Nickel(0) Catalyzed [2+2] Cross-addition of Bicyclo[2.2.1]heptene Derivatives with Electron-deficient Olefins[1)]

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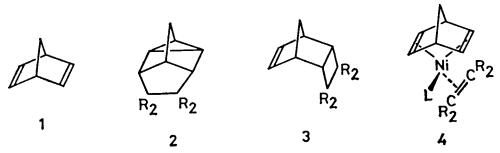
In the presence of bis(acrylonitrile)nickel(0) or bis(1,5-cyclooctadiene)nickel(0), *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene cycloadds to acrylonitrile and methyl acrylate to give *anti*- and *syn*-3-cyano-*exo*,*exo*-tetracyclo[4.3.1.$0^{2,5}$.$0^{7,9}$]-decane or the corresponding methoxycarbonyl derivatives. The cycloaddition with dimethyl maleate proceeds with retention of configuration. Benzonorbornadiene also enters into the 2+2 reaction, while *endo*-tricyclo-[3.2.1.$0^{2,4}$]oct-6-ene, bicyclo[2.2.1]heptene, and 5-methylenebicyclo[2.2.1]heptene are unreactive. Origins of the observed selectivities in the catalyzed reaction are discussed.

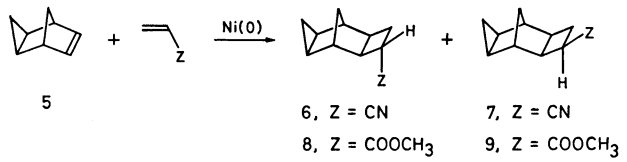
Under the influence of Ni(0) catalysts, bicyclo-[2.2.1]heptadiene (**1**), a homoconjugated diene[2)] having large strain energy (25.6 kcal/mol[3)]), undergoes a variety of cycloadditions. The diene dimerizes readily to give various regio- and stereoisomers.[4)] Reactions with acetylene and its derivatives afford different types of cycloadducts depending on the nature of the substituents.[4)] Electron-deficient olefins such as methyl acrylate, acrylonitrile, crotononitrile, and dimethyl maleate also react smoothly to yield the formal homo-Diels-Alder adducts of type **2**,[4,5)] while certain strained olefins such as methylenecyclopropane give the endo [2+2] cycloadducts of type **3** as the major product.[6,7)] The endo stereochemistry is considered as originating from the mixed ligand complex, depicted as **4**, in which the diene **1** coordinates to the Ni(0) atom as an endo bidentate ligand. This paper describes a Ni(0) catalyzed reaction of several bicyclo[2.2.1]heptene derivatives that are structurally related to the diene **1**. The principal aim was to determine how, and to what extent, the structural modification of one of the double bonds would affect the reaction course and reactivity with respect to those of the parent diene **1**.



1 2 3 4

Results and Discussion

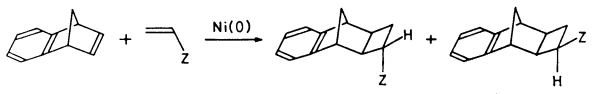
Nickel(0) Catalyzed [$_{\pi}2+_{\pi}2$] *Cross-addition.* When a solution of the cyclopropanated hydrocarbon **5** in acrylonitrile was kept at 70 °C for 120 h in the presence of a catalytic amount of bis(acrylonitrile)-nickel(0) [Ni(an)$_2$], the [2+2] cycloadducts **6** and **7** were obtained in 55% yield in a ratio of 63:37. Neither other cycloadducts nor dimeric products were obtained. Neither were rearrangement products of the starting hydrocarbon **5** detected. Similarly, the reaction of **5** with methyl acrylate (45 °C, 48 h) in the presence of bis(1,5-cyclooctadiene)nickel(0) [Ni-(cod)$_2$] gave a 78:22 mixture of **8** and **9** in 72% yield. Reaction of **5** with 1,2-disubstituted olefins proceeds more sluggishly. Dimethyl maleate and **5** in toluene



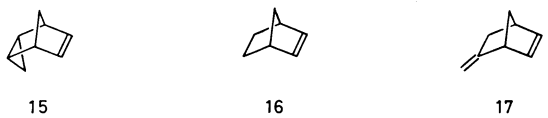
5 6, Z = CN 7, Z = CN 8, Z = $COOCH_3$ 9, Z = $COOCH_3$

10 11 Z = $COOCH_3$

in the presence of Ni(cod)$_2$ (35 °C, 72 h) afforded **10** and **11** (97:3) in 10% yield. Since dimethyl fumarate did not give any adducts under similar conditions, the origin of the production of **11** as a stereo impurity is presently unknown.[8)] The reaction of the benzo derivative **12** and methyl acrylate in the presence of Ni(cod)$_2$ afforded an 87:13 mixture of the stereoisomeric cycloadducts **13** and **14** in 34% yield. On the other hand, the endo cyclopropane isomer of **5** (**15**), bicyclo[2.2.1]heptene (**16**), and 5-methylene-bicyclo[2.2.1]heptene (**17**) gave no or very little cycloadducts with electron-deficient olefins.



12 13 14 Z = $COOCH_3$

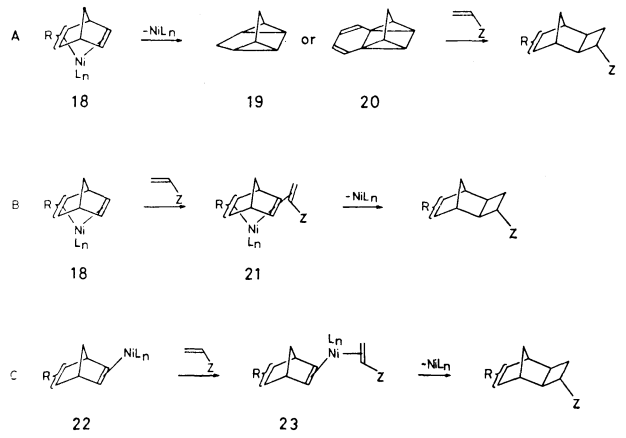


15 16 17

Thus the hydrocarbons **5** and **12** react with olefins in the presence of Ni(0) catalysts under mild reaction conditions to give formal [$2_{\pi}+2_{\pi}$] cycloadducts as the sole products. Characteristic features of these Ni(0)-catalyzed reactions include: (a) The reactions provide new examples of completely selective [2+2] cross-additions promoted by transition metal complexes. (b) The reactions afford only exo adducts, in contrast with the reaction of **1** with methylenecyclopropane

which produced endo adducts as the major products.[6] (c) The cycloaddition proceeds with a high degree of stereospecificity concerning the electron-deficient olefinic substrates. (d) The reactivities of the bicyclo-[2.2.1]heptenes are highly sensitive to the structural change at the site remote from the reacting double bond.

Possible Reaction Paths. Three paths, A, B, and C, may be conceivable "*a priori*" as possible mechanisms which are consistent with the characteristics of the reactions (Scheme 1). The first two, A and



Scheme 1.

B, involve the coordination complex **18** where the strained hydrocarbon is acting as an endo bidentate ligand.[9,10] Thus path A assumes initial metal catalyzed skeletal change of **18** to **19**[11] or **20** and subsequent uncatalyzed, symmetry-allowed [$_{\sigma}2+_{\sigma}2+_{\pi}2$] cycloaddition,[12,13] whereas path B involves the donor-acceptor complex **21** in which the electron-deficient olefin is interacting with the bicycloheptene double bond from the side opposite the coordinated metal atom.[14] Reaction *via* path C goes through the metal complexes **22** and **23** in which the strained olefin binds to the Ni(0) atom as an exo unidentate ligand.

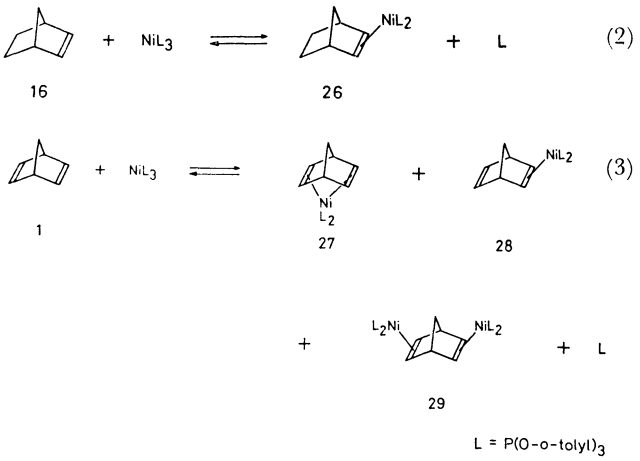
Operation of the path A could be readily dismissed on the basis of the following experiments. Gas chromatographic analysis of the reaction mixture of **5** with methyl acrylate did not indicate the presence of **19**. Moreover, when separately prepared **19**[11] was exposed to the Ni(0) catalyst in methyl acrylate, no traces of cycloadducts **8** and **9** were formed; the compound **19** was recovered unchanged.

Elucidation of the Mode in the Coordination of the Strained Olefins to Nickel(0) Complex. In order to differentiate the remaining two possibilities, B and C, the mode of coordination of the initial strained olefins to the Ni(0) atom was examined by Tolman's method. An olefinic substrate and a Ni(0) complex are known to exist in equilibrium as depicted in Eq. 1.[15]

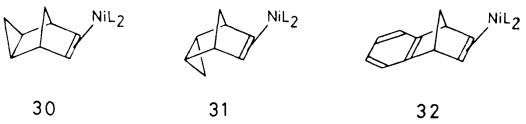
$$\underset{\mathbf{24}}{\text{Olefin}} + \text{NiL}_3 \rightleftharpoons \underset{\mathbf{25}}{\text{(olefin)NiL}_2} + \text{L} \qquad (1)$$

$$\text{L} = \text{P(O-}o\text{-tolyl)}_3$$

A monoolefin of an appropriate concentration reacts with Ni[P(O-*o*-tolyl)$_3$]$_3$ to give a single 1:1 complex **25**. whose electronic spectrum exhibits an absorption maximum around 350 nm and a shoulder near 400 nm irrespective of the structure of the olefins. Thus two isosbestic points are to be observed when the spectra are taken at various concentration of olefins. The compound **16** presents a typical example (Eq. 2 and Fig. 1). On the other hand, the diene **1** exhibited the complex spectra shown in Fig. 2, where no absorption maxima were observed over the range 300—550 nm. This is ascribed to the fact that **1** acts as both an endo bidentate and an exo unidentate ligand to give a mixture of **27**—**29** (Eq. 3).[15] The



hydrocarbons **5**, **12**, and **15** displayed spectroscopic behavior quite similar to that observed for the monoolefin **16** (Figs. 3, 4, and 5), which indicates that these strained hydrocarbons coordinate to Ni(0) atom as exo unidentate ligands to give complexes **30**—**32**. Although the structure and properties of the complex **24** are different from those of the catalysts employed



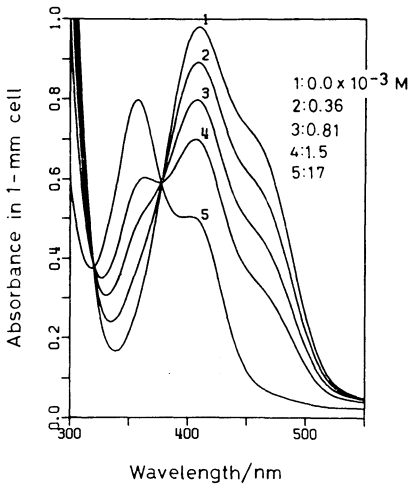


Fig. 1. Electronic spectra of benzene solution containing 1.94×10^{-3} M (1 M = 1 mol dm^{-3}) of Ni[P(O-*o*-tolyl)$_3$]$_3$ and increasing concentration of **16** at 24 °C.

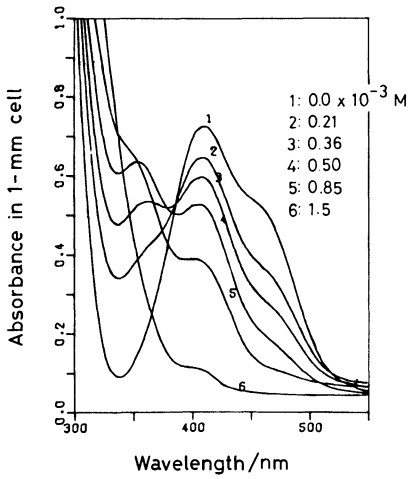


Fig. 2. Electronic spectra of benzene solution containing 1.32×10^{-3} M of Ni[P(O-*o*-tolyl)$_3$]$_3$ and increasing concentration of **1** at 24 °C.

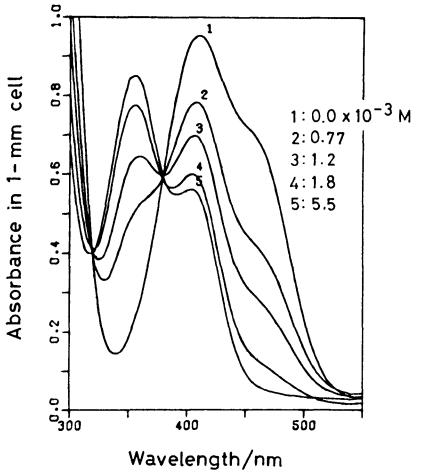


Fig. 3. Electronic spectra of benzene solution containing 1.78×10^{-3} M of Ni[P(O-*o*-toly)$_3$]$_3$ and increasing concentration of **5** at 24 °C.

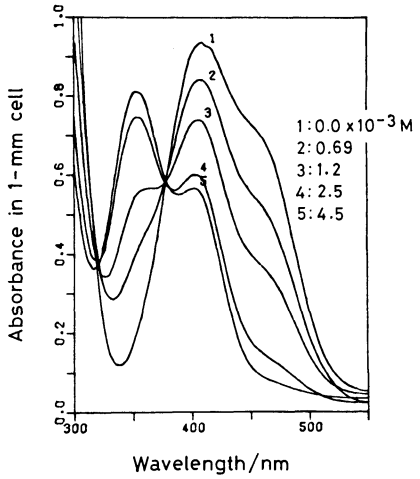


Fig. 4. Electronic spectra of benzene solution containing 1.83×10^{-3} M of Ni[P(O-*o*-toly)$_3$]$_3$ and increasing concentration of **15** at 24 °C.

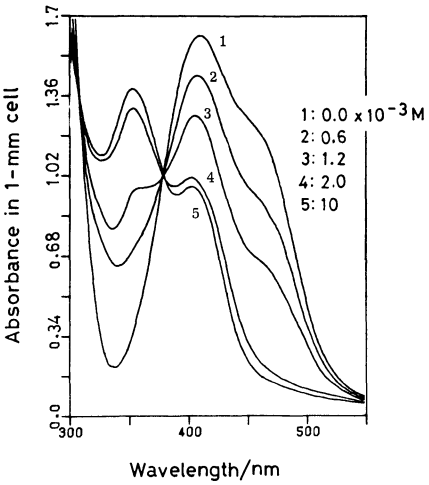


Fig. 5. Electronic spectra of benzene solution containing 1.93×10^{-3} M of Ni[P(O-*o*-tolyl)$_3$]$_3$ and increasing concentration of **12** at 24 °C.

in the actual catalytic reactions, these results strongly suggest that complexes of a similar type play an important role in the present catalytic reactions. Thus path C is thought to be most probable.

Determination of the Equilibrium Constant of the Complex Formation. Based on the electronic spectra (Figs. 1—5) of the mixtures of the complex **24** and the strained olefins, the equilibrium constants of the complex formation at 24 °C were calculated following Tolman's procedure.[15] The results are summarized in Table 1.

Reactivity of the Strained Olefins. The rate of the reaction of the strained olefins with methyl acrylate catalyzed by Ni(cod)$_2$ was measured at 40 °C. The results are listed in Table 1. The relative reactivities decrease in the order **5**>**12**>**15**. The competition experiments using **5** and **15** at 40 °C showed that the presence of varying amounts of **15** does not affect the reactivity of **5**.

Homoconjugation in the Olefinic Substrates. The existence of homoconjugation in **1**,[2] **5**,[2b] and **12**[2c] has been well-established mainly on the basis of photoelectron and charge-transfer spectra. The influence

TABLE 1. EQUILIBRIUM CONSTANTS FOR [olefin + $NiL_3 \rightleftharpoons$ (olefin)NiL_2 + L] IN BENZENE AT 24 °C

Olefin	K[a]	Relative reactivity
1-Hexene	0.32±0.04	—
16	3.8±0.5	≈0
15	10.3±0.1	≈0
5	30±6	1.6—2.4
12	320±30	1.0
1	—[b]	—

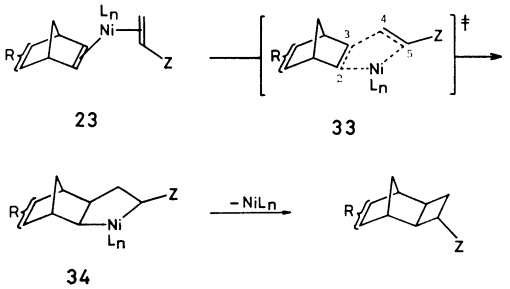
a) K=[(olefin)NiL_2][L]/[olefin][NiL_3]. b) Very large.

of stereoelectronic factors on the degree of these through-space interactions are considerable. In exo derivative **5**, there is substantial homoconjugation which arises from the direct overlap between the π-orbital of the double bond and the Walsh-orbital of the cyclopropane ring. On the other hand, the cyclopropane ring of the endo isomer **15** does not participate

in the cyclic homoconjugation with the double bond.[2b] The extent of the homoconjugative interaction decreases in the order **1**>**12**>**5**≫**15**.

Discussion. It should be emphasized that in these catalytic reactions the benzene ring or cyclopropane rings which are located remote from the reacting carbon–carbon double bond exert definitive influences on the reactivities of the strained hydrocarbons. In certain cases the reactivities of the strained olefinic hydrocarbons can be gauged from the strain energies of these hydrocarbons.[16] There is no appreciable difference in strain energies between these hydrocarbons, because the carbocyclic frameworks are quite similar to each other. Further, as can be seen from the values of equilibrium constants and the results of competitive experiments, there no good correlation seems to exist between the reactivity and the coordination ability of the strained olefins with the Ni(0) atom. For instance, the compound **12** has a large equilibrium constant, but is less reactive than **5**. The exo cyclopropane derivative **5** has an equilibrium constant only three times larger than that of the endo isomer **15**, but only the former compound reacts with methyl acrylate.

The present catalytic reactions can be considered to proceed in a stepwise manner with the initial formation of a transitory five-membered metallacycle **34** as outlined in Scheme 2.[17,18] The observed structure-reactivity relationship leads us to consider that the cyclic homoconjugation between the double bond and cyclopropane or the benzene ring exerts a great influence on lowering the energy of the transition state **33** which gives rise to the metallacyclopentane intermediate **34**. MO considerations are consistent with this assumption; the cyclic homoconjugation in bicyclo[2.2.1]heptene system reduces the bond order of the C=C bond and consequently increases the free valency of C_2 and C_3. This effect facilitates the bonding interaction between C_2 and Ni, and C_3 and C_4, which results in lowering the transition state energy. If the formation of **34** *via* **33** is the rate-determining step, such effects are conceived to determine the reactivity of the strained olefins in the present catalysis.[19]



Scheme 2.

Experimental

General. The nuclear magnetic resonance (NMR) spectra were recorded either on a Varian HA-100D (100 MHz) or a JEOL JNM-FX 100 (100 MHz, FT-NMR) spectrometer. Chemical shifts were indicated as parts per million down field from tetramethylsilane as an internal standard. Singlet, doublet, triplet, and multiplet are abbreviated to s, d, t, and m. Infrared (IR) spectra were taken on a JASCO Model DS-402G spectrophotometer in carbon tetrachloride. Analytical gas chromatography (GLC) was done on Hitachi Model 063 instrument equipped with a flame ionization detector using nitrogen as the carrier gas. Preparative gas chromatography was performed on a Varian Model 1700 instrument using helium as the carrier gas. The columns used follow: A, 3 mm×2 m 10% Silicone DCQF-1 on 100—120 mesh Chromosorb W AW; B, 10 mm× 3 m 10% Silicone DCQF-1 on 100—120 mesh Neosorb; C, 3 mm×2 m 10% Silicone DCQF-1 on 100—120 mesh Neopak 1A; D, 1/8 inch×4 m 10% Silicone DCQF-1 on 80—100 mesh Chromosorb W AW; E, 3 mm×2 m 5% poly(ethylene glycol) 20M on 80—100 mesh Chromosorb G NAW. The visible spectra were recorded on a Hitachi Model 323 spectrometer using a 1-mm cell equipped with a serum cap. Low-resolution mass spectra were obtained at 70 eV on Hitachi Model RMU-6C instrument. High resolution mass spectra were taken on a JEOL JMS-D300 spectrometer equipped with JMA-2000 mass data analysis system. Analytical thin layer chromatography (TLC) was done on E. Merck Kieselgel PF_{254} precoated plates (0.25-mm layers). Preparative TLC separation was performed using 20 cm×20 cm glass plates coated with a 1.0-mm thick layer of E. Merck Kieselgel PF_{254}. The positions of spots were visualized by exposure to iodine vapor or a spray of a solution of Cerium(IV) sulfate in 1 mol dm^{-3} H_2SO_4 followed by heating on a hot plate.

Materials. Guaranteed grade 1-hexene and benzene for spectrometry, and reagent grade methyl acrylate, acrylonitrile, acetonitrile, diethyl ether, and hexane for handling air-sensitive metal complexes were distilled under argon over powdered calcium hydride and stored in Schlenk tubes under argon. E. Merck norbornadiene and norbornene were distilled over calcium hydride and stored in the presence of a small amount of hydroquinone. Other reagent grade solvents and reagents were distilled before use.

Ni(an)$_2$-catalyzed Reaction of ***5*** *and Acrylonitrile.* $Ni(an)_2$ was prepared in a glass ampoule from $Ni(CO)_4$ (34.0 mg, 0.20 mmol) and acrylonitrile (2.5 ml) by the literature procedure[20] and to this was added a solution of **5**[21] (240 mg, 2.26 mmol) in acrylonitrile (1.5 g, 28 mmol). The tube was sealed under argon and the mixture was kept at 70 °C for 120 h. After addition of dichloromethane (20 ml) to the reaction mixture, the nickel complex was decomposed by air. The resulting precipitates were removed by filtration through Celite 545 and the filtrate was evaporated to give a colorless oil. Fractional distillation by Kugelrohr afforded a mixture of *anti*-3-cyano-*exo*,*exo*-tetracyclo[4.3.1.-$0^{2,5}.0^{7,9}$]decane (**6**) and its syn isomer **7** (210 mg, 55% combined yield), bp 90—100 °C (3 mmHg††). No other products were detected by TLC analysis (R_f 3.9, **6**, and **7** unseparable, hexane–ether 10:1). GLC analysis (column A, 150 °C) indicated that **6** (t_R 25.6 min) and **7** (t_R 28.8 min) produced in a ratio of 63:37. Analytical samples of **6** and **7** were obtained by preparative GLC (column B, 180 °C). Spectral and analytical data of the products follow: **6**: IR 2235 cm^{-1} (CN); NMR δ 0.00 (dt, $J_{8a,8s}=J_{8a,7}=J_{8a,9}=7.0$ Hz, H_{8a}), 0.38 (dt, $J_{8s,7}=J_{8s,9}=3.0$ Hz, H_{8s}), 0.59 (dd, H_7, H_9), 0.97 (A part of ABq, $J_{10s,10a}=12.0$ Hz, H_{10s}), 1.12 (B part of ABq, H_{10a}), 1.6—2.0 (m, H_5), 2.13 (broad s, H_6), 2.26 (broad s, H_1), 2.3—2.7 (m, H_2, H_3, $2H_4$). Mass spectrum *m/e* 158 (M^+-1). Found: C, 82.76; H, 8.13; N, 8.58%. Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80%. **7**: IR 2230

†† 1 mmHg≈133.322 Pa.

cm^{-1} (CN); NMR δ −0.03 (dt, $J_{8a,8s}$=8.0 Hz, $J_{8a,7}$=$J_{8a,9}$=6.5 Hz, H_{8a}), 0.44 (dt, $J_{8s,7}$=$J_{8s,9}$=3.0 Hz, H_{8s}), 0.55 (dd, H_7, H_9), 1.09 (A part of ABq, $J_{10s,10a}$=13.0 Hz, H_{10s}), 1.62 (B part of ABq, H_{10a}), 1.6—1.9 (m, H_5), 2.12 (broad s, H_1), 2.2—2.6 (m, H_2, $2H_4$, H_6), 3.0—3.4 (m, H_{3n}). Mass spectrum *m/e* 158 (M^+-1). Found: C, 83.14; H, 8.25; N, 8.61%. Calcd for $C_{11}H_{13}N$: C, 82.97; H, 8.23; N, 8.80%.

Preparation of the Authentic Samples of ***6*** *and* ***7***. *anti*- and *syn*-3-cyano-*exo*-tricyclo[4.2.1.0^{2,5}]oct-7-ene (**35**) and (**36**) were prepared by the application of the reported procedure.[12] In a 20-ml reaction ampoule were placed quadricyclane (500 mg, 5.43 mmol), acrylonitrile (3.0 ml), and hydroquinone (3 mg) and the tube was sealed under argon. The mixture was kept at 95 °C for 72 h. Distillation of the reaction mixture *in vacuo* afforded a mixture of **35** and **36** (700 mg, 92%). GLC analysis (column C, 140 °C) indicated that **35** (t_R 14.0 min) and **36** (t_R 12.0 min) were produced in 33:67. Pure samples of the adducts were obtained by GLC purification (column D, 130 °C). Spectral properties of **35** and **36** follow: **35**: NMR ($CDCl_3$) δ 1.40 (d, $J_{9a,9s}$=10.0 Hz, H_{9a}), 1.59 (d, H_{9s}), 2.71 (broad s, H_6), 2.80 (broad s, H_1), 5.99 (m, H_7, H_8), 1.2—2.6 (m, other protons). High resolution mass spectrum. Found: *m/e* 145.087. Calcd for $C_{10}H_{11}N$: *m/e* 145.089. **36**: NMR ($CDCl_3$) δ 1.49 (d, $J_{9s,9a}$=10.0 Hz, H_{9s}), 2.02 (d, H_{9a}), 2.73 (broad s, H_6), 2.98 (broad s, H_1), 3.0—3.4 (m, H_{3n}), 6.01 (broad s, H_7, H_8), 1.5—2.7 (m, other protons). High resolution mass spectrum. Found: *m/e* 145.090. Calcd for $C_{10}H_{11}N$: *m/e* 145.089. Conversion of **35** to **6** was performed by the cyclopropanation by gaseous diazomethane catalyzed by bis[*N*-(1-phenylethyl)salicylideneaminato]copper(II).[22] Purification by GLC (column B, 180 °C) gave pure sample of **6**. Compound **7** was obtained from **36** by the similar procedure. NMR and mass spectra of the authentic samples were superimposable on those of **6** and **7** obtained by metal catalysis.

Ni(cod)$_2$-catalyzed Reaction of ***5*** *and Methyl Acrylate.* In a 30-ml glass ampoule equipped with a serum cap was placed $Ni(cod)_2$[23] (1.50 g, 5.51 mmol) under argon and to this was added **5** (1.06 g, 10.0 mmol) and methyl acrylate (10.0 ml) with a syringe. The reaction tube was sealed under argon and kept at 45 °C for 72 h. After opening the tube dichloromethane (20 ml) was added to the mixture and air was bubbled gently for 2 h to decompose the nickel complex. The resulting black precipitates were filtered off by passage through a short column packed with Celite 545. The filtrate was concentrated and the residue was analyzed by GLC (column A, 150 °C) indicating that essentially two products *anti*-3-methoxycarbonyl-*exo*,*exo*-tetracyclo[4.3.1.0^{2,5}.0^{7,9}]decane (**8**) (t_R 15.3 min) and its syn isomer **9** (t_R 14.2 min) were produced in a ratio of 78:22. Distillation by Kugelrohr (1 mm, 150 °C) gave a mixture of **8** and **9** (1.46 g, 72% yield). Analytical samples of **8** and **9** were obtained by preparative GLC separation (column B, 180 °C). The structures of **8** and **9** were determined by the comparison of their spectral data with those of authentic samples prepared as follows. A mixture of **35** and **36** (20 g, 0.138 mol) and KOH (15 g, 0.21 mol) in 80% aqueous ethylene glycol was kept at 140 °C for 12 h. The reaction mixture was acidified by HCl and the resulting carboxylic acid was taken up into ether. Esterification by adding a solution of diazomethane in ether to the acid afforded a mixture of *anti*- and *syn*-3-methoxycarbonyl-*exo*-tricyclo[4.2.1.0^{2,5}]oct-7-enes (16.4 g, 67%). The ester (5.6 g, 31.5 mmol) was cyclopropanated by the reported procedure[22] to give a mixture of **8** and **9** (4.0 g, 66%). Separation by preparative GLC (column B, 180 °C) gave pure samples of **8** and **9**. The stereochemistry of the ester groups was determined on the basis of the NMR spectra taken in the presence of $Eu(fod)_3$. Physical properties of **8**: IR 1735 cm^{-1} (C=O); NMR δ −0.06 (dt, $J_{8a,8s}$=$J_{8a,7}$=$J_{8a,9}$=7.0 Hz, H_{8a}), 0.36 (dt, $J_{8s,7}$=$J_{8s,9}$=3.0 Hz, H_{8s}), 0.56 (dd, H_7, H_9), 0.93 (A part of ABq, $J_{10s,10a}$=12.0 Hz, H_{10s}), 1.22 (B part of ABq, H_{10a}), 1.5—1.8 (m, H_5), 2.09 (broad s, H_6), 2.18 (broad s, H_1), 2.2—2.6 (m, H_2, H_3, $2H_4$), 3.61 (s, OCH_3). When the $Eu(fod)_3$-induced shifts were plotted against the relative molar ratios of the shift reagent and the substrate, a linear relationship was observed. The gradients, ppm/mol of $Eu(fod)_3$ per mole of substrate, of these lines were 26.6 (OCH_3), 25.0 (H_3), 20.5 (H_{4n}), 20.0 (H_2), 10.0 (H_5), 7.8 (H_{4x}), 6.1 (H_1), 6.1 (H_{10a}), 3.8 (H_6), 3.3 (H_{10s}). Values for cyclopropane protons could not be determined. Mass spectrum *m/e* 192 (M^+). Found: C, 75.04; H, 8.32%. Calcd for $C_{12}H_{16}O_2$: C, 74.97, H, 8.39%. Physical properties of **9**: IR 1738 cm^{-1} (C=O); NMR δ −0.11 (dt, $J_{8a,8s}$=$J_{8a,7}$=$J_{8a,9}$=7.0 Hz, H_{8a}), 0.31 (dt, $J_{8s,7}$=$J_{8s,9}$=3.0 Hz, H_{8s}), 0.50 (dd, H_7, H_9), 0.78 (A part of ABq, $J_{10s,10a}$=12.0 Hz, H_{10s}), 1.22 (B part of ABq, H_{10a}), 2.07 (broad s, H_6), 1.8—2.6 (m, H_2, $2H_4$, H_5), 3.0—3.4 (m, H_{3n}), 3.60 (s, OCH_3). The gradients of the lines derived from the $Eu(fod)_3$-induced spectra were 19.5 (OCH_3), 20.2 (H_{10a}), 14.6 (H_1), 12.3 (H_{4x}), 9.9 (H_2), 7.8 (H_{4n}), 6.0 (H_{10s}), 5.1 (H_5), 5.0 (H_{3n}), 3.8 (H_6). Values for cyclopropane protons could not be determined. Mass spectrum *m/e* 192 (M^+). Found: C, 75.06; H, 8.33%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

Ni(cod)$_2$-catalyzed Reaction of ***5*** *and Dimethyl Maleate.* In a 10-ml reaction ampoule was placed $Ni(cod)_2$ (50 mg, 0.18 mmol) under argon and to this was added at −60 °C, a mixture of **5** (110 mg, 1.04 mmol), dimethyl maleate (710 mg, 4.87 mmol), and toluene (1.8 ml). The reaction tube was sealed and dipped in a water-bath kept at 30 °C for 72 h. The colorless oil obtained after the usual work-up was analyzed by GLC (column C, 175 °C) indicating that the adducts *anti*,*anti*-3,4-bis(methoxycarbonyl)-*exo*,*exo*-tetracyclo[4.3.1.0^{2,5}.0^{7,9}]decane (**10**) (t_R 21.0 min) and its *anti*,*syn*-isomer **11** (t_R 14.0 min) were produced in 10 and 0.3% yields respectively. The GLC analysis also revealed that the recovered diester consisted of dimethyl maleate (30%) and dimethyl fumarate (70%). Pure samples of **10** and **11** (mp 81.0—81.5 °C) were isolated by preparative GLC (column B, 200 °C). Spectral properties of **10**: IR 1740 cm^{-1} (C=O); NMR (benzene as a lock signal): δ −0.02 (dt, $J_{8a,8s}$=$J_{8a,7}$=$J_{8a,9}$=7 Hz, H_{8a}), 0.36 (dt, $J_{8s,7}$=$J_{8s,9}$=3 Hz, H_{8s}), 0.60 (dd, H_7, H_9), 0.93 (A part of ABq, $J_{10s,10a}$=12 Hz, H_{10s}), 0.99 (B part of ABq, H_{10a}), 2.16 (broad s, H_1, H_6), 2.64 (broad s, H_2, H_5), 2.5—2.8 (m, H_3, H_4), 3.57 (s, $2OCH_3$); mass spectrum *m/e* 250 (M^+). Found: C, 67.17; H, 7.35%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.23%. Spectral properties of **11**: IR 1734 cm^{-1} (C=O); NMR (benzene as a lock signal): δ −0.07 (dt, $J_{8a,8s}$=$J_{8a,7}$=$J_{8a,9}$=7 Hz, H_{8a}), 0.34 (dt, $J_{8s,7}$=$J_{8s,9}$=3 Hz, H_{8s}), 0.53 (dd, H_7, H_9), 0.70 (A part of ABq, $J_{10s,10a}$=13 Hz, H_{10s}), 1.11 (B part of ABq, H_{10a}), 2.24 (broad s, H_6), 2.32 (broad s, H_1), 2.1—2.6 (m, H_2, H_3, H_5), 2.95 (dd, J=4 Hz, J'=7 Hz, H_4), 3.58 (s, OCH_3), 3.60 (s, OCH_3); mass spectrum *m/e* 250 (M^+). Found: C, 66.93; H, 7.27%. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.23%. The authentic samples of **10** and **11** were prepared by the cyclopropanation[22] of *anti*,*anti*- and *anti*,*syn*-3,4-bis(methoxycarbonyl)-*exo*-tricyclo[4.2.1.0^{2,5}]oct-7-ene,[12] respectively. NMR and IR spectra as well as GLC behavior of **10** and **11** were identical with those of authentic samples.

Attempted Ni(cod)$_2$-catalyzed Reaction of ***5*** *with Dimethyl Fumarate.* To $Ni(cod)_2$ (46 mg, 0.17 mmol) placed in

a 10-ml reaction ampoule was added a mixture of **5** (117 mg, 1.10 mmol), dimethyl fumarate (287 mg, 1.99 mmol), and toluene (3.0 ml) at −60 °C under argon. The reaction tube was sealed and kept at 30 °C for 72 h with occasional shaking. The reaction mixture was worked up as usual and analyzed by GLC (column C, 175 °C), indicating that no 1:1 adducts were formed.

*Ni(cod)$_2$-catalyzed Reaction of Benzonorbornadiene (**12**) and Methyl Acrylate.* In a 10-ml reaction ampoule equipped with a serum cap was placed Ni(cod)$_2$ (270 mg, 0.99 mmol) and the system was flushed with argon. To this was added a mixture of degassed **12**[24] (250 mg, 1.76 mmol) and methyl acrylate (3.0 ml) with a hypodermic syringe. The reaction tube was sealed and the mixture was kept at 40 °C for 5 d. After opening the tube, the remaining nickel complex was decomposed by introduction of a gentle stream of air. The solid substance was removed by filtration and evaporation of methyl acrylate under reduced pressure gave 460 mg of a colorless oil. Distillation *in vacuo* (160 °C (0.1 mm)) afforded a mixture of *anti*-3-methoxycarbonyl-7,8-benzo-*exo*-tricyclo[4.2.1.0^{2,5}]non-7-ene (**13**) and its syn isomer **14** (130 mg, 32%). GLC analysis (column A, 200 °C) indicated that **13** (t_R 5.4 min) and **14** (t_R 4.9 min) were produced in 80:20 ratio. No distinct coupling between H_1 and H_3, and H_5 and H_6 were observed in NMR spectra of **13** and **14**, which support the exo fusion of cyclobutane rings in these products. The stereochemistries of the ester groups were determined on the basis of the Eu(fod)$_3$-aided NMR spectra. Spectral properties of **13**: IR 1734 cm^{-1} (C=O); NMR δ 1.78 (A part of ABq, $J_{9s,9a}$=10.0 Hz, H_{9s}), 1.6—2.7 (m, H_2, H_3, $2H_4$, H_5), 2.12 (B part of ABq, H_{9a}), 3.13 (broad s, H_6), 3.22 (broad s, H_1), 3.62 (s, OCH_3), 6.8—7.2 (m, aromatic protons). The gradients of the lines derived from the Eu(fod)$_3$-induced spectra were 11.8 (OCH_3), 12.7 (H_3), 11.0 (H_{4n}), 9.7 (H_2), 5.1 (H_{4x}), 3.6 (H_5), 3.0 (H_1), 3.0 (H_{9a}), 1.6 (H_{9s}), 1.5 (H_6). Mass spectrum *m/e* 228 (M^+). Found: C, 79.01; H, 7.02%. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06%. Spectral properties of **14**: IR 1737 cm^{-1} (C=O); NMR δ 1.62 (A part of ABq, $J_{9s,9a}$=11.0 Hz, H_{9s}), 1.9—2.6 (m, H_2, $2H_4$, H_5, H_{9a}), 3.0—3.5 (m, H_3), 3.12 (broad s, H_6), 3.32 (broad s, H_1), 3.69 (s, OCH_3), 6.8—7.2 (m, aromatic protons). High resolution mass spectrum. Found: *m/e* 228.1146. Calcd for $C_{15}H_{16}O_2$: *m/e* 228.1150.

*Attempted Ni(cod)$_2$-catalyzed Reaction of **15** and Methyl Acrylate.* Ni(cod)$_2$ (380 mg, 1.38 mmol) was placed in a 20-ml reaction ampoule under argon and the tube was cooled to −70 °C in a Dry Ice–methanol bath. To this was added a solution of **15** (0.56 g, 5.28 mmol) in methyl acrylate (5.0 ml). The sealed reaction tube was kept at 45 °C for 48 h. After decomposition and removal of the resulting precipitates the reaction mixture was analyzed by GLC (column A, 140 °C) indicating that no 1:1 adducts were formed.

*Attempted Ni(cod)$_2$-catalyzed Reaction of **16** with Methyl Acrylate.* In a 10-ml glass ampoule was placed Ni(cod)$_2$ (60 mg, 0.22 mmol) under argon. Then a solution of **16** (100 mg, 1.06 mmol) in methyl acrylate (2.0 ml) was added to this and the tube was sealed. The mixture was kept at 45 °C for 48 h. After opening the tube and addition of dichloromethane (2.0 ml) the catalyst was decomposed by the introduction of a gentle stream of air. Black precipitates were filtered off through a pad of Celite 545 and the filtrate was analyzed by GLC (column A, 140 °C), which revealed that no 1:1 addition compounds were produced.

*Attempted Ni(cod)$_2$-catalyzed Reaction of **17**.* A solution of **17**[25] (56 mg, 0.53 mmol) in methyl acrylate (2.0 ml) was added to Ni(cod)$_2$ (100 mg, 0.37 mmol) placed in a 10-ml reaction ampoule under argon. The yellow solution was kept at room temperature for 20 h and then at 50 °C for 12 h. After the usual work-up, the reaction mixture was analyzed by GLC (column A, 140 °C). No products were detected.

*Comparison of the Reactivities of **5** and **12**.* A competition experiment was done by keeping a mixture of **5** (117 mg, 1.11 mmol), **12** (153 mg, 1.08 mmol), and Ni(cod)$_2$ (100 mg, 0.37 mmol) in methyl acrylate (3.0 ml) at 45 °C under argon. Aliquots of the reaction mixture were taken out with hypodermic syringes after appropriate time intervals and analyzed by GLC (column A, 200 °C). The ratio (**8**+**9**)/(**13**+**14**) varied from 1.6 to 2.4.

*Ni(cod)$_2$-catalyzed Reaction of **5** and Methyl Acrylate with or without Added **15**.* Solutions of Ni(cod)$_2$ (0.37 mmol) and eicosane (0.13 mmol, an internal standard for GLC analysis) in methyl acrylate (2 ml) containing varying amounts of **5** (0.13—0.64 mmol) and **15** (0.56—0 mmol) were kept at 40 °C for 22 h under argon. After the usual work-up, the reaction mixtures were analyzed by GLC (column E, 180 °C). The initial rates of reactions of **5** were calculated based on the above experiments. The results indicated that the presence of varying amounts of **15** caused little change in the reactivity of **5** (only by a factor of 1.0—1.1).

*Spectrophotometric Determination of the Modes and Equilibrium Constants of the Coordination of the Olefins **5**, **12**, and **15** on Nickel Atom.* Special precautions were necessary to get rid of oxygen for handling air-sensitive dilute solutions of the nickel(0) complexes. The olefinic compounds **1**, **5**, **12**, **15**, and **16** were distilled over CaH_2 under argon before use. The complex [P(O-*o*-tolyl)$_3$]$_3$Ni(0) (**24**)[26] was obtained by the procedure described by Tolman. All liquid materials were transferred with gas-tight syringes. The 5 mM (1 M= 1 mol dm^{-3}) benzene solution of **24** (2.0 ml) was freshly prepared just before use and was placed in a 5-ml flask equipped with a Teflon stopcock. To this was added an appropriate amount of the olefinic substrate in benzene. Finally the volume of the solution was adjusted strictly to 5 ml by adding benzene. Thus, 0.8 M solution of **24** in benzene containing variable concentrations (10^{-1} to 10^{-4} M) of strained olefins were prepared. For measurements of visible spectra these solutions were transferred into quartz cells of 1-mm path capped with rubber septa under argon by the use of a gas-tight syringe. The following procedure for determination of the equilibrium constants of the reaction of **5** and **24** is representative for all the other olefins. Visible spectra of a solution of **24** with variable concentration of **5** are shown in Fig. 3. The values of [(olefin)NiL$_2$] where L is P(O-*o*-tolyl)$_3$ were obtained from the loss of absorbance at 450 nm due to the complex **24**, and K was calculated according to the Eq. 4. To minimize the error, which becomes large when the K value is much greater than unity, appropriate amounts of the phosphite ligand were added so that the apparent K values become close to unity. Addition of phosphite ligand, however, causes the formation of NiL$_4$ species as shown in Eq. 5. Thus, the concentration of the each species in Eq. 4 was obtained at first assuming that K is zero, and then the concentration of NiL$_4$ was calculated using the reported formation constant.[15] Finally from the corrected concentration of the each species in

$$K = \frac{[(\text{olefin})\text{NiL}_2][\text{L}]}{[\text{olefin}][\text{NiL}_3]}, \quad (4)$$

$$\text{NiL}_3 + \text{L} \overset{k}{\rightleftharpoons} \text{NiL}_4, \quad (5)$$

Eq. 4, equilibrium constants were obtained (Table 1). Visible

spectra of the solution of **24** and other olefins are shown in Figs. 1, 2, 4, and 5.

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