

BISBUTADIENE[1,2-BIS(DIMETHYLPHOSPHINO)ETHANE] TITANIUM(0) OLEFIN DIMERIZATIONS CATALYZED BY TITANIUM AND ZIRCONIUM BUTADIENE COMPLEXES

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Summary

The complex $\text{Ti}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$ ($\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$) was prepared by Na/Hg reduction of $\text{TiCl}_4(\text{dmpe})$ in the presence of butadiene. The compound is a poorer Lewis base than is $\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$, as it fails to form seven-coordinate adducts analogously to the Zr complex. Both complexes catalyze the dimerization of ethylene to 1-butene and, by cross dimerization with additional ethylene, 3-methyl-1-pentene and 2-ethyl-1-butene. Propene is converted to 2,3-dimethyl-1-butene. *cis*-2-Butene is very slowly dimerized to 3,4-dimethyl-1-hexene. On the basis of the products formed and their distribution, a mechanism involving formation of a metallocyclopentane complex is proposed. The reaction is first-order in olefin and is slowed by increasing substitution. Formation of a mono(olefin) complex is the probable rate-determining step.

Introduction

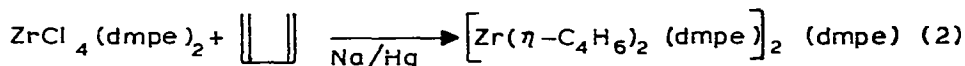
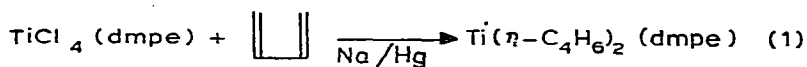
Complexes containing Group IV metals in low oxidation states are generally characterized by extreme reactivity. This reactivity arises from the highly reducing nature of these metal ions and, in some cases, simultaneous coordinative unsaturation. For example, dicyclopentadienyltitanium(II) and related derivatives exhibit both nucleophilic and electrophilic behavior, as exemplified by complexation of nitrogen [1] on the one hand, and reactions involving insertions into CH bonds [1,2] on the other. Indeed, the facility of reactions involving formal oxidation or partial transfer of charge from metal(II) [3] or, in a few cases, metal(0) [4] ($M = \text{Ti, Zr, Hf}$) ions is a ubiquitous feature of Group IV chemistry. Recently, we reported a series of complexes $\text{Zr}(\text{butadiene})_2(\text{dmpe})\text{L}$ ($\text{dmpe} = 1,2\text{-bis}(\text{dimethylphosphino})\text{ethane}$; $\text{L} = \text{Lewis base}$) [5]. Although these species are stabilized by some degree of charge transfer from Zr to the butadiene ligand, they formally contain zirconium(0) and are easily oxidized. Further, these adducts are in equilibrium with the coordinatively unsaturated fragment $\text{Zr}(\text{butadiene})_2(\text{dmpe})$

[5b]. This paper deals with olefin dimerizations catalyzed by this complex, a reaction which proceeds because of the simultaneous coordinative unsaturation and electron rich nature of the metal center. Additionally, we report the preparation and chemistry of the analogous titanium complex for comparative purposes.

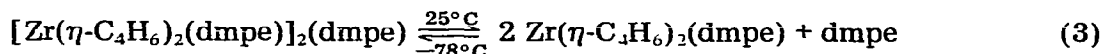
Results and discussion

Ti(η -C₄H₆)₂(dmpe) and its properties

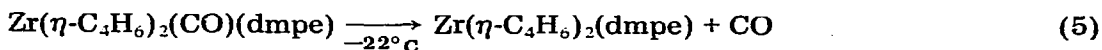
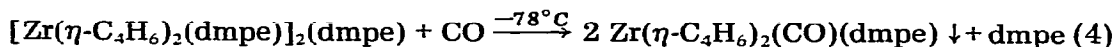
Preparation. In 1965 Chatt reported that reduction of TiCl₄ with sodium naphthalene in the presence of excess dmpe gave successive color changes, suggestive of the formation of low-valent titanium complexes, but that addition of the fourth equivalent of reductant led to the deposition of titanium metal [6]. Apparently, any binary phosphine-titanium(0) or, possibly, naphthalene-titanium(0) complexes* formed in the reaction are not stable. However, in the presence of good π -accepting ligands stable titanium(0) complexes may be isolated. Thus, Na/Hg reduction of TiCl₄(dmpe) [8] in the presence of butadiene affords the, formally, titanium(0) complex indicated in eq. 1. Analogous reactions with ZrCl₄(dmpe)₂ have previously been shown to give the zirconium(0)-



dmpe-bridged dimer in eq. 2 [5]. The coordinatively saturated dimer is in equilibrium with the 16-electron monomer Zr(η -C₄H₆)₂(dmpe), the predominant species at room temperature.



Indeed, this complex has been isolated by the carbonylation-decarbonylation sequence in eq. 4 and 5 [5b].



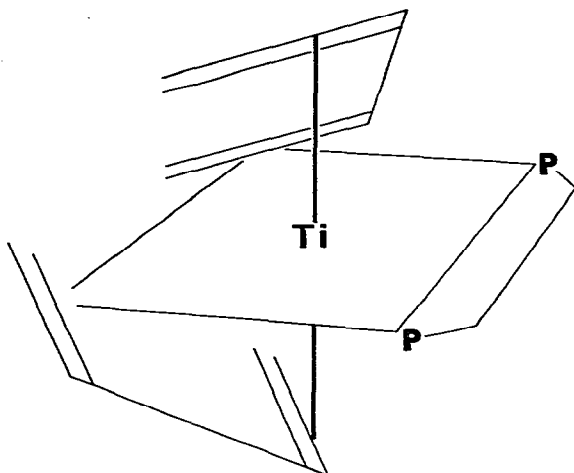
On the basis of its spectroscopic properties, Ti(η -C₄H₆)₂(dmpe) is structurally analogous to the Zr complex, for which a C₂-distorted octahedral structure has been suggested** [5b].

The 16-electron Zr complex is an intense purple; the Ti analog is deep blue.

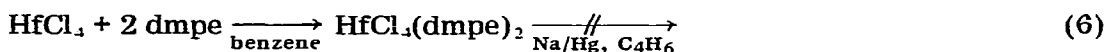
The Hf analog was not accessible by Na/Hg reduction. The adduct HfCl₄(dmpe)₂, prepared by direct reaction (eq. 6), was recovered unchanged after

* Naphthalene complexes are frequently formed when sodium naphthalene is used as a reductant [7].

** This structure accounts for the chemical equivalence of the ends of the dmpe chelate and of the butadiene groups. The methylene carbons are presumed accidentally degenerate or rendered equivalent by an undefined exchange process.

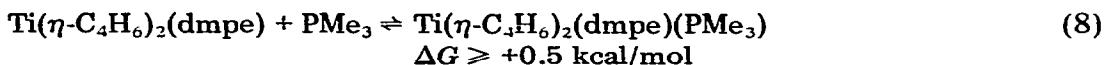
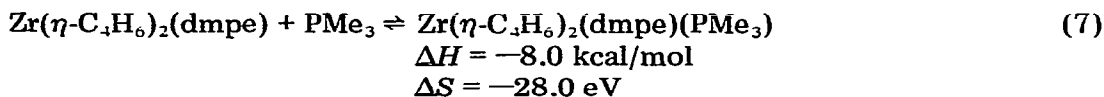


shaking with Na/Hg in the presence of butadiene. A small amount of [Zr-



$(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})_2(\text{dmpe})$ was observed by ^{31}P NMR in these reactions, presumably arising from a Zr impurity in the HfCl_4 .

Comparative Lewis basicity. Although $\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$ readily forms seven-coordinate adducts with small ligands at low temperatures, e.g. formation of the dmpe-bridged dimer and carbonyl adduct in eq. 3 and 5 [5b], The Ti complex does not. Reduction of $\text{TiCl}_4(\text{dmpe})$ in the presence of butadiene and excess dmpe gives only the 16-electron adduct. Similarly, addition of dmpe to $\text{Ti}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$, leaves the Ti complex unchanged. Further, the ^{31}P NMR resonance of $\text{Ti}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$ is unshifted on cooling to -100°C in the presence of dmpe. The Ti complex does not react with 1 atm of CO at -78°C or at 25°C ; the Zr analog reversibly complexes CO at -78°C (eq. 4 and 5) and irreversibly reduces it at 25°C [5b]. Similarly, although $\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$ forms its most stable phosphine adduct with PMe_3 (eq. 7) [5b], no interaction is observed for an equimolar mixture of the Ti complex and PMe_3 at -90°C by ^{31}P NMR. Assuming that 5% of an adduct could have been detected, it follows that ΔG



for adduct formation is more endothermic than $+0.5 \text{ kcal/mol}$ at -90°C .

Solutions of the Ti complex do not react with 1 atm of hydrogen at 25°C . In contrast, the Zr complex rapidly evolves butane on treatment with hydrogen and, in some circumstances, functions as a hydrogenation catalyst [5b].

The reluctance of the Ti complex to expand its coordination sphere in contrast to $\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$ is, presumably, a steric consequence. Similar behavior has been observed for Group IV organometallic and inorganic derivatives in different oxidation states. The complex $(\eta\text{-C}_5\text{Me}_5)_2\text{ZrH}_2$ forms adducts with CO and

PF₃ [9]; apparently, (η -C₅Me₅)₂TiH₂ does not [1b]. Nitrogen forms a bridged adduct, [(η -C₅Me₅)₂Ti]₂(N₂), with (η -C₅Me₅)₂Ti [10] but gives [(η -C₅Me₅)₂Zr-(N₂)₂]₂(N₂) with zirconocene generated in situ [11]. Similarly, although (η -C₆H₆)₂Ti can be isolated from the reaction of Ti vapor and benzene [4a], no stable products are obtained from similar reactions with Hf or Zr vapor unless PMe₃ is present. In the latter case (η -C₆H₆)₂M(PMe₃) (M = Zr, Hf) is produced [4b].

Olefin condensations

Although neither Zr(η -C₄H₆)₂(dmpe) nor the Ti analog form an observable ethylene adduct (as determined by ³¹P NMR measurements), such an adduct is, apparently, kinetically accessible, as both complexes catalyze the dimerization of ethylene and do so with remarkable product selectivity.

Most of the studies described below have been performed with the dmpe-bridged dimer [Zr(η -C₄H₆)₂(dmpe)]₂(dmpe). However, saturated benzene solutions of this complex at room temperature contain the coordinatively unsaturated Zr(η -C₄H₆)₂(dmpe) as the predominant species (ca. 91% [5b]), as shown in eq. 3. The dimeric complex is used as a convenient source of the 16-electron monomer.

Ethylene dimerization and trimerization. Stirring toluene or hexane solutions of [Zr(η -C₄H₆)₂(dmpe)]₂(dmpe) under 1 or more atmospheres of ethylene at temperatures between 50 and 70°C leads to formation of 1-butene and branched trimers of ethylene. Major products and yields for the condensation of ethylene and other olefins are listed in Table 1. The product distribution for ethylene

TABLE 1
PRODUCTS OF OLEFIN CONDENSATIONS CATALYZED BY [Zr(η -C₄H₆)₂(dmpe)]₂(dmpe)

Substrate	Products (% Yield ^a)	Conditions
Ethylene	Ethylene (6) 1-Butene (13) 3-Methyl-1-pentene (29) 2-Ethyl-1-butene (46) 1-Hexene (trace)	Toluene solvent, 320 mmol substrate, 1 mmol catalyst, 70°C, 50 h
Propene	Propene (86) 2,3-Dimethyl-1-butene (9)	Toluene solvent, 320 mmol substrate, 1 mmol catalyst, 70°C, 50 h
Cyclopropane	Cyclopropane (98)	Toluene solvent, 320 mmol substrate, 1 mmol catalyst, 70°C, 50 h
<i>cis</i> -2-Butene	<i>cis</i> -2-Butene (99) 3,4-Dimethyl-1-hexene (1)	Hexane solvent, 123 mmol substrate, 1.3 mmol catalyst, 70°C, 250 h
Isobutene	Isobutene (96) No dimers detected ^b	Hexane solvent, 300 mmol substrate, 1 mmol catalyst, 70°C, 250 h
Butadiene	Butadiene (42) Complex mixture of C ₈ H ₁₂ isomers Polymer	Hexane solvent, 320 mmol substrate, 1 mmol catalyst, 70°C, 50 h
1,7-Octadiene	Complex mixture of other <i>n</i> -octadienes (95)	Neat, 109 mmol substrate, 0.7 mmol catalyst, 110°C, 50 h ^c

^a Mol % of olefin initially present. ^b No C₈ hydrocarbons observed by GLC. ^c No or negligible reaction after heating at 50°C or 70°C, see experimental section.

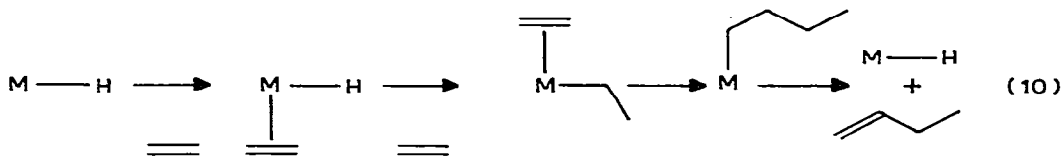
TABLE 2
TIME DEPENDENCE OF PRODUCT DISTRIBUTION FROM ETHYLENE CONDENSATION ^a

Reaction time (h)	Yields ^b		
	Recovered ethylene (%)	1-butene (%)	hexanes (%) ^c
20	60	31	4
50	47	36	12
120	27	45	18

^a Conditions are presented in the experimental section; total consumption of ethylene would represent ca. 120 turnovers. ^b Yields are reported as mol% of ethylene originally present. ^c Hexenes are a mixture of 3-methyl-1-pentene and 2-ethyl-1-butene.

condensation as a function of time is presented in Table 2. Hexenes do not appear in significant concentration until moderate amounts of 1-butene have been formed, suggesting hexenes are formed by codimerization of 1-butene and ethylene, rather than by direct trimerization. Octenes, formed by codimerization of ethylene and hexenes, were not directly observed. However, reactions carried to near completion did show trace amounts of products having retention times similar to n-octane. In addition to the two major branched hexenes, 1-hexene and an unidentified C₆ hydrocarbon were formed in trace amounts. No 2-butene was detected throughout the reaction (<1%).

These products can be accounted for by an insertion mechanism (eq. 10) similar to that proposed for the Rh-catalyzed dimerization of ethylene to 1-butene [12]. However, this mechanism requires M-H elimination-addition steps to



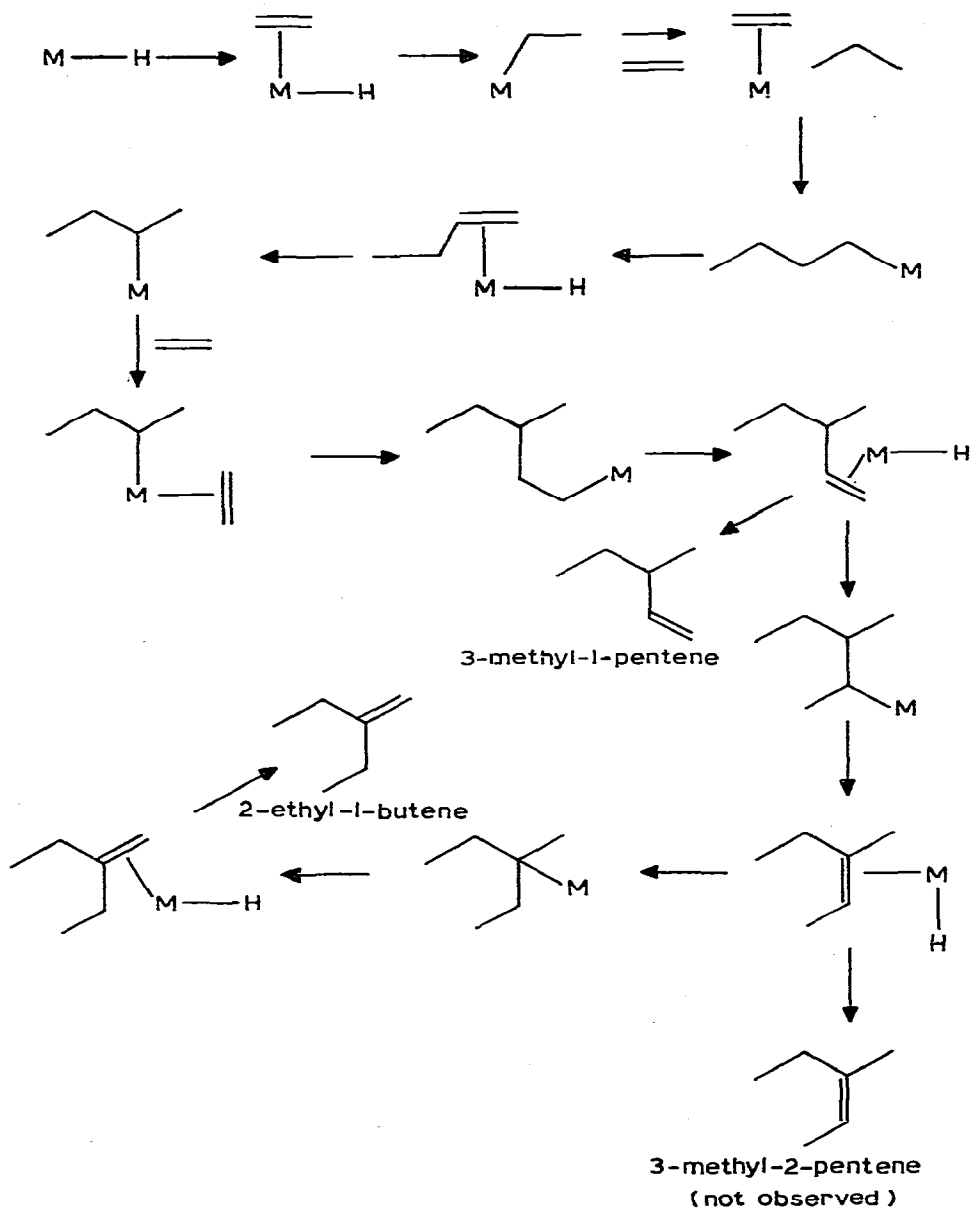
account for branched hexenes and, consequently, predicts the presence of unobserved C₄ and C₆ isomers, e.g. 2-butene, 3-methyl-2-pentene, and internal n-hexenes. Further, as shown in Scheme 1 this mechanism requires that the metal complex of 3-methyl-2-pentene be a precursor to the complex of 2-ethyl-1-butene and the liberated olefin (a major product). Inasmuch as 3-methyl-2-pentene is thermodynamically more stable than 2-ethyl-1-butene *, the absence of the former can only be accounted for if the olefins are decomplexed irreversibly and if the rate of dissociation of 2-ethyl-1-butene is fastest. This is an unlikely circumstance, particularly since trisubstituted olefins should dissociate faster than disubstituted olefins **.

The absence of 3-methyl-2-pentene and isomerized products is strong evidence against an insertion mechanism.

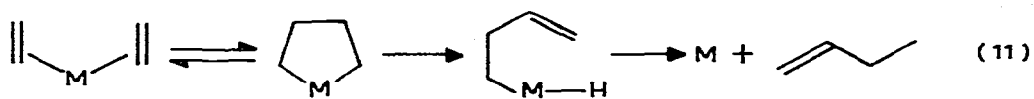
* Compare $\Delta G_f^\circ(298)$ kcal/mol: *cis*-3-Methyl-2-pentene, 17.5; *trans*-3-methyl-2-pentene, 17.04; 2-ethyl-1-butene, 19.11 [13].

** Increasing substitution lowers the binding constant for olefins [14], a reflection, in part, of an increased rate of dissociation.

SCHEME 1



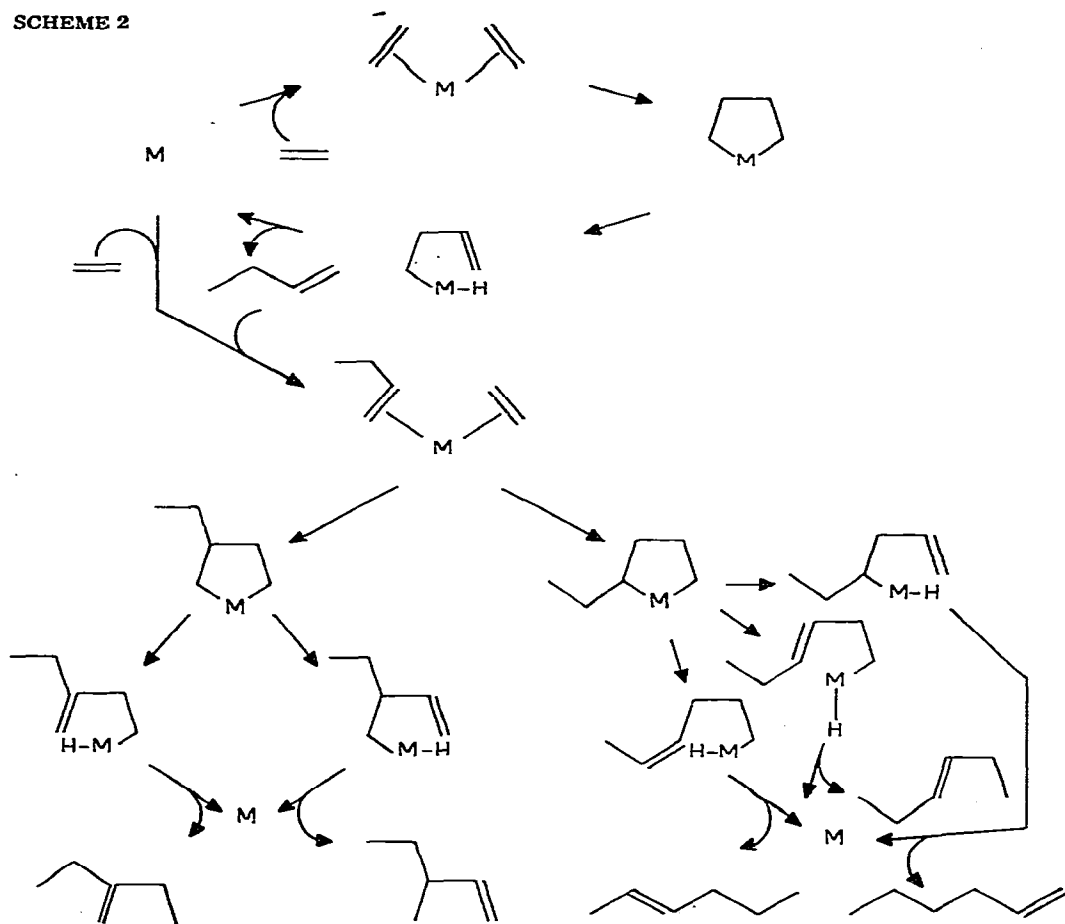
An alternate possibility is based on the steps in eq. 11. The condensation of



olefins with labile metal complexes to form metallocyclopentane complexes has been observed for tetrafluoroethylene [15], norbornadiene [16], methylenecyclopropane [17], and ethylene [9,18]. The equilibrium in eq. 11 has been

directly or indirectly observed for diethylene or metallocyclopentane complexes of titanium [19], nickel [20], and rhodium [21]. Metallocyclopentane complexes have been shown to decompose to ethylene, cyclobutane, or 1-butene (presumably, but not necessarily * by the β -elimination sequence in eq. 11) depending on the conditions, coordination number, oxidation state, and nature of the metal ion [19,20a,22–24]. Indeed, metallocyclopentane or substituted metallocyclopentane complexes of nickel and tantalum catalyze the dimerization of ethylene to 1-butene and have been proposed to do so by a mechanism based on eq. 11 [23,24].

SCHEME 2

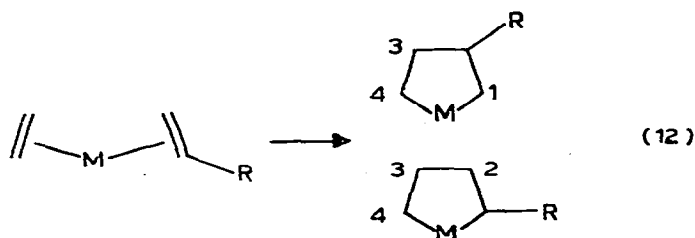


The observed codimers can be accounted for by Scheme 2. This scheme predicts 1-butene, 2-ethyl-1-butene, and 3-methyl-1-pentene as the only products, providing steric effects require placement of substituents on C₂ of the metallocycle, rather than adjacent to the metal atom, or providing that the 2-substituted metallocycle eliminates olefin faster than the 1-substituted isomer **. The observa-

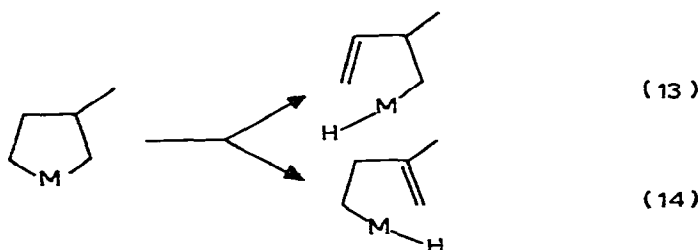
* Intermolecular hydrogen transfer and α -elimination have been suggested as other decomposition paths leading to 1-butene [22].

** Recent results by Schrock, et al. suggest that elimination of the olefin may be more complex than depicted in the last step of eq. 11 [25].

tion of only trace amounts of 1-hexene and unidentified C_6 hydrocarbons is con-

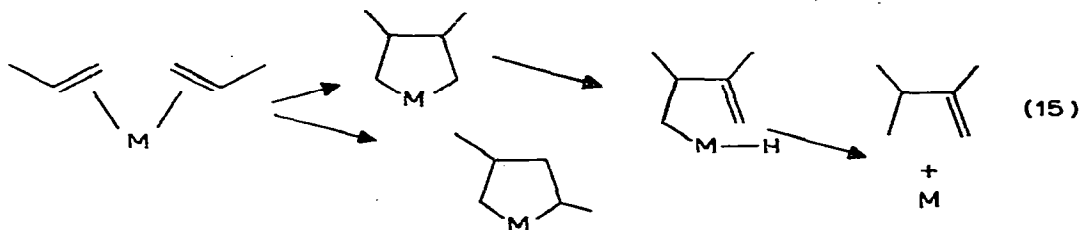


sistent with this hypothesis. Further, the preponderance of 2-ethyl-1-butene suggests that β -elimination preferentially occurs from the unsubstituted methylene group (C_3) rather than from the substituted, tertiary center (C_2). Similarly, the tantalum metallocycle $(\eta-C_5H_5)TaCl_2(CH_2)_4$ catalyzes the condensation of



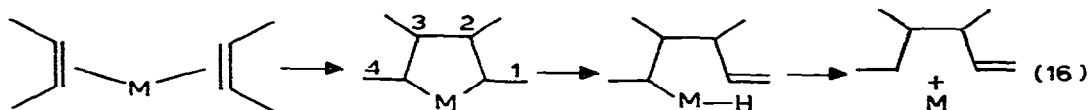
ethylene to 1-butene and only two (unidentified) codimers of ethylene and butene [23].

Substituted olefins. Propene is dimerized to 2,3-dimethyl-1-butene (Table 1), suggesting metallocycle formation occurs so as to place substituents on C_2 and C_3 of the ring or that olefin forms faster from the 2,3-substituted metallocycle. Indeed, the isolated tantalocycle, $(\eta-C_5H_5)TaCl_2(CH_2CH(Me)CH(Me)CH_2)$,



formed from reaction of propene and $(\eta-C_5H_5)TaCl_2(CHCMe_3)$ is 2,3-substituted and has *trans*-methyl groups [23].

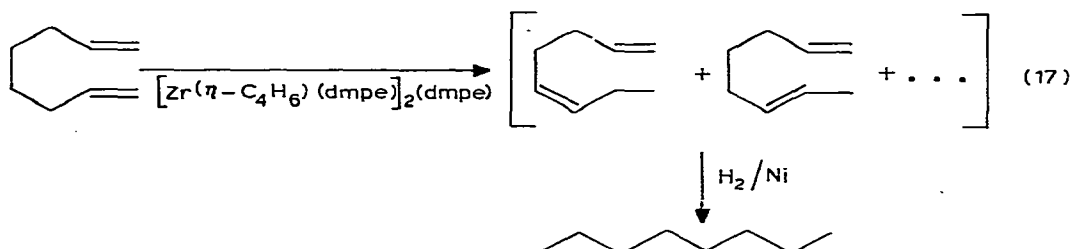
Dimerization of *cis*-2-butene gives (in very low yield) 3,4-dimethyl-1-hexene (Table 1), as would be expected for the metallocyclic mechanism in eq. 16, pro-



viding β -elimination occurs exclusively from the acyclic methyl group attached to C_1 .

The absence of 1- or *trans*-2-butene in the recovered C₄ fraction is consistent with the lack of long-lived metal hydride as a reaction intermediate or impurity.

Heating 1,7-octadiene with [Zr(η -C₄H₆)₂(dmpe)]₂(dmpe) at the temperature used for dimerization of other olefins did not result in significant substrate isomerization. At higher temperatures 1,7-octadiene is converted to a complex mixture of isomers. However, no methylenemethylcyclohexane or cyclic isomers are formed, as hydrogenation of the product mixture gave only n-octane (eq. 17).



The substrate 1,7-octadiene, apparently, either prevents metallocycle formation or blocks some subsequent step; higher energy pathways then become observable, e.g., double bond isomerization. Since 1,7-octadiene forms a metallocycle when treated with $[(\eta\text{-C}_5\text{H}_5)_2\text{Ti}]_2(\text{N}_2)$ (as shown by formation 2-hydroindanone on carbonylation) [19b] or $(\eta\text{-C}_5\text{H}_5)\text{TaCl}_2(\text{CHCMe}_2)$ [23], the latter possibility is likely. Indeed, the tantalocycle derived from 1,7-octadiene is said to be thermally more stable than monocyclic derivatives [23].

Similarly, isobutene is not dimerized by the Zr catalyst. No 2,4,4-trimethyl-1-pentene or other dimers were formed.

Butadiene is converted to a complex mixture of C₈H₁₂ hydrocarbons and substantial amounts of polymerized material when warmed with $[\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})]_2(\text{dmpe})$.

Cyclopropane does not react under the standard conditions.

Rates of dimerization. The consumption of ethylene or propene, catalyzed by the Zr or Ti complexes, follows first-order kinetics over at least three half-lives. Rate constants so measured are presented in Table 3.

$$\frac{-d[\text{olefin}]}{dt} = k_{\text{obs}}[\text{olefin}] \quad (18)$$





Assuming a first-order dependence on catalyst (i.e. the rate law given in eq. 19) and assuming that the dmp-bridged dimer is totally dissociated to $\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$ as in eq. 3, the second-order rate constant is given by the expression in eq. 20. Calculated second-order rate constants are listed in Table 3.

$$\frac{-d[\text{olefin}]}{dt} = k'[\text{metal}][\text{olefin}] \quad (19)$$

$$k' = k_{\text{obs}}/[\text{metal}] \quad (20)$$

Although *cis*-2-butene is dimerized under these conditions (products listed in Table 1), it reacts too slowly to allow accurate rate measurements. It is apparent that 1,2-disubstituted olefins are dimerized substantially slower than monosubstituted olefins, which themselves react more slowly than ethylene. However, the

TABLE 3
RATES OF OLEFIN DIMERIZATION ^a

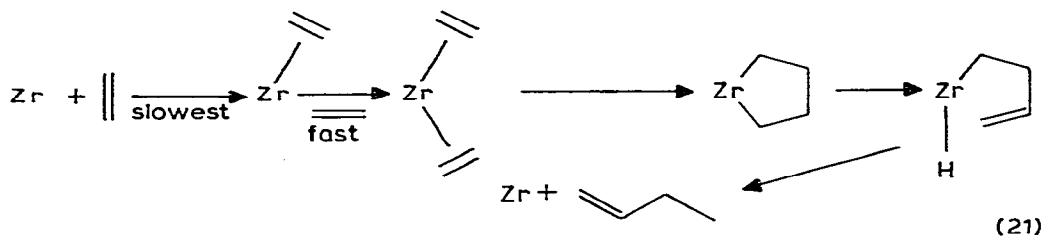
Catalyst	Substrate	$k_{\text{obs}}(\text{h}^{-1})$ ^b	$k'(\text{h}^{-1} \text{M}^{-1})$ ^c
$[\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})]_2(\text{dmpe})$		1.43 ± 0.03	11.0 ± 0.2
$[\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})]_2(\text{dmpe})$		$(2.67 \pm 0.26) \times 10^{-3}$	$(3.1 \pm 0.3) \times 10^{-2}$
$[\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})]_2(\text{dmpe})$		<i>d</i>	<i>d</i>
$\text{Ti}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$		0.79 ± 0.04 ^e	7.2 ± 0.40

^a Conditions are given in the experimental section, $T = 49^\circ\text{C}$. ^b Pseudo first-order rate constant. ^c Second order rate constant derived by assuming a first-order dependence on metal (see text). ^d Too slow to measure. ^e Error limits are the standard error from the least squares fits.

rate of cross dimerization between ethylene and, for example, 1-butene must be approximately equal to that for dimerization of ethylene alone, otherwise no codimers (i.e. hexenes) would be formed. The rate of dimerization, therefore, follows the order:

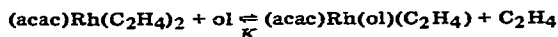


The first-order dependence on olefin and the olefin substituent effects suggest that formation of the initial olefin complex is slowest*. Formation of butene-



ethylene codimers requires that the second association step (formation of the bis(olefin) complex) not discriminate between monosubstituted olefins and ethylene. ³¹P NMR spectra of solutions of the catalyst in the presence of ethylene under dimerization conditions show no signals other than that of $\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$, implying that relatively little Zr is complexed with ethylene and involved in the catalytic cycle at any given time. This observation is consistent with the first step in eq. 21 being slow and subsequent steps being fast. In some

* Equilibrium constants for metal olefin complexes reflect similar steric effects, presumably, because of a slower rate of association as well as a faster dissociation rate. Compare K for

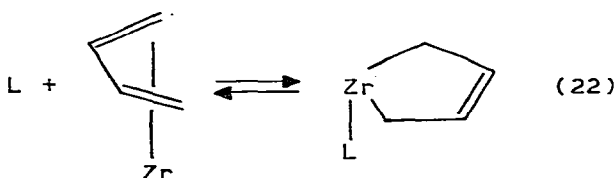


$$K(\text{C}_2\text{H}_4) = 1, K(\text{propene}) = 0.08, K(\text{cis-2-butene}) = 0.004 \text{ [14].}$$

cases, the subsequent step may become sufficiently slow as to be rate determining, e.g., 1,7-octadiene.

The somewhat slower rate for the $\text{Ti}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$ catalyzed dimerizations likely reflects a slower formation of olefin complex, as expected on the basis of the decreased tendency to form Lewis base adducts (vide supra).

Nature of the catalytic species. No induction period was observed in the $[\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})]_2(\text{dmpe})$ -catalyzed dimerization of ethylene. Further, the catalyst can be recovered unchanged (no loss of butadiene) from the reaction mixture. Inasmuch as the rate-determining formation of the olefin adduct affords a coordinatively saturated complex, $\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})(\text{olefin})$, some ligand dissociation step must precede formation of a bis(olefin) complex and, subsequently, products. Since formation of a $1,2\text{-}\eta^2\text{-C}_4\text{H}_6$ unit, i.e. dissociation of one end of a butadiene ligand, would likely lead to loss of butadiene, dissociation of one end of the dmpe chelate or formation of a $1,4\text{-}\eta^2\text{-C}_4\text{H}_6$ group is indicated. That is, coordinative unsaturation may be achieved by the equilibrium in eq. 22.



Although equilibria of this type have not been directly observed, complexes containing $1,4\text{-}\eta^2$ butadiene ligands have been prepared [26].

Experimental

All manipulations were performed in vacuo or under an atmosphere of prepurified nitrogen or argon. Solvents were purified by distillation from sodium benzophenone ketyl. Volatile olefins were dried by passage through a 3 cm column of P_2O_5 . 1,7-Octadiene was distilled from sodium. The complexes $[\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})]_2(\text{dmpe})$ [5] and $\text{TiCl}_4(\text{dmpe})$ [8] were prepared by published procedures. GLC analyses for hexenes and lower boiling hydrocarbons were performed on a $20' \times 1/4''$ column of 10% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb-P at temperatures between 30 and 45°C . Higher boiling hydrocarbons were analyzed on a similar $6' \times 1/4''$ column at 50°C . Quantitative measurements were made on a Varian 920 gas chromatograph interfaced with a Varian CDS-111 Integrator. Cyclohexane or cyclohexene were used as internal standards for the estimation of C_6 hydrocarbons; 1,7-octadiene was used for C_8 hydrocarbons.

^{13}C NMR chemical shifts are relative to TMS.

Preparation of $\text{Ti}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$

Butadiene (51.4 mmol) was condensed at -196°C into a flask containing 4.34 g (12.8 mmol) of $\text{TiCl}_4(\text{dmpe})$, 200 ml of THF, and 50 ml of 0.75% Na/Hg. The vessel was warmed to room temperature and shaken for 1/2 h, resulting in the formation of a dark solution. The supernatant was decanted, filtered through a pad of Celite, and evaporated to dryness. The black residue was slowly heated to 90°C over a period of 3 h to remove residual dmpe. The residue was then

extracted with 300 ml of hot hexane. The resulting deep blue solution was filtered and concentrated; cooling to -20°C afforded blue crystals of $\text{Ti}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$. Three crops (1.4 g, 4.6 mmol, 36%) were collected. Anal.: Found: C, 54.90; H, 9.14; P, 20.06. $\text{C}_{14}\text{H}_{28}\text{P}_2\text{Ti}$ calcd.: C, 54.91; H, 9.22; P, 20.23%. Mass spectrum m/e 306 [$^{12}\text{C}_{14} \text{ } ^1\text{H}_{28} \text{ } ^{31}\text{P}_2 \text{ } ^{48}\text{Ti}$] $^+$ and 252 [$\text{P}-\text{C}_4\text{H}_6$] $^+$. ^1H NMR (benzene- d_6) 4.37 (m, 4 H, butadiene methine protons), 8.34 (m, 4 H, butadiene methylene protons), 8.55 (d, 4 H, dmpe methylene protons), 9.15 (t, 12 H, dmpe methyl groups), and τ 9.94 (m, 4 H, butadiene methylene protons). $^{31}\text{P}\{^1\text{H}\}$ NMR (toluene- d_8) 36.9 ppm downfield from 85% H_3PO_4 . ^{13}C NMR (benzene- d_6) 45.9 (t, J 145.7 Hz, butadiene $\text{C}_{1,4}$), 106.2 ppm (d, J 157.7 Hz; butadiene $\text{C}_{2,3}$).

Olefin condensations catalyzed by $[\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})]_2(\text{dmpe})$

Typically, 1 mmol of $[\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})]_2(\text{dmpe})$ and 30 ml of solvent were charged to a 150 ml Hoke bomb. The vessel was cooled to -196°C and evacuated; 320 mmol of olefin were condensed onto the frozen solution. The bomb was sealed, warmed to room temperature, and, then, heated to 70°C for 50 h. At the end of this period, volatile components were distilled in vacuo from the bomb. Separation and identification of the products are described below for each case. The results and conditions are summarized in Table 1.

(1) *Ethylene*. The reaction mixture was slowly distilled through traps maintained at -78 , -126 (methylcyclohexane slush), and -196°C . Ethylene (identified by mass spectroscopy and comparison of its ^1H NMR spectrum and GLC retention time to those of an authentic sample) was recovered from the -196°C trap. 1-Butene (identified similarly) was recovered from the -126°C trap; no 2-butenes were detected. The -78°C trap contained a solution of hexenes in the toluene solvent. The two major and one of the two minor products were isolated by preparative GLC and identified as 3-methyl-1-pentene, 2-ethyl-1-butene, and 1-hexene by comparison of ^{13}C NMR and mass spectral data with those for authentic samples. GLC traces showed an additional unidentified minor product in the C_6 region ($<2\%$) and a few unidentified peaks ($<1\%$ of total products) in the C_8 region.

3-Methyl-1-pentene: ^{13}C NMR (benzene- d_6) 11.9 (q, J 125.9 Hz, C_5), 20.1 (q, J 125.2 Hz, CH_3), 29.8 (t, J 127.6 Hz, C_4), 40.1 (d, J 128.5 Hz, C_3), 112.7 (t, J 160.0 Hz, C_1), 144.4 ppm (d, J 150.6 Hz, C_2).

2-Ethyl-1-butene: ^{13}C NMR (benzene- d_6) 12.8 (q, J 125.6 Hz, $\text{C}_{3,6}$), 29.1 (t, J 124.0 Hz, $\text{C}_{3,5}$), 106.9 (t, J 154.8 Hz, C_1) 152.8 ppm (s, C_2).

(2) *Propene*. The reaction mixture was slowly distilled through traps at -78 and -196°C . Unreacted propene was recovered from the -196°C trap. The -78°C trap contained a solution of hexenes in the toluene solvent. The major product was isolated by preparative GLC and identified as 2,3-dimethyl-1-butene by ^{13}C NMR and mass spectroscopy. Three minor products observed in the C_6 region of the GLC traces were unidentified. Cumulatively these three peaks contained $<5\%$ of the area of the 2,3-dimethyl-1-butene peak.

2,3-Dimethyl-1-butene: ^{13}C NMR (benzene- d_6) 20.3 (q, J 123.0 Hz, $\text{CH}_3\text{-C}_3$), 21.7 (q, J 127.0 Hz, $\text{C}_{1,5}$), 35.7 (d, J 121.0 Hz, C_2), 108.2 (t, J 150.0 Hz, C_4), 151.4 ppm (s, C_3).

(3) *cis-2-Butene*. The reaction mixture was analyzed as described above. Un-

reacted *cis*-2-butene was recovered from the -196°C trap. No *trans*-2-butene or 1-butene was detected by GLC or ^1H NMR. The -78°C trap contained a small amount of butene dimer in the hexane solvent. The dimer was shown to be 3,4-dimethyl-1-hexene by GLC co-injection with an authentic sample. No other products were detected.

(4) *Butadiene*. A similar workup allowed recovery of butadiene (-196°C trap) and collection of dimers in the hexane solvent (-78°C trap). Solid polymer was found in the bomb. GLC analysis of the hexane solution indicated a complex mixture of species having retention times suggestive of C_8 hydrocarbons. These peaks were collected together and shown to be isomers of C_8H_{12} by mass spectral analysis.

(5) *Cyclopropane*. A similar fractional condensation allowed quantitative recovery of cyclopropane. No propene or ethylene was detected by GLC analysis.

(6) *Isobutene*. Similarly, isobutene was quantitatively recovered. No dimers were found by GLC analysis of the hexane solution retained in the -78°C trap.

(7) *1,7-Octadiene*. After 50 h at 50°C a solution of 0.67 mmol of $[\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})]_2(\text{dmpe})$ in 108.5 mmol neat 1,7- C_8H_{14} was analyzed by GLC. No conversion of substrate to other hydrocarbons was observed. After 250 h at 70°C only ca. 15% of the substrate had been converted to other products. After 50 h at 110°C over 95% of the substrate had been consumed. GLC traces showed the presence of many products. These were shown to be isomers of linear octadiene by hydrogenating the mixture (W-2 Raney Ni, 1500 psi H_2 , 70°C) and observing that n-octane was the sole product (as determined by GLC and ^1H NMR).

Time dependent ethylene condensations

Aliquots (15 ml) of a solution, prepared by dissolving 1.63 mmol of $[\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})]_2(\text{dmpe})$ in 50 ml of toluene, were placed in each of three 2-l bulbs. The bulbs were cooled to -196°C , evacuated, and to each was added 123 mol of ethylene. Each bulb was heated at 68°C for a specified period of time and opened. The products were analyzed as described above; results are presented in Table 2.

Rates of olefin dimerization

In a representative experiment, 0.05 mmol of $[\text{Zr}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})]_2(\text{dmpe})$ (or 0.10 mmol $\text{Ti}(\eta\text{-C}_4\text{H}_6)_2(\text{dmpe})$) was placed in a calibrated NMR tube. The tube was cooled to -196°C , evacuated, and 5.0 mmol of olefin and 2.5 mmol of benzene were condensed onto the solid. Enough benzene- d_6 was then added to bring the volume to the mark and the tube was sealed. The tube was placed in a constant temperature bath ($49.0^{\circ}\text{C} \pm 0.5^{\circ}$) and the concentration of the olefin measured at intervals by integration of its ^1H NMR resonances against that of the residual protons of benzene. Plots of $-\ln$ (area of ethylene peak/area of benzene peak) versus time were linear over at least three half-lives. The slopes (k_{obs}) showed no variation when only 3.0 mmol ethylene was used. The results are summarized in Table 3.

HfCl₄(dmpe)₂

To a flask was charged 39.8 g HfCl_4 (0.124 mmol), 350 ml toluene, and 37.3 g

(0.248 mmol) dmpe. The solution was refluxed for 10 min, filtered through a Celite pad, and evaporated to dryness. The white solid was recrystallized from 1/1 toluene/hexane; 55.6 g (0.090 mol, 72%) white crystals were obtained. $^{31}\text{P}\{^1\text{H}\}$ NMR (benzene- d_6) 0.3 ppm upfield from 85% H_3PO_4 . Anal.: Found: C, 23.10; H, 4.90. $\text{C}_{12}\text{H}_{32}\text{Cl}_4\text{HfP}_4$ calcd.: C, 23.23; H, 5.20%.

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