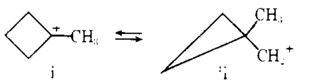

example, in 41) can be expected to alter this equilibrium ratio. Similarly, geometrically enforced deviations from the bisected geometry in ii would work to decrease its relative stability.

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Influence of Structural Features on the Course of Transition Metal Catalyzed 1,8-Bishomocubane Rearrangements[1]

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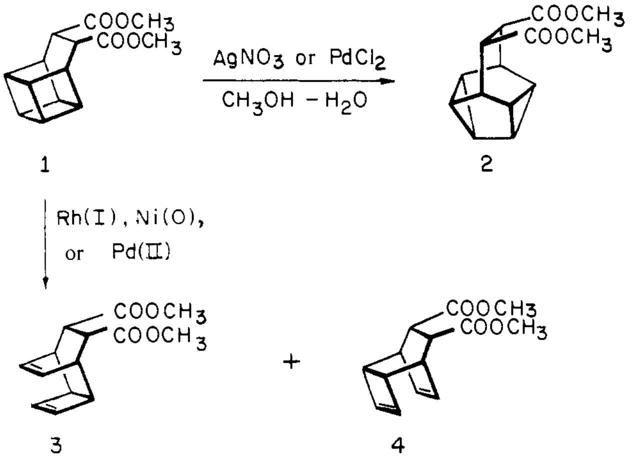
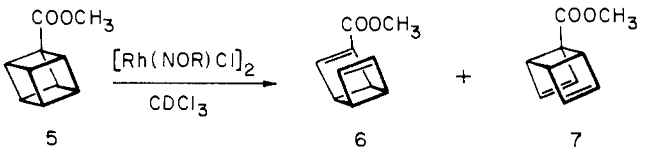
Abstract: Evidence is presented that the rearrangements of several 1,8-bishomocubane derivatives by various Rh(I) and Pd(II) catalysts are sensitive not only to the nature of the ligands attached to the metal but also to the level of substitution at the reaction site (C_4 and C_5). Thus, the level of snoutane production increases in the order $[Rh(NOR)Cl]_2 < PdI_2(PPh_3)_2 < PdCl_2(PPh_3)_2 < PdCl_2(PhCN)_2$ irrespective of the degree or nature of the bishomocubane substitution pattern. The observed effect is sometimes very large varying from 0 to 100% of snoutane during progression through this series of catalysts. This trend indicates decreased formation of snoutane as the metal ion is made softer. Also, as steric hindrance is gradually increased at the remote bishomocubyl corners, greater proportions of snoutane appear in the product mixture. The effect is significantly greater with $PdI_2(PPh_3)_2$ than for $[Rh(NOR)Cl]_2$ indicating that the palladium complex is more responsive in its catalytic action to these influences. Kinetic data point up the fact that steric retardation with $PdI_2(PPh_3)_2$ is a far more serious issue than it is with Ag(I) catalysis. The isomerizations appear to be less sensitive to electronic effects. Since the distribution of dienes derived from 9,10-disubstituted bishomocubanes is generally such that the endo isomer predominates, preferential approach from the direction proximal to these groups is kinetically favored in most (but not all) cases. Additional trends in these rearrangements are discussed.

Supplementing the previous stereochemical[4] and kinetic[5] investigation of Ag(I)-promoted bishomocubane-snoutane rearrangements, we here describe the considerably more varied behavior of such compounds toward Pd(II) and Rh(I) catalyst systems. Previously, Dauben had shown that reaction of diester **1** with $PdCl_2$ in aqueous methanol similarly led in quantitative yield to snoutane **2**.[6] However, Pd(II) complexes having ligands (*e.g.*, phosphites) which are strong π acceptors but weak σ donors were found to promote competing isomerization leading to moderate levels of **3** and **4**. With palladium complexes containing ligands of the σ donor-π acceptor type, *e.g.*, $PdI_2(PPh)_3$, essentially complete conversion to **3** and **4** was noted. The rearrangement of **1** to **3** and **4** likewise operates exclusively when $Ni(COD)_2$[8] and a series of Rh(I) complexes[6] are employed. These findings conform to earlier discoveries that Rh(I) catalysis leads to efficient cyclobutane-diolefin valence isomerization. Examples include the rearrangements of quadricyclane to norbornadiene,[9] hexamethylprismane to hexamethyl(Dewar benzene),[10] cubane to tricyclooctadiene,[11] and cuneane to semibullvalene.[12] The choice of catalysis mode is therefore seemingly predicated upon the ability of the metal ion for oxidative addition which facilitates the cyclobutane-diolefin transformation or for σ electron acceptance which favors conversion to snoutane.[6]



However, it was apparent when the present work was initiated that these mechanistic inferences had been drawn exclusively from substrates lacking substituents at the reaction site. A detailed examination of substituent effects as they affect the environment where reaction occurs, and consequently the reaction course as well, comprises the principal objective of this investigation. The only previous observation to be made on the subject of substituent influences is the response of carbomethoxycubane (**5**) to the catalytic effect of $[Rh(NOR)Cl]_2$.[11] At 40° in deuteriochloroform solution, **5** experiences isomerization to **6** and **7** at a rate 16 times slower than cubane and gives principally that diene

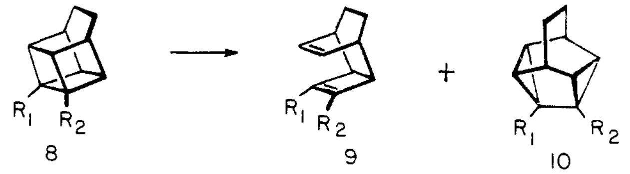


(**6**) which arises from σ bond cleavage to the carbon atom bearing the electron withdrawing group (71%). Statistical factors necessarily gain importance in these examples, and the underlying preference for formation of **6** is not completely understood. As noted previously,[5] the 1,8-bishomocubyl framework restricts transition metal attack to one of two surfaces which, depending upon substitution, may be equivalent. As far as diene production is concerned, these two pathways are easily recognizable because the ring opened products differ in their overall stereochemistry.

The focus of our interest required that we have 4- and 4,5-substituted 1,8-bishomocubanes at our disposal. The previous reports[4,5] detail the methodology utilized to gain synthetic entry to these highly strained molecules.

Results

Hydrocarbon Derivatives. When a dry benzene solution of parent hydrocarbon **8a** (3.8×10^{-2} *M*) was heated with 1.0×10^{-2} *M* $[Rh(NOR)Cl]_2$ at 75° for 29 hr, clean isomerization occurred to yield 99.5% of diene **9a** accompanied by approximately 0.5% of snoutane (**10a**). The identity of the nicely crystalline **9a** was founded on its characteristic pmr spectrum. The structure proof for **10a** was based upon comparison with an authentic sample obtained from silver-catalyzed rearrangement.[5] Treatment of **8a** with $PdI_2(PPh_3)_2$ under comparable conditions resulted in slower bond reorganization. After 344 hr at 75°, the composition of the product mixture was 95.5% of **9a** and 4.5% of **10a.** When recourse was made to $PdCl_2(PPh_3)_2$, the rate of reaction returned qualitatively to that exhibited by the rhodium catalyst, but a further decrease in product selectivity was noted, the proportion of diene **9a** now dropping to 71.1%. The conditions used for these reactions and the results are summarized in Table I.

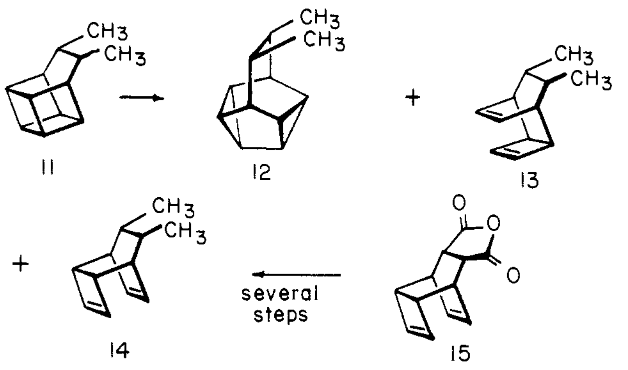


a, $R_1 = R_2 = H$; b, $R_1 = CH_3$, $R_2 = H$; c, $R_1 = R_2 = CH_3$

We next turned our attention to the effect of 4-methyl substitution. Interestingly, $[Rh(NOR)Cl]_2$ did not promote exclusive rearrangement of **8b** to **9b** but produced 7.7% of snoutane **10b** as well. The behavior of $PdI_2(PPh_3)_2$ toward **8b** was still more striking. After 96 hr at 75° in anhydrous benzene, isomerization had progressed to the extent of 45.2% and diene **9b** and snoutane **10b** had been produced in near equal amounts (see Table I). When the reaction was allowed to proceed to the 94.3% level (272 hr), the normalized amounts of these isomers were seen to be 53.9 and 46.1%, respectively. The reaction of **8b** with $PdCl_2(PPh_3)_2$ followed the trend established earlier with **8a** in the sense that isomerization was relatively rapid (complete in 26 hr) and snoutane production was additionally favored (94.4%).

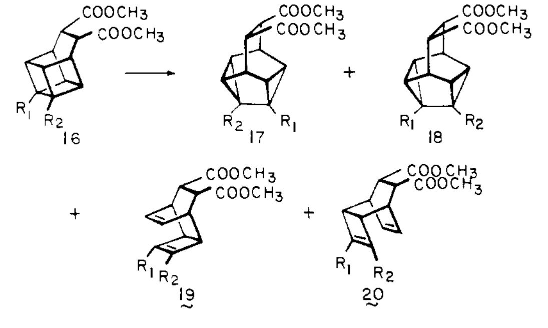
The behavior of 4,5-dimethyl derivative **8c** is best characterized as an extreme example of substituent effects. With all three catalysts, the rates (qualitative) of isomerization were significantly slowed, presumably for steric reasons. Surprisingly, however, the levels to which snoutane **9c** was produced were totally unprecedented. In the case of $[Rh(NOR)Cl]_2$, 28% of **10c** resulted and this value rose to 89.2% for $PdI_2(PPh_3)_2$. Catalysis by $PdCl_2(PPh_3)_2$ led exclusively to **10c!**

These findings suggested to us that substitution by an alkyl group at C_4 is capable of directing a greater proportion of reaction into that channel which operates during Ag(I) catalysis and that this effect is further magnified when a second group is positioned at the remaining remote corner. To remove the unlikely possibility that mere alkyl substitution of the 1,8-bischomocubyl nucleus elsewhere than at C_4 and C_5 would produce comparable effects, we have also examined the behavior of the cis 9,10-dimethyl derivative **11.** Product analysis (vpc) of the mixtures obtained from its $[Rh(NOR)Cl]_2$ and $PdI_2(PPh_3)_2$-catalyzed rearrangement indicated that small amounts of snoutane **12** were formed. However, the 1-5% yields clearly do not compare with the behavior of **8c.** An added point of interest was the finding that Rh(I) favored production of diene **14** while the Pd(II) catalyst gave relatively higher amounts of diene **13.** The structural assignments to **13** and **14** follow again from their pmr data and from independent synthesis of **14** beginning with the cyclooctatetraene-maleic anhydride adduct of known stereochemistry (**15**).



9,10-Dicarbomethoxybishomocubanes. The intricate substituent-linked response of **8a–8c** to rearrangement by Rh(I) and Pd(II) complexes led us to seek more information about these reactions *via* a study of the readily accessible 9,10-dicarbomethoxybishomocubanes. When the polar ester functions are cis oriented, two isomeric dienes (**19** and **20**) can be produced depending upon the direction of approach by the catalyst. Direct comparison with the behavior of **11** becomes possible as well.

Treatment of **16a** with catalytic quantities of rhodium norbornadiene chloride dimer in benzene solution at 40° for 40 hr gave rise exclusively to the dienes **19a** (19.5%) and **20a** (80.5%). This fourfold preference for ring opening of the bischomocubyl framework from the direction syn to the 9,10-substituents (compare **11** where the same is true) is significantly diminished when $PdI_2(PPh_3)_2$ is employed as catalyst (see Table II). The small levels of snoutane which are produced under the latter conditions parallel the observations made above with the hydrocarbon derivatives. Addition of $PdCl_2(PPh_3)_2$ to benzene solutions of **16a** resulted after 41 hr at 80° in conversion to still higher levels (53%) of **17a.** At this point, we were prompted to investigate the catalytic effects of $PdCl_2(PhCN)_2$ on **16a.** The benzonitrile ligands are weak σ donors-π acceptors and nonpolarizable,



a, $R_1 = R_2 = H$; b, $R_1 = CH_2OAc$, $R_2 = H$; c, $R_1 = CH_3$, $R_2 = H$; d, $R_1 = R_2 = CH_3$

Table I. Rh(I) and Pd(II) Promoted Isomerizations of 1,8-Bishomocubanes **8** and **11**

Compd	Catalyst	Solvent	Temp, °C	Time, hr	Composition, % **8**	**9**	**10**
8a	$[Rh(NOR)Cl]_2$	C_6H_6	75	29		99.5	0.5
	$PdI_2(PPh_3)_2$	C_6H_6	75	344		95.5	4.5
	$PdCl_2(PPh_3)_2$	C_6H_6	75	29		71.1	28.9
8b	$[Rh(NOR)Cl]_2$	C_6H_6	75	29		92.3	7.7
	$PdI_2(PPh_3)_2$	C_6H_6	75	96	54.8	23.3	21.9
						(51.6)^{a}	(48.4)^{a}
				272	5.7	50.8	43.4
						(53.9)^{a}	(46.1)^{a}
	$PdCl_2(PPh_3)_2$	C_6H_6	75	26		5.6	94.4
8c	$[Rh(NOR)Cl]_2$	C_6H_6	75	24	11.7	63.4	24.9
						(71.8)^{a}	(28.2)^{a}
				72		72.5	27.5
	$PdI_2(PPh_3)_2$	C_6H_6	75	72	100		
				2570^{b}	89.3	1.1	9.1
						(10.8)^{a}	(89.2)^{a}
	$PdCl_2(PPh_3)_2$	C_6H_6	75	32	4.2		95.8
				127			100
11	$[Rh(NOR)Cl]_2$	C_6H_6	75	22	1 (**12**)	24 (**13**)	75 (**14**)
	$PdI_2(PPh_3)_2$	C_6H_6	80	89	5 (**12**)	56 (**13**)	39 (**14**)

[a] Values normalized to 100%. [b] 107 days.

Table II. Rh(I) and Pd(II) Promoted Isomerizations of Several 9,10-Dicarbomethoxybishomocubanes (**16**)

Compd	Catalyst	Solvent	Temp, °C	Time, hr	**16**	Composition, % **17/18**	**19**	**20**
16a	$[Rh(NOR)Cl]_2$	C_6H_6	40	40			19.5	80.5
	$PdI_2(PPh_3)_2$	C_6H_6	80	63	39.4	4.2	20.6	35.7
						(7)^{a}	(34)^{a}	(59)^{a}
				161	19.6	7.6	26.5	46.2
						(9)^{a}	(33)^{a}	(58)^{a}
		$CHCl_3$	65	256	14	(9)^{a}	(35)^{a}	(56)^{a}
	$PdCl_2(PPh_3)_2$	C_6H_6	80	41		53	11	36
		$CHCl_3$	40	45	4	37	23	36
	$PdCl_2(PhCN)_2$	C_6H_6	80	38	8.3	88.9	0.7	2.1
				135		96	1	3
16b	$[Rh(NOR)Cl]_2$	C_6H_6	40	40			19	81
	$PdI_2(PPh_3)_2$	C_6H_6	80	236	77	9	4	10
						(39)^{a}	(17)^{a}	(43)^{a}
				622	33	31	7	29
						(47)^{a}	(10)^{a}	(43)^{a}
				1700	15	40	8	37
						(17/30)^{a}	(9)^{a}	(44)^{a}
	$PdCl_2(PPh_3)_2$	C_6H_6	80	53		52/48		
	$PdCl_2(PhCN)_2$	C_6H_6	80	19		100		
16c	$[Rh(NOR)Cl]_2$	C_6H_6	40	90	5.5	1.6/1.0	17.4	72.8
						(1.7/1.0)^{a}	(18.4)^{b}	(77.1)^{a}
	$PdI_2(PPh_3)_2$	C_6H_6	80	800	7.8	15.3/27.3	8.3	41.3
						(16/30)^{a}	(9)^{a}	(45)^{a}
	$PdCl_2(PPh_3)_2$	C_6H_6	80	23		50.2/47.9	0.4	1.5
	$PdCl_2(PhCN)_2$	C_6H_6	80	47	3.3	41.0/55.0	0.2	0.4
16d	$[Rh(NOR)Cl]_2$	C_6H_6	80	26	14	19	4	63
				40	7.7	13.2	4.5	74.6
				160		22	4	74
	$PdI_2(PPh_3)_2$	C_6H_6	80	600	84	5.9	1.6	8.5
						(37)^{a}	(10)^{a}	(53)^{a}
	$PdCl_2(PPh_3)_2$	C_6H_6	80	119		100		
	$PdCl_2(PhCN)_2$	C_6H_6	80	120	0.9	96.6	1.0	1.5

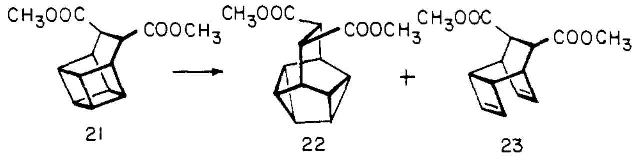
[a] Values normalized to 100%.

and are conducive to formation of exceptionally high levels of snoutane. After 135 hr in benzene at 80°, 96% of **17a** was produced and the **19a**/**20a** ratio again favored **20a** by a small but significant margin (Table II).

Replacement of the C_4 hydrogen in **16a** by $-CH_2OAc$ had little effect on the response to $[Rh(NOR)Cl]_2$ catalysis. Rearrangement in benzene solution was again complete in 40 hr, and only **19b** and **20b** were produced. The ratio of these dienes (19:81) was seen to be entirely comparable with that found for the parent diester. In contrast, the relative reactivity of **16b** toward $PdI_2(PPh_3)_2$ was notably decreased and the proportion of snoutanes **17b** and **18b** in the product mixture was measurably enhanced (Table II). It is interesting and mechanistically relevant that distal isomer **18b** is formed preferentially under these conditions and to an extent (64% **18b**; 36% **17b**) identical with that realized upon Ag(I) catalysis.[4] When $PdCl_2(PPh_3)_2$ was employed, the only products were these two snoutanes. However, the small structural change in the catalyst proved to be a sufficient perturbation to cause a changeover in isomer distribution with **17b** (52%) now predominating over **18b** (48%). The replacement of iodine by chlorine in the catalyst is also adequate to generate a meaningful kinetic change. With $PdI_2(PPh_3)_2$ the level of isomerization of **16b** after 1700 hr at 80° is only 85%, while with $PdCl_2(PPh_3)_2$ conversion to the snoutanes is complete after 53 hr under the same conditions.

Substitution by methyl at C_4 has a greater impact than acetoxymethyl on Rh(I) catalysis. Rearrangement is not only slower but small amounts of snoutanes **17c** (1.7%) and **18c** (1.0%) are observed as well. This preference for proximal diester **17c** differs from the behavior of this bishomocubane toward Ag(I).[4] As one progresses through the series of catalysts $PdI_2(PPh_3)_2$, $PdCl_2(PPh_3)_2$, and $PdCl_2(PhCN)_2$, the expected increase in snoutane production is seen. What was not anticipated was the vacillation in the proportion of proximal isomer. Like $[Rh(NOR)Cl]_2$, $PdCl_2(PPh_3)_2$ promotes preferential formation of **17c.** On the other hand, catalysis by $PdI_2(PPh_3)_2$ and $PdCl_2(PhCN)_2$ promotes more favorable bond switching in the direction leading to **18c.**

As in the case of **16a,** the action of diiodobis(triphenylphosphine)palladium(II) on trans diester **21** affords chiefly the ring opened diene **23** (92%), while rhodium norbornadiene chloride dimer gives rise essentially completely to **23.**



Consequently, when the transition is made from a bishomocubyl diester (**16a**) having two differing available reaction sites to one (**21**) having a pair of equivalent cubyl surfaces, little change arises in product distribution.

4,5-Dimethyl substitution as in **16d** engendered the anticipated kinetic retardation. Higher levels than usual of snoutane formation were again evidenced, and the proportion of **17d** was seen to increase in passing from Rh(I) to Pd(II) catalysts and with structural modification of the latter. Diester **16d** paralleled **16a-c** in giving rise preferentially to endo diene **20d.** The formation of exo isomer **19d** was not completely precluded however. In all instances, the major diene ester **20** was identified by direct comparison with authentic samples prepared by Diels-Alder reaction of the appropriately substituted cyclooctatetraene with maleic anhydride, methanolysis, and esterification of the acid with diazomethane. Structural assignment to the exo isomers **19** followed from their closely analogous pmr and mass spectra. Vpc analysis served to separate certain of the individual diene isomers and snoutane pairs. In the case of **16b,** the mixture of **17b-18b** was collected and subsequently analyzed quantitatively by pmr methods (C_6H_6 solutions).[4] Suitable control experiments demonstrated that each of the bishomocubanes examined were stable to the reaction conditions in the absence of the catalysts.

Kinetic Data. Although the major intent of this study was to gain information on product distributions, some quantitative insight into structural effects on rate seemed desirable. A more exhaustive analysis of kinetic factors was conducted in the homocubane series as reported in the accompanying paper.[13] To this end, rates of $PdI_2(PPh_3)_2$-promoted rearrangement of several bishomocubanes were determined in anhydrous benzene solution at 80.6°. As clearly evidenced in Table III, long range inductive effects operate to retard somewhat the response of esters **16a** and **21** relative to hydrocarbon **11.** Substitution by methyl at C_4 causes a tenfold decrease in rate, while 4-acetoxymethyl derivative **16b** isomerizes some 15 times more slowly than **16a** (contrast effects on Ag(I) catalysis). By comparison, **16d** undergoes bond reorganization very slowly, the values cited being a generous upper limit obtained by extrapolation.

Discussion

The present results demonstrate that the two extreme possibilities for transition metal catalyzed rearrangement of bishomocubane derivatives are delicately dependent upon the nature of the complex. Arguments analogous to those developed by Dauben and Kielbania[6] point to control of the competitive pathways by the σ electron acceptor ability of the complex and by the σ donor-π acceptor capability of its ligands. Irrespective of the degree or nature of bishomocubane substitution, progression through the series $[Rh(NOR)Cl]_2$, $PdI_2(PPh_3)_2$, $PdCl_2(PPh_3)_2$, and $PdCl_2(PhCN)_2$ results in an increase in the relative amount of snoutane produced. In certain cases such as **16b,** the extent of the observed selectivity in mechanistic fractionation is truly large: 0% snoutane with $[Rh(NOR)Cl]_2$, 100% snoutane with $PdCl_2(PhCN)_2$. In the Pd(II) complexes, the halogen effect is rather impressive. These ligands are expected to contribute by their differing electronegativities to the overall softness of the palladium center, the more highly electronegative chloride atoms imparting a greater degree of hardness relative to iodine. The observed trends indicate decreased formation of snoutane as the metal is made softer through coordination to iodine. The notable kinetic differences between these two Pd(II) catalysts may also have their origin in such ligand variation, although the varied steric size of the two substances should not be overlooked.

Table III. Isomerization Rate Data (7.3×10^{-3} *M* $PdI_2(PPh_3)_2$, anhydrous C_6H_6, 80.6°)

Compd	k, M^{-1} sec^{-1}	Rel rate	Rel reactivity toward $AgClO_4$-C_6H_6[a]
11	7.0×10^{-3}	4.7	11
16a	1.5×10^{-3}	1.0	1
21	1.1×10^{-3}	0.7	0.5
16c	1.4×10^{-4}	0.09	9
16b	6.5×10^{-5}	0.04	0.14
16d	6.8×10^{-6}	>0.005	4

[a] Data taken from ref 5.

Our data require further that the course of these skeletal bond relocations be significantly dependent upon steric factors. Thus, structural changes of the sort exemplified by **8a, 8b,** and **8c** in which substitution is gradually increased at the two cubyl corners remote from the ethano bridge leads progressively to greater proportions of snoutane in the product mixture. The sensitivity to introduction of methyl groups at these sites is less for $[Rh(NOR)Cl]_2$ (0.5, 7.7, and 24.9%, respectively) than for $PdI_2(PPh_3)_2$ (4.5, 46.1, 89.2%), indicating that the palladium complex is more responsive in its catalytic action to these influences.

The same trend is witnessed with the 9,10-dicarbomethoxybishomocubanes. Added substituents at C_4 and C_5, whether electron donating or withdrawing, decrease the over-all rate of rearrangement. When both C_4 and C_5 are substituted, steric retardation becomes a serious issue, one which is far more overwhelming than observed for Ag(I) catalyzed isomerizations.[5] The substitution patterns examined appear to retard formation of diene products more so than snoutane isomers. The factored rate constant for conversion of **16a** to **17a** with $PdI_2(PPh_3)_2$ is 1.3×10^{-4} M^{-1} sec^{-1}. For **16b** and **16c,** the relevant catalytic rate constants are 3.1×10^{-5} and 6.4×10^{-5} M^{-1} sec^{-1}, respectively. The spread in reactivity is consequently approximately 4. Similar treatment of the data for combined conversion to **19** and **20** gives k_{cat} values of 1.36×10^{-3}, 3.4×10^{-5}, and 7.6×10^{-5}, respectively, or an 18-fold reactivity difference.

The isomerizations appear to be considerably less sensitive to electronic effects (Table III). Failure to observe a rate enhancement with C_4 methyl substitution could argue against development of carbonium ion character in the transition state. It could also reflect the offsetting of a favorable kinetic effect by more untoward steric complications. Discussion of this particular aspect of mechanism is taken up in the following paper[13] where a much wider range of substitution has been examined. It is relevant to note particularly at this time the wide differences in kinetic behavior of the several bishomocubanes toward $PdI_2(PPh_3)_2$ and $AgClO_4$ (Table III). The most striking example of this contrasting reactivity is dimethyl diester **16d** which isomerizes four times *more* rapidly than parent diester **16a** under conditions of Ag(I) catalysis. In the presence of $PdI_2(PPh_3)_2$, it is perhaps 1000 times *less* reactive.

The behavior of **11** toward $[Rh(NOR)Cl]_2$ indicates that approach from the direction proximal to the 9,10-methyl groups is kinetically favored (75% of **14**). The $PdI_2(PPh_3)_2$ catalyst system is seemingly not as greatly influenced since it produces 56% of **13.** In general, the cis 9,10-methoxycarbonyl and -methyl groups have the effect of enhancing diene formation from the proximal cubyl surface, particularly when $[Rh(NOR)Cl]_2$ is the catalyst. The rather variable distribution of snoutane isomers **17** and **18** remains difficult to rationalize either in terms of directional specificity or favored initial bond cleavage.[4,5]

In summary, the evidence is strong that complexes of Rh(I) and particularly Pd(II) are particularly responsive to steric factors and less so toward electronic influences. Variation in substitution at the reaction site not only leads to kinetic deceleration but also serves to generate surprisingly large differences in the distribution of snoutane and diene products.

Experimental Section

Proton magnetic resonance spectra were obtained with Varian A60-A, Varian HA-100, and Jeolco MH-100 spectrometers; apparent splittings are given in all cases. Infrared spectra were determined with Perkin-Elmer Model 137 and 467 instruments. Mass spectra were recorded on an AEI-MS9 spectrometer at an ionization potential of 70 eV. Elemental analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative vpc work was done on a Varian-Aerograph A90-P3 instrument equipped with a thermal conductivity detector. Analytical work and the kinetic measurements were achieved with the aid of a Hewlett-Packard 5750 unit (flame ionization detector) equipped with an electronic integrator.

General Remarks. The rearrangement reactions conducted at 40° were carried out in nmr tubes while those performed at 80° made use of sealed glass ampoules. In both instances, the vessels were cleansed thoroughly with acid (HNO_3 or HF), rinsed repeatedly with dilute ammonium hydroxide solution, and washed exhaustively with distilled water prior to drying. The various catalysts were prepared by literature methods and carefully purified.[14] Each container was charged with substrate and an anhydrous benzene (or chloroform) solution of catalyst. The ampoules were sealed under nitrogen at 25 mm pressure.

Reaction mixtures were processed by adding the cooled contents to a small volume (*ca.* 1 ml) of pentane, washing the mixture with saturated aqueous potassium cyanide solution (two 1.5-ml portions) and water (two 3-ml portions), and drying over magnesium sulfate. The dried solutions were analyzed directly by vpc methods with the aid of several columns.[15] Precautions were exercized at all times to ensure that purely thermal isomerization of the bishomocubanes to the isomeric snoutanes did not occur in the injector port of the gas chromatograph. In this connection, recourse to a polyethylene liner and direct on-column injection were found to be particularly advantageous.

Reaction of 8a with $[Rh(NOR)Cl]_2$. A dry benzene solution 3.8×10^{-2} *M* in **8a** and 4.5×10^{-3} *M* in catalyst was heated in a sealed ampoule at 75° for 29 hr. After work-up, there was obtained diene **9a** (99.5%) and snoutane **10a** (0.5%) (analysis on column a).[15] The latter hydrocarbon was characterized by direct comparison with an authentic sample.[4] Preparative vpc isolation of **9a** using column f[15] at 100° afforded the pure white solid: mp 61-62°; δ_{TMS} ($CDCl_3$) 5.90-6.04 (m, 2, olefinic), 5.88 (s, 2, cyclobutene), 2.40-2.72 (m, 4, bridgehead), 1.34-1.40 (m, 4, methylenes).

Anal. Calcd for $C_{10}H_{12}$: C, 90.85; H, 9.15. Found: C, 90.46; H, 8.83.

Reaction of 8a with $PdI_2(PPh_3)_2$. Reaction of a 5.7×10^{-2} *M* benzene solution of **8a** which was also 9.7×10^{-3} *M* in catalyst was heated in a sealed tube at 75° for 344 hr and gave 95.5% of **9a** and 4.5% of **10a** (analysis on column a).[15]

Reaction of 8a with $PdCl_2(PPh_3)_2$. When a benzene solution 3.8×10^{-2} *M* in **8a** and 4.5×10^{-3} *M* in catalyst was heated at 75° for 29 hr, there was obtained 71.1% of **9a** and 28.9% of **10a** (analysis on column a).[15]

Reaction of 8b with $[Rh(NOR)Cl]_2$. A reaction mixture 3.4×10^{-2} *M* in **8b** and 1.2×10^{-2} *M* in catalyst (C_6H_6 solvent) gave after 29 hr at 75° 92.3% of diene **9b** and 7.7% of snoutane **10b** (column a).[15] These were separated on column g.[15] Identification of **10b** was made by direct comparison with authentic hydrocarbon. *anti*-3-Methyltricyclo[4.2.2.0^{2,5}]deca-3,7-diene (**9b**) was obtained as a colorless oil: δ_{TMS} ($CDCl_3$) 5.90-6.01 (m, 2, olefinic), 5.53-5.60 (m, 1, cyclobutene), 2.33-2.58 (m, 4, bridgehead), 1.52-2.58 (m, 4, methylenes), 1.36 (br s, 3, methyl).

Anal. Calcd for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.49; H, 9.67.

Reaction of 8b with $PdI_2(PPh_3)_2$. Heating of a benzene solution 5.9×10^{-2} *M* in **8b** and 1.3×10^{-2} *M* in catalyst for 272 hr gave a product mixture containing **8b** (5.7%), **9b** (50.8%), and **10b** (43.4%) (analysis on column a).[15]

Reaction of 8b with $PdCl_2(PPh_3)_2$. When a dry benzene solution 3.4×10^{-2} *M* in **8b** and 4.5×10^{-3} *M* in catalyst was kept at 75° for 26 hr, there was produced 5.6% of **9b** and 94.4% of **10b** (analysis on column a).[15]

Reaction of 8c with $[Rh(NOR)Cl]_2$. A reaction mixture 7.8×10^{-2} *M* in **8c** and 1.2×10^{-2} *M* in catalyst was kept at 75° for 72 hr and analyzed on column a.[15] A mixture of **9c** (72.5%) and **10c** (27.5%) had been formed, and the isomers were separated on column g.[15] The snoutane proved identical with an authentic sample.[4] Diene **9c** was isolated as a colorless oil: δ_{TMS} ($CDCl_3$) 5.84-6.05 (m, 2, olefinic), 2.25-2.63 (br m, 4, bridgehead), 1.47 (s, 6, methyl), 1.28-1.45 (m, 4, methylenes).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.79; H, 9.91.

Reaction of 8c with $PdI_2(PPh_3)_2$. Heating a benzene solution 7.8×10^{-2} *M* in **8c** and 1.3×10^{-2} *M* in catalyst at 75° for 107 days gave a product mixture consisting of unreacted **8c** (89.3%), **9c** (1.1%), and **10c** (9.1%) (analysis on column a).[15]

Reaction of 8c with $PdCl_2(PPh_3)_2$. A dry benzene solution 5.2×10^{-2} *M* in **8c** and 4.5×10^{-3} *M* in catalyst was heated at 75° in a sealed ampoule for 127 hr. The single product formed was identified as snoutane **9c.**

Reaction of 11 with $[Rh(NOR)Cl]_2$. To 5.1 mg of **11** was added a solution of the catalyst (3 mg) in benzene (0.5 ml). This solution was sealed in a clean glass tube under vacuum and heated at 75° for 22 hr. The cooled reaction mixture was diluted with pentane and washed with aqueous potassium cyanide solution and water. Analysis of the dried organic phase on column e[15] at 120° showed starting material to be completely consumed. Three products were formed and these were shown to be **12** (1%), **13** (24%), and **14** (75%). The identities of **12** and **14** were established by comparison with anthentic samples. The structure of **13** follows from spectral data obtained on a sample isolated from a preparative scale reaction: δ_{TMS} ($CDCl_3$) 5.93-6.12 (m, 2, olefinic), 5.84 (s, 2, cyclobutene), 2.83-3.03 (m, 2), 2.16-2.45 (m, 2), 1.63-2.05 (m, 2), 0.83-1.08 (m, 6, methyls).

Calcd for $C_{12}H_{16}$ *m/e* 160.1252; found 160.1254.

Reaction of 11 with $PdI_2(PPh_3)_2$. An ampoule was charged with 2 mg of **11** and 0.5 ml of 0.0019 *M* catalyst solution in benzene, sealed, and heated at 80° for 89 hr. Vpc analysis of the processed reaction mixture on column d[15] revealed the presence of **12** (5%), **13** (56%), and **14** (39%).

***cis*-7,8-Bis(hydroxymethyl)-*anti*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene.**[16] A solution of 23.5 g (0.116 mol) of **15**[17] in 200 ml of tetrahydrofuran was added dropwise during 1 hr to a refluxing mixture of lithium aluminum hydride (6.6 g, 0.174 mol) in 200 ml of the same solvent. Heating was continued for 2.5 hr, whereupon the mixture was cooled in ice and treated dropwise with saturated aqueous sodium sulfate solution until the solids were white. The solids were separated by filtration and washed with 100 ml of tetrahydrofuran. Evaporation of the combined filtrates gave 19.6 g (87.4%) of the diol as a white crystalline solid, mp 116-117° (lit.[18] mp 117°).

***cis*-7,8-Bis(methanesulfonyloxymethyl)-*anti*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene.**[16] The diol (19.55 g, 0.102 mol) dissolved in 100 ml of pyridine was added dropwise over 60 min to a mechanically stirred solution of methanesulfonyl chloride (32.0 g, 0.28 mol) in 350 ml of pyridine chilled in ice at such a rate that the temperature did not exceed 10°. The mixture was stirred at 0° for an additional 2 hr, then 1.5 l. of 10% hydrochloric acid was added slowly below 10°. The dimesylate which precipitated as a white powder was filtered, washed with water, and air dried. There was obtained 34.5 g (97%) of white crystals: mp 138–139° (from methanol); δ_{TMS} ($CDCl_3$) 6.05 (m, 2, olefinic), 5.87 (br s, 2, cyclobutene), 4.17 (m, 4, $-CH_2O-$), 3.03 (s, 6. methyls), 2.77 (m, 4, bridgehead), 2.28 (m, 2, methine).

Anal. Calcd for $C_{14}H_{20}O_6S_2$: C. 48.26; H. 5.74; S, 18.41. Found: C, 48.09; H, 5.78; S, 17.97.

***cis*-7,8-Dimethyl-*anti*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene (14).** To a slurry of lithium aluminum hydride (800 mg, 21 mmol) in ether (50 ml) was added the dimesylate (500 mg, 1.44 mmol) and the mixture was heated at reflux with stirring for 22 hr. The reaction was arrested by addition of water and 15% sodium hydroxide solution in the usual manner. The precipitated salts were filtered and washed with ether, and the filtrates were evaporated. The residue was taken up in pentane and passed through a short silica gel column. Concentration of the pentane eluate gave 190 mg (83%) of **14** as a colorless oil. A Kugelrohr distillation at 130° and 25 mm gave purified product: δ_{TMS} ($CDCl_3$) 5.75–6.08 (m, 4, olefinic), 2.58–2.80 (m, 2, bridgehead), 2.17–2.48 (m, 2, bridgehead), 1.43–2.04 (m, 2, methine), 0.68–0.98 (m, 6, methyls).

Anal. Calcd for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 89.94; H, 10.14.

Rearrangement of 16a with [Rh(NOR)Cl]$_2$. A solution of 14 mg (0.056 mmol) of **16a** and 3.5 mg (0.008 mmol) of catalyst in 0.5 ml of anhydrous benzene was heated at 40° for 40 hr. There was produced 19.5% of **19a** and 80.5% of **20a** (analysis on column d).[15] The spectral features of **20a** were identical with those of an authentic sample (see below). The most distinguishing pmr signal of **19a** is its methoxyl singlet at δ 3.30 (in C_6H_6); the mass spectral fragmentation pattern of **19a** (*m/e* 248) is identical with that of **20a.**

***cis*-7,8-Dicarbomethoxy-*anti*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene (20a).** A solution of 2.0 g (0.10 mmol) of **15** in 50 ml of methanol was heated at reflux for 6 hr, cooled, and evaporated. The residue was treated with a slight excess of ethereal diazomethane and this solution was evaporated. The residue was recrystallized from hexane to give 1.56 g (63%) of **20a:** mp 53–54°; δ_{TMS} (C_6D_6) 6.10 (m, 2, olefinic), 5.71 (s, 2, cyclobutene), 3.43 (s, 6, methyl), 2.60–2.92 (br m, 2), 2.38 (m, 2).

Calcd for $C_{14}H_{16}O_4$, *m/e* 248.1049; Found 248.1052.

Rearrangement of 16a with PdI$_2$(PPh$_3$)$_2$. A. Benzene Solution. Reaction of 14 mg (0.056 mmol) of **16a** and 7 mg (0.01 mmol) of catalyst in 1 ml of benzene at 80° for 161 hr (sealed ampoule) gave 19.6% of recovered **16a,** 7.6% of **17a,**[4] 26.5% of **19a,** and 46.2% of **20a** (analysis on column d[15] at 180°).

B. Chloroform Solution. Heating 5 mg (0.020 mmol) of **16a** with 2.7 mg (0.007 mmol) of the catalyst in a sealed glass tube with 1.0 ml of chloroform for 256 hr returned 14% of **16a.** The three products were identified (normalized percentages) as **17a** (9%), **19a** (35%), and **20a** (56%) (analysis on column d).[15]

Rearrangement of 16a with PdCl$_2$(PPh$_3$)$_2$. A. Benzene Solution. A solution of 13 mg (0.052 mmol) of **16a** and 2 mg (0.004 mmol) of catalyst in 1 ml of dry benzene was heated at 80° for 41 hr. Vpc analysis on column d[15] showed that 53% of **17a,** 36% of **19a,** and 11% of **20a** was formed.

B. Chloroform Solution. A solution of 25 mg (0.10 mmol) of **16a,** 8 mg (0.0011 mmol) of catalyst, and 1.0 ml of chloroform was sealed in an ampoule and heated at 40° for 45 hr. Analysis of the processed reaction mixture on column d[15] revealed that 4% of **16a** remained and that **17a** (37%), **19a** (23%), and **20a** (36%) had been formed.

Rearrangement of 16a with PdCl$_2$(PhCN)$_2$. Heating 10 mg (0.040 mmol) of **16a** with 3 mg (0.008 mmol) of catalyst in 0.5 ml of benzene for 135 hr at 80° gave 96% of **17a,** 1% of **19a,** and 3% of **20a** (analysis on column d).[15]

Isomerization of 16b with [Rh(NOR)Cl]$_2$. A solution of 100 mg (0.31 mmol) of **16b** and 10 mg (0.02 mmol) of catalyst in 0.3 ml of anhydrous benzene was placed in an nmr tube and heated at 40° for 40 hr. There was produced 19% of **19b** and 81% of **20b** (analysis on column c).[15] The spectral data for the isolated **20b** were identical with those of an authentic sample. The distinguishing methoxyl signal of **19b** (in C_6D_6) appears at δ 3.08; its mass spectral fragmentation pattern (*m/e* 320) is identical with that of **20b.**

3-Acetoxymethyl-*cis*-7,8-dicarbomethoxy-*anti*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene (20b). A solution of 3-acetoxymethyltricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic anhydride[4] (100 mg, 0.365 mmol) in 5 ml of methanol was refluxed for 5 hr, cooled, and treated with an excess of ethereal diazomethane. Evaporation gave **20b** as an oil which was purified by silica gel chromatography (elution with 2% ether in benzene). There was obtained 82 mg (70%) of the diester; δ_{TMS} ($CDCl_3$) 6.00 (m, 2, olefinic), 5.77 (br s, 1, cyclobutene), 4.39 (br s, 2, $-CH_2O-$), 3.58 (s, 6, methyl), 2.92 (s, 2), 2.04 (s, 3).

Calcd for $C_{17}H_{20}O_6$, *m/e* 320.1260; found 320.1263.

Isomerization of 16b with PdI$_2$(PPh$_3$)$_2$. Reaction of 40 mg (0.13 mmol) of **16b** with 7 mg (0.01 mmol) of catalyst in 400 μl of dry benzene for 1700 hr at 80° gave a product mixture consisting of **16b** (15%), **17b–18b** (40%), **19b** (8%), and **20b** (37%) (analysis on column b).[15] The snoutane mixture was analyzed by pmr in benzene-d_6 solution and found to contain 14% of **17b** and 26% of **18b.**

Isomerization of 16b with PdCl$_2$(PPh$_3$)$_2$. Reaction of 20 mg (0.063 mmol) of **16b** with 5 mg of catalyst (0.01 mmol) in 0.2 ml of benzene at 80° for 53 hr gave only the snoutanes **17b** (52%) and **18b** (48%) (pmr analysis).

Isomerization of 16b with PdCl$_2$(PhCN)$_2$. When a dry benzene solution (0.5 ml) of **16b** (10 mg, 0.031 mmol) and catalyst (5 mg, 0.01 mmol) was heated at 80° for 19 hr, there was produced only the snoutanes **17b** and **18b** (analysis on column b).[15]

Reaction of 16c with [Rh(NOR)Cl]$_2$. A 20-mg (0.076 mmol) sample of **16c** and 4 mg (0.009 mmol) of catalyst were taken up in 0.3 ml of benzene and heated at 40° in an nmr tube for 90 hr. Vpc analysis on column d[15] showed the presence of unreacted **16c** (5.5%), a mixture of **17c–18c** (2.6%, determined by integration to be a 1.6:1.0 ratio), **19c** (17.4%), and **20c** (72.8%). The spectral data for **20c** were identical with those of an authentic sample. The distinguishing methoxyl signal of **19c** (in $CDCl_3$) appears at δ 3.70; its mass spectral fragmentation pattern (*m/e* 262) is identical with that of **20c.**

***cis*-7,8-Dicarbomethoxy-3-methyl-*anti*-tricyclo[4.2.2.0^{2,5}]deca-3,9-diene (20c).** A solution of 3-methyltricyclo[4.2.2.0^{2,5}]deca-3,7-diene-9,10-dicarboxylic anhydride (80 mg, 0.37 mmol)[4] in 10 ml of anhydrous methanol was heated at reflux for 4 hr, cooled to 0°, and treated with excess ethereal diazomethane. Evaporation led to an oily solid which was taken up in methanol, triturated to the cloud point with water, and cooled to −78° with scratching. A white powder precipitated (50 mg) and an additional 20 mg (total yield 73%) was isolated from the filtrate. Recrystallization from aqueous methanol gave pure **20c:** mp 59–60.5°; δ_{TMS} ($CDCl_3$) 5.92–6.05 (m, 2, olefinic), 5.55 (br s, 1, cyclobutene), 3.57 (s, 6, methyl), 2.70–3.07 (m, 4, bridgehead), 2.35–2.70 (m, 2), 1.57 (br s, 3, methyl).

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.49; H, 6.97.

Reaction of 16c with PdI$_2$(PPh$_3$)$_2$. A solution of 8 mg (0.031 mmol) of **16c** and 8 mg (0.01 mmol) of catalyst in 0.5 ml of benzene was heated in a sealed tube for 800 hr. Work-up and vpc analysis on column d[15] showed the product mixture to contain 7.8% of **16c,** 42.6% of snoutanes **17c** and **18c** (15.3:27.3 ratio), 8.3% of **19c,** and 41.3% of **20c.**

Reaction of 16c with PdCl$_2$(PPh$_3$)$_2$. A solution of 10 mg (0.038 mmol) of **16c** and 3.5 mg (0.007 mmol) of catalyst in 0.5 ml of benzene was heated at 80° for 23 hr and gave 50.2% of **17c,** 47.9% of **18c,** 0.4% of **19c,** and 1.5% of **20c** (vpc analysis on column d).[15]

Reaction of 16c with PdCl$_2$(PhCN)$_2$. Heating 10 mg (0.038 mmol) of **16c** and 3 mg (0.008 mmol] of catalyst in 0.5 ml of benzene at 80° for 47 hr gave 3.3% of returned **16c,** 41% of **17c,** 55% of **18c,** 0.2% of **19c,** and 0.4% of **29c** (vpc analysis on column d).[15]

Rearrangement of 16d with [Rh(NOR)Cl]$_2$. A solution of 30 mg (0.11 mmol) of **16d** and 40 mg (0.09 mmol) of catalyst in 1 ml of benzene was heated at 80° for 160 hr to give 22% of **17d,** 4% of **19d,** and 74% of **20d.** Snoutane **17d** and diene **20d** were identical with authentic samples. Vpc-mass spectral analysis of **19d** showed this diester to have a fragmentation pattern (*m/e* 276) entirely comparable to that of **20d.**

cis-7,8-Dicarbomethoxy-3,4-dimethyl-_anti_-tricyclo[4.2.2.$0^{2,5}$]-deca-3,9-diene (20d). A solution of 300 mg (1.3 mmol) of 3,4-dimethyltricyclo[4.2.2.$0^{2,5}$]deca-3,7-diene-9,10-dicarboxylic anhydride[4] in 15 ml of dry methanol was heated at reflux for 5.5 hr, cooled to 0°, and treated with excess diazomethane in ether. The solution was kept overnight at room temperature and evaporated to leave a residue which was crystallized from aqueous methanol. Pure **20c** was obtained as white crystals: mp 61.5–63°; δ_{TMS} ($CDCl_3$) 5.96 (m, 2, olefinic), 3.52 (s, 6, methyl), 2.86 (br s, 2), 2.73–3.0 (m, 2), 2.5 (m, 2), 1.52 (br s, 6, methyl). Calcd *m/e* 276.1361; found 276.1366.

Anal. Calcd for $C_{16}H_{20}O_4$: C, 69.55; H, 7.30. Found: C, 69.54; H, 7.28.

Rearrangement of 16d with $PdI_2(PPh_3)_2$. Reaction of 11 mg (0.040 mmol) of **16d** with 3 mg (0.005 mmol) of catalyst in 0.5 ml of benzene for 600 hr at 80° returned 84% of unchanged **16d** and gave 5.9% of **17d**, 1.6% of **19d**, and 8.5% of **20d** (analysis on column d).[15]

Rearrangement of 16d with $PdCl_2(PPh_3)_2$. Reaction of 3 mg (0.011 mmol) of **16d** with 4 mg (0.009 mmol) of catalyst in 0.5 ml of benzene for 119 hr at 80° gave 100% of snoutane **17d** (analysis on column d).[15]

Rearrangement of 16d with $PdCl_2(PPh_3)_2$. Reaction of 3 mg (0.011 mmol) of **16d** with 3 mg (0.008 mmol) of catalyst in 0.5 ml of benzene for 120 hr at 80° gave 0.9% of **16d**, 96.6% of **17d**, 1.0% of **19d**, and 1.5% of **20d** (analysis on column d).[15]

Isomerization of 21 with $PdI_2(PPh_3)_2$. Heating 6 mg of **21**[4] with 0.5 ml of 0.0019 *M* catalyst solution in benzene at 79° for 119.5 hr gave 8% of snoutane **22**[4] and 92% of diene **23**; δ_{TMS} ($CDCl_3$) 5.70–6.15 (m, 2, olefinic), 5.83 (s, 2, cyclobutene), 3.73 and 3.67 (two s, 3 each, methyls), 2.58–3.30 (br m, 6).

Anal. Calcd for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.64; H, 6.76.

Isomerization of 21 with $[Rh(NOR)Cl]_2$. A solution of 43.5 mg of **21** and 14 mg of catalyst in 1.4 ml of benzene was heated in a sealed ampoule at 40° for 44 hr. Work-up gave 26.9 mg of an oily product, vpc analysis of which on column f[15] showed it to be single substance. Isolation and pmr analysis gave proof that this material was uniquely **23**.

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References and Notes

(1) Part XXIX of the series dealing with Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. Part XXVIII is L. A. Paquette, J. S. Ward, R. A. Boggs, and W. B. Farnham, *J. Amer. Chem. Soc.*, **97**, 1101 (1975).

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(15) (a) Column 10 ft × 0.125 in. 5% Carbowax 20 M on Chromosorb G; (b) 14 ft × 0.125 in. 3% UCON 50HB2000P on Chromosorb W; (c) 2 ft × 0.125 in. 5% Carbowax 20 M on Chromosorb P; (d) 16 ft × 0.125 in. 7.7% OV-25 and 5.8% Carbowax 20M on Chromosorb G; (e) 15 ft × 0.125 in. 4% OV-25 and 2% Carbowax 20M on Chromosorb G; (f) 6 ft × 0.25 in. 5% SE-30 on Chromosorb G; (g) 10 ft × 0.25 in. 8% Carbowax 20 M on Chromosorb G.

(16) We thank Dr. Denise Cottrell for this experiment.

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Rhodium(I)- and Palladium(II)-Promoted Rearrangements of Homocubanes. A Comparison of Kinetic Reactivity and Product Distribution with Substituent Alteration[1]

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Abstract: The effect of varied 4-substitution of the homocubane ring system on the course of Rh(I) and Pd(II) catalyzed rearrangements was probed both by direct examination of product ratios and kinetically in the case of $[Rh(NOR)Cl]_2$. Comparison of the rate data with catalytic rate constants previously determined from Ag(I)-promoted bond switching reactions revealed a greatly diminished sensitivity of Rh(I) to the *electronic* nature of the substituent at C_4 but an increase in its response to *steric* factors. The range of k_{Rh} values, excluding those for the 4-*tert*-butyl and 4,5-dimethyl examples, is but a factor of 60 (compare Ag(I) where it is 500-fold). The rhodium norbornadiene chloride dimer promoted isomerization of 4-trideuteriomethylhomocubane shows essentially nil deuterium isotope effect ($k_H/k_D = 1.011 \pm 0.005$). This behavior is attributed to the absence of carbonium ion character in the rate-determining transition state. The compatibility of these findings with an oxidative addition pathway is discussed, as are several additional quantitative relationships uncovered in this study.

In the preceding paper of this series,[1] complexes of Rh(I) ($4d^8$) and Pd(II) ($4d^8$) were shown to promote the rearrangement of 1,8-bishomocubanes. In many instances, the isomerizations were observed to differ in type from the exclusive bond switching pathway catalyzed by Ag(I) ($4d^{10}$) salts,[3] dienes and not snoutanes arising as the major products. These diverse catalytic properties cannot be distinguished simply on the basis of the differing electronic configurations of the transition metals (d^8 *vs.* d^{10}) but are seemingly dependent to a greater extent on more subtle fac-