Table I. Optimum Pyramidilization Angle (β_{opt}), Stabilization Energy, SE = $[E(\alpha = \beta = 0) - E(\alpha = 0, \beta = \beta_{opt})]$, and Barrier to Rotation about the TiC Bond at $\beta = \beta_{opt}$, $\Delta E = [E(\alpha = 90°) - E(\alpha = 0°)]$, for Some L_2TiCH_2 Complexes

L	β_{opt}, deg	SE,[a] eV	ΔE, eV
H	75	0.26	−0.01
Cl	57.5	0.28	0.61
Cp	34	0.14[a]	1.57

[a] SE = E(Cp orientation 1, $\alpha = 0$, $\beta = \beta_{opt}$) − E(Cp orientation 2, $\alpha = \beta = 0$).

orbitals have exchanged roles: the σ-bond is formed from the $Ti_{d_{x^2-y^2}}$ orbital and the carbene σ frontier orbital, which is now composed mainly of the C_{2p_y} orbital, and the $Ti_{d_{z^2}}$ orbital assumes the role of a low-lying, unoccupied, nonbonding orbital. A π-bond is again formed from the $Ti_{d_{yz}}$ orbital and the carbene π frontier orbital, but now the front, or rear, lobes, rather than the right-hand lobes, of the $Ti_{d_{yz}}$ orbital are used and the carbene π frontier orbital has become the C_{2p_z} orbital.

Several fascinating possibilities arise including that (1) the complex gradually becomes less stable as β increases so that this distortion corresponds to a soft vibrational mode, (2) the complex is less stable at intermediate angles, $0 < \beta < 90°$, and geometries I and III correspond to two minima on the potential surface that are separated by an energy barrier, and (3) the complex is more stable at intermediate angles and the equilibrium geometry is a nonclassical, nonplanar structure pyramidal at the metal center. Provided the barrier in (2) is low, these three possibilities are consistent with the known chemistry of related compounds.[6] The equilibrium structure anticipated in (3) is similar to that predicted for the alkyl Cp_2TiR[7c] and leaves one side of the metal atom readily accessible to an incoming donor.

In order to investigate these possibilities further, we used the extended Hückel (EH) molecular orbital method[7] to calculate potential energy curves for pyramidilization at the metal center. The curves obtained for the carbenes L_2TiCH_2, L = H, Cl, and Cp, are shown in Figure 1. They favor the third possibility above, but the first two cannot be ruled out on the basis of EH results alone. However, our results appear to constitute evidence that in these systems pyramidilization at the metal center is at least a soft vibrational mode.[8]

The optimum pyramidilization angles, stabilization energies, and barriers to rotation about the TiC bond at the optimum pyramidilization angles are presented in Table I. That the rotational barrier for the hydride is slightly negative suggests that the equilibrium structure for this system is one in which the metal and carbene fragment planes are not only skew, but also perpendicular. We have computed the barriers to rotation about the TiC bond for conformers I and III also. In H_2TiCH_2 and Cl_2-$TiCH_2$ they correlate well with the relative energies of the lig-and–split metal orbitals from which the TiC π-bond is formed. In Cp_2TiCH_2 pyramidilization is complicated by steric interactions
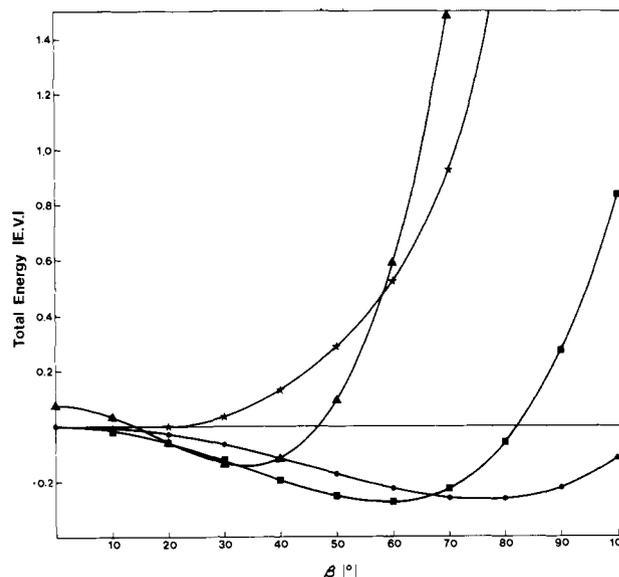

Figure 1. Total energy of transition-metal carbene L_2TiCH_2 as a function of β: (●) L = H; (■) L = Cl; (▲) L = Cp, Cp orientation 1; (☆) L = Cp, Cp orientation 2. For the first, second, and fourth, $\beta = 0$ is taken as the zero of energy; for the third, Cp orientation 2, $\beta = 0$ is taken as the zero of energy.

between the methylene fragment and the Cp rings. These soon become severe if, as we have done, β is varied while the rings are held fixed. Additional stabilization might be expected if the rings are allowed to rotate about the normals to them as β is varied.

Walsh orbital correlation diagrams indicate that pyramidilization at the metal center should be much harder in the corresponding d^3 and d^4 complexes and that these complexes should have the classical "planar" structure.

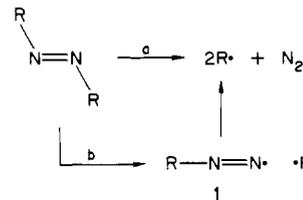A full account of this work will be presented elsewhere.

Direct Studies of Photodissociation of Azomethane Vapor Using Transient CARS Spectroscopy

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A central and persistent question in azoalkane chemistry involves the mechanism of primary bond cleavage: do the two C–N bonds break in a synchronous (a) or a sequential (b) fashion?[1,2]

$$
\begin{array}{c}
R \\
\backslash \\
N{=}N \xrightarrow{\quad a \quad} 2R\cdot \; + \; N_2 \\
/ \\
R
\end{array}
$$

$$\xrightarrow{\quad b \quad} R{-}N{=}N\cdot \quad \cdot R$$

$$\mathbf{1}$$

A sequential mechanism implies a diazenyl radical intermediate

(6) E.g., (a) the ready dimerization of $Cp_2ZrCH(CH_2CMe_3)$ (b) the facile addition of acetylenes to $Cp_2Ti{=}CH_2$, and (c) the low activation energy for olefin metathesis of $Cp_2TiCH_2CH_2CH_2$. (a) Hartner, W. H.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640. (b) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coalbaugh, T. S.; Tebbe, F. N. *J. Am. Chem. Soc.* **1981**, *103*, 5584. Tebbe, F. N.; Harlow, R. S. *J. Am. Chem. Soc.* **1980**, *102*, 6151. (c) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7419.

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(8) Hehre (Hehre, W. J., personal communication, Aug 27, 1984) has informed us that "a normal mode analysis carried out on the STO-3G structure of planar $H_2Ti{=}CH_2$[5b,c] confirms that it is a minima on the overall potential energy surface."

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Communications to the Editor

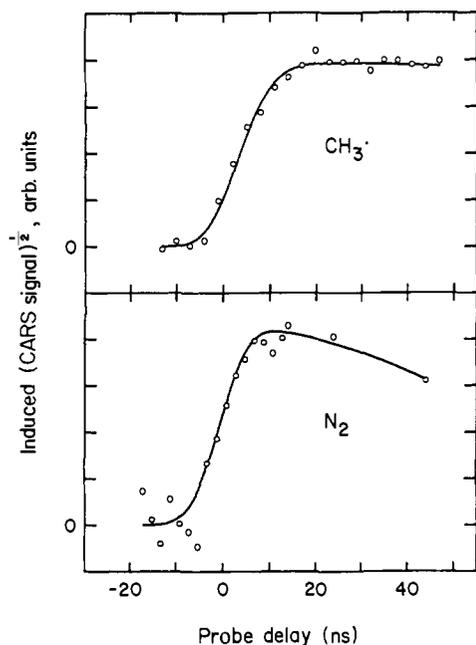*J. Am. Chem. Soc., Vol. 107, No. 7, 1985* 2181

Figure 1. Appearance kinetics of the photoproducts of azomethane. (Top) Circles show methyl concentrations measured at a 3004-cm^{-1} Raman frequency in a sample of 11 torr of azomethane plus 410 torr of SF$_6$. The solid curve is a kinetic fit based on the instrumental function and a 4-ns rise time representing thermalization. (Bottom) Circles show N$_2$ ($v = 0$) concentrations measured at 2328 cm^{-1} in 6 torr of azomethane plus 200 torr of He. The rise of the solid curve was computed from the instrumental function only, with no resolvable molecular rise time.

(1) whereas a synchronous reaction requires that alkyl radicals and N$_2$ be formed directly and at the same rate. In this paper we report the results of kinetic vibrational spectroscopy of the photofragments formed from azomethane (CH$_3$N=NCH$_3$), the simplest stable azoalkane.[3] We find that fragmentation is complete within 2 ns and that the nascent N$_2$ vibrational distribution appears consistent with a theoretical prediction of sequential bond cleavage.

Our experimental method uses coherent anti-Stokes Raman spectroscopy (CARS) as a probe of transient species.[4] A static sample of azomethane vapor is first irradiated by a 355-nm photolyzing laser pulse. Then, after a variable delay, a separate analyzing laser system probes the CARS susceptibility of the excited sample volume. Excitation and probing beams are derived from Q-switched Nd:YAG-based laser systems that provide a time profile of ca. 7 ns and a spectral resolution of 1 cm^{-1}. Computer control is used to obtain CARS spectra at fixed probe delays as well as kinetic scans at fixed Raman frequencies. A full description of our apparatus and data processing methods will be reported separately.[5]

Both photoproducts of azomethane are detectable by their Raman-active vibrations: N$_2$ appears near 2330 cm^{-1} as the Q branch of its fundamental transition, whereas the methyl radical is seen near 3004 cm^{-1} in its recently uncovered symmetric C–H stretching band, ν_1.[6] We have performed kinetic scans at these frequencies to measure the appearance rates of both species. Figure 1 (top) shows the data obtained for methyl in the presence of SF$_6$, which was added to relax the substantial excess vibrational

Figure 2. CARS spectrum of the nascent vibrational distribution of N$_2$ photoproduct. The circles are data obtained at delays of <20 ns in a sample of 7 torr of azomethane plus 200 torr of He. The solid curves show computed spectral fits based on the known spectroscopic constants of N$_2$ and adjusted resonant and nonresonant components.

energy of the nascent radicals. The solid line is a fit computed as the convolution of our instrument's response function with a methyl rise time of ~4 ns. In Figure 1 (bottom) we show the growth of the N$_2$ $v = 0 \rightarrow 1$ signal when helium is present to thermalize the rotational motion. The computed best fit for nitrogen implies a prompt (<2 ns) appearance time.

Vibrational anharmonicity in N$_2$ is large enough that the strong Q branches of its $v = 0 \rightarrow 1$, $v = 1 \rightarrow 2$, ... bands are easily distinguishable. By scanning this region of the CARS spectrum at early delays after excitation, we have determined the nascent vibrational distribution of the N$_2$ photoproduct. Figure 2 shows these data, from which the following distribution is computed: 84 ± 3% in $v = 0$, 16 ± 2% in $v = 1$, and <3% in $v > 1$. We have also obtained higher resolution spectra of the $v = 0$ band at early delays in the absence of helium buffer gas which indicate a rotational distribution corresponding to a temperature near 425 K.

Because we find that nitrogen as well as methyl radicals are both formed promptly after excitation of azomethane to its lowest $^1(n,\pi^*)$ state, it is clear that the reaction mechanism involves no diazenyl intermediate having a lifetime longer than 2 ns. Still, the question remains as to whether dissociation is stepwise with a short-lived intermediate or truly synchronous. There is a long-standing prediction that the large change in N–N separation from reactant (1.25 Å) to product (1.10 Å) will cause substantial N$_2$ vibrational excitation in the synchronous case.[7] However, we suggest that product excitation is better predicted by three factors: the change in N–N separation from transition state to product, the internal energy available at the transition state, and impulsive force effects in the exit channel. From the few detailed studies of other ground-state dissociations,[8,9] we expect the first two of these to dominate. Theoretical calculations on azomethane predict sequential dissociation involving a second transition state having an N–N distance of only 1.115 Å.[2d,10] This separation would allow little "Franck–Condon" excitation of the nitrogen, in contrast to the H$_2$ formed from formaldehyde.[8,11] Our data show the vibrational and rotational energy contents of the N$_2$ to be only ~400 and ~300 cm^{-1}, out of 16 800 cm^{-1} of total fragment energy.[12]

In summary, we view the photodissociation of *trans*-azomethane as proceeding through high levels of the ground electronic surface

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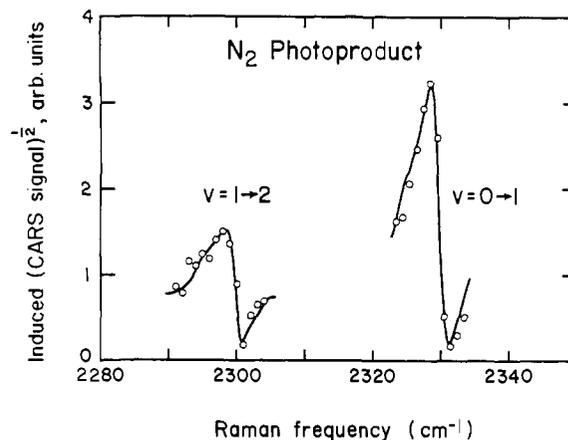
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(12) Decomposition of azomethane to two methyl radicals plus N$_2$ is endothermic[1] by 32.5 kcal/mol. Substracting this value from the 80.5 kcal/mol energy of 355-nm photons gives the energy available to the fragments.

formed by rapid (10^{-11} s) $S_1 \rightarrow S_0$ internal conversion.[13] These energized S_0^* molecules, which interconvert freely between trans and cis forms, dissociate fully in less than 2 ns through a process believed to involve a short-lived but real diazenyl intermediate.[2d,10,14,15] This view may be confirmed by a quantitative theoretical interpretation of the product state distribution or by further experimental studies of the methyl energetics and of related azoalkanes.

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Mechanisms of Phenylacetylene Polymerization by Molybdenum and Titanium Initiators

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We are reporting that while phenylacetylene, a few of whose molecules are doubly labeled by ^{13}C's on the triple bond, is polymerized by some catalysts including titanium tetrabutoxide plus triethylaluminum to give poly(phenylacetylene) in which the labels are separated by a double bond (eq 1), when the initiator is molybdenum pentachloride plus tetraphenyltin, the labels are separated by a single bond (eq 2). This tallies with the idea that
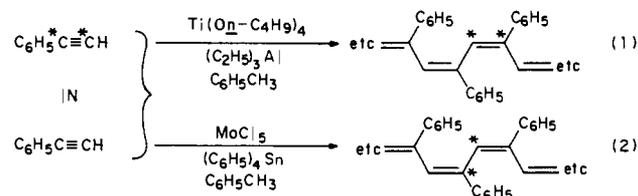
derivatives of molybdenum are effective initiators of both olefin metatheses[1,2] and acetylene polymerizations,[3,4] not by coincidence, but because the acetylene polymerizations they induce *are* olefin metatheses (eq 3).[5,6] In contrast, the titanium-initiated acetylene
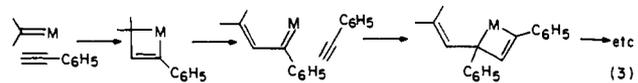
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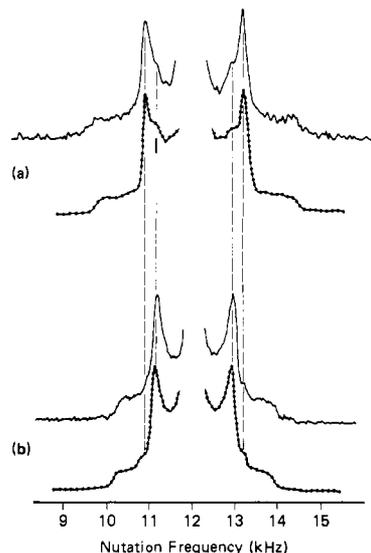
Figure 1. ^{13}C NMR nutation spectra of poly(phenylacetylene) at 77 K. (a) Sample prepared according to eq 1. The cross-polarization time was 0.5 ms and the recycle time 1 s. The number of scans was 144 000. (b) Sample prepared according to eq 2. The cross-polarization time was 1.0 ms and the recycle time 0.5 s. The number of scans was 115 200. The dotted curves are simulated spectra, calculated as described in the text. The center peaks, due to isolated ^{13}C nuclei, have been cropped for clarity. The inner and outer pairs of dashed lines mark, respectively, the peaks of curves arising from ^{13}C's separated by single and double bonds.

polymerizations—both the one reported here and one reported earlier, in which titanium tetrabutoxide plus triethylaluminum polymerized unsubstituted acetylene[7]—seem to follow an insertion mechanism like that believed to apply to the titanium-catalyzed polymerization of ethylene.[8]

Whether the labeled carbons are separated in the polymers by single or by double bonds was analyzed by nutation NMR spectroscopy.[7,9] Thus the spectra displayed in Figure 1 exhibit Pake doublets, produced by the dipole–dipole interaction of adjacent ^{13}C nuclei, that are coincidence, by 2196 Hz in a sample prepared with the titanium catalyst and by 1765 Hz in one prepared with the molybdenum catalyst. The best theoretical simulations, also displayed in the figure, correspond in the first sample to 91% of the carbons being separated by 1.36 Å and 9% by 1.48 Å. In the second sample (made with the molybdenum catalyst), the analysis is optimized if 88% of the carbons are separated by 1.48 Å and 12% by 1.36 Å. The only parameters in the theoretical simulations are the two bond lengths, the fraction of the bonds having these lengths, and a natural width (75 Hz) for lines assumed to be Lorentzian.[9] The accuracy of the nutation method and fitting procedure is demonstrated by the measured C–C length for acetic acid agreeing with X-ray diffraction measurements within 0.7%,[9] by the C≡C length in phenylacetylene agreeing with microwave measurements within 1.8%,[10] and by the single- and double-bond lengths analyzed above agreeing with those (averaging 1.47 ± 0.01 and 1.35 ± 0.01 Å) determined for a variety of polyenes.[11]

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