# Coarctate Transition States: The Discovery of a Reaction Principle[†]

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A computer aided classification of more than 80 000 reactions from reaction databases and manual classification of several thousand reactions from the literature suggested that there are three major topologies of electron redistribution in single step reactions. The linear (e.g., addition, substitution, elimination) and the cyclic (pericyclic) topology correspond to the most common and fundamental ways of mechanistic thinking in organic chemistry. Among the remaining reactions, there is a third class sharing a common topology of electron redistribution that we call "coarctate". We proved that the obvious relationships of these reactions are based on a common physical principle. They seem to form a third, small but important category of organic reactions that hitherto never have been described in a coherent context.

## INTRODUCTION

The number of well characterized and documented chemical reactions is well over $10^6$. Maybe $10^4$–$10^5$ of them can be regarded as being synthetically useful. The number of fundamental reaction types an experienced synthetic chemists is able to immediately apply on a synthetic problem probably is in the order of 100, even though he or she is aware of a much larger number of published reactions.[1] To cope with the multitude of individual reactions, particularly for solving synthetic problems, different organizing principles have found favor in organic chemistry. Most frequently used are name reactions (e.g., Diels–Alder, Wittig, Beckmann, Eschenmoser, Ugi), mechanistic descriptors (e.g., substitution, addition, cycloaddition, rearrangement, oxidation, reduction), and formal descriptors (e.g. C–C linking, functional group interconversion, umpolung, protection group reactions). However, none of these (historically grown) principles is formal and unequivocal enough to form the basis of a computer aided reaction classification. Retrieval systems for large reaction data bases and synthesis planning programs demanded the development of a number of formal, computerizable classification algorithms.[2] The disadvantage of these methods is that they group reactions whose relationship already is well recognized. To unravel novel interrelations, inherent regularities, or even reaction principles within a large number of reactions in nowadays readily available reaction data bases, we had to follow a different and even more formal (less biased) strategy.

Well suited for this purpose is the reverse process of our reaction generation principles[3–5] (Figure 1), which is based on the Ugi–Dugundji model of constitutional chemistry.[6–8]

Reactions are classified in hierarchical order by first removing those bonds whose bond order does not change during the reaction (together with the corresponding atoms, e.g., substituents). In the second step the remaining atoms are replaced by a variable element. The resulting "basic reaction" thus comprises the set of conceivable hetero reactions. The last step and highest level of abstraction is the reaction category, that only gives information about the sequence of increasing and decreasing bond orders.[9,10] It is synonymous with the array of electron pushing arrows in the conventional way of writing mechanisms. In the case of concerted reactions, the reaction category defines the delocalized system of electrons
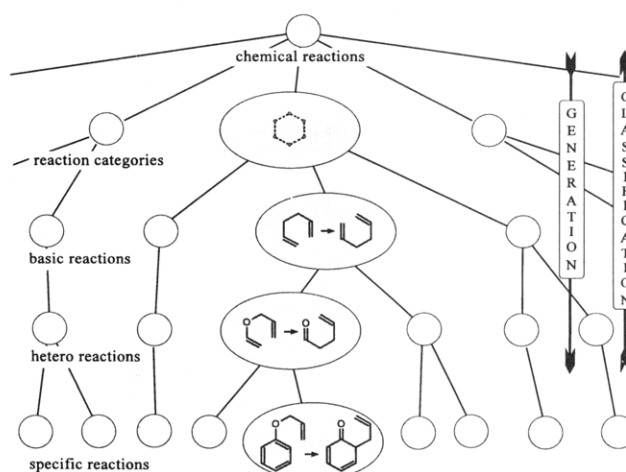


**Figure 1.** Hierarchical classification and generation of chemical reactions.



**Figure 2.** Topologies of bond redistribution patterns according to the classification of reactions from reaction databases and Houben Weyl.
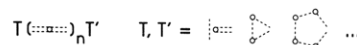


**Figure 3.** Formal "aufbau principle" of complex reactions.

in the transition state.

## TOPOLOGIES OF REACTION CATEGORIES

Figure 2 shows the final result of our attempts to classify more than 80 000 reactions from data bases available through the ORAC and REACCS reaction retrieval systems and a few thousand reactions mainly from Houben Weyl.[11]

The numbers do not add up to 100%. Some reactions could not be classified since they were not stoichiometric or they
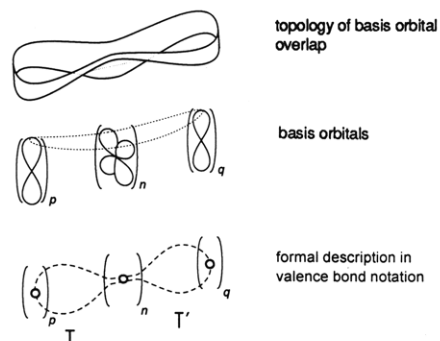
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**Figure 4.** Topology of basis orbital overlap and formal description of coarctate transition states.
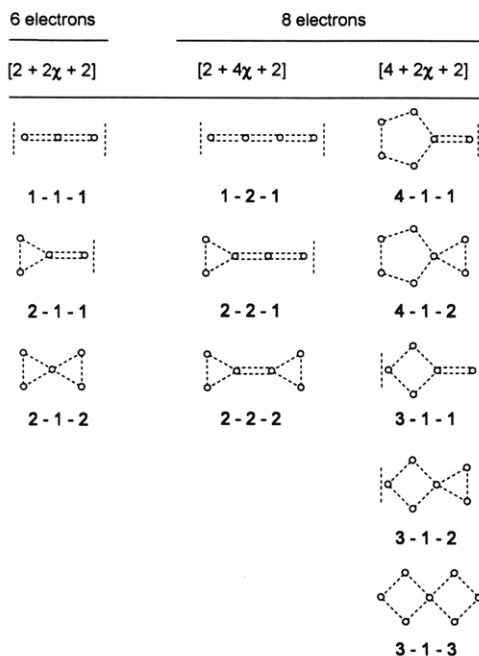


**Figure 5.** Coarctate transition states with six to eight mobile electrons. For definition of the notation see text.
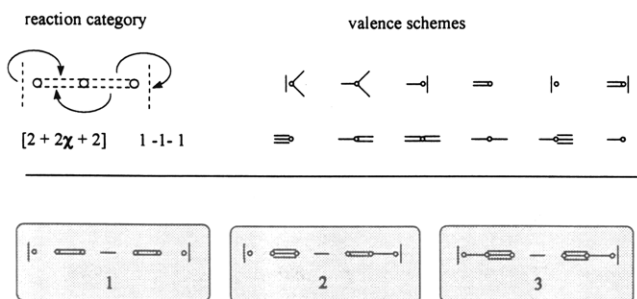


**Figure 6.** Complex basic reactions with two lone pair terminators and a linear subsystem of $n = 1$ (1–1–1). Lone pairs are represented by |, and the variable elements in the reaction centers by O. The chemistry of the elements is defined by the "allowed" valence schemes given on top. As a further boundary condition, reactions with triple bonds or allene structures in 3-, 4-, and 5-membered rings are eliminated. Reactions are written with the lone pair bearing atoms on the educt side of the reaction equation. Reverse reactions are not separately listed.

comprised multistep reactions. Considerable manual intervention during classification was necessary, while using the databases. Therefore the numbers in each category are not absolutely correct. Nevertheless they should give a good estimate of the population and importance of the different reaction categories. At a first glance the results are not surprising.
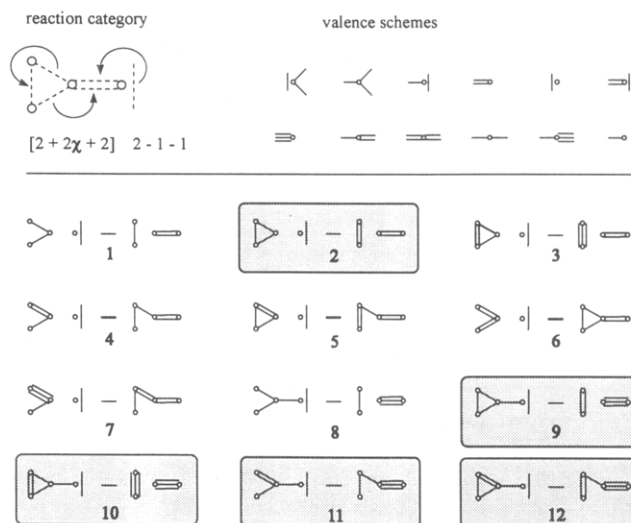


**Figure 7.** Complex basic reactions with a 3-ring and a lone pair terminator and a linear subsystem of $n = 1$ (2–1–1). For definition of the notation and boundary conditions see Figure 6.
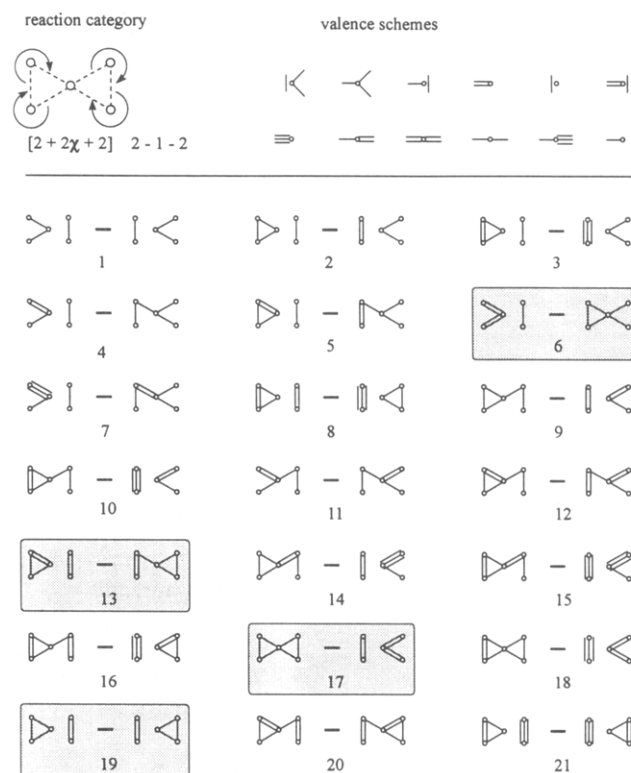


**Figure 8.** Complex basic reactions with two 3-ring terminators and a linear subsystem of $n = (2–1–2)$. For definition of the notation and boundary conditions see Figure 6.

Most of the organic reactions investigated are of linear topology. They can be depicted by a linear array of electron pushing arrows. Since electrons are shifted over a linear sequence of atoms, they always imply the forming and removing of charges that usually are eliminated in a subsequent tautomerization step. Nucleophilic addition, substitution, and elimination are the most important examples of reactions with a linear topology of electron redistribution. The second largest group of reaction categories is of cyclic topology. They can be depicted by a cyclic arrangement of electron pushing arrows and are called pericyclic, if they are concerted. Within the remaining data set, however, we discovered a third group of reactions with a more complicated electron redistribution pattern. We therefore provisionally termed them "complex
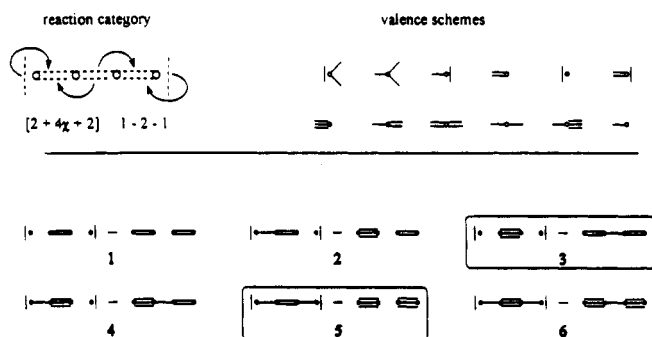
**Figure 9.** Complex basic reactions with two lone-pair terminators and a linear subsystem of $n = 2$ (1–2–1). For definition of the notation and boundary conditions see Figure 6.
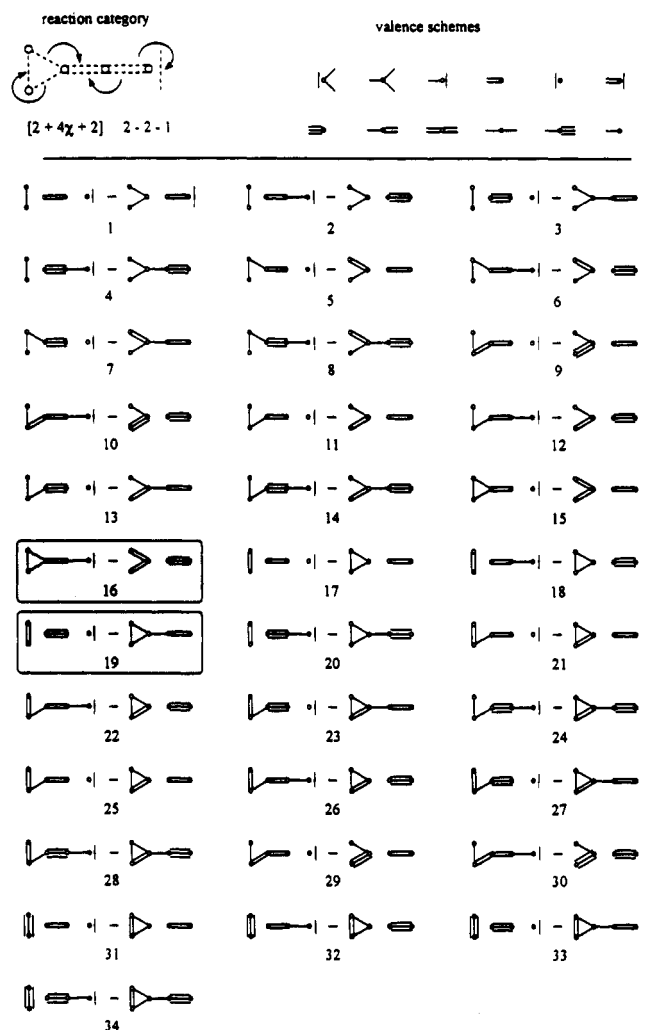
**Figure 10.** Complex basic reactions with a 3-ring and a lone pair terminator and a linear subsystem of $n = 2$ (2–2–1). For definition of the notation and boundary conditions see Figure 6.

**Figure 11.** Complex basic reactions with two 3-ring terminators and a linear subsystem of $n = 2$ (2–2–2). For definition of the notation and boundary conditions see Figure 6.

reactions". The topology of electron shift resembles a coarctate (constricted) circle. Complex reactions have the following features in common (Figure 3):

1. They consist of at least one atom or a linear sequence of atoms at which two bonds are broken and made simultaneously. This part corresponds to the coarctations in the electron redistribution pattern.

2. The coarctation is bound by "terminators". Terminators are atoms with a lone pair, two atoms complementing the electron shift to a three membered ring, three atoms to form a four membered ring, or larger terminators. Any combination of two terminators is allowed.

In the first instance, this organizing principle is purely formal and descriptive and the question arises:

*Are these relationships purely accidental, or is there any underlying physical principle that favors such reactions or transition states?*

## MECHANISM OF COMPLEX REACTIONS (COARCTATE TRANSITION STATES)

To answer this question, we made the following *ad hoc* assumptions:
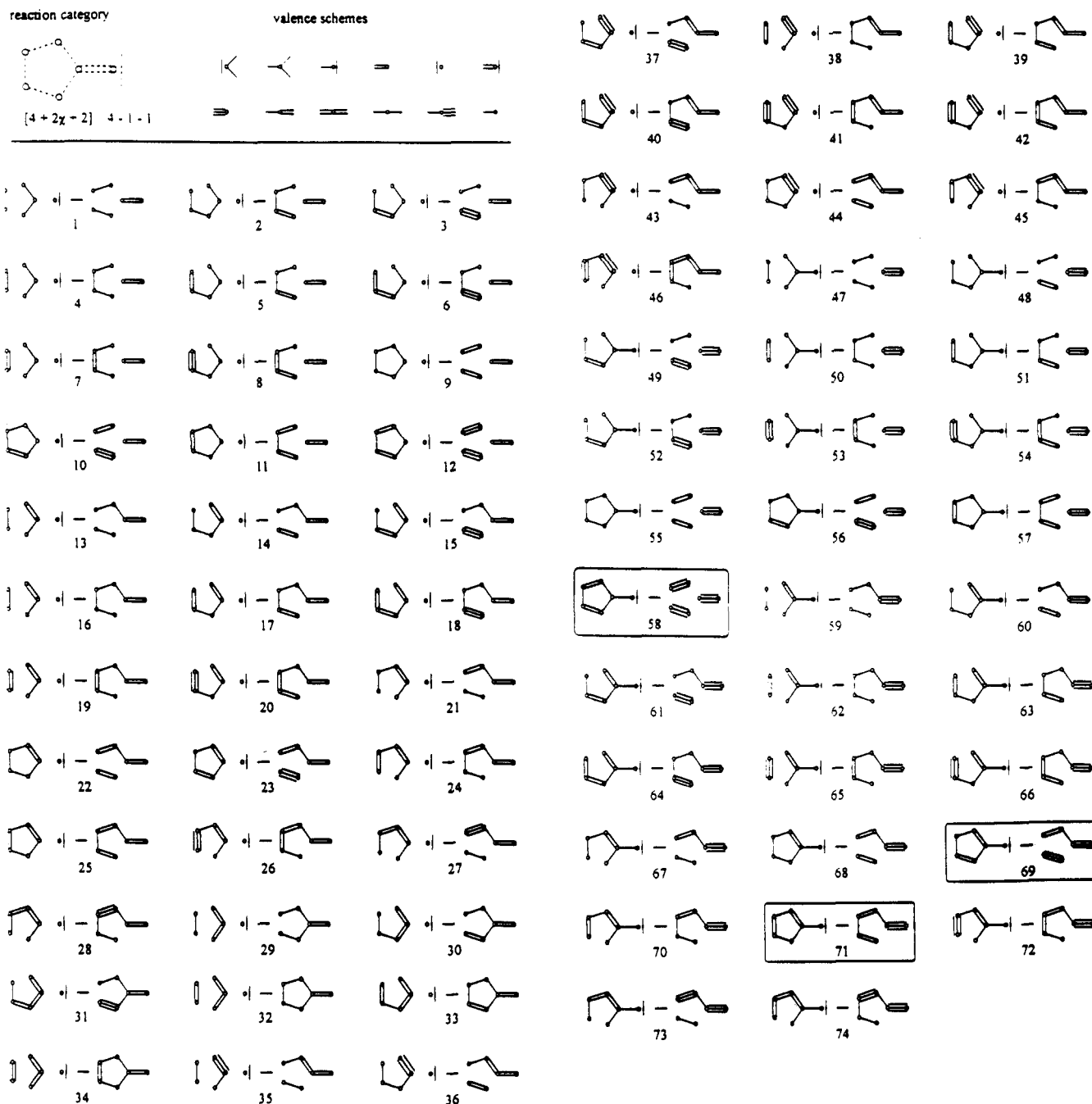
1. The reactions are concerted.

**Figure 12.** Complex basic reactions with a 5-ring and a lone pair terminator and a linear subsystem of $n = 1$ (4–1–1). For definition of the notation and boundary conditions see Figure 6.

2. The transition states are stabilized by "aromaticity" (similar to pericyclic reactions).

The plausibility of concerted reactions decreases with an increasing number of bonds that have to be formed and broken simultaneously.[12] Nevertheless, there is a number of reactions particularly within the pericyclic reaction categories that proceed concertedly via an extended system of bond making and breaking. The low barrier of activation of these reactions is explained by aromatic stabilization of their transition states.[13-15] Thus we followed the argument that a similar effect could also be operative in complex reactions.

There are several methods to approach the problem. In order to avoid an extensive quantum theoretical formalism and because a detailed theoretical treatment will appear elsewhere,[16] a brief summary of the topological approach should serve as a simplistic explanation:

The starting point of our topological model of coarctate transition states is the well-known Hückel–Möbius method[17] or the Dewar–Evans principle[18] for treating pericyclic reactions.[19] Both models are based on the assumption that the "mobile electrons" and the corresponding basis orbitals can be treated separately from those valence electrons and basis orbitals which are not affected by the reaction. There are only two determinants defining if a concerted pericyclic reaction is allowed or forbidden: (1) the topology of overlap of the basis orbitals and (2) the number of mobile electrons in the transition state. If the overlap of basis orbitals has Hückel topology and the number of electrons is $4n + 2$, the transition state is said to be Hückel aromatic[20] (stabilized by aromaticity similar to aromatic structures) and the reaction will be thermochemically allowed. Reactions with antiaromatic transition states are thermochemically forbidden.

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reaction category

valence schemes
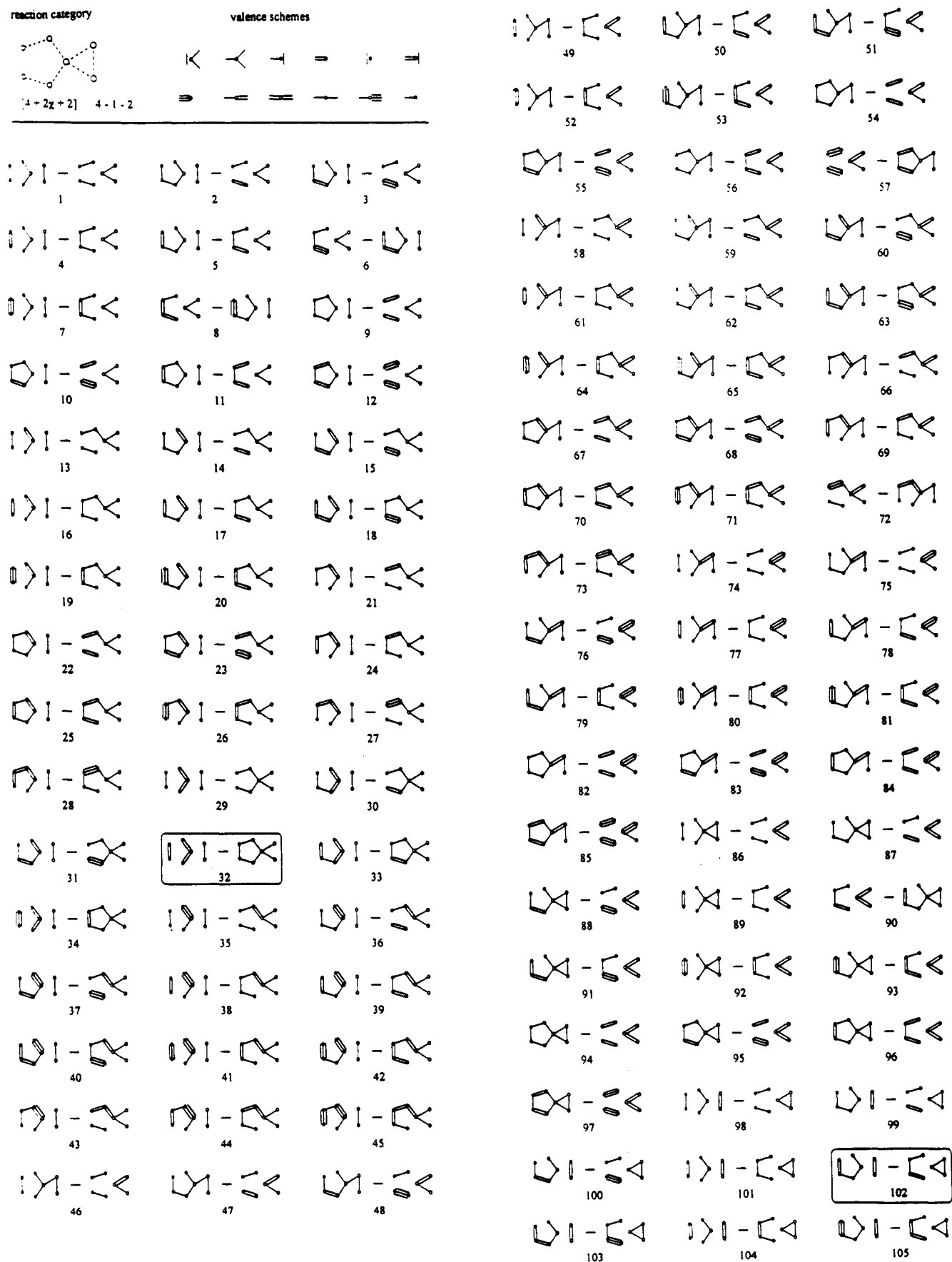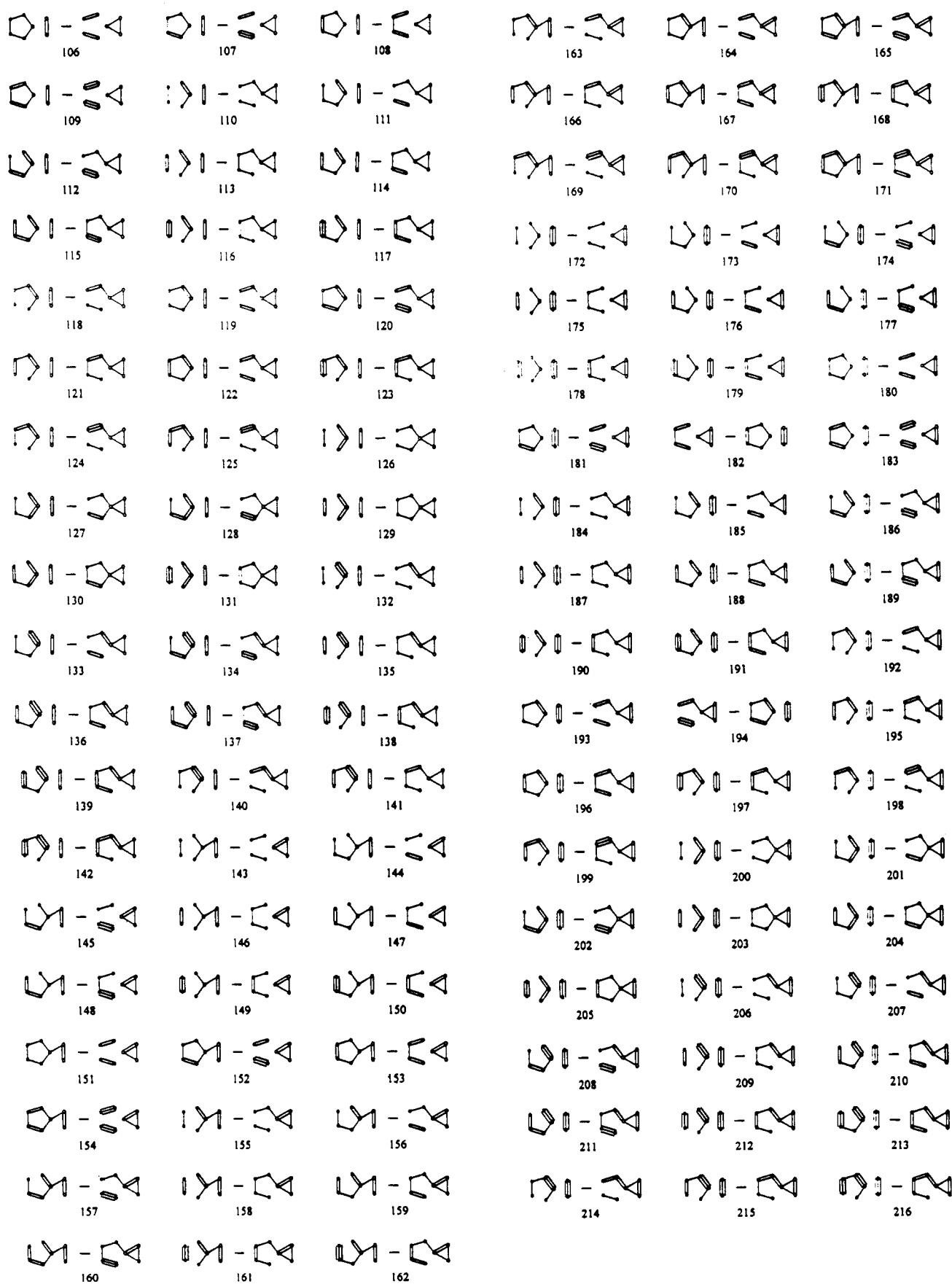
$[4 + 2\chi + 2]$   4 - 1 - 2

Figure 13. Complex basic reactions with a 5-ring and a 3-ring terminator and a linear subsystem of $n = 1$ (4–1–2). For definition of the notation and boundary conditions see Figure 6.
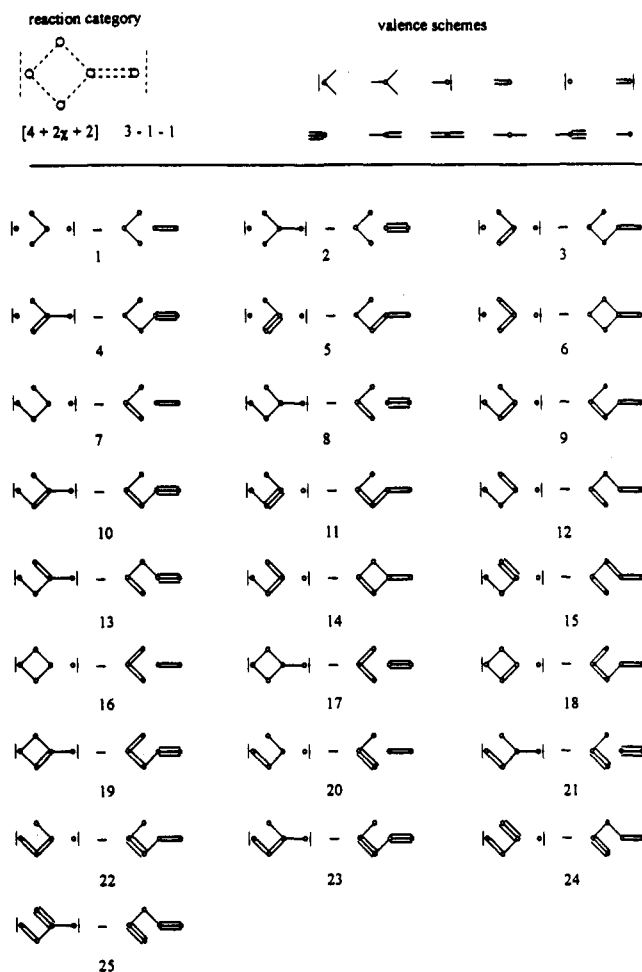
(Figure 13 continued)

COARCTATE TRANSITION STATES

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**Figure 14.** Complex basic reactions with a 4-ring and a lone pair terminator and a linear subsystem of $n = 1$ (3-1-1). For definition of the notation and boundary conditions see Figure 6.

We could prove that the transition states of thermochemical complex reactions also are stabilized by aromaticity.[16] The topology of the overlap of basis orbitals in the transition state of complex reactions corresponds to an intersecting ribbon, both ribbon planes being perpendicular where they intersect. The intersecting part corresponds to the coarctations (atoms at which two bonds are made and broken simultaneously), and the two loops form the terminators (Figure 4).

Since the orbital overlap is still cyclic and of Hückel topology, coarctate transition states profit from the same principle of stabilization as pericyclic transition states.

Thus the obvious relationships of complex reactions at the formal and descriptive level seem to correspond at the level of quantum theory with the Hückel approximation. However, before we accept the theory of coarctate transition states as a reaction principle in organic chemistry, we have to answer two major questions:

1. Is our simplistic qualitative model valid at a higher level of quantum theory, or are the conjugative effects small and probably obscured by much larger effects, e.g., electron correlation?

2. Is our topological model of coarctate transition states useful in practice?

To answer the first question we performed high level *ab initio* calculations on the energy hypersurface of a number of known complex reactions.[16] In most cases examined, an energetically low lying coarctate transition states was found.[21] Predictions concerning the stereochemistry in these cases agree with our topological model and the experimental facts. A

comparison of the molecular orbitals in the transition state of the cyclopropylcarbene fragmentation and the furfurylidene rearrangement obtained by high level *ab initio* calculations with our topological model show excellent agreement.[16] Our topological model thus holds on higher levels of quantum chemistry, and its application is justified from a theoretical point of view.

The second question is more difficult to answer. To be useful in practice, a novel theory should be able to give a correct prediction and explanation of a *large number* of experimental facts. A theory with a very limited scope may be correct but useless.[22] Our topological model is able to predict reactivity and stereochemistry of nearly a hundred rearrangement, addition, and fragmentation reactions from nine different reaction categories. The predictions are in agreement with experimental findings or with *ab initio* calculations (performed when experimental data were not available). In some cases for the first time a simple explanation for the reactivity of different substrates could be given.[16]

Thus the formal and purely descriptive relationships of complex reactions (listed in Figure 3.) have a sound theoretical basis. On the other hand the theory of coarctate transition states now can be reduced again to a descriptive level. Using the reverse process of our reaction classification (Figure 1), we should be able to predict novel complex reactions.

## PREDICTION OF COMPLEX REACTIONS

With the aid of our "aufbau" principle of complex reactions (Figure 3) and the computer program IGOR,[23] or our algorithm for generating spanning subgraphs,[24] we are able to generate the complete set of conceivable comples basic reactions under given boundary conditions. An exhaustive listing of complex basic reactions should be interesting from two points of view:

1. Comparison of the known reactions with those that are conceivable from a purely combinational basis should give further information about chemical characteristics affecting the plausibility or feasibility of complex reactions.

2. The unknown reactions can be predicted and possibly (depending on their plausibility) verified in the laboratory.

A similar attempt to generate the "symbolic equations of linear–cyclic bond redistribution topologies" was performed by Zefirov *et al.*[25] There are three reaction categories with six mobile electrons (breaking and making of three bonds) and eight reaction categories with eight mobile electrons (making and breaking of four bonds) (see Figure 5).

Analogous to the pericyclic reactions, we propose the following two notations for complex reactions: The first notation counting atoms has the general form $t - q - t'$, where $t$ and $t'$ give the number of atoms in both terminators and $q$ indicates the number of atoms in the coarctations.[26] The second definition counting electrons has the general form $[n + p\chi + n']$. $n$ and $n'$ indicate the number of mobile electrons in both terminators, and $p$ is the number of mobile electrons in the coarctations (which is usually two electrons per atom). The Greek symbol $\chi$ (chi) should depict that there are two orthogonal basis orbitals[27] located at these atoms (instead of one per atom in the terminators). The first definition is substrate related; the second gives information about the electronic structure of the transition state.

Each of these reaction categories comprises a number of basic reactions that form the second level in our hierarchical system of reaction generation (Figure 1). The boundary conditions for the generation of basic reactions are the electron redistribution pattern (R-matrix)[8] and the "valence schemes"
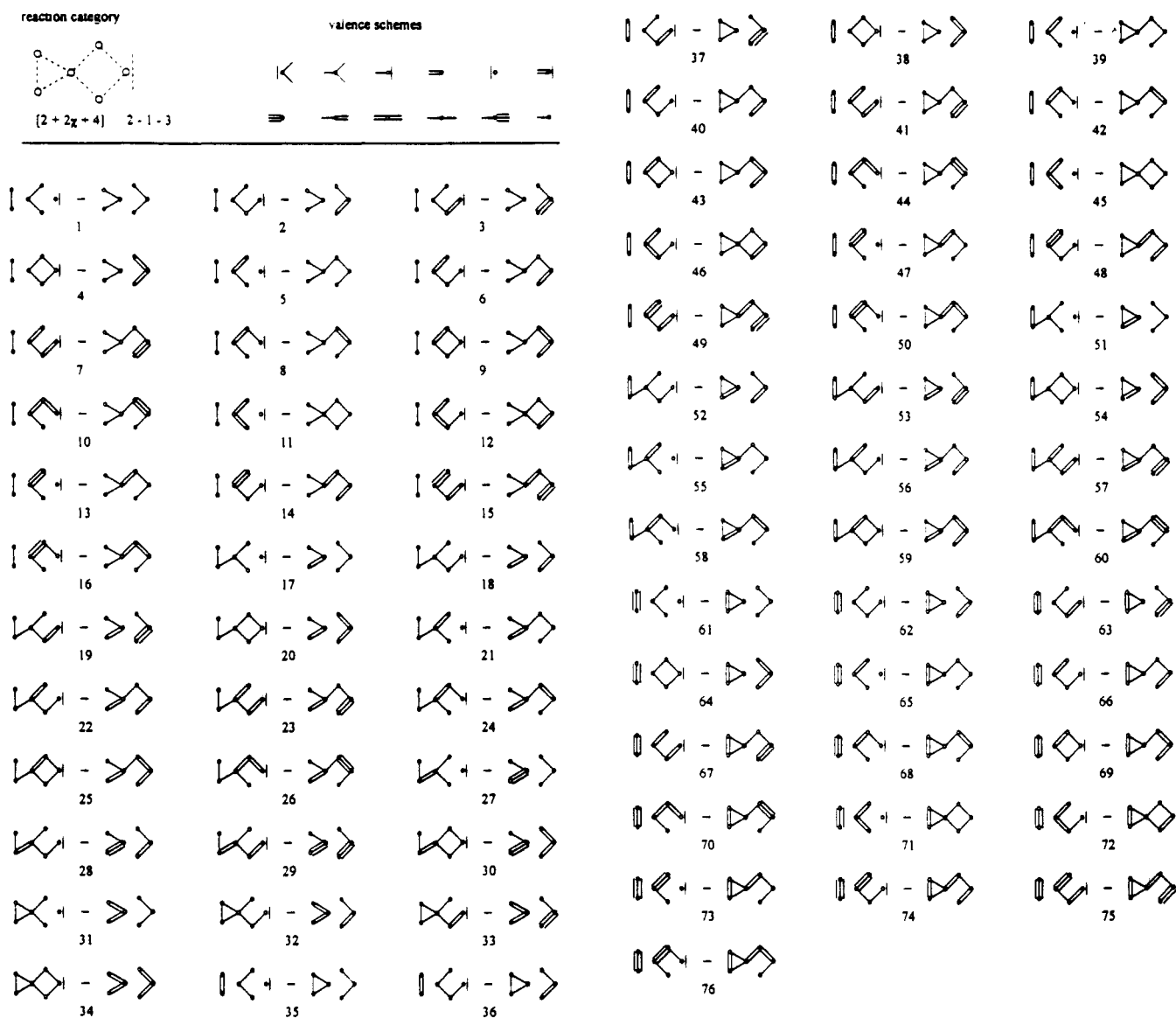
**Figure 15.** Complex basic reactions with a 4-ring and a 3-ring terminator and a linear subsystem of $n = 1$ (3-1-2). For definition of the notation and boundary conditions see Figure 6.

of the atoms in the reaction center. It is useful from a chemical viewpoint to allow the coordination patterns of carbon, including carbene structures as valence schemes for the variable element in the reaction centers, because this includes the chemistry of the most important heteroatoms as well.[28] As a second chemically meaningful condition, we excluded those reactions with allene or triple bonds in 3-, 4-, and 5-membered rings in educt or product. The combinatorial multitude of conceivable basic reactions of course increases with the number atoms and electrons involved and decreases with an increasing degree of symmetry. For instance the category with a linear subsystem of one atom and two lone pair terminators 1-1-1 contains three basic reactions, and the corresponding category with a 5-ring and a 3-ring terminator 5-1-3 comprises 216 basic reactions. In Figures 6–16 the complete set of conceivable basic reactions of the 11 complex reaction categories with 6 and 8 electrons and 3 to 7 atoms involved in the reaction are listed. Basic reactions with known examples in the literature are highlighted with a box.

The basic reactions are generated by combinatorial methods, and there is no inherent chemical information available during the generation process except the electron shift pattern (R-matrix), the allowed valence schemes (chemistry of the atoms involved), and ring strain constraints. Thus additional

chemical considerations such as empirical knowledge or quantum chemical calculations are needed to rate the plausibility of the generated reactions. By comparing the known reactions (that are plausible since they exist) with the unprecedented (that may be more or less plausible), we should obtain information about additional principles favoring a complex mechanism.

For a number of basic reactions within the three [2 + 2$\chi$ + 2] categories (1-1-1, 2-1-1, and 2-1-2), we found precedence in the literature.[16] Figures 17–19 give one prominent literature example for each of these basic reactions.

It is extremely difficult to prove experimentally that these reactions are concerted.[39] Reaction 1 in the 1-1-1 category most probably proceeds via an ylid[40] and reaction 10 in the 2-1-1 category via a diradical intermediate.[41] Concerning reaction 3 in the 1-1-1 category, reactions 2, 9, and 12 in the 2-1-1 category, and reaction 19 in the 2-1-2 category, all available evidence suggests a concerted mechanism.[42]

The eight 8-electron categories 1-2-1, 2-2-1, 2-2-2, 4-1-1, 4-1-2, 2-1-3, 3-1-1, 3-1-3 (or, in electron count notation, [2 + 4$\chi$ + 2], [4 + 2$\chi$ + 2], and [3 + 2$\chi$ + 3]) comprise a much larger number of basic reactions. The number of literature precedents (see Figure 20), however, is lower, compared to the 6-electron reactions.
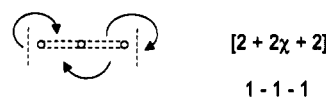
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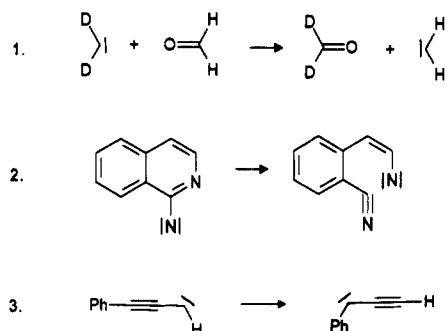


**Figure 16.**

**(Figure 16 continued)**
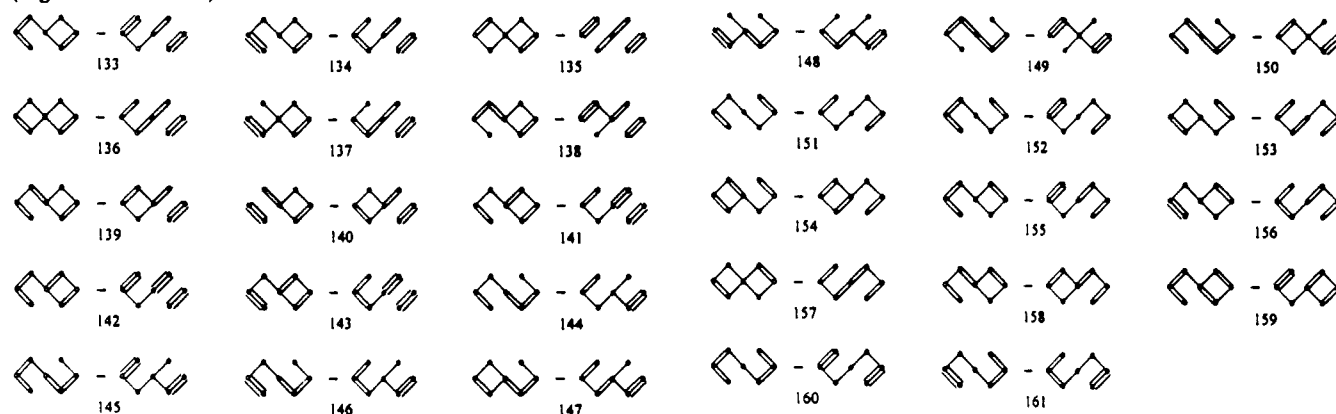


**Figure 16.** Complex basic reactions with two 4-ring terminators and a linear subsystem of $n = 1$ (3–1–3). For definition of the notation and boundary conditions see Figure 6.
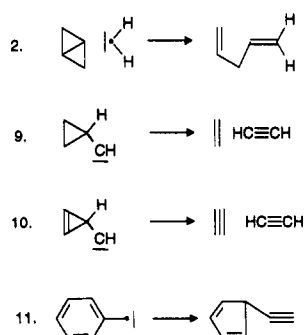
reaction category:



$[2 + 2\chi + 2]$

1 - 1 - 1

examples:



**Figure 17.** Literature examples for the complex category 1–1–1.[29,30,40]

reaction category:



$[2 + 2\chi + 2]$

2 - 1 - 1

examples:



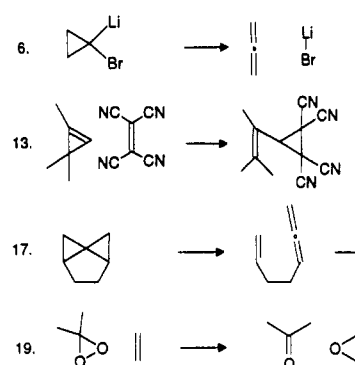**Figure 18.** Literature examples for the complex category 2–1–1.[31–34]

Scrutinizing the known reactions (e.g., Figures 17–20) in comparison with the conceivable ones (Figures 6–16), the following heuristic rules can be derived. (They are similar to those of pericyclic reactions.)

1. Complex reactions are the less probable the more bonds (and atoms) are involved in the transition state.

reaction category:



$[2 + 2\chi + 2]$

2 - 1 - 2
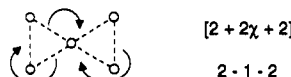
examples:



**Figure 19.** Literature examples for the complex category 2–1–2.[35–38]

2. Breaking and making single bonds, especially C–C bonds, are less favorable than shifting double or triple bonds.

3. Hydrogen is by far the easiest group to be transferred. Oxygen in epoxidation reactions is the only exception.

4. sp³-hybridized atoms do not react with each other.

5. All known reactions are thermodynamically highly favorable. They either start from extremely unstable educts, such as carbenes or nitrenes, or small and stable products are formed, such as nitrogen, carbon dioxide, or compounds with C≡N triple bonds.

6. No example of a complex reaction with a 4-ring terminator was found, even though such reactions are conceivable.

## CONCLUSION

Comprehensive reaction databases with efficient retrieval capabilities can be used to search for hidden reaction principles. The formal "aufbau principle" of complex reactions was found in such a way (Figure 3). Searching for physical principles favoring these reactions led to the development of the theory of coarcate transition states. The following flow chart comprises the three stages in chronological order.
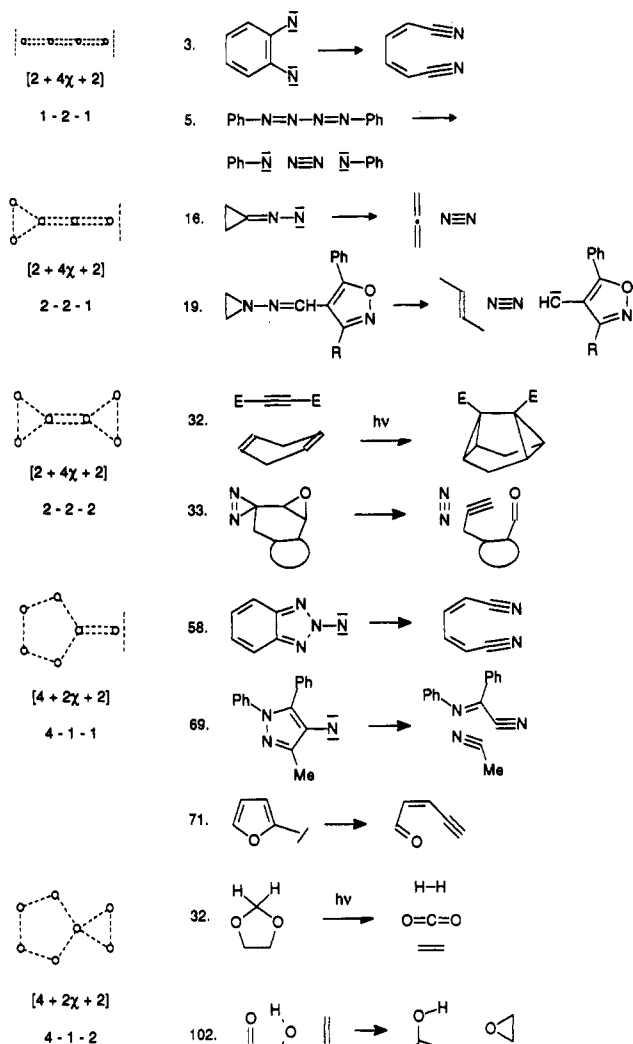
**Figure 20.** Literature examples for the complex categories 1-2-1, 2-2-1, 2-2-2, 4-1-1, and 4-1-2.[43-53]
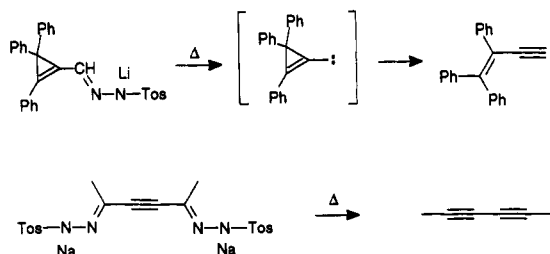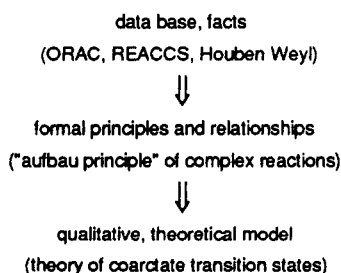


**Figure 21.** Complex reactions that were theoretically predicted and subsequently verified experimentally.



The theory of coarctate transition states predicts the mechanism and stereochemistry of the complex reactions. The formal aufbau principle of complex reactions can be used to predict unprecedented reactions of this class (Figures 6–16). Two of these, reaction 12 of the 2–1–1 category (Figure 7)

and reaction 6 of the 1–2–1 category (Figure 9), have been verified in our laboratory (Figure 21).

We are sure that a number of other complex reactions remain to be discovered.

## ACKNOWLEDGMENT

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(20) There are pericyclic reactions with Moebius type transition states. They are thermochemically allowed with 4n electrons delocalized in the transition state.

(21) In some cases even semiempirical calculations that are known to notoriously favor strongly asymmetrical or diradical mechanisms predict concerted or even synchronous transition states.

(22) Our topological model is only applicable on concerted reactions. If a large number of complex reactions were nonconcerted, this would considerably limit our theory.

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