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]

Acknowledgment. We thank the Ministry of Education of the Japanese Government for support of this work (Grant No. 303023). Partial financial support by the Matsunaga Science Foundation, the Takeda Science Foundation, the Kurata Science Foundation, and the Ito Science Foundation is also gratefully acknowledged.

Registry No. 1, 185-94-4; **2**, 51794-28-6; **3**, 3211-90-3; **4**, 3211-87-8; **5**, 35436-49-8; **6**, 23057-38-7; **7**, 16646-41-6; **8**, 35436-47-6; **9**, 51725-16-7; **10**, 51725-17-8; **11**, 51725-18-9; **12**, 51725-19-0; **13**, 35436-50-1; **14**, 35436-51-2; **15**, 35436-52-3; **16**, 4098-47-9; **17**, 51773-59-2; **18**, 51725-15-6; **19**, 51773-58-1; **20**, 51830-07-0; **28**, 77429-78-8; **29**, 77429-79-9; **30**, 22177-48-6; bis(acrylonitrile)nickel(0), 77450-60-3; acrylonitrile, 107-13-1; methyl acrylate, 96-33-3; dideuteriodiiodomethane, 15729-58-5; cyclobutene, 822-35-5; dimethyl fumarate, 624-49-7; dimethyl maleate, 624-48-6; tetrakis(triphenylphosphine)platinum(0), 22372-53-8; $(ma)_2Ni(dipy)$, 35039-19-1.

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.

(44) Prinzbach, H.; Martin, H. D. *Chimia* **1969**, *23*, 37; *Chem. Abstr.* **1960**, *70*, 87777.

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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Received February 13, 1981

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

(1) Nickel-Catalyzed Reactions Involving Strained Bonds. 17. Part 16: Takaya, H.; Suzuki, T.; Kumagai, Y.; Yamakawa, M.; Noyori, R. *J. Org. Chem.*, preceding paper in this issue.

(2) Part of this work was reported in a preliminary form: (a) Noyori, R.; Suzuki, T.; Kumagai, Y.; Takaya, H. *J. Am. Chem. Soc.* **1971**, *93*, 5894. (b) Noyori, R. *Tetrahedron Lett.* **1973**, 1691. (c) Noyori, R.; Kawauchi, H.; Takaya, H. *Ibid.* **1974**, 1749.

(3) Wiberg, K. B.; Ciula, R. P. *J. Am. Chem. Soc.* **1959**, *81*, 5261.

(4) (a) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. *J. Am. Chem. Soc.* **1970**, *92*, 2377. (b) Chang, S.; McNally, D.; Shary-Tehrany, S.; Hickey, M. J.; Boyd, R. H. *Ibid.* **1970**, *92*, 3109.

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

(6) (a) Frey, H. M.; Stevens, I. D. R. *Trans. Faraday Soc.* **1965**, *61*, 90. (b) Srinivasan, R.; Levi, A. A.; Haller, I. *J. Phys. Chem.* **1965**, *69*, 1775. (c) Lemal, D. M.; Menger, F.; Clark, G. W. *J. Am. Chem. Soc.* **1963**, *85*, 2529.

(7) See ref 5, p 76.

(8) Bishop, K. C., III. *Chem. Rev.* **1976**, *76*, 461.

(9) (a) Wiberg, K. B.; Lampman, G. M.; Ciula, R. P.; Connor, D. S.; Schertler, P.; Lavanish, J. *Tetrahedron* **1965**, *21*, 2749. (b) Blanchard, E. P., Jr.; Cairncross, A. *J. Am. Chem. Soc.* **1966**, *88*, 487. (c) Doering, W. v. E.; Coburn, J. F. *Tetrahedron Lett.* **1965**, 991. (d) Lemal, D. M.; Shim, K. S. *Ibid.* **1964**, 3231. (e) Moore, W. R.; Ward, H. R.; Merritt, R. F. *J. Am. Chem. Soc.* **1961**, *83*, 2019. (f) Meinwald, J.; Swithenbank, C.; Lewis, A. *Ibid.* **1963**, *85*, 1880. (g) Galantay, E.; Paolella, N.; Barcza, S.; Coombs, R. V.; Weber, H. P. *Ibid.* **1970**, *92*, 5771.

(10) (a) Paquette, L. A. *Acc. Chem. Res.* **1971**, *4*, 280. (b) Paquette, L. A.; Zon, G. *J. Am. Chem. Soc.* **1974**, *96*, 224 and references cited therein. (c) Sakai, M.; Westberg, H. H.; Yamaguchi, H.; Masamune, S. *Ibid.* **1971**, *93*, 4611. (d) Murata, I.; Nakasuji, K. *Tetrahedron Lett.* **1973**, 47 and references cited therein.

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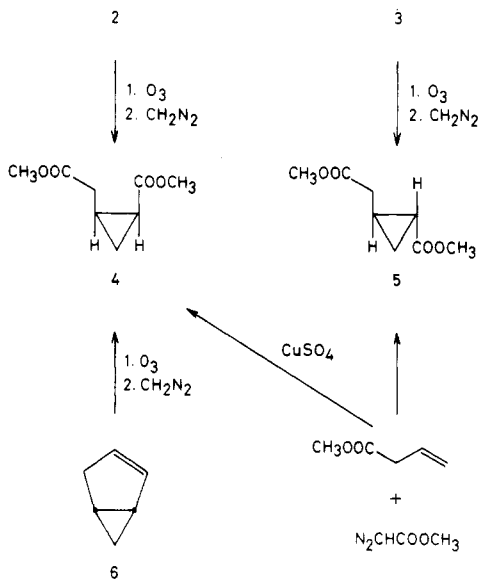
Scheme I

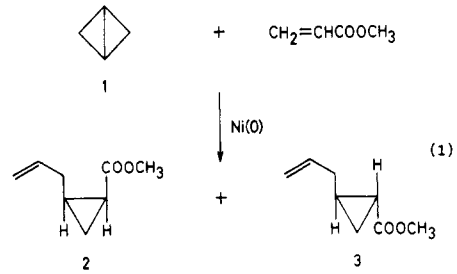


were 1,3-dienes arising from a geminal two-bond cleavage reaction.[9] As to the mechanism, the reaction has been considered to proceed by forming the allylcarbene–transition-metal complexes, followed by collapse through 1,2 hydrogen transfer with loss of the metal residue. Indeed, Dauben and Masamune isolated the carbene–Pd complex at low temperatures and characterized it on the basis of NMR spectral data.[15]

Some years ago, noting the eminent π character of the central bond of 1,[16] we initiated an examination of the catalysis with Ni(0) complexes. In this investigation, our attention has been focused on the reaction mode and the intermolecular trapping, in a formal sense, of the reactive intermediate.[17]

Results and Discussion

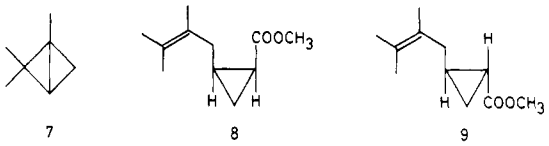
Nickel(0)-Catalyzed Reaction of Bicyclo[1.1.0]butane (1) and Methyl Acrylate. As the catalyst, sparingly soluble bis(acrylonitrile)nickel(0) [$Ni(an)_2$] or readily soluble bis(1,5-cyclooctadiene)nickel(0) [$Ni(cod)_2$] was used. When a mixture of 1, methyl acrylate (1:10 ratio), and a catalytic amount of $Ni(an)_2$ was heated at 60 °C for 36 h under nitrogen, two cyclopropane adducts, 2 and 3 (65:35 ratio), were obtained in a 95% combined yield (eq 1). The reaction with $Ni(cod)_2$ catalyst[18] proceeded smoothly even at 0 °C, affording a mixture of 2 and 3 (65:35) in 92% yield. Structures of the products were



determined on the basis of spectral data[19] and chemical conversions. As shown in Scheme I, ozonolysis of the adducts 2 and 3 followed by methylation with diazomethane gave the diesters 4 and 5, respectively. The Z diester 4 was independently prepared from bicyclo[3.1.0]hex-2-ene (6) by a similar oxidative structural modification. Reaction of methyl vinylacetate and methyl diazoacetate in the presence of cupric sulfate gave a mixture of 4 and 5 with the latter predominating.

The reaction was only successful with electron-deficient olefins, and no coupling products were obtained with simple alkene substrates. Attempted skeletal change of 1 in the absence of electron-deficient olefins failed. Thus treatment of 1 in toluene solution with $Ni(cod)_2$ or $Ni(CO)_4$ at 25 °C resulted in essential recovery of the starting hydrocarbon 1. Only a trace amount of butadiene was detected. This could be ascribed to the fact that the affinity of 1 to nickel atom is not high enough to displace the cyclooctadiene or carbonyl ligand.[22] Reaction with the toluene-insoluble catalyst, $Ni(an)_2$, at 60 °C was likewise unsuccessful. Thus the production of soluble, coordinatively unsaturated Ni(0) complexes is crucial for the smooth catalysis of 1.[18b,c]

Mode of the Two-Bond Cleavage Reaction and the Nature of the Reactive Intermediate. Apparently the Ni(0)-catalyzed reaction of 1 and methyl acrylate involves cleavage of two σ bonds of the strained hydrocarbon 1. Unfortunately, however, the high degree of symmetry incorporated in the simple hydrocarbon 1 makes elucidation of the reaction mode virtually impossible. We have therefore chosen the trimethylbicyclobutane 7 and its



deuterated derivative 10 as the substrates and examined the mode of the two-bond cleavage reaction. When the undeuterated bicyclobutane 7 was treated with $Ni(an)_2$ in methyl acrylate at 60 °C, there was obtained a 65:35 mixture of 8 and 9 in 70% combined yield.

In the same manner, reaction with the deuterio derivative 10 was carried out to afford a mixture of 11 and 12 (eq 2). The deuterium positioning in these products was readily determined by comparison of their NMR spectra with those of the undeuterated products (see the paragraph

(11) (a) Gassman, P. G.; Meyer, G. R.; Williams, F. J. *J. Am. Chem. Soc.* **1972**, *94*, 7741. (b) Sakai, M.; Yamaguchi, H.; Masamune, S. *Chem. Commun.* **1971**, 486.

(12) Gassman, P. G.; Atkins, T. J. *J. Am. Chem. Soc.* **1971**, *93*, 1042, 4597.

(13) Gassman, P. G.; Reitz, R. R. *J. Am. Chem. Soc.* **1973**, *95*, 3057 and references cited therein.

(14) Moriarty, R. M.; Chen, K.-N.; Flippen, J. L. *J. Am. Chem. Soc.* **1973**, *95*, 6489.

(15) (a) Dauben, W. G.; Kielbania, A. J., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 3669. (b) Masamune, S.; Sakai, M.; Darby, N. *J. Chem. Soc., Chem. Commun.* **1972**, 471.

(16) (a) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 767. (b) Pomerantz, M.; Hillenbrand, D. F. *Ibid.* **1973**, *95*, 5809. See also: (c) Wiberg, K. B.; Ellison, G. B.; Peters, K. S. *Ibid.* **1977**, *99*, 3941.

(17) For Ni(0)-catalyzed reactions of strained hydrocarbons and olefins, see ref 1 and the references cited therein.

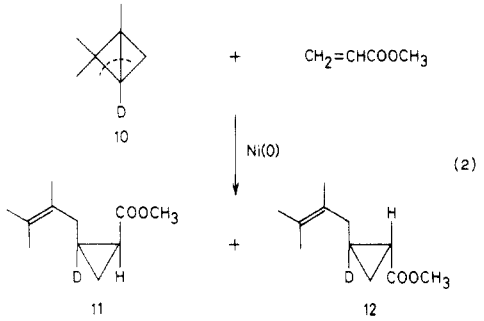
(18) Cyclooctadiene ligands of $Ni(cod)_2$ are readily displaced by electron-deficient olefins to give coordinatively unsaturated nickel(0) complexes. (a) Fritz, H. P.; Schrauzer, G. N. *Chem. Ber.* **1961**, *94*, 650. (b) Schrauzer, G. N. In "Advances in Organometallic Chemistry"; Stone, F. G. A., West, R. Eds.; Academic Press: New York, 1964; Vol. II, p 1. (c) Herberhold, M. In "Metal π-Complexes"; Elsevier: Amsterdam, 1972; Vol. II, Part 1, pp 284–287.

(19) The stereochemical assignment was established on the basis of the allylic methylene signals; the E isomer 3 showed the absorption at δ 1.9–2.3, whereas the corresponding signals of the Z isomer 2 appeared at a slightly lower field, δ 2.1–2.4, due to the anisotropy effect of the adjacent ester group.[20] Moreover, one of cyclopropane methylene protons of 3 trans to the carbomethoxyl group is most shielded and gave the signal at $\delta \sim 0.5$.[21]

(20) Seyden-Penne, J.; Strzalko, T. *C. R. Hebd. Seances Acad. Sci.* **1965**, *260*, 5059.

(21) Pavia, A. A.; Wylde, J.; Wylde, R.; Arnal, E. *Bull. Soc. Chim. Fr.* **1965**, 2709.

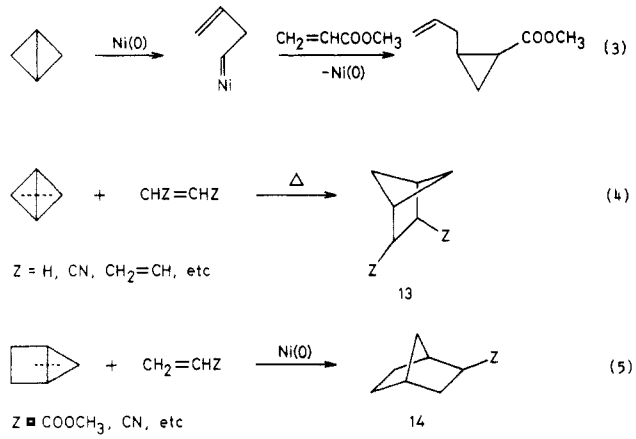
(22) Takaya, H.; Yamakawa, M.; Noyori, R. *Chem. Lett.* **1973**, 781. See also ref 1.



(2)

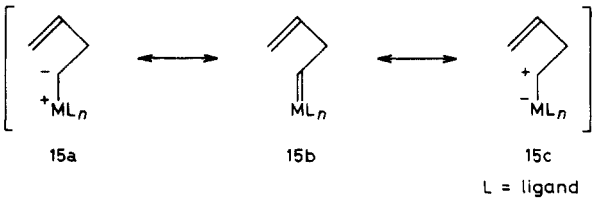
at the end of the paper about supplementary material). Thus the Ni(0)-promoted reaction has proved to involve breakage of the geminal C-1,C-3 and C-2,C-3 bonds of bicyclobutanes. Any other modes of the bond fission could not explain the experimental findings.

The present coupling reaction as outlined by eq 3 is viewed, in a formal sense, as an intramolecular retro-carbene addition of the bicyclobutanes followed by an intermolecular trapping of the resulting allylcarbene intermediate with an external olefin. The transition-metal-promoted cycloaddition lies in a marked contrast to the corresponding purely thermal reaction. Certain olefins are known to react with bicyclobutanes, without transition metal catalysts, giving the $[_{\pi}2 + _{\sigma}2]$-type cycloadducts (eq 4).[5] Under the purely thermal conditions,



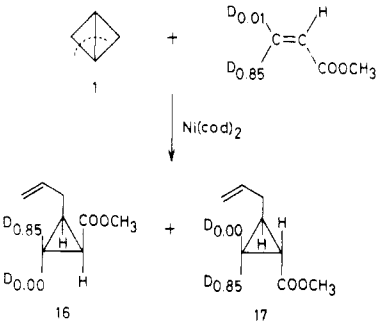
the bicyclobutane substrates appeared to suffer cleavage of only one σ bond. In addition, the overall course of the Ni(0)-catalyzed reaction of bicyclobutanes and olefins should be compared with that involving the higher homologue, bicyclo[2.1.0]pentane, which affords the $[_{\sigma}2 + _{\pi}2]$ adducts of type **14**.[1]

Another point to be noted is the eminent nucleophilicity of the carbene moiety in the intermediary Ni(0)/carbene π complex, L_nNi–:CHR, or metallaethene species, L_nNi=CHR, in which Ni is in a formal 2+ oxidation state. This phenomenon could be most reasonably explained by considering the electropositive property of Ni(0) atom. In general, metal-complexed carbene intermediates, if one takes metallaethene formulation, can be represented as the resonance hybrid, **15a** (ylide) ↔ **15b** (ylene) ↔ **15c** (inverse ylide). When M is an electron-donating Ni atom, the

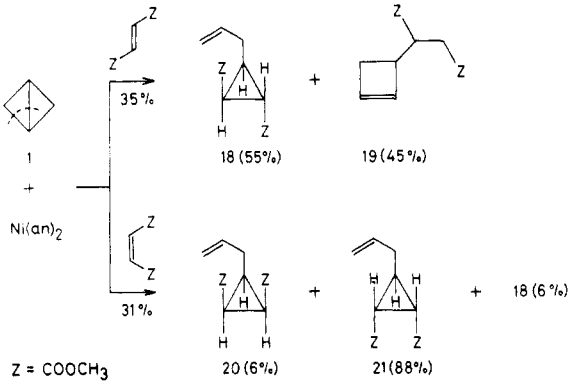


structures **15b** and **15c** become important in the hybrid.[23]

Scheme II



Scheme III



Consequently, the carbenoids can enter into cyclopropanation with electron-deficient olefins facilely but do not react with simple alkenes.[24,25] The fact that the nickel carbenoid, unlike other metal carbenoids, showed little tendency to collapse into a 1,3-diene and Ni(0) residue is also compatible with this view. The well-known alkylcarbene (or the metal complex) to olefin isomerization has been shown to occur via 1,2-migration of hydrogen to the electron-deficient carbenic carbon.[26] The observed propensity of other allylcarbene–metal complexes to give 1,3-dienes[10–13] would be ascribed to the electronegative nature of the metal ions or complexes which increases the inverse ylide character (**15c**) of the carbenoids.

Stereochemistry of the Reaction of the Nickel Carbenoid with Olefins. The stereochemical course of the cyclopropanation with allylcarbene–nickel complexes was examined by the reaction with deuterium-labeled acrylate. When a yellow-orange mixture of **1**, methyl (*Z*)-β-deuterioacrylate, and a small amount of $Ni(cod)_2$ was maintained at 32 °C, the cycloadducts **16** and **17** were obtained (Scheme II). No noticeable isomerization of the starting olefin had taken place during the reaction, as shown by NMR analysis of the recovered acrylate. Although the cyclopropane adducts **16** and **17** exhibited NMR spectra too complicated to analyze directly, their structures could be substantiated by comparison of their well-resolved spectra taken with the shift reagent $Eu(fod)_3$ with those of the corresponding undeuterated products **2**

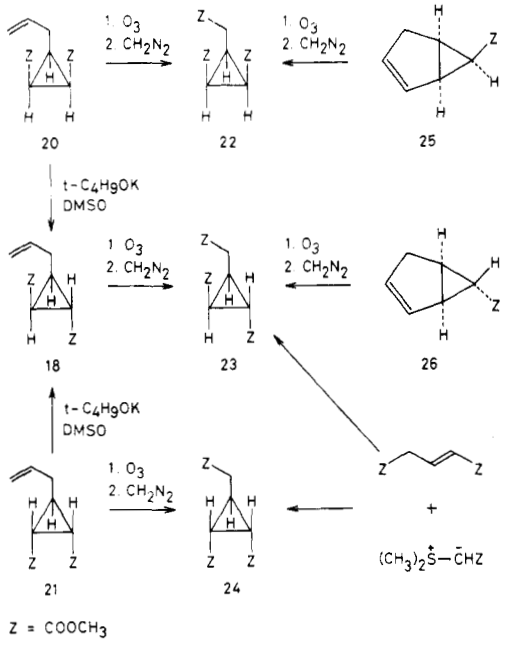
(23) Both theoretical and experimental evidence for the significance of $M^{\delta+}$–$CH_2^{\delta-}$-type polarization has been presented for carbene complexes of electropositive metals: (a) Rappé, A. K.; Goddard, W. A., III. *J. Am. Chem. Soc.* **1977**, *99*, 3966; (b) Gassman, P. G.; Johnson, T. H. *Ibid.* **1977**, *99*, 622; (c) Kirchner, R. M.; Ibers, J. A.; Saran, M. S.; King, R. B. *Ibid.* **1973**, *95*, 5775; (d) Schrock, R. R. *Ibid.* **1975**, *97*, 6578; (e) Guggenberger, L. J.; Schrock, R. R. *Ibid.* **1975**, *97*, 6578.

(24) A similar intermolecular reaction with the aid of Rh(I) complex was reported: Gassman, P. G; Reitz, R. R. *J. Organomet. Chem.* **1973**, *52*, C51.

(25) For intramolecular carbene reactions of the Rh(I) carbenoids, see: Gassman, P.; Nakai, T. *J. Am. Chem. Soc.* **1972**, *94*, 2877.

(26) Kirmse, W. "Carbene Chemistry", 2nd ed.; Academic Press: New York, 1971; Chapter 12.

Scheme IV

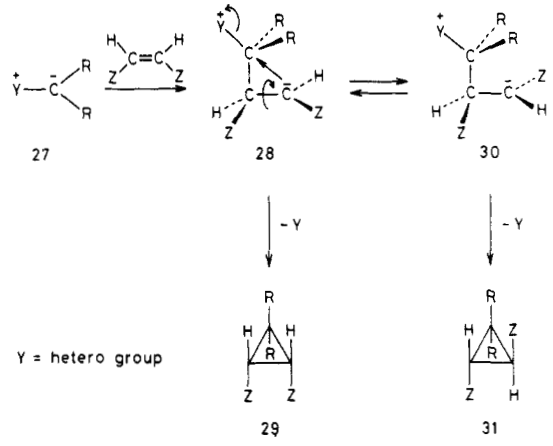


and 3 (see the paragraph at the end of the paper about supplementary material). The assignments were made on the basis of careful integration of signals obtained by using the field-sweep mode of the spectrometer. The result shows that the *Z* configuration of the starting olefin is retained in the cyclopropane products, indicating the cyclopropanation of the intermediary nickel carbenoid is proceeding with excellent stereospecificity.

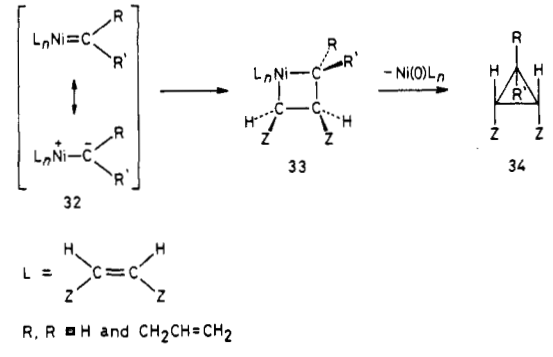
The reactions of 1 were carried out with a pair of *E* and *Z* 1,2-disubstituted olefins as well. The results are summarized in Scheme III. Dimethyl fumarate and maleate entered into the catalytic reaction rather sluggishly compared with methyl acrylate. The reaction of 1 and dimethyl fumarate in the presence of $Ni(an)_2$ in benzene (40 °C, 60 h) gave a single cyclopropane adduct, 18, in which the *E* stereochemistry of the fumarate is retained, in 19% yield. In addition, the cyclobutene adduct **19** (a mixture of threo and erythro isomers) was obtained in 16% yield. The reaction of 1 and dimethyl maleate gave a mixture of the 1:1 adducts in 31% yield. This consisted of the stereoretaining addition products **20** and **21** as well as a small amount of the stereoinverted addition product **18**. Formation of **19** was negligible in this case. The stereochemical assignment of the cyclopropane adducts **18**, **20**, and **21** was made on the basis of their stereocontrolled oxidation to triesters and independent synthesis of the latter, as outlined in Scheme IV. Apparently the cyclopropanation across the fumarate double bond was completely stereospecific (cis addition), while the stereospecificity with respect to maleate was >91%, as determined by the ratio (**20** + **21**)/(**18** + **20** + **21**). The observed lack of stereospecificity in the latter case would probably be ascribed to the reaction of fumarate ester formed by isomerization of the starting maleate. During the catalytic reaction, in fact, dimethyl maleate isomerized slowly, and the recovered unsaturated esters contained 1–3% of dimethyl fumarate. Dimethyl fumarate did not undergo the geometrical isomerization under the catalytic conditions. Additionally, a control experiment suggested that diethyl fumarate reacts about 6 times as fast as diethyl maleate.

It is worthwhile pointing out that the intermediary allylcarbene–nickel complexes, regardless of the considerable ylide character,[23] cycloadd to electron-deficient olefins with a high degree of stereospecificity. As shown in Scheme V,

Scheme V



Scheme VI



certain ylides of type **27**, particularly those containing a sulfur group, are known to undergo a nonstereospecific bimolecular alkylidene transfer reaction with electron-poor olefins (CHZ=CHZ).[27] Since Y in **27** has a closed-shell structure, the electropositive carbon undergoes the Michael-type nucleophilic attack on the carbon–carbon double bond, followed by cyclization via an intramolecular backside displacement, ejecting the small molecule Y to produce the cyclopropane adduct **29**. In the zwitterionic intermediate **28**, there is negligible electrostatic interaction between the charged moieties. Accordingly, the conformation cannot be fixed, and the rotation around the CHZ–⁻CHZ single bond can take place, leading to **30** which gives the stereoisomeric product **31**. In the initially formed intermediate **28**, various conformations are possible, and thus some attractive interactions between the charged groups could be obtained. The conformer, however, cannot cyclize by the intramolecular S_N2-type mechanism. On the other hand, the stereochemical course of the present nickel carbenoid reaction could be explained by Scheme VI, which for the sake of simplicity is given by valence bond description. The carbenic moiety in **32** could react with the olefinic substrate coordinated to the same metal atom,[18] giving the nickelacyclobutane intermediate **33**. Subsequent elimination of Ni(0) species gives rise to the cyclopropane adduct **34**.[28] The stereospecific nature of

(27) For example: (a) Truce, W. E.; Badiger, V. V. *J. Org. Chem.* **1964**, *29*, 3277; (b) Johnson, C. R.; Haake, M.; Schroeck, C. W. *J. Am. Chem. Soc.* **1970**, *92*, 6594; (c) Johnson, C. R.; Schroeck, C. W. *Ibid.* **1971**, *93*, 5303.

(28) Recently it was suggested that metallacyclobutanes are intermediates for olefin metathesis reactions and that cyclopropanes are formed from such intermediates by reductive elimination: (a) Casey, C. P.; Burkhardt, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 7808; (b) Casey, C. P.; Tuinstra, H. E.; Saeman, M. C. *Ibid.* **1976**, *98*, 608; (c) Gassman, P. G.; Johnson, T. H. *Ibid.* **1976**, *98*, 6055; (d) Grubbs, R. H.; Miyashita, A. *Ibid.* **1978**, *100*, 7418. For a reverse process starting from cyclopropanes, see: (e) Gassman, P. G.; Johnson, T. H. *J. Am. Chem. Soc.* **1976**, *98*, 6057; (f) Gassman, P. G.; Johnson, T. H. *Ibid.* **1976**, *98*, 6057.

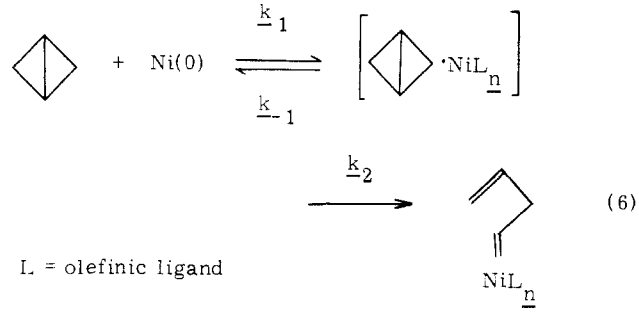
Table I. Kinetic Data of the Ni(0)-Catalyzed Reaction of Bicyclobutanes and Methyl Acrylate at 25 ± 0.1 °C[a]

bicyclobutane	k, M^{-1} s^{-1} [b]	rel rate	color of soln
bicyclo[1.1.0]butane	3.39×10^{-2}	1.0	yellow
1-methylbicyclo[1.1.0]butane	8.22×10^{-2}	2.4	yellow
1,2,2-trimethylbicyclo[1.1.0]butane	6.53×10^{-1}	19	yellow
1-(carbomethoxy)bicyclo[1.1.0]butane	1.50×10^{-3}	0.04	dark orange
1-(carbomethoxy)-3-methylbicyclo[1.1.0]butane	1.12×10^{-3}	0.03	dark orange

[a] For the details, see the Experimental Section. [b] These rate data pertain to the initial rate of disappearance of bicyclobutanes.

the overall transformation would be a result of (1) the presence of a carbon–metal σ bond or the related bonding interactions in **33**, thereby preventing the inversion of stereochemistry, and (2) the operation of a concerted mechanism in the reductive elimination **33** → **34**.[29] Reverse process of the final step, viz., cyclopropane → metallacyclobutane conversion, is well documented.[30]

Kinetic Results and Some Mechanistic Considerations. The kinetic behavior of the catalytic reaction of 1 was investigated by using a solution of 1 and $Ni(cod)_2$ in methyl acrylate. The rate of disappearance of 1 at 0 °C was monitored by NMR measurement. When $\log [1]_0/[1]_t$ was plotted against time, t, a straight line was obtained, indicating that the catalytic reaction is a second-order process depending upon the concentration of both $Ni(cod)_2$ and 1. This result was further supported by the following facts: (a) doubling the catalyst concentration resulted in a twofold increase of the slope of the line derived from plotting $\log [1]_0/[1]_t$ vs. t; (b) the half-life of 1 was independent of its initial concentration. Then rate constants for several substituted bicyclobutanes were measured in methyl acrylate at 20 °C.[31] The results (Table I) show that the reaction of bicyclobutanes with an electron-withdrawing group at an angular position, which are expected to have a larger coordination tendency to zerovalent nickel species,[32,33] proceeds more slowly than that of alkyl-substituted bicyclobutanes. When carbomethoxy or cyano derivatives were mixed with $Ni(cod)_2$ in methyl acrylate, a dark orange to wine-red color developed without any significant reaction, which suggests the formation of intermediary metal complexes.[34,35] Such phenomena were generally observed for other strained hydrocarbons such as 1,4-bis(carbomethoxy)bicyclo[2.1.0]pentane[1] and 2,3-bis(carbomethoxy)quadricyclane[36] upon interaction with $Ni(cod)_2$ in methyl acrylate. The above results suggest that the reaction proceeds with the formation of a complex of the strained hydrocarbon 1 and Ni(0) species as shown in eq 6.[37] An electron-donative alkyl substituent may facilitate the rearrangement of strained molecules coordinated to a nickel atom.



(6)

Experimental Section

General Methods. Nuclear magnetic resonance spectra (NMR) were recorded on a Varian Model HA-100D or a JEOLCO Model C-60H spectrometer in CCl_4 unless otherwise indicated. All chemical shifts are recorded as δ values in parts per million downfield from internal tetramethylsilane. Singlet, doublet, triplet, and multiplet were abbreviated to s, d, t, and m, respectively. Infrared (IR) spectra were taken in CCl_4 by using a JASCO Model DS-402G spectrometer. Analyses by gas–liquid chromatography (GLC) were carried out on a Yanagimoto Model G-8 (FID) or a Hitachi Model 063 (FID) using nitrogen as the carrier gas. Preparative separation was performed on a Varian Model 1700 (TCD) using helium as the carrier gas. The columns used are as follows: A, 2 m × 3 mm, 5% poly(ethylene glycol) succinate on Neosorb NC; B, 2 m × 4 mm, 10% poly(ethylene glycol) 20M on Celite 545 coated with silver nitrate; C, 2 m × 3 mm, 5% poly(ethylene glycol) 4000 on Celite 545); D, 2 m × 3 mm, 5% bis(ethylene glycol) succinate on Neopak 1A; E, 4.9 m × 9 mm, 15% bis(ethylene glycol) succinate on Neopak 1A; F, 2 m × 3 mm, 30% 4-benzylbiphenyl on Chromosorb W AW; G, 2 m × 3 mm, 5% poly(ethylene glycol) adipate on Neopak 1A; H, 2 m × 3 mm, 5% bis(ethylene glycol) succinate on Neopak 1A. Mass spectra were recorded at an ionization voltage of 70 eV on a Hitachi Model RMU-6C spectrometer. For analytical thin-layer chromatography (TLC), silica gel GF_{254} precoated plates (E. Merck) of 0.25-mm thickness were used, and compounds were

(29) Collman, J. P.; Hegedus, L. S. In "Principles and Applications of Organo-transition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980, Chapter 4, and references cited therein.

(30) (a) Bailey, N. A.; Gillard, R. D.; Keeton, M.; Mason, R.; Russell, D. R. *Chem. Commun.* **1966**, 396. (b) Binns, S. E.; Cragg, R. H.; Gillard, R. D.; Heaton, B. T.; Pilbrow, M. F. *J. Chem. Soc. A* **1969**, 1227. (c) Gillard, R. D.; Keeton, M.; Mason, R.; Pilbrow, M. F.; Russell, D. R. *J. Organomet. Chem.* **1971**, *33*, 247. (d) Moriarty, R.; Chen, K.-N.; Yeh, C.-L.; Flippen, J. L.; Karle, J. *J. Am. Chem. Soc.* **1972**, *94*, 8944. (e) McQuillin, F. J.; Powell, K. G. *J. Chem. Soc., Dalton Trans.* **1972**, 2123. (f) Lenarda, M.; Ros, R.; Granziani, M.; Belluco, U. *J. Organomet. Chem.* **1974**, *65*, 407. (g) Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Chem. Soc., Chem. Commun.* **1976**, 626. (h) Brown, D. B.; Viens, V. A. *J. Organomet. Chem.* **1977**, *142*, 117. (i) Cushman, B. M.; Earnest, S. E.; Brown, D. B. *Ibid.* **1978**, *159*, 431 and references cited therein. (j) Al-Essa, R. J.; Puddephatt, R. J.; Quyser, M. A.; Tipper, C. F. H. *J. Am. Chem. Soc.* **1979**, *101*, 364.

(31) Details of the Ni(0)-catalyzed reaction of 1-methylbicyclo[1.1.0]butane, 1-(carbomethoxy)bicyclo[1.1.0]butane, and 1-(carbomethoxy)-3-methylbicyclo[1.1.0]butane will be described in a separate paper.

(32) Tolman, C. A. *J. Am. Chem. Soc.* **1974**, *96*, 2780.

(33) Yamamoto, T.; Yamamoto, A.; Ikeda, S. *J. Am. Chem. Soc.* **1971**, *93*, 3350.

(34) There has been presented considerable evidence for the existence of strained hydrocarbon–transition-metal complexes: (a) Volger, H. C.; Hogeveen, H.; Gaasbeek, M. M. P. *J. Am. Chem. Soc.* **1969**, *91*, 2137; (b) Hogeveen, H.; Nusse, B. J. *Tetrahedron Lett.* **1974**, 159; (c) Paquette, L. A.; Wilson, S. E.; Henzel, R. P.; Allen, G. R., Jr. *J. Am. Chem. Soc.* **1972**, *94*, 7761.

(35) The color change was not attributable to the complex formation between the cyano or carbomethoxyl group and Ni(0), because such phenomena could not be observed when $Ni(cod)_2$ was brought into contact with acetonitrile or ethyl acetate (see ref 32).

(36) Noyori, R.; Umeda, I.; Kawauchi, H.; Takaya, H. *J. Am. Chem. Soc.* **1975**, *97*, 812.

(37) When this mechanism is operating, the reaction adheres to the following equation

$$\frac{-d[1]}{dt} = \frac{k_2K[1][\text{catalyst}]}{K[1]+1}$$

and at higher concentration levels of 1, a zero-order dependence of 1 should be observed. The initial rates of conversion were measured as a function of bicyclobutane concentration. When the initial rate calculated from these rate constants was plotted against the initial concentration of 1, $[1]_0$, a nearly linear relationship was obtained throughout the measured concentration range (0.64–3.06 M). This means that the reaction proceeds with a small equilibrium constant, $K \leq 0.05$ M^{-1}.

visualized by irradiating with UV light or spraying with iodine vapor, 2% ceric sulfate in 2 N H_2SO_4, or 5% $KMnO_4$. Preparative TLC separations were carried out by using 1-mm-thick silica gel GF_{254} plates. Microanalyses were performed at the Department of Industrial Chemistry, Faculty of Engineering, Kyoto University. Yields were determined by GLC analyses with appropriate internal standards unless otherwise stated. All boiling points are uncorrected.

Materials. Bicyclo[1.1.0]butane (1),[38] 1,2,2-trimethylbicyclo[1.1.0]butane (7),[39] 1,2,2-trimethylbicyclo[1.1.0]butane-*3-d* (10),[40] and methyl (*Z*)-β-deuterioacrylate[41] were prepared by the literature procedures. The deuterium content at the angular position of 10 proved to be 98% by NMR analysis. Bis(1,5-cyclooctadiene)nickel(0) [Ni(cod)$_2$][42] and bis(acrylonitrile)nickel(0) [Ni(an)$_2$][43] were obtained by the standard method. Methyl acrylate (CP grade) was heated at reflux over powdered CaH_2 for 3 h under argon in the presence of a small amount of hydroquinone, distilled into a Schlenk tube under argon (dried at −90 °C) atmosphere, and stored in the dark. GR grade benzene and toluene were dried (CaH_2) and distilled. Cyclohexane (GR grade), methyl laurate (EP grade), methyl caproate (EP grade), and diethyl succinate (EP grade) were degassed by bubbling dry argon through them for 5 min and were used as standards for GLC analyses.

Nickel(0)-Catalyzed Reaction of Bicyclo[1.1.0]butane (1) with Methyl Acrylate. (a) Catalysis by Ni(an)$_2$. The catalyst was prepared in a 20-mL sealed tube from 25 mg (0.15 mmol) of $Ni(CO)_4$. The orange-red crystals were washed with three 5-mL portions of benzene, and to this was added a solution of 1 (280 mg, 5.20 mmol) in 4 mL of methyl acrylate. The tube was sealed in a nitrogen atmosphere and kept at 60 °C for 36 h. The reaction vessel was opened, and air was introduced through the reaction mixture to decompose the catalyst. Solid material was filtered by the aid of Celite 545, and the filter cake was washed with four 5-mL portions of methylene chloride. The combined filtrates were evaporated to give a colorless oil (610 mg). GLC analysis (column A, 60 °C), using methyl caproate as an internal standard, indicated that (*Z*)-1-(carbomethoxy)-2-(2-propenyl)cyclopropane (2) and its *E* isomer 3 were formed in 95% yield in a ratio of 65:35. The products 2 and 3 had retention times (t_R) of 4.8 and 6.3 min, respectively. Short-path distillation of the residue gave 552 mg (80%) of an essentially pure sample of 2 and 3. Analytically pure samples of 2 and 3 were obtained by a combination of preparative TLC (hexane–ether, 10:1) and GLC separation (column B, 97 °C, t_R = 13.2 (for 2) and 15.2 min (for 3)). Mass spectra of 2 and 3 exhibited molecular ion peaks at *m/e* 140. Other spectral properties of 2 were as follows: IR 1733, 1195, 1172 (ester), 3055, 1640, 994, 915 cm^{-1} (vinyl); NMR δ 0.7–1.2 (m, H_{3c}, H_{3t}), 1.0–1.5 (m, H_2), 1.4–1.9 (m, H_1), 2.0–2.4 (m, 2 H_4), 3.59 (s, OCH_3), 4.7–5.3 (m, 2 H_6), 5.4–6.1 (m, H_5). The following coupling constants were determined on the basis of the spectra taken in the presence of Eu(fod)$_3$: $J_{1,2} = J_{1,3t} = J_{2,3t}$ = 8.3 Hz, $J_{1,3c} = J_{2,3c}$ = 7.0 Hz, and $J_{3c,3t}$ = 4.5 Hz. Anal. ($C_8H_{12}O_2$) C, H. Spectral properties of 3: IR 1733, 1203, 1171 (ester), 3055, 1643, 993, 914 cm^{-1} (vinyl); NMR δ 0.5–0.9 (m, H_{3t}), 0.9–1.7 (m, H_1, H_2, H_3), 1.9–2.3 (m, 2 H_4), 3.60 (s, OCH_3), 4.8–5.2 (m, 2 H_6), 5.4–6.1 (m, H_5). The coupling constants determined on the basis of the Eu(fod)$_3$-aided spectra were as follows: $J_{1,2} = J_{1,3c} = J_{3c,3t}$ = 4.5 Hz, $J_{1,3t} = J_{2,3c}$ = 8.5 Hz, and $J_{2,3t}$ = 7.0 Hz. Anal. ($C_8H_{12}O_2$) C, H.

(b) Catalysis by Ni(cod)$_2$. The nickel catalyst (68 mg, 0.25 mmol) was placed in a 20-mL glass tube under a nitrogen atmosphere. To this was added a solution of 1 (270 mg, 5.0 mmol) in 15 mL of methyl acrylate at −40 °C. The tube was sealed under nitrogen, and the mixture was kept at 0 °C for 12 h. Air was introduced into the reaction mixture for 5 min at 0 °C, and the resulting precipitates were removed by filtration. Evaporation of the solvent gave a mixture of 2 and 3 in 92% yield (65:35 ratio).

Conversion of 2 and 3 to the Corresponding 1-(Carbomethoxy)-2-[(carbomethoxy)methyl]cyclopropanes 4 and 5. Ozone was introduced into a solution of 2 (50 mg, 0.36 mmol) in methanol (5 mL) at −70 °C until the olefin was consumed completely. Excess ozone was removed by introducing a gentle stream of nitrogen at this temperature. The temperature of the solution was then raised gradually up to −30 °C. Then hydrogen peroxide (30%, 2.5 mL) was added with stirring, and the temperature was again raised up to 0 °C. At this point 1 mL of 30% NaOH was added to this mixture, and the solution was further stirred at 0 °C for several hours. The reaction mixture was acidified with concentrated HCl, and the solvent was evaporated to give a crystalline mass, which was dissolved in the ether and esterified by adding a solution of diazomethane in ether to give the cis diester 4 in 55% (34 mg) yield. Similarly, 3 (35 mg, 0.25 mmol) was converted to the trans diester 5 in 58% (25 mg) yield. Spectral properties of 4: IR 1740, 1195, 1170 (ester), 3060, 1007 cm^{-1} (cyclopropane); NMR δ 0.7–1.3, 1.3–2.0 (m, cyclopropane methine and methylene protons), 2.55 (d, *J* = 6.0 Hz, CH_2COOCH_3), 3.60 (s, 2 OCH_3); mass spectrum, *m/e* 172 (M^+). Anal. ($C_8H_{12}O_4$) C, H. Spectral properties of 5: IR 1736, 1200, 1168 (ester), 3060, 1007 cm^{-1} (cyclopropane); NMR δ 0.5–0.9, 1.0–2.0 (m, cyclopropane methine and methylene protons), 2.26 (d with fine splitting of the lower field signal, *J* = 6.0 Hz, CH_2COOCH_3), 3.63 (s, 2 OCH_3); mass spectrum, *m/e* 172 (M^+). Anal. ($C_8H_{12}O_4$) C, H. The authentic sample of 4 was prepared from bicyclo[3.1.0]hex-2-ene (6) by the reported procedure.[44] The compound 5 was obtained as follows. Methyl diazoacetate (500 mg, 5.00 mmol) was added dropwise with stirring to a mixture of anhydrous $CuSO_4$ (300 mg, 1.88 mmol) and methyl 3-butenoate (4.0 g, 40 mmol) at 70 °C over a period of 4 h, and the mixture was stirred further at this temperature for 0.5 h. The catalyst was removed by filtration, and the solid was washed with three 5-mL portions of methylene chloride. The combined filtrate and washings were evaporated, and the residue was distilled in vacuo to give 0.8 g (93%) of a 25:75 mixture of 4 and 5, bp 100–120 °C (15 mm). The compounds 4 and 5 were obtained in pure form by preparative GLC (column C, 120 °C). IR and NMR spectra and GLC retention times (column A, 120 °C, t_R = 6.0 (4) and 8.5 min (5)) of 4 and 5 were identical with those of authentic specimens.

Ni(an)$_2$-Catalyzed Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane with Methyl Acrylate. A 10-mL reaction ampule was washed with 2% KOH in methanol and dried prior to use. Reaction of 1,2,2-trimethylbicyclo[1.1.0]butane (7; 113 mg, 1.18 mmol) in methyl acrylate (4 mL) in the presence of Ni(an)$_2$ (0.1 mmol) was done at 60 °C for 36 h under nitrogen. The usual workup gave 131 mg (70%) of a 65:35 mixture of (*Z*)-1-(carbomethoxy)-2-(2,3-dimethyl-2-butenyl)cyclopropane (8) and its *E* isomer 9. The analytical samples of 8 and 9 were obtained by preparative TLC (hexane–benzene, 1:1, three developments). Both adducts showed strong IR absorptions at 1735 (ester carbonyl), 1440, and 1390 cm^{-1}. Other spectral properties of 8 were as follows: NMR δ 0.7–1.9 (m, cyclopropane protons), 1.67 (s, 3 CH_3), 2.22 (d, *J* = 6.0 Hz, allylic methylene), 3.65 (s, OCH_3); mass spectrum, *m/e* 182 (M^+). Anal. ($C_{11}H_{18}O_2$) C, H. For 9: NMR δ 0.5–1.8 (m, cyclopropane protons), 1.66 (s, 3 CH_3), 1.9–2.3 (m, allylic methylene), 3.60 (s, OCH_3); mass spectrum, *m/e* 182 (M^+). Anal. ($C_{11}H_{18}O_2$) C, H.

Ni(an)$_2$-Catalyzed Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane-3-*d* (10) and Methyl Acrylate. A mixture of methyl acrylate (3 mL), Ni(an)$_2$ (0.38 mmol), and a solution of 10 in decalin (0.5 mL, 40 mg (0.41 mmol) of 10) was placed in a 20-mL ampule under nitrogen and kept at 60 °C for 40 h with occasional shaking. After the usual workup distillation of the crude product gave 200 mg of colorless oil (boiling point up to 100 °C (20 mm)) in which the two products 11 (R_f 0.34) and 12 (R_f 0.30) were detected (TLC analysis; ether–hexane, 1:10). Purification by TLC (ether–hexane, 1:15, three developments) gave pure *Z* isomer 11 (13.7 mg, 18%) and *E* isomer 12 (5.8 mg, 8%). The structures of 11 and 12 were determined by comparing their NMR spectra with those of undeuterated compounds 8 and 9 (see paragraph at the end of paper about supplementary material). When the spectra of the *Z* isomers 8 and 11 were com-

(38) Sieja, J. B. *J. Am. Chem. Soc.* **1971**, *93*, 130.
(39) Scattbøl, L. *Tetrahedron Lett.* **1970**, 2361.
(40) Moore, W. R.; Taylor, K. G.; Müller, P.; Hall, S. S.; Gaibel, Z. L. F. *Tetrahedron Lett.* **1970**, 2365.
(41) Majerski, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 665.
(42) Bogdanovič, B.; Kroner, K.; Wilke, G. *Justus Liebigs Ann. Chem.* **1966**, *699*, 1.
(43) Schrauzer, G. N. *Chem. Ber.* **1961**, *94*, 642.
(44) Roth, W. R. *Justus Liebigs Ann. Chem.* **1964**, *671*, 10.

pared, the doubletlike signal at δ 2.22 for the methylene protons of 8 changed to a broad singlet in the latter deuterated product. These signals showed no change in the relative intensity. Similarly, in going from the *E* adduct 9 to 12, the two-proton multiplet (AB part of ABM system) appearing at δ 2.06 was replaced by a broad singlet.

Ni(cod)$_2$-Catalyzed Reaction of Bicyclo[1.1.0]butane and Methyl (*Z*)-β-Deuterioacrylate. Ni(cod)$_2$ (22.8 mg, 0.83 mmol) was placed in a glass tube at −60 °C under argon, and to this was added a mixture of bicyclobutane (159 mg, 2.69 mmol), methyl (*Z*)-β-deuterioacrylate (511 mg, 5.88 mmol), and toluene (0.5 mL). The homogeneous orange-yellow mixture was kept at 32 °C for 24 h. After removal of the decomposed catalyst, unchanged deuterated acrylate was recovered with toluene by distillation with a ball-tube distillation apparatus at 50–60 °C (150 mm). Then a mixture of 16 and 17 (252 mg, 62%) was obtained at 100–110 °C (18 mm) as a colorless oil. GLC (column D, 70 °C) indicated that 16 (t_R = 14.0 min) and 17 (t_R = 18.0 min) were formed in a 60:40 ratio. Analytically pure samples were obtained by preparative GLC (column E, 110 °C). For 16: NMR δ 1.00 (t, J = 8.0 Hz, H_{3t}), 1.1–1.4 (m, H_2), 1.70 (t, J = 8.0 Hz, H_1), 1.9–2.6 (m, 2 H_4), 3.60 (s, OCH_3), 4.8–5.3 (m, 2 H_6), 5.5–6.0 (m, H_5). For 17: NMR δ 0.67 (dd, J = 8.5, 7.0 Hz, H_{3t}), 1.2–1.6 (m, H_1, H_2), 1.9–2.3 (m, 2 H_4), 3.60 (s, OCH_3), 4.8–5.2 (m, 2 H_6), 5.5–6.1 (m, H_5) (see the paragraph at the end of the paper about supplementary material). NMR analysis of the recovered methyl (*Z*)-β-deuterioacrylate indicated that no cis–trans isomerization had occurred during the catalytic reaction.

Ni(an)$_2$-Catalyzed Reaction of 1 with Dimethyl Fumarate. A solution of 1 (96.3 mg, 1.78 mmol) and dimethyl fumarate (500 mg, 3.47 mmol) in benzene (5 mL) was added to Ni(an)$_2$ (prepared from Ni(CO)$_4$; 25 μL, 32.8 mg, 0.192 mmol) in a 10-mL glass ampule under nitrogen, and the mixture was kept at 60 °C for 48 h. After removal of the decomposed catalyst by filtration, the organic solution was concentrated to give 0.58 g of a colorless liquid. GLC analysis (column A, 110 °C, methyl parmitate as a standard) indicated that 18 (t_R = 12.0 min) and 19 (t_R = 21.0 min) were formed in a 35% combined yield in a ratio of 55:45. Analytical TLC (ether–hexane, 1:2) showed that apart from the starting dimethyl fumarate (R_f 0.20), 18 (R_f 0.26) and 19 (R_f 0.16) were the only detectable products. Preparative TLC (one development with 1:5 ether–hexane and two developments with 1:2 ether–hexane) separation followed by short-path distillation (bp 100–120 °C (1 mm)) gave analytically pure samples of 18 and 19. Compound 18 had the following spectral properties: IR 1730, 1195, 1175 (ester), 3060, 1643, 992, 917 cm^{-1} (vinyl); NMR δ 1.5–2.5 (m, cyclopropane methine and allylic methylene), 3.62 (s, 2 OCH_3), 4.8–5.2 (m, $CH{=}CH_2$), 5.4–6.1 (m, $CH{=}CH_2$); mass spectrum, m/e 198 (M^+). Anal. ($C_{10}H_{14}O_4$) C, H. Compound 18 was converted to 23 by ozonolysis followed by esterification as described for the conversion of 2 to 4. Spectral data of 23: IR 1743, 1730, 1193, 1167 cm^{-1} (ester); NMR δ 1.8–2.7 (m, cyclopropane methines), 2.65 (d, J = 7.0 Hz, CH_2COOCH_3), 3.61 (s, OCH_3), 3.66 (s, 2 OCH_3). Anal. ($C_{10}H_{14}O_6$) C, H. For 19: IR 1740, 1190, 1173 cm^{-1} (ester); NMR δ 2.0–2.5 (m, allylic methylene, CH_2COOCH_3), 2.5–3.0 (m, allylic methine, $CHCOOCH_3$), 3.61 (s, 2 OCH_3), 5.66 (m, CH=CH); mass spectrum, m/e 198 (M^+). Anal. ($C_{10}H_{14}O_4$) C, H. The product 19 was converted to dimethyl 3,4-bis(carbomethoxy)adipate[45] by ozonolysis followed by oxidative workup and esterification of the resulting acid with diazomethane: IR 1742, 1200, 1165 cm^{-1} (ester); NMR δ 2.1–3.5 (m, methine and methylene protons), 3.60 (s, 2 OCH_3), 3.65 (s, 2 OCH_3); mass spectrum, m/e 234 (M^+).

Ni(an)$_2$-Catalyzed Reaction of 1 with Dimethyl Maleate. To Ni(an)$_2$ (0.19 mmol) placed in a 20-mL ampule was added a solution of 1 (120 mg, 2.2 mmol) in dimethyl maleate (1.8 g, 12.5 mmol) under argon. The tube was sealed and kept at 40 °C for 60 h. GLC analysis (column A, 125 °C) of the mixture indicated that 1:1 adducts 18 (t_R = 11.5 min), 20 (t_R = 25.0 min), and 21 (t_R = 28.0 min) were produced in 31% combined yield in a ratio of 6:6:88. Analytical samples of these products were obtained by preparative TLC (ether–hexane, 1:5, three developments). For 20: IR 1736, 1200, 1162 (ester), 3055, 1640, 992, 914 cm^{-1} (vinyl); NMR δ 1.1–1.7 (m, $CHCH_2CH{=}CH_2$), 1.9–2.3 (m, 2 $CHCOOCH_3$), 2.4–2.7 (m, $CH_2CH{=}CH_2$), 3.61 (s, 2 OCH_3), 4.8–5.2 (m, $CH{=}CH_2$), 5.5–6.0 (m, $CH{=}CH_2$); mass spectrum, m/e 198 (M^+). Anal. ($C_{10}H_{14}O_4$) C, H. For 21: IR 1738, 1202, 1164 (ester), 3060, 1643, 995, 918 cm^{-1} (vinyl); NMR δ 1.6–2.3 (m, cyclopropane protons), 3.59 (s, 2 OCH_3), 4.8–5.3 (m, $CH{=}CH_2$), 5.4–6.0 (m, $CH{=}CH_2$); mass spectrum, m/e 198 (M^+). Anal. ($C_{10}H_{14}O_4$) C, H. The products 20 and 21 were converted to triesters 22 and 24, respectively, by successive ozonolysis, oxidative workup, and esterification with diazomethane. Physical properties of 22: IR 1743, 1197, 1168 cm^{-1} (ester); NMR δ 1.6–2.3 (m, cyclopropane methines), 2.84 (d, J = 7.0 Hz, methylene), 3.62 (s, 3 OCH_3). Anal. ($C_{10}H_{14}O_6$) C, H. For 24: IR 1742, 1200, 1165 cm^{-1} (ester); NMR δ 1.8–2.5 (m, methine and methylene protons), 3.63 (s, 3 OCH_3). Anal. ($C_{10}H_{14}O_6$) C, H.

Preparation of the Authentic Samples of 22–24. The authentic samples of 22 and 23 were obtained from methyl *endo*- and *exo*-6-(carbomethoxy)bicyclo[3.1.0]hex-2-enes (25 and 26) by ozonolysis followed by the usual workup and esterification of the acid with diazomethane, respectively. The starting olefins 25 and 26 were prepared as follows.[46] A solution of cyclopentadiene (4.0 mL) and methyl diazoacetate[47] (1.0 g, 10 mmol) in pentane (10 mL) was placed in a Pyrex tube and irradiated with a 200-W high-pressure mercury lamp with a $CuSO_4$ solution as a filter for 15 h. The solvent was evaporated, and the residue was distilled in vacuo. A fraction (boiling point up to 120 °C (1.5 mm)) was collected to give a mixture of 25 and 26 (4.9 g) contaminated with a large amount of dicyclopentadiene. TLC purification (benzene, three developments) afforded pure samples of 25 (30 mg, 2% yield) and 26 (415 mg, 30% yield). The authentic samples of 23 and 24 were obtained by the following procedure. Methyl (dimethylsulfuranylidene)acetate[48] (1.6 g, 12 mmol) was placed in a 30-mL two-necked flask equipped with a reflux condenser and a nitrogen inlet tube. The top of the condenser was connected to a bubbler. The system was flushed with dry nitrogen, and to this were added methylene chloride (12 mL) and dimethyl glutaconate[49] (1.9 g, 12 mmol). The resulting pale yellow solution was heated at reflux for 18 h. The solvent was evaporated, and the residue was distilled in vacuo to give a colorless oil: 1.0 g; bp 100–130 °C (0.1 mm). Preparative TLC (repeated developments with ether–hexane, 1:4, 1:3, and 1:2 (twice)) gave pure samples of 23 (R_f 0.59) and 24 (R_f 0.40).

Isomerization of 20 and 21 to 18. To a mixture of 20 and 21 (1:1 ratio, 2 μL) and methyl parmitate (1 μL, GLC reference) in dry dimethyl sulfoxide (5 μL) was added a 3 M solution of $(CH_3)_3COK$ in dimethyl sulfoxide (10 μL), and the mixture was allowed to stand at room temperature for 3 h. GLC analysis (column A, 130 °C) indicated that about 95% of 20 and 21 isomerized to 18.

NMR Study of the Kinetics of the Ni(0)-Catalyzed Reaction of Bicyclo[1.1.0]butane (1) with Methyl Acrylate. Into an NMR tube surrounded by a dry ice–methanol bath (−70 °C) were introduced 0.50 mL of the standard solution (0 °C) of Ni(cod)$_2$ (6.19×10^{-2} M) in methyl acrylate and 0.50 mL of a solution (0 °C) of 1 (1.28 M) and benzene (0.67 M, internal standard) in the same solvent, thus giving a solution of the catalyst (3.10×10^{-2} M), 1 (0.64 M), and benzene (0.34 M) in methyl acrylate. The tube was sealed under argon and kept at −70 °C. The tube was shaked vigorously for 1 min in an ice–water bath to ensure complete mixing and then was inserted into the probe of the 60-MHz NMR spectrometer which had been kept at 0 °C. The rate of disappearance of 1 was measured at appropriate intervals by integrating NMR signals due to benzene protons and angular protons of 1. The plots of log $[1]_0/[1]_t$ vs. time (seconds) were linear. The rate constant k (1.38×10^{-3} M^{-1} s^{-1}) was calculated from the slope of the line. Then the rate constants were obtained by varying initial concentration (0.64–3.06 M) of 1, and the initial

(45) (a) Alder, K.; Schumacher, M. *Justus Liebigs Ann. Chem.* **1949**, *564*, 96. (b) Avram, M.; Dinulescu, I. G.; Dinu, D.; Mateesen, G.; Nenitzesen, C. D. *Tetrahedron* **1963**, *19*, 309.

(46) (a) Warkentin, J.; Singleton, E.; Edgar, J. F. *Can. J. Chem.* **1965**, *43*, 3456. (b) Garin, D. L.; Henderson, K. O. *Tetrahedron Lett.* **1970**, 2009.

(47) Womack, E. B.; Nelson, A. B. "Organic Syntheses"; Wiley: New York, 1955; Collect. Vol. III, p 392.

(48) Payne, G. B. *J. Org. Chem.* **1967**, *32*, 3351.

(49) Schaeffer, H. J.; Baker, B. R. *J. Org. Chem.* **1958**, *23*, 625.

rates of conversion of 1 were calculated on this basis.

Kinetic Study of the $Ni(cod)_2$-Catalyzed Reaction of 1 and Methyl Acrylate. This experiment is illustrative for kinetic measurements of Ni(0)-catalyzed reaction of bicyclobutanes and methyl acrylate at 25 °C. Twelve 20-mL reaction ampules were equipped with serum caps and flushed with argon for 2.5 min. Into each tube was placed $Ni(cod)_2$ (14.3 ■ 0.3 mg, 5.18×10^{-2} mmol), and the vessel was again flushed with argon for 2 min at -50 °C. To this were added methyl acrylate (5.0 mL) and a solution (5 mL) of 1 (7.10×10^{-2} M) and cyclohexane (5.87×10^{-2} M) in methyl acrylate by using hypodermic syringes. The reaction tube was flushed with argon for 1 min at -50 °C and sealed. The reaction vessels were placed in a constant-temperature bath kept at 25.0 ± 0.1 °C for a time and shaked vigorously for 1.5 min to dissolve the catalysts. The resulting orange-yellow solutions were kept at this temperature for a specified time and then cooled to -60 °C. After each tube was opened, bis(diphenylphosphino)-ethane (diphos; 40 mg, 0.10 mmol) was added to the mixture to quench the reaction. It was then exposed to air at -30 °C for 2 h, and the pale yellow solution was subjected to GLC analysis (column F, 35 °C, 15 mL/min, t_R = 3.8 (1) and 15.2 min (cyclohexane)) to determine the quantity of the unchanged 1. The rate constant calculated on the basis of the experiments is given in Table I.

Kinetic measurements of $Ni(cod)_2$-catalyzed reaction of 1-methylbicyclo[1.1.0]butane (35) and methyl acrylate were carried out in a similar manner by using initial bicyclobutane and catalyst concentrations of 6.05×10^{-2} and 5.25×10^{-3} M, respectively. The quantity of the unreacted 35 was determined by GLC (column F, 35 °C, t_R = 5.1 (35) and 15.0 min (cyclohexane)). For the trimethyl derivative 7, lower concentrations of 7 (2.24×10^{-2} M) and the catalyst (2.65×10^{-3} M) were used because of the high reaction rate. Methyl laurate was added after the workup as a GLC standard (column G, 130 °C, t_R = 14.3 (8), 15.3 (9), and 24.3 min (methyl laurate)). Relatively high initial concentrations were employed for less reactive 1-(carbomethoxy)bicyclo[1.1.0]butane (36; 6.00×10^{-2} M, and a catalyst concentration of 1.41×10^{-2} M) and 1-(carbomethoxy)-3-methylbicyclo[1.1.0]butane (37; 6.37 $\times 10^{-2}$ M, and a catalyst concentration of 1.43×10^{-2} M). GLC analysis (column H, 65 °C) of 36: t_R = 5.4 (methyl caproate), 13.3 min (36). GLC analysis (column H, 65 °C) of 37: t_R = 7.6 (methyl caproate), 17.4 min (37).

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Supplementary Material Available: NMR spectra for compounds 2, 3, 8, 9, 11, 12, 16, and 17 taken with or without added $Eu(fod)_3$ (4 pages). Ordering information is given on any current masthead page.

Synthesis of Functional Chelating Diphosphines Containing the Bis[2-(diphenylphosphino)ethyl]amino Moiety and the Use of These Materials in the Preparation of Water-Soluble Diphosphine Complexes of Transition Metals[1]

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Acylation of bis[2-(diphenylphosphino)ethyl]amine provides a flexible synthesis of functionalized chelating diphosphines. This reaction offers a route to diphosphine complexes of transition metals having a wide range of structures and physical properties and especially to water-soluble complexes. The aqueous solubility of the free ligands and of the complexes prepared from them depend on the ligand, on the metal, and on other materials (especially surfactants) present in the solution. We describe typical preparations of ligands and outline the properties of their complexes with certain transition metals.

Homogeneous catalysis and asymmetric synthesis increasingly require complex organic structures incorporating ligands capable of coordinating a transition-metal center. In earlier papers,[2-4] we described a flexible synthesis of functionalized, water-soluble, chelating diphosphines and presented examples of applications of these materials. This paper provides experimental procedures for these syntheses and outlines factors affecting the properties of the resulting materials in aqueous solutions.

Results and Discussion

All syntheses are based on bis[2-(diphenylphosphino)-ethyl]amine 1 (Scheme I).[5] This compound, isolated as a crystalline, air-stable hydrochloride, can be acylated at

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(2) Wilson, M. E.; Whitesides, G. M. *J. Am. Chem. Soc.* 1978, *100*, 306-307.

(3) Wilson, M. E.; Nuzzo, R. G.; Whitesides, G. M. *J. Am. Chem. Soc.* 1978, *100*, 2269-2270.

(4) Nuzzo, R. G.; Feitler, D.; Whitesides, G. M. *J. Am. Chem. Soc.* 1979, *101*, 3683-3685.

(5) Compound 1 was first prepared by: Sacconi, L.; Marassi, R. *J. Chem. Soc. A* 1968, 2997-3002.

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