coordination compounds exist with atomic hydrogen as well as with molecular dihydrogen as ligands,[21] only hydride ligands need to be considered, because η^2-H_2 complexes are extremely labile.[21]

Recently, Minot et al.[22] performed calculations on the hydrogenation of small Pt_n (n = 2–13) clusters using the extended Hückel method and reported stable complexes like $Pt_4H_{16}(H_2)_2$ and $Pt_6H_{12}(H_2)_4$. Although this suggests that high H/Pt values may be possible, synthesis of hydride complexes of Pt with H:Pt > 2 has rarely been reported. When Pt, Rh, and Ir are compared, we expect Pt to coordinate less ligands than Rh and Ir in the same oxidation state, because Pt has one electron more. Rh and Ir differ in the fact that higher oxidation states are more stable for Ir than for Rh, and since the M–H band can formally be described as M^+–H^-, higher H/M values are expected for Ir. In accordance with this Garlaschelli et al.[23] prepared polyhydride complexes with H:Ir = 5, while the same procedure for Rh yielded only H:Rh = 2. So the H/M stoichiometries in polyhydride complexes increase in the order H/Pt < H/Rh < H/Ir.

The results of this study show that hydrogen chemisorption measurements cannot be used directly to determine particle sizes in highly dispersed catalysts. Above H/M = 0.7, the $H/M_{surface}$ stoichiometry exceeds unity; below H/M = 0.7, the uncertainty in the metal–metal coordination number is too high to determine the $H/M_{surface}$ stoichiometry. However, for one particular metal the hydrogen chemisorption results can always be used to compare metal particle sizes in a qualitative way. By means of the EXAFS technique a calibration can be made, and then H/M values can be quantitatively related to the percentage of exposed metal atoms. The observed differences in H/M values for Pt, Rh, and Ir are analogous to the differences in stability of their polyhydride complexes. Details of this and related studies will be published elsewhere.[11]

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On the Question of Heavy Atom Tunneling in the 2-Norbornyl Cation

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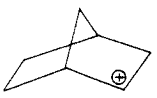
The controversy concerning the structure of the 2-norbornyl cation (**1**) has focused on two questions: (a) Is the ion symmetrical, as indicated in **3**? (b) If it is unsymmetrical, is it a normal classical secondary carbocation? Chemical evidence[1] and the chemical shifts in its ESCA spectrum[2] suggest that the answer to the second question is "no". Equally, the integrated areas of the ESCA bands show unambiguously[3] that the ion is *not* symmetrical. The relationship between the structures can be seen clearly by writing them in the form **2**–**4**. While **2** and **4** are represented, for convenience, as classical carbenium ions, the evidence, as noted above suggests that they are best formulated as unsymmetrical π complexes,[4] derived by displacing the apical methylene group in **3** toward one end or other of the basal C=C bond.



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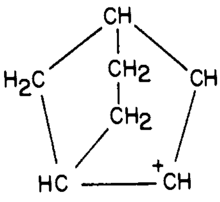

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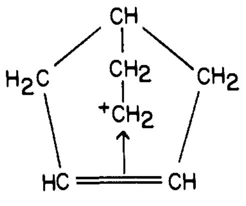

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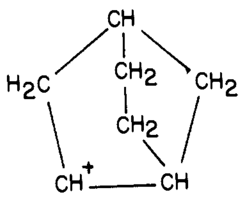

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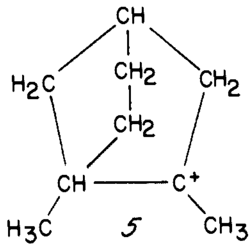

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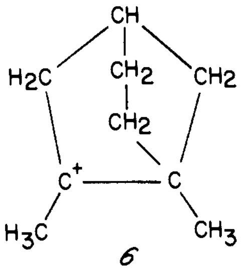

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The NMR spectrum of the ion corresponds, however, to a symmetrical structure, even at liquid helium temperatures.[5] The only way to reconcile this evidence with the ESCA results is to suppose that **2** and **4** interconvert rapidly even at 4 K. Classical interconversion, by crossing an energy barrier, could be fast on the NMR time scale at this temperature only if the barrier height were less than 0.2 kcal/mol. Apart from the improbability of this being the case, it is not clear that so low a barrier would be consistent with the ESCA measurements, given that these were carried out at 77 K where $kT \simeq 0.2$ kcal/mol.

A simple solution of this problem was proposed by Fong[6] and by Brickmann,[7] i.e., that the interconversion of **2** and **4** takes place by tunneling. While this suggestion has been ignored because of the belief that tunneling involving heavy atoms (*heavy atom tunneling*, HAT) cannot be fast, Carpenter[8] has recently shown that it can be, and we[9] have confirmed his suggestion. Indeed, using a better procedure,[10] we found the rate of HAT in the system he studied (automerization of cyclobutadiene) to be even greater

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Table I. Calculated MINDO/3 Classical Rate Constants

process	T, K	E_a, kcal/mol	$\Delta S^{\ddagger}$, cal/deg·mol	k, s^{-1}
2 to **4**	100	1.88	−0.98	2.69×10^{8}
	273		−2.87	1.14×10^{11}
	323		−3.17	1.98×10^{11}
2 to **4**	100	1.0	−0.98	2.26×10^{10}
	273		−2.87	5.79×10^{11}
	323		−3.17	7.80×10^{11}
5 to **6**	100	7.3	−1.27	3.32×10^{-4}
	200		−2.14	4.07×10^{4}
	300		−2.71	2.09×10^{7}
5 to **6**	100	6.3	−1.27	5.08×10^{-2}
	200		−2.14	5.04×10^{5}
	300		−2.71	1.12×10^{8}

than he supposed. We have also demonstrated the likely importance of HAT in a number of other automerizations.[11]

While the suggestion by Fong and Brickmann is thus reasonable, Myhre et al.[12] have recently claimed to have refuted it by NMR studies of a "model" system, i.e., 1,2-dimethyl-2-norbornyl cation (**5**). They showed this to be unsymmetrical by freezing out interconversion with its mirror image (**6**). Interconversion of **5** and **6** by tunneling must therefore be slow on the NMR time scale. Assuming the rates of tunneling in **2** and **5** to be similar, Myhre et al. concluded that tunneling must be likewise unimportant in **2**.

This argument is, however, fallacious. HAT is expected to be significant only when the motions of the heavy atoms are small and when the classical barrier to reaction is low. The automerization of **5** involves motion of more heavy atoms than that of **2** and the corresponding barrier is expected[13] to be much higher. The evidence presented by Myhre et al. does not therefore have any bearing on the structure of **1**.

Ab initio calculations have failed to establish its structure. Studies of simple systems have shown that a very high level of theory is needed to reproduce the relative energies of classical and nonclassical isomers of simple carbocations correctly.[14] Such procedures cannot be applied to ions as large as **2** or **5** without making unacceptable assumptions.[15] However, while the relative energies of **2** and **3** cannot be predicted reliably, the error is likely to be much the same for **2** as it is for **5** and the same should be true for any errors in their vibration frequencies, in particular the imaginary frequency corresponding to translation along the reaction coordinate at the (symmetrical) transition state. Since Miller's treatment[10] of tunneling depends only on these quantities,[18] any reasonably good procedure should give a reasonable estimate of the relative rates of tunneling in **2** and **5**.

Table II. Calculated MINDO/3 Tunneling Rate Constants

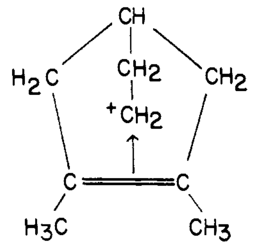
process	E_a, kcal/mol	k_t, s^{-1}
2 to **4**	1.88	5.5×10^{3} [a]
2 to **4**	1.0	1.88×10^{9} [a]
5 to **6**	7.3	1.06×10^{-6} [b]
5 to **6**	6.3	7.68×10^{-4} [b]

[a] Vibration in the direction of the barrier, $h\omega_f = 242$ cm^{-1}; imaginary frequency, $h\omega_i = 115.35$ cm^{-1}. [b] Vibration in the direction of the barrier, $h\omega_f = 214.28$ cm^{-1}; imaginary frequency, $h\omega_i = 299.06$ cm^{-1}.

The obvious choice in this connection is the MINDO/3 model,[19] given that this has been shown[14] to reproduce the results of "state-of-the art" calculations for small carbocations surprizingly well, better indeed than any lower level ab initio treatment. Furthermore, MINDO/3 predicts[20] **1** to exist as two mirror image isomers separated by a low barrier, a result which would be consistent with the experimental evidence if tunneling is fast. We have now used it to study tunneling in **2** and **5**. The calculations were carried out using the standard procedures embodied in the MOPAC[21] package of computer programs. The results for **1** duplicated the earlier calculation.[20]

5 (ΔH_f = 198.06 kcal/mol) was found to be 7.3 kcal/mol lower in energy than the corresponding π-complex nonclassical structure (**7**; ΔH_f = 205.36 kcal/mol), which is the transition state (TS) for the interconversion of the two classical ions **5** and **6**. In the case of **2** (ΔH_f = 214.17 kcal/mol), the corresponding nonclassical ion (**3**) (ΔH_f = 216.05 kcal/mol) is only 1.88 kcal/mol less stable. The classical rates for conversion of **2** to **4** and of **5** to **6**, from the calculated enthalpies and entropies of activation, are shown in Table I.

The rates of interconversion by tunneling of **2** with **4**, and of **5** with **6**, were calculated by the procedure described previously[10] (see[9]), using the barrier heights and the imaginary frequencies for motion along the transition coordinate in **3** or **7**, calculated by MINDO/3. The results are shown in Table II. For comparison classical and tunneling rates are also listed for activation energies (E_as) less by 1 kcal/mol than the MINDO/3 values.



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Our results correctly[12] predict tunneling to be unimportant in the case of **5**. Equally, however, they predict it to be very important in the case of **2**, if the barrier to rearrangement is less than 2 kcal/mol. Such a barrier is consistent with all the available evidence. Our calculations thus confirm the conclusion that the results reported by Myhre et al.[12] have no bearing on the situation in **2** and support the suggestion[3] that the "2-norbornyl cation" is a "nonclassical classical" carbocation, i.e., an unsymmetrical π complex, which undergoes interconversion with its mirror image isomer rapidly by tunneling, even at the lowest temperatures.

Acknowledgment. This work was supported by the Air Force Office of Scientific Research (AFOSR 86-0022), the Robert A. Welch Foundation (Grant F-126), the National Science Foundation (Grant CHE82-17948), and the Tektronix Foundation.

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(15) The most elaborate attempt of this kind yet reported,[16] using a large basis set with allowance for correlation by Moeller–Plesset (MP) perturbation theory, was claimed to show **1** to have the symmetrical structure (**3**). The calculation was, however, carried out by using geometries calculated by much simpler models which are known to give unsatisfactory results for simple carbocations.[14] The simplification is not acceptable in cases such as this where small differences in energy are involved, particularly when the molecules in question involve unusual kinds of bonding. The conclusion reached, i.e., that **3** is not only lower in energy than **2** but *much* lower, is in conflict with the experimental evidence, that the ion is unsymmetrical in magic acid. It is extremely unlikely that differential solvation of two such similar structures could have so large an effect. It also seems unlikely that the experimental evidence can be in error, given that the ESCA measurements have led to similar results in two different laboratories.[17]

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(18) The width of the barrier, corresponding to the geometrical displacement of atoms involved in the rearrangement, is taken into account indirectly by using an assumed form for the barrier shape.

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