1,8-NAPHTHALENEDIYLZINC

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ABSTRACT

1,8-Naphthalenediylzinc (**1b**) was prepared from the corresponding mercury derivative **1c** by stirring with metallic zinc for 3 weeks at 50 °C in THF; an intermediate **1g** has been tentatively identified. Association measurements showed that **1b** is a dimer like **1c** and the group 14 analogues.

INTRODUCTION

In view of the successful application of 1,8-naphthalenediylmagnesium (**1a**) [1] for the preparation of four-membered metallacycles [2] and of 1,8-dilithionaphthalene [3] for the preparation of several organic [4] and organometallic [5] 1,8-substituted derivatives of naphthalene, 1,8-naphthalenediylzinc (**1b**) appeared to be an attractive reagent for similar synthetic applications.

There is one brief mention of **1b** by Leznoff et al. [6], who prepared it *in situ* from 1,8-diiodonaphthalene, zinc bromide and metallic lithium. To our knowledge, however, detailed information on the isolation or properties of **1b** has not been reported.

EXPERIMENTAL

General

All manipulations involving organometallic compounds were carried out in fully sealed glassware using standard high vacuum techniques. Solvents were dried by distillation from liquid Na/K alloy after predrying on NaOH. Zinc shot was used as commercially available (Alfa Europe Products, 99.999%). NMR spectra were measured on a Bruker AC 200 spectrometer (¹H NMR: 200 MHz; ¹³C NMR: 50.3 MHz) and on a Bruker MSL 400 spectrometer (¹H NMR: 400.1 MHz; ¹⁹⁹Hg NMR: 71.6 MHz). GCMS analyses were performed on a HP 5890 GC/ 5970 MS combination, operating at 70 eV and equipped with a Chrompack BP1 (QSGE) 50 m/ 0.25 mm column.

Synthesis of 1,8-naphthalenediylzinc (**1b**)

1,8-Naphthalenediylmercury (**1c**) [7] (6.24 g, 19.1 mmol) and zinc (37.8 g, 0.6 mol) in 180 mL of THF were stirred for 3 weeks at 50 °C in the dark. A brown solution with a black precipitate was obtained. The solution was separated from the excess of zinc and the black precipitate by careful decantation. Titration [8] of an aliquot indicated the formation of **1b** in 77% yield (14.7 mmol). After evaporation of THF, the brown residue was washed several times with 60 mL of benzene to furnish pure **1b**. It was again dissolved in 180 mL of THF whereafter a light yellow solution was obtained; the yield was 51% as determined by titration after hydrolysis [8].

1b: ¹H NMR (200 MHz, THF-*d*₈, ref. THF-*d*₇ δ(H(2)) = 1.75 ppm): δ = 7.69 (dd, ³J_{HH} = 6.5 Hz, ⁴J_{HH} = 1.4 Hz, 2H, H(2,7)), 7.52 (dd, ³J_{HH} = 8.1 Hz, ²J_{HH} = 1.3 Hz, 2H, H(4,5)), 7.19 (dd, ²J_{HH} = 8.0 Hz, ³J_{HH} = 6.5 Hz, 2H, H(3,6)). ¹³C NMR (62.9 MHz, THF-*d*₈, ref. THF-*d*₈ δ(C(1)) = 67.4 ppm) δ = 177.8 (bs), 159.1 (bs), 135.3 (dd, ¹J_{CH} = 151.5 Hz, ³J_{CH} = 8.0 Hz), 134.7 (bs), 127.5 (d, ¹J_{CH} = 153.5 Hz), 124.4 (d, ¹J_{CH} = 152.5 Hz).

Reaction of **1b** with deuterium oxide

To a solution of **1b** (ca. 0.1 mmol) in 1 mL of THF, an excess of deuterium oxide was added at room temperature. After addition of diethyl ether, the reaction mixture was hydrolyzed, extracted with diethyl ether and examined by GCMS. The only product observed was [1,8-D₂]naphthalene (**3**).

3: ^1H NMR (200 MHz, CDCl_3 , ref. CHCl_3 δ = 7.26 ppm): δ = 7.9–7.8 (m, 2H, H(4,5), 7.47 bd, $^3J_{\text{HH}}$ = 5.6 Hz, 4H H(2,3,6,7)). This second order ^1H NMR spectrum was simulated with the program PANIC [9] which gave the best fit using $^3J(\text{D}(1)\text{H}(2))$ = 1.5 Hz, $^4J(\text{D}(1)\text{H}(3))$ = 0.2 Hz, $^5J(\text{D}(1)\text{H}(4))$ = 0.0 Hz, $^3J(\text{H}(2)\text{H}(3))$ = 6.0 Hz, $^4J(\text{H}(2)\text{H}(4))$ = 1.4 Hz and $^3J(\text{H}(3)\text{H}(4))$ = 8.6 Hz, and a $\Delta\delta(\text{H}(4,5)\text{--H}(2,3,6,7))$ = 0.38 ppm; in accordance with the data reported for **3** as obtained from the reaction of **1a** with deuterium oxide [1b]. GCMS m/z (rel. int.): 131 (11), 130 (M^+ ; 100), 129 (16), 128 (7), 127 (3).

Reaction of **1c** with metallic zinc: formation of intermediate **1g**

Compound **1c** (5.0 g, 15.3 mmol) was stirred with zinc (30.2 g, 0.48 mol) in 180 mL of THF. After 1 week stirring in the dark, the resulting light brown suspension was allowed to settle. The light brown THF solution was decanted from the excess of zinc, zinc amalgam and unreacted **1c**. A sample of the THF solution was evaporated to dryness and the residue was dissolved in $\text{THF-}d_8$. The ^1H NMR spectrum showed the presence of **1b** and **1g** in a ratio of 3:1. Titration [8] of an aliquot of the THF solution indicated the formation of (**1b** + **1g**) in 23% yield.

1g: ^1H NMR (200 MHz, $\text{THF-}d_8$, ref. $\text{THF-}d_7$ δ = 1.75 ppm; tentative assignments by comparison with data of **1b** and **1c** [7]): δ = 7.84 (dd, $^3J_{\text{HH}}$ = 7.6 Hz, $^4J_{\text{HH}}$ = 1.4 Hz, 1H, H(7)), 7.62 (dd, $^3J_{\text{HH}}$ = 6.9 Hz, $^4J_{\text{HH}}$ = 1.4 Hz, 1H, H(2)), 7.55 (dd, $^3J_{\text{HH}}$ = 7.6 Hz, $^4J_{\text{HH}}$ = 1.4 Hz, 1H, H(4)), 7.37 (dd, $^3J_{\text{HH}}$ = 6.6 Hz, $^4J_{\text{HH}}$ = 1.3 Hz, 1H, H(5)), 7.30 (dd, $^3J_{\text{HH}}$ = 7.6 Hz, $^3J_{\text{HH}}$ = 6.6 Hz, 1H, H(3 or 6)), 7.26 (dd, $^3J_{\text{HH}}$ = 7.5 Hz, $^3J_{\text{HH}}$ = 6.6 Hz, 1H, H(3 or 6)). ^{13}C {H} NMR (62.9 MHz, $\text{THF-}d_8$, ref. $\text{THF-}d_8$ $\delta(\text{C}(1))$ = 67.4 ppm) δ = 164.2 (C(8)), 152.2 (C(1)), 136.5 (C(7)), 133.9 (C(4)), 128.5 (C(5)), 127.5 (C(2)), 124.9 (C(3 or 6)), 124.6 (C(3 or 6)). ^{199}Hg NMR (71.6 MHz, $\text{THF-}d_8$, ref. Me_2Hg δ = 0 ppm): δ = -326.4.

Reaction of **1g** with deuterium oxide: formation of **2**

To a 3:1 mixture of **1b** and **1g** (ca. 0.1 mmol) in THF obtained as described above, an excess of deuterium oxide was added at room temperature. After addition of diethyl ether, a colorless solution with a fine grey precipitate was obtained. After settling of the precipitate, the supernatant solution was decanted, evaporated to dryness and the residue was examined by GCMS which showed the presence of **3** only. The grey precipitate was dissolved in $\text{DMSO-}d_6$ and a ^1H NMR spectrum was measured which showed **2** as the only compound. The spectrum was in accordance with a ^1H NMR spectrum of **2** simulated with the program PANIC [9]; for the undeuterated parent compound (unresolved ^1H NMR spectrum!) see ref. [10].

2: ^1H NMR (200 MHz, $\text{DMSO-}d_6$, ref. $\text{DMSO-}d_5$ δ = 2.50 ppm): 7.95 (dd, $^3J_{\text{HH}}$ = 8.2 Hz, $^4J_{\text{HH}}$ = 1.4 Hz, 1H, H(5)), 7.87 (dd, $^3J_{\text{HH}}$ = 6.7 Hz, $^4J_{\text{HH}}$ = 1.2 Hz, 1H, H(2)), 7.83 (dd, $^3J_{\text{HH}}$ = 8.2 Hz, $^4J_{\text{HH}}$ = 1.2 Hz, 1H, H(4)), 7.60 (dd, $^3J_{\text{HH}}$ = 6.7 Hz, $^3J_{\text{HH}}$ = 8.1 Hz, 1H, H(3)), 7.56 (dd, $^3J_{\text{HH}}$ = 6.8 Hz, $^4J_{\text{HH}}$ = 1.4 Hz, 1H, H(7)), 7.50 (dd, $^3J_{\text{HH}}$ = 8.2 Hz, $^3J_{\text{HH}}$ = 6.8 Hz, 1H, H(6)).

Association measurements of **1b**

The association measurements of **1b** were performed by the method of stationary isothermal distillation [11]. Relevant data are presented in Table 1.

Table 1. Degree of association of 1,8 naphthalenediylzinc (**1b**) in THF at 301 K.

$[\text{C}_{10}\text{H}_6\text{Zn}]^a$	S_{th}^b	S_a^c	i^d
2.968	0.1244	0.0628	1.98
5.659	0.2371	0.1135	2.09
8.111	0.3398	0.1669	2.04
10.35	0.4338	0.2082	2.08
12.41	0.5201	0.2521	2.06
14.31	0.5996	0.2915	2.06

^a $[\text{C}_{10}\text{H}_6\text{Zn}]$ = formal concentration of monomeric $\text{C}_{10}\text{H}_6\text{Zn}$ in $\mu\text{mol}\cdot\text{g}^{-1}$. ^b S_{th} = theoretical rate of evaporation (in $\text{mm}\cdot\text{h}^{-1}$) = $[\text{C}_{10}\text{H}_6\text{Zn}]\cdot S_s$, where S_s is the standard rate of evaporation found by calibration of the apparatus with triphenylmethane, $S_s = 41.90 \text{ mm}\cdot\text{h}^{-1}\cdot\text{mmol}^{-1}\cdot\text{g}$. ^c Apparent rate of evaporation in $\text{mm}\cdot\text{h}^{-1}$. ^d Association number $i = S_{\text{th}}/S_a$.

RESULTS AND DISCUSSION

Inspired by the successful preparation of 1,2-phenylenezinc by transmetalation of 1,2-phenylenemercury with metallic zinc [12], we envisaged the synthesis of **1b** in a similar fashion from 1,8-naphthalenediylmercury (**1c**) [7] (Scheme 1).

For this purpose, **1c** was reacted with metallic zinc in THF at room temperature. The progress of the reaction was monitored by the disappearance of the sparingly soluble **1c**. After four days of stirring, only 8% of **1b** (and/or **1g**, vide infra) had been formed as indicated by titration after hydrolysis of a sample [8]. When the reaction mixture was heated to 50 °C, the combined yield of **1b** and **1g** was increased to 23% after one week of stirring. At this stage, a sample was obtained by decanting the clear light brown solution from the slurry of insoluble **1c**, zinc amalgam and excess of zinc. According to the ^1H NMR spectrum of this sample in $\text{THF-}d_8$, two compounds were present: **1b** and **1g**.

Scheme 1

The latter was identified as follows. In the ¹⁹⁹Hg NMR spectrum of the sample, a resonance at $\delta = -326.4$ ppm was observed which indicated the presence of one aryl-Hg-aryl bond since in **1c**, the resonance for the mercury nucleus is found at $\delta = -298.0$ ppm. Furthermore, when the sample was deuterolyzed, [1,8-D₂]naphthalene (**3**; GCMS, ¹H NMR) and a grey precipitate were formed. The precipitate was identified as [8,8'-D₂]-1,1'-dinaphthylmercury (**2**) (Scheme 1) by its ¹H NMR spectrum in DMSO-*d*₆. From these results, we tentatively suggest that **1g** is an intermediate in the transmetalation reaction of **1c** with zinc.

After prolonged stirring of the reaction mixture for three weeks at 50 °C, the resulting clear brownish solution was carefully decanted from the amalgam to give **1b** in 77% yield according to titration. Pure **1b** was isolated by evaporation of the THF solution and washing the residue with benzene. Although **1b** is slightly soluble in benzene, it could be isolated in 51% yield as determined by titration after hydrolysis [8]. Unfortunately, crystals suitable for an X-ray crystal structure determination could not be obtained. However, the structure of **1b** in THF solution was determined by the method of stationary isothermal distillation [11] which furnished a concentration independent degree of association of 2.05 (Table 1), suggesting a dimeric structure as indicated in Scheme 1.

Scheme 2

X-Ray crystal structures of analogous dimers with eight-membered central rings have been reported for **1c** [7] and for the group 14 analogues **1d,e** [13] and **1f** [14]. Due to strong Hg...Hg interactions, the structure of **1c** is slightly distorted, but as a whole, the molecule is practically planar. As zinc is a much stronger Lewis acid than mercury, it is probably coordinated by two molecules of THF per zinc atom as was experimentally observed for dimeric 1,2-phenylenezinc [12]. This substitution pattern is expected to cause too much strain for the structure to remain planar; therefore, we assume that **1b** will adopt a structure with a chair-like folding of the central eight-membered ring similar to that found in the crystal structures of **1d-f** where E resides slightly above and below the planes of the naphthalene ring systems (Scheme 2).

However, in **1d-f**, the bond angles C-E-C are 123 – 128° which deviates considerably from the normal

tetrahedral values. The ensuing strain will be less severe in **1b** because in diorganozinc compounds in which the zinc atom is surrounded by two organic groups and two THF molecules, C-Zn-C bond angles usually are 140 - 160°, and as a consequence, the distortion of the naphthalene moiety from planarity of **1b** is probably less pronounced. A boat conformation is unlikely, because in that case, the two syn THF ligands will suffer from steric congestion across the eight-membered ring.

The dimeric structure of **1b** is in line with expectation. It is not surprising that **1b** is not a monomer because the strain in the four-membered ring (see compounds **1**; $n = 1$ with both C-Zn bonds represented by solid lines) would be prohibitive. As the C-Zn bonds do interchange in solution, the system will tend to adopt the thermodynamically most favorable situation. Associates higher than dimeric are not observed and are not likely either for the following reasons. Once the most serious strain has been relieved by changing from monomer to dimer, further oligomerization would leave the strain situation unaffected because the unfavorable *peri*-interactions remain essentially the same in a trimer or in a higher associate. At the same time, as entropy becomes more negative by the decrease of particles, the system is protected against further oligomerization. In this regard, only the magnesium analogue **1a** is an exception as it is a tetramer consisting of a central tetrahedron of four magnesiums surrounded by four naphthalenediyl units and four THF ligands; this has been rationalized as being due to the increased ionic character of the magnesium-carbon bond [1,2]. However, the balance between the different oligomers may be subtle as illustrated by the related case of 1,2-phenylenezinc which is strictly trimeric in solution, but it crystallizes as the dimer [12].

CONCLUSION

The cyclic organozinc compound **1b** was prepared from the corresponding cyclic organomercury compound **1c** by transmetalation with metallic zinc; this conversion takes place via the intermediate zinc-mercury derivative **1g**. Compound **1b** is dimeric as determined by its degree of association in THF solution. Due to the presumably tetrahedral coordination of the zinc atoms to two carbons and two THF ligands, it is suggested that the structure of **1b** closely resembles that of **1d-f**, the analogous 1,8-bis(dimethylelement)naphthalenes of group 14.

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