

# Synthesis of 2,7-Disubstituted Derivatives of 1,8-Naphthalenediol. Unusual Structure of a Chlorotitanium 1,8-Naphthalenediolate

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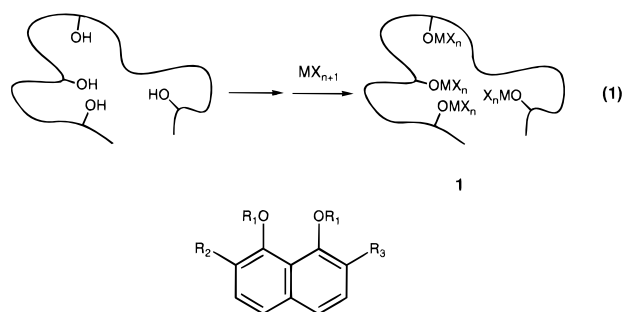
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A variety of 2,7-disubstituted derivatives of 1,8-naphthalenediol (**2**) of potential value as ligands for the complexation of transition metals can be prepared from 1,8-naphthalenediyl bis(diethylcarbamate) (**3**) and 1,8-bis(methoxymethoxy)naphthalene (**9**) by directed ortho-metalation and subsequent functionalization. The reaction of TiCl<sub>4</sub> with 1,8-naphthalenediol (**2**) in the presence of diisopropyl ketone produced an adduct of a novel chloride-bridged dimer of [1,8-naphthalenediolato(2<sup>-</sup>)-O,O']dichlorotitanium (**16**; R = H). Its unusual structure indicates that complexes derived from 1,8-naphthalenediols can have features not normally observed in complexes derived from simple phenols.

## Introduction

Multidentate Lewis acids interest chemists because they can be designed so that their multiple electrophilic sites are held in orientations favoring the recognition, binding, and chemical activation of molecules with complementary arrangements of basic sites.<sup>3</sup> We have shown that a convenient method for synthesizing multidentate Lewis acids is to add metal salts MX<sub>n+1</sub> or related species to compounds containing hydroxyl groups or similar sites suitably oriented by an organic framework (eq 1).<sup>4</sup> This yields metal alkoxides **1** with multiple



- |   |  |
|---|--|
| <b>2</b> (R <sub>1</sub> = R <sub>2</sub> = R <sub>3</sub> = H)   | <b>8</b> (R <sub>1</sub> = H, R <sub>2</sub> = R <sub>3</sub> = Ph)  |
| <b>3</b> (R <sub>1</sub> = CON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , R <sub>2</sub> = R <sub>3</sub> = H)  | <b>9</b> (R <sub>1</sub> = CH <sub>2</sub> OCH <sub>3</sub> , R <sub>2</sub> = R <sub>3</sub> = H)                                   |
| <b>4</b> (R <sub>1</sub> = CON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , R <sub>2</sub> = R <sub>3</sub> = Si(CH <sub>3</sub> ) <sub>3</sub> )               | <b>10</b> (R <sub>1</sub> = CH <sub>2</sub> OCH <sub>3</sub> , R <sub>2</sub> = Ph, R <sub>3</sub> = H)                              |
| <b>5</b> (R <sub>1</sub> = CON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , R <sub>2</sub> = R <sub>3</sub> = Si(C <sub>2</sub> H <sub>5</sub> ) <sub>3</sub> ) | <b>11</b> (R <sub>1</sub> = CH <sub>2</sub> OCH <sub>3</sub> , R <sub>2</sub> = R <sub>3</sub> = Ph)                                 |
| <b>6</b> (R <sub>1</sub> = CON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , R <sub>2</sub> = R <sub>3</sub> = Br)   | <b>12</b> (R <sub>1</sub> = H, R <sub>2</sub> = R <sub>3</sub> = CH <sub>3</sub> )   |
| <b>7</b> (R <sub>1</sub> = CON(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> , R <sub>2</sub> = R <sub>3</sub> = Ph)   | <b>13</b> (R <sub>1</sub> = CH <sub>2</sub> OCH <sub>3</sub> , R <sub>2</sub> = R <sub>3</sub> = CH <sub>3</sub> )                   |
|   | <b>14</b> (R <sub>1</sub> = CH <sub>2</sub> OCH <sub>3</sub> , R <sub>2</sub> = R <sub>3</sub> = Si(CH <sub>3</sub> ) <sub>3</sub> ) |

Lewis acidic sites OMX<sub>n</sub>. In an attempt to use this procedure to convert organic diols into rigid bidentate Lewis acids with two nearby electrophilic sites, we have

synthesized a series of 2,7-disubstituted derivatives of 1,8-naphthalenediol (**2**), and we have determined the structure of an adduct of the naphthalenediolate formed when compound **2** reacts with TiCl<sub>4</sub>.<sup>5</sup>

## Results and Discussion

Treatment of 1,8-naphthalenediol (**2**)<sup>6</sup> with diethylcarbamoyl chloride in the presence of K<sub>2</sub>CO<sub>3</sub> provided bis(carbamate) **3** in 82% yield. Sequential addition of excess chlorotrimethylsilane and *tert*-butyllithium to compound **3** at -95 °C then gave the bis(carbamate) **4** of 2,7-bis(trimethylsilyl)-1,8-naphthalenediol in 84% yield. An analogous reaction with chlorotriethylsilane produced the expected bis(carbamate) **5** in 38% yield, but similar silylations did not occur with chlorotriisopropylsilane or chlorotriphenylsilane. Unfortunately, attempts to make the corresponding 2,7-bis(silylated)-1,8-naphthalenediols by using LiAlH<sub>4</sub> or KOH to deprotect carbamates **4** and **5** led to desilylation and the recovery of unsubstituted 1,8-naphthalenediol (**2**).

For this reason, we decided to introduce substituents at C<sub>2</sub> and C<sub>7</sub> that would be resistant to cleavage. Treatment of the bis(carbamate) **4** of 2,7-bis(trimethylsilyl)-1,8-naphthalenediol with Br<sub>2</sub> in CCl<sub>4</sub> caused bromodesilylation and gave the bis(carbamate) **6** of 2,7-dibromo-1,8-naphthalenediol in 87% yield. Coupling of compound **6** with phenylboronic acid under modified Suzuki conditions<sup>7</sup> then provided the bis(carbamate) **7** of 2,7-diphenyl-1,8-naphthalenediol (**8**) in 95% yield. Deprotection again proved troublesome, however, and naphthalenediol **8** could not be recovered when bis-

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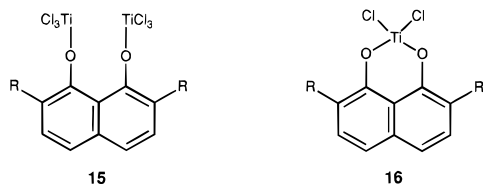
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(carbamate) **7** was treated with  $\text{LiAlH}_4$ ,  $\text{KOH}$ , or methyllithium under various conditions.

The synthesis of 2,7-diphenyl-1,8-naphthalenediol (**8**) was finally achieved in the following way. Treatment of 1,8-naphthalenediol (**2**) with  $\text{KH}$  and chloromethyl methyl ether provided the corresponding bis(methoxymethyl) ether **9** in 56% yield. Directed ortho-monometalation of compound **9** using *n*-butyllithium at  $-15^\circ\text{C}$ , followed by addition of 1,2-dibromotetrafluoroethane,<sup>8</sup> gave the corresponding monobromide. Without purification, this compound was subjected to modified Suzuki coupling with phenylboronic acid. These steps produced the diether **10** of 2-phenyl-1,8-naphthalenediol in 88% overall yield. Repetition of these steps then gave the diether **11** of 2,7-diphenyl-1,8-naphthalenediol in 69% overall yield from diether **9**. Deprotection of compound **11** with  $\text{HCl}$  in aqueous methanol provided 2,7-diphenyl-1,8-naphthalenediol (**8**) in 99% yield as a highly air-sensitive solid.

A related sequence of steps could be used to make 2,7-dimethyl-1,8-naphthalenediol (**12**). Directed metalation of diether **9** using *n*-butyllithium at  $-15^\circ\text{C}$ , addition of iodomethane, remetalation, and readdition of iodomethane in a single flask produced the diether **13** of 2,7-dimethyl-1,8-naphthalenediol (**12**) in 87% overall yield. Normal deprotection of compound **13** then gave 1,8-naphthalenediol **12** in 96% yield. In addition, the bis(methoxymethyl) ether **14** of 2,7-bis(trimethylsilyl)-1,8-naphthalenediol could be prepared in 27% yield by treating bis(methoxymethyl) ether **9** with chlorotrimethylsilane and *tert*-butyllithium.

Treatment of simple phenols with  $\text{TiCl}_4$  in a 1:1 ratio is known to produce trichlorotitanium phenoxides.<sup>9</sup> Because titanium aryloxides tend to have  $\text{Ti}-\text{O}-\text{C}$  angles close to  $180^\circ$ ,<sup>10,11</sup> we hoped that the reactions of 1,8-naphthalenediols **2**, **8**, and **12** with  $\text{TiCl}_4$  in a 1:2 ratio would give derivatives of bidentate Lewis acid **15**



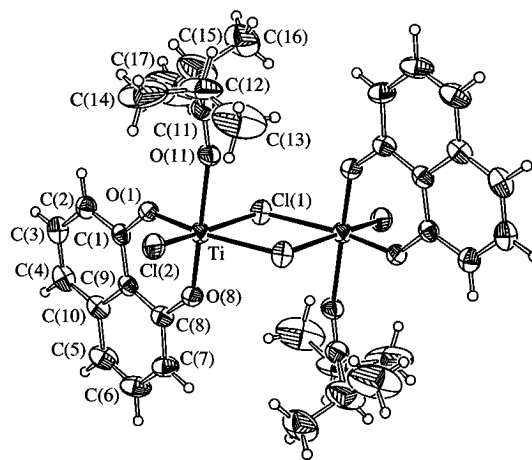
rather than alternative structures derived from mono-

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**Figure 1.** ORTEP drawing of the structure of the chloride-bridged dimer of the 1:1 adduct of (1,8-naphthalenediolato-*O,O'*)dichlorotitanium (**16**;  $\text{R} = \text{H}$ ) with diisopropyl ketone. Hydrogen atoms appear as spheres of arbitrary size, and other atoms are represented by ellipsoids corresponding to 40% probability.

**Table 1.** Atomic Coordinates and Isotropic Thermal Parameters for the Dimer of the 1:1 Adduct of (1,8-Naphthalenediolato-*O,O'*)dichlorotitanium (**16**;  $\text{R} = \text{H}$ ) with Diisopropyl Ketone

atom	<i>x</i>	<i>y</i>	<i>z</i>	$B_{\text{iso}}^a$ ( $\text{\AA}^2$ )
Ti	0.36680(8)	0.09557(7)	0.93332(5)	3.46(3)
Cl(1)	0.51756(12)	-0.06355(9)	0.91438(7)	4.09(4)
Cl(2)	0.26736(13)	0.25396(10)	0.97480(8)	4.67(4)
O(1)	0.3070(3)	0.1073(3)	0.8185(2)	3.59(10)
O(8)	0.2140(3)	0.0109(2)	0.9396(2)	3.75(10)
O(11)	0.5493(3)	0.1838(2)	0.9156(2)	4.08(11)
C(1)	0.1973(4)	0.0626(3)	0.7633(3)	3.3(1)
C(2)	0.1829(5)	0.0871(4)	0.6778(3)	3.8(2)
C(3)	0.0683(5)	0.0426(4)	0.6188(3)	4.5(2)
C(4)	-0.0288(5)	-0.0243(4)	0.6458(3)	4.7(2)
C(5)	-0.1217(5)	-0.1177(4)	0.7625(4)	5.2(2)
C(6)	-0.1125(6)	-0.1368(4)	0.8474(4)	5.3(2)
C(7)	0.0004(5)	-0.0942(4)	0.9067(3)	4.5(2)
C(8)	0.1045(5)	-0.0315(3)	0.8807(3)	3.6(1)
C(9)	0.0977(4)	-0.0072(3)	0.7929(3)	3.3(1)
C(10)	-0.0184(5)	-0.0512(4)	0.7329(3)	4.0(2)
C(11)	0.6351(5)	0.2450(4)	0.8920(3)	4.5(2)
C(12)	0.6765(7)	0.3478(5)	0.9371(6)	8.2(3)
C(13)	0.6827(9)	0.3329(7)	1.0336(5)	11.9(3)
C(14)	0.5601(9)	0.4315(6)	0.8984(7)	14.8(4)
C(15)	0.7031(8)	0.2247(8)	0.8160(5)	10.1(3)
C(16)	0.8495(7)	0.1886(6)	0.8392(5)	8.9(3)
C(17)	0.6105(9)	0.1663(10)	0.7472(5)	16.4(4)

<sup>a</sup>  $B_{\text{iso}}$  is the mean of the principal axes of the thermal ellipsoid.

dentate dichlorotitanium naphthalenediolate **16**. The addition of excess diisopropyl ketone to a suspension produced by treating 1,8-naphthalenediol (**2**) in  $\text{CHCl}_3$  with 2 equiv of  $\text{TiCl}_4$  yielded a homogeneous solution from which deep purple crystals formed. Their structure was determined by X-ray crystallography, and the results are summarized in Figure 1 and Tables 1–3. The product can be described as a chloride-bridged dimer of a 1:1 adduct of diisopropyl ketone and the unexpected (1,8-naphthalenediolato-*O,O'*)dichlorotitanium (**16**;  $\text{R} = \text{H}$ ). Several features of this structure are unusual. In particular, both aryloxy  $\text{Ti}-\text{O}-\text{C}$  angles are conspicuously bent ( $133.1(3)$  and  $134.2(3)^\circ$ ). In addition, the dichlorotitanium 1,8-naphthalenediolate units are bridged by chloride, whereas in the dimeric structures of dichlorotitanium diphenoxide and other closely related dichlorotitanium aryloxides, bridging involves atoms of oxygen.<sup>11</sup> We attribute these unexpected features to the

**Table 2. Selected Bond Lengths and Angles for the Dimer of the 1:1 Adduct of (1,8-Naphthalenediolato-*O,O'*)dichlorotitanium (16; R = H) with Diisopropyl Ketone**

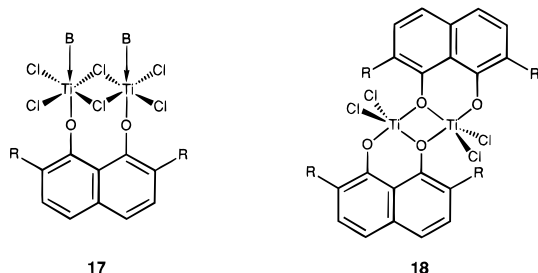
Bond Lengths (Å)			
Ti-Cl(1)	2.476(1)	Ti-O(1)	1.816(3)
Ti-Cl(1) <sup>a</sup>	2.500(1)	Ti-O(8)	1.794(3)
Ti-Cl(2)	2.319(1)	Ti-O(11)	2.094(3)
O(11)-C(11)	1.214(6)		
Bond Angles (deg)			
Cl(1)-Ti-Cl(1) <sup>a</sup>	80.43(4)	Cl(1) <sup>a</sup> -Ti-Cl(2)	89.17(5)
Cl(1)-Ti-Cl(2)	167.47(6)	Cl(1) <sup>a</sup> -Ti-O(1)	170.96(10)
Cl(1)-Ti-O(1)	91.21(10)	Cl(1) <sup>a</sup> -Ti-O(8)	93.73(10)
Cl(1)-Ti-O(8)	91.24(10)	Cl(1) <sup>a</sup> -Ti-O(11)	89.45(9)
Cl(1)-Ti-O(11)	84.24(9)		
Cl(2)-Ti-O(1)	98.68(10)	O(1)-Ti-O(8)	89.87(14)
Cl(2)-Ti-O(8)	96.42(11)	O(1)-Ti-O(11)	86.26(13)
Cl(2)-Ti-O(11)	88.73(9)	O(8)-Ti-O(11)	173.98(13)
Ti-Cl(1)-Ti <sup>a</sup>	99.57(5)	Ti-O(8)-C(8)	134.2(3)
Ti-O(1)-C(1)	133.1(3)	Ti-O(11)-C(11)	166.5(3)

<sup>a</sup> Equivalent position: 1 - x, -y, 2 - z.

**Table 3. Crystallographic Data for the Dimer of the 1:1 Adduct of (1,8-Naphthalenediolato-*O,O'*)dichlorotitanium (16; R = H) with Diisopropyl Ketone**

formula	C <sub>34</sub> H <sub>40</sub> Cl <sub>4</sub> O <sub>6</sub> Ti <sub>2</sub>
fw	782.30
system	monoclinic
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>
cell consts	
<i>a</i> , Å	9.388(4)
<i>b</i> , Å	12.388(5)
<i>c</i> , Å	15.898(8)
<i>B</i> , deg	100.41(4)
cell vol, Å <sup>3</sup>	1818.5(14)
<i>Z</i>	4
<i>T</i> , K	215
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	1.429
<i>μ</i> <sub>calcd</sub> , mm <sup>-1</sup>	6.88
radiation (λ, Å)	graphite-monochromated Cu Kα (1.540 56)
cryst dimens, mm	0.30 × 0.45 × 0.56
scan width	0.80 ± 0.14 tan θ
2θ <sub>max</sub> , deg	45
data colln range	± <i>h</i> , ± <i>k</i> , ± <i>l</i>
no. of reflns collcd	12 205
no. of reflns retained	2562
no. of params refined	208
goodness-of-fit	2.78
<i>R</i>	0.055
<i>R</i> <sub>w</sub>	0.064

characteristic geometry of the 1,8-naphthalenediolate ligand. Specifically, adducts **17** of a base B with



hypothetical trichlorotitanium aryloxyde **15** may be disfavored because the expected Ti...Ti distance (2.7 Å) is too short to permit chloride bridging without introducing significant amounts of strain. In contrast, the normal Ti...Ti distance in octahedral chloride-bridged

adducts of TiCl<sub>4</sub> is approximately 3.8 Å.<sup>12</sup> Furthermore, adducts of conventional oxygen-bridged dimer **18** may be destabilized by steric repulsion involving substituents at C<sub>2</sub> and C<sub>2'</sub> even when R = H.

Other features of the structure shown in Figure 1 are well precedented. For example, each atom of titanium attains octahedral coordination, and the average distances from titanium to the bridging chlorides (2.488(1) Å), terminal chlorides (2.319(1) Å), aryloxyde oxygens (1.805(3) Å), and carbonyl oxygens (2.093(3) Å) are similar to those observed in related complexes.<sup>10-12</sup>

## Conclusions

Our work provides efficient methods for converting 1,8-naphthalenediol (**2**) into 2,7-disubstituted derivatives that promise to serve as novel ligands for the complexation of transition metals. Our observations indicate that complexes derived from 1,8-naphthalenediols can have unique structural features not observed in complexes derived from simple phenols.

## Experimental Section

CH<sub>3</sub>CN and CHCl<sub>3</sub> were dried by distillation from CaH<sub>2</sub>, and tetrahydrofuran (THF) was dried by distillation from the sodium ketyl of benzophenone. TiCl<sub>4</sub> was purified by distillation under Ar. Other commercial reagents were used without further purification. Flash chromatography was performed in the normal way.<sup>13</sup>

**1,8-Naphthalenediol (2).** 1,8-Naphthalenediol (**2**) was prepared by modifying published procedures.<sup>6</sup> A mechanically stirred mixture of KOH (75 g, 1.3 mol) and NaOH (75 g, 1.9 mol) was melted in a stainless steel beaker heated in an oil bath at 260 °C. To the stirred melt was added 1,8-naphthosultone (25.0 g, 0.121 mol) in small portions. This yielded a black liquid, which was stirred at 260 °C for 1 h, poured onto aluminum foil, and allowed to solidify. The solid was broken up and added in small portions to vigorously stirred 10% aqueous HCl (1.2 L), and the resulting mixture was then heated at reflux for 10 min. The solution was cooled and extracted with ether, and volatiles were removed from the combined extracts by evaporation under reduced pressure. Sublimation of the residue at 120 °C/0.2 Torr provided 1,8-naphthalenediol (**2**; 13.4 g, 0.0837 mol, 69%) as a colorless solid: mp 139–140 °C (lit.<sup>6c</sup> 140 °C); IR (CHCl<sub>3</sub>) 3589, 3192 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 6.81 (dd, 2H, <sup>3</sup>*J* = 7.4 Hz, <sup>4</sup>*J* = 1.1 Hz), 7.30 (t, 2H, <sup>3</sup>*J* = 7.4 Hz), 7.39 (dd, 2H, <sup>3</sup>*J* = 7.4 Hz, <sup>4</sup>*J* = 1.1 Hz), 7.59 (bs, 2H); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 109.4, 114.4, 120.5, 126.7, 137.0, 152.5.

**1,8-Naphthalenediyl Bis(diethylcarbamate) (3).** A mixture of 1,8-naphthalenediol (**2**; 286 mg, 1.79 mmol), diethylcarbamoyl chloride (604 mg, 4.45 mmol), and K<sub>2</sub>CO<sub>3</sub> (616 mg, 4.46 mmol) in dry CH<sub>3</sub>CN (30 mL) was stirred and heated at reflux under dry N<sub>2</sub> for 12 h. Water was then added, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>, and volatiles were removed from the combined extracts by evaporation under reduced pressure. Recrystallization of the residue from hexane/ethyl acetate (10:1) provided 1,8-naphthalenediyl bis(diethylcarbamate) (**3**; 523 mg, 1.46 mmol, 82%) as a beige solid: mp 132–133 °C; IR (CHCl<sub>3</sub>) 1707 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.23 (t, 6H, <sup>3</sup>*J* = 7.1 Hz), 1.29 (t, 6H, <sup>3</sup>*J* = 7.1 Hz), 3.43 (q, 4H, <sup>3</sup>*J* = 7.1 Hz), 3.48 (q, 4H, <sup>3</sup>*J* = 7.1 Hz), 7.10 (d, 2H, <sup>3</sup>*J* = 7.6 Hz), 7.42 (dd, 2H, <sup>3</sup>*J* = 8.1 Hz, <sup>3</sup>*J* = 7.6 Hz), 7.72 (d, 2H, <sup>3</sup>*J* = 8.1 Hz); <sup>13</sup>C NMR (75.4 MHz, CDCl<sub>3</sub>) δ 13.6, 14.4, 42.0, 42.3, 120.1, 122.8, 125.8, 126.0, 136.7, 146.6, 154.8; HRMS (EI) (*m/e*) calcd for C<sub>20</sub>H<sub>26</sub>N<sub>2</sub>O<sub>4</sub> 358.1892, found 358.1886.

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Anal. Calcd for  $C_{20}H_{26}N_2O_4$ : C, 67.02; H, 7.31. Found: C, 65.92; H, 7.17.

**2,7-Bis(trimethylsilyl)-1,8-naphthalenediyl Bis(diethylcarbamate) (4).** A solution of 1,8-naphthalenediyl bis(diethylcarbamate) (**3**; 1.57 g, 4.38 mmol) in dry THF (50 mL) was stirred at  $-95^\circ\text{C}$  under dry Ar and treated dropwise with chlorotrimethylsilane (2.85 g, 26.2 mmol) and a solution of *tert*-butyllithium (10.3 mL, 1.7 M in hexane, 18 mmol). The resulting green solution was kept at  $-95^\circ\text{C}$  for 1 h and then at  $25^\circ\text{C}$  for 12 h. Saturated aqueous  $\text{NH}_4\text{Cl}$  was added, the mixture was extracted with ether, and volatiles were removed from the combined extracts by evaporation under reduced pressure. The residue was washed with hexane and dried to give pure 2,7-bis(trimethylsilyl)-1,8-naphthalenediyl bis(diethylcarbamate) (**4**; 1.85 g, 3.68 mmol, 84%) as a colorless solid: mp  $204\text{--}205^\circ\text{C}$ ; IR ( $\text{CHCl}_3$ )  $1715\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.34 (s, 18 H), 1.21 (t, 6H,  $^3J = 7.1\text{ Hz}$ ), 1.31 (t, 6H,  $^3J = 7.1\text{ Hz}$ ), 3.30–3.41 (m, 8H), 7.47 (d, 2H,  $^3J = 8.1\text{ Hz}$ ), 7.66 (d, 2H,  $^3J = 8.1\text{ Hz}$ );  $^{13}\text{C NMR}$  (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$   $-0.6, 13.4, 13.9, 41.5, 41.5, 123.5, 125.4, 128.7, 130.6, 138.2, 151.4, 153.9$ ; HRMS (EI) (*m/e*) calcd for  $C_{26}H_{42}N_2O_4Si_2$  502.2683, found 502.2636.

**2,7-Bis(triethylsilyl)-1,8-naphthalenediyl Bis(diethylcarbamate) (5).** When chlorotriethylsilane was used in place of chlorotrimethylsilane in the previous procedure, 1,8-naphthalenediyl bis(diethylcarbamate) (**3**; 50 mg, 0.14 mmol) was converted into 2,7-bis(triethylsilyl)-1,8-naphthalenediyl bis(diethylcarbamate) (**5**; 31 mg, 0.053 mmol, 38%): mp  $208\text{--}210^\circ\text{C}$ ; IR ( $\text{CHCl}_3$ )  $1715\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.85–1.01 (m, 30 H), 1.21 (t, 6H,  $^3J = 7.1\text{ Hz}$ ), 1.31 (t, 6H,  $^3J = 7.1\text{ Hz}$ ), 3.17–4.30 (m, 8H), 7.45 (d, 2H,  $^3J = 8.0\text{ Hz}$ ), 7.68 (d, 2H,  $^3J = 8.0\text{ Hz}$ );  $^{13}\text{C NMR}$  (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  3.4, 7.3, 13.4, 14.1, 41.5, 41.5, 123.8, 125.4, 125.7, 131.4, 138.0, 151.6, 153.8; MS (EI) (*m/e*) 586, 557.

**2,7-Dibromo-1,8-naphthalenediyl Bis(diethylcarbamate) (6).** Bromine (382 mg, 2.39 mmol) was added dropwise at  $0^\circ\text{C}$  to a stirred suspension of 2,7-bis(trimethylsilyl)-1,8-naphthalenediyl bis(diethylcarbamate) (**4**; 600 mg, 1.19 mmol) in  $\text{CCl}_4$  (100 mL). The mixture was kept at  $0^\circ\text{C}$  for 48 h, and excess bromine was then destroyed by the addition of saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$ . The mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , and volatiles were removed from the combined extracts by evaporation under reduced pressure. Crystallization of the residue from hexane/ethyl acetate (1:1) provided 2,7-dibromo-1,8-naphthalenediyl bis(diethylcarbamate) (**6**; 536 mg, 1.04 mmol, 87%) as a colorless solid: mp  $160\text{--}162^\circ\text{C}$ ; IR ( $\text{CHCl}_3$ )  $1722\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  1.26 (t, 6H,  $^3J = 7.1\text{ Hz}$ ), 1.38 (t, 6H,  $^3J = 7.1\text{ Hz}$ ), 3.23–3.41 (m, 4H), 3.47–3.56 (m, 2H), 3.82–3.91 (m, 2H), 7.57 (d, 2H,  $^3J = 8.9\text{ Hz}$ ), 7.65 (d, 2H,  $^3J = 8.9\text{ Hz}$ );  $^{13}\text{C NMR}$  (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  13.4, 14.2, 42.3, 42.5, 117.4, 125.6, 127.0, 130.5, 134.5, 143.3, 152.9; MS (EI) (*m/e*) 514, 435; HRMS (EI) (*m/e*) calcd for  $C_{20}H_{24}^{79}\text{Br}_2\text{N}_2\text{O}_4$  514.0103, found 514.0126.

**2,7-Diphenyl-1,8-naphthalenediyl Bis(diethylcarbamate) (7).** A stirred mixture of 2,7-dibromo-1,8-naphthalenediyl bis(diethylcarbamate) (**6**; 311 mg, 0.602 mmol), phenylboronic acid (734 mg, 6.02 mmol), and tetrakis(triphenylphosphine)palladium (21 mg, 0.018 mmol) in a mixture of DME (25 mL) and 2 N aqueous  $\text{Na}_2\text{CO}_3$  (25 mL) was heated at reflux for 12 h under Ar. Water was added, the resulting mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , and volatiles were removed from the combined extracts by evaporation under reduced pressure. Flash chromatography (silica, hexane (84%)/ethyl acetate (16%)) of the residue provided pure 2,7-diphenyl-1,8-naphthalenediyl bis(diethylcarbamate) (**7**; 292 mg, 0.572 mmol, 95%) as a colorless solid: mp  $169\text{--}170^\circ\text{C}$ ; IR ( $\text{CHCl}_3$ )  $1703\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.64 (t, 6H,  $^3J = 7.1\text{ Hz}$ ), 1.02 (t, 6H,  $^3J = 7.1\text{ Hz}$ ), 2.78 (dq, 2H,  $^2J = 14.2\text{ Hz}$ ,  $^3J = 7.1\text{ Hz}$ ), 2.96 (dq, 2H,  $^2J = 14.2\text{ Hz}$ ,  $^3J = 7.1\text{ Hz}$ ), 3.40 (m, 4H), 7.31–7.45 (m, 12H), 7.79 (d, 2H,  $^3J = 8.4\text{ Hz}$ );  $^{13}\text{C NMR}$  (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  13.0, 13.1, 41.7, 42.8, 123.5, 125.6, 126.9, 127.7, 128.1, 128.2, 128.3, 129.1, 133.8, 135.3, 138.7, 143.2, 154.2; HRMS

(EI) (*m/e*) calcd for  $C_{32}H_{34}N_2O_4$  510.2519, found 510.2484. Anal. Calcd for  $C_{32}H_{34}N_2O_4$ : C, 75.27; H, 6.71. Found: C, 75.18; H, 6.81.

**1,8-Bis(methoxymethoxy)naphthalene (9).** 1,8-Naphthalenediol (**2**; 1.48 g, 9.24 mmol) was added in portions to a stirred suspension of KH (3.2 g, 80 mmol) in dry DMF (100 mL) at  $0^\circ\text{C}$  under dry  $\text{N}_2$ . Chloromethyl methyl ether (4.46 g, 55.4 mmol) was then added dropwise, and the resulting mixture was kept at  $25^\circ\text{C}$  for 3 h. Water was added cautiously, and volatiles were removed by evaporation *in vacuo*. The residue was partitioned between  $\text{H}_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$ , the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$ , and volatiles were removed from the combined extracts by evaporation under reduced pressure. Recrystallization of the residue from pentane yielded 1,8-bis(methoxymethoxy)naphthalene (**9**; 1.28 g, 5.16 mmol, 56%) as a colorless solid: mp  $76\text{--}77^\circ\text{C}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.62 (s, 6H), 5.31 (s, 4H), 7.11 (dd, 2H,  $^3J = 7.7\text{ Hz}$ ,  $^4J = 1.0\text{ Hz}$ ), 7.37 (dd, 2H,  $^3J = 8.3\text{ Hz}$ ,  $^4J = 7.7\text{ Hz}$ ), 7.52 (dd, 2H,  $^3J = 8.3\text{ Hz}$ ,  $^4J = 1.0\text{ Hz}$ );  $^{13}\text{C NMR}$  (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  56.3, 96.4, 112.7, 119.2, 122.7, 126.1, 137.4, 153.5; MS (EI) (*m/e*) 248, 172; HRMS (EI) (*m/e*) calcd for  $C_{14}H_{16}O_4$  248.1049, found 248.1037.

**1,8-Bis(methoxymethoxy)-2,7-diphenylnaphthalene (11).** A solution of 1,8-bis(methoxymethoxy)naphthalene (**9**; 1.01 g, 4.07 mmol) in dry THF (50 mL) was stirred at  $-15^\circ\text{C}$  under dry Ar and treated dropwise with a solution of *n*-butyllithium (4.9 mL, 2.5 M in hexane, 12 mmol). The resulting black mixture was kept at  $-15^\circ\text{C}$  for 30 min, and then 1,2-dibromotetrafluoroethane (2.12 g, 8.16 mmol) was added. The mixture was then treated with saturated aqueous  $\text{Na}_2\text{S}_2\text{O}_3$  and partitioned between  $\text{H}_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$ . The aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$ , and volatiles were removed from the combined organic extracts by evaporation under reduced pressure. A stirred mixture of the crude monobromide, phenylboronic acid (1.99 g, 16.3 mmol), and tetrakis(triphenylphosphine)palladium (228 mg, 0.197 mmol) in DME (20 mL) and 2 N aqueous  $\text{Na}_2\text{CO}_3$  (20 mL) was heated at reflux for 20 h. Water was added, the resulting mixture was extracted with  $\text{CH}_2\text{Cl}_2$ , and volatiles were removed from the combined extracts by evaporation under reduced pressure. Flash chromatography (silica, hexane (94%)/ethyl acetate (6%)) provide crude 1,8-bis(methoxymethoxy)-2-phenylnaphthalene (**10**; 1.16 g, 3.58 mmol, 88%) as a colorless liquid. A solution of this intermediate in dry THF (40 mL) was treated sequentially with *n*-butyllithium (4.3 mL, 11 mmol) and 1,2-dibromotetrafluoroethane (1.86 g, 7.16 mmol) under the conditions described above, and the product of bromination was isolated in the same manner. A stirred mixture of this product, phenylboronic acid (1.31 g, 10.7 mmol), and tetrakis(triphenylphosphine)palladium (201 mg, 0.174 mmol) in DME (15 mL) and 2 N aqueous  $\text{Na}_2\text{CO}_3$  (15 mL) was heated at reflux for 48 h. The product was isolated in the manner described above and purified by flash chromatography (silica, hexane (95%)/ethyl acetate (5%)). Recrystallization from hexane/ethyl acetate (15:1) then gave 1,8-bis(methoxymethoxy)-2,7-diphenylnaphthalene (**11**; 1.13 g, 2.82 mmol, 69%) as a colorless solid: mp  $147\text{--}149^\circ\text{C}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.83 (s, 6H), 4.98 (s, 4H), 7.36 (t, 2H,  $^3J = 7.8\text{ Hz}$ ), 7.45–7.50 (m, 6H), 7.64 (d, 4H,  $^3J = 8.4\text{ Hz}$ ), 7.71 (d, 2H,  $^3J = 8.4\text{ Hz}$ );  $^{13}\text{C NMR}$  (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  56.9, 100.4, 122.1, 124.8, 126.8, 127.9, 128.5, 130.4, 133.9, 136.7, 139.4, 148.8. Anal. Calcd for  $C_{26}H_{24}O_4$ : C, 77.97; H, 6.04. Found: C, 77.60; H, 6.10.

**2,7-Diphenyl-1,8-naphthalenediol (8).** A solution of 1,8-bis(methoxymethoxy)-2,7-diphenylnaphthalene (**11**; 226 mg, 0.564 mmol) in a deoxygenated mixture of  $\text{CH}_3\text{OH}$  (10 mL) and  $\text{CH}_2\text{Cl}_2$  (10 mL) was stirred at  $25^\circ\text{C}$  under Ar and treated with deoxygenated aqueous 12 N HCl (1.9 mL). The mixture was kept at  $25^\circ\text{C}$  for 12 h, and then volatiles were removed by evaporation *in vacuo*. The residue was pure 2,7-diphenyl-1,8-naphthalenediol (**8**; 175 mg, 0.560 mmol, 99%) in the form of a colorless air-sensitive solid: mp  $167\text{--}168^\circ\text{C}$  dec; IR ( $\text{CHCl}_3$ )  $3528, 3425\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42

(m, 6H), 7.53 (t, 4H,  $^3J = 7.4$  Hz), 7.62 (d, 4H,  $^3J = 7.1$  Hz), 7.94 (s, 2H);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  114.2, 120.1, 122.5, 127.5, 128.7, 128.9, 129.5, 135.8, 137.3, 149.3.

**1,8-Bis(methoxymethoxy)-2,7-dimethylnaphthalene (13).** A solution of 1,8-bis(methoxymethoxy)naphthalene (**9**; 287 mg, 1.16 mmol) in dry THF (20 mL) was stirred at  $-15^\circ\text{C}$  under dry Ar and treated dropwise with a solution of *n*-butyllithium (1.4 mL, 2.5 M in hexane, 3.5 mmol). The resulting black mixture was kept at  $-15^\circ\text{C}$  for 15 min, and then iodomethane (494 mg, 3.48 mmol) was added dropwise. A second portion of *n*-butyllithium was added, followed by a second portion of iodomethane. The mixture was then partitioned between  $\text{H}_2\text{O}$  and  $\text{CH}_2\text{Cl}_2$ , the aqueous phase was extracted with  $\text{CH}_2\text{Cl}_2$ , and volatiles were removed from the combined extracts by evaporation under reduced pressure. Flash chromatography (silica, hexane (91%)/ethyl acetate (9%)) of the residue provided pure 1,8-bis(methoxymethoxy)-2,7-dimethylnaphthalene (**13**; 280 mg, 1.01 mmol, 87%) as a colorless liquid:  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.52 (s, 6H), 3.62 (s, 6H), 5.07 (s, 4H), 7.24 (d, 2H,  $^3J = 8.3$  Hz), 7.50 (d, 2H,  $^3J = 8.3$  Hz);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  17.2, 57.6, 100.9, 121.6, 124.4, 126.8, 128.4, 135.1, 149.0.

**2,7-Dimethyl-1,8-naphthalenediol (12).** A solution of 1,8-bis(methoxymethoxy)-2,7-dimethylnaphthalene (**13**; 280 mg, 1.01 mmol) in deoxygenated  $\text{CH}_3\text{OH}$  (15 mL) was stirred at  $25^\circ\text{C}$  under Ar and treated with deoxygenated aqueous 12 N HCl (1.7 mL). The mixture was kept at  $25^\circ\text{C}$  for 12 h, and then volatiles were removed by evaporation *in vacuo*. The residue was pure 2,7-dimethyl-1,8-naphthalenediol (**12**; 182 mg, 0.967 mmol, 96%) in the form of a colorless air-sensitive solid: mp  $147\text{--}148^\circ\text{C}$ ; IR ( $\text{CHCl}_3$ ) 3600, 3440  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  2.37 (s, 6H), 7.15 (d, 2H,  $^3J = 8.3$  Hz), 7.27 (d, 2H,  $^3J = 8.3$  Hz), 7.48 (bs, 2H);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$  15.4, 114.2, 117.1, 119.8, 128.7, 134.4, 149.2.

**1,8-Bis(methoxymethoxy)-2,7-bis(trimethylsilyl)naphthalene (14).** A solution of 1,8-bis(methoxymethoxy)naphthalene (**9**; 1.00 g, 4.03 mmol) in dry THF (50 mL) was stirred at  $-78^\circ\text{C}$  under dry Ar and treated dropwise with chlorotrimethylsilane (2.63 g, 24.2 mmol) and then with a solution of *tert*-butyllithium (8.3 mL, 1.7 M in hexane, 14 mmol). The resulting green mixture was kept at  $-78^\circ\text{C}$  for 18 h, brought to  $25^\circ\text{C}$ , and then recooled to  $-78^\circ\text{C}$ . Second portions of chlorotrimethylsilane (1.71 g, 15.7 mmol) and *tert*-butyllithium (6.8 mL, 12 mmol) were then added. The cooling bath was removed, and the mixture was kept at  $25^\circ\text{C}$  for 12 h. Saturated aqueous  $(\text{NH}_4)_2\text{SO}_4$  was then added, the mixture was extracted with ether, and volatiles were removed from the combined extracts by evaporation under reduced pressure. Heating the residue in a Kugelrohr permitted distillation of unreacted 1,8-bis(methoxymethoxy)naphthalene (**9**; 0.203 g, 0.818 mmol, 20%). Flash chromatography (silica, hexane (95%)/ethyl acetate (5%)) of the residue from the distillation yielded 1,8-bis(methoxymethoxy)-2,7-bis(trimethylsilyl)naphthalene (**14**; 0.341 g, 0.868 mmol, 27% based on unrecovered starting material): mp  $60\text{--}61^\circ\text{C}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  0.48 (s, 18H), 3.50 (s, 6H), 5.11 (s, 4H), 7.53 (d, 2H,  $^3J = 8.2$  Hz), 7.60 (d, 2H,  $^3J = 8.2$  Hz);  $^{13}\text{C}$  NMR (75.4 MHz,  $\text{CDCl}_3$ )  $\delta$   $-0.2$ , 58.2, 100.7, 119.7, 123.6, 129.0, 131.5, 139.4, 157.0; HRMS (EI) (*m/e*) calcd for  $\text{C}_{20}\text{H}_{32}\text{O}_4\text{Si}_2$  392.1839, found 392.1825.

**Reaction of  $\text{TiCl}_4$  with 1,8-Naphthalenediol (**2**) in the Presence of Diisopropyl Ketone and X-ray Crystallographic Study of the Product.** At  $25^\circ\text{C}$  under dry Ar,

diisopropyl ketone (0.303 mg, 2.65 mmol) was added to a stirred suspension produced by treating a solution of 1,8-naphthalenediol (**2**; 107 mg, 0.668 mmol) in dry  $\text{CHCl}_3$  (5 mL) with  $\text{TiCl}_4$  (253 mg, 1.33 mmol). The resulting solution yielded purple crystals of the chloride-bridged dimer of a 1:1 adduct of diisopropyl ketone with (1,8-naphthalenediolato-*O,O'*)-dichlorotitanium (**16**; R = H) (68.7 mg, 0.176 mmol, 26%). Crystallographic data are summarized in Table 3. A single crystal of the complex was mounted quickly in air on an Enraf-Nonius CAD4 diffractometer. Unit cell parameters were determined from 25 well-centered reflections in the range  $20^\circ \leq \theta \leq 22.5^\circ$ . The orientation was checked every 400 measurements, and the intensity was checked every 1 h using five standard reflections. The largest variations were within  $\pm 1.5\%$  of the mean. Corrections were introduced for the Lorentz effect and polarization, and an absorption correction was applied using a Gaussian integration technique (grid,  $20 \times 20 \times 20$ ; transmission factors, 0.10–0.27). The structure was solved by direct methods (SHELX-86) and difference-Fourier calculations (SHELX-76).<sup>14</sup> The structure was refined on  $|F_o|$  by full-matrix least-squares procedures. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated at idealized coordinates. Anomalous dispersion was included for all atoms. Refinement converged to  $R_f = 0.055$ ,  $R_w = 0.064$ , and goodness-of-fit = 2.78 for 208 parameters refined. The final  $\Delta F$  map was essentially featureless with a general background below  $\pm 0.24 \text{ e } \text{\AA}^{-3}$ . The scattering curves for the non-hydrogen atoms<sup>15</sup> and the hydrogen atoms<sup>16</sup> were taken from standard sources.

Atomic coordinates and isotropic thermal parameters are listed in Table 1, and selected bond lengths and angles are compiled in Table 2. Tables of complete bond lengths and angles, anisotropic thermal parameters, calculated hydrogen atom coordinates, and distances to weighted least-squares planes are included as Supporting Information.

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**Supporting Information Available:**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compounds **5**, **8**, **12**, and **13** and tables of complete bond lengths and angles, anisotropic thermal parameters, calculated hydrogen atom coordinates, and distances to the weighted least-squares planes for the dimer of the 1:1 adduct of (1,8-naphthalenediolato-*O,O'*)dichlorotitanium (**16**; R = H) with diisopropyl ketone (15 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any masthead page for ordering information.

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