

CALIFORNIA INSTITUTE OF TECHNOLOGY

Submitted in Partial Fulfillment for the
Degree of Master of Science

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October 23, 1980

REACTIONS OF AN ALUMINUM
STABILIZED TITANIUM ALKYLIDENE

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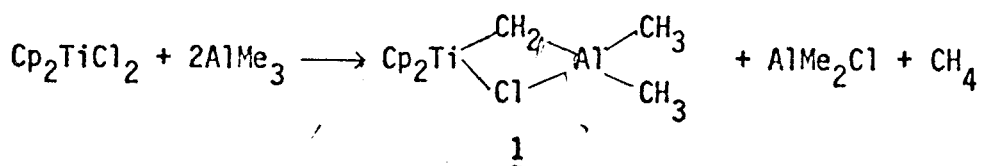
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INTRODUCTION

In recent years there has been a great deal of interest in organometallic alkylidene complexes as they are one of the postulated intermediates for the currently accepted mechanism of metathesis. Our interest was drawn to an aluminum stabilized titanium alkylidene because it had been reported to catalyze metathesis and to demonstrate other novel reactivity. This paper reports our results in the study of the chemistry of this complex.

Part 1The Preparation of Enol Ethers from Esters by a
Titanium-Aluminum Carbenoid Complex

Recently, Tebbe prepared a series of titanium methylene bridged complexes¹ which he found to be methylene transfer reagents for homologation of olefins and for methylenation of carbonyl functionalities both in ketones and esters. The compound he isolates is the first well characterized one of its type, but similar systems had been proposed as early as 1961.² Specifically, the reaction we were interested in is the following:

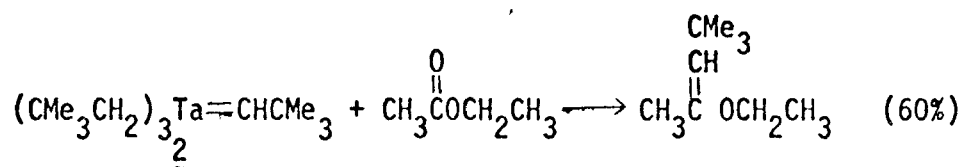


It was found by Tebbe that compound 1, when reacted with ethyl acetate, formed the enol ether. To date, the direct production of enol ethers

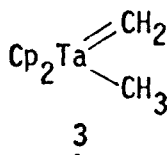


from esters has not been a general reaction. Phosphorous ylides have been successful in this reaction only in cases where the ester is highly activated (e.g. oxalic and cyanoacetic esters).³ However, recent evidence indicates ylides derived from transition metal complexes may be more reactive than their phosphorous counterparts.

Schrock, in his search for reactive carbenoid complexes, recently isolated a tantalum neopentylidene reagent 2 which reacts with ethyl acetate to form the tert-butyl vinyl ether.⁴



However, these results should not cause one to believe all tantalum carbenoid species will readily react in a Wittig type manner. Schrock also prepared a methylene carbenoid species 3 which reacts with acetone to form isobutylene only at elevated temperature and apparently does not react at all with esters.⁵

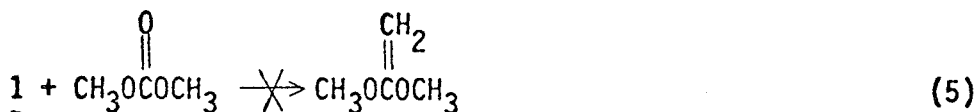
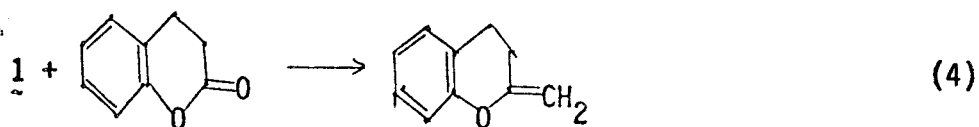
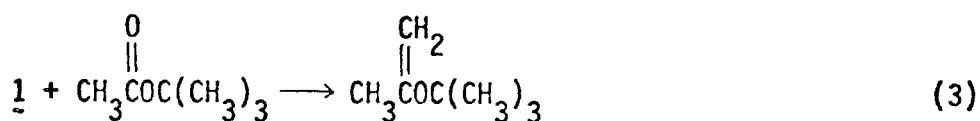


With this evidence in mind, we began to explore equation (1) in more detail. Specifically, we were interested in the scope and synthetic utility of the reaction.

The first question to be confronted dealt with the stoichiometry of the reaction. Initial results had indicated that in order for the reaction to go to completion, two equivalents of the methylene complex 1 are required. In an attempt to quantitatively answer this question, a series of NMR experiments was initiated. The specific ester chosen was tert-butyl acetate with anisol as an internal standard. After following the system using varying amounts of the methylene

transfer reagent 1, it is clear the reaction actually proceeds with a 1:1 stoichiometry. This is a fortunate result as it makes the reaction more synthetically useful.

Next, the scope of the reaction was studied. The specific esters dealt with by this student were the following:

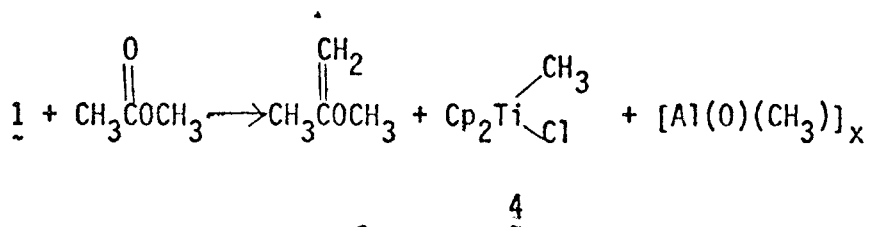


Reaction (2) was verified by gas chromatography and no yield was calculated. Reactions (3,4,5) were studied solely by NMR in perdeuterobenzene, and no products were isolated. In reactions (3) and (4), internal standards indicate they proceed in approximately 100% yield. Reaction times vary considerably, with (4) going to completion within half an hour, while (3) requires 24 hours. This can most likely be attributed to steric factors. There is also a distinct reaction in system (5). It is exothermic and goes to completion almost instantly; however, the desired product is not observed. Analysis of the NMR indicates polymerization has probably occurred. Interestingly, the presence of titanium and aluminum as components

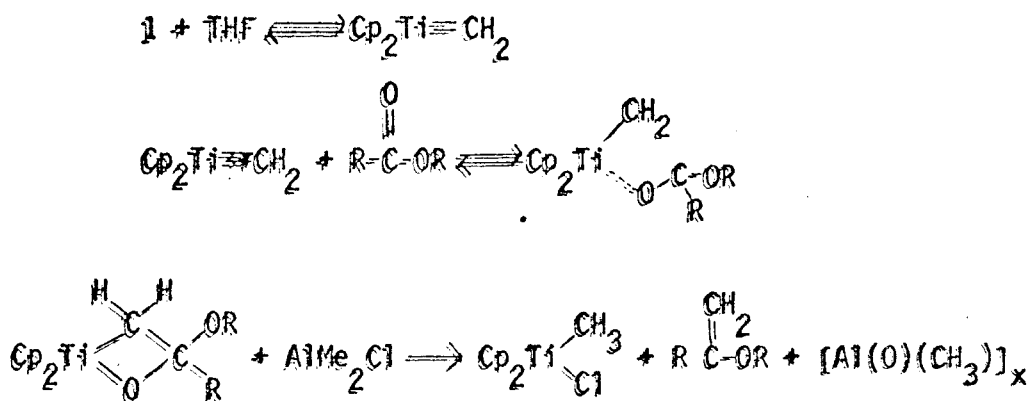
of the reaction mixture does not induce polymerization of the enol ethers. Products remain unchanged after several days in the NMR tube.

The scope of these methylenation reactions were studied to a much more extensive degree by Stanley Pine.^{6,7} He isolated a series of the enol ethers in yields of 80 - 97%. Reaction (4) was later examined by him where the isolated yield of the cyclic enol ether was 85%. Therefore, it has been proven the titanium carbenoid complex 1 is a general reagent for the preparation of enol ethers from esters.

In order to gain some insight into the mechanism of this methylene transfer reaction, it was decided to isolate the final titanium product. Since, at the end of the reaction, the NMR indicates the cyclopentadienyl functionality is a singlet, it would appear that essentially only one titanium complex remains. Therefore, a reaction was set up using methyl acetate as the ester. Upon recrystallization, a 60% yield of 4 is obtained. The postulated net reaction follows:



Unfortunately, this does not provide any mechanistic information. The only other mechanistic information is the observation that the rate of reaction increases if tetrahydrofuran or pyridine is added to the reaction mixture. For example, reaction (3) requires 24 hours for completion in perdeuterobenzene, but if tetrahydrofuran is added, the reaction is complete in less than two hours. Considering these observations, the following mechanism is postulated.

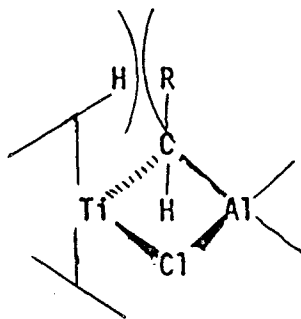


The first step has also been postulated by Tebbe,⁸ but the other steps are speculative.

Once the titanium-aluminum carbenoid has been studied, it was desirable to ascertain whether this type of system could be extended to other transition metals. The complex Cp_2WCl_2 was reacted with trimethylaluminum under a variety of conditions; and, even though in every case methane was evolved, no identifiable complex could be isolated. This line of research was terminated when it was discovered that Tebbe had already examined the tungsten system and a large number of other transition metals, but had been unable to isolate a complex analogous to the titanium case.⁸

The compound developed by Tebbe is an extremely useful methylene transfer reagent; however, the utility of this system would be magnified if it could be extended to other alkyl groups. In an attempt to determine whether these compounds are possible, Cp_2TiCl_2 was reacted with both triethyl aluminum and triisopropyl aluminum. In both cases, the desired product was not isolated. There are two potential reasons for the lack of formation of the carbene complex. First, β -hydride elimination, which competes with the desired α -hydride elimination,

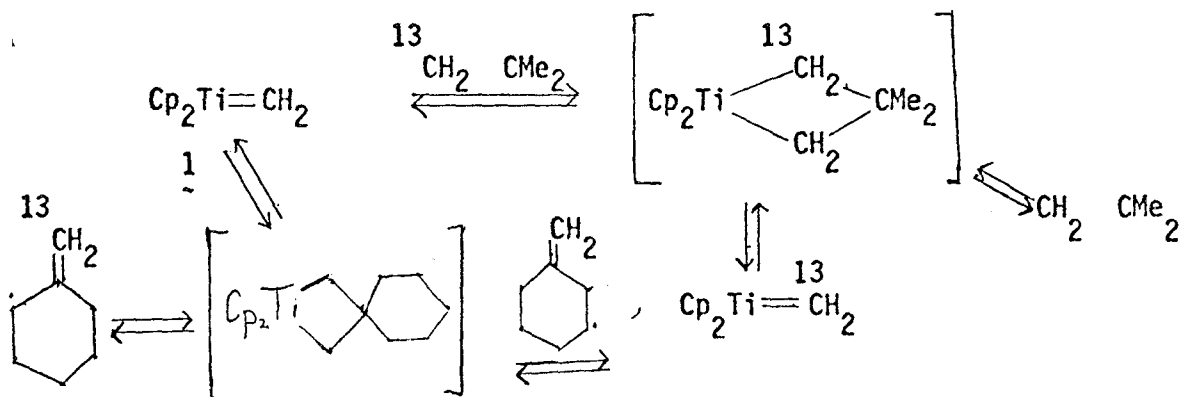
could be more facile. Second, steric hindrance with the cyclopentadienyl functionality could preclude formation of the intended complex.



In any case, this line of inquiry was terminated.

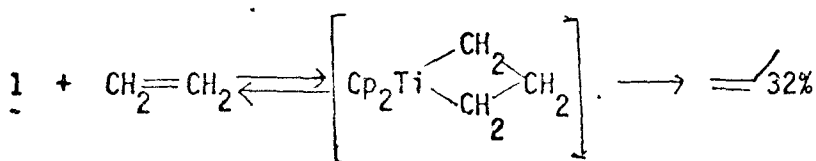
Part 2Synthesis of Metallacyclobutanes

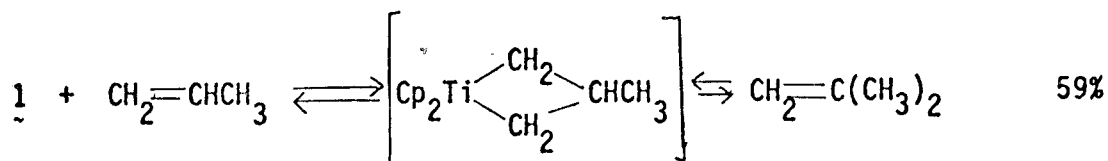
In addition to the novel ester reactivity of the titanium methylene species, **1**, we were also interested in its metathesis activity. Tebbe and coworkers had noted that, **1** catalyzes a metathesis process in which the methylene groups of isobutene and methylenecyclohexane exchange.^{9,10} The following mechanism was postulated by these workers to explain their observations.



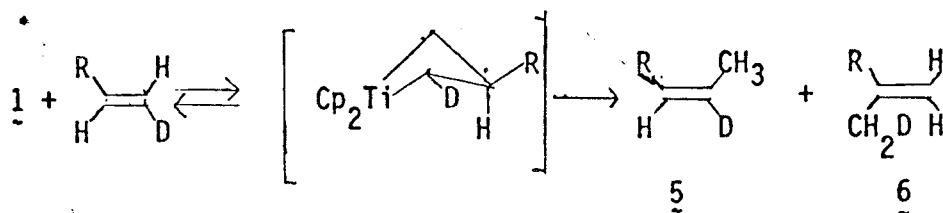
This is an example of the alkylidene/metallacycle mechanism now generally accepted as the olefin metathesis mechanism with conventional catalysts.¹¹

This scheme is also thoroughly consistent with the one previously postulated by Tebbe for homologation of ethylene and propylene.¹ With these olefins, which contain a hydrogen substituent at both ends of the double bond, the postulated metallacycle intermediate undergoes facile β -hydrogen transfer and olefin elimination.





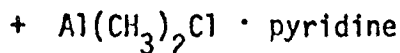
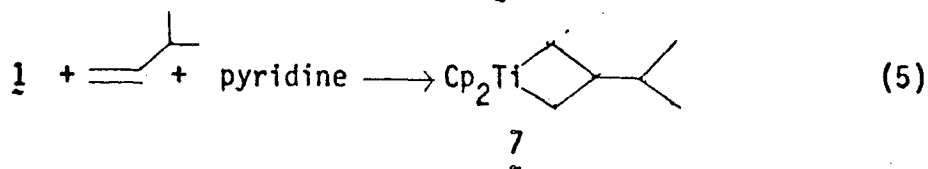
As part of a study of the factors controlling the stereochemistry of metathesis using unsymmetrical analogs of 1, (η^5 -1,2,4-trimethylcyclopentadienyl) (η^5 -C₅H₅) TiCH₂·AlCl(CH₃)₂, we reexplored the methanation reaction. Specifically, we were interested in whether olefin stereochemistry would be retained during the homologation reaction. This issue could be examined by the use of trans deuterium labelled olefins.



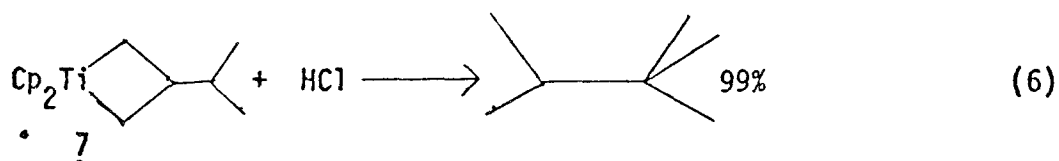
R = phenyl, isopropyl

Compounds 5 and 6 should be produced in approximately equal amounts if no cis-trans isomerization occurs during the β hydrogen transfer and olefin elimination. Initially it was assumed this reaction could be followed by NMR spectroscopy. However, at room temperature no apparent reaction occurred and as the temperature was raised to 50°C the spectrum became unidentifiable due to line broadening. Tebbe had made the observation that the rate could be increased by addition of Lewis bases like tetrahydrofuran to the reaction mixture;⁸ but, this method again gave an unidentifiable reaction mixture. However, when one equivalent of pyridine was added to a reaction mixture containing 1 and 3-methyl-1-butene a clean spectrum was immediately obtained of

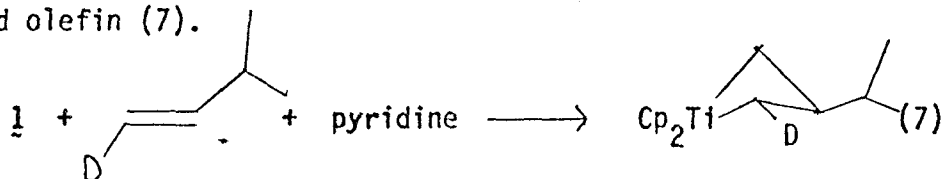
a single product. Therefore, the reaction was expanded to synthetic scale and a red crystalline material, **7**, obtained.¹²



The material was identified by its NMR spectrum (Figure 1) and chemical reactions (6) to be a metallacyclobutane.



The key features in the ¹H-NMR spectrum are the barely resolvable AB quartets for protons H_a and H_b and the high field shift of H_c. The latter may be a result of H_c being forced into the shielding environment of the [Cp₂Ti] fragment due to puckering of the metallacycle ring. The downfield assignment of H_a, the equatorial protons, was made by forming the metallacycle with specifically trans deuterium labelled olefin (7).



Implicit in this assignment is the assumption the isopropyl group occupies an equatorial position and cis/trans isomerization does not occur during formation of the metallacycle.

At this point it is desirable to briefly review the chemistry of metallacyclobutanes. The first metallacyclobutanes were made by

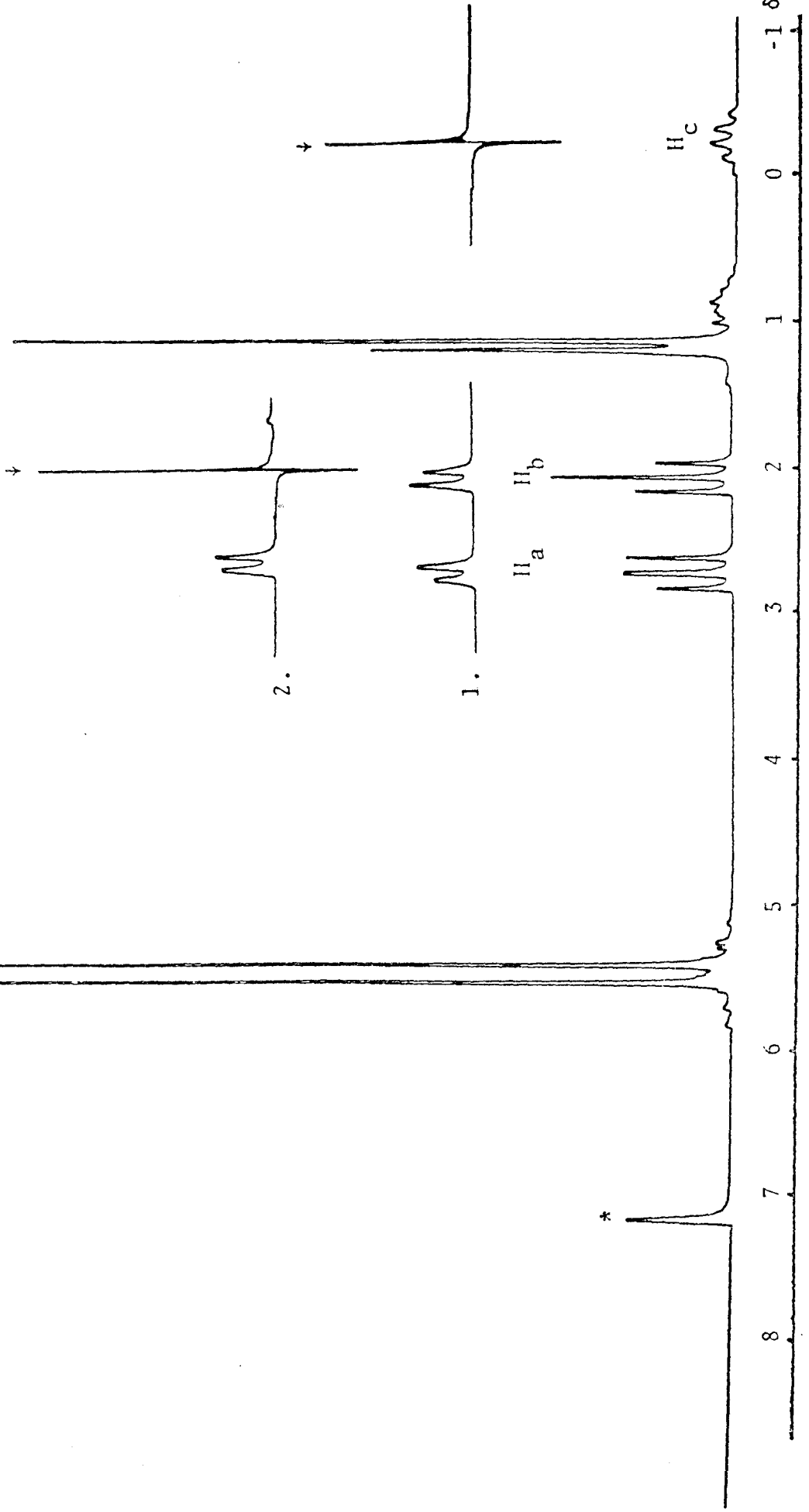
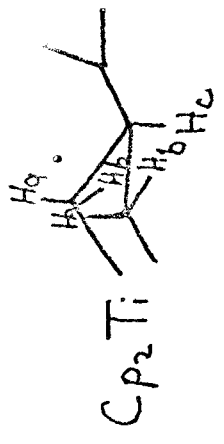
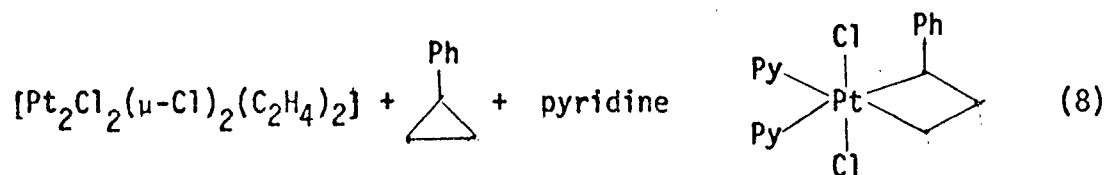


Figure Captions

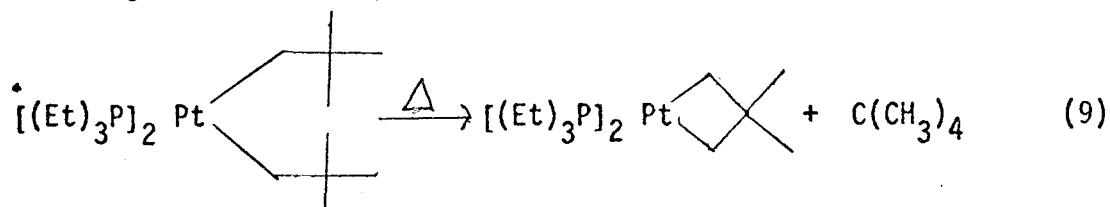
Figure 1. $^1\text{H-NMR}$ of $\underline{7}$ in benzene- d_6 (*), 90 MHz at 34°C .

One and two show H_a and H_b region in selective homo-decoupling of H_c and H_b respectively. + Indicates the position of the decoupling power. 1) AB quartet, $J_{AB} = 8.1$ Hz. 2) $J_{AC} = 8.0$ Hz. 3) $\underline{7-d}_1$, see reaction scheme for the structure, H_a (-d).

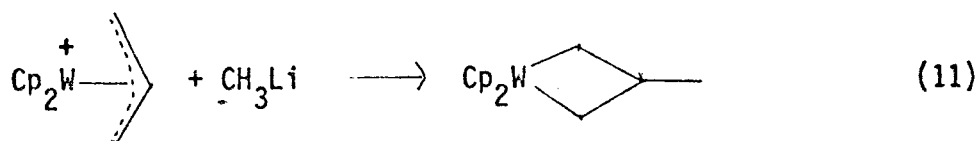
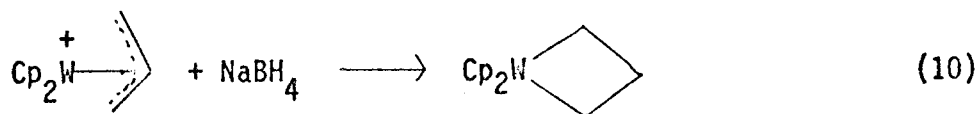
reaction of platinum complexes with cyclopropanes, an example of which is the reaction explored by Puddephatt and coworkers (8).¹³



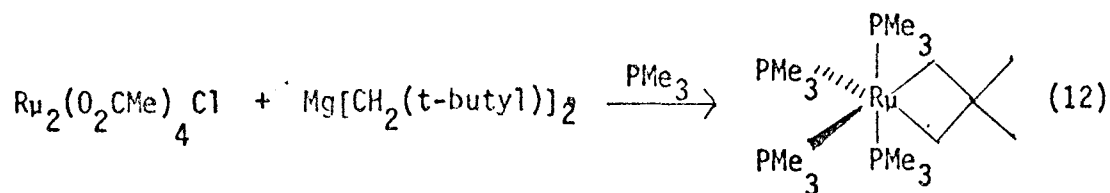
A large number of platinacyclobutanes have been made by this general technique. Another method for making platinacyclobutanes was recently developed by Whitesides,¹⁴ and involves oxidative addition of platinum into a gamma C-H bond (9).



Green and coworkers have recently reported the preparation of a new class of metallacyclobutanes.^{15,16} These stable tungsten and molybdenum complexes were prepared by the reduction of the corresponding η^3 -allyl complexes (10), (11).



The last known metallacyclobutane was synthesized by Wilkinson and coworkers (12).¹⁷

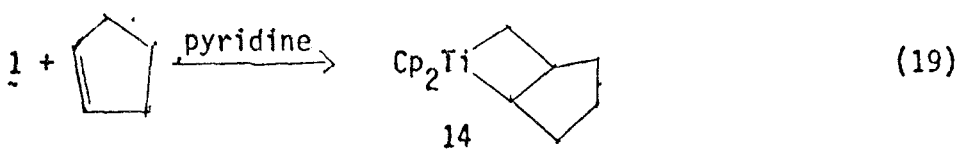
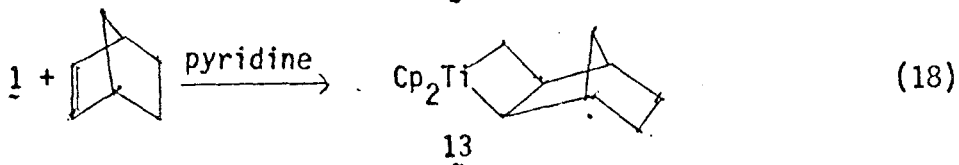
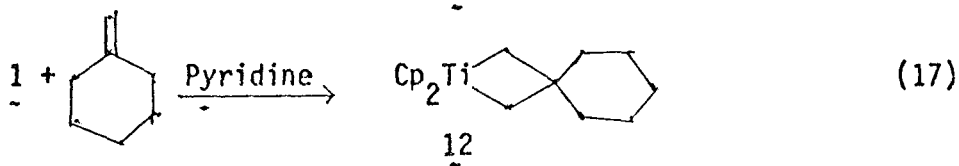
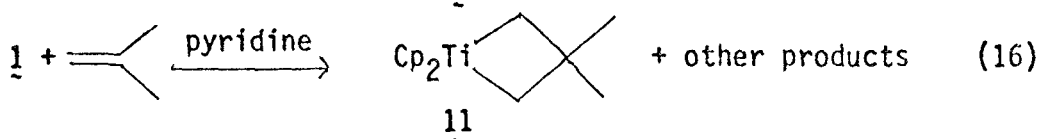
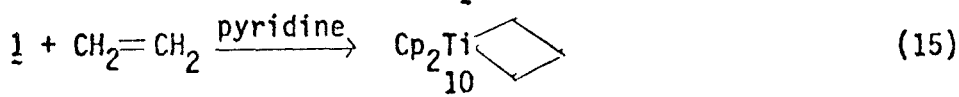
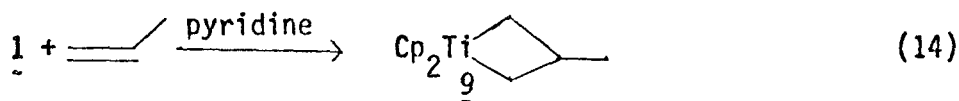
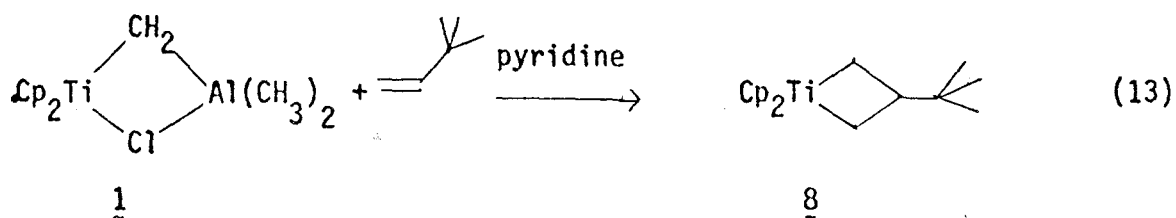


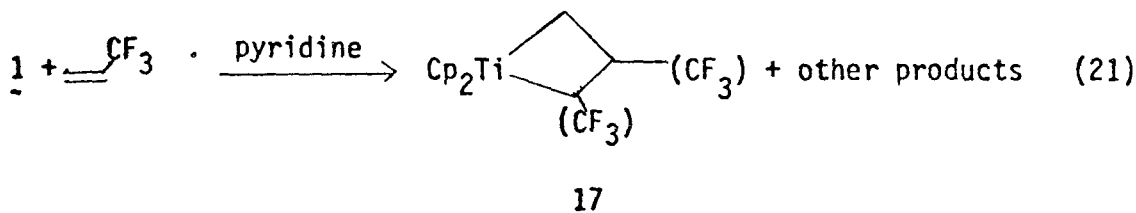
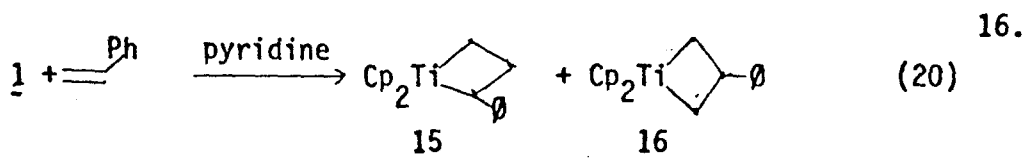
To date this complex is not well characterized. In any case, none of the metallacyclobutanes have been reported as doing any metathesis chemistry. This is understandable in the case of platinum and ruthenium as they are not metathesis metals. However, this is not an expected result for molybdenum and tungsten because they are the most efficient metathesis metals known. As will be seen in later discussions, this class of titanacyclobutanes are the first isolated metallacyclobutanes which actually do metathesis chemistry. In addition, this system represents an example of the first metallacyclobutanes synthesized by addition of an olefin to an alkylidene, an important development as this is the method of production postulated in the metathesis reaction. Lastly, this system represents the only case in which both of the postulated metathesis intermediates can be isolated and studied. For these reasons, extensive work into the chemistry and scope of these reactions was initiated.

Originally this reaction was run by mixing pyridine with a toluene solution of 1 and 3-methyl-1-butene. However, this was inconvenient as the pyridine-dimethylchloroaluminum adduct and 7 can only be separated with great difficulty by repeated recrystallization from hexane/tetrahydrofuran. It was subsequently found that 4-vinylpyridine-styrene copolymer (1:1) served as a more convenient Lewis base. In a typical reaction, the polymer was stirred with 1 and the olefin in toluene for 3.5 hours, the solution was filtered and the solvent removed to obtain essentially pure metallacycle. Other Lewis bases have also proven effective in the reaction. For example, dimethylaminopyridine has been successfully used in the production of some metallacycles. Most likely, the reaction proceeds because pyridine (or its derivatives)

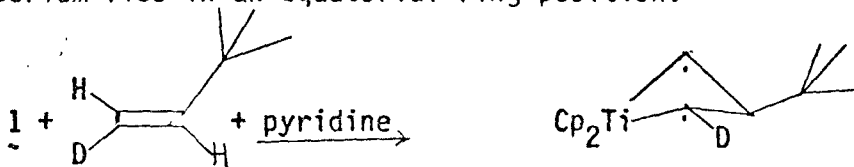
removes the dimethylaluminumchloride from 1 and the reactive $[\text{Cp}_2\text{TiCH}_2]$ fragment was trapped immediately by the olefin in the metallacycle form. This scheme is consistent with Tebbe's belief that his inability to isolate the titanacyclobutane was due to the presence of aluminum in the system.¹⁰

Once 7 had been identified the scope of this reaction was examined. The olefins which gave NMR spectra consistent with metallacyclobutane formation are listed below (13)-(21).

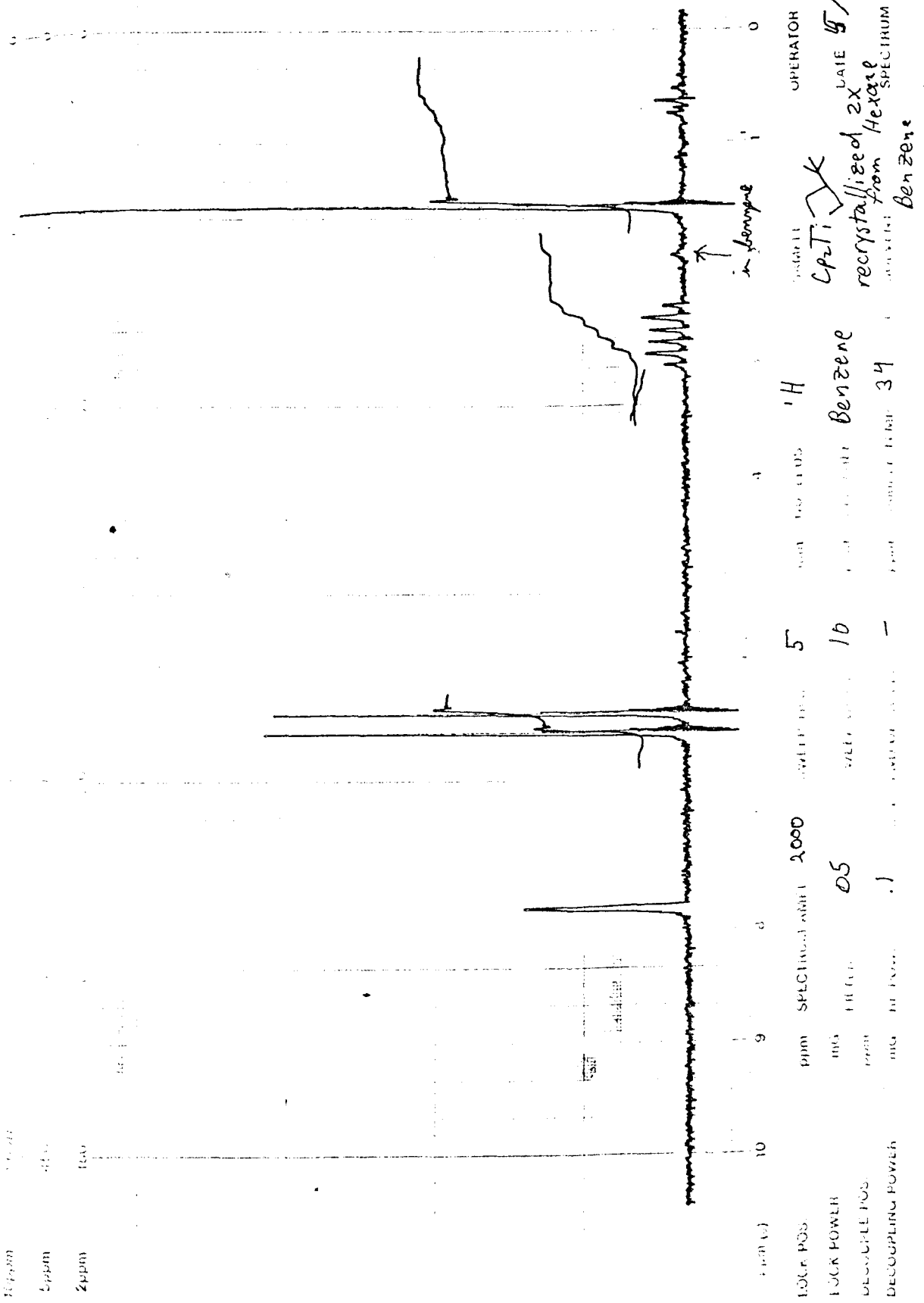




The reactions, with the exception of (16), (20) and (21) gave very clean spectra with only one product obtained. At the time of this writing, only four of these products have been isolated and crystallized, 7, 8, 10 and 13. The NMR spectrum of 8 is analogous to that of 7 (Figure 2) with the barely resolvable AB quartet for protons H_a and H_b and the high field shift of H_c . The assignments for H_a and H_b were made by reacting 1 with trans-1-d,-3,3-dimethyl-1-butene and assuming the deuterium lies in an equatorial ring position.



The reaction of 1 with styrene is of particular interest. Most of the alkyl monosubstituted olefins reacted cleanly to give metallocyclobutanes substituted at the three position. This was an expected result largely for steric reasons. Also, these results are consistent with metathesis selectivity experiments in which either electronic¹⁸ or steric¹⁹ arguments were invoked. However, with styrene both of the possible isomers, 15 and 16, were formed in what is believed to be a 2:1 ratio, respectively. This result can be rationalized by electronic arguments. Previous experiments with 1 with carbonyl functionalities



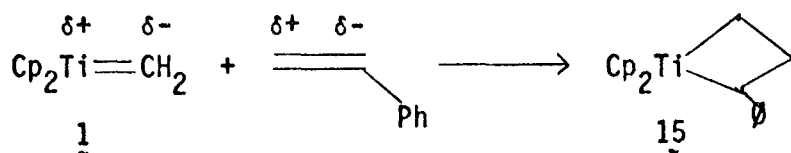
OPERATOR Howard
 DATE 5/8/80
 C₆H₆ K
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1H
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Figure 2

demonstrated its nucleophilic reactivity; therefore, reaction with polarized styrene resulted in the two substituted isomer.

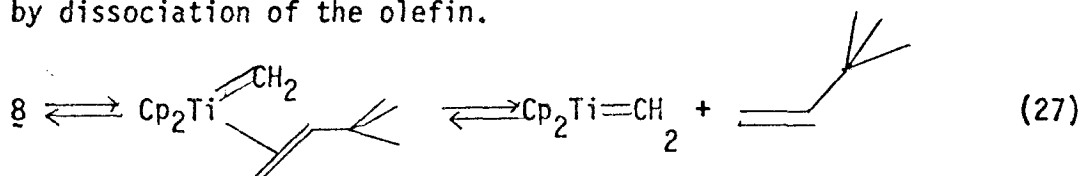


To date, purification of 15 and 16 has not been accomplished, but work is progressing in this area. To further probe the issue of electronic control of stereochemical orientation in titanacycle formation, 1 was reacted with the highly polarized 3,3,3-trifluoropropene. In this case only one isomer was obtained, but, unfortunately, the reaction did not proceed cleanly even at -78°C . It is not yet possible to definitively assign the obtained isomer and much work is yet to be done on this system.

A large number of other olefins, when reacted with 1, failed to produce a metallacyclobutane: cyclohexene, cyclooctene, cis-2-butene, trans-2-butene, 2-methyl-2 butene and 2,3-dimethyl-2-butene. In each of these cases there was no reaction until pyridine was added at which time an immediate reaction occurred to produce unidentifiably broadened NMR spectra. There are several possibilities as to how this reaction proceeds. If pyridine is added to 1 without the presence of olefin, there is an immediate reaction to produce analogous spectra, so possibly these olefins do not react at all. Also, the olefins might be reacting directly to form some paramagnetic material. Lastly, the olefins might be reacting to form metallacyclobutanes then rapidly decomposing. Low temperature NMR experiments should be performed to resolve this issue.

Initially metallacycle **8** was chosen to be studied more closely. This titanacycle is the most thermally stable one yet isolated, completely stable in the solid state at room temperature and not decomposing in solution until approximately 60°C. In comparison, all the other metallacycles decompose at different rates in solution at room temperature. For example, **7** decomposes within 48 hours at room temperature while **15** and **16** are completely decomposed within an hour. At present there is no obvious explanation for the thermal stability of **8**; however, a crystal structure is in progress and this might provide some clue. In addition, as more metallacycles are made their thermal stability will be studied with the hope that some pattern will be established.

Some of the reactions of **8** are outlined in Figure 3. The HCl decomposition (22) was as expected and helped verify the structure. The thermal decomposition (23) is illuminating and some inferences about its mechanism can be drawn. The major mode of decomposition proceeds through an alkylidene/metallacycle mechanism (27) followed by dissociation of the olefin.



The unstable alkylidene thus formed scavenges protons and evolves methane. The proton source is probably the cyclopentadienyl protons. This is a reasonable assumption as titanium is known to readily insert into the C-H bonds of its cyclopentadienyl rings;²⁰ however, the positive identification of the proton source must be left to deuterium labelling experiments. Some of the olefin formed is also reduced to the corresponding hydrocarbon, 2,2-dimethylbutane, and a small portion

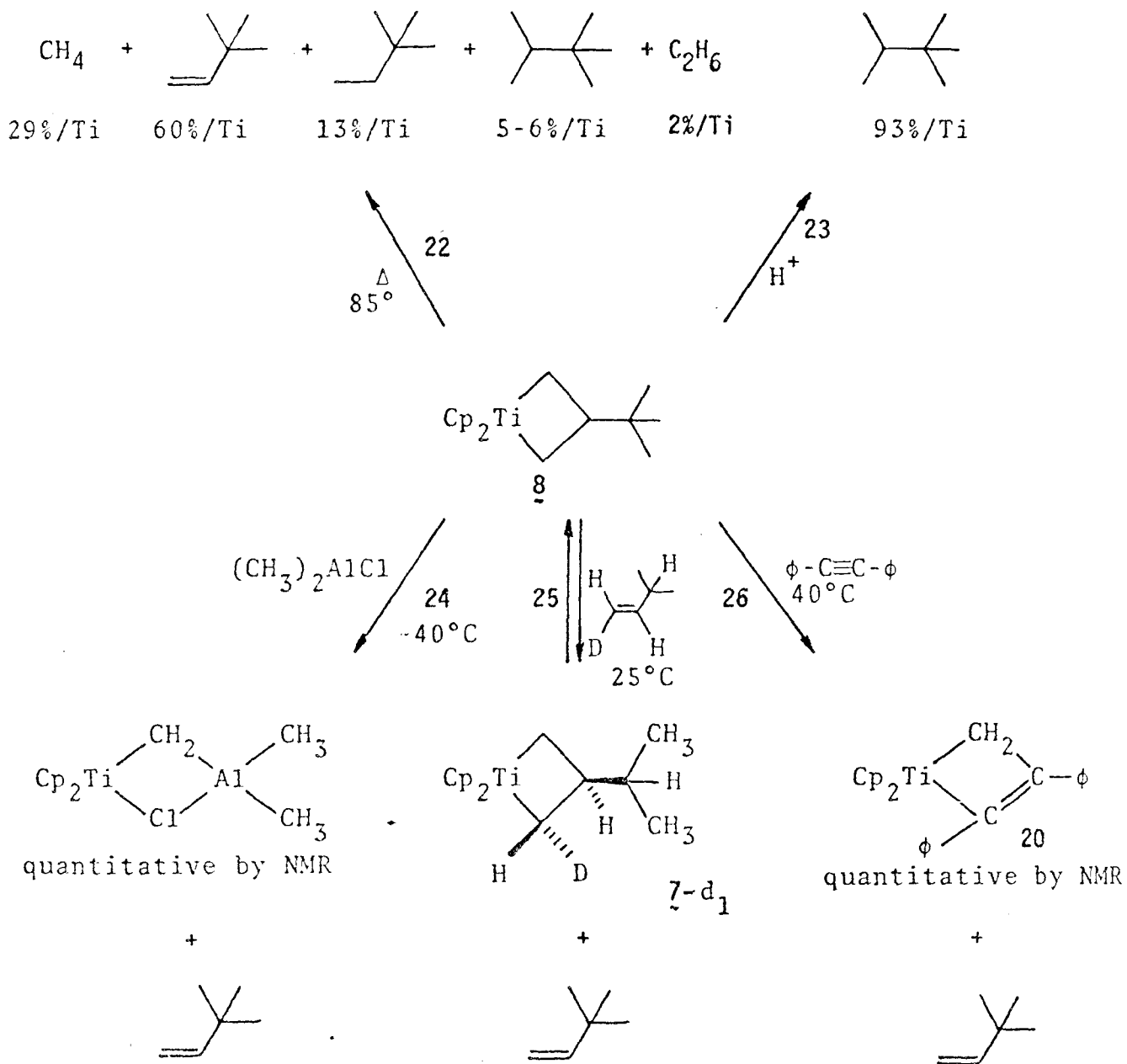
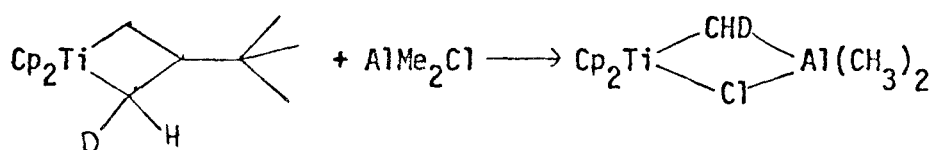


Figure 3

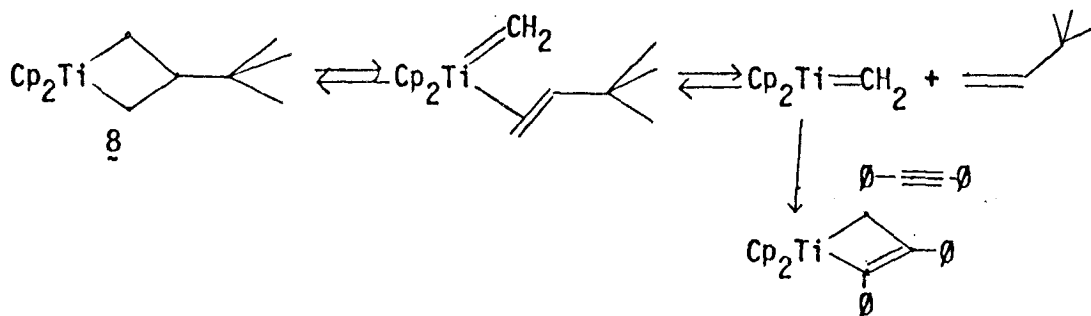
of the metallacycle directly scavenges protons to form the C-7 hydrocarbon 2,2,3-trimethylbutane.

The reaction of 8 with dimethylaluminum chloride, (24), is of particular importance as it helps to define the role of the cocatalyst in the metathesis system. First, in this case the aluminum alkyl is essential for alkylidene formation, the initiation step in metathesis. Second, the Lewis acid cocatalyst apparently facilitates the alkylidene/metallacycle equilibrium. Lastly, the formation of 8 coupled with reaction 24 provides the necessary metathesis steps for this system. This was further verified by reaction of 8-d₁ with dimethylaluminum-chloride.



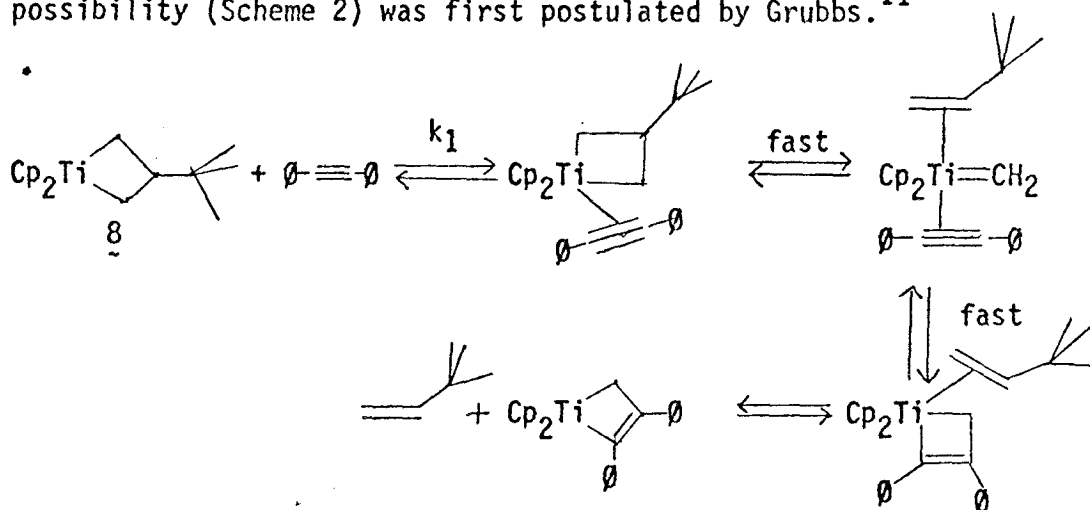
Thus the metathesis cycle is complete in a manner consistent with the mechanism first postulated by Chauvin.²¹

The exchange reactions, (25) and (26), are also consistent with metathesis reactivity. We were particularly interested in the exchange reaction with diphenylacetylene (26) as a model for the metathesis reaction suitable for a kinetics study. This reaction is desirable for this study because it is quantitative by NMR, irreversible, and easily resolved from the starting material by NMR spectroscopy. Specifically, the issue we wished to resolve was whether the exchange reaction was first or second order. Scheme 1 outlines the anticipated mechanism for a first order reaction.



Scheme 1

This mechanism postulates the intermediacy of a free alkylidene in the metathesis system and is an example of Chauvin's mechanism. The second possibility (Scheme 2) was first postulated by Grubbs.¹¹

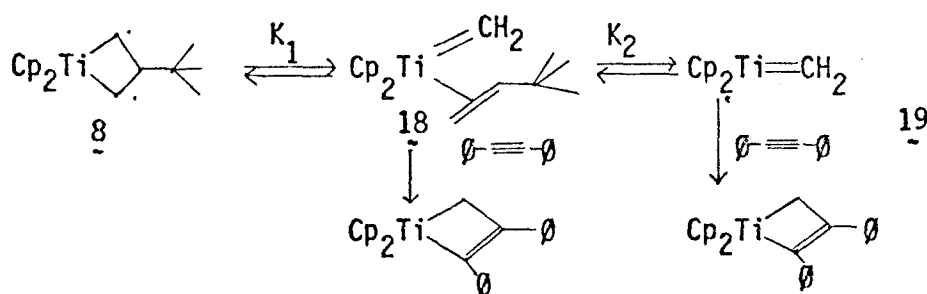


Scheme 2


In this scheme the metallacycle is the major intermediate. Complexation of the olefin induces the C-C bond fragmentation to produce a monoalkylidene fragment as a transient intermediate. It is well known that complexation of an olefin to a metal-alkyl compound facilitates reductive cleavage of the metal-carbon sigma bond.²² However, in this case the rate determining step is believed to be k_1 , the coordination of diphenylacetylene, and the overall reaction should demonstrate

second order kinetics. The reaction was followed by NMR by observing the appearance of the methylene unit on the metallacyclobutene or by observing the disappearance of the metallacyclobutane cyclopentadienyl resonance. A large number of reactions were run with varying amounts of diphenylacetylene and first order kinetics in metallacycle and zero order in acetylene were found $K_{313^{\circ}\text{K}} = 3.67 \times 10^{-4} \text{ sec}^{-1}$.

In order to ascertain the actual reactive species, further study of the potential mechanism can be done. It is possible the reactive species is actually the alkylidene/olefin complex and the system never proceeds to a free alkylidene.



If 18 is the reactive species, then K_1 is the rate determining step. If 19 is the reactive species, either K_1 or K_2 could be the rate determining step. If K_2 is rate determining an olefin dependence should be observed, implying the alkylidene is the reactive species. This particular study has only been performed once and it was found addition of olefin inhibited the rate (Table 1).

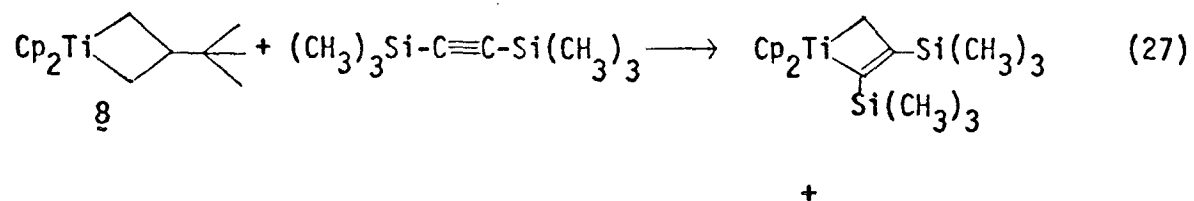
$[\phi \equiv \phi]$		40°C rate (sec ⁻¹)
0.494	0.0	3.68X10 ⁻⁴
0.535	0.258	3.4X10 ⁻⁴
0.483	0.516	2.98X10 ⁻⁴
0.501	1.032	2.68X10 ⁻⁴

concentration of $\underline{8}$ - 0.241 M/l
anisole was used as an internal standard
all concentrations are given in Moles/liter

Table 1

However, the dependence is small and there has been a great deal of difficulty encountered in obtaining reproducible results from this study. Consequently, these experiments need to be repeated before definitive arguments should be advanced. In any case, initial results indicate $\underline{19}$ is formed during the reaction and is, at least in part, an intermediate in the reaction.

Work has also been begun to determine whether these first order kinetics are general for the transformation of metallacyclobutanes to metallacyclobutenes. Initial results with bis (trimethylsilyl) acetylene indicate the reaction is first order (27) with the same rate constant as the diphenylacetylene exchange.

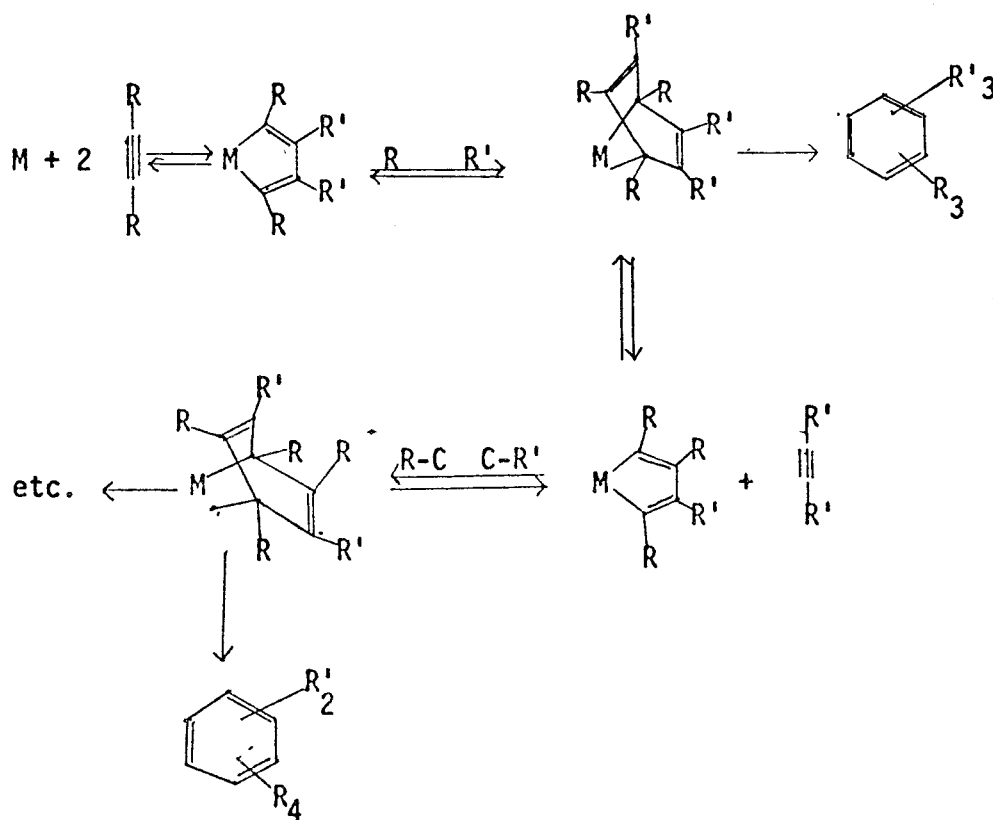


In conclusion, we have now isolated an intermediate from a true metathesis system. These reactions appear to be general for mono-substituted olefins and also effective for some disubstituted olefins. These compounds provide us with a unique opportunity to study the metathesis reaction and work is in progress to extend our knowledge of this system.

Part 3Titanium Metallacyclobutenes

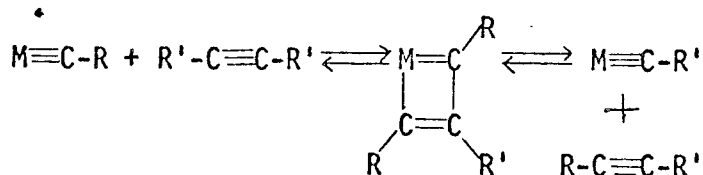
In addition to the novel ester and olefin reactivity of the carbenoid species 1, it also reacts in a facile manner with disubstituted acetylenes to form titanium metallacyclobutenes. These series of compounds could be important in elucidating the mechanism of acetylene metathesis.

To date, the mechanism of acetylene metathesis is virtually unstudied; however, at least two mechanisms have been proposed in the literature. One of the earliest involves a reversible Diels-Alder reaction as the main scrambled step.²³



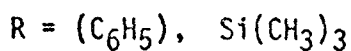
At present, this mechanism appears unlikely. From recent studies which involve addition of acetylenes to metallacyclopentadienes, aromatic formation is essentially the sole product. If metathesis activity is a potential side product of this acetylene trimerization, some aromatics with scrambled alkyl groups should be observed. However, these types of products have not been reported in the studies of this reaction.²⁴

Another mechanism which has been postulated is analogous to the olefin metathesis system. Instead of a carbene catalyst, a carbyne catalyst is considered.¹⁸



Although at this point this mechanism has not been disproven, there is no supporting evidence.

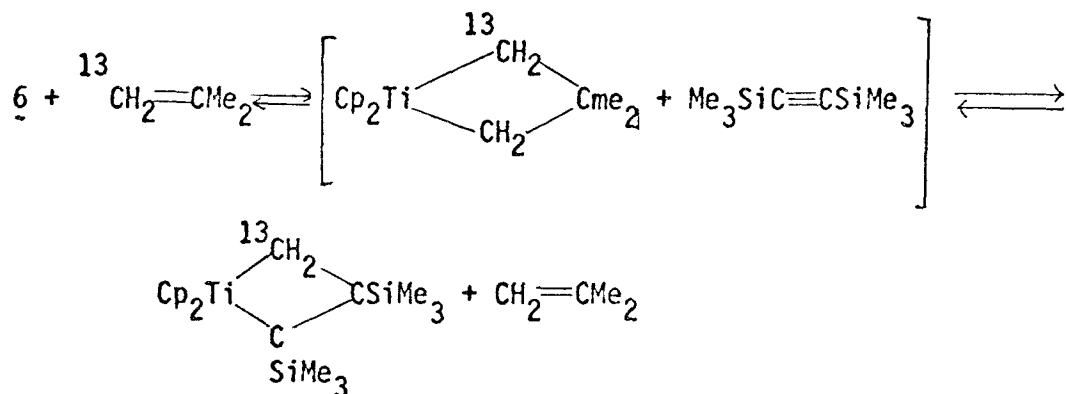
The recently reported isolation of thermally stable metallacyclobutenes suggests an alternate mechanism of acetylene metathesis. Tebbe found the reaction of 1 with diphenylacetylene or bis (trimethylsilyl) acetylene produces the corresponding metallacyclobutene.²⁵



20

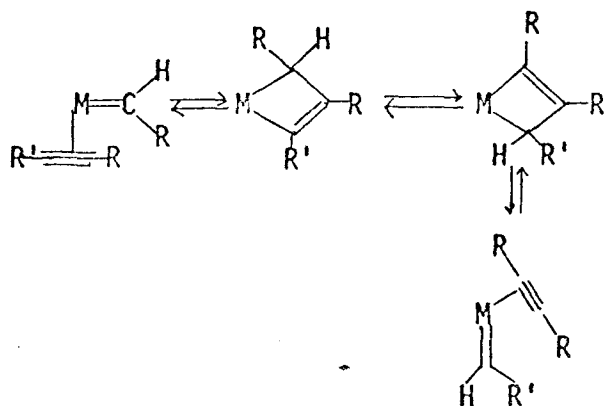
21

In the trimethylsilyl case, he also found the reaction with 1 to be reversible. In addition, complexes 1 and 21 catalyze olefin metathesis, in what Tebbe believes to be the following manner.²⁵



•

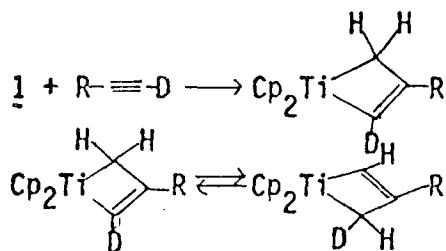
Combining the acetylene reaction (28) with a second reaction provides a potential scheme for acetylene metathesis. The important step to examine is the 1,3 hydrogen shift.



Whether this step can be thermally induced is unknown. Many of the catalyst systems contain a phenolic functionality which might indicate the necessity of a co-catalyst.¹¹

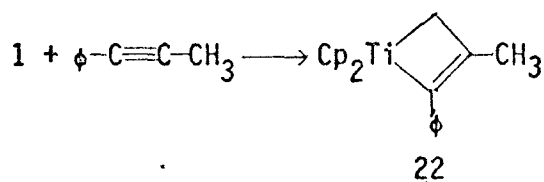
It is our intention to examine the feasibility of the 1,3 hydrogen shift. The most desirable approach would be to carry out the

reaction with deuterium labelled terminal acetylenes. This would allow us to directly explore the exchange by observing the accumulation of deuterium in the methylene position.



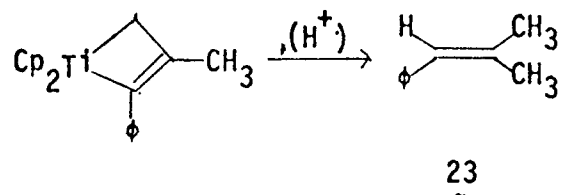
The first terminal acetylene utilized in the synthesis was phenyl acetylene. However, after numerous attempts, none of the desired complex was isolated. As it is possible an acid-base reaction occurred rather than the intended one, less acidic terminal acetylenes were used. Unfortunately, the reaction failed with both trimethylsilylacetylene and 1-pentyne. It was later discovered that Tebbe had attempted the same reaction with an equal lack of success.⁸

At the time this work was being pursued, it was not known that complex 21 had been prepared. Therefore, we considered the possibility that the formation of 20 was a special case. In order to probe this issue, a study of activity of 1 with other disubstituted acetylenes was initiated. The complex, 1, was reacted with methylphenylacetylene in tetrahydrofuran to obtain 22 in 85% recrystallized yield.



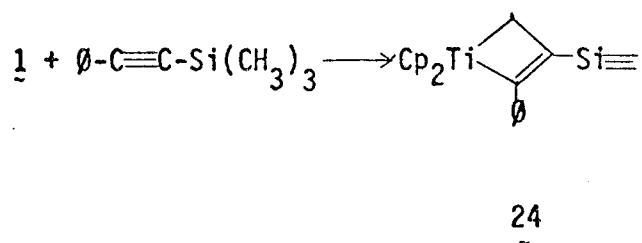
This complex was identified by its NMR spectrum and by its acid decomposition product. Upon addition of two equivalents of acetic acid, the

only detectable organic compound was 23.

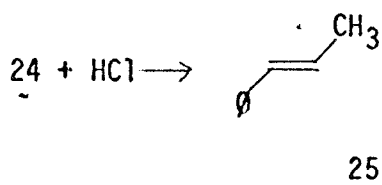


It is interesting to note that 22 was the only isomer of the organo-metallic reaction. The reason for this is not clear, but the most likely explanation is steric. Tebbe took a crystal structure of 20 and found the metallacyclobutene component to be essentially planar with the phenyl functionalities lying in the plane. If the same situation exists in solution with complex 22, it is possible the planar phenyl group would be sterically less demanding than the methyl group.

In a second synthesis of this nature, 1 is reacted with trimethylsilylphenylacetylene in tetrahydrofuran to form the titanium metallacyclobutene, 24.

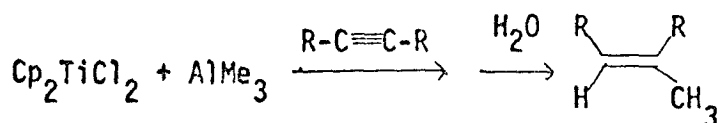


The reaction proceeds in 80% recrystallized yield with only one isomer isolated. The compound was identified by its NMR spectra and its HCl decomposition product.



Upon addition of a large excess of HCl gas to a stirred hexane solution of 24, 25 was produced in 83% yield. Apparently desililation of the originally formed trisubstituted olefin occurs readily under the reaction conditions. Again the fact that only one isomer was obtained in this reaction is probably attributable to steric factors.

In addition to supplying a possible mechanism for acetylene metathesis, these metallacyclobutenes might answer another important question. A number of reactions have been reported in the literature where disubstituted acetylenes have been transformed to cis-trisubstituted olefins by reaction of trimethylaluminum with zirconium and titanium cyclopentadienyl complexes.^{26,27} The following series of reactions reported by Negishi is an example.

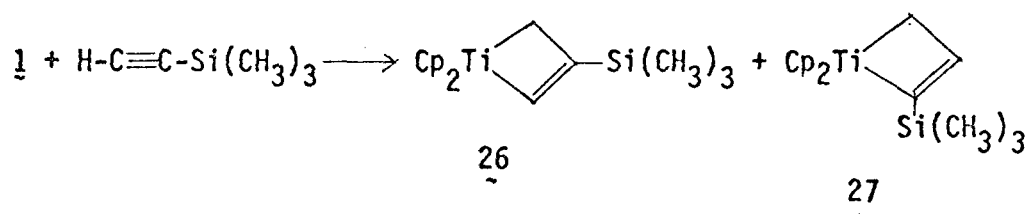


It has been thought these systems produce noncyclic species of the type RMeC=CRM (where $\text{M} = \text{Ti}$ or Al).²⁶ However, in light of the above systems, it seems possible these reactions are going through a metallacyclobutene intermediate. Therefore, these results could be useful in answering a mechanistic question and in developing these complexes into important reagents for the organic synthesis of trisubstituted olefins.

At this point, another attempt was made to synthesize a metallacyclobutene using terminal acetylenes. It has been found by Tebbe that upon heating 21 with diphenylacetylene, an exchange reaction occurs to produce 20. Consequently, it was decided to try analogous exchange reactions with terminal acetylenes. The complex 21 was

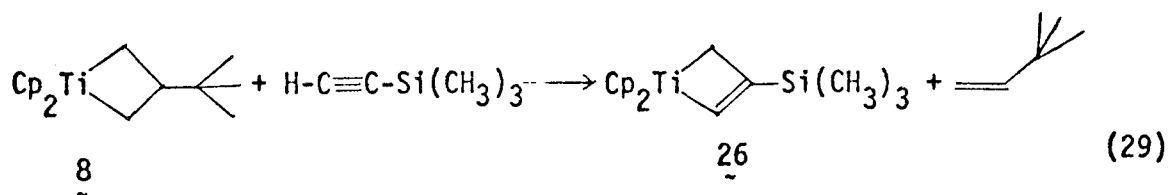
was reacted with phenylacetylene in a NMR tube without solvent at 85°C. The only reaction observed is polymerization. Interestingly, even though polymerization of phenylacetylene occurs, 21 is not destroyed during the process. However, the series of complexes desired cannot be isolated in his manner.

A very promising approach to the synthesis of the desired metallacyclobutenes has recently been found. When pyridine was added to a perdeuterobenzene solution of 1 and trimethylsilylacetylene, the NMR spectrum indicated that both 26 and 27 were formed in approximately a 3:1 ratio, respectively.



Unfortunately, to date, these compounds have not been isolated. All attempts to do so have led to decomposition to a paramagnetic material. NMR experiments indicate the products are thermally unstable and, at least while in solution, unstable to vacuum. In addition, this reaction is not a general one for the formation of metallacyclobutenes from mono-substituted acetylenes. The reaction produces paramagnetic material with ethynylbenzene, 3,3-dimethyl-1-butyne and 3-methyl-1-butyne.

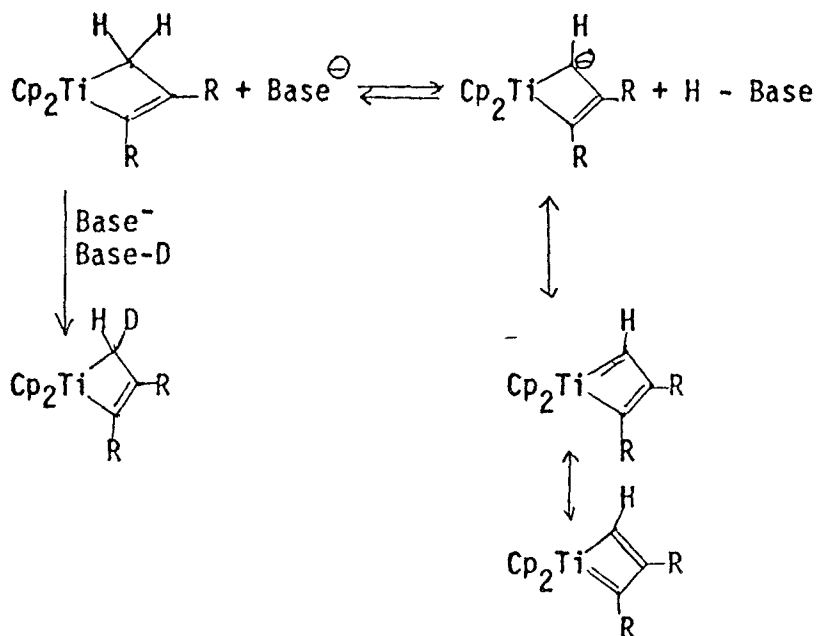
Another promising approach to the synthesis of metallacyclobutenes is based on the exchange reaction of acetylenes with metallacyclobutenes (29).



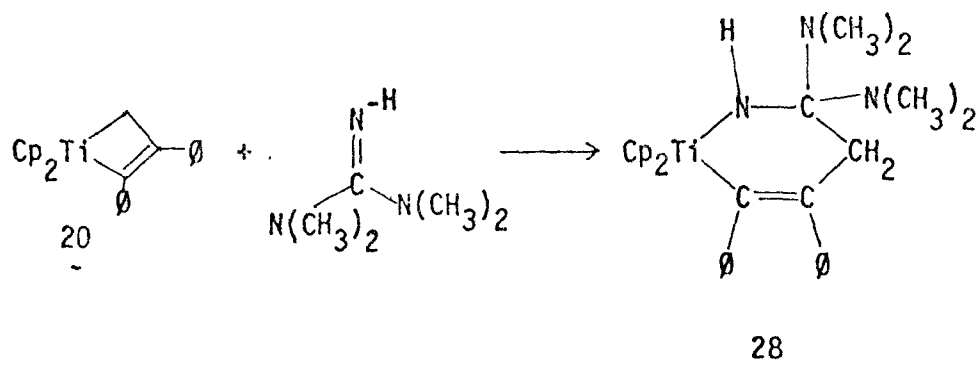
In this case only a single isomer was obtained, 26. Also, this reaction can be extended to other monosubstituted acetylenes. For example, 3,3-dimethyl-1-butyne and 3-methyl-1-butyne both participate in this exchange reaction. The problem encountered was that the exchange at room temperature was very slow, taking three days, and extensive thermal decomposition occurred at these temperatures. However, as the temperature was lowered the reaction slowed. Studies are proceeding to determine the optimum conditions for this reaction.

Acidity Studies

The determination of the acidity of metallacyclobutenes is important in establishing its potential role in metathesis of acetylenes. Consequently, we decided to treat some of the stable metallacyclobutenes with a series of bases to attempt to produce deprotonated intermediates. Also, it is hoped some interesting complexes might be formed by these reactions



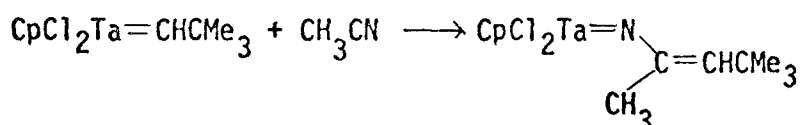
To date, only 20 has been treated with any bases. It does not react with triphenylphosphine, pyridine, sodium phenoxide or sodium methoxide. With *n*-butyl lithium and potassium *t*-butoxide, the complex is destroyed. Only with tetramethylguanadine does a clean reaction proceed to produce a yellow, air stable, crystalline material. The structural assignment of this compound, 28, can be tentatively made based upon its NMR, and by analogy to the other products obtained by reaction of metallacyclobutenes with imines.²⁸



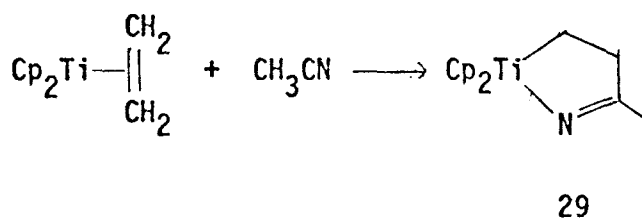
This product is formed by insertion of the imine into the titanium-carbon bond. These studies will be continued with other bases and with other metallacyclobutenes.

Addition of Acetonitrile

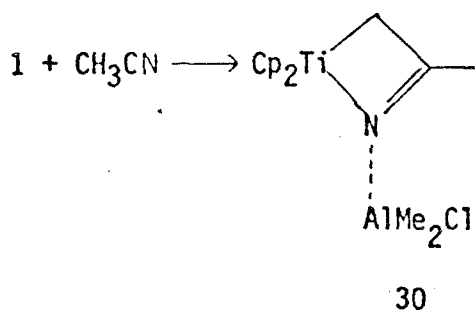
It has been found that acetonitrile will insert into metal carbene bonds.²⁹



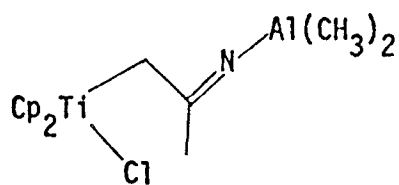
In this case performed by Schrock, the product is noncyclic. However, recent work in John Bercaw's laboratory indicates cyclic products of this nature are also possible.³⁰



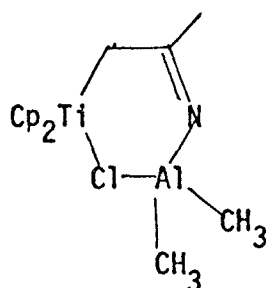
We decided to determine if a four membered ring complex analogous to 29 could be synthesized by addition of 1 to acetonitrile. A reaction occurred almost immediately at -50°C in tetrahydrofuran to obtain a product in 60% isolated yield which had an I.R. stretch at 1610 cm^{-1} and by proton NMR analysis could be 30.



Upon addition of aqueous hydrochloric acid to the reaction mixture, gas chromatography analysis indicated the formation of acetone; unfortunately, this data is also consistent with at least two other possible structures, 31 and 32.



31



32

To date, no chemical methods have been found to differentiate between these three possible structures. It might be necessary to take a crystal structure in order to definitively determine which isomer exists.

Experimental

Reaction (3): Synthesis of 2-Methoxypropene

Complex 1 (0.5 grams, 1.8 mmoles) was reacted with methyl acetate (0.13 mls, 1.8 mmoles) in dry, degassed toluene. After four hours, wet ether was added. The solid was filtered and the filtrate was eluted through a silica column with pet ether. The pet ether solution was injected into a 32-foot carbowax column resulting in a retention time of 339 seconds. Coinjection with an authentic sample of 2-methoxypropene indicated the correct material was obtained. No methylacetate was detectable by gas chromatography indicating a high yield was obtained.

Reaction (4): Synthesis of 2-(t-butoxy) Propene

Complex 1 (0.1 grams, 0.35 mmoles) was dissolved in dry, degassed perdeuterobenzene in an NMR tube and t-butyl acetate (0.048 mls, 0.35 mmoles) was added. The reaction was followed by NMR, and its completion was reached after 24 hours. An internal standard of anisol indicated a yield of approximately 100%. NMR (C_6D_6) δ 4.95 (broad singlet, 2H), δ 1.85 (S,9A). The CH_3 peak was buried in Al- CH_3 peaks.

Reaction (5): Synthesis of Enol Ether from Dihydrocoumarin

Complex 1 (0.1 grams, 0.35 mmoles) was reacted with dihydrocoumarin (0.045 mls, 0.35 mmoles) in the same manner as (4) to obtain

an approximately 100% yield of the product. NMR (C_6D_6) δ 7.1 (m,4H), δ 4.9, 4.2 (d,2H), 3.5 (m,4H).

Bis (Cyclopentadienyl) Titanium Methyl Chloride 4

Into a schlenk tube under argon was placed 1 (1.3 grams, 4.6 mmoles) followed by 10 mls of dry, degassed toluene. Methyl acetate (0.4 mls, 5 mmoles) was added by syringe techniques. The solution was stirred for 5 hours at ambient temperature. The solvent was pumped off to obtain an orange solid. The solid was dissolved in the minimum amount of toluene and one-fourth volume of pet ether was added. After cooling at $-45^\circ C$ for 24 hours, an orange crystalline solid (0.63 grams, 60% yield) was filtered and washed twice with pet ether. NMR (C_6D_6) δ 6.0 (s,10H), δ 1.0 (s,3). Elemental Analysis; Found, C-57.21, H-5.78, Cl-15.7; Calculated, C-57.7, H-5.73, Cl-15.5.

4-vinylpyridine/styrene Copolymer (1:1)

Styrene (42 grams; 0.4 moles) was stirred with 4-vinylpyridine (41.7 grams; 0.4 moles) and α, α' azobisisobutyronitrile (1.3 grams; 8 mmoles) in 400 mls of dry, degassed tetrahydrofuran under argon at $60^\circ C$ for 24 hours. The polymer was then precipitated by dropwise addition of the reaction mixture to stirred diethyl ether (20 mls of diethyl ether for every ml of the reaction mixture). The resulting white powder was filtered, washed with diethyl ether then dried by being placed under high vacuum for 24 hours. Yield-61 grams; 73%.

Metallacyclobutanes

All manipulations were performed on a vacuum line under argon or in a dry box with a nitrogen atmosphere. All solvents have been rigorously dried and degassed.

7

Complex 1 (1 gram; 3.5 mmoles) was dissolved in 25 mls of toluene. One ml of 3-methyl-1-butene (1 ml; 8.9 mmoles) was added followed by one gram of polymer (4-vinylpyridine/styrene 1:1). The mixture was stirred for 3.5 hours then the polymer was removed by filtration through a coarse frit and washed with toluene until the wash was clear. The toluene was evaporated and the resulting red solid was dissolved in the minimum amount of a 10:1 hexane/tetrahydrofuran solution then filtered through a fine frit to remove a brown powder. The solution was cooled to -40°C for 24 hours then filtered to obtain red crystals. Yield 0.6 grams, 64%. NMR-- see discussion.

HCl decomposition of 7

The metallacycle 7 (0.3 grams; 1.1 mmoles) was dissolved in 1 ml of pentane and three equivalents of HCl (generated by addition of H_2SO_4 to NaCl) vacuum transferred into the reaction mixture at liquid nitrogen temperature. The reaction mixture was allowed to warm to room temperature and the volatiles vacuum transferred. The products were identified by gas chromatography/mass spectroscopy. If the reaction was allowed to warm quickly an approximately equimolar amount of 2,3-dimethylbutane and 2,3-dimethyl-1-butane was found. However, when the reaction was slowly warmed in a dry ice/acetone bath only one product, 2,3-dimethylbutane was

obtained in 99% yield. The yield was determined by gas chromatography with a flame ionization detector using hexane as an internal standard with response factors independently determined with authentic samples.

8

Complex 1 (1 gram; 3.5 mmoles) was reacted with 3,3-dimethyl-1-butene (1 ml; 7.8 mmoles) and 1 gram of polymer (4-vinylpyridine/styrene copolymer 1:1) in the same manner as 7. The product was recrystallized from hexane to obtain red needles. Yield 0.62 grams; 64%. When the same reaction is run in an NMR tube with pyridine as the Lewis base and using anisole as an internal standard, the yield is 100%. NMR--see discussion.

Elemental Analysis Calc: C-73.91; H-8.76; Ti-17.34

Found: C-73.88; H-8.81; Ti-17.44

Crystals suitable for x-ray diffraction analysis were obtained by slow evaporation from hexane under nitrogen.

HCl decomposition of 8

The decomposition was run in the same manner as the HCl decomposition of 7. The product, 2,2,3-trimethylbutane, was identified by G.C/M.S. The yield 93% was determined by G.C. (durapack, 17 feet, 100°C) with a flame ionization detector using heptane as an internal standard. The response factors were independently determined using authentic samples. The olefin 2,3,3-trimethyl-1-butene was synthesized by the method of Negishi³¹ and the corresponding hydrocarbon, 2,2,3-trimethylbutane, formed by catalytic hydrogenation of the olefin.

Thermal Decomposition of 8

NMR experiments indicated thermal decomposition began at approximately 60°C. The metallacycle, 8, (0.3 grams; 1.1 mmoles) was dissolved in 2 mls of toluene, the solution evacuated and degassed, and the flask then placed in an 85°C oil bath for 16 hours. Methane was collected by Toepler pump at -100°C (Yield 29%/Ti). The remaining volatiles were vacuum transferred and identified by G.C./M.S. using authentic samples as standards. Yields were determined by G.C. (dura-pack, 17 feet, 100°C) with a flame ionization detector and response factors were independently determined. Products: ethane-2%/Ti; 3,3-dimethyl-1-butene-60%/Ti; 2,2-dimethylbutane-13%/Ti; 2,2,3-trimethylbutane-6%/Ti.

Reaction of 8 with $\text{Al}(\text{CH}_3)_2\text{Cl}$ (24)

This reaction was followed by NMR. The metallacycle 8 (0.025 grams; 0.09 mmoles) was dissolved in 0.3 mls of benzene with 10 μl s. of anisole in an NMR tube equipped with a septum cap. The tube was cooled to -40°C and $\text{Al}(\text{CH}_3)_2\text{Cl}$ added (15 μl , excess). The NMR was taken at -40°C immediately after addition of the aluminum alkyl and a quantitative reaction had occurred.

Reaction of 8 with 3-methyl-1-butene (25)

The reaction was followed by NMR. The metallacycle (0.025 grams; 0.09 mmoles) was dissolved in 0.3 mls of benzene in an NMR tube equipped with a septum cap. The olefin (20 μl s; excess) was added by syringe and the reaction followed for three days. A steady concentration of 7 was observed; however, because this compound is thermally unstable, after three days all of material had decomposed.

trans-1-d₁-3,3,-dimethyl-1-butene.

Deuterated olefins were prepared from Cp₂Zr(H)(Cl) and the corresponding acetylenes by the method of Schwartz.³² Cp₂Zr(H)(Cl) (5 grams; 20 mmoles) was placed in a 250 ml round bottomed flask equipped with a sidearm with 125 mls of benzene and 3,3-dimethyl-1-butyne (3.1 mls, 25 mmoles). The mixture was stirred for 18 hours under argon at room temperature, most of the benzene evaporated, and the reaction quenched by addition of D₂O. After filtration, the solution was vacuum transferred then the product collected by preparative gas chromatography (SE-30, 8 feet, 100°C). Yield 1.4 grams, 82%. NMR (C₆D₆) δ5.9 (m, 1H), δ5.0 (d, 1H), δ1.1 (s, 9H).

This product was then reacted with complex 1 and polymer to produce deuterated metallacyclobutane in the same manner as the analogous nondeuterated metallacyclobutane.

NMR Experiments to Determine Scope of Metallacyclobutane Formation

All of these experiments were run in the same manner. Complex 1 (0.025 grams; 0.088 mmoles) was dissolved in 0.3 mls of perdeutero-benzene in an NMR tube equipped with a septum cap. The olefin (excess) was injected into the tube and the NMR spectrum taken. In all cases studied there was no reaction at this point. Pyridine was then injected and the spectrum taken immediately. For those olefins which produced the metallacyclobutane, the most distinctive feature on the NMR was the doublet formed by the cyclopentadienyl ring protons (with the exception of ethylene).

Kinetics Experiments (26)

A large number of reactions were run. A typical example is given. Five tubes were prepared by weighing 1, 2, 3, 4 and 5 equivalents of diphenylacetylene into NMR tubes. The tubes were marked at the 0.3 ml level then taken into the dry box. A standard solution of metallacyclobutane 8 was prepared by placing 0.2 grams of 8 and 0.05 mls of anisole (internal standard) into a volumetric flask and raising the solvent level to 2 mls by addition of perdeuterobenzene. A known amount (0.2 mls) of the stock solution of 8 was added to each tube and the volume of the tubes is then raised to 0.3 mls (if the olefin dependence were to be determined, the olefin would be injected and the volume then raised) by addition of perdeuterobenzene. The tubes are then frozen and sealed and the reaction followed on an EM-390 by observing the formation of the methylene group on the metallacyclobutene or by the disappearance of the metallacyclobutane cyclopentadienyl peaks.

Metallacyclobutenes (20, 21, 22, 24)

All manipulations were performed in a dry box with a dinitrogen atmosphere using dry, degassed solvents or an a vacuum line under argon.

The disubstituted acetylene was dissolved in THF and cooled to -40°C . Complex 1 was added and the solution was allowed to react at -40°C for 24 hours at which time the solvent was evaporated. The residue was dissolved in the minimum amount of toluene and an equivalent volume of pet ether was added. After cooling for 24 hours, the solid obtained was filtered and washed with cold pet ether resulting in the isolation of room temperature stable purple crystals.

20

Complex 1 (2 grams, 7.05 mmoles) was reacted and purified by the above method with diphenylacetylene (1.26 grams, 7.05 mmoles) to obtain the corresponding metallacycle (1.93 grams, 74% yield). NMR (C_6D_6) δ 7.0 (m,10H), δ 5.6 (s,10H), δ 3.4 (s,2H).

21

Complex 1 (2 grams, 7.05 mmoles) was reacted and purified by the above method with bis (trimethylsilyl) acetylene (1.21 grams, 7.05 mmoles) to obtain the corresponding metallacycle (1.3 grams, 52% yield). NMR (C_6D_6), δ 5.2 (s,10H), δ 4.6 (s,2H), δ 0.3 (s,9H), δ 0.2 (s,9H).

22

Complex 1 (2 grams, 7.05 mmoles) was reacted and purified by the above method with methylphenylacetylene (0.87 mls, 7.05 mmoles) to obtain the corresponding metallacycle (1.85 grams, 85% yield). NMR (C_6D_6) δ 7.15 (m,5H), δ 5.65 (s,10H), δ 3.35 (s,2H), δ 1.65 (s,3H).

Compound 22 was then added to a toluene solution of glacial acetic acid. After sitting for 10 minutes, the solution was filtered then eluted through a neutral alumina column. The resulting solution was separated on a 10-foot SE-30 column to obtain a single product. NMR (CCl_4) δ 7.15 (m,5H), δ 6.2 (m,1H), δ 1.89 (d,3H), δ 1.80 (d,3H). This corresponds to the published value.³³

23

Complex 1 (2 grams, 7.05 mmoles) was reacted and purified by the above method with methyl (trimethylsilyl) acetylene (1.24 grams, 7.05 mmoles) to obtain the corresponding metallacycle (2.0 grams, 80%

yield). NMR (C_6D_6) δ 7.1 (m, 5H), δ 5.45 (s, 10H), δ 4.35 (s, 2H), δ 0.10 (s, 9H).

Complex 23 (1.5 grams; 4.1 mmoles) was stirred with 25 mls of hexane at $-78^\circ C$. HCl was then bubbled into the reaction mixture for ten minutes. The mixture was allowed to warm to room temperature. The Cp_2TiCl_2 was filtered off and the hexane evaporated. The resulting liquid was placed on a silica column and eluted with hexane. After evaporation of solvent, 0.4 grams (83% yield of *trans*- β -methylstyrene) was obtained. NMR (C_6D_6) δ 7.2 (m, 5H), δ 6.2 (m, 2H), δ 1.8 (d, 3H). The NMR matched that of an authentic sample supplied by Aldrich.

26, 27

These two metallacyclobutenes have only been seen on the NMR by adding pyridine to an NMR tube containing 1 and trimethylsilylacetylene.

26 NMR (C_6D_6) δ 6.6 (t, 1H), δ 5.6 (s, 10H), δ 3.8 (d, 2H), δ 0.4 (s, 9H) :

27 NMR (C_6D_6) δ 5.4 (s, 10H), δ 4.1 (d, 2H), δ 0.3 (s, 9H) the single proton cannot be definitely assigned.

Imine Insertion Product 28

Compound 20 (0.5 grams, 1.35 mmoles) and tetramethylguanidine (0.4 grams, 3.53 mmoles) were dissolved in 10 mls of toluene for 12 hours to produce an orange solution. Hexane (10 mls) was added and the solution cooled to $-40^\circ C$ to precipitate a yellow powder. This powder was dissolved in toluene and one half volume of hexane added. The solution was cooled to $-40^\circ C$ and yellow crystals were formed. NMR (C_6D_6) δ 7.3 (m, 10H), δ 5.8 (s, 10H), δ 2.7 (m, 12H), δ 2.6 (s, 2H).

Acetonitrile Addition Product (30, 31, 32)

The reactants 1 (1 gram, 3.53 mmoles) and acetonitrile (0.19 mls, 3.53 mmoles) were cooled to -40°C in the dry box. These compounds were then added simultaneously to 5 mls of dry, degassed THF cooled to -40°C . After five minutes, the products are precipitated by addition of cold pet ether. The liquid was decanted and the red oil washed twice with approximately 15 mls of cold pet ether. Additional pet ether was added and stirred over the red oil for 24 hours to obtain a brown solid. After filtration, the brown solid was dissolved in the minimum amount of toluene and pet ether was added until the solution became cloudy. The solution was cooled at -40°C for 24 hours then filtered to obtain a brown powder (0.48 grams, 47% yield). NMR (C_6D_6) δ 5.85 (S,10H), δ 2.10 (S,2H), δ 1.85 (S,3H), δ 0.15 (S,6H).

The solid was dissolved in THF and an excess of aqueous 1 M HCL was added. After ten minutes the toluene layer was separated, and a small sample injected at 40°C into a G.C. 20-foot SE-30 and a 20-foot carbowax column. The retention times matched those of an authentic sample of acetone.

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