

Novel supramolecular architectures in group 13 perfluoroaryl complexes. Synthesis and structures of $[\text{AlMe}(\text{C}_6\text{F}_5)(\mu\text{-Me})]_2$ and $\text{GaMe}(\text{C}_6\text{F}_5)_2$ †

Gregory S. Hair, Alan H. Cowley,* John D. Gordon, Jamie N. Jones, Richard A. Jones* and Charles L. B. Macdonald

The University of Texas at Austin, Chem. & Biochem. Dept., 1 University Station A5300, Austin, Texas 78712-0165, USA. E-mail: cowley@mail.utexas.edu; Tel: 512 471 7484. E-mail: rajones@mail.utexas.edu; Tel: 512 471 1706

Received (in Columbia, MO, USA) 5th October 2002, Accepted 12th December 2002

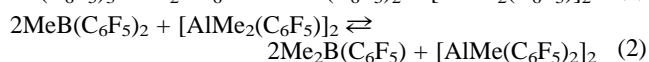
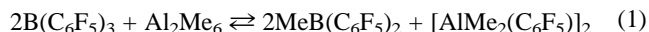
First published as an Advance Article on the web 15th January 2003

Novel supramolecular architectures are observed in the solid state structures of $[\text{AlMe}(\text{C}_6\text{F}_5)(\mu\text{-Me})]_2$ (**1**) and $\text{Ga}(\text{C}_6\text{F}_5)_2\text{Me}$ (**2**) via π - π stacking between C_6F_5 rings and intermolecular aryl-F \rightarrow Ga interactions, respectively.

Noncovalent attractive forces such as hydrogen bonding and π - π interactions are now recognized as key features in the self-assembly of multicomponent molecular architectures.^{1,2} For the group 13 elements, large supramolecular assemblies involving dative covalent interactions between Lewis acid centers and nitrogen or oxygen donor bases or halogens are well known.³

In this report we describe the synthesis and structures of two group 13 organometallics which exhibit novel supramolecular structures, namely $[\text{AlMe}(\text{C}_6\text{F}_5)(\mu\text{-Me})]_2$ (**1**) and $\text{GaMe}(\text{C}_6\text{F}_5)_2$ (**2**). In **1**, intermolecular π - π stacking between pairs of offset C_6F_5 rings creates an unusual zig-zag one-dimensional chain. In **2**, a linear chain-like supramolecular assembly is formed via intermolecular aryl-F \rightarrow Ga interactions.

Strong group 13 Lewis acids such as $\text{B}(\text{C}_6\text{F}_5)_3$ and $\text{Al}(\text{C}_6\text{F}_5)_3$ are currently of significant interest as components of olefin polymerization catalyst systems. The aluminium derivatives $\text{Al}(\text{C}_6\text{F}_5)_3(\text{arene})$ (arene = benzene, toluene) may be conveniently prepared by the reaction of $\text{B}(\text{C}_6\text{F}_5)_3$ with AlMe_3 in an arene solvent.^{4,5} This process no doubt occurs via a series of mixed ligand species (eqn. 1,2).



Recently Klosin *et al.* reported the detection of such dinuclear aluminium species in these reaction mixtures.⁶ They were also able to isolate and characterize the unsymmetrical aluminium species $(\text{C}_6\text{F}_5)_3\text{Al}_2\text{Me}_3$ when an excess of AlMe_3 was used. These kinds of mixed alkyl/perfluorophenyl aluminium compounds are also of interest since it has been claimed that species such as $[\text{Et}(\text{C}_6\text{F}_5)_2\text{Al}]_x$ alone act as catalysts or catalyst precursors for the polymerization of olefins.⁷

The initial products from the exchange reaction between $\text{B}(\text{C}_6\text{F}_5)_3$ and Al_2Me_6 should be $\text{MeB}(\text{C}_6\text{F}_5)_2$ and $\text{Al}_2\text{Me}_4(\text{C}_6\text{F}_5)_2$. In fact, the latter compound was isolated recently by Roesky *et al.* from the reaction of $\text{C}_6\text{F}_5\text{Li}$ with Me_2AlCl in hexane solution.⁸ Thermal decomposition results in a disproportionation to give $\text{Al}(\text{C}_6\text{F}_5)_3$ and Al_2Me_6 .

We have prepared compound **1** by the direct reaction of $\text{Al}(\text{C}_6\text{F}_5)_3(\text{toluene})$ with AlMe_3 in toluene solution at room temperature.⁹ It was recrystallized from toluene at -20°C as clear colorless crystals in 75% yield. The related gallium complex $\text{GaMe}(\text{C}_6\text{F}_5)_2$ (**2**) was prepared via the exchange reaction between $\text{B}(\text{C}_6\text{F}_5)_3$ and GaMe_3 in toluene solution at room temperature and was isolated in pure form by sublimation at 50°C and 0.1 torr.⁹

The solution NMR data for **1** are consistent with a fluxional system on the NMR time scale.⁹ In the solid state, **1** crystallizes

in the triclinic space group $P\bar{1}$ with two independent dimeric molecules per unit cell.[‡] The asymmetric unit contains two Al atoms, each in a different dimer. Each dimer features an inversion center located at the midpoint of the Al–Al vector. A view of the atom numbering scheme for the two crystallographically independent molecules is shown in Fig. 1.

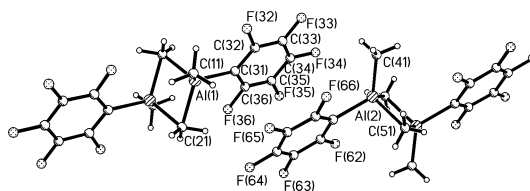


Fig. 1 View of two independent molecules of $[\text{AlMe}(\text{C}_6\text{F}_5)(\mu\text{-Me})]_2$ (**1**) showing the atom numbering scheme.

Each dimeric unit of **1** bears two C_6F_5 groups and, as a consequence, a novel supramolecular architecture is achieved by offset π - π interactions between pairs of C_6F_5 groups from different molecules. This creates a one-dimensional zig-zag framework as shown in Fig. 2. There are two sets of offset π - π interactions between C_6F_5 groups. In each case the dihedral angle between the aryl rings is 7.6° . The distances between the centroids of the π -stacked aryl rings are 3.713 Å and 4.465 Å. The latter distance is consistent with significantly more offset interactions between the fluoroaryl rings. These π - π interactions are clearly supramolecular in nature and not simply the result of unit cell packing. Calculations¹⁰ have shown that intramolecular π - π interactions between C_6F_5 groups should be favorable, although there appear to be few examples of such interactions in organometallic chemistry. Thus similar close π - π interactions are completely absent in the solid state structures of the related $\text{Al}-\text{C}_6\text{F}_5$ complexes $(\text{C}_6\text{F}_5)_3\text{Al}_2\text{Me}_3$ ⁶ and $\text{Al}(\text{C}_6\text{F}_5)_3\text{PhMe}$.⁵ Mountford and coworkers have described the titanium imide $\text{Ti}(\text{NC}_6\text{F}_5)\text{Cl}_2(\text{NHMe}_2)_2$ in which both C_6F_5 - C_6F_5 π - π stacking as well as $\text{Ti}-\text{Cl}\cdots\text{H}-\text{N}$ interactions are observed.¹¹ In this compound the separation between the C_6F_5 planes is 3.23 Å. Examples of intramolecular π - π interactions between two C_6F_5 rings are also known for a few ferrocene derivatives.¹²⁻¹⁴ For example, in $\text{Fe}(\text{C}_6\text{F}_5\text{Cp})_2$ ¹⁴ the distance between the aryl ring centroids is 3.58 Å and intramolecular C–F distances of 3.23 and 3.27 Å are observed between fluoroaryl rings. In **1** the closest C–F interactions are 3.190(3) Å (F35–C62) and 3.298(3) Å (F35–C63). A more detailed view of these interactions in one of the π -stacked fluoroaryl pairs is shown in Fig. 3 and full details of the other interactions are given in the Supporting Information†.

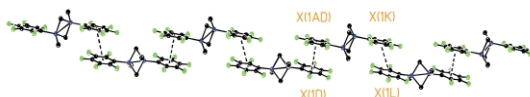


Fig. 2 View of the π - π interactions that create the linear zig-zag supramolecular structure in **1**. Distances between ring centroids: X(1AD)–X(1D) = 3.713(4) Å, X(1K)–X(1L) = 4.456(4) Å.

† Electronic supplementary information (ESI) available: Experimental procedures for the preparation of **1** and **2** and X-ray experimental details. See <http://www.rsc.org/suppdata/cc/b2/b210024j>

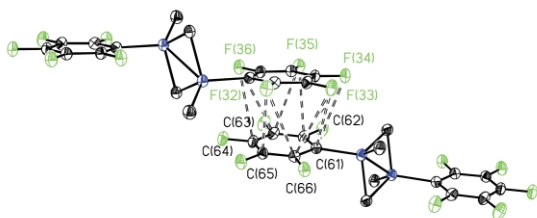


Fig. 3 View of π - π interactions in the C_6F_5 rings of **1**. Close C-F interactions are F(35)-C(63) 3.190(3) Å and F(35)-C(63) 3.298(3) Å.

The related gallium complex **2** is essentially mononuclear, possibly due to the presence of two bulky C_6F_5 groups per metal *vs.* one in the case of **1**. Thus, the presence of σ -bonded C_6F_5 and Me groups in **2** results in a nearly planar three-coordinate environment at gallium. However, in the solid state, there are also two intermolecular aryl-F \rightarrow Ga interactions from the *m*-F atoms on each C_6F_5 group (F(25) and F(15)) (Fig. 4).[‡] Thus, the localized geometry around Ga is that of a pseudo trigonal bipyramid and the overall supramolecular architecture comprises an interesting linear linked chain-like structure (Fig. 5). The Ga \cdots F contacts of 2.715(3) Å (Ga(1)-F(15)) and 2.727(3) Å (Ga(1)-F(25)) are shorter than the sum of the van der Waals radii (3.45 Å),¹⁵ but both are considerably longer than the sum of the covalent radii (1.91 Å).¹⁵ These distances may be compared with other short Ga \cdots F interactions; for example the intramolecular contacts in [2,4,6-(CF_3)₃ C_6H_2]₃Ga fall within the range 2.665–2.844 Å.¹⁶

The use of novel supramolecular structures such as those found in **1** and **2** to engineer the preparation of nanostructured materials is currently under investigation.

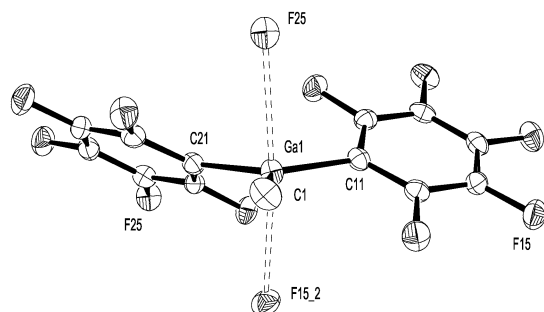


Fig. 4 View of the molecular structure of $GaMe(C_6F_5)_2$ (**2**) showing the localized geometry about Ga and the atom numbering scheme. Ga(1)-C(1) 1.922(2) Å, Ga(1)-C(21) 1.978(2) Å, Ga(1)-C(11) 1.975(2) Å.

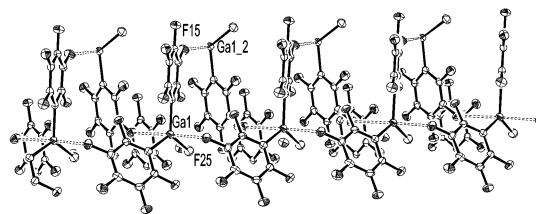


Fig. 5 View of supramolecular framework structure of **2**.

We are grateful for support from the Robert A. Welch Foundation (Grants F135 and F816).

Notes and references

[‡] CCDC reference numbers 196548 and 196549. See <http://www.rsc.org/suppdata/cc/b2/b210024j/>

- L. F. Lindoy and I. M. Atkinson, *Self-Assembly in Supramolecular Systems*, Cambridge University Press, UK, 2000.
- I. Haiduc and F. T. Edelman, *Supramolecular Organometallic Chemistry*, Wiley-VCH, 1999.
- See for example, F. P. Gabbaï, A. Schier and J. Riede, *Angew. Chem., Int. Ed.*, 1998, **37**, 622; J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle and K. S. Suslick, *Comprehensive Supramolecular Chemistry*, Vol. 9, Pergamon, Oxford, 1996.
- P. Biagini, G. Lugli, L. Abis and P. Andressi, U.S. Patent 5,602,269, Enichem, 1997.
- G. S. Hair, A. H. Cowley, R. A. Jones, B. G. McBurnett and A. Voigt, *J. Am. Chem. Soc.*, 1999, **121**, 4922.
- J. Klosin, G. R. Roof, E. Y.-X. Chen and K. A. Abboud, *Organometallics*, 2000, **19**, 4684.
- J. S. Kun, L. M. Wojcinski, S. Liu, J. C. Sworen and A. Sen, *J. Am. Chem. Soc.*, 2000, **122**, 5668.
- T. Belgardt, J. Storre, H. W. Roesky, M. Noltemeyer and H.-G. Schmidt, *Inorg. Chem.*, 1995, **34**, 3821.
- See Supplementary Information[†].
- S. Lorenzo, G. R. Lewis and I. Dance, *New J. Chem.*, 2000, **24**, 295.
- N. Adams, A. R. Cowley, S. R. Dubberley, A. J. Sealey, M. E. G. Skinner and P. Mountford, *Chem. Commun.*, 2001, 2738.
- P. A. Deck, M. J. Lane and J. L. Montgomery, *Organometallics*, 2000, **19**, 1013.
- M. P. Thornberry, C. Sledobnick and P. A. Deck, *Organometallics*, 2000, **19**, 5352.
- M. D. Blanchard, R. P. Hughes, T. E. Concolino and A. R. Rheingold, *Chem. Mat.*, 2000, **12**, 1604.
- J. E. Huheey, E. A. Keiter and R. L. Keiter, *Inorganic Chemistry Principles of Structure and Reactivity*, 4th ed., Harper Collins, New York, 1993, p. 292.
- R. D. Schluter, H. S. Isom, A. H. Cowley, D. A. Atwood, R. A. Jones, F. Olbrich, S. Corbelin and R. J. Lagow, *Organometallics*, 1994, **13**, 4058.