Inorganic Ring Systems

Synthesis of Hexa- and Dodecanuclear Organoaluminum Ring Structures Incorporating the "Magic" $Ph_2C(X)$ Group ($X = O^-$, NH^-)**

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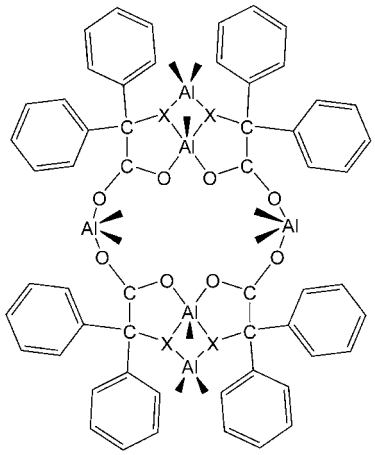
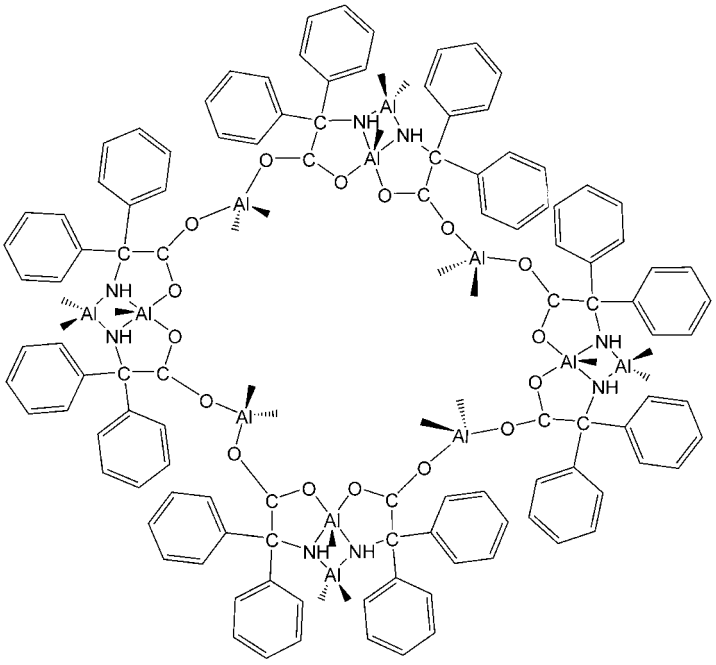
Organoaluminum carboxylates are attracting attention owing to their biological relevance[1] and their usefulness as precursors in materials science.[2] Bifunctional carboxylic acid ligation has been extensively studied by Lewiński and coworkers. A number of adducts, both bi- and tetranuclear, were isolated and structurally characterized and a preference for *anti* binding of aluminum at a carboxylic acid group was identified.[3–6] We have been intrigued by the ring formation of a number of *N*,*N*′- and *N*,*O*-chelate ligands on treatment with Group 13 alkyl derivatives. In our work, we have previously structurally characterized rings containing two, four, six, and eight Group 13 metal centers. For example, anthranilic acid, 1,2-$(H_2N)C_6H_4CO_2H$, afforded a macrocyclic deca-ring system $[\{Me_2Al(MeAl)(\mu_3\text{-}O)(\mu_2\text{-}O)L\}_3]$ (L = quinazoline heterocycle), whilst the Schiff-base ligand 3,5-tBu$_2$-2-$(OH)C_6H_2CHNC_6H_4$-2-(CO_2H) affords the tetrameric systems $[\{M[3,5\text{-}t\text{Bu}_2\text{-}2\text{-}(O)C_6H_2CHNC_6H_4\text{-}2\text{-}(CO_2)]_2\}_2(\mu\text{-}MMe_2)]$ (M = Al, Ga; X = Me, Cl).[7] In our search for related ligand systems containing both amino and carboxylic acid functionalities, we have turned our attention to amino acids and related ligands. In the present work, the reaction of Me_3Al with the amino acid 2,2-diphenylglycine as well as with the closely related benzilic acid (diphenylglycolic acid) is studied. The products are the remarkable 16-membered macrocyclic structures **1** and **2**, each of which contains six aluminum centers (in three different environments), and a nonsymmetric 32-membered ring complex **3** containing twelve aluminum centers. Despite being recrystallized from acetonitrile, none of the products **1**–**3** are the result of MeCN insertion into aluminum–nitrogen bonds, which we have previously observed for a number of anilines and hydrazines.[7a] All three structures contain the common structural motif $\{[Ph_2C(X)(CO_2)]_2(Me_2Al)(MeAl)\}(AlMe_2)$ (X = O or NH) (**I**). The structure **II** has recently been postulated for a glycine-derived product,[6] and a closely related motif **III** has been characterized following reaction of Me_3Al with a number of sterically hindered diols.[8]



1 (X=NH), **2** (X=O)



3

Addition of 1.5 molar equivalents of Me_3Al to diphenylglycine, 2,2′-$Ph_2C(NH_2)(CO_2H)$, in refluxing toluene results in rapid evolution of methane and formation of a colorless solution. Following workup, small colorless prisms of **1**, suitable for an X-ray analysis using synchrotron radiation,[9] were grown from solutions in acetonitrile on prolonged

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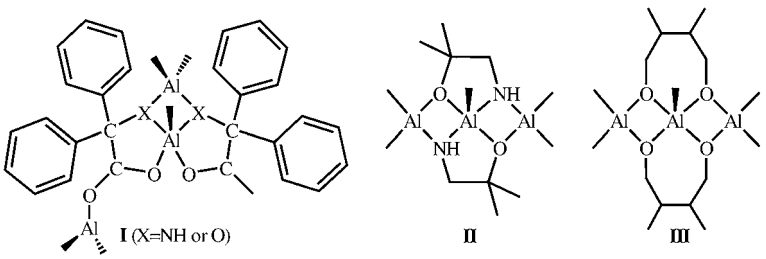


standing at ambient temperature in about 55% yield. The molecular structure of the acetonitrile solvate is shown in Figure 1. The structure is made up of two of the subunits **I**

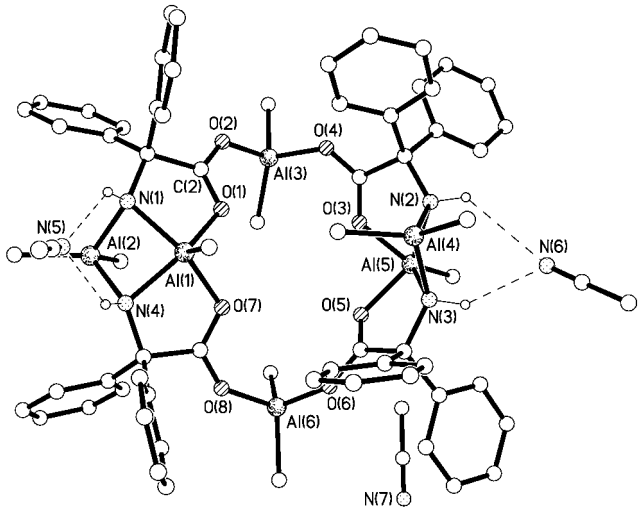


Figure 1. Molecular structure of **1**.[15] Selected bond lengths [Å] and angles [°]: Al(1)-N(1) 2.0010(12), Al(1)-O(1) 1.8964(10), Al(1)-N(4) 1.9816(12), Al(1)-O(7) 1.9108(10), Al(2)-N(1) 1.9632(12), Al(2)-N(4) 1.9598(12), Al(3)-O(2) 1.8580(11), Al(3)-O(4) 1.8295(12); O(7)-Al(1)-O(1) 84.79(4), N(4)-Al(1)-N(1) 81.37(5), O(1)-Al(1)-N(1) 80.69(4), N(4)-Al(1)-O(7) 81.73(4), N(4)-Al(2)-N(1) 82.88(5), Al(1)-O(1)-C(2) 120.01(9), C(2)-O(2)-Al(3) 130.11(9).

(X = NH) linked by the Me_2Al bridges to form a 16-membered macrocyclic ring system; there is no overall symmetry for the molecule (Figure 1). The six aluminum centers possess three very different environments. The five-coordinate Al(1)-type centers are square-based pyramids with an apical methyl group and basal O and N atoms each derived from two diphenylglycine ligands. For the latter, the N atoms are bridged by a pseudo-tetrahedral Al(2)-type center with angles in the range of 82.9–121.2°. The Al(1)···Al(2) distance of 2.84 Å is not indicative of any metal–metal interaction. The geometries at the bridging aluminum centers (Al(3)-type) are only slightly distorted from tetrahedral, with angles ranging between 100.2 and 123.9°. Throughout the structure the carboxylate groups bind in an *anti*/*syn* fashion and in each case the aluminum centers pretrude somewhat out of the plane of the carboxylate group (0.02–0.15 Å for type 1, 0.06–0.66 for type 3) resulting in an overall puckering of the macrocycle. The presence of the inwardly directed methyl groups results in an essentially self-filling macrocycle with no obvious cavity. The ^{1}H NMR spectrum supports this formulation with peaks in the region $\delta = -0.25$ to -1.46 ppm integrating to 30 H for the Al-Me groups. The NH groups are observed at $\delta = 2.41$ ppm and 3313 cm^{-1} in the ^{1}H NMR and IR spectra, respectively.

Encouraged by the synthesis of the ring complex **1**, we then investigated the related ligand benzilic acid, 2,2′-$Ph_2C(OH)(CO_2H)$. A similar procedure to that employed for **1** yielded small colorless prisms suitable for X-ray crystallography using synchrotron radiation[9] in about 17% yield. The product here was remarkably similar to **1**, incorporating two of the subunits (X = O) bridged by the Me_2Al units to afford an Al_6-containing 16-membered macrocyclic ring. Figure 2 empha-

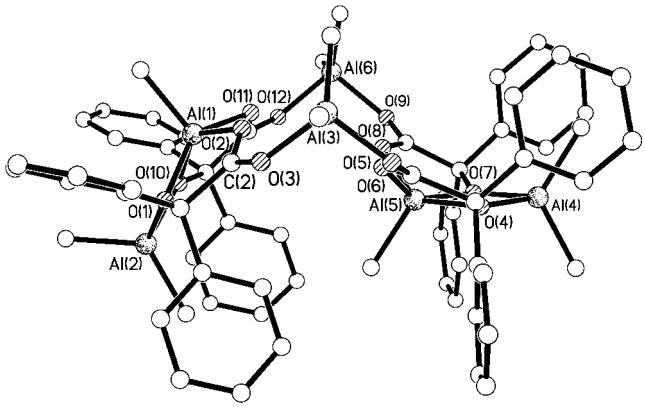


Figure 2. Molecular structure of **2**.[15] Selected bond lengths [Å] and angles [°]: Al(1)-O(2) 1.8582(17), Al(1)-O(11) 1.8679(18), Al(1)-O(10) 1.8788(17), Al(1)-O(1) 1.8974(17), Al(2)-O(1) 1.8519(17), Al(2)-O(10) 1.8612(18), Al(3)-O(3) 1.8392(18), Al(3)-O(6) 1.8469(18); O(2)-Al(1)-O(1) 82.62(7), Al(3)-O(3)-C(2) 134.90(17).

sizes the folded geometry adopted by the asymmetric rings **1** and **2**; the asymmetry is best highlighted by the Al(1)/Al(2) and Al(4)/Al(5) vectors which are almost vertical and horizontal, respectively. The rings **1** and **2** differ in the degree of associated solvent (**1**·3 MeCN and **2**·MeCN), doubtless due to H-bonding interactions with the NH groups in **1**.

Unsuspectingly, on increasing the ratio of Al to ligand for the diphenylglycine reaction from 1.5:1 to 2:1, we selectively crystallized the 32-membered ring system shown in Figure 3. The homogeneity of the sample was verified by measuring the unit cell dimensions of eight crystals picked at random from several different reactions and crystallizations. The molecule has no overall symmetry and can be viewed as a "doubling-up" of the complex **1**, such that we now have four subunits **I** each linked through the Me_2Al bridges. Overall the macrocycle adopts a bowl-like conformation with aluminum centers 2, 5, 8, and 11 forming the rim of the bowl. The Al–N, Al–O, and Al–C bond lengths in **3** are all similar to those observed in **1**. In total for **3**, there are about 15.5 MeCN of crystallization, four of which are involved in bifurcated hydrogen bonding to NH groups as observed in **1**·3 MeCN.

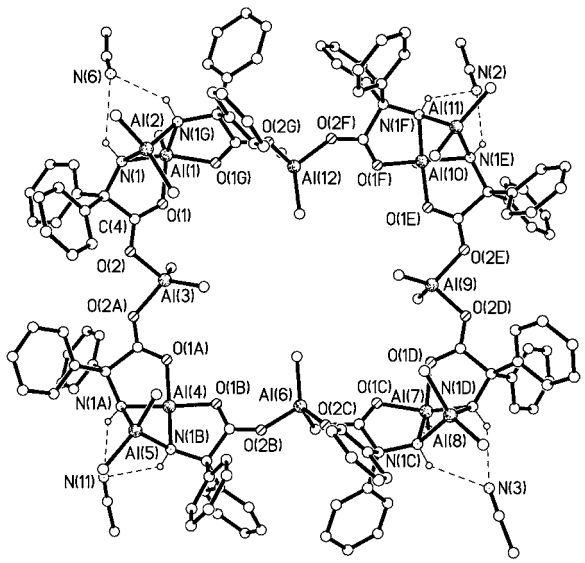
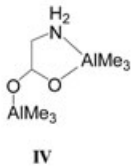


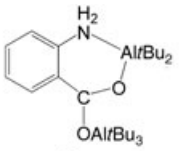
Figure 3. Molecular structure of **3**. Selected bond lengths [Å] and angles [°]: Al(1)-O(1) 1.877(4), Al(1)-O(1G) 1.901(4), Al(1)-N(1G) 1.986(4), Al(1)-N(1) 1.990(4), Al(2)-N(1G) 1.961(4), Al(2)-N(1) 1.965(4), Al(3)-O(2A) 1.842(4), Al(3)-O(2) 1.855(4); O(1)-Al(1)-O(1G) 85.54(16), Al(3)-O(2)-C(4) 123.9(4).

Unfortunately, cryoscopic molecular weight measurements (in benzene) proved to be uninformative with these systems.

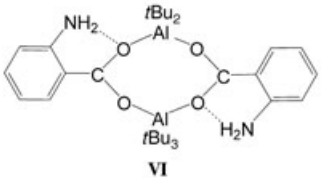
The formation of the products **1** or **3** is dependent on the ligand to aluminum ratio employed in the reaction. Recent work by Lewiński and co-workers on both anthranilic acid and glycine has shown how quite different products can arise through the use of differing amounts of Me_3Al. In particular, for the amino acid glycine, use of two equivalents of Me_3Al affords the adduct **IV**, in which only the carboxylate is deprotonated.[6] Adduct **IV** can either be further deprotonated at the amine functionality or can



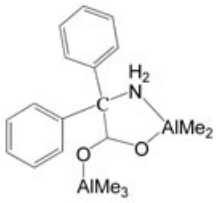
IV



V

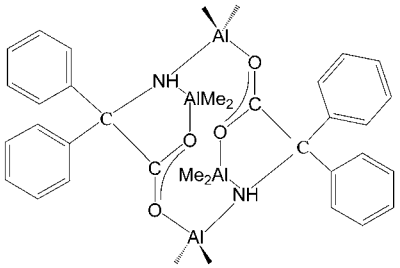


VI

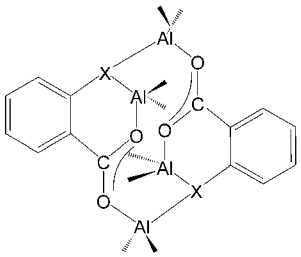


VII

monoalkylation of the carboxylate occur. A related adduct **V** has been isolated (and structurally characterized) from the reaction of Al*t*Bu$_3$ and anthranilic acid.[3] Interestingly, mechanical grinding of **V** results in expulsion of Al*t*Bu$_3$ and formation of the dimeric carboxylate **VI**. Clearly, in our case (diphenylglycine), subsequent C alkylation (as in the formation of **II**) does not occur. It is possible that the formation of **1** and **3** involves the initial formation of the adduct **VII**—the diphenylglycine analogue of **IV** and **V**. Two molecules of this adduct **VII** would then need to combine in the presence of a further equivalent of Me_3Al with concomitant loss of methane to afford the motif **I**. Alternatively, a tetranuclear adduct **IX**, similar to those (**VIII**) reported for salicylic acid and phthalic acid,[4,5] and proposed for anthranilic acid[6] is plausible, which can rearrange to the motif **I** with concomitant loss of Me_3Al. It is also possible that rapidly equilibrating species are present in solution and that an increase in the aluminum to ligand ratio promotes (or induces) the crystallization of **3**.[10] Equilibria involving polynuclear species have been observed previously, most notably for palladium-based molecular triangles and squares.[11] With this in mind, peaks in the electrospray mass spectra[12] of **3** can tentatively be assigned to both Al_6- and Al_9-containing species. However, we have not carried out any mechanistic studies and as yet have not observed any intermediates prior to isolation of **1**–**3** (^{1}H NMR spectra for **1**–**3** show little change over the range +20 °C to −50 °C). It is noteworthy that **1**–**3** contain the



VIII



IX (X = O, CO_2, NH)

"magic" diarylhydroxy(or amino)methyl group, the ability of which to enhance selectivity in asymmetric synthesis is now well documented.[13]

The use of only one equivalent or an excess (three equivalents) of Me_3Al under similar conditions repeatedly failed to yield any crystalline material, whilst reactions between diphenylglycine and Me_3Ga yielded the known complex $[(Me_2Ga)_4(MeGa)_2\{HNC(Me)C(CN)CH(NCMe)_2\}_2]$ as the only crystalline product.[14] Attempts to convert ring system **1** into the larger ring system **3** by using varying amounts of Me_3Al were also unsuccessful; on each occasion unreacted **1** was retrieved.

In conclusion, we have identified a structural motif, which is the building block for a number of new organoaluminum macrocycles, and observed that subtle changes in reaction stoichiometry can lead to the isolation of quite different products. Here, for example, we have shown that both 16- and 32-membered macrocycles are readily accessible from diphenylglycine and Me_3Al. The reasons why excess Me_3Al should promote increased ring size are as yet unclear; however, further work is now in progress to explore this chemistry in more detail.

Experimental Section

All manipulations were performed under N_2 by using standard Schlenk techniques and dried, deoxygenated solvents.

Complexes **1**–**3** were prepared by heating Me_3Al (5 mL, 2.0 M, 0.01 mol) and the appropriate acid (0.01 or 0.005 mol) under reflux for 12 h. Volatile components were then removed in vacuo, and the products were obtained by extraction into hot acetonitrile (40–50 mL). Colorless prisms were obtained on prolonged standing at ambient temperature.

1: Yield 56%; elemental analysis calcd (%) for $C_{66}H_{74}N_4O_8Al_6 \cdot 3$MeCN: C 61.8, H 6.0, N 7.0; found: C 61.9, H 5.9, N 6.4 (sample dried in vacuo for 12 h); IR: $\tilde{\nu} =$ 3337 (ν(NH)), 1576 (ν(CO) (broad)) cm^{-1}; ^1H NMR ([D_8]toluene, 400 MHz, 298 K): $\delta = 7.48$ (m, 16H; aryl-H), 7.05 (overlapping m, 24H; aryl-H), 2.39 (s, 4H; NH), 0.73 (s, 15H; MeCN), −0.25 (s, 6H; Me_2Al), −0.36 (s, 12H; Me_2Al), −0.81 (s, 6H; Me_2Al), −1.46 ppm (s, 6H; MeAl); ES-MS: 689 (**I**·2MeCN); m.p. > 350 °C (decomp).

2: Yield 17%; elemental analysis calcd (%) for $C_{66}H_{70}O_{12}Al_6 \cdot$MeCN: C 65.3, H 6.1, N 0.6; found: C 65.2, H 5.8, N 0.8% (sample dried in vacuo for 24 h); IR: $\tilde{\nu} =$ 1632 (ν(CO)), 1613 (ν(CO)) cm^{-1}; ^1H NMR (C_6D_6, 400 MHz, 298 K): $\delta = 6.68$–8.21 (5 × m, 40H; aryl-H), 0.50 (s, 15H; MeCN), 0.09 (s, 6H; Me_2Al), 0.02 (s, 12H; Me_2Al), 0.00 (s, 6H; Me_2Al), −2.21 ppm (s, 6H; MeAl); m.p. > 350 °C (darkens at 285 °C).

3: Yield 49%; elemental analysis calcd (%) for $C_{132}H_{148}N_8O_{16}Al_{12} \cdot 12$MeCN: C 64.1, H 6.4, N 9.6; found: C 63.6, H 6.4, N 9.5 (sample dried in vacuo for 24 h); IR: $\tilde{\nu} =$ 3313 (ν(NH)), 1603 (ν(CO)) cm^{-1}; ^1H NMR (C_6D_6, 400 MHz, 298 K): $\delta = 7.48$ (m, 32H; aryl-H), 7.01 (m, 48H; aryl-H), 2.43 (s, 8H; NH), 0.63 (s, 16.5H; MeCN), −0.23 (s, 12H; Me_2Al), −0.32 (s, 24H; Me_2Al), −0.80 (s, 12H; Me_2Al), −1.41 ppm (s, 12H; MeAl); ES-MS: 1213 (**1**), 1861 (3**I**·MeCN), 1943 (3**I**·3MeCN); m.p. > 350 °C (decomp).

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[15] Crystal data for **1**·3MeCN: $C_{66}H_{74}Al_6N_4O_8 \cdot 3CH_3CN$, $M_r =$ 1336.34, orthorhombic, space group *Pbca*, colorless, 0.19 × 0.12 × 0.06 mm^3, $a = 24.1743(6)$, $b = 19.2565(5)$, $c =$ 31.6425(8) Å, $V = 14730.0(6)$ Å^3, $T = 160(2)$ K, $Z = 4$, $\rho_{calcd} =$ 1.205 g cm^{-3}, $2\theta_{max} = 56.98°$, synchrotron, $\lambda = 0.6928$ Å, ω scans with narrow frames, 102505 data measured on a Bruker SMART 1K CCD diffractometer (Bruker SMART software), 18684 independent, ($R_{int} = 0.047$), Lp and absorption corrections applied (based on symmetry equivalent and repeated measurements), $\mu = 0.144$ mm^{-1}, min and max trans: 0.97, 0.99, solved by direct methods (Bruker SHELXTL software), $wR2 = 0.123$ (all data), $R1 = 0.044$ (14097 unique data with $F^2 > 2\sigma(F^2)$) refined on F^2 (SHELXTL), for 851 parameters with H atoms constrained, largest difference map features within ±0.37 e Å^{-3}. Crystal data for **2**·MeCN: details as above except $C_{66}H_{70}Al_6O_{12} \cdot CH_3CN$, $M_r = 1258.15$, triclinic, space group $P\bar{1}$, 0.06 × 0.05 × 0.01 mm^3, $a = 10.8136(10)$, $b = 13.7496(13)$, $c = 23.423(2)$ Å, $\alpha =$ 92.891(2), $\beta = 97.964(2)$, $\gamma = 92.453(2)°$, $V = 3440.2(6)$ Å^3, $T =$ 150(2) K, $Z = 2$, $\lambda = 0.6861$ Å, 27917 data measured, 13310 independent, ($R_{int} = 0.050$), $\mu = 0.152$ mm^{-1}, min and max trans: 0.99, 1.00, $wR2 = 0.125$, $R1 = 0.049$ (8859 unique), 795 parameters, largest difference map features within ±0.35 e Å^{-3}. Crystal data for **3**·15.5MeCN: details as above except $C_{132}H_{148}Al_{12}N_8O_{16} \cdot 15.5\,CH_3CN$, $M_r = 3068.69$, monoclinic, space group $P2_1/n$, 0.80 × 0.21 × 0.16 mm^3, $a = 21.9995(18)$, $b = 25.854(2)$, $c =$ 31.963(3) Å, $\beta = 94.131(2)$, $V = 18133(3)$ Å^3, $T = 160(2)$ K, $Z =$ 4, $Mo_{K\alpha}$, $\lambda = 0.71073$, 92789 data measured, 23712 independent ($R_{int} = 0.131$), $\mu = 0.126$ mm^{-1}, min and max trans: 0.91, 0.98, $wR2 = 0.176$, $R1 = 0.068$ (11627 unique), 1854 parameters, largest difference map features within ±0.48 e Å^{-3}. A total of 4.5MeCN were badly disordered and were modeled as diffuse electron density with the Platon "Squeeze" procedure.[16] CCDC-244038—CCDC-244040 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
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