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The Amination and Dimerization of Norbornadiene with Nickel, Palladium, and Rhodium Complexes

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The reactions of norbornadiene in amine by the use of nickel, palladium and rhodium complexes have been studied in the presence of protic acid. A catalytic system of $Ni(COD)_2$ (**1**)-*n*-Bu_3P gives a mixture of 5-*exo*-(*o*-tolyl)-2-norbornene (**3**) and 5-*exo*-(*N*-amino)-2-norbornene (**4**). Bis(triphenylphosphine)(maleic anhydride)-palladium (**5**) gives 3-(*N*-amino)nortricyclene (**6**). Dichlorotetrakis(cyclooctene)dirhodium (**10**) gives a [2+4] cycloaddition product (**11**). All these reactions mechanisms are discussed from the point of view of an acid-promoted reaction on low-valent transition metal complexes.

The amination or telomerization of 1,3-dienes is of interest from the points of view of both synthetic chemistry and mechanistic study. It has been clarified that controlled amounts of some protic acids enhanced the reactions remarkably.[1] However, the transition metal-catalyzed addition of an amine to olefin or homoconjugated diene has so far been lacking. Norbornadiene is here employed as the diolefinic substrate in order to determine whether or not the anchimeric participation of one double bond might result in a transition metal-catalyzed addition of amine similar to that observed for 1,3-dienes, if the amination is possible.

On the other hand, the dimerization of norbornadiene by transition metals has been extensively studied.[2] The normal products in an aprotic solvent are [2+2] or [4+2] cycloaddition compounds. Previous work in this laboratory has shown a novel dimerization of norbornadiene by some nickel catalysts in an amine, giving 5-*exo*-(*o*-tolyl)-2-norbornene as the major product.[3] This reaction is also explicable in terms of an acid-promoted dimerization on a zerovalent nickel complex. Consequently, we expected that the amination and the dimerization might occur competitively. It appeared to us that the reaction patterns can, to a great extent, be altered mainly by adjusting the acidity of the catalytic system or by controlling the amount of protic acid added. Accordingly, we undertook a study of the effect of added acid on the reaction. This paper will be concerned with a systematic investigation of the reactions of norbornadiene by several nickel-, palladium-, and rhodium complexes.

Results and Discussion

The polymerization of norbornadiene catalyzed by low-valent nickel or palladium complexes proceeded rapidly in an alcohol, but in an amine no appreciable polymerization occurred. The use of amine as a solvent was favorable for the reaction of norbornadiene. Consequently, under these conditions the dimerization and the amination occurred competitively when trifluoroacetic acid was added. Among the amines used, cyclic amines such as morpholine and piperidine gave the best results. Accordingly, these amines were used.

Nickel Catalysts. Bis(1,5-cyclooctadiene)nickel (**1**) was used in the presence of tri-*n*-butylphosphine. The reaction in morpholine or piperidine proceeded smoothly at 90 °C. Without trifluoroacetic acid, only the [2+2]cycloaddition compound (**2**) was formed in a *ca.* 60% yield.

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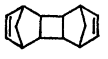

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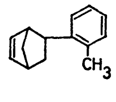

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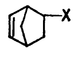

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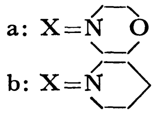


A striking change in the reaction occurred when a small amount of trifluoroacetic acid (1 equiv. to Ni) was added to the system. The product (**2**) was no longer formed; instead 5-*exo*-(*o*-tolyl)-2-norbornene (**3**) was obtained as the sole dimeric product, accompanied by a small amount of 5-*exo*-(*N*-amino)-2-norbornene (**4**). The identifications of the products were based on the mass, infrared-, and NMR-spectra. The *endo* proton on the C-5 atom of **4** can couple only with two neighboring protons on the C-6 carbon atom, not with the bridge-head, giving a double doublet at 8.0 τ for **4a**. The spectral data of **3** have been reported previously.[3]

The further addition of the acid prevented the formation of **3**, but promoted that of **4**. These results are graphically shown in Fig. 1.

This reaction pattern is explicable in terms of a mechanism similar to that proposed in the dimerization

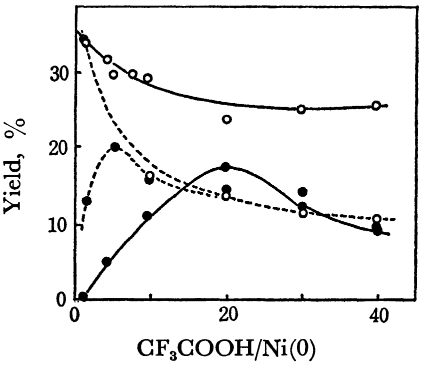


Fig. 1. Effect of [CF_3COOH] on the reaction by Ni at 90 °C.
(○), 5-*exo*-(*o*-Tolyl)-2-norbornene; (●), 5-*exo*-(N-amino)-2-norbornene.
(——), in morpholine; (······), in piperidine.
Conditions: [$Ni(COD)_2$]=0.05 mmol, [*n*-Bu_3P]=0.2 mmol, [norbornadiene]=2 mmol; amine, 0.4 ml; 15 hr.

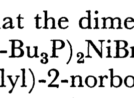
and amination of 1,3-dienes; a large amount of the added acid prevents the homolytic coupling of norbornadiene on the ligand-containing zerovalent nickel NiL_X, because the reaction of protic acid with the zerovalent nickel complex lies in the following equilibrium:[4]

$$HX + NiL_X \rightleftharpoons [HNiL_X]^+X^- \qquad (1)$$

On the other hand, the first step in the amination appears to involve a metal-hydride initiated mechanism; metal-hydride adds to one of the carbon-carbon double bonds of norbornadiene. A similar reaction scheme was established in the reaction of 1,3-diene, which proceeds through a π-allyl intermediate.

It has already been reported in a previous paper[3] that the dimerization of norbornadiene in amine by the $(n\text{-}Bu_3P)_2NiBr_2$–$NaBH_4$ (1 : 1) system gives 5-*exo*-(*o*-tolyl)-2-norbornene. In this case, only the dimer was obtained, no appreciable amount of the reaction product of amine with norbornadiene being formed. The present results (Fig. 1) are consistent with the previous results, because the mixture of $(n\text{-}Bu_3P)_2NiBr_2$–$NaBH_4$ (1 : 1) is considered to give a system consisting of zerovalent nickel and an equimolar amount of hydrogen bromide (that is, the HX/Ni(0) ratio is unity); thus, the major product of the previous study is 5-*exo*-(*o*-tolyl)-2-norbornene.

Palladium Catalyst. Bis(triphenylphosphine)(maleic anhydride)palladium was effective in the reaction of norbornadiene with amines. The most marked difference in the catalysis between the palladium and nickel complexes lies in the reaction product. No dimeric product was formed; 3-(*N*-amino)nortricyclene was the sole reaction product. In this case, however, a higher temperature, 110 °C, was favorable for the desired reaction. The product was identified as follows; the infrared spectrum has strong absorptions at 3080 and 805 cm^{-1} due to its nortricyclyl structure,[5] and no absorption due to olefinic protons is observed in its NMR spectrum.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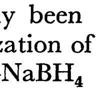
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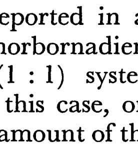
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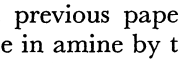
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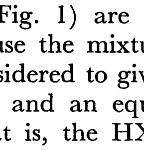


In this catalytic system, trifluoroacetic acid plays an important role. No obvious reaction occurs without the added acid (Fig. 2). The added acid has a promoting effect on the formation of a palladium hydride. The equilibrium of Eq. 1 is applicable to the palladium complex also. However, in this case the equilibrium is considered to lie far to the right. This assumption is consistent with the fact that stable metal hydrides of the platinum group can be isolated.[6] Consequently, the coupling of norbornadiene no longer occurs on the palladium complex, but the reaction of the hydride with norbornadiene predominates; thus, a nortricyclyl palladium intermediate is formed. The addition of a large amount of the acid resulted in the formation of polymeric products. It is noteworthy that an acid-base reaction between the added acid and amine occurs competitively with the reaction of Eq. 1. Therefore, as the co-catalyst a quaternary ammonium salt such as piperidine hydrochloride can be used instead of the acid. However, its efficiency was far lower.

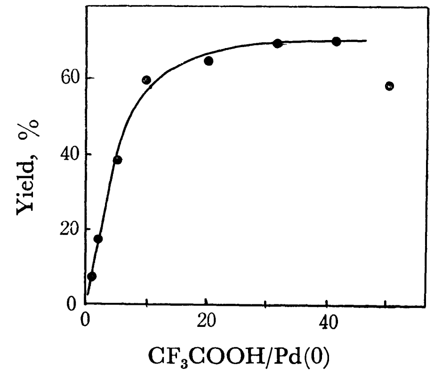


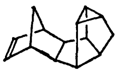
Fig. 2. Effect of $[CF_3COOH]$ on the reaction by Pd at 110 °C.
Conditions: $Pd(PPh_3)_2(C_4H_2O_3)$, 0.015 mmol; norbornadiene, 2 mmol; piperidine, 0.4 ml; 5 hr.

The stereochemistry of this amination is interesting to study. Complex **7**[7] was prepared for this purpose. When the pale-yellow complex **7** was added to morpholine, the complex turned black immediately. The gas-chromatographic analysis showed a single component(**8**). The presence of the infrared bands at 800 and 820 cm^{-1} indicated the formation of a derivative of nortricyclene. The chemical shift of the proton at C-5 (the carbomethoxy-bearing carbon) is very close to that of 3-carbomethoxynortricyclene.[8] From the spectral data, it may be concluded that the environment of the proton at the C-5 atom is not influenced by introducing the amino group at the C-3 atom. This fact indicates that the amino group is located in an *exo* configuration with respect to the methylene bridge. This stereochemistry suggests that the reaction of the amino group occurs in the opposite direction from the palladium atom. The reaction mechanism of this model compound seems to be applicable to the acid-promoted catalytic reaction with **5**. The only difference lies in the point that the intermediate in the catalytic reaction has a hydrogen atom instead of the methoxy group at the C-5 atom.

Rhodium Catalyst. As has been described above, the metal-hydride is an active species in the amination. From this point of view, hydridocarbonyltris(triphenylphosphine)rhodium (**9**) was used. However, the hydride was too stable to catalyze the amination.

$HRh(CO)(PPh_3)_3$ **9**

$[RhCl(C_8H_{14})_2]_2$ **10**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The catalytic activity of dichlorotetrakis(cyclooctene)dirhodium (**10**) was low in reaction to the amination or

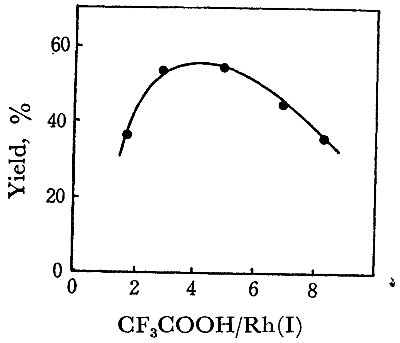

Fig. 3. Effect of [CF_3COOH] on the reaction by Rh at 110 °C.
Conditions: [$RhCl(COE)_2]_2$, 0.02 mmol; norbornadiene, 5.4 mmol; 8 hr.

dimerization in the presence of tri-*n*-butylphosphine and trifluoroacetic acid, and **4** was obtained in a low yield, accompanied by a small amount of the hydrogenation product of **4**. In the absence of the phosphine, however, **10** showed a specific activity for the formation of **11**. The identification of **11** was done by comparing its NMR spectrum with the reported one.[9] As is shown in Fig. 3, the yield was also influenced by the presence of acid. The maximum yield was realized when 4 equivalents of trifluoroacetic acid to **10** were added to the system. This catalytic system is characteristic in the point that **11** is selectively formed. The ordinary rhodium catalyst gives a mixture of dimers,[14] and the selectivity of **11** is not so high as in the present case. In this dimerization, the presence of amine has no effect on the reaction.

Experimental

Materials. Bis(1,5-cyclooctadiene)nickel,[10] dichlorobis(6-methoxybicyclo[2.1.1]hept-2-ene)dipalladium,[7] and bis(triphenylphosphine)(maleic anhydride)palladium,[11] hydridocarboxyltris(triphenylphosphine)rhodium,[12] and dichlorotetrakis(cyclooctene)dirhodium[13] were prepared according to the reported methods. Amines and norbornadiene were dried by the usual methods and, if necessary, distilled under an atmosphere of argon and stored over a Molecular Sieve 3 Å. Commercially-available trifluoroacetic acid and *n*-butylphosphine were used without further purification. Gas-chromatographic analyses were carried out on a Silicone DC 550 column on Celite 545 (3m, 150 °C), using tetralin as the internal standard.

Catalytic Reaction with Nickel Complex. All the reactions were carried out under an argon atmosphere in a sealed glass tube.

A. Without the Acid. In a glass tube (8 mm in diameter), 0.05 mmol of bis(1,5-cyclooctadiene)nickel was placed under an argon atmosphere, and then 0.2 mmol of Bu_3P, 0.4 ml of morpholine and 0.2 ml (2 mmol) of norbornadiene were added (in this order). The tube was sealed with a flame and heated without agitation at 90 °C for 15 hr. Subsequent gas-chromatographic analysis showed that the dimer (**2**) was formed in a 60% yield.

B. With the Acid. The following procedure is illustrative. To 0.05 mmol of $Ni(COD)_2$ in the glass tube was added 0.4 ml of morpholine containing 0.25 mmol (variable, as is shown in Fig. 1) of trifluoroacetic acid, 0.2 mmol of *n*-Bu_3P, and 0.2 ml of norbornadiene. The tube was sealed and heated without agitation at 90 °C for 15 hr. Subsequent gas-chromatographic analysis showed the formation of 5-*exo*-(*o*-tolyl)-2-norbornene, **3** (in a 30% yield) and 2-*exo*-(*N*-morpholino)-2-norbornene, **4a** (in a 20% yield). The products were separated by gas-chromatography. The identification was based on the infrared, NMR, and mass spectra. The NMR spectrum ($CDCl_3$) showed peaks at 3.9, 4.1, (quartet), and 8.0 τ (double doublet). The yields under other conditions are shown graphically in Fig. 1.

*Catalytic Reactions with Palladium Complex (**5**).* The procedure was similar to those described above. The results are shown in Fig. 2. The infrared spectrum of **6a** showed strong absorptions at 800 and 810 cm^{-1} due to the nortricyclyl framework. The NMR spectrum ($CDCl_3$) showed multiplets centered at 8.0 (1H), 8.4 (1H), 8.9(1H), 8.2(2H), and 9.8 τ (4H).

*Reaction of **7** with Morpholine.* To 0.55 g (1 mmol) of **7** we added 4 ml of morpholine. The yellow complex, **7** immediately turned black. The solution was then stirred at room temperature for 5 hr. Subsequent gas-chromatographic analysis showed the formation of **8** in a 45% yield. The NMR spectrum has singlets at 8.7 (3H), 8.4 (1H), 8.0 (2H), and 6.6 τ (3H of methoxy group) and two multiplets centered at 7.7(4H, of morpholine) and 6.3 τ (4H of morpholine). The mass spectrum has a peak due to the molecular ion at *m/e* 209.

*Catalytic Reaction of the Rhodium Complex (**10**).* The reaction was carried out such as has been described above. The reaction conditions are shown in Fig. 3. The identification of the product (**11**) was based on the NMR spectrum.[9]

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