

ChemComm

Chemical Communications

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: X. Tao, C. G. Daniliuc, K. Soloviova, C. A. Strassert, G. Kehr and G. Erker, *Chem. Commun.*, 2019, DOI: 10.1039/C9CC04199K.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.

COMMUNICATION

Aryllallenes and the Halogeno-B(C₆F₅)₂ Reagents: Facile Formation of 2-BorylindenesReceived 00th January 20xx,
Accepted 00th January 20xxXin Tao,^a Constantin G. Daniliuc,^a Kateryna Soloviova,^b Cristian A. Strassert,^b Gerald Kehr^a and Gerhard Erker

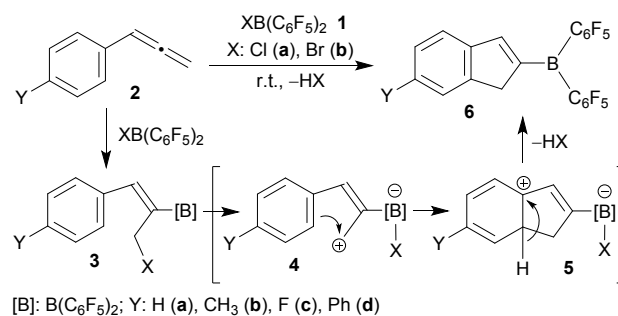
DOI: 10.1039/x0xx00000x

Phenylallene reacts rapidly with ClB(C₆F₅)₂ to give the respective 2-borylindene. Several substituted allenylarenes form the respective 2-B(C₆F₅)₂ boryl-substituted indenenes upon treatment with ClB(C₆F₅)₂ or BrB(C₆F₅)₂ as well. Bis- and tris-allenylarenes form the corresponding products featuring multiple five-membered ring annulations, including a symmetrical tris-borylated dihydro-1H-trindene derivative. The B(C₆F₅)₂ borylindenes show fluorescence properties.

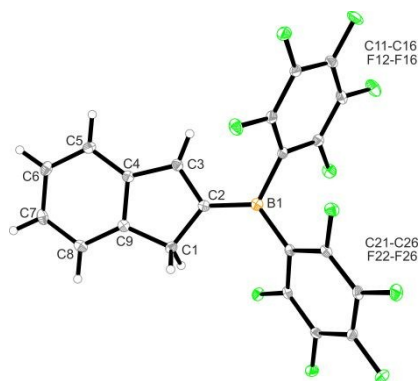
Allenes are important synthetic building blocks.¹ We had recently shown that the parent allene was selectively cyclotrimerized to 1,3,5-trimethylenecyclohexane² under metal-free conditions with Piers' borane [HB(C₆F₅)₂]³ serving as an efficient catalyst. Several mono-alkyl substituted allenes were likewise cyclotrimerized to single trialkyl-1,3,5-trimethylenecyclohexane diastereoisomers² at the HB(C₆F₅)₂ catalyst. The reaction of phenylallene with HB(C₆F₅)₂ took a different course. Here we observed initial stoichiometric head to head dimerization with borylation followed by a Cope rearrangement to give the respective borylated 1,6-diphenyl-1,5-hexadiene product.⁴ We have recently developed a new convenient synthetic route to the strongly electrophilic halogenoboranes X-B(C₆F₅)₂ (X: Cl, Br).⁵ These also served as catalysts for the alkylallene cyclotrimerization reaction.⁶ We have now reacted the XB(C₆F₅)₂ reagents with a small series of aryllallenes.⁷ This gave a surprising result, that will be presented and discussed in this account.

We treated phenylallene (**2a**) with ClB(C₆F₅)₂ (**1a**) in d₂-dichloromethane solution. NMR spectroscopy showed that the reaction went to completion within 5 min at r.t. and gave the 2-borylindene product **6a** (Scheme 1). We performed the reaction on a preparative scale and isolated compound **6a** as a white crystalline solid in 83% yield. It was characterized by C,H

elemental analysis, by spectroscopy and by X-ray diffraction. The NMR spectra at 299 K (in CD₂Cl₂) showed a ¹¹B NMR resonance in the typical range of a strongly Lewis acidic trigonal planar borane with this substituent situation. The large Δδ¹⁹F_{m,p} NMR chemical shift difference is accord with this characterization (Table 1). The ¹⁹F NMR spectrum shows three signals (o,p,m-C₆F₅) of the pair of symmetry-equivalent pentafluorophenyl ligands at boron at 299 K. Lowering the monitoring temperature resulted in broadening of all three signals and splitting into two o-F, two p-F and two m-F ¹⁹F NMR resonances below 213 K. This observation of a pair of inequivalent C₆F₅ groups at B at very low temperature indicates freezing of the rotation around the indenyl C2-B bond under these conditions, with both the B-C₆F₅ groups still rotating freely.



Scheme 1. 2-Borylindene synthesis from allenylbenzenes.



^a Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster, Corrensstraße 40, 48149 Münster, Germany. E-mail: erker@uni-muenster.de

^b Photophysical measurements; Institut für Anorganische und Analytische Chemie – CeNTech, Westfälische Wilhelms-Universität Münster, Heisenbergstrasse 11, D-48149 Münster Germany.

Electronic Supplementary Information (ESI) available: details on the characterization of the new compounds and experimental details. See DOI: 10.1039/x0xx00000x

Figure 1. A view of the molecular structure of the 2-borylindene product **6a** (thermal ellipsoids are given with a 30% probability).

The X-ray crystal structure analysis of compound **6a** confirmed that formation of the indene framework had taken place by borane induced ring closure of the arylallene functionality. The $B(C_6F_5)_2$ group is attached at the indene five-membered ring at carbon atom C2 and there is some indication of conjugative interaction of the indene π system with the borane Lewis acid: the C2-B1 linkage in compound **6a** is markedly shorter than the B1-C(sp²) bonds to the pair of C_6F_5 groups, and the planar boryl group is oriented coplanar with the indene plane (Table 1 and Figure 1).

The cyclization reaction of phenylallene works also well with $BrB(C_6F_5)_2$ (r.t., 5 min) and we isolated the product **6a** in 68% yield. We then carried out the analogous reactions of the arylallenes **2b-d**⁷ with the $CIB(C_6F_5)_2$ reagent **1a** to give the substituted 2-borylindenes **6b-d** (Scheme 1 and Table 1). The reactions of the allenes **2b** (Y: CH₃) and **2d** (Y: Ph), went to completion within ca. 5 min as well. The reaction of the fluorine substituted system **2c** with $CIB(C_6F_5)_2$ was slower (ca. 1 h at r. t.) but also gave the respective borylindene **6c** in >80% yield after workup. The analogous reactions were also achieved cleanly under analogous conditions with the $BrB(C_6F_5)_2$ reagent **1b**. The X-ray crystal structure analysis of compound **6d** (Y: Ph) shows that the π -conjugation ranged all the way from the trigonal planar borane to the distal phenyl group (see the ESI, Figure 48). This showed up in the photophysical properties of the compound (see below).

Table 1. Selected structural parameters^a and spectroscopic features of the 2-borylindene compounds **6a-d**.

	6a	6b	6c	6d
Y	H	CH ₃	F	Ph
B1-C2	1.519(3)	1.519(12)	1.517(13)	1.523(3)
B1-C11	1.590(3)	1.577(9)	1.606(11)	1.578(3) ^b
B1-C21	1.577(3)	1.602(8)	1.582(12)	1.588(3)
C11-B1-C2-C3	4.6(3)	7.0(4)	-173.2(14)	-0.5(3) ^c
NMR ^d				
¹¹ B	57.0	56.0	56.4	56.2
$\Delta\delta^{19}F_{m,p}$	10.8	10.6	10.8	10.8

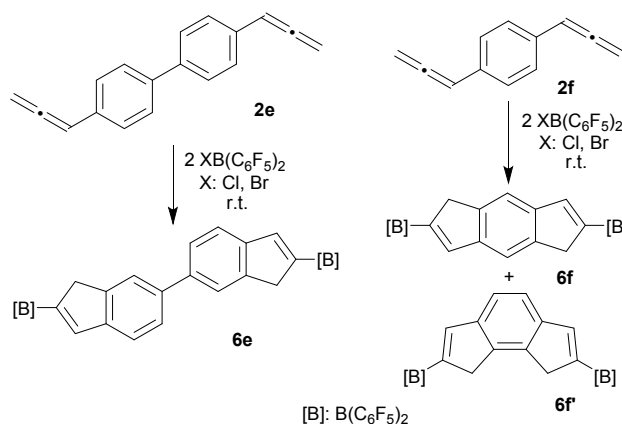
^a Bond lengths in Å, angles in °; the structures of the compounds **6b-d** are depicted in the ESI. ^b B1-C31. ^c C31-B1-C2-C3. ^d in CD₂Cl₂ at 299 K; in ppm δ -scale.

The reactions of the arylallenes **2** with the reagents **1** yield the borylated indene products **6** with loss of the HCl or HBr, respectively. This might be rationalized by a reaction pathway as depicted in Scheme 1. In the case of the reaction of the arylallene **2c** (Y: F) with $BrB(C_6F_5)_2$ (**1b**) we have observed the intermediate formation of the 1,2-halogenoboration⁸ product **3** (X: Br, Y: F) by NMR spectroscopy at low temperature, and we monitored its subsequent slow conversion to the final product **6c** at r.t. (see the ESI, Scheme S12).

We then turned to the cyclization reaction of bis-allenylarene substrates with the halogeno- $B(C_6F_5)_2$ reagents **1a** and **1b**.

Bis(allenyl)biphenyl **2e** cleanly underwent the boryl cyclization reaction upon treatment with $CIB(C_6F_5)_2$ in dichloromethane (1 h, r.t.) to give the bis-indene product **6e**, which we isolated in 77% yield (Scheme 2). It shows the typical NMR features of the pair of symmetry-equivalent subunits [¹¹B: δ 56.9, $\Delta\delta^{19}F_{m,p}$ = 10.9, ¹H: 8.10 (3-H), 3.91 (CH₂)]. The analogous cyclization of **2e** with $BrB(C_6F_5)_2$ took slightly longer (3 h, r.t.) and we isolated the product **6e** in 70% yield from the workup procedure (see the ESI, chapter F).

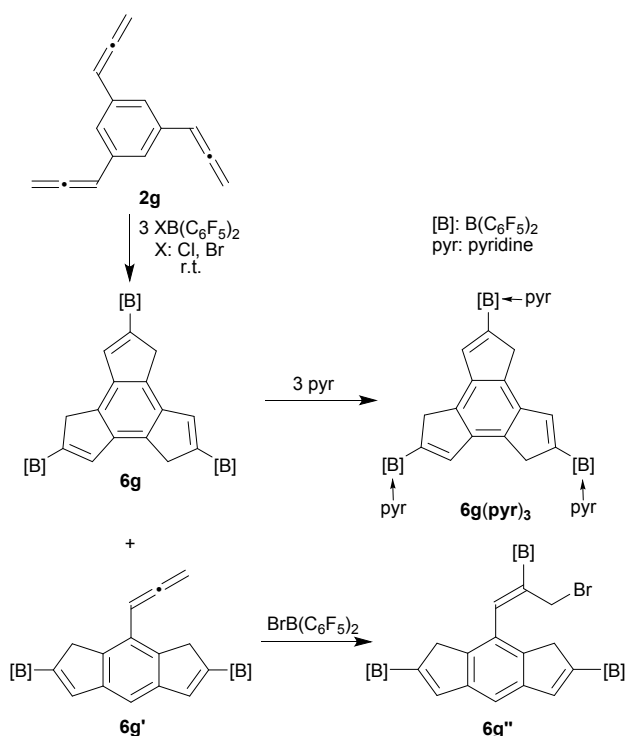
1,4-Bis(allenyl)benzene **2f** underwent a clean twofold cyclization with borylation under analogous conditions. In this case there is a competition for the formation of two different cyclization products. From the reaction of **2f** with two molar equivalents of $CIB(C_6F_5)_2$ (CH₂Cl₂, r.t., 1 h) we isolated a ca. 60:40 mixture of the regio-isomeric doubly borylated s- and a-dihydroindacene products **6f** and **6f'** in a combined yield of 93%. The reaction of **2f** with the $BrB(C_6F_5)_2$ reagent (3 h, r.t.) gave the same mixture in slightly lower yield (70%). We note that the specific features of our allene-cyclization pathway (Scheme 1) enforce the positioning of the indene double bonds which leads to the selective formation of the C_{2h} symmetric framework of the s-dihydroindacene derivative **6f** and the C_{2v} framework of the a-dihydroindacene compound **6f'**. Compound **6f** shows a single ¹H NMR resonance of the central aromatic subunit at δ 7.88 (¹³C: δ 121.2) and the indene resonances of the pair of annulated five-membered rings at δ 8.10 (3-H) and δ 3.88 (CH₂) [¹³C: δ 161.2 (C3), 153.4 (br, C2), 150.3 (C4), 146.4 (C6), 41.9 (CH₂)]. The regio-isomer **6f'** shows the respective arene ¹H NMR signal at δ 7.75 (¹³C: δ 125.2) and the five-membered ring resonances at δ 8.12 (3-H) and δ 3.89 (CH₂) [¹³C: δ 161.7 (C3), 152.5 (br, C2), 146.2 (C4), 146.1 (C6), 40.9 (CH₂)]. The ¹⁹F and ¹¹B NMR features of the products **6f** and **6f'** are only marginally different from each other (see the ESI, chapter G).



Scheme 2. Formation of 2-borylindene products from bis(allenyl)arenes.

Eventually, we reacted 1,3,5-tris(allenyl)benzene **2g** with three molar equiv. of $CIB(C_6F_5)_2$ (CH₂Cl₂, r.t., 1 h) (Scheme 3). During this time, a yellow precipitate had formed which was isolated in 32% yield and shown (see below) to be the product **6g** of the three-fold ring closure reaction.⁹ It contained the C_{3h}-symmetric dihydro-1*H*-trindene core, the formation of which was again enforced by the specific reaction pathway involved. From the filtrate we isolated the product **6g'**, formed by twofold allene

derived ring formation (the reaction of the tris-allene **2g** with $\text{BrB}(\text{C}_6\text{F}_5)_2$ gave a similar result). Consequently, compound **6g'** features the C_{2v} -symmetric substituted *s*-dihydroindacene framework. This composition of compound **6g'** was confirmed by its X-ray crystal structure analysis (Figure 2).



It shows the planar framework with the pair of $\text{B}(\text{C}_6\text{F}_5)_2$ substituents at the central five-membered indene ring subunits (C2, C2A) and the remaining allenyl group at the central carbon atom C7 oriented almost coplanar with the *s*-dihydroindacene core. In solution (CD_2Cl_2) compound **6g'** shows a single olefinic indenyl ^1H NMR resonance (at δ 8.09) and the corresponding CH_2 signal at δ 3.95. The single remaining allenyl substituent shows typical ^1H NMR signals at δ 6.54 ($=\text{CH}-$) and δ 5.22 ($=\text{CH}_2$), respectively (^{13}C NMR signals at δ 213.0 ($=\text{C}=\text{C}$), 89.3 ($=\text{CH}-$) and 78.9 ($=\text{CH}_2$). Compound **6g'** shows a ^{11}B NMR resonance at δ 57.2, which is typical for a strongly Lewis acidic borane with these substituents.

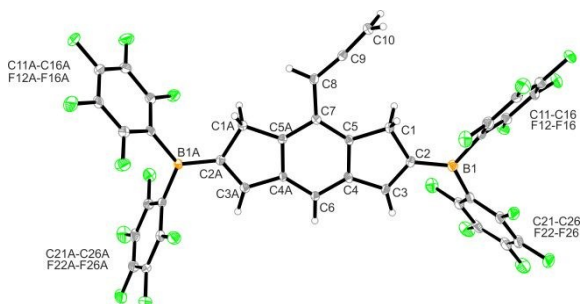


Figure 2. A view of the molecular structure of compound **6g'** (thermal ellipsoids are given with a 15% probability). Selected bond lengths (Å) and angles ($^\circ$): B1-C2 1.528(17), B1-C11 1.587(18), B1-C21 1.575(17), C2-C3 1.364(14), C1-C2 1.519(15), C1-C2-C3 108.3(9), C11-B1-C21 114.8(13).

Compound **6g**, the product of three-fold ring closure, shows the pair of ^{13}C NMR resonances of the per-substituted central arene ring at δ 149.0 and δ 139.6, with the respective signals of the three symmetry-equivalent annulated five-membered rings at δ 158.3 (C3), 151.3 (br, C2), and δ 41.4 (CH_2), respectively [^1H NMR resonances at δ 8.22 (3-H) and δ 4.12 (CH_2)]. It shows a $\Delta\delta^{19}\text{F}_{\text{m,p}} = 11.3$ ppm chemical shift difference, indicating the presence of a planar-tricoordinate boron Lewis acid functionality.

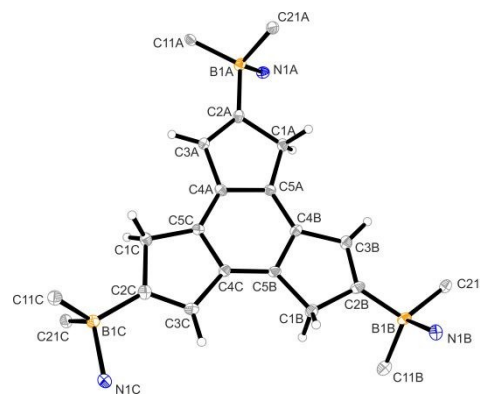


Figure 3. Molecular structure of the tris-pyridine adduct **6g(pyr)₃** of the tris-borylated dihydro-1*H*-trindene derivative **6g** (thermal ellipsoids are given with a 15% probability; substituents at B1A, B1B, and B1C are omitted for clarity except their ipso-atoms). Selected bond lengths (Å) and angles ($^\circ$): N1A-B1A 1.645(10), B1A-C1A 1.605(11), B1A-C11A 1.640(11), B1A-C21A 1.653(11), C2A-C3A 1.348(10), C1A-C2A 1.527(10), C1A-C2A-C3A 107.3(6), C11A-B1A-C21A 106.5(6), C11A-B1A-C2A-C3A -7.2(12).

We reacted compound **6g** with excess pyridine and isolated the tris-pyridine adduct **6g(pyr)₃** in 95% yield. It showed the NMR features of three symmetry-equivalent pyridine ligands at boron (^{11}B : δ -2.1) and the typical NMR resonances of the central dihydro-1*H*-trindene core [^1H : δ 6.70 ($\text{CH}=\text{C}$), 3.31 (CH_2); ^{13}C : δ 154.8 (br, $=\text{CB}$), 132.8 ($=\text{CH}-$), 41.5 (CH_2), arene core: δ 139.9 and 133.8]. Compound **6g(pyr)₃** was characterized by an X-ray crystal structure analysis (Figure 3). It shows the newly formed planar close to C_{3h} symmetric dihydro-1*H*-trindene core. The three $\text{B}(\text{pyridine})(\text{C}_6\text{F}_5)_2$ moieties are bonded to the central carbon atoms of the three five-membered ring systems, each in a different conformational orientation to the central core. Two pyridine units show a close to trans-orientation to each other whereas the third is found oriented more towards an in-plane orientation to the central core.

The reaction of the tris-allene **2g** with the $\text{BrB}(\text{C}_6\text{F}_5)_2$ reagent took a similar course. We isolated the products **6g** and **6g'** from the reaction mixture. In this case we also observed the formation of the follow-up product **6g''** which was apparently formed by $\text{BrB}(\text{C}_6\text{F}_5)_2$ addition to the terminal allene carbon-carbon double bond of compound **6g'** (see the ESI, Scheme S22). We note that compound **6g''** is related to the alleged intermediate **3** in the possible mechanistic scheme of the formation of the 2-borylindene products formed in this study (Scheme 1).

The borylindenes **6** prepared in this study are fluorescent in solution (CH_2Cl_2 , 10^{-5} M, room temperature) as well as in the solid state (see the ESI, Figure S110). In general, the photoluminescence peaks are in the blue-green region of the electromagnetic spectrum. A bathochromic shift is observed for

the broad emission bands arising from compounds **6d** and **6g**, if compared with **6a**, **6b** and **6c**, most probably due to the extended π -systems leading to an enhanced conjugation. Photoluminescence quantum yields (Φ_f) and time-resolved excited state decays (τ) were also measured, both in the solid state and in solution (Table S1). The emission is originated from relatively long-lived excited singlet states (multiexponential decays in the 10 ns-range). The photo-luminescence quantum yields are enhanced for the solid compounds, due to the lack of rotovibrational and collisional relaxation associated to the liquid phases. Interestingly, the Stokes-shift is smaller in the solid state than in solution. Moreover, an incipient vibrational progression can be observed for the amorphous solids. This indicates a sizeable interaction between the excited states of the luminophores and the solvent molecules in solution.

sp^2 -Carbon borylated carbo- and heterocycles serve as important synthetic building blocks. In many cases those systems can conveniently be obtained by means of selective C-H activation processes.¹⁰ The formation of borylated indoles may serve as typical examples.¹¹ This is different for the indenenes. 2-Borylated indenenes are still mostly made by conventional methods, namely formation of the indene bromohydrin, followed by acid induced dehydration, metalation of the resulting 2-bromoindene and reaction with the respective boron halide reagent.¹² Our approach by means of formation of the 2-borylindene framework by borylating carbon-carbon bond formation starting from the readily available allenylarenes provides an attractive alternative. The sp^2 -carbon bonded $B(C_6F_5)_2$ group had previously been shown to be active in e.g. Suzuki-Miyaura coupling.¹³ We could show that the borylated indenenes **6a** and **6d** serve as reagents in metal-catalyzed cross-coupling reactions with p-iodotoluene to give the respective 2-arylated indene products in good yields (see chapter J of the ESI for details). The photophysical properties of the $(C_6F_5)_2B$ -indenenes described in this study also indicate a potential of such building blocks for the design of respective organo-element materials.

Financial support from the European Research Council is gratefully acknowledged. K. S. thanks the Alexander von Humboldt Foundation for a Georg-Forster postdoctoral fellowship.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- (a) A. S. K. Hashmi, *Angew. Chem. Int. Ed. Engl.*, 2000, **39**, 3590; (b) N. Krause and A. S. K. Hashmi (Eds), *Modern Allene Chemistry*, Wiley-VCH, Weinheim, Germany, 2004; (c) S. Ma, *Chem. Rev.*, 2005, **105**, 2829; (d) N. Krause and C. Winter, *Chem. Rev.*, 2011, **111**, 1994; (e) S. Yu and S. Ma, *Angew. Chem. Int. Ed.*, 2012, **51**, 3074; (f) W. Yang and A. S. K. Hashmi, *Chem. Soc. Rev.*, 2014, **43**, 2941.
- X. Tao, G. Kehr, C. G. Daniliuc and G. Erker, *Angew. Chem. Int. Ed.*, 2017, **56**, 1376.
- (a) D. J. Parks, R. E. H. Spence and W. E. Piers, *Angew. Chem. Int. Ed. Engl.*, 1995, **34**, 809; (b) D. J. Parks, W. E. Piers and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492; (c) M. Hoshi, K. Shirakawa and M. Okimoto, *Tetrahedron Lett.*, 2007, **48**, 8475; (d) A. Schnurr, K. Samigullin, J. M. Breunig, M. Bolte, H.-W. Lerner and M. Wagner, *Organometallics*, 2011, **30**, 2838; (e) J. Zhang, S. Park and S. Chang, *Angew. Chem. Int. Ed.*, 2017, **56**, 13757.
- (a) X. Tao, C. G. Daniliuc, D. Dittrich, G. Kehr and G. Erker, *Angew. Chem. Int. Ed.*, 2018, **57**, 13922; (b) see for a comparison: B. Inés, D. Palomas, S. Holle, S. Steinberg, J. A. Nicasio and M. Alcarazo, *Angew. Chem. Int. Ed.*, 2012, **51**, 12367.
- (a) A. Ueno, J. Li, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Eur. J.*, 2018, **24**, 10044. See also: b) R. D. Chambers and T. Chivers, *J. Chem. Soc.*, 1965, 3933; (c) W. E. Piers and R. E. H. Spence, *Acta Cryst.*, 1995, **C51**, 1688; (d) M. Bochmann, S. J. Lancaster and O. B. Robinson, *J. Chem. Soc., Chem. Commun.*, 1995, 2081; (e) W. E. Piers, *Adv. Organomet. Chem.*, 2004, **52**, 1.
- X. Tao, C. Wölke, C. G. Daniliuc, G. Kehr and G. Erker, *Chem. Sci.*, 2019, **10**, 2478.
- The arylallenes were prepared from the respective alkynylarenes according to: J. Huang and S. Ma, *J. Org. Chem.*, 2009, **74**, 1763.
- (a) M. F. Lappert and B. Prokai, *J. Organomet. Chem.*, 1964, **1**, 384; (b) S. Hara, H. Dojo, S. Takinami and A. Suzuki, *Tetrahedron Lett.*, 1983, **24**, 731; (c) Y. Satoh, H. Serizawa, S. Hara and A. Suzuki, *J. Am. Chem. Soc.*, 1985, **107**, 5225; (d) J. R. Lawson, E. R. Clark, I. A. Cade, S. A. Solomon and M. J. Ingleson, *Angew. Chem. Int. Ed.*, 2013, **52**, 7518 and references cited herein.
- In contrast to our synthetic scheme, the conventional dihydro-1H-trindene synthesis (starting by aldol condensation of three equiv. of cyclopentanone, followed by a bromination/debromination sequence) gives a mixture of the two dihydro-1H-trindene double bond isomers, see e.g.: (a) T. J. Katz and W. Slusarek, *J. Am. Chem. Soc.*, 1980, **102**, 1058; (b) T. J. Lynch, M. C. Helvenston, A. L. Rheingold and D. L. Staley, *Organometallics*, 1989, **8**, 1959; (c) M. C. Helvenston and T. J. Lynch, *J. Organomet. Chem.*, 1989, **359**, C50; (d) S. Santi, L. Orian, A. Donoli, A. Bisello, M. Scapinello, F. Benetollo, P. Ganis and A. Cecon, *Angew. Chem. Int. Ed.*, 2008, **47**, 5331; (e) T. J. Lynch, J. M. Carroll, M. C. Helvenston, T. L. Tisch, A. L. Rheingold, D. L. Staley and A. Mahmoudkhani, *Organometallics*, 2012, **31**, 3300; (f) A. Donoli, A. Bisello, R. Cardena, C. Prinzivalli and S. Santi, *Organometallics*, 2013, **32**, 1029.
- (a) N. Kuhl, M. N. Hopkinson, J. Wencel-Delord and F. Glorius, *Angew. Chem. Int. Ed.*, 2012, **51**, 10236; (b) T. Gensch, M. N. Hopkinson, F. Glorius and J. Wencel-Delord, *Chem. Soc. Rev.*, 2016, **45**, 2900.
- (a) Q. Zhong, S. Qin, Y. Yin, J. Hu and H. Zhang, *Angew. Chem. Int. Ed.*, 2018, **57**, 14891 and references cited therein; (b) see also: M.-A. Légaré, M.-A. Courtemanche, É. Rochette and F.-G. Fontaine, *Science*, 2015, **349**, 513.
- (a) H. D. Porter and C. M. Suter, *J. Am. Chem. Soc.*, 1935, **57**, 2022; (b) E. G. Ilpeij, F. H. Bijer, H. J. Arts, C. Newton, J. G. de Vries and G.-J. M. Grute, *J. Org. Chem.*, 2002, **67**, 169; (c) A. C. Möller, R. H. Heyn, R. Blom, O. Swang, C. H. Görbitz and J. Kopf, *Dalton Trans.*, 2004, 1578.
- (a) N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457; (b) C. Chen, G. Kehr, R. Fröhlich and G. Erker, *J. Am. Chem. Soc.*, 2010, **132**, 13594; (c) C. Chen, T. Voss, R. Fröhlich, G. Kehr and G. Erker, *Org. Lett.*, 2011, **13**, 62; (d) G. Kehr and G. Erker, *Chem. Commun.*, 2012, **48**, 1839; (e) G. Kehr and G. Erker, *Chem. Sci.*, 2016, **7**, 56.