

In the preparation of the γ -hydroxamic acid **8a** from the anhydride, it was desirable to minimize the formation of the corresponding α -hydroxamic acid. Nucleophiles are known to attack almost exclusively at the γ -carbonyl of *N,N*-phthaloylglutamic anhydride,¹¹ presumably for steric reasons. However, the phthaloyl protecting group could not be employed since conditions used for its incorporation into β -chloroglutamate led to elimination of HCl.¹² Consequently, model studies were undertaken to examine steric and electronic aspects of attack by several nucleophiles on various *N*-protected glutamic anhydrides. The reactions of *N*-(triphenylmethyl)- or *N*-Boc-glutamic anhydride with NH_2OH , $\text{NH}_2\text{OCH}_2\text{Ph}$, or NH_2OCPh_3 under a variety of temperature and solvent conditions yielded unacceptable mixtures of α and γ isomers. The reaction of the Boc-anhydride with PhSH/NEt_3 in THF, followed by NH_2OH ,¹³ proceeded with a high degree of preference for the desired γ -hydroxamic acid; however, these conditions were too severe for the corresponding Boc- β -chloroglutamic anhydride, even at lower temperatures and when NEt_3 was replaced by the more hindered $\text{NEt-}i\text{-Pr}_2$. On the basis of a hypothesis that an anionic nucleophile had a stronger preference for the γ rather than the α carbonyl,¹⁴ a charged nucleophile which also would be a good leaving group for displacement by NH_2OH was sought. The lithium salt of *N*-hydroxyphthalimide (**12**) was found to be quite effective and showed an overwhelming preference for attack at the γ -carbonyl moiety of Boc- and Cbz-protected anhydrides. Furthermore, the product of this reaction (**7**) could be smoothly converted to the γ -hydroxamic acid with aqueous hydroxylamine. Analogous reactions with *N*-hydroxyphthalimide or PhSLi in place of **12** were less satisfactory. Thus, the reaction of **6a** with **12** in THF at -30 to -50 °C led to precipitation of **7**, which was not purified but was treated directly with a concentrated (~ 4 M) aqueous solution of hydroxylamine at pH 6 to afford **8a-NH₂OH**^{7d} (mp 123.5–125 °C (dec)), which precipitated from the reaction mixture, and **8a-DCHA**^{7e} (mp 119–120 °C (dec)), obtained after extractive workup followed by addition of DCHA, in a 66% combined overall yield from **6a**. The salts of **8a** were allowed to cyclize (NEt_3 , pH 11, room temperature) via the free acid to Cbz-tricholomic acid (**9a**) (foam; DCHA salt,^{7f} mp 163–168 °C (dec)), which was treated with diphenyldiazomethane¹⁵ to afford **10a**^{7g} (foam; 74%, after chromatography, from **8a** salts).

The diastereomeric (*L-threo*) diprotected tricholomic acid **10b** was prepared from the anhydride **6b** by the same series of reactions as for the natural isomer except that the conversions were performed on unpurified or partially purified (i.e., extractive workup) intermediates because of the failure of intermediates **7b** and **8b-NH₂OH** to precipitate from the reaction mixtures. The overall yield for the four steps leading to pure **10b**^{8e} (mp 161–162 °C) after chromatography was 46%. For analytical purposes, **8b** was characterized as the DCHA salt^{8d} (mp 147–149 °C (dec)).

The natural diprotected tricholomic acid **10a** was converted to **11a**^{7h} (mp 113–115 °C) with excess dichlorotris(dimethylamino)phosphorane¹⁵ in refluxing THF¹⁶ in a 54% purified yield. Removal of the Cbz and benzhydryl protecting groups was effected simultaneously in trifluoroacetic acid containing 8 equiv of thioanisole¹⁷ to afford natural **1a** (87%) which was in all respects identical with the natural material.¹⁸ Unnatural **1b**^{8g} was prepared

from **10b** in an analogous fashion in a 57% yield for the last two steps. The integrity of the chiral centers at each major stage in the syntheses and the stereospecificity of the isoxazole ring-forming reactions were demonstrated by deprotection followed by high-voltage paper electrophoresis (pH 1.9, 4.2 kV) of the resulting amino acids, which showed that pertinent intermediates were free from diastereomeric impurities.

The synthesis of **1a** reported here was carried out in eight steps from **4a** in a 17% overall yield (**1b** from **4b**, 15%).¹⁹ Moreover, the required starting materials and reagents are commercially available or readily prepared, and most are quite inexpensive, especially in the early stages of the synthesis. The procedural manipulations are simple and three of the reactions are carried out in aqueous media; only one step from **4**, the formation of **10a**, requires chromatography.

Acknowledgment. We are grateful to Dr. David G. Martin (Upjohn Co.) for a generous donation of natural AT-125 (U-42,126), to Dr. Wendell Wierenga (Upjohn Co.) for experimental details of certain related reactions, and to the National Institutes of Health (Grant CA 21156) and the Research Corp. for financial support.

(18) The synthetic material was identical with AT-125 (kindly donated by Dr. David Martin of Upjohn Co.) by NMR, IR, MS, ORD, high-voltage electrophoresis, and TLC (20:5:1 MeOH/H₂O/pyridine); $[\alpha]_D^{25} +148^\circ$ (*c* 8.45 mg/mL, H₂O). For **1b**: IR (KBr) 891, 1363, 1395, 1515, 1590, 1605 cm^{-1} ; $[\alpha]_D^{25} -109^\circ$ (*c* 11.2 mg/mL, H₂O).

(19) Unless otherwise noted, satisfactory analyses for all elements except O were obtained for the following compounds: **4a**, **5a**, **6a**, **8a-NH₂OH-H₂O**, **10a**, **11a**, **1b**, **4b**, **5b**, **6b**, **8b-DCHA** (H, N, Cl), **10b**, **11b**.

Structures of Titanacyclobutanes

J. Bosco Lee, Gregory J. Gajda, William P. Schaefer, Thomas R. Howard, Takao Ikariya, Daniel A. Straus, and Robert H. Grubbs*

Contribution No. 6483 from the Laboratories of Chemistry
California Institute of Technology
Pasadena, California 91125

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It has become apparent that the fundamental step of olefin metathesis¹ and other related catalytic reactions² involves equilibration between metal-alkylidene and metallacyclobutanes.³⁻⁵ Although many of the structural features of metal-alkylidene species are established,³ similar data are not available for metallacyclobutanes which undergo this important reaction. Two important structural parameters relating to catalytic reactions are the conformation of the ring and the ease of distorting the ring toward potential reactive intermediates. The degree of puckering

(1) Grubbs, R. H. *Prog. Inorg. Chem.* **1979**, *24*, 1. Grubbs, R. H.; Hoppin, C. *J. Am. Chem. Soc.* **1979**, *101*, 1499.

(2) Metallacyclobutanes have also been invoked as key intermediates in hydrocarbon cracking and isomerization reactions and olefin polymerization. Dartigues, J. M.; Chambellan, A.; Gault, F. G. *J. Am. Chem. Soc.* **1976**, *98*, 856. Foger, K.; Anderson, J. R. *J. Catal.* **1978**, *54*, 318. Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604. Parshall, G. W.; Herskovitz, T.; Tebbe, F. N.; English, A. D.; Zeile, J. V. In "Fundamental Research in Homogeneous Catalysis"; Tsutsui, M., Ed.; Plenum Press: New York, 1979; Vol. 3.

(3) (a) Wengrovius, J. H.; Schrock, R. R.; Churchill, M. R.; Wissert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515. (b) Schrock, R. R.; Rocklage, S.; Wengrovius, J. H.; Rupprecht, G.; Fellman, J. *J. Mol. Catal.* **1980**, *8*, 73.

(4) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Tebbe, F. N.; Parshall, G. W.; Ovenall, D. W. *Ibid.* **1979**, *101*, 5074. (c) Tebbe, F. N.; Harlow, R. L. *Ibid.* **1980**, *102*, 6151.

(5) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. This reaction has been found to be very general.

(11) (a) King, F. E.; Kidd, D. A. *J. Chem. Soc.* **1949**, 3315–3319. (b) King, F. E.; Jackson, B. S.; Kidd, D. A. *Ibid.* **1951**, 243–246.

(12) *L-threo-N,N*-Phthaloyl- β -(mesyloxy)- γ -(hydroxamido)glutamic acid also has been shown to cyclize nonstereospecifically to a mixture of diastereomers of *DL-N,N*-phthaloyltricholomic acid: Wierenga, W., private communication.

(13) Wieland, T.; Weidenmüller, H. L. *Justus Liebigs Ann. Chem.* **1955**, *597*, 111–122.

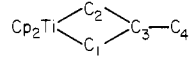
(14) When *erythro-N*-Boc- β -chloroglutamic anhydride was treated with PhSH followed by NH_2OCPh_3 , and deprotected, a 1:1 mixture of γ -hydroxamate/ α -hydroxamate was obtained; when $\text{PhSH}/\text{NEt-}i\text{-Pr}_2$ was used, no α -hydroxamate was observed, but the yield of γ -hydroxamate was low.

(15) Appel, R.; Schöler, H. *Chem. Ber.* **1977**, *110*, 2382–2384.

(16) Experimental details for a related reaction were kindly provided to us by Dr. W. Wierenga of Upjohn Co., for which we are very grateful.

(17) Kiso, Y.; Ukawa, K.; Akita, T. *J. Chem. Soc., Chem. Commun.* **1980**, 101–102.

Table I. Selected Bond Angles and Distances for Metallacycles of General Type

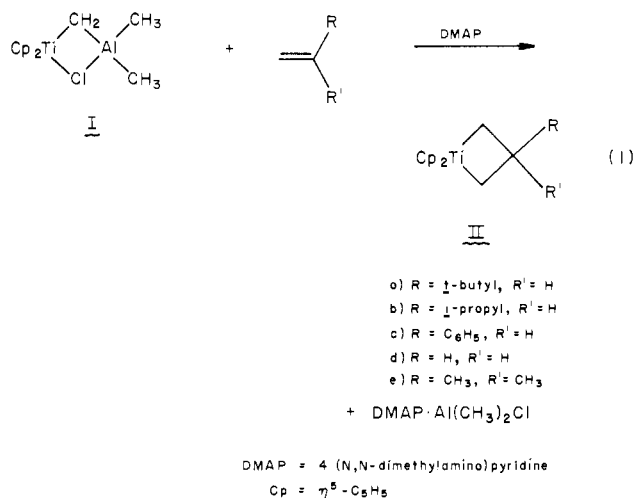


	IIa	IIc	IIe
Bond Angles (deg)			
C ₁ -Ti-C ₂	75	75.3 (1)	74.8 (3)
Ti-C ₁ -C ₃	84	86.0 (2)	87.2 (4)
Ti-C ₂ -C ₃	85	85.7 (2)	87.0 (4)
C ₂ -C ₃ -C ₁	116	112.0 (3)	110.9 (6)
C ₁ -C ₃ -C ₄	118	115.9 (3)	108.9 (6)
			[110.3 (6)] ^a
C ₂ -C ₃ -C ₄	115	109.1 (3)	111.4 (6)
			[108.3 (6)] ^a
Bond Distances (Å)			
Ti-C ₁	2.16	2.127 (3)	2.138 (8)
Ti-C ₂	2.14	2.113 (4)	2.152 (7)
C ₁ -C ₃	1.55	1.546 (5)	1.59 (1)
C ₂ -C ₃	1.53	1.579 (5)	1.58 (1)
C ₃ -C ₄	1.52	1.521 (5)	1.51 (1)
			[1.55 (1)] ^a
Ti-C(η ⁵)	2.07-2.51	2.36-2.40	2.38-2.44

^a Corresponding value for the second methyl group.

of the ring is important since several stereochemical models⁶ have been advanced to explain the moderate stereospecificity⁷ observed in the metathesis of acyclic olefins. The central argument in these proposals is the conformational preference of the presumed metallacyclobutane intermediate. This assumption is largely based on the structural data from a series of stable platinumacyclobutanes where puckering of the metallacyclic ring has been reported.⁸ Unfortunately, these systems do not engage in metathesis.

Recently we reported the isolation of a metallacyclobutane II from the reaction of a well-defined metal-alkylidene metathesis catalyst I with terminal olefins and demonstrated that such intermediates take part in metathesis reactions (eq 1).⁵



A detailed structural analysis of this intermediate is indispensable for the understanding of metathesis¹ and related catalytic reactions. In this Communication we report the X-ray crystallographic studies on three such complexes, IIa, IIc, and IIe,⁹ and

(6) (a) Katz, T. J. *Adv. Organomet. Chem.* **1977**, *16*, 283. (b) Katz, T. J.; McGinnis, J. L. *J. Am. Chem. Soc.* **1975**, *97*, 1592. (c) Casey, C. P.; Albin, L. D.; Burkhardt, T. J. *Ibid.* **1977**, *99*, 2533. (d) Casey, C. P.; Tuinstra, H. E. *Ibid.* **1978**, *100*, 2270. (e) Leconte, M.; Bassett, J. M. *Ibid.* **1979**, *101*, 7296.

(7) (a) Wang, J.; Menapace, H. R. *J. Org. Chem.* **1968**, *33*, 3794. (b) Hughes, W. B. *Chem. Commun.* **1969**, 431. (c) Bassett, J. M.; Bilhou, J. L.; Mutin, R.; Theolier, A. *J. Am. Chem. Soc.* **1975**, *97*, 7376.

(8) (a) Gillard, R. D.; Keeffon, M.; Mason, R.; Pilbrow, M. F.; Russell, D. R. *J. Organomet. Chem.* **1971**, *33*, 247. (b) Yarrow, D. J.; Ibers, J. A.; Lenarda, M.; Grazini, M. *Ibid.* **1974**, *70*, 133.

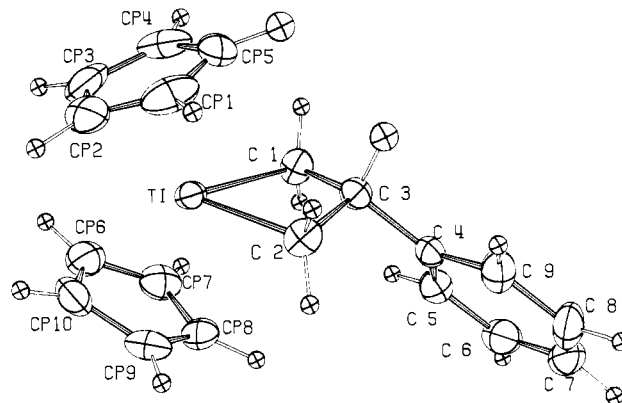


Figure 1. ORTEP drawing of the molecular structure of complex IIc.

Table II. ¹³C Chemical Shifts (ppm)^a

	T, °C	C ₁	C ₃	C ₂	δ C ₂
IIa	25	67.954	18.695	67.954	
IIa-d ₂		67.163	18.452	68.014	0.060
IIc	-10	73.861	11.708	73.861	
IIc-d ₂		<i>b</i>	11.405	73.982	0.121
IId	0, -70	76.671	-11.633	76.671	
IId-d ₂		75.913	-11.896	76.716	0.045

^a Chemical shifts relative to benzene-d₆ (128.0 ppm) for IIa and toluene-d₈ (137.5 ppm) for IIc and IId. Experimental error ±0.007 ppm and ±0.9 Hz. ^b Not observed due to low solubility.

the solution structure of IIa, IIc, and IId as determined through deuterium isotope effects on ¹³C chemical shifts.

The molecular structure of IIc is shown in Figure 1 with selected bond angles and distances listed for all three compounds in Table I. Although difficulty was encountered in the refinement of the structure of IIa due to disorder,¹¹ the data are included for comparison.

It is interesting to note that despite the asymmetry at the C(3) position, the metallacyclic ring is nearly planar. This is evident in the displacement of C(3) from the plane defined by C(1)-Ti-C(2), 0.09 Å, 0.05 Å (3.25° displacement), and less than 0.01 Å for IIa, IIc, and IId, respectively. It appears that in both monosubstituted structures, the R (*tert*-butyl or phenyl)-Cp interaction is being relieved by a rocking motion of the C(3) fragment in the plane instead of puckering. The factors governing this choice are not apparent. The question of the symmetry of the metallacyclic plane is more subtle. The difference between

(9) Crystal data: Complex IIa, space group P3₁12 with *a* = 25.108 (18) Å and *c* = 6.222 (7) Å; cell volume 3394 (5) Å³ with 9 molecules in the cell, formula weight 276.28, ρ(calcd) = 1.21 (2) g/cm³. Most work was done for a cell with *a* = 14.496 (10) Å, *c* = 6.222 (7) Å, and volume = 1131 (2) Å³, with 3 molecules in the cell of symmetry P3₁21. Complex IIc, space group P2₁/c with *a* = 6.153 (1) Å, *b* = 14.294 (7) Å, *c* = 17.449 (10) Å, and β = 107.81 (2)°; cell volume 1463 (1) Å³ with 4 molecules in the cell, formula weight 296.27, ρ(calcd) = 1.36 (1) g/cm³. Diffraction data (IIa: 2065 reflections with 1623 > 0, 747 reflections in the smaller cell with 685 > 0; IIc: 1931 reflections with 1783 > 0) were collected at room temperature on a Syntex P2₁ diffractometer using monochromatized Mo Kα radiation. Data were corrected for Lorentz and polarization factors and the structures were solved by a combination of Patterson and structure factor difference Fourier techniques. IIa could not be refined by least squares because of disorder.¹¹ Fourier refinement led to a model with a final *R* index of 0.172 and a goodness of fit of 5.7 (*R* = Σ||F_o - |F_c||/Σ|F_o|; GOF = [Σw(F_o² - |F_c²)²/(N_o - N_p)]^{1/2}, where N_o = 757 and N_p = 75). Full-matrix least-squares refinement of IIc led to a final *R* index of 0.056 [0.036 for data with F_o² > 3σ(F_o²)] and GOF = 1.32 for 1931 data and 181 parameters.

(10) Complex IIe, space group P2₁2₁2₁ with *a* = 7.918 (3) Å, *b* = 9.141 (3) Å, and *c* = 18.133 (6) Å; cell volume = 1312 (2) Å³ with 4 molecules in the cell, formula weight 248.23, ρ(calcd) and 1.261 (1) g/cm³. Full-matrix least-squares refinement of IIe (using computer-generated hydrogen positional parameters) led to a final *R* index of 0.065 [0.042 for data with F_o² > 3σ(F_o²)] and a GOF = 1.32 for 1004 data and 145 parameters.

(11) There is a twofold disorder of the cyclopentadienyl groups about the axis between them and the titanium atom, a twofold disorder of the metallacyclic ring, and an additional twofold disorder (at least) of the *tert*-butyl group in the small cell. We could not resolve these disorders in the large cell.

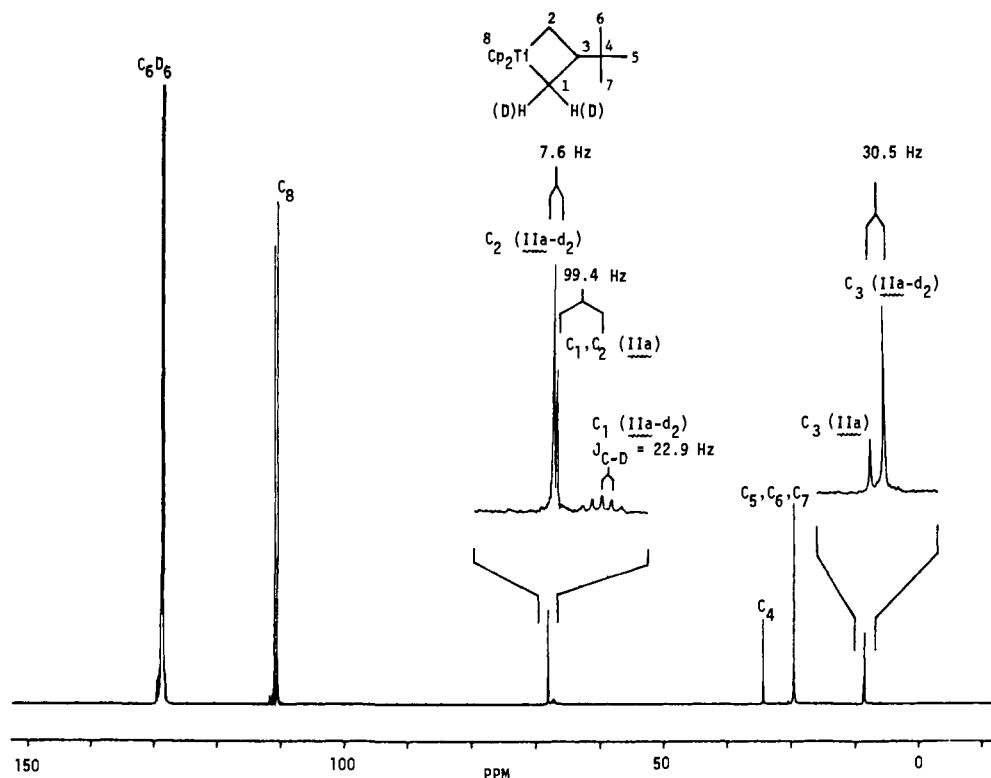
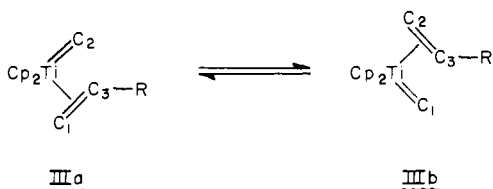


Figure 2. 125.7-MHz ^{13}C NMR spectrum of a 4:1 mixture of IIa-d_2 and IIa at 25°C in benzene- d_6 .

the two independent titanium-carbon distances in IIc is 0.014 \AA while the $\text{C}(1)\text{-C}(3)$ and $\text{C}(2)\text{-C}(3)$ distances differ by 0.033 \AA and the internal angles $\text{Ti-C}(1)\text{-C}(3)$ and $\text{Ti-C}(2)\text{-C}(3)$ are identical. The bond length differences appear to be outside experimental error and may suggest a slight distortion. Complex IIe does not show significant distortion from C_{2v} symmetry. If indeed the metal-alkylidene-olefin structures, IIIa and IIIb , are



important as recent calculations¹² and the reactivity of the complexes suggest,¹³ a highly distorted metallacycle would be expected. This does not seem to be the case. Compound IIc probably represents a limiting case since conjugation is increased in structure III . The ^{13}C NMR studies that follow probe this question further.

Deuterium isotope effects on carbon chemical shifts have been used as a tool for the determination of solution structures.¹⁴ Saunders and co-workers¹⁵ have presented a criterion, based on the relative isotopic splitting, δ/Δ ,¹⁶ for differentiating symmetrical molecules from systems that are asymmetrical but appear symmetrical on the NMR time scale due to rapid degenerate rearrangement. They propose that the relative splitting is much greater for equilibrium processes than for resonance phenomena. If the titanacycles presented here were in fact rapidly equilibrating alkylidene-olefin complexes, deuteration of one of the α carbons

should lift this degeneracy and result in a significant shift of the ^{13}C resonance of the other α carbon. Consequently, labeled ($\alpha,\alpha\text{-d}_2$) IIa,c,d were prepared and their ^{13}C NMR spectra were measured.¹⁷ The results are collected in Table II. In the ^{13}C NMR spectrum (Figure 2) of a 4:1 mixture of IIa-d_2 and IIa ,¹⁸ the deuterium-labeled carbon (C_1) appears as a 1:2:3:2:1 quintet ($J_{\text{C-D}} = 22.9 \text{ Hz}$), 99.4 Hz (0.791 ppm) upfield from the corresponding resonance of the nondeuterated complex. An interesting finding is the resonance for C_2 of IIa-d_2 , which appears 7.6 Hz (0.060 ppm) downfield from the corresponding resonance of IIa . Similar downfield shifts were also observed for C_2 of IIc-d_2 and IId-d_2 . The other carbon shifts show the normal intrinsic isotope effect.¹⁹ The splitting, δ , in these systems ranges from 0.045 ppm for IId-d_2 to 0.121 ppm for IIc-d_2 (the structure which shows some distortion). The expected (or static) shift, Δ , is estimated from a series of known metal-alkylidene complexes (groups 4 and 5) and the only known group 4 ethylene complex²⁰ to be $\sim 100 \text{ ppm}$. Thus we obtain δ/Δ to be of the order of $10^{-3}\text{-}10^{-4}$ for these titanacycles. Rather large changes in Δ will have a small effect on this relative splitting. Previously reported¹⁵ symmetrical allyl cation systems have values of 10^{-3} while unsymmetrical systems are near 10^{-1} . The allyl cations serve as excellent models for the deuterium shifts in these cases. The above observations are consistent with a symmetric but easily distorted metallacycle structure.

These structural studies suggest that metallacyclobutanes involved in metathesis may be planar and symmetrical. If this is

(17) $^{13}\text{C}\{^1\text{H}\}$ spectra were obtained on a Bruker WM-500 spectrometer operating at 125.7 MHz ; probe temperatures were measured to $\pm 1^\circ\text{C}$ with a thermocouple.

(18) Nondeuterated complex was added as an internal reference.

(19) The decomposition of IIa-d_2 through the carbene-olefin complex shows a large secondary isotope effect favoring the formation of protio-metal-methylene products.¹³ If, deuteration distorts the metallacycle toward the carbene-olefin structure, the nondeuterated carbon should become more carbenoid and hence be shifted downfield.¹⁸

(20) (a) $\text{Cp}_2\text{Ta}(\text{CH}_2)(\text{CH}_3)$, ^{13}C δ 228; $\text{Cp}_2\text{Ta}(\text{CH}_2\text{AlMe}_3)(\text{CH}_3)$, δ 177; Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389. (b) $\text{Cp}_2\text{TiCH}_2\text{AlClMe}_2$, δ 188; $\text{Cp}_2\text{TiCH}_2\text{AlMe}_3$, δ 204; ref 4a. (c) $(\text{Cp}_2\text{TiCH}_2)_2$, δ 236; Ott, K. C.; Grubbs, R. H., *J. Am. Chem. Soc.* **1981**, *103*, 5922. (d) $\text{Cp}_2^*\text{Ti}(\text{C}_2\text{H}_4)$, δ 105; Cohen, S.; Bercaw, J. E., private communication, [$\text{Cp}^* = \eta^5\text{-}(\text{CH}_3)_5\text{C}_5\text{H}_5$].

(12) Eisenstein, O.; Hoffmann, R.; Rossi, A. R. *J. Am. Chem. Soc.* **1981**, *103*, 5582. However, a second calculation shows a symmetrical structure. Rappé, T.; Goddard, W. A., private communication.

(13) Lee, J. B.; Grubbs, R. H., unpublished results.

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

(15) (a) Saunders, M.; Telkowsi, L.; Kates, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 8070. (b) Saunders, M.; Kates, M. R. *Ibid.* **1977**, *99*, 8071. (c) Saunders, M.; Kates, M. R.; Wiberg, K. B.; Pratt, W. *Ibid.* **1977**, *99*, 8072.

(16) δ is the isotope splitting and Δ the chemical shift difference estimated for the static equilibrium.

the case, the source of stereoselection in olefin metathesis may result from factors other than those arising from the conformational effects due to puckering of the intermediate. In this titanium system, the symmetrical metallacyclobutane appears to rest at the minimum of a broad potential surface, such that distortion toward the required transition state for metathesis is facile.

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Supplementary Material Available: Atomic coordinates, thermal parameters, and structure factors for compounds IIc and IIe (19 pages). Ordering information is given on any current masthead page.

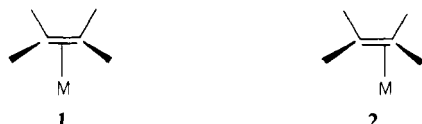
Reactivity of Distorted $C_5H_5Fe(CO)_2$ (olefin) Cations toward Nucleophilic Attack

T. C. T. Chang, Bruce M. Foxman,* M. Rosenblum,* and C. Stockman

Department of Chemistry, Brandeis University
Waltham, Massachusetts 02254

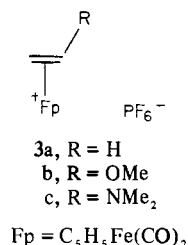
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It has recently been suggested that endogenous activation of metal-complexed olefins for nucleophilic attack is derived from displacement of the metal fragment, in the course of reaction, toward one end of the olefin ($1 \rightarrow 2$). Calculations show that



such a deformation leads to stabilization and increased localization of the fragment ligand LUMO ($\pi^* - \lambda b_2$) through its interaction with the olefin π orbital.¹ The results of these changes is to greatly increase the overlap population associated with the interaction of the nucleophile orbital and the olefin-centered LUMO.

Complexes whose *ground-state* structures are distorted, as in **2**, might therefore be expected to exhibit enhanced reactivity, in the absence of compensating factors. The crystal structures of two such distorted complexes (**3b** and **3c**) together with a com-



parison of their reactivities and that of the undistorted parent complex **3a** with the comparatively soft nucleophile Fp (η^1 -allyl)² (**4**) are now reported.

The preparation of Fp(vinyl ether)PF₆ complexes has previously been described.³ The vinylamine complex (**3c**) is readily obtained

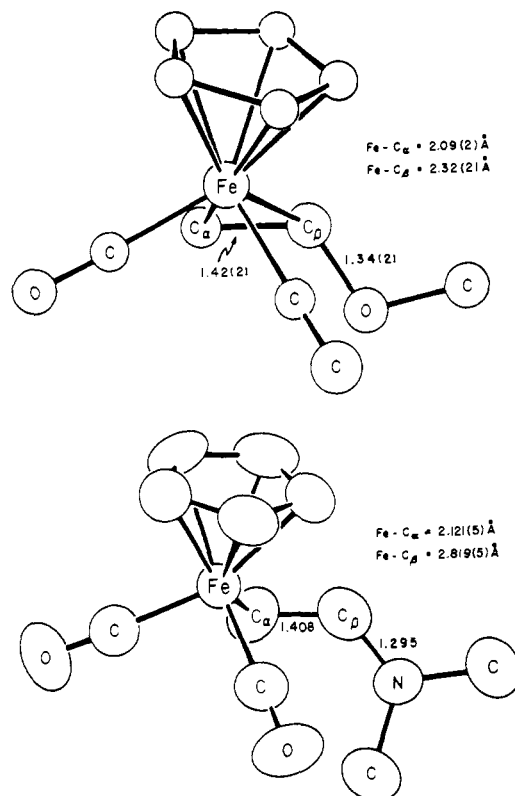


Figure 1. Molecular structures: (top) $[(\eta^5-C_5H_5)Fe(CO)_2-(CH_2CHOCH_3)]$ cation (**3b**); (bottom) $[(\eta^5-C_5H_5)Fe(CO)_2(CH_2CHN(CH_3)_2)]$ cation (**3c**).

from **3b** by treatment with excess dimethylamine in ether (30 °C, 10 min, then 25 °C, 10 min). The product is filtered and recrystallized from Et₂O-CH₂Cl₂ to give **3c** as yellow crystals, dec 158 °C (94%).⁴ Complex **3b** forms as monoclinic crystals, with $a = 13.494(4)$ Å, $b = 7.539(2)$ Å, $c = 16.501(5)$ Å, $\beta = 121.09(4)^\circ$, $Z = 4$, $\rho_{\text{calcd}} = 1.76 \text{ g}\cdot\text{cm}^{-3}$, $\rho_{\text{obsd}} = 1.78 \text{ g}\cdot\text{cm}^{-3}$ ($\lambda(\text{MoK}\alpha) = 0.71073$ Å). The complex occupies a $2a$ site in space group $C2/m$, requiring disorder of the cation. Full-matrix least-squares refinement of positional and thermal parameters for all nonhydrogen atoms using 1620 data for which $|F_o| > 3.92\sigma(|F_o|)$ led to $R = \sum(|F_o| - |F_c|)/\sum|F_o| = 0.080$. Crystals of complex **3c** belong to the monoclinic system, space group $P2_1/n$ with $a = 7.447(2)$ Å, $b = 25.642(6)$ Å, $c = 8.293(2)$ Å, $\beta = 100.11(3)^\circ$, $Z = 4$, and $\rho_{\text{calcd}} = 1.67 \text{ g}\cdot\text{cm}^{-3}$ ($\lambda(\text{MoK}\alpha) = 0.71073$ Å). Full-matrix least-squares refinement of positional and anisotropic thermal parameters for all nonhydrogen atoms using 1897 data for which $|F_o| > 3.92\sigma(|F_o|)$ gave $R = 0.048$.

Inspection of Figure 1 indicates that the ligand in the vinyl ether complex **3b** is an unsymmetrically bound η^2 -olefin, while the ligand in the vinylamine complex **3c** is more nearly σ bonded, its geometry closely approximating that expected for an iminium ion, with a C=N length of 1.295 (7) Å. Despite the long Fe-C_β distance (2.819 (5) Å), it is likely that this complex retains some η^2 -olefinic character.⁵ This is clearly evidenced by the short C_α-C_β bond length (1.408 (8) Å)⁶ and by the Fe-C-C-N torsion angle of 102.3°, which is indicative of interaction⁷ between the Fe-C_α σ

(4) IR (KBr) 2020, 1975, 1645 cm⁻¹; NMR (CD₃NO₂) δ 8.0 (t, 1, CHNMe₂), 5.25 (s, 5, Cp), 3.5, 3.1 (2 s, 6, NMe₂), 2.05 (d, 2, J = 9 Hz, FpCH₂). The BF₄⁻ salt has been analyzed. Anal. Calcd for C₁₁H₁₄BF₄FeO₂N: C, 39.40; H, 4.19; N, 4.18. Found: C, 39.26; H, 4.23; N, 4.12. Madhavarao, M. Ph.D. Thesis, Brandeis University, 1977.

(5) A similar interaction has been observed and discussed previously in $[(\eta^5-C_5H_5)Fe(CO)_2(CH_2COOH)]_2$, where the Fe-C_β distance is 2.85 (2) Å: Ariyaratne, J. K. P.; Bierrum, A. M.; Green, M. L. H.; Ishaq, M.; Prout, C. K.; Swanwick, M. G. *J. Chem. Soc. A* 1969, 1309.

(6) It would appear that the C_α-C_β and C-N bond lengths are indicative of 50% double-bond character in each of these bonds: (a) Ammon, H. L. *Acta Crystallogr., Sect. B* 1974, B30, 1731. (b) Lubke, B.; Behrens, U. *J. Organomet. Chem.* 1978, 149, 327.

(1) Eisenstein, O.; Hoffmann, R. *J. Am. Chem. Soc.* 1980, 102, 6148.
(2) Lennon, P. J.; Rosan, A.; Rosenblum, M.; Tancredi, J.; Waterman, P. *J. Am. Chem. Soc.* 1980, 102, 7033.
(3) Cutler, A.; Raghu, S.; Rosenblum, M. *J. Organomet. Chem.* 1974, 77, 381.