View Article Online
View Journal

Dalton Transactions

An international journal of inorganic chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: R. Lorenz, D. Reger, R. Weller, N. Jux and N. Burzlaff, *Dalton Trans.*, 2020, DOI: 10.1039/D0DT02729D.

ROYAL SOCIETY OF CHEMISTRY

rsc.li/dalton

View Article Online
DOI: 10.1039/D0DT02729D

ARTICLE

Hexa-*peri*-hexabenzocoronene decorated with an allenylidene ruthenium complex – almost a flyswatter‡

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

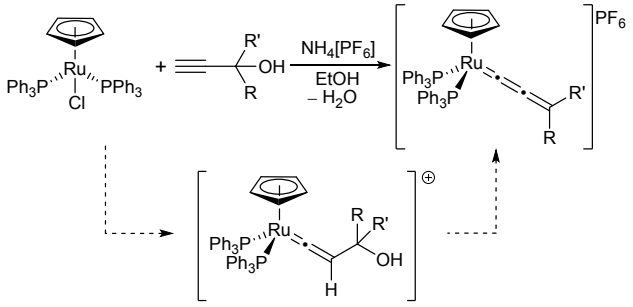
Rebecca Lorenz,[a] David Reger,[b] Ruth Weller,[ac] Norbert Jux *[b] and Nicolai Burzlaff*[a]

Carbon-rich ruthenium allenylidene complexes bearing either a hexaarylbenzene (HAB) or a hexa-*peri*-hexabenzocoronene (HBC) substituent were synthesised. This was achieved via the corresponding propargyl alcohols with HAB and HBC substituents, which were accessible via 3 or 4 step reaction cascades. Reaction of the propargyl alcohols HC≡C(OH)Ph(HAB) and HC≡C(OH)Ph(HBC) with [RuCl(η^5-C_5H_5)(PPh_3)$_2$] yielded the complexes [Ru(η^5-C_5H_5)(=C=C=C(HAB)(Ph))(PPh_3)$_2$]PF_6 and [Ru(η^5-C_5H_5)(=C=C=C(HBC)(Ph))(PPh_3)$_2$]PF_6. The latter of which shows interesting π-π-stacking behaviour in the solid state as well as aggregation in solution.

Hexa-*peri*-hexabenzocoronenes (HBCs) are all benzenoid polycyclic aromatic hydrocarbons (PAHs) with remarkable properties, such as an impressive chemical and thermal stability.[1,2] The unsubstituted HBC aggregates in a columnar fashion, which makes them promising candidates for the application as charge transport layers in various electronic devices.[2,3] Since the first synthesis of the parent HBC by Clar and co-workers back in 1958, sophisticated synthetic procedures have been developed to obtain a large variety of HBCs.[1,4] Hexa(alkyl)-HBCs undergo facile self-assembly into columnar mesophases with high charge carrier mobility.[5] Their behaviour as semiconducting organic materials makes these molecules suitable candidates for the application in organic field-effect transistors (OFETs) and as donor materials in organic photovoltaics (OPVs).[6]

Inspired by this, several transition metal complex decorated HBCs have been synthesised and the interactions between the π-systems and the metal centres have been studied during the last decade. Among the first examples was a chromium tricarbonyl HBC half-sandwich complex by Herwig *et al.*[7] In analogy to this complex, several half-sandwich HBC rhodium complexes have been reported.[8] DFT calculations for chromium and ruthenium sandwich complexes have been conducted, however to the best of our knowledge no HBC full-sandwich complex was reported until now.[9] Moreover, it was possible to attach ferrocenyl units via an alkynyl bridge to a HBC.[10] It was also shown that new triarylphosphine ligands can be designed by using HBC units.[11] A different approach showed that HBCs can be modified with *N*,*N*-chelating motifs that can coordinate ruthenium, palladium and rhenium fragments.[12] Furthermore, σ-bonded platinum complexes have been synthesised by El Hamaoui *et al.*[13] Acetylene units can also serve as a connection point between metal fragments and HBC. Several platinum and gold complexes were synthesised following this concept.[14] Furthermore, acetylene complexes derived from dicobalt octacarbonyl have been reported.[15]

In recent years, various research groups focused on the synthesis and investigation of ruthenium allenylidene complexes.[17,18,19] Our group reported on a panoply of these complexes [Ru]=C=C=CR_2, either with the charge neutral [Ru(bdmpza)Cl(PPh_3)] fragment (bdmpza = bis(3,5-dimethyl-pyrazol-1-yl)acetate) or the cationic [Ru(η^5-C_5H_5)(PPh_3)$_2$]$^+$ fragment.[20–23] The synthesis of these ruthenium allenylidene complexes follows a synthetic concept published by Selegue (**Scheme 1**).[16]



Scheme 1 Synthesis of allenylidene in analogy to the procedure developed by Selegue.[16] R = Ph, R' = HBC, HAB.

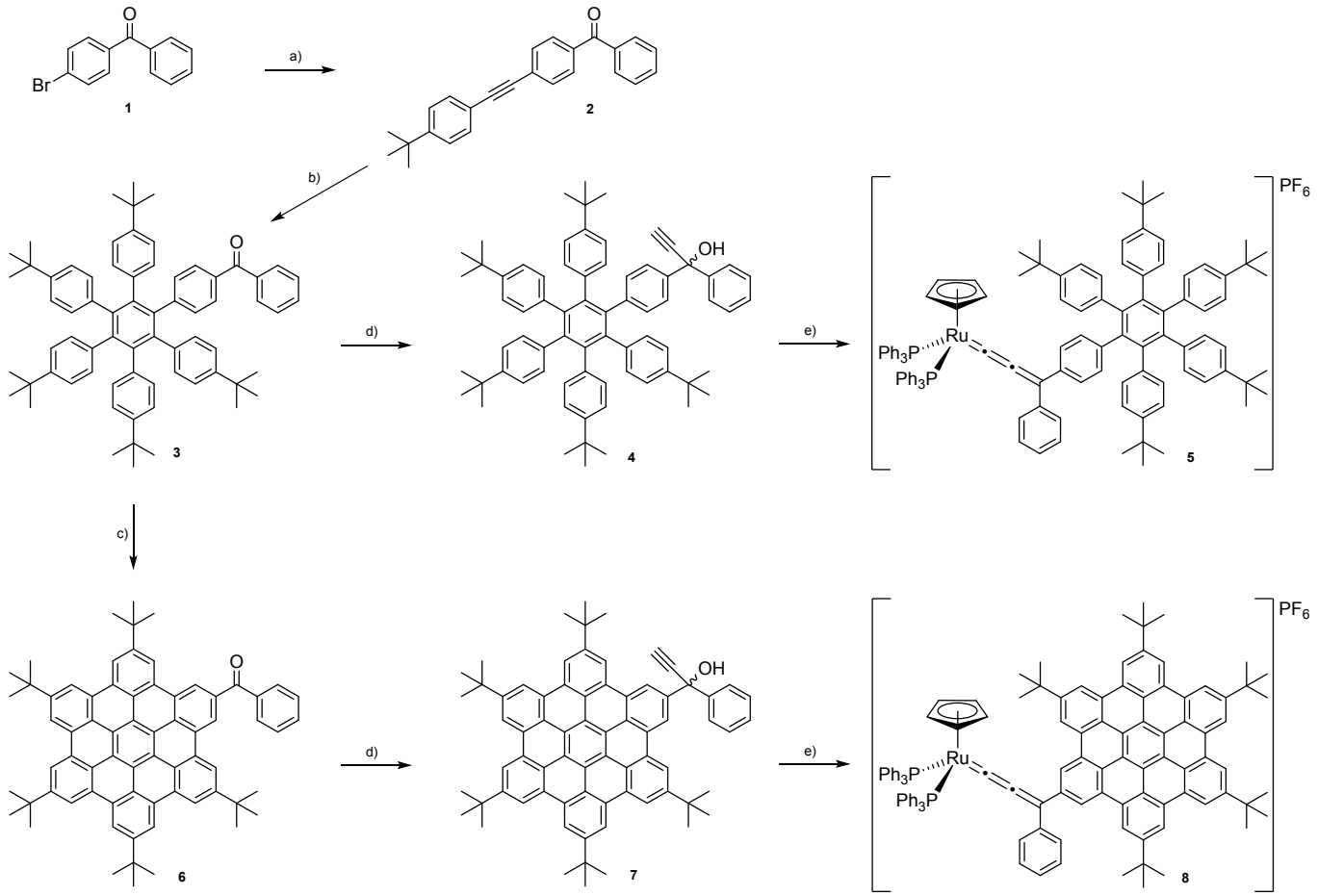
The focus in these studies lay on allenylidene complexes with carbon-rich and/or polycyclic aromatic substituents R and was mainly driven by interesting possible applications in molecular electronics[24] and novel opto-electronic materials[19]. Also other groups showed that the combination of allenylidene complexes and carbon-rich fragments, for instance, the conjunction with fullerenes, leads to new molecules with

[a] Department Chemistry and Pharmacy, Interdisciplinary Center of Molecular Materials (ICMM), University of Erlangen-Nuernberg, Egerlandstr. 1, 91058 Erlangen, Germany.
[b] Department Chemistry and Pharmacy, University of Erlangen-Nuernberg, Nicolaus-Fiebiger-Str. 10, 91058 Erlangen, Germany.
[c] Fb. 15 – Chemie, Philipps-University Marburg, Hans-Meerwein-Straße 4, 35032 Marburg, Germany.

† Electronic supplementary information (ESI) available: Experimental details, X-ray crystallographic data for 6 and NMR spectra for all new compounds. See DOI: 10.1039/x0xx00000x

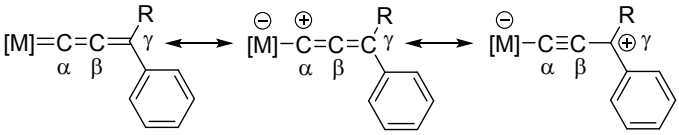
diverse properties.[25] Due to possible synergistic effects between these properties and those of HBC, we were now interested in the synthesis of allenylidene complexes with a HBC as substituent R (**Scheme 1**).

Thus, herein we report on the synthesis and characterisation of two novel carbon-rich ruthenium allenylidene complexes bearing either a HAB or a HBC moiety. To prepare these compounds the reaction procedure introduced by SELEGUE was adapted (**Scheme 1**). As this reaction route is a wet-chemical approach a *t*-butylated HBC was used to ensure sufficient solubility.[26] In order to demonstrate the influence of the conjugated π-system of the HBC the corresponding HAB complex was synthesised as well. The required propargyl alcohols were synthesised following a 3 or 4 step procedure, depicted in **Scheme 2**. The reaction cascade starts from commercially available 4-bromobenzophenone **1**. The precursor was converted into the acetylene derivative **2** via a SONOGASHIRA coupling followed by a DIELS-ALDER reaction with tetrakis-(4-tert-butylphenyl)cyclopentadienone to obtain HAB-benzophenone derivative **3**. Tetrakis-(4-tert-butylphenyl)cyclopentadienone was synthesised according to literature procedures.[27–29] Branching off at that point the propargyl alcohol of HAB **4** was obtained by nucleophilic addition of a trimethylsilylacetylene anion followed by an *in situ* desilylation reaction. By applying the procedure reported by SELEGUE, the desired deep purple allenylidene complex [Ru(η^5-C_5H_5)(=C=C=C(HAB)(Ph))(PPh_3)$_2$]PF_6 (**5**) was obtained. By oxidative closure of **3** under SCHOLL conditions, HBC **6** was prepared. The propargyl alcohol **7** was synthesised in analogy to compound **4**. The desired dark green-blue allenylidene complex [Ru(η^5-C_5H_5)(=C=C=C(HBC)(Ph))(PPh_3)$_2$]PF_6 (**8**) was obtained in analogy to complex **5**. The yields of the allenylidene complexes **5** and **8** are rather low due to purification of the cationic complexes by column chromatography, which is a lossy procedure. The ^{13}C NMR spectra of both allenylidene complexes **5** and **8** show the characteristic signal of Cα in the downfield region at 290.5 and 290.7 ppm, respectively. Due to the ^2J coupling with the phosphorous nuclei, both signals split into triplets with coupling constants of 18 Hz. Both values are in good agreement with the already reported ones.[23] Interestingly, the nature of the PAH residue on Cγ does not seem to have a large.



Scheme 2 Synthesis of complexes **5** and **8**: a) 4-*tert*-butylphenylacetylene (1.05 eq.), $Pd(PPh_3)_2Cl_2$ (2 mol%), CuI (1 mol%), THF/DIPA 1:1; b) tetrakis-(4-*tert*-butylphenyl)cyclopentadienone (1.00 eq.), toluene; c) $FeCl_3$ (16 eq.) in $MeNO_2$ (300 mg/mL), CH_2Cl_2; d) trimethylsilylacetylene (10 eq), *n*-BuLi (10 eq) in THF; e) [Ru(η^5-C_5H_5)Cl(PPh_3)$_2$] (1.00 eq), $NH_4[PF_6]$ (1.00 eq), MeOH

influence on the chemical shift of Cα. Since this chemical shift directly correlates with the contribution of the allenylidene versus the alkynyl resonance structure (**Scheme 3**), it can be concluded that the nature of the cumulene chain is similar in both complexes.



Scheme 3 Limiting resonance structures and conventional designation in allenylidene complexes.[17,18d,19] Right: allenylidene; left: alkynyl form. Further delocalisation over the aromatic and polyaromatic residues at Cγ is possible. R = PAH.

The bond lengths obtained from crystal structure analysis of compound **8** show the characteristic elongation of the Ru–Cα and Cβ–Cγ bond due to a significant single bond contribution (**Fig. 1**).‡ This results in a shortened Cα-Cβ bonds due to the triple bond character of this bond. Comparison with literature known allenylidene complexes substantiates the pronounced contribution of the alkynyl structure. The ideal angle of the cumulene chain (Ru-Cα-Cβ and Cα-Cβ-Cγ) is 180°. However, the measured angles are 171.2(2) and 169.3(3)°, respectively. This deviation might be due to the steric hindrance provided by the HBC moiety and the flexibility of both groups attached to Cγ. Similar deviations were observed for large rigid organic substituents, before.[20,22,23]

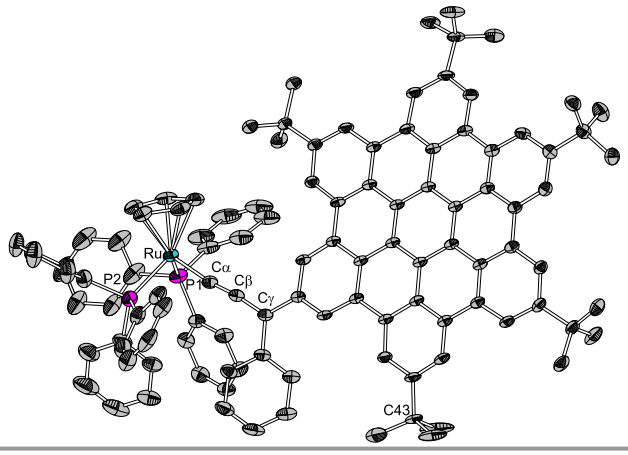


Fig. 1 Molecular structure of **8**. Thermal ellipsoids are shown at a 50% probability level. Hydrogen atoms, solvent molecules and hexafluorophosphate anion are omitted for clarity. Only majority positions are shown for clarity. Selected bond lengths (Å) and angles (°): Ru-P1 2.3462(8), Ru-P2 2.3162(8), CCp-Ru 1.8975(1), Ru-Cα 1.897(3), Cα-Cβ 1.255(4), Cβ-Cγ 1.357(4), P1-Ru-P2 97.60(3), Ru-Cα-Cβ 171.2(2), Cα-Cβ-Cγ 169.3(3).

The investigation of the packing motif reveals the formation of a dimer with interplanar distances of 3.592 Å (**Fig. 2**). The ruthenium units are located on opposing sites in the dimer. Furthermore, the *t*-butyl groups point to the periphery of the dimer which leads to an out-of-plane bending of the HBC moiety. The most significant deviation from the planar arrangement amounts to 0.788 Å. This deviation is measured from the central six-membered ring plane to the central atom of the *t*-butyl group (C43). A similar behaviour has already been observed for the simple *t*-butyl substituted HBC. The parent HBC molecule shows a slightly smaller interplanar distance of 3.44 Å. Between pairs of dimers solvent molecules are intercalated.[7] Within one dimer the arrangement is similar to the one adopted by two layers of graphene (interplanar distance: 3.35 Å),[30] where one carbon atom is projected to the middle of the six-membered ring of the neighbouring layer (**Fig. 2**).[31]

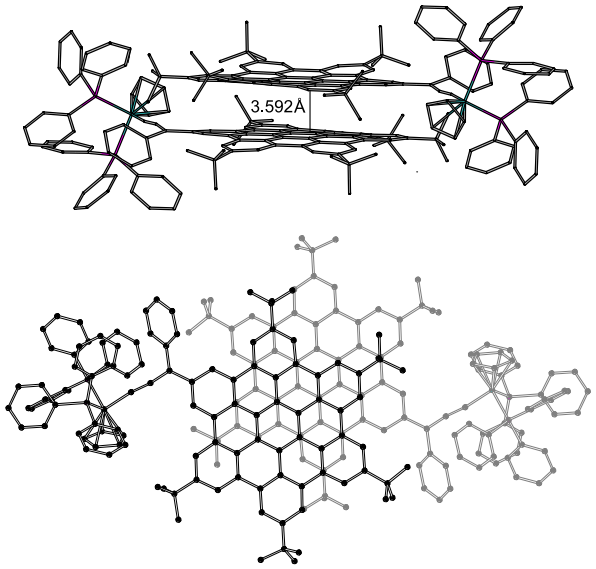


Fig. 2 Packing motif of **8**. Dimer formation due to π-π-stacking. Interplanar distance is 3.592 Å.

The UV/Vis absorption spectrum of [Ru(η^5-C_5H_5)(=C=C=C(HAB)(Ph))(PPh_3)$_2$]PF_6 (**5**) shows an absorption maximum in the near-UV region at 252 nm (63700 L mol^{-1} cm^{-1}), which is characteristic for such non-planar structures. Additionally, a small absorption band is located at 340 nm (9200 L mol^{-1} cm^{-1}) and another maximum is observed at 532 nm (30600 L mol^{-1} cm^{-1}) (**Fig. 3**). The latter one is usually assigned to a metal perturbed π-π^*transition of the allenylidene unit.[17] The shift of this transition is similar to the one of a simple diphenyl allenylidene complex bearing a trispyrazolylborate (Tp) ligand [Ru(=C=C=C(Ph_2)(PPh_3)$_2$(Tp)]SbF_6, which is detected at 527 nm.[32]

In contrast, [Ru(η^5-C_5H_5)(=C=C=C(HBC)(Ph))(PPh_3)$_2$]PF_6 (**8**) shows an absorption throughout the visible spectrum. The highest extinction coefficient (33300 L mol^{-1} cm^{-1}) is observed for the absorption maximum at 359 nm.

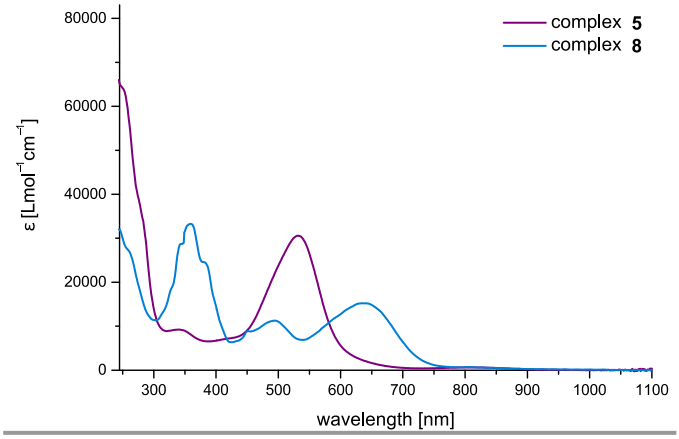


Fig. 3 UV/Vis absorption spectra of **5** and **8** in CH_2Cl_2 (245-1100 nm).

View Article Online
DOI: 10.1039/D0DT02730D

The characteristic maxima of the HBC unit are located between 343 and 382 nm.[2] Interestingly, two additional absorption bands are observed at 495 and 636 nm (**Fig. 3**). These maxima correspond to metal-perturbed π-π* transitions of the allenylidene moiety. In comparison with the simple diphenyl and the HAB decorated allenylidene complex **5**, this maximum experiences a significant bathochromic shift.

In order to investigate the aggregation behaviour in solution, UV/Vis titration experiments with pyrene were conducted. The resulting Job's plots show a maximum at χ_R = 0.5, which indicates the formation of a 1:1 aggregate, for complex **5** (**Fig. 4**). The plot of complex **8** reveals a different shape. Two maxima at χ_R = 0.4 and 0.65 (**Fig. 4**) can be observed. These values indicate the formation of 1:2 and 2:1 aggregates in solution. This leads to the assumption that in solution either aggregates of two HBC moieties are formed compared to those in the solid state, between those dimers an additional pyrene molecule can be incorporated, or oligomeric chains are formed with alternating HBC dimers and pyrene moieties.

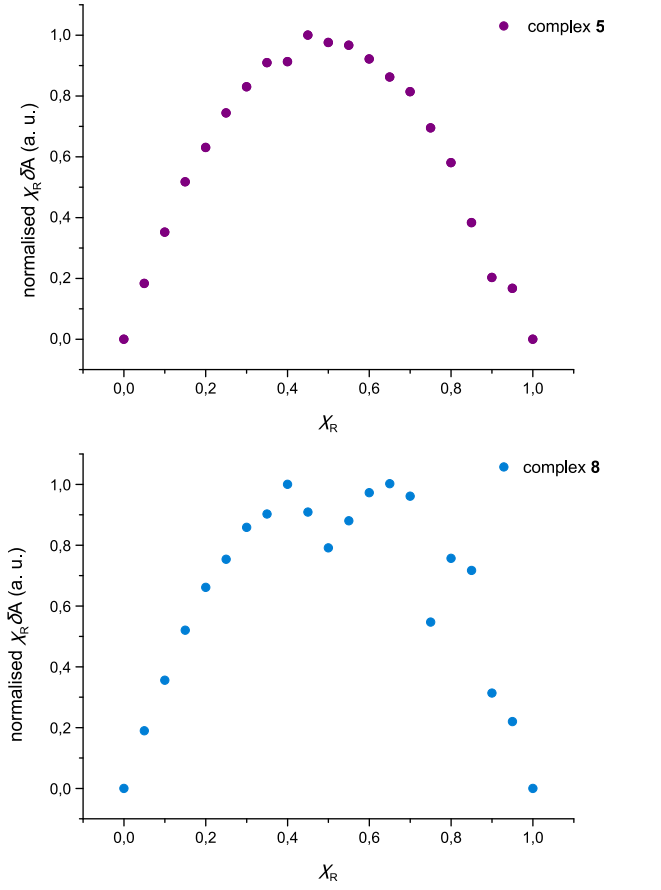


Fig. 4 Job's plots of the aggregation of **5** and **8** with pyrene in CH_2Cl_2. δA was calculated from variation in absorption maximum at 532 nm and 636 nm, respectively.

To investigate and compare the electrochemical properties of complex **5** and **8** cyclic voltammetry was conducted. For complex **5** one oxidation and two reduction processes could be observed (**Fig. 5, Fig. S29-31**). The oxidation event occurs at 0.896 V and may correspond to the Ru(II)/Ru(III) oxidation.[22,23,32,33] The two reduction processes are observed at −0.863 and −1.94 V, respectively and exhibit quasi-reversible character. They might correspond to two one electron reductions of the allenylidene unit or to the reduction of the organic ligand.

The measurements of complex **8** revealed one reduction and one oxidation process (**Fig. 5**, **Fig. S32**-**S34**). The oxidation event shows an irreversible process at 1.02 V. Multiple scans of the high potential region led to the disappearance of the oxidation sweep. A similar behaviour has already been observed for thienyl-substituted ruthenium allenylidene complexes.[34] In this case, the oxidation was assigned to happen at the organic ligand and not as often reported at the metal centre.[22,23,32,33] Due to the analogous behaviour, a ligand-centred oxidation is assumed for HBC-based ruthenium allenylidene complex **8**. The reduction wave at −1.26 V exhibits a quasi-reversible character. By comparing this value to other ruthenium allenylidene complexes, it can be readily assigned to the reduction of the allenylidene moiety.[22,23]

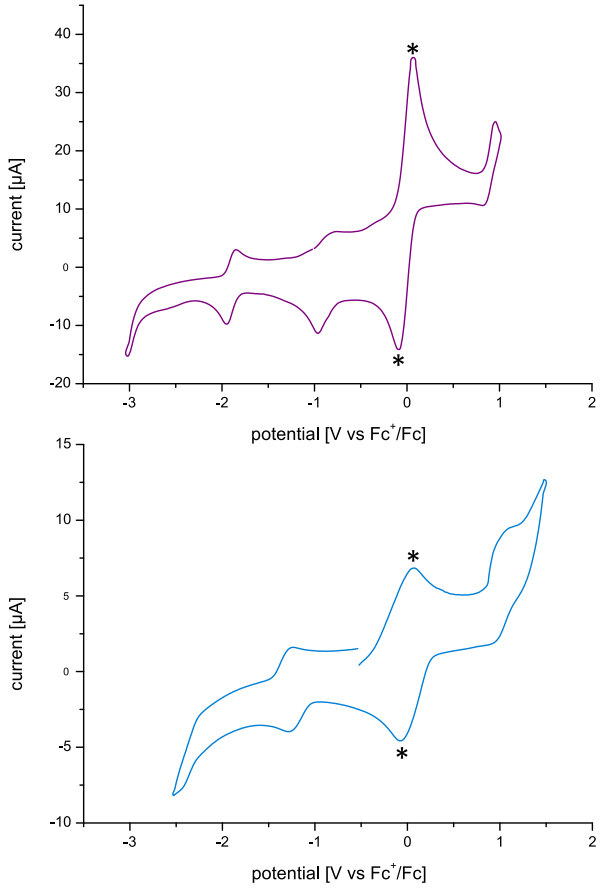


Fig. 5 Cyclic voltammogram of **5** (top) and **8** (bottom) (0.001 M) on a Au electrode (0.1 V s^{-1}, 0.2 M *n*-Bu_4NPF_6/CH_2Cl_2, referenced to internal Fc^+/Fc). * marks the redox sweep of the Fc^+/Fc reference redox couple.

In summary, we synthesised two novel carbon-rich ruthenium complexes in a 5 and 6 step reaction cascade. The HBC complex **8** is, to the best of our knowledge, an allenylidene complex with one of the most extended conjugated systems. The planarisation of the π-system seems to have a major influence on the aggregation properties. Furthermore,

absorption and electrochemical properties were examined and discussed. By fully conjugating the polycyclic aromatic system, it is possible to vary and broaden the absorption properties significantly.

This work was generously supported by 'Solar Technologies go Hybrid', an initiative of the Bavarian State Ministry for Science, Research and Art. Funding of a Bruker AVANCE III HD 400 MHz spectrometer and a Bruker AVANCE III HD 600 MHz spectrometer as well as a Super Nova A S2 (Dual) diffractometer with Atlas S2 CCD detector and Nova (Cu) and Mova (Mo) X-ray sources by the German Research Council (DFG) is gratefully acknowledged. Partly funded by the Deutsche Forschungsgemeinschaft (DFG) – Projektnummer 182849149 – SFB 953. D.R. and R.L. thank the Graduate School Molecular Science (GSMS) for financial support.

Experimental details

Materials and methods

All air-sensitive compounds were prepared under a dry N_2 or Ar atmosphere using conventional SCHLENK techniques. The solvents were purchased from Sigma-Aldrich, Roth, Fluka or Fisher Scientific (*p.a.* grade, < 50 ppm H_2O). Solvents were degassed prior to use and stored under N_2 or Ar atmosphere over molecular sieves. Tetrakis-(4-*tert*-butylphenyl)cyclo-pentadienone was synthesised following known literature procedures.[27–29] All commercially available substances were purchased from Sigma-Aldrich or abcr and used without further purification. Thin layer chromatography (TLC) was performed on Merck or Macherey-Nagel silica 60 F254, detected by UV-light (254 nm, 366 nm). ^{1}H NMR, ^{13}C{^{1}H} NMR, APT ^{13}C{^{1}H} NMR and ^{31}P{^{1}H} NMR spectra were measured with a *JEOL JNM EX* 400 MHz, *JEOL JNM GX* 400 MHz, *Bruker Avance* 400 MHz, *Bruker AVANCE III HD 400 MHz* and *Bruker AVANCE III HD 600 MHz* instrument. The δ values are given in ppm relative to tetramethylsilane and were referenced by the solvent peaks of the deuterated solvent. For ^{31}P{^{1}H} NMR spectra H_3PO_4 was used as an internal standard. The resonance multiplicities are indicated as "s" (singlet), "d" (doublet), "t" (triplet), "q" (quartet), "sept" (septet) and "m" (multiplet). Signals referred to as bs (broad singlet) are not clearly resolved or significantly broadened. Para-substituted phenyl rings with an AA'BB' spin system are termed as multiplets. IR spectra were recorded with a *Bruker Alpha* FT-IR spectrometer equipped with Alpha's Platinum ATR single reflection diamond ATR module. IR spectra in solution were measured in CaF_2 cuvettes (0.2 mm) with a *Jasco* FT-IR 4100 or a *Shimadzu* IRTracer-100. LDI/MALDI-ToF mass spectrometry was performed on a *Shimazu AXIMA Confidence* (nitrogen laser, 50 Hz, 337 nm). In case of MALDI, the following matrix were used: 2,5-dihydroxybenzoic acid (DHB), sinapic acid (SIN) or trans-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB). High resolution mass spectrometry was performed on an Electrospray-ionization mass spectrometry ESI-ToF mass spectrometer *Bruker maXis 4G* UHR MS/MS spectrometer or a *Bruker* micrOToF II focus ToF MS spectrometer. ESI MS spectra were recorded on an UHR time-of-flight (ToF) *Bruker Daltonik* maXis plus 5G, an ESI-quadrupole time-of-flight (q-ToF) MS capable of resolution of at least 60.000 FWHM. The flow rates were 180 µL/h. The machine was calibrated prior to each experiment via direct infusion of the Agilent ESI-ToF low concentration tuning mixture, which provided a m/z range of the singly charged peaks up to 2700 Da. Peaks were identified using simulated isotopic patterns create by Bruker Data Analysis software. Cyclic voltammetry experiments were carried out using a *Methrom Autolab PGSTAT 100.* A three-electrode setup was used, using a gold disk working electrode, a platinum wire counter electrode, and a silver wire as a pseudo-reference electrode.

Synthetic procedures

4-(4-*tert*-butylphenylacetylene)benzophenone (2)

A round-bottom pressure-flask (100 mL) equipped with a magnetic stirring bar was charged with 4-bromobenzophenone **1** (2.00 g, 7.66 mmol), $[Pd(PPh_3)_2Cl_2]$ (0.110 g, 0.150 mmol), CuI (15.2 mg, 0.0800 mmol), THF (25 mL) and diisopropylamine (25 mL). The mixture was degassed by N_2 bubbling for 10 min. 4-*tert*-butylphenylacetylene (1.27 g, 1.45 mL, 8.04 mmol) was added and the flask was closed. The reaction mixture was stirred for 18.5 h at 100 °C. After completion of the reaction all solvents were removed under reduced pressure and the remaining solids were purified by column chromatography (silica, hexanes/CH_2Cl_2 1:2 v/v). All fractions containing the product were collected, the solvents were evaporated and the remaining brownish solid was recrystallized from hot *n*-pentane (30 mL).The product was dried under vacuum and was obtained as a white solid with a yield of 78 % (1.99 g, 5.88 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz, rt.): δ [ppm] = 7.79–7.77 (m, 4H), 7.62–7.56 (m, 3H), 7.50–7.46 (m, 4H), 7.39–7.37 (m, 2H), 1.32 (s, 9H).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz, rt.): δ [ppm] = 195.9, 152.2, 137.5, 136.6, 132.5, 131.5, 131.4, 130.1, 130.0, 128.3, 127.9, 125.5, 119.7, 92.8, 88.1, 34.9, 31.2.

HRMS (APPI, CH_2Cl_2): *m/z* = 339.1754 $[M+H]^+$. Calculated: 339.1743.

HAB-benzophenone derivative 3

A round-bottom pressure-flask (250 mL) equipped with a magnetic stirring bar was charged with 4-(4-*tert*-butylphenylacetylene)benzophenone **2** (1.00 g, 2.95 mmol), tetrakis-(4-*tert*-butylphenyl)cyclo-pentadienone (1.80 g, 2.95 mmol) and toluene (15 mL). The flask was purged with N_2 and was closed. The mixture was stirred for 60 h at 220 °C. After completion of the reaction MeOH (50 mL) was added and a white solid precipitated. The white solid was filtered off, washed with an excess of MeOH and dried under vacuum. The product was obtained in a yield of 71 % (1.90 g, 2.07 mmol).

^{1}H NMR ($CDCl_3$, 400 MHz, rt.): δ [ppm] = 7.53–7.51 (m, 2H), 7.50–7.46 (m, 1H), 7.36–7.32 (m, 2H), 7.29–7.27 (m, 2H), 6.98–

View Article Online DOI: 10.1039/D0DT02729D

6.96 (m, 2H), 6.85–6.83 (m, 4H), 6.82–6.79 (m, 6H), 6.71–6.64 (m, 10H), 1.12 (s, 18H), 1.08 (s, 27H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, rt.): δ [ppm] = 196.9, 147.9, 147.54, 147.51, 146.2, 141.0, 140.7, 139.9, 138.8, 138.0, 137.7, 137.6, 137.4, 133.8, 132.0, 131.5, 131.1, 131.0, 129.8, 128.5, 128.0, 123.4, 123.11, 123.07, 34.1, 34.0, 31.21, 31.16.

MS (MALDI-ToF, dhb): m/z = 919 $[M]^+$, 942 $[M+Na]^+$, 958 $[M+K]^+$.

HRMS (APPI, toluene): *m/z* = 918.57286 $[M]^+$. Calculated: 918.57342.

HAB-Phenylpropargyl alcohol 4

TMS-acetylene (0.765 mL, 5.38 mmol) was dissolved in THF (5.0 mL) and cooled to −60 °C. *n*-BuLi (2.15 mL, 2.5 M in *n*-hexane, 5.38 mmol) was added and the solution was allowed to stir for 30 minutes. This mixture was added dropwise to a solution of HAB-benzophenone derivative **3** (495 mg, 0.538 mmol) in THF (100 mL). The colourless solution was allowed to warm to room temperature and stirred for one day. Afterwards it was hydrolysed with water (6.0 mL) and filtered. The solvent was removed, the white solid was purified by column chromatography (silica, $CHCl_3$/*n*-hexane, 2:1. v/v) (Rf = 0.37). The white solid was dried under vacuum. The product was isolated in a yield of 86 % (437 mg, 462 µmol).

^1H NMR ($CDCl_3$, 400 MHz, rt.): δ [ppm] = 7.34 (dd, $^3J_{H,H}$ = 1.7, 8.0 Hz, 2H, *o*-$C_{Ar}H$), 7.26–7.24 (m, 3H, *m*/*p*-PhH), 7.10 (d, $^3J_{H,H}$ = 8.4 Hz, 2H, *o*-PhH), 6.84–6.80 (m, 12H, $C_{Ar}H$), 6.71–6.66 (m, 10 H, *m*-$C_{Ar}H$), 2.72 (s, 1H, C≡CH), 2.58 (bs, 1H, OH), 1.12 (s, 18H, $C(CH_3)_3$), 1.11 (s, 27H, 3×$C(CH_3)_3$).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 151 MHz, rt.): δ [ppm] = 147.8 (C_{Ar}), 147.6 (C_{Ar}), 147.6 (C_{Ar}), 144.8 (C_{Ar}), 141.3 (C_{Ar}), 140.8 (C_{Ar}), 140.7 (C_{Ar}), 140.7 (C_{Ar}), 140.3 (C_{Ar}), 139.6 (C_{Ar}), 138.0 (C_{Ar}), 138.0 (C_{Ar}), 137.9 ($C_{Ar}H$), 131.6 ($C_{Ar}H$), 131.3 ($C_{Ar}H$), 131.2 (2×$C_{Ar}H$), 128.2 ($C_{Ar}H$), 127.7 (C_{Ar}), 126.2 ($C_{Ar}H$), 124.5 ($C_{Ar}H$), 123.3 ($C_{Ar}H$), 123.2 ($C_{Ar}H$), 123.2 ($C_{Ar}H$), 86.6 (C≡CH), 75.2 (C≡CH), 74.2 (COH), 34.2 ($C(CH_3)_3$), 34.2 ($C(CH_3)_3$), 31.4 ($C(CH_3)_3$), 31.3 ($C(CH_3)_3$).

HRMS (ESI/+MS/MeOH): *m/z* (%) = 927.5880 (100) $[M-OH]^+$, 957.5804 (85) $[M+Na]^+$, 983.5540 (50) $[M+K]^+$. Calculated: 927.5863, 967.5788, 983.5528.

EA: $C_{71}H_{76}O$ (945.39 $gmol^{-1}$) [%]: calcd: C 90.20, H 8.10; found: C 90.11, H 8.08.

IR: ν [cm^{-1}] = 3548 (ν O–H, w)3307 (ν C≡C–H, w), 3035 (ν C_{Ar}–H, w), 2960 (ν C_{alkyl}–H, s), 2901 (ν C_{alkyl}–H, m), 2864 (ν C_{alkyl}–H, m), 1460 (C_{alkyl}–H, m), 1393 (δ C_{alkyl}–H/ δ O–H, m), 1360(δ C_{alkyl}–H/ δ O–H, m), 1018 ($\delta_{out\ of\ plane}$ C_{Ar}–H, s), 832 ($\delta_{out\ of\ plane}$ C_{Ar}–H, s), 761 ($\delta_{out\ of\ plane}$ C_{Ar}–H, m), 698 ($\delta_{out\ of\ plane}$ C_{Ar}–H, m).

[Ru(η^5-C_5H_5)(=C=C=C(Ph)(HAB))(PPh_3)$_2$][PF_6] (5)

The propargyl alcohol **4** (90.0 mg, 0.0952 mmol), [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (69.1 mg, 0.0952 mmol) and ammonium hexafluorophosphate (15.5 mg, 0.0952 mmol) were suspended in MeOH (40.0 mL). The suspension was stirred at room temperature for four days. Afterwards, the solvent was removed and the dark purple solid was purified by column chromatography (silica, CH_2Cl_2/acetone 11:1, v/v) (R_f = 0.5). The product was isolated in a yield of 17 % (29.0 mg, 16.4 µmol).

^1H NMR (CD_2Cl_2, 600 MHz, rt.): δ[ppm] = 7.60 (t, 1H, $^3J_{H,H}$ = 7.4 Hz, *p*-PhH), 7.33–7.28 (m, 8H, $C_{Ar}H$), 7.26–7.23 (m, 5H, $C_{Ar}H$) 7.06 (t, 12H, $^3J_{H,H}$ = 7.3, *m*-PPh_3), 7.03–6.99 (m, 13H, *o*-PPh_3, 1×$C_{Ar}H$), 6.88 (d, 4H, $^3J_{H,H}$ = 8.2, $C_{Ar}H$), 6.83 (t, 6H, $^3J_{H,H}$ = 7.7, *p*-PPh_3), 6.79 (d, 4H, $^3J_{H,H}$ = 8.2, $C_{Ar}H$), 6.70 (d, 2H, $^3J_{H,H}$ = 8.1, $C_{Ar}H$), 6.67 (d, 4H, $^3J_{H,H}$ = 8.2, $C_{Ar}H$), 4.96 (s, 5H, $C_{Cp}H$), 1.10 (s, 27H, 3×$C(CH_3)_3$), 1.06 (s, 18H, 2×$C(CH_3)_3$).

$^{13}C\{^1H\}$ NMR (CD_2Cl_2, 151 MHz, rt.): δ[ppm] = 290.5 (t, $^2J_{C,P}$ = 18.3 Hz, C_α), 204.5 (C_β), 161.1 (C_γ), 148.8 (C_{Ar}), 148.5 (C_{Ar}), 148.5 (C_{Ar}), 147.7 (C_{Ar}), 144.3 (*i*-Ph), 141.8 (C_{Ar}), 141.4 (C_{Ar}), 140.4 (C_{Ar}), 140.0 (C_{Ar}), 139.2 (C_{Ar}), 138.1 (C_{Ar}), 138.0 (C_{Ar}), 137.9 (C_{Ar}), 135.5–135.1 (m, *i*-PPh_3), 133.4 (t, $^3J_{C,P}$ = 5.0 Hz, *o*-PPh_3), 133.1 ($C_{Ar}H$), 132.0 ($C_{Ar}H$), 131.5 (2×$C_{Ar}H$), 131.3 (2×$C_{Ar}H$), 131.3 ($C_{Ar}H$), 130.9 (*p*-PPh_3), 130.6 ($C_{Ar}H$), 130.0 ($C_{Ar}H$), 129.2 ($C_{Ar}H$), 128.8 (t, $^4J_{C,P}$ = 5.0 Hz, *m*-PPh_3), 123.9 ($C_{Ar}H$), 123.7 (2×$C_{Ar}H$), 123.7 (2×$C_{Ar}H$), 93.3 (C_{Cp}), 34.5 (2×$C(CH_3)_3$), 34.4 ($C(CH_3)_3$), 34.4 (2×$C(CH_3)_3$), 31.4 (2×$C(CH_3)_3$), 31.3 (3×$C(CH_3)_3$).

$^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 162 MHz): δ[ppm] = 46.7 (s, PPh_3), −144.3 (sept, $^2J_{P,F}$ = 713 Hz, PF_6).

HRMS (ESI/+MS/MeOH): *m/z* (%) = 1617.7030 (100) $[M-PF_6]^+$. Calculated: 1617.7043.

EA: $C_{112}H_{109}F_6P_3Ru$ (1763.09 $gmol^{-1}$): calcd [%]: C 76.30, H 6.23; $C_{112}H_{109}F_6P_3Ru$ × CH_2Cl_2 (1848.01$gmol^{-1}$): calcd: C 73.44, H 6.05; found: C 73.44, H 6.20 %.

IR (CH_2Cl_2): ν [cm^{-1}] = 2965 (ν C_{alkyl}–H, m), 2905(ν C_{alkyl}–H, w), 2868 (ν C_{alkyl}–H, w), 1935 (ν C=C=C, m), 1595 (ν C_{Ar}=C, m), 1090 (δ P–C/ ν C_{Ar}–C_{Ar}, w).

HBC-benzophenone derivative 6

A round-bottom SCHLENK-flask (500 mL) equipped with a magnetic stirring bar was charged with HAB-benzophenone derivative **3** (0.600 g, 0.650 mmol) and CH_2Cl_2 (400 mL). The solution was degassed with N_2 for 40 min and meanwhile cooled to 0 °C in an ice bath. Dry $FeCl_3$ (1.69 g, 10.4 mmol) dissolved in $MeNO_2$ (5.60 mL) was added portion wise. After complete addition of the $FeCl_3$ and solution degassing, cooling was continued for 1 h. The ice-bath was removed, the N_2 stream was stopped and the dark mixture was stirred for further 4 h at room temperature. The reaction was quenched by addition of MeOH (150 mL). All solvents were evaporated and the remaining solids were filtered over a plug of silica with CH_2Cl_2. The yellow product fraction was collected the solvents were concentrated and the product was precipitated from the CH_2Cl_2 solution by addition of MeOH. The yellow solid was filtered off, washed with a small amount of MeOH and dried under vacuum. The product was obtained as a bright yellow solid with a yield of 94 % (0.550 g, 0.610 mmol).

^1H NMR ($CDCl_3$, 400 MHz, rt.): δ [ppm] = 9.45 (s, 2H), 9.23 (s, 2H), 9.22 (s, 2H), 9.19 (s, 2H), 9.17 (s, 2H), 9.05 (s, 2H), 8.18–8.15 (m, 2H), 7.77–7.74 (m, 1H), 7.68–7.64 (m, 2H), 1.83 (s, 9H), 1.82 (s, 18H), 1.74 (s, 18H).

$^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz, rt.): δ [ppm] = 197.3, 149. 2, 149.1, 149.0, 138.1, 134.4, 132.7, 130.7, 130.5, 130.4, 130.3, 130.2, 130.1, 129.8, 128.4, 128.1, 123.7, 123.65, 123.57, 123.0,

121.3, 121.1, 120.3, 119.28, 119.26, 118.93, 118.89, 35.75, 35.71, 35.69, 32.0, 31.9.

MS (MALDI-ToF, dhb): *m*/z = 907 $[M]^+$.

HRMS (APPI, toluene): *m/z* = 906.48046 $[M]^+$. Calculated: 906.47952.

HBC-Phenylpropargyl alcohol 7

TMS-acetylene (0.862 mL, 6.06 mmol) was dissolved in THF (10 mL) and cooled to −60 °C. *n*-BuLi (2.42 mL, 2.5 M in *n*-hexane, 6.06 mmol) was added and the solution was allowed to stir for 1 h. This mixture was added dropwise to a solution of HBC-benzophenone derivative **6** (550 mg, 0.606 mmol) in THF (80 mL). The yellow solution was allowed to warm to room temperature and stirred for 21 h. Afterwards, it was hydrolysed with water (3 mL) and filtered. The solvent was removed, the yellow solid was dissolved in CH_2Cl_2 (80 mL) and washed with water (3 × 100 mL). The combined organic phases were dried (Na_2SO_4). The solvent was removed and the yellow solid dried under vacuum. The product was isolated in a yield of 99 % (562 mg, 602 µmol)

^{1}H NMR ($CDCl_3$, 400 MHz, rt.): δ[ppm] = 9.41 (s, 2H, CH_{Ar}), 9.34 (3 partially overlapping s, 4H, CH_{Ar}), 9.31 (s, 2H, CH_{Ar}), 9.29 (s 2H, CH_{Ar}), 9.16 (s, 2H, CH_{Ar}), 7.92 (d, 2H, $^3J_{H,H}$ = 7.4 Hz, *o*-PhH), 7.48 (t, 2H, $^3J_{H,H}$ = 7.6 Hz, *m*-PhH), 7.40 (t, 1H, $^3J_{H,H}$ = 7.3 Hz, *p*-PhH), 3.31 (br, 1H, OH), 3.20 (s, 1H, C≡CH), 1.87 (s, 9H, $C(CH_3)_3$), 1.86 (s, 18 H, 2×$C(CH_3)_3$), 1.80 (s, 18H, 2×$C(CH_3)_3$).

^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt.): δ[ppm] = 149.3 (C_{Ar}), 149.2 (C_{Ar}), 144.7 (*i*-Ph), 142.0 (C_{Ar}), 142.0 (C_{Ar}), 131.0 (C_{Ar}), 131.0 (C_{Ar}), 130.7 (C_{Ar}), 130.6 (C_{Ar}), 130.5 (C_{Ar}), 130.5 (C_{Ar}), 130.2 (C_{Ar}), 128.7 (*m*-Ph), 128.3 (*p*-Ph), 126.7 (*o*-Ph), 125.5 (C_{Ar}), 124.1 (C_{Ar}), 124.0 (C_{Ar}), 121.0 (C_{Ar}), 120.9 (C_{Ar}), 120.6 (C_{Ar}), 120.2 (C_{Ar}), 119.7 (CH), 119.4 (CH), 119.3 (CH), 119.1 (CH), 119.1 (CH), 119.0 (CH), 87.1 (C≡CH), 76.3 (C≡CH), 75.4 (C–OH), 35.9 ($C(CH_3)_3$), 35.9 ($C(CH_3)_3$), 35.9 ($C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$).

HRMS (ESI/+MS/MeOH): *m/z* (%) = 915.4902 (99) $[M–OH]^+$, 932.4928 (100) $[M]^+$, 955.4823 (22) $[M+Na]^+$. Calculated: 915.4930, 932.4957, 955.4849.

EA: $C_{71}H_{64}O$ (933.29 $gmol^{-1}$): calcd [%]: C 91.37, H 6.91; found: C 89.95, H 7.04.

IR: ν [cm^{-1}] = 3538 (ν O–H, w), 3287 (ν C≡C–H, w), 2951 (ν C_{alkyl}–H, m), 2864 (w, C_{alkyl}–H), 1605 (ν C_{Ar}=C, m), 1579 (ν C_{Ar}=C, m), 1460 (ν C_{alkyl}–C, m), 1368 (ν C_{alkyl}–C, m), 867 (δ C_{Ar}–H, s), 757 (δ O–H, m), 747 (C_{Ar}–H), 696 (C_{Ar}–H).

[Ru(η^5-C_5H_5)(=C=C=C(Ph)(HBC))(PPh_3)$_2$][PF_6] (8)

The propargyl alcohol **7** (200 mg, 0.214 mmol), [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (233 mg, 0.321 mmol) and ammonium hexafluorophosphate (52.3 mg, 0.321 mmol) were suspended in MeOH (120 mL). The suspension was stirred at room temperature for 4 days. Afterwards, the solvent was removed and the dark green-blue solid was purified by column chromatography (silica, CH_2Cl_2/acetone 11:1, v/v) (R_f = 0.62). The product was isolated in a yield of 29 % (109 mg, 62.3 µmol).

^{1}H NMR ($CDCl_3$, 600 MHz, rt.): δ[ppm] = 9.69 (s, 2H, C_{Ar}H), 9.40–9.39 (two overlapping s, 4H, C_{Ar}H), 9.37 (overlapping s, 4H, C_{Ar}H), 9.17 (s, 2H, C_{Ar}H), 7.87 (t, 1H, $^3J_{H,H}$ = 7.5 Hz, *p*-PhH), 7.69 (d, 2H, $^3J_{H,H}$ = 7.5 Hz, *o*-PhH), 7.55 (t, 2H, $^3J_{H,H}$ = 7.7 Hz, *m*-PhH), 7.32 (t, 6H, $^3J_{H,H}$ = 7.0 Hz, *p*-PPh_3H), 7.20–7.14 (m, 25H, *o*-/m- PPh_3H), 5.25 (s, 5H, C_{Cp}H), 1.87 (s, 9H, $C(CH_3)_3$), 1.86 (s, 18H, 2×$C(CH_3)_3$), 1.75 (s, 18H, 2×$C(CH_3)_3$).

^{13}C{^{1}H} NMR ($CDCl_3$, 151 MHz, rt.): δ[ppm] = 290.7 (t, $^2J_{C,P}$ = 18.1 Hz, C_α), 209.0 (C_β), 159.9 (C_γ), 150.2 (C_{Ar}), 149.9 (d, $^2J_{C,P}$ = 7.0 Hz, *i*-PPh_3), 144.7 (*i*-Ph), 141.3 (C_{Ar}), 135.4 (C_{Ar}), 135.3 (C_{Ar}), 135.0 (*p*-PPh_3), 134.8 (C_{Ar}), 133.3 (t, $^3J_{C,P}$ = 5.0 Hz, *o*-PPh_3), 132.1 (*p*-Ph), 131.9 (C_{Ar}), 131.0 (C_{Ar}), 130.9 (*o*-Ph), 130.8 (C_{Ar}), 130.4 (C_{Ar}), 129.8 (C_{Ar}), 129.3 (*m*-Ph), 129.0 (C_{Ar}), 128.7 (t, $^4J_{C,P}$ = 5.0 Hz, *m*-PPh_3), 124.4 (C_{Ar}), 123.9 (C_{Ar}), 123.8 (C_{Ar}), 123.7 (CH), 122.4 (C_{Ar}), 121.6 (C_{Ar}), 121.1 (C_{Ar}), 120.3 (C_{Ar}H), 120.0 (C_{Ar}), 119.6 (C_{Ar}H), 119.4 (C_{Ar}H), 119.3 (C_{Ar}H), 119.3 (C_{Ar}H), 93.9 (C_{Cp}), 36.0 ($C(CH_3)_3$), 36.0 (2×$C(CH_3)_3$), 32.2 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$), 32.1 ($C(CH_3)_3$).

^{31}P{^{1}H} NMR ($CDCl_3$, 162 MHz): δ[ppm]= 46.1 (PPh_3), −144.2 (sept, $^2J_{P,F}$ = 713 Hz, PF_6).

HRMS (ESI/+MS/MeOH): *m/z* (%) = 1605.6104 (96.0) $[M–PF_6]^+$. Calculated: 1605.6135

EA: $C_{112}H_{97}F_6P_3Ru$ (1750.99 $gmol^{-1}$): calcd [%]: C 76.83, H 5.58; found: C 77.23, H 5.82.

IR (CH_2Cl_2): ν[cm^{-1}] = 2980 (C_{alkyl}–H), 1927 (C=C=C), 1607 (C_{Ar}=C), 1591 (C_{Ar}=C), 1435 (P–C).

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ CCDC 2005956 contains 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/structures.

References

1 E. Clar, C. T. Ironside and M. Zander, *J. Chem. Soc.*, 1959, 142.

2 H. Seyler, B. Purushothaman, D. J. Jones, A. B. Holmes and W. W. H. Wong, *Pure Appl. Chem.*, 2012, **84**, 11910.

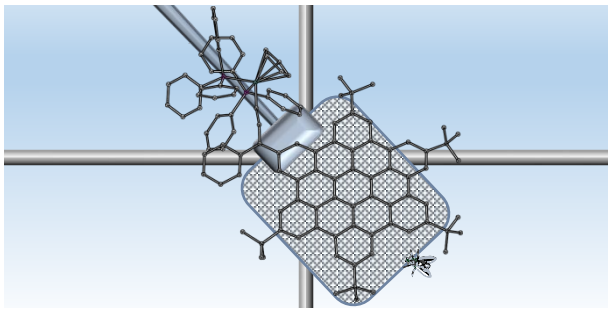
3 a) R. Goddard, M. W. Haenel, W. C. Herndon, C. Krueger and M. Zander, *J. Am. Chem. Soc.*, 1995, **117**, 30; b) A. Keerthi, I. C.-Y. Hou, T. Marszalek, W. Pisula, M. Baumgarten and A. Narita, *Chem. - Asian J.*, 2016, **11**, 2710; c) A. Kratzer, J. M. Englert, D. Lungerich, F. W. Heinemann, N. Jux and A. Hirsch, *Faraday Discuss.*, 2014, **173**, 297; d) A. Narita, X.-Y. Wang, X. Feng and K. Müllen, *Chem. Soc. Rev.*, 2015, **44**, 6616; e) Y. Segawa, H. Ito and K. Itami, *Nat. Rev. Mater.*, 2016, **1**, 95.

4 a) S. Suzuki, Y. Segawa, K. Itami and J. Yamaguchi, *Nat. Chem.*, 2015, **7**, 227; b) D. Lungerich, D. Reger, H. Hölzel, R. Riedel, M. M. J. C. Martin, F. Hampel and N. Jux, *Angew. Chem., Int. Ed.*, 2016, **55**, 5602.

5 a) W. Pisula, M. Kastler, D. Wasserfallen, M. Mondeshki, J. Piris, I. Schnell and K. Müllen, *Chem. Mater.*, 2006, **18**, 3634; b) A. Bashir, A. Heck, A. Narita, X. Feng, A. Nefedov, M. Rohwerder, K. Müllen, M. Elstner and C. Wöll, *Phys. Chem. Chem. Phys.*, 2015, **17**, 21988.
6 J. M. Warman, J. Piris, W. Pisula, M. Kastler, D. Wasserfallen and K. Müllen, *J. Am. Chem. Soc.*, 2005, **127**, 14257.
7 P. T. Herwig, V. Enkelmann, O. Schmelz and K. Müllen, *Chem. Eur. J.*, 2000, **6**, 1834.
8 A. Woolf, A. B. Chaplin, J. E. McGrady, M. A. M. Alibadi, N. Rees, S. Draper, F. Murphy and A. S. Weller, *Eur. J. Inorg. Chem.*, 2011, 1614.
9 a) M. R. Philpott and Y. Kawazoe, *J. Phys. Chem. A*, 2008, **112**, 2034; b) M. Lein, *Aust. J. Chem.*, 2018, **71**, 222.
10 D. J. Roberts, D. Nolan, G. M. Ó. Máille, G. W. Watson, A. Singh, I. Ledoux-Rak and S. M. Draper, *Dalton Trans.*, 2012, **41**, 8850.
11 J. N. Smith, J. M. Hook and N. T. Lucas, *J. Am. Chem. Soc.*, 2018, **140**, 1131.
12 a) S. M. Draper, D. J. Gregg, E. R. Schofield, W. R. Browne, M. Duati, J. G. Vos and P. Passaniti, *J. Am. Chem. Soc.*, 2004, **126**, 8694; b) Y. Fogel, M. Kastler, Z. Wang, D. Andrienko, G. J. Bodwell and K. Müllen, *J. Am. Chem. Soc.*, 2007, **129**, 11743; c) A. B. S. Elliott, R. Horvath, X.-Z. Sun, M. G. Gardiner, K. Müllen, N. T. Lucas, M. W. George and K. C. Gordon, *Inorg. Chem.*, 2016, **55**, 4710; d) J. R. Wright, J. D. Crowley and N. T. Lucas, *Chem. Commun. (Cambridge, U. K.)*, 2016, **52**, 12976; e) X. Qiao, Q. Li, R. N. Schaugaard, B. W. Noffke, Y. Liu, D. Li, L. Liu, K. Raghavachari and L.-S. Li, *J. Am. Chem. Soc.*, 2017, **139**, 3934.
13 B. El Hamaoui, F. Laquai, S. Baluschev, J. Wu and K. Müllen, *Synth. Met.*, 2006, **156**, 1182.
14 a) K.-Y. Kim, S. Liu, M. E. Köse and K. S. Schanze, *Inorg. Chem.*, 2006, **45**, 2509; b) D. Nolan, B. Gil, F. A. Murphy and S. M. Draper, *Eur. J. Inorg. Chem.*, 2011, **2011**, 3248–; c) D. Nolan, B. Gil, L. Wang, J. Zhao and S. M. Draper, *Chemistry*, 2013, **19**, 15615.
15 a) J. Wu, B. El Hamaoui, J. Li, L. Zhi, U. Kolb and K. Müllen, *Small*, 2005, **1**, 210; b) B. El Hamaoui, L. Zhi, J. Wu, J. Li, N. T. Lucas, Ž. Tomović, U. Kolb and K. Müllen, *Adv. Funct. Mater.*, 2007, **17**, 1179.
16 J. P. Selegue, *Organometallics*, 1982, **1**, 217.
17 R. F. Winter and S. Záliš, *Coord. Chem. Rev.*, 2004, **248**, 1565.
18 a) V. Cadierno, M.P. Gamasa and J. Gimeno, *Coord. Chem. Rev.*, 2004, **248**, 1627; b) S. W. Roh, K. Choi and C. Lee, *Chem. Rev.*, 2019, **119**, 4293; c) P. J. Low and S. Bock, *Electrochim. Acta*, 2013, **110**, 681; d) V. Cadierno and J. Gimeno, *Chem. Rev.*, 2009, **109**, 3512.
19 C. Coletti, A. Marrone and N. Re, *Acc. Chem. Res.*, 2012, **45**, 139.
20 F. Strinitz, A. Waterloo, J. Tucher, E. Hübner, R. R. Tykwinski and N. Burzlaff, *Eur. J. Inorg. Chem.*, 2013, **2013**, 5181.
21 S. Spörler, L. Müller, A. R. Waterloo, R. R. Tykwinski and N. Burzlaff, *J. Organomet. Chem.*, 2016, **821**, 122.
22 F. Strinitz, J. Tucher, J. A. Januszewski, A. R. Waterloo, P. Stegner, S. Förtsch, E. Hübner, R. R. Tykwinski and N. Burzlaff, *Organometallics*, 2014, **33**, 5129.
23 S. Spörler, F. Strinitz, P. Rodehutskors, L. Müller, A. R. Waterloo, M. Dürr, E. Hübner, I. Ivanović-Burmazović, R. R. Tykwinski and N. Burzlaff, *New J. Chem.*, 2016, **40**, 6127.
24 a) P. F. H. Schwab, M. D. Levin and J. Michl, *Chem. Rev.*, 1999, **99**, 1863; b) P. J. Low, *Dalton Trans.*, 2005, 2821; c) C. Olivier, B. Kim, D. Touchard and S. Rigaut, *Organometallics*, 2008, **27**, 509.
25 Y.-W. Zhong, Y. Matsuo and E. Nakamura, *Chem. - Asian J.*, 2007, **2**, 358.
26 V. S. Iyer, K. Yoshimura, V. Enkelmann, R. Epsch, J. P. Rabe and K. Müllen, *Angew. Chem., Int. Ed.*, 1998, **37**, 2696.
27 D. Lungerich, J. F. Hitzenberger, M. Marcia, F. Hampel, T. Drewello and N. Jux, *Angew. Chem., Int. Ed.*, 2014, **53**, 12231.
28 U. T. Mueller-Westerhoff and M. Zhou, *Tetrahedron Lett.*, 1993, **34**, 571.
29 D. Reger, P. Haines, F. W. Heinemann, D. M. Guldi and N. Jux, *Angew. Chem., Int. Ed.*, 2018, **57**, 5938.
30 A. H. R. Palser, *Phys. Chem. Chem. Phys.*, 1999, **1**, 4459.
31 D. D. L. Chung, *J. Mater. Sci.*, 2002, **37**, 1475–1489.
32 S. Hartmann, R. F. Winter, B. Sarkar and F. Lissner, *Dalton Trans.*, 2004, 3273.
33 S. Rigaut, J. Perruchon, S. Guesmi, C. Fave, D. Touchard and P. Dixneuf, *Eur. J. Inorg. Chem.*, 2005, 447.
34 G. A. Koutsantonis, P. A. Schauer and B. W. Skelton, *Organometallics*, 2011, **30**, 2680.

View Article Online
DOI: 10.1039/D0DT02729D

Hexa-*peri*-hexabenzocoronene decorated with an allenylidene ruthenium complex – almost a flyswatter



A ruthenium allenylidene complex bearing a hexa-*peri*-hexabenzocoronene (HBC) substituent was synthesised, resembling yet another strategy to decorate HBCs with transition metal fragments.