The Cobalt-Way to Heterophenylenes: Syntheses of 2-Thianorbiphenylenes, Monoazabiphenylenes, and Linear 1-Aza[3]phenylene {Biphenyleno[2,3-*a*]-cyclobuta[1,2-*b*]pyridine}

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Abstract: $CpCo(CO)_2$ catalyzes the cocyclization of *ortho*-diethynylthiophenes and -pyridines with alkynes to construct the corresponding thia- and azaphenylenes. This strategy is applied to the synthesis of linear 1-aza[3]phenylene, the first higher heterophenylene.

Key words: alkynes, cobalt, cyclization, heterocycles, transition metals

The [N]phenylenes are a new class of polycyclic cyclohexatrienoid hydrocarbons, in which the alternating fusion between benzene and cyclobutadiene rings causes unusual activation of the π - and σ -framework.¹ As such, they have garnered increasing recent attention as electronically² and otherwise functional materials.³ In a similar vein, heteropolyarenes, in particular thiopheneand pyridine-derived systems, are also the subject of intense current scrutiny for such applications.^{4,5} Consequently, heterophenylenes appear to be attractive targets of investigation. However, few such systems are known (or claimed), all restricted to the biphenylene nucleus.⁶ We report that cobalt-catalyzed cocyclization of orthodiethynylarenes with alkynes, a strategy employed for the assembly of the all-carbon phenylenes,¹ seems applicable to the synthesis of heteroanalogues.

An initial foray exploring this notion started with 3,4-diethynylthiophene (1)⁷ and its reaction with irradiated (hv), boiling (Δ) bis(trimethylsilyl)acetylene (BTMSA, **2a**) as the solvent in the presence of catalytic CpCo(CO)₂ (ca. 15 mol%). Gratifyingly (Scheme 1), the desired 2-thianorbiphenylene **3a** formed, but only in 10% yield, in addition to an array of CpCo(cyclobutadiene) and diyne autocyclization products.⁸ The corresponding reaction of **2** with *o*-diethynylbenzene is nearly quantitative,⁹ and the poor outcome in the case of **1** may be the result of the cumulatively deleterious effect of the widened enediyne bond angles,¹⁰ the potential interference of the metal with the sulfur frame,¹¹ and the activated nature of the benzocyclobutadieno-fused thiophene ring. Chemical structure proof was attained by protodesilylation (TFA–CH₂Cl₂, 70%) to give the known parent **3** (R = H), which had been synthesized by the bis-Wittig reaction of 1,2-benzocyclobutadienequinone with bis(triphenylphosphoranylidenemethyl) sulfide.¹² The success (if limited) of the cocyclizations of **2b** (6 equiv) and **2c** (0.9 equiv), rendering **3b** and **3c** (Scheme 1),⁸ point to some generality of the process. In an attempt to access the 2-thianor[3]phenylene analogue of **3a**, diyne **3c** was protodesilylated and subjected to cocyclotrimerization with **2a**, resulting in decomposition. The pyrrole relatives of **1**, 3,4diethynylpyrrole¹² and (hitherto unknown) 3,4-diethynyl-1,2,5-trimethylpyrrole,⁸ failed to furnish 2-azanorbiphenylenes.





The relatively poor outcome of the above experiments notwithstanding, they suggested that employment of a less sensitive heteroaromatic core might be more successful. Attention was therefore directed at the synthesis of azaphenylenes from appropriate ethynylpyridines. Thus, protodesilylation of 3,4-bis[(trimethylsilyl)ethynyl]pyridine¹³ [K₂(CO)₃, MeOH–Et₂O (1:3)] generated (unisolated) **4**, which was immediately cocyclized with **2a** to assemble 6,7-bis(trimethylsilyl)-2-azabiphenylene (**5**) in 61% yield (Scheme 2).⁸ Protodesilylation (TfOH–cyclohexane, 69%) gave the known parent system.^{6,14}

Similarly, 2,3-bis[(trimethylsilyl)ethynyl]pyridine, accessed more directly than reported,¹⁵ namely by Sono-gashira trimethylsilylethynylation of commercial 2,3-



Scheme 2

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dibromopyridine,⁸ was converted into the 1-aza derivative **7** via (unisolated) diyne **6** (Scheme 3).⁸ Again, protodesilylation (as above for **5**; 81%) led to the known 1-azabiphenylene.^{6,14} Iododesilylation (ICl, CCl₄, 58%) furnished 6,7-diiodo-1-azabiphenylene.⁸ These results, while preliminary, make the underlying strategy clearly the approach of choice for the synthesis of substituted derivatives of both azabiphenylenes.





Encouraged by these findings, we embarked on the more ambitious goal of extending the series to the first higher heterophenylenes, specifically substituted linear 5-azaand 1-aza[3]phenylenes 9 and 13, respectively. Approaching the first entailed quadruple alkynylation of 2,3,5,6tetrabromopyridine¹⁶ to produce **8**,⁸ which was deprotected (KF·2H₂O, 18-crown-6, DME) in situ and reacted with 2a in the presence of CpCo(CO)₂. Surprisingly, the only product that could be detected was 10, evidently derived from 9 by insertion of 2a into the four-membered-ring bond proximal to nitrogen (Scheme 4). Its structural, in particular regiochemical, assignment rests on the spectral data.⁸ Most clearly diagnostic is the NOE between H_a and H_b. The formation of **10** can be viewed in the context of the well-precedented activation of the strained ring in biphenylene by transition metals toward insertion of unsaturated moieties¹⁷ and the relatively high reactivity of the a-position in pyridine in metal-mediated transformations.¹⁸ Considering the relative stability of **5** and **7** to the conditions of their generation, it appears that the second strained ring in 9 labilizes the σ frame of the first. Such an effect has also been observed for the all-carbon analogue, linear [3]phenylene.9,19

In light of the detrimental positioning of the nitrogen in 5azaphenylene **9**, the core of the target was changed to that of its 1-azaisomer (Scheme 5). For this purpose, **6** was cocyclized with trivne **11**²⁰ to provide **12**.⁸ In situ protodesilylation, followed by another cyclization, now with **2a**, gratifyingly engendered the novel 1-aza[3]phenylene **13**.⁸ Attaining the ultimate goal, parent **14**, was approached with trepidation, since desilylation of **13** with acid was expected to lead to addition reactions to the central activated ring,^{1,9} and treatment with base, successful in the synthesis of the carbon analogue linear [3]phenylene, was considered risky in view of the hydrolytic instability of azabiphenylene derivatives.²¹ In the event, the latter concerns proved unfounded and **14** evolved from **13** through the action of potassium *tert*-butoxide.⁸

The spectral properties of **13** and **14** parallel those of their carbon counterparts,^{1a,9} except for the perturbation in-



Scheme 4



Scheme 5

duced by the presence of the nitrogen atom. Specifically, the NMR signals of the nuclei adjacent to the cyclobutadienoid rings are unusually shielded, as exemplified by $\delta_{H-5} = 6.40$ ppm, $\delta_{H-10} = 6.48$ ppm (CDCl₃), $\delta_{C-5} = 112.2$ ppm, and $\delta_{C-10} = 111.4$ ppm (CD₂Cl₂) for **14** (compare the corresponding values for linear [3]phenylene: $\delta = 6.24$ and 111.2 ppm). The electronically activated nature of these molecules is also confirmed by their deep red color, quantified by their longest wavelength UV/vis absorptions at 437 (**13**) and 433 nm (**14**), respectively. The bathochromic shift experienced by the 1-azabiphenylene frame on benzocyclobutannelation to **14** is 75 nm, identical to that observed when going from biphenylene to linear [3]phenylene. It thus seems that the azaderivatives

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have potential as building blocks for interesting materials, similar to that of their carbocyclic analogues, with the added advantage of bearing the tunable heteroatom.

Because of the novelty of these systems,²² X-ray crystallographic analyses of 12 and 14 were performed, in addition to DFT calculations (B3LYP/6-311G**) of the parent 1-azabiphenylene and 14 (Figures 1 and 2).



Figure 1 Structural details (bond lengths and angles) of a: pyridine in the gas phase ('best fit' data;²³ top left), **b**: 1-azabiphenylene by computation (B3LYP/6-311G**), c: biphenylene in the crystal [standard deviations 0.002–0.004 (bond lengths) and 0.2 (angles)],²⁴ and \mathbf{d} : 12 in the crystal [data are the mean values from two independent molecules in the unit cell; standard deviations 0.006-0.007 (bond lengths) and 0.4-0.5 (angles)]. All four-membered-ring angles deviate <1° from 90°.

Inspection of the structure of 12 in Figure 1 (d) reveals that the presence of the nitrogen accentuates the distortions induced by the cyclobutadienoid ring in biphenylene (see c).^{1a,6,25} Thus, there is pronounced bond alternation of the pyridine nucleus toward an azacyclohexatriene configuration with a bond localization index $L_i = 0.22$.²⁶ For comparison, the corresponding values for pyridine (see a) and biphenylene are 0.15 and 0.14, respectively. This feature is also apparent in the calculated structure of the parent 1-azabiphenylene (see b), which also provided the opportunity to compare the geometric details of the unsubstituted cyclohexatrienoid ring with that in biphenylene. The two are remarkably similar $(L_i = 0.11 \text{ and } L_i = 0.11 \text{ and } L_i$ 0.14, respectively), indicating that the nitrogen atom exerts its effect primarily on its immediate surroundings.

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Turning to Figure 2, analysis of the experimental structure of 14 (see a) is obfuscated by the disorder of the nitrogen over all four topological-symmetry-equivalent positions. The unit cell features two independent flat molecules, one containing an inversion center. The packing shows a sandwich-herringbone motif,²⁷ depicted in Figure 3, with nearest neighbor planes at an angle of 94°.



Figure 2 Structural details (bond lengths and angles) of a: linear 1aza[3]phenylene (14) in the crystal [the nitrogen atom is disordered over four positions, modeled as the superposition of 0.25 N and 0.75 C; data are the mean values from two independent molecules in the unit cell; standard deviations 0.002 (bond lengths) and 0.1-0.2 (angles)], b: computed data for 14 (B3LYP/6-311G**), and c: X-ray data for linear [3]phenylene (center of inversion).²⁸ All four-memberedring angles deviate <1° from 90°.

Because of the disorder of the N atom in a, recourse was taken to a computed structure of 14 (see b) for a comparison of bond lengths and angles with those in linear [3] phenylene (see \mathbf{c}).²⁸ Averaging the structural details of **b** to reflect the disorder in **a** reproduced the data for the latter fairly well (e.g., averaged bonds to N in b: 1.348 and 1.405 Å; versus those in a: 1.346 and 1.415 Å, respectively; averaged angle at N: 114.4° versus 114.0°). Analogous to the findings pertaining to Figure 1, introducing the heteroatom into the linear [3]phenylene frame affects the heterocycle the most ($L_i = 0.19$). The center ring retains its characteristic bis- π -allyl frame and is unaltered ($L_i = 0.07$ in both **b** and **c**), similar to the terminal carbocycle $(L_i = 0.14 \text{ vs. } 0.15).$



Figure 3 Crystal packing diagram of 14

In summary, we have shown that $CpCo(CO)_2$ educes the potential of ortho-diethynylthiophenes and -pyridines to function as cooligomerization partners with alkynes on route to the corresponding heterophenylenes, a transformation that should be general for a variety of derivatives. An iterative sequence gives rise to linear 1-aza[3]phenylene, the first higher heterophenylene. Its properties resemble those of the carbon analogue, with the exception of the local perturbations induced by the heteroatom. One can anticipate that the chemistry disclosed herein is applicable to the assembly of other members of the family of heterophenylenes.

Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synlett.

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Selected Data

Compound 3a: colorless crystals; mp 80-81 °C (EtOH-H₂O). IR (hexanes): 3010, 1364, 1250, 1064, 1031, 854 cm⁻ ¹. ¹H NMR (300 MHz, CDCl₃): δ = 7.18 (s, 2 H), 6.53 (s, 2 H), 0.32 (s, 18 H). ¹³C NMR (75 MHz, CDCl₃): δ = 148.2, 147.7, 144.8, 124.1, 113.2, 2.63. MS (EI, 70 eV): m/z $(\%) = 302(100) [M]^+, 273(12), 272(22), 271(85), 215(13),$ 73 (58). UV/Vis (EtOH): λ_{max} (log ε) = 257 sh (5.04), 262 (5.16), 337 (4.37), 353 (4.43) nm. Anal. Calcd for C₁₆H₂₂SSi₂: C, 63.51; H, 7.33. Found: C, 63.84; H, 7.58. Compound **5**: opaque oil. ¹H NMR (400 MHz, CDCl₃): $\delta = 8.12$ (d, J = 5 Hz, 1 H), 7.60 (br s, 1 H), 7.32 (s, 1 H), 7.27 (s, 1 H), 6.38 (d, J = 5 Hz, 1 H), 0.30 (s, 18 H). MS (EI, 70 eV): m/z (%) = 297 (100) [M]⁺, 282 (70), 266 (20), 239 (12), 73 (53). HRMS (EI): *m/z* [M]⁺ calcd for C₁₇H₂₃NSi₂: 297.1369; found: 297.1361. UV/Vis (hexane): λ_{max} (log

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 ε) = 231 (3.56), 301 (3.02), 325 (3.25), 340 (3.31) nm. Compound 7: opaque oil. ¹H NMR (500 MHz, CDCl₃; assignments by 2D NMR): $\delta = 7.64 (d, J = 5.5 Hz, 1 H, H^2)$, 7.26 (s, 1 H, H⁸), 7.16 (s, 1 H, H⁵), 6.74 (d, J = 6.5 Hz, 1 H, H^4), 6.51 (dd, J = 6.25, 6.25 Hz, 1 H, H^3), 0.34 (s, 9 H, Me₃Si), 0.33 (s, 9 H, Me₃Si). ¹³C NMR (100 MHz, CDCl₃): $\delta = 173.1 (C^{8b}), 152.7 (C^{8a}), 150.9 (C^{6/7}), 150.5 (C^{4b}), 150.2$ (C^{4a}), 149.3 (C^{6/7}), 145.7 (C²), 124.6 (C⁵), 124.3 (C⁸), 122.4 (C³), 122.0 (C⁴), 2.00 (SiCH₃), 1.99 (SiCH₃). MS (EI, 70 eV): m/z (%) = 297 (100) [M]⁺, 282 (72), 266 (32), 239 (17), 73 (55). HRMS (EI): *m*/*z* [M]⁺ calcd for C₁₇H₂₃NSi₂: 297.1369; found: 297.1361. UV/Vis (hexane): λ_{max} (log ε) = 241 (4.01), 270 (3.76), 347 (3.50), 362 nm (3.40). Compound 14: deep red crystals; mp 225-226 °C (dec.; hexane). IR (neat): 3069, 2929, 2855, 1643, 1585, 1415, 1349, 1246, 1186, 1153, 865, 733 cm⁻¹. ¹H NMR (400 MHz, CDCl₃; assignments by 2D NMR): $\delta = 7.48$ (dd, J = 6.0, 1.2Hz, 1 H, H²), 6.72 (m, 2 H, H^{7,8}), 6.53 (m, 2 H, H^{6,9}), 6.48 (d, J = 1.2 Hz, 1 H, H¹⁰), 6.45 (dd, J = 6.8, 1.2 Hz, 1 H, H⁴), 6.40 $(s, 1 H, H^5), 6.39 (dd, J = 6.4, 6.4 Hz, 1 H, H^3).$ ¹³C NMR $(150 \text{ MHz}, \text{CD}_2\text{Cl}_2): \delta = 172.2 \text{ (C}^{10b}), 155.4 \text{ (C}^{4b/10a}), 155.0$ $(C^{4b/10a}), 153.9 (C^{5a/9b}), 153.6 (C^{5a/9b}), 150.4 (C^{5b/9a}), 150.1$ $(C^{5b/9a}), 148.9 (C^{4a}), 145.2 (C^2), 129.2 (C^{7/8}), 129.0 (C^{7/8}),$ 122.3 (C³), 119.2 (C⁴), 117.1 (C^{6/9}), 117.0 (C^{6/9}), 112.2 (C⁵), 111.4 (C¹⁰). MS (EI, 70 eV): m/z (%) = 227 (100) [M]⁺, 201 (30), 174 (7), 150 (4), 123 (3), 113 (14), 100 (22). HRMS (EI): *m/z* [M]⁺ calcd for C₁₇H₉N: 227.0735; found: 227.0739. UV/Vis (hexane): λ_{max} (log ε) = 266 (5.48), 275 (5.60), 299 (4.97), 311 (4.91), 387 sh (4.68), 407 (5.07), 421 sh (5.02), 433 (5.28) nm.

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