The Free Internet Journal for Organic Chemistry

Paper

Archive for Organic Chemistry

Arkivoc **2017**, part iii, 191-204

Reactivity of 3-halopropynols: X-ray crystallographic analysis of 1,1-dihalocumulenes and 2+2 cycloaddition products

Nurbey Gulia, Bartłomiej Pigulski, and Sławomir Szafert*

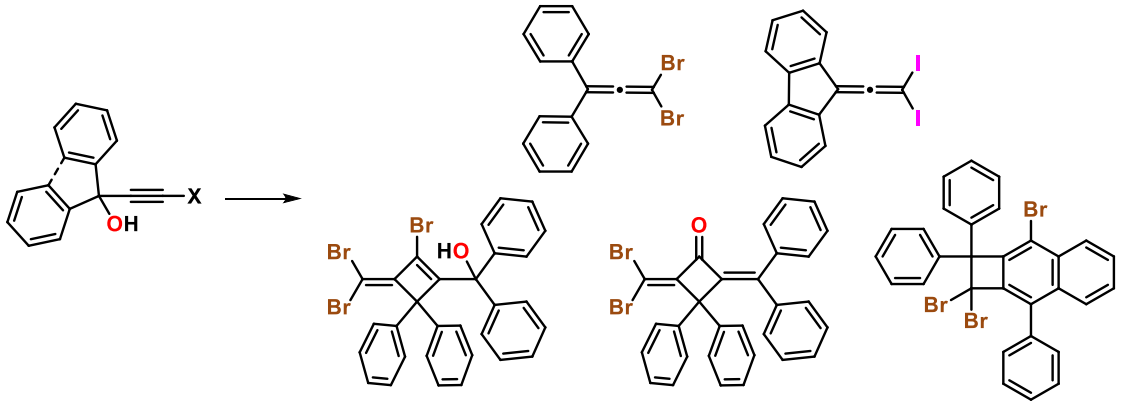
Faculty of Chemistry, University of Wrocław, 14 F. Joliot-Curie, 50-383 Wrocław, Poland
Email: slawomir.szafert@chem.uni.wroc.pl

Dedicated to Prof. Oleg A. Rakitin on the occasion of his 65th birthday

Received 04-10-2017 **Accepted** 06-08-2017 **Published on line** 07-05-2017

Abstract

Reactions of 3-halopropynols and their butadiyne analogues with $BF_3{\cdot}Et_2O$ or $HX_{(aq)}$ were investigated. Depending on the end group and the reaction conditions, different products were obtained which belonged to two classes: (i) 1,1-dihaloallenes, and (ii) products of 2+2 cycloaddition. The resulting species were identified using single crystal X-ray analysis and NMR spectroscopy.



Keywords: Allenes, 1-haloalkynes, 2+2 cycloaddition, heavy atom effect, ^{13}C NMR, X-ray crystallography

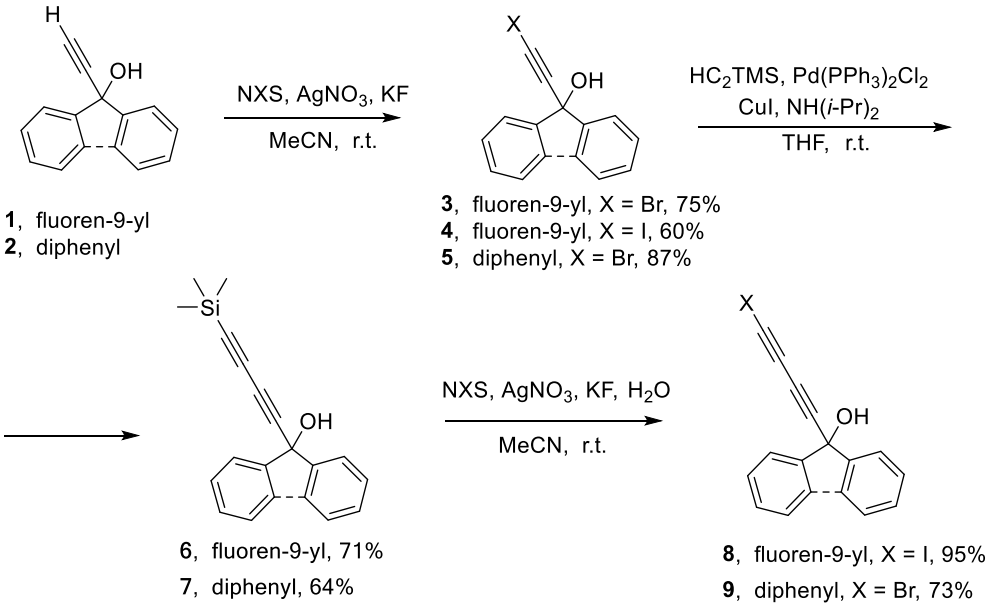
Introduction

During the last few decades enormous progress in the chemistry of allenes has been made and compounds of this type are now being used as versatile synthetic precursors in many organic reactions.[1] Moreover, their extended analogues - cumulenes - are attracting a significant interest in scientific circles as model compounds of the linear, allotropic form of carbon - carbyne.[2] Nevertheless, known 1,1-dihalocumulenes remain rare and only the synthesis and reactivity of tetrafluorobutatriene has been widely explored. The compound was first obtained in 1959 by Martin and Sharkey,[3] but an X-ray solid state structure of this extremely unstable compound was determined in 2002.[4] To date, this perfluorinated butatriene was used as a ligand for organometallic iridium[5,6] and rhodium[6] complexes or as dienophile in Diels-Alder reaction.[7] Perchlorinated,[8] perbrominated[9] and periodinated[10] analogues are known but no reactivity studies were performed. 1,1-Dibromo- or 1,1-diiodo-cumulenes have a significant potential as building blocks for more complex, all-carbon scaffolds and may be obtained from 1-halobutadiynes. In our group, we have been conducting continuous studies on the syntheses and reactivity of 1-haloalkynes and 1-halopolyynes[11-16] and we attempted to use them as precursors of 1,1-dihalocumulenes. On the other hand, (2+2) cycloaddition of allenes has been intensively explored for many years.[17,18] Dimerization proceeds through diradical intermediates affording different isomers of 2-dimethylenecyclobutane derivatives.[19] Their subsequent transformations provide complex molecules with broad carbon core diversification.[20-22] Herein, we report on the preparation and characterization of two 1,1-dihaloallenes and some products of their cycloaddition. Because of the complicated molecular structure of these compounds, we focused on X-ray crystallographic methods for structure determination.

Results and Discussion

Synthesis

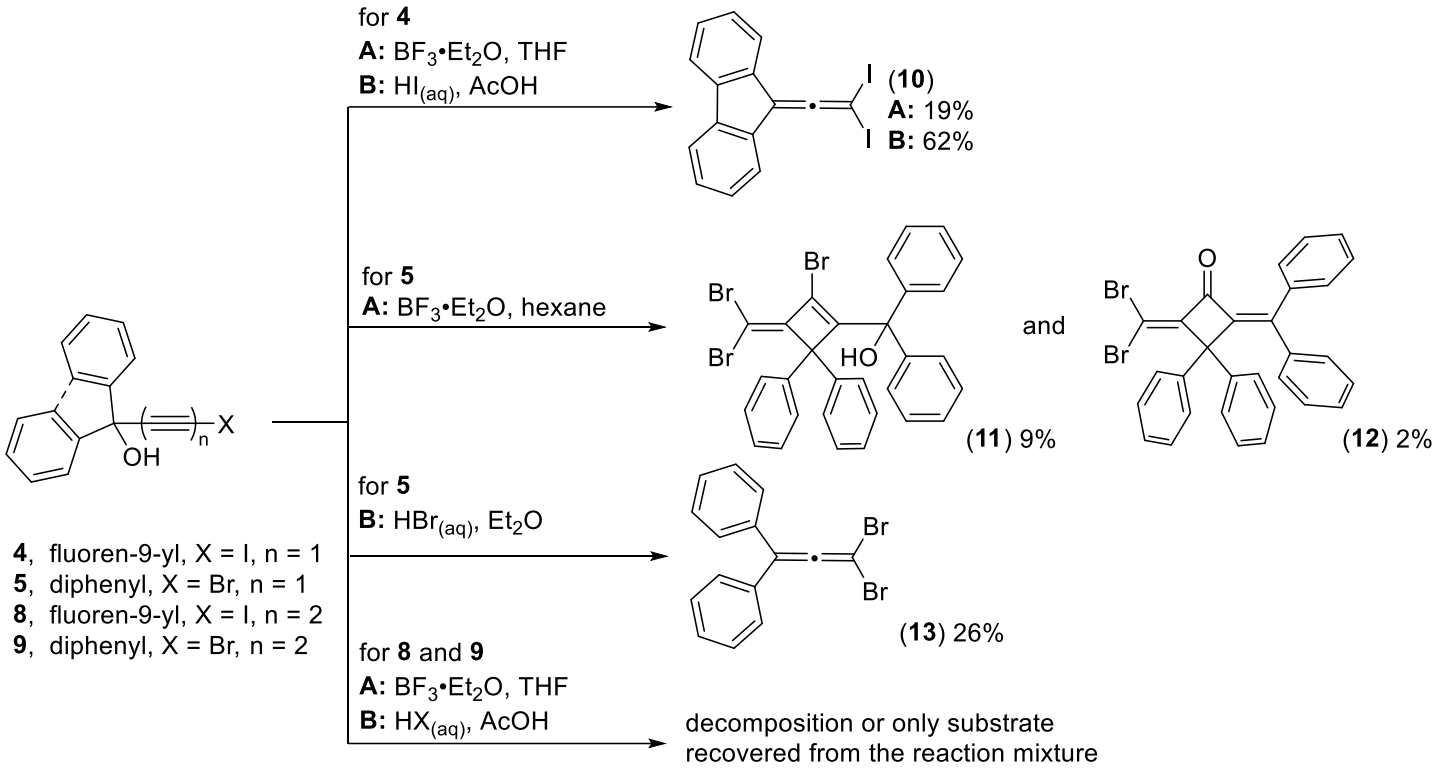
Syntheses of 1-haloalkyne precursors started from commercially available alkynols **1** and **2** as shown in Scheme 1. In the first step, halogenations with the use of *N*-bromosuccinimide (NBS) or *N*-iodosuccinimide (NIS) were performed to yield 1-haloalkynes **3-5**.



Scheme 1. Synthesis of 1-haloalkyne precursors.

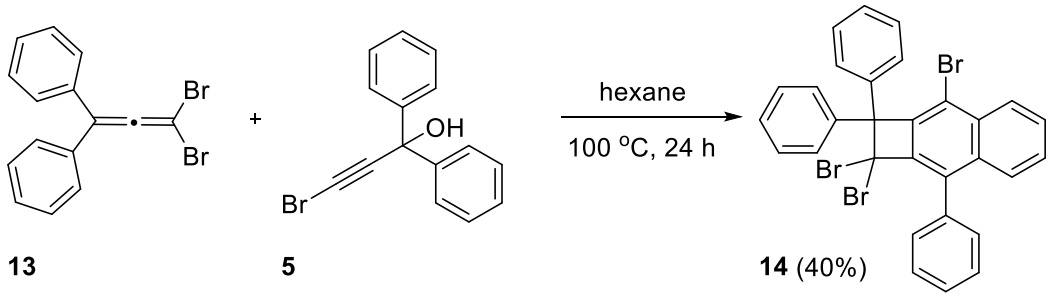
Next, 1-bromoalkynes **3** and **5** were used for Cadiot-Chodkiewicz cross-coupling with trimethylsilyl acetylene to give butadiynes **6** and **7**. Final 1-halobutadiynes **8** and **9** were obtained using NXS/$AgNO_3$ halogenations.

Our primary synthetic goal was to obtain 1,1-dihaloallenes and 1,1-dihalocumulenes from the 1-haloalkyne precursors **4**, **5**, **8** and **9**. Therefore, their reactions with $BF_3{\cdot}Et_2O$ (with and without an external source of halogen) and $HX_{(aq)}$ were carried out as shown in Scheme 2. It is known that the reaction of polyynes such as R-$(C{\equiv}C)_n$-$C(OH)R_2$ with $BF_3{\cdot}Et_2O$ leads to a cationic intermediate.[23-24] Therefore we hoped that the unstable cationic cumulene can be halogenated by an external source of halogen. Higher cumulenes are highly moisture sensitive[25] and thus we focused on the development of moisture free conditions. In the first thrust, the reaction of **4** with $BF_3{\cdot}Et_2O$ was performed. As a result we obtained **10** as a main product (19%) but other unknown minor products were also formed. Unfortunately, our attempts to increase the yield of **10** by addition of iodine source (I_2, NaI, NIS, tetrabutylammonium iodide (TBAI)) failed and we decided to switch to 'wet' conditions. We used literature procedure[21] and the reaction of **4** with $HI_{(aq)}$ gave **10** in 62% yield. The reaction of **5** with $BF_3{\cdot}Et_2O$ gave a complex mixture of products. After extensive silica gel chromatography workup we obtained and characterized two major components of this mixture - products of 2+2 cycloaddition **11** and **12**. It is noteworthy, that no formation of **13** was observed. The reaction of **5** with $HBr_{(aq)}$ gave expected, pure **13**.[26] Unfortunately, the reaction of butadiynes **8** and **9** with $BF_3{\cdot}Et_2O$ did not occur and only slow decomposition of substrates was observed. The use of $HX_{(aq)}$ caused only much quicker decomposition of substrates.

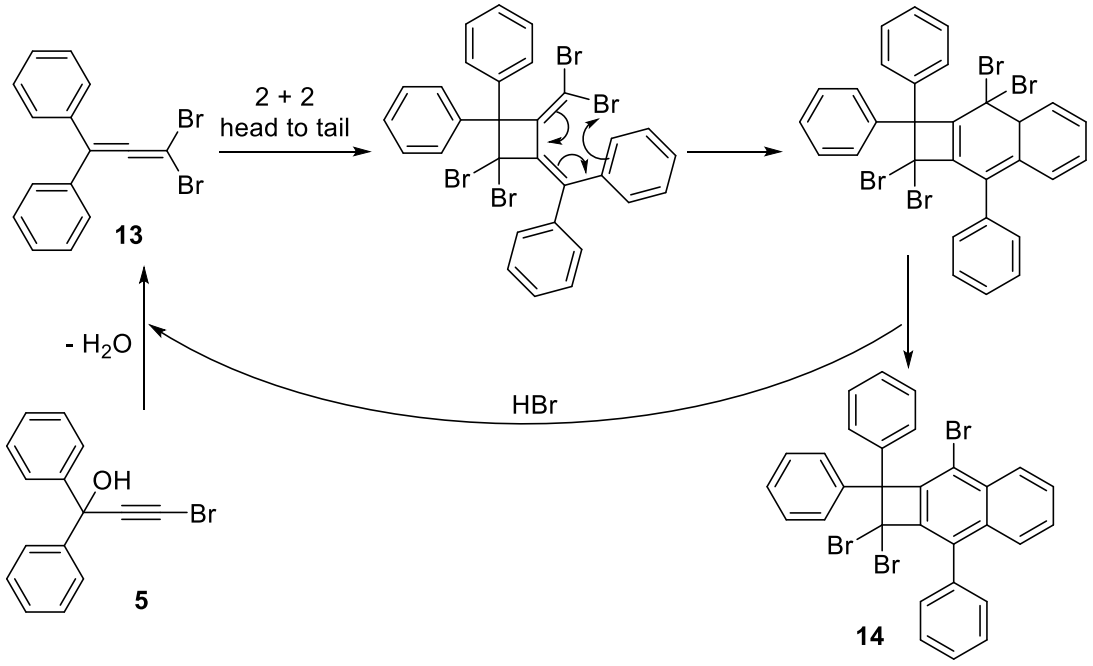


Scheme 2. Attempts to prepare 1,1-dihaloallenes and 1,1-diahalocumulenes.

We assumed that **11** and **12** might be the result of 2+2 cycloaddition of **5** and **13** formed *in situ*.[27] Therefore we carried out a reaction of **5** and **13** in pure hexane at 100 °C in a sealed vial as shown in. However, we did not find formation of **11** and/or **12**; the main product was the cyclobuta[*b*]naphthalene **14** in 40% yield. Compound **14** was obtained by dimerization of pure **13** in hexanes solution under the similar condition with only 18%. It is also possible to obtain **14** directly from **5** by Lewis acid mediated dimerization.[28] Therefore, we assume that the precursor of **14** are both compounds that underwent reaction according to the proposed mechanism (Scheme 4).



Scheme 3. The attempted reaction of **13** with **5**.



Scheme 4. The proposed mechanism for the formation of **14** from **13** and **5**.

We decided to look closer at the ^{13}C NMR spectra of allenes **10** and **13** (see Figure 1). The chemical shifts of signals of the three allenic carbon atoms of **10** and **13** are given in Table 1. ^{13}C NMR spectrum of **13** is a standard spectrum of allene with slightly upfield shifted signal of C1 (54.4 ppm). The situation for **10** is different and the carbon signal derived from C1 atom is extremely strongly shifted upfield (-46.4 ppm) which is considerably outside the typical chemical shift range used for ^{13}C NMR measurements. The examples of 1,1-diiodoallenes are very rare in the literature and the majority of them were obtained in pre-^{13}C NMR era.[29] Therefore, it is hard to perform a comparison of the obtained results with the literature data since useful ^{13}C NMR spectra are available only for perhalobutatrienes. Carbon chemical shifts of allenic part of **10** and **13** are compared in Table 1 with those for butatrienes $I_2(C{=}C)_2I_2$[10] and $Br_2(C{=}C)_2Br_2$.[9]. The chemical shift of a signal derived from C=**C**I_2 carbon strongly depends on solvent and in cyclohexanone it is also strongly upfield shifted (-27.5 ppm). The explanation for the very strong shielding may be the heavy atom effect. This phenomenon is observed for instance for an alpha carbon signal in 1-iodoalkynes[30] and also leads to upfield shift of that signal. The strength of that effect intimately depends on Lewis basicity of a solvent. Solvents that are Lewis bases result in less upfield-shifted carbon signal of the C≡**C**-I atom. That may explain the difference between the chemical shift of C=**C**I_2 atom for **10** (-46.4 ppm in $CDCl_3$) and that for $I_2C_4I_2$ (-27.5 ppm in cyclohexanone). We suggest that the unusual chemical shift of the signal derived from C1 carbon of **10** is most likely to be due to an extremely strong heavy atom effect.

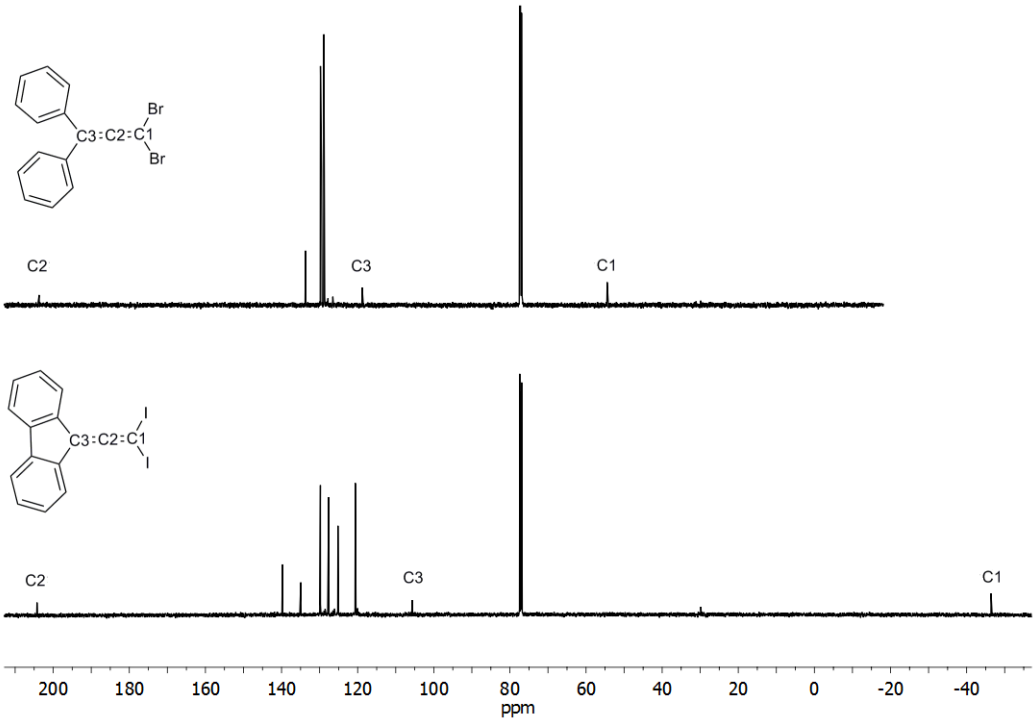


Figure 1. ^{13}C NMR spectra of **10** and **13** ($CDCl_3$, 126 MHz, 300 K).

Table 1. Chemical shifts of selected ^{13}C NMR signals for **10**, **13**, $I_2C_4I_2$ and $Br_2C_4Br_2$

Compound	Solvent	C1 [ppm]	C2 [ppm]	C3 [ppm]
10	$CDCl_3$	-46.4	204.3	105.7
13	$CDCl_3$	54.4	203.7	118.8
$I_2C_4I_2$[10]	DMSO-d_6	37.7	121.2	-
$I_2C_4I_2$[10]	pyridine-d_5	-14.9	163.5	-
$I_2C_4I_2$[10]	cyclohexanone with cyclohexane-d_{12}	-27.5	162.9	-
$Br_2C_4Br_2$[9]	DMSO-d_6	65.4	153.5	-

X-ray single crystal diffraction

Monocrystals of allenes **10** and **13** were obtained by slow evaporation of their hexane solutions. Compound **10** crystallizes in *P*-1 space group, triclinic system with Z = 4, whereas **13** crystallizes in $P2_1/n$ space group, monoclinic system with Z = 8 (see the Table S1 in the Supplementary Material). In both crystal structures there are two molecules in the asymmetric unit. Molecular structures are shown in Figures 2 and 3.

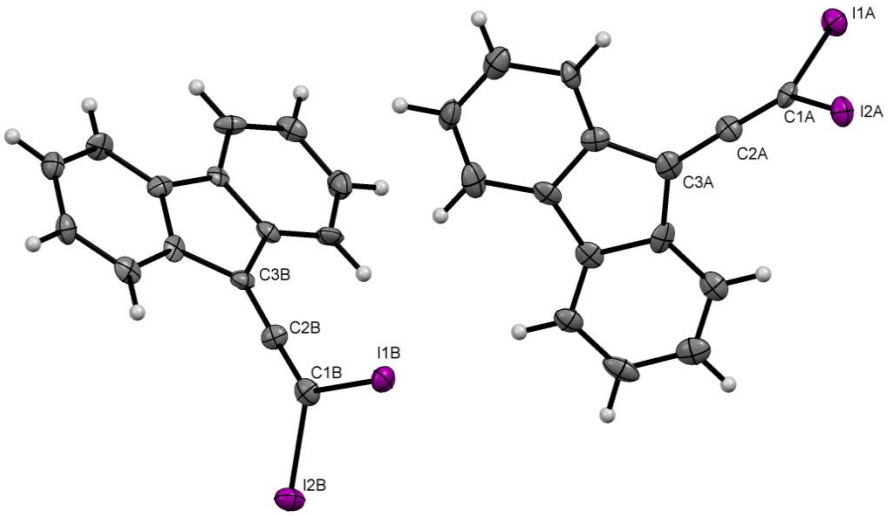


Figure 2. The molecular structure of **10**. Two molecules in the asymmetric unit.

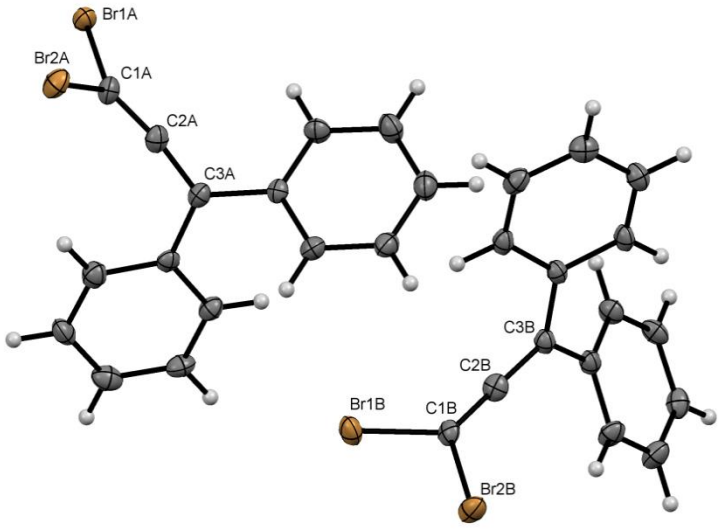


Figure 3. The molecular structure of **13**. Two molecules in the asymmetric unit.

Selected bond lengths and angles for **10** and **13** are given in the supplementary material Table S2. Single diffraction X-ray structures of 1,1-dibromo and 1,1-diiodoallenes are rare in the literature and only the structures of tetrabromo and tetraiodobutatrienes are known.[9-10] For both **10** and **13** C1-C2 double bond (1.276-1.295 Å) are shorter than C2-C3 double bond (1.306-1.339 Å). Analogous bond lengths for tetraiodobutatriene are C1-C2 = 1.316 Å and C2-C3 = 1.225 Å, whereas for tetrabromobutatriene they are C1-C2 = 1.296 and C2-C3 = 1.285 Å. The angles between the plane containing C1, X1 and X2 atoms and the plane containing C3 atom and carbon atoms directly connected with it are nearly 90° and the exact values are 86.4° and 87.9° for **10** and 89.6° and 85.8° for **13**. Those values are typical for allenes.

Monocrystals of **11**, **12** and **14** were obtained under identical conditions i.e. by slow evaporation of DCM from DCM/hexane solutions (1/1). All three compounds crystallize in monoclinic system in $P2_1/n$ (**11**, **14**) and *Cc* (**12**) space groups (see the Table S1 in the Supplementary Material). The molecular structures of **11**, **12** and **14** are shown in Figures 7-9. The interatomic distances and angles within carbon four-membered rings were

analyzed. In all three structures this part of the molecules is almost ideally planar, however, the distances and angles between carbon atoms in these fragments contain substantial distortions from the ideal four-membered ring. In each structure, the smallest bond angle "lies" at the carbon with the biggest substituent. In **14** (molecule 14B) it is 82.3(2)° for angle C2B-C1B-C4B. Structures **11** and **12** contain similar angle distortion at corresponding atoms (see the Table S3 in the Supplementary Material). The bond length in four-membered rings of **11** and **12** are within the normal range for the corresponding bond types. However, in **14** we observed unusually long C(sp^3)-C(sp^3) bonds in both molecules (two molecules in the asymmetric unit) which are 1.644(5) and 1.662(5) Å for C2A-C1A and C2B-C1B. Such extremely long C(sp^3)-C(sp^3) covalent bond may occur in some other cyclobutanaphthalene derivatives.[22,31]

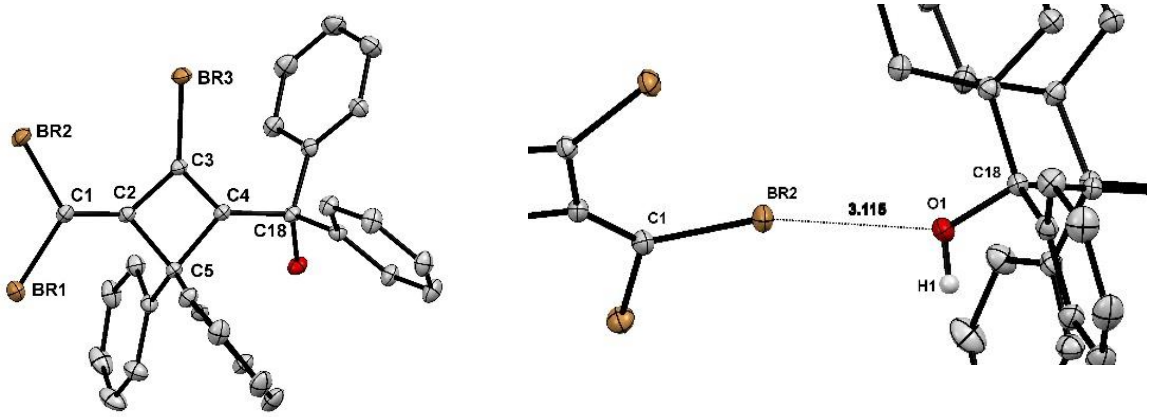


Figure 4. The molecular structure of **11**; the intermolecular halogen bond.

In structures of **11**, **12** and **14**, van der Waals forces are the predominant intermolecular interactions. Nevertheless, in the structure of **11** halogen bond Br-O of 3.115(2) Å (the sum of vdW radii of Br and O is 3.37 Å, Figure 7) occurs. Additionally, the OH group of **11** remains disengaged in the hydrogen bond. To confirm that we used infrared spectroscopy. The IR spectrum showed the stretching frequency and signal shapes (sharp peak at 3592 cm^{-1}) supporting non-hydrogen-bonded OH groups. The relative position of two molecules of **11** enables the hydrogen O-H···Br bonding after rotation around O1-C18 bond (Figure 7). However, halogen bond better stabilizes the structure in this particular example.

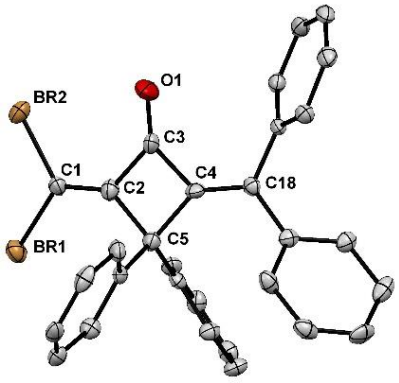


Figure 5. The molecular structure of **12**.

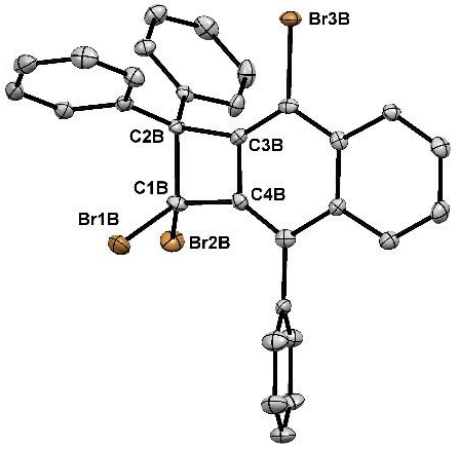


Figure 6. The molecular structure of **14** (two molecules in the asymmetric unit).

Conclusions

Two 1-haloalkynes and two 1-halobutadiynes were investigated as precursors of 1,1-diahaloallenes and 1,1-dihalocumulenes. All new compounds were fully characterized by spectroscopic methods. For 1,1-diiodoallene an extremely strong heavy atom effect on the ^{13}C NMR spectrum was observed. Five products presented in this work were characterized by X-ray crystallography. They belong to two classes: 1,1-dihaloallenes and products of 2+2 cycloaddition of allenes that contain a carbon four-membered ring in their structure.

Experimental Section

General. All reactions were conducted under N_2 by using standard Schlenk techniques unless stated otherwise. Glassware was pre-dried at 120 °C. Solvents were treated as follows: THF was distilled from Na/benzophenone, CH_2Cl_2 and CH_3CN were distilled from P_2O_5, Et_2O, AcOH and hexane (pure for analysis) were used as received. $AgNO_3$ (puriss p.a., POCH), AgF (98%, Alfa Aesar), KF (puriss p.a., POCH), NaI (puriss p.a., POCH), I_2 (puriss p.a., POCH), NIS (97% Alfa Aesar), NBS (99%, Aldrich), TBAI (98%, Aldrich), $HI_{(aq)}$ (57%, Fluka), $HBr_{(aq)}$ (48%, Lancaster), $BF_3{\cdot}Et_2O$ (Aldrich), $Pd(PPH_3)_2Cl_2$ (99.5% Aldrich), CuI (99.999%, Aldrich), trimethylsilylacetylene (98%, Aldrich), NH*i*Pr_2 (99.5%, Aldrich) ethynyltrimethylsilane (98%, Fluorochem)were used as received. Silica gel (0.063-0.200) were used for column chromatography. Syntheses were started from commercially available **1** and **2** and compounds **3**, **6**, and **7** are known.

^1H and ^{13}C NMR spectra were recorded using a 500 MHz Bruker Avance spectrometer with an inverse broadband probe. For all the ^1H NMR spectra, the chemical shifts are given in ppm relative to the solvent residual peaks ($CDCl_3$, ^1H: 7.26 ppm, ^{13}C: 77.16 ppm). Coupling constants are given in Hz. ^{13}C NMR spectra were measured with proton decoupling. HRMS spectra were recorded using Bruker MicOTOF-Q spectrometers with ESI ion source and time-of-flight mass analyzer. IR spectra were recorded using a Bruker 66/s FTIR spectrometer. Microanalyses were conducted with an Elementar CHNS Vario EL III analyzer.

X-ray diffraction. X-ray diffraction data were collected with a KUMA KM4 CCD or an Agilent Sapphire2 diffractometer (*ω* scan technique). The space groups were determined from systematic absences and Lorentz and polarization corrections were applied. Absorption correction was applied with the use of CrysAlisPro software.[32] The structures were solved by direct methods and refined by full-matrix, least-squares on F^2 by use of the SHELXTL Package.[33] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and added to the structure factor calculations but were not refined. The position of **H**-O (**11**) was found in electron density map then hydrogen was placed and refined (AFIX 147).

Synthetic procedures

9-(Bromoethynyl)-9*H*-fluoren-9-ol[34] (**3**). 9-Ethynyl-9*H*-fluoren-9-ol (**1**, 1.083 g, 5.25 mmol) and NBS (1.133 g, 6.30 mmol) were dissolved in 25 mL of acetonitrile. Next, KF (0.305 g, 5.25 mmol) and $AgNO_3$ (0.892 g, 5.25 mmol) were added. The mixture was stirred for 2 h and after this time solvent was removed under reduced pressure. Crude product was purified by elution through short silica gel plug (hexane/Et_2O; v/v; 1/1) yielding 1.362 g of yellow solid (4.78 mmol, 75%). IR (cm^{-1}, nujol mull) 2211 (C≡C), 3524 (OH). ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 2H), 7.63 – 7.60 (m, 2H), 7.41 (td, *J* 7.5, 1.2 Hz, 2H), 7.36 (td, *J* 7.4, 1.2 Hz, 2H), 2.65 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.4, 139.1, 130.0, 128.7, 124.4, 120.4, 80.0, 75.6, 44.4. Elemental analysis: calcd for $C_{15}H_9BrO$ (285.14): C 63.18, H 3.18. Found: C, 62.97; H, 3.01 %.

9-(Iodoethynyl)-9*H*-fluoren-9-ol (**4**)

According to the procedure for **3**, 9-ethynyl-9*H*-fluoren-9-ol (**1**, 0.986 g of, 4.78 mmol), $AgNO_3$ (0.812 g, 4.78 mmol, KF (0.278 g, 4.78 mmol), NIS (1.330 g, 5.73 mmol), H_2O (172 µL), and acetonitrile (40 mL) were used. Time: 24 h, purification: silica gel plug (hexane/DCM; v/v; 1/2), yield: 0. 953 g (2.87 mmol, 60%), yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (ddd, *J* 7.4, 1.1, 0.7 Hz, 2H), 7.62 (ddd, *J* 7.5, 1.1, 0.7 Hz, 2H), 7.41 (td, *J* 7.5, 1.2 Hz, 2H), 7.36 (td, *J* 7.4, 1.2 Hz, 2H), 2.54 (bs, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.6, 139.3, 130.0, 128.8, 124.5, 120.4, 94.0, 76.3, 1.5. HRMS(ESI): *m/z* calcd for $C_{19}H_9OINa$: 354.9590 $[M+Na]^+$; found: 354.9564.

3-Bromo-1,1-diphenylprop-2-yn-1-ol[35] (**5**). 1,1-Diphenylprop-2-yn-1-ol (**2**, 1.00 g, 4.80 mmol) was dissolved in acetonitrile (30 mL) with an addition of water (0.220 mL, 12.2 mmol). The flask was wrapped with aluminum foil and NBS (1.04 g, 5.84 mmol), $AgNO_3$ (0.245 g, 1.44 mmol), and KF (0.167 g, 2.87 mmol) were added. The mixture was stirred for 20 h. After this time solvent was removed on rotary evaporator. Mixture of DCM/hexane (v/v, 1/1) was poured onto greasy residual and this mixture was passed through a short (10 cm) silica gel plug. **5** (1.203 g, 4.19 mmol, yield 87%) was obtained as beige solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 – 7.56 (m, 4H), 7.37 – 7.32 (m, 4H), 7.31 – 7.27 (m, 2H), 2.80 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 128.5, 128.1, 126.2, 82.8, 75.6, 48.4.

9-[(Trimethylsilyl)buta-1,3-diyn-1-yl]-9*H*-fluoren-9-ol (**6**). 9-(Bromoethynyl)-9*H*-fluoren-9-ol (**3**, 0.721 g, 2.53 mmol), $Pd(PPh_3)_2Cl_2$ (0.036 g, 0.051 mmol), CuI (0.019 g, 0.10 mmol), ethynyltrimethylsilane (0.43 mL, 3.0 mmol) were dissolved in 20 mL of THF. Next NH*i*-Pr_2 (0.89 mL, 6.3 mmol) was added and the mixture was stirred for 2 h. After this time solvent was removed under reduced pressure and product was purified by silica gel chromatography (hexane/Et_2O; v/v; 1/1) yielding **6** (0.545 g, 1.80 mmol, 71%) as yellow oil. IR (cm^{-1}, nujol mull) 2104 (C≡C), 2222 (C≡C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.67 (m, 2H), 7.63 – 7.60 (m, 2H), 7.41 (td, *J* 7.5, 1.2 Hz, 2H), 7.35 (td, *J* 7.5, 1.2 Hz, 2H), 2.52 (bs, 1H, OH), 0.16 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.2, 139.3, 130.1, 128.8, 124.5, 120.5, 88.1, 87.5, 77.5, 75.2, 68.1, -0.4.

1,1-Diphenyl-5-(trimethylsilyl)penta-2,4-diyn-1-ol[36] (**7**). To the solution of 3-bromo-1,1-diphenylprop-2-yn-1-ol (**5**, 0.627 g, 2.18 mmol) in THF (15 mL) ethynyltrimethylsilane (0.453 mL, 3.27 mmol), CuI (0.021 g, 0.11 mmol), and $Pd(PPh_3)_2Cl_2$ (0.077 g, 0.11 mmol) were added. Next, NH*i*Pr_2 (0.770 mL, 5.49 mmol) was added dropwise and the mixture was stirred for 2 h. Next, the solvent was removed under reduced pressure and the residue was purified by silica gel flash-chromatography (DCM/hexane, 1/1). **7** (0.423 g, 1.39 mmol, 64%) was obtained as beige solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 4H), 7.37 – 7.31 (m, 4H), 7.31 – 7.26 (m, 2H), 2.77 (s, 1H), 0.21 (m, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.1, 128.6, 128.2, 126.2, 89.5, 87.3, 79.4, 75.1, 72.4, -0.3.

9-(Iodobuta-1,3-diyn-1-yl)-9*H*-fluoren-9-ol (**8**). According to the procedure for **3**, 9-[(trimethylsilyl)buta-1,3-diyn-1-yl]-9*H*-fluoren-9-ol (**6**, 0.210 g, 0.695 mmol), AgF (0.091 g, 0.69 mmol), NIS (0.194 g, 0.836 mmol), H_2O (25 µL, 1.4 mmol), and acetonitrile (20 mL) were used. Time: 16 h, purification: silica gel plug (hexane/Et_2O, 1:1, v/v), yield: 0.236 g (0.663 mmol, 95%), white solid. IR (cm^{-1}, nujol mull) 2221 (C≡C). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 2H), 7.62 (dd, *J* 7.3, 0.9 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.35 (td, *J* 7.5, 1.1 Hz, 2H), 2.51 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1, 139.3, 130.2, 128.8, 124.5, 120.5, 78.1, 74.9, 74.7, 68.7, 0.7. HRMS(ESI): *m/z* calcd for $C_{17}H_9OINa$: 378.9590 $[M+Na]^+$; found: 378.9552.

5-Bromo-1,1-diphenylpenta-2,4-diyn-1-ol (**9**). According to the procedure for **3**, 1,1-diphenyl-5-(trimethylsilyl)penta-2,4-diyn-1-ol (**7**, 0.152 g, 0.500 mmol), $AgNO_3$ (0.026 g, 0.15 mmol), KF (0.029 g, 0.50 mmol), NBS (0.107 g, 0.601 mmol), H_2O (23 µL, 1.3 mmol), and acetonitrile (10 mL) were used. Time: 20 h, purification: silica gel (hexane/DCM, 1:1, v/v), yield: 0.114 g (0.366 mmol, 73%), beige viscous oil. IR (cm^{-1}, KBr) 3411 (O-H, broad), 2234 (C≡C), 2138 (C≡C), 1490, 1450, 697. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 4H), 7.37 – 7.32 (m, 4H), 7.31 – 7.27 (m, 2H), 2.77 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 128.6, 128.3, 126.2,

75.0, 72.4, 64.9, 43.7 (1C is missing). HRMS(ESI): *m/z* calcd for $C_{17}H_{11}BrONa$: 332.9885 $[M+Na]^+$; found: 332.9886.

9-(2,2-Diiodovinylidene)-9*H*-fluorene (10)

Procedure A: 9-(Iodoethynyl)-9*H*-fluoren-9-ol (**4**, 0.475 g, 1.43 mmol) was dissolved in 25 mL of THF and the solution was cooled to 0 °C. $BF_3{\cdot}Et_2O$ (0.21 mL, 1,70 mmol) was added and the mixture was stirred for 1 h. After this time solvent was removed under reduced pressure and product was purified by elution through short silica gel plug (hexane) yielding 0.120 g (0.271 mmol, 19%) of white solid.

Procedure B: 9-(Iodoethynyl)-9*H*-fluoren-9-ol (**4**, 0.232 g, 0.699 mmol) was dissolved in 10 mL of AcOH and cooled down to 0 °C. Next $HI_{(aq)}$ (0.74 mL, 57%) in 2 mL of H_2O was added dropwise. The mixture was stirred for 2 h at room temperature and the product precipitated as yellow solid. Crude product was filtered off and purified by elution through short silica gel plug (hexane) yielding 0.190 g (0.430 mmol, 62%) of white solid. IR (cm^{-1}, nujol mull) 1919 (C=C), 1926 (C=C). ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 – 7.66 (m, 2H), 7.58 – 7.54 (m, 2H), 7.38 – 7.31 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 204.3, 139.8, 135.0, 129.8, 127.6, 125.2, 120.6, 105.7, -46.4. Elemental analysis: calcd for $C_{15}H_8I_2$ (442.03): C 40.76, H 1.82. Found: C 40.79, H 1.64 %.

[2-Bromo-3-(dibromomethylene)-4,4-diphenylcyclobut-1-en-1-yl]diphenylmethanol (**11**) **and 2-(Dibromomethylene)-4-(diphenylmethylene)-3,3-diphenylcyclobutan-1-one** (**12**). 3-Bromo-1,1-diphenylprop-2-yn-1-ol (**5**, 0.330 g, 1.15 mmol) was dissolved in dry hexane (10 mL) and $BF_3{\cdot}Et_2O$ (0.170 mL, 1.38 mmol) was added in one portion. After 24 h at room temperature hexane was evaporated under reduce pressure and the residue was separated using column chromatography (silica gel, hexane/DCM 50→100%).

(**11**) (0.033 g, 0.052 mmol, yield 9%) was obtained as yellow solid. R_f = 0.50 (silicagel, hexane/DCM 50%). IR (cm^{-1}, KBr) 3592 (O-H, sharp), 1563, 1493, 1447, 846, 756, 697. ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.43 (m, 4H), 7.25 – 7.13 (m, 16H), 2.44 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 13C NMR (126 MHz, CDCl3) δ 165.1, 145.8, 142.9, 137.6, 129.4, 128.1, 127.9, 127.6, 127.6, 123.6, 116.4, 80.7, 78.2, 70.8. HRMS(ESI): *m/z* calcd for $C_{30}H_{21}Br_3ONa$: 658.9014 $[M+Na]^+$; found: 658.9046.

(**12**) (0.007 g, 0.013 mmol, yield 2%) was obtained as yellow solid. R_f = 0.36 (silicagel, hexane/DCM 50%). IR (cm^{-1}, KBr) 1725, 1568, 1095, 755, 700, 556. ^1H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.22 (m, 15H), 7.16 (t, *J* 7.8 Hz, 1H), 6.97 (t, *J* 7.8 Hz, 2H), 6.65 (d, *J* 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 183.5, 155.6, 150.7, 149.9, 140.4, 138.6, 137.9, 130.0, 129.6, 129.1, 128.5, 128.2, 128.1, 127.9, 127.3, 126.5, 94.6, 67.3. HRMS(ESI): *m/z* calcd for $C_{30}H_{21}Br_2O$: 556.9933 $[M+H]^+$; found: 556.9932.

(3,3-Dibromopropa-1,2-diene-1,1-diyl)dibenzene[26] (**13**). 3-Bromo-1,1-diphenylprop-2-yn-1-ol (**5**, 0.574 g, 2.00 mmol) was dissolved in diethyl ether (5 mL) and a mixture of $HBr_{(aq)}$ (48%, 5 mL) and water (5 ml) was added in one portion. Two phase clear solution was mixed vigorously over 2h. Product was extracted with diethyl ether and passed through 10 cm of silica gel with hexane to yield 0.189 g (26%) of white crystalline solid. IR (cm^{-1}, KBr) 1927, 1442, 770, 730, 691, 574. ^1H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.36 (m, 10H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.7, 133.7, 129.8, 129.5, 128.9, 118.8, 54.4.

1,1,3-Tribromo-2,2,8-triphenyl-1,2-dihydrocyclobuta[*b*]naphthalene (14). (3,3-Dibromopropa-1,2-diene-1,1-diyl)dibenzene (**13**, 0.020 g, 0.057 mmol), 3-bromo-1,1-diphenylprop-2-yn-1-ol (**5**, 0.016 g, 0.056 mmol) and dry hexane (2 mL) were sealed in a screw cap vial and stirred at 100 °C for 24 h. **14** was isolated by chromatography (silica gel, hexane/DCM 5→30%, R_f = 0.30 (silicagel, hexane/DCM 20%). Yield 0.014 g (40%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.42 (d, *J* 8.5 Hz, 1H), 7.82 (d, *J* 8.5 Hz, 1H), 7.70 – 7.63 (m, 3H), 7.59 – 7.51 (m, 4H), 7.50 – 7.44 (m, 4H), 7.41 – 7.34 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.0, 140.6, 139.0, 135.7, 135.1, 135.0, 133.7, 130.7, 130.5, 128.6, 128.4, 128.1, 128.1, 127.7 (2C), 127.3, 127.1, 116.2, 67.1, 29.9.

Acknowledgements

The authors thank the National Science Centre Poland (Grants UMO-2015/19/B/ST5/02917) and Foundation for Polish Science (START scholarship) for support of this research.

Supplementary Material

For full details, including copies of ^{1}H, ^{13}C and NMR spectra and X-ray crystallography details, see the Supporting Information. CCDC 1540598(**10**), 1540596(**11**), 1540595(**12**), 1540599(**13**) and 1540597 (**14**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

References

1. Krause, N.; Hashimi, A. S. K. *Modern Allene Chemistry* Wiley-VCH: Weinheim, 2004. https://doi.org/10.1002/9783527619573
2. Januszewski, J. A.; Tykwinski, R. R. *Chem. Soc. Rev.* **2014**, *43*, 3184-203. https://doi.org/10.1039/c4cs00022f
3. Martin, E. L.; Sharkey, W. H. *J. Am. Chem. Soc.* **1959**, *81*, 5256-5258. https://doi.org/10.1021/ja01528a056
4. Bach, A.; Lentz, D.; Luger, P.; Messershmidt, M.; Olesch, C.; Patzschke, M. *Angew. Chem. Int. Ed.* **2002**, *41*, 296-299. https://doi.org/10.1002/1521-3773(20020118)41:2<296::AID-ANIE296>3.0.CO;2-A
5. Hughes, R. P.; Laritchev, R. B.; Zakharov, L. N.; Rheingold, A. L. *J. Am. Chem. Soc.* **2004**, *126*, 2308-2309. https://doi.org/10.1021/ja031598o
6. Akkerman, F. A.; Lentz, D. *Angew. Chem. Int. Ed.* **2007**, *46*, 4902-4904. https://doi.org/10.1002/anie.200701081
7. Ehm, C.; Lentz, D. *Chem. Commun.* **2010**, *46*, 2399-2401. https://doi.org/10.1039/b922424f
8. Heinrich, B.; Roedig, A. *Angew. Chem. Int. Ed.* **1968**, *7*, 375-376. https://doi.org/10.1002/anie.196803751
9. Liu, P.-H.; Li, L.; Webb, J. A.; Zhang, Y.; Goroff, N. S. *Org. Lett.* **2004**, *6*, 2081-2083. https://doi.org/10.1021/ol049734x
10. Webb, J. A.; Liu, P.-H.; Malkina, O. L.; Goroff, N. S. *Angew. Chem. Int. Ed.* **2002**, *41*, 3011-3014. https://doi.org/10.1002/1521-3773(20020816)41:16<3011::AID-ANIE3011>3.0.CO;2-0
11. Gulia, N.; Pigulski, B.; Charewicz, M.; Szafert, S. *Chem. Eur. J.* **2014**, *20*, 2746-2749. https://doi.org/10.1002/chem.201303680
12. Gulia, N.; Pigulski, B.; Szafert, S. *Organometallics* **2015**, *34*, 673-682. https://doi.org/10.1021/om501105w
13. Tomilin, D. N.; Pigulski, B.; Gulia, N.; Arendt, A.; Sobenina, L. N.; Mikhaleva, A. I.; Szafert, S.; Trofimov, B. A. *RSC Adv.* **2015**, *5*, 73241-73248. https://doi.org/10.1039/C5RA08820H

14. Pigulski, B.; Gulia, N.; Szafert, S. *Chem. Eur. J.* **2015**, *21*, 17769-17778. https://doi.org/10.1002/chem.201502737
15. Pigulski, B.; Arendt, A.; Tomilin, D. N.; Sobenina, L. N.; Trofimov, B. A.; Szafert, S. *J. Org. Chem.* **2016**, *81*, 9188-9198. https://doi.org/10.1021/acs.joc.6b01732
16. Pigulski, B.; Męcik, P.; Cichos, J.; Szafert, S. *J. Org. Chem.* **2017**, *82*, 1487-1498. https://doi.org/10.1021/acs.joc.6b02685
17. Alcaide, B.; Almendros, P.; Aragoncillo, C. *Chem. Soc. Rev.* **2010**, *39*, 783-816. https://doi.org/10.1039/B913749A
18. López, F.; Mascarenas, J. *Chem. Eur. J.* **2011**, *17*, 418-428. https://doi.org/10.1002/chem.201002366
19. Skraba, S. L.; Johnson, R. P. *J. Org. Chem.* **2012**, *77*, 11096-11100. https://doi.org/10.1021/jo302176k
20. Harrington, L. E.; Britten, J. F.; McGlinchey, M. J. *Org. Lett.* **2004**, *6*, 787-790. https://doi.org/10.1021/ol049967o
21. Banide, E. V.; Molloy, B. C.; Ortin, Y.; Muller-Bunz, H.; McGlinchey, M. J. *Eur. J. Org. Chem.* **2007**, 2611-2622. https://doi.org/10.1002/ejoc.200600905
22. Toda, F. *Eur. J. Org. Chem.* **2000**, 1377-1386. https://doi.org/10.1002/(SICI)1099-0690(200004)2000:8<1377::AID-EJOC1377>3.0.CO;2-
23. Bartik, T.; Weng, W.; Ramsden, J. A.; Szafert, S.; Faloon, S. B.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1998**, *120*, 11071-11081. https://doi.org/10.1021/ja981927q
24. Szafert, S.; Haquette, P.; Faloon, S. B.; Gladysz, J. A. *J. Organomet. Chem.* **2000**, *604*, 52-58. https://doi.org/10.1016/S0022-328X(00)00201-1
25. Januszewski, J. A.; Hampel, F.; Neiss, C.; Gorling, A.; Tykwinski, R. R. *Angew. Chem. Int. Ed.* **2014**, *53*, 3743-3747. https://doi.org/10.1002/anie.201309355
26. Kollmar, H.; Fisher, H. *Tetrahedron Lett.* **1968**, *9*, 4291-4294. https://doi.org/10.1016/S0040-4039(00)76410-0
27. Siebert, M. R.; Osbourn, J. M.; Brummind, K. M.; Tantillo, D. J. *J. Am. Chem. Soc.* **2010**, *132*, 11952-11966. https://doi.org/10.1021/ja102848z
28. Feng, A.-H.; Chen, J.-Y.; Yang, L.-M.; Lee, G.-H.; Wang, Y.; Luh T.-Y. *J. Org. Chem.* **2001**, 66, 7922-7924. https://doi.org/10.1021/jo015882e
29. Kai, F.; Seki, S. *Tetrahedron* **1968**, *24*, 415-420. https://doi.org/10.1016/0040-4020(68)89039-8
30. Rege, P. D.; Malkina, O. L.; Goroff, N. S. *J. Am. Chem .Soc.* **2002**, *124*, 370-371. https://doi.org/10.1021/ja016290g
31. Kaupp, G.; Boy, J. *Angew. Chem. Int. Ed.* **1997**, *36*, 48-49. https://doi.org/10.1002/anie.199700481
32. *CrysAlisPRO*, Oxford Diffraction /Agilent Technologies UK Ltd: Yarnton, England.
33. Sheldrick, G. M. *Acta crystallographica. Section A, Foundations of crystallography* **2008**, *64*, 112-122. https://doi.org/10.1107/S0108767307043930
34. Bovonsombat, P.; Mc Nelis, E. *Tetrahedron. Lett.* **1994**, *35*, 6431-6432.

https://doi.org/10.1016/S0040-4039(00)78238-4
35. Chodkiewicz, W. *Ann. Chim. (Paris)* **1957**, *2*, 819-869.
36. Holmes, A. B.; Jennings-White, C. L. D.; Schulthess, A. H. *J. Chem. Soc., Chem. Commun.* **1979**, 840-842. https://doi.org/10.1039/c39790000840

