

were collected on a Picker FACS-I automatic diffractometer using Cu K α radiation ($0 < 2\theta \leq 100^\circ$). The structure was solved by direct methods²¹ and has been refined to a conventional *R* factor of 0.058.²² The compound forms as discrete ion pairs in the crystal (Figure 1) with the lithium ion coordinated by two hydridic hydrogens from the [(Mes)₂BH₂]⁻ group and four oxygen atoms from two DME molecules. The molecule possesses twofold symmetry. The structure shows two rather unusual features. One is the markedly asymmetric manner in which the DME molecules bond to the lithium atom, the difference in the two Li-O distances being 0.353 (8) Å. This difference does not find precedent in other complexes, e.g., those alkali metal macrocyclic ethers^{23,24} which do not experience significant intermolecular bonding interactions. A second feature is the opening of the C(1)-B-C(1') angle to 116.8 (2)° from its normal tetrahedral value. It is felt that this is due solely to intramolecular repulsions between the mesityl groups rather than to any partial contribution from boron-lithium direct overlap analogous to that proposed for a Cu-BH₄ complex.²⁵ The structure accounts for the observed increase in $\nu(\text{B-H})$ of LDMBH₂·2DME compared to that for LDMBH₂ since in the former complex the formal positive charge on the lithium ion is partially accommodated by the coordinated DME groups.

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Supplementary Material Available. A listing of atomic coordinates will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-274.

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Hydrogenolysis of Substituted Nortricyclenes over Supported Metal Catalysts. Methyl Migrations and Skeletal Rearrangements

Sir:

Hydrogenolysis of cyclopropyl rings normally occurs with simple ring cleavage.¹ We wish to report that hydrogenolysis of the strained hydrocarbons 3,3-dimethylnorbornene (3,3-dimethyltricyclo[2.2.1.0^{2,6}]heptane (1)) and the related cyclopropyl compound, spiro[tricyclo[2.2.1.0^{2,6}]heptane-3,1'-cyclopropane (5), gives products arising from reactions involving carbon-

carbon bond breaking and re-forming under certain conditions. Hydrogenolysis of either compound over platinum in acetic acid solution gave the products of simple ring cleavage, 2,2-dimethylnorbornane (2) and 7,7-dimethylnorbornane (3), with the latter predominating. These were also the only products from hydrogenolyses of 1 in the temperature range 80–200° over palladium on silica or platinum on either silica or pumice. In contrast, hydrogenolysis of 1 over palladium on pumice in the same temperature range gave di-*exo*-, di-*endo*-, and *trans*-2,3-dimethylnorbornanes (4) in addition to 2 and 3 (see Table I). Samples of 2 and 3 were

Table I. Product Distributions from Hydrogenolyses of 1

Catalyst ^d	H ₂ flow rate, cm ³ min ⁻¹	T, °C	Product composition, % ^a					
			2 + <i>trans</i> -4	3	<i>cis</i> - <i>exo</i> -4	<i>cis</i> - <i>endo</i> -4	Recovd 1	
2% Pt/pumice	9	108	20	80				
	9	158	30	70				
	9	200	50	50				
2% Pd/silica	7	100	15 ^b	85				
	7	180	20	80				
2% Pd/pumice	9	108	7.1	5.1	2.0	4.1	81.6	
	9	130	23.2	2.3	8.2	20.2	46.0	
	9	190	44.7 ^c	7.0	14.1	34.1	0.5	
PtO ₂ in acetic acid		30	15	85				

^a A Perkin-Elmer F11 gas chromatograph fitted with a 2-m capillary column packed with Apieson L (10%) on Chromosorb P was used at 16 psi nitrogen pressure and at 110°. Separation of 2 and *trans*-4 could not be achieved. ^b Identified as pure 2,2-dimethylnorbornane after preparative glc using an Autoprep A-700 with a 6-m column of Apiezon L (30%) on Chromosorb P at 110°, with helium pressure 18 psi. ^c Identified by nmr as mainly *trans*-2,3-dimethylnorbornane after preparative glc. ^d Catalysts were prepared by the impregnation of 60–85 mesh (B.S.S.) Whatman S. G. silica gel and of 22–60 mesh pumice stone of Hopkins and Williams Ltd. with aqueous chloroplatinic acid or palladium(II) chloride dissolved in hydrochloric acid. The catalysts were reduced in a stream of hydrogen with the temperature being elevated gradually to 330°.

recovered unchanged after passage over the palladium on pumice catalyst at 140° and the nortricyclene 1 did not react when passed over either silica or pumice in the absence of metal at 120°. The kinetically controlled rearrangement product contains a high proportion of 2,3-*endo*-dimethylnorbornane. The di-*endo* compound was shown to isomerize at higher temperatures over the palladium on pumice catalysts in agreement with previous work,² thus accounting for the increase of di-*exo* and *trans* compounds in the product mixture at these temperatures. Additionally, it was not possible to separate *trans*-2,3-dimethylnorbornane and 2,2-dimethylnorbornane with the glc facilities available, but preparative glc of the product from a reaction at 190° showed that the first eluted peak was pure *trans*-4 and did not contain a detectable amount (by nmr) of 2.

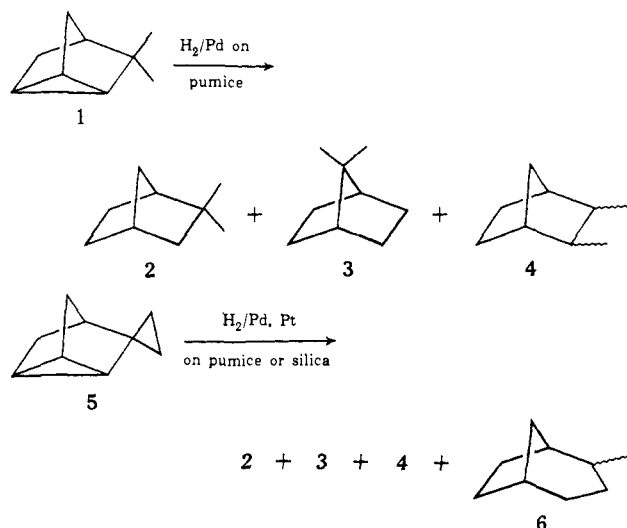
Rearrangement products predominated when the cyclopropylnortricyclene (5) was hydrogenolyzed over palladium or platinum catalysts (see Table II). In addition to the 2,3-dimethylnorbornanes (4), *exo*- and *endo*-2-methylbicyclo[3.2.1]octanes (6) were formed.

- (2) H. A. Quinn, W. R. Jackson, M. A. McKervey, and J. J. Rooney *J. Amer. Chem. Soc.*, **92**, 2911 (1970); H. A. Quinn, J. H. Graham, M. A. McKervey, and J. J. Rooney, *J. Catal.*, **26**, 333 (1972).

Table II. Product Distributions from the Hydrogenolysis of **5**

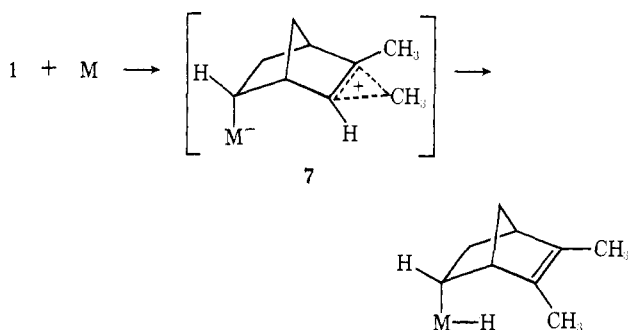
Catalyst	H ₂ flow rate, cm ³ min ⁻¹	T, °C	Product composition, %							Unidentified comps, incl. dimers ^a	
			Recovd 5	<i>trans</i> - 4 + 2	3	<i>cis-exo-4</i>	<i>cis-endo-4</i>	<i>exo-6</i>	<i>endo-6</i>		
2% Pd/pumice	9.5	140	85				2.4	12.2	0.4		
	9.5	195		7.1	0.6		7.5	4.6	56.0	8.0	
	9.5	250		6.5			8.2	10.7	50.4	16.2	9.0
2% Pt/SiO ₂	9	82		43.4	23.7		13.5	8.1	5.3	5.3	
	9	140		7.7	1.5		11.5	15.2	38.7	13.7	
	9	242		1.3	0.8		15.6	10.4	38.0	7.5	26.0
PtO ₂ in acetic acid	2-mol uptake 1 mol	30		15.0	85.0						
		30	>98% of 1								

^a Identified using an MS30 gas chromatographic-mass spectral system.



Again, the pumice support was shown to be inactive (at 200°) in the absence of metal. Reactions at higher temperatures, especially over platinum, gave increasing amounts of dimeric (mol wt 244) and oligomeric material.

These are the first examples of 1,2-alkyl shifts during hydrogenolysis of strained C₈-ring hydrocarbons in excess hydrogen over supported metals. The products can be explained by metal insertion into the C₃ ring to give initially a metallocarbonium ion, *e.g.*, **7**. The more



sterically hindered C-C bond of the C₃ ring is preferred because the resulting carbonium ion is stabilized by charge delocalization arising from the simultaneously migrating methyl group. Hydrogenation of 2,3-dimethylbicyclo[2.2.1]hept-2-ene gives mainly the *endo*-methyl compound **4**.³ The postulated mechanism is very similar to that suggested for isomerizations of strained C₈-ring hydrocarbons homogeneously

(3) K. Alder and W. Roth, *Chem. Ber.*, **88**, 407 (1955).

catalyzed by Ag⁺, Rh⁺, and other metal cations.⁴ We are currently investigating why these reactions are so sensitive to catalyst, support, and reaction medium.

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(4) See D. J. Cardin, B. Cetinkaya, M. J. Doyle, and M. F. Lappert, *Chem. Soc. Rev.*, **2**, 99 (1973).

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Intermolecular Ligand Exchange in Cationic Nickel, Palladium, and Platinum Hydrides of the Type HML₃+X⁻ in the Presence of Added Phosphine Ligand

Sir:

We present, for the first time, direct nmr spectroscopic evidence for the rates of ligand association in a series of four-coordinate group VIII complexes (HML₃⁺ species) relative to the rate of intramolecular rearrangement within the five-coordinate intermediate or transition state (HML₄⁺) (M = Ni(II), Pd(II), Pt(II); L = P(C₂H₅)₃).

The hydride region ¹H nmr spectrum (all nmr parameters are given in Table I) for an acetone-*d*₆ solution of HPt[P(C₂H₅)₃]₃+B(C₆H₅)₄⁻ consists of a doublet of triplets (with ¹⁹⁵Pt satellite lines) indicating that the cation has a square planar structure (1) in solution.^{1,2} As P(C₂H₅)₃ is added, the triplets broaden and then sharpen into singlets. The limiting spectrum in the presence of a large excess of ligand is a doublet in which the *J*_{HP₁} couplings have been lost while the *J*_{HP₂} coupling has been retained.

The ³¹P{¹H} Fourier mode nmr spectrum (Figure 1) in the absence of added ligand is an A₂B pattern together with an A₂BX pattern (34% ¹⁹⁵Pt). As ligand is added (Figure 1) the resonances assigned to the A spins (L₁) broaden and eventually coalesce with the free ligand resonance. By contrast the resonances assigned to the B spin (L₂) are simply decoupled from the A spins and only slightly broadened by the exchange process. The ¹H and ³¹P data indicate that the Pt-L₁ bond is broken in the exchange process and that there is no concomitant

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