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# Synthesis and structure of fluorinated dialacycles

Martin Tschinkl [a], T. Matthew Cocker [b], Robert E. Bachman [b], R.E. Taylor [a], François P. Gabbaï [a],*

[a] *Department of Chemistry, Texas A&M University, College Station, TX 77843-3255, USA*
[b] *Department of Chemistry, Georgetown University, Washington, DC 20057, USA*

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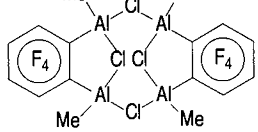
**Abstract**

Addition of THF to a solution of dimeric 1,2-bis(chloromethylalumino) tetrafluorobenzene (**1**) induces a ring contraction process that results in the formation of a mixture of three dialacycles as shown by $^{1}$H- and $^{19}$F-NMR. The three diaalacycles have been identified as 9-methyl-10-chloro-9,10-dihydro-9,10-diala-octafluoroanthracene bis(THF) adduct (**2a**), 9,10-dichloro-9,10-dihydro-9,10-diala-octafluoroanthracene bis(THF) adduct (**2b**) and 9,10-dimethyl-9,10-dihydro-9,10-diala-octafluoroanthracene bis(THF) adduct (**2c**). A co-crystal of these three compounds was examined by X-ray crystallography, confirming the structure of the dialacycle and revealing that the central six-membered ring is in a chair conformation. In **2**, each aluminum center is four-coordinate with a slightly distorted tetrahedral geometry. The coordination sites of the aluminum are occupied by the *ipso*-carbon atoms of the tetrafluorophenylene units, the oxygen atom of a coordinated THF molecule, and either a methyl group (50%) or a chloride ion (50%). © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Aluminum; Perfluorinated; Lewis acid; Dialacycle

## 1. Introduction

Organo-Group 13 derivatives with perfluorinated ligands have recently received renewed attention because of their ability to function as co-catalysts for the metallocene catalyzed Ziegler–Natta polymerization of olefins [1,2]. While the boron derivatives have been investigated in detail [1], the chemistry of the corresponding aluminum compounds is considerably less well developed [2–6]. This disparity can be partly explained by the lower stability of fluorinated organoaluminum compounds toward C–F bond activation and Al–F bond formation. As part of our efforts to prepare aluminum bifunctional Lewis acids with a perfluorinated backbones, we recently discovered that the reaction 1,2-bis(trimethylstannyl)tetrafluorobenzene with dimethylaluminumchloride cleanly yields the unusual dimeric compound 1,2-bis(chloromethylalumino)tetrafluorobenzene (**1**) in high yield [7]. In this paper, we would like to report our initial studies regarding the reaction of **1** with Lewis basic solvents and its rearrangement to a mixture of 9,10-dihydro-9,10-diala-anthracene derivatives. Such 9,10-dihydroanthracene derivatives of the Group 13 elements are well known in the case of boron [8–10] and indium [11,12] but have only rarely been observed for aluminum or gallium [13].



**1**

## 2. Results and discussion

Addition of THF to a solution of **1** in hexane followed by slow evaporation of the solvent resulted in the formation of a crystalline material **2** (Scheme 1). Analysis of this material by $^{19}$F-NMR revealed the existence of a mixture of compounds. Two sets of signals whose multiplicity is consistent with two independent higher

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* Corresponding author. Fax: + 1-979-8454719.
*E-mail address:* gabbai@mail.chem.tamu.edu (F.P. Gabbaï).

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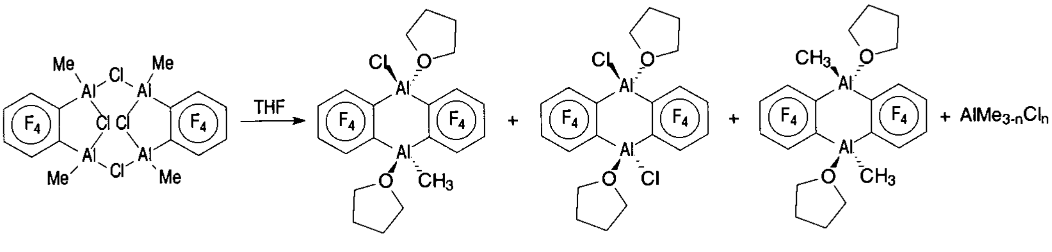
order AA′BB′ spin systems were detected at −121.85/−156.4 ppm and −123.3/−159.0 ppm. For comparison, **1** gives rise to two sets of signals which feature a similar splitting pattern but exhibit markedly different chemical shift (−121.22/−151.88 ppm) [7]. The spectrum of mixture **2** exhibits four additional signals whose multiplicity and intensity is consistent with a higher order ABCD spin systems were observed at −122.4, −122.9, −157.2 and −158.1 ppm. These observations suggest that the crystalline material contains three individual species. Complex **2a**, which contains an unsymmetrically substituted tetrafluorophenylene group, gives rise to the four independent $^{19}$F-NMR signals. We have successfully simulated the multiplicity of these signals giving us confidence in the assignment of the structure of **2a** (Fig. 1). The two symmetrically substituted species (**2b** and **2c**) then can be assigned to the two independent AA′BB′ spin systems. The respective intensity of the signals is in agreement with an approximate molar ratio 1/0.45/0.25 for **2a**/**2b**/**2c**. The proton spectrum of the mixture **2** contains the expected two AlMe resonances for **2a** and **2c** as well as signals consistent with the presence of coordinated THF molecules. Owing to the high air and water sensitivity of these compounds, we were unable to separate the three isomers.

Slow evaporation of the solvent produced crystalline material that was suitable for X-ray crystallographic studies. These structural studies confirm that presence of the dialacycle ring in compounds **2a**–**2c**. The ring contraction process responsible for the formation of the cyclic structure is apparently induced by addition of the basic THF to a solution of **1** and necessitates the elimination of $AlMe_{3-n}Cl_n$ species. Similar ring closure reactions have been observed previously in the formation of 9,10- dibora- [10] and 9,10-diinda-octafluoroanthracene derivatives [11c].

Compounds **2a**–**2c** apparently co-crystallize in the triclinic space group $P\bar{1}$ with two independent disordered half-molecules (molecule I and II) in the asymmetric unit. Both molecules possess crystallographically imposed inversion symmetry with the inversion center



**1** **2a** **2b** **2c**

Scheme 1.

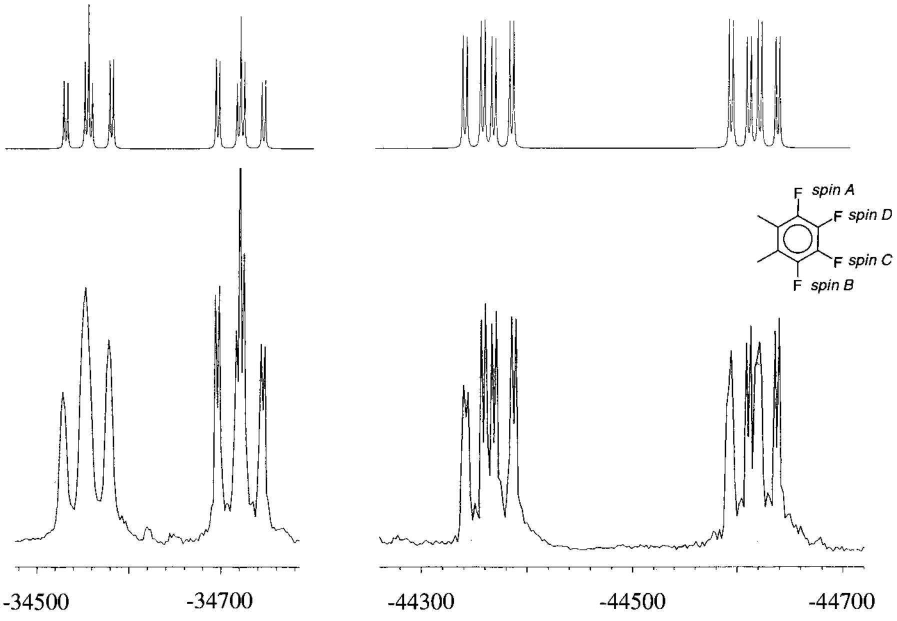


Fig. 1. Simulated (top) and observed (bottom) $^{19}$F-NMR signals for **2a**.

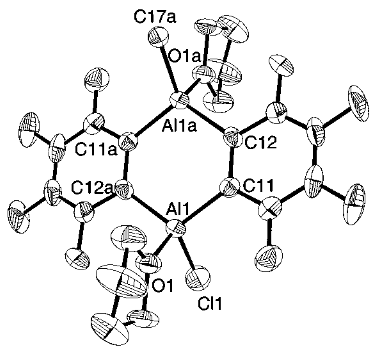


Fig. 2. Structure of molecule I in crystals of **2**. The disordered atoms C(27) and Cl(1a) are not shown for clarity.

Table 1
Selected bond lengths and angles for molecule I [a]

| | |
|---|---|
| *Bond lengths* (Å) | |
| Cl(1)–Al(1) | 2.112(6) [2.091(9)] |
| Al(1)–O(1) | 1.865(3) [1.870(3)] |
| Al(1)–C(12a) | 1.979(5) [1.980(4)] |
| Al(1)–C(11) | 1.986(4) [1.985(4)] |
| Al(1)–C(17) | 1.87(3) [1.96(4)] |
| *Bond angles (°)* | |
| O(1)–Al(1)–C(12a) | 106.21(17) [103.12(15)] |
| O(1)–Al(1)–C(17) | 102.1(12) [103.3(12)] |
| C(12a)–Al(1)–C(17) | 115.6(12) [113.4(13)] |
| O(1)–Al(1)–C(11) | 106.46(16) [105.29(16)] |
| C(12a)–Al(1)–C(11) | 111.42(18) [112.12(17)] |
| C(17)–Al(1)–C(11) | 113.9(12) [117.7(12)] |
| O(1)–Al(1)–Cl(1) | 104.9(3) [106.4(3)] |
| C(12a)–Al(1)–Cl(1) | 113.4(3) [114.6(3)] |
| C(11)–Al(1)–Cl(1) | 113.7(3) [114.0(3)] |

[a] The corresponding distances in molecule II are given in brackets.

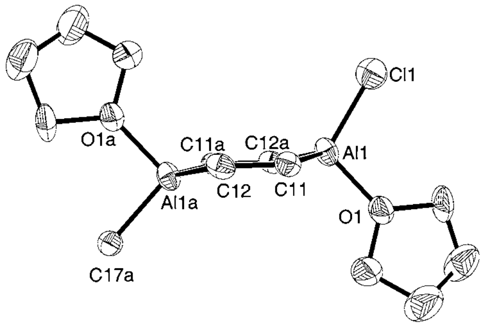


Fig. 3. Side-view of the central six-membered dialacycle of molecule I in the crystals. At the exception of *ipso*-C atoms, the tetrafluorophenylene backbones are not shown for clarity reasons.

positioned at the center of the dimetalla-six-membered rings. Fig. 2 shows the structure of molecule I as both of the independent molecules have very similar geometry. Selected metrical parameters are assembled in Table 1. The dimetallacycle deviates slightly from planarity and adopts a chair-like conformation (Fig. 3). The aluminum centers are displaced by 0.230 Å (Al(1)) and 0.111 Å (Al(2)) from the plane defined by the respective *ipso*-carbon atoms. In that respect, the structure of **2a**–**2c** differs from that of the 9,10-dimethyl-9,10-dihydro-9,10-digallaanthracene bis(pyridine) adduct which possesses a practically planar central six-membered ring [13].

Both aluminum atoms are in a slightly distorted tetrahedral environment composed of the *ipso*-carbon atoms of the perfluorinated aromatic ring, the oxygen atom of a THF molecule and disordered methyl group/chloride ion. Regardless of the model chosen, the relative occupancies of these two moieties consistently refined to a 1:1 ratio. This result agrees well with the relative molar ratio of **2a**, **2b** and **2c** determined by NMR in solution which indicates a relative ratio of 55:45 (chloride:methyl), assuming a completely random distribution of the three species throughout the crystal. Such an assumption is reasonable in light of the similar size of a methyl group and a chloride and the similar bond lengths expected in each case. The Al–C(aryl) distances in **2** range from 1.978(5) to 1.986(5) Å and are comparable to those observed in the related complexes $(C_6F_5)_3Al$–(THF) (av. 1.99 Å) [6], $(C_6F_5)_3Al$–(Toluene) (av. 1.98 Å) [3a], and $(C_6F_5)_3Al$–(Benzene) (av. 1.98 Å) [3a], as well as those seen in **1** (av. 1.958(5) Å). Likewise, the Al–O bond distances in **2** (av. 1.87 Å) are close to those observed for $(C_6F_5)_3Al$–(THF) (1.86 Å) [6].

We note that the results of the X-ray analysis are also in agreement with the existence of a crystal that would contain pure disordered **2a**. The hypothesis of a **2a**–**2c** co-crystal is however favored because of the confirmed existence of a mixture in solution.

## 3. Conclusions

In this paper, we report for the first time the structural characterization of 9,10-dihydro-9,10-diala-anthracene derivative. In this peculiar case, the phenylene backbone is perfluorinated, which enhances the Lewis acidity to the aluminum centers. We note that related 9,10-dibora-octafluoroanthracene derivatives are powerful Lewis acids that have been used as co-catalysts in the metallocene catalyzed polymerization of olefins [14]. Finally, this structural report elaborates on the series of previously characterized six-membered dialacycles which is so far limited to 1,4-dialumina-2,5-cyclohexadienes [15].

## 4. Experimental

### 4.1. General considerations

$^{19}$F-NMR (282.2 MHz) spectra were recorded in $C_6D_6$ on a VARIAN UNITY PLUS 300 spectrometer at 25°C with $CFCl_3$ as an external standard. $^1$H-NMR (300 MHz) and $^{13}$C-NMR (75.4 MHz) spectra were recorded in $C_6D_6$ on the same instrument at 25°C with TMS as an external standard. The NMR simulation was performed with the spin simulation software within the Varian VNMR 6.1B software package. The atom numbering scheme used to report the NMR data is in accordance with the IUPAC nomenclature [16]. All experiments were carried out under a dry inert atmosphere of $N_2$ using standard Schlenk technique or a glove box (Unilab, M. Braun). THF was dried over Na/K and distilled prior to use. Hexane was dried over $CaH_2$ and distilled prior to use. All solvents were dried, distilled and stored over molecular sieves before use. Compound **1** was prepared by following the published procedure [7].

### *4.2. Preparation of 9,10-dihydro-9,10-dialaoctafluoroanthracenes mixture*

**Great caution must be exercised. Aluminum compounds with fluorinated organic ligands have been reported to explode** [6]. Compound **1** has also been found to explode. THF (0.5 ml) was added to a hexane (1 ml) solution of **1** (200 mg, 0.33 mmol) at 25°C. The resulting solution was allowed to stand for 3 days during which the solvent slowly evaporated to yield a crystalline residue (150 mg) which was separated from the remaining solution by decantation and identified as mixture **2**. Due to the potential explosivity of these compounds, no further purification efforts were undertaken. As shown by $^1$H- and $^{19}$F-NMR, mixture **2** contained small amounts of impurities. Melting point experiments did not allow the detection of a sharp transition but revealed a progressive decomposition initiating between 60 and 70°C. $^1$H-NMR $\delta$ $-0.34$ (2c, s, 3H, $AlCH_3$), $-0.41$ (2a, s, 3H, $AlCH_3$). $^{13}$C-NMR $\delta$ $-6.8$ (2c, s, $AlCH_3$), $-9.4$ (2a, s, $AlCH_3$). $^{19}$F-NMR: 2a: $\delta$ $-122.4$ (F(4,5) or F(1,8), spin A), $-122.9$ (F(4,5) or F(1,8), spin B), $-157.2$ (F(2,7) or F(3,6), spin C), $-158.1$(F(2,7) or F(3,6), spin D) with $|J_{AB}| = 23.0$, $|J_{AC}| = 4.1$, $|J_{AD}| = 27.3$, $|J_{BC}| = 27.7$, $|J_{BD}| = 4.1$, $|J_{CD}| = 17.00$; 2b: $\delta$ $-123.4$ (F(1,4,5,8), spin A/A′) $-159.0$(F(2,3,6,7), spin B/B′) with $|J_{AA'}| = 24.5$, $|J_{AB}| = 3.5$, $|J_{AB'}| = 27.0$, $|J_{A'B}| = 27.0$, $|J_{A'B'}| = -3.5$, $|J_{BB'}| = 19.0$; 2B: $\delta$ $-121.86.4$ (F(1,4,5,8), spin A/A′) $-156.34$(F(2,3,6,7), spin B/B′) with $|J_{AA'}| = 23.5$, $|J_{AB}| = 5.5$, $|J_{AB'}| = 28.0$, $|J_{A'B}| = 28.0$, $|J_{A'B'}| = 5.5$, $|J_{BB'}| = 16.0$.

### *4.3. Structural study of **2***

Due to the reactive nature of **2**, the crystals were handled under a blanket of dry mineral oil during mounting. Despite this precaution, the crystals were observed to rapidly decompose with the evolution of gas during the mounting process. A colorless crystal ca. $0.3 \times 0.2 \times 0.1$ mm$^3$ in size was selected for data collection, mounted on a glass fiber with epoxy cement and rapidly transferred to the cold $N_2$ stream on the instrument. The unit cell determination and data collection were performed as described previously [17] to yield a total of 12 597 reflections to a resolution of 0.75 Å ($3.84 > 2\theta > 56.52°$). The data were corrected for Lorentz and polarization effects and an absorption correction was applied on the basis of equivalent reflection measurements using the method of Blessing as incorporated into the program SADABS [18] ($T_{max} = 0.9673/T_{min} = 0.7195$). Other key crystallographic parameters are as follows: $C_{21}H_{19}Al_2ClF_8O_2$, M = 544.7; triclinic space group $P\bar{1}$; $a = 10.641(7)$, $b = 10.768(5)$, $c = 11.673(6)$ Å, $\alpha = 88.99(5)$, $\beta = 65.51(5)$, $\gamma = 78.38(3)°$, $V = 1189.0(11)$ Å$^3$, $Z = 2$; $\mu = 0.314$ mm$^{-1}$. The data set was truncated at 0.90 Å resolution ($2\theta = 24.71°$) on the basis of intensity statistics yielding a final data set (99.7% complete) of 9120 reflections (4036 unique, $R_{int} = 0.0606$). The structure was solved by direct methods and refined against $F^2$ using the SHELXTL/PC (ver. 5.10) package. During refinement, a variety of disorder models were attempted for the methyl group and the chlorine atom in order to determine if the distribution of **2a**, **2b** and **2c** in the crystal was truly random. All such models converged to an ca. 1:1 ratio of the two groups at each position. Based on these results, a completely random distribution of the three species in the co-crystal was assumed and the occupancy of each function was set at 50%, consistent with the inversion symmetry present, and held fixed for the remainder of the refinement. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in calculated positions using a standard riding model. The final refinement converged [19] with residuals of $wR_2(F^2) = 0.1395$ (all data), $R_1(F) = 0.0562$ ($I > 2\sigma(I)$) and Goodness-of-Fit = 0.931 for 313 parameters and 4036 data.

## 5. Supplementary material

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 141211 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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[19] [$R_1 = \Sigma|F_o - F_c|/\Sigma F_o$; $wR_2 = \{\Sigma w|F_o^2 - F_c^2|^2/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = [\sigma^2(F_o^2) + (aP)^2 + bP]$ with $P = [2F_c^2 + \max(F_o^2, 0)]/3$ and $a$ and $b$ are fitted parameters.