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From Solvolysis to Self-Assembly*

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Abstract

My sojourn from classical physical-organic chemistry and solvolysis to self-assembly and supramolecular chemistry, over the last forty years, is described. My contributions to unsaturated reactive intermediates, namely vinyl cations and unsaturated carbenes, along with my decade long involvement with polyvalent iodine chemistry, especially alkynyliodonium salts, as well as my more recent research with metal-ligand, coordination driven and directed self-assembly of finite supramolecular ensembles are discussed.

Introduction

During a forty-year career of active research, I have had the pleasure of being involved in and making contributions in three distinct research areas. In the first third of my career I was a classical physical-organic chemist in the area of unsaturated reactive intermediates. In the middle portion I was involved in polyvalent iodine as well as some organometallic chemistry. Since the early 1990's my contributions have primarily been in supramolecular chemistry and self-assembly. In this perspective I shall discuss how and why I got involved in each area, what the critical prior discoveries were and literature results that provided the background and groundwork for our contributions and what our own seminal contributions were to the field. During each period there were also key persons who had an impact and influence on the course of events that I shall mention as well. However, as will be seen, this is a personal narrative based on recollection of events, dependent upon the frailties of human memory, beclouded by the passage of time.

I first became interested in chemistry in high school in Hungary where I grew up. As a freshman in Gymnasium in 1955 I had a chemistry course that was the equivalent of what we now teach in general chemistry to first year students in college in this country. Moreover, in those days in Hungary there were no restrictions on the purchase, even by a teenager, of common chemicals such as inorganic salts, NaOH, common acids, etc., easily available in the corner drug store and elsewhere, so that I was able to set up my own home laboratory and experiments. I clearly recall making "slow burning" black gunpowder from readily available potassium nitrate, sulfur and charcoal powder. Phenolphthalein, used as a primitive laxative by the then pharmacist and as an indicator by the chemist, was available for acid-base titrations and the fascinating color changes that it underwent. When my family moved to the U.S.A. in 1956 I continued with chemistry in high school. I was also fortunate to have a dedicated, inspiring college chemistry teacher Robert C. Miller who invited me to do research with him in organophosphorous chemistry in my sophomore year at DePaul University. He also motivated his students to go to the best graduate schools anywhere in the country.

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I was a graduate student at UC-Berkeley from the fall of 1963 until the fall of 1966 in the group of Andrew Streitwieser, Jr. My Ph.D. Dissertation was on the “Kinetics and Mechanism of Boron Fluoride-Alcohol Alkylations.” A classical physical-organic study of Friedel-Crafts alkylations¹ including an investigation of the stereochemistry of the alkylation of benzene with chiral 1-propanol-1-d₃.² During this period the Streitwieser and Noyce groups held joint research group meetings. Among the interests of Professor D. Noyce and his group were electrophilic additions to alkynes and vinyl cations.³ Early work on vinyl cations involved essentially only electrophilic additions to alkynes.⁴ Unlike the rich chemistry on the solvolytic generation of carbonium ions⁵ little was known about the direct solvolytic generation of vinyl cations. Only systems substituted by an aromatic ring,⁶ a vinyl group,⁷ or a cyclopropyl ring⁸ directly attached to the carbon bearing the leaving group, underwent solvolysis, resulting in “stabilized” vinyl cations. Even the normally highly reactive arenesulfonates, like the 1-cyclohexenyl tosylate and brosylate and the cis-2-buten-2-yl tosylate and brosylate, reacted via an addition-elimination mechanism rather than unimolecular ionization and vinyl cations.⁹

Sometime during this period, Streitwieser visited the DuPont Company where he was a consultant, and became aware of trifluoromethanesulfonic acid, CF₃SO₃H, also known as triflic acid.¹⁰ Triflic acid, first reported by Haszeldine and Kidd,¹¹ is known to be the strongest Brønsted acid, much stronger than such common acids as HNO₃, H₂SO₄ or even HClO₄.¹⁰ I remember Streitwieser requesting a sample of Ba(OSO₂CF₃)₂ from the 3M Company in St. Paul, Minnesota, from which the acid was obtained by reaction with fuming H₂SO₄ and distillation. He and co-workers¹² used CF₃SO₃H to prepare CH₃CH₂OSO₂CF₃, as well as the deuterio analogs CD₃CH₂OTf, and CH₃CD₂OTf, and via solvolytic studies establish that the reaction occurs via “a transition state with comparatively little positive charge and substantial bonding to a nucleophilic solvent molecule.” In other words, mostly an S_N2 process with little, if any S_N1 character,¹² despite the superior leaving ability of the triflate group.

By December 1966 I had obtained my Ph.D. and left for Princeton for postdoctoral studies with Paul v.R. Schleyer. The 50's and 60's were the golden age of physical-organic chemistry and among the challenges was the so-called nonclassical ion¹³ problem, typified by the 2-norbornyl system. Hence, I became involved in the study of “remote” methoxy groups as probes for delocalized cations and their substituent effects on 2-norbornyl solvolysis rates.¹⁴ However, Schleyer also encouraged his co-workers and, in particular, postdoctoral fellows to develop independent projects.

It was at this point that I put two and two together to see if one could generate simple alkylvinyl cations via solvolysis. I told Schleyer about triflic acid and encouraged him to obtain some Ba(OSO₂CF₃)₂ from 3M, which he did. From literature data,¹⁵ as well as work in progress in both the Streitwieser¹² and Schleyer¹⁶ groups, it was known that a triflate was almost 10⁴ times more reactive¹⁷ than a comparable tosylate in solvolytic reactions. So the challenge was to prepare a simple alkylvinyl triflate and investigate its solvolytic behavior. Ultimately we succeeded by the direct addition of CF₃SO₃H to alkynes, in a sealed tube, and established¹⁸ that cis-2-buten-2-yl triflate, **2c**, reacted in aqueous ethanol via an S_N1 process and the elusive simple alkylvinyl cation, **3c** Scheme 1.

This was the first example of the preparation of a vinyl trifluoromethanesulfonate (of immense importance in cross coupling reactions, vide infra) and the observation of a simple alkylvinyl cation generated via solvolysis and bond heterolysis.

Throughout my graduate and postdoctoral period I was pretty sure I was interested in an academic career. I liked research, I liked the opportunity of working with young people, I enjoyed teaching (as a TA in Berkeley and as instructor for a year at Princeton) and above all

I appreciated the challenge and independence that an academic career afforded. By the late 60's the academic market started to tighten (one of those periodic cycles that seem to occur every 12–15 years). In 1967/68 I interviewed at 6–9 places (I no longer recall the exact number) and received four offers. I was particularly attracted by Utah for a number of reasons: (1) it was a growing department on the move; (2) it had just received an NSF Centers of Excellence Grant; (3) it had just attracted Robert W. Parry from the University of Michigan, a distinguished inorganic chemist, founding editor of *Inorganic Chemistry* (later ACS President) and was negotiating with Cheves Walling from Columbia University, a distinguished physical-organic chemist and a pre-eminent free-radical expert (already a member of the U.S. National Academy of Sciences, later Editor of *JACS*); (4) it just completed in 1968 a brand new chemistry building with excellent facilities, (5) my wife to be, Christine, whom I met at Berkeley, although originally from Germany, grew up in San Francisco and was a westerner (as was I after having been in the midwest, B.S. in Chicago, the west at Berkeley and the east at Princeton) and Salt Lake was as far “east” as she was willing to move; (6) I found it to be a very collegial place. So in late 1968 I accepted the offer from the University of Utah, effective July 1 of 1969. I have never regretted this decision and after 40 years and a half dozen outside offers (three as chair of major research institutions) I am still at Utah and will likely remain here for the rest of my career. Many colleagues and friends in the chemical profession thrive by moving, with the challenges and opportunities that a new position and place offer. However, just as many, or even more, thrive by staying at the same place, developing their career parallel with the growth and development of the department at their “home” institution.

Independent Career

First Period

Like all young assistant professors I was now faced with starting my own research. I decided to investigate the generation, nature and chemistry of vinyl cations. It was an area that was different from my Ph.D. work, different from the main thrust of my postdoctoral work but still in the realm of physical-organic chemistry that I was trained in, knew something about, and enjoyed. Moreover, and most important, it was my own idea, developed all on my own from careful observations at Berkeley, reading the literature and with encouragement from my mentors. Furthermore, I had excellent preliminary results as described above,¹⁸ that served as a platform for starting an independent career in, at that time, a very active and highly visible area.

The challenge was to generalize the formation of vinyl triflates so that any and all types of alkenyl triflates could be made and investigated, not just the limited number and type accessible by addition of $\text{CF}_3\text{SO}_3\text{H}$ to alkynes. We were fortunate to discover (independently, but simultaneously with Schleyer and Hanack) that this could be accomplished by reacting enolizable carbonyl compounds, such as aldehydes and ketones with triflic anhydride, $(\text{CF}_3\text{SO}_2)_2\text{O}$, in the presence of a weak base.^{17,19} To this date, this is the way all vinyl(enol) triflates are prepared and currently widely used in cross-coupling reactions.²⁰ For us, this opened up the entire spectrum of solvolytic generation of a variety of vinyl cations^{4a,21} and allowed us to examine cyclic vinyl cations;²² rearrangements of vinyl cations;^{19b,23} deuterium isotope effects in the generation of vinyl cations²⁴ and the effect different substituents, various solvents and nucleophiles²⁵ have on their generation. We also examined Friedel-Crafts type alkylation of aromatic substrates using enol triflates.²⁶

A typical example of our investigations of vinyl cations was the detailed study of the solvolysis of cis and trans-3-phenyl-2-buten-2-yl triflates. Using kinetic deuterium isotope effects, Hammett sigma-rho effects, stereochemistry and product studies, we established that the E-isomer, **4**, reacted via a vinylidene phenonium ion, **5**, analogous to the well-known σ -bridged

phenonium ion,²⁷ first prepared by Cram,²⁸ whereas the Z-isomer, **6**, reacted via the open vinyl cation, **7**, as shown in Scheme 2.^{24a,29}

Of course we were not alone in our study of vinyl cations; as in any active area there were many investigators, key among them, C. Grob (Basel), M. Hanack (Tübingen); G. Modena (Padova); R.G. Bergman (then Caltech); P.v. Schleyer (then Princeton), and Z. Rappoport (Jerusalem), as described and summarized in our two monographs on this topic.^{21b,c} Hence, by the late 70's and early 80's vinyl cations were fully accepted members of the family of reactive intermediates, and in fact observed³⁰ by NMR, analogous to the NMR observation of carbocations in the seminal work of Olah.⁵ Therefore, it was time to move on to a different area. Moreover, one needed to be active and productive in more than one area to be successful in academia.

While investigating vinyl cations, taking advantage of the superior¹⁷ leaving group ability (nucleofugality) of triflates, it occurred to us that this superior nucleofugality of triflates could also be applied to the generation of unsaturated carbenes from primary vinyl triflates and cognates.

A large amount of work had been done in carbene chemistry since the pioneering studies of H. Meerwein, J. Hine, W. v. E. Doering, P. Skell and G. Closs.³¹ Besides simple carbenes, **8**, vinylidene carbenes, **9a**, and allenidene carbenes, **9b**, were already known. Vinylidene carbenes, **9a**, were generated via the elimination of HX from primary vinyl halides by bases,³² deamination of vinyl amines,³³ photofragmentation,³⁴ and base decomposition of 5,5-disubstituted N-nitrosooxazolidones,³⁵ none of which were ideal, whereas allenidene carbenes, **9b** were mostly generated from popargyl halides and/or haloallenes in the presence of bases.³⁶

In the 70's and early 80's we established³⁷ that primary vinyl triflates,³⁸ (R)₂C=CHOSO₂CF₃, and silylvinyl triflates,³⁹ (R)₂C=C(SiMe₃)OSO₂CF₃, serve as progenitors par excellence for vinylidene carbenes, **9a**. We showed that triflate generated carbenes are singlets,⁴⁰ electrophilic⁴¹ and behave as free carbenes⁴² rather than carbenoids.^{31,43} We demonstrated via stereochemical and computational investigations that R₂C=: addition to alkenes is stereoselective and proceeds via a "C₂-inward" transition state.⁴⁴ Via isotopic labeling we determined⁴⁵ that the rearrangement of β-aryl or β-alkyl vinylidene carbenes to afford alkynes occur via the free carbene rather than by the Fritsch-Buttenberg-Wiechell type of organometallic intermediate⁴⁶ and a carbenoid.

Addition of R₂C=: to π-systems provided a simple and general means of entry to interesting small and strained ring compounds,⁴⁷ including alkylidenecyclopropanes,⁴⁸ **10** and m-xylylene,⁴⁹ **11a**. The parent m-xylylene, **11b**, was just recently spectroscopically fully characterized and investigated via matrix isolation.⁵⁰ Likewise, reaction with azoarenes afforded 2(H)-Indazoles, **12**, via an ylide type process.⁵¹ Furthermore, reaction with isonitriles

gave heterocumulenes,⁵² **13**, and interaction with isocyanates resulted in vinyl carbamates,⁵³ **14**.

Insertion of R₂C=C: into diphenyl diselenide and diphenyl ditelluride yielded little known phenylseleno, **15**, and phenyltelluro, **16**, ketals, respectively.⁵⁴

We also established that insertion of unsaturated carbenes into Si-H bonds occurs stereospecifically via a concerted three-centered transition state⁵⁵ analogous to the insertion of Br₂C: and C₁₂C: into chiral NpPhMeSiH.⁵⁶ Insertion of R₂C=C: into enethiols gave divinylsulfides, **17**.⁵⁷

We were also able to extend our unsaturated carbene studies to previously unknown, longer, congeners, alkadienylidenecarbenes, **19**, and alkatetraenylidenecarbenes, **21** as shown in Scheme 3.³⁷ Carbene **19** was readily available from 1-(ethynyl)-vinyl triflates,⁵⁸ **18**, and **21** from 1-(butadiynyl)-vinyl triflates,⁵⁹ **20**. As previously, we established^{60,61} that both **19** and **21** are singlets, electrophilic and free carbenes. Insertion of **19** into group 4 hydrides resulted in the formation of novel Si, Ge, and Sn functionalized cumulenes, **22**.⁶²

The impact and legacy of this work in unsaturated reactive intermediates is interesting. Vinyl (enol) triflates, that are the precursors to the solvolytic generation of vinyl cations and that we were the first to prepare and report,^{18,19} are now widely used in metal catalyzed cross coupling protocols.²⁰ Enol triflates serve as the premier electrophilic coupling partners in a variety of cross coupling reactions that are of importance in natural product synthesis⁶³ as well as materials science.

Unsaturated carbenes have recently been found and are among the most abundant carbon containing species in interstellar space.^{64,65} Moreover, metal vinylidenes and allenylidenes and metallacumulenes are extensively employed in alkene metathesis^{66,67} and various catalytic reactions,⁶⁸ including pericyclic reactions⁶⁹ and substitution reactions.⁷⁰

Middle Period

By the mid-1980's, it became obvious to me that we had exhausted the chemistry of unsaturated reactive intermediates. Moreover, in the late 1970's, early 1980's, a senior colleague at Utah wisely counseled me to broaden my horizons and look beyond the generation, nature and chemistry of reactive intermediates as, by this time, the bloom was off classical physical-organic chemistry and, in particular, carbocations and carbenes. At the time, I thought that there may still be interest in the solvolytic generation of the elusive alkynyl cations $RC\equiv C^+$, and I describe below how our quest for this high-energy species led us to polyvalent iodine chemistry. However, I also took this advice to heart and began looking for new areas. Furthermore, I enjoyed the challenge of venturing into new territory and learning and mastering new chemistry. Initially, we explored two areas that were tangential to and an outgrowth of our previous work. First, our interest in selenium, tellurium, germanium and tin compounds, **15**, **16**, and **22**, led us to organometallic chemistry. Hence, we explored the interaction of various organometallic nucleophiles with our vinyl, **2**, ethynylvinyl, **18**, and butadiynylvinyl, **20**, triflates. We discovered that these precursors readily undergo reactions with cobalt species to give vinyl-cobaloxime complexes,⁷¹ **23**, and σ -butatrienyl

23

24

cobaloxime complexes⁷² **24**. Likewise, vinyl triflates as well as, **18**, readily react with $(Ph_3P)_4Pt$ to yield four-coordinate cationic σ -vinyl Pt(II) complexes⁷³ and σ -butatrienyl cationic Pt(II) complexes.⁷⁴ Similarly, we explored the reaction of Vaska's compound, $(Ph_3P)_2Ir(CO)Cl$, with various triflates.⁷⁵ We examined the mechanism of formation and the chemistry of vinylic acyl Pt(II) complexes.⁷⁶ We investigated the formation of heterobimetallic Ir-Pt complexes.⁷⁷ We prepared and studied Rh and Pt π -cumulene complexes,^{78,79} **25**, and **26** and **27**, **28** below. We also investigated the mechanism, oxidative addition⁸⁰ and reductive elimination,⁸¹ of metal mediated vinylic cross-coupling reactions, using our previously prepared, readily available vinyl(enol) triflates.

25 **26** **27** **28**

This brief excursion into organometallics at this stage of my career, and what I learned about various metals and their complexes, in particular platinum chemistry, served me well later when we employed metal-ligand interactions in abiological self-assembly (*vide infra*).

Second, a combination of my interest in small and strained ring chemistry via alkylidene carbene additions to π -bonds, briefly described above, and a fortuitous event in 1982, got us involved in alkylidenecyclopropenes. That year Professor Brian Halton, from Victoria University in Wellington, New Zealand, spent a year with me at Utah as a senior Fulbright Scholar. Brian's interest and expertise was in strained organic molecules and, in particular, cyclopropenes.⁸² Because of their strain and consequent high energy, such molecules have novel physical, spectral and chemical properties that are both of theoretical as well as synthetic interest and challenge.⁸³ Among the intriguing and more strained hydrocarbons are the ortho-bridged aromatics. The parent member of the family, benzyne, **29** is easily generated and well known as a transient intermediate,⁸⁴ but observed spectroscopically only in an Armatrix at 8K.⁸⁵ Cyclopropabenzene, **30**, the next homologue, is an isolable compound, despite its nearly 70 kcal/mole strain energy.⁸² The cross-conjugated fulvenes,⁸⁶ **31**, and radialenes, **32**, represent another class of alluring strained hydrocarbons.⁸³

29 **30** **31** **32**

Hence, Brian and I decided to combine our expertise to investigate the preparation, characterization, properties and chemistry of the then unknown alkylidenecyclopropenes, e.g. **33**, a unique class of strained hydrocarbons that combine into a single molecular framework the features of the ortho-bridged benzene **30**, and the cross-conjugated triafulvene, **31**, and **32**:

Due to the then unknown nature of **33**, and its anticipated high strain of about 80 kcal/mole, and hence possible instability at room temperature, we decided to focus our initial efforts on **38** for two reasons. First, strained derivatives of naphthalene are known⁸⁴ to be more stable than those of benzene and, furthermore, alkyl substituents stabilize double bonds. Second, we anticipated that **37** would be easily accessible via an alkylidene carbene, **34**, addition to tetrahydronaphthalene, **35**, a reaction known⁸⁷ to give adduct, **36**, followed by oxidation to the desired **38** as shown in Scheme 4. However, all attempts to oxidize **36** to **38**, with numerous reagents under a wide variety of conditions, failed. Only unreacted starting material and/or partially oxidized hydrocarbon, **37**, was observed.⁸⁸

Brian's year at Utah, from a chemical perspective, was a year of frustration, with no progress and publication. However, after Brian's return to Wellington, the alternative Peterson olefination⁸⁹ of **39** worked well⁸⁸; that started a decade-plus long trans-oceanic collaboration⁹⁰ with Brian, which resulted not only in nearly 20 joint publications, but also a lifelong friendship. In a collaborative fashion we investigated the electrochemical properties,⁹¹ photoelectron spectra,⁹² polarity,⁹³ ¹³C-NMR⁹⁴ and ambiphilicity⁹⁵ of these novel strained hydrocarbons. We explored their reactions with both electrophiles⁹⁶ and nucleophiles.⁹⁷ We used them as unique ligands in the formation of interesting Pt, Pd, and Rh-complexes.⁹⁸ We prepared and characterized related benzocalicenes and benzotriaheptafulvalenes.⁹⁹

During this period, we were still intrigued by the possible solvolytic generation of alkynyl cations, $\text{RC}\equiv\text{C}^+$, the only remaining member of the family of ubiquitous carbocations that were not known in solution. Although they were detected in interstellar space,¹⁰⁰ and in the gas phase by mass spectrometry,¹⁰¹ there was no evidence of their formation in the condensed phase. In fact, both experimental data and theoretical calculations indicated that the parent ethynyl cation, $\text{HC}\equiv\text{C}^+$ has a heat of formation of about 400 kcal/mole.¹⁰² However, given the superior leaving ability of triflate, I reasoned that alkynyl triflates, like $\text{ArC}\equiv\text{COSO}_2\text{CF}_3$ might afford this elusive species in solution. Unfortunately, alkynyl esters of any kind, carboxylate, **40**, sulfonate, **41**, or phosphate, **42**, were unknown compounds prior to the 1980's. At this point two serendipitous events occurred that resulted in a major change and new direction in my research. I had a phone conversation with a former Ph.D. student of mine, Albert G. Anderson (Ph.D. 1977, University of Utah), who was at Central Research at DuPont, and I mentioned the fact that alkynyl esters were unknown. He suggested that I consider using iodonium species as possible progenitors and called my attention to the seminal work of Koser¹⁰³ on alkynyl tosylates that appeared in 1981. This was the beginning of my interest in polyvalent iodine chemistry that occupied my interest for over a decade, from the mid 1980's onward and ultimately also led to my involvement in abiological self-assembly (vide infra). My interest and involvement in polyvalent iodine species was further facilitated by the arrival of a very talented postdoctoral fellow, Dr. Viktor Zhdankin from N. Zefirov's group at Moscow State University in Russia, during this time. He was not only very talented, dedicated, hardworking and creative, but was already familiar with polyvalent iodine species as well as the extensive Russian literature in this area.

Iodine was discovered in 1811 and most commonly occurs in the monovalent form with an oxidation state of -1 in organoiodine compounds. However, because it is the largest, most polarizable and least electronegative of the halogens, iodine also readily forms stable, polycordinate, high-valent compounds, generally as I(III) and I(V) species. Over 120 years ago, the German chemist, C. Willgerodt reported¹⁰⁴ the preparation of PhICl_2 , followed by the preparation¹⁰⁵ of PhI(OAc)_2 and numerous¹⁰⁶ diaryliodonium salts, $\text{Ar}_2\text{I}^+\text{X}^-$. Since then, interest and activity in multi-coordinate iodine species waxed and waned until the early 1980's when the chemistry of hypervalent, multi-coordinate iodine experienced a renaissance.¹⁰⁷

Our primary interest in this area was focused on alkynyliodonium species,¹⁰⁸ $\text{RC}\equiv\text{CI}^+\text{Ph}$, as potential progenitors of alkynyl sulfonate esters, **41** and, in particular, alkynyl triflates as possible solvolytic precursors of $\text{RC}\equiv\text{C}^+$. Beringer and Galton¹⁰⁹ were the first to report an alkynyliodonium species, **43**, but only in 10–20% yield (Scheme 5). Moreover, **43** decomposed at room temperature in a few hours, as shown in Scheme 5. The first stable, crystalline iodonium salt, **44**,

was reported by Merkushev and co-workers,¹¹⁰ but it was characterized only by IR and its hydrolysis product. A major advance was made by Koser and co-workers¹⁰³ in the formation of alkynyl(phenyl)iodonium tosylates, **46**, via addition of what has become known as “Koser’s reagent,” **45**,¹¹¹ to terminal alkynes. Although this early work had serious limitations,¹⁰⁸ it galvanized the field. Improvements rapidly followed so that by the mid-1980's a variety of alkynyl(phenyl)iodonium salts were readily available as stable microcrystalline compounds.^{112,113}

Arguably, the most general and widely used methods¹¹⁴ of preparing alkynyliodonium species involves alkynylsilanes and in situ Zefirov’s reagent,¹¹⁵ **48**, or the use of stannylalkynes,¹¹⁶ **49**, and iodonium triflate, **50**,¹¹⁷ as shown in Scheme 7. This later methodology affords a wide variety of β - functionalized alkynyliodonium salts, **51**. This procedure is also applicable to the preparation of the parent system,¹¹⁸ $\text{HC}\equiv\text{CI}^+\text{Ph} \text{ } ^-\text{OTf}$, as well as $\text{PhI}^+\text{C}\equiv\text{C}^+\text{Ph} \text{ } 2^-\text{OTf}$,¹¹⁹ and other bis-alkynyliodonium compounds.¹²⁰ Similar procedures have been developed for the ready preparation of alkenyliodonium species,^{121–123} as well as heteroaryliodonium salts.¹²⁴

All pure alkynyliodonium species are microcrystalline solids sparingly soluble in most organic solvents, the best solvent being acetonitrile. Their stability depends both on the counter-anion and the β -substituent on the alkyne. The more nucleophilic the counter-ion, the less stable the alkynyliodonium compound, the most stable and hence most widely employed being the triflates, tetrafluoroborates and tosylates. They have highly characteristic signals in both the IR and NMR; in particular C-13 NMR.¹²⁵ X-ray analysis indicates a pseudobipyramidal or T-shaped structure, **52**, with the alkyne and counter ion in an axial arrangement, and the phenyl

group and two lone pairs on the iodine in the equatorial position,^{118a,126} in accord with the hypervalent (10-I-3) nature of these salts.¹²⁷

The reactions of alkynyliodonium salts may be described in three broad classes: (1) interaction with nucleophiles; (2) cycloadditions; (3) cross coupling reactions. In a formal sense alkynyliodonium salts can serve as electrophilic acetylene equivalents or as “alkynylating” agents “ $\text{RC}\equiv\text{C}^+$ ”. Indeed they undergo reactions with a wide variety of nucleophiles, including C, N, O, S, P, As, Se, Te, and organometallic nucleophiles as described below. The actual mechanism of reaction of course does not involve the high-energy alkynyl cation but goes through ylids and carbenes as summarized in Scheme 8.

The preponderance of evidence^{107c,d} indicates that the mechanism of these reactions involves a conjugate addition of the nucleophile to the electron-deficient β -carbon to form an iodonium ylide, **53**, (Scheme 8). Loss of iodobenzene forms the alkylidenecarbene, **54**, which rearranges via migration of either R or the nucleophile to provide the final product, **56**. Among the evidence for this mechanism is that in the presence of acid, ylide **53** can be trapped to give stable alkenyliodonium salts, **55**. Moreover, if either the alkyl group or the Nu on the β -carbon of **54** has a 1,5-C-H bond, the carbene can insert and provide a cyclopentene or five-membered

heterocycle **57** (vide infra). Both the ylide, **53**, and carbene, **54**, have been trapped.¹²⁸ The addition of the nucleophile to the β -alkynyl carbon (Michael type addition) is facilitated by the strong inductive electron-withdrawing nature of the PhI^+ moiety ($\sigma_1=1.24$ for PhI^+ vs. $\sigma_1=0.39$ for I-itself).¹²⁹

Only “soft” carbon nucleophiles, such as β -dicarbonyl compounds, react with alkynyliodonium salts; enolates of simple aldehydes, or ketones analogous to hard nucleophiles, like RO^- , result in decomposition products. This reaction represents a convenient way of directly introducing the $\text{RC}\equiv\text{C}$ -group into a variety of β -dicarbonyl compounds.¹³⁰

Reaction with $\text{R}_1\text{R}_2\text{NLi}$ affords aminoalkynes $\text{RC}\equiv\text{CNR}_1\text{R}_2$.¹³¹ Sulfur nucleophiles provide ready access to $\text{RC}\equiv\text{CSCN}$,¹³² $\text{RC}\equiv\text{CS}(\text{O})_2\text{Ar}$,¹³³ $\text{RC}\equiv\text{CSS}(\text{O})_2\text{Ar}$,¹³⁴ and $\text{RC}\equiv\text{CP}(\text{S})(\text{OR}_1)_2$.¹³⁵ Phosphorus nucleophiles provide alkynyl phosphonium salts, $\text{RC}\equiv\text{CP}^+\text{Ph}_3\text{X}^-$,¹³⁶ and $\text{RC}\equiv\text{CP}(\text{O})(\text{OR}_1)_2$.¹³⁷ Acetylenic arsonium salts, $\text{RC}\equiv\text{CAs}^+\text{Ph}_3\text{BF}_4^-$,¹³⁸ selenides, $\text{RC}\equiv\text{CSeAr}$,¹³⁹ and tellurides, $\text{RC}\equiv\text{CTeAr}$ ¹³⁹ are obtained from reactions with Ph_3As , NaSeAr and NaTeAr , respectively. Organometallic nucleophiles, such as $(\text{Ph}_3\text{P})_2\text{M}(\text{CO})(\text{Cl})$ $\text{M}=\text{Ir}, \text{Rh}$, and others, provide interesting organometallic complexes.^{120c,140,141}

However, the most interesting reaction is the formation of the previously unknown alkynyl esters, **40–42**, that combine two of the most common and important functional groups in organic chemistry, namely the carbon-carbon triple bond and esters into a single moiety.¹⁴² Simple carboxylate, phosphate and sulfonate esters are important in synthetic, mechanistic and biochemistry and are so ubiquitous that they are often taken for granted by most chemists. As described in all introductory text books of organic chemistry, esters are most readily made by the reaction of acid halides, $\text{RC}(\text{O})\text{X}$, $(\text{RO})_2\text{P}(\text{O})\text{X}$, $\text{RS}(\text{O})_2\text{X}$, with an alcohol. Likewise, vinyl (enol) esters are made by the reaction of enolates with acid halides. Therein was the problem. The preparation of alkynyl esters by an analogous process requires hydroxyalkynes, **58a**, or ynols that are the triple-bond analogs of enols, **59a**. Whereas enols are readily accessible,¹⁴³ in the case of ynols the tautomeric equilibrium is completely on the side of ketenes, **58b**, and hence ynols **58a** are not available. Theoretical calculations¹⁴⁴ indicate that the ketene-ynol, $\text{CH}_2=\text{C}=\text{O} \rightleftharpoons \text{HC}\equiv\text{COH}$, energy difference is 37 kcal/mole in favor of the ketene, while the energy difference between CH_3CHO and $\text{CH}_2=\text{CHOH}$ is only 14 kcal/mole.

We prepared these unique esters by interaction of alkynyl(phenyl)iodonium triflates with ArCO_2Na for the carboxylate esters,¹⁴⁵ **40**, CuOTf or AgOTf for the sulfonate esters,^{112a,b} **41**, and $(\text{R}'\text{O})_2\text{P}(\text{O})\text{ONa}$ for the phosphate esters,¹⁴⁶ **42**, as shown in Scheme 9. X-ray structure determination of the carboxylate ester,¹⁴⁷ **40**, and the sulfonate ester,¹⁴⁸ **41**, established, as anticipated, that the $\text{C}_{\text{sp}}\text{--O}$ bond is considerably shorter than the $\text{C}_{\text{sp}^2}\text{--O}$ bond of ordinary esters with a value of 1.366 Å vs 1.445 Å for carboxylate esters and 1.331 Å vs. 1.465 Å for the sulfonate esters respectively.^{147,148}

Acid-catalyzed hydrolysis of these esters proceeds via an $\text{A}_{\text{E}}2$ process involving a rate-limiting proton transfer to the β -carbon and formation of a vinyl cation that rapidly reacts with H_2O to give the respective acids as final products.¹⁴⁹ Whereas the base-catalyzed reaction involves OH^- attack on the acyl moiety, $\text{C}=\text{O}$, $\text{P}=\text{O}$, SO_2 , and the usual standard mechanistic steps.¹⁴⁹ Since alkynyl esters are electron-rich acetylenes they do not undergo Diels-Alder type cycloadditions but do react with an azete to give interesting Dewar pyridines.¹⁵⁰

These alkynyl esters, **40–42**, also have interesting biological activity. Both alkynyl carboxylates, **40**, and alkynyl phosphates, **42**, are potent serine protease inhibitors.¹⁵¹ Moreover, the alkynylphosphate esters, **42**, are potent inhibitors of bacterial phosphotriesterase.¹⁵² For example, 1-hexynyl diethyl phosphate, $\text{n-BuC}\equiv\text{COP}(\text{O})(\text{OEt})_2$ effectively inhibits the phosphotriesterase from *Pseudomonas diminuta* in less than one minute with <1% residual activity.^{152b,c} As I had no background in biochemistry these studies were carried out in collaboration with Y. Shalitin at the Technion in Israel and F. Raushel at Texas A. & M.

However, as shown in Scheme 8, the reaction of a nucleophile with alkynyl iodonium salts, besides resulting in a wide variety of functionalized acetylenes, **56**, as just described, can take an alternative route. If there is a 1,5-C-H bond available the intermediate carbene, **54**, instead of rearranging to **56**, will undergo intramolecular C-H insertion, resulting in a cyclopentene, **57**. This tandem Michael-addition/carbene-insertion process provides an efficient means to some interesting cyclopentene derivatives.¹⁵³ We have taken advantage of this process to prepare¹⁵⁴ a variety of interesting cyclopentenones with yields of 44–75% at room temperature

in CH₂Cl₂. This provides a nice alternative to the Nazarov¹⁵⁵ and Pauson-Khand^{156,157} reactions for the synthesis of cyclopentenones. Feldman and co-workers have also used this tandem Michael-addition/carbene-insertion procedure to prepare highly substituted dihydropyrrole derivatives¹⁵⁸ as well as polycyclic alkaloids.¹⁵⁹ This method has also been used to prepare thiazoles¹⁶⁰ as well as benzofurans,¹⁶¹ furopyridines¹⁶² and 2-mercaptothiazoles.¹⁶³

The second type of reaction that alkynyl(phenyl)iodonium species undergo is cycloadditions, β - Functionalized alkynyliodonium salts, **51**, undergo Diels-Alder cycloadditions with symmetrical dienes^{114c} under mild conditions, to give cycloadducts, **60**, and **61**, in good yields as shown in Scheme 10, whereas unsymmetrical dienes¹⁶⁴ result in mixtures of products with little, if any, regioselectivity. Similarly bisiodonium triflate **62** reacts with furan or cyclopentadiene, at room temperature to give **63** (Scheme 10).^{119b,165}

Since alkynyliodonium salts are also excellent 1,3-dipolarophiles, various [3+2]-cycloadditions have been studied. Nitrile oxides, **64**, give cycloadducts,¹⁶⁶ **65**, as sole products, whereas ethyl diazoacetate, **66**, yields regioisomeric pyrazoles, **67**, in only moderate yields as shown in Scheme 11. Organic azides, PhN₃ and CH₃N₃, give triazolylidonium salts, and diazocarbonyl compounds afford pyrazolylidonium salts, but only in low yields.¹⁶⁸

Because of the superior leaving ability of the PhI⁺ moiety, various iodonium species are excellent electrophilic partners in a range of metal-catalyzed cross-coupling reactions.^{169,170} Perhaps the most interesting of these is the preferential and selective coupling of alkenyliodonium salt, **68**, with alkynes, in the presence of a triflate in the same molecule, to give conjugated enynes, **69**, stereospecifically,¹⁷¹ as shown in Scheme 12.

Finally, alkynyliodonium and other iodonium salts have significant biological activity;^{107b,c} specifically alkynyl and aryl mono- and diiodonium salts are effective inhibitors of PQQ, **70**, an organic co-factor in certain biological redox processes,¹⁷² and have very potent in vitro activity against oral and dental anaerobes.¹⁷³

70: PQQ

Although we did not succeed in our original goal of the generation of alkynyl cations, RC≡C⁺, that has only been accomplished¹⁷⁴ via nuclear decay processes involving tritium and ³He, we have uncovered some very interesting chemistry. The legacy and significance of this work is the increasing use and involvement of polyvalent iodine species in contemporary

organic chemistry.¹⁷⁵ Examples include Feldman and Cutarrellis¹¹⁶ elegant synthesis of pareitropone,¹⁷⁶ a potent anti-cancer alkaloid, the synthesis of discorhabdin,¹⁷⁷ and morphinandienone and neospirinedienone¹⁷⁸ and many others. Most recently, the unique reactivity of polyvalent iodine reagents in conjunction with Pd(O) and Pd(II) complexes has been exploited for a wide range of synthetically useful organic transformations.¹⁷⁹

Third Period

At this juncture, another serendipitous and fortunate event occurred that started and influenced my current interest and involvement in abiological self-assembly. In 1991 I visited the University of Nevada at Reno and gave a seminar on the above described polyvalent iodine chemistry. During the question and answer period, Professor Lawrence Scott (then at Reno, now at Boston College) asked whether, given the pseudotrigonal pyramidal nature and concomitant 90° angle of alkynyliodonium species, **52**, I had thought of making macrocyclic systems. I had not, but immediately grasped the significance of his suggestion and, upon returning to Utah, discussed it with my theoretical colleague Jack Simons and with V. Zhdankin, my postdoctoral fellow already mentioned. In collaboration with Jack, we examined the structures, stabilities and vibrational frequencies of square planar tetraalkynyl and tetraaryl tetraiodonium salts,¹⁸⁰ **71–73**, and with Dr. Zhdankin started the synthesis of the triflate salt of **73** as shown in Scheme 13. Although we succeeded in the preparation of **78** from commercially available **74** in just three steps, the overall yield was only 7–10%.¹⁸¹ Moreover, getting satisfactory structure proof (mass spec, NMR, etc) proved to be a challenge and frustration due to the insolubility of **78** and hence this even delayed publication.¹⁸¹ Although more recently we succeeded¹⁸² in improving the overall yield for the formation of **78** to 70%; at the time this made me think of how one could make such macrocycles in a simpler, better way in much higher yields. My aforementioned experience in organometallic chemistry, and in particular Pt(II) chemistry and the square planar nature and concomitant 90° angle of Pt(II) complexes, provided the insight that transition metal chemistry, metal-ligand dative interactions¹⁸³ and likely self-assembly were an answer.

Self-assembly is a process whereby appropriate complementary molecular subunits spontaneously assemble according to the specific information encoded within their structures. Nature is the supreme and consummate master of self-assembly and supramolecular chemistry. It embraces the principles of, and adroitly exploits, noncovalent interactions of all types in a multitude of ways to enable and facilitate countless biological processes. All living organisms,

from the simplest to humans, depend upon some form of molecular self-assembly. Nature performs the most amazing feats of self-assembly with an artistry and facility we can only admire and all too often take for granted. Protein folding,¹⁸⁴ nucleic acid assembly and tertiary structures,¹⁸⁵ phospholipid membranes,¹⁸⁶ ribosomes, microtubules, etc. are but some representative examples of self-assembly in nature that are of critical importance in living organisms.¹⁸⁷ The protein coat of all viruses around their nucleic acid consists of a self-assembled spherical capsid, in the shape of either a dodecahedron or an icosahedron.¹⁸⁸

The power and beauty of spontaneous self-assembly derives from its ability to rapidly, and deceptively simply, generate large, complex and sophisticated “supramolecules” from easily available building blocks with maximum efficiency, generally under mild conditions (at or near room temperature, at 1-atm.) in water or other common solvents. Self-assembly depends upon appropriate direction and control being exerted at all stages of the process via preprogramming of the subunits or building blocks such that the requisite recognition elements for self-assembly are contained in the subunits. Nature’s repertoire of information to guide self-assembly includes hydrogen bonding, π - π stacking, hydrophobic-hydrophilic interactions, electrostatic and van der Waals interactions, conformations, etc., all commonly referred to as “weak interactions.” Among the difficulties encountered in our attempts to mimic nature’s elegant self-assembly processes, particularly in the formation of ensembles with well defined shapes and sizes such as polyhedra like dodecahedra, is our inability to use the directionality of the “weaker interactions” nature employs. In contrast, because of d-orbital involvement, dative, metal-ligand bonds are highly directional. Moreover, 3rd row metal ligand bonds have bond energies of ca. 15–25 kcal/mol, much less than covalent bonds (ca. 60–120 kcal/mol) but stronger than the weak interactions of biology (ca. 0.5–10 kcal/mol). Hence, coordination kinetics can be modulated to engage in self-repair to achieve thermodynamic control of superstructure. Furthermore, by being stronger than weak interactions one dative metal-ligand bond can replace several hydrogen bonds in the self-assembly process.

An important and critical feature of coordination driven, and indeed all self-assembly processes, is that they must occur under thermodynamic control with kinetically rapid reversible equilibria between starting materials, intermediates and products. As the equilibrium is reversible, the process is self-correcting: an “incorrectly” formed bond can dissociate and reassociate “correctly.” However, to be practically useful, any thermodynamic self-assembly process must generate one product, which is substantially more stable than any starting material, intermediate or competitors, thus ensuring a near-quantitative yield. This is generally, albeit not always, the case in coordination driven self-assembly. In such a thermodynamically controlled, kinetically rapid, self-assembly process, all components are continuously being formed and are in thermodynamic equilibrium.^{189,190}

Elegant, pioneering work by J.-M. Lehn and J.-P. Sauvage (Strasbourg) demonstrated¹⁹¹ the feasibility and usefulness of coordination driven self-assembly in the formation of infinite helicates, grids, ladders and racks.¹⁹² Inspired by this work, my interest in molecular squares such as **71–73**, and my experience with square planar Pt(II), the logical place to start was the formation of supramolecular squares via coordination driven self-assembly. Indeed, reaction of dppp-chelated Pt and Pd bis-triflates **79** with dipyrindine afforded¹⁹³ the desired squares **80**, in essentially quantitative yields as determined by NMR and high isolated yields, as shown in Scheme 14. Furthermore, X-ray data unambiguously established the structure and exact geometry (Figure 1a) as well as the novel solid-state packing of the cationic portion of molecular square **80a** (Figure 1b).

This initial success was rapidly followed by the formation of a wide variety of squares of different sizes and composition¹⁹⁴ such as mixed,¹⁹⁵ neutral-charged Pt-Pt and Pt-Pd, as well

as hybrid¹⁹⁶ Pt-iodonium, early-late¹⁹⁷ transition metal, large nanoscale¹⁹⁸ and porphyrin¹⁹⁹ based squares, all in essentially quantitative yields.

These achievements in turn made me think of the broader implications and advantages of metal directed and driven abiological self-assembly and in particular of different types of finite, closed, rigid 2D and 3D architectures with pre-designed shapes and sizes. As a consequence, together with Bogdan Olenyuk (then a graduate student at Utah, now an Assistant Professor of Chemistry at the University of Arizona) we developed²⁰⁰ the so called “directional bonding” approach for the ready, modular assembly of a wide range of 2D polygons and 3D cages as illustrated in Figure 2. This methodology combines rigid electron-poor metal centers and complementary rigid electron-rich organic donors. The two most significant factors that largely determine the supramolecular structure so obtained are the shape and size of the individual component-building units (tectons). The shape of the donor/acceptor units is dominated by the turning angle, defined as the angle formed between the open valencies of a ditopic or tritopic donor or acceptor. For example, as seen in Figure 2, four 90° square planar Pt-units in combination with four linear donor units, such as bipyridine, afford a $A^2_4L^2_4$ molecular square or eight mutually perpendicular, tritopic angular, units in combination with 12 ditopic, linear units, can form a $A^3_8L^2_{12}$ molecular cube. Furthermore, the size of the individual building units determines the overall size of the self-assembled supramolecular species. As previously described,^{200b} symmetry considerations also play an important role in this abiological self-assembly protocol.

Our “directional bonding” approach, which has been widely used and adopted,²⁰¹ allowed us to prepare other polygons such as triangles,²⁰² various rhomboids,²⁰³ diverse rectangles²⁰⁴ and hexagons,²⁰⁵ all in near quantitative yields as expected for a self-correcting, self-healing process.

Of course, as in all active, cutting-edge research such as coordination driven self-assembly, we were and are not alone in the field. M. Fujita (University of Tokyo) and co-workers were pioneers in this area and reported the self-assembly of the first molecular square²⁰⁶ as well as many other interesting metallacycles and metallacages.²⁰⁷ K. Raymond (UC-Berkeley) and co-workers²⁰⁸ have developed and applied a protocol based upon incommensurate n-fold symmetry axes, and C. Mirkin (Northwestern) and co-workers pioneered a methodology based upon the weak-link approach²⁰⁹ and, more recently, a new protocol using a halide induced ligand rearrangement reaction.²¹⁰ The late Professor Albert Cotton and co-workers employed di-metal building blocks in their approach.²¹¹

We proceeded to investigate both 2D²¹² and 3D²¹³ chiral self-assembled supramolecular species. Chiral supramolecular systems²¹⁴ are particularly interesting because of their applications in asymmetric catalysis, chiral-host-guest events, chiral sensing, and their potential to mimic complex biological processes.

Likewise, functionalized supramolecular metal-organic assemblies are of considerable interest because of their potential uses in a variety of electronic, magnetic, catalytic, photonic, mechanic and sensor applications.²¹⁵ There are at least three ways of incorporating functionalities into metal-organic supramolecular architectures: (1) edge or corner functionalization; (2) “inside” or endo functionalization via covalent attachment; (3) “outside” or exo functionalization via covalent linking as shown in Figure 3.

Initially we prepared corner functionalized ferrocene²¹⁶ and crown ether and calixrene²¹⁷ systems; more recently we self-assembled various edge functionalized metal-organic architectures.²¹⁸ Most recently we self-assembled a series of dendrimer,²¹⁹ ferrocene,²²⁰ and crown-ether²²¹ exo-functionalized architectures. A novel aspect of this work is the direct “one

pot" self-assembly, via orthogonal none-covalent interactions of hexagonal cavity-cored poly [2]pseudorotaxanes²²¹ as shown in Figure 4.

Similarly we have developed a functionalized rectangle as a chromogenic supramolecular optical sensor for Ni(II), Cd(II) and Cr(III) as illustrated in Scheme 15.

The vast majority of self-assembled supramolecular metallacycles are charged.²²³ However, recently we²²⁴ and others²²⁵ have also prepared a range of neutral supramolecular ensembles via self-assembly. Similarly, ambidentate ligands, usually a pyridyl carboxylate, have also been employed^{226,227} in the formation of self-assembled metallacycles.

In some cases, instead of a simple product, there is an equilibrium between two species such as a triangle and square^{202b} or a rhomboid and hexagon.²²⁸ In some instances there is also restricted rotation around the Pt-N bond^{199b,229} resulting in AB multiplets due to the inequivalent α - and β - protons of the pyridyl moiety. This has been investigated using variable temperature NMR by us²³⁰ and others,²³¹ and a free energy of activation, $\Delta G^\ddagger$, for the rotation of the bipyridine unit was determined to be about 74 kJ/mol.

The mutual recognition of complementary components within a complex mixture, that is self-sorting, is a critical phenomenon in biological systems. Self-sorting allows for the formation of multiple higher-order supramolecular structures from complex multicomponent mixtures when specific recognition information is encoded within the structure of molecular subunits.²³² Therefore, we,²³³ and many other groups,²³⁴ investigated self-sorting in metal-ligand coordination driven abiological self-assembly. As shown in Scheme 16, only head-to-tail ensembles, **83** and **85** were observed,^{233c} with no trace of head-to-head analogs in the reaction of the ambidentate pyridylcarboxylate unit **81** with acceptors **82** and **84**, respectively. Likewise, over 90% self-recognition, with but minor amounts of oligomers, and formation of the respective rectangle **87**, square **88**, and triangle **89**, were observed,^{233d} after equilibration for about 120 hours, in the reaction of mixtures of tectons, **82**, **84**, and **86** with 4,4'-bipyridine, as shown in Scheme 17. Hence, these coordination driven abiological self-assembly processes undergo self-selection via self-recognition analogous to biological systems and provide further evidence for the thermodynamic control, via fairly rapid kinetic pathways, in the self-assembly of these nanoscale supramolecular ensembles.

Molecular-based devices,²³⁵ e.g. molecules that possess the ability to act as sensors, switches, motors, machines, memory components, etc. - represent perhaps the ultimate in minaturization of functional machinery. Such devices, when properly designed and controlled, constitute the backbone of the nascent nanotechnology that has the potential to revolutionize manufacturing and consumer goods in the 21st century. *Nanotechnology*, however, will only develop to its full potential if preceded by *nanoscience*: a solid foundation and understanding of the fundamental properties of molecules at the nanoscale and of "bottom up" nanofabrication.²³⁶

As already described above, the synthesis and characterization of self-assembled 2D and 3D coordination based supramolecular architectures is well established, as are their solution and solid-state properties.²²⁹ Very little is known, however, about their behavior on surfaces. While solution phase studies are essential for the establishment and understanding of many of the configurational, physical, optical, and dynamic properties of molecules, and solid-state studies provide unequivocal structural information, neither phase is ideal for the design and fabrication of molecular devices.²³⁷ Where the solution state lacks coherence and orientational control, and the solid state often imparts too much rigidity and confinement, the deposition of molecules and supramolecules on surfaces provides²³⁸ a means of controlling and integrating them with other known materials in typical device settings, provided that they can be aligned, distributed, and addressed appropriately. For these reasons, investigating the behavior and properties of

these species on surfaces will provide the necessary nanoscience foundation that is critical for the design, development, and fabrication of nanomolecular devices.

The advantages of incorporating functional organic and organometallic molecules into device settings by integrating them onto/into surfaces have been known for some time. Surface confined molecular films that contain functional electronic materials include photovoltaic devices, optical and non-linear optical materials, light emitting diodes, and field-effect transistors.²³⁹ The reduced symmetry of surface confined, molecular film-based components and devices offers the opportunity to systematically manipulate and tune their collective optical, electronic and other properties through molecular design in a manner that is often more effective than may be achieved by the same components in the less coherent solution phase. Even with the great many successes²³⁹ of molecular film-based devices, the use of self-assembled supramolecular metallacycles provide additional advantages owing to the ease with which large, symmetric, structurally complex polygons and polyhedra can be prepared. It is in this regard that the incorporation of metallacycles onto surfaces can be considered multi-tiered self-assembly: the supramolecules are first themselves self-assembled and then they are collectively self-assembled onto the desired surface. Taking advantage of thermodynamically-driven self-assembly processes at each step avoids many of the time consuming and costly elements of device fabrication, such as multistep covalent synthetic procedures, high-vacuum sublimation-deposition of monolayers, harsh surface treatments necessary for etching, and the like.

The primary method of characterizing and understanding surface confined nanoscale molecules is scanning probe microscopy²³⁷ and, in particular, the primary instruments are scanning tunneling microscopes (STM) and electrochemical STM (ECSTM).²⁴⁰ STM has unparalleled spacial resolution and is thereby able to provide real-time, real-space, 3D surface structural information up to atomic resolution in the exploration of single molecules and their aggregates on surfaces.²⁴⁰

To date, a large number of surface-confined complex organic, inorganic, and biological molecules have been studied.²⁴¹ There have been, however, very few investigations of the structure and properties of nanosized 2D metallacycles or 3D metallasupramolecular cages on surfaces.²⁴² Therefore we,²⁴³ in collaboration with Professor L. J. Wan at the Institute of Chemistry in Beijing, China, and others²⁴⁴ investigated surface confined metallacycles and metallacages. Figure 5 demonstrates that molecular square, **80a**, physisorbs on a Au(111) surface and, as seen in Figure 6, supramolecular rectangles physisorb on both HOPG and on Au(111) surfaces and self-organize to form highly ordered adlayers. Interestingly, as seen in Figure 6, the rectangles uniformly adopt an edge on orientation on HOPG but a flat orientation on Au(111). The reason for this difference of orientation on the two different surfaces, graphite and gold, is not fully understood, but likely has to do with the stronger π -Au interactions on gold vs. the weaker substrate-surface interaction on graphite. These results nicely demonstrate that nanoscale supramolecular metallacycles do indeed form well-ordered adlayers on surfaces and hence it will be possible to integrate these molecules into devices such as molecular sensors, switches, etc.

A fascinating and important aspect of abiological coordination driven self-assembly is the formation of three dimensional supramolecular polyhedra and cages.^{223,245} Such systems may be self-assembled via either a face-directed or edge/corner directed approach. We have used the face directed approach to self-assemble a truncated tetrahedron²⁴⁶ and cuboctahedra²⁴⁷ (Scheme 18) as well as various molecular prisms.^{231c,248}

The edge/corner directed approach was used in the self-assembly of a variety of 3D cages²⁴⁹ as well as dodecahedra²⁵⁰ (Scheme 19).

This last reaction is truly remarkable as fifty individual building units have to combine in just the right way to form the desired dodecahedron in quantitative yield as observed.²⁵⁰ Although we do not have an X-ray structure of the dodecahedra, various spectral techniques, including spin-echo NMR and TEM (Figure 7) establish their structure with a high level of confidence.

Similarly, Fujita²⁵¹ and Raymond²⁵² have self-assembled a remarkable array of interesting metallacages and investigated their host-guest properties and used them as nano reaction vessels.

These rationally designed self-assembled coordination based metallacages are also related to metal-organic-frameworks (MOF) that are currently very topical because of their potential use in gas (H₂, CO₂, etc.) uptake and storage.²⁵³

Our own contributions to this burgeoning field of abiological self-assembly via coordination has been the introduction of the “directional bonding” approach for the rational design of metallacycles and metallacages; the self-assembly of the first chiral architectures and the demonstration that they form highly ordered adlayers on HOPG and gold surfaces. The significance of this work lies in providing insights, by analogy, into biological self-assembly processes and, more importantly, in the nascent nanotechnology area by providing a means of rationally designing new materials, methods for “bottom-up” fabrication and new platforms for devices such as biomedical sensors, molecular machines and switches etc.

Summary and Conclusions

I have been fortunate to make contributions in three distinct areas in three different phases of my career. Early on I was involved in physical-organic chemistry and unsaturated reactive intermediates, in particular vinyl cations and unsaturated carbenes that has enriched the family of reactive carbon intermediates. Perhaps the most important legacy of this work is the discovery and first preparation of vinyl(enol) trifluoromethanesulfonates (triflates) that have become important and widely used in contemporary metal catalyzed cross coupling reactions. In the middle of my career I was involved in polyvalent iodine chemistry and some organometallic chemistry as well as strained, unusual aromatic hydrocarbons. The significance of this work is our discovery of several new iodonium reagents, in particular PhICNOTf, and a general method for the ready formation of alkynyliodonium species that are increasingly being employed in synthetic organic chemistry. For the last 15–18 years I have been involved in supramolecular chemistry and self-assembly where we have developed an entire new paradigm for the rational design of complex, nanoscale, finite metallacycles and metallacages that has impact upon nanoscience and nanotechnology and inspired numerous young scientists to enter the field.²⁵⁴ A common thread in all three areas has been my “mechanistic” thinking and approach acquired during my training as a physical-organic chemist. I continue to see a bright future for physical-organic chemistry and the rigorous thinking and approach that it demands and affords. My own involvement for the remainder of my active career will undoubtedly be in the area of supramolecular chemistry and self-assembly where there is a wealth of exciting and new things to be discovered and exploited.

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254. An indication of this in the over 1600 citations to date of our chemical review article, 223 published in 2000, and the over 600 citations to date of our Accounts article, 200a published in 1997, where we first described the directional bonding approach as summarized in Figure 2.

Figure 1.

(a) Geometry of Pt-square **80a** based upon X-ray data; (b) solid-state stacking diagram of the cationic part of **80a**.

Figure 2. Directional bonding approach to the formation of 2D polygons and 3D cages via the combination of various angular (A) and linear (L) tectons.

Figure 3. Different ways of incorporating functionality into self-assembled supramolecular metallacycles.

Figure 4.
Orthogonal, one-pot self-assembly of poly[2]pseudorotaxanes.

Figure 5.

(A) Large-scale STM image of self-assembled squares adsorbed on a Au(111) surface. (B) High-resolution STM image of the adlayer also showing the underlying Au(111)-(1x1) lattice in the upper right corner. (C) Proposed structural model for the adlayer.

Figure 6.

(A) Low-resolution image of a supramolecular rectangle on HOPG, showing the underlying HOPG surface in the lower left corner. (B) High-resolution STM image of the supramolecular rectangle on HOPG. (C) A proposed structural model for the adlayer of the rectangle on HOPG. (D) A large-scale (60 × 60 nm) image of the same supramolecular rectangle on Au(111). (E) High-resolution image of the rectangle adlayer, showing the underlying Au(111) lattice in the lower left corner. (F) A proposed structural model for the adlayer of the rectangle on the Au (111) surface.

Figure 7.
TEM micrograph of individual dodecahedra deposited on a carbon film at low concentrations and dried at $-130\text{ }^{\circ}\text{C}$.^{250a}

Scheme 1.
Solvolytic Generation of a Vinyl Cation¹⁸

Scheme 2.
Mechanism of reaction of E-3, and Z-3-aryl-2-buten-2-yl triflates.²⁹

Scheme 3.
Generation of extended unsaturated carbenes.

Scheme 4.
Preparation of alkylidenecycloproparene **38**

Scheme 5.
Formation and decomposition of **43**.

Scheme 6.

Formation of alkynyl(phenyl)iodonium tosylates.

Scheme 7.
Formation of alkynyl(phenyl)iodonium triflates.

Scheme 8.

The mechanism of alkynyliodonium salts via ylids and carbenes.

Scheme 10.
Diels-Alder reactions involving alkynyliodonium salts.

Scheme 12.
Coupling of alkenyliodonium salt **68** with alkynes.

Scheme 13.
Synthesis of macrocyclic tetraaryltetraiodonium compound **78**.

Scheme 14. Self-Assembly of dppp-chelated Pt and Pd macrocyclic molecular squares **80**.

Scheme 15.
Supramolecular chromogenic sensor for Ni, Cd, and Cr.

Scheme 16.
 Self-selection in self-assembly.

Scheme 17.
Self-recognition in self-assembly.

Scheme 18.

Face directed self-assembly of a cuboctahedron from triangle-tectons and 12 connectors.

Scheme 19.
Self-assembly of a nanoscale dodecahedra.