

**Figure 1.**  $^1\text{H}$  NMR spectra, 300 MHz, of  $\text{Cu}_2\text{Co}_2\text{SOD}$  in  $\text{H}_2\text{O}$  (spectra A at 30 °C and C at 40 °C) and  $\text{D}_2\text{O}$  (spectra B at 30 °C and D at 40 °C) solutions at pH (or  $\text{pH}^*$ ) 5.5.

magnetically coupled to copper(II) could be estimated from the above spectra to be above 95%, since no signal from  $\text{E}_2\text{Co}_2\text{SOD}$  species could be detected. The  $\text{Cu}_2\text{Co}_2\text{SOD}$  derivative was prepared by addition of solid sodium dithionite under helium atmosphere until the copper(II) d-d band disappeared.

The 300-MHz  $^1\text{H}$  NMR spectrum of  $\text{Cu}_2\text{Co}_2\text{SOD}$  in water solution at pH 5.5 and 30 °C is reported in Figure 1 (spectrum A); the downfield region of the spectrum at 40 °C is also shown (spectrum C). The spectra show at least nine isotropically shifted signals (labeled a-i) which can be straightforwardly assigned to residues coordinated to the cobalt(II) chromophore. With the likely exception of the upfield signals h and i the resonances are in positions typical of ring protons of coordinated histidines.<sup>14-17</sup> In the native enzyme the zinc ion is coordinated to N1 of His-69, of His-78, and of the bridging histidinato 61 ion. If the latter residue is still coordinated to cobalt(II) but not to copper(I) it should bear an exchangeable proton on the N3 nitrogen analogously to the other two coordinated histidines. Therefore three signals are expected to disappear upon deuteration of the sample.

$\text{Cu}_2\text{Co}_2\text{SOD}$  samples that are 95% deuterated give rise to spectra B and D at 30 and 40 °C, respectively. Indeed, it appears that signals a, c, and f are lost almost completely upon deuteration, while the rest of the spectrum (including signals i and h, not shown) is the same, although the signals are somewhat broader. This is to us a definite proof that the imidazolato bridge is broken on the copper(I) side, leaving His-61 regularly coordinated to the cobalt(II) ion. Owing to the close similarity of  $\text{Cu}_2\text{Co}_2\text{SOD}$  to  $\text{Cu}_2\text{Zn}_2\text{SOD}$  even with respect to the catalytic properties,<sup>4</sup> this conclusion can be confidently extended to the native enzyme, thus settling an important issue in the overall knowledge of the system.

As a final comment, we can assign signals b, d, and e, which are of line widths comparable to or smaller than the NH signals, to the metalike protons of the three histidines coordinated to cobalt(II). Signal g is definitely broader and can possibly be assigned to one of the ortholike protons, whereas the other two may be below the c,d,e group or broad beyond detection. Finally, in analogy with other cobalt(II)-substituted proteins containing histidines coordinated through N1, signals h and i can be assigned to two of the  $\beta$ -methylene protons.

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periment. The 300-MHz  $^1\text{H}$  NMR spectra were recorded at the High Field NMR Service Center, CNR, Bologna, superbly run by Prof. L. Lunazzi; technical assistance of D. Macciantelli is gratefully acknowledged.

## Early Transition-Metal Carbene Complexes $\text{L}_2\text{M}=\text{CH}_2$ : Equilibrium Structures and Rotational Barriers

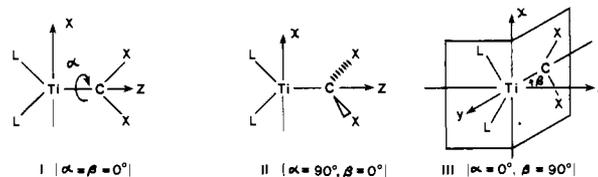
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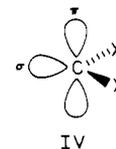
In the course of an ongoing experimental and theoretical investigation, which has the synthesis and characterization of hybrid Fischer-Schrock<sup>2</sup> complexes as its ultimate goal, we have obtained theoretical results which predict that some early transition-metal carbene complexes have novel structures. In particular, we have been investigating the structures of a number of  $d^2$  complexes of the type  $\text{L}_2\text{TiC(X)H}$  and  $\text{L}_2\text{TiCX}_2$ , where  $\text{L} = \text{H}, \text{Cl}$ , and  $\eta^5$ -cyclopentadienyl (Cp) and  $\text{X} = \text{H}, \text{OH}$ , and  $\text{SH}$ , with a view to understanding the nucleophilicity of an alkylidene carbon coordinated to an electron-poor metal atom<sup>2</sup> and how it might be adjusted for synthetic advantage.<sup>3,4</sup>

Theoretical studies of some of these complexes have been reported,<sup>5</sup> but to date only the familiar "planar", I, and



"perpendicular", II, conformers have been investigated. Limiting geometrical studies to these conformers has the effect of constraining the carbene carbon atom to lie in the plane of the  $\text{L}_2\text{Ti}$  fragment. However, the directional properties of the metal d orbitals are such that a geometry III, with the planes of the metal and carbene fragments vertical and intersecting at 90° along the x axis, affords the opportunity for the formation of  $\sigma$ - and  $\pi$ -bonds that are as strong, in a first approximation, as those formed in the "planar" geometry, I.

In geometry I, the  $\sigma$ -bond is formed from the metal  $d_{z^2}$  orbital and the  $\sigma$  frontier orbital of the carbene fragment (IV), which



is composed mainly of the  $\text{C}_{2p_z}$  orbital. The  $\pi$ -bond is formed from the metal  $d_{yz}$  orbital and the  $\pi$  ( $2p_y$ ) frontier orbital of the carbene fragment. The metal  $d_{x^2-y^2}$  orbital is left unused as a low-lying nonbonding orbital. In geometry III, the metal  $d_{x^2-y^2}$  and  $d_{z^2}$

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

L	$\beta_{\text{opt}}$ , deg	SE, <sup>a</sup> eV	$\Delta E$ , eV
H	75	0.26	-0.01
Cl	57.5	0.28	0.61
Cp	34	0.14 <sup>a</sup>	1.57

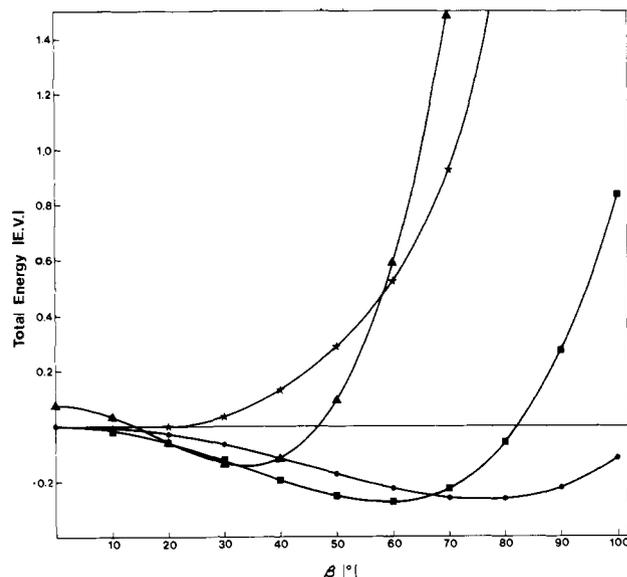
<sup>a</sup>SE =  $E(\text{Cp orientation 1}, \alpha = 0, \beta = \beta_{\text{opt}}) - E(\text{Cp orientation 2}, \alpha = \beta = 0)$ .

orbitals have exchanged roles: the  $\sigma$ -bond is formed from the  $Ti_{d_{2z}}$  orbital and the carbene  $\sigma$  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  $\pi$ -bond is again formed from the  $Ti_{d_{yz}}$  orbital and the carbene  $\pi$  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  $\pi$  frontier orbital has become the  $C_{2p_x}$  orbital.

Several fascinating possibilities arise including that (1) the complex gradually becomes less stable as  $\beta$  increases so that this distortion corresponds to a soft vibrational mode, (2) the complex is less stable at intermediate angles,  $0 < \beta < 90^\circ$ , 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.<sup>6</sup> The equilibrium structure anticipated in (3) is similar to that predicted for the alkyl  $Cp_2TiR^c$  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 Huckel (EH) molecular orbital method<sup>7</sup> 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.<sup>8</sup>

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  $Cl_2TiCH_2$  they correlate well with the relative energies of the ligand-split metal orbitals from which the TiC  $\pi$ -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  $\beta$ : (●)  $L = H$ ; (■)  $L = Cl$ ; (▲)  $L = Cp$ , 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,  $\beta$  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  $\beta$  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.

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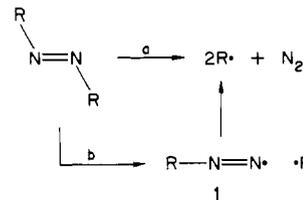
## Direct Studies of Photodissociation of Azomethane Vapor Using Transient CARS Spectroscopy

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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?<sup>1,2</sup>



A sequential mechanism implies a diazenyl radical intermediate

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(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  $H_2Ti=CH_2$ <sup>5bc</sup> confirms that it is a minima on the overall potential energy surface."