Titanium Carbenes: Reactions with Selected Carbonyl Compounds and Ring-Opening Metathesis Polymerization of Cyclic Olefins

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ABSTRACT

The reaction of "$(C_5H_5)_2Ti{=}CH_2$" with acid anhydrides and imides yielded several useful organic transformations, including stereoselective ring formation applicable to alkaloid synthesis. Further studies developed an *in situ* preparation of Tebbe's reagent for large-scale methylenation of ketones and esters. Additionally, the reaction of proton sources with titanacyclobutanes was briefly surveyed and found to give both ring-opened and carbene-trapped products.

The polymerization of strained cyclic olefins initiated by metal carbenes was investigated. Endcapping of polynorbornene produced by titanacyclobutanes was followed by UV and NMR. These analyses along with molecular weight measurements established the high efficiency of the endcapping reaction and the absence of polymer degradation during the reaction. The ring-opening polymerization of cyclopentene by titanacyclobutanes gave polymers that were close to being monodisperse. Kinetic studies showed that the rate of polymerization was first order in cyclopentene. Block copolymers (both A-B and A-B-A) containing monodispersed segments were synthesized with alternating "hard" and "soft" blocks. In these block copolymerization studies the polymerization of *exo*-dicyclopentadiene by titanacyclobutanes was shown to be a true "living" system. The polymerization of norbornene by the tungsten alkylidene, $W(CHtBu)(NAr)[OCMe(CF_3)_2]_2$ (Ar= 2,6-diisopropylphenyl), was investigated and found not to be a living system. Finally, the heteroolefin, N-methyl-7-azabenzonorbornadiene, was ring-opened metathesis polymerized and the resulting polymer dehydrogenated and doped to give a conducting material (10^{-3} to 10^{-4} Scm^{-1}).

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CHAPTER 1.

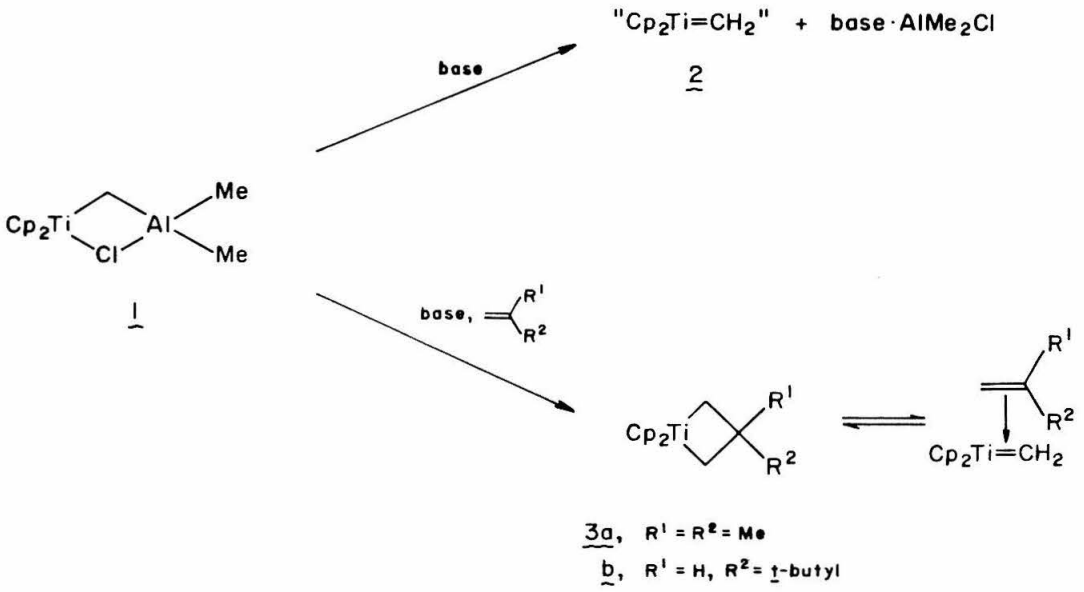
Chapter 1

Reactions of "$Cp_2Ti{=}CH_2$" Sources with Acid Anhydrides and Imides[1a]

Introduction

In 1978 Tebbe and co-workers reported[1b] the isolation of the titanium alkylidene **1** and the subsequent reactions with several substrates, including the conversion of cyclohexanone into methylenecyclohexane. Further studies by other investigators[2] have developed a variety of useful synthetic transformations of carbonyl substrates with this reagent and titanacyclobutanes, both of which serve as sources of the highly reactive titanocene methylidene **2** (Scheme I).

Scheme I. Sources of "$Cp_2Ti{=}CH_2$"

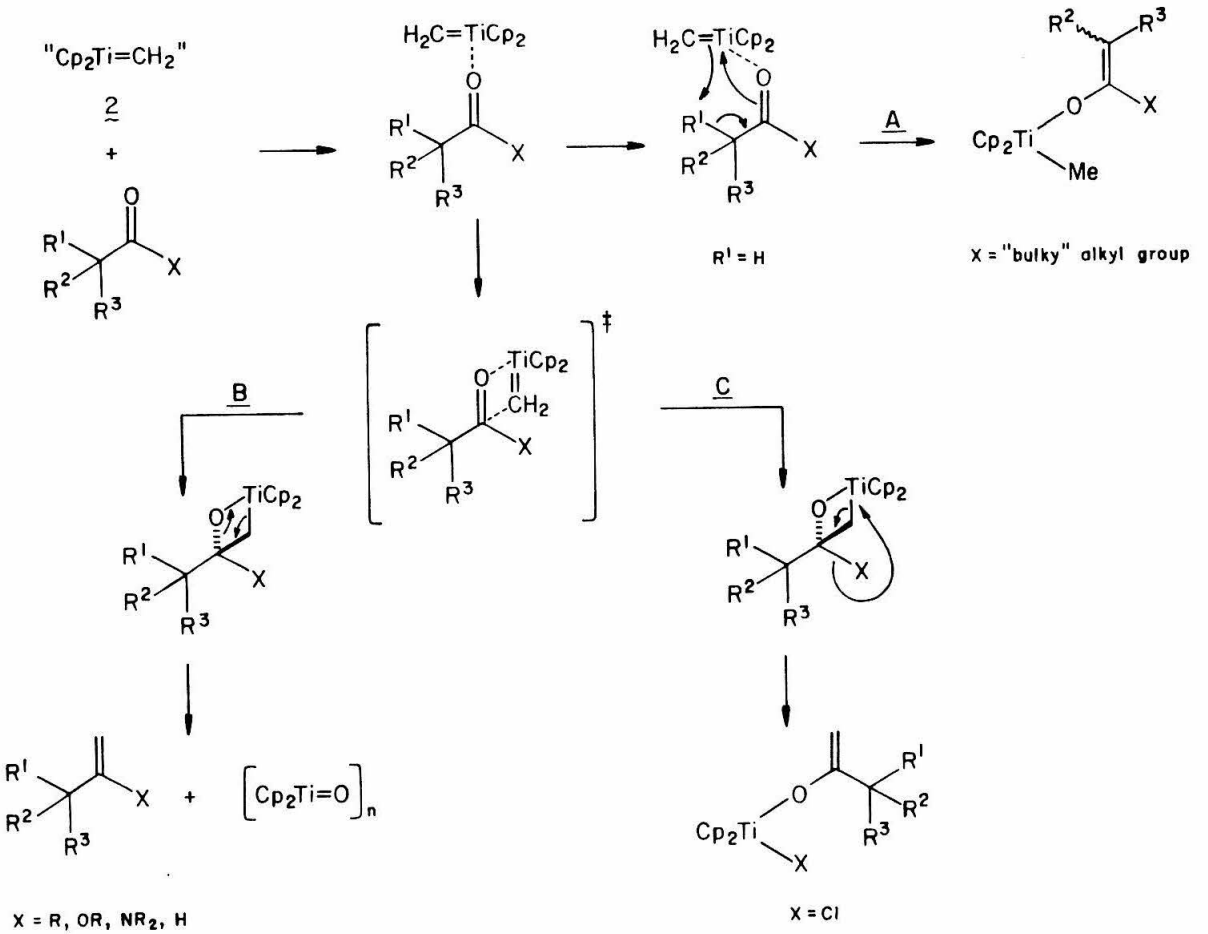


3a, $R^1 = R^2 = Me$
b, $R^1 = H$, $R^2 = t$-butyl

Principally, three pathways of reactivity of **2** with carbonyl compounds are known (Scheme II). The different reactivity patterns may be explained by the following sequence of steps. Initial coordination of the carbonyl oxygen to the titanium in **2** gives a Lewis acid-base complex. This is followed by formation of an oxymetallacycle intermediate except for hindered ketones where the lower energy pathway

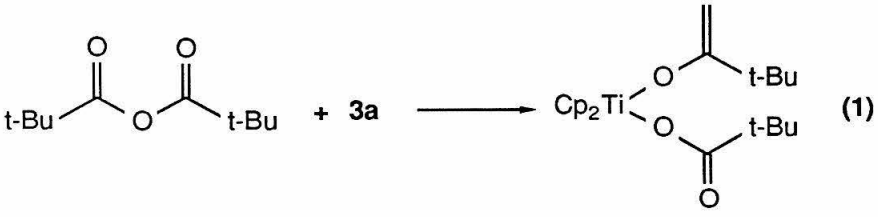
appears to be deprotonation of the ketone to yield the titanium enolate of the original ketone[3] (Path A). Decomposition of the oxymetallacycle produces $(Cp_2Ti{=}O)_n$ and the methylene-transfer product for unhindered ketones,[3] aldehydes,[4] esters,[5] and amides[6] (Path B). Alternatively, the intermediate derived from **2** and acid chlorides rearranges to give an enolate[7] (Path C), presumably due to the lability of the chloride substituent as compared to those of the other complexes. In this chapter the reactions of **2** with acid anhydrides and imides, which show examples of all three pathways, are discussed. These examples show all three reaction paths in selected systems and demonstrate the subtle features that control the relative rates of each pathway.

Scheme II. Reactivity of **2** with Carbonyl Compounds

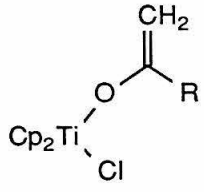


Results and Discussion

Reaction of 2 with Acid Anhydrides. Pivalic anhydride (trimethylacetic anhydride) upon treatment with the metallacycle **3a** gave the enolate **4a** (Eq. 1). Apparently the carboxylate substituent of the oxymetallacycle intermediate is comparable in lability to the chloride, as none of the product resulting from methylenation was observed. An NMR tube reaction in C_6D_6 with 1.2 equivalents of anhydride led to a 70% yield of enolate, which was stable over several hours at room temperature to excess anhydride still present (^{1}H NMR). Isolation of **4a** was achieved in 55% yield with a 1:1 ratio of reactants in pentane. Recrystallization from pentane afforded crystals of **4a** that were unsuitable for structure analysis as were crystals isolated from toluene/pentane, ether, and THF/hexane. Upon very slow cooling of the solutions over many days (to obtain crystals for structure determination) significant decomposition of the enolate occurred and the crystals obtained were of much lower purity with the impurities present being $Cp_2Ti(OC(O)t\text{-}Bu)_2$ (**7a**)[8] and the methyl ketone pinacolone (^{1}H NMR). Compound **4a** did not react with pivaldehyde at room temperature nor at higher temperatures at which the enolate decomposed. In contrast, the analogous reaction employing the enolate **11a** leads to a 67% yield of the aldol product.[7a]



4a



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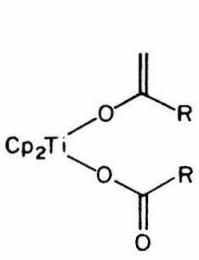
a R= t-Bu

Upon treatment with **3a** in C_6D_6, acetic anhydride was transformed into the enolate **4b** (^{1}H NMR). Acidolysis with anhydrous HCl precipitated Cp_2TiCl_2 and gave acetone and acetic acid in the supernatant (identified by ^{1}H NMR and GC analysis). Reaction of the initially formed enolate with starting materials present in solution was also observed, yielding additional products (*vide infra*). Similar results were also obtained with propionic and butyric anhydrides.



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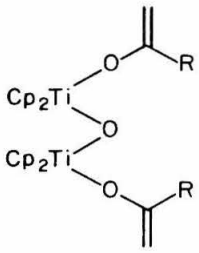

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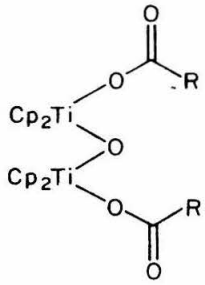
a, R = t-Bu
b, R = Me
c, R = Ph



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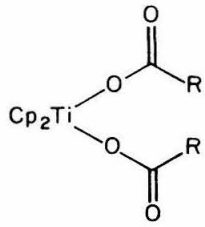

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A series of NMR tube experiments were conducted to study the subsequent reactions of the enolate **4b**. It was found that the yield of **4b** (based on limiting reagent) varied depending dramatically upon the ratio of anhydride to **3a** employed (Table I). The highest yield of **4b** was obtained with a 1:1 ratio of reactants although substantial amounts of side products were still present. The presence of excess **3a** gave a lower yield of **4b** and increase in formation of $(Cp_2Ti(OC(Me)=CH_2))_2O$ (**5b**). In contrast, a lower yield of **4b** and an increase in formation of $(Cp_2Ti(OC(O)Me))_2O$ (**6b**) and $Cp_2Ti(OC(O)Me)_2$ (**7b**) was observed when excess anhydride was employed. Attempted isolation of **4b** using a 1:1 ratio of reactants was unsuccessful with a variety of solvents, temperatures, and reaction times. In one trial with ether as a solvent and a reaction time of 80

Table I. Products from **3a** and $(MeCO)_2O$

ratio of reactants	% yield based on limiting reagent[a]			
3a/$(MeCO)_2O$	**4b**[b]	**5b**[b]	**6b**[c]	**7b**[c]
0.10	d	d	d	d
0.5	25	0	5	20
0.8	43	17	20	11
0.9	46	18	16	16
1.0	47	37	13	6
1.1	40	40	15	4
1.4	19	54	20	10
1.9	d	50	20	d
2.2	e	e	e	e

a. Percent yields based on NMR peak heights ($\pm$ 5%).

b. Identified by comparison of ^{1}H NMR to similar compounds.

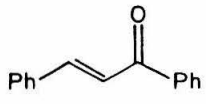
c. Identified by ^{1}H NMR comparison to authentic samples (**6b**,[8] **7b**[9]).

d. Not observable by NMR ($\leq$5%).

e. Spectrum uninterpretable.

minutes at 0-5°C, an impure sample of **6b** was isolated in an 11% yield from the reaction mixture. NMR analysis of the supernatant indicated a complex mixture of **4b**, **5b**, **7b**, and other compounds present. Compound **6b** was identified by ^{1}H and ^{13}C NMR, IR and acidolysis with anhydrous HCl to give acetic acid and Cp_2TiCl_2. It underwent slow conversion to **7b** and $(Cp_2Ti{=}O)_n$ upon standing at room temperature in C_6D_6 or $CDCl_3$.

The reaction between **3a** and benzoic anhydride produced the enolate **4c** (R= Ph), but further reaction of the enolate was again observed. The product was obtained in 40-60% crude yield after workup. NMR analysis of a typical sample collected gave approximately 60% **4c**, 10% **5c**,[8] 10% **6c**,[10] and 10% **7c**.[11] Reaction of **4c** with benzaldehyde was slow at room temperature (several hours) and was accompanied by decomposition of the enolate. At 50°C the reaction proceeded quickly (15 minutes) with less decomposition of the enolate (^{1}H NMR). Workup of the mixture afforded the dehydrated aldol product chalcone (**8**) in an unoptimized 27% yield.



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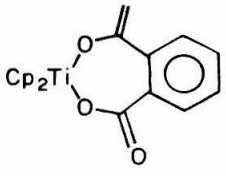

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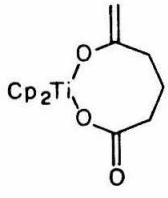

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Phthalic anhydride upon treatment with **3a** gave the enolate **9** in 46 % yield (NMR tube reaction). By varying the ratio of reactants it was found that **3a** rapidly decomposed **9**, while the anhydride led to much slower decomposition. In an NMR tube experiment, employing two equivalents of anhydride, the initial spectrum recorded six minutes after thawing the sample showed little decomposition of the

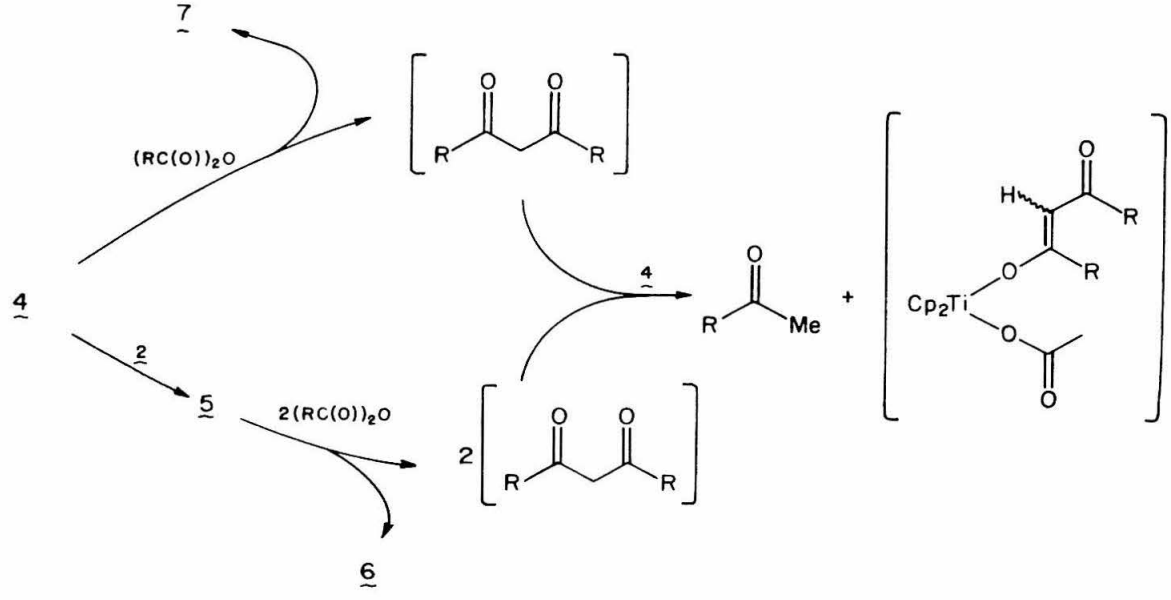
enolate with unreacted **3a** and anhydride still present. After eleven minutes no **3a** remained and decomposition of **9** had occurred with an increase in the broad signal at 6.4 ppm, indicative of $(Cp_2Ti{=}O)_n$. Excess anhydride was still present and after one hour little increase in enolate decomposition was observed. An impure sample of **9** was isolated in ~10% yield (after several attempts under different reaction conditions) and spectrally characterized. The reaction of **3a** with glutaric anhydride gave the enolate **10** in 44% yield (NMR tube reaction), which was found to decompose in the same manner as **9**. Maleic and succinic anhydrides upon treatment with **3a** gave only insoluble polymeric material and no observable enolate by NMR.

Because of the complexity of the reaction of anhydrides with **3a**, no quantitative kinetic runs were performed. Qualitatively, anhydrides with less bulky alkyl groups reacted faster and also decomposed faster. **4c** was formed and decomposed at an intermediate rate. Comparison of rates of formation of enolates by treatment of **3a** with acid chlorides and anhydrides, respectively, was investigated. Previous work[7b] has shown benzoyl chloride reacts twenty times faster than pivaloyl chloride with **3a**. A similar experiment using a 1:1 ratio of benzoic anhydride and pivaloyl chloride with **3a** gave a ratio of 14:1 (NMR integration). Therefore, to a first approximation, acid chorides react 1.4 (20/14) times faster than the corresponding acid anhydrides with **3a**.

As previously mentioned, the enolates formed from acid anhydrides and **3a** undergo further reactions once formed in solution. An overall mechanism consistent with the products observed is presented in Scheme III. The further reactions of **4** are proposed to occur as follows. Acylation of the enolate by excess anhydride affords the corresponding β-diketone with concomitant formation of the titanocenedicarboxylate **7**. The acidic β-diketone protonates another molecule of enolate to give the methyl ketone and a titanocenecarboxylate-β-diketonate complex. Additionally,

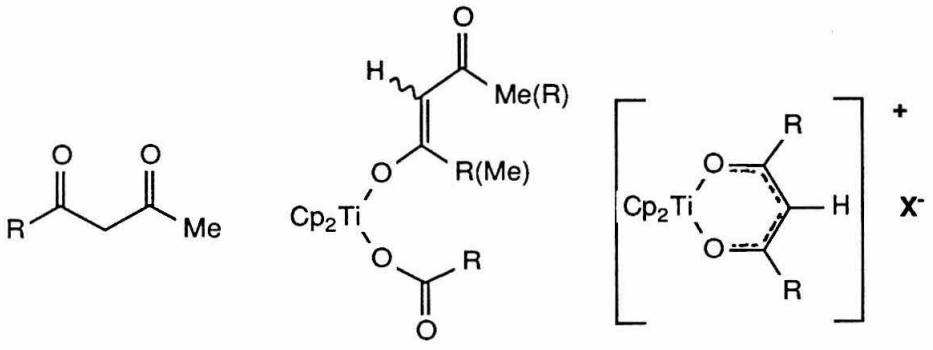
4 can react with **2** present, yielding the μ-oxo complex **5**. This complex behaves similarly to **4**, giving the new μ-oxo complex **6** and two moles of β-diketone, upon reaction with anhydride.

Scheme III. Subsequent Reactions of **4**

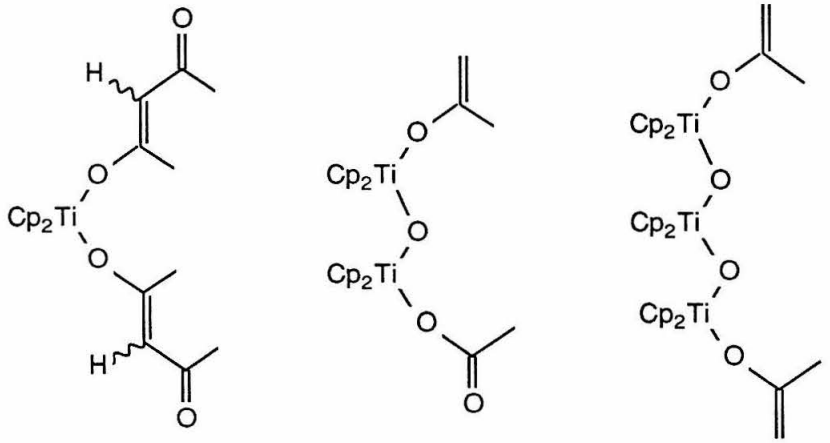


In order to establish the pathways presented in Scheme III, the following experiments were performed.

4a, b, and **c** were separately combined with acetic anhydride and each subsequent reaction was followed by ^{1}H NMR. In every case the formation of the methyl ketone was observed and for **4b** was also confirmed by GC analysis. The characteristic signals of **7a, b**, and **c** were also seen in each case, respectively. Identification or isolation of the corresponding β-diketones **19** was unsuccessful under a variety of reaction conditions. NMR signals characteristic of the subsequent



19 20 21
a R= Me; X= Cl

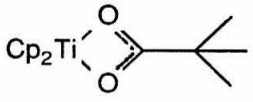


22 23 24

β-diketonatecarboxylate complexes **20** were observed, but because of the overlapping of other signals no definite assignment could be made. Acidolysis of the reaction mixtures with anhydrous HCl resulted in no observable formation of **19**, either by NMR or GC, whereas acidification with acetic acid gave new unassignable signals in the NMR and unknown compounds in the GC traces. All known titanocene(IV) β-diketonate complexes **21** are cations isolated as salts with noncoordinating counterions.[31] Attempted synthesis of **20** by the combination of **21a** (generated *in situ*) and NaOAc gave a mixture of products by NMR, one of which may have been the desired product. The synthesis of a similar compound **22** with Cp_2TiCl_2

and two equivalents of Na(acac) resulted in the formation of a bright yellow titanocene β-diketonate polymer. Combination of **4a** with 2,4-pentanedione (acacH) gave pinacolone and a mixture of titanocene β-diketonate complexes. Acidolysis with anhydrous HCl produced a minor fraction of the original 2,4-pentanedione (^{1}H NMR).

Attempts to synthesize the μ-oxo titanocenes **23** and **24** with **7b**[9] and either one or two equivalents of **3a**, respectively, were unsuccessful (^{1}H NMR). The reaction between **4a** and **3a** to generate **5a** proceeded very slowly at room temperature with decomposition of the starting materials before any reaction. However, treatment of **4c** with one equivalent of **3a** resulted in formation of **5c**, which was identified by ^{1}H, ^{13}C NMR and IR. It underwent slow decomposition at room temperature in benzene to form unidentifiable paramagnetic species. As mentioned previously, an impure sample of **6b** was isolated in the attempted synthesis of **4b** and fully characterized.



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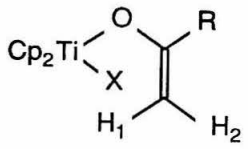
Thermal instability of **4**, both in solution and the solid state, was also observed in separate cases. Attempts at recrystallization of **4a** as mentioned earlier led to significant decomposition. Among the products formed were pinacolone, **7a**[8], and **25**.[8] Isolated samples of **4c** slowly underwent decomposition over several days at room temperature to give paramagnetic metal species, **7c**, and the methyl ketone



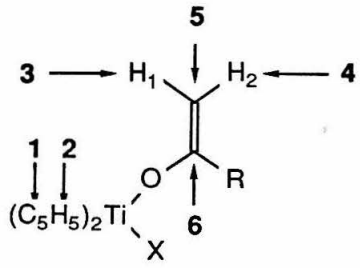
11 X= Cl
4 X= O_2CR

Figure 1. Interaction of H_1 and X

acetophenone. Similarly, decomposition of **9** was observed, but no decomposition products were identified. The mechanism(s) of these decompositions is unknown.

NMR Spectra. Pertinent ^1H and ^{13}C NMR chemical shifts of four examples each of **11** and **4** are given in Tables II and III, respectively. The assignment of H_1 and H_2 for **11** has been previously done on the basis of a difference NOE experiment[7b] and the same experiment was repeated with **4a**. Irradiation of the *t*-butyl group adjacent to the vinyl group led to enhancement of the downfield signal at 3.86 ppm, which was then assigned to the proton *cis* to the *t*-butyl group.[32] The shifts for this proton in **11** and **4** are nearly identical for corresponding compounds, whereas the shift of the other enolate proton, H_1, differs significantly. This can be rationalized by the different environment of H_1 in the two respective compounds when they are in the conformation shown in Figure 1. The chemical shifts of the Cp protons are also nearly the same. The ^{13}C NMR spectra show good correlation between **11** and **4** for the Cp and vinyl group carbons, indicative of similar bond strengths between the enolate and titanium in each case.

IR Spectra. Analysis of IR data of **11** and **4** leads to similar conclusions as before. The values of ν(C=C) for two examples of **11** (R= *t*-butyl and ClC_6H_4-) are 1620 and 1590 cm^{-1}, respectively, while the same stretching modes in **4a** and **c** (R= *t*-butyl and C_6H_5-) are 1614 and 1615 cm^{-1}, respectively. The value for the μ-oxo



11 X= Cl
4 X= O_2CR

Table II. Titanocenechloroenolates **11** (NMR Shifts in ppm[a])

R	1	2	3	4	5	6
Et	117.1	6.02	3.80	3.89	84.8	176.4
t-Bu	117.2	6.03	3.44	3.84	82.2	182.4
Ph	b	6.03	4.32	4.77	b	b
Cl-C_6H_4	117.9	b	b	b	87.4	169.3

Table III. Titanocenecarboxylatoenolates **4** (NMR Shifts in ppm[c])

R	1	2	3	4	5	6
Et	b	6.05	3.67	3.89	b	b
t-Bu	116.2	6.06	3.26	3.86	80.8	181.1
Ph	117.1	6.05	4.06	4.77	86.1	170.1
-C_6H_4-	118.8	5.99	4.29	4.67	91.1	172.9

a. ^1H NMR recorded in C_6D_6 ; ^{13}C NMR in CD_2Cl_2.

b. Spectrum not recorded.

c. ^1H and ^{13}C NMR recorded in C_6D_6.

compound **5c** is 1615 cm^{-1} and this is in good agreement with the rest of the values. The carboxylate ligand of **4** is potentially bidentate, but the large difference in the frequencies of the asymmetric and symmetric stretching vibrations indicates only monodentate binding.[33] The same conclusion can also be reached upon comparision of the values for **4a** and **c** with the analogous titanocenedicarboxylates **7a** and **c** as shown in Table IV. The carboxylate ligands in **7** have been postulated to be monodentate[34] and a single crystal X-ray structure of **7c**[11] has verified this. The μ-oxo-carboxylate **6b** (υ(C=O): 1640, 1364, 1300 cm^{-1}) appears to be in the same class. The assignment of the structure of the μ-oxo compounds **5c** and **6b** from NMR data was further confirmed by the observation in the IR of the Ti-O-Ti stretch at 720 and 730 cm^{-1}, respectively. The related μ-oxo compound $[Cp_2TiCl]_2O$ has been assigned a value of 720 cm^{-1} for this stretching mode.[35]

Table IV. Comparision of **4** and **7**: υ(C=O) in cm^{-1} [a]

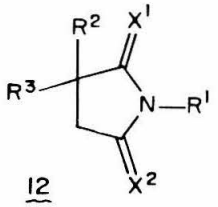
compound	asymmetric	symmetric	Δ (υ)
4a	1645	1300, 1290	335-345
7a	1636	1310, 1294	326-342
4c	1640	1320, 1300	320-340
7c	1640	1350, 1300	290-340

a. Recorded in C_6D_6 .

Reaction of 2 with Imides. Imides, analogous in structure to acid anhydrides, were expected to undergo methylenation upon reaction with **2** beacause of the poor leaving group ability of -NRC(O)R compared to that of -OC(O)R (Scheme II). Wittig reagents are known to react with imides to give alkenylation products in low yields.[12] The reaction appears to be limited by steric hindrance with low yields reported for succinimides (2,5-pyrrolidinediones) and in only exceptional cases could glutarimides (2,6-piperidinediones) be alkenylated.

A. Succinimides. Treatment of 1-phenyl-2,5-pyrrolidinedione (**12a**) (Chart I) with one equivalent of **3a** yielded a 1:1:1 mixture of starting material and the methylene-transfer products **12b** and **c** (^{1}H NMR). Employing two equivalents of **3a** led to quantitative formation (^{1}H NMR) of **12c**, which rapidly isomerized upon contact with moisture in the air to the pyrrole **13a**.[13] In reacting 1.9 equivalents of **12a** with **3a** , a 69:31 ratio of **12b** to **c** was observed (^{1}H NMR). Similar results were obtained utilizing **1** as a source of **2**. Additionally, 1-methyl-2,5-pyrrolidinedione (**12d**) gave in the same manner the methylene-transfer products **12e** and **f** and the pyrrole **13b**.[13] Apparently, the rates of methylene-transfer from **2** to the pyrrolidinediones **12a** and **d** and the methylenepyrrolidinones **12b** and **e** are very similar under the conditions employed, giving the observed product ratios. Unfortunately, **3a** is not reactive at lower temperatures (less than 0°C) where regioselectivity may be possible and use of **1** (–40°C, THF) on a preparative scale necessitates a basic aqueous workup that would isomerize and/or decompose the products. The dimethylene compounds **12c** and **f** could serve as potential sources of 1,2,5-trisubstituted pyrroles upon alkylation or acylation.

A single methyl group adjacent to one of the imide carbonyls imparted partial regioselectivity as evidenced by a 60:20:20 ratio of the methylenepyrrolidinone **12h**, the dimethylenepyrrolidine **12i**, and the starting pyrrolidinedione **12g** upon treatment of **12g** with one equivalent of **3a** (^{1}H NMR). Use of **1** at –40°C was not



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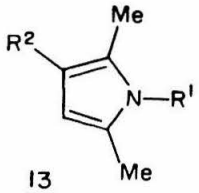

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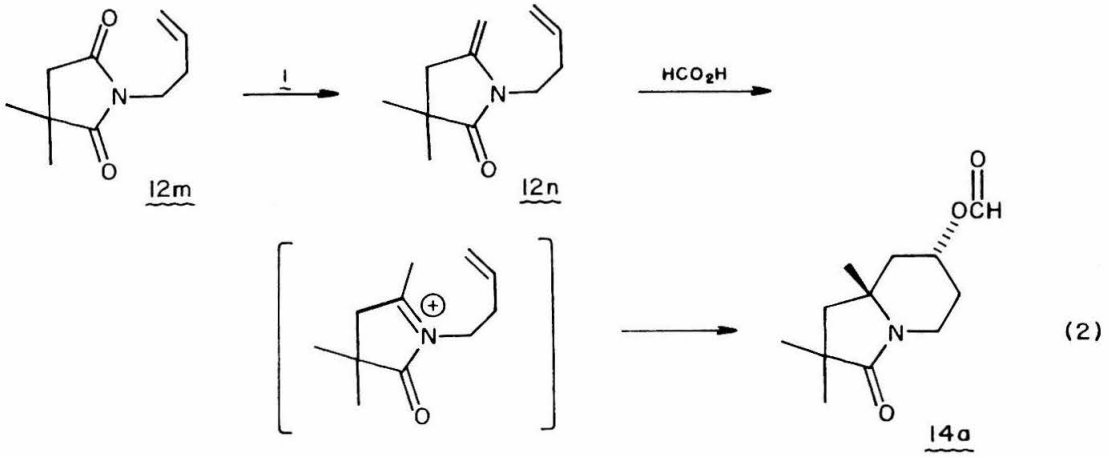
Chart I

cmpd.	R^1	R^2	R^3	X^1	X^2
12a	Ph	H	H	O	O
b	Ph	H	H	CH_2	O
c	Ph	H	H	CH_2	CH_2
d	Me	H	H	O	O
e	Me	H	H	CH_2	O
f	Me	H	H	CH_2	CH_2
g	Ph	Me	H	O	O
h	Ph	Me	H	O	CH_2
i	Ph	Me	H	CH_2	CH_2
j	Ph	Me	Me	O	O
k	Ph	Me	Me	O	CH_2
l	Ph	Me	Me	CH_2	CH_2
m	3-butenyl	Me	Me	O	O
n	3-butenyl	Me	Me	O	CH_2
o	2,6-dimethylphenyl	Me	Me	O	O
p	2,6-dimethylphenyl	Me	Me	O	CH_2
13a	Ph	H			
b	Me	H			
c	Ph	Me			

successful as **12h** and **i** decomposed upon workup of the reaction mixture and only the pyrrole **13c**[30] was isolated (8% yield).

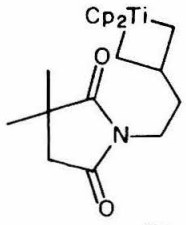
Introduction of two methyls into one of the α-positions of **12a**, to give **12j**, resulted in highly regioselective methylene-transfer to the least hindered carbonyl. Employing **3a** produced a 96:4 ratio of **12k** to **12l** (^{1}H NMR), while use of **1** at –40°C followed by basic aqueous workup gave in very high yield exclusively **12k**. Thus, quaternization of one of the α carbons leads to both high regioselectivity and increased stability of the methylene-transfer product.



(2)

Exploitation of this reactivity was accomplished by transformation of the pyrrolidinedione **12m** (synthesized by the procedure of Mitsunobu[29]) to the methylene-pyrrolidinone **12n**. Subsequent treatment with HCO_2H[14] gave exclusively the cyclized product **14a** (69% isolated yield) presumably by trapping the intermediate α-acyl iminium ion (Eq. 2). In treating **12m** with **1**, the crude product obtained after workup contained unreacted **12m**, even when excess **1** was employed. An NMR tube reaction with **3a** as a source of **2** yielded a mixture (3:1) of **12n** to the metallacycle **18**. This type of metallacycle[15] (with a single β-substituent) is stable at room temperature, and heating at 50°C for 20 minutes was needed to complete

decomposition. Unfortunately, the yield of **12n** did not increase after decomposition of **18**, and **12m** was recovered after workup. Using **1** as the methylene source, the total isolated yield of **14a** was 51% based on **12m**.



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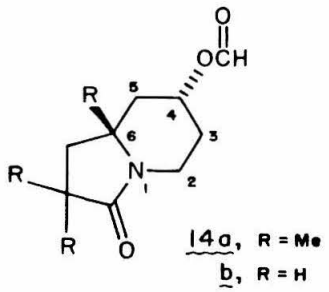
Assignment of the stereochemistry of **14a** is based upon comparison of its ^{1}H NMR spectrum to the related compound **14b** synthesized by Speckamp and coworkers[16a] (see Table V). The shift of the formate protons are nearly identical in both structures, while the value for H_4, H_2-e and H_2-a are very similar. More importantly, for both compounds the splitting patterns and coupling constants for these protons are the same. The assignment of trans stereochemistry (relative to the formate group) of the methyl group on C6 is based upon the presumed trans coplanar addition of the olefin to the α-acyliminium ion.[16b] No other isomers of **14a** were observed by ^{1}H NMR in either the crude reaction mixture or the purified product. Speckamp and coworkers have made extensive use of the α-acyliminium ion in a number of alkaloid syntheses[17], and use of the above sequence of reactions could potentially provide useful precursors to alkaloid analogues.

B. Glutarimides. Treatment of imide **15a** with one equivalent of **1** at –40°C in THF gave upon workup a quantitative yield of the original imide (Chart II). In an attempt to understand this result, an NMR tube experiment utilizing **3a** as a source of **2** was conducted. The ^{1}H NMR showed a 69:31 ratio of the enolate **16a** to the methylene-transfer product **15b**, indicating that treatment with **1** at –40°C



14a, R = Me
b, R = H

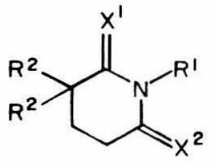
TABLE V. Selected Shifts (ppm) and Coupling Constants (Hz) from ^{1}H NMR Spectra[a] of **14a** and **b**

proton	**14a**	**14b**
OC-H	8.03 (s)	8.05 (s)
H_4	5.22 (t of t, J_1= 12 Hz, J_2= 11 Hz, J_3=J_4= 4.4 Hz)	5.05 (t of t, J_1=J_2= 11 Hz J_3=J_4= 4 Hz)
H_2(e)	4.15 (m, J_1= 14 Hz, J_2= 5.4, J_3= 2 Hz)	4.25 (m, J_1= 14 Hz, J_2= 5.5 Hz, J_3= 2 Hz)
H_2(a)	2.86 (t of d, J_1= 13 Hz, J_2= 14 Hz, J_3= 3 Hz)	2.76 (t of d, J_1=J_2= 14 Hz, J_3= 3 Hz)

a. Recorded in $CDCl_3$ (values for **14b** from Ref. 16a).

had given exclusively **16a** (which was protonated upon workup), while the NMR tube reaction had followed both Paths A and B, Scheme II. Similarly, treatment of the imide **15c** with **3a** resulted in a mixture of the starting imide **15c** (20%), methylene-transfer products **15d** (55%) and **e** (10%), the combined methylene-transfer and enolized product **16b** (9%), and the enolate **16c** (7%), while use of two equivalents of **3a** with **15c** gave **15e** (55%), **16b** (40%), and **16c** (7%) (^{1}H NMR).

The more sterically hindered glutarimides **15f** and **g** were treated with **3a**,



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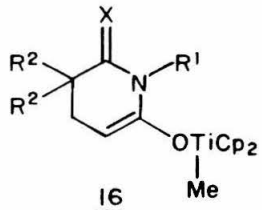

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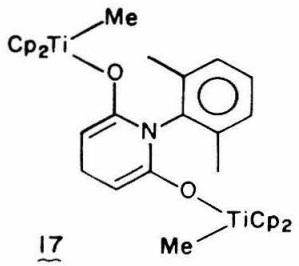
Chart II.

cmpd.	R^1	R^2	X^1	X^2
15a	Ph	Me	O	O
b	Ph	Me	O	CH_2
c	Ph	H	O	O
d	Ph	H	O	CH_2
e	Ph	H	CH_2	CH_2
f	2,6-dimethylphenyl	Me	O	O
g	2,6-dimethylphenyl	H	O	O
h	CH_2Ph	Me	O	CH_2
i	CH_2Ph	Me	O	CH_2
j	Me	Me	O	O
k	Me	Me	O	CH_2
16a	Ph	Me	O	
b	Ph	H	CH_2	
c	Ph	H	O	
d	2,6-dimethylphenyl	Me	O	
e	2,6-dimethylphenyl	H	O	
f	CH_2Ph	Me	O	



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giving exclusively the enolates **16d** and **e**, respectively (in the reaction of **15g** with **3a** a small amount of the proposed dienolate **17** (5%) was also observed) (^{1}H NMR). Compound **16d** was quite stable thermally and showed no decomposition or reaction with 3 equivalents of benzaldehyde in C_6D_6 after 2.5 days at 60°C. Synthesis of **16d** (44% isolated yield) from **3a** and **15f** produced analytically pure crystals that were unfortunately unsuitable for x-ray structure analysis.

The less sterically hindered glutarimide **15h** upon reaction with **3a** (NMR tube experiment) gave a 50:50 mixture of the methylene-transfer product **15i** and the enolate **16f**. Use of **1** (–40°C, THF) and workup afforded a 42% yield of **15i** after chromatography. In an attempt to optimize the yield of methylene-transfer product, the reaction of imide **15j** with several sources of **2** under a variety of conditions was studied with the results summarized in Table VI. Utilization of **1** gave lower yields of methylenation (runs 1-9) compared to **3a-b** (runs 10-11). The trend toward higher yields of **15k** with increasing temperature implies that entropy favors methylenation over enolization in this system.

C. Enolization vs. Methylenation. As discussed above, the reaction of **2** with imides proceeds by two pathways. 2,5-Pyrrolidinediones undergo methylenation exclusively, while 2,6-piperidinediones are predominantly enolized. However, methylenation does proceed to some degree when the substituent on nitrogen is less bulky. In an attempt to observe enolization of a 2,5-pyrrolidinedione by **2**, the

Table VI. Reaction of **15j** with "$Cp_2Ti{=}CH_2$" Sources[a]

run	% yield of **15k**	temp. °C	solvent[a]	"$Cp_2Ti{=}CH_2$" source
1	54, 57[b]	–78	PhMe, pyr	**1**
2	59	–40	PhMe, pyr	**1**
3	60	–20	PhMe, pyr	**1**
4	62	20	PhMe, pyr	**1**
5	63, 65[b]	60	PhMe, pyr	**1**
6	55	–40	THF	**1**
7	52	–40	THF, pyr	**1**
8	56	–78	THF, PhMe	**1**
9	62	0	C_6D_6 , pyr	**1**
10	72	20	C_6D_6	**3a**
11	71	58	C_6D_6	**3b**

a. See Experimental Section for procedures.

b. Values of two different trials.

imide **12o** (containing a very bulky nitrogen substituent) was allowed to react with **3a** in an NMR tube experiment and gave exclusively the methylenation product **12p** (none of the enolized product was observed). Treatment of **12o** with **1** (-40°C, THF) also gave only **12p**. In contrast, the 2,6-piperidinedione analog **15f** yielded only the enolate **16d** under the same experimental conditions (*vide supra*).

A possible explanation for the different reactivities of **12o** and **15f** towards **2** is as follows. Steric inhibition (by the 2,6-dimethylphenyl group on the nitrogen) towards formation of the oxymetallacycle intermediate needed for methylenation is

essentially identical for both imides. Therefore, the controlling factor in pathway determination appears to be the "availability" (for enolization) of the hydrogens on the carbon adjacent to the carbonyl. As expected, x-ray structures of several 2,5-pyrrolidinediones have shown the five-membered ring to be essentially planar with both α hydrogens in pseudoequatorial positions.[18] However, structures of 2,6-piperidinediones have shown one α proton to be axial and one to be equatorial for the six-membered, half-chair ring with very small torsional angles for the C4-C5-N-C1 and C5-N1-C1-C2 frameworks (the C3 carbon is out of the plane by $\sim$ 0.6 Å).[19] Preferential enolization of the axial hydrogen α to the carbonyl in cyclohexanone is presumably due to stabilization of the developing filled p-orbital of the enolized carbon with the p-orbitals of the C-O framework.[20] From above, 2,6-piperidinediones contain an enolizable axial hydrogen while 2,5-pyrrolidinediones do not, and therefore one may conclude the observed enolization of the former is due to the favored (*vide supra*) axial hydrogen abstraction.

Another possibility is that the increased flexibility of the six-membered ring of 2,6-piperidinediones (compared to 2,5-pyrrolidinediones) allows for proper orientation of the hydrogen for enolization to proceed. Further studies are needed to determine the geometrical requirements of enolization of 2,6-piperidinediones by **2**.

Conclusion

In summation, the reaction of the titanocene methylidene **2** with anhydrides and imides proceed by the three known pathways (enolate formation, methylenation, and enolization) of carbonyl compound reactivity towards **2**. Anhydrides are transformed into titanium enolates, presumably by migration of the carboxylate substituent of the oxymetallacycle intermediate. Succinimides (2,5-pyrrolidinediones) cleanly undergo methylenation at both carbonyl moieties with regioselectivity possible when one carbonyl is sterically hindered. Glutarimides (2,6-piperidinediones) are predominantly enolized by **2** (forming titanium enolates) with methylenation also observed as a competing reaction.

Experimental Section

General Procedures. All work involving air- and/or moisture-sensitive compounds was performed using standard high vacuum or Schlenk line techniques under argon purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves, and a Vacuum Atmospheres dry box under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Associates EM-390 (90 MHz ^{1}H), XL-200 (200.15 MHz ^{1}H, 50.4 MHz ^{13}C), or a JEOL FX-90Q (89.60 MHz ^{1}H, 22.53 MHz ^{13}C). Chemical shifts are referenced to residual protiosolvent residues. IR spectra were recorded on a Beckman 4240. GC analysis was done using a Varian 1400 flame-ionization instrument equipped with a Spectra-Physics System I computing integrator and 10 ' 10% FFAP on 80/100 Chromosorb PAW column. Thin-layer chromatography (TLC) was performed on precoated TLC plates (silica gel 60 F-254, EM Reagents). Flash chromatography was performed by the procedure of Still et al.[21] using silica gel 60 (230-400 mesh ATM, EM Reagents). Melting points were recorded on a Thomas Hoover melting point apparatus and are uncorrected. Elemental analysis was performed by L. Henling at the analytical facility of the California Institute of Technology.

Materials. Tebbe's reagent (**1**),[22] and the metallacycles **3a**[15] and **b**[15] were synthesized according to established procedure. All acid anhydrides except pivalic anhydride were purchased from Aldrich and were purified before use as follows: liquid anhydrides were fractionally distilled and stored under nitrogen; solid anhydrides were dissolved in an organic solvent, washed with 5% $NaHCO_3$ (aqueous) (3X), H_2O (1X), dried (Na_2SO_4), evacuated to dryness, recrystallized, dried under high vacuum and stored under nitrogen. Pivalic anhydride was made by the procedure of Ansell[23] and stored under nitrogen. 1-Phenyl-2,5-pyrrolidinedione (**12a**) (Pfaltz & Bauer) and 1-methyl-2,5-pyrrolidinedione (**12d**) (Alfa Products) were recrystallized (EtOH) before use. 3-Methyl-1-phenyl-2,5-pyrrolidinedione

(**12g**), 3,3-dimethyl-1-phenyl-2,5-pyrrolidinedione (**12j**), and 1,3,3-trimethyl-2,6-piperidinedione (**15j**) were made according to the procedure of Speckamp et al.[24] 1-Phenyl-2,6-piperidinedione (**15c**) was synthesized by the procedure of Devlin et al.[25] $NaO_2CC(CH_3)_3$ was synthesized by treating the organic precursor with alcoholic NaOH, washing the collected salt liberally with Et_2O and drying under high vacuum at 50°C for 1 h. Benzaldehyde (Aldrich) was prepurified by the procedure of Perrin, Armarego and Perrin.[26] Pivaldehyde (Aldrich) was dried over $MgSO_4$ before use. Cp_2TiCl_2 (Boulder) was purified by soxhlet extraction with CH_2Cl_2 before use. Toluene, benzene, THF, and diethyl ether were dried (CaH_2), transferred to sodium benzophenone ketyl and later distilled into solvent flasks equipped with a Teflon screw-type valve. Pentane and hexane were stirred over conc H_2SO_4, washed with H_2O, dried over $MgSO_4$, transferred to sodium benzophenone ketyl in tetraglyme and later distilled as above. Methylene chloride was dried over P_2O_5, degassed on the vacuum line for several minutes and distilled as above. Benzene-d_6 (Merck, Sharp & Dohme) was transferred to sodium benzophenone ketyl, later distilled and stored in the dry box.

General Procedures for NMR Tube Reactions. Reagents (if solids) were weighed and added to an NMR tube in the dry box and the tube capped with a rubber septum. The tube was brought out and cooled to –20°C in a dry ice-acetone bath. C_6D_6 was first added slowly from a gas-tight syringe so that it froze before mixing with the solid(s) present. Any liquid reagents were added on top of the C_6D_6 by syringe. The tube was thawed by hand warmth, shaken vigorously for several minutes, and the spectrum recorded.

Synthesis of $(C_5H_5)_2Ti(OC(O)t\text{-}Bu)(OC(t\text{-}Bu)=CH_2)$ (4a). To a Schlenk tube cooled to –10°C and charged with **3a** (0.395 g, 1.59 mmol) were added 3 mL of –10°C pentane via syringe. Pivalic anhydride (0.296 g, 1.59 mmol) was added via syringe and the mixture briefly stirred, warmed to 2°C, and stirring

continued for another 90 min. The solution was allowed to warm to room temperature and the dark supernatant transferred to another argon-filled Schlenk tube via cannula. The remaining orange solid was washed (1X, 1 mL, pentane), the washing added to the supernantant and this combined mixture slowly cooled to –50°C. The large orange-red crystals that deposited were collected, washed (2X, 0.5 mL pentane, –50°C) and dried under high vacuum to give 0.329 g of **4a** (55% yield, ^{1}H NMR integration with an internal standard gave ≥90% purity): ^{1}H NMR (C_6D_6) δ 6.06 (s, 10H), 3.87 (s, 1H), 3.26 (s, 1H), 1.33 (s, 9H), 1.13 (s, 9H); ^{13}C NMR (C_6D_6) δ 182.7, 181.1, 116.2, 80.8, 40.2, 37.8, 28.5, 28.2; IR (C_6D_6) 2960, 1636, 1614, 1480, 1391, 1307, 1290, 1206, 1182, 1034, 1016, 810 cm^{-1}.

NMR Studies of the Reaction Between 3a and Acetic Anhydride (results presented in Table I). Reactions were NMR tube experiments in which the concentrations of the reactants, reaction conditions, and times at which the spectra were recorded were duplicated as best as possible for each run. ^{1}H NMR (C_6D_6) **4b**: δ 6.05 (s, 10H), 3.95 (s, 1H), 3.78 (s, 1H), 1.98 (s, 3H), 1.71 (s, 3H); **5b**: 6.03 (s, 20H), 3.97 (s, 2H), 3.78 (s, 2H), 1.77 (s, 6H); **6b**: see preparation of **6b** this section; **7b**[9]; 6.13 (s, 10H), 1.94 (s, 6H).

Synthesis of $(C_5H_5)_2Ti(OC(O)Ph)(OC(Ph)=CH_2)$ (4c). To a Schlenk tube charged with **3a** (0.228 g, 0.919 mmol) and $(PhCO)_2O$ (0.209 g, 0.924 mmol) and cooled to –10°C were added 2 mL of –10°C Et_2O. The mixture was stirred and allowed to warm to 0°C. An orange precipitate began to form after 20 min and stirring was continued another 25 min. The mixture was then recooled to –20°C, the fine orange precipitate collected, washed (2X, 0.5 mL, Et_2O, -20°C) and dried under high vacuum to give 0.154 g (40% yield) of impure product containing 60% **4c**: ^{1}H NMR (C_6D_6) δ 8.49 (m, 2H), 7.70 (m, 2H), 7.20 (m, 6H), 6.05 (s, 10H), 4.77 (s, 1H), 4.06 (s, 1H); ^{13}C NMR (C_6D_6) δ 171.5, 170.1, 135.9, 131.4, 130.3, 127.0, 125.7, 117.1, 86.1; IR (C_6D_6) 3238, 1640, 1615, 1445, 1320, 810 cm^{-1} along with

10% **5c** (see below), 10% **6c** (^{1}H NMR (C_6D_6) δ 8.49 (m, 4H), 7.20 (m, 6H), 6.12 (s, 20H)) and 10% **7c**[11] (^{1}H NMR (C_6D_6) δ 8.49 (m, 4H), 7.20 (m, 6H), 6.15 (s, 10H)).

Reaction of 3a and 4c to Produce 5c. An NMR tube experiment was performed using a previously prepared sample of **4c** (50% **4c** by NMR, 0.026 g total wt, 0.031 mmol of **4c**) and **3a** (0.012 g, 0.048 mmol) in C_6D_6 . The ^{1}H NMR was recorded shortly afterwards and the ^{13}C NMR then recorded overnight. Another ^{1}H NMR followed, which showed partial decomposition of the sample during the night. A similarly prepared sample of **5c** was used to record the IR: ^{1}H NMR (C_6D_6) δ 7.70 (m, 4H), 7.20 (m, 6H), 6.03 (s, 20H), 4.81 (s, 2H), 4.11 (s, 2H); ^{13}C NMR (C_6D_6) δ 169.6, 140.0, 130.1, 126.9, 125.5, 116.2, 86.3; IR (C_6D_6) 3235, 1615, 1445, 1320, 810, 720 cm^{-1}.

Synthesis of $[(C_5H_5)_2Ti(OC(O)CH_3]_2O$ (6b). To a precooled (–10°C) Schlenk tube charged with **3a** (0.204 g, 0.822 mmol) and 2 mL of Et_2O were added $(MeCO)_2O$ (0.071 g, 0.706 mmol) via syringe. The mixture was warmed to 0°C and stirred 80 min, at which time a yellow precipitate had formed. The Schlenk tube was recooled to –20°C, the solid collected, washed (2X, 0.5 mL, Et_2O, –20°C) and dried under high vacuum to give 0.032 g (11% yield) of crude product : ^{1}H NMR (C_6D_6) δ 6.03 (s, 20H), 2.04 (s, 6H); ^{13}C NMR (C_6D_6) δ 176.7, 115.9, 24.0; IR (C_6D_6) 1640, 1364, 1300, 1015, 730 (Ti-O-Ti) cm^{-1}.

Synthesis of $(C_5H_5)_2Ti(OC(O)t\text{-}Bu)_2$ (7a). To a Schlenk tube charged with Cp_2TiCl_2 (0.519 g, 2.09 mmol) and $NaO_2C(CH_3)_3$ (0.562 g, 4.53 mmol) were added 20 mL of toluene via syringe. The mixture was stirred for 12 h, at which time it had become orange in color with no undissolved Cp_2TiCl_2. After filtration through Celite under argon the resulting clear orange solution was reduced in volume under vacuum to 10 mL and slowly cooled to –50°C. The small orange crystals that deposited were collected, washed (2X, 0.5 mL, toluene, –50°C) and dried under high

vacuum to give 0.280 g (35% yield) of **7a**. The supernatant was evacuated to dryness to give an additional 0.133 g for an overall yield of 52% : ^{1}H NMR (C_6D_6) δ 6.06 (s, 10H), 1.27 (s, 18H); ^{13}C NMR (C_6D_6) δ 182.5, 117.7, 40.1, 28.0; IR (C_6D_6) 2945, 1645, 1481, 1395, 1294, 1188, 815 cm^{-1}. Anal. Calcd. for $C_{20}H_{28}O_4Ti$: C, 63.16; H, 7.42. Found: C, 63.07; H, 7.19.

Synthesis of Chalcone (8). A Schlenk tube was charged with a previously prepared impure sample of **4c** (65% **4c** by NMR, 0.313 g total wt, 0.486 mmol of **4c**) and 2 mL of benzene added via syringe. The mixture was briefly stirred to dissolve the solid, benzaldehyde (0.140 g, 1.3 mmol) added via syringe and the mixture stirred for 30 min at 47-49°C. It was then allowed to cool to room temperature, 10 mL of saturated NH_4Cl (aqueous) added, and stirring continued in the air for 10 min. The organic layer was separated, washed with saturated NaCl (aqueous) (2X), and H_2O (1X), dried ($MgSO_4$), purified by filtration through silica gel and evaporated under partial vacuum to give a yellow oil. Pentane (6 mL) was added and the solution slowly cooled to –50°C with the appearance of white crystals. They were collected, washed (pentane, 2X, 0.5 mL, –50°C) and dried under high vacuum to give 0.027 g (27% yield based on mmol of **4c**) of product: mp 55-56°C (lit[27] 58°C): ^{1}H NMR ($CDCl_3$) δ 8.02 (m, 2H), 7.51 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 190.5 (C=O), 144.8, 138.2, 134.8, 132.7, 130.5, 128.9, 128.4, 122.0. An independently synthesized sample[28] had identical ^{1}H and ^{13}C NMR spectra.

Synthesis of 9. To a Schlenk tube cooled to –10°C and charged with **3a** (0.160 g, 0.645 mmol) and phthalic anhydride (0.083 g, 0.56 mmol) were added 2 mL of Et_2O at -10°C. The mixture was stirred briefly and warmed to –3°C. Additional stirring for 0.5 h produced an orange-yellow precipitate. The mixture was then recooled to –20°C, the solid collected, washed (2X, 0.5 mL, Et_2O, –20°C) and dried under high vacuum to give 0.083 g of fine orange-yellow solid. NMR analysis with an internal standard gave ~25% product with substantial amounts of unidentified

titanocene compounds. This gives an overall 10% yield: ^{1}H NMR (C_6D_6) δ 8.46 (m, 1H), 7.53 (m, 1H), 7.12 (m, 2H), 5.99 (s, 10H), 4.67 (s, 1H), 4.29 (s, 1H); ^{13}C NMR (C_6D_6) δ 172.9, 162.7, 141.2, 134.8, 132.9, 124.9, 118.8, 91.1.

NMR Studies of Imides. Reactions were NMR tube experiments performed in C_6D_6 with the product ratios determined by integration of characteristic ^{1}H NMR shifts of each compound. The spectral data for the known compounds **12a, d, g, j, 13a, b, 15c,** and **j** are listed in Chart III. Values for the new compounds **12k, m-p, 15a, f-i, k** and **16d** are listed elsewhere in this section. NMR shifts of all other new compounds are listed in Chart IV.

Chart III

compound	^{1}H NMR
12a	7.40 (m, 2H), 7.20 (m, 3H), 1.77 (s, 4H)
12d	2.58 (s, 3H), 1.62 (s, 4H)
12g	7.40 (m, 2H), 7.20 (m, 3H), 1.84 (m, 3H), 0.84 (d, 3H)
12j	7.40 (m, 2H), 7.20 (m, 3H), 2.01 (s, 2H), 0.87 (s, 6H)
13a	6.95 (m, 5H), 6.15 (s, 2H), 1.99 (s, 6H)
13b	6.01 (s, 2H), 2.67 (s, 3H), 1.96 (s, 6H)
15c	7.10 (m, 5H), 2.04 (t, 4H), 1.03 (m, 2H)
15j	3.06 (s, 3H), 2.13 (t, 2H), 0.94 (t, 2H), 0.86 (s, 6H)

Attempted Synthesis of 3-Methyl-5-methylene-1-phenyl-2-pyrrolidinone (12h). Imide **12g** (0.175 g, 0.925 mmol) was treated in the same manner as **12j** (see below) to give 0.200 g of a yellow oil, which by ^{1}H NMR was a complex mixture of products. TLC (3:1 $CHCl_3$/pet ether) also indicated many products present. Flash chromatography (3:1 $CHCl_3$/pet ether) gave only one fraction (R_f=

Chart IV

compound	^{1}H NMR	^{13}C NMR
12b	7.14 (m, 5H), 4.10 (m, 1H), 3.88 (m, 1H), 2.06 (m, 4H)	
12c	7.14 (m, 5H), 3.86 (m, 2H), 3.80 (m,2H), 2.40 (s, 4H)	152.4, 129.8, 128.8, 127.9, 127.1 77.4, 28.4
12f	3.80 (s, 2H), 3.76 (s, 2H), 2.51 (s, 3H), 2.21 (s, 4H)	
12h	7.20 (m, 5H), 4.16 (m, 1H), 3.89 (m,1H, 2.34 (m, 3H), 1.06 (d, J = 6.3 Hz, 3H)	
12i	7.20 (m, 5H), 3.84 (s, 2H), 3.78 (s, 2H), 2.34 (m, 3H), 0.81 (d, J = 6.3Hz, 3H)	
16a	7.05 (m, 5H), 5.43 (s, 10H), 3.83 (t, J = 4.0 Hz, 1H), 2.14 (d, J = 4.0 Hz, 2H), 1.34 (s, 6H), 0.70 (s, 3H)	
16b	7.10 (m, 5H), 5.50 (s, 10H), 3.86 (s, 1H), 3.66 (s, 1H), ... 0.72 (s, 3H)	
16c	7.10 (m, 5H), 5.42 (s, 10H), ... 0.69 (s, 3H)	
16e	6.98 (m, 3H), 5.44 (s, 10H), 3.85 (t, J=4.0 Hz, 1H), 2.52 (t, J = 4.0 Hz, 2H), 2.10 (s, 6H), 2.05 (m, 2H), 0.57 (s, 3H)	170.7,157.1, 137.4, 137.2, 129.7, 129.2, 113.2, 77.7, 40.6, 33.6, 19.0, 18.1
16f	7.10 (m, 5H), 5.54 (s, 10H), 3.55 (t, J = 4.2 Hz, 1H), 2.05 (m, 2H), 1.34 (s, 6H), 0.77 (s, 3H)	

0.70) of 0.027 g (8% yield) of a slightly yellow oil, which was identified by ^{1}H and ^{13}C NMR as the known pyrrole **13c**:[30] ^{1}H NMR ($CDCl_3$) δ 7.30 (m, 2H), 7.10 (m, 3H), 5.81 (s, 1H), 1.98 (s, 3H), 1.90 (s, 3H), 1.82 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 139.3, 129.0, 128.0, 127.5, 127.4, 107.7, 12.7, 11.2, 10.6.

3,3-Dimethyl-5-methylene-1-phenyl-2-pyrrolidinone (12k). Imide **12j** (0.203 g, 1.00 mmol) was dissolved in 2 mL of THF, cooled to –40°C and a solution of **1** (0.313 g, 1.10 mmol) in 3.5 mL of PhMe added dropwise over several minutes. The resulting mixture was stirred 0.5 h at –40°C and allowed to warm to room temperature over an additional 15 min period. Workup according to Pine et al.[5] gave 0.195 g (96% yield) of crude product, mp 97-100°C. Recrystallization (EtOH) afforded 0.090 g of pure **12k**, mp 98-101°C. ^{1}H NMR ($CDCl_3$) δ 7.38 (m, 5H), 4.14 (m, 2H), 2.68 (m, 2H), 1.31 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 180.3, 145.8, 135.3, 129.2, 127.8, 127.4, 86.2, 40.8, 40.3, 25.0. Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.39; H, 7.38; N, 6.94.

1-(3-Butenyl)-3,3-dimethyl-2,5-pyrrolidinedione (12m). 3,3-Dimethyl-2,5-pyrrolidinedione[24] (1.30 g, 10.2 mmol) was converted by the method of Mitsunobu[29] to **12m**. After flash chromatography (99:1 $CHCl_3$/THF) the resulting yellow oil was distilled under reduced pressure (bp 93°C, 5 torr) affording 1.08 g of pure **12m** (58% yield): ^{1}H NMR ($CDCl_3$) δ 5.65 (m, 1H), 5.04 (m, 1H), 4.91 (m, 1H), 3.54 (t, J= 6.8 Hz, 2H), 2.48 (s, 2H), 2.32 (d of t, J_1= 6.8 Hz, J_2= 7.1 Hz, 2H), 1.26 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 183.2, 175.8, 134.5, 117.5, 43.6, 39.9, 37.6, 32.0, 25.7. Anal. Calcd. for $C_{10}H_{15}NO_2$: C, 66.27; H, 8.34; N, 7.73. Found: C, 65.98; H, 8.27; N, 7.65.

1-(3-Butenyl)-3,3-dimethyl-5-methylene-2-pyrrolidinone (12n). Imide **12m** (0.181 g, 1.00 mmol) was treated in the same manner as **12j** (see above). Workup[5] yielded 0.200 g of crude product as a mixture of **12n** and **m** (2.8:1.0). **12n**: ^{1}H NMR ($CDCl_3$) δ 5.61 (m, 1H), 5.07 (m, 1H), 4.92 (m, 1H), 4.21 (m, 1H),

4.12 (m, 1H), 3.51 (t, J= 7.2 Hz, 2H), 2.48 (m, 2H), 2.29 (d of t, J_1= 6.8 Hz, J_2= 6.9 Hz, 2H), 1.15 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 180.9, 144.4, 134.9, 116.9, 84.2, 40.5, 39.7, 39.0, 30.9, 25.4.

3,3-Dimethyl-1-(2,6-dimethylphenyl)-5-methylene-2-pyrrolidinone (12p). Imide **12o** (0.231 g, 1.00 mmol) was treated in the same manner as **12j**, affording a quantitative crude yield of product, mp 85-87°C. Recrystallization (EtOH) provided an analytical sample of **12p**, mp 87.0°C: ^{1}H NMR ($CDCl_3$) δ 7.14 (m, 3H), 4.08 (m, 1H), 3.79 (m, 1H), 2.72 (m, 2H), 2.11 (s, 6H), 1.34 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 179.6, 143.7, 136.2, 128.4, 128.1, 85.3, 40.7, 40.3, 25.5, 17.3. Anal. Calcd. for $C_{15}H_{19}NO$: C, 78.56; H, 8.35; N, 6.11. Found: C, 78.35; H, 8.38; N, 6.04.

1-Aza-4-formyloxy-6,8,8-trimethyl-bicyclo(4.3.0)nonane-9-one (14a). A crude sample of **12n** (74% **12n** and 26% **12m** by ^{1}H NMR, 0.200 g total wt, 0.74 mmol of **12n**) was dissolved in 15 mL of HCO_2H and let stir 18 h.[14] The solution was then evaporated under reduced pressure, dissolved in 50 mL of $CHCl_3$, washed (2 X 100 mL, 5% $NaHCO_3$ (aqueous); 1 X 100 mL, H_2O), dried (Na_2SO_4), and evaporated under reduced pressure to give 0.220 g of a yellow oil. Flash chromatography (2:1 pet ether/acetone) afforded 0.115 g (69% yield based on starting material) of **14a** (R_f= 0.38) as a slightly yellow oil. 0.035 g of **12m** (R_f= 0.74) was also recovered. ^{1}H NMR ($CDCl_3$) δ 8.03 (s, 1H), 5.22 (t of t, J_1= 12.0 Hz, J_2= 11.0 Hz, J_3= J_4= 4.4 Hz, 1H), 4.15 (m, J_1= 14.0 Hz, J_2 = 5.4 Hz, J_3= 2.0 Hz, 1H), 2.76 (t of d, J_1= 13.0 Hz, J_2= 14.0 Hz, J_3= 3.0 Hz, 1H), 2.15-1.4 (m, 4H), 1.91 (s, 1H), 1.89 (s, 1H), 1.38 (s, 3H), 1.23 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 177.5, 160.3, 68.5, 56.7, 49.7, 44.7, 40.2, 34.6, 30.8, 27.8, 27.6, 25.0.

Imides 12o, 15a, f, g and h. These imides were prepared by the method of Devlin et al.[25] Yields after recrystallization or distillation were 66% (**12o**), 42%

(**15a**), 55% (**15f**), 75% (**15g**), and 73% (**15h**). Melting points, spectral data, and elemental analyses for each compound are as follows.

3,3-Dimethyl-1-(2,6-dimethylphenyl)-2,5-pyrrolidinedione (12o). Mp 97-98°C (EtOH): ^{1}H NMR ($CDCl_3$) δ 7.16 (m, 3H), 2.75 (s, 2H), 2.10 (s, 6H), 1.44 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 181.6, 174.3, 135.4, 130.1, 129.1, 128.3, 43.7, 40.4, 25.3, 17.4. Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.53; H, 7.32; N, 6.02.

3,3-Dimethyl-1-phenyl-2,6-piperidinedione (15a). Mp 115-117 °C (EtOH): ^{1}H NMR ($CDCl_3$) δ 7.40 (m, 3H), 7.05 (m, 2H), 2.87 (t, J= 6.9 Hz, 2H), 1.95 (t, J= 6.9 Hz, 2H), 1.37 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 177.7, 171.9, 135.4, 128.7, 128.0, 127.9, 38.2, 30.5, 28.4, 24.9. Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.49; H, 6.84; N, 6.36.

3,3-Dimethyl-1-(2,6-dimethylphenyl)-2,6-piperidinedione (15f). Mp 84-86°C (EtOH): ^{1}H NMR ($CDCl_3$) δ 7.13 (m, 3H), 2.89 (t, J= 6.3 Hz, 2H), 2.02 (s, 6H), 1.96 (t, J= 6.3 Hz, 2H), 1.38 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 176.8, 171.2, 134.8, 128.1, 38.5, 31.0, 29.6, 25.1, 17.3. Anal. Calcd. for $C_{15}H_{19}NO_2$: C, 73.44; H, 7.81; N, 5.71. Found: C, 73.34; H, 7.76; N, 5.62.

1-(2,6-Dimethylphenyl)-2,6-piperidinedione (15g). Mp 139-140 °C (EtOH): ^{1}H NMR ($CDCl_3$) δ 7.15 (m, 3H), 2.83 (t, J= 6.6 Hz, 4H), 2.10 (m, J= 6.6 Hz, 2H), 2.07 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 171.5, 134.8, 133.3, 128.3, 128.0, 32.6, 17.3, 17.1. Anal. Calcd. for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.73; H, 6.95; N, 6.40.

1-Benzyl-3,3-dimethyl-2,6-piperidinedione (15h). Bp 140°C (0.5 torr): ^{1}H NMR ($CDCl_3$) δ 7.27 (m, 5H), 4.94 (s, 2H), 2.73 (t, J= 7.0 Hz, 2H), 1.80 (t, J= 7.0 Hz, 2H), 1.27 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 177.7, 171.8, 137.3, 128.1, 127.0, 42.8, 38.2, 30.6, 29.5, 25.3. Anal. Calcd. for $C_{14}H_{17}NO_2$: C, 72.70; H, 7.41; N, 6.06. Found: C, 72.51; H, 7.48; N, 5.94.

1-Benzyl-3,3-dimethyl-6-methylene-2-piperidinone (15i). Imide **15h** (0.231 g, 1.00 mmol) was treated in the same manner as **12j** (see above), affording 0.261 g of a yellow oil as a mixture of **15h** and **i** (1:1). Flash chromatography on silica gel (9:1 pet ether/acetone) gave 0.097 g (42% yield) of **15i** as a slightly yellow oil. ^{1}H NMR ($CDCl_3$) δ 7.20 (m, 5H), 4.93 (s, 2H), 4.16 (s, 1H), 4.07 (m, 1H), 2.55 (t, J= 6.4 Hz, 2H), 1.74 (t, J= 6.4 Hz, 2H), 1.31 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 175.6, 144.0, 137.5, 128.3, 126.6, 126.3, 91.8, 46.4, 38.5, 34.0, 27.1, 27.0.

Reaction of 15j with "$Cp_2Ti{=}CH_2$" Sources (results presented in Table VI). In runs # 1-5, **15j** was dissolved in 1 mL of PhMe, 0.1 ml of pyridine added, and the mixture stirred at the desired temperature. **1** (in 6 mL of PhMe) was added dropwise over 5 min, stirring continued for 0.5 h at temperature listed and an additional 0.25 h without temperature bath. Workup[5] gave a quantitative yield of **15k** and unreacted **15j** as a yellow oil. ^{1}H NMR integration gave percent yield of **15k**. In runs # 6-7 THF was used in place of PhMe, while in run # 8 the imide was dissolved in THF and **1** in PhMe. Runs # 9-11 were NMR tube experiments. Spectral data of **15k**: ^{1}H NMR ($CDCl_3$) δ 4.21 (s, 1H), 4.12 (m, 1H), 3.12 (s, 3H), 2.56 (t, J= 6.4 Hz, 2H), 1.69 (t, J= 6.4 Hz, 2H), 1.24 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 176.3, 145.7, 90.4, 38.5, 34.5, 34.4, 27.0, 26.7.

The Titanium Enolate of 3,3-Dimethyl 1-(2,6-dimethylphenyl) 2,6-piperidinedione (16d). To a Schlenk tube charged with **3a** (0.085 g, 0.34 mmol) and **15f** (0.095 g, 0.35 mmol) were added 2 mL of PhMe via syringe. The resulting mixture was stirred 0.5 h with the formation of a bright orange precipitate. Additional PhMe was added (7 mL) to give a clear orange solution, which was slowly cooled to −50°C. Isolation of the resulting orange crystals gave 0.065 g (44% yield) of **16d**: ^{1}H NMR ($CDCl_3$) δ 6.96 (m, 3H), 5.47 (s, 10H), 3.81 (t, J= 4.5 Hz, 1H), 2.13 (d, J= 4.5 Hz, 2H), 2.10 (s, 6H), 1.34 (s, 6H), 0.58 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 173.8, 155.8, 137.7, 137.1, 129.6, 129.4, 113.1, 76.0, 40.6, 38.1, 34.4, 25.2. Anal.

Calcd. for $C_{26}H_{31}NO_2Ti$: C, 71.39; H,7.14; N, 3.20. Found: C, 71.25; H, 7.11; N, 3.18.

Synthesis of Titanocene (III) Pivalate (25). To a Schlenk tube charged with Cp_2TiCl (0.509 g, 2.44 mmol) and $NaO_2C(CH_3)_3$ (0.329 g, 2.70 mmol) were added 20 mL of toluene and the resulting mixture stirred for 4 h, at which time the solution had become deep blue. It was filtered through Celite under argon, reduced in volume until a few crystals appeared and then slowly cooled to –50°C. The large deep navy blue crystals that formed were collected, washed (2X, 0.5 mL, toluene, –50°C) and dried under high vacuum to give 0.370 g (56% yield) of product: m.p. 185-186°C (lit m.p.[36] 178-180°C); IR (C_6D_6) 2962, 1508, 1490, 1441, 1227, 1015, 790, 613 cm^{-1}.

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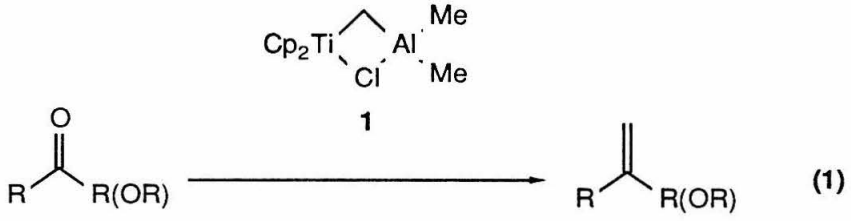
Chapter 2

Further Chemistry of Titanium Carbenes and Metallacycles

In Situ Preparation of μ-Chloro-μ-methylene-bis(cyclopentadienyl)-titanium Dimethylaluminum (Tebbe's Reagent)[1]

Introduction

The titanium alkylidene **1** (Tebbe's reagent) is a versatile methylenation agent for the conversion of ketones to olefins and esters to vinyl ethers (Eq. 1).[2] Unfortunately, this commercially available reagent (Strem, Alfa) is expensive for large-scale reactions and currently one needs to employ vacuum line and Schlenk techniques for its synthesis.[3]



(1)

We felt there was a need to develop a facile method for the *in situ* generation of **1** (utilizing only an inert gas manifold and standard synthetic organic techniques), which could also be applied to large-scale synthesis.

Results and Discussion

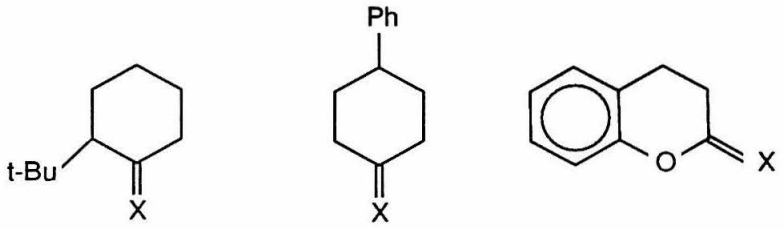
It was found that the crude reaction mixture formed by the combination of titanocene dichloride and 2 equivalents of $AlMe_3$ (2.0 M in PhMe) could be used directly to effect methylene-transfer. Optimization of reaction conditions were performed by allowing the crude mixture, containing **1** and approximately one equivalent of $AlMe_2Cl$ in PhMe, to react with a THF solution of 2-*tert*-butylcyclohexanone (**2**). Workup afforded a combined quantitative yield of starting ketone and the methylenation product **3** as an oil upon which ^1H NMR analysis gave the equivalents of **1** consumed by the ketone (Table I).

Table I. Equivalents of **1** Produced Under Different Reaction Conditions[a]

run	preparation	equivalents of **1** produced
1	68°C, 11 h	0.40
2	72°C, 11 h	0.47
3	87°C, 11 h	0.23
4	60°C, 11.5 h	0.30
5	50°C, 18.5 h	0.55
6	RT, 72 h	0.65

a. See Experimental Section for preparation of **1** and determination of equivalents produced.

On a 50 mmol scale performed using the parameters of run # 6 (Table I) under slightly modified conditions, 1.3 equivalents of 4-phenylcyclohexanone (**4**) were methylenated by the *in situ* Tebbe's reagent (**1**) derived from one equivalent of titanocene dichloride to give an 82% isolated yield (94% crude yield) of the olefin **5**.



2 X= O
3 X= CH_2

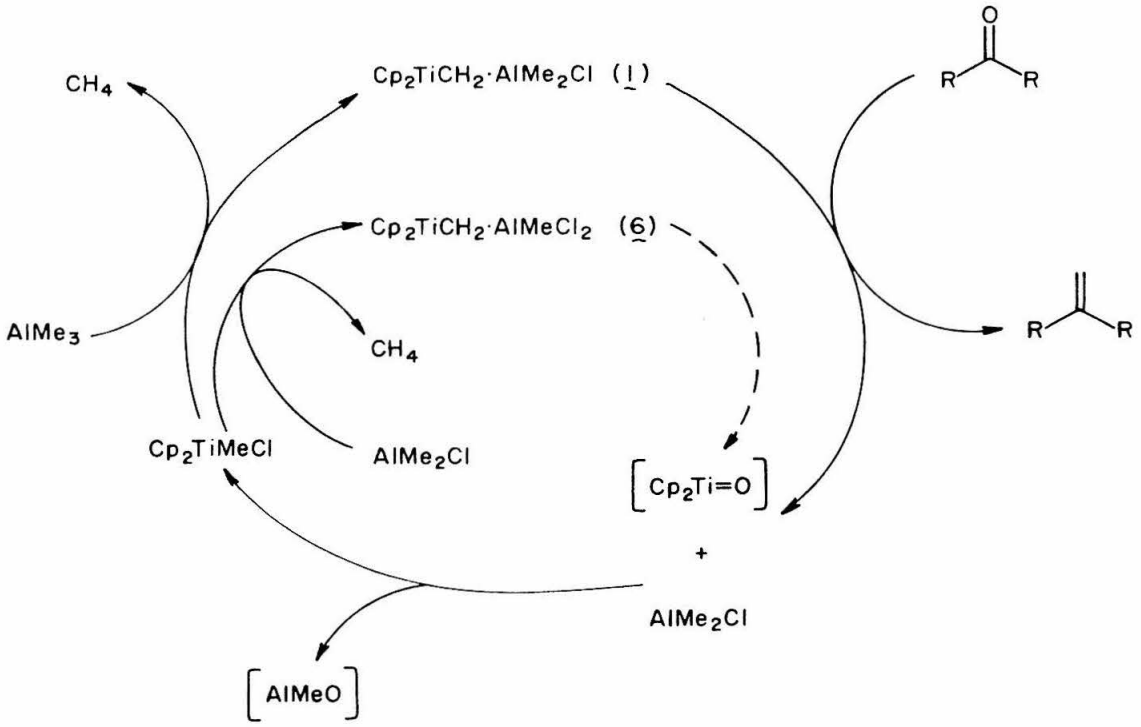
4 X= O
5 X= CH_2

7 X= O
8 X= CH_2

This surprising result may be due to regeneration of **1** during the reaction as shown in Scheme I. Conversion of the methylenation byproduct ($Cp_2Ti{=}O$) (Cp= cyclopentadienyl) to $Cp_2TiMeCl$ by $AlMe_2Cl$[4] and its reaction with $AlMe_3$ could yield **1**.[5a] Alternatively, $AlMe_2Cl$ may react with $Cp_2TiMeCl$ to give $Cp_2TiCH_2 \cdot AlMeCl_2$ (**6**),[5a] a less reactive methylenation agent.[5b]

In addition, 1.0 equivalent of the ester dihydrocoumarin (**7**) was converted to the vinyl ether **8**[1b] in 76% isolated yield upon treatment with **1** generated as above, while use of 1.3 equivalents of ester gave unreacted ester upon workup.

Scheme I. Regeneration of 1



Conclusion

The procedures listed in the Experimental Section for methylenation of **4** and **7** may be used as general guides for ketones and esters, respectively. One potential side reaction of ketones is the formation of the metallacyle (**9**) by the combination of the olefin produced and excess **1**. These compounds serve as good methylenation agents when heated above their decomposition point[6] and normally react with ketone present to form two equivalents of olefin and ($Cp_2Ti{=}O$).[7] If unquenched by ketone, **9** will be hydrolyzed upon workup to give the gem-dimethyl product **10**.[8] Therefore, use of a slight excess of ketone or warming the reaction above approximately 60°C before quenching is advised. Conversely, metallacycle formation with vinyl ethers has never been observed and should present no problem in reacting *in situ* **1** with esters. Potential side reactions of carbonyl starting materials and methylenation products with organoaluminum species present during these reactions do not appear to proceed to a significant degree.

9

10

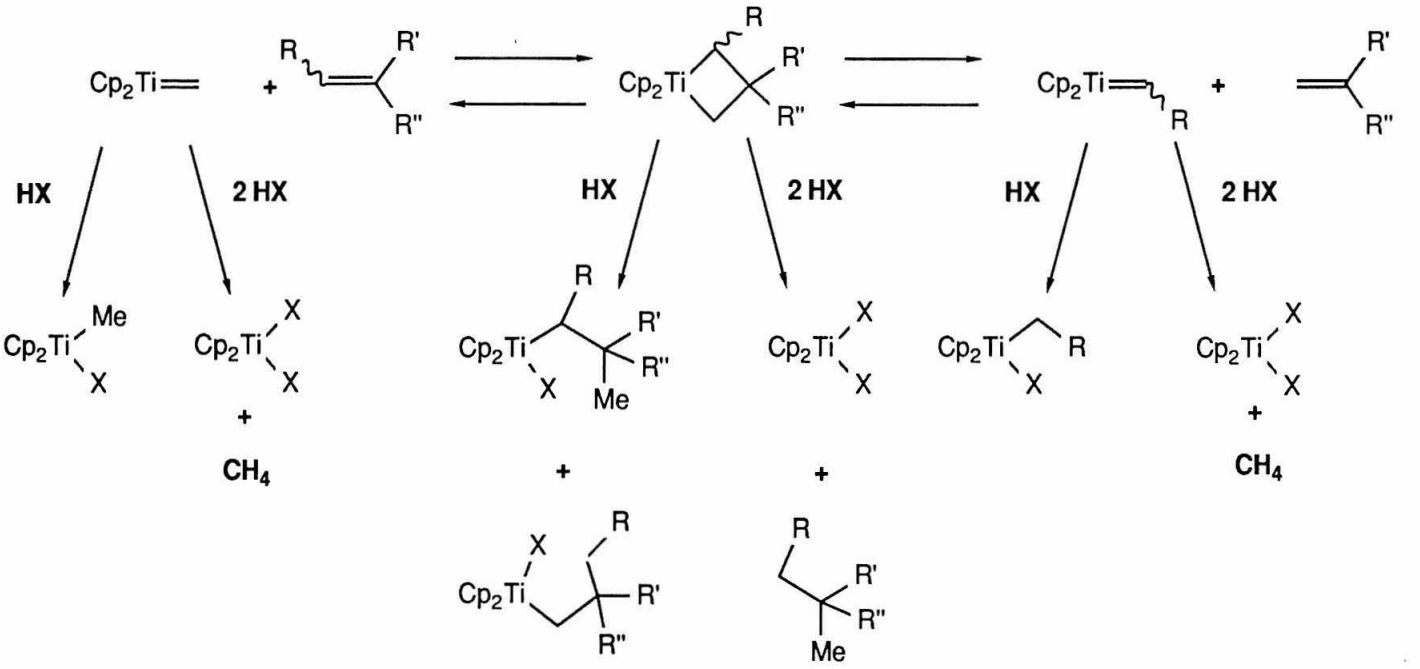
Reaction of Titanacyclobutanes with Proton Sources

Introduction

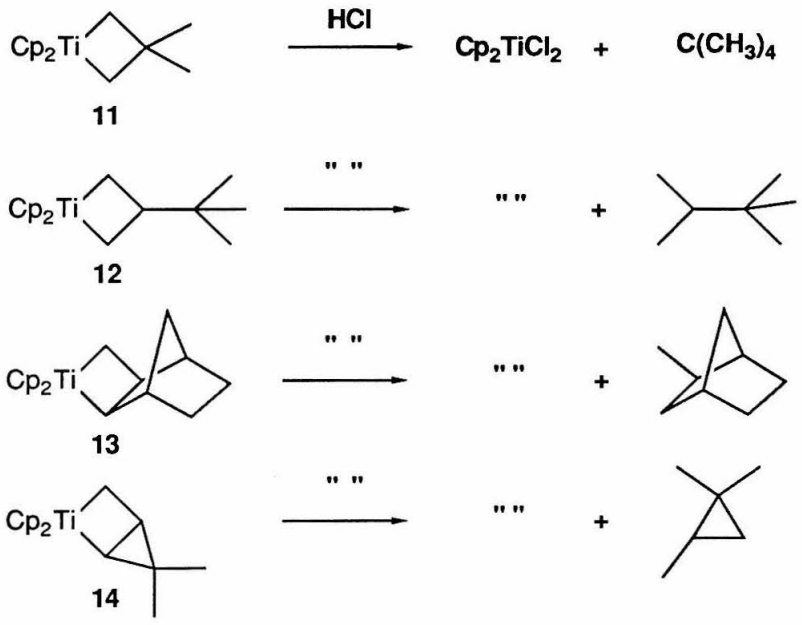
Treatment of metal alkyls with protons sources of the type HX (X^-= coordinating anionic ligand) normally gives the free alkane and MX[9] (Eq. 2). Titanacyclobutanes, a type of metal alkyl, have been intensively studied as synthetic organic reagants,[7] metathesis polymerization catalysts,[10] and in the area of organometallics.[11] Thermal decomposition of these metallacycles yields titanium carbenes, which are in rapid equilibrium with the parent metallacycle (Scheme II). Reaction of titanacyclobutanes with HX, as above, would be expected to give the products shown in Scheme II, depending upon the temperature of the reaction and equivalents of HX added. As expected, treatment of the metallacycles **11**[7], **12**[12], **13**[10], and **14**[13] below their decomposition temperature with anhydrous HCl (g) gives Cp_2TiCl_2 and the corresponding alkane (Scheme III).

$$M-R + H-X \longrightarrow R-H + M-X \quad (2)$$

Scheme II. Proposed Reactions of Titanacyclobutanes with HX

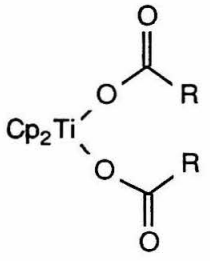


Scheme III. Treatment of Titanacyclobutanes with HCl

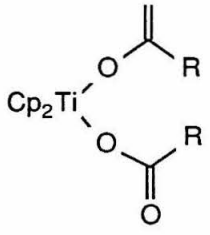


Results and Discussion

It became necessary to synthesize the dicarboxylates **15** in order to establish their identity as side products in the synthesis of the enolates **16**.[14] *A priori*, a facile method appeared to be treatment of metallacycle **11** with 2 equivalents of RCO_2H below the decomposition temperature (5°C) of **11**. In an initial experiment **11** was allowed to react with 2 equivalents of CH_3CO_2H in C_6D_6 at 0°C. Surprisingly, the formation of **15a** was not detected and only paramagnetic titanium species were implied (^{1}H NMR). Additionally, the absence of isobutylene (δ 4.72, 1.58; C_6D_6) indicated the metallacycle reacted before decomposition to the carbene. IR analysis gave a spectrum similar to that reported for the carboxylate **17a**.[15] Use of 1 equivalent of acid gave the same result. The experiment was repeated with 1 equivalent of pivalic (trimethylacetic) acid and the subsequent IR was identical to that of the independently synthesized[14] titanocene (III) carboxylate **17b**.



15



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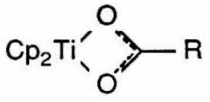


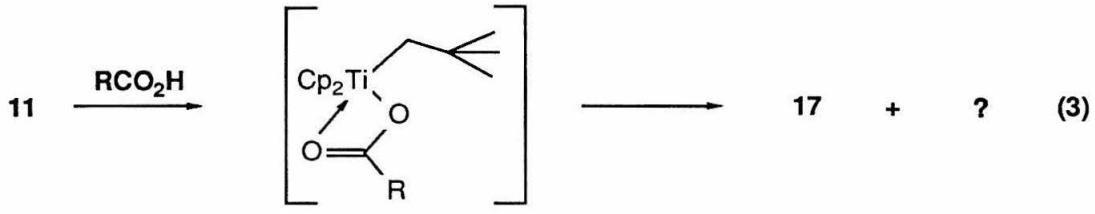
17

a R= Me

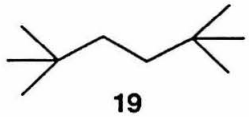
b R= t-Bu

The above results imply that the reaction of **11** with carboxylic acids produces the corresponding Ti (III) carboxylates. Apparently the intermediate titanocene alkyl carboxylate **18** rapidly decomposes to give **17** and as yet unidentified organic products (Eq. 3). The ^{1}H NMR spectra of the two reactions did contain signals

(δ 1.14 (s, 1.0), 0.88 (s, 4.5)) attributable to the neopentyl dimer **19**, but no further evidence was obtained to confirm this assignment.[16] One can postulate the coordination of a lone pair of the carbonyl oxygen destablizes the intermediate **18**, leading to the observed products. A similar mechanism has been proposed in the base-assisted decomposition of organocobalamins.[17]

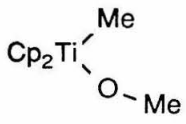


18



19

To further probe the chemistry of proton addition to titanacyclobutanes, **11** was allowed to react with MeOH. At –20°C (below the decomposition temperature to the carbene) no reaction was observed after **3.3** hours (^{1}H NMR). Warming to room temperature resulted in rapid formation of the alkoxide **20** (^{1}H NMR). Apparently MeOH does react with the titanium-carbon bonds of **11** at –20°C. However, the carbene derived from **11** is rapidly trapped to give the resulting metal alkoxide **20**. The more stable metallacycle **12** was treated with MeOH at room temperature (again below the decomposition temperature), and slow formation (**2.3** hours) of the metallacycle-trapped product **21** was observed in quantitative yield (^{1}H NMR). Therefore, MeOH will protonate titanium-carbon bonds of titanacyclobutanes at room temperature, but at a much slower rate than carboxylic acids.



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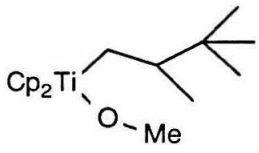

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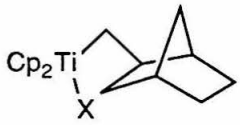
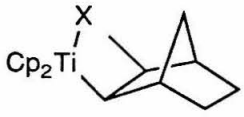


22



23

24

a X= OMe
b X= OPh
c X= OAr (Ar= 2,6-dimethylphenyl)
d X= O_2CMe
e X= O_2CF_3
f X= $O_2CC(CH_3)_3$
g X= Cl

The reaction of alcohols was further probed using the metallacycle **13**. The reaction with MeOH proceeded slowly at room temperature with 60% of the original metallacycle consumed after 22 hours. An extra equivalent of MeOH was added to complete the reaction in an additional 12 hours. The experiment was repeated at 72°C and the same conversion noted after 0.5 hours. In both experiments a mixture of products was observed (^{1}H and ^{13}C NMR). In the first, signals assignable to the alkoxides **22a** (55%) and **23a** (12%), and CpH (15%) were observed (percentage based on integration of the Cp region). The yield of **22a** decreased in the second experiment along with an increase in CpH. Treatment of **13** with PhOH initially gave the alkoxides **22b** and **23b** in a 3:1 ratio (^{1}H NMR). After 2 days the quantity of **23b** decreased with the appearance of $Cp_2Ti(OPh)_2$ and the alkane **24**. The experiment was repeated with 2,6-dimethylphenol and slow disappearance of **13**

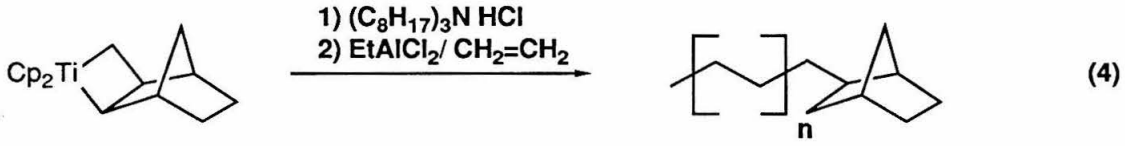
observed at room temperature. The new compounds **22c** and $Cp_2Ti(OAr)_2$(Ar= 2,6-dimethylphenyl) formed at equal rates and after consumption of 1 equivalent of ArOH, the three complexes **13**, **22c** and $Cp_2Ti(OAr)_2$ were present in equal amounts.

Therefore, it appears that MeOH will protonate both titanium-carbon bonds of **13**, predominantly at the tertiary carbon. Additionally, the Cp's are protonated at a slower rate. Phenol reacts more quickly, giving the two alkoxides, again with a preference to protonate the tertiary over the secondary carbon. Steric bulk ortho to the hydroxyl group of the phenol slows the reaction drastically and also presumably destabilizes the resulting unobserved alkoxide **23c** as evidenced by its presumed subsequent rapid protonation to form $Cp_2Ti(OAr)_2$.

The protonation chemistry of **13** by carboxylic acids was also investigated. Treatment of **13** with 1 equivalent of CH_3CO_2H gave cleanly the alkoxide **22d** (^1H and ^{13}C NMR), while use of trifluoroacetic and pivalic acids gave the corresponding alkoxides **22e** and **f**, respectively. Apparently, **22d-f** are more stable than the proposed intermediate **18** derived from **11**. Both **22d** and **f** decomposed at $-20°C$ in solution over several days to give uncharacterized Ti (III) species. The decomposition of **22f** gave a very broad peak at 3.5 ppm, which was also observed in the reaction of **11** with pivalic acid.[18] The alkoxide **22e** is more robust as little decomposition was observed after 6 days at $-20°C$. This parallels the reported stability of titanocene dicarboxylates (**15**).[19]

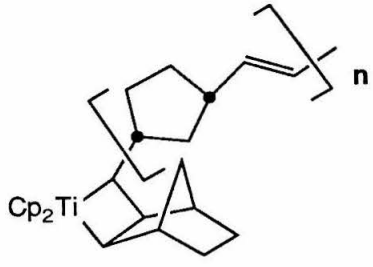
Finally, the addition of amine hydrochlorides to **13** was examined. The reaction with NH_4HCl was complicated by the its insolubility in organic solvents. The reaction was slow at room temperature and led to decomposition of **13**, giving a complex mixture of products. The more soluble amine·HCl, *t*-$BuNH_2$·HCl, (still only partially soluble) gave similar results. The solubility problem was solved by use of $(C_8H_{17})_3N$·HCl[20], which was completely soluble in Et_2O, benzene and

toluene. An NMR tube reaction (thawing of tube) of **13** and $(C_8H_{17})_3N{\cdot}HCl$ gave predominantly the alkyl chloride **22g** with other minor unidentified Ti (IV) products observed. Repeating the experiment at room temperature gave a 54% yield, while use of 2 equivalents of the amine·HCl resulted in a 40% yield. Possibly the lower yields are due to a competing reaction that produces an unobserved Ti (III) product.



13 (4)

Titanocene alkyl chlorides are well known as Ziegler-Natta polymerization catalysts[21] and therefore **22g** was tested by treatment with $EtAlCl_2$ at 0°C under an atmosphere of ethylene (Eq. 4). Slow uptake of ethylene was observed (0.6 equivalents of ethylene/Ti/minute), and after 1 hour the polymerization was quenched and the polymer collected (yield gave 71 equivalents of ethylene/Ti polymerized). The experiment was repeated but quenched 30 seconds after addition of the $EtAlCl_2$. Capillary GC analysis versus C_nH_{2n+2} standards indicated the majority of polyethylene chains were endcapped by a norbornane fragment and only a minor fraction was initiated by $Cp_2Ti(Et)Cl$.[22] Attempts to extend this reaction with **25** to give a diblock polymer were unsuccessful.



25

Conclusion

The chemistry of proton addition to titanacyclobutanes follows several pathways. MeOH will slowly add to give the corresponding alkoxide. However, the carbene derived from thermal decomposition of the metallacycle is rapidly trapped to produce the titanocene alkoxide methyl complex. Stronger acids (phenols, carboxylic acids and amine·HCl's) will protonate the titanium-carbon bonds with addition to tertiary carbons preferred over secondary carbons. In the reaction of carboxylic acids with titanacyclobutanes the product is unstable and decomposes to give the corresponding titanocene (III) carboxylate at a rate dependent upon the alkyl group present.

Experimental Section

General Procedures. All work involving air- and/or moisture-sensitive compounds was performed using standard high-vacuum or Schlenk-line techniques under argon purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves, and a Vacuum Atmospheres dry box under nitrogen. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a Varian Associates EM-390 (90 MHz ^{1}H), FX-90Q (89.6 MHz ^{1}H, 22.53 MHz ^{13}C, 84.3 MHz ^{19}F) or a JEOL GX-400 (399.65 MHz ^{1}H, 100.67 MHz ^{13}C). Chemical shifts are referenced to residual protiosolvent residues. IR spectra were recorded on a Beckman 4240. Capillary GC analysis was done using a Shimadzu GC-Mini 2 flame ionization instrument modified for capillary use and equipped with a Hewlitt-Packard Model 339A integrator (column 0.24 mm X 15 m DBI). Elemental analysis was performed by L. Henling at the analytical facility of the California Institute of Technology.

Gel permeation chromatographic (GPC) analyses utilized Shodex KF-803 and KF-804 columns, a Spectroflow 757 absorbance detector (λ =254 nm), and a Knauer differential refractometer. All GPC analyses were performed on 0.20 % w/v solutions of polymer in CH_2Cl_2. An injection volume of 0.100 mL and a flow rate of 1.0 mL/min were used.

Materials. Titanocene dichloride (Boulder) was purified by soxhlet extraction with CH_2Cl_2 before use. $AlMe_3$ (2.0 M in PhMe) was purchased from Aldrich (packaged under nitrogen in Sure/Seal bottles). 2-Tert-butylcyclohexanone (**2**), 4-phenylcyclohexanone (**4**), and dihydrocoumarin (**7**) were also purchased from Aldrich and used as received. Dry THF was previously distilled from sodium benzophenone ketyl and stored in solvent flasks equipped with Teflon screw-type valves. Solvents listed as reagent or technical were used as received. Silica gel (60, 230-400 mesh ATM) was purchased from EM Reagents.

Titanacyclobutanes **11**[6], **12**[12], **13**[10], and **14**[13] were synthesized according to established procedure. The alcohols and carboxylic acids were reagant grade and used without further purification. Ammonium chloride was dried under high vacuum at 50°C for 2 h before use. The amine hydrochloride *t*-$BuNH_2$·HCl was prepared by treating the amine (in Et_2O) with HCl (g), and the resulting salt collected and dried as above. $(C_8H_{17})_3N$·HCl was prepared according to a literature procedure[20] and dried as above. Toluene, THF, and diethyl ether were dried (CaH_2), transferred to sodium benzophenone ketyl and later distilled into solvent flasks equipped with a Teflon screw-type valve. Pentane was stirred over conc H_2SO_4, washed with H_2O, dried over $MgSO_4$, transferred to sodium benzophenone ketyl in tetraglyme and later distilled as above. Benzene-d_6 and toluene-d_8 (Merck, Sharp & Dohme) were transferred to sodium benzophenone ketyl, later distilled and stored in the dry box. A standard solution of norbornene was prepared under argon as follows: to 8.10 g (86.1 mmol) of freeze-pump-thaw degassed norbornene was added by syringe 0.5 mL of octane and finally benzene, to give a total volume of 50.0 mL (1.72 M in norbornene).

"Titration" of *in Situ* Solutions of 1. Solutions of **1** were prepared as below using titanocene dichloride (2.49 g, 10.0 mmol) and $AlMe_3$ (2.0 M in PhMe, 10 mL, 20.0 mmol of $AlMe_3$). After stirring as described in Table I, 2-tert-butylcyclohexanone (**2**)(1.54 g, 10.0 mmol) in 30 mL of THF was treated with the prepared solution of **1** as below with stirring continued 0.5 h at –40°C and an additional 15 min at room temperature. Workup as below gave quantitative crude yields of organic product as a mixture of ketone and olefin. ^{1}H NMR integration of the *tert*-butyl resonances of **2** and **3** was used to calculate equivalents of **1** produced.

Preparation of (4-Methylenecyclohex-1-yl)benzene (5). A three-neck 250 mL round-bottom flask equipped with a magnetic stir bar and oil bubbler was charged with titanocene dichloride (12.45 g, 50.0 mmol), flushed with argon,

and $AlMe_3$ (2.0 M in PhMe, 55 mL total, 110 mmol of $AlMe_3$) was added by cannula from a graduated cylinder (the graduated cylinder was previously flushed with argon, capped with a rubber septum and charged by cannula from an Aldrich Sure/Seal bottle). The resulting dark red mixture was stirred at room temperature with initial evolution of CH_4 through the bubbler. After 72 h of stirring, additional $AlMe_3$ (2.0 M in PhMe, 20 mL total, 40 mmol of $AlMe_3$) was added by the above method and stirring continued for 12 h.

A 500 mL round-bottom flask equipped with magnetic stir bar and charged with 4-phenylcyclohexanone (**4**) (11.32 g, 65.0 mmol) was flushed with argon and capped with a rubber septum. 80 mL of dry THF were added by syringe and the resulting solution stirred and cooled to –40°C . The previously prepared solution of **1** was added via cannula over a 10 min period while maintaining the resulting mixture at or below –40°C. Stirring was continued for 0.5 h at –40°C , 1.5 h at –40°C to 0°C , and finally 1 h at room temperature. The resulting dark-red mixture was diluted with 50 mL of reagent THF added by syringe, vigorously stirred, and cooled to –10°C. A 40 mL sample of 15% NaOH (aq) was added initially in 0.2-0.3 mL portions by syringe with vigorous evolution of CH_4, while maintaining the mixture at –10°C or below. When the mixture became too viscous for magnetic stirring, the flask was swirled by hand with frequent cooling and the remainder of the NaOH solution was added in much larger portions to the open flask. Additional stirring at room temperature produced a mixture containing a pale orange supernantant with a large amount of slightly bluish precipitate, which turned white upon standing. The aluminoxane polymer formed serves as an excellent drying agent and no further drying was required. The mixture was filtered through a Celite pad on a coarse frit with suction and the precipitate and pad liberally washed with technical Et_2O. The combined filtrate and washings were evaporated under reduced pressure to afford a clear orange toluene solution of crude product, which was diluted with

300 mL of reagent pentane to precipitate a large amount of orange solid. After filtration through a silica gel pad (on a coarse frit with suction) with liberally washing of the precipitate with reagent pentane, the combined washing and filtrate were evaporated under reduced pressure to give 10.57 g (94% yield) of product as a yellow oil. Vacuum distillation (bp 88°C, 2 torr) afforded 9.21 g (82% yield) of pure **5** as a colorless oil: ^{1}H NMR (CD_2Cl_2) δ 7.26 (m, 5H), 4.72 (m, 2H), 2.89-1.45 (m, 9H); ^{13}C NMR (CD_2Cl_2) δ 149.4, 147.5, 128.8, 127.3, 126.4, 107.6, 44.6, 36.1, 35.7. Anal. Calcd. for $C_{13}H_{16}$: C, 90.64; H, 9.36. Found: C, 90.66; H, 9.50.

Preparation of 3,4-Dihydro-2-methylene-2H-1-benzopyran (8). Dihydrocoumarin (**7**) (7.41 g, 50.0 mmol) was treated as above to give toluene solution of crude **8**. Due to the insolubility of **8** in pentane, an alternative method of purification was employed. This consisted of evaporation of the toluene solution of **8** under reduced pressure at 50°C to give a deep orange oil containing significant quantities of titanocene compounds (^{1}H NMR), followed by vacuum distillation to afford 5.56 g (76% yield) of **8**[2b] as a slightly yellow oil: ^{1}H NMR (CD_2Cl_2) δ 7.04 (m, 4H), 4.54 (s, 1H), 4.17 (m, 1H), 2.74 (m, 2H), 2.64 (m, 2H); ^{13}C NMR (CD_2Cl_2) δ 156.8, 153.6, 129.2, 128.1, 123.5, 121.6, 116.3, 89.5, 27.0, 25.7 Anal. Calcd. for $C_{10}H_{10}O$: C, 82.16; H, 6.89. Found: C, 81.77; H, 6.98.

General Procedures for NMR Tube Reactions. Reagents (if solids) were weighed and added to an NMR tube in the dry box and the tube capped with a rubber septum. The tube was brought out and cooled to –20°C in a dry ice-acetone bath. C_6D_6 was first added slowly from a gas tight syringe so that it froze before mixing with the solid (s) present. Any liquid reagents were added on top of the C_6D_6 by syringe. The tube was thawed by hand warmth, shaken vigorously for several minutes, and the spectrum recorded.

Addition of Proton Sources to Titanacyclobutanes. Reactions were NMR tube experiments performed in C_6D_6 unless otherwise indicated. A brief

description for each experiment is given below. When the number of hydrogens is not listed after a proton shift, the number in parentheses signifies the relative integration compared to the other shifts. Partial assignments of NMR and IR spectra are given when relevant to structure identification.

Reaction of 11 with CH_3CO_2H. **11** (0.031 g, 0.12 mmol) and CH_3CO_2H (0.0084 g, 0.14 mmol, 1.2 eq) were combined to give initially a dark brown solution which turned green after several minutes. A ^1H NMR containing broad signals was recorded 3 min after mixing and the IR recorded shortly afterward. The experiment was repeated with 2 eq of acid and identical ^1H NMR and IR spectra obtained: ^1H NMR (C_6D_6) δ 1.14 (s, 1.0), 0.88 (s, 4.5); IR (C_6D_6) 2957, 2865, 1535 (C=O), 1470 (C=O), 1455, 1366, 1124, 1017, 942, 820, 794, 690 cm^{-1}. The IR of the proposed product **17a** is as follows[15]: IR (C_6D_6) 3140, 3080, 1525 (C=O), 1460 (C=O), 1460, 1120, 1005, 835, 785, 590 cm^{-1}.

Reaction of 11 with Pivalic Acid. **11** (0.035 g, 0.14 mmol) and pivalic acid (0.014 g, 0.14 mmol, 1.0 eq) were combined to give a green-brown solution which formed a blue precipitate after several hours. A ^1H NMR was recorded 5 min after thawing to give a spectrum with broad peaks. An IR was recorded shortly afterwards and was identical to an authentic sample of **17b**[14]: ^1H NMR (C_6D_6) δ 3.40 (width at baseline ~90 Hz, 3.0), 1.14 (s, 1.0), 0.89 (s, 4.9).

Reaction of 11 with MeOH. **11** (0.027 g, 0.11 mmol) and MeOH (0.0056 g, 0.18 mmol, 1.6 eq) were combined to give an orange solution rapidly. ^1H NMR indicated isobutylene (δ 4.72, 1.58) and the product **20**: ^1H NMR (C_6D_6) δ 5.63 (s, 10 H), 3.78 (s, 3H), 0.70 (s, 3H). The experiment was repeated by addition of MeOH to a d_8-toluene solution of **11** precooled to –20°C. The tube was kept at –20°C to –15°C for 3.3 h. It was then allowed to warm to room temperature and the ^1H NMR recorded, which showed only **20** and isobutylene present.

Reaction of 12 with MeOH. 12 (0.025 g, 0.090 mmol) and MeOH (0.00395 g, 0.12 mmol, 1.3 eq) were combined and the reaction observed to proceed slowly at room temperature (^{1}H NMR). After 2.3 h the reaction was complete, giving the product **20**: ^{1}H NMR (C_6D_6) δ 5.67 (s, 5H), 5.59 (s, 5H), 3.82 (s, 3H), 1.78 (m, 2H), 1.03 (s, 9H), 0.85 (d, J= 5.9 Hz, 3H), 0.80 (m, 1H); ^{13}C NMR (C_6D_6) δ 112.3, 111.8, 66.1, 56.5, 48.8, 35.7, 28.0, 16.0.

Reaction of 13 with MeOH. 13 (0.024 g, 0.084 mmol) and MeOH (0.003 g, 0.094 mmol, 1.1 eq) were combined and the reaction observed to proceed slowly at room temperature (^{1}H NMR) with ~60 % of **13** consumed after 22 h. An additional 1.1 eq of MeOH were added and after 12 h (31 h total) **13** was completely consumed. The following products were identified by ^{1}H NMR (percentage based on original Cp's): CpH (15 %) (identified by comparision to an authentic sample); **22a** (55%) (^{1}H NMR (C_6D_6) δ 5.65 (s, 5H), 5.64 (s, 5H), 3.83 (s, 3H), 2.28 (m, 1H), 1.92 (m, 1H), 1.80-0.84 (m, 11H); ^{13}C NMR (C_6D_6) δ 111.9, 111.8, 66.5, 64.8, 49.2, 46.6, 44.7, 37.9, 36.3, 31.0, 29.9); **23a** (12%) (^{1}H NMR (C_6D_6) δ 6.05 (s, 5H), 5.84 (s, 5H)...); and **24** (12%) (comparison to an authentic sample). The experiment was repeated at 72°C. After 0.5 h ~60% of **13** was consumed. An additional 1.0 eq of MeOH was added and after 0.5 h (1 h total) **12** was completely consumed (^{1}H NMR). NMR indicated a more complex mixture of titanium products than before (including **22a** in lower and CpH in higher yields than before).

Reaction of 13 with PhOH. 13 (0.022 g, 0.077 mmol) and PhOH (0.007 g, 0.074 mmol, 1.0 eq) were combined to give a clear orange solution. The ^{1}H and ^{13}C NMR spectra were recorded 20 min after thawing and indicated a 3:1 ratio of **22b** to **23b**. After 2 days a ratio of 6:1:1.5 of **22b** to **23b** to $Cp_2Ti(OPh)_2$ was observed along with **24** (^{1}H NMR): **22b** (^{1}H NMR (C_6D_6) δ 7.20 (m, 2H), 6.82 (m, 1H), 6.43 (m, 2H), 5.71 (s, 5H), 5.68 (s, 5H), 2.27 (m, 1H), 2.02 (m, 1H), 1.81-1.10 (m, 11H); ^{13}C NMR (C_6D_6) δ 169.3, 129.5, 119.2, 117.6, 112.89, 112.86, 69.5, 49.0, 46.4, 45.2,

37.8, 36.3, 30.9, 29.9); **23b** (^{1}H NMR (C_6D_6) δ 7.20 (m, 2H), 6.82 (m, 1H), 6.43 (m, 2H), 5.73 (s, 5H), 5.64 (s, 5H), 2.67 (m, 1H), 1.81-1.10 (m, 11H), 1.00 (d, J= 6.8 Hz, 3H); ^{13}C NMR (C_6D_6) δ 169.2, 129.5, 119.2, 117.61, 117.60, 113.3, 93.2, 51.2, 49.5, 46.0, 39.2, 31.4, 28.9, 22.0); $Cp_2Ti(OPh)_2$ (^{1}H NMR (C_6D_6) δ 7.20 (m, 4H), 6.82 (m, 2H), 6.43 (m, 4H), 5.88 (s, 10H); ^{13}C NMR (C_6D_6) δ 170.8, 129.5, 119.4, 117.7, 116.0).

Reaction of 13 with 2,6-dimethylphenol. **13** (0.021 g, 0.073 mmol) and the phenol (0.009 g, 0.073 mmol, 1.0 eq) were combined. After 10 min 90% of **13** remained (^{1}H NMR). After 2.2 h ~50% of **13** remained along with 25% $Cp_2Ti(OAr)_2$ and 25% **22c**. After 48 h 30% of **13** remained along with equal amounts of $Cp_2Ti(OAr)_2$, **22c**, and **24**: (**22c** ^{1}H NMR (C_6D_6) δ 7.2-6.8 (m, 3H), 5.71 (s, 5H), 5.70 (s, 5H).....).

Reaction of 13 with CH_3CO_2H. **13** (0.020 g, 0.070 mmol) and CH_3CO_2H (0.044 g, 0.073 mmol, 1.0 eq) were combined to give a dark-orange solution. ^{1}H and ^{13} NMR spectra (containing broad signals) were recorded 20 min after thawing and indicated exclusive formation of **22d**. After 4 days at –20°C only 50 % of **22d** remained with no new titanocene (IV) compounds present (^{1}H NMR): ^{1}H NMR (C_6D_6) δ 5.81 (s, 5H), 5.80 (s, 5H), 2.17 (s, 1H), 1.81 (s, 1H), 1.79 (s, 3H), 1.75-0.86 (m, 11H); ^{13}C NMR (C_6D_6) δ 173.9, 114.3, 76.1, 49.1, 46.1, 44.5, 37.7, 36.2, 30.9, 29.8, 23.7.

Reaction of 13 with CF_3CO_2H. **13** (0.022g, 0.077 mmol) and CF_3CO_2H (0.0077 g, 0.068 mmol, 0.9 eq) were combined to give a dark red-brown solution. The ^{1}H and ^{13}C NMR spectra (broadened signals), recorded 20 min after thawing, indicated formation of **22e** in high yield. After 6 days at –20°C, little decomposition was observed (^{1}H NMR): ^{1}H NMR (C_6D_6) δ 5.75 (s, 5H), 5.73 (s, 5H), 2.17 (s, 1H), 1.95 (m, 1H), 1.80-0.84 (m, 11H); ^{13}C NMR (C_6D_6) δ 159.5 (q, $^2J_{C-F}$= 38.0 Hz),

116.5 (q, $^1J_{C-F}$= 288 Hz), 115.5, 86.4, 49.6, 46.1, 44.2, 37.6, 36.2, 30.7, 29.6; ^{19}F NMR (C_6D_6) δ 88.0 (s) vs. C_6F_6.

Reaction of 13 with Pivalic Acid. **13** (0.024 g, 0.084 mmol) and pivalic acid (0.010g, 0.098 mmol, 1.2 eq) were combined to give a dark-brown solution. ^1H and ^{13}C NMR spectra (broad signals) were recorded 1 h after thawing and indicated exclusive formation of **21f**. After 2 days at room temperature **22f** had disappeared with appearance of unidentified organics (2.6-0.8 ppm) and a broad peak at 3.5 ppm (~400 Hz in width): ^1H NMR (C_6D_6) δ 5.90 (s, 5H), 5.86 (s, 5H), 2.20 (m, 1H), 1.79 (m, 1H), 1.60-0.90 (m, 11H), 1.14 (s, 9H); ^{13}C NMR (C_6D_6) δ 181.2, 114.4, 78.7, 48.9, 46.7, 45.1, 40.2, 37.6, 36.6, 29.8, 28.4.

Reaction of 13 with NH_4Cl. **13** (0.048 g, 0.168 mmol) and NH_4Cl (0.090 g, 0.168 mmol, 1.0 eq) were combined in a Schlenk tube, 4 mL of THF added and the resulting dark-red heterogeneous mixture stirred at room temperature. After 46 h the solution was deep orange-red with undissolved NH_4Cl still present. The solution was evacuated to dryness and analyzed by ^1H NMR, which indicated a complex mixture of products present.

Reaction of 13 with $tBuNH_2Cl$. **13** (0.048 g, 0.168 mmol) and $tBuNH_2Cl$ (0.0184 g, 0.168 mmol, 1.0 eq) were combined in THF as above. After 24 h of stirring there was little change in appearance of the mixture. ^1H NMR indicated mostly starting material present along with unidentified titanocene compounds.

Reaction of 13 with $(C_8H_{17})_3N{\cdot}HCl$. **13** (0.019 g, 0.066 mmol) and the the amine·HCl (0.024 g, 0.062 mmol, 0.94 eq) were combined and the ^1H NMR indicated the product **22g**, unreacted **13**, and the free amine. The experiment was repeated with PhOMe as an internal standard (using 1.1 eq of the amine·HCl), which gave a 75 % yield of **22g**. The experiment was repeated again with 1.0 eq of the amine·HCl at room temperature (no freezing of the C_6D_6) and gave a purple-red solution containing a 54% yield of **22g** (^1H NMR). Addition of an extra 1.0

eq of the amine·HCl reduced the amount of **22g** to 41% . Starting with 2.0 eq of amine·HCl at room temperature, a 40% yield of **22g** was observed (^{1}H NMR).

Preparation of 22g. **13** (0.097 g, 0.34 mmol) and $(C_8H_{17})_3N$·HCl (0.132 g, 0.34 mmol, 1.0 eq) were combined in a Schlenk tube, the tube cooled to 0°C and 4 mL of Et_2O added. The resulting mixture was stirred for 15 min at 0°C and then 15 min at room temperature. The mixture was evacuated to give a red oil containing a small amount of orange precipitate. The oil was redissolved in pentane, filtered through Celite under argon and the resulting clear red solution reduced in volume to 10 mL. The red solution was slowly cooled to –50°C, giving orange-red crystals and some gummy solid. The crystals were collected, washed with pentane at –50°C and analyzed by NMR: ^{1}H NMR (C_6D_6) δ 5.83 (s, 5H), 5.82 (s, 5H), 2.17 (m, 1H), 1.83 (d, J= 3.0 Hz, 1H), 1.75 (d of d, J_1= 4.1 Hz, J_2= 6.0 Hz, 1H), 1.6-1.0 (m, 10H); ^{13}C NMR (C_6D_6) δ 115.5, 115.4, 83.7, 49.7, 46.4, 44.6, 37.6, 36.3, 30.8, 29.7.

Polymerization of Ethylene by 22g. **13** (0.050 g, 0.17 mmol) and $(C_8H_{17})_3N$·HCl (0.068 g, 0.17 mmol, 1.0 eq) were combined in a Schlenk tube, the tube cooled to 0°C and 15 mL of PhMe added by syringe. The mixture was stirred 15 min at 0°C , 15 min at room temperature, and recooled to 0°C. A separate Schlenk tube was charged with $EtAlCl_2$ (0.072 g, 0.57 mmol, 3.3 eq), which was dissolved in 2.5 mL of PhMe and cooled to 0°C. Both tubes were purged with ethylene for 15 min. The Al solution was added by cannula to the toluene solution of **22g**. Stirring was continued at 0°C under a static atmospheric pressure of ethylene. A slow uptake of ethylene was observed as evidenced by a pressure change of 10 mm of Hg/min. More ethylene was added to maintain the pressure. The head volume was ~200 mL and therefore the rate of consumption of ethylene was ~0.1 mmol/min (0.6 eq/Ti/min) by the ideal gas law. After 1 h the solution had become viscous and developed a film on the surface. 50 mL of MeOH were added to quench the polymerization. The resulting mixture was added to 100 mL of rapidly

stirring MeOH to precipitate the polymer, giving 0.347 g (equivalent to 12 mmol of ethylene) of light-brown powder after drying under high vacuum overnight. This represents 71 eq of ethylene consumed/eq of Ti.

The experiment was repeated, but 30 s after mixing of the solutions the polymerization was quenched with 10 mLs of 1:1 conc. HCl/MeOH. The organic layer was separated, washed (10% NaOH (aq)), dried (Na_2SO_4) and evacuated to give a gummy solid. The solid was redissolved in toluene and analyzed by capillary GC (see General Procedures).

Attempted Polymerization of Ethylene by 25. A Schlenk tube was charged with **13** (0.058 g, 0.20 mmol) and 2 mL of benzene added to dissolve the metallacycle. This solution was added to a tube equipped with a Teflon valve and charged with a benzene solution (total volume= 5 mL) of norbornene (0.81 g, 8.6 mmol, 43 eq). The resulting mixture was stirred at 62°C and the disappearance of norbornene followed by capillary GC. After 36 eq of norbornene were consumed, the mixture was allowed to cool to room temperature and evacuated overnight at under high vacuum. The red polymer was redissolved in 5 mL of toluene, cooled to 0°C and the amine·HCl (0.088 g, 0.23 mmol, 1.2 eq) in 5 mL of toluene at 0°C added. The resulting mixture was stirred 40 min at 0°C and then allowed to warm to room temperature with a slight color change to orange-red. One-half of the solution was treated in the same manner as **22g** with $EtAlCl_2$ and ethylene as above to give a green solution, but no uptake of ethylene was observed. After several minutes the solution turned brown and polymerization started. The other half of the solution was added to stirring MeOH to precipitate the polymer. GPC analysis of the soluble portion of the two different samples of polymer gave identical molecular weights. Repeating the experiment with no warming to room temperature during the generation of **22g** gave the same results.

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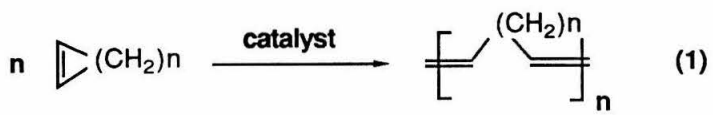
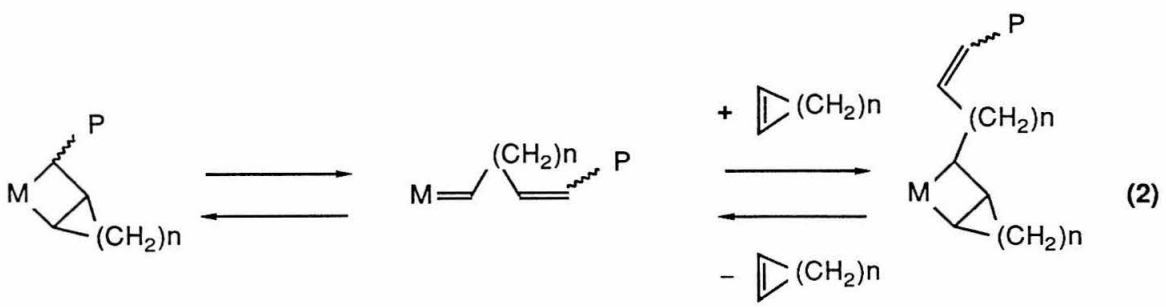
Chapter 3

Ring-Opening Metathesis Polymerization of Cyclic Olefins by Titanacyclobutanes and Tungsten Alkylidenes

Introduction

The ring-opening metathesis polymerization (ROMP) of cyclic olefins (Eq. 1) was first reported by Natta and coworkers in 1964 as a competing reaction to the normal Ziegler-Natta addition polymerization.[1] Since this initial discovery, olefin metathesis polymerization has been extensively studied.[2] Mechanistics studies have now firmly established the intermediacy of alternating chain-propagating metal carbenes and metallacycles[2d] (Eq. 2).



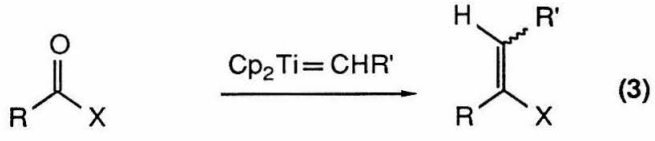


The past few years have seen a growing interest in the ring-opening metathesis polymerization (ROMP) of cyclic olefins[3]. Currently, several polymers, including *trans*-polyoctenamer[4] and polynorbornene[5], are produced industrially. This highly versatile reaction is catalyzed by a variety of metal systems[2]. The Grubbs research group has been employing several titanium[6] and tungsten[7] ROMP catalysts and has synthesized, to date, endcapped-polyalkenamers[8], block copolymers[9], conducting polymers[10], rigid polyalkanamers[11] and chelating polyethers[12].

In this chapter several different aspects of metathesis polymerization employing titanium and tungsten catalysts are discussed. The first section involves the end capping of polynorbornene produced by a living polymerization system involving intermediate titanacyclobutanes. Results on investigations on the polymerization of cyclopentene by titanacyclobutanes are presented in the second section. The third section describes the production of block copolymers containing monodisperse segments. A preliminary study on the polymerization of norbornene by a stable tungsten alkylidene is outlined in the fourth section. The last section presents the synthesis of a novel, conducting polymer produced by metathesis polymerization of a hetero-olefin.

End Capping of Polynorbornene Produced by Titanacyclobutanes[13]

Previous work[14] has shown that titanium carbenes, generated from titanacyclobutanes and other sources, react with aldehydes, ketones, esters, amides, and imides to give Wittig-type products in excellent yields (Eq. 3). The novel combination of the organic and polymer chemistry of titanium carbenes should make possible the controlled synthesis of polymers with a variety of end groups. Among the potential uses are efficient removal of the catalyst, modification of the bulk properties of the original ROMP-derived polyalkenamer, and introduction of moieties for further chemical transformations and/or polymerization.



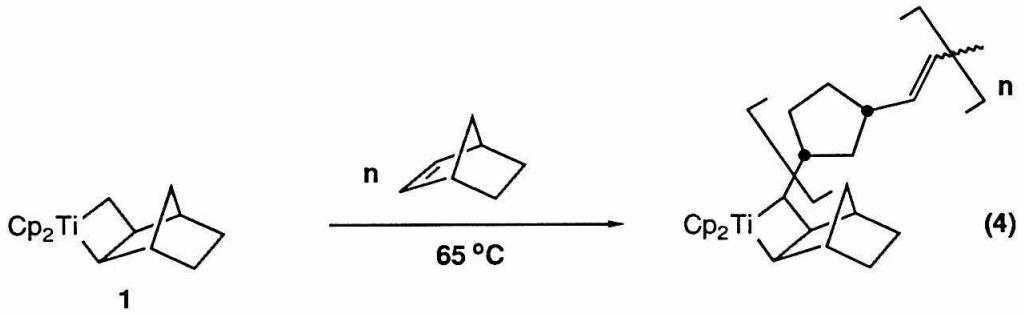
(3)

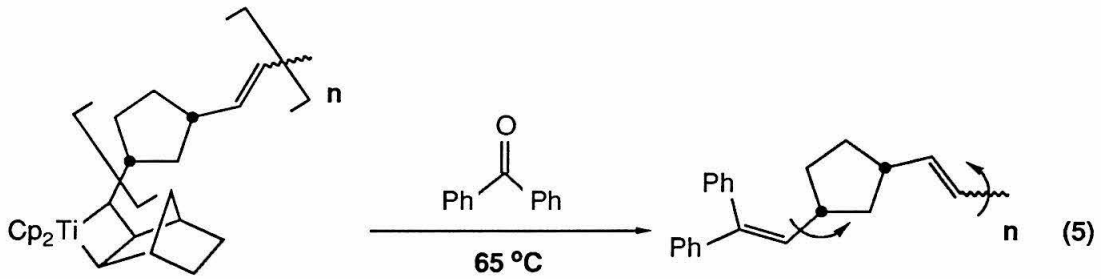
X= H, R", OR", NR"R"', N(R")C(O)R"'

In this section the end capping of polynorbornene with benzophenone utilizing the Wittig-type chemistry of titanium carbenes is described. The efficiency of the end capping reaction as well as its effect on polymer molecular weights and polydispersities are examined.

Results and Discussion

By the use of **1** as a catalyst, norbornene was polymerized (Eq. 4), and the resulting living polymer was allowed to react with benzophenone to give diphenylethylene- capped polynorbornene (Eq. 5). This capping group was chosen for its favorable ^{1}H NMR and UV properties to faciliate end group analysis. On the basis of model studies, benzophenone is also a good test of a sterically demanding ketone.





To establish the efficiency of the reaction, both ^{1}H NMR and UV analyses were used to determine the quantity of diphenylethylene end cap present in the isolated samples of end-capped polymer. Comparision of these values with the expected theoretical values (based on the molecular weights of the polymers derived from GPC and assuming 100% active catalyst) gave the percentage of chains containing the end cap.

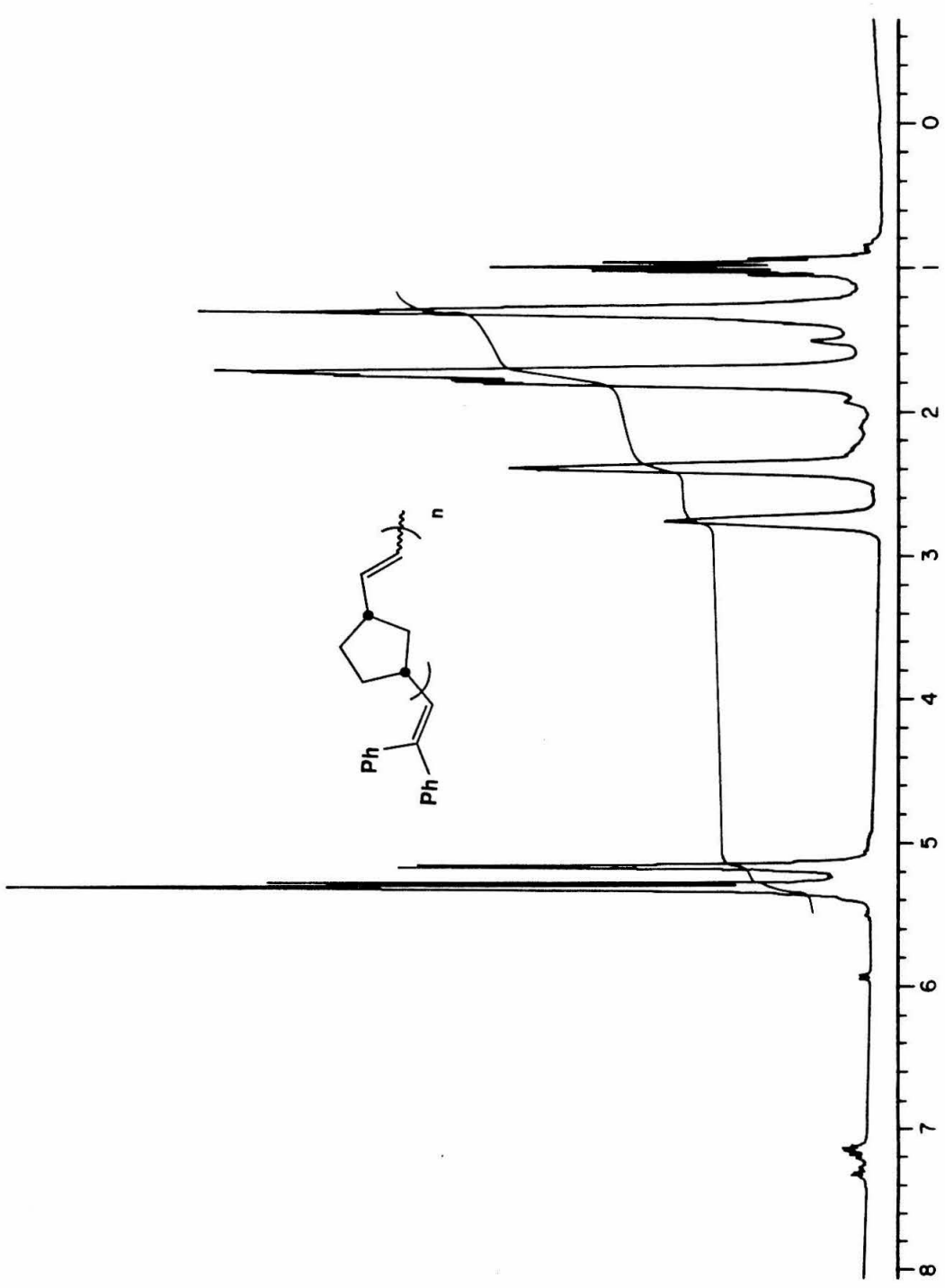
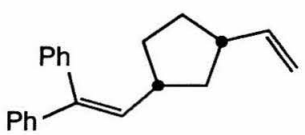


Figure 1. 400 MHz ^{1}H NMR spectrum in CD_2Cl_2 of diphenylethylene-capped polynorbornene (n= 47).

A typical ^1H NMR spectrum of the capped polymer (in CD_2Cl_2) is given in Figure 1. Both the aromatic protons (δ 7.10 - 7.40, m, 10H) and the olefinic proton (δ 5.95, d, J= 11 Hz, 1H) of the endcap (Ph_2C=CH-) were observable. The olefinic protons of the polymer (δ 5.10 - 5.40, m) overlap the residual solvent signal of the NMR solvent and could not be used for integration purposes. However, the allylic protons of the polymer (δ 2.40, 2.78) were well-resolved and were integrated and compared to the integration of the aromatic protons of the end cap. In this manner the ratio of monomer units of polymer to endcap was determined (Table I).

During GPC analysis (see Experimental Section) of the polymers, the UV trace (λ= 254 nm) was also recorded. Because of the much higher extinction coefficient of the end group compared to the polymer, the absorbance due to the polymer was minimal and could be easily subtracted from the trace by comparison to the UV trace of uncapped polymer samples of identical concentrations. The capped monomer **2** was synthesized as previously described[3a] and the UV trace of a standard solution (1.02×10^{-4} M in CH_2Cl_2) was used to calibrate the response factor of the UV detector. Integration of the UV trace of the capped polymer following the above analysis was used to determine the quantity of end group in the polymer sample and therefore to give the ratio of monomers to end cap (Table I).



2

Previous work has shown that GPC (using polystyrene standards) gives approximately twice the correct value of molecular weight for polynorbornene.[3a,15]

Table I. Percentage of Chains End Capped

run	monomers/end cap[a]		M_n[b]	monomers/chain[c]	% end capped[d]	
	NMR[e]	UV[f]			NMR[g]	UV
1	51	65	8,500	45	88	69
2	47	63	9,000	48	102	76
3	79	83	12,400	66	84	80

a. See text.

b. Determined by gel permeation chromatography (versus polystyrene standards).

c. $M_n \div$ (2)(MW of norbornene).

d. ((Monomers/chain)$\div$ (monomers/end cap)) $\times$ 100 % .

e. (Allylic protons of polymer/2) $\div$ (aromatic protons of end cap/10).

f. (Wt of polymer in sample/MW of monomer) $\div$ (wt of end cap in sample/MW of end cap).

g. Values have an error of $\pm$ 5 % from ^{1}H NMR integration.

If the M_n values from GPC (divided by 2) are used as the correct values of average molecular weight of the polymer samples prepared, the average number of monomers per polymer chain can be calculated (Table I). Comparison of the number of monomers per end cap (determined by ^1H NMR and UV) to the average number of monomers per chain gives the percentage of chains that contain the end cap (Table I). Both sets of values are in good agreement (70-100%), indicating the end-capping reaction to be highly efficient.[16]

Table II. Molecular Weight Analysis of Capped and Uncapped Polynorbornene[a]

run		M_n[b]	M_w[b]	n[c]
1	uncapped	10,400	12,600	1.21
	capped	11,100	13,600	1.23
2	uncapped	9,000	12,400	1.38
	capped	9,100	13,100	1.44

a. See Experimental Section for synthesis.

b. Determined by gel permeation chromatography (polystyrene standards).

c. Polydispersity.

Another important aspect of the end-capping reaction is the potential degradation of the polymer under the conditions of the reaction.[17] Generation of titanium hydrides and/or radical species during end-capping would lead to rapid cross-linking of the olefin-rich polymer. To examine this question, samples of uncapped and capped polynorbornene were prepared under identical conditions (see Experimental Section) and analyzed by GPC (Table II). The molecular weights and polydispersities remained relatively unchanged, indicative of minimal degradation of polynorbornene upon end-capping.[18]

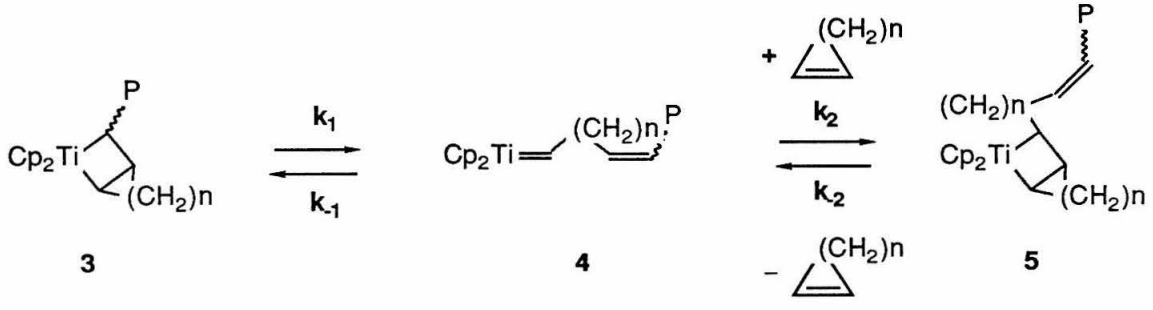
Conclusion

The successful combination of polymer and Wittig chemistry of titanium carbenes demonstrated herein provides the opportunity to synthesize polymers with a variety of end groups. Further research in the promising area is in progress.

Effect of Ring Strain on the Olefin Metathesis Polymerization of Cyclic Olefins

Mechanistic studies have firmly established the intermediacy of alternating chain-propagating metal carbenes and metallacycles during metathesis polymerizations[2d], but the factors affecting the kinetics of the reaction are not as well understood. Investigation of the polymerization of norbornene by titanacyclobutanes demonstrated that the polymerization proceeds with a rate independent of monomer concentration[3a]. This result is best explained by a rate-determining unimolecular cleavage of metallacycle **3** followed by rapid trapping of the subsequent carbene **4** with norbornene to give the new metallacycle **5** (Scheme I; $k_1 \gg k_{-1}$, $k_2 \gg k_{-2}$, $k_2 \gg k_1$).

Scheme I. Metallacycle-Carbene Equilibrium



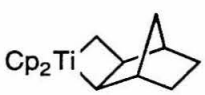
Relief of ring strain of the norbornane fragment of **3** promotes cleavage to 4 and conversely prevents the back reaction ($k_1 \gg k_{-1}$). The difference in ring-strain of norbornene vs. norbornane and the relative stabilities of titanium carbenes and

alkenes vs. titanacyclobutanes, respectively, combine to drive the formation of **5** and inhibit the reverse reaction ($k_2 \gg k_{-2}$).

In this section the polymerization by titanacyclobutanes of cyclopentene is examined. The results presented herein further elaborate the factors affecting the rates of the different steps in olefin metathesis polymerization.

Results and Discussion

Initiation of Polymerization.[19] Reaction of metallacycle **7** (synthesized from **6**[6c] and cyclopentene) with 2 equivalents of cyclopentene at 20-85°C over 3 hours resulted in metallacycle decomposition (to unknown products) with no observable (^{1}H NMR) polymer formation. Decomposition of **7** at 35°C in the presence of an excess of benzophenone gives exclusively 1,1-diphenylethylene in high yield[20], confirming that **7** cleaves exclusively to give "$Cp_2Ti{=}CH_2$" and cyclopentene upon thermolysis, rather than in a productive manner, to initiate polymerization. The norbornene-derived metallacyle **1** is known to cleave productively at 65 °C (70:30 productive/nonproductive metathesis)[3a], but treatment with 14 equivalents of cyclopentene at 65°C for 12 hours gave only cyclopentene and unidentified titanium products.[21] Metallacycle **8** produces exclusively the carbene **9** at 23°C (Eq. 6)[6b] and polymerizes norbornene at 65°C to give narrow-dispersed polynorbornene.[3a] Reaction of **8** with cyclopentene at 23°C was monitored by ^{1}H NMR. Exactly 2 equivalents of the olefin were consumed. This result and ^{1}H NMR signals characteristic of titanacyclobutanes observed in the cyclopentadienyl region (δ 5.36 and 5.30), the α-region (δ 4.77 and 2.77) and the β-region (δ 0.44 and –0.21) suggest formation of metallacycle **10** (Eq. 7). These observations indicate successful initiation of the polymerization to give a stable chain-carrying species.



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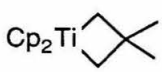

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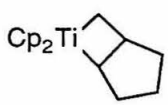

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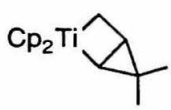

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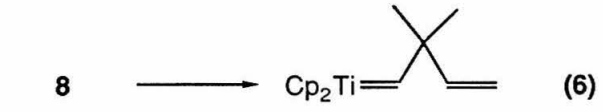

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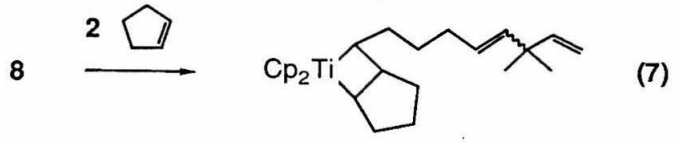

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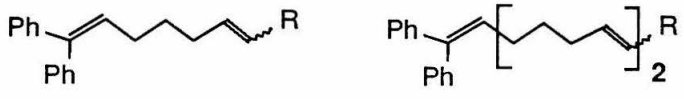


11 12

R = $C(CH_3)_2CH{=}CH_2$

Propagation of Polymerization.[19] Reaction of **10** with excess benzophenone gave two major organic products. Although these products were not isolated, analogy with trapping experiments on the norbornene metallacycle **1**[3a] and high resolution mass spectra support their formulation as olefins **11** and **12**. The formation of both metallacycle cleavage products in a ratio of 3:1 (**11:12**) indicates that, although the non-productive cleavage pathway predominates, reaction in the direction of polymerization does occur (Scheme I, $k_{-2}/k_1 \approx 3$). Nevertheless, when **10** was heated to 45°C in the presence of 3 equivalents of cyclopentene, the metallacycle decomposed without consuming any of the olefin. Subsequent polymerization of norbornene in the presence of cyclopentene revealed that **10** is active toward polymerization of strained olefins. No consumption of cyclopentene occurred. These results are consistent with observations made in attempted cyclopentene polymer-

izations with a variety of other metathesis catalysts.[22] The large enthalpy change for the polymerization of strained olefins drives the reaction. Cyclopentene has a relatively low strain energy. At lower monomer concentrations, the unfavorable entropy change term overwhelms gains in enthalpy and polymerization is impossible.

Polymer Synthesis. Polymerization was finally achieved with 20-220 equivalents of cyclopentene in benzene or toluene, using **8** as a catalyst. The results are summarized in Table III. The polymerizations were followed by capillary VPC with the expected consumption of cyclopentene observed. No other low molecular weight compounds were detected in the VPC traces as has been noted for other cyclopentene polymerizations[22], although they may have gone unobserved under the experimental conditions.

Polymer Analysis. The resulting polymers were isolated by precipitation into MeOH and analyzed by NMR and GPC. The NMR was consistent with that previously reported for polypentenamer.[23] Additional peaks attributable to the end group, $-C(CH_3)_2CH{=}CH_2$, derived from the catalyst were observed[24] and used as an internal standard to determine the number of monomers/chain by integration against the olefinic signal of the polymer (see Table IV). The molecular weights as determined by GPC (vs. polystyrene standards) were higher than the NMR-derived values with a conversion factor of 1.6 suggested. The polydispersities(M_w/M_n), although not unity were still in the range of living systems. The increase in dispersity with longer reaction times is very suggestive of secondary metathesis of the carbon double bonds of the polymer by the active catalyst. The percentage of *trans* double bonds in the polymer was in the range of 79-88% , with slight variations observed with changes in temperature, reaction times and initial monomer concentration. All these factors have previously been noted to change the *cis/trans* ratio, but no attempt was made in this study to confirm these results.

Table III. Polymerization of Cyclopentene[a]

run	% *trans*[b]	total time (h)	temp(°C)	$[cyclopentene]_o$(M)	solvent[c]	[**9**](10^{-3} M)
1	86	21;6.5[d]	23;48[d]	5.68	B	35
2	82	159	23	5.68	B	42
3	88	172	23	2.84	B	38
4	79	148	23	8.52	T	38
5	85	145	25	5.68	T	42
6	84	98.3	25	5.68	T	42
7	80	8.8	34	5.68	T	42
8	84	19.5	34	5.68	T	42
9	85	23.5	34	2.84	T	38
10	80	23.0	34	8.52	T	38
11	-	27.0	34	1.42	T	38
12	-	28.0	34	0.71	T	37

a. See Experimental Section for procedure.

b. Determined from ^{13}C NMR($CDCl_3$) (*trans*, δ 130.1, *cis*, δ 129.5).

c. B= benzene; T= toluene.

d. 21 h at 23°C, then 6.5 h at 48°C.

Table IV. Polymer Molecular Weights

run	eq of cyclopentene consumed[a]	MW[b] (NMR)	M_n[c] (GPC)	M_w[c] (GPC)	n[d] (GPC)	correction factor[e]
1	45	4280	6130	11500	1.88	1.4
2	61	4500	8240	13080	1.59	1.8
3	30	2640	4500	6470	1.43	1.7
4	65	4800	7630	12400	1.62	1.6
5	68	4300	7770	12100	1.55	1.8
6	54	3880	6610	9800	1.48	1.7
7	37	1500	-	-	-	-
8	36	2860	4370	5720	1.31	1.5
9	17	1770	3250	4610	1.42	1.8
10	58	3600	5970	8240	1.38	1.4
11	-	630	1440	1880	1.30	2.3
12	3	200	1200	1520	1.27	6

a. Determined by VPC vs. an internal standard (see Experimental Section).

b. Determined by ^{1}H NMR: ((CH_3 protons of end group/6) ÷ (-CH=CH- protons of polymer/2) × (MW of cyclopentene).

c. Determined by gel permeation chromatography (polystyrene standards).

d. Polydispersity.

e. M_n(GPC)/MW(NMR); average of runs 1-10 (comparable MW's) = 1.6.

Kinetics of Polymerization. The overlap of signals in the ^{1}H NMR spectra of cyclopentene and poly(1-pentylene) precluded use of ^{1}H NMR for kinetic studies. Attempts to measure accurately the consumption of cyclopentene by VPC to determine the kinetics of the reaction were of limited success. The volatility of cyclopentene (bp 44°C) and the temperature of the polymerization (33°C) made it difficult to sample the mixture without loss of cyclopentene. Qualitatively, the general trend of increasing rates of polymerization with higher concentrations of cyclopentene was observed.

To obtain quantitative kinetic data, an exact method of measurement was required. Recently, ^{13}C NMR was employed to determine the kinetics of the polymerization of ethylene by a scandium catalyst.[25] Utilizing this method, the polymerization of cyclopentene by **9** was monitored at 36.7±0.5°C[26] for several concentrations of monomer to determine initial rates of polymerization (Table V). Assuming that the initial rates observed are good approximations of the instantaneous rate at the initial cyclopentene concentration, the rate data were used to examine the validity of Scheme I.

Table V. Rates of Cyclopentene Polymerization[a]

run	[cyclopentene] (M)	rate (10^{-5}) Ms^{-1}
1	1.42	8.17±1.56
2	2.84	10.6±1.5
3	5.70	19.8±1.0

a. See Experimental Section.

In reexamining Scheme I, it was noted that the propagating metallacycles **3** and **5** are indistinguishable during the polymerization and therefore a new simpler

scheme with just the metallacycle **3** and the carbene **4** was used (Scheme II). A rate expression for the polymerization was derived from Scheme II, using the steady-state approximation since the concentration of the unstable propagating carbene **4** is very small[27] and therefore approximately constant. Additionally, the concentration of the metallacycle **3** was replaced by the concentration of the catalyst employed. This was justified by the predominance of the propagating metallacycle **3** over the propagating carbene **4** during the polymerization.[27] Using these approximations, the time dependence of the concentration of carbene **4** and the resulting expression for [**4**] were derived in Eqs. 8 and 9, respectively ([C]= concentration of catalyst; [M]= concentration of monomer).

$$\frac{d[4]}{dt} = 0 = k_1[C] + k_{-2}[C] - k_{-1}[4] - k_2[4][M] \qquad (8)$$

$$[4] = \frac{(k_1 + k_{-2})[C]}{k_{-1} + k_2[M]} \qquad (9)$$

$$-\frac{d[M]}{dt} = k_2[M][4] - k_{-2}[C] \qquad (10)$$

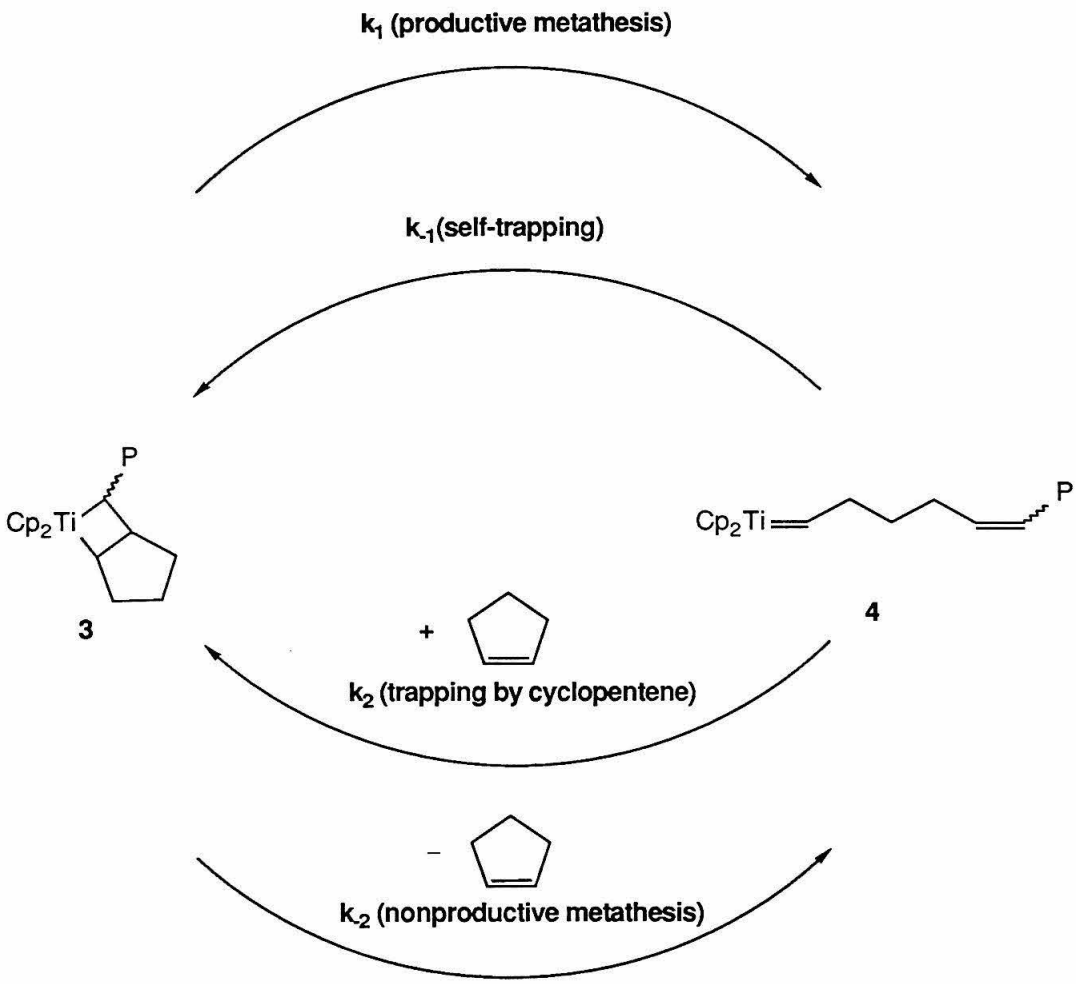
$$-\frac{d[M]}{dt} = \frac{k_2[M][C](k_1 + k_{-2})}{k_{-1} + k_2[M]} - k_{-2}[C] \qquad (11)$$

$$-\frac{d[M]}{dt} = \left[k_2[M] \frac{k_1 + k_{-2}}{k_{-1} + k_2[M]} - k_{-2} \right][C] \qquad (12)$$

Using Eq. 9, the rate of polymerization (change in monomer concentration with time) was derived in Eqs. 10-12.

The derived rate expression (Eq. 12) predicts a first-order dependence of the rate upon the concentration of catalyst (a question not examined in these studies)

Scheme II


k1 (productive metathesis)
k-1(self-trapping)
P
Cp2Ti
3
Cp2Ti
P
4
+
k2 (trapping by cyclopentene)
–
k-2 (nonproductive metathesis)

and a more complex relationship between the concentration of monomer and the rate of polymerization. The effect of monomer concentration upon the rate would, however, be more straightforward for two special cases. In the first, if $k_2[M] \gg k_{-1}$, then Eq. 12 simplifies to the expression given in Eq. 13 and the rate of the polymerization would be independent of monomer concentration.

$$- \frac{d[M]}{dt} = k_1[C] \qquad (13)$$

$$- \frac{d[M]}{dt} = \left[k_2[M] \frac{k_1 + k_2}{k_{-1}} - k_2 \right] [C] \qquad (14)$$

In the second case, if $k_{-1} \gg k_2[M]$, the rate would be represented by Eq. 14 and a first- order dependence of the rate on monomer concentration should be observed. Additionally, one would expect a negative y-intercept in the plot of rate vs. monomer concentration.

A plot of rate vs. cyclopentene concentration (Figure 2) indicates that the rate of polymerization is linear with respect to [M] and therefore can be expressed by Eq. 14. The result implies that even at higher concentrations of cyclopentene (runs 2 and 3), k_{-1} is still much greater than $k_2[M]$ and therefore the rate of self-trapping (k_{-1}) is much faster than trapping by cyclopentene (k_2). The y-intercept of Figure 2 is a small positive value; Eq. 14 predicts a negative y-intercept. The approximations used in assigning instantaneous rates (*vide supra*) may be responsible for this discrepancy.

A interesting dilemma arises when one examines the implication of the above analysis. If the rate of self-trapping (k_{-1}) is much faster than k_2 (cyclopentene

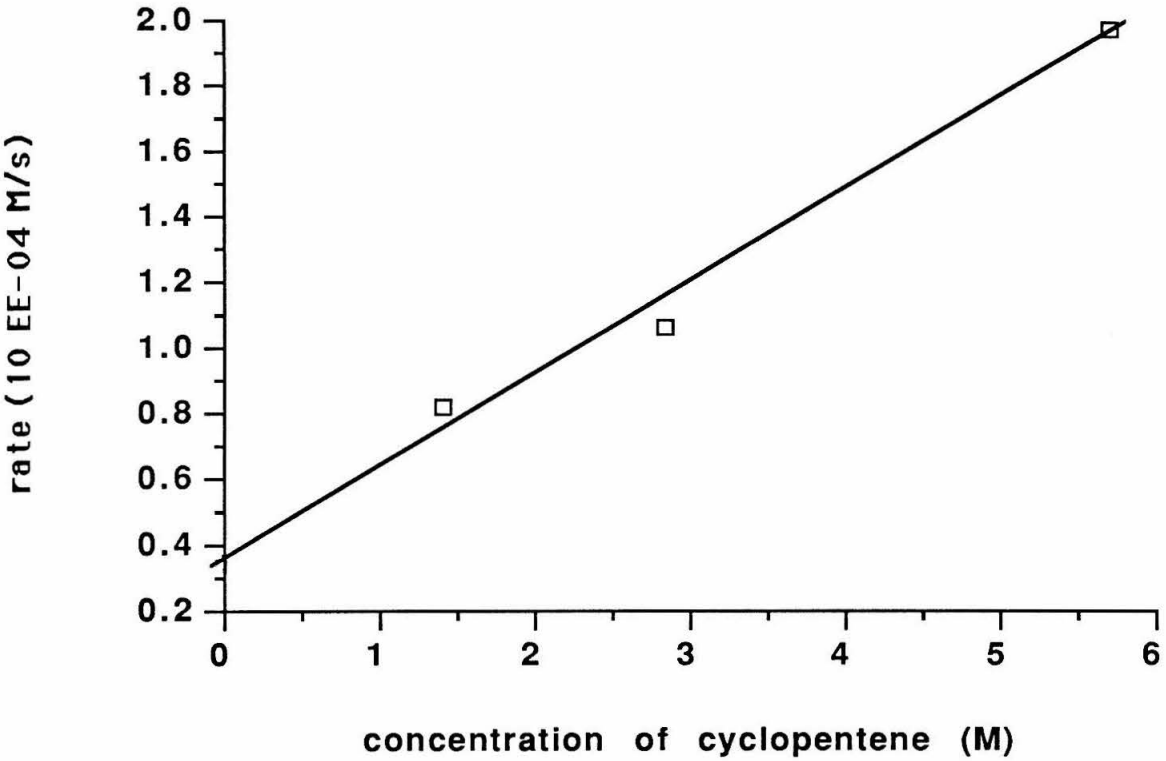
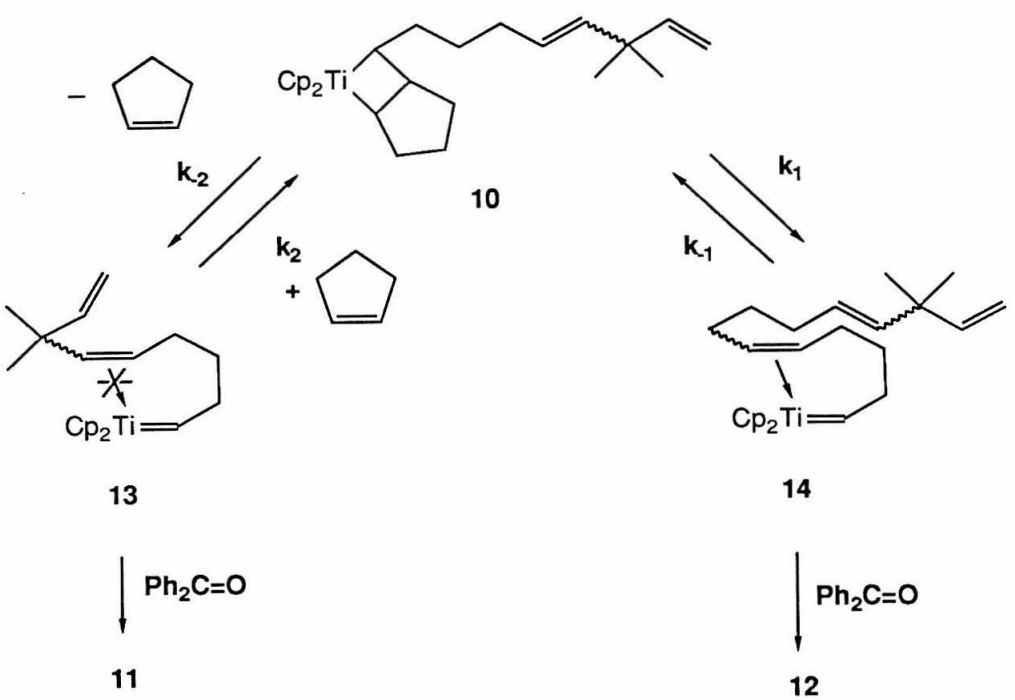


Figure 2. Plot of rate of polymerization vs. concentration of cyclopentene. The line was derived from a least-squares fit of the data points (correlation= 0.99).

trapping) and the rate of nonproductive metathesis (k_{-2}) is three times the rate of productive metathesis (k_1) (from trapping experiments of metallacycle **10** with benzophenone), then the overall result would be depolymerization!

This conclusion necessitates a reexamination of the kinetic data and trapping experiments. The data derived from the kinetic runs are consistent with Eq. 14. The ratio of rates (k_{-2}/k_1) from trapping experiments of **10** may, however, be in error. This ratio is valid only if the intermediate carbenes are trapped at the same rate by benzophenone. It is possible that the intermediate carbene **14** (Scheme III) derived from the productive metathesis of **10** is complexed by the pendent olefin[28] and reacts more slowly than the carbene **13** (Scheme III) derived from loss of cyclopentene from **10**, which is not complexed (the *gem*-dimethyl group α to the carbon-carbon double bond of **13** would sterically inhibit formation of the carbene olefin complex). Because of the equilibrium between **13** and **14** (Scheme III), the trapping of **13** by benzophenone would decrease the quantity of **14** present (via **10**) and give the ratio of products observed. The ratio of the trapped products would not therefore be a true reflection of the ratio of k_{-2} to k_1.

Scheme III



Conclusion

Titanacyclobutanes ring-open metathesis polymerize cyclopentene, a relatively strain-free monomer as has been reported for other metathesis catalysts. The polymers produced have low polydispersities that approach living systems for low molecular weight samples. Kinetic analysis of the polymerization demonstrated that the rate of polymerization is first-order in monomer and implies that the intermediate carbenes are more rapidly trapped intramolecularly than intermolecularly. For the polymerization to proceed, this implies that productive metathical cleavage of the chain-carrying metallacycles is much more favorable than nonproductive cleavage.

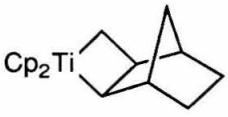
Block Copolymers Containing Monodispersed Segments Produced by Ring-Opening Metathesis Polymerization of Cyclic Olefins

The study and utilization of block copolymers (both diblock and triblock) have proceeded rapidly since their initial discovery in the early 1960s.[29] Key to development of this unique and highly useful class of copolymers is the concurrent discovery of living polymerization systems[30] that produce well-defined monodispersed segments of controlled molecular weight. Ring-opening metathesis polymerization (ROMP) is developing into a method of controlled polymerization comparable to known living anionic, cationic, and group-transfer systems. To date, the living polymerization of the cyclic olefin norbornene has been reported for titanium[3a], tantalum[31], and tungsten[32] metathesis systems. In further developing titanacyclobutanes as highly versatile metathesis polymerization catalysts, we are currently exploring their use for block copolymer synthesis. We have previously reported the blocking of norbornene with 3,4-diisopropylidene-cyclobutene to give a conducting polymer with mechanical properties that are superior to the parent cyclobutene polymer.[10a]

In this section the results of investigations into block copolymer synthesis via titanacyclobutanes are discussed.

Results and Discussion

Metathesis Polymerization by Titanacyclobutanes. In order to understand the use of titanacyclobutanes in metathesis polymerization, a brief review is needed. Gilliom and Grubbs[3a] have demonstrated that metallacycles **1** and **8** (derived from norbornene and 3,3-dimethylcyclopropene, respectively) upon reaction with norbornene (**15**) give monodispersed polynorbornene (**16**) (PDI $\simeq$ 1.1) with virtually no chain transfer or termination. The catalyst is active at higher temperatures ($\geq$ 65°C) and upon cooling to room temperature the living polymer is stable for several days. If stored at room temperature under an inert atmosphere, this system retains some activity even after several months. Rapid decomposition is observed, however, at the polymerization temperature in the absence of monomer.



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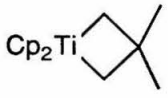

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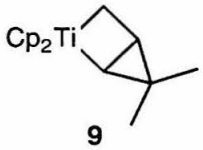

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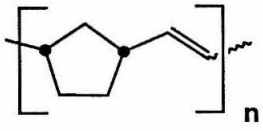
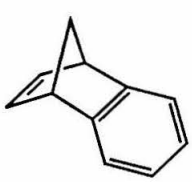


16

Initial Studies. In order to synthesize block copolymers, it was necessary to find cyclic olefin monomers other than norbornene that titanacyclobutanes would

metathesis polymerize to give living systems. Previous work has shown that cyclopentene, although polymerized by **8**, is not a true living system as broader molecular weight dispersities are observed as the polymerization proceeds.[33] The polymerization of benzonorbornadiene (**17**) by WCl_6/Ph_4Sn has been reported to give polybenzonorbornadiene (**18**).[34] The attempted polymerization of 11 equivalents of **17** by the metallacycle **6**[35] was complicated by the onset of precipitation of the resulting polymer after 5-6 equivalents of monomer had reacted (determined by capillary VPC). Precipitation of the polymer from the reaction mixture (PhMe, 70°C) completely stopped the polymerization after 9 equivalents of **17** were consumed. The isolated sample of polybenzonorbornadiene (polymer **19**, Table VI) was only sparingly soluble in organic solvents.



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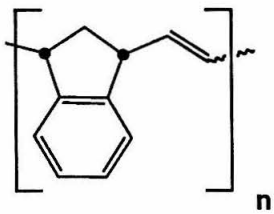


18

A portion of the living polymer was treated with 60 equivalents of norbornene (**15**) at 70°C to give the diblock polymer **20**[36] (Table VI). During the polymerization, the living polymer redissolved and the rate of polymerization increased. GPC analysis of **20** indicated a large reduction in the polydispersity from the original polymer **19** (Table VI). In an attempt to solubilize the polybenzonorbornadiene produced by **6**, a sample of polynorbornene (polymer **21**, Table VI) was synthesized first and 13 equivalents of benzonorbornadiene (**17**) added. Again, the polymerization was stopped by the insolubility of the resulting diblock polymer **22** (Table VI). The experiment was repeated with the random copolymerization of norbornene and benzonorbornadiene utilized in hopes of solubilizing the second block.

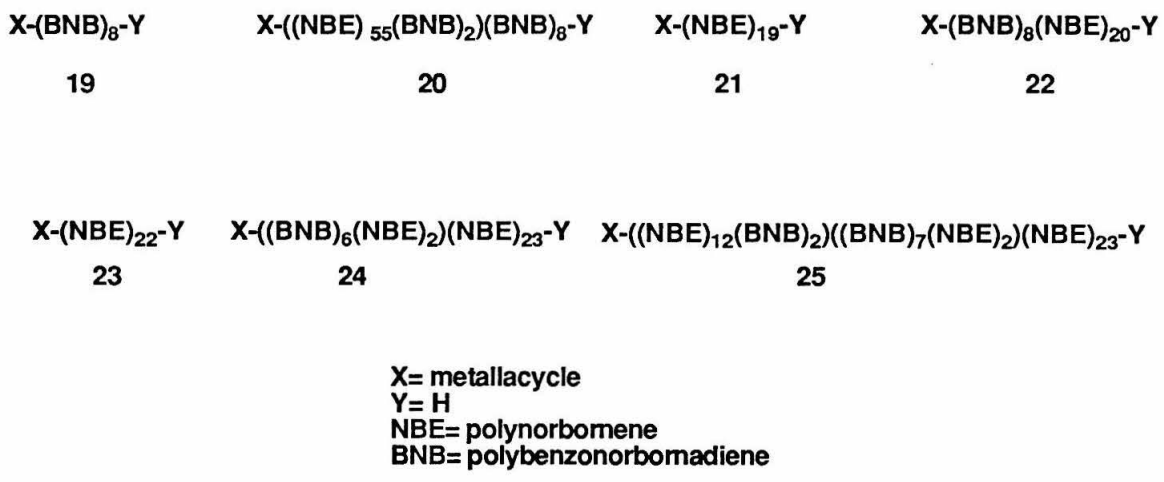


Table VI. Block Copolymers of Polynorbornene and Polybenzonorbornadiene Produced by **6**[a]

polymer[b]	isolated yield (%)	theoretical MW	M_n[c]	M_w[c]	PDI[d]
19	84	1330	1550	2810	1.81
20	91	6890	26700	32800	1.23
21	78	2070	6900	12300	1.78
22	77	3350	5250	9420	1.60
23	98	2360	5310	10600	2.30
24	99	2360	6430	14100	2.19
25	96	4950	16200	29100	1.80

a. See Experimental Procedure for details of synthesis.

b. The number of monomers in each block was estimated by assuming 100% active catalyst and dividing the equivalents of monomer consumed (capillary VPC) by the equivalents of catalyst present.

c. Determined by gel permeation chromatography vs. polystyrene standards. The polymers **19** and **20** were analyzed a few days after synthesis. The rest of the polymers had decomposed over several months (see text) before analysis.

d. Polydispersity index.

The resulting diblock **24** and triblock **25** (Table VI) still had only limited solubilities that hampered the polymerizations. The consumption of monomers throughout the polymerizations and high yields of collected polymer coupled with the observation of increasing molecular weights (GPC) indicate that the diblock and triblock polymers were successfully synthesized. The living polymers described above slowly decomposed over several months at ambient temperature in the dry box to give mostly insoluble yellow solids. GPC analysis (Table VI) of the CH_2Cl_2-soluble portion indicated, by broader molecular weight distributions, that the materials had become crosslinked, possibly due to titanium-carbon bond homolysis of the metallacycle end groups followed by radical-initiated crosslinking.

Further Studies. Several steps were taken to improve the synthesis of the block copolymers. Removal of the metallacycle end group, which was deemed necessary in order to stabilize the polymer produced, was accomplished by end capping of the living block copolymers with acetone.[37] The metallacyle **8**, which initiates polymerization without an induction period[3a], was used instead of **6**. Additionally, the solvent used in the polymerizations was thoroughly deoxygenated and dried by stirring over "titanocene" before use.[38] Under these modified conditions block copolymers were again synthesized. The results for polymers **26-32** are presented in Table VII. The isolated polymers were white amorphous solids, which did not decompose over several months in the dry box. Samples exposed to ambient atmosphere, however, turned yellow and became brittle over several weeks.[39]

Further analysis of the polymers **26, 27,** and **28** (a series of monoblock, diblock, and triblock copolymers) was performed. The rates of polymerization of norbornene in the first and third blocks (**26** and **28**, respectively) were identical, indicating no catalyst decomposition throughout the polymerization. The correct elemental analyses of the three polymers confirmed the purity of the samples isolated after end capping. ^{1}H NMR analysis gave the ratio of norbornene and benzonorbornadiene

X-$(NBE)_{46}$-Y
26

X-$((BNB)_5(NBE)_3)(NBE)_{46}$-Y
27

X-$(NBE)_{44}((BNB)_5(NBE)_3)(NBE)_{46}$-Y
28

X-$(NBE)_{66}$-Y
29

X-$((NBE)_2(BNB)_{10})(NBE)_{66}$-Y
30

X-$(NBE)_{46}$-Y
31

X-$(NBE)_{51}(NBE)_{46}$-Y
32

X= -CH=C$(Me)_2$
Y= -C$(Me)_2$CH=CH_2
NBE= polynorbornene
BNB= polybenzonorbornadiene

Table VII. Block Copolymers of Polynorbornene and Polybenzonorbornadiene Produced By **8**[a]

polymer[b]	isolated yield(%)	theoretical MW	M_n[c]	M_w[c]	PDI[d]
26	42	4460	11300	12100	1.07
27	71	5450	14000	15400	1.10
28	63	9730	27600	33300	1.21
29	61	6340	14900	15900	1.07
30	52	7950	20100	24600	1.22
31	74	4460	10300	11000	1.07
32	62	9260	23500	24700	1.05

a. See Experimental Procedure for details of synthesis.

b. The number of monomers in each block was estimated by assuming 100% active catalyst and dividing the equivalents of monomer consumed (capillary VPC) by the equivalents of catalyst present.

c. Determined by gel permeation chromatography vs. polystyrene standards.

d. Polydispersity index.

Table VIII. Ratio of Polynorbornene and Polybenzonorbornadiene in Polymers **26**, **27**, and **28**

polymer	polynorbornene/polybenzonorbornadiene	
	by ^{1}H NMR[a]	by VPC[b]
26	-	-
27	11.4	9.8
28	18.1	19.6

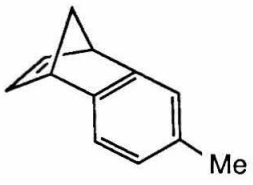
a. Determined by integration of the allylic protons of polynorbornene (**16**) vs. the allylic protons of polybenzonorbornadiene (**18**). The methylene protons of **18** overlap the allylic protons of **16** and this was taken into account.

b. Determined by consumption of **15** and **17** during the polymerization (see Experimental Section).

incorporated into each polymer. Comparison of these values with those calculated from the amount of the monomer consumed during the polymerization (by capillary VPC) is presented in Table VIII. The good agreement of these ratios indicates that the assignment of the number of monomer units in each block from consumption of monomer by VPC is a valid approximation.

In testing the improved procedures polynorbornene was blocked with itself (polymers **31** and **32**). Analysis by GPC showed that the polydispersity remained low and the theoretical and experimental molecular weights maintained a constant ratio. The insolubility of polybenzonorbornadiene still presented a problem, though, and only short blocks of this polymer could be added before polymerization stopped because of precipitation of the living polymer system from the reaction mixture.

In hopes of producing a more soluble polymer, 6-methylbenzonorbornadiene



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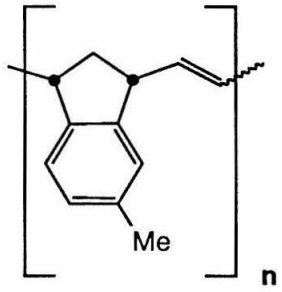

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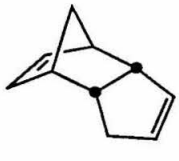
(**33**) was polymerized by the metallacycle **8**, but the polymer produced (**34**) still became insoluble after 7-9 equivalents of monomer were consumed. Two more solutions to the problem were tested. First, one possibility of insoluble polymer formation might be a radical-induced crosslinking (initiated during the polymerization at 70°C) due to trace amounts of impurities present in the monomer **17** that were not removed by distillation from CaH_2. As a further purification step, therefore, the monomers employed were filtered through alumina several times before further treatment as before. The other solution tested was to examine the polymerization of monomers besides **17** and **33**. Previous work has shown that *endo*-dicyclopentadiene (**35**) can be polymerized by the metallacycles **8** or **9** to give low molecular weight samples of the ring-opened polymer **36**[19a], and therefore this monomer was employed in the next set of experiments. Additionally, *exo*-dicyclopentadiene (**37**) was used in hopes of giving the corresponding polymer **38**.



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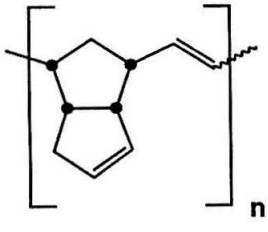

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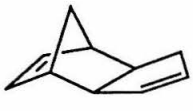

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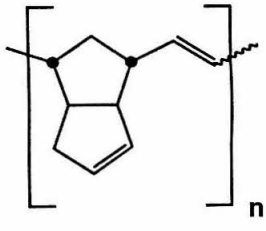

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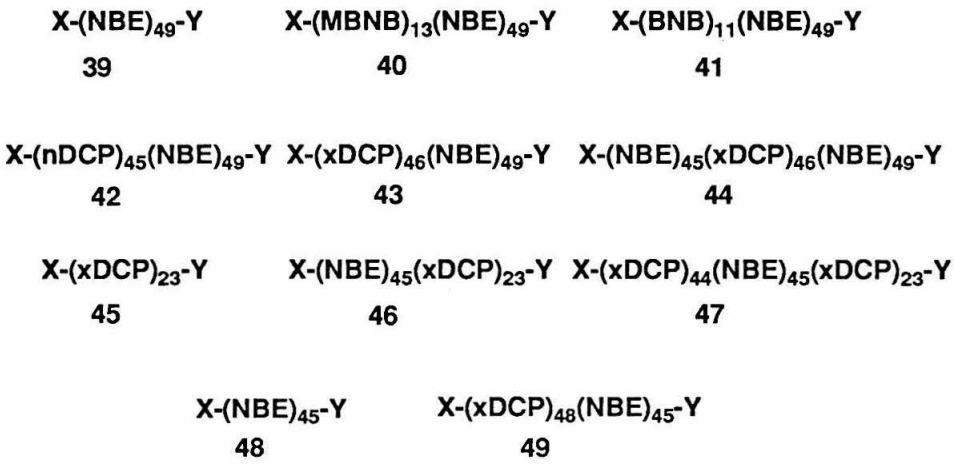


X= $-CH=C(Me)_2$
Y= $-C(Me)_2CH=CH_2$
NBE= polynorbornene
BNB= polybenzonorbornadiene
MBNB= poly(6-methylbenzonorbornadiene)
xDCP= poly(exo-dicyclopentadiene)
nDCP= poly(endo-dicyclopentadiene)

Table IX. Block Copolymers of Polynorbornene, Polybenzonorbornadiene, Poly(6-methylbenzonorbornadiene), Poly(*exo*-dicyclopentadiene), and Poly(*endo*-dicyclopentadiene) Produced By **8**[a]

polymer[b]	isolated yield (%)	theoretical MW	M_n[c]	M_w[c]	PDI[d]
39	75	4740	10200	12100	1.19
40	58	6770	18100	20800	1.15
41	58	6300	15500[e]	17200[e]	1.11[e]
42	90	10700	23900	27400	1.15
43	66	10820	27700	32000	1.16
44	63	15100	46200	58800	1.27
45	96	3200	6840	8290	1.21
46	68	7400	23900	25900	1.08
47	85	13200	43500	49500	1.14
48	78	4400	10500	11200	1.07
49	47	10700	28100	32100	1.14

a. See Experimental Procedure for details of synthesis.

b. The number of monomers in each block was estimated by assuming 100% active catalyst and dividing the equivalents of monomer consumed (capillary GC) by the equivalents of catalyst present.

c. Determined by gel permeation chromatography vs. polystyrene standards.

d. Polydispersity index.

e. A small amount of high molecular weight polymer ($M_n \approx 400{,}000$) was also present and was not used to calculate the molecular weight data.

Once again the synthesis of block copolymers was attempted and the results for the isolated polymers **39-49** are displayed in Table IX. Polymers **40-44** were all prepared from a sample of polynorbornene (**39**), which was isolated as a living polymer and stored in solution at ambient temperature overnight. The polydispersity of **39** (Table IX) indicated that partial decomposition occurred, presumably induced by metallacycle decomposition[40]; however, the resulting block copolymers produced from **39** were very close to mono-disperse. The block copolymerizations of norbornene and benzonorbornadiene were still complicated by the insolubility of the resulting block copolymers; therefore, this insolubility is most likely a property of the polymer and not a result of decomposition. The polymers produced from *endo* and *exo* dicyclopentadiene were, however, completely soluble, thus permitting the synthesis of blocks containing up to 46 monomer units. ^{1}H NMR was employed as before to determine the ratio of the different monomers incorporated into the block copolymers of polynorbornene and poly(*exo*-dicyclopentadiene) (Table X). Overlapping of the signals of the two respective blocks complicated the analysis and an algebraic approximation was used (see Experimental Section). The values are once again in good agreement with the VPC-derived numbers.

The GPC traces of these block copolymers revealed that more than one molecular weight distribution was present. A second smaller peak corresponding to twice the molecular weight of the major distribution usually appeared. The formation of this "dimer" would have to occur at either the start or the end of the polymerization. Constant "dimer" formation throughout the polymerization would broaden the entire molecular weight range, not produce separate ranges. Trace impurities present in either the monomer or catalyst were considered good candidates for cause of the formation of this "dimer." The monomer **37** was therefore further purified by stirring over sodium at 90°C for 12 hours before distillation. The polymerization of **37** by **9** was repeated and aliquots were removed at set intervals and analyzed

Table X. Ratio of Polynorbornene to Poly(*exo*-dicyclopentadiene) in Polymers **43**, **44**, **46**, **47**, and **49**

polymer	polynorbornene/poly*exo*-dicyclopentadiene	
	by NMR[a]	by VPC[b]
43	1.2	1.1
44	2.0	2.0
46	2.4	2.0
47	0.79	0.67
49	0.94	0.96

a. Determined by integration of the aliphatic and olefinic regions of the ^{1}H NMR spectrum (see Experimental Section).

b. Determined by consumption of **15** and **37** during the polymerization.

by GPC. The results are presented in Table XI. The GPC traces indicated much less "dimer" present ($\leq$5%) and the lower polydisperties reflect this fact. Further purification of the catalyst and/or monomer or addition of a radical inhibitor may totally eliminate this problem. One important note in the polymerization of **37** is that a plot of percent conversion vs. molecular weight (Figure 3) gives a straight line with an intercept of zero, indicating that the polymerization is a living process for this monomer.[30]

Rates of Polymerization of Different Monomers. Previous work has shown that the rate of polymerization of norbornene by titanacyclobutanes is independent of monomer concentration and is first order in catalyst concentration.[3a] Although no quantitative kinetic analysis was undertaken in the work reported herein, qualitatively, the polymerizations of benzonorbornadiene, 6-methylbenzonorborna-

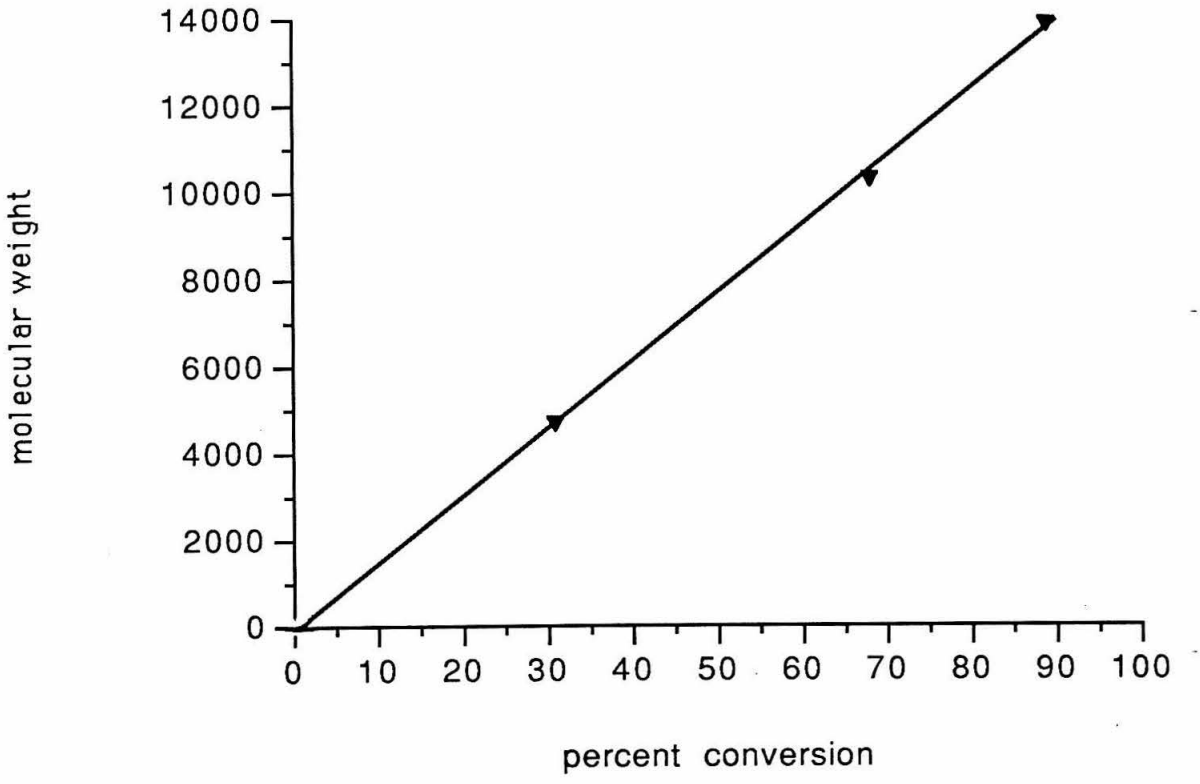


Figure 3. A plot of molecular weight vs. percent conversion for the polymerization of *exo*-dicyclopentadiene (**37**). The line was derived from a least-squares fit of the data (correlation= 0.999).

Table XI. The Living Polymerization of *Exo*-dicyclopentadiene(**37**)[a]

equiv of **37** consumed[b]	% conversion[c]	theoretical MW	M_n[d]	M_w[d]	PDI[e]
16	31	2240	4730	5190	1.10
34	68	4620	10300	11500	1.12
44	89	5940	13800	15200	1.10

a. See Experimental Section for procedure.

b. Determined by capillary VPC vs. an internal standard.

c. Based on 50 equivalents of monomer added.

d. Determined by gel permeation chromatography vs. polystyrene standards.

e. Polydispersity index.

diene, and *exo* and *endo* dicyclopentadiene were similar to above. The rates of polymerization were constant during the synthesis of each block and changed the appropriate amount upon change in the catalyst concentration. Benzonorbornadiene and 6-methylbenzonorbornadiene polymerized at slightly faster rates than norbornene in their respective homopolymerizations and at a comparable rate to norbornene during copolymerizations with norbornene. *Exo*-dicyclopentadiene (**37**) polymerized 5-6 times slower than norbornene (homopolymerizations), and *endo*-dicyclopentadiene (**35**) 15-20 times slower. The copolymerization of **35** and **37** was indirectly studied in each polymerization of **37** as this monomer contained 95% **37** and 5% **35** (19:1 ratio). Typically, at the end of the polymerization ($\leq$5% of monomer remaining) the ratio of **37** to **35** was 1.4 to 1 implying that **37** polymerizes 14 times faster than **35** in the copolymerization of the two monomers.

The rates of the homopolymerizations of norbornene derivatives by titanacy-

clobutanes are determined by the stability of the chain-carrying metallacycles whose decomposition to the carbene controls the rate of polymerization.[3a] The data presented above indicate that the metallacycles derived from the respective monomers are comparative in stability as evidenced by similar rates. The rates observed in the copolymerizations can be rationalized by the relative trapping abilities by the different monomers of the intermediate titanium carbenes.

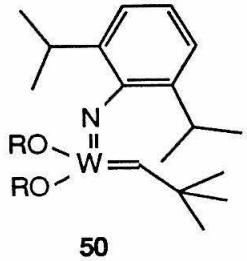
Morphology of the Block Copolymers. The physical properties of block copolymers lead to desirable characteristics (i.e., elasticity, toughness, processibility) not attainable with the respective homopolymers or their physical blends.[29] The block copolymers synthesized in this work appear to exhibit these modified properties. Polynorbornene samples are soft plastics and melt under 115°C. Polybenzonorbornadiene, poly(6-methylbenzonorbornadiene), and poly(*exo*-dicyclopentadiene) were isolated as powders, which remained solid at 115°C. The block copolymers obtained had characteristics intermediate in nature. Further studies are needed in order to quantitatively describe the properties of these polymers.

Conclusion

The synthesis of block copolymers by metathesis polymerization of cyclic olefins with titanacyclobutanes has been achieved. The use of blocks that remain in solution throughout the polymerization permits the synthesis of blocks containing 50 monomer units. Impurities present in the monomer and/or catalyst, which cause formation of "dimers," can be removed to give block copolymers containing essentially monodisperse segments. Finally, the block copolymers produced have different physical properties than the respective homopolymers.

Ring-Opening Metathesis Polymerization of Norbornene by W(CHtBu)(NAr)[(OCMe(CF$_3$)$_2$]$_2$ (Ar= 2,6-diisopropylphenyl)[41]

Recently, tungsten metathesis catalysts have been reported that are much more active than titanium catalysts and show a greater tolerance for polar functional groups.[3e,f,7] One of these has been shown to produce a growing alkylidene in the polymerization of norbornene.[7b] Since a variety of ligand combinations are now available, it should be possible to fine-tune catalyst activity precisely to the point required for controlled polymer synthesis. The complex W(CH*t*Bu)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (Ar= 2,6-diisopropylphenyl) (**50a**)[7a] will react rapidly with ordinary olefins to give isolable tungstenacyclobutane complexes or alkylidene complexes (depending upon the degree of substitution of the tungstenacyclobutane ring), and will metathesize an internal olefin such as *cis*-2-pentene at a rate whose lower limit is 1000 turnovers per minute at 25°C. One important advantage of this catalyst is that no cocatalyst is needed to activate it as is the case for all other tungsten metathesis catalysts reported to date.[2] In this section the activity of this catalyst toward polymerization of norbornene is examined.



50
a R= OCMe(CF$_3$)$_2$
b R= Ot-Bu

Results and Discussion

In an initial experiment W(CH*t*-Bu)(NAr)[OCMe$(CF_3)_2$]$_2$ (Ar= 2,6-diisopropyl phenyl) (**50a**) was allowed to react with 288 equivalents of norbornene in toluene at –40°C to –20°C over several hours. Aliquots were withdrawn at intervals and the isolated polymers analyzed by GPC (vs. polystyrene standards). *All* of the samples had the same high molecular weight values ($M_n \approx 400{,}000$; $M_w \approx 650{,}000$; n = 1.6), indicating slow initiation followed by very rapid propagation and finally termination.[42] Analysis by ^{13}C NMR indicated essentially 100% *cis* double bonds.[43]

The polymerization was investigated further in a series of sealed NMR tube experiments in d_8-toluene. The initial ^1H NMR (–80°C) showed no catalysts or catalyst-derived signals present (only monomer and polymer were observed). The polymerizations were followed at –60°C and a constant rate of polymer formation (zero order in monomer) seen.[44] As the reaction proceeded, signals attributable to decomposed catalyst slowly increased and reached maximum intensity at 100% completion.[45] Upon warming to room temperature, the expected doublet signal for the alkylidene proton of the growing chain appeared at 9.24 ppm (J_{HH}=7.3 Hz). However, the intensity was only 5-10% of that expected if all the initial alkylidene was transformed into the propagating alkylidene. An approximately equal amount of a signal due to the starting catalyst reappeared, but most of the initial tungsten complex apparently decomposed in an as yet undefined manner. At 25°C the all *cis* polymer isomerized to predominantly *trans* over several days. GPC analyses of the polymers formed at low temperature gave comparable values to the initial polymerization (*vide supra*). Samples allowed to isomerize to predominantly *trans* polymer showed the expected increase in polydispersity. Finally, in a polymerization (74 equivalents of norbornene) initiated at –80°C , but then rapidly warmed to room temperature, much lower molecular weights (M_n= 9,400; M_w= 21,000) were obtained, although the polydispersity remained high.

Further work has shown that the analog **50b** produces monodisperse polynorbornene containing 10-20% of a higher molecular weight fraction.[32a] This fraction was postulated to be formed by a trace of an extremely active, as yet unidentified, tungsten-carbene species present during the polymerization. One possibility was that traces of water might have produced this unknown, very active catalyst. To resolve this question, the behavior of the alkylidene **50a** in the presence of small amounts of H_2O was examined.

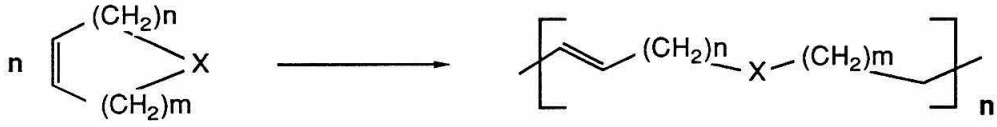
In three separate experiments identical amounts of the alkylidene **50a** were treated with approximately 100 equivalents of norbornene. To the second experiment was added 0.01 equivalent of H_2O/W and to the third, 0.10 equivalent. After the polymerization, the resulting isolated polymers were analyzed by GPC. In the first experiment with no added water the predominant molecular weight range was at ~90,000, with a much smaller range at ~7,000. Analysis of the second experiment showed a decrease in the amount of higher molecular weight fraction and an increase in the lower molecular weight range. The GPC trace of the polymer from the third experiment indicated approximately equal quantities of the two fractions. These results imply that added H_2O decreases the molecular weight of the resulting polymer and therefore it is not the cause of the higher molecular weight fractions observed with the alkylidene **50b**.

Conclusion

The ring-opening metathesis polymerization of norbornene by the tungsten alkylidene W(CH*t*Bu)(NAr)[OCMe(CF_3)$_2$]$_2$ (Ar= diisopropylphenyl) is not a living polymerization system and gives high molecular weight polynorbornene at low conversions. Decomposition of the catalyst during the polymerization gives an as yet unidentified species. The addition of small amounts of H_2O to the active catalyst produces lower molecular weight polymers.

Ring-Opening Metathesis Polymerization of N-Methyl-7-Azabenzonorbornadiene

The metathesis polymerization of heterocyclic olefins is virtually unknown[2] (Eq. 15). Recently, it has been shown that 7-oxanorbornene derivatives upon polymerization by several olefin metathesis catalysts yield the corresponding ring-opened polymers.[12,19a] Polymerization of the analogous 7-azanorbornenes has not been reported to date. In general, introduction of a Lewis base into the ring of the monomer would be expected to inactivate most olefin metathesis catalysts employed because of the Lewis acidic nature of the monomer..

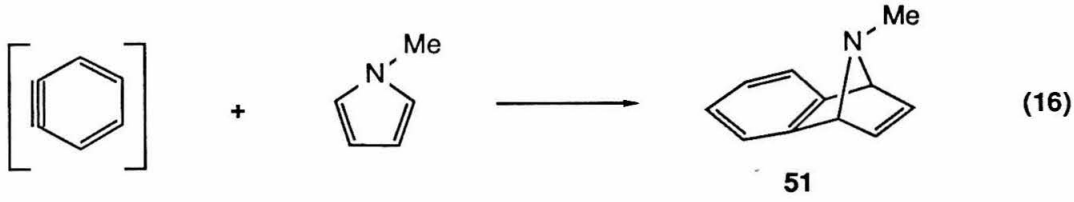


(15)

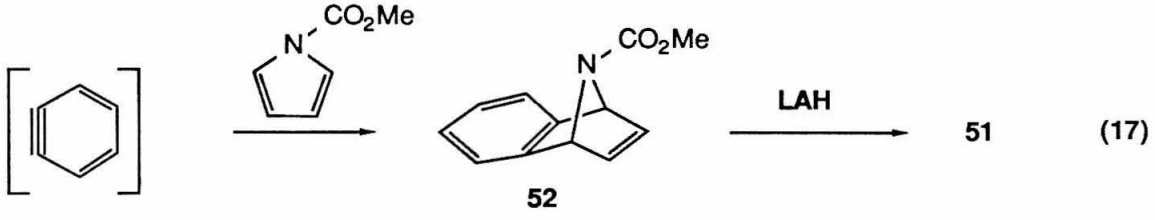
In this section the successful metathesis polymerization of *N*-methyl-7-azabenzonorbornadiene and further transformation into a conducting polymer are discussed.

Results and Discussion

Synthesis of Monomers. The synthesis of N-methyl-7-azabenzonorbornadiene (**51**) has been reported by several different researchers.[46,47,48] Attempts to synthesize **51** by the method of Wittig and Behnisch[46] (eq 16) gave a complex mixture of products (^{1}H NMR and TLC) from which the isolation of **51** was not achieved, either by distillation or chromatography. Vernon and coworkers[47] reported a two-step procedure for the synthesis of **51**, which is given in Eq. 17. The intermediate **52** has also been reported by other workers[49], and their procedure (with improvements in the isolation procedure) was used to give **52** in a 50% isolated yield.

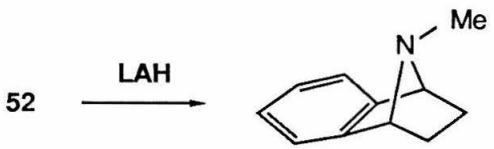


51 (16)



52 **51** (17)

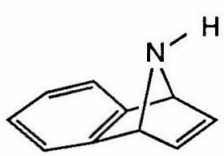
Attempts to reduce the carbomethoxy group of **52** with lithium aluminum hydride (LAH) to give **51** according to the published procedure[47] were unsuccessful and instead gave the corresponding benzonorbornene **53** (Eq. 18). Use of less than



53 (18)

one equivalent of LAH yielded a mixture of **51** and **53**. This surprising result has already been reported by Marchand and Allen.[50]

Hydrolysis of the carbomethoxy group of **52** (KOH/H_2O) gave the free amine **54**.[51] Yoskekawa and coworkers[48] reported that the "methylation" of **54** (no mention of procedure) gives the desired methyl amine **51**. Attempted reaction of **54** with MeI/K_2CO_3 in CH_2Cl_2 gave only α-napthyl methylamine (**55**) (^1H NMR). Treatment of **54** with $NaCNBH_3/CH_2{=}O$[52] was successful and gave **51** in a 45% yield after distillation.



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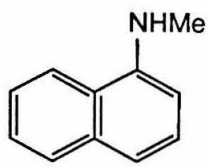
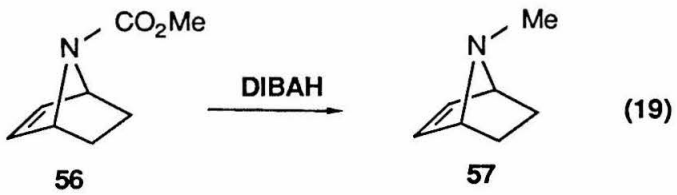


55

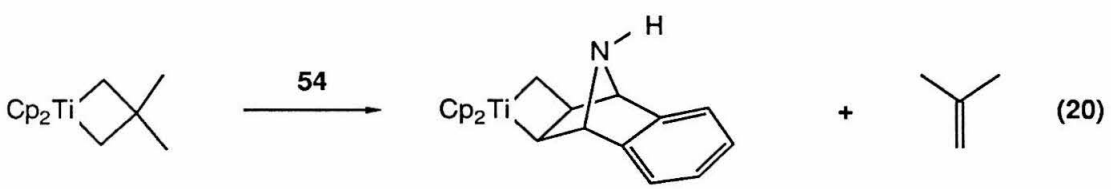
It was decided to shorten the synthesis of **51** and therefore the reduction of **52** was reinvestigated. Marchand and Allen reported that the reduction of the azanorbornene **56** with diisobutylaluminum hydride (DIBAL-H) gives N-methyl-7-azanorbornene **57** (Eq. 19).[53] The reduction of **52** was attempted by this method and the desired product **51** obtained in a 73% yield after distillation.



56 57 (19)

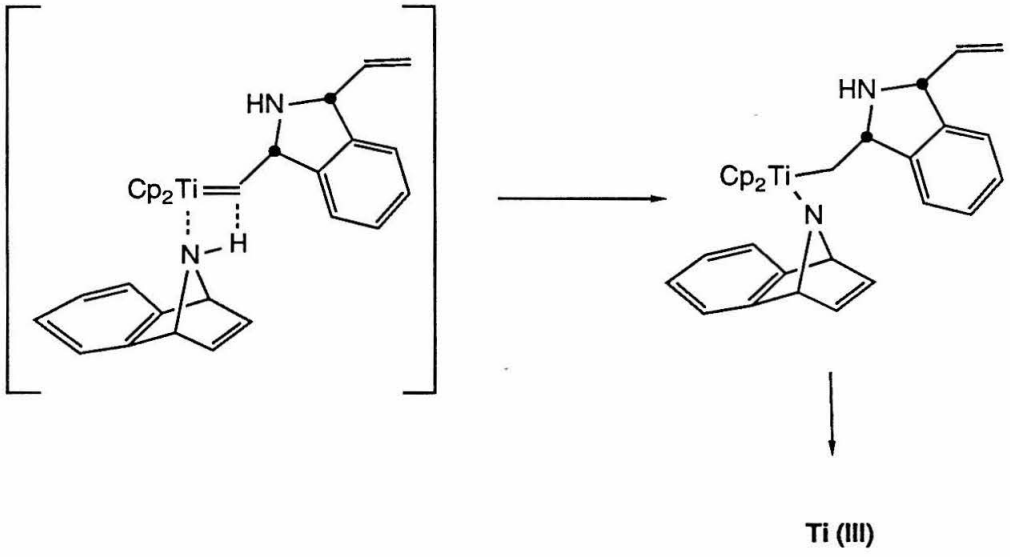
In summary, N-methyl-7-azabenzonorbornadiene (**51**) and 7-azabenzonorbornadiene (**54**) were synthesized from the same intermediate, N-carbomethoxy-7-azabenzonorbornadiene (**52**). The literature procedures for the synthesis of these compounds were vague and irreproducible. The well-defined procedures described in the Experimental Section now make possible the rapid synthesis of these monomers in multigram quantities.

Synthesis of Polymers. Reaction of 7-azabenzonorbornadiene (**54**) with the titanacyclobutane **6**[6c] (derived from "$Cp_2Ti{=}CH_2$" and isobutylene) cleanly gave the new metallacycle **58** (Eq. 20) (^{1}H NMR). Addition of 6-12 equivalents of the monomer **54** to **58** and heating to initiate the polymerization resulted in decomposition of **58** to give an uncharacterized Ti (III) species. It is possible that this result occurred by reaction of the carbene derived from the azametallacyle **58** with the N-H bond of the monomer, followed by decomposition of this adduct at the polymerization temperature (Scheme IV).

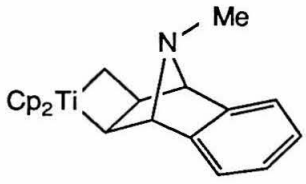


6 58 (20)

Scheme IV



The monomer **51** (a tertiary amine without a N-H bond) was reacted with **6** to give the new metallacycle **59**. Reaction of **59** with 10 equivalents of **51** in an NMR tube reaction led to catalyst decomposition as before, but new signals attributable to the ring-opened polymer **60** were observed (^{1}H NMR). The experiment was repeated using the metallacycle **8**[6b] (derived from 3,3-dimethylcyclopropene) and Tebbe's reagant (**61**)[54] as catalysts and similar results were obtained. In all of the above experiments with **51**, approximately 4-6 equivalents of monomer were consumed before the polymerization stopped. On a preparative scale 6.7 equivalents of **51** were polymerized by the metallacycle **6** and the resulting polymer **60** isolated in a 91% yield after chromatography. GPC analysis (vs. polystyrene standards) gave M_n= 690 and M_w= 922 (polydispersity index= 1.33), indicating that the polymerization was close to a living system. Unfortunately, an absolute molecular weight was not obtained, although the low molecular weights from the GPC indicate that the average chain contains only a few monomer units.



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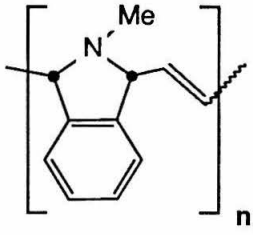

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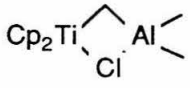
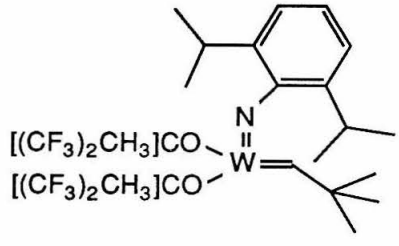
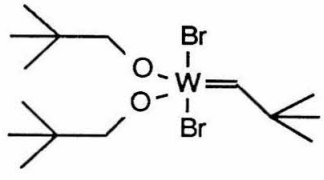


61

In an attempt to produce longer polymer chains, other metathesis catalysts were tried. The two-component metathesis system composed of the tungsten catalyst **62**[7b] and $AlBr_3$ instantly decomposed upon addition of the amine **51** (^{1}H NMR). The experiment was repeated in the absence of $AlBr_3$ and the same result obtained. Presumably the basic amine instantly forms an acid-base complex with **62**, which then rapidly decomposes.



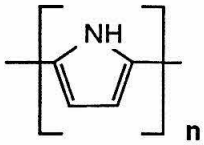
50a



62

The tungsten alkylidene **50a**[7a,32] was treated with 20 equivalents of **51** to give the polymer **60** with complete consumption of monomer observed (^{1}H NMR). On a preparative scale 50 equivalents of **51** were polymerized by **50a** to give an 83% isolated yield of **60**. Apparently, **50a** is not as sensitive to the amine functionality as is **62**, and the polymerization proceeds. ^{1}H NMR integration of the *t*-butyl end group of the polymer (derived from **50a**) versus the allylic region of the polymer gave 47 monomers per chain, indicating good catalyst stability during the polymerization.

The isolated polymer **60** from the above methods was a light brown solid (lighter in color upon further purification), which was slightly soluble in aromatic solvents and soluble in chloroform and tetrahydrofuran (THF). The polymer also formed films upon evaporation of the solvent. The polymer was further characterized by ^{13}C NMR and IR.



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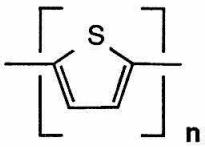

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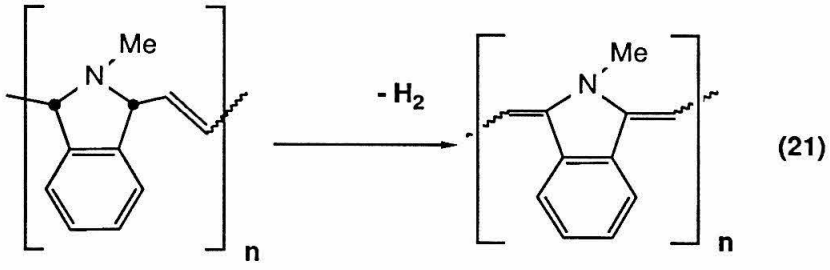

60 65 (21)

Synthesis of a Conducting Polymer. Research into the area of conducting polymers has increased tremendously over the last few years.[55] Previous work has shown that conjugated polymers such as polypyrrole (**63**) and polythiophene (**64**), when oxidized or reduced by chemical dopants, give materials with measurable conductivities.[56] Dehydrogenation of polymer **60** would yield a similar polymer (**65**) containing a π-conjugated system of electrons along the chain (Eq. 21). In an attempt to dehydrogenate polymer **60**, samples were dissolved in THF and treated with one equivalent of 2,3-dichloro-5,6-dicyanoquinone (DDQ) at room temperature, instantaneously giving a fine black precipitate. Soxhlet extraction with ethyl acetate

yielded a fine black solid free of DDQ and $DDQH_2$ (TLC, NMR). The solid was insoluble in organic solvents as well as in aqueous acids. A sample diluted with calcium carbonate was analyzed by solid state ^{13}C NMR (CP-MAS) and gave the appropriate spectra for the polymer **65**, indicating that the reaction was successful.

Samples of **65** were exposed to iodine vapor and then evacuated under high vacuum. The increase in weight of these doped samples indicated that approximately one equivalent of iodine per monomer unit polymer had been incorporated. The conductivity of pressed pellets of these samples was $10^{-3}$to 10^{-4} Scm^{-1}. The conductivities of samples before doping were $10^{-4}$to 10^{-5} Scm^{-1}. This surprising result may arise from charge defects introduced by hydride abstraction by the DDQ to give cations on the polymer backbone (with $DDQH^-$ counterions), resulting in the observed conductivity.

Conclusion

The successful olefin metathesis polymerization of cyclic olefins containing a nitrogen in the ring has been achieved. The polymer formed can be dehydrogenated to give a new polymer with a conjugated π-electron system. Doping of this conjugated polymer gives a material with conductivites of $10^{-3}$to 10^{-4} Scm^{-1}.

Experimental Section

General Procedures. All work involving air- and/or moisture-sensitive compounds was performed using standard high-vacuum or Schlenk techniques under argon purified by passage through columns of BASF RS-11 (Chemalog) and Linde 4Å molecular sieves and a Vacuum Atmospheres drybox under nitrogen. ^{1}H, ^{2}H, and ^{13}C NMR spectra were recorded on a Varian Associates EM-390 (90 MHz ^{1}H), a JEOL FX-90Q (89.6 MHz ^{1}H, 22.53 MHz ^{13}C), and a JEOL GX-400 (399.65 MHz ^{1}H, 61.35 MHz ^{2}H, 100.67 MHz ^{13}C). Chemical shifts are referenced to residual protiosolvents. Solid-state NMR spectra were obtained on a home-built spectrometer operating at a carbon frequency of 50.36 MHz with a spinning rate of 3-5 KHz. Data manipulation was performed on a Nicolet computer using left-shifts and nonlinear base-line fits to eliminate the rolling base line. Chemical shifts were referred to an external standard of adamantane. Analytical gas chromatographic analyses (VPC) were performed on a Shimadzu GC-Mini 2 flame ionization instrument modified for capillary use and equipped with a Hewlett-Packard Model 339A integrator (column: 0.24 mm × 15 m DBI). Thin layer chromatography (TLC) was performed on precoated TLC plates (silica gel 60 F-254, EM Reagants). Flash chromatography was performed by the procedure of Still et al.[57], using silica gel 60 (230-400 mesh ATM, EM Reagants). High-vacuum evacuation of samples were performed at 10^{-5} torr. Elemental analysis was performed by L. Henling at the analytical facilities of the California Institute of Technology.

Gel permeation chromatographic (GPC) analyses utilized Shodex KF-803, 804, 805, and 805.5 columns, a Spectroflow 757 absorbance detector (λ= 254 nm), and a Knauer differential refractometer. GPC analyses were performed on 0.20 or 0.40 % w/v solutions of polymer in CH_2Cl_2. Typically, an injection volume of 0.100 mL and a flow rate of 1.5 mL/min were used. Calibration was based on narrow dispersity polystyrene standards (Polysciences) ranging from MW= 3550 to

600,000. The molecular weight averages and distribution were calculated by standard procedures[58] from the refractive index trace and were not corrected for peak broadening. UV integration was performed by weighing photocopies of the traces recorded on an Omniscribe recorder (Houston Instruments) and averaging five copies per trace. Conductivities were measured by the DC four-point method[59], using a Signatone four-point probe, Model S-301-5. Oil bath temperatures for all polymerizations were maintained by use of an I^2R Therm-O-Watch, Model L6-1000SS. Polymerizations were carried out in heavy-walled glass tubes equipped with a stir bar, female 14/20 joint and a Teflon valve (see Figure 4)

Materials. Metallacycle **1**[3a], capped monomer **2**[3a], and the metallacycles **6**[6c]and and **8**[3a] were prepared as previously described. The cyclic olefin, 3,3-dimethylcyclopropene (used to synthesize **8**), was kindly provided by S. C. Virgil and the tungsten alkylidene **50a**[7a] supplied by R. R. Schrock. Tebbe's reagant (**61**) was prepared as previously described[59] and the tungsten alkylidene **62**[7b] was kindly provided by T. M. Swager.

The monomers used in the polymerizations were prepared and purified as follows. Norbornene was purchased from Aldrich, refluxed over sodium and distilled prior to use. The norbornene-2,3-d_2[61] employed was kindly provided by Dr. J. K. Stille and purified as above. Cyclopentene was purchased from Aldrich, filtered through alumina (neutral grade, EM Sciences), dried over CaH_2, and distilled prior to use. Benzonorbornadiene (**17**) and 6-methylbenzonorbornadiene (**33**) were prepared by the method of Wittig and Knauss[62] and originally purified by vacuum distillation from CaH_2. In later experiments (see synthesis of polymers **39-49**), the monomers were filtered through alumina, stirred over CaH_2 overnight, and then vacuum-distilled from CaH_2. Pure *endo*-dicyclopentadiene **35** was synthesized by allowing freshly prepared cyclopentadiene to dimerize at 0°C over a two-month period (82% conversion)[63], removing the unreacted cyclopentadiene by rotary evaporation, and vacuum distillation of the product from CaH_2. In later experiments

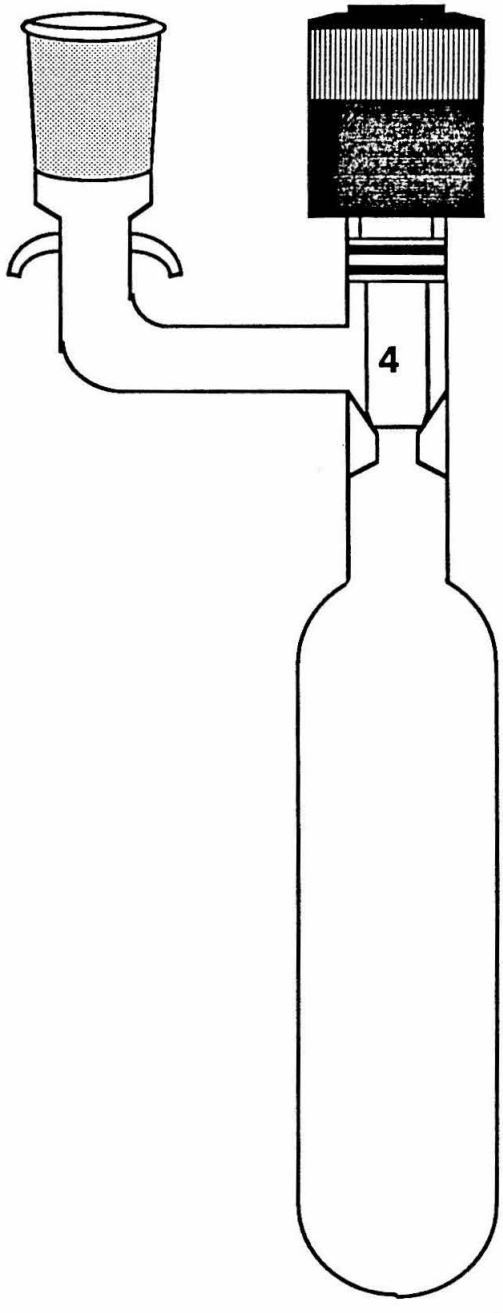

Figure 4. Design of heavy-walled glass tubes used for polymerizations (actual size).

it was further purified as above. *Exo*-dicyclopentadiene (**37**) (95% *exo*, 5% *endo*) was purchased from Wiley Organics and purified as above. In the last set of experiments (see text) the monomer was stirred over sodium at 90°C overnight and then vacuum-distilled from sodium. N-methyl-7-azabenzonorbornadiene (**51**) and 7-azabenzonorbornadiene (**54**) were prepared and purified as described in the experimental procedures of this section. All monomers listed above were deoxygenated by three freeze-pump-thaw degassing cycles and stored in the dry box or in tubes equipped with Teflon valves.

Benzophenone was purchased from Baker and used as received. The benzaldehyde used for end capping was purified by the procedure of Perrin, Armarego, and Perrin.[64] The d_6-acetone used for end capping was dried over 4Å sieves, vacuum-transferred and deoxygenated as above before use. The acetone employed for end capping was purified by refluxing over $KMnO_4$ until the purple color persisted, drying ($CaSO_4$), further drying (4Å molecular sieves) and deoxygenation by three freeze-pump-thaw degassing cycles. The purified material was stored in a flask equipped with a Teflon valve. Anthranilic acid (MCB) and isoamyl nitrite (Aldrich) were used as received. N-carbomethoxypyrrole was prepared by the method of Acheson and Vernon[65] from potassium pyrrole[66] and methyl chloroformate (Aldrich). DIBAL-H was obtained from Alfa as a neat liquid and stored in the dry box. DDQ was purchased from Aldrich. Octane and *p*-xylene (used for VPC internal standards) were distilled from CaH_2 and deoxygenated as above before use. BHT was purchased from Aldrich (Gold Label).

The solvents used in polymerizations and organometallic syntheses were purified as follows. Tolulene, benzene, THF, and diethyl ether were dried (CaH_2), transferred to sodium benzophenone ketyl and later distilled into solvent flasks equipped with Teflon screw-type valves. Toluene for polymerizations in later experiments was further purified by stirring prepurified material (distilled from sodium

benzophenone ketyl) over "titanocene"[38] overnight and then vacuum-transferring into a flask equipped with a Teflon valve. Benzene-d_6 and toluene-d_8 (Merck, Sharp & Dohme) were transferred to sodium benzophenone ketyl, later distilled and stored in the dry box. The solvents used in organic synthesis were purified as above if listed as "dry." Otherwise the solvents were reagant grade. Methanol for precipitation of polymers was reagant grade and used without further purification.

Polymerization of Norbornene in End Capping Studies. A standard solution of norbornene was prepared under argon as follows: To 8.10 g (86.1 mmol) of freeze-pump-thaw degassed norbornene were added by syringe 0.5 mL of octane and finally benzene to give a total volume of 50.0 mL (1.72 M in norbornene).

In the original set of experiments only end-capped polynorbornene was synthesized. In later experiments both uncapped and capped polymers were made by the following procedure.

In A Schlenk tube **1** (20 mg, 0.07 mmol) were dissolved in 2.0 mL of the standard norbornene solution (3.5 mmol, 50 eq of norbornene). The resulting mixture was transferred by syringe into two separate tubes (1.0 mL in each). The solutions were stirred in the same oil bath at 65°C and both polymerizations followed by capillary VPC. In each case the concentration of norbornene remained the same in each tube (VPC). At 95% completion the contents of one tube were allowed to cool to 23°C. The resulting red solution was added to 50 mL of rapidly stirred MeOH, and the precipitated red amorphous polymer dried under high vacuum and stored under inert atmosphere. To the other tube was added by syringe a solution of 0.065g (0.36 mmol, 10 eq/Ti) of benzophenone in 1.0 mL of benzene and stirring continued at 65°C. The initial dark-red solution became pale orange after 0.5 h and capillary VPC indicated no further polymerization of norbornene. After allowing to cool to 23°C, the solution was flash-chromatographed (benzene) and the polymer isolated by precipitation into MeOH and dried under high vacuum at

115 °C overnight. The resulting white amorphous solid (60-70 % yield) was stored under inert atmosphere. The capped polymer samples were free of benzophenone and organotitanium species (TLC).

End Capping of Polynorbornene With Benzaldehyde. The metallacycle **8** (0.039 g, 0.15 mmol) was used to polymerize norbornene (0.298 g, 3.17 mmol, 21 eq) (see synthesis of **19** for procedure) to 90% completion (19 eq). One-half of the living polymer was end capped with acetone (see **26**) to give a clear sticky oil. This sample of low molecular weight polynorbornene was analyzed by GPC: MW (theoretical)= 1,900; M_n= 3,740; M_w= 4,240; PDI= 1.13. To the other half of the living polymer (0.320 g, 0.075 mmol) in PhMe (1.0 mL total volume) was added benzaldehyde (0.077 g, 0.72 mmol, 10 eq/Ti) by syringe (in the dry box) and the mixture stirred and heated at 70°C for 0.5 h to give a pale-orange solution. Purification (see **26**) gave a light-yellow, slightly sticky solid. ^{1}H NMR (CD_2Cl_2) integration of the aromatic protons of the end cap (δ 7.15 (m)) vs. the allylic protons of the polymer (δ 2.40, 2.78) indicated that 78% of the polymer chains were end capped (assuming 19 eq of monomer/chain). The polymer was also analyzed by GPC: MW (theoretical)= 1,960; M_n= 4,040; M_w= 4,510; PDI= 1.12.

End Capping of Polynorbornene With $(CD_3)_2C$=O. The metallacycle **8** (0.020g, 0.075 mmol) was used to polymerize a mixture of norbornene (0.130 g, 1.39 mmol, 18.5 eq) and norbornene-2,3-d_2 (0.027 g, 0.28 mmol, 3.7 eq) as above to 96% completion (18 eq of norbornene, 3.6 eq of norbornene-d_2). The living polymer was end capped with $(CD_3)_2C$=O (0.160 g, 2.5 mmol, 33 eq/Ti) and collected as above to give a clear, sticky solid. ^{2}H NMR (PhMe, C_6D_6 internal standard) integration of the methyl deuteriums of the end cap (δ 1.45, 1.55) vs. the olefinic deuteriums of the polymer (δ 5.50) indicated that 102% of the polymer chains were end capped (assuming 3.6 eq of norbornene-d_2/chain). The polymer was also analyzed by GPC: MW (theoretical)= 2,160; M_n= 4,740; M_w= 5,320; PDI= 1.12.

Attempted Polymerization of Cyclopentene With 7.[19] In the dry box an NMR tube was charged with **6**[6c](0.020 g, 0.081 mmol), capped with a septum and brought out. In a Schlenk tube cyclopentene (0.017 g, 0.25 mmol, 3 eq) was dissolved in 0.4 mL of d_8-toluene and both the Schlenk tube and NMR tube cooled to –78°C. The cyclopentene/benzene solution was transferred by cannula to the NMR tube. The tube was warmed to –5°C and the reaction followed by ^{1}H NMR. After 20 min with an increase in temperature to 20°C, the formation of **5** was complete. Continued heating to 85°C over a 3 h period resulted in metallacyle decomposition with no change in cyclopentene concentration or new signals attributable to poly-1-pentylene.

Attempted Polymerization of Cyclopentene with 1.[19] To a Schlenk tube charged with **1** (0.040 g, 0.14 mmol) was added by syringe 1.0 mL of benzene. Cyclopentene (0.135 g, 1.98 mmol, 14 eq) was introduced by vacuum-transfer. The tube was warmed to room temperature, equipped with a condenser and stirred 12 h at 65 °C under argon. Methanol precipitation yielded no polymer and ^{1}H NMR analysis ($CDCl_3$) indicated only cyclopentene, norbornene and unidentified titanium products present.

Preparation of Metallacyle 10.[19] Cyclopentene (0.040 g, 0.6 mmol, 3 eq) was added to a 5 mm NMR tube containing **8** (0.050 g, 0.2 mmol) and benzene-d_6 at 10°C. The tube was placed in the probe of the NMR, a spectrum was recorded at 10°C, and the sample was warmed to 25°C. Consumption of cyclopentene was monitored by integration of spectra recorded at regular intervals. After 1.25 h, no peaks attributable to **8** remained and two equivalents of cyclopentene had reacted. Metallacycle **10** was obtained as a red oil by removal of volatiles under vacuum. It was redissolved in benzene-d_6 and a ^{1}H NMR spectrum recorded. ^{1}H NMR (C_6D_6) δ 5.91 (dd), 5.59 (s), 5.37 (s,Cp), 5.36 (s,Cp), 5.31 (s,Cp), 5.30 (s,Cp), 5.05 (d), 4.97 (d), 4.76 (m), 2.76 (m), 2.29 (m), 2.21-1.32 (m), 1.15 (s, Me), 1.09 (s), 1.03 (s),

0.43 (m), –0.21 (m). The ratio of the olefinic region (δ 6.0 to 4.0) to the aliphatic region (δ 3.0 to –1.0) by NMR integration was approximately 2:3.

Reaction of 10 With Benzophenone.[19] A sample of **10** (0.2 mmol) prepared as described above from 0.050 g of **8** was stirred with benzophenone (0.075 g, 0.4 mmol, 2 eq) in 1.0 mL of benzene for 5 h at 60°C. After cooling to 23°C, the solution was diluted with 10 mL of petroleum ether. The resultant yellow precipitate was removed by rapid filtration through silica gel. Evaporation of the solvent under vacuum yielded 0.048 g of a yellow oil. Analysis by capillary VPC indicated two major products eluting at moderate (peak 1) and long (peak 2) retention times, respectively.

Peak 1 (**11**): MS, *m/e* 316 (M+), 246, 233, 206, 193, 167, 129, 115, 91 (base). ***Exact mass*** calcd. for $C_{24}H_{28}$: 316.2191. Found: 316.2195.

Peak 2 (**12**): MS. *m/e* 384 (M+), 245, 206, 193, 167, 115, 91 (base), 44. ***Exact mass*** calcd. for $C_{29}H_{36}$: 384.2817. Found: 384.2818.

A small amount of material coeluted with each peak having *m/e* of 318 and 386, repectively. Persumably these products arise from secondary hydrogenation of **12** and **13**.

Thermolysis of 10 in the Presence of Cyclopentene.[19] A sample of **10** was prepared as described above. Prior to removal of excess cyclopentene under vacuum, the sample was heated to 45°C. Decomposition of **10** was indicated by disappearance of its cyclopentadienyl signals. The excess cyclopentene was not affected.

Polymerization of Norbornene With 10.[19] To metallacyle **8** (0.020 g, 0.08 mmol) dissolved in 0.5 mL of benzene-d_6 in a 5 mm NMR tube was added cyclopentene (0.015 g, 0.23 mmol, 3 eq). The reaction of **8** to give **10** was monitored by ^{1}H NMR spectroscopy. After conversion was complete, norbornene (0.025 g,

0.27 mmol, 3 eq) in 0.1 mL of benzene-d_6 was added. The tube was heated in the probe to 50 °C. Polymerization of norbornene was indicated by reduction in signals assigned to the monomer and by the appearance of signals attributable to ring-opened polynorbornene. No consumption of cyclopentene was observed. In fact, 0.7 eq of additional cyclopentene was released by the reaction of **10** with norbornene.

Polymerization of Cyclopentene. In the polymerizations several different concentrations of **8** and cyclopentene were employed at different temperatures in benzene or toluene (see Table III). A typical procedure is given below (run # 7).

In a Schlenk tube **8** (20 mg, 0.077 mmol) was dissolved in 1.0 mL of toluene and 1.0 ml of cyclopentene added by syringe. The resulting mixture was briefly stirred and transferred by cannula into a tube equipped with a Teflon valve closure. The solution was stirred in an oil bath at 34°C and the polymerization followed by capillary VPC. The toluene of the mixture was used as an internal standard to determine the concentration of cyclopentene remaining. The mixture darkened slightly with time, but remained red. After 8.8 h (37 eq of cyclopentene consumed (VPC, see Table IV)), the resulting red solution was added to 50 mL of rapidly stirred MeOH, and the polymer precipitated as a dark, red-brown oil. It was dried under high vacuum overnight and stored under inert atmosphere.

^{13}C NMR Kinetics. A stock solution of **8** (0.020 g, 0.077 mmol) in 500 μL of C_6D_6 was prepared in the dry box. To each of four NMR tubes (equipped with a glass tube extension for flame-sealing) were added 125 μL of the stock solution of **8**. To each tube were then added C_6D_6 and cyclopentene as given in Table XII below to give a total volume of 500 μL ([**8**]= 0.038 M).

The tubes were flame-sealed and stored at −50°C. To run the kinetics each tube was placed in the NMR probe and allowed to equilibrate at 37.6± 0.5°C for 5 min. ^{13}C NMR spectra were recorded every 10 min (256 scans) with a short pulse

Table XII. Sample Preparation For Kinetics

tube	μL of C_6D_6	μL of cyclopentene
1	125	250
2	250	125
3	312.5	62.5

delay. Integration of the signal of the C4 carbon of cyclopentene (δ 23.8) versus residual benzene (δ 128.2, 128.0, 127.8) of the NMR solvent gave the concentration of cyclopentene remaining (assuming the first spectrum corresponds to the initial concentration of the sample). After 0.75-1.0 h 10% completion of polymerization was reached and the data accumulation ended. Least-squares analysis of plots of [cyclopentene] vs. time gave the rates listed in Table V. The experiment was repeated for the first two tubes (1 and 2) with alternating accumulations with short pulse delays (256 scans) and 100 s pulse delays (12 scans). The same concentrations were observed in each case.

Polymerization of Benzonorbornadiene (17) By 6. The metallacycle **6** (0.020 g, 0.081 mmol) was dissolved in 0.4 mL of C_6D_6 in an NMR tube and **17** (0.012g, 0.081 mmol) added by syringe. After 40 min ^{1}H and ^{13}C NMR spectra were recorded, which indicated quantitative formation of isobutylene and the new metallacycle derived from $Cp_2Ti{=}CH_2$ and **17**: ^{1}H NMR (C_6D_6) δ 7.14 (m, 4H), 5.50 (s, 5H), 5.18 (s, 5H), 3.36 (d, J= 9.0 Hz, 1H), 3.11 (bs, 1H), 2.84 (dd, J_1= 9.3 Hz, J_2= 8.8 Hz), 1.88 (pt, J_1= 8.8 Hz, J_2= 8.8 Hz, 1H), 0.34 (pq, J_1= 9.0 Hz, J_2= 9.3 Hz, J_3= 8.8 Hz); ^{13}C NMR (C_6D_6) δ 153.1, 148.7, 125.9, 124.6, 121.6, 118.8, 110.3, 109.5, 103.7, 74.2, 53.8, 49.3, 45.1, 19.1 (the spectra are similar to that for metallacycle **1** derived from norbornene: see Ref. 19a, p. 85).

To the metallacycle generated above were added an additional 6 eq of **17** by syringe. The NMR tube was heated at 70°C in the NMR probe and consumption of the monomer observed with the appearance of polymer peaks at δ 7.20 (m), 5.95 (bs), 5.75 (bs), 4.15 (bs) and 3.75 (bs), 2.68 (bs) and 1.80 (bs). After approximately 5 eq of monomer were consumed, the polymerization stopped. The contents of the tube were dark, red-brown with a pink precipitate.

Synthesis of 19. A stock solution of **17** (2.237 g, 15.7 mmol) was prepared with 0.2 mL of octane (internal VPC standard) and additional PhMe to give 25.00 mL total volume ([**17**]= 0.63 M). The metallacycle **6** (0.045 g, 0.18 mmol) and 3.0 mL of stock solution (0.268 g, 1.89 mmol, 11 eq of **17**) were combined in a vial in the dry box and transferred by pipette to a glass tube. The tube was brought out of the dry box and attached to a hose on the vacuum line via the joint. The deep-red mixture was stirred 0.5 h and the isobutylene produced by reaction of **6** with **17** was removed by three freeze-pump-thaw degassing cycles.

Stirring was continued at 67-68°C in an oil bath. Samples were withdrawn periodically by dipping an oven-dried pipette (purged with argon) into the polymerization solution under a stream of argon. The small amount retained in the tip of the pipette by capillary action was diluted with acetone to precipitate the polymer and the supernatant was analyzed by VPC. The ratio of **17** to octane was used to determine the eq of **17** remaining. A fine precipitate began to form 20 min after the start of the polymerization and more appeared as the polymerization proceeded. After 50 min at the polymerization temperature (9 eq of **17** consumed), the tube was allowed to cool to room temperature, freeze-pump-thaw degassed and transferred to the dry box. 1.0 mL of the solution was removed to a vial, the vial brought out and its contents added to stirring MeOH to precipitate **19** (0.067 g, 84% yield based upon percent completion) as a fine pink powder. The polymer was analyzed by GPC (see Table VI) and NMR: ^{1}H NMR ($CDCl_3$) δ 7.15 (bs, 4H),

(5.75 (bs), 5.65 (bs) (2H)), (4.21 (bs), 3.79(bs) (2H)), (2.68 (bs), 1.84 (bs) (2H)), ^{13}C NMR ($CDCl_3$) δ 146, 134, 133, 127, 124, 123.5, 48, 43. The ^{1}H and ^{13}C NMR spectra were consistent to those reported in the literature.[34]

Synthesis of The Diblock Polymer 20. A stock solution of norbornene in toluene with an internal standard of octane was prepared as before. To the remaining mixture from the synthesis of **19** consisting of the living polymer (0.160 g, 0.12 mmol) and **17** (0.037 g, 0.26 mmol, 2.2 eq/Ti) in PhMe (2.0 mL total volume) were added 4.0 mL of the stock norbornene solution (0.685 g, 7.27 mmol, 61 eq/Ti of norbornene). The polymerization was performed as before. The precipitate originally present disappeared as the polymerization progressed. After 15.5 h (57 eq of norbornene and 2 eq of benzonorbornadiene consumed by VPC) the tube was allowed to cool to room temperature. The polymer (0.756 g, 79% yield) was collected as before and analyzed by GPC (see Table VI).

Synthesis of Polymers 21-25. These polymers were synthesized by the same procedure listed for the polymers **19** and **20**. The results are presented in Table VI.

Synthesis of Polymers 26-32. The method used for polymerization and isolation of the resulting polymers was modified from before as follows.

The toluene was further dried (see Materials). The metallacycle **8** was employed instead of **6**. The polymerizations were performed at 71-72°C. The polymers produced were end capped with acetone and purified by flash chromatography on silica gel. A typical end capping and isolation procedure for polymer **26** is given below.

To a tube equipped with a Teflon valve and containing a solution of living polynorbornene (0.211 g, 0.046 mmol, 46 eq of norbornene/chain) in toluene (1.0 mL total volume) was added 0.1 mL (0.079 g, 1.36 mmol, 30 eq/Ti) of acetone by syringe. The resulting mixture was stirred at 71°C for 15 min to give a clear pale-orange solution. The mixture was allowed to cool, diluted with PhMe and filtered

through a pad of silica gel with suction. The pad was liberally washed with PhMe and the combined filtrate and washings reduced in volume by rotary evaporation to approximately 2 mL. The resulting PhMe solution of product was added dropwise to a stirring MeOH solution to precipitate the polymer. The pure white amorphous solid was dried under high vacuum overnight.

The polymers **26, 27,** and **28** were submitted for elemental analysis.

26. Anal. Calcd. for $C_4H_7(C_7H_{10})_{46}C_5H_9$: C, 89.23; H, 10.77. Found: C, 89.10; H, 10.55 (no detectable ash).

27. Anal. Calcd. for $C_4H_7(C_{11}H_{10})_5(C_7H_{10})_3\ (C_7H_{10})_{46}C_5H_9$: C, 89.71; H, 10.29. Found: C, 89.31; H, 10.29 (no detectable ash).

28. Anal. Calcd. for $C_4H_7(C_7H_{10})_{44}\ (C_{11}H_{10})_5(C_7H_{10})_3\ (C_7H_{10})_{46}C_5H_9$: C, 89.58; H, 10.42. Found: C, 89.40; H, 10.23 (no detectable ash).

Polymerization of 6-Methylbenzonorbornadiene (33). The polymerization was performed by the same procedure as for **26-32** except that the isolated polymer was not end capped. The product was a fine pink solid which was only sparingly soluble in PhMe or CH_2Cl_2. GPC analysis gave M_n= 3,590; M_w= 6,330; PDI= 1.76. The polymer was also analyzed by NMR: ^{1}H NMR ($CDCl_3$) δ 7.15 (m, 3H); 5.70 (bs), 5.52 (bs) (2H); 4.15 (bs), 3.85 (bs) (2H); 2.65(bs), 1.80(bs) (2H); 2.38 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 146, 143, 136, 133, 127, 124.5, 123.5, 48, 43, 22.

Living Polymerization of exo-Dicyclopentadiene (37). The polymerization was performed as above with the metallacycle **8** (0.017 g, 0.065 mmol) and **37** (0.430 g, 3.25 mmol, 50 eq) in PhMe (2.0 mL total volume). At set intervals during the polymerization aliquots of the mixture were removed and end capped with acetone and the isolated polymers analyzed by GPC (see Table XI.)

Synthesis of Polymers 39-49. These polymers were synthesized by the same procedure as used for polymers **26-32**. The monomers were more thoroughly

purified as described in the Materials section. The polymerization temperature was increased to 75°C.

NMR Determination of the Ratio of Homopolymers in Block Coplymers 43, 44, 46, 47, and 49 (Table X). The overlap of the ^1H NMR of polynorbornene and poly(dicyclopentadiene) prevented a simple integration to determine the ratio of the polymers present. An algebraic approximation was used instead as follows. The olefinic region of the NMR was modeled as arising from two olefinic protons per monomer unit of polynorbornene and four olefinic protons per monomer unit of poly(dicyclopentadiene). Similarly, the aliphatic region was modeled as arising from eight protons each per monomer unit of polynorbornene and poly(dicyclopentadiene), respectively. These relationships are given in Eqs. 22 and 23 below.

$$2x + 4y = (\text{olefinic protons})\,z \qquad (22)$$

$$8x + 8y = (\text{aliphatic protons})\,z \qquad (23)$$

$$\frac{x}{y} = \frac{2(\text{aliphatic}) - 4(\text{olefinic})}{4(\text{olefinic}) - (\text{aliphatic})} \qquad (24)$$

x = monomer units of polynorbornene
y = monomer units of polydicyclopentadiene
z = correction factor of integration to actual number of protons

Solving these two equations in three unknowns (x,y,z) yields an expression for the ratio of polynorbornene to poly(dicyclopentadiene) present in the block copolymers as given in Eq. 24 below.

Polymerization of Norbornene By 50a. The following list of experiments were performed in studying the polymerization chemistry of **50a**.

Experiment 1. 50a (0.010 g, 0.013 mmol) was dissolved in 4.0 mL of PhMe in a tube, the tube cooled to –78°C, and the mixture rapidly added by cannula to 2.0 mL of a toluene solution of norbornene (0.342 g, 3.64 mmol, 288 eq) and octane (0.020 g, internal standard for VPC), also cooled to –78°C and in a similar tube. The resulting mixture was stirred 2.5 h at –78°C, 4.5 h at –40°C, and finally 5 h at –20°C. During the polymerization small aliquots (0.1 mL) of the reaction mixture were removed by pipette under argon and added to MeOH. The resulting supernatants were analyzed by VPC and the precipitated polymer by GPC. At the end of the polymerization the remaining solution was treated as above. The total amount of polymer collected throughout the experiment was 0.045 g (13% yield based on initial monomer). The concentration of norbornene remained relatively unchanged during the polymerization (VPC). All of the polymer samples gave the same GPC values: M_n= ~400,000; M_w= ~650,000; PDI= 1.6. ^1H and ^{13}C NMR analyses of the polymer samples showed them to be essentially 100% *cis*-polynorbornene.

Experiment 2. 50a (0.0036g, 0.0045 mmol) was dissolved in 0.4 mL of d_8-toluene and transferred to an NMR tube. Norbornene (0.0945 g, 1.00 mmol, 222 eq) was vacuum-transferred to the tube (cooled in liq N_2) and the tube flame-sealed. The tube was thawed at –78°C and very briefly shaken to mix the norbornene with the catalyst solution. The tube was rapidly transferred to the precooled probe (–81°C) and an initial ^1H NMR spectrum recorded, which showed only monomer and polymer present (7.5% conversion by integration of the olefinic protons of the monomer and polymer). After 0.5 h more polymer had formed (16.2% conversion). The probe was warmed to –61°C and the polymerization followed by ^1H NMR (results presented in following table).

After 110 min at –61°C, the tube was recooled to –80°C, and the contents rapidly added to MeOH to precipitate a yellow polymer. ^1H and ^{13}C NMR gave 100% *cis* polymer and GPC gave M_n= 390,000; M_w= 660,000; PDI= 1.7.

Table XIII. Experiment 2

time (min)	% conversion
0	25.9
10	28.2
20	30.1
30	33.8
40	38.3
50	41.1
60	43.0
70	46.4
80	48.4
90	51.7
100	54.6
110	57.8

Experiment 3. 50a (0.0047 g, 0.0059 mmol) was dissolved in 0.3 mL of d_8-toluene and transferred to an NMR tube. Norbornene (0.0296 g, 0.314 mmol, 53 eq) in 0.2 mL of d_8-toluene was vacuum-transferred to the NMR tube (cooled in liq N_2) and the tube flame-sealed. The tube was thawed at –78°C to give a homogeneous solution. The tube was then rapidly transferred to the precooled probe (–81°C) and an initial ^{1}H NMR spectrum recorded, which showed only monomer and polymer present (13.7% conversion). After 1 h more polymer had formed (18.3% conversion). The probe was warmed to –61°C and the polymerization followed by ^{1}H NMR (results presented in table below).

After 50 min at –61°C, the tube was warmed to –40°C for 10 min at which time the polymerization was complete (^{1}H NMR). As the polymerization had pro-

Table XIV. Experiment 3

time (min)	% conversion
0	39.6
5	45.5
10	48.4
15	52.0
20	54.3
25	56.7
30	58.2
35	61.8
40	63.7
45	65.8
50	68.1

gressed, the following peaks slowly appeared and reached maximum intensity at 100% polymerization: δ 6.72 (t, J= 7 Hz), 6.26 (t, J= 8 Hz), 4.73 (m), 4.23 (m), 3.67 (m), 0.55 (t, J= 8 Hz), 0.28 (t, J= 8 Hz) and –0.02 (bs). Each peak had the same integration, which corresponded to 30% of the integration expected for one proton of the original catalyst. This estimation was based upon integration vs. the polymer olefinic protons.

The tube was rapidly warmed to ambient temperature and an initial ^{1}H NMR recorded. It showed the appearance of the propagating alkylidene complex (δ 9.24 (H_{alpha}, d, J_{HH}= 7 Hz)) in 6% yield, and also present was 8% of the original catalyst (**50a**). The tube was kept at ambient temperature for 56 h with observation by NMR of the isomerization of the polymer double bonds from 100% *cis* to 81% *trans*. The catalyst and the unidentified peaks remained at approximately the same

intensity. The contents of the tube were added to stirring MeOH to precipitate a yellow polymer. GPC analysis gave M_n= 22,500; M_w= 47,200 and PDI= 2.1.

Experiment 4. **50a** (0.0068 g, 0.0086 mmol) was dissolved in 0.4 mL of d_8-toluene and transferred to an NMR tube which was sealed with a septum. Norbornene (0.060 g, 0.64 mmol, 74 eq) was dissolved in 0.3 mL of d_8-toluene and drawn into a gas tight syringe that was sealed. The tube was cooled to –78°C and the ^{1}H NMR recorded (clean spectrum of catalyst observed). The norbornene solution was added slowly at –80°C, the tube shaken briefly, and the ^{1}H NMR recorded, which showed only monomer and polymer. The tube was quickly warmed to room temperature and allowed to stand 2 h, at which time the ^{1}H NMR showed polymer (93% *cis*), alkylidenes and unidentified species as before (see Experiment 3). The contents of the tube were added to stirring MeOH to precipitate a yellow polymer. GPC analysis gave M_n= 9,400; M_w= 21,000; PDI= 2.2.

Experiment 5. An NMR tube containing **50a** (0.0269 g, 0.034 mmol) and norbornene (0.0438 g, 0.465 mmol, 13.7 eq) in 0.5 mL of d_8-toluene was prepared as in Experiment 3. The tube was rapidly transferred to the probe (precooled to –91°C) and an initial ^{1}H NMR recorded, which showed most of the catalyst still present along with monomer (30%) and polymer (70%). Slow warming over a 15 min period to –71°C finished the polymerization (^{1}H NMR) with the simultaneous appearance of the propagating alkylidene (5% of the initial alkylidene). The initial alkylidene remained at roughly the same concentration, but upon warming to ambient temperature was quickly reduced to approximately 5% concentration along with the appearance of the unidentified peaks (30% of one proton of the initial alkylidene). The propagating alkylidene remained at roughly the same concentration. After 82 h at ambient temperature the polymer had isomerized to 90% *trans* with the tungsten species remaining as observed before.

The experiment was repeated with **50a** (0.0545 g, 0.0689 mmol) and norbornene (0.015 g, 0.159 mmol, 2.31 eq) and similar results obtained.

Experiment 6. An NMR tube containing **50a** (0.0351 g, 0.0444 mmol) and norbornene-d_2 (0.0563 g, 0.587 mmol, 13.2 eq) in 0.63 mL of PhMe and 0.020 mL of d_8-toluene was prepared as in Experiment 3. The tube was kept at –80°C for 1 h and then allowed to warm to ambient temperature. After 6 h at room temperature a ^{2}H NMR was recorded overnight. The spectrum (signal/noise= 55) contained only signals attributable to olefinic polymer deuteriums. None of the unidentified peaks previously mentioned were observed. The tube was evacuated (10^{-5} torr) for several hours and the orange residue redissolved in d_8-toluene. A ^{1}H NMR was then recorded, which showed no alkylidene protons and was missing the unidentified peaks at δ 6.26, 4.73, and –0.02. All other peaks were present.

Addition of H_2O to the Polymerization of Norbornene By 50a. A "wet" solution of PhMe was prepared by combining dry, deoxygenated PhMe and H_2O in a tube under argon and stirring the resulting mixture overnight. The mixture was then allowed to stand for 24 h. The toluene layer was transferred by cannula and stored in a tube equipped with a Teflon valve. Experiments with tritiated water have shown that 100 mL of "wet" PhMe prepared as above contains 1.85 mmol of H_2O.[67]

A stock solution of **50a** (0.0843 g, 0.106 mmol) in 0.65 mL of PhMe was prepared in the dry box and 0.2 mL (0.0327 mmol of **50a**) portions of the solution placed in three different tubes equipped with Teflon valves. Additionally, to each tube was added PhMe (in the dry box), 0.8 mL of a toluene solution of norbornene (0.298 g, 3.17 mmol, 96.9 eq) (by vacuum-transfer) and "wet" PhMe (by vacuum-transfer) as described in Table XV.

All three tubes were simultaneously thawed in a –78°C bath, stirring initiated and the bath removed. After warming to room temperature (15 min), the pale yellow solutions were added to stirring MeOH to precipitate the respective polymers, which were analyzed by GPC (see text).

Table XV. Preparation of **50a**/H_2O Mixtures

tube	mL of dry PhMe	mL of "wet" PhMe	eq H_2O/W
1	1.0	0	0
2	0.98	0.020	0.01
3	0.80	0.20	0.10

Preparation of N-methyl-7-azabenzonorbornadiene (51). Under argon N-carbomethoxy-7-azabenzonorbornadiene (**52**) (10.68 g, 53.1 mmol, see synthesis below) was dissolved in 120 mL of benzene and a solution of DIBAL-H (28.7 g, 202 mmol) in 90 mL of benzene added dropwise over 4 h at room temperature to the stirring solution. Stirring was continued an additional 13 h. The reaction was quenched by slow addition of MeOH with cooling in an ice bath. The resulting mixture was diluted with Et_2O and filtered through Celite to remove the large amount of aluminum salts. The pale-yellow filtrate was evaporated to give 7.71 g (92% yield) of crude product as a yellow oil. The crude amine was dissolved in 200 mL of ether and cooled to 0°C, and the ether solution extracted with 1 N HCl (aq) (3X100 mL) at 0°C. The aqueous layer was made basic with KOH (s), extracted with Et_2O (3X150 mL) and the ether layer dried ($MgSO_4$), evaporated and the resulting yellow oil redissolved in CH_2Cl_2 and dried (CaH_2). The dichloromethane solution was evacuated to dryness and the product isolated by vacuum distillation (b.p. 80°C, 4 torr) from NaOH (s) to give a colorless oil. A ^1H NMR ($CDCl_3$) spectrum of the product was identical to that reported in the literature.[49]

Synthesis of N-carbomethoxy-7-azabenzonorbornadiene (52). The reaction was performed under argon as follows. To a refluxing solution of N-carbomethoxypyrrole[65] (15.25 g, 122 mmol) in 80 mL of dry THF were added simultaneously by separate syringe pumps THF solutions (40 mL each) of anthranilic

acid (16.73 g, 122 mmol) and isoamyl nitrite (14.29 g, 122 mmol), respectively. After 2.5 h the addition was complete and refluxing continued an additional 1.5 h. The resulting dark brown solution was evacuated by rotary evaporation, redissolved in 100 mL of $CHCl_3$, and the organic layer washed with H_2O (2X100 mL), sat $NaHCO_3$ (aq) (2X100 mL), H_2O (1X100 mL) and dried (Na_2SO_4). The chloroform solution was evacuated to dryness by rotary evaporation followed by high vacuum to give the crude product as a dark brown oil. Vacuum distillation (b.p. 118°C, 0.02 torr) afforded 12.2 g (50% yield) of product as a clear oil, which solidified upon standing (lit[68] m.p.= 55°C; b.p.= 130-140°C, 0.05 torr).

Preparation of 7-azabenzonorbornadiene (54). A mixture of N-carbomethoxy-7-azabenzonorbornadiene (**52a**) (9.38 g, 46.6 mmol, see synthesis above) and 125 mL of 10% NaOH (aq) was refluxed for 20 h. The mixture was then extracted with Et_2O (3X50 mL) and the combined ether fractions dried ($MgSO_4$) and evacuated to dryness to give a dark brown oil. Vacuum-distillation (b.p. 65°C, 0.8 torr; lit[68] b.p.= 60°C, 0.4 torr) from CaH_2 gave 5.6 g (84% yield) of **54** as a colorless oil.

Preparation of poly(vinylidenemethylisoindole)(60). Method A. To a Teflon valve-equipped tube was transferred by syringe a freshly prepared solution of the metallacycle **6** (0.095 g, 0.38 mmol) in 2.0 mL of benzene. To this solution was added by syringe the monomer **51** (0.400 g, 2.54 mmol, 6.7 eq). The resulting mixture was stirred at 75°C for 4 h to give a dark-brown solution. The mixture was evacuated to dryness under high vacuum, redissolved in 4 mL of chloroform and stirred overnight. The chloroform solution was flash-chromatographed (1:1 chloroform/MeOH) to give 0.363 g (91% yield) of dark-brown polymer, the isolated solids or solutions of which turned purple in color upon exposure to the air over several hours. The purple impurity was undetectable by ^1H NMR and could be removed by flash chromatography (THF). The product **60** was submitted to NMR,

IR and GPC analysis: ^{1}H NMR ($CDCl_3$) δ 7.27 (m, 4H), 5.87 (bs, 2H), 5.38 (m, $=CH_2$), (4.71 (bs), 4.22 (bs) (2H)), 2.89 (m, -CH_3, 3H); ^{13}C NMR ($CDCl_3$) δ 141.8, 135.1, 134.2, 127.3, 122.2, 72.8, 67.0, 37.9; IR (KBr) 2930 (m), 2770 (m), 1690 (m), 1610 (m), 1560 (w), 1475 (s), 1460 (vs), 1360 (w), 1320 (w), 1280 (s), 1190 (m), 1160 (w), 1115 (w), 1070 (w), 1020 (sh), 990 (sh), 970 (vs), 920 (w), 895 (w), 795 (w), 740 (vs), 660 (w); GPC M_n= 690, M_w= 922, PDI= 1.33.

Method B. To a tube was added by syringe a freshly prepared solution of **50a** (0.050 g, 0.063 mmol) in 3.5 mL of PhMe. The solution was cooled to –78°C and the monomer **51** (0.500 g, 3.18 mmol, 50 eq) added by syringe. The resulting mixture was stirred for 10 min at –78°C and then allowed to warm to room temperature over 0.5 h. After an additional 4 h of stirring at ambient temperature, the orange solution was added dropwise to 40 mL of stirring MeOH. The precipitated polymer (an off-white powder) was triturated in MeOH, collected by centrifugation and dried under high vacuum overnight to give 0.415 g (83% yield).

Dehydrogenation of 60 with DDQ. THF solutions of **60** were treated with THF solutions of DDQ (1 eq/ monomer unit of polymer) to give instantly a dark black precipitate. The precipitate was purified by soxhlet extraction with ethyl acetate to give samples free of $DDQH_2$ and DDQ (TLC, NMR). The precipitate after extraction was insoluble in H_2O, conc H_2SO_4, chloroform, THF or PhMe. The yield was quantitative. The entire procedure was performed under argon or air with similar results. Solid-state ^{13}C NMR (CP-MAS) analysis gave a spectrum with broad signals at δ 135 and 30.

Doping of 65 with I_2. Samples of **65** were exposed to iodine vapor under vacuum at room temperature for several days with no change in appearance. The samples were then evacuated under high vacuum and by weight uptake had incorporated one iodine atom/monomer unit. Pressed pellets of the doped material typically gave conductivites of 10^{-4} to 10^{-5} Scm^{-1}.

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17. It has been observed that the living polymer quickly decomposes after complete consumption of norbornene at 65°C(see Ref. 3a). Therefore end capping was performed at 95% completion of the polymerization (see Experimental Section).

18. This work was performed prior to optimization of reaction conditions that now give polydispersities as low as 1.08 (see Ref. 3a). Current studies with acetone as an endcapping reagent routinely provide samples with polydispersities less than 1.10 (see section on block copolymers in this chapter).

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24. ^{1}H NMR ($CDCl_3$) δ 5.80 (dd, J_1= 10.5 Hz, J_2= 17.3 Hz, 1 H, -CH=); 4.88 (ddd, J_1= 10.7 Hz, J_2= 17.6 Hz, J_3= 1.4 Hz, 2 H, =CH_2); 1.06(s, 6 H, $C(CH_3)_2$ α to *trans* double bond of polymer); 0.91 (s, 6 H, $C(CH_3)_2$ α to *cis* double bond). Typically, the ratio of the signals at δ 1.06 and 0.91 indicated the first double bond of the polymer was approximately 90 % *trans*.

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26. The temperature of the probe was determined from the chemical shift of a MeOH standard: Gordon, A. J.; Ford, R. A. The Chemist's Companion; Wiley: New York, 1972, p. 303.

27. Titanium carbenes derived from titanacyclobutanes have never been observed during polymerizations (^{1}H NMR, $\leq$5%).

28. The presence of carbene-olefin complexes in the metathesis chemistry of titanacyclobutanes has been implied by kinetic studies: see Anslyn, E. V.; Grubbs, R. H. *J. Am. Chem. Soc.* **1987**, *109*, 0000.

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30. (a) Living polymerizations are characterized by narrow and controlled molecular weights in product polymers, absence of chain transfer or termination and characterizable chain-carrying intermediates: see Flory, P. *J. Am. Chem. Soc.* **1940**, *62*, 1561. (b) The term "living" is also used to describe polymerization systems, where the catalyst is part of the polymer chain and its activity remains even after the polymerization has ended. A quick experimental test to identify a true "living" polymerization system is to plot the molecular weights of the resulting polymers vs. the percent conversion of the monomer during the polymerization. A straight line with a zero intercept indicates that a system is living: see Odian, G. Principles of Polymerization; 2nd ed.; Wiley-Interscience: New York, 1981.

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33. See preceding section of this chapter.

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35. The metallacycle **6** decomposes to give "$Cp_2Ti{=}CH_2$" and isobutylene. The carbene is rapidly trapped by **17** giving the corresponding metallacycle, which initiates polymerization. The isobutylene was removed by freeze-pump-thaw degassing before the polymerization was started (see Experimental Section).

36. The second block contained a small amount of polybenzonorbornadiene because of residual monomer present from the previous block. Typically, the blocks synthesized contained a minor amount of the other polymer. The living polymer decomposes in the absence of monomer at 70°C. Therefore, the polymerizations were run to 95% completion.

37. See the section on end capping of polynorbornene in this chapter.

38. The procedure for the synthesis of "titanocene" was provided by the J. E. Bercaw research group, California Institute of Technology.

39. The significant quantities of ozone present in the atmosphere in Pasadena, CA, may have accelerated this process. Samples of polynorbornene containing 1% BHT (2,6-di-*tert*-butyl-4-methylphenol) by weight were completely air-stable over several months.

40. Thermal instability of metallacycles in solution has been previously observed. See Ref. 6.

41. This section is part of a more complete study on this catalyst system: see Ref. 32a.

42. For similar results: Dolgolplosk, B. A.; Makavetsty, T. G.; Golenko, T. G.; Korshak, Y. U.; Timyakova, E. I. *Eur. Polym. J.* **1974**, *10*, 901.

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44. In a typical experiment with [W] = 0.012 M and [norbornene] = 0.628 M, the rate was 18 eq/hr.

45. The following signals appeared, each of approximately equal intensity (30% integration of one proton of original catalyst): δ 6.72 (t, J= 7 Hz), 6.26 (t, J= 8 Hz), 4.73 (m), 4.23 (m), 3.67 (m), 0.55 (t, J = 8 Hz), 0.28 (t, J = 8 Hz), – 0.02 (br s). Other additional peaks may be obscured by polymer. Upon use of norbornene- d_2 (deuterated at the double bond), only polymer olefinic signals were observable by ^{2}H NMR. The corresponding ^{1}H NMR was missing the signals at δ 6.26, 4.73 and – 0.02.

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