Clearly, on the basis of previous reports and the present case, the transition state for this formally simple displacement reaction is remarkably sensitive to substituent variation in the substrate, the nucleophile, and variation of solvent.

Recent evidence from a variety of sources has begun to elucidate the importance that desolvation of attacking anions can play in nucleophilic displacements. In the present instance, we are at least dealing with nucleophiles which do not require extensive desolvation and which are probably producing completely dissociated ions in the solvents used[28] at our working concentrations.

References and Notes

(1) H. C. Brown, D. H. McDaniel, and O. Hafliger, "Determination of Organic Structures by Physical Methods", Academic Press, New York, N.Y., 1955.
(2) H. C. Brown, J. Chem. Soc. 1248 (1956).
(3) M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. C. Beauchamp, D. Holtz, and R. W. Taft, J. Am. Chem. Soc., 94, 1369 (1972).
(4) R. W. Taft, J. Am. Chem. Soc., 96, 1236 (1974).
(5) R. W. Taft in "Proton Transfer Reactions", E. F. Caldin, Ed., Chapman and Hall, London, in press.
(6) C. L. Liotta, E. M. Perdue, and H. P. Hopkins, Jr., J. Am. Chem. Soc., 96, 7308 (1974).
(7) D. Aue, private communication.
(8) J. M. Cook, N. L. Dassanyake, C. D. Johnson, A. R. Katritsky, and T. W. Toone, J. Chem. Soc., Perkin Trans. 2, 1069 (1974).
(9) Most of the thermodynamic data for the protonation of pyridines in solution are compared in ref 6 and 8 and E. M. Arnett and G. Scorrano, Adv. Phys. Org. Chem., in press; L. Helpler and J. Larson in "Solute-Solvent Interactions", J. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969.
(10) B. G. Ramsey and F. A. Walker, J. Am. Chem. Soc., 96, 3314 (1974).
(11) E. M. Arnett, E. J. Mitchell, and T. S. S. R. Murty, J. Am. Chem. Soc., 96, 3875 (1974).
(12) R. W. Alder, Chem. Ind. (London), 20, 983 (1973).
(13) M. G. Ahmed, R. W. Alder, G. H. James, M. L. Sinnott, and M. G. Whiting, Chem. Commun., 23, 1533 (1968).
(14) P. Beak, D. S. Mueller, and J. Lee, J. Am. Chem. Soc., 96, 3867 (1974).
(15) E. M. Arnett, W. G. Bentrude, J. J. Burke, and P. M. Duggleby, J. Am. Chem. Soc., 87, 1541 (1965).
(16) J. F. Coetzee, personal communication.
(17) H. C. Brown and G. K. Barbaras, J. Am. Chem. Soc., 69, 1137, (1947).
(18) R. W. Taft (Irvine) and L. Bell (University of Pittsburgh), unpublished work.
(19) J. Delpuech and G. Serratrice, Bull. Soc. Chim. Fr., 2500 (1974).
(20) A. Fischer, W. J. Galloway and J. Vaughan, J. Chem. Soc., 3591 (1964).
(21) H. Z. van Halban, Z. Phys. Chem., 67, 129 (1909).
(22) M. H. Abraham, Prog. Phys. Org. Chem., 11, 1 (1974); M. H. Abraham and P. L. Grellier; J. Chem. Soc., Perkin Trans. 2, 623 (1975).
(23) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, N.Y., 1941, p 417.
(24) M. M. Kreevoy, "Technique of Organic Chemistry", Volume VIII, Part II, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience, New York, N.Y., 1963, p 1382.
(25) P. Haberfield, A. Nudelman, A. Bloom, R. Romar, and H. Ginsberg, J. Org. Chem., 36, 1792 (1971).
(26) R. W. Alder, R. Baker, and J. M. Brown, "Mechanism in Organic Chemistry", Wiley-Interscience, New York, N.Y., 1971, p 50.
(27) D. C. Wigfield and B. Lem, Tetrahedron, 31, 9 (1975).
(28) G. J. Janz and R. P. T. Tomkins, "Nonaqueous Electrolytes Handbook", Vol. I, Academic Press, New York, N.Y., 1972.
(29) E. S. Amis, "Solvent Effects on Reaction Rates and Mechanisms", Academic Press, New York, N.Y., 1966.

Peri- and Regioselectivities of the Nickel(0)-Catalyzed Valence Isomerization of the 1,8-Bishomocubane System. A Molecular Orbital Consideration[1]

R. Noyori,* M. Yamakawa, and H. Takaya

Contribution from the Department of Chemistry, Nagoya University, Chikusa, Nagoya 464, Japan. Received April 23, 1975

Abstract: Skeletal isomerization of cis-9,10-dicarbomethoxypentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (4) with nickel(0) complexes has been investigated under various reaction conditions. In ordinary cases, exo- and endo-cis-9,10-dicarbomethoxytricyclo[4.2.2.0^{2,5}]deca-3,7-dienes (5 and 6) are produced in high yield. cis-9,10-Dicarbomethoxypentacyclo[4.4.0.0^{2,4}.0^{3,8}.0^{5,7}]decane (7), if any, is formed only in a small amount. The ease with which the isomerization takes place is profoundly influenced by the catalyst system employed. Bis(1,5-cyclooctadiene)nickel(0) or bis(acrylonitrile)nickel(0) alone does not effect the catalytic transformation. With the aid of appropriate ligands, such as electron-deficient olefins or triphenylphosphine, the isomerization proceeds smoothly, indicating that the formation of soluble, coordinatively unsaturated nickel(0) complexes is crucial for the isomerization of 4. By the use of the catalyst system derived from bis(1,5-cyclooctadiene)-nickel(0) and tetracyanoethylene, the dicyclopropyl isomer 7 is obtained as the major product. The production of Ni^{2+} species would be the cause of the change in the reaction course. The origin of the clean peri- and regioselectivities of the isomerization is explained in terms of the molecular orbital treatment. Judging from the shape of molecular orbitals of 1,8-bishomocubane, only the C(2)–C(5) and the structurally equivalent bonds can have a positive interaction with nickel(0) atom. The catalytic two-bond cleavage of 4 is considered to proceed by a mechanism involving the C(2)–C(5) edge-on coordination complex. The possibility of the concerted process through face-on metal coordination is ruled out.

Numerous examples have been presented of the transition metal-promoted skeletal change of strained polycyclic hydrocarbons.[2] Among a variety of hydrocarbon systems so far investigated, cubane (1) is particularly interesting in that the reaction course is dramatically dependent on the transition metal catalysts employed. Two types of symmetry-forbidden (in a formal sense) transformation can be possible with the aid of transition metals. For example, Rh(I) complexes promote the cleavage of a cyclobutane ring in a [$_\sigma2_s + _\sigma2_s$] fashion to give the tricyclooctadiene 2.[3] In the presence of Ag$^+$ ion, the cyclobutane → diolefin conversion does not take place, but instead there is obtained the

Table I. Nickel(0)-Catalyzed Isomerization of 4 under Various Reaction Conditions[a]

Ni(0) complex	Solvent	Additive	Color of soln	Temp, °C (time, h)	Conversion,[b] %	Product distribution, %[b]		
						5	6	7
Ni(COD)₂	Toluene[c]	Methyl acrylate	Wine-red	35 (36)	100	51	49	0
Ni(COD)₂	Methyl acrylate[d]	None	Wine-red	23 (19)	100	54	46	0
Ni(COD)₂	Toluene	Methyl crotonate	Yellow	39 (36)	50	47	53	0.4
Ni(COD)₂	Toluene	Dimethyl maleate	Orange	39 (36)	89	63	37	0.3
Ni(COD)₂	Toluene	Dimethyl fumarate	Orange	39 (36)	52	54	42	4
Ni(COD)₂	Toluene	Fumaronitrile	Red	39 (36)	28	48	52	0
Ni(COD)₂	Toluene	Tetracyanoethylene	Yellow[e]	39 (36)	66	8	24	68
Ni(COD)₂	Toluene	Triphenylphosphine	Wine-red	39 (36)	91	42	57	1.5
Ni(COD)₂	Toluene	DIPHOS[f]	Yellow	39 (36)	12	67	33	0
Ni(COD)₂	Toluene	P(OR)₃[g]	Yellow	39 (36)	9	66	34	0
Ni(COD)₂	Toluene[c]	Acrylonitrile	Colorless[e]	23 (48)	0			
Ni(COD)₂	Toluene[c]	None	Yellow	23 (48)	0			
Ni(AN)₂	Toluene[c]	Methyl acrylate	Wine-red	60 (48)	100	59	41	0
Ni(AN)₂	Toluene[c]	None	Colorless[e]	60 (36)	0			
Ni(AN)₂	Acrylonitrile[c]	None	Colorless[e]	35 (36)	0			
Ni(CO)₄	Benzene-d₆[c]	None	Colorless	35 (24)	0			
Ni[P(OR)₃]₃[h]	Toluene	None	Red	39 (36)	26	64	36	0

[a] Unless otherwise stated, reactions were carried out by use of 4 (0.10 mmol), Ni(0) complex (0.033 mmol), and the indicated additive (0.10 mmol) in 3.0 ml of the solvent. No isomerization took place in the absence of the Ni(0) complex. [b] Obtained by GLC analysis. [c] For the details of the reaction, see Experimental Section. [d] The reaction was done in 0.5 ml of the solvent. [e] Heterogeneous mixture. [f] Bis(diphenylphosphino)ethane. [g] Tri-o-tolyl phosphite. [h] Tris(tri-o-tolyl phosphite)nickel(0).


2   1   3
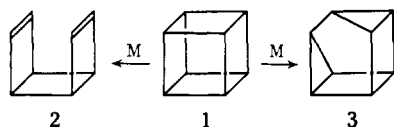
rearranged product, cuneane (3).[4] The latter reaction can be formally viewed as a bicyclo[2.2.0]hexane → dicyclopropyl conversion ([$_\sigma 2_a + _\sigma 2_a$] process). Homocubane, 1,8-bishomocubane, and their derivatives exhibit the same metal dependency of the reaction course; Rh(I) complexes cause the cyclobutane → diolefin valence isomerization,[5,6] while Ag⁺ promotes the bicyclohexane → dicyclopropyl bond-switching reaction.[7-11] In cubane, which has an O_h symmetry, the 12 strained σ bonds are structurally all equivalent, while the homo- and 1,8-bishomocubane skeletons of C_{2v} symmetry consist of four and five different types of carbon–carbon σ bonds, respectively. Therefore, the observed regioselectivity of the reaction of the latter[5-8,10,11] should be associated with the lower degree of symmetry incorporated in the molecule. Thus, the system serves as a good model for understanding the nature of the interaction between transition metal and strained carbon–carbon σ bond. This paper describes the nickel(0)-catalyzed reaction of a bishomocubane and a straightforward explanation on the origin of the reaction selectivities.[12]

Results and Discussion

Nickel(0)-Catalyzed Valence Isomerization of cis-9,10-Dicarbomethoxypentacyclo[4.4.0.0²,⁵.0³,⁸.0⁴,⁷]decane (4). A toluene solution of the 1,8-bishomocubane 4, methyl acrylate (1:1 mole ratio), and a small amount of bis(1,5-cyclooctadiene)nickel(0) [Ni(COD)₂] placed in a nitrogen-filled glass tube exhibited characteristic wine-red color. When the solution was allowed to stand at 35° for 36 h, a 51:49 mixture of 5 and 6 was obtained in quantitative yield (Scheme I). Bis(acrylonitrile)nickel(0) [Ni(AN)₂] can be used in place of Ni(COD)₂. Structures of 5 and 6 were determined by comparison of their spectral and chromatographic properties with those of authentic specimens obtained by the Rh(I)-catalyzed reaction of 4.[13] Neither the dicyclopropyl isomer 7 nor methyl acrylate adduct of 4[14] was detected in the product mixture. Thus, the Ni(0) cata-

Scheme I

5   6

7

Z = COOCH₃
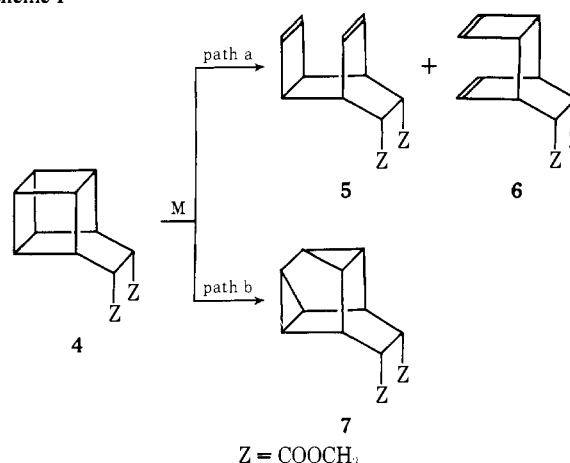
lysts derived from Ni(COD)₂ and methyl acrylate have proved to cause the isomerization of 4 exclusively via path a.

The catalyzed reactions of 4 were then carried out with Ni(0) complexes under various conditions, and the products were analyzed carefully by GLC. The results are summarized in Table I. The dienes 5 and 6 were usually, with one exception, the major products, and the dicyclopropyl derivative, if any, was obtained only in a small amount. The product distribution was not affected significantly by the reaction conditions. Notably, the ease of the isomerization with nickel complexes was profoundly influenced by the added ligands, however. Ni(COD)₂ complex alone did not cause the isomerization. Upon addition of electron-deficient olefins or triphenylphosphine, a smooth isomerization occurred. Bis(diphenylphosphino)ethane, a bidentate phosphine ligand, and tri-o-tolyl phosphite were not as effective as triphenylphosphine but still activated the Ni(0) catalyst. Attempted reaction with Ni(AN)₂ or nickel tetracarbonyl in hydrocarbon solvents resulted in recovery of the starting material 4. The failure with Ni(AN)₂ catalyst could be due to its insolubility in hydrocarbons. The lack of reactivity of soluble Ni(COD)₂ or Ni(CO)₄ would be ascribed to the fact that the affinity of the saturated compound 4 for Ni(0) atom is not high enough to displace the cyclooctadiene or

carbonyl ligands of the metal complexes. Tertiary phosphines and phosphites are widely used to replace olefinic ligands coordinated to transition metals. Methyl acrylate and other electron-deficient olefins are also known to have a tenacity with which Ni(0) binds the ligand,[15,16] and the production of soluble coordinatively unsaturated Ni(0) complexes[17] seems to be the essential sequence for the catalytic isomerization of **4**. The coordinatively unsaturated Ni(0) complex, tris(tri-o-tolylphosphite)nickel(0),[18] exhibited moderate catalytic reactivity. Thus, the additives used, though not participating in the reaction products, appear to be playing an important role in modifying the catalyst activity. Finally, the effect of tetracyanoethylene (TCNE), coexistent in the catalytic system, is worthy to note. The addition of TCNE caused a considerable change in the product distribution and produced the dicyclopropyl derivative **7** as the major isomer.

Since no deep-color development was observed upon mixing the diene **5** or **6** with $Ni(COD)_2$ in toluene or methyl acrylate, the deep coloration observed with the reaction systems causing the rapid valence isomerization may be responsible for the presence of certain Ni(0)–σ bond interaction. Similar phenomena were observed with the Ni(0)-catalyzed reactions of certain bicyclo[1.1.0]butane and bicyclo[2.1.0]pentane derivatives[19] and Rh(I)-catalyzed isomerization of a quadricyclane.[20]

The Periselectivity of the Catalyzed Reaction of 4. The transition metal-promoted rearrangements of **4** are classified into two types (Scheme I), the two-bond cleavage reaction leading to the dienes **5** and **6** (path a) and the bond-switching reaction to afford the dicyclopropyl derivative **7** (path b). Dauben and Kielbania have examined the catalytic reaction of **4** extensively with various Rh(I) and Pd(II) complexes and concluded that the electronic nature of the metal, as well as the property of the ligand, is guiding the reaction course; metals having distinct ability of oxidative addition such as Rh(I) complexes facilitate the reaction via path a, and, on the other hand, metals with great σ acceptor ability, such as Ag^+ ion, favor the conversion via path b.[5,6] Particularly interesting is the dual behavior of Pd(II) complexes which is affected profoundly by the electronic nature of the ligands. Recently Paquette et al. further pointed out that choice of the reaction course is delicately dependent on the substituents on the strained hydrocarbon skeleton as well.[6,11] Since the Ni(0) atom is known to be more electropositive than Rh(I) species,[18,21] the present observation for the catalyses of **4** gives further credence to these interpretations.

The isomerization with $Ni(COD)_2$ and TCNE favors the formation of the dicyclopropyl derivative **7** (path b). This is not so surprising, because under these conditions electron transfer from the Ni(0) atom to the cyano olefins is known to occur, producing Ni^{2+} and TCNE·⁻ ions.[22] In this case, therefore, the catalytic system is considered to contain Ni^{2+} species which can act as the Ag^+ ion does. In other usual cases, the reaction course forming the dienes **5** and **6** (path a) is predominant, but the certain systems indeed produce a small amount of **7**. At present it is not clear whether the extent of the formation of this minor component is correlated to the electronic nature of the major catalyst species coordinated with electron-deficient olefins or phosphine (or phosphite) ligands, or the production is actually due to the presence of some paramagnetic impurities in the reaction system.[23]

The Regioselectivity of the Transition Metal Catalyses. Dauben and Kielbania assumed that the Rh(I)-catalyzed reaction, **4** → **5** + **6** (path a), is proceeding through a bidentately coordinated complex of type **8**, whereas metals with strong σ accepting ability, such as Ag^+ and Pd(II),


8   9
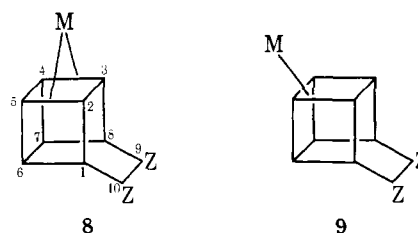
promote rearrangement, **4** → **7**, via an edge-on coordination complex **9** which gives an intermediate with an electron-deficient center.[5] This consideration is in accord with the experimental findings but not sufficient enough to explain the origin of the clean regioselectivity attending the isomerization of **4**. Here, the metal complexation at C(2)–C(5) and/or the diagonally situated equivalent bond, if operating, seems somewhat curious in view of the well-recognized relationship between strain energy and coordination tendency.[24] Since an x-ray analysis of a bishomocubane derivative indicated that these bonds are less distorted from the normal structure than the C(4)–C(5) bond (particularly, the bond-angle distortion),[8] the latter bond might be expected to be more susceptible to metal coordination from this point of view. With Ni(0) or Rh(I) complexes, three types of cyclobutane–diolefin transformation could be conceived a priori (Scheme II), but, in fact, only one process involving

Scheme II

Z = $COOCH_3$
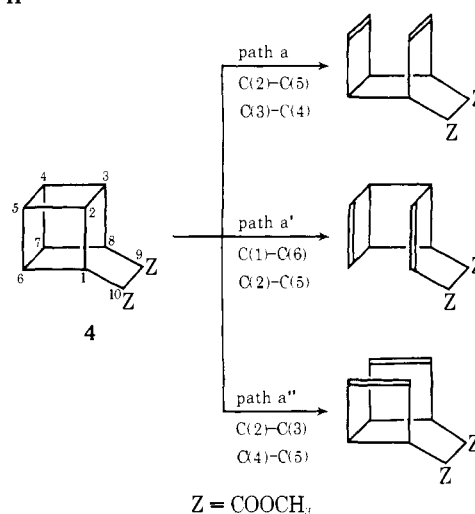
C(2)–C(5) and C(3)–C(4) cleavage (path a) is taking place specifically, no trace of products via path a′ or path a″ being obtained. The second basic point which remained to be answered is on the Ag^+-catalyzed rearrangement (path b). Detailed study by Paquette et al. indicated that the reaction goes after formation of a complex **10** by a mechanism involving the delocalized cation **11** as essential reactive intermediate (Scheme III).[11,25] Other cationic interme-

Scheme III

10   11

Z = $COOCH_3$
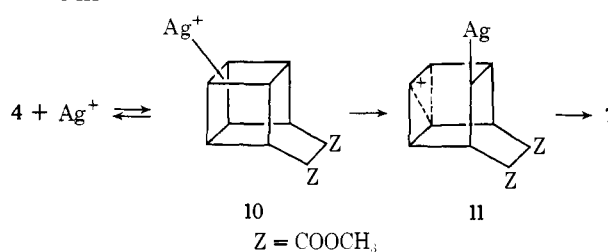
diates, if produced, may lead to products other than **7**. The reason why this cationic species **11** can be formed so specifically is of considerable interest but has as yet remained unclear.
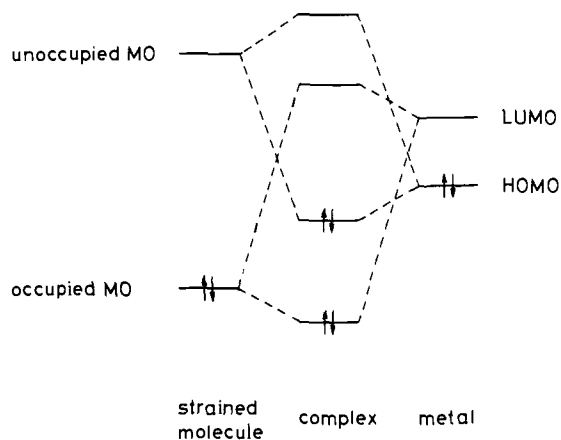
Figure 1. Correlation diagram of the energy levels of a strained molecule and a transition metal.
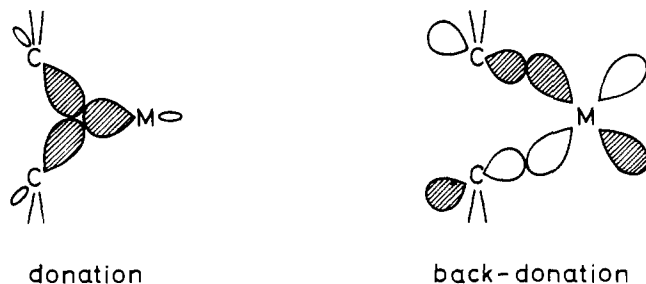

Figure 2. The edge-on interaction of a strained carbon-carbon σ bond and a transition metal.

We find we can give a new simple explanation on these matters in terms of the molecular orbital (MO) treatment, at least with the cases involving no complexity associated with steric factors. The selectivities of the catalyzed reaction of **4**, we postulate, result primarily from the site of initial metal approach; as well as the nature of the resulting edge-on complexes.

In order to elucidate the feature of the metal–strained hydrocarbon interaction, both the electronic nature of the metal and detailed structure of the hydrocarbon should be taken into account. As shown in Figure 1, the principal bonding interaction between a transition metal and a strained hydrocarbon molecule is based on overlapping of a high-lying occupied molecular orbital of the strained molecule and the lowest unoccupied molecular orbital (LUMO) of the metal (σ interaction) and a low-lying unoccupied molecular orbital of the strained molecule and the highest occupied molecular orbital (HOMO) of the metal (π interaction).[26] Figure 2 illustrates schematically the σ donation from a carbon-carbon bond to a metal and the π back-donation from the metal to the carbon-carbon bond in an edge-on complex. The MO contribution of the carbon-carbon bond that participates in the metal π complexation must be bonding in nature in any appropriate high-lying filled orbital and, at the same time, must have a strong antibonding character in a low-lying vacant orbital. Thus the mode of the interaction and the stability of the π complex are governed by both shape and energy levels of these MO's.[27] If the phases of the MO's coincide with each other, the LUMO of transition metals or the ions, as usual, can accept readily an electron from the high-lying MO of the strained hydrocarbon ligand. Here, when the metal has a substantially high-lying HOMO, the back-donation from the metal to an unoccupied MO of the hydrocarbon is facilitated, thereby stabilizing the π-type complex (case 1). Ni(0) (3d^{10}) has eminent π donor ability (HOMO -7.6 eV

5a$_2$ E = -1.0 eV

6b$_2$ (LUMO) E = -2.1 eV

7b$_1$ (HOMO) E = -11.8 eV

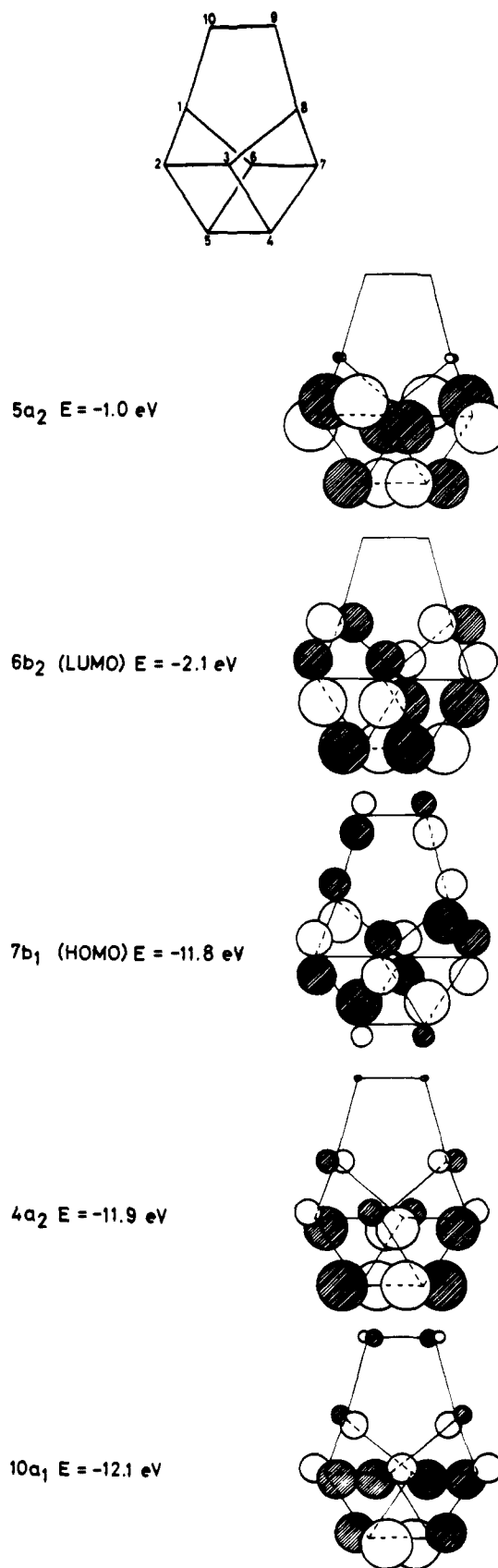4a$_2$ E = -11.9 eV

10a$_1$ E = -12.1 eV

Figure 3. Selected high-lying occupied and low-lying unoccupied MO's of 1,8-bishomocubane.

and LUMO -4.8 eV[15]) and provides a typical example of this type.[15,16] Rh(I) species (4d^8) could also be categorized into this case.[18,21] On the other hand, when the metal HOMO is not high enough to have an interaction with an appropriate unoccupied MO of the ligand, only the σ inter-
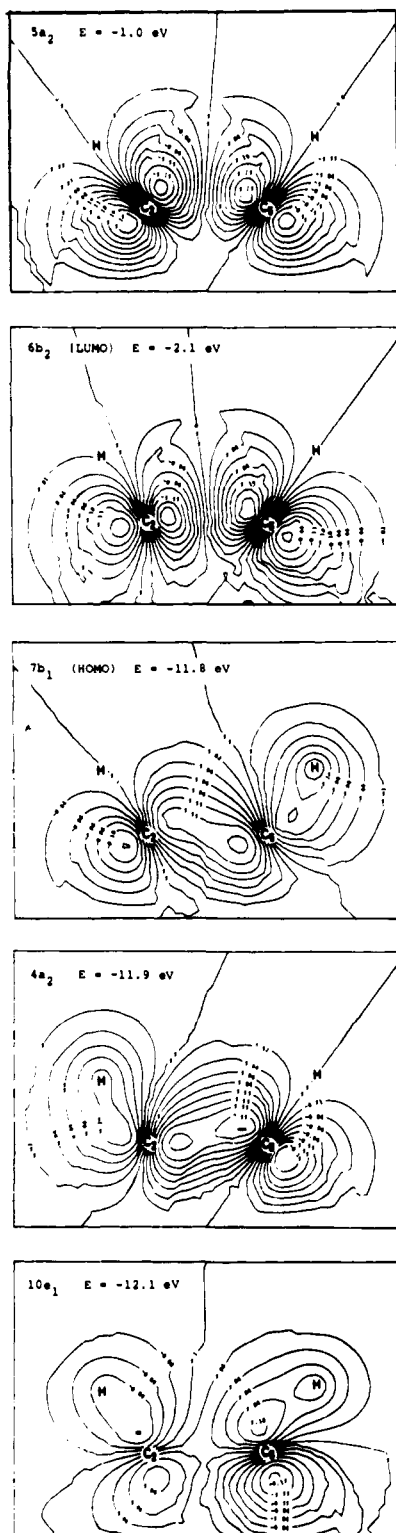
Figure 4. Contour maps of selected MO's of 1,8-bishomocubane around the C(2)–C(5) bond in the plane bisecting the C(4)–C(5)–C(6) angle.
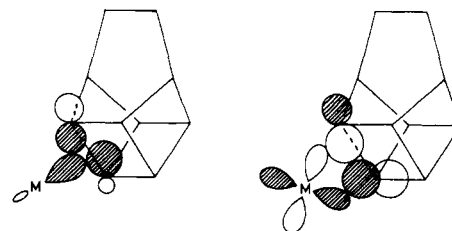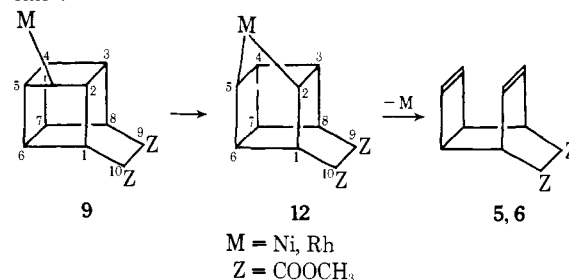

Figure 5. The HOMO–LUMO interactions between metal complexes and 1,8-bishomocubane at the C(2)–C(5) bond. The metal is situated in the plane bisecting the C(4)–C(5)–C(6) angle.

of HOMO and LUMO of reagent and substrate.[27] In the saturated hydrocarbon systems, unlike ordinary π-electron systems, there are several σ levels which are close in energy to these frontier MO's. Therefore, the nature of interactions with these orbitals should be carefully examined as well. The MO calculations on 1,8-bishomocubane were performed by the extended Hückel (EH) method. Figure 3 shows the energy levels and three-dimensional views of some selected high-lying occupied MO's and low-lying unoccupied MO's. Apparently, among the strained carbon–carbon bonds, the C(2)–C(5) and the structurally equivalent bonds have MO shapes suitable for the edge-on π complexation, but other bonds do not satisfy the prerequisite for the metal coordination. The orbital symmetries rule out positive interactions of a metal with a C(2)–C(3), C(4)–C(5), or C(6)–C(7) bond. Detailed contour maps of the orbitals around the C(2)–C(5) bond in the plane bisecting the C(4)–C(5)–C(6) angle are given in Figure 4. The HOMO is set up for good σ donation to a metal atom attacking the C(2)–C(5) bond. The next HOMO is situated at a slightly lower level and shows similar MO appearance around the C(2)–C(5) bond.[29] The LUMO appears to be nicely set up for π back-donation from the metal approaching the C(2)–C(5) bond. The next LUMO has also antisymmetric nature around the C(2)–C(5) bond. However, this MO is far removed in energy and hence is not suitable for the metal interaction. Consequently, it is not unreasonable to assume simply that Ni(0) or Rh(I) species (case 1) cause the maximum MO overlapping with bishomocubane at the C(2)–C(5) bond through the HOMO–LUMO interactions, as illustrated in Figure 5. Thus only this MO approach can rationalize why these metals have an initial interaction with C(2)–C(5) or the equivalent bonds and not with other bonds.

The bishomocubane ligand in the complex 9 undergoes oxidative addition to the π-donating metal atom to produce the intermediate 12 containing carbon–metal σ bonds,[30,31] which in turn experiences the second carbon–carbon bond breakage selectively at C(3)–C(4), yielding the final products 5 and 6 (Scheme IV). Although the reactive intermedi-

action is dominant in stabilizing the hydrocarbon complex (case 2). The Ag$^+$ ion (4d^{10}, HOMO -21.5 eV, and LUMO -7.6 eV[21]) is representative of this case. Pd(II) species (4d^8) are situated electronically intermediate between these two extreme cases. With such metals, the bonding nature, as well as the complex stability, is subtly influenced by other ligands attached to the metal.[5,28]

According to the frontier orbital theory, reaction courses are controlled primarily by the interaction between two sets

Scheme IV

M = Ni, Rh
Z = COOCH$_3$

ate 12 contains two metallocyclopentane structures, the metathetic transformation involving the metallocycle M–C(2)–C(1)–C(6)–C(5) does not occur because the ring structure, particularly at the C(1) position, is distorted con-
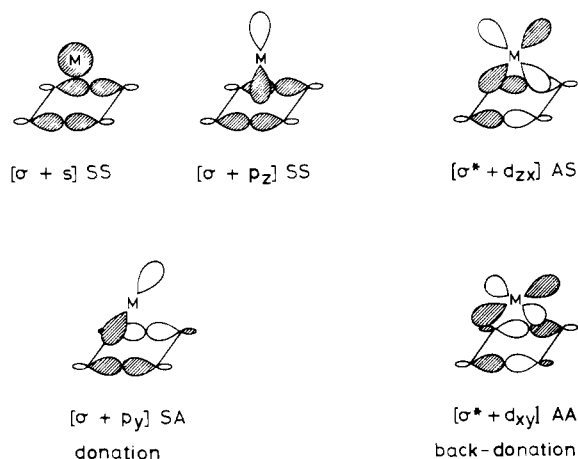
[σ + s] SS   [σ + p_z] SS   [σ* + d_zx] AS

[σ + p_y] SA   [σ* + d_xy] AA

donation   back-donation

Figure 6. The face-on interaction in a d^{10} metal complex.

SS   AS
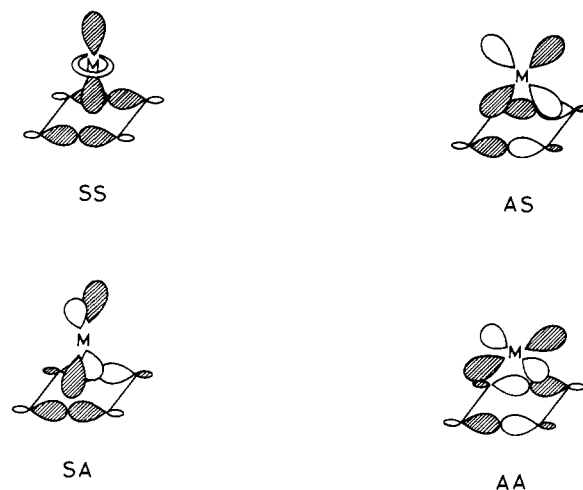

SA   AA

Figure 7. The face-on interaction in a d^8 metal complex.

siderably from the ideal geometry, as can be easily seen from molecular models.[32]

Mango and Schachtschneider have claimed that the transition metal-catalyzed cyclobutane–diolefin valence isomerization proceeds in a concerted manner through a bidentate cyclobutane coordination complex (Scheme V).[2d,33] The

Scheme V
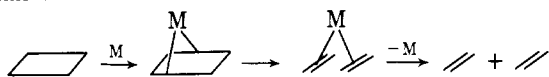
face-on coordination to a four-membered ring may be feasible with d^{10} or d^8 metals. The modes of the orbital interactions are given in Figures 6 and 7.[34] Judging from Figure 3, however, the orbitals appear to spread in directions appropriate to only formation of the unidentate edge-on coordination complex **9**. In view of the MO symmetry and direction of spatial development (see the C(2)–C(3)–C(4)–C(5) surface), one cannot find out any appropriate sets of MO's built up for the alternative face-on complexation. Therefore, obviously the concept outlined in Scheme V cannot be applied to the reaction of a bishomocubane skeleton. Any concerted mechanisms involving a unidentate face-on complex are not likely to be operating either.

The Ag^+-promoted rearrangement via path b can be also understood by looking at the shape of a frontier orbital of bishomocubane. The Ag^+ LUMO (5s atomic orbital) can interact strongly with the bishomocubane HOMO at the bonding C(2)–C(5) position to form the complex **10** (case 2). In the hydrocarbon HOMO, as illustrated in Figures 3 and 4, the C(2) and C(5) contributions are not equal; the orbital contribution at C(2) is greater and spatially suitable for the metal interaction compared with that of C(5). Therefore, the initially formed Ag^+ complex, even if formulated simply as **10**, has considerable character of **13**. Thus

13
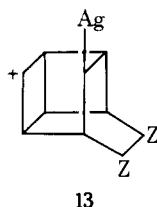
the metal ion–hydrocarbon interaction leads to the site selective carbocation generation. Subsequent ejection of Ag^+ species from **11** produces the formal cyclobutyl → cyclopropylcarbinyl rearrangement product **7** (Scheme III).[35]

In conclusion, the observed clean peri- and regioselectivities in the transition metal catalyzed reaction of **4** can be

simply, but entirely, accounted for by the present MO treatment.

Details of Molecular Orbital Calculation of Pentacyclo[4.4.0.0^{2,5}.0^{3,8}.0^{4,7}]decane (1,8-Bishomocubane)

The MO computation based on the extended Hückel (EH) calculation[36] was done using the Fortran program. Computation was performed on a FACOM 230-60 computer at the Computation Center of Nagoya University.

The geometry of the carbocyclic skeleton was based on the x-ray diffraction data reported by Dauben et al.[8] The reported values were employed for the carbon–carbon bond lengths. The bond angles were determined by a least-squares procedure using the reported values: $\angle C(1)$–C(2)–C(3), 110.8°; $\angle C(1)$–C(2)–C(5), 90.3°; $\angle C(2)$–C(3)–C(4), 89.1°; $\angle C(3)$–C(4)–C(5), 90.9°; $\angle C(3)$–C(4)–C(7), 85.0°; $\angle C(2)$–C(1)–C(10), 117.7°; $\angle C(8)$–C(9)–C(10), 110.8°; $\angle C(2)$–C(1)–C(6), 87.1°.

The following assumptions were set for hydrogen atoms: all C–H bonds were assigned a length of 1.09 Å; $\angle H$–C(9)–H and $\angle H$–C(10)–H set at 109.5° (tetrahedral angle); the H–C(9)–H and H–C(10)–H planes bisect $\angle C(8)$–C(9)–C(10) and $\angle C(1)$–C(10)–C(9), respectively, and each plane is perpendicular to the C(8)–C(9)–C(10) plane. Other angles $C(i)$–C(j)–H were set so that the total energy calculated by CNDO/2 method becomes minimum: $\angle C(1)$–C(2)–H, 118.2°; $\angle C(3)$–C(2)–H, 118.3°; $\angle C(4)$–C(5)–H, 126.0°; $\angle C(10)$–C(1)–H, 110.8°.

The schematic drawing of the MO's (Figure 3) was made according to the simplified approach suggested by Haselbach and Schmelzer.[37] Contour maps were drawn using CALCOMP Model 1136/915 XY Plotter. Coordinates of atoms in 1,8-bishomocubane were given in Table II.

Experimental Section

Gas–liquid phase chromatography (GLC) analysis was done on a Yanagimoto Model G-8 gas chromatograph equipped with a glass column packed with 5% poly(ethylene glycol succinate) on 80–120 mesh Neosorb (3 mm × 2 m) (column A) or a Hitachi Model 063 gas chromatograph equipped with a 5% diethylene glycol succinate on 80–120 mesh Neopak 1A (3 mm × 2 m) (column B), and a flame ionization detector, using nitrogen as the carrier gas. The product ratios were determined by peak area of GLC traces. Commercially available precoated silica gel plates (0.25-mm layers of E. Merck 60 F-254 silica gel) were used for analytical thin-layer chromatography (TLC). Compounds were detected on these plates by exposure to iodine vapor or spray of 2% ceric sulfate in 2 N H_2SO_4 followed by heating. Preparative TLC was done on 1.0-mm layers of E. Merck GF-254 silica gel prepared in this laboratory.

Table II. Coordinates of Atoms in 1,8-Bishomocubane

Atom	x	y	z
C(1)	1.4119	−1.3254	0.0
C(2)	2.3716	−0.7849	1.0475
C(3)	2.3716	0.7849	1.0475
C(4)	3.5139	0.7600	0.0
C(5)	3.5139	−0.7600	0.0
C(6)	2.3716	−0.7849	−1.0475
C(7)	2.3716	0.7849	−1.0475
C(8)	1.4119	1.3254	0.0
C(9)	0.0	0.7900	0.0
C(10)	0.0	−0.7900	0.0
H_1	1.4126	−2.4154	0. 0
H_2	2.4338	−1.3021	2.0049
H_3	2.4338	1.3021	2.0049
H_4	4.3962	1.3999	0.0
H_5	4.3962	−1.3999	0.0
H_6	2.4338	−1.3021	−2.0049
H_7	2.4338	1.3021	−2.0049
H_8	1.4126	2.4154	0.0
H_{9a}	−0.5209	1.1496	0.8874
H_{9b}	−0.5209	1.1496	−0.8874
H_{10a}	−0.5209	−1.1496	0.8874
H_{10b}	−0.5209	−1.1496	−0.8874

Reagent grade acrylonitrile and methyl acrylate were distilled over calcium hydride under reduced pressure in an argon atmosphere. Benzene and toluene were distilled after refluxing over sodium metal for several hours under argon and stored in Schlenk tubes. Nickel tetracarbonyl was stored under water in a refrigerator and used without further purification. Bis(acrylonitrile)nickel [Ni(AN)$_2$],[38] bis(1,5-cyclooctadiene)nickel [Ni(COD)$_2$],[39] and tris(tri-o-tolylphosphite)nickel[40] were prepared by the standard procedures. cis-9,10-Dicarbomethoxypentacyclo[4.4.0.0^{2,5}.0^{3,8}. 0^{4,7}]decane (4)[8] was synthesized by the uv irradiation of endo-cis-9,10-dicarbomethoxytricyclo[4.2.2.0^{2,5}]deca-3,7-diene (6) obtained by the esterification of the thermal cycloadduct of cyclooctatetraene and maleic anhydride,[41] mp 81.5–82.5° (from n-hexane) (lit.[13] 80–82°).

Ni(COD)$_2$-Catalyzed Isomerization of 4 into 5 and 6 in the Presence of Methyl Acrylate or Other Added Ligands. In a 20-ml glass ampule were placed 4 (310 mg, 1.00 mmol) and Ni(COD)$_2$ (27.0 mg, 0.10 mmol), and the system was filled with nitrogen by five freeze–pump–thaw cycles. Methyl acrylate (86 mg, 1.0 mmol) in toluene (1.5 ml) was added, and the tube was sealed under nitrogen. The solid materials were dissolved by shaking, and the resulting deep wine-red solution was allowed to stand at 35° for 36 h. The tube was opened, and the catalysts were decomposed by introducing a slow stream of air. The solid precipitates were removed by filtration through a pad of Celite 545. The solvent was evaporated by a rotary evaporator, and the last traces of the solvent and cyclooctadiene were removed under reduced pressure (0.1 mm at 50°) to give 325 mg of viscous oil. TLC and NMR analyses of the residue indicated that it was composed of only 5 and 6, showing that the isomerization proceeded in essentially quantitative yield. Neither the dicyclopropyl compound 7 nor 1:1 adduct of 4 and methyl acrylate was detected by NMR, GLC (column B, column temperature 180°, injection temperature 180°), and TLC analyses. Analysis by GLC (column A, column temperature 150°, injection temperature 180°, 35 ml/min) indicated that 5 and 6 were formed in a ratio of 51:49. Peaks attributed to 5 and 6 appeared with retention times of 9.4 and 15.2 min, respectively, while the authentic samples of 4 and 7 had retention times of 14.0 and 20.5 min. The pure samples of 5 and 6 were obtained by preparative TLC separation (ether-n-hexane 2:5). The compounds 5 and 6 had R_f values of 0.30 and 0.50, respectively. The diene 6 melted at 50–52°.[13] Structures of these products were confirmed by comparison of the NMR spectra, GLC, and TLC behavior with those of authentic samples obtained by the Rh(I)-catalyzed reaction of 4.[5]

Similar reactions were carried out using Ni(0) complex (0.033 mmol), 4 (0.10 mmol), and an added ligand (0.10 mmol) under the specified reaction conditions, and the results are summarized in Table I.

Isomerization of 4 by Ni(AN)$_2$ in the Presence of Methyl Acrylate. Ni(AN)$_2$ (16.0 mg, 0.1 mmol) was freshly prepared in a

20-ml ampule, and to this was added a solution of 4 (31.0 mg, 0.10 mmol) and methyl acrylate (0.5 ml) in toluene (0.5 ml) under nitrogen. The tube was sealed and the wine-red reaction mixture was kept at 60° for 48 h with occasional shaking. The vessel was opened, and after an introduction of a gentle stream of air, the resulting solid was removed by filtration. The residue was washed with three 3-ml portions of methylene chloride. The combined filtrate and washings were evaporated, and the residue was vacuum-dried at 50° (0.1 mm) to give 35.0 mg of a colorless oil. Analysis by NMR, TLC, and GLC showed that 5 and 6 were the only detectable products. The yield was quantitative, and the 5:6 ratio was 59:41.

Attempted Isomerization of 4 by Ni(COD)$_2$ or Ni(AN)$_2$ in Toluene. Ni(COD)$_2$ (12.0 mg, 0.044 mmol) was placed in a 10-ml glass ampule, and the system was flushed with nitrogen. To this was added a solution of 4 (28.0 mg, 0.090 mmol) in toluene (1.0 ml), and the tube was sealed under nitrogen. The yellow solution was allowed to stand at room temperature for 48 h. Decomposition of the nickel complex with air followed by filtration of the precipitates and evaporation of the solvent gave 36.5 mg of white solid. The NMR analysis indicated that the starting 1,8-bishomocubane (4) was recovered unchanged.

A similar experiment was carried out using 4 (31.0 mg, 0.10 mmol), Ni(AN)$_2$ (16 mg, 0.10 mmol), and toluene (0.5 ml) at 60° for 36 h. Analysis by NMR showed no trace of 5 and 6. Another experiment with 4 (20.0 mg, 0.06 mmol), Ni(AN)$_2$ (32.0 mg, 0.20 mmol), and acrylonitrile (1.0 ml) at 35° for 36 h resulted in the complete recovery of the starting diester 4 as well.

Attempted Isomerization of 4 by Ni(CO)$_4$ in Benzene-d_6. A solution of 4 (10.0 mg, 0.032 mmol) in benzene-d_6 (0.44 ml) was placed in an NMR tube under argon. To this solution was added Ni(CO)$_4$ (9.1 mg, 0.05 mmol) in the dark. The colorless solution was kept at 35° for 24 h in the dark place with occasional shaking. The NMR analysis revealed that no isomerization of 4 took place.

References and Notes

(1) Nickel-Catalyzed Reactions Involves Strained Bonds. XIII. Part XII: R. Noyori, I. Umeda, H. Kawauchi, and H. Takaya, J. Am. Chem. Soc., 97, 812 (1975).
(2) Reviews: (a) R. Pettit, H. Sugahara, J. Wristers, and W. Merk, Discuss. Faraday Soc., No. 47, 71 (1969); (b) J. Halpern, Acc. Chem. Res., 3, 386 (1970); (c) L. A. Paquette, ibid., 4, 280 (1971); (d) F. D. Mango and J. H. Schachtschneider, "Transition Metals in Homogeneous Catalysis", G. N. Schrauzer, Ed., Marcel Dekker, New York, N.Y., 1971, p 223.
(3) L. Cassar, P. E. Eaton, and J. Halpern, J. Am. Chem. Soc., 92, 3515 (1970).
(4) L. Cassar, P. E. Eaton, and J. Halpern, J. Am. Chem. Soc., 92, 6366 (1970).
(5) W. G. Dauben and A. J. Kielbania, Jr., J. Am. Chem. Soc., 93, 7345 (1971).
(6) L. A. Paquette, R. A. Boggs, W. B. Farnham, and R. S. Beckley, J. Am. Chem. Soc., 97, 1112 (1975).
(7) L. A. Paquette and J. C. Stowell, J. Am. Chem. Soc., 92, 2584 (1970).
(8) W. G. Dauben, C. H. Schallhorn, and D. L. Whalen, J. Am. Chem. Soc., 93, 1446 (1971).
(9) N. B. Chapman, J. M. Key, and K. J. Toyne, Tetrahedron Lett., 5211 (1970); L. A. Paquette and J. S. Ward, ibid., 4909 (1972); E. W. Turnblom and T. J. Katz, J. Am. Chem. Soc., 95, 4292 (1973); L. A. Paquette, J. S. Ward, R. A. Boggs, and W. B. Farnham, ibid., 97, 1101 (1975).
(10) W. G. Dauben, M. G. Buzzolini, C. H. Schallhorn, D. L. Whalen, and K. J. Palmer, Tetrahedron Lett., 787 (1970); J. E. Byrd, L. Cassar, P. E. Eaton, and J. Halpern, Chem. Commun., 40 (1971); L. A. Paquette and J. C. Stowell, J. Am. Chem. Soc., 93, 2459 (1971); L. A. Paquette, R. S. Beckley, D. Truesdell, and J. Clardy, Tetrahedron Lett., 4913 (1972).
(11) L. A. Paquette and R. S. Beckley, J. Am. Chem. Soc., 97, 1084 (1975); L. A. Paquette, R. S. Beckley, and W. B. Farnham, ibid., 97, 1089 (1975).
(12) The preliminary observation has been reported: H. Takaya, M. Yamakawa, and R. Noyori, Chem. Lett., 781 (1973).
(13) W. G. Dauben and D. L. Whalen, Tetrahedron Lett., 3743 (1966).
(14) For Ni(0)-catalyzed reactions between strained hydrocarbons and electron-deficient olefins, see R. Noyori, T. Odagi, and H. Takaya, J. Am. Chem. Soc., 92, 5780 (1970); R. Noyori, T. Suzuki, Y. Kumagai, and H. Takaya, ibid., 93, 5894 (1971); R. Noyori, T. Suzuki, and H. Takaya, ibid., 93, 5896 (1971); R. Noyori, Y. Kumagai, I. Umeda, and H. Takaya, ibid., 94, 4018 (1972); R. Noyori, Y. Kumagai, and H. Takaya, ibid., 96, 634 (1974); R. Noyori, H. Kawauchi, and H. Takaya, Tetrahedron Lett., 1749 (1974); see also ref 1.
(15) C. A. Tolman and W. C. Seidel, J. Am. Chem. Soc., 96, 2780 (1974).

(16) G. N. Schrauzer, *Chem. Ber.*, **94**, 642 (1961); R. Ugo, *Coord. Chem. Rev.*, **3**, 319 (1969); T. Yamamoto, A. Yamamoto, and S. Ikeda, *J. Am. Chem. Soc.*, **93**, 3350, 3360 (1971).
(17) Cyclooctadiene ligands of Ni(COD)$_2$ are readily replaced by electron-deficient olefins: M. Herberhold, "Metal π Complexes", Vol. II, Part I, Elsevier, Amsterdam, 1972, p 284; G. N. Schrauzer, *Adv. Organomet. Chem.*, **2**, 1 (1964).
(18) C. A. Tolman and W. C. Seidel, *J. Am. Chem. Soc.*, **96**, 2774 (1974).
(19) R. Noyori, unpublished observation.
(20) H. Hogeveen and B. J. Nusse, *Tetrahedron Lett.*, 159 (1974).
(21) R. S. Nyholm, *Proc. Chem. Soc., London*, 273 (1961).
(22) G. N. Schrauzer and S. Eichler, *Chem. Ind. (London)*, 1270 (1961); see also, O. W. Webster, W. Mahler, and R. E. Benson, *J. Org. Chem.*, **25**, 1470 (1960); I. H. Elson, D. G. Morrell, and J. K. Kochi, *J. Organomet. Chem.*, **84**, C7 (1975).
(23) G. N. Schrauzer, *Chem. Ber.*, **94**, 642 (1961).
(24) J. G. Traynham and J. R. Olechowski, *J. Am. Chem. Soc.*, **81**, 571 (1959); M. A. Muhs and F. T. Weiss, *Ibid.*, **84**, 4697 (1962); J. P. Visser, A. J. Schipperijn, J. Lukas, D. Bright, and J. J. de Boer, *Chem Commun.*, 1266 (1971); J. Mantzaris and E. Weissberger, *J. Am. Chem. Soc.*, **96**, 1880 (1974); R. Noyori, T. Ishigami, N. Hayashi, and H. Takaya, *ibid.*, **95**, 1674 (1973).
(25) Paquette[11] argued that the intermediate formation of the π complex **10** is a prelude to rearrangement and not an inconsequential cul de sac.
(26) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, C79 (1951); J. Chatt and L. A. Duncanson, *J. Chem. Soc.*, 2939 (1953). Review: P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, **2**, 271 (1973).
(27) K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology", P.-O. Löwdin and B. Pullman, Ed., Academic Press, New York, N.Y., 1964, p 513 ff; K. Fukui, *Acc. Chem. Res.*, **4**, 57 (1971); E. Hellbronner and H. Bock, "Das HMO-Modell und Seine Anwendung", Verlag Chemie, GmbH, Weinheim/Bergstr., Germany, 1968; M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry", McGraw-Hill, New York, N.Y., 1969; N. D. Epiotis, *J. Am. Chem. Soc.*, **94**, 1924 (1972); W. C. Herndon, *Chem. Rev.*, **72**, 157 (1972); K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, *J. Am. Chem. Soc.*, **95**, 7287 (1973).
(28) G. Distefano, G. Innorta, S. Pignataro, and A. Foffani, *J. Organomet. Chem.*, **14**, 165 (1968).
(29) The MO computation based on the CNDO/2 formalism does not change the relative energy levels of the occupied orbitals shown in Figure 3.
(30) L. Cassar and J. Halpern, *Chem. Commun.*, 1082 (1970).
(31) The π-type complex **9** and the oxidative addition product **12** are indistinguishable in the present MO treatment.
(32) Musso and coworkers interpreted the regioselectivity of the palladium-catalyzed hydrogenolysis of **4** in terms of the extent of strain release upon the carbon–carbon σ bond rupture: N. A. Sasaki, R. Zunker, and H. Musso, *Chem. Ber.*, **106**, 2992 (1973).
(33) F. D. Mango and J. H. Schachtschneider, *J. Am. Chem. Soc.*, **89**, 2484 (1967).
(34) The unidentate face-on coordination requires a pair of donation and back-donation interactions, whereas in order to form the bidentate face-on complex two sets of such overlappings are necessary.
(35) The theoretical scrutiny should be made carefully by combination with experimental observations. The present argument on the Ag$^+$-catalyzed reaction of bishomocubanes is fully consistent with the Dauben–Paquette mechanism which involves the edge argentation. The MO consideration alone, however, cannot rule out a priori the following alternative pathways. In an extreme case with metals having σ acceptor ability but negligible π donor ability, the hydrocarbon–metal interaction other than π complexation may become energetically favorable [J.-M. Lehn and G. Wipff, *J. Chem. Soc., Chem. Commun.*, 747 (1973)]. Thus Ag$^+$ ion may attack electrophilically the C(2) corner (with stereochemical retention or inversion) which has a great MO coefficient and substantial p character. Secondly, the rearrangement might proceed via a mechanism involving a charge transfer from bishomocubanes to Ag$^+$ ion [K. L. Kaiser, R. F. Childs, and P. M. Maitlis, *J. Am. Chem. Soc.*, **93**, 1270 (1971); G. F. Koser and J. N. Faircloth, 170th National Meeting of the American Chemical Society, Chicago, Ill., Aug 25–29, 1975, Abstract ORGN-46].
(36) R. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
(37) E. Haselbach and A. Schmelzer, *Helv. Chim. Acta*, **54**, 1299 (1971).
(38) G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5310 (1959).
(39) B. Bogdanović, M. Kröner, and G. Wilke, *Justus Liebigs Ann. Chem.*, **699**, 1 (1966); M. F. Semmelhack, *Org. React.*, **19**, 161 (1972).
(40) C. W. Gosser and C. A. Tolman, *Inorg. Chem.*, **9**, 2350 (1970).
(41) W. Reppe, O. Schlichting, K. Klager, and T. Toepel, *Justus Liebigs Ann. Chem.*, **560**, 1 (1948).

Ring Contraction of 2-Azidopyridine 1-Oxides and Related Compounds.[1,2] 2-Cyano-1-hydroxypyrroles and -imidazoles

Rudolph A. Abramovitch* and Berkeley W. Cue, Jr.

Contribution from the Department of Chemistry, University of Alabama, University, Alabama 35486. Received June 8, 1975

Abstract: A series of 2-azidopyridine 1-oxides was prepared from the corresponding 2-aminopyridine 1-oxides, and their thermal decomposition in benzene, methanol, and aniline was studied. In benzene, decomposition occurred smoothly at 85–95° to give 2-cyano-1-hydroxypyrroles as the exclusive products in good yields. The decomposition of 3-substituted-2-azidopyridine 1-oxides led to 2-substituted-2-cyano-2*H*-pyrrole 1-oxides which readily formed 1:1 adducts with phenyl isocyanate. In methanol or aniline, 2-cyanopyrroles and 3-substituted-2,3-dihydro-2-pyrrolones were isolated involving nucleophilic addition of a solvent molecule to the open-chain intermediate. 2-Azidopyrazine 1-oxide in benzene gave 2-cyano-1-hydroxyimidazole. A possible mechanism is suggested which does not invoke the formation of a nitrene but involves a concerted elimination of nitrogen and ring opening followed by ring contraction.

The thermal and photochemical decomposition of 3- and 4-azidopyridine 1-oxides have been studied,[3,4] and the products obtained appear to result from nitrene intermediates. On the other hand, the chemistry of 2-azidopyridine 1-oxide (**3a**) has received little attention.[5] In a related study, Kamiya[6] observed that the decomposition of 6-azidopyridazine 1-oxide is faster than that of some 3-azidopyridazine 1-oxides, but the products were not isolated. In principle, the properties of the nitrene derived from **3a** could be modified appreciably from those expected of an electrophilic arylnitrene by the presence of the ortho *N*-oxide oxygen. For example, it could exhibit 1,4-dipole behavior (**4**). Alternatively, **3a** could undergo ring contraction with elimination of nitrogen, as has been observed for some cyclic azides.[7] This

could involve formation of a nitrene (**4**) or be a concerted process, ring opening accompanying nitrogen elimination. With a view to deciding between these various possibilities, we prepared a series of 2-azidopyridine 1-oxides (**3a–h**) and investigated their thermal decomposition in benzene, methanol, aniline, and morpholine in one case. To date, we have not observed any 1,4-dipolar behavior but have observed ring contraction leading to 2-cyano-1-hydroxypyrroles.

There is little known about *N*-hydroxypyrroles. The first example was prepared by Knorr[8a] who treated 3,4-dicarbethoxyhexa-2,5-dione with hydroxylamine to get 2,5-dimethyl-1-hydroxypyrrole-3,4-dicarboxylic ester. This was hydrolyzed and decarboxylated to 2,5-dimethyl-1-hydroxypyrrole. The same compounds were also prepared from di-