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Journal of Organometallic Chemistry 689 (2004) 2186–2191

Journal of Organo metallic Chemistry

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A structural study of dimethylaluminum carboxylato and hydrazonato complexes

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Received 24 February 2004; accepted 29 March 2004

Dedicated to Professor Alan H. Cowley, University of Texas at Austin, for his many important contributions to chemistry, chemical education, and service to the scientific community.

Abstract

The reaction of trimethylaluminum with 2,4,6-triphenylbenzoic acid and the isoelectronic fluoren-9-one phenylhydrazone results in the formation of the dialkylaluminum complexes $[(CH_3)_2Al\{\mu\text{-}O_2CPh(Ph_3)\}]_2$ (**4**) and $[Me_2AlN(C_6H_5)N{=}C_{13}H_8]_2$ (**5**). The synthesis of these complexes, as well as their spectroscopic and structural characterization are reported. X-ray crystallographic studies show that the carboxylato complex **4** adopts a dimeric structure containing an 8-membered O–Al–O–C core whereas the hydrazonato complex **5** likewise is dimeric in the solid state, but exhibits a 6-membered N–Al–N heterocyclic ring.

Keywords: Aluminum; Carboxylate ligands; Hydrazones; Group 13 elements; N ligands; O ligands

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1. Introduction

The coordination chemistry and reactivity of aluminum carboxylato complexes (**A**) and related ligands such as amido (**B**), amidinato (**C**), hydrazonato (**D**) and triazenido (**E**) (Fig. 1) have been of importance recently, particularly in the areas of olefin polymerization [1,2] and materials science [3,4]. One of the reasons these ligands are of such interest is due to the variety of bonding modes possible [5], which can affect not only the structure but also the reactivity of the complexes.

We recently reported the syntheses of monomeric *m*-terphenyl amidine **1** [6] and bis-amidine [7] aluminum complexes. As a continuation of this work, we have chosen to study the coordination chemistry of two isoelectronic species 2,4,6-triphenylbenzoic acid **2** and fluoren-9-one phenylhydrazone **3**, which can also be considered a structural isomer of an amidine in which the positions of the imino carbon and nitrogen atoms have been reversed (Fig. 2). To the best of our knowledge, there have been no reports to date of monomeric dialkylaluminum carboxylato complexes, however base-stabilized monomeric dialkylaluminum hydrazonato complexes are known [8].

Herein we report our attempts to enforce small ring sizes or monomeric structures using in one case, steric factors, and in the other, electronic factors. By maintaining the steric bulk of **1** in the carboxylato ligand **2**, the coordination chemistry with aluminum should also be maintained. In the case of the hydrazonato ligand **3**, the electron withdrawing ability of the fluorenylidene portion will alter the electronic environment around the nitrogen atoms and therefore also affect the coordination chemistry to aluminum.

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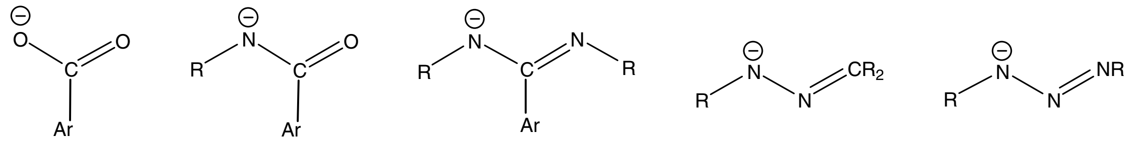
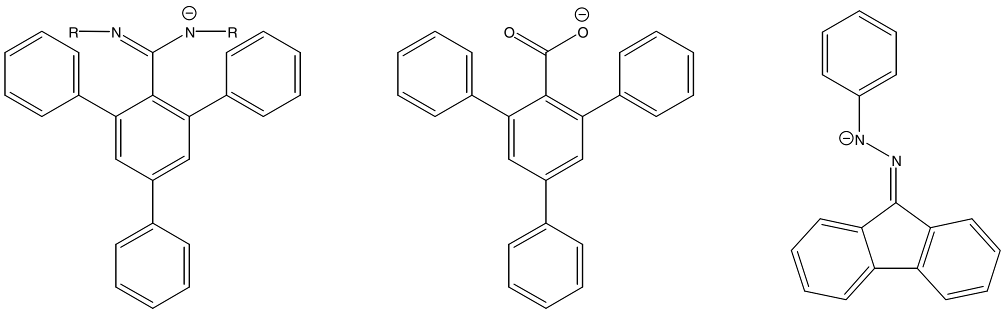
doi:10.1016/j.jorganchem.2004.03.043



A **B** **C** **D** **E**

Fig. 1. Isoelectronic carboxylato (**A**), amido (**B**), amidinato (**C**), hydrazonato (**D**) and triazenido (**E**) ligands.



R = Isopropyl or cyclohexyl

1 **2** **3**

Fig. 2. Amidinato **1**, carboxylato **2** and hydrazonato **3** ligands.

2. Experimental

2.1. General

An MBraun UL-99-245 dry box and standard Schlenk techniques on a double manifold vacuum line were used in the manipulation of air and moisture sensitive compounds. NMR spectra were recorded on a Varian AS 500 MHz spectrometer or a Bruker AMX 600 MHz spectrometer in five millimeter quartz tubes. ^{1}H and ^{13}C{^{1}H} chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) and are calibrated to the residual signal of the solvent. Infrared spectra were obtained using a Bomem MB spectrometer with the percent transmittance values reported in cm^{-1}. Melting points were measured using a Mel-Temp apparatus and are uncorrected. Elemental analysis were obtained by M.K. Yang on a Carlo Erba Model 1106 CHN analyzer. UV–Vis spectra were recorded on a Shimadzu UV-3150 spectrometer. 2,4,6-Triphenylbenzoic acid [9] and fluoren-9-one phenylhydrazone [10,11] were synthesized according to literature procedures. All other reagents and solvents were purchased from Aldrich and used without further purification.

2.1.1. *Preparation of* $[(CH_3)_2Al\{\mu\text{-}O_2CPh(Ph_3)\}]_2$ *(**4**)*

2,4,6-Triphenylbenzoic acid (0.20 g, 0.57 mmol) was suspended in 10 mL anhydrous CH_2Cl_2. To this solution, trimethylaluminum (2.0 M in toluene, 0.34 mL, 0.68 mmol) was added dropwise. The solvent was evaporated slowly at room temperature to give colourless crystals. Additional crystals formed upon cooling the solution to −30 °C. The solvent was removed via cannula and the crystals were characterized as **4**. Yield: 0.15 g, 64%; m.p. 265–266 °C. ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.61 (s, 2 H, C_6H_2), 7.37–7.49 (m, 15H, C_6H_5), −1.51 (s, 6H, $AlCH_3$); ^{13}C NMR (CD_2Cl_2, 125 MHz) δ 174.7, 142.9, 141.8, 140.5, 139.7, 131.7, 129.2, 128.9, 128.5, 128.4, 128.3, 128.1, 127.4, −12.4. IR (nujol, cm^{-1}) 1624 (vs), 1598 (vs), 1503 (s), 1418 (s), 1262 (w), 1200 (s), 1192 (s), 1030 (m), 892 (s), 805 (m), 756 (s), 698 (vs). Elem. Anal. Calc. $C_{54}H_{48}Al_2O_4$: C, 79.59; H, 5.94. Found: C, 79.44; H, 5.71%.

2.1.2. *Preparation of* $[Me_2AlN(C_6H_5)N{=}C_{13}H_8]_2$ *(**5**)*

Fluoren-9-one phenylhydrazone (0.22 g, 0.83 mmol) was dissolved in ca. 10 mL anhydrous CH_2Cl_2. To this solution, trimethylaluminum (2.0 M in hexane, 0.83 mL, 1.6 mmol) was added dropwise. The solvent was evaporated slowly at room temperature to give dark purple crystals. Yield: 0.16 g, 59%; m.p. 207 °C (dec). ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 8.37 (br s, 1H), 8.21 (d, 7 Hz, 1H), 7.60 (d, $J = 7$ Hz, 1H), 7.56 (d, $J = 7$ Hz, 1H), 7.52 (t of d, $J = 7$ Hz, 1 Hz, 1H), 7.45 (t of d, $J = 7$ Hz, 1 Hz, 1H), 7.35 (t of d, $J = 7$ Hz, 1 Hz, 1H), 7.17 (t of d, $J = 7$ Hz, 1 Hz, 1H), 6.81 (t, $J = 8$ Hz, 2H), 6.59 (d, $J = 8$ Hz, 2H), 6.44 (t, $J = 7$ Hz, 1H), −0.44 (br, 6H, $AlCH_3$); ^{13}C NMR (150 MHz, CD_2Cl_2) δ 129.8, 129.7, 128.5, 128.2, 124.7, 122.1, 121.1, 121.0, 113.9, 25.9 (quaternary carbon signals not observed due to low solubility). IR (cm^{-1}) 3378 (w), 3057 (w), 2922 (m), 1602 (s), 1569 (vs), 1508 (s), 1492 (s), 1447 (s), 1426 (m), 1307 (m), 1260 (vs), 1226 (s), 1195 (s), 1124 (s), 1087 (s), 1070 (m), 1016 (m), 886 (m), 779 (s), 749 (s), 726 (vs), 687 (vs). Elem. Anal. Calc. $C_{42}H_{38}Al_2N_4$: C, 77.28; H, 5.87; N, 8.58. Found: C, 77.60; H, 6.19; N, 7.92%. UV–Vis (toluene) λ 550 nm (ε 1038).

2.2. *X-ray crystallography*

Crystals of **4** and **5** were grown from concentrated CH_2Cl_2 solutions. A colourless chip of **4** was broken loose from a cluster of crystals and was mounted on a glass fibre. Data for **4** were collected at room temperature (21 °C) on a Nonius κ-CCD diffractometer with COLLECT (Nonius B.V., 1998). The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using DENZO (Nonius B.V., 1998). The data were scaled using SCALEPACK (Nonius B.V., 1998). The SHELXTL-NT V6.1 (Sheldrick, G.M.) suite of programs was used to solve the structure by direct methods. Subsequent difference Fouriers allowed the remaining atoms to be located. The two methyl groups were each modeled as six half-hydrogen atoms.

A single crystal of **5** was mounted on a glass fibre. Data for **5** were collected at −60 °C on a Seimens 1K SMART/CCD diffractometer using Mo Kα radiation. Lorentz and polarization corrections were applied and data were also corrected for absorption using redundant data and the SADABS program. Direct methods and Fourier techniques were used to solve the crystal structures. Refinement was conducted using full-matrix least-squares calculations and SHELX-TL PC V 5.03.

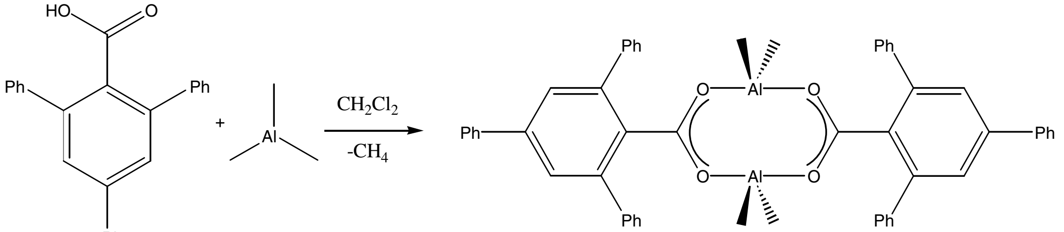
All of the non-hydrogen atoms for **4** and **5** were refined with anisotropic thermal parameters. The hydrogen atom positions were calculated geometrically and were included as riding on their respective carbon atoms. The largest residual electron density peak for **4** (0.173 e/Å^3) was associated with one of the phenyl rings. The largest residual electron density peak for **5** (0.223 e/Å^3) was associated with Al(2). There was one molecule of methylene chloride per dimer in the lattice of **5**.

3. Results and discussion

Spectroscopic evidence for dimeric dialkylaluminum carboxylato complexes was first presented as early as 1970 [12] however it was not until recently that Barron and co-workers [3] published the first structural characterization of dialkylaluminum carboxylato complexes as part of their study of alumoxane materials. Amidinates, on the other hand, have been shown to chelate a single aluminum centre to form monomeric complexes [2,6,7]. In the case of amides, Lin and co-workers [13] have shown that changing the steric properties of the ligand can have a large effect on the coordination mode adopted at the aluminum centre. As the carboxylate ligand **2** has similar steric requirements to amidine **1** [6], and is bulkier than the carboxylates studied by Barron and co-workers [3], we expected a monomeric complex, possibly with a 4-membered AlO_2C ring, which, to the best of our knowledge, remain unreported for dialkylaluminum complexes.

Addition of trimethylaluminum to a solution of 2,4,6-triphenylbenzoic acid **2** in dichloromethane results in the formation of **4** (Scheme 1). Colourless crystals were formed upon evaporation of solvent or cooling of the solution. The compound was characterized using ^1H and ^{13}C NMR spectroscopy, IR spectroscopy and X-ray crystallography. The ^1H NMR spectrum shows a distinctive singlet at −1.51 ppm attributed to the aluminum methyl groups. The aromatic protons of the flanking phenyls appear as a multiplet ranging from 7.37–7.49 ppm, while the two protons of the central phenyl appear as a singlet at 7.61 ppm. In the infrared spectrum, we observed a diagnostic shift of ν(C=O) from 1696 cm^{-1} in the free ligand to 1624 cm^{-1} in the complex, as well as the disappearance of ν(O–H) at 3438 cm^{-1} in the free ligand.

X-ray crystallographic studies (Table 1) revealed that **4** exists as a symmetrical dimer in the solid state (Fig. 3) with an 8-membered O–Al–O–C heterocyclic core in which the benzoate ligands bridge two aluminum centres. Complex **4** has an Al···Al distance of 4.320 Å, which falls in the middle of the range (4.217–4.463 Å) of



2 **4**

Scheme 1. Synthesis of **4**.

Table 1
Crystallographic data

Compound	**4**	**5**
Empirical formula	$C_{54}H_{46}Al_2O_4$	$C_{21.50}H_{20}AlClN_2$
Formula weight (g/mol)	812.87	368.83
Temperature (K)	294(2)	213(2)
Crystal system	$P\overline{1}$	Pca2(1)
Space group	Triclinic	Orthorhombic
a (Å)	9.9702(2)	17.560(2)
b (Å)	10.6813(2)	10.1087(12)
c (Å)	11.3952(2)	21.888(3)
α (°)	77.0130(10)	90
β (°)	85.6730(10)	90
γ (°)	74.0890(10)	90
Volume (Å^3)	1137.06(4)	3885.3(8)
Z	1	8
Density (calculated) (Mg/m^3)	1.187	1.261
μ (mm^{-1})	0.109	0.248
F(000)	428	1544
Crystal size (mm^3)	$0.58 \times 0.48 \times 0.15$	$0.25 \times 0.3 \times 0.3$
Theta range for data collection (°)	2.79 to 27.50	1.86 to 26.50
Index ranges	$-12 \leq h \leq 12, -13 \leq k \leq 13, -14 \leq l \leq 14$	$-14 \leq h \leq 22, -12 \leq k \leq 12, -27 \leq l \leq 27$
Reflections collected	20440	21576
Independent reflections	5208 [*R*(int) = 0.041]	8008 [*R*(int) = 0.0330]
Absorption correction	Integration	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	5208/0/277	8008/1/460
Goodness-of-fit on F^2	1.038	1.019
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0433, wR^2 = 0.1128$	$R1 = 0.0411, wR^2 = 0.0896$
R indices (all data)	$R1 = 0.0596, wR^2 = 0.1231$	$R1 = 0.0602, wR^2 = 0.0937$

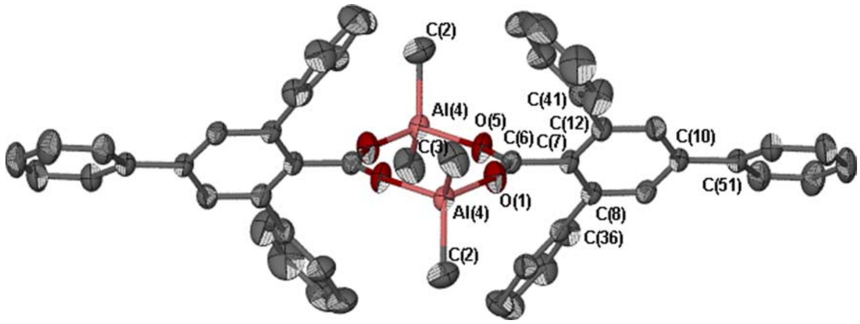
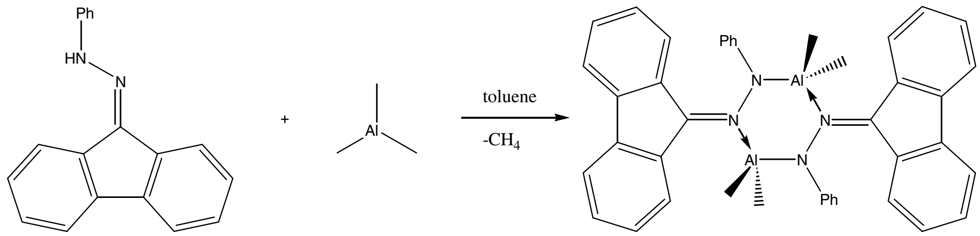


Fig. 3. ORTEP diagram of aluminum carboxylato complex **4**. Hydrogen atoms have been removed for clarity. Selected bond lengths (Å): Al(4)–O(1) = 1.8095(11), O(1)–C(6) = 1.2482(18), C(6)–O(5) = 1.2502(17), O(5)–Al(4a) = 1.8090(11), Al(4)···Al(4a) = 4.320. Selected bond angles (°): Al(4)–O(1)–C(6) = 152.97(10), O(1)–C(6)–O(5) = 124.20(13), C(6)–O(5)–Al(4a) = 152.79(10), O(5a)–Al(4)–O(1) = 107.89(6).

previously characterized aluminum carboxylato dimers [3]. The C(6)–O(1) and C(6)–O(5) bond lengths of 1.248(2) and 1.250(2) Å, respectively, are the same within experimental error and show that there is complete delocalization within the O–C–O fragment. The Al(4)–O(1) and Al(4)–O(5) bond lengths of 1.810(1) and 1.809(1) Å support this conclusion, and are comparable to literature values for similar compounds [3]. The aluminum atoms themselves exhibit the expected tetrahedral geometry, with O–Al–C bond angles ranging from 105.26(8)–107.89(6)° and the C(3)–Al(4)–C(2) bond angle of 123.8(1)°.

The O–Al–O–C ring of **4** is nearly flat, with a maximum deviation from the heterocyclic plane of ±0.066 Å for O(5). Due to the steric constraints imposed by the *ortho*-phenyls of the ligand, the heterocyclic core of **4** is twisted out of the plane of the central phenyl with an O(1)–C(6)–C(7)–C(12) torsion angle of 61.7°. A similar effect, with a twist angle of 42.6°, was reported by Barron and co-workers [14] in a gallium–carboxylato complex based on *ortho*-toluic acid. No unusual intra- or intermolecular π-interactions were observed.

Although they are not used as commonly as the previously discussed carboxylato ligands, the coordination



3 **5** **5**

Scheme 2. Synthesis of **5**.

chemistry of hydrazone derivatives also promised to be very interesting. Studies performed by Uhl et al. [4] on related hydrazines have shown that varying the sterics of the ligand can lead to the formation of 6-membered Al_2N_4, 5-membered Al_2N_3, or 4-membered Al_2N_2 heterocycles, while Cowley and co-workers [15] described a ladder-like tetranuclear structure for a 1,1-dimethylhydrazine aluminum complex. Studies by Barron's group on isoelectronic triazenides have shown that the preferred coordination geometry is chelation a single four- [16] or six-coordinate aluminum centre with the number of triazenido ligands controlled by the presence or absence of other strong Lewis bases in solution [17,18]. Thus, we were eager to examine the coordination chemistry of our hydrazonato ligand **3**.

Treatment of fluoren-9-one phenylhydrazone **3** with trimethylaluminum (Scheme 2) results in the immediate formation of an intense purple solution, with a UV–Vis absorption at $\lambda_{max} = 550$ nm. Dark purple crystals formed upon slow evaporation of the dichloromethane solution. Complex **5** was characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy and X-ray crystallography. The ^1H NMR spectrum showed a broad singlet at −0.44 ppm that was assigned to the methyl protons bound to the aluminum. Similarly, in the ^{13}C NMR spectrum, a singlet at 25.9 ppm was identified as the aluminum methyl carbons.

Analysis of the solid state structure of **5** (Fig. 4) revealed that the aluminum complex exists as a dimer. Also included in the crystal lattice is a molecule of dichloromethane. The N–Al bond lengths in **5** vary, suggesting that the nitrogen attached to the phenyl forms a covalent bond with the aluminum (N(1)–Al(2) = 1.899(2) Å, N(3)–Al(1) = 1.889(2) Å), while the other makes a dative bond (N(2)–Al(1) = 2.036(2) Å, N(4)–Al(2) = 2.043(2) Å). As is expected in four-coordinate aluminum, the N–Al covalent bond lengths are slightly longer than the normal N–Al bond length of 1.78(2) Å while the N–Al dative bond lengths are well within the range of other N–Al dative bonds in four-coordinate aluminum complexes (1.94–2.10 Å) [19].

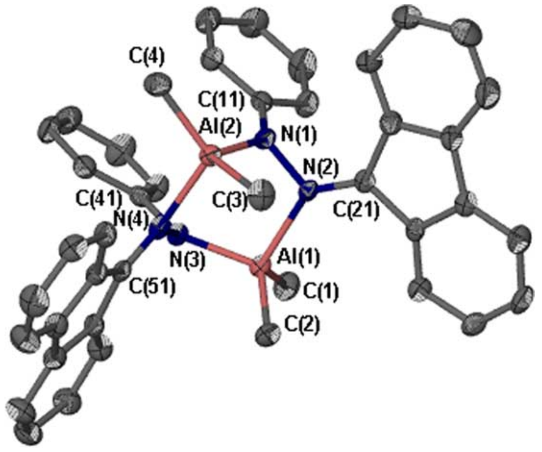


Fig. 4. ORTEP diagram of **5**. Hydrogen atoms and solvent have been removed for clarity. Selected bond lengths (Å): Al(1)–N(3) = 1.889(2), Al(1)–N(2) = 2.036(2), Al(2)–N(1) = 1.899(2), Al(2)–N(4) = 2.043(2), N(1)–N(2) = 1.445(2), N(3)–N(4) = 1.449(2), Al(1)···Al(2) = 3.477. Selected bond angles (°): N(3)–Al(1)–N(2) = 99.30(8), N(1)–Al(2)–N(4) = 99.08(9), N(2)–N(1)–Al(2) = 108.93(13), N(1)–N(2)–Al(1) = 108.37(13), N(4)–N(3)–Al(1) = 110.44(13), N(3)–N(4)–Al(2) = 108.40.

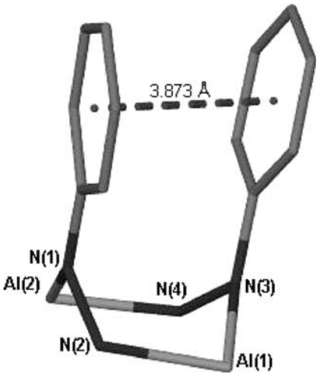


Fig. 5. Stick diagram of the twist-boat conformation of the core of **5** and the phenyl substituents.

The N–Al–N heterocyclic core of **5** adopts a twist-boat conformation. This conformation was also seen in Uhl's dialkylaluminum hydrazone [$Me_2AlN(CHMe_2)$-$NCMe_2$]$_2$ [20]. Chair conformations are found for other hydrazide derivatives [21,22]. The conformation is likely determined by steric factors. The two phenyl substituents in **5** are stacked in an offset face-to-face fashion with a centroid···centroid distance of 3.873 Å. Typical π–π stacking distances are in the range of 3.3–3.6 Å [23], so it is unlikely that this contributes to the stabilization of the molecule and the alignment is probably coincidental. Similarly, no unusual intermolecular π-interactions were observed (see Fig. 5).

In summary, the synthesis of two dimeric aluminum complexes was accomplished. The carboxylato complex **4** is one of very few structurally characterized molecules featuring an 8-membered O–Al–O–C heterocyclic core. The hydrazonato complex **5** features a 6-membered Al_2N_4 heterocycle and expands the use of hydrazones as ligands in organometallic chemistry.

4. Supplementary Information

Crystallographic data for the structural analyses of **4** and **5** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 230826 (**4**) and 231268 (**5**). 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).

Acknowledgements

Funding for this research was provided by the Natural Sciences and Engineering Research Council of Canada (NSERC), Simon Fraser University, University of Western Ontario and Saint Mary's University. The authors would like to thank Marcy Tracey (SFU) for the collection of NMR data.

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