formed in the high-pressure ion source by interaction between $(CO)_5Mn^+$ and CH_4 (reaction 2). Multiple ion-molecule collisions in the high-pressure ion source provided thermalization of the weakly bound complex. The present experiments do not allow us to identify the exact nature of the interaction between CH_4 and $(CO)_5Mn^+$.

$$(CO)_5Mn^+ + CH_4 \rightarrow (CO)_5Mn^+/CH_4 \qquad (2)$$

Combining the present results with those of ref 13 yields the potential energy surface shown in Figure 2. Exchange of the CH_4 unit in the complex with CD_4 was not successful. This can be ascribed to lack of a coordination site for the incoming CD_4.

The high-pressure mass spectrum of $Mn_2(CO)_{10}/CH_4$ also showed the presence of $[Mn, C_5, O_5, H_2]^+$ and $[Mn, C_5, O_6, H_2]^+$ (ca. 7% and 2% of m/z 391, respectively[17]). The CID mass spectra of these ions were dominated by $(CO)_5Mn^+$, corresponding with loss of H_2 and H_2O, respectively. The energy dependence of the CID spectra suggests that these species are weakly bound $(CO)_5Mn^+/H_2$ and $(CO)_5Mn^+/H_2O$ complexes.

In summary, we have obtained unambiguous evidence for the existence of weakly bound organometallic/CH_4 complexes, which may play an important role in reductive elimination and oxidative addition reactions. Further experiments are in progress to establish the reaction mechanism that generates the $(CO)_5Mn^+/CH_4$ complex and to obtain a more accurate binding energy of this complex. Preliminary results indicate that other organometallic species, e.g., $Re_2(CO)_{10}$, yield similar complexes.

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Kinetic Acidity of Cubane

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We have determined the kinetic acidity of cubane by the application of a ^3H NMR spectroscopic approach.[1] An earlier measurement of the acidity of cubane[2] has been subject to some controversy.[3]

Kinetic acidities are a useful measure of the acidity of weak carbon acids[4] and are obtained by measuring rates of base-catalyzed proton-exchange reactions. It has been found that one-bond $^{13}C-^1H$ NMR coupling constants ($^1J_{CH}$) correlate closely with kinetic acidities for cyclic aliphatic hydrocarbons[5] (see Figure 1). This correlation holds even for strongly strained systems such as cyclopropane. Cubane, a strained polycycloalkane, would be anticipated to also fit this correlation. On the basis of its $^1J_{CH}$ value of 155 Hz,[6] the predicted kinetic acidity of cubane from the correlation is 1.4×10^{-4} times that of benzene.

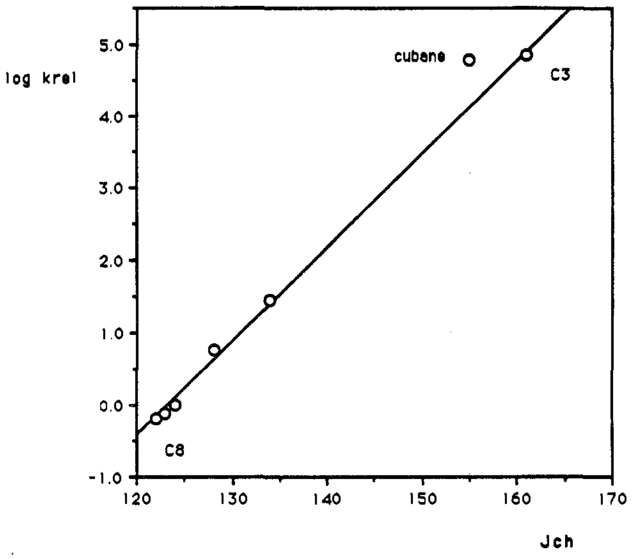

Figure 1. Logarithm of kinetic acidity (CsCHA tritiodeprotonation) relative to cyclohexane vs one-bond $^{13}C-^1H$ NMR coupling constant. The point for cubane is superimposed on the previous correlation (ref 5b) based on cycloalkanes, n = 3-8.

Table I. Cubane Tritium Incorporation and Loss

experiment	[CsCHA][a]	cubane:[b] 10^6k_1[c]	p-xylene ring:[b] 10^4k_1[c]	rel rate: curbane/ p-xylene
tritodeprotonation	0.123	2.9	4.4	0.0066
protiodetritiation	0.086	0.88	1.7	0.0052

[a] Calculated from the volume of 0.2 N CsCHA added. [b] Pseudo-first-order rate constant (s^{-1}). [c] Statistically corrected.

It thus came as a surprise when it was reported by Luh and Stock[2] that the kinetic acidity of cubane is 1.2 times that of benzene, a value almost 4 orders of magnitude greater than predicted on the basis of $^1J_{CH}$. Ritchie and Bachrach were prompted by this result to do calculations[3] on the cubane system, in an attempt to explain its behavior. They concluded that cubane is thermodynamically more acidic than cyclopropane, and they rationalized the results on the basis of greater rehybridization in the cubane system on deprotonation.[7] On the other hand, the value of the Laplacian at the bond critical point for the C-H bond suggests a lower acidity for cubane.[3]

We had planned to reinvestigate the kinetic acidity of cubane for some time, but the experimental techniques available were difficult to apply. The detection methods we have used routinely for kinetic acidity studies (scintillation counting, mass spectrometry) do not always guarantee the identity of the substance being analyzed for isotopic exchange, thus leading to potential errors due to the presence of impurities. The application of tritium NMR spectroscopy as a new technique for monitoring proton exchange kinetics[1] presented us with the opportunity to study cubane.

The exchange experiments on cubane were accomplished by incorporating tritium (tritiodeprotonation) from N-tritiated cyclohexylamine (CHA), catalyzed by cesium cyclohexylamide (CsCHA), in an analogous manner to that described previously.[1] The rate of tritium incorporation at 297 K was determined in a competition experiment with p-xylene, for which the kinetic acidity is known.[1] The tritium NMR spectrum of the sample consisted of four singlets at δ 7.24 (xylene ring), δ 4.25 (cubane), δ 2.45 (xylene methyl), and δ 1.36 (amino position of CHA). For this study we also conducted a protiodetritiation experiment, as follows: the sealed NMR tube containing the substrates from the trit-

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iodeprotonation run was opened, and the contents (1.2 mL) were syringed into a flask containing ca. 10 g of polyphosphoric acid (PPA). The reaction of PPA with CHA proceeded slowly, and the flask was heated gently for 1 h. The hydrocarbons were then vacuum transferred from the flask into an NMR tube containing CsCHA and [^{1}H]CHA, and the detritiation reaction was monitored at 297 K. The measured rate constants are tabulated in Table I. All of the rate constants refer to rates/hydrogen.

It can be shown that our tritiodeprotonation and protiodetritiation rates are directly comparable, because they result from tracer experiments. The average rate of exchange of cubane is then 0.0060 times that of the ring position in *p*-xylene. Since this position exchanges 0.11 times as fast as benzene,[1] the kinetic acidity of cubane is 6.6×10^{-4} that of benzene. Figure 1 shows that its acidity (6.3×10^4 times that of cyclohexane) is still, however, almost 5 times that predicted from $^1J_{CH}$ values (1.3×10^4 times that of cyclohexane), indicating that there is indeed an enhanced acidity for cubane, but it is much smaller than previously reported. Our result thus supports the enhanced rehybridization effect shown by the calculations. Cubane is also kinetically less acidic than cyclopropane (7.1×10^4 times the kinetic acidity of cyclohexane),[5] which is qualitatively correct on the basis of s character (31% for cubane vs 32% for cyclopropane). Additional experiments and calculations are in progress to further define the relationships between thermodynamic and kinetic acidities on related systems.

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Surprising Differences in the Reactivity of Cyanoaromatic Radical Anions Generated by Photoinduced Electron Transfer

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Cyanoaromatics such as 9,10-dicyanoanthracene (DCA) are widely used as "sensitizers" in photochemical electron transfer reactions.[1-17] Although it is generally accepted that the excited cyanoaromatics undergo single electron transfer (SET) reduction to generate the corresponding anion radicals (and these anion radicals are frequently observed, as intermediates, via laser flash photolysis techniques),[8,9] the reported fate of the cyanoaromatic can be quite varied, depending upon the other reagents present. Thus in some cases, they may function as true sensitizers with no net consumption,[2] such as in a number of cases where strained hydrocarbons are induced to rearrange via photochemical SET.[3] In other instances, the cyanoaromatics undergo net reactions as diverse as substitution,[1] addition, or net two-electron reduction to the corresponding dihydro compounds.[18] In several cases it is clear that the cyanoaromatic anion radical, or some species derived from it, must be undergoing reaction with reagents that are normally regarded as relatively unreactive. In this paper, we report some studies that indicate that the reactivity of photogenerated cyanoaromatic anion radicals is strongly affected by the medium in which they are generated; interestingly we report conditions under which potentially reactive anion radicals of DCA and 2,6,9,10-tetracyanoanthracene (TCA) can be the stable "end products" of photoinduced redox reactions.

In 1979 Ohashi et al.[19] described a remarkable reaction in which DCA was converted into 9-amino-10-cyanoanthracene and acetaldehyde when irradiated in the presence of amines and water in acetonitrile solvent. Related chemistry was subsequently explored by Mariano et al.[20] Although a precise mechanism has not been established, it was determined that the amino nitrogen came from acetonitrile and, given the low reactivity of acetonitrile toward nucleophiles, that a highly reactive intermediate had to be involved. We have found that the simple addition of an inert salt suppresses this reaction and 9,10-dicyanoanthracene radical anion ($DCA^{\bullet-}$) is produced as a stable final product. A number of reports[21-23] indicate that added salts dramatically enhance the lifetime (and reduce the reactivity) of radical ions. This may be in part a medium effect, but the major effect is the stabilization of the radical ion by the presence of a stable, unreactive counterion. When a vacuum-degassed solution of DCA (1.22×10^{-4} M), triethylamine (0.22 M), and tetra-*n*-butylammonium dihydrogen phosphate (5.4×10^{-3} M) is irradiated with a 450-W medium-pressure mercury lamp filtered to pass light from 370 to 440 nm, the characteristic absorption spectrum[24] of DCA radical anion appears and is stable for weeks at a time. The fate of triethylamine is not clear except for NMR evidence that can be assigned to diethylamine.[25] When oxygen is admitted, the radical anion is quickly converted back to DCA. The conversion of DCA to stable DCA radical anion is not complete and of low quantum yield, however, and depends on a number of experimental variables. For example, both the quantum and chemical efficiency of radical ion

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$$A \xrightarrow{h\nu} A^{1*} \quad (1)$$

$$A^{1*} + Et_3N \rightarrow A^{\bullet-} + Et_3N^{\bullet+} \quad (2)$$

$$Et_3N^{\bullet+} \xrightarrow{-H^+} Et_2N\dot{C}HCH_3 \quad (3)$$

$$Et_2N\dot{C}HCH_3 + A \rightarrow A^{\bullet-} + Et_2N^+{=}CHCH_3 \quad (4)$$

$$Et_2N^+{=}CHCH_3 + H_2O \rightarrow Et_2NH + CH_3CHO \quad (5)$$

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