Synthesis, Characterization, and Reactivity of Permethyltitanocene Monoethylene Complex

Thesis by

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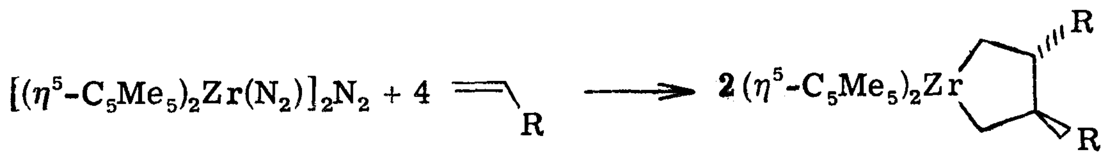
Introduction

The lability of the dinitrogen ligands for the compounds $[(\eta^5\text{-}C_5Me_5)_2M]_2(N_2)_n$ [M = Ti n = 1; M = Zr n = 3] makes them convenient sources of the very reactive fragments $(\eta^5\text{-}C_5Me_5)_2M$.[1,2] Previously, the reactions of these electron deficient metallocenes with the π acids CO, olefins, acetylenes, isocyanides, and nitriles have been investigated.[3,4] During the course of this work it was found that the reaction of $[(\eta^5\text{-}C_5Me_5)_2Zr]_2(N_2)_3$ **1** and ethylene, propylene or 1-butene in toluene at room temperature gives bis(pentamethylcyclopentadienyl)zirconacyclopentanes **2** in quantitative yield (eq 1).[5]



(1)

1 **2**

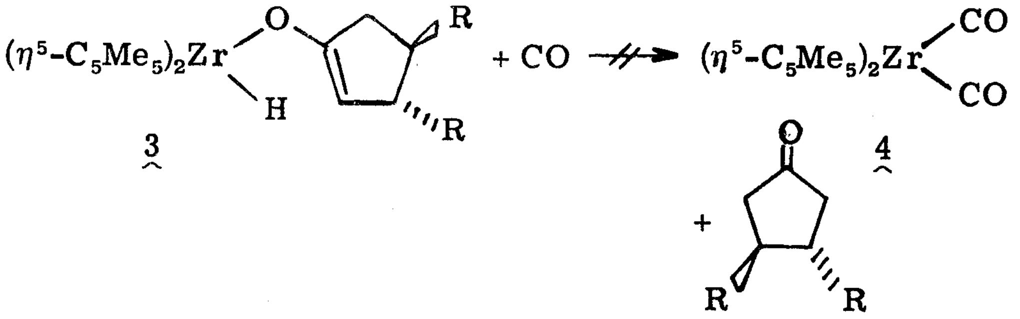
(R = H, CH_3, CH_2CH_3)

Zirconacyclopentanes react with carbon monoxide according to equation 2. The zirconium enolates formed were stable to further

(2)

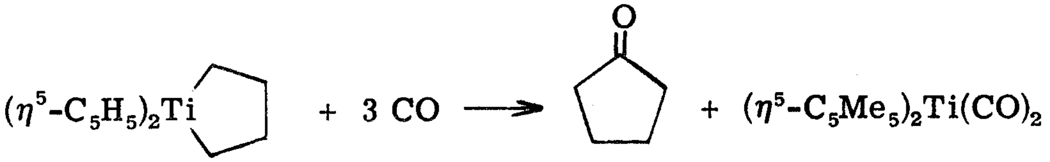
2 **3**

reaction with CO (e.g. eq 3) at 25°C.



3 4 (3)

In contrast, Whitesides reported the reaction of CO with an analogous titanocyclopentane yields titanocene dicarbonyl and free cyclopentanone (eq. 4).[6] This metallocycle, which was



5 6 (4)

prepared from 1,4-dilithiobutane and $(\eta^5\text{-}C_5H_5)_2TiCl_2$, was much less stable than the zirconium analog, decomposing above -40°C. Production of cyclopentanone was not catalytic under these reaction conditions.

As can be seen from the above example, there are often differences between the organometallic chemistry of titanium and zirconium.[7,8] In addition, it has frequently been observed that the pentamethylcyclopentadienyl ligand leads to transition metal complexes of greater stability than those with the $(\eta^5\text{-}C_5H_5)$ ligand.[9-11]

The possibility of generating a catalytic synthesis of substituted cyclopentanones from olefins and carbon monoxide starting with $[(\eta^5\text{-}C_5Me_5)_2Ti]_2N_2$ as a source of $(\eta^5\text{-}C_5Me_5)_2Ti$ was therefore investigated. The greater steric constraints imposed by $(\eta^5\text{-}C_5Me_5)_2Ti$, relative to $(\eta^5\text{-}C_5Me_5)_2Zr$, did result in different chemistry, but not of the type that was originally anticipated.

Results and Discussion

Whereas the complex $[(\eta^5\text{-}C_5Me_5)_2Zr(N_2)]_2(N_2)$ reacts with 1 atm ethylene at 25° in toluene to give bis(pentamethylcyclopentadienyl)zirconacyclopentane in quantitative yield (^1H NMR), $[(\eta^5\text{-}C_5Me_5)_2Ti]_2N_2$ (**7**) reacts with ethylene under analogous conditions to give primarily a bis(pentamethylcyclopentadienyl)titanium monoethylene complex (**8**), which may be isolated as bright green crystals (eq 5).

$$\underset{\mathbf{7}}{[(\eta^5\text{-}C_5Me_5)Ti]_2N_2} + 2C_2H_4 \longrightarrow \underset{\mathbf{8}}{2(\eta^5\text{-}C_5Me_5)_2Ti(\eta^2\text{-}C_2H_4)} + N_2 \qquad (5)$$

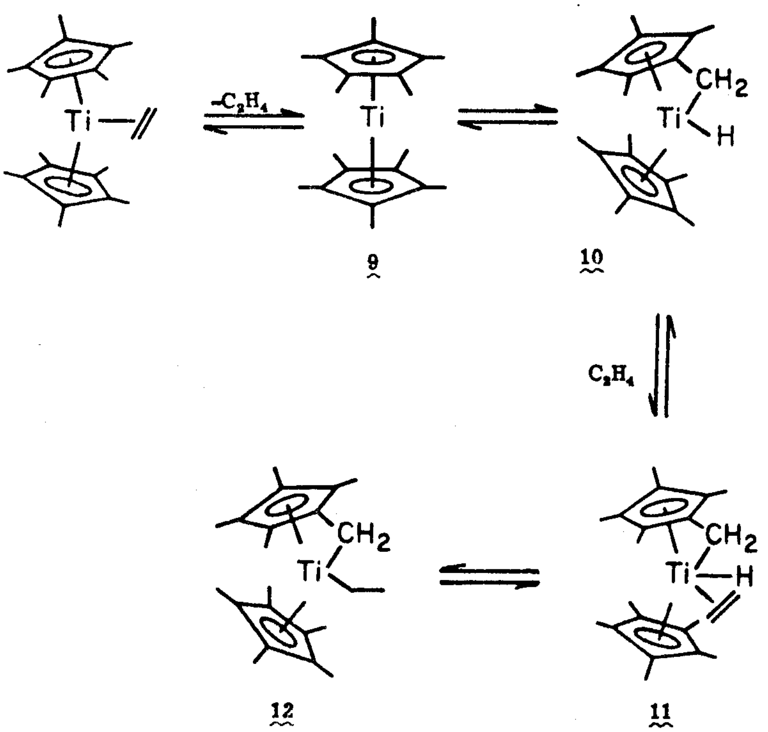
Toepler pump measurements indicated 0.96 mol ± 0.05 mol ethylene per mol titanium is taken up in reaction 5. Molecular weight measurements indicate that **8** is monomeric in benzene. Proton NMR spectra in benzene-$\underline{d}_6$ exhibit a singlet at 1.63 δ, attributable to the pentamethylcyclopentadienyl protons, and a singlet at 1.91 δ, due to the protons of coordinated ethylene. An upfield shift of this magnitude for the olefinic protons upon coordination has been attributed to a major contribution of the metallocyclopropane type resonance structure.[12,13]

Complex 8 may also be prepared in good yield by reduction of $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ with 2% sodium amalgam in toluene under one atmosphere of ethylene (see Experimental).

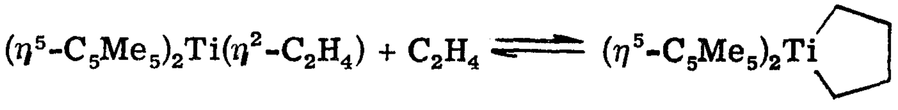
$$(\eta^5\text{-}C_5Me_5)_2TiCl_2 + 2Na + C_2H_4 \longrightarrow (\eta^5\text{-}C_5Me_5)_2Ti(\eta^2\text{-}C_2H_4) + 2NaCl \tag{6}$$

Hydrogen-deuterium exchange between the methyl groups of the $(\eta^5\text{-}C_5Me_5)$ ligands and ethylene is observed for $\{\eta^5\text{-}C_5(CH_3)_5\}_2Ti\text{-}(\eta^2\text{-}C_2D_4)$. In the presence of excess C_2D_4 exchange is observed for both free and complexed ethylene. By analogy with mechanisms of H/D exchange proposed earlier for $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ and $(\eta^5\text{-}C_5Me_5)_2Zr(H)(CH_2CHMe_2)$, a mechanism such as that shown in Scheme I appears to be operative.[12, 13]

Scheme I



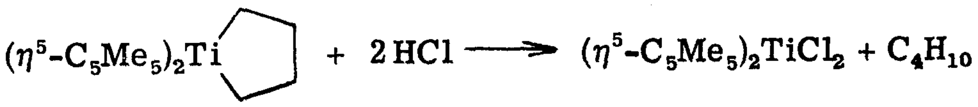
In the presence of excess ethylene a new singlet is observed in the ^{1}H NMR spectrum of 8 which is assigned to the (η^5-C_5Me_5) protons of bis(pentamethylcyclopentadienyl)titanocyclopentane (eq 7).


(7)

8 13

This assignment is supported by the observation that treatment of 8 with *ca* 10 atm ethylene and removal of excess ethylene at -80°, followed by treatment with excess HCl releases a 60:40 mixture of ethane and butane in approximate agreement with the ratio of (η^5-C_5Me_5) signals for 8 and 13 observed under these conditions by ^{1}H NMR spectrometry. The reversibility of eq 7 is demonstrated by the

$$(\eta^5\text{-}C_5Me_5)_2Ti(C_2H_4) + 2\,HCl \longrightarrow (\eta^5\text{-}C_5Me_5)_2TiCl_2 + C_2H_6 \qquad (8)$$


(9)

complete recovery of 8 when toluene and excess ethylene are removed from a mixture of 8 and 13 under reduced pressure at 25°. Furthermore, the log of K_{eq} for eq 7 varies linearly with temperature as expected (Figure 1).

Complex 10, when treated with hydrogen, methyl iodide, or carbon monoxide yielded the complexes (η^5-C_5Me_5)$_2$TiH$_2$, (η^5-C_5Me_5)$_2$Ti(CH$_3$)(I), and (η^5-C_5Me_5)$_2$Ti(CO)$_2$, (eqs 10-12).

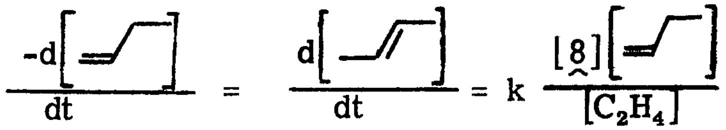
$$10 + 2H_2 \longrightarrow C_2H_6 + (\eta^5\text{-}C_5Me_5)_2TiH_2 \tag{10}$$

$$10 + 2CO \longrightarrow C_2H_4 + (\eta^5\text{-}C_5Me_5)_2Ti(CO)_2 \tag{11}$$

$$10 + MeI \longrightarrow C_2H_4 + (\eta^5\text{-}C_5Me_5)_2Ti(CH_3)(I) \tag{12}$$

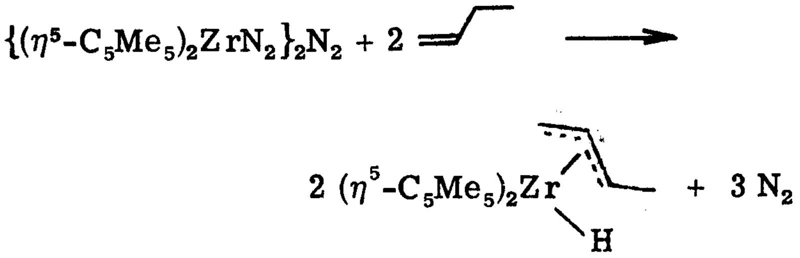
No stable adducts were isolated from the reaction of $[(\eta^5\text{-}C_5Me_5)_2Ti]_2N_2$ with propene. For this olefin complete displacement of N_2 from 7 occurred only under forcing conditions, which resulted in a large number of unidentified products. Similarly, no clean conversion of $[(\eta^5\text{-}C_5Me_5)_2Ti]_2N_2$ (7) to an olefin adduct could be observed with either 1-butene or 1-hexene; however, these primary olefins were rapidly and catalytically converted to <u>trans</u>-2-butene and trans-2-hexene, respectively, in high yield in the presence of 7. The ethylene adduct 8 also effects olefin isomerization, but at a rate more amenable to kinetic studies. The isomerization exhibits a first order dependence on both 8 and 1-butene with E_a = 23.8 (1.4) kcal• mol^{-1} Furthermore, the rate of isomerization of 1-butene is inhibited by added ethylene. The rate of isomerization of 1-butene at 106 °C containing 0.0253 - 0.277 <u>M</u> added ethylene appears to vary linearly with $[C_2H_4]^{-1}$ with an intercept ($[C_2H_4] \rightarrow \infty$) of zero, within experimental error (Figure 2). Since under these conditions the concentration of 13 is diminishingly small (13:8 $\leq$ 0.004 by extrapolation from Figure 1), the observed $[C_2H_4]^{-1}$ dependence of the rate of

1-butene isomerization is consistent with $(\eta^5\text{-}C_5Me_5)_2Ti$ as the catalytically active species, generated by dissociation of ethylene from **8**, or more readily by dissociation of N_2 from **7**. Thus the rate law observed obeys that of eq 13.



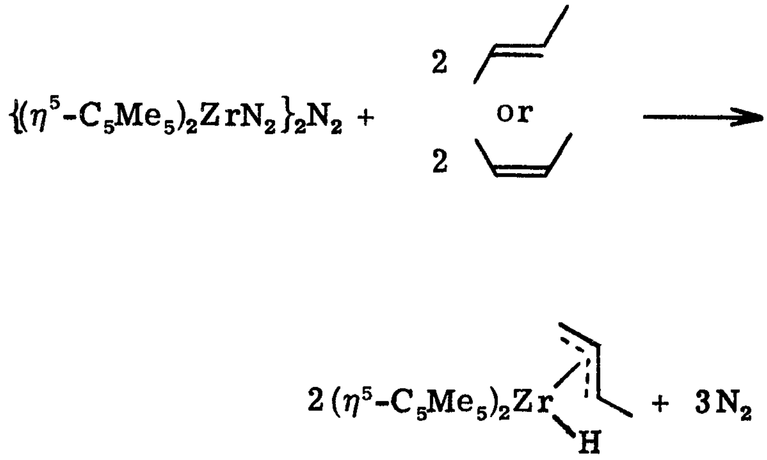
(13)

Whereas no intermediates could be detected directly in the $(\eta^5\text{-}C_5Me_5)_2Ti$ catalyzed isomerization of 1-butene or 1-hexene, some previous results from our laboratory with the analogous zirconium system suggest a probable mechanism.[5, 13] Treatment of $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ with 2.0 equivalents of 1-butene yields a stable η^3-allyl hydride complex (**14**) (eq 14).



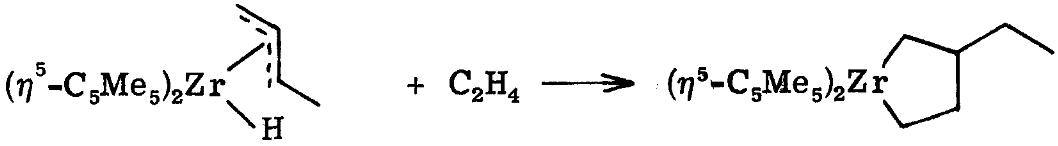
(14)

With cis- or trans-2-butene, even in excess, this same trans-allyl hydride complex is obtained (eq 15). Furthermore, ethylene

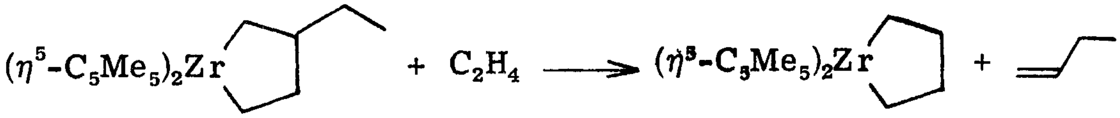


(15)

rapidly and quantitatively displaces 1-butene from **14** as shown in eqs 16 and 17. These reactions (and their microscopic reverse) form



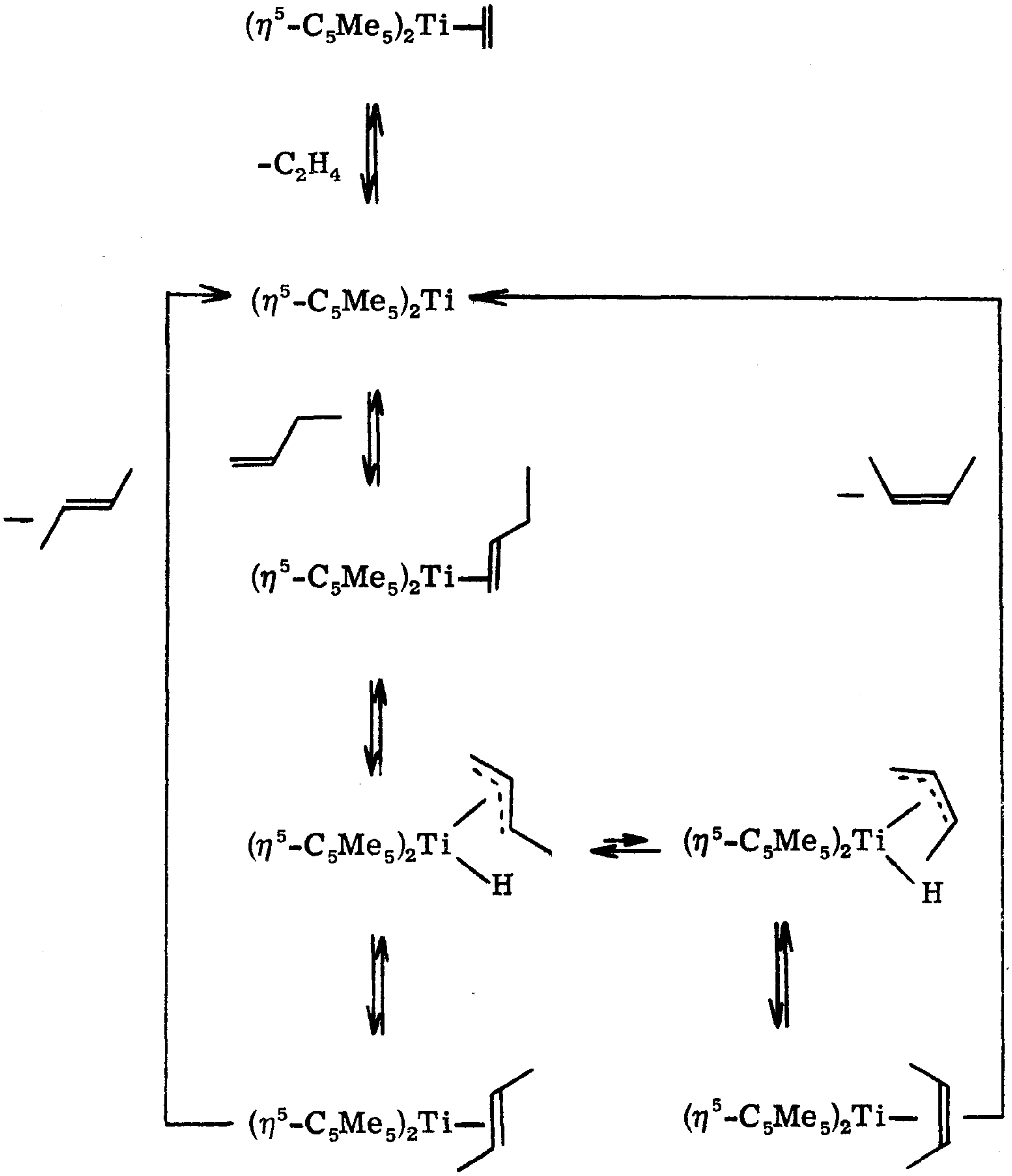
(16)



(17)

the framework of the proposed mechanism outlined in Scheme II.

Scheme II



The primary differences between the permethyltitanocene and permethylzirconocene systems are the relative stabilities of the mono-olefin complexes, allyl hydride, and metallacyclopentanes. Unlike the very stable (to 120°C) zirconocyclopentanes, titanacyclopentanes do not provide a thermodynamic "sink", presumably due to unfavorable steric crowding with the bulky (η^5-C_5Me_5) rings about the smaller titanium center. This feature thus allows for a much more active olefin isomerization catalyst.

The mechanism of Scheme II could be consistent with the observed rate law and may also be used to explain the high stereospecificity of the isomerizations of 1-butene and 1-hexene. No cis-2-butene is observed until well after a thermodynamic mixture of 1-butene and trans-2-butene (11% and 89%, respectively, at 110°C)[14] is obtained in the isomerization. The initial absence of cis-2-butene may be understood in terms of the steric requirement of the catalyst; its precursor, the cis-allyl hydride complex of permethyltitanocene (Scheme II) is expected to be sterically disfavored relative to the trans-allyl hydride complex, since the contact between the methyl groups of the (η^5-C_5Me_5) rings and the methyl substituent of the allyl group is minimized for the trans-allyl ligand. This preference for the trans-allyl geometry is manifested in the zirconium system as well, since only the trans isomer is observed even when

$(\eta^5\text{-}C_5Me_5)_2Zr(\eta^3\text{-}C_4H_7)(H)$ is prepared from $\{(\eta^5\text{-}C_5Me_5)_2ZrN_2\}_2N_2$ and cis-2-butene. Similar steric arguments may be offered to explain the absence of 3-hexenes even after long periods of isomerization of 1-hexene (3.4% 1-hexene and 96.6% trans-2-hexene after 72 hrs at 81 °C). Apparently none of the allylic intermediates which would lead to 3-hexenes (or cis-2-hexene) are formed due to the steric crowding for these species.

The permethyltitanocene system thus appears to belong to a rather small class of olefin isomerization catalysts[15,16] which operate via the fundamental transformation (Scheme III):

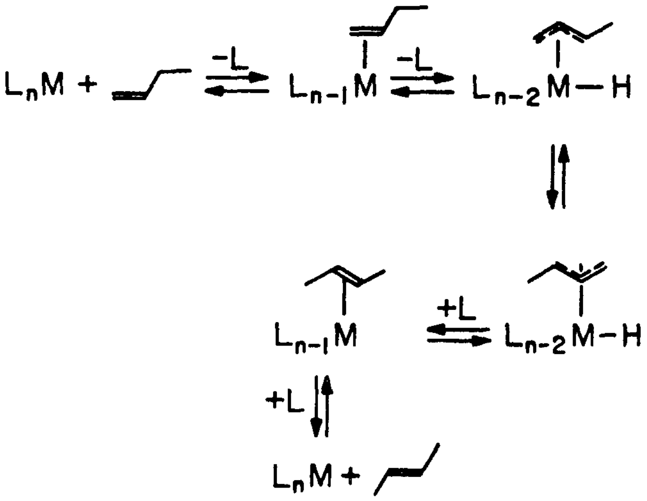
$$\text{M(olefin)} \rightleftharpoons \text{M(allyl)(H)} \rightleftharpoons \text{M(olefin}'\text{)}.$$

A much larger class involves (an often fortuitous) transition metal hydride and operates via (Scheme IV):

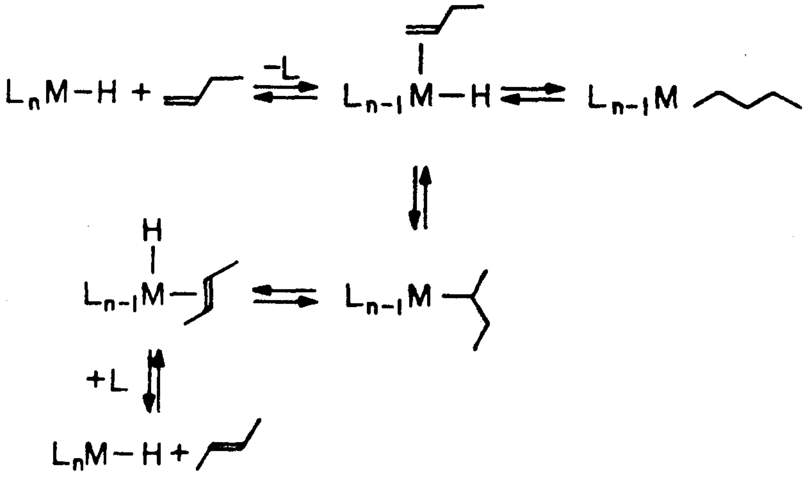
$$\text{M(H)(olefin)} \rightleftharpoons \text{M(alkyl)} \rightleftharpoons \text{M(H)(olefin}'\text{)}.$$

Olefin isomerization catalyzed by iron(O)carbonyls ($Fe(CO)_5$, $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$) thus far represents the only system in which the π-allyl hydride mechanism (Scheme III) has been unambiguously established.[17-21] The classic differentiation between Scheme III and Scheme IV is a cross-over experiment in which a mixture of deuterated and nondeuterated olefins are isomerized.[21] In this manner it is possible

Scheme III



Scheme IV



to establish whether the isomerization is intramolecular, and thus proceeds without intermolecular exchange of hydrogen and deuterium between olefins as would be expected if the isomerization proceeds via Scheme IV. The isomerization of a 1:1 mixture of 1-butene-$\underline{d}_8$ and 1-butene-$\underline{d}_0$ has been carried out, and gc/ms analysis of the results is now in progress. These experiments are described in the Appendix.

Conclusion

Differences between the chemistry of $(\eta^5\text{-}C_5Me_5)_2Zr$ and $(\eta^5\text{-}C_5Me_5)_2Ti$ fragments demonstrates the greater steric constraints imposed by the smaller metal center especially when flanked by the bulky (C_5Me_5) ligand system. Steric constraints disfavor the formation of stable metallacyclopentane derivatives of $(\eta^5\text{-}C_5Me_5)_2Ti$ and control the stereochemistry of olefin isomerization effected by $(\eta^5\text{-}C_5Me_5)_2Ti(C_2H_4)$. Primary olefins, 1-butene and 1-hexene, are isomerized to thermodynamic mixtures of the primary olefin and the trans-2 isomer, uncontaminated by the cis-2-isomer or in the case of hexene by any of the 3-olefin. The mechanism of olefin isomerization is currently under investigation and at this time is thought to proceed via a π-allyl hydride intermediate. This will represent the second well documented case of olefin isomerization mediated via the π-allyl hydride mechanism.

Experimental

Physical Measurements. ^{1}H NMR spectra were recorded on a Varian EM 390 Spectrometer. Infrared spectra were recorded on a Beckman IR 12 Model Spectrophotometer. Infrared spectra of solids were recorded as Nujol mulls using NaCl plates and spectra of gases were measured using a 10 cm pathlength cell (NaCl windows) with a stopcock and a ball joint for attachment to a vacuum line. Elemental analysis and molecular weight determinations were performed by Alfred Bernhardt Analytische Laboratorien, Germany.

Materials. All manipulations were performed using high-vacuum or glovebox techniques. Solvents were purified by vacuum transfer from $LiAlH_4$, then from "titanocene", prepared as described earlier.[1] NMR solvents, benzene-$\underline{d}_6$ (Aldrich) and toluene-$\underline{d}_8$ (Stohler), were vacuum distilled from 4 Å molecular sieves, then from "titanocene". Argon and nitrogen were purified by passage over activated, linde 4 Å molecular sieves and MnO on vermiculite.[2] Carbon monoxide (Matheson) was used directly from the cylinder. Ethylene (Union Carbide), propylene, 1-butene, cis-2-butene, trans-2-butene, anhydrous HCl (all Matheson) and 1-butene-$\underline{d}_8$ (Merck, Sharpe, and Dohme) were purified by at least two freeze, pump, thaw cycles at -196°C.

1-hexene (Aldrich) was vacuum distilled from sodium metal. Methyl iodide (MCB) was vacuum transferred from calcium hydride. $[(\eta^5\text{-}C_5Me_5)_2Ti]_2N_2$ was prepared as previously described.[3]

(1) $(C_5Me_5)_2TiC_2H_4$. (a) from $[(C_5Me_5)_2Ti]_2N_2$. To a stirred solution of 200 mg (0.301 mmol) $[(\eta^5\text{-}C_5Me_5)_2Ti]_2N_2$ in 20 mls toluene at -78° was added 1.55 mmol ethylene. The dry ice bath was removed and the solution allowed to warm slowly to 25°, then magnetically stirred overnight. Residual gases were removed *in vacuo* and passed through three -196° traps. Nitrogen (0.353 mmol, 1.17 mmol/mmol **1**) was collected with a Toepler pump . After warming the traps to -78°, 0.97 mmol ethylene was collected; thus 0.58 mmol C_2H_4 (0.96 mmol/mmol Ti) was consumed. Toluene was removed *in vacuo* and the bright green crystals which formed in the reduced volume of solution were isolated by filtration: 79 mg (38%); ^{1}H NMR (benzene-$\underline{d}_6$), δ 1.63 (s, 30 H, $\eta^5\text{-}C_5(C\underline{H}_3)_5$), δ 1.91 (s, 4 H, $\eta^2\text{-}C_2\underline{H}_4$).

(b) from $(\eta^5\text{-}C_5Me_5)TiCl_2$. To a stirred solution of 2.00 g (5.16 mmol) of $(\eta^5\text{-}C_5Me_5)_2TiCl_2$ in 100 ml toluene was added 14.4 ml of mercury and 1.8 ml of 40% sodium amalgam via syringe against a counterflow of argon. Upon completion of the addition argon was immediately replaced with an atmosphere of ethylene. The solution was maintained at room temperature and magnetically stirred for three days or until gas uptake was complete (no noticeable change on the manometer for 6 hrs). Residual gases were removed by three freeze, pump, thaw cycles and the reaction vessel was transferred to the glove box. After the mercury settled, the solution was filtered twice through sintered glass frits and transferred to a vacuum-line frit assembly. Bright-green crystals were isolated from a reduced volume of the toluene solution by filtration and dried *in vacuo* (56%) ^1H NMR (benzene-d_6), δ 1.63 (s, 30 H, $C_5(C\underline{H}_3)_5$), δ 1.91 (s, 4 H, $C_2\underline{H}_4$).

Anal. calcd. for $C_{12}H_{34}Ti$: C, 76.28; H, 9.89. Found: C, 76.14; H, 9.89. Mol weight: Calcd, 346; Found, 334 (osmometry in benzene).

(2) Reaction of $(\eta^5\text{-}C_5Me_5)_2TiC_2H_4$ with H_2. To an NMR tube was added 30 mg (0.867 mmol) of **5**. Benzene-$\underline{d}_6$ was added by vacuum transfer and the tube was sealed under 700 torr H_2 while cooling to -78°. ^1H NMR taken at ambient temperatures within 5 minutes after sample preparation showed quantitative formation of $(\eta^5\text{-}C_5Me_5)_2TiH_2$ (based on comparison with spectra of authentic $(\eta^5\text{-}C_5Me_5)_2TiH_2$).

(3) Reaction of $(\eta^5\text{-}C_5Me_5)_2TiC_2H_4$ and MeI. To an NMR tube was added 42 mg (0.12 mmol) of **5**. Benzene-$\underline{d}_6$ was added by vacuum transfer. Subsequently 0.600 mmol MeI was condensed into the tube at -196° and the tube was sealed *in vacuo.* ^1H NMR spectra taken at ambient temperatures within 5 minutes of sample preparation showed peaks characteristic of both the starting material and products.

^1H NMR spectra taken approximately 1 hr after sample preparation showed quantitative formation of $(\eta^5\text{-}C_5Me_5)_2TiMeI$ (based on comparison to the authentic sample ^1H NMR (benzene-d_6), δ 1.56 (s, 30 H, $C(C\underline{H}_3)_5$), δ 1.86 (3 H, $C\underline{H}_3$).

(4) Reaction of $(\eta^5\text{-}C_5Me_5)_2TiC_2H_4$ and CO. To an NMR tube was added 37 mg (0.107 mmol) of $\underset{\frown}{5}$. Benzene-d_6 was added by vacuum transfer, and the tube was sealed under 700 torr CO while cooling to -78°. ^1H NMR spectra taken at ambient temperature within 5 minutes of sample preparation showed quantitative formation of $(\eta^5\text{-}C_5Me_5)_2Ti(CO)_2$.

(5) Reaction of $[(\eta^5\text{-}C_5Me_5)_2Ti]_2N_2$ and C_2D_4. To an NMR tube was added 29 mg (0.044 mmol) $[(\eta^5\text{-}C_5Me_5)_2Ti]_2N_2$. Toluene-$\underline{d}_8$ was added by vacuum transfer. At -196° ethylene-$\underline{d}_7$ (0.58 mmol) was condensed into the tube, which was sealed in vacuo. Incorporation of protons into free ethylene was noticeable (^1H NMR) only upon heating the tube to 54° in an oil bath for 15 minutes. No reaction was noted at room temperature, even after 48 hours.

(6) Reaction of $(\eta^5\text{-}C_5Me_5)_2TiC_2H_4$ and excess ethylene. $(\eta^5\text{-}C_5Me_5)_2TiC_2H_4$ (50.5 mg, 0.146 mmol) was transferred to a 50 ml bomb and toluene was added by vacuum transfer. Ethylene (13.2 moles) was condensed into the evacuated vessel at -196°. The apparatus was allowed to warm and then magnetically stirred overnight. The solution was then cooled to -78° and excess ethylene removed *in vacuo*. While the bomb was maintained at -196°, 0.784 mmol anhydrous HCl was added. The solution was warmed to -78° resulting in an instantaneous reaction. Residual gases were pumped into a -196 trap and, subsequently, into a gas bulb containing 120 mg NaOH in 1 ml H_2O. Gases were identified by IR and ^1H NMR as ethane and butene in a 60:40 ratio.

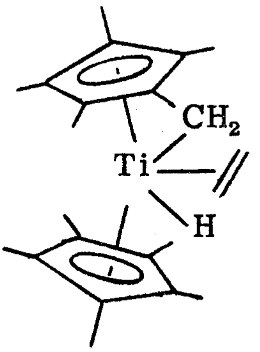
(7) Measurement at the rate of isomerization of 1-butene in the presence of $(\eta^5\text{-}C_5Me_5)_2TiC_2H_4$. Standard solutions were prepared containing 61.60 ± 0.18 mg/ml (0.18 M), $(\eta^5\text{-}C_5(CH_3)_5)_2TiC_2H_4$ and 54.63 ± 0.68 mg/ml (0.29 M) of ferrocene as an internal standard. To 0.5 ml of this solution in an NMR tube maintained at -196° was added 0.92 mmol 1-butene, and the tube was sealed. The tube was heated in a constant temperature oil bath and rates at reaction measured by ^1H NMR spectrometry, E_a was determined by measuring the rate at 334, 345, 354 K.

(8) Measurement of equilibrium constant for eq 7. To an NMR was added 67.4 mg (0.364 mmol) $(\eta^5\text{-}C_5H_5)_2Fe$ and 22.2 mg (0.064 mmol) $(\eta^5\text{-}C_5Me_5)_2TiC_2H_4$. Toluene-$d^8$ (0.5 ml) was distilled onto the solids *in vacuo* and 0.7103 mmols ethylene was condensed into the tube at -196°C. The tube was sealed and concentrations of $(\eta^5\text{-}C_5Me_5)_2TiC_2H_4$ and $(\eta^5\text{-}C_5Me_5)_2TiC_4H_8$ were measured by variable temperature NMR (-20 - +65°C).

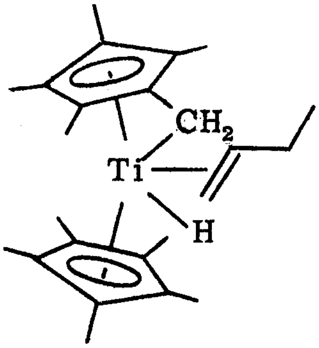
Appendix

Awaited GC mass spectral data from several experiments outlined in this section will further elucidate the mechanism of olefin isomerization. As stated previously one distinguishing characteristic of olefin isomerization via π-allyl hydrides is the lack of scrambling predicted from the coisomerization of 1-butene-$\underline{d}_8$ and 1-butene-$\underline{d}_0$ (cf. Scheme III). A 50:50 mixture of d-butene-$\underline{d}_8$ and 1-butene-$\underline{d}_0$ was co-condensed into a solution of $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{C}_2\text{H}_4)$ in benzene-$\underline{d}_6$ and allowed to react through two half lives. Data from this experiment will also determine the existence of a kinetic isotope effect.

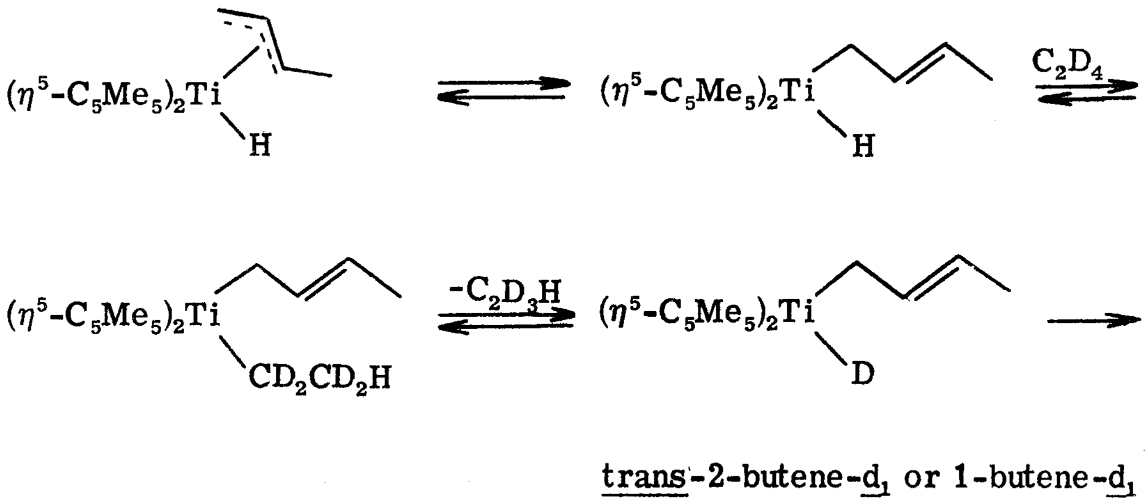
During the course of this work it was observed that ethylene-$\underline{d}_4$ exchanged deuterium for protons from the pentamethylcyclopentadienyl ligands of $[(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}]_2\text{N}_2$ or $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{C}_2\text{H}_4)$ (cf. Scheme I). A control experiment was run to determine whether proton exchange between $(\eta^5\text{-C}_5\text{Me}_5)_2\text{Ti}(\text{C}_2\text{H}_4)$ and 1-butene-$\underline{d}_8$ was possible by a similar mechanism. Exchange seems unlikely based on the greater steric crowding predicted in the analogous intermediates:



vs.



To determine if deuterium incorporation into 1-butene-$\underline{d}_0$ could occur via ethylene insertion into the π-allyl hydride intermediate (Scheme V), 1-butene-$\underline{d}_0$ was isomerized with $(\eta^5\text{-}C_5Me_5)_2Ti(C_2H_4)$ in the presence of added ethylene-$\underline{d}_4$. Arguments based on steric crowding predict that such a process should be unfavorable.



Appendix Experimental

(1) Reaction of 1-butene-d_8 and $(\eta^5\text{-}C_5Me_5)_2TiC_2H_4$. To an NMR tube was added 0.5 ml of the standard kinetic solution (0.9 mmols $(\eta^5\text{-}C_5Me_5)_2TiC_2H_4$). After two freeze pump thaw cycles 0.58 mmol d^8 1-butene was condensed into the tube at -196°C. The sealed tube was maintained at 63°C is a constant temperature oil bath for 5 hr. The tube was then opened and gas collected by freeze pump thaw cycles.

(2) Reaction of 1-butene-d_8 and 1-butene-d_0 and $(\eta^5\text{-}C_5Me_5)_2Ti(C_2H_4)$. (a) To an NMR tube was added 30 mg (0.0876 mmols) $(\eta^5\text{-}C_5Me_5)_2TiC_2H_4$. After evacuations 0.5 mls benzene-d_6 and 0.45 mmols each of 1-butene-d_0 and 1-butene-d_8. The sealed tube was maintained at 63°C in a constant temperature oil bath for 1 hr 45 min. The tube was opened and gas collected by freeze pump thaw cycles.

(b) 5 mls standard kinetic solution was added to an NMR tube. After the solution was freeze pump thawed 0.44 mmol each 1-butene-d_8 and 1-butene-d_0 was condensed into the tube. The sealed tube was maintained at 61° in a constant temperature oil bath for 1 hr 45 min. The tube was opened and gas collected by freeze pump thaw cycles.

(3) Reaction of ethylene-d_4, 1-butene-d_0 and $(\eta^5\text{-}C_5Me_5)_2Ti(C_2H_4)$. To an NMR tube was added 0.5 ml of the standard kinetic solution.

After two freeze pump thaw cycles 0.58 mmols 1-butene and 0.29 mmols ethylene-$\underline{d}_4$ were condensed into the tube at -196°C. The sealed tube was maintained at 105°C in a constant temperature oil bath for 1 hr 45 min. The tube was opened and residual gases collected by freeze pump thaw cycles.

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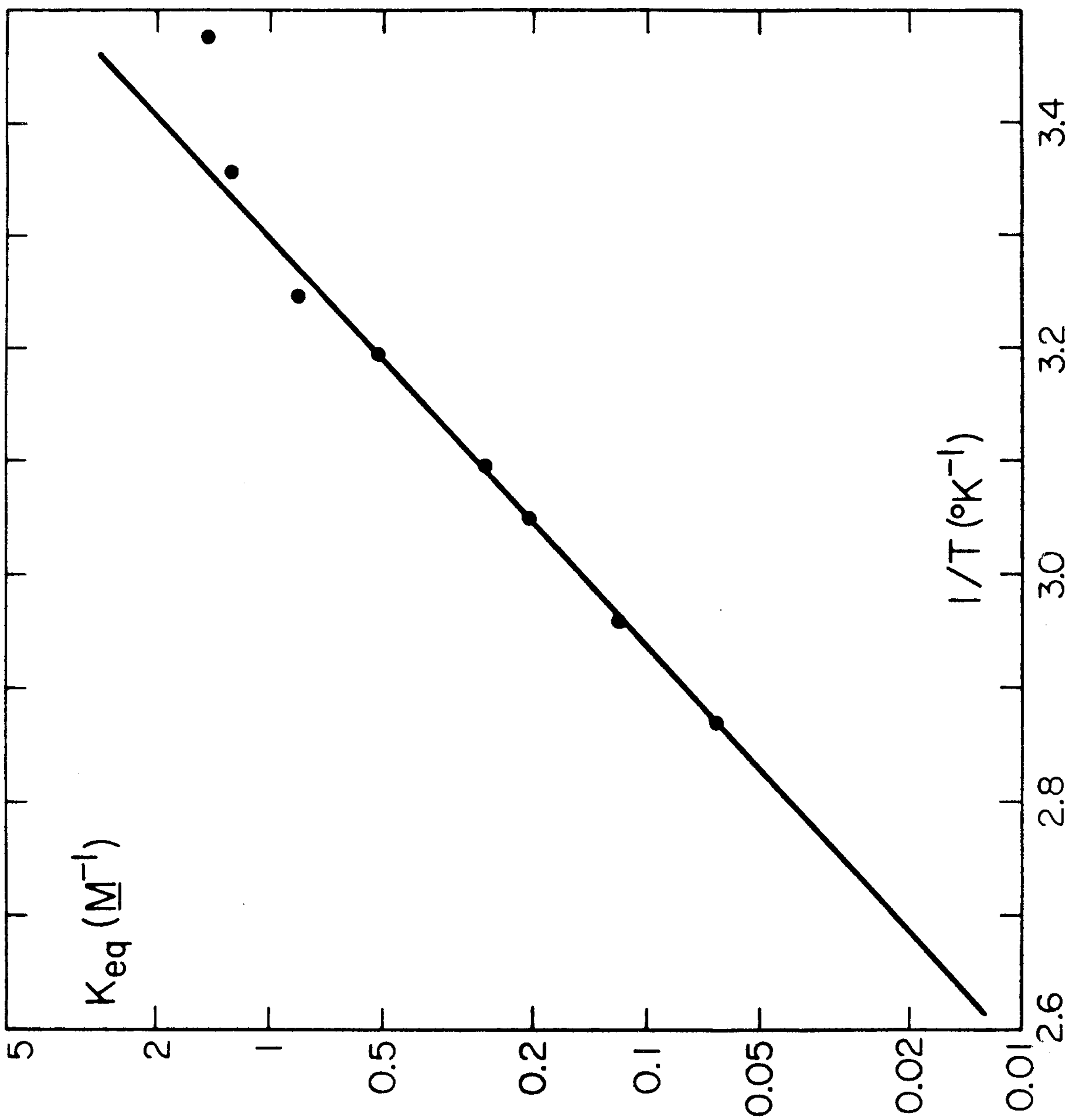

Figure 1. Temperature dependence of K_{eq} for eq 7.

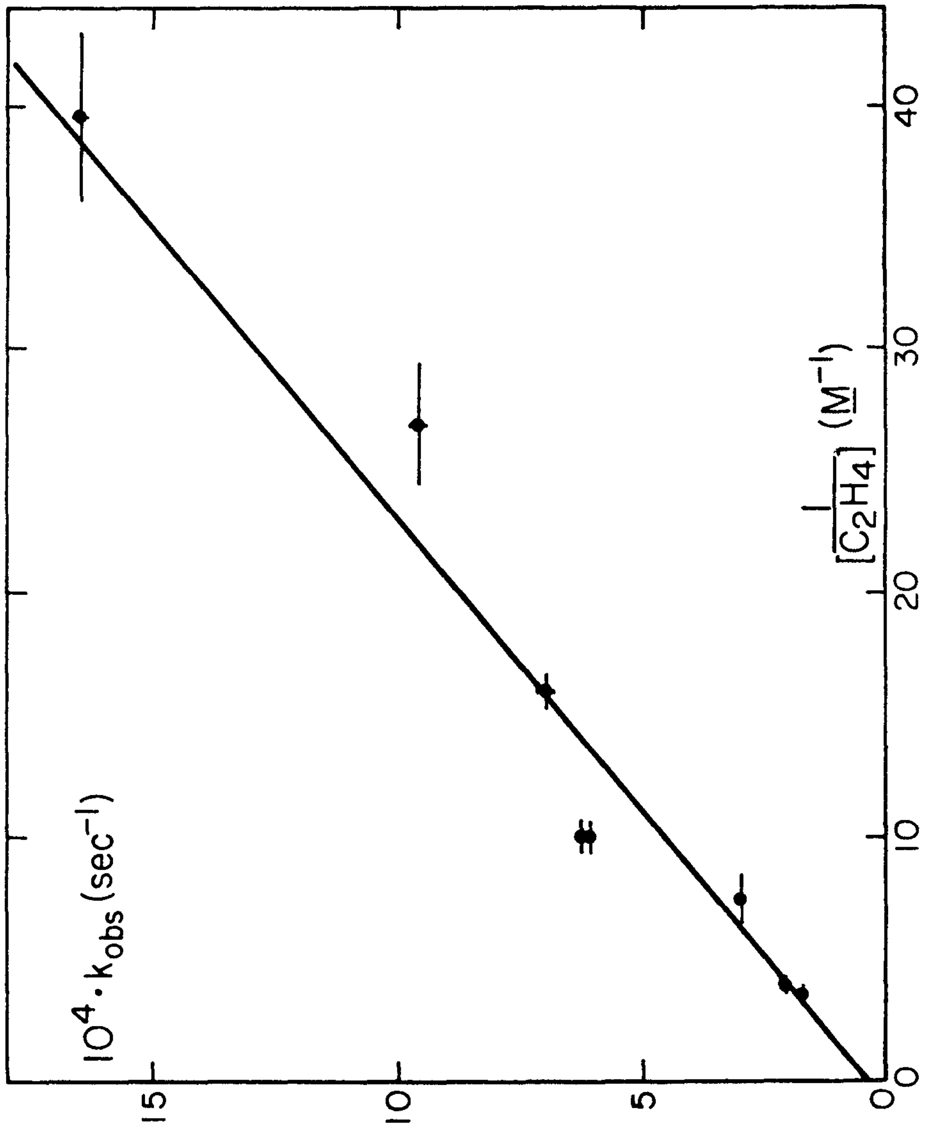

Figure 2. Dependence of rate of isomerization of 1-butene on added ethylene.