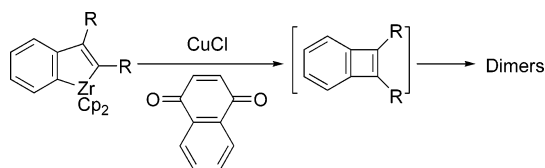# Generation of Benzocyclobutadiene Derivatives from Zirconaindene Derivatives

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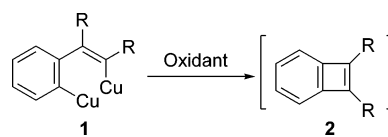
cjxi@tsinghua.edu.cn

Zirconaindene derivatives produced benzocyclobutadiene derivatives in situ in the presence of CuCl and 1,4-naphthoquinone, which afforded their dimers, 6a,10b-dihydrobenzo[a]biphenylenes and dibenzosemibullvalenes or dibenzo[a,e]-cyclooctenes.

Benzocyclobutadiene and its dimers are some of the most attractive molecules.[1] A variety of methods for generating benzocyclobutadiene are known,[2] such as (i) dehalogenation of 1,2-dihalobenzocyclobutene with zinc or lithium amalgam or $Fe_2(CO)_9$,[2a,b,c,j,k] (ii) 1-bromobenzocyclobutene mediated by transition metals,[2e,o,p] and (iii) cycloaddition of benzyne with alkyne.[2n] A conceptually new and simple method using intramolecular oxidative "decomposition" of organic cuprates **1** with oxidants can be considered as a preparative method for the preparation of benzocyclobutadiene derivatives **2**, as shown in Scheme 1. However, this reaction pattern is rarely reported.[3]

SCHEME 1

SCHEME 2

Takahashi et al. reported on the generation of cyclobutadienes from the reaction of zirconacyclopentadienes with CpCo-(PPh₃)₂.[4] Recently, we and another group reported the intramolecular coupling reaction of zirconacyclopentadienes in the presence of CuCl and benzoquinone produced cyclobutadiene derivatives, which easily transformed into cyclooctatetraene (COT) derivatives.[3] Accordingly, we envisioned that the coupling reaction of zirconaindenes **3** under optimized conditions could give benzocyclobutadiene derivatives **2**. Herein we report that zirconaindene derivatives **3** produce benzocyclobutadiene derivatives **2** in situ in the presence of CuCl and 1,4-naphthoquinone (Scheme 2), which easily transformed into their corresponding dimers.

Treating Cp₂ZrPh₂ generated by the reaction of dichlorobis-(cyclopentadienyl)zirconium and PhLi[5] with 3-hexyne, a coupling reaction took place to give zirconaindene **3a**.[6] It was found that **3a** did not undergo intramolecular coupling to afford benzocyclobutadiene even in the presence of 1,4-naphthoquinone. Copper catalyzed or mediated carbon−carbon bond formation reactions of zirconacycles have been reported, and transmetalation of Zr−C bonds to Cu−C bonds has been proven to be an effective methodology for activation of Zr−C bonds.[7] Consequently, addition of 2 equiv of CuCl to the THF solution of **3a** at room temperature in the presence of 1 equiv of 1,4-naphthoquinone afforded only 5,6,6a,10b-tetraethyl-6a,10b-dihydrobenzo[a]biphenylene **4a** within 12 h in good isolated yield (Scheme 3). The ¹H NMR and ¹³C NMR spectra of **4a** were identical with those obtained from an authentic sample of **4a**. Similarly, compounds **4b** and **4c** were isolated in 65% and 58% yield, respectively. Additive adducts of the organic species to 1,4-naphthoquinone were not detected in any of the cases, only naphthlene-1,4-diol was detected.
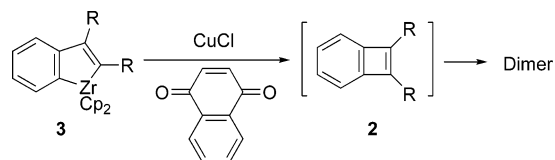
(1) (a) Cava, M. P.; Mitchell, M. J. *Cyclobutadiene and Related Compounds*; Academic Press: New York, 1967. (b) Turro, N. J.; Liu, J.-M.; Zimmerman, H. E.; Factor, R. *J. Org. Chem.* **1980**, *45*, 3511. (c) Miller, L. S.; Grohmann, K.; Dannenberg, J. J. *J. Am. Chem. Soc.* **1981**, *103*, 6249. (d) Heubes, M.; Dietz, T.; Quast, H.; Seefelder, M.; Witzel, A.; Gadgil, V. R.; Williams, R. V. *J. Org. Chem.* **2001**, *66*, 1949. (e) Goren, A. C.; Hrovat, D. A.; Seefelder, M.; Quast, H.; Borden, W. T. *J. Am Chem. Soc.* **2002**, *124*, 3469.
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(6) (a) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.
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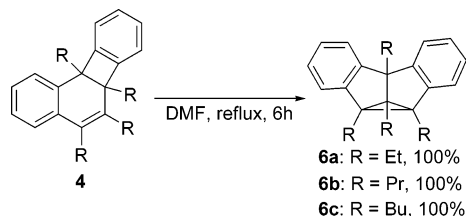
SCHEME 3

SCHEME 4

SCHEME 5

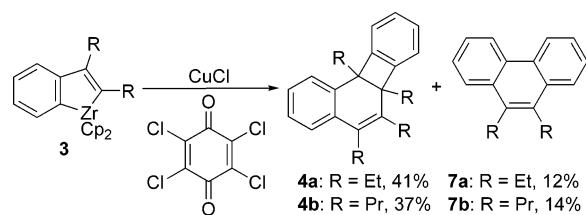6a: R = Et, 100%
6b: R = Pr, 100%
6c: R = Bu, 100%
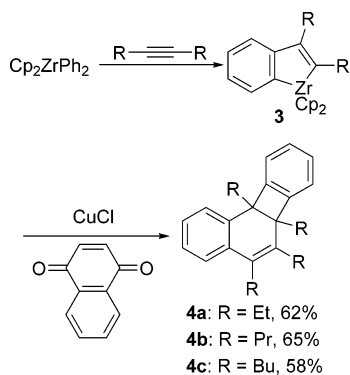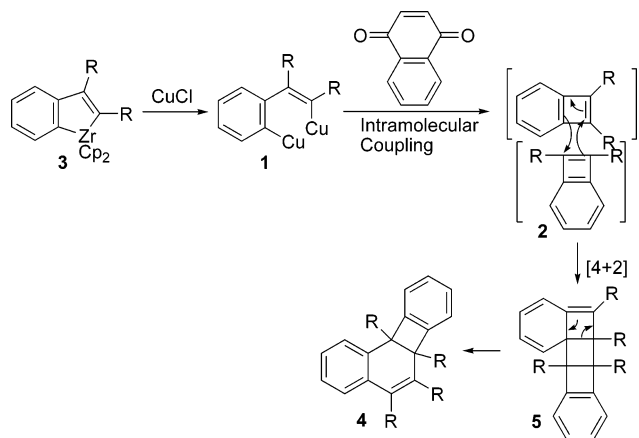
Although the benzocyclobutadiene **2** was not directly obtained, **2** was the most likely intermediate with respect to the above-obtained results. Thus the reaction could be explained by intramolecular oxidative coupling of the 1,4 sp^2 carbon center of **1** to afford benzocyclobutadiene **2**. It underwent intermolecular [4+2] cycloaddition of two molecules of **2** followed by rearrangement of initially formed dimer **5** to give dimer **4**[8,2b,e,j,k] as shown in Scheme 4.
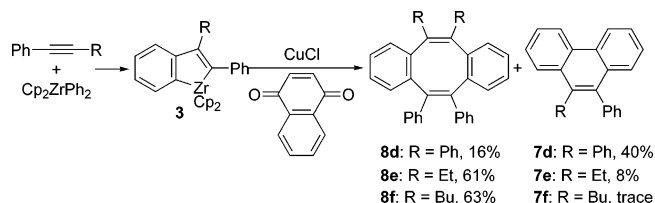
To obtain further experimental evidence for dimeric products, the isolated compound **4** was dissolved in DMF and the solution was heated to reflux (Scheme 5). Within 6 h, **4** disappeared completely and transformed into dibenzosemibullvalence derivatives **6** in a quantitative yield.[2e,k,8] Compound **6** was stable at room temperature and its structure was determined by X-ray analysis (R = Et).[9]

During the course of our study we examined oxidants such as 1,4-benzoquinone, 1,4-naphthoquinone, and *p*-chloranil. 1,4-

(8) (a) Cava, M. P.; Napier, D. R. *J. Am. Chem. Soc.* **1957**, *79*, 1701. (b) Trahanovsky, W. S.; Arvidson, K. B. *J. Org. Chem.* **1996**, *61*, 9528. (c) Wang, K. K.; Liu, B.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 6860.

SCHEME 6

4a: R = Et, 41% 7a: R = Et, 12%
4b: R = Pr, 37% 7b: R = Pr, 14%

SCHEME 7

8d: R = Ph, 16% 7d: R = Ph, 40%
8e: R = Et, 61% 7e: R = Et, 8%
8f: R = Bu, 63% 7f: R = Bu, trace

Naphthoquinone worked as a good oxidant for the generation of benzocyclobutadienes. When 1,4-benzoquinone was used as the oxidant, a complex mixture was obtained. In contrast with the reaction of zirconacyclopentadienes with 1,4-benzoquinone,[3a] this result may be attributed to a proper tuning of the reactivity of zirconaindene and 1,4-naphthoquinone. When *p*-chloranil was used as the oxidant, the intramolecular coupling reaction of zirconaindene in the presence of CuCl at room temperature produced **4**, together with some amount of compound **7**[10] (Scheme 6).

It is noteworthy that in this work no incorporation of quinone species was observed in the product.[11] In other words, quinone is not available to trap the benzocyclobutadienes. Apparently, the quinone is reduced faster than the generation of the proposed reactive intermediate.

To extend the scope of the reaction, diphenyl-substituted zirconaindene **3d** generated in situ by the reaction of Cp$_2$ZrPh$_2$ with diphenyl acetylene was treated with CuCl and 1,4-naphthoquinone. However, 5,6,6a,10b-tetraphenyl-6a,10b-dihydrobenzo[*a*]biphenylene **4d** was not observed, rather 9,10-diphenylphenanthrene **7d** was isolated in 40% yield, together with 5,6,11,12-tetraphenyldibenzo[*a,e*]cyclooctene **8d** in 16% isolated yield. The structure of product **7d** was confirmed by X-ray analysis.[12] Reaction of substituted zirconaindene **3e** or **3f** bearing one phenyl substitutent mainly afforded dibenzo-[*a,e*]cycloctene **8e** or **8f**, together with some amount of **7e** or **7f**. No formation of product **4e** or **4f** was observed. The results indicated that these reactions proceeded by a [2+2] cycloaddition[3a,8] instead of [4+2] cycloaddition due to the steric hindrance of the large substituent.

To clarify whether the product **7** was from zirconaindene or from Cp$_2$ZrPh$_2$ and alkyne, compound **3d** was isolated first[13] and then reacted under the same condition. Compound **8d** was

(9) Crystallographic data for **6a**: colorless plate, triclinic, space group *P*1̄ (no. 2), *a* = 8.5368(8) Å, *b* = 8.8167(10) Å, *c* = 14.2494(15) Å, α = 86.753(8)°, β = 83.833(7)°, γ = 62.065(7)°, *Z* = 2, R1 = 0.0487, *w*R2 = 0.0932, GOF = 1.049.

(10) Kanno, K.-I.; Liu, Y.; Iesato, A.; Nakajima, K.; Takahashi, T. *Org. Lett.* **2005**, *7*, 5453.

(11) Cava, M. P.; Mitchell, M. J.; Deana, A. A. *J. Org. Chem.* **1960**, *25*, 1481.

(12) Crystallographic data for **7d**: colorless needle, tetragonal, space group *P*4$_1$/*a* (no. 88), *a* = 26.953(3) Å, *b* = 26.953(3) Å, *c* = 9.978(3) Å, α = 90°, β = 90°, γ = 90°, *Z* = 16, R1 = 0.0800, *w*R2 = 0.0889, GOF = 0.795.

(13) Choi, S.-B.; Boudjouk, P.; Qin, K. *Organometallics* **2000**, *19*, 1806.

only obtained in 46% yield. No formation of compound **7d** was observed. This result indicated product **7** did not come from compound **3**. Thus, the formation of product **7** was proposed by the reaction of alkynes with benzyne[2n,14] generated from Cp_2-$ZrPh_2$.

In summary, a new and simple method for the preparation of benzocyclobutadiene derivatives via zirconaindene derivatives in the presence of CuCl and quinones has been developed, which provides access to various dimers of benzocyclobutadiene. Further investigation into the mechanism and the scope of the reaction is in progress.

Experimental Section

Typical Procedure for the Preparation of 5,6,6a,10b-Tetra-ethyl-6a,10b-dihydrobenzo[*a*]biphenylene (4a). To a solution of Cp_2ZrCl_2 (1.0 mmol, 0.292 g) in THF (5.0 mL) was added PhLi (2.0 M in Bu_2O, 2.00 mmol) at 0 °C and the mixture was stirred for 1 h. To this solution of diphenylzirconocene in THF was added 3-hexyne (228 μL, 2.0 mmol). The reaction mixture was warmed to room temperature and heated at 80 °C until the solution turned red (about 24 h). After the solution was cooled to 0 °C, CuCl (0.200 g, 2.00 mmol) was added, and the reaction mixture was stirred for 5 min. Then 5.0 mL of THF followed by 1,4-naphthoquinone (1.2 mmol, 190 mg) was added to the suspension. The mixture was stirred at room temperature for 12 h and quenched with 3 N HCl and aqueous layers were extracted with 15 mL of Et_2O five times. The combined organic layers were dried over $MgSO_4$. The solvent was evaporated and the product was purified by column chroma-tography with petroleum ether as eluant to afford a colorless liquid **4a**, 98 mg (isolated yield 62%). ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 0.93 (t, $J = 7.5$ Hz, 3H), 1.04 (t, $J = 7.5$ Hz, 3H), 1.19−1.28 (m, 6H), 2.13−2.32 (m, 3H), 2.44−2.72 (m, 5H), 7.10−7.14 (m, 1H), 7.18−7.31 (m, 5H), 7.38−7.41 (m, 1H), 7.57−7.60 (m, 1H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 11.3, 11.5, 14.2, 15.0, 21.5, 23.7, 25.6, 30.1, 55.8, 59.3, 120.0, 120.6, 123.7, 126.0, 126.2, 126.3, 127.1, 127.5, 131.1, 132.9, 138.3, 138.5, 150.3, 150.7. HRMS calcd for $C_{24}H_{28}$ 316.2191, found 316.2193.

5,6,6a,10b-Tetrapropyl-6a,10b-dihydrobenzo[*a*]biphenylene (4b). A white fatty liquid (121 mg, isolated yield 65%). ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 0.90 (t, $J = 7.5$ Hz, 3H), 0.94 (t, $J = 7.5$ Hz, 3H), 1.00−1.09 (m, 6H), 1.15−1.39 (m, 4H), 1.45−1.62 (m, 4H), 1.88−2.16 (m, 3H), 2.27−2.56 (m, 5H), 7.05−7.29 (m, 7H), 7.51−7.54 (m, 1H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 14.4, 14.6, 14.8, 15.3, 19.9, 20.1, 22.67, 23.7, 30.9, 33.9, 356.0, 40.2, 55.5, 59.0, 120.0, 120.4, 123.7, 125.9, 126.1, 126.2, 127.1, 127.5, 129.3, 133.0, 138.0, 138.9, 150.3, 150.8. HRMS calcd for $C_{28}H_{36}$ 372.2817, found 372.2816.

5,6,6a,10b-Tetrabutyl-6a,10b-dihydrobenzo[*a*]biphenylene (4c). A colorless liquid (124 mg, isolated yield 58%). ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 0.81−0.99 (m, 12H), 1.15−1.33 (m, 8H), 1.43−1.54 (m, 8H), 1.90−2.17 (m, 3H), 2.27−2.54 (m, 5H), 7.00−7.19 (m, 6H), 7.23−7.26 (m, 1H), 7.46−7.49 (m, 1H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 13.91, 13.96, 14.00, 14.1, 23.2, 23.4, 23.6, 23.9, 28.5, 28.7, 29.0, 31.2, 31.6, 32.5, 33.3, 37.8, 55.4, 58.9, 120.0, 120.5, 123.7, 125.9, 126.1, 126.2, 127.1, 127.5, 129.3, 133.1, 137.9, 138.8, 150.3, 150.8. HRMS calcd for $C_{32}H_{44}$ 428.3443, found 428.3442.

Typical Procedure for the Preparation of 1,2,5,8-Tetra-ethyldibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (6a). A solution of

4a (80 mg) in 5.0 mL of DMF was heated to reflux for 6 h. Then the solution was cooled to room temperature and 20 mL of deionized water was added. The mixture was extracted with 15 mL of hexane five times. The combined organic layers were dried over $MgSO_4$. The solvent was evaporated and the product was purified by column chromatography with petroleum ether as eluant to afford a white solid **6a**, 80 mg (isolated yield 100%). Mp 104−105 °C. ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 1.06 (t, $J = 7.5$ Hz, 3H), 1.14−1.23 (m, 9H), 1.99 (q, $J = 7.5$ Hz, 2H), 2.13−2.23 (m, 2H), 2.31−2.41 (m, 2H), 2.52 (q, $J = 7.5$ Hz, 2H), 7.02−7.06 (m, 6H), 7.21−7.24 (m, 2H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 10.8, 12.5, 12.9, 18.4, 21.0, 21.7, 54.0, 65.1, 70.4, 119.1, 123.6, 125.4, 125.8, 141.8, 153.1. HRMS calcd for $C_{24}H_{28}$ 316.2191, found 316.2193.

1,2,5,8-Tetrapropyldibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (6b). A white solid (isolated yield 100% from **4b**). Mp 111−112 °C. ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 0.91 (t, $J = 7.5$ Hz, 3H), 0.98−1.06 (m, 9H), 1.36−1.65 (m, 8H), 1.77−1.83 (m, 2H), 1.91−2.01 (m, 2H), 2.16−2.26 (m, 2H), 2.32−2.37 (m, 2H), 6.96−6.99 (m, 6H), 7.12−7.15 (m, 2H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 15.0, 15.1, 15.3, 19.8, 21.3, 21.5, 28.7, 31.2, 31.7, 53.2, 64.7, 69.9, 119.1, 123.6, 125.3, 125.8, 141.9, 153.1. HRMS calcd for $C_{28}H_{36}$ 372.2817, found 372.2819.

1,2,5,8-Tetrabutyldibenzotricyclo[3.3.0.0^{2,8}]octa-3,6-diene (6c). A white fatty liquid (isolated yield 100% from **4c**). ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 0.94 (t, $J = 7.5$ Hz, 3H), 1.00−1.05 (m, 9H), 1.32−1.39 (m, 4H), 1.44−1.67 (m, 12H), 1.84−1.89 (m, 2H), 1.98−2.06 (m, 2H), 2.22−2.32 (m, 2H), 2.39−2.44 (m, 2H), 7.00−7.04 (m, 6H), 7.17−7.20 (m, 2H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 14.11 (4C), 23.7, 23.8, 24.0, 26.0, 28.6, 29.0, 30.2, 30.4, 53.0, 64.7, 69.6, 119.1, 123.6, 125.3, 125.8, 142.0, 153.1. HRMS calcd for $C_{32}H_{44}$ 428.3443, found 428.3444.

5,6,11,12-Tetraphenyldibenzo[*a,e*]cyclooctene (8d).[15] A yellow solid (41 mg, isolated yield 16%). Mp 186−190 °C. ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 6.77−6.97 (m, 4H), 7.06−7.10 (m, 20H), 7.16−7.36 (m, 4H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 126.7, 127.7, 127.9, 128.2, 130.5, 141.2(2C), 143.2. HRMS calcd for $C_{40}H_{28}$ 508.2191, found 508.2194.

5,6-Diethyl-11,12-diphenyldibenzo[*a,e*]cyclooctene (8e). Colorless liquid (125 mg, isolated yield 61%). ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 0.95 (t, $J = 7.5$ Hz, 6H), 2.42−2.50 (m, 4H), 2.80−2.87 (m, 4H), 7.10−7.19 (m, 10H), 7.29−7.32 (m, 8H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 13.89, 27.38, 125.85, 126.48, 126.57, 127.08, 127.72, 128.43, 131.06, 139.44, 140.888, 141.60, 143.24, 143.49. HRMS calcd for $C_{32}H_{28}$ 412.2191, found 412.2193.

5,6-Dibutyl-11,12-diphenyldibenzo[*a,e*]cyclooctene (8f).[3a] A white crystal (147 mg, isolated yield 63%). Mp 109−111 °C. ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 0.77 (t, $J = 7.2$ Hz, 6H), 1.20−1.29 (m, 4H), 2.36−2.47 (m, 4H), 2.74 (t, $J = 7.6$ Hz, 4 H), 7.02−7.19 (m, 10H), 7.23−7.30 (m, 8H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 13.89, 23.28, 31.56, 34.55, 125.70, 126.42, 126.63, 127.11, 127.72, 128.52, 131.12, 138.53, 140.80, 141.52, 143.41, 143.50. HRMS calcd for $C_{36}H_{36}$ 468.2817, found 468.2815.

9,10-Diethylphenanthrene (7a).[10] A white solid (28 mg, isolated yield 12%). Mp 104−106 °C. ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 1.38 (t, $J = 7.5$ Hz, 6H), 3.18 (t, $J = 7.5$ Hz, 4H), 7.56−7.62 (m, 4 H), 8.06−8.13 (m, 2 H), 8.69−8.72 (m, 2H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 15.2, 22.3, 123.1, 124.8, 125.6, 126.8, 130.0, 131.2, 135.0. HRMS calcd for $C_{18}H_{18}$, 234.1409, found. 234.1411.

9,10-Dipropylphenanthrene (7b).[10] A white solid (37 mg, isolated yield 14%). Mp 94−95 °C. ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 1.20 (t, $J = 7.5$ Hz, 6H), 1.78 (m, 4H), 3.18 (t, $J = 8.4$ Hz, 4H), 7.62−7.65 (m, 4 H), 8.13−8.16 (m, 2 H), 8.74−8.77 (m, 2H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 14.8, 24.0, 31.5, 122.9, 124.7, 125.3, 126.5, 129.8, 131.3, 133.8. HRMS calcd for $C_{20}H_{22}$ 262.1722, found 262.1725.

(14) Selected papers for phenanthrenes formed from one alkyne and two benzynes: (a) Pena, D.; Escudero, S.; Perez, D.; Guitian, E.; Castedo, L. *Angew. Chem.*, *Int. Ed.* **1998**, *37*, 2659. (b) Pena, D.; Perez, D.; Guitian, E.; Castedo, L. *Org. Lett.* **1999**, *1*, 1555. (c) Pena, D.; Perez, D.; Guitian, E.; Castedo, L. *J. Am. Chem. Soc*. **1999**, *121*, 5827. (d) Radhakrishnan, K. V.; Yoshikawa, E.; Yamamoto, Y. *Tetrahedron Lett.* **1999**, *40*, 7533. (e) Yoshikawa, E.; Radhakrishnan, K. V.; Yamamoto, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7280.

(15) Holland, J. M.; Jones, D. W. *J. Chem. Soc. C* **1971**, 608.

9,10-Diphenylphenanthrene (7d).[10] A white solid (66 mg, isolated yield 45%). Mp 238−240 °C. ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 7.10−7.32 (m, 10H), 7.36−7.41 (m, 2H), 7.51−7.56 (m, 2H), 7.63−7.74 (m, 2H), 8.78 (d, J = 8.1 Hz, 2H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 122.6, 126.5, 126.6, 126.8, 127.7, 128.0, 130.1, 131.2, 131.4, 132.0, 137.3, 139.7. HRMS calcd for C$_{26}$H$_{18}$ 330.1409, found 330.1406.

9-Ethyl-10-phenylphenanthrene (7e).[16] A Colorless solid (23 mg, isolated yield 8%). Mp 161−163 °C. ^{1}H NMR (CDCl$_3$, SiMe$_4$) δ 1.28 (t, J = 7.5 Hz, 3H), 2.98 (q, J = 7.5 Hz, 2H), 7.28−7.60 (m, 8H), 7.64−7.71 (m, 2H), 8.23−8.26 (m, 1H), 8.78−8.88 (m, 2H); ^{13}C NMR (CDCl$_3$, SiMe$_4$) δ 15.44, 23.69, 122.40, 123.25, 125.29, 125.80, 126.22, 126.43, 126.91, 127.17, 127.67, 128.52, 129.33, 130.22, 130.64, 130.74, 132.55, 136.01, 136.74, 140.63. HRMS calcd for C$_{22}$H$_{18}$ 282.1409, found 282.1410.

Procedure for the Preparation of 2,3-Diphenyl-1-zirconaindene (3d).[13] To a solution of Cp$_2$ZrCl$_2$ (4.0 mmol, 1.128 g) in toluol (30.0 mL) was added PhLi (2.0 M in Bu$_2$O, 8.00 mmol) at 0 °C and the mixture was stirred for 1 h. To this solution of diphenylzirconocene in tolune was added diphenyl acetylene (5.0 mmol, 0.890

g). The reaction mixture was refluxed for 24 h to give an orange solution. Concentration of this solution led to the precipitation of an orange solid. Washing with hexane (5 × 20 mL) gave 2,3-diphenyl-1-zirconaindene (**3d**) in 70% yield.

Procedure for the Reaction of Isolated 2,3-Diphenyl-1-zirconaindene (3d) with 1,4-Naphthoquinone in the Presence of CuCl. 2,3-Diphenyl-1-zirconaindene (**3d**) (1.08 mmol) was dissolved in THF (5 mL). Then CuCl (2.16 mmol, 211 mg) and 1,4-naphthoquinone (1.3 mmol, 205 mg) were added. The mixture was stirred at room temperature for 12 h. Compound **8d** was obtained in 46% isolated yield after normal workup.

Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for all new compounds and single-crystal data for **6a** and **7d**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Bradsher, C. K.; Rapoport, L.; Anderson, P. *J. Am. Chem. Soc.* **1946**, *68*, 2152.