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In-depth ^{27}Al NMR investigation of $Al(C_6F_5)_3$ and its complexes with Lewis bases

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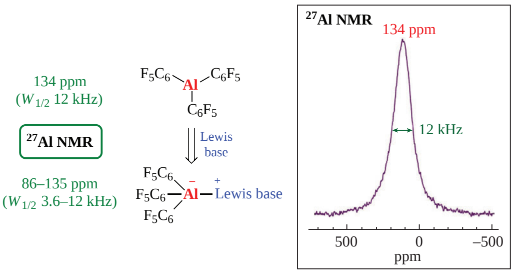
For the first time, a correct ^{27}Al chemical shift and $W_{1/2}$ for $Al(C_6F_5)_3$ as the most widely used Al-based 'super-electrophilic' Lewis acid was determined. A step-by-step proper way for acquisition and processing challenging ^{27}Al spectra is suggested, which is applicable for any organoaluminium compounds with asymmetric environment of Al. Using this procedure, several Lewis pairs of $Al(C_6F_5)_3$ with *N,O,S,P*-centered Lewis bases were characterized.



Keywords: tris(pentafluorophenyl)aluminium, super-electrophilic Lewis acids, ^{27}Al NMR, organoaluminium compounds, frustrated Lewis pairs.

Carbocationic transformations induced by 'super-electrophilic' Lewis acids are currently on the frontiers of organic synthesis.[1–3] They demonstrate unprecedented way of reactivity control based on highly reactive carbocation with weakly-coordinating anion (WCA) interactions resulting in various unique C–H and C–F activation processes that were developed in past decade.[4–6] Compound $Al(C_6F_5)_3$ and its complexes with Lewis bases are currently widely used as super-electrophilic Lewis acid (SLA) catalysts or sources of WCA in various carbocationic transformations.[7] Additionally, $Al(C_6F_5)_3$ was found to be highly efficient as a catalyst itself or as a catalyst component in a variety of carbocationic polymerization processes.[8–12] Moreover, $Al(C_6F_5)_3$-based Frustrated Lewis Pairs (FLP) are intensively studied currently for activation of H_2, CO_2 and other small molecules.[13–15]

Such remarkable interest to $Al(C_6F_5)_3$ and related Al-based Lewis acids makes it necessary to have a method to control the ligand environment of Al atom directly in reaction mixture. ^{27}Al NMR could be the most informative for this purpose because ^{27}Al chemical shifts and a peak width would give information about the current state of the reactive center of aluminum-based Lewis acid in the reaction medium, while other methods are usually ineffective for highly reactive complexes. Liquid-state NMR spectroscopy itself is extremely powerful method for in-depth studying of molecular structure of reactive intermediates. Unfortunately, it is still very limited when nuclei with high quadrupole moment like ^{27}Al are to be investigated. All issues with such nuclei resulted from extremely broad signals when they have asymmetric environment. This results in low sensitivity, difficulties in chemical shift determination, as well as impeded analysis when two or more compounds are presented in analyzing mixture. Nevertheless, the employment of this method is not impossible provided the further development of specialized approaches for recording and analysis.

Another serious problem that is special for ^{27}Al NMR is high background signal resulted from glass of NMR tube and glass components of NMR probe, which clogs to a large extent the target signals. The combination of both these problems leads to the fact that ^{27}Al NMR very rarely could be successfully acquired and used for analysis. Aluminum from NMR tube can be excluded by usage of quartz or Teflon tubes. However, for highly air- and moisture sensitive organoaluminium compounds, most often Young NMR tubes are used that are always made from glass. Nevertheless, issues associated with aluminum from glass (or even more expensive sapphire) components of NMR probe could not be avoided at all. So, the only way is to carefully subtract the background signal, which might be challenging task especially for synthetic chemists. As the result, ^{27}Al data for most of reported organoaluminium compounds are either not provided at all, or a note of blank spectrum is given. As for the rest, it is often unclear whether the chemical shift was determined correctly or signal maximum at distorted baseline was simply measured.

Therefore, the current work was aimed, first of all, to revise published ^{27}Al NMR data of $Al(C_6F_5)_3$ as the most widely used Al-based 'super-electrophilic' Lewis acid, and second, to summarize the detailed procedure how to acquire and process ^{27}Al NMR spectra in challenging cases to obtain clear data. Initial $Al(C_6F_5)_3$ **1** was synthesized as $Al(C_6F_5)_3 \cdot 0.5\,PhMe$ complex $\mathbf{1} \cdot 0.5\,PhMe$ by well-known procedure that involves ligand exchange between $B(C_6F_5)_3$ and $AlMe_3$ in toluene/*n*-hexane solution (Scheme 1).[16] Its ^{19}F NMR data were in a good agreement with the data published by many researchers. However, the only ^{27}Al spectra reported for this Lewis acid was found to be erratic and most likely attributed to ^{27}Al spectrum of glass (*e.g.*, 50–60 ppm, Table 1, entries 1 and 2).[17]

$$\mathrm{B(C_6F_5)_3 + AlMe_3 \xrightarrow[64\%]{i} Al(C_6F_5)_3{\cdot}0.5\,PhMe}$$

1·0.5 PhMe

Scheme 1 *Reagents and conditions*: i, PhMe, *n*-hexane, room temperature.

We were able to register a good ^{27}Al spectrum from the solution of Al(C_6F_5)$_3$ **1** in C_6D_6 or in C_6H_6 (concentration 50 mg in 0.6 ml of benzene, Figure 1, curve *1*). The major signal component in this spectrum is that at *ca*. 67 ppm from glass in NMR tube and NMR probe. After subtracting of ^{27}Al spectrum from standard NMR tubes (the method that works well for simple ^{27}Al spectra) we obtained spectra (*2*) and (*3*) in Figure 1 that still contain residual glass peaks. Subtraction of ^{27}Al NMR from strictly the same NMR tube under exactly the same acquisition parameters afforded a very good and clear spectrum (curve *4*).

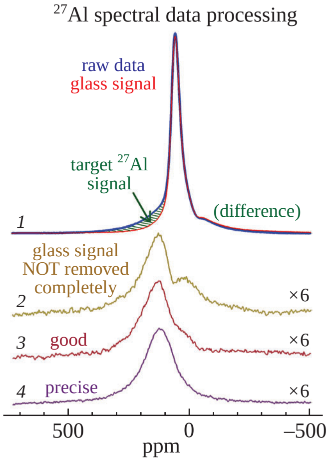


Figure 1 (*1*) Initial ^{27}Al NMR spectrum of Al(C_6F_5)$_3$ **1** (raw data, blue) and ^{27}Al glass signal (red); (*1*)–(*4*) processed ^{27}Al difference spectra: (*2*) typical processed ^{27}Al NMR spectrum with glass signal NOT removed completely (brown); (*3*) good processing, but with residual perturbations from glass (dark red); (*4*) properly processed clear ^{27}Al NMR of **1** (violet).

Determination of chemical shift and $W_{1/2}$ also has some peculiarities compared to usual ^{1}H NMR. In fact, simple peak maximum is incorrect as such a wide signal can be often somewhat distorted and non-symmetric, and also it can give a large error in value. So, it is better to use signal mass center (*i.e*. the position of the middle of integral curve). However, the most correct chemical shift will be obtained by line shape simulation that can be easily performed using standard TopSpin software package (Figure 2). This resulted in chemical shift of 134 ± 2 ppm with $W_{1/2}$ of 12 kHz and $W_{1/8}$ of 28 kHz for

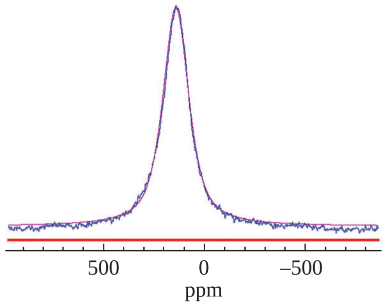
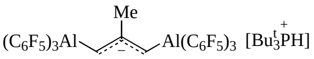
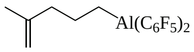
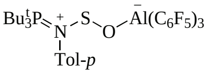


Figure 2 Example of line shape analysis of ^{27}Al NMR signal of compound **1** to get signal parameters using ‘solid line shape analysis’ program package (‘SOLA’) in Bruker TopSpin software (key optimization parameters: δ = 135.0 ppm, LB = 12 000 Hz, $xG/(1-x)L = 0.3$).

Table 1 ^{27}Al NMR data of **1** and complexes of Al(C_6F_5) with Lewis bases in comparison with selected literature examples.

Entry	Compound	Solvent	This work		Lit.[a]		Reference
			δ/ppm	$W_{1/2}$/kHz	δ/ppm	$W_{1/2}$/kHz	
1	Al(C_6F_5)$_3$·0.5 PhH	C_6D_6	–	–	52	6.3	17
2	Al(C_6F_5)$_3$·0.5 PhMe	C_6D_6	134 ± 2	12 ($W_{1/2}$) 28 ($W_{1/8}$)	61	6.4	17
3	Al(C_6F_5)$_3$·CyH	C_6D_5Br	–	–	failed[b]		18
4	EtAl(C_6F_5)$_2$	C_6D_5Br	–	–	failed[b]		18
5	Al(C_6F_5)$_3$·Pyridine	C_6D_6	127 ± 1	4.0	–	–	–
6	Al(C_6F_5)$_3$·2,6-Lutidine	C_6D_6	117 ± 1	3.6	–	–	–
7	Al(C_6F_5)$_3$·THF	C_6D_6	129 ± 2	4.5	–	–	–
8	Al(C_6F_5)$_3$·P(OEt)$_3$	C_6D_6	110 ± 2	4.0	–	–	–
9	Al(C_6F_5)$_3$·MeCN	C_6D_6	86 ± 5	11.5	–	–	–
10	Al(C_6F_5)$_3$·Me$_2$S	C_6D_6	135 ± 2	5.5	–	–	–
11	Li(Et$_2$O)$_2$[Al(C_6F_5)$_4$]	THF-d_8	–	–	116.3	n.d.[c]	19
12	[Bu$^t_3$PH][Al(C_6F_5)$_4$]	C_6D_5Br	–	–	116	0.5	20
13		C_6D_5Br	–	–	139	2.4	20
14		C_6D_5Br	–	–	failed[b]		20
15	[Et$_4$N][ClAl(C_6F_5)$_3$]	C_6D_5Br	–	–	123	1.5	18
16	[Et$_4$N][HAl(C_6F_5)$_3$]	C_6D_5Br	–	–	115	1.0	18
17	[Et$_4$N][EtAl(C_6F_5)$_3$]	C_6D_5Br	–	–	134	2.0	18
18	[Et$_4$N][H(Al(C_6F_5)$_3$)$_2$]	C_6D_5Br	–	–	failed[b]		18
19	[Bu$^t_3$PH][H(Al(C_6F_5)$_3$)$_2$]	C_6D_5Br	–	–	failed[b]		18
20	[Mes$_3$PH][H(Al(C_6F_5)$_3$)$_2$]	C_6D_5Br	–	–	failed[b]		18
21		Toluene-d_8	–	–	*ca*. 118	*ca*. 1.8	21
22	[Bu$^t_3$PH][PhC≡CAl(C_6F_5)$_3$]	CD_2Cl_2	–	–	105.18	n.d.	22
23	*E*-(*o*-Tol$_3$P)C(Ph)=C(H)Al(C_6F_5)$_3$	DCE-d_4	–	–	116.52	n.d.	22

[a] Literature data are presented as in original publication. [b] An attempt was published, but no signal was detected. [c] No data presented.

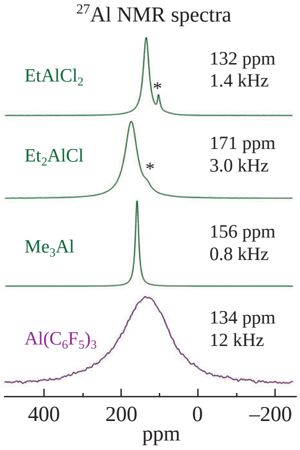


Figure 3 Comparison of precisely processed and clear ^{27}Al NMR spectra and signal parameters of Al(C_6F_5)$_3$ **1** (violet), Me_3Al, Et_2AlCl, and $EtAlCl_2$ (green); * stands for oxidation impurities in a commercial source reagent.

Al(C_6F_5)$_3$ in benzene solution (see Table 1, entry 2). As the result, we obtained for the first time correct ^{27}Al NMR signal of ‘free’ Al(C_6F_5)$_3$ **1** and used it for further analysis. If compared to more ordinary and widely used organoaluminium compounds like Me_3Al, Et_2AlCl, and $EtAlCl_2$ existing as dimers in non-polar solvents, ^{27}Al chemical shift of Al(C_6F_5)$_3$ appears in the range 120–170 ppm that is typical for alkyl/aryl organoaluminium compounds (Figure 3).[23] As can be seen from these data, influence of substituents on the absolute value of ^{27}Al chemical shift is not straightforward and further investigations are required. Notably, the Al(C_6F_5)$_3$ signal is much wider than those of Me_3Al, Et_2AlCl, $EtAlCl_2$ as it was expected from much larger substituents and lower molecule symmetry.

Interestingly, H to D exchange of solvated toluene was noted when analyzing ^{1}H and ^{13}C NMR data of **1** in C_6D_6. The exchange is not complete (~60–70%) and a mixture of partially deuterated toluenes is presented in solution (as well as a significantly increased C_6D_5H signal), but this fact clearly demonstrates well-known extremely high Lewis acidity of Al(C_6F_5)$_3$.

When working with so extremely air- and moisture sensitive compounds like Al(C_6F_5)$_3$, it is required to be sure that the compound acquired in NMR tube is the target compound and not any decomposition product. In our case, we were able to grow single crystals of C_6H_6 solvate of **1**, Al(C_6F_5)$_3$(C_6H_6)$\cdot$0.5C_6H_6, from our NMR sample (after NMR experiments) after 2 months storage in a fridge at 5 °C (Figure 4).[†]

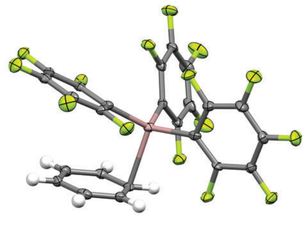


Figure 4 X-ray of Al(C_6F_5)$_3$(C_6H_6)$\cdot$0.5C_6H_6 after NMR analysis.

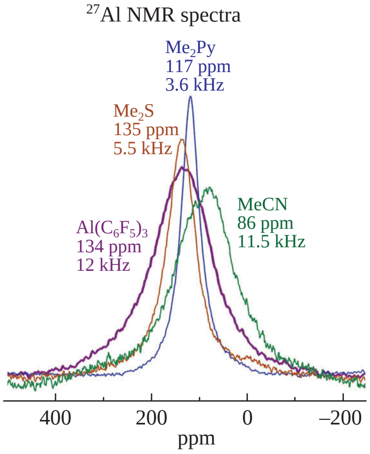


Figure 5 Comparison of precisely processed and clear ^{27}Al NMR spectra and signal parameters of Al(C_6F_5)$_3$ **1** (violet) and its complexes with 2,6-lutidine (Me_2Py, blue), Me_2S (orange), and MeCN (green).

Complexation of Al(C_6F_5)$_3$ with any *O,N,P,S*-centered Lewis bases makes ^{27}Al NMR signal much narrower and easier for registration (see Table 1, entries 5–10). Several *N,O,S,P*-centered Lewis bases were tested, including pyridine, 2,6-lutidine, Me_2S, THF, P(OEt)$_3$ and MeCN (Figure 5). In most cases, ^{27}Al signals were downfield shifted to 110–127 ppm along with signal narrowing to 3.5–5.5 kHz (entries 5–8). The only exception is MeCN, for which signal was downfield shifted dramatically to 86 ppm, while being similarly broad as for ‘free’ Al(C_6F_5)$_3$ (entry 9). Complexation with Me_2S causes only narrowing without signal shift (entry 10).

Remarkably, we noted that pyridine formed quite weak complex with Al(C_6F_5)$_3$, and only one set of pyridine signals was observed in ^{1}H and ^{13}C NMR (with an excess of pyridine). On the contrary, complex with 2,6-lutidine is more robust and two sets of lutidine signals in ^{1}H and ^{13}C NMR were observed. This fact is somewhat unusual, and the reason for this is unclear yet.

In conclusion, we have for the first time determined a correct ^{27}Al chemical shift and $W_{1/2}$ for Al(C_6F_5)$_3$ as the most widely used Al-based ‘super-electrophilic’ Lewis acid. Moreover, we described step-by-step correct way to acquire and process ^{27}Al spectra that are of high importance when organoaluminium compounds with non-symmetric ligand environment of Al are employed. Using this procedure we characterized several Lewis pairs of Al(C_6F_5)$_3$ with *N,O,S,P*-centered Lewis bases, including pyridine, 2,6-lutidine, Me_2S, THF, P(OEt)$_3$ and MeCN.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.09.002.

[†] *Crystal data for* Al(C_6F_5)$_3$(C_6H_6)$\cdot$0.5C_6H_6. Crystals of $C_{27}H_9AlF_{15}$ (M = 645.32) are triclinic, space group $P\bar{1}$, at 100 K: a = 7.3615(5), b = 11.3190(9) and c = 15.5278(11) Å, V = 1213.87(15) Å^3, Z = 2, d_{calc} = 1.766 g cm^{-3}, μ(MoKα) = 0.217 mm^{-1}, F(000) = 638. 7361 reflections were measured, and 7361 independent reflections (R_{int} = 0.056) were used in a further refinement. The refinement converged to wR_2 = 0.1892 and GOF = 1.172 for all independent reflections [R_1 = 0.097 was calculated against F for 5178 observed reflections with $I > 2\sigma(I)$]. X-ray diffraction datasets for Al(C_6F_5)$_3$(C_6H_6)$\cdot$0.5C_6H_6 were collected on an in-lab Bruker QUEST diffractometer [graphite monochromator, φ and ω scan mode, λ = 0.71073 Å (MoKα)].

Structure was solved by direct method and refined in anisotropic approximation for non-hydrogen atoms with the ShelXL program. Hydrogen atoms of aromatic fragments were calculated according to the idealized geometry and refined with constraints applied to C–H bond lengths and equivalent displacement parameters [U_{eq}(H) = 1.2U_{eq}(X), X is central atom of the XH group; U_{eq}(H) = 1.5U_{eq}(Y), Y is central atom of the YH group]. All structures were solved with the ShelXT program and refined with the ShelXL program.

CCDC 2258828 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

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