

# Pyramidal Mono- and Dications: Bridge between Organic and Organometallic Chemistry

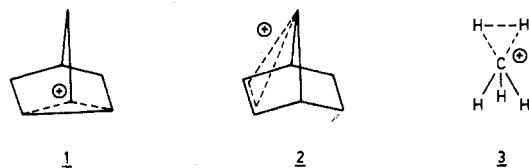
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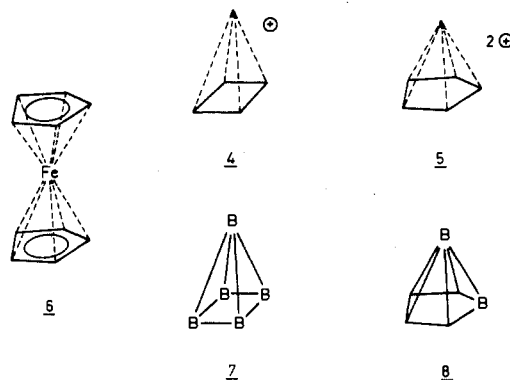
Considerable differences between organic and organometallic chemistry arise from the divergent structural and bonding properties of organic and organometallic compounds. Carbonium ions increasingly are becoming a link between these two fields of chemistry. They belong to organic chemistry but show several structural features and bonding properties which are quite familiar to organometallic chemists.

An example is the coordination number of carbon, which in organic chemistry is usually not found to be higher than four. In the field of organometallic chemistry, e.g. carboranes, coordination numbers for carbon of five and six have been observed,<sup>1</sup> (Table I). The idea that in some carbonium ions the carbon atom might be pentacoordinated was first suggested by Wilson<sup>2</sup> and was developed by Winstein, Olah, Brouwer, and Hogeveen, and others.<sup>3</sup> Nonclassical carbonium ions like norbornyl (1) and 7-norbornenyl (2) cations and  $\text{CH}_5^+$  (3) are especially common rep-



representatives of this phenomenon. This Account deals with the pyramidal<sup>4</sup> monocation  $(\text{CH})_5^+$  (4) and dication  $(\text{CH})_6^{2+}$  (5) and their derivatives. These carbonium ions not only involve a pentacoordinated and a hexacoordinated carbon atom, respectively, but also show another structural analogy with the well-known organometallic sandwich compounds. The structure of ferrocene, 6, the first example of such a compound,<sup>7</sup> is that of two five-membered rings with an iron atom in between. Dication 5 can then be viewed as a semisandwich: one five-membered ring with a C-H group on top of it.

The strong analogy between carbonium ions and boranes<sup>8</sup> is due to the isoelectronic relationship of boron and a carbonium ion center. For example the



square-pyramidal structure of pentaborane, 7, made Williams<sup>9</sup> suggest the square-pyramidal structure for a  $(\text{CH})_5^+$  carbonium ion. Stohrer and Hoffmann<sup>10</sup> were the first to develop the idea of a square-pyramidal structure for this carbonium ion by using molecu-

(1) R. N. Grimes, "Carboranes", Academic Press, New York, N.Y., 1970.  
(2) T. P. Nevell, E. de Salas, and C. L. Wilson, *J. Chem. Soc.*, 1188 (1939).

(3) S. Winstein and D. S. Trifan, *J. Am. Chem. Soc.*, 71, 2953 (1949). For reviews see: S. Winstein, *Q. Rev., Chem. Soc.*, 23, 1411 (1969); G. A. Olah, *Angew. Chem., Int. Ed. Engl.*, 12, 173 (1973); D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, 9, 179 (1972).

(4) Proposed to be the generic name of this class of carbonium ions.<sup>5,6</sup>  
(5) H. Hogeveen and P. W. Kwant, Abstracts of papers presented at the Second International Symposium on the Chemistry of Nonbenzenoid Aromatic Compounds, Lindau, Sept 1974.

(6) H. Hogeveen, P. W. Kwant, J. Postma, and P. Th. van Duynen, *Tetrahedron Lett.*, 4351 (1974).

(7) G. Williamson, M. Rosenblum, M. C. Whiting, and R. B. Woodward, *J. Am. Chem. Soc.*, 74, 2125 (1952).

(8) K. Wade, *New Sci.*, 615 (1974).

(9) R. E. Williams, *Inorg. Chem.*, 10, 210 (1971).

(10) W. D. Stohrer and R. Hoffmann, *J. Am. Chem. Soc.*, 94, 1661 (1972).

Hepke Hogeveen was born in 1935 in Groningen, and obtained the Ph.D. degree in 1961 with J. F. Arens, W. Drenth, and H. Wynberg at the University of Groningen. Subsequently he spent two postdoctoral years with F. Montanari at the University of Bologna, and then joined the Organic Chemistry group of Shell Research Laboratory in Amsterdam. In 1970 he acted as assistant to Lord Rothschild in London, being occupied with research administration. He was appointed Professor of Organic Chemistry at Groningen in 1971. His research interests lie mainly in the areas of stable carbonium ions, modified reactivity of organic molecules by transition-metal complexes, and strained ring systems. At home, Professor Hogeveen shares the hobbies of his wife and two daughters: music and a country life.

Peter Kwant is employed by Shell Research Laboratory in Amsterdam. He studied both law and chemistry at the University of Groningen, obtaining his law degree in 1971, and the Ph.D. (with Professor Hogeveen) in 1974.

Table I

Coordination no. of carbon	Examples
0	Free carbon atoms <sup>a</sup>
1	Carbynes ( $:\dot{\text{C}}\text{H}$ ) <sup>b</sup>
2	Carbenes ( $:\text{CH}_2$ )
3	Carbonium ions ( $\text{CH}_3^+$ ), carbanions ( $\text{CH}_3^-$ ), radicals ( $\text{CH}_3$ )
4	Covalent compounds ( $\text{CH}_4$ )
5	Carbonium ions 1, 2, and 3 ( $\text{CH}_5^+$ ), <sup>c</sup> carboranes
6	( $\text{CCH}_3$ ) <sub>6</sub> <sup>2+</sup> dication, carboranes

<sup>a</sup> P. S. Skell, K. J. Klabunde, J. H. Plonka, J. S. Roberts, and D. L. Williams-Smith, *J. Am. Chem. Soc.*, 95, 1547 (1973), and previous papers. <sup>b</sup> O. P. Strausz, G. J. A. Kennepohl, F. X. Garneau, T. Do Minh, B. Kim, S. Valenty, and P. S. Skell, *J. Am. Chem. Soc.*, 96, 5723 (1974). <sup>c</sup> H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, 87, 319 (1968); D. M. Brouwer and H. Hogeveen, *Prog. Phys. Org. Chem.*, 9, 179 (1972).

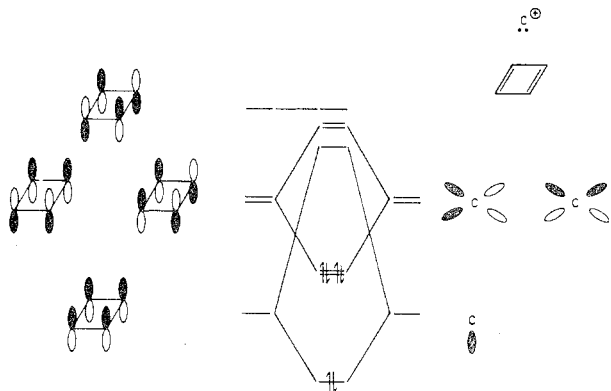
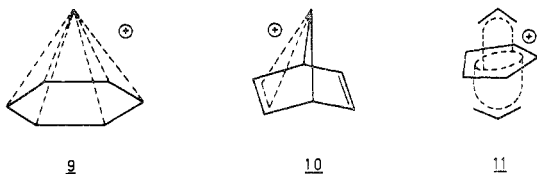


Figure 1. Interaction diagram showing how the orbitals of 4 are constructed from cyclobutadiene and  $\text{CH}^+$ .<sup>10</sup>

lar orbital calculations, thus providing the impetus for much research in this field. The dication 5 also has a borane prototype: the  $\text{C}_4\text{B}_2\text{H}_6$  carborane, which was shown by microwave spectroscopy to possess structure 8.<sup>11</sup>

Besides the ions 4 and 5 and their derivatives, a third pyramidal structure, 9, has once been suggested as a possible description for the norbornadienyl cation  $(\text{CH})_7^+$ .<sup>12</sup> However, this does not appear to be an appropriate description of this carbonium ion. Norbornadienyl cation is preferably described by 10 using a two-electron, three-center bond.<sup>13</sup>



As a class of  $\sigma$ -delocalized carbonium ions related to pyramidal carbonium ions, the armilenium<sup>14</sup> cations have to be mentioned. Here, just as in the pyramidal carbonium ions, a description in terms of two-electron, three-center bonds fails to give a correct impression about the actual bonding and symmetry. Thus far only one armilenium cation, 11, is known in the literature.<sup>14</sup>

### $(\text{CH})_5^+$ : MO Calculations

In 1972 Stohrer and Hoffmann reported extended Hückel quantum mechanical calculations on  $(\text{CH})_5^+$  cation. A number of possible structures were calculated and several rearrangement pathways were explored. The authors proposed the square-pyramidal structure 4 to be the unique stable structure in this system. Insight into the electronic structure of 4 was gained by drawing an interaction diagram (Figure 1) showing how the orbitals of 4 are constructed from cyclobutadiene and  $\text{CH}^+$ .<sup>10</sup>

In a number of subsequent papers several authors report additional calculations on  $(\text{CH})_5^+$  cations. Use of the CNDO/2 method<sup>15</sup> and of another modified CNDO method<sup>16</sup> substantiated the conclusion that 4

is the most stable of the geometrical  $(\text{CH})_5^+$  structures. The latter study reveals also that there is an additional energy minimum, associated with structure 12, 45 kcal/mol above that of 4. Dewar and Haddon,<sup>17</sup> using the MINDO/3 method, also reached the conclusion that 4 and 12 are the only minima on the  $(\text{CH})_5^+$  potential-energy surface. Although 12 is stabilized by 14.4 kcal/mol compared to 4, according to these calculations, the calculated activation energy of 43 kcal/mol for the conversion of 4 to 12 makes it likely that 4, once formed, is a stable species. Ab initio calculations, reported by Hehre and Schleyer,<sup>18</sup> indicate the minimum for the square-pyramidal structure 4 to lie 55 kcal/mol above the singlet cyclopentadienyl structures.



12

Ab initio calculation of the stabilizing effect of substitution by phenyl and methyl reveals that phenyl substitution is vastly superior in stabilizing cyclopentadienyl ions, but less so in stabilizing 4. Substitution at a base position of 4 is better than at the apex. Permethyl substitution stabilizes all forms markedly, favoring the pyramidal ion slightly over cyclopentadienyl.<sup>18</sup>

From a steric point of view it is interesting that several calculations indicate the basal hydrogens in 4 to be directed upward, permitting a better orientation of the cyclobutadiene  $\pi$  system toward the apical  $\text{CH}^+$ .<sup>15,17,18</sup>

The triplet state of cyclopentadienyl cation was also calculated using the MINDO/3 method; it was found to be more stable than 12 by 1.6 kcal/mol.<sup>19</sup> Ab initio calculations indicate the triplet cyclopentadienyl cation to be 17 kcal/mol more stable than the lowest singlet.<sup>18</sup> This is in agreement with the recent EPR study of cyclopentadienyl cation at 78 K, which shows this  $(\text{CH})_5^+$  isomer to be a ground-state triplet.<sup>20</sup> A number of substituted cyclopentadienyl cations, however, appear to be ground-state singlets.<sup>21</sup>

### $(\text{CH})_5^+$ : Experimental Work

Experimental work on the parent square-pyramidal carbonium ion 4 has not yet been reported, but a dimethyl-substituted species has recently been prepared. The results of solvolysis experiments with 13-OBs do not demand the intermediacy of a square-pyramidal cationic intermediate.<sup>22</sup> However, by dissolving 13-OH and 13- $\text{OCH}_3$  or isomeric homotetra-

(16) H. Kollmar, H. O. Smith, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 5834 (1973).

(17) M. J. S. Dewar and R. C. Haddon, *J. Am. Chem. Soc.*, **95**, 5836 (1973).

(18) W. J. Hehre and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **95**, 5837 (1973).

(19) M. J. S. Dewar and R. C. Haddon, *J. Am. Chem. Soc.*, **96**, 255 (1974).

(20) M. Saunders, R. Berger, A. Jaffe, J. M. McBride, J. O'Neill, R. Breslow, J. M. Hoffmann, C. Perchonock, E. Wasserman, R. S. Hutton, and V. J. Kuck, *J. Am. Chem. Soc.*, **95**, 3017 (1973).

(21) R. Breslow, H. W. Chang, and W. A. Yager, *J. Am. Chem. Soc.*, **85**, 2033 (1963); R. Breslow, H. W. Chang, R. Hill, and E. Wasserman, *ibid.*, **89**, 1112 (1967); R. Breslow, *Acc. Chem. Res.*, **6**, 393 (1973); W. Broser, H. Kurreck, and P. Siegle, *Chem. Ber.*, **100**, 788 (1967); W. Broser, P. Siegle, and H. Kurreck, *ibid.*, **101**, 69 (1968).

(22) S. Masamune, M. Sakai, and H. Ona, *J. Am. Chem. Soc.*, **94**, 8955 (1972).

(11) J. P. Pasinski and R. A. Beudet, *J. Chem. Soc., Chem. Commun.*, 928 (1973).

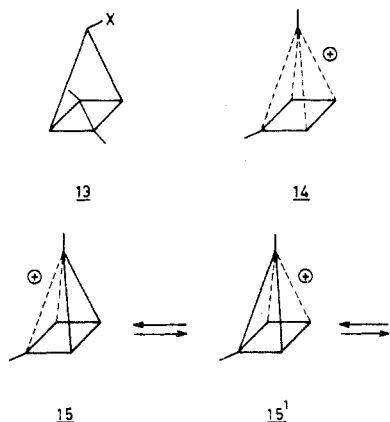
(12) S. Winstein and C. Ordonneau, *J. Am. Chem. Soc.*, **82**, 2084 (1960).

(13) R. K. Lustgarten, M. Brookhart, and S. Winstein, *J. Am. Chem. Soc.*, **94**, 2347 (1972); P. R. Story, L. C. Snyder, D. C. Douglas, E. W. Anderson, and R. L. Kornegay, *ibid.*, **85**, 3630 (1963).

(14) M. J. Goldstein and S. A. Kline, *J. Am. Chem. Soc.*, **95**, 935 (1973).

(15) S. Yoneda and Z. Yoshida, *Chem. Lett.*, 607 (1972).

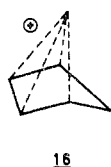
hedranes in  $\text{FHSO}_3\text{-SO}_2\text{ClF}$  at  $-78^\circ$ , the same  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained, which were ascribed to the pyramidal cation 14. Quenching of these solutions at low temperature afforded cyclopentenes.



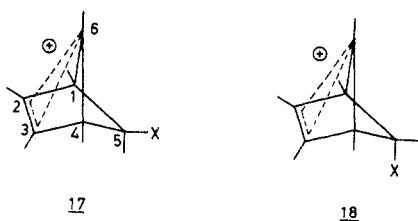
These results can be explained either by 14 or by a cyclopentadienyl cation, but the latter was judged to be incompatible with the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. On the same basis a number of other species were eliminated, leaving only 14 and a rapidly equilibrating system of less symmetrical structures 15 as possible structures for the observed cation. On the NMR time scale these two possibilities are equivalent, and the available data did not provide a clear distinction,<sup>23</sup> although the very high-field  $^{13}\text{C}$  NMR chemical shift for C-5 could be an indication for structure 14. In subsequent papers the authors use only 14 as the structural formula of this ion.<sup>24,25</sup>

### Homo-(CH)<sub>5</sub><sup>+</sup> Cations

Insertion of a methylene group into one of the four-membered ring bonds of 4 would give rise to the homo derivative 16. Bicyclo[2.1.1]hexenyl cations possess the geometrical prerequisites for such an electronic structure.



A number of hexamethylbicyclo[2.1.1]hexenyl cations (17, X = H, OH; 18 X = H, Cl, Br,  $\text{SO}_2\text{SbF}_5^-$ )



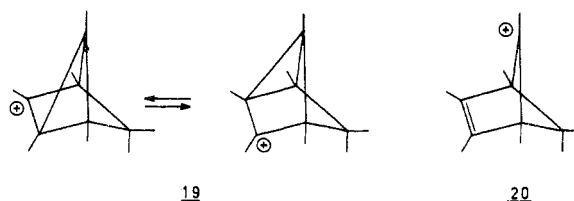
were prepared and experimental data were obtained in order to get information about the degree of delocalization of the positive charge.<sup>26-30</sup> Several elec-

(23) S. Masamune, M. Sakai, H. Ona, and A. L. Jones, *J. Am. Chem. Soc.*, **94**, 8956 (1972).

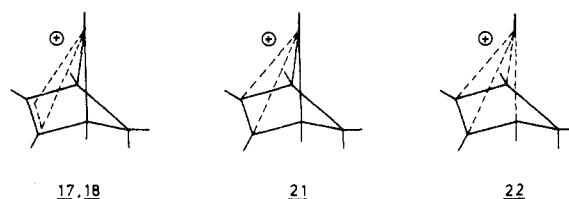
(24) S. Masamune, M. Sakai, A. V. Kemp-Jones, H. Ona, A. Venot, and T. Nakashima, *Angew. Chem.*, **85**, 829 (1973).

(25) A. V. Kemp-Jones, N. Nakamura, and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 109 (1974).

tronic structures were considered for these ions. Classical structures 19 and 20 were rejected on the basis



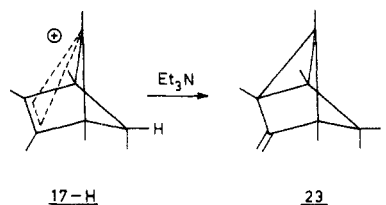
of: the rate of carbonylation<sup>31</sup> of the ions 17-H and 18-H; the ESCA spectrum of ion 18-Cl, showing a broad signal,<sup>32</sup> and the  $^{13}\text{C}$  NMR chemical shifts compared with those of model compounds.<sup>28</sup> Three nonclassical possibilities were considered: 17 and 18, 21, and 22. In order to obtain an indication of the relative importance of these structures, the  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts of ions 17 and 18 were scrutin-



ized. These shifts permit us to establish the following sequence in the charge density: C-2,3 > C-6 > C-1,4. Structure 22 therefore is only a minor resonance contributor to the actual structure. The preferred representation of the ions is shown by structure 17, 18 rather than structure 21, because the dotted line between C-2 and C-3 indicates the presence of at least some positive charge at C-6.<sup>28,29</sup>

This conclusion on the electronic structure of ions 17 and 18 is in good agreement with the reactivity of these ions. Triethylamine reacts with methyl-substituted carbonium ions to abstract a proton. This proton abstraction is a kinetically controlled process occurring at the methyl group adjacent to the carbon atom bearing the highest positive charge.<sup>33</sup>

Reactions of 17-H and 18-Br,Cl give rise to the formation of 23 and 24, respectively.<sup>33,34</sup> These products can be explained by proton abstraction at C-2,3 of ions 17 and 18, thus substantiating the conclusion that the positive charge is highest at these carbon



(26) H. Hogeveen and H. C. Volger, *Recl. Trav. Chim. Pays-Bas*, **87**, 385 (1968); **87**, 1042 (1968); **88**, 353 (1969).

(27) L. A. Paquette, G. R. Krow, J. M. Bollinger, and G. A. Olah, *J. Am. Chem. Soc.*, **90**, 7147 (1968).

(28) H. Hogeveen and P. W. Kwant, *J. Am. Chem. Soc.*, **95**, 7315 (1973).

(29) P. W. Kwant, Thesis, Groningen 1974.

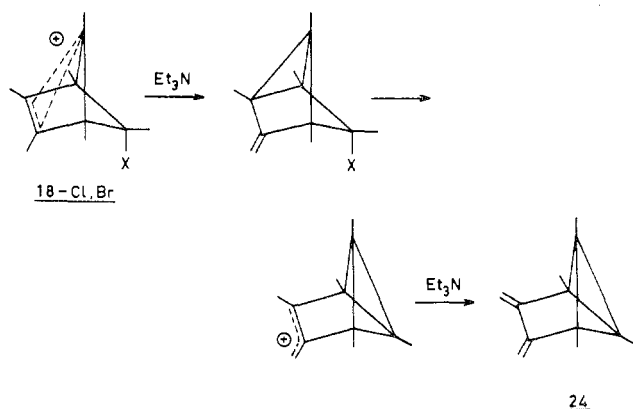
(30) H. Hogeveen, P. W. Kwant, E. P. Schudde, and P. A. Wade, *J. Am. Chem. Soc.*, **96**, 7518 (1974).

(31) H. Hogeveen and C. J. Gaasbeek, *Recl. Trav. Chim. Pays-Bas*, **89**, 395 (1970).

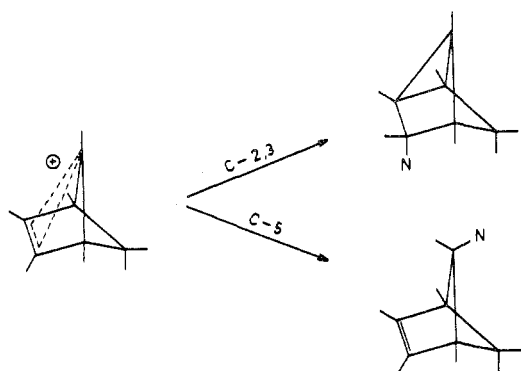
(32) R. Hüttel, P. Tauchner, and H. Forkl, *Chem. Ber.*, **105**, 1 (1972).

(33) H. Hogeveen and P. W. Kwant, *J. Org. Chem.*, **39**, 2624 (1974).

(34) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 5357 (1972); 3747 (1973).

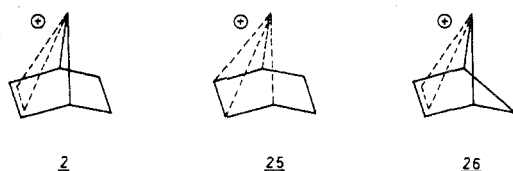


atoms.<sup>28</sup> Reactions of ions 17 and 18 with a number of nucleophiles have been performed. These experiments yield bicyclic as well as tricyclic products (Scheme I). The observation that hard nucleophiles usually prefer attack at C-2,3 again indicates that the charge at C-2,3 is higher than at C-6. Reactions of ions 17 and 18 with a nucleophile at C-1,4 have not been observed.<sup>28,29</sup>



It is of interest to check, using the available literature data, whether the conclusion that 22 is only a minor resonance contributor holds also for the parent structure and for the related 7-norbornenyl cation. CNDO calculations of the norbornenyl cation 2 indicate nonclassical  $\sigma$ -electron delocalization over C-1, -2, -3, -4, and -7.<sup>35</sup> The overlap population of the 1-7 bond of 7-norbornenyl cation, calculated by using the CNDO/2 technique, amounted to 0.616, a value somewhat smaller than the overlap population in a normal C-C bond (e.g., neopentane, 0.704).<sup>36</sup> However, examination of the reported <sup>1</sup>H<sup>13</sup> and <sup>13</sup>C NMR<sup>37</sup> indicates that there is not a high positive charge on C-1 and C-4 of 7-norbornenyl cation. Structure 2 therefore is a better representation of the actual structure of 7-norbornenyl cation than 25.

The parent ion 26 has been prepared, both under



(35) H. O. Ochorodnyk and D. P. Santry, *J. Am. Chem. Soc.*, **91**, 4711 (1969).

(36) S. Yoneda, Z. Yoshida, and S. Winstein, *Tetrahedron*, **28**, 2395 (1972).

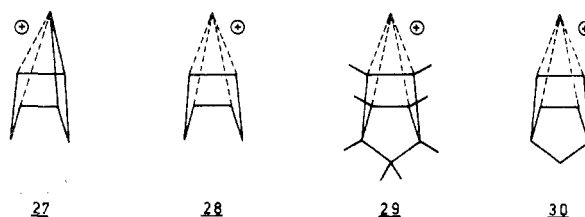
(37) G. A. Olah, A. M. White, J. R. DeMember, A. Commeyras, and C. Y. Lui, *J. Am. Chem. Soc.*, **92**, 4627 (1970).

solvolytic conditions<sup>38</sup> and in strong acid.<sup>39</sup> The <sup>1</sup>H NMR chemical shifts of 26 in FHSO<sub>3</sub> at -60° and those of 7-norbornenyl cation 2 are quite similar,<sup>39,40</sup> indicating that the electronic structures of 26 and 2 are comparable.

We conclude that ions 2, 17, 18, and 26, which possess the geometrical prerequisites for an electronic structure related to 4, fail to show such an extensive delocalization of the positive charge. These ions prefer a structure which can be described using a two-electron, three-center bond.

### Bishomo-(CH)<sub>5</sub><sup>+</sup> Cations

The trishomocyclopropenyl cation 27 has been the subject of a number of solvolytic studies.<sup>41</sup> The authors felt that the experimental results could equally well be explained with the intermediacy of the more symmetrical bishomo-(CH)<sub>5</sub><sup>+</sup> cation 28. To obtain more information, the ion was generated in SbF<sub>5</sub>-SO<sub>2</sub> and the <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded at -110°. Although no conclusive distinction could be made between a rapidly equilibrating system of ions 27 and a static ion 28, structure 28 is preferred on the basis of related theoretical and experimental work.<sup>24</sup>



Recent MINDO/2 calculations on bishomo-(CH)<sub>5</sub><sup>+</sup> carbonium ions indicate the square-pyramidal form to be favored energetically over less symmetrical structures.<sup>42</sup>

Two substituted bishomo-(CH)<sub>5</sub><sup>+</sup> ions have also been reported. Hart and Kuzuya<sup>43</sup> studied the permethyl species 29 in strongly acidic solution and Masamune and coworkers<sup>25</sup> used the same technique for the parent ion 30, which is perhaps also present as an intermediate in solvolysis.<sup>44</sup> The <sup>1</sup>H (at ca. -120°) and <sup>13</sup>C NMR spectra of both ions are in principle consistent either with the presence of 29 and 30 or with degenerate, rapidly equilibrating systems of less symmetrical structures.

### (CCH<sub>3</sub>)<sub>6</sub><sup>2+</sup>: Preparation and Chemical Behavior

The first—and thus far only—representative of the (CH)<sub>6</sub><sup>2+</sup> type pyramidal carbonium ion is the hexamethyl derivative 31.<sup>45</sup> This ion, the structure of which will be discussed below, is formed when a variety of ionic and covalent precursors are treated with

(38) S. Masamune, S. Takada, N. Nakatsuka, R. Vukov, and E. N. Cain, *J. Am. Chem. Soc.*, **91**, 4322 (1969).

(39) S. Masamune, E. N. Cain, R. Vukov, S. Takada, and N. Nakatsuka, *Chem. Commun.*, 243 (1969).

(40) R. K. Lustgarten, M. Brookhart, S. Winstein, P. G. Gassman, D. S. Patton, H. G. Richey, and J. D. Nichols, *Tetrahedron Lett.*, 1699 (1970).

(41) R. K. Lustgarten, *J. Am. Chem. Soc.*, **94**, 7602 (1972); S. Masamune, R. Vukov, M. J. Bennett, and J. T. Purdham, *ibid.*, **94**, 8239 (1972); P. G. Gassman and X. Creary, *ibid.*, **95**, 2729 (1973).

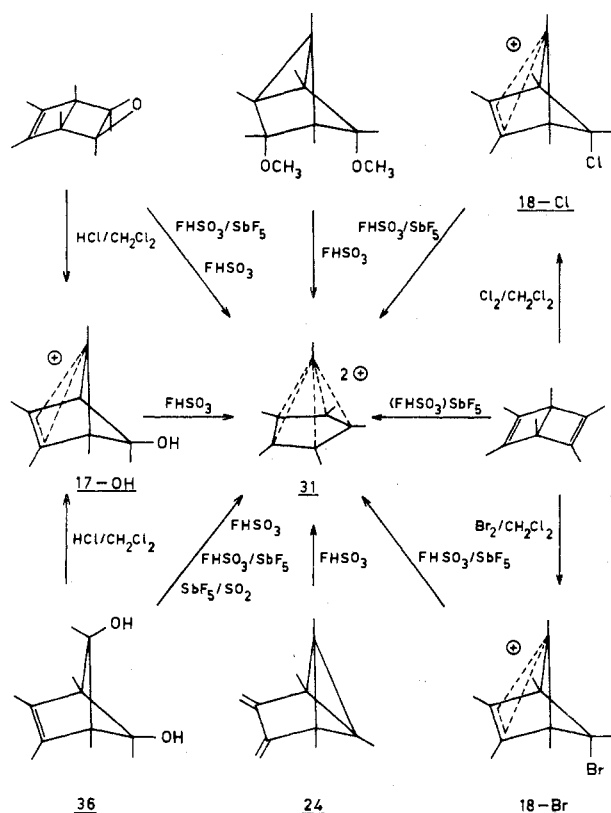
(42) K. Morio and S. Masamune, *Chem. Lett.*, 1107 (1974).

(43) (a) H. Hart and M. Kuzuya, *J. Am. Chem. Soc.*, **94**, 8958 (1972); (b) *ibid.*, **95**, 4096 (1973); (c) *ibid.*, **96**, 6436 (1974); (d) H. Hart and M. Kuzuya, *Tetrahedron Lett.*, 4123 (1973).

(44) R. M. Coates and K. Yano, *Tetrahedron Lett.*, 2289 (1972).

(45) H. Hogeveen and P. W. Kwant, *Tetrahedron Lett.*, 1665 (1973).

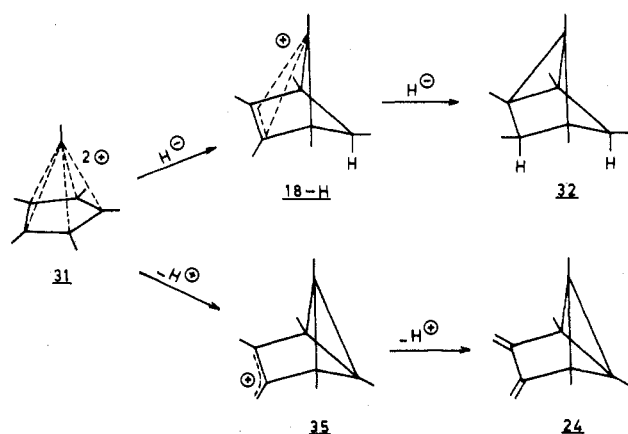
Scheme II



strong acids ( $\text{FHSO}_3$ ,  $\text{FHSO}_3\text{-SbF}_5$ ) at low temperature,<sup>6,29,46</sup> (Scheme II). Presumably all of these reactions involve first the formation of 5-substituted monocations **17** and **18** followed by reaction with the strong acid solvent in a subsequent step.

In reactions of the dication with nucleophiles the reverse pathway is followed. For example, the quenching of solutions of **31** with lithium aluminum hydride in ether or with triethylamine to give **32** and **24**, respectively, can be explained with monocations as intermediates (Scheme III). Such a mechanism ex-

Scheme III

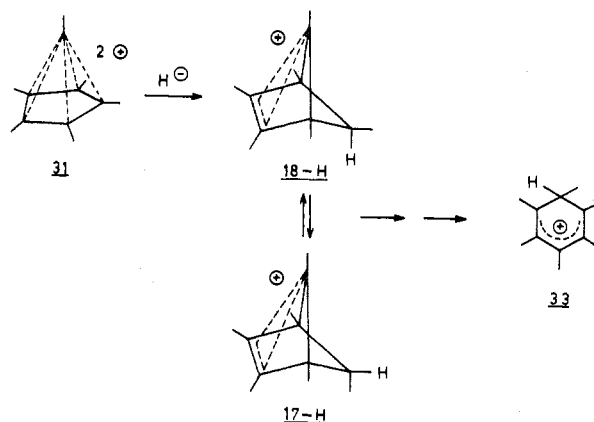


plains the tricyclic structure of the products as well as their stereochemistry.<sup>28</sup> The intermediacy of monocations is nicely illustrated by the hydride uptake reaction of **31** in strongly acidic solution. The rate of this reaction, which yields hexamethylbenzenium ion **33**, was observed to decrease with increasing solvent

(46) H. Hogeveen and P. W. Kwant, *J. Am. Chem. Soc.*, **96**, 2208 (1974).

acidity. Upon addition of reagents able to donate hydride ions, such as isopentane, the rate of hydride uptake is so much enhanced that under these conditions the intermediate ions **18-H** and **17-H** (1:3 equilibrium ratio)<sup>26</sup> can be observed by  $^1\text{H}$  NMR (Scheme IV). This substantiates the conclusion that in the first step dication **31** takes up hydride to give monocations.<sup>46</sup> The isomerization of **18-H** and **17-H** was already known<sup>26</sup> from previous studies.

Scheme IV



Apart from this hydride uptake, at temperatures up to  $100^\circ$  no reactions of the dication in strongly acidic solution have been observed. As the rate of hydride uptake is acidity dependent, the use of the strongest acids available ( $\text{HF-SbF}_5$  and  $\text{FHSO}_3\text{-SbF}_5$ , both 1:1 molar ratio) minimizes the dication decomposition, so that it can be handled at room temperature.

#### $(\text{CCH}_3)_6^{2+}$ : Structure

The dicarbonium ion nature of the  $(\text{CCH}_3)_6^{2+}$  dication was derived from the observation that **31** can be formed from precursors containing two different functional groups and that quenching of solutions of **31** provides products with incorporation of two identical substituents. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopic data are in agreement with this conclusion.<sup>29,45,46</sup>

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Figure 2) of dication **31**—which show 5:1 peak ratios—and the tricyclic structure of the quenching products were used to rule out a number of possibilities for the structure of the dication. Only two possible structures, indistinguishable on this basis, remained: the nonclassical, fivefold symmetrical, static structure **31** and a rapidly equilibrating set of structures **34** (Scheme V), which have only a plane of symmetry and in which the top carbon atom describes a circle during the degenerate process.<sup>29,46</sup>

In carbonium ion chemistry, rapidly equilibrating structures are frequently encountered and the degenerate rearrangement of Scheme V is strongly related to the "cyclopropane merry-go-round" observed in polymethylbicyclo[3.1.0]hexenyl cations.<sup>47</sup> If this fivefold degenerate rearrangement is sufficiently rapid to make five carbon atoms (with the attached methyls) equivalent on the NMR time scale, the 5:1

(47) R. F. Childs and S. Winstein, *J. Am. Chem. Soc.*, **90**, 7146 (1968); R. F. Childs, M. Sakai, and S. Winstein, *ibid.*, **90**, 7144 (1968); V. A. Koptuyug, L. I. Kuzubova, I. S. Isaev, and V. I. Mamatyuk, *J. Org. Chem. USSR (Engl. Transl.)*, **6**, 2265 (1970).

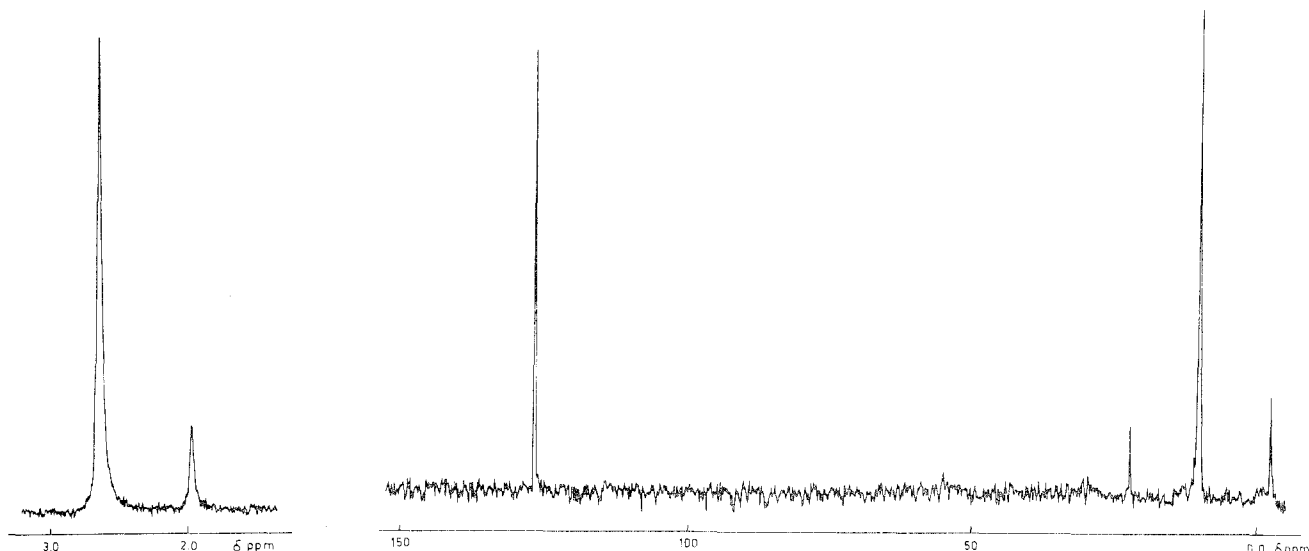
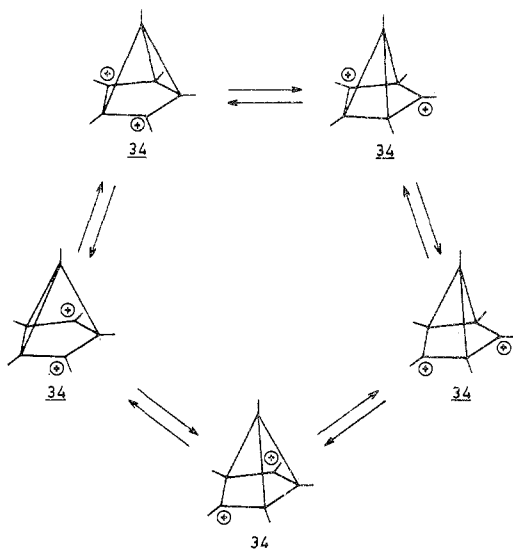


Figure 2.  $^1\text{H}$  (left) and  $^{13}\text{C}$  NMR (right) spectra of dication 31.

Scheme V



ratio is accounted for. It should be noted that this only holds for a rapid Wagner–Meerwein shift in the manner indicated in Scheme V.<sup>29,46</sup>

A number of techniques have been employed to obtain information which might enable one to express preference for one of the two alternatives. Although the evidence is not absolute, the data permit one to express strong preference for the nonclassical structure 31.<sup>29,45,46</sup>

The observation that at  $-140^\circ$  the  $^1\text{H}$  NMR spectrum of the dication displays no line broadening permits calculation of an upper limit of 5 kcal/mol for the free enthalpy of activation of the rapid Wagner–Meerwein shift causing the degenerate system of Scheme V. This would be a low barrier compared with those of polymethylbicyclo[3.1.0]hexenyl cations.<sup>47</sup> This argument, however, is not conclusive because it might be argued that in the latter case allylic stabilization in the ground state adds to the free enthalpy of activation, so that the barrier of less than 5 kcal/mol for ion 34 would still be compatible with such a classical structure.

The  $^{13}\text{C}$  NMR spectrum of the dication provides two arguments for the nonclassical structure. The use

of model compounds<sup>48</sup> in order to predict the average chemical shift of the five-membered ring carbon atoms of classical ion 34 affords a value (166.1 ppm) which proved inconsistent with the observed one (126.3 ppm). Furthermore, the  $^{13}\text{C}$  NMR chemical shift of the apical methyl carbon, found to lie even upfield from  $\text{Me}_4\text{Si}$  ( $-2.0$  ppm), cannot be explained with 34. In structure 31 either a ring current or a steric effect can serve as an explanation.<sup>29</sup>

The dication can be viewed as the protonated monocation 35 (see Scheme II). This monocation is expected to be stabilized owing to its nature as an allylic cation with additional stabilization by delocalization of the positive charge into the adjacent cyclopropane ring.<sup>49</sup> However, the  $^1\text{H}$  NMR spectrum does not show the presence of any other ion besides the dication. Moreover, it was noticed that the deuterium incorporation in  $\text{DFSO}_3$  solution is extremely low.<sup>29</sup> When we compare this result with the literature data on allylic cations stabilized by a cyclopropane group—these cations are not protonated in  $\text{FHSO}_3$  to give dications to a detectable extent<sup>49</sup>—it is obvious that unusually large stabilization of the dication is responsible for the equilibrium lying on the dication side.

As the rate of carbonylation appeared to provide a useful indication about the stability of carbonium ions,<sup>50</sup> carbonylation of the dication with pivaloyl cation as the carbon monoxide donor was attempted. No carbonylation was noticed, in contrast to the behavior of dimethylcyclopropylcarbinyl cation, which reacts with CO even at much lower temperatures.<sup>31</sup> The latter ion is considered to be the best available model for classical structure 34.

Strongly acidic solutions of the dication show no uv absorption with molar extinction greater than 100. Absorptions due to the solvent and decomposition products prohibit drawing conclusions about the presence of possible absorptions with smaller extinctions. Model systems for classical ion 34, cyclopropylcarbinyl cations, show absorptions with large molar extinctions ( $>10^4$ ) in the region 270–290 nm.<sup>51</sup> From

(48) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801 (1969).

(49) T. S. Sorensen and K. Rajeswari, *J. Am. Chem. Soc.*, **93**, 4222 (1971); K. Rajeswari and T. S. Sorensen, *ibid.*, **95**, 1239 (1973).

(50) H. Hogeveen, *Adv. Phys. Org. Chem.*, **10**, 29 (1973).

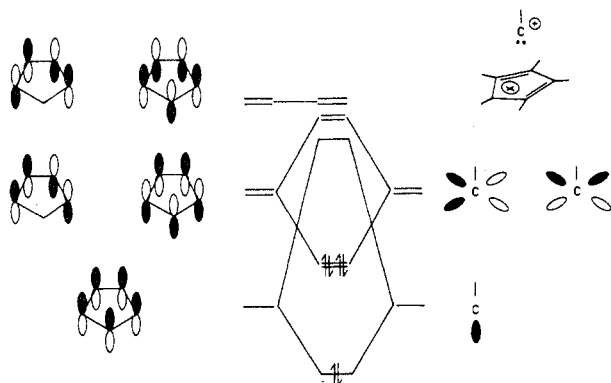


Figure 3. Interaction diagram of pentamethylcyclopentadienyl cation and  $\text{CCH}_3^+$ , showing how the orbitals of 31 are constructed from those of these two parts.

this consideration it is difficult to see why 34, with two positive centers interacting with the cyclopropyl group, would have no observable uv absorption. Unfortunately no models are available for structure 31. However, the results of ab initio calculations on the electronic structure of several states of parent ion 5 (see below) are in agreement with the absence of an uv absorption of the dication 31.<sup>6</sup>

Moreover, in view of the known instability of dications, the thermal stability of the dication is very hard to explain when a classical structure is adopted.<sup>29,46</sup>

Since the experimental evidence presented above strongly indicates 31 to represent the actual structure of the dication, some discussion about the nature of this structure is warranted. The  $(\text{CCH}_3)_6^{2+}$  structure can be treated in the same way as that of  $(\text{CH})_5^+$  (see Figure 1) with an interaction diagram (Figure 3) showing how the orbitals of 31 are constructed from  $\text{CCH}_3^+$  and pentamethylcyclopentadienyl cation.

The two stabilizing interactions seen in Figure 3 are clearly revealed in the ab initio calculations of 5.<sup>52</sup> The overlap populations are greatest between the  $\sigma$  and  $\pi$  orbitals of the apical CH group and the  $\pi$  orbitals of the ring.<sup>52</sup> The charge distribution in dication 31 can be estimated from the  $^{13}\text{C}$  NMR spectral data and the reactivity toward nucleophiles, which indicate that the positive charge resides mainly on the ring, rather than on the top.<sup>29,46</sup> This is in agreement with the predictions of ab initio calculations on the parent ion 5 (see below).

### $(\text{CH})_6^{2+}$ : Ab Initio Calculations

The stability arguments for the nonclassical structure 31 are supported strongly by the ab initio quantum mechanical calculations of Jonkman and Nieuwpoort<sup>52</sup> on the parent  $(\text{CH})_6^{2+}$  dication. These authors calculated the energies of many structures with C-6 at different positions above the five-membered ring. The energy was found to decrease when C-6 approaches a point above the center of the ring—that is, the pyramidal structure 5.

Preliminary results indicate the presence of a second minimum on the  $(\text{CH})_6^{2+}$  potential-energy surface, a chair form of benzene dication, which is found to be somewhat less stable than the pyramidal struc-

ture. As to the question whether this  $(\text{CH})_6^{2+}$  isomer has a triplet or a singlet ground state, the calculations have not yet provided an unambiguous answer.<sup>53</sup> Experimental results concerning the related hexachlorobenzene dication show that this ion has a triplet ground state.<sup>54</sup>

Using the ab initio program GAUSS 70, it was calculated that the gross atomic orbital populations for the apical CH group are  $\sigma_{\text{CH}}^2\pi^{1.76}\sigma^{0.96}$ . Starting from  $\sigma_{\text{CH}}^2\pi^2\sigma^0$  one might say that 0.96 electron has been donated to the empty  $\sigma$  orbital of  $\text{CH}^+$  accompanied by a  $\pi$  back donation of 0.24 electron to the  $(\text{CH})_5^+$  ring. This would result in a positive charge of 0.28 unit at the top, which resides, according to the calculations, almost entirely on the hydrogen atom, and 1.71 units in the ring, distributed over C (0.08 unit) and H (0.28 unit). The bond length of the five-membered ring bonds is calculated to be 1.45 Å and the top carbon atom is found at 1.21 Å above the center of the five-membered ring in the energy minimum of 5.<sup>52</sup>

Open-shell ab initio calculations (using the computed equilibrium geometry), which might correlate with uv absorptions, led to the conclusion that the highest wavelength maximum in the electronic spectrum of 5 as a single ion in vacuum is at 148 nm. The combined effect of solvent and methyl substitution was estimated to be 40–50 nm, so that the first allowed transition of 31 lies below 200 nm, which explains the absence of an observable uv absorption of this ion.<sup>6</sup>

### Current Research and Prospective Developments

At the moment a number of projects concerning the  $(\text{CCH}_3)_6^{2+}$  dication are being carried out in cooperation with other research groups. The ESCA<sup>55</sup> and Raman<sup>56</sup> spectroscopic techniques are being explored to obtain spectroscopic information about the structure of the dication. However, technical problems associated with the use of the strongly acidic solvents have prohibited the recording of satisfactory ESCA and Raman spectra thus far. Preliminary data concerning the heat of formation<sup>57</sup> add to the data presented above which indicate the high stability of the dication. Solvolysis experiments are planned<sup>58</sup> in order to investigate the occurrence of 31 under solvolytic conditions. Mass spectrometric experiments are being performed<sup>59</sup> to get insight into the nature of the  $(\text{CCH}_3)_6^{2+}$  particle which is observed in the mass spectrum of both hexamethylbenzene and hexamethyl(Dewar benzene).<sup>29</sup>

The synthesis of other  $(\text{CH})_6^{2+}$  derivatives, such as 37–39, is at present being actively investigated in this

(53) P. Th. van Duynen, H. T. Jonkman, W. C. Nieuwpoort, and J. Postma, private communications.

(54) E. Wasserman, R. S. Hutton, V. J. Kuck, and E. A. Chandross, *J. Am. Chem. Soc.*, **96**, 1965 (1974).

(55) Dr. G. A. Sawatsky and Mr. A. Heeres, Department of Physical Chemistry, The University, Groningen, The Netherlands.

(56) Dr. N. C. Rol and Mr. I. L. C. Freriks, Koninklijke/Shell-Laboratorium Amsterdam (Shell Research B.V.), The Netherlands.

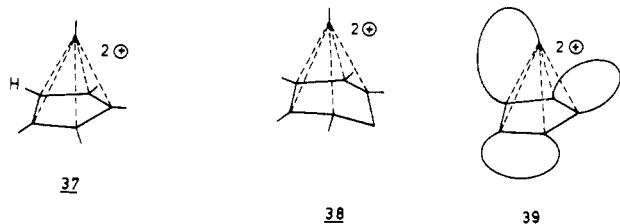
(57) The heat of formation of the dication from diol 36 (see Scheme II) in  $\text{FHSO}_3$  was measured to be  $-25.7$  kcal/mol at  $-60^\circ$ . Professor Dr. E. M. Arnett and Dr. J. L. About kindly provided us with these data.

(58) Professor Dr. M. Hanack, Universität des Saarlandes, Saarbrücken, Federal Republic of Germany.

(59) Dr. N. M. M. Nibbering, Laboratory for Organic Chemistry, University of Amsterdam, The Netherlands.

(51) G. A. Olah, C. U. Pittman, and M. C. R. Symons, "Carbonium ions", Vol. 1, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1968, Chapter 5.

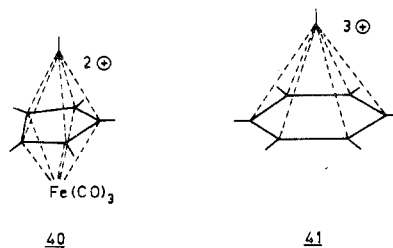
(52) H. T. Jonkman and W. C. Nieuwpoort, *Tetrahedron Lett.*, 1671 (1973).



laboratory by exploiting procedures which to some extent have already been developed.<sup>33,60</sup> These dications could well reveal a number of interesting details about the bonding in this type of carbonium ions and could open further synthetic perspectives.

(60) G. Capozzi and H. Hogeveen, *J. Am. Chem. Soc.*, **97**, 1479 (1975); R. F. Heldeweg and H. Hogeveen, *Tetrahedron Lett.*, 1517 (1975); H. Hogeveen and E. M. G. A. van Kruchten, research in progress; H. Hogeveen, J. Jorritsma, P. A. Wade, F. van Rantwijk, J. B. Koster, J. J. Prooi, A. Sinneema, and H. van Bekkum, *Tetrahedron Lett.*, 3915 (1974).

Futuristic structures such as **40**,<sup>61</sup> an "inverted sandwich", and trication **41**, a logical extension of the pyramidal series,<sup>43c</sup> could also be the result of continuing research in the field of pyramidal carbonium ions.



(61) For a related organometallic species see: V. R. Miller, L. G. Sneddon, D. C. Beer, and R. N. Grimes, *J. Am. Chem. Soc.*, **96**, 3090 (1974); L. G. Sneddon, D. C. Beer, and R. N. Grimes, *ibid.*, **95**, 6623 (1973).

## Some Approaches to the Theory of Chemisorption

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Chemisorption may be defined as adsorption involving significant electron sharing or transfer. Thus it is not only more specific than physisorption, but generally much stronger, with energies of 1–5 eV.

Chemisorption seems to be strongest on transition metals probably because of the presence of available, rather localized, highly directional d orbitals. Almost all elements can be adsorbed. Saturated molecules are strongly adsorbed only upon dissociation into atoms or fragments. Chemisorption invariably involves some charge transfer. For adsorbates with low ionization potential  $I$  (i.e., alkalis or alkaline earths) considerable electron deficiency, i.e., polar or even ionic adsorption, is the rule. For substances of high  $I$  electron transfer is usually to the adsorbate and  $\leq 0.1$  electron charge. Within a given system there are qualitative differences from crystal plane to crystal plane, and it is also known that distinct binding states occur on a given plane. The greatest variety of modes occurs on body-centered cubic (bcc) rather than face-centered cubic (fcc) substrates; the former are atomically less closely packed, and this suggests that the existence of different modes is connected with adsorbate–substrate geometry. The latter have not been elucidated for more than a handful of states.

In the last few years the experimental study of chemisorption has been revolutionized by a number

of new techniques culminating in various electron spectroscopies which promise to reveal the electronic structure of the adsorption complex. These developments seem to have stimulated theoretical efforts, and the theory of chemisorption on metals is now progressing rapidly. Much of the theory is also applicable, with some modifications, to semiconductors.

### Cluster Models

The bonding of an adsorbate atom or molecule to a metal surface is not very different in principle from other chemical bonding except that a very large number of substrate atoms and electrons are involved. This necessarily introduces some modifications, for instance the possibility that discrete bonding and antibonding orbitals are replaced by more or less broad resonances. In addition the close spacing in energy of metal electrons gives much greater weight to screening (for instance image effects) than in small molecules. One approach is to make essentially "chemical" calculations on clusters consisting of a small number (5–10) of substrate atoms plus an adsorbate<sup>1</sup> and to hope that the results will simulate the actual system closely enough to allow significant conclusions to be drawn. This approach can take account of image effects and the contribution to bonding of continuum states only by putting in "by hand" such terms at the end of the calculation, if at all. More important, it must ignore the flow of electrons into and out of clusters (imagined as part of the metal adsorbate system). Finally it cannot utilize what is known about the clean metal and its surface. Despite these

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(1) K. H. Johnson and R. P. Messmer, *J. Vac. Sci. Technol.*, **11**, 236 (1974).