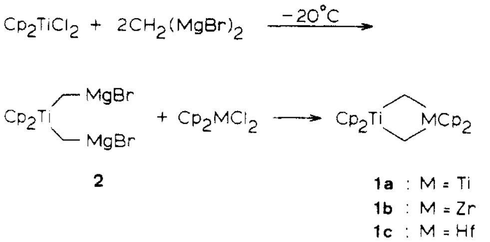
Table I. NMR Spectra of 1,3-Dimetallacyclobutanes 1

	^{1}H NMR[a]			^{13}C NMR[b]		
compd	Cp_2M	Cp_2Ti	CH_2	Cp_2M	Cp_2Ti	CH_2
1a[c]	6.23	6.23	8.72	112.1 [d, 172][d]	112.1 [d, 172][d]	235.8 [t, 125.2]
1b	6.2	6.22	7.63	110.1 [d, 171][d]	111.7 [d, 172][d]	205.7 [t, 124.5]
1c	6.15	6.25	6.26	109.3 [d, 172][d]	112.6 [d, 172][d]	193.3 [t, 120.9]

[a] δ in ppm; 90 MHz; C_6D_6 (C_6HD_5 as internal standard at 645 Hz; integrals in agreement with the number of protons). [b] δ in ppm [multiplicity; ^1J(C,H) in Hz]; 62.89 MHz; C_6D_6. [c] See also ref 4. [d] Additional long-range coupling leads to quasi-quintets with ^2J(C,H) ≈ ^3J(C,H) = 6 Hz.

Scheme I



intermediacy in catalytic processes.[3] In this context, 1,3-metallatitanacyclobutanes[1c–f,4] are of special interest because the replacement of a carbon atom by an additional metal may be expected to change the bonding situation, the ease of fragmentation to metal–carbene complexes such as $Cp_2Ti{=}CH_2$, the catalytic activity, etc. The only 1,3-metallatitanacyclobutane known so far is 1,1,3,3-tetracyclopentadienyl-1,3-dititanacyclobutane ($Cp_2TiCH_2TiCp_2CH_2$, **1a**), obtained by Ott and Grubbs[4] in the thermal decomposition of titanacyclobutanes.[5] On the basis of the recently developed bimetallic di-Grignard reagent $Cp_2Ti(CH_2MgBr)_2$ (**2**),[1d] we present here a new access not only to **1a** but also to other, mixed group 4 analogues $Cp_2MCH_2TiCp_2CH_2$ (**1b**, M = Zr; **1c**, M = Hf) (Scheme I).

In a typical experiment, dichlorodicyclopentadienyltitanium (Cp_2TiCl_2; 0.342 mmol) was converted to **2** by stirring in a sealed glass vessel for 1 hour at −20 °C with 2 molar equiv of bis(bromomagnesio)methane, $CH_2(MgBr)_2$[6] (0.684 mmol), in ether/benzene (1:1, 20 mL); **2** was obtained as a dark red, viscous precipitate in 40% yield.[1d] On addition of Cp_2MCl_2 (M = Ti, Zr, Hf; 0.274 mmol), followed by warming up to room temperature, the precipitate dissolved and yielded a solution of **1** which was purple-red in the case of **1a**[4] and brownish in the case of **1b** and **1c**. The isolation of **1** was achieved by evaporation of the solvent, extraction of the residue with toluene (10 mL), filtration, and concentration of the filtrate followed by crystallization at −80 °C; in this way, **1a** was obtained as dark purple crystals, **1b** as brown crystals, and **1c** as light brownish crystals in 33, 31, and 36% yield, respectively, relative to the Cp_2TiCl_2 used for the preparation of **2**. The new compounds were characterized by elemental analysis[7] and by their NMR spectra (Table I).

The data of Table I reveal some interesting trends which are, however, not fully understood at the moment. Most remarkable are the low field shifts of the protons and carbon nuclei of the methylene groups. While low field shifts of a much less dramatic degree have been observed in titanacyclobutanes bearing a group 14 atom at position 3,[1] the presence of two group 4 metals in the four-membered ring leads to values reminiscent of metal carbenes[8,9] and metal–carbene complexes.[2b,5,10] Theory[2a] predicts that the tendency to form such metal–carbene structures decreases for the higher elements, in line with the upfield shifts observed for **1a**, **1b**, and **1c**, respectively. The same trend would be expected on the basis of electronegativity considerations, although we feel that the electronegativity differences are not sufficient to explain the magnitude of the effects observed. Alternatively, low field shifts of bridging methylene groups have been connected to metal–metal bonding,[9] which results in a relatively acute M–C–M angle. Interestingly, the decrease of the carbon–proton coupling constant of the methylene group in the sequence **1a** → **1c** (Table I) would be in line with an increasing M–C–M angle, caused by increasing s character of the carbon to metal bond. A final distinction will only be possible if a crystal structure has been determined; unfortunately, the crystals obtained so far were not suitable for this purpose.

Acknowledgment. We thank Mr. A. F. Hamminga, University of Groningen, for performing the elemental analyses.

Registry No. 1a, 79389-12-1; 1b, 96227-73-5; 1c, 96213-70-6; 2, 96213-71-7; Cp_2TiCl_2, 1271-19-8; Cp_2ZrCl_2, 1291-32-3; Cp_2HfCl_2, 12116-66-4; $CH_2(MgBr)_2$, 27329-47-1.

---

(3) (a) Tebbe, F. N.; Parshall, G. W.; Overall, D. W. *J. Am. Chem. Soc.* **1979**, *101*, 5074. (b) Ott, K. C.; Lee, J. B.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 2942. (c) Lee, J. B.; Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1982**, *104*, 7491. (d) Weiss, K. In "Transition Metal Carbene Complexes"; Fischer, H., Weiss, K., Eds.; Verlag Chemie: Weinheim, 1983; p 228. (e) Ivin, K. J.; Rooney, J. J.; Stewart, C. D.; Green, M. L. H.; Mahtab, R. *J. Chem. Soc., Chem. Commun.* **1978**, 604.

(4) Ott, K. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1981**, *103*, 5922.

(5) Analogous dizirconacyclobutanes are known: Hartner, F. W.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640.

(6) (a) Bruin, J. W.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *Tetrahedron Lett.* **1983**, *24*, 3935. (b) Bruin, J. W.; Schat, G.; Akkerman, O. S.; Bickelhaupt, F. *J. Organomet. Chem.*, in press.

(7) Anal. Calcd for **1b**: C, 61.80; H, 5.66. Found: C, 61.93; H, 5.82. Anal. Calcd for **1c**: C, 51.33, H, 4.70. Found: C, 50.74; H, 4.78.

(8) Schrock, R. R.; Sharp, P. R. *J. Am. Chem. Soc.* **1978**, *100*, 2389.

(9) Herrmann, W. A. *J. Organomet. Chem.* **1983**, *250*, 319 and references cited therein.

(10) (a) Tebbe, F. N.; Parshall, G. W.; Reddy, G. S. *J. Am. Chem. Soc.* **1978**, *100*, 3611. (b) Eisch, J. J.; Piotrowski, A. *Tetrahedron Lett.* **1983**, *24*, 2043.

Kinetic Control in Catalytic Olefin Isomerization. An Explanation for the Apparent Contrathermodynamic Isomerization of 3-Pentenenitrile[†]

Ronald J. McKinney

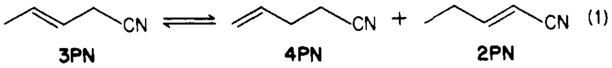
Central Research & Development Department
Experimental Station
E. I. du Pont de Nemours & Company
Wilmington, Delaware 19898

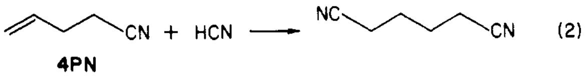
Received March 20, 1985

Summary: The isomerization of 3-pentenenitrile with homogeneous cationic nickel hydride or palladium catalysts is kinetically controlled, initially producing the terminal olefin 4-pentenenitrile in preference to the conjugated and thermodynamically favored isomer 2-pentenenitrile by ratios as high as 70:1.

[†] Contribution No. 3437.

The isomerization of the internal olefin **3PN** to the terminal olefin **4PN** (eq 1) is a critical step in the industrially important hydrocyanation of **3PN** to adiponitrile (eq 2).[1] Unfortunately, the undesired conjugated isomer **2PN**, a yield loss, is also produced.





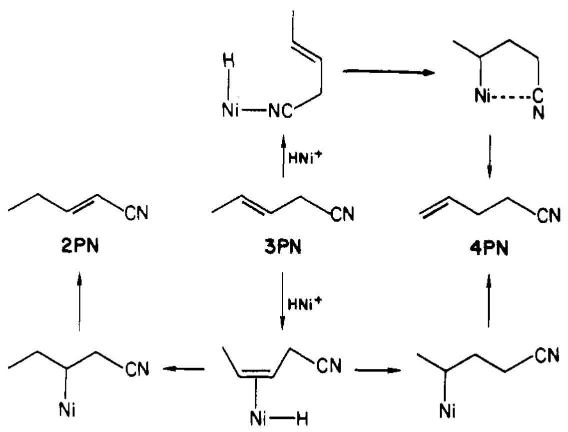
On-going studies in this laboratory have led us to believe that a cationic nickel hydride complex, $HNi[P(OR_3)]_4^+$ (R = alkyl or aryl), is an important catalytic species in the isomerization process. We have, therefore, studied the isomerization of **3PN** in the presence of $Ni[P(OR)_3]_4$ complexes treated with trifluoromethanesulfonic acid, CF_3SO_3H (triflic acid). The reaction of strong acids with NiL_4 complexes produces $HNiL_4^+$ complexes[2] which are rapid olefin isomerization catalysts.[3]

When *trans*-**3PN**[4] containing $Ni[P(O\text{-}p\text{-tolyl})_3]_4$ (0.030 M) **3PN**:Ni = 330) and $P(O\text{-}p\text{-tolyl})_3$ (0.120 M) is treated with CF_3SO_3H (1 equiv/Ni) at 50 °C, rapid isomerization occurs for less than 30 s before catalytic activity ceases (the solution remains homogeneous). During this short burst of isomerization **4PN** and **2PN** are produced in a ratio of 70:1. Similar results are obtained at 40 and 25 °C. If hydrogen cyanide and the Lewis acid triphenylboron, $B(C_6H_5)_3$, are used in place of triflic acid, the initial ratio of **4PN**:**2PN** produced is >65:1. Similar results are obtained with hydrogen cyanide and other Lewis acids, e.g., $ZnCl_2$, $SnCl_2$, and $AlCl_3$. The use of acid in the absence of nickel does not cause isomerization.

When a different phosphite ligand is used, the ratio of **4PN** to **2PN** initially produced is altered significantly; isomerization with $Ni[P(OC_2H_5)_3]_4$ and triflic acid at 50 °C, which is active for several hours, produces a kinetic **4PN**:**2PN** ratio of 17.5:1. In contrast, when 2-hexene is treated with this same catalyst system, the initial ratio of 1-hexene to 3-hexene produced is <2:1.

This unprecedented kinetic preference for isomerization of an internal olefin to a terminal olefin is in stark contrast to the strong thermodynamic preference for the conjugated isomer **2PN**; the thermodynamic distribution at 50 °C is 78.3:20.1:1.6 (**2PN**:**3PN**:**4PN**).[5] It should be emphasized that the ratio of **4PN**:**3PN** never goes above the equilibrium ratio of about 0.07[6] but arrives at that equilibrium ratio before any significant production of **2PN** occurs. A possible explanation is illustrated in Scheme I. Nitrile coordination may direct nickel hydride addition across the double bond as illustrated in the upper portion of Scheme I, whereas, without nitrile coordination, the direction of nickel hydride addition is nonselective (lower portion of scheme I). A strong preference for nitrile coordination over double-bond coordination of **3PN** toward NiL_4 has been previously illustrated.[7] Apparently the nature of the phosphite ligand affects the preference for one path over another but whether this is due to electronic or steric factors remains to be elucidated.

Scheme I



Such kinetically controlled isomerization is not limited to nickel-catalyzed systems. A recent report by Sen and Lai[8] prompted us to isomerize **3PN** with $[Pd(CH_3CN)_4](BF_4)_2$.[9] At room temperature, **4PN** is produced more than 25 times faster than **2PN**. Though a different mechanism of isomerization has been proposed for this catalyst (allylic), it still may be that prior nitrile coordination directs the position of allylic formation.

A more detailed mechanistic study with these catalyst systems is underway.

Registry No. $Ni(P(O\text{-}p\text{-tolyl})_3]_4$, 36700-08-0; $P(O\text{-}p\text{-tolyl})_3$, 620-42-8; CF_3SO_3H, 1493-13-6; $[PdCCH_3CN)_4](BF_4)_2$, 21797-13-7; *trans*-3PN, 16529-66-1.

---

[1] Tolman, C. A.; McKinney, R. J.; Seidel, W. C.; Druliner, J. D.; Stevens, W. R. *Adv. Catal.*, in press.

[2] Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 4217-4222.

[3] Tolman, C. A. *J. Am. Chem. Soc.* **1972**, *94*, 2994-2999.

[4] Cis-trans isomerization also occurs rapidly under these conditions. It does not appear to matter whether mixtures or pure cis or trans isomers are utilized.

[5] Obtained by repeated sequential treatment of several different PN mixtures with neutral alumina (Woelm N, Akt. 1) and $Ni[P(OEt)_3]_4$ + CF_3SO_3H at 50 °C until no further change in distribution is observed.

[6] Tolman, C. A.; Seidel, W. C.; Druliner, J. D.; Domaille, P. J. *Organometallics* **1984**, *3*, 33.

[7] Tolman, C. A. *Organometallics* **1983**, *2*, 614.

[8] Sen, A.; Lau, T.-W. *Inorg. Chem.* **1984**, *23*, 3257-3258.

[9] Purchased from Strem Chemicals, Inc.

A Model for Metal-Templated Catalytic Asymmetric Induction via π-Allyl Fragments

Barry M. Trost* and Dennis J. Murphy

McElvain Laboratories of Organic Chemistry
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received February 19, 1985

Summary: Asymmetric induction in metal-catalyzed allylic alkylations with stabilized nucleophiles places severe demands on the nature of the inducing ligands because of the distal relationship between the incoming nucleophile and the chiral environment. A model invoking creation of "chiral pockets" led to the generation of a series of chiral and optically active ligands derived from the commercially available 1,1′-binaphthol. Asymmetric syntheses of nearly 70% ee are accessible at practical operating temperatures between +25 and +66 °C.

Despite impressive strides in catalytic asymmetric induction in the formation of C–O and C–H bonds, such advances in the formation of C–C bonds remain more elusive.[1] Earlier reports of good asymmetric induction in

---

[1] For a case of C–C bond formation in a cross-coupling reaction in which both groups are bound to the metal prior to C–C bond formation see: Hayashi, T.; Konishi, M.; Fukushima, M.; Kanehira, K.; Hioka, T.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2195.

0276-7333/85/2304-1143$01.50/0