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Building Bridges Between Inorganic and Organic Chemistry (Nobel Lecture)**

By Roald Hoffmann*

Robert B. Woodward, a supreme patterner of chaos, was one of my teachers. I dedicate this lecture to him, for it is our collaboration on orbital symmetry conservation, the electronic factors which govern the course of chemical reactions, which is recognized by half of the 1981 Nobel Prize in Chemistry. From Woodward I learned much: the significance of the experimental stimulus to theory, the craft of constructing explanations, and the importance of aesthetics in science. I will try to show you how these characteristics of chemical theory may be applied to the construction of conceptual bridges between inorganic and organic chemistry.

Fragments

Chains, rings, substituents—those are the building blocks of the marvelous edifice of modern organic chemistry. Any hydrocarbon may be constructed on paper from methyl groups (CH_3), methylenes (CH_2), methynes (CH), and carbon atoms (C). By substitution and the introduction of heteroatoms all of the skeletons and functional groupings imaginable, from ethane to tetrodotoxin, may be obtained.

The last thirty years have witnessed a remarkable renaissance of inorganic chemistry, and the particular flowering of the field of transition-metal organometallic chemistry. The complexes 1—9 are a selection of some of the simpler creations of the laboratory in this rich and ever-growing field. ,

Structures 1—3 illustrate at a glance one remarkable feature of transition-metal fragments. Here are three tricarbonyliron complexes of organic moieties—cyclobutadiene, trimethylenemethane, and 1-hydroxy-1,3-butadiene—which on their own would have little kinetic or thermodynamic stability. Yet complexed to $Fe(CO)_3$ these molecules are relatively stable: they exist in a bottle. The inorganic fragment is not merely a weakly attached innocent bystander: it transforms essentially and strongly the bonding relationships in the molecule.

Structures 4—6 contain the ubiquitous cyclopentadienyl ligand (Cp), two of them in the archetypical ferrocene, one in $CpMn(CO)_3$, two bent back in $Cp_2Ti(CO)_2$. Structures 7—9 introduce us to the simplest representatives of the

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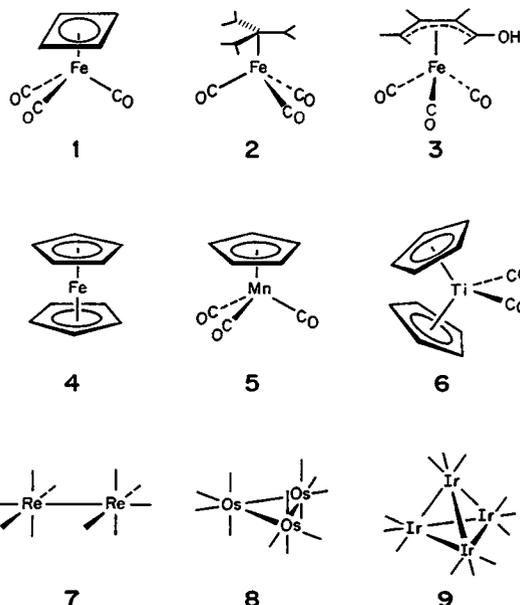
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burgeoning class of clusters—assemblages of two or more metal atoms embellished with external ligands.

If we seek order, unity, a way of thinking about these complexes, it is not difficult to perceive that the molecules contain as building blocks transition metal-ligand fragments, ML_n, such as $M(CO)_5$, $M(CO)_4$, $M(CO)_3$, or MCp. It must be said immediately that there is nothing special about the carbonyl ligand. It is merely a representative and common component of organometallic complexes. Phosphanes, olefins, alkyls will do as well.

To reconstruct the complexes 1—9, we need to know the electronic structure of the fragments. For the simple qualitative picture of the bonding in these molecules that we seek, we do not need to know every last detail of the electronic structure of each molecule. It will suffice that we know the frontier orbitals of the fragments—the higher occupied and the lower unoccupied levels—in other words the valence active orbitals of each fragment. It is *Kenichi Fukui* who taught us the importance of the frontier orbitals. We shall soon see that it is the resemblance of the frontier orbitals of inorganic and organic moieties that will provide the bridge that we seek between the subfields of our science.

Over the last eight years my coworkers and I have built up a library of the orbitals of ML_n fragments[1-3]. We have done so using entirely qualitative, approximate molecular orbital calculations of the extended Hückel type (a procedure for its time, developed with another of my teachers, *William N. Lipscomb*) and symmetry arguments (the value of which I first learned from still another of my teachers, *Martin P. Gouterman*). Molecular orbital theory, *Robert S. Mulliken*'s great contribution to chemistry, is fundamental to our approach, be it in the construction of the very orbitals of the fragments, their changes on molecular deformation, or the interaction of several such fragments to restore the composite molecule. Yet when I seek the simplest of all possible ways to tell you of the orbitals of these fragments, I am led back to the valence bond picture introduced into chemistry by *Linus Pauling*[4].

Let us go back to the building blocks. The general fragments ML_n, 10—13, may be viewed in many ways. One convenient approach is to consider them as pieces of an octahedron.

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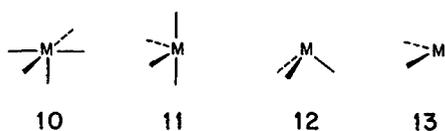
This is quite analogous to perceiving CH_3, CH_2, and CH in a tetrahedron. If not a unique viewpoint, it is a useful one. Given that we have an octahedron, or pieces thereof, let us prepare the metal atom for octahedral bonding, and then introduce the appropriate number of ligands.

The valence orbitals of the transition metals are nd, $(n+1)s$ and $(n+1)p$, with $n = 3, 4, 5$. To prepare the metal atom for bonding we must form six equivalent octahedral hybrids. This is accomplished (cf. 14), by using all of the s and p functions and two of the d's. Three d functions, d_{xz}, d_{xy}, and d_{yz}, are left unhybridized. They may be described

as the t_{2g} set of the crystal field, ligand field, or molecular orbital theories of an octahedral complex[5].
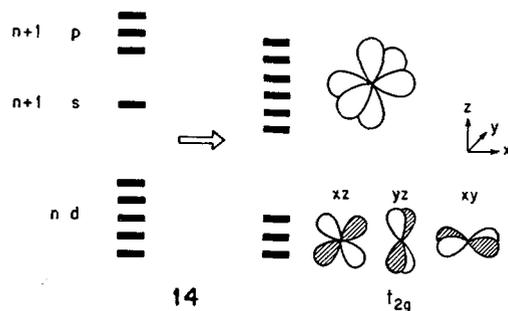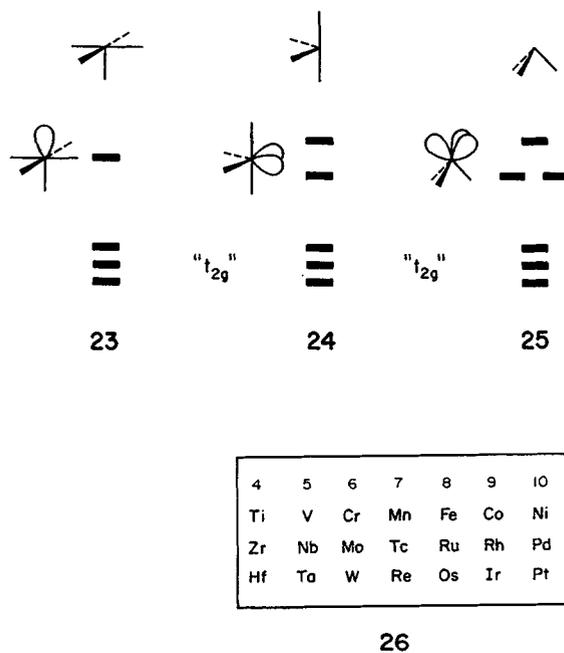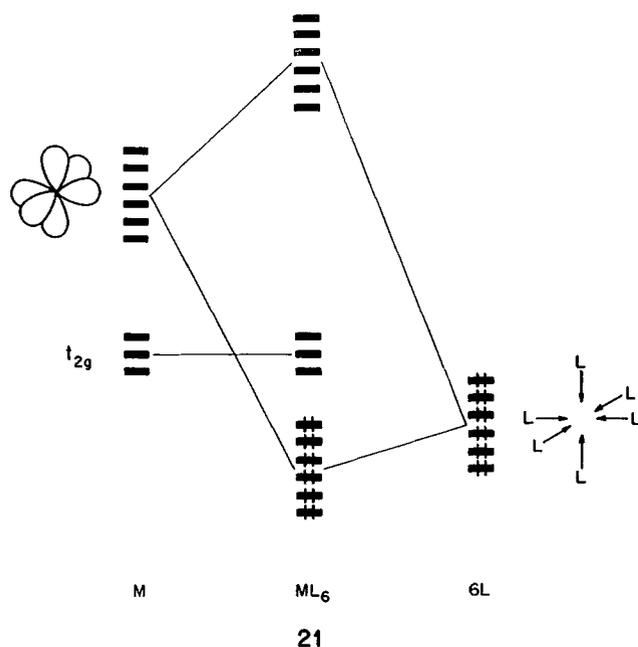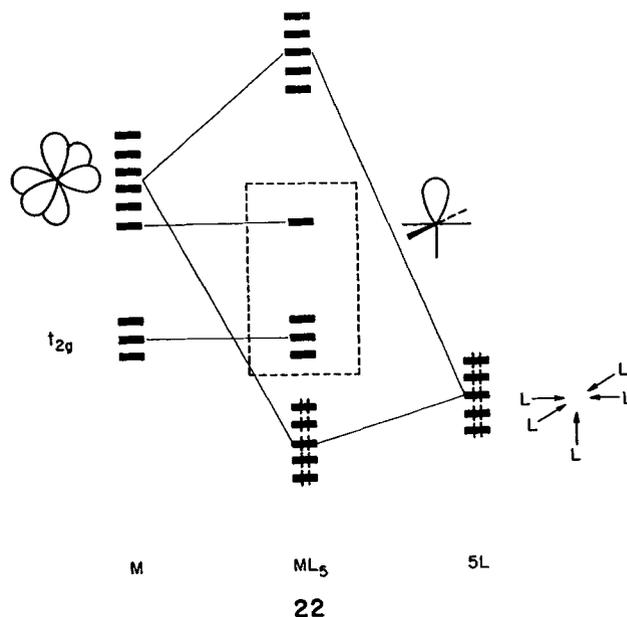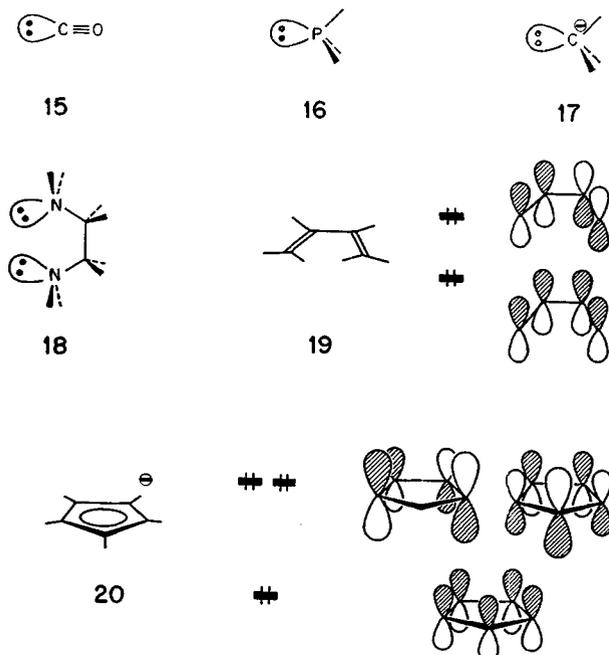

To form an octahedral complex we would introduce six ligands to make use of the six octahedral hybrids. Perhaps it is appropriate to digress here and make clear our ligand convention, which is to consider the ligand always as an even-electron Lewis base. While acceptor character or Lewis acidity is a desirable feature in a ligand, Lewis basicity or donation is essential. We see the basicity in the form of the lone pairs of CO, PH_3, and CH_3^- (15—17), in bidentate four-electron ligands, be they ethylenediamine (18) or butadiene (19), or in the electronically tridentate $C_5H_5^-$ (Cp$^-$, 20), the equivalent of three two-electron bases[6].

Let six two-electron ligands approach the metal atom prepared for octahedral bonding (cf. 21). Sizable σ overlaps lead to formation of strongly metal-ligand σ bonding combinations, and their strongly metal-ligand σ^* antibonding counterparts. The six electron pairs of the ligands enter the six bonding combinations. Any electrons the metal contributes enter the t_{2g} orbital left behind. Indeed, for $Cr(CO)_6$ with its 6 metal electrons we attain a nice closed shell configuration, a situation we have learned to associate with relative kinetic and thermodynamic stability in organic chemistry.

What if we have not six ligands coming in, but only five? This situation is depicted in 22. Five hybrids interact strongly, are removed from the frontier orbital region, just as all six were in 21. One hybrid, the one pointing toward where no ligand is, remains roughly untouched, relatively low-lying in energy. The frontier orbitals, enclosed in a dashed box in 22, now contain the t_{2g} set plus one hybrid.

What if we have four ligands (ML_4) or three (ML_3)? Much the same thing happens. In ML_4 two hybrids are left behind, in ML_3 three. We have thus reached the simplest of all possible pictures of the electronic structure of the ML_n fragments with $n = 5, 4, 3$, namely that given in 23—25. The ML_n fragment's frontier orbitals consist of the descendants of an octahedral t_{2g} set at relatively low energy, and above them $6 - n$ (one for $n = 5$, two for $n = 4$, three for $n = 3$) hybrids pointing toward the missing octahedral vertices.

What remains is to decide how many electrons to place into these frontier orbitals, and here the ever-useful Mendeleev Table, modified in 26 for electron counting purposes, tells us that Fe in oxidation state zero will have eight electrons in $Fe(CO)_4$ or $Fe(CO)_3$, and so will Co^I or Ni^{II}.

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M ML₅ 5L

M ML₆ 6L

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4	5	6	7	8	9	10
Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

26

The reader had best beware. The account given here is simplified, as much as I dare simplify it. In that process, perforce, is lost the beautiful detail and complexity that makes $Fe(CO)_3$ different from $FeCl_3^{3-}$. There is a time for detail and there is a time for generality. The reader of my papers will know that my coworkers and I do not stint on detail, whether it is in explication or in perusal of the literature. But the time now, here, is for building conceptual frameworks and so similarity and unity take temporary precedence over difference and diversity.

Recall that the reason for building up the frontier orbitals of inorganic fragments is that we wish to use these orbitals in the construction of organometallic and inorganic complexes. We are now ready for that task. For instance, if

we want tricarbonyl(trimethylenemethane)iron we construct a molecular orbital interaction diagram (cf. 27). On one side are the orbitals of $Fe(CO)_3$ just discussed, on the other side the older, better known frontier orbitals of $C(CH_2)_3$. We interact the two, using the full armament of group theory and perturbation theory[7] to follow what happens.

I will not trace this argument any further, for the primary purpose of this lecture is not the description of the electronic structure of organometallic complexes. My coworkers and I have done this comprehensively elsewhere[1,8]. Instead, I wish to describe a bridge between organic and inorganic chemistry that becomes possible the moment we gain knowledge of the orbitals of the ML_n fragments.
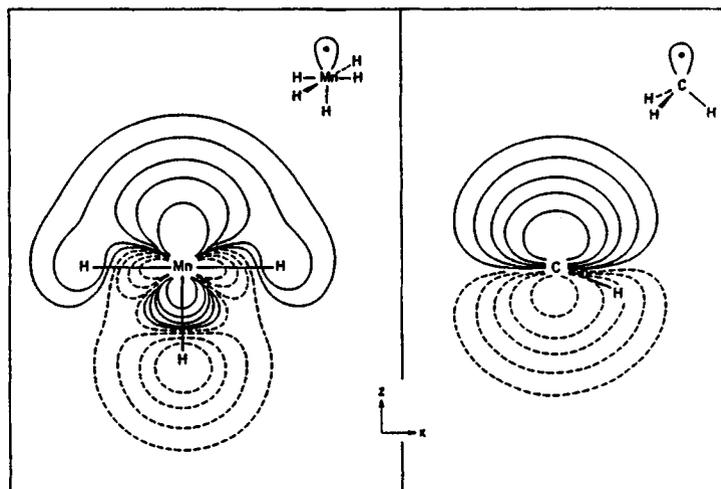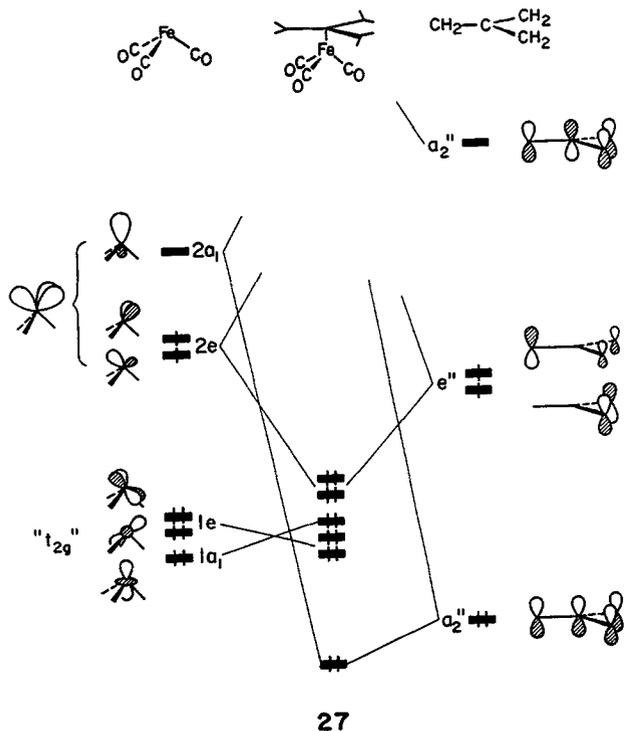
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Fig. 1. Contour diagram of the isolobal a_1 orbitals of MnH_5^{5-} (left) and CH_3 (right), as computed by the extended Hückel method. The contours of Ψ, plotted in a plane passing through Mn and three H's (left) and C and one H (right), are ± 0.2, ± 0.1, ± 0.055, ± 0.025, ± 0.01.

The Isolobal Analogy

Consider the d^7-fragment, $Mn(CO)_5$ (or $Co(CN)_5^{3-}$). Above the three lone pairs in the t_{2g} set this doublet molecule has a single electron in a hybrid pointing away from the ML_5. The similarity to CH_3, the methyl radical, is obvious (cf. **28**).

d^7-ML_5 CH_3

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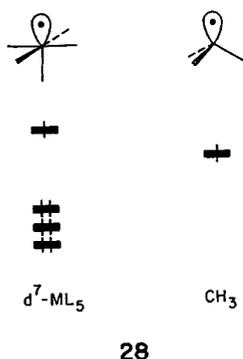
The representation **28** is, of course, schematic. Figure 1 shows the a_1 orbitals of MnH_5^{5-} and CH_3, so as to provide a more realistic comparison.

If d^7-ML_5 is like CH_3 then they should both behave similarly. Let us think about what a methyl radical does. It dimerizes to ethane and starts radical chains. $Mn(CO)_5$ or $Co(CN)_5^{3-}$ do similar things. They dimerize to $Mn_2(CO)_{10}$ or $Co_2(CN)_{10}^{6-}$ (cf. **29**), and each has a rich radical-type chemistry[9]. One can even codimerize the organic and inorganic fragments to give $(CO)_5MnCH_3$. That may not be the preferred way to make this quite normal organometallic alkyl complex in the laboratory, but the construction on paper is quite permissible.

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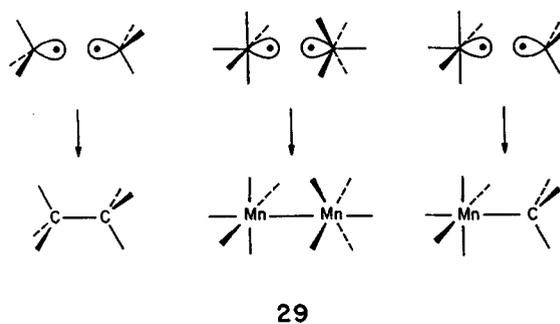
CH_3 and d^7-ML_5 resemble each other. Another way we can see that resemblance, traceable to their singly occupied a_1 orbitals, is to compare the overlap of both orbitals with a probe ligand, let us say a hydrogen atom. This is done in Figure 2. Note the remarkable parallelism of the two overlaps. The H—CH_3 overlap is everywhere smaller than the H—MnL_5 overlap, but the dependence of both on the distance is quite similar.
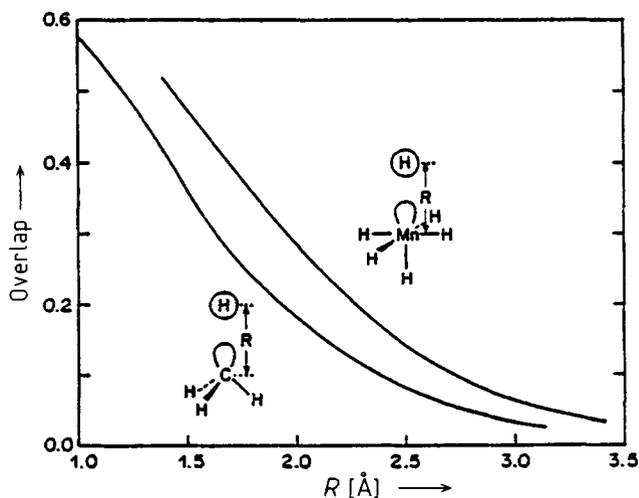

Fig. 2. Overlap integrals between the a_1 frontier orbital of MnH_5^{5-} and CH_3 and a H 1s orbital at a distance R from the Mn or c atom.

A word is needed to describe the resemblance of the two fragments, CH_3 and d^7-ML_5. They are certainly not isostructural, nor are they isoelectronic. However, both possess a frontier orbital which looks approximately the same for the two fragments. We will call two fragments *isolobal* if the number, symmetry properties, approximate energy and shape of the frontier orbitals and the number of electrons in them are similar—not identical, but similar[10]. Thus CH_3 is isolobal with $Mn(CO)_5$. We will introduce a symbol for the isolobal relationship: a "two-headed" arrow with half an orbital below. Thus,

$$CH_3 \xleftrightarrow{} Mn(CO)_5$$

Let's extend the definition a little:

1) If $Mn(CO)_5$ is isolobal with CH_3, so are $Tc(CO)_5$ and $Re(CO)_5$, as well as $Fe(CO)_5^+$. The shape of the a_1 hybrid will vary slightly with different principal quantum numbers, but essentially it is only the d-electron count that matters.
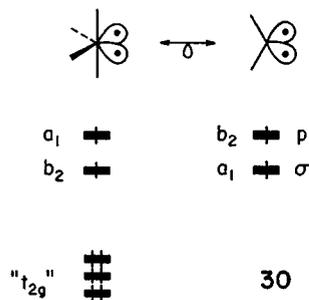
2) If $Mn(CO)_5$ is isolobal with CH_3, then $Cr(CO)_5$, $Mo(CO)_5$ or $W(CO)_5$ are isolobal with CH_3^+, and $Fe(CO)_5$ (square pyramidal!) is isolobal with CH_3^-.

3) If $Mn(CO)_5$ is isolobal with CH_3, so are $Mn(PR_3)_5$ or $MnCl_5^{5-}$ or any d^7-ML_5 species. And so is $CpFe(CO)_2$, a ubiquitous fragment. The procedure here is to write $CpFe(CO)_2$ as $Cp^-Fe^+(CO)_2$, and to replace the Cp^- by its isolobal equivalent of three carbonyls, reaching $Fe(CO)_5^+$, which is isoelectronic with $Mn(CO)_5$.

Let us go on to the ML_4 fragment. It is clear that a d^8-ML_4 species, e.g. $Fe(CO)_4$, is isolobal with a methylene or (carbene, CH_2).

$$Fe(CO)_4 \xleftrightarrow{} CH_2$$
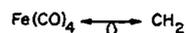
As **30** reveals, both fragments have two electrons in delocalized a_1 and b_2 orbitals which are the equivalent of two localized hybrids. There are explicable differences in the ordering of the two combinations[11]. The different order-

ing has, however, no grave consequences—recall that we are not so much interested in the fragments themselves as in their bonding capabilities. The moment we interact $Fe(CO)_4$ or CH_2 with another ligand, the initial ordering of a_1 and b_2 becomes relatively unimportant since both are typically strongly involved in the bonding.

Dimerize, conceptually, the isolobal fragments $Fe(CO)_4$ and CH_2. One gets the known ethylene, **31**, the tetracarbonyliron carbene complex, **32**, derivatives of which are known[12], and $Fe_2(CO)_8$, **33**. The last molecule is unstable,

and so far has been observed only in a matrix[13]. We come here to a cautionary note on the isolobal analogy. The isolobal analogy carries one between organic and inorganic molecules of similar electronic structure. But there is no guarantee that the result of such an isolobal mapping ($31 \xleftrightarrow{} 33$) leads one to a molecule of great kinetic stability. It might, or it might not.
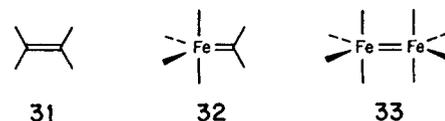
Lest the reader be concerned about this limitation of the analogy let me remind him or her of what happens as one proceeds from ethylene down Group IV. Si, Ge, Sn, Pb substitution leads to olefin analogues, but they are kinetically and thermodynamically so unstable that it has taken great effort to provide evidence for their fleeting existence.

$Fe_2(CO)_8$, **33**, has π and π^* levels similar to those of ethylene. But the low energy of its π^* makes this molecule coordinatively unsaturated. It can, for instance, add another CO to reach the stable enneacarbonyldiiron. More interesting, as we will soon see, is the strategy of stabilizing the unstable $Fe_2(CO)_8$ by making a complex of it, just as is routinely done for unstable organic molecules (**1**—**3**).

$Fe(CO)_4$, $Ru(CO)_4$, or $Os(CO)_4$ may be trimerized in various combinations with methylene, as in **34**—**37**. These cyclopropanes, ranging from all-organic to all-inorganic, are known. But note that when I show the "all-metallic" three-membered ring I have to go to Os. It is well known that the
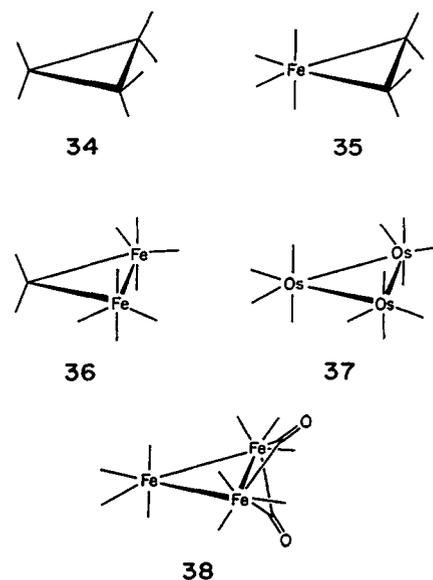

ground state structure of $Fe_3(CO)_{12}$ is **38**, with two bridging carbonyls[14]. Another limitation of the isolobal analogy is exposed here: the unbridged Fe structure analogous to **37** is certainly not much higher in energy than **38**, but nevertheless the lowest energy structure is bridged. Movement of some ligands (e.g. carbonyls, but not phosphanes) in and out of bridging sites is an experimental reality, a facile process, for transition metal complexes, especially of

the first transition series. Such easy terminal to bridging interconversions are rare in organic chemistry, with the exception of carbonium ions. Bridging in inorganic structures, when it does occur, does not cause a major perturbation in the nature of the frontier orbitals.

Consider next the d^9-ML_3 fragment, e.g. $Co(CO)_3$. This is isolobal with a methylidyne (or carbyne) CH, as shown in 39. Once again there are differences, though of no great


$$d^9\text{-}ML_3 \longleftrightarrow CR$$

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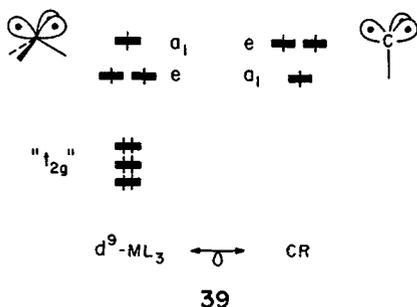
significance, in the a_1 versus e energy ordering between the two fragments. Their similarity is revealed most strikingly by the existence of the entire series of mixed organic and inorganic tetrahedranes, 40—44. To be sure, 41 can be

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43   **44**
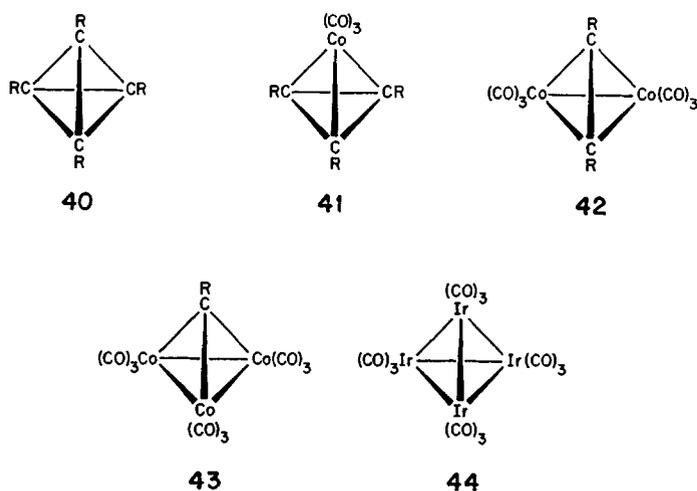
called a cyclopropenyl complex and 42 a binuclear acetylene complex, but I believe something is gained in seeing the entire series as a progression of isolobal substitution.

The fundamentals of the isolobal analogy have now been exposed. Just how far-reaching the relationships written here

$$d^7 \text{ - } ML_5 \longleftrightarrow CH_3$$
$$d^8 \text{ - } ML_4 \longleftrightarrow CH_2$$
$$d^9 \text{ - } ML_3 \longleftrightarrow CH$$
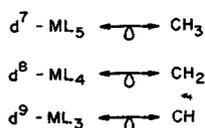
are, will become clearer shortly. For the moment it is important to note that the isolobal analogy is not solely the creation of my research group. In his fruitful explorations of the reactivity of d^8-square planar complexes Halpern often made use of the similarity of such an ML_4 entity to a carbene[9a]. He did the same for d^7-ML_5 and organic free radicals[9a]. Dahl, in a beautiful series of structural studies of transition metal clusters, saw clearly the relationship of

the orbitals of an ML_n fragment to a chalcogen or pnicogen atom, which of course are easily related to CR[15, 16]. And most importantly, Wade[17] and Mingos[18] independently developed a comprehensive and elegant picture of the electronic structure of transition- metal clusters by relating them to the polyhedral boron hydrides (which Lipscomb and I studied—the circle closes!). It is a trivial step from BH to CH^+. All of these workers saw the essence of the isolobal analogy.

Structural Implications of the Isolobal Analogy

How quickly the hands and mind of man provide us with the problem of choice! The molecules I would need to illustrate the isolobal analogy at work did not exist thirty years ago. Now they are around us, in superabundance. I have made a selection, based in part on the ease with which these lovely molecules illustrate the principles, in part on the ambiguous and ephemeral basis of recent (1981) appearance in the literature.

One obvious use of the isolobal analogy is in the structural sense. The analogy allows us to see the simple essence of seemingly complex structures. I should like to show you some examples centering on the ML_4 fragment.

Last year there appeared a structure of the cluster $HRe_3(CO)_{12}Sn(CH_3)_2$ from the work of Kaesz et al.[19]. The unique hydrogen was not located; presumably it bridges one Re—Re bond. If we remove the hydrogen as a proton, a convention we have found useful[8n], we reach $Re_3(CO)_{12}Sn(CH_3)_2^-$, **45**. Not a usual molecule, but the isolobal chain

$$Re(CO)_4^{\ominus} \longleftrightarrow Fe(CO)_4 \longleftrightarrow CR_2 \longleftrightarrow SnR_2$$
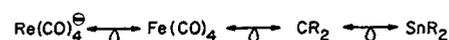
allows us immediately to see the very close similarity of this structure to the previously known **46**[20] and **47**[21].


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46   **47**
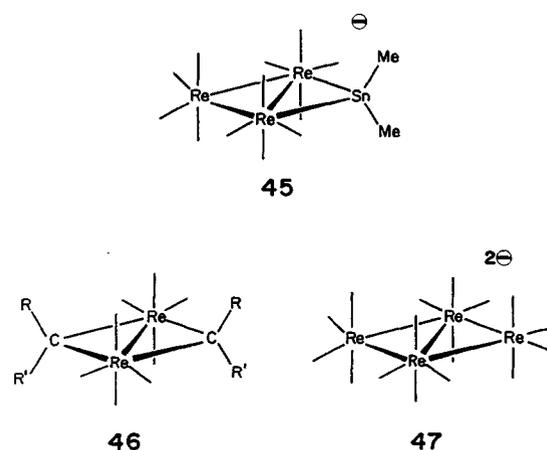
It is interesting to speculate when we might see the missing members of the series on the organic side, $(CO)_4Re(CH_2)_3^+$ and $(CH_2)_4^{2+}$.

Two ML_4 fragments united yield the aforementioned unstable $Fe_2(CO)_8$ system, **48**. It was hinted before that one should think of stabilizing this species by complexation. A pretty example is at hand, **49**[22]. Two $Fe_2(CO)_8$ units are complexed by a tin atom! Note the pinning back of the

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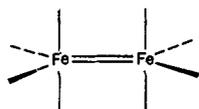
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equatorial carbonyls, analogous to the bending back of hydrogens in a transition metal complexed olefin. Alternatively, and interestingly, this can be considered as a spiropentane.
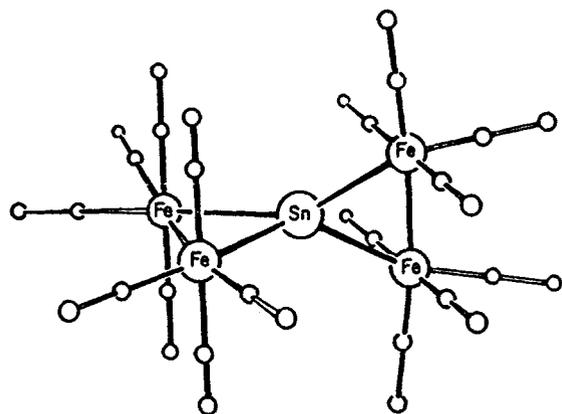
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Earlier last year, *Lewis, Johnson et al.* published a synthesis and structure of $Os_5(CO)_{19}$[23]. The structure, **50**, appears terribly complicated until one realizes it is really **51**, a typical trigonal bipyramidal $Os(CO)_5$ derivative, with two of the equatorial carbonyls substituted by olefins, or rather by the $Os_2(CO)_8$ olefin analogues. The "olefin" orientation is just as it should be[1k, o].
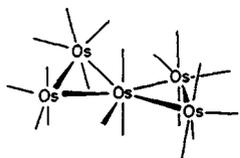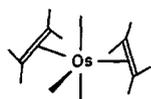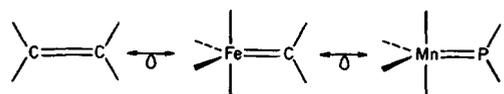
50 **51**

Another system isolobal to ethylene and $Fe_2(CO)_8$ is the "mixed dimer" $(CO)_4FeCH_2$. Upon formally shifting an electron from the metal to the carbon, a bit of alchemy, one gets to a phosphido complex **52**:

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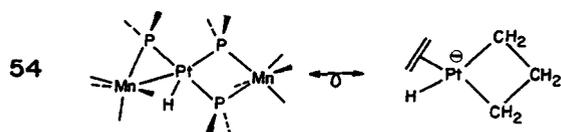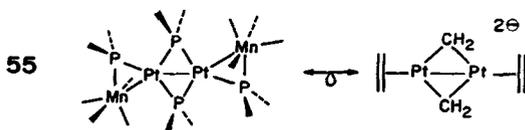The reason for this transformation sequence is that complexes of $Mn(CO)_4PR_2$ have been made. *Braunstein, Grandjean et al.* have reported a remarkable set of structures, among them the three shown with their isolobal analogues in **53**—**55**[24]. In each structure we can see the obvious ethylene-like $(CO)_4MnPR_2$ entity.
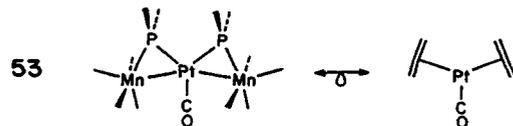
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At the same time that these structures were published there appeared a structure of **56**, synthesized in an entirely different way by *Haines, Steen, and English*[25]. Unbridge the two semibridged carbonyls, do a bit more electronic alchemy relating Mn—Pt to Fe—Rh, and the relationship to **55** becomes crystal clear.
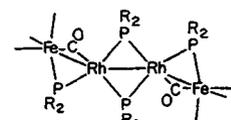
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Realizing that $Fe(CO)_4$ ⟶ $CpFe(CO)^-$ ⟶ CpRhCO, we see immediately that **57** is yet another $Fe_2(CO)_8$ analogue.

57

Thus, the methylene complex, **58**, synthesized by *Herrmann* is a two-thirds inorganic cyclopropane[26].
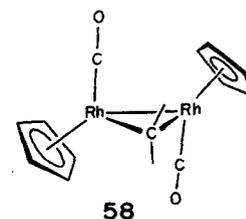
58

There are a few more fascinating $Cp_2Rh_2(CO)_2$ structures to be shown, but first we need to examine one extension of the isolobal concept.

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The Relationship between ML_n and ML_{n-2} Fragments

Earlier in the discussion we looked at two octahedral fragments, ML_5 and ML_4, in which a pair of axial ligands remained. If we remove these ligands (cf. **59**) an interesting extension of the isolobal analogy emerges.

59————————————————————————

If the z-axis is oriented along the direction of the vanishing ligands, then it is clear that the main result of this perturbation is that the metal d_{z^2} atomic orbital is lower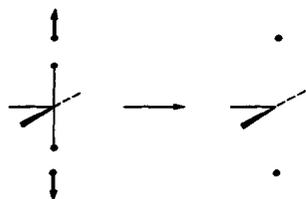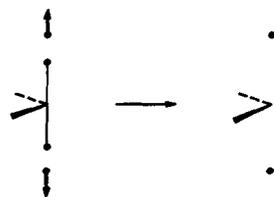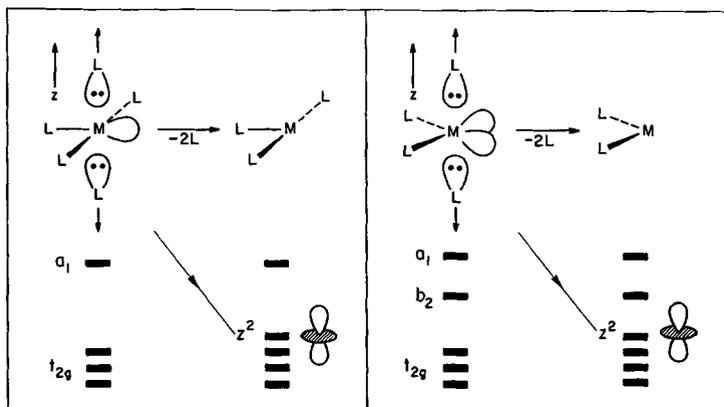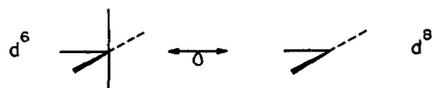ed in energy. It returns from the metal-ligand σ-antibonding manifold to become a non-bonding orbital (cf. **60**, **61**)[1o,3c].

60   **61**

The high-lying orbitals (one in ML_5, two in ML_4) remain[27]. The obvious relationships that emerge then are those between a d^n-ML_5 and a $d^{n+2}(C_{2v})$- or T-shaped ML_3; and between $d^n(C_{2v})$-ML_4 and d^{n+2}-ML_2. Or to put it explicitly in terms of the most common fragments, **62**.

62

So we now add some further diversity to the non-isomorphic mapping which is the isolobal relationship:

$$CH_3^\oplus \xrightarrow{\;0\;} Cr(CO)_5 \xrightarrow{\;0\;} PtCl_3^\ominus$$

$$CH_2 \xrightarrow{\;0\;} Fe(CO)_4 \xrightarrow{\;0\;} Ni(PR_3)_2$$
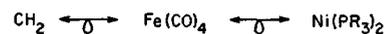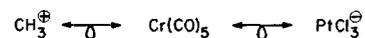
An obvious application is to olefin complexes; the similarity of $(CO)_4Fe(C_2H_4)$ to $(PR_3)_2Ni(C_2H_4)$, and that of $(CO)_5Cr(C_2H_4)$ to Zeise's salt emerges directly[1o,x].

Returning to the $[CpRh(CO)]_2$ analogue of ethylene, we can now think about some other structures. First, it turns out that moving the carbonyl groups into the bridge does little to change the ethylene-like nature of the dirhodium fragment, **63**[1u].

63
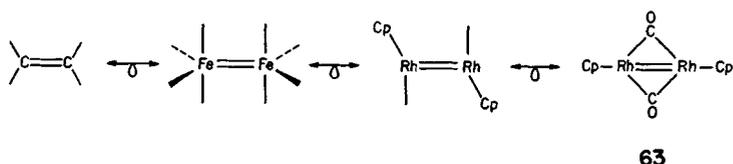
Since $CH_2 \xrightarrow{\;0\;} Fe(CO)_4 \xrightarrow{\;0\;} Pt(CO)_2 \xrightarrow{\;0\;} Rh(CO)_2^-$, it is possible to see in the compound of *Bergman et al.*, **64**[28], an analogue of *Herrmann's* compound **58**.
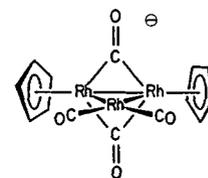
64

Essentially the same fragment, **63**, reappears in the fantastic $[CpRh(CO)]_4Pt$ structure, **65**, of *Stone et al.*[29] $(Cp = \eta^5$-$C_5Me_5)$ and can be related to the $(RC\equiv CR)_2Pt$ structure, **66**, earlier synthesized by the same group[30].
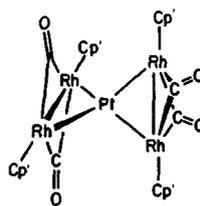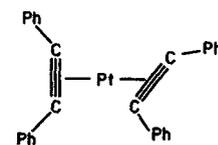
65   **66**

Into the t_{2g} Shell

It turns out that not only is d^9-$Co(CO)_3$ isolobal with CH, but so is d^5-$CpW(CO)_2$. To see how this comes about let us first relate the Cp complex to a simple ML_n.

$$CpW(CO)_2 \xrightarrow{\;0\;} CpCr(CO)_2 \xrightarrow{\;0\;} Cr(CO)_5^\oplus$$

As was shown earlier, $Cr(CO)_5^+$ is isolobal with CH_3^{2+}. That is not a very productive analogy. So let us examine

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$Cr(CO)_5^+$ in more detail. The electronic structure of an ML_5 fragment was given earlier. It is repeated in more detail on the left of **67**. The ML_5–CH_3 analogy concentrates on the hybrid of $\sigma(a_1)$ symmetry. But the t_{2g} set, even if it is less "directional" than the hybrids, has extent in space and well-defined symmetry properties. In particular, two of the t_{2g} orbitals are of π pseudosymmetry, one of δ-type. If, as we are forced to by the electron deficiency, we extend our view at least to the π component of the t_{2g} set (dotted lines at right in **67**), we see a clear relationship between d^5-ML_5 and CH, just as there is between d^7-ML_5 and CH_3.

67
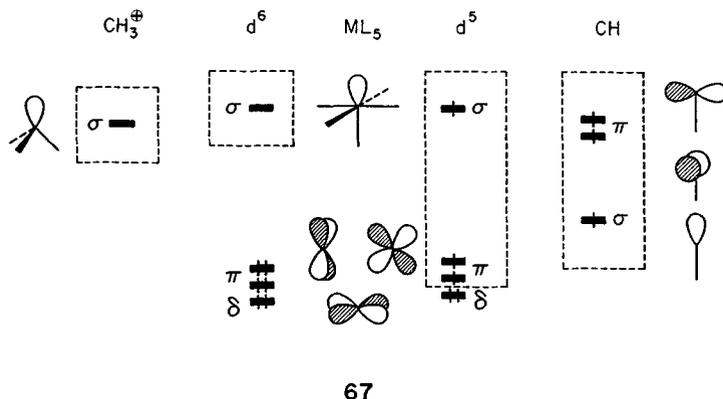
A little further reflection will show that by using one half of the π set of the t_{2g} we can get a relationship between d^6-ML_5 and CH_2.

To summarize:

$$d^7\text{-}ML_5 \longleftrightarrow CH_3$$
$$d^6\text{-}ML_5 \longleftrightarrow CH_2$$
$$d^5\text{-}ML_5 \longleftrightarrow CH$$

or to put it another way

$$d^6\text{-}ML_5 \longleftrightarrow CH_3^\oplus$$
$$d^6\text{-}ML_5 \longleftrightarrow CH_2$$
$$d^6\text{-}ML_5 \longleftrightarrow CH^\ominus$$

This gives us another way of looking at things, a *deprotonation analogy*. In what way is CH_3^+ like CH_2 or CH^-? Let us draw out their orbitals schematically, including CH_4 for good measure, in **68**.

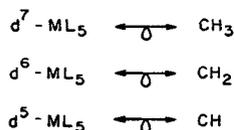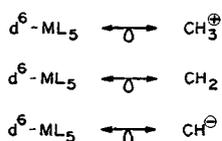Taking away a proton from each molecular fragment does not change its ability to function as a donor (though its quality or donor strength will be *very* different). Each fragment, from CH_4 to C^{4-}, is in principle an eight-electron donor.

To recapitulate: the isolobal analogy is not a one-to-one mapping. A d^6-ML_5 fragment is isolobal with CH_3^+, CH_2, and CH^-. This is why the d^5-$CpW(CO)_2$ is isolobal with CH.

The isolobal analogy for low d-electron count metals has been exploited most notably in the work of *Stone*'s group at Bristol. Just four compounds from their many beautiful examples are shown in **69**—**72**[31].

68
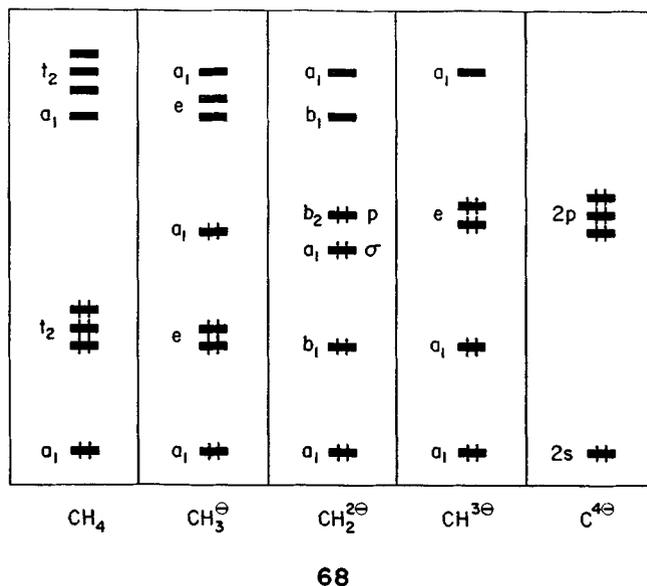
Since d^6-$Cr(CO)_5 \longleftrightarrow CH_2 \longleftrightarrow d^{10}$-$Pt(PR_3)_2$, **69** corresponds to cyclopropane. Since $CpW(CO)_2$ is isolobal with CR, **70** corresponds to cyclopropene. Both isomers **71** and **72** are related to $(CO)_3Fe(cyclobutadiene)$, **1**, or for that matter to the organic square-pyramidal $C_5H_5^+$[32].

69 **70** **71** **72**
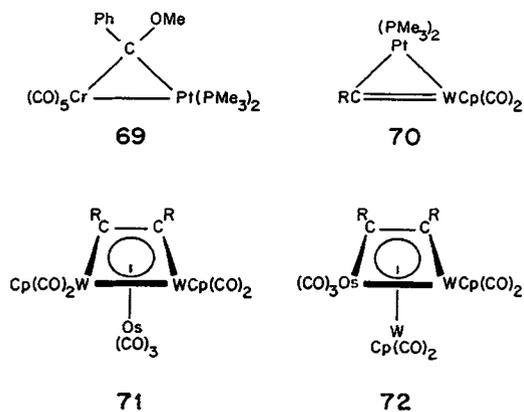
From Inorganic to Organic Chemistry

The psychological direction of the isolobal analogy in general has been to make one feel more comfortable about the structures of complex inorganic molecules by relating them to known, presumably simpler, organic molecules. It is interesting to reverse this process and think about as yet unsynthesized organic structures related to known inorganic ones. The mapping from one realm of chemistry to the other must be accompanied by the warning already given: there is no guarantee that the "product" of an isolobal transformation is as stable, kinetically or thermodynamically, as the "reactant"[33].

$Fe(CO)_3$ is isolobal with CH^+. Thus, **1** is related to $C_5H_5^+$, **73**[32], and the ubiquitous ferroles, **74**[34], are related to $C_6R_6^{2+}$, **75**[35]. Another product of the interaction of acetylenes with carbonyliron species is the "flyover bridge" molecule, **76**, a binuclear ring-opened fulvene complex[34]. The isolobal replacement carries over to **77**.

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1 → **73**

74 **75**
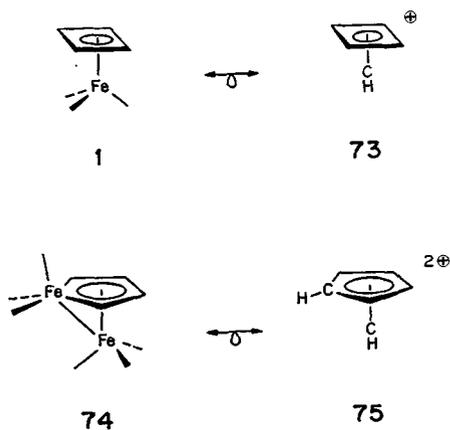
This is an unusual hydrocarbon $C_8H_8^{2+}$ of C_2 symmetry, a hypothetical doubly homoallylic cation. It is not a geometry one would normally have thought of for a heptafulvene dication, yet once reached by the isolobal mapping it appears to be geometrically reasonable[36]. More mappings of this type await exploitation.

76 **77**
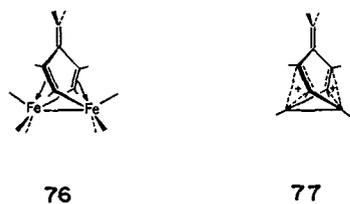
From Organic to Inorganic Reaction Mechanisms

Puddephatt, Tipper et al.[37] have discovered a remarkable rearrangement of a platinacyclobutane, **78**, in which a carbon atom adjacent to the metal, with its substituents,

78

exchanges in a very specific way with the carbon atom opposite the metal[37]. The labeling experiment of *Casey et al.* showing this phenomenon most directly is given in **79**[38]. How does this happen?

79

Kinetic evidence for a primary dissociative step to $Cl_2(py)Pt(CH_2)_3$ exists[37]. Suppose the ML_3 fragment can distort from its original T-shape to a C_{3v} geometry. Since d^8-$PtCl_2(py)$ is isolobal with CH^+, we can see a relationship to the cyclobutyl cation, **80**.

80

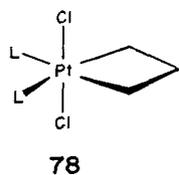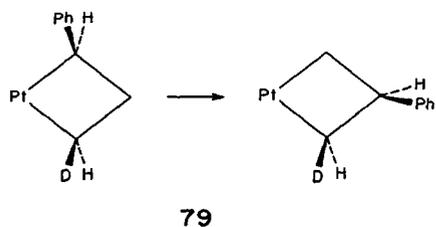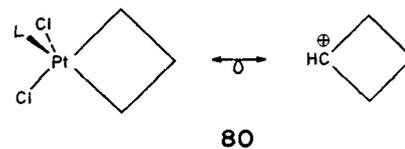This association immediately brings to mind the entire complex of speculations and facts surrounding the facile rearrangement of cyclobutyl cations through "bicyclobutonium" waypoints[39]. The motions likely to occur are shown in **81**. Ligand loss is followed by geometric reorganization at the metal, approach to a "bicyclobutonium structure", an itinerary around the periphery of a Jahn-Teller wheel through "cyclopropyl carbinyl" waypoints, and exit through an isomeric "bicyclobutonium" structure.

$M = PtLCl_2$

81
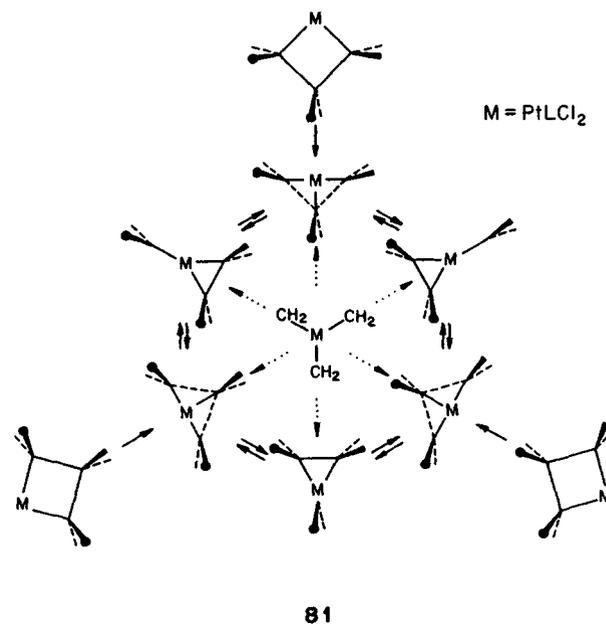
This is but one instance among many where the isolobal analogy is useful in moving between organic and inorganic reaction mechanisms.

Beyond the Octahedron

The octahedron was a most useful starting point for generating fragment frontier orbitals, thereby engendering the isolobal analogy. But the octahedral polytype is not unique for six-coordinate complexes, and higher coordination numbers are feasible. We seek another more far-ranging derivation and find one based on the 18-electron rule.

An (unoriginal) justification of this rule goes as follows: Consider n ligands, $n \leq 9$, approaching a metal with its 9 valence orbitals (cf. **82**). A little group theory shows that for the octahedron and most, but not quite all, coordination geometries the n ligand orbitals will find a match in number, symmetry properties, and extent in space among the hybrid sets that can be formed from the nine metal orbitals. The exceptions are very well understood[40]. Given this match, n M—L σ bonding combinations will go down in energy, n M—L σ* antibonding combinations will go up, and 9 − n metal orbitals will remain relatively un-

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82
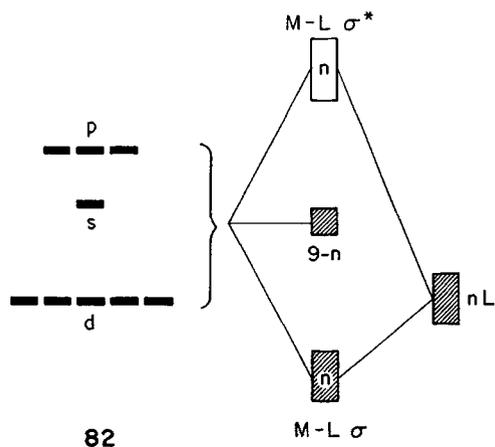
touched, approximately non-bonding. The 18-electron rule then is the statement: "Thou shalt not fill antibonding orbitals". Filling bonding (n) + nonbonding $(9-n)$ orbitals leads to 9 electron pairs or 18 electrons.

This "proof" is trivial but not silly. Upon a little reflection it will lay bare the limitations of the 18-electron rule on the left and right side of the transition series, for special symmetry cases, and for weak field ligands.

We next remove a ligand, a base, from the 18-electron complex. A localized hole on the metal, a directional hybrid, is created. The electron pair leaves with the ligand (cf. **83**). To put it in another way, in some localized description of the bonding, one M—L σ bond was formed by interaction of a ligand pair of electrons with a metal-based hybrid. Reversing the process, breaking the bond, frees that hybrid.

$$ML_n \longrightarrow ML_{n-1} + L$$

83
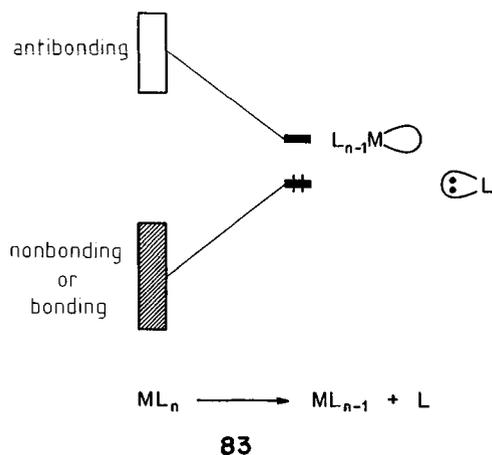
A parallel analysis for main group elements leads to the octet rule, since only s and p are considered as valence orbitals. Hybrids are freed by removing ligands, so that CH_3^+ has one vacant directional orbital, CH_2^{2+} has two such.

The parallel between ML_n and EL_n fragments (M = transition metal, E = main group element) is derived from the generation of similar hybrid patterns on removal of ligands from 18- or 8-electron configurations. For instance, if the octahedral polytype is used as a starting point, the 18-electron rule is satisfied for a d^6-ML_6. Then d^6-ML_5 will have one hybrid and no electrons in the gap between antibonding and bonding or nonbonding levels, just like CH_3^+, **84**:

d^6-ML_4 will have two empty hybrids, so will CH_2^{2+}. The common form of the isolobal analogy follows from this.

84

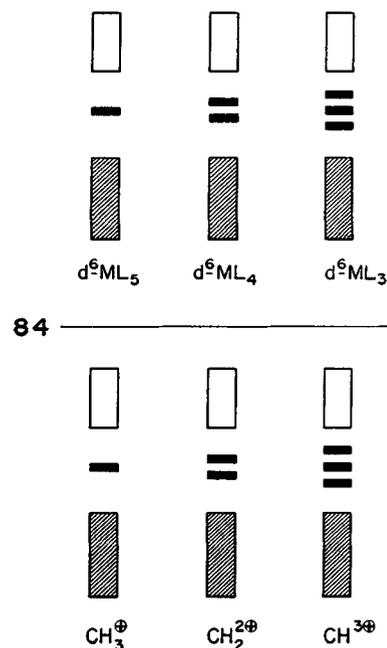The advantage of this alternative derivation is that it is easily extended to higher coordination numbers. For instance in any of the multitude of seven-coordinate geometries[8g] the 18-electron configuration is d^4. It follows immediately for fragments derived from these seven-coordinate structures that

$$d^5\text{-}ML_6 \longleftrightarrow CH_3$$
$$d^6\text{-}ML_5 \longleftrightarrow CH_2$$
$$d^7\text{-}ML_4 \longleftrightarrow CH$$
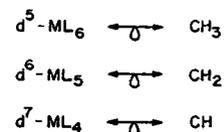
From an eight-coordinate starting point[8p], where the 18-electron configuration is d^2:

$$d^3\text{-}ML_7 \longleftrightarrow CH_3$$
$$d^4\text{-}ML_6 \longleftrightarrow CH_2$$
$$d^5\text{-}ML_5 \longleftrightarrow CH$$
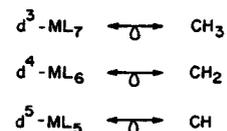
The conclusions may be summarized in Table 1. Note once again the nonisomorphic, "many-to-one" nature of the isolobal analogy. Also, the results of the previous section on "Into the t_{2g} Shell" are contained in the present discussion.

Table 1. Isolobal Analogies.

Organic Fragment	Transition Metal Coordination Number on which Analogy is Based				
	9	8	7	6	5
CH_3	d^1-ML_8	d^3-ML_7	d^5-ML_6	d^7-ML_5	d^9-ML_4
CH_2	d^2-ML_7	d^4-ML_6	d^6-ML_5	d^8-ML_4	d^{10}-ML_3
CH	d^3-ML_6	d^5-ML_5	d^7-ML_4	d^9-ML_3	

L = neutral two electron ligand.

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Miscellanea

The general rules in hand, the cautions understood, one can proceed to apply the isolobal analogy. Indeed my strategy has been to show the applications as I introduced extensions of the model. Here are some additional examples:

In a recent study of binuclear acetylene complexes the discussion focused on four structural types, **85—88**[41].

Now it is simple—the inorganic chain **89** *is* really *n*-heptane!

One of Many Bridges

The isolobal analogy is a model. It is the duty of our scientific craft to push it to its extremes, and being only a model it is certain to fail somewhere, for any model, as ingenious a construction as it might be, is bound to abstract

That these were isolobal with tetrahedrane, an olefin, bicyclobutane and cyclobutene was not only a curiosity, but actually made easier for us the complicated analysis of the interconversions of these molecules. And the isolobal analogy points to the synthesis of the as yet unknown "isomers" in the series, dimetallacyclobutadienes and butadienes, already known in complexed form.

Finally for amusement, consider the chain, **89**, assembled by *Vahrenkamp et al.*[42] (no implication is made in the simplified drawing of the chain stereochemistry.) There had better be a relationship to *n*-heptane! And so there is. We proceed using Table 1 as needed. CpCr(CO)₃ appears in a seven-coordinate guise here, so does CpCr(CO)₂; while Co(CO)₃ and Fe(CO)₄ are in a five-coordinate environment. It follows that:

only a piece of reality. The reader has seen just how far the model can be pushed and where it breaks down.

The pleasing aspect of this particular model is that it brings together different subfields of our central science. We are separated, split as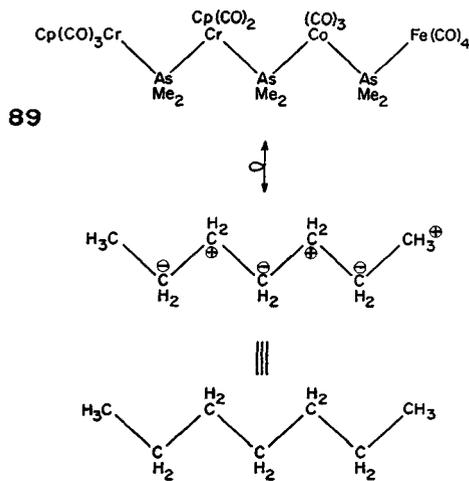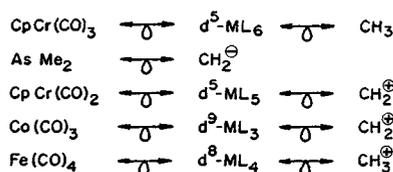under—organic, inorganic, physical, biological, analytical chemists—by the very largesse of our creation. The variety of molecules we create, and the methods we use to study them breed jargon and specialization. Yet underneath the seeming complexity there must be a deep unity. I think this approach would have pleased *R. B. W.*

It should be obvious to the reader that the spirit of this new line of work of my group owes much to what went on before. In particular I owe a direct debt of gratitude to my teachers M. P. Gouterman, W. N. Lipscomb, Jr., E. J. Corey, R. B. Woodward and my younger collaborators in the "organic days". E. L. Muetterties helped me learn inorganic chemistry. But it is my coworkers—graduate students, postdoctoral fellows, senior visitors—who in long group meetings, patiently yet with inspiration helped me shape this view of a piece of chemical experience. In rough chronological order of passing through Baker Lab in the "inorganic days" they are: M. Elian, N. Rösch, A. R. Rossi, J. M. Howell, M. M.-L. Chen, D. M. P. Mingos, A. B. Anderson, P. D. Mollére, P. J. Hay, J. C. Thibeault, P. Hofmann, J. W. Lauher, R. H. Summerville, T. A. Albright, D. L. Thorn, D. L. DuBois, Nguyen Trong Anh, A. Dedieu, E. M. Shustrovich, P. K. Mehrotra, M.-H. Whangbo, B. E. R. Schilling, K. Tatsumi, J. K. Burdett, H. Berke, A. R. Pinhas, S. Shaik, E. D. Jemmis, D. Cox, A. Stockis, R. D. Harcourt, R. D. Bach, O. Eisenstein, R. J. Goddard, H. H. Dunken, P. Kubáček, D. M. Hoffman, C. Mealli, Z. Havlas, C. N. Wilker, T. Highbanks, S.-Y. Chu, S. Wijeyesekera, C. Minot, S. Cain, S. Sung, M. Kertész, C. Zheng. Kaz Tatsumi was especially helpful in the preparation of this paper.

I am in the business of communicating ideas to people. The graphical aspect of this enterprise, be it lecture slides or published articles, is critical. Throughout these years nearly

[1] Some selected papers from my group on this subject are the following: a) M. Elian, R. Hoffmann, *Inorg. Chem. 14* (1975) 1058; b) R. Hoffmann, P. Hofmann, *J. Am. Chem. Soc. 98* (1976) 598; c) J. W. Lauher, R. Hoffmann, *ibid. 98* (1976) 1729; d) J. W. Lauher, M. Elian, R. H. Summerville, R. Hoffmann, *ibid. 98* (1976) 3219; e) M. Elian, M. M.-L. Chen, D. M. P. Mingos, R. Hoffmann, *Inorg. Chem. 15* (1976) 1148; f) R. H. Summerville, R. Hoffmann, *J. Am. Chem. Soc. 98* (1976) 7240; *101* (1979) 3821; g) R. Hoffmann, M. M.-L. Chen, D. L. Thorn, *Inorg. Chem. 16* (1977) 503; h) T. A. Albright, P. Hofmann, R. Hoffmann, *J. Am. Chem. Soc. 99* (1977) 7546; i) D. L. Thorn, R. Hoffmann, *Inorg. Chem. 17* (1978) 126; j) Nguyen Trong Anh, M. Elian, R. Hoffmann, *J. Am. Chem. Soc. 100* (1978) 110; k) R. Hoffmann, T. A. Albright, D. L. Thorn, *Pure Appl. Chem. 50* (1978) 1; l) A. Dedieu, R. Hoffmann, *J. Am. Chem. Soc. 100* (1978) 2074; m) B. E. R. Schilling, R. Hoffmann, D. L. Lichtenberger, *ibid. 101* (1979) 585; n) B. E. R. Schilling, R. Hoffmann, *ibid. 101* (1979) 3456; o) T. A. Albright, R. Hoffmann, J. C. Thibeault, D. L. Thorn, *ibid. 101* (1979) 3801; p) T. A. Albright, R. Hoffmann, Y.-C. Tse, T. D'Ottavio, *ibid. 101* (1979) 3812; q) A. Dedieu, T. A. Albright, R. Hoffmann, *ibid. 101* (1979) 3141; r) S. Shaik, R. Hoffmann, C. R. Fisel, R. H. Summerville, *ibid. 102* (1980) 4555; s) R. J. Goddard, R. Hoffmann, E. D. Jemmis, *ibid. 102* (1980) 7667; t) E. D. Jemmis, A. R. Pinhas, R. Hoffmann, *ibid. 102* (1980) 2576; u) A. R. Pinhas, T. A. Albright, P. Hofmann, R. Hoffmann, *Helv. Chim. Acta 63* (1980) 29; v) R. Hoffmann, *Science 211* (1981) 995; w) K. Tatsumi, R. Hoffmann, *J. Am. Chem. Soc. 103* (1981) 3328; x) O. Eisenstein, R. Hoffmann, *ibid. 103* (1981) 4308; *102* (1980) 6148; y) Beautiful contour plots of the frontier orbitals of the most important fragments have been made in a rare unpublished pamphlet: T. A. Albright "A Holiday Coloring Book of Fragment Molecular Orbitals", Cornell University, 1977. Some orbitals are reproduced in [3a].

[2] Others have contributed much to the development of the fragment formalism in inorganic chemistry. For some early references see: a) J. K. Burdett, *J. Chem. Soc. Faraday Trans. II 70* (1974) 1599; b) T. H. Whitesides, D. L. Lichtenberger, R. A. Budnik, *Inorg. Chem. 14* (1975) 68; c) S. F. A. Kettle, *J. Chem. Soc. A 1966*, 420; *Inorg. Chem. 4* (1965) 1661; d) M. L. H. Green: *Organometallic Compounds*, Vol. 2, Methuen, London 1968, p. 115; e) K. Wade, *Chem. Commun. 1971*, 792; *Inorg. Nucl. Chem. Lett. 8* (1972) 559, 563; *Electron Deficient Compounds*, Nelson, London 1971; f) D. M. P. Mingos, *Nature (London) Phys. Sci. 236* (1972) 99; g) P. S. Braterman, *Struct. Bonding (Berlin) 10* (1972) 57; h) F. A. Cotton, W. T. Edwards, F. C. Rauch, M. A. Graham, R. N. Perutz, J. J. Turner, *J. Coord. Chem. 2* (1973) 247; i) D. V. Korolkov, H. Miessner, *Z. Phys. Chem. (Leipzig) 253* (1973) 25.

[3] Three recent overviews of the fragment formalism by some of the most active workers in the field: a) J. K. Burdett: *Molecular Shapes*, Wiley-Interscience, New York 1980; b) D. M. P. Mingos in G. Wilkinson, F. G. A. Stone, E. W. Abel: *Comprehensive Organometallic Chemistry*, Pergamon, Oxford 1981; c) T. A. Albright, *Tetrahedron 38* (1982) 1339.

[4] a) L. Pauling: *The Nature of the Chemical Bond*, 3rd Ed., Cornell University Press, Ithaca, NY 1960; *Die Natur der chemischen Bindung*, 3. Aufl., Verlag Chemie, Weinheim 1976; b) in recent times Pauling has returned to the problem of the electronic structure of transition metal complexes. See *e.g.*: L. Pauling, *Proc. Nat. Acad. Sci. USA 72* (1975) 3799, 4200; *73* (1976) 274, 1403, 4290; *74* (1977) 2614, 5235; *75* (1978) 12, 569; *Acta Crystallogr. Sect. B 34* (1978) 746.

[5] For a leading reference see: C. J. Ballhausen: *Introduction to Ligand Field Theory*, McGraw-Hill, New York 1962.

[6] An excellent introduction to the conventions and achievements of organometallic chemistry is J. P. Collman, L. S. Hegedus: *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley 1980.

[7] For an introduction to the methology see E. Heilbronner, H. Bock: *The HMO Model and its Application*: Wiley, London/Verlag Chemie, Wein-

heim 1976; W. L. Jorgensen, L. Salem: *The Organic Chemist's Book of Orbitals*, Academic Press, New York 1973; R. Hoffmann, *Acc. Chem. Res. 4* (1971) 1.

[8] a) N. Rösch, R. Hoffmann, *Inorg. Chem. 13* (1974) 2656; b) R. Hoffmann, M. M. L. Chen, M. Elian, A. R. Rossi, D. M. P. Mingos, *ibid. 13* (1974) 2666; c) A. R. Rossi, R. Hoffmann, *ibid. 14* (1975) 365; d) P. J. Hay, J. C. Thibeault, R. Hoffmann, *J. Am. Chem. Soc. 97* (1975) 4884; e) R. Hoffmann, J. M. Howell, A. R. Rossi, *ibid. 98* (1976) 2484; f) S. Komiya, T. A. Albright, R. Hoffmann, J. Kochi, *ibid. 98* (1976) 7255; *99* (1977) 8440; g) R. Hoffmann, B. F. Beier, E. L. Muetterties, A. R. Rossi, *Inorg. Chem. 16* (1977) 511; h) B. L. Barnett, C. Krüger, Y.-H. Tsay, R. H. Summerville, R. Hoffmann, *Chem. Ber. 110* (1977) 3900; i) R. Hoffmann, D. L. Thorn, A. E. Shilov, *Koord. Khim. 3* (1977) 1260; j) D. L. DuBois, R. Hoffmann, *Nouv. J. Chim. 1* (1977) 479; k) D. L. Thorn, R. Hoffmann, *J. Am. Chem. Soc. 100* (1978) 2079; *Nouv. J. Chim. 3* (1979) 39; l) T. A. Albright, R. Hoffmann, *Chem. Ber. 111* (1978) 1578; *J. Am. Chem. Soc. 100* (1978) 7736; m) T. A. Albright, R. Hoffmann, P. Hofmann, *Chem. Ber. 111* (1978) 1591; n) R. Hoffmann, B. E. R. Schilling, R. Bau, H. D. Kaesz, D. M. P. Mingos, *J. Am. Chem. Soc. 100* (1978) 6088; o) P. K. Mehrotra, R. Hoffmann, *Inorg. Chem. 17* (1978) 2187; p) J. K. Burdett, R. Hoffmann, R. C. Fay, *ibid. 17* (1978) 2553; q) B. E. R. Schilling, R. Hoffmann, *J. Am. Chem. Soc. 100* (1978) 7224; *Acta Chem. Scand. B 33* (1979) 231; r) H. Berke, R. Hoffmann, *J. Am. Chem. Soc. 100* (1978) 7224; s) B. E. R. Schilling, R. Hoffmann, J. W. Faller, *ibid. 101* (1979) 592; t) A. R. Pinhas, R. Hoffmann, *Inorg. Chem. 18* (1979) 654; u) C. Krüger, J. C. Sekutowski, H. Berke, R. Hoffmann, *Z. Naturforsch. B 33* (1978) 1110; v) E. D. Jemmis, R. Hoffmann, *J. Am. Chem. Soc. 102* (1980) 2570; w) A. Stockis, R. Hoffmann, *ibid. 102* (1980) 2952; x) K. Tatsumi, R. Hoffmann, M.-H. Whangbo *J. Chem. Soc. Chem. Commun. 1980*, 509; y) K. Tatsumi, R. Hoffmann, *Inorg. Chem. 19* (1980) 2656; *J. Am. Chem. Soc. 103* (1981) 3328; *Inorg. Chem. 20* (1981) 3781; z) R. J. McKinney, D. L. Thorn, R. Hoffmann, A. Stockis, *J. Am. Chem. Soc. 103* (1981) 2595; aa) K. Tatsumi, R. Hoffmann, A. Yamamoto, J. K. Stille, *Bull. Chem. Soc. Jpn. 54* (1981) 1857; ab) P. Kubáček, R. Hoffmann, *J. Am. Chem. Soc. 103* (1981) 4320; ac) O. Eisenstein, R. Hoffmann, A. R. Rossi, *ibid. 103* (1981) 5582; ad) M. Kamata, K. Hirotsu, T. Higuchi, K. Tatsumi, R. Hoffmann, S. Otsuka, *ibid. 103* (1981) 5772; ae) D. N. Cox, D. M. P. Mingos, R. Hoffmann, *J. Chem. Soc. Dalton Trans. 1981*, 1788; af) D. M. Hoffman, R. Hoffmann, *Inorg. Chem. 20* (1981) 3543.

[9] a) J. Halpern, *Discuss. Faraday Soc. 1968*, 467; *Adv. Chem. Ser. 70* (1968) 1; b) J. Kwiatek, J. K. Seyler, *ibid. 70* (1968) 207.

[10] The term "isolobal" was introduced in [1e], but the concept, as we will see below, is older.

[11] In methylene a_1 is below b_2, because the latter is a pure p orbital, while the former has some s character. In Fe(CO)₄ the a_1 and b_2 can be thought of as being derived from the e_g orbital (z^2, $x^2 - y^2$) of the octahedron. Removal of two *cis*-ligands stabilizes $x^2 - y^2$ (b_2) more than it does z^2 (a_1). Were the ligands removed *trans*, to reach the square-planar ML₄ fragment, the situation would be reversed. Cf. also [3].

[12] E. O. Fischer, H.-J. Beck, C. G. Kreiter, J. Lynch, J. Müller, E. Winkler, *Chem. Ber. 105* (1972) 162; R. Pfiz, J. Daub, *J. Organomet. Chem. 152* (1978) C32–C34; H. LeBozec, A. Gorgues, P. H. Dixneuf, *J. Am. Chem. Soc. 100* (1978) 3946; M. F. Lappert, P. L. Pye, *J. Chem. Soc. Dalton Trans. 1977*, 2172.

[13] M. Poliakoff, J. J. Turner, *J. Chem. Soc. A 1971*, 2403.

[14] C. H. Wei, L. F. Dahl, *J. Am. Chem. Soc. 91* (1969) 1351.

[15] A. S. Foust, M. S. Foster, L. F. Dahl, *J. Am. Chem. Soc. 91* (1969) 5631 and references therein.

[16] See also J. E. Ellis, *J. Chem. Educ. 53* (1956) 2 for an extensive exposition of this analogy.

[17] K. Wade, *Adv. Inorg. Chem. Radiochem. 18* (1976) 1; *Chem. Br. 11* (1975) 177; cf. also [2e].

[18] D. M. P. Mingos, *Adv. Organomet. Chem. 15* (1977) 1; R. Mason, D. M. P. Mingos, *MTP Int. Rev. Sci. Phys. Sci. Ser. II 11* (1975) 121; D. M. P. Mingos, *Trans. Am. Crystallogr. Assoc. 16* (1980) 17; cf. also [2f] and [3b].

[19] B. T. Huie, S. W. Kirtley, C. B. Knobler, H. D. Kaesz, *J. Organomet. Chem. 213* (1981) 45.

[20] E. O. Fischer, T. L. Lindner, H. Fischer, G. Huttner, P. Friedrich, F. R. Kreissl, *Z. Naturforsch. B 32* (1977) 648.

[21] R. Bau, B. Fontal, H. D. Kaesz, M. R. Churchill, *J. Am. Chem. Soc. 89* (1967) 6374.

[22] J. D. Cotton, J. Duckworth, S. A. R. Knox, P. F. Lindley, I. Paul, F. G. A. Stone, P. Woodward, *Chem. Commun. 1966*, 253; J. D. Cotton, S. A. R. Knox, I. Paul, F. G. A. Stone, *J. Chem. Soc. A 1967*, 264.

[23] D. H. Farrar, B. F. G. Johnson, J. N. Nicholls, P. R. Raithby, M. J. Rosales, *J. Chem. Soc. Chem. Commun. 1981*, 273.

[24] P. Braunstein, D. Matt, O. Bars, M. Louër, D. Grandjean, J. Fischer, A. Mitschler, *J. Organomet. Chem. 213* (1981) 79.

[25] R. J. Haines, N. D. C. T. Steen, R. B. English, *J. Chem. Soc. Chem. Commun. 1981*, 587.

Angew. Chem. Int. Ed. Engl. 21 (1982) 711–724

723

[26] W. A. Herrmann, C. Krüger, R. Goddard, I. Bernal, *Angew. Chem. 89* (1977) 342; *Angew. Chem. Int. Ed. Engl. 16* (1977) 334; P. Hofmann, *Angew. Chem. 91* (1979) 591; *Angew. Chem. Int. Ed. Engl. 18* (1979) 554.

[27] There are some further details, not discussed here but treated elsewhere [1o, 1x, 3c]. In particular, the ML₂ will have another relatively low-lying orbital when L is a π acceptor.

[28] W. D. Jones, M. A. White, R. G. Bergman, *J. Am. Chem. Soc. 100* (1978) 6770.

[29] a) M. Green, J. A. K. Howard, R. N. Mills, G. N. Pain, F. G. A. Stone, P. Woodward, *J. Chem. Soc. Chem. Commun. 1981*, 869; b) For some other compounds containing a similar unit see L. M. Cirjat, J.-S. Huang, Z.-H. Zhu, L. F. Dahl, *J. Am. Chem. Soc. 102* (1980) 6623.

[30] N. M. Boag, M. Green, D. M. Grove, J. A. K. Howard, J. L. Spencer, F. G. A. Stone, *J. Chem. Soc. Dalton Trans. 1981*, 2170.

[31] a) F. G. A. Stone, *Acc. Chem. Res. 14* (1981) 318 and references therein; L. Busetto, M. Green, J. A. K. Howard, B. Hessner, J. C. Jeffery, R. M. Mills, F. G. A. Stone, P. Woodward, *J. Chem. Soc. Chem. Commun. 1981*, 1101; T. V. Ashworth, M. J. Chetcuti, L. J. Farrugia, J. A. K. Howard, J. C. Jeffery, R. Mills, G. N. Pain, F. G. A. Stone, P. Woodward *Reactivity of Metal-metal Bonds, ACS Symposium Series 155* in M. H. Chisholm: Washington 1982, p. 299. b) For futher molecules of type 71 and 72 see E. Sappa, A. m. Manotti Lanfredi, A. Tiripicchio, *J. Organomet. Chem. 221* (1981) 93; J. R. Shapley, J. T. Park, M. R. Churchill, C. Bueno, H. J. Wasserman, *J. Am. Chem. Soc. 103* (1981) 7385; G. Jaouen, A. Marinetti, B. Mentzen, R. Mutin, JK.-Y. Saillard, B. G. Sayer, M. J. McGlinchey, unpublished results.

[32] a) W.-D. Stohrer, R. Hoffmann, *J. Am. Chem. Soc. 90* (1972) 1661; b) R.

E. Williams, *Inorg. Chem. 10* (1971) 210; *Adv. Inorg. Chem. Radiochem. 18* (1976) 67; c) S. Masamune, M. Sakai, H. Ona, *J. Am. Chem. Soc. 94* (1972) 8955; S. Masamune, M. Sakai, H. Ona, A. L. Jones, *ibid. 94* (1972) 8956; d) H. Hart, M. Kuzuya, *ibid. 94* (1972) 8958.

[33] See in this context: J. Chandrasekhar, P. v. R. Schleyer, H. B. Schlegel, *Tetrahedron Lett. 1978*, 3393.

[34] Cf. [1i] for the relevant literature citations.

[35] H. Hogeveen, P. W. Kwant, *Acc. Chem. Res. 8* (1975) 413. For some related main group structures see: P. Jutzi, F. Kohl, P. Hofmann, C. Krüger, Y.-H. Tsay, *Chem. Ber. 113* (1980) 757.

[36] But apparently not a stable structure after all: A. Sevin, A. Devaquet, *Nouv. J. Chim. 1* (1977) 357; T. Clark, P. v. R. Schleyer, *ibid. 2* (1978) 665.

[37] R. J. Al-Essa, R. J. Puddephatt, P. J. Thompson, C. F. H. Tipper, *J. Am. Chem. Soc. 102* (1980) 7546 and references therein.

[38] C. P. Casey, D. M. Scheck, A. J. Shusterman, *J. Am. Chem. Soc. 101* (1979) 4233.

[39] Cf. M. Saunders, H.-U. Siehl, *J. Am. Chem. Soc. 102* (1980) 6868 and references therein.

[40] The exceptions include Zr(BH₄)₄, W(RCCR)₃(CO), Cp₃M and Cp₃MR, Cp₄U, UO₂L₆; among others. For the relevant references see S.-Y. Chu, R. Hoffmann, *J. Phys. Chem. 86* (1982) 1289 and [3a].

[41] D. M. Hoffmann, R. Hoffmann, C. R. Fisel, *J. Am. Chem. Soc. 104* (1982) 3858; D. M. Hoffmann, R. Hoffmann, *J. Chem. Soc. Dalton Trans.*, in press.

[42] H. J. Langenbach, E. Keller, H. Vahrenkamp, *J. Organomet. Chem. 191* (1980) 95.

Polarity of Binary Liquid Mixtures

By Heinz Langhals*

In contrast to the thoroughly studied polarity properties of pure liquids, only little is known about the polarity of mixtures of liquids, although the majority of mechanistic and preparative work is not carried out in pure phases. Using a widely applicable two-parameter equation, polar behavior of binary liquid mixtures can be described quantitatively as a function of their composition. Based on this equation, satisfactory explanations are found for deviations observed for binary solvent mixtures from the linear correlation of polarity scales, as well as for the unusual activation parameters estimated by *Winstein* for solvolysis of *tert*-butyl chloride. Applications of the equation range from a rapid test for determining water contents of solvents, the study of reaction mechanisms, to polymer chemistry.

1. Introduction

Solvent polarity has been interesting to chemists for some considerable time[1-4]. Macroscopic physical quantities, such as dielectric constant or refractive index are of only limited use for studying chemical reaction behavior and the associated molecular processes[1,5-8]: the development of the empirical polarity scales, however, was a substantial advance. The oldest, the Y-scale of *Winstein* and *Grunwald*[9-11], shown in equation (1), is based on the solvolysis of *tert*-butyl chloride and often correctly describes the influence of solvents on the rate of chemical reactions.
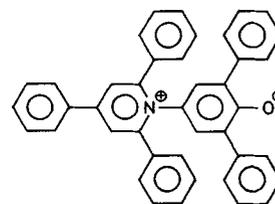
$$\lg \frac{k}{k_0} = Y \qquad (1)$$

k = rate constant of the solvolysis of $(CH_3)_3CCl$ in the medium to be studied

k_0 = rate constant of the solvolysis of $(CH_3)_3CCl$ in 80% ethanol-water.

2. Empirical Polarity Scales

Today, the *Winstein* Y-values are widely used as a primary polarity scale. Being derived from a solvolysis reaction, the Y-scale is, however, confined to polar media. Therefore, a number of other polarity scales[1] of wider applicability were developed, based on reaction kinetics or spectroscopic data. Scales derived from solvatochromism of dyes are noted for their straightforward and precise measurement[12,13]. Most remarkable is the $E_T(30)$-scale of *Dimroth* and *Reichardt*[14,15], which has become the most widely used scale: the solvatochromic dye pentaphenyl pyridiniumphenolate 1, which serves as reference substance,

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