derivatives of hemocyanin has copper(I) ions ligated by three imidazole ligands.[15] While the role of an endogenous ligand in the binding of molecular oxygen to hemocyanin is still uncertain, it appears certain that the binding of CO requires no other ligands in addition to imidazole to reproduce the spectroscopic properties for HcCO. We are currently examining the reaction of Cu(timm)$^+$ with other biologically important small molecules, including O_2.

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(15) It should be noted that Zolla has reported that the carbonyl derivative of the half-apo form of hemocyanin [one Cu(I)] does *not* show any luminescence, even though the remaining single copper ion should still be bound by three imidazoles ligands and CO: Zolla, L.; Calabrese, L.; Brunori, M. *Biochim. Biophys. Acta* **1984**, *788*, 206-213. It may be that the absence of the second copper results in a conformational change that allows the active site to be exposed to solvent, quenching the luminescence. The monomeric imidazole complexes reported here only show luminescence *when isolated in a glass*; in solution, the emission is quenched. Solvent quenching of emission has been observed for a number of Cu(I) complexes when the solvent can coordinate to the metal (see ref 14).

2,3-Bis(trimethylsilyl)- and 2,3,8,9-Tetrakis(trimethylsilyl)[4]phenylene

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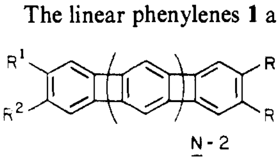
The linear phenylenes **1** are of great theoretical importance as



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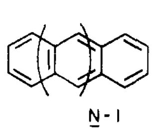
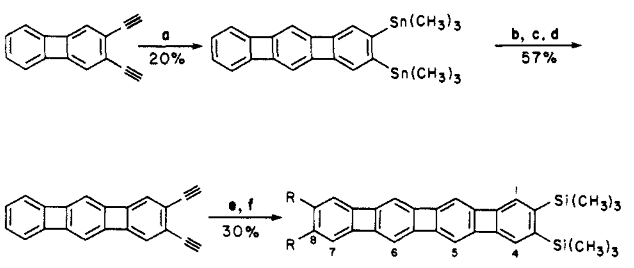


2

novel synthetic oligomers on which to probe the aromaticity criterion. These substances are unusual because the aromatic benzene ring is juxtaposed to the antiaromatic cyclobutadiene nucleus in an alternating manner, giving rise to new electronic, perhaps conducting, properties.[1] In contrast to the acenes **2**,[2] the series is alternating between a $4n$ (N even) and $4n + 2$ (N odd) π-electron count. We recently described the synthesis of [3]phenylene **1** ($N = 3$, $R^1 = R^2 = R^3 = R^4 = H$),[1] and the unusual reactivity and spectral properties of this system raised several questions: (a) Is the next higher benzocyclobutadienolog, [4]phenylene, capable of existence? (b) If it is, will it be paratropic? (c) How will such a polycycle accommodate unfavorable cyclobutadienoid[3] character? We now report the synthesis of the [4]phenylene nucleus **3**,[4] crucial in order to understand the basic electronic features associated with this novel class of compounds, and as another step to the higher members of the series. The approach to **3a** also incorporates a novel cobalt-catalyzed alkyne cyclization[5] involving bis(trimethylstannyl)acetylene.

Scheme I[a]

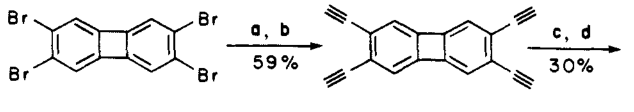


4

3a (R = H)

[a] (a) $(CH_3)_3SnC{\equiv}CSn(CH_3)_3$, $CpCo(CO)_2$, xylenes, Δ, $h\nu$, 3.5 h; (b) I_2, $CHCl_3$, 1 h, 80%; (c) $(CH_3)_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, Et_3N, 23 °C, 20 h, 75%; (d) KOH, CH_3OH, 1 h, 95%; (e) $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$, $CpCo(CO)_2$, THF, Δ, $h\nu$, 9 h, 30%; (f) CO (1 atm), 90 °C, 16 h, 100%.

Scheme II[a]



5

3b [R = (CH3)3Si]

[a] (a) $(CH_3)_3SiC{\equiv}CH$, $PdCl_2(PPh_3)_2$, piperidine, 24 h, 90-100 °C, 60%; (b) KOH, ether, CH_3OH, 2 h, 98%; (c) $(CH_3)_3SiC{\equiv}CSi(CH_3)_3$, $CpCo(CO)_2$, THF, Δ, $h\nu$, 13 h, 30%; (d) CO (1 atm), 120 °C, 72 h, 99%.

The original strategy involved an extension of our cyclobutabenzoannelation scheme[1] employing 2,3-bis(trimethylsilyl)[3]phenylene **1** [$N = 3$, $R^1 = R^2 = Si(CH_3)_3$, $R^3 = R^4 = H$] as a starting point. However, iododesilylation of this system proved impossible, electrophilic attack occurring at the reactive central ring.[6] Therefore, the synthetic plan was revised to (a) explore the utility of the trimethylstannyl group as a masked halogen[7] in cobalt-catalyzed [2 + 2 + 2] cycloadditions, starting from 2,3-diethynylbiphenylene[1] (Scheme I) or (b) to employ the new tetrayne **5**, thought to be accessible from 2,3,6,7-tetrabromobiphenylene[8] (Scheme II).[9] Gratifyingly, both strategies were successful, Scheme I in particular demonstrating the feasibility of trimethylstannyl alkyne cyclizations and the stability of the [3]phenylene nucleus in the presence of Pd^{2+}. Minor byproducts in the cyclization of **4** were **6** (one stereoisomer) and in that of **5** they were **7** (one stereoisomer) and **8** (stereochemistry tentative).

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(1) Berris, B. C.; Hovakeemian, G. H.; Lai, Y.-H.; Mestdagh, H.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1985**, *107*, 5670.

(2) Clar, E. *Polycyclic* Hydrocarbons; Academic Press: New York, 1964; Vol. 1.

(3) Vollhardt, K. P. C. *Top. Curr. Chem.* **1975**, *59*, 113.

(4) An attempt to synthesize [4]phenylene by dimerization of 2,3-didehydrobiphenylene failed: Losey, E. N.; LeGoff, E. *J. Org. Chem.* **1972**, *37*, 3812.

(5) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539.

(6) Hovakeemian, G. H.; Vollhardt, K. P. C., unpublished results.

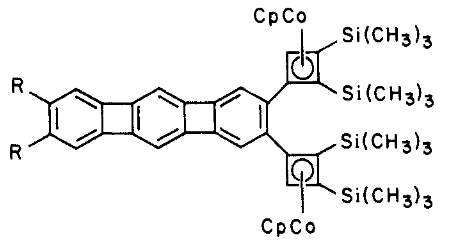
(7) Evnin, A. B.; Seyferth, D. *J. Am. Chem. Soc.* **1967**, *89*, 952.

(8) Figeys, H. P.; Defay, N.; Martin, R. H.; McOmie, J. F. W.; Ayres, B. E.; Chadwick, J. B. *Tetrahedron* **1976**, *32*, 2571.

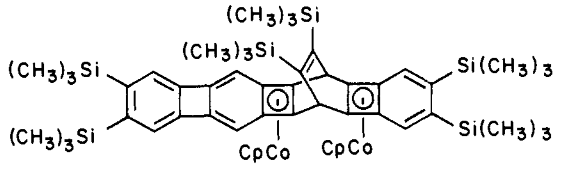
(9) All new compounds gave satisfactory analytical and/or spectral data. For selected data, **3a**-CpCo: ^1H NMR (C_6D_6) δ 0.32 (s, 18 H), 4.54 (s, 5 H), 6.57 (s, 2 H), 6.72 (s, 2 H), 6.75 (m, 4 H), 7.44 (s, 2 H). **3a**: HRMS *m/e* (relative intensity) 444.1735 (M^+, 100), calcd for $C_{30}H_{28}Si_2$ 444.1722; ^1H NMR (C_6D_6) δ 0.31 (s, 18 H), 5.73 (s, 2 H, H_6), 5.89 (s, 2 H, H_5), 6.17 (dd, $J = 4.97$, 2.84 Hz, 2 H, H_7), 6.44 (dd, $J = 4.97$, 2.84 Hz, 2 H, H_8), 6.81 (s, 2 H, H_1); ^{13}C NMR (C_6D_6) δ 2.23, 109.31, 109.50, 115.04, 120.35, 128.30, 147.53, 150.14, 150.84, 151.16, 151.21, 152.10, 153.46; UV (THF) λ_{max} (log ϵ) 247 (3.60), 253 (3.80), 259 (4.00), 300 (4.20), 316 (4.13), 364 (3.20), 377 (3.20), 458 (3.50), 488 nm (3.64). **3b**-CpCo: ^1H NMR (C_6D_6) δ 0.32 (s, 36 H), 4.59 (s, 5 H) 6.72 (s, 4 H), 7.45 (s, 4 H); ^{13}C NMR (C_6D_6) δ 2.23, 74.05, 80.09, 114.90, 125.21, 143.24, 147.99, 148.96. **3b**: MS, *m/e* (relative intensity) 588 (M^+, 100), 573 (2.5), 516 (9.8), 294 (21), 207 (75); ^1H NMR (C_6D_6) δ 0.31 (s, 36 H), 5.89 (s, 4 H, H_5), 6.81 (s, 4 H, H_1); ^{13}C NMR (C_6D_6) δ 2.20, 109.6, 120.4, 147.5, 150.1, 151.3, 153.5. **8**: MS, *m/e* (relative intensity) 1006 (M^+, 0.4), 836 (8.8), 712 (7.1), 369 (15), 57 (100); ^1H NMR (C_6D_6) δ 0.29 (s, 18 H), 0.34 (s, 18 H), 0.40 (s, 18 H), 4.37 (s, 2 H), 4.69 (s, 10 H), 6.25 (s, 2 H), 7.10 (s, 2 H), 7.57 (s, 2 H).

(10) (a) Duclos, R. I.; Vollhardt, K. P. C.; Yee, L. S. *J. Organomet. Chem.* **1979**, *174*, 109. (b) Gorgues, A.; Le Coq, A. *J. Chem. Soc., Chem. Commun.* **1979**, *767*; *Tetrahedron Lett.* **1979**, 4829. (c) Balci, M.; Cakmak, O.; Harmandar, M. *Ibid.* **1985**, *26*, 5469.

0002-7863/86/1508-2481$01.50/0



6 (R = H)
7 [R = $(CH_3)_3Si$]



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The structural assignment of **8** is based on analytical and spectral data, particularly comparison of the ^{1}H NMR spectrum with that of model compounds.[6,9,10,12] Compound **8** constitutes the first example of a (formal) Diels–Alder-type addition to the phenylene nucleus, signaling increasing reactivity along the series, as in the acenes.[2,11] This conclusion is corroborated by the tenacity with which the [4]phenylene nucleus holds on to complexed CpCo, both desired cyclization products emerging initially attached to the metal. On the basis of models[10a,12] and symmetry (for **3b**–CpCo) the cobalt unit must be complexed to the central ring, maximizing aromatic character[13] in the system. Decomplexation with CO (Schemes I and II) furnished **3** as deep red-brown, very air-sensitive solids which decomposed on attempted melting point determination.

On cyclobutabenzoannulation of [3]phenylene **1** ($N = 3$) the UV spectrum[9] experiences strong bathochromic shifts ($\Delta\lambda_{max} = 52$ nm for the highest wavelength band) as predicted by theory[2,14] and clearly indicative of through-conjugation. Particularly instructive are the ^{1}H NMR spectra of **3a** and **3b**[9] in comparison with those of its analogue **1** ($N = 3$).[1] While the outside benzene ring hydrogens have approximately the *same* chemical shifts, their inside counterparts experience a noticeable upfield movement when going from the [3]- to the [4]phenylene nucleus. A possible interpretation of this finding is that the outside benzenes attempt to maximize their aromatic character at the expense of that in the other two. In support of this conclusion, the chemical shift of H^3 in 1,2-bis(trimethylsilyl)benzocyclobutadiene (**9**)[10a] is δ 5.75, almost identical with those of H^5 and H^6 in **3a**. Striking is the effect of CpCo complexation on the chemical shift of the hydrogens in **3**,[9] all nuclei undergoing deshielding in increments ranging from 0.32 to 0.99 pm, pointing to substantial "aromatization" of the system[13] as also observed for **9**.[10a] Unprecedented is the remote effect on the outside rings, the molecule now appearing to adopt a "double biphenylenoid" electronic structure.[15] It thus appears that in the phenylenes, the properties of local π-electronic circuits override those expected based on the total π-electron count.[16] The preparation of [5]phenylene, currently under way, is necessary to clarify this point.

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Registry No. **1** ($N = 2$; $R^1 = R^2 = H$; $R^3 = R^4 = C_2H$), 87710-28-9; **1** ($N = 3$; $R^1 = R^2 = H$; $R^3 = R^4 = Sn$), 101471-34-5; **1** ($N = 2$; $R^1 = R^2 = R^3 = R^4 = Br$), 62754-84-1; **3a**, 101471-35-6; **3b**, 101471-37-8; **4**, 101471-38-9; **5**, 101471-36-7; **6**, 101471-39-0; **7**, 101471-40-3; **8**, 101471-41-4; $(CH_3)_3SnC{\equiv}CSn(CH_3)_3$, 2117-50-2; $CpCo(CO)_2$, 12078-25-0; $(CH_3)_3SiC{\equiv}CH$, 1066-54-2; $PdCl_2(PPh_3)_2$, 13965-03-2.

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(11) Biermann, D.; Schmidt, W. *J. Am. Chem. Soc.* **1980**, *102*, 3163.
(12) Hirthammer, M.; Hestdagh, H.; Vollhardt, K. P. C., manuscript in preparation.
(13) Chinn, J. W., Jr.; Hall, M. B. *Organometallics* **1984**, *3*, 284. Anderson, A. B.; Fitzgerald, G. *Inorg. Chem.* **1981**, *20*, 3288. Herndon, W. C. *J. Am. Chem. Soc.* **1980**, *102*, 1538; *Isr. J. Chem.* **1980**, *20*, 276. Bursten, B. E.; Fenske, R. F. *Inorg. Chem.* **1979**, *18*, 1760. Clack, D. W.; Warren, K. D. *Inorg. Chim. Acta* **1978**, *27*, 105.
(14) Vollhardt, K. P. C.; Wirz, J., manuscript in preparation.
(15) Lloyd, D. *Non-benzenoid Conjugated Carbocyclic Compounds*; Elsevier: New York, 1984.
(16) Minsky, A.; Meyer, A. Y., Hafner, K.; Rabinovitz, M. *J. Am. Chem. Soc.* **1983**, *105*, 3975. Rabinovitz, M.; Willner, I.; Minsky, A. *Acc. Chem. Res.* **1983**, *16*, 298.

Triphenylsilyl Cation

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We wish to report the preparation and characterization in solution of the triphenylsilyl cation, the silicon analogue of the trityl cation. Although numerous attempts have been made to prepare this species,[2] all have met with failure. The only silylenium ion prepared to date is tris(2-propylthio)silyl, an esoterically substituted species in which the sulfur atoms serve to stabilize the electron deficient silicon center through polarization and resonance.[3]

We now report that the triphenylsilyl cation[4] may be prepared by the Corey method[5] as the ion pair in dichloromethane or 1,2-dichloroethane and as the free ion in acetonitrile or sulfolane. The reaction involves hydride transfer from the silane to the trityl cation (eq 1).

$$Ph_3SiH + Ph_3C^+ \, ClO_4^- \rightarrow Ph_2Si^+ \, ClO_4^- + Ph_3CH \quad (1)$$

The ^{1}H and ^{13}C spectra of a solution from the reaction of equimolar amounts of triphenylsilane and trityl perchlorate in CD_2Cl_2 show the clean production of a single species. Thus the ^{13}C aromatic region contains only one set of four resonances from the product (plus the peaks from triphenylmethane at known positions).

Solutions have been examined in a number of solvents with high polarity (to promote ionization) but with low nucleophilicity or donor number (to avoid complexation with solvent). The molar conductance (mho cm^2 mol^{-1}) is only 1.13 in CH_2Cl_2 or 0.28 in 1,2-dichloroethane but 179.5 in acetonitrile and 12.0 in sulfolane.[6] A log–log plot of molar conductance vs. concentration indicates whether the formed species exists as an ion pair or as free ions. For acetonitrile and sulfolane, the plot is linear and horizontal, as expected for free ions (the increase in conductance at higher

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[1] This work was supported by the National Science Foundation (Grant CHE83-12285).
(2) For a review, see: Corriu, R. J. P.; Henner, M. *J. Organomet. Chem.* **1974**, *74*, 1–28.
(3) Lambert, J. B.; Schulz, W. J., Jr. *J. Am. Chem. Soc.* **1983**, *105*, 1671–1672.
(4) With some trepidation we suggest the name *sityl* (rhymes with *trityl*) for this cation.
(5) Corey, J. Y. *J. Am. Chem. Soc.* **1975**, *97*, 3237–3238.
(6) The apparently low value in sulfolane is caused by its very high viscosity (9.87) in comparison with acetonitrile (0.325) and dichloromethane (0.393), since conductivity is inversely proporational to viscosity.

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