theless, in comparison with simulations of other systems of similar complexity, the agreement found between simulation and experiment is impressive.

The batch behavior is reproduced almost quantitatively. The ability of a mechanism to yield both bistability and oscillations of the correct amplitude and wave form *with the actual experimental parameters* is almost unprecedented in the literature of oscillating reactions. The prediction of the oscillation period, though not exact, is within a factor of 2, good agreement for this type of study. It remains to be seen whether the calculated region of bistability between stationary and oscillatory states will be found experimentally.

As pointed out elsewhere,[6,8] this reaction is an ideal one for detailed kinetic studies. The availability of a reliable mechanism should make it an even more attractive system for further investigation.

Acknowledgment. This work was supported by the National Science Foundation (CHE8419949) and by a U.S.–Hungarian Cooperative Grant from the NSF (INT8613532) and the Hungarian Academy of Sciences. We are grateful to Prof. Kenneth Showalter for sharing his results with us prior to publication. We thank Prof. Kenneth Kustin for a critical reading of the manuscript.

Mechanism of Titanocene Metallacyclobutane Cleavage and the Nature of the Reactive Intermediate

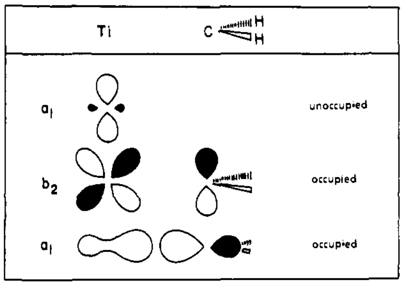
Eric V. Anslyn and Robert H. Grubbs*

Contribution No. 7519 from the Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology, Pasadena, California 91125. Received December 10, 1986

Abstract: The mechanism of titanocene metallacyclobutane cleavage to give a titanocene methylidene is examined in detail. The reaction of titanocene metallacyclobutanes with acetylenes or olefins displays either first- or second-order kinetics depending upon the metallacycle, its reaction temperature, and the trapping reagent. The rate-determining step for cleavage is the formation of an olefin–titanocene methylidene complex. Evidence for this complex is presented by competition experiments and kinetic studies of titanocene methylidene phosphine adducts. Deuterium isotope effect studies on an α-d_2 metallacycle reveal a preference for cleavage toward placing deuterium in the liberated olefin. The studies presented allow for the rational control of the catalytic activity of titanocene metallacyclobutanes.

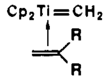
Titanocene metallacyclobutanes[1] show a wide variety of reactivities with organic and inorganic reagents. Their reactions include methylene transfer to organic carbonyls,[2] formation of enolates,[2a,e,3] electron transfer from activated alkyl chlorides,[4] olefin metathesis,[5] ring-opening polymerization,[6] and complexation with metal halides.[7] All these reactions presumably occur through a reactive intermediate that exhibits behavior consistent with that of a transition-metal carbene. The intermediate has been postulated to be free titanocene methylidene[5d] A or a titanocene methylene olefin complex[5d] B. The cleavage of the metallacycle

Chart I



$Cp_2Ti{=}CH_2$

A



$Cp_2Ti{=}CH_2 \leftarrow (R)HC{=}CH(R)$

B

to give the reactive intermediate is the rate-determining step in all the above reactions. Controlling the rate of cleavage and understanding the nature of the reactive intermediate could lead to better catalyst design, better selectivity in organic reactions, and higher stereocontrol in polymerization.[8]

The metallacycle can be envisioned to lose olefin in a one-step process or by a slipping mechanism in which a methylidene–olefin complex forms first and then the olefin dissociates. This question has been approached theoretically by several groups. Rappē has

---

[1] Lee, J. B.; Gajda, G. J.; Schaefer, W. P.; Howard, T. R.; Ikariga, T.; Straus, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 7358.

[2] (a) Clawson, L. E.; Buchwald, S. L.; Grubbs, R. H. *Tetrahedron Lett.* **1984**, *50*, 5733. (b) Brown-Wensley, K. A. Ph.D. Thesis, California Institute of Technology, Pasadena, California, 1981. (c) Pine, S. H.; Yahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270. (d) Pine, S. H.; Pettit, R. J.; Geib, G. D.; Cruz, S. G.; Gallego, C. H.; Tijerina, T.; Pine, R. D. *J. Org. Chem* **1985**, *50*, 2316. (e) Cannizzo, L. F.; Grubbs, R. H. *J. Org. Chem.* **1985**, *50*, 2316. (f) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 855. (g) For review see: Brown-Wensley, K. A.; Buchwald, S. L.; Cannizzo, L. F.; Clawson, L. E.; Ho, S.; Meinhart, J. D.; Stille, J. R.; Strauss, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733.

[3] (a) Stille, J. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1983**, *105*, 1664. (b) Chou, T.; Huang, S. *Bull. Inst. Chem., Acad. Sin.* **1984**, *31*, 41.

[4] Buchwald, S. L.; Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 1766.

[5] (a) Tebbe, F. N.; Parshall, G. W.; Overall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074. (b) Klabunde, U.; Tebbe, F. N.; Parshall, G. W.; Harlow, R. L. *J. Mol. Catal.* **1980**, *8*, 37. (c) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 6876. (d) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491. (e) Straus, D. A.; Grubbs, R. H. *J. Mol. Catal.* **1985**, *28*, 9.

[6] (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733. (b) For a review on ring-opening polymerization: Calderon, J. J. *Macromol. Sci. Rev.* **1972**, C7(1), 105. Katz, J. J.; Lee, S. J.; Shippey, M. A. *J. Mol. Catal.* **1980**, *8*, 219.

[7] (a) Mackenzie, P. B.; Ott, K. C.; Grubbs, R. H. *Pure Appl. Chem.* **1984**, *56*, 59. (b) Park, J. W.; Mackenzie, P. B.; Schaefer, W. P.; Grubbs, R H. *J. Am. Chem. Soc.* **1986**, *108*, 6402–6404.

[8] (a) Thoi, H. H.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1982**, *15*, 245. (b) Leconte, M.; Basset, J. M. *J. Am. Chem. Soc.* **1979**, *202*, 7296. (c) Calderon, N.; Lawerence, J. P.; Ofstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.

0002-7863/87/1509-4880$01.50/0

found, by the generalized valence bond method[9] and the orbital phase continuity principle,[10] that an olefin can react with the methylidene in a concerted 2 + 2 reaction which is allowed due to the second angular node present in d orbitals.[11] He found no energy well for an olefin–methylidene complex. However, Hoffmann and co-workers[12] have studied this system by using the extended Hückel method and found the metallacycle substantially less stable than the olefin–methylidene complex (by approximately 20 kcal/mol). Furthermore, they found the global potential energy minimum to be the geometry Rappé found to be a saddle point, namely, the olefin–methylidene complex. Thus, two radically opposing views exist on the stability of a titanocene methylidene olefin complex.

The nature of the titanocene methylidene has also been studied theoretically by several groups, all of which agree on its basic features.[13] The titanocene methylidene has its π-bond electron density in a plane between the two cyclopentadienyl rings and has an empty orbital of A_1 symmetry in the same plane. Chart I represents the frontier orbitals of methylidene and CH_2.[14] The hypothetical free uncoordinated titanocene methylidene is a 16-electron species which has an empty orbital to which Lewis bases could possibly coordinate. Addition of a two-electron donor Lewis base would achieve a full 18e count for the titanium. Herein, we report that the reactivity of the titanocene methylidene is intimately tied to the nature of empty and bonding orbitals and whether or not a Lewis base adduct is stable.

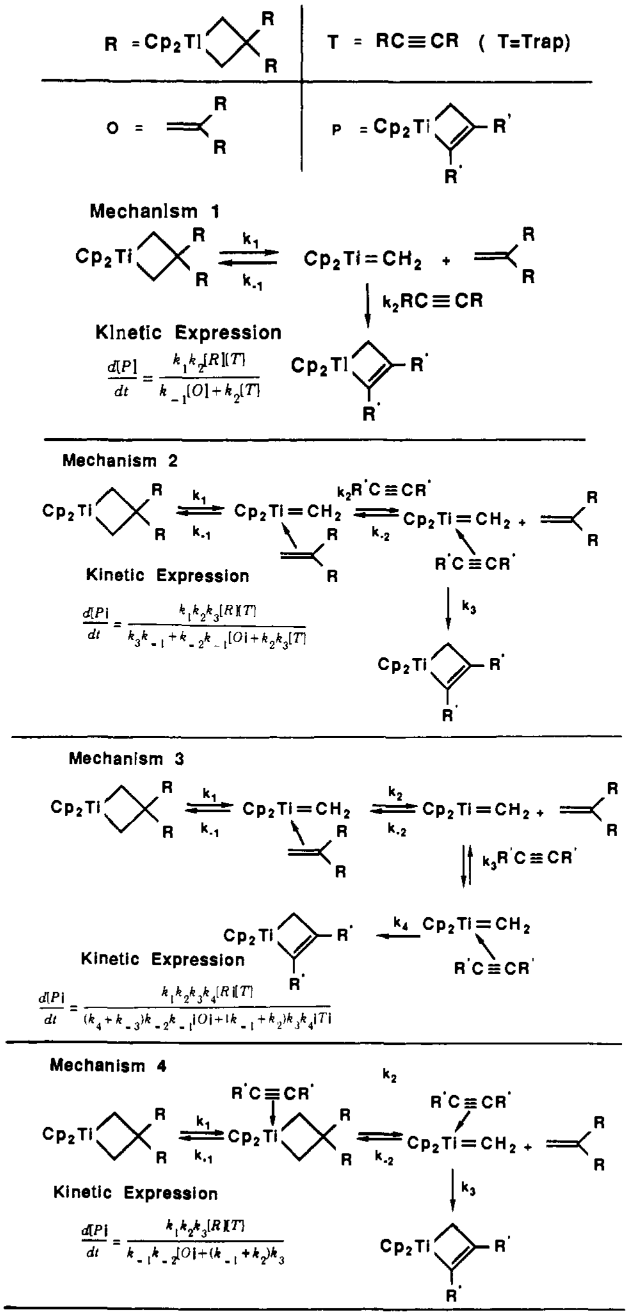
For later transition-metal olefin metathesis systems,[15] the metallacycle is the unstable reactive intermediate which can cleave nonproductively to give starting materials or in a productive manner to yield metathesized olefin. Because of the reversibility of this process, the product distribution is thermodynamically controlled. Only in the case where metathesized olefin cannot react with the carbene is relative reactivity information gained.

The reactivity of the titanocene metathesis system directly contrasts the later metal systems. The stable chain-propagating catalyst is the metallacycle, not the methylidene. The methylidene can be trapped with olefins and internal acetylenes to yield metallacyclobutanes and metallacyclobutenes, respectively. These olefin and acetylene traps can be chosen so that the reaction is not reversible. In these systems relative reactivity information can be obtained.

Results and Discussion

A. Rate Expressions and Reaction Orders. In order to probe the reaction mechanism, we first chose to study the reaction order of several metallacycles. The reaction order gives information on the number of molecules that are involved in the rate-determining step, or in multistep reactions, it can reflect contributions from several different steps. This information therefore gives some initial insight into relative sizes of rate constants in multistep reactions and plausible mechanisms. This was done because preliminary results suggested that the reaction order changed with metallacycle and substrate.

Scheme I. Metallacycle Proposed Mechanisms



The proposed mechanisms of metallacycle cleavage to a reactive titanocene methylidene intermediate are presented in Scheme I. In mechanisms 1 and 3, the reactive intermediate is free titanocene methylidene A. In mechanisms 2 and 4, the reactive intermediate is a titanocene methylidene olefin complex B. Mechanism 3 also involves the titanocene methylidene olefin intermediate, but it then forms the free titanocene methylidene which reacts with the trapping reagent. The rate expressions for each mechanism are also presented and were derived by using the steady-state approximation for all intermediates. The basic form of the kinetic expressions for mechanisms 1, 2, and 3 are the same. They all have a product of rate constants preceding the [R][T] term in the numerator and additive [O] and [T] terms in the denominator with a constant for mechanism 2. In contrast, mechanism 4 has no trap term in the denominator. The mathematical form was tested by manipulation of reaction orders and observation of saturation behavior. Table I presents the compounds discussed and the temperatures which give roughly equal rates of cleavage.

Mechanisms 1, 2, and 3 will exhibit first-order behavior under the appropriate conditions. For mechanisms 1 and 3, the rate expression reduces to first-order when [T] ≫ [O] or when the

---

[9] Bobrowicz, F. W.; Goddard, W. A., III In *Modern Theoretical Chemistry: Methods of Electronic Structure Theory*, Schaefer, H. F., III, Ed.; Plenum: New York, 1977; Vol. 3, Chapter 4, pp 79–127.

[10] (a) Nelson, C. W., Jr.; Goddard, W. A., III *J. Chem. Phys.* **1969**, *51*, 716. (b) Steigerwald, M. L.; Goddard, W. A., III *J. Am. Chem. Soc.* **1984**, *106*, 308.

[11] Upton, T. H.; Rappé, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 1206.

[12] Eisenstein, O.; Hoffmann, R.; Rossi, A. R. *J. Am. Chem. Soc.* **1981**, *103*, 5582.

[13] (a) Francl, M. M.; Hout, R. F.; Hehre, W. J. *Organometallics* **1983**, *2*, 815. (b) Gregory, A. P.; Mintz, E. A. *J. Am. Chem. Soc.* **1985**, *107*, 2179. (c) Rappé, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 297.

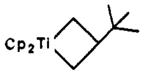
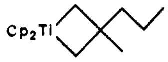
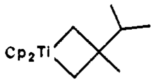
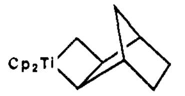
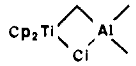
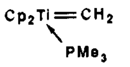
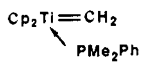
[14] Lauder, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729.

[15] (a) Hughes, W. B. *J. Am Chem. Soc.* **1970**, *92*, 532. (b) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (c) Calderon, N.; Lawrence, J. P.; Olstead, E. A. *Adv. Organomet. Chem.* **1979**, *17*, 449.

[16] Hartner, F. W., Jr.; Schwartz, J.; Cleft, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 601.

[17] (a) Tebbe, F. N.; Harlow, R. L. *J. Am. Chem. Soc.* **1980**, *102*, 6149. (b) McKinney, R. J.; Tulip, T. H.; Thorn, D. L.; Coolbaugh, T. S.; Tebbe, F. N. *Ibid.* **1981**, *103*, 5584. (c) Howard, T. R.; Lee, J. B.; Grubbs, R. H. *Ibid.* **1980**, *102*, 6876. (d) Meinhart, J. D.; Santarsiero, B. D.; Grubbs, R. H. *Ibid.* **1986**, *108*, 3318.

Table I

Compound	Number	Cleavage Temperature
	1	55
	2	0
	3	5
	4	-5
	5	65
	6	45
	7	-78 with added pyridine
 $Cp_2Ti{=}CH_2 \cdot PMe_3$	8	20
 $Cp_2Ti{=}CH_2 \cdot PMe_2Ph$	9	0

rate constants preceding [T] in the denominator are much greater than the rate constants preceding [O]. Conditions for attaining first-order behavior for mechanism 2 are more stringent. When $[T] \gg [O]$, k_{-1} must also be small compared to $k_2[T]$ before first order behavior is observed. Finally in mechanism 4, first-order behavior only occurs for high concentrations of trapping reagent.

When the olefin and trap terms of the denominator are comparable in mechanism 1, 2, or 3, then reduction to first-order is not possible. This occurs when the rate constants preceding [O] and [T] are roughly equal. The reaction is now second-order because [O] is going up exactly proportional to the drop in [T] and because the initial [R] and [T] are roughly equal. The denominator is now approximately a constant. Therefore, the observation of both first- and second-order behavior can be due to the ability of the trap and the olefin to compete for the reactive intermediate. When the free olefin produced by the metallacycle is competitive with the added trapping reagent, the reaction displays second-order behavior. When the added trap is much better at trapping the reactive intermediate than the olefin produced, the reaction displays first-order behavior for mechanisms 1, 2, and 3.[18]

In Figure 1a, a first-order plot of the reaction of metallacycle **1** with 1 equiv of diphenylacetylene is displayed. In Figure 1b, a second-order plot of the same reaction is displayed. Clearly the reaction more closely follows first-order behavior. Figure 2a shows the first-order plot of **3** when trapped with 1 equiv of diphenylacetylene. In Figure 2b, the second-order plot of the same data is displayed. The reaction now more closely follows second-order behavior. Mechanism 4 can be ruled out solely on the basis of these data since it should display only second-order behavior under these conditions. This behavior can, however, be explained by mechanisms 1, 2, and 3. It is due to a greater difference between the trapping rate constants of the trap vs. the olefin released for metallacycle **1** compared to metallacycle **3**. In other words, isobutylene is a more comparable trap to diphenylacetylene at a

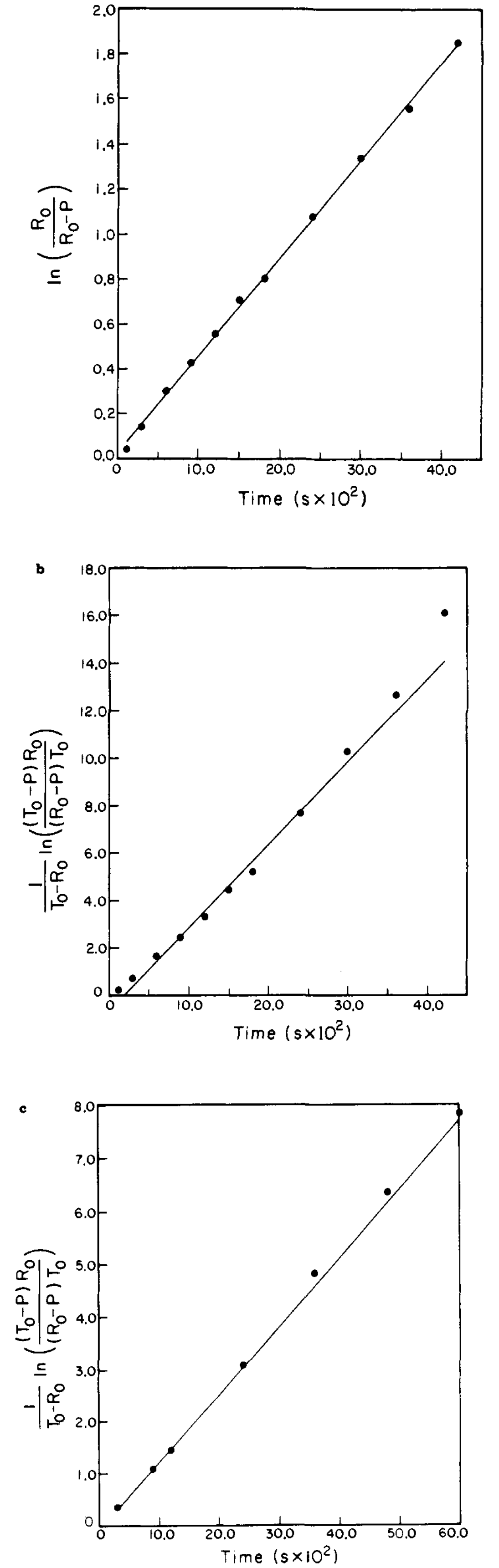


Figure 1. a. First-order plot for the reaction of **1** with 1.1 equiv of diphenylacetylene. The graph is linear, $\rho = 0.999$, and standard deviation $y = 0.0224$. B. Second-order plot for the reaction of **1** with 1.1 equiv of diphenylacetylene. The graph curves up, $\rho = 0.993$, and standard deviation $y = 0.578$. c. Second-order plot for the reaction of **1** with 1.1 equiv of diphenylacetylene and 2.5 equiv of neohexene. The graph is linear, and $\rho = 0.998$.

---

[18] The simplifications are extensions of reasoning presented in first year physical chemistry books such as: Moore, W. J. *Physical Chemistry*, 4th Ed.; Prentice Hall: New Jersey, 1964; Chapter 9, p 324.

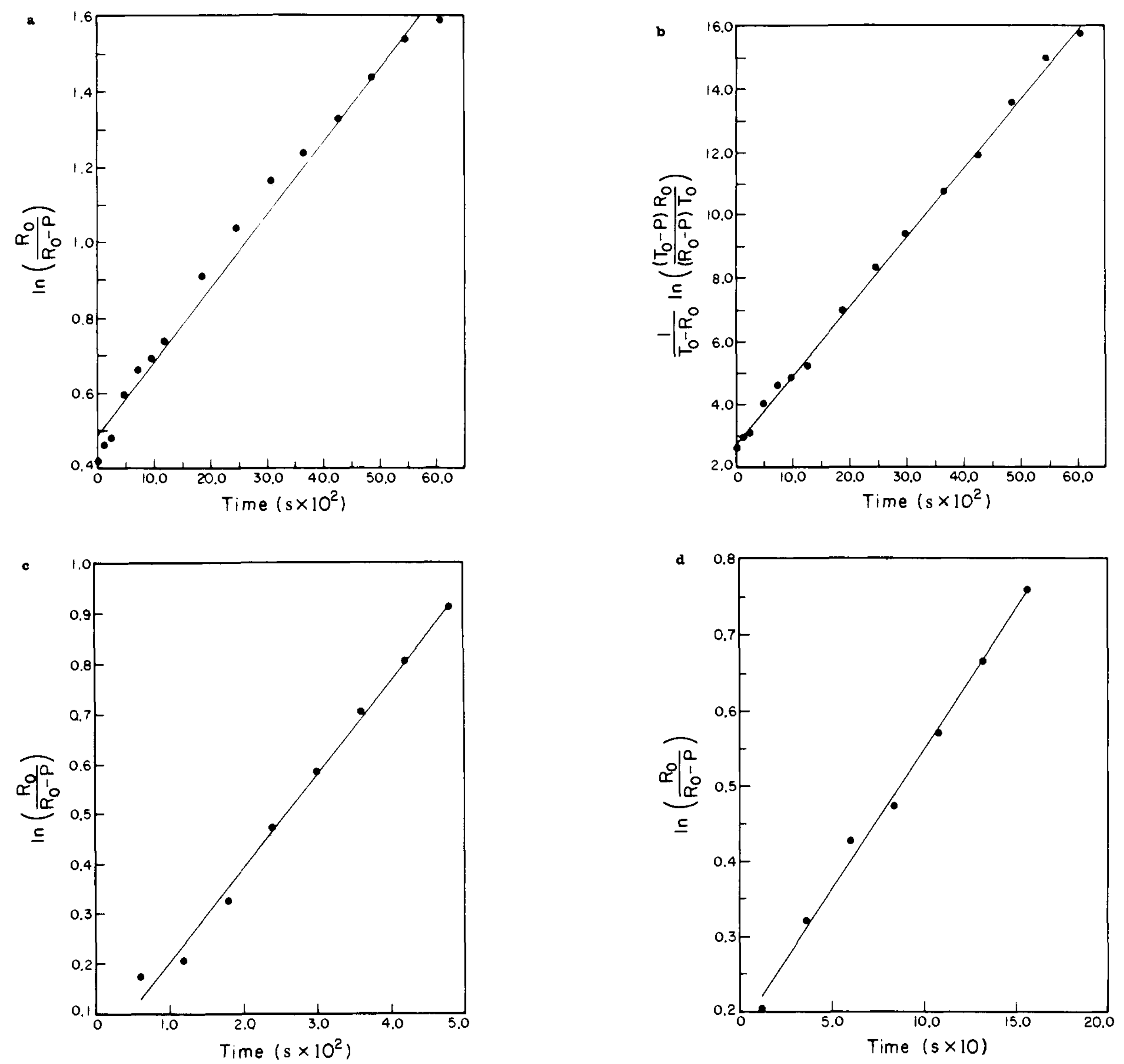


Figure 2. a. First-order plot for the reaction of **3** with 1.1 equiv of diphenylacetylene. The graph curves down, $\rho = 0.993$, and standard deviation $y = 0.047$. b. Second-order plot for the reaction of **3** with 1.1 equiv of diphenylacetylene. The graph is linear, $\rho = 0.998$, and standard deviation $y = 0.257$. c. First-order plot for the reaction of **3** with 8 equiv of diphenylacetylene. The graph is linear, $\rho = 0.995$, and standard deviation $y = 0.0169$. d. First-order plot for the reaction of **3** with 1.1 eq of dimethylacetylene. The graph is linear, $\rho = 0.997$, and standard deviation $y = 0.0172$.

temperature of 10 °C than is neohexene at a temperature of 55 °C. For metallacycle **3**, the denominator of the rate expressions cannot be simplified by neglecting the olefin term as it can be in the reaction of **1**.

Along with each graph is presented the ρ value for the line and the standard deviation of the y value. Very often, scatter can contribute to a low ρ or high standard deviation, and yet the line will be linear. In contrast, a high ρ or small standard deviation can be associated with low scatter, and yet the line will be visually curved. Since the scatter in all our graphs are low, we relied mostly on visual inspection of the graphs rather than relying solely on mathematical error analysis. The graphs shown are typical examples of the experimental data, and the rate constants derived were always repeatable with an error margin of ten percent.

The reaction orders can also be reversed by using different traps or by changing concentrations. Figure 1c shows the kinetics of the reaction of **1** with diphenylacetylene when 3.9 equiv of neohexene is added. Now the reaction displays second-order behavior and is slower (the rate dropped by 30%). This is due to the terms in the denominator of the rate expressions becoming closer in value since the olefin concentration has been increased. Conversely, the reaction of **3** with diphenylacetylene is first-order and faster if a large excess of diphenylacetylene is used (Figure 2c). Now the trap term in the denominator of the kinetic expressions for mechanism 1, 2, and 3 is much larger than the olefin term. The same effect can be achieved by using a better acetylene trap for **3**. If 2-butyne is used as the acetylene trap (Figure 2d), then the reaction is first-order in **3**. Now, the rate constants of the trap term are so large that the olefin cannot compete for the reactive intermediate.

These studies have shown the delicate balance between reaction orders in the titanocene metallacycle systems. The reaction order is determined by a competition between the free olefin released and the trapping reagent for the reactive intermediate. This competition can be manipulated easily by changing traps or trap concentrations and therefore changing reaction orders. The rate of reaction of olefins vs. acetylenes for the reactive intermediate are, therefore, comparable.

It must be emphasized that the conclusion of first- or second-order behavior is based on whether the graphs *better fit* a first- or second-order logarithm. The reactions really are in between first- and second-order behavior since it would be unlikely that the olefin reaction term was exactly equal to zero (pure first-order behavior) or that the olefin and trap terms were exactly equal to one another (pure second-order behavior).

B. Saturation Behavior. Mechanisms 1, 2, and 3 predict a pseudo-first-order rate constant that approaches k_1 as the concentration of the trap increases whereas mechanism 4 does not.

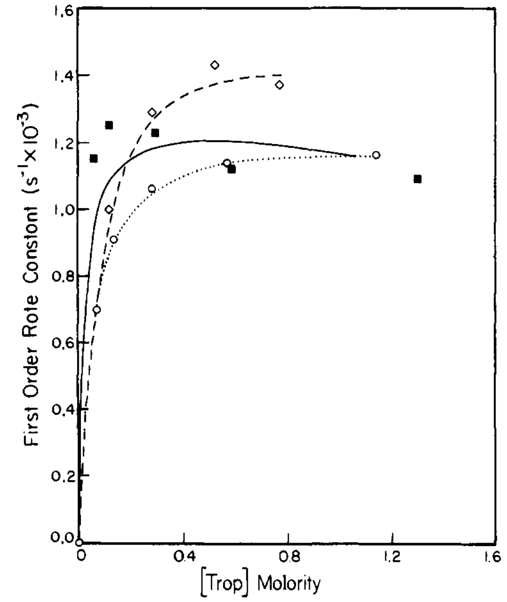


Figure 3. Saturation kinetics on 0.1 M **2** with diphenylacetylene (□), dimethylacetylene (■), and neohexene (○).

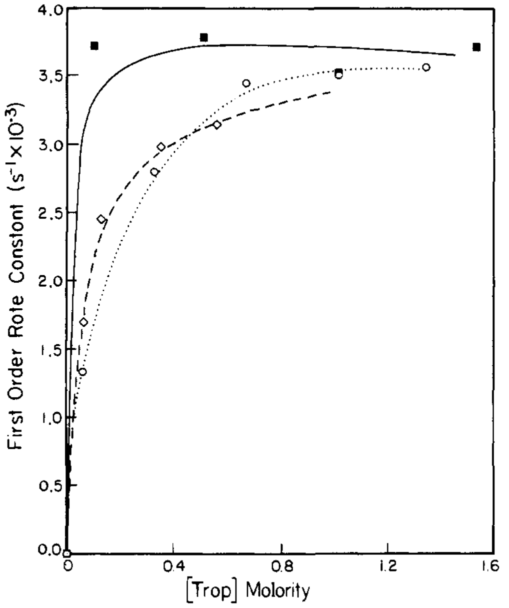


Figure 4. Saturation kinetics on 0.1 M **3** with dimethylacetylene (■), diphenvlacetylene (◇), and neohexene (○).

Mechanism 4 would not saturate because there is no trap term in the denominator of the kinetic expression, and, therefore, the reaction cannot reduce to first order. In order to test for this behavior and also to determine the k_1 values for different metallacycles, the reactions were monitored under saturation conditions.

In all metallacycles studied, the rate-determining step in the reaction of the metallacycle with a trap at high concentration is the formation of a reactive titanocene methylidene intermediate. All of the metallacycles studied show saturation behavior at high trapping concentrations. This behavior is predicted by mechanisms 1, 2, and 3. In these three mechanisms, as the trapping term becomes large compared to the olefin term in the denominators, all of the expressions reduce to first order in metallacycle and give a rate which is independent of trap concentration.

Figures 3 and 4 show saturation behavior of metallacycles **2** and **3** with three different traps: neohexene, 2-butyne, and diphenylacetylene. The more efficient trapping agent shows more rapid approach to saturation as predicted by all three mechanistic schemes. The better trapping agent competes more effectively than the olefin at a lower trapping agent concentration. All the traps saturate to the same level as predicted above. The trapping ability of the acetylenes increases with the electron richness of the triple bond and decreases with increasing size of the R groups. Error bars are excluded on these graphs for clarity but would be plus or minus 10%. Metallacycles **1**, **2**, **3**, **5**, and **6** have all been studied under saturation conditions. Figure 4 represents a typical case. Figure 3 shows our worst case.

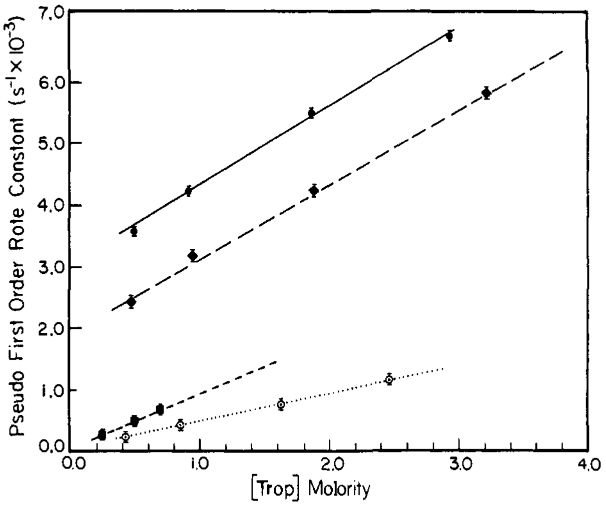


Figure 5. Pseudo-first-order kinetics on 0.1 M **8** with 4-octyne (●), 3-hexyne (♦), diphenylacetylene (□), and neohexene (○).

Mechanism 4[19] could saturate at high trap concentrations analogous to Michaelis–Menton enzyme kinetics.[20] In order for this to be true, however, the rate-determining step would have to be dissociation of the metallacycle–olefin complex. This would mean that at the point of saturation, the concentration of this complex would be substantial and detectable. No intermediates are ever seen when following these reactions by ^{1}H NMR.

There is another argument against this alternative. If the incoming trap induces cleavage of the metallacycle by prior coordination, each trap should do this at a different rate. Each trapping reagent would show saturation behavior with the metallacycles to a different rate-determining k_1. Figures 3 and 4 show this not to be the case. Therefore, prior coordination of the olefin is rejected.

In summary, these studies show that the olefin term in the denominator can be ignored at high trap concentrations reducing the reaction order to first order. This also shows that the rate-determining step is metallacycle cleavage and that the trapping rates are orders of magnitude faster. Finally, only mechanisms 1, 2, and 3 are consistent with the data of the last two sections.

C. Phosphine Adduct Kinetics Analogy. Titanocene methylidene phosphine adducts can be synthesized from metallacycles.[16] These adducts also yield metallacycles when reacted with olefins or acetylenes. A study was commenced on these adducts in order to enter the same reaction pathway as the metallacycles via a different route and also because titanocene methylidene phosphine adducts could show similar associative or dissociative reaction pathways as an olefin complex and hence serve as a model for the post rate-limiting steps.

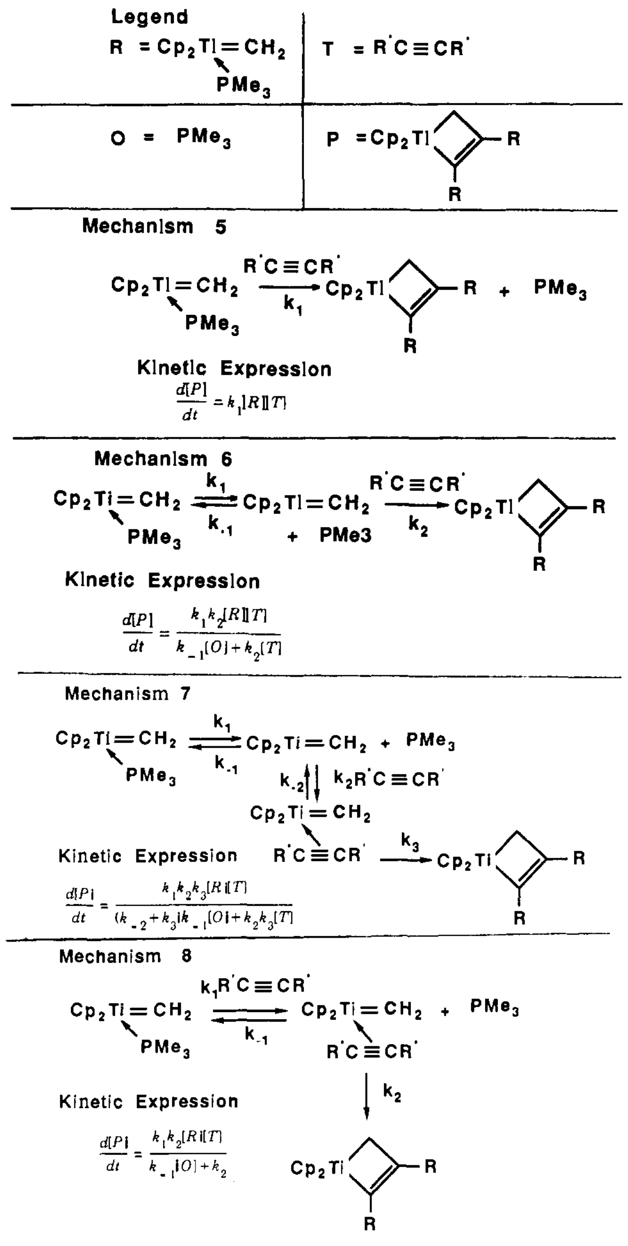
Mechanisms 5, 6, 7, and 8 represent the alternatives for phosphine adduct reactions with trapping reagents (Scheme II). With use of ideas presented in sections A and B, mechanisms 6 and 7 would show saturation kinetics and first-order kinetics (in phospine adduct) with high concentration of trap or with very good traps. Mechanisms 5 and 8 would give second-order behavior (first order in phosphine adduct and first order in trap) or pseudo-first-order behavior for high trap concentrations. Mechanism 8, however, would also show inhibition by added phosphine. Figure

---

(19) *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Perganon: Oxford, 1900; Vol. 3, p 324.

(20) Stryer, L. *Biochemistry*; W. H. Freeman: San Francisco, 1975; Chapter 1, p 124.

Scheme II



5 shows pseudo-first-order behavior for **8** with several trapping reagents. The lines remain linear even to 25-fold excess of trapping reagents. Therefore there is no saturation behavior, and instead second-order kinetics are obeyed for all trapping agent concentrations.

In an extreme case, mechanisms 6 and 7 could also show second-order behavior. If the back reaction of phosphine with free methylidene in mechanisms 6 and 7 is so great that the [O] term in the kinetic expressions outweighs the other term in the denominator, even at very high trap concentrations, then the kinetic expressions would never reduce to first-order behavior. This possibility was tested for by measuring the relative trapping abilities of trimethylphosphine vs. 3-hexyne. This was done by adding trimethylphosphine and 3-hexyne to a solution of Tebbe's reagent. There was intermediate formation of phosphine adduct and metallacyclobutene. The reaction of phosphine adduct to metallacyclobutene was then followed by NMR. The kinetics were then extrapolated back to time zero to determine the initial ratio of phosphine adduct and metallacyclobutene. It was found to be 10.9. This yields the relative trapping abilities. A calculation was then performed to determine the extent of saturation that should be present when the trap is in a 25-fold excess (as with 3-hexene, Figure 5), and the trapping rate constant by phosphine is 10.9 times that of the acetylene. The result is approximately 70%. (See Experimental Section for details). It is clear that at 70% of the saturated level, there should be curvature in the pseudo-first-order plots. This is not observed and so mechanisms 6 and 7 are ruled out. This narrows the possibilities to mechanisms 5 and 8.

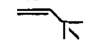
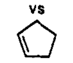
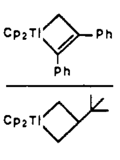
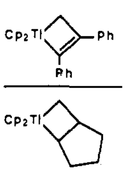
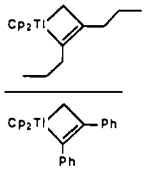
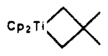
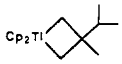
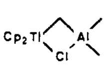
When free phosphine (1 equiv) is added to the reaction of the phosphine adduct with diphenylacetylene, the observed rate is cut in half. This result along with the second-order behavior is enough to narrow the phosphine adduct possibilities to mechanism 8. The phosphine adduct reacts with the trap in a reversible step. The intermediate then has two competing pathways: a second-order pathway involving free phosphine to give starting material or a first-order pathway to give product. We propose this intermediate to be an acetylene or olefin complex with the methylidene.

Accepting mechanism 8 for phosphine adduct reactions, we return to the metallacycle reaction. Two analogies can be drawn from the phosphine adduct mechanism. First, since an acetylene–methylidene complex is involved in the phosphine adduct reaction, it is conceivable that it is also a viable intermediate in the metallacycle reaction. Secondly, the phosphine adduct is a good model for an acetylene–methylidene complex. Although the phosphine complex is a more stable adduct, it could show similar displacement or dissociative reaction pathways. Taking what we have learned from the phosphine adduct mechanism gives mechanisms 2 and 3 as the viable possibilities for metallacycle cleavage. In the reaction of the phosphine adducts, the traps displace the phosphine in a pseudo S_N2 manner giving an acetylene–methylidene intermediate. Presumably an olefin can likewise displace another olefin or acetylene in a pseudo S_N2 process. The key difference between the phosphine–methylidene and olefin–methylidene is their stability. An olefin–methylidene complex could be so much more unstable that it rapidly dissociates to free olefin and free methylidene before a trap can displace the olefin. This is the key difference between mechanisms 2 and 3. These schemes, however, can be easily differentiated if several methylidene sources are competitively trapped with two different trapping reagents.

D. Competition Trapping. The titanocene methylidene in mechanisms 1 and 3 is independent of the olefin produced by cleavage of the metallacycle. Mechanism 2, however, involves a titanocene methylidene olefin complex. Therefore, if several different methylidene sources are competitively trapped with two different trapping reagents, the ratio of products derived from the two competing traps should be the same for mechanisms 1 and 3 but not necessarily the same for mechanism 2. Mechanism 2 could show a memory of its origin because of the coordinated olefin. To test this possibility a number of titanocene methylidene sources that would yield a range of $Cp_2Ti{=}CH_2{\cdot}L$ species were studied.

Table II shows several different titanocene methylidene sources, all of which give different trapping ratios with several different traps. Successive experiments showed that the ratios were reproduced within 15% of each other. This lends credence to mechanism 2. In addition, the metallacycles give very different trapping ratios than the phosphine adducts, confirming that different reactive intermediates are generated from the two species. Further analysis of Table II uncovers several trends. When competing diphenylacetylene against neohexene, the differences in product ratios derived from several metallacycles are small (case 1). When competing diphenylacetylene against cyclopentene, the differences in product ratios (case 2) become larger, and finally when competing 4-octyne and diphenylacetylene, the differences are on the order of a factor of 2 (case 3). The different product ratios (for an individual titanocene methylidene source) reflect the different ability of the traps to displace the olefin or phosphine from the titanocene methylidene source. As the inequivalence between the traps increases, so does the difference in product ratios between the different titanocene methylidene sources. In case 1, diphenylacetylene and neohexene are equally efficient trapping reagents and therefore displace the leaving groups equally well. In cases 2 and 3, one trap is significantly better than the other,

Table II

methylidene	case 1	case 2	case 3
Source	PhC≡CPh vs 	PhC≡CPh vs 	 vs PhC≡CPh
			
	2.2	5.9	9.9
	2.1	4.8	10.8
	1.9	3.8	5.2
$Cp_2Ti{=}CH_2$ PMe_3	2.7	10.2	22.2
$Cp_2Ti{=}CH_2$ PMe_2Ph	2.6	8.6	18.9
	2.8	9.5	22.7

and therefore the difference in product ratios can be observed. In case 3, 4-octyne is a much better trap than diphenylacetylene and therefore displaces the most selective (harder to displace) leaving group more efficiently. This is analogous to traditional S_N2 chemistry. A good leaving group reacts less selectively (more statistically) with nucleophiles than a poor leaving group.[21]

The magnitude of the differences between the ratios of products in cases 1, 2, and 3 are small compared to organic S_N2 reactions. Pseudo S_N2 reactions at metal centers have not been extensively studied. We propose three reasons for this small difference. If the transition state for S_N2 displacement is late along the reaction coordinate, it will not have much character of the leaving group. A second possible explanation is that the mechanism of metallacycle reaction is a combination of mechanisms 2 and 3. In other words, there are two reactive intermediates, both the titanocene methylidene complex and a free titanocene methylidene. To whatever extent the free methylidene exists in solution, it would suppress the difference in trapping ratios between different starting reactants. Other studies in our group support this theory. Thirdly, the initial differences in displacement of the metallacycle olefin from the olefin–titanocene methylidene complex by two different traps could be washed out by scrambling of the traps. In other words, the trap–titanocene methylidene complex can react with other traps and therefore the initial influence of the metallcycle olefin would be lost. The product ratio would then more reflect the relative rate of closure of the trap–titanocene methylidene complexes and not the initial rate of displacement of olefin. This dependence on the rate of closure of the trap–titanocene methylidene complex is an outcome of the Curtin–Hammett principle.[22]

Besides giving evidence for a different intermediate from several different titanocene methylidene sources, competition kinetics can reveal differences in selectivities of the reactive intermediates. We were intrigued that the metallacycle reaction orders were different from one metallacycle to another. As already explained, this behavior is due to the differential reactivity of the intermediate toward olefin or trapping agent. This competition between olefin and trap should have a temperature dependence. A temperature dependence could reveal differences in ΔS for trapping the reactive intermediate with olefins or acetylenes.

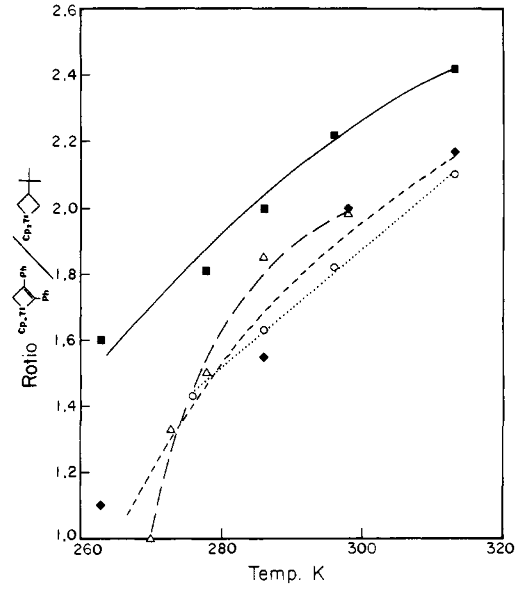


Figure 6. Competition kinetics vs. temperature using diphenylacetylene and neohexene as traps: ■, 7; ◆, 3; △, 2; ○, 8.

In section A, the behaviors of **1** and **3** were contrasted. In addition, metallacycles **2** and **4** more closely exhibit second-order behavior than first-order behavior when reacted with diphenylacetylene. In contrast metallacycle **5** more closely exhibits first-order behavior than second-order.[6] The available data suggest that metallacycles that decompose at higher temperatures show first-order behavior whereas those which cleave at lower temperatures show second-order behavior. In fact, as the temperature is lowered in the reaction of metallacycle **1** with diphenylacetylene, the first-order kinetic plots start to curve and begin to suggest second-order behavior. Conversely, as the temperature is raised in the reaction of **3** with diphenylacetylene, the curves bend more to resemble first order. In section A, the reaction orders were related to a competition between the olefin (liberated by the metallacycle) and the trap for the reactive intermediate. Thus it appears that as the temperature is raised, the olefin becomes a poorer trap relative to an acetylene.

To test this behavior, we undertook competition trapping studies of several metallacycles with an olefin and an acetylene trap at different temperatures. As seen in Figure 6, at high temperature, the acetylene preferentially traps the intermediate. This trend is also observed in competitive trapping studies with phosphine adducts and Tebbe's reagent.[7] We were restricted to diphenylacetylene and neohexene traps since these substrates are roughly equal in trapping ability and hence the trends can be uncovered. The data in Figure 6 confirm that at higher temperatures the diphenylacetylene is a better trap than the olefin released.

The neohexene used to compete against diphenylacetylene is not the olefin released from **2**, **3**, or **4**. Therefore, this temperature-dependent trend is only applicable to the explanation of observed first- or second-order kinetics for **2**, **3**, and **4** if the critical difference between the traps is that one is an alkene and one is an alkyne. We propose that the critical difference is in the steric interaction on approach of the trap to the titanocene methylidene. The terminal R groups of an olefin are forced to interact with the cyclopentadienyl ligands as the metallacycle is formed. The

---

(21) Collins, C. J.; Bowman, N. S. *Isotope Effects in Chemical Reactions*; Van Nostrand Reinhold: New York, 1970.

(22) Finch, W. C.; Ansyln, E. V.; Grubbs, R. H., unpublished results.

(23) Straus, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.

(24) Meinhart, J. D.; Grubbs, R. H., unpublished results.

(25) Yoshida, T.; Negishi, E. I. *J. Am. Chem. Soc.* **1981**, *103*, 1276.

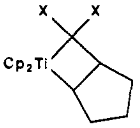
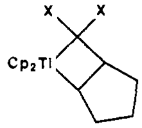
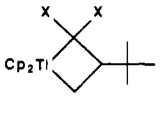
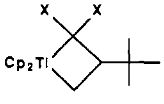
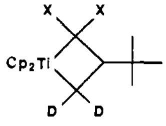
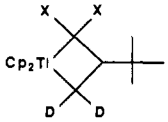
(26) Ott, K. C.; de Boer, E. J. M.; Grubbs, R. H. *Organometallics* **1984**, *3*, 223.

(27) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *J. Am. Chem. Soc.* **1975**, *97*, 679.

(28) Supplied as part of the JEOL FX-90Q operator software.

(29) Gordon, A. J. *The Chemists' Companion: A Handbook of Practical Data, Techniques and References*; Wiley: New York, 1972.

Table III[a]

Reactant	Eq. of Trap	k_H/k_D
	1.1	1.30
	8	1.45
	1.1	1.23
	8	1.17
	1.1	1.26
	8	1.29

[a] X = H or D.

alkyne R groups will begin to bend back out of the way of the cyclopentadienyl ligands as the metallacycle is formed. This steric argument is also confirmed by the Rappé calculation.[11] He found that as ethylene approaches the titanium of $Cl_2Ti{=}CH_2$, the chlorines bent back to avoid the incoming olefin. This steric hindrance should be accentuated in the real system since cyclopentadienyl ligands are undeniably larger than chlorines and the olefins all have alkyl or aryl substituents, not just hydrogens. If steric hindrance is taken as contributing to $\Delta S^{\ddagger}$, then $\Delta S^{\ddagger}$ should be more positive for acetylenes than for olefins since their approach to the titanocene moiety is less sterically crowded. Therefore, the temperature dependence can be explained if $\Delta S^{\ddagger}$ is greater for alkynes, and hence they will be favored over alkenes as the temperature is raised.

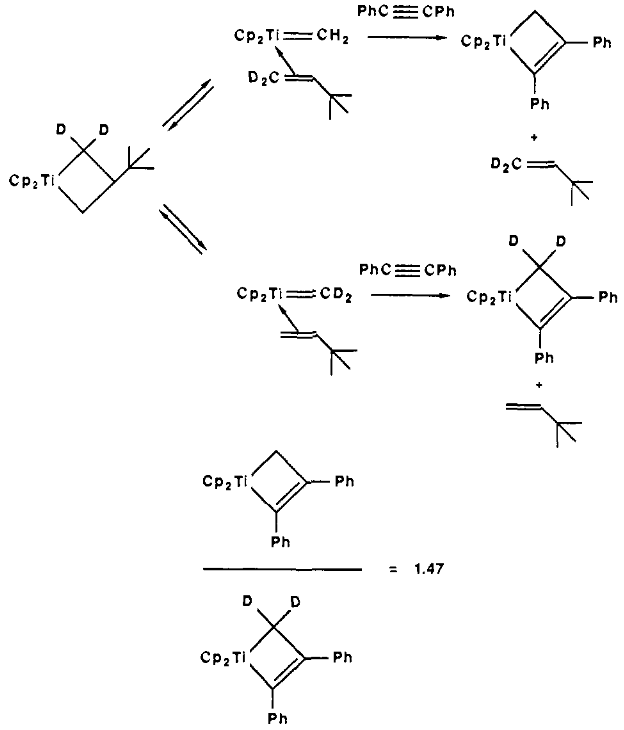
In summary, these experiments reveal an image of the transition state for reaction of titanocene methylidene with an acetylene being less crowded than reaction with an olefin. This, combined with the fact that an acetylene is more electron rich than an alkene and thus is a better trapping agent for the electrophilic titanocene methylidene, makes an acetylene an overall better trap electronically and a more entropically favored trap. These experiments also lend further credence to the existence of an olefin–titanocene methylidene complex since each titanocene methylidene source gave different product ratios when competitively trapped.

E. Deuterium Isotope Effects. The past four sections have concentrated on identifying the mechanism of reaction of metallocyclobutanes and phosphine–titanocene methylidene adducts. Strong evidence was presented for the role of an olefin–titanocene methylidene adduct in these reactions. To further develop our understanding of the rate-determining step of metallacyclobutanes and the bonding in the olefin–titanocene methylidene adduct, we undertook the examination of several secondary deuterium isotope effects.

There are two possible isotope effects in these systems to study. The first isotope effect studied was on the rate of cleavage of the metallacycles. The second was an intramolecular competitive isotope effect on the direction of cleavage of the metallacycles.

Table III summarizes the kinetic deuterium isotope effects on the rate of cleavage of metallacycles **1** and **6** with diphenylacetylene. In both cases, the effect of deuterium substitution on the methylene carbons of the metallacycle decreases the rate of cleavage. When a metallacycle cleaves, the hybridization of the α-carbons change from sp^3 to sp^2. A secondary isotope effect of $k_H/k_D \simeq 1.2$ was observed and is in the correct range for rehybridization changes of this type.[21] Each isotope effect experiment was repeated two to three times, and the measured values were always within seven percent of each other.

Scheme III

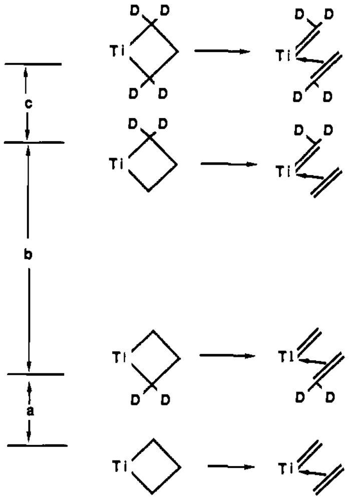


In the case of metallacycle 6, the isotope effect is due to the deuteriated metallacycle going directly to deuteriated methylidene. The case of **1**-d_2 is a combination of effects. The deuterium can either end up on the olefin or on the methylidene. Finally, in the case of **1**-d_4, the effect is due to both carbons changing from a deuteriated sp^3 carbon to a deuterated sp^2 carbon. As each α-carbon of the metallacycle is deuteriated, an isotope effect of approximately 1.2 was observed. Therefore the zero-point energy difference between **1**-d_0 and **1**-d_2 that lead to the isotope effects is approximately the same as the difference between **1**-d_2 and **1**-d_4. In addition, since these isotope effects are independent of trap concentration, the effect is solely in the rate-determining cleavage of the metallacycle to the titanocene methylidene and is not reflecting any rate differences in subsequent steps.

When large trapping agent concentrations are used, one can obtain a competitive isotope effect by trapping metallacycle **1**-d_2 (Scheme III). This metallacycle can cleave in two directions to give two intermediates, which are immediately trapped due to the high trap concentration. When the deuterium incorporated in the metallacyclobutene product is measured in comparison to the deuterium incorporated in the olefin liberated, the competitive isotope effect is found to be 1.47 favoring deuterium incorporation in the olefin.

An intramolecular secondary effect of 1.47 favoring deuterium incorporation in the olefin is quite large. This effect must be due to a significant zero-point energy difference between deuteriated methylidene and deuteriated olefin in the olefin–titanocene methylidene complex. The transition state should resemble the olefin–titanocene methylidene adduct since the reaction is endothermic by approximately 25 kcal/mol and the transition state is therefore late along the reaction coordinate. This assumption is also predicted by the Rappé calculation which places the transition state for metallacycle cleavage at almost the same geometry as an olefin–titanocene methylidene complex. Therefore the competitive isotope effect can be used to gain insight into the

Scheme IV



bonding of the olefin–titanocene methylidene adduct.

The large intramolecular competitive isotope effect of 1.47 is due to the carbon–hydrogen bonds of the methylidene carbon being significantly weaker than the carbon–hydrogen bonds of the olefin carbon. This effect is the same (within experimental error) as the k_{H_4}/k_{D_4} isotope effect on metallacycle **1** and the k_{H_2}/k_{D_2} effect of metallacycle 6. These results all taken together demonstrate that the majority of the isotope effect stems from the metallacycle α-carbons undergoing the most hybridization change when transforming to the methylidene carbon rather than to the olefin carbon. A qualitative energy diagram (Scheme IV) shows the relative activation energy differences for the reactions studied.

Separation **a** gives the activation energy difference between perprotio metallacycle cleavage and dideuterio metallacycle cleavage to yield dideuterio olefin. This should be roughly the same activation energy difference between tetradeuterio metallacycle cleavage and dideuterio metallacycle cleavage to yield dideuterio methylidene (separation **c**). Finally the largest separation **b** is the difference between dideuterio metallacycle placing deuterium on the olefin vs. methylidene during cleavage. Activation energy difference **b** accounts for the intramolecular competitive isotope effect, whereas **a** + **b** accounts for the isotope effect on metallacycle **5** and **a** + **b** + **c** accounts for the k_{H_4}/k_{D_4} isotope effect on metallacycle **1**. This energy diagram explains the seeming coincidence of three different isotope effects since a and c are small compared to b. Attempts to quantify these energy differences are now under way.

The results can also be used as further support for the concerted nature of the reaction. If the reaction was stepwise starting with either heterolytic or homolytic Ti–C bond cleavage, the intramolecular competitive isotope effect would have been the reverse of that observed due to the propensity of deuterium preferring a sp^3 center.

F. Ramifications and Future Studies. We have presented strong evidence for the existence of a olefin–titanocene methylidene adduct. Very few adducts of this type have been synthesized or observed spectroscopically.[30] Several predictions arise from this study. They are all imbedded in the movement of the olefin from the metallacycle to a π metal complex. This movement involves moving the R groups on the β-carbon in toward the cyclopentadienyl ligands. Therefore, any large bulky R groups on the olefin or on the cyclopentadienyl ligands should slow the reaction. If, however, the olefin were lost from the metallacycle without movement of the alkyl groups toward the cyclopentadienyl ligands, bulky groups would be predicted to speed the rate of cleavage. Preliminary results show that the reaction is slowed by bulky groups.

It has been shown previously that the metallacycle cleavage temperature correlates well with the substitution pattern of the olefin released.[23] It was found that disubstituted metallacycles cleave at lower temperatures than monosubstituted metallacycles. Therefore, there exists an interplay between large sterics of the olefin increasing the energy of activation and disubstitution decreasing the energy of activation for metallacycle cleavage.

Electronic effects can now also be predicted. Since the olefin is sliding into an empty orbital (as presented in the introduction), any effect to make this orbital more electrophilic should speed the reaction. Therefore, substituents on the cyclopentadienyl rings should effect the rate of cleavage in a predictable fashion. Preliminary results also support these predictions.[22] To whatever extent the reactive intermediate is a methylidene olefin complex, the outgoing olefin could influence the approach of the incoming olefin and therefore influence stereochemistry. Preliminary studies in ring-opening polymerizations support this notion.[31] Studies taking advantage of this predictability of reaction rates and the nature of the reactive intermediate are currently being performed and will be published in the near future.

Conclusion

The work presented lends insight into the manner in which titanocene metallacyclobutanes cleave to form a titanocene methylidene intermediate. Competition trapping experiments and kinetics on a phosphine adduct strongly implicate an olefin–titanocene methylidene complex as an intermediate. The fundamental conclusions can thus be summarized as follows: (1) the latent olefin of the metallacycle slides toward the titanium to coordinate to an empty orbital in the rate-determining step, (2) this complex can then rapidly react by an S$_N$2 process where the olefin is displaced by another Lewis base. It has not been rigorously ruled out that the olefin can also dissociate in an S$_N$1 manner to yield uncoordinated titanocene methylidene which also rapidly reacts with traps. The nature of the movement of the olefin lends itself to steric and electronic manipulation and therefore rational control of catalytic activity can be achieved.

The results can be compared to the theoretical results of Rappê and Upton.[11] We have presented evidence for the existence of an olefin–titanocene methylidene complex whereas the theoretical generalized valence bond method found no such intermediate in an energy well for the $Cl_2Ti{=}CH_2(CH_2{=}CH_2)$ system. Our other results are consistent with the theoretical development presented by Rappê and Upton. We view the reaction preceding in the manner they present by the orbital phase continuity principle except that there exists a small energy well for olefin coordination preceeding the 2 + 2 reaction.

Experimental Section

General Considerations. All manipulations were performed by using glovebox or standard Schlenk line techniques. Argon was purified by passage through Chemalog R3-11 and activated Linde 4A molecular sieves. Deuteriated solvents were purchased from Cambridge Isotope Laboratories and purified by vacuum transfer from sodium benzophenone ketyl. All acetylenes and phosphines were purchased from Aldrich Chemical Co. and used as supplied.

Synthesis of all titanocene metallacyclobutanes,[23] titanocene methylidene phosphine adducts,[6,24] and of Tebbe's reagent[25] were from literature preparations. Deuteriated metallacycles were synthesized from selectively labeled olefins. D^8 Tebbe's reagent was synthesized by a literature preparation[26] and deuteriated neohexene was synthesized by hydrozirconation using Cp_2ZrHCl[27] and monodeuteriated *tert*-butylacetylene and quenching with D_2O.

^{1}H NMR spectra were recorded on a JEOL FX-90Q and/or JEOL GX-400. Spectra were taken in benzene-d_6 or toluene-d_8 solutions and referenced to residual protons on the solvent. All kinetics were followed by an automated kinetic routine which took spectra at programmable intervals.[28] All reactions were followed to at least 3 half-lives. The temperatures reported for the NMR probe were determined by the chemical shift difference of methanol.[29] Reactant and product concentrations and/or ratios were determined by integration of the cyclopentadienyl resonances.

---

(30) (a) Foley, H. C.; Strubinger, L. M.; Fargos, T. S.; Geoffroy, G. L. *J. Am. Chem. Soc.* **1983**, *105*, 3064. (b) Casey, C. P.; Shusterman, A. J.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc.* **1982**, *104*, 2417 and references therein.

(31) Swager, T. M.; Cannizzo, L. F.; Novak, B. M.; Virgil, S.; Grubbs, R. H., unpublished results.

Table IV. Reaction Order Studies[a]

metallacycle	trap	mg or μL of trap	equiv of trap	solv	T, °C	order	k_{obsd}, s^{-1}	additional comments
1	A	7.0	1.1	Ben	55	1st	4.33×10^{-4}	
3	A	6.5	1.1	Tol	4	2nd	2.47×10^{-3} M^{-1}	
1	A	7.0	1.1	Ben	55	2nd	2.53×10^{-4} M^{-1}	20 μL of neohexene

[a] A = diphenylacetylene; Ben = C_6D_6; Tol = toluene-d_8.

Table V. Saturation Kinetics on **2**[a]

metallacycle	trap	mg or μL of trap	equiv of trap	solv	T, °C	order	k_{obsd}, s^{-1}
2	A	10.0	1.4	Tol	5	1st	1.00×10^{-3}
2	A	21.7	3.5	Tol	5	1st	1.29×10^{-3}
2	A	40.5	6.6	Tol	5	1st	1.43×10^{-3}
2	A	59.3	9.7	Tol	5	1st	1.36×10^{-3}
2	B	2.0	0.7	Tol	5	1st	1.25×10^{-3}
2	B	4.0	1.5	Tol	5	1st	1.22×10^{-3}
2	B	10.0	3.7	Tol	5	1st	1.22×10^{-3}
2	B	20.0	7.4	Tol	5	1st	1.12×10^{-3}
2	B	45.0	16.3	Tol	5	1st	1.09×10^{-3}
2	C	4.0	0.9	Tol	5	1st	6.98×10^{-4}
2	C	8.0	1.8	Tol	5	1st	9.10×10^{-4}
2	C	16.0	3.6	Tol	5	1st	1.14×10^{-3}
2	C	30.0	7.2	Tol	5	1st	1.11×10^{-3}
2	C	60.0	14.3	Tol	5	1st	1.18×10^{-3}

[a] A = diphenylacetylene; B = dimethylacetylene; C = neohene; Tol = toluene-d_8.

Table VI. Saturation Kinetics on **3**[a]

metallacycle	trap	mg or μL of trap	equiv of trap	solv	T, °C	order	k_{obsd}, s^{-1}
3	A	4.0	0.77	Tol	0	1st	1.3×10^{-4}
3	A	20.0	4.1	Tol	0	1st	2.8×10^{-4}
3	A	40.0	8.4	Tol	0	1st	3.45×10^{-4}
3	A	80.0	16.8	Tol	0	1st	3.56×10^{-4}
3	A	6.0	0.84	Tol	0	1st	1.7×10^{-4}
3	A	15.0	1.6	Tol	0	1st	2.45×10^{-4}
3	A	31.4	4.4	Tol	0	1st	2.98×10^{-4}
3	A	50.0	7.0	Tol	0	1st	3.15×10^{-4}
3	B	4.0	1.27	Tol	0	1st	3.72×10^{-4}
3	B	20.0	6.4	Tol	0	1st	3.78×10^{-4}
3	B	40.0	12.7	Tol	0	1st	3.52×10^{-4}
3	B	60.0	19.2	Tol	0	1st	3.72×10^{-4}

[a] A = diphenylacetylene; B = dimethylacetylene; Tol = toluene-d_8.

Table VII. Pseudo-First-Order on **8**[a]

metallacycle	trap	mg or μL of trap	equiv of trap	solv	T, °C	order	k_{obsd}, s^{-1}
8	D	10.0	1.8	Ben	25	1st	1.45×10^{-3}
8	D	25.0	4.6	Ben	25	1st	2.32×10^{-3}
8	D	50.0	9.2	Ben	25	1st	3.12×10^{-3}
8	D	100.0	18.3	Ben	25	1st	4.28×10^{-3}
8	D	150.0	27.4	Ben	25	1st	5.73×10^{-3}
8	E	5.0	1.2	Ben	25	1st	9.52×10^{-4}
8	E	20.0	5.2	Ben	25	1st	3.58×10^{-3}
8	E	40.0	9.4	Ben	25	1st	4.28×10^{-3}
8	E	80.0	18.8	Ben	25	1st	5.43×10^{-3}
8	E	120.0	28.0	Ben	25	1st	6.67×10^{-3}
8	A	15.2	2.3	Ben	25	1st	2.95×10^{-4}
8	A	31.6	4.8	Ben	25	1st	4.78×10^{-4}
8	A	46.7	7.0	Ben	25	1st	6.76×10^{-4}
8	C	6.0	1.2	Ben	25	1st	1.8×10^{-4}
8	C	20.0	4.2	Ben	25	1st	3.38×10^{-4}
8	C	40.0	8.3	Ben	25	1st	5.27×10^{-4}
8	C	80.0	16.1	Ben	25	1st	7.75×10^{-4}
8	C	120.0	24.7	Ben	25	1st	1.23×10^{-3}

[a] D = 4-octyne; E = 3-hexyne; A = diphenylacetylene; C = neohexene; Ben = C_6D_6.

All sample weighing and preparation was done in a VAC Dri-Train MO 40-1 drybox using either a Sartorius pan loader with a precision of 1 mg or an Sartorius Analytical balance with a precision of 0.1 mg. The 5-mm NMR samples were capped with a septum and then the septa wrapped with parafilm. This allowed for easy syringing of solvents and reactants. The NMR solvents were loaded in volumetic flasks in the drybox, then capped with a septum, and wrapped with parafilm. This allowed for easy transport of small amounts of deuteriated solvents to the NMR spectrometer where the final combination of reactants and solvents took place. The time required for equilibration of the sample in the NMR probe was determined to be 3 min.

In all kinetic runs 10 mg of the metallacycle or phosphine adduct was used. If the trapping reagent was solid, then it was weighed into the 5-mm NMR tube prior to transfer into the drybox. If the trapping reagent was a liquid, then it was syringed into the NMR tube immediately after the solvent was added and immediately before putting the sample in the NMR probe. The NMR probe was always stabilized at the reaction temperature for at least 5 min before starting an experiment. Tables IV through VII summarize the kinetic results and conditions for data presented in sections A–C.

Competition Kinetics vs. Temperature on 2, 3, 7, and Tebbe's Reagent. Five NMR tubes was loaded with 10 mg of Tebbe's reagent. Four NMR tubes were loaded with 10 mg of **2**. Three NMR tubes were loaded with 10 mg of 2. Four NMR tubes were loaded with 10 mg of **7** Diphenylacetylene (1.14 g, 10 equiv) was put in a 10-mL round-bottom flask and covered with a septum. The round-bottom flask was then purged with Ar. Toluene (6.8 mL) was added along with 83 μL (10 equiv) of neohexene. This mixture was stirred to dissolve the acetylene. Constant temperature baths at −10, 0.0, 15, 25, and 40 °C were prepared.[29] The trap solution (0.4 mL) was syringed onto **2**, **3**, and Tebbe's reagent (along with 10 μL of pyridine) at −20 °C and shaken vigorously. The NMR tubes were then put in the 0.0 °C bath for 10 h. The trap solution (0.4 mL) was syringed into **2**, **3**, **7**, and Tebbe's reagent (along with 10 μL of pyridine) at −20 °C and shaken vigorously. The four NMR tubes were then put in the 15 °C bath for 5 h. The trap solution (0.4 mL) was syringed into **2**, **3**, **7**, and Tebbe's reagent (along with 10 μL of pyridine) at −20 °C and shaken vigorously. The four NMR tubes were then put into the 25 °C bath for 1 h. The trap solution (0.4 mL) was syringed onto **2**, **7**, and Tebbe's reagent (along with 10 μL of pyridine) at −20 °C and shaken vigorously. The three NMR tubes were then put in the 40 °C bath for 15 min. After the allotted time period for each experiment, the solvent was removed in vacuo and the NMR tubes were then taken into a drybox where 0.4 mL of C_6D_6 was syringed in. The cyclopentadienyl ^{1}H NMR resonances of the products were integrated to determine the product ratios.

Deuterium Isotope Effects on 1. Two NMR tubes were loaded with 10 mg of **1**. Two NMR tubes were loaded with 10 mg of **1**-d_2. Two NMR tubes were loaded with 10 mg of **1**-d_4. In a 5-mL round-bottom flask was loaded 20.3 mg (1.1 equiv) of diphenylacetylene, 1.6 mL of C_6D_6, and 12 μL of toluene (as internal standard). In another 5-mL round-bottom flask was loaded 180 mg of diphenylacetylene (6.5 equiv), 1.6 mL of C_6D_6, and 12 μL of toluene (as internal standard). The NMR spectrometer was stabilized at 55 °C. Right before each experiment, 0.4 mL of one trapping solutions was added to one NMR tube of each of the three sets of compounds at room temperature. The other trap solution (0.4 mL) was then added to the other NMR tube of the three sets at room temperature. The NMR tubes were shaken vigorously and immediately put in the NMR probe. The determined reaction rates for equivalent protio and deuterio reactions were ratioed to give the isotope effect.

Deuterium Isotope Effects on 4. Two NMR tubes were loaded with 10 mg of **4**. Two NMR tubes were loaded with 10 mg of **4**-d_2. In a 5-mL round-bottom flask was added 22.5 mg of diphenylacetylene (1.1 equiv), 1.2 mL of C_6D_6, and 9 μL of toluene (as internal standard). In another 5-mL round-bottom flask was added 136 mg of diphenylacetylene (6.5 equiv), 1.2 mL of C_6D_6, and 9 μL of toluene. The NMR spectrometer was stabilized at 50 °C. Right before each experiment 0.4 mL of one of the trapping solutions was added to one NMR tube of each of the two sets of compounds at room temperature. The other trap solution (0.4 mL) was then added to the other NMR tube of the two sets at room temperature. The NMR tubes were shaken vigorously and immediately put in the NMR probe. The determined reaction rates for equivalent protio and deuterio reactions were ratioed to give the isotope effect.

Competitive Isotope Effect. A NMR tube was charged with 10 mg of **1**-d_2, 45 mg of diphenylacetylene, and 4 mL of C_6D_6. The tube was sealed and warmed to 55 °C for 4 h. The reaction was cooled to room temperature, and the α-hydrogens of the metallacyclobutene and the methylene hydrogens of the neohexene were integrated by NMR. The procedure was repeated in C_6H_6 and the deuterium incorporation also determined by ^2H NMR.

Competitive Trapping Tebbe's Reagent with Trimethylphosphine and 3-hexyne. Tebbe's reagent (10 mg) was loaded in a NMR tube. A solution of 0.2 mL of C_6D_6, 100 μL of 3-hexyne, and 70 μL of trimethylphosphine was made up in a 2-mL volumetric flask. The NMR spectrometer was stabilized at 25 °C. C_6D_6 (0.2 mL) was syringed onto the Tebbe's reagent. The NMR tube was shaken to dissolve the Tebbe's reagent. Then 0.2 mL of the trap solution was syringed into the NMR tube at the same time that a stop watch was started. The reaction was then followed by an automated kinetic routine. At the time of addition of the traps, the Tebbe's reagent is completely converted to **8** and metallacyclobutene. **8** then reacts with 3-hexyne to form more of the metallacyclobutene. The pseudo-first-order rate constant is $1.24 \times 10^{-3}\ s^{-1}$. At the time that $t = 0$, the logarithm intercept was 0.1215. With use of this intercept and the first-order logarithm expression, it can be calculated that the ratio of products from trimethylphosphine and 3-hexyne is 10.9. When the kinetic expression for mechanism 7 is factored as shown below, then the terms that cause the expression to saturate are in parentheses.

$$\text{rate} = k[\text{R}]\left(\frac{k_2[\text{T}]}{k_{-1}[\text{O}] + k_2[\text{T}]}\right)$$

If now [O] is taken to be 1 and the [T] to be 27.9 (as in the case of a 27.9-fold excess of 3-hexyne) and the [O] rate constants to be 1 compared to the 10.9 (as found above) for the [T] rate constants, then the following expression results.

$$\text{rate} = k_1[\text{R}]\left(\frac{1 \times 27.9}{10.9 \times 1 + 1 \times 27.9}\right) \Rightarrow \text{rate} = 0.719k_1[\text{R}]$$

Therefore 71.9% of the rate-determining k_1 should have been reached when the 3-hexyne is in a 27.9-fold excess.

Competition Trapping Experiments. Three 10-mg samples of compounds **2**, **3**, **7**, **8**, and **9** and Tebbe's reagent were measured into individual NMR tubes. In a 10-mL round bottom was measured out 364 μL (10 equiv) of neohexene, 50 mg of diphenylacetylene (10 equiv), and 3 mL of toluene. In another 10-mL round-bottom 252 μL of cyclopentene (10 equiv), 500 mg of diphenylacetylene (10 equiv), and 3 mL of toluene were measured out. In a third 10-mL round-bottom 399-μL of 4-octyne (10 equiv), 500 mg of diphenylacetylene (10 equiv), and 3 mL of toluene were measured out. Each solution (0.4 mL) was syringed onto each of compounds **2**, **3**, **7**, **8**, and **9** and Tebbe's reagent (along with 10 μL of pyridine) in individual NMR tubes at 25 °C. The reactions were then shaken vigorously and allowed to stand for 1 h. The solvent is then removed in vacuo and each NMR sample taken into the drybox where 0.4 mL of C_6D_6 is added. The product ratios are determined by integrating the cyclopentadienyl resonances.

Acknowledgment. We gratefully acknowledge financial support from the National Science Foundation (Grant CHE-8214668) and National Institutes of Health (Grant GM-31332).

Ion Pairing in Transition-Metal Carbonylates Modeled by ab Initio Calculations on BH_2COM_a (M_a = Li, Na)

Keith H. Pannell,*[†] Krishan S. RaghuVeer,[†,‡] Janet E. DelBene,[§] and Francis Nathan[†]

Contribution from the Departments of Chemistry, University of Texas at El Paso, El Paso, Texas 79968, Rhode Island College, Providence, Rhode Island 02908, and Youngstown State University, Youngstown, Ohio 44555. Received August 6, 1985

Abstract: Ab initio calculations carried out on the title molecules provide an excellent model for the type of ion pairs that have been observed spectroscopically, and by X-ray crystal determination, for various transition-metal carbonylate salts. Three stable ion pair structures have been identified: one involves the alkali metal bonded to the terminal O atom of the CO group with a linear COM_a linkage; the second has a direct alkali-metal–boron bond with essentially tetrahedral geometry around boron; and the third is a π-complex in which the alkali metal is bonded to the CO π-system orthogonal to the plane of the BH_2 group, i.e., stabilization requires an extended π-system involving the nonbonding electrons on B. A study on ion pairing with an (acyl)$BHCOM_a$ system reveals a chelate complex, as has been identified experimentally in related acyl transition-metal carbonylates. Calculated infrared stretching frequencies for the CO group in the various minimum energy structures change from one structural form to the other in a manner exactly paralleling those obtained experimentally for the metal carbonylate ion pairs, e.g., $[BH_2CO]^-$, 2030 cm^{-1}, $[BH_2COLi]$, 1944 cm^{-1}, and $[LiBH_2CO]$, 2103 cm^{-1}. Addition of a water molecule to the alkali-metal ion also causes changes in the CO stretching frequencies that are consistent with experimental data for solvent effects.

The great interest that has been generated by the study of organometallic transition-metal chemistry has in part been stimulated by the hope of creating new synthetic pathways for organic molecules based upon catalytic and stoichiometric use of transition-metal complexes containing direct metal–carbon σ bonds. Excellent recent textbooks attest to this activity.[1,2] A major route to the formation of transition-metal complexes containing a direct metal–carbon σ bond is the reaction of various transition-metal carbonylate salts with organic halides, as illustrated below for two common salt systems.[3,4]

$$[(\eta^5\text{-}C_5H_5)Fe(CO)_2]^-Na^+ + CH_3I \rightarrow [(\eta^5\text{-}C_5H_5)Fe(CO)_2CH_3] + NaI$$

$$[Mn(CO)_5]^-Na^+ + CH_3I \rightarrow [Mn(CO)_5CH_3] + NaI$$

Due to the central position of this type of salt elimination reaction, a considerable amount of study into the physical and chemical properties of the metalate salts has been published.[5,6] It has become clear that the solution structures of these salts are dependent upon many variables such as temperature, solvent composition, and countercation. An excellent review of this ion pairing aspect has been published.[7] Furthermore, it is abundantly clear that the chemical reactivity of the salts is directly related to the various structural modifications exhibited in solution, e.g.,

---

[†] University of Texas at El Paso.

[‡] Rhode Island College.

[§] Youngstown State University.

(1) Lukehart, C. M. *Fundamental Transition Metal Organometallic Chemistry*; Brooks/Cole: Monterey, CA, 1985.

(2) Collman, J. P.; Hegedus, L. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(3) Piper, T. S.; Wilkinson, G. *J. Inorg. nucl. Chem.* **1956**, *3*, 104.

(4) Clossen, R. D.; Kozikowski, J.; Coffield, T. H. *J. Org. Chem.* **1957**, *22*, 598.

(5) King, R. B. *Acc. Chem. Res.* **1970**, *3*, 417.

(6) Jonas, K. *Adv. Organomet. Chem.* **1981**, *19*, 97.

(7) Darensbourg, M. Y. *Adv. Inorg. Chem.* **1985**, *33*, 221.

0002-7863/87/1509-4890$01.50/0