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Tail-to-Tail Dimerization of Acrylonitrile Catalyzed by Low-Valent Ruthenium Complexes

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Zero-valent ruthenium complexes, [Ru(cod)(cot)] and [Ru(cod)(benzene)], are effective catalyst precursors for the tail-to-tail dimerization of acrylonitrile. Hydrogen pressure is necessary for the catalytic reaction, and the turnover number for dimers is greatly improved in neat acrylonitrile. Under the conditions of 150 °C and 25 atm of H_2 (initial pressure at room temperature), the conversion of acrylonitrile is 61% and the yield of tail-to-tail dimers is 42% (selectivity 69%) in 3 h. The turnover number for the dimers is 2060, which is much higher than those reported so far. From the results of a catalytic reaction under D_2 pressure, a reaction mechanism is proposed, in which two successive insertions of acrylonitrile into dihydridoruthenium complex are involved. A fast and reversible insertion of the third acrylonitrile is responsible for the H–D exchange of acrylonitrile in the deuterium labeling experiment.

The tail-to-tail dimerization of C3 functional olefins by homogeneous catalysts would be an attractive alternative route to industrial production of hexamethylenediamine and adipic acid, which are precursors of Nylon-6,6.[1)] Among the C3 olefins, much work has been devoted to the dimerization of acrylonitrile,[2—10)] methyl acrylate,[11)] and acrolein[12)] by transition metal catalysts. In the dimerization of acrylonitrile (AN) by transition metal catalysts, Ru(II) and Ru(III) complexes have been widely used as catalyst precursors. For example, Misono et al. reported the first example of the tail-to-tail dimerization of AN by $RuCl_3 \cdot 3H_2O$ under hydrogen pressure, in which a turnover number (TON) for dimer was 87.[2b)] Since then, effects of various additives have been studied on the $RuCl_3 \cdot 3H_2O$-based catalysts, and a recent patent described how $RuCl_3 \cdot 3H_2O$ in the presence of $HSnBu_3$ under H_2 improved the TON to about 530.[8i)] For the catalytic reaction under H_2 pressure, a mechanism involving successive insertion of two AN molecules into a ruthenium-hydride species was proposed.[6)]

On the other hand, a catalytic system without using H_2 pressure has been explored, but in most cases the conversion of AN was decreased while the selectivity to dimer was increased due to the suppression of propionitrile formation. Along this line, Tkatchenko reported the catalytic dimerization of AN by $[RuClCp^*(an)]_3$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl),[7)] but details of the data have not been published. Similar results were described in a patent, where $[RuClCp^*(cod)]$ (cod = cycloocta-1,5-diene) gave a TON of 100.[8j)] Recently, Sugise and Murai et al. reported that a catalytic system $[RuCl_2(dmso)_4]$/EtCOONa/DMSO/carboxylic acid (dmso = dimethyl sulfoxide) gave linear dimers of AN (TON = 1206) without the formation of propionitrile.[9)] So far this is the highest TON value to our knowledge in the tail-to-tail dimerization of AN by transition metal complexes, and they proposed a mechanism involving insertion of Ru into a vinylic C–H bond of AN.

In the course of our study on the reactions of low valent Ru complexes with nitriles and olefins,[13)] we have found that [Ru(cod)(cot)] (cot = cycloocta-1,3,5-triene) and [Ru(cod)(benzene)] work as effective catalyst precursors for the tail-to-tail dimerization of AN under H_2 pressure. The TON was increased to > 2000 in neat AN. A catalytic reaction using D_2 was also done, and incorporation of deuterium into products was analyzed. Here we report the results of the catalytic reactions and some mechanistic studies.

Results and Discussion

Catalytic Reactions in Neat Acrylonitrile. The tail-to-tail dimerization of AN by Ru complexes yielded a mixture of *cis*-1,4-dicyanobut-1-ene (*cis*-DCB), *trans*-1,4-dicyanobut-1-ene (*trans*-DCB), and adiponitrile (ADN) (Eq. 1). Propionitrile (PN) was a by-product resulting from simple hydrogenation of AN. Dimers and PN were isolated by atmospheric and Kugelrohr distillations, and they were characterized by NMR and GC/MS.

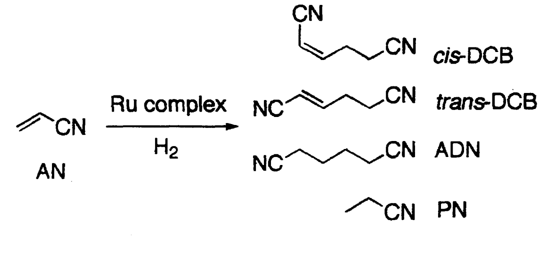

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Table 1 summarizes the results of catalytic reactions using various Ru complexes having ene ligands. In the reaction by [Ru(cod)(cot)] (**1**) at 150 °C for 3 h under H_2 (25 atm of initial pressure) in neat AN (Run 1), the conversion of AN was 61%. Products and their yields based on the charged AN were as follows: *cis*-DCB (20%), *trans*-DCB (20%), ADN (2%), and PN (19%). Thus, the overall yield of tail-to-tail dimer was 42%, and the selectivity to dimer was 69%. It is notable that a TON of 2060 is greater than those reported previously.[2—9] Neither head-to-tail nor head-to-head dimers were produced in Run 1. We also obtained a yellow powder in a very low yield (<1%), which was not assignable to poly-AN but to a Ru-DCB adduct (vide infra).

[Ru(cod)(benzene)] (**2**) gave almost the same high activity as **1** (Run 2), and a slightly lower activity was obtained for [Ru(cod)(naphthalene)] (Run 3). $RuCl_3 \cdot 3H_2O$ showed lower activity than **1** and **2** (Run 4), although the neat AN condition gave a higher TON of 1200 for $RuCl_3 \cdot 3H_2O$ than that using alcohol solvents in the previous reports.[2)] Lower TON values were obtained for other Ru ene complexes such as $[RuCl_2(nbd)]_n$ (nbd = bicyclo[2.2.1]hepta-2,5-diene), $[Ru(C_8H_{11})(C_8H_{12})]BF_4$, and $[RuH(C_2H_4)(PPh_2C_6H_4)(PPh_3)_2]$ (Runs 5, 6, and 7). No dimer was formed by using $[RuHCl(CO)(PPh_3)_3]$, $[Ru_3(CO)_{12}]$, or $[Ru(\eta^1 : \eta^3\text{-}C_8H_{10})(PMe_3)_3]$.[14)]

Optimization of the Reaction Conditions. Some optimizations of reaction temperature and initial H_2 pressure were done for the catalytic reaction by **1** in neat AN. Figure 1 shows the dependence of yield of dimer (*cis*-DCB, *trans*-DCB, and ADN) and PN on the reaction temperature, where 150 °C gives a maximum yield of dimer. In Fig. 2, the dependence of yield of dimer on the initial H_2 pressure is depicted. No reaction occurred under 1 atm of H_2, but the catalytic dimerization of AN proceeded at higher H_2 pressures than 5 atm. The yield of dimer increased with increase in the H_2 pressure up to 25 atm, but decreased at 100 atm. The yield of PN also increased with H_2 pressure up to 50 atm. Thus, the highest selectivity to dimer was obtained at 25 atm, and for this reason, we used the reaction temperature of 150 °C and the initial H_2 pressure of 25 atm as the standard reaction conditions. Under these conditions, the yield of dimer reached about 40% in 90 min and longer reaction time gave a slight change in the yield. The *cis*/*trans* ratio of DCB was about 1.0 at each reaction time, which was in contrast to the result by the H_2-free $[RuCl_2(dmso)_4]$ system.[9)]

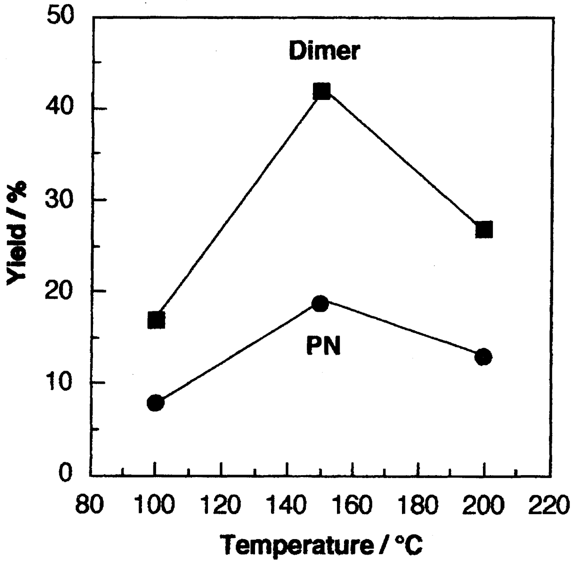

Fig. 1. Dependence of the product yield on the reaction temperature. Other conditions: see Table 1.

In Fig. 3, the observed gauge pressure of H_2 at 150 °C is plotted against the reaction time, where the gauge pressure decreased to 7 atm after 90 min. After 120 min, the autoclave was cooled to room temperature, recharged with 25 atm of H_2, and again heated to 150 °C. However, there was no more reaction. Possibly, the active species turned inactive at low H_2 pressure or at room temperature.[15)]

The effects of ethanol and benzene as solvents were studied for the catalytic reaction by **1**. Figure 4 shows the plots of yield versus mol% of AN in EtOH. At 26 mol%, the yield of PN was larger than that of dimer. As the mol% of AN was increased, the yield of PN was decreased but that of dimer changed only slightly. Thus, both TON and selectivity to dimer were increased with an increase in the mol% of AN (Fig. 5). A similar effect was observed when benzene was used as a solvent. From these results, we have concluded that the neat AN condition gives better results than using

Table 1. Dimerization of Acrylonitrile by Ru Complexes under Hydrogen Pressure[a)]

Run	Catalyst	AN conv.	Yield of product (%)				Dimer sel.[c)]	TON[d)]
		%	*cis*-DCB[b)]	*trans*-DCB[b)]	ADN[b)]	PN	%	
1	[Ru(cod)(cot)]	61	20	20	2	19	69	2060
2	[Ru(cod)(benzene)]	63	20	20	2	19	67	1990
3	[Ru(cod)(naphthalene)]	58	18	18	2	19	66	1700
4	$RuCl_3 \cdot 3H_2O$	44	13	12	1	15	63	1200
5	$[RuCl_2(nbd)]_n$	26	10	9	0	7	73	770
6	$[Ru(C_8H_{11})(C_8H_{12})]BF_4$	30	9	7	2	12	60	710
7[e)]	$[RuH(C_2H_4)(PPh_2C_6H_4)(PPh_3)_2]$	26	4	2	1	9	27	325

a) Reaction conditions: Ru 0.035—0.045 mmol, AN/Ru = ca. 5×10^3, Initial H_2 pressure 25 atm, 150 °C, 3 h. b) [(mol of dimer)×2] / (mol of charged AN)×100. c) [(total mol of dimer)×2] / (mol of converted AN)×100. d) [(total mol of dimer)×2 / (mol of Ru). e) Higher oligomer and polymer are also formed.

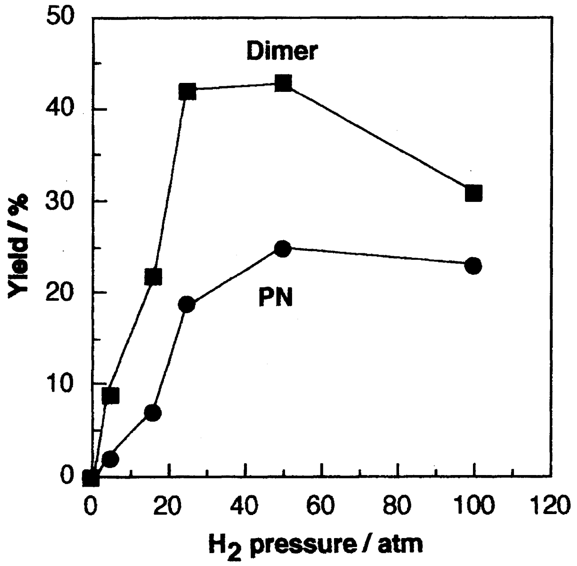

Fig. 2. Dependence of the product yield on the initial H_2 pressure. Other conditions: see Table 1.

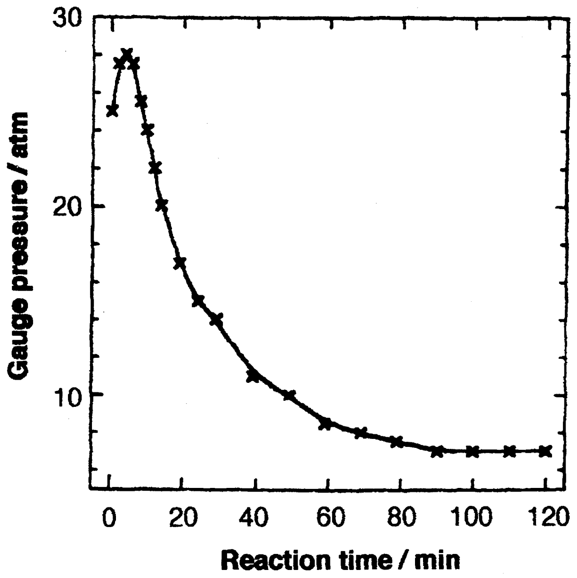

Fig. 3. Plots of the gauge pressure against the reaction time. Conditions: see Table 1.

solvents.

NMR Tube Reactions of 1 with AN. In order to clarify the mechanism of these catalytic reactions, NMR tube reactions of **1** with AN were done in C_6D_6. Immediately after three equiv AN was added to **1** under N_2 at room temperature, no significant change was observed although the peaks of AN were slightly shifted to high field (Fig. 6c). After 1 h, the peak intensities of AN and **1** were reduced and resonances due to free COD appeared at $\delta=5.57$ and 2.21 (Fig. 6d). Formation of yellow powder (**4**) was also observed in the reaction mixture. The amount of powder **4** was increased after 24 h, and in the NMR spectrum (Fig. 6e) the peaks of AN and **1** almost disappeared and only free COD was observed (60% based on initial **1**). No free COT was detected in this reaction.

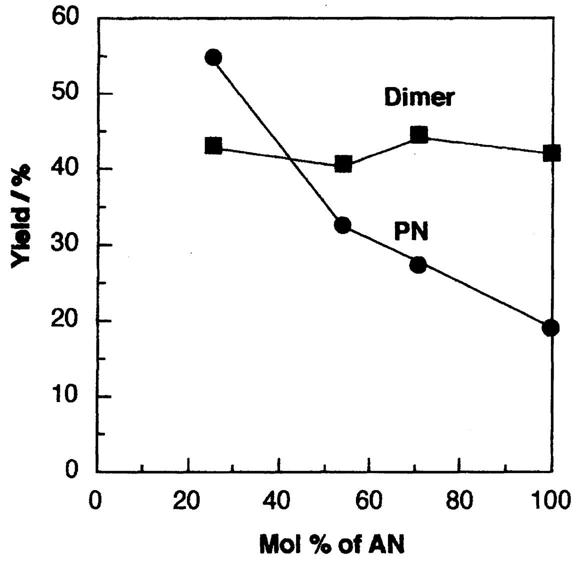

Fig. 4. Effect of ethanol as an additive on the product yield. Conditions: see Table 1.

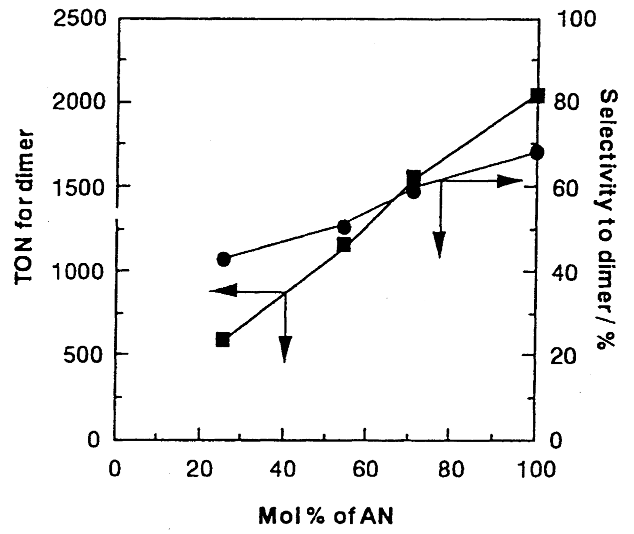

Fig. 5. Effect of ethanol as an additive on dimer's TON and selectivity.

In similar NMR tube reactions at the AN/**1** ratios of 1 and 2, the peaks of **1** were still observed with free COD while AN completely disappeared after 24 h. On the other hand, at the ratio of AN/**1** of 5, the peaks of **1** were not observed while approximately two equiv free AN and one equiv free COD were seen in the NMR spectrum. These results imply that **1** reacts with three equiv AN to release only COD, resulting in the formation of powder **4** as precipitates. Although full characterization of **4** was not successful due to its poor solubility in organic solvents, **4** may be assigned to a polymeric complex $[Ru(C_8H_{10})(an)_3]_n$ by considering the data of IR and elemental analysis. The observed ν(CN) band at 2203 cm^{-1} for **4**, which is different from that of poly-AN (2248 cm^{-1}) and slightly lower than that of free AN (2229 cm^{-1}), suggests the coordination of AN by C=C double bond to Ru,[2d] although possible coordination by the CN group cannot be completely excluded. The broad band at

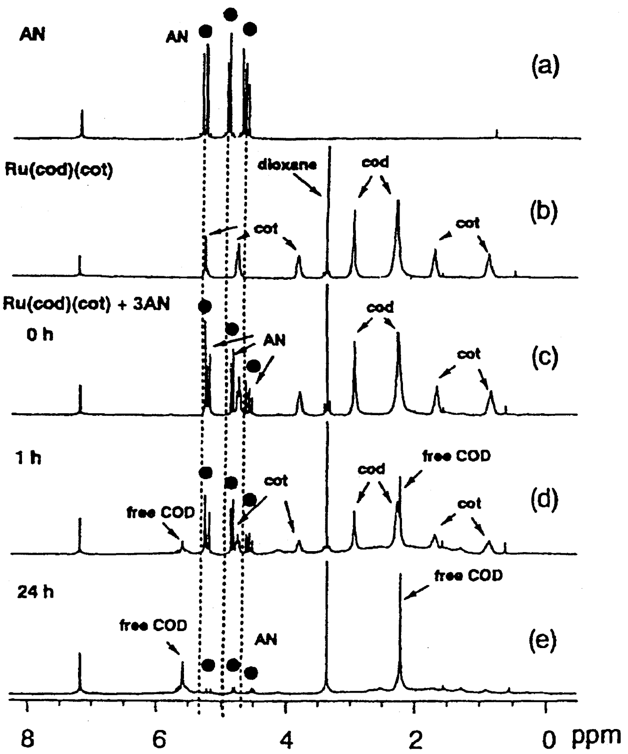

Fig. 6. NMR spectra of the reaction of **1** with AN: (a) AN; (b) **1**; (c) reaction of **1** with 3 equiv AN at 0 h; (d) 1 h, (e) 24 h. Conditions: C_6D_6, room temperature. Three solid circles represent the peaks due to free AN.

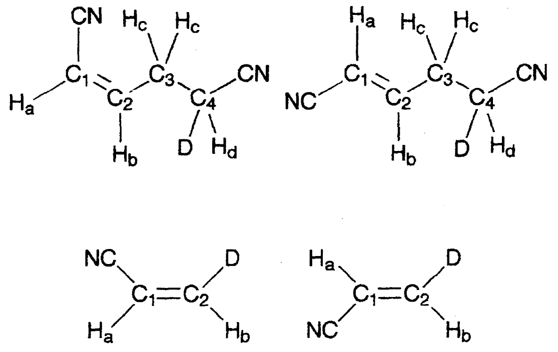

Fig. 7. *cis*- / *trans*-Dicyanobut-1-ene-d_1 and *cis* / *trans*-acrylonitrile-d_1.

about 1640 cm^{-1} may ascribe to ν(C=C) of an uncoordinated double bond of C_8H_{10}. Elemental analysis of **4** was in good accordance with a formula of $Ru(C_8H_{10})(an)_3$.[16]

In a catalytic reaction using **4** as a precursor, we obtained high activity and selectivity similar to those of **1** (55% conversion of AN and 65% selectivity to dimer under the conditions of Table 1). Therefore, this complex is suggested to be one intermediate or precursor involved in the catalytic cycle.

Catalytic Reaction Using D_2. To discover the role of hydrogen in the catalytic reaction, D_2 gas was used in place of H_2, and incorporation and distribution of deuterium in the products were analyzed. The catalytic reaction was done under conditions similar to those in Table 1: initial D_2 pressure 14 atm, 150 °C, and 5 h. In gas chromatographic analysis of the reaction products, the AN conversion was 52% (recovered AN 19 mmol), and the products were DCB (21 mmol, 31% yield, *cis*/*trans* ratio = 1.0), ADN (1 mmol, 1%), and PN (21 mmol, 15%), thus the selectivity to dimer was 62%. The products were isolated and characterized by NMR and GC/MS.

In the ^{1}H NMR spectrum of *cis*-DCB, a triplet of triplets appeared at $\delta=2.56$, which was assigned to H_d having couplings with H_c and D ($J_{HH}=7$, $J_{HD}=3$ Hz) (Fig. 7). No H–D coupling was observed for H_a, H_b, or H_c. The ratio of integral values for H_a, H_b, H_c, and H_d was 1 : 1 : 2 : 1, suggesting that one of the two hydrogens at C_4 position is completely deuterated. $^{13}C\{^1H\}$ NMR of *cis*-DCB showed the complete incorporation of one deuterium at C_4 more clearly; a characteristic triplet due to a coupling with one D was observed at $\delta=15.9$ ($J_{CD}=21$ Hz). GC/MS of *cis*-DCB also gave an M^+ peak at $m/z=107$. Similar NMR and GC/MS results were obtained for *trans*-DCB. Accordingly, DCB contains only one deuterium at C_4 with nearly 100% of deuterium incorporation. Further detailed inspection of the ^{1}H and $^{13}C\{^1H\}$ NMR spectra of *cis*- and *trans*-DCB indicates that H_b and H_c at C_2 and C_3 are also partially deuterated (about 15%), though the precise estimation of deuteration was unsuccessful due to extensive overlapping of the peaks.

As is expected from these results, ^{1}H and $^{13}C\{^1H\}$ NMR spectra of recovered AN gave small signals due to AN-d_1 along with those of AN-d_0. In ^{1}H NMR, two small doublets appeared at $\delta=6.23$ ($J_{HH}=18$ Hz) and $\delta=6.08$ ($J_{HH}=12$ Hz) with equal intensities, which were assignable to H_b of *trans*- and *cis*-AN-d_1, respectively (Fig. 7). They were observed at slightly higher fields than those of big doublets of AN-d_0 due to the isotope anisotropy. Two small doublets of triplets due to H_a of *trans*- and *cis*-AN-d_1 appeared at $\delta=5.674$ and 5.669, respectively. From the integral values, the deuterium incorporation was estimated to be 19% in the recovered AN. In $^{13}C\{^1H\}$ NMR, a small triplet also appeared at $\delta=137.0$, being assignable to C_2 with a C–D coupling ($J_{CD}=25$ Hz). From these data, it was seen that 19% of recovered AN (19 mmol) was AN-d_1 only at C_2 position (*cis*/*trans* ratio = 1.0). This result suggests the facile reversible insertion of AN into Ru–H (or Ru–D), where only Ru–CH(CN)CH_3 is formed. A certain amount of deuterium was also incorporated both in C_1 and C_2 positions of PN, though the contents were not accurately estimated due to extensive overlapping. MS data qualitatively suggests the existence of PN-d_1 with a small amount of PN-d_2. This result demonstrates that PN is not formed by the simple hydrogenation of AN with hydrogen.

By combining these results, the following important facts were obtained. DCB contains one deuterium at the C_4 position. Small amounts of deuterium are distributed into the C_2 position of recovered AN, C_2 and C_3 positions of DCB, and PN, implying extensive H–D scrambling at the C_2 position in AN during the reaction. The amount of deuterium at C_4 of DCB is approximately the same as the sum of all other distributed ones, indicating that one D of D_2 is incorporated into DCB, but the other is extensively exchanged with H in

AN during the catalytic process.

Reaction Mechanism. Kinetics was not intensively analyzed in this study, but the following features were obtained related to the reaction mechanism; (1) H_2 pressure is necessary for the catalytic reaction, (2) PN is always formed as a by-product with the molar ratio of PN/dimer of about 1.0, (3) the *cis*/*trans* ratios for DCB and AN-d_1 are about 1.0 at each reaction time, (4) polymeric $[Ru(C_8H_{10})(an)_3]_n$ as an active precursor was isolated from the reaction of **1** with AN, (5) in the deuterium labeling experiment, all DCB contained one deuterium at C_4, and (6) H–D exchange took place at C_2 in AN, C_3 and C_4 in DCB, and C_1 and C_2 in PN.

Although the mechanisms involving metallacyclopentane[1c] and vinylic C–H activation of AN[9] are also capable of producing DCB-d_1 in the deuterium labeling experiment, they cannot fully explain features (1)—(6). Therefore, it seems most likely that the mechanism involves the insertion of AN to ruthenium hydride (Fig. 8), as proposed by Tsou et al. for the $[RuCl_2(an)_3]$-catalyzed dimerization of AN under H_2.[6] In the presence of excess AN, **1** is converted to $[RuH_2L_n]$ species (**5**, L=an) by the reaction of **1** with H_2 possibly via $[Ru(C_8H_{10})(an)_3]$. Formation of such dihydridoruthenium(II) complexes in the reactions of **1** with H_2 in the presence of tertiary phosphine ligands has been well established.[17,18] The first insertion of AN to **5** gives (2-cyanoethyl)(hydrido)ruthenium species (**6**), and the second insertion of AN to **6** is very fast to form (1,4-dicyanobutyl)(hydrido)ruthenium species (**7**). As we obtained only linear dimers, the modes of the first and the second insertions are completely reverse. Probably, **5** adds to AN by the anti-Markovnikov mode, and then the nucleophilic 2-cyanoethyl group of **6** would attack to C_2 of AN to give **7**. The third AN molecule inserts into the remaining Ru–H bond of **7** by the Markovnikov mode to form (1-cyanoethyl)(1,4-dicyanobutyl)ruthenium species (**8**), and the third insertion is also fast and reversible. Therefore, in the deuterium labeling experiment, the H–D exchange reaction proceeds at the C_2 position of the 1-cyanoethyl group of **8** after repeated cycles of insertion and β-elimination at this step in the presence of a large excess of AN. The reason why only **8** is formed without the formation of (2-cyanoethyl)(1,4-dicyanobutyl)ruthenium species in this process is not clear. Alternatively, selective and reversible oxidative addition of a vinylic C–H bond to give a (2-cyanovinyl)(hydrido)ruthenium(IV) intermediate can also interpret the selective H–D exchange at C_2 position of AN.[9,19] However, we suppose that the Ru(IV) intermediacy is unlikely under hydrogen pressure. β-Hydrogen elimination from **8** is faster than reductive elimination to give *cis*/*trans*-DCB and (1-cyanoethyl)(hydrido)ruthenium species (**9**), which undergoes reductive elimination to form PN and Ru(0) species (**10**). Oxidative addition of H_2 to **10** regenerates **5**. When the reactions were done in solvent or under high pressure of H_2, the ratio of dimer to PN decreased (Figs. 2, 4, and 5), implying the involvement of a minor hydrogenation process under these reaction conditions.

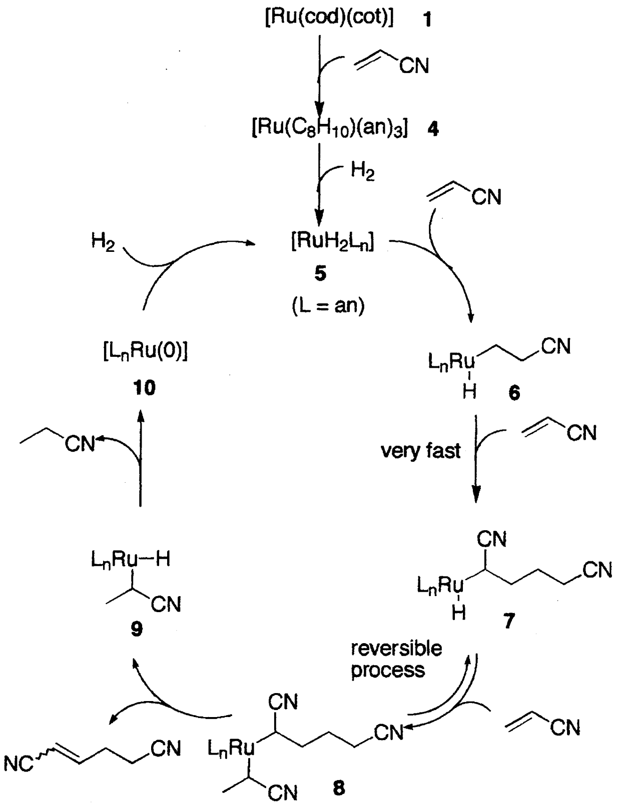

Fig. 8. A proposed mechanism for the catalytic reaction using H_2.

In conclusion, high catalytic activity (TON > 2000) has been obtained in the tail-to-tail dimerization of acrylonitrile under H_2 pressure by using low-valent Ru complexes as precursors. Neat acrylonitrile condition gives high activity, which has the advantage of no use of organic solvents. In the proposed mechanism, one tail-to-tail dimer is formed by the successive insertion of acrylonitrile to ruthenium-hydride, and one propionitrile is also formed as a by-product in the catalytic cycle.

Experimental

All manipulations were done under N_2 or Ar atmosphere using standard Schlenk techniques[20] unless otherwise noted. Acrylonitrile was dried over CaH_2 and distilled under N_2. Solvents were dried over appropriate agents and distilled under N_2 (methanol : $Mg(OMe)_2$, benzene : Na/benzophenone ketyl, benzene-d_6 : Na, chloroform-d_1 : P_4O_{10}). The following complexes were prepared according to the methods in the literature: [Ru(cod)(cot)],[21] [Ru(cod)(benzene)],[22] [Ru(cod)(naphthalene)],[23] $[RuCl_2(nbd)]_n$,[24] $[Ru(C_8H_{11})(C_8H_{12})]BF_4$,[25] $[RuH(C_2H_4)(PPh_2C_6H_4)(PPh_3)_2]$.[26] $RuCl_3 \cdot 3H_2O$ and commercially available pure hydrogen and deuterium were used without further purification. Kugelrohr distillation was done using a Shibata GTO350RD. IR spectra were obtained on a JASCO FT-IR-5M using KBr disks. NMR spectra were measured on a JEOL LA-300 spectrometer (^1H 300 MHz, ^{13}C 75 MHz). GC/MS and GC were done using a Shimadzu GCMS QP-2000A (EI 70 eV) and a Shimadzu GC-14B (FID), respectively (columns: GL Sciences Inc. TC-WAX 0.25 mm×30 m). Elemental analyses were done using a

Perkin–Elmer type 2400 series II CHN analyzer.

Catalytic Reaction. A typical experimental procedure is as follows (Table 1, Run 1): Ru(cod)(cot) (12.0 mg, 0.0381 mmol) was dissolved in AN (9.86 g, 186 mmol) under N_2, and the mixture with a magnetic stir bar was transferred to a 50 ml stainless steel autoclave with a glass liner (Taiatsu Glass) under N_2. The autoclave was charged with 25 atm of H_2 at room temperature, and was heated to 150 °C in an oil bath with stirring. After 3 h, the autoclave was cooled to room temperature and the remaining H_2 pressure was released. The autoclave was opened and the reaction mixture was transferred to a Schlenk tube under N_2. Naphthalene was added as an internal standard and the products were quantitatively analyzed by GC.

According to the preceding reports,[11g,12] yield and selectivity were defined as the following case of *cis*-DCB: yield of *cis*-DCB = [(mol of *cis*-DCB×2] / (mol of charged AN)×100, selectivity to *cis*-DCB = [(mol of *cis*-DCB)×2] / (mol of converted AN)×100. Turnover number for dimer was also defined based on the converted AN: TON = [mol of dimers)×2] / [mol of Ru].

From the catalytic reaction mixture, yellow powder **3** was obtained by filtration from the catalytic reactions. Yield less than 1%. IR (KBr, cm^{-1}): 2939 (m), 2244 (s), 2226 (m), 1638 (m), 1452 (m), 965 (m).

NMR Tube Reaction of 1 with AN. **1** (11.5 mg, 0.0365 mmol) was dissolved in C_6D_6 in an NMR tube, and dioxane (0.018 mmol) was added as an internal standard. To the solution was added AN (0.110 mmol, AN/Ru = 3.0), and NMR spectra were measured at room temperature. Similar experiments were also done using various AN/Ru ratios.

Characterization of $[\mathbf{Ru(C_8H_{10})(an)_3}]_n$ (4). **4** was obtained as a yellow powder from the NMR tube reaction described above. Alternatively, it was prepared by the reaction of **1** (28 mg, 0.089 mmol) with AN (1 mL) at room temperature for 12 h. The yellow powder precipitated was filtered, washed with hexane, and dried under vacuum. Yield: 23 mg, 99%. **4** was soluble in acrylonitrile and crotononitrile, slightly soluble in chloroform, and insoluble in benzene, toluene, dichloromethane, DMSO, THF, acetonitrile, methanol, acetone, ether, or DMF. Moderately air-sensitive as solid, and unstable as solutions in AN and chloroform. IR (KBr) 2919 (s), 2846 (s), 2203 (s), 1450 cm^{-1} (m). Anal. Found: C, 55.53; H, 5.49; N, 11.22%. Calcd for $C_{17}H_{19}N_3Ru$: C, 55.72; H, 5.23; N, 11.47%.

Catalytic Reaction Using $\mathbf{D_2}$. The reaction was done in a 50 ml autoclave as described above, and the reaction conditions were as follows: **1** 0.037 mmol, AN 138 mmol, initial D_2 pressure 14 atm, 150 °C, and 5 h. The reaction mixture was separated by atmospheric and Kugelrohr distillations.

***cis*-DCB-$\boldsymbol{d_1}$.** Yield 16%. ^{1}H NMR ($CDCl_3$) $\delta = 6.54$ (dt, $J_{HH} = 11$, 8 Hz, 1H, H_b), 5.55 (d, $J_{HH} = 11$ Hz, 1H, H_a), 2.77 (t, $J_{HH} = 7$ Hz, 2H, H_c), 2.56 (tt, $J_{HH} = 7$, $J_{HD} = 3$ Hz, 1H, H_d). ^{13}C{^{1}H} NMR ($CDCl_3$) $\delta = 149.1$ (NC–*C*H=), 117.8 and 114.9 (*C*N), 102.9 (NC–C=*C*H–), 27.0 (*C*H$_2$), 15.9 (t, $J_{CD} = 21$ Hz, NC–*C*H(D)–). MS (EI, 70 eV) *m*/*z* (rel intensity) 109 (1), 108 (6), 107 (M$^+$; 20), 66 (100), 39 (51).

***trans*-DCB-$\boldsymbol{d_1}$.** Yield 16%. ^{1}H NMR ($CDCl_3$) $\delta = 6.70$ (dt, $J_{HH}=16$, 7 Hz, 1H, H_b), 5.54 (d, $J_{HH}=16$ Hz, 1H, H_a), 2.60 (t, $J_{HH}=7$ Hz, 2H, H_c), 2.54 (tt, $J_{HH}=7$, $J_{HD}=2$ Hz, 1H, H_d). ^{13}C{^{1}H} NMR ($CDCl_3$) $\delta = 150.0$ (NC–*C*H=), 117.7 and 116.3 (*C*N), 103.1 (NC–C=*C*H–), 28.6 (*C*H$_2$), 15.8 (t, $J_{CD} = 20$ Hz, NC–*C*H(D)–). MS (EI, 70 eV) *m*/*z* (rel intensity) 109 (0.5), 108 (7), 107 (M$^+$; 18), 66 (100), 39 (33). Observation of peaks at 108 in MS spectra of both *cis*- and *trans*-DCB indicated the presence of DCB-d_2, and its content was roughly estimated to be 20% by assuming a natural abundance of C and fragmentation. Deuterium content was also estimated to be about 15% in ^{1}H NMR, which was in accord with the MS data. The d_3 species was negligible.

PN. Yield 15%. ^{1}H NMR ($CDCl_3$) $\delta = 2.37$ (q, $J_{HH} = 7$ Hz, –CH$_2$–), 1.30 (t, $J_{HH} = 7$ Hz, CH$_3$). The content of PN-d_1 was not estimated because of extensive overlapping in NMR and fragmentation in MS. However, peaks at *m*/*z* (rel intensity)=57 (PN-d_2, 7), 56 (PN-d_1, 20), and 55 (PN-d_0, 59) qualitatively indicate the presence of PN-d_1 and -d_2.

AN-$\boldsymbol{d_1}$. ^{1}H NMR ($CDCl_3$) $\delta = 6.23$ (d, $J_{HH}=18$ Hz, 1H, =C(*H*)(D) of *trans*-isomer), 6.08 (d, $J_{HH}=12$ Hz, 1H, =C(*H*)(D) of *cis*-isomer), 5.674 (dt, $J_{HH}=18$, $J_{HD} = 1.9$ Hz, 1H, (NC)(*H*)C= of *trans*-isomer), 5.669 (dt, $J_{HH}=12$, $J_{HD} = 2.8$ Hz, 1H, (NC)(*H*)-C= of *cis*-isomer. ^{13}C{^{1}H} NMR ($CDCl_3$) $\delta = 137.0$ (t, $J_{CD} = 25$ Hz, =*C*(H)(D) of *cis*- and *trans*-isomers), 116.9 (s, *C*N), 107.3 (s, =*C*(H)(CN)). Content of AN-d_1 was estimated to be 19% from the integration of ^{1}H NMR. MS *m*/*z* (rel intensity) 55 (AN-d_2, 2), 54 (AN-d_1, 28), 53 (AN-d_0, 100). The MS data also indicated the existence of d_1 species, and by assuming the natural abundance of C and fragmentation the contents of AN-d_1 was roughly estimated to be 19%. The amount of AN-d_2 was negligible.

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15) As described before, small amount of pale-yellow powder (**3**) was formed from the reactions at high AN conversions. Powder **3** was insoluble in most organic solvents, and its NMR spectrum could not be obtained. IR spectrum of powder **3** showed different frequencies from those of poly-AN, but it resembled the spectrum of DCB. Hence powder **3** may be an adduct of Ru catalyst and DCB, which is a deactivated form of Ru catalyst. In fact, **3** gave very low activity when used as a catalyst precursor. One possible explanation for the maximum conversion of AN at 60% is that the active Ru species reacts with DCB accumulated in the reaction mixture to form the inactive adduct. We expect that effective removal of DCB from the reaction mixture and continuous supply of AN would keep the high activity of the Ru catalyst.

16) Low solubility of complex **4** may arise from its polymeric structure due to extensive bridging using extra C=C double bond and cyano group in C_8H_{10} and AN ligands.

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18) The dependence of H_2 pressure to yields (Fig. 2) are not fully explained by the proposed mechanism. However, up to 25 atm, the formation of **5** seems to increase with H_2 pressure. Over 25 atm, formation of other Ru species may suppress more formation of **5**. Another plausible effect of H_2 pressure is to keep the intermediates **5**—**10** active in the catalytic cycle.

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