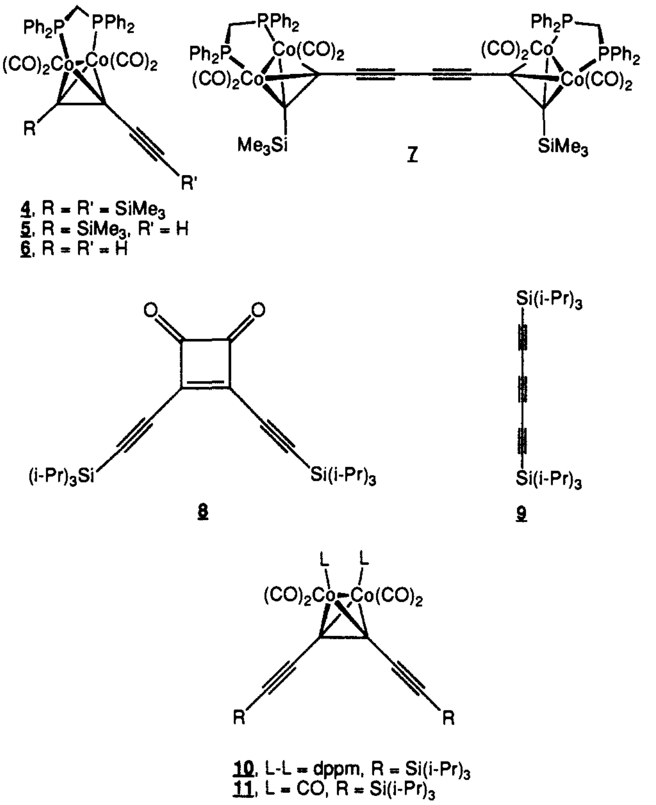
Scheme II



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); ^{1}H 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 {^{1}H} 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{^{1}H} 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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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-H$^{•+}$ 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

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

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

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.

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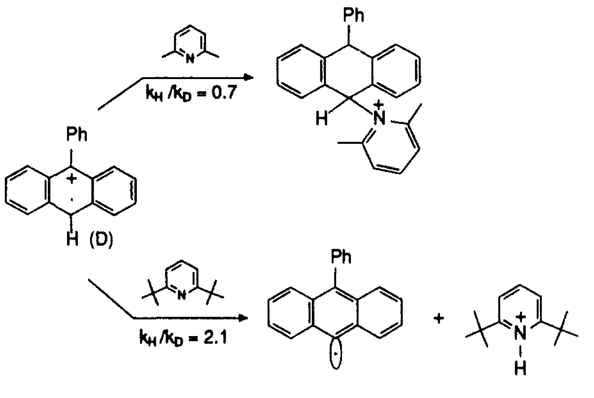
(4) Parker, V. D.; Reitstöen, B.; Tilset, M. *J. Phys. Org. Chem.* **1989**, *2*, 580.

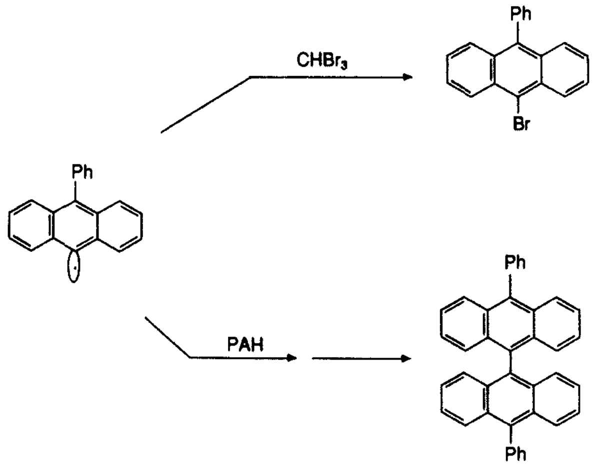
(5) Reitstöen, B.; Norrsell, F.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 8463.

0002-7863/90/1512-4968$02.50/0

Scheme I



Scheme II



attack on the cation radical with rate constants ranging from 10^5 to 10^7 M^{-1} s^{-1}.[3] We now find that 2,6-lutidine (LUT) reacts with $PAH^{\bullet+}$ under the same conditions with a second-order rate constant of 1.1×10^3 M^{-1} s^{-1}, about 4 orders of magnitude slower than the corresponding reaction with pyridine as the nucleophile. An inverse kinetic isotope effect, $k_H/k_D = 0.75$, was observed for the reaction between $PAH^{\bullet+}$ and 2,6-lutidine. This is readily explained by the hybridization change, sp^2 to sp^3,[6] that takes place at the PAH 10-position during nucleophilic attack on the cation radical. A 1 order of magnitude decrease in the second-order rate constant, 1.3×10^2 M^{-1} s^{-1}, was observed for the reaction of 2,6-di-*tert*-butylpyridine (TBP) with $PAH^{\bullet+}$ under the same conditions. This reaction was accompanied by a normal deuterium kinetic isotope effect, $k_H/k_D = 2.1$. The kinetic results are a clear indication of a mechanism change as the nitrogen center becomes more highly sterically congested. TBP is essentially non-nucleophilic toward $PAH^{\bullet+}$ and undergoes attack on the proton at the 10-position to generated $PA^{\bullet}$ while LUT, like pyridine, acts as a nucleophile toward the cation radical. The two reaction pathways are shown in Scheme I.

The formation of free aryl radicals during the reaction of $PAH^{\bullet+}$ with TBP was substantiated by the observation that in the presence of bromoform a partitioning between bromine atom abstraction and dehydro-dimer formation was observed (Scheme II). The rate constant for the abstraction of bromine from CBr_4 by phenyl radical has been determined to be equal to 5×10^9 M^{-1} s^{-1} at 318 K,[7] and $CHBr_3$ reacts about 1 order of magnitude slower than CBr_4 with α-naphthyl and 4-nitrophenyl radicals.[8] Preparative electrolyses in acetonitrile resulted in yields of 9-bromo-10-phenylanthracene of 5, 20, and 32% at $CHBr_3$ concentrations of 0.1, 0.4, and 0.8 M, respectively.[9]

It is of interest to compare the observed activation energies for the two processes. Nuclophilic attack on $PAH^{\bullet+}$ by LUT gives rise to an Arrhenius activation energy (E_a) of 4 kcal/mol and a rate constant at 298 K of 1120 M^{-1} s^{-1}. When the nitrogen-centered base was TBP, a negative E_a (−7 kcal/mol) and a 1 order of magnitude lower rate constant (130 M^{-1} s^{-1}) were observed. Under similar conditions, the nucleophilic attack of pyridine on $PAH^{\bullet+}$ is accompanied by an E_a of 2.4 kcal/mol and a second-order rate constant equal to 10^7 M^{-1} s^{-1}.[3]

The data support our current view[3-5] for the mechanism of electrophilic reactions of cation radicals. The low E_a values are a consequence of a preequilibrium (reactions 3) with a negative ΔH before rate-determining nucleophilic attack (reaction 4). A

$$PAH^{\bullet+} + N \rightleftarrows PAH^{\bullet+}/N \qquad (3)$$

$$PAH^{\bullet+}/N \rightarrow PAH^{\bullet}\text{-}N^+ \qquad (4)$$

$$PAH^{\bullet+}/N \rightarrow PA^{\bullet} + N\text{-}H^+ \qquad (5)$$

branching of the mechanism takes place after step 3. The normal pathway when N is LUT or less highly substituted pyridines is nucleophilic attack (reaction 4). But when N is highly hindered TBP, the π-complex ($PAH^{\bullet+}/N$) cannot rearrange (reaction 4) and undergoes internal proton transfer followed by dissociation (reaction 5). The fact that E_a is substantially lower in the latter case indicates that the activation energy for reaction 4 is greater when N is LUT than that for reaction 5 when N is TBP, assuming that ΔH for reaction 3 is less affected by the nature of N. Pyridine reacts about 10^4 times more rapidly than LUT, indicating that the presence of the 2- and 6-methyl groups does appreciably hinder the reaction, although not to the extent that proton transfer becomes more favorable. The substantially negative E_a observed for the highly hindered base strongly supports the assumption of preequilibrium step 3.

Since LUT is only about a factor of 10 more reactive than TBP and the former reacts exclusively via reaction 4, it follows that LUT does not give rise to a larger rate constant for reaction 5 than the more hindered base. This result is in contrast to those observed for the proton abstraction from hexamethylbenzene cation radical ($ArCH_3^{\bullet+}$) in acetonitrile.[10] A substantial steric effect was observed with LUT reacting about 120 times faster than TBP. This indicates that abstraction of an aryl proton is less susceptible to steric effects than is abstraction of an arylmethyl proton.

The aryl proton abstraction reaction appears to be general for 9-substituted anthracene cation radicals with TBP.[11] Data for both 9-cyano- and 9-nitroanthracene cation radical with LUT and TBP parallel that for $PAH^{\bullet+}$. On the other hand, we were unable to observe proton abstraction from either 9,10-diphenylanthracene or thianthrene cation radicals with TBP under the same conditions. We conclude that there must be appreciable positive charge at the position of attachment of the proton in order for the reaction to be favorable. Further work is in progress to define the scope of the aryl proton transfer reaction.

Acknowledgment. The National Science Foundation (CHE-8803480) is gratefully acknowledged for generous support of this work.

Registry No. 9-Phenylanthracene cation radical, 40807-34-9; 10-deuterio-9-phenylanthracene cation radical, 123289-29-2; 2,6-lutidine, 108-48-5; 2,6-*tert*-butylpyridine, 585-48-8; 9-cyanoanthracene cation radical, 84985-64-8; 9-nitroanthracene cation radical, 84367-93-1; 9,10-diphenylanthracene cation radical, 34480-04-1; thioanthrene cation radical, 34507-27-2.

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(11) A referee correctly pointed out that the 9-substituted anthracene cation radicals are expected to be significantly less acidic than benzene cation radical by virtue of their lower oxidation potentials.