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# Forty-Five Years of Chemical Discovery Including a Golden Quarter-Century

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Inorganic chemistry became a passion for me as a graduate student in the 1950s. It was exciting to be part of the renaissance of the discipline, and I am pleased to have contributed to its strength. Physical concepts applied to the understanding of the properties of transition metal compounds guided our work initially. In the 1970s, probably as a direct result of the world abandoning the gold standard, the chemistry of gold was awakened after a long sleep. Much of the chemistry covered in this review of our work relates to novel compounds of gold and the properties they display which have been uncovered during the last 25 years of the 20th century. Stable metal–metal bonded Au(II) and organometallic Au(III) compounds, bi- and trimetallic oxidative addition, phosphorescent species with microsecond lifetimes, gold chains resulting from aurophilic bonding stronger than H-bonding, and recently, gold binding to organic $\pi$ acids have intrigued my group and other gold chemists during this period.

**Introduction.** There are few times in a scientist's career that the opportunity arises to describe a major portion of his own work in a journal as important as *Inorganic Chemistry*. I am delighted to be invited to do this and herein will attempt to describe my primary contributions, especially those that relate to gold chemistry, recognizing that the real work was that of my students and postdoctorals who are acknowledged in the references and tables.

My inorganic chemistry interest began at Valparaiso University when I did undergraduate research studies with Byron Ferguson on the use of thioacetamide, $CH_3C(S)NH_2$, as a reagent to precipitate metal sulfides.[1] With some metal ions, coordination compounds of unknown structure form prior to metal sulfide precipitation. Unfortunately I was able to contribute little then to the knowledge of these materials which subsequently decompose into metal sulfides. Success came easier with $\beta$-diketonate studies at the Massachusetts Institute of Technology under the guidance of F. A. Cotton. Although I had entered MIT to work in radiochemistry, Charles Coryell encouraged me to explore the developing opportunities in physical inorganic chemistry with Cotton. The structural discovery, using the rudimentary X-ray crystallography of the day, that the nickel(II) complex of acetylacetone, $Ni(acac)_2$, was a trimer[2] (Figure 1) with a paramagnetic, six-coordinate Ni(II) was novel. It was not the "high-spin" square planar complex most had suggested it to be. Later we showed spectroscopically that $Ni(acac)_2$ was a diamagnetic, planar molecule in the gas phase.[3] Many new results were obtained[4] which related to the oligomerization of metal $\beta$-ketoenolates generally, including base adducts of some of these complexes. After I wrote a major review covering metal $\beta$-ketoenolates in 1966,[5] I remained interested in the synthesis and properties of metal complexes of these ligands for many more years. Some of our most significant work that followed related to the influence of the Jahn−Teller, JT, effect[6] (Figure 2) on the structural and spectroscopic properties of metal complexes with $\beta$-ketoenolates and related ligands.

**Jahn−Teller Studies.** Our first effort with group 11 chemistry was developed with $\beta$-ketoenolate complexes of Cu(II). The JT behavior of six-coordinate Cu(II) and then Cr(II) and Mn(III) complexes was a focus of our work for a

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Fackler is a Distinguished Professor of Chemistry (since 1987) at Texas A&M University. Born and raised in Toledo, OH, he attended parochial and public schools there through high school and the Massachusetts Institute of Technology in 1952. He graduated, B.A., from Valparaiso University (Indiana) in 1956, and returned to MIT to obtain a Ph.D. (1960), where he studied under the current Texas A&M's Professor F. A. Cotton. He is married to Naomi P. Steege, and they have five children. He taught at U. C. Berkeley (1960–1962) and Case Western Reserve (1962–1982), where he headed the Chemistry Department from 1972 to 1977, becoming the Teagle Professor in 1978. He was a visiting Associate Professor at U. C. Santa Barbara in 1969. He came to Texas A&M as Dean of the College of Science (1983–1991) and Professor of Chemistry (1983–1987). He has advised over 30 Ph.D. and over 40 postdoctoral students and has published over 300 research papers and one undergraduate text and two edited books. Fackler has been active in several research/education professional activities including the American Chemical Society (Cleveland section chair, 1975, and Inorganic Division chair, 1979), National Science Foundation and National Institutes of Health sponsored research programs, the American Association for the Advancement of Science (Fellow and Division Chair elect), Undergraduate Research Programs (director for six years), Fulbright and NSF programs in Colombia, South America, Gordon Research Conferences on Inorganic Chemistry (chair, 1979), Science Education (chair, Europe, 1994). Board of Trustees (chair, 1989). Among special honors are a J. S. Guggenheim Fellowship, the Morley (1987), Southwest Regional (1990), and Distinguished Service in the Advancement of Inorganic Chemistry (2001) Award of the American Chemical Society, and the Manchot Research Professorship (1992) at the Technical University of Munich, Germany, and several named lectureships. He was a University Distinguished Lecturer at Texas A&M in 2000. He has an Honorary Doctorate from Valparaiso University. Fackler is currently on the editorial advisory boards of *Cluster Science* and *Inorganic Chemistry* and is editor of *Comments on Inorganic Chemistry*. He edited the *Modern Inorganic Chemistry Series* for Plenum until 2000. He currently edits *Profiles in Inorganic Chemistry* for Kluwer/Plenum.

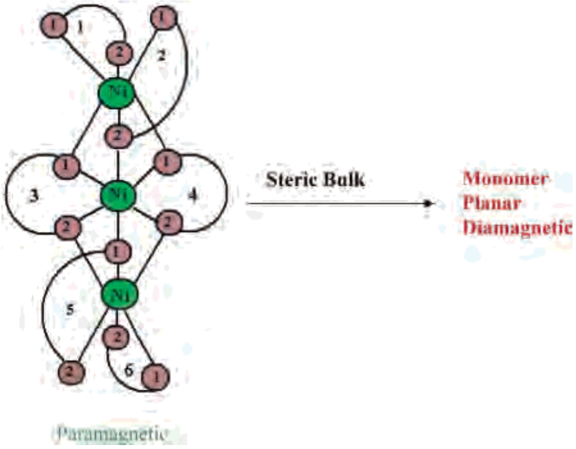

**Figure 1.** Nickel acetylacetonate trimer structure and the change that takes place when bulky $\beta$-ketoenolate ligands are used.

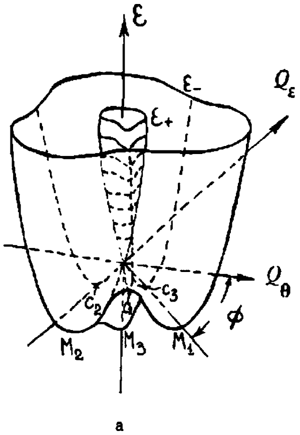

**Figure 2.** Jahn–Teller potential energy surface.

number of years and involved the studies of some gifted people.[7–11] Optical powder reflectance, single-crystal polarized electronic, and electron paramagnetic resonance spectroscopic studies were important, and the EPR spectra showed that JT distortion barriers could be very small, even in the solid state. A liquid crystal technique we developed later was applied by Hoffman[12] to studies of inorganic and biological materials. This work showed that the EPR of "flat" molecular metal $\beta$-ketoenolates could be used to determine spin-polarization directions in frozen liquid crystals.[13] In our Jahn–Teller studies, we were fortunate to recognize that the previously reported, nearly octahedral structure of the $MnO_6$ bonding in $Mn(acac)_3$ was incompatible with its visible spectrum and successfully showed[14] that the molecule actually is tetragonally distorted. The previously reported

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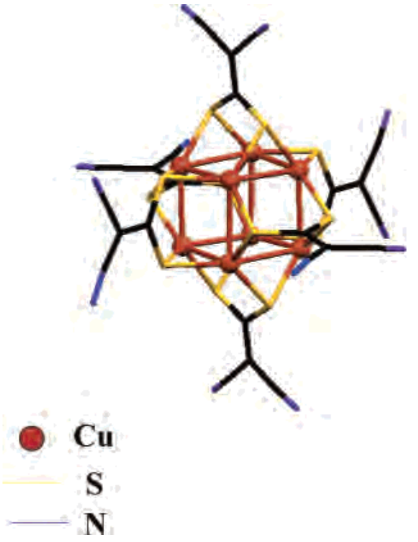

**Figure 3.** An X-ray structural drawing of the $[Cu_8(i\text{-}MNT)_6]^{4-}$ showing the cube of copper atoms. It is surrounded by the nearly regular icosahedron of sulfur atoms giving the anion a $T_h$ point group symmetry.

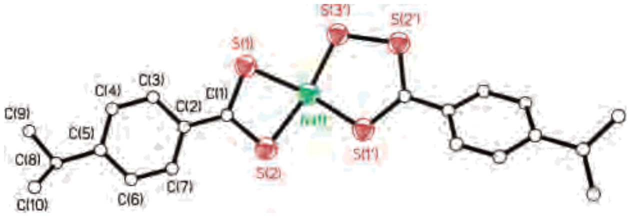

**Figure 4.** Sulfur-rich dithiocumate chelate ring formed by sulfur addition to the Ni(II) dithio acid complex.

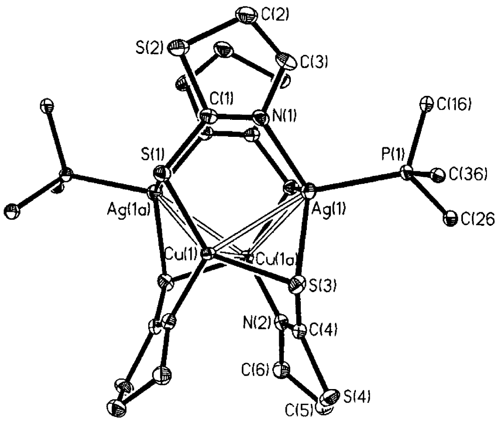

**Figure 5.** Butterfly structure of the Cu(I)/Ag(I) MTP (MTP = 1-mercaptothiazoline) and Cu(I) clusters and their adducts with phosphines and amines.

structure of $Mn(acac)_3$ apparently was that of $Cr(acac)_3$, accidentally mounted on the diffractometer by a technician not familiar with the different colors of these materials. V. Day later found[15] another tetragonally distorted polymorph of $Mn(acac)_3$. Incidentally, we also demonstrated that water forms H-bonds to this and other metal $\beta$-ketoenolates, producing a chelated water O−H stretch vibration seen in the infrared.[16] A very successful and enjoyable outcome of our Jahn−Teller work was my editing of the important comprehensive "Modern Inorganic Chemistry Series" volume on the Jahn−Teller effect by Isaac Bersuker.[6]

**Metal−Sulfur Chemistry.** Metal−sulfur coordination chemistry was developed very successfully in my laboratory with the advent of Dimitri Coucouvanis. Dimitri's work involved excellent syntheses with 1,1-dithiolate ligands. This led to the first copper(I) metal cubane structure[17] (Figure 3) as found in the anion $[Cu_8(i\text{-}MNT)_6]^{4-}$. Dimitri also developed the chemistry of "sulfur-rich" complexes with their disulfide containing chelate rings (Figure 4).[18] Other students[19] also contributed substantially to this new metal−sulfur chemistry.[20] David Fries[21] (along with Kerro Knox) taught me how to do X-ray crystallography. Al Sattelberger taught our group much organometallic synthesis as a postdoctoral, although we published only one paper together.[22] Recently, my group has returned to copper− and silver−sulfur cluster chemistry with the first result being the beautiful butterfly cluster structures (Figure 5) of the mercaptothiazolines.[23] We found that dithiophosphates[24] not only readily form typical tetrahedral clusters like the 1,1-dithiolates but also form cubanes, but with an anion such as $S^{2-}$, $Br^-$, or $Cl^-$ in the center of the cube[25] (Figure 6). A former student has continued studies in this area and has found that $Se^{2-}$ also can be incorporated into a $[Cu_8Se_{12}]$ cube.[26]

The chemistry of sulfur ligand complexes like the dithiophosphates, -phosphonates, and -phosphinates, xanthates, dithiocarbamates, and dithioacid derivatives has fascinated my group[27] for nearly 40 years.[28] Could it have been the industrial job offer that I received when I was finishing my Ph.D., or my undergraduate research, that stimulated my desire to do research with these molecules? Union Carbide had wanted me to work on xanthate flotation agents. After Coucouvanis left Case Western Reserve University, he

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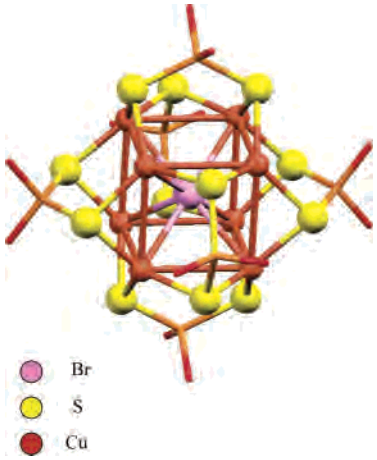

**Figure 6.** The skeletal portion of the cation of {Cu$_8$[S$_2$P(OC$_3$H$_7$)$_2$]Br}PF$_6$.

continued to be a leader in the development of new chemistry of metal−sulfur compounds, particularly those compounds relevant to biological processes.[29]

**Catalysis.** Interest in metal-based catalysis has stimulated work in my group for many years although I have published relatively little in this area. It is my general belief that industry often is better poised to make practical advances than academicians, although clearly there are many prominent exceptions. Ni(SacSac)ClPR$_3$ and its chemistry[30] got me interested in Zeigler−Natta catalysts. As a result I consulted with BFGoodrich and Firestone (now Bridgestone) for many years on Zeigler elastomer polymerization catalysis,[31] and on metal−sulfur chemistry related to vulcanization[32] and the adhesion of rubber to steel belts. This is copper−sulfur chemistry since the steel cord in tires is coated with copper which bonds to the sulfur linkages in the vulcanized rubber. One of the nickel-based catalytic systems that I worked on actually became a commercial process for production of *cis*-polybutadiene. I have worked at Texas A&M with an engineering colleague, Aydin Akgerman, and a few postdoctorals on metal-based hydroformylation and hydrogenation catalysis in supercritical CO$_2$.[33] Gold cluster catalysis also has taken an important place in my work[34,35] through collaboration with my colleague D. Wayne Goodman.

**Gold Chemistry Begins.** My interest in gold chemistry began in the 1970s when my second Greek student asked about doing some gold(III) chemistry. Since other $d^8$ metal complexes long had been studied in our group and we were recognizing catalytic potential for some of them, I thought that gold(III) compounds might be able to produce stable organometallic species that would mimic organometallic intermediates possibly present in commercial catalytic processes. The stability of the Au−C bond seemed to be more pronounced than Rh−C or Pd−C bonds. Furthermore Au was not then known, nor now, to form binary hydrides. This latter fact would reduce the likelihood that organometallic intermediates would decompose by hydride elimination.[36] Reduction to the element was a potential problem, however. The neutral ylides, CH$_2$Y, where Y = PR$_3$, SOR$_2$, or SR$_2$, looked like good candidates for the formation of stable, nonreducing Au−C bonds (vide infra). This turned out to be the case, and we successfully synthesized and characterized the first air-stable gold(III) compounds which contained only $\sigma$ Au−C bonding[37] (Figure 7).

The sulfoxide- and sulfur-ylide analogues of the phosphorus Wittig reagents are particularly interesting since the ylides themselves are very reactive. When phosphines and other bases are added to a solution containing the gold ylide complex, the ylide is removed in situ to react in its usual manner with ketones or other carbonyls in the solution.[37] The only other tetracoordinate Au(III) complex with four

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**Figure 7.** The structure of $(CH_3)_3AuCH_2PPh_3$.

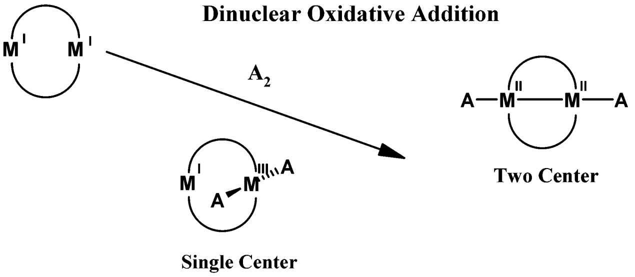

**Figure 8.** The two isomers formed upon oxidative addition of $A_2$ to a dinuclear ylide complex.

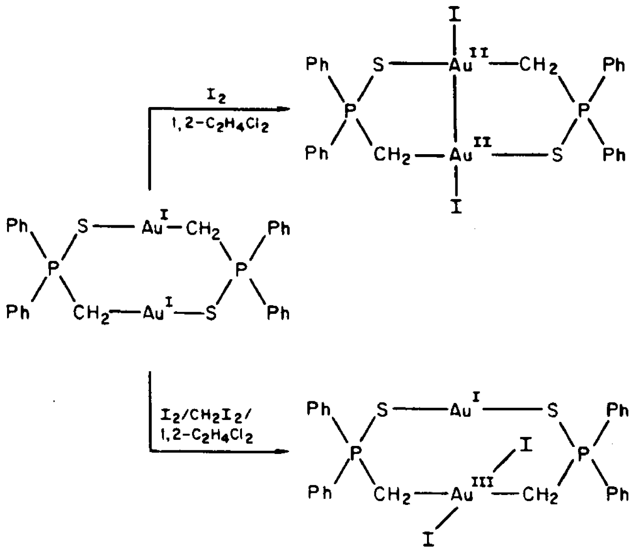

**Figure 9.** Line drawing of the Au(III)/Au(I) and Au(II)−Au(II) isomers of the MTP complex.

Au−C aliphatic $\sigma$ bonds known at the time, the anion $[Au(CH_3)_4]^-$, is pyrophoric in air. This remarkable stability of the ylide complexes appears to be attributable to the presence of positive charge on the P or S atom which gives rise to a large, electron-holding dipole moment for the compounds.[38,39] This helps prevent decomposition by the well-established Kochi electron-transfer mechanism.[40]

**Metal−Metal Bonding in Oxidative Addition.** Hubert Schmidbaur[41] at the Technical University in Munich (Garching) also recognized the importance of ylide complexes of gold and reported that the ylide anions produced dinuclear Au(I) compounds which display a fascinating oxidative addition chemistry (Figure 8). Although the structure was not determined at that time, Schmidbaur suggested that $CH_3I$ added to $[Au(CH_2)_2PR_2]_2$ to form a stable Au(II) compound, $CH_3[Au(CH_2)_2PR_2]_2I$. This was very interesting to me[42] and started us on a very fruitful chemistry that related to the formation of a Au(II) metal−metal bond in the oxidative addition process. Bosnich[43] had demonstrated that adjacent metal ions inhibit oxidative addition by the very presence of a “positive” metal atom being near to the metal atom undergoing the oxidative addition. Goddard[44a] had suggested that, for metal atoms with a low-lying excited state, promotion to an open-shell excited state is required in oxidative addition. As a result we rationalized that, if an adjacent metal atom is capable of stabilizing this excited state through acceptance of electron density from the excited state or by metal−metal bond formation, Schmidbaur’s interesting oxidative addition might be explained. Formation of a Au−Au bond in the excited state could promote the oxidative addition process for these dinuclear ylide compounds by stabilizing this state. Our work over the next few years established the formation of a short Au(II)−Au(II) bond in the products of oxidative addition. Indeed, Che and Miskowski[45] recently demonstrated by resonance Raman spectroscopy that Au−Au bond formation occurs in the photoexcited state of related dinuclear gold(I) compounds.

A large number of new substances resulted from competition with the Garching (Munich) group, in which the dinuclear Au(I) complexes were converted into new metal−metal bonded Au(II) species.[46,47] New dinuclear Au(III) compounds also resulted from further oxidation and rupture of the metal−metal bond. The isolation and X-ray structural characterization of both the Au(II)−Au(II) and Au(I)···Au(III) isomeric products[48] with the anionic ligand diphenylmethylenethiophosphinato, MTP, $[CH_2P(S)Ph_2]^{2-}$, was a major breakthrough for us (Figure 9). Many of the ylide materials studied in our group have been reviewed

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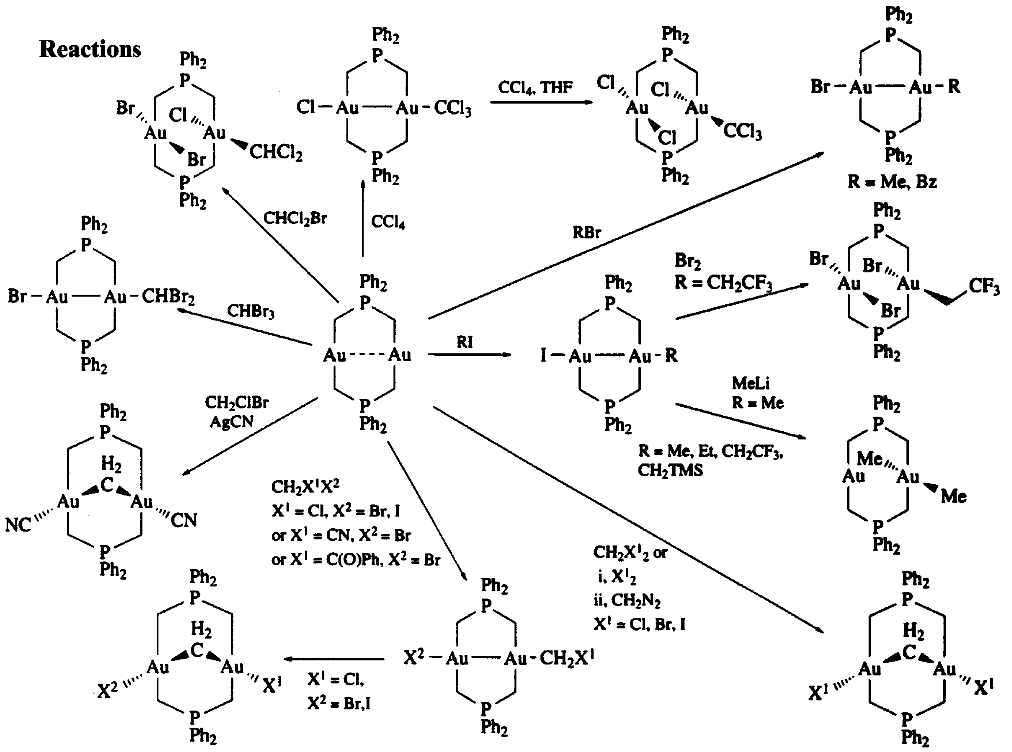

**Figure 10.** Reactions of dinuclear gold ylide complexes.

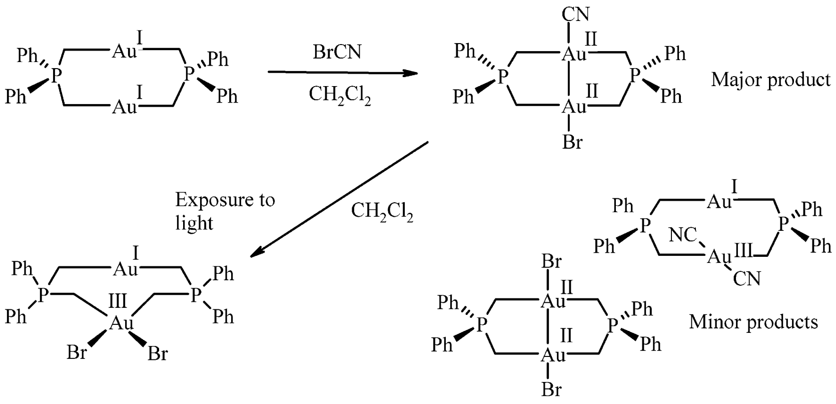

**Figure 11.** Various isomers of dinuclear gold ylides. Synthesis of the *cis*-Au(III)···Au(I) dibromide.

(Figure 10).[40] While Mazany pioneered the MTP work and moved with me from Case Western Reserve to Texas A&M, it was Hal Murray, my first postdoctoral at A&M, who guided my group and taught them much excellent synthesis. We even used colored glassware and put yellow filters on fluorescent lights to prevent them from destroying some of our light sensitive Au(I) compounds. Murray also helped write up the results which came fast and furiously at the time I was learning how to be a dean. I kept my group in the Laboratory for Molecular Structure and Bonding directed by Al Cotton since this ensured a continuous, critical evaluation of the work. A good student crystallographer of mine[49] and Larry Falvello, Cotton's expert crystallographer at the time, helped make sure that the X-ray crystallography was done correctly. All of our students learned this tool and used it well.

I believe that our success with X-ray structures prompted Schmidbaur to develop routine use of crystallography in his laboratory, a tool he has exploited beautifully. A few years later, Richard Staples[50] contributed much to the X-ray crystallography of my group, as he still does periodically in his current position at Harvard. A synthetic outcome (Figure 11) of the work with the ylide complexes of gold was the success we achieved in isolating and characterizing a number of different isomers of dinuclear gold(II) and gold(III). The various diphenyl ylide isomers of gold(II) and gold(III) that have been obtained and characterized are pictured (Figure 12).

A very important finding in the dinuclear gold chemistry is that the ground state of the closed-shell Au(I) system has a HOMO which is "antibonding" between the two Au(I) centers. The distances, however, between the centers are

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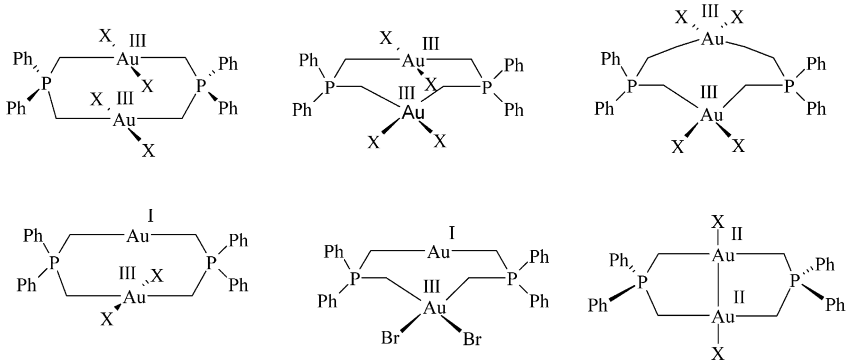

**Figure 12.** Isomers of Au(II)−Au(II), Au(III)···Au(I), and Au(III)···Au(III) ylide complexes isolated and characterized structurally.

relatively short, shorter than van der Waals Au(I) separations were predicted to be. In the dinuclear dithiocarbamate, [Au($S_2CNEt_2$)]$_2$, this distance is so short (less than 2.8 Å) that interpreting the frequency of the Au−Au stretch was not easily nor correctly done[51] until long after it became known that the molecules undergo oxidative addition with halogens.[52] This special feature of the bonding of gold compounds has been labeled as "aurophilic" bonding by Schmidbaur even though the symmetry of the orbital functions of the ground state which are directed along the intermetallic axis is antibonding. The origin of the aurophilic behavior is thought to be related to relativistic and correlation effects associated with the heavy Au(I) atoms and their 6s valence shell.[53] The role of the relatively accessible bonding excited state in contributing to this aurophilic bonding has not been well evaluated, although it is obvious from emission spectra that we and others have obtained that the triplet excited state in dinuclear gold compounds may be as close as 2 eV from the ground state. For closed-shell ions, this is a very small energy gap.

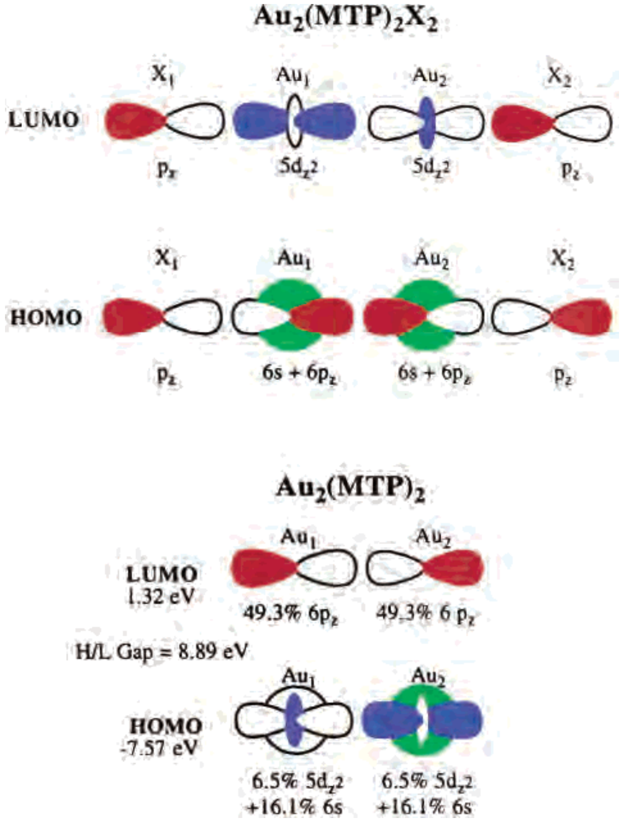

**Figure 13.** Orbital shapes for the HOMO and LUMO and Fenske−Hall energies for the Au(I) and Au(II) MTP complexes.

Most of us learned early in our chemical career that electron pair bonds require two electrons and two orbitals, one from each of the atoms in the bond. For the products obtained in the oxidative addition of halogens to dinuclear Au(I) compounds, [AuL]$_2$, the three new bonds formed involve an electron from each of the two Au(I) atoms and two electrons from the $X_2$. One pair of these electrons is used to form the metal−metal bond in this system (Figure 13). In the Goddard argument, the two gold electrons available for the metal−metal bond are a result of promotion from the filled $d_{z^2}$ orbital on each Au(I) to the hybrid (d-sp) orbital along the Au−Au axis. Thus it was most exciting when David Briggs discovered[54] that the trinuclear [$Au^I(MTP)_2Pt^{II}(MTP)_2Au^I$] complex (Figure 14) had produced an oxidative addition product across the metal atoms with new metal−metal bonds between each Au−Pt atom pair. The formation of four electron pair bonds (two Au−X and two Au−Pt) requires that the [$Au^IPt^{II}Au^I$] unit contribute six of the eight electrons and six of the orbitals needed for the new product. The expected result, especially if the central metal atom is only a spectator, is seen in the upper sketch of Figure 14. Once the structure was obtained, we realized that the Pt(II) atom in the oxidized product looked structurally like Pt(IV), with six covalent bonds surrounding it. It became apparent that the Pt(II) atom in [Au(MTP)$_2$Pt(MTP)$_2$Au] was being promoted from its ground state with its filled $5d_{z^2}$ orbital (square planar $PtS_4$ coordination), into an open-shell state, analogous to the excitation of the Au(I) atoms. The empty $6p_z$ orbital (on Pt(II)) directed toward the Au atoms provided the accessible accepting orbital (Figure 15). The [$Au^IPt^{II}Au^I$] cluster had undergone an oxidative addition in which the trinuclear unit had lost two electrons to the halogen. As far as "oxidation" was concerned, the [AuPtAu] unit in the product can be formulated as either [$Au^IPt^{IV}Au^I$]$^{6+}$ or [$Au^{II}Pt^{II}Au^{II}$]$^{6+}$. While the latter formula-

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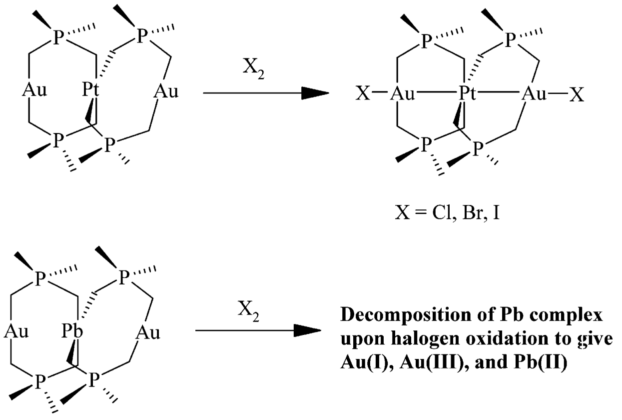

**Figure 14.** The oxidative addition of halogens to trinuclear complexes. Addition occurs to Au−Pt−Au but fails with Au−Pb−Au. Oxidative addition at single gold center for the Au−Pt−Au complex has not been achieved.

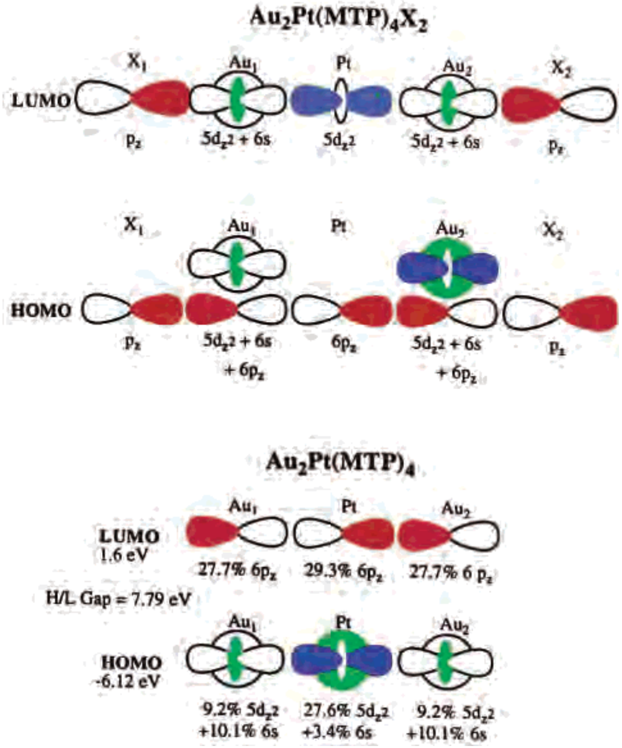

**Figure 15.** Representation of the HOMO and LUMO orbitals for the trinuclear AuPtAu MTP complex and its oxidized product.

tion for the gold atoms better explains their structural features, it is abundantly clear that all three metal atoms are involved in a process which takes $[AuPtAu]^{4+}$ to $[AuPtAu]^{6+}$. To date we have not isolated a one electron oxidation product. Halide exchange for the $X[Au(MTP)_2Pt(MTP)_2]X$ products was found to be facile, and other terminal ligands can be attached to the oxidized cluster.[55] Furthermore, if the central atom is Pb(II), a four-coordinate ion with no readily available empty orbital directed toward the Au(I) centers to which electron promotion can occur, halogen oxidation produces Au(III), Pb(II), and Au(I) decomposition products (Figure 14). Incidentally, the coordination about the Pb(II) is that of a flattened tetrahedron.

*The important outcome of this work is that neighboring atom electronic features can promote or inhibit oxidative addition depending upon the ease of metal−metal bond formation between the metal atoms involved.*

Cotton has since discovered a number of similar trinuclear systems[56] with other metals. When one of the elements involved cannot participate in metal−metal bond formation because there are no available electrons or orbitals or both, such as in $[Au^IPb^{II}Au^I]^{4+}$, oxidative addition does not occur. With gold, the trinuclear $[Au^IPt^{II}Au^I]^{4+}$ system unfortunately appears to be unique, to date, although one might anticipate that similar results could occur with $[Au^IIr^IAu^I]^{3+}$ or $[Au^IPd^{II}Au^I]^{4+}$ clusters. The $[Au^I(ylide)_2Au^{III}(ylide)_2Au^I]^+$ (ylide = $(CH_2)_2PPh_2$) cation, which is electronically similar to the $[Au^IPt^{II}Au^I]^{4+}$ cluster, apparently shows no oxidative addition chemistry.[41,57] The isoelectronic mercury complex, $[Hg^{II}(MTP)_2Pt^{II}(MTP)_2Hg^{II}]^{2+}$, also does not undergo oxidative addition with halogens.[41b]

Chains of metal atoms able to undergo oxidation and metal−metal bond formation now exist. With gold, the longest chain to date involves six gold atoms with terminal $C_6F_5$ units.[58] However, not all Au−Au bonds are alike in this system, and reductive elimination to a stable hexanuclear species does not take place.

Regarding metal−metal bonded species, Yam has successfully isolated and characterized an unsupported Au(II)−Au(II) compound, with no bridging ligands, the only example to date.[59]

The absence of formation of a stable metal−metal bond by oxidative addition did not preclude interesting properties from being found with many other dinuclear and trinuclear Au(I) compounds. The relatively accessible excited state with Au(I), which is capable of being perturbed by different ligands and neighboring metal atoms, has led to a rich photoluminescence chemistry with Au(I) compounds. This has been especially true with those compounds that have intermolecular aurophilic bonds. $[Au(MTP)_2]$, for example, forms chains of gold atoms with intermolecular distances, 3.2 Å, only slightly longer than the 3.0 Å intramolecular distance. The solid state material is strongly luminescent. The trinuclear $[Au^IPt^{II}Au^I]^{4+}$ and $[Au^IPb^{II}Au^I]^{4+}$ species also form linear chain materials which are luminescent in the solid state. The latter compound also shows semiconducting properties.[60] Interestingly, this compound, upon crystallization with THF, displays a very different color and a different emission spectrum from the compound formed without any solvent in the lattice. These unusual optical properties suggest the possibility of device formation such as has been established by Mann[61] for linear chain Pt compounds and recently by Eisenberg[62] with a Au(I) dithiocarbamate.

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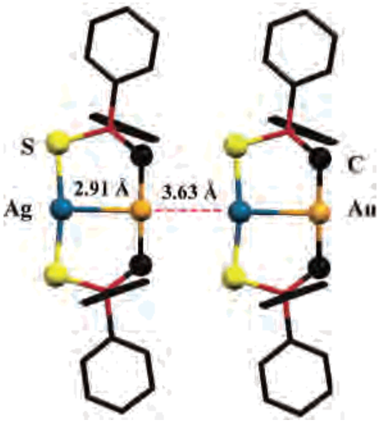

**Figure 16.** Linear chain structure for the mixed-metal Au(I)···Ag(I) MTP complex.

**Table 1.** Intramolecular and Intermolecular Distances Observed for Dinuclear MTP Complexes[a]

| M, M′ | intramolecular | intermolecular |
|---|---|---|
| Au, Au | ∼3.0 | ∼3.2 |
| Ag, Ag | ∼3.0 | ∼3.2 |
| Ag, Au | ∼2.9 | ∼3.6 |

[a] All three compounds crystallize in the same space group (*C*2/*c*).

Before I comment on developments from our laboratory regarding the optical properties of Au(I) compounds, I want to mention that the Ag(I) ylide system also has intrigued us. Schmidbaur[63] reported a detailed synthesis[64] for the dinuclear complex $[Ag(CH_2)_2PMe_2]_2$. Over several years I had students try to repeat this synthesis but always without success. After having a couple of postdoctorals fail to reproduce it, I suggested to a CWRU undergraduate that the problem may be light sensitivity. By avoiding fluorescent lights, fixtures not present in the Schmidbaur laboratory when the synthesis was performed there, the synthesis was successful. Hence when I moved to Texas A&M, I covered all fluorescent lights in our laboratory with UV-blocking translucent paper and we did most of our early work in Schlenk equipment made from UV-blocking glass. Later Suning Wang prepared[65] and characterized the $[Ag(MTP)_2]_2$. Recently the mixed-metal complex $[AgAu(MTP)_2]$ (Figure 16) has been prepared[66] and characterized. This compound has a shorter M−M intramolecular interaction than either the homonuclear Au(I) or Ag(I) products. The mixed-metal structure, unlike the Au(I) and Ag(I) complexes but like one of the isomers of the $[HgAu(MTP)_2]^+$ cation,[67] has two M−S (Ag−S) bonds on one metal center. It is believed that the polarity of the metal−metal interaction contributes to the short intramolecular distance observed (Table 1). Incidentally, Suning Wang also contributed substantially to the discovery of a new insertion reaction[68] and the syntheses and characterization of the AuTl,[69] AuHg,[70] and AuPbAu[71] complexes.

**Gold Clusters.** I would be remiss not to describe here the contribution another postdoctoral, Richard Winpenny, made to gold cluster chemistry while with me.[72] A close-packed “magic number” $Au_{55}$ structure had been proposed for a cluster involving $PPh_3$ and halide coordination.[73] Lou Pignolet had repeated the synthesis of this species, and by using $^{252}Cf$ plasma desorption mass spectroscopy, a tool invented at Texas A&M by R. D. Macfarlane, we were able to demonstrate that the synthetic procedure reported in *Inorganic Syntheses* gives, in our hands, a mixture of gold clusters.[70] Catherine McNeal, Macfarlane’s scientific colleague, provided the expertise for the interpretation of the spectra. The most reasonable conclusion was that the clusters synthesized are composed of linked icosahedra, similar to the mixed Ag/Au clusters characterized structurally by Teo.[74] This work led to our subsequent contributions to the gold cluster catalysis currently underway in collaboration with the Goodman group.[75]

The chelating ylide and MTP chemistry suggested that dithiophosphates and related sulfur compounds of Au(I) might produce similar dinuclear Au(I) complexes of interest. Little work had been reported previously. This chemistry was pursued beautifully by a Ph.D. student who synthesized many new dithiophosphates, -phosphinates, and -phosphonates.[76]

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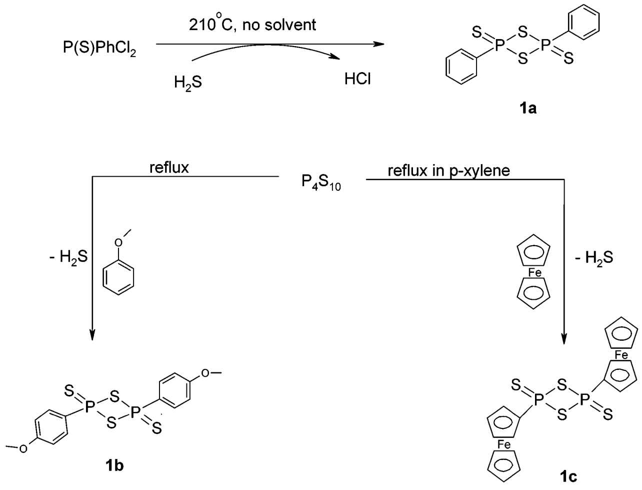

Figure 17. Synthesis of new dithiophosphonate precursors.

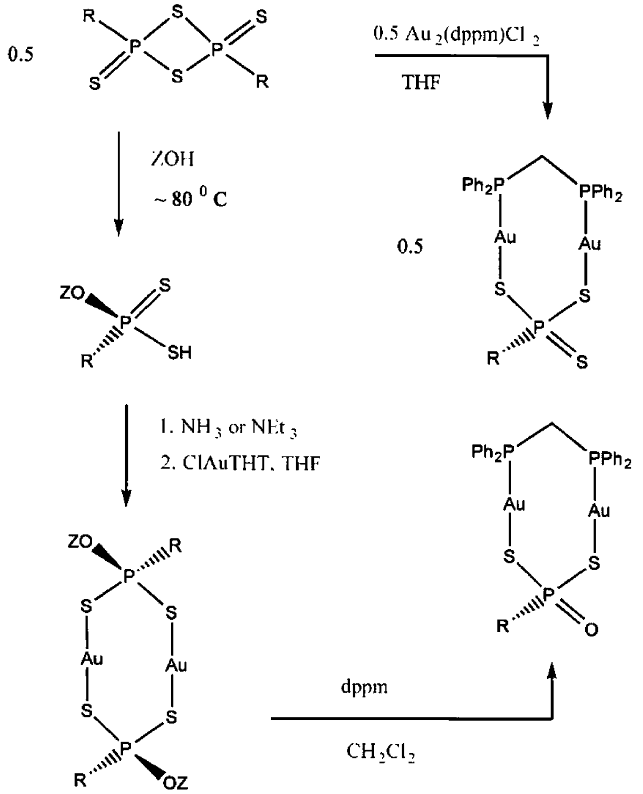

Figure 18. Synthesis of gold dithiophosphonates and related materials.

Related work is continuing in my laboratories. New synthetic procedures (Figures 17 and 18) have been developed, and a very nice example of reversible oxidative halogen addition and elimination has been achieved (Figure 19).[76] The chemistry has opened up a new class of luminescent materials with considerable versatility.[77] Linear chain products form with many of these dithiophosphorus compounds and show room temperature emission spectra with low-energy bands not present in the isolated molecules, which are generally luminescent only at low temperatures.

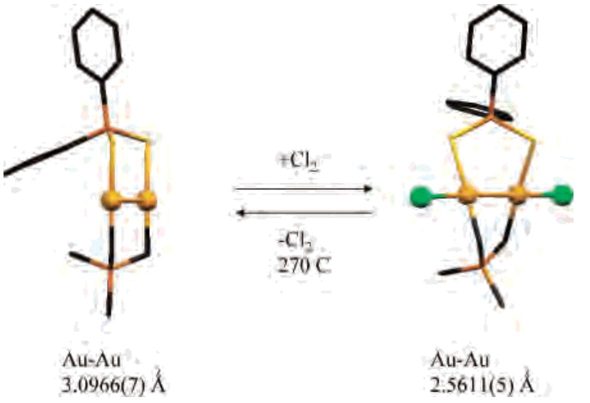

Figure 19. Reversible oxidative addition of chlorine to a dinuclear, mixed-ligand dithiophosphinate/ylide complex of dinuclear Au(I).

**Emission Spectra.** The emission spectroscopy of Au(I) compounds has led to many interesting results in our group, a portion of which has been reviewed.[78] Visible luminescence is observed in mononuclear, three-coordinate Au(I) compounds in the solid state or in solution. These luminescent compounds often show an excitation to a state which lives for microseconds, a surprising result considering the large spin−orbit effects for heavy atoms. Dinuclear and other aurophilically bonded Au(I) compounds generally also luminesce under UV excitation, but some of them do this only at temperatures below room temperature.

With strong donors such as phosphines and sulfur ligands, ligand-to-metal charge transfer, LMCT, can occur to an excited state which converts to a metal-centered triplet in the complexes. For the three-coordinate phosphine complexes, the excited state appears to be a triplet state involving an orbital perpendicular to the trigonal plane of the molecule and an orbital in this plane. A transition back to the ground state singlet is symmetry and spin forbidden. This excited state is easily perturbed by ligands that can coordinate to the trigonal gold axis to produce four-coordinate, “tetrahedral” products. With the triphosphaadamantane ligand, TPA (Figure 20), it was possible to isolate and characterize four-coordinate, nearly perfectly tetrahedral, nonluminescent products.[79] However, with a 3:1 ligand-to-metal ratio in a water solution, the liquid phase is strongly luminescent. The luminescence is pH dependent since the pH influences the equilibrium distribution of two-, three-, and four-coordinate products in solution, with only the three-coordinate species being emissive. Unfortunately the three-coordinate TPA product could not be isolated. However, with the tris-sulfonated triphenylphosphine ligand, TPPTS (Figure 20), the Au(I) product exists as a three-coordinate species in water even with excess TPPTS present. Thus with some good fortune, a student was able to isolate crystals of the cesium

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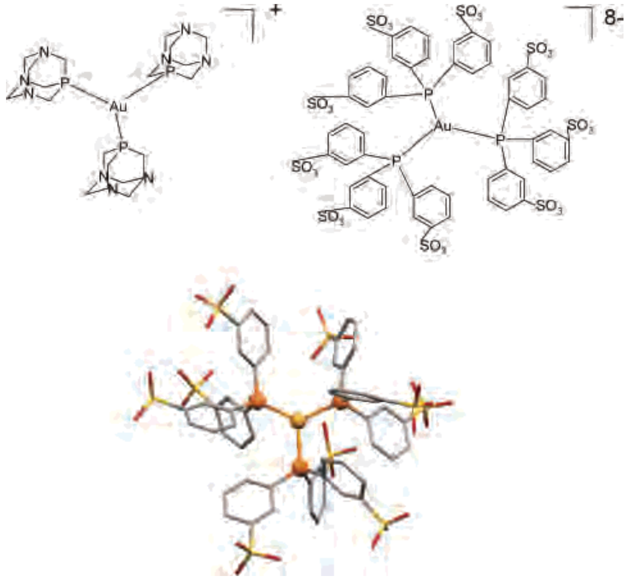

**Figure 20.** Water soluble complexes of Au(I) with TPA and TPPTS ligands. The X-ray structure of the $[Au(TPPTS)_3]^{8-}$ anion as found in the cesium salt is seen in the color drawing.

salt and a good crystal structure was obtained.[80] The large size of the TPPTS ligand prevents a fourth TPPTS ligand from bonding to the Au(I). TPA and other small ligands will quench the visible luminescence, however, presumably by interacting with or coordinating to the Au(I) to form a four-coordinate complex. Water which remains present in the crystal lattice does not quench the luminescence. A paper describing details of this work is in press.[80b] The geometry about the Au(I) clearly influences the emission spectra for these mononuclear compounds, but electron transfer quenching also can take place from halocarbons and other "oxidizing" ligands. The possibilities for spectrochemical sensing applications are abundant.

The first evidence of visible luminescence with gold compounds was discovered by Zvi Dori.[81] Gray[82] and a number of his former students, and their students, also have contributed substantially to the understanding of luminescence in closed-shell systems. Roundhill has written a book which has surveyed some of the advances in this area.[83] For studies of gold, my review with Forward and Assefa[78] and the review by Bowmaker[84] should be consulted. A recent review paper by Yam[85] focuses upon results from her group with phosphine complexes. With metallic species in which a metal−metal bond can be formed in the excited state, excitation and emission are described in terms of LMMCT (metal−metal). The implication in LMMCT nomenclature is that the excited state is produced from excitation out of largely a ligand-based ground state and that this excited state involves more than a single metal center. In this case metal−metal bond formation occurs in the excited state.[85] Clearly this also is the situation with many compounds studied in our laboratory. While this work will not be reviewed and critiqued here, it is important to point out that intermolecular metal−metal interactions produce some very interesting results, some of which appear to lead to the formation of electronic devices.[86]

With dinuclear Au(I)···Au(I) compounds such as the dithiocarbamates, dithiophosphates, and related materials which have both intermolecular and intramolecular aurophilic interactions, emission (from the solid) can be sensitive to the presence or absence of small molecules in the lattice.[62] Furthermore the absorption (and emission) energies vary with changes that can occur in the Au(I)···Au(I) distance which can be influenced by temperature or the presence of small molecules in the lattice.[87] We have noted that the presence of intermolecular interactions in a series of dithiophosphates and dithiophosphonates leads to the appearance of a low-energy emission band which is absent in similar compounds which have no intermolecular Au(I)···Au(I).[88] We have examined this with a number of new dinuclear dithiophosphinates and, so far, find no exceptions. It appears that intermolecular aurophilic interactions induce the formation of a relatively long-lived LMMCT transition that is perturbed by the neighboring Au(I) atoms. The results of Eisenberg with the dithiocarbamate complex $[Au(S_2CN(C_5H_{11})_2]_2$, which changes crystal structure upon reaction with VOCs (volatile organic compounds), appear to be similar.[62]

**Trinuclear Au(I) Compounds.** An especially interesting class of Au(I) compounds are those materials that have three Au(I) atoms bridged by −N═C− or −N═N− ligands, the carbeniates, benzylimidazolates, and pyrazolates (Figure 21). Several years ago we recognized that oxidative addition to the trinuclear 2,5-diphenylpyrazolate complex of Au(I), [Au(pyraz)]$_3$, occurs at only one $Au^I$ center. Using aqua regia, halogen addition to the pyrazolate rings occurs as well, with two of the gold centers remaining Au(I).[89] This does not appear to be the case with the carbeniates or benzimidazolates where all three gold atoms can be oxidized stepwise to Au(III).[90]

Several of the benzimidazolates and the carbeniates aurophilically bond intermolecularly in the solid state with four of the six gold atoms in a hexanuclear unit having short Au(I)···Au(I) contacts. No evidence for a similar structure has been published with the pyrazolates, but a polymorph under current investigation shows aurophilic behavior.[91] In 1997 Balch[92] made a spectacular discovery that a special

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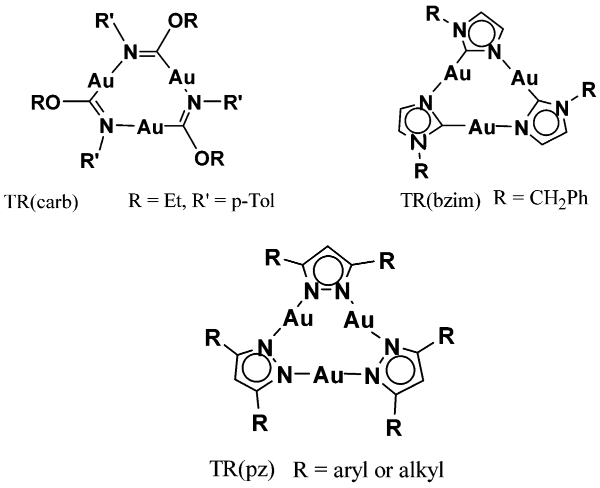

**Figure 21.** Trinuclear gold carbeniates, benzylimidazolates, and pyrazolates.

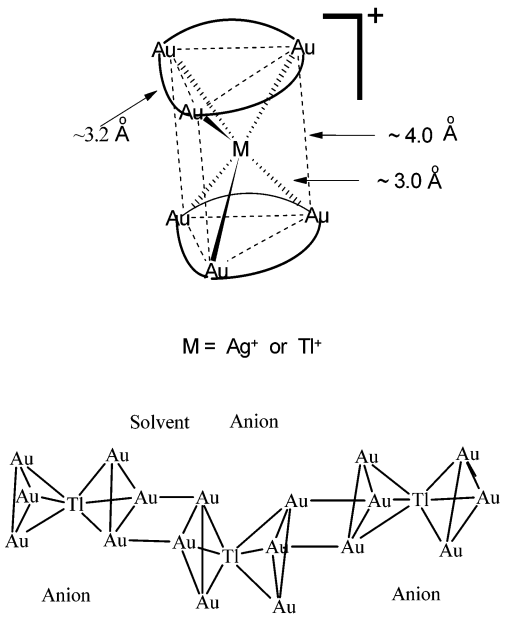

**Figure 22.** Line drawing of the product produced by incorporating silver or thallium cations into trinuclear carbeniate and benzylimidazolate chains. Anions and solvent molecules found in lattice.

carbeniate, $[Au(MeN{=}COMe)]_3$, stacked in an arrangement which produces three infinite linear chains of Au(I) atoms, triangles stacked upon each other. Yet, in the hexagonal crystal structure, there is also a stacking in which the triangular $[Au(MeN{=}COMe)]_3$ units are offset, rotated by 60°. Irradiation of these crystals with UV light causes the material to emit red light with a long-lived emission. When a drop of solvent such as methylene chloride is placed upon the irradiated crystals in the dark, a bright yellow burst of light is observed. Balch called this a “solvoluminescence”. The light energy somehow is stored and then released suddenly when solvent reacts with the crystals. Unfortunately, to date, the observation appears to be unique with $[Au(MeN{=}COMe)]_3$.

When Alfredo Burini and co-workers in Camerino, Italy, discovered that trinuclear benzylimidazolates appear to interact with silver salts in some previously unknown fashion, he contacted me regarding our interest in what has now become a very fruitful collaboration. We were able to learn that Ag(I) and Tl(I) were intercalated (Figure 22) into stacked chains of the trinuclear gold benzylimidazolate and carbeniate complexes.[93] Furthermore, these new materials showed interesting luminescent properties in the solid state. It became apparent that this is a general property of the trinuclear Au(I) carbeniate and benzylimidazolates and that the possibility existed that other aurophilic entities also might bond to the six Au(I) atoms of two trinuclear gold units. Furthermore, the structures showed that there is, in these compounds, an infinite chain ABAABA pattern, where B is Ag(I) or Tl(I) and A is the trinuclear gold unit. The two

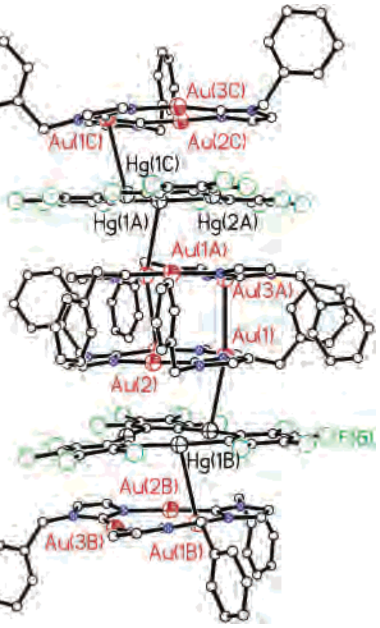

**Figure 23.** The stacked product of the acid−base reaction between $[Hg(C_6F_4)]_3$ and TR(bzim).

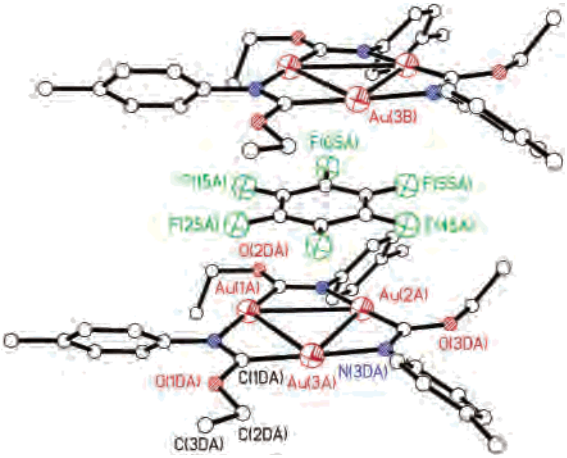

**Figure 24.** The stacked acid−base complex formed from $C_6F_6$ and a TR(carb).

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**Table 2.** Listing of Co-Workers

Doctoral Students from the Fackler Group with Date of Degree in Parentheses

Thomas S. Davis (1967); Dimitri Coucouvanis (1967); John Fetchin (1969); William C. Seidel (deceased) (1969); Joel Levy (1970); Judy Mayhew Andrews (1970); John Michael Burke (1971); Robert G. Fischer (1971); Jaime Pradilla-Sorzano (1972); William J. Zegarski (1973); Alex Avdeef (1973); Ivan Lin (1975); Christos Paparizos (1977); Hsiang-Wen Chen (1977); Judith Stein (1979); Wie-Hin Pan (1979); Lap-Tak Chan (1981); John Basil (1982); Rosario del Pilar Neira (1983); Anthony M. Mazany (1984); Douglas Dudis (1984); Barbara Trzcinska-Bancroft (1985); Dwight Heinrich (1987); Raphael Raptis (1988); César A. López Villagrán (1992); Thomas C. Carlson (1993); Rosa M. Davila (1993); Shu-Jen Liu (1993); Chen Wie (David) Liu (1994); Tiffany A. Grant (1998); Werner Van Zyl (1998); Hanan Abdou

Master of Science Degree Students with Date of Degree in Parentheses

Joyce T. Hashagen Chremos (1964); James L. Marini (1965); Martin M. Mittleman (1965); Jaime Pradilla-Sorzano (1966); Sidney Lehr (1981); Julie Shain Diebold (1987); David Briggs (1987); Michele Harless (1993); R. Theron Stubbs; David Neitling (1995); Belinda Prihoda (Education) (1998)

Bachelor's Degree Undergraduates Who Have Worked with Fackler,
Who Have Then Studied for an Advanced Degree in Chemistry

Geoff Dolbear; Sheldon Kopperl; Ray Reeder; Greg Kubas; Phil Rakita; Walter Holloway; J. P. Jones; Larry McCandlish; David Briggs; Brian McBurnett

Postdoctoral Research Associates and Visiting Faculty with Approximate
Date of Association in Parentheses

Ishwar D. Chawla (1962), Kansas State; David G. Holah (1963), University of Hull (England); Helmut Weigold (1967), Manchester; Sister Dolores Abood (1970), Notre Dame College; Max Weeks (1966), Imperial College; James A. Smith (1968), Ohio State; Dominic Hunt (1969), Notre Dame; David Fries (1970), Case Western; Juan Costamagna (1970), Universidad de Buenos Aires, Argentina; David Schussler (1972), Purdue; Luis J. Matienzo, (1974), Maryland; Loren D. Thompson (1974), Providence; Alfred P. Sattelberger (1975), Indiana; Anthony F. Masters (1977), Australian National University, Australia; Howard Knachel (1983), University of Dayton; Joanne H. Tocher (1983), Edinburgh, U.K.; David O. Marler (1984), Texas A&M; Leigh C. Porter (1984), UC—Irvine; Barbara Trzcinska-Bancroft (1985), CWRU; H. H. Murray (1983), Yale University; Guillermo Garzon (1986), Northwestern; Ju-Chun Wang (1987), Louisiana State University; Richard Winpenny (1988), Edinburgh, U.K.; Suning Wang (1987), Yale; Raphael Raptis (1989), Texas A&M; Chris King (1987), University of Tulane; Md. Nazrul I. Khan (1985), CWRU; Roman Kesinski (1990), University of Birmingham; Anabel Elduque (1990), Universidad de Zaragoza; Rosa M. Davila (1993), Texas A&M; Zerihun Assefa (1992), University of Maine; Richard Staples (1990), University of Toledo; Jennifer M. Forward (1993), Oxford University; José María López-de-Luzuriaga (1993), Zaragoza, Spain; Angelo Maspero (1998), Milano, Italy; Mohammed A. Omary (1999), University of Maine; Manal Omary (1999), University of Maine; Ibrahim Kani (2000), Turkey; Ahmed Mohamed (2001), University of Maine

aurophilic Au(I)···Au(I) bonds formed between "intermolecular" A units apparently contribute to the luminescence of the materials and to their structural stability. The trinuclear A units, TR(carb) and TR(bzim), display a very strong nucleophilic character. We also asked ourselves, can an ABAB chain pattern also be found, and if so, would this pattern produce different properties? Would electrically neutral, $\pi$ acidic species also bond with the TR(carb) and TR(bzim) to form stacked acid—base pairs as observed for the cations?

This latter question was answered first. My colleague Francois Gabbaï had been working with the very acidic $[Hg(C_6F_4)]_3$ complex.[94] We discussed with him the acid—base ideas of Dennis Dougherty[95] and then successfully formed a $[TR(bzim)][Hg(C_6F_4)]_3$ adduct (Figure 23)[96] while his group was finding that even benzene gave a $\pi$ base interaction with $[Hg(C_6F_4)]_3$.[97] By density functional calculations we examined the $\pi$ base character of the TR(carb) and TR(bzim) along with the $\pi$ acid character of the $[Hg(C_6F_4)]_3$. It was not surprising that this theory showed the gold compound to be a strong base and the mercury compound to be a strong acid.[97]

In parallel with our studies involving small acidic $\pi$ organics interacting with the TR(carb) and TRbzim) species, Balch[98] noted the $\pi$ base character of the trinuclear carbeniates he was studying and was able to find that "large" $\pi$ acid aromatic compounds such as 2,7-dinitro-, 2,4,7-trinitro-, and 2,4,5,7-tetranitro-9-fluorenones stack with the gold carbeniates. He avoided $\pi$ acids containing potential ligands such as TCNQ, believing that the nitrogen of this $\pi$ acid would bond to the gold as a typical ligand and decompose it. This proved not to be the case. Both ABAABA and ABAB patterns could be found with $\pi$ acids. We have found that $C_6F_6$ produces the ABAB chain pattern with a TR(carb) (Figure 24) while the $\pi$ acceptor TCNQ gives the ABAABA pattern that had been found with Ag(I), Tl(I), and $[Hg(C_6F_4)]_3$.[99] The TCNQ product also shows an interesting luminescence and semiconducting behavior by electron microscopy. A large single crystal showed no significant conductivity, however. Very recently, we have determined by $^{31}$P HOESY and PGSE NMR that aggregation of these TR(carb) and TR(bzim) species with $[Hg(C_6F_4)]_3$ occurs in solution.[100]

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(97) Burini, A.; Fackler, J. P., Jr.; Galassi, R.; Grant, T. A.; Omary, M. A.; Rawashdeh-Omary, M. A.; Pietroni, B. R.; Staples, R. J. Supramolecular Chain Assemblies Formed by Interaction of a $\pi$ Molecular Acid Complex of Mercury with $\pi$-Base Trinuclear Gold Complexes. *J. Am. Chem. Soc.* **2000**, 122, 11264.

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Much remains to be understood regarding the luminescence of Au(I) complexes, but it is clear that aurophilic interactions influence strongly emission behavior. LMCT states also play very important roles. With the TR(carb) complex, a vibronic pattern in the emission spectrum, with a spacing consistent with a Raman line observed at 1425 cm$^{-1}$,[101] implicates the carbeniate ligand in a LMCT or possibly a LMMCT transition. Further studies are needed.

**Abbreviations:** acac (acetylacetonato), pentane-2,4-dionato; JT, Jahn−Teller; EPR, electron paramagnetic resonance; i-MNT, maleonitrile-1,1-dithiolate, $[S_2CC(CN)_2]^{2-}$; SacSac, pentane-2,4-dithionato; MTP, diphenylmethylenethiophosphinato, $[CH_2P(S)Ph_2]^{2-}$; ylide ligands (most often as anions), $[(CH_2)_2PR_2]^{-}$; THF, tetrahydrofuran, $C_4H_8O$; LMCT, ligand-to-metal charge transfer; LMMCT, ligand-to-metal charge transfer when the excited state involves two or more metal atoms; TPA, triazaphosphaadamantane, $C_9H_{18}N_3P$; TPPTS, tris(*m*-sulfonatophenyl)phosphine, $[P(m\text{-}SO_3Ph)_3]^{3-}$; pyraz, [3,5-diphenylpyrazolato]$^{-}$, [di-3,5-Ph-$N_2C_3H$]$^{-}$; carb, [RN═C-(OR)]$^{-}$; bzim, [1-N,3-N(R)$C_3H_2$]$^{-}$.

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