

The intercalator free fingerprints of Rsa I and Bgl I show all the partial fragments; however, Rsa I produces a weak 2244-bp band, whereas the fragments produced by Bgl I appear equally. From these fingerprints the relative cutting order may be assigned for each set of restriction sites. Using the Eco RI cleavage site to define the zero point, the order for Rsa I is 3846 > 164, 2281 and for Bgl I is 928 > 1162, 3481. Finally, Mst I displays a prominent set of partial bands, the 4263-, 3266-, and 3168-bp fragments, which correlates with an order of reactivity for Mst I of 1355 > 1453 > 260 > 3587 (Table I).

In a typical run, BMSp (or EB), DNA, and assay buffer (50 mM of tris/HCl, pH 7.4, 6 mM of NaCl, 6 mM of dithiothreitol, 6 mM of MgCl₂, and 100 μg/mL bovine serum albumin) were mixed and allowed to equilibrate for 1 h. The restriction enzyme was added at time 0. At the proper intervals a 10-μL sample was withdrawn and terminated with 5 μL of 5% sodium dodecyl sulfate. The ethidium and intercalator free samples were then prepared for electrophoresis. Because BMSp can affect the mobility of DNA, BMSp was removed on a BioRad AG 50W-X8 column before preparing the samples for electrophoresis.²⁴ The samples were then electrophoresed in 5% polyacrylamide.

The addition of EB at 30% saturation ([EB]/[BP] = 0.16) induces no changes in the Rsa I and Bgl I fingerprints. There is only a reduction in the rate of restriction; therefore, no selective action is indicated. Conversely, the addition of BMSp at 30% saturation ([BMSp]/[BP] = 0.08) alters the fingerprints of all three enzymes. The 2244-bp partial of Rsa I disappears. The order of appearance of the 2553- and 2042-bp partials of Bgl I is reversed (the 2042-bp fragment now appears before the 2553-bp fragment), and Mst I shows a new set of prominent partials. The Mst I 2232/2227- and 2129-bp fragments appear in preference to the 4263, 3266, and 3168-bp partials. These changes correspond to inhibition at 164 for Rsa I, at 928 for Bgl I, and at 1355/1453 for Mst I (Figure 1).

Why BMSp can selectively compete with a restriction enzyme while EB shows no selective effects may simply be a demonstration of the enhanced sequence selectivity of a dimer (BMSp) over a monomer (EB).¹¹ Alternatively, BMSp and EB may both bind selectively, but only BMSp competes effectively with the restriction enzyme as a consequence of the relative binding affinities of the enzyme, BMSp, and EB.^{10,11} BMSp seems to preferentially inhibit restriction sites in the first third of the plasmid.²⁵ This corresponds to the BMSp saturation (30%) and suggests that the entire region, base pairs 164-1453, may be the preferred binding site of BMSp. A third interpretation is nonselective binding with sequence selective alteration of the plasmid DNA by BMSp (but not EB) which inhibits enzyme cleavage. Previous evidence that BMSp and EB bind rAdT in preference to dAdT suggests that the specificity of the intercalators may be due to the preferential binding of specific conformations of the nucleic acid double helix.^{10d,e,11,26}

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Registry No. BMSp, 79919-41-8; EB, 1239-45-8.

Supplementary Material Available: Electrophoretic data for Rsa I, Bgl I, and Mst I (2 pages). Ordering information is given on any current masthead page.

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(25) Studies with ³²P end labeled linear pBR322 DNA show that BMSp protects a region in the first third of the plasmid from DNase degradation.

(26) (a) Krugh, T. R.; Reinhardt, C. G. *J. Mol. Biol.* **1975**, *97*, 133-162. (b) Krugh, T. R.; Wittling, F. N.; Cramer, S. P. *Biopolymers* **1975**, *14*, 197-210. (c) Kastrop, R. V.; Young, M. A.; Krugh, T. R. *Biochemistry* **1978**, *17*, 4855-4865. (d) Patel, D. J.; Carmel, J.-L. *Proc. Natl. Acad. Sci. U.S.A.* **1976**, *73*, 3343-3347.

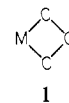
Titanacyclobutane: Structural Considerations

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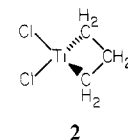
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Metalloacyclobutane complexes have been implicated in several organometallic reactions including olefin dimerization,¹ polymerization,² and metathesis.³ Indeed, such complexes have been

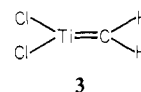


isolated,^{4,5} and a few platinum complexes⁵ have been structurally characterized. However, for early transition metals where the catalytic processes occur, the structural characterization is less complete.⁶

Herein we report the structure for a simple metalloacyclobutane obtained from ab initio theoretical studies and provide relative



energetics for its equilibrium with free ethylene plus the metal alkylidene complex.



For the metalloacyclobutane **2** we find⁷ a planar, symmetric ring

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(6) A recent X-ray study [J. B. Lee, G. J. Gajda, W. P. Schaefer, T. R. Howard, T. Ikariya, D. A. Straus, and R. H. Grubbs, *J. Am. Chem. Soc.*, submitted for publication] of three substituted titanacyclobutanes leads to results quite compatible with our structural study. Most significantly, all three complexes were found to have a planar metalloacyclobutane ring.

(7) The structural calculations for **2-4** were ab initio Hartree-Fock. All electrons of the Ti, C, and H were considered by using valence double- ζ basis sets (the H was unscaled). The Cl was described by a molecularly optimized minimum basis⁸ using the SHC effective potential⁹ to replace the core electrons. Generalized valence bond (GVB) calculations were carried out at the optimized geometry to obtain the orbitals in Figure 1. Constraints in the geometric optimizations were $\angle\text{ClTiCl} = 142^\circ$ for **2** and $R_{\text{TiCl}} = 2.238 \text{ \AA}$ for **2** and **3** (based on the calculated geometry for **4**; in addition, the CH₂ plane of **2** was taken to pass through the diagonally opposite atom; A. K. Rappé, Ph.D. Thesis, California Institute of Technology, October 1980.

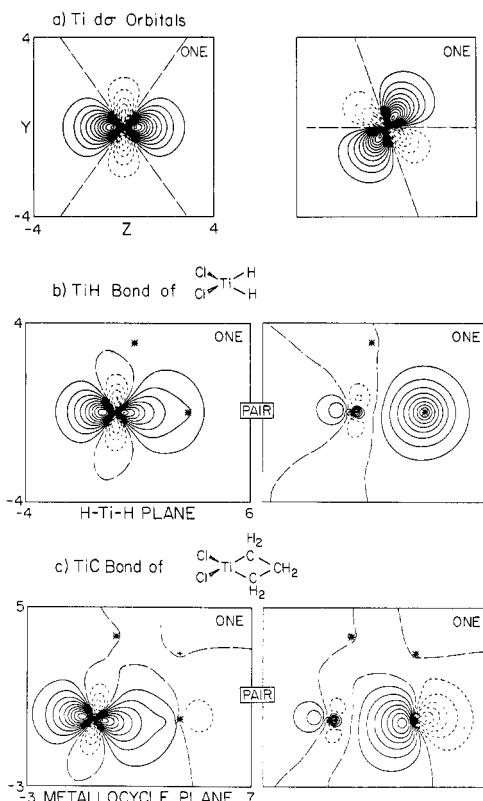
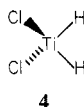


Figure 1. (a) The $d\sigma$ and $d\sigma'$ orbitals for Ti; $d\sigma'$ was obtained by rotating $d\sigma$ by 54.73561° . It should be noted that $\langle d\sigma|d\sigma' \rangle = 0$. (b) The GVB orbitals for one of the TiH bonds of **4**. (c) The GVB orbitals for one of the TiC bonds of **2**. In all figures, the nodal line is shown by long dashes. Solid lines indicate positive amplitude, and dotted lines indicate negative amplitude. The spacing between contours is 0.0625 a. u.

with $\angle\text{CTiC} = 75.6^\circ$, $\angle\text{CCC} = 105.4^\circ$, $\angle\text{CCTi} = 89.5^\circ$ (two), and $\angle\text{HCH} = 111.0^\circ$ (three). In comparisons for cyclobutane similar calculations¹⁰ lead to a puckering of 20° (with a well depth of 1.2 kcal) and $\angle\text{CCC} = 89.5^\circ$ and $\angle\text{HCH} = 108.3^\circ$. The calculated bond lengths for **2** are $R_{\text{TiC}} = 2.02$, $R_{\text{CC}} = 1.56$, and $R_{\text{CH}} = 1.09$ Å. For the alkylidene **3** we find^{8,11} $R_{\text{TiC}} = 1.885$ Å, $R_{\text{CH}} = 1.084$ Å, $\angle\text{HCH} = 116.5^\circ$, and $\angle\text{CITiCl} = 144.4^\circ$.

It is particularly interesting that the metalocycle is planar. This is in sharp contrast to the common assumption that metalocyclobutanes are strongly puckered (an assumption which has been used to explain the stereochemistry of olefin metathesis¹²). On the other hand, the metalocycle is quite floppy with respect to puckering. Using a fixed puckering angle of 10° , we reoptimized the geometry and found the energy to be only 0.3 kcal/mol above that of the optimum planar molecule.

Also intriguing is the CTiC angle of 75.6° . The value seems small but what angle should be optimum for two unstrained sigma bonds to Ti? Replacing the metalocycle with two Ti-H bonds



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(8) W. A. Goddard III and A. K. Rappé, in "Potential Energy Surfaces and Dynamics Calculations", D. G. Truhlar, Ed., Plenum Press, New York, 1981, pp 661-684.

(9) A. K. Rappé, T. A. Smedley, and W. A. Goddard III, *J. Phys. Chem.*, **85**, 1662 (1981).

(10) F. A. Cotton and B. A. Frenz, *Tetrahedron*, **30**, 1587 (1974); G. A. Segal, *J. Am. Chem. Soc.*, **96**, 7892 (1979); W. J. Hehre and J. A. Pople, *ibid.*, **97**, 6941 (1975); D. Cremer, *ibid.*, **99**, 1307 (1977); A. C. Legon, *Chem. Rev.*, **80**, 231 (1980).

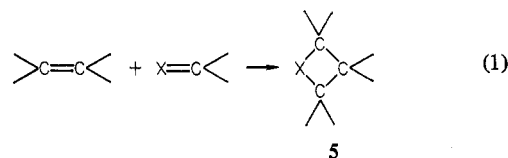
(11) The optimizations for **3** are the same as for **2** except that d functions were included on the C. See ref 8 for more details.

(12) T. J. Katz and J. McGinnis, *J. Am. Chem. Soc.*, **97**, 1592 (1971); C. P. Casey, L. D. Albin, and T. J. Burkhardt, *ibid.*, **99**, 2533 (1977).

leads to an optimum HTiH angle of 74.9° , suggesting that the C-Ti-C part of the metalocyclobutane is not strained. [However, the orbital plots (Figure 1c) indicate some residual strain in this bond.] The CCC angle (105.4°) of the metalocycle **2** is intermediate between that of cyclobutane (89.5°) and that of propane¹³ (112.5°), suggesting that the strain is reduced but still present for the metalocycle.

Compared with cyclobutane, the CTiC part of the metalocycle is much more open, allowing the CCC part to relax. The result is opening of the CCC angle from 90 to 105° . This apparently reduces the nonbonded interactions (eclipsed CH bonds) responsible for puckering in cyclobutane, allowing the metalocycle to be planar.

Considering the cycloaddition



we find that

$$\Delta H_{300} = -34.5 \text{ kcal/mol}^{14,15}$$

for $\text{X} = \text{TiCl}_2$ [i.e., formation of **3**], whereas

$$\Delta H_{300} = +17 \text{ kcal/mol}^{8,16}$$

for $\text{X} = \text{CrCl}_4$ and

$$\Delta H_{300} = +8 \text{ kcal/mol}^{8,16}$$

for $\text{X} = \text{MoCl}_4$. Thus, binding energies of **5** increase as one goes to the left and down the periodic table, as one would expect from trends in sizes of d orbitals. These results can be compared with those for hydrocarbon analogues, e.g.,

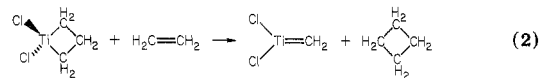
$$\Delta H_{300} = -18.7 \text{ kcal/mol}^{17}$$

for $\text{X} = \text{CH}_2$.

As indicated in Figure 1, the two Ti-C bonds of **2** are quite covalent, as are the two Ti-H bonds of **4**. Each bond can be accurately described as having one electron in a d orbital of the

(13) D. R. Lide, *J. Chem. Phys.*, **33**, 1514 (1960).

(14) This energy is obtained from ab initio GVB-CI calculations on the energy of reaction for



using experimental geometries for cyclobutane and ethylene. Vibrational frequencies (either estimated, experimental, or calculated) were used to obtain zero-point energies (for ΔH_0) and C_p (for $\Delta H_{300} - \Delta H_0$). For **2** both Ti-C bonds were correlated as well as the analogous C-C bonds (two) of cyclobutane. For **3**, both Ti-C σ and π bonds were correlated along with the analogous C-C (σ and π) bonds of ethylene. In each case a full CI was performed among the uniquely defined GVB orbitals (four orbitals for each molecule). For these correlated calculations, d functions were included on both carbons of ethylene, the CH_2 carbon of **3**, and the carbon involved in both correlated bonds of cyclobutane. This leads to total energies of $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4) = -1883.42709$, $\text{C}_4\text{H}_8 = -155.86557$, $\text{Cl}_2\text{TiCH}_2 = -1805.50877$, and $\text{C}_2\text{H}_4 = -77.97647$ H. This results in $\Delta H_{300} = +18.3$ kcal/mol for reaction 2. Using the experimental¹⁵ $\Delta H_{300} = -18.7$ kcal/mol for $\text{X} = \text{CH}_2$ leads to $\Delta H_{300} = -37.0$ kcal/mol for $\text{X} = \text{TiCl}_2$. The differential effect of not including d functions on the remaining three carbon atoms of the cyclic structures was examined using a Hartree-Fock wave function, leading to total energies of $\text{Cl}_2\text{Ti}(\text{C}_2\text{H}_4) = -1883.34843$ (without d functions), -1883.38757 (with d functions), $\text{C}_4\text{H}_8 = -155.82814$ (d functions on one carbon), and -155.87131 H (d functions on all carbons). This results in a 2.5-kcal differential effect and a final $\Delta H_{300} = -34.5$ kcal for reaction 1 with $\text{X} = \text{TiCl}_2$.

(15) S. W. Benson, "Thermochemical Kinetics", Wiley, New York, 1976.

(16) A. K. Rappé and W. A. Goddard III, *J. Am. Chem. Soc.*, submitted for publication.

(17) T. H. Edwards, N. K. Moncur, and L. E. Snyder, *J. Chem. Phys.*, **46**, 2139 (1967); R. A. Hill and T. H. Edwards, *ibid.*, **42**, 1391 (1965).

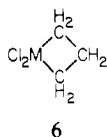
Ti bonded to an appropriate orbital on the ligand (1s for H or an sp^3 hybrid orbital for C). On the other hand, the two Ti-Cl bonds are quite ionic and can be rather accurately visualized as two chloride (Cl^-) ligands. Thus the electronic states of the Ti can be most accurately described as Ti(II) with both d electrons of the d^2 configuration involved in covalent bonds to the C (or H) ligands. Often such a system would be described formally as Ti(IV), with the C (or H) ligands considered as anions. We recommend strongly against such formal assignments of the oxidation state since it provides a distorted picture of where the electrons are actually located.

An interesting question here is what bond angle is expected for a d^2 system making two covalent bonds. An s^2 atom leads to bond angles of 180° (e.g., BeH_2) and p orbitals lead to bond angles of $90-92^\circ$ [e.g., SiH_2 , PH_2 , and SH_2 . See, e.g., W. A. Goddard III and L. B. Harding, *Annu. Rev. Phys. Chem.*, **29**, 363 (1978)]. For two $d\sigma$ orbitals to be orthogonal, they must be at 54.7° (or 125.3°), as in Figure 1a. However, intraatomic electron repulsion destabilizes this optimum $d\sigma d\sigma'$ configuration¹⁸ and favors a $d\sigma d\delta$ configuration that would lead to a 90° bond angle. The observed optimum angle of $\sim 75^\circ$ is a compromise between these two effects.

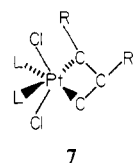
The highly covalent character of the Ti-C (or Ti-H) bonds is critically dependent upon the highly ionic character in the Ti-Cl bonds. Similar results should obtain if the two Cl are replaced by other electronegative ligands such as cyclopentadienyl (Cp), F, or alkoxy.

The same considerations should apply to Zr and Hf and with similar energetic factors so that similar bond angles are expected.

For systems such as



where $M = Ni, Pd, \text{ or } Pt$, the above results suggest ionic M-Cl bonds and fairly covalent M-C bonds so that these systems are best described as d^8 with two singly occupied d orbitals involved in M-C bonds and the remaining three d orbitals doubly occupied. [Often **6** would be denoted as involving the M(IV) oxidation state.] The arguments for d^2 systems of Ti, Zr, and Hf apply equally to these d^8 systems of Ni, Pd, Pt, Rh, and Ir, and hence we expect similar geometries, $\theta(CMC) = 75^\circ$. Indeed, structural studies⁵ on



lead to $\theta = 74-76^\circ$.

In summary, we find that tetracoordinate compounds of the Ti and Ni columns having two bonds to electronegative species (e.g., Cl, Cp, OR) and two bonds to alkyl groups (or hydrogens) have covalent metal-alkyl (or metal-H) bonds involving nearly pure d orbitals on the metal. Because of bonding and electron repulsion considerations for these d^2 and d^8 systems, the optimum CMC angle is $\sim 75^\circ$ for a system without large strain or steric effects.

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Registry No. 2, 79953-32-5; **3,** 79899-81-3; **4,** 79953-33-6.

(18) For example, a p^2 configuration leads to one triplet state (3P), while a d^2 configuration leads to two triplet states (3F and 3P), separated by ~ 20 kcal/mol. It should be pointed out that previous theoretical work on preferred bond angles [e.g., J. W. Lauher and R. Hoffman, *J. Am. Chem. Soc.*, **96**, 1729 (1976)] has ignored this intraatomic electron repulsion effect.

Deuterium Isotope Effects on Carbon-13 Chemical Shifts in Cyclophanes. Deshielding Intrinsic Through-Space and Through-Bond Effects

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Deuterium isotope effects on ^{13}C NMR chemical shifts are often used for spectral assignments,¹ and studies on their correlation with molecular structure are therefore desirable. Most deuterium isotope effects on ^{13}C shifts reported so far are *shielding*,² and only relatively few examples of *deshielding* effects have been observed.³ Some of these unusual deshielding effects^{3f} are rationalized^{4,5} in terms of isotopic perturbations of degenerate conformational equilibria;⁶ others^{3d,3e} could be a consequence of the slightly different hydrogen-bonding abilities of OH relative to OD groups. The deshielding by deuterium of the positively charged carbon in classical static β -deuteriocarbocations (C^+-C-D) results from less efficient hyperconjugative electron release by C-D compared to C-H bonds.^{3h}

We now report the first examples of *intrinsic through-space* deuterium isotope effects on ^{13}C chemical shifts as well as a number of long-range *through-bond* effects in cyclophanes carrying deuterated methyl groups.⁷ Importantly, the majority of both types of isotope shifts are *deshielding*. Table I contains the data,^{8,9}

(1) Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden: London, 1978; pp 107-110.

(2) For a list of pertinent references, see: Hansen, P. E.; Led, J. J. *Org. Magn. Reson.* **1981**, *15*, 288-293.

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(4) Anet, F. A. L.; Dekmezian, A. H. *J. Am. Chem. Soc.* **1979**, *101*, 5449-5451.

(5) Andrews, G. C.; Chmurny, G. N.; Whipple, E. B. *Org. Magn. Reson.* **1981**, *15*, 324-325.

(6) Anet, F. A. L.; Basus, V. J.; Hewett, A. P. W.; Saunders, M. *J. Am. Chem. Soc.* **1980**, *102*, 3945-3946.

(7) All compounds apart from **1d** were prepared via the aldehydes which were obtained by formulation of [2.2]paracyclophane, 4-methyl[2.2]paracyclophane, and [2.4](1,2,4,5)cyclophane, respectively, with dichloromethyl methyl ether/TiCl₄. The aldehydes were reduced with LiAlH₄ or LiAlD₄ as appropriate, the alcohols treated with PBr₃, and the bromides reduced with LiAlH₄ (LiAlD₄) to give the methyl derivatives. Compound **3a** had mp 198-199 °C (from petroleum ether); **1d** was obtained via the sequence $RH \rightarrow RCOCH_3 \rightarrow RCO_2H \rightarrow RCD_2OH \rightarrow RCD_2Br \rightarrow RCD_3$ (R = [2.2]-paracyclophane-4-yl).

(8) 100.6-MHz ^{13}C and 400.1-MHz 1H NMR spectra were recorded. Molar ratios of deuterated and nondeuterated compounds were distinctly different from unity to facilitate distinction between the resonances of the two species. Narrow spectral widths and Lorentzian-to-Gaussian transformation [Ferrige, A. G.; Lindon, J. C. *J. Magn. Reson.* **1978**, *31*, 337-340] were used to resolve small chemical shift differences.

(9) Assignment of the ^{13}C NMR spectra was made by selective $^{13}C\{^1H\}$ double resonance, by SFORD, by comparison of the spectra with those of a number of dimethyl[2.2]paracyclophanes and of [2.4](1,2,4,5)cyclophane, respectively, and from two- and three-bond C,D coupling constants. The 1H NMR spectra were assigned by homonuclear decoupling and extensive NOE difference experiments. ^{13}C chemical shifts (relative to $CDCl_3$, δ 77.05): **1a**, 139.49, 139.37, 139.35 (C-6,11,14), 138.20 (C-3), 136.97 (C-4), 135.32 (C-5), 134.13 (C-8), 133.26, 133.20 (C-12,13), 132.03 (C-16), 129.94 (C-7), 127.62 (C-15), 35.42 (C-10), 35.04 (C-9), 33.89 (C-1), 33.43 (C-2), 20.16 (CH_3); **2a**, 139.29 (C-11,14), 137.82 (C-3,6), 136.30 (C-5,8), 134.28 (C-4,7), 132.37 (C-13,16), 128.46 (C-12,15), 33.59 (C-1,10), 33.06 (C-2,9), 19.64 (CH_3); **3a**, 141.76, 141.71, 141.26 (C-6,8,11,15,12,14), 140.35 (C-3,5), 139.85 (C-16), 139.00 (C-4), 137.24 (C-7), 132.94 (C-13), 34.33, 33.26 (C-9,18,10,17), 32.23 (C-1,20), 29.06 (C-2,19), 18.80 (CH_3).