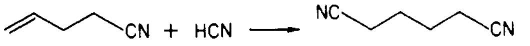
The isomerization of the internal olefin **3PN** to the terminal olefin **4PN** (eq 1) is a critical step in the industrially important hydrocyanation of **3PN** to adiponitrile (eq 2).[1] Unfortunately, the undesired conjugated isomer **2PN**, a yield loss, is also produced.

3PN **4PN** **2PN** (1)



4PN (2)

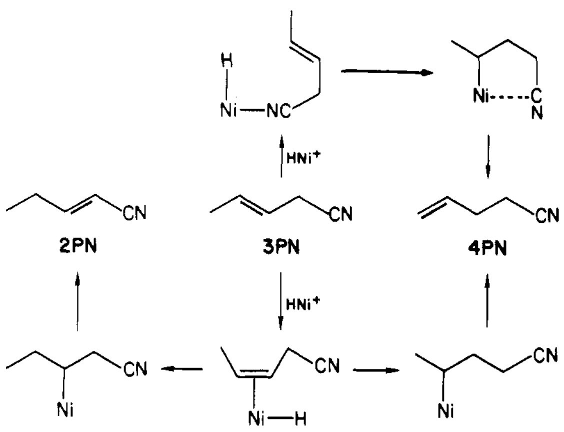
On-going studies in this laboratory have led us to believe that a cationic nickel hydride complex, $HNi[P(OR_3)]_4^+$ (R = alkyl or aryl), is an important catalytic species in the isomerization process. We have, therefore, studied the isomerization of **3PN** in the presence of $Ni[P(OR)_3]_4$ complexes 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.

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[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

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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

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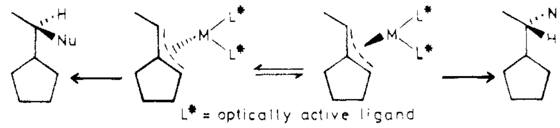
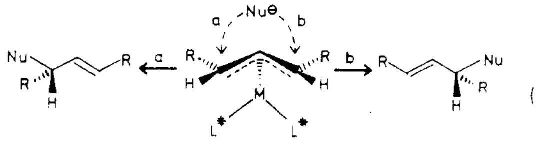
[1] For a case of C–C bond formation in a cross-coupling reaction in which both groups are bound to the metal prior to C–C bond formation see: Hayashi, T.; Konishi, M.; Fukushima, M.; Kanehira, K.; Hioka, T.; Kumada, M. *J. Org. Chem.* **1983**, *48*, 2195.

palladium-catalyzed allylic alkylation involved chiral π-allyl fragments bound to chiral metal templates in which interconversion between the two diastereomeric complexes must be rapid relative to the rate of alkylation (see eq 1).[2,3]



(1)

It has been suggested that, in such cases, the asymmetric induction depends upon the equilibrium between the two diastereomeric intermediates and thus relies upon thermodynamic control.[3] An alternative approach, which is necessarily kinetic, envisions the use of a meso π-allyl fragment bound to a chiral template in which the latter steers the nucleophile to one of the two ends of the allyl fragment to lead to one of the two enantiomeric products (eq 2).



(2)

Unlike the successful catalytic asymmetric epoxidation and hydrogenation systems in which *both* partners are bound to the metal template prior to bond formation, metal-catalyzed allylic alkylation with stabilized nucleophiles requires the nucleophile to approach the allyl fragment distal[4] to the chiral ligands—a fact making transmission of the asymmetric environment to the newly forming C–C bond more difficult. Our approach therefore involves creation of an asymmetric environment, as in a "chiral pocket", for good asymmetric induction.

As an initial working model, the notion that a chiral barrier is created by bidentate chiral ligands (vide infra) leads schematically to structures **1**–**3** (Figure 1). C–P–K molecular models predict that enlarging the ring of the bidentate ligand leads to greater embracing of the allyl fragment by the metal template and consequently higher asymmetric induction. From such a simplistic model, asymmetric induction should increase in the order **1** < **2** < **3**.

We chose the lactone **8** as the substrate and bis(benzenesulfonyl)methane as the nucleophile. The L_nPd^0 catalyst (1–5 mol %) was generated in situ by reaction of palladium acetate or palladium trifluoroacetate with 2.0 or 3.0 equiv of bidentate ligand per palladium in THF followed by addition of a reducing agent (1-hexene or *n*-butyllithium). Addition of the lactone **8**, nucleophile, BSA[5] as base, and heating at reflux gave the alkylated product which was characterized after esterification with diazomethane (eq 3).[6] With the exception of **5**, the degree of asymmetric induction increased in the predicted order; however, induction reached only 38% with **7**.

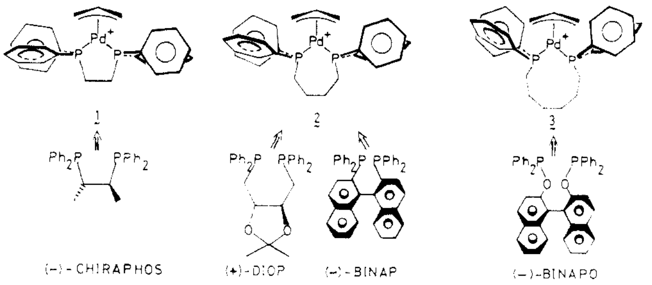


Figure 1. Schematic model for chiral barriers.

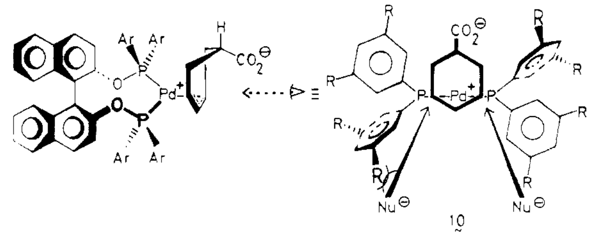
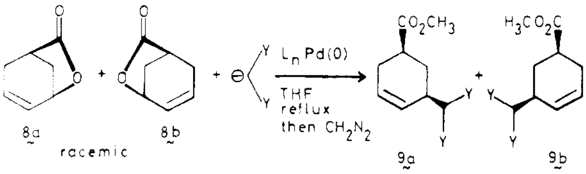


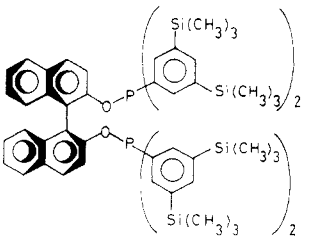
Figure 2. A model for asymmetric induction.

By analogy to the rhodium-based asymmetric hydrogenation systems, the phenyl groups of the ligand in the postulated catalytically active intermediate **10** can be viewed as a propellor (Figure 2). This may account for the asymmetric induction,[7,13] and indeed, this model correctly predicts the absolute configuration as depicted in **9a**.[8] Introduction of substituents in the meta positions of the aryl rings should further extend the chiral barriers toward the approaching nucleophile and perhaps increase the % ee. We therefore placed a trimethylsilyl substituent at the meta position as in **11** (see eq 5 and ref 9 for synthesis). As shown in eq 3, the % ee jumped to *nearly 70% at the temperature of refluxing THF*!



(3)

L	Y	% **9a**	% **9b**	% ee	% yield
4	SO_2Ph	59	41	18	73
5	SO_2Ph	58	42	16	82
6	SO_2Ph	65	35	31	92
7	SO_2Ph	69	31	38	66
11	SO_2Ph	85	15	69	82



11

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(2) Trost, B. M.; Dietsche, T. J. *J. Am. Chem. Soc.* **1973**, *95*, 8200. Trost, B. M.; Strege, P. E. *Ibid.* **1977**, *99*, 1649.

(3) Bosnich, B.; Mackenzie, P. B. *Pure Appl. Chem.* **1982**, *54*, 189.

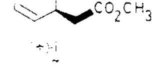
(4) Trost, B. M.; Weber, L.; Strege, P. E.; Fullerton, T. J.; Dietsche, T. J. *J. Am. Chem. Soc.* **1978**, *100*, 3426. Also see: Backvall, J.-E.; Nordberg, R. E.; Zetterberg, K.; Åkermark, B.; Hayashi, T.; Koniski, M.; Kumada, M. *J. Chem. Soc., Chem. Commun.* **1984**, 107.

(5) BSA = *N,O*-bis(trimethylsilyl)acetamide.

(6) Enantiomeric excess was determined by ^1H NMR using tris(3-heptafluorobutyryl-*d*-camphorato)europium(III) $[Eu(hfbc)_3]$ in $CDCl_3$ at 200 or 270 MHz. Cf. Fraser, R. R.; Petit, M. A.; Saunders, J. K. *J. Chem. Soc., Chem. Commun.* **1971**, 1450.

(7) Knowles, W. S.; Vineyard, B. D.; Sabacky, M. J.; Stults, B. R. *Fundam. Res. Homogeneous Catal.* **1979**, *3*, 537.

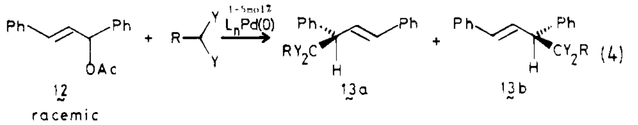
(8) Determined in the case of malonate as the nucleophile (Y = CO_2Me) by decarbomethoxylation to the known (+)-i.[2]



(+)-i

Organometallics **1985,** *4,* 1145–1147 1145

Allyl acetate 12 also undergoes alkylation using 6 or 7 as the optically active ligands as summarized in eq 4. Phase-transfer conditions were required for the bis(benzenesulfonyl)methane system since no alkylation occurred with BSA in THF. Strikingly, only a small effect of either temperature or steric demand of the nucleophile is observable as delineated in eq 4. The absolute configuration of **13a**, assigned by degradation to dimethyl (+)-S-2-phenylsuccinate[10] can also be rationalized by a model similar to that depicted in Figure 2. The reversal of the sense of induction of 13 with BINAP is potentially due to syn–anti interconversion (which is not possible with lactone 8).



12
racemic

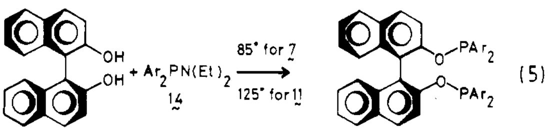
13a

13b

(4)

L	R	Y	condtns	% 13a	% 13b	% ee	% yield
6	CH_3	CO_2Me	BSA, THF, 66 °C	25	75	50	81
7	H	CO_2Me	BSA, THF, 66 °C	78	22	55	87
7	CH_3	CO_2Me	BSA, THF, 25 °C	84	16	68	75
7	H	SO_2Ph	$(n\text{-Bu})_4NOH$, 25 °C CH_2Cl_2, H_2O	83	17	66	85

The high asymmetric induction for C–C bond formation ultimately possible in all the reactions reported herein demonstrates that diastereomeric complexes need not be the source of asymmetric induction in metal-catalyzed allylic alkylations. An electronic effect as observed in enantiomerically pure stoichiometric molybdenum complexes[11] appears unlikely as the source of the asymmetric induction. The observation of good ee in spite of the unfavorable orientation of the incoming nucleophile with respect to the centers of asymmetry supports the notion that these ligands begin to create chiral pockets. The practical operating temperature of these alkylations combined with the ready availability of the chiral ligands from the commercially available, optically active 1,1′-binaphthol[12] according to eq 5[12] enhances the utility of this approach. It is interesting to note that the *more flexible* ligand 7 provides higher induction than the more rigid ligand 6 in contrast to other asymmetric catalytic reactions such as hydrogenation.[13]



(5)

Acknowledgment. We wish to thank the National Science Foundation for their generous support of our programs. We thank Johnson Matthey and Englehardt for generous supplies of palladium salts and Dr. Larry Truesdale and Hoffmann La Roche Inc. for a generous gift of optically pure BINAP.

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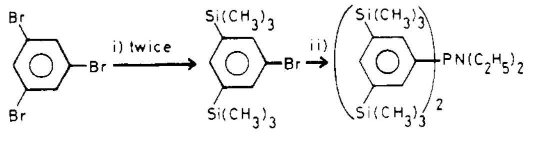
[9] The synthesis of the requisite 14 (Ar = 3,5-bis(trimethylsilyl)phenyl) proceeds simply from 1,3,5-tribromobenzene as depicted.



(i) n-C_4H_9Li, ether, −78 °C, then Me_3SiCl; (ii) n-C_4H_9Li, THF, −78 °C; then 0.4 equiv of Cl_2PNEt_2, −78 °C–room temperature

[10] Petterson, K. *Ark. Kem.* **1954,** *7,* 39, 347.

[11] Faller, J. W.; Chao, K.-H. *J. Am. Chem. Soc.* **1983,** *105,* 3893; *Organometallics* **1984,** *3,* 927.

[12] Available from Aldrich Chemical Co. or by direct oxidative coupling of β-naphthol in the presence of *d*-amphetamine. See: Brussee, J.; Jansen, A. C. A. *Tetrahedron Lett.* **1983,** *24,* 3261. In our hands, more forcing conditions (toluene, 85 °C) were required than those reported by: Grubbs, R. H.; DeVries, R. A. *Tetrahedron Lett.* **1977,** 1879.

[13] It should be noted that less than 3 equiv of chiral ligand 11/Pd led to substantially lower % ee. The significance of this important observation with respect to the exact structure of the active catalyst is not known. In other cases, we have observed variation of ee with the ratio of phosphine to palladium. In these cases, the conditions which give the highest ee are reported.

Ancillary Ligand Involvement in the Activation of Dihydrogen by Iridium(III) Complexes

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Summary: Oxidative addition of methyl iodide to the Ir(I) complexes $Ir(\eta^2\text{-}C_8H_{14})[N(SiMe_2CH_2PR_2)_2]$ (R = Ph, *i*-Pr) yields monomeric, five-coordinate methyl iodide derivatives $Ir(CH_3)I[N(SiMe_2CH_2PR_2)_2]$. Spectroscopic and crystallographic data indicate that these species are square pyramidal with the methyl ligand in the apical position. The complex $Ir(CH_3)I[N(SiMe_2CH_2P(i\text{-}Pr)_2)_2]$ is monoclinic, crystallizing in the $P2_1/m$ space group with a = 9.6295 (7) Å, b = 15.2327 (5) Å, c = 10.4068 (9) Å, α = 90°, β = 111.774 (4)°, γ = 90°, Z = 2, and R_w = 0.029. Under dihydrogen, these complexes rapidly form the Ir(III) amine hydrides $Ir(CH_3)I(H)[NH(SiMe_2CH_2PR_2)_2]$ having a stereochemistry which corresponds to an overall trans addition of H_2. Unit cell parameters for $Ir(CH_3)I(H)[NH(SiMe_2CH_2P(i\text{-}Pr)_2)_2]$, which is triclinic and belongs to the $P\bar{1}$ space group, are as follows: a = 11.412 (2) Å, b = 14.712 (3) Å, c = 9.9133 (13) Å, α = 106.972 (9)°, β = 112.406 (8)°, γ = 70.989 (13)°, Z = 2, and R_w = 0.040. Crystallographic data for both of these complexes were collected at 22 °C by using an Enraf-Nonius CAD4-F diffractometer with Mo Kα radiation. It would appear that H_2 activation by these iridium complexes occurs via an oxidative addition/reductive transfer pathway rather than a direct heterolytic cleavage of H_2.

The activation of dihydrogen by transition-metal complexes can occur via oxidative addition, homolysis, or heterolysis depending upon the nature of the metal center, its oxidation state, coordinated ligands, and the solvent basicity.[1] Although heterolytic cleavage is purported to occur for a number of Rh(III)[2,3] and Ir(III)[4] species under H_2, the evidence for this mechanism vs. an oxidative ad-

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[†] Fellow of the Alfred P. Sloan Foundation (1984–1986).

[1] Brothers, J. P. *Prog. Inorg. Chem.* **1981,** *28,* 1.

[2] Halpern, J.; Harrod, J. F. *Can. J. Chem.* **1959,** *37,* 1933.

[3] James, B. R.; Rempel, G. L. *Can. J. Chem.* **1966,** *44,* 233.

[4] James, B. R. "Homogeneous Hydrogenation"; Wiley: New York, 1973; p 313.

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