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The Effects of Phosphorus Ligands on the Stereoselectivity of the Nickel-catalyzed Dimerization of Norbornadiene

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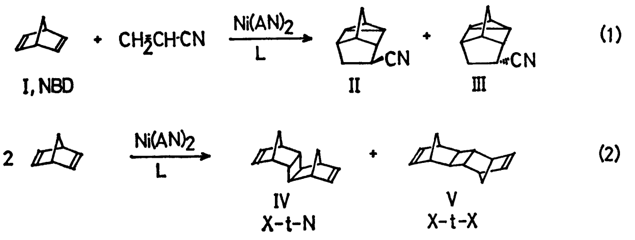
The effects of phosphorus ligands on the stereoselectivity of the nickel-catalyzed 2+2 cyclodimerization of norbornadiene have been studied. The electronic factor, $\nu_{CO}(A_1)$, of $Ni(CO)_3L$ (where L is the ligand) is correlated with the ratio of the *exo-trans-exo* (X-t-X) to the *exo-trans-endo* (X-t-N) isomers of the product, but no simple correlation is apparent between the steric parameter and the selectivity. A three-coordinated Ni(0) species is proposed as the intermediate. The values of $\Delta H^{\ddagger}_{\text{X-t-X}}-\Delta H^{\ddagger}_{\text{X-t-N}}$ and $\Delta S^{\ddagger}_{\text{X-t-X}}-\Delta S^{\ddagger}_{\text{X-t-N}}$ are large and negative.

Ligand effects in homogeneous catalytic reactions are generally divided into electronic and steric factors. Contrary to the electronic factor, the estimation of the steric factor is rather complicated, and little appears to be known about the steric effect on the selectivity of a reaction. Stereoselective organic syntheses have been attracted increasing interest in recent years. Our work in this series was initiated in order to clarify the factors which control the steric course of some homogeneous catalytic reactions. In the previous paper we described that the steric effect of trivalent phosphorus ligands dominates the steric course of the 4+2 cycloaddition of norbornadiene (NBD) with acrylonitrile (AN) catalyzed by bis(acrylonitrile)nickel $Ni(AN)_2$ (Eq. 1).[1]



A steric parameter, the cone angle,[2] was correlated with the ratio of the stereo-isomers (II and III). It seems to us that the reaction of norbornadiene is simple enough for the evaluation of the effect of the added ligands, because both isomerization and retroreaction can be minimized by temperature control under these conditions. The dimerization (Eq. 2) is catalyzed by various transition metal complexes.[3] In the nickel carbonyl-catalyzed dimerization,[4] irradiated $Ni(CO)_4$ with ultraviolet gives a different selectivity from that of the dark reaction.[5] If a ligand added to this system, instead of irradiating, alters the stereoselectivity, the effects of the ligand can be evaluated from the product distribution.

This paper will deal with the dominant role of the electronic effect in the 2+2 cyclodimerization of norbornadiene (Eq. 2).

Results

The present study employed bis(acrylonitrile)nickel $Ni(AN)_2$ combined with phosphorus ligands as the catalyst. Early in the reaction, $Ni(AN)_2$ was insoluble, but it was gradually dissolved by complexing with the phosphorus ligands. With a strong donor ligand, $Ni(AN)_2$ was rapidly dissolved and the system turned reddish-yellow. During the reaction, the acrylonitrile, which was coordinated to the nickel, reacted with norbornadiene to give II and III as the by-products. The radio of II and III was controlled by the cone angle of the phosphorus ligands used, as has been described in the previous paper.

The dimers, *exo-trans-endo* (IV, abbreviated as X-t-N) and *exo-trans-exo* (V, X-t-X), were the major products.[6] The ratio of IV to V is considered to reflect the stereoselectivity of the reaction under these conditions (65.8—130 °C), because neither isomerization nor retroreaction occurred. In fact, the purified product, IV or V was heated with the catalyst. In this case, however, the isomer was recovered unchanged. Figure 1 shows the effects of the added triphenylphosphine on the yield and on the ratio of IV to V. An inspection of Fig. 1 reveals that the selectivity is independent of the amount of triphenylphosphine (P/Ni>2). This observation shows that the active species is specified not by the amount but by the kind of the phosphorus ligand added. This is consistent with the previous observation.[1] A correlation for the temperature indicated that the IV isomer was preferably formed as the temperature rises.

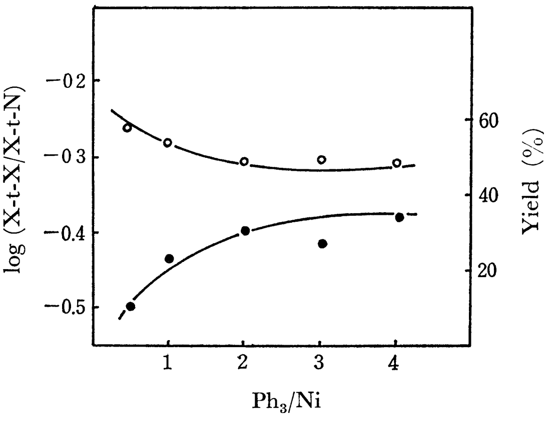


Fig. 1. Effects of added triphenylphosphine on the yield and the selectivity. ○, selectivity; ●, yield. Conditions: NBD, 8 mmol; $Ni(AN)_2$, 0.04 mmol; 100 °C for 5 h.

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As has been reported earlier,[1] the electronic and steric factors of the ligands were estimated by means of the $\nu_{CO}(A_1)$ of $Ni(CO)_3L$ and the cone angle, θ, respectively. The ratio of IV to V was correlated with ν_{CO} rather than with θ, as is shown in Figs. 2 and 3. No simple correlation is apparent between the cone angle and the selectivity. For example, ligands of different bulkiness, $(O\text{-}o\text{-}C_6H_4CH_3)_3P$ (**11**), $(O\text{-}m\text{-}C_6H_4CH_3)_3P$ (**12**), $(C_6H_5O)_3P$ (**10**), and $CH_3C(CH_2O)_3P$ (**21**), gave a similar ratio. This is in marked contrast to the 4+2 cycloaddition of norbornadiene with acrylonitrile, where a clear-cut correlation of the bulkiness of the ligands with the selectivity was found.

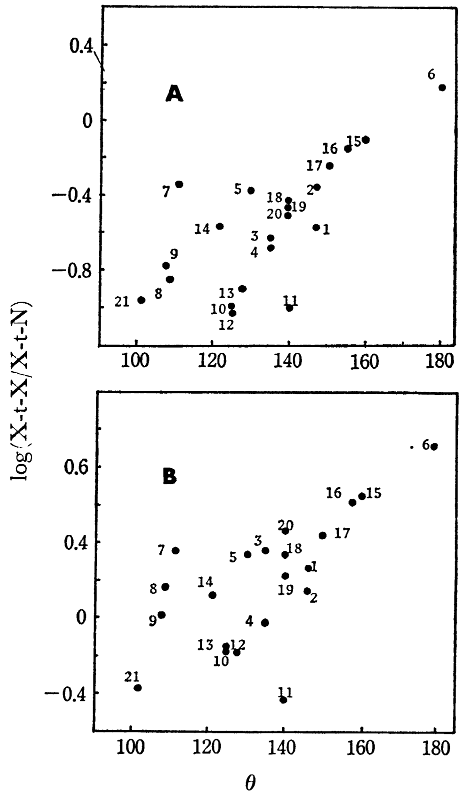


Fig. 2. Selectivity *vs.* cone angle. A, 110°; B, 7.15 °C. Ligands numbers refer to Experimental section.

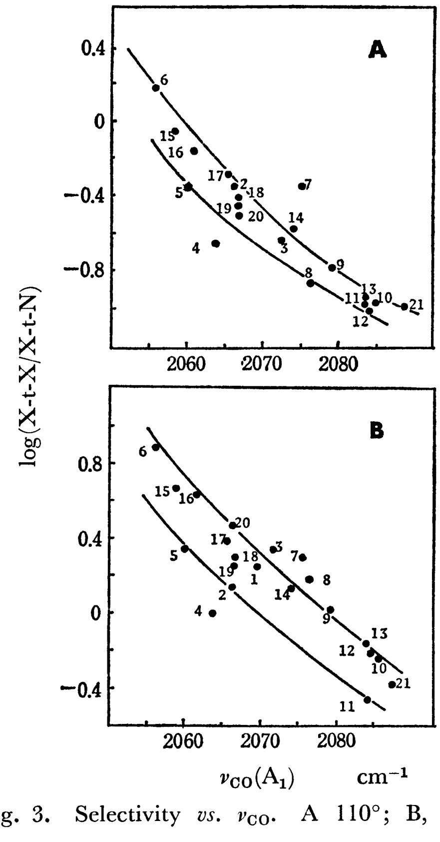


Fig. 3. Selectivity *vs.* ν_{CO}. A 110°; B, 71.5 °C.

On the other hand, the importance of the electronic effect is indicated by the rather good correlation between $\nu_{CO}(A_1)$ and log V/IV. No appreciable difference in the effects was observed between phosphines and phosphites, except that the former gave higher yields than the latter.

The solvent effect was investigated by using PPh_3 as the auxiliary ligand at 92 and 110 °C. Solvents similar in their volume to norbornadiene were used. Figure 4 shows the relation between their molar polarizability and the selectivity. Acetonitrile behaved differently from the other solvents. This is attributable to the coordination of the CN group to the nickel. The increase in the polarity of the solvent preferred the formation of the X-t-X isomer. However, the solvent effect was smaller than that of the ligand.

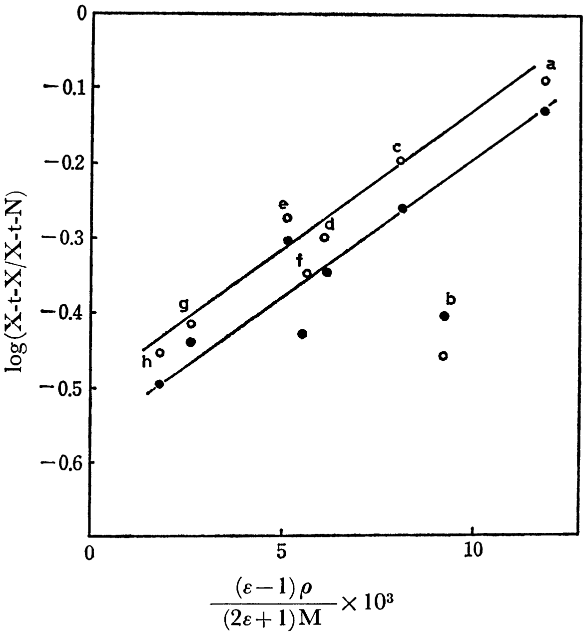


Fig. 4. Solvent effect. a, methanol; b, acetonitrile: c, ethanol; d, 2-propanol; e, tetrahydrofuran; f, pyridine; g, benzene; h, triethylamine. ●, 110 °C; ○, 92 °C. Conditions: NBD, 6 mmol; $Ni(AN)_2$, 0.04 mmol; PPh_3, 0.12 mmol; solvent, 1 ml; 3 h.

It is noteworthy that the 4+2 cycloaddition of norbornadiene to acrylonitrile is strongly influenced by the cone angle of the ligands coordinated to the nickel, while the 2+2 cyclodimerization of norbornadiene is influenced by their electronic factor. This difference is attributable to the limited coordination number of the central metal. Due to a steric interaction of reactants in the coordination sphere, the reaction follows an unexpected course. The reaction of acetylenes with norbornadiene is an example.[7] Bulky diphenylacetylene undergoes 2+2 cycloaddition with norbornadiene on nickel, while dicarbomethoxyacetylene undergoes 4+2 cycloaddition. The failure of the 4+2 cycloaddition of diphenylacetylene may be ascribed to the steric interaction of the bulky phenyl group. In the reaction (Eq. 1) the tetrahedral configuration around the nickel was assumed. Zerovalent nickel (d^{10}) has the maximum coordination number 4, and the stabilization energy of its ligand field is highest. However, the steric interaction caused by adding the fourth bulky ligand may cost more energy than would be gained by completing the coordination number, 4. In fact, Seidel and Tolman[8] have reported that, in the homolog of NiL_4, coordinatively unsaturated NiL_3 is obtained with bulky $P(O\text{-}o\text{-}C_6H_4CH_3)_3$.

A supposed intermediate of the dimerization is shown in Fig. 5, where one molecule of norbornadiene is bidentately coordinated, and the other, unidentately, by assuming that the C–Ni bond is 2.1 Å. In this configuration the cone angle of the ligand coordinated to the fourth site must be smaller than 95°. None of the phosphorus ligands used in the present study can occupy the site, because they are too bulky to be coordinated to the nickel. Therefore, a three-coordinated Ni(0) species is here proposed as the intermediate.[9] This assumption is in striking contrast to that used for the reaction of norbornadiene with acrylonitrile.[1]

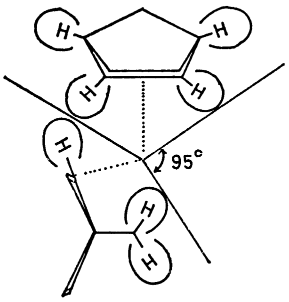


Fig. 5. Proposed coordination of bidentate and unidentate norbornadiene.

Plots of V/IV (the ratio of X-t-X to X-t-N formed) against $1/T$ were used to determine the values of $\Delta H^{\neq}_{\text{X-t-X}}-\Delta H^{\neq}_{\text{X-t-N}}$ ($\Delta\Delta H^{\neq}$) and $\Delta S^{\neq}_{\text{X-t-X}}-\Delta S^{\neq}_{\text{X-t-N}}$ ($\Delta\Delta S^{\neq}$), by assuming that the ratio of the products formed reflects that of the rate constants. The values of $\Delta\Delta H^{\neq}$ and $\Delta\Delta S^{\neq}$ are large and negative, in general (Fig. 6). The isokinetic temperature is derived as 79 °C.

The thermally "forbidden" dimerization of norbornadiene is here considered to proceed *via* a metal-carbon bonded intermediate.[10] In fact, an analogous iridocycle has been prepared and can be regarded as a stabilized intermediate.[11] The stereochemistry of the carbon–carbon bond formation on the iridium metal is not altered during the reductive elimination, which gives the 2+2 cycloaddition products. That is, no isomerization is involved in these steps. Before the coupling of two double bonds, the coordination of both reactants to the central metal is required. In the nickel-catalyzed 2+2 cycloaddition of norbornadiene with a strained olefinic double bond, the transient bidentate (*endo*) coordination of norbornadiene is assumed, because this catalytic system gives exclusively an adduct having *endo* stereochemistry.[12] The mode of the coordination before the coupling is considerd to determine the stereochemistry of the products.

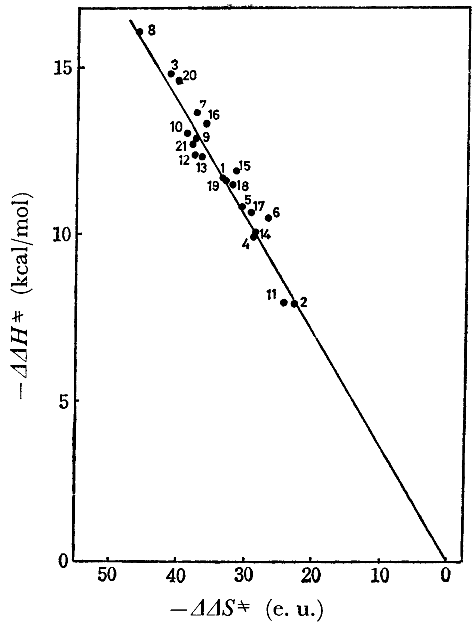
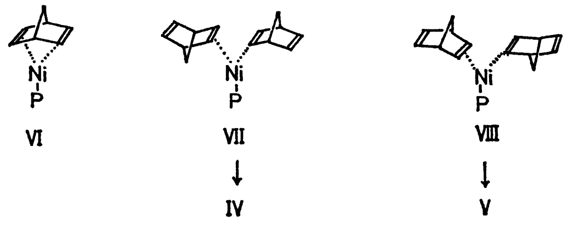


Fig. 6. Isokinetic relation. Ligands numbers refer to Experimental section.

In general, due to its strain each double bond of norbornadiene can participate in the coordination;[9] thus, the *endo* coordination through chelation is inherent in the present reaction. Consequently, prior to the coupling of norbornadiene, the corresponding *exo-endo* (VII) and *exo-exo* (VIII) coordinations can be assumed with likelihood; they afford *exo-trans-endo* (IV) and *exo-trans-exo* (V) isomers respectively.



No sufficient explanation of the electronic effect of the phosphorus ligands on the reaction can be made on the basis of the present study. However, the following explanation is possible. The donor ligand increases the electron density of the nickel. The coordination of norbornadiene on the less-hindered *exo* side gives a greater overlap of the orbitals between the nickel and the double bond.[13] The terms of enthalpy dominates the formation of VIII. On the other hand, the formation of VII is favorable in terms of its smaller entropy loss on the basis of the assumption that both VII and VIII are derived from VI by substituting one and two double bonds of the originally *endo*-coordinated norbornadiene with the incoming norbornadiene. A higher temperature also favors the formation of IV (Fig. 3). Therefore, the entropy term is considered to be dominant in the formation of VII. If the intermediates (VII and VIII) participate in the product-determining step, the selectivity is determined by the ease of their formation.

Experimental

Commercially available phosphorus compounds were used without further purification. All the reactions were carried out in glass tubes (8 mm in diameter) without stirring. The reaction conditions are indicated in the figures. The separation of the isomers was performed by gas chromatography on a Silicon DC 550 column (3 m) at 180 °C. They were identified by comparing the NMR spectra of the gas chromatographically collected samples with those of the reported ones.[4d] The yields were determined by gas chromatography, using tetralin as the internal standard. The total yields (X-t-X and X-t-N formed) of a typical reaction (NBD, 8 mmol) in the presence of $Ni(AN)_2$ (0.04 mmol) and the ligand (0.12 mmol) in benzene (1 ml) are as follows (% at 71.5 °C for 15 h, 110 °C for 3 h): $(C_6H_5)_3P$ (**1**), (65.2, 49.0); $(p\text{-}CH_3C_6H_4)_3P$ (**2**), (70.2, 59.2); $(C_6H_5)_3As$ (**3**), (46.4, 4.8); $(C_2H_5)_2(C_6H_5)P$ (**4**), (55.0, 3.7); $(n\text{-}C_4H_9)_3P$ (**5**), (43.9, 35.7); $(C_6H_{11})_3P$ (**6**), (36.6, 24.5); $(C_4H_9O)_3P$ (**7**), (47.1, 15.3); $(C_2H_5O)_3P$ (**8**), (27.4, 3.6); $(CH_3O)_3P$ (**9**), (20.8, 1.9); $(C_6H_5O)_3P$ (**10**), (32.2, 1.4); $(O\text{-}o\text{-}C_6H_4CH_3)_3P$ (**11**), (31.6, 0.9); $(O\text{-}m\text{-}C_6H_4CH_3)_3P$ (**12**), (27.6, 0.5); $(O\text{-}p\text{-}C_6H_4CH_3)_3P$ (**13**), (36.7, 0.9); $(C_2H_5O)_2(C_6H_5)P$ (**14**), (35.4, 6.9); $(o\text{-}C_6H_4CH_3)_3P$ (**15**), (42.3, 31.6); $(o\text{-}C_6H_4OCH_3)_2(C_6H_5)P$ (**16**), (59.8, 23.1); $(o\text{-}C_6H_4OCH_3)(C_6H_5)_2P$ (**17**), (55.0, 20.1); $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (**18**), (47.6, 10.4); $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (**19**), (36.2, 15.9); $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_3$ (**20**), (41.6, 7.3); $CH_3C(CH_2O)_3P$ (**21**), (25.8, 3.6).

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