An analytical sample of **34** was collected by preparative vpc on a 19% Carbowax 20M Chromosorb W column at 70°, $n^{24}D$ 1.4218.

Anal. Calcd for $C_8H_{16}O$: C, 74.94; H, 12.58. Found: C, 74.77; H, 12.56.

Rhodium Dicarbonyl Acetylacetonate (39). This complex was prepared according to the procedure of Bonati and Wilkinson.[40] It was shown by mass spectrometry that the material was at least 99% pure.

Treatment of 3 with 39 in Chloroform. A chloroform solution of **3** was treated with 2 mol % of **39** utilizing the same general experimental procedure described above for the reaction of **3** with rhodium dicarbonyl chloride dimer. Analysis of the product mixture by vpc indicated the formation of 58% of **4** and 11% of **12**.

Treatment of 3 with 39 in Methanol. The same general procedure was used in this experiment as has been previously outlined for the reaction of **3** with methanol in the presence of rhodium dicarbonyl chloride dimer. The major difference in the two reactions was that **39** caused a somewhat slower reaction. Vpc analysis of the products from this reaction indicated the formation of 84% of **34** and 13% of **12**.

Addition of an amount of sodium methoxide equivalent to 10% of the amount of **39** caused no perceptible change in the reaction. The yields of **34** and **12** remained the same.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

Transition Metal Complex Promoted Rearrangements. The Effect of the Metal and of the Attached Ligands on the Mode of Cleavage of Methylated Bicyclo[1.1.0]butanes[1]

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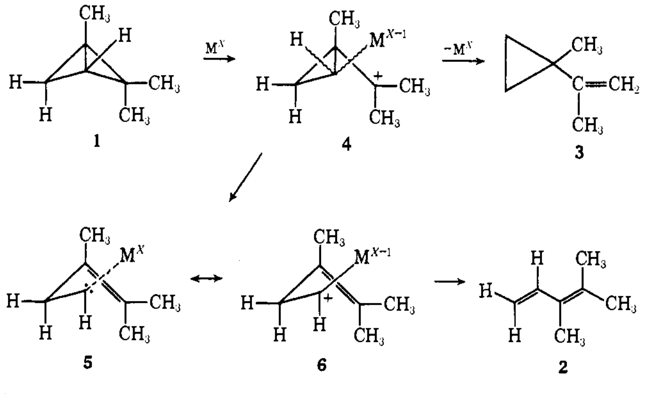
Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210. *Received February 18, 1972*

Abstract: A study has been carried out in order to determine the effect of the metal, of the oxidation state of the metal, and of the ligands attached to the metal, in the transition metal complex promoted isomerization of methyl-substituted bicyclo[1.1.0]butanes. The results of these studies have been compared to our results with derivatives of rhodium(I). We found that derivatives of chromium, cobalt, copper, gold, iridium, manganese, mercury, palladium, platinum, rhenium, rhodium, ruthenium, tin, and zinc promoted the isomerization of methylated bicyclo[1.1.0]butanes. The nature of the products formed was dependent on the metal, the oxidation state of the metal, and on the ligands attached to the metal. The dependency on the attached ligand was amply demonstrated by the formation of different products (resulting from the cleavage of different bonds) when bisbenzonitrile palladium(II) chloride was replaced by π-allylpalladium(II) chloride dimer. The mechanisms of these isomerizations are discussed. A stepwise process of bond cleavage is suggested. In general, insufficient evidence prohibits any definitive explanation of the specificity of the various metal derivatives which we have used in our investigation of the transition metal promoted isomerization of bicyclo[1.1.0]butane derivatives.

In the preceding paper[1] we have discussed in detail the rhodium dicarbonyl chloride dimer promoted isomerizations of methylated bicyclo[1.1.0]butane derivatives. We presented evidence in support of an overall mechanism which is shown below for the conversion of 1,2,2-trimethylbicyclo[1.1.0]butane (**1**) into a mixture of **2** and **3**. We suggested that the transition metal complex behaves initially as a very specific Lewis acid type species, which attacks the bicyclo[1.1.0]butane moiety, producing cleavage of a side bond to give the most stable cyclopropylcarbinyl cation (**4**). Proton transfer and loss of the metal would then explain the formation of **3**.[2] An alternate mechanistic path, which **4** could follow, would involve cleavage of the central bond to yield a resonance hybrid represented by the transition metal complexed carbene **5** and the transition metal bonded carbocation **6**. Again, hydrogen transfer and loss of the metal complex would give the observed product **2**.[2] In view of the extremely unusual nature of these rhodium dicarbonyl chloride dimer promoted rearrangements, we decided to investigate the use of derivatives of other transition metals in the rearrangement of derivatives of bicyclo[1.1.0]butane. We now wish to present the details of this investigation.[4-7]



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(1) Paper XXXIII of a series on The Chemistry of Bent Bonds. For the previous paper in this series see P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **94**, 7733 (1972).

(2) Ample precedent exists for the protonolysis of carbon–metal bonds.[3] We feel that it may be possible for this protonolysis to occur *via* initial proton transfer from carbon to metal and then from metal to carbon. We are currently investigating this aspect of these rearrangements.

(3) For a recent leading reference see T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **93**, 1049 (1971); see also M. Orchin, *Advan. Catal.*, **16**, 1 (1966).

(4) For preliminary reports of part of this work see P. G. Gassman and F. J. Williams, *Tetrahedron Lett.*, 1409 (1971); P. G. Gassman, T. J. Atkins, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1812 (1971); P. G. Gassman, G. R. Meyer, and F. J. Williams, *Chem. Commun.*, 842 (1971).

Rearrangements of 1,2,2-Trimethylbicyclo[1.1.0]butanes. The reaction of 1,2,2-trimethylbicyclo[1.1.0]butane (**1**) with many transition metal complexes paralleled the reaction of **1** with rhodium dicarbonyl chloride dimer. For instance, **1** reacted with dichlorotricarbonylruthenium to give 59% of **2** and 24% of **3**. This can be compared with the reaction of **1** with *p*-toluenesulfonic acid, which gave **3** as the only isolable product. Similarly, the Lewis acids—zinc tetrafluoroborate, zinc iodide, cupric tetrafluoroborate hexahydrate, mercuric bromide, and stannous chloride—promoted the conversion of **1** into only **3**. Table I lists the yields and reaction times for the isomerization of 50 mg of **1** in 2 ml of chloroform containing 2 mol % of the specified reagent at 25°.

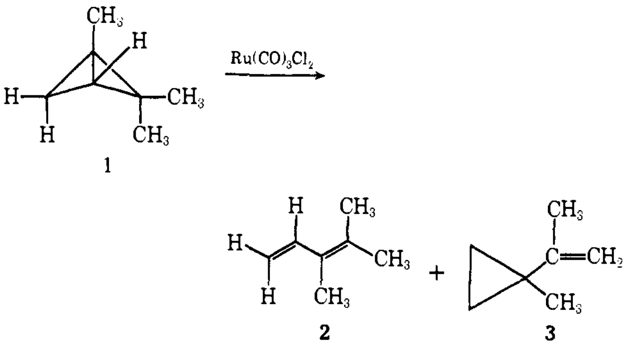
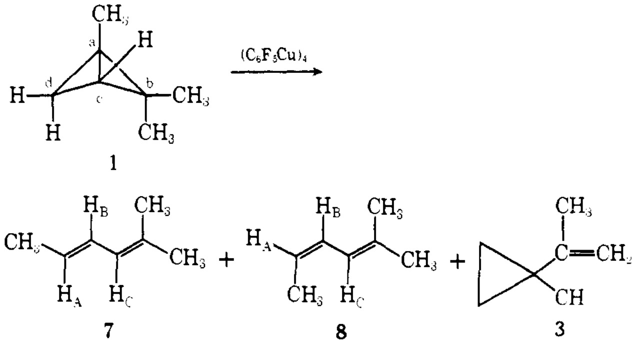


Table I. Reagents for the Isomerization of 1,2,2-Trimethylbicyclo[1.1.0]butane (**1**) to **2** and **3**

Reagent	Time, hr[a]	% of **2**[b,c]	% of **3**[b,c]
$Co(CO)_8$[d]	2	24	42
$Cu(BF_4)_2 \cdot 6H_2O$[d]	3		43
$Mn_2(CO)_{10}$[d]	5	12	22
$HgBr_2$[d]	24		58
$(C_6H_5CN)_2PdCl_2$[e]	0.02[f]	29	5
$[Rh(CO)_2Cl]_2$[e]	0.1	58	30
$Ru_3(CO)_{12}$[d]	18	30	38
$[Ru(CO)_3Cl_2]_2$[d]	4	59	24
$RuCl_3$[e]	13	26	49
$SnCl_2$[e]	5		62
ZnI_2[e]	24		71
$Zn(BF_4)_2$[e]	17		54
$CH_3C_6H_4SO_3H$[g]	6		44

[a] Reaction times reflect the time at which diene absorption in the uv maximized (for those reactions which gave **2**), or the time when the presence of **1** could no longer be detected by nmr (for those reactions which gave only **3**). [b] Yields were determined by vpc analysis using 2,2,4-trimethylpentane as an internal standard. The yields are all averages of at least two runs. [c] With several reagents the yields maximized and then decreased. In these instances higher molecular weight materials were formed. [d] The reagent was not completely dissolved in the solvent. [e] Completely dissolved in the chloroform. [f] This reaction was carried out at 0° with 3.7 mol % of reagent. Even at this temperature the yields of **2** and **3** decreased with time. [g] For this reaction, 10 mol % of acid was used (not completely dissolved, but more than 2 mol % in solution).

In contrast to the behavior discussed above, **1** reacted with pentafluorophenylcopper tetramer[8] to produce a mixture of **7**, **8**, and **3**, in 39, 33, and 11% yields, respectively.[4,9] The structures of **7** and **8** were established on the basis of both chemical and spectroscopic evidence. Although the dienes, **7** and **8**, appeared as a single peak on most vpc columns, we eventually accomplished separation on a 25 ft × 1/4 in. 20% D.C. Silicone Fluid No. 200 on 60–80 Chromosorb P column at 75°. Since this separation was only attained with great difficulty, **7** and **8** were catalytically hydrogenated as the mixture. Reduction over 5% palladium on carbon gave only 2-methylhexane, which was identical with an authentic sample[10] in all respects.



An independent synthesis of **7** and **8** was accomplished starting with commercially available[10] **9**, which was converted into the corresponding acetate **10**, with acetic anhydride in pyridine. Pyrolysis of **10** in the vapor phase at 450° gave a mixture of **7**, **8**, and **11** in the ratio of 28:22:50.[11] Separation of **11** from the mixture of **7** and **8** was readily accomplished by preparative vpc. The mixture of **7** and **8** obtained from **10** was spectroscopically almost identical with the mixture of **7** and **8** obtained from **1**. In addition, pure **7** was synthesized from *trans*-2-butenal (**12**) *via* a Wittig reaction with **13**.

The stereochemistry of samples of **7** and **8**, isolated from the reaction mixture obtained from **1**, was rigorously established spectroscopically. The infrared spectrum of **7** showed a strong absorption at 10.44 μ (trans olefin) while the spectrum of **8** had a strong absorption at 14.02 μ (cis olefin). The nmr spectrum of **7** had absorptions at τ 8.28 (9 H, s), 4.48 (1 H, m), 4.25

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(5) For preliminary reports from other laboratories on silver ion promoted isomerizations of methylated bicyclo[1.1.0]butanes see (a) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *J. Amer. Chem. Soc.*, **93**, 1288 (1971); (b) L. A. Paquette, R. P. Henzel, and S. E. Wilson, *ibid.*, **93**, 2335 (1971); (c) M. Sakai, H. Yamaguchi, H. H. Westberg, and S. Masamune, *ibid.*, **93**, 1043 (1971); (d) M. Sakai and S. Masamune, *ibid.*, **93**, 4610 (1971); (e) M. Sakai, H. H. Westberg, H. Yamaguchi, and S. Masamune, *ibid.*, **93**, 4611 (1971); (f) M. Sakai, H. Yamaguchi, and S. Masamune, *Chem. Commun.*, 486 (1971).

(6) For preliminary reports from other laboratories on palladium(II)-promoted rearrangements of methylated bicyclo[1.1.0]butanes see ref 5c,d,f.

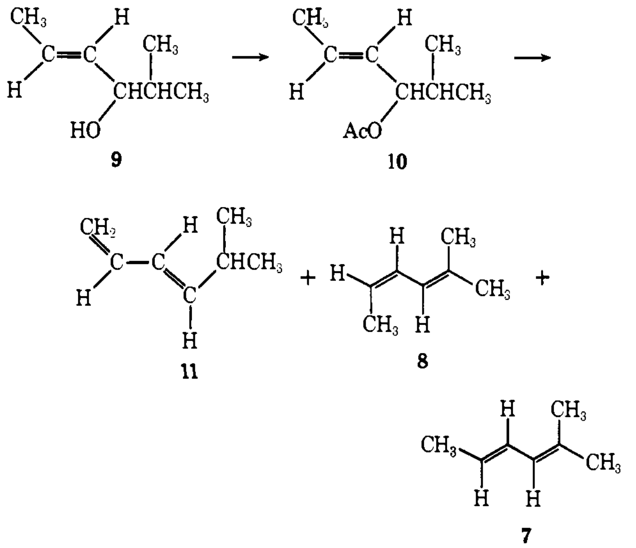
(7) The use of transition metal derivatives as reagents which promote the rearrangement of derivatives of bicyclo[1.1.0]butane is an outgrowth of the use of various transition metal complexes and of silver ion in the rearrangement of other highly strained ring systems. For typical examples see H. Hogeveen and H. C. Volger, *J. Amer. Chem. Soc.*, **89**, 2486 (1967); P. G. Gassman and D. S. Patton, *ibid.*, **90**, 7276 (1968); W. Merk and R. Pettit, *ibid.*, **89**, 4788 (1967); R. Pettit, H. Sugahara, J. Wristers, and W. Merk, *Discuss. Faraday Soc.*, 47, 71 (1969); H. Dietl and P. M. Maitlis, *Chem. Commun.*, 759 (1967); H. C. Volger and H. Hogeveen, *Recl. Trav. Chim. Pays-Bas*, 86, 830 (1967); H. C. Volger and M. M. P. Gaasbeek, *ibid.*, **87**, 1291 (1968); H. Hogeveen and H. C. Volger, *Chem. Commun.*, 1133 (1967); H. C. Volger, H. Hogeveen, and M. M. P. Gaasbeek, *J. Amer. Chem. Soc.*, **91**, 218, 2137 (1969); T. J. Katz and S. Cerefice, *Tetrahedron Lett.*, 2509, 2561 (1969); T. J. Katz and S. A. Cerefice, *J. Amer. Chem. Soc.*, **91**, 2405, 6519 (1969); B. L. Booth, R. N. Haszeldine, and M. Hill, *Chem. Commun.*, 1118 (1967); P. V. Balakrishnan and P. M. Maitlis, *ibid.*, 1303 (1968); J. W. Kang, K. Mosley, and P. M. Maitlis, *ibid.*, 1304 (1968); J. W. Kang and P. M. Maitlis, *J. Amer. Chem. Soc.*, **90**, 3259 (1968).

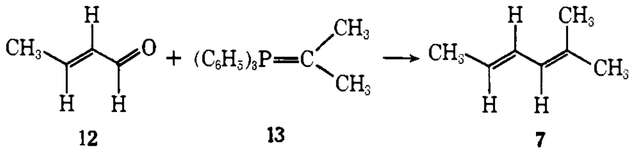
(8) A. Cairncross, H. Omura, and W. A. Sheppard, *ibid.*, **93**, 248 (1971). We wish to thank Dr. Sheppard for generously supplying us with a sample of pentafluorophenylcopper tetramer.

(9) It is interesting to note that Paquette and coworkers have observed that silver ion reacts with **1** to give the same products as were obtained with pentafluorophenylcopper tetramer.[5]

(10) Purchased from Chemical Samples Co., Columbus, Ohio.

(11) For a closely related reaction see F. L. Greenwood, *J. Org. Chem.*, 27, 2308 (1962).

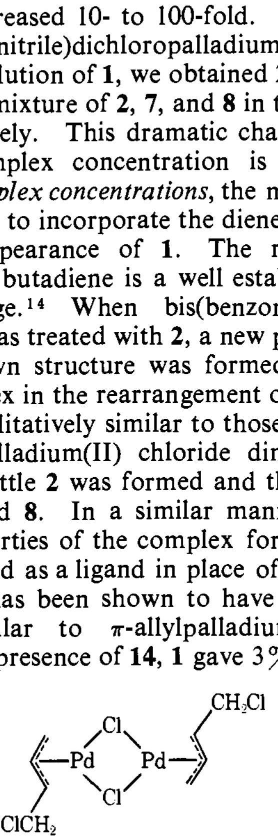




(1 H, m), and 3.77 (1 H, m). Spin decoupling of the methyl hydrogens permitted determination of J_{AB} = 15, J_{BC} = 11, and J_{A-CH_3} = 7 Hz. The value of J_{AB} supported the structure assigned on the basis of the infrared spectrum. The nmr spectrum of **8** showed absorptions at τ 8.27 (9 H, m), 4.60 (1 H, m), and 3.85 (2 H, m). Irradiation of the methyl hydrogen multiplet centered at τ 8.27 simplified H_A into a doublet with J_{AB} = 9 Hz. This substantiated the stereochemical assignment.

The results discussed above provide the basis for some perplexing thought. Clearly, pentafluorophenylcopper tetramer is an efficient material for promoting the rearrangement of **1**. However, a dramatic difference exists between pentafluorocopper tetramer and transition metal complexes such as rhodium dicarbonyl chloride dimer. Whereas the latter bring about the cleavage of the a–c and b–c bonds of **1**, the use of pentafluorophenylcopper tetramer results in the cleavage of the a–b and a–c bonds of **1**. This amazing specificity indicates the presence of factors which are far from being understood.

Following our discovery of the dramatic differences observed in the reaction of **1** with rhodium dicarbonyl chloride dimer as compared with pentafluorophenylcopper tetramer, we found that a spectrum of results could be obtained, depending on the metal, the ligands attached to the metal, and the oxidation state of the metal. As shown in Table I, when **1** was treated with 3.7 mol % of bis(benzonitrile)dichloropalladium(II) at 0°, a 5:1 mixture of **2**:**3** was obtained as the only volatile material. When π-allylpalladium(II) chloride dimer was used to promote the rearrangement, **1** gave 3% of **3** and 72% of a 3:56:41 mixture of **2**:**7**:**8** after 35 min at 0°. Although both complexes involved palladium(II), the bis(benzonitrile)dichloropalladium gave neither **7** nor **8**, while the π-allylpalladium chloride dimer gave only a 2% yield of **2**.[12] These observations allow us to arrive at two important conclusions which have far reaching consequences relative to the transition metal complex promoted isomerizations of highly strained polycyclic molecules. First, it has been established that *the mode of cleavage can be controlled by the ligands attached to the transition metal* since bis(benzonitrile)dichloropalladium promoted cleavage of the a–c and b–c bonds of **1**, while π-allylpalladium chloride dimer caused major cleavage of the a–b and a–c bonds of **1**.[13] Secondly, the observed transformations required that there was very little, if any, ligand exchange during the course of the reaction *under the conditions described above*. This second conclusion was supported by experiments in which the transition metal complex to **1** ratio was decreased 10- to 100-fold. When 0.2 mol % of bis(benzonitrile)dichloropalladium was added to a chloroform solution of **1**, we obtained 20% of **3** and a 37% yield of a mixture of **2**, **7**, and **8** in the ratio of 20:49:31, respectively. This dramatic change in product ratio with complex concentration is reasonable if, *at the lower complex concentrations*, the metal undergoes ligand exchange to incorporate the diene **2**, prior to the complete disappearance of **1**. The replacement of benzonitrile by butadiene is a well established type of ligand exchange.[14] When bis(benzonitrile)dichloropalladium(II) was treated with **2**, a new palladium complex of unknown structure was formed. The use of this new complex in the rearrangement of **1** gave results which were qualitatively similar to those observed with other π-allylpalladium(II) chloride dimer type complexes. Very little **2** was formed and the major products were **7** and **8**. In a similar manner we investigated the properties of the complex formed when butadiene was used as a ligand in place of benzonitrile.[14] This complex has been shown to have structure **14**,[15] which is similar to π-allylpalladium(II) chloride dimer. In the presence of **14**, **1** gave 3% of **3** and 40% of a 55:26:19 mixture of **2**:**7**:**8**. This showed that **14** was intermediate in properties between the palladium(II) complexes described above.



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As shown in Table II, the dependency on ligands observed for palladium(II) was also evident for rhodium(I). However, the changes with rhodium(I) were much less dramatic in that only a few per cent of **7** and **8** was formed (when the reaction was carried out with tris(triphenylphosphine)rhodium carbonyl hydride). With rhodium(III) the amounts of **7** and **8** exceeded the amount of **2**. Since rhodium(I) dicar-

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[12] Suitable control reactions demonstrated that the dienes were not interconverted under the reaction conditions. A complicating factor involved the finding that both catalysts slowly promoted the polymerization of the product dienes. However, this catalyzed disappearance of the dienes could not be used to explain the observed selective isomerizations of **1** since the rates of disappearance of the three different dienes were qualitatively comparable. Hence, the observed diene ratios must approximate the initially formed product composition.

[13] Both palladium(II) complexes gave cyclopropane derived from the cleavage of the b–c bond of **1**. However, the very low yield (3%) of this material, when π-allylpalladium chloride dimer was used, precludes any significant interpretation of this observation.

[14] P. E. Slade and H. B. Jonassen, *J. Amer. Chem. Soc.*, **79**, 1277 (1957).

[15] B. L. Shaw, *Chem. Ind. (London)*, 1190 (1962).

Table II. Product Composition as a Function of the Attached Ligands in the Transition Metal Complexed Isomerization of **1**

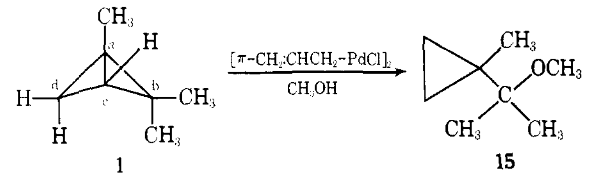
Complex	% yields **3**	**2**	**7**	**8**
$(C_6H_5CN)_2PdCl_2$	5^a	29^a		
	20^b	7^b	18^b	11^b
14	3	22	10	8
$PdCl_2$	33	33	14	8
$[⟨⟨\text{–}PdCl]_2$	3	2	40	30
$[Rh(CO)_2Cl]_2$	30	58		
$[Rh(norbornadiene)_2Cl]_2$	3	58		
$Rh(CO)_2AcAc$	11	58		
$((C_6H_5)_3P)_3RhCl$	42	17	1	1
$((C_6H_5)_3P)_3Rh(H)CO$	18	46	3	3
$RhCl_3 \cdot H_2O$	50	6	7	4
$Rh(AcAc)_3$	54	4	13	7
$(C_6F_5Cu)_4$	11		39	33
AuI_3	15	15	6	6
$AgBF_4{}^c$	8		74	16

[a] Carried out with 3.7 mol % of complex at 0°. [b] Carried out with 0.2 mol % of complex at 25°. [c] For the source of the silver fluoroborate numbers see ref 5b.

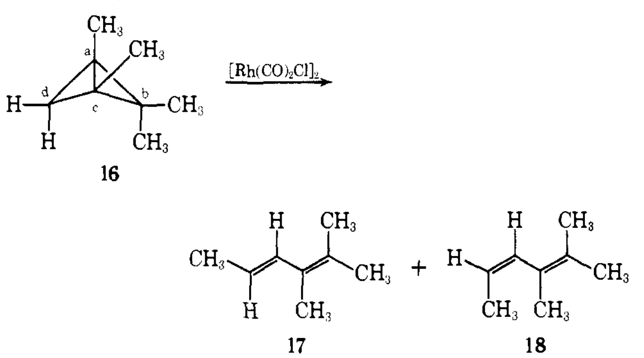
bonylacetylacetonate gave 58% of **2**, while rhodium(III) triacetylacetonate gave 4% of **2**, 13% of **7**, and 7% of **8**, it seems highly probable that the oxidation state of the metal also plays a part in determining the mode of bond cleavage of derivatives of bicyclo[1.1.0]butane. From the last part of Table II, it can be seen that derivatives of copper, gold, and silver can react with **1** to give significant amounts of **7** and **8**. Of the derivatives of these three metals which were studied, only gold triiodide gave significant amounts of **2**.

The results of our studies of the transition metal complex promoted isomerization of **1**, as detailed above, provide ample evidence for the general nature of this type of isomerization. It was particularly interesting to us that derivatives of all of the metals, which we tried, caused rearrangement of **1**. We strongly suspect that there are derivatives of all of the transition metals which will promote these facile rearrangements of **1**.

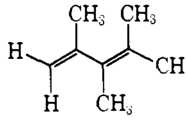
In order to show that the trapping of an intermediate cation was not limited to the rhodium dicarbonyl chloride dimer promoted rearrangement of **1**, we treated **1** with π-allylpalladium chloride dimer in methanol. After 1 min at room temperature we obtained 94% of **15** which was identified by comparison with an authentic sample. It seems clear that in methanol only the b–c bond is broken by π-allylpalladium chloride dimer. Thus, it appears that the solvent can also play an important part in determining which bond is initially cleaved.[16]



1,2,2,3-Tetramethylbicyclo[1.1.0]butane. 1,2,2,3-Tetramethylbicyclo[1.1.0]butane (**16**) was studied in far less detail than **1**. As previously noted,[1] **16** was readily rearranged by rhodium dicarbonyl chloride dimer to give a mixture of **17** and **18** in 50 and 46% yields, respectively.



In contrast to the behavior of **1** with rhodium dicarbonyl chloride dimer, **16** gave no vinylcyclopropane derivative and the dienes had mixed stereochemistry. In this instance, the transition metal complex promoted process is dramatically different from the thermal process which gave **19**.[17] Whereas



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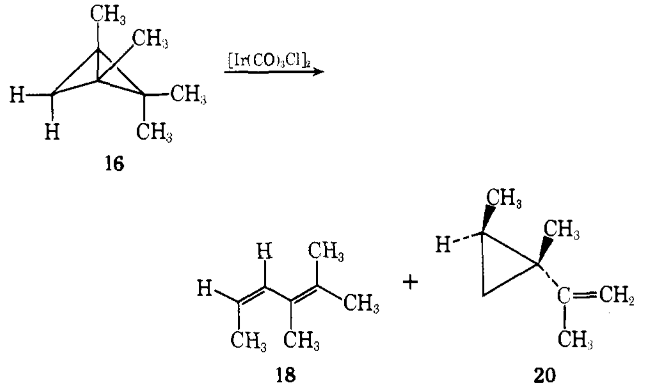
the thermal rearrangement of **16** involved cleavage of the a–b and c–d bonds, the transition metal promoted cleavage occurred *via* fracture of the a–b and a–c bonds.

When a solution of **16** in chloroform was treated with 2 mol % of chlorotricarbonyliridium dimer, we obtained 48% of **18** and 36% of **20**. The structure



of **18** was established by comparison with a previously identified sample.[1] The structure of **20** was established primarily on the basis of its nmr spectrum which showed peaks at τ 5.30 (2 H, m) (terminal methylene), 8.30 (3 H, d, J = 1 Hz) (allylic methyl), 8.86 (3 H, s) (C_1 methyl), 8.92 (3 H, d, J = 5 Hz) (C_2 methyl), 9.09 (2 H, t, br m), and 10.00 (1 H, m). The multiplet at τ 9.09 was due to one of the geminal hydrogens and the ring hydrogen at C_2. The peak at τ 10.00 was due to the proton at C_2 which was cis to the two cis methyl groups. The cisoid nature of the two methyl groups was assigned on the basis of a comparison of the nmr of **20** with those of **3** and the monodeuterated analogs of **3**.[1]

The results obtained in the reaction of **16** with chlorotricarbonyliridium dimer differed dramatically from

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[16] The cause of this solvent effect is currently under study. It is not known whether this is due merely to the solvation of the reactants or to an exchange reaction between the π-allylpalladium chloride dimer and the methanol.

[17] W. R. Moore, K. G. Taylor, P. Müller, S. S. Hall, and Z. L. F. Gaibel, *Tetrahedron Lett.*, 2365 (1970).

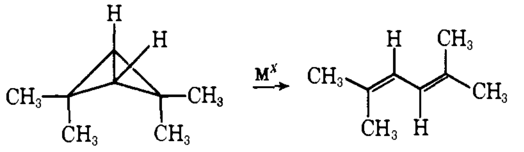
those obtained with rhodium dicarbonyl chloride dimer. The major difference was the formation of **20** with chlorotricarbonyliridium dimer *vs.* the formation of **17** when rhodium dicarbonyl chloride dimer was used. Superficially it might appear either that **17** and **18** were being equilibrated by the complex present in solution or that **20** was converted to **17** by rhodium dicarbonyl chloride dimer. Control experiments demonstrated that **17**, **18**, and **20** were not interconvertible when treated at the temperature and time of the reaction with rhodium dicarbonyl chloride dimer in chloroform. This indicates either that **17** and **18** are formed directly from **16** by the rhodium dicarbonyl chloride dimer, or that **18** or **20** was converted into **17** by some transitory intermediate generated in the reaction of **16** with rhodium dicarbonyl chloride dimer.[18] It should be noted that the formation of **18** and **20** from **16** in the presence of chlorotricarbonyliridium dimer involves the same stereospecificity as was observed for the rearrangement of 1-deuterio-2,3,3-trimethylbicyclo[1.1.0]butane in the presence of rhodium dicarbonyl chloride dimer.[1]

2,2,4,4-Tetramethylbicyclo[1.1.0]butane. As shown in Table III, we have found that derivatives of copper, chromium, gold, iridium, manganese, mercury, palladium, rhenium, rhodium, ruthenium, and zinc readily isomerized 2,2,4,4-tetramethylbicyclo[1.1.0]butane (**21**) to 2,5-dimethyl-2,4-hexadiene (**22**). This isomerization seemed to be relatively insensitive to the nature of the derivative of the transition metal and to the oxidation state. However, yields did vary significantly depending on the nature of the transition metal complex. Unfortunately, due to differing solubilities of these various derivatives, no pattern could be discerned among the yields.

Table III. Isomerization of 2,2,4,4-Tetramethylbicyclo[1.1.0]butane by Derivatives of Transition Metals

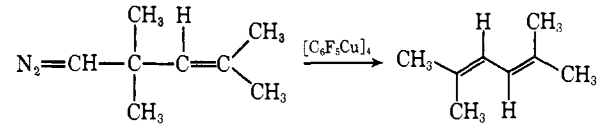
Reagent	Time, hr	Yield of 2,5-dimethyl-2,4-hexadiene,[a,b] %
$Cu(BF_4)_2 \cdot 6H_2O$	3	92
CuOAc	0.3	52
$[C_6F_5Cu]_4$	3[c]	67
$Cr(CO)_6$	24	35
AuI_3	0.2	56
AuCN	24	40
$[Ir(CO)_3Cl]_2$	12[c]	87
$Mn_2(CO)_{10}$	1.5	53
$HgBr_2$	0.2	71
$(C_6H_5CN)_2PdCl_2$	0.2	55
$[\langle\langle\text{-PdCl}]_2$	0.1	60
$Re_2(CO)_{10}$	1.5	58
$[Rh(CO)_2Cl]_2$	12[c]	85
$((C_6H_5)_3P)_3Rh(H)CO$	6	51
$((C_6H_5)_3P)_3RhCl$	4	70
$RuCl_3$	3	31
$Ru_3(CO)_{12}$	4	90
$Ru(CO)_3Cl_2$	2	74
ZnI_2	0.2	68
$Zn(BF_4)_2$	3	37
$CH_3C_6H_4SO_3H$	4	77

[a] All yields are the average of at least two runs. [b] In addition to the formation of **22**, significant amounts of higher molecular weight intractable material were formed. [c] The uv experiment was not performed. The exothermicity and color change indicate that reaction is instantaneous.



21 **22**

The various mechanistic possibilities for the conversion of **21** into **22** have been discussed previously.[1] The only thing which we can add to that discussion as a result of this study is that conversion of the diazo compound **23** into **22** was not restricted to rhodium dicarbonyl chloride dimer. For instance, pentafluorophenylcopper tetramer smoothly converts **23** into **22** in high yields as the only product (*ca.* 85% yield).



23 **22**

Summary

The various studies presented in this paper illustrate the diverse nature of the derivatives of transition metals which readily promote the rearrangement of methylated derivatives of bicyclo[1.1.0]butane. Important conclusions which can be reached as a result of this study indicate that the isomerization of bicyclo[1.1.0]butanes by transition metal complexes depends on the metal, oxidation state of the metal, ligands attached to the metal, nature of the substitution on the bicyclo[1.1.0]butane, and, perhaps, on the nature of the solvent used for the reaction.

We are continuing to explore the detailed aspects of these fascinating isomerizations.

Experimental Section

Melting points and boiling points are uncorrected. Infrared spectra were taken on a Perkin-Elmer Model 137 Infracord or Beckman IR-9 spectrophotometer. Ultraviolet spectra were obtained on a Cary Model 16 recording ultraviolet spectrophotometer. Nuclear magnetic resonance spectra were obtained on either a Varian Associates A-60-A or HA-100 spectrometer and reported in τ units relative to tetramethylsilane ($\tau = 10.00$) as the internal standard.

General Procedure for the Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane (1) with the Transition Metal Derivatives Listed in Table I. To a solution of 100 mg of **1** in 2 ml of chloroform was added 2 mol % of the desired transition metal derivative. After stirring overnight, the solvent and products were vacuum transferred away from the nonvolatile material (25° (0.1 mm)). The products were separated and collected by preparative vpc and identified as previously described.[1]

Determination of Reaction Time for the Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane (1) with Transition Metal Derivatives. To a stirred solution of about 20 mg of **1** in 2 ml of chloroform was added 2 mol % of the transition metal derivative. The progress of the reaction was followed by removal of 5-μl aliquots, dilution to 5 ml with chloroform, and uv absorption determination at 238 nm (maximum for 3,4-dimethyl-1,3-pentadiene). The yield of each reaction was obtained at the time when the uv absorption due to **2** remained constant or started to decrease. Each reaction was run in duplicate. Nmr spectral analysis of the crude reaction mixture showed the presence of products and the absence of **1**.

Determination of Yields for the Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane (1) with Transition Metal Derivatives. To a stirred solution of 50 mg of 1,2,2-trimethylbicyclo[1.1.0]butane (**1**) in 2 ml

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[18] For a discussion of evidence for the existence of this type of equilibration–isomerization in a different system see P. G. Gassman, T. J. Atkins, and T. Lumb, *J. Amer. Chem. Soc.*, **94**, 7757 (1972).

of chloroform was added 2 mol % of the transition metal derivative. The yield was determined by vpc analysis in duplicate (at the time indicated by the maximum ultraviolet absorption) using 2,2,4-trimethylpentane as the internal standard on a 10 ft × 1/8 in. 20% D.C. Silicone Fluid No. 200, 1000 cs on a 60–80 Columpak column at 60°.

Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane (1) with Pentafluorophenylcopper. A solution of 500 mg of **1** in 5 ml of chloroform was cooled in an ice–water bath and stirred under a nitrogen atmosphere. To this solution was added 96 mg (2 mol %) of pentafluorophenylcopper tetramer. The reaction mixture immediately became warm and turned a dark green-black with simultaneous formation of a green precipitate. After stirring for 3 hr the solvent and products were vacuum transferred away from the nonvolatile material (25° (0.1 mm)). The products were separated into two fractions, one containing a mixture of **7** and **8** and the other containing **3**, by preparative vpc on a 20% D.C. Silicone Fluid No. 200, 1000 cs on a 60–80 Columpak (1/4 in. × 9 ft) column at 70°.

The minor component, **3**, had infrared (CCl_4) and nmr spectra identical with the known sample of **3** obtained from the acid-catalyzed opening of **1**.

The mixture of **7** and **8** had infrared absorptions (CS_2) at 3.25 (olefinic C–H), 6.03, 6.13 (C=C), 7.23 ($C-CH_3$), 10.44 (trans-disubstituted olefin), and 14.02 μ (cis-disubstituted olefin). The mixture had $\lambda_{max}^{isooctane}$ 235 nm (ϵ 20,940). An exact mass determination of the mixture showed an observed *m/e* of 96.0941 and a calculated mass of 96.0939.

A 25-mg sample of this mixture was hydrogenated over a 5% Pd/C catalyst to give 2-methylhexane which had infrared and nmr spectra identical with an authentic sample.[10]

The mixture of **7** and **8** was separated into two components on an analytical vpc on a 24 ft × 1/8 in. 5% SF-96 on 60–80 Chromosorb G column at 50°. Enrichment with an authentic sample of **7** allowed identification of the major component of the mixture as **7**. The mixture consisted of 54% of **7** and 46% of **8**. Compounds **7** and **8** were isolated in greater than 95% purity by preparative vpc on a 25 ft × 1/4 in. 20% D.C. Silicone Fluid No. 200 on 60–80 Chromosorb P column at 75°. The trans isomer **7** had a strong absorption in the infrared (CS_2) at 10.44 μ (trans-disubstituted olefin) and complete absence of the absorption at 14.02 μ (cis-disubstituted olefin). The nmr of **7** ($CHCl_3$) had a 9 H singlet at τ 8.28, a 1 H multiplet at 4.48, a 1 H multiplet at 4.25, and a 1 H multiplet at 3.77.

Single irradiation of the methyl groups at τ 8.28 simplified H_a into a doublet at τ 4.48 with J_{AB} = 15 Hz. The coupling constant was consistent with the assignment of trans stereochemistry. Finally, the ir spectrum of **7** was identical with the spectrum of an authentic sample.

The cis isomer **8** had a strong absorption in the infrared (CS_2) at 14.02 μ (cis-disubstituted olefin) and complete absence of the absorption at 10.44 μ (trans-disubstituted olefin). The nmr spectrum of **8** ($CHCl_3$) had a 9 H multiplet centered at τ 8.27, a 1 H multiplet at 4.60, and a 2 H multiplet at 3.85. Single irradiation at τ 8.27 simplified H_a into a doublet at τ 4.60 with J_{AB} = 9 Hz, which supports the assignment of cis stereochemistry.

Finally, both dienes **7** and **8** were shown to be stable under the reaction conditions.

Yields were obtained by vpc using 2,2,4-trimethylpentane as an internal standard as described previously.

***trans*-2-Methyl-4-hexene 3-Acetate (10).** A solution of 10 g of *trans*-2-methyl-4-hexen-3-ol[10] (>99% pure) in 100 ml of dry pyridine was stirred while 11.2 g of acetic anhydride was added dropwise. The solution was stirred overnight at room temperature and poured onto a mixture of dilute hydrochloric acid and Skelly F. The layers were separated and the aqueous layer was extracted well with Skelly F. The combined organic layers were washed with dilute hydrochloric acid, water, sodium bicarbonate, water, and a saturated salt solution. After drying over magnesium sulfate, filtration, and removal of the solvent, the residue was distilled *in vacuo* to give 13.12 g (96%) of **10**, bp 76–77° (22 mm), $n^{24.6}$D 1.4218.

Pyrolysis of *trans*-2-Methyl-4-hexene 3-Acetate (10). A neat solution of 6.0 g of **10** was added dropwise (1 drop/7 sec) through a 34 in. × 1 in. vertical Pyrex column packed with 6-mm glass beads and maintained at 450°. A very slow nitrogen flow was maintained throughout the reaction. The pyrolyzed material was collected in a trap at −70° and was dissolved in 25 ml of ether and washed with water, aqueous sodium bicarbonate, water, and saturated brine solution. After drying over magnesium sulfate and removal of the drying agent by filtration, the solvent was removed by distillation and the residue was distilled to give 2.77 g (53%), bp 95–96°, of a mixture shown to consist of 28% of **7**, 22% of **8**, and 50% of **11**, by vpc on a 24 ft × 1/8 in. 5% SF-96 on 60–80 Chromosorb G column at 50°.

The three components were separated by preparative vpc on a 25 ft × 1/4 in. 20% D.C. Silicone Fluid No. 200 on 60–80 Chromosorb P column at 75°. Compounds **7** and **8** had identical ir spectra with the two dienes obtained from the transition metal complex promoted rearrangement of **1**. Compound **11** was identified on the basis of the following spectral data. The infrared absorption of **11** (CCl_4) had characteristic absorptions at 3.20 (olefinic C–H), 6.05, 6.20 (olefin), 7.24, 7.34 (geminal dimethyl), and 11.16 μ (terminal methylene). The nmr spectrum (CCl_4) of **11** had a broad 3 H multiplet centered at τ 4.10, a 2 H multiplet centered at 5.0, a 1 H septuplet at 7.66, and a 6 H doublet centered at 9.0 (*J* = 7 Hz). Finally, the ultraviolet spectrum of **11** showed $\lambda_{max}^{isooctane}$ 224 nm (ϵ 21,800). The trans stereochemistry was assigned on the basis of the previously reported work of Greenwood.[11]

Triphenylisopropylphosphonium Bromide. A mixture of 35 g (0.13 mol) of triphenylphosphine and 30 g (0.24 mol) of isopropyl bromide was heated at 130–140° in a glass bomb for 2 days. The bomb was cooled and the product washed with ether to give 51 g of **13**, mp 234–238° (lit.[19] mp 238°).

***trans*-2-Methyl-2,4-hexadiene (7).** To 24 ml (0.056 mol) of a 15% solution of *n*-butyllithium in hexane in a 250-ml three-necked round-bottomed flask equipped with a reflux condenser, addition funnel, mechanical stirrer, and nitrogen inlet tube, was added 100 ml of anhydrous ether and 21.6 g (0.056 mol) of triphenylisopropylphosphonium bromide. The mixture was stirred at room temperature for 15 hr. *trans*-2-Butenal[10] (3.57 g, 0.051 mol) was added and the reaction mixture was stirred at room temperature for 24 hr and then refluxed for 24 hr. The red solution turned milky yellow upon addition of the aldehyde. The reaction mixture was allowed to cool. The precipitate was filtered and washed with 125 ml of ether, which was combined with the rest of the reaction mixture and dried over calcium chloride. The ether and calcium chloride were removed and the product distilled through a 9-in. glass helices packed column, bp 98°. The product was homogeneous by vpc analysis and had an ir (CS_2) maximum at 10.44 μ and nmr ($CHCl_3$) absorptions at τ 8.28 (9 H, s), 4.48 (1 H, m), 4.25 (1 H, m), and 3.77 (1 H, m).

Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane (1) with 3.7 Mol % of Bis(benzonitrile)dichloropalladium(II). A solution of 38 mg of **1** in 2 ml of chloroform was cooled to 0° and stirred. To this solution was added 5.6 mg (3.7 mol %) of bis(benzonitrile)dichloropalladium(II). After stirring for 28 min the solvent and products were vacuum transferred away from the transition metal complex (0.1 mm). The crude product was purified to give a mixture of **2** and **3** by preparative vpc on a 20% D.C. Silicone Fluid No. 200, 1000 cs on a 60–80 Columpak (1/4 in. × 9 ft) column at 60°.

The minor component **3** had ir and nmr spectra identical with the vinylcyclopropane derivative obtained from the acid-catalyzed opening of **1**, while the major component **2** had ir and nmr spectra identical with the diene obtained in the reaction of **1** with chlorodicarbonylrhodium(I) dimer.[1] Yields (28% of **2** and 4% of **3**) were obtained by vpc analysis using 2,2,4-trimethylpentane as an internal standard as described previously.

Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane (1) with π-Allylpalladium(II) Chloride Dimer. A solution of 53 mg of **1** in 2 ml of chloroform was cooled to 0° and stirred. To this solution was added 4.3 mg (2 mol %) of π-allylpalladium(II) chloride dimer. After stirring for 35 min the solvent and products were vacuum transferred away from the transition metal complex (0.1 mm). The 1-methyl-1-(2-propenyl)cyclopropane (**3**) was separated from the mixture of dienes (**2**, **7**, and **8**) by preparative vpc on a 20% D.C. Silicone Fluid No. 200, 1000 cs on a 60–80 Columpak (1/4 in. × 9 ft) column at 70°. The yield for the reaction was determined as an average of three runs by vpc analysis using 2,2,4-trimethylpentane as an internal standard. The composition of the diene mixture was determined by a combination of vpc analysis and quantitative ir spectral studies. The ratio of *cis*-diene **8** to **2** and **7** was determined by vpc on a 24 ft × 1/8 in. 5% SF-96 on 60–80 Chromosorb G column at 60°. The ratio of **2** to **7** was then calculated by infrared analysis on a Beckman IR-9 spectrophotometer using a 5% solution in carbon disulfide. The characteristic absorptions of **2** at 890 cm^{-1} and **7** at 952 cm^{-1} were used in this determination.

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(19) U. H. M. Fagerlund and D. R. Idler, *J. Amer. Chem. Soc.*, **79**, 6473 (1957).

Control Reactions. (a) 1-Methyl-1-(2-propenyl)cyclopropane (3) and Bis(benzonitrile)dichloropalladium(II). A chloroform solution of **3** was stirred with the bis(benzonitrile)dichloropalladium overnight. Nmr analysis indicated that, although some of **3** had disappeared, no dienes were formed.

(b) Treatment of *trans*-2-Methyl-2,4-hexadiene (7) with Bis(benzonitrile)dichloropalladium(II). To a stirred solution of 49 mg of **7** in 2 ml of chloroform was added 4 mg (2 mol %) of bis(benzonitrile)-palladium chloride. After stirring overnight, nmr analysis indicated that, although some of **7** had polymerized, it had not isomerized.

(c) Treatment of 2,3-Dimethyl-2,4-pentadiene (2) with Bis(benzonitrile)dichloropalladium(II). To a solution of 52 mg of **2** in 2 ml of chloroform was added, with stirring, 8.4 mg (4 mol %) of the transition metal complex. After stirring overnight, nmr analysis indicated that, although some of **2** had polymerized, it had not isomerized.

(d) Treatment of 1-Methyl-1-(2-propenyl)cyclopropane (3) with π-Allylpalladium(II) Chloride Dimer. A chloroform solution of **3** was stirred with π-allylpalladium chloride dimer overnight. Vpc analysis indicated that, although some of **3** had disappeared, no dienes were formed.

(e) Treatment of *trans*-2-Methyl-2,4-hexadiene (7) with π-Allylpalladium(II) Chloride Dimer. To a solution of 53 mg of **7** in 2 ml of chloroform was added, with stirring, 5.5 mg (2 mol %) of π-allylpalladium chloride dimer. After stirring for 17 hr, nmr analysis of the product mixture indicated that, although some of **7** had polymerized, it had not isomerized.

(f) Treatment of *cis*- and *trans*-2-Methyl-2,4-hexadiene (7 and 8) with π-Allylpalladium(II) Chloride Dimer. To a solution of 51 mg of a mixture of **7** and **8** in 2 ml of chloroform was added 5.3 mg (2 mol %) of π-allylpalladium chloride dimer. Vpc analysis of the reaction mixture on a 24 ft × $^1/_8$ in. 5% SF-96 on 60–80 Chromosorb G column at 62° indicated no change in the cis:trans ratio after 14 hr.

Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane (1) with 0.2 Mol % of Bis(benzonitrile)dichloropalladium(II). To a stirred solution of 100 mg of **1** in 2 ml of chloroform was added 0.7 mg (0.2 mol %) of bis(benzonitrile)dichloropalladium(II). After stirring at room temperature for 12 hr, the solvent and products were vacuum transferred (0.1 mm) away from the transition metal complex. The olefinic products were isolated as a mixture of **2**, **7**, and **8** and identified as previously described. Yields and diene composition were obtained by a combination of vpc (using 2,2,4-trimethylpentane as internal standard) and infrared techniques as previously described.

Ligand Exchange Reaction using 3,4-Dimethyl-1,3-pentadiene (2) and Bis(benzonitrile)dichloropalladium(II). To a solution of 37.4 mg of **2** in 2 ml of chloroform was added 2.9 mg (2 mol %) of bis(benzonitrile)dichloropalladium(II). (The solution was initially deep red and turned to orange after 10 min.) After stirring for 24 hr, the mixture was vacuum transferred (25° (0.3 mm), 0.5 hr) and 35 mg of **1** in 2 ml of chloroform was added to the residue. The mixture was stirred overnight. Nmr analysis of the vacuum transferred material showed the presence of a mixture of **7** and **8** and **2** in a 4:1 ratio.

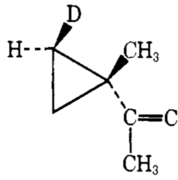
Preparation of 14. The complex **14** was prepared following the procedure of Slade and Jonassen.[14]

Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane with 14. A solution of 192 mg of **1** in 3 ml of chloroform was stirred with 9.2 mg (1 mol %) of **14**[20] at room temperature for 4 hr. The solvent and products were vacuum transferred away from the transition metal complex (25° (0.1 mm)) and the vacuum transferred mixture was analyzed as described above for the reaction of **1** with π-allylpalladium(II) chloride dimer.

General Procedure for Reaction of 1,2,2-Trimethylbicyclo[1.1.0]-butane with Transition Metal Complexes Listed in Table II. To a solution of 100 mg of **1** in 5 ml of chloroform was added 2 mol % of the transition metal complex ($PdCl_2$, $[Rh(CO)_2Cl]_2$, [Rh(norbornadiene)$_2$Cl]$_2$, $Rh(CO)_2AcAc$, $((C_6H_5)_3P)_3RhCl$, $((C_6H_5)_3P)_2Rh(H)CO$, $RhCl_3 \cdot H_2O$, $Rh(AcAc)_3$, or AuI_3). After stirring for an appropriate length of time, the solvent and products were vacuum transferred (0.1 mm) away from the transition metal complex. In the cases where only **2** and **3** were formed, the reaction mixtures were analyzed as described above for the reaction of **1** with bis(benzonitrile)dichloropalladium(II). In the cases where **2**, **3**, **7**, and **8** were formed, the reaction mixtures were analyzed as described above for the reaction of **1** with π-allylpalladium(II) chloride dimer.

Reaction of 1,2,2-Trimethylbicyclo[1.1.0]butane (1) with π-Allylpalladium Chloride Dimer in Methanol. To a solution of 300 mg of **1** in 3 ml of methanol was added 12 mg (2 mol %) of π-allylpalladium chloride dimer. After 1 min at 25° the solvent and volatile product were vacuum transferred (0.1 mm). The only volatile product obtained was **15** which was identified by comparison with an authentic sample.[1] The yield, 94%, of this product was determined by vpc using 1-butanol as an internal standard.

Reaction of 1,2,2,3-Tetramethylbicyclo[1.1.0]butane (16) with Chlorotricarbonyliridium Dimer. To a solution of 200 mg of **16** in 2 ml of chloroform cooled in an ice–water bath was added 55.5 mg (5 mol %) of the transition metal complex. The solution was allowed to sit overnight at room temperature and the volatile material was then vacuum transferred (25° (0.3 mm)). The two components of the mixture were separated and collected by preparative vpc on a 20% D.C. Silicone Fluid No. 200, 1000 cs on 60–80 Columpak ($^1/_4$ in. × 9 ft) column at 80°. The second peak was found to have an ir spectrum identical with that of an authentic sample of **18**.[1] The first peak had an ir (CCl_4) maximum at 11.2 μ and nmr (CCl_4) absorptions at τ 5.30 (2 H, m), 8.30 (3 H, d, J = 1 Hz), 8.86 (3 H, s), 8.92 (3 H, d, J = 5 Hz), 9.09 (2 H, t, br m), and 10.00 (1 H, m). The cisoid nature of the two methyl groups was assigned on the basis of a comparison of the nmr spectrum with that of **3** and **24**. Attention was focused on the resonance of the cyclopropyl protons of each compound. The two-proton multiplet appearing at τ 9.58 in the nmr spectrum of **3** was assigned to the cyclopropyl protons cis to the methyl group while the two-proton multiplet appearing at τ 9.36 was assigned to the cyclopropyl protons cis to the vinyl group.[1] This assignment was supported by the nmr spectrum of **24**, which showed a one-proton multiplet at τ 9.58 and a two-proton multiplet at τ 9.36. The nmr of **20** shows that the *upfield* cyclopropyl proton resonance of **3** (τ 9.58) is shifted further upfield to τ 10.00, by virtue of the presence of the added methyl group, and integrates for one proton—a shift in the expected direction. On the other hand, the *downfield* cyclopropyl proton resonance of **3** (τ 9.36) is shifted further downfield at τ 9.09 (and integrates for two protons) with the addition of the methyl group. An exact mass determination on the compound showed an observed *m/e* of 110.1094 and a calculated mass of 110.1095.



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The product yields were determined using 2,2,4-trimethylpentane as an internal standard as previously described.

General Procedure for Reaction of 2,2,4,4-Tetramethylbicyclo-[1.1.0]butane (21) with the Transition Metal Complexes Listed in Table III. To a solution of 100 mg of **21** in 2 ml of chloroform was added 2 mol % of the specified transition metal complex. After stirring for the specified length of time, the nmr spectrum indicated that the only product was 2,5-dimethyl-2,4-hexadiene (**22**).[1] Yields were determined using 2,2,4-trimethylpentane as an internal standard as previously described.[1]

Determination of Reaction Time for the Reaction of 2,2,4,4-Tetramethylbicyclo[1.1.0]butane (21) with Various Transition Metal Complexes. To a stirred solution of about 20 mg of 2,2,4,4-tetramethylbicyclo[1.1.0]butane in 2 ml of chloroform was added 2 mol % of the transition metal complex. The progress of the reaction was followed by removal of 5-μl aliquots, dilution to 5 ml with chloroform, and uv absorption determination at 238 nm (maximum for 2,5-dimethyl-2,4-hexadiene). The yield of each reaction was determined at the time when the uv absorption due to the product remained constant or started to decrease.

Nmr spectral analysis of each reaction mixture (in duplicate) after the time indicated by uv spectral analysis showed the presence of only **22** and the absence of **21**.

Determination of Yields for the Reaction of 2,2,4,4-Tetramethylbicyclo[1.1.0]butane (21) with Various Transition Metal Complexes. To a stirred solution of 50 mg of **21** in 2 ml of chloroform was added 2 mol % of the specified transition metal complex. The yields were determined as described above for the reaction of **1** with various transition metal complexes.

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(20) The catalyst was shown to contain less than 1% of bis(benzonitrile)dichloropalladium(II) by ir analysis.

Reaction of 23 with Pentafluorophenylcopper Tetramer. Three separate weighed aliquots of a mixture of **23** and tetrahydrofuran were diluted with chloroform and a small amount of pentafluorophenylcopper tetramer (*ca.* 5 mg) was added. An immediate exothermic reaction took place with the simultaneous evolution of nitrogen. An internal standard (2,2,4-trimethylpentane) was then added and the solution analyzed by vpc on a 10 ft × $^{1}/_{8}$ in. 20% D.C. Silicone Fluid No. 200 on 60–80 Chromosorb P column at 75°. The yield of 2,5-dimethyl-2,4-hexadiene (**22**), which was the only product, was 48% based on the tosylhydrazone precursor of **23**. Prior to the analytical run a preparative scale reaction was run and the product was collected and shown to be identical in all respects with an authentic sample.

Acknowledgment. We are indebted to the National Science Foundation for a grant which supported this investigation.

Transition Metal Complex Promoted Rearrangements. Tricyclo[4.1.0.0^{2,7}]heptane and 1-Methyltricyclo[4.1.0.0^{2,7}]heptane[1]

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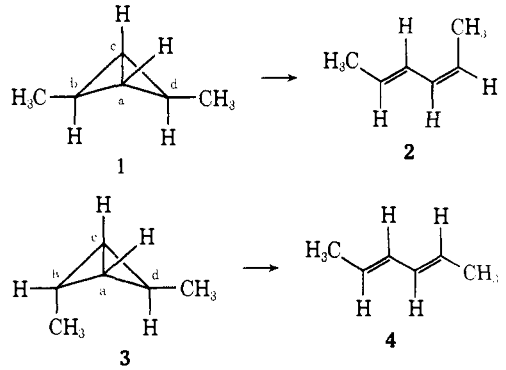
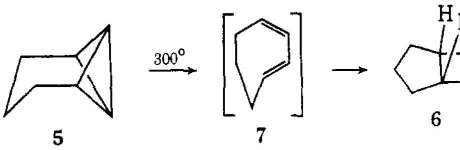
Abstract: The transition metal complex promoted isomerization of tricyclo[4.1.0.0^{2,7}]heptane (**5**) and 1-methyltricyclc[4.1.0.0^{2,7}]heptane (**13**) has been studied in detail. Derivatives of copper, iridium, mercury, palladium, platinum, rhodium, ruthenium, tin, and zinc were found to readily bring about the rearrangement of **5** to norcarene, 3-methylenecyclohexene, or 1,3-cycloheptadiene. Similarly, certain transition metal derivatives readily isomerize **13** to methylated derivatives of norcarene, 3-methylenecyclohexene, 1,3-cycloheptadiene, or bicyclo[3.2.0]hept-6-ene. The yields and nature of the products formed were shown to be very dependent on the nature of the metal, the ligands attached to the metal, and the presence of the methyl group on **13**. Mechanistically, it appears that the transition metal promoted isomerization of these highly strained tricyclic molecules occurred *via* a stepwise process. A mechanism is proposed which involves initial attack of the transition metal complex at the bridgehead of the bicyclo[1.1.0]butane moiety to cleave a side bond of the bicyclo[1.1.0]butane portion of the molecule. This mechanistic scheme utilizes the transition metal complex as a highly selective Lewis type acid which generates a cyclopropylcarbinyl type cation in cleaving the aforementioned side bond. Consistent with this mechanistic scheme were experiments in which some initially generated intermediate was trapped by nucleophilic solvent. An overall mechanistic picture is presented which provides a reasonable explanation of the processes which lead to each of the observed products.

Since the first reported synthesis of bicyclo[1.1.0]butane and its derivatives, numerous workers have investigated its thermal isomerization to 1,3-diene derivatives.[3] The mechanism of this rearrangement has been discussed in detail,[4,5] and has been shown to involve a conrotatory mode of ring opening of one cyclopropane ring concomitant with a disrotatory mode of ring opening of the other cyclopropane ring. For example, *exo,exo*-2,4-dimethylbicyclo[1.1.0]butane (**1**) gives 93% of *cis,trans*-2,4-hexadiene (**2**) and *endo,exo*-2,4-dimethylbicyclo[1.1.0]butane (**3**) gives 95% of *trans,trans*-2,4-hexadiene (**4**).[4c] The formation of **2**, for example, may be viewed as occurring by cleavage of either of the opposite pairs of side bonds (a–b and c–d, or a–d and b–c) followed by conrotatory rotation of one pair of developing orbitals and disrotatory rotation of the other set of orbitals to give the observed stereochemistry. The thermal opening of tricyclo[4.1.0.0^{2,7}]heptane (**5**) has been reported[4b] to give bicyclo[3.2.0]hept-6-ene (**6**). It was suggested that *cis,*-*trans*-1,3-cycloheptadiene (**7**) was initially formed. It was further postulated that **7** was very unstable due to the strain of the trans double bond and thus underwent rapid ring closure under the thermolysis conditions to give **6**. It should be noted that there is no currently





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[1] Paper XXXIV of a series on The Chemistry of Bent Bonds. For the preceding paper in this series see P. G. Gassman, G. R. Meyer, and F. J. Williams, *J. Amer. Chem. Soc.*, **94**, 7741 (1972).

[2] National Science Foundation Trainee, 1968–1972.

[3] For a detailed listing of references to the thermal cleavage of bicyclo[1.1.0]butanes, see P. G. Gassman, G. R. Meyer, and F. J. Williams, *J. Amer. Chem. Soc.*, **94**, 7741 (1972).

[4] (a) K. B. Wiberg and J. M. Lavinish, *ibid.*, **88**, 5272 (1966); (b) K. B. Wiberg and G. Szeimies, *Tetrahedron Lett.*, 1235 (1968); (c) G. L. Closs and P. E. Pfeffer, *J. Amer. Chem. Soc.*, **90**, 2452 (1968).

[5] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969). In particular, see pp 810–814.