient, and NMR signals of the nuclei A may become broad and weak. In the absence of other processes giving rise to marked broadening of spin-1/2 A NMR signals, the coupling constants J(A,X) can be calculated if T^Q(X) is known (Eq. 1) [1, 2], where $\Delta\nu_b$ is the broadening of the A NMR signal caused by scalar relaxation of the second kind, S_X is the spin of the nucleus X).

$$\Delta\nu_b = 4/3\pi S_X(S_X+1)[J(A,X)]^2[T^Q(X)] \quad (1)$$

This procedure can be tested for $^1J(^{13}C,^{11}B)$ in trialkylboranes which are known to be monomers, and for which interactions with non-coordinating solvents can be neglected in this context. The situation is more complex in the case of $^1J(^{27}Al,^{13}C)$, since most trialkylalanes are dimers which may undergo fast or slow exchange processes, and therefore, the line widths of the ^{13}C NMR signals can be a function of various effects. However, tri(*tert*-butyl)aluminum **1** is a monomer in solution and in the gas phase [3] (although weakly associated in the solid state [4]), and it should be a suitable candidate for determining $^1J(^{27}Al,^{13}C)$ for the first time in a tri-coordinate organoaluminum compound. Corresponding NMR data for the analogous borane **1B** have been determined in this work (Scheme 1). In addition, we have included herein the calculations for the trimethylaluminum dimer $\mathbf{2_2}$, and for trimethylaluminum **2** and 1-aluminaadamantane **3** as monomers, for which experimental data are inaccessible. For comparison, experimental and calcu-



Scheme 1. Aluminum and boron compounds considered in this work.

lated NMR data of the corresponding boranes **2B** and **3B** are known [5]. Experimental coupling constants $^1J(^{27}Al,^{13}C)$ and $^1J(^{13}C,^{11}B)$ are available for the anions $[AlMe_4]^-$ **4** [6] and $[BMe_4]^-$ **4B** [7], respectively, and in this work, we have determined a complete NMR data set for $Li[AlBu^t_4]$ **5** [8] under various conditions, and for the adduct $Me_2AlC(SiMe_3)_3$-THF **6** [9].

Results and Discussion

^{13}C NMR spectra of $AlBu^t_3$ **1** have been reported [8, 10], although the assignment appears to be tentative, and the line shapes have neither been mentioned nor discussed. Numerous adducts of **1** have been studied by ^1H and ^{13}C NMR [11], and again information on line shapes is missing. This is also true for $Li[AlBu^t_4]$ **5** [8]. In the case of **5**, the line shapes of both ^{13}C and ^1H NMR signals critically depend on the conditions of measurement (*vide infra*). The determination of $^1J(^{27}Al,^{13}C)$ by line shape analysis of the ^{13}C NMR signals, taking the ^{27}Al spin relaxation into account, has been used for the trimethylaluminum dimer $\mathbf{2_2}$ [12] and also for other combination of spin-1/2 with quadrupolar nuclei [2]. Results of our measurements, literature data and our calculated NMR data are given in Table 1.

DFT calculations

The DFT calculations of the NMR data were based on the optimized gas phase geometries. In the case of **1B**, the X-ray structural analysis has revealed negligible intermolecular interaction, and therefore, the calculated geometry should be very similar to that determined experimentally for the solid state [4b]. This is shown in Fig. 1. As in the solid state, the atoms

angles (deg)	M = B	Al
M-C-C1,2,3	121.7	115.9
X-Ray	120.6(2)	114.4(mean)
M-C-C	107.4	108.1
X-Ray	108.7(2)	105.3(mean)

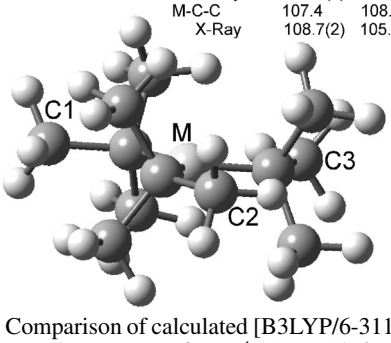


Fig. 1. Comparison of calculated [B3LYP/6-311+G(d,p)] and experimental structures of MBu^t_3 (M = Al: **1**, B: **1B**).

Table 1. Experimental and calculated NMR parameters[a] of comparable aluminum and boron compounds.

Compound	$AlBu^t_3$ **1**	$AlMe_3$ **2**	1-AlC_9H_{15}[b] **3**	$[AlMe_4]^-$ **4**	Li[$AlBu^t_4$]	$Me_2AlC(SiMe_3)_3$-THF	$Me_2AlMe_2AlMe_2$
Parameter	BBu^t_3 **1B**	BMe_3 **2B**	1-BC_9H_{15}[c] **3B**	$[BMe_4]^-$ **4B**	**5**	**6**[d]	$\mathbf{2_2}$
$\delta^{13}C$ exp. [calcd.]	21.0 (br[e], C)	– [−6.1]	– [38.4] (CH)	n.r.[f] [−8.5]	19.6 (C)	−2.4 (br, $AlMe_2$)	−8.2 (Me_t) [−9.5]
	[25.2]		– [35.1, 39.9] (CH_2)		35.2 (Me)	1.4 (br, AlCSi)	−5.6 (Me_b) [−3.7]
	30.6 (Me) [30.9]				25.7, 68.2 (THF)	6.4 ($SiMe_3$)	
		14.8 [15.5]	39.0 (CH) [42.2]	6.2 [17.4]		24.5, 71.9 (THF)	
	30.5 (br, C)		45.2, 38.8 [54.9, 43.1]				
	[35.5]						
	31.5 (Me) [32.2]						
$\delta^{27}Al$ exp. [calcd.]	250 [257.2]	– [306.3]	– [308.1]	n.r. [134.1]	143.4	173	157 [139.7]
$\delta^{11}B$ exp. [calcd.]	83.2 [90.2]	86.0 [88.5]	82.6 [84.6]	−21.5 [−22.0]			
$^1J(^{27}Al,^{13}C)$ exp. [calcd.]	93 ± 5 [76.3]	– [76.7]	– [67.0]	71.5 [64.9]	76.0		110 (Me_t) [108.5]
							19 (Me_b) [46.4]
$^1J(^{13}C,^{11}B)$ exp. [calcd.]	52.0 [51.5]	51.0 [49.1]	49.0 [47.7]	42.0 [41.0]			

[a] B3LYP/6-311+G(d,p); calcd. $\sigma(^{13}C)$ data are converted to $\delta^{13}C$ data by $\delta^{13}C = \sigma(^{13}C)$ [$SiMe_4$] – $\sigma(^{13}C)$, with $\sigma(^{13}C)$ [$SiMe_4$] = 184.0, $\delta^{13}C$ [$SiMe_4$] = 0; calcd. $\sigma(^{11}B)$ data are converted to $\delta^{11}B$ data by $\delta^{11}B = \sigma(^{11}B)$ [B_2H_6] – $\sigma(^{11}B)$ + 18, with $\sigma(^{11}B)$ [B_2H_6] = 84.1, $\delta^{11}B$ [B_2H_6] = 18.0 and $\delta^{11}B$ [BF_3-OEt_2] = 0; calcd. $\sigma(^{27}Al)$ data are converted to $\delta^{27}Al$ data by $\delta^{27}B = \sigma(^{27}Al)$ [$Al(BH_4)_4^-$] – $\sigma(^{27}Al)$ + 34 with $\sigma(^{27}Al)$ [$Al(BH_4)_4^-$] = 509.7, $\delta^{27}Al$ [$Al(BH_4)_4^-$] = 34 and $\delta^{27}Al$ [$Al(H_2O)_6^{3+}$] = 0; [b] 1-aluminaadamantane; [c] 1-boraadamantane; [d] $\delta^{29}Si = -4.3$; $^1J(^{29}Si,^{13}C_{Me}) = 50.0$ Hz; $^1J(^{29}Si,^{13}C_{CAl}) = 30.5$ Hz; [e] $h_{1/2} = 18$ Hz; [f] n.r. = not reported.

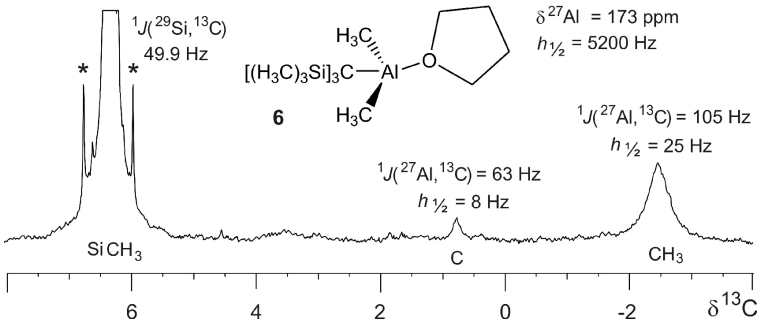


Fig. 2. 125.8 MHz $^{13}C\{^1H\}$ NMR spectrum of $Me_2AlC(SiMe_3)_3$-THF in C_6D_6. The line widths of the ^{13}C(Al–C) and ^{13}C(Al–CH_3) signals are markedly different, indicating different coupling constants $^1J(^{27}Al,^{13}C)$ as calculated from Eq. 1. The geometry of $Me_2AlC(SiH_3)_3$-THF was optimized [B3LYP/6-311+G(d,p)], and the NMR parameters were calculated: $\delta^{27}Al$ = 161.2; $^1J(^{27}Al,^{13}C_C)$ = 41.5 Hz and $^1J(^{27}Al,^{13}C_{Me})$ = 97.8 Hz.

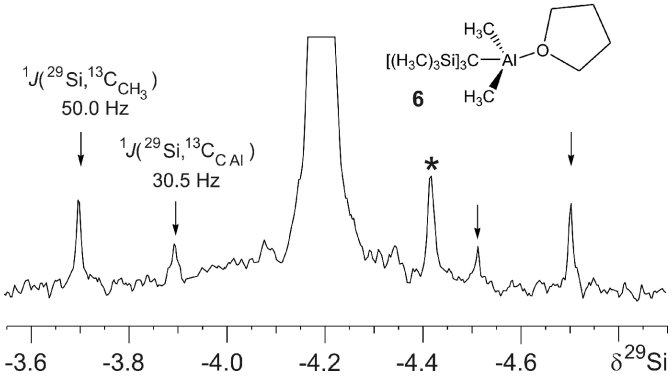


Fig. 3. 49.7 MHz $^{29}Si\{^1H\}$ NMR spectrum (refocused INEPT) of $Me_2AlC(SiMe_3)_3$-THF in C_6D_6. The information on $^1J(^{29}Si,^{13}C_{AlC})$ could not be obtained from the ^{13}C NMR spectrum.

C1, C2 and C3 are exactly coplanar with the central boron atom and the intervening carbon atoms linked directly to boron. There is also good agreement between the respective calculated and experimental B–C–C bond angles. The calculated structure of **1** is analogous to that of **1B** except of the Al–C–C bond angles. Again, the calculated structural data agree well with experimental findings for the solid state [4] and also with results from the gas phase electron diffraction study [3b], given for the fact that the molecules of **1** are weakly associated in the crystal lattice, and the determination of the latter has not been particularly precise. This association must be weak, since the trigonal planar surroundings of the aluminum atom are almost undistorted. Hyperconjugation has been invoked to explain certain structural features of **1** and **1b** [4b], and this is supported by experimental and calculated NMR parameters, at least for trialkylboranes [5].

The calculated coupling constants $^1J(^{13}C,^{11}B)$ are in almost perfect agreement with experimental data, irrespective whether these were obtained from observed splitting in the ^{13}C NMR spectra or by line shape analysis of the respective ^{13}C NMR signals. The calculated data $^1J(^{27}Al,^{13}C)$ for **1** and **4** appear to be too small by $\approx 15\,\%$, when compared with experimental data, a fact which has already been noted for $^1J(^{29}Si,^{13}C)$ calculated by the same procedure [13]. There appears to be a systematic error in the calculations for third row element nuclei such as ^{29}Al, ^{29}Si, and potentially ^{31}P. However, the trends of the experimental $^1J(^{27}Al,^{13}C)$ data are well reproduced. The experimental $^1J(^{27}Al,^{13}C)$ data for the dimer of $AlMe_3$, $\mathbf{2_2}$ [12], may be inaccurate, in particular for the bridging methyl group. In the case of $\mathbf{2_2}$, the line shape analysis of the ^{13}C NMR signals as a result of spin dynamics is hampered by dynamic processes involving intra- and inter-molecular exchange.

Further examples of line shape analysis

An application of the line shape analysis for ^{13}C(Al–C) NMR signals is shown in Fig. 2 for the THF adduct of $Me_2AlC(SiMe_3)_3$ **6** [9]. The aluminum atom bears two greatly different types of alkyl groups, and this should be mirrored by different coupling constants $^1J(^{27}Al,^{13}C)$, evident from the different line widths of the relevant ^{13}C NMR signals. These experimental findings are supported by the calculated coupling constants $^1J(^{27}Al,^{13}C)$, when the model compound $Me_2AlC(SiH_3)_3$-THF is used.

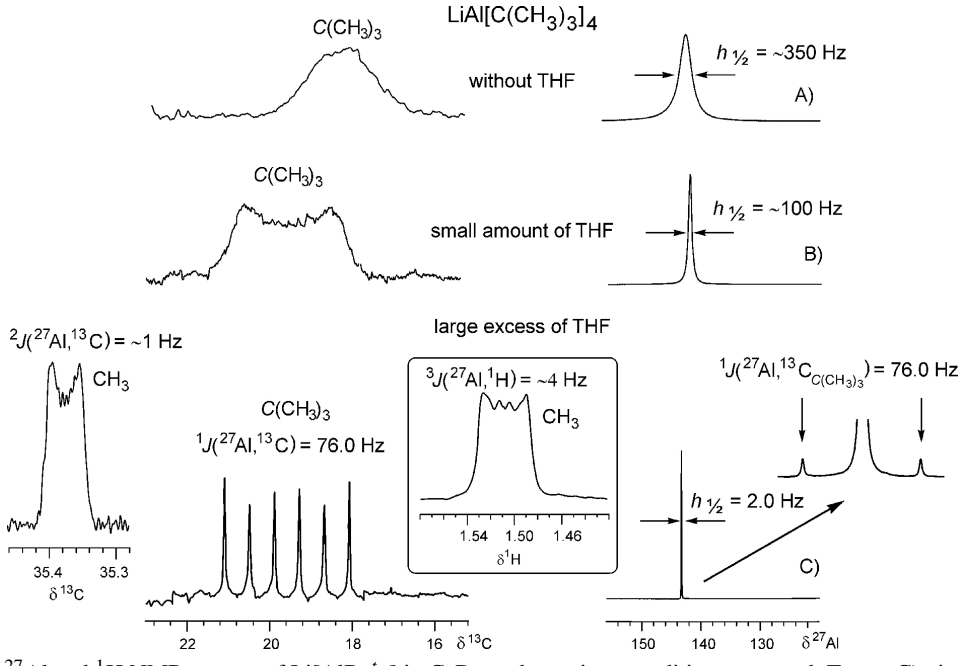


Fig. 4. ^{13}C, ^{27}Al and ^1H NMR spectra of $Li[AlBu^t_4]$ in C_6D_6 under various conditions as stated. Traces C) give all relevant information on coupling constants involving ^{27}Al. The ^{13}C satellites in the $^{27}Al\{^1H\}$ NMR spectrum do not show any appreciable isotope-induced chemical shift $^1\Delta^{12/13}C(^{27}Al)$ (< 0.5 ppb).

As can be seen from Fig. 2, ^{29}Si satellites are readily assigned for the $^{13}C(SiMe_3)$ NMR signals. However, there is no chance to detect the ^{29}Si satellites for the broad and weak ^{13}C(Al–C–Si) NMR signal. The alternative for determining $^1J(^{29}Si,^{13}C)$ is provided by ^{29}Si NMR spectra, for which almost perfect line shapes with an excellent signal-to-noise ratio can be achieved using $^1H\rightarrow{}^{29}Si$ polarization transfer (*e. g.* INEPT [14]), as shown in Fig. 3. The relatively small value $^1J(^{29}Si,^{13}C_{AlC}) = 30.5$ Hz is typical of such silanes [13, 15].

NMR spectroscopy of $Li[AlBu^t_4]$

Addition of one equivalent of $LiBu^t$ to $AlBu^t_3$ **1** gives $Li[AlBu^t_4]$ **5** as reported [8]. If the $LiBu^t$ in pentane is added to a pre-cooled (0 – 5 °C) solution of **1**, there are no side reactions, and pure **5** can be obtained and used in solutions without further purification. As shown in Fig. 4, the information from the NMR spectra is greatly affected by the conditions. Without THF, the lithium seeks for coordinative saturation by interactions with the *tert*-butyl groups. Therefore, the tetrahedral surroundings of the ^{27}Al nucleus are significantly distorted, and quadrupole-induced relaxation is relatively fast (traces A). This is changed by adding THF. In the presence of a large excess of THF, the ions apparently become separated, and the tetrahedral symmetry around the ^{27}Al nucleus is largely restored. Consequently, the ^{27}Al relaxation rate is much slower. In fact, the line width of 2 Hz of the ^{27}Al NMR signal is the smallest line width of any ^{27}Al NMR signal reported so far (see *e. g.* [16]). It is the hitherto first known example for observing ^{13}C satellites in an ^{27}Al NMR spectrum. Therefore, the typical splitting patterns owing to resolved or partially resolved ^{27}Al-^{13}C and ^{27}Al-^1H spin-spin coupling across one, two and three bonds are clearly visible in the ^{13}C and ^1H NMR spectra, respectively (traces C).

Experimental Section

The preparation and the handling of samples were carried out observing the necessary precautions to exclude air and traces of moisture. The solvents used were carefully dried by established methods. Starting materials such as $LiBu^t$ (1.7 M in pentane) (Aldrich) and aluminum trichloride (anhydrous, 99.99+ % Al) (STREM Chemicals) were commercial products. Tri(*tert*-butyl)aluminum **1** [3a, 17] [^1H NMR (250.1 MHz, C_6D_6, 298 K): δ ($^1J(^{13}C,^1H)$) = 1.03 (123.7)

(s, 27H, CH_3)], the corresponding borane **1B** [18] and $Me_2AlC(SiMe_3)_3$-THF **6** [9] [^{1}H NMR (250.1 MHz, C_6D_6, 298 K): δ ($^1J(^{13}C,^1H)$ [$^2J(^{29}Si,^1H)$] = −0.39 (111.4) (s, 6H, $AlCH_3$), 0.40 (117.9) [6.1] (s, 27H, $Si(CH_3)_3$), 1.05, 3.45 (m, m, 8H, THF)] were prepared by literature procedures.

NMR spectra were recorded at 23 °C on Bruker ARX 250 and DRX 500 or Varian Inova 400 spectrometers: ^{1}H, ^{13}C, ^{27}Al, and ^{29}Si NMR (refocused INEPT [14] based on $^2J(^{29}Si,^1H) = 7$ Hz), all equipped with multinuclear units, using C_6D_6 solutions (*ca.* 5 %) in 5 mm tubes. Chemical shifts are given with respect to Me_4Si [d^1H (C_6D_5H) = 7.15, d^{13}C (C_6D_6) = 128.0, δ^{29}Si = 0 for $\Xi(^{29}Si)$ = 19.867184 MHz]; δ^{11}B = 0 for BF_3-OEt_2 with $X(^{11}B)$ = 32.083971 MHz; external 1.1 M $Al(NO_3)_3$ in D_2O [δ^{27}Al = 0 for $\Xi(^{27}Al)$ = 26.056890 MHz].

Lithium-tetra(tert-butyl)alanate ***5***

A solution of **1** (136 mg, 0.68 mmol) in C_6D_6 (1 mL) was cooled to 0 – 5 °C, and $LiBu^t$ (0.4 mL of a 1.7 M solution in pentane, 0.68 mmol) was added. The mixture was warmed to r. t. and stirred for 10 min, and volatile materials were then removed *in vacuo*. The remaining solid was dissolved in C_6D_6 (0.6 mL), the solution was centrifugated, and the liquid was collected. Then THF (finally 0.5 mL) was added in portions. **5**: ^{1}H NMR (500.1 MHz, C_6D_6, 298 K): δ = 1.39 (m, 36H, CH_3), 1.53, 3.39 (m, m corresponding to 32H, excess of THF).

All calculations were performed using the GAUSSIAN 03 program package [19]. Optimization of the gas phase geometries was carried out with DFT methods (B3LYP) [20] and the 6-311+G(d,p) basis set [21]. Frequencies were calculated analytically to characterize the stationary points of the optimized geometries as minima by the absence of imaginary frequencies. Chemical shifts (GIAO [22]) and coupling constants [23] were calculated in the framework of the GAUSSIAN 03 program [19].

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