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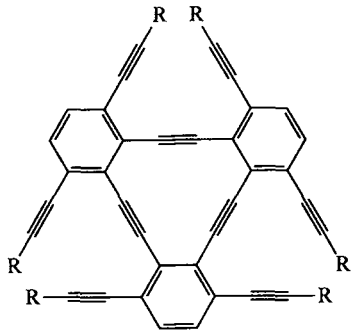
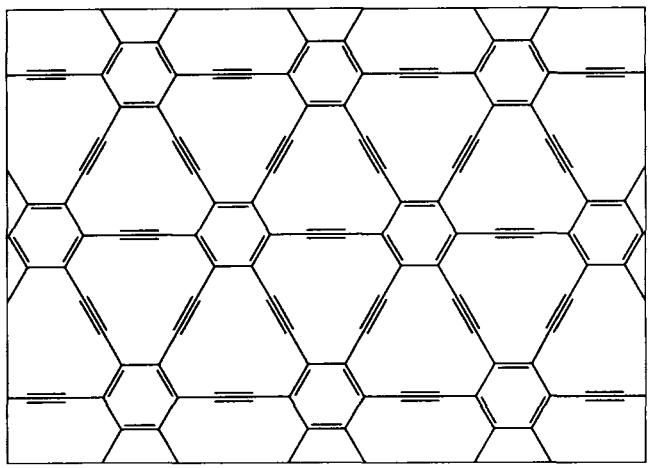
5,6,11,12,17,18-Hexadehydro-1,4,7,10,13,16-hexaethynyltribenzo[*a*,*e*,*i*]cyclododecene: Synthesis and CpCo-Catalyzed Cycloisomerization to the First Superdelocalized Oligophenylenes**

Christian Eickmeier, Heiko Junga, Adam J. Matzger, Frank Scherhag, Moonsub Shim, and K. Peter C. Vollhardt*

The title molecule ("hexaethynyltribenzocyclyne") **1a** is of great interest as a subunit of graphyne **2**,[1] a partially carbomeric[2] graphitic carbon allotrope,[3] as an extended π framework for ligating transition metals with unusual properties,[4] and as a precursor to antikekulene **3** by means of threefold CpCo-catalyzed cycloisomerization.[5] Compound **3** constitutes a much theoretically scrutinized[6] member of the as yet unknown circular phenylenes.[7]



1a, R = H
1b, R = $Si(CH_3)_2[C(CH_3)_2CH(CH_3)_2]$
1c, R = Pr
1d, R = $CH_2C_6H_{11}$



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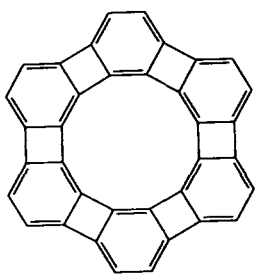
Compound **3** is intriguing in its juxtaposition to kekulene **4**,[8] which has the same number of rings but inner and outer π perimeters with a $4n+2$ electron count, whereas in **3**, the corresponding circuits are of the $4n$ type. However, in **4**, the annulenoid resonance forms suffer from the disruption of all benzenoid circuits and appear to be negligible contributors, as borne out by theory[6c, e, f, 9] and experiment.[8] In contrast, the nonannulenoid resonance alternatives to that depicted in **3** are all expected to be considerably destabilized by cyclobutadienoid antiaromaticity, an underlying feature of all phenylenes.[7] Thus, **3** might be a better candidate than **4** for probing the phenomenon of superdelocalization, although the notion of the



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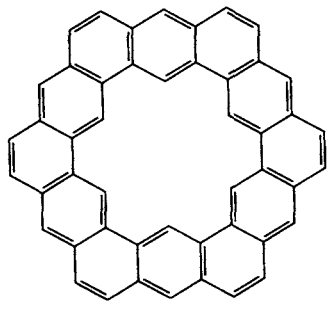

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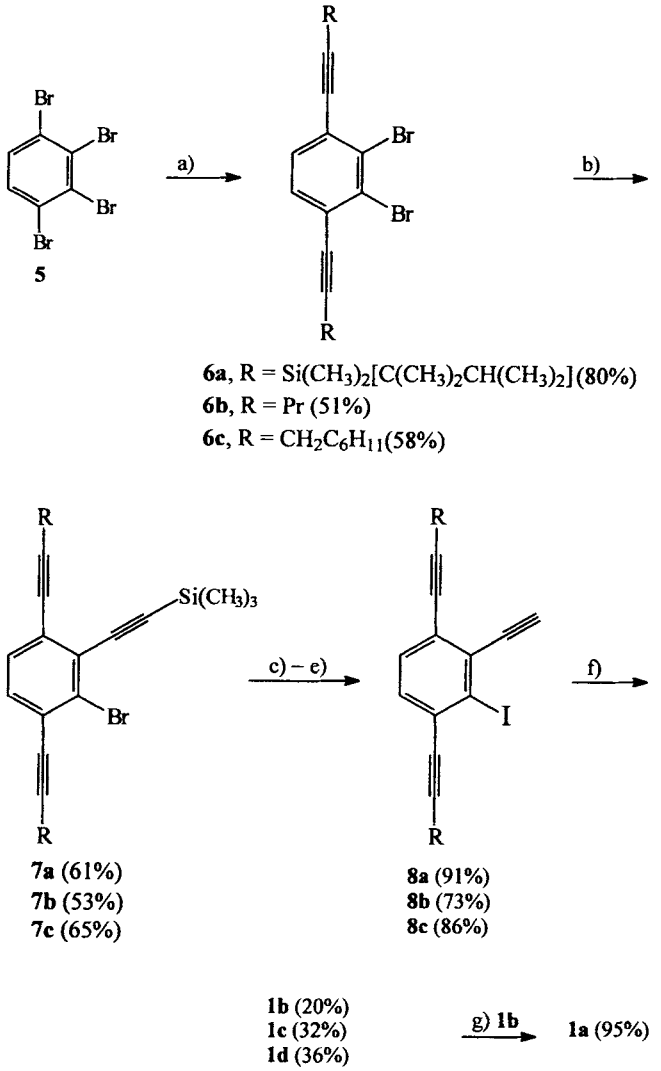
latter has been met with skepticism by some theoreticians.[6] We report here the total synthesis of **1a–d** and their reactivity in the presence of $[CpCo(CO)_2]$, which has led to the first superdelocalized oligophenylenes **9a,b** and **10a,b**.

Scheme 1 details the synthetic strategy toward **1**, which has as its cornerstone the discovery that 1,2,3,4-tetrabromobenzene



Scheme 1. a) RC≡CH, 1–2% CuI, 1–2% $[PdCl_2(PPh_3)_2]$, Et_3N, 23–60 °C, 3 d; b) $(CH_3)_3SiC_2H$, 1–2% CuI, 1–2% $[PdCl_2(PPh_3)_2]$, Et_3N, 100 °C, 4 h–2.5 d; c) BuLi, $(CH_3CH_2)_2O$, −78 °C, 30 min; d) I_2, $(CH_3CH_2)_2O$, −78 → 23 °C; e) K_2CO_3, CH_3OH or NaOH, CH_3OH or $Bu_4N^+F^-$, THF, 1 h; f) CuCl, NH_4OH, EtOH (DMSO for **8c**), pyridine, Δ, 6 h; g) $Bu_4N^+F^-$, THF, CH_3CN, 5 h.

(**5**)[10] can be regioselectively alkynylated at C1 and C4 to furnish **6**, then at C3 to give **7**, using Pd catalysis.[11] The regiochemistry of **6** was confirmed by debromination to the *p*-dialkynylbenzenes (1. *t*BuLi, 2. H_2O) and further transformations (vide infra). The bromine substituent in **7** is unsuitable for the protocol that constructs the tribenzocyclyne frame of **1**[12] and therefore was replaced by iodine. The C2-ethynyl group was selectively deprotected and cyclization of **8a–c** yielded **1b–d**.

The parent nonayne **1a** was readily accessible by desilylation of **1b**. It is relatively stable even in the solid state, and it can be conveniently handled in solution, which bodes well for its continuing elaboration into larger networks. Models show that the R groups in **1** are severely congested and indeed the X-ray structural analysis of **1d** (Figure 1)[13] reveals a severely distorted cyclyne frame with local C_2 symmetry, dihedral angles between the mean planes of the three benzene rings of 25.4, 30.8, and 31.4°, and deviations from linearity of the triple bonds within (average 174.3°, range 169.6–178.1°) and without (average 175.5°, range 171.7–179.9°) the cyclyne ring. All cyclohexyl groups adopt chair conformations. Apart from these features, the molecular structure is remarkably similar to that of the unsubstituted core system.[14b] The most noteworthy aspect of the spectral data of **1** (Table 1) is the much lower intensity of the longest wavelength UV band ($\pi-\pi^*$ transition) observed for the parent tribenzocyclyne at 290 nm ($\lg\varepsilon = 5.57$), which was associated with the rigid planarity of the latter,[14] a characteristic that is absent in **1**.

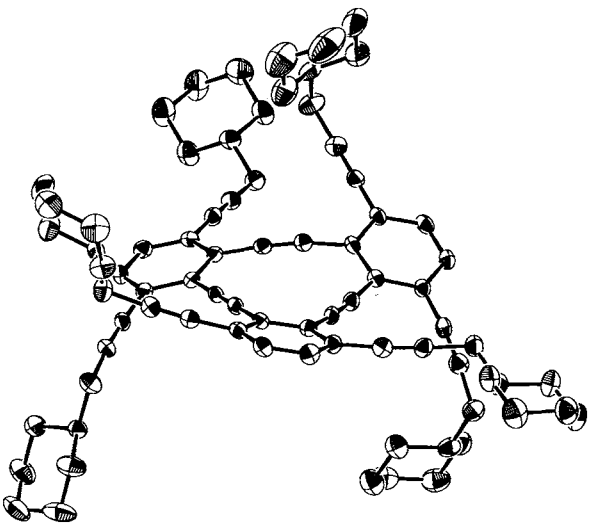


Figure 1. Molecular structure of **1d** in the crystal.

With **1a** in hand, our first concern was its potential to isomerize to **3** in the presence of $[CpCo(CO)_2]$. Calculations were encouraging in this respect, suggesting each of the three individual [2+2+2]cycloadditions to be exothermic (−14.5, −13.4, and −10.0 kcal mol^{-1} (PM3);[15a] for the last step: −31.0 kcal mol^{-1} (HF/6-31G*),[15b] −45.50 kcal mol^{-1} (B3LYP/6-31G*);[15b] comparable to the values calculated for the cyclization to angular [3]phenylene). Unfortunately, in practice, **1a** gave only insoluble dark brown powders. Suspecting lack of solubility of the target (or intermediates en route) as a potential problem in these experiments, we turned to the substituted nonaynes **1b–d**, with better, albeit not complete, success. Thus, while **1b** gave intractable mixtures, **1c** and **1d** provided **9a,b** and **10a,b**, respectively, either directly as mixtures or by a stepwise sequence (Scheme 2, Table 1).[11] The isolation of **9a,b** was possible because they cyclize noticeably slower than **1c,d**. This trend continues for **10a,b** which, despite extensive experimentation with conditions (solvent, temperature, addition rates, light sources), could not be induced to furnish the antikekulene core, but rather gave either recovered starting material or decomposition (>170 °C, sulfolane or 1-methylnaphthalene).

Because of the novelty of the "circularly" conjugated phenylenes **9** and **10**, X-ray structural determinations of **9b** and **10b** were carried out (Figures 2 and 3, respectively).[13] Similar to **1d** (Figure 1), the twelve-membered ring in **9b** is significantly (although less) distorted from planarity; the plane of the nonphenylene benzene forms an angle of 18.4° with the mean plane of the dehydro[12]annulene cycle. Unlike the parent angular

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Table 1. Selected physical data for **1a**, **1b**, **1d**, **9b**, **10a,b**, and **11** [11].

1a: yellow solid ($CHCl_3$), m.p. > 100 °C (decomp); MS (70 eV): *m/z* (%): 444 (M^+, 10), 149 (100); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (s, 6H), 3.32 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, [D$_{10}$]1,2-dimethoxyethane): δ = 133.4, 128.9, 126.0, 106.5, 99.2, 94.9; IR (KBr): $\tilde{\nu}$ = 3292, 2957, 2924, 2854, 2108, 1461, 830, 660, 621 cm^{-1}; UV/Vis (isooctane): λ_{max} (lgε) = 222 (3.20), 243 (3.31), 261 (3.34), 288 (3.30), 306 (3.37), 316 (3.29), 329 (3.66) nm

1b: yellow crystals (*i*PrOH), m.p. 197–198 °C; MS (70 eV): *m/z* (%): 1298 (M^+, 20), 1213 (22), 1129 (100), 1044 (50); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (s, 6H), 1.73 (sept, *J* = 6.9 Hz, 6H), 0.93 (s, 36H), 0.90 (d, *J* = 6.9 Hz, 36H), 0.28 (s, 36H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 132.2, 129.4, 126.2, 104.0, 102.3, 96.8, 34.5, 23.8, 20.8, 18.7, −2.40; IR (KBr): $\tilde{\nu}$ = 2958, 2866, 2153, 1462, 1250, 838, 822, 776, 674 cm^{-1}; UV/Vis (isooctane): λ_{max} (lgε) = 253 (4.71), 285 (4.93), 308 (4.97), 340 (4.81), 385 sh (3.8) nm. High-resolution FAB-MS calcd for $C_{84}H_{121}Si_6$: 1297.8084; found: 1297.8075

1d: yellow crystals (*i*PrOH/CH_2Cl_2), m.p. 144–145 °C; FAB-MS: *m/z* (%) : 1021 (M^+,100); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (s, 6H), 2.31 (d, *J* = 6.8 Hz, 12H), 1.91–1.79 (m, 12H), 1.72—1.52 (m, 24H), 1.28–0.93 (m, 30H); $^{13}C\{^1H\}$ NMR and DEPT 135 (100 MHz, $CDCl_3$): δ = 132.0 (CH), 129.0, 126.2, 96.0, 95.8, 80.1, 37.6 (CH), 32.9 (CH_2), 28.0 (CH_2), 26.3 (CH_2), 26.1 (CH_2); IR (KBr): $\tilde{\nu}$ = 2923, 2851, 2226, 1465, 1448, 1118, 827 cm^{-1}; UV/Vis (isooctane): λ_{max} (lgε) = 232 (4.73), 243 sh (4.77), 248 (4.83), 275 (4.97), 301 (4.90), 313 (4.89), 319 sh (4.82), 336 (5.02), 382 (3.87), 402 (3.84) nm. High-resolution MS calcd for $C_{78}H_{84}$: 1020.6573; found: 1020.6564

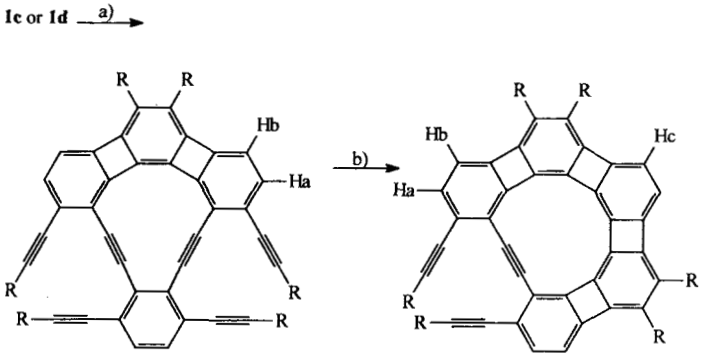
9b: orange crystals (*i*PrOH/CH_2Cl_2), m.p. 210–211 °C; FAB-MS: *m/z* (%): 1021 (M^+, 100); ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.16 (s, 2H), 7.00 (d, *J* = 7.4 Hz, 2H), 6.61 (d, *J* = 7.3 Hz, 2H), 2.34 (d, *J* = 6.9 Hz, 4H), 2.30 (d, *J* 6.9 Hz, 4H), 2.15 (d, *J* = 7.0 Hz, 4H), 1.91–1.82 (m, 8H), 1.81–1.48 (m, 24H), 1.48–1.38 (m, 2H), 1.33–0.86 (m, 32H); $^{13}C\{^1H\}$ NMR and DEPT 135 (100 MHz, CD_2Cl_2): δ = 151.5, 150.2, 146.6, 134.5 (CH), 133.6, 132.8 (CH), 131.6, 128.8, 126.6, 125.1, 118.0 (CH), 116.4, 96.7, 94.3, 94.0, 93.4, 81.2, 80.4, 39.4, (CH), 38.2 (CH), 38.1 (CH), 37.2 (CH_2), 34.0 (CH_2), 33.3 (CH_2, 2C), 28.3 (CH_2), 26.9 (CH_2), 26.8 (CH_2), 26.73 (CH_2), 26.71 (CH_2), 26.59 (CH_2, 2C); IR (KBr): $\tilde{\nu}$ = 2923, 2850, 2224, 1448, 1068, 824 cm^{-1}; UV/Vis (THF): λ_{max} (lgε) = 250 (4.94), 261 (4.81), 269 (4.81), 306 (5.05), 327 (4.67), 335 sh (4.59), 372 (4.18), 389 (4.34), 399 sh (4.23), 415 (4.08), 444 (3.94), 484 (3.78), 516 (3.11) nm. High-resolution MS calcd for $C_{78}H_{84}$: 1020.6573; found: 1020.6584

10a: red solid (CH_2Cl_2), m.p. > 250 °C (decomp); MS (70 eV): *m/z* (%): 696 (M^+, 100), 207 (6), 97 (6), 83 (8), 69 (13), 57 (22); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.93 (d, *J* = 7.2 Hz, 2H), 6.54 (d, *J* = 7.2 Hz, 2H), 6.30 (s, 2H), 2.39 (t, *J* = 7.8 Hz, 4H), 2.33–2.25 (m, 8H), 1.68–1.46 (m, 12H), 1.02 (t, *J* = 7.8 Hz, 6H), 0.97 (br t, *J* = 7.8 Hz, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, CS_2): δ = 151.6, 150.4, 149.3, 148.5, 146.0, 135.0, 134.4, 134.3, 133.0, 132.8, 132.0, 125.4, 117.8, 116.8, 116.7, 94.8, 91.9, 81.1, 31.7, 31.6, 30.4, 23.52, 23.49, 23.2, 22.7, 14.8, 14.3; IR (KBr): $\tilde{\nu}$ = 2959, 2928, 2226, 1457, 1384, 818 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} = 263, 294, 326, 343, 379, 480, 554 nm. High-resolution MS calcd for $C_{54}H_{48}$: 696.3756; found: 696.3760

10b: dark red crystals (CCl_4), m.p. 290–295 °C; MS (70 eV): *m/z* (%): 1021 (M^+, 7), 285 (7), 263 (24), 207 (47), 169 (56), 146 (62), 103 (72), 69 (100); ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 6.93 (d, *J* = 7.4 Hz, 2H), 6.54 (d, *J* = 7.3 Hz, 2H), 6.30 (s, 2H), 2.40–0.70 (m, 78H); ^{1}H NMR (500 MHz, C_6D_6): δ = 7.03 (d, *J* = 7.3 Hz, 2H), 6.27 (s, 2H), 6.25 (d, *J* = 7.3 Hz, 2H), 2.44 (d, *J* = 6.8 Hz, 4H), 2.20 (d, *J* = 6.9 Hz, 4H), 2.11 (d, *J* = 6.8 Hz, 4H), 1.94 (dm, *J* = 11.6 Hz, 4H), 1.87 (dm, *J* = 11.3 Hz, 4H), 1.80 (dm, *J* = 12.5 Hz, 4H), 1.75–0.85 (m, 54H); IR (KBr): $\tilde{\nu}$ = 2922, 2850, 2222, 1449, 1262, 1176, 1096, 1032, 818 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 255 sh (4.96), 264 (5.03), 295 (4.93), 326 (4.61), 342 (4.54), 380 (4.46), 399 sh (4.12), 432 (3.82), 456 (3.74), 484 (3.68), 520 (3.00), 554 (3.13) nm

11: red crystals (CH_2Cl_2), m.p. 230–232 °C; MS (70 eV): *m/z* (%): 458 (M^+, 100), 398 (13), 229 (10), 200 (9); ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 6.97 (m, 4H), 6.90 (m, 2H), 6.83 (m, 2H), 6.47 (s, 2H), 6.17 (s, 2H), 2.36 (t, *J* = 7.3 Hz, 4H), 1.62 (sex, *J* = 7.4 Hz, 4H), 0.98 (t, *J* = 7.4 Hz, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2): δ = 151.8, 149.9, 149.5, 148.9, 143.4, 137.8, 136.4, 132.9, 131.5, 129.5, 128.2, 119.1, 118.6, 117.7, 116.2, 34.9, 23.0, 14.0; IR (KBr): $\tilde{\nu}$ = 2959, 2925, 2854, 1262, 1098, 1023, 802, 737 cm^{-1}; UV/Vis (CH_2Cl_2): λ_{max} (lgε) = 262 (4.82), 273 (4.86), 330 (4.69), 352 (4.71), 4.02 (3.81), 4.30 (3.93), 454 (3.93) nm

[3]phenylene,[5] the phenylene subunit in **9b** is slightly curved (dihedral angles between the mean planes of adjacent benzene and cyclobutadiene rings between 0.44 and 3.14°), a phenomenon that appears to be general.[16] In other respects, the structure of this unit, especially the pronounced bond alternation of its central benzene ring, is remarkably similar to that of the parent system; small deviations are due to the presence of the additional substituents, especially the alkyne groups which generally cause slight elongations in attached benzene ring



9a, R=Pr (13.8%)
9b, R=$CH_2C_6H_{11}$ (45%)

10a (13.6%)
10b (40%)

Scheme 2. a) [$CpCo(CO)_2$] (0.3–1 equiv), *m*-xylene, △, *hv*, 20 min; b) as in a) but with 1,2,4-trichlorobenzene as solvent, 160 °C, 3 h.

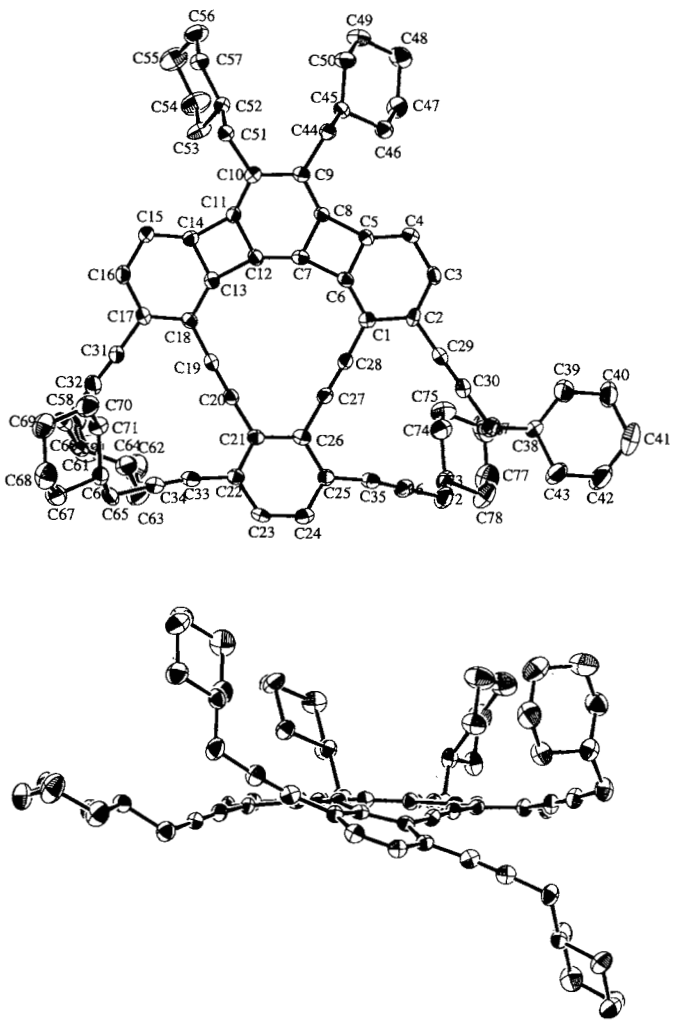


Figure 2. Structure of **9b** in the crystal: views from above (top) and the side (bottom). Selected distances [Å] and angles [°], averaged for idealized symmetry: C1–C2 1.430(4), C2–C3 1.400(4), C3–C4 1.400(4), C4–C5 1.371(4), C5–C6 1.418(4), C6–C1 1.381(4), C6–C7 1.499(4), C7–C8 1.459(4), C8–C5 1.505(4), C8–C9 1.357(4), C9–C10 1.465(4), C7–C12 1.353(4), C1–C28 1.429(4), C21–C22 1.410(4), C22–C23 1.399(4), C23–C24 1.375(4), C24–C25 1.399(4), C25–C26 1.410(4), C26–C27 1.432(4), C27–C28 1.204(4); C1-C2-C3 121.0(3), C2-C3-C4 122.9(3), C3-C4-C5 116.2(3), C4-C5-C6 121.1(3), C5-C6-C1 123.5(3), C5-C6-C7 90.5(3), C6-C7-C8 89.8(2), C7-C8-C5 88.7(2), C8-C5-C6 91.1(2), C7-C8-C9 126.7(3), C8-C9-C10 116.5(3), C12-C7-C8 116.9(3).

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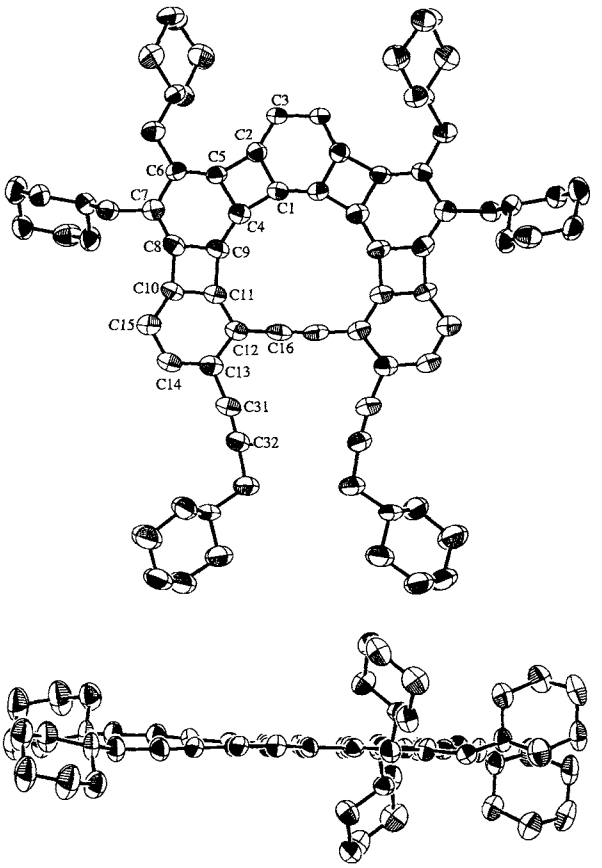
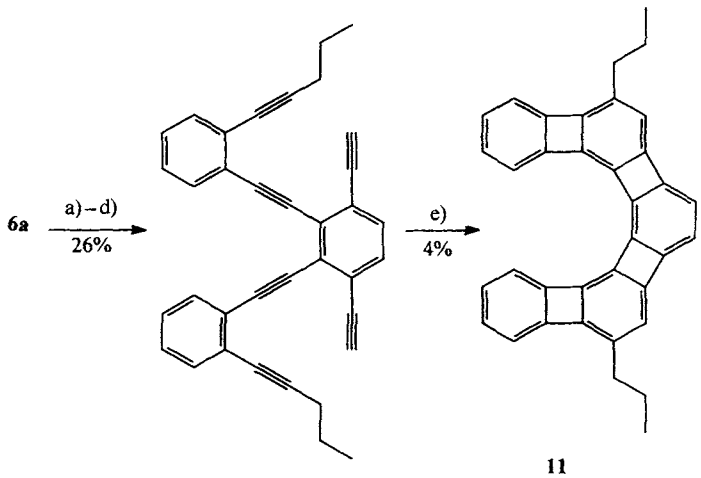


Figure 3. Structure of **10b** in the crystal: views from above (top) and the side (bottom). Selected distances [Å] and angles [°]: C1–C1′ 1.34(1), C1–C2 1.449(8), C2–C3 1.367(8), C3–C3′ 1.41(1), C1–C4 1.479(8), C4–C5 1.473(8), C2–C5 1.527(8), C5–C6 1.351(8), C6–C7 1.472(8), C7–C8 1.352(9), C8–C9 1.461(9), C9–C4 1.351(8), C8–C10 1.507(8), C10–C11 1.433(9), C9–C11 1.496(8), C11–C12 1.387(8), C12–C13 1.440(8), C13–C14 1.398(9), C14–C15 1.399(9), C10–C15 1.357(8), C12–C16 1.423(8), C16–C16′ 1.21(1), C13–C31 1.446(9), C31–C32 1.190(8); C1′-C1-C2 118.9(4), C1-C2-C3 122.1(6), C2-C3-C3′ 119.0(4), C1-C2-C5 89.8(5), C2-C5-C4 88.3(5), C1-C4-C5 90.9(5), C2-C1-C4 91.0(5), C4-C5-C6 125.2(6), C5-C6-C7 116.9(6), C6-C7-C8 117.1(7), C7-C8-C9 125.9(6), C4-C8-C9 117.1(6), C5-C4-C9 117.8(6), C8-C9-C11 90.9(6), C9-C11-C10 89.5(5), C8-C10-C11 91.5(5), C9-C8-C10 88.1(6), C10-C11-C12 124.8(6), C11-C12-C13 112.8(7), C12-C13-C14 121.9(7), C13-C14-C15 123.0(7), C10-C15-C14 116.5(7), C11-C12-C16 123.3(6), C12-C16-C16′ 177.5(5).

bonds.[1c, 3e, 14b] While the overall rigidity of the carbon frame increases noticeably when going from **1d** to **9b**, this effect is much more pronounced when continuing from **9b** to **10b** (Figure 3). The latter lies on a C_2 axis and exhibits a slightly helical angular [5]phenylene frame (dihedral angles between the mean planes of adjacent rings between 0.53 and 2.31°). The distances between the three alkyne units that would be called on in cyclotrimerization increase along the series **1**, **9**, **10**. That, along with the increasing rigidity of the structures, provides a rationale for their decreasing reactivity in the presence of [CpCo].

Because the parent angular [5]phenylene[17] could not be obtained in the form of crystals suitable for X-ray analysis and hence comparison with **10b**, the appropriately crystalline dipropyl derivative **11** (Table 1)[11] was prepared by a new, much shorter route (five steps) starting from **6a** (Scheme 3) in a variation of Scheme 1. The crystal structure of **11** is shown in Figure 4. The molecule is more pronouncedly helical than **10b** (dihedral angles between adjacent ring planes between 0.94 and 4.91°), and there is no significant contact between 5-H and 26-H (distance 2.59 Å, assuming a C–H bond length of 1.08 Å). Otherwise, the two structures are quite similar; minor deviations can be ascribed to the presence of the adjacent cyclohexylmethyl substituents and the added alkyne functions (vide supra) in **10b**. As indicated by the ^{1}H NMR data (Table 1),[17] the internal benzene rings have significant cyclohexatriene character. The bridging triple bond (C16–C16′) flattens **10b** relative to **11** and decreases the distance between the terminal benzene rings some-



Scheme 3. a) $(CH_3)_3SiC_2H$ (excess), 15% CuI, 15% $[PdCl_2(PPh_3)_2]$, piperidine, 110 °C, 7 d; b) K_2CO_3, CH_3OH, THF, 1 h; c) 1-iodo-2-(1-pentynyl)benzene (4 equiv), 10% CuI, 10% $[PdCl_2(PPh_3)_2]$, Et_3N, 100 °C, 7 d; d) $Bu_4N^+F^-$, THF, 1 h; e) $[CpCo(CO)_2]$ (2 equiv), xylenes, △, *hv*, 1 h.

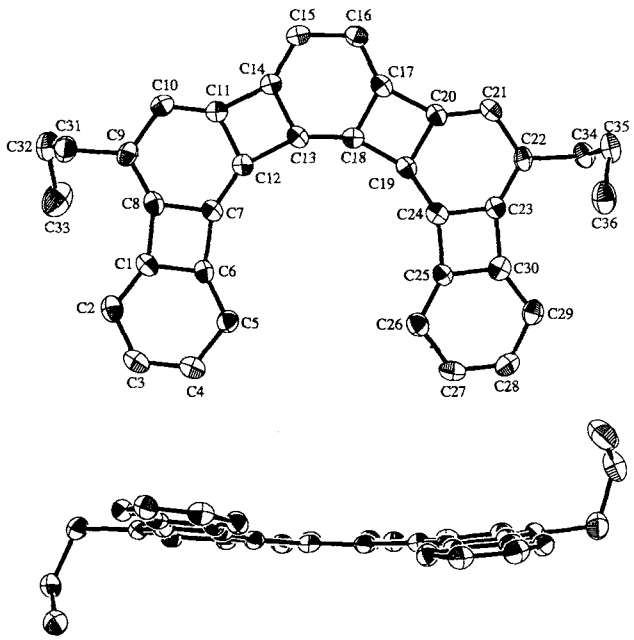


Figure 4. Structure of **11** in the crystal: views from above (top) and the side (bottom). Selected distances [Å] and angles [°], averaged for idealized symmetry: C1–C2 1.371(3), C2–C3 1.405(3), C3–C4 1.378(3), C4–C5 1.407(3), C5–C6 1.362(3), C1–C6 1.415(2), C6–C7 1.504(2), C7–C8 1.448(2), C1–C8 1.508(2), C8–C9 1.364(3), C9–C10 1.443(3), C10–C11 1.354(3), C11–C12 1.449(2), C7–C12 1.352(3), C12–C13 1.496(2), C13–C14 1.443(2), C11–C14 1.506(2), C14–C15 1.366(3), C15–C16 1.423(3), C13–C18 1.352(3); C1-C2-C3 116.1(3), C2-C3-C4 121.9(3), C3-C4-C5 122.0(3), C4-C5-C6 115.8(3), C1-C6-C5 122.7(3), C2-C1-C6 121.5(3), C1-C6-C7 90.2(2), C6-C7-C8 90.0(2), C1-C8-C7 88.8(2), C6-C1-C8 91.1(2), C7-C8-C9 125.8(3), C8-C9-C10 115.9(3), C9-C10-C11 118.8(3), C10-C11-C12 124.5(3), C7-C12-C11 117.7(3), C8-C7-C12 117.4(3), C11-C12-C13 90.3(2), C12-C13-C14 90.1(2), C11-C14-C13 90.2(2), C12-C11-C14 89.5(2), C13-C14-C15 124.0(3), C14-C15-C16 118.0(3), C18-C13-C14 118.0(3).

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what (e.g. C5–C26 in **11**: 4.69 Å; calculated for its planar conformer: 4.55 Å; C12–C12′ in **10b**: 4.06 Å). This change does not appear to greatly alter bond angles and lengths.[18] Thus, as perhaps expected, the X-ray data for **9b** and **10b** do not reveal any structural evidence for superdelocalization imparted by the bridging alkyne units.

Much more sensitive probes for such a phenomenon are UV and, especially, ^{1}H NMR measurements. Indeed, the longest wavelength maxima in the electronic spectra of **9a,b** (λ_{max} = 514 and 516 nm, respectively) and **10a,b** (554 nm) are drastically bathochromically shifted relative to those of angular [3]- (394 nm)[19] and [5]phenylene (470 nm),[17] considerably more than expected by simple substituent contributions,[7, 20] and consistent with increased antiaromaticity[21] due to superdelocalization. The latter would be expected to increase the cyclobutadienoid character of the four-membered rings, causing increased shielding of close-lying benzenoid hydrogens. Indeed, H_b in **9a,b** is shielded ($\Delta\delta$ = 0.28; all measurements in CD_2Cl_2), relative to the corresponding nuclei in angular [3]phenylene.[17] More convincingly, in **10a,b**, not only is H_b shielded ($\Delta\delta$ = 0.33) relative to the parent angular [5]phenylene (and **11**), but also the remote H_c ($\Delta\delta$ = 0.21). While H_a in **9** and **10**, respectively, appear unchanged in these comparisons, we believe that they experience the same shielding effect as H_b and H_c, since the added *ortho*-alkynyl substitution causes deshielding by $\Delta\delta \approx 0.2$ (and negligible *meta* and *para* effects).[7, 22] The operation of aromatic π-stacking effects[23] on the observed chemical shifts was ruled out by measurements at varying concentrations (5–170 mM). Moreover, the slight increase in σ-strain introduced by the alkyne bridge is unlikely to be the cause of these shieldings, since the δ(H) values of highly strained biphenylene derivatives are normal.[24]

We conclude that superdelocalization effects are operational in annelated oligophenylenes[25] of the type **9** and **10** and anticipate that they will be accentuated in **3**. The successful execution of the final cyclization step from **10** may have to rely on derivatives in which the [5]phenylene grid is rendered more flexible by chemical alteration.

Experimental Section

Cycloisomerization of **1d**: To degassed, boiling *m*-xylene (100 mL) was added within 10 s a degassed solution of **1d** (110 mg, 1.08 mmol) and $[CpCo(CO)_2]$ (41 μL, 0.324 mmol) in *m*-xylene (20 mL). The reaction mixture was irradiated with a 300 W projector lamp (60 V). After 20 min, the solvent was evaporated, and the crude product was dissolved in CH_2Cl_2, absorbed on silica gel, and chromatographed on silica gel (35 × 3 cm, 18–32 μm) eluting with hexanes/CH_2Cl_2 (20:1–10:1) to provide **9b** as an orange solid (49 mg, 45%), followed by **10b** as a red solid (5 mg, 5%).

Cycloisomerization of **9b**: A solution of compound **9b** (20 mg, 0.02 mmol) in degassed, boiling 1,2,4-trichlorobenzene (100 mL) was irradiated with a 300 W projector lamp (60 V) while a solution of $[CpCo(CO)_2]$ (7 μL, 0.055 mmol) in 1,2,4-trichlorobenzene (12 mL) was added with a syringe pump over 3 h. The solvent was evaporated and the crude product was chromatographed on a silica gel preparative TLC plate (1 mm), eluting with hexanes/CH_2Cl_2 (4:1) to provide **10b** (8.1 mg, 40%).

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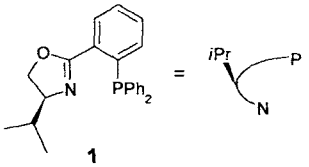
Palladium-Catalyzed Allylic Alkylation with Phosphinoaryldihydrooxazole Ligands: First Evidence and NMR Spectroscopic Structure Determination of a Primary Olefin–Pd^0 Complex**

Henning Steinhagen, Michael Reggelin,* and Günter Helmchen*

Palladium-catalyzed allylic substitution reactions are well established in organic synthesis.[1] We and others showed that an enantioselective reaction can be realized with ligands containing electronically different donor centers;[2] of these, chiral phosphinoaryldihydrooxazole (phosphinooxazoline) ligands were found to be particularly useful.[3] With the prototype **1** of this ligand class it was possible to obtain substitution products with enantiomeric purity of $\geq 98\%$ from acyclic substrates.



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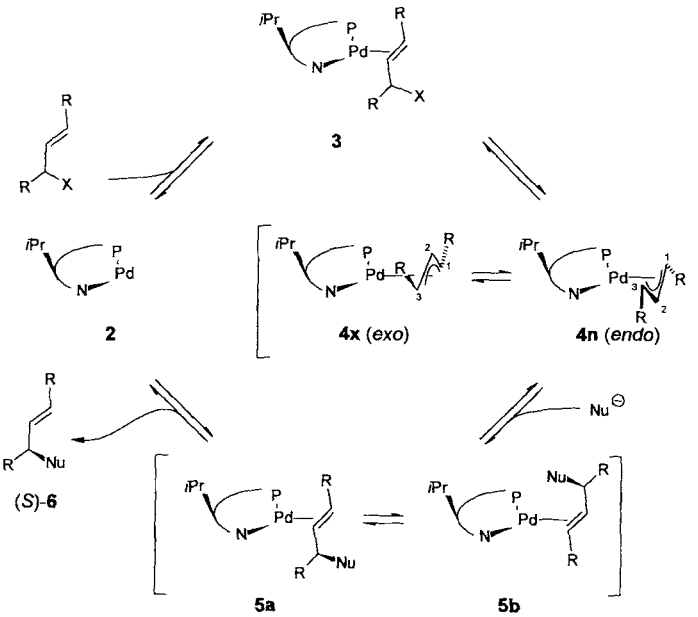
The postulated catalytic cycle for the examined system is shown in Scheme 1. The cycle contains the essential intermediates **2**–**5**, of which only the easily preparable allylic complexes **4** could be characterized so far. In the case of an unsymmetrical ligand such as **1**, an *exo*- (**4x**) and an *endo*-π-complex (**4n**) are fundamentally possible; these are in equilibrium through π-σ-π rearrangement.[4] As a consequence, there are in principle four reaction pathways, of which two lead to the preferred product (*S*)-**6**. Attack of the nucleophile can occur at C-3 of **4x** or at C-1 of **4n**. In spite of contrary assumptions (early[4, 5b] and late transition state[5a]), mechanistic interpretations up to now were all based on the postulate that the first reaction pathway is the faster one. We were now able to detect a primarily formed η^2-olefin–Pd^0 complex in the catalytic cycle and unambiguously determine its conformation. Therefore, it is now possible to make a well-founded statement about a late transition state.



Scheme 1. Catalytic cycle of the Pd-catalyzed allylic substitution; R = Ph, X = OAc, Nu = $CH(COOCH_3)_2$.

Initially the stoichiometric reaction between the π-allyl complexes **4**[6] (10:1 mixture of **4x** and **4n**) and sodium dimethylmalonate (NaDMM) as a nucleophile was examined. A solution of the complexes in [D_8]THF (0.5 mL, 88 mM), prepared at room temperature, was cooled to −78 °C, and a precooled solution of NaDMM (20.3 mg, 0.132 mmol) in [D_8]THF (0.5 mL) added. The sample was allowed to warm to room temperature inside the NMR probehead, and the progress of the reaction was monitored by ^{31}P NMR spectroscopy (Figure 1).

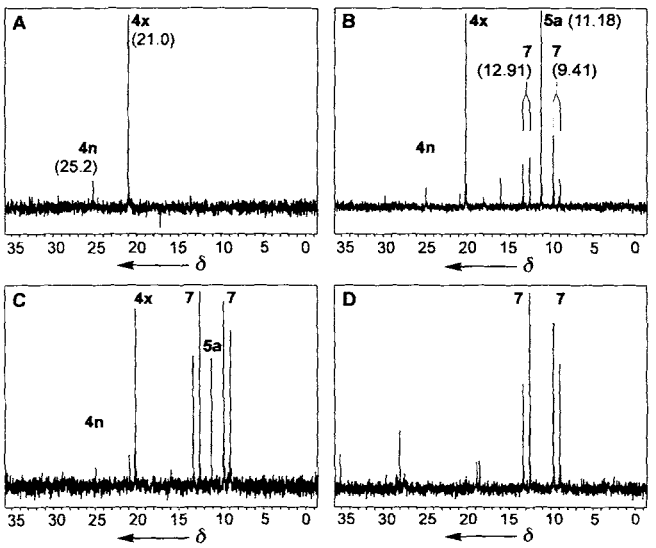


Figure 1. $^{31}P\{^1H\}$ NMR spectra recorded at various times during the reaction (161.98 MHz, −60 °C): A) equilibrating π-allyl complexes **4x** and **4n**; B–D) reaction mixtures at 370 s, 500 s, and 1 h, respectively, after addition of NaDMM.

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