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Frontiers of Inorganic Chemistry

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I want to thank the organizers and the sponsors of this symposium for inviting me to participate in honoring my long time friend Professor Vittorio Carassiti on his 70th birthday. I recall reading his papers in the 1950s on the photochemistry of cyano molybdenum complexes, and I have always viewed him as the "father of photochemistry of metal complexes in Italy." His influence in this area of chemistry is very apparent today as his former students and their students continue to do excellent research in photochemistry,[1] some of which is reported here in this special issue of *Coordination Chemistry Reviews*. The role of Carassiti in Italy was much the same as that of Adamson introducing photochemistry of metal complexes in the USA, so it was most appropriate that Professor A. W. Adamson be present to contribute to the success of this delightful symposium. Since our research group has published very little on the photochemistry of metal complexes[2] and since Carassiti is an inorganic chemist having been President of the Inorganic Division of the *Italian Chemical Society*, I take the liberty to discuss the early status of research in inorganic chemistry in the USA, and to mention some of the current areas of research in inorganic chemistry that I think are at the forefront of the field. Other inorganic chemists would make different choices, but I believe they would agree on several of the areas presented here.

My generation of chemistry students in the USA were primarily interested in organic chemistry. This is understandable because exciting research was being done on commercially important organic polymers, plastics, pharmaceuticals, and petroleum chemistry. Good textbooks of organic chemistry were available, and it was possible to teach organic chemistry in a meaningful systematic manner on the basis of properties of functional groups. For example, the reaction of ROH with R'COOH to form an ester R'COOR was much the same regardless of the nature of R. Before World War II, inorganic chemistry in the USA was relegated to the manufacture of heavy chemicals such as H_2SO_4, NH_3, and HNO_3. Good textbooks of inorganic chemistry were lacking, and most colleges and universities did not teach a course in inorganic chemistry. General chemistry courses did contain a considerable amount of inorganic reactions and syntheses, mostly dealing with industrial processes for producing H_2SO_4, steel, etc. The excitement of research in inorganic chemistry was largely nonexistent, for very little research was being done. This created a feeling that inorganic chemistry was synonymous with the heavy chemical industry which was doing well and in no need of research. What then did

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happen to turn things around and make research in inorganic chemistry arguably as exciting and important as organic chemistry?

Since much of this turn around in the US happened on my watch (B.Ed. 1940, Ph.D. 1943, industrial chemist 1946, university faculty 1990, emeritus professor to present) I feel comfortable relating my views on how and why this change occurred in the status of inorganic chemistry relative to organic chemistry. Several factors contributed to this, but in my opinion the turn around towards inorganic chemistry happened during World War II with the Manhattan Project on nuclear fission. Many chemists trained in something other than inorganic chemistry were involved in doing research on fission products and on uranium and transuranium elements. This meant doing research on the solution chemistry of metals, which several of the chemists found challenging and interesting. At the end of the war these people took positions elsewhere, and they brought with them their desire to continue research in inorganic chemistry. As a result the Manhattan project spawned a new generation of young talented inorganic chemists who then were largely responsible for the beginning of the *renaissance* of inorganic chemistry in the USA.

Research in the Manhattan Project not only provided the necessary human resources of chemists doing research in inorganic chemistry, but it also helped make available some of the necessary tools required to do modern inorganic chemistry. Isotopes such as ^{2}H, ^{18}O, and ^{36}Cl were immediately put to use to investigate the kinetics and mechanisms of inorganic reactions. For example, Henry Taube was able to use ^{36}Cl in his discovery of the *inner and outer-sphere electron transfer* mechanism which won him the Nobel Prize in 1983.

Starting in the late sixties a variety of scientific instruments became available, making it possible to do high quality research in inorganic chemistry. When I was a student it was possible to characterize an organic compound by its melting point or mixed melting point, and to follow their rates of reaction which are generally slow by conventional means. Not so for inorganic compounds which generally do not melt and often react very fast. Research progress with inorganic systems had to await the commercial development of scientific instruments such as the X-ray diffractometer for structural studies and the stopped-flow equipment for monitoring fast reactions. Today chemists have an arsenal of computers and sophisticated instruments which makes it possible to do first-rate research with equal ease on both inorganic and organic systems.

Once good sound research in inorganic chemistry started to make its mark in the 50s and 60s, chemists began to focus on the entire periodic table and not just the elements C, H, O, N mostly encountered in organic compounds. Demands of industrialized countries and of high-tech industries required the use of inorganic compounds and of new materials. By the mid-to-late fifties most of our colleges and universities offered a one quarter or one semester course in inorganic chemistry, and good textbooks on inorganic chemistry began to appear. Surely the most important contribution to the current high status of inorganic chemistry in the US is the choice made by many talented students to do research in inorganic chemistry. With the study of the chemistry of all the elements in the periodic table exciting discoveries have been made over the years, such as ferrocene (P. Pauson and

S. A. Miller, 1951), xenon fluorides (N. Bartlett, 1962), M–N_2 complexes (A. D. Allen, 1965), and $(\eta^2\text{–}H_2)M$ compounds (G. Kubas). The Division of Inorganic Chemistry now presents more papers and posters at annual *American Chemical Society* meetings than does any other ACS Division. This is due to the young people entering the field in increasing numbers and to the wide breadth of research that involves inorganic systems. As more and more of our very best students choose to do research in inorganic chemistry, they and the results of their research will provide the driving force for a continuing bright future for inorganic chemistry.

Here, in my opinion, are listed some current *frontier* areas of research in inorganic chemistry (Table I).

Table I. Frontiers of Inorganic Chemistry in 1992

(1) Bioinorganic Chemistry
(2) Kinetics, Thermodynamics and Mechanisms of Inorganic Reactions
(3) Main Group Element Chemistry
(4) Metal Cluster Chemistry
(5) Photochemistry and Solar Energy
(6) Solid State Inorganic Chemistry
(7) Transition Metal Organometallic Chemistry

This list is deliberately put in alphabetical order to avoid my choice of rank order, and it is realized that other inorganic chemists would compile different lists but I do feel they would in some way include most of these topics. For each of these frontier areas a few specific topics will be tabulated and some general comments made, but no attempt will be made to do more than just mention the topics, giving only one or two references for each.

Bioinorganic chemistry is making a tremendous contribution to our understanding of biological reactions of metalloproteins by focussing on the coordination chemistry of the metal in the protein. Biological systems present very complicated ligands, but at the active site the metal is in a coordination environment not unlike metals in classical Werner complexes. Some of the research currently being done in the area of bioinorganic chemistry is shown in Table II.

Table II. Bioinorganic Chemistry

(1) Nitrogenase
(2) Cancer Chemotherapy and Radioactive Imaging Agents
(3) Ligands Designed to Selectively Sequester Metal Ions
(4) Long Range Electron Transfer in Biological Systems

At long last the X-ray structure of nitrogenase has been determined by Rees and coworkers.[3] This is an extremely important accomplishment for it should provide new insights into the chemistry of this most significant enzyme which has been the subject of extensive studies the past two decades by outstanding scientists worldwide. Much spectroscopic information was obtained and interpreted in terms of possible structures of nitrogenase. One thing the investigators finally seemed to agree on was elemental analyses of the FeMo−cofactor having an Fe:Mo:S ratio of (7±1):1:(8±1). This prompted bioinorganic chemists to synthesize metal sulfur clusters of this composition in an attempt to mimic the behavior of nitrogenase.[4] For example, two of the clusters reported are shown in Figure 1.

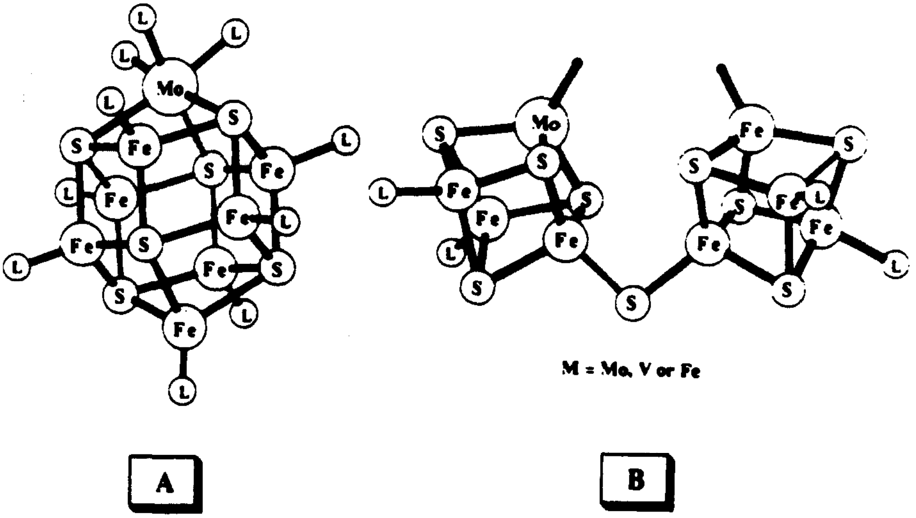


Figure 1. Proposed models for the Fe/Mo/S center in nitrogenase: A, the pentlandite model;[5] B, the double-cubane model.[6]

Structure A which was prepared in Holm's laboratory[5] is related to the mineral pentalandites, whereas Coucouvanis and coworkers[6] prepared structure B which consists of two cubane units singly bridged by a μ_2-S^{2-} ligand. Both are cleverly designed structures and represent considerable achievements in syntheses, but neither one corresponds to the X-ray structure of the nitrogenase[3] MoFe−protein from *Azotobacter vinelandii* at 2.7 Å resolution (Fig. 2).

One way to describe the nitrogenase structure is in terms of two six-membered 3Fe:3S rings, held together by two bridging Ss, and capped on one side by Fe and the other by Mo. The two 3Fe:3S rings are eclipsed such that at Fe_3--Y--Fe_7 (Fig. 2) the Y could perhaps be N_2, resulting in the formation of $Fe_3-N{\equiv}N-Fe_7$ which may activate N_2 towards reduction and bond cleavage to afford NH_3. This immediately raises the question of the role of Mo in the cofactor. The double-cubane model (Fig. 1B) had been prepared to permit the formation of $Mo-N{\equiv}N-Fe$ and perhaps allow the heterometal system to activate the N_2 bridge. Another point of interest is that the pentlandite model (Fig. 1A)

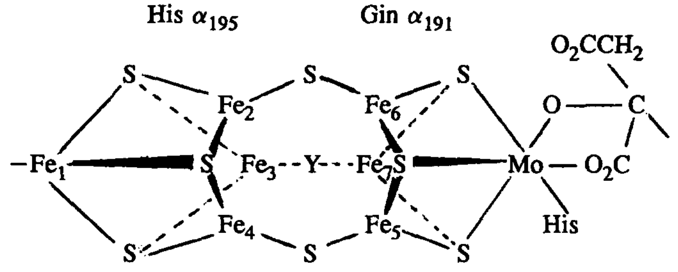


Fig. 2. Schematic representation of the MoFe-cofactor model, where Y represents the bridging ligand with relatively light electron density.

prepared by outstanding coordination chemists has the plausible staggered six-membered 3Fe:3S ring structure in order to permit interaction between the Fes and Ss of adjacent rings. Mother Nature being less of a coordination chemist but more of a pragmatist in the design of nitrogenase to reduce N_2 chose the eclipsed six-ring structure allowing for the formation of $Fe-N\equiv N-Fe$. Clearly the structure of nitrogenase answers some questions but raises others, so it is time for scientists working in this area to get back to their laboratories.

Other areas of bioinorganic chemistry beyond the ones listed in Table II are likewise currently under active investigation by inorganic chemists interested in the role of metals in biological reactions. The landmark discovery in 1969 by Rosenberg[7] that *cis*-$[Pt(NH_3)_2Cl_2]$, first prepared[8] in 1845, has antitumor activity focused attention on the possible use of metal complexes in medicinals. Huge amounts of research have been done in attempts to understand the workings of this cancer chemotherapy, and international scientific conferences are held to present new findings and books[9] on the subject are available. Much the same is true for research on diagnostic techniques using radioactive imaging reagents, in particular technetium-99m.[10]

Of all the natural and synthetic iron(III) chelating agents, the microbial iron transport agent (siderophore) enterobactin has the largest metal-ligand stability constant[11] of log $K_f \approx 49$. The chelating agent is a sexadentate tris-catechol, and this prompted Raymond and coworkers[12] to design the syntheses of sequestering agents specific for high oxidation state metal cations. One such octadentate ligand selectively removes 80-90% of toxic plutonium from animals in one administration of the ligand. A very desirable ligand yet to be reported is one that would specifically sequester and remove Pb^{2+} from people.

The classical *inner-* and *outer-sphere* mechanisms of electron transfer in metal complexes cited for the 1983 Nobel Prize to Henry Taube[13] has recently been extended to studies of long range electron transfer in biological systems. Typical of the excellent research being done by several different investigators is the work reported from the laboratory of Gray.[14] Electron tunneling in Ru-modified cytochrome c is being assessed by measuring intramolecular electron-transfer rates between Fe^{2+} and Ru^{3+} at different distances varying from approximately 8 to 15 Å. The rates are found to correlate with the lengths of σ-tunneling pathways consisting of covalent bonds, hydrogen bonds, and no-bond space jumps from the Ru-histidines to the heme group. No doubt much more research is in the offing for a more complete understanding of the various electron transfer processes vital to life itself.

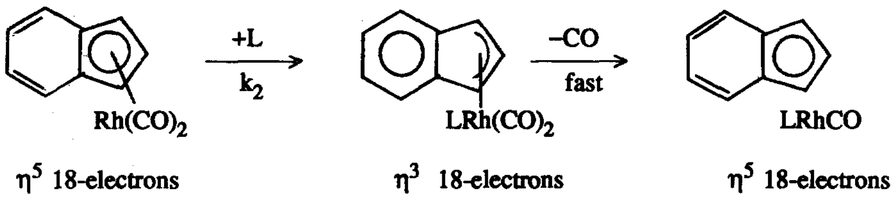
Kinetics, Thermodynamics and Mechanisms of Reactions as applied to classical Werner metal complexes was of immense interest to inorganic chemists a half-century ago. Following Werner's coordination chemistry theory[15] in 1893 (exactly one century ago) extensive work was carried out on the syntheses and reactions of metal complexes. This meant that in the 1940-50s the time was right to obtain quantitative thermodynamic data on the stability constants[16] of metal complexes in solution, and to address the kinetics and mechanisms of their reactions.[17] Chemists know that kinetics and thermodynamics are fundamental to all chemical syntheses and reactions, making it imperative that such information be available. The time is now right to gather this information on transition metal organometallic compounds, because of the large amount of research that has been done on these systems since the discovery of ferrocene in 1951 by Pawson[18] and by Miller.[18] A few current studies of this type are shown in Table III.

Table III. Kinetics, Thermodynamics, and Mechanisms of Inorganic Reactions

(1) Ligand Substitution Reactions Related to Homogeneous Catalysis
(2) Ziegler-Natta Polymerization Type Reactions
(3) Bond Dissociation Energies and Syntheses of Organometallic Compounds
(4) Radical Reactions Involving Transition Metal Complexes

One extremely important aspect of transition metal organometallic chemistry is the use of some of these compounds as homogeneous catalysts for the preparation of desired products. Excellent books[19] provide many examples of such catalytic cycles, and research in this area abounds particularly with fascinating attempts to prepare desired chiral compounds using chiral homogeneous catalysts.[20]

Ligand substitution is generally one or more of the necessary steps in a catalytic cycle for homogeneous catalysts. Therefore, it is important that quantitative kinetic data on ligand substitution be gathered and that it be understood what factors promote substitution lability in organometallic compounds. Only two examples will be cited. One is the discovery[21] of a *ring-slippage* mechanism in 1966 which permits an 18-electron metal complex to react by an associative pathway providing a pair of electrons can be localized on a ligand to vacate a low energy metal orbital for ready nucleophilic attack. This phenomenon has been widely used in organometallic chemistry,[22] and Mawby[23] later was able to show that indenyl metal complexes react more rapidly than do corresponding cyclopentadienyl compounds. For example, rates may differ by as much as 10^8 times (eq. 1).



(1)

This large rate enhancement is referred to as the *indenyl ligand effect*[24] and it has been attributed to the driving force of the increase aromaticity of the fused 6-ring in the transition state for reaction. However, recent calorimetric studies by Hoff and coworkers[25] show that in compounds of the type (η^5-ring)M$(CO)_3$H, where M = Mo, W, the M-indenyl ground-state bond energy is 10 to 14 kcal/mol less than for M-cyclopentadienyl. This suggests the indenyl effect is a result of contributions from both ground-states and transition states.

A second important example of ligand substitution lability that impacts on homogeneous catalysis is the discovery in 1978 by Brown and coworkers[26] that metal carbonyl radicals are substitution labile. It was later determined[27] that 17-electron metal carbonyls may react 10^{10} times faster than do 18-electron systems (eq.).

$$M(CO)_6 + P(n\text{–}Bu)_3 \longrightarrow M(CO)_5P(n\text{–}Bu)_3 + CO \qquad (2)$$

M =	Cr	V
Relative rates	1	10^{10}
	18-electrons	17-electrons

These very fast reactions are believed to involve an associative pathway *via* attack at the half-filled orbital of the 17-electron metal compound. However, if such an attack by the entering nucleophile is not possible then ligand substitution takes place by a dissociative process and the rates of reaction of corresponding 17-electron and 18-electron systems are approximately the same.[28] It appears the electron count has little effect on M–L bond breaking but it has a large effect on M-nucleophile bond making.

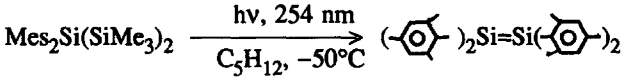
Quantitative thermodynamic data on bond dissociation energies of transition metal organometallic compounds are now being actively determined and made use of in the synthesis of desired compounds and hopefully of homogeneous catalysts.[29] Ziegler and Natta obtained the Nobel Prize in chemistry in 1963 for their work on olefin polymerization, and it may be astonishing to note that excellent research continues to be done on the mechanisms of reactions of this type. Investigations on surface-bound metal hydrocarbonyls show the organometallic connections between heterogeneous and homogeneous catalysis.[30] For example, studies of heterogeneous catalysts prompted the design and synthesis of the efficient homogeneous polymerization catalyst $[(\eta5\text{–}C_5H_5)ThCH_3]^+$, $[B(C_6F_5)_4]^-$. Also transition metals because of their variable oxidation states are known to promote radical reactions and mechanisms of these reactions continue to be actively investigated.[31]

Main group element chemistry has always been a significant area of research for inorganic chemists. Not so, however, in the USA where for two or three decades after the 1940s most inorganic chemists worked on transition metal chemistry. Again there are various reasons for this, but one was surely the exposure chemists got to *d*-element and to *f*-element chemistry on the Manhattan project. This has now taken a sudden change in the USA, where there is also at present outstanding research being done on the chemistry of the main group elements (Table IV).

Table IV. Main Group Element Chemistry

(1) New Diene Compounds
(2) Inorganic Polymers
(3) Single Source III/V Precursors for Syntheses of Semiconductors
(4) New Quasi-Aromatic Ring Systems

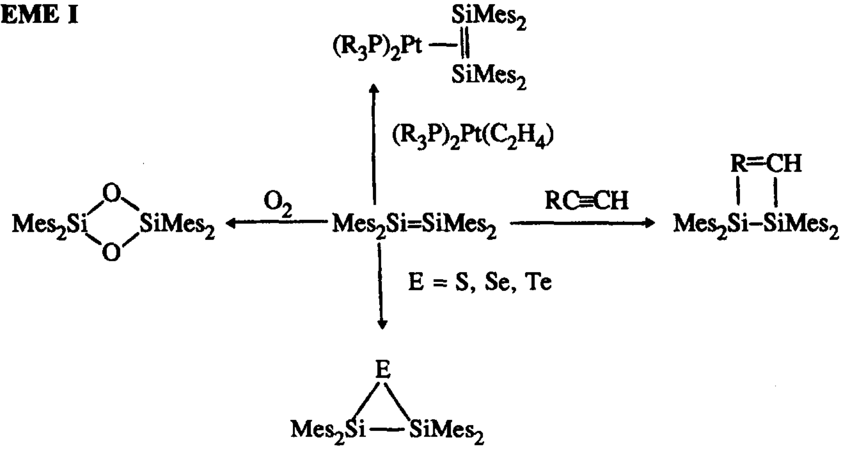
For many years chemists believed multiple bonds could only be formed between elements in the first period of the periodic table, e.g. C=C, C≡C. Research later showed multiple metal-metal bonding in compounds, including even a quadruple bond M≣M.[32] Still it was believed that main group elements of the second period and beyond had orbitals incapable of efficient overlap to permit multiple bonding between two such elements. This was all changed by the discovery in 1981 of West and coworkers[33] of disilene by the photochemical reaction of $Mes_2Si(SiMe_3)_2$ (eq. 3).



(3)

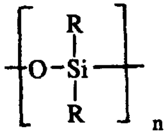
Extensive studies have been made of the reactions of disilenes, and some of the reactions are analogous to those of olefins (Scheme I).

SCHEME I



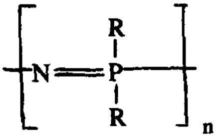
Other diene compounds[34] (Sn=Sn, P=P, As=As, and B=B) have been prepared and are being actively investigated.

There has been a long and continuing concern with making inorganic polymers which may have desirable properties not obtainable with organic polymers. This means polymers with backbones other than $(-C-C)_n$, even one day possibly $(M-M)_n$ backbone polymers. Silicones (I) have been known for years but only now are the new polymers polyphosphazenes (II) and polysilanes (III) being utilized.



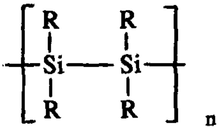
$\left[-O-\overset{R}{\underset{R}{Si}}-\right]_n$

Silicones (I)



$\left[-N=\overset{R}{\underset{R}{P}}-\right]_n$

Polyphosphazenes (II)

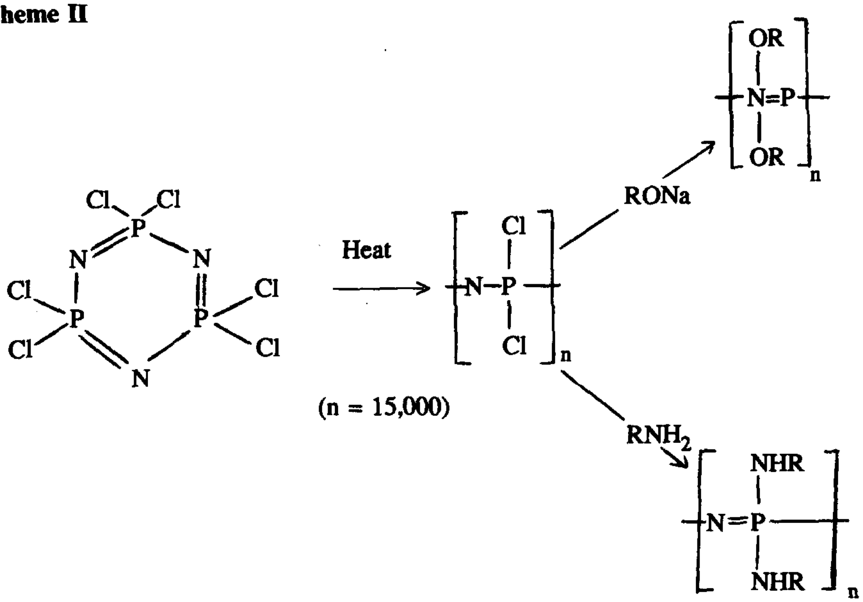


$\left[-\overset{R}{\underset{R}{Si}}-\overset{R}{\underset{R}{Si}}-\right]_n$

Polysilanes (III)

An excellent book entitled **Inorganic Polymers** was recently published.[35] Allcock and coworkers[36] are responsible for the discovery and the development of polyphosphazenes. They achieved this by a ring-opening polymerization of the well known 6-ring $P_3N_3Cl_6$ followed by the ready replacement of Cl^- by OR^- or NHR^- (Scheme II).

Scheme II



This rational approach has resulted in the syntheses of approximately 300 different polyphosphazenes and several of these have properties that make them useful commercially in a variety of applications not achieved by organic polymers.

A fascinating aspect of main group elements chemistry is one involving novel quasiaromatic systems. Borazine ($B_3N_3H_6$) or *inorganic benzene* discovered by Stock[37] in 1926 was recently joined by an "aluminazine" [$MeAlN(2,6-iPr_2C_6H)]_2$ reported by Power and coworkers.[38] Other quasi-aromatic main group systems are being considered and investigated (Fig. 3).

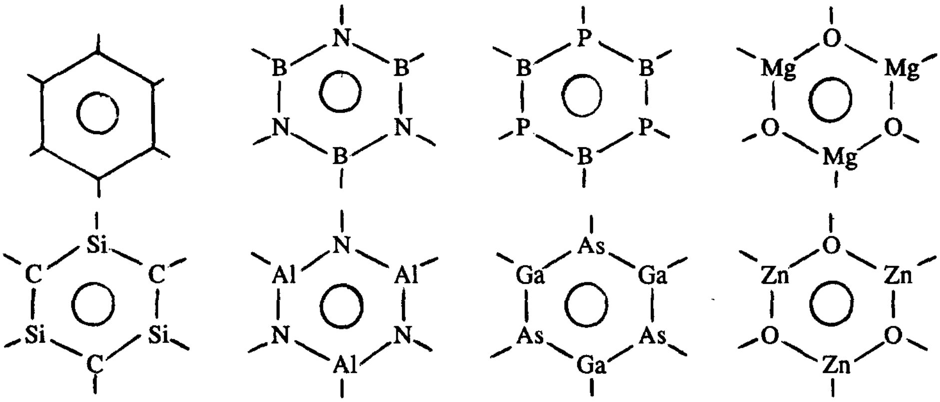


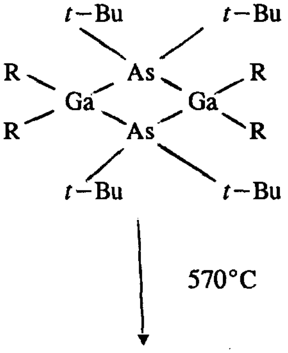
Figure 3. Some quasi-aromatic 6-rings with the same number of valence electrons as benzene or borazine.

Finally mention should be made of research being done with main group elements to prepare single-source III/V precursors for the OMCVD (organometallic compound vapor deposition) production of GaAs and related semiconductors.[39] There are several disadvantages to the present method used to prepare GaAs films (eq. 3),

$$Me_3Ga + AsH_3 \xrightarrow{\text{heat}} GaAs + 3CH_4 \qquad (3)$$

It is possible to prepare volatile organometallic compounds containing equivalent amounts of the desired group III and V elements (eq. 4).

$$2GaCl_3 + 2t\text{-}Bu_2AsLi + 4RLi \longrightarrow 6LiCl + \qquad (4)$$



(5)

$$4(CH_3)_2C{=}CH_2 + 2GaAs + 4RH$$

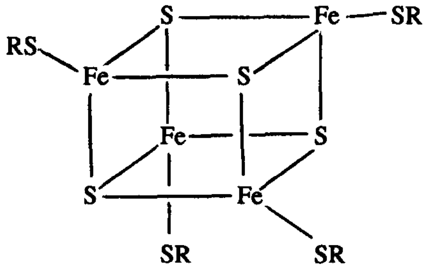
The organometallic compound can then be pyrolyzed (eq. 5) to give the desired semiconductor film.

Metal cluster compounds have been known for many years,[40] starting with clusters of the type $[M_6Cl_8]^{4+}$ (M = Mo, W). Some research with these systems continued over the years, but the use of transition metal organometallic clusters as homogeneous catalysts[19] triggered a tremendous amount of research activity on these systems. Another reason was perhaps the success of Chini[41] with his rational syntheses of metal carbonyl clusters and the early X-ray structural work of Dahl.[41] A few of the topics of research on metal clusters are listed in Table V.

Table V. Metal Cluster Chemistry

(1) Solution Syntheses of Molecular Cluster Complexes.
(2) Gas Phase Formation of Metal Cluster Complexes
(3) Reactions of Metal Cluster Complexes

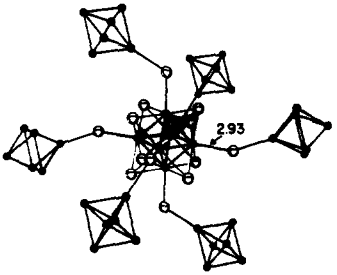
Considerable effort has been made over the years to synthesize metal clusters as models for natural metalloproteins. Much of this effort has involved the solution syntheses of metal-sulfur clusters. Mentioned earlier were the syntheses of nitrogenase related clusters.[4] The classical example of the synthesis of $[Fe_4S_4(SR)_4]^{2-}$ with a cubane structure (IV) by Holm and coworkers[42] illustrates how some of these clusters may be prepared in solution.



(IV)

Since the metal complexes involved are ligand substitution labile, the syntheses generally take place readily in reaction mixtures containing the appropriate reagents, solvent and counter ions. This is the good news, but the bad news is this is largely an empirical approach and the cluster chemist can not be certain of what product will be obtained. This approach of making clusters from smaller molecules in solution is referred to as "synthesis by self-assembly," which means the cluster obtained represents the thermodynamic sink for the system. Fortunately the thermodynamic sink metal cluster core is often that found in natural proteins, as it was with the 4Fe–4S core of ferredoxin.[42]

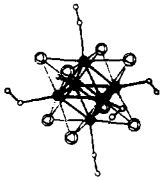
The ferredoxin research also showed it was possible to obtain the desired cluster by ligand substitution reactions permitting core extrusion from the metalloprotein. With the successful experience of this method, it is of interest to note that cluster chemists are now applying the same approach of "cluster extrusion" from extended solid-state metal complexes.[43] Some of the nonmolecular solid metal complexes are extended arrays containing discrete clusters, independent except for the bridging interactions between them. Examples of such extended structures are Re_3Cl_9,[44] NbSeBr,[45] and $PbMo_6S_8$,[46] which have discrete triangular $[Re_3(\mu_2\text{-}Cl)_3]$ cubane $[Nb_4(\mu_3\text{-}Se)_4]$, and face-capped octahedral $[Mo_6(\mu_3\text{-}S)_8]$ clusters that are connected through metal-halide or metal-chalcogenide bridges. For example, the face-capped cluster (V) of Nb_6I_{11}



Nb_6I_{11} (V)

has been excised by its reaction with $MeNH_2$ (eq. 6).

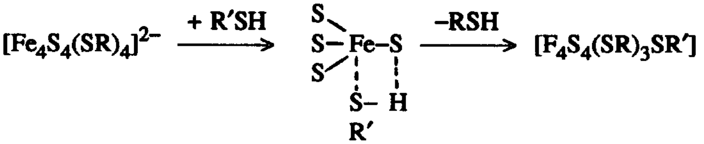
$$Nb_6I_{11} \xrightarrow[\text{in MeOH}]{MeNH_2} \qquad (6)$$



There are many such examples in the literature,[43] but as solution cluster chemists become aware of the rich variety of clusters in the solid-state more use will be made of this approach to the syntheses of molecular metal clusters. Of further help to synthetic cluster chemistry will be the recent development of a topological procedure for isomer enumeration using a matrix method which calculates all possible structures for a given cluster.[47]

Gas phase formation of clusters is having a dramatic impact on chemistry now that C_{60} buckminsterfullerene, first detected in the gas phase,[48] is being produced in sufficient quantity to do chemistry.[49] The recent discovery by Castleman and coworkers[50] of the gas phase formation of metal complex clusters called *metallo-carbohedrenes* provides cluster chemists with a new class of compounds at the frontier of cluster chemistry. The development of the chemistry of these compounds M_8C_{12} (M = Ti, V, Zr, Hf) and the proposed double-cage $M_{14}C_{21}$ and triple-cage $M_{18}C_{29}$ compounds will depend on finding ways to make these metallo-carbohedrenes in quantity.

Reactions of metal clusters in solution have been extensively studied, but much more research needs to be done in this area related to biological systems, and to homogeneous catalysis by organometallic clusters. Suffice to mention only the Fe–S clusters show what has been done and what can be done. The most important reactions of synthetic Fe–S clusters are ligand substitution and electron transfer. Ligand substitution forms the basis of the core extrusion method[51] used to identify certain clusters present in proteins. Ligand substitution follows a second-order rate law,[52] being first-order in both the cluster and the thiol concentrations. This suggests possibly a four-centered reaction pathway (eq. 7).



$$[Fe_4S_4(SR)_4]^{2-} \xrightarrow{+\,R'SH} \begin{array}{c} S\diagdown \quad\quad \\ S-Fe-S \\ S\diagup\ \vdots \quad \vdots \\ \quad S-H \\ R' \end{array} \xrightarrow{-RSH} [F_4S_4(SR)_3SR'] \qquad (7)$$

The electron transfer reactions involve the following equilibria (8).

$$\underset{4Fe(II)}{[Fe_4S_4(SR)_4]^{4-}} \rightleftharpoons \underset{\substack{3Fe(II)\\+\ Fe(III)}}{[Fe_4S_4(SR)_4]^{3-}} \rightleftharpoons \underset{\substack{2Fe(II)\\+\ 2Fe(III)}}{[Fe_4S_4(SR)_4]^{2-}} \rightleftharpoons \underset{\substack{Fe(II)\\+\ 3Fe(III)}}{[Fe_4S_4(SR)_4]^{-}} \qquad (8)$$

The formal oxidation state of each iron is shown below each complex, but most coordination chemists would expect electron delocalization among all four irons in the cubane so that each would have the same charge. However, there is Mössbauer[53] and NMR[54] evidence that in ferredoxin electron delocalization involves only two of the irons, perhaps because the ligand symmetry is the same at only two irons in the protein. Thus, what is formally represented as 3Fe(II) + Fe(III) is perhaps (Fe^{2+} + Fe^{2+}) + ($Fe^{2.5+}$ + $Fe^{2.5+}$) in the natural protein.

Although *photochemistry and solar energy* is listed as one of the frontiers of inorganic chemistry (Table I), it is not necessary that it be discussed here for most of the papers in this special issue honoring Professor Carassiti deal with inorganic photochemistry.

Not unlike main group element chemistry, *solid state inorganic chemistry* research got a late start in the USA. Yet the ever increasing demand for new materials has resulted in this rapidly becoming one of the most important areas of research at the frontiers of inorganic chemistry. The reason for this is clear, these new materials will be prepared by solid state inorganic chemists, not by materials scientists and physicists who will study the properties of the new materials. Some of the current areas of research in solid state inorganic chemistry are given in Table VI.

Bednorz and Müller[55] reported in 1986 the importance of Cu–O layers in high-temperature (T_c > 35°K) superconductors for the La–Ba–Cu–O system. This was immediately followed a year later by the report of Chu, Wu and coworkers[56] of the "1:2:3" system $YBa_2Cu_3O_7$ with a $T_c \sim 90$°K. This sparked an avalanche of research activity in attempts to make even higher temperature superconductors by making extensive use of the

Table VI. Solid State Inorganic Chemistry

(1) Syntheses of High Temperature Superconductors
(2) Use of Coordination Chemistry in Solid State Syntheses
(3) Preparation of Synthetic Metals
(4) Syntheses of Molecular Magnets
(5) Syntheses of Nonlinear Optical Materials

periodic table to generate analogous mixed metal oxide solids. One example of a recent advance in such studies is provided by Poeppelmeier and coworkers[57] who report the synthesis and structure of a new family of cuprate superconductors, the Ca doped $LnSr_2Cu_2GaO_7$ system (Fig. 4).

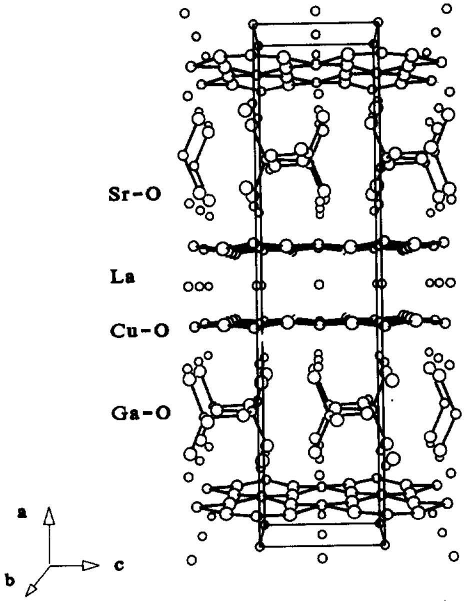


Figure 4. Structure of $LaSr_2Cu_2GaO_7$ as viewed down the *b* axis. Thermal ellipsoids are of arbitrary size.

This is the first time that superconductivity has been achieved in layered cuprates with nonmagnetic and fixed oxidation state cations separating the Cu–O planes, and further theoretical work will be required to clarify the relationships and locations of all energy bands and bonding interactions in these systems. One other example of current research in this area is that of producing highly oriented films of these materials by OMCVD as reported by Marks and coworkers.[58]

To most traditional solution inorganic chemists, solid state syntheses seems more of an art than a science, "shake and bake" and take what you get as product. This is surely an overstatement, but it is gratifying to see that coordination chemistry considerations can be helpful in the design of solid state syntheses. An illustration of this is provided by Ibers and coworkers[59] where they use the concept of linking chains of $NbSe_2$ trigonal prisms with the square planar coordination properties of Pd to form $Nb_2Pd_3Se_8$ (Fig. 5)

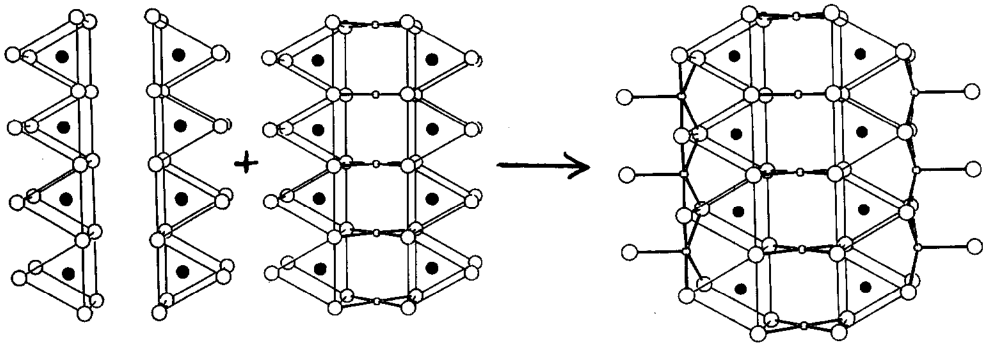


Figure 5. Chains of NBS trigonal prisms combine with Pd to form individual chains of $Nb_2Pd_3Se_8$, where Nb, O Se, o Pd.

This approach considering preferred coordination geometries of metal atoms taken from coordination chemistry promises to be useful in understanding solid state structures and more rational syntheses of new compounds.

The remaining topics listed (Table VI) are synthetic metals,[60] molecular magnets,[61] and nonlinear optical materials.[62] All of these are the subject of numerous publications and very good reviews for each are referenced in the previous sentence, so no discussion is included here except to say these are important areas of research in solid state chemistry.

Finally, *transition metal organometallic chemistry* has become an established area of chemistry with several excellent books[63] written on the subject, but still important frontier research continues to be done in this broad area of chemistry. Some of the current "hot" research topics are listed in Table VII.

Of all eight research topics listed in Table VII, I choose to comment briefly only on the first, that of $(\eta^2\text{-}H_2)ML_n$ complexes. The 1983 Kubas[64] discovery that molecular H_2 behaves as a ligand to form stable metal complexes is in my opinion the most important discovery made in transition metal organometallic chemistry in the past decade. This is because H_2 is ubiquitous in this area of chemistry, being used in important industrial processes such as hydrogenation of alkenes and hydroformylation. In this respect the discovery of H_2 as a ligand ranks in importance with the earlier discovery of the ligand behavior of N_2 by Allen and Senoff.[65] Ironically the two discoveries in each case came after outstanding chemists had at times unknowingly had in their laboratories such metal complexes.

Table VII. Transition Metal Organometallic Chemistry

(1) $(\eta^2\text{–}H_2)\ ML_n$ Complexes
(2) Metal Complexes with C_{60}
(3) Homogeneous Catalysis
(4) "Living" Catalyst Systems and Block Polymers
(5) Stereoselective Catalysts
(6) "Designer" Inorganic Polyoxoanion-based Catalysts
(7) New High Oxidation State Metal Systems
(8) Hydrodesulfurization in Petroleum Chemistry

Since the initial Kubas report there have been hundreds of publications on the syntheses of new $(\eta^2\text{–}H_2)ML_n$ compounds and on their properties. The syntheses of these compounds are of four general types: (1) addition of H_2 to an "unsaturated" precursor as done with the discovery of $W(CO)_3[P(i\text{–}Pr)_3]_2(H_2)$, (2) protonation of metal hydride complexes, (3) reduction of metal complexes with $NaBH_4$, and (4) the photolysis of metal carbonyls in the presence of H_2.

The $(\eta^2\text{–}H_2)M$ bond, believed to be analogous to that of a metal-olefin bond, is shown in Fig. 6.

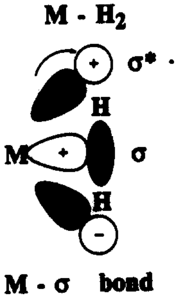


Figure 6. Bonding model for a metal-H_2 complex.

The metal-olefin complex uses the olefin π bonding and antibonding orbitals, whereas the metal-H_2 uses the H_2 σ bonding and antibonding orbitals. It follows from this bonding model that what is required for a stable $M\text{–}H_2$ bond is a good balance of σ-bonding of electrons from H_2 to M and of back σ^* bonding of electrons from M to H_2. In the simplest terms this window of $M\text{–}H_2$ stability will depend on the electron density of the metal. If the electron density on the metal is too low it will not react with H_2, if the electron density is too high then electrons will transfer to the H_2 resulting in the formation of classical metal hydrides. Only when there is a balance of electron density between these extremes will stable $M\text{–}H_2$ systems result (Fig. 7).

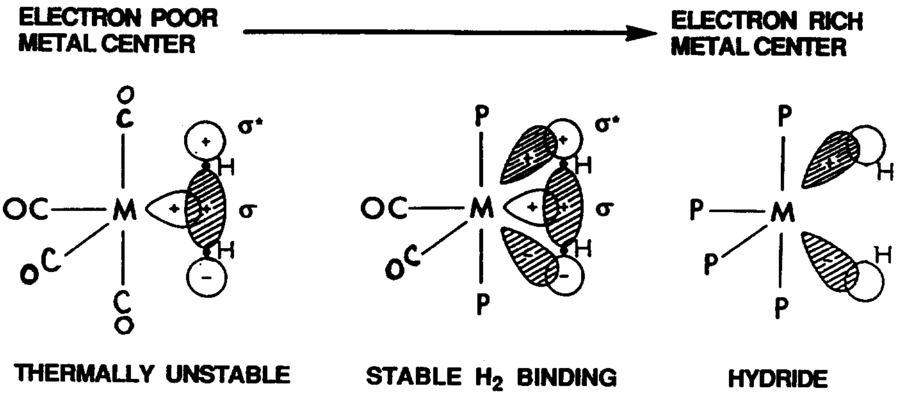


Figure 7. Changing from a system of low electron density on the metal ($M(CO)_4$) to one of high electron density ($M(PR_3)_4$) results in no $M-H_2$ interaction to H–M–H formation. The intermediate electron density on the metal ($M(CO)_2(PR_3)_2$) affords stable $M-H_2$ complexes.

One further point of interest is the strength of η^2-H_2 as a ligand compared to other common ligands.[66] Figure 8 shows that towards $W(CO)_3[P(C_6H_{11})_3]_2$ the heats of binding for H_2 is 5 kcal/mole less than for N_2 and 20 kcal/mole less than for CO.

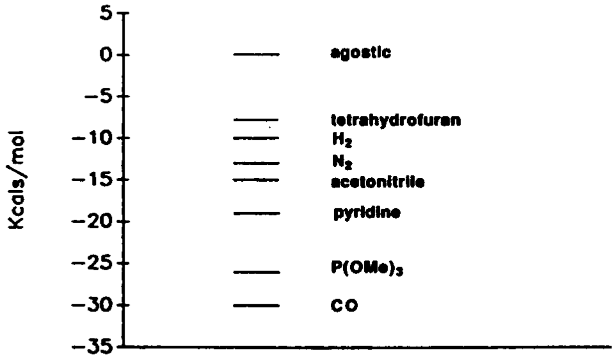


Figure 8. Enthalpies of ligand addition (kcal/mole) to $W(CO)_3[P(C_6H_{11})_3]_2$.

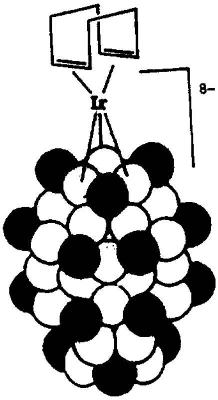
The recent explosion of publications on $(\eta^2-H_2)ML_n$ complexes is certain to continue, because H_2 has a major role to play in transition metal organometallic chemistry.

The remaining seven research topics in Table VII will only be mentioned and a significant reference given for each. Fagan and coworkers[67] have taken advantage of the availability of buckminsterfullerene (C_{60}) to attach metal complexes directly to the exterior of the C_{60} framework by means of reactions in solution to form $M-C_{60}$ bonds. This was accomplished by the reaction of $M(PEt_3)_4$ (M = Ni, Pd, Pt) with C_{60} to afford $(Et_3P)_2M(\eta^2-C_{60})$, or with an excess of the complex to afford $[(Et_3P)_2M]_6(\eta^2-C_{60})$. The structures of these compounds show the metal is bound to only two of the carbons of C_{60} in a manner similar to its bonding to an olefin.

Marks and coworkers[68] have investigated the nature of $Cp_2Th(CH_3)_2$ on surfaces used for heterogeneous catalysis for olefin polymerization, and as a result developed the efficient homogeneous catalyst $[Cp_2ThCH_3]^+[B(C_6F_5)_4]^-$. The active catalyst both on the surface or in solution appears to be $[Cp_2ThCH_3]^+$, which is "coordinatively unsaturated." Grubbs and coworkers[69] and Schrock and coworkers[70] have developed "living" ring-opening metathesis polymerization, which also permits making block polymers.

Taube states[70] "traditional coordination complexes such as the metalammines have not figured prominently in the field of organometallic chemistry. It therefore comes as somewhat of a surprise that the organometallic chemistry of osmiumammines is proving to be very rich." One example of this was his use of $[Os(NH_3)_5]^{2+}$ as a catalyst to selectively hydrogenate benzene to cyclohexene.[72] There has been a long going interest in stereoselective catalysis to produce chiral compounds. Burk and coworkers[20] recently reported excellent success using a special chiral diphosphine ligand in a DUPHOS-Rh(I) catalyzed asymmetric hydrogenation of olefin precursors to desirable chiral amino acids of interest to the pharmaceutical industry.

Finke and coworkers[73] have prepared "designer" inorganic polyoxoanion-based catalysts, using heteropoly acids to make anions of the types $[P_2W_{17}Mn^{III}O_{61}]^{7-}$ and $[(COD)IrP_2W_{15}Nb_3O_{62}]^{8-}$ (VI).



(VI)

The Mn system is an oxidation catalyst of the Groves[74] type, but has the advantage that there is no carbon in the phosphotungstate to oxidize as with the porphyrin ligand. The Ir system has the good leaving group cyclooctadiene (COD) which readily allows for an open coordination site on the metal for catalysis applications.

Hermann and coworkers[75] have prepared $CpRe(O)_3$ and even $CH_3Re(O)_3$ where Re(VII) is the oxidation state of the metal, and they have used these compounds as oxidation catalysts. Studies of this type stress the point that metals in high oxidation states can play an important role in organometallic chemistry. Finally, Angelici and coworkers[76] have investigated the mechanism of the catalysis of hydrodesulfurization (HDS) of thiophenes using organometallic complexes. Such studies are important to a better understanding of the large-scale commercial application of catalytic HDS processes used in the petroleum industry.

In *conclusion* it is sufficient to repeat that inorganic chemistry during the last three or four decades has established itself as a most significant subdiscipline of chemistry. This is destined to continue into the 21st century as more demands are made on higher degrees of sophisticated technology, but most importantly as our better students choose to do research in inorganic chemistry. They will make new, and at present unthinkable, discoveries using all the natural resources available as typified by the elements in the periodic table.

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