The Frustrated Lewis Pair Inducedd Formation of a Pentafulvene [6+4] Cycloaddition Product

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Supporting Information

General considerations

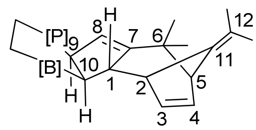
All manipulations were performed under Ar using Schlenk-type glassware or in a glove box. Solvents were dried according to the procedure by Grubbs or were distilled from appropriate drying agents and stored under an argon atmosphere.

Melting points were obtained with a DSC Q20 (*TA Instruments*). IR spectra were recorded on a *Varian* 3100 FT-IR (Excalibur Series). Elemental analyses were performed on a *Elementar Vario El III*. NMR spectra were recorded on a *Varian* UnityPlus 600 (^{1}H: 599.9 MHz, ^{13}C: 150.8 MHz, ^{19}F: 564.4 MHz, ^{11}B: 192.4 MHz, ^{31}P: 242.7 MHz). ^{1}H NMR and ^{13}C NMR: chemical shifts δ are given relative to TMS and referenced to the solvent signal. ^{19}F NMR: chemical shifts δ are given relative to $CFCl_3$ (external reference), ^{11}B NMR: chemical shifts δ are given relative to $BF_3{\cdot}Et_2O$ (external reference), ^{31}P NMR: chemical shifts δ are given relative to H_3PO_4 (85% in H_2O) (external reference). NMR assignments were supported by additional 2D NMR experiments. X-ray crystal structure analysis: Data sets were collected with a Nonius KappaCCD diffractometer. Programs used: data collection COLLECT (Nonius B.V., 1998), data reduction Denzo-SMN (Z. Otwinowski, W. Minor, *Methods in Enzymology*, **1997**, *276*, 307-326), absorption correction Denzo (Z. Otwinowski, D. Borek, W. Majewski, W. Minor, *Acta Cryst.* **2003**, *A59*, 228-234), structure solution SHELXS-97 (G.M. Sheldrick, *Acta Cryst.* **1990**, *A46*, 467-473), structure refinement SHELXL-97 (G.M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122), graphics XP (BrukerAXS, 2000). R-value is given for the observed reflections, wR^2-value for all refelctions. Thermal ellipsoids are shown with 50 % probability.

Materials

Dimesitylvinylphosphine [P. Spies, G. Erker, G. Kehr, K. Bergander, R. Fröhlich, S. Grimme and D. W. Stephan, *Chem. Commun*., 2007, 5072] and $HB(C_6F_5)_2$ [a) D. J. Parks, R. E. von H. Spence and W. E. Piers, *Angew. Chem. Int. Ed. Engl*., 1995, **34**, 809; *Angew. Chem.,* 1995, **107**, 895; b) W. E. Piers, D. J. Parks and G. P. A. Yap, *Organometallics*, 1998, **17**, 5492] were synthesized according to literature procedures. 6,6-Dimethylpentafulvene **3** was synthesized according to a procedure described by Stone and Little: K. J. Stone and R. D Little, *J. Org. Chem.*, 1984, **49**, 1849.

Synthesis of 6



[P]: $PMes_2$; [B]: $B(C_6F_5)_2$

Dimesitylvinylphosphine (100 mg, 0.34 mmol) and bis(penta-fluorophenyl)borane were dissolved in pentane (10 mL) and stirred for 15 min and 6,6-dimethylfulvene **(3)** (358 mg, 3.4 mmol) was added to the solution. After the reaction mixture had been stirred for 2 d, a white powder started to precipitate. The reaction mixture was stirred for another 5 d, and then the precipitate was isolated *via* cannula filtration. After washing with pentane (2×3 mL), the white-yellow powder was dried *in vacuo* to afford **6** (126 mg, 43%). Crystals suitable for the X-ray crystal structure analysis were obtained by diffusion of heptane into a benzene solution of **6**.

Melting point (DSC): 131 °C.

IR (KBr): $\tilde{\nu}$ /cm^{-1} = 2970 (s), 2927 (s), 2853 (m), 2361 (m), 1641 (m), 1606 (s), 1558 (w), 1511 (s), 1446 (s), 1382 (m), 1292 (w), 1269 (s), 1203 (w), 1175 (w), 1111 (w), 1075 (s), 1025 (w), 966 (vs), 891 (m), 855 (vs), 806 (m), 777 (m), 740 (m), 691 (s), 652 (m), 631 (w), 553 (m).

Exact mass (ESI-HRMS): calc. for C48H46BF10PH: 855.3343. Found: 855.3359.

Found: C, 66.46; H, 4.64. **Calc.** for $C_{48}H_{46}BF_{10}P$ (854.65 g/mol): C, 67.46; H, 5.43.

^{1}H NMR (600 MHz, 253 K, [d_2]-CH_2Cl_2): δ = 6.86 (1H, br, *m*-Mes^{A}), 6.83 (1H, br, *m*'-Mes^{A}), 6.79 (1H, br, *m*-Mes^{B}), 6.77 (1H, br, *m*'-Mes^{B}), 5.98 (1H, dd, $^{3}J_{HH}$ = 6.1 Hz, $^{3}J_{HH}$ = 2.8 Hz, 4-H), 5.91 (1H, dd, $^{3}J_{HH}$ = 6.1 Hz, $^{3}J_{HH}$ = 2.8 Hz, 3-H), 4.65 (1H, m, 8-H), 4.64 (1H, m, 9-H), 3.00 (1H, dm, $^{3}J_{PH}$ = 41.7 Hz, 10-H), 2.93, 2.77 (each 1H, each m, $^{P}CH_2$), 2.59 (1H, m, 1-H), 2.56 (1H, d, $^{3}J_{HH}$ = 2.8 Hz, 5-H), 2.48 (1H, br, 2-H), 2.43 (6H, s, *o*-CH_3^{MesA}, *o*'-CH_3^{MesB}), 2.26 (3H, s, *p*-CH_3^{MesA}), 2.19 (3H, s, *p*-CH_3^{MesB}), 2.14 (1H, m,), 0.28 (1H, m) ($^{B}CH_2$), 1.88 (3H, s, *o*'-CH_3^{MesA}), 1.85 (3H, s, *o*-CH_3^{MesB}), 1.48 (3H, s, 12-CH_3), 1.03 (3H, s, 12'-CH_3), 0.71 (3H, s, 6-CH_3), 0.64 (3H, s, 6'-CH_3).

^{13}C{^{1}H} NMR (151 MHz, 253 K, [d_2]-CH_2Cl_2): δ = 159.0 (d, $^{3}J_{PC}$ = 13.1 Hz, C7), 143.4 (*o*'-Mes^{B}), 142.6 (*o*-Mes^{A}), 142.8 (d, $^{4}J_{PC}$ = 2.6 Hz, *p*-Mes^{A}), 142.6 (*p*-Mes^{B}), 141.7 (C11), 140.8 (d, $^{2}J_{PC}$ = 7.5 Hz, *o*-Mes^{B}), 140.4 (d, $^{2}J_{PC}$ = 7.5 Hz, *o*'-Mes^{A}), 135.7 (C4), 133.2 (C3), 132.5 (d, $^{3}J_{PC}$ = 9.8 Hz, *m*-Mes^{B}), 131.2 (d, $^{3}J_{PC}$ = 10.1 Hz, *m*'-Mes^{A}), 131.1 (d, $^{3}J_{PC}$ = 10.9 Hz, *m*-Mes^{A}), 131.0 (d, $^{3}J_{PC}$ = 10.9 Hz, *m*'-Mes^{B}), 123.4 (d, $^{2}J_{PC}$ = 8.7 Hz, C8), 122.3 (d, $^{1}J_{PC}$ = 74.8 Hz, *i*-Mes^A), 122.2 (d, $^1J_{PC}$ = 65.0 Hz, *i*-Mes^B), 115.9 (C12), 54.4 (d, $^3J_{PC}$ = 4.3 Hz, C1), 52.3 (C5), 46.5 (d, $^4J_{PC}$ = 6.8 Hz, C2), 45.7 (d, $^1J_{PC}$ = 27.1 Hz, C9), 41.4 (d, $^4J_{PC}$ = 3.3 Hz, C6), 35.7 (br, C10), 26.3 (d, $^5J_{PC}$ = 4.4 Hz, 6-CH_3), 26.2 (6'-CH_3), 25.4 (br d, $^1J_{PC}$ ~ 36 Hz, $^PCH_2$), 25.1 (d, $^3J_{PC}$ = 2.1 Hz, *o*-CH_3^{MesA}), 24.6 (*o*'-CH_3^{MesB}), 22.5 (d, $^3J_{PC}$ = 6.2 Hz, *o*'-CH_3^{MesA}), 22.3 (d, $^3J_{PC}$ = 4.2 Hz, *o*-CH_3^{MesB}), 20.8 (*p*-CH_3^{MesA}), 20.6 (*p*-CH_3^{MesB}), 19.9 (12-CH_3), 17.7 (12'-CH_3), 15.8 (br, $^BCH_2$), n.o. (C_6F_5).

^{1}H TOCSY (600 MHz, 253 K, [d_2]-CH_2Cl_2): δ $^1H_{irr}$ / δ $^1H_{res}$ = 6.86 / 6.83, 2.43, 2.26, 1.88 (*m*-Mes^A / *m*'-Mes^A, *o*-CH_3^{MesA}, *p*-CH_3^{MesA}, *o*'-CH_3^{MesA}), 6.79 / 6.77, 2.43, 2.19, 1.85 (*m*-Mes^B / *m*'-Mes^B, *o*'-CH_3^{MesB}, *p*-CH_3^{MesB}, *o*-CH_3^{MesB}), 5.98 / 5.91, 2.59, 2.56, 2.48 (4-H / 3-H, 1-H, 5-H, 2-H), 5.91 / 5.98, 2.59, 2.56, 2.48 (3-H / 4-H, 1-H, 5-H, 2-H), 3.00 / 4.64, 2.59, 2.48 (10-H / 9-H, 1-H, 2-H), 2.93, 2.77 / 2.14, 0.28 ($^PCH_2$ / $^BCH_2$), 2.59 / 5.98, 5.91, 4.65, 3.00, 2.48 (1-H / 4-H, 3-H, 8-H, 10-H, 2-H), 2.48 / 5.98, 5.91, 3.00, 2.59, 2.56, (2-H / 4-H, 3-H, 10-H, 1-H, 5-H), 2.26 / 6.86, 6.83, 2.43, 1.88 (*p*-CH_3^{MesA} / *m*-Mes^A, *m*'-Mes^A, *o*-CH_3^{MesA}, *o*'-CH_3^{MesA}), 2.19 / 6.79, 6.77, 2.43, 1.85 (*p*-CH_3^{MesB} / *m*-Mes^B, *m*'-Mes^B, *o*'-CH_3^{MesB}, *o*-CH_3^{MesB}), 2.14, 0.28 / 2.93, 2.77 ($^BCH_2$ / $^PCH_2$), 1.88 / 6.86, 6.83, 2.43, 2.26 (*o*'-CH_3^{MesA} / *m*-Mes^A, *m*'-Mes^A, *o*-CH_3^{MesA}, *p*-CH_3^{MesA}), 1.85 / 6.79 / 6.77, 2.43, 2.19 (*o*-CH_3^{MesB} / *m*-Mes^B, *m*'-Mes^B, *o*'-CH_3^{MesB}, *p*-CH_3^{MesB}), 1.48 / 1.03 (12-CH_3 / 12'-CH_3), 1.03 / 1.48 (12'-CH_3 / 12-CH_3), 0.71 / 0.64 (12-CH_3 / 6'-CH_3), 0.64 / 0.71 (6'-CH_3 / 6-CH_3).

^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 253 K, [d_2]-CH_2Cl_2): δ (^{1}H, ^{1}H) = 6.86 / 6.83, 2.43, 2.26, 1.88 (*m*-Mes^A / *m*'-Mes^A, *o*-CH_3^{MesA}, *p*-CH_3^{MesA}, *o*'-CH_3^{MesA}), 6.83 / 6.86, 2.43, 2.26, 1.88 (*m*'-Mes^A/ *m*-Mes^A, *o*-CH_3^{MesA}, *p*-CH_3^{MesA}, *o*'-CH_3^{MesA}), 6.79 / 6.77, 2.43, 2.19, 1.85 (*m*-Mes^B / *m*'-Mes^B, *o*'-CH_3^{MesB}, *p*-CH_3^{MesB}, *o*-CH_3^{MesB}), 6.77 / 6.79, 2.43, 2.19, 1.85 (*m*'-Mes^B / *m*-Mes^B, *o*'-CH_3^{MesB}, *p*-CH_3^{MesB}, *o*-CH_3^{MesB}), 5.98 / 5.91, 2.56 (4-H / 3-H, 1-H), 5.91 / 5.98, 2.48 (3-H / 4-H, 2-H), 4.65, 4.64 / 3.00, 2.59, 2.48 (8-H, 9-H / 10-H, 1-H, 2-H), 3.00 / 4.65, 4.64, 2.59 (10-H / 8-H, 5-H, 1-H), 2.93, 2.77 / 2.14, 0.28 ($^PCH_2$ / $^BCH_2$), 2.59 / 4.65, 4.64, 3.00, 2.48 (1-H / 8-H, 9-H, 10-H, 2-H), 2.56 / 5.98, 1.03, 0.71 (5-H / 4-H, 12'-CH_3, 6-CH_3), 2.48 / 5.91, 4.65, 4.64, 1.48 (2-H / 3-H, 8-H, 9-H, 12-CH_3), 2.43 / 6.86, 6.77 (*o*-CH_3^{MesA}, *o*'-CH_3^{MesB} / *m*-Mes^A, *m*'-Mes^B), 2.26 / 6.83 (*p*-CH_3^{MesA} / *m*'-Mes^A), 2.19 / 6.79, 6.77 (*p*-CH_3^{MesB} / *m*'-Mes^A, *m*-Mes^A), 2.14, 0.28 / 2.93, 2.77 ($^BCH_2$ / $^PCH_2$), 1.88 / 6.83 (*o*'-CH_3^{MesA} / *m*'-Mes^A), 1.85 / 6.79 (*o*-CH_3^{MesB} / *m*-Mes^B), 1.48 / 2.48 (12-CH_3 / 2-H), 1.03 / 2.56 (12'-CH_3 / 5-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 253 K, [d_2]-CH_2Cl_2): δ (^{1}H) / δ (^{13}C) = 6.86 / 131.1 (*m*-Mes^A), 6.83 / 131.2 (*m*'-Mes^A), 6.79 / 132.5 (*m*-Mes^B), 6.77 / 131.0 (*m*'-Mes^B), 5.98 / 135.7 (4-H), 5.91 / 133.2 (3-H), 4.65 / 123.4 (8-H), 4.64 / 45.7 (9-H), 3.00 / 35.7 (10-H), 2.93, 2.77 / 25.4 ($^PCH_2$), 2.59 / 54.4 (1-H), 2.56 / 52.3 (5-H), 2.48 / 46.5 (2-H), 2.43 / 25.1, 24.6 (*o*-CH_3^{MesA}, *o*'-CH_3^{MesB}), 2.26 / 20.8 (*p*-CH_3^{MesA}), 2.19 / 20.6 (*p*-CH_3^{MesB}), 2.14, 0.28 / 15.8 ($^BCH_2$), 1.88 / 22.5 (*o*'-CH_3^{MesA}), 1.85 / 22.3 (*o*-CH_3^{MesB}), 1.48 / 19.9 (12-CH_3), 1.03 / 17.7 (12'-CH_3), 0.71 / 26.3 (6-CH_3), 0.64 / 26.2 (6'-CH_3).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 253 K, [d_2]-CH_2Cl_2): δ (^{1}H) / δ (^{13}C) = 6.86 / 131.2, 122.3, 25.1, 20.8 (*m*-Mes^A / *m*'-Mes^A, *i*-Mes^A, *o*-CH_3^{MesA}, *p*-CH_3^{MesA}), 6.83 / 131.1, 122.3, 22.5, 20.8 (*m*'-Mes^A / *m*-Mes^A, *i*-Mes^A, *o*'-CH_3^{MesA}, *p*-CH_3^{MesA}), 6.79 / 131.0, 122.2, 22.3, 20.6 (*m*_Mes^B / *m*'-Mes^B, *i*-Mes^B, *o*-CH_3^{MesB}, *p*-CH_3^{MesB}), 6.77 / 132.5, 122.2, 24.6, 20.6 (*m*'-Mes^B / *m*-Mes^B, *i*-Mes^B, *o*'-CH_3^{MesB}, *p*-CH_3^{MesB}), 5.98 / 141.7, 52.3, 46.5 (4-H / C11, C5, C2), 5.91 / 141.7, 52.3, 46.5 (3-H / C11, C5, C2), 4.65 / 159.0, 41.4 (8-H / C7, C6), 4.64 / 54.4 (9-H / C1), 2.56 / 159.0, 141.7, 133.2, 46.5, 41.4 (5-H / C7, C3, C2, C6), 2.43 / 143.4, 142.6, 131.1, 131.0, 122.2 (*o*-CH_3^{MesA}, *o*'-CH_3^{MesB} / *o*-Mes^A, *o*'-Mes^B, *p*-Mes^B, *m*-Mes^A, *m*'-Mes^B, *i*-Mes^B), 2.26 / 140.4, 131.2, 122.3 (*p*-CH_3^{MesA} / *o*'-Mes^A, *m*'-Mes^A, *i*-Mes^A), 2.19 / 142.6, 132.5, 131.0, 122.2 (*p*-CH_3^{MesB} / *p*-Mes^B, *m*-Mes^B, *m*'-Mes^B, *i*-Mes^B), 1.88 / 140.4, 131.2, 122.3 (*o*'-CH_3^{MesA} / *o*'-Mes^A, *m*'-Mes^A, *i*-Mes^A), 1.85 / 140.8, 132.5, 122.2 (*o*-CH_3^{MesB} / *o*-Mes^B, *m*-Mes^B, *i*-Mes^B), 1.48 / 141.7, 115.9, 17.7 (12-CH_3 / C11, C12, 12'-CH_3), 1.03 / 141.7, 115.9, 19.9 (12'-CH_3 / C11, C12, 12-CH_3), 0.71 / 159.0, 52.3, 41.4, 26.2 (6-CH_3 / C7, C5, C6, 6'-CH_3), 0.64 / 159.1, 52.3, 41.4, 26.3 (6'-CH_3 / C7, C5, C6, 6-CH_3).

^{11}B{^{1}H} NMR (192 MHz, 253 K, [d_2]-CH_2Cl_2): δ = –14.0 ($\nu_{1/2}$ = 160 Hz).

^{11}B NMR (192 MHz, 253 K, [d_2]-CH_2Cl_2): δ = –14.0 ($\nu_{1/2}$ = 170 Hz).

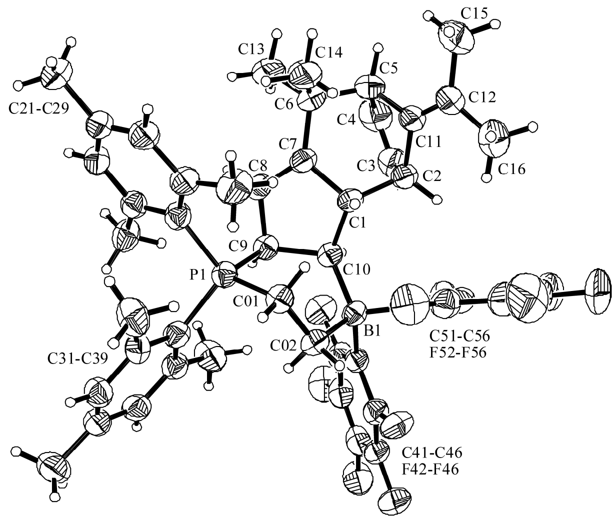
^{31}P{^{1}H} NMR (242 MHz, 253 K, [d_2]-CH_2Cl_2): δ = 33.2 ($\nu_{1/2}$ = 15 Hz).

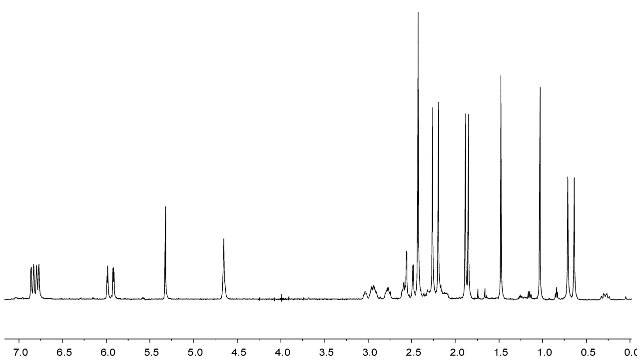
^{31}P NMR (242 MHz, 253 K, [d_2]-CH_2Cl_2): δ = 33.2 ($\nu_{1/2}$ = 110 Hz).

^{19}F{^{1}H} NMR (564 MHz, 253 K, [d_2]-CH_2Cl_2): δ = –129.2 (1F, *o*), –134.1 (1F, *o*'), –163.3 (1F, *p*), –165.6 (1F, *m*), –166.0 (1F, *m*') [$\Delta\delta_{m,p}$ = 2.3/2.7] ($C_6F_5^A$), –129.9 (1F, *o*), –138.6 (1F, *o*'), –163.5 (1F, *p*), –165.5 (1F, *m*), –166.9 (1F, *m*') [$\Delta\delta_{m,p}$ = 2.0/3.4] ($C_6F_5^B$).

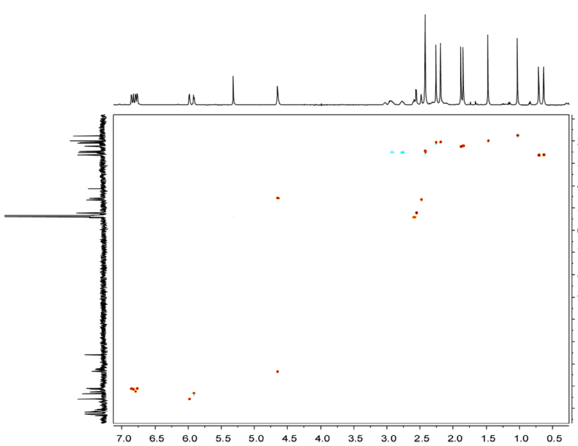
^{19}F,^{19}F GCOSY (564 MHz / 564 MHz, 253 K, [d_2]-CH_2Cl_2): δ (^{19}F) / δ (^{19}F) = –129.2 /–165.6 (*o*-$C_6F_5^A$ / *m*-$C_6F_5^A$), –129.9 / –165.5 (*o*-$C_6F_5^B$ / *m*-$C_6F_5^B$, *m*-$C_6F_5^B$), –134.1 /–166.0 (*o*'-$C_6F_5^A$ / *m*'-$C_6F_5^A$), –138.6 /, –166.9 (*o*'-$C_6F_5^B$ / *m*'-$C_6F_5^B$), –163.3 / –165.6,–166.0 (*p*-$C_6F_5^A$ / *m*-$C_6F_5^A$, *m*'-$C_6F_5^A$), –163.5 / –165.5, –166.9 (*p*-$C_6F_5^B$ / *m*-$C_6F_5^B$, *m*'-$C_6F_5^B$), –165.5 / –129.9, –163.5 (*m*-$C_6F_5^B$ / *o*-$C_6F_5^B$, *p*-$C_6F_5^B$), –165.6 / –129.2, –163.3 (*m*-$C_6F_5^A$ / *o*-$C_6F_5^A$, *p*-$C_6F_5^A$), –166.0 / –134.1, –163.3 (*m*'-$C_6F_5^A$ / *o*'-$C_6F_5^A$, *p*-$C_6F_5^A$),–166.9 / –138.6,–163.5 (*m*'-$C_6F_5^B$ / *o*'-$C_6F_5^B$, *p*-$C_6F_5^B$).

X-ray crystal structure analysis of 6: formula $C_{48}H_{46}BF_{10}P$ * 1.5 C_6H_6, *M* = 971.79, colorless crystal 0.30 x 0.15 x 0.07 mm, *a* = 12.3700(4), *b* = 11.0380(3), *c* = 36.1547(9)Å, *β* = 90.729(1)º, *V* = 4936.2(3) Å^3, ρ_{calc} = 1.308 g cm^{-3}, μ= 1.139 mm^{-1}, empirical absorption correction (0.726 ≤ *T* ≤ 0.925), *Z* = 4, monoclinic, space group $P2_1$/n (No. 14), λ= 1.54178 Å, *T* = 223(2) K, ω and φ scans, 26710 reflections collected (±*h*, ±*k*, ±*l*), [(sinθ)/λ] = 0.60 Å^{-1}, 8274 independent (R_{int} = 0.055) and 5776 observed reflections [*I* ≥ 2 σ(*I*)], 632 refined parameters, *R* = 0.053, wR^2 = 0.139, max. (min.) residual electron density 0.29 (-0.28) e Å^{-3}, hydrogen atoms calculated and refined as riding atoms.

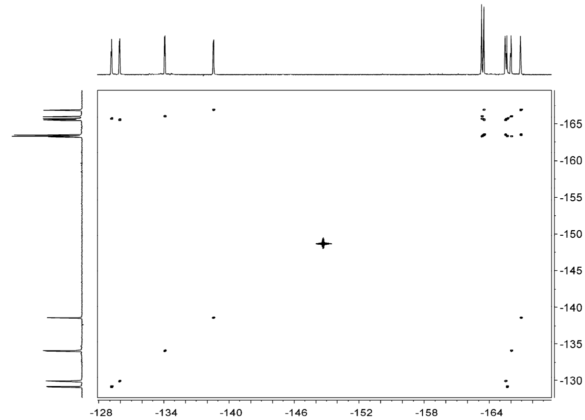




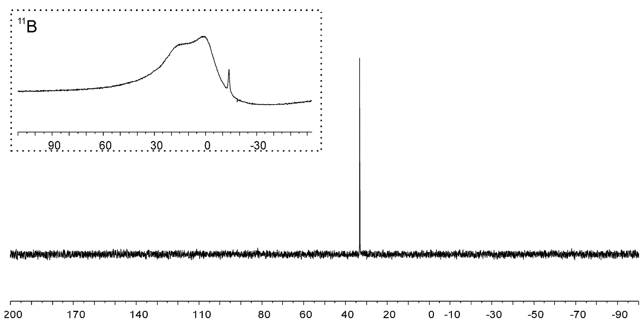
^{1}**H NMR** (600 MHz, 253 K, [d_2]-CH_2Cl_2).



^{1}**H,**^{13}**C GHSQC** (600 MHz / 151 MHz, 253 K, [d_2]-CH_2Cl_2).

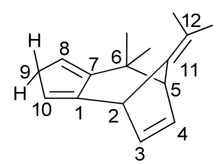


^{19}**F,**^{19}**F GCOSY** (564 MHz / 564 MHz, 253 K, [d_2]-CH_2Cl_2).



^{31}**P{**^{1}**H} NMR** (242 MHz, 253 K, [d_2]-CH_2Cl_2) and ^{11}**B{**^{1}**H} NMR** (192 MHz, 253 K, [d_2]-CH_2Cl_2).

Synthesis of 7



Heating of a deuterated benzene (1 mL) solution of **6** (74 mg, 0.08 mmol) for 6 h at 85 °C yielded **7**. After filtration through silica gel (eluent: pentane) and evaporation of pentane *in vacuo* **7** could be isolated (6.6 mg, 36%) with pentane as impurity, since prolonged drying of the compound *in vacuo* led to the loss of the product due to its volatility.

Exact mass (GC-MS, t_R: 9.57 min, EI^+): calc. for $C_{16}H_{20}$: 212.1565. Found: 212.1573; calc. for $[C_{16}H_{20}+H]^+$: 213.1599. Found: 213.1519.

^{1}**H NMR** (600 MHz, 298 K, [d_6]-benzene): δ = 6.13 (1H, dd, $^{3}J_{HH}$ = 5.9 Hz, 3.0 Hz, 3-H), 6.02 (1H, dd, $^{3}J_{HH}$ = 5.9 Hz, 3.0 Hz, 4-H), 5.96 (1H, m, 8-H), 5.76 (1H, m, 10-H), 3.97 (1H, d, $^{3}J_{HH}$ = 3.0 Hz, 2-H), 2.83 (1H, d, $^{3}J_{HH}$ = 3.0 Hz, 5-H), 2.69, 2.68 (each 1H, ABX_2, $^{2}J_{HH}$ = 23.8 Hz, $^{3}J_{HH}$ = 1.6 Hz, 9-H), 1.61 (3H, s, 12-CH_3), 1.60 (3H, s, 12'-CH_3), 1.25 (3H, s, 6-CH_3), 1.21 (3H, s, 6'-CH_3).

^{1}**H{**^{1}**H}-HD** (600 MHz, 298 K, [d_6]-benzene): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 5.96 / 2.69, 2.68 (8-H / 9-H (ABX, $^{2}J_{HH}$ = 23.8 Hz,

$^{3}J_{HH}$ = 1.6 Hz)), 5.76 / 2.69, 2.68 (10-H / 9-H (ABX, $^{2}J_{HH}$ = 23.8 Hz, $^{3}J_{HH}$ = 1.6 Hz)), 5.96, 5.76 / 2.69, 2.68 (8-H, 10-H / 9-H (AB, $^{2}J_{HH}$ = 23.8 Hz)).

^{13}C{^{1}H} NMR (151 MHz, 298 K, [*d*$_6$]-benzene): δ = 154.1 (C7), 145.5 (C1), 141.4 (C11), 137.5 (C3), 134.2 (C4), 126.3 (C8), 119.4 (C10), 117.3 (C12), 52.7 (C5), 44.8 (C2), 40.7 (C6), 39.4 (C9), 32.4 (6-CH_3), 27.8 (6'-CH_3), 20.3 (12'-CH_3), 19.7 (12-CH_3).

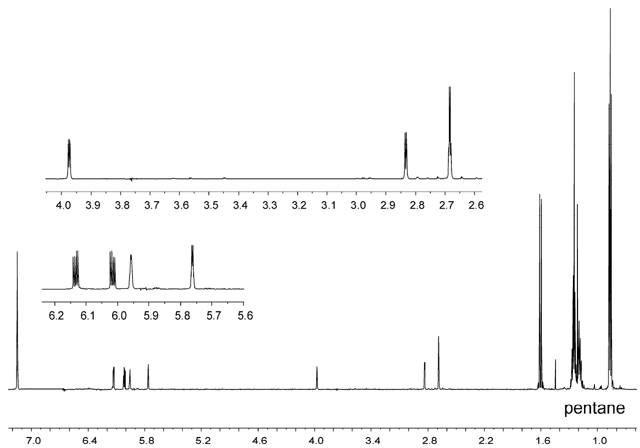
^{1}H TOCSY (600 MHz, 298 K, [*d*$_6$]-benzene): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 6.13 / 6.02, 3.97, 2.83, 2.68 (3-H / 4-H, 2-H, 5-H, 9-H), 6.02 / 6.13, 3.97, 2.83, 2.68, 1.60 (4-H / 3-H, 2-H, 5-H, 9-H, 12'-CH_3), 5.96 / 5.76, 3.97, 2.83 (8-H / 10-H, 2-H, 5-H), 5.76 / 5.96, 3.97, 2.83 (10-H / 8-H, 2-H, 5-H), 3.97 / 6.13, 6.02, 2.83, 2.68 (2-H / 3-H, 4-H, 5-H, 9-H), 2.83 / 6.13, 6.02, 3.97 (5-H / 3-H, 4-H, 2-H), 2.68 / 5.96, 5.76, 3.97 (9-H / 8-H, 10-H, 2-H).

NOE-DIFF (600 MHz, 298 K, [*d*$_6$]-benzene): δ $^{1}H_{irr}$ / δ $^{1}H_{res}$ = 6.13 / 6.02, 3.97 (5-H / 4-H, 6-H), 6.02 / 6.13, 2.83, 1.21 (4-H / 5-H, 3-H, 2'-CH_3), 5.96 / 5.76, 2.69, 2.68, 1.25, 1.21 (8-H / 10-H, 9-H, 9-H, 6-CH_3, 6'-CH_3), 5.76 / 5.96, 3.97, 2.69, 2.68 (10-H / 8-H, 2-H, 9-H, 9-H), 3.97 / 6.13, 5.76, 1.61 (2-H / 3-H, 10-H, 12-CH_3), 2.83 / 6.02, 1.60, 1.25, 1.21 (5-H, 4-H, 12'-CH_3, 6-CH_3, 6'-CH_3), 2.69, 2.68 / 5.96, 5.76 (9-H / 8-H, 10-H).

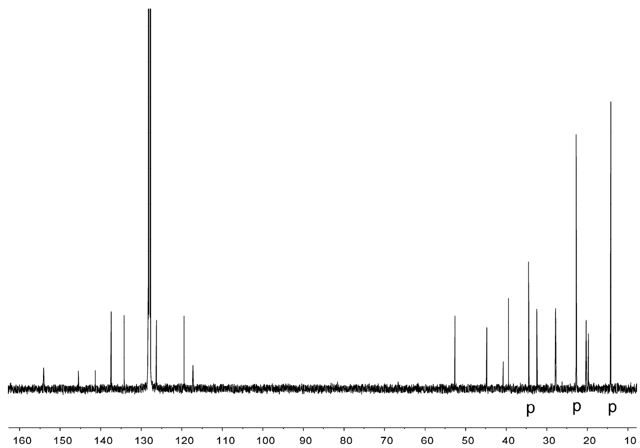
^{1}H,^{1}H GCOSY (600 MHz / 600 MHz, 298 K, [*d*$_6$]-benzene): δ (^{1}H, ^{1}H) = 6.13 / 6.02, 3.97 (3-H / 4-H,2-H), 6.02 / 6.13, 3.97, 2.83 (4-H / 3-H, 2-H, 5-H), 5.96 / 5.76, 3.97, 2.69, 2.68, 1.25 (8-H / 10-H, 2-H, 9-H, 9-H, 6-CH_3), 5.76 / 5.96, 3.97, 2.69, 2.68 (10-H / 8-H, 2-H, 9-H, 9-H), 3.97 / 6.13, 6.02, 5.96, 5.76, 2.83, 2.69, 2.68, 1.60 (2-H / 3-H, 4-H, 8-H, 10-H, 5-H, 9-H, 9-H, 12'-CH_3), 2.83 / 6.13, 6.02, 3.97, 1.61, 1.21 (5-H / 3-H, 4-H, 2-H, 12-CH_3, 6'-CH_3), 2.69, 2.68 / 5.96, 5.76, 3.97, 1.60, 1.25 (9-H / 8-H, 10-H, 2-H, 12'-CH_3, 6-CH_3), 1.61 / 2.83 (12-CH_3 / 5-H), 1.60 / 3.97, 2.69, 2.68 (12'-CH_3 / 2-H, 9-H, 9-H), 1.25 / 2.69, 2.68 (6-CH_3 / 9-H, 9-H), 1.21 / 2.83 (6'-CH_3 / 5-H).

^{1}H,^{13}C GHSQC (600 MHz / 151 MHz, 298 K, [*d*$_6$]-benzene): δ (^{1}H) / δ (^{13}C) = 6.13 / 137.5 (3-H), 6.02 / 134.2 (4-H), 5.96 / 126.3 (8-H), 5.76 / 119.4 (10-H), 3.97 / 44.8 (2-H), 2.83 / 52.7 (5-H), 2.69, 2.68 / 39.4 (9-H), 1.61 / 19.7 (12-CH_3), 1.60 / 20.3 (12'-CH_3), 1.25 / 32.4 (6-CH_3), 1.21 / 27.8 (6'-CH_3).

^{1}H,^{13}C GHMBC (600 MHz / 151 MHz, 298 K, [*d*$_6$]-benzene): δ (^{1}H) / δ (^{13}C) = 6.13 / 141.4, 134.2, 52.7, 44.8 (3-H / C11, C4, C5, C2), 6.02 / 141.4, 137.5, 52.7, 44.8 (4-H / C11, C3, C5, C2), 5.96 / 154.1, 145.5, 119.4, 39.4 (8-H / C7, C1, C10, C9), 5.76 / 154.1, 145.5, 126.3, 39.4 (10-H / C7, C1, C8, C9), 3.97 / 154.1, 145.5, 137.5, 134.2, 119.4, 117.3, 52.7 (2-H / C7, C1, C3, C4, C10, C12, C5), 2.83 / 154.1, 141.4, 137.5, 134.2, 117.3, 44.8, 40.7, 32.4 (5-H / C7, C11, C3, C4, C12, C2, C6, 6-CH_3), 2.68, 2.69 / 154.1, 145.5, 126.3, 119.4, 32.4 (9-H / C7, C1, C8, C10, 6-CH_3), 1.61 / 141.4, 117.3, 40.7, 20.3, 19.7 (12-CH_3 / C11, C12, C6, 12'-CH_3, 12-CH_3), 1.60 / 145.5, 141.4, 137.5, 117.3, 40.7, 20.3, 19.7 (12'-CH_3 / C1, C11, C3, C12, C6, 12'-CH_3, 12-CH_3), 1.25 / 154.1, 52.7, 40.7, 32.4, 27.8 (6-CH_3 / C7, C5, C6, 6-CH_3, 6'-CH_3), 1.21 / 154.1, 52.7, 40.7, 32.4, 27.8 (6'-CH_3 / C7, C5, C6, 6-CH_3, 6'-CH_3).



^{1}H NMR (600 MHz, 298 K, [*d*$_6$]-benzene).



^{13}C{^{1}H} NMR (151 MHz, 298 K, [*d*$_6$]-benzene) [p: pentane].

Notes

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