

Comparative Dimerization of 1-Butene with a Variety of Metal Catalysts, and the Investigation of a New Catalyst for C–H Bond Activation

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Abstract: Catalytic dimerization of 1-butene by a variety of catalysts is carried out, and the products are analyzed by gas chromatography and mass spectrometry. Catalysts based on cobalt and iron can produce highly linear dimers, with the cobalt-based dimers exceeding 97 % linearity. Catalysts based on vanadium and aluminum prefer to make branched dimers, which are most often methyl-heptenes in the case of vanadium and almost exclusively 2-ethyl-1-butene in the case of aluminum. The

vanadium catalyst also produces substantial amounts of dienes and alkanes, suggesting a competing hydrogenation/dehydrogenation pathway that appears to involve vinyl C–H bond activation. Nickel catalysts are generally less selective than those based on iron or cobalt for making linear dimers, but

Keywords: C–H activation • dimerization • homogeneous catalysis • vanadium

they can make dimers with 60 % linearity. The major by-products for the nickel systems are trisubstituted internal olefins. An important side reaction that must be considered for dimerization reactions is 1-butene isomerization to 2-butene, which makes recycling the butene difficult for a linear dimerization process. Aluminum, iron, and vanadium systems promote very little isomerization, but nickel and cobalt systems tend to isomerize the undimerized substrate heavily.

Introduction

The dimerization of olefins by homogeneous catalysts is an area of academic as well as commercial importance.^[1] For example, ethylene dimerization to 1-butene is a potentially attractive way to produce polyethylene comonomer, especially in regions where other sources of 1-butene are scarce.^[2] Dimerization of propylene and 1-butene is practiced widely, with the generally branched dimers finding application as plasticizer alcohol precursors or gasoline additives. The dimerization of 1-butene is a particularly interesting area to study, since there are a number of different processes that can happen during the reaction, some of which in-

clude branched dimer formation, linear dimer formation, 1-butene isomerization, and butene oligomerization.

Recent reports by Wasserscheid et al.^[3] and by ourselves^[4] illustrate the desirability of catalysts that promote linear dimerization. While Keim and Wasserscheid reported that nickel complexes with fluorinated acetylacetonate (acac) ligands dissolved in buffered ionic liquids catalyze linear dimerization (TONs < 3000, 50–70 % linearity), we reported that tridentate pyridine bisimine iron complexes, when activated with alumoxanes, are highly active and selective for this process (TONs ≥ 75 000, 65–80 % linearity). This unprecedented combination of activity and selectivity prompted an investigation of several other catalysts and a comparison of their tendencies regarding olefin dimerization. Herein are reported the results of this study.

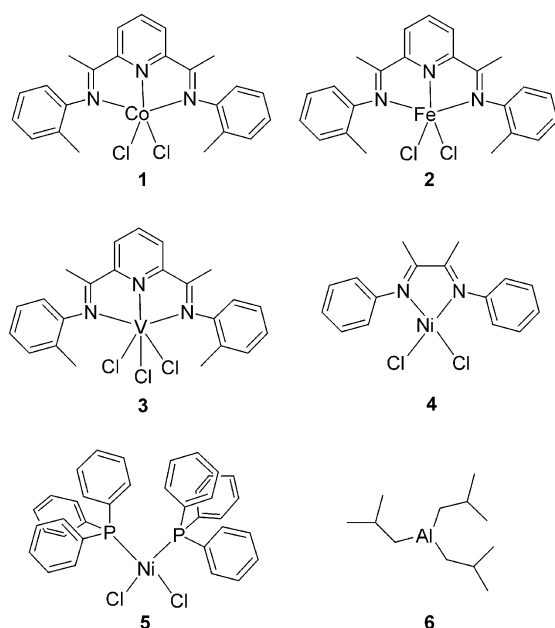
Results and Discussion

Although a number of different catalysts have been reported for dimerizing olefins, the catalyst precursors utilized in this work were chosen because they provide ample room for comparison between well-known and newly emerging homogeneous systems. These six complexes are shown in Scheme 1. Complexes **1–3**, all of which may be activated by alkyl alumoxanes, compare a series of pyridine bisimine catalysts, using the recently reported iron-based system as a useful benchmark. Diimine nickel complex **4**, on which

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 Supporting information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author. ¹H NMR of vanadium-based 1-butene dimer; GC of vanadium-based 1-butene dimer, 1-butene trimer, and 1-hexene dimer with signals identified from MS data; GC/MS of vanadium-based propylene dimer with signals identified.



Scheme 1. Precatalysts for the dimerization of 1-butene.

Brookhart and Svejda have disclosed variations for propylene dimerization,^[5] is included to extend the comparative study of nitrogen-based ligands to nickel. Complex **5**, which is activated with diethylaluminum chloride, resembles the types of catalysts used in the IFP Dimersol Process,^[6] and is included as an example of a relatively non-selective catalyst. Catalyst **6**, which is known to selectively make vinylidene (2-alkyl-1-alkene) dimers,^[7] is incorporated to illustrate the diverse products that can be made from olefin dimerization.

To test each of the catalyst **1–6** for dimerization activity and selectivity, a 500-mL Zipperclave reactor was used, and an inert gas head pressure of at least 100 psig was used to drive the butene into the reactor as a liquid and to keep the butene liquefied during reaction heating.^[8] The reactions were typically run for three hours, but catalyst **3** was run

longer to improve the conversion. Table 1, which presents the dimerization data, allows a number of comparisons to be made regarding catalyst selectivity and productivity.

In terms of activity, the iron catalyst **2** is by far the highest, outpacing the other systems by approximately an order of magnitude. This trend was not surprising, especially upon comparison of the iron catalyst to its cobalt analogue **1**. Previous reports of these systems for ethylene oligomerization^[9] have shown that iron is significantly more active than cobalt. However, the activity of cobalt catalyst **1** compared very favorably to that of catalysts **3–5**. In fact, complex **1** is significantly more active than the nickel or vanadium systems studied.

Along with the dimerization reaction, several of the catalysts promoted the side reaction of butene isomerization. For both nickel systems and for cobalt, isomerization is rapid, and the amount of isomerized butene tends to exceed the amount of dimer formed. In a process where linear dimerization is desired, isomerization is detrimental because incorporation of internal olefins, if they are able to incorporate, will cause the formation of branched products. Catalysts **2** and **6** only promote modest isomerization, with the highly active iron complex **2** preferring dimerization to isomerization by a factor of >20:1. Vanadium system **3**^[10] does not heavily isomerize the starting olefin either, but it promotes a unique hydrogen transfer process that leads to several unexpected products. The mechanism of catalyst **3** will be discussed in this report.

All of the catalysts **1–6** (Table 1) are quite selective for producing dimers preferentially to higher oligomers. As a first approximation, assuming that the sterically hindered di- and trisubstituted dimer products do not react further (excluding possible isomerization) once they have undergone chain transfer from the metal, the degree of dimer formation is simply a factor of the catalysts' relative rates of propagation and chain transfer. Thus, in complexes of type **1–5**, in which decreased steric bulk of the ligands has been shown to promote oligomerization relative to polymerization, the propensity for forming dimers is somewhat expect-

Table 1. Results for the dimerization of 1-butene by catalysts **1–6**.

Catalyst	Reaction conditions	Yield [g]	% Conv.	% Dim.	% LD ^[a]	% MBD ^[b]	% DBD ^[c]	Dimer branch index (BI) ^[d]	Total TON ^[e]	Dim./isom ratio ^[f]
1 /MMAO ^[g]	25 mg 1 , Al:Co = 500:1, 250 g C ₄ , 30 °C, 3 h	97.7	39	99	97	3	trace	0.03	38 000	0.7:1
2 /MMAO	10 mg 2 , Al:Fe = 500:1, 250 g C ₄ , 30 °C, 3 h	153	61	82	70	30	trace	0.30	147 000	>20:1
3 /MMAO	25 mg 3 , Al:V = 500:1, 250 g C ₄ , 30 °C, 16 h	45.1	18	84	36 ^[h]	62 ^[h]	2	0.66	16 000	>30:1
4 /MMAO	25 mg 4 , Al:Ni = 500:1, 250 g C ₄ , 30 °C, 3 h	31.6	13	72	62	38	trace	0.38	8300	1.1:1
5 /DEAC ^[i]	25 mg 5 , Al:Ni = 500:1, 250 g C ₄ , 60 °C, 3 h	26.1	10	84	55	31	13	0.57	12 200	<0.1:1
6	16.6 g 6 , 700 g C ₄ , 1200 psig N ₂ , 200 °C, 3 h	140	20	98	9	90	1	0.91	30	>20:1

[a] LD = linear dimer. [b] MBD = mono-branched dimer; further analysis included in Table 2. [c] DBD = di-branched dimer. [d] BI = average number of branches per molecule in the C₈ product fraction. [e] TON = moles of butene dimerized or oligomerized per mole of pre-catalyst. [f] Approximate ratio of moles of 1-butene dimerized or oligomerized to moles of butene isomerized; since this value may change with changing substrate concentration, it is only a general expression of a catalyst system's tendency to isomerize or dimerize α -olefins. [g] MMAO = isobutyl-modified methylalumoxane, purchased from Akzo. [h] Refer to the discussion on catalyst **3** and to Table 2 for more details on these numbers. [i] DEAC = diethylaluminum chloride.

ed. The cobalt catalyst **1** is the most selective, producing only traces of higher butene oligomers.

The composition of the C₈ products made by catalysts **1–6** illustrates the diverse pathways for dimerizing α -olefins. Table 1 breaks the C₈ products from each reaction into linear, monobranched, and dibranched components. The branch index simply refers to the average number of branches per C₈ molecule. As is seen from the table, which was composed using GC/MS data, the iron system produces predominantly linear octenes, but the octenes made by the cobalt catalyst are 97% linear. We have recently reported additional studies involving highly selective cobalt catalysts for linear dimerization and isomerization.^[11] Nickel catalysts **4** and **5** are also moderately selective for linear dimer formation, although the branch index of the bisphosphine complex **5** is inflated by its formation of dibranched products. In addition, the high levels of 2-butenes made by **4** and **5** tend to make them poor candidates for linear dimerization, since butene recycle or high substrate conversion (if possible) would lead to significant increases in product branching. Catalysts **3** and **6**, on the other hand, make predominantly branched dimers, albeit with different structures from each other.

To more carefully analyze the branched dimers, Table 2 was constructed, and all of the monobranched dimers were analyzed by GC/MS. While the iron and cobalt catalysts make primarily 5-methyl-2-heptenes and 5-methyl-3-heptenes, the vanadium system produces a mixture of methyl-heptenes, vinylidene (2-ethyl-1-hexene), and methyl-heptane. The origin of this saturated species will be discussed in detail. The nickel systems make predominantly trisubstituted internal olefins, while the aluminum catalyst makes almost exclusively 2-ethyl-1-hexene.

To better understand the different selectivities reported, it is useful to examine Scheme 2, which illustrates the various pathways available for 1-butene dimerization. Similar schemes have been presented by Keim and Beach for analyzing butene dimers.^[12] To simplify the picture somewhat, incorporation of 2-butene has been omitted, since it is as-

Table 2. Analysis of mono-branched dimers.

Catalyst	% Vinylidene (2-ethyl-1-hexene)	% Internal trisubstituted methyl-heptene	% Internal disubstituted methyl-heptene
1 /MMAO	trace	trace	> 99
2 /MMAO	1.5	0.5	98.0
3 /MMAO	24.3 ^[a]	trace	75.7 ^[a]
4 /MMAO	trace	90.7 ^[b]	9.3
5 /DEAC	trace	77.8 ^[b]	22.0
6	98.2	1.8	trace

[a] Only the mono-branched, mono-olefins were included in this analysis (products made by proposed complexes **9** and **12** in Scheme 2).

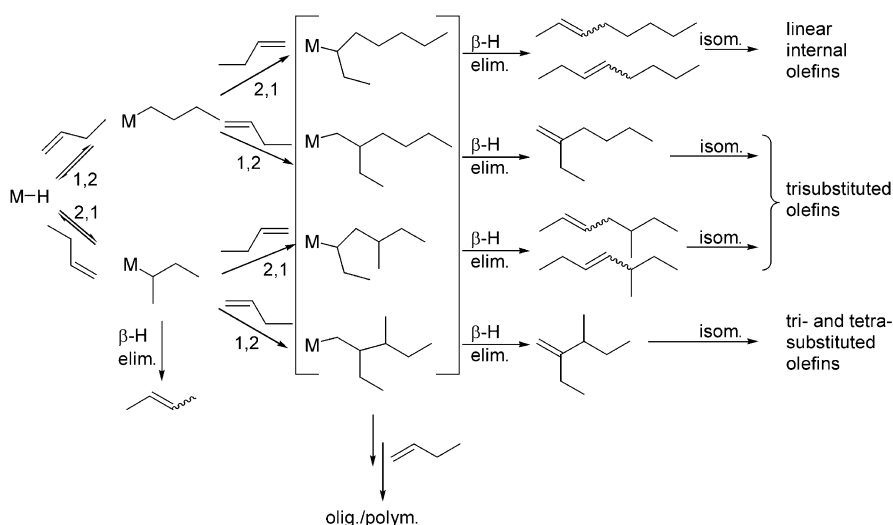
[b] Nickel catalysts **4** and **5** are capable of isomerizing the products.

sumed to constitute only a negligible percentage of product formation. The various products shown in Scheme 2 can be matched to the different dimers listed in Tables 1 and 2, thus allowing the data in the tables to be presented in a mechanistic format.

Upon analysis of the dimers made by vanadium catalyst **3**, the mass spectral data indicated a substantial presence of both dienes and saturated species in the C₈ products. Approximately 28 mol% of the total C₈ products were identified as dienes, while about 19 mol% were identified as C₈ alkanes. The fairly equal levels of these di-olefins and non-olefins suggested that some form of hydrogen transfer was responsible for the results, rather than only a dehydrogenation step that would generate hydrogen gas. One possible mechanistic explanation for this process is the dehydrogenation of mono-olefins by the catalyst, followed by transfer of the hydrogen to a second mono-olefin to generate a saturated species. However, several pieces of evidence made this scenario unlikely. First, since the olefin with the highest concentration in solution is 1-butene, the transfer of hydrogen would be expected to form much more butane than saturated C₈ products. Analysis of the products indicated only slightly elevated levels of butane, a result that may be better explained by a different mechanism. Also, no dehydrogenation of the heptane internal standard to heptenes was observed;

if a dehydrogenation mechanism were at work, one might surmise that C₇ paraffins and C₈ mono-olefins should both be susceptible to this process. Furthermore, activation of heptane by the catalyst would not necessarily result in chain transfer to form heptenes. A vanadium heptyl complex might be able to react with butene to produce C₁₁ species. No C₁₁ species were observed in the products, thus indicating the relative inertness of heptane in this process.

Further analysis of the products provided the best clues regarding the vanadium dimerization mechanism. The mass spec-



Scheme 2. Pathways for 1-butene dimerization by migratory insertion.

tral data showed that virtually all of the saturated C_8 products contained methyl branches, and that almost all of the dienes were linear. This segregation of alkanes and dienes between the branched and the linear products, respectively, combined with the relatively equal amounts of the two product types, suggested a mechanism whereby the creation of a molecule of one product would eventually lead to the creation of a molecule of the other. Upon consideration of this mole balance constraint, the dimerization mechanism in Scheme 3 is proposed, in which competitive mechanisms of chain transfer can be used to rationalize the unique product distribution. Beginning with the unobserved vanadium-hydride ('V-H') species shown, an initial primary (1,2) insertion of 1-butene produces the vanadium-*n*-butyl complex **7**, which can insert a second butene with secondary (2,1) or primary (1,2) regiochemistry to give the two vanadium-octyl complexes **8** and **9**, respectively. Species **8**, which according to the product distribution represents the less likely insertion product, may then undergo β -H elimination or β -H transfer to form the linear internal olefin. Species **9**, on the other hand, undergoes a competing mechanism of chain transfer. The catalyst may yield the product via the similar β -H mechanism of **8** to produce 2-ethyl-1-hexene, or it can undergo a net vinyl C-H bond metathesis reaction between the vanadium-carbon bond and the vinyl carbon-hydrogen

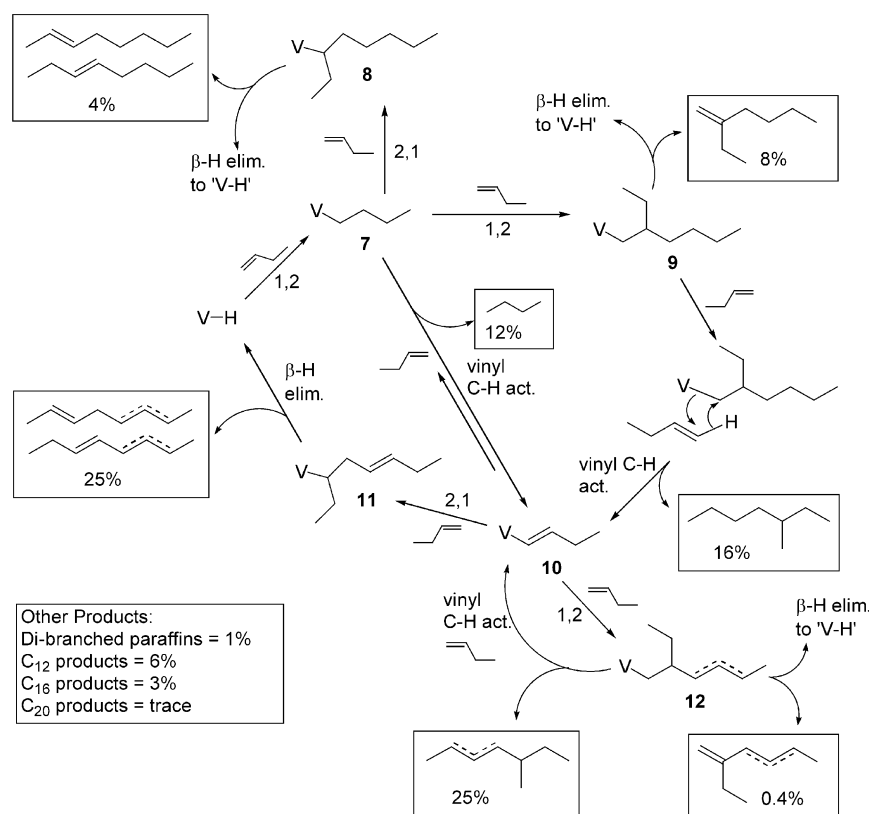
bond of an incoming molecule of 1-butene. This reaction generates an equivalent of 3-methyl-heptane and a new complex **10** with a vanadium-butenyl group.

The vinylic C-H activation seems unlikely when one considers that such a C-H bond (ca. 465 kJ mol⁻¹)^[13] is much stronger than, for example, a C-H bond^[14] of an alkane (≥ 420 kJ mol⁻¹; 423 kJ mol⁻¹ for ethane) or the H-H bond (436 kJ mol⁻¹).^[15] Surprisingly, despite these bond enthalpy differences, metathesis reactions involving vinylic C-H and metal-carbon bonds have often been proposed^[16] to explain such phenomena as formation of polymers and oligomers with saturated end groups. These interpretations will be discussed in the next section.

At this juncture, an obvious question is why complexes **8** and **9** undergo different mechanisms of chain transfer. The apparent answer is due to sterics, since **8** possesses an ethyl branch at the α -carbon atom to the vanadium center, while **9** has an ethyl branch at the β -position. Complex **8** is apparently too sterically hindered to facilitate the metathesis reaction preferred by complex **9**. Following the chain transfer step of **9**, the vanadium-butenyl species **10** may undergo the same reactions as the vanadium-butyl complex; specifically 2,1 insertion of butene to form complex **11** or 1,2 insertion to produce species **12**. Both **11** and **12** will then undergo chain transfer processes identical to their saturated ana-

logues **8** and **9**, only this time the products will be linear C_8 dienes and methyl-branched C_8 mono-olefins, with a very small amount (~0.4%) of mono-branched dienes.

Worth noting, the vanadium-butenyl complex **7** prefers the second insertion of butene to occur with primary (1,2) regiochemistry, but butenyl complex **10** has an approximately equal propensity for 1,2 and 2,1 insertion. These tendencies are estimated by adding the respective amounts of branched and linear products that result from each complex. To further investigate why complexes **7** and **10** prefer somewhat different modes of insertion, we considered that the methyl-heptene made by complex **12** could be made by a different route; specifically by successive 2,1 insertions followed by β -H elimination (see Scheme 2). Formation of methyl-heptenes via this route would produce both 5-methyl-2-heptene and 5-methyl-3-heptene, for a total of four products when the *cis* and *trans* isomers are counted. Complex **12**, however, would only make 5-



Scheme 3. Proposed mechanism for dimerization by vanadium complex **3**. All of the percentages were determined by GC/MS. The presence of vinylidene product was confirmed by ¹H NMR spectroscopy. All of the percentages refer to mole percent values. The dotted bond lines on products refer to ambiguities in the location of the bonds due to the suggested isomerization/insertion mechanism of **10**. The *trans* isomers are depicted for clarity, but *cis* isomers are likely present for all of the disubstituted internal olefins.

methyl-3-heptene. By use of commercially available GC standards, the only methyl-heptene identified in the product was *trans*-5-methyl-2-heptene, a result that is inconsistent with *either* mechanism. This odd result may suggest that complex **10** undergoes a double bond shift upon conversion to **11** or **12**, or that our speculative mechanism is incorrect.

In addition to the questions regarding species **7** and **10**, their respective insertion products **9** and **12** apparently exhibit quite different tendencies in their modes of chain transfer. Complex **9** undergoes chain transfer with only a slight preference for the vinyl C–H activation route, while complex **12** almost exclusively prefers this mechanism. Since **9** and **12** differ only in the presence of a double bond on the alkyl fragment of complex **12**, the disparate product compositions are another interesting and yet unexplained phenomenon.

Another consideration of the cycle proposed in Scheme 3 involves the disposition of vanadium complex **7**. If relatively unhindered species such as **9** and **12** undergo chain transfer via a metathesis step, complex **7** would also be expected to display this behavior to produce *n*-butane. In fact, by careful inspection of Scheme 3, the amount of butane may be approximated by subtracting the number of moles of alkanes from the number of moles of dienes: (mol. butane) = (mol. diene) – (mol. alkane)

From the GC data, it was possible to calculate a total C₈+ yield of 45.1 g, which included 37.9 g of C₈ fractions, 4.1 g of C₁₂ fractions, and 2.9 g of C₁₆ fractions. The molar ratio of C₈ dienes to C₈ alkanes (from GC/MS) was then assumed to be constant for the C₁₂ and C₁₆ fractions, for which the GC/MS data could not be deconvoluted.^[17] From the overall diene to alkane ratio, the amount of “missing” *n*-butane was predicted to be 2.2 g, or about 9 mol% of the total product (*n*-butane, C₈, C₁₂, C₁₆). Finally, by using the residual *n*-butane and 1-butene signals and the reaction conversion (18%), the amount of *n*-butane formed in the reaction was estimated at 3.0 g, or about 12 mol% of the total product. These predicted and observed butane levels are in fairly close agreement considering the limitations of the experiment.

In separate experiments, 1-hexene was dimerized (16,000:1 hexene:V ratio) to 60% conversion, in order to determine the amount of *n*-hexane formed. The *n*-hexane constituted 7.5 mol% of the final product (*n*-hexane, C₁₂, C₁₈); but as with the butene trimers, we were not able to achieve sufficient separation of the C₁₂ species to quantify the amounts of dienes and alkanes, thus preventing estimation of the predicted amount of *n*-hexane formation. Finally, propylene was also dimerized by catalyst **3** to see if any additional information could be gained from examining the C₆ products. As with the 1-butene and 1-hexene dimerizations, numerous alkane and diene species were identified. However, quantitative analysis was limited by the formation of substantial amounts of higher oligomers. In addition, the propylene dimers do not appear to form by the same regiochemical (2,1 versus 1,2) and steric constraints as the butene dimers. GC/MS data for both the propylene and 1-hexene dimerizations are included in the Supporting Information.

If the catalytic cycle in Scheme 3 is correct, it is possible to establish the following ‘rules’ for the vanadium-catalyzed dimerization:

- 1) The first insertion of an α -olefin at vanadium occurs with 1,2 regiochemistry (98 + %).
- 2) If the second insertion is 2,1, then β -H elimination/transfer to generate linear internal olefins is the preferred chain transfer step (99 + %).
- 3) If the second insertion is 1,2, then vinyl hydride transfer (metathesis) is preferred.
- 4) The methylene (terminal) hydride of the incoming olefin transfers exclusively when vinyl-hydride activation occurs, thus giving an *n*-butenyl–vanadium complex.

Discussion

The proposed competing chain transfer pathways in Scheme 3 raise the question of literature precedent for vanadium and other metals. For example, in polypropylene produced with a Sc-based constrained geometry catalyst, Bercaw et al.^[16b] found no evidence of vinylidene chain ends (from H-transfer to monomer or metal center); hence, it was speculated that olefin C–H bond metathesis might be an important termination process. Ziegler et al.^[18] published several computational papers that examined vinylic σ -bond metathesis as a chain transfer route for scandium and titanium catalysts. Specifically, their computations indicated that such a process would generally be less favorable than the parallel C=C bond insertion (in terms of both overall exothermicity and reaction barrier). However, the computed energetics are not prohibitive enough to rule out vinylic C–H metathesis as a minor process. Apparently, a well-defined complex (i.e. adduct) with ethylene (or olefin) in a head-on orientation toward the metal center is formed; it is stabilized by an agostic interaction involving the vinylic C–H bond as well as electrostatic interaction between the olefin and the electron deficient metal center.

Recently the groups of Gibson and Gal have independently reported the isolation of tridentate pyridinebisimine Co^I alkyl complexes. These Co^I species do not undergo olefin insertion, and the authors speculate that the catalysts may achieve an active Co^{III} state via oxidative addition of a vinyl C–H bond. These researchers clearly state that this activation step is one of several possible ways to generate the active species, if indeed the active catalyst is a Co^{III} species.^[19] In the case of vanadium complex **3**, it is not clear if the oxidation state of the metal in the active form is +3 (the same as the catalyst precursor) or if it is somewhat reduced. In any case, the described system likely consists of a dⁿ system with $n \geq 2$. The agostic interactions and electrostatic stabilization that are deemed to favor vinylic C–H activation in the case of the Sc^{III} or Ti^{IV} catalysts would not be that strong in the case of the vanadium catalyst. However, this seemingly unlikely mode of chain transfer should not be ruled out, particularly because there appears to be no other good explanation for the formation of the alkane products.

Furthermore, it is also noted that complex **3** possesses a significantly different ligand set than the Sc^{III} or Ti^{IV} catalysts. Bearing that in mind, it is not inconceivable that the nitrogen-based ligand could also be involved in the C–H activation chemistry proposed for vanadium. The proposed mechanism of Scheme 3 should at this point only be invoked to rationalize the product distribution, rather than to argue for a specific mode of activation.

Although σ -bond metathesis and vinyl C–H bond activation are known for a variety of transition metal complexes, subsequent functionalization of the activated hydrocarbon is less common. One area where several studies have been undertaken is in the field of ethylene polymerization. Specifically, it has been proposed by Reinking et al. and Kissin et al. that Zr- and V-based polymerization catalysts can promote long-chain branching (LCB) by intramolecular or intermolecular σ -bond metathesis reactions with polyethylene chains.^[20,21] This theory has been proposed as an alternative to the prevailing idea that LCB arises from the reincorporation of polymer chains with unsaturated end groups into another growing polymer chain. However, in systems that utilize hydrogen as a chain transfer agent, the number of available terminal olefin groups can be quite small, which indicates another mechanism may be responsible for LCB. Additionally, Reinking showed that simple alkanes such as *n*-heptane and cyclohexane can be activated by VCl_4 on silica with an alkylaluminum cocatalyst.^[20] In the presence of hydrogen and ethylene, the vanadium system produces alkylcyclohexanes catalytically from cyclohexane, indicative of C–H bond activation followed by ethylene insertion. The authors propose that this phenomenon is a model for the LCB mechanism since it demonstrates how saturated species can be incorporated into a polymer chain.

Due to the unique product distribution, a catalytic cycle involving a formal oxidative addition of butene to vanadium catalyst **3**, followed by successive steps involving migratory insertion and reductive elimination, appears unlikely. Although 1-butene could conceivably oxidatively add to a low-valent vanadium center, followed by successive migratory insertion and reductive elimination reactions to generate the products shown, the *absence* of products such as *n*-octane, coupled with the roughly equal amounts of linear dienes and branched paraffins, argue against this mechanism. Vinyl C–H bond metathesis coupled with β -hydride elimination/transfer remains the most likely pathway; since both processes are known to occur with early metals, the unique features of this system are the proposed steric-based competition between the two mechanisms and the high catalytic activity toward the vinyl C–H bond activation route.

As a final consideration, the prevalence of vinyl C–H bond activation in the vanadium system magnifies a reaction that may be occurring to a lesser extent in a variety of other catalytic systems, ranging from Ziegler–Natta polymerizations and oligomerizations to catalytic olefin dimerization. As presented in this work, the presence of trace amounts of dienes in any of these processes may possibly be attributed to small amounts of chain transfer by vinyl C–H bond activation to generate vinyl–metal bonds.

Conclusion

The dimerization of 1-butene by a selected variety of transition metal catalysts has been used to demonstrate a number of mechanistic pathways that are available during α -olefin dimerization. Cobalt catalysts form almost completely linear dimers, while iron and nickel systems can make predominantly linear products. The iron catalysts, however, are at least an order of magnitude faster than nickel, and they do not tend to isomerize the substrate or the product substantially. Aluminum, albeit with low activity, is highly selective for producing vinylidene dimers, and the vanadium catalyst discussed herein dimerizes olefins by a unique mechanism that produces significant and roughly equal amounts of branched alkanes and linear dienes. Future work will involve attempts to better understand the speculative mechanism of the vanadium catalyst.

Experimental Section

Materials: Anhydrous THF and methanol were purchased from Aldrich and used without further purification. Anhydrous cyclohexane was purchased from Aldrich and stored over 3A molecular sieves. 1-hexene and 1-butene were obtained as commercial grades of Chevron Phillips' Normal Alpha Olefins. 1-hexene was degassed and dried over 3A molecular sieves. MMAO-3A, triisobutylaluminum, and diethylaluminum chloride were purchased from Akzo Nobel. 2,6-Diacetylpyridine, iron(II) chloride tetrahydrate, and all substituted anilines were purchased from Aldrich and used without further purification. Nickel(II) chloride, dimethoxyethane adduct; vanadium(III) chloride, tris-tetrahydrofuran adduct; bis(triphenylphosphine) nickel(II) chloride; and cobalt(II) chloride hexahydrate were purchased from Strem.

Catalyst preparation: Complexes **1**,^[9,11] **2**,^[9] and **4**^[5] were prepared by described literature methods. Synthetic details for complex **3** are detailed below:

2,6-Bis[1-(2-methylphenylimino)ethyl]pyridine vanadium(III) chloride (3**):** 2,6-Bis[1-(2-methylphenylimino)ethyl]pyridine (1.00 g, 2.9 mmol) and vanadium(III)chloride–tetrahydrofuran adduct (1.04 g, 2.8 mmol) were added together under inert conditions to a 100 mL flask with a stirbar. THF (25 mL) was added, and the reaction was stirred for 16 h in hot THF (55°C). Pentane was added, and the reaction was filtered and washed with ether and pentane to give, after drying, 1.35 g (97%) of complex **3**. Analytical data for pre-catalyst complex **3**: MS ($[M^+ - Cl]$): 464/462; elemental analysis (%): calcd C 55.39, H 4.65, N 8.42; found: C 55.34, H 5.10, N 7.94.

Dimerization of 1-hexene: A dry two-necked flask with a stirbar was charged with 1-hexene (100 mL) and pre-catalyst **3** (25 mg) under inert atmosphere (16000:1 olefin:V ratio). The flask was transferred to a Schlenk manifold and placed under a slow nitrogen purge. The pre-catalyst was slurried in the 1-hexene by rapidly stirring the liquid. MMAO-3A in heptane (100:1 Al:V) was then added via syringe. Samples were taken for GC analysis after 3 h and after 24 h. The reaction had formed about 50% of its final product after 3 h.

Dimerization of 1-butene: A 500-mL Zipperclave reactor was heated under vacuum at 50°C for several hours. The reactor was cooled to room temperature under an inert gas. The pre-catalyst was then added to the reactor in a sealed NMR tube by tying the tube to the stirrer shaft, and the reactor was resealed and placed under vacuum. A glass sample charger was then attached to the injection port of the reactor. The internal standard and the cocatalyst were added. The reactor was then quickly sealed and charged with liquid butene. The reactor was further pressurized with at least 100 psi of nitrogen or argon to keep the butene in the liquid phase.^[8] Stirring was begun, thus breaking the NMR tube and initiating the reaction. The temperature was monitored using a thermocou-

ple. Internal cooling and external heating were used to maintain the desired reactor temperature.

Product analysis: For the butene dimerization, the reactor was slowly vented. The aluminum cocatalysts in all of the reactions were neutralized by pouring the liquid products into a water wash. After removal of the cocatalysts, the products were analyzed by gas chromatography (GC). A Hewlett Packard 6890 Series GC System with an HP-5 50 m or 30 m column with a 0.2 mm inner diameter was used for dimer as well as α -olefin characterization. An initial temperature of 35°C and a rate of 2.4°Cmin⁻¹ were used to raise the temperature to 52°C, followed by a rate of 15.0°Cmin⁻¹ to raise the temperature to 157°C. A final ramp rate of 22.5°Cmin⁻¹ was used to reach the final temperature of 250°C. ChemStation from Hewlett Packard was used to analyze the collected data. GC/MS data were obtained using an Agilent 5973 Benchtop Mass Spectrometer using electron impact ionization interfaced to an Agilent 6890 gas chromatograph. The GC column was a J&W Scientific DB-5MS, 60 m × 0.25 mm i.d. with a 0.25 µm film thickness. After an initial time of 5.0 min, a ramp rate of 3.0°Cmin⁻¹ was used to raise the oven temperature to 300°C. The Wiley275 L computerized database was used to assign the mass spectrum signals. Due to ambiguities in classifying all of the dimer products for catalyst **3** by GC/MS, ¹H NMR spectroscopy was used for further characterization. In particular, NMR spectroscopy resolved a GC/MS discrepancy, resulting in correct classification of the vinylidene dimer made from 1-butene. At first, the GC/MS data indicated that the vinylidene species was actually a trisubstituted dimer, which could be formed by isomerization of a vinylidene or a methyl-heptene. However, control experiments with the activated vanadium catalyst **3** and 2-ethyl-1-hexene or disubstituted internal methyl-heptenes showed no isomerization behavior. ¹H NMR spectroscopy confirmed that the species in question was indeed a vinylidene and not a trisubstituted olefin. GC data were then used to make all of the quantitative assessments, since the NMR spectra could not distinguish between the dimeric and trimeric products.

The conversions and yields were determined by comparing the product to the internal standard integrals, and by assuming equal response factors of the standard and the products. For hexene dimerization, unreacted 1-hexene was the internal standard, and for the butene experiments cyclohexane was used.

Acknowledgement

We thank Dr. M. Jeansonne and Dr. J. B. Green for help with dimer characterization, and A. J. Marcucci and Eric Fernandez for performing several of the dimerization experiments. Furthermore, we thank Dr. M. M. Johnson, Dr. P. K. Das and Dr. D. E. Lauffer for helpful mechanistic discussions.

- [1] a) Y. Chauvin, H. Olivier, in *Applied Homogeneous Catalysis with Organometallic Compounds*, Vol. 1 (Eds.: B. Cornils, W. A. Herrmann), VCH, New York **1996**, pp. 258–268; b) G. W. Parshall, S. D. Ittel in *Homogeneous Catalysis: the Applications and Chemistry of Catalysis by Soluble Transition Metal Complexes* 2nd ed., Wiley, **1992**, pp. 72–76; c) J. Skupinska, *Chem. Rev.* **1991**, *91*, 613; d) W. Keim, *Angew. Chem.* **1990**, *102*, 251; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 235–244.
- [2] a) A. M. Al-Jarallah, J. A. Anabtawi, M. A. B. Siddiqui, A. M. Aitani, A. W. Al-Sa'doun, *Catal. Today* **1992**, *14*, 1; b) A.-H. Wu (Phillips) U. S. Pat. 5414178, **1995**.
- [3] a) B. Ellis, W. Keim, P. Wasserscheid, *Chem. Commun.* **1999**, 337; b) P. Wasserscheid, M. Eichmann, *Catal. Today* **2001**, *66*, 309.
- [4] B. L. Small, A. J. Marcucci, *Organometallics* **2001**, *20*, 5738.
- [5] S. A. Svejda, M. Brookhart, *Organometallics* **1999**, *18*, 65.
- [6] a) H. Olivier-Bourbigou, J.-A. Chodorge, P. Travers, *Petroleum Technology Quarterly* **1999**, *Autumn*, 141; b) Y. Chauvin, J. F. Gaillard, D. V. Quang, J. W. Andrews, *Chem. Ind.* **1974**, 375; c) D. Commercuc, Y. Chauvin, J. Gaillard, J. Léonard, J. W. Andrews, *Hydrocarbon Process.* **1984**, 118.
- [7] K.-F. Lin, G. E. Nelson, C. W. Lanier, (Ethyl) U. S. Pat. 4973 788, **1990**.
- [8] For catalyst **6**, a 2-L reactor was used. Care should be taken when working with liquid butene at the elevated temperature described for catalyst **6** ($\geq 180^\circ\text{C}$). The reactor should be rated for at least 1400 psig, and the reaction should be heated slowly to avoid sudden temperature increases.
- [9] a) B. L. Small, M. Brookhart, *J. Am. Chem. Soc.* **1998**, *120*, 7143; b) G. J. P. Britovsek, S. Mastroianni, G. A. Solan, S. P. D. Baugh, C. Redshaw, V. C. Gibson, A. J. P. White, D. J. Williams, M. R. J. Elsegood, *Chem. Eur. J.* **2000**, *6*, 12, 2221.
- [10] a) D. Reardon, F. Conan, S. Gambarotta, G. Yap, Q. Wang, *J. Am. Chem. Soc.* **1999**, *121*, 9318; b) R. Schmidt, U. Hammon, M. B. Welch, H. G. Alt, B. E. Hauger, R. D. Knudsen (Phillips) U. S. Pat. 6458905, **2002**.
- [11] B. L. Small, *Organometallics* **2003**, *22*, 3178.
- [12] a) W. Keim, B. Hoffmann, R. Lodewick, M. Penckert, G. Schmitt, J. Fleischhauer, U. Meier, *J. Mol. Catal.* **1979**, *6*, 79; b) D. L. Beach, J. E. Bozik, C.-Y. Wu, Y. V. Kissin, *J. Mol. Catal.* **1986**, *34*, 345.
- [13] a) K. M. Ervin, S. Gronert, S. E. Barlow, M. K. Gilles, A. G. Harrison, V. M. Bierbaum, C. H. DePuy, W. C. Lineberger, G. B. Ellison, *J. Am. Chem. Soc.* **1990**, *112*, 5750; b) J. J. Russell, S. M. Senkan, J. A. Seetula, D. Gutman, *J. Phys. Chem.* **1989**, *93*, 5184.
- [14] J. Berkowitz, G. B. Ellison, D. Gutman, *J. Phys. Chem.* **1994**, *98*, 2744.
- [15] K. P. Huber, G. Herzberg, in *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules*, Van Nostrand, New York, **1979**.
- [16] a) H. H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R. M. Waymouth, *Angew. Chem.* **1995**, *107*, 1255–1283; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1143–1170; b) B. J. Burger, M. E. Thomson, W. D. Cotter, J. E. Bercaw, *J. Am. Chem. Soc.* **1990**, *112*, 1566; c) M. E. Thomson, S. M. Buxter, A. R. Bulls, B. J. Burger, M. C. Nolan, B. D. Santasiero, W. P. Schaefer, J. E. Bercaw, *J. Am. Chem. Soc.* **1987**, *109*, 203; d) P. L. Watson in *Selective Hydrocarbon Activation* (Eds.: J. A. Davis, P. L. Watson, J. F. Liebman, A. Greenberg), VCH Publishers, New York, **1990**.
- [17] GC/MS was used to obtain peak MW values for the C₁₂ fraction, indicating substantial amounts of C₁₂ alkanes (MW=170) and C₁₂ dienes (MW=166). Reliable intensities, however, could not be obtained due to multiple overlapping signals.
- [18] a) T. Ziegler, E. Folga, A. Berces, *J. Am. Chem. Soc.* **1993**, *115*, 636; b) T. K. Woo, L. Fan, T. Ziegler, *Organometallics* **1994**, *13*, 2252; c) T. K. Woo, P. M. Margl, T. Ziegler, *Organometallics* **1997**, *16*, 3454.
- [19] a) V. C. Gibson, M. J. Humphries, K. P. Tellman, D. F. Wass, A. J. P. White, D. J. Williams, *Chem. Commun.* **2001**, 2252; b) T. M. Kooistra, Q. Knijnenburg, J. M. M. Smits, A. D. Horton, P. H. M. Budzelaar, A. W. Gal, *Angew. Chem.* **2001**, *113*, 4855; *Angew. Chem. Int. Ed.* **2001**, *40*, 4719.
- [20] M. K. Reinking, G. Orf, D. McFaddin, *J. Polym. Sci. Polym. Chem. Ed.* **1998**, *36*, 2889.
- [21] Y. V. Kissin, T. E. Nowlin, R. I. Mink, *Macromolecules* **1993**, *26*(9), 2151.

Received: March 13, 2003

Revised: October 27, 2003 [F4945]