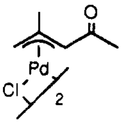
was also observed for **2b** and **2c**. It then may well be that in the decarbonylation reaction of dienol silyl ether 1 with $PdCl_2(PhCN)_2$ in benzene (eq 2) the formation of **2** is slow so that the decarbonylation catalyst $PdCl_2(PhCN)_2$ is always present to force most of **2** formed to undergo the decarbonylation.

Scheme I outlines a possible mechanism of the decarbonylation reaction. The silylcarbonyl-substituted complex **2a** is converted to the η^1-allyl complex A, in which β-elimination of the trimethylsilyl groups affords the vinylketene complex intermediate B.[7] No intermolecular exchange of the coordinated ketene occurs, because treatment of a mixture of **2b** and **2c** with a catalytic amount of $PdCl_2(PhCN)_2$ afforded only **4b** and **4c**, but no crossover products.[8] Subsequent addition of the silylpalladium moiety to the ketene in the reverse direction affords acylpalladium complex C, from which decarbonylation gives rise to the (η^1-allyl)palladium complex D[9] and then (η^3-allyl)palladium complex **4a**.

Treatment of the complex **5**[1c] or **6**[1b] containing methyl or hydrogen attached to the carbonyl carbon, respectively, instead of the silyl group, with a catalytic amount of $PdCl_2(PhCN)_2$ resulted in no decarbonylation reaction.



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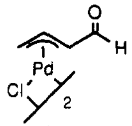

6

Thus, the decarbonylation needs the trimethylsilyl group attached to the carbonyl carbon, and the step from A to B in Scheme I appears to be the key to the overall decarbonylation. A facile syn elimination of (trimethylsilyl)palladium iodide from (β-silylalkyl)palladium iodide has been reported.[10] Such an interaction between palladium and a silyl group is also important in other new transformations of the complexes of type **2**, which we will report in the near future.

Acknowledgment. Partial support of this work by Grants-in-Aid from the Ministry of Education, Science, and Culture is acknowledged. Thanks are also due to the Analytical Center, Faculty of Engineering, Osaka University, for the use of JEOL GSX-400 and Bruker AM600 spectrometers.

Supplementary Material Available: Typical experimental procedures and spectral data for all compounds prepared (3 pages). Ordering information is given on any current masthead page.

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[7] It is possible that in eq 1 3 is formed by the reaction of $PdCl_2$ with methyl crotonate, which may have been generated by trapping of vinylketene by MeOH. The reaction of **1a** with 2 equiv of $PdCl_2(PhCN)_2$ in MeOH with Li_2CO_3 gave a larger amount of **3** (39%) together with **2a** (30%).

[8] A mixture of 17.3 mg of **2b** (0.05 mmol), 29.7 mg of **2c** (0.1 mmol), and 5.7 mg of $PdCl_2(PhCN)_2$ (0.015 mmol) was dissolved in 1 mL of C_6D_6. After 24 h, the reaction mixture was examined by ^1H NMR spectroscopy (**2b**, 9%; **4b**, 77% (syn/anti = 83/17); **2c**, 70%; **4c**, 29% (syn/anti = 59/41)).

[9] The (3-butenoyl)palladium complexes analogous to C underwent decarbonylation to afford (η^3-allyl)palladium complexes: Ozawa, F.; Son, T.; Osakada, K.; Yamamoto, A. *J. Chem. Soc., Chem. Commun.* **1989**, 1067.

[10] Karabelas, K.; Hallberg, A. *J. Org. Chem.* **1989**, *54*, 1773.

Stereoselective Formation of Dimethylcyclopentanes through Intramolecular Ziegler–Natta Alkene Insertion[†]

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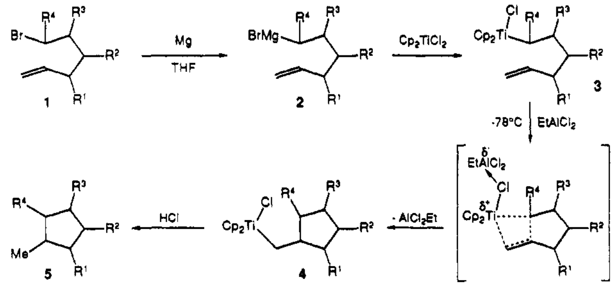
Summary: The intramolecular olefin insertion into titanium–carbon bonds results in efficient five-membered ring formation from 5-hexen-1-yl ligands. Cyclization of substrates having methyl groups on the alkyl tether proceeds with high diastereoselectivity (>94:6) in the formation of dimethylcyclopentane products.

The multitude of early transition-metal/Lewis acid complexes known as Ziegler–Natta catalysts includes some of the most efficient and selective reagents for organic reactions.[1] In 1955, Natta first reported the polymerization of propylene using a titanium catalyst ($TiCl_4/AlEt_3$), which sequentially formed hundreds of C–C bonds prior to chain termination.[1c,2] Each insertion of propylene into the metal–polymer bond occurred with high regioselectivity and was accompanied by the formation of a new asym-

Scheme I. Lewis Acid Promoted Intramolecular Alkene Insertion



	R^1	R^2	R^3	R^4
a	H	H	H	H
b	Me	H	H	H
c	H	Me	H	H
d	H	H	Me	H
e	H	H	H	Me

[†] Dedicated to the memory of John K. Stille, a colleague, mentor, friend, and father whose loss has been felt very deeply by so many people.

[1] For reviews in Ziegler–Natta polymerization and the catalysts used, see: (a) *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Kodenska: Tokyo, 1986. (b) Sinn, H.; Kaminsky, W. *Adv. Organomet. Chem.* **1980**, *18*, 99. (c) Pino, P.; Mulhaupt, R. *Angew. Chem., Int. Ed. Engl.* **1989**, *18*, 99. (d) Boor, J., Jr. *Ziegler–Natta Catalysts and Polymerization*; Academic Press: New York, 1979. (e) Reichert, K. H. In *Transition Metal Catalyzed Polymerizations. Alkenes and Dienes*; Quirk, R. P., Ed.; Harwood Academic: New York, 1983; Part B, p 465.

[2] Natta, G.; Pino, P.; Corradini, F.; Danusso, F.; Mantica, E.; Mazzanti, G.; Moraglio, G. *J. Am. Chem. Soc.* **1955**, *77*, 1708.

Table I. Distribution of Reaction Products Following Protonolysis of Organometallic Species

		relative ratio of C_7 protonolysis products[c]				
			dimethylcyclopentanes			
reaction[a]	yield[b]	uncyclized	1,2-trans:1,2-cis		1,3-trans:1,3-cis	
1b → **5b**	96%	*d*	79	21		
1b → **2b**	100%	88	10	2		
2b → **3b**	100%	87	10	3		
3b → **4b**	93%	0	92	8		
1c → **5c**	96%	14			19	67
1c → **2c**	98%	83			3	14
2c → **3c**	96%	85			3	12
3c → **4c**	93%	0			3	97
1d → **5d**	88%	*d*			59	41
1d → **2d**	100%	85			9	6
2d → **3d**	64%	77			14	9
3d → **4d**	94%	0			92	8
1e → **5e**	83%	17	19	64		
1e → **2e**	93%	79	7	12[e]		
2e → **4e**	72%	16	22	55[e]		

[a] 1 → 5: Bu_3SnH, AIBN, C_6H_6, 80 °C, 0.05 M. 1 → 2: Mg, THF, 45 °C. 2 → 3: Cp_2TiCl_2, CH_2Cl_2, −45–25 °C. 3 → 4: $EtAlCl_2$, toluene, 30 min, −78 °C. [b] Yield of C_7 protonolysis products determined by capillary gas chromatography analysis.[13] [c] Organometallic species were quenched with HCl/Et_2O (1 M) at −78 °C. [d] The amount of reduced product could not be quantified because of overlap with the solvent peak. [e] The balance of the mixture consisted of the three possible *β*-hydrogen elimination products.[15]

metric center. The reaction proceeded with high relative asymmetric induction that produced stereocenters, which, in long sections of the polymer, contained the same absolute configuration (isotactic). Over the past 35 years, the stereoselectivity, kinetics, and mechanistic aspects of Ziegler–Natta polymerization have been examined with a focus on the soluble group IV metallocene catalysts. From work on Ti(IV) and Zr(IV) metallocenes and alkylaluminum Lewis acids such as $EtAlCl_2$, a great deal of information has been acquired about the copolymerization of 1-alkenes with ethylene.[3] Recently, the use of methylaluminoxane[4] has made it possible to promote *α*-olefin insertion and study the effect of the Ti, Zr, and Hf metallocene ligand environment on the tacticity and enantioselectivity of polypropylene formation.[5] An example of the use of $EtAlCl_2$ to activate a titanocene complex toward C–C bond formation involved an intramolecular olefin insertion of **3a** to **4a** (Scheme I).[6] This system was used in an elegant mechanistic study of the Ziegler–Natta alkene insertion process and, as a result, was found to be an efficient tool for the formation of five-membered rings.

This report describes the effect of an asymmetric alkyl chain on stereoselective cyclopentane ring formation during the cyclization of **3** to **4**. Preparation of the 5-hexen-1-yltitanocene substrates **3** was accomplished by transmetalation of the Grignard complexes **2** with Cp_2TiCl_2 following an established procedure.[7] In the case of the unsubstituted alkyl tether **3a**, we found that the initial metalation of **1a** occurred with small amounts of cyclization (3–7%) to produce some of the (cyclopentylmethyl)magnesium bromide complex during the electron-transfer process.[8] Substrates **1b–e**[9] underwent ring formation to a slightly greater extent (12–19%) during the metalation process than for **1a** (Table I), presumably due to the Thorpe–Ingold substituent effect.[12] In each case, the trans:cis dimethylcyclopentane ratios resulting from cyclization and protonolysis of the Grignard mixture correlated well with the ratios produced by free-radical cyclization of the same bromides.[13] Continued heating of the Grignard products under these reaction conditions did not produce further cyclization. Subsequent transmetalation of the primary alkenyl ligands from magnesium (**2**) to titanium (**3**) was found to occur without any additional generation of cyclic products, except in the transformation from **2d** to **3d**, the system with the *α*, *β*, and *γ* carbons analogous to those of a growing polypropylene chain.[14] In the case of **3d**, the MgX_2 produced during transmetalation was thought to promote intramolecular olefin insertion more readily than for those substrates lacking a *β* substituent. On the other hand, the formation of **2e** and subsequent reaction with Cp_2TiCl_2 produced a 29:71 ratio of trans:cis **4e** as the only organometallic products.[15] The complete organometallic cyclization in the absence of $EtAlCl_2$ and the similarity to the 23:77 product ratio formed under free-radical conditions both

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(3) For a concise summary of early transition-metal metallocene catalysts and their use in polymerization studies, see ref 1d, pp 115–117.

(4) Andreson, A.; Cordes, H.-G.; Herwig, J.; Kaminsky, W.; Merck, A.; Mottweiler, R.; Pein, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 630.

(5) (a) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355. (b) Kaminsky, W.; Kulper, K.; Brintzinger, H. H.; Wild, F. R. W. P. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 507. (c) Kaminsky, W. In *Catalytic Polymerization of Olefins*; Keii, T., Soga, K., Eds.; Kodenska: Tokyo, 1986; p 293. (d) Ewen, J. A.; Haspeslagh, L.; Atwood, J. L.; Zhang, H. *J. Am. Chem. Soc.* **1987**, *109*, 6544. (e) Pino, P.; Cioni, P.; Wei, J. *J. Am. Chem. Soc.* **1987**, *109*, 6189. (f) Ewen, J. A.; Jones, R. L.; Razavi, A.; Ferrara, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 6255. (g) Kaminsky, W.; Ahlers, A.; Moller-Lindenhof, N. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1216. (h) Roll, W.; Brintzinger, H. H.; Rieger, B.; Zolk, R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 279. (i) Mallin, D. T.; Rausch, M. D.; Lin, Y.-G.; Dong, S.; Chien, J. C. W. *J. Am. Chem. Soc.* **1990**, *112*, 2030.

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(7) Waters, J. A.; Mortimer, G. A. *J. Organomet. Chem.* **1970**, *22*, 417.

(8) Ligand cyclization during Grignard formation and subsequent protonolysis, to an extent of 2–5%, has been well documented by: Ashby, E. C.; Oswald, J. *J. Org. Chem.* **1988**, *53*, 6068 and references therein.

(9) All bromoalkene substrates were prepared from the corresponding alcohols[10] by bromination with *N*-bromosuccinimide/PPh_3.[11]

(10) (a) **1b–1d**: Beckwith, A. L. J.; Easton, C. J.; Lawrence, T.; Serelis, A. K. *Aust. J. Chem.* **1983**, *36*, 545. (b) **1e**: Peterson, P. E.; Karat, R. J. *J. Am. Chem. Soc.* **1969**, *91*, 4521.

(11) (a) Trippett, S. *J. Chem. Soc.* **1962**, 2337. (b) Bose, A. K.; Lai, B. *Tetrahedron Lett.* **1973**, 3937.

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(13) Yields for these volatile compounds were determined by capillary gas chromatographic analysis of the quenched reaction mixture (HCl/Et_2O) using internal standards and correcting for detector response. Authentic samples of the reaction products were obtained from Aldrich Chemical Co. or Wiley Organics, and analyses were made by using a 60-m RSL-200 column (5% methyl phenyl silicone) with helium or hydrogen as the carrier gas.

(14) The distinction between products resulting from protonolysis of **2** or **3** was made based on two observations that support complete transmetalation. First, **2** was not soluble in the toluene/hexane mixture used to extract **3** from the reaction mixture. In addition, treatment of **2** with $EtAlCl_2$ did not produce ligand cyclization at 25 °C. Complete cyclization of the alkenyl ligand after the transmetalation and filtration procedures led us to believe that the only organometallic complexes present were those of titanium.

(15) Removal of the volatiles and quenching of the organometallics with HCl/Et_2O produced a solution containing only the 1,2-dimethylcyclopentanes. The volatiles removed from the organometallic species contained predominantly 1-heptene, as well as traces of the 1,6- and 2,6-heptadienes, and the 1,2-dimethylcyclopentanes.

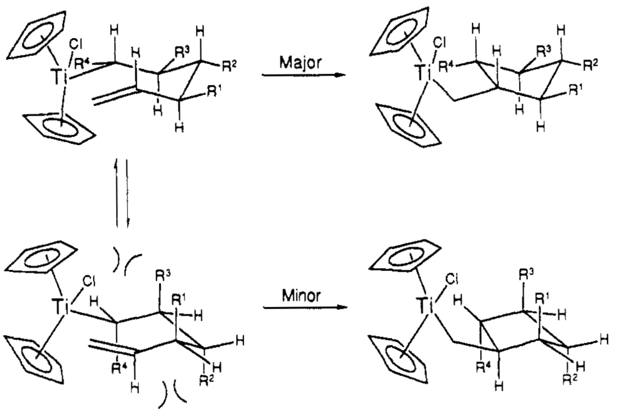
support the presence of radical intermediates during transmetalation rather than intramolecular alkene insertion into a secondary Ti–C bond.

Several general features of the intramolecular Ziegler–Natta olefin insertion, with respect to the reaction selectivity and efficiency, deserve highlighting. Activation of organotitanium complexes **3b–d** with $EtAlCl_2$ in toluene at −78 °C produced complete conversion to the corresponding cyclic organometallic products **4** within 30 min.[16] In each case, intramolecular olefin insertion occurred with exo regiospecificity. Methylcyclohexane, the product of endo cyclization, and methyl-1,5-hexadiene or methylmethylenecyclopentane, the potential products of β-hydride elimination, were not observed as products under these conditions.[17] In all intramolecular olefin insertion reactions involving primary bromide substrates (**3b–d**), >94:6 diastereoselective ring formation was observed. Finally, this Lewis acid catalyzed ring formation of disubstituted cyclopentane products occurred in >90% yields as a diastereomeric mixture.

A methyl substituent on the tether had a significant effect on the stereochemical formation of the C–C bond (Table I). Treatment of the mixture containing **3b** with $EtAlCl_2$ produced complete conversion to **4b**, which resulted in a 92:8 ratio of trans:cis 1,2-dimethylcyclopentane upon protonolysis. Taking into account the amount of the minor cis isomer already generated during Grignard formation, the Lewis acid promoted intramolecular olefin insertion into the Ti–C bond step occurred with 94:6 selectivity. Substrate **3c** resulted in higher overall stereoselectivity (**1c** to **5c**) of 3:97 trans:cis 1,3-dimethylcyclopentane with the Ziegler–Natta cyclization and protonolysis (**3c** to **5c**) proceeding with >99:1 cis selectivity. When the methyl substituent was located on the β carbon (**3d**), the compound analogous to that of an active polypropylene catalyst, cyclization proceeded with high (92:8) overall selectivity for *trans*-1,3-dimethylcyclopentane, and Lewis acid promoted insertion exhibited a >99:1 preference for the trans product. The fact that the cyclizations of **3c** and **3d** both gave common cyclic organometallic products (**4c** is equivalent to **4d**) with opposite product selectivities shows that this insertion process was not under reversible equilibrium reaction conditions.

Cyclization reactions were typically carried out by using the following general procedure under an inert atmosphere. Bromide **1** (354 mg, 2 mmol) was added to a 45 °C suspension of Mg (122 mg, 5 mmol) in 2 mL of THF over the period of 4–5 h. After an additional 2 h, the mixture was cooled to room temperature and transferred via cannula to a −45 °C flask containing a suspension of Cp_2TiCl_2 (598 mg, 2.4 mmol) in 8 mL of CH_2Cl_2. Residual Mg turnings were washed with THF (1 mL), which was also transferred to the reaction vessel. The reaction mixture was then stirred for 30 min at −45 °C, during which time it became a homogeneous deep-red solution; it was then warmed to ambient temperature and stirred an additional 4 h. Concentration of the mixture in vacuo to a total volume of 4 mL, followed by the addition of a toluene/hexane mixture (1:1, 10 mL) at 0 °C, caused the precipitation of all magnesium salts.[18] The solids were removed by filtration and then washed with 2 × 5 mL toluene/hexane (1:1). The soluble portion and washings were combined, evaporated to a dark-red oil, and kept under vacuum for 1 h. After dissolving the organometallics in toluene (14 mL), the mixture was cooled to −78 °C and $EtAlCl_2$ (0.56 mL, 1.0 mmol, 1.8 M in toluene) added via syringe. The reaction was stirred for 30 min at −78 °C and was then quenched with HCl (1.0 M in Et_2O) to produce the dimethylcyclopentanes.

Scheme II. Model for Diastereoselective Five-Membered Ring Formation



Due to the sterically crowded nature of this active center, the titanocene species plays an important role in the high degree of diastereoselective control achieved during formation of dimethylcyclopentane. Other metals, such as aluminum and lithium, have also been reported to mediate stereoselective five-membered ring formation without evidence of radical intermediates. Mixtures of diethylaluminum intermediates corresponding to the titanium species **3b** and **3c**, a separate mixture analogous to **3b** and **3d**, as well as a mixture containing the organoaluminum analogue of **3e**, have been generated from Et_2AlH and the corresponding methyl-substituted 1,5-hexadiene. After heating to 60 °C and subsequent hydrolysis, these mixtures produced dimethylcyclopentanes with trans selectivities of 98:2, 9:91, 96:4, and 28:72 from intermediates corresponding to **3b**, **3c**, **3d**, and **3e**, respectively.[19] The lithium complexes analogous to **3b** and **3e** have demonstrated trans selectivities of 93:7 and >44:1, respectively.[20] The selectivities exhibited by the titanium-, aluminum-, and lithium-mediated cyclizations demonstrate the involvement of the metal in the C–C bond-forming step as well as provide evidence for the negligible contribution from the less selective radical intermediates during cyclic product formation.

The ability of the titanocene complex to enhance product selectivity can be rationalized by the ordered transition-state model shown in Scheme II. In this model, eclipsing interactions on the tether are minimized and the complex can adopt the preferred arrangement where the Ti–C bond is coplanar with the alkene. Stereochemical selectivity is derived from the substantial preference for the substituent to occupy the pseudoequatorial position of the chairlike transition state. In a pseudoequatorial position, sterically unfavorable interactions with the bulky cyclopentadienyl ligands can be minimized. In each case

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[16] The intermediate in Scheme I is meant to provide a pictorial representation of the bond-making and -breaking process that occurs but is not intended to imply any mechanistic character.

[17] The use of toluene as the only solvent optimized product formation. In the presence of THF or Et_2O, an excess of Lewis acid is required to promote the reaction, and if the solution contained the CH_2Cl_2 from the transmetalation process, extensive β-hydride elimination was observed (>50%) by the formation of 1,5-hexadiene and methylenecyclopentane for substrate **3a**.

[18] Complex **3** was much less sensitive to the presence of oxygen or hydrolytic conditions than the corresponding Grignard, and similar compounds have been reportedly prepared by removal of solvent by using rotary evaporation.[7]

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examined, the experimental dimethylcyclopentane product formation was in agreement with this model.

In addition to the high diastereoselective control achieved for the synthesis of 1,2- and 1,3-disubstituted cyclopentanes, these studies also provide insight into the microstructure of poly(1,5-hexadiene) produced by Ziegler–Natta catalysts. Polymerization of 1,5-hexadiene has been found to proceed predominantly through an alternating intermolecular insertion/intramolecular cyclization addition of each monomer unit, and the resulting polymer contained repeating units of cyclopentane rings bridged by methylene groups.[21] Recent studies in this area have focused on determining the stereochemistry of these cyclization reactions. Using $TiCl_3/EtAlCl_2$ as the polymerization catalyst, Cheng and Khasat have determined that the polymer consists of a 46:54 ratio of trans:cis disubstituted cyclopentane rings by ^{13}C NMR.[22] This observation is opposite that observed for the titanocene intramolecular olefin insertion of **3d** to **4d** (>99:1, trans:cis). Using a zirconocene catalyst, which was more closely related to the titanocene system **3d**, Waymouth has observed a selectivity of 91:9 for polymerization of 1,5-hexadiene at −78 °C.[23] Thus, the metallocene compounds of both zirconium and titanium were found to have parallel selectivities in the formation of trans 1,3-disubstituted cyclopentane rings in the synthesis of polymers and monomeric cyclization, and these catalysts have shown much higher selectivities than the $TiCl_3/EtAlCl_2$ catalyst system. Thus, in addition to providing a method of highly selective C–C bond formation in the preparation of five-membered rings, these titanocene complexes appear to be accurate models for study of the Ziegler–Natta polymerization process.

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