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Transition metal-free vs. metal-catalyzed cyclotrimerization of didehydro[8]annulenes (COTynes): a complex pathway to non-planar PAHs – Dewar benzenes vs. benzotri[8]annulenes†

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The formation of non-planar PAHs from didehydro[8]annulene (COTyne) cycloadditions was investigated under both transition metal-catalyzed (Pd, Ru) and metal-free conditions. The observed reactivity depended on the planarity of the COTyne and the reaction conditions. Parent COTyne **1a** dimerized into naphthocyclooctatetraene under TM-free conditions, whereas Pd(0) catalysis promoted its cyclotrimerization into benzotri[8]annulene **7**. X-ray characterization and its dynamic behavior in solution was investigated. Planar dibenzoCOTyne **1b** exhibited different reactivity depending on its formation method (*in situ* or preformed), the metal catalyst (Pd, Ru), and absence of catalysts. Under Pd(0) catalysis, cyclotrimerization yielded benzo-fused tri(dibenzo[8]annulene) **3** with moderate efficiency, regardless of how **1b** was generated. The presence of K⁺ had no significant effect compared to tribenzoCOTyne **1c**. Without metal catalysts, **1b** predominantly formed the corresponding Dewar benzene derivative **2**. With Ru(II) catalysts, reactivity was influenced by both the generation method of **1b** and the Cp ligand. When generated *in situ*, **1b** was an inefficient ligand for CpRu, leading to Dewar benzene formation, whereas preformed **1b** produced **3** in moderate yields. The competition between Dewar benzene and benzo-fused tri(dibenzo[8]annulene) formation increased with greater steric hindrance at the Ru center (CpRu vs. Cp^{*}Ru catalysts). Dewar benzene formation likely proceeds *via* a cyclobutadiene intermediate followed by cycloaddition.

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) have garnered increasing attention since the discovery of planar graphene¹ structures, which exhibit exceptional electronic and optical properties.² The synthesis of planar PAHs typically requires regioselective fusion of multiple rings. Over the years, significant progress has been made in addressing this challenge.^{1,2a,3} Metal-catalyzed cycloadditions have proven particularly effective, as they efficiently form aromatic rings – examples include triphenylene⁴ and biphenylene cores,⁵ as well as helicenes⁶ and helicene-like molecules.⁷ More recently, non-planar (curved)⁸ PAHs with bowl-⁹ and saddle-shaped¹⁰ geometries have emerged as fascinating systems, as they can modify and improve the electronic and optical properties of their planar counterparts (Fig. 1).

Although the metal-catalyzed trimerization ([2 + 2 + 2] cycloadditions) of planar arynes is well established (Scheme

1A),¹¹ the cyclotrimerization of cycloocta-1,3,5-trien-7-ynes (COTynes or didehydro[8]annulenes) and their symmetrical benzo-fused derivatives (benzoCOTynes) into benzo-fused tri[8]annulenes *via* transition metal (TM) catalysis has been scarcely investigated.¹² The few reported cases have produced puzzling and unexpected outcomes, as stated below.

The structure of cubic graphite containing benzoannulated eight-membered rings – a hypothetical three-dimensional sp²-carbon allotrope with intriguing ion transport properties – has become one of the most attractive synthetic targets for exploring cyclotrimerizations.¹³ In this context, Müllen and coworkers, in their pursuit of a molecular model of cubic graphite, reported that *in situ* generated saddle-shaped COTyne **1d** (phenanthrene-

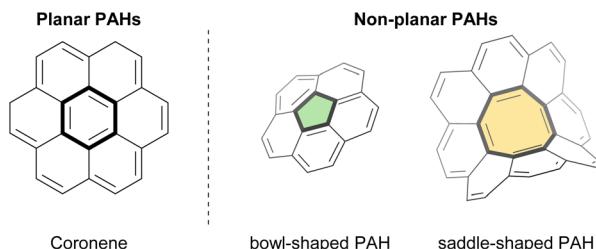
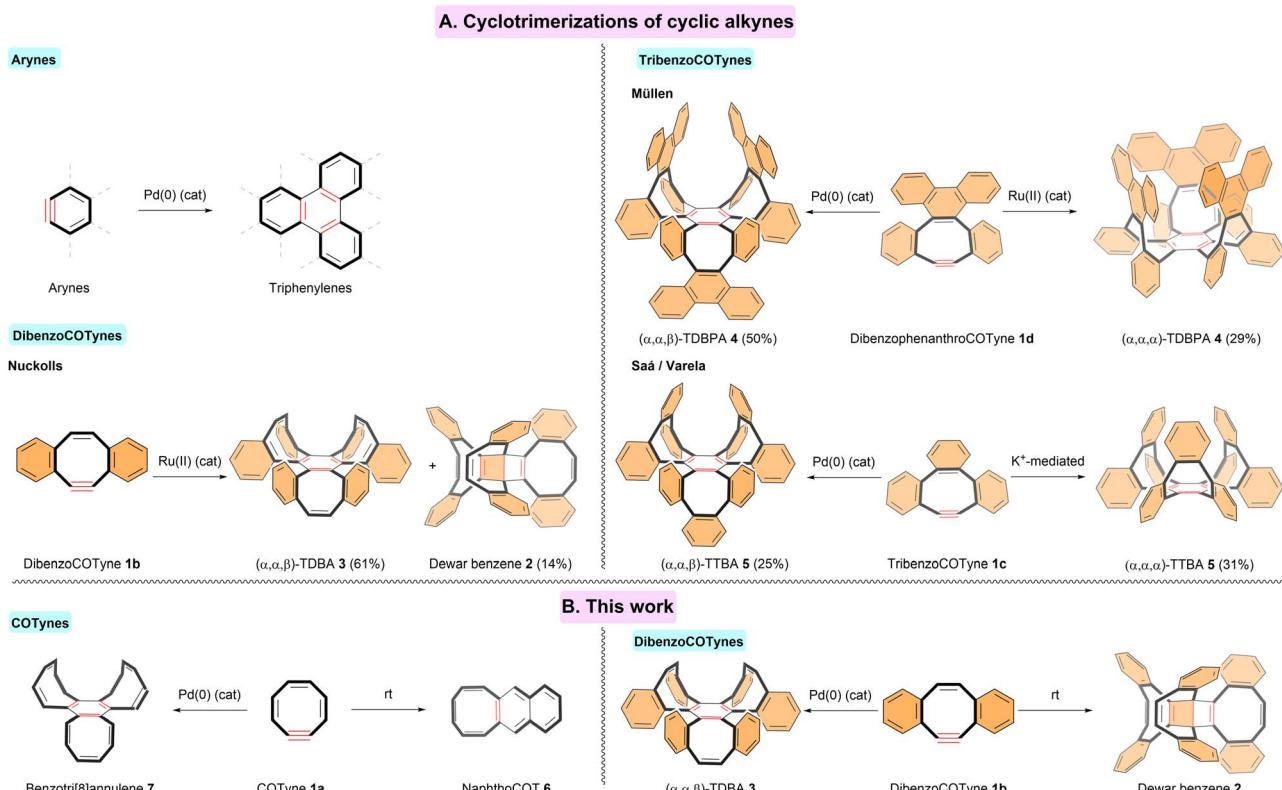


Fig. 1 Benzannulated PAHs and non-planar bowl- and saddle-shaped PAHs.

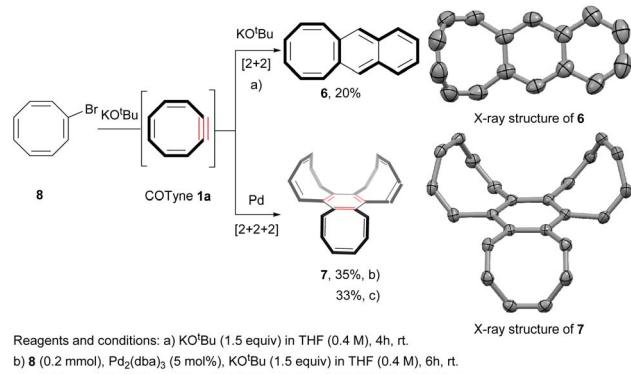
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Scheme 1 (A) Cyclotrimerizations of cyclic alkynes: arynes, dibenzoCOTynes and tribenzoCOTynes. (B) Transition-metal-free and metal-catalyzed cycloadditions of COTyne **1a** and dibenzoCOTyne **1b**.



Scheme 2 Transition-metal free and Pd-catalyzed cycloadditions of COTyne **1a**. ORTEP drawing of naphthoCOT **6** and benzotri[8]annulene **7** showing thermal ellipsoids at the 50% probability level, H atoms have been omitted for clarity.

dibenzofused COTyne) could be trimerized into the (α,α,β) - or (α,α,α) stereoisomers of tri[8]annulene **4** (TDBPA) using two different transition metal catalysts, $\text{Pd}(\text{dba})_2$ and $[\text{CpRu}(\text{CH}_3\text{CN})_3]\text{PF}_6$ (Scheme 1A).¹⁴ More recently, our group demonstrated that *in situ* generated saddle-shaped tribenzoCOTyne **1c** can be selectively trimerized into the non-interconvertible (α,α,β) - or (α,α,α) -benzofused tris(tribenzo[8]annulenes) **5** (TTBA) *via* Pd-catalyzed or K^+ -mediated processes, respectively (Scheme 1A). DFT calculations have been used to rationalize the selective formation of the (α,α,α) -stereoisomer, which represents a true

open fragment of the proposed cubic graphite structure under K^+ -mediated conditions.¹⁵

In contrast, Nuckolls and coworkers previously reported the formation of Dewar benzene derivative **2** (DB) and the (α,α,β) -stereoisomer of benzofused tri(dibenzo[8]annulene) **3** (TDBA) from planar dibenzoCOTyne **1b** using $[\text{CpRu}(\text{CH}_3\text{CN})_3]\text{PF}_6$ as the catalyst (Scheme 1A).¹⁶ Unfortunately, no clear mechanistic explanation was provided to account for the observed selectivity of Ru-catalyzed reactions involving both planar dibenzo- and non-planar tribenzoannulated COTynes.

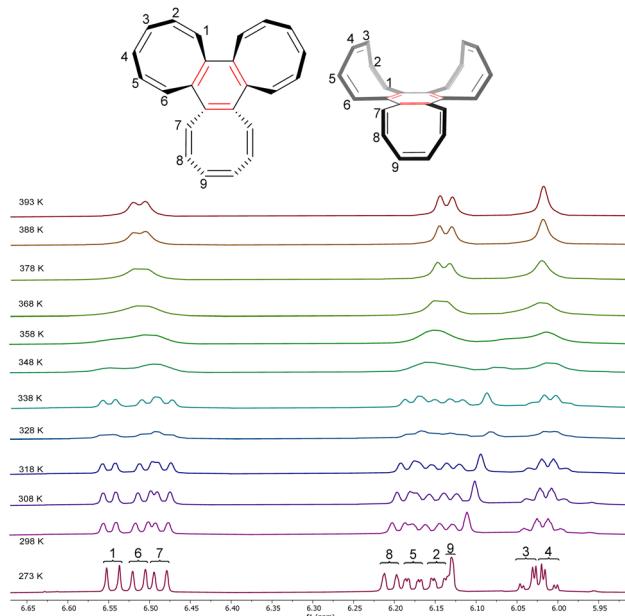
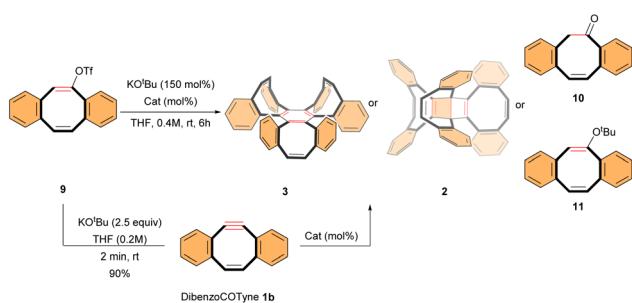
From these results, it appears that both the reaction conditions and the geometry of the cyclic alkynes (COTynes), ranging from saddle-shaped to nearly planar (depending on the absence or presence of benzoannelated rings), determine the reaction outcome. To clarify these aspects and address the previously puzzling results on COTyne cyclotrimerizations, we present here the intriguing structure-dependent reactivity of COTynes, cycloocta-1,3,5-trien-7-yne (COTyne **1a**) and 5,6-didehydrodibenzo[*a,e*][8]annulene (dibenzoCOTyne **1b**), in their respective cyclotrimerizations to non-planar PAHs (Scheme 1B).

Results and discussion

COTyne **1a**

Based on previously published results, it remains unclear whether the planar intermediate COTyne **1a**, generated from bromoCOT **8** (ref. 17) in the presence of $\text{KO}'\text{Bu}$, undergoes cyclotrimerization or cyclodimerization. The cyclotrimerization



Fig. 2 VT-¹H NMR spectra of (α,α,β)-benzotri[8]annulene 7.Table 1 Transition metal-free and metal-catalyzed cycloadditions of dibenzoCOTyne 1b^a

Entry	Starting material	Catalyst (mol%)	Product (yield) ^b
1	9	Pd ₂ (dba) ₃ (5)	3 (25%)
2 ^c	9	[CpRu(CH ₃ CN) ₃]PF ₆ (10)	10 (40%)
3	9	[CpRu(CH ₃ CN) ₃]PF ₆ (10)	2 (44%)
4	9	—	2 (60%)
5 ^d	1b	—	2 (17%)
6 ^e	1b	—	2 (17%)
7 ^f	1b	—	11 (50%)
8	1b	Pd ₂ (dba) ₃ (5)	3 (40%)
9 ^c	1b	[CpRu(CH ₃ CN) ₃]PF ₆ (10)	3 (30%) + 2 (13%)
10 ^c	1b	[Cp [*] Ru(CH ₃ CN) ₃]PF ₆ (10)	3 (8%) + 2 (33%)
11 ^c	1b	Cp [*] RuCl(cod) (10)	2 (52%)

^a Conditions: SM (0.2 mmol), with or w/o [M], with or w/o KO'Bu in THF (0.4 M) at rt. ^b Isolated yield. ^c DCM instead of THF. ^d THF (0.4 M) at rt.

^e THF (0.4 M) at rt, in the presence of K[B(ArF₅)₄] (1.5 equiv). ^f THF (0.4 M) at rt, in the presence of KO'Bu (1.5 equiv).

of COTyne 1a has been suggested based on EPR spectroscopic measurements of the tri[8]annulenylene radical. However, doubts persist due to the lack of a described synthesis procedure and spectroscopic data for the proposed cyclotrimer.¹⁸

In contrast, Krebs previously reported that a similar treatment of 8 with KO'Bu yielded a dimeric product of the COTyne intermediate, naphthoCOT 6, in low yield, rather than the trimeric annulene 7.¹⁹ To resolve these conflicting results and determine whether dimerization or trimerization occurs under basic conditions, we subjected bromoCOT 8 to the same basic conditions. We obtained naphthoCOT 6 in low yield (20%), with no trace of the corresponding benzotri[8]annulene 7 (Scheme 2). The molecular structure of naphthoCOT 6 was determined by X-ray diffraction analysis.²⁰

We then explored transition metal-catalyzed processes. To our delight, treatment of bromoCOT 8 under our optimized Pd-catalyzed trimerization conditions for tribenzoCOTyne¹⁵ successfully yielded the expected (α,α,β)-benzotri[8]annulene 7 in 33–35% yield (Scheme 2). The (α,α,β) conformational structure of 7 was verified by X-ray crystallography²⁰ and further supported by the presence of nine signals in its ¹H NMR spectrum in *o*-C₆Cl₂D₄ solution, indicating a symmetry plane. The signals of 7 were assigned based on ¹H and ¹³C NMR data, as well as 2D HSQC, HMBC and COSY spectra (Fig. 2 and ESI[†]).

To investigate conformational exchange among the three degenerate conformers of (α,α,β)-benzotri[8]annulene 7, variable-temperature NMR (VT-NMR) spectroscopy was used to study the dynamics of the (α,α,β) isomer (Fig. 2). As expected, the nine signals in the ¹H NMR spectrum at room temperature merged into three signals – two doublets and one singlet – when heated to 388 K. This change occurred due to rapid exchange between conformers, resulting in an averaged signal for each proton type.

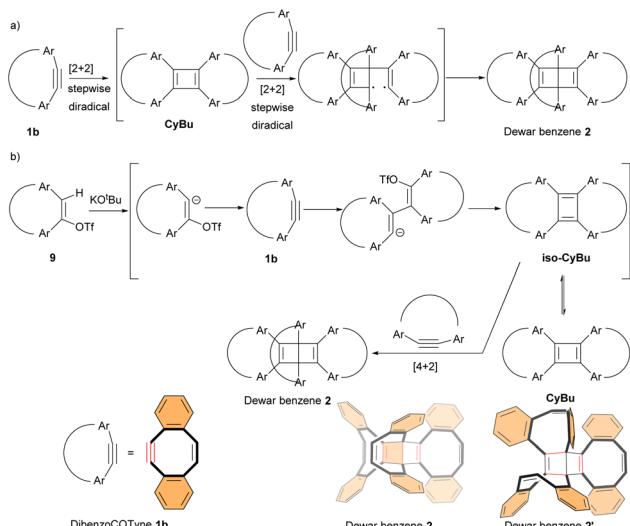
The coalescence temperature (T_c) for selected protons (6,7 and 3,4) at 348 K allowed us to estimate the activation free energy (ΔG^\ddagger) for the flipping of the cyclooctatetraene ring in 7 as 17.8 kcal mol⁻¹.²¹ DFT calculations yielded a theoretical ΔG^\ddagger of 18.4 kcal mol⁻¹ for the interconversion between degenerate (α,α,β)-7 conformers and 19.9 kcal mol⁻¹ for the interconversion between (α,α,β) and (α,α,α) isomers. The (α,α,β) isomer was found to be 1.8 kcal mol⁻¹ more stable than the (α,α,α) isomer.²²

DibenzoCOTyne 1b

Next, we analyzed the influence of benzo-fused rings on the reactivity of COTyne. Treatment of vinyl triflate 9 (ref. 23) under similar Pd-catalyzed conditions yielded benzfused tri(dibenzo[8]annulene) 3 (TDBA) in low yield (25%, Table 1, entry 1). This result clearly indicates that the dibenzoCOTyne intermediate 1b is less reactive than the COTyne 1a in Pd-catalyzed trimerizations. Although the X-ray structure of the (α,α,β)-TDBA 3 had been previously reported, the NMR spectra were not described.^{16b} Our results confirm the (α,α,β)-conformer, as indicated by the presence of 15 signals in the ¹H NMR spectrum and 24 signals in the ¹³C NMR spectrum, 9 of which correspond to quaternary carbons, suggesting a plane of symmetry.²²

Surprisingly, when vinyl triflate 9 was reacted under basic conditions with [CpRu(CH₃CN)₃]PF₆ as a catalyst, we obtained moderate yields of either ketone 10 (40% in DCM) or DB 2 (44% in THF) (Table 1, entries 2 and 3),²⁴ but no TDBA 3 was detected. Interestingly, in a control experiment without a Ru catalyst, treatment of vinyl triflate 9 under basic conditions at room temperature produced DB 2 in a relatively high yield of 60%





Scheme 3 Plausible transition metal-free routes to DB 2: (a) from dibenzoCOTyne **1b**; (b) from vinyl triflate **9** + $\text{KO}'\text{Bu}$.

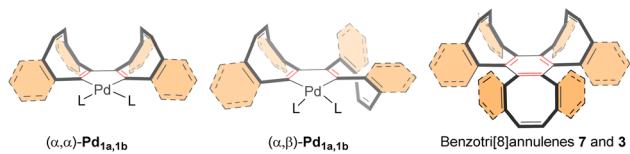


Fig. 3 Palladacycle intermediates on the cyclotrimerization of COTyne **1a** and dibenzoCOTyne **1b**.

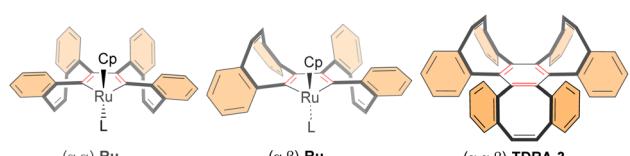


Fig. 4 Ruthenacycle intermediates on the cyclotrimerization of dibenzoCOTyne **1b**.

(Table 1, entry 4), establishing an alternative, transition metal-free route to this product.²⁵

The formation of dibenzoCOTyne **1b** appears to be involved in this process, as a THF solution of preformed **1b**²⁶ generated DB 2, albeit in a surprisingly low yield of 17% (Table 1, entry 5).²⁷ The effect of K^+ salts was then investigated.¹⁵ A similar outcome was observed when potassium salt $\text{K}[\text{BarF}_5]_4$ was added to a THF solution of **1b** (Table 1, entry 6). However, when the reaction was conducted in the presence of $\text{KO}'\text{Bu}$, the primary product was vinyl ether **11** (50%, Table 1, entry 7), suggesting that **1b** was captured in this form.²²

As expected, the Pd-catalyzed trimerization of dibenzoCOTyne **1b** produced the (α,α,β) -TDBA **3** in an improved 40% yield (Table 1, entries 1 vs. 8), demonstrating that efficient cyclotrimerization requires alkyne coordination to Pd. Similar to Ru-catalyzed trimerizations, the presence of alkynes is essential for a successful cyclotrimerization.^{12b}

In our hands, subjecting dibenzoCOTyne **1b** to $[\text{CpRu}(\text{CH}_3\text{CN})_3]\text{PF}_6$ 10 mol%, DCM, rt, yielded tri[8]annulene **3** as the major product (30%) and DB **2** as the minor product (13%) (Table 1, entry 9). However, using the more electron-rich and sterically hindered catalyst, $[\text{Cp}^*\text{Ru}(\text{CH}_3\text{CN})_3]\text{PF}_6$, resulted in an inverted product ratio, with **3** as the minor product (8%) and DB **2** as the major product (33%) (Table 1, entry 10). Since the overall yield remained nearly unchanged, the steric hindrance at the Ru center is likely the key factor influencing this outcome.

Furthermore, employing the neutral catalyst $\text{Cp}^*\text{RuCl}(\text{cod})$ completely inhibited the cyclotrimerization of **1b**, yielding DB **2** as the sole isolated product (Table 1, entry 11).

Variable-temperature VT^1H NMR studies on (α,α,β) -TDBA **3** showed no significant variations within the examined temperature range (298–373 K, Fig. S1, ESI†), indicating no interconversion between isomers. DFT calculations further supported this, revealing very high activation free energy barriers (ΔG^\ddagger) of 44.8 kcal mol⁻¹ for interconversion between degenerate (α,α,β) conformers and 53.0 kcal mol⁻¹ for transformation from the (α,α,β) to the (α,α,α) isomer. Additionally, the (α,α,β) isomer was found to be 3.2 kcal mol⁻¹ more stable than the (α,α,α) isomer.²²

Transition metal-free cyclotrimerization of dibenzoCOTyne **1b**: formation of Dewar benzene derivative **2** (DB)

The thermal dimerization and cyclotrimerization of linear substituted alkynes are well-documented processes, both experimentally and through DFT calculations.²⁸ These calculations suggest that the cyclotrimerization of the cyclic alkyne dibenzoCOTyne **1b** proceeds through the initial formation of a cyclobutadiene (**CyBu**) intermediate *via* a stepwise $[2+2]$ diradical cycloaddition of two dibenzoCOTyne **1b** units (Scheme 3a). This **CyBu** intermediate then undergoes another stepwise $[2+2]$ diradical cycloaddition with a third dibenzoCOTyne **1b** molecule, leading to the formation of the “cyclophane” DB **2** as the final cyclotrimer. Notably, DB **2** remains stable and does not undergo the typical ring-opening to the corresponding benzene, since this transformation would generate a highly strained *p*-[6]-cyclophane.^{28a,29}

Notably, entries 4 and 5 in Table 1 reveal that the yield of DB **2** is higher when dibenzoCOTyne **1b** is generated *in situ* under basic conditions (entry 4) compared to when preformed/isolated **1b** is used (entry 5). This observation prompted an investigation into an alternative pathway for the dimerization/trimerization leading to Dewar benzene formation. It is plausible that the **iso-CyBu** cyclobutadiene isomer could form directly from the initial vinyl triflate **9** under basic conditions (Scheme 3b). These two valence isomers can interconvert *via* a relatively low-energy barrier,³⁰ and capturing this **iso-CyBu** isomer in a favorable $[4+2]$ cycloaddition with dibenzoCOTyne **1b** would directly yield DB **2**.

Interestingly, unlike Cp^3 -annelated cyclobutadienes, no tetramerization of the **CyBu** or **iso-CyBu** cyclobutadiene intermediates was detected.³¹ Furthermore, cyclotrimerization to form dibenzotri[8]annulene **3** was also not observed,³² suggesting that the formation of the alternative “non-cyclophane” DB **2'** intermediate is not favored.³³

Mechanistic hypotheses for Pd(0)- and Ru(II)-catalyzed cyclotrimerizations

Pd-catalyzed cyclotrimerization ($[2 + 2 + 2]$ cycloadditions) of arynes is a well-established method for synthesizing triphenylene and its benzo-fused derivatives.^{11c} This process involves the formation of a palladacycle intermediate (a square planar palladacyclopentadiene), followed by the insertion of a third alkyne unit and a final reductive elimination. Arynes are typically generated *in situ* from their corresponding *o*-(trimethylsilyl)triflates precursors in the presence of fluoride sources.

A similar Pd-catalyzed cyclotrimerization occurs when the parent COTyne **1a** and dibenzoCOTyne **1b** – either preformed or generated *in situ* from their bromo- and triflate COT precursors **8** and **9** – are involved. Due to the non-planar structure of COTs in palladacycles, conformers must be taken into account. Additionally, the reactivity of COTynes is inversely related to the number of fused benzene rings (*i.e.*, the more strained the COTyne, the more reactive it is).

From COTyne **1a**, two possible palladacycle intermediates can form: one where both COT units are on the same face (α,α) and another where they are on opposite faces (α,β). These intermediates can interconvert through a simple flap process. Given the low steric hindrance of the unsubstituted COT ring, the insertion of a third alkyne unit should ultimately yield the thermodynamically favored (α,α,β)-tri[8]annulene **7** (Fig. 3).

A similar mechanism is expected for the formation of tri[8]annulene **3** when dibenzoCOTyne **1b** (preformed or generated *in situ* from **9**) participates in Pd-catalyzed cyclotrimerization (Fig. 3). However, in this case, significant steric hindrance from the benzofused rings could impede the COT core flap process.

According to the accepted mechanism for the Ru(II)-catalyzed alkyne cyclotrimerization,³⁴ two possible intermediates – ruthenacyclopentadiene or ruthenacyclobiscarbene – can form, adopting either an (α,α) or (α,β) configuration. In both cases, the Cp ligand is positioned on the opposite face of the tetrahedral geometry around the Ru center (Fig. 4).³⁵ Following coordination of the third alkyne (dibenzoCOTyne), a formal $[2 + 2]$ cycloaddition occurs, placing the new benzene rings of the incoming dibenzoCOTyne on the opposite face of those already present in the ruthenacyclopentadiene/ruthenacyclobiscarbene intermediate. As a result, the formation of (α,α,β)-dibenzotri[8]annulene (TDBA) **3** is favored, regardless of whether the initial intermediate adopts an (α,α) or (α,β) configuration (Fig. 4).

For Ru(II)-catalyzed cyclotrimerization of preformed dibenzoCOTyne **1b** (Table 1, entries 9–11), the formation of DB **2** – either predominantly (in Cp*Ru complexes) or partially – may originate from the trapped **iso-CyBu** cyclobutadiene isomer. This intermediate could be generated through reductive elimination from a ruthenacyclobiscarbene species.³⁶

Conclusions

In summary, we have investigated the cycloadditions of COTynes under both catalyzed (Pd, Ru) and non-catalyzed conditions. The observed reactivity depended on the nature of the COTyne and the reaction conditions. The parent COTyne **1a** led to the

dimerization product, naphthocyclooctatetraene **6**, under thermal conditions, whereas in the presence of Pd(0) catalysts, it underwent cyclotrimerization to form benzotri[8]annulene **7**.

For the planar dibenzoCOTyne **1b**, its reactivity varied based on its mode of formation (*in situ* or preformed), the choice of metal catalyst (Pd, Ru), and the absence of catalysts. Under Pd catalysis, cyclotrimerization yielded benzo-fused tri(dibenzo[8]annulene) **3** in moderate yields, regardless of how dibenzoCOTyne **1b** was generated. In contrast, under transition metal-free conditions, dibenzoCOTyne **1b** consistently evolved into Dewar benzene derivative **2** (DB), although yields varied. No beneficial effect of K⁺ on its reactivity was observed.

Interestingly, the reactivity of dibenzoCOTyne **1b** under Ru(II) catalysis depended on its formation mode and the steric properties of the Cp ligand at the Ru center. When generated *in situ*, **1b** was unable to coordinate effectively to the CpRu catalyst, leading to DB **2** as the predominant product. However, when preformed dibenzoCOTyne **1b** was used with a CpRu(II) catalyst, cyclotrimerization proceeded in moderate yields to afford benzo-fused tri(dibenzo[8]annulene) **3**. The competition between DB **2** and tri[8]annulene **3** formation was more pronounced with increased steric hindrance at the Ru center (CpRu *vs.* Cp*Ru catalysts).

The formation of DB **2** likely proceeds through an initial cyclobutadiene intermediate, either a radical or ionic mechanism, depending on the reaction conditions, followed by cycloaddition with dibenzoCOTyne **1b**.

Functionalizations and further applications of benzotribenzo-fused tri[8]annulenes are currently in progress in our lab.

Data availability

All experimental data associated with this work are provided in the ESI.† Crystallographic data for **6** and **7** have been deposited at the CCDC under 2418247 and 2427818, respectively, and can be obtained from http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Author contributions

J. Bello-García performed the experimental work and data analysis. J. A. Varela and C. Saá conceived the project, supervised the investigation and wrote the manuscript. All authors discussed the results and contributed to the preparation of the final manuscript.

Conflicts of interest

There are no conflicts to declare.

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