Scheme I

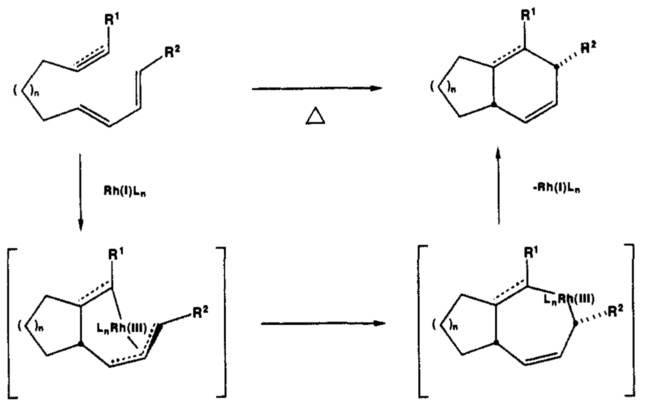
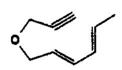
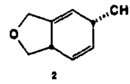
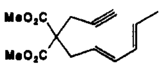
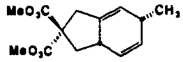
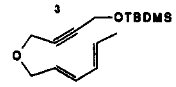
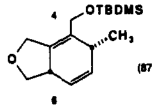
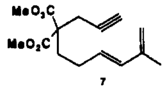
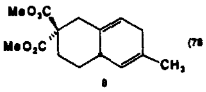
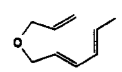
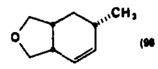
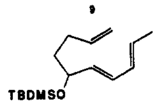
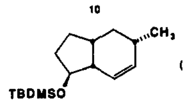


Table I. Rh(I)-Catalyzed [4 + 2] Cycloadditions

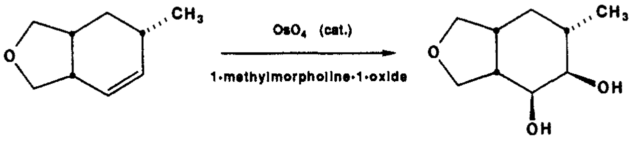
Substrate	Product	(yield %)	Reaction Conditions
 1	 2	(96 %)	$(Ph_3P)_3RhCl$ · TFE 55 °C, 15 min
 3	 4	(93 %)	$(Ph_3P)_3RhCl$ · TFE 55 °C, 45 min
 5	 6	(87 %)	$[(i\text{-}C_3HF_6O)_3P]_2Rh^+$ - THF [13] 55 °C, 15 min
 7	 8	(78 %)	$(Ph_3P)_3RhCl$ · TFE 55 °C, 45 min
 9	 10	(98 %)	$[(i\text{-}C_3HF_6O)_3P]_2RhCl$ · THF 25 °C, 60 h
 11	 12	(61 %)	$[(i\text{-}C_3HF_6O)_3P]_2RhCl$ · THF 55 °C, 18 h

formylations[9] results in dramatic increases in reaction efficiency. Accordingly, several new Rh(I) complexes were generated in situ by the reaction of $[RhCl(cyclooctene)_2]_2$ with various phosphite ligands (2 equiv)[10] and examined for efficacy in the intramolecular [4 + 2] cycloaddition reaction. In consonance with the findings of Van Leeuwen and Roobeck,[8,9] a significant enhancement in cyclization efficiency was observed when d^8 rhodium complexes modified by 1,1,1,3,3,3-hexafluoro-2-propoxy bearing phosphite ligands were employed as catalysts. In addition, these highly active catalyst systems were found to be effective in THF solution at temperatures as low as 25 °C.

The generality of the rhodium-catalyzed intramolecular [4 + 2] cycloaddition reaction for the elaboration of 5/6 and 6/6 ring systems was subsequently demonstrated by its application to several representative substrates (Table I).[11]

Several synthetically pertinent features serve to differentiate the reactivity profile of Rh(I) catalysts from their Ni(0) counterparts.[3] *Of primary interest is the observation that these cycloadditions are not confined to substrates bearing nonterminal alkynes as [4 + 2] addends. Terminal alkynes and, more importantly, alkenes readily participate in representative cyclizations to provide the corresponding bicyclic products in good to excellent yield.* In addition, Rh(I)-catalyzed cycloadditions were found to proceed with excellent levels of diastereoselection. In every instance examined to date, Rh(I)-catalyzed cyclization under optimized conditions led to the formation of an exclusive cycloadduct as determined by GC as well as ^1H and ^{13}C NMR.[5,7]

In the case of **10**, rigorous proof of relative stereochemistry was provided by single-crystal X-ray diffraction analysis of the corresponding crystalline diol **13**.



10 13

The preceding examples indicate that the Rh(I)-catalyzed [4 + 2] cycloaddition reaction is an effective means for the elaboration of a range of bicyclic intermediates from acyclic precursors under exceedingly mild reaction conditions. The utilization of chiral phosphines in enantioselective variations of this novel annulation process as well as its application to problems of synthetic interest will be the topics of future reports from this laboratory.

Acknowledgment. Support for this research by grants from the Alfred P. Sloan Foundation and the National Institutes of Health are gratefully acknowledged. The authors thank Ray Larsen of the MSU X-ray facility for obtaining the crystal structure for diol **13**.

Supplementary Material Available: Spectroscopic and physical data (^1H NMR, IR, high-resolution mass spectra, and mp) for the cycloadducts **2–12** and the diol **13** (3 pages). Ordering information is given on any current masthead page.

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(8) van Leeuwen, P. W. N. M.; Roobeek, C. F. *Tetrahedron* **1981**, *37*, 1973.

(9) van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Organomet. Chem.* **1983**, *258*, 343.

(10) Larock, R. C.; Oertle, K.; Potter, G. F. *J. Am. Chem. Soc.* **1980**, *102*, 190.

(11) In a representative experiment, a 12-cm test tube containing $[(C_8H_{14})_2RhCl]_2$ (17.9 mg, 0.025 mmol) was flushed with Ar and then charged with dry THF (4 mL). To the stirred solution was added $(i\text{-}C_3HF_6O)_3P$ (53.1 mg, 0.100 mmol) followed by **9** (276 mg, 2.000 mmol). The pale yellow solution was then allowed to stir at 25 °C for 60 h (or, alternatively, was warmed to 55 °C for 2.5 h). The reaction mixture was filtered through 3 g of alumina (30% EtOAc–C_6H_{14} for elution), and the solvents were evaporated. Flash chromatography of the residue on silica gel followed by evaporative distillation provided **10** (270 mg, 98%).

(12) In this instance, cyclization was effected by exposure of **5** to 5 mol % of the cationic complex prepared by the sequential treatment of $[(C_8H_{14})_2RhCl]_2$ with AgO_3SCF_3 (1.0 equiv/Rh)[13] followed by $(i\text{-}C_3HF_6O)_3P$ (2.2 equiv).

(13) Schrock, R. R.; Osborn, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 3089.

Synthesis and Crystal Structure of a Stable Hexacobalt Complex of Cyclo[18]carbon

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University of California
Los Angeles, California 90024-1569

Received February 12, 1990

Recently, we reported the gas-phase formation of neutral cyclo[18]carbon (C_{18}) from a stable precursor prepared by synthesis and characterized by X-ray crystallography.[1,2] We now report the synthesis and the structure of C_{18}, stabilized as the transition-metal complex **1** (Scheme I).

Conceptually, the synthesis of **1** originates from the ≡C—C angle bending that occurs in alkynes upon formation of (μ-acetylene)dicobalt hexacarbonyl complexes. The bending angle after complexation lies between 136.2° and 144.4° for complexes of known X-ray crystal structure.[3] Dicobalt hexacarbonyl

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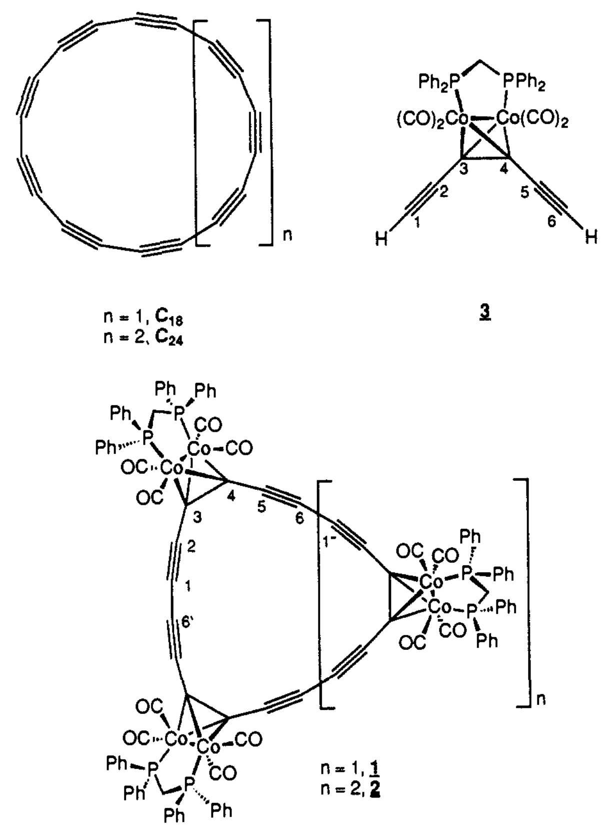
(1) Diederich, F.; Rubin, Y.; Knobler, C. B.; Whetten, R. L.; Schriver, K. E.; Houk, K. N.; Li, Y. *Science* **1989**, *245*, 1088–1090.

(2) For other precursors to the cyclo[*n*]carbons, see: (a) Rubin, Y.; Diederich, F. *J. Am. Chem. Soc.* **1989**, *111*, 6870–6871. (b) Rubin, Y.; Knobler, C. B.; Diederich, F. *J. Am. Chem. Soc.* **1990**, *112*, 1607–1617.

(3) (a) Bird, P. H.; Fraser, A. R.; Hall, D. N. *Inorg. Chem.* **1977**, *16*, 1923–1931. (b) Baert, F.; Guelzim, A.; Coppens, P. *Acta Crystallogr.* **1984**, *B40*, 590–595. (c) Gregson, D.; Howard, J. A. K. *Acta Crystallogr.* **1983**, *C39*, 1024–1027. (d) Meyer, A.; Gorgues, A.; Le Floc'h, Y.; Pineau, Y.; Guillevic, J.; Le Marouille, J. Y. *Tetrahedron Lett.* **1981**, *22*, 5181–5182.

0002-7863/90/1512-4966$02.50/0

Scheme I



fragments[4,5] have been used as protecting groups to allow geometrically disfavored cyclization reactions by bending an alkyne moiety,[6] or to stabilize strained alkynes.[7]

Complex **5** was prepared first as a model to test the Eglinton–Glaser oxidative coupling of (μ-acetylene)dicobalt complexes bearing a free terminal alkyne unit. Ligand exchange of two carbonyls on [(μ-bis(trimethylsilyl)butadiyne)$Co_2(CO)_6$][8] with bis(diphenylphosphino)methane (dppm)(benzene, reflux, 12 h, 85%) afforded **4**, which was deprotected at the alkynyl group to **5** with tetrabutylammonium fluoride (TBAF) (THF/CH_3OH, 10:1, 12 h, 97%) (Scheme II).[9] The butadiyne complex **6** was obtained as stable, deep red crystals when stronger desilylation conditions were used (TBAF, moist THF, 25 °C, 83%). Oxidative coupling of **5**, using standard Eglinton–Glaser conditions[10] ($Cu(OAc)_2$, pyridine, 25 °C, 24 h, 75%), furnished dimer **7**, demonstrating the applicability of this method to the coupling of $(dppm)Co_2(CO)_4$ derivatives like **3**.[11]

Next, triyne **9**[12] was prepared in gram quantities by flash vacuum pyrolysis of cyclobutenedione **8**[2b] in 69% yield.[13] The reaction of **9** with $Co_2(CO)_8$ (n-hexane, 25 °C, 12 h) and subsequent ligand exchange with dppm (toluene, reflux, 2 h) furnished **10** in 75% yield (Scheme II). The bulky triisopropylsilyl groups in **9** were chosen to direct complexation toward the less hindered 3,4-triple bond. Deprotection of **10** with TBAF (moist THF, 25 °C, 5 min, 100%) gave the hexatriyne complex **3** as stable, dark

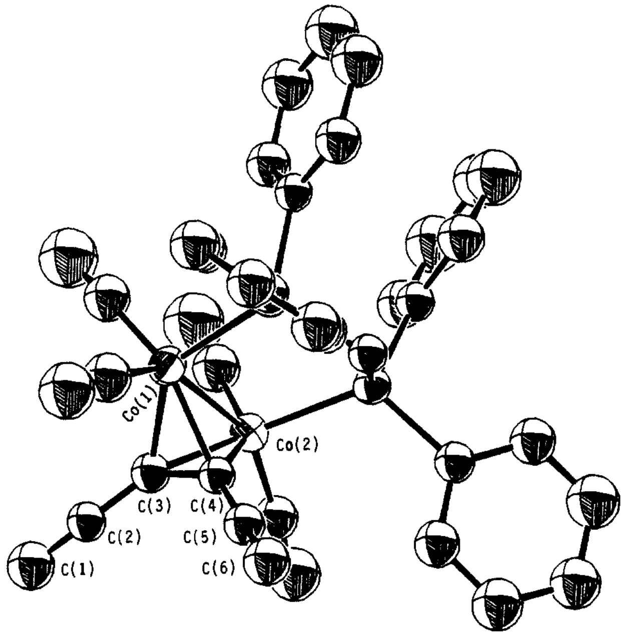


Figure 1. X-ray crystal structure of 3.

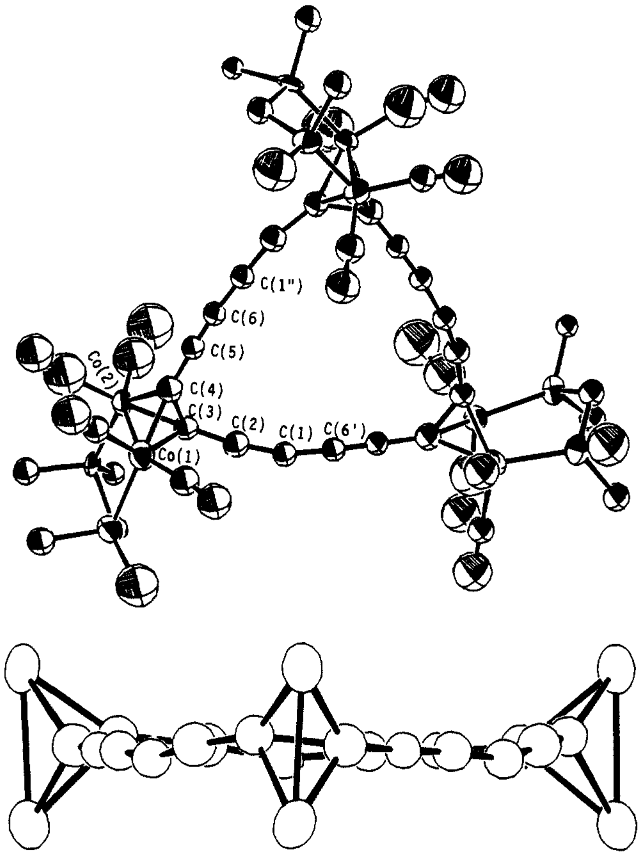


Figure 2. X-ray crystal structure of 1. Above: all except the ipso carbons from the phenyl groups omitted for clarity. Below: edge view with CO and dppm ligands omitted for clarity.

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[4] Dickson, R. S.; Fraser, P. J. *Adv. Organomet. Chem.* **1974**, *12*, 323–377.

[5] (a) Nicholas, K. M.; Nestle, M. O.; Seyferth, D. *Transition Metal Organometallics in Organic Synthesis*, Alper, H., Ed.; Academic: New York, 1978; Vol. II. (b) Vollhardt, K. P. C. *Angew. Chem.* **1984**, *96*, 525–541; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539–556.

[6] (a) Magnus, P.; Carter, P. A. *J. Am. Chem. Soc.* **1988**, *110*, 1626–1628. (b) Krafft, M. E. *J. Am. Chem. Soc.* **1988**, *110*, 968–970. (c) Magnus, P.; Becker, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 7495–7498. (d) Schreiber, S. L.; Sammakia, T.; Crowe, W. E. *J. Am. Chem. Soc.* **1986**, *108*, 3128–3130.

[7] Bennett, M. A.; Schwemlein, H. P. *Angew. Chem.* **1989**, *101*, 1349–1373; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296–1320.

[8] Pannell, K. H.; Crawford, G. M. *J. Coord. Chem.* **1973**, *2*, 251–255.

[9] Spectroscopic data (^1H NMR, ^{13}C NMR, IR, EI-MS or FAB-MS, UV–vis) and elemental analyses support the structures proposed for all new compounds.

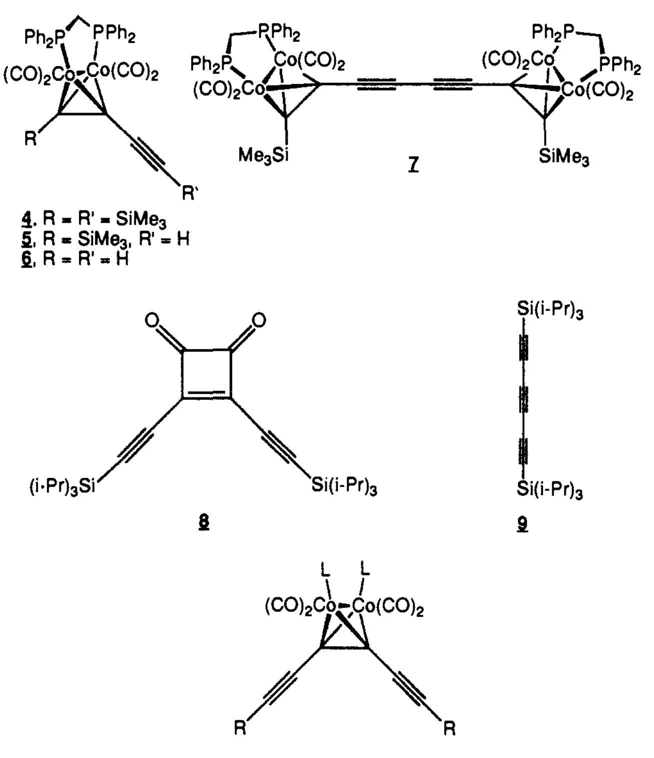
[10] Behr, O. M.; Eglinton, G.; Galbraith, A. R.; Raphael, R. A. *J. Chem. Soc.* **1960**, 3614–3625.

[11] Magnus, P.; Becker, D. P. *J. Chem. Soc., Chem. Commun.* **1985**, 640–642.

[12] Blanco, L.; Helson, H. E.; Hirthammer, M.; Mestdagh, H.; Spyroudis, S.; Vollhardt, K. P. C. *Angew. Chem.* **1987**, *99*, 1276–1277; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1246–1247.

[13] This new method for the preparation of 9 and other triynes and pentaynes will be reported later: Rubin, Y.; Knobler, C. B.; Diederich, F., unpublished results.

Scheme II



red crystals, characterized by X-ray crystallography[14] (Figure 1). In contrast, attempts to deprotect the $Co_2(CO)_6$ complex **11**, prepared in 62% yield from **9** as described above, were unsuccessful. With values of 137.7° and 138.8°, respectively, the angles C(2)–C(3)–C(4) and C(3)–C(4)–C(5) in **3** are of similar magnitude to those of previously described (μ-acetylene)$Co_2(CO)_6$ complexes.[3] Compounds **6** and **3** provide stable, well-characterized cobalt complexes of the explosive compounds 1,3-butadiyne[15] and 1,3,5-hexatriyne.[16,17]

The oxidative cyclization of **3** ($Cu(OAc)_2$, pyridine, 45 °C, 48 h, [**3**] = 0.01 M) afforded trimer **1** (33%) and tetramer **2** (5.4%), both as air-stable shiny black needles.[18] Recrystallization of **1** from 1,2-dichloroethane/methylcyclohexane provided crystals suitable for X-ray analysis[19] (Figure 2). The crystal structure shows that **1** is formally a complex of cyclo[18]carbon. The C_{18} ring is nearly planar, the largest deviation from the least-squares plane through the 18 carbon atoms being 0.19 Å. The angles C(2)–C(3)–C(4) and C(3)–C(4)–C(5) are 131 (4)° and 134 (4)°. The diyne units show considerable deviation from linearity as a result of C≡C—C bending; the C(2)–C(1)–C(6′) angle, 161 (5)°, is the smallest.

Cyclo[18]carbon is highly stabilized as a ligand in complex **1**. It differs from free C_{18} by variations in bond lengths and angles,[1] by partial deconjugation of the π-system,[20] and by the steric shielding provided by the three $(dppm)Co_2(CO)_4$ units. Attempts to free C_{18} of the protecting groups by mild oxidation of **1** are now under way.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Experimental details of the crystal structure determinations for **1** and **3**, fully labeled views of the two structures, and tables of their atomic coordinates, equivalent isotropic thermal parameters, bond angles, and bond lengths (18 pages); tables of observed and calculated structure factors for **1** and **3** (21 pages). Ordering information is given on any current masthead page.

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(14) X-ray crystal data for **3** ($C_{35}H_{24}O_4Co_2P_2 \cdot CHCl_3$): M_r = 807.8; monoclinic; space group = $P2_1$; Z = 2; a (Å) = 8.487 (2); b (Å) = 18.443 (3); c (Å) = 11.842 (2); β = 101.290 (5)°; V (Å^3) = 1818; D_{calcd} (g cm^{-3}) = 1.26. Data were collected on a Huber diffractometer constructed by Professor C. E. Strouse, UCLA, using Mo Kα radiation, $2\theta \leq 45°$, giving 2460 unique reflections; the structure was solved by direct methods (MULTAN80), yielding R = 0.047 and R_w = 0.058 for 2157 reflections with $I > 3\sigma(I)$.

(15) Bonrath, W.; Pörschke, K. R.; Wilke, G.; Angermund, K.; Krüger, C. *Angew. Chem.* **1988**, *100*, 853–855; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 833–835.

(16) The preparation of a $[Co_2(CO)_6]_2$ complex of 1,3-butadiyne and a $[CO_2(CO)_6]_3$ complex of 1,3,5-hexatriyne in very low yields has been reported: Peyronel, G.; Ragni, A.; Trogu, E. F. *Gazz. Chim. Ital.* **1967**, *97*, 1327–1343.

(17) Dellaca, R. J.; Penfold, B. R. *Inorg. Chem.* **1971**, *10*, 1269–1275.

(18) Spectral data for **1**, **2**, and **3**. Compound **3**: mp > 120 °C dec; IR ($CHCl_3$) ν (≡CH) 3305, (C≡C) 2075, (C≡O) 2053, 2047, 1993 cm^{-1}; UV (CH_2Cl_2) λ_{max} (nm) 280 (ϵ 26 800), 340 sh (11 100), 393 sh (2430); ^1H NMR (360 MHz, CD_2Cl_2) δ 3.76 (t, $^5J_{HP}$ = 1.4 Hz, 1,6-H); ^{13}C NMR (90.6 MHz, CD_2Cl_2, gated decoupling) δ 69.2 (br s, C-3,4), 84.5 (d, $^1J_{CH}$ = 252.2 Hz, C-1,6), 85.7 (d, $^2J_{CH}$ = 49.9 Hz, C-2,5). Compound **1**: IR (CH_2Cl_2) ν (C≡C) 2107, (C≡O) 2057, 2042, 2000 cm^{-1}; UV (CH_2Cl_2) λ_{max} (nm) 254 sh (ϵ 119 500), 291 (106 000), 370 (91 400), 445 sh (36 700), 546 sh (12 400); $^{13}C\{^1H\}$ NMR (90.6 MHz, CD_2Cl_2) δ 72.0 (br s, C-3,4), 84.0 (br s, C-2,5), 88.0 (s, C-1,6). Compound **2**: IR ($CHCl_3$) ν (C≡C) 2100, (C≡O) 2043, 2033, 1993 cm^{-1}; UV (CH_2Cl_2) λ_{max} (nm) 268 sh (ϵ 141 700), 381 (122 700), 453 sh (50 900), 560 sh (15 000); $^{13}C\{^1H\}$ NMR (90.6 MHz, CD_2Cl_2) δ 70.6 (br s, C-3,4), 85.0 (br s, C-2,5), 88.0 (s, C-1,6). The highly characteristic electronic absorption spectra of **1** and **2**, their similar IR and NMR spectra, and their R_f values (TLC, SiO_2, CH_2Cl_2/hexane, 1:1; **1**, R_f = 0.12; **2**, R_f = 0.08) strongly suggest that **2** is a cyclic tetramer.

(19) X-ray crystal data for **1** ($C_{105}H_{66}O_{12}Co_6P_6$); M_r = 2059.13; hexagonal; space group = $P6_3$; Z = 2; a (Å) = 20.922 (5); c (Å) = 16.385 (4); V (Å^3) = 6211; D_{calcd} (g cm^{-3}) = 1.20; data collection as in footnote 14, $2\theta \leq 42°$, 4914 unique reflections, solution by heavy-atom methods gave R = 0.126 and R_w = 0.161 for 1856 reflections with $I > 3\ \sigma(I)$. Highly disordered solvent prevented further refinement.

(20) (a) Reference 4, pp 334–337. (b) Sautet, P.; Eisenstein, O.; Canadell, E. *New J. Chem.* **1987**, *11*, 797–806.

Kinetic Isotope Effects and Negative Activation Energies for Proton Transfer from 9-Phenylanthracene Cation Radical to Hindered Nitrogen-Centered Bases

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Received December 4, 1989

The pK_a of benzene cation radical in acetonitrile has been estimated to be equal to −4.[1] This suggests that reaction 1, where $Ar\text{-}H^{\bullet+}$ is a benzene cation radical and B is pyridine or a substituted pyridine, has an equilibrium constant of the order of 10^{10} or greater in acetonitrile at 298 K. Yet, there has been no

$$Ar\text{-}H^{\bullet+} + B \rightleftarrows Ar^{\bullet} + B\text{-}H^{+} \qquad (1)$$

$$Ar\text{-}H^{\bullet+} + B \rightleftarrows ArH^{\bullet}\text{-}B^{+} \qquad (2)$$

convincing evidence reported that this reaction takes place in solution. Twenty years ago it was suggested[2] that the primary reactions during the oxidation of benzene and biphenyl in acetonitrile consist of formation of the cation radicals followed by deprotonation to give the corresponding aryl radicals. However, no evidence was presented to support the proton transfer reactions, and subsequent work has shown that arene cation radicals undergo addition reactions 2 with nucleophiles in essentially barrier-free reactions rather than proton transfer.[3-5] We now report the first evidence for reaction 1 and show that this reaction can only compete with reaction 2 when the base is rendered non-nucleophilic by steric constraints.

The reactions of 9-phenylanthracene (PAH) cation radical with 4-substituted pyridines in acetonitrile at 293 K involve nucleophilic

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(1) Nicholas, A. M. de P.; Arnold, D. R. *Can. J. Chem.* **1982**, *60*, 2165.

(2) Osa, T.; Yildiz, A.; Kuwana, T. *J. Am. Chem. Soc.* **1969**, *91*, 3994.

(3) Parker, V. D.; Tilset, M. *J. Am. Chem. Soc.* **1987**, *109*, 2521.

(4) Parker, V. D.; Reitstöen, B.; Tilset, M. *J. Phys. Org. Chem.* **1989**, *2*, 580.

(5) Reitstöen, B.; Norrsell, F.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 8463.