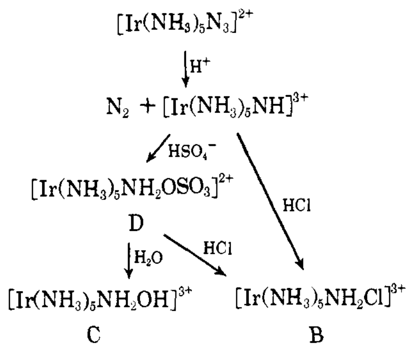
Scheme I



The intermediate nitrene complex behaves as an extremely powerful electrophile as does nitrene (NH) itself, which gives analogous products (NH_2Cl and NH_2OH) in aqueous solution.[11] Such behavior is expected for singlet nitrenes, where a valence-shell orbital is unoccupied, and is observed for the singlet aminonitrenes, R_2N-N.[12]

The formation of coordinated nitrene from the Ir(III) azide is in marked contrast to the behavior found for many other azido complexes, where only acid-catalyzed aquation occurs.[10,13] The difference could be attributed to a lowering of the energy of the transition state for nitrene formation by π donation from the t_{2g} orbitals on Ir(III). This proposed $d\pi \rightarrow p\pi$ interaction is analagous to the $p\pi \rightarrow p\pi$ interaction which is invoked to explain the unusual stability and the singlet (rather than triplet) ground state of the aminonitrenes, R_2N-N.[12]

Acknowledgment. We wish to thank Mr. T. R. Weaver for experimental assistance and helpful discussions. This research was supported by a grant from the NSF. One of us (J. W. M.) wishes to acknowledge the support of a predoctoral NIH fellowship.

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Reactions of Methylene in Solution. Selective Abstraction Reactions of $^1CH_2$ and $^3CH_2$

Sir:

Recently we utilized chemically induced nuclear spin polarization (CIDNP) to assign singlet (triplet) spin multiplicity to methylene generated by direct irradiation (photosensitized decomposition) of diazomethane.[1] However, one important question remained unanswered. In carbon tetrachloride the same abstraction–recombination product was formed from both spin multiplicities, and thus the same signal was enhanced (in emission or absorption) during both modes of decomposition. Therefore, it was impossible to decide whether methylene was formed exclusively in one spin state or only predominantly in one state and to a lesser extent in the other one.[2-6] This ambiguity can be resolved by studying multiplicity-specific reactions of methylene. Reactions of this type were found in the gas phase, where methylene attacks substrates containing both hydrogen and halogen atoms in a selective and multiplicity-specific manner.[7,8] Although reactions in solution are not necessarily comparable to those in the gas phase, we investigated reactions of methylene in solutions of substrates similar to those successfully employed in the gas phase.

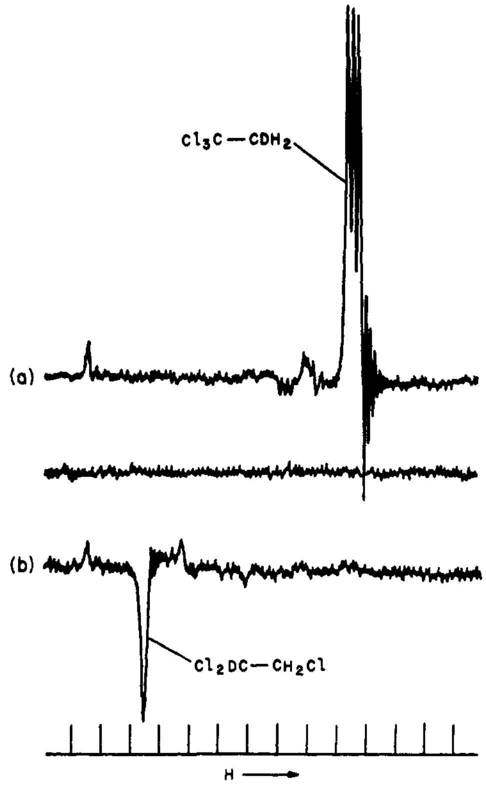

Figure 1. Proton nmr spectra (60 MHz) of diazirine solutions in deuteriotrichloromethane during triplet-sensitized (a) and direct (b) photolysis. A spectrum of the same region without irradiation is shown between traces a and b. A frequency scale (10.6 Hz between markers) is given below trace b. The resonance of diazirine (~200 Hz upfield of **3**) is not included in the spectra.

In this study we used diazirine (**1**)[9] as the source of methylene because diazomethane is so readily decomposed by even relatively stable free radicals (such as trichloromethyl).[1,10] Deuteriotrichloromethane was chosen as substrate because the nmr spectra of its po-

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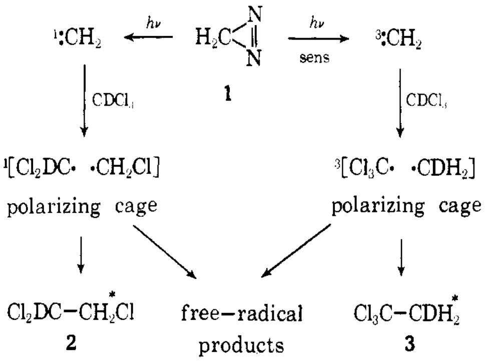
tential insertion products are simple. When diazirine is photolyzed in $CDCl_3$ solution a CIDNP spectrum is observed (Figure 1b). The dominating emission signal is attributed to spin-polarized 1-deuterio-1,1,2-trichloroethane (**2**), formed by chlorine abstraction and in-cage coupling of the resulting radical pair, $[Cl_2DC\cdot\ \cdot CH_2Cl]$. The observed signal direction is the same as in the case of the chloromethyl–trichloromethyl radical pair.[1] The factors determining the signal direction (in-cage coupling, negative *a* value, negative Δg) are the same for both radical pairs. Consequently, the emission signal observed for **2** establishes the singlet as the initial spin multiplicity of the parent radical pair and thus of the methylene involved in its formation.

When the decomposition of **1** in $CDCl_3$ is photosensitized, a new signal is observed, a 1:1:1 triplet in strongly enhanced absorption (Figure 1a). This signal has the chemical shift of 1,1,1-trichloroethane; its splitting pattern indicates the presence of a nucleus of spin 1 in the molecule; the magnitude of the observed coupling ($J \sim 1.9$ Hz) identifies this interaction as a geminal proton–deuteron coupling. The observed product, 2-deuterio-1,1,1-trichloroethane (**3**), is obviously formed by abstraction of the deuterium atom from deuteriotrichloromethane and recombination of the resulting radical pair (Scheme I). Since the polarized protons originate in the radical with negative Δg[11] and a negative *a* value, an absorption signal is compatible with a radical pair initially of triplet spin multiplicity and consequently with $^3CH_2$ as intermediate.

Scheme I[a]



[a] An asterisk denotes polarization.

It is noteworthy that the spectrum obtained during the photosensitized decomposition of **1** (Figure 1a) does not exhibit a signal of **2**. Earlier, we had observed that $^3CH_2$ (as well as $^1CH_2$) abstracts chlorine atoms from CCl_4.[1] Now we find that in $CDCl_3$, where hydrogen abstraction competes with halogen abstraction, $^3CH_2$ rather selectively abstracts hydrogen. We view the halogen abstraction by $^3CH_2$, a relatively stable ground-state[14] species, as kinetically unfavorable but certainly thermodynamically feasible.

Of equal significance is the complete absence (within the limit of detectability) of spin-polarized **3** in the singlet spectrum (Figure 1b). Barring the fortuitous cancellation of an enhanced absorption signal by a signal in enhanced emission of equal intensity, this observation means that $^1CH_2$ selectively abstracts chlorine atoms, that no triplet methylene is formed in the direct irradiation, and that the reactions of $^1CH_2$ with $CDCl_3$ are faster than the intersystem crossing to the triplet ground state.[15] The absence of an enhanced signal, of course, does not mean that the corresponding product is not formed; it only means that this product is not formed *via* a reaction sequence which allows the generation and observation of polarized nuclear spins. Consequently, our CIDNP evidence should not be interpreted as an argument against the well-established (one step) insertion reaction of methylene into carbon–hydrogen bonds.[16]

Concluding, we recall the results of Setser and coworkers, who inferred a similar specificity of singlet and triplet methylene for gas-phase reactions.[7] Their conclusion was based on kinetic studies of the photodecomposition of ketene and diazomethane in the presence of simple chloro-substituted alkanes and inert gases. It is gratifying and encouraging that an entirely different technique leads to essentially identical conclusions for the corresponding liquid-phase reactions.

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[15] Studies aimed at determining the intersystem crossing rate of $^1CH_2$ in solutions of chlorinated alkanes and inert diluents are now underway.

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X-Ray Determination of the Absolute Configuration of Metal Complexes in Quasiracemic Crystals. Λ-(−)$_{546}$-Cobalt(III) Acetylacetonate

Sir:

The number of dissymmetric metal complexes whose absolute configurations have been unambiguously established by X-ray methods is still quite small, and nearly all of the compounds studied to date are diamine complexes.[1] X-Ray studies of a wider variety of metal chelates are needed in order to test empirical spectroscopic criteria[2,3] for relating optical rotatory power and absolute configuration. We report here a simple X-ray method for determination of the absolute configuration of metal complexes in quasiracemic crystals and its application to Λ-(−)$_{546}$-cobalt(III) acetylacetonate.[4] The only other tris-β-diketonate complex

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