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The preparation of 1,3-dizincapropanes via a boron–zinc transmetallation

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Abstract

The reaction of 1,3-diethylborylpropane and the corresponding 3-mercurio derivatives were prepared by hydroboration of the allylic precursor and were treated with diethylzinc leading to the corresponding 1,3-bimetallic reagents which, based on their sharp NMR signals, were tentatively considered as eight-membered rings. Their reaction with reactive electrophiles like allylic bromides or propargyl bromide, benzoyl chloride and ethyl propiolate in the presence of CuCN·2LiCl provided the desired 1,3-adducts in fair to good yields. These sensitive 1,3-dimetallics proved not to be suited for reactions with less reactive organic electrophiles, and hydride-transfer reactions were observed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Zinc; Boron; Transmetallation

1. Introduction

1,3-Dimetallic compounds of main group elements are useful building blocks for the preparation of metallacyclic transition metal complexes [1]. Applications of these dimetallic species for organic synthesis has been less frequent due to the difficult preparation of these organometallics. Thus, the reaction of 1,3-dibromopropane with various metals including lithium, magnesium or zinc affords cyclopropane as the major reaction product and 1,3-dimetallic compounds can only be obtained in modest yields [2]. Recently, we reported the preparation of 1,3-dizincapropanes **1a-b** [3] using a boron–zinc exchange reaction [4]. Herein, we wish to report some of the aspects of the reactivity of **1a-b** toward organic electrophiles as well as the preparation and reactivity of the corresponding mixed 1,3-bimetallic of zinc and mercury (**2**).

2. Results and discussion

The reaction of allylic zinc bromides **3a-b** [5] with diethylthiophenylborane (**4**) [6] furnishes the allylic diethylboranes **5a-b**. The sensitive organoboranes can be isolated in pure form by distillation under reduced pressure (53–67%). The hydroboration of **5a-b** with diethylborane [4] gives the expected 1,3-diethylborylpropane derivatives **6a-b** in 82–85% yield as a clear oil. Similarly, the hydroboration of diallylmercury (**7**) [7] with diethylborane [4,8] at −30°C affords the mixed 1,3-bimetallic of mercury and boron (**8**) (Scheme 1).

The 1,3-bimetallic **8** was directly used for the preparation of **2** since all attempts to purify this compound led to decomposition. The 1,3-diboron derivatives (**6a-b**) and **8** undergo a smooth boron–zinc exchange reaction by treatment with Et_2Zn (four equivalents, neat, 0°C, 0.5 h) leading, after removal of the excess Et_2Zn by vacuum, to the crude 1,3-dizincapropanes **1a-b**, which are obtained as sole products as shown by ^1H- and ^{13}C-NMR analysis (see Scheme 2 and Section 4).

Based on NMR experiments as well as on the extensive studies of Bickelhaupt on the structural behavior of

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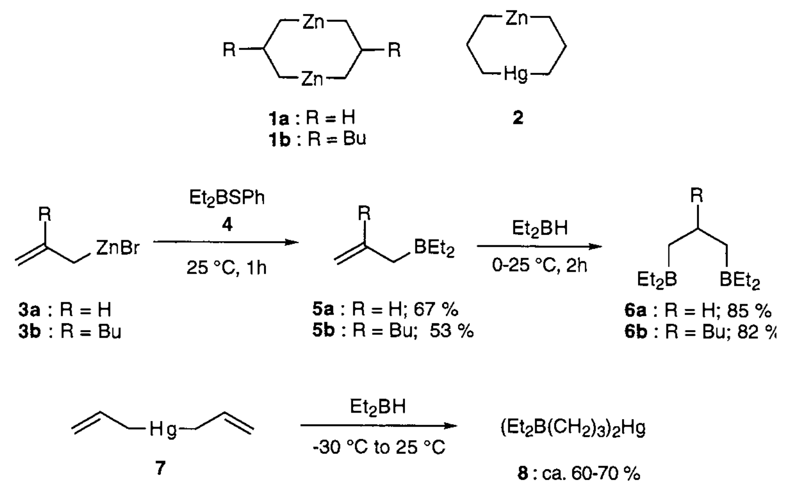


Scheme 1.

1,5-, 1,6- and 1,7-dizincaalkanes [9], we favor an eight-membered cyclic structure for **1a-b**, as well as for **2**, rather than an open-chain polymeric structure ($(-ZnCH_2CH_2CH_2-)_n$ or $((CH_2)_3Hg-(CH_2)_3-Zn)_n$, since the ^{13}C-NMR spectra of **1b** shows a sharp set of signals with two signals for carbon C(1), C(2) and C(3), which can be explained assuming the existence of *cis* and *trans* isomers, respectively *cis*-**1b** and *trans*-**1b**, in an approximate ratio of 46:54 (Scheme 3).

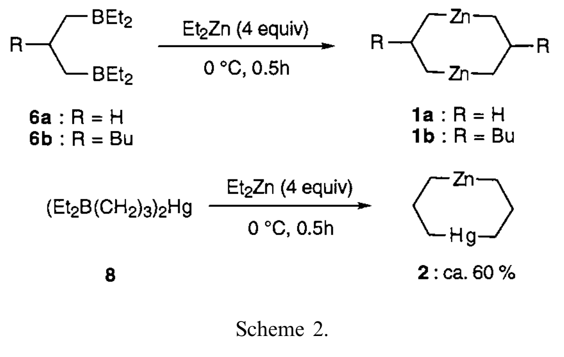
These 1,3-bimetallics of zinc display a low reactivity toward organic electrophiles like most organozinc compounds. However, after transmetallation to the corresponding copper–zinc compounds by adding the terahydrofuran (THF) soluble copper salt CuCN·2LiCl, the reaction with reactive electrophiles like allylic halides furnishes the expected allylated products **9a**–**d** in 84–88% yield. With propargyl bromide, the formation of the 1,3-bisallenylated product (**10**) is obtained in 48% yield. Unsaturated electrophiles like ethyl propiolate provide the bisMichael adduct (**11**) in 40% yield. Finally, the reaction of **1a-b** with benzoyl chloride in the presence of CuCN·2LiCl furnishes the 1,5-diketone (**12a-b**) in 38–40% yield (Scheme 4). Reactions with other classes of electrophiles like aldehydes, less reactive acid chlorides or enones did not lead to the desired 1,3-adducts. Reduction of several of these electrophiles (tosyl cyanide [10], benzaldehyde) was observed showing that **1a-b** play the role of a hydride donor.

The 1,3-bimetallic of zinc and mercury has a similar chemical behavior and reacts in the presence of CuCN·2LiCl [11] with allylic halides, benzoyl chloride, nitrostyrene, ethyl propiolate and 3-iodo-2-cyclohexen-1-one [12] affording the expected polyfunctional diorganomercurials (**13a**–**e**) in 40–58% yield (Scheme 5).

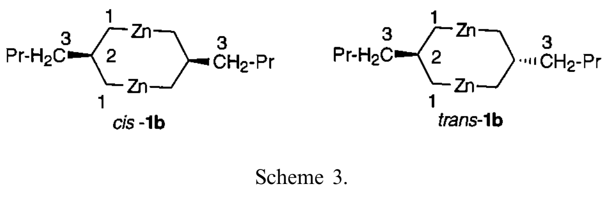
As a synthetic application, we have examined the performance of cyclization reactions using bisfunctional electrophiles. Thus, the reaction of **1b** with 1,4-dibromo-2-butyne (**14**) [13,14] in the presence of CuCN·2LiCl affords the sensitive 1,2-bis(*exo*-methylene)cyclopentane (**15**) in 48% yield (Scheme 6).

3. Conclusion

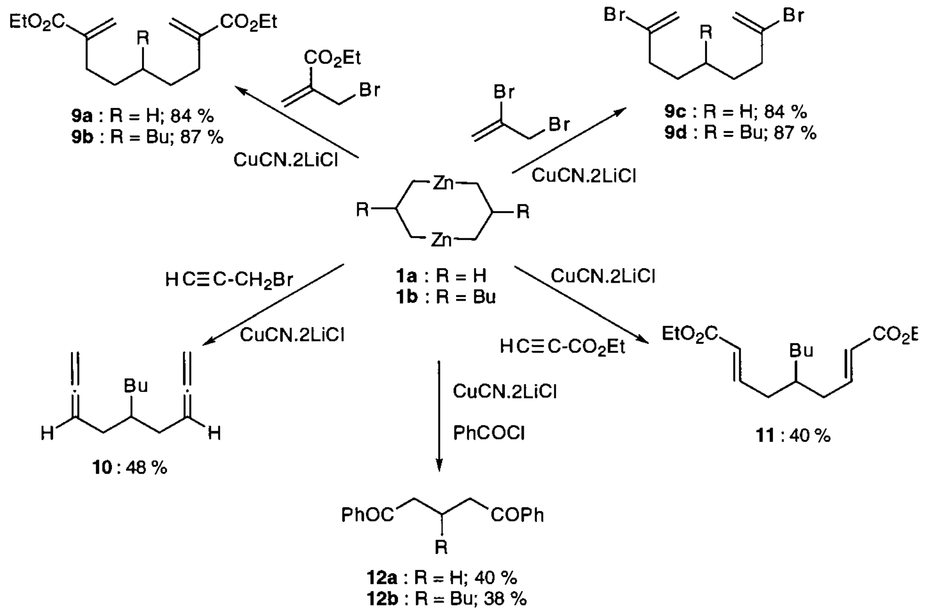
We have prepared several 1,3-bimetallic compounds of zinc and mercury and have reacted them with organic electrophiles in the presence of a copper catalyst leading to 1,3-disubstituted products in good to moderate yield. A new access method to polyfunctional diorganomercurials was developed and a new cyclization to a bis(*exo*-methylene)cyclopentane was performed. The limited stability of the bis-metallic reagents **1a-b** and **2** did not allow further extension of the scope of these quenching reactions.



Scheme 2.



Scheme 3.



Scheme 4.

4. Experimental

All reactions were carried out under argon atmosphere using standard Schlenk techniques. THF was distilled from sodium benzoquinone immediately before use. Diethylthiophenylborane (**4**) [6], diallylmercury (**7**) [7], allylzinc bromide [5], 3-iodo-2-cyclohexen-1-one [12], 1,4-dibromo-2-butyne [14], ethyl (2-bromomethyl)acrylate [15] were prepared according to the literature procedures.

4.1. General experimental procedure

4.1.1. Preparation of allyl(diethyl)borane (5a)

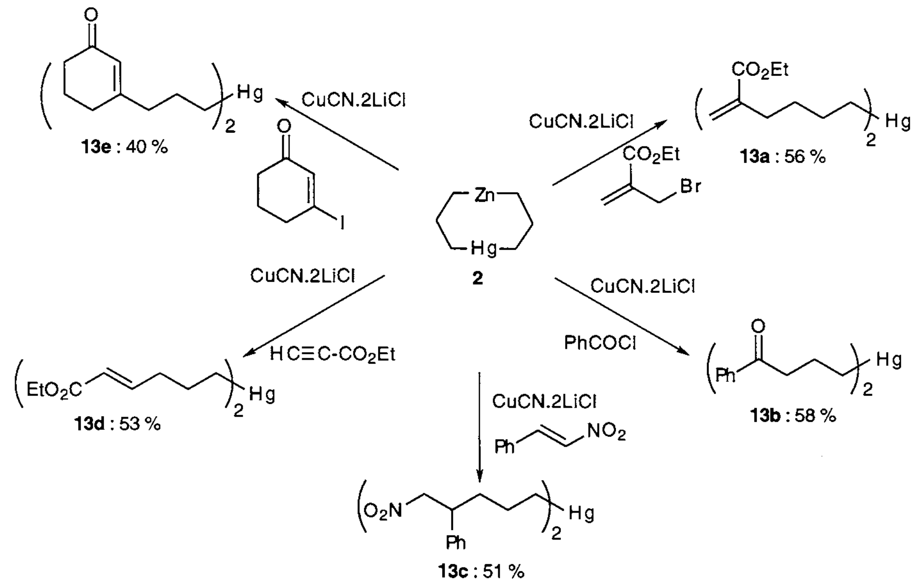
A 250 ml three-necked flask equipped with a magnetic stirrer, an argon inlet, an addition funnel and a thermometer was charged with cut zinc foil (10.5 g, 160 mmol), THF (8 ml) and 1,2-dibromoethane (900 mg, 4.8 mmol). The flask was briefly heated to activate the zinc foil. The reaction mixture was treated with chlorotrimethylsilane (290 mg, 2.7 mmol) and cooled after 5 min to 0°C. Allyl bromide (19.4 g, 160 mmol) in THF (70 ml) was added slowly in order to keep the temperature below 8°C. After the end of the addition, the reaction mixture was stirred for 1 h and the resulting allylzinc bromide was ready to use [5]. Gas chromatography analysis of hydrolyzed and iodolyzed reaction aliquots (containing an internal standard like decane) allow a yield estimate of ca. 80%. This zinc reagent was treated with diethylthiophenylborane (**4**) [6] (28.5 g, 160 mmol) at 0°C. The reaction mixture was allowed to warm to 25°C and the solvent was distilled off by treating with an oil bath to 150°C, the fractions at 110–115°C were collected and contained the sensitive allylic borane **5a**, which was characterized by NMR spectroscopy (11.8 g, 107 mmol, 67% yield). ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 5.77–5.98 (m, 1H), 4.70–4.95 (m, 2H), 2.00–2.20 (s, br, 2H), 1.00–1.25 (m, 4H), 0.70–1.00 (m, 6H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 135.8, 113.5, 34.0 (br), 19.5 (br), 7.8.

4.1.2. Preparation of (2-butylallyl)borane (5b)

The same procedure as described for **5a** was applied using zinc foil (6.86 g, 92 mmol), 2-bromomethylhexene (11.33 g, 64 mmol) and diethylthiophenylborane (**4**) (11.40 g, 64 mmol). The crude product was purified rapidly with fast distillation by heating the reaction flask to 100°C. This product was redistilled carefully furnishing the desired product (**5b**) (8.51 g, 49 mmol, 53% yield). ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 4.58–4.77 (m, 1H), 4.37–4.58 (m, 1H), 2.04–2.25 (m, 2H), 1.88 (t, 2H, $J = 7.3$ Hz), 1.27–1.42 (m, 4H), 1.16 (q, 4H, $J = 7.7$ Hz), 0.90 (t, 3H, $J = 7.6$ Hz), 0.85–0.92 (m, 6H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 149.1, 109.5, 38.6, 37.0 (br), 30.1, 22.6, 20.0 (br), 14.0, 8.2.

4.1.3. Preparation of 1,3-bis(diethylboryl)propane (6a)

Diethylborane was prepared by mixing commercially available $BH_3 \cdot Me_2S$ and Et_3B in the ratio 1:2. The resulting solution can be stored in the refrigerator for several weeks [8]. Diethylborane (12 mmol) was cooled to 0°C and diethylallylborane (**5a**) (1.32 g, 12 mmol) was added. The reaction mixture was stirred for 2 h at 25°C and the unreacted boranes and methyl sulfide was evaporated at 0°C under vacuum (0.1 mmHg). The air-sensitive 1,3-diborane (**6a**) was characterized only by NMR spectroscopy. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 1.46–1.58 (m, 2H), 1.12–1.24 (m, 12H), 0.85–0.95 (t,



Scheme 5.

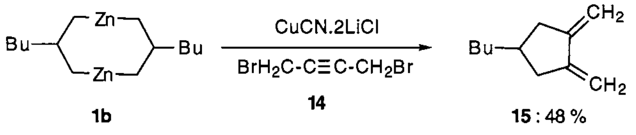
12H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 31.5 (br), 19.2 (br), 18.9, 8.2.

*4.1.4. Preparation of 1,3-bis(diethylboryl)-2-butylpropane (**6b**)*

The product **6b** was prepared using the same procedure as for **6a** with the allylic borane **5b** (2.14 g, 12.9 mmol) and diethylborane (12.9 mmol) resulting in the formation of **6b** as a clear liquid after evaporation of the solvents. This sensitive material was characterized only by NMR spectroscopy. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.00–1.40 (m, 19H), 0.78–1.00 (m, 15H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 40.8, 37.6 (br), 32.5, 30.2, 23.0, 19.9 (br), 14.2, 8.3.

*4.1.5. Preparation of bis(3-diethylborylpropyl)mercury (**8**)*

Diallylmercury (**7**) [7] (420 mg, 1.5 mmol) was dissolved in dry ether and cooled at −30°C in a Schlenk tube protected from light (wrapped in aluminium foil). Diethylborane (5 mmol) was added dropwise and the reaction mixture was allowed to warm to r.t. and was stirred for 1.5 h. Excess diethylborane was pumped off at 0°C (0.1 mmHg) resulting in the formation of the sensitive 1,3-dimetallic **8**, which was used directly for the next step (preparation of **2**). It was only characterized by ^{1}H- and ^{13}C-NMR spectroscopy. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 1.94 (q, 2H, $J=8$ Hz), 1.27 (t, 2H, $J=8$ Hz), 1.17 (q, 4H, $J=8$ Hz), 1.05 (t, 2H, $J=8$ Hz), 0.91 (t, 6H, $J=8$ Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 48.2, 34.0 (br), 23.6, 18.9 (br), 8.2.



Scheme 6.

*4.1.6. Preparation of 1,5-dizincacyclooctane (**1a**)*

The 1,3-diboron derivative **6a** (5 mmol) was treated neat with Et_2Zn (2.0 ml, 20 mmol) and the reaction mixture was stirred for 0.5 h at 0°C and the excess Et_2Zn was removed by vacuum (3 h, 0.1 mmHg followed by 1 h at 25°C and 0.1 mmHg). The resulting crude **1a** is a gray oil containing small amounts of zinc powder. The dizinc reagent can be stored at 0°C for 24 h with little decomposition. This sensitive material was characterized by NMR spectroscopy and used crudely for the next step (reaction with electrophiles). ^{1}H-NMR (THF-d_8, 300 MHz): δ 1.82 (m, 4H), 0.22 (m, 8H). ^{13}C-NMR (THF-d_8, 75.5 MHz): δ 27.7, 22.4.

*4.1.7. Preparation of 1,5-dizinca-3,7-dibutylcyclooctane (**1b**)*

This product was prepared as described for **1a** using the 1,3-diborane derivative **6b** (464 mg, 1.97 mmol) and Et_2Zn (0.79 ml, 7.88 mmol). The crude product **1b** was used directly for further transformations (reactions with electrophiles). It was characterized only by NMR spectroscopy. ^{1}H-NMR (THF-d_8, 500 MHz): δ 2.10–2.20 (m, 2H), 1.10–1.35 (m, 12H), 0.80–0.95 (m, 6H), 0.30–0.55 (m, 8H). ^{13}C-NMR (THF-d_8, 125 MHz): δ 49.2, 48.5, 39.0, 38.6, 32.1, 31.6, 31.6, 31.3, 24.5, 15.0.

*4.1.8. Preparation of 1-zinca-5-mercuriocyclooctane (**2**)*

The crude mercury compound **8** prepared in the quantities as described above was treated with Et_2Zn

(0.6 ml, 6 mmol) at 0°C and was stirred for 0.5 h. The excess of Et_2Zn was removed by vacuum (0°C, 0.1 mmHg, 2 h and 25°C, 2 h) providing the crude zinc reagent **2** which was used directly for further transformations. This sensitive material was characterized by NMR spectroscopy. ^{1}H-NMR (THF-d_8, 300 MHz): δ 2.59 (m, 2H), 1.05 (t, 2H, $J = 10.0$ Hz), 0.20 (t, 2H, $J = 10.0$ Hz). ^{13}C-NMR (THF-d_8, 75.5 MHz): δ 49.2, 29.2, 18.8.

*4.1.9. Typical procedure for the reaction of a 1,3-dimetallic reagent (**1a** or **1b**) with an electrophile. Preparation of 2,8-dibromo-1,8-nonadiene (**9c**)*

The 1,3-bimetallic reagent **1a** prepared from the 1,3-diboron derivative **6a** (0.88 g, 4.9 mmol) was treated with Et_2Zn (2.0 ml, 20 mmol) as described above. The resulting 1,3-dizinc reagent **1a** was diluted in THF (8 ml) cooled to − 60°C and a solution of CuCN (890 mg, 10 mmol) and LiCl (850 mg, 20 mmol) in THF (12 ml) was added, followed after 5 min with 2,3-dibromopropene (2.93 g, 16.7 mmol). The reaction mixture was allowed slowly to warm to 25°C and stirred for 0.5 h. After the usual work-up, the resulting crude oil obtained after evaporation of the solvents was purified by flash chromatography using hexanes:ether (19:1) affording the desired product (**9c**) (1.16 g, 4.1 mmol, 84% yield) as a yellowish oil. IR (neat): 2938 (s), 1630 (s), 885 (s), 734 (w) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.55 (m, 2H), 5.38 (m, 2H), 2.44 (t, 4H, $J = 7.3$ Hz), 1.58 (q, 4H, $J = 7.5$ Hz), 1.22–1.38 (m, 2H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 134.5, 116.4, 41.2, 27.5, 27.0. EI-MS: 203 (M^+–Br, 3), 201, 121 (29), 82 (11), 81 (100), 79 (19), 67 (18). CH-Anal. Calc. for $C_9H_{14}Br_2$ (282.02): C, 38.33; H, 5.00. Found: C, 38.28; H, 5.04%.

*4.1.10. Analytical data of products **9a-b**, **9d**, **10**, **11**, **12a-b** prepared according to the typical procedure (Scheme 4)*

*4.1.10.1. 2,8-Dicarbethoxy-1,8-nonadiene (**9a**).* Compound **9a** (1.23 mg, 4.57 mmol, 88% yield) was obtained using ethyl (2-bromomethyl)acrylate [15] (3.49 g, 18.1 mmol). The crude product was purified by flash chromatography (hexanes:ether, 19:1). IR (neat): 3104 (w), 2982 (s), 2934 (vs), 1719 (vs), 1632 (s), 1179 (vs, br) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 6.04 (s, 2H), 5.42 (s, 2H), 4.11 (q, 4H, $J = 7.1$ Hz), 2.21 (t, 4H, $J = 7.2$ Hz), 1.29–1.45 (m, 6H), 1.21 (t, 6H, $J = 7.1$ Hz). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 167.1, 140.8, 124.0, 60.3, 31.6, 28.6, 28.0, 14.0. EI-MS: 268 (M^+, 4), 223 (30), 194 (83), 149 (42), 148 (40), 121 (100), 81 (97). CH-Anal. Calc. for $C_{15}H_{24}O_4$ (268.35): C, 67.14; H, 9.01. Found: C, 66.85; H, 9.17%.

*4.1.10.2. 5-Butyl-2,8-dicarbethoxy-1,8-nonadiene (**9b**).* Compound **9b** (1.32 g, 4.07 mmol, 84% yield) was obtained using ethyl (2-bromomethyl)acrylate [15] (3.26 g, 16.9 mmol). The crude product was purified by flash chromatography (hexanes:ether, 19:1). IR (neat): 2982 (s), 2934 (vs), 1719 (vs), 1632 (s), 940 (s), 883 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.08 (s, 2H), 5.48 (s, 2H), 4.13 (q, 4H, $J = 7.1$ Hz), 2.20–2.30 (m, 4H), 1.37–1.47 (m, 5H), 1.21–1.31 (m, 12 H), 0.83–0.90 (m, 3H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 167.0, 141.2, 123.8, 60.2, 36.6, 32.7, 32.0, 28.8, 28.5, 22.7, 13.9, 13.8. EI-MS: 324 (M^+, 3), 278 (13), 250 (72), 221 (26), 193 (34), 177 (57), 80 (100). CH-Anal. Calc. for $C_{19}H_{32}O_4$ (324.46): C, 70.34; H, 9.94. Found: C, 70.12; H, 9.68%.

*4.1.10.3. Preparation of 5-butyl-2,8-dibromo-1,8-nonadiene (**9d**).* Compound **9d** (1.41 g, 4.2 mmol, 87% yield) was obtained using 2,3-dibromopropene (3.83 g, 19.2 mmol). The crude product was purified by flash chromatography (hexanes:ether, 19:1). IR (neat): 2928 (vs), 1629 (vs), 1456 (w), 885 (vs) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.56 (s, 2H), 5.37 (s, 2H), 2.41 (t, 4H, $J = 7.6$ Hz), 1.47–1.57 (m, 4H), 1.34–1.45 (m, 1H), 1.21–1.34 (m, 6H), 0.89 (t, 3H, $J = 6.7$ Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 135.0, 116.3, 38.7, 35.1, 32.8, 31.4, 28.6, 23.0, 14.1. EI-MS: 259, 257 (M^+–Br, 1), 177 (14), 137 (17), 95 (99), 81 (100), 67 (61). CH-Anal. Calc. for $C_{13}H_{22}Br_2$ (338.12): C, 46.18; H, 6.56. Found: C, 46.24; H, 6.63%.

*4.1.10.4. Preparation of 5-butyl-1,2,7,8-nonatetraene (**10**).* Compound **10** (0.34 g, 1.93 mmol, 40% yield) was obtained using propargyl bromide (4.09 g, 19.5 mmol). The crude product was purified by flash chromatography (hexanes) affording a sensitive compound that did not give a correct elementary analysis and did not show the molecular peak in mass spectrometric analysis. However, clean ^{1}H- and ^{13}C-NMR spectra could be obtained. IR (neat): 2926 (vs), 1956 (s), 1440 (m), 841 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300MHz): δ 5.02 (q, 2H, $J = 7.1$ Hz), 4.58–4.65 (m, 4H), 1.97–2.07 (m, 4H), 1.49 (sept, 1H, $J = 6.1$ Hz), 1.21–1.39 (m, 6H), 0.83–0.95 (m, 3H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 209.2, 87.8, 73.9, 37.9, 32.6, 32.2, 28.8, 22.9, 13.9. EI-MS: 147 (M^+–C_2H_5, 5), 133 (15), 122 (47), 105 (54), 91 (68), 79 (74), 41 (100).

*4.1.10.5. Preparation of (E),(E)-1,7-dicarbethoxy-4-butyl-1,6-heptadiene (**11**).* Compound **11** (540 mg, 2.25 mmol, 40% yield) was obtained using ethyl propiolate (1.65 g, 16.8 mmol) and the 1,3-diboron derivative **6b** (1.01 g, 5.6 mmol), and performing the reaction at − 15°C for 3 h. The crude product was purified by flash chromatography (hexanes:ether, 8:1). IR (neat): 2982 (s), 1722 (vs), 1655 (s), 1368 (s), 1268 (s, br), 1044 (s), 980 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 6.81 (dt, 2H, $J = 15.6$ and 9.0 Hz), 5.71 (dt, 2H, $J = 15.7$ and 1.5 Hz), 4.06 (q, 4H, $J = 7.1$ Hz), 2.12 (q, 4H, $J = 7.4$ Hz), 1.53 (q, 2H, $J=7.4$ Hz), 1.16 (t, 6H, $J=7.1$ Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 165.9, 147.5, 121.6, 59.7, 30.9, 25.9, 13.8. EI-MS: 240 (M^+, 8), 195 (51), 166 (44), 121 (27), 98 (31), 93 (63), 81 (100). CH-Anal. Calc. for $C_{13}H_{20}O_4$ (240.30): C, 69.98; H, 8.39. Found: C, 69.76; H, 8.39%.

*4.1.10.6. Preparation of 1,5-diphenyl-1,5-pentadione (**12a**).* Compound **12a** (560 mg, 2.22 mmol, 42% yield) was obtained using benzoyl chloride (1.80 g, 12.8 mmol) and the 1,3-diboron derivative **6a** (0.96 g, 5.33 mmol). The crude product was purified by flash chromatography (hexanes:ether, 9:1). The product was obtained as a white solid (m.p. 61°C). IR (KBr): 3064 (w), 2970 (w), 1679 (vs), 1281 (s), 730 (s), 688 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.88–8.02 (m, 4H), 7.32–7.54 (m, 6H), 3.08 (t, 4H, $J=7.0$ Hz), 2.12–2.21 (q, 2H, $J=7.0$ Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 199.6, 136.7, 132.9, 128.4, 127.9, 37.4, 18.7. EI-MS: 252 (M^+, 12), 133 (18), 120 (29), 105 (100), 77 (49), 51 (10). CH-Anal. Calc. for $C_{17}H_{16}O_2$ (252.12): C, 80.93; H, 6.39. Found: C, 80.74; H, 6.50%.

*4.1.10.7. Preparation of 1,5-diphenyl-3-butyl-1,5-pentadione (**12b**).* Compound **12b** (600 mg, 1.93 mmol, 38% yield) was obtained using benzoyl chloride (2.14 g, 15.2 mmol) and starting from the 1,3-diboron derivative **6b** (1.20 g, 5.1 mmol). The crude product was purified by flash chromatography (hexanes:ether, 6:1). IR (neat): 3063 (w), 2929 (s), 1769 (m), 1684 (vs), 1597 (m), 1449 (s), 753 (s), 690 (vs) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.86–7.94 (m, 4H), 7.32–7.50 (m, 6H), 2.86–3.10 (m, 4H), 2.67 (sept, J = 6.5 Hz, 1H), 1.32–1.43 (m, 2H), 1.12–1.31 (m, 4H), 0.78 (t, 3H, $J=7.1$ Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 199.9, 137.1, 132.9, 128.5, 128.1, 43.0, 33.8, 31.2, 29.0, 22.7, 13.9. EI-MS: 308 (M^+, 1), 189 (34), 105 (100), 77 (44). CH-Anal. Calc. for $C_{21}H_{24}O_2$ (308.42): C, 81.78; H, 7.84. Found: C, 81.88; H, 7.93%.

*4.1.11. Typical procedure for the reaction of the 1,3-bimetallic of mercury and zinc (**2**) with electrophiles in the presence of CuCn · 2LiCl*

*4.1.11.1. Preparation of bis(5-carbethoxy-5-hexenyl)mercury (**13a**).* The 1,3-bimetallic **2**, prepared as described above, was dissolved in THF (5 ml). A solution of CuCN (270 mg, 3 mmol) and LiCl (250 mg, 6 mmol) in THF (3 ml) was added at −78°C. The reaction mixture was warmed up to 0°C and cooled back to −78°C after 5 min. Ethyl (2-bromomethyl)acrylate [15] (410 mg, 2.1 mmol) in THF (2 ml) was added and the reaction mixture was warmed up to 0°C and kept for 2 h. It was worked-up as usual. The crude product obtained after evaporation of the solvents was purified by flash chromatography (hexanes:ether, 19:1) yielding the compound **13a** as an oil (300 mg, 56% yield). IR (neat): 2924 (s), 1717 (s), 1630 (m), 1160 (s), 861 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 6.05 (s, 2H), 5.44 (s, 2H), 4.13 (q, 4H, $J=7.2$ Hz), 2.24 (t, 4H, $J=6$ Hz), 1.72–1.86 (m, 4H), 1.36–1.48 (m, 4H), 1.23 (t, 4H, $J=7$ Hz), 0.99 (t, 6H, $J=7.2$ Hz). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 167.8, 141.6, 124.5, 60.9, 44.3, 34.5, 32.1, 28.8, 14.6. EI-MS: 512 (M^+, 0.1), 510 (M^+, 0.1), 357 (2), 200 (0.6), 156 (49), 155 (66), 127 (51), 109 (88), 81 (100). CH-Anal. Calc.: C, 42.30; H, 5.93. Found: C, 42.26; H, 6.16%.

*4.1.11.2. Preparation of bis(4-phenyl-4-oxobutyl)mercury (**13b**).* Compound **13b** (510 mg, 58% yield) was obtained by the reaction of the 1,3-bimetallic **2** (2.5 mmol) with benzoyl chloride (490 mg, 3.5 mmol) at −10°C for 6 h. The crude product was purified by flash chromatography (hexanes:ether, 9:1) yielding the compound **13b** as a solid (m.p. 77°C). IR (neat): 2929 (s), 1681 (s), 1206 (m), 742 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 7.86– 7.90 (m, 8H), 7.36–7.46 (m, 12H), 2.91 (t, 4H, $J=7$ Hz), 2.09–2.24 (m, 4H), 0.98 (t, 4H, $J=7.2$ Hz). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 201.1, 137.2, 132.8, 128.5, 128.1, 43.5, 42.7, 24.2. EI-MS: 496 (M^+, 0.3), 494 (M^+, 0.2), 202 (1), 147 (94), 105 (100), 77 (53), 28 (4). CH-Anal. Calc.: C, 48.52; H, 4.49. Found: C, 48.23; H, 4.35%.

*4.1.11.3. Preparation of bis(5-nitro-4-phenylpentyl)mercury (**13c**).* Compound **13c** (315 mg, 51% yield) obtained by the reaction of β-nitrostyrene (313 mg, 2.1 mmol) with the 1,3-bimetallic **2** (1.5 mmol). Reaction conditions were 0°C, 12 h. The crude product was purified by flash chromatography (hexanes:ether, 5:1). IR (neat): 2921 (s), 1551 (s), 1494 (s), 1453 (s), 764 (s), 702 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 7.07–7.24 (m, 10H), 4.43 (m, 8H), 3.35–3.42 (m, 2H), 1.52–1.59 (m, 8H), 0.87–0.90 (m, 4H). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 138.7, 127.9, 126.5, 126.4, 80.0, 43.1, 42.3, 37.5, 25.0. EI-MS: 586 (M^+, 0.2), 584 (M^+, 0.1), 192 (10), 145 (95), 131 (100), 77 (11). CH-Anal. Calc.: C, 45.17; H, 4.82; N, 4.78. Found: C, 44.91; H, 4.90; N, 4.96%.

*4.1.11.4. Preparation of (E)-bis(5-carbethoxy-4-pentenyl)mercury (**13d**).* Compound **13d** (450 mg, 53% yield) was obtained by the reaction of ethyl propiolate (340 mg, 3.5 mmol) with the bimetallic **2** (2.5 mmol). Reaction conditions were −78°C, 14 h. The crude product was purified by flash chromatography (hexanes:ether, 85:15). IR (neat): 2926 (s), 1719 (s), 1654 (s), 1267 (s), 1043 (m), 987 (m) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 6.81–6.96 (m, 2H), 5.73 (d, 2H, $J=15.6$ Hz), 4.10 (q, 4H, $J=7.2$ Hz), 1.89–2.20 (m, 8H), 1.21 (t, 6H, $J=7$ Hz), 0.96 (t, 4H, $J=7.4$ Hz). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 165.5, 148.9, 120.8, 59.1, 41.9, 36.2, 26.6, 13.3. EI-MS: 484 (M^+, 14), 482 (M^+, 1), 202 (8), 200 (1), 141 (49), 113 (84), 68 (47), 28 (100). CH-Anal. Calc.: C, 39.79; H, 5.43. Found: C, 39.61; H, 5.38%.

*4.1.11.5. Preparation of bis(3-(3-oxocyclohexenyl)propyl)mercury (**13e**).* Compound **13e** (200 mg, 40% yield) was obtained by the reaction of 3-iodo-2-cyclohexenone [12] (460 mg, 2.1 mmol) and the bimetallic **2** (1.5 mmol). Reaction conditions were −10°C, 48 h. Purification by flash chromatography (hexanes:ether, 1:4). IR (neat): 2926 (s), 1665 (s), 1621 (s), 1252 (s), 1192 (s), 886 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 200 MHz): δ 5.80 (s, 2H), 2.14–2.30 (m, 12 H), 1.91–2.02 (m, 8H), 0.95 (t, 4H, $J = 7.4$ Hz). ^{13}C-NMR ($CDCl_3$, 50 MHz): δ 199.9, 167.3, 126.3, 43.6, 43.2, 37.7, 29.9, 26.7, 23.0. EI-MS: 476 (M^+, 1), 474 (M^+, 1), 137 (24), 123 (11), 110 (100), 95 (11). CH-Anal. Calc.: C, 45.52; H, 5.52; Found: C, 45.30; H, 5.65%.

*4.1.12. Preparation of 1-butyl-3,4-dimethylenecyclopentane (**15**)*

Compound **15** (390 mg, 2.6 mmol, 48% yield) was obtained using the typical procedure with the 1,3-diboron derivative **6b** (1.30 g, 5.5 mmol) and 1,4-dibromo-2-butyne (1.46 g, 6.9 mmol) [14]. The crude product was purified by flash chromatography (hexanes) yielding a sensitive compound which was pure by 95% as judged by ^{13}C-NMR and ^{1}H-NMR spectroscopy. IR (neat): 3440 (s, br), 2956 (vs), 2923 (vs), 1672 (s), 1466 (m), 894 (s) cm^{-1}. ^{1}H-NMR ($CDCl_3$, 300 MHz): δ 5.33 (s, 2H), 4.85 (s, 2H), 2.49–2.63 (m, 2H), 2.01–2.13 (m, 2H), 1.81–1.97 (m, 1H), 1.21–1.37 (m, 6H), 0.89–0.95 (m, 3H). ^{13}C-NMR ($CDCl_3$, 75.5 MHz): δ 148.5, 103.5, 40.7, 37.5, 34.9, 30.4, 22.9, 14.1. EI-MS: 150 (M^+, 12), 107 (18), 93 (100), 91 (36), 79 (28).

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