times, after which analysis by NMR showed no detectable ≡CH.

To 0.76 g of lithium aluminum deuteride in 30 mL of refluxing tetrahydrofuran was slowly added 1.88 g of 3-chloro-1-deuterio-1-pentyne in 10 mL of tetrahydrofuran. During the addition process the product allene was allowed to slowly distill from the reaction mixture (along with some tetrahydrofuran) at 55 °C. The distillate was repeatedly washed with cold water until no tetrahydrofuran was detectable by NMR. To the final product (~0.42 g) was added 0.405 g of unlabeled ethylallene, and the resulting mixture was analyzed by mass spectrometry, giving a H_2/D_2 ratio of 0.957 ± 0.003.

Addition of Benzenethiol to a Mixture of 4 and 4-d_2. Benzenethiol (0.0337 g) was added to 0.0550 g of the mixture of 4 and 4-d_2 (H_2/D_2 ratio of 0.957 ± 0.003). The reaction mixture was placed in direct sunlight for 30 min and was then allowed to stand overnight. The unreacted allene was removed on a vacuum line and was analyzed by mass spectrometry, giving a H_2/D_2 ratio of 1.015 ± 0.012.

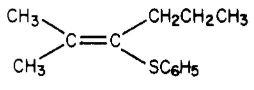
The adduct mixture was separated by preparative GLC on a 15 ft × $^3/_8$ in. Carbowax 20M on Chromosorb P column at 230 °C. The first peak, comprised of **8** and **9**, had a H_2/D_2 ratio of 0.998 ± 0.005 (corrected for P + 2 and P − 2 contributions determined with unlabeled **8**). The second peak (**7**) had a H_2/D_2 ratio of 0.922 ± 0.005, while the third peak (**10**) had a H_2/D_2 ratio of 0.893 ± 0.007.

The yields of the products were determined by a combined GLC and NMR analysis. The yields of the adducts derived from 4 and the mixture of 4 and 4-d_2 are given below the structures in Scheme I. The overall deuterium balance was within 0.1% of the starting amount of 4-d_2.

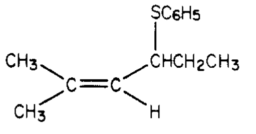
Measurement of the Relative Rates. Approximately 0.4 mmol of ethylallene and 0.4 mmol of the monoalkylallene or 1,1-dimethylallene, or 0.4 mmol of 1,1-dimethylallene and 0.4 mmol of the other di-, tri-, and tetraalkylallenes, were carefully weighed into a small reaction vessel equipped with a Minert valve (Kontes Glass Co.). Approximately 20–25 mg of pentane or heptane as an internal standard (depending on the relative GLC retention times of the allenes and the standards) was added, and the reaction vessel was carefully weighed. Several 0.15-μL samples were removed and analyzed by GLC on a 10-ft Apeizon M on Chromosorb P column at 70 °C, and the ratios of allene to internal standard were calculated. The reaction vessel was again weighed, and the initial amounts of the allenes added to the vessel were corrected for the losses incurred during the GLC analyses. Approximately 0.4 mmol of benzenethiol was added, and the reaction vessel was again carefully weighed to determine exactly the amount of the benzenethiol added. The reaction vessel was placed in direct sunlight for 30 min. Aliquots were then removed and analyzed by GLC, and the ratios of the allenes to internal standard were calculated. The changes in the allene–internal standard ratios were used to calculate the number of millimoles of each allene reacted, and the relative rates were calculated by using an iterative computer program.

Product distributions were determined from reactions carried out with pure allenes as reported in the previous paper[1] or as reported herein. Mass balance calculations agreed to within ±2% of the complete utilization of the benzenethiol.

Addition of Benzenethiol to 3-Ethyl-1,1-dimethylallene. To 53.6 mg (0.56 mmol) of the allene was added 47.4 mg (0.43 mmol) of benzenethiol. The mixture was allowed to stand in direct sunlight for 2 h, and then the excess allene was removed on a vacuum line. The NMR spectrum of the residue indicated the presence of two adducts I and II by comparison of the chemical shifts with those reported in the accompanying article for similar adducts: adduct I, NMR characteristic peaks ($CDCl_3$) δ 0.91 (t, *J* = 7.2 Hz), 1.91 and 2.02 (s, $=C(CH_3)_2$); adduct II, NMR δ 1.13 (t, *J* = 6.8 Hz), 5.97 (d, *J* = 6.9 Hz). The NMR spectrum of the mixture also contained overlapping multiplets at δ 1.56 and 2.23. Integration of the NMR spectrum indicated a ratio of I/II of 84.7:15.3. Analysis by GC/MS indicated the presence of two adducts in a ratio of 80.3:19.7. Exact mass on the mixture calcd for $C_{13}H_{18}S$ 206.113, found 206.112.

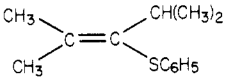


I



II

Addition of Benzenethiol to Tetramethylallene.[2] To 31.7 mg (0.33 mmol) of tetramethylallene was added 26.2 mg (0.24 mmol) of benzenethiol. The reaction mixture was allowed to stand in direct sunlight for 2 h, and then the excess unreacted allene was removed on a vacuum line. The NMR showed the presence of a single adduct having structure III:[2] NMR δ ($CDCl_3$) 1.22 (d, *J* = 6.8 Hz, 6 H), 2.32 and 2.36 (s, 3 H each), 3.81 (septet, *J* = 6.8 Hz, 1 H), 7.62 (br s, 5 H).



III

Acknowledgment. This research was supported by the National Science Foundation (Grant No. CHE77-08627).

Registry No. 1, 598-25-4; 4, 591-95-7; 3-ethyl-1,1-dimethylallene, 29212-09-7; tetramethylallene, 1000-87-9; butylallene, 2384-90-9; isobutylallene, 13865-36-6; isopropylallene, 13643-05-5; *tert*-butylallene, 26981-77-1; 1-ethyl-1-methylallene, 7417-48-3; 1-*tert*-butyl-1-methylallene, 7417-50-7; allene, 463-49-0; trimethylallene, 3043-33-2; benzenethiol, 108-98-5; deuterium, 7782-39-0.

Nickel(0)-Catalyzed Reactions of Bicyclo[2.1.0]pentane and Electron-Deficient Olefins[1,2]

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Received February 13, 1981

In the presence of a catalytic amount of bis(acrylonitrile)nickel(0), bicyclo[2.1.0]pentane suffers from the cleavage of the central σ bond and cycloadds to electron-deficient olefins such as methyl acrylate, acrylonitrile, dimethyl maleate, and dimethyl fumarate to give bicyclo[2.2.1]heptane derivatives. The stereochemistry and mechanism of the catalyzed cycloadditions have been elucidated by use of deuterated bicyclo[2.1.0]pentanes.

In connection with the activation of saturated hydrocarbons via homogeneous catalysis, we have examined reactions of various strained hydrocarbon systems which have unique steric and electronic structures.[1-4] Strained

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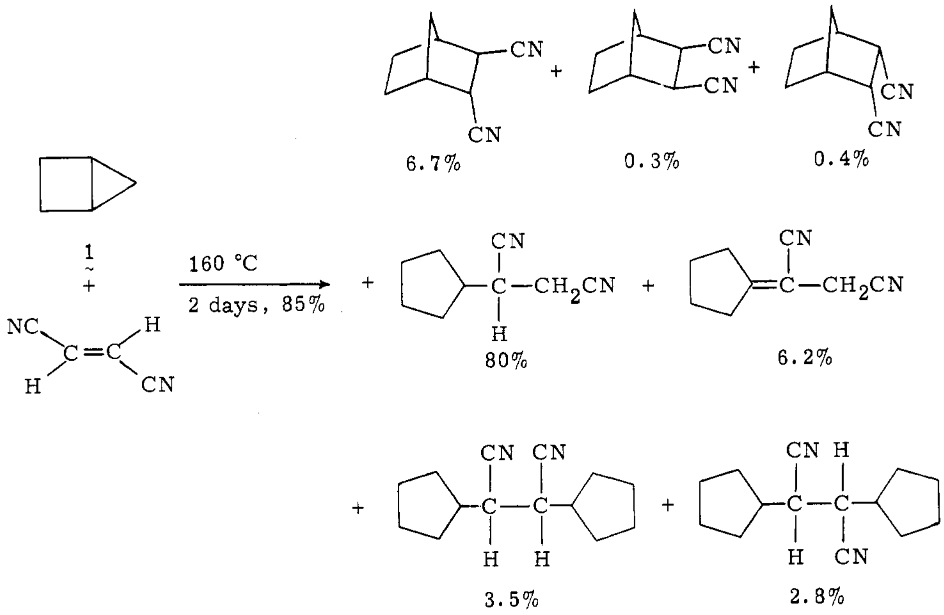
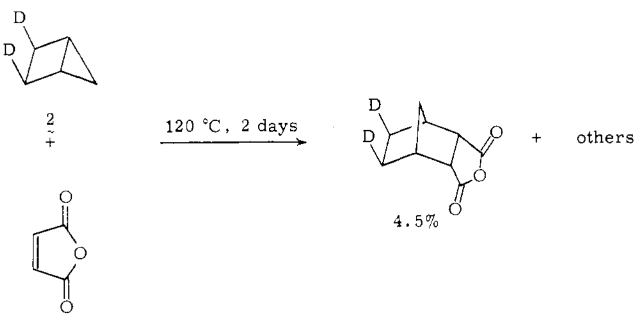
Scheme I

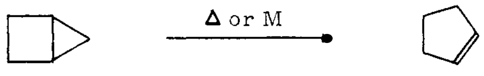


Scheme II



carbon–carbon σ bonds, though formally classified as a single bond, have considerable π bonding character, and hence information obtained with these substrates should mediate between the well-documented transition-metal chemistry of alkenes and the rather unclarified alkane chemistry.

Bicyclo[2.1.0]pentane (1) is a highly strained hydrocarbon (calculated strain energy 57 kcal/mol).[5] The central bond contains the highest strain energy and upon its cleavage ca. 50 kcal/mol of the energy is released. Despite these characteristics, the hydrocarbon is thermally stable and decomposes only at temperatures over 300 °C.[6a] The strained central σ bond, however, is kinetically labile and suffers readily attack of electrophilic reagents to form the monocyclic compounds.[7] In a continuing effort to investigate behavior of strained carbon–carbon bonds in the presence of nickel(0) complexes,[1–3,8] we have chosen this peculiar molecule as a substrate. There have been several literature reports which deal with the transition-metal-promoted reactions of 1 or its derivatives. In the presence of platinum catalysts, the parent hydrocarbon 1 undergoes a facile hydrogenolysis of the central bond giving cyclopentane.[6] Several transition-metal catalysts such as



1

Rh(I), Rh(III), Ir(I), Ir(III), Ru(III), Pt(IV), and Ag(I) complexes promote intramolecular skeletal change of the strained hydrocarbons, but they are not effective for the intermolecular reactions which form carbon to carbon bonds.[4b,9–11] On the other hand, the Ni(0) catalyst system induces facilely the intermolecular coupling reaction between the hydrocarbon and electron-deficient olefins.[2]

Throughout the investigation, we have paid particularly attention to the contrasting reaction modes between the purely thermal and transition-metal-catalyzed reactions and the origins. Characteristics of the thermal addition of the strained molecule to electron-poor olefins, studied extensively by Gassman,[12] could be summarized as follows. Scheme I illustrates as a typical example the reaction of 1 and fumaronitrile.[13] The first point to be noted is that

---

(1) Nickel-Catalyzed Reactions Involving Strained Bonds. 16. Part 15: Noyori, R.; Yamakawa, M.; Takaya, H. *Tetrahedron Lett.* **1978**, 4823.

(2) Part of this work was published in preliminary form: (a) Noyori, R.; Suzuki, T.; Takaya, H. *J. Am. Chem. Soc.* **1971**, *93*, 5896; (b) Noyori, R.; Kumagai, Y.; Takaya, H. *Ibid.* **1974**, *96*, 634.

(3) (a) Noyori, R.; Odagi, T.; Takaya, H. *J. Am. Chem. Soc.* **1970**, *92*, 5780. (b) Noyori, R.; Suzuki, T.; Kumagai, Y.; Takaya, H. *Ibid.* **1971**, *93*, 5894. (c) Noyori, R.; Kumagai, Y.; Umeda, I.; Takaya, H. *Ibid.* **1972**, *94*, 4018. (d) Noyori, R.; Umeda, I.; Takaya, H. *Chem. Lett.* **1972**, 1189. (e) Noyori, R. *Tetrahedron Lett.* **1973**, 1691. (f) Takaya, H.; Yamakawa, M.; Noyori, R. *Chem. Lett.* **1973**, 781. (g) Takaya, H.; Hayashi, N.; Ishigami, T.; Noyori, R. *Ibid.* **1973**, 813. (h) Noyori, R.; Kawauchi, H.; Takaya, H. *Tetrahedron Lett.* **1974**, 1749. (i) Noyori, R.; Umeda, I.; Kawauchi, H.; Takaya, H. *J. Am. Chem. Soc.* **1975**, *97*, 812. (j) Noyori, R.; Yamakawa, M.; Takaya, H. *Ibid.* **1976**, *98*, 1471. (k) Noyori, R.; Suzuki, T.; Kumagai, Y.; Hosoya, M.; Kawauchi, H.; Takaya, H. *J. Org. Chem.*, following paper in this issue.

(4) Reviews: (a) Mango, F. D. *Coord. Chem. Rev.* **1975**, *15*, 109; (b) Bishop, K. C., III *Chem. Rev.* **1976**, *76*, 461.

(5) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, 92, 2377.

(6) (a) Criegee, R.; Rimmelin, A. *Chem. Ber.* **1957**, *90*, 414. (b) Baldwin, J. E.; Andrews, G. D. *J. Org. Chem.* **1973**, *38*, 1063.

(7) Review: Wiberg, K. B. *Adv. Alicyclic Chem.* **1968**, *2*, 185.

(8) Noyori, R.; Ishigami, T.; Hayashi, N.; Takaya, H. *J. Am. Chem. Soc.* **1973**, *95*, 1674.

(9) Gassman, P. G.; Atkins, T. J.; Lumb, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 7757.

(10) Wiberg, K. B.; Bishop, K. C. III *Tetrahedron Lett.* **1973**, 2727.

(11) McKinney, M. A.; Chou, S. K. *Tetrahedron Lett.* **1974**, 1145. For Ag^+-catalyzed rearrangement of *anti*-tricyclo[3.1.0.0^{2,4}]hexanes, see: Wissner, A.; Meinwald, J. *J. Org. Chem.* **1973**, *38*, 1697. Ag(I)-catalyzed rearrangement of dehydronoriceane was also observed: Katsushima, T.; Yamaguchi, R.; Kawanishi, M.; Osawa, E. *J. Chem. Soc., Chem. Commun.* **1976**, 39.

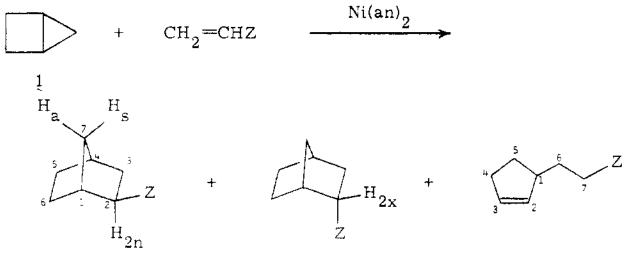
(12) Gassman, P. G. *Acc. Chem. Res.* **1971**, *4*, 128.

(13) Gassman, P. G.; Mansfield, K. T.; Murphy, T. J. *J. Am. Chem. Soc.* **1969**, *91*, 1684.

the reaction requires the forcing thermal conditions in spite of the large strain energy of the hydrocarbon substrate **1**. The second point is the poor selectivity of the reaction; the [$_{\sigma}2 + _{\pi}2$] cycloaddition is achieved in only low yields, and the monocyclic adducts are the major products.[14] The third characteristic is lack of stereospecificity in the cycloaddition; the trans olefin forms both trans and cis adducts. These would be ascribed to the orbital symmetry forbiddenness of the [2 + 2] type reaction,[15] and the operation of a multistep mechanism via diradical intermediates was suggested.[12,13] Scheme II shows the fourth, the most intriguing feature of the cycloaddition; Gassman elegantly demonstrated that maleic anhydride approaches from the end side of the bicyclo envelope of **2**, and consequently the strained molecule undergoes the reaction with inversion of stereochemistry at both angular positions.[12,13] We have discovered in this work these features of the cycloaddition are changed dramatically by the added Ni(0) catalysts.

Results and Discussion

Nickel(0)-Catalyzed Reaction of Bicyclo[2.1.0]pentane (1) with Electron-Deficient Olefins. In the presence of a Ni(0) complex and electron-poor olefins, the central σ bond of **1** was cleaved readily under mild reaction conditions. When a mixture of **1** and 5 mol % of bis(acrylonitrile)nickel(0) [Ni(an)$_2$] in acrylonitrile was heated at 70 °C for 36 h under a nitrogen atmosphere, the adducts **3** (47%), **4** (28%), and **5** (16%) were produced. The Ni(0)-promoted reaction of **1** and methyl acrylate proceeded at 40 °C and gave the adducts **6** (33%), **7** (33%), and **8** (22%). In addition, small amounts of the acrylonitrile adducts **3**–**5** were formed. The identity of these products was established by comparison with authentic samples.[16,17] The reaction of **1** with either acrylonitrile or methyl acrylate was observed only with the aid of the Ni(0) catalyst, and in the absence of the complex no reaction took place under comparable thermal conditions. Addition of triphenylphosphine (2 equiv/equiv of Ni(an)$_2$) to the reaction system retarded the catalytic coupling reactions. In the absence of the electron-deficient olefins, **1** did not undergo skeletal change even with the aid of the Ni(0) complexes such as bis(1,5-cyclooctadiene)nickel(0) and nickel carbonyl. These facts indicate that the coordination ability of **1** for nickel(0) atom is not high enough to displace the cyclooctadiene or carbonyl ligand and that the soluble, coordinatively unsaturated nickel(0) complexes bearing electron-deficient olefins are true, active catalysts for the reaction of **1**.[3f,j,18]



1

3, Z = CN

4, Z = CN

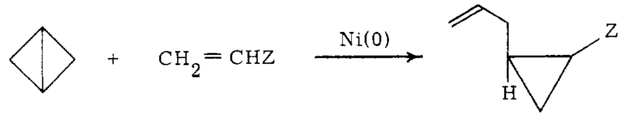
5, Z = CN

6, Z = COOCH$_3$

7, Z = COOCH$_3$

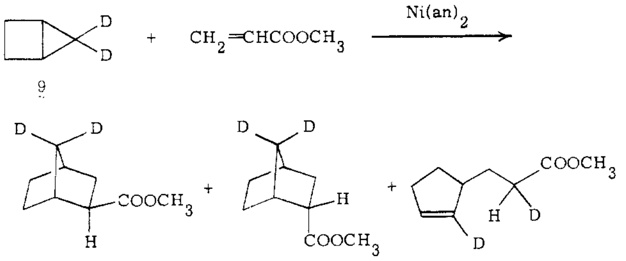
8, Z = COOCH$_3$

Apparently the strained σ bond of **1** is activated by Ni(0) catalyst and reacts with olefinic substrates under mild reaction conditions. The mode of the major reactions is viewed formally as a thermally forbidden [2 + 2] process. In addition, the yield of this type of products is increased to a great extent (66–75%) compared with the purely thermal reaction (few percent for the reaction of Scheme I). Notably, the hydrocarbon **1** experiences bond breakage only at the central σ bond and the behavior is strikingly contrasted to that of the lower homologue, bicyclo[1.1.0]butane. The latter hydrocarbon under similar catalytic conditions suffers from a geminal two-bond cleavage and couples with olefinic substrates as allylcarbene.[3b,e,k]



Z = electron-withdrawing group

In order to gain insight into the reaction pathway of the production of the cyclopentene adducts **5** or **8**, the reaction was examined with 5,5-dideuterated bicyclopentane **9**. When the catalytic reaction of **9** and methyl acrylate was carried out at 60 °C, there were obtained the 1:1 adducts **10**–**12**. The monocyclic adduct **12** gave a NMR spectrum too complicated to analyze directly. The location of deuterium atoms, however, could be clearly determined on the basis of the well-resolved spectrum taken with the added shift reagent Eu(fod)$_3$ (see the paragraph at the end of the paper about supplementary material). In going from the undeuterated adduct **8** to the dideuterio derivative **12**, the relative intensity for the ester-substituted methylene protons was reduced to half the initial value. In the absence of Eu(fod)$_3$, signals for the vinylic protons of **9** were not separated. In the presence of the shift reagent, however, the signal for the C-2 proton occurred at lower field as compared with the C-3 proton, since the former lies closer to the coordinative ester group. In the spectrum of the deuterated product **12**, the signal due to the C-3 proton occurred at the same position, but the C-2 proton signal disappeared completely. Thus this experiment provided convincing evidence that the formation of the monocyclic adduct involves a specific deuterium shift. No indication of deuterium scrambling during the reaction was provided. By comparison, Rh(I)-catalyzed reaction of the dideuterio



10 11 12

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[14] Dicyanoacetylene reacts with 1 at room temperature to give a mixture of bicyclic and monocyclic adducts.[12]

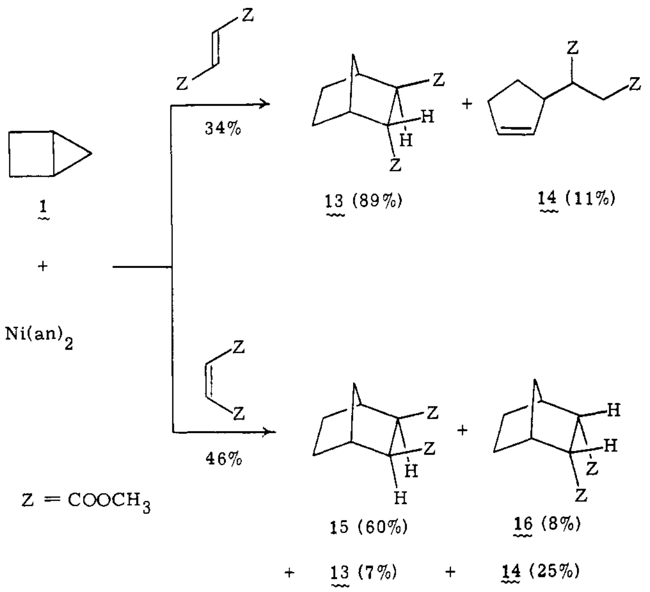
[15] Woodward, R. B.; Hoffmann, R. "The Conservation of Orbital Symmetry"; Academic Press: New York, 1970.

[16] (a) Diels, O.; Alder, K. *Justus Liebigs Ann. Chem.* **1931**, *490*, 236. (b) Alder, K.; Heimbach, K.; Reubke, R. *Chem. Ber.* **1958**, *91*, 1516.

[17] (a) Noller, C. R.; Adams, R. *J. Am. Chem. Soc.* **1926**, *48*, 2444. (b) Julia, M.; Le Goffic, F. *Bull. Soc. Chim. Fr.* **1965**, 1555.

[18] It has been well established that methyl acrylate and other electron-deficient olefins react readily with bis(1,5-cyclooctadiene)nickel or nickel carbonyl to form coordinatively unsaturated Ni(0) complexes: (a) Schrauzer, G. N. *Chem. Ber.* **1961**, *94*, 642; (b) Schrauzer, G. N. *Adv. Organomet. Chem.* **1964**, *2*, 1; (c) Ugo, R. *Coord. Chem. Rev.* **1969**, *3*, 319; (d) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350, 3360. (e) Herberhold, M. "Metal π Complexes"; Elsevier: Amsterdam, 1972; Vol. II, Part I, p 284.

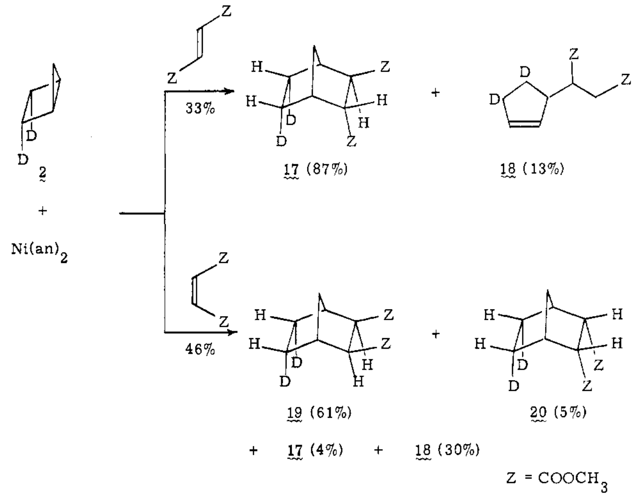
Scheme III



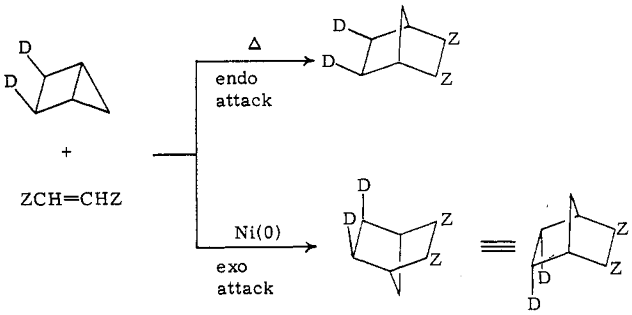
derivatives **2** and **9** is known to afford cyclopentene-d_2 in which the deuterium atoms are completely scrambled.[9] The locations of the deuterium atoms in compounds **10** and **11** were also unequivocally determined by comparison of Eu(fod)$_3$-induced NMR spectra of **10** and **11** with those of undeuterated **6** and **7** (see the paragraph at the end of the paper about supplementary material).

Stereochemical Course with Respect to the Olefinic Substrates. The stereochemistry of the cycloaddition was examined by using 1,2-disubstituted olefins having *Z* and *E* configurations. Reaction with dimethyl fumarate or maleate proceeded rather sluggishly compared with that involving monosubstituted olefins but indicated the high degree of stereospecificity of the [2 + 2] cycloaddition. The results are summarized in Scheme III. When **1** was allowed to react with dimethyl fumarate in benzene containing Ni(an)$_2$ at 60 °C for 45 h, a single cycloadduct, **13**, in which the *E* configuration of the starting olefin is retained was obtained. In addition, a small amount of the monocyclic adduct **14** was also produced. The cycloadduct **13** was identical with an authentic sample in all respects.[19] The spectral data of **14** were identical with those reported,[20] though the detailed stereochemistry (threo or erythro) is unknown. The reaction of **1** with dimethyl maleate afforded a mixture of coupling products **13–16**. Structures of **15** and **16** were substantiated by comparison with authentic specimens.[19] Compound **14** produced by this reaction was indistinguishable from that derived from **1** and dimethyl fumarate. The stereospecificity of the cycloaddition was at least 91%, as determined by the ratio (**15** + **16**)/(**13** + **15** + **16**). Unsaturated esters recovered from the reaction of **1** and maleate consisted of maleate and fumarate (97:3). Therefore, some of the stereoimpurity **13** probably arose from the fumarate formed during the catalytic reaction. It is worthwhile pointing out that in contrast to the purely thermal cycloaddition which occurs in a nonstereospecific manner (Scheme I) the present catalysis leads to a highly, though not completely, stereospecific addition.

Scheme IV



Scheme V



Stereochemical Course with Respect to Bicyclopentane Skeleton. Next, the catalytic cycloaddition was done with 2,3-*exo*,*exo*-dideuteriobicyclo[2.1.0]pentane (**2**) in order to elucidate the direction of the olefin approach to the bicyclo envelope. Scheme IV exhibits the results of the Ni(an)$_2$-catalyzed reaction of **2** and dimethyl fumarate or maleate at 60 °C. In all cycloadducts, deuterium atoms were located in the endo position of the bicyclo[2.2.1]heptane skeleton. The deuterium atom positioning was unambiguously established by comparison of their NMR spectra with those of the undeuterated and exo,-exo-dideuterated derivatives, which were prepared by palladium-catalyzed reduction of the 5,6-dehydro derivatives with H_2 or D_2, respectively[21] (see the paragraph at the end of the paper about supplementary material). Thus the stereochemistry of the Ni(0)-catalyzed cycloaddition is virtually the reverse of that encountered in the purely thermal reaction. In the absence of the transition-metal complex, electron-deficient olefins approach bicyclopentane from the endo side, and, consequently, the [2 + 2]-type cycloaddition takes place with inversion at both angular positions (Scheme V).[12,13] On the other hand, in the presence of the Ni(0) complexes the metal interacts with **1** from the exo side, and then the hydrocarbon enters into the cycloaddition without a change of the original configuration. An exo approach of the transition-metal complex has been suggested for the Rh(I)-catalyzed isomerization of bicyclopentane derivatives.[10]

Mechanism of the Catalyzed Reactions. The above-described findings would be most reasonably explained by the mechanism outlined in Scheme VI. First, the Ni(0) complex interacts with the bicyclopentane **21** at the central bond which has considerable π-bond character, giving the complex **22**. In analogy with other transition-metal catalyses,[4] oxidative addition[22] of the strained σ bond

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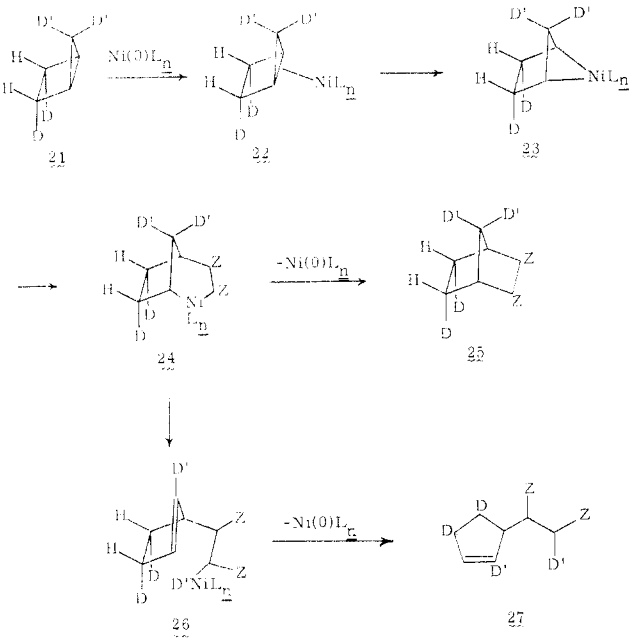
(19) Bode, H. *Ber. Dtsch. Chem. Ges.* **1937**, *70*, 1167.

(20) de Mayo, P.; Reid, S. T.; Yip, R. W. *Can. J. Chem.* **1964**, *42*, 2828.

(21) Arnold, D. R.; Trecker, D. J.; Whipple, E. B. *J. Am. Chem. Soc.* **1965**, *87*, 2596.

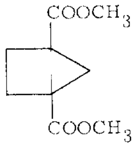
Scheme VI



to the Ni(0) atom ($d^{10} \rightarrow d^8$ conversion)[23] forms the metallabicyclic intermediate **23**.[24] Insertion of the coordinated olefin into the carbon–nickel σ bond[25] produces the new organonickel species **24**, from which the organic moiety eliminates reductively ($d^8 \rightarrow d^{10}$ conversion) to give the formal [2 + 2] cycloadduct **25**. Here the zerovalent Ni catalyst is regenerated. The monocyclic 1:1 adduct **27** can be derived from the common intermediate **24** through the intramolecular β metal hydride (or deuteride) elimination[26] followed by the reductive elimination, **24** → **26** → **27**. The regiospecific β elimination in **24** would be a result of steric constraints due to the presence of the CHZCHZ bridge. In this scheme, as a matter of simplicity, the oxidative addition concept is employed. At present, however, it is indistinguishable whether the edgewise-coordinated complex **22** and the complex **23** can exist as two distinct chemical entities or actually are canonical forms in a resonance hybrid.[27]

One remaining question relates to the origin of the exo approach of the Ni(0) complex to the bicyclopentane central bond. The exo side of the flap is, of course, sterically less hindered as compared with the endo side, and thus the approach from this side may be favored on steric grounds. We feel, however, the direction of the metal approach is mainly associated with the orbital symmetry factors, since certain olefins, unlike transition metals, interact with the σ bond from the opposite, more hindered endo side. A molecular orbital calculation of **1** has indeed indicated that the exo side of the flap, with respect to the charge distribution of the central bond, has a considerable symmetric, bonding character and the endo region, on the other hand, mainly an antisymmetric, antibonding character.[28] Irregardless of whether $[_\pi 2 + {}_\sigma 2]$ reaction is concerted or nonconcerted in nature, approach of the two-electron systems via an S + S combination is unfavorable.[15] Thus in the uncatalyzed reaction, an electron-poor olefin may attack the back lobe of the angular carbon of **1** to produce diradical or zwitterionic intermediates,[12] which result in nonselective and nonstereospecific reactions. Alternatively, in order to make the concerted cycloaddition feasible, olefins may have an S + A pericyclic interaction with the central σ bond from the weakly bonding endo side.[29] In contrast, the attraction between the Ni(0) atom and the strained σ bond is of a $[_d 2 + {}_\sigma 2]$ type, and hence, the metal atom possessing an occupied, antisymmetric d orbital approaches preferentially from the strongly bonding, symmetric, exo side. Thus the orbital symmetry effects, rather than simple steric factors, could explain distinctly the contrasting stereochemistries of the uncatalyzed and catalyzed cycloadditions.

Attempted Isolation of the Reactive Intermediates. We have carried out several experiments in an effort to obtain and characterize the reactive organometallic intermediates of type **22** or **23**[24] but have not as yet gained successful results. Reaction of **1** and $Ni(cod)_2$ in benzene at 60 °C resulted in recovery of the starting materials. Attempted reaction of **1** with diethyldipyridylnickel(II) $[(C_2H_5)_2Ni(dipy)]$[30] in methyl acrylate or with bis(methyl-acrylate)dipyridylnickel(0) $[(ma)_2Ni(dipy)]$[31] in benzene did not give any stable adducts. In general, olefins having electron-withdrawing groups give stable Ni(0) π complexes.[30-32] In addition, 1,1,2,2-tetracyanocyclopropane is known to react with a zerovalent platinum or palladium complex to give a stable metallacyclobutane derivative.[24a] In these contexts, we have tried the reactions of 1,4-bis(carbomethoxy)bicyclo[2.1.0]pentane (**28**) and certain nickel complexes. When **28** was treated with $Ni(cod)_2$ in methyl acrylate at 10 °C, the starting strained compound was recovered, however. Reaction of **28** and $(C_2H_5)Ni(dipy)$ in benzene at 100 °C caused decomposition of the nickel complex. When **28** was allowed to react with $(ma)_2Ni(dipy)$ in benzene at 45 °C, the cyclopentene derivative **29** was produced, but no stable organonickel compound was obtained. The structure of **29** was substantiated by the spectral data. Reaction of **28** in benzene



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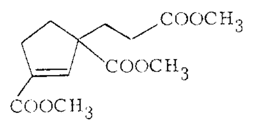

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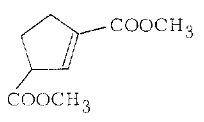

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solution with $(C_2H_5)_2$Ni(dipy) or $(ma)_2$Ni(dipy) was monitored by UV-visible spectra, but no indication for the formation of the σ complexes of type **23** was provided.

Next, in view of the high stability of metallacycles containing a platinum atom,[33] some reactions of **1** or **28** with Pt(0) complexes were examined. However, when **1** was treated with bis(triphenylphosphine)ethyleneplatinum(0) in benzene at 90 °C, no reaction was observed. The Pt(0) complex did not react with **28** at 55 °C either. Tetrakis(triphenylphosphine)platinum(0) in toluene did not give any 1:1 complexes with **28** below 35 °C. At 110 °C, the isomeric product **30** was formed. Thus the initial experiments to obtain stable metal complexes of bicyclopentanes were totally unsuccessful.

Conclusion

The modes of the catalyzed intermolecular reaction of bicyclo[2.1.0]pentane (**1**) and electron-deficient olefins are significantly different from those of the uncatalyzed, purely thermal reactions. In summary, the present reaction system exhibits clearly the intriguing operations of transition-metal complexes in organic reactions, namely, (1) the activation of strained carbon–carbon β bonds under mild reaction conditions, (2) the promotion of cycloaddition involving such β bonds with high efficiency, and (3) the reversal of stereochemical consequence observed for the purely thermal reaction. The final effect was discovered first in the present catalytic system.

Experimental Section

General Methods. Nuclear magnetic resonance (NMR) spectra were recorded with either a Varian Model HA-100D (100 MHz) or a JEOLCO Model C-60H (60 MHz) spectrometer as solutions in CCl_4 with tetramethylsilane as an internal standard. Chemical shifts were recorded in parts per million from tetramethylsilane. Singlet, doublet, triplet, and multiplet were abbreviated s, d, t, and m, respectively. Infrared spectra (IR) were measured on a JASCO Model DS-402G spectrometer as $CHCl_3$ solutions unless stated otherwise. Mass spectra were taken on a Hitachi RMU-6C spectrometer at an ionization voltage of 70 eV. The analytical thin-layer chromatography (TLC) was performed on commercially prepared silica gel glass plates (E. Merck Kieselgel PF_{254} precoated plates (0.25-mm layers)). Preparative TLC plates (20 × 20 cm glass plates with 1.0-mm-thick layers) were prepared in this laboratory by using E. Merck Kieselgel PF_{254}. Silver nitrate impregnated TLC plates were prepared as follows. E. Merck precoated plates for analytical use were dipped in a solution of silver nitrate (10.0 g) in a mixture of acetonitrile (50 mL) and ethanol (100 mL) for a few minutes and then dried at 100 °C for 30 min in the dark.

Analyses by gas–liquid chromatography (GLC) were done on a Hitachi Model 063 or a Yanagimoto Model G-8 instrument equipped with flame-ionization detector. Preparative GLC separation was performed on a Yanagimoto 3D or Varian Model 1700 gas chromatograph. The columns used were as follows: A, 3 mm × 2 m, 5% ethylene glycol succinate polyester on 80–100-mesh Neosorb NC; B, 3 mm × 1.5 m, 5% ethylene glycol succinate polyester on 80–100-mesh Neosorb NC; C, 4 mm × 2 m, 5% Carbowax 20M on 80–100-mesh Celite 545; D, 3 mm × 3 m, 12% diisodesyl phthalate on Celite 545; E, 3 mm × 2 m, 30% 4-benzylbiphenyl on 60–80 mesh Chromosorb W AW; F, 3 mm × 2 m, 5% ethylene glycol adipate polyester on 80–100-mesh Neosorb NC; G, 4 mm × 5 m 20% ethylene glycol adipate polyester on 80–100-mesh Neosorb NC; $^3/_8$ in. × 4 m, 15% ethylene glycol adipate polyester on 80–100-mesh Neosorb NC.

Materials. Commercial reagent grade organic solvents were distilled before use. Benzene, acrylonitrile, methyl acrylate, petroleum ether, and dimethyl maleate were distilled over CaH_2 under argon into Schlenk tubes and used for air-sensitive metal complexes. Commercial dimethyl fumarate was recrystallized from benzene. Bis(acrylonitrile)nickel was prepared from nickel tetracarbonyl and acrylonitrile.[32b] Bicyclo[2.1.0]pentane,[34] *exo*,-*exo*-2,3-dideuteriobicyclo[2.1.0]pentane,[35] 1,4-bis(carbomethoxy)bicyclo[2.1.0]pentane,[36] Ni(cod)$_2$,[37] $(C_2H_5)_2$Ni(dipy),[30] $(ma)_2$Ni(dipy),[31] $(C_2H_4)Pt[P(C_6H_5)_3]_2$,[38] and $[(C_6H_5)_3P]_4Pt$[39] were obtained according to the reported procedures. Nitrogen (99.999%) and argon (99.99%) were used as obtained.

Synthesis of Bis(acrylonitrile)nickel(0). $Ni(an)_2$ is unstable in solution as well as in the solid state if a trace amount of oxygen is present, and hence the complex for catalysis was freshly prepared in reaction ampules before use. A 20 mM solution of $Ni(CO)_4$ in dry, degassed acrylonitrile was prepared at −40 °C under nitrogen. This solution (5 mL) was transfered into a 20-mL reaction ampule with a 20-cm narrow neck by a syringe under nitrogen. To this was added petroleum ether (1.0 mL), and the vessel was connected to a bubbler. The neck of the ampule was surrounded by crushed dry ice. When the tube was placed in an oil bath heated at 70–75 °C, red crystals of $Ni(an)_2$ appeared immediately. After being heated for 1 h, the reaction mixture was cooled at −50 °C while a gentle stream of nitrogen was introduced. The liquid phase was removed by a syringe, and the remaining solid was washed twice with 5 mL of degassed benzene at room temperature. The complex thus prepared was used for catalytic reaction of **1**.

$Ni(an)_2$-Catalyzed Reaction of Bicyclo[2.1.0]pentane (1) with Acrylonitrile. To $Ni(an)_2$ (0.1 mmol) placed in a 20-mL reaction ampule was added a solution of **1** (162 mg, 2.38 mmol) in acrylonitrile (6.0 mL) under nitrogen. The tube was sealed, and the mixture was kept at 70 °C for 36 h with occasional shaking. The solid material was removed by filtration through a pad of Celite 545. An aliquot of the filtrate was analyzed by GLC (column A, 95 °C) with cyclooctanone as an internal standard, indicating that *exo*- and *endo*-2-cyanobicyclo[2.2.1]heptanes (**3** and **4**, unseparated, t_R = 6.75 min) were produced in a 76% combined yield accompanied by 3-(2-cyclopentenyl)propionitrile (**5**; t_R = 8.25 min, 14% yield). The mixture of **3** and **4** was obtained by GLC separation (column C, 95 °C) and was heated at reflux for 20 h in a saturated solution of hydrogen chloride in methanol. The resulting methyl esters **6** and **7** and a small amount of the corresponding acids were poured into water, extracted with ether, and treated with a solution of diazomethane in ether to give a mixture of **6** and **7**. The intensity of NMR signals due to ester methyl protons indicated that **3** and **4** were produced in a ratio of 60:40. The pure samples of **3**–**5** were obtained by preparative TLC using a $AgNO_3$-impregnated silica gel plate (benzene-hexane (1:1), two developments). For **3**: IR 2998 (w), 2950 (s), 2870 (s), 2240 (m), 1455 (m), 1313 (w), 1298 (w), 1135 (w), 1068 (w), 1035 (w), 918 (w), 879 (w), 840 (w), 825 cm^{-1} (w); NMR δ 0.7–2.0 (m, 8 H), 2.0–2.8 (m, 3 H); mass spectrum, *m/e* 121 (M^+) and 120 ($M^+ - 1$). For **4**: IR 3000 (m), 2950 (s), 2880 (s), 2240 (m), 1480 (w), 1455 (m), 1325 (w), 1315 (w), 1306 (w), 1267 (w), 1171 (w), 1068 (w), 1049 (w), 982 (w), 932 (w), 875 (w), 828 cm^{-1} (w); NMR δ 0.8–2.1 (m, 8 H), 2.1–2.9 (m, 3 H); mass spectrum, *m/e* 121 (M^+), 120 ($M^+ - 1$). The authentic samples of **3** and **4** were prepared by the hydrogenation of *exo*- and *endo*-5-cyanobicyclo[2.2.1]-oct-2-ene[16] on Raney nickel in methanol. The spectral properties of **5** are as follows: 3040 (m), 3000 (m), 2920 (s), 2840 (s), 2240 (m), 1675 (w), 1613 (w), 1460 (w), 1448 (m), 1425 (m), 1363 (w), 1350 (w), 1325 (w), 1310 (w), 1135 (w), 1032 cm^{-1} (w); NMR δ 0.9–2.1 (m, 4 H), 2.1–3.3 (m, 5 H), 5.76 (m, CH=CH); mass spectrum, *m/e* 121 (M^+), 120 ($M^+ - 1$), 67 ($M^+ - CH_2CH_2CN$). The product **5** was also converted to methyl ester **8** by being heated in a saturated hydrogen chloride in absolute methanol at 65 °C for 4 h. The authentic sample of **8** was prepared by the

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silver acetate catalyzed decomposition of 1-(2-cyclopenten-1-yl)-3-diazo-2-propanone at 70 °C in a mixture of triethylamine and methanol.[17] The IR, NMR, and mass spectra and GLC retention time of the authentic sample were identical with those of 8.

$Ni(an)_2$-Catalyzed Reaction of 1 and Methyl Acrylate. To $Ni(an)_2$ (0.1 mmol) prepared in a 20-mL ampule was added degassed and freshly distilled methyl acrylate (5.0 mL) followed by a solution of 1 (279 mg, 4.1 mmol) in methyl acrylate (2.0 mL), and the tube was sealed. The mixture was kept at 40 °C for 36 h. After the tube was opened and a gentle stream of air introduced into the reaction mixture, the solid precipitates were removed by filtration through Celite 545. An aliquot of the filtrate was analyzed by GLC (column A, 80 °C) with cyclohexanone as the internal standard. The cycloadducts 6 and 7 (t_R = 5.5 min) were produced in a 75% combined yield in a ratio of 50:50 accompanied by monocyclic ester 8 (t_R = 7.5 min, 12% yield). Evaporation of methyl acrylate followed by Kugelrohr distillation of the residue gave 0.38 g (60% yield) of a colorless oil which was composed of essentially three products, 6–8. Analytically pure samples of these products were obtained by preparative GLC (column C, 95 °C).

For **6**: IR 3020 (w), 2960 (s), 2880 (m), 1730 (s), 1454 (m), 1436 (s), 1360 (m), 1310 (s), 1285 (m), 1270 (w), 1256 (w), 1195 (s), 1175 (s), 1155 (m), 1115 (w), 1063 (s), 1038 (w), 1030 (w), 948 (w), 920 (w), 903 (w), 880 (w), 852 (w), 835 cm^{-1} (w); NMR δ 1.0–1.7 (m, H_{3n}, H_{5n}, H_{5x}, H_{6n}, H_{6x}, H_{7a}, H_{7s}), 1.7–2.0 (m, H_{3x}), 2.1–2.4 (m, H_{2n}), 2.28 (br s, H_4), 2.45 (br s, H_1), 3.61 (s, OCH_3). When the chemical shifts observed on addition of $Eu(fod)_3$ were plotted against the relative molar ratios of the shift reagent and the substrate, a linear relationship was observed. The gradients [ppm/mol of $Eu(fod)_3$/mol of substrate] of these lines were 12.0 (H_{2n}), 11.5 (OCH_3), 11.1 (H_{3x}), 9.0 (H_1), 8.4 (H_{7s}), 5.3 (H_{3n}), 2.8 (H_{7a}), and 2.4 (H_4). The values for H_{5n}, H_{5x}, H_{6n}, and H_{6x} could not be obtained because of the unsatisfactory resolution of the signals. The following coupling constants were determined: $J_{1,6x} = 3.5$, $J_{2n,3n} = 9.5$, $J_{2n,3x} = 5.5$, $J_{3n,3x} = 13.0$, $J_{3n,7a} = 2.5$, $J_{7a,7s} = 9.5$ Hz. Mass spectrum, *m/e* 154 (M^+), 123, 95, 87, 81, 67.

For **7**: IR 3020 (w), 2950 (s), 2870 (m), 1728 (s), 1478 (w), 1454 (m), 1435 (s), 1353 (m), 1310 (s), 1300 (w), 1253 (m), 1195 (s), 1173 (s), 1140 (w), 1117 (m), 1072 (m), 1053 (w), 1035 (m), 990 (w), 968 (w), 950 (w), 912 (w), 876 cm^{-1} (w); NMR δ 1.2–1.7 (m, H_{3n}, H_{3x}, H_{5n}, H_{5x}, H_{6n}, H_{6x}), 1.38 (br s, H_{7a} and H_{7s}), 2.25 (br s, H_4), 2.47 (br s, H_1), 2.5–2.8 (m, H_{2x}), 3.62 (s, OCH_3). The gradients of the lines derived from the $Eu(fod)_3$-aided spectra were 14.0 (H_{2x}), 13.1 (OCH_3), 13.1 (H_{3n}), 11.7 (H_{6n}), 8.4 (H_1), 5.8 (H_{3x}), 5.0 (H_{5n}), 4.3 (H_{6x}), 2.9 (H_4), 2.5 (H_{5x}), 1.8 (H_{7s}), and 0.8 (H_{7a}). The coupling constants were as follows: $J_{1,2x} = J_{1,6x} = 4.0$, $J_{2x,3n} = 5.0$, $J_{2x,3x} = 13.0$, $J_{3n,3x} = 13.0$ Hz. Mass spectrum, *m/e* 154 (M^+), 123, 122, 95, 87, 81, 67.

For **8**: IR 3050 (w), 3020 (m), 2955 (s), 2850 (m), 1732 (s), 1617 (w), 1454 (m), 1438 (s), 1420 (w), 1359 (w), 1328 (w), 1312 (w), 1282 (w), 1250 (s), 1195 (s), 1172 (s), 1075 (w), 1030 (w), 1015 (w), 990 (w), 946 (w), 910 (w), 890 (w), 855 (w), 840 cm^{-1} (w); NMR (CCl_4) δ 1.2–1.8 (m, 2 H_5 and 2 H_6), 1.9–2.4 (m, 2 H_4), 2.25 (t, J = 7.5 Hz, 2 H_7), 2.4–2.8 (m, H_1), 3.61 (s, OCH_3), 5.5–5.8 (m, H_2 and H_3). The gradients of the lines obtained by plotting the magnitude of the induced chemical shifts caused by $Eu(fod)_3$ were 13.1 (H_7), 12.2 (OCH_3), 8.7 (H_6), 3.9 (H_1), 2.2 (H_2), and 1.2 (H_3). The values for H_4 and H_5 could not be obtained because of the poor signal resolution. Mass spectrum, *m/e* 154 (M^+), 123, 122, 95, 87, 81, 80, and 67.

The above-described spectral data for products 6–8 were identical with those of samples prepared by the reported procedures.[16,17]

Preparation of Dideuteriodiiodomethane. Dideuteriodiiodomethane was obtained by the reported procedure[40] with slight modification. Absolute methanol (150 mL) was introduced under nitrogen into a 300-mL, two-necked flask equipped with a reflux condenser and a three-way stopcock which was connected with a nitrogen-inlet tube and a bubbler. To this was added sodium metal (3.72 g, 0.162 mol) cut in small pieces. After all of the sodium metal had dissolved, excess methanol was removed by distillation under reduced pressure (30 mm). The last trace of methanol was stripped off at 50 °C (2 mm and then 0.05 mm for 5 h). Dry sodium iodide (22.2 g, 148 mmol) was added to this solid followed by dry dioxane (50 mL), D_2O (30 mL), and diiodomethane (50 g, 187 mmol). The mixture was heated at reflux for 10 h (bath temperature 110 °C), cooled to room temperature, and extracted with three 75-mL portions of pentane. The combined organic layer was washed twice with 50 mL of water and dried over magnesium sulfate. Distillation in vacuo gave 39.1 g (78%) of deuterated diiodomethane. The deuteration procedure was repeated to give 32.9 g (65% overall yield) of dideuteriodiiodomethane. NMR analysis showed the presence of 7.2% of $CHDI_2$.

Preparation of 5,5-Dideuteriobicyclo[2.1.0]pentane (9). Cyclobutene was prepared by retro-Diels–Alder reaction of 7,8-bis(carbomethoxy)tricyclo[4.2.2.$0^{2,5}$]deca-7,9-diene.[41] A mixture of cyclobutene (1.698 g, 31.4 mmol) and dideuteriodiiodomethane (12.8 g, 47.4 mmol) in 15 mL of dry toluene was placed in a 100-mL pressure bottle under nitrogen. The mixture was stirred, and to this was added diethylzinc[42] (4.48 g, 36.4 mmol) over a period of 1 h at room temperature. About 10 mL of dry air was introduced by a syringe to accelerate the reaction, and the solution was stirred at room temperature for 2 h. More air (20 mL) was introduced, and the mixture was stirred for 24 h at room temperature giving white precipitates. Water (20 mL) was added dropwise with stirring and cooling with an ice–salt bath. After the vigorous evolution of gas had ceased, the mixture was filtered by the aid of Celite 545. The aqueous layer was extracted twice with 3-mL portions of toluene, and the combined organic layer was washed with two 10-mL portions of cold water. The organic layer was dried over Na_2SO_4. Dideuteriobicyclo[2.1.0]pentane (**9**) was distilled at a bath temperature of 60 °C with the introduction of a slow stream of nitrogen. About 5 mL of the distillate was collected. Analysis by GLC (column D, 50 °C, 10 mL/min) indicated the formation of **9** (t_R = 10.6 min) and ethyl iodide (t_R = 23.2 min) in comparable amounts. To this mixture was added 30 mL of dry toluene followed by 20 g (76.3 mmol) of triphenylphosphine. The mixture was kept at 60 °C for 48 h, and the precipitated phosphonium salt was filtered off. The filtrate was washed with two 20-mL portions of cold water, and the organic layer was dried over Na_2SO_4. GLC analysis (column E, 40 °C, 10 mL/min, t_R = 10.5 min) showed no trace of ethyl iodide remained. To this mixture was added 2.0 g (7.63 mmol) of triphenylphosphine, and the mixture was kept further at 60 °C for 24 h. The product **9** and toluene were distilled at 65 °C with the introduction of a slow stream of nitrogen for a period of 60 h. Analysis of the distillate (ca. 3.5 mL) by GLC using cyclohexane as the internal standard showed that 370 mg (17%) of **9** was formed. The mixture was stored over 3A molecular sieves.

$Ni(an)_2$-Catalyzed Reaction of 5,5-Dideuteriobicyclo[2.1.0]pentane (9) with Methyl Acrylate. A mixture of **9** (370 mg, 5.45 mmol), methyl acrylate (10 mL), and toluene (3 mL) was chromatographed through a short column of neutral alumina under an argon atmosphere. The solution was treated with $Ni(an)_2$ (49.4 mg, 0.30 mmol) in a 20-mL glass ampule. The nickel complex was decomposed gradually to produce metallic nickel as a black precipitate, which was removed by filtration through Celite 545 under argon. The filtrate was again added to $Ni(an)_2$ (49.2 mg, 0.30 mmol) and a small amount of hydroquinone in a 20-mL ampule, and the tube was sealed under argon. The mixture was kept at 40 °C for 72 h. The tube was opened, and the solid material was removed by filtration through Celite 545 with the aid of a slight positive pressure of nitrogen. The filtrate was distilled at 50 °C (150 mm), and the distillate was collected in a trap surrounded by a dry ice–methanol bath (–70 °C). Dichloromethane (10 mL) was added to the residue, and the precipitates were filtered off. The solvent was evaporated by a rotary evaporator at room temperature, and the remaining brown oil (1.32 g) was distilled under reduced pressure to give 0.712 g (85%) of a mixture of 1:1 adducts **10**–**12**. The GLC analysis (column F, 90 °C, 15 mL/min) showed that the products **10** (t_R = 24.2 min), **11** (t_R = 22.4 min), and **12** (t_R = 30.8 min) were formed in a ratio

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of 57:11:32. The pure samples of **10**–**12** were obtained by preparative GLC (column G, 150 °C). The structure of each product was determined by NMR spectra taken with added $Eu(fod)_3$ (see the paragraph at the end of the paper about supplementary material).

For **10**: NMR δ 1.0–1.7 (m, H_{3n}, H_{5n}, H_{5x}, H_{6n}, H_{6x}), 1.6–2.0 (m, H_{3x}), 2.1–2.4 (m, H_{2n}), 2.28 (br s, H_4), 2.45 (br s, H_1), 3.61 (s, OCH_3).

For **11**: NMR δ 1.2–1.7 (m, H_{3n}, H_{3x}, H_{5n}, H_{5x}, H_{6n}, H_{6x}), 2.25 (br s, H_4), 2.47 (br s, H_1), 2.5–2.8 (m, H_{2x}), 3.62 (s, OCH_3).

For 12: NMR δ 1.2–1.9 (m, 2 H_5, 2 H_6), 1.9–3.0 (m, H_1, 2 H_4, H_7), 3.61 (s, OCH_3), 5.6–5.8 (m, H_3).

Ni(an)$_2$-Catalyzed Reaction of 1 with Dimethyl Fumarate. Benzene (3.0 mL) was added to $Ni(an)_2$ (0.2 mmol) prepared in a 20-mL reaction ampule, and the mixture was cooled to −30 °C. To this was added dimethyl fumarate (0.50 g, 3.5 mmol), and the system was flushed with nitrogen. Then a solution of **1** (78.9 mg, 1.16 mmol) in benzene (2.0 mL) was added, and the ampule was sealed. The mixture was kept at 60 °C for 45 h, and the solid compounds were removed by filtration. GLC analysis using methyl parmitate (column B, 125 °C) indicated that the bicyclic adduct **13** (t_R = 12.0 min) and the olefinic diester **14** (t_R = 15.0 min) were produced in a 34% combined yield in a ratio of 89:11. The reaction mixture was distilled in vacuo, and the colorless distillate contaminated with the starting dimethyl fumarate was subjected to preparative GLC (column C, 150 °C) to give analytically pure samples of **13** and **14**. The spectroscopic properties of **13** were identical with those of an authentic specimen which was obtained by the Diels–Alder reaction of cyclopentadiene and dimethyl fumarate followed by hydrogenation of the cycloadduct over Raney nickel.[19] The spectral data of **14** were identical with those reported,[20] but the stereochemistry (threo and/or erythro) remained unknown.

Ni(an)$_2$-Catalyzed Reaction of 1 and Dimethyl Maleate. To $Ni(an)_2$ (0.2 mmol) prepared in a 20-mL ampule was added a solution of **1** (78.9 mg, 1.16 mmol) in dimethyl maleate (5.33 g, 3.70 mmol), and the tube was sealed under nitrogen. The mixture was kept at 60 °C for 45 h. After the usual workup the reaction mixture was analyzed by GLC (column B, 125 °C) with methyl parmitate as the internal standard, indicating that **15** (t_R = 20.0 min), **16** (t_R = 22.0 min), **14** (t_R = 15.0 min), and **13** (t_R = 12.0 min) were formed in a 46% combined yield in a ratio of 60:8:25:7. Analytically pure samples were obtained by distillation of the reaction mixture followed by preparative GLC (column C, 155 °C). The authentic samples of **15** and **16** were prepared by Raney nickel catalyzed hydrogenation of *exo,exo*-5,6-bis(carbomethoxy)bicyclo[2.2.1]hept-2-ene and its endo,endo isomer.[19] The NMR, IR, and mass spectra of **15** and **16** were superimposable on those of the authentic samples.

Ni(an)$_2$-Catalyzed Reaction of 2,3-*exo,exo*-Dideuteriobicyclo[2.1.0]pentane (2) with Dimethyl Fumarate. To $Ni(an)_2$ (0.13 mmol) placed in a 20-mL ampule was added benzene (1.0 mL) under a nitrogen atmosphere, and the mixture was cooled to −50 °C. To this were added dimethyl fumarate (398 mg, 2.76 mmol) and a solution of **2** (100 mg, 1.43 mmol) in benzene (2.0 mL). The tube was sealed under nitrogen and placed in an oil bath kept at 60 °C for 48 h. GLC analysis of the reaction mixture with methyl parmitate as the internal standard (column B, 125 °C) showed that **17** and **18** were produced in 33% combined yield in a ratio of 87:13. Air was bubbled into the reaction mixture to decompose the nickel complex, and the resulting solid material was removed by filtration. The filtrate was concentrated, and from the residue was removed the unreacted dimethyl fumarate as much as possible by recrystallization three times from benzene. The liquid phase was concentrated, and the residue was distilled in vacuo (120 °C, 2 mm) to give a mixture of **17**, **18**, and dimethyl fumarate. Analytical samples of **17** and **18** were obtained by preparative GLC (column H, 200 °C). The location and stereochemistry of deuterium atoms could be unequivocally determined by comparison of $Eu(fod)_3$-aided NMR spectra of **13**, **17**, and the 5,6-*exo,exo*-dideuterio derivative.

For **17**: NMR δ 1.25, 1.55 (AB q with fine splitting, $J_{7a,7s}$ = 10.5 Hz, $J_{1,7a}$ = $J_{4,7a}$ = 1.7 Hz, H_{7a}, H_{7s}), 1.3–1.6 (m, H_{5x}, H_{6x}), 2.4–2.7 (m, H_1, H_4), 2.72 (dd, $J_{2x,3}$ = 5.3 Hz, $J_{3,4}$ = 1.7 Hz, H_3), 3.22 (ddd, $J_{1,2}$ = 4.5 Hz, $J_{2,6x}$ = 1.5 Hz, H_2), 3.63 (s, OCH_3), 3.65 (s, OCH_3). The authentic sample of 2,3-*endo,exo*-bis(carbomethoxy)-5,6-*exo,exo*-dideuteriobicyclo[2.2.1]heptane was obtained by catalytic deuteration of the corresponding bicyclo[2.2.1]hept-2-ene over 10% Pd/C in pentane at 25 °C. The deuterated positions in compound **18** were determined by NMR analysis. In going from **14** to **18**, the signal intensities due to the five-membered-ring methylenes appearing around δ 1.5–2.3 ppm[20,43] were reduced from 4 H to 2 H.

Ni(an)$_2$-Catalyzed Reaction of 2 with Dimethyl Maleate. A solution of **2** (500 mg, 7.13 mmol) in degassed dimethyl maleate (3.50 g, 24.4 mmol) was added to $Ni(an)_2$ (0.10 mmol) placed in a 20-mL reaction tube under nitrogen. The tube was sealed and kept at 60 °C for 48 h. Analysis of an aliquot of the reaction mixture by GLC with methyl parmitate as the internal standard (column B, 125 °C) showed that the bicyclic products **19**, **20**, and **17** and the ene type reaction product **18** were produced in a 46% combined yield (61:5:4:30). Isolation of each product was attained by preparative GLC (column H, 200 °C) after the usual workup. The GLC analysis (column A, 90 °C) of the recovered dimethyl maleate revealed that about 1% of the starting maleate was isomerized to fumarate during the catalytic reaction. The authentic specimens of exo,exo-dideuterated derivatives of **19** and **20** were obtained by deuteration of the corresponding dehydro compounds over 10% Pd/C at an atmospheric pressure of deuterium. The stereochemistries of the deuteriums in **19** and **20** were unequivocally determined by comparison of their NMR spectra with those of undeuterated compounds **15** and **16** and those of the *exo,exo*-dideuterio derivatives (see the paragraph at the end of the paper about supplementary material).

For **19**: NMR δ 1.21, 2.03 (AB q with fine splitting, $J_{7a,7s}$ = 10.5 Hz, $J_{1,7a}$ = $J_{4,7a}$ = 1.7 Hz), 1.57 (br s, H_{5x}, H_{6x}), 2.4–2.6 (m, H_1, H_4), 2.59 (d, $J_{1,2}$ = $J_{3,4}$ = 1.7 Hz, H_2, H_3), 3.54 (s, 2 OCH_3).

For **20**: NMR δ 1.3–1.5 (m, H_{5x}, H_{6x}, H_{7a}, H_{7s}), 2.47 (br s, H_1, H_4), 2.84 (br s, H_2, H_3), 3.57 (s, 2OCH_3).

Attempted Reaction of 1 with $(C_2H_5)_2Ni(dipy)$ in Methyl Acrylate. A solution of **1** (800 mg, 11.0 mmol) in methyl acrylate (1.0 mL, 11 mmol) was added to $(C_2H_5)_2Ni(dipy)$ (200 mg, 0.72 mmol) placed in a 10-mL ampule under argon at −78 °C. The tube was sealed, and the dark green solution was warmed up to room temperature. The color of the solution became dark red, and $(ma)_2Ni(dipy)$ precipitated as red-brown crystals. The mixture was kept at room temperature for 24 h and then at 80 °C for 24 h. When the mixture cooled the crystals of $(ma)_2Ni(dipy)$ separated again. The precipitates were removed by filtration through a pad of Celite 545, and the filtrate was evaporated. The residue was analyzed by GLC, indicating that no trace of **6** and **7** was produced.

Reaction of 28 with $(ma)_2Ni(dipy)$ in Benzene. In a 5-mL ampule was placed $(ma)_2Ni(dipy)$ (139 mg, 0.36 mmol) under argon, and to this was added **28** (137 mg, 0.74 mmol) in benzene (1.0 mL). The tube was sealed, and the mixture was kept at 45 °C for 24 h. The initial dark red color turned green. No crystalline material was obtained after cooling to room temperature. The reaction mixture was worked up as usual to give an oil (141 mg). NMR analysis using cyclooctene as the internal standard showed that the adduct **29** was obtained in 30% yield: IR (CCl_4) 1738 and 1725 cm^{-1} (C=O); NMR δ 1.7–2.7 (m, 4 CH_2), 3.62 (s, OCH_3), 3.69 (s, OCH_3), 3.72 (s, OCH_3), 6.53 (t, *J* = 0.2 Hz, an olefinic proton); mass spectrum, *m/e* 270 (M^+). Anal. ($C_{13}H_{18}O_6$) C, H.

Attempted Reaction of 28 and $Ni(cod)_2$. $Ni(cod)_2$ (50 mg, 0.18 mmol) was placed in a 5-mL glass ampule under argon, and to this was added a solution of **28** (150 mg, 0.82 mmol) in methyl acrylate (1.0 mL). The reaction mixture was kept at 40 °C for 12 h. TLC analysis of the reaction mixture indicated that the starting ester was recovered unchanged.

Attempted Reaction of 28 and $(C_2H_5)_2Ni(dipy)$. A mixture of $(C_2H_5)_2Ni(dipy)$ (150 mg, 0.55 mmol) and **28** (100 mg, 0.55 mmol) in benzene placed in a 5-mL ampule was kept at room temperature for 12 h under argon. Then the temperature of the dark green mixture was raised to 50 °C and kept at this temperature for 2 h. Dark green precipitates appeared. The temperature was further raised to 100 °C over a period of 2 h. During this time, the precipitates disappeared to give a dark green so-

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lution. After the usual workup the mixture was analyzed by TLC and NMR. Only the starting **28** and bipyridyl were detected.

Attempted Reaction of 1 and $[(C_6H_5)_3P]_2Pt(C_2H_4)$. A mixture of **1** (0.1 mL, 0.88 mmol) and $[(C_6H_5)_3P]_2Pt(C_2H_4)$ (24 mg, 0.03 mmol) in benzene (0.6 mL) was placed in a NMR sample tube under argon, and the reacton was monitored by NMR after the mixture was kept for 24 h at room temperature and then at 90 °C for 12 h. The starting **1** was not consumed under the above-mentioned reaction conditions.

Attempted Reaction of 28 with Tetrakis(triphenylphosphine)platinum(0). Tetrakis(triphenylphosphine)platinum(0) (100 mg, 0.083 mmol) was placed in a 20-mL Schlenk tube under argon, and to this was added benzene (15.0 mL). The crystals were dissolved at 80 °C, and the solution was cooled to room temperature. Then a solution of **28** (75.0 mg, 0.38 mmol) in benzene (1.0 mL) was added, and the mixture was stirred at room temperature for 24 h and then at 35 °C for 12 h. Analysis by IR and NMR spectra indicated that most of **28** remained unreacted. The mixture was further heated at 110 °C for 24 h. NMR analysis of the mixture showed that besides the starting **28** and the platinum complex only **30** was formed. NMR spectrum of **30**: δ 1.9–2.4 (m, CH_2), 2.4–2.7 (m, $=CCH_2$), 3.4–3.8 (m, $=CHCH$), 3.59 (s, OCH_3), 3.62 (s, OCH_3), 6.5–6.6 (m, $=CH$). The spectral data of **30** were identical with those of the authentic sample obtained by the thermal isomerization of **28** at 140 °C.[44]

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Supplementary Material Available: NMR spectra for compounds **6–8**, **10–13**, **15–17**, **19**, and **20** taken with or without added $Eu(fod)_3$ (6 pages). Ordering information is given on any current masthead page.

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Nickel(0)-Catalyzed Reactions of Bicyclo[1.1.0]butanes. Geminal Two-Bond Cleavage Reaction and the Stereospecific Olefin Trapping of the Carbenoid Intermediate[1,2]

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Zerovalent nickel complexes such as bis(acrylonitrile)nickel(0) or bis(1,5-cyclooctadiene)nickel(0) catalyze the reaction of bicyclo[1.1.0]butanes and electron-deficient olefins such as methyl acrylate and acrylonitrile to give the corresponding allylcyclopropane derivatives in excellent yields. The reaction of 3-deuterio-1,2,2-trimethylbicyclo[1.1.0]butane indicates that the two-bond cleavage occurs at the central σ bond and one of the four peripheral bonds of bicyclo[1.1.0]butanes to generate an allylcarbene–nickel complex as the reactive intermediate. The reaction of bicyclo[1.1.0]butane with (*Z*)-β-deuterioacrylate or a pair of *E* and *Z* 1,2-disubstituted olefins proceeded with a high degree of stereospecificity. The mechanism of cycloaddition is discussed.

Since the first synthesis of a bicyclo[1.1.0]butane derivative was reported by Wiberg in 1959,[3] extensive studies on the chemistry of the smallest bicyclic hydrocarbon system have been done. The parent hydrocarbon **1**, regardless of the high strain energy (66 kcal/mol[4]), is rather stable in the gas phase or in hydrocarbon solvents.[5,6] Thermolysis of **1** and its derivatives at temperatures as high as 200 °C breaks two σ bonds to give 1,3-butadiene. The central bond remains intact during the purely thermal, symmetry-controlled reactions.[7] With the aid of transition-metal catalysts, however, it experiences skeletal change quite facilely.[8,10–14] In most cases, the products

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