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## Dichlorotitanacyclopropane. The Structure and Reactivity of a Metallacyclopropane<sup>†</sup>

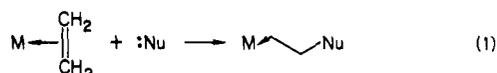
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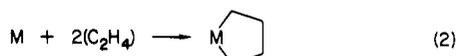
**Abstract:** We have studied the electronic structure of  $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4)$  and found wave functions describing both the metallacyclopropane and  $\pi$ -complex forms. The metallacyclopropane form is lower in energy than the  $\pi$ -complex form at all geometries we investigated. We show that the three-membered ring is strained and that simple  $2_s + 2_s$  reactions of the Ti-C bonds can relieve this strain. The ability of the metallacycle to undergo these pericyclic reactions sets it apart from the simple acid-base  $\pi$ -complex.

### I. Introduction

The chemistry of the enormous number of transition-metal olefin complexes reported in the literature is quite varied.<sup>1</sup> For example, in some cases transition metals are known to activate olefins toward nucleophilic attack (eq 1),<sup>2</sup>

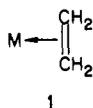


while in other systems, oxidative cycloaddition (eq 2)

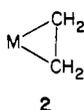


occurs.<sup>3</sup> It is the case that metal systems that facilitate reaction 1 do not facilitate reaction 2 and vice versa.

In an attempt to determine the electronic reason for the different reactivities of various metal-olefin complexes, we were led to examine whether a given metal-olefin complex should be regarded (i) as a  $\pi$ -complex (1)



that is, an acid/base complex with donation of the C-C  $\pi$ -bonding electrons onto the metal supplemented by backbonding of the metal  $d\pi$  electron pair into the antibonding orbital of the olefin  $\pi$  bond; or (ii) as a metallacyclopropane (2)

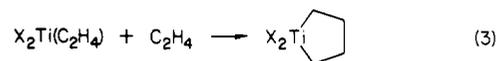


having two metal-carbon  $\sigma$  bonds and only a single carbon-carbon bond.<sup>4</sup>

We have concluded that *some* metal-olefin complexes should be viewed as 1 and others should be viewed as 2, and most importantly those species that are best described by 1 will show reactivity as in (1), and species that are described as 2 will show reactivity as in (2). We suggest that whether a complex has the form of 1 or 2 depends upon the metal, its oxidation state, the nature of the auxiliary ligands around the metal, and the nature of the olefin. This suggests strategies that one might use in designing systems that will show one type of reactivity in contrast to another.

### II. Results and Discussion

**A. Structure of a Metallacyclopropane.** Complexes of the form  $\text{X}_2\text{Ti}(\text{C}_2\text{H}_4)$  (X = anion ligand such as  $\eta^5$ -cyclopentadienyl) have been reported to react with added olefin to give titanacyclopentanes (eq 3).<sup>5</sup> Inasmuch as the predominance of this mode of reactivity



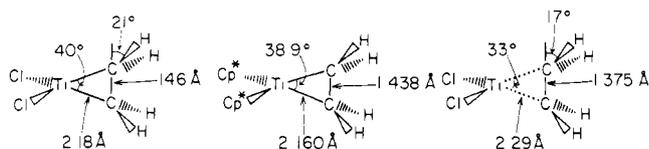
(1) (a) H. Alper, Ed. "Transition Metal Organometallic Chemistry in Organic Synthesis", Academic Press, New York, 1976, Vol. 1. (b) M. L. H. Green, "Organometallic Compounds. The Transition Elements", Chapman and Hall, London, 1968, Vol. 1, Chapter 1. (c) S. D. Ittel and J. A. Ibers, *Adv. Organomet. Chem.*, **14**, 33 (1976). (d) G. Henrici-Olivé and S. Olivé, "Coordination and Catalysis", Verlag Chemie, Weinheim, 1977. (e) J. P. Collman and L. S. Hegeudus, "Principles and Applications of Organotransition Metal Chemistry", University Science Books, Mill Valley, CA, 1980, Chapter 3.

(2) See, for example, ref 1c, Chapter 12, and references therein.

(3) (a) R. R. Schrock, S. McLain, and J. Sancho, *Pure Appl. Chem.*, **52**, 729 (1980). (b) G. Erber and K. Kropp, *J. Am. Chem. Soc.*, **101**, 3659 (1979). (c) D. R. McAlister, D. K. Erwin, and J. E. Bercaw, *Ibid.*, **100**, 5966 (1978). (d) A. P. Fraser, P. H. Bird, S. A. Bezman, J. R. Shapley, R. White, and J. A. Osborn, *Ibid.*, **95**, 597 (1973). (e) J. X. McDermott, M. E. Wilson, and G. M. Whitesides, *Ibid.*, **98**, 6529 (1976).

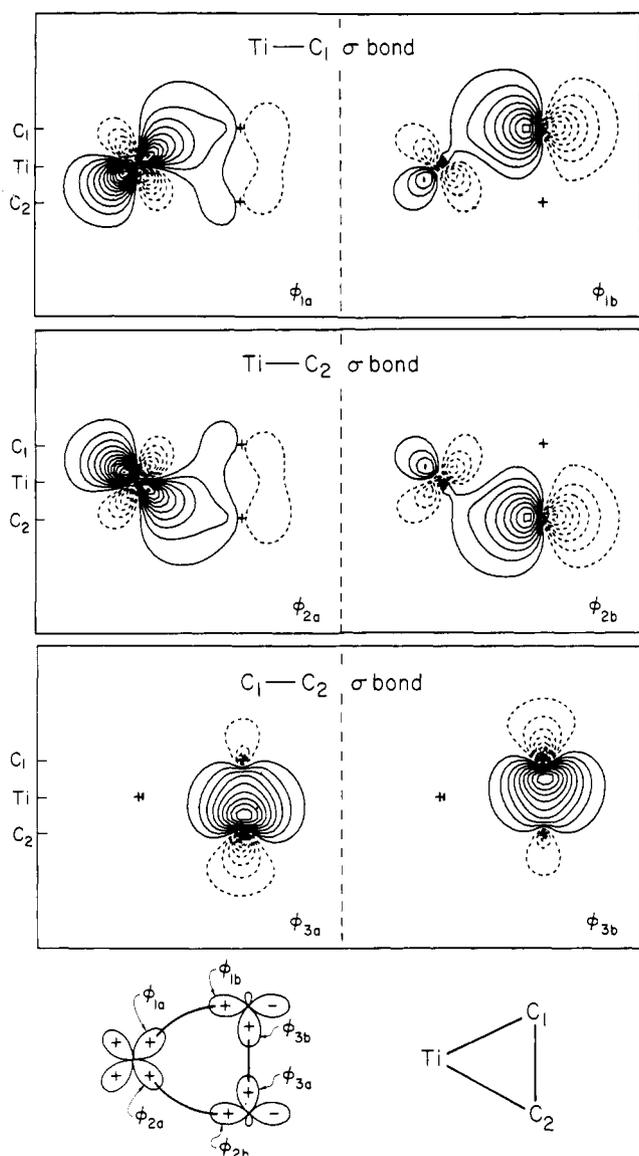
(4) The question of  $\pi$  complex vs. metallacycle is not a new one. See: (a) M. J. S. Dewar and G. P. Ford, *J. Am. Chem. Soc.*, **101**, 783 (1979). (b) T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *Ibid.*, **101**, 3801 (1979). (c) B. Åkermark, M. Almémarte, J. Almlöf, J.-E. Bäckvall, B. Roos, and Å. Stogå, *Ibid.*, **998** 4617 (1977).

<sup>†</sup>  $2_s + 2_s$  Reactions at Transition Metals. Part 3.



**Figure 1.** Calculated and observed geometries of complexes  $X_2Ti(C_2H_4)$ : (a) dichlorotitanacyclopropane (this work), (b)  $Cp_2^*Ti(C_2H_4)$  (ref 5b), (c) dichlorotitanium (ethylene) (this work).

#### Valence Bonds in Dichlorotitanacyclopropane



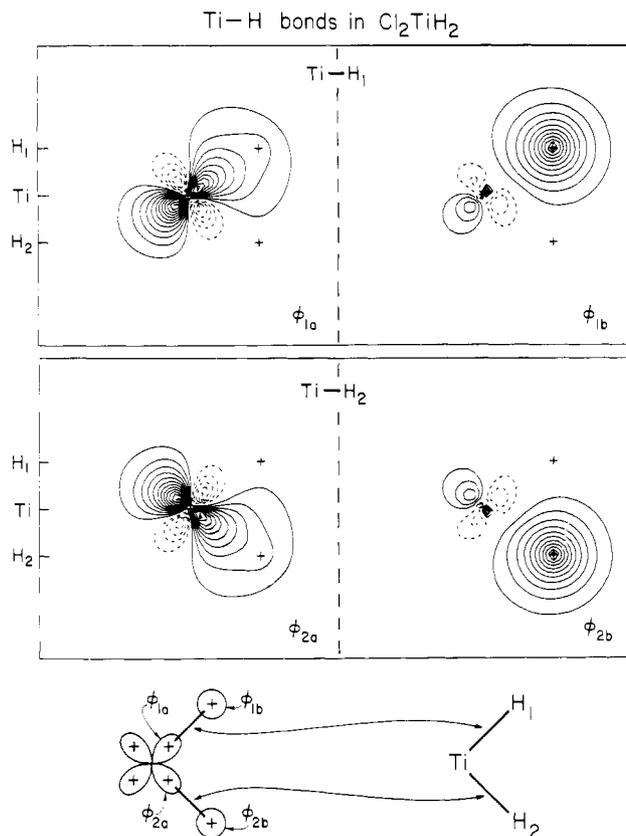
**Figure 2.** GVB orbitals describing the valence space of dichlorotitanacyclopropane. Spacing between contours is 0.05 au. The characteristic dimension of the plot is 6.0  $a_0$ .

over the others open to these olefins complexes is difficult to predict by using a simple acid/base model of the complexes 1,<sup>6</sup> we undertook the detailed investigation of their electronic structure. As a model we chose  $Cl_2Ti(C_2H_4)$  (3).

Using the procedure outlined in the Appendix [based on the generalized valence bond (GVB) method], we optimized the ge-

(5) (a) See ref 3e. (b) S. A. Cohen, P. R. Auburn, and J. E. Bercaw, *J. Am. Chem. Soc.*, **105**, 1136 (1983). (c) S. A. Cohen, Ph.D. Thesis, California Institute of Technology, 1982.

(6) See, however: (a) F. D. Mango and J. H. Schachtschneider, *J. Am. Chem. Soc.*, **93**, 1123 (1971). (b) R. G. Pearson, "Symmetry Rules for Chemical Reactions", Wiley-Interscience, New York, 1976, p 423. (c) J. W. Lauber and R. Hoffmann, *J. Am. Chem. Soc.*, **98**, 1729-1742 (1976).



**Figure 3.** Plots of the two Ti-H bonds in  $Cl_2TiH_2$  (ref 10). Spacing between contours is 0.05 au, and the characteristic dimension of the plots is 6.0  $a_0$ .

ometry of this complex. The resulting geometry is shown in Figure 1a. This calculated geometry should be compared with the structure of  $Cp_2^*Ti(C_2H_4)$  (4) recently determined by Cohen, Auburn, and Bercaw<sup>5b</sup> and shown in Figure 1b. The theory and experiment agree quite closely (disagreements of 0.02 Å in Ti-C and C-C bond lengths), indicating that the chlorine ligands in 3 are reasonable models for the Cp\* ligands in 4.<sup>7</sup>

We also optimized the geometry of  $Cl_2Ti(C_2H_4)$  using the Hartree-Fock (HF) method (the generalization of the molecular orbital method) and found the results shown in Figure 1c (5). This indicates that the electron correlation effects included in GVB<sup>8</sup> must be taken into account for an accurate description of systems such as 3.

The optimum valence bond orbitals for the Ti-C and C-C bonds of 3 are shown in Figure 2 where we see that the wave function has the form of a metallacycle, 2. Here bond 1 is a *bent* sigma bond between a d orbital on the titanium and a p orbital on the upper carbon. Similarly, bond 2 is a *bent* sigma bond between a second titanium d orbital and a p orbital on the lower carbon. Bond 3 is a *bent* sigma bond between the two carbons of the CH<sub>2</sub>CH<sub>2</sub> moiety. Thus the GVB wave function describes the electronics of a *strained* three-membered ring.<sup>9</sup> The strain in the ring is obvious from Figure 2 because of the C-Ti-C angle is seen to be 40° (both computationally and experimentally), but the angle between the

(7) Using  $[EA(X) + 1/R(M-X)] = \alpha(X)$  as a gauge of the propensity for X to form ionic bonds to M, and using  $R(Ti-Cp) = 2.08$  Å [G. Fachinetti, C. Floriani, F. Marchetti, and M. Mellini, *J. Chem. Soc., Dalton Trans.* 1398 (1978)],  $r(Ti-Cl) = 2.328$  Å (this work),  $EA(Cl) = 3.62$  eV [H. Hotop and W. C. Lineberger, *J. Phys. Chem. Ref. Data* **4**, 539 (1975)], and  $EA(C_2H_5) = 2.2$  eV [H. N. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *Ibid.*, **6**, 736 (1977)], one sees that  $\alpha(Cl) = 9.8$  eV and  $\alpha(Cp) = 9.1$  eV. Thus the tendency of Cp and Cl to form ionic bonds is similar, and the gross features of the electronic structure of metal complexes with these ligands should be similar.

(8) W. A. Goddard III, T. J. Dunning, Jr., W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368-376 (1973).

(9) S. W. Benson, "Thermochemical Kinetics", Wiley-Interscience, New York, 1976, 2nd ed., p 60.

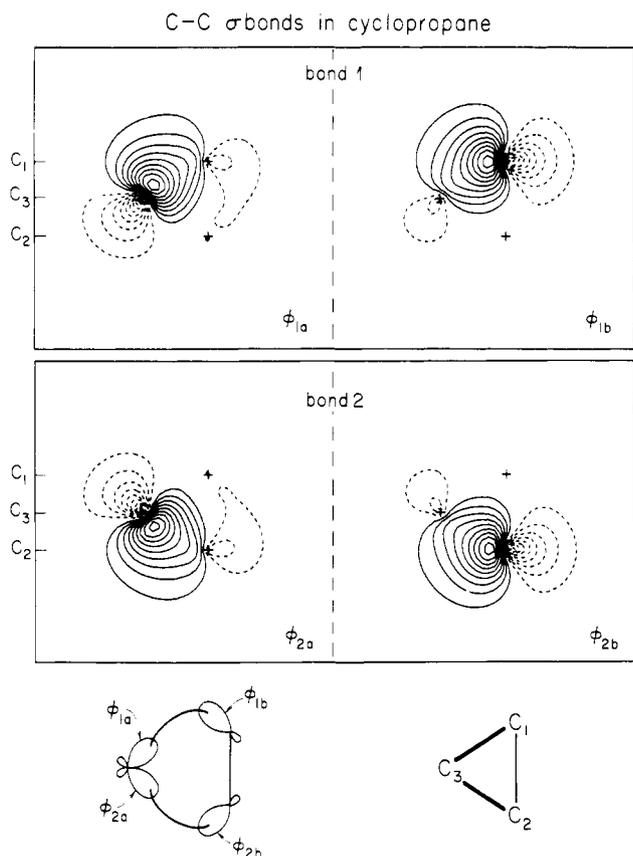
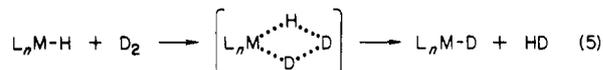


Figure 4. Plots of two of the C-C bonds in cyclopropane.

two bonding orbitals on Ti ( $\varphi_{1a}$  and  $\varphi_{2a}$  in Figure 2) is  $75^\circ$ .<sup>10</sup> This situation should be compared with our observation that in the unstrained system ( $\text{Cl}_2\text{TiH}_2$ , **6**), the H-Ti-H angle is  $75^\circ$ , and the angle between the two Ti-centered bonding orbitals ( $\varphi_{1a}$  and  $\varphi_{2a}$  in Figure 3) is also  $75^\circ$ . The orbitals of Figure 2 should also be compared with the C-C bond orbitals from cyclopropane (Figure 4). Here the C-C-C bond angle is  $60^\circ$ , but the angle between the two bonding orbitals at the same carbon is  $100^\circ$ .<sup>11</sup> Our conclusion is that the  $\text{Ti}(\text{C}_2\text{H}_4)$  complexes (**3** and **4**) are *metallacyclopropanes*, not  $\pi$ -complexes.

**B. Reactivity of a Metallacyclopropane.** The distinction of an acid-base  $\pi$ -complex **1** from a metallacyclopropane **2** is not significant in a practical way unless one can see a clear difference in the reactivities of the two different forms. The question then is, what reactivity is expected from the dichlorotitanacyclopropane?

Recently we have examined exchange reactions of  $\text{H}_2$  with several metal-hydrogen bonds<sup>12</sup> (eq 4) and found that the concerted, suprafacial  $2 + 2$  reaction shown in eq 5 is allowed (that



is, it has a low activation barrier) if (1) the M-H bond is covalent (little or no charge transfer to the hydrogen or to the metal) and if (2) the metal half of this covalent bond is predominantly d in character. The reason that this pericyclic  $2_s + 2_s$  reaction leads to a low activation energy (i.e., is characterized by strong bonding in the transition state) is that the metal d orbital has a pattern of nodes that allows both of the active bonds to be *retained* at the transition state of the reaction. With regard to this nodal

(10) A. K. Rappé and W. A. Goddard III, *J. Am. Chem. Soc.*, **104**, 297 (1982).

(11) This angle is measured from the plots shown in Figure 6 and is the angle between the lines of maximum amplitude of the two orbitals on the same center.

(12) M. L. Steigerwald and W. A. Goddard III, *J. Am. Chem. Soc.*, **106**, 308 (1984).

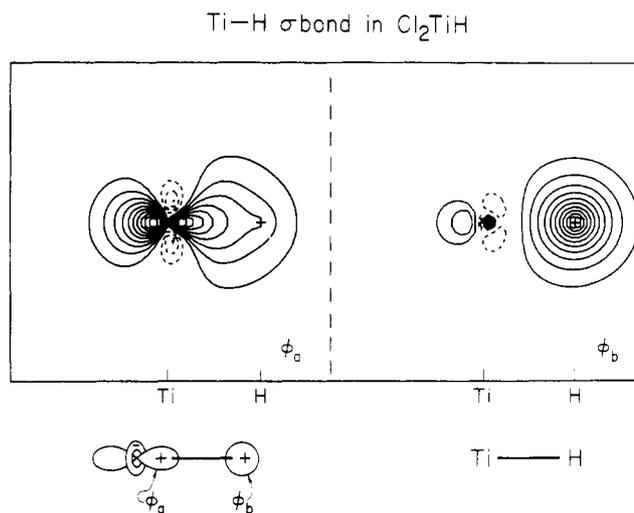


Figure 5. GVB orbitals describing the Ti-H bond in  $\text{Cl}_2\text{TiH}$ .

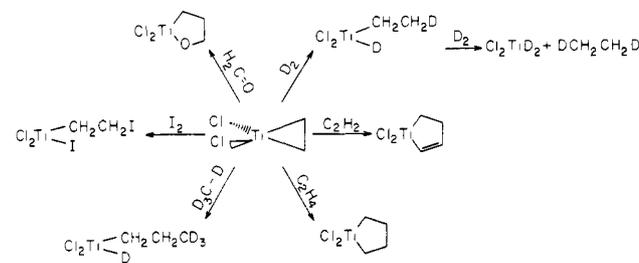


Figure 6. Expected reactions of dichlorotitanacyclopropane.

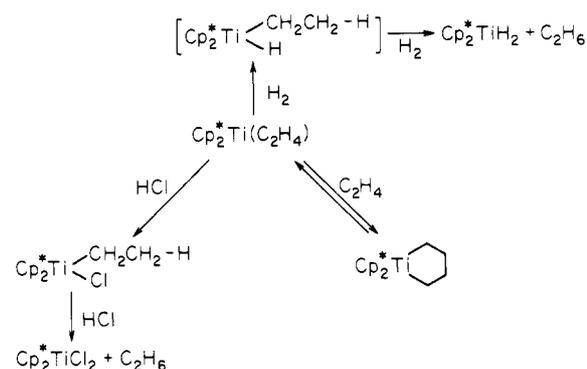
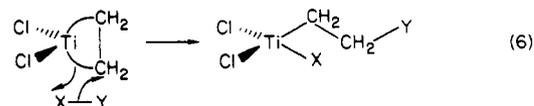


Figure 7. Observed reactions of  $\text{Cp}_2^*\text{Ti}(\text{C}_2\text{H}_4)$  (ref 5b).

pattern, there is no difference between. for example, the Ti-H bond in  $\text{Cl}_2\text{TiH}$  (see Figure 5) and the Ti-C bond shown in Figure 2. The electronic structure of the titanacyclopropane and our studies of the  $2 + 2$  reactions at metals, when taken together, suggest that **3** should undergo reactions as outlined in eq 6, where XY is some nonpolar reagent. Examples of this expected re-



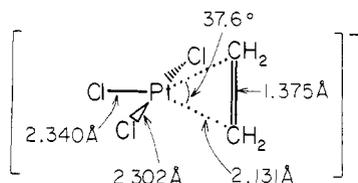
activity are shown in Figure 6 (assuming favorable heats of reaction). Several of these reactions have been observed by Cohen and Bercaw in the  $\text{Cp}_2^*\text{Ti}(\text{C}_2\text{H}_4)$  system<sup>5b,c</sup> (Figure 7). This agreement between the chemistry expected of a metallacyclopropane and that found for **4** confirms that *these  $\text{Ti}(\text{C}_2\text{H}_4)$  complexes are metallacyclopropanes*.

**C. The Titanium-Olefin  $\pi$ -Complex.** In the above sections we argue that  $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4)$  and  $\text{Cp}_2^*\text{Ti}(\text{C}_2\text{H}_4)$  should be viewed as titanacyclopropanes. We next must consider whether this form is significantly different from that of the classical  $\pi$ -complex.<sup>13</sup> In order to explore this issue, we *restricted* the GVB calculations so that there would be two bonds between the carbon atoms (as

**Table I.** Total Energies for  $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4)^a$ 

level of calculation	geometry				$\Delta E_R^b$ (kcal/mol)
	1a		1c		
	metallacycle	$\pi$ -complex	metallacycle	$\pi$ -complex	
GVB-PP(3/6)	-1844.48314	-1844.45670	-1844.47708	-1844.46380	12.1
GVB-CI	-1844.50897	-1844.48006	-1844.50229	-1844.48531	14.8

<sup>a</sup>Except for  $\Delta E_R$ , all energies are in hartrees. <sup>b</sup> $\Delta E_R = E(\text{metallacycle at geometry 1a}) - E(\pi\text{-complex at geometry 1c})$ .

**Figure 8.** Structure of Zeise's salt (ref 14).

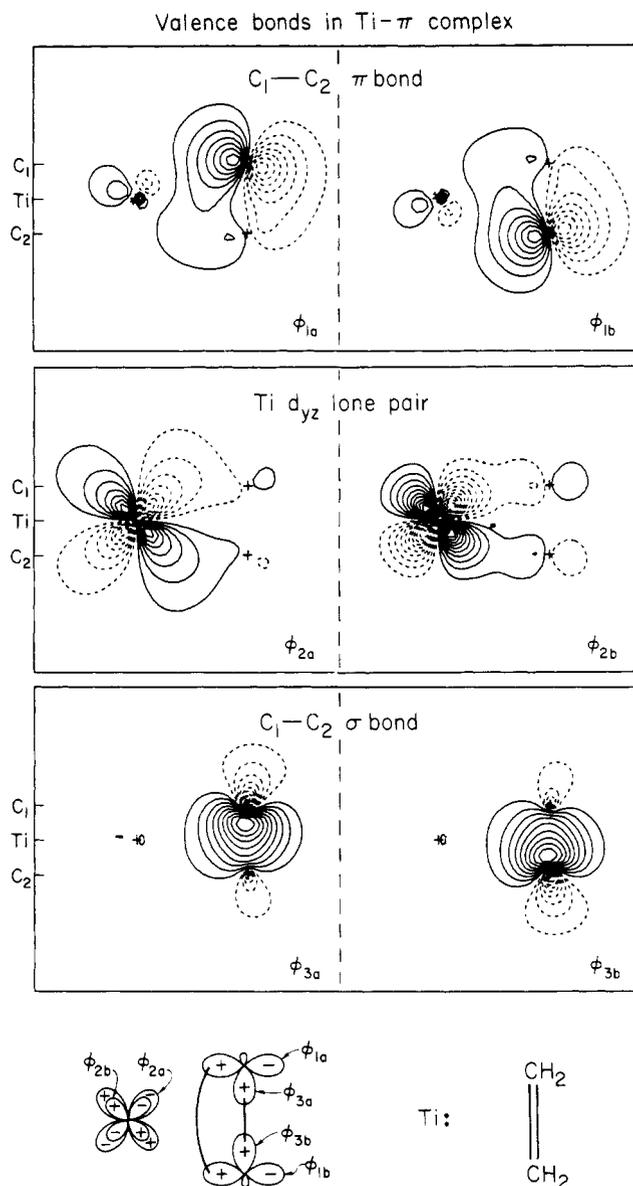
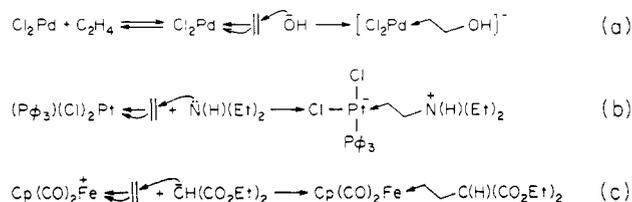
in the free olefin) and a lone pair of electrons occupying a d orbital on the metal having the proper symmetry to donate from the metal to the  $\pi^*$  system of the olefin. The geometry preferred for this "Dewar-Chart-Duncanson"-type complex is that of Figure 1c. As would be expected, the  $\pi$ -complex **1** has a shorter C-C bond and a longer TiC bond than does the metallacycle **2** (compare parts a and c in Figure 1). In fact, the C-C bond length in the  $\pi$ -complex form (Figure 1c) is quite close to the C-C bond length in Zeise's salt<sup>14</sup> (Figure 8), long considered as a typical  $\pi$ -complex.

In Table I we report local energies of both the metallacyclopropane and  $\pi$ -complex forms of  $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4)$ . At two different levels of calculation it is apparent that the metallacyclo form is significantly lower in energy than the  $\pi$ -complex form. This further substantiates our claim that **4** and  $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4)$  are best viewed as metallacycles.

**D. The Reactivity of a  $\pi$ -Complex.** The optimized GVB orbitals describing the  $\pi$ -complex are shown in Figure 9. Pair 1 ( $\phi_{1a}$  and  $\phi_{1b}$ ) shows a basic C-C  $\pi$  bond delocalized onto the acidic metal, and pair 2 ( $\phi_{2a}$  and  $\phi_{2b}$ ) shows the delocalization of the basic doubly occupied Ti d orbital into the acidic  $\pi^*$  orbital of the olefin. Pair 3 ( $\phi_{3a}$  and  $\phi_{3b}$ ) shows the C-C  $\sigma$  bond that has been distorted by the acid-base bonds of pairs 1 and 2. Note that *simple* four-electron  $2 + 2$  suprafacial reaction described above is no longer allowed because the ability of the transition metal to form the reactive metal-carbon "d bond" has been quenched. In this way the "transition-metal" character of the bonding has been eliminated and the "main group" Woodward-Hoffmann rules apply.<sup>15</sup>

These plots indicate that the C-C  $\pi$  bond and the Ti lone pair are still intact. The *spin-recoupling* that results in the disintegration of these two entities and subsequent formation of two metal-carbon bonds of the metallacycle has not occurred. We view this bonding as the interaction of two "closed-shell" molecules,  $\text{Cl}_2\text{Ti}$  (singlet) and  $\text{C}_2\text{H}_4$  (as opposed to the bonding in the metallacyclopropane, which is the interaction of two higher spin fragments, "triplet"  $\text{Cl}_2\text{Ti}$  and "triplet"  $\text{C}_2\text{H}_4$ ). This being the case, the chemistry of the  $\pi$ -complex should be dominated by "closed-shell" processes, i.e., reactions in which the electrons of a bonding pair delocalize *together* across the same paths. [This is distinct from the pericyclic reactions in which *one* member of each electronic pair delocalizes while the other remains localized (ideally) on one center<sup>1,12</sup>].

It is known that when the central metal is an oxidized late transition metal [Pd(II),<sup>16</sup> Pt(II),<sup>17</sup> Fe(II)<sup>18</sup>], the sense of acid-base

**Figure 9.** GVB orbitals describing the valence space of (ethylene)dichlorotitanium. Spacing between the contours is 0.05 au, and the characteristic dimension of the plots is  $6.0 a_0$ .**Figure 10.** Some representative reactions of metal-olefin  $\pi$ -complexes.

bonding is acceptor-metal/donor-olefin. In these cases, the intrinsic Lewis acidity of the metal is transferred to the olefin, and thus the olefin is activated toward nucleophilic attack. Examples of this activation are shown in Figure 10. In cases where this

(13) (a) Reference 4. (b) See also: M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, C71 (1951).

(14) R. A. Love, T. F. Koetzle, G. S. B. Williams, L. C. Andrews, and R. Bau, *Inorg. Chem.*, **14**, 2653 (1975).

(15) R. B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry", Verlag Chemie, Weinheim, 1971.

(16) G. W. Parshall, "Homogeneous Catalysis", Wiley Interscience, New York, 1980, Chapter 6 and p 25.

(17) N. Belluco, "The Organometallic and Coordination Chemistry of Platinum", Academic Press, New York, 1974, p 374.

(18) M. Rosenblum, *Acc. Chem. Res.*, **7**, 122 (1974).

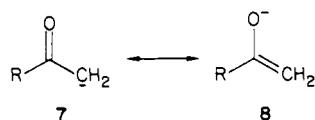
mode of bonding obtains, the geometry of the olefinic ligand is not expected to deviate substantially from that of the free olefin. This is due to the persistence of the double bond between the two carbon atoms. Since this bond remains, the overlap between the two carbon  $p\pi$  orbitals that form the olefinic  $\pi$  bond is still required and a short C-C internuclear distance results.

Complexes between simple unactivated olefins and highly reduced late transition metal centers ( $\text{Ni}^0$ ,<sup>19</sup>  $\text{Fe}^0$ ,<sup>20</sup>  $\text{Co}^{-1}$ ,<sup>21</sup>  $\text{Pt}^0$ ,<sup>22</sup>) are also quite well known. The chief mode of reactivity of these complexes is olefin dissociation, and in this way these olefin complexes are usually used simply as sources of low-valent metals in homogeneous reactions.<sup>23</sup> These complexes react at the olefin with electrophiles such as proton acids, but extensive olefinic reactivity is absent in these complexes. These observations, as well as several quantum chemical studies and spectroscopic studies,<sup>24</sup> are consistent with the bonding in these complexes being of the acid/base type, in the sense donor-metal/acceptor-olefin.

Complexes of this form are expected to have C-C bond distances that are long relative to that of a normal C-C double bond. [For example, the C-C bond length in  $(\text{PPh}_3)_2\text{Ni}(\text{C}_2\text{H}_4)$  is 1.43 Å<sup>25</sup> and that in  $\text{Li}_2\text{Fe}(\text{C}_2\text{H}_4)_2$  is 1.43 Å,<sup>20</sup> compare these with  $r(\text{C}-\text{C}) = 1.34$  Å in  $\text{C}_2\text{H}_4$ .] This may be rationalized either by noting that occupation of the antibonding  $\pi^*$  orbital reduces the C-C bond order<sup>13b</sup> or by noting that more effective stabilization of the metal-centered lone pair is realized if the two participating carbon  $p\pi$  orbitals overlap the two lobes of the doubly occupied d orbital more. This would tend to open the C-M-C angle more toward 90° (thus lengthening the C-C bond) and bend the  $\text{CH}_2$  units out of the plane of the olefin.

**E. Metallacycle vs.  $\pi$ -Complexes.** In the discussion above, we pointed out that there are two distinct forms of an  $\text{M}(\text{C}_2\text{H}_4)$  complex, **1** and **2**. We showed that the metallacycle form is preferred in **3** and **4**. Of course, the full wave function of such a complex will be a mixture or *resonance* of these two forms.<sup>26</sup> We find the stabilization of this mixing to be 2 kcal/mol,<sup>27</sup> further indicating that the metallacycle form is preferred. Even so, the less favored  $\pi$ -complex form can play a role in chemistry, but only after paying a 12-kcal penalty due to loss of the favorable metallacycle character.

This situation is analogous to that of the enolate anion, which has two important resonance structures, **7** and **8**



with their relative importance determined by the character of substituents and solvent.<sup>28</sup> Even when more stable, the use of

structure **7** alone to describe the enolate would not explicitly recognize the oxygen-centered nucleophilicity of the molecule; similarly, exclusion of **7** from consideration would mask the carbon-centered nucleophilicity. The use of this concept of resonance of molecules is fruitful because each resonance structure has its own characteristics and distinct behavior. By determining which canonical form is more important in a given chemical structure, one may estimate the relative importance of the two manifolds of reactivity.<sup>29</sup> This being the case, it is necessary to come to an understanding of which physical characteristics of the constituent parts of a metal-olefin complex increase the importance of one canonical form over the other. In the same way that different chemical environments will enhance the importance of **7** or **8**, different environments (reaction medium, ligands, different metal centers, etc.) will favor **1** over **2**. To make our theory useful, we must outline rules for estimating the relative importance of **1** and **2**.

We can state rules for deciding when the metallacycle form will predominate over the  $\pi$ -complex form:

(1) **High-Spin Metal Fragment:** The  $\pi$ -complex form requires a doubly occupied d orbital on the metal that may backbond into the  $\pi^*$  space on the olefin.<sup>13b</sup> Thus metals that have stable low-spin states (i.e., low-lying states with doubly occupied d orbitals) will be more likely to form acid-base type complexes. Conversely, metal centers that prefer high-spin coupling of the valence of shells (such as  $d^2$   $\text{Ti}^{\text{II}}$ ,  $d^2$   $\text{Ta}^{\text{III}}$ , and  $d^2$   $\text{Nb}^{\text{III}}$ )<sup>30</sup> will be more likely to form metallacyclopropanes. Thus, early transition metals will tend to form metallacycles and late metal will tend to form  $\pi$  complexes.<sup>31</sup>

(2) **Weak C-C  $\pi$  Bond in the Free Olefin:** Formation of the metallacyclopropane requires the cleavage of a C-C  $\pi$  bond. Therefore the metallacyclopropane form will be more important as the C-C  $\pi$  bond of the free olefin is weaker. Thus, acetylenes and olefins with strained  $\pi$  bonds (methylenecyclopropane, cyclopropenes, norbornadiene, allenes, etc.)<sup>32</sup> will be more likely to adopt a metallacycle form than will simple olefins. Also, olefins with electron-withdrawing substituents that weaken the C-C  $\pi$  bond will favor metallacyclopropane formation.<sup>33</sup> Since the C-C  $\pi$  bond in  $\text{C}_2\text{H}_4$  is one of the strongest C-C  $\pi$  bonds known,<sup>34</sup> ethylene will be the olefin least likely to form a metallacyclopropane.

(3) **Strong M-C  $\sigma$  Bonds:** Since the major force stabilizing the metallacyclopropane is the formation of metal-carbon covalent bonds, metal fragments that tend to make stronger covalent bonds will favor the metallacycle form. Thus  $\text{Cl}_2\text{Ti}$  will favor metallacyclopropane less than will  $\text{Cl}_2\text{Zr}$  or  $\text{Cl}_2\text{Hf}$  owing to the greater radial extent of the bonding orbitals of  $\text{Cl}_2\text{Zr}$  and  $\text{Cl}_2\text{Hf}$ .<sup>35</sup> Late transition metals will favor metallacycles less than will corresponding early transition metals for the same reason.<sup>35</sup>

**F. Implications.** When a complex having the form  $\text{M}(\text{C}_2\text{H}_4)$  is judged by the above criteria to be predominantly metallacyclic, it should demonstrate chemistry associated with that of two *isolated*, and *strained*, metal carbon bonds. Therefore, we suggest that the oxidative cyclization reaction **2**, which has been observed

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(29) Reference 26b, Chapter 8, especially paragraph 8.2.

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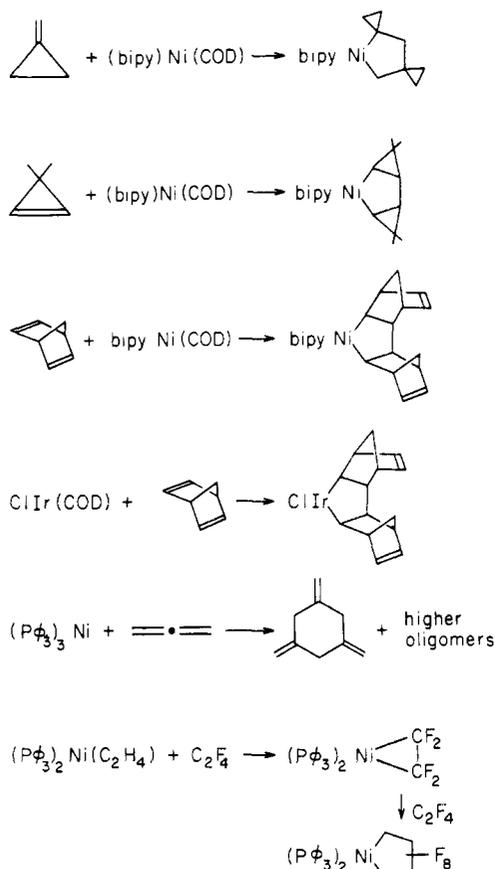
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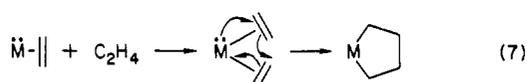
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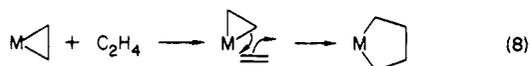


**Figure 11.** Some reaction of low-valent group 8 metals with olefin having weak  $\pi$  bonds.

for  $M = \text{Cp}_2^*\text{Zr}$ ,<sup>3c</sup>  $\text{Cp}_2^*\text{Ti}$ ,<sup>5b</sup> and  $\text{CpCl}_2\text{Ta}$ ,<sup>3a</sup> should be viewed not as a six-electron process (eq 7)<sup>6</sup> but rather as the simpler

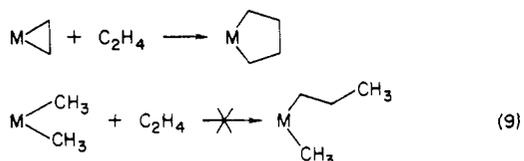


four-electron insertion process (eq 8).

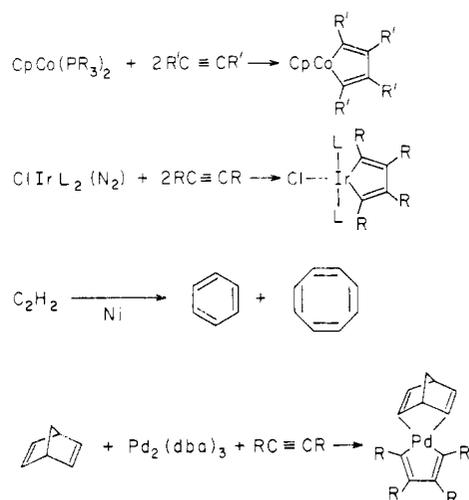


Furthermore, we suggest that reaction 2 is not oxidative at all; the "divalent" metal in the metallacyclopropane participates in the pericyclic migratory insertion reaction<sup>12</sup> to give the "divalent" metal in the metallacyclopentane.

Why is it that these metallacyclopropanes react with olefins (see Figure 6), while the corresponding dialkyl complexes do not (eq 9)?<sup>36</sup>



The beautiful simplicity of the metallacyclopropane form is apparent in the plots of Figure 2. The strain in the three-membered ring, which is manifest in the valence bond description, stimulates the migratory insertion reaction. Cyclopropane itself is stable in



**Figure 12.** Some reactions of low-valent group 8 metals with acetylenes.

**Table II.** Parameters Characterizing GVB Orbital Pairs Mentioned in This Study

molecule	electron pair	GVB orbitals	
		overlap	$\Delta\epsilon$ (kcal/mol)
$\text{Cl}_2\text{Ti} \begin{array}{c} \text{CH}_2 \\ \diagdown \\ \text{CH}_2 \end{array}$	C-C bond	0.85	8.2
	Ti-C bond	0.63	19.5
$\text{Cl}_2\text{Ti} \begin{array}{c} \text{CH}_2 \\ \diagdown \\ \text{CH}_2 \end{array}$	C-C $\pi$ bond	0.72	12.6
	C-C $\sigma$ bond	0.87	6.3
	Ti lone pair	0.84	3.1
	ethane	C-C bond	0.83
cyclopropane	C-C bond	0.81	10.0
ethylene	C-C $\pi$ bond	0.64	9.5
	C-C $\sigma$ bond	0.88	6.3
$\text{Cl}_2\text{Ti}^a$	Ti lone pair	0.89	1.9
	Ti-C bond	0.64	23.2
$\text{Cl}_2\text{Ti} \begin{array}{c} \text{CH}_3 \\ \diagdown \\ \text{H} \end{array}$	Ti-C bond	0.64	23.2

<sup>a</sup>Reference 45. <sup>b</sup>Reference 44.

the presence of simple olefins *only* because for carbon the  $2_s + 2_p$  reaction is forbidden<sup>15</sup> (eq 10).



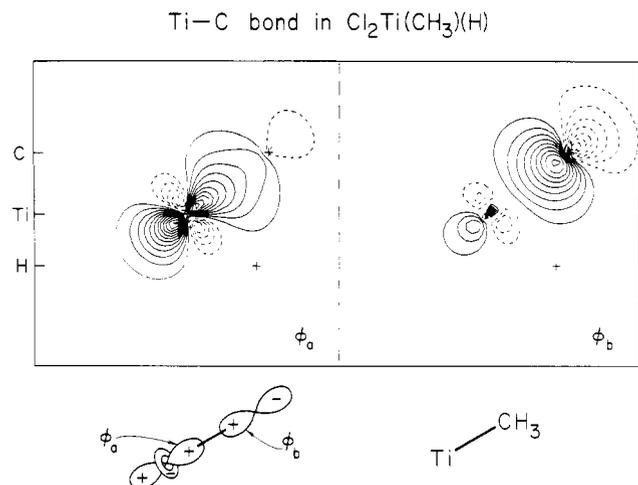
The presence of the metal at the apical site and, importantly, the use of the metal valence  $d$  orbitals in the covalent metal-carbon bond allows the intrinsic strain of the three-membered ring to be relieved by a very simple  $2 + 2$  reaction.

It is important to note that the metal fragments ( $\text{Cp}_2^*\text{Ti}$ ,  $\text{Cp}_2^*\text{Zr}$ ,  $\text{CpCl}_2\text{Ta}$ , etc.) affording the reaction shown in (2) are all expected to be high-spin  $d^2$  species.<sup>30</sup> According to the first rule mentioned in section II.E, the complex formed between each of these fragments and ethylene should be a metallacyclopropane.

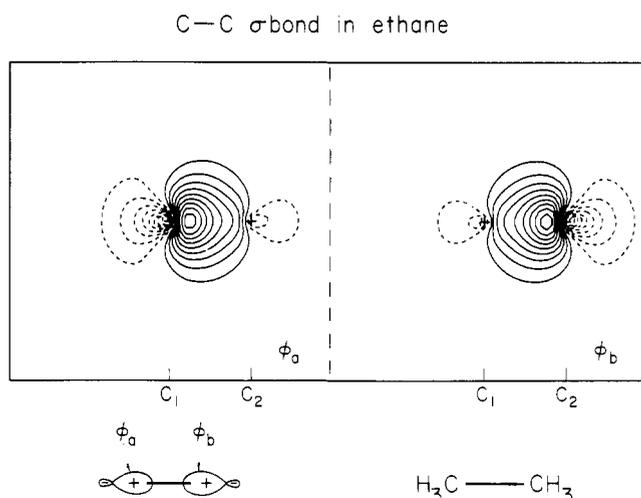
There are also several examples in the literature where metal fragments that do *not* have high-spin  $d$  shells promote "oxidative cycloaddition" to give metallacyclopropanes when they are treated with olefins.  $\text{Ni}(0)$  and  $\text{Ir}(1)$ <sup>3d,32</sup> (Figure 11). In a similar way, low-valent group 8 metals are known to react with 2 equiv of acetylene to give metallacyclopentadienes<sup>37</sup> (Figure 12). In all of these cases the metal is introduced into the (often catalytic) reaction sequence as a low-valent complex that is transformed to

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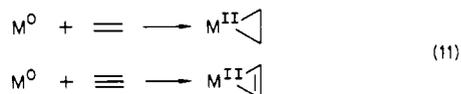


**Figure 13.** GVB orbitals describing the Ti—C bond in  $\text{Cl}_2\text{Ti}(\text{H})(\text{CH}_3)$ . Spacing between the contours is 0.05 au, and the characteristic dimension of the plots is  $6.0 a_0$ .



**Figure 14.** GVB orbitals describing the C—C bond in ethane.

the higher valent metallacyclic product. We suggest that the change in valency occurs upon the addition of the *first* equivalent of olefin (or acetylene) to give the metallacyclopropane (or propene)<sup>33,38</sup> (eq 11).

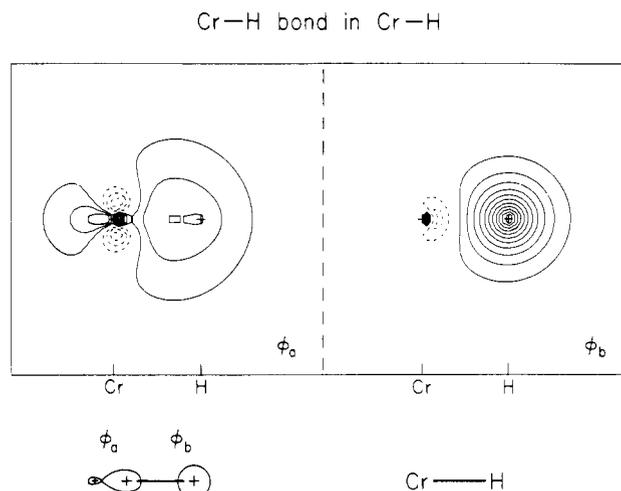


Note that in all of the above cases the active  $\pi$  bonds are *weak* ones (due to strain, electron-withdrawing substituents, or the intrinsic weakness of acetylene  $\pi$  bonds). This was mentioned above as the second criterion for predicting predominance of a metallacyclic structure over a  $\pi$ -complex form.

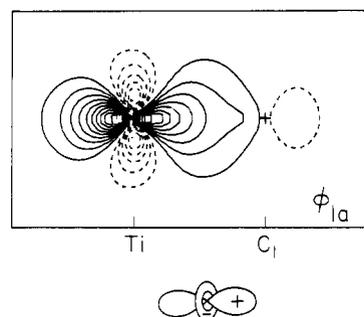
### III. Conclusions

The GVB calculations on  $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4)$  lead to a metallacyclopropane resonance structure that predominates over the  $\pi$ -complex resonance structure. The chemistry expected from this metallacyclopropane form involves  $2 + 2$  suprafacial reactions with the strained Ti—C bond. This reactivity is consistent with experimental observation.

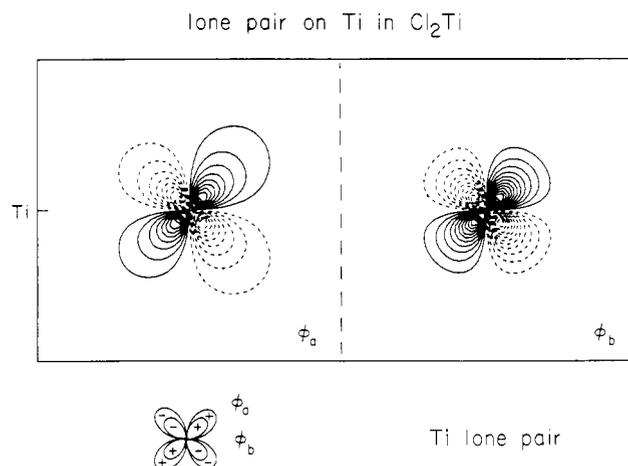
(38) (a) Reference 1e, p 108. (b) J. L. Thomas, *Inorg. Chem.*, **17**, 1507 (1978). (c) J. L. Thomas, *J. Am. Chem. Soc.*, **95**, 1838 (1973). (d) H. Hoberg, D. Schaefer, and G. Burkhardt, *J. Organomet. Chem.*, **228**, C21 (1982). (e) M. Kadonaga, N. Yasuoka, and N. Kasai, *J. Chem. Soc., Chem. Commun.* 1597 (1971). (f) R. J. DePasquale, *J. Organomet. Chem.*, **32**, 381 (1971).



**Figure 15.** GVB orbitals describing the Cr—H bond in CrH.



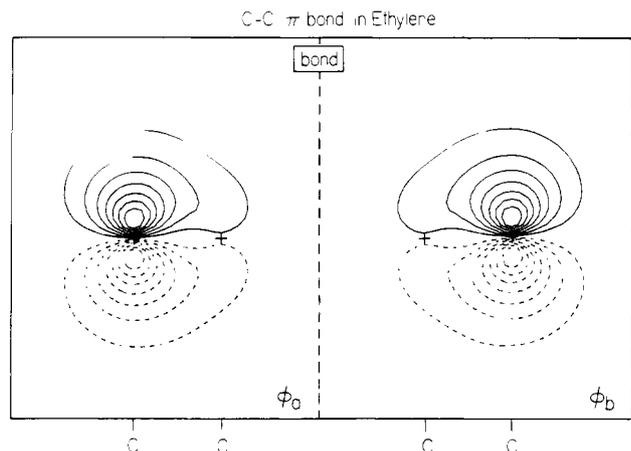
**Figure 16.** Plot of the Ti-centered GVB orbital in the Ti—C  $\sigma$  bond in dichlorotitanacyclopropane. The plane of this plot is perpendicular to the plane of the Ti—C—C ring and contains the Ti and C atoms of the bond.



**Figure 17.** Lone pair on (bent)  $\text{TiCl}_2$ .

We have emphasized that the metallacyclopropane and  $\pi$ -complex forms are not truly separate and distinct; however, we expect that one form will take precedence over the other in any one system. This leads to the partitioning of the chemistry of olefin complexes into two classes, that of the metallacycle and that of the  $\pi$ -complex. The chemistry of the metallacyclopropane is dominated by  $2_2 + 2_2$ -type reactions,<sup>12</sup> while the chemistry of the  $\pi$ -complex is dominated by acid-base reactions resulting from enhancement of the electrophilicity of the olefin.<sup>2</sup>

By examining the wave function of one metallacyclopropane in detail, we have been able to see the ring strain that is not at all apparent in the  $\pi$ -complex form. We have seen how this ring strain plays an important role in metallacyclopropane chemistry, owing to the suprafacial  $2 + 2$  reaction that, although forbidden



**Figure 18.** GVB orbitals describing the  $\pi$  bond in ethylene. The spacing between the contours is 0.05 au, and the characteristic dimension of the plots is  $6.0 a_0$ .

in main group chemistry, is possible at a transition metal to carbon covalent bond!

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#### Appendix: Details of the Calculations

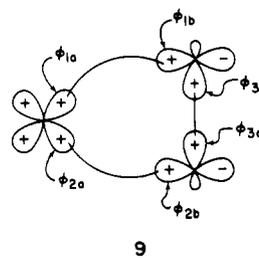
**A. Basis Sets and Effective Potentials.** We calculated GVB(3/6) wave functions for the  $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4)$  complex. The titanium, carbon, and hydrogen centers were described in a fully ab initio, all-electron fashion, using valence double- $\zeta$  basis sets on each.<sup>39</sup> The core electrons (1s, 2s, 2p) on chlorine were replaced with the SHC ab initio core effective potential,<sup>40</sup> and the valence electrons on chlorine were described by using a minimal basis set optimized for molecular environments.<sup>40</sup>

**B. Geometry Variation.** During the geometry searches,  $C_{2v}$  molecular symmetry was assumed. This is justified for several reasons. Firstly, all tetra- and divalent four-coordinate titanium complexes are pseudotetrahedral.<sup>41</sup> It seems unlikely that the  $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4)$  complexes would deviate from this. Secondly, Bercaw and co-workers have studied  $\text{Cp}_2^*\text{Ti}(\text{C}_2\text{H}_4)$  crystallographically and found that the ethylene moiety occupies two of the "tetrahedral sites" about the titanium atom.<sup>5b</sup> Finally, our experience with similar complexes of titanium [ $\text{Cl}_2\text{TiH}_2$ ,  $\text{Cl}_2\text{TiH}$ ,  $\text{Cl}_2\text{TiH}^+$ ,  $\text{Cl}_2\text{-Ti}=\text{CH}_2$ , and  $\text{Cl}_2\text{Ti}(\text{CH}_2)_3$ ] also indicate that there is little force driving the two "organic" ligands out of the plane that bisects the Cl–Ti–Cl angle.<sup>10,12</sup>

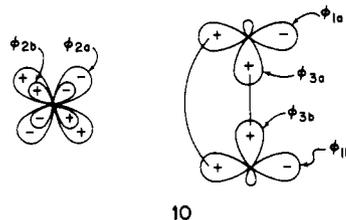
Throughout these calculations, the Ti–Cl bond length was fixed at 2.328 Å, and the Cl–Ti–Cl angle was fixed at 142°. These are the parameters calculated for  $\text{Cl}_2\text{TiH}_2$ ,<sup>10</sup> and since the chlorine ligands are used here singly as *model* "anionic" ligands, the fixing of their positions is justified. The C–H bonds in the complex were fixed at 1.091 Å and not varied, although the angle of depression of the methylene units was optimized.<sup>1c</sup>

The geometry of the complex was optimized for the GVB-PP(3/6) level wave function in which the motions of three pairs of electrons are correlated. Each pair requires two valence

bond-like orbitals so that six orbitals are used for the three pairs (hence, 3/6). These six electrons are the "active electrons" in this complex. This wave function has the flexibility to describe either the three bonds of a metallacyclopropane **9**



or the three parts of a  $\pi$ -complex (a lone pair on the metal, a C–C  $\sigma$  bond, and a C–C  $\pi$  bond) **10**



The geometry search was conducted as follows: (1) With  $R(\text{CC}) = 1.432 \text{ \AA}$  and  $R(\text{TiC}) = 2.14 \text{ \AA}$ , the angle of depression of the  $\text{CH}_2$  units from the ethylene plane was optimized at 21°. (2) With this angle set at 21° and  $R(\text{C–C})$  set at 1.432 Å, the TiC distance was bound to be 2.181 Å. (3) With the angle of depression set at 21° and  $R(\text{Ti–C})$  set at 2.181 Å, the carbon–carbon distance was optimized at 1.460 Å. In this way the structure shown in Figure 1a was found. [A similar geometry variation procedure using a purely HF (molecular orbital) wave function gave the geometry shown in Figure 1c.]

The GVB(3/6) wave function that was variationally determined is that wave function described by the orbitals in Figure 2. No symmetry or equivalence restrictions were placed on the wave function to force the metallacyclopropane structure.

Using symmetry restrictions, we were able to force the  $\text{Cl}_2\text{-Ti}(\text{C}_2\text{H}_4)$  system to have a wave function describing the  $\pi$ -complex form. This was done by requiring that two covalent bonds be retained between the two carbon atoms. As expected, the GVB(3/6) ( $\pi$ -complex) wave function prefers the geometry of Figure 1c (by 4.5 kcal/mol) over the geometry of Figure 1a.

We compared the energies of the metallacyclopropane and  $\pi$ -complex forms of  $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4)$  at both the GVB-PP(3/6) and GVB-CI levels (Table I). Comparison at the GVB-PP level is qualitatively in agreement with the more accurate GVB-CI comparison, although the CI results show the metallacyclopropane to be slightly more favored over the  $\pi$ -complex form than at the GVB-PP level. In a GVB-CI wave function for these GVB(3/6) systems, all sextuple excitations from the dominant configuration are allowed into the six orbitals of the active space. The only restriction implied is that there be at least one electron and at most three electrons in a given GVB pair.

We were also curious about the location of triplet states of the  $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4)$ . At the  $\text{Ti}(\text{C}_2\text{H}_4)$  geometry of Figure 1b, we found the lowest triplet having one electron in the "back-bonding" d-orbital to be 22 kcal/mol above the metallacyclopropane. Since there is no experimental evidence for triplet states in these systems, they were not studied further.

It is valuable to examine the GVB orbitals describing these structures in more detail. Recall that in the valence bond formalism a covalent bond results from the overlap of two *singly-occupied* electronic orbitals, say  $\varphi_a$  and  $\varphi_b$ . Also recall that the valence bond wave functions,  $\psi_{\text{VB}}$ , can be written as a sum of two molecular orbital configurations (eq 12), where  $\sigma$  and  $\sigma^*$  correspond to bonding and antibonding localized molecular orbitals

$$\psi^{\text{VB}} = (ab + ba) = (a + b)^2 - \lambda^2(a - b)^2 \equiv \sigma^2 - \lambda^2\sigma^{*2} \quad (12)$$

(39) The Ti basis set is from Rappé et al.: A. K. Rappé, T. A. Smedley, and W. A. Goddard III, *J. Phys. Chem.*, **85**, 2607 (1981). The carbon and hydrogen (scaled, double- $\zeta$ ) basis sets can be found in Dunning and Hay: T. H. Dunning, Jr., and P. J. Hay, in "Modern Theoretical Chemistry: Methods of Electronic Structure Theory", H. F. Schaefer III, Ed., Plenum Press, New York, 1977, Vol. 3, and references therein.

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and  $\lambda \sim 0.1$  for a strong bond (overlap = 0.8).<sup>42</sup> The GVB pair lowering,  $\Delta E$ , is the energetic destabilization realized in replacing the GVB pair ( $\sigma^2 - \lambda^2\sigma^{*2}$ ) by the one configuration (molecular orbital) term ( $\sigma^2$ ). A small overlap of the two GVB orbitals indicates large pair lowering energy, and in this case a valence bond description is greatly preferred over the MO description.

In Table II we list these calculational results for the GVB(3/6) wave functions describing the metallacyclopropane and  $\pi$ -complex resonance structures. For comparison, we include the analogous data for the two carbon-carbon bonds in ethylene,<sup>43</sup> the carbon-carbon bond in ethane,<sup>43</sup> the carbon-carbon bond in cyclopropane,<sup>43</sup> the titanium-carbon bond in  $\text{Cl}_2\text{Ti}(\text{CH}_3)(\text{H})$ ,<sup>44</sup> and the lone pair on Ti in  $\text{Cl}_2\text{Ti}$ .<sup>45</sup>

From these and other data we may generalize that Ti-C bonds are characterized by bond orbitals having an overlap of  $\sim 0.6$ - $0.65$ . This is significantly smaller than the overlap of bonding orbitals in a carbon-carbon  $\sigma$  bond ( $\sim 0.8$ - $0.85$ ). Also, the inclusion of the second configuration ( $\sigma^{*2}$ ) in the molecular wave function is energetically twice as important in the titanium-carbon bond as in the carbon-carbon bond.

Data in Table II indicate that the Ti-C bonds in the metallacyclopropane are quite similar to the "normal" TiC bond in  $\text{Cl}_2\text{Ti}(\text{CH}_3)(\text{H})$ . Contour plots of the orbitals of this TiC bond are shown in Figure 13. Comparison of these orbitals with the orbitals describing the Ti-C bond in the metallacyclopropane (Figure 2) shows the bent character of the latter bond. Similar plots of the orbitals of the C-C bond in ethane are shown in Figure 14. These two bonding orbitals point directly at one another, unlike the corresponding orbitals of the C-C bond in cyclopropane (Figure 4). Comparison of the two carbon-carbon bonds with the two titanium-carbon bonds shows that there is the same relationship between the two Ti-C bonds as between the two C-C bonds. In this way an evaluation of these GVB wave functions makes the strain in the titanacyclopropane apparent.

The nonpolarity of the Ti-C bonds in both the metallacyclopropane and  $\text{Cl}_2\text{Ti}(\text{CH}_3)(\text{H})$  is also apparent from the plots of the GVB orbitals. Note that in each case there is one orbital that

is centered on the metal atom and one orbital centered on the carbon. As a contrasting example, the two GVB orbitals for the Cr-H bond of the  $d^5$  sextet state of  $\text{CrH}$ <sup>46</sup> are shown in Figure 15. This bond is polar ( $\text{Cr}^+ \rightarrow \text{H}^-$ ) because both orbitals ( $\psi_a$  and  $\psi_b$ ) are centered on the hydrogen. Not surprisingly, this polarity also results in a higher overlap (0.77) in this bond than in a typical nonpolar M-H bond (overlap = 0.62 in the Ti-H bond in  $\text{Cl}_2\text{TiH}_2$ ).

Finally, we can assess the shape of the titanium bonding orbital in the metallacyclopropane by plotting the amplitude of this orbital in the plane perpendicular to the Ti-C ring and along one of the Ti-C bond axes. This plot is shown in Figure 16. From this it is apparent that the Ti bonding orbital is shaped like a  $d_z^2$  orbital, just as in  $\text{Cl}_2\text{Ti}^+-\text{H}$ ,  $\text{Cl}_2\text{Ti}-\text{H}$ ,  $\text{Cl}_2\text{TiH}_2$ ,  $\text{Cl}_2\text{Ti}(\text{CH}_3)(\text{H})$ ,  $\text{Cl}_2\text{Ti}(\text{CH}_2)_3$ ,  $\text{Cl}_2\text{Sc}-\text{H}$ ,  $\text{Cl}_2\text{ZrH}$ , and  $\text{Cl}_2\text{ZrH}_2$ .<sup>10,12,47</sup> The shape of this bonding orbital is critical when evaluating the propensity of this bond to participate in 2 + 2 reactions, as mentioned in the above text. The fact that there is a ring of negative amplitude about the waist of the "dumbbell" of positive amplitude in this orbital means that the  $2_s + 2s$  substrate can approach the reaction bond from any azimuthal direction to form the quadrilateral transition state required for the pericyclic reaction.

The wave function that describes the  $\pi$ -complex form is not surprising. The orbitals in Figure 17 show a doubly occupied d orbital in the singlet state of  $\text{Cl}_2\text{Ti}$ . Comparison of these plots with the corresponding plots for the  $\pi$ -complex form of  $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4)$  shows only minor changes. The changes observed in the two carbon-carbon bonds in the  $\text{C}_2\text{H}_4$  unit, when complexed to the metal, are not surprising. These bond orbitals in the  $\pi$ -complex indicate some distortion from the normal double bond in ethylene (Figure 18), but the ring strain is not nearly as clearly demonstrated here as in the metallacyclopropene form. Furthermore, it is not clear from the  $\pi$ -complex wave function that the ring strain is actually relieved along the 2 + 2 reaction pathway. In this way the ring strain, a *thermodynamic* quantity, can at least qualitatively be related to the *kinetics* of the 2 + 2 migratory insertion reaction.

Registry No. 3, 97391-51-0; 4, 83314-27-6; ethane, 74-84-0; cyclopropane, 75-19-4; ethylene, 74-85-1.

(42) This is the overlap of the two GVB orbitals describing the H-H bond in  $\text{H}_2$ .

(43) Geometry of this species taken from "Landolt-Börnstein Numerical Data and Functional Relationships in Science and Technology. Group II, Volume 7, Structure Data of Free Polyatomic Molecules", K.-H. Hellwege, Ed.; Springer Verlag, Berlin, 1976.

(44) For these model calculations we kept the  $\text{Cl}_2\text{Ti}$  fragment frozen, assigned  $r(\text{Ti}-\text{H}) = 1.70 \text{ \AA}$  (ref 12),  $r(\text{Ti}-\text{C}) = 2.02 \text{ \AA}$  (ref 10), and  $\vartheta(\text{C}-\text{Ti}-\text{H}) = 75^\circ$  (ref 10).

(45)  $r(\text{Ti}-\text{Cl}) = 2.328 \text{ \AA}$  and  $\vartheta(\text{Cl}-\text{Ti}-\text{Cl}) = 140^\circ$ .

(46) The geometry of this diatomic was taken from Huber and Herzberg: K. P. Huber and G. Herzberg, "Molecular Spectra and Molecular Structure. IV. Constants of Diatomic Molecules", Van Nostrand Reinhold Co., New York, 1979. Value  $r(\text{Cr}-\text{H}) = 1.655 \text{ \AA}$  was used. See also: S. P. Walch and C. W. Bauschlicher, Jr., *J. Chem. Phys.*, **78**, 4597 (1983).

(47) M. L. Steigerwald and W. A. Goddard III, *Organometallics*, to be submitted.

## Barriers to Rotation Adjacent to Double Bonds

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**Abstract:** The barriers to internal rotation about C—C single bonds adjacent to C=O or C=C groups have been calculated via ab initio MO theory, and the results are compared with experimental data. With acetaldehyde, acetone, and propene, the calculated barrier is almost independent of basis set, is not significantly affected by correction for electron correlation, and agrees well with the experimental value. On the other hand, the calculated barriers for propanal, 2-butanone, and 1-butene are strongly basis set dependent, and only the 6-31G\* set, which includes polarization functions at carbon, gives relative energies which are in reasonable agreement with experiment. Electron correlation has a small effect on the barrier height. The components of the barrier are discussed. The barriers for acetaldehyde, acetone, propene, and 1-butene appear to have the same origin as that for ethane. With propanal and 2-butanone, there are additional terms which arise from a dipole-induced dipole interaction between the carbonyl group and the C—C bond of the ethyl group, and from the overlap of the bond orbitals of these groups.

Our studies of the enthalpies of hydrolysis of acetals, ketals, and ortho esters<sup>1-4</sup> has led us to investigate the effect of structure

on the energies and conformations of the above, as well as their hydrolysis products, the aldehydes, ketones, and esters. This report