Main-Group Metal Complexes

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Barium Dibenzopentalenide as a Main-Group Metal η^8 Complex: Facile Synthesis from 1,4-Dilithio-1,3-butadienes and $Ba[N(SiMe_3)_2]_2$, Structural Characterization, and Reaction Chemistry**

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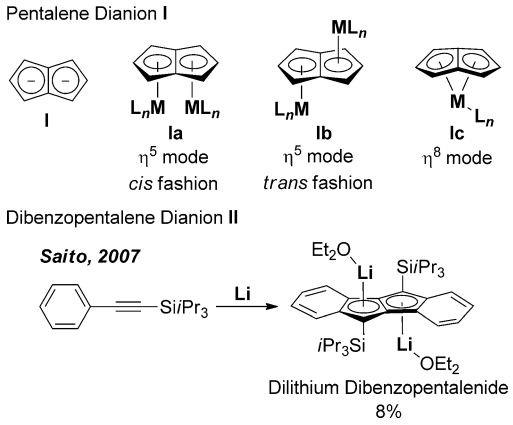
The pentalene dianion (**I**, Scheme 1), a 10π aromatic system, can be considered as a fused-ring system of two cyclopentadienyl monoanions.[1] These dianions have been very useful as unique ligands in transition-metal and f-element organometallic chemistry.[1–3] The dianion **I** is known to coordinate with two metal centers in an η^5 mode, both in *cis* fashion (**Ia**) and *trans* fashion (**Ib**).[2] The dianion **I** may also coordinate to a single metal in an η^8 mode (**Ic**).[3] For the coordinating mode **Ic**, the metal center is usually an f- or d-block element.[1–3] Main-group metals for the coordinating mode **Ic** have not been reported to date, owing to the high instability caused by the extreme distortion.[4] Much less investigation has been carried out on the dibenzopentalene dianion **II** (Scheme 1), which is more π-extended than the pentalene dianion **I**.[5] In 2007, Saito and co-workers reported the first molecular structure of a dibenzopentalene dianion, dilithium dibenzopentalenide, obtained in 8% yield by reduction of phenyl(triisopropylsilyl)acetylene with lithium (Scheme 1).[6] The two lithium atoms are bonded to the adjacent 5-membered rings in a *trans* position with an η^5 mode.



Scheme 1. Pentalene dianion and dibenzopentalene dianion.

In 2000, Brintzinger, Knoll and co-workers reported the synthesis of dibenzylbarium by the reaction between benzyllithium and $Ba[N(SiMe_3)_2]_2$, in which the Li–C bond was transferred to its corresponding Ba–C_{sp^3} bond.[7] As we were interested in the reaction chemistry of 1,4-dilithio-1,3-butadienes **1**,[8,9] we investigated the transmetalation of 1,4-dilithio-1,3-butadienes **1** with $Ba[N(SiMe_3)_2]_2$, expecting that a novel reaction might occur because of the higher ionicity and reactivity of the resulting Ba–C_{sp^2} bonds.[10,11] Herein we report the synthesis and structural characterization of barium dibenzopentalenide **2**, which is, among all pentalene and dibenzopentalene complexes, the first example of a complex in which a main-group metal binds in an η^8 mode. Moreover, the reaction chemistry of barium dibenzopentalenides was also investigated, affording dibenzopentalene derivatives, which have recently attracted considerable attention because of their unique planar structures and antiaromatic character.[12,13]

The pure phenyl-substituted 1,4-dilithio-1,3-butadiene **1a** could be prepared in high yields by lithiation of the corresponding 1,4-diiodo-1,3-butadiene after filtration of LiI followed by recrystallization from hexane/THF/Et_2O.[14] An X-ray structural analysis of **1a** (Figure 1) revealed a monomeric pattern with a double dilithium bridge (see the Supporting Information for detailed structural information).[6a,14b,15] The Li1 and Li2 atoms were coordinated with two THF and one Et_2O molecule, respectively.

Treatment of **1a** with $Ba[N(SiMe_3)_2]_2$ (1 equiv) in hexane resulted in deep-red precipitates, which indicated the occurrence of transmetalation, because both **1a** and $Ba[N(SiMe_3)_2]_2$ are readily soluble in hexane. After recrystallization of the deep-red solids from THF at room temperature, barium dibenzopentalenide **2a** was isolated in 61% yield (Scheme 2). Hydrolysis of the isolated intermediate **2a** with H_2O afforded its corresponding product **3a** in quantitative yield. Moreover, barium dibenzopentalenide **2a** could also be generated quantitatively by the reaction between **3a** and $Ba[N(SiMe_3)_2]_2$ (Scheme 2).

Shown in Figure 2 is the structure of **2a** determined by single-crystal X-ray structural analysis. The single barium atom is coordinated to the parent pentalene in an η^8 fashion, which is, among all pentalene and dibenzopentalene com-

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Supporting information (including experimental details, X-ray crystallographic data, and NMR spectra of all new products) for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201305254.

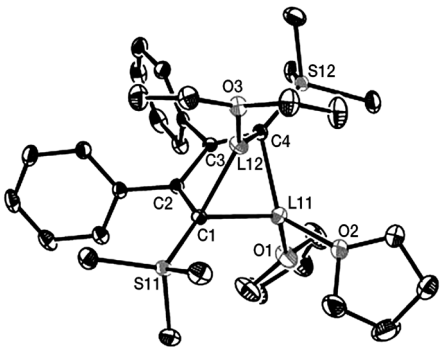
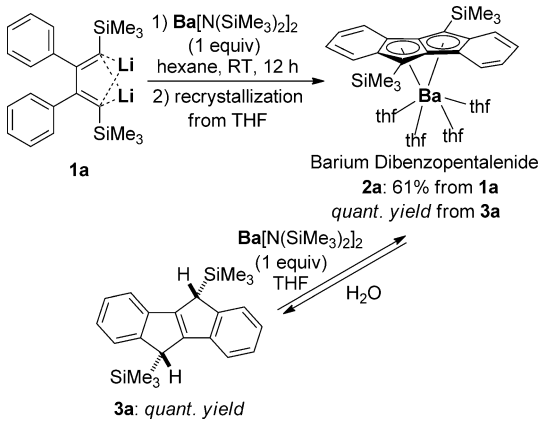


Figure 1. ORTEP drawing of the structure of **1a** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1–C2 1.359(2), C2–C3 1.536(2), C3–C4 1.359(2), C1–Li1 2.176(4), C1–Li2 2.123(4), C4–Li1 2.207(4), C4–Li2 2.092(4), Li1–O1 1.993(4), Li1–O2 1.994(4), Li2–O3 1.946(3).[17]



Scheme 2. Synthesis of barium dibenzopentalenides **2**.

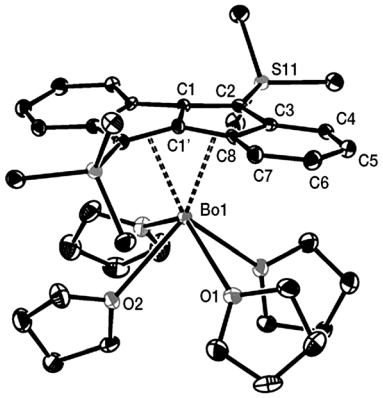
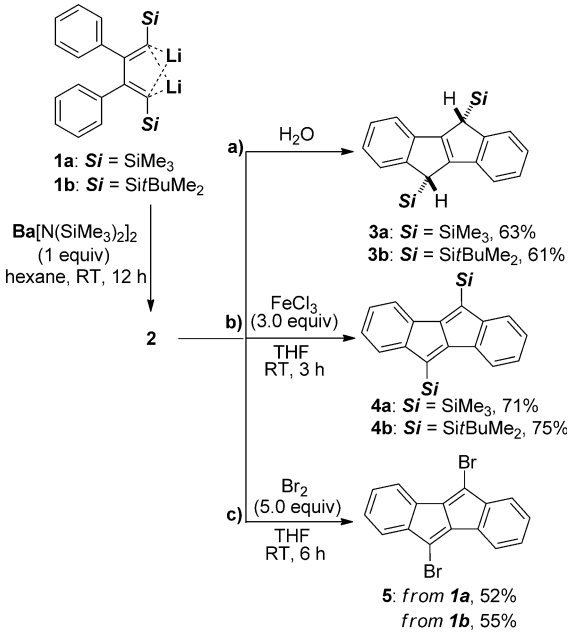


Figure 2. ORTEP drawing of the structure of **2a** with 30% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å]: C1–C2 1.464(7), C2–C3 1.432(7), C3–C8 1.460(7), C8–C1′ 1.441(7), C1–C1′ 1.432(9), C3–C4 1.425(7), C4–C5 1.365(7), C5–C6 1.404(8), C6–C7 1.382(7), C7–C8 1.399(7), Ba1–O1 2.766(4), Ba1–O2 2.766(4), Ba1–C1 2.801(5), Ba1–C2 3.107(5), Ba1–C3 3.277(5), Ba1–C8 3.152(5), Ba1–C1′ 2.801(5).[17]

plexes, the first example of a complex in which a main-group metal binds in an η^8 mode. Meanwhile, the π framework was slightly distorted, thereby resulting in bending of the dibenzopentalene about the bridgehead C1–C1′ bond by about 13.5°; this angle is smaller than those of all reported pentalene complexes with an η^8 coordination mode.[1,3] The large ionic radii of Ba^{2+}(1.35 Å) might be the major reason.[16] In contrast to the nearly equal C–C bond lengths (1.432–1.464 Å) in the five-membered rings, a remarkable difference was observed among the C–C bond lengths in the benzenoid rings (1.365–1.425 Å).

With these unprecedented barium dibenzopentalenides in hand, we investigated their reaction chemistry (Scheme 3). Treatment of phenyl-substituted 1,4-dilithio-1,3-butadiene **1a**



Scheme 3. Reactivity of barium dibenzopentalenides **2**.

and **1b** with $Ba[N(SiMe_3)_2]_2$ (1 equiv) in hexane in situ led to the formation of their corresponding barium dibenzopentalenides **2a** and **2b**. When the in situ generated barium dibenzopentalenides **2** were quenched with H_2O, 5,10-dihydro-dibenzopentalenes **3a** and **3b** were isolated in 63% and 61% yield, respectively (Scheme 3a). According to their NMR spectra and the X-ray crystallographic analysis of **3b** (Figure 3), only the *cis* stereoisomer was observed. This is probably because the η^8 coordinating mode of barium dibenzopentalenides allows the proton to attack only at the other face, thus resulting in the *cis* stereoisomer only.

When the in situ generated **2a** was treated with $FeCl_3$, the dibenzopentalene derivative **4a** was isolated in 71% yield as an oxidation product (Scheme 3b). Similarly, the dibenzopentalene derivative **4b** was isolated in 75% yield from the reaction of **2b** with $FeCl_3$. Iodine was also applied as an oxidation reagent for compounds **2**. However, much lower yields of their corresponding products **4** were obtained.[6] Treatment of the in situ generated barium dibenzopentale-

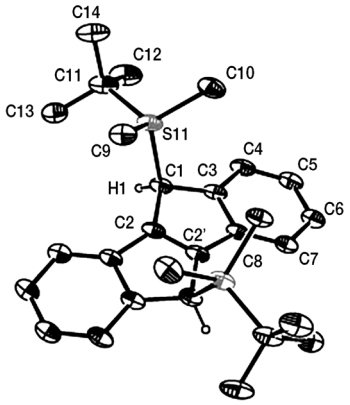
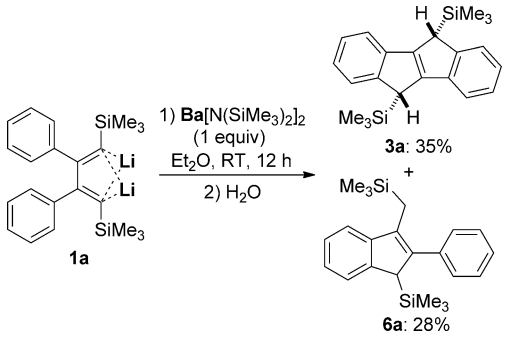


Figure 3. ORTEP drawing of the structure of **3b** with 20% thermal ellipsoids. Selected bond lengths [Å]: C1–C2 1.494(5), C2–C2′ 1.333(8), C8–C2′ 1.461(5), C1–C3 1.501(6), C3–C4 1.387(5), C4–C5 1.364(7), C5–C6 1.385(6), C6–C7 1.393(5), C7–C8 1.354(6), C1–Si1 1.946(3).[17]

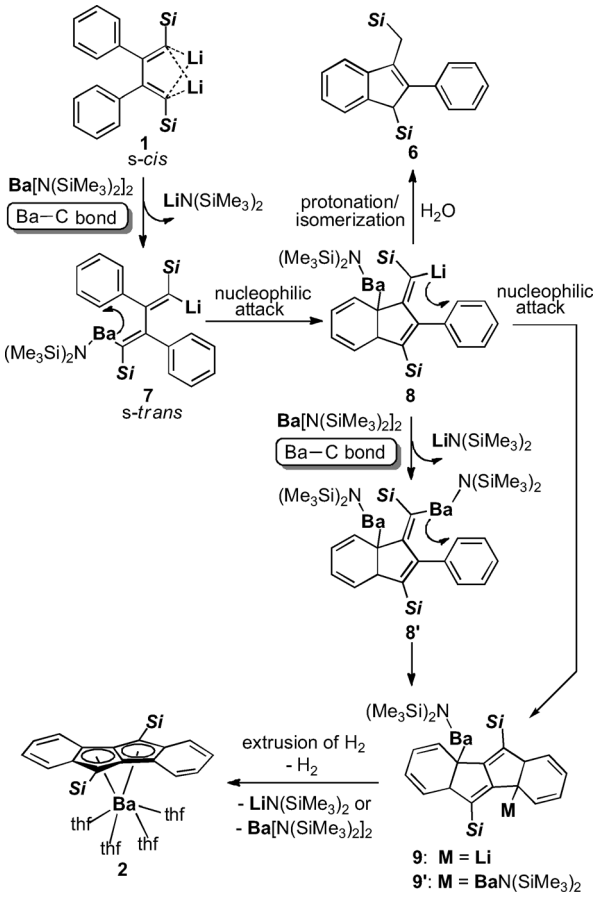
nides **2a** and **2b** with Br_2 in THF afforded their corresponding 5,10-dibromodibenzopentalene **5** in 52% and 55% yield, respectively (Scheme 3c). Orita and Otera have demonstrated that the dihalo-substituted dibenzopentalenes **5** could be applied for the synthesis of a series of phenylethynyl- and/or phenyl-substituted dibenzopentalenes and dibenzopentalene oligomers.[13k]

When the reaction between 1,4-dilithio-1,3-butadiene **1a** and $Ba[N(SiMe_3)_2]_2$ was carried out in Et_2O instead of hexane (Scheme 4), quenching of the reaction mixture afforded the 5,10-dihydro-dibenzopentalene **3a** in 35% yield, along with the unpredicted indene derivative **6a** in 28% yield, which is useful for understanding the reaction process.



Scheme 4. Transmetalation of 1,4-dilithio-1,3-butadiene **1a** with $Ba[N(SiMe_3)_2]_2$ in Et_2O generating **3a** and **6a**.

A proposed mechanism for the formation of barium dibenzopentalenides **2** is given in Scheme 5. First, the transmetalation of 1,4-dilithio-1,3-butadienes **1** occurred and afforded the corresponding barium species **7**. Owing to the breakage of the dilithium bridged structure of **1**, the s-*trans* configuration became favorable. Then, an intramolecular nucleophilic attack to the phenyl ring would lead to **8**. Meanwhile, **8** might react with a second $Ba[N(SiMe_3)_2]_2$, forming the barium species **8′**. Next, an intramolecular nucleophilic attack would generate the intermediate **9** or **9′**.



Scheme 5. Proposed mechanism for the formation of dibenzopentalene dianion **2** and indene derivative **6**.

Finally, **9** or **9′** would be converted into the final dibenzopentalene dianion **2** by extrusion of dihydrogen. A similar dihydrogen extrusion process has been proposed by Saito and co-workers.[6a] The formation of the indene derivative **6** indicated the formation of the proposed intermediate **8** or **8′**.

In summary, we have successfully established a novel synthesis of dibenzopentalene dianions **2** through the introduction of Ba–C bonds to 1,4-butadienyl skeletons. Among all pentalene and dibenzopentalene complexes, the barium dibenzopentalenide **2** is the first example of a complex, in which a main group metal binds with an η^8 mode. Preliminary studies of the reaction chemistry of thus obtained barium dibenzopentalenides **2** has demonstrated that synthetically useful applications can be expected.

Experimental Section

Isolation of **2a**: $Ba[N(SiMe_3)_2]_2(thf)_{1.6}$ (0.25 mmol) was added to the solution of 1,4-dilithio-1,3-butadiene **1a** (0.25 mmol) in hexane (10 mL) at room temperature. After 12 h, deep-red precipitates of barium dibenzopentalenide **2a** formed. The resulting precipitates were rinsed with hexane. Recrystallization of the deep-red solids from THF at room temperature afforded pure barium dibenzopentalenide **2a** (deep-red solid, 118 mg, 61%). ^1H NMR (400 MHz, C_4D_8O, $SiMe_4$): $\delta = 0.04$ (s, 18H, CH_3), 1.75–1.77 (m, 16H, CH_2), 3.59–3.63 (m, 16H, CH_2), 7.00–7.69 ppm (m, 8H, CH). Anal. Calcd. for $C_{38}H_{58}BaO_4Si_2$: C, 59.09; H, 7.57. Found: C, 59.30; H, 7.32.

Recrystallization of **2a** from THF at room temperature afforded single crystals for X-ray analysis.

Crystallographic data for **2a**: $C_{38}H_{58}BaO_4Si_2$, $M_w = 772.36\ g\,mol^{-1}$, $T = 173(2)$ K, monoclinic, space group $C2/c$, $a = 22.0250(19)$, $b = 9.270(3)$, $c = 21.292(5)$ Å, $\alpha = 90.000(14)$, $\beta = 120.230(12)$, $\gamma = 90.000(10)°$, $V = 3756.1(13)$ Å^3, $Z = 4$, $GOF = 1.176$, reflections collected: 16198, independent reflections: 4301 [R(int) = 0.0973], final R indices [$I > 2\sigma I$]: $R_1 = 0.0783$, $wR_2 = 0.1155$, R indices (all data): $R_1 = 0.0931$, $wR_2 = 0.1206$.

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[17] CCDC-942570 (**1a**), 937746 (**2a**), and 942571 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

