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Cobalt and iron metallates as catalysts for cyclization reactions of diynes and triynes: [2+2+2] Cycloaddition vs. Garratt-Braverman reaction

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ABSTRACT

Highly reduced anthracene and naphthalene cobaltates and ferrates catalyze the cyclization of diynes and triynes, furnishing expected [2 + 2 + 2] cycloaddition products as well as unexpected annulation products from Garratt-Braverman cyclization reactions. The anionic Cp*Fe-naphthalene complex exclusively catalyzes the latter reaction. The Garratt-Braverman reactions show a large solvent-dependent substrate conversion. Diynes and triynes afforded the corresponding substituted 1,3-dihydronaphthofurane products with yields up to 91% isolated yield.

Introduction

The cyclotrimerization of alkynes is a prime example for the versatility and virtuosity of transition metal complexes as catalysts for the assembly of complex molecular structures [1]. Mechanistic investigations over several decades have shed light on the many mechanistic varieties and their intricacies [2]. The applications have led to numerous functionalized aromatic molecules, which would have been difficult to synthesize otherwise [3]. Asymmetric versions of the cyclotrimerization reaction allow the synthesis of chiral molecules, possessing different stereochemical elements [4]. Concordantly and alternatively to the development of second or third row transition metal catalysts, the focus has been directed to developing catalysts based on 3d metals in recent years [5].

Usually, cyclotrimerization reactions utilize the most common oxidation states of the individual transition metal catalyst. For the middle to late (groups 6–9) transition metals few examples rely on zero-valent metal or anionic metal complexes, e.g. molybdenum complexes [6]. Nonetheless, there is increasing evidence that in the case of cobalt not only Co(I) but also Co(0) complexes are catalytically active species in *in situ* generated catalytic systems [7]. Early examples for zero-valent metal complexes that are active in [2 + 2 + 2] cycloadditions were iron-arene complexes prepared by Zenneck and co-workers by metal vapor synthesis [8]. Jacobi von Wangelin and co-workers also proposed the formation of a zero-valent Fe(0) species from Fe(II) precursors, furnishing a catalytically active complex for arene synthesis from alkyne building blocks [9]. The application of pyrimidinediimine ligands in *in situ* generated Fe(0) complexes allows the 1,3,5-isomer-selective cyclotrimerization of terminal alkynes [10]. Very recent work indicated the possibility of using sterically shielded non-innocent heterocyclic ligands like phenanthrolines, thus allowing formal Fe(0) species to be used as precursor in alkyne cyclotrimerization [11]. The synthesis and catalytic usability of Fe(I) complexes for [2 + 2 + 2] cycloadditions of alkynes has been reported by Tilley and coworkers and others [12]. The utilization of formal CpFe(0) fragments for cyclotrimerization reactions has been reported by Fürstner et al. [13]. In this case, triynes were converted to the corresponding benzene product using 10 mol% of the Fe catalyst (Scheme 1).

In 2011, one of us reported that a potassium bis(anthracene) ferrate [14], originally synthesized by Ellis and co-workers [15], is an active (pre)catalyst in cross-coupling reactions of Grignard reagents with aryl halides (Scheme 2). Based on these results, we investigated the catalytic properties of a series of highly reduced cobalt and iron complexes bearing arene or alkene ligands. Although these complexes are generally highly reactive compounds and susceptible towards air and moisture, they can provide access towards very selective reactions. This was showcased in 2014 [16], when the cobaltate **Cat1** and also **Cat2** were observed to exhibit catalytic activity in the hydrogenation of various

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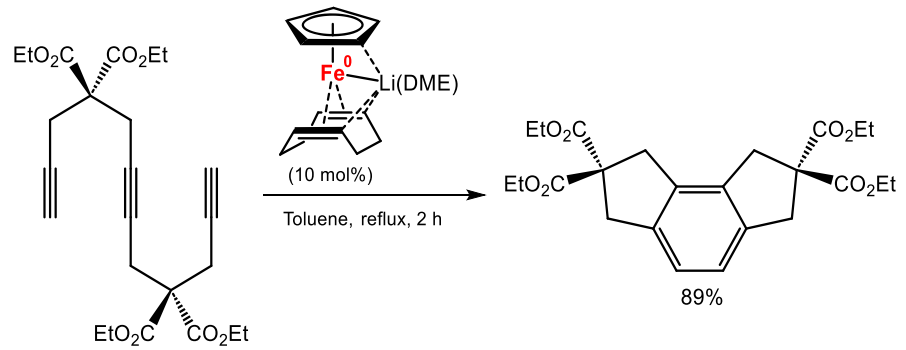
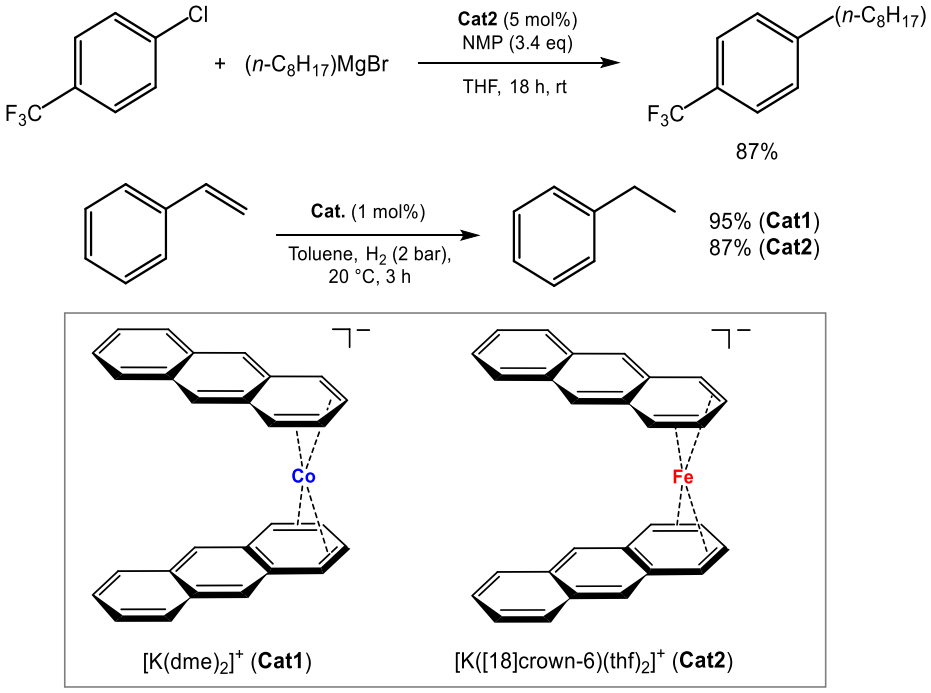


Scheme 1. Cyclotrimerization reactions with formal CpFe(0)-diolefin complex reported by Fürstner and co-workers.



Scheme 2. Highly reduced iron and cobalt complexes (below) in cross-coupling (top) and hydrogenation reactions (middle).

alkenes, imines and ketones under mild conditions. Subsequent investigations demonstrated the versatility of such metallates also including other ligands like α-diimino ligands for addition reactions [17]. With this in mind, we were interested in investigating the reactivity of such highly reduced metallate complexes towards cyclization reactions of (oligo-)alkynes.

Experimental details

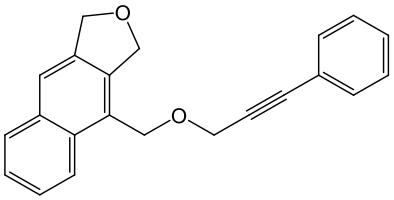
General remarks

The precatalysts **Cat1** to **Cat6** were synthesized according to the literature [18]. The cyclization reactions were performed under argon atmosphere (purity: 6.0, purchased from Linde Gas GmbH) and were assembled in a LABmaster Pro glovebox from M. Braun. Solvents for the cyclization reactions were obtained either from a MB SPS 7 solvent purification system from M. Braun (tetrahydrofurane (THF), *n*-hexane, toluene, dichloromethane (DCM) and acetonitrile (MeCN)) or from Acros Organics in septum bottles stored over molecular sieve (dimethyl sulfoxide (DMSO), *N,N*-dimethylformamide (DMF), *N*-methyl-2-pyrrolidone (NMP)). Deuterated solvents were obtained from Eurisotop or Deutero GmbH. Degasification of the solvents was achieved *via* the freeze-pump-thaw method. Further details concerning the synthesis of substrates and analytical methods are provided in the supporting information. Chemical shifts are stated in parts per million (ppm) on the delta scale (δ). Axis calibration was performed using the residual protic solvent signals (^{1}H NMR: $CDCl_3$: 7.26 ppm, d_3-MeCN: 1.94 ppm, THF-d_8: 1.72 ppm, toluene-d_8: 2.08; ^{13}C NMR: $CDCl_3$: 77.16 ppm, d_3-MeCN: 1.32 ppm, THF-d_8: 25.31, toluene-d_8: 20.43). Multiplicities are stated as s (singlet), d (doublet), t (triplet), dd (doublet of doublets), q (quartet) or m (multiplet).

*General procedure for the cyclization of triynes and diynes with precatalyst **Cat6** (GP1)*

An oven-dried 10 mL vial was subsequently charged with **Cat6** (0.010 mmol, 6.2 mg, 10 mol%), MeCN or THF (2 mL), a magnetic stirring bar as well as the desired substrate **1, 3, 7, 10–13, 18** (0.100 mmol) or **20–23** (0.100 mmol) before the vial was sealed with a crimp cap by means of a crimper. After stirring for 19 to 60 h at room temperature, the reaction was quenched by stirring for 5 min at atmospheric conditions. The crude product was directly charged on silica gel and the product purified by flash column chromatography with the stated eluent composition on silica gel, followed by removal of the eluent in vacuo.

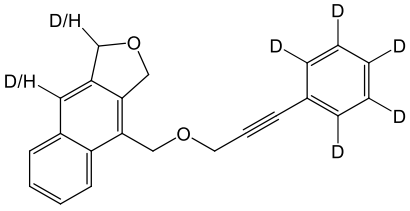
■ Yield of **5**: 53% (16.6 mg, 0.053 mmol)



Eluent composition: *n*-heptane/acetone (v/v 20:1)

^{1}H NMR (300 MHz, d_3-MeCN): δ = 8.24–8.22 (m, 1H,), 7.90–7.88 (m, 1H), 7.74 (s, 1H), 7.55–7.46 (m, 4H), 7.42–7.36 (m, 3H), 5.29 (s, 2H), 5.15 (s, 2H), 5.04 (s, 2H), 4.42 (s, 2H); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.26–8.22 (m, 1H,), 7.86–7.82 (m, 1H), 7.67 (s, 1H), 7.55–7.45 (m, 4H), 7.37–7.32 (m, 3H), 5.41 (s, 2H), 5.25 (s, 2H), 5.09 (s, 2H), 4.44 (s, 2H), ^{13}C{^{1}H} NMR (125 MHz, d_3-MeCN): δ = 140.1, 139.2, 134.8, 132.7, 132.5, 129.8, 129.6, 129.4, 127.0, 126.7, 126.6, 125.0, 123.4, 121.0, 86. 9, 86.5, 73.4, 72.8, 67.0, 58.6; HRMS(ESI+) *m/z*: $[M + H]^+$ calcd for $C_{22}H_{18}O_2$, 315.1380; found 315.1380.

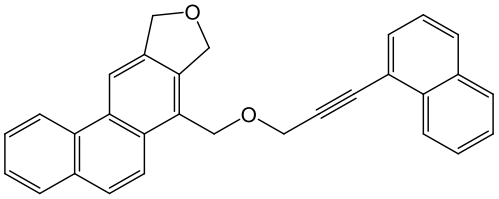
Yield of **d_x-5**: 41% (12.8 mg, 0.041 mmol)



Eluent composition: *n*-heptane/acetone (v/v 20:1)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.67 (s, 0.94H/D), 5.40 (s, 2H), 5.24–5.22 (m, 1.64H/D), 5.08 (s, 2H), 4.42 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 138.89, 138.86, 137.8, 137.7, 133.8, 131.9, 131.5 (t, *J* = 24.5 Hz), 128.2–127.8 (m), 126.1–125.3 (m), 125.4, 123.7, 122.4, 120.22, 120.2, 86.9, 85.1, 73.2, 72.6, 66.3, 58.1.

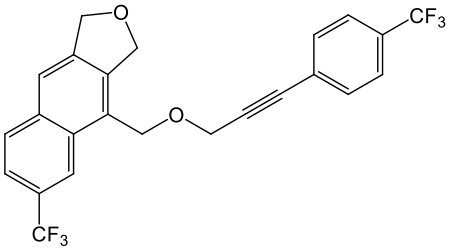
Yield of **6**: 65% (27.0 mg, 0.065 mmol)



Eluent composition: *n*-heptane/acetone (v/v 20:1)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.66 (d, *J* = 8.3 Hz, 1H), 8.57 (s, 1H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.21 (d, *J* = 9.2 Hz, 1H), 7.91–7.86 (m, 3H), 7.82–7.73 (m, 2H), 7.96–7.52 (m, 4H), 7.48–7.44 (m, 1H), 5.48 (s, 2H), 5.35 (s, 2H), 5.20 (s, 2H), 4.63 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 139.1, 138.3, 133.5, 133.3, 131.8, 130.94, 130.88, 130.60, 130.58, 129.3, 128. 7, 128.5, 127.4, 127.1, 126.81, 126.77, 126.7, 126.5, 126.2, 125.4, 122.8, 122.7, 120.3, 115.2, 89.9, 85.2, 73.8, 73.1, 66.8, 58.4; HRMS(ESI+) *m/z*: $[M+NH_4]^+$ calcd for $C_{30}H_{22}O_2$, 32.1958; found 432.1959.

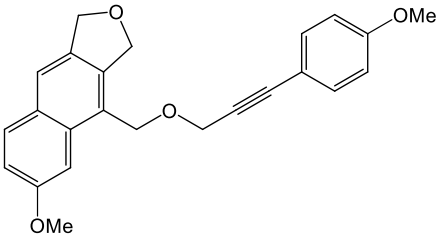
Yield of **8**: 43% (19.4 mg, 0.043 mmol)



Eluent composition: *n*-heptane/acetone (v/v 20:1)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.52 (s, 1H,), 7.95–7.92 (m, 1H), 7.72–7.54 (m, 6H), 5.40 (s, 2H), 5.26 (s, 2H), 5.08 (s, 2H), 4.48 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 140.4, 140.3, 135.2, 132.1, 130.9, 130.6 (q, *J* = 32.6 Hz), 129.7, 128.1 (q, *J* = 31.8 Hz), 126.6, 126.2, 125.5 (q, *J* = 3.6 Hz), 124.5 (q, *J* = 272.2 Hz), 124.0 (q, *J* = 272.2 Hz), 121.9 (q, *J* = 4.4 Hz), 121.6 (q, *J* = 3.1 Hz), 120.3, 87.2, 85.9, 73.1, 72.5, 66.3, 58.3; ^{19}F NMR (470 MHz, $CDCl_3$): δ = –62.9, –62.1; HRMS(ESI+) *m/z*: $[M+NH_4]^+$ calcd for $C_{24}H_{16}F_6O_2$, 468.1393; found 468.1387.

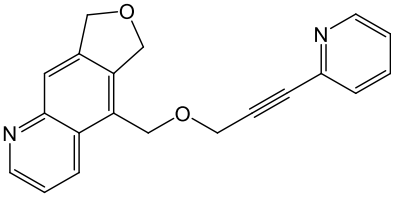
Yield of **14**: 15% (5.61 mg, 0.015 mmol)



Eluent composition: DCM/acetone (v/v 20:1)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 8.9 Hz, 1H), 7.59 (s, 1H), 7.54 (d, *J* = 2.6 Hz, 1H), 7.44–7.39 (m, 2H), 7.16–7.12 (m, 1H), 6.88–6.84 (m, 2H), 5.38, (s, 2H), 5.21 (s, 2H), 5.02 (s, 2H), 4.42 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 160.0, 158.1, 139.4, 135.3, 133.4, 133.3, 129.9, 129.3, 124.2, 120.1, 118.3, 114.7, 114.2, 103.0, 86.9, 83.8, 73.2, 72.7, 66.4, 58.0, 55.45, 55.44; HRMS(ESI+) *m/z*: $[M + H]^+$ calcd for $C_{24}H_{22}O_4$, 375.1564; found 375.1591.

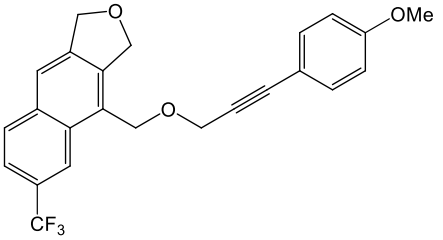
Yield **15**: 67% (21.2 mg, 0.067 mmol)



Eluent composition: *n*-heptane/acetone (v/v 1:1)

^{1}H NMR (500 MHz, d_3-MeCN): δ = 8.8.87–8.85 (m, 1H), 8.63–8.54 (m, 2H), 7.90 (s, 1H), 7.78–7.73 (m, 1H), 7.51–7.46 (m, 2H), 7,36–7.32 (m, 1H), 5.32 (s, 2H), 5.20 (s, 2H), 5.05 (s, 2H), 4.46 (s, 2H); ^{13}C{^{1}H} NMR (125 MHz, d_3-MeCN): δ = 151.3, 151.2, 149.8, 143.6, 143.2, 140.5, 137.7, 133.6, 128.3, 127.7, 127.2, 124.6, 122.6, 122.1, 87.0, 85.9, 73.5, 72.8, 66.9, 58.7; HRMS(ESI+) *m/z*: $[M + H]^+$ calcd for $C_{20}H_{16}N_2O_2$, 317.1285; found 317.1289.

Yield of **17**: 59% (24.3 mg, 0.059 mmol)



Eluent composition: DCM/acetone (v/v 20:1)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.52 (s, 1H), 7.94–7.91 (m, 1H), 7.70 (s, 1H), 7.66–7.62 (m, 1H), 7.45–7.40 (m, 2H), 6.89–6.84 (m, 2H), 5.40 (s, 2H), 5.25 (s, 2H), 5.07 (s, 2H), 4.44, (s, 2H), 3.82 (s, 3H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 160.0, 140.4, 140.2, 135.1, 133.4, 130.9, 129.6, 127.9 (q, *J* = 32.1 Hz), 126.9, 124.5 (q, *J* = 271.7 Hz), 122.1 (q, *J* = 4.3 Hz), 121.5 (q, *J* = 3.1 Hz) 120.1, 114.5, 114.1, 87.3, 83.2, 73.1, 72.5, 65.8, 58.4, 55.4; ^{19}F NMR (282 MHz, $CDCl_3$): −62.0; HRMS(ESI+) *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{19}F_3O_4$, 435.1176; found 435.1170.

Yield of **19**: 57% (17.4 mg, 0.057 mmol)

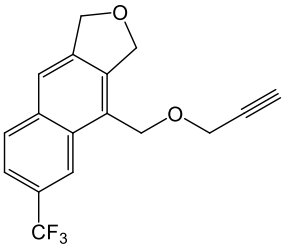
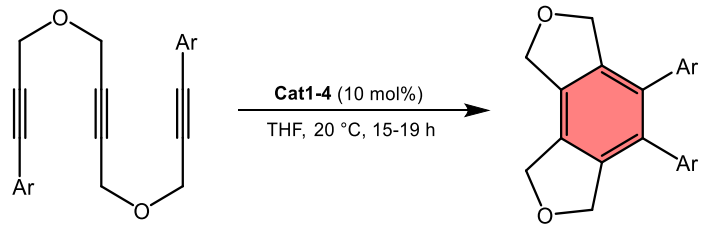


Table 1
Catalytic screening of precatalysts **Cat1–4**.



1 (Ar = Ph)
3 (Ar = 1-Naphthyl)

2 (Ar = Ph)
4 (Ar = 1-Naphthyl)

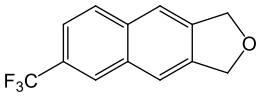
Entry	Substr.	Cat.	Reaction time [h]	Recovered Substr.[%][a]	Yield [%][a]
1	**1**	**Cat1**	15	32	48
2	**1**	**Cat2**	15	24	66
3	**1**	**Cat3**	15	–	71
4	**1**	**Cat4**	15	20	65
5	**3**	**Cat1**	19	39	51
6	**3**	**Cat2**	19	17	58
7	**3**	**Cat3**	19	–	69
8	**3**	**Cat4**	19	9	57

[a] Isolated compound.

Eluent composition: *n*-heptane/acetone (v/v 20:1)

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.50 (s, 1H), 7.95–7.92 (m, 1H), 7.72 (s, 1H), 7.66–7.63 (m, 1H), 5.37 (s, 2H), 5.25 (s, 2H), 5.02 (s, 2H), 4,25 (d, J = 2.3 Hz, 2H), 2.58 (t, J = 2.37 1H,); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 140.4, 140.3, 135.1, 130.9, 129.6, 128.1 (q, J = 272.5 Hz), 126.5, 124.6 (q, J = 272.2 Hz), 122.0 (q, J = 4.5 Hz), 121.6 (q, J = 3.1 Hz), 120.2, 79.4, 75.6, 73.1, 72.5, 65.9, 57.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.1; HRMS(ESI+) *m/z*: $[M+NH_4]^+$ calcd for $C_{17}H_{13}F_3O_2$, 324.1206; found 324.1206.

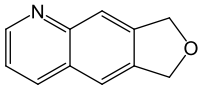
Yield **24**: 91% (21.6 mg, 0.091 mmol)



Eluent: DCM

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.08 (s, 1H), 7.88–7.86 (m, 1H), 7.68–7.67 (m, 2H), 7.91–7.59 (m, 1H), 5.22 (s, 4H); ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 140.9, 139.9, 134.4, 132.0, 128.9, 127.7 (q, J = 32.3 Hz), 125.6 (q, J = 4.5 Hz), 124.4 (q, J = 272.7 Hz) 121.4 (q, J = 3.1 Hz), 120.4, 119.5, 72.8, 72.7; ^{19}F NMR (282 MHz, $CDCl_3$): δ = −62.2; HRMS (ESI+) *m/z*: $[M+NH_4]^+$ calcd for $C_{13}H_9F_3O$, 256.0944; found 256.0946.

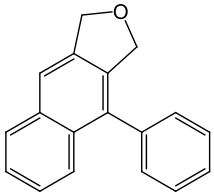
Yield of **25**: 72% (12.3 mg, 0.072 mmol)



Eluent composition: *n*-heptane/acetone (v/v 3:1)

The analytical data agrees with the values stated in the literature [20].

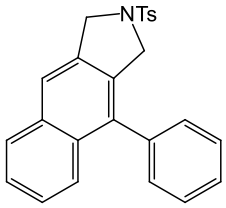
Yield of **26**: 85% (20.91 mg, 0.085 mmol)



Eluent: DCM

The analytical data agrees with the values stated in the literature [21].

Yield of **27**: 11% (calculated by integration of the CH_2 peak at 4.83 ppm of the product relative to the integrated peak of cyclohexane at 1.43 ppm).

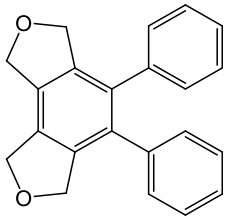


The analytical data agrees with the values stated in the literature [21].

*General procedure for the cyclization of triynes with precatalysts **cat1–6** (GP2)*

The screening reactions were performed in analogy to GP1. Scale of the screening reactions: triyne **1** or **7** (0.050 mmol), **Cat1** (3.2 mg, 0.005 mmol, 10 mol%), **Cat2** (3.9 mg, 0.005 mmol, 10 mol%), **Cat3** (3.0 mg, 0.005 mmol, 10 mol%), **Cat4** (1.6 mg, 0.005 mmol, 10 mol%), **Cat5** (2.0 mg, 0.005 mmol, 10 mol%), **Cat6** (3.1 mg, 0.005 mmol, 10 mol%). The workup for the reactions with all precatalysts except for **Cat4** deviated from GP1 in that the solvent was removed by rotary evaporation, the obtained crude product was dissolved in $CDCl_3$ (800 μL), and cyclohexane was added followed by filtration with a 0.2 μm PTFE syringe filter into an NMR tube. The yields were calculated by comparison of normalized integrated signal intensities (triyne **7**: 4.39 ppm, product **8**: 5.08 ppm and product **9**: 4.97 ppm) relative to the integrated signal intensity of cyclohexane as internal standard at 1.43 ppm. The results of the screening reactions are summarized in Table 1.

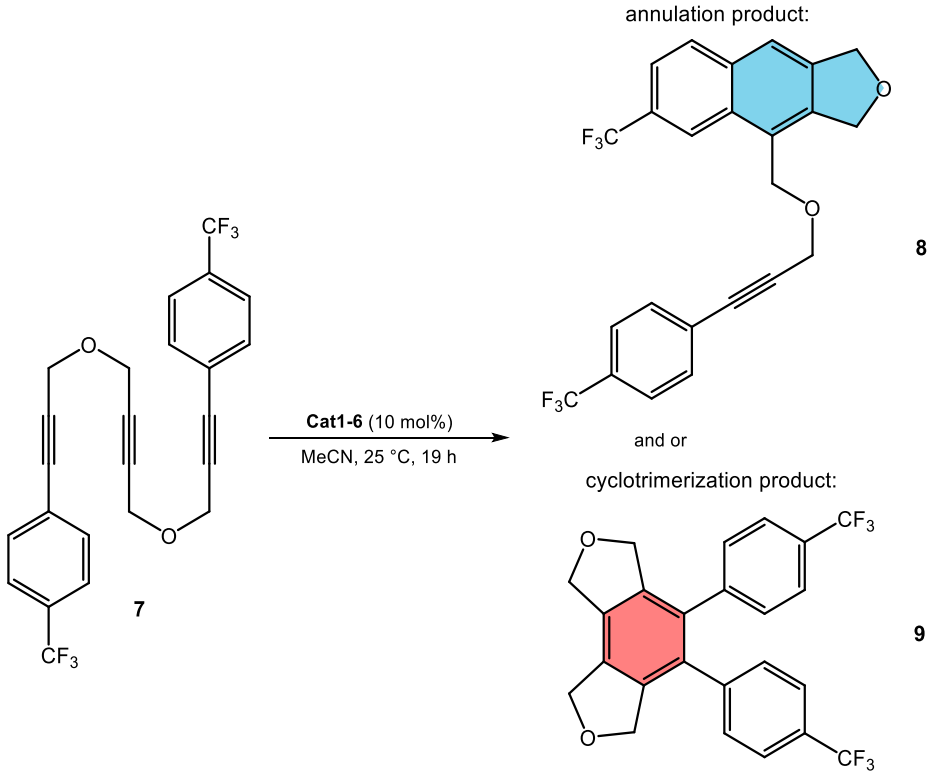
Yield of **2**: 20% (6 mg, 0.020 mmol)



Eluent composition: *n*-heptane/acetone (v/v 15:1)

The analytical data agrees with the values stated in the literature [19].

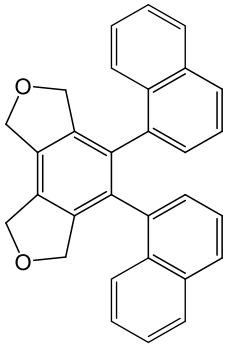
Table 2
Screening of precatalysts **Cat1–6** with triyne **7** as test substrate.



Entry	Cat.	Unreacted **7** [%]	Product **8** [%]	Product **9** [%]
1	**Cat1**	29	31	32
2	**Cat2**	14	48	–
3[a]	**Cat3**	~41	~35	~23
4	**Cat4**	–	–	96[b]
5	**Cat5**	56	–	41
6	**Cat6**	32	52	–

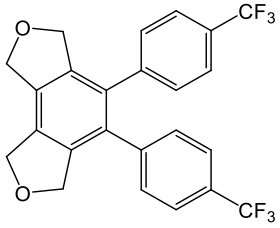
[a] Due to very broad signals, yields and conversion were estimated by NMR integration of the signals at 5.36 (**8**), 5.16–4.96 (**8** and **9**) and 4.62–4.21 (**8** and **7**) ppm (see SI).
[b] Isolated yield.

Yield of **4**: 36% (15.0 mg, 0.036 mmol)



Eluent composition: *n*-heptane/acetone (v/v 15:1)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79–7.44 (m, 9H), 7.25–6.82 (m, 5H), 5.30–5.21 (m, 4H), 4.81–4.67 (m, 4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 140.1, 140.0, 136.0, 135.6, 133.6, 133.5, 133.39, 133.36, 131.64, 131.55, 131.4, 131.0, 128.5, 128.16, 128.13, 127.73, 128.70, 126.4, 126.1, 125.9, 125.8, 125.73, 125.65, 125.63, 125.1, 124.7, 73.9, 73.8, 73.1, 73.0.

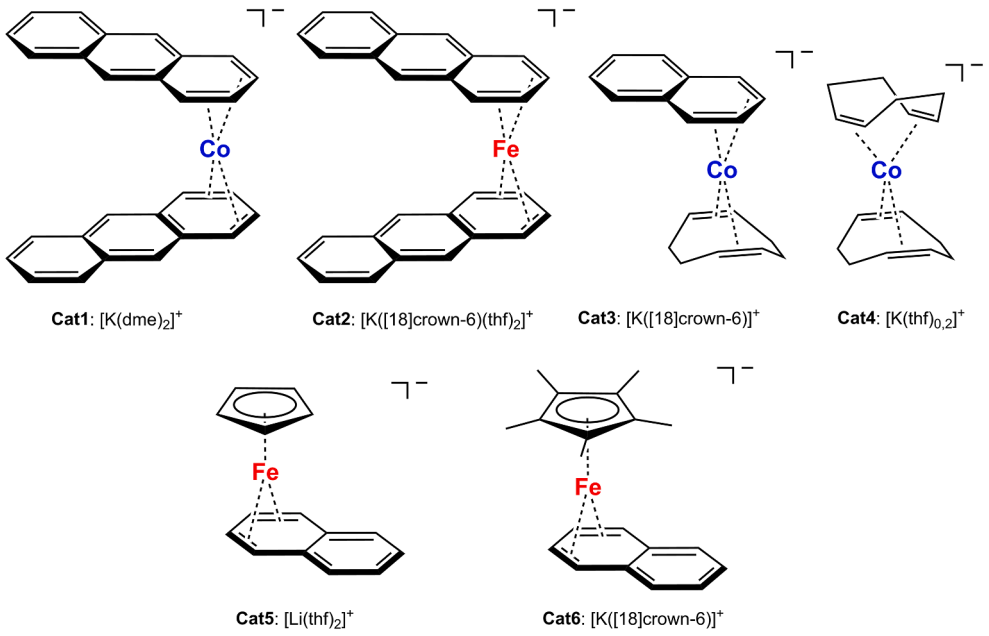
Yield of product **9** obtained from the reaction with precatalyst **Cat4**: 96% (21.4 mg, 0.048 mmol).



Eluent composition: *n*-heptane/acetone (v/v 15:1)
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48 (d, *J* = 8.1 Hz, 4H), 7.15 (d, *J* = 8.1 Hz, 4H), 5.16 (s, 4H, CH_2), 4.97 (d, 4H); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): δ = 141.9, 139.2, 132.8, 132.6, 129.9, 129.6 (q, *J* = 32.8 Hz), 125.4 (q, *J* = 3.6 Hz), 124.1 (q, *J* = 272.2 Hz), 73.6, 72.9; ^{19}F NMR (470 MHz, $CDCl_3$): δ = -62.6; HRMS(ESI+) *m/z*: $[M+Na]^+$ calcd for $C_{24}H_{16}F_6O_2$, 473.0947; found 473.0950.

*General procedure concerning the solvent screening for the cyclization of triyne **7** with precatalyst **Cat6** (GP3)*

The reactions, the workup and the determination of the yield were carried out in analogy to GP2 with **Cat6**, in *n*-hexane, THF, MeCN, DMF, DMSO, DCM, 1,4-dioxane, NMP and toluene as solvent (2 mL each)



Cat1: $[K(dme)_2]^+$ **Cat2**: $[K([18]crown\text{-}6)(thf)_2]^+$ **Cat3**: $[K([18]crown\text{-}6)]^+$ **Cat4**: $[K(thf)_{0,2}]^+$

Cat5: $[Li(thf)_2]^+$ **Cat6**: $[K([18]crown\text{-}6)]^+$

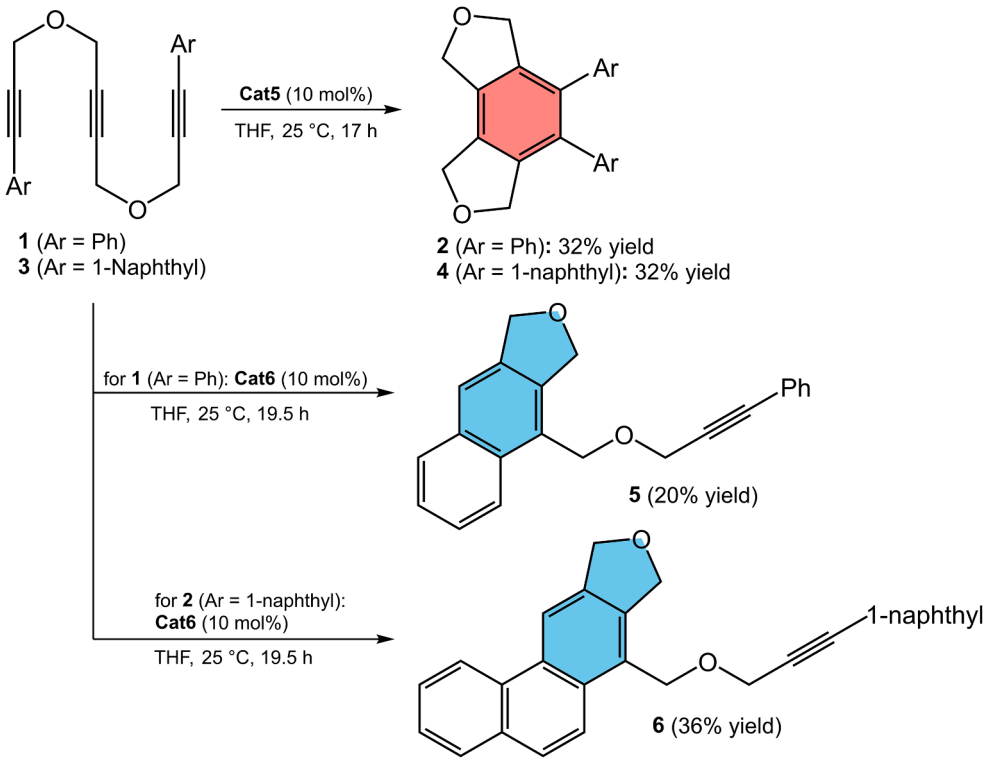
Scheme 3. Investigated cobaltate and ferrate complexes.

whereas DMF, DMSO and NMP were condensed into a cooling trap under high vacuum at 100 °C. The results of the screening reactions are summarized in Table 2.

Results

We investigated a series of anionic iron and cobalt complexes for the cyclization of differently substituted triynes. The cobaltates and ferrates used are depicted in Scheme 3 and are comprised of different ligand sets. **Cat1** and **Cat2** contain two anthracene ligands, **Cat3** features one naphthalene and one 1,5-cyclooctadiene (cod) ligand, **Cat4** features two cod ligands, while **Cat5** and **Cat6** carry one naphthalene ligand and a Cp or Cp* ligand, respectively. All precatalysts are used as potassium salts except **Cat5**, which possesses a lithium cation.

As described above complexes related to **Cat5** and **Cat6** have been used before for initiating cyclotrimerization reactions, but the scope has remained rather limited [13]. For evaluation of the general reactivity of **Cat1–6** we investigated the intramolecular cyclization of two terminally substituted triynes at room temperature, using THF as reaction solvent (Scheme 4). The results for the reactions with catalyst **Cat1–4** are



Scheme 4. Screening of the cyclotrimerization activity with precatalysts **Cat5** and **Cat6**.

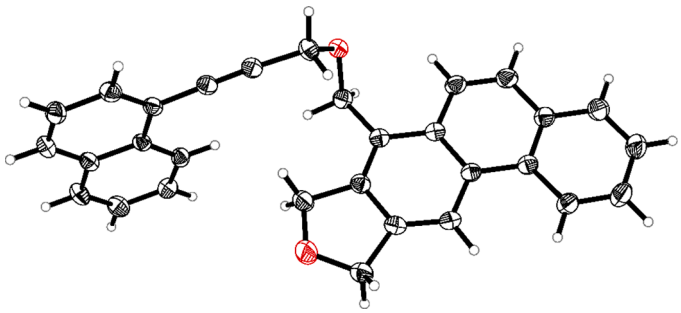


Fig. 1. Solid-state molecular structure of annulation product **6** (thermal ellipsoids drawn at the 50% probability level).

displayed in Table 1. In all cases a cyclization reaction was observed, leading to the formation of cyclization products **2** or **4** from the corresponding triynes **1** and **3**. The size of the arene group did not play a significant role and the observed yields were consistently in the range of 48–71%. In the case of **Cat1** most of the remaining starting material **1** and **3** could be retrieved (Table 1, Entries 1 and 5). This was also observed to a somewhat lesser extent for **Cat2** (Entries 2 and 6). For precatalyst **Cat3** the best conversions to products **2** or **4** were observed (Entries 3 and 7), however, no starting material could be reisolated. Yields for the $[Co(cod)_2]^-$ salt **Cat4** were somewhat lower than for **Cat3**; however, it was possible to reisolate small amounts of the corresponding starting materials (Entries 4 and 8).

Beside the anionic cobaltates and ferrates containing only neutral polyarene or alkene ligands, ferrates containing Cp and Cp* groups as steering ligands have also found to exhibit interesting capabilities for cyclization reactions. Therefore, we decided to evaluate the CpFe complex **Cat5** and Cp*Fe complex **Cat6** as suitable precatalysts in this cyclization reaction (Scheme 4).

These investigations revealed the participation of an unexpected cyclization process. Precatalyst **Cat5** afforded the expected cyclotrimerization products **2** and **4** with significantly lower yield compared to precatalysts **Cat1–4**, which suggests that the reaction is much less selective than for **Cat1** to **Cat4**. Furthermore, a completely different reaction outcome was observed for **Cat6**. Instead of yielding the expected cyclotrimerization products, the formal arene C—H insertion products **5** and **6**, whose formation included C—C coupling and H shift, were detected in this case. The structure of product **6** was unambiguously proven by a single crystal X-ray structure analysis (Fig. 1). Switching from Cp to the more electron-rich Cp* ligand covalently bound to the iron centre appears to facilitate this particular annulation reaction. Mechanistic assumptions and precedents will be discussed at a later stage of the reported investigations.

Further experimentation was guided by the consideration that a more coordinating solvent might further stabilize any reactive intermediate of the observed annulation reaction. Therefore, we decided to test MeCN as solvent and for the screening chose a different internal triyne **7** as substrate since the compound's fluorine atoms represent an additional feature for NMR spectroscopic characterization of possible products. The results for the screening reaction are shown in Table 2.

The application of **Cat1** in MeCN led to the formation of nearly equal amounts of cyclotrimerization product **9**, annulation product **8** and unreacted **7** (Table 2, Entry 1). The iron congener **Cat2** exclusively delivered **8** with little remaining starting material, which is comparable to Cp*Fe complex **Cat6** (Entries 2 and 6). Similar to **Cat1**, almost no selectivity was observed, when the heteroleptic complex **Cat3** was used as a precatalyst (Entry 3). An astonishing result was obtained with **Cat4**, which yielded the cyclotrimerization product **9** almost quantitatively under these very mild conditions (Entry 4). Consistent with the general reactivity depicted in Scheme 4, the lithium ferrate **Cat5** also selectively yielded the cyclotrimerization product **9** from triyne **7** when the reaction was performed in MeCN (Entry 5).

The formation of these rather unusual reaction products **5, 6** and **8** can be rationalized by looking into the comparable reactions of diynes in

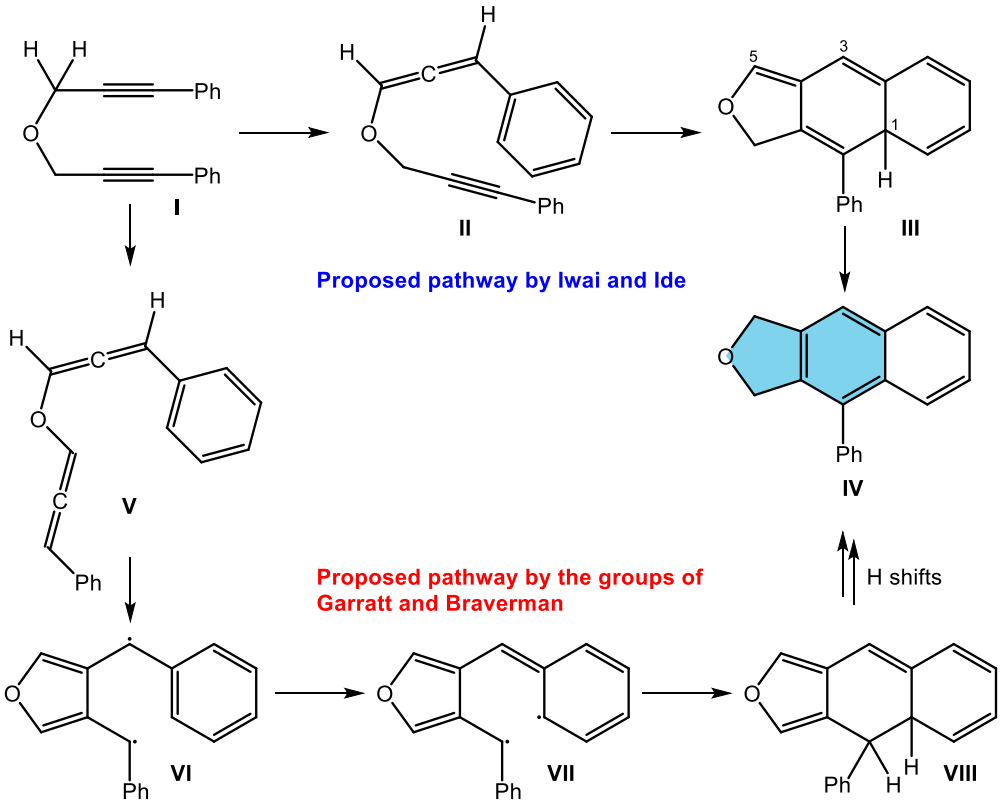
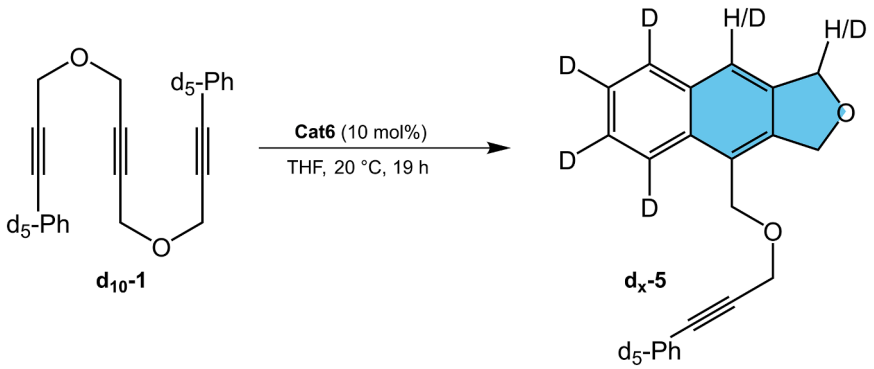
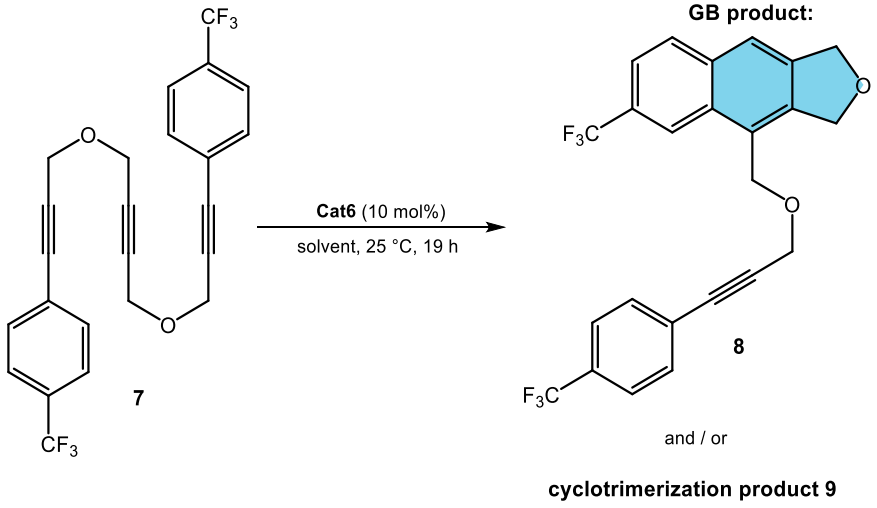


Fig. 2. Proposed reaction pathways for the Garratt-Braverman cyclization for dipropargyl ethers.



Scheme 5. Cyclization of compound $\mathbf{d_{10}}$**–1** using catalyst **Cat6**.

Table 3
Screening results with precatalyst **Cat6** in various solvents.

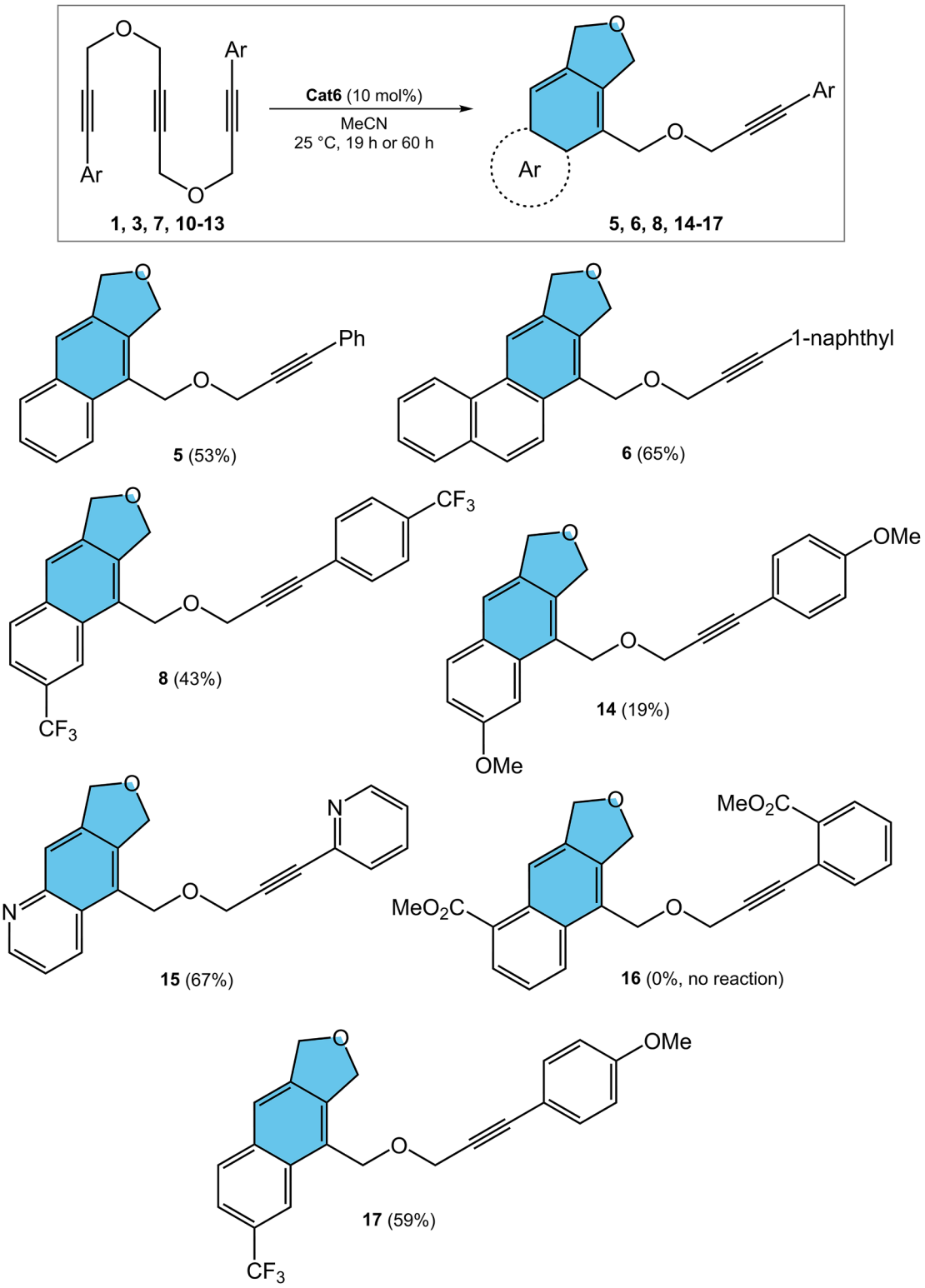


Entry	Solvent	Conversion of **7** [%][a]	Product **8** [%]	Product **9** [%]
1	*n*-Hexane	25	6	–
2	THF	27	16	–
3	MeCN	69	52	–
4	DMF	28	25	–
5	DMSO	51	37	–
6	DCM	7	–	4
7	1,4-Dioxane	12	8	–
8	NMP	82	27	–
9	Toluene	12	7	–

[a] Determined with internal standard.

the presence of strong bases as a possible pathway for the transformation [22]. This generally less well-known reaction is called the Garratt-Braverman (GB) reaction. Mechanistic considerations imply alkyne-allene isomerization and subsequent cyclization. Possible mechanistic pathways are displayed in Fig. 2 and follow early suggestions. Iwai and Ide proposed an alkyne-allene isomerization by the base (**II**), followed by an allene-ene-alkyne intramolecular Diels-Alder-type cycloaddition process (**III**) [23]. The so-constructed annellated phenyl ring then leads to the naphthalene product (**IV**) after hydrogen shifts and aromatization. Contrary to this, Braverman and Garratt proposed the formation of a bisallene (**V**), which rearranges *via* ring closure to a biradical (**VI**) [24]. Shifting one of the radicals lead to a neighboring rearrangement, allowing simple ring closure (**VII** → **VIII**). Again, shifting hydrogens allow the formation of the annellated naphthalene product **IV**.

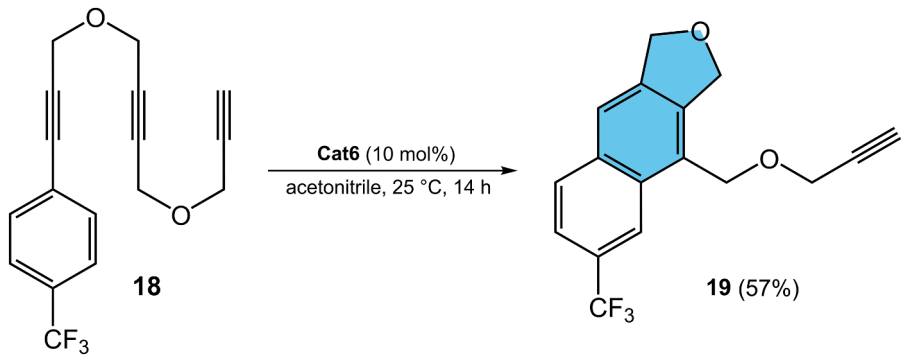
We have synthesized an aryl group-deuterated version of compound **1** ($\mathbf{d_{10}}$**–1**) and subjected the compound to the reaction conditions described above (Scheme 5), an experiment already suggested and executed by Das, Bag and Basak [25]. The cyclization gave the expected reaction product $\mathbf{d_X}$**-5**, possessing deuterium on the newly formed aromatic ring and the former propargylic position. The NMR analysis points towards ca. 36% incorporation into the alkyl position and about 6% in the aromatic position. The deuterium must come from the deuterated phenyl ring of the substrate and confirms the C-D activation that must have occurred during the annulation process. Deuterium redistribution on the newly formed annulated ring and the former propargylic position most likely have occurred during the bond rearrangement in the rearomatization process. Although the incorporation of D in the aromatic



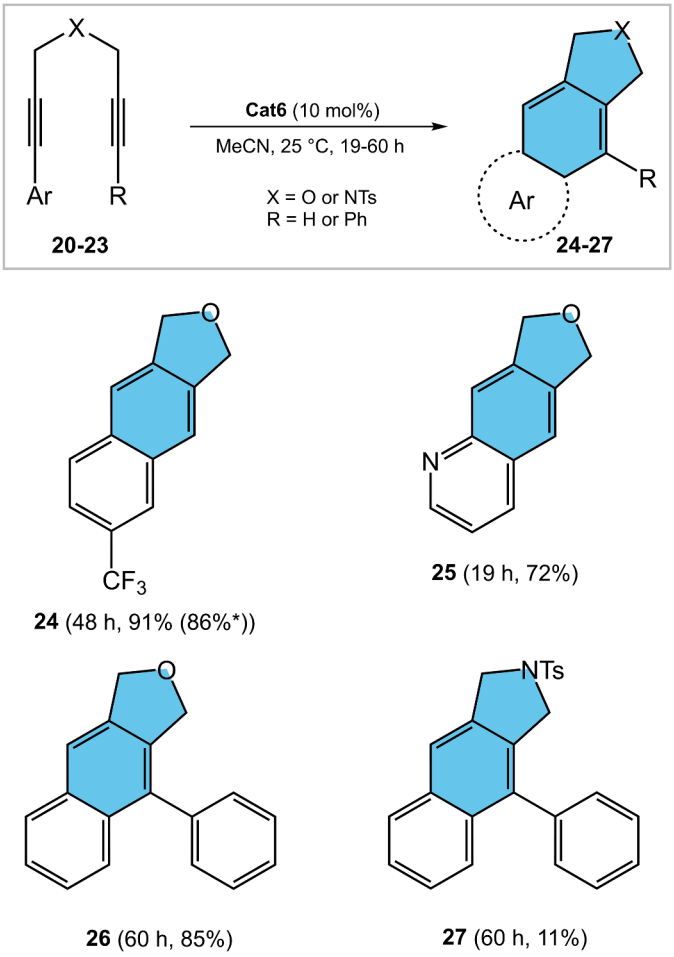
Scheme 6. Application of precatalyst **Cat6** to selectively form annulation products from different triyne substrates.

position is of relatively small extent, similar slightly higher values were already reported in the cited literature and point towards the non-radical version of the mechanism [25]. In the structurally related sulfone-bridged diyne substrate no D incorporation at the aromatic position was found, making the radical pathway most likely. In the case of the O-bridged diyne, the experimental data from the literature demonstrate the difference compared to the sulfone, allowing D incorporation on the aromatic ring as well as the annulated furane ring by 1,3-D and 1,5-D shifts (see **III** in Fig. 2). The postulation of the formation of radicals could also interfere with the presence of the metallate complexes by redox processes.

This initial observation of reactivity reminiscent to the GB cyclization was investigated further by evaluating reaction solvents with different polarities in reactions catalyzed by complex **Cat6**, which gave



Scheme 7. Reactivity of precatalyst **Cat6** with mono-arylated triyne **13**.



Scheme 8. Reactivity of precatalyst **Cat6** towards arylated diynes. (* Reaction was performed on a 1 mmol scale with 24 h reaction time.)

the best result for the GB reaction. The results for the cyclization of test triyne **7** are given in Table 3. The best results were obtained using MeCN as solvent, selectively furnishing the GB product **8** with 52% yield (Table 3, Entry 3). Other polar solvents including DMF, DMSO, and NMP were in general beneficial for the selective synthesis of product **8** (Entries 4, 5 and 8), while THF and 1,4-dioxane displayed the same selectivity but with reduced yields of **8** (Entries 2 and 7). Nonpolar solvents like toluene and *n*-hexane yielded only very small amounts of **8** (Entries 1 and 9). Contrary to all other screened solvents, a very small amount of cyclotrimerization product **9** was observed instead of GB product **8** when the reaction was performed in DCM (Entry 6).

Following the reaction solvent screening we investigated the scope of the GB reactions using precatalyst **Cat6** and different triynes in MeCN (Scheme 6). Applying the phenyl-substituted triyne **1** or 1-naphthyl-substituted triyne **3**, the corresponding GB products were obtained with 53% (product **5**) and 65% (product **6**) isolated yield, respectively. This observation further validated the beneficial effect of MeCN compared to THF as reaction solvent. Triyne **10** bearing *para*-methoxy substituted phenyl rings resulted in diminished yield of the annulation product **14** (19%) when compared to the unsubstituted product **5**. The trifluoromethylated substrate **7** gave the product **8** with 43% isolated yield. It is noteworthy that the 2-pyridyl-substituted triyne **11** was converted with a yield of 67% to the annulated quinoline product **15**, demonstrating the possibility of also performing this reaction with pyridines. Upon employing carboxy methyl substituents on the *ortho* position of the phenyl ring as electron-withdrawing groups, no

conversion to the expected product **16** was observed. From earlier experiments we found that the corresponding triyne **12** containing the electron-withdrawing ester group can be cyclized using $CoCl(PPh_3)_3$ as catalyst, yielding the corresponding cyclotrimerization product with 51% yield [26]. Finally, synthesis of unsymmetrically aryl-substituted triyne **13**, bearing an electron-withdrawing as well as electron-donating group on the aryl substituent gave exclusive GB reaction on the CF_3-substituted aryl ring. Under the reaction conditions a yield of 59% for compound **17** was obtained, displaying the significantly different reactivities already observed in the cyclization of compounds **8** and **14**.

We also exemplarily investigated the reaction with the monoarylated triyne **18** to evaluate whether in this case a possible alternative reaction pathway with the terminal alkyne was possible (Scheme 7). Terminally unsubstituted alkynes often proved to be more reactive in cyclotrimerization reactions. We made similar observations, as the yield of **19** is slightly higher than when the annulation was performed with the diarylated triyne **7** (57% compared to 43%, see Scheme 6).

Next, we investigated the cyclization behavior of diynes with precatalysts **Cat6** using MeCN as reaction solvent (Scheme 8). The reaction was performed at room temperature and allowed the annulation of ether-bridged diynes (**20–22**), affording the GB products **24–26** in very good yields albeit with longer reaction times (up to 60 h). The reaction for compound **24** was also performed on a 1 mmol scale, resulting in only slightly inferior yield compared to the original scale (86 vs. 91%). Basak and co-workers reported the synthesis of product **25** by using a strong base (KO*t*-Bu) under reflux conditions with slightly higher yield (80%) [21b].

Compound **25** was also prepared in the presence of Triton B and NaH in DMSO at room temperature with 32% yield, interpreted to be initiated by an anionic Diels-Alder reaction [20]. Contrary to product **26**, the tosylated amine-bridged analogue **23** gave only 11% of the expected GB product **27**. Thus, it can be speculated that the N-tosyl group might be detrimental for the successful cyclization.

In an attempt to gain insight into the catalytic mechanism, stoichiometric 1:1 reactions of **Cat6** with triyne **1** were conducted in THF-d_8 and d_3-MeCN (for the spectra, see SI). Conversion of the catalyst was determined by comparison of the integrals of free naphthalene ($\delta = 7.50$, 7.88 ppm) generated in the reaction with [18]crown-6 ($\delta = 3.50$ ppm). Whilst a reaction time of 18 h was necessary to completely convert the ferrate in THF-d_8, full conversion was detected after 1 h when the reaction was conducted in d_3-MeCN. This is in agreement with the observed slower reaction rate for the catalytic reaction in THF, when compared to MeCN. Besides free naphthalene and [18]crown-6, unidentified signals were observed in the aliphatic region at 1.78, 1.72 and 0.96 ppm. No signals of **1** or a triyne cyclization product were identified in the NMR spectra. The absence of any product signal might be explained by the formation of a substantial amount of insoluble red powder during the reaction. Attempts to characterize this product by X-ray crystallography have so far been unsuccessful. Upon aqueous workup of the reaction, naphthalene, [18]crown-6 and Cp*H, as well as traces of **5** could be observed *via* mass or NMR spectroscopy. As the observed red powder was hypothesized to be a possible intermediate in the catalytic cycle, another equivalent of triyne **1** was added to the reaction mixture of **Cat6** and one equiv. of **1** in d_3-MeCN. This led to the complete dissolution of the powder, surprisingly accompanied not by the appearance of **5**, but by the clean formation of cyclotrimerization product **2**. When the reaction of **Cat6** and two equiv. of **1** was performed in THF, Garratt-Braverman cyclization product **5** and cycloaddition product **2** were both observed together with unreacted triyne **1** in a ratio of 1 : 0.5 : 1.6, respectively. Altogether, these experiments show that the competitive mechanisms for the formation of the [2 + 2 + 2] cycloaddition and the Garratt-Braverman cyclization products are not only governed by the catalyst structure, but the solvent and the substrate – catalyst ratio also seem to play a major role in determining product formation.

Conclusion

The present study uncovered the dichotomic behavior of cobaltates and ferrates containing neutral ligands (arenes, olefins) and cyclopentadienyl ligands (Cp, Cp*) in catalytic cyclization reactions of diynes and triynes, which afford either [2 + 2 + 2] cycloaddition products or arene annulation products at room temperature. Cobaltates and ferrates containing either anthracene, naphthalene or 1,5-cyclooctadiene catalyze the cyclotrimerization of triynes with yields up to 71% without formation of significant amounts of byproducts in THF as reaction solvent. The ferrate complex **Cat6** containing a Cp* ligand, however, yielded the annulation product of two alkyne units with the terminal aromatic ring of the substrate in modest yields in THF. The formation of such products is known from non-catalytic Garratt-Braverman reactions of diynes in the presence of strong bases. Investigation of the *para*-trifluoromethylphenylated triyne **7** with the different catalysts preponderantly delivered the cyclotrimerization product or a mixture of the cyclotrimerization and annulation product. Using the Cp*Fe-naphthalene ferrate **Cat6** in acetonitrile allowed the exclusive formation of the Garratt-Braverman product with up to 67% yield for triynes and up to 91% for diyne cyclization. The investigation provided further evidence for the exceptional reactivity of these metallates for catalytic cyclotrimerization reactions under mild conditions as well as a promising catalytic version of the Garratt-Braverman reaction.

Credit author statement

Benedikt N. Baumann: Synthesis of substrates, cyclization experiments, data collection and writing of the manuscript and supporting information.

Helge Lange: Initial investigations of the metallate catalysts and cyclization reactions during his MSc thesis.

Felix Seeberger: Synthesis of metallates, investigations towards the reaction mechanism, writing of the manuscript.

Philipp Büschelberger: Initial investigations of the metallate catalysts and cyclization reactions, collaboration with Helge Lange.

Robert Wolf and Marko Hapke: Conceptualization of project, supervision of students, funding acquisition, writing of originally drafted manuscript.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

Robert Wolf reports financial support was provided by Deutsche Forschungsgemeinschaft (RTG Ion Pairs in Molecular Reactivity, Project 426795949).

Data availability

Data will be made available on request.

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Supplementary materials

Supplementary material associated with this article can be found, in

the online version, at doi:10.1016/j.mcat.2023.113482.

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