

Organometallics Roundtable 2011

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These are turbulent times for much of chemistry as well as underlying global economies, but organometallic chemistry is heading higher, say the participants in the 2011 Organometallics Roundtable. In the inaugural version of this feature, our panelists take the pulse of the field, threshing out the big picture as well as the minutiae.

have a broader range of high-valent metal oxo complexes that contain easily tunable non-porphyrin ligands. This would allow us to rapidly identify parameters important in achieving our goal of using nitrous oxide at ambient temperatures and pressures.



We are living in an era of unprecedented change in academic, industrial, and government-based research worldwide, and navigating these rough waters requires “all hands on deck”. Toward this end, *Organometallics* has assembled a panel of seventeen experts who share their thoughts on a variety of matters of importance to our field.

In constituting this panel, an attempt was made to secure representation from a number of countries and career stages, as well as from industry. We were fortunate that so many busy experts could take the time to spend with us. The following pages constitute an edited transcript of the panel discussion held on August 29, 2011, which was structured around the 10 questions summarized in the side bar and repeated below.

(1) *Organometallics*: As a way of warming up our crystal balls, let us talk synthesis in the context of your own research. Suppose Santa Claus could have bought you one new reaction, process, ligand, etc. for Christmas to help the chemistry in your research group during 2012. What would have been your wish, and why?

Jennifer Schomaker: We do a lot of oxidation chemistry in our group, and we’re particularly intrigued with using nitrous oxide as a very selective and mild oxidant. I would love to

Bernhard Rieger: We have been engaged in CO₂ chemistry for several years and have been trying to incorporate the carbon atom from CO₂ into value-added products. A couple of months ago, we succeeded in obtaining acrylic acid esters from ethylene and CO₂ using nickel-based complexes. My wish would be to somehow close the cycle to achieve a new catalytic reaction. I have the feeling we are very close.

Suzanne Blum: Rather than a synthetic technique, my group could really use a new analytical method to assay our reactions much more quickly, something that could look at lots of air-sensitive reactions and would be cheap enough for routine use in academic environments. This would allow us to investigate many different reaction conditions and optimize much more quickly than we currently can do.

Al Sattelberger: Did you look at combinatorial methods or are you thinking about those?

Suzanne Blum: We are certainly screening ligands and metals that way, but what we could really use is something that doesn’t require a special institute or center that’s been

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funded with expensive robotic equipment. We need to have the ability to look at reactions much more quickly and optimize more easily.



Suzanne Blum, *University of California—Irvine*

Tobin Marks: Look at everything we've learned recently about N-heterocyclic carbene ligands or pincer ligands or other porphyrins. What I'd like are ligands that make homogeneous catalysts behave more like heterogeneous catalysts in terms of thermal stability, durability, recyclability. I throw this out as a broader challenge than just one ligand. Bernard Rieger and I were talking about a related matter before we started. If you look at how long it's taken to discover some of these ligands, are there ways to speed the discovery process? And once they are discovered, we need to get them into the community faster.

Organometallics: That's a very provocative and interesting statement. On the scientific side, is the presence of C–H bonds a debit in realizing these types of ligands? They would seem to be the Achilles heel in many cases.

Tobin Marks: Sure, ligand substituents will be the key. If you look at our community, there are people running homogeneous catalytic reactions at universities at far higher temperatures than we would have ever imagined doing before and getting really interesting results. And that's because of the much more durable ligands and metal complexes, but the C–H bond could be one thing we might want to protect.

Joachim Ritter: My team is involved with converting biomass to feedstock chemicals, as opposed to new polymers. There are a lot of intermediates that have been promoted over the years, for example the candidates from the 2004 DOE report (Top Value Added Chemicals from Biomass Volume I—Results of Screening for Potential Candidates from Sugars and Synthesis Gas, DOE 2004). For many of these, there is really no commercially viable chemistry available: for example, hydroxymethyl furfural (HMF), which can be accessed from glucose or fructose. I would like to see the homogeneous catalysis community get more interested in these areas. Since this is a Christmas present question: I would like to see a homogenous catalyst with a very stable ligand like Tobin Marks pointed out that is capable of converting glucose to HMF in 90–95% yield at temperatures below 80 °C.

Organometallics: Would that make a lot of money, or be worth patenting at least?

Joachim Ritter: Yes.

Jim Mayer: I would like to extend what Tobin Marks said to solvents, not just ligands. I think we have a need for inert inexpensive solvents, and ideally usable as NMR solvents. We need solvents that would be stable to the kinds of conditions people are pushing their systems to—whether it is harsh conditions involving acid or base or oxidative conditions.

Organometallics: Jim, for classic organic molecules, the range of available liquids seems pretty well established. Are you thinking of “neoteric” solvents such as ionic liquids or certain special categories?

Jim Mayer: I was thinking more about pure and simple chemical stability. As we get more stable ligands, such as the pincer ligands that Alan Goldman, Jensen and Kaska, and Brookhart and others have developed, people are doing reactions at higher temperatures and under more forcing conditions. Alkane functionalization reactions, for instance, would ideally be done in a solvent that could dissolve ions and that would not be reactive under conditions that attack unactivated C–H bonds.



Guy Bertrand, *University of California—Riverside*

Guy Bertrand: Let me throw out a new type of answer to the question being discussed. My dream is to replace transition metals by main-group elements to achieve novel bonding motifs, new catalysts, new materials, etc. Some of this is motivated by pure intellectual curiosity. But one practical aspect would be toxicity considerations. For example, boron and silicon are much more benign than many metals.

Organometallics: Anyone else?

Bernhard Rieger: Maybe we could have a programmable polymerization catalyst that assembles monomers according to a built-in protocol that can be altered. This is admittedly very visionary, but this may be something that has the potential to change polymerization catalysis and the way we design polymer materials enormously.

Vy Dong: Hydroformylation is a very useful industrial transformation. The related process hydroacylation has the potential to be useful but remains very limited in scope. If I'm asking Santa Claus for a reaction, I would like a general hydroacylation method to couple simple aldehydes and olefins or ketones, with perfect atom economy. Since we're talking to Santa Claus, let's have this method be catalyzed by iron complexes. It would be great to have a unified and broadly applicable strategy for making various organic motifs, including aldol products, Mannich products, heterocycles, macrocycles, etc.

To follow up on Tobin Marks' comment about ligand design, I would add that while there are so many chiral phosphine ligands for use in enantioselective reductions, we barely have any chiral ligands available for enantioselective oxidation chemistry.

Organometallics: What kind of chiral ligands would you need? Are you thinking about nitrogen donor ligands, which

SUMMARY OF PANEL QUESTIONS

(1) As a way of warming up our crystal balls, let's talk synthesis in the context of your own research. Suppose Santa Claus could have bought you one new reaction, process, ligand, etc. for Christmas to help the chemistry in your research group during 2012. What would have been your wish, and why?

(2) After Christmas comes New Year's. That's an occasion for looking back. What do you see as some of the top organometallic achievements of 2011 when it comes time to sing Auld Lang Syne?

(3) Let's reduce the previous question to "attention-getting molecules". Are there any nominations for an "organometallic molecule of the year" for 2011 (or 2010)?

(4) What are the major challenges for organometallic chemistry, either within the field or in the context of the "grand challenges" for society. What specific problems should be attracting organometallic chemists?

(5) In January of 2011, Whitesides and Deutsch published an essay in *Nature*, "Let's Get Practical", in which they state "Business as usual is not an option". Do you perceive a message for organometallic chemists in this opinion piece?

(6) Suppose one of your students will start an academic research group in 2012. What would be your advice?

(7) "Frustrated Lewis Pairs", which have been on the scene for about five years, could be viewed as a "new" reactivity mode, i.e. a previously unrecognized or ungeneralized mechanism of activation. Are more of these coming down the line, or are the organometallic chemist's bag of tricks pretty much on the table?

(8) What influences are computational chemistry and new instrumentation or instrumental techniques having on organometallic chemistry? Are there trends or developments of note?

(9) What other factors may be limiting the advancement of the field? Do you perceive any shortcomings that need to be addressed in the area of human capital, education, training, infrastructure, meetings or public forums, publishing venues, etc.?

(10) Would anyone like to add anything more regarding organometallics and the year 2012, or challenges for the future?

one often sees in oxidation catalysts? These are frequently pyridine systems, and a stereocenter may have to be remote.

Vy Dong: Sounds right. In 2009, the Sasai group from Japan reported the use of a spiro bis(isoxazoline) ligand that allows an oxidative Pd-catalyzed cyclization.¹ That's one of the few examples of asymmetric catalysis using higher valent

palladium. We just don't have many of these ligands available for screening.



Vy Dong, *University of Toronto*

Ekkehardt Hahn: I'd like to make a remark coming back to the idea of self-assembly. Let's look at what's popular in this field now like MOFs. Now look at Ken Raymond's tetrahedral assemblies from polycatechol ligands. How about substituting these ligand building blocks with ligands from organometallic chemistry, or for compounds essentially forming organometallic derivatives in the end. Take a polycatecholate and make it a polycarbon donor ligand. Of course, only a few donor groups are available, which most likely would be isocyanides or carbenes (NHCs). In the field of molecular compounds one can make polymetallic assemblies with polycarbene ligands. The question is: can one make something that is like a MOF, where the organic building block would be ligands from organometallic chemistry like a polycarbene or polyisocyanide or something like this? And this is what I think would be a real challenge, because it would not only lead to new self-assembly materials, but the metals in these compounds would be coordinated by carbon donors rather than oxygen or nitrogen donors like in the classical MOFs. They might thus retain their catalytic activity, so you may end up with a zeolite type assembly that contains catalytically active metals, which are only coordinated by carbon donors. I believe this constitutes a challenge and is something I'm dreaming about for many years now. Some initial progress has been made, but we are far from reaching the target.

Organometallics: Is there anyone besides you thinking about this or working on it?



Ekke Hahn, *Westfälische Wilhelms-Universität Münster*

Ekkehardt Hahn: I've known a couple of people trying to make compounds similar to benzenetricarboxylic acid that

feature three carbene donors and then use these together with suitable metals to assemble networks, for instance. But that is difficult because these things in the end turn out to be not too soluble. So how are you going to characterize them? If you want to make a molecular cage, that appears possible—but a polymer, I don't know of any.

Zach Ball: This touches on coordination chemistry ideas we are thinking about. To me, the fundamental problem is that most of these ligands participate in kinetic, irreversible ligation events. And MOFs perhaps require finding a thermodynamic minimum. So how do you approach that problem?

Ekkehardt Hahn: That can be controlled, and we had just recently a paper published where this has been done. If you have silver carbenes for instance, they are not inert, they can rearrange, and we have seen polycarbene ligands forming different polynuclear assemblies depending on what is thermodynamically most stable, breaking for instance carbene-silver bonds in the process. It does not work with carbene-platinum or carbene-palladium bonds, but with silver it works. So once you have made silver carbenes, they are not at the end point thermodynamically, and they can still react further. That is the basis for the transmetalation reaction—you can take a silver carbene and transmetalate it to gold or whatever.

Zach Ball: And do you have hope that if you design the right carbene ligands that you could get exchangeable carbene ligands for platinum or other systems? Is it a ligand design problem?



Zachary Ball, Rice University

Ekkehardt Hahn: That has already been shown with NHCs. One can take a tetracarbene, stick four silver cations to the carbene donors, and then transmetalate the carbene ligand to get the tetragold derivative. In any case we're talking about dreams here, right?

Organometallics: Thank you, Ekke. Are there any other dreams, goals, or Christmas presents for your group?

Mark Humphrey: We've been building metal arylalkynyl containing oligomers and dendrimers and so on for a while. What would be nice would be a Sonogashira coupling catalyst that works easily with no particularly air-sensitive manipulations, no steric problems, and no alkyne homocoupling, and that works with aryl chlorides, electron-rich alkynes, and all the other difficult systems—it would be great to avoid the need for trans-halogenations or other modifications.

If I can be greedy and have a second present, I'd like broadly applicable methods for the controlled syntheses of high-nuclearity carbonyl clusters—what I'm really after is where one can

“dial up” the cluster size and composition. The area is still dominated by the old “heat-it-and-hope” and redox condensation approaches.

Jerzy Klosin: We do a lot of ligand synthesis and we have a state-of-the-art reactor high-throughput facility. However, often the limiting step is just making ligands. Even with the recent advances in organic synthesis such as various cross-coupling chemistries, it often takes us one week to make one ligand. So there is a mismatch between screening and synthesis capabilities—we can actually screen about 200 reactions a day, but at times we can only make one or two ligands per week. So for our lab, the dream improvement would be the development of high-throughput synthesis, because it doesn't actually exist now for many ligand families.

Organometallics: Do microfluidics enter into the possibility for you here or are there limitations such as scalability?

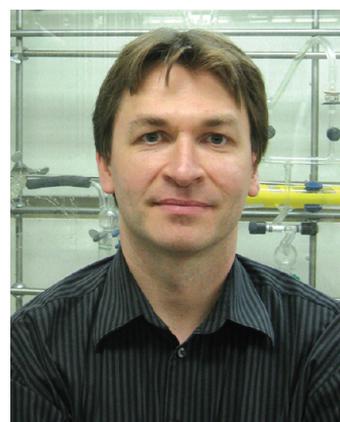
Jerzy Klosin: Yes, we probably need a little bit more than that.

Joachim Ritter: I was involved with high-throughput work at Dupont about 10 years ago, and we built a facility to synthesize about 100 phosphite ligands per week under air- and moisture-free conditions. But it takes serious commitment. Ultimately, you have to recognize the immense staffing needs required to sustain such a facility.

Jerzy Klosin: Agreed.

Joachim Ritter: Furthermore, there is no such thing as 100 or more clean ligands falling into your hands within a week unless you're focusing on a particular class of ligand, chemistry, and isolation technique.

Jerzy Klosin: Absolutely right—there are some ligands we used when we were involved in asymmetric hydroformylation chemistry that are easy to prepare using parallel synthesis. We actually made dozens of them within a week. You can make various imines using the high-throughput approach. However, when you do, for example, Suzuki-type chemistry within a multistep reaction sequence it's difficult to envision what kind of a high-throughput methodology would allow one to streamline such synthesis.



Jerzy Klosin, The Dow Chemical Company

Tobin Marks: Maybe this is more of a question, but if you think of how our discipline has advanced, one very important thing is tools, such as NMR, mass spectroscopy, single molecule spectroscopy, and calorimetry. One of the subjects I hope we can discuss today would be some of the new emerging tools.

Jerzy Klosin: I have one more wish for the chemistry Christmas list, but it diverges from Tobin Marks' direction.

We've been involved in olefin polymerization for a number of years and one of the holy grails in this field has been efficient copolymerization of ethylene and/or propylene with polar monomers. This has been accomplished on a very small scale, with late transition metals, but these systems are far from being practical, as they are mainly based on palladium. So I guess my Christmas wish would be the discovery of highly efficient and inexpensive catalysts that would be able to copolymerize ethylene with monomers containing polar functionalities.

Vivian Yam: As I have been working more on the materials and energy side, I would love to have an organometallic metal complex system that is highly luminescent and robust, resistant to oxygen and moisture with a photoluminescence quantum yield of unity and very high electroluminescence quantum efficiency for white OLED's for solid-state lighting. I also would like to have an organometallic metal complex system with a long-lived charge-separated state for solar energy conversion and a robust photocatalyst for water splitting.

(2) *Organometallics*: After Christmas comes New Year's. That is an occasion for looking back. What do you see as some of the top organometallic achievements of 2011 when it comes time to sing Auld Lang Syne? Said differently, was there any work that made you highly envious? Obviously there will be a lot of subjectivity in the responses.

Bill Jones: Since I've been in the area of CH activation for a long time, I look back and ask "what have we really accomplished?". One of the earliest and most useful things was the formation of olefins from alkanes. Jensen and Goldman did the first catalytic examples of that chemistry, but the real use for that has really come on stream in the past couple of years, with alkane metathesis. This involves generation of an olefin, subsequent metathesis, and rehydrogenation to a new distribution of alkanes. I think that was a significant accomplishment to be able to combine both of those steps and turn it into something useful.

The next development, reported this past year (Scheme 1),² is the formation of *o*-xylene from octane, where you dehydrogenate octane several times to form a triene, then do an electrocyclicization, and then dehydrogenate to form product. It also appears that this may be commercially viable. The researchers noticed early on small amounts of benzene in their alkane metathesis studies. And following up on that a year or two later, they discovered how to optimize that process and then found out that with octane as the feed, *o*-xylene was formed with high

selectivity. It's exciting and interesting to me as one of the great recent discoveries.

Vy Dong: My students had a debate regarding this very question last year, and they chose the Mo-catalyzed Z-selective olefin metathesis reaction developed by Amir Hoveyda and Richard Schrock as the top achievement in organometallic chemistry last year (Scheme 1).³ There are many exciting aspects of that work. For one, the complex itself has a unique structure, bearing a pyrrolide, a tunable imido, and an axially chiral binol-derived ligand. In addition, these chiral-at-molybdenum alkylidenes exhibited unprecedented levels of reactivity and selectivity and provided the first example of a highly efficient catalytic Z-selective cross-metathesis reaction. This study also featured insights from computational chemistry by Odile Eisenstein. This work will undoubtedly inspire future developments in catalyst design. It's also a rare and relevant example of stereoselective synthesis using a chiral-at-metal complex.

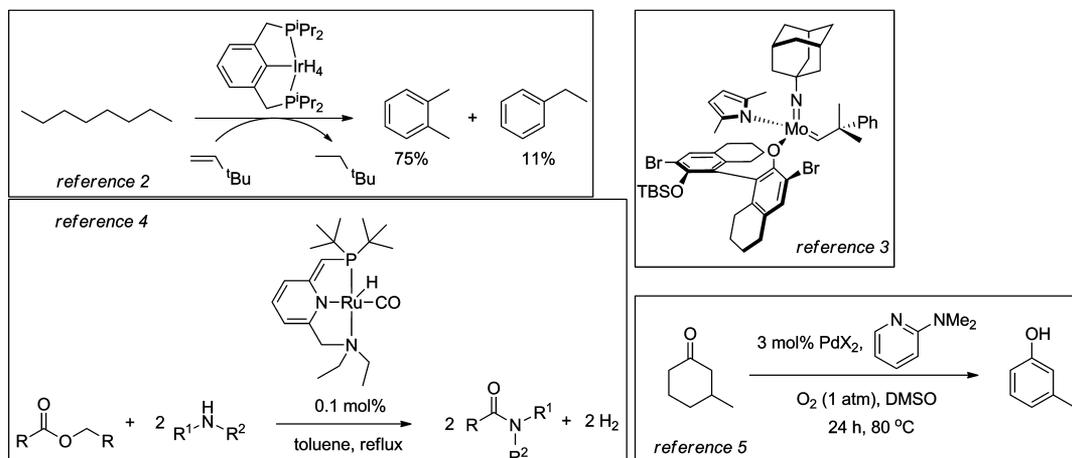


Mark Humphrey, Australian National University

Mark Humphrey: I think that the dehydrogenative couplings—for example of amines and alcohols to make amides—that have come out of David Milstein's group are really slick (Scheme 1).⁴ Given the inexpensive building blocks, there seems to be the potential for new commodity chemical processes.

Jennifer Schomaker: Along the lines of dehydrogenation chemistry, a recent paper by the Stahl group reported a very nice Pd-catalyzed aerobic conversion of substituted

Scheme 1. Panel Picks, Part 1 (See Text for Others)



cyclohexanones to phenols (Scheme 1).⁵ One exciting aspect of this method is that in contrast to the conventional ortho and para substitution patterns obtained from electrophilic aromatic substitution of phenols, meta-substituted phenols can be obtained readily. The variety of well-established chemistries for accessing the cyclohexanone substrates is another attractive feature of the method.

Zach Ball: On the subject of dehydrogenation and its use to trigger other processes, I'd like to point to work that's come out of Krische's lab at the University of Texas (Scheme 2).⁶ I'm convinced that these systems are powerful new synthetic approaches that work in very complex structures encountered in target-directed synthesis. So it gets away from the demonstration of new reactivity and is a different approach to truly create useful processes. Honestly, 5 years ago I wouldn't have believed these sorts of transformations were possible.

Joachim Ritter: I'll use the opportunity to pick up dehydrogenation in the area of biomass conversions using organometallic catalysis. I was really impressed by Bergman's and Ellman's paper basically disproportionating lignin models by first ruthenium-catalyzed dehydrogenation and then hydrogenation to create mixtures of monofunctional carbonyl and hydroxylic products (Scheme 2).⁷ I also think Hartwig's work on nickel-catalyzed hydrogenolysis is equally impressive (Scheme 2).⁸ There's a long way to go, but this is a very important area for a sustainable future, and I would like to see more organometallic chemists engaged in this area.

The big picture here would be sustainable solutions for today's chemicals. I think there is still this perception out there that one takes biomass and creates new molecules or materials. That is usually a very steep uphill battle. A commodity is defined as something that already exists today abundantly. New materials are very difficult to introduce. It can take decades. A sustainable future will require some new materials, but it will also require sustainable solutions coming up soon for the base materials, including aromatic commodities. The work I mentioned is certainly leading the way in this context on a very fundamental level.

Bill Jones: In my view, the key point here involves maximizing non-petroleum-based resources.

Bernhard Rieger: I have another example maybe from polymerization catalysis. The CO₂/propylene oxide copolymerization is now 40 years old, and over the entire time, we never had catalysts active enough to allow commercialization.

A couple of years ago, Lee from South Korea came up with a specifically substituted cobalt salen complex. These authors showed for the first time that we can have extremely high polymerization activities. I think this is an important signal for the industry, with respect to a new and sustainable polymer chemistry, which is no longer oil based. So I believe this represents an important recent breakthrough.



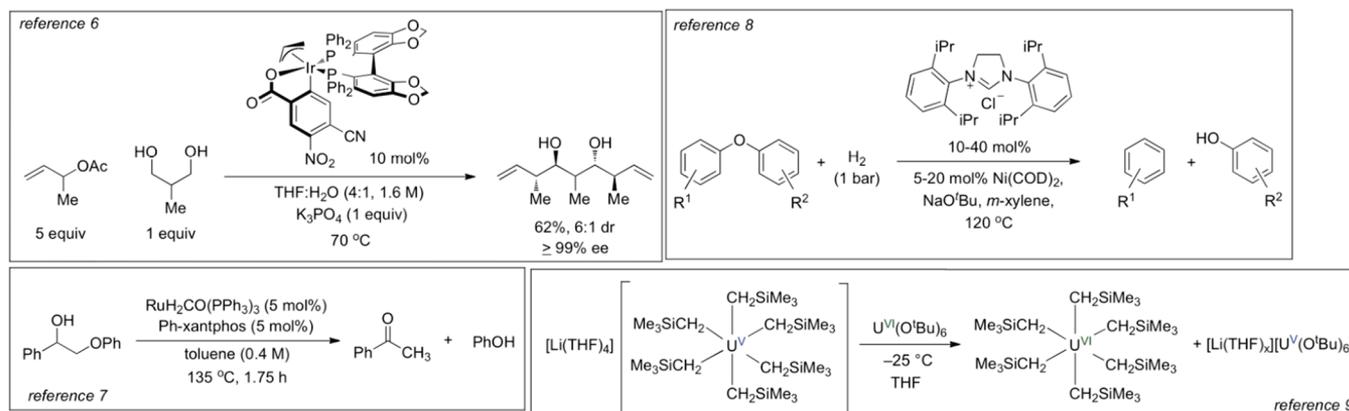
Bernhard Rieger, Technische Universität München

Jerzy Klosin: In a somewhat different vein, I think olefin metathesis is going to be a big force, and not only in the fine chemical industry. However, one complication for making commodity materials containing polar functionalities via metathesis is the use of expensive ruthenium. So going back to the Christmas wish list, it would be particularly worthwhile to develop metathesis catalysts that are based on the first-row metals.

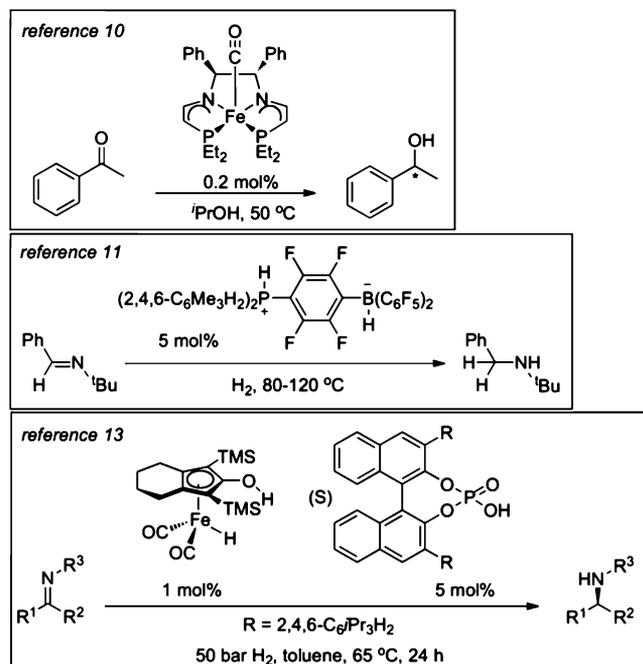
Al Sattelberger: A number of us around the table have worked on uranium alkyls from time to time, and I must confess that I'm really impressed with what Trevor Hayton is doing at UC Santa Barbara. He published a paper recently on homoleptic uranium(V) alkyls and has compelling evidence for a homoleptic uranium(VI) alkyl in solution (Scheme 2).⁹

Vy Dong: We were encouraged to think of recent reports that made us especially envious, and it's always tempting to covet one's own neighbor's chemistry. In Toronto, Bob Morris has developed an iron catalyst for asymmetric transfer hydrogenation,¹⁰ while Doug Stephan has reported boron catalysts for hydrogenations with H₂ (Scheme 3).¹¹ Along with Paul Chirik's earlier work,¹² these exciting advances give hope that

Scheme 2. Panel Picks, Part 2 (See Text for Others)



Scheme 3. Panel Picks, Part 3 (See Text for Others)



other important metal-catalyzed transformations, like hydrogenation, may be possible, without using precious metals.

Al Sattelberger: I also noticed an interesting case where Beller combined a Brønsted acid and a transition-metal complex to create a novel catalyst system for enantioselective imine hydrogenation (Scheme 3).¹³ The transition-metal complex activated the H₂, whereas the Brønsted acid was the source of the chirality. I think we're going to see a lot more mixed catalyst systems with task-specific components.

(3) **Organometallics:** Let us reduce the previous question to “attention-getting molecules”. Are there any nominations for an “organometallic molecule of the year” for 2011 (or 2010)? What qualities do you seek to recognize?



Bill Jones, University of Rochester

Bill Jones: Although this is just outside the time frame provided, I liked the methane complex that Brookhart and Goldberg characterized fully and reported (Scheme 4).¹⁴ I thought that was pretty cool.

Zach Ball: Mine is of a similar vintage. We think a lot about organometallics in biological systems. From that perspective,

Watanabe has reported a rhodium(I) organometallic complex with ferritin that is shockingly beautiful.¹⁵ They treated ferritin with a rhodium complex, and the complex goes into a pocket in the middle of the protein, and inserts norbornadiene across a cysteine–rhodium bond, generating an absolutely remarkable bio-organometallic structure. It's just a beautiful structure and an amazing set of reactivities.

Jim Mayer: As long as we're talking about biology, I'll note that Serena DeBeer and co-workers have reported that the central atom in nitrogenase is carbon, making it an organometallic cluster.¹⁶

Ian Manners: If I could take one, or a set of compounds from the materials area (which is an area of organometallics that I view as underdeveloped), it's the cyclometalated iridium(III) phenylpyridyl complexes, which over the years have been found to be really useful for phosphorescent light-emitting diodes where you can achieve desired colors very efficiently. There's a nice paper recently by the Fuyou Li group in China¹⁷ where the specific imaging of cell nuclei has been achieved. You can treat cells with the iridium complex with two labile ligands, and the complex is actually nonemissive unless you actually coordinate the histidine from a histidine-rich protein in the nucleus. For me, it's a nice example of how organometallic chemistry has a lot of potential in an area where you would not a priori expect much utility. It shows once again that an organometallic compound with an iridium–carbon bond can be tremendously useful. And I think if we can sort of go back to point 1 about the wish list, there's probably a need for many more organometallic compounds with the right ligands that can impart the right stability to water and air. If this area can be expanded, they are likely to be useful for a lot of applications.

Zach Ball: I'll second that. That was actually my second choice for the molecule of the year. It brings up a lot more questions than it answers, which is always a good thing.

Vy Dong: Meyer and Smith synthesized an unusual iron nitride complex and provided unambiguous evidence for an Fe(V) oxidation state, which was previously unknown.¹⁸ This work gives chemists tools to develop new interesting metal complexes and new iron catalysts.

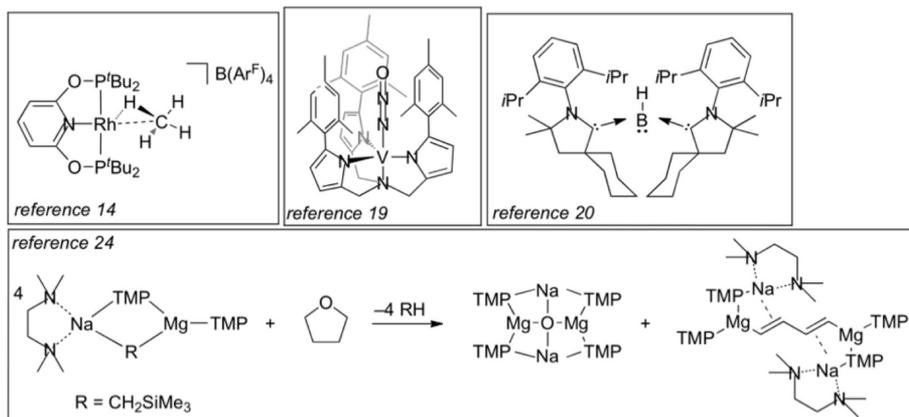
Jennifer Schomaker: This isn't an organometallic molecule, but I really liked Chris Chang's report of the first single-crystal X-ray structure of a nitrous oxide complex of vanadium (Scheme 4).¹⁹ The metal center is supported by a substituted tris(pyrrolylmethyl)amine ligand and the group's studies indicate a linear, N-bound metal–N₂O complex. It will be interesting to see if they can achieve catalytic oxidation using this complex.

Organometallics: Some panelists may be a little too modest with respect to their own work. Guy, what's the prettiest molecule that you think you've made in the last two years? What's your number one favorite?

Guy Bertrand: I really like what we published last week (Scheme 4).²⁰ It's a neutral basic tricoordinate boron derivative. The idea is that all of us are using nitrogen-based ligands, phosphorus-based ligands, carbene ligands, and we have in hand a brand new family of ligands based on boron, since these novel compounds are isoelectronic with amines and phosphines, it's very interesting.

Bill Jones: One thing I've noticed just over the past couple of years is that there has been an explosion in main-group chemistry of compounds with multiple bonds. I'm not sure where this is going in terms of reaction chemistry, but all of a

Scheme 4. Panel Picks, Part 4 (See Text for Others)



sudden after 30 years of only isolated examples of silicon–silicon double bonds, it seems like this area is exploding. It seems like everybody has examples of this now.

(4) *Organometallics*: Let us turn to another question. What are the major challenges for organometallic chemistry, either within the field or in the context of the “grand challenges” for society. What specific problems should be attracting organometallic chemists? Some have already spoken about biomass utilization, an issue that certainly belongs here. What are others, or who has more to say about this one?

Joachim Ritter: I’d like to continue with the deoxygenation of carbohydrates. This field has been dominated mostly by engineers, with the exception of a few pioneers from the organometallic community (Marcel Schlaf has been most persistent). More recently more chemists are getting involved but I believe there is still an unfilled need for fundamental investigations using homogeneous catalysts. There is a paradigm shift if you want to move from petroleum-based resources to biomass-based resources. Of course there are also carbon-rich renewable feeds in the form of vegetable oils, and known hydrocarbon chemistries such as metathesis can play a good role. But for the rest of biomass, we need deoxygenation technologies. When you move from a petroleum-based CH/CH_2 feedstock to a biomass CH_2O feedstock you’ll need selective deoxygenation vs selective C–H activation. So as important as C–H activation was and still is, I think selective deoxygenation is a major challenge and I would love to see organometallic chemists getting more involved.

Bill Jones: My sound bite on this subject would be “oxygenations”, either of abundant hydrocarbons or in a highly selective sense in a complex multifunctional molecule. This starts at the other end of the spectrum from Joachim Ritter’s deoxygenations, and meets in the middle.

Jim Mayer: If I can just generalize that, it’s worth noting that organometallic chemists know how to work with highly reducing compounds, but not strongly oxidizing ones. We have gloveboxes, we know how to dry our solvents and get rid of oxygen, and members of our community routinely handle compounds with potentials of -1 , -2 , even -2.5 V vs. NHE. However, there’s almost no organometallic chemistry with compounds that have potentials of $+1$ V or $+1.5$ V. We don’t know what ligands are stable and we don’t know what solvents we can use. It’s a large area of organometallic chemistry that just hasn’t yet been very successfully explored.



Tobin Marks, Northwestern University

Tobin Marks: I’ll come back to a very old biological process, but still a fascinating one: nitrogen fixation with nitrogenase. We still need better ways to do catalytic chemistry with dinitrogen. Paul Chirik has done some really nice work in this area, but there could be a lot more.

(5) *Organometallics*: In January of 2011, Whitesides and Deutch published an essay in *Nature*, “Let us Get Practical”, in which they state “Business as usual is not an option”.²¹ Do you perceive a message for organometallic chemists in this opinion piece? Do we need a paradigm shift in the way we train co-workers or select research topics?

Joachim Ritter: This article really resonates with a lot of thoughts I have had concerning the relationship of academic and industrial chemistry. I do believe there is a need to teach students practical problems, and then apply creative and cutting edge science to solve them. Basic research and independent science is important, but I do feel there is a huge benefit of understanding the problems of the real world. And one of the things that I would advocate in education is that every graduate student take a course in industrial organic and inorganic chemistry, so the student learns early how actual commercial processes relate to their work. What is involved in not just making 100 mg or a gram of a material, but 100 million pounds, and what are the implications? Challenges in the industrial world include space–time yields, purification methods, catalyst recovery and lifetime, solvent usage, etc. These topics sound straightforward, but when you’re actually working in industry developing new processes with broadly trained junior chemists coming straight out of top schools, sometimes you see that very

talented chemists have a hard time connecting to these challenges. So I do feel there is something to be done in education. In addition to an in-depth drive toward the newest cutting edge developments in science, there needs to be a perspective of today's problems in the context of chemistry. And then I think young chemists will pick up on approaches to solve those problems, but people need to be aware of what those are.

Tobin Marks: I would fold some business concepts into that course.

Jerzy Klosin: I wholeheartedly second Joachim's analysis. I often visit the websites of university professors and you can sometimes see on these sites what type of chemistries have been reviewed during group meetings. It turns out that this is nearly exclusively outtakes from other professors' research. Very little is actually devoted to industrial processes that would highlight the difficulties with commercializing new technologies. It would be highly useful for students' education to send them to industry for a semester or a summer stay. There is also discussion of sending researchers from industry for a short sabbatical stay at academic labs to get a different perspective on the current trends in chemistry. I think this exchange between industry and academia would be highly beneficial for everybody.

Jim Mayer: I very much agree with that. And certainly I've been very eager to encourage my students to do it—I think you'd find lots of academics would encourage their students to spend some time in an industrial laboratory. The students get a lot out of it, and I think they can contribute to a research lab even if they're only there for a summer. I hope that more companies will sponsor such programs.

However, chemists work in all different areas these days, not only in large-scale commodity production. Students and post-docs from my group have not only gone on to work at large chemical and oil companies, but also to fine chemical businesses, to process chemistry groups in pharmaceutical companies, into nuclear medicine. The challenges are very different in these different areas.

I think we also want to be very careful in going down the path of training chemistry students in the details of cost estimation and commercialization. When I was a postdoc at DuPont, discussions of such topics were led by expert engineers, with people who could for instance estimate capital costs of a plant. I think we can sensitize our students that such issues are important, but I don't think it's valuable for academic chemists like me to try to decide what kinds of processes are practical. Practical means that somebody could make money practicing the technology, and even the professionals aren't so good at predicting that.

Joachim Ritter: I agree with you, but there is something to be said for raising awareness in a structured way. And also maybe making them aware of simple tools; things like primary raw material analysis is really not that difficult to do if you're aware of it. We were talking earlier about using ligands that are more stable. I think it's helpful to think about ligands that are within a certain cost range such that you can afford to apply them. I'll give an example: there's a lot of people running studies on dissolving lignocellulose in ionic liquids, and I think it's important to look into this option from a fundamental point of view. But at the same time, promoting this concept as an industrial process is audacious. You can estimate with very little effort that you'd have to recover about 99.99% of the ionic liquid, which is extremely challenging.



Jim Mayer, *University of Washington*

Jim Mayer: I concur, except I know someone at a major US chemical company who is very actively pursuing a process with ionic liquids. I think they are interested in using a thin film of the ionic liquid. So generalizations can be problematic.

Joachim Ritter: It may be possible for a specialty chemical. But for a commodity chemical (that is C_6 and C_5 carbohydrates in this case) worth 10–15 cents a pound the math does not add up, if you consider the cost of the ionic liquid and the recovery rate needed. Again this is just an example. I'm not talking about teaching Ph.D. students to learn the trade of detailed technoeconomic analysis, but to give them the tools to develop the skills to estimate what may make economic sense. In my opinion it would foster work in more relevant areas of research. After all, we want organometallic chemists to be relevant also outside the organometallic research community. Raising awareness and applying crude but insightful models to estimate minimum cost can help develop sound judgment. There is a place for fundamental science, a place for applying fundamental science towards a practical problem in applied science. When we try to place either one of those fields in the wrong context, we lose relevance.

Jerzy Klosin: One could argue, on the other hand, that a substantial discovery can be made with a super-expensive ligand or impractical process. So I wouldn't necessarily teach students to limit their thinking to problems based on practicality of the chemistry. At the same time, I think that having a course, or elements of the course devoted to industrial chemistry would be helpful. Discussion related to problems that industrial chemists face on a routine basis would be of high value as well.

Mark Humphrey: Asking students to carry out economic analyses will increasingly crop up when benchmarking the performance of molecules. We're continually trying to improve some materials performance, some molecular property, and increasingly we'll have to consider if you get enough bang for your buck. In my group we've estimated costs of making various organics and organometallics while trying to optimize two-photon absorption capability. All sorts of molecules are being explored in NLO, and trying to compare them is tough. Up until now, a molecule's performance has been scaled by molecular weight for comparative purposes, but there are several other scaling factors that might be more useful—for example, scaling by volume, by cost, by environmental impact (which ultimately flows into cost), etc. We tried the cost and volume approaches earlier this year—an enormous amount of work for the student involved, which he wasn't keen to repeat

as he'd rather have been in the lab, but a useful exercise with interesting outcomes.²²

Jim Mayer: I appreciate these comments and I think it would be great if cost information were more readily accessible. Perhaps *Organometallics* could help with this, either with a website or a tutorial that would help academics find cost information. That could stimulate attention on these kinds of questions.



Joachim Ritter, *DuPont Central Research and Development Experimental Station*

Joachim Ritter: There are general models and cost info available. As far as cost models are concerned, third-party reviews (e.g. from SRI Nexant and others) are helpful. For commodity chemical prices, there are services such as CMAI.

Jim Mayer: Yes, but the good third-party reviews have to be purchased, and they are expensive. I'm not eager to spend \$2000 on an SRI report that may or may not have the information I want.

Joachim Ritter: Well, again, I'm not advocating that a doctoral student needs to be an expert in technoeconomic analysis. I'm not advocating stifling creativity, but what I'm advocating is to raise the awareness. That may require additional resources.

Bernhard Rieger: I got a totally different message from this Whitesides/Deutsch publication. We collaborate with a couple of industries, and there the money pressure on the decision makers is enormously high. But the time between basic inventions and innovations is more or less the same—10 years and more. Therefore, some companies just tend to turn away from basic research. For me the major question is how can we keep decision makers interested in our fundamental approach? In addition, I personally do not believe that we should train our students to think about cost structures. I think we should go for the fascinating new research.

Bill Jones: I just wanted to chime in also on this article, as it evoked a response. We've talked about economics and those issues that figure into getting practical and we've heard that maybe our students aren't necessarily the ones to do the economic analysis. But one thing I can say about our students is their intersection with industrial scientists is almost zero. So to get a group of industrial chemists together and talk about what are the problems that they face day to day, these are totally unknown to our students. I think if you could share that knowledge somehow, that would serve as a way for students to start thinking about practicality. Not in specifics in terms of economics, but in "oh, I didn't know that was a problem". And

somehow trying to find a way for them to at least talk once in a while, I think, would be a huge improvement in their education.

Bernhard Rieger: Just as a quick answer, with WACKER we work closely together in the area of silicon chemistry and for example with BASF on other fields. In this we always have a very close communication between students and researchers from industry. I fully agree with you, it is definitely a good thing to combine basic research from the very beginning on with industrialists.

Bill Jones: And I think different countries have different models for doing this. I think the US industry is very bad about interacting with students. You go to Japan and it's the opposite. The academics and the students are involved with industry almost from day one.

Organometallics: Reto, in this regard, can you bring us up to date on the situation in Switzerland? One often hears about the close cooperation between academia and industry there.

Reto Dorta: I am not a big expert on the Swiss system yet. For the contacts I have with industry, they came about because there was natural overlap between what we were doing and their needs. From then on, they were hands-off with what we were doing. For the practicality of our research, I have the impression that my independent research is more practical than what I had done before. But overall, I'm clearly on the university side and I think we should just be able to do research, whether it has practical aspects or not. We do still get money for good basic fundamental research in Switzerland, but there is more and more emphasis on practical problems. I don't think it's really a good development. We wouldn't have exciting "molecules of the year" if we were only doing practical research.



Reto Dorta, *University of Zurich*

Ekkehardt Hahn: I am coming back to the phrase "business as usual is not an option". Well there's two things: I remember when I started as a postdoc, and that was 25 years ago in Berkeley, there was an initiative by NSF to define what the future of chemistry should be and Clayton Heathcock wrote an article, which I still remember vividly—it was very impressive. It said chemistry or science is best if you leave people alone to do what they can do best. This is, I think, what was considered the business as usual. Leave them alone, and they will come up with something that will be good. And that worked for 100 years. On the other hand, I'm from Berlin in Germany. You just move 100 miles east and you come to the former eastern bloc where three or four hundred million people, you take the Chinese on top of that and that is 1.5 billion people, were told until 20 years ago what is useful and what they do research on.

The administration there had all the power to direct research, and they erected huge research facilities. They managed in some fields. The Russians managed to get into space and to build spaceships. But let us look at the general outcome of this planned research. Has anybody seen a toaster from Romania from the seventies? Have you been in a car from Russia or run a computer from Czechoslovakia built in the eighties? I believe in general it does not work if administrators or people not in the business tell you what's important to do research on.

My worry is that we get too much into being told and accepting what is trendy. When I was at Berkeley, superconductivity was trendy. This dropped like a rock within 10 years. Up to now, few of the dreams of the late 80's like transporting energy through superconducting cables have become reality. The number of people who entered the field, which was then considered trendy, was very large and the drive was not from industry, I must admit. Rather, the impetus came from academicians who said "let's do research on this topic". In any case, many researchers have left the field again. I'm fully convinced that we should look at where our research is going. But I'm reluctant to accept that the need of something by industry should determine what we are doing. Good science comes from independent people, having the resources, which they have less and less of, available to do what they can do best. There is a lot of truth, even today, in the Heathcock document.



Ian Manners, *University of Bristol*

Ian Manners: I'll concur with a lot of that. I remember when I started my doctoral work at Bristol, which was regarded as a top place for fundamental organometallic chemistry, we were, at that time, generally discouraged from thinking about anything applied, as applications were regarded as dirty chemistry, and research in universities should all be fundamental and curiosity-driven. And you know, that's one extreme opinion. In the Whitesides article, you've got the exact opposite message. What I don't understand is why people have to see things as a black and white like this, just one way or the other. I mean, humans have been on Earth for hundreds of thousands of years, but the real developments in our civilization, in terms of technology, have come in last 200 years or so. And why is that? In my view, it's for some of the reasons that Ekkehardt Hahn mentioned. People thinking and using their talents, and people also being very motivated by practical problems has also been absolutely vital for sure. On the other hand, there are many things that have come from curiosity-driven research. For example NMR, and ultimately the MRI machines in hospitals, came from people simply trying to flip nuclear spins with radio

waves, and you can't really get much more fundamental than that. In my view we have come to where we are now as a civilization from an essential combination of both curiosity-driven and application-driven research. And so that's what should continue. Neither alone is sufficient. And that's the real problem with the message from this article. Whitesides is a brilliant scientist, one of the most brilliant, no question, but the problem with this article is that it regards science as black and white. What it describes is one way, one recipe for doing future science, and it's a great way. But the spectrum of science that we need is really a continuum from fundamental to applied research. Both ends of the spectrum and the middle are all essential. Moreover, people have to use their talents—we need to recognize that some are good at one or the other and some at both. We have to note, in my view, that it is still very important just to give the most creative people money to play around and see what they come up with, because some people come up with just fabulous things, over and over again during their career and, down the road, people can often find uses for these discoveries. That's a concept and message completely neglected in this article.

Vivian Yam: I totally agree that basic science is important. I guess a lot of people are saying that chemistry is a mature subject and so that's why people think that chemistry should play a more supportive role to biologists and physicists or whatever. But I totally disagree with that, because the thought that chemistry is a very mature subject is not true, since there are still a lot of things that we don't understand very well, like C–H bond activation, activating methane, or water splitting. So a lot of things are still unknown. Thus, I don't really agree with a lot of people commenting that chemistry is a mature subject. I think there is still a lot to be done. I think we should keep our minds open and to work on interdisciplinary areas. I believe this is important. Like the energy issues—I am not really a catalysis maven, I'm more on the materials side and I think there are a lot of new opportunities and applications out there for metal-carbon bonds, as in light-emitting diodes, solar cells and solar energy conversion, and medicinals and drugs. So I think we should keep our minds open as organometallic chemists. But then we have to stick to fundamentals. Really it's the fundamentals that will help to advance our knowledge. We have to allow for curiosity-driven research.

Tobin Marks: Vivian's comments resonate with me because one of the things I read in the Whitesides/Deutsch editorial is about crossing disciplines. In other words, not to be afraid to talk to someone in your materials science department if you could collaborate in a way that would make a big advance in some field. The same is true with your physics department or your biology department—not to be too insulated. It's amazing what impact the right organometallic compound might have on, for example, a light-emitting diode and it's critical not to sort of sit in a silo and say "well, I'm totally uninterested in that". Rather, sit down with a colleague, start talking about how they work, and maybe soon you will be saying "gee. I have just the molecule that would be fun to try".

Jerzy Klosin: If organometallic chemists were only a curiosity-driven group, we might have disappeared 20 years ago. I think the purpose of this panel and your interest is to examine what can be done in the near future to assure survival of the field for, let's say, the next several decades. Observing the field, it is quite clear that substantial amount of research that is being done nowadays by organometallic chemists is highly practical in nature. So I'm not concerned at all about what is

happening in academic laboratories will make the field obsolete. I would like for a second to go back to what Bill Jones said a couple of minutes ago related to education and the decoupled state of affairs between academic and industrial worlds. A couple of years ago, there was the CENTC (Center for Enabling New Technologies Through Catalysis) meeting in Seattle, and (pointing) you participated in this, Bill. There were chemists from Eastman and Dow and we gave talks about the chemistry that is being investigated and practiced in our companies. I found there was a lot of interest from graduate students about our work as shown by a lot of follow-up questions. There was also a lot of interest about life in industry beyond chemistry. More meetings of this type would be very useful for graduate students.

Ekkehardt Hahn: I want to modify a little of what I said before. I didn't want to give the impression that an industrial problem is not a viable academic challenge. With original research, however, you try to make an impact rather than to be seen as someone who just follows in a given path. And very often we don't even know about the problems industry has. I recently had visitors from BASF who were just sitting in my office waiting for a seminar to begin. They couldn't go anywhere, so I said 'tough luck for you, now you've gotta listen to what we are doing'. There was 20 min of time, and I gave an 18 min presentation on what we're doing, and the next day they called me and said look, you have on the shelf compounds we could possibly use to solve one of our problems making car coatings. I had not the slightest clue that the compounds we had in stock could have an impact on car coatings. The next problem was that the confidentiality agreement to be signed was longer than the paper we had discussed. Industry is always very secretive to disclose what they are actually interested in. So it is not only the academics who are challenged to provide solutions to industry, but it is also a challenge to industry to find a way to transmit what they are interested in and to do it in a way that one can associate with. Industry partners have to make money and they have to protect their intellectual properties—I understand that—but both sides have not found the optimal way to communicate yet.

Zach Ball: From my perspective, it seems there been a rise in university IP restrictions, and a desire to maintain rights on both sides that make it difficult to work on the science.

Joachim Ritter: I would second that, especially in the US it is very difficult to come up with an agreement with a university. This is in part because universities have expectations as to how they would participate in a revenue stream.

Jerzy Klosin: Principal investigators are easy to work with, but in the past we also struggled to reach satisfactory research agreements with tech transfer offices due to their high expectations regarding the value of future technologies.



Alfred Sattelberger, Argonne National Laboratory

Al Sattelberger: There is enormous pressure on the universities to bring in more revenue to support on-campus activities. It's not a good situation. Some schools are reducing salaries, furloughing staff, eliminating positions, dealing with large budget cuts, etc. This is especially pronounced at state institutions.

(6) Organometallics: Suppose one of your students will start an academic research group in 2012. What would be your advice? Let us try to get comments from countries around the world on this one.

Suzanne Blum: This is the question that I feel the most strongly about, and my advice is not going to be country dependent. My advice to somebody starting out would be to make a large departure from what is already going on; to be creative to develop a program that isn't just $n + 1$ but to really go out there and make use of this time to pioneer a creative new area that they have come up with.

Jennifer Schomaker: In principle, I agree whole-heartedly with Suzanne. Many of us chose our careers because we believed we could be truly independent and creative. Unfortunately, the system makes it quite difficult to deviate too far from what the scientific elite think is important right now (which may or may not turn out to be all that important in the future). One of the best pieces of advice I can give to my students is to be stubborn! As a young faculty member, the majority of time is spent convincing potential students, colleagues and reviewers that your ideas are worth something. You've got to be convinced they are, because initially, no one else will be. Another piece of advice I give my students is to be yourself and don't stoop to letting style win over substance, no matter how tempting the professional rewards may be. Don't be afraid to try some wild and crazy ideas and just have fun with the science.

Organometallics: How could we better train our coworkers for the challenges raised in these two responses? One of our Editors just refereed a postdoc proposal for the Deutsche Forschungsgemeinschaft (DFG), and the applicant proposed to do exactly the same kind of work he could have kept on doing in his doctoral institution, as opposed to something that would exploit the training opportunities in the proposed host group.

Suzanne Blum: One thing we can do as academics is to be straightforward with our students as to what constitutes a small departure in the literature versus a larger, creative departure. A creative departure is often more than providing a solution to a big-picture problem, it's identifying and defining the big-picture problem in the first place. Similarly, when students come to us with independent proposals, we can be frank with them about what the pros and cons are of their ideas. At Irvine, we have a second-year exam that includes a proposal component. Very few times would anybody actually want to do the proposals students describe at this stage of their graduate training. Nevertheless, if we can be straightforward and have conversations with students about developing their independent ideas in the long term, we provide helpful direction. I know many of us have been on hiring committees and perhaps have found that there wasn't as much departure or as much creativity in the proposed research programs as we would desire in new colleagues. Some of this lack of creativity can trace back to the education that we provide when mentoring graduate students. It's important to be straightforward about what is going to constitute a big enough departure to be a creative research program.



Jennifer Schomaker, *University of Wisconsin—Madison*

Jennifer Schomaker: I have found the managerial aspects of running a research group to be quite daunting. We're used to being very critical of each other in so many ways. It's different when you're a graduate student or postdoc and then you move into this environment where now even the littlest frown on your face has a big impact. So I would tell my students to really think about your management style, positive reinforcement, make sure you set clear expectations of your students—very high expectations—but make the expectations clear; have a way to monitor these expectations. Talk to colleagues right away about how they have managed these issues; mentoring can be very helpful.

Tobin Marks: I think I'd add on top of that the ability to multitask. Think of all the things that young faculty, or senior faculty, do: walk in from giving a freshman lecture to a Ph.D. exam to some frustrating committee, follow this up with an hour mandatory on-line ethics training, correct your latest page proofs, interview the faculty candidate, etc. etc. This plethora of activities hits all of us hard, and also affects new faculty transitioning from industry to academia.

Bill Jones: The advice I would give to the students is to read the literature broadly, because as they do their doctoral work, they usually focus, focus, focus. They know the literature in their thesis area fully, so if you want to ask them to come up with a new idea, guess what area it's going to be in? Almost always it's just a slight departure from something they've already done. But by reading the literature a little more broadly outside their comfort zone, you learn about other areas and you'll think, oh, I know about this topic, I could see how it could apply to this other topic. And one of the things I miss about our electronic journals now is it used to be that it was the article just before or just after the one you were searching for that attracted your attention. And I guess that can still happen with electronic browsing, but it used to just hit me more often. When searching in *Chemical Abstracts* by formula indexing, I found another compound with the same formula and realized, "oh I didn't think about that". But reading the literature broadly will get you to go outside of your comfort zone and apply ideas from one field to another subject.

Guy Bertrand: I think I would say to a young assistant professor, give some freedom to your students. Very often they are very close to students and want to have results very quickly and the students feel they have no chance to think, no chance to solve the problem, but they have to learn to solve

their own problems, and this is the best way to become creative.

Vy Dong: I agree with Suzanne that it is important to be creative and try something new. To play the devil's advocate, however, I wonder if we put too much emphasis on departing from something we know well and have been trained to do well? On some level, it makes sense to encourage students to build upon certain things that they've already learned. In the field of biology, many people base their independent careers upon results from their postdoctoral work, and that doesn't seem to be a problem. I'm also curious about how this attitude differs among countries? For example, I've talked to a colleague in China whose professor advised "If you don't do palladium chemistry, how will people know you are my student?"

Jennifer, I agree that group management is key. My simple strategy is free food—worked really well for me as a student.

Bernhard Rieger: I encourage my doctoral students to spend Friday afternoons to follow their own ideas. I provide them with a budget and if they come by later and ask me to discuss their results, which I did not know about before, I feel that they have a good chance to start their own research carrier.

Jim Mayer: I want to comment that the NSF center that Bill Jones and I are a part of, the Center for Enabling New Technologies through Catalysis (CENTC), holds regular brainstorming sessions. Only occasionally do good ideas come out of them, but the students are full partners and they learn, first of all, that the professors don't on average have any better ideas than they do. This sounds sort of funny, but actually it's very liberating for them. They don't feel like they have to come up with some fully formed idea, such as the ones they see groups running on. In general, I like group meetings where people present prospective ideas, as opposed to just what they've done, as these are ways to get the students pushed into thinking more broadly.

Ian Manners: One of the things I talk to my students about is to decide what you want to do and to then suggest where they might do it. For example, is it at the curiosity-driven end of the spectrum or is it more at the directed end of the spectrum, and to then consider the countries where that's best achieved. If you want to do curiosity-driven research these days, to be honest, I don't recommend the US. I recommend Germany or Switzerland or Canada to my students. On the other hand, some students are really fired up in problems in energy and bio and materials, then that opens up additional possibilities in addition to those destinations. One thing I've found from moving around and working in different countries myself is that every country has a different kind of scientific culture. In fact the culture mentioned by Suzanne Blum of people doing something different and trying to pioneer a different area once they start their independent careers is really a North American concept. It has filtered across to some extent to Europe, but it's really pioneered in North America, and I actually believe 100% in that concept; I think that's the way to go. But there are still in a lot of countries where the idea is that your job is to continue the same line of research and, in a way, to take up the relay baton from your mentor. So there are a lot of country-specific possibilities. For example in some countries people get really much more fired up about fundamental than applied chemistry, and they have allocated very good funding for that, whereas in others that is not the case. I think that's also very much worth considering when choosing a career.



Vivian Yam, *The University of Hong Kong*

Vivian Yam: My advice would be quite similar to that of Suzanne Blum in that you've got to be creative and innovative and you have to start off working toward important problems rather than try to be derivative of what other people have been doing. Don't worry about initially proposing wild and crazy ideas. I also agree with Bill Jones that students have to read very widely in a very broad sense. So actually, in my group, what I have been asking my students is not just to read articles in *Inorganic Chemistry*, *Organometallics*, or *JACS*, but rather to read papers on analytical chemistry, biochemistry, and other topics that are very different from what we have been doing. A lot of times this will lead to cross-fertilization and creative ideas. And in response to the earlier comment on colleagues in China, my experience with Chinese co-workers, the ones I've come across, is that they are quite free to work on their own projects. Of course if you are going into a state key laboratory or institute that focuses on a certain direction, then you have to be on that direction because otherwise you don't get funding. But then they still allow you the freedom to explore within that general direction. For example, in a state key laboratory focusing on a certain area of chemistry, then it could be anything related to that area of chemistry justifying the project topic. So there is certain flexibility. I think in the old days you had to work under big professors, but now they really are moving towards the American system, where they have a tenure system for some major universities like Peking University, and they also have independent groups. So long as you are a principal investigator, you can just work on your own projects. In my opinion, things have been changing.

Mark Humphrey: Apart from having ideas of science to pursue, there are some practical considerations that the student needs to be aware of. You can't run an organometallic chemistry research group without funding. You can't get initial funding in Australia or many other places without a competitive track record (publications, awards, fellowships, etc.). In Australia, the majority of funding for fundamental research comes from the Australian Research Council's Discovery program, and if you miss that, there really isn't a good plan B apart from dribbles of internal institutional money (its unlike the US situation where there are other possible sources of funding). So the student should have picked up lots of advice from their advisor and others to ensure their track record ticks all the boxes, and they'll also need plenty of strategic advice to ensure their initial grant application is funded—once the first grant gets up, things become easier.

Ekkehardt Hahn: To a certain extent, the problem is complicated by the geographical location someone is going.

I had a very good student who wanted to go back to India, he came from an IIT and wanted to go back to an IIT. To get hired there, it was the number of publications that was of utmost importance. To me it appeared that it was not primarily the quality or what was in there or if your *Organometallics* paper was 30 pages long, it was the number of publications. There is a strong competition in the hiring process there. If you have 10 applicants, one has 8 publications, the next one has 5 and the others 2 or 3, then the one with 8 papers makes it. Hence, it is very difficult with all the philanthropic advice to be creative, to read the literature, and to do something new, when you come out in the real world where numbers and research fields force you in a specific direction. China, in my opinion, is a classic example of where numbers are very important.

Vivian Yam: My understanding is that they are changing. Quality is now more important than quantity.

Ekkehardt Hahn: I hope so, because today even the 28-year-old junior researchers in China know their H indexes—the values might be still low but they know. So you meet people who introduce themselves saying their name and “I have a H index of 10”. And you wonder who has trained them? Is this how science works, that you look only at the H index? That index may become important in some contexts as you get older but it is not so important for young researchers. So apart from encouraging creativity, junior researchers should be placed in a surrounding where they can do research without looking for the immediate impact of that research. I think this is more or less our job.

(7) Organometallics: “Frustrated Lewis Pairs”, which have been on the scene for about five years, could be viewed as a “new” reactivity mode, i.e. a previously unrecognized or ungeneralized mechanism of activation. Are more of these coming down the line, or are the organometallic chemist's bag of tricks pretty much on the table?

Ian Manners: Just a quick comment on this. I think this emphasizes that we need to keep doing curiosity-driven research, because I don't think Doug Stephan, for example, was trying to solve a practical problem when this was discovered. So, it's beautiful, potentially useful chemistry that's come from curiosity-driven research. It's an example par excellence.

Bill Jones: I don't think that we have exhausted our bag of tricks at all. It's just that we don't foresee new reactivity pathways until we discover them. I would put in the same ballpark heterolytic hydrogen cleavage, as exemplified by the Shvo catalyst systems. Who would have thought this was possible? If someone had written that on an exam as an answer to how hydrogenation occurred, you'd give the person a zero (back in the old days). But now it's accepted. So I think these things are out there, we just haven't thought of them. If we had, we'd be out there doing them now. I'll bet on more discoveries of this type.

Ekkehardt Hahn: I guess with the advent of anything which you might call cooperative reactivity or supramolecular reactivity, it starts all over again. If you look at the diverse chemistry of mononuclear complexes, imagine what the future would hold in polynuclear systems for cooperative reactivity in catalysis or related fields. I think we are just seeing the beginning of that, the toolbox is not even half full.

Mark Humphrey: That's right—one nice example is Mulvey's bimetallic bases (e.g. Zn/Na, Mg/Na, Mn/Na). He's used them to demonstrate some really unusual transformations of THF (Scheme 4).^{23,24} The broad applicability of this hasn't been examined. In general, there is enormous potential when

employing combinations of metals and this hasn't been widely exploited yet.

Jerzy Klosin: There remain some old chemistries that we still don't have a detailed understanding of. A prime example in my field is Ziegler–Natta catalysts. Many billions of pounds of polyethylene are produced annually using this process, yet mechanistic details still remain unresolved. There has been debate over the years about the oxidation state of titanium in Ziegler–Natta systems and how titanium interacts with the support. The problem is that this is not easy chemistry to study—this is not only solid state but also paramagnetic chemistry.

Bernhard Rieger: Some companies are more or less convinced that most of the really new and exciting chemistry is already discovered. This is a refrain that appears in the literature periodically. However, it is our job to convince them that it's worth spending money for basic research, because otherwise they invest it just for process development.

Jim Mayer: If someone thinks that everything already has been discovered, ask them to predict what the world will look like in 25 years.

Joachim Ritter: I believe there is still a lot to discover. I think maybe that some comments have been prompted by the fact that the industrial world is often not ready for a new ligand or process, because the steps to take it out of the lab to a pilot and demonstration plant require large investments. Today's chemical companies are busy reacting to rapid market swings and trends, which does not leave a lot of room for risky long-term projects. Furthermore, there has been a lot of manufacturing and R&D chemistry moving out of the US into China and India. Addressing the short-term cost pressures consumes a larger portion of research than in the past. That's just a reality. We certainly are open for the next big things, new chemistry included, and I'm looking forward to seeing them. Especially in the area of CO₂ utilization, solar energy, and chemistries relevant to biomass based energy and chemicals.

(8) Organometallics: The first question prompted some discussion of instrumental needs, but let us try to address that more formally now. What influences are computational chemistry and new instrumentation or instrumental techniques having on organometallic chemistry? Are there trends or developments of note?

Jerzy Klosin: I would like to mention some developments at the University of Wisconsin. Clark Landis has been developing NMR spectroscopy on a millisecond time scale, which is exciting, as we all love using NMR spectroscopy because it is such an information-rich technique.²⁵ We deal with many catalytic processes, where very fast reactions are common and reaction rates can't be measured easily. I think this is a very exciting development and Landis' group has made some nice progress already.

Jennifer Schomaker: Speaking of NMR as a very information-rich technique, I would love to have a way to get the same information about paramagnetic compounds as easily as I can for diamagnetic compounds.

Bernhard Rieger: I think computational chemistry has significantly developed over the last decade. Maybe 10, 15 years ago it was just good to explain some curious results, but now it can help to even predict reactivity to some extent. If you have tons of parameters to find a new catalyst, it helps a lot if you get suggestions, even solutions.

Al Sattelberger: Here I push back a little bit, as I still think there is a lot of rationalization after the fact. I haven't seen

many cases where predictive capabilities are demonstrated in an intellectually honest fashion.

Bill Jones: I want to add something on calculations. I tend to agree that they have not been used as a predictive tool than as a rationalization tool. In my opinion, when you try to use calculations as a predictive tool, the problem is that you don't consider all the side reactions that might be more favorable. This compromises predictive power. Another issue, coming from just having dabbled in this a little bit, is that solvation models are still extremely naïve. With systems where there is charge transfer or charged ligands coming and going, you can get different answers depending what solvation model you are using. I'd like to see that area developed for organometallic systems, because they're certainly not all neutral. Sometimes there are charged species or development of charge in transition states, and this would really be useful. That's also a problem with paramagnetic systems. Another issue involves weak interactions. At least if you use a program like Gaussian, when we're talking about a weak interaction it doesn't know what that interaction is. Most transition states are up there in the weak interaction region, so they're kind of right but they're not as good as the ground states.

Tobin Marks: So better functionals for weak interactions.

Bill Jones: I'm not sure, because I don't know enough about what goes into these models, but certainly there's room for improvement.

Jerzy Klosin: We frequently use computational chemistry, but sometimes we find that, depending on the catalytic system we study, computational results are not in line with experimental data. The difference of 1–2 kcal for a catalytic system can be very significant, but computational methods have often difficulty with such small energy differences. But give it another 5–10 years and advances in processor speeds and computational methods will allow computational chemists to tackle very complex catalytic systems with high accuracy. There will be a lot of predictive power coming from computational chemistry as the time to crunch large molecules with all the atoms included will be reduced significantly.

Zach Ball: I'd say one of the analysis issues we struggle with is dealing with ensemble systems or solutions that are complex, not composed of a single species. Modern mass spectrometric methods, for example, have changed the way we solve many of our most important problems.

Reto Dorta: This kind of goes back on to that Christmas list. For my part, I was really amazed by a particular scientific paper that came out perhaps a couple of years ago and described AFM pictures where you could see the actual molecule. You could even see the C–H bonds of that molecule. In 20–50 years from now, who knows, maybe you can put your solution into some microscopy instrument, scan the surface and you would see the molecules in it. That would be really cool.

Jerzy Klosin: That's what Suzanne Blum is trying to pioneer.

Suzanne Blum: Yes, we have developed a fluorescence microscopy technique that is providing insight into questions like Zach Ball's and Reto Dorta's. To put this in a broader perspective, if you look at what other disciplines have learned by imaging—spectroscopy where you also get localization information—it's a great deal about their systems. For example, the 2008 Nobel prize in chemistry was awarded for the development of the green fluorescent protein and its application to imaging biological systems. As synthetic and mechanistic chemists, we want to understand reactivity at the highest level of detail so that we can manipulate molecules for



synthetic causes. For example, we want to determine the nature of the catalytically active species and sometimes that means figuring out its location: where IS the active catalyst? Is it a nanoparticle that decayed from a homogeneous precursor? Or is it actually the soluble molecular catalyst? If we had imaging techniques in chemistry with resolution at the single-molecule and -particle level, we could answer questions about the nature of catalysts by direct observation while at the same time removing the ensemble averaging challenges present in prior analytical methods. My group has recently developed techniques in this area.²⁶

(9) *Organometallics*: What other factors may be limiting the advancement of the field? Do you perceive any shortcomings that need to be addressed in the area of human capital, education, training, infrastructure, meetings or public forums, publishing venues, etc.?

Jim Mayer: I have a question about this question. It's not clear what you mean by "the field". Tobin Marks talked about nitrogenase as one of the grand challenges, but it is not evident to me that the work in this area would be publishable in *Organometallics*. I'm concerned about the field of organometallic chemistry and its future. For instance, we have not captured the organic side as well as we might have: that community prefers to publish in *Organic Letters* rather than *Organometallics*. And that is a real loss for our community, in my view.

***Organometallics*:** Do you think that we—meaning the field—are not inclusive enough, or need to reach out more effectively?

Jim Mayer: I think the community leaders are way broader than the field of organometallic chemistry as we define it. I think many of the leaders of our field have projects in their groups that would not be publishable in the journal of *Organometallics*. And I think many of the challenges that we are interested in are much broader than this field has become.

Ekkehardt Hahn: I guess since we depend on public funds we also have to make ourselves understood to the public. Apart from having resources and whatever, in my opinion the chemical community performs poorly in transmitting to the general public what they are actually doing. Fifty years ago, chemists were considered problem solvers. Today if you open

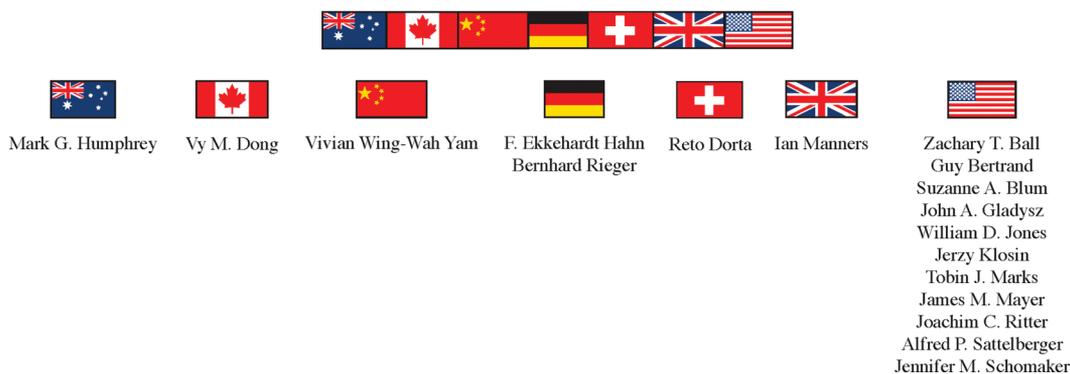
any newspaper, we are the problem makers. That is written by people who cannot distinguish uranium from urine, mostly, but still, they determine the public forum. The chemists have almost no voice in the public forum. I do public lectures, for more than 10 years now, called *Alchemy for Beginners*. In these lectures I take some brandy, orange juice or Chanel No. 5 and show that these are chemicals. We burn hydrogen over a glass flask and collect the water. I noticed that most people don't know that water comes from a chemical reaction. Or we make liquid oxygen and even many chemists have not seen that liquid oxygen is blue. The subtitle of these lectures is "Natural Chemistry". I try to convince the audience that nothing is more natural than chemistry, and that every orange is a chemical factory making vitamin C and whatever else is in the orange. We do not transmit that very well, and that is where we run into problems. In Germany, the top talent does not want to study chemistry anymore because they do not want to be with the pollutants or the people who destroy our planet. This is the image of chemistry that we have to fight. Our public image is not as good as it must be, based on what we achieve. That is one important point in my opinion. I do not know if the ACS taking up a similar initiative, but the German Chemical Society now tries to train journalists so that there are some people out there who know that the world is made up from chemical elements, not bio stuff, but from chemical elements, and that studying chemistry is not a waste of money.

Bernhard Rieger: I heard of an interesting recent study. Students at high schools were asked what they think of chemistry as a science and chemistry with respect to industrial applications and the answer for me was surprising. They judged all chemistry as a science very high and they shifted the problems that Ekkehardt Hahn mentioned to industry. So they distinguished between industry and chemistry as a science. I don't think that this is really true, but they looked at it that way.

Jerzy Klosin: Companies such as BASF, DuPont, and Dow are spending millions of dollars to improve the image of the chemical industry. But it's not going to be easy to change public perception.

Joachim Ritter: I'd like to return to the training part of the question on the floor. I think as far as training is concerned, and I am not referring to training for the chemical industry but training in general, problem solving in an interdisciplinary fashion should be a focus. I had a really big eye-opener when I joined DuPont and had the opportunity to work with people in different fields on the same problem. Our project teams have experts in all disciplines needed to drive a project to commercial success: analytical chemists, chemical engineers, biochemists, chemists with materials science backgrounds—whatever specialty is required. I've seen amazing success stories happen in a very short period of time when you apply interdisciplinary problem solving power to a project and you avoid compartmentalizing research. I know it is important to keep organometallic chemistry as a distinct entity, but at the same time I believe already at the student level we should expose chemists to interdisciplinary problem solving and working on teams. And they can learn how their discipline can impact other areas. I believe the ability to work successfully within a team environment is a prerequisite for a successful industrial and academic career.

Bernhard Rieger: Maybe when it comes to research, I have a feeling that photochemistry is underestimated. If one thinks about sustainability, then you have to think about different



forms of energy and photochemistry comes automatically to my mind.

Ian Manners: I don't know if this goes to this point or the previous one, but I was just thinking that organometallic chemistry has been successful and that it has kind of "grown up" in many ways and so now you find it in organic journals and physical journals and bio and materials journals. I just wonder whether something could be done to illustrate this in *Organometallics*. For example, an article in every issue or maybe once a month which actually shows highlights of where organometallic chemistry has been used in different disciplines so people can see that organometallics is out there all over the place and the journal *Organometallics* is just, if you like, something that focuses on mainly on fundamental organometallic chemistry.

Organometallics: That's a great idea. It would be an excellent mechanism for keeping our readers aware of how organometallic chemistry is impacting so many disciplines.

One could also consider training from a textbook angle. There is a very nice book from two German authors, Weissmehl and Arpe, entitled "*Industrial Organic Chemistry*".²⁷ Organometallic chemistry represents only a fraction of the content, but the point would be whether certain types of monographs would help our co-workers.

Joachim Ritter: There is a second book I would recommend in addition, namely Wittcoff and Reuben: "*Industrial Organic Chemicals*".²⁸ And of course there are similar books on inorganic industrial chemistry.

Bill Jones: I was going to add another bottleneck or problem in our discipline. Organometallic chemistry has grown so much in 50 years that if you think about what you had to learn when you were in graduate school, Collman and Hegedus²⁹ was the sum of all knowledge. Now take a look at Hartwig's book that has come out recently and contemplate the difference in the volume of material.³⁰ It's frightening. So how do you get across to a new student that volume of material? I find that to be a major challenge and a bottleneck for students, just to have an awareness of the breadth of what's been done in the field historically and up to the current date.

Jennifer Schomaker: I agree with Bill that educating students thoroughly in organometallic chemistry is difficult. Not only the volume of material, but the manner in which the subject is approached. Even if a graduate program offers an "organometallic" course, the content will be heavily influenced by the background of the person teaching it. Some students want to understand how to use organometallic compounds as catalysts for synthesis, but others want a completely different

perspective on the topic. For the most part, I tell my students to get Hartwig's book and learn as they go.

(10) Organometallics: Would anyone like to add anything more regarding organometallics and the year 2012, or challenges for the future?

Bill Jones: I wrote down three topics that I thought we could talk about. First, and somebody mentioned this already, there is a strong future for organometallic chemistry in organic applications. We're seeing more and more of that in their literature, in our literature, and I think that's one growth area for the future. Second, catalysis will always be important. No one's going to say "alright, we have enough catalysis, let's not do that, let's do something else". The third thing that we have not touched too much on today is energy, and fuel applications. I think that is going to be a huge area in the future and I think organometallic chemistry can play a big part in that. The CO₂ problem constitutes one entry point, but I think there are other entry points in which organometallic compounds can be important.

Tobin Marks: I would say not just fuels but lots of other energy-related problems, hinging on photovoltaics, lighter, stronger materials, alternative materials. And let's not forget old unsolved issues like selective carbon monoxide reduction to oxygenates.

Vivian Yam: I strongly agree with what had been said. We need to be more open to diversity and to exploring new opportunities. Apart from catalysis, like in materials, we can develop organometallics as phosphorescent materials, single-source precursors, organic transistors and semiconductors, energy-related materials for solar energy conversion, photovoltaics, hydrogen storage, etc. Also organometallics as drugs, sensors, and diagnostics which are more bio-related, as well as others that are more related to the environment, like carbon dioxide activation, sequestration, green chemistry and many, many others.

Organometallics: On that note, we will conclude our inaugural *Organometallics* Roundtable. The Editors would like to warmly thank all of the panelists for their time, engagement, and many valuable insights.

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