

# Activated Phenacenes from Phenylenes by Nickel-Catalyzed Alkyne Cycloadditions\*\*

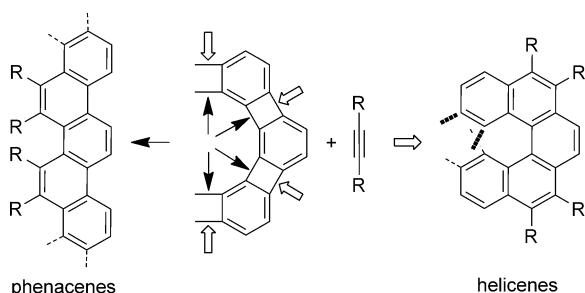
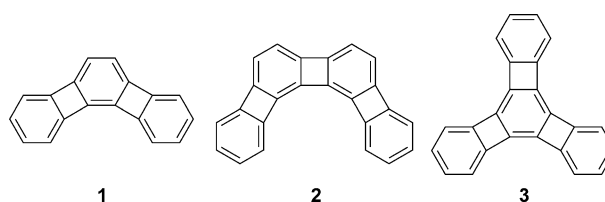
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Polycyclic aromatic hydrocarbons have emerged as key components of future (opto)electronic and other nanodevices.<sup>[1]</sup> Functional constraints, such as air-sensitivity, instability, unfavorable band-gap, insolubility, and encumbered processability require tunable synthetic approaches to specific targets.<sup>[2]</sup> We report the Ni-catalyzed cycloaddition of alkynes to the angular phenylene motif,<sup>[3,4]</sup> which engenders novel sterically and electronically activated extended phenacenes<sup>[5]</sup> with extensive selectivity. The potential of phenacenes as components for light-emitting diodes, field-effect transistors, and superconductors has been discovered only recently.<sup>[6]</sup>

In principle, the angular phenylene frame could undergo attack by alkynes at either the bay (full arrows) or the non-bay region (open arrows), which, if complete and regiochemically pristine, would furnish only one of the two extremes, phenacenes or helicenes, respectively (Figure 1). In the absence of such selectivity, the number of possible products is substantial: 5 for parent system **1**, 17 for angular

[4]phenylene **2**, and 6 for  $C_3$ -symmetric [4]phenylene **3**. We report a more optimistic experimental picture that is associated with an unexpected bifurcation in mechanism, as pinpointed by DFT computations.

The results of a comparative study of the [Ni(cod)-(PMe<sub>3</sub>)<sub>2</sub>]-catalyzed cycloaddition (cod = 1,5-cyclooctadiene) of diphenylacetylene (dpa) to equimolar amounts of **1**, **2**, and **3**, respectively, under identical reaction conditions are shown



**Figure 1.** The two extremes of angular phenylene reactivity in cycloadditions to alkynes.

in Table 1.<sup>[7]</sup> Inspection of the product structures reveals remarkable selectivity toward the formation of phenacene (sub)units derived from multiple insertions, even though only one equivalent of alkyne reagent is present. Consequently, varying amounts of starting phenylenes are recovered, but the mass balances are good to excellent.

Each one of the ensuing topologies (six of which were detailed by X-ray analysis; Table 1)<sup>[7]</sup> exhibits unique features as a result of  $\pi$ -activation through benzocyclobutadienofusion and/or extreme  $\sigma$ -distortion from planarity caused by the crowded 4,5-diphenylphenanthrene<sup>[8]</sup> substructures. Thus, yellow **4** presents the unknown benzo[3,4]cyclobuta[1,2-*a*]-phenanthrene connectivity.<sup>[9]</sup> Its phenyl groups are rotated extensively relative to the attached  $\pi$ -core (as also seen for the other structures), the center of one of which (at C11) is located directly above H10 of the biphenylene fragment (distance 2.496 Å), causing extraordinary shielding of this nucleus ( $\delta$  = 4.01 ppm!). This phenomenon is also observed for **6**, **7**, and **9**.<sup>[7,10]</sup> The activation of the phenanthrene nucleus is structurally evident in the change in the sequence of bond alternation in the annelated terminal ring<sup>[7]</sup> and in the electronic spectrum [e.g., highest  $\lambda_{\text{max}}$  = 420 nm; cf. phenanthrene: 345 nm, or the “hexagonal squeeze”<sup>[11]</sup> [4]phenacene (chrysene): 360 nm].<sup>[12]</sup> These effects are even more pronounced in the [*a,i*] and [*a,c*] doubly fused and topologically new<sup>[13]</sup> red phenanthrenes (air sensitive) **6** ( $\lambda_{\text{max}}$  = 484 nm; cf. [5]phenacene (picene): 376 nm)<sup>[12]</sup> and **9** ( $\lambda_{\text{max}}$  = 503 nm; cf. benzo[*g*]chrysene: 371 nm).<sup>[7,14]</sup> Turning to the [5]phenacene structures, colorless derivative **5** ( $\lambda_{\text{max}}$  = 405 nm) suffers the consequences of severe twisting caused by the 5,6,7,8-tetraphenyl substitution, most dramatically illustrated by the

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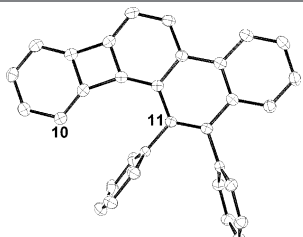
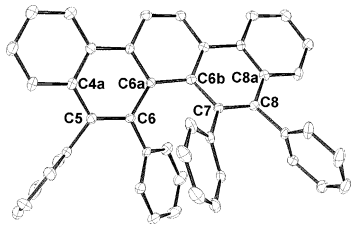
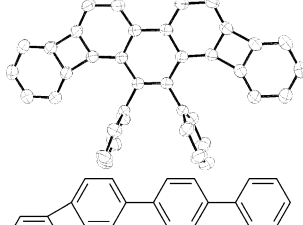
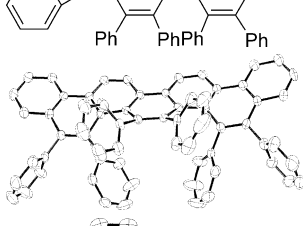
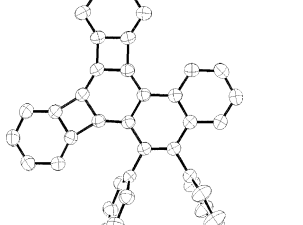
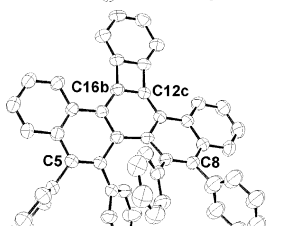
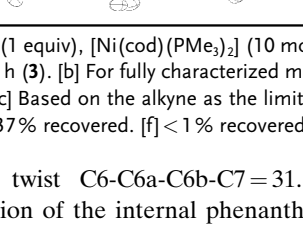
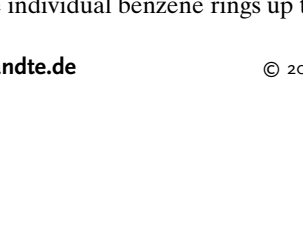
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**Table 1:** Phenylated phenacenes by the Ni-catalyzed cycloaddition of dpa to **1–3**.<sup>[a]</sup>

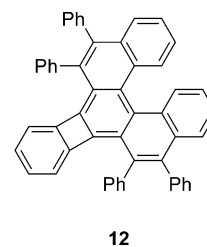
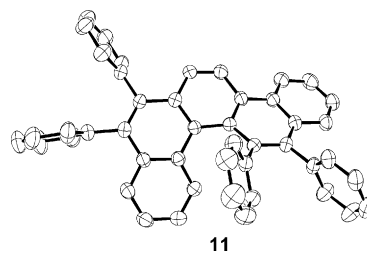
Phenylene	Products <sup>[b]</sup>	Yield [%] <sup>[c]</sup>
<b>1</b> <sup>[d]</sup>		<b>4</b> 20
		<b>5</b> 59
		<b>10</b> 66
<b>2</b> <sup>[e]</sup>		<b>6</b> 33
		<b>7</b> 27
		<b>8</b> 28
<b>3</b> <sup>[f]</sup>		<b>9</b> 33
		<b>11</b> 20

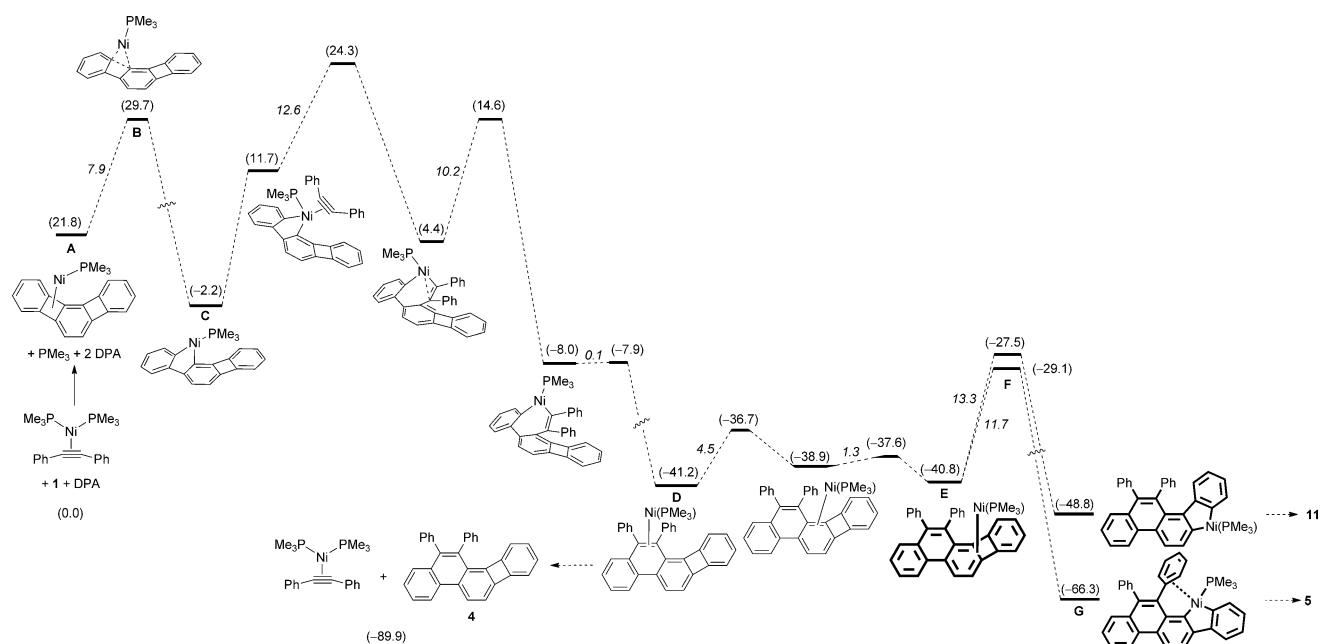
[a] Ph-C≡C-Ph (1 equiv), [Ni(cod)(PMe<sub>3</sub>)<sub>2</sub>] (10 mol %), THF, 75 °C, 23 h (**1**), 5 h (**2**), 48 h (**3**). [b] For fully characterized minor other isomers, see reference [7]. [c] Based on the alkyne as the limiting reagent. [d] 10 % recovered. [e] 37 % recovered. [f] < 1 % recovered.

bay region twist C6-C6a-C6b-C7=31.1°, the associated deplanarization of the internal phenanthrene unit (dihedral angles in the individual benzene rings up to 23°), the extreme

dihedral angle of the bonds to the attached 6,7-phenyls of 76.2°, and bond elongation (relative to [5]phenacene) along the path C4a–C8a. As a consequence, the molecule is chiral and configurationally rigid, as evidenced by the NMR spectra, which reveal dissymmetry of both aryl groups at –60 °C.<sup>[7]</sup> Those at C5/8 exhibited coalescence by rotation on warming to room temperature,  $\Delta G_{287}^\ddagger = (13.0 \pm 0.1) \text{ kcal mol}^{-1}$ . The *ortho* and *meta* CH signals of the bay phenyls remained anisochronous up to 70 °C, when slight line broadening occurred, suggesting a barrier to rotation and/or enantiomerization<sup>[15]</sup> of > 20 kcal mol<sup>–1</sup>. An attempt to model a meso diastereomer in silico led to a highly distorted array, 54 kcal mol<sup>–1</sup> more energetic than **5**.<sup>[7]</sup> Phenyleneoactivation is again evident in the air-sensitive red **7** [ $\lambda_{\text{max}} = 456 \text{ nm}$ ; cf. [6]phenacene (fulminene): 384 nm]<sup>[16]</sup> and **10** [ $\lambda_{\text{max}} = 510 \text{ nm}$  (sh); cf. benzo[s][5]phenacene: 350 nm).<sup>[17]</sup> Both show encumbrance of the phenyl groups in the NMR experiment similar to that of **5**, quantified for the relatively faster phenyl rotation at C5 and C8 in **10**:  $\Delta G_{287}^\ddagger = (13.2 \pm 0.1) \text{ kcal mol}^{-1}$ .<sup>[7]</sup> The [5]phenacene warping is similar to that in **5**. As in **6**, the atypically<sup>[3]</sup> short phenacene bond of benzofusion C16b–C12c in **10** (1.379 Å)<sup>[7]</sup> heralds increased benzocyclobutadienoid character and hence reactivity toward oxygen. Such could be verified by deliberate oxygenolysis of this bond to the corresponding ring-opened dione (72 %).<sup>[7,18]</sup> Finally, colorless [7]phenacene **8** [ $\lambda_{\text{max}} = 427 \text{ nm}$ ; p-band 388 nm; cf. [7]phenacene: p-band 344 nm]<sup>[19]</sup> is even more twisted than **5**, with averaged dihedral angles C6(8)–C6a(8a)–C6b(8b)–C7(9) (bay carbons) = 35.4°, Ph–C6(8)–C7(9)–Ph = 88.2°, and the associated deplanarization of the internal [5]phenacene unit (dihedral angles in the individual benzene rings up to 26°). It adopts approximate meso symmetry, the corresponding chiral isomer computed to lie 4.1 kcal mol<sup>–1</sup> higher in energy.<sup>[7]</sup> Configurational rigidity is manifest in the NMR spectra (not quantified), with locked central phenyl groups at room temperature, whereas the outside phenyl signals begin to decoalesce < 0 °C.<sup>[7]</sup>

A simple (if counterintuitive) rationale for the disproportionate generation of multiple adducts would be increasing reactivity of the phenylene frame with successive cycloadditions. However, subsection of **4** and **9**, respectively, to renewed reaction not only proceeded about an order of magnitude more slowly, but the former gave colorless isomer **11** (calculated to be more stable by 4.4 kcal mol<sup>–1</sup>;  $\lambda_{\text{max}} = 406 \text{ nm}$ ; cf. benzo[c]chrysene: 386 nm)<sup>[14]</sup> instead of **5**, the latter the air-sensitive, red **12** ( $\lambda_{\text{max}} = 496 \text{ nm}$ ) and not **10** as the main products.<sup>[7]</sup> There must be alternative pathways to these respective assemblies.





**Figure 2.** Computed relative free energies,  $\Delta G_{298}$  ( $\text{kcal mol}^{-1}$ ) for the conversion of **1** with  $[\text{Ni}(\text{dpa})(\text{PMe}_3)_2]$  and dpa (0  $\text{kcal mol}^{-1}$ ). Free energies of activation are indicated in italics.

A series of semi-quantitative experiments, focused on **1** and its products and monitored by  $^1\text{H}$  NMR spectroscopy, was carried out to shed some light on this mechanistic problem. Thus, to rule out a competitive dinuclear catalytic species,<sup>[4c]</sup> the catalyst concentration was varied from 7 to 35 to 50 mol % with 0.003 molar **1** and dpa in THF. The rate of disappearance of **1** increased proportionally. Surprisingly, the initial ratios of **4**:**5** with different nickel catalyst loadings were identical and high (10:1), and constant up to 20% conversion. On further reaction, the concentration of **4** leveled, whereas that of **5** increased to furnish the eventually isolated proportion of 2:3 (Table 1). No intermediates were detectable by  $^1\text{H}$  NMR spectroscopy. That this change in relative rates was due to the amount of dpa present in the mixture was ascertained by varying the latter: higher starting concentrations of dpa slowed the overall reaction, but the rate of formation of **5** more than that of **4** (e.g., 50 mol % catalyst, 4 equiv dpa, 40 °C; **4**:**5** = 20:1; to 20% conversion). This effect of added dpa was reproduced by other ligands, such as  $\text{PMe}_3$  or cod. Conversely, the production of **5** maximized when keeping the level of dpa low. This finding could be exploited preparatively by applying high dilution conditions (10 mol % catalyst, syringe pump addition of 2 equiv dpa, boiling THF, 13 h) converting **1** quantitatively (NMR) to **5** (87%) and **4** (13%).<sup>[7]</sup>

Turning to the behavior of **4**, an analogous change in product ratios **11**:**5** with alkyne concentration was recorded: 2:1 with 1 equivalent, 13:1 with 3 equivalents. Similarly, following the conversion of **4** with 1 equivalent of alkyne by  $^1\text{H}$  NMR spectroscopy (50 mol % catalyst, 60 °C, THF) revealed an initial ratio of 5:1 (0.7 h), which changed gradually to the final number of 2:1 (72 h), in the absence of any other species. Finally, **1** appears inert to the catalyst (1:1) (20–60 °C) on its own,<sup>[21]</sup> but addition of the alkyne (1 equiv) caused immediate quantitative formation of  $[\text{Ni}(\text{PMe}_3)_2(\text{dpa})]^{[20]}$  (and cod), cycloaddition commencing slowly only on warming to 40 °C.

Armed with these experimental data, further mechanistic input was sought by DFT calculations.<sup>[7]</sup> This task was complicated by the appearance of several energetically close-lying Ni species in the starting mixture, the following transition state (TS) for the first insertion, and the resulting products.<sup>[7]</sup> Gratifyingly, however,  $[\text{Ni}(\text{PMe}_3)_2(\text{dpa})]$  emerged as the lowest-energy initial species (Figure 2; 0  $\text{kcal mol}^{-1}$ ), in consonance with observation. Similarly, TS **B** was computed as the most favorable structure for the ring opening step, and **C** for its product, replicating the experimental selectivity for bay region attack. The regioselectivity of this step may be due to relative stabilization of the polarized Ni–C( $\alpha$ -biphenylene) bond in **C** by the electron-withdrawing neighboring cyclobutadienoid ring,<sup>[3]</sup> a notion also supported by the finding that in the reaction of **2** (50 mol % catalyst, 1 equiv dpa, 40 °C) the first new species is **6** exclusively, before the gradual appearance of **7** and then **8**. The precursor nickelacyclopentadiene would enjoy double adjacent strained ring stabilization. From **C**, dpa adds and inserts regioselectively to eventually render ligated **4** in the form of **D**. We postulate this species to be the crucial bifurcating point from which, possibly favored by excess dpa (or other ligand), **4** escapes in an exothermic, but reversible, step. Alternatively, at low dpa loading, the attached metal moiety can undergo rapid haptotropism,<sup>[22]</sup> thus positioning itself for the second insertion from **E**. Again in accord with experiment, renewed bay region addition is favored kinetically (**F**), as well as thermodynamically, enjoying anchimeric assistance of the neighboring phenyl group in producing **G**,<sup>[22]</sup> which cascades on to **5**.<sup>[7]</sup>

To rationalize the finding that **4** proceeds preferentially to **11** at high dpa concentrations, we propose a different Ni species, e.g., **H** (Figure 3), for which computation suggests a

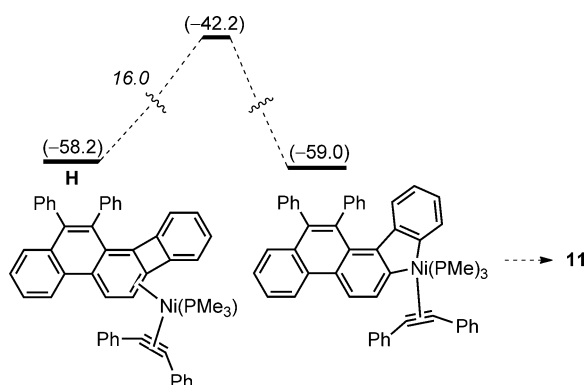
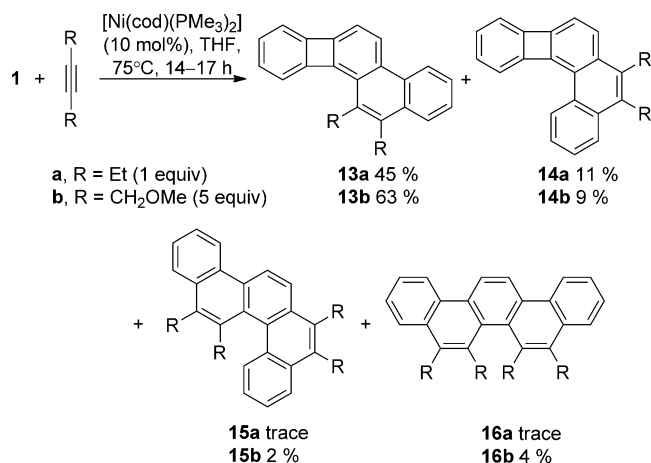


Figure 3. A computed route to **11** through Ni species **H**.

sterically prohibited bay region attack by dpa, but a kinetically feasible route to product. **H** might arise directly from **4** by  $[\text{Ni}(\text{PMe}_3)(\text{dpa})]$  ligation or by interception of the  $\text{D} \rightleftharpoons \text{E}$  manifold.

A brief excursion was undertaken to probe the generality of this chemistry by variation of the alkyne (Scheme 1). The selectivity of addition was less pronounced than that occurring with dpa, notably some non-bay first addition product **14**, albeit minor, now detectable.



Scheme 1. Ni-catalyzed cycloadditions of 3-hexyne and 1,4-dimethoxy-2-butyne to **1**.

Moreover, further reaction to **15** and **16** was much more sluggish. It appears that reactivity and selectivity is quite dependent on the structure of the alkyne and that the presence of a potentially ligating substituent (i.e. MeO in 1,4-dimethoxybutyne) is beneficial in these respects, as reflected by **G** in Figure 2.

In summary, we have shown that the embedded strain in the phenylenes can be exploited in multiple cycloadditions of alkynes catalyzed by Ni. These reactions have the potential to be highly regioselective and tunable, as demonstrated in the case of dpa as the substrate. For this alkyne and **1**, DFT calculations in conjunction with experiments provide a plausible mechanistic rationale, pointing to the operation of

two different catalysts, whose viability appears alkyne concentration dependent. It is reasonable to assume that a similar mechanistic bifurcation characterizes the transformations of **2** and **3**. Our results suggest that with variation of catalyst,<sup>[23]</sup> substrate, and reaction conditions extensive, if not complete, designed control of the outcome of these processes might be attainable.

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