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An Evaluation of the Effects of the Phosphorus Ligands on the Stereoselectivity of a Nickel-catalyzed Reaction. The Reaction of Norbornadiene with Acrylonitrile

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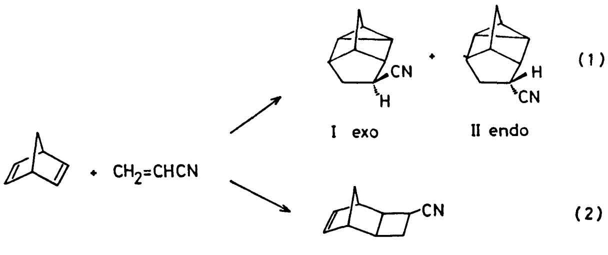
The effects of nineteen phosphorus ligands on the nickel-catalyzed 4+2 cycloaddition reaction of norbornadiene to acrylonitrile have been studied. The cone angle and the ν_{CO} stretching frequency of $Ni(CO)_3L$ (where L is the phosphorus ligand) are used as measures of their steric and electronic parameters respectively. The steric factor of the phosphorus ligands is correlated with the ratio of the *exo-* and *endo*-isomers of the product. Consequently, this effect is important in determining the steric course of the reaction. The electronic property and the solvent effect are less influential.

Many stereoselective reactions are catalyzed by transition metal complexes. In these catalytic reactions, the reaction participants are both electronically and sterically influenced by the effects of the ligands. Therefore, the transition metal-catalyzed homogeneous reactions have many advantages, *e.g.*, the available coordination sites for the reactions can be modified by adding some appropriate ligands, thus controlling a desired reaction. Such a modification has widely been used in synthetic and mechanistic studies of such transition metal-catalyzed reactions as the polymerization and oligomerization of olefins, hydrogenation, hydroformylation, and so on.[1] The electronic properties of phosphorus ligands have been evaluated from the infrared stretching frequencies of the ν_{CO} of $Ni(CO)_3L$ (where L is the phosphoru sligand).[2] On the other hand, the steric parameters of phosphorus ligands are somewhat complicated. Tolman has proposed the concept of a "cone angle", which encloses the van der Waals radii of the outermost atoms of the phosphorus ligand.[3–5] Until now, though, no satisfactory study of the electronic and steric effects of the phosphorus ligand on the transition metal-catalyzed homogeneous reaction has been made, because the reaction consists of many complicated steps. It seems that only a simple reaction can be discussed.

The reaction of norbornadiene with acrylonitrile is known to occur catalytically by means of nickel complexes.[6] This 4+2 cycloaddition is one of the most satisfactory model reactions for the evaluation of the stereochemical course of a transition metal-catalyzed reaction, because the *endo-exo* isomerization of the products is negligibly slow under the reaction conditions and the reaction can probably be explained by a simple intermediate which involves the coordination of two reactants and the phosphorus ligand.[7,8] In the past several years, the reactions of diolefins catalyzed by nickel complexes have been developed in our laboratory, and mechanistic studies have also been carried out.[9] The present study forms a part of this systematic investigation. This paper will deal with an evaluation of the effects of both the electronic and the steric factors of the phosphorus ligands on the reaction of norbornadiene with acrylonitrile as a model reaction.

Results and Discussion

The reaction of norbornadiene with acrylonitrile gives two products, I and II (Eq. 1). Around 100 °C no appreciable 2+2 reaction (Eq. 2) occurs.



Some nickel catalysts are effective for the reaction (Eq. 1) at lower temperatures. Schrauzer and Eicheler have reported the bis(acrylonitrile)nickel-catalyzed reaction in the presence of a phosphorus ligand, but they did not discuss the stereoisomers in detail.[6] It has been found that the catalytic reaction, unlike the thermal reaction, affords the *exo* isomer predominantly, and that this stereoselectivity is influenced delicately by an added phosphorus ligand.[10] To gain insight into the effects of the ligands on the stereoselectivity of the reaction, various phosphorus compounds and triphenylarsine were prepared and used with bis(acrylonitrile)nickel, $Ni(AN)_2$. Bis(acrylonitrile)nickel itself, without a phosphorus ligand, had no catalytic activity under these conditions. Metal acetylacetonates, such as $Cr(C_5H_7O_2)_2$, $Mn(C_5H_7O_2)_3$, $Fe(C_5H_7O_2)_3$, $Co(C_5H_7O_2)_3$, $Ni(C_5H_7O_2)_2$, $Cu(C_5H_7O_2)_2$, and $V(C_5H_7O_2)_3$, combined with sodium borohydride were used in the presence of triphenylphosphine. None of these complexes except $Ni(C_5H_7O_2)_2$ catalyzed the reaction.

Before the systematic investigation, the optimum ratio of triphenylphosphine to the nickel complex was studied. The yields were increased with the amount of added triphenylphosphine, while the ratio of the *exo* to *endo* isomers was not influenced by its amounts (Fig. 1). Bis(acrylonitrile)nickel is slightly soluble under the present reaction conditions. The addition of triphenylphosphine seems to increase the solubility of $Ni(AN)_2$, thus increasing the yield. This observation reveals that the active species is specified only by the kind of the phosphorus ligand, not by its amount.

All the reactions were carried out between 70 and 130

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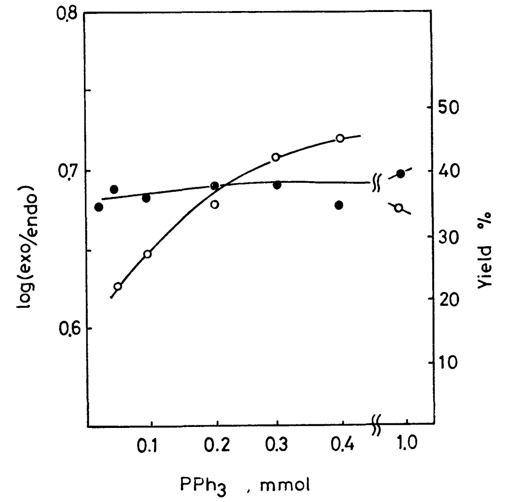

Fig. 1. Effect of added $(C_6H_5)_3P$ on the reaction at 80 °C. Conditions: $Ni(AN)_2$, 0.05 mmol; C_3H_3N, 6 mmol; C_7H_8, 6 mmol; reaction time, 10 hr.
(○): Yield (●): Isomer ratio

°C. Under these conditions, neither *retro*-reaction nor isomerization occurred. That is, the product (I or II) was separated by gas chromatography and heated in the presence of $Ni(AN)_2-(C_6H_5)_3P$ at 100 °C. After 20 hr, no isomerization occurred and I or II was recovered unchanged. Consequently, the isomeric ratio reflects the ratio of the rates of their formation; thus the reaction is kinetically controlled.

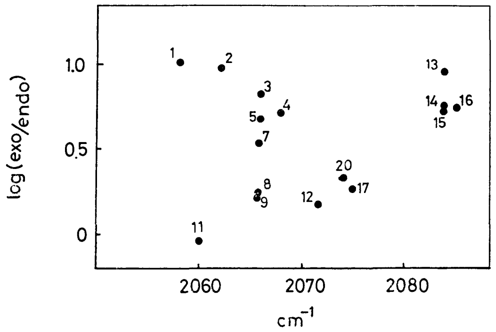

Fig. 2. Plot of *exo*/*endo* ratio at 80 °C against $\nu_{CO}(A_1)$ of $Ni(CO)_3L$ of phosphorus ligand (L) used with $Ni(AN)_2$. Ligand number refers to experimental section.

In general, ligand effects may be separated into electronic and steric factors. The electronic properties of the phosphorus ligands have been estimated by means of the ν_{CO} stretching frequency of $Ni(CO)_3L$ complex (where L is the phosphorus compound).[2] This spectrochemical estimation is applicable to some discussion of the catalytic process. Wilkinson and his co-workers[11] have employed this estimation for the explanation of the catalysis of tris(triarylphosphine)rhodium chloride. As is shown in Fig. 2, however, there is no correlation between the *exo*/*endo* ratio at 80 °C or 130 °C and the electronic properties of the added ligands. For example, there is a marked difference in the electronic properties between $(o\text{-}CH_3OC_6H_4)_3P$ and $(o\text{-}CH_3C_6H_4O)_3P$ (**1** and **13** in Fig. 2). The ratio of the isomers is nearly equal. All the phosphite ligands $P(OR)_3$ except $(o\text{-}CH_3C_6H_4O)_3P$ gave products in similar yields (see Experimental section). The electronic character of the phosphorus ligand has no appreiable influence on the reaction rate. This is a marked contrast to the dimerization of olefins or acetylenes. For example, the ratio of the stereoisomers (*exo-trans-exo* and *endo-trans-exo*) of the 2+2 cyclodimer of norbornadiene is strongly influenced by the electronic factor.[12]

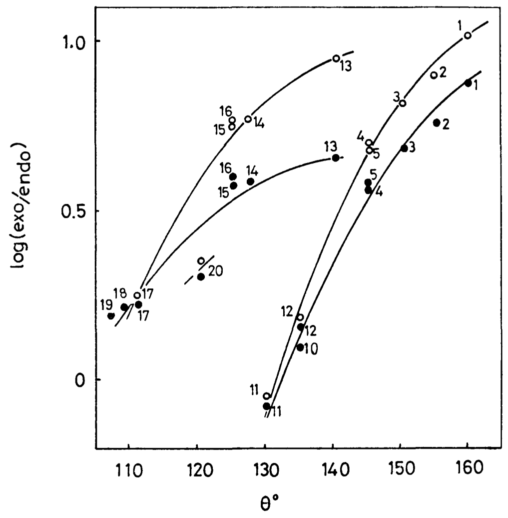

Fig. 3. Plot of *exo*/*endo* ratio against cone angle (θ) of the phosphorus ligands.
(○): 80 °C (●): 130 °C

Contrary to the electronic factor, an estimation of the steric factor of the phosphorus ligand is rather complicated. One measure of its bulkiness is the cone angle, θ, which is the maximum clearance angle for the rotation of the phosphorus ligand around its three-fold axis.[3] When this value is used as a measure of the steric parameter, it is shown in Fig. 3 that the steric factor is much more important than the electronic factor in determining the steric course of the reaction. The cone angles of the phosphorus ligand used and the ratio of *exo*/*endo* are correlated with each other. In Fig. 3 the phosphorus ligands are divided mainly into two groups; the first is a phosphite group, and the other, phosphine. The effect of $(C_6H_5)(C_2H_5O)_2P$ (**20**) is intermediate between those of the phosphites and phosphines. Within the phosphorus homologs, excellent correlations of log *exo*/*endo* with the cone angles are observed. The steric effect is more predominant at 80 °C than at 130 °C. These facts can reasonably be explained in terms of steric interaction between the coordinated acrylonitrile and the phosphorus ligand in the coordination sphere of the reaction intermediate.

Here it may be postulated that, among the four available coordination sites of the zero-valent nickel, two are occupied by diene and one by acrylonitrile,[8] and that their coordination takes place in the less-hindered tetrahedral configuration between the CN group and the phosphorus ligand (Fig. 4). Therefore, when a bulky phosphorus ligand is used, the less hindered coordination (Fig. 4 right) is favorable; thus the *exo* isomer is formed.

The steric effect of the phosphorus ligand on the reaction is further illustrated by the following facts. When

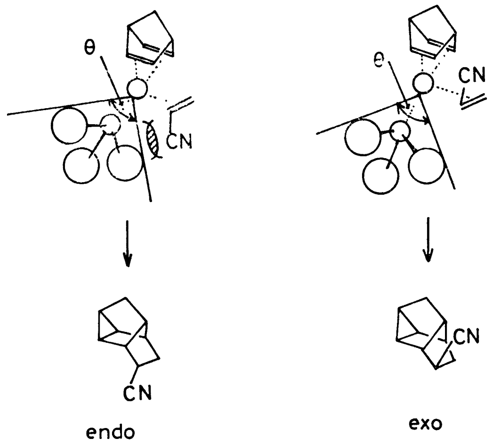

Fig. 4. Proposed structure of the intermediates.

the more bulky $(o\text{-}CH_3C_6H_4)_3P$ was used as the ligand, no appreciable reaction occurred between 80 and 130 °C. In the case of $(CH_3OC_6H_4)_3P$, the *ortho* isomer gave a lower yield than the other isomers. The fact that phosphites have a different steric effect on the reaction from that of the phosphine analogue cannot be explained by the present study. The effect of diphosphines (**7**—**9**) is too complicated to discuss, since diphosphines coordinate to the nickel competitively with norbornadiene and retard the reaction.

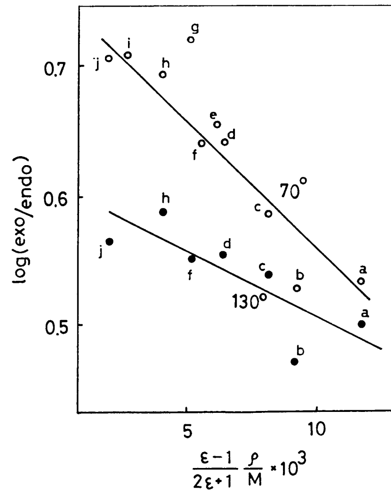

Fig. 5. Plot of *exo*/*endo* ratio against molar polarization of the solvent used.
(○): 70 °C (●): 130 °C
a, methanol; b, acetonitrile; c, ethanol; d, acetone; e, 2-propanol; f, pyridine; g, tetrahydrofuran; h, ethyl acetate; i, benzene; j, triethylamine.

The solvent effect was also investigated by using aprotic and protonic solvents, using triphenylphosphine as the auxiliary ligand. A linear free-energy relationship was observed for all the solvent. The polar solvent preferred the *endo* isomer. This can be explained by the dipolar interaction between the intermediate (Fig. 4) and the solvent. Thus, the intermediate (Fig. 4), which gives the *endo* isomer, is considered to have a larger total dipole moment than the other intermediate giving the the *exo* isomer and is stabilized by the polar solvent.[13] However, this effect on the reaction is smaller than that of the ligands.

Experimental

Commercially available phosphorus compounds were used without further purification. The other phosphorus compounds were prepared by the known methods. The products of the reaction of norbornadiene with acrylonitrile were identified by comparing their infrared and NMR spectra with those of the reported ones. Quantitative analyses were performed by gas chromatography on a column, Silicon DC 550 on Celite, 3 m at 150 °C, using tetralin as the internal standard. The *exo* isomer was eluted faster than the *endo* isomer. The cone angles and the stretching frequencies of $\nu_{CC}(A_1)$ were estimated by the reported methods. The Stewart molecular model was used for the estimation of the cone angle (θ). The values estimated in the present study are as follows: $P(C_6H_5)(o\text{-}C_6H_4OCH_3)_2$ (**2**), 155; $P(C_6H_5)_2(o\text{-}C_6H_4OCH_3)$ (**3**), 150; $P(p\text{-}C_6H_4CH_3)_3$ (**5**), 145; $P(C_6H_5)(C_2H_5)_2$ (**10**), 135; $As(C_6H_5)_3$ (**12**), 135; $P(O\text{-}o\text{-}C_6H_4CH_3)_3$ (**13**), 140; $P(O\text{-}m\text{-}C_6H_4CH_3)_3$ (**14**), 127; $P(O\text{-}p\text{-}C_6H_4CH_3)_3$ (**15**), 125; $P(O\text{-}n\text{-}C_4H_9)_3$ (**17**), 111; $P(C_6H_5)(OC_2H_5)_2$ (**20**), 121.

Reaction. All the reactions were carried out in a glass tube (8 mm in diameter), as in the case of the dimerization of butadiene reported earlier.[14] In the glass tube, $Ni(AN)_2$ (0.05 mmol), the solvent (1 ml), norbornadiene (6 mmol), acrylonitrile (6 mmol), the phosphorus ligand (0.2 mmol), and tetralin (130 mg, as the internal standard for the gas chromatographic analysis) were placed under an atmosphere of argon. The tube was sealed with a flame and then heated without agitation. The total yields (*exo* and *endo* isomers) of the reactions in the presence of the various ligands shown in Figs. 2 and 3 are as follows (% at 80, 130 °C for 10 hr): $P(o\text{-}C_6H_4OCH_3)_3$ (**1**) (26.9, 12.4), **2** (27.9, 11.2), **3** (27.4, 17.7), $P(C_6H_5)_3$ (**4**) (48.9, 28.1), **5** (42.5, 30.9), $NiBr_2[P(C_6H_5)_3]_2$ (**6**) (18.6, 15.7), $(C_6H_5)_2P(CH_2)_3P(C_6H_5)_2$ (**7**) (59.7, 28.4), $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$ (**8**) (47.9, 25.0), $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (**9**) (17.6, 19.1), $P(C_6H_5)(C_2H_5)_2$ (**10**) (42.1, 27.0), $P(n\text{-}C_4H_9)_3$ (**11**) (16.6, 8.4), **12** (17.6. 5.9), **13** (24.8, 12.9), **14** (49.9, 26.7), **15** (50.4, 29.5), $P(OC_6H_5)_3$ (**16**) (47.9, 26.7), **17** (58.7, 28.1), $P(OC_2H_5)_3$ (**18**) (58.2, 26.1), $P(OCH_3)_3$ (**19**) (57.2, 25.0), **20** (57.2, 27.5).

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