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THE RHODIUM(I)-CATALYZED REARRANGEMENT OF *syn*-1,3-BISHOMOCYCLOHEPTATRIENE

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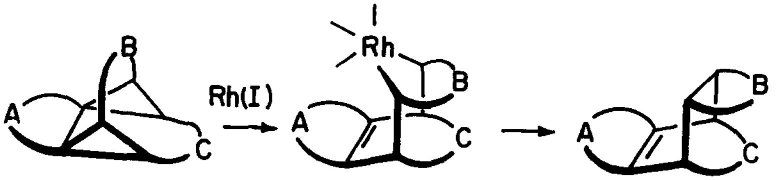
Catalysis of strained ring rearrangements by rhodium(I) complexes continues to attract much mechanistic and synthetic interest.[2] For dicyclopropyl systems fixed in an *S-cis* conformation by one (A) or two (B and C) bridges as in 1, a general type of *four electron* reorganization has been identified involving oxidative addition of Rh(I) to give 2 and ultimate reductive loss of the metal to deliver product (3). The facile conversions of quadricyclane to norbornadiene[3] and of 4 and 6 to 5 and 7, respectively,[4] are exemplary. This preference for net four electron change is quite marked and still dominates in cases ideally suited for six electron rearrangement. Thus, while diademane (8) readily opens to triquinacene (9) in the presence of acid or Ag(I) and when heated, conversion to snoutene (10) is the only rearrangement pathway followed when Rh(I) is added.[5] We here report discovery of the first example of a *six-electron* rhodium-catalyzed isomerization of a dicyclopropyl compound and elucidation via deuterium labeling of a homo[3,3]sigmatropic carbon shift alternative.



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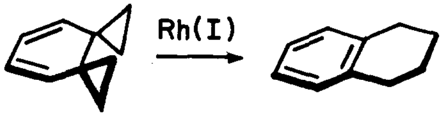

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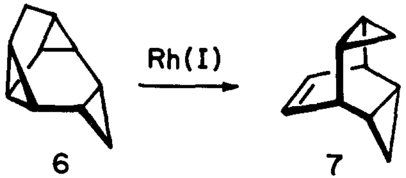

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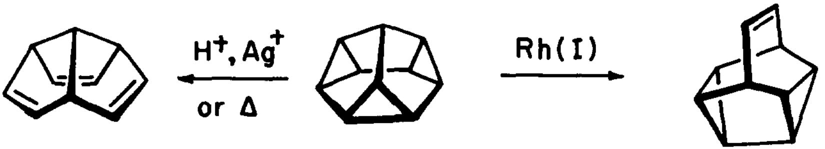
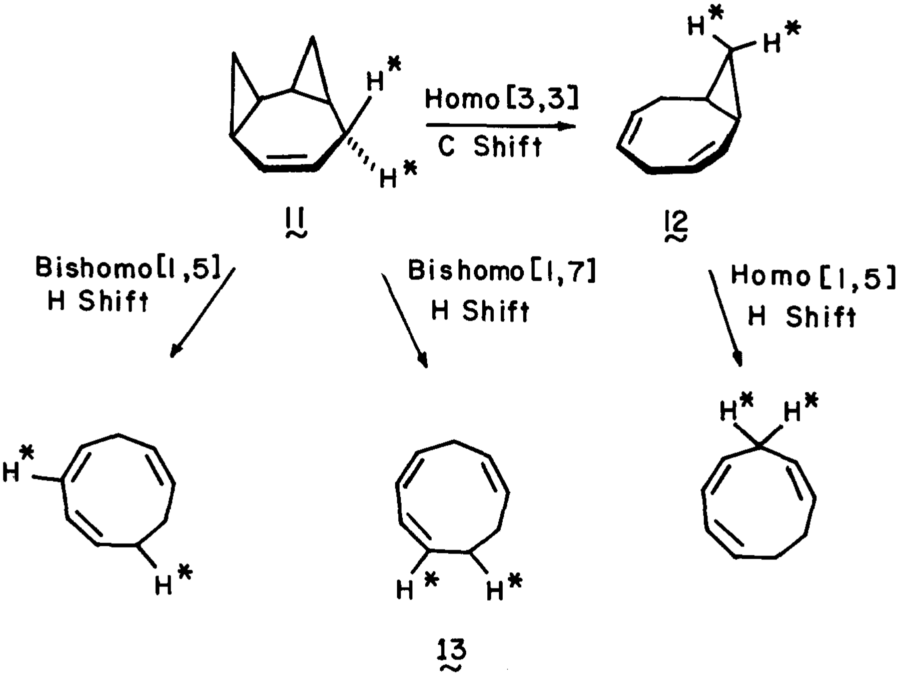


9 8 10

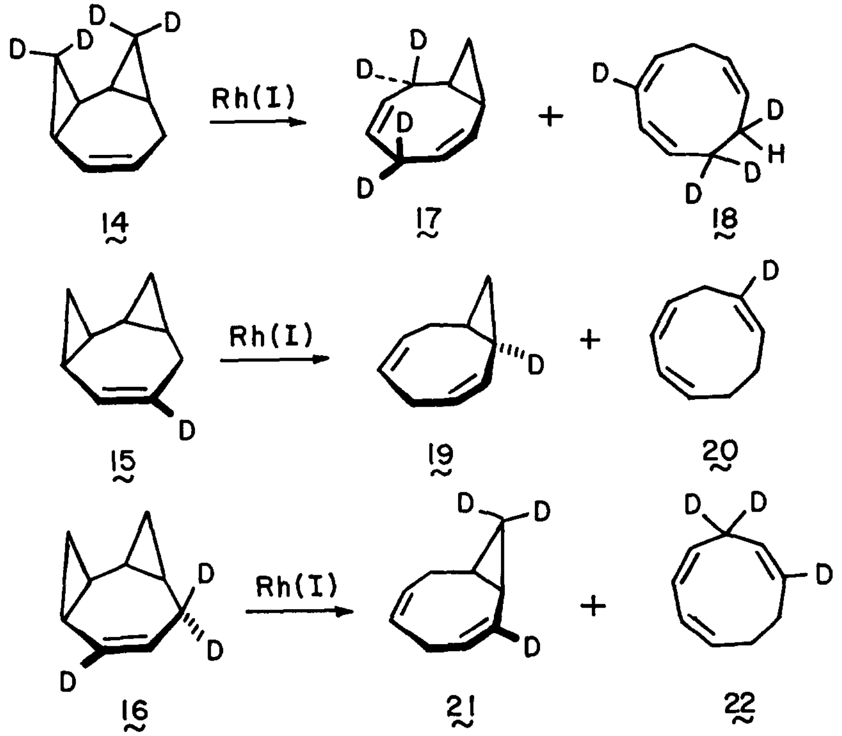
Heating (60°, 12 hr) of a benzene solution of *syn*-1,3-bishomocycloheptatriene (**11**)[6] containing 8 mol percent rhodium dicarbonyl chloride dimer led smoothly to a 59:41 mixture of bicyclo[6.1.0]nona-2,5-diene (**12**) and *cis*^{3}-1,3,6-cyclononatriene (**13**) as attested to by direct spectral comparison with authentic samples.[7] Suitable control experiments revealed that both **11** and **13** were stable to the reaction conditions in the absence of catalyst. Expectedly,[7] **12** underwent conversion to **13** at this temperature at a rate which was not measurably altered by the Rh(I) complex. These data, together with the time dependence of the product ratio, established **12** to be the primary product of catalysis.

The bond reorganization leading from **11** to **12** may be interpreted as a net homo[3,3]sigmatropic shift. Homo[1,5]dienyl hydrogen translocation within **12** can give rise to **13**. Alternatively, this nine-membered cyclic triene might also arise in part from **11** through Rh(I)-catalyzed bishomo[1,5]- or bishomo[1,7]dienyl hydrogen migration. These mechanistic options are illustrated below for a simple $7,7\text{-}d_2$ derivative of **11**. Of course, the possibility remains that more complex skeletal rearrangements are involved.



In order to address these mechanistic questions, the deuterium labeled bishomocycloheptatrienes **14**,[6] **15**,[8] and **16**[9] were prepared and similarly treated with $[Rh(CO)_2Cl]_2$. The action of this catalyst on **14** resulted in conversion to **17** and **18** (59:41, 78°, 12 hr; 7:93, 85°, 30 hr) whose ^1H NMR spectra serve as the basis for structural assignment. In the case of **17**, no integratable allylic absorptions were seen alongside those attributable to the four olefinic and four cyclopropyl protons.[11] The spectrum of **18** is characterized by a 5:3 ratio of olefinic to allylic protons, with the doubly allylic methylene triplet due to the pair of H_5's remaining unchanged from its appearance in the unlabeled compound.

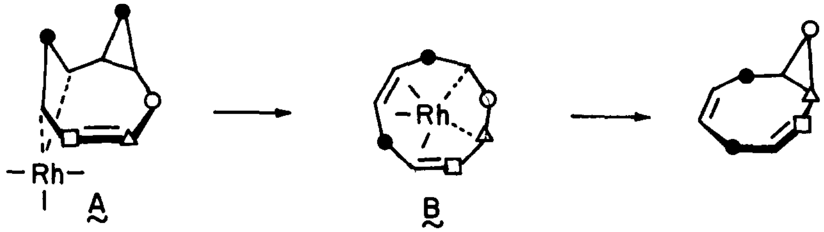
The isomerization of 15 (78°, 22 hr) produced 19 and 20 (30:70). The spectrum of 19 is closely identical to that of 12 except for the absence of the allylic cyclopropyl proton signal at δ 1.47.[11] The samples of 20 displayed a 5:6 ratio of olefinic to allylic protons with the H_5's appearing as a doublet (J = 7 Hz) centered at δ 2.68.



When trideuterio bishomotropilidene 16 was treated with 7 mol percent $[Rh(CO)_2Cl]_2$ in benzene at 70° (21 hr), a 52:48 ratio of 21 and 22 was realized. These were separated as before by preparative gas chromatography and characterized again by ^1H NMR. A typical sample of 21 lacked the cyclopropyl methylene proton absorptions at δ 0.68 and -0.11 together with the proximate olefinic hydrogen, while 22 was completely devoid of an H_5 signal and exhibited a 5:4 ratio of olefinic and allylic protons.[11]

The observed distribution of the deuterium labels (5 of the 9 constituent carbon atoms of 11 were so tagged) reveals the catalyzed rearrangement leading to 12 to involve a net [3,3]homodienyl sigmatropic shift, followed by thermally induced 1,5-homodienyl hydrogen migration. Thus, in this instance the Rh(I) complex promotes a formal six electron bond reorganization instead of a conventional four electron isomerization. Since the remaining bis- and trishomocycloheptatrienes[6] were found to be stable to $[Rh(CO)_2Cl]_2$ under conditions of prolonged heating, the spatial orientation and relative positioning of the cyclopropane rings about the central cycloheptane core are crucial to the success of the reaction.

A hypothetical mechanism consistent with the above data would involve rate-determining oxidative addition of rhodium into the fused bond of the central cyclopropane ring as in A,



followed in a subsequent more rapid step by [3,3]homodienyl Rh shift with relief of structural strain to give **B**, and ultimate reductive extrusion of the metal to construct a new three-membered ring. Although the conversion of **A** to **B** need not occur synchronously, the overall chemical change represents a previously unobserved and novel facet of organorhodium chemistry.[1]

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(8) This monodeuterio hydrocarbon was prepared by $NaBD_4$ reduction of *syn*-3,5-bishomocycloheptadienone,[6] reaction of the epimeric mixture of α-deuterio alcohols with sulfene, and subsequent elimination of methanesulfonic acid with KO*tert*Bu in refluxing benzene.

(9) This trideuterio bishomotropilidene was synthesized by deuterium exchange of *syn*-3,5-bishomocycloheptadienone (Na_2CO_3, D_2O-THF; *p*-TsOH, CH_3OD) conversion to the tosylhydrazone, and decomposition of the latter with lithium 2,2,6,6-tetramethylpiperidide.[10]

(10) R. H. Shapiro and M. Heath, *J. Am. Chem. Soc.*, **89**, 5734 (1967).

(11) Small corrections for residual protium content (1-5%) at the isotopically labeled sites in **14**-**16** were made in analyzing these spectra.

(12) We are grateful to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support.