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Using the Wittig reaction to produce alkenylcarbaboranes

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Supporting Information

Preparation of 9-[2-(1-carboranyl)-vinyl)]anthracene. (**E-1** and **Z-1**)
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Experimental

General Details. IR spectra were recorded from KBr pellets on a Shimadzu FTIR-8300 spectrophotometer. The ^{1}H, ^{1}H{^{11}B}-NMR (300.13 MHz), ^{11}B-NMR (96.29 MHz) spectra were recorded on a Bruker ARX 300 spectrometer. All NMR spectra were recorded from $CDCl_3$ solutions at 25ºC. Chemical shift values for ^{11}B NMR spectra were referenced to external $BF_3{\cdot}OEt_2$, and those for ^{1}H and ^{1}H{^{11}B} spectra were referenced to $Si(CH_3)_4$. Chemical shifts are reported in units of parts per million downfield from reference, and all coupling constants are reported in Hertz.
X-ray studies. Intensity data sets for compounds E-1 and E,E-2 were collected using a Bruker X8 Kappa APEXII diffractometer (Mo-Kα radiation, λ = 0.71073 Å) equipped with a graphite monochromator. The ω and φ scan technique was employed to measure the intensities. Both compounds were measured at 100 K. Decomposition of the crystals did not occur during data collection. The intensities of all data sets were corrected for Lorentz and polarization effects. Absorption effects in all compounds were corrected using the program SADABS [1]. The crystal structures of all compounds were solved by direct methods. Crystallographic programs used for structure solution and refinement were those of SHELX97 [2]. Scattering factors were those provided with the SHELX program system. Missing atoms were located in the difference Fourier map and included in subsequent refinement cycles. The structures were refined by full-matrix least-squares refinement on F^2. The positions of the hydrogen atoms of C_{cage}-H groups were determined from Fourier map and refined with U_{iso} constrained at 1.2 times U_{eq} of the carrier C atom. Other hydrogen atoms were placed geometrically and refined using a riding model with U_{iso} constrained at 1.2 times U_{eq} of the carrier C or B atom. For all structures, non-hydrogen atoms were anisotropically refined. In the last cycles of refinement of all structures a weighting scheme was used, with weights calculated using the following formula $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$, where $P= (F_o^2+2F_c^2)/3$. ORTEP3 drawings [3] with the numbering schemes used are shown in Figures 1–2 (see below).

All reactions were performed under an atmosphere of dinitrogen employing standard schlenk techniques. THF was distilled form sodium benzophenone prior to use. Ortho-carborane was purchased from Katchem Ltd. (Prague) and 9-(chloromethyl)anthracene was purchased from Aldrich. Both compounds were used as received. C-formyl-carborane [4] and 9,10-Bis[(chloromethyl)]anthracene [5] were prepared by literature procedures. The phosphonium salts 9-(Triphenylphosphoniumchloride)methyl-anthracene and 9-10-Bis[(Triphenylphosphoniumchloride)]dimethylanthracene were prepared respectively from 9-(chloromethyl)anthracene and 9,10-Bis[(chloromethyl)]anthracene following the method described in reference [6].

Preparation of 9-[2-(1-carboranyl)-vinyl)]anthracene. (1E and 1Z)

9-(Triphenylphosphoniumchloride)methylanthracene (0.489 g, 1 mmol) and potassium *tert*-butoxide (0.123 g, 1.1 mmol) were dissolved in dry THF (60 mL) immediately forming a dark red solution. This was allowed to stir at room temperature for 1 h to complete the formation of the ylide. A dry THF (20 mL) solution of C-formyl-carborane (0.172 g, 1.1 mmol) was added and the reaction heated to reflux for 3 h yielding a yellow solution that was stirred overnight at room temperature. This mixture was then washed with 10% aqueous HCl solution (30 mL), followed by water (30 mL). The organic layer was evaporated to dryness to yield a yellow oil. The product was obtained from silica column chromatography (90:10, hexane:ethyl acetate) as a mixture of the E and Z isomers. Yield: 0.240 g (69%). E:Z ratio: 60:40 (estimated from the ^{1}H NMR of the mixture of both isomers). The E/Z mixture could be separated by successive preparative TLC using hexane as eluent.

Compound 1E: yellow solid. Melting point: 182-184º C. ^{1}H-NMR δ/ppm: 8.43 (1H, s, 10-Anth), 8.00 (4H, m, 1,4,5,8-Anth), 7.74 (1H, d, $^3J_{HH}$= 15.9, $C_{cluster}$-CH=C), 7.51 (4H, m, 2,3,6,7-Anth), 6.18 (1H, d, $^3J_{HH}$= 15.9, Anth-CH=C), 3.88 (1H, br s, $C_{cluster}$-H). IR/cm^{-1}: 3059 ($C_{cluster}$-H), 2588 (s, υ B-H), 2361, 2341 (s, υ =CH), 1443, 1350, 1157, 1072, 1014 (Anth), 883 (Anth), 841, 791, 729 (Anth), 667, 687, 532, 517. ^{11}B{^{1}H} NMR δ/ppm: -1.0, -2.5, -3.9, -5.5, -8.1, -9.7, -11.7, -13.4.

Compound 1Z: very pale yellow solid. Melting point: 132-136º C. ^{1}H-NMR δ/ppm: 8.49 (1H, s, 10-Anth), 8.04 (2H, d, 1,8-Anth), 7.96 (2H, d, 4,5-Anth), 7.53 (4H, m, 2,3,6,7-Anth), 7.21 (1H, d, $^3J_{HH}$= 12.3, $C_{cluster}$-CH=C), 6.44 (1H, d, $^3J_{HH}$= 12.3, Anth-CH=C), 2.96 (1H, s, $C_{cluster}$-H). IR/cm^{-1}: 3055 ($C_{cluster}$-H), 2924, 2854 (s, υ =CH), 2619, 2573 (s, υ B-H), 1443, 1335, 1157, 1072, 1014 (Anth), 883 (Anth), 845, 787, 733 (Anth), 525, 436. ^{11}B{^{1}H} NMR δ/ppm: -1.5, -3.0, -8.4, -9.9, -11.3, -12.2, -13.8.

Preparation of 9,10-Bis{[2-(1-carboranyl)-vinyl)]}anthracene. (2)

This compound was prepared using the same procedure as for **1**, starting from 9,10-Bis[(Triphenylphosphoniumchloride)]dimethylanthracene (0.582 g, 0.728 mmol) and potassium *tert*-butoxide (0.090 g, 0.80 mmol) in dry THF (30 mL). After formation of the ylide, C-formyl-carborane (0.250 g, 2.2 mmol) was added in dry THF (30 mL). After work-up, the compound was obtained as an oily mixture of all possible isomers. From solutions of this mixture in THF/hexane single crystals of the major isomer (E,E) were obtained.

X-ray analysis

Single crystals of compounds **E-1** and **E,E-2** were obtained by slow evaporation of THF/hexane solutions. The crystal structure of **E-1** contains four crystallographically non-equivalent molecules while the structure of **E,E-2** presents half molecule situated at an inversion centre.

Both compounds present *ortho*-carborane moieties linked to an anthracene unit through an ethylene spacer (-HC=CH-). Compound 1 is a 9-monosubstituted anthracene while compound 2 is a disubstituted anthracene on the positions 9 and 10 (see Figures 1 and 2).

In all cases, the carborane substituents are distorted icosahedra with no particularly unusual bond distances or angles. The B-B and C-B bond lengths are within expected values. The C_{cage}-C_{cage} distances between the cluster carbon atoms are elongated respect *ortho*-carborane (1.62 Å), which is normal for substituted carboranes. These distances are, however, longer than the one found in the related compound 1-(2-(3,4,5-trimethoxyphenyl)ethenyl)-carborane, 1.626 Å [7], but shorter than the ones found in related methyl-carborane derivatives as 1-propenyl-2-methyl-carborane, 1.688 Å [8], and 1-(Buta-1,3-dienyl)-2-methyl-carborane, 1.683 Å [9]. The steric hindrance of the extra methyl group of the last two examples explains the longer Cc-Cc distances.

	Cc-Cc	Cc-CH	-HC=CH-	Cc-Cc-CH=CH
E-1				
Unit A	C1-C2: 1.639(6)	C1-C3: 1.497(6)	C3-C4: 1.188(6)	-14.6(10)
Unit B	C101-C102: 1.655(6)	C101-C103: 1.508(6)	C103-C104: 1.277(6)	-113.0(6)
Unit C	C201-C202: 1.654(6)	C201-C202: 1.496(6)	C203-C204: 1.263(6)	132.5(6)
Unit D	C301-C302: 1.642(6)	C301-C303: 1.483(5)	C303-C304: 1.325(6)	-158.1(5)
E,E-2				
Unit A	C1-C2: 1.674(9)	C1-C3: 1.430(6)	C3-C4: 1.323(7)	52.2(7)

Table S.1. Selected bond lengths (Å) for **E-1** and **E,E-2**.

A very interesting thing about compound **E-1** is the fact that it presents four crystallographically non-equivalent molecules in the asymmetric unit. The difference among them is the different conformation around the ethylene linker. This is reflected in the value of the Cc-Cc-CH=CH torsion angle (the torsion angle that involves the carborane cage carbon atoms and the carbon atoms of the ethylene spacer). This wide range in the torsion angle values is possibly due to the lack of an extra group on the other carbon atom of the carborane cage.

Crystal packing

Although the molecular structure of this type of compounds is usually not very different to previous known ones in terms of bond lengths and angles, these compounds are very interesting as model compounds to study the secondary interactions that determine the supramolecular structure of carborane containing molecules. The only different groups present in the molecules are BH and CH groups from the carborane cage and aromatic CH groups from the ethylene linker and the anthracene moiety. The intermolecular interactions that direct the crystal packing of these compounds are of three types: (i) B-H…H-C interactions ("dihydrogen" bond) which are dipole-dipole interactions established between the partially negatively charged B-H groups (hydridic hydrogen atoms) of the *ortho*-carborane moiety and the partially positively charged C-H of the organic fragments of the molecules; (ii) van der Waals B-H…H-B interactions and (iii) interactions with the п cloud of the anthracene unit (п-п stacking and X-H…п interactions, X= C, B).

Compound **E-1** crystallizes in the non-centrosymmetric space group Pn. The main secondary interaction in the crystal packing of this compound is a π-stacking interaction among the anthracene groups. Thus, the anthracene groups stack along the crystallographic *b* axis, as shown in Figure 3. The π-π interactions can be described as strong (see data in Table 4) and parallel displaced [10]. These interactions involve the central rings of the anthracene units, creating continuous chains of anthracene groups parallel to the *b* axis. Besides these π-π interactions, within these chains the molecules establish B-H…H-C, B-H…H-B and C-H…π interactions with neighbouring molecules in the same direction, reinforcing the interactions along the crystallographic *b* axis (see data in Tables 2, 3 and 5, repectively). If we take a close look at one of those chains, we see that the ethylene-carboranyl side groups on the anthracene moieties spiral along the anthracene row, forming a helix. This helical structure is responsible for the non-centrosymmetry of the crystal packing. These helices interact with each other through "dihydrogen" B-H…H-C and van der Waals B-H…H-B interactions completing the three-dimensional packing of the compound. Figure 4 shows a global view of the *ac* plane, as seen down the *b* axis. The interactions among different helices occur along three directions: the diagonal of the *ac* plane [1 0 1], the crystallographic *a* axis and the other diagonal of the *ac* plane [1 0 -1]; see Figures 5, 6 and 7, respectively, for the details of the interactions along those three directions and Tables 2 and 3 for data.

The more symmetrical compound **E,E-2** crystallizes in the centric space group P21/c. The crystal packing of this compound is very influenced by the shape of the molecule: the E disposition of both double bond spacers makes it very difficult for the anthracene moiety to establish π-π interactions. Thus, the minimum distance between centroids of neighbouring anthracenes is as long as 5.734 Å. Instead, every anthracene establish weak C-H…*π* interactions with the ethenyl spacer and very weak van der Waals interactions with B-H groups of carborane cages located above and below the anthracene plane, in the direction of the diagonal of the *ac* plane [1 0 1], as shown in Figure 8 (data in Tables 5 and 6). The carborane groups also interact with the outer rings of the anthracene moiety. These interactions arrange the molecules in a plane which is parallel to the *ac* crystallographic plane, as shown in Figure 8. The carborane groups also establish two van der Waals BH…HB interactions along the crystallographic *a* axis (see Figure 8 and data in Table 3), reinforcing the interactions within these planes. These planes interact with nearby planes in the *b* direction completing the three-dimensional packing of the compound. Thus, the CH groups of the carboranes cages point out these planes establishing weaker van der Waals interactions with boron atoms of nearby planes (data in Table 2).

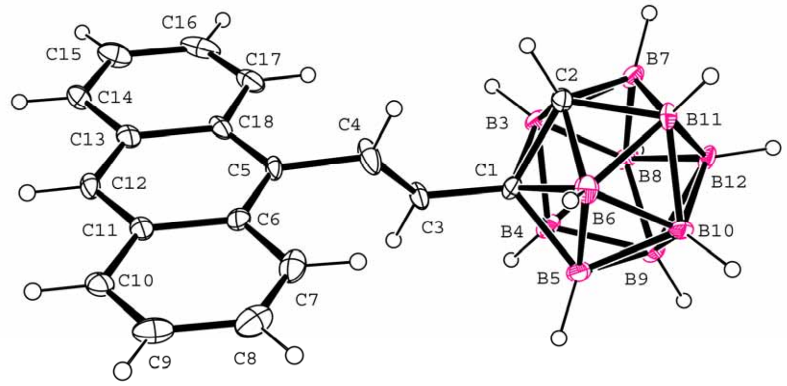

Figure S.1: Molecular structure of **E-1** showing the labelling scheme.

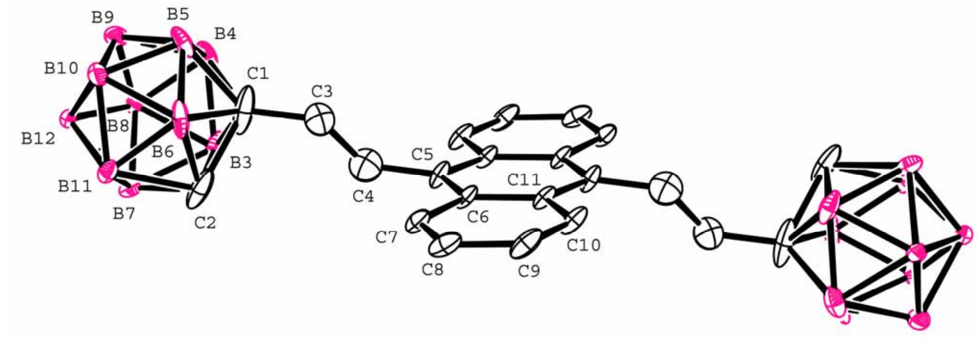

Figure S.2: Molecular structure of **E,E-2** showing the labelling scheme. Hydrogen atoms have been omitted for clarity.

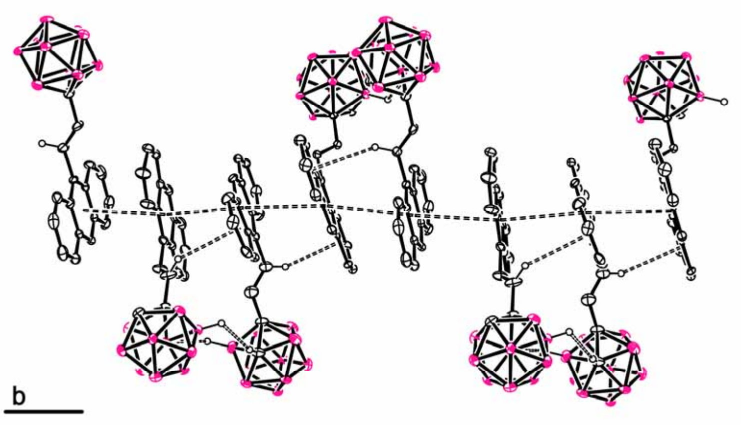

Figure S.3: Crystal packing diagram for **E-1** along the crystallographic *b* axis.

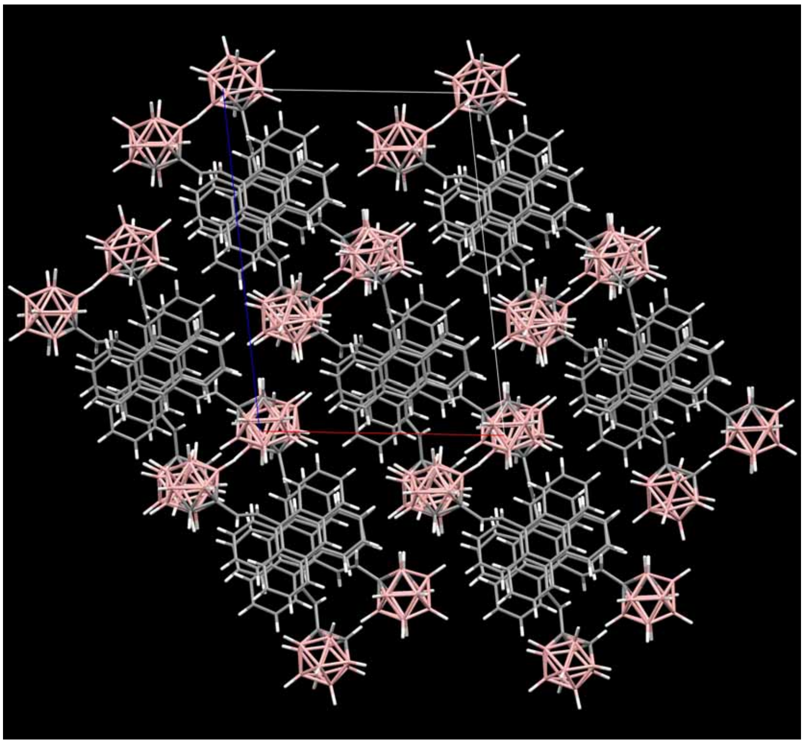

Figure S.4: Crystal packing diagram for **E-1** as seen down the crystallographic *b* axis (*a* axis is shown in red; *c* axis is shown in blue).

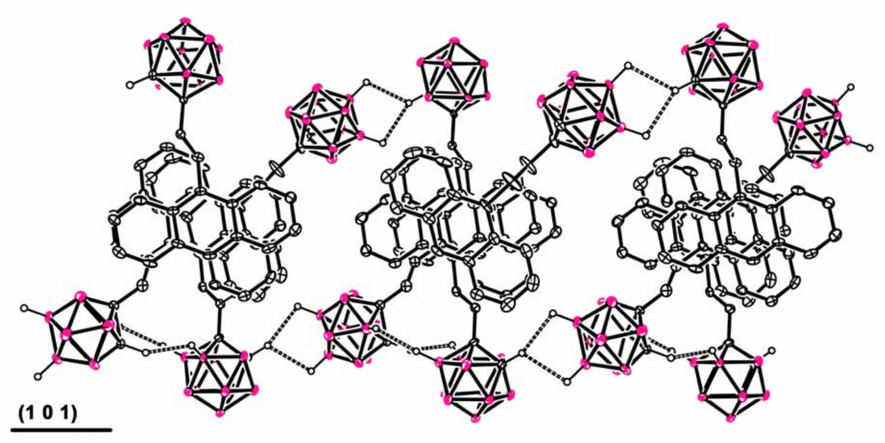

Figure S.5: Crystal packing diagram for **E-1** along the (1 0 1) direction.

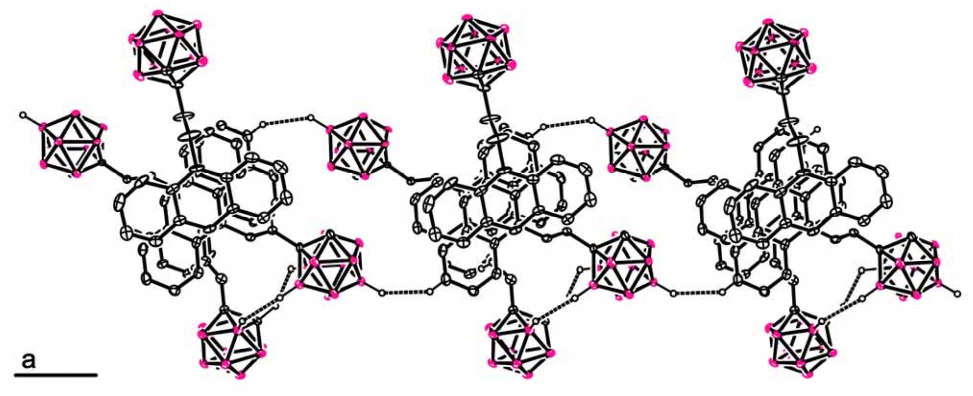

Figure S.6: Crystal packing diagram for **E-1** along the *a* axis.

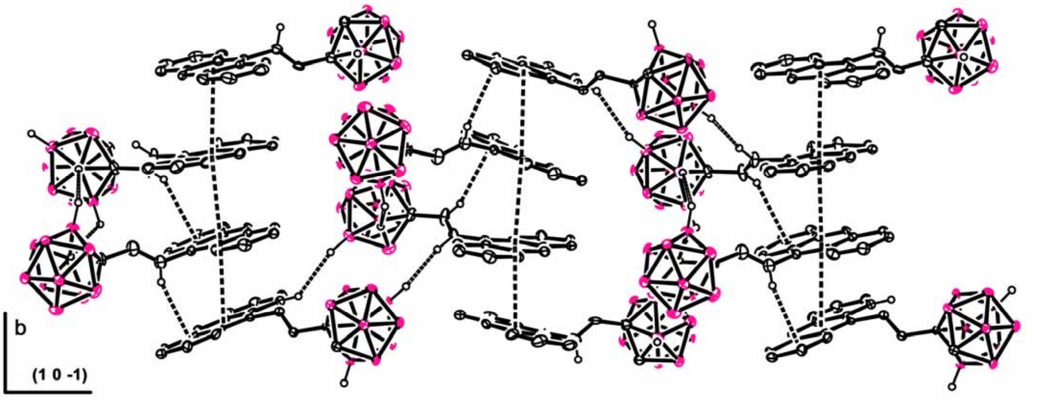

Figure S.7: Crystal packing diagram for **E-1** along the (1 0 -1) direction.

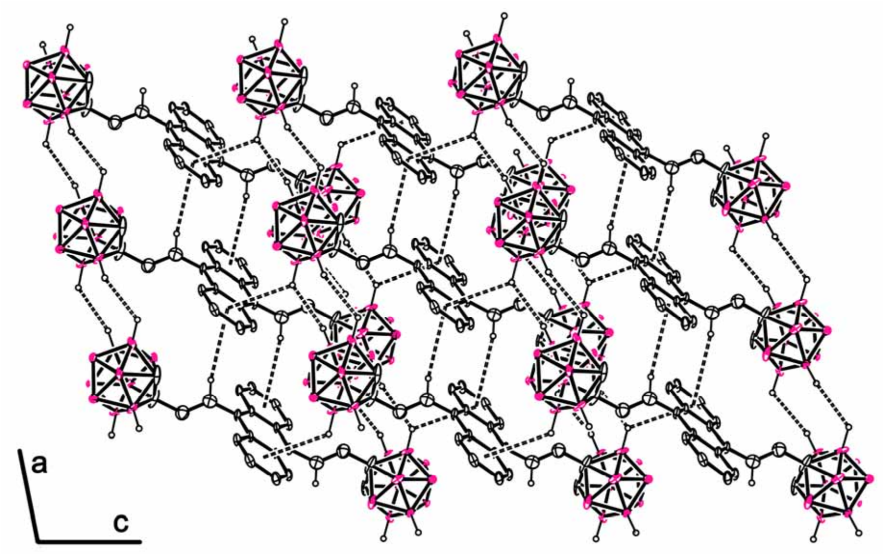

Figure S.8: Crystal packing diagram for **E,E-2** in the AC plane.

References:

[1] G. M. Sheldrick. SADABS: Program for absorption correction using area detector data. University of Göttingen, Germany, 1996.
[2] SHELX97 [Includes SHELXS97, SHELXL97, CIFTAB] - Programs for Crystal Structure Analysis (Release 97-2). G. M. Sheldrick, Institüt für Anorganische Chemie der Universität, Tammanstrasse 4, D-3400 Göttingen, Germany, 1998.
[3] ORTEP3 for Windows - L. J. Farrugia, *J. Appl. Crystallogr.* 1997, **30**, 565.
[4] P. Dozzo, R. A. Kasar, S. B. Kahl, *Inorg. Chem.*, 2005, **44**, 8053-8057.
[5] M. W. Miller, R. W. Amidon, P. O. Tawney, *J. Amer. Chem. Soc.*, 1955, **77**, 2845-2848.
[6] I. Cade, N. J. Long, A. J. P. White, D. J. Williams, *J. Organomet. Chem.*, 2006, **691**, 1389-1401.
[7] Z. Qiu; Z. Xie, *Angew. Chem. Int. Ed.*, 2008, **47**, 6572-6575.
[8] G.V.Grintselev-Knyazev, M.Yu.Antipin, S.P.Knyazev, V.N.Kirin, E.A.Chernyshev, *Acta Crystallogr.,Sect.E:Struct.Rep.Online*, 2002, **E58**, o16-o17.
[9] J. C. Clark, F. R. Fronczek, M. G. H. Vicente, *Tetrahedron Lett.*, 2005, **46**, 2365-2368.
[10] C. Janiak, *J. Chem. Soc. Dalton Trans.*, 2000, 3885-3896.

Table S.2: B-H…H-C interactions

B-H…H-C	**H…H (Å)**	**B…C (Å)**	**B-H…H (º)**	**H…H-C (º)**
E-1				
B(305)-(H305)…H(30b)-C(304) INTRA	2.356	3.186	98.6	131.9
b axis				
B(104)-H(104)…H(202)-C(202)	2.195	3.888	129.1	156.1
[1 0 1] direction				
B(10)-H(10)…H(302)#1-C(302)#1	2.334	3.732	105.0	141.1
B(12)-H(12)…H(302)#1-C(302)#1	2.347	3.721	105.2	135.3
B(209)-H(209)…H(102)#4-C(102)#2	2.353	3.833	104.4	166.5
B(212)-H(212)…H(102)#4-C(102)#2	2.522	3.728	99.9	119.0
a axis				
B(112)-H(112)…H(10f)#3-C(109)#3	2.373	3.986	139.3	135.3
B(312)-H(312)…H(30e)#6-C(309)#4	2.393	4.030	136.7	144.5
[1 0 -1] direction				
B(110)-H(110)…H(30c)#2-C(307)#5	2.377	4.086	144.1	140.0
B(309)-H(309)…H(10c)#5-C(104)#6	2.241	4.290	170.4	169.1
E,E-2				
B(3)-H(3)…H(4a)-C(4) INTRA	2.266	3.084	99.6	124.0
B(11)-H(11)…H(9a)#2-C(9)#2	2.410	4.063	140.9	139.8

Symmetry codes:
(**1**) #1: x+0.5,-y+1,z+0.5; #2: x-0.5, -y+1, z-0.5; #3: x+1,y,z; #4: x-1,y,z; #5: x+0.5,-y+1,z-0.5; #6: x-0.5,-y+1,z+0.5.
(**2**) #2: x+1, 1.5-y, z+0.5.

Table S.3: B-H…H-B interactions

B-H…H-B	H…H (Å)	B…B (Å)	B-H…H (º)	H…H-B (º)
E-1 (b axis)				
B(105)-H(105)…H(206)-B(206)	2.296	4.035	145.2	136.5
B(3)-H(3)…H(303)#1-B(303)#7	2.390	4.081	151.9	125.5
E,E-2 (a axis)				
B(5)-H(5)…H(8)#1-B(8)#1	2.387	4.132	125.1	150.9
B(6)-H(6)…H(7)#1-B(7)#1	2.394	4.097	152.5	119.1

Symmetry codes:
(**1**) #7: x,-y+1,z
(**2**) #1: x+1,y,z

Table S.4: π-π interactions

π-π	Cg-Cg (Å)[a]	alpha[b]	beta[c]	gamma[d]	Cg(I)_J[e]	Cg(J)_I[f]
E-1 (b axis)						
inner1-inner2	3.644	6.74	18.23	11.54	3.571	3.461
inner2-inner 3	3.698	11.55	11.19	16.40	3.548	3.628
inner3-inner4	3.666	2.26	17.20	18.77	3.471	3.502
Inner4-inner1#8	3.735	9.07	20.12	24.31	3.403	3.506

[a] Centroid-Centroid distance. [b] Dihedral angle between the ring planes. [c] Angle between the centroid vector Cg(I)…Cg(J) and the normal to the plane I. [d] Angle between the centroid vector Cg(I)…Cg(J) and the normal to the plane J. [e] Perpendicular distance of Cg(I) on ring plane J. [f] Perpendicular distance of Cg(J) on ring plane I.

Symmetry codes: (**1**) #8: x,y+1,z

Table S.5: C-H…π interactions

C-H…π	H…Cg (Å)	C…Cg (Å)	C-H…Cg (º)	min$_{(H…C)}$ (Å)	max$_{(H…C)}$ (Å)
E-1 (b axis)					
C(4)-H(4a)…outer3#8	3.069	3.849	140.4	2.802C(306)	3.859 C(309)
C(103)-H(10b)…outer3	2.951	3.740	141.3	3.121 C(216)	3.449 C(213)
C(204)-H(20b)…outer4	2.805	3.502	131.0	2.918, C(316)	3.348, C(318)
E,E-2 (a axis)					
C(4)-H(4a)…outer#1	3.248	4.185	169.1	2.898, C(9)	4.076, C(6)

Symmetry codes:
(**1**) #8: x, y+1, z. (**2**) #1: x+1,y,z

Table S.6: B-H…π interactions

B-H…π	H…Cg (Å)	B…Cg (Å)	B-H…Cg (º)	min$_{(H…C)}$ (Å)	max$_{(H…C)}$ (Å)
E,E-2 (very weak)					
B(5)-H(5)…outer#3	3.060	3.794	123.4	2.632, C(10)	3.970, C(7)

Symmetry codes:
(**1**) #3: -x+1,-y+2,-z+2