(C_9O_9, $C_9'O_9'$) practically lie in this plane: $C_9CrC_9'/PC_1C_1'P'$ interplane angle 6.46° ± 0.4°. Conversely, the plane of the two other carbonyls (C_8O_8, $C_8'O_8'$) is almost orthogonal to the biphosphinine plane (94.94° ± 0.05°). When the structures of **2** and **10** are compared, several significant differences appear. Whereas the two P$\overset{\cdots}{-}$C and two N$\overset{\cdots}{-}$C bonds of **2** are almost strictly equal (1.707 and 1.709 Å; 1.367 and 1.358 Å) as in (bipy)Cr$(CO)_4$[13] indicating that the two aromatic rings are not disturbed by the bridge, the two internal P$\overset{\cdots}{-}$C bonds of **10** are notably longer than the two external ones (1.737 vs 1.711 Å). Theoretical calculations are currently underway to establish whether or not delocalization occurs in the five-membered metallacycle of **10**. In addition, we are trying to improve the yield of the bridging step (eq 2), and we are starting to investigate the coordination chemistry of **10**.

Supplementary Material Available: ^1H NMR, ^{13}C NMR, and mass spectra of **4a,b** and **5–7**, X-ray structural determination for **10** including experimental details, and tables of bond distances and angles and their estimated standard deviations, positional parameters and their estimated standard deviations for all non-hydrogen atoms, and β_{ij} with their estimated standard deviations for **10** (6 pages). Ordering information is given on any current masthead page.

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[13] Main data for (bipy)Cr$(CO)_4$: N–C, 1.347 (3) Å (mean); C–C bridge, 1.471 (5) Å; N–Cr, 2.089 (3) Å (mean). This structure will be fully described elsewhere.

Cubane Radical Cation in Liquid Hydrocarbons: Time-Resolved Fluorescence Detected Magnetic Resonance Study†

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The structure and rearrangement of strained hydrocarbons and radical cations in general, and those of the $(CH)_8$ group in particular, have attracted considerable experimental and theoretical attention.[1-8] The electronic structure of the cubane radical cation (cubane$^{•+}$) is particularly interesting, since the cubane molecule has the highest strain energy of the set and belongs to the O_h point group.[8] The photoelectron spectroscopic study and ab initio STO-3G and MINDO/3 calculations by Heilbronner et al. indicate that cubane has triply degenerate highest occupied molecular orbitals (t_{2g} orbitals).[1] Upon ionization it undergoes Jahn–Teller distortion:[9] the symmetry is lowered from O_h to C_{2v}. An EPR study of cubane photolyzed in a neon matrix at 4 K was reported by Knight et al. in 1987.[2] However, Knight repeated these experiments recently and concluded that cubane$^{•+}$ was not observed in his experiments.[10] In view of this finding, we conclude that the cubane radical cation was not observed previously and that in our studies of cubane$^{•+}$ rearrangements in Freon matrices we could not directly observe the EPR spectrum of cubane$^{•+}$ in several Freon matrices at 77 K. Cubane$^{•+}$ undergoes rearrangement at 80 K and higher temperatures, and one cannot utilize a Freon matrix to stabilize and observe its EPR spectrum in the temperature range (110–120 K) where resolved EPR spectra of radical cations in $CF_2ClCFCl_2$ are usually obtained.[7]

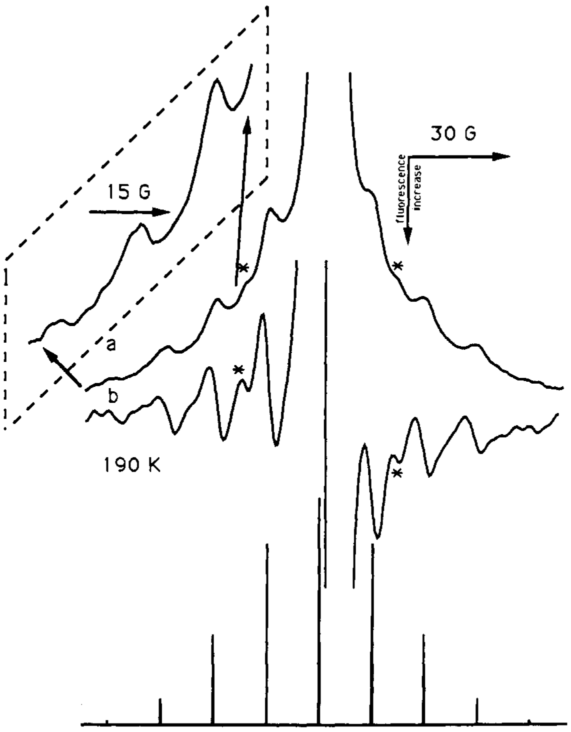

Figure 1. (a) FDMR spectrum observed at 190 K in cyclopentane containing 10^{-3} M cubane and 10^{-4} M perdeuterated anthracene. The asterisks indicate the signals from the cyclopentane solvent.[20] The insertion is the enlargement of the left outermost three peaks. (b) First-derivative FDMR spectrum of part a.

We report here a time-domain study of cubane$^{•+}$, utilizing the time-resolved fluorescence detected magnetic resonance (FDMR) technique.[11] We have observed a radical cation, which we assign to cubane$^{•+}$ in liquid hydrocarbon solution. The observed FDMR spectrum is consistent with the presence of eight protons (a_{8H} = 16.1 G) of the cation which are equivalent.

Cubane$^{•+}$ was produced in cyclopentane solutions 10^{-3} M in cubane and 10^{-4} M in perdeuterated anthracene (A) using pulsed electron beam (12-ns width) irradiation, generated by a 3 MeV electron Van de Graaff generator. The ionizing radiation creates singlet-phased radical ion pairs in cyclopentane (c-C_5H_{10}, gas-phase ionization potential (IP) = 10.4 eV[12]) consisting of a cyclopentane radical cation (c-$C_5H_{10}^{•+}$) and an electron, most of which recombine geminately in a few picoseconds. A small part of c-$C_5H_{10}^{•+}$ reacts by transferring positive charge to dissolved cubane (IP = 9.1 eV[1]) to form cubane$^{•+}$, while some of the electrons are converted to the scintillator radical anion ($A^{•-}$). The resulting radical ion pairs consisting of cubane$^{•+}$ and $A^{•-}$ are still spin-correlated. Upon their recombination, an excited singlet state

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(^{1}A*) is generated, resulting in detectable fluorescence.

The time-resolved FDMR spectra (Figure 1) of radical ion pairs of cubane$^{\bullet+}$ and A$^{\bullet-}$ at 190 K which recombine to give ^{1}A* was obtained by measuring the fluorescence intensity as a function of applied magnetic field. The resonant decrease in the intensity of fluorescence was induced by the application of a single 100-ns microwave pulse immediately following the electron beam pulse. An FDMR spectrum provides parameters such as those provided by an EPR spectrum. However, an FDMR spectrum is the fluorescence decrease induced by the pulse of microwave at resonance. The modulation depth, the line width, and thus the spectral resolution are dependent on the lifetime of the radical ion species, the microwave power, and the sampling-time window (microwave pulse width).[11] The criterion that is important is whether a *distinct* hyperfine decrease of fluorescence is present. Its intensity vis-à-vis background intensity should not be compared to that of the conventional EPR spectra.

Figure 1a consists of an intense central line (off scale) due to the unresolved FDMR lines of scintillator radical ions superimposed on the wider, multiplet FDMR spectrum assigned to cubane$^{\bullet+}$. This observed spectrum was not seen when cubane was absent or when other isomeric C_8H_8 hydrocarbons were used in its stead.[13] The multiplet is analyzed as a binomial nine-line pattern with a spacing of 16.1 G resulting from the interaction of the electron with the eight equivalent protons of the cubane molecule (cf. the stick spectrum). The two outermost lines are weak in both the experimental and the simulated stick spectrum. The first derivative (computer generated) in Figure 1b shows the lines more decisively. The eight protons must be equivalent, either by symmetry in a static structure, or by a dynamic Jahn–Teller distortion of cubane$^{\bullet+}$ in which they are averaged. Similar results were obtained in cyclopentane in a temperature range of 190–240 K. The signal-to-noise ratio is better at lower temperatures. The nature of the FDMR experiment tells us that we are observing a *radical cation* and the scintillator (perdeuterated anthracene) *radical anion* which recombine to give the excited state whose emission is being detected. An additional clue is provided by the behavior of cubane solution in hydrocarbons where we find that a given solution can be used very briefly, i.e., one cannot deliver many electron beam pulses to this solution because the intensity of the FDMR signal decreases as the number of pulses increases. This means that the species giving rise to the radical cation is sensitive to the buildup of the radiolysis products that have lower IP, such as olefins, that can compete in charge transfer. This means that the species giving rise to the nine-line spectrum must have an IP lower than that of the alkane being used as a solvent and higher than the IP of the olefin derived from this alkane, which is the main radiolysis product having lower IP. The cyclopentane/cyclopentene (IP = 9.0 eV[14]) and *n*-pentane (IP = 10.2 eV[15])/2-pentene (IP = 9.0 eV[16]) provide the IP bracketing. This is not the case when we study cyclooctatetraene (COT) or semibullvalene solutes, since such solutions are not sensitive to the buildup of the olefin product as COT (IP = 8.4 eV[8]) and semibullvalene (IP = 8.4 eV[8]) have IP values lower than the IP values of these olefins. Such considerations provide additional proof that we are observing a radical cation of cubane.

We have used semiempirical MO calculations such as AM1-UHF[17] to provide qualitative insights into how spin-density distributions, and consequently the coupling constants, depend on the distortions in the structure of cubane$^{\bullet+}$. Heilbronner et al.[1] calculated the ground-state cubane$^{\bullet+}$ by an open-shell MINDO/3 model, suggesting that the cubane radical cation is distorted from O_h to C_{2v}. Twelve equivalent structures of C_{2v} are on the potential surface of the cation. The "transition states" that interconvert these structures were not obtained, however. Indeed, we find static molecular distortions of the cubane radical cation by an AM1-UHF model that can undergo dynamic Jahn–Teller averaging to give an average coupling constant[18] similar to the experimentally observed one. These qualitative calculations suggest that the static distortion (Archimedean antiprism) of cubane, in which all protons are equivalent, is much higher in energy than several other structures of cubane$^{\bullet+}$ in which dynamic Jahn–Teller averaging could occur. A more quantitative analysis awaits development of more sophisticated calculations.

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(13) Preliminary results show that under similar conditions the FDMR spectra observed when cyclooctatetraene was solute consist of at least 19 lines with a spacing of 1.6 G; while those observed when semibullvalene was solute consist of a triplet (a_{2H} = 36.5 G) superimposed on the background signals. Qin, X.-Z.; Trifunac, A. D., unpublished results.

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Activation in Transition-Metal Catalysis by Catalyst Relay. A Synthetic Approach to (−)-Dendrobine

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Probing fundamental factors that control selectivity in transition-metal-catalyzed reactions is a major task in order to improve their applicability in complex synthesis. Defining the role that functionality *remote* from the reaction site in a substrate may play becomes significant in designing appropriate substrates and thereby synthetic strategy. We record a most unusual effect of a distant unsaturation on a transition-metal-catalyzed allylic alkylation[1] discovered in the course of a synthesis of (−)-dendrobine (**1**), an alkaloid constituent of the Chinese ornamental orchid *Dendrobine nobile*, the extracts of which form the basis of the Chinese herbal medicine Chin-Shih-Hu[2] and for which no asymmetric synthesis has been recorded.[3]

Our retrosynthetic analysis of (−)-dendrobine envisioned creation of the perhydroindane nucleus **2** via a palladium-catalyzed cycloisomerization[4] of **3**, which in turn would be available by a palladium-catalyzed allylic alkylation via **4** or **5**. Of these two, the former a priori appears to be the preferred substrate because of its sterically more accessible olefin for initial coordination to Pd(0).

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