Supplementary data

A Simple Cobalt Catalyst System for the Efficient and Regioselective Cyclotrimerisation of Alkynes

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Experimental section:

All reactions were performed in an argon atmosphere using the Schlenk technique.

Synthesis of diimine complexes:

Ligands were synthesized as previously described in the literature. The complexes were synthesized by suspending anhydrous $CoBr_2$ (1.68 g, 10.0 mmol) and ligand (10.0 mmol) in anhydrous THF (40 mL) at r.t. After stirring overnight the solvent was removed *in vacuo* and the solid product used without further characterisation.

Representative procedure:

A suspension of $CoBr_2$(cy-diimine) (44 mg, 0.1 mmol, 5.0 mol%), zinc dust (13 mg, 0.2 mmol, 10.0 mol%) and anhydrous ZnI_2 (64 mg, 0.2 mmol, 10.0 mol%) in anhydrous CH_3CN (1.0 mL) under Argon atmosphere was boiled up and allowed to cool to room temperature. After 15 min the alkyne (2.0 mmol) was added and the mixture stirred at room temperature for terminal alkynes or 80 °C for internal alkynes. The reaction was monitored by TLC and GC/MS. After complete conversion the brown reaction mixture was passed through a pad of silica using CH_2Cl_2 as eluent. The solvents were removed in vacuo and the crude product purified by FC. The spectroscopic characteristics of already known products were compared with published data.

Competetive reaction of Phenylacetylene and Isoprene in THF:

Similarly to the representative procedure Isoprene (0.24 mL, 2.0 mmol) and Phenylacetylene (0.22 mmol, 2.4 mmol were reacted in THF at r.t. for 5 h. The brown reaction mixture was passed through a pad of silica using CH_2Cl_2 as eluent. The solvents were removed in vacuo and the crude product purified by FC using Pentan as eluent giving **5** (161 mg, 0.95 mmol), **6** (63 mg, 0.23 mmol) and **1**/**2** (50 mg, 0.16 mmol).

1: 1,2,4-Triphenylbenzene / **2**: 1,3,5-Triphenylbenzene: The isomeric ratio was determined as previously described via careful integration of ^{1}H NMR-spectra.[1,2,3]

6: 6-Methyl-2,3-diphenyl-cycloocta-1,3,6-triene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 7.42 (d, 4H, J = 7.3, H_{ar}), 7.25 (m, 4H, H_{ar}), 6.23 (t, 1H, J = 7.7 Hz, CH), 6.20 (t, 1H, J = 7.7, CH), 5.56 (td, 1H, J = 5.0, 0.7 Hz), 2.86 (broad, 4H, CH_2), 1.87 (s, 3H, Me).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 141.1 (C), 140.6 (C), 138.9 (C_{ar}), 135.1 (C_{ar}), 128.5 (CH_{ar}), 127.1 (CH_{ar}), 126.8 (CH_{ar}), 123.9 (CH), 123.4 (CH), 120.2 (CH), 34.0 (CH_2), 28.3 (CH_2), 27.3 (CH_3).

MS (70 eV), m/z (%): 272 (47, M^+), 257 (23, M^+-Me), 244 (100,), 229 (51), 217 (24), 202 (14), 178 (17), 165 (23), 115 (19), 91 (17).

HRMS calcd. for $C_{21}H_{20}$ 272.1565, found: 272.1559.

Table **2**, Entry **1**:

A: 1,2,4-Tributyl-benzene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 7.07 (d, 1H, J = 7.6 Hz, H_{ar}), 6.97 (m, 2H, H_{ar}), 2.59 (m, 6H, CH_2), 1.58 (m, 6H, CH_2), 1.41 (m, 6H, CH_2), 0.97 (m, 9H, CH_3).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 140.3 (C_{ar}), 140.1 (C_{ar}), 137.6 (C_{ar}), 129.2 (CH_{ar}), 128.9 (CH_{ar}), 125.7 (C_{ar}), 35.3 (CH_2), 33.8 (CH_2), 33.6 (CH_2), 33.6 (CH_2), 32.5 (CH_2), 32.0 (CH_2), 22.9 (CH_2), 22.9 (CH_2), 22.5 (CH_2), 14.0 (2 x CH_3), 14.0 (CH_3).

B: 1,3,5-Tributyl-benzene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 6.84 (s, 3H, H_{ar}), 2.59 (m, 6H, CH_2), 1.58 (m, 6H, CH_2), 1.41 (m, 6H, CH_2), 0.97 (m, 9H, CH_3).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 142.7 (C_{ar}), 125.8 (CH_{ar}), 35.7 (CH_2), 33.8 (CH_2), 22.5 (CH_2), 14.0 (CH_3)

MS (70 eV), m/z (%): 246 (23, M^+), 203 (25), 161 (100), 147 (15), 119 (12), 105 (17).

Identified spectroscopically by comparison with literature data.[3] The regioisomeric ratio was determined by ^{1}H-NMR using signals at δ = 7.07, 6.97 and 6.84.

Table **2**, Entry **2**: Hexaphenylbenzene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 6.83 (s, 30H, H_{ar}).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 140.6 (C_{ar}), 140.3 (C_{ar}), 131.4 (CH_{ar}), 126.6 (CH_{ar}), 125.2 (CH_{ar}).

MS (70 eV), m/z (%): 534 (100, M^+).

HRMS calcd. for $C_{42}H_{30}$ 534.2347, found: 534.2350.

Identified spectroscopically by comparison with literature data.[4]

Table **2**, Entry **3**: Hexaethylbenzene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 2.63 (q, 12H, *J* = 7.4 Hz, CH_2), 1.19 (t, 18H, *J* = 7.4 Hz, CH_3).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 137.4 (C_{ar}), 21.7 (CH_2), 15.3 (CH_3).

MS (70 eV), m/z (%): 246 (55, M^+), 231 (100, M^+-Me), 217 (12).

Identified spectroscopically by comparison with literature data.[3]

Table **2**, Entry **4**:

A: 1,2,4-Trimethyl-3,5,6-triphenylbenzene

^{1}H NMR (300 MHz, 300K, C_6D_6): δ = 7.35 – 6.92 (m, 18H, H_{ar}), 2.17 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.10 (s, 3H, CH_3).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 142.5 (C_{ar}), 141.6 (C_{ar}), 133.9 (C_{ar}), 131.9 (C_{ar}), 131.3 (C_{ar}), 130.3 (CH_{ar}), 129.4 (CH_{ar}), 128.4 (CH_{ar}), 127.3 (CH_{ar}), 126.5 (CH_{ar}), 125.7 (CH_{ar}), 19.4 (CH_3), 18.3 (CH_3), 18.1 (CH_3).

B: 1,3,5-Trimethyl-2,4,6-triphenylbenzene

^{1}H NMR (300 MHz, 300K, C_6D_6): δ = 7.35 – 6.92 (m, 18H, H_{ar}), 2.07 (s, 9H, CH_3).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 142.5 (C_{ar}), 132.9 (C_{ar}), 130.3 (C_{ar}), 127.3 (CH_{ar}), 125.7 (CH_{ar}), 19.4 (CH_3).

MS (70 eV), m/z (%): 348 (100, M^+).

HRMS calcd. for $C_{27}H_{24}$ 348.1878, found: 348.1874.

Identified spectroscopically by comparison with literature data.[5] The regioisomeric ratio was determined by ^{1}H-NMR using signals at δ = 2.17, 2.14, 2.10 and 2.07.

Table **2**, Entry **5**:

A: 1,2,4-Triethyl-3,5,6-trimethylbenzene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 2.86 (m, 6H, CH_2), 2.45 (s, 9H, CH_3), 1.31 (m, 9H, CH_3).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 138.5 (C_{ar}), 137.7 (C_{ar}), 137.6 (C_{ar}), 132.3 (C_{ar}), 132.2 (C_{ar}), 131.1 (C_{ar}), 23.6 (CH_2), 23.0 (CH_2), 16.1 (CH_3), 16.1 (CH_3), 15.2 (CH_3), 14.9 (CH_3), 14.8 (CH_3), 13.8 (CH_3).

B: 1,3,5-Triethyl-2,4,6-trimethylbenzene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 2.86 (m, 6H, CH_2), 2.45 (s, 9H, CH_3) 1.31 (m, 9H, CH_3).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 138.7 (C_{ar}), 131.2 (C_{ar}), 23.6 (CH_2), 15.2 (CH_3), 13.7 (CH_3).

MS (70 eV), m/z (%): 204 (49, M^+), 189 (100, M^+-Me), 175 (16), 161 (9), 147 (7), 129 (7), 119 (6), 105 (5), 91 (6), 77 (3).

Identified spectroscopically by comparison with literature data.[6,7] The regioisomeric ratio was determined via GC.

Table **2**, Entry **6**:

A: 1,2,4-Tris(trimethylsilyl)benzene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 7.83 (s, 1H, H_{ar}), 7.65 (d, 1H, J = 7.3 Hz, H_{ar}), 7.49 (dd, 1H, J = 7.3, 1.3 Hz, H_{ar}), 0.37 (s, 9H, TMS), 0.35 (s, 9H, TMS), 0.26 (s, 9H, TMS).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 146.6 (C_{ar}), 144.8 (C_{ar}), 138.8 (CH_{ar}), 138.3 (C_{ar}), 134.4 (CH_{ar}), 132.8 (CH_{ar}), 2.0 (CH_3), 1.9 (CH_3), -1.2 (CH_3).

B: 1,3,5-Tris(trimethylsilyl)benzene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 7.68 (s, 3H, H_{ar}), 0.27 (s, 9H, TMS)

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 140.0 (CH_{ar}), 139.3 (C_{ar}), -1.0 (CH_3)

MS (70 eV), m/z (%): 294 (12, M^+), 279 (100, M^+-Me), 263 (80), 191 (38), 124 (14), 73 (63).

Identified spectroscopically by comparison with literature data.[3] The regioisomeric ratio was determined by ^{1}H-NMR using signals at δ = 7.83, 7.68, 7.65 and 7.49.

Table **2**, Entry **7**:

A: 1,2,4-Triisopropenyl-benzene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 7.12 (m, 2H, H_{ar}), 6.95 (d, 1H, *J* = 7.8 Hz, H_{ar}), 5.16 (m, 1H, C=C$\underline{H}$), 4.91 (m, 2H, CH_2), 4.87 (m, 2H, CH_2), 4.82 (m, 1H, C=C$\underline{H}$),1.95 (m, 3H, CH_3), 1.86 (m, 6H, CH_3).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 146.6 (C_{ar}), 146.0 (C_{ar}), 142.8 (C_{ar}), 141.6 (C), 140.9 (C), 139.8 (C), 128.5 (CH_{ar}), 125.7 (CH_{ar}), 124.0 (CH_{ar}), 115.2 (2 x CH_2), 112.3 (CH_2), 23.8 (CH_3), 23.7 (CH_3), 21.8 (CH_3).

B: 1,3,5-Triisopropenyl-benzene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 7.01 (s, 3H, H_{ar}), 4.91 (m, 6H, CH_2), 1.98 (m, 9H, CH_3).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 143.6 (C_{ar}), 141.4 (C), 122.1 (CH_{ar}), 112.7 (CH_2), 22.0 (CH_3).

MS (70 eV), m/z (%): 198 (64, M^+), 183 (100, M^+-Me), 168 (29), 155 (66), 143 (55), 128 (53), 115 (29).

HRMS calcd. for $C_{15}H_{18}$ 198.1409 , found: 198.1404.

The regioisomeric ratio was determined by ^{1}H-NMR using signals at δ = 7.12, 7.01 and 6.95.

Table **2**, Entry **8**:

A: 1,2,4-Tris-(2-acetoxypropyl)benzene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 7.06 (m, 1H, H_{ar}), 6.97 (m, 2H, H_{ar}), 5.06 (m, 3H, CH), 3.10-2.93 (m, 2H, CH_2), 2.88 – 2.63 (m, 4H, CH_2), 1.97 (m, 9H, $COCH_3$), 1.22 (dd, 3H, *J* = 5.4, 1.0 Hz, CH_3), 1.19 – 1.16 (m, 6H, CH_3).

B: 1,3,5-Tris-(2-acetoxypropyl)benzene

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 6.87 (s, 3H, H_{ar}), 5.06 (m, 3H, CH), 2.88 – 2.63 (m, 3H, CH_2), 1.97 (m, 9H, $COCH_3$), 1.19 – 1.16 (m, 6H, CH_3).

The regioisomers and diastereoisomers in the ^{13}C NMR are not seperatly assigned:

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 170.1 / 170.1 (CO), 137.5 (C_{ar}), 136.0 / 135.9 (C_{ar}), 135.6 / 135.6 (C_{ar}), 134.2 / 134.1 (C_{ar}), 131.4 / 131.4 (CH_{ar}), 130.3 (CH_{ar}), 128.5 / 128.5 (CH_{ar}), 127.4 (CH_{ar}), 71.1 (broad signal, CH), 41.8 (CH_2), 41.5 / 41.5 (CH_2), 38.7 (CH_2), 38.4 (CH_2), 21.0 (CH_2), 19.4 (CH_3), 19.2 – 19.1 (broad signal, CH_3).

HRMS calcd. for $C_{21}H_{30}O_6$ 401.194009 (M+Na), found: 401.193325.

The regioisomeric ratio was determined by ^{1}H-NMR using signals at δ = 7.06, 6.97 and 6.87.

Table **2**, Entry **9**:

A: Benzene-1,2,4-tricarboxylic acid trimethyl ester

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 8.34 (d, 1H, J = 1.7 Hz, H_{ar}), 8.12 (dd, 1H, J = 8.0, 1.7 Hz, H_{ar}), 7.67 (d, 1H, J = 8.0 Hz, H_{ar}), 3,88 (s, 3H, Me), 3,87 (s, 6H, Me).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 167.4 (C), 166.6 (C), 165.2 (C), 136.1 (C_{ar}), 132.3 (C_{ar}), 132.1 (CH_{ar}), 131.4 (C_{ar}), 130.1 (CH_{ar}), 128.7 (CH_{ar}), 52.7 (CH_3), 52.7 (CH_3), 52.4 (CH_3).

B: Benzene-1,3,5-tricarboxylic acid trimethyl ester

^{1}H NMR (300 MHz, 300K, $CDCl_3$): δ = 8.76 (s, 3H, H_{ar}), 3.91 (s, 9H, Me).

^{13}C NMR (75 MHz, 300K, $CDCl_3$): δ = 165.2 (C), 131.0 (C_{ar}), 134.4 (CH_{ar}), 52.4 (CH_3).

MS (70 eV), m/z (%): 252 (3, M^+), 221 (100, M^+-Me).

Identified spectroscopically by comparison with literature data.[8,9] The regioisomeric ratio was determined by ^{1}H-NMR using signals at δ = 8.76, 8.34, 8.12 and 7.67.

1 J. E. Hill, G. Balaich, P. E. Fanwick, I. P. Rothwell, *Organometallics*, 1993, **12**, 2911.

2 L. Yong, H. Butenschön, *Chem. Commun.*, 2002, 2852.

3 C. Breschi, L. Piparo, P. Pertici, A. M. Caporusso, G. Vitulli, *J. Organomet. Chem.*, 2000, **602**, 1-2, 57.

4 L. Eshdat, A. Ayalon, R. Beust, R. Shenhar, M. Rabinoritz. *J. Am. Chem. Soc.*, 2000, **122**, 12637.

5 A. K. Jhingan, H. Jiang, M. Chen, *J. Org. Chem.*, 1987, **52**, 1161.

6 T. Yokota, Y. Sakurai, S. Sakaguchi, Y. Ishii, *Tetrahedron Lett.*, 1997, **38**, 3923.

7 R. Rathore, S. V. Lindeman, J. K. Kochi, *J. Am. Chem. Soc.*, 1997, **119**, 9393.

8 H. Neunhoeffer, G. Werner, *Liebigs Ann. Chem.*, 1985, **4**, 852.

9 B. Nakhle, S. A. Trammwell, K. M. Sigel, T. J. Meyer, B. W. Erickson, *Tetrahedron*, 1999, **55**, 2835.