

## Synthesis and Structural Characterization of a Novel Aluminum Amidato Derivative Exhibiting a Rare 16-Membered Wheel Containing Four Aluminum Centers

Vanessa Tabernero, Marta E. G. Mosquera,\* and Tomás Cuenca\*

Departamento de Química Inorgánica, Universidad de Alcalá, Campus Universitario, E-28871 Alcalá de Henares, Spain

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Reaction of 2 equiv of AlMe<sub>3</sub> with  $1,2-C_6H_4\{NHC(t-Bu)O\}_2$  gives the tetranuclear aluminum compound  $[\{AlMe_2(1,2-C_6H_4\{NC(t-Bu)O\}_2)\}AlMe_2]_2$  (1), the molecular structure of which exhibits a novel central 16-membered ring formed by four AlMe<sub>2</sub> units and four NCO fragments. Treatment of 1 with 1 equiv of  $B(C_6F_5)_3$  affords the ionic species  $[\{(AlMe_2)_3(AlMe)(1,2-C_6H_4\{NC(t-Bu)O\}_2)_2]][MeB(C_6F_5)_3]$  (2).

Aluminum derivatives bearing oxygen donor ligands play important roles in a broad array of areas ranging from catalysis to biochemistry and material chemistry.<sup>1–8</sup> In particular, aluminum carboxylato complexes have been used as precursors for aluminum oxides<sup>9,10</sup> and exhibit biological relevance.<sup>11,12</sup> Species containing N,O-donor ligands are also of interest in catalytic reactions; thus alkoxido and amino-alkoxido aluminum derivatives are very active species in many catalytic polymerization processes.<sup>13–16</sup> Nevertheless, the chemistry of aluminum with the related amidato ligands has been far less explored. After the initial studies published by Wade<sup>17</sup> and Lappert<sup>18</sup> in 1968, only a few of

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these complexes have been reported, <sup>19–23</sup> despite the excellent properties that some of these derivatives have shown in polymerization processes of polar monomers.<sup>24</sup>

We have investigated the reactivity of aluminum compounds toward *N*,*N'*-alkyl-1,2-phenylenediamines and the related amide reagents due to the interesting steric and donor characteristics exhibited by this kind of ligand.<sup>25,26</sup> The diamines 1,2-C<sub>6</sub>H<sub>4</sub>(NHR)<sub>2</sub> (R = CH<sub>2</sub>t-Bu, *n*-Pr) react with 2 equiv of AlMe<sub>3</sub> in toluene solution, affording amido aluminum dinuclear compounds [Al<sub>2</sub>{1,2-C<sub>6</sub>H<sub>4</sub>(NCH<sub>2</sub>R)<sub>2</sub>}Me<sub>4</sub>].<sup>25</sup> The extension of our investigations to the related diamide reagent 1,2-C<sub>6</sub>H<sub>4</sub>{NHC-(*t*-Bu)O<sub>2</sub> has allowed us to isolate a novel tetranuclear derivative that shows a rare 16-membered ring structure; its synthesis, structural characterization, and reactivity toward tris(pentafluorophenyl)borane are described in this report.

## **Results and Discussion**

The diamide  $1,2-C_6H_4\{NHC(t-Bu)O\}_2$  was prepared by lithiation of the corresponding commercially available 1,2-phenylenediamine, and further reaction with pivaloyl chloride was carried out according to the methods described in the literature.<sup>27–29</sup> Addition of 2 equiv of AlMe<sub>3</sub> to 1,2-C<sub>6</sub>H<sub>4</sub>-{NHC(t-Bu)O}<sub>2</sub> in toluene at room temperature affords the

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<sup>\*</sup>Corresponding authors. Tel: +34-918854655. Fax: +34-918854683. E-mail: tomas.cuenca@uah.es; martaeg.mosquera@uah.es.



tetranuclear aluminum compound [{AlMe<sub>2</sub>(1,2-C<sub>6</sub>H<sub>4</sub>{NC-(*t*-Bu)O<sub>3</sub>)}AlMe<sub>2</sub>]<sub>2</sub>(1), as shown in Scheme 1. The route to 1 involves an initial aminolysis process of aluminum–carbon bonds with loss of methane to create the aluminum–nitrogen and aluminum–oxygen bonds. Four "AlMe<sub>2</sub>" units are connected through four amidato functionalities to adopt the final structure. The same complex is obtained even when the reaction is performed using different reagent stoichiometries under analogous reaction conditions. Compound 1 is isolated in 59% yield as an analytically pure colorless solid, airand moisture-sensitive but thermally stable in solution and in the solid state. Spectroscopic data and elemental analysis concur with the proposed structure. Single crystals for X-ray diffraction were obtained, and the molecular structure was confirmed (see below).

The <sup>1</sup>H NMR spectrum of **1** (CDCl<sub>3</sub> at room temperature) shows a resonance for the *tert*-butyl group protons at  $\delta$  1.38 accompanied by two multiplets corresponding to an AA'BB' spin system for the aromatic phenyl ring protons at  $\delta$  7.18 and 6.77. Three resonances for the methyl groups coordinated to the aluminum atoms are observed, one signal at  $\delta$ -0.76 integrating for 12 protons and two singlets at  $\delta - 0.36$ and -0.81 for six protons each. The same spectroscopic features are observed in the  ${}^{13}C{}^{1}H$  NMR spectral data. On the basis of this spectroscopic pattern and the elemental analysis, the suggested structure of 1 in solution is the tetranuclear disposition shown in Scheme 1. This structure was confirmed by X-ray diffraction studies, which shows each amidato group coordinating two aluminum atoms through both nitrogen and oxygen atoms (see below). Thus, the four methyl ligands linked to the aluminum coordinated through the oxygen atom are equivalent, while the methyl groups attached to the diamido-aluminum fragment have different chemical environments, with the two located near the phenylene ring experiencing the anisotropic effect of the ring.

We were interested in exploring the acid/base properties of this new aluminum macrocycle derivative. Thus we analyzed the reaction toward B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> as a Lewis acid reagent.<sup>30</sup> One equivalent of  $B(C_6F_5)_3$  was added to a solution of 1 in bromobenzene ( $C_6D_5Br$ ) at room temperature, and the spectroscopic study of the reaction suggested the formation of the ionic species  $[{(AIMe_2)_3(AIMe)(1,2-C_6H_4{NC(t-Bu)O}_2)_2][MeB(C_6F_5)_3] (2)$ (Scheme 1). Unfortunately it was not possible to obtain suitable crystals of 2 for a structure determination by X-ray diffraction methods, and complex 2 was characterized in solution by NMR spectroscopy. The elemental analysis of this compound shows that the contents of C and H are slightly lower than the calculated values due to its high air sensitivity at room temperature. The <sup>1</sup>H NMR spectrum of 2 (CDCl<sub>3</sub> at  $-40 \,^{\circ}\text{C}$  or C<sub>6</sub>D<sub>5</sub>Br at room temperature) indicates methyl abstraction, resulting in two nonequivalent sides derived from the initial symmetric ring present in molecule 1. Subsequently, four signals of the phenyl ligand, two singlets of the tert-butyl group protons, and six resonances for the methyl groups (one integrating for 6 protons) are observed with the presence of a broad singlet at  $\delta$  0.39 corresponding to a methyl group bonded to the boron atom.

In order to study the nature of complex 2, we carried out a diffusion-ordered NMR (DOSY) study to deduce the connection between the cationic and anionic units in solution. The <sup>1</sup>H DOSY spectrum of **2** in  $C_6D_5Br$  solution at room temperature resolves into 2D peaks placed in one single horizontal line in the diffusion dimension, indicating that the signal corresponding to the methylborate group protons has the same diffusion coefficient as the cation fragment resonances. Estimating the expected volume of the corresponding ionic species in compound 2 and consequently the related different hydrodynamic radius of the diffusing ionic fragments, this qualitative PGSE NMR result at room temperature is consistent with the existence of a cation-anion interaction. Cation-anion interactions depend on the structural and chemical characteristics of the ionic fragments. Ion-pairing effects have been claimed to have an important role in stoichiometric and catalytic reactions mediated by ionic transition metal complexes.<sup>31</sup> As an example, ionpairing phenomena in the single-site group 4 metal derivatives as a precatalyst system for the olefin polymerization reaction exhibit a strong influence on the properties of the resulting polyolefinic polymer.32-34

To achieve a better knowledge of the structure of **2** for studying the position of the methyl borate anion in this compound, 2D NOESY NMR measurements in  $C_6D_5Br$  at room temperature and in CDCl<sub>3</sub> at -40 °C were carried out. Exchange cross-peaks between the resonances assigned to the protons of the methyl group abstracted by boron to form the anionic unit and those corresponding to the methyl groups attached to the aluminum atoms in the cationic fragment are revealed. Although the crystal structure of the neutral compound **1** shows the methyl groups pointing out of the 16-membered ring, in solution at room temperature an alternative conformation could be easily induced. In this conformation the aluminum atoms, and consequently the methyl groups, are directed toward the core of the wheel, allowing a proximity that might favor the exchange process. Exchange between terminal

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Figure 1. ORTEP view of the structures of the diamide  $1,2-C_6H_4$ {NH(CO)*t*-Bu}<sub>2</sub> (a) and compound 1 (b) with ellipsoids of 30% probability. Hydrogen atoms bonded to carbon atoms are omitted for clarity.

Table 1. Selected Bond	Lengths (Å) and	Angles (deg)	for Com-
	pound 1		

molecule I		molecule II			
Al(2)-O(1)	1.804(2)	Al(3)-O(4)	1.800(2)		
$Al(2) - O(2)^a$	1.812(2)	Al(3) - O(3)	1.805(2)		
Al(1) - N(1)	1.973(2)	Al(4) - N(3)	1.987(3)		
Al(1) - N(2)	1.983(2)	$N(4) - Al(4)^b$	1.972(3)		
O(1) - C(1)	1.288(3)	O(3) - C(3)	1.286(4)		
C(1) - N(1)	1.341(4)	N(3) - C(3)	1.331(4)		
O(2) - C(2)	1.277(3)	O(4) - C(4)	1.281(4)		
C(2) - N(2)	1.336(4)	C(4) - N(4)	1.341(4)		
$O(1) - Al(2) - O(2)^{a}$	96.93(10)	O(4) - Al(3) - O(3)	98.77(11)		
C(1) - O(1) - Al(2)	161.2(2)	C(3) - O(3) - Al(3)	162.2(2)		
$C(2) - O(2) - Al(2)^{a}$	163.42(19)	C(4) - O(4) - Al(3)	163.6(2)		
O(1) - C(1) - N(1)	121.0(3)	O(4) - C(4) - N(4)	121.8(3)		
O(2) - C(2) - N(2)	121.4(3)	O(3) - C(3) - N(3)	122.5(3)		
C(1) - N(1) - Al(1)	131.8(2)	C(3) - N(3) - Al(4)	132.7(2)		
C(1)-N(1)-C(15)	119.1(2)	C(3) - N(3) - C(49)	119.2(2)		
C(15) - N(1) - Al(1)	107.48(17)	C(49) - N(3) - Al(4)	106.80(18)		
C(2) - N(2) - Al(1)	131.6(2)	$C(4) - N(4) - Al(4)^{b}$	131.3(2)		
C(21) - N(2) - Al(1)	107.54(17)	$C(44) - N(4) - Al(4)^{b}$	107.79(18)		
C(2)-N(2)-C(21)	119.2(2)	C(4) - N(4) - C(44)	119.2(2)		
N(1) - Al(1) - N(2)	87.47(10)	$N(4)^{b} - Al(4) - N(3)$	87.46(10)		
a - x, -y + 2, -z + 1, b - x + 1, -y + 1, -z + 2.					

and abstracted methyl groups has been extensively studied for zirconocene-borate systems.<sup>32,34–36</sup>

**Single-Crystal Structure.** The molecular structure of **1** has been determined by X-ray crystallography. The crystal structure of **1** is shown in Figure 1b, and Table 1 summarizes selected bond lengths and angles. In the asymmetric unit, two half molecules (molecules I and II in Table 1) are observed, and the whole structures are generated by an inversion center, rendering two chemically equivalent but crystallographically independent 16-membered rings. Figure 2a highlights the structure of the central 16-membered-ring core formed by four AlMe<sub>2</sub> units and four NCO fragments. Two AlMe<sub>2</sub> units are coordinated to two oxygen atoms from different amidato

ligands (COAlOC), while the other two AlMe<sub>2</sub> fragments are bonded to two nitrogen atoms (CNAlNC) within a diamido environment. Thus, the phenylene-bis-amidato groups behave as tetradentate ligands bridging two dimethylaluminum units through the two oxygen atoms and chelating a central aluminum moiety through the two nitrogen atoms.

A crystallographic study of  $1,2-C_6H_4$ {NHC(*t*-Bu)O}<sub>2</sub> (Figure 1a) showed that the C-N distances are slightly longer (1.346(4) and 1.348(4) Å) and the bond lengths for C–O slightly shorter (1.227(3) - 1.221(3) Å) in the free ligand in comparison with the coordination disposition in **1**. As such, bond lengths for C–N are 1.341(4) and 1.336(4) Å in molecule I and 1.331(4) and 1.341(4) Å in the chemically equivalent molecule II, and the bond lengths for C–O fall in the range 1.277(3)– 1.288(3) Å, indicating a partially delocalized structure within the OCN fragment.<sup>37</sup> Distances of 1.308(2) Å for C–N bonds and 1.302(2) Å for C–O bonds have been found in analogous aluminum compounds with formato bridging ligands, for which a delocalized structural disposition within the OCN fragment is suggested.<sup>23</sup> The distances Al-N (1.972(3)-1.987(3) Å range) are shorter than those reported for donor N-Al bonds.<sup>38</sup> On the basis of these structural findings, we propose that complex 1 could be described as a zwitterionic compound, formed by two anionic moieties [AlMe<sub>2</sub>(1,2-C<sub>6</sub>H<sub>4</sub>{NC(*t*-Bu)- $O_{2}$ ]<sup>-</sup> linked by the C=O groups to two cationic fragments  $[AIMe_2]^+$ , rendering a 16-membered macrocycle.

In view of this zwitterionic structure with its anionic contribution from the aluminum-diamido fragment and its cationic contribution from the aluminum centers connected to the oxygen atoms, the Lewis acid  $B(C_6F_5)_3$  in the reaction described in Scheme 1 should attack on the more nucleophilic aluminum-methyl bond, suggesting the abstraction of one methyl group bonded to the aluminum-amido unit to generate the structural disposition shown in Scheme 1.

In the side view of the ring, the atoms forming the inner core  $(COAlOC)_2$  are nearly coplanar, while the nitrogen atoms come slightly out of that plane in a chair orientation

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**Figure 2.** (a) Central 16-membered ring of the structure of **1**. (b) Side view of the ring disposition. (c) Side view showing the methyl groups and phenyl rings disposition. In (a) and (c) H atoms and *t*-Bu groups have been omitted for clarity. In (b) H atoms, Ph, and *t*-Bu groups have been omitted for clarity.

(Figure 2b), which is the preferred disposition for this kind of derivative.<sup>39</sup> The distance between the aluminum centers in the "CNAINC" fragments in the central ring is 8.195 Å for molecule I (8.222 Å for molecule II), and that between aluminum centers in the "COAlOC" moieties is 8.630 Å for molecule I (8.593 Å for molecule II). This central cavity is covered by the two phenylene rings (Figure 2a and c). The disposition of the rings suggests the existence in the solid state of  $\pi$ -stacking intramolecular interactions, although the distances between the centroids of these aligned rings are relatively long, 4.198 and 4.299 Å, indicating that this effect probably occurs for steric rather than electronic reasons. The methyl groups bonded to the Al centers are oriented toward the outside of the ring. They are placed in two perpendicular planes that are also nearly perpendicular to the plane formed by the central core, surrounding it on four sides in a wall-like fashion (Figure 2b and c).

The five-membered chelate aluminum-diamido rings are not planar, and the phenylenediamido ligand is folded along the N–N vector with a fold angle,  $\Theta$ , of 17.55° and 18.33°. Similar folding has been previously observed in analogous compounds.<sup>26,29</sup> Both phenyl ligands are placed in an *anti* direction (see Figure 2c).

Metal-carboxylato interactions have been addressed because of their biological interest, and attempts have been made to determine which lone pair of the oxygen atoms of the carboxylato group is preferred for metal binding.<sup>2</sup> Upon comparison with these carboxilato derivatives, an analysis of the structure of 1 indicates that the aluminum moieties are bonded to the oxygen atoms in an *anti-anti* disposition. This orientation has proven to be the most likely disposition in carboxylato compounds.<sup>2</sup> Several coordination modes for the amidato ligand bonded to aluminum are possible,<sup>17,18,23,40,41</sup> and the factors affecting the different coordination modes have been studied.<sup>23</sup> It is note-worthy to point out that few molecular  $Al_4$  rings have been described where the aluminum atoms are connected by symmetric bridges.<sup>2,42</sup> The unusual 16-membered ring arrangement observed in **1** with a partially delocalized "Al–N–C–O" unit seems to be imposed by the particular nature of this bis-amidato ligand.

Polymerization Studies. The electrophilicity of 2 could enhance substrate coordination to the cationic aluminum center and is active in the polymerization behavior. An initial test of cyclohexene oxide (CHO) polymerization with compound 2 in the standard conditions was carried out (25 °C; catalyst/CHO, 1/2000; 30 min; 5.6 × 10<sup>-5</sup> moles of Al), showing low activity (5% yield,  $M_n = 2.9 \times 10^4$ ;  $M_w = 7.0 \times 10^4$ , polydispersity = 2.5). The broad polydispersity index suggests multiple reaction sites or a low exchange of the growing chain between aluminum centers.<sup>43,44</sup> These preliminary results are in accordance with the cationic-anionic interactions and the methyl exchange effect of the ion pairs observed for compound 2 in solution. The low activity could be attributed to the fact that the initiation step in this polymerization process requires the coordination of the monomer molecule to the active metal centers, and in compound 2 these centers seem to be blocked by the coordination of the methylborate anion.

In conclusion, the polyfunctional diamide  $1,2-C_6H_4-$ {NHC(*t*-Bu)O}<sub>2</sub> behaves as a good precursor for the formation of novel high-nuclearity macrocycle derivatives in the

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reaction with trialkyl aluminum compounds. It is expected that the use of bulky ligands would produce low nuclearity derivatives; however the electronic and steric characteristics of this diamide generate multinuclear metal rings. The ring structure of the tetranuclear 1 (both in solution and in the solid state) displays potential donor and acceptor sites, and it is expected to show wide coordinative abilities that could lead to interesting catalytic properties.

## **Experimental Section**

**General Considerations.** All manipulations were conducted using Schlenk techniques or in an inert atmosphere glovebox. All solvents were rigorously dried prior to use. NMR spectra were recorded at 400.13 (<sup>1</sup>H), 376 (<sup>19</sup>F), and 100.60 (<sup>13</sup>C) MHz on a Bruker AV400. Chemical shifts ( $\delta$ ) are given in ppm using CDCl<sub>3</sub> or C<sub>6</sub>D<sub>5</sub>Br as solvent. <sup>1</sup>H and <sup>13</sup>C resonances were measured relative to solvent peaks considering TMS  $\delta = 0$ ppm, while <sup>19</sup>F was measured relative to external CFCl<sub>3</sub>. Elemental analyses were obtained on a Perkin-Elmer Series II 2400 CHNS/O analyzer. All reagents were commercially obtained (Aldrich) and used without further purification. The diamide 1,2-C<sub>6</sub>H<sub>4</sub>{NHC(*t*-Bu)O}<sub>2</sub> was prepared according to the reported methods.<sup>27,28</sup>

Synthesis of [{AlMe<sub>2</sub>(1,2-C<sub>6</sub>H<sub>4</sub>{NC(*t*-Bu)O}<sub>2</sub>)}AlMe<sub>2</sub>]<sub>2</sub>(1). A 0.434 mL amount of AlMe<sub>3</sub> (2 M, 0.869 mmol) was added to a solution of 1,2-C<sub>6</sub>H<sub>4</sub>{NHC(*t*-Bu)O}<sub>2</sub> (0.120 g, 0.434 mmol) in toluene at room temperature. After 4 h, the solvent was removed *in vacuo* to give a solid, which was recrystallized in hexanes. Compound 1 was obtained as a colorless solid. Yield: 59% (0.200 g, 0.258 mmol). Anal. Calcd (%) for C<sub>40</sub>H<sub>68</sub>Al<sub>4</sub>N<sub>4</sub>O<sub>4</sub> (776.32 g/mol): C, 61.87; H, 8.76; N, 7.21. Found: C, 61.33; H, 8.88; N, 7.80. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  7.18 (AA'BB' spin system, 4H, Ph), 6.77 (AA'BB' spin system, 4H, Ph), 1.38 (s, 36H, *t*-Bu), -0.36 (s, 6H, Me), -0.76 (s, 12H, Me), -0.81 (s, 6H, Me). <sup>13</sup>C NMR (100.60 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$  183.5 (CO), 137.3 (*ipso*-Ph), 124.9, 124.4 (Ph), 42.0 (*ipso-t*-Bu), 28.5 (*t*-Bu), -0.46, -6.99, -7.52 (AlMe).

Synthesis of [{(AlMe<sub>2</sub>)<sub>3</sub>(AlMe)(1,2-C<sub>6</sub>H<sub>4</sub>{NC(*t*-Bu)O}<sub>2</sub>)<sub>2</sub>][MeB-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>] (2). In the drybox an PTFE-valved J-Young NMR tube was charged with B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (0.010 g, 0.019 mmol) and compound 1 (0.014 g, 0.019 mmol). Then the mixture was taken out of the drybox, and CDCl<sub>3</sub> was added at -78 °C, affording a dark solution. NMR monitoring was done at -40 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, -40 °C):  $\delta$  7.25 (m, 2H, Ph), 7.15 (m, 2H, Ph), 6.93 (m, 2H, Ph), 6.86 (m, 2H, Ph), 1.42 (s, 18H, *t*-Bu), 1.35 (s, 18H, *t*-Bu), 0.39 (br, 3H, BMe), -0.34 (s, 3H, AlMe), -0.81 (s, 3H, AlMe), -1.65 (s, 3H, AlMe). <sup>13</sup>C NMR (400 MHz, CDCl<sub>3</sub> -40 °C):  $\delta$  190 (CO), 188.3 (CO), 148.8, 146.6, 137.9, 137.1, 135.9, 134.9 (C<sub>6</sub>F<sub>5</sub>), 137.9, 137.6 (*ipso-*Ph), 128.8, 127.9, 124.3, 123.8 (Ph), 41.7, 41.8 (*ipso-t*-

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Bu), 27.2, 27.1 (*t*-Bu), 10.0 (br, BMe), 0.42, -1.54, -2.60, -9.34, -10.81, -10.96, -11.72 (AlMe). <sup>19</sup>F NMR (376.40 MHz., CDCl<sub>3</sub>  $-40 \,^{\circ}\text{C}$ ):  $\delta -133.5$  (d,  $J = 23.5 \,\text{Hz}$ ,  $o-\text{C}_6\text{F}_5$ ), -164.4 (t,  $J = 20.0 \,\text{Hz}$ ,  $p-\text{C}_6\text{F}_5$ ), -167.1 (s br,  $m-\text{C}_6\text{F}_5$ ). Compound **2** could not be isolated as a pure substance since decomposition occurs in solution at room temperature, which prevented us from obtaining correct elemental analysis.

Single-Crystal X-ray Structure Determination of 1,2-C<sub>6</sub>H<sub>4</sub>-{**NHC**(*t*-**Bu**)**O**}<sub>2</sub> and Compound 1. Details of the X-ray experiment, data reduction, and final structure refinement calculations are summarized in the table in the Supporting Information. Suitable single crystals of  $1,2-C_6H_4\{NHC(t-Bu)O\}_2$  and 1 for the X-ray diffraction study were selected. Data collection was performed at 200(2) K on a crystal covered with perfluorinated ether oil. The crystals were mounted on a Bruker-Nonius Kappa CCD singlecrystal diffractometer equipped with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Multiscan<sup>45</sup> absorption correction procedures were applied to the data. The structures were solved, using the WINGX package,<sup>46</sup> by direct methods (SHELXS-97) and refined by using full-matrix least-squares against  $F^2$  (SHELXL-97).<sup>47,48</sup> All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms except for the ones bonded to the nitrogen atoms in  $1,2-C_6H_4\{NHC(t-Bu)O\}_2$ , which were found in the difference Fourier map and refined. Half of a toluene molecule per molecule of 1 is present in the unit cell. This solvent molecule was found in the difference Fourier map but was very disordered, and it was not possible to get a chemically sensible model for it; therefore, the Squeeze procedure<sup>49</sup> was used to remove its contribution from the structure factors. Full-matrix least-squares refinements were carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$  with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. The final residual electron density maps showed no remarkable features.

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Supporting Information Available: General procedure for the polymerization experiments and table of crystallographic data, including fractional coordinates, bond lengths and angles, anisotropic displacement parameters, and hydrogen atom coordinates in CIF format of the diamide  $1,2-C_6H_4$ {NHC(*t*-Bu)-O}<sub>2</sub> and complex 1. This material is available free of charge via the Internet at http://pubs.acs.org.

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