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The $B(C_6F_5)_3$ Boron Lewis Acid Route to Arene-Annulated Pentalenes

Chao Chen,[a] Marcel Harhausen,[a, b] Aiko Fukazawa,[b] Shigehiro Yamaguchi,*[b] Roland Fröhlich,[a] Constantin G. Daniliuc,[a] Jeffrey L. Petersen,[c] Gerald Kehr,[a] and Gerhard Erker*[a]

Abstract: 4,5-Dimethyl-1,2-bis(1-naphthylethynyl)benzene (**12**) undergoes a rapid multiple ring-closure reaction upon treatment with the strong boron Lewis acid $B(C_6F_5)_3$ to yield the multiply annulated, planar conjugated π-system **13** (50% yield). In the course of this reaction, a C_6F_5 group was transferred from boron to carbon. Treatment of **12** with $CH_3B(C_6F_5)_2$ proceeded similarly, giving a mixture of **13** (C_6F_5-transfer) and the product **15**, which was formed by CH_3-group transfer. 1,2-Bis(phenylethynyl)benzene (**8a**) reacts similarly with $CH_3B(C_6F_5)_2$ to yield a mixture of the respective C_6F_5- and CH_3-substituted dibenzopentalenes **10a** and **16**. The reaction is thought to proceed through zwitterionic intermediates that exhibit vinyl cation reactivities. Some $B(C_6F_5)_3$-substituted species (**26**, **27**) consequently formed by in situ deprotonation upon treatment of the respective 1,2-bis(alkynyl)benzene starting materials (**24**, **8**) with the frustrated Lewis pair $B(C_6F_5)_3/P(o\text{-tolyl})_3$. The overall formation of the C_6F_5-substituted products formally require $HB(C_6F_5)_2$ cleavage in an intermediate dehydroboration step. This was confirmed in the reaction of a thienylethynyl-containing starting material **21** with $B(C_6F_5)_3$, which gave the respective annulated pentalene product **23** that had the $HB(C_6F_5)_2$ moiety 1,4-added to its thiophene ring. Compounds **12**–**14**, **23**, and **26** were characterized by X-ray diffraction.

Keywords: conjugation · cyclization · dibenzopentalenes · internal alkynyl coupling · Lewis acids

Introduction

Their extended conjugated π-systems at planar polycyclic frameworks make dibenzopentalenes and their derivatives very interesting substrates for the development of advanced organic materials.[1] There are surprisingly few viable synthetic entries to dibenzopentalene systems. Most of them involve metal-induced or metal-catalyzed reactions. Some of them require quite harsh reaction conditions; some otherwise very attractive pathways still give rather low yields.[2] Nevertheless, there has been a small number of attractive dibenzopentalene syntheses described in the recent literature involving typical metal-catalyzed coupling reactions. Here are a few typical examples: Tilley et al. utilized the Pd-catalyzed coupling of compounds **1a** and **2** to produce the diphenyl-substituted dibenzopentalene system **3** (and a number of related derivatives) at high temperature (> 130 °C).[3] Kawase et al. found that acetylenic substrates such as **1b** could be homocoupled by treatment with zinc powder and a nickel catalyst to give the dibenzopentalene derivatives **4** (see Scheme 1).[4] Saito et al. found a unique synthetic entry to dibenzopentalenes by means of treatment of alkyne **5** with elemental lithium. The dianion of the corresponding dibenzopentalene **4** was probably formed in a radical pathway. Subsequent oxidation with I_2 gave **4** (Scheme 2).[5,6]

[a] Dr. C. Chen,[+] Dr. M. Harhausen,[+] Dr. R. Fröhlich,[++] Dr. C. G. Daniliuc,[++] Dr. G. Kehr, Prof. G. Erker
Organisch Chemisches Institut der Universität Münster
Corrensstrasse 40, 48149 Münster (Germany)
E-mail: erker@uni-muenster.de

[b] Dr. M. Harhausen,[+] Prof. A. Fukazawa, Prof. S. Yamaguchi
Department of Chemistry Graduate School of Science
Nagoya University
Furo, Chikusa, Nagoya, 464-8602 (Japan)
E-mail: yamaguchi@chem.nagoya-u.ac.jp

[c] Prof. J. L. Petersen[++]
Bennett Department of Chemistry
West Virginia University
P.O. Box 6045, Morgantown, WV 26506 (USA)

[+] These authors contributed equally to this work.

[++] X-ray crystal structure analyses.

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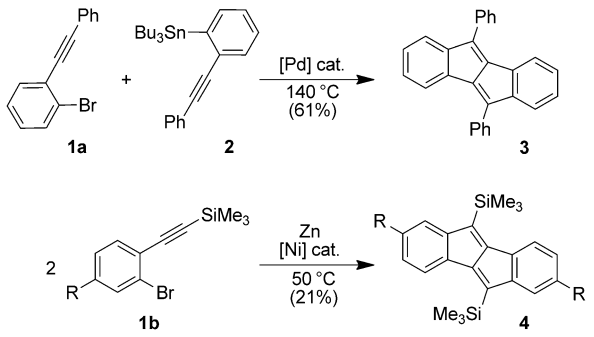
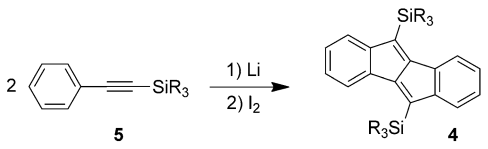
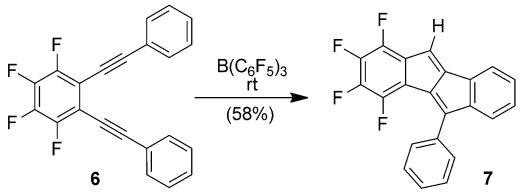


Scheme 1. Examples of previously reported dibenzopentalene systems.



Scheme 2. Redox pathway to a dibenzopentalene derivative.

In a recent communication we disclosed a novel metal-free entry to dibenzopentalene systems. Our new $B(C_6F_5)_3$-induced reaction is also special in the sense that it yields unsymmetrically substituted dibenzopentalenes by a simple isomerization reaction of *o*-dialkynylbenzene derivatives under very mild reaction conditions. The formation of **7** from **6** is an example (see Scheme 3).[7]



Scheme 3. $B(C_6F_5)_3$-induced synthesis of **7**.

In some cases we observed a more complex reaction pathway with competing C_6F_5-transfer. Typical examples are the reactions of the starting materials **8a**,**b** with $B(C_6F_5)_3$ which gave mixtures of the products **9a**,**b**, **10a**,**b**, and **11a**,**b** (Scheme 4). The formation of the stoichiometric C_6F_5-transfer products **10** involved a dehydroboration reaction, which was supported by internal $HB(C_6F_5)_2$ trapping in a bis-thienyl-substituted derivative, and we also observed some $B(C_6F_5)_3$-substituted deprotonation products in conjunction with trapping experiments using bulky amine bases.[7] The indene-type products **11** also involved stoichiometric C_6F_5-transfer reactions. These compounds were, however, probably formed as secondary products from a boron-containing species during the work-up procedure.[7,8]

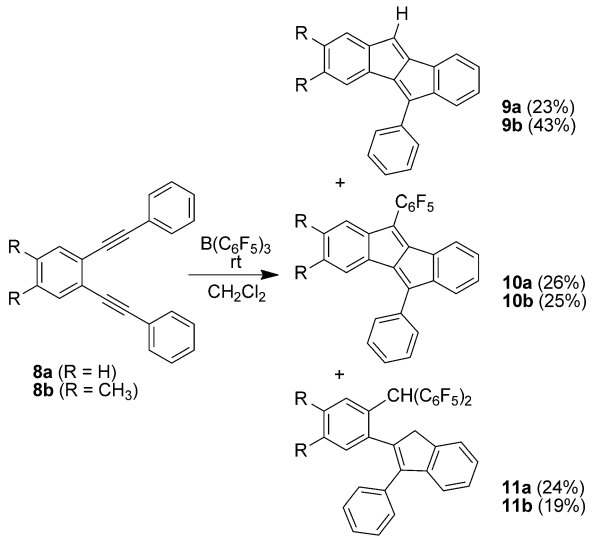
We have now substantially extended this reaction and obtained additional mechanistic evidence to understand the potentially competing pathways taken in the reactions of *o*-1,2-bis(arylalkynyl)benzenes with the strongly electrophilic $RB(C_6F_5)_2$ reagents.[9,10] These new and extended examples will be described in this account.

Results and Discussion

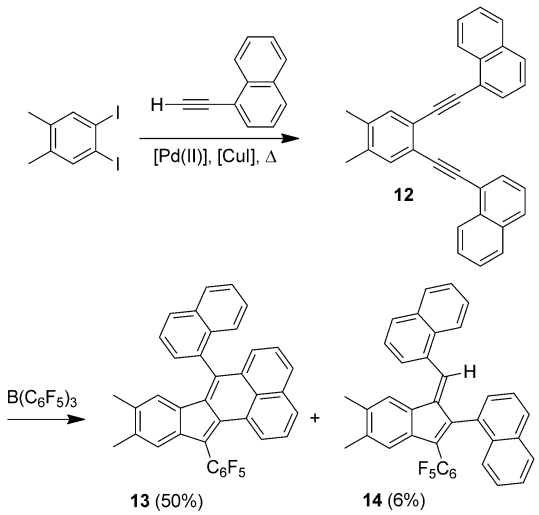
Reaction of Naphthyl-Substituted Bisalkynylbenzenes

We prepared 1,2-diiodo-4,5-dimethylbenzene from *o*-xylene according to a literature procedure.[11] This was then Sonogashira coupled[12] with 1-ethynylnaphthalene[13] to give the bisalkynylbenzene derivative **12** (39%). Compound **12** shows acetylenic ^{13}C NMR resonances of the pair of symmetry-equivalent C≡C-naphthyl substituents at δ 93.9 and 90.9 ppm, and a respective IR band at $\tilde{\nu}=2172\ cm^{-1}$. Compound **12** was furthermore characterized by X-ray diffraction. It shows the typical structural features of doubly substituted alkyne moieties. The conformational arrangement of the pair of naphthyl substituents at the ends of the linear alkyne units is close to C_2-symmetric (the structure is depicted in the Supporting Information).

We mixed **12** with $B(C_6F_5)_3$ (1 molar equiv) at low temperature in CH_2Cl_2 (−20 °C) and then let the mixture warm to room temperature, followed by stirring for 2 days. Work-up involving chromatographic separation eventually gave the product **13** as a dark red solid in 50% yield and the minor component **14** (6%) (see Scheme 5). In both cases, a C_6F_5 substituent was transferred concurrently with the ring-closure reactions. Consequently, we have monitored five ^{19}F NMR resonances of the C_6F_5 substituent of the



Scheme 4. Preparation of the products **9–11**.



Scheme 5. Formation of the products **13** and **14**.

product **13** at δ −138.0/−138.2 (*o*), −155.2 (*p*), and −161.39/−161.44 ppm (*m*-F of C_6F_5), indicating a hindered rotation of the ring (with respect to the NMR time scale). We have monitored the typical signal of the remaining 1-naphthyl substituent in **13** and those of the annulated $C_{10}H_6$ unit. Compound **13** features ^{1}H NMR methyl singlets at δ 2.14 (3H) and 1.82 ppm (3H) and the resonances of their adjacent CH units at δ 6.73 and 5.73 ppm (each 1H), respectively.

Both the products **13** and **14** were characterized by X-ray diffraction. The structure of the major product **13** in the crystal shows the presence of the phenalene framework that is annulated with the substituted indene building block. The pentacyclic annulated framework is planar and completely unsaturated. The indene six-membered ring bears a pair of methyl substituents and the adjacent five-membered carbocycle bears the C_6F_5-substituent that had been transferred from the $B(C_6F_5)_3$ Lewis acid during the reaction. It is rotated almost perpendicular to the indene plane (dihedral angle C34-C33-C1-C2 −114.6(4)°). The next six-membered ring of **13** has the remaining 1-naphthyl substituent attached to it (θ C14-C13-C23-C32 −98.0(4)°) (see Figure 1).

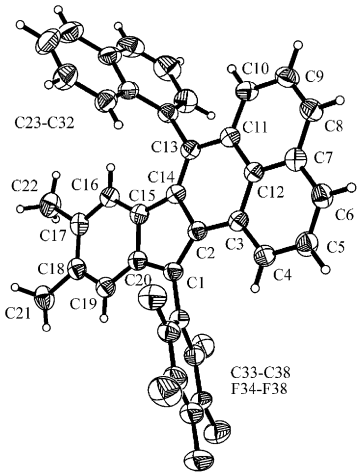
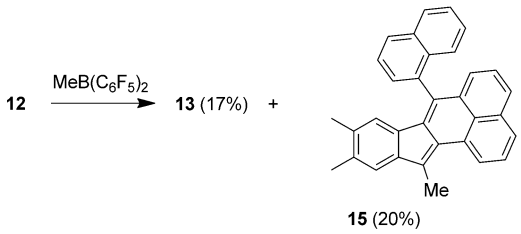


Figure 1. A projection of the molecular structure of compound **13** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å): C1–C2 1.388(4), C2–C14 1.467(4), C14–C15 1.467(4), C15–C20 1.409(4), C2–C3 1.451(4), C3–C12 1.435(4), C12–C11 1.419(4), C11–C13 1.453(4), C13–C14 1.358(4), C3–C4 1.376(4), C4–C5 1.402(4), C5–C6 1.360(5), C6–C7 1.401(5), C7–C12 1.415(5), C15–C16 1.393(4), C16–C17 1.391(4), C17–C18 1.399(5), C18–C19 1.398(4).

The minor reaction product **14** shows the NMR resonances of a pair of different naphthyl substituents. We have monitored the ^{1}H/^{13}C NMR features of the exocyclic fulvene=CH[naphthyl] unit at δ 7.25/134.6 ppm. In addition, this product also contains a C_6F_5 substituent at the indene five-membered carbocycle (^{19}F NMR: δ −137.9/−138.0 (*o*), −155.6 (*p*), −162.8/−162.9 ppm (*m*-F of C_6F_5). Compound **14** was also characterized by X-ray diffraction (see the Supporting Information for details).

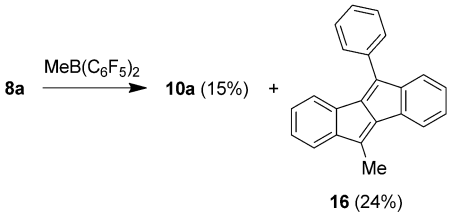
We also reacted the naphthyl-substituted starting material **12** with the methyl group-containing borane $CH_3B(C_6F_5)_2$.[10] From the chemistry of the alkyl-$B(C_6F_5)_2$-induced 1,1-carboborations[14,15] we might have expected to find a reaction route favored by selective methyl-group transfer. However, it turned out that the reaction of $CH_3B(C_6F_5)_2$ with **12** is rather unselective. We have observed the formation of the products **13** and **15**, formed by C_6F_5 or CH_3 transfer, respectively, in a close to 1:1 molar ratio (Scheme 6). The products



Scheme 6. Preparation of the products **13** and **15**.

were separated by column chromatography. The new product **15** was characterized by spectroscopy (CH_3: ^{1}H NMR: δ: 2.68, 2.22, and 1.81 ppm; for further details, see the Experimental Section and the Supporting Information).

A similar result was obtained when the doubly phenyl-substituted starting material **8a** (see Scheme 4) was reacted with the boron Lewis acid $CH_3B(C_6F_5)_2$. Stirring the mixture for 2 days at room temperature in dichloromethane gave a mixture of the respective products **10a** (formed by C_6F_5-transfer) and **16** (formed by transfer of the CH_3-group) (see Scheme 7). The products were separated by chromatography, and the new product **16** was characterized by spectroscopy (CH_3: δ 2.25 (^{1}H), 12.1 ppm (^{13}C), see the Experimental Section for details).



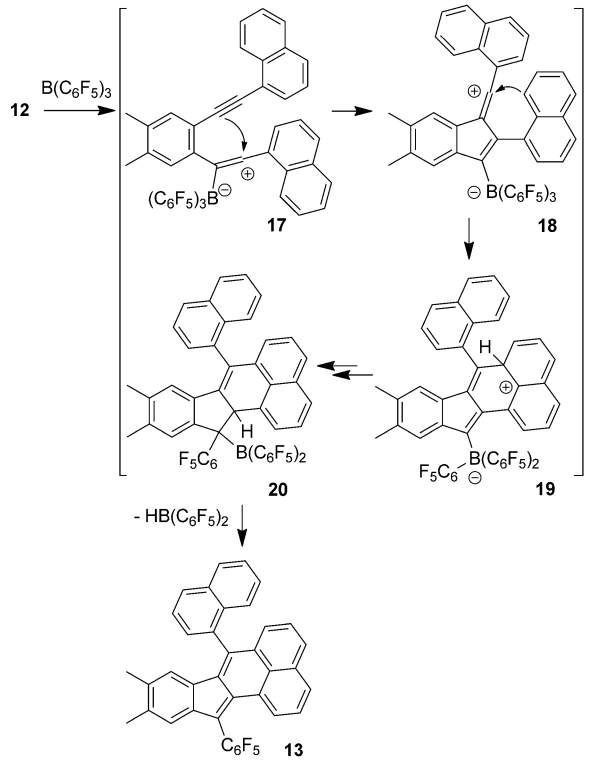
Scheme 7. Preparation of the compounds **10a** and **16**.

Variations and Mechanistic Implications

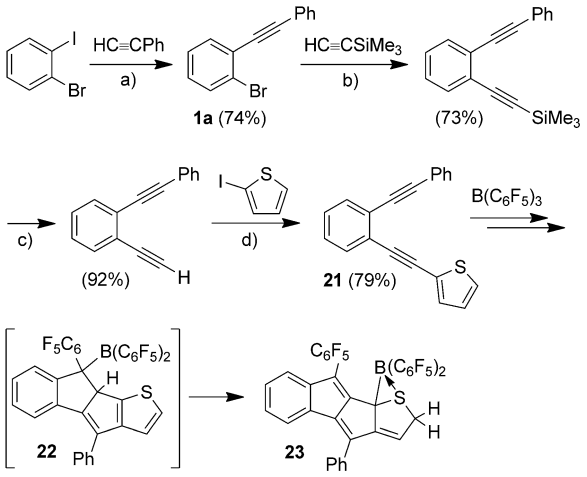
We have shown with a series of examples that 1,2-bis(arylethynyl)benzenes can readily be converted into substituted dibenzopentalenes and related systems containing extended π-systems at planar polycyclic carbon σ-frameworks. The overall boron Lewis acid induced reaction sequences involve typical carbocation reactivities. This can be formulated for both the naphthyl- and phenyl-substituted examples. The re-

action sequence followed in the naphthyl series[1a] can probably be described as follows (see Scheme 8). We assume that the reaction starts by $B(C_6F_5)_3$ addition to the proximal acetylene carbon atom of **12**. The ensuing vinyl cation reactivity of a resulting zwitterionic intermediate (**17**) allows for the subsequent closure of the five-membered ring to generate **18**, which then might be prone for electrophilic attack on the adjacent 1-naphthyl substituent (**19**). C_6F_5-substituent migration (**20**) with subsequent elimination of $HB(C_6F_5)_2$ would then directly lead to the observed major product **13**. This general pathway that formally involves a variant of a 1,1-carboboration at an acetylene carbon atom[1a,15] is supported by our findings in the corresponding phenyl- and thienyl-substituted series (see below), where we were able to deprotonate the $B(C_6F_5)_3$-substituted intermediate with P-(*o*-tolyl)$_3$ as the Lewis base (utilizing the frustrated Lewis pair effect[16]). We also could trap the $HB(C_6F_5)_2$ product from the necessary dehydroboration reaction in the thienyl series.

We have obtained the supporting evidence for several of the proposed steps by studying the reactions of a variety of different substituted 1,2-bis(alkynyl)benzene derivatives with $B(C_6F_5)_3$ under special conditions. Let us first address the retro-hydroboration reaction that we have proposed to take place at the stage of the reactive intermediate **20** (see Scheme 8). For that purpose we prepared the unsymmetrical thienyl-containing bis(alkynyl)benzene derivative **21** by means of the synthetic sequence outlined in Scheme 9. Compound **21** was then reacted with one molar equivalent of B-



Scheme 8. Formal mechanistic pathway of the formation of compound **13**.



Scheme 9. a) NEt_3, rt, 24 h, $[Pd(PPh_3)_2Cl_2]$ cat., CuI. b) NEt_3, 60 °C, 3 days, $[Pd(PPh_3)_2Cl_2]$ cat., CuI. c) K_2CO_3, MeOH, rt, 4 h. d) $[Pd(PPh_3)_2Cl_2]$ cat., CuI.

$(C_6F_5)_3$ in pentane at room temperature overnight. Work-up eventually gave the product **23** as a red-brown solid, isolated in 40 % yield. The X-ray crystal structure analysis (single crystals were obtained from CH_2Cl_2/pentane at room temperature by the diffusion method) revealed that the $HB(C_6F_5)_2$ addition product to a thieno-annulated benzopentalene system[17,18] had been obtained. Product **23** features a C_6F_5 group and a phenyl substituent at the central pentalene-derived unit. It shows a $B(C_6F_5)_2$ substituent at the junction with the thiophene framework, whose sulfur atom forms a dative bond to the adjacent boron Lewis acid [C2-B1 1.589(3) Å, S1-B1 1.984(2) Å, C2-S1 1.887(2) Å] (see Figure 2).

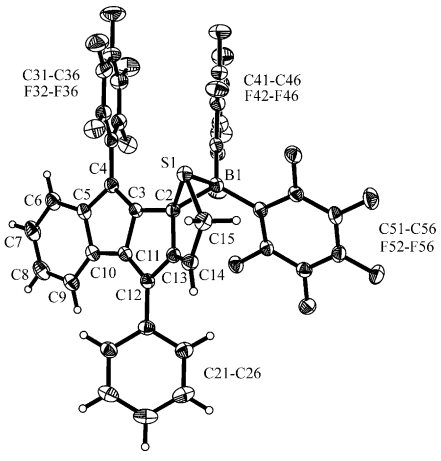
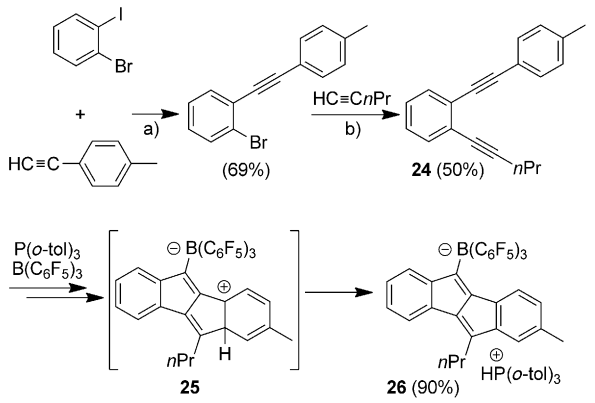


Figure 2. Molecular structure of compound **23** (thermal ellipsoids are shown with 30 % probability). Selected bond lengths (Å) and angles (°): C2–B1 1.589(3), S1–B1 1.984(2), C2–S1 1.887(2), C2–C13 1.505(2), C13–C14 1.333(3), C14–C15 1.500(3), C2–C3 1.477(2), C3–C4 1.357(3), C3–C11 1.469(3), C11–C12 1.372(3), C11–C10 1.467(3), C12–C13 1.471(3); C3-C2-S1 128.5(1), C3-C2-B1 128.8(2), C4-C3-C2 142.7(2).

In solution the internal hydroboration product **23** shows ^{1}H NMR resonances of the CH_2 group of the dihydrothiophene moiety at δ 4.09 and 3.59 ppm ($^{2}J_{HH}$ = 17.0 Hz) and of the adjacent =C-H proton at δ 5.43 ppm. Compound **23** shows six separate *o*-C_6F_5 ^{19}F NMR resonances and three separate *p*-C_6F_5 resonances of the C_6F_5 substituent at carbon and both chemically inequivalent C_6F_5 groups at boron (^{11}B: −6.9 ppm).

The formation of product **23** indicates that a retro-hydroboration is likely to proceed after the C_6F_5-transfer from boron to a carbon atom of the pentalene framework had occurred to generate **22** (see Scheme 9; which is the thiophene-containing equivalent of intermediate **20** in Scheme 8). In the case of **22**, the liberated $HB(C_6F_5)_2$ is then apparently trapped internally by 1,4-addition to the annulated thiophene framework at this specific arene/hetarene-annulated pentalene framework.[7]

We have also obtained some experimental support for the involvement of a dibenzopentalene borate intermediate (see **19**, Scheme 8) by using the unsymmetrically substituted bis(alkynyl)benzene derivative **24** as the starting material for the cyclization reaction with $B(C_6F_5)_3$. Compound **24** was readily prepared by a twofold Sonogashira coupling reaction starting from *o*-bromoiodobenzene (Scheme 10). We then



Scheme 10. a) NEt_3, rt, 24 h, $[Pd(PPh_3)_2Cl_2]$ cat., CuI. b) $HNiPr_2$, 80 °C, 3 days, $[Pd(PPh_3)_2Cl_2]$ cat., CuI.

reacted the starting material **24** with the intermolecular frustrated Lewis pair (FLP) $B(C_6F_5)_3$/P(*o*-tolyl)$_3$[16,19] in pentane at room temperature. Product formation was apparently initiated by $B(C_6F_5)_3$ Lewis acid addition to the C≡C-(*p*-tolyl) unit, followed by ring closure with the adjacent C≡C-*n*-propyl function and subsequent electrophilic aromatic substitution to generate the alleged intermediate **25**. This was then effectively deprotonated under the applied reaction conditions by the bulky P(*o*-tolyl)$_3$ Lewis base component of the FLP to give the observed product **26**.

The phosphonium/dibenzopentalenylborate salt **26** was isolated as a brown solid in 90% yield. In solution it features the typical ^{1}H NMR resonances of the *n*-propyl substituent, a ^{11}B NMR resonance at δ −16.1 ppm, a ^{31}P NMR resonance of the [P]H unit at δ −13.2 ppm with a typical coupling constant of $^{1}J_{PH}$ = 482 Hz, and a total of 15 separated ^{19}F NMR features of the $B(C_6F_5)_3$ substituent, which contains a chiral propeller conformational geometry that is "frozen" on the NMR time scale under the applied monitoring conditions at 298 K.

Compound **26** was also characterized by X-ray diffraction (single crystals were obtained from a layered CH_2Cl_2/*n*-heptane mixture at room temperature). The X-ray crystal structure analysis (see Figure 3) confirmed the regioselective for-

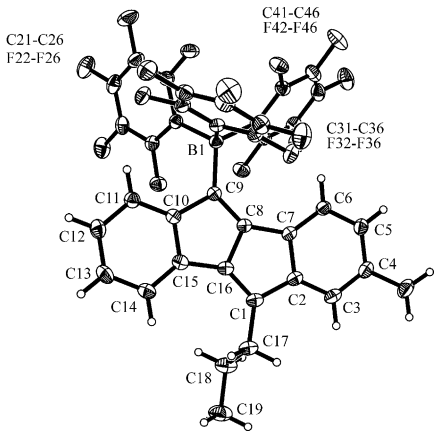
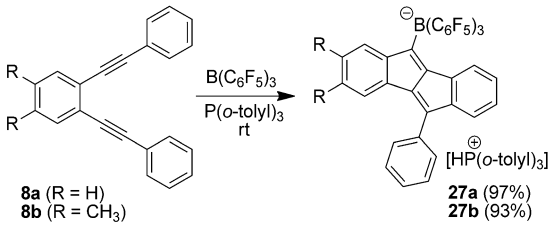


Figure 3. Molecular structure of the anion of salt **26** (thermal ellipsoids are shown with 30% probability). Selected bond lengths (Å) and angles (°): C1–C2 1.482(3), C2–C7 1.424(3), C7–C8 1.482(3), C8–C9 1.371(3), C9–C10 1.505(3), C10–C15 1.419(3), C15–C16 1.454(3), C16–C1 1.364(3), C1–C17 1.497(3), C9–B1 1.627(3); C8-C9-B1 133.8(2), C10-C9-B1 120.7(2), C2-C1-C17 125.4(2), C16-C1-C17 128.2(2).

mation of the triply substituted dibenzopentalene framework. Compound **26** shows the methyl group at the terminal phenylene ring syn-oriented to the *n*-propyl substituent at the dibenzopentalene "C-ring" and the bulky $B(C_6F_5)_3$ propeller arranged at the opposite sector at the adjacent central five-membered ring system. The structure features an independent $[HP(o\text{-tolyl})_3]^+$ phosphonium counter cation in the crystal.

We also treated the bis(phenylethynyl)benzene starting materials **8a** and **8b** with the $B(C_6F_5)_3$/P(*o*-tolyl)$_3$ FLP. Under similar reaction conditions, this resulted in the formation of the related salts **27a**,**b** in high yield (see Scheme 11).



Scheme 11. Formation of the salts **27a**,**b**.

Electronic Structure and Properties of Dibenzopentalenes and Related π-Electron Systems

The synthesized dibenzopentalenes and related π-electron systems are an attractive class of molecules with planar polycyclic skeletons. Kawase and coworkers have already reported that dibenzopentalene derivatives exhibit characteristic absorption spectra with a very weak absorption band in the long-wavelength region around 600 nm.[3b,4,17] They also demonstrated that this absorption band is attributable to forbidden HOMO–LUMO transitions, which are one of the characteristics of 4nπ electron systems. We have recently reported the electronic effect of electron-withdrawing C_6F_5 groups on the electronic structure of dibenzopentalenes, leading to significant bathochromic shifts of the absorption bands.[7] With a new phenalene-containing π-conjugated system in hand, we were interested in the perturbation by a phenalene moiety in **13** to the electronic structure.

We first evaluated the photophysical properties of the indenophenalene π system **13** in comparison with the dibenzopentalene derivative **10b**. Figure 4 displays the UV/Vis absorption spectra of compounds **13** and **10b** in acetonitrile.

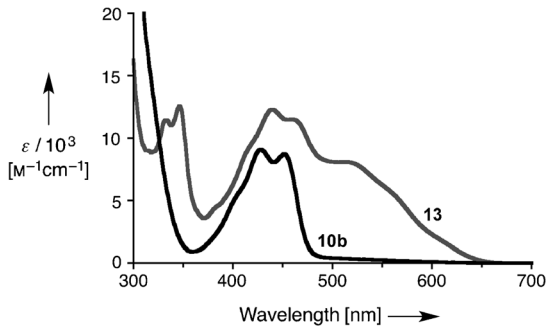


Figure 4. UV/Vis absorption spectra of **10b** (black) and **13** (gray) in acetonitrile.

Compound **13** exhibits the longest-wavelength absorption band with the maximum wavelength (λ_{max}) of 513 nm with a relatively large molar extinction coefficient ($\varepsilon = 8100$), which contrasts the fact that the longest-wavelength absorption band of the dibenzopentalene derivative **10b** around 600 nm is very weak. This result indicates that the extension of the π-conjugated skeleton with a phenalene skeleton significantly alters the electronic structure and thus the photophysical properties.

To gain insights into the difference in the electronic structure between dibenzopentalenes and indenophenalenes, DFT calculations were conducted for **10b** and **13** at the B3LYP/6-31G(d) level (Figure 5). In **13**, both the HOMO and LUMO are effectively delocalized over the indenophenalene skeleton. Although the character of the LUMOs in **10b** and **13** resembles each other, the HOMO and HOMO −1 in **10b** switch the order in **13**, presumably due to the expanded π conjugation in the phenalene substructure in the HOMO of **13**. As a result, **13** has a higher-lying HOMO

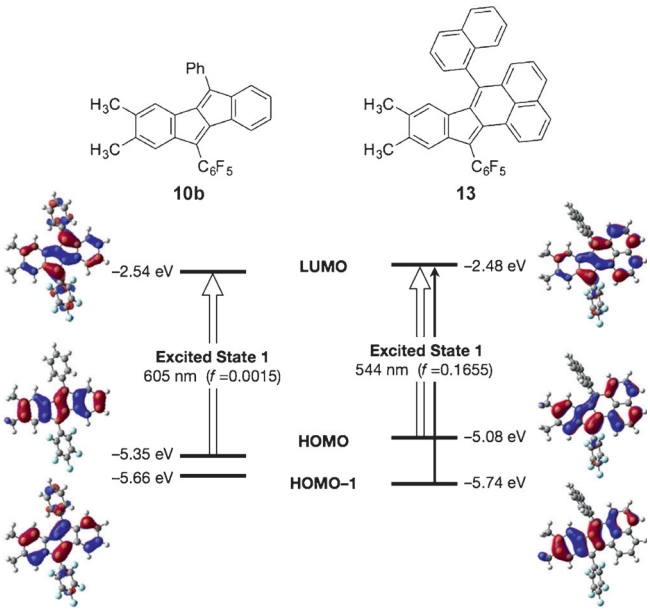


Figure 5. Energy diagrams and pictorial representations of the HOMO-1, HOMO, and LUMO of the dibenzopentalene **10b** and the relevant phenalene-fused system **13** calculated at the B3LYP/6-31G(d) level, and their lowest energy transitions estimated by TD-DFT calculations at the B3LYP/6-31G(d) level.

than **10b**. Based on time-dependent DFT (TD-DFT) calculations, the HOMO–LUMO transition is mainly responsible for the longest-wavelength absorption in **13**. The blue shift as well as the significantly larger ε value in the longest-wavelength absorption band of **13** compared to **10b** is consistent with the results of the calculated values (**13**: $\lambda =$ 554 nm, $f = 0.0015$; **10b**: $\lambda = 605$ nm, $f = 0.1655$).

Another notable feature of the indenophenalene **13** is the high electrochemical stability as verified by cyclic voltammetry (Figure 6). Compound **13** showed reversible redox waves

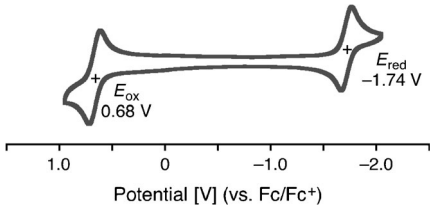


Figure 6. Cyclic voltammogram of **13** measured in CH_2Cl_2 (sample: 1 mM; $Bu_4N^+PF6^-$: 0.1 M; scan rate: 100 mV s^{-1}). Fc = ferrocene.

with first oxidation and reduction potentials of $E_{1/2} = 0.68$ V and −1.74 V (versus Fc/Fc^+), respectively. These results demonstrate that the incorporation of the phenalene-fused structure strongly perturbs the electronic structure, and also indicate the potential application of this new ring-fused π skeleton as a building block of redox-active functional organic dyes.

Conclusions

Our study shows that rather complex, extended, fully conjugated and annulated organic π-systems can rather easily be obtained by means of sequential carbon–carbon coupling reactions initiated and mediated by strongly electrophilic RB-$(C_6F_5)_2$-type Lewis acids. There are still some selectivity issues that need attention but we have found promising examples that indicate a potential usefulness of this method for forming such extended π-systems easily from readily available acetylenic precursors.

Experimental Section

General procedures

All syntheses involving air- and moisture-sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of argon. Solvents were dried and stored under an argon atmosphere. NMR spectra were recorded on a Bruker AC 200P, on a Bruker AV 300, on a Bruker AV 400, on a Varian Inova 500, and on a Varian UnityPlus 600 spectrometer. ^{1}H NMR and ^{13}C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ (external reference, $\delta=0$), ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference, $\delta=0$), ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (85% in H_2O) (external reference, $\delta=0$). NMR assignments were supported by additional 2D NMR experiments. Elemental analyses were performed on an Elementar Vario El III instrument. IR spectra were recorded on a Varian 3100 FT-IR spectrometer (Excalibur Series). Melting points were obtained with a DSC Q20 instrument (TA Instruments). Electrospray ionization mass spectra (MS-ESI) were recorded on a Bruker Micro-TOF machine. Prior exact mass (EM) measurement calibration was performed using sodium formiate clusters. The spectra are described by listing the calculated mass and the observed signals or by comparison of the isotopic pattern of the calculated and the measured signals of the mass. A preparative gel permeation chromatography (GPC) system [LC-9201 (Japan Analytical Industry) equipped with a polystyrene gel column (JAIGEL 1H and 2H, Japan Analytical Industry)] was used for further purification of diyne and pentalene derivatives. UV/VIS spectra were recorded in Nagoya using a Shimadsu UV-3150 UV-VIS NIR spectrophotometer. Listed are the solvent, the wavelength of the extinction maxima (λ_{max}), and the molar extinction coefficient ε. X-Ray diffraction: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection, COLLECT; data reduction, Denzo-SMN;[26] absorption correction, Denzo;[27] structure solution, SHELXS-97;[28] structure refinement, SHELXL-97;[29] and graphics, XP (BrukerAXS, 2000). Thermals ellipsoids are shown with 30% probability, R-values are given for observed reflections, and wR^2 values are given for all reflections. Exceptions and special features: Compound **14** crystallized with one half dichloromethane molecule per asymmetric unit. The structure was refined with Flack parameter of 0.37(4). CCDC 981779 (**12**), CCDC 981780 (**13**), CCDC 981781 (**14**), CCDC 981782 (**23**), CCDC 981783 (**26**) 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.

Compounds **8a**,[20] **8b**,[20] 1,2-diiodo-4,5-dimethylbenzene,[11,20] 1-bromo-2-(phenylethynyl)benzene,[21,22] 1-bromo-2-(p-tolylethynyl)benzene,[23] 1-(trimethylsilylethynyl)-2-(phenylethynyl)benzene,[24] and 2-ethynyl-1-(phenylethynyl)benzene,[22] were prepared according to procedures described in the literature.

*Preparation of 4,5-dimethyl-1,2-bis(1-naphthylethynyl)benzene (**12**)[20]*

1,2-Diiodo-4,5-dimethylbenzene (4.2 g, 12 mmol), $[Pd(PPh_3)Cl_2]$ (750 mg, 1.1 mmol), and CuI (400 mg, 2.1 mmol) were dissolved in degassed NEt_3 (50 mL). After 1-ethynylnaphthalene (4.0 mL, 35.3 mmol) was added, the resulting black mixture was heated to 100 °C for 12 h. Then all the volatiles were removed in vacuum, and the residue was extracted with diethyl ether (3×50 mL). After filtration, diethyl ether was removed in vacuo. The crude product was washed with a mixture of *n*-pentane and CH_2Cl_2 (6:1, 20 mL) and dried to finally give the product as a brown solid (1.9 g, 4.7 mmol, 39%). M.p. 147 °C; ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): $\delta=$ 8.54 (d, $^3J=8.4$ Hz, 1H, 9^N-H), 7.88 (d, $^3J=8.2$ Hz, 1H, 4^N-H), 7.86 (d, $^3J=8.2$ Hz, 1H, 6^N-H), 7.81 (d, $^3J=7.1$ Hz, 1H, 2^N-H), 7.55 (s, 1H, 2-H), 7.47 (m, 1H, 3^N-H), 7.43 (m, 1H, 7^N-H), 7.13 (m, 1H, 8^N-H), 2.36 ppm (s, 3H, Me); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): $\delta=$138.2 (C-1), 133.59 (C-10^N), 133.56 (C-5^N), 133.52 (C-2), 131.0 (C-2^N), 129.2 (C-4^N), 128.5 (C-6^N), 127.2 (C-8^N), 126.76 (C-7^N), 126.75 (C-9^N), 125.6 (C-3^N), 123.3 (C-3), 121.3 (C-1^N), 93.9 (C-4), 90.9 (C-5), 19.8 ppm (Me); IR (ATR): $\tilde{\nu}=2172$ cm^{-1} (C≡C); HRMS (ESI): m/z calcd for $C_{32}H_{22}+Ag^+$: 513.0767 [$M+Ag^+$]; found: 513.0767.

*X-ray crystal structure analysis of compound **12***

Formula $C_{32}H_{22}$, M=406.50, colorless crystal, 0.28×0.23×0.12 mm, $a=$ 8.1726(2), $b=$11.0699(3), $c=$13.3109(4) Å, $\alpha=$101.795(1), $\beta=$99.307(1), $\gamma=$104.491(2)°, $V=$1112.14(5) Å^3, $\rho_{calc}=1.214$ gcm^{-3}, $\mu=0.069$ mm^{-1}, empirical absorption correction ($0.981\le T\le 0.991$), $Z=2$, triclinic, space group $P\bar{1}$ (No. 2), $\lambda=0.71073$ Å, $T=223(2)$ K, ω and φ scans, 5568 reflections collected ($\pm h$, $\pm k$, $\pm l$), [(sinθ)/λ]=0.59 Å^{-1}, 3775 independent ($R_{int}=0.031$) and 3184 observed reflections [$I>2\sigma(I)$], 291 refined parameters, $R=0.055$, $wR^2=0.141$, max. (min.) residual electron density 0.25 (−0.14) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

*Preparation of 1-(2-thienylethynyl)-2-(phenylethynyl)benzene (**21**)*

2-Ethynyl-1-(phenylethynyl)benzene (1.11 g, 5.57 mmol, 1 equiv) was dissolved in THF (20 mL) and then degassed for 30 min. In another Schlenk flask *o*-iodothiophene (1.00 g, 6.01 mmol, 1.1 equiv) was dissolved in NEt_3 (20 mL) and tetrahydrofuran (20 mL), and then degassed. After 30 min, $[Pd(PPh_3)_4]$ (318 mg, 5 mol%) and CuI (104 mg, 10 mol%) were added to the Schlenk flask. Subsequently, the diyne solution was transferred via a canula and the reaction mixture was stirred for 1 day at 60 °C. Then the reaction mixture was filtered and the filtrate was concentrated in vacuo. The obtained residue was first purified by column chromatography (*n*-hexane) and then purified by GPC ($CHCl_3$) yielding compound **21** (1.23 g, 4.32 mmol, 79%) as a yellow brown solid. M.p. 81 °C; ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): $\delta=$7.65 (2H), 7.40 (3H)(each m, Ph), 7.59, 7.37 (each m, each 2H, C_6H_4), 7.37 (2H), 7.07 ppm (1H)(m, C_4H_3S); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): $\delta=$132.6, 128.2, 127.7, 123.4 (C_4H_3S), 132.1, 131.9, 128.7, 128.5, 125.79, 125.75 (C_6H_4), 132.0, 129.0, 128.8, 123.4 (Ph), 94.1 (≡CPh), 92.3, 88.4 (≡C), 87.0 ppm (≡C-[C_4H_3S]); IR (ATR): $\tilde{\nu}=2175$ cm^{-1} (C≡C); HRMS (ESI): m/z calcd for $C_{20}H_{12}S+Na^+$: 307.0552 [$M+Na^+$]; found: 307.0529.

*Preparation of 2-hexynyl-1-(p-tolylethynyl)benzene (**24**)*

1-Bromo-2-(p-tolylethynyl)benzene (1.35 g, 5 mmol, 1 equiv), $[Pd(PPh_3)_2Cl_2]$ (140 mg, 4 mol%), and CuI (300 mg, 32 mol%) were dissolved in degassed $HNiPr_2$ (50 mL). Then 1-pentyne (1 mL, 10 mmol, 2.0 equiv) was added. The resulting black mixture was heated to 80 °C for 3 days. Subsequently, all volatiles were removed in vacuum, and the obtained residue was extracted with diethylether (3×50 mL). After filtration of the ether suspension, the solvent was removed in vacuum, and the residue was purified by column chromatography (*n*-pentane). Compound **24** was obtained as an orange-red liquid (644 mg, 2.49 mmol, 50%). ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): $\delta=$7.56 (m, 1H, 3-H), 7.50 (m, 2H, *o*-tol), 7.48 (m, 1H, 6-H), 7.29 (m, 2H, 4,5-H), 7.23 (m, 2H, *m*-tol), 2.54 (2H), 1.72 (2H), 1.13 (3H)(each m, *n*-Pr), 2.41 ppm (s, 3H, Me); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): $\delta=$139.2 (*p*-tol), 132.3 (C-6), 132.1 (C-3), 131.9 (*o*-tol), 129.6 (*m*-tol), 128.3, 127.7 (C-4,5), 126.9, 126.1 (C-1,2), 120.6 (*i*-tol), 95.2 (≡C-*n*-Pr), 93.4 ((≡Ctol), 88.3 ((C≡^{tol}), 79.9 (C≡$^{n\text{-}Pr}$), 22.7, 22.0, 13.8 (*n*-Pr), 21.7 ppm (Me); IR (ATR): $\tilde{\nu}=2216$ cm^{-1} (C≡C);

HRMS (ESI): *m*/*z* calcd for $C_{20}H_{18}$+Ag^+: 365.0454 [*M*+Ag^+]; found: 365.0450.

Reaction of ***12*** *with* $B(C_6F_5)_3$*: Preparation of compounds* ***13*** *and* ***14***

$B(C_6F_5)_3$ (256 mg, 0.5 mmol, 1 equiv) was dissolved in cold CH_2Cl_2 (−20 °C, 5 mL) and added to a solution of 4,5-dimethyl-1,2-bis(1-naphthylethynyl)benzene (**12b**) (202 mg, 0.5 mmol, 1 equiv) in cold CH_2Cl_2 (−20 °C, 5 mL). The resulting dark red solution was allowed to warm to room temperature and stirred for 2 days before diethyl ether (grade p.a., 5 mL) was added. Then all volatiles were removed in vacuo. The obtained residue was purified by column chromatography (cyclohexane:CH_2Cl_2 = 20:1) to give the products **13** (142 mg, 0.25 mmol, 50 %) and **14** (18 mg, 0.03 mmol, 6 % [ca. 85 % pure $^1H(CD_2Cl_2)$]) as dark red solids. Compound **13**: M.p. 311 °C; ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 8.16 (dm, ^3J = 8.3 Hz, 1H, 4^N-H), 8.06 (dm, ^3J = 8.2 Hz, 1H, 6^N-H), 7.90 (dm, ^3J = 8.1 Hz, 1H, 11-H), 7.87 (dm, ^3J = 8.0 Hz, 1H, 13-H), 7.77 (dm, ^3J = 7.8 Hz, 1H, 9-H), 7.75 (dd, ^3J = 8.3 ^3J = 7.0 Hz, 1H, 3^N-H), 7.68 (dm, ^3J = 8.5 Hz, 1H, 9^N-H), 7.64 (dd, ^3J = 7.0 Hz, J = 1.2 Hz, 1H, 2^N-H), 7.53 (m, 1H, 10-H), 7.53 (m, 1H, 7^N-H), 7.36 (dd, ^3J = 8.0 Hz, 7.4 Hz, 1H, 14-H), 7.31 (m, 1H, 8^N-H), 7.18 (dd, ^3J = 7.4 Hz, ^4J = 1.1 Hz, 1H, 15-H), 6.73 (s, 1H, 4-H), 5.73 (s, 1H, 1-H), 2.14 (s, 3H, 3-Me), 1.82 ppm (s, 3H, 2-Me); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): δ = 141.3, 137.5 (C-5,18), 139.5 (C-17), 137.0 (C-3), 135.4 (C-1^N), 134.2 (C-5^N), 134.1 (C-2), 133.6 (C-12), 133.0 (C-16), 132.9 (C-7), 132.7 (C-10^N), 131.21 (C-13), 131.15 (C-19), 130.0 (C-15), 129.5 (C-11), 129.1 (C-4^N), 128.9 (C-8), 128.7 (C-6^N), 127.9 (C-2^N), 127.4, 126.7 (C-10,7^N), 127.0 (C-14), 126.9 (C-8^N), 126.3 (C-3^N), 126.2 (C-20), 126.1 (C-9^N), 125.4 (C-1), 125.2 (C-9), 120.6 (C-4), 119.2 (br, C-6), 20.24 (2-Me), 20.20 ppm (3-Me), [C_6F_5 not listed]; ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ = −138.0, −138.2 (each m, each 1F, *o*-C_6F_5), −155.2 (t, ^3J = 20.7 Hz, 1F, *p*-C_6F_5), −161.39, −161.44 ppm (each m, each 1F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 6.2]; UV/Vis (CH_3CN): λ_{max} (log ε) = 350 nm (4.04), 439 nm (4.09), 513 nm (3.91); HRMS (ESI): *m*/*z* calcd for [$C_{38}H_{21}F_5$+Na^+]: 595.1456 [*M*+Na^+]; found: 595.1457.

X-ray crystal structure analysis of compound ***13***

Single crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a solution of **13** in CH_2Cl_2. Formula $C_{38}H_{21}F_5$, M = 572.55, red crystal, 0.20 × 0.17 × 0.03 mm, a = 30.7143(10), b = 7.4972(2), c = 24.9464(8) Å, β = 110.193(2)°, V = 5391.4(3) Å3, ρcalc = 1.411 gcm-3, μ = 0.878 mm-1, empirical absorption correction (0.843 ≤ T ≤ 0.974), Z = 8, monoclinic, space group *C*2/*c* (No. 15), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 22682 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å-1, 4541 independent (R_{int} = 0.064) and 3141 observed reflections [$I > 2\sigma(I)$], 390 refined parameters, R = 0.061, $wR2$ = 0.157, max. (min.) residual electron density 0.18 (−0.26) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Compound **14**: M.p. 210 °C; ^1H NMR (500 MHz, CD_2Cl_2, 299 K): δ = 8.01 (m, 1H, 19^N-H), 7.92 (dm, ^3J = 8.5 Hz, 1H, 4^N-H), 7.91 (dm, ^3J = 8.6 Hz, 1H, 6^N-H), 7.89 (m, 1H, 16^N-H), 7.88 (m, 1H, 14^N-H), 7.79 (dm, ^3J = 7.1 Hz, 1H, 2^N-H), 7.73 (dm, ^3J = 8.1 Hz, 1H, 9^N-H), 7.54 (m, 1H, 3^N-H), 7.53 (m, 1H, 12^N-H), 7.51 (m, 1H, 13^N-H), 7.50 (m, 3H, 7^N,17^N,18^N-H), 7.41 (ddd, ^3J = 8.1, 6.9 Hz, ^4J = 1.4 Hz, 1H, 8^N-H), 7.25 (s, 1H, 9-H), 7.04 (s, 1H, 1-H), 6.82 (s, 1H, 4-H), 2.23 (s, 3H, 3-Me), 2.03 ppm (s, 3H, 2-Me); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 299 K): δ = 143.8 (C-7), 143.1 (C-8), 140.9 (C-5), 137.5 (C-3), 134.7 (C-2), 134.6 (C-9), 134.1, 133.98, 133.96, 132.1 (C-1^N,5^N,11^N,15^N), 133.3 (C-20^N), 132.2 (C-10), 131.8 (C-10^N), 129.4 (C-4^N), 128.9 (C-14^N), 128.81 (C-6^N), 128.77 (d, J = 1.1 Hz, C-12^N), 128.5 (C-16^N), 128.1 (m, C-6), 127.7 (C-2^N), 126.72 (C-8^N), 126.68 (d, J = 1.5 Hz, C-19^N), 126.6 (C-7^N), 126.5 (C-18^N), 126.3 (C-17^N), 125.6 (C-3^N), 125.5 (C-13^N), 125.2 (C-9^N), 125.2 (C-1), 120.9 (C-4), 20.23 (3-Me), 20.15 ppm (2-Me). [n.o. (C_6F_5); ^{t} tentatively assigned]; ^{19}F NMR (470 MHz, CD_2Cl_2, 299 K): δ = −137.9, −138.0 (each m, each 1F, *o*-C_6F_5), −155.6 (t, ^3J = 20.9 Hz, 1F, *p*-C_6F_5), −162.8, −162.9 ppm (each m, each 1F, *m*-C_6F_5), [$\Delta\delta^{19}F_{mp}$ = 7.2, 7.3]; HRMS (ESI): *m*/*z* calcd for [$C_{38}H_{23}F_5$+Na^+]: 597.1612 [*M*+Na^+]; found: 597.1618.

X-ray crystal structure analysis of compound ***14***

Single crystals suitable for the X-ray crystal structure analysis were obtained by slow evaporation of a solution of **14** in CH_2Cl_2. Formula $C_{38}H_{23}F_5$·0.5 CH_2Cl_2, M = 617.03, colorless crystal, 0.30 × 0.05 × 0.01 mm, a = 12.0940(6), b = 31.8452(12), c = 7.5845(2) Å, V = 2921.1(2) Å^3, ρ_{calc} = 1.403 gcm^{-3}, μ = 1.672 mm^{-1}, empirical absorption correction (0.634 ≤ T ≤ 0.983), Z = 4, orthorhombic, space group *P*nc2 (No. 30), λ = 1.54178 Å, T = 223(2) K, ω and ϕ scans, 12101 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 4295 independent (R_{int} = 0.060) and 3354 observed reflections [$I > 2\sigma(I)$], 413 refined parameters, R = 0.052, wR^2 = 0.135, max. (min.) residual electron density 0.16 (−0.22) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Reaction of ***12*** *with* $MeB(C_6F_5)_2$*: Preparation of compounds* ***13*** *and* ***15***

$MeB(C_6F_5)_2$ (183 mg, 0.5 mmol, 1 equiv) was dissolved in cold CH_2Cl_2 (−20 °C, 5 mL) and added to a solution of diyne **12** (202 mg, 0.5 mmol, 1 equiv) in cold CH_2Cl_2 (−20 °C, 5 mL). The dark red reaction solution was then allowed to warm to room temperature and stirred for 2 days before diethyl ether (p.a., 5 mL) was added. Subsequently, all volatiles were removed in vacuo. The obtained residue was purified by column chromatography (cyclohexane:CH_2Cl_2 = 20:1) to give the products **13** (48 mg, 0.08 mmol, 17 %) and **15** (58 mg, 0.10 mmol, 20 %), each as a dark red solid. Compound **15**: M.p. 212 °C; ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 8.27 (d, ^3J = 7.8 Hz, 1H, 9-H), 8.12 (d, ^3J = 8.3 Hz, 4^N-H), 8.03 (d, ^3J = 8.2 Hz, 1H, 6^N-H), 7.83 (d, ^3J = 7.8 Hz, 1H, 11-H), 7.79 (d, ^3J = 8.0 Hz, 1H, 13-H), 7.73 (t, ^3J = 7.8 Hz, 1H, 10-H), 7.72 (dd, ^3J = 8.3 Hz, 6.9 Hz, 1H, 3^N-H), 7.63 (d, ^3J = 8.6 Hz, 1H, 9^N-H), 7.58 (dd, ^3J = 6.9 Hz, ^4J = 1.1 Hz, 1H, 2^N-H), 7.50 (ddd, ^3J = 8.2 Hz, 6.7 Hz, ^4J = 1.0 Hz, 1H, 7^N-H), 7.30 (dd, ^3J = 8.0, 7.3 Hz, 1H, 14-H), 7.26 (ddd, ^3J = 8.6 Hz, 6.7 Hz, ^4J = 1.1 Hz, 1H, 8^N-H), 7.20 (s, 1H, 4-H), 7.02 (d, ^3J = 7.3 Hz, 1H, 15-H), 5.64 (s, 1H,1-H), 2.68 (s, 3H, 6-Me), 2.22 (s, 3H, 3-Me), 1.81 ppm (s, 3H, 2-Me); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): δ = 143.7 (C-5), 138.4 (C-18), 136.4 (C-3), 136.2 (C-1^N), 135.4 (C-17), 134.9 (C-6), 134.3 (C-5^N), 134.0 (C-16), 133.8 (C-12), 133.4 (C-2), 132.9 (C-10^N), 131.9 (C-19), 131.1 (C-8), 129.5 (C-13), 128.71 (C-7), 128.68 (C-4^N), 128.63 (C-6^N), 128.0 (C-2^N), 127.5 (C-15), 127.3 (C-10), 127.0 (C-11), 126.9 (C-20), 126.7 (C-8^N), 126.6 (C-14), 126.5 (C-7^N), 126.3 (C-3^N), 126.1 (C-9^N), 125.4 (C-9), 125.0 (C-1), 120.6 (C-4), 20.3 (3-Me), 20.2 (2-Me), 14.1 ppm (6-Me); UV/Vis (CH_3CN): λ_{max} (log ε) = 342 nm (4.11), 417 nm (3.94), 510 nm (3.74); HRMS (ESI): *m*/*z* calcd for [$C_{33}H_{24}$+Na^+]: 443.1770 [*M*+Na^+]; found: 443.1770.

*Reaction of 1,2-bis(phenylethynyl)benzene (****8a****) with* $MeB(C_6F_5)_2$*: Preparation of compounds* ***10a*** *[7,20] and* ***16***

$MeB(C_6F_5)_2$ (360 mg, 1.0 mmol, 1 equiv) was dissolved in cold CH_2Cl_2 (−20 °C, 5 mL) and added to a solution of the diyne **8a** (278 mg, 1.0 mmol, 1 equiv) in cold CH_2Cl_2 (−20 °C, 5 mL). The resulting dark red solution was allowed to warm to room temperature and then stirred for 2 days before diethyl ether (p.a., 5 mL) was added. Subsequently, all volatiles were removed in vacuo, and the obtained residue was purified by column chromatography (cyclohexane:dichloromethane = 20:1) to give the products **16** (71 mg, 0.24 mmol, 24 %) and **10a** (65 mg, 0.15 mmol, 15 %), each as a yellow solid. Compound **16**: M.p. 146 °C.; ^1H NMR (500 MHz, CD_2Cl_2, 298 K): δ = 7.64 (m, 2H, *o*-Ph), 7.51 (m, 2H, *m*-Ph), 7.44 (m, 1H, *p*-Ph), 7.26 (dm, ^3J = 7.4 Hz, 1H, 9-H), 7.12 (dm, ^3J = 7.4 Hz, 1H, 1-H), 7.05 (dm, ^3J = 7.4 Hz, 1H, 12-H), 6.98 (m, 1H, 10-H), 6.93 (m, 3H, 3,4,11-H), 6.82 (m, 1H, 2-H), 2.25 ppm (s, 3H, Me); $^{13}C\{^1H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): δ = 151.6 (C-5), 149.6 (C-13), 143.4 (C-7), 143.3 (C-15), 139.1 (C-14), 138.9 (C-6), 135.9 (C-8), 135.3 (C-16), 134.3 (*i*-Ph), 128.99 (*m*-Ph), 128.96 (*p*-Ph), 128.9 (*o*-Ph), 128.3 (C-3), 127.7 (C-2), 127.45, 127.42 (C-10,11), 122.6 (C-12), 122.4 (C-9), 121.7 (C-1), 121.2 (C-4), 12.1 ppm (Me); UV/Vis (CH_3CN): λ_{max} (log ε) = 406 nm (3.88), 514 nm (1.80); HRMS (ESI): *m*/*z* calcd for $C_{23}H_{16}$+Ag^+: 399.0298 [*M*+Ag^+]; found: 399.0298.

Preparation of compound ***23***

The diyne **21** (60.0 mg, 211 μmol, 1 equiv) was mixed with dry *n*-pentane (5 mL). Then $B(C_6F_5)_3$ (108 mg, 211 μmol, 1 equiv) dissolved in dry *n*-

pentane (5 mL) was added at room temperature. The reaction mixture turned dark red-brown immediately, and the obtained suspension was stirred overnight. Then the supernatant was removed with a pipette, and the solid residue was washed with *n*-pentane (3×2 mL). After drying in vacuo, the product was isolated as a brown solid (67.2 mg, 84.3 μmol, 40%). Decomp. 147 °C; ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 7.86 (dm, ^3J = 7.6 Hz, 1H, 1-H), 7.77 (m, 2H, *o*-Ph), 7.60 (m, 2H, *m*-Ph), 7.56 (m, 1H, *p*-Ph), 7.31 (td, ^3J = 7.6 Hz, ^4J = 1.1 Hz, 1H, 3-H), 7.18 (td, ^3J = 7.6 Hz, ^4J = 1.1 Hz, 1H, 2-H), 6.94 (ddm, ^3J = 7.6 Hz, J_{FH} = 4.1 Hz, 1H, 4-H), 5.43 (dd, ^3J = 3.8 Hz, 2.3 Hz, 1H, 11-H), 4.09 (dd, ^2J = 17.0 Hz, ^3J = 3.8 Hz, 1H, 10-H^a), 3.59 (dd, ^2J = 17.0 Hz, ^3J = 2.3 Hz, 1H, 10-H^b); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = 160.1 (m, C-12), 149.7 (C-14), 147.0 (C-5), 146.4 (C-7), 143.0 (d, J = 1.8 Hz, C-13), 133.1 (*i*-Ph), 130.49 (*p*-Ph), 130.45 (C-15), 129.7 (C-3), 129.4 (*m*-Ph), 129.3 (*o*-Ph), 125.7 (C-2), 124.1 (C-1), 120.7 (d, J = 3.5 Hz, C-4), 113.5 (br, C-6), 111.5 (C-11), 75.7 (br, C-8), 46.5 ppm (C-10), [C_6F_5 not listed]; ^{11}B{^{1}H} NMR (192 MHz, CD_2Cl_2, 298 K): δ = −6.9 ppm ($\nu_{1/2}$ ~300 Hz); ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ = −129.1 (m, *o*), −132.8 (m, *o′*), −154.5 (t, $^3J_{FF}$ = 20.0 Hz, *p*), −162.1 (m, *m′*), −162.6 (m, *m*) (each 1F, BC_6F_5), [$\Delta\delta^{19}F_{pm}$ = 7.6, 8.1]; −130.8, −132.1 (each br m, *o*), −155.5 (t, $^3J_{FF}$ = 19.9 Hz, *p*), −162.57, −162.62 (each m, *m′*) (each 1F, BC_6F_5), [$\Delta\delta^{19}F_{pm}$ = 7.1]; −135.0, −136.3 (each m, *o*), −154.9 (t, $^3J_{FF}$ = 20.4 Hz, *p*), −161.5, −162.8 ppm (each m, *m*) (each 1F, C_6F_5), [$\Delta\delta^{19}F_{pm}$ = 6.6, 7.9]; HRMS (ESI): *m*/*z* calcd for $C_{38}H_{12}BF_{15}S-H^+$: 795.0447 [*M*−H]; found: 795.0448.

X-ray crystal structure analysis of compound ***23***

Crystals suitable for the X-ray crystal structure analysis were obtained by diffusion method of a layered CH_2Cl_2/*n*-heptane solution at room temperature. Formula $C_{38}H_{12}BF_{15}S$, M = 796.35, orange crystal, 0.37×0.15×0.10 mm, a = 16.9719(7), b = 8.8408(3), c = 21.3311(5) Å, β = 102.748(2)°, V = 3121.73(18) Å^3, ρ_{calc} = 1.694 gcm^{-3}, μ = 2.038 mm^{-1}, empirical absorption correction (0.519 ≤ T ≤ 0.822), Z = 4, monoclinic, space group $P2_1/c$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 26907 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 5423 independent (R_{int} = 0.041) and 4904 observed reflections [I > 2σ(I)], 497 refined parameters, R = 0.036, wR^2 = 0.112, max. (min.) residual electron density 0.22 (−0.21) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of compound ***26***

The diyne **24** (50.0 mg, 194 μmol, 1 equiv) and tri(*o*-tolyl)phosphane (59.1 mg, 194 μmol, 1 equiv) were dissolved in dry *n*-pentane (5 mL). Then a solution of $B(C_6F_5)_3$ (99.6 mg, 194 μmol, 1 equiv) in dry *n*-pentane (5 mL) was added at room temperature. The reaction mixture turned dark red-brown immediately. The obtained suspension was stirred overnight. Subsequently, the supernatant was removed with a pipette, and the solid residue was washed with *n*-pentane (3×2 mL). After drying in vacuo, the product was isolated as a brown solid (188 mg, 175 μmol, 90%). M.p. 213 °C; ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = pentalene anion: 7.00 (dm, ^3J = 7.4 Hz, 1H, 1-H), 6.92 (dm, ^3J = 7.4 Hz, 1H, 4-H), 6.68 (tm, ^3J = 7.4, 7.4 Hz, 1H, 2-H), 6.64 (m, 1H, 12-H), 6.63 (tm, ^3J = 7.4, 7.4 Hz, 1H, 3-H), 6.33 (d, ^3J = 7.7 Hz, 1H, 10-H), 5.36 (dd, ^3J = 7.7 Hz, J_{FH} = 4.5 Hz, 1H, 9-H), 2.51 (m, 2H, 14-CH_2), 2.15 (s, 3H, 11-Me), 1.61 (m, 2H, CH_2), 1.00 (t, ^3J = 7.4 Hz, 3H, CH_3). [HP(*o*-tol)$_3$] cation: 8.37 (d, $^1J_{PH}$ = 482.5 Hz, 1H, PH), 7.79 (m, 3H, *p*-^{o}tol), 7.57 (m, 3H, *m′*-^{o}tol), 7.45 (m, 3H, *m*-^{o}tol), 7.14 (dd, $^3J_{PH}$ = 16.0 Hz, ^3J = 7.9 Hz, 3H, *o*-^{o}tol), 2.38 ppm (s, 9H, Me); ^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 298 K): δ = pentalene anion: 157.8 (m, C-5), 151.5 (C-13), 146.9 (C-7), 146.5 (C-15), 136.98 (C-14), 136.0 (C-16), 135.9 (C-8), 135.2 (C-11), 126.8 (C-3), 126.2 (C-10), 124.9 (C-2), 123.8 (d, J = 6.1 Hz, C-9), 123.2 (dm, J = 8.1 Hz, C-4), 121.0 (C-12), 120.5 (C-1), 28.5 (14-CH_2), 22.6 (CH_2), 21.3 (11-Me), 14.7 (CH_3), n.o. (C-6), [C_6F_5 not listed]. [HP(*o*-tol)$_3$] cation: 143.8 (d, $^2J_{PC}$ = 9.0 Hz, *o′*-^{o}tol), 137.00 (*p*-^{o}tol), 135.0 (d, $^2J_{PC}$ = 12.8 Hz, *o*-^{o}tol), 133.5 (d, $^3J_{PC}$ = 10.8 Hz, *m′*-^{o}tol), 128.8 (d, $^3J_{PC}$ = 13.9 Hz, *m*-^{o}tol), 111.9 (d, $^1J_{PC}$ = 87.8 Hz, *i*-^{o}tol), 21.1 ppm (d, $^3J_{PC}$ = 8.6 Hz, Me); ^{11}B{^{1}H} NMR (192 MHz, 298 K, CD_2Cl_2): δ = −16.1 ppm ($\nu_{1/2}$ ≈ 50 Hz); ^{19}F NMR (564 MHz, CD_2Cl_2, 298 K): δ = −127.2 (*o*), −129.8 (*o′*), −163.9 (t, $^3J_{FF}$ = 20.4 Hz, *p*), −166.7 (*m′*), −168.1 (*m*) (each m, each 1F, BC_6F_5), [$\Delta\delta^{19}F_{pm}$ = 2.8, 4.2]; −127.3 (*o*), −133.0 (*o′*), −164.1 (t, $^3J_{FF}$ = 20.5 Hz, *p*), −167.1 (*m*), −167.3 (*m′*) (each m, each 1F, BC_6F_5), [$\Delta\delta^{19}F_{pm}$ = 3.0, 3.2]; −127.8 (*o*), −133.6 (*o′*), −163.8 (t, $^3J_{FF}$ = 20.4 Hz, *p*), −166.0 (*m*), −166.9 ppm (*m′*) (each m, each 1F, BC_6F_5), [$\Delta\delta^{19}F_{pm}$ = 2.2, 3.1]. ^{31}P NMR (243 MHz, 298 K, CD_2Cl_2): δ = −13.2 ppm (dm, $^1J_{PH}$ ≈ 482 Hz); HRMS (ESI): *m*/*z* calcd for $(C_{21}H_{21}P)_2+Ag^+$: 717.1807 [M_2+Ag$^+$]; found: 717.1809; *m*/*z* calcd for $C_{38}H_{17}BF_{15}^-$: 769.1184 [M^-]; found: 769.1218.

X-ray analysis of compound ***26***

Crystals suitable for X-ray crystal structure analysis were obtained by the diffusion method of a layered CH_2Cl_2/*n*-heptane solution at room temperature. Formula $C_{59}H_{39}BF_{15}P$, M = 1074.68, orange crystal, 0.40×0.20×0.15 mm, a = 12.6060(3), b = 20.7988(3), c = 19.4554(6) Å, β = 104.734(2)°, V = 4933.3(2) Å^3, ρ_{calc} = 1.447 gcm^{-3}, μ = 1.356 mm^{-1}, empirical absorption correction (0.613 ≤ T ≤ 0.822), Z = 4, monoclinic, space group $P2_1/n$ (No. 14), λ = 1.54178 Å, T = 223(2) K, ω and φ scans, 48272 reflections collected (±h, ±k, ±l), [(sinθ)/λ] = 0.60 Å^{-1}, 8606 independent (R_{int} = 0.043) and 7850 observed reflections [I > 2σ(I)], 693 refined parameters, R = 0.047, wR^2 = 0.125, max. (min.) residual electron density 1.06 (−0.45) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

Preparation of compound ***27a***

Compound **8a**[20] (25.0 mg, 89.8 μmol, 1 equiv) and tri(*o*-tolyl)phosphane (27.3 mg, 89.8 μmol, 1 equiv) were dissolved in dry *n*-pentane (5 mL). Then a solution of $B(C_6F_5)_3$ (46.0 mg, 89.8 μmol, 1 equiv) in dry *n*-pentane (5 mL) was added at room temperature. The mixture turned dark red-brown immediately. The obtained suspension was stirred overnight. Subsequently, the supernatant was removed with a pipette, and the solid residue was washed with *n*-pentane (3×2 mL). After drying in vacuo, the product was obtained as a brown solid (95 mg, 86.8 μmol, 97%). M.p. 116 °C; ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = pentalene anion: 7.50 (m, 2H, *o*-Ph), 7.42 (m, 2H, *m*-Ph), 7.37 (m, 1H, *p*-Ph), 7.00 (dm, ^3J = 7.5 Hz, 1H, 4-H), 6.94 (dm, ^3J = 7.5 Hz, 1H, 1-H), 6.85 (dm, ^3J = 7.5 Hz, 1H, 12-H), 6.72 (td, ^3J = 7.5 Hz, ^4J = 1.1 Hz, 1H, 11-H), 6.66 (td, ^3J = 7.5 Hz, ^4J = 1.3 Hz, 1H, 3-H), 6.58 (td, ^3J = 7.5 Hz, ^4J = 1.2 Hz, 1H, 10-H), 6.57 (td, ^3J = 7.5 Hz, ^4J = 1.1 Hz, 1H, 2-H), 5.63 (dd, ^3J = 7.5 Hz, J_{FH} = 4.5 Hz, 1H, 9-H). [HP(*o*-tol)$_3$] cation: 8.31 (br d, $^1J_{PH}$ = 483.3 Hz, 1H, PH), 7.74 (m, 3H, *p*-^{o}tol), 7.52 (m, 3H, *m′*-^{o}tol), 7.40 (m, 3H, *m*-^{o}tol), 7.10 (dd, $^3J_{PH}$ = 16.0 Hz, ^3J = 7.8 Hz, 3H, *o*-^{o}tol), 2.32 ppm (s, 9H, Me); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2, 298 K): δ = pentalene anion: 160.4 (br, C-6), 157.8 (d, J_{FC} = 4.4 Hz, C-5), 150.2 (C-13), 147.0 (C-7), 146.5 (C-15), 138.4 (C-8), 135.35 (C-14), 135.32 (C-16), 135.1 (*i*-Ph), 129.2 (*o*-Ph), 128.69 (*m*-Ph), 128.1 (*p*-Ph), 127.8 (C-3), 126.1 (C-10), 125.6 (C-11), 125.5 (C-2), 124.5 (d, J_{FC} = 6.4 Hz, C-9), 123.7 (d, J_{FC} = 7.7 Hz, C-4), 121.1 (C-12), 120.3 (C-1), [C_6F_5 not listed]. [HP(*o*-tol)$_3$] cation: 143.8 (d, $^2J_{PC}$ = 9.0 Hz, *o′*-^{o}tol), 136.9 (d, $^4J_{PC}$ = 2.8 Hz, *p*-^{o}tol), 134.9 (d, $^2J_{PC}$ = 12.8 Hz, *o*-^{o}tol), 133.4 (d, $^3J_{PC}$ = 10.7 Hz, *m′*-^{o}tol), 128.67 (d, $^3J_{PC}$ = 13.8 Hz, *m*-^{o}tol), 111.9 (d, $^1J_{PC}$ = 87.8 Hz, *i*-^{o}tol), 21.0 ppm (d, $^3J_{PC}$ = 8.6 Hz, Me); ^{11}B{^{1}H} NMR (160 MHz, CD_2Cl_2, 298 K): δ = −16.0 ppm ($\nu_{1/2}$ ≈ 50 Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): δ = −127.0 (*o*), −129.6 (*o′*), −163.4 (t, $^3J_{FF}$ = 20.6 Hz, *p*), −166.5 (*m*), −167.8 (*m′*) (each m, each 1F, BC_6F_5), [$\Delta\delta^{19}F_{pm}$ = 3.1, 4.4]; −127.1 (*o*), −132.7 (*o′*), −163.5 (t, $^3J_{FF}$ = 20.4 Hz, *p*), −166.7 (*m′*), −167.1 (*m*) (each m, each 1F, BC_6F_5), [$\Delta\delta^{19}F_{pm}$ = 3.2, 3.6]; −127.8 (*o*), −133.5 (*o′*), −163.3 (t, $^3J_{FF}$ = 20.3 Hz, *p*), −165.6 (*m′*), −166.6 ppm (*m*) (each m, each 1F, BC_6F_5), [$\Delta\delta^{19}F_{pm}$ = 2.3, 3.3]; ^{31}P NMR (202 MHz, CD_2Cl_2, 298 K): δ = −13.0 ppm (br d, $^1J_{PH}$ ≈ 483 Hz); elemental analysis calcd (%) for $C_{61}H_{35}BF_{15}P$: C 66.93, H 3.22; found: C 67.21, H 3.18.

Preparation of compound ***27b***

Compound **8b**[20] (25.0 mg, 81.3 μmol, 1 equiv) and tri(*o*-tolyl)phosphane (24.7 mg, 81.3 μmol, 1 equiv) were dissolved in dry *n*-pentane (5 mL). Then a solution of $B(C_6F_5)_3$ (41.7 mg, 81.3 μmol, 1 equiv) in dry *n*-pentane (5 mL) was added at room temperature. The reaction mixture turned dark red-brown immediately. After stirring the suspension overnight, the supernatant was removed with a pipette, and the solid residue was washed with *n*-pentane (3×2 mL). After drying in vacuo, the product was obtained as a brown solid (85 mg, 75.7 μmol, 93%). M.p. 124 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ = pentalene anion: 7.52 (m, 2H, *o*-Ph),7.42 (m, 2H, *m*-Ph), 7.35 (m, 1H, *p*-Ph), 6.83 (dm, ^3J = 7.5 Hz, 1H,

12-H), 6.77 (s, 1H, 4-H), 6.73 (s, 1H, 1-H), 6.69 (td, $^{3}J=7.5$ Hz, $^{4}J=1.0$ Hz, 1H, 11-H), 6.53 (td, $^{3}J=7.5$ Hz, $^{4}J=1.0$ Hz, 1H, 10-H), 5.58 (dd, $^{3}J=7.5$ Hz, $J_{FH}=4.5$ Hz, 1H, 9-H), 1.94 (s, 6H, 2,3-Me). [HP(*o*-tol)$_3$] cation: 8.33 (br d, $^{1}J_{PH}=482.3$ Hz, 1H, PH), 7.76 (m, 3H, *p*-°tol), 7.54 (m, 3H, *m*′-°tol), 7.42 (m, 3H, *m*-°tol), 7.11 (dd, $^{3}J_{PH}=16.0$ Hz, $^{3}J=7.8$ Hz, 3H, *o*-°tol), 2.33 ppm (s, 9H, Me); $^{13}C\{^{1}H\}$ NMR (126 MHz, CD_2Cl_2, 298 K): $\delta=$ pentalene anion: 160.7 (br, C-6), 155.9 (d, $J_{FC}=4.7$ Hz, C-5), 150.2 (C-13), 146.9 (C-15), 146.5 (C-7), 138.4 (C-8), 135.6 (C-3),135.4 (*i*-Ph), 134.0 (C-14), 133.2 (C-2), 133.1 (C-16), 129.2 (*o*-Ph), 128.6 (*m*-Ph), 127.9 (*p*-Ph), 125.8 (C-10), 125.4 (dm, $J_{FC}=8.1$ Hz, C-4),125.3 (C-11), 124.2 (d, $J_{FC}=6.3$ Hz, C-9), 121.9 (C-1), 120.8 (C-12), 20.1 (3-Me), 19.7 (2-Me), [C_6F_5 not listed]. [HP(*o*-tol)$_3$] cation: 143.8 (d, $^{2}J_{PC}=9.1$ Hz, *o*′-°tol), 136.9 (br, *p*-°tol), 134.9 (br d, $^{2}J_{PC}=12.8$ Hz, *o*-°tol), 133.4 (br d, $^{3}J_{PC}=10.7$ Hz, *m*′-°tol), 128.7 (br d, $^{3}J_{PC}=13.5$ Hz, *m*-°tol), 111.9 (br d, $^{1}J_{PC}=88.1$ Hz, *i*-°tol), 21.0 ppm (d, $^{3}J_{PC}=8.9$ Hz, Me); $^{11}B\{^{1}H\}$ NMR (160 MHz, CD_2Cl_2, 298 K): $\delta=-16.1$ ($\nu_{1/2}\approx50$ Hz). ^{19}F NMR (470 MHz, CD_2Cl_2, 298 K): $\delta=-126.9$ (*o*), -129.8 (*o*′), -163.5 (t, $^{3}J_{FF}=20.2$ Hz, *p*), -166.7 (*m*), -167.9 (*m*′) (each m, each 1F, BC_6F_5), [$\Delta\delta^{19}F_{pm}=3.2$, 4.4]; -127.2 (*o*), -132.5 (*o*′), -163.7 (t, $^{3}J_{FF}=20.8$ Hz, *p*), -166.9 (*m*′), -167.2 (*m*) (each m, each 1F, BC_6F_5), [$\Delta\delta^{19}F_{pm}=3.2$, 3.5]; -127.8 (*o*), -133.5 (*o*′), -163.4 (t, $^{3}J_{FF}=20.2$ Hz, *p*), -165.7 (*m*′), -166.7 ppm (*m*) (each m, each 1F, BC_6F_5), [$\Delta\delta^{19}F_{pm}=2.3$, 3.3]; ^{31}P NMR (202 MHz, CD_2Cl_2, 298 K): $\delta=-13.0$ ppm (br d, $^{1}J_{PH}\approx482$ Hz); elemental analysis calcd (%) for $C_{63}H_{39}BF_{15}P$: C 67.40, H 3.50; found: C 67.02, H 3.34.

Photophysical properties

UV/VIS spectra were recorded using a Shimadzu UV-3150 UV-VIS-NIR spectrophotometer with a resolution of 0.5 nm. Dilute solutions in spectral grade solvents in a 1 cm square quartz cuvette were used for the measurements.

Electrochemical properties

Cyclic voltammograms were recorded on an ALS/CHI-617A electrochemical analyzer (BAS). The CV cell consisted of a glassy carbon electrode, a Pt counter electrode, and an $Ag/AgNO_3$ reference electrode. The measurements were carried out under an argon atmosphere using CH_2Cl_2 solutions of samples with a concentration of 1 mM and 0.1 M tetrabutylammonium hexafluorophosphate as a supporting electrolyte. Redox potentials were calibrated with the ferrocene/ferrocenium couple as an internal standard.

Computational method

Geometry optimization of a series of dibenzopentalene derivatives were performed with the B3LYP theory and 6-31G(d) basis set, implemented in the Gaussian 09 Program.[25] All stationary points were optimized without any symmetry assumptions and characterized by normal coordinate analysis at the same level of theory (the number of imaginary frequencies, NIMAG, was 0). Time-dependent density functional theory (TD-DFT) vertical excitation calculations were performed using the B3LYP theory and 6-31G(d) basis set as implemented in the Gaussian 09 program.

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