and acetophenone at 77°K are 74.5 and 73.6 kcal/mol, respectively, whereas in benzene at room temperature they were found to be 72.0 and 72.6 kcal/mol, respectively, which shows that under the latter conditions the triplet energy of butyrophenone is even *lower* than that of acetophenone. Furthermore, it was observed[17] that in rigid matrices propiophenone and higher homologs of alkyl phenyl ketones exhibit two emissions ("dual phosphorescence") in varying ratios depending mainly on the viscosity of the glassy solvent. The higher energy ("anomalous") emission has been attributed[17] to a torsional distortion of the triplet molecule and to hindrance to conformational change in the rigid glass.

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# Nickel(0)-Catalyzed Reaction of Quadricyclane with Electron-Deficient Olefins[1]

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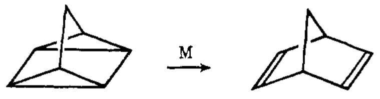
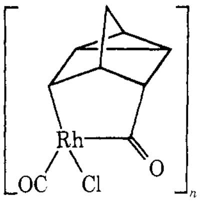
**Abstract:** Quadricyclane (**1**) upon treatment with a catalytic amount of nickel(0) complexes isomerizes in a $[_{\sigma}2 + {}_{\sigma}2]$ fashion to yield norbornadiene (**2**). The reactive intermediate can be trapped intermolecularly, in a formal sense, by activated olefins such as acrylonitrile or acrylic acid esters, giving the adducts, endo- and exo-8-substituted tetracyclo[4.3.0.0$^{2,4}$.0$^{3,7}$]nonanes **7** and **8.** Methyl $\alpha$,*cis*-$\beta$-dideuterioacrylate enters into the catalytic cycloaddition stereospecifically with retention of configuration. The course of the reaction is formally viewed as a $[_{\sigma}2_s + {}_{\pi}2_s]$ process and lies in marked contrast with the corresponding uncatalyzed reaction which leads to the $[_{\sigma}2 + {}_{\sigma}2 + {}_{\pi}2]$ cycloaddition products, tricyclo[4.2.1.0$^{2,5}$]non-7-enes. Comparative studies on the catalytic reactions of **1** and **2** with acrylates lead to conclusions that (1) **2** reacts with acrylates at a much lower rate than **1**, (2) the presence of **2** results in lowering of the rate of both the isomerization **1** → **2** and the cycloaddition of **1** with olefins giving **7** and **8**, and (3) the product distribution of the cycloaddition (**7**:**8** ratio) does not depend on whether the starting hydrocarbon is **1** or **2** but solely on the reaction conditions. These findings suggest both reactions involve a common intermediate(s) in the product-determining step.

Under the influence of transition metal complexes, strained carbon–carbon $\sigma$ bonds are activated under mild reaction conditions and undergo characteristic transformations.[2] Quadricyclane (**1**) is a molecule which received early attention in this area. Thermal isomerization of the hydrocarbon to norbornadiene (**2**) proceeds only slowly ($t_{1/2} > 14$ hr at 140°)[3] despite the extraordinarily high strain energy (total 78.7 kcal/mol)[4] which can be released through the isomerization. The remarkable thermal stability of **1** should reflect the fact that the cyclobutane–diolefin transformation, though energetically favorable, is restricted by the orbital symmetry conservation rules.[5] Upon addition of Rh(I) complexes, however, it undergoes the $[_{\sigma}2 + {}_{\sigma}2]$ valence isomerization very facilely even at low temperature;[6] the presence of 2 mol % of di-$\mu$-chloro-bis(norbornadiene)dirhodium is known to accelerate the reaction by a factor of $10^{19}$ ($t_{1/2}$ of **1** in 0.7 *M* $CHCl_3$ solution 45 min at −26°).[6a] Pd(II)[6a] and Ag(I)[6c] also catalyze the isomerization.[7] The apparent removal of the symmetry constraints had attracted much theoretical interest, and Pettit, Mango, and Schachtschneider interpreted the phenomenon in terms of the concerted mechanism involving interaction between the strained $\sigma$ bonds and appropriate d orbitals of the transition metals which may conserve the molecular orbital symmetry throughout the skeletal change.[8] Later Cassar and Halpern isolated the stable acylrhodium complex **3** derived from a stoichiometric reaction of **1** and di-$\mu$-chloro-tetracarbonyldirhodium(I) and suggested the stepwise mechanism involving the Rh(III) intermediate **4** for the catalytic transformation **1** → **2**.[9] Similar nonconcerted processes involving the oxidative addition mechanism have been advanced for the catalyses of other strained hydrocarbon systems.[2a,b,10] Thus the mechanistic implication of the concertedness incipiently postulated[8] is losing its importance or at least would have to be reexamined.[11] In any event, however, transition metal complexes do promote various processes which are not easily attainable because of the orbital-symmetry restrictions. Of numerous metal catalysts so far investigated, only Ni(0) complexes could catalyze the intermolecular cycloadditions involving carbon–carbon $\sigma$ bonds effectively. Equations 1–3 illustrate examples of the coupling reactions of certain strained hydrocarbons with electron-deficient olefins ($Z$ = CN, $COOCH_3$, etc.). The catalyses with other transition metal complexes, with few exceptions,[15,16] have been limit-



1 2



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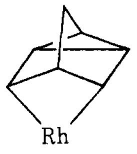

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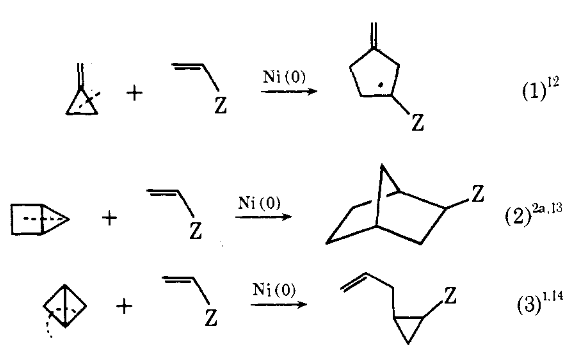
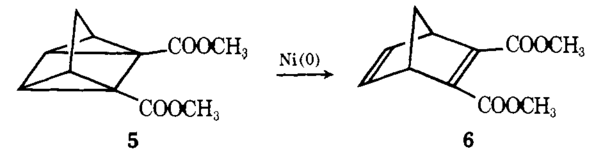


ed to *intramolecular* skeletal changes or incorporation of protic solvents.[7,17] In view of the intriguing operation of Ni(0) catalysts, we have examined the intermolecular, in a formal sense, trapping with external olefins of the reactive species generated from the hydrocarbon **1** and the transition metal. Comparison of the reactivity profile with that encountered on the uncatalyzed thermal reaction and the mechanistic correlation with the well-known Ni(0)-catalyzed reaction of **2** and olefins[18] are also subjects of our interest.

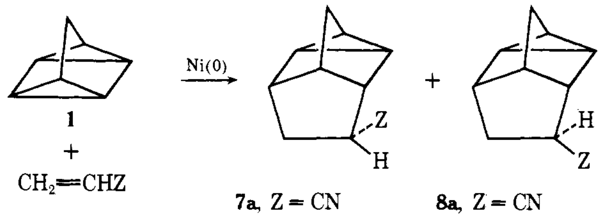
## Results and Discussion

**Nickel(0)-Catalyzed Isomerization of Quadricyclane (1) to Norbornadiene (2).** Treatment of **1** with 5 mol % of bis(acrylonitrile)nickel(0) [Ni(AN)$_2$] suspended in toluene at 20° for 48 hr under a nitrogen atmosphere gave a mixture of **2** (87% yield) and unchanged **1** (10%).[19] In addition, a small amount (<3%) of a mixture of norbornadiene dimers[18c] was formed. The Ni(AN)$_2$-catalyzed isomerization did not occur below 0°. The reaction took place at much lower temperature with bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)$_2$] as a soluble Ni(0) catalyst; treatment of **1** with 5 mol % of Ni(COD)$_2$ in toluene at −20° for 48 hr gave **2** in 85% yield.

Isomerization of dicarbomethoxyquadricyclane (**5**)[20] was also effected by Ni(COD)$_2$ to give the diene **6** in 88% yield after 48-hr reaction at −15°.



**Nickel(0)-Catalyzed Cycloaddition of 1 and Electron-Deficient Olefins.** When the reaction of **1** and Ni(AN)$_2$ in toluene at 20° was carried out in the presence of fivefold excess of acrylonitrile, the cycloadducts **7a** and **8a** (51:49 ratio) were obtained in 50% combined yield at the expense of **2** (*ca.* 30% yield). Structures of **7a** and **8a** were confirmed by their independent synthesis from thermal reaction of **2** and acrylonitrile.[21] Similarly, reaction of **1** and methyl acrylate gave a stereoisomeric mixture of **7b** and **8b**[21] (60:40 ratio) in 58% yield accompanied by small amounts of the acrylonitrile adducts **7a** and **8a**. Ethyl, *n*-butyl, or *tert*-butyl acrylate may be used to afford the corresponding adducts **7c–e** and **8c–e**. Ni(COD)$_2$ in place of Ni(AN)$_2$ could effect the catalysis of **1** at a temperature as low as −20° but gave the same cycloadducts in somewhat reduced yield.



**7a**, Z = CN
**b**, Z = $COOCH_3$
**c**, Z = $COOC_2H_5$
**d**, Z = COO-*n*-$C_4H_9$
**e**, Z = COO-*t*-$C_4H_9$

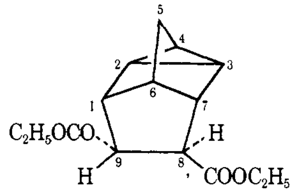
**8a**, Z = CN
**b**, Z = $COOCH_3$
**c**, Z = $COOC_2H_5$
**d**, Z = COO-*n*-$C_4H_9$
**e**, Z = COO-*t*-$C_4H_9$

Attempted reaction of **1** with methacrylonitrile or methyl methacrylate resulted in only the isomerization giving **2**. When a mixture of **5** and methyl acrylate was exposed to the above described catalytic conditions, only the diene **6** was obtained.

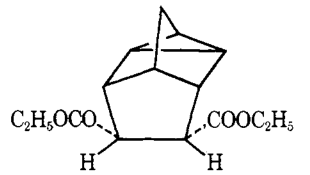
Nortricyclane, which is structurally related but less strained (total strain energy 38.8 kcal/mol)[4] with respect to **1**, was inert to the above described conditions. Control experiments showed that, with or without the Ni(0) catalysts, the electron-deficient olefins react with neither **1** nor **2** under the conditions used for the catalytic reactions.

**Effects of Phosphine Ligands on the Catalysis.** The addition of tertiary phosphine ligands to the catalyst system caused a significant decrease in reaction rate and some change in product distribution. The Ni(AN)$_2$-catalyzed reaction of **1** and excess acrylonitrile (1:15 mol ratio) in the presence of triphenylphosphine [1 equiv per equiv of Ni(AN)$_2$] at 20° for 48 hr afforded a mixture of **7a** and **8a** (10% combined yield) in a ratio of 33:67, together with the diene **2** (55% yield). Bis(diphenylphosphino)ethane, a chelating ligand, exhibited an efficient inhibitory effect on the catalytic cycloaddition. The isomerization **1** → **2** was also retarded but could not be completely quenched by adding 1 equiv of the bidentate phosphine ligand. Effects of the diene **2** on the catalysis of **1** will be described later.

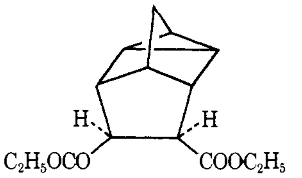
**Stereochemistry of the Ni(0)-Catalyzed Cycloaddition.** The reaction of **1** with diethyl fumarate in the presence of Ni(AN)$_2$ (20°, 72 hr) gave the isomer **2** in 91% yield. The 1:1 cycloadduct **9** was obtained in only 3.7% yield.[22] Diethyl maleate gave no traces of cycloadducts at a temperature of −20° or below where the diene **2** does not produce the olefin adducts (*vide infra*). At an elevated temperature (~10°, 24 hr), a mixture of **2** (62%), the endo,endo adduct **10** (7.8%), and exo,exo adduct **11** (0.2%) was obtained. Neither crotononitrile nor methyl crotonate underwent the catalytic cycloaddition with **1** below 30°.



**9**



**10**



**11**

Thus use of 1,2-disubstituted olefins which gave a preference to the isomerization **1** → **2** over the cycloaddition allowed only partial analysis of the stereochemistry of the cycloaddition involving breakage of the carbon–carbon $\sigma$ bond. Information to establish the stereochemical course was gained by examining the reaction with a deuterium-labeled acrylate. The reaction of **1** and methyl $\alpha$,*cis*-$\beta$-dideuterioacrylate in toluene containing Ni(AN)$_2$ under the above described conditions gave rise to a mixture of the stereoisomeric adducts **12** and **13**. The starting acrylate had not been appreciably isomerized under the reaction condi-

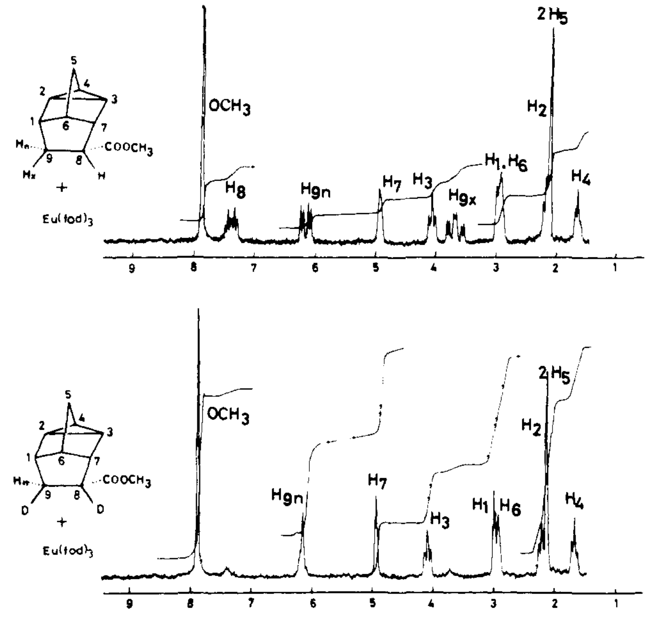


**Figure 1.** Nmr spectra of *endo*-8-carbomethoxytetracyclo-[4.3.0.0$^{2,4}$.0$^{3,7}$]nonane (**7b**) and its dideuterated derivative **12** taken with Eu(fod)$_3$ (0.24 *M* solution of the substrate in CCl$_4$ containing 0.43 mol equiv of Eu(fod)$_3$, 100 MHz).

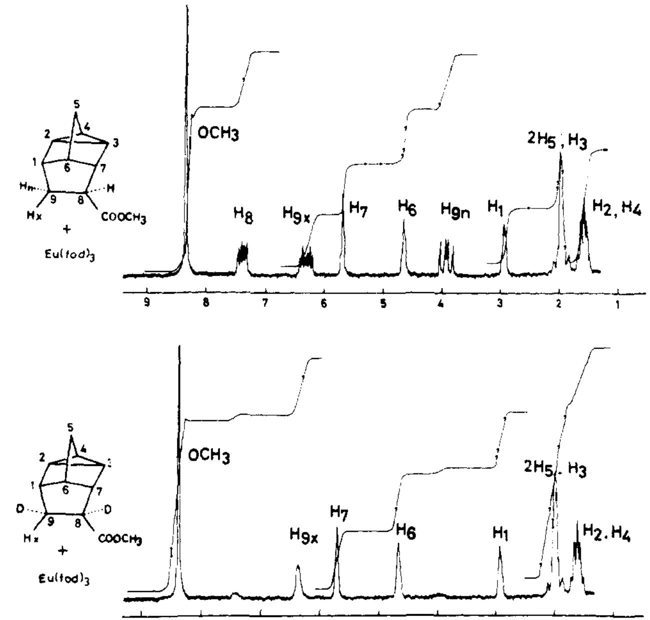
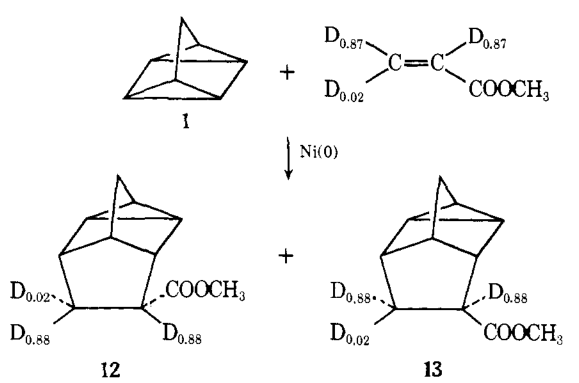


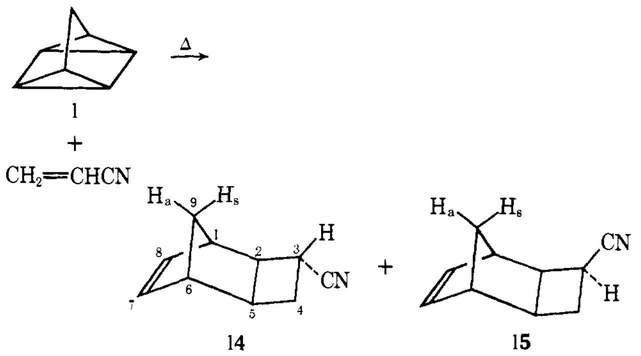
**Figure 2.** Nmr spectra of *exo*-8-carbomethoxytetracyclo-[4.3.0.0$^{2,4}$.0$^{3,7}$]nonane (**8b**) and its dideuterated derivative **13** taken with Eu(fod)$_3$ (0.25 *M* solution of the substrate in CCl$_4$ containing 0.46 mol equiv of Eu(fod)$_3$, 100 MHz).

**Scheme I**

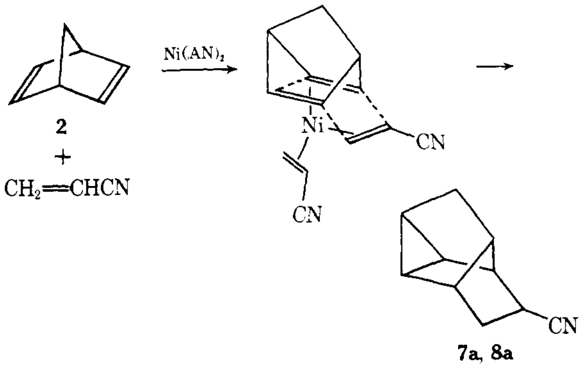


tions. The value of isotopic incorporation in the products was determined by nmr analysis of the samples isolated by preparative scale glpc. The integration of signals was carried out carefully with variable field modulation on the spectra taken with the aid of the Eu(fod)$_3$ shift reagent (Figures 1 and 2). The results shown in Scheme I clearly indicate that the catalytic cycloaddition proceeds with a high degree of stereospecificity. Thus the present reaction provides a new example of transition-metal promoted [$_\sigma2_s$ + $_\pi2_s$] processes which can be envisaged formally as a ground-state disallowed transformation.

**Comparison of the Catalyzed and Uncatalyzed Reactions of 1 with Electron-Deficient Olefins.** The course of the present catalytic cycloaddition is in dramatic contrast with the corresponding uncatalyzed, thermal reaction which leads to the [$_\sigma2$ + $_\sigma2$ + $_\pi2$] adducts. In the absence of transition metals, though under rather forcing conditions, quadricyclane (**1**) and its derivatives react with electron-deficient olefins in a concerted manner to give tricyclo-[4.2.1.0$^{2,5}$]non-7-enes.[23] We have found that acrylonitrile can also enter into the cycloaddition. When a mixture of **1** and excess acrylonitrile was heated in a sealed tube at 95° for 72 hr, the tricyclic adducts **14** and **15** (33:67 ratio) were obtained in 92% combined yield. The stereochemical assignment of **14** and **15** was substantiated by nmr analysis. An AB quartet due to the methylene protons H$_s$ and H$_a$ of **14** occurred at $\delta$ 1.42 and 1.58 ($J$ = 10 Hz), whereas the corresponding signals of **15** appeared at $\delta$ 1.54 and 2.05 ($J$ = 10 Hz). The large chemical shift difference observed for the latter should be ascribed to the anisotropy effect of the cyano group.



**The Homo Diels–Alder Reaction of Norbornadiene (2) and Electron-Deficient Olefins.** Thermal, symmetry-allowed cycloaddition of **2** and dienophiles is known as the homo Diels–Alder reaction.[21,24] Thus reaction of **2** and acrylonitrile or methyl acrylate proceeds smoothly at a temperature above 100° and gives the tetracyclic adducts **7** and **8**.



(4)

Schrauzer and his coworkers found that, in the presence of Ni(AN)$_2$, the cycloadditon takes place under much milder

**Table I.** Homo Diels–Alder Reactions of Norbornadiene (**2**) and Electron-Deficient Olefins

| Olefin | Product | Thermal reaction[a] % yield (**7**:**8**)[c] | Catalytic reaction[b] % yield (**7**:**8**)[c] |
|---|---|---|---|
| Methyl acrylate | **7b**, **8b** | 55 (84:16) | 78 (55:45) |
| Ethyl acrylate | **7c**, **8c** | 50 (83:17) | 76 (53:47) |
| *n*-Butyl acrylate | **7d**, **8d** | 52 (83:17) | 81 (51:49) |
| *tert*-Butyl acrylate | **7e**, **8e** | 44 (76;24) | 67 (45:55) |
| Diethyl fumarate | **9** | 19[d] | 6[e] |
| Diethyl maleate | **10**, **11** | 11 (65:35)[d,f] | 39 (95:5)[d,f,g] |

[a] A mixture of **2** (10 mmol) and acrylate (22 mmol) was heated at 150° for 48 hr. [b] Unless otherwise stated, the reaction was done at 25° for 24 hr with a mixture of **2** (1.7–1.8 mmol), acrylate (11 mmol), and toluene (2.0 ml) in the presence of 5 mol % of $Ni(COD)_2$. [c] Values determined by glpc. [d] The reaction was done by heating a mixture of **2** (19 mmol) and the olefin (10 mmol) at 180° for 60 hr. [e] 50°, 48 hr. [f] Ratio of **10** to **11**. [g] 25°, 36 hr.

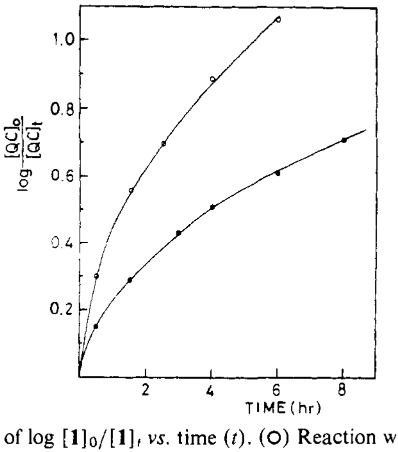


**Figure 3.** Plot of log $[\mathbf{1}]_0/[\mathbf{1}]_t$ *vs.* time ($t$). (○) Reaction was done with 0.380 *M* of **1** and 0.020 *M* of $Ni(COD)_2$ in toluene at −15°. (●) Reaction was carried out at −15° with 0.455 *M* of **1** and 0.024 *M* of $Ni(COD)_2$ in 1:3 methyl acrylate–toluene. The data are from Figure 4. QC = quadricyclane (**1**).

reaction conditions and with higher yield and claimed operation of the concerted, $\pi$-complex multicenter mechanism outlined by eq 4 where acrylonitrile is chosen as substrate.[18] The catalyzed and uncatalyzed homo Diels–Alder reactions gave different product distributions as shown in Table I.

**Comparison of the Reactivities of 1 and 2 in the Presence of Ni(0) Catalysts.** We had been prompted to compare the catalytic reactivities of **1** and **2** in detail, because (1) the two hydrocarbons have a close structural relationship to each other, (2) **1** upon treatment with Ni(0) catalysts undergoes facile isomerization giving **2**, and (3) both hydrocarbons in the presence of Ni(0) complexes give the same type of olefin adducts **7** and **8**. For the clarity in interpreting observations, we employed acrylic acid esters as olefinic substrate and $Ni(COD)_2$ as the catalyst which provide a *homogeneous* system during the reaction. Since electron-deficient olefins are known to displace readily the COD ligand of the complex,[25,26] the actual catalysts effecting the reaction would be free from COD. The catalyses were carried out by use of the hydrocarbons **1** and **2** separately and with a mixture of **1** and **2**.

**(A) Separate Comparisons.** Firstly, the behavior of **1** and **2** under the strictly same catalytic conditions was determined. The reaction of **1** and methyl acrylate in the presence of a catalytic amount of $Ni(COD)_2$ at −20° for 65 hr gave a 58:42 mixture of **7b** and **8b** in 22% combined yield. The remainder consisted of unchanged **1** (10%), the isomer **2** (62%), and its dimers (3%). The corresponding reaction of **2** and methyl acrylate in the presence of $Ni(COD)_2$ proceeded very slowly and afforded the adducts **7b** and **8b** in only 1% combined yield. Notably the **7b**:**8b** ratio was identical, within the limits of the accuracy of glpc analysis, with that obtained from the reaction of **1** and methyl acrylate. This is also the case for the catalyses with ethyl, *n*-butyl, or *tert*-butyl acrylate. Some representative results are summarized in Table II. The reaction with *tert*-butyl acrylate is particularly enlightening.

Careful examination revealed that no trace of **1** was produced during the catalytic reactions involving **2**.

**(B) Reaction of 1 in the Presence of 2.** With the expectation that the catalytic reaction of **1** may follow the second-order kinetic rate law depending on the concentration of **1** and the Ni(0) catalyst, we attempted the kinetic investigation of the reaction. In fact, however, when log $[\mathbf{1}]_0/[\mathbf{1}]_t$ was plotted against reaction time, a marked deviation from linearity was observed as shown in Figure 3. With methyl acrylate as solvent, this tendency was even more pronounced, thereby making the detailed kinetic study difficult. Apparently this trend is due to the retarding effect of the diene **2** which forms from **1** and in turn coordinates to the Ni(0) catalyst.[27,28] Thus the ease with which the isomerization **1** → **2** and the $[_\sigma2 + {}_\pi2]$ cycloaddition take place is markedly affected by the diene **2** coexistent in the reaction system. Figure 4 outlines the progress of the reactions in toluene and methyl acrylate. When 4.5-fold excess of **2** was present in the catalytic system from the beginning, rate of the conversion **1** → **2** fell by a factor 3–4. Also, yield of the cycloadducts **7b** and **8b** was reduced from 14% obtained after a 14-hr reaction under the above described conditions

**Table II.** Nickel(0)-Catalyzed Reactions of Acrylates $CH_2{=}CHZ$ with **1** or **2**

| Z | Solvent | *T*, °C (time, hr) | 7 and 8 from 1: % yield[a,b] | 7 and 8 from 1: **7**:**8** ratio[c] | 7 and 8 from 2: % yield[a,d] | 7 and 8 from 2: **7**:**8** ratio[c] |
|---|---|---|---|---|---|---|
| ● $COOCH_3$ | Toluene | −20 (48) | 12 | 58:42 | 1 | 57:43 |
| $COOCH_3$ | Toluene | −20 (65) | 22 | 58:42 | 1 | 57:43 |
| $COOCH_3$ | None | −10 (21) | 25 | 58:42 | 2 | 58:42 |
| $COOCH_3$ | None | 0 (13) | 25 | 58:42 | 7 | 59:41 |
| $COOC_2H_5$ | Toluene | −20 (48) | 15 | 60:40 | 0.8 | 60:40 |
| $COOC_2H_5$ | Toluene | −20 (60) | 20 | 59:41 | 1 | 59:41 |
| $COOC_2H_5$ | None | 0 (13) | 29 | 75:43 | 6.5 | 58:42 |
| COO-*n*-$C_4H_9$ | Toluene | −20 (48) | 19 | 59:41 | 0.5 | 59:41 |
| COO-*n*-$C_4H_9$ | None | −20 (48) | 22 | 56:44 | <0.5 | *e* |
| COO-*n*-$C_4H_9$ | None | 0 (13) | 38 | 57:43 | 13 | 57:43 |
| COO-*n*-$C_4H_9$ | None | 0 (8) | 33 | 56:44 | 5 | 57:43 |
| COO-*t*-$C_4H_9$ | Toluene | −20 (48) | 8 | 58:42 | 1 | 57:43 |
| COO-*t*-$C_4H_9$ | None | 0 (13) | 23 | 53:47 | 4 | 52:48 |
| COO-*t*-$C_4H_9$ | None | 20 (3.5) | 24 | 48:52 | 13 | 49:51 |

[a] Determined by glpc. [b] The remainder consisted of **1**, **2**, and small amounts of the dimers of **2**. [c] Duplicates deviated less than 1% from the mean. [d] Mainly unchanged. [e] The accurate ratio could not be determined because of the low yield.

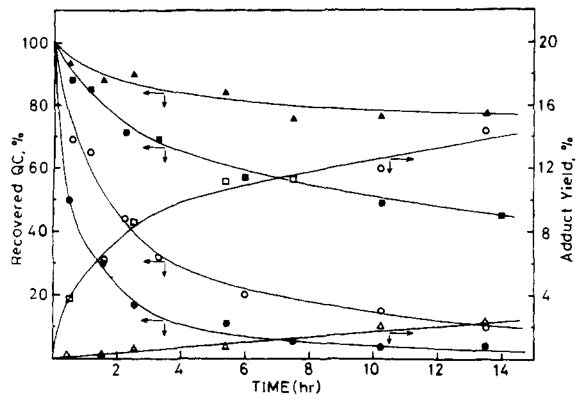


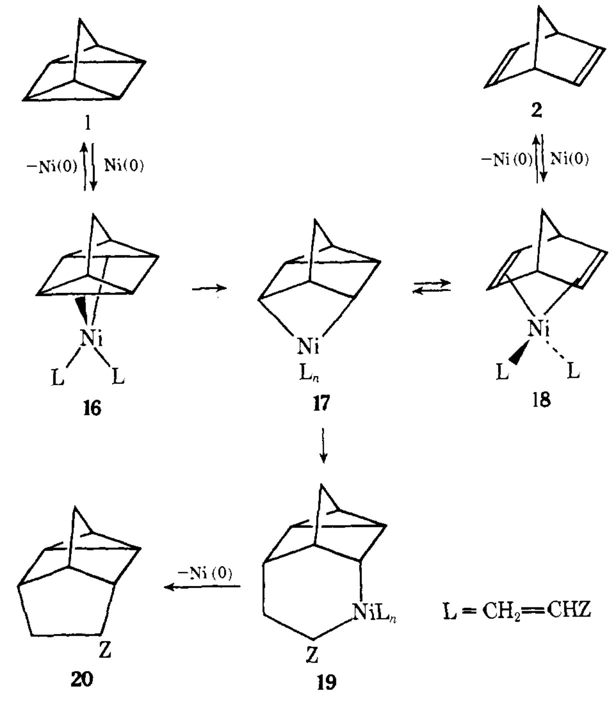
**Figure 4.** Plot of the amount of recovered **1** *vs.* time (*t*). (●) Isomerization of **1** in toluene without added **2**. (■) Isomerization of **1** in toluene in the presence of 4.5 equiv of **2**. (○,□) Reaction of **1** in a mixture of methyl acrylate and toluene without added **2**. (▲,△) Reaction of **1** in a mixture of methyl acrylate and toluene in the presence of 4.5 equiv of **2**.

(without added **2**) to only 2% by the addition of 4.5-fold excess of **2**. Here the isomeric ratio of the cycloadducts, **7b**:**8b** = 58:42, remained unchanged.

Thus these comparative studies lead to conclusions that (1) under the conditions given in Table II, **2** reacts with acrylates at a much *lower* rate than **1**, (2) the presence of **2** retards both the isomerization of **1** to **2** and the $[_\sigma 2 + _\pi 2]$ cycloaddition of **1** and acrylates, and (3) the product distribution of the cycloaddition, **7**:**8** ratio, does not depend on whether the starting hydrocarbon is **1** or **2** but depends crucially on the catalysis conditions. The observed kinetic deceleration by **2** implies the existence of the preequilibrium, Ni(0) + **2** $\rightleftharpoons$ Ni(0)-**2** complex. In spite of the easiness of the formation of the latter diene complex, further reaction proceeds only slowly.

**Mechanistic Consideration of the Catalytic Reactions.** All these findings can reasonably be accounted for by assuming the mechanism outlined in Scheme II. The reactions with **1** and with **2** proceed by way of the mixed ligand complex(es) **17** as the common, product-determining intermediate.

**Scheme II**



The highly strained $\sigma$ bond of **1** through the initial, edgewise coordination[29,30] undergoes oxidative addition[2b,31] to the $d^{10}$ Ni(0) atom to form the organonickel intermediate **17**.[32,33] This process is a consequence of the combination of eminent $\sigma$-donor ability of **1**[34] and strong $\pi$-donor ability of Ni(0) atom.[26,28,34,35] Ligand isomerization followed by extrusion of the Ni(0) catalyst produces the isomeric diene **2**,[9] while insertion of the coordinated olefin to the Ni-C bond gives **19** which through elimination of the Ni(0) complex leads to the cycloaddition products **20**. The transformations **16** → **17** → **18** and **16** → **17** → **19** are expected to be facile because of the apparent relief of a large amount of strain. By contrast, the conversion of **18** to **17** would be energetically unfavorable because of the significant increase in the strain energy that should occur.[36,37] It is not surprising, therefore, that with the saturated (in a formal sense) hydrocarbon **1** the cycloaddition forming **20** is quite facile, whereas with the diene **2** having the strong coordination tendency to Ni(0) atom the reaction proceeds only sluggishly. Rather, **2** acts as an inhibitor of the catalysis of **1**. The reaction of **2** at an elevated temperature [as high as 30° in the case of the $Ni(COD)_2$ catalysis] could surmount the kinetic barrier and afforded the cycloadducts **7** and **8** in good yield (*cf.* Table I).

In Scheme II, the oxidative addition concept is employed as a matter of simplicity. At present, however, it is indistinguishable experimentally whether the edgewise coordinated cyclopropane-metal complex of type **21** and the corresponding metallacyclobutane **22** can exist as two distinct tautomers or actually are canonical forms in a resonance hybrid.[38,39] If the latter were the case, the complex **16** (or the corresponding unidentately coordinated complex) could also serve as reasonable intermediate which is common to the reaction of **1** and that of **2**. The Ni(II) complex **19** (*n* = 2) could be derived directly from the 18-electron Ni(0) complex **16** *via* oxidative coupling between the coordinated strained $\sigma$ bond and olefinic ligand L.[40]

**21**

**22**

Although an excellent stereospecificity was observed for the catalytic cycloaddition, operation of a concerted mechanism which gives **20** directly from **16** seems unlikely in view of the 16- and 18-electron rule.[40] The conversion, **16** → **20** + Ni(0), through which the number of valence electrons of Ni(0) reduces by six (or four if coordination of the cyclopropane ring of **20** to Ni(0) is taken into consideration), is severely restrained; the 18-electron complex **16** could not undergo any associative reactions.

The previously discovered Ni(0)-catalyzed cycloaddition of **2** and electron-deficient olefins,[18] though the conditions employed there were somewhat different from those of the present work, could also be explained in terms of the stepwise mechanism outlined here rather than by the concerted mechanism which violates the 16- and 18-electron rule. A question regarding the concertedness of the Rh-catalyzed dimerization of **2** was first raised by Katz, and evidence for the stepwise mechanism was presented.[41,42]

## Experimental Section

**General.** All boiling temperatures are uncorrected. Nuclear magnetic resonance (nmr) spectra were recorded on either a Varian Associates Model HA-100D or Japan Electron Optics Lab. Co. Model C-60H spectrometer in carbon tetrachloride solution. All chemical shifts were recorded as in parts per million downfield from internal tetramethylsilane standard. Singlet, doublet, triplet, and multiplet were abbreviated s, d, t, and m, respectively. Infrared (ir) spectra were taken in carbon tetrachloride on a JASCO Model DS-402 spectrophotometer. Mass spectra were recorded on a Hitachi Model RMU-6C mass spectrometer at 70 eV ionizing radiation. Gas-liquid phase chromatography (glpc) analysis was carried out on a Yanagimoto Model G-8 gas chromatograph equipped with a flame ionization detector by use of nitrogen as the carrier gas. Preparative separation was performed on a Varian Associates Model 1800 instrument fitted with a thermal conductivity detector with helium as the carrier gas. The following columns were used: A, 4 m × 4 mm 11% diisodecyl phthalate on 80–120 mesh Neosorb; B, 2 m × 4 mm 5% poly(ethylene glycol) succinate on 80–120 mesh Celite 545; C, 4 m × 4 mm 5% poly(ethylene glycol) succinate on 80–120 mesh Celite 545; D, 7 ft × ⅜ in. 30% diisodecyl phthalate on 80–120 mesh Neosorb; E, 13 ft × 0.25 in. 15% poly(ethylene glycol) adipate on 80–120 mesh Neosorb; and F, 13 ft × 0.25 in. 10% silicone DC QF-1 on 80–120 mesh Chromosorb W AW. Yields were determined by cut-and-weigh integration of glpc traces by using internal standards. For analysis of acid-sensitive quadricyclane (**1**), the injection port was thoroughly washed with dimethylformamide, water, and 0.5% methanolic NaOH, and the columns were silylated with hexamethyldisilazane before use. Precoated silica gel plates (0.25-mm layers of E. Merck 60 F-254 silica gel) were used for analytical thin-layer chromatography (tlc), and compounds were visualized by ultraviolet illumination, exposure to iodine vapor, or spray of 2% ceric sulfate in 2 *N* $H_2SO_4$ or 5% aqueous $KMnO_4$. Preparative scale tlc was also conducted on silica gel plates (1.0-mm layers of E. Merck GF-254 silica gel). Microanalyses were performed at the Department of Industrial Chemistry, Faculty of Engineering, Kyoto University.

**Materials.** Commercial (reagent grade) acrylonitrile, methyl acrylate, ethyl acrylate, *n*-butyl acrylate, norbornadiene (**2**), and 1,5-cyclooctadiene were distilled over calcium hydride under reduced pressure in a nitrogen atmosphere and stored in a refrigerator over molecular sieves 3A. Triphenylphosphine was recrystallized twice from ethanol and dried in a vacuum desiccator. Bis(diphenylphosphino)ethane (Arapahoe Chemicals) was used without further purification. Benzene and toluene were distilled after refluxing over calcium hydride for 3 hr in a nitrogen atmosphere and stored under nitrogen. Quadricyclane (**1**),[43] and dicarbomethoxyquadricyclane (**5**),[44] and nortricyclane[45] were prepared by the standard procedure. *tert*-Butyl acrylate was obtained from acryloyl chloride and *tert*-butyl alcohol in 73% yield by the application of the method of preparation of *tert*-butyl acetate.[46] Methyl α,*cis*-β-dideuterioacrylate was synthesized through retro-Diels–Alder reaction of methyl *cis*-11,12-dideuterio-9,10-ethanoanthracene-11-carboxylate, which was prepared by the method of Hill and Newkome[47] with modification by Majerski and Schleyer.[48] Bis(acrylonitrile)nickel(0) [Ni(AN)$_2$] was prepared in a reaction ampoule from nickel tetracarbonyl and acrylonitrile by the procedure of Schrauzer.[49] The sparingly soluble orange-red crystals were washed with three 2-ml portions of benzene before use. Bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)$_2$] was obtained by the reduction of bis(acetylacetonato)nickel(II) with triethylaluminum in the presence of 1,5-cyclooctadiene[50] and recrystallized twice from toluene. Since these nickel(0) complexes are highly air sensitive, care to avoid contact with air was exercised; all catalytic reactions were run in 10-ml or 20-ml ampoules of heavy-walled glass tubing with predawn neck under strictly anaerobic conditions using oxygen-free nitrogen or argon. All liquid reagents were degassed by bubbling dry nitrogen or argon for 30 min at room temperature before use.

**Ni(AN)$_2$-Catalyzed Isomerization of 1 into 2.** A solution of **1** (184 mg, 2.0 mmol) and benzene (78 mg, 1.0 mmol, internal standard for glpc analysis) in toluene (2.0 ml) was added to Ni(AN)$_2$ (16 mg, 0.1 mmol) in a reaction ampoule at −40°, and the tube was sealed under nitrogen. The mixture was kept at 20° for 48 hr with occasional shaking. The reaction tube was opened, and a slow stream of air was introduced at −20° to decompose the catalysts. The solid precipitates were removed by filtration through a pad of Celite 545, and the filtrate was analyzed by glpc (column A, column temperature 65°, injection temperature <150°, 30 ml/min). Peaks attributed to benzene, norbornadiene (**2**), unreacted quadricyclane (**1**), and toluene appeared with retention times ($t_r$) of 15.5, 18.0, 38.4, and 42.5 min, respectively. The yield of **2** was 87%. Ten per cent of **1** was recovered unchanged. The structure of **2** was confirmed with a sample obtained by glpc (column D, 70°) by comparison of the nmr and ir spectra with those of an authentic sample.

**Ni(AN)$_2$-Catalyzed Reaction of 1 and Acrylonitrile.** Ni(AN)$_2$ (16 mg, 0.1 mmol) was made in a 10-ml ampoule, to which was added a solution of **1** (184 mg, 2.0 mmol), acrylonitrile (0.54 g, 10 mmol), and benzene (78 mg, 1.0 mmol, internal standard) in toluene (2.0 ml) under an atmosphere of nitrogen. The reaction tube was sealed and kept at 20° for 48 hr with occasional shaking. After the mixture was cooled to −20°, the catalysts were decomposed by introducing a gentle stream of air. The resulting solid was removed by filtration. Glpc analysis of the filtrate (column A, 65°) showed the isomerization product **2** was formed in 30% yield. Methyl laurate (214 mg, 1.0 mol) was added to the filtrate as the glpc standard. Evaporation of the mixture and analysis of the residue by glpc (column B, 120°, 15 ml/min) indicated that **7a** and **8a** were obtained in 50% combined yield in a ratio of 51:49. Methyl laurate, **7a**, and **8a** had the retention times of 4.4, 10.4, and 8.3 min, respectively. The analytically pure samples were obtained by tlc separation (*n*-hexane–benzene 1:1) followed by preparative glpc (column E, 140°). Ir and nmr spectra of **7a** and **8a** were identical with those of the authentic samples prepared by thermal reaction of **2** and acrylonitrile.[18]

**Ni(AN)$_2$-Catalyzed Reaction of 1 and Acrylonitrile in the Presence of Triphenylphosphine.** Ni(AN)$_2$ (16 mg, 0.1 mmol) and triphenylphosphine (26 mg, 0.1 mmol) were mixed in a 10-ml glass tube, to which was added toluene (1.0 ml) at −40°. The mixture was warmed up to room temperature with shaking to dissolve the nickel complex as much as possible. The resulting deep red solution was cooled again to −40°, and then was added a mixture of **1** (92 mg, 1.0 mmol), acrylonitrile (0.79 g, 15 mmol), benzene (78 mg, 1.0 mmol), and toluene (1.0 ml). The reaction tube was sealed under nitrogen and allowed to stand at 20° for 48 hr. A solution of methyl laurate (107 mg, 0.5 mmol) in toluene (1.0 ml) was added to the reaction mixture, and the catalysts were decomposed by admitting air into the solution. Removal of the solid materials by filtration followed by glpc analysis indicated the production of **7a** and **8a** (33:67) in 10% yield together with the diene **2** (55%). Reaction of **1** (92 mg, 1.0 mmol) and acrylonitrile (0.79 g, 15 mmol) in the presence of Ni(AN)$_2$ (16 mg, 0.1 mmol) and bis(diphenylphosphino)ethane (40 mg, 0.1 mmol) was carried out under the same reaction conditions. The reaction mixture was worked up as above and analyzed by glpc. Only trace amounts (<3%) of the adducts **7a** and **8a** were detected. In the absence of acrylonitrile, 25% of **1** was isomerized to **2** under similar reaction conditions.

**Ni(AN)$_2$-Catalyzed Reaction of 1 with Methyl Acrylate.** The reaction of **1** (150 mg, 1.5 mmol) and methyl acrylate (1.5 ml, 17 mmol) in the presence of Ni(AN)$_2$ (32 mg, 0.2 mmol) was carried out as described for the reaction with acrylonitrile. After the catalysts had been decomposed with air at −20° and removed by filtration, the reaction mixture was subjected to preparative tlc (20:1 *n*-hexane–ether, two developments) affording **7b** ($R_f$ 0.31, 92.4 mg, 35%) and **8b** $R_f$ 0.39, 61.6 mg, 23%). In addition, a mixture of **7a** and **8a** ($R_f$ 0.21, 14.0 mg, 7%) was obtained. Pure samples of **7b** and **8b** were obtained by preparative glpc (column E, 140°), and the structures were determined by comparison of ir and nmr spectra with those of authentic specimens prepared by thermal reaction of **2** and methyl acrylate.

**Ni(AN)$_2$-Catalyzed Reaction of 1 and Methyl α,*cis*-β-dideuterioacrylate.** A mixture of Ni(AN)$_2$ (32 mg, 0.2 mmol), **1** (1.5 g, 16.5 mmol), α,*cis*-β-dideuterioacrylate (0.48 g, 5.4 mmol), and toluene (0.5 ml) was prepared in a 10-ml ampoule under nitrogen. The reaction tube was sealed and allowed to stand at 20° for 72 hr. The catalysts were decomposed with air, and the resulting solid materials were removed by filtration. Unchanged methyl acrylate-$d_2$ was recovered together with **2** and toluene by distillation *in vacuo*, bp 80° (700 mm). No change was observed in the nmr spectrum of the acrylate compared with that of the starting one. Distillation of the residue under reduced pressure gave a crude oil (1.0 g), bp 90° (3 mm). Glpc analysis showed the fraction consisted of the adducts **11** and **12** (58:42) (50% combined yield) and some norbornadiene dimers. The analytical samples were obtained by preparative glpc separation (column E, 150°). The deuterium contents of the starting material and products were determined carefully by nmr analysis (100 MHz, variable field modulation) with dilution technique with the aid of the undeuterated substances. The value of isotopic incorporation represents a mean for ten integrations and the deviation was within ±2%. The proton assignments of **7b** and **8b** and their deuterated derivatives **11** and **12** were based on initial chemical shifts, coupling constants, and decoupling experiments on their parent spectra and, more easily, on the Eu(fod)$_3$-aided spectra (Figures 1 and 2). Nmr spectrum of **7b**, $\delta$ 0.8–1.0 (m, $H_2$ and $H_3$), 1.0–1.2 (m, $H_4$), 1.51 (s, 2 $H_5$), 1.6–2.1 (m, $H_{9n}$ and $H_{9x}$), 1.79 (broad s, $H_6$), 1.99 (broad s, $H_1$), 2.2–2.3 (m, $H_7$), 2.7–3.0 (m, $H_8$), and 3.65 (s, $OCH_3$). When the Eu(fod)$_3$-induced shifts were plotted against the relative molar ratios of the shift reagent and the substrate, linear relationship was observed. The gradients, ppm/mol of Eu(fod)$_3$ per mole of substrate, of these lines were 10.5 ($H_8$), 9.81 ($OCH_3$), 9.26 ($H_{9n}$), 7.25 ($H_3$), 6.40 ($H_7$), 4.25 ($H_{9x}$), 2.90 ($H_2$), 2.70 ($H_6$), 2.35 ($H_1$), and 1.45 ($H_4$ and $H_5$). The following coupling constants were determined: $J_{1,9n} = 0$, $J_{1,9x} = 5.0$, $J_{7,8} = 4.5$, $J_{8,9n} = 4.8$, $J_{8,9x} = 11.4$, and $J_{9n,9x} = 13.0$ Hz. Nmr spectrum of **8b** was: $\delta$ 0.8–1.0 (m, $H_2$ and $H_3$), 1.0–1.2 (m, $H_4$), 1.54 (s, 2 $H_5$), 1.7–2.1 (m, $H_{9n}$ and $H_{9x}$), 1.95 (broad s, $H_6$), 2.00 (broad s, $H_1$), 2.15 (broad s, $H_7$), 2.5–2.8 (m, $H_8$), and 3.60 (s, $OCH_3$). The gradients of the lines derived from the Eu(fod)$_3$-induced spectra were 10.6 ($OCH_3$ and $H_8$), 9.90 ($H_{9x}$), 7.95 ($H_7$), 6.10 ($H_6$), 4.75 ($H_{9n}$), 2.45 ($H_1$ and $H_3$), 1.65 ($H_2$), 1.25 ($H_4$), and 1.15 ($H_5$). The coupling constants determined were: $J_{1,9n} = 0$, $J_{1,9x} = 5.0$, $J_{7,8} = 0$, $J_{8,9n} = 12.0$, $J_{8,9x} = 5.0$, and $J_{9n,9x} = 12.0$ Hz.

**Ni(AN)$_2$-Catalyzed Reaction of 2 and Olefinic Substrates $CH_2{=\!=}CHZ$.** The reaction of **2** and acrylonitrile or methyl acrylate in the presence of Ni(AN)$_2$ was carried out in the same fashion as described for the reaction with **1**. In each case, only small amounts (<1%) of the adducts **7** and **8** were detected by glpc analysis. The reaction of **2** and acrylonitrile at 40° for 38 hr gave only 2% of the adducts **7a** and **8a**, the isomeric ratio being 49:51.

**Attempted Reaction of Nortricyclane and Olefinic Substrate $CH_2{=\!=}CHZ$ in the Presence of Ni(AN)$_2$.** A mixture of nortricyclane (190 mg, 2.0 mmol), acrylonitrile or methyl acrylate (2.0 ml), and toluene (2.0 ml) was added to Ni(AN)$_2$ (32 mg, 0.2 mmol) in a 10-ml ampoule under nitrogen. The reaction mixture was kept at 25°. Neither glpc (column C, column temperature 110°) nor tlc analysis of the filtrate could detect the 1:1 adducts. Quantitative recovery of unchanged nortricyclane was shown by glpc (column A, 50°). The reaction was done in the same scale with Ni(COD)$_2$ as a catalyst at 0° for 72 hr. No addition products, however, were noticed by glpc or tlc analysis.

**Ni(AN)$_2$-Catalyzed Reaction of 1 with Diethyl Fumarate.** A mixture of **1** (184 mg, 2.00 mmol) and diethyl fumarate (1.50 g, 8.72 mmol) in toluene (2.0 ml) was added to freshly prepared Ni(AN)$_2$ (32 mg, 0.20 mmol) in a 10-ml ampoule, and the vessel was sealed under nitrogen. The mixture was kept at 20° for 72 hr with occasional shaking. The tube was opened, and to this mixture were added a solution of benzene (120 mg, 1.54 mmol) and diethyl sebacate 15.9 mg, 0.062 mmol) in toluene (1.0 ml). The catalysts were decomposed with air at −20°. After the removal of the solid materials by filtration, the filtrate was evaporated to give colorless liquid (1.70 g). The glpc analysis showed the formation of the diene **2** (column A, 65°) (91% yield) accompanied by the single 1:1 adduct **9** (column B, 170°, 14 ml/min, $t_r$ 22.6 min) (3.7%). A pure sample of **9** was obtained by preparative glpc (column E, 190°) of the crude product obtained by carrying five runs: ir 3067 (w), 2982 (m), 2952 (m), 2872 (w), 1730 (s), 1433 (w), 1373 (w), 1310 (m), 1276 (w), 1253 (m), 1246 (m), 1177 (s), 1096 (w), 1040 (m), 956 (w), and 860 (w) cm$^{-1}$; nmr $\delta$ 0.8–1.3 (m, $H_2$, $H_3$, and $H_4$), 1.28 (t, $J = 7.0$ Hz, 2 $CH_3$), 1.53 (s, 2 $H_5$), 2.01 (broad s, $H_6$), 2.23 (broad s, $H_1$), 2.3–2.4 (m, $H_7$), 3.11 (dd, $J_{8,9} = 4.5$ and $J_{1,9} = 2.6$ Hz, $H_9$), 3.30 (dd, $J_{7,8} = 4.5$ Hz, $H_8$), and 4.10 and 4.13 (two sets of q, $J = 7.0$ Hz, 2 $OCH_2CH_3$); mass spectrum *m/e* 264 ($M^+$). *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 67.95; H, 7.69. The structure of **9** was established by the comparison of ir and nmr spectra with those of an authentic sample prepared by thermal reaction of **2** and diethyl fumarate at 180° for 48 hr (19%). Under comparable catalytic reaction conditions, **2** and diethyl fumarate gave **9** in only 0.2%.

**Ni(AN)$_2$-Catalyzed Reaction of 1 with Diethyl Maleate.** The reaction of **1** (156 mg, 1.70 mmol) and diethyl maleate (1.52 g, 8.83 mmol) in toluene (2.0 ml) in the presence of Ni(AN)$_2$ (32 mg, 0.20 mmol) was done at 10° for 24 hr as described for the reaction with **1** and diethyl fumarate. Decomposition of the catalysts followed by removal of the precipitates and evaporation of the solvent gave colorless liquid (1.64 g) which was analyzed by glpc (column B, 170°, 14 ml/min). The endo,endo isomer **11** ($t_r$ 37.0 min) and the exo,exo isomer **12** ($t_r$ 30.8 min) were obtained in 8% yield in a ratio of 97:3 accompanied by the diene **2** (62%). Under comparable reaction conditions, **2** and diethyl maleate gave 10% of **11** and **12** in a ratio of 97:3. Neither **1** nor **2** gave the adducts below −20° after 48-hr reaction. Structures of **11** and **12** were established by comparison of the ir and nmr spectra with those of authentic specimen obtained by thermal reaction of **2** and diethyl maleate (180°, 48 hr, 11% yield, **10**:**11** 65:35). Spectral and analytical data of the adducts were: (**11**) ir 3066 (w), 2981 (s), 2951 (s), 2871 (m), 1740 (s), 1445 (w), 1373 (m), 1350 (m), 1320 (m), 1290 (w), 1240 (m), 1208 (m), 1192 (s), 1175 (s), 1100 (w), 1072 (m), 1064 (m), 1053 (m), 1040 (w), 946 (w), and 865 (w) cm$^{-1}$; nmr $\delta$ 1.0–1.4 (m, $H_2$, $H_3$, and $H_4$), 1.24 (t, $J = 7.0$ Hz, 2 $CH_3$), 1.49 (s, 2 $H_5$), 1.78 (broad s, $H_6$), 2.23 (broad s, $H_1$ and $H_7$), 3.07 (broad s with find splitting, $H_8$ and $H_9$), and 4.05 (q, $J = 7.0$ Hz, 2 $OCH_2CH_3$); mass spectrum *m/e* 264 ($M^+$). *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.32; H, 7.83. (**12**) Ir 3067 (w), 2987 (s), 2942 (s), 2872 (m), 1735 (s), 1448 (w), 1375 (m), 1351 (w), 1332 (m), 1317 (w), 1298 (w), 1277 (w), 1260 (m), 1243 (m), 1213 (w), 1193 (s), 1179 (s), 1150 (s), 1099 (w), 1048 (m), 1008 (w), 967 (w), 903 (w), and 854 (w) cm$^{-1}$; nmr $\delta$ 0.8–1.0 (m, $H_2$ and $H_3$), 1.0–1.3 (m, $H_4$), 1.24 (t, $J = 7.0$ Hz, 2 $CH_3$), 1.61 (s, 2 $H_5$), 2.24 (broad s, $H_1$ and $H_7$), 2.44 (broad s, $H_6$), 3.01 (sharp s, $H_8$ and $H_9$), and 4.00 (q, $J = 7.0$ Hz, 2 $OCH_2CH_3$); mass spectrum *m/e* 264 ($M^+$). *Anal.* Calcd for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63. Found: C, 68.05; H, 7.82.

**Thermal Reaction of 1 and Acrylonitrile.** A mixture of **1** (0.65 g, 7 mmol) and acrylonitrile (3.7 g, 70 mmol) was placed in a 10-ml glass tube. The system was deoxygenated by five freeze–thaw cycles, sealed under nitrogen, and heated at 95° for 72 hr. Distillation *in vacuo* gave a mixture of the adducts **14** and **15** (0.93 g, 92%, 33:67 ratio), bp 80–90° (2 mm). The isomers were separated by glpc (column F, 130°). Spectral properties of **14** were: ir 3063 (w), 2973 (s), 2246 (m), 1478 (w), 1438 (w), 1323 (m), 852 (w), and 700 (m) cm$^{-1}$; nmr $\delta$ 1.42 and 1.58 (AB q, $J_{AB} = 10$ Hz, $H_{9s}$ and $H_{9a}$), 1.6–2.6 (m, $H_2$, $H_3$, 2 $H_4$, and $H_5$), 2.70 (broad s, $H_6$), 2.84 (broad s, $H_1$), and 5.9–6.1 (m, $H_7$ and $H_8$). *Anal.* Calcd for $C_{10}H_{11}N$: C, 82.72; H, 7.64; N, 9.65. Found: C, 82.51; H, 7.61; N, 9.33. Mass spectra of **14** and **15** exhibited molecular ion peaks at *m/e* 145 and characteristic fragment peaks resulting from retrocycloaddition at *m/e* 92 and 66. Spectral properties of **15** were: ir 3065 (w), 2973 (s), 2248 (m), 1470 (w), 1436 (w), 1328 (m), 1298 (w), 1083 (w), 898 (w), 835 (w), 718 (w), and 687 (m) cm$^{-1}$; nmr $\delta$ 1.54 and 2.05 (AB q, $J_{AB} = 10$ Hz, $H_{9s}$ and $H_{9a}$), 1.5–2.7 (m, $H_2$, 2 $H_4$, and $H_5$), 2.74 (broad s, $H_6$), 3.02 (broad s, $H_1$), 3.1–3.5 (m, $H_3$), and 6.00 (broad s, $H_7$ and $H_8$). *Anal.* Calcd for $C_{10}H_{11}N$: C, 32.72; H, 7.64; N, 9.65. Found: C, 82.63; H, 7.40; N, 9.79.

**Ni(COD)$_2$-Catalyzed Isomerization of 1 into 2.** Ni(COD)$_2$ (27 mg, 0.1 mmol) was placed in a 10-ml reaction ampoule under argon atmosphere, and to this was added toluene (2.0 ml). The mixture was shaken at room temperature until the complex dissolved completely, and the yellow solution was placed in a Dry Ice–methanol bath cooled at −40°. A solution of **1** (184 mg, 2.0 mmol) and benzene (78 mg, 1.0 mmol) in toluene (2.0 ml) was added, and the tube was sealed under argon. The mixture was placed in a refrigerator and kept at −20° for 48 hr. The ampoule was opened, and the catalysts were decomposed by exposure to air at −20° for a few minutes. The precipitates were separated by filtration through a pad of Celite 545, and the filtrate was analyzed by glpc (column A, 65°) to show the formation of **2** in 85% yield and the recovery of **1** in 5%.

**Ni(COD)$_2$-Catalyzed Isomerization of Dicarbomethoxyquadricyclane (5) into the Diene 6.** The quadricyclane **5** (115 mg, 0.533 mmol) in toluene (3.0 ml) was added to Ni(COD)$_2$ (27 mg, 0.1 mmol) in a 10-ml reaction ampoule under argon, and the tube was sealed. After 48 hr at −15°, the catalysts were decomposed with air and removed by filtration. Evaporation of the solvent gave a crude oil (0.125 g) which was analyzed by nmr with tetralin as an internal standard, indicating that 2,3-dicarbomethoxynorbornadiene (**6**) was formed in 88% yield. Analytical sample of **6** was obtained by preparative tlc (*n*-hexane–ether 10:1), and the structure was confirmed by comparison of its nmr spectrum with that of an authentic sample.

**Ni(COD)$_2$-Catalyzed Reaction of 1 or 2 and Acrylate.** The following is illustrative for the reaction of **1** or **2** and acrylic esters catalyzed by $Ni(COD)_2$. $Ni(COD)_2$ (27 mg, 0.1 mmol) was placed in a 10-ml reaction tube in an atmosphere of nitrogen, and the vessel was cooled at −50°. Then was added a mixture of methyl acrylate (1.0 ml, 0.93 g, 10.8 mmol) and toluene (1.0 ml) containing benzene (78 mg, 1.0 mmol, internal standard). The mixture was warmed to room temperature with shaking, and after the nickel complex was dissolved, the homogeneous yellow-orange solution was cooled again to −50°. A solution of **1** (184 mg, 2.0 mmol) in toluene (1.0 ml) was added, and the mixture was kept at −20° for 65 hr. Addition of toluene (0.5 ml) containing methyl laurate (43 mg, 0.4 mmol, internal standard) at −20° was followed by decomposition of the catalysts with air at this temperature. Glpc analysis of the colorless organic layer (column A, 65°; column C, 125°) revealed the formation of a 58:42 mixture of the adducts **7b** and **8b** (22% combined yield) accompanied by **2** (62%). The remainder consisted of unchanged **1** (10%) and dimers of **2** (3%). A series of reactions of **1** or **2** with methyl, ethyl, *n*-butyl, and *tert*-butyl acrylate were done under variable reaction conditions, and the results are summarized in Table II. Experiments with **2** and various acrylates were carried out at 25° in a similar manner, and the results are shown in Table I. The spectral and analytical data of the products were: (**7c**) ir 3065 (w), 2945 (s), 2870 (m), 1732 (s), 1375 (w), 1324 (m), 1293 (w), 1184 (s), 1174 (s), 1072 (w), and 1043 (m) cm$^{-1}$; nmr $\delta$ 1.8–2.2 (m, $H_2$, $H_3$, and $H_4$), 1.27 (t, $J$ = 7.0 Hz, $OCH_2CH_3$), 1.52 (s, 2 $H_5$), 1.5–2.2 (m, $H_1$, $H_6$, and 2 $H_9$), 2.2–2.3 (m, $H_7$), 2.84 (ddd, $J$ = 4.5, 4.5, and 10.5 Hz, $H_8$), and 4.10 (q, $J$ = 7.0 Hz, $OCH_2CH_3$); mass spectrum *m/e* 192 ($M^+$). *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.87; H, 8.59. (**8c**) Ir 3085 (w), 2960 (s), 2887 (m), 1731 (s), 1371 (m), 1348 (w), 1321 (w), 1285 (w), 1261 (w), 1242 (w), 1216 (w), 1178 (s), 1156 (s), 1097 (w), 1063 (w), and 1038 (m) cm$^{-1}$; nmr $\delta$ 0.8–1.2 (m, $H_2$, $H_3$, and $H_4$), 1.25 (t, $J$ = 7.0 Hz, $OCH_2CH_3$), 1.55 (s, 2 $H_5$), 1.8–2.1 (m, $H_1$, $H_6$, and 2 $H_9$), 2.15 (broad s, $H_7$), 2.5–2.7 (m, $H_8$), and 4.05 (q, $J$ = 7.0 Hz, $OCH_2CH_3$); mass spectrum *m/e* 192 ($M^+$). *Anal.* Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.07; H, 8.61. (**7d**) Ir 3069 (w), 2964 (s), 2869 (m), 1728 (s), 1457 (w), 1387 (w), 1337 (w), 1314 (m), 1290 (m), 1248 (m), 1170 (s), 1070 (m), 1027 (w), 988 (w), and 942 (w) cm$^{-1}$; nmr $\delta$ 0.7–1.2 (m, $H_2$, $H_3$, and $H_4$), 0.98 (t, $J$ = 6.3 Hz, $CH_3$), 1.2–2.2 (m, $H_1$, $H_6$, 2 $H_9$, and $OCH_2CH_2CH_2CH_3$), 1.51 (s, 2 $H_5$), 2.2–2.3 (m, $H_7$), 2.84 (ddd, $J$ = 4.5, 4.5, and 11.0 Hz, $H_8$), and 4.04 (t, $J$ = 6.3 Hz, $OCH_2$); mass spectrum *m/e* 220 ($M^+$). *Anal.* Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.44; H, 9.16. (**8d**) Ir 3066 (w), 2958 (s), 2871 (m), 1728 (s), 1455 (w), 1349 (w), 1322 (w), 1285 (w), 1261 (w), 1241 (m), 1216 (w), 1173 (s), 1155 (s), 1066 (m), and 1022 (w) cm$^{-1}$; nmr $\delta$ 0.8–1.2 (m, $H_2$, $H_3$, and $H_4$), 0.97 (t, $J$ = 7.0 Hz, $CH_3$), 1.1–1.8 (m, $OCH_2CH_2CH_2CH_3$), 1.55 (s, 2 $H_5$), 1.8–2.1 (m, $H_1$, $H_6$, and 2 $H_9$), 2.15 (broad s, $H_7$), 2.5–2.7 (m, $H_8$), and 4.00 (t, $J$ = 7.0 Hz, $OCH_2$); mass spectrum *m/e* 220 ($M^+$). *Anal.* Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.27; H, 9.14. (**7e**) Ir 3065 (w), 2980 (s), 2940 (s), 2870 (m), 1726 (s), 1476 (w), 1458 (w), 1395 (w), 1370 (m), 1318 (w), 1292 (w), 1250 (w), 1214 (w), 1155 (s), 1070 (w), and 853 (w) cm$^{-1}$; nmr $\delta$ 1.8–2.2 (m, $H_2$, $H_3$, and $H_4$), 1.45 (s, 3 $CH_3$), 1.50 (s, 2 $H_5$), 1.5–2.1 (m, $H_1$, $H_6$, and 2 $H_9$), 2.1–2.3 (m, $H_7$), and 2.78 (ddd, $J$ = 4.5, 4.5, and 11.0 Hz, $H_8$); mass spectrum *m/e* 220 ($M^+$). *Anal.* Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.57; H, 9.00. (**8e**) Ir 3066 (w), 2943 (s), 2870 (m), 1724 (s), 1455 (w), 1390 (w), 1370 (s), 1326 (w), 1287 (w), 1244 (w), 1220 (w), 1150 (s), 1016 (w), and 849 (w) cm$^{-1}$; nmr $\delta$ 0.8–1.2 (m, $H_2$, $H_3$, and $H_4$), 1.50 (s, 3 $CH_3$), 1.60 (s, 2 $H_5$), 1.7–2.2 (m, $H_1$, $H_6$, and 2 $H_9$), 2.14 (broad s, $H_7$), and 3.63 (dd, $J$ = 5.5 and 8.5 Hz, $H_8$); mass spectrum *m/e* 220 ($M^+$). *Anal.* Calcd for $C_{14}H_{20}O_2$: C, 76.32; H, 9.15. Found: C, 76.51; H, 8.98.

**$Ni(COD)_2$-Catalyzed Reaction of 2 with Diethyl Fumarate or Maleate.** A mixture of **2** (159 mg, 1.73 mmol), diethyl fumarate (1.72 g, 10.0 mmol), and toluene (2.0 ml) was kept at 50° for 48 hr, and the mixture was worked up as described for the reaction with $Ni(AN)_2$ as the catalyst to give colorless liquid (1.82 g). Analysis by glpc indicated that **9** was formed in 6% yield. Similarly, a mixture of **2** (166 mg, 1.81 mmol), diethyl maleate (1.72 g, 10.0 mmol), and toluene (2.0 ml) was allowed to stand at 25° for 36 hr and worked up in the usual manner. Glpc analysis of the product showed that **10** and **11** were formed in 39% yield in a ratio of 95:5.

**Attempted Reaction of 5 with Methyl Acrylate in the Presence of $Ni(COD)_2$.** A solution of **5** (117 mg, 0.563 mmol) and $Ni(COD)_2$ (45.5 mg, 0.166 mmol) in degassed methyl acrylate (5.0 ml) was kept at −15° for 65 hr under argon atmosphere, and the reaction mixture was worked up as described for the isomerization of **5** in toluene. Analysis of the crude product (0.141 mg) by nmr and tlc indicated that **6** was the only product (84%). No signs of the formation of the expected 1:1 adducts were observed.

**Thermal Homo Diels–Alder Reaction of Norbornadiene (2) and Acrylic Acid Esters.** A mixture of **2** (0.92 g, 10.0 mmol), methyl acrylate (1.91 g, 22.2 mmol), and hydroquinone (10 mg) was placed in a 10-ml ampoule and degassed by three freeze–thaw cycles. The system was sealed under nitrogen, and the mixture was heated at 150° for 48 hr. Evaporation of the excess methyl acrylate left a colorless oil (1.2 g) which consisted mainly of the homo Diels–Alder reaction products. Yield of the adducts **7b** and **8b** and the product ratio were determined by glpc (column C, 125°). Similar reactions with ethyl, *n*-butyl, and *tert*-butyl acrylate were run under comparable reaction conditions, and the results are summarized in Table I. The analytical sample of each isomer was obtained by preparative glpc (column E, 140–160°).

**$Ni(COD)_2$-Catalyzed Isomerization of 1 into 2 with or without Added 2.** $Ni(COD)_2$ (27 mg, 0.1 mmol) was placed in a 10-ml ampoule, and the air was replaced by argon. To this was added toluene (3.0 ml), and the catalysts were dissolved by shaking at room temperature. The yellow solution was cooled to −60°, and 2.0 ml of a solution of **1** (175 mg, 1.90 mmol) and benzene (71 mg, 0.92 mmol) in toluene was added. The tube was sealed and allowed to stand at −15° with occasional shaking. After a specified reaction period, the system was opened, and the catalysts were decomposed by contact with air at −20° for a few minutes. The precipitates were removed by filtration through a pad of Celite 545 under slightly positive pressure of nitrogen, and the filtrate was analyzed by glpc (column A, 65°). Reactions by use of solution of $Ni(COD)_2$ (27 mg, 0.1 mmol) in toluene (3.0 ml) and 2.0 ml of a mixture of **1** (175 mg, 1.90 mmol), **2** (0.9 ml, 8.8 mmol), and benzene (73 mg, 0.94 mmol) in toluene were carried out under the strictly same reaction conditions as described above. The results are shown in Figure 4.

**$Ni(COD)_2$-Catalyzed Reaction of 1 and Methyl Acrylate with or without Added 2.** A mixture of methyl acrylate (1.0 ml, 10.8 mmol) and toluene (2.0 ml) was added to $Ni(COD)_2$ (27 mg, 0.1 mmol) in a 10-ml ampoule under argon at −40°. This mixture was warmed up to room temperature and shaken vigorously until the catalysts dissolved completely. The solution was cooled to −60° and mixed with 1.2 ml of a solution of **1** (176 mg, 1.91 mmol) and benzene (79 mg, 1.01 mmol) in toluene, and the system was sealed. After the reaction mixture had been kept at −15° for a specified time, the tube was opened, and the catalysts were decomposed by exposure to air for a few minutes. A solution of methyl laurate (14.7 mg, 0.0687 mmol, internal standard) in toluene (1.0 ml) was added to this mixture, and the solid precipitates were removed by filtration. The amount of unreacted **1** and the yields of **7b** and **8b** were determined by glpc analysis (column A, 65°, and column C, 135°). Reactions with a solution of $Ni(COD)_2$ (27 mg, 0.1 mmol) in toluene (2.0 ml) and 1.2 ml of a mixture of **1** (180 mg, 1.96 mmol), **2** (0.9 ml, 8.8 mmol), and benzene (79 mg, 1.01 mmol) in toluene were run under conditions comparable to those described above. The results are shown in Figures 3 and 4. The **7b**:**8b** ratio (58:42) did not change within the limits of experimental error throughout the reaction.

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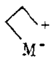

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