CHEMISTRY LETTERS, pp. 941 - 944, 1984.

KINETIC AND THERMODYNAMIC CONTROL OF ASYMMETRIC INDUCTION BY CHIRAL DIPHOSPHINE IN RING CONTRACTION OF (CHIRAL DIPHOSPHINE)$\overline{NiCH_2CH_2CH_2COO}$ TO (CHIRAL DIPHOSPHINE)$\overline{NiCH(CH_3)CH_2COO}$

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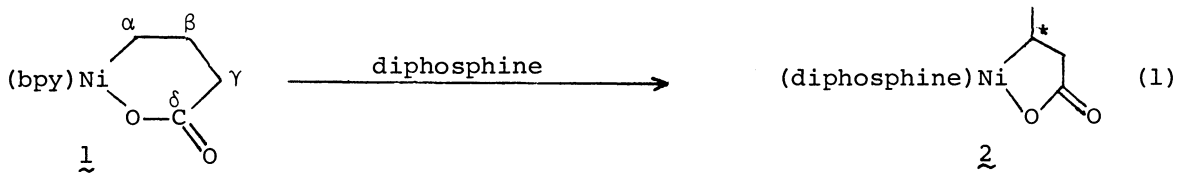
An (*S*,*S*)-CHIRAPHOS-coordinated six-membered ring complex $\overline{NiCH_2CH_2CH_2COO}$ undergoes facile ring contraction to give a mixture of ((*S*,*S*)-CHIRAPHOS)-(*R*)-$\overline{NiCH(CH_3)CH_2COO}$ (2a) and ((*S*,*S*)-CHIRAPHOS)-(*S*)-$\overline{NiCH(CH_3)CH_2COO}$ (2b). Complex 2a is kinetically favored, whereas 2b is thermodynamically favored; a thermodynamically equilibrated mixture contains 2b in 54% de.

Recent development in studies of asymmetric olefin hydrogenation by transition metal catalysts having chiral ditertiary phosphine ligands clarified the interaction between the olefin and metal complex having the chiral ligands and infuluence of the chiral ligands on rate-determining step of hydrogenation.[1-6] However, only a little is known about the infuluence of the chiral ligands on the stereochemistry of the metal-bonded alkyl group where the asymmetry is induced in the asymmetric synthesis.[2,3]

Previously we observed a ring contraction reaction of a 6-membered nickel-containing cyclic ester 1 to a 5-membered nickel-containing cyclic ester 2 induced by displacement of a 2,2'-bipyridine ligand by sterically more demanding diphosphine like 1,2-bis(diphenylphosphino)ethane.[7]



1 2 (1)

By formation of the methyl-substituted nickel-containing cyclic ester, a chiral center as marked by * is generated at the α-carbon bonded to Ni and use of chiral

diphosphine ligand is expected to induce formation of unequal amounts of diastereomers. We report here the kinetic and thermodynamic control of chiral diphosphines on distribution of the two diastereomers formed in the ring contraction.

Addition of (*S*,*S*)-CHIRAPHOS to a solution of 1 at room temperature led to an instant ring contraction as proved by ^{1}H- and $^{13}C\{^{1}H\}$-NMR and IR of the compound recovered after addition of (*S*,*S*)-CHIRAPHOS. The $^{31}P\{^{1}H\}$-NMR spectrum observed immediately after addition of (*S*,*S*)-CHIRAPHOS (Fig. 1a) shows two sets of two doublets arising from the two diastereomers.

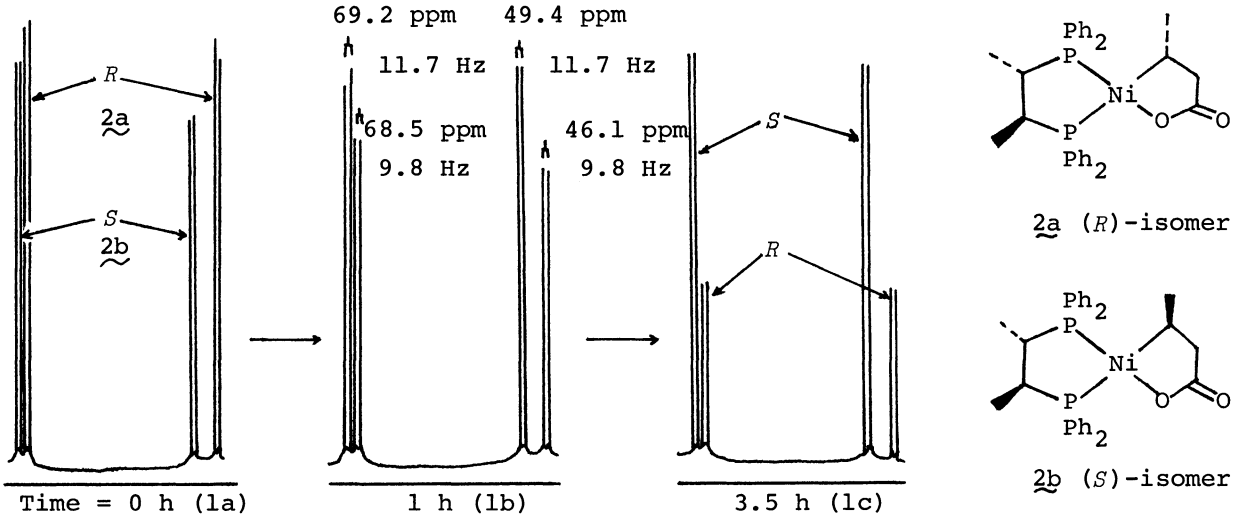
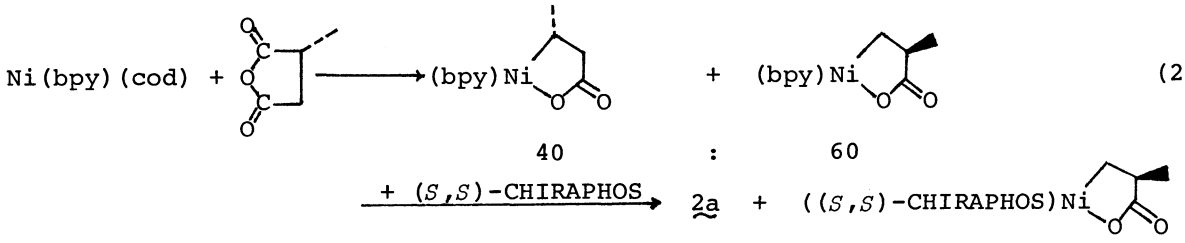


Fig. 1. Change of $^{31}P\{^{1}H\}$-NMR spectrum of 2 with time.

Complex 2a was independently prepared through the reaction of (*R*)-methylsuccinic anhydride (100% ee) with Ni(bpy)(cod),[7,8]



(2)

The reaction 2 proceeds via ring opening of methylsuccinic anhydride followed by decarbonylation, and the processes most likely proceed with the stereochemical retention at the methyl-substituted carbon.[9]

Figure 1 shows that the (*R*)-isomer which is present in 16% diastereomer excess (de)[10] in the beginning decreases with reversal of its configuration eventually to give the (*S*)-isomer in 54% de after 10 h at 24 °C, demonstrating that the kinetically favored diastereomer (2a) and thermodynamically favored diastereomer

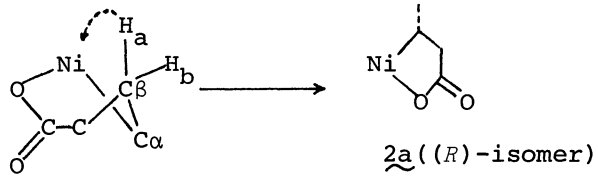
(2b) are different in the present system. The present finding represents the first example, to our knowlege, of observation of configurational reversal from the kinetically controlled chiral alkyl complex to the thermodynamically controlled chiral alkyl complex of the reverse configuration.

The isomerization between 2a and 2b obeys the first-order kinetics, giving 1.2×10^{-4} s^{-1} and 3.7×10^{-5} s^{-1} for the rate constants, k_1 and k_{-1}, respectively at 24 °C.

$$2a \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2b$$

From temperature dependence of the k_1 and k_{-1} values, the kinetic parameters for k_1 are calculated as $\Delta H_1^{\ddagger} = 93 \pm 2$ kJ/mol, $\Delta S_1^{\ddagger} = -8 \pm 6$ J/mol·k, and $\Delta G_1^{\ddagger} = 95$ kJ/mol at 24 °C. From the temperature dependence of the equilibrium constant, $K = k_1/k_{-1}$, the thermodynamic parameters for the equilibrium were obtained: $\Delta H° = 13 \pm 2$ kJ/mol $\Delta S° = 54 \pm 6$ J/mol·K, and $\Delta G° = -3.0$ kJ/mol at 24 °C.

The kinetic and thermodynamic control of the asymmetric induction observed in the present system seems to be elucidated on the basis of molecular models of the 6-membered and 5-membered complexes coordinated by (*S*,*S*)-CHIRAPHOS. If the coordinating (*S*,*S*)-CHIRAPHOS takes a δ-conformation as observed in several transition metal complexes,[1,4] the CPK molecular model of ((*S*,*S*)-CHIRAPHOS)-$\overline{NiCH_2CH_2CH_2COO}$ (3) initially formed by the ligand exchange suggests that the 6-membered cyclic ester ring would prefer the λ-conformation[11] where one of two hydrogens attached to the β-carbon (H_a) situated at a closer distance than the other (H_b) to the nickel atom to be preferentially abstracted. Ni-assisted 1,2-shift (presumably through β-elimination) of H_a to the α-carbon (C_α) leads to the formation of 2a.



3 (λ-form) 2a ((*R*)-isomer)

Reversal of configuration of 2a to 2b then reflects the thermodynamic preference of the (*S*)-isomer as imposed by the template of (*S*,*S*)-CHIRAPHOS which is in the δ-conformation. Examination on the steric model indicates the preference of the (*S*)-isomer in the 5-membered complex.

When (*R*,*R*)-DIPAMP, which takes a reverse conformation (λ) to (*S*,*S*)-CHIRAPHOS,[1,4] was employed, the thermodynamically equilibrated product after the ring contraction contained the (*R*)-isomer in 50% de in contrast to the result obtained

with CHIRAPHOS. This result also agrees with the conclusion obtained from the CPK molecular model of the corresponding 5-membered complex. The initial product obtained immediately after the ring contraction, however, contains more amount of (*S*)-isomer than the equilibrated product, and the isomerization from the (*S*)-isomer to (*R*)-isomer also obeyed the first order kinetics with rate constant 5.5×10^{-5} s^{-1} at 24 °C.

The authors express their grateful acknowledgement to Dr. Knowles of Monsanto Co. for donating (*R*,*R*)-DIPAMP through Professor Ojima of State University of New York.

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8) ^{31}P-NMR spectrum showed no peak assigned to 2b, indicating that reaction 2 proceeds with high stereoselectivity.

9) T. C. Flood, "Topics in Stereochemistry," ed by G. L. Geoffroy, John Wiley, New York (1981), Vol. 12.

10) Since it takes 0.5-1 h for measuring the ^{31}P-NMR of the solution of 2 prepared by mixing 1 with (*S*,*S*)-CHIRAPHOS, the initial de of 2a is considered to be somewhat higher than 16%.

11) δ and λ conformations concerning the 6-membered ring in 3 is defined by the direction of tortion of a line connecting the β and C=O (or δ) carbons (cf. Eq. 1) from the molecular plane.

(Received April 3, 1984)