

Review

Synthesis and Reactions of Dibenzo[*a,e*]pentalenes

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Abstract: Pentalene has recently received a considerable amount of attention as a ligand in sandwich-type transition metal complexes. In contrast, dibenzo[*a,e*]pentalene (hereafter denoted as dibenzopentalene), which is more π -extended than pentalene, has received less attention, despite its potential usefulness as a building block of ladder-type π -conjugated molecules, which have recently received growing interest. However, very recently, several novel efficient methods for the synthesis of dibenzopentalenes have been reported. This review surveys recent advances in the synthesis and reactions of dibenzopentalenes and describes the aromaticity of their ionic species.

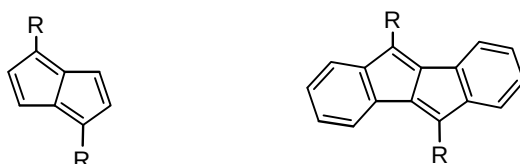
Keywords: dibenzopentalene; thermolysis; skeletal rearrangement; reductive cyclization; catalyst; redox reaction

1. Introduction

The parent pentalene has 8π electrons, which indicates its antiaromatic nature, and is very highly reactive, having only been observed using a matrix isolation technique at $-196\text{ }^{\circ}\text{C}$ (Chart 1) [1,2]. In contrast, its dianion has 10π electrons and is calculated to have considerable aromaticity [3]. The stable pentalene dianion was first synthesized in 1962 [4,5] and the X-ray crystal structure of its dilithium salt was reported in 1991 [6]. On the other hand, no reports on the generation of a pentalene dication have appeared to date, and its aromaticity is still controversial [3,7]. The pentalene dianions are now widely used as ligands of sandwich-type transition metal complexes [8-11]. However, the dibenzo[*a,e*]pentalenes (hereafter denoted as dibenzopentalenes), which are more π -extended than the pentalenes have received less attention despite their potential usefulness as building blocks of ladder-type π -conjugated molecules, which are of growing recent interest (Figure 1). The main reason for this

is a limited number of methods for the synthesis of dibenzopentalene frameworks, even though synthesis of a dibenzopentalene was first reported in 1912 [12]. However, very recently, efficient and unique methods for the synthesis of dibenzopentalenes together with reports of their reactivity have successively appeared. It is therefore time to briefly survey the recent advances in the synthesis and reactions of dibenzopentalenes and to discuss the aromaticity of their derivatives.

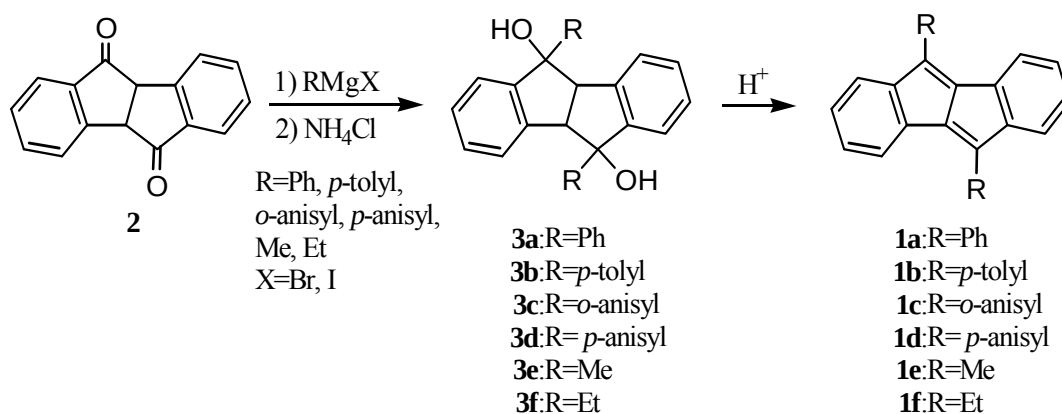
Figure 1. Pentalene and Dibenzo[*a,e*]pentalene.



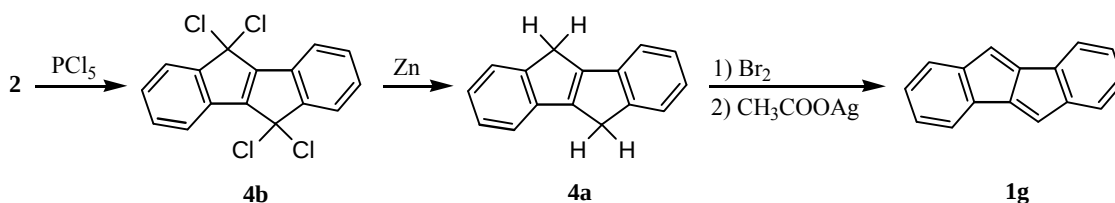
2. Early Studies on the Preparation of Dibenzopentalenes

The first synthesis of dibenzopentalenes **1a–b** was reported by Brand in 1912 [12]. The key starting compound was diphenylsuccindanedione **2** [13–15], which was synthesized from diphenylsuccinic acid. Treatment of **2** with phenylmagnesium bromide and *p*-tolylmagnesium bromide followed by an addition of ammonium chloride afforded the corresponding diols **3a** and **3b**, respectively (Scheme 1) [12]. Diols **3a** and **3b** were treated with formic acid to provide dibenzopentalenes **1a** and **1b**. This method could be applied to introduce other aryl or alkyl groups, such as *o*-anisyl [16], *p*-anisyl [16], methyl [17] and ethyl [17] groups, leading to the formation of dibenzopentalenes **3c–3f** (Scheme 1).

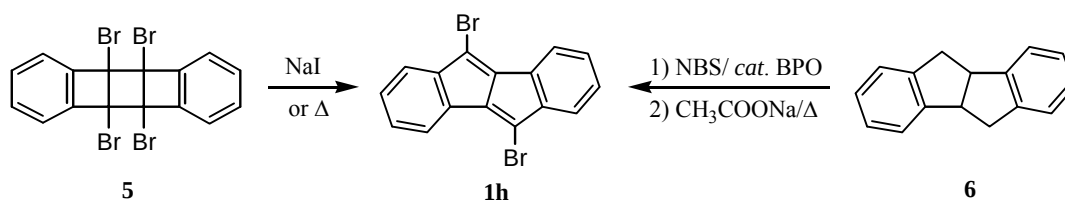
Scheme 1. Early Studies on the Preparation of Dibenzopentalenes from Diphenylsuccindanedione **2**.



The parent dibenzopentalene **1g** was first synthesized from dihydrodibenzopentalene **4a**, which was prepared from diphenylsuccindanedione **2** via tetrachlorodibenzopentalene **4b** (Scheme 2) [18]. Diphenylsuccindanedione **2** reacted with phosphorus pentachloride to afford **4b** [19,20], which was treated with zinc to provide **4a** [20]. Treatment of **4b** with bromine followed by silver acetate provided the parent dibenzopentalene **1g** in 59% yield (Scheme 2) [18].

Scheme 2. Preparation of the Parent Dibenzopentalene **1g**.

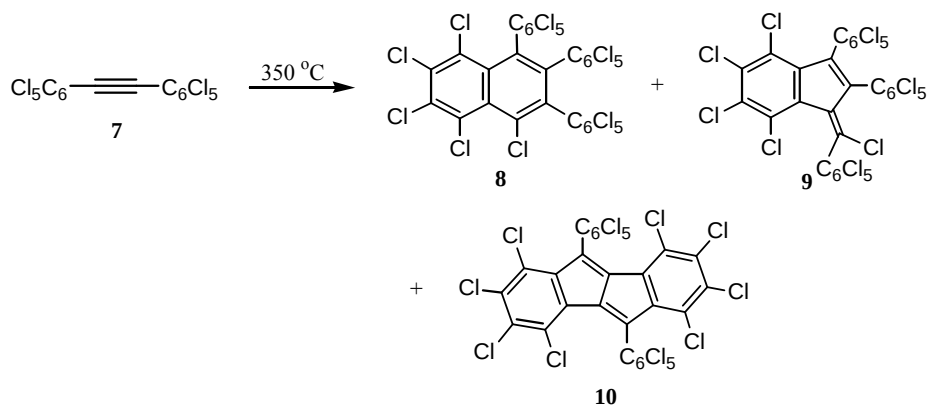
Dibromodibenzopentalene **1h** was prepared by the thermolysis of dibenzotricyclic tetrabromide **5** [21] and by the reaction of **5** with sodium iodide (Scheme 3) [22]. Bromination of tetrahydrodibenzopentalene **6** followed by dehydrobromination also afforded **1h** (Scheme 3) [22].

Scheme 3. Preparation of the Dibromodibenzopentalene **1h**.

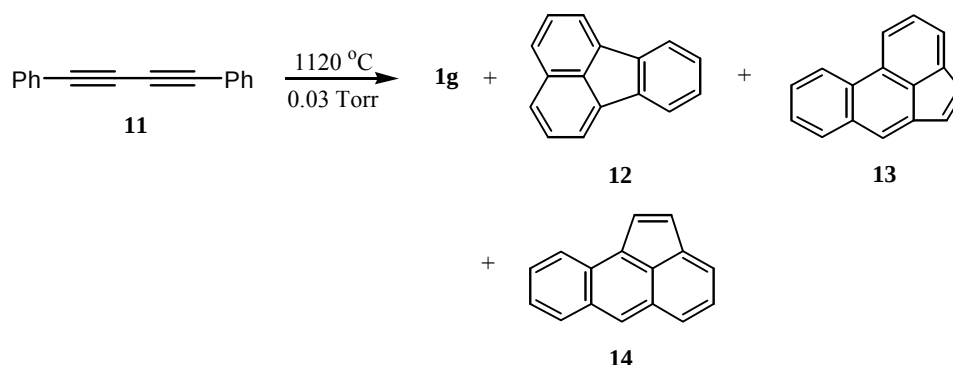
3. Preparation of Dibenzopentalenes by Thermolysis

Thermolysis, such as the flash vacuum pyrolysis (FVP) technique, is sometimes a very powerful tool for the creation of rigid π -frameworks through somewhat unexpected and complex reaction pathways.

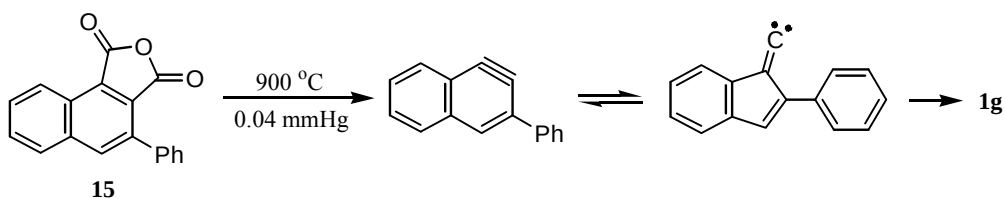
Bis(pentachlorophenyl)acetylene **7** was heated at 350 °C for 45 min to afford perchloro-1,2,3-triphenylnaphtalene **8** (42%) as a main product with perchloro-2,3,8-triphenylbenzofulvene **9** (31%) and perchlorodibenzopentalene **10** (1%) (Scheme 4) [23]. Prolonged heating of **7** for 2 h revealed an increase of the yield of **10** (23%) and a decrease of the yields **9** (10%): hence, dibenzopentalene **10** was formed via **9**.

Scheme 4. Thermolysis of Perchloro-1,2,3-triphenylnaphtalene **8**.

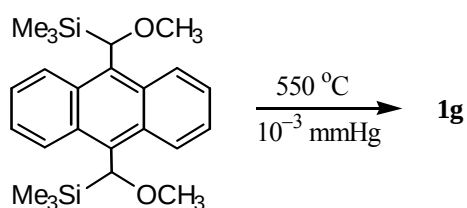
Flash vacuum pyrolysis of diphenylbutadiyne **11** at 1120 °C/0.03 Torr gave a pyrolysate (22% mass recovery), which consisted of dibenzopentalene **1g** (19%), fluoranthene **12** (59%), acephenanthrylene **13** (13%), aceanthrylene **14** (2%) and unreacted **11** (7%) (Scheme 5) [24].

Scheme 5. Flash Vacuum Pyrolysis of Diphenylbutadiyne **11**.

Flash vacuum pyrolysis of 3-phenylnaphthalene-1,2-dicarboxylic anhydride **15** at 900 °C/0.04 mmHg also gave dibenzopentalene **1g** (95%) and a plausible mechanism for the formation of **1g** was proposed (Scheme 6) [25].

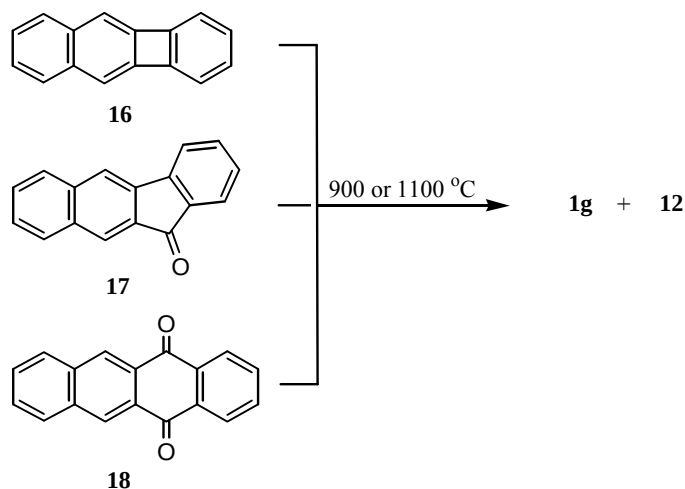
Scheme 6. Flash Vacuum Pyrolysis of 3-Phenylnaphthalene-1,2-dicarboxylic Anhydride **15**.

Flash vacuum pyrolysis of 9,10-bis[(methoxysilyl)methyl]anthracene **16** at 550 °C/10⁻³ mmHg also gave dibenzopentalene **1g** (48%), and a very complicated mechanism was proposed (Scheme 7) [26].

Scheme 7. Flash Vacuum Pyrolysis of 9,10-Bis[(methoxysilyl)methyl]anthracene **16**.

Benzo[*b*]biphenylene **16**, benzo[*b*]fluorenone **17** and 5,12-naphthacene quinone **18** were also heated in the gas phase to provide dibenzopentalene **1g** and fluoranthene **12**, and the ratios of **1g** to **12** were dependent on the reaction temperature (Scheme 8) [27].

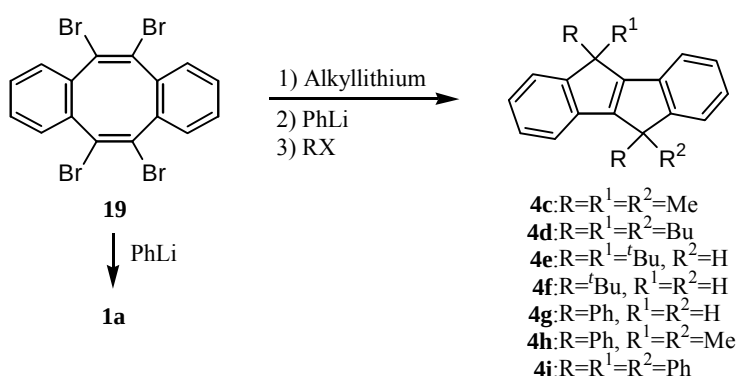
Thermolysis is indeed efficient for the preparation of dibenzopentalenes. However, it needs a special apparatus: hence, it is rather difficult to carry out. Moreover, it is difficult to prepare functionalized dibenzopentalenes using thermolysis.

Scheme 8. Flash Vacuum Pyrolysis of Benzannulated Compounds.

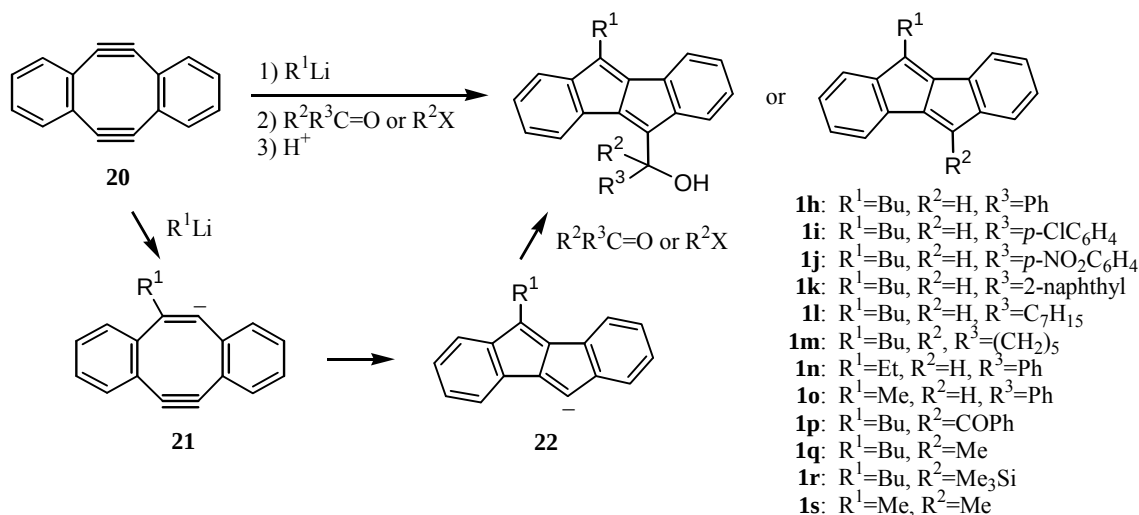
4. Preparation of Dibenzopentalenes from Dibenzocyclooctene Derivatives through Skeletal Rearrangement

Anionic dibenzocyclooctene derivatives are known to undergo skeletal rearrangements to afford the corresponding dibenzopentalenes.

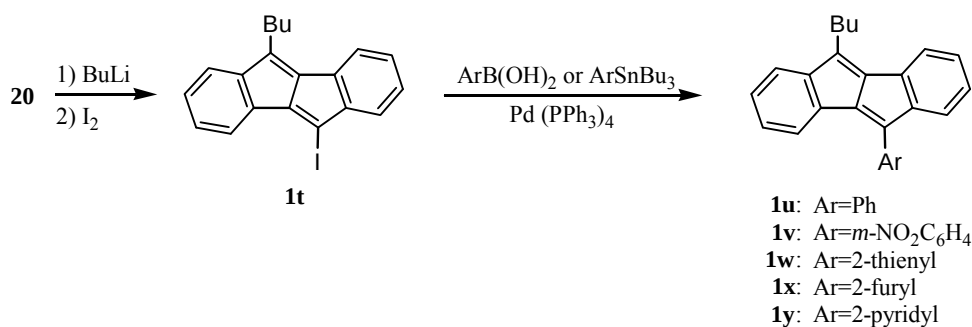
Treatment of 5,6,11,12-tetrabromodibenzo[*a,e*]cyclooctatetraene **19** with alkyllithiums followed by an addition of phenyllithium and electrophiles provided dihydrodibenzopentalenes **4c-4i** (Scheme 9) [28]. However, when compound **19** was treated with phenyllithium without a treatment with electrophiles, 5,10-diphenyldibenzopentalane **1a** was also obtained.

Scheme 9. Reactions of 5,6,11,12-Tetrabromodibenzo[*a,e*]cyclooctene **19** with Lithium Reagents.

A similar method starting from dibenzocyclooctadiyne **20** was very recently reported [29]. Dibenzocyclooctadiyne **20** reacted with alkyllithiums to provide the corresponding anionic intermediates **21**, which underwent isomerization to anionic dibenzopentalenes **22**. The reactions were terminated with electrophiles to afford dibenzopentalenes **1h-1s** in very good yields (61–78%) (Scheme 10) [29].

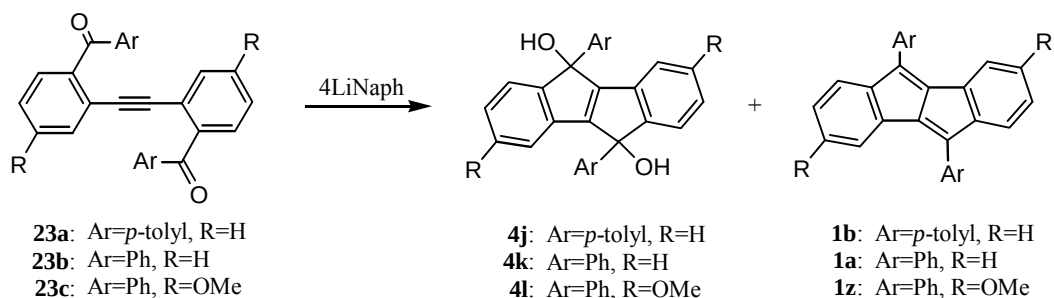
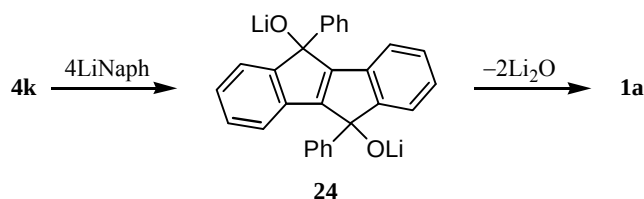
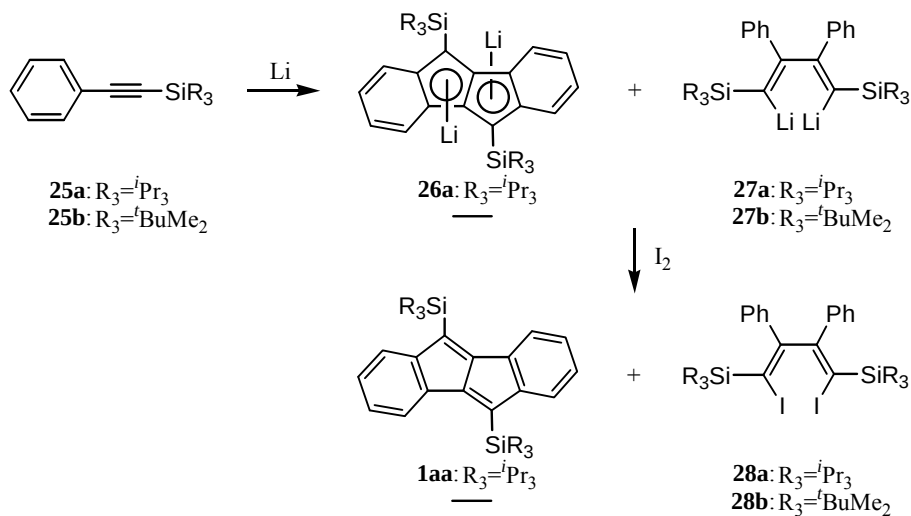
Scheme 10. Preparation of Dibenzopentalenes from Dibenzocyclooctadiene **20**.

To introduce an aryl group to the dibenzopentalene skeleton, treatment of **20** with butyllithium followed by iodine afforded iodo-derivative **1t**, which reacted with arylboronic acids and aryltributylstannanes through Suzuki-Miyaura and Migita-Kosugi-Stille coupling reactions, respectively, to provide the corresponding aryl derivatives **1u-1y** in good yields (50–70%) (Scheme 11) [29].

Scheme 11. Preparation of Aryl-substituted Dibenzopentalenes.

5. Preparation of Dibenzopentalenes through Reductive Cyclization

The intramolecular cyclization reactions of *o*-substituted phenylacetylenes are of considerable use for the preparation of benzannulated five-membered ring compounds, such as indenenes, indoles, benzofurans and benzothiophenes [30,31]. A very sophisticated application of this methodology to prepare dibenzopentalene skeletons was very recently reported by Yamaguchi [32]. Reduction of *o,o'*-bis(arylcarbonyl)diphenylacetylenes **23** with lithium naphthalenide produced dibenzopentalenes **1** (8–25% yields) together with 5,10-dihydroxy-5,10-dihydrodibenzopentalenes **4** (29–52% yields) (Scheme 12). Since dihydroxy derivative **4k** reacted with lithium naphthalenide to afford the corresponding dibenzopentalenes **1a** in 49% yield (Scheme 13), Li_2O was eliminated from dilithium alkoxide intermediate **24**.

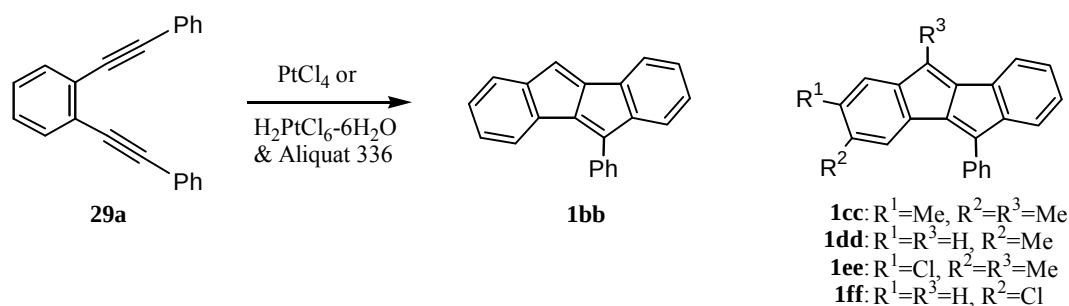
Scheme 12. Reductive Cyclization of *o,o'*-Bis(arylcarbonyl)diphenylacetylenes **23**.**Scheme 13.** Mechanism for the Formation of Dibenzopentalene.**Scheme 14.** Formation of Dibenzopentalene by Reduction of Phenylsilylacetylene.

Another example of reductive cyclization of a phenylacetylene to form a dibenzopentalene is rather unexpected. We recently reported the reduction of phenyl(tri-*i*-propylsilyl)acetylene **25a** with lithium providing dilithium dibenzopentalenide **26a** as well as 1,4-dilithio-1,3-butadiene **27a**, which were treated with iodine to afford the corresponding dibenzopentalene **1aa** (8%) and 1,4-diiodo-1,3-butadiene **28a** (28%), respectively (Scheme 14) [33]. Since phenylsilylacetylenes are usually reduced by lithium to afford 1,4-dilithio-1,3-butadienes [34,35], the formation of dilithium dibenzopentalenide **26a** is surprising and unprecedented. However, the reduction of phenyl(*t*-butyldimethylsilyl)acetylene **25b** with lithium produced only the corresponding 1,4-dilithio-1,3-butadiene **27b**: thus, the reaction mode is quite sensitive to bulkiness of the silyl substituent of phenylsilylacetylene, even though the reason for this is still unclear.

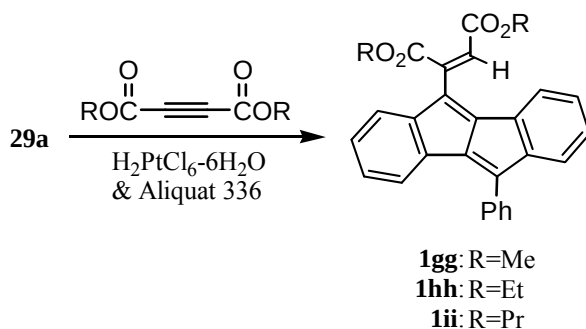
6. Preparation of Dibenzopentalenes in the Presence of Catalysts

Catalytic reactions for the preparation of dibenzopentalenes have also been reported. In early studies, the key starting compound was 1,2-bis(phenylethynyl)benzene (**29a**), treatment of which with PtCl_4 in benzene afforded a Pt-complex of dibenzopentalene **1bb**, an unstable compound that converted to **1bb** during purification (Scheme 15) [36,37]. The yield of **1bb** was 85%. This method was later applied for the preparation of dibenzopentalenes **1cc–1ff** (Scheme 15) [38]. When PdCl_2 was used as a catalyst, a Pd-complex of **1bb** was isolated and treatment of the resulting complex with triphenylphosphine provided **1bb**, even though the yield was very low. A mixture of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and Aliquat 336[®] (Aliquat = methyltriocetylammmonium chloride) was also used as a catalyst for the preparation of **1bb** with 80% yield [39]. When the reactions were carried out in the presence of dialkyl acetylenedicarboxylates, the corresponding adducts **1gg–1ii** were obtained (25–36% yields) together with **1bb** (Scheme 16) [40].

Scheme 15. Formation of Dibenzopentalene from 1,2-Bis(phenylethynyl)benzene (**29a**).

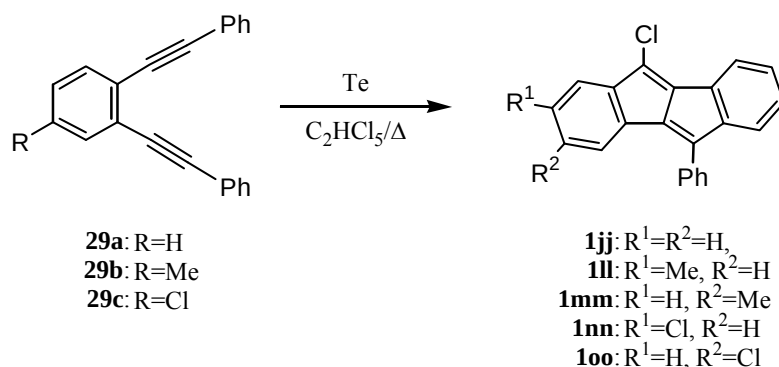


Scheme 16. Cyclization of 1,2-Bis(phenylethynyl)benzene (**29a**) in the Presence of Dialkyl Acetylenedicarboxylates.

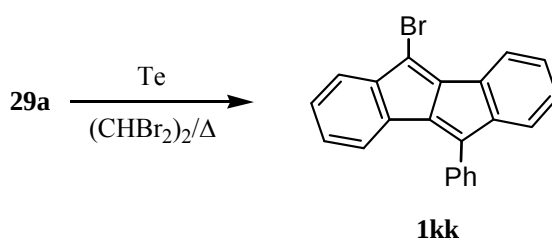


The cyclization reactions of 1,2-bis(phenylethynyl)benzenes to afford dibenzopentalenes were surprisingly catalyzed by tellurium (Scheme 17) [38]. Heating of **29a** with a catalytic amount of tellurium in pentachloroethane (PCE) under reflux provided dibenzopentalene **1jj** in 61% yield through a halogen transfer reaction (Scheme 17). When **29a** was heated with a catalytic amount of tellurium in tetrabromoethane at 170 °C, the corresponding bromodibenzopentalene **1kk** was obtained in 6% yield (Scheme 18) [38]. Treatment of **29b** with a catalytic amount of tellurium in PCE under reflux produced a 1:1 mixture of **1ll** and **1mm** in 79% yield. Likewise, **29c** reacted in PCD in the presence of a catalytic amount of tellurium to afford an 1:1 mixture of **1nn** and **1oo** in 83% yield.

Scheme 17. Cyclization of 1,2-Bis(phenylethynyl)benzenes Catalyzed by Tellurium in Pentachloroethane.



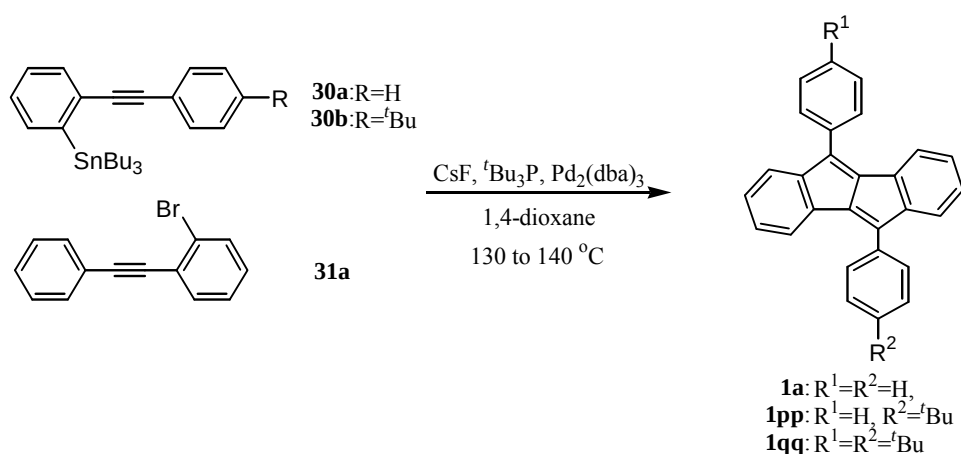
Scheme 18. Cyclization of 1,2-Bis(phenylethynyl)benzenes Catalyzed by Tellurium in Tetrabromoethane.



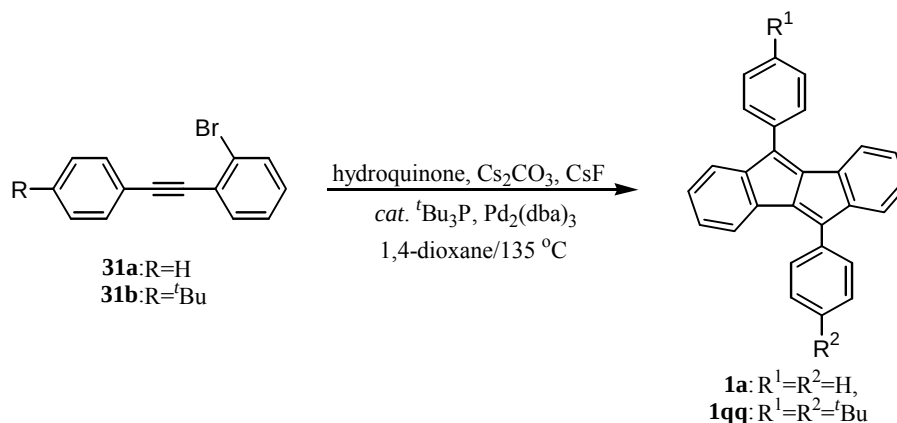
Two phenylacetylenes, one of which has a halogen atom and the other of which has a Bu₃Sn group were coupled in the presence of CsF, ^tBu₃P and Pd₂(dba)₃ to give dibenzopentalenes (Scheme 19) [41]. The coupling reaction of **30a** and **31a** under the reaction conditions shown in Scheme 19 provided dibenzopentalene **1a** in 61% yield. A crossover coupling reaction of **30b** and **31a** under the same conditions afforded homocoupled products **1a** (20% yield) and **1qq** (trace), as well as the crossover-coupled product **1pp** (40% yield), suggesting that the homocoupling reaction of **31a** would proceed.

Heating of **31a** and **31b** afforded **1a** and **1qq**, respectively in very high yields with 2 equivalents of hydroquinone, Cs₂CO₃ and CsF in the presence of catalytic amounts of ^tBu₃P and Pd₂(dba)₃ in 1,4-dioxane at 135 °C (Scheme 20) [41]. This method could be applied for the preparation of a variety of dibenzopentalenes (55–72% yields) (Scheme 21) [41]. The most striking feature of this catalytic system is that a heteroaromatic analog **34** of a dibenzopentalene was able to be synthesized.

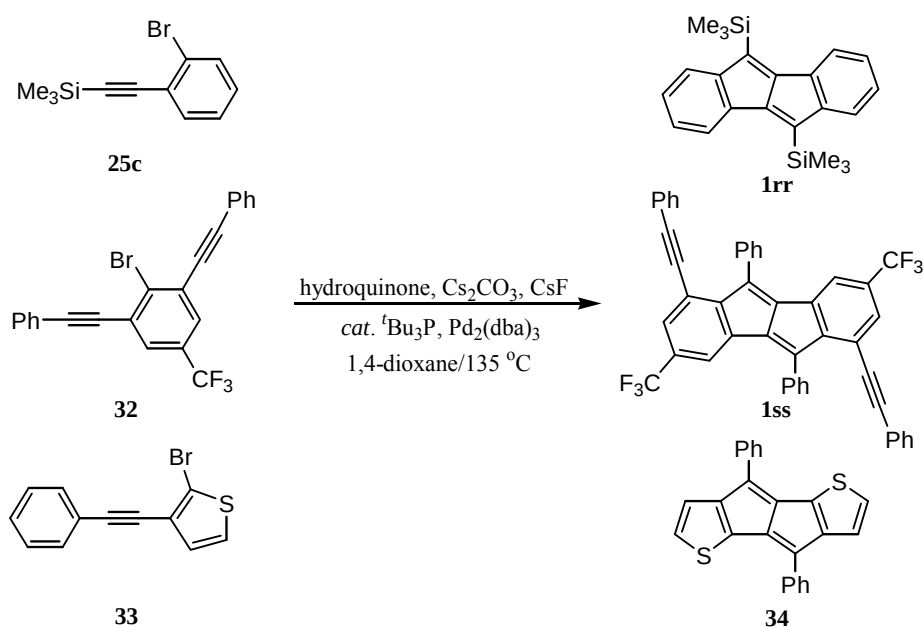
Scheme 19. Coupling of Two Acetylenes in the Presence of CsF, ^tBu₃P and Pd₂(dba)₃.



Scheme 20. Homocoupling of Acetylenes with hydroquinone, Cs_2CO_3 and CsF in the Presence of $t\text{Bu}_3\text{P}$ and $\text{Pd}_2(\text{dba})_3$.

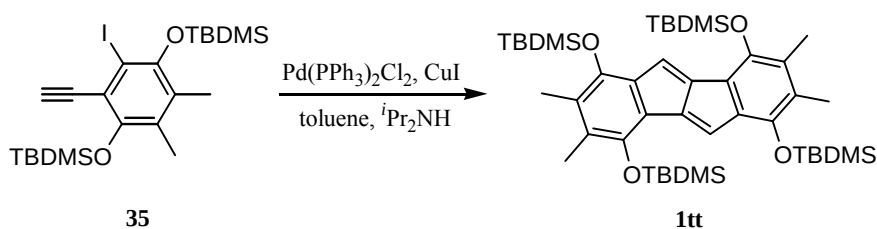


Scheme 21. Preparation of a Variety of Functionalized Dibenzopentalenes.



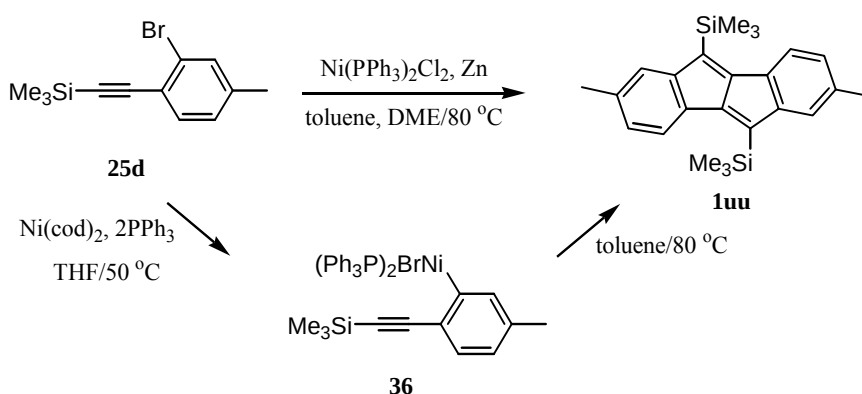
Another catalytic synthesis of a dibenzopentalene from 2-halophenylacetylene was carried out using $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ and CuI (Scheme 22) [42]. Heating of a mixture of 2-iodophenylacetylene **35** with $\text{Pd}(\text{PhCN})\text{Cl}_2$, PPh_3 and CuI in toluene and diisopropylamine at 90 °C provided dibenzopentalene **1tt** in 67% yield (Scheme 22). Although this system is simpler than that in Scheme 21, no further applications for the synthesis of dibenzopentalenes have been reported.

Scheme 22. Preparation of Dibenzopentalene from 2-Iodophenylacetylene.

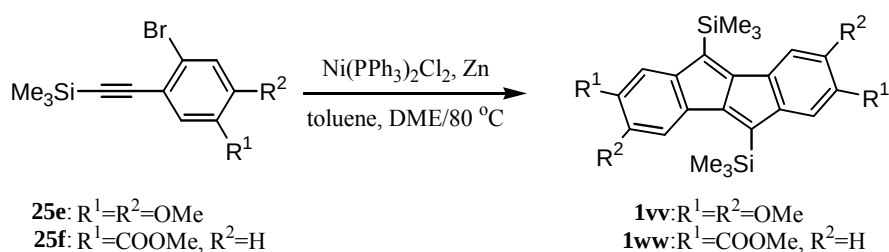


Being inspired by this catalytic system, an extremely simple synthesis of dibenzopentalenes from 2-bromoethynylbenzenes was reported. Treatment of 2-bromoethynylbenzene **25d** with an equivalent of $\text{Ni}(\text{PPh}_3)_2\text{Cl}_2$ and 1.5 equivalents of Zn at 80 °C produced dibenzopentalene **1uu** in 41% yield (Scheme 23) [43]. Reaction of **25d** with $\text{Ni}(\text{cod})_2$ and PPh_3 at 50 °C afforded Ni complex **36**, which was transformed into **1uu** at 80 °C. In the initial step, a generated intermediate Ni(0) complex $\text{Ni}(\text{PPh}_3)_2$ therefore underwent oxidative addition to **25d** to give **36**. The yield of **1uu** was improved to 46% in the presence of $\text{Ni}(\text{cod})_2$, PPh_3 and Zn at 110 °C. This method enabled the synthesis of a variety of dibenzopentalenes (13–24% yields) (Scheme 24 and 25) [43]. It is noted that the electronic nature of substituents on the aromatic rings did not affect the formation of dibenzopentalenes.

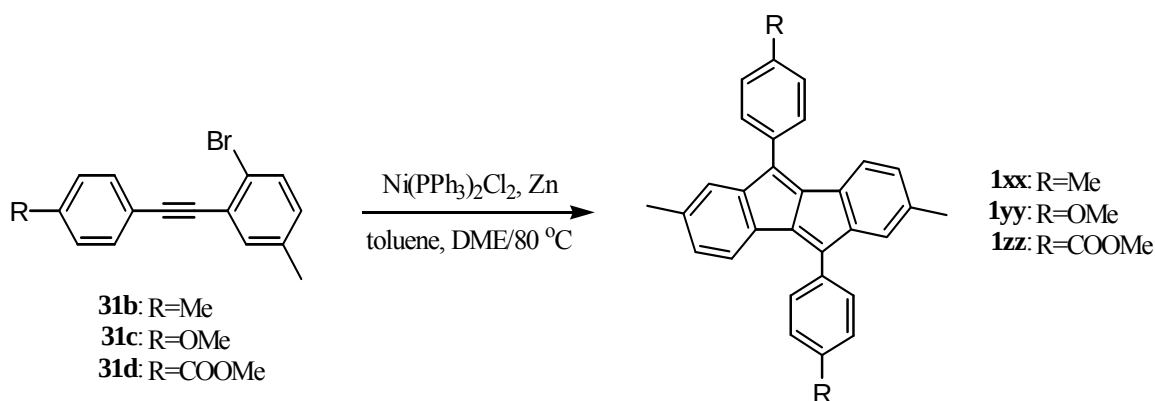
Scheme 23. Preparation of Dibenzopentalene with Ni(0) Catalyst.



Scheme 24. Preparation of Functionalized Dibenzopentalenes with Ni(0) Catalyst.



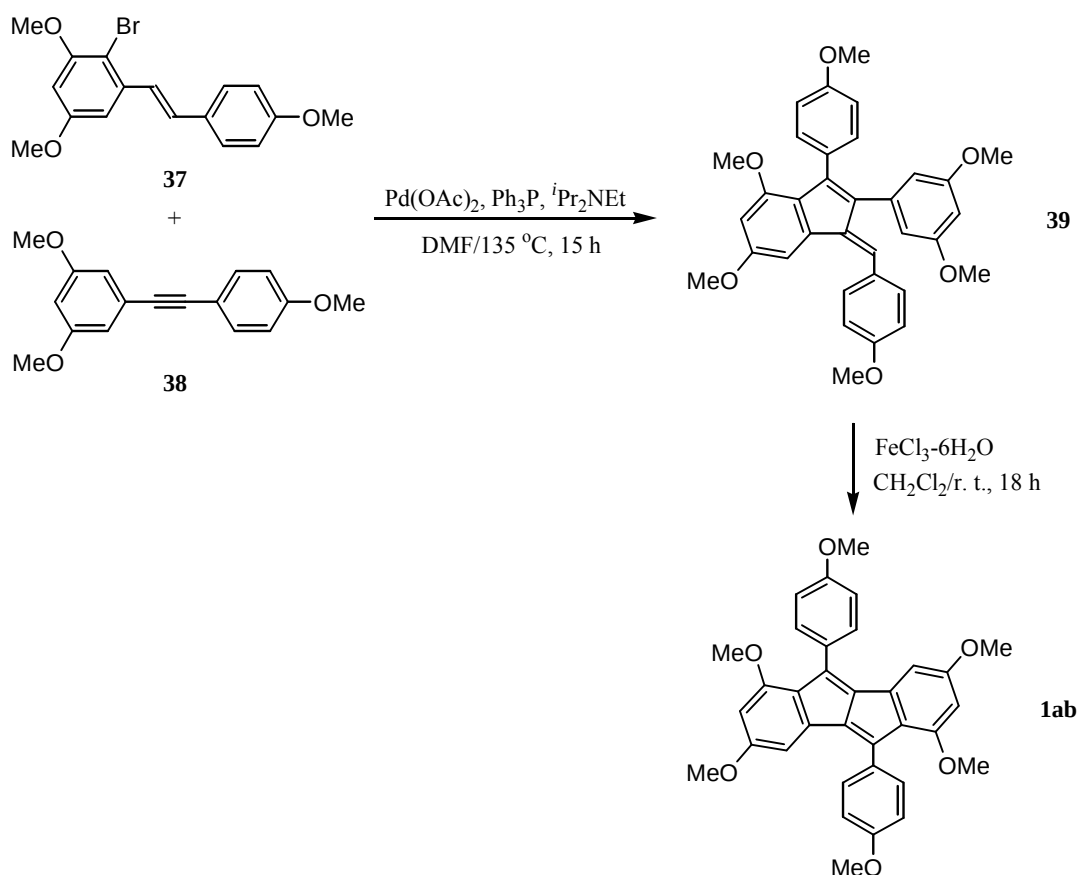
Scheme 25. Preparation of Diaryl-substituted Dibenzopentalenes with Ni(0) Catalyst.



A unique two-step synthesis of a dibenzopentalene was also reported recently. The two starting compounds **37** [44] and **38** were prepared from commercially available 3,5-dimethoxybenzaldehyde in

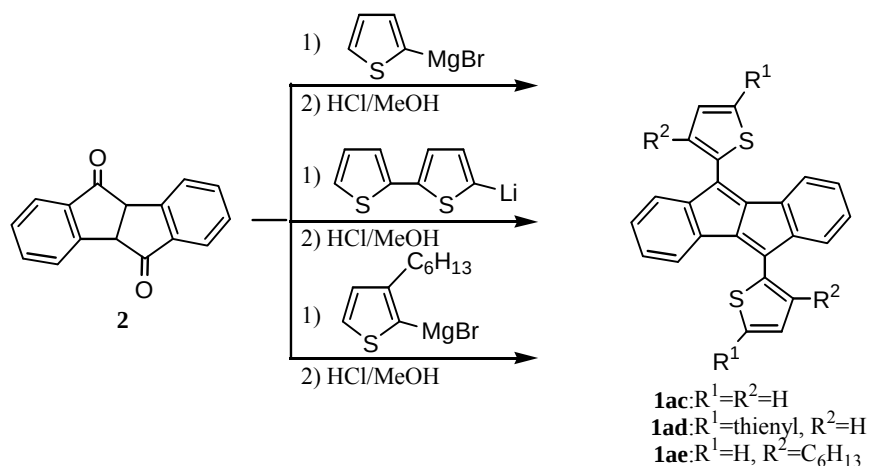
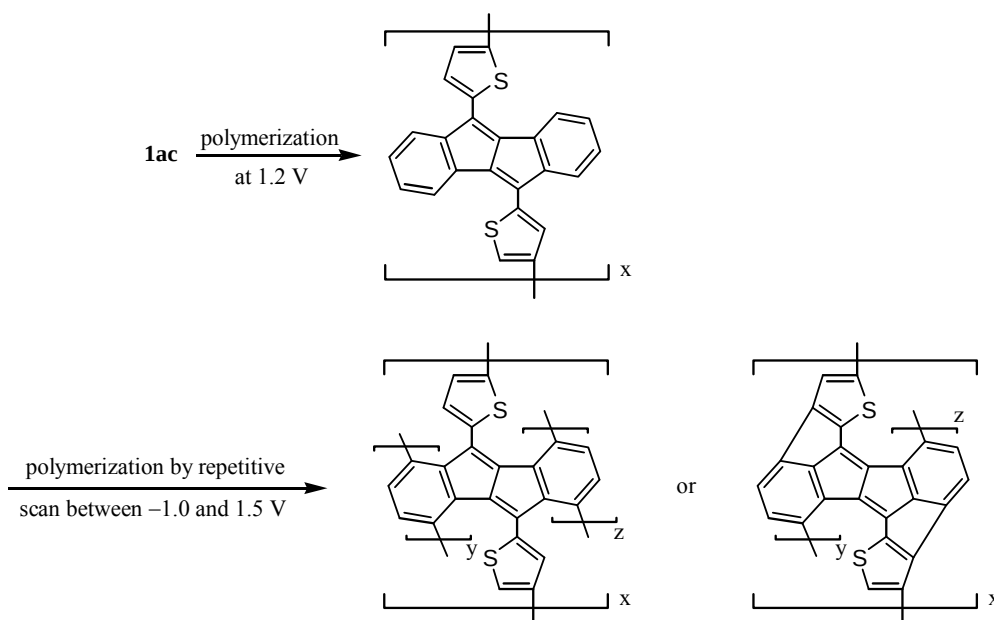
five and three steps, respectively. Compounds **37** and **38** were subjected to standard Heck reaction conditions to afford indene derivative **39** in 53% yield (Scheme 26) [45]. Oxidative cyclization of **39** occurred in the presence of FeCl_3 to provide dibenzopentalene **1ab** in 38% yield (Scheme 26) [45].

Scheme 26. Preparation of Dibenzopentalene through a Coupling Reaction of Stilbene and Tolane.



7. Preparation of Dibenzopentalene Polymer by Electrochemical Polymerization

Starting from diketone **2**, thienyl-substituted dibenzopentalenes were synthesized by the classical method (Scheme 27) [15]. Diketone **2** reacted with thienyllithium or thienylmagnesium bromide to afford the corresponding adducts, which were treated with acid to provide thienyl-substituted dibenzopentalenes **1ac-1ae**. When a cyclic voltammetric analysis of **1ac** was carried out, the growth of a new redox system was observed upon scanning between -1.0 and 1.2 V and the electrode was modified, suggesting polymerization of **1ac** on the electrode. The anodic study of the modified electrode between -1.0 and 1.5 V revealed that the original species on the modified electrode was further modified, perhaps due to intramolecular cyclization or polymerization through the benzene moiety (Scheme 28) [15]. The band gap of the resulting polymer was estimated to be about 2.2 V.

Scheme 27. Preparation of Thienyl-substituted Dibenzopentalenes from Diketone **2**.**Scheme 28.** Electrochemical Polymerization of Dibenzopentalene **1ac**.

8. Aromaticity of Dibenzopentalenes

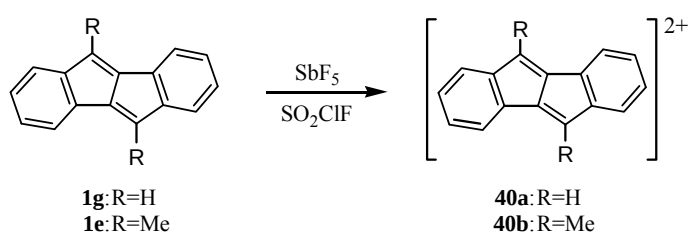
To evaluate aromaticity of dibenzopentalene, current densities in π -systems induced by external magnetic fields were calculated [46]. The current pattern of dibenzopentalene has three distinct regions, and the central paratropic ring current in the two five-membered rings is bordered by diatropic ring currents in the two benzene rings. The paratropic ring current in the central five-membered rings is derived from two π -electrons in the HOMO, whereas the diatropic benzene ring currents arise from several orbitals that lie just below the HOMO. This regional character of the current patterns is consistent with NICS [47] values for individual rings: the NICS values of the five- and six-membered rings are 7.4 and -9.8 ppm, respectively.

9. Ionic Species of Dibenzopentalenes

Redox behavior of dibenzopentalenes is of considerable interest because two-electron oxidation and reduction of dibenzopentalenes afford the corresponding 14π dications and 18π dianions, respectively, which are both expected to be aromatic.

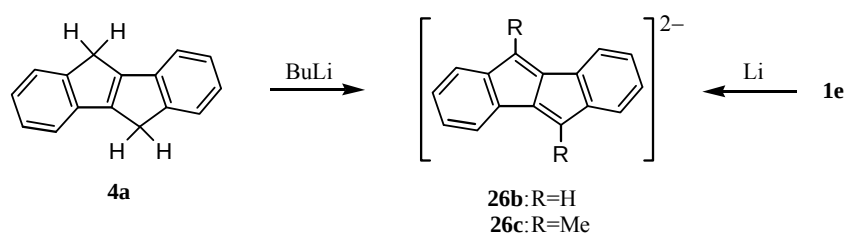
Treatment of dibenzopentalenes **1e** and **1g** with excess SbF_5 in SO_2ClF resulted in dark green and violet-purple solutions, respectively, attributed to the formation of dications **40** (Scheme 29) [48,49]. The ^1H NMR spectra of the resulting solutions showed considerable downfield resonances, compared with those of the starting **1e** and **1g**, suggesting that dications **40** are aromatic.

Scheme 29. Formation of Dications of Dibenzopentalenes.

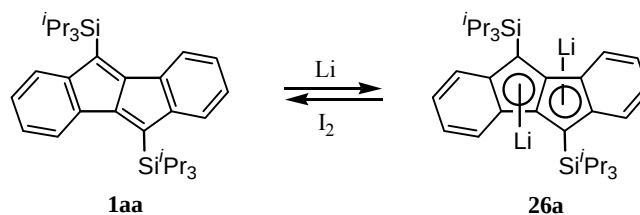


Dianion **26b** of the parent dibenzopentalene **1g** was synthesized by the reaction of dihydrodibenzopentalene **4a** with butyllithium (Scheme 30) [48,49]. Although the H1 and H9 resonated upfield, compared with those of **1g**, the other protons on the benzene rings were deshielded, suggesting diatropic ring current over the perimeter of the framework. It is therefore concluded that **26b** should be regarded as a peripheral aromatic dianion. Dianion **26c** of dibenzopentalene **1e** was synthesized by the reaction of **1e** with lithium, and a considerably aromatic character was observed (Scheme 30) [48,49].

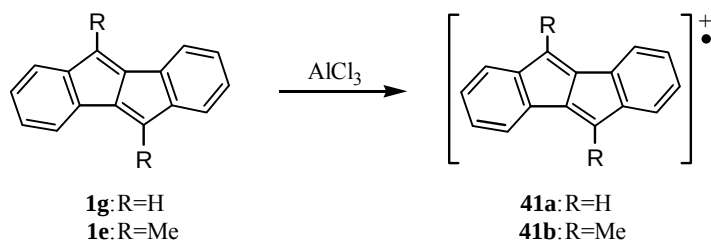
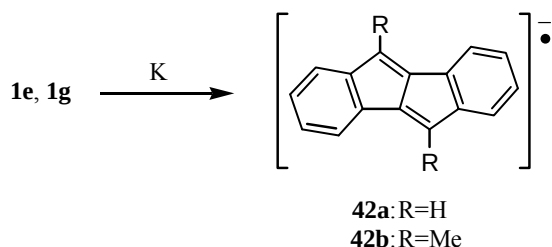
Scheme 30. Formation of Dianions of Dibenzopentalenes.



Very recently, the first report on the molecular structure of a dianion of a dibenzopentalene has appeared (Scheme 14) [33]. The X-ray crystallographic analysis of **26a** revealed that the five-membered rings contain nearly equalized C–C bond lengths, whereas a slight bond alternation in those of the six-membered ring is found, suggesting preferable aromatic delocalization in the five-membered ring over benzenoid delocalization. Similar trends were also found in some benzannulated anions [50–56]. Dianion **26a** was also synthesized by the reaction of the corresponding dibenzopentalene **1aa** with lithium (Scheme 31) [57]. Oxidation of **26a** occurred by treatment with iodine to provide **1aa**.

Scheme 31. Reversible Redox Behavior of Dibenzopentalene **1aa**.

Dications and dianions are formed through the cation radical and the anion radical, respectively. The synthesis of cation radicals **41a** and **41b** of dibenzopentalenes were accomplished by the reactions of dibenzopentalenes **1e** and **1g** with aluminum trichloride, the formation of which was evidenced by ESR spectroscopy (Scheme 32) [58]. Respective anion radicals **42a** and **42b** of **1e** and **1g** were synthesized by the reactions of **1e** and **1g** with potassium (Scheme 33) [58].

Scheme 32. Formation of Cation Radicals of Dibenzopentalenes.**Scheme 33.** Formation of Anion Radicals of Dibenzopentalenes.

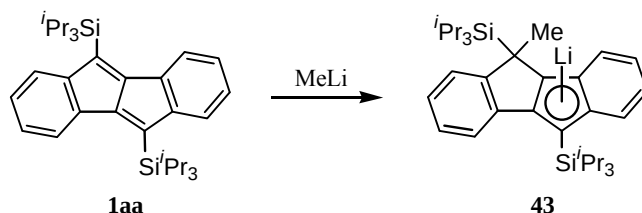
Subsequent challenging tasks are to characterize molecular structures of cation radicals, anion radicals and dications of dibenzopentalenes.

10. Reactions of Dibenzopentalenes

Although a variety of dibenzopentalenes can now be synthesized, their reactivity has been explored very little. Very recently, unique reactions of a dibenzopentalene were reported. Dibenzopentalene **1aa** reacted with methyllithium to quantitatively produce lithium 5-methyldibenzopentalenide **42**, the structure of which was established by X-ray crystallographic analysis (Scheme 34) [57]. Since 6,6-dimethylfulvene derivative reacted with methyllithium to give the corresponding lithium *t*-butylcyclopentadienide [59], **1aa** reacted with methyllithium as a fulvene to give **43**. The C–C bond lengths of the cyclopentadienyl anion moiety differ slightly, in contrast to dilithium dibenzopentalenide **26a** [33], which displays no alternation of the C–C bonds in the five-membered ring. The six-membered ring adjoining the anionic five-membered ring also has different C–C bond

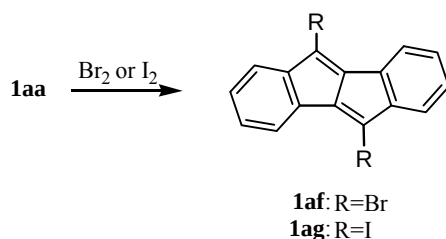
lengths in the anion. On the other hand, remarkable alternation of the C–C bonds is found in the cyclopentadiene ring of **43**. Nucleus-Independent-Chemical-Shifts (NICS) values calculated at 1.0 Å above (−12.5 ppm) and below (−12.9 ppm) the cyclopentadienide ring [47,60] of the model compound of **43** are negative, suggesting aromatic character of the cyclopentadienide ring.

Scheme 34. Reaction of Dibenzopentalene **1aa** with Methyllithium.



Dibenzopentalene **1aa** reacted with bromine and iodine to provide the corresponding dihalodibenzopentalenes **1af** and **1ag** in very high yields (Scheme 35) [57]. Dihalodibenzopentalenes would be good starting compounds for further functionalization of dibenzopentalenes.

Scheme 35. Reaction of Dibenzopentalene **1aa** with Halogens.



11. Summary and Outlook

Dibenzopentalenes have long been known, and their unique redox behavior leading to 14π and 18π aromatic species is well established. However, their chemistry is still limited because of the lack of versatile synthetic methods. Very recently, there have been reported several efficient methods for the synthesis of a wide variety of dibenzopentalenes, together with their unique reactions. It is therefore appropriate to cultivate a new chemistry of dibenzopentalenes, which would be applied as building blocks of new π -extended sandwich complexes and redox-active materials.

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