

Reaction energetics of a dissociative olefin metathesis mechanism for dichlorotitanacyclobutane

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As shown in Figure 2, the nickel atom is in a trigonal environment, and the bonding in the nickelacyclopropane unit is slightly unsymmetrical, with the Ni-C(2) distance being somewhat shorter than the Ni-C(1) distance. The α twist of the C(1)-C(2) bond, measured¹³ as the angle between the C(1)-C(2) line and the NiCIP(1) plane is 8.5 (7)°, so that C(1) and C(2) deviate by 0.05 and 0.26 Å, respectively, from the mean least-squares coordination plane of the nickel atom. As expected the ylidic P(2)-C(2) distance at 1.77 (1) Å is appreciably shorter than the average P(2)-Me bond length (1.81 (2) Å). Conversion of 2 to its isomer 1d is sufficiently slow to allow detailed NMR studies to be carried out. The results of these studies, which are summarized in Figure 3, conclusively show that the solid-state structure of this compound is maintained in solution.¹⁴

Work is now in progress to clarify the mechanism of this unusual rearrangement and to ascertain the potential role of 2 and of the other related species as intermediates in alkyne transformations induced by transition-metal complexes.

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Supplementary Material Available: Tables of crystal data, atomic coordinates, bond distances and angles, and thermal parameters for 1b and 2 (12 pages). Ordering information is given on any current masthead page.

(12) Crystal data: C₂₆H₃₇NiOP₂; *M_r* = 509.7; orthorhombic; space group *Pbca*; *a* = 20.638 (5) Å, *b* = 20.09 (1) Å, *c* = 12.913 (5) Å; *V* = 53 54 Å³; *D_{calc}* = 1.26 g cm⁻³; *Z* = 8; *F*(000) = 2160; μ (Mo K α) = 9.59 cm⁻¹. Diffraction intensity data were collected on an Enraf-Nonius CAD-4F diffractometer using the ω -2 θ scan technique. Of the 4669 reflections measured in an octant out to 2 θ = 40°, 1277 unique reflections were considered observed (*I* ≥ 3 σ (*I*)). The structure was solved by Patterson and Fourier techniques and refined by least squares to an *R* value of 5.6%. The carbon atoms were considered isotropic. The hydrogen atoms were geometrically placed and included with fixed contributions in the refinement cycles, except H(1) whose coordinates, taken from a Fourier difference map, were refined.

(13) See for instance; Jolly, P. W. In "Comprehensive Organometallic Chemistry", Wilkinson, G., Stone, F. G. A., Eds.; Pergamon Press: Oxford, 1982, Vol. 6, Chapter 37.5 and references therein.

(14) The assignment has been confirmed by selective decoupling experiments. The spectra were recorded in C₆D₆ at 250 MHz (¹H) and at 101.2 MHz (³¹P). IR (Nujol mull, cm⁻¹): 1600 (ν (CO)). Anal. Calcd for C₂₆H₃₇OP₂ClNi: C, 58.9; H, 7.3. Found: C, 57; H, 7.3.

Reaction Energetics of a Dissociative Olefin Metathesis Mechanism for Dichlorotitanacyclobutane

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Summary: We have studied the rearrangement of dichlorotitanacyclobutane to the corresponding (olefin)titanium methylidene complex, characterizing in detail the wave functions, geometries, and energetics of each

complex and the transition state connecting them. We find that the metallacycle is more stable than the olefin alkylidene complex by 11.5 kcal/mol and that there is no activation barrier for the rearrangement. We have further determined the olefin coordination energy to be 10.4 kcal/mol. From straightforward kinetic arguments we conclude that metathesis of the dichlorotitanacyclobutane complex, proceeding via a dissociative mechanism, should have an activation enthalpy of 21.9 kcal/mol.

Olefin metathesis¹ is a transition-metal-assisted reaction that occurs quite easily with early transition metals. For example the Arrhenius activation energy for this reaction has been measured^{1a} to be as low as 6.6 kcal/mol. The generally accepted mechanism for olefin metathesis¹ involves the reaction of a metal alkylidene with an olefin to form a metallacyclobutane that then decomposes to generate a new olefin and a new alkylidene complex. If the metal-carbon π bond is considered to be at least partially covalent, then this is a thermal 2 + 2 reaction, predicted to be "forbidden" by orbital symmetry rules.²

In this study we consider the isomerization of the parent dichlorotitanacyclobutane to form an ethylenetitanium methylidene complex. Previous work³ has shown this chloride system to be a reasonable structural and energetic model of dicyclopentadienyltitanacyclobutane, a moderately active olefin metathesis catalyst.⁴ We present calculations⁵ characterizing the initial metallacycle and the final olefin methylidene complex as well as the transition state connecting them, demonstrating this reaction to have a very low barrier.

The geometry of the metallacycle is shown schematically in Figure 1a. The carbon-carbon bond distances (1.57 Å) are comparable to typical aliphatic carbon-carbon distances. The configuration at C₂ is nearly tetrahedral, but there are substantial departures from tetrahedral configurations at C₁ and C₃, with extremely small skeletal angles of 88.1°. The cyclopentadienyl analogue of this metallacycle, dicyclopentadienyltitanacyclobutane, displays a similar arrangement of bond lengths and angles at the carbon atoms.^{4b} Our calculated Ti-C bond lengths of 2.12 Å are also in good agreement with the observed 2.15 Å. The bonding interactions are as discussed previously.^{3a}

The product olefin methylidene complex is shown schematically in Figure 1c. The dichlorotitanium methylidene moiety is only weakly perturbed by the presence of the olefin from the configuration found previously to be optimum for the isolated alkylidene complex.^{3a} Principle differences arise from steric interactions between the chloride ligands and the olefin, as the chlorides bend substantially out of the titanium-methylidene plane. The olefin seeks to reduce its interaction with the methylene group, and assumes an asymmetric orientation, with the Ti-C₂ distance 0.1 Å greater than the Ti-C₃ distance. Similarly, the angle subtended by the C₁-Ti axis and the

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C_3 -Ti- C_2 bisector is about 96° . The ethylene unit itself is very weakly perturbed: it is essentially planar, and all bond distances and angles depart only slightly from the corresponding gas-phase values. The titanium-methylene bonding interaction is essentially unchanged from that of the dichlorotitanium methyldiene complex discussed elsewhere.^{3a}

From differences in total energies of the reactants and products and the calculated vibrational frequencies, we estimate the thermodynamics of the isomerization reaction to have a ΔH_{298} of +11.5 kcal/mol, a ΔS_{298} of +6.5 cal/(deg mol), and a ΔG_{298} of +9.6 kcal/mol. The relative stability of the metallacycle is consistent with the experimentally observed thermodynamic preference for the metallacycle in the dicyclopentadienyl analogue.⁴

Given the greater stability of the metallacycle, we would expect the transition state in the isomerization reaction to bear a resemblance to the olefin methyldiene complex, and indeed this is the case. The calculated transition state is shown schematically in Figure 1b. The only major differences between the product and the transition state appear in the position of the olefin atoms. The angle between the C_1 -Ti axis and the C_3 -Ti- C_2 bisector decreases in the transition state to 90° , the C_3 -Ti and C_2 - C_1 distances are significantly shorter (by 0.16 and 0.22 Å, respectively, relative to the product), and the C_2 -Ti and C_1 -Ti distances shorten only slightly (by 0.05 and 0.01 Å, respectively, relative to the product). Thus the reaction coordinate involves both a rotation of the olefin center of mass about the Ti atom away from C_1 and a rotation of the olefin about its center of mass. The energy change along this coordinate possesses a negative second derivative, and calculated gradients in the energy at the geometry shown are zero, identifying this as a saddle point.

(5) All of the calculations reported here were carried out by using Cartesian Gaussian basis sets. For both Cl^{50} and Ti, an effective potential was used to replace the core electrons. For geometry optimizations a (7s,4p/3s,2p) basis was used for carbon^{5c} and a (4s/2s) basis for hydrogen.^{5d} The carbon basis was augmented with a single set of d Gaussians ($\zeta = 0.75$) for a final set of calculations at the optimum geometries. For chlorine a valence minimum basis (3s,3p/1s,1p)^{5c} was used. For Ti, the core potential was obtained by using the method of Kahn.^{5e} A valence double ζ (3s,2p,4d/2s,2p,2d) basis^{5c} was used with this potential. Both Hartree-Fock (HF) and generalized valence bond (GVB)^{5f} wave functions were obtained during each step in the geometry optimization procedure. Near the reaction saddle point, however, a more general form of self-consistent wave function was used that allowed optimization of spin couplings as well.^{5g} Thermodynamic estimates were obtained by using the GVB orbitals as a basis for configuration interaction (CI) calculations.^{5h} The reactant, product, and transition-state geometries were optimized by calculating analytic first derivatives (with respect to coordinate variation) for the total Hartree-Fock energy, using the method of Dupuis and King.⁵ⁱ Second derivatives were estimated by constructing an approximate force constant matrix from molecular vibrational data and correcting it after each new test geometry via finite difference of analytic first derivatives, essentially as outlined by Schlegel.^{5j} (b) Rappé, A. K.; Smedley, T. A.; Goddard III, W. A. *J. Phys. Chem.* **1981**, *85*, 1662-1666. (c) Rappé, A. K.; Goddard III, W. A. In "Potential Energy Surfaces and Dynamics Calculations"; Truhlar, D. G., Ed.; Plenum Press: New York, 1981; pp 661-684. (d) Dunning, T., Jr.; Hay, P. J. In "Modern Theoretical Chemistry: Methods of Electronic Structure Theory"; Schaefer III, H. F., Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 1, p 1. (e) Hay, P. J.; Wadt, W. R.; Kahn, L. R. *J. Chem. Phys.* **1978**, *68*, 3059-3066. (f) Bobrowicz, F. W.; Goddard III, W. A. In "Modern Theoretical Chemistry: Methods of Electronic Structure Theory"; Schaefer III, H. F., Ed.; Plenum Press: New York, 1977; Vol. 3, Chapter 4, pp 79-127. (g) A computational procedure developed by F. W. Bobrowicz, based upon: Ladner, R. C.; Goddard III, W. A. *J. Chem. Phys.* **1969**, *51*, 1073-1087, and: Bobrowicz, F. W. Ph. D. Thesis, California Institute of Technology, 1974. (h) Total energies from configuration interaction calculations are as follows: metallacycle, -1884.0677; π complex, -1884.0534; transition state, -1884.0498; alkylidene + olefin, -1884.0344. (i) Dupuis, M.; King, H. F. *J. Chem. Phys.* **1978**, *68*, 3998-4004. Dupuis, M.; Rys, J.; King, H. F. *QCPE* **1981**, *13*, 403. (j) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214-218.

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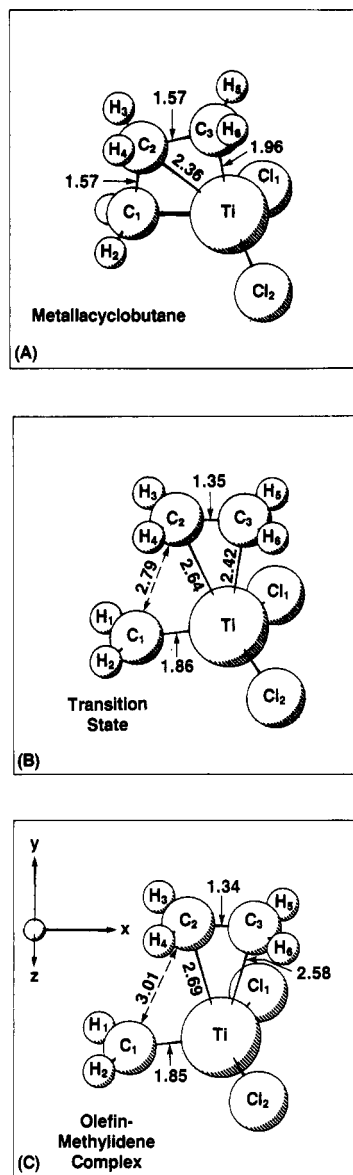
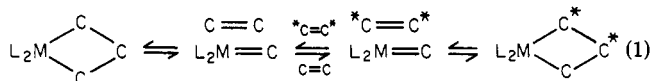


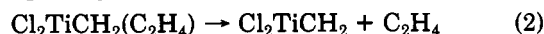
Figure 1.

The transition-state energetic minimum found here lies only 2.3 kcal/mol above the olefin methyldiene complex and is essentially degenerate with it after the zero point correction. The activation barrier for conversion of the metallacycle to the olefin methyldiene complex is thus equivalent to the thermodynamic difference of 11.5 kcal/mol.

For the metathesis process, the metallacycle is presumed to open into the π complex and subsequently exchange olefins as shown in eq 1. To address the kinetics of this



reaction, we have also carried out calculations measuring the binding energy of the olefin in the π complex (eq 2)

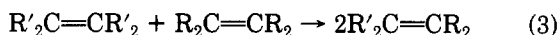


and obtain $\Delta H_{298} = 10.4$ kcal/mol. From a straightforward analysis of the kinetics of the metathesis reaction we conclude that the observed rate should reflect an activation enthalpy of approximately 21.9 kcal/mol (10.4 + 11.5 kcal/mol). Experimentally, the irreversible reaction of a *β*-*tert*-butyldicyclopentadienyltitanacyclobutane with di-

phenylacetylene has been found to possess an activation enthalpy of 26.9 kcal/mol,^{4d} qualitatively consistent with our results. Alternatively, the measured activation energy could be associated with a rate-limiting conversion of the metallacycle to the π complex, which would only be valid if the barrier for the reverse reaction (π complex to metallacycle) is similar in magnitude to the olefin binding energy (~ 10 kcal/mol). This interpretation is inconsistent with our calculated barrier (~ 0 kcal/mol) but leads to relative thermodynamic placements of the metallacycle and π complex similar to those presented here (eq 2). Finally, an associative mechanism (where both olefins are bound to the alkylidene complex) is possible for our coordinatively unsaturated dichloro complex (the bis(olefin) complex would be a 12-electron system) and in fact has a barrier lower than the dissociative mechanism described above (~ 10 kcal/mol lower). This associative mechanism is not likely for the experimental dicyclopentadienyl system as the bis(olefin) complex would be a 20-electron system (barring cyclopentadienyl ring slippage) but is possible for other highly coordinately unsaturated systems.

Hoffmann and co-workers⁵ have studied the olefin metathesis reaction pathway using the extended Hückel method. The set of complexes they examined included $\text{Cp}_2\text{Ti}(\text{CH}_2)(\text{C}_2\text{H}_4)$, for which they obtained results diametrically opposed to other theoretical work,³ experiment,⁴ and the work reported here. Specifically, they find the metallacyclobutane substantially less stable than the olefin methylenide complex (by approximately 20 kcal/mol). Further, they find the global potential energy surface minimum to be associated with a geometry close to that found here for the saddle point. This minimum was found to be approximately 6 kcal/mol below the olefin methylenide complex. A point of agreement common to our work, experiment, and Hoffmann and co-workers is that the observed barrier should be small.

The extension of the above results to olefin metathesis (eq 3) in general is straightforward. As discussed above



we find this process to have a very low kinetic barrier. As noted previously^{3a,4} the difficulty for titanium systems is the thermodynamic instability of titanium methylenide complexes. For Cr, Mo, and W oxo dichloride methylenide systems, with appropriate cocatalysts, the thermodynamics are balanced.⁷ The activation energetics presented here suggests that these Cr, Mo, and W oxo systems will be quite active catalysts with small kinetic and thermodynamic barriers. Thus, our theoretical results are in agreement with the experimental evidence from the Schrock group.⁸

Registry No. $\text{Cl}_2\text{TiCH}_2(\text{C}_2\text{H}_4)$, 91158-49-5; dichlorotitanacyclobutane, 79953-32-5; dicyclopentadienyltitanacyclobutane, 80122-08-3.

Supplementary Material Available: Details of computational procedures employed to obtain complex geometries and thermodynamic data (2 pages). Ordering information is given on any current masthead page.

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"Open Cobaltocene" Chemistry. The Dimerization of Bis(2,4-dimethylpentadienyl)cobalt

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Summary: The reaction of cobaltous chloride with 2 equiv of the 2,4-dimethylpentadienyl anion ($2,4\text{-C}_7\text{H}_{11}^-$) leads to a dimeric product in which each cobalt atom is coordinated by an $\eta^5\text{-2,4-C}_7\text{H}_{11}$ ligand and by an $\eta^4\text{-buta-1,3,7,9-decatetraene}$ portion of half a bridging 2,4,7,9-tetramethyl-2,4,6,8-decatetraene ligand, which was formed by the intermolecular coupling of two $2,4\text{-C}_7\text{H}_{11}$ ligands. The coupled ligand is unusual in that an isomerization from a 1,3,7,9-decatetraene ligand seems to have taken place.

We have recently shown that the pentadienyl ligand forms a wide range of stable compounds with transition metals.² Of initial interest have been the bis(pentadienyl)metal complexes, wherein the metal may be titanium, vanadium, chromium, iron, or ruthenium, and a wide range of structural, spectroscopic, chemical, and theoretical studies have now been reported for these "open metallocenes".^{2,3} As all of the above compounds possess electron configurations in the range of 14-18 (less than or equal to the noble-gas configuration), it was clearly of interest to investigate the nature of "open metallocenes" formally having even greater electron counts.⁴

The reaction of cobaltous chloride with 2 equiv of the 2,4-dimethylpentadienyl anion in THF at -78°C leads to the formation of a deep red-brown solution, which seems to initially contain monomeric bis(2,4-dimethylpentadienyl)cobalt.⁵ On standing at low temperature, however, slow deposition of a less soluble material takes place, occasionally yielding a homogeneous crop of small crystalline material in yields of up to 80%. Initial analytical and mass spectral data suggested a dimeric formulation,⁷ $[\text{Co}(\text{C}_7\text{H}_{11})_2]_2$, which was ultimately confirmed

(1) NSF Predoctoral Fellow, 1980-1983.

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(4) This, of course, assumes that both ligands are η^5 bound, which may not be the case.

(5) (a) The monomeric species may well contain one η^5 and one η^3 -pentadienyl ligand.⁶ (b) Treatment of the initial solution with ferricinium tetrafluoroborate led to a yellow-orange product, insoluble in pentane but soluble in THF and methylene chloride. A mass spectrum indicated the expected $\text{Co}(\text{C}_7\text{H}_{11})_2\text{BF}_4$ composition. A single-crystal X-ray diffraction study was undertaken^{6c} and the cobalt atom and BF_4^- unit were readily located. It appeared that two 2,4-dimethylpentadienyl ligands were present, but these were badly disordered. Attempts are being made to prepare this cation as a salt with other anions. (c) Hutchinson, J. P.; Wilson, D. R.; Ernst, R. D., unpublished results.

(6) (a) It can be noted that $(\text{C}_5\text{H}_5)_2\text{Cr}(\text{C}_8\text{H}_8)$ has been formulated as a 17-electron complex with an $\eta^3\text{-C}_8\text{H}_8$ ligand,^{6b} while $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{C}_8\text{H}_8)$ is a 17-electron complex with an $\eta^3\text{-C}_8\text{H}_8$ ligand.^{6c} (b) Müller, J.; Menig, H. *J. Organomet. Chem.* **1975**, *96*, 83. (c) Van Oven, H. O.; de Liefde Meijer, H. J. *Ibid.* **1969**, *19*, 373.

(7) (a) Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{Co}$: C, 67.46; H, 8.90. Found: C, 66.71; H, 9.11. (b) In addition to the expected parent ion (m/e 498, relative abundance = 3%), other expected fragments were observed, e.g., Co (59, 12%), C_7H_{11} (95, 29%), and $(\text{C}_7\text{H}_{11})_2$ (190, 20%). A monomeric fragment (m/e 249) was not observed. (c) The crude dimer solutions react cleanly with potential ligands such as phosphites to yield good yields of the appropriate ligand adducts of mono(2,4-dimethylpentadienyl)cobalt.