



IDW
2014

Université de Montréal

November 14th – 16th 2014

Getting there

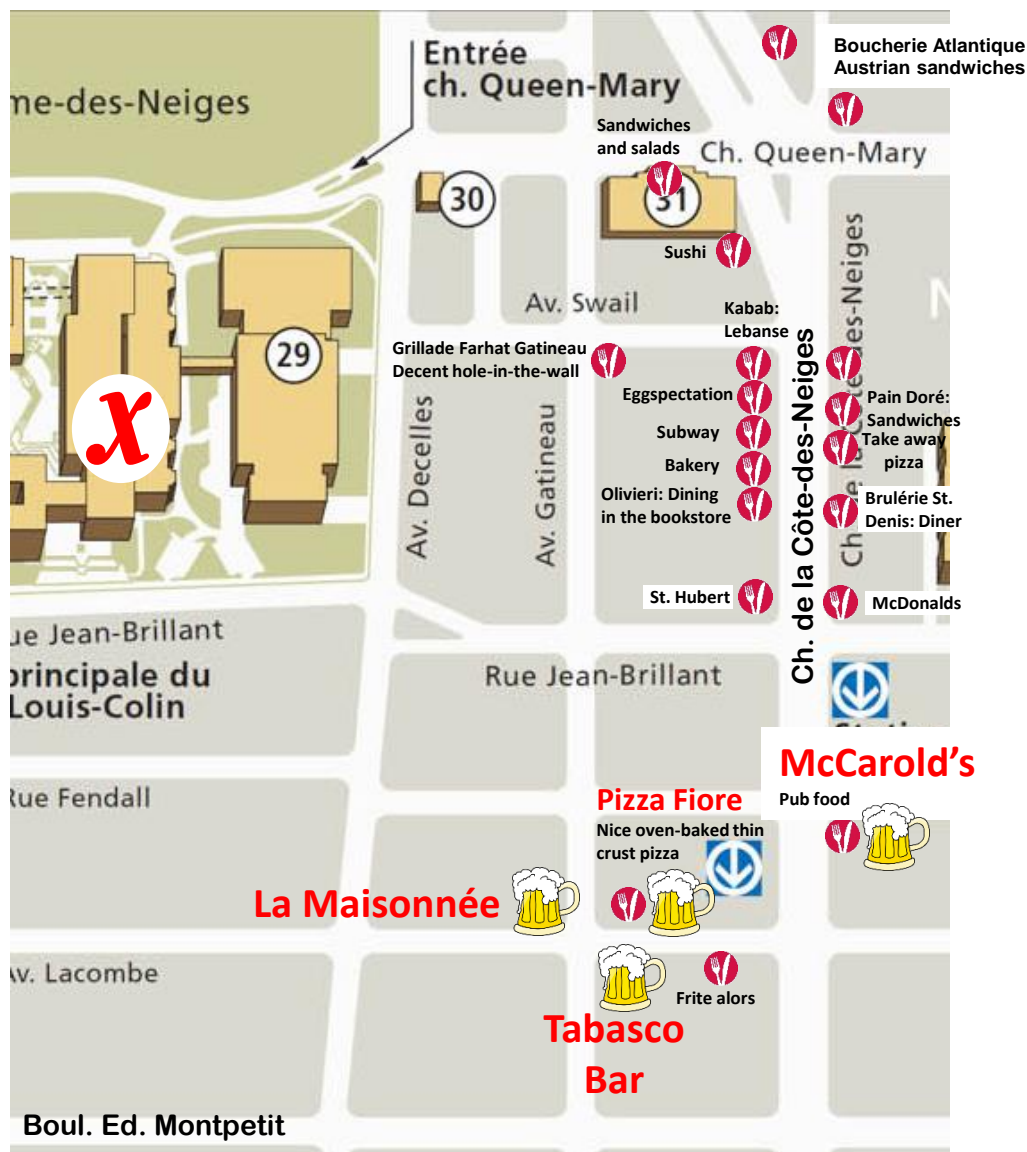
The conference including poster session and banquet will be held on the 2nd floor of 3200 Rue Jean-Brillant on the Université de Montréal campus.



Public transport is the easiest way to reach the conference. Metro stations "Université de Montréal" or "Côte-de-Neiges" (blue line) and several bus stops (i. e. 166 and 55) are in easy walking distance.

Parking is available at the Garage Louis Colin (5255, av. Louis-Colin) for \$12/day. It is advisable to exit the garage and take the street towards 3200 Jean-Brillant. Free parking might be found in the residential streets around the conference venue, but be aware of Montreal's sometimes cryptic parking signs which restrict parking to residents in certain sections (\$52 per offense).

Inorganic Discussion Weekend, Montréal 2014



Lunch

You will find a number of lunch spots around campus, in particular on Av. Côte-des-Neiges, all less than 10 minutes walking away.

Some organizers recommendations:

Grillade Farhat Gatineau: If you want to go for a fast meat skewer

Olivieri: For the more fancy French experience

Pizza Fiore: Nice pizzeria

After-banquet watering holes

La Maisonnée: The most popular choice. Fun to the sound of karaoke and the smell of stale beer

Tabasco Bar: Somewhat less popular and less crowded

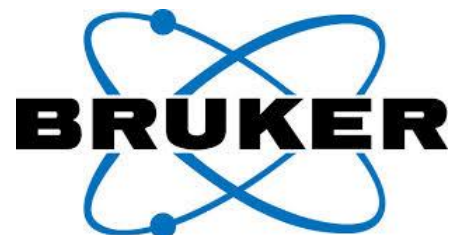
Pizza Fiore: An order of fries comes with each pitcher

Pub McCarold's: A very decent selection of beer for a less decent price

Grande Gueule: A bit out of the way and significantly quieter

Grande Gueule 

Gold Sponsors



Silver Sponsors



Bronze Sponsors



Agenda

Friday, November, 14th

19:30-22:00 MBraun Mixer at the “Sir Winston Churchill Pub – Karina Lounge”
at 1455-1459 Crescent Street

Saturday, November, 15th

8:00-8:30 *Coffee Break* (3200 Jean Brillant, 2nd floor, Cafétéria Chez Valère)

8:30 Opening remarks (B-2245)

9:00-10:20 Oral presentations O1-O8 (B-2325 and B-2245)

10:20-10:40 *Coffee Break*

10:40-12:00 Oral presentations O9-O16 (B-2325 and B-2245)

12:00-14:00 *Lunch Break* (see map at the end of the booklet for possibilities)

14:00-15:20 Oral presentations O17-O24 (B-2325 and B-2245)

15:20-15:40 *Coffee Break*

15:40 Plenary Lecture (B-2245): Prof. John E. Bercaw, *CALTECH*

17:00-19:00 Poster Session (3200 Jean Brillant, 2nd floor)

19:00-22:00 *Conference banquet* (Cafétéria Chez Valère, 2nd floor)

Sunday, 16. Nov. 2014

8:30-9:00 *Coffee Break*

9:00-10:20 Oral presentations O25-O32 (B-2325 and B-2245)

10:20-10:40 *Coffee Break*

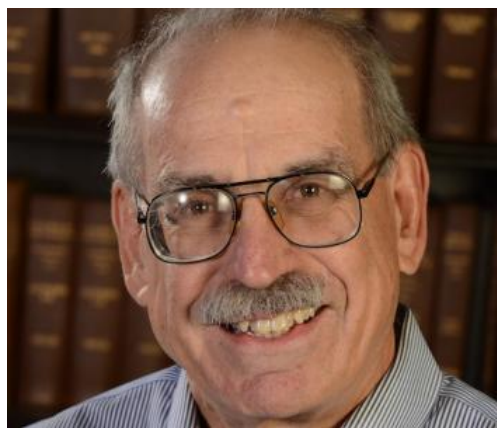
10:40-11:20 Oral presentations O33-O36 (B-2325 and B-2245)

11:30 Plenary Lecture (B-2245): Prof. Joseph A. Schwarcz, *McGill University*

appr. 13:00 Closing remarks (B-2245)

Prof. John E. Bercaw

*Centennial Professor of Chemistry
California Institute of Technology, Pasadena, USA.*



Prof. John E. Bercaw received his Ph. D. in chemistry from the University of Michigan in 1971. He joined the Californian Institute for Technology in 1972, where he became a faculty member in 1974. He is author of over 300 scientific publications and his contributions to organometallic chemistry have been noted with several prestigious awards, such as ACS awards for Pure Chemistry (1980), Organometallic Chemistry (1990), Advancement of Inorganic Chemistry (1997), the George A. Olah Award (1999), the

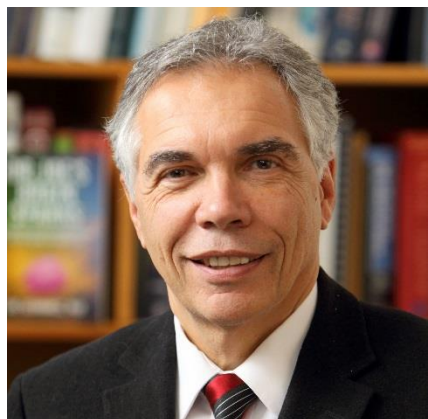
Arthur C. Cope scholar Award (2000), the Bailar Medal (2003), the Basolo Medal (2005), the Tolman Medal (2013) and the Willard Gibbs Medal (2014). He was named a fellow of the American Association for the Advancement of Science, of the National Academy of Sciences and of the American Academy of Arts and Sciences.

Hydrocarbon Upgrading to Fuels and Chemicals: Progress towards Homogeneous Catalysts

Current technologies for conversion of natural gas and petroleum to fuels and commodity chemicals are energy intensive and polluting. New catalytic processes that are more efficient and “greener” are required to reduce CO₂ emissions and to more effectively utilize our fossil fuel reserves. Discussed will be fundamental research efforts directed towards developing (1) a selective, homogeneous catalyst for direct, partial oxidation of light alkanes, (2) a homogeneous catalyst system for converting syngas (a mixture of CO and H₂), obtained by steam reforming of light alkanes, to C_{n>1} products, and (3) a catalytic tandem olefin dimerization/hydrogen transfer scheme for upgrading light alkane/alkene mixtures to transportation fuels.

Prof. Joseph A. Schwarcz

Director of the Office for Science & Society, McGill University, Montreal, Canada.



Prof. Joe Schwarcz received his Ph. D. in chemistry from McGill University in 1973, but he is best known for his entertaining public lectures on scientific topics. He hosts "The Dr. Joe Show" on Montreal's CJAD and is the author of several bestselling books popularizing science, such as "Science, Sense and Nonsense", "Radar, Hula Hoops and Playful Pigs" and "The Right Chemistry". His contributions to chemistry have been recognized with several awards, including the Royal Society of Canada's McNeil Medal in 1992, the ACS Grady-Stack Award for demystifying chemistry 1999, the Sandford Fleming Award from the Royal Canadian Institute in 2005 and the CSC "Montreal Medal" in 2010.

Hey! There are cockroaches in my chocolate ice cream!

No, there really are no cockroaches in chocolate ice cream. But one of my radio listeners did jump to this conclusion after misinterpreting what had been said about a certain food colorant. Being on one end of a microphone and in front of television cameras for over thirty years has afforded some fascinating insight into the public's perception of science. It has also provided an opportunity to separate sense from nonsense in areas ranging from nutrition and medications to cosmetics and pesticides. This highly visual and entertaining presentation examines some serious as well as some frivolous experiences in dealing with the public and emphasizes the importance of fostering critical thinking.

Oral presentations

Saturday, 8:30 : Opening remarks (B-2245)

	Group A (B-2325)	Group B (B-2245)
9:00-9:20	O1 Nuclearity control at iron(II) with hemilabile SNS pincer-type ligands: Facile C-S bond activation and imine coupling to redox-active N ₂ S ₂ Ligand Uttam K. Das <i>University of Ottawa</i>	O2 Direct synthesis of silver nanocatalyst from bulk metal: cellulose nanocrystals as active support and reductant Madhu Kaushik <i>McGill University</i>
9:20-9:40	O3 Synthesis and Reactivities of New NCN-Type Pincer Complexes of Nickel Jean-Philippe Cloutier <i>Université de Montréal</i>	O4 Gold Chemical Vapour Deposition Using Gold(I) Amide Precursors Sara E. Koponen <i>Carleton University</i>
9:40-10:00	O5 Cyclometallation and Coupling of a Rigid 4,5-Bis(imino)acridanide Pincer Ligand Promoted by Yttrium Edwin W. Y. Wong <i>McMaster University</i>	O6 Metal-Containing Micro-/Nano-Structures from the Pyrolysis of Ion Exchanged Phosphonium Polymer Blend Films Vanessa A. Béland <i>University of Western Ontario</i>
10:00-10:20	O7 Ketone Asymmetric Hydrogenation Catalyzed by P-NH-P' Pincer Iron Catalysts: an Experimental and Computational Study Kai Yang Wan <i>University of Toronto</i>	O8 Synthesis and Characterization of Thiophene Functionalized Dithiatetrazocines François Magnan <i>University of Ottawa</i>

10:20-10:40 : Coffee Break

	Group A (B-2325)	Group B (B-2245)
10:40-11:00	O9 Emission Properties of Three Coordinated Organoboron Compounds Containing B=N Soren Mellerup <i>Queen's University</i>	O10 Activation of Robust Bonds by Aluminum(I) Terry Chu <i>Brock University</i>
11:00-11:20	O11 Tuning Luminescence Properties of Au(I) Compounds through Au(I)-Au(I) Interactions: Application of Pressure-Dependent Spectroscopy to Dithiocarbamates Nicolas B. Desmarais <i>Université de Montréal</i>	O12 Reaction and Coordination Chemistry of Poly-(Chalcogenotrimethylsilanes) Mahmood A. Fard <i>University of Western Ontario</i>
11:20-11:40	O13 On the Coordination Chemistry of N,N'-Disubstituted Amidine-N-oxides Mihaela Cibian <i>Université de Montréal</i>	O14 Creating Phosphine Based Polymer Networks Using Air-Stable Primary Phosphines Ryan Guterman <i>University of Western Ontario</i>

Inorganic Discussion Weekend, Montréal 2014

- 11:40-12:00 **O15** Pure hydrogen evolution from small organic molecules using iron photocatalysts
Jacob M. Sommers
University of Ottawa
- O16** The Highly Lewis Acidic Dicationic Phosphonium Salt: [(SIMes)PFPh₂][B(C₆F₅)₄]₂
Meera Mehta
University of Toronto

12:00-14:00 : Lunch Break

	Group A (B-2325)	Group B (B-2245)
14:00-14:20	O17 Platinum Complexes of an Alane-Appended Analogue of ,1'-Bis(diphenylphosphino)ferrocene Bradley E. Cowie <i>McMaster University</i>	O18 Synthesis and Reactivity of Novel Low Valent Cationic Gallium Complexes Jeremy L. Bourque <i>Western University</i>
14:20-14:40	O19 Coordination of phosphido-boratabenzene ligands to transition metals to obtain zwitterionic complexes Viridiana Perez <i>Université Laval</i>	O20 Facile 1,1-carboboration of mono- and bis(alkynyl)tellurides Fu An Tsao <i>University of Toronto</i>
14:40-15:00	O21 New Designs for 1,2,3,5- dithiadiazolyl Radical Ligands Carolyn A. Michalowicz <i>University of Guelph</i>	O22 Synthesis of 1,2,4,6-Thiatriazinyl and 1,2,4,6-Selenatriazinyl π -Radicals for Molecular Electronics Nathan Yutronkie <i>University of Ottawa</i>
15:00-15:20	O23 Isolation and Characterization of a Tetramethyliron(III) Ferrate: An Intermediate in the Reduction of Ferric Salts with MeMgBr Malik H. Al-Afyouni <i>University of Rochester</i>	O24 Rhenium Complexes of Carboxamides Acids Zhijie Chua <i>McGill University</i>

15:20-15:40 : Coffee Break

15:40 : Plenary Lecture: Prof. John E. Bercaw, *CALTECH* (B-2245)

17:00 : Poster Session (3200 Jean Brillant, 2nd floor)

- Authors with odd numbers, please be present from 17:00-18:00 at your poster
- Authors with even numbers, please be present from 18:00-19:00 at your poster

19:00 : Conference banquet (Caf  teria Chez Val  re, 2nd floor)

Inorganic Discussion Weekend, Montréal 2014

Sunday, Nov. 16

	Group A (B-2325)	Group B
9:00-9:20	O25 Synthesis and Reactivity of Metal Fluorocarbene Complexes Graham M. Lee <i>University of Ottawa</i>	O26 The First Family of Lanthanide Molecule-Based Magnets Assembled from Crown Ether Ligands Majeda Al Hareri <i>Brock University</i>
9:20-9:40	O27 Elucidating effects of nucleophile variation in (SciOPP)FeX ₂ catalyzed Kumada cross-coupling reactions: the case of alkyl-alkynyl couplings Jared L. Kneebone <i>University of Rochester</i>	O28 A strategy to create a class III mixed-valence complex via a non-innocent terpyridine structural mimic Katie L. M. Harriman <i>University of Ottawa</i>
9:40-10:00	O29 Titanocene-based Catalysts for the Dehydrocoupling/Dehydrogenation of Amine-Boranes Titel Jurca <i>University of Bristol</i>	O30 Synthesis and characterization of new half sandwich ruthenium silyl complexes Van Hung Mai <i>Brock University</i>
10:00-10:20	O31 Palladium-Catalyzed Carbonylative C-H Functionalization of Heterocycles Jevgenijs Tjutrins <i>McGill University</i>	O32 The Destructive Interaction of Dirhodium(II) Tetraacetate and Human Metallothionein Daisy L. Wong <i>University of Western Ontario</i>

10:20-10:40 : Coffee Break

Saturday	Group A (B-2325)	Group B
10:40-11:00	O33 Reduction of Ketones using Fe(II)(P-NH-N-P') Catalysts Samantha A.M. Smith <i>University of Toronto</i>	O34 Mechanism of a Cu-Catalyzed Phenolic Oxygenation Mohammad S. Askari <i>Concordia University</i>
11:00-11:20	O35 What causes isomerization during olefin metathesis? Carolyn S. Higman <i>University of Ottawa</i>	O36 Ligand and Redox Derivatives of a Core Heteroligated Analogue of the Nitrogenase Cofactor Lay Ling Tan <i>University of Waterloo</i>

11:30 : Plenary Lecture: Prof. Joseph A. Schwarcz, *McGill University* (B-2245)

13:00 : Closing remarks (B-2245)

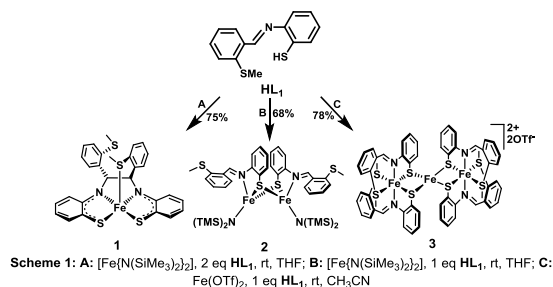
O1

Nuclearity control at iron(II) with hemilabile SNS pincer-type ligands: Facile C-S bond activation and imine coupling to redox-active N₂S₂ Ligand

Uttam K. Das,¹ Stephanie L. Daifuku,² Serge I. Gorelsky,¹ Ilia Korobkov,¹ Michael L. Neidig,² and R. Tom Baker*¹

¹University of Ottawa, Ottawa, ON K1N 6N5, Canada, udas091@uottawa.ca, ²University of Rochester, Rochester, NY 14627, USA

Two simple SNS pincer-type ligands, (*thiolate*-L₁ and *amido*-L₂) are prepared in one and two steps, respectively from commercial sources. Depending on solvent and order of addition, reactions of HL₁ with Fe[N(SiMe₃)₂]₂ and Fe(OTf)₂ afford 5-coordinate mononuclear-, 4-coordinate thiolate-bridged binuclear- and 6-coordinate trinuclear Fe(II) complexes (**Scheme 1**). Complex **3** reacts with P(OMe)₃ to generate thiolate-bridged 6-coordinate binuclear Fe(II) complexes, [{FeL₂(μ-SNS)}₂](OTf)₂ whereas [FeX(PMe₃)₄](X') (X = Cl, OTf; X' = BPh₄, OTf) and HL₁ yield mononuclear [Fe(SNS)(PMe₃)₃](X') that converts slowly to trivalent [Fe(SNC)(PMe₃)₃](X') via facile C-S bond activation. In another reaction, imine coupling occurs to afford a 5-coordinate mononuclear Fe(II) complex with a redox-active N₂S₂ ligand. Finally, HL₂ reacts with Fe[N(SiMe₃)₂]₂ to produce 6-coordinate mononuclear diamido complex [Fe(SNS)₂] which features two short Fe-S bonds to 5-membered ring thioethers and two long Fe-S bonds to the 6-membered ring thioethers. The latter reaction also yields some of the 4-coordinate complexes with only one 5-membered ring coordinated thioether, demonstrating the hemilabile nature of these SNS amido ligands. Products are characterized by elemental analysis, IR, NMR, UV/vis and Mössbauer spectroscopy, MCD, TD-DFT and single crystal X-ray diffraction. To assess their suitability as catalyst precursors for reductive transformations, preliminary reactivity studies of these complexes will be presented.



Notes

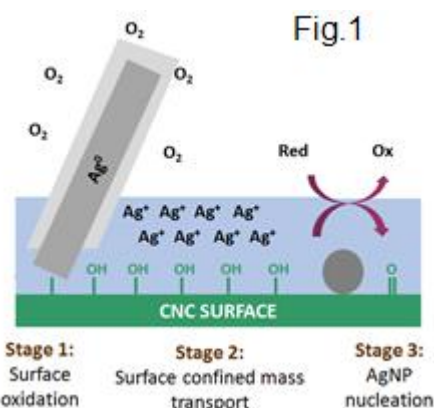
O2

Direct synthesis of silver nanocatalyst from bulk metal: cellulose nanocrystals as active support and reductant

Madhu Kaushik, Alain Li, Reuben Hudson, Chao-Jun Li, and Audrey Moores*

McGill University, Montreal, QC H3A 0B8, madhu.kaushik@mail.mcgill.ca

CNCs are derived from the biopolymer, cellulose, through acid hydrolysis by concentrated sulphuric acid. CNCs have well-defined size and morphology, high specific surface area and aspect ratio, high crystalline order and chirality, superior mechanical strength, and controllable surface chemistry. In addition, CNCs are inexpensive, renewable, biodegradable, non-toxic, and accessible industrially in large scale.¹ We exploit CNCs as reducing agents in the facile synthesis of Ag nanoparticles onto the CNC surface, directly from bulk Ag metal. The synthesis of silver nanoparticle Ag salts onto the CNC surface have been reported to include the reduction of Ag salts in presence of external reducing agents.² We use the surface hydroxyl groups on the CNC for reducing the Ag (I) generated from the bulk Ag wire in the CNC suspension (Fig.1). This CNC-hybrid composite material shows excellent conversions of aromatic aldehydes into their corresponding alcohols at 40 bars of H₂ and 100 °C in water. This reaction provides a fast and simple method to access alcohol from aldehyde in water.



1. Klemm, D.; Kramer, F.; Moritz, S.; Lindström, T.; Ankerfors, M.; Gray, D.; Dorris, A. *Angew. Chem. Int. Ed.* **2011**, *50*, 5438

2. Liu, H.; Wang, D.; Song, Z.; Shang, S. *Cellulose* **2011**, *18*, 67

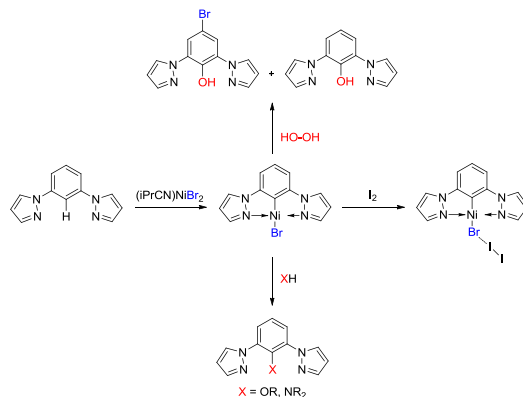
Notes

O3 **Synthesis and Reactivities of New NCN-Type Pincer Complexes of Nickel**

Jean-Philippe Cloutier, Boris Vabre, Berline MOUNGANG-SOUMÉ and Davit ZARGARIAN*

Université de Montréal, Montreal, QC H3C 3J7, jphilippecloutier@gmail.com, Montreal, QC H4G 1N1

Preparation, characterization and reactivities of a new family of Ni(II) complexes based on the tridentate pyrazole NCN-type pincer ligands. Refluxing these ligands in xylene with (*i*-PrCN)NiBr₂ and NEt₃ gave the complexes (NCN^{Pz})NiBr and (MeO-NCN^{Pz})NiBr via C-H nickelation. Reaction of the bromo complexes with aq. H₂O₂ (30%) gave the functionalized ligands Br-NC(OH)N^{Pz} and NC(OH)N^{Pz} or MeO-NC(OH)N^{Pz}, whereas **1** reacted with I₂ to generate (NCN^{Pz})NiBr·I₂, an iodine adduct displaying weak Br—I interactions. Heating **1** in EtOH in air generated NC(OEt)N^{Pz}, and this ligand derivatization could be extended to other alcohols and amines.



Notes

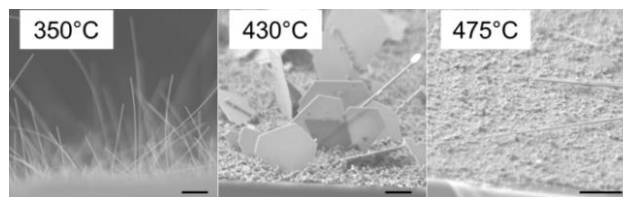
O4 Gold Chemical Vapour Deposition Using Gold(I) Amide Precursors

**Sara E. Koponen,¹ Matthew B. E. Griffiths,¹ David J. Mandia,¹ Jennifer F. Mcleod,¹
Jason P. Coyle,¹ Javier B. Giorqi,² Seán T. Barry¹**

¹Carleton University, Ottawa, ON K1S 5B6, sarakoponen@cmail.carleton.ca ²University of Ottawa, Ottawa, ON K1N-6N5

Gold thin films generated by chemical vapour deposition (CVD) are of interest for a number of optical and microelectronic applications. CVD is better suited to these applications than physical vapour deposition (PVD) techniques owing to the improved film uniformity and conformality that can be achieved with CVD.

Two novel Au(I) amide CVD precursors, trimethylphosphine gold(I) hexamethyldisilazide **1** and 1,3-diisopropyl-imidazolin-2-ylidene gold(I) hexamethyldisilazide **2**, were studied. Film morphology, thickness, and composition were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS), respectively. Under comparable deposition conditions, these precursors yield films with vastly different morphologies. Compound **1** produces spherical nanoparticles, which is typical for gold CVD. Compound **2** produces a mixture of nanoflakes, nanowires, and nanoparticles. The lower-dimensional nanostructures, which are unprecedented in CVD-generated gold films, are particularly interesting for plasmonic applications. Promisingly, nanocrystal shape exhibits a temperature dependence. Nanoflakes dominate at temperatures ranging from 400 to 470 °C. Nanowire growth is favoured outside of this temperature range, in particular at lower temperatures. Higher temperatures yield predominately nanoparticulate films. The possibility that the supporting ligand is directing growth, and the implications for nanocrystal shape control by CVD, will be discussed.



Scale bars 1 μm

Notes

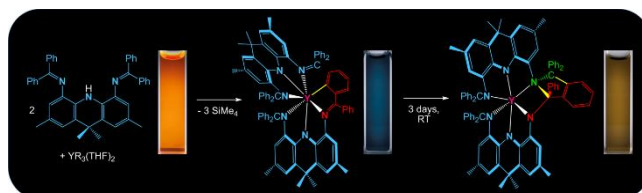
O5

Cyclometallation and Coupling of a Rigid 4,5-Bis(imino)acridanide Pincer Ligand Promoted by Yttrium

Edwin W. Y. Wong¹ and David J. H. Emslie^{*,1}

¹McMaster University, Hamilton, ON L8S 4M1, emslied@mcmaster.ca

Rigid, dianionic xanthene-based ligands have been used by the Emslie group to isolate rare examples of neutral and cationic organothorium and organouranium complexes. These successes in actinide chemistry led us to pursue analogous organoyttrium complexes using new rigid, monoanionic acridanide ligands due to their potential to catalyze a range of transformations such as α -olefin polymerization and hydroamination. An extremely rigid NNN-donor proligand, H[AIm₂], was prepared and its reaction with [Y(CH₂SiMe₃)₃(THF)₂] (0.5 equiv.) afforded deep blue [Y(AIm₂)(AIm₂')] (**1**; AIm₂' = cyclometallated AIm₂). Compound **1** slowly isomerizes to form green-brown **2**, in which the AIm₂ and AIm₂' ligands are coupled together to form a single hexadentate ligand. The unexpected orange colour of H[AIm₂] and blue colour of **1** were investigated using TD-DFT calculations and the results will be discussed. The kinetics of the isomerization and a proposed mechanism will also be described.



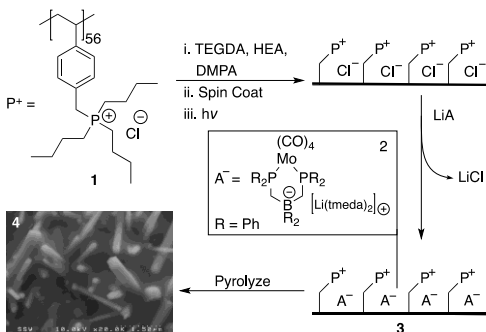
Notes

O6

Metal-Containing Micro-/Nano-Structures from the Pyrolysis of Ion Exchanged Phosphonium Polymer Blend Films

Vanessa A. Béland,¹ Matt A. S. Ross, Jonathan W. Dube, Ryan Guterman and Paul J. Ragogna^{*,1}

¹University of Western Ontario, City of London, ON N6A 3K7, vbeland@uwo.ca



In the last two decades there has been extensive research into surface functionalization^{1,2} and polymer-derived ceramics.³ When combining these two emerging fields it is ideal to start with an easily shaped surface for the subsequent deposition of the ceramic char. In this context, we have synthesized a highly crosslinked metal-functionalized surface; first by UV-curing a phosphonium polymer (**1**) blend to produce a thin film; followed by ion exchange on the surface with a molybdenum tetracarbonyl bis(phosphino)borate (**2**).⁴ The result was 45% exchange of (**2**) on to possible phosphonium sites by ATR-IR spectroscopy. The synthesis, characterization, pyrolysis and resulting nanostructures (**4**) of these

ion exchanged polymer blend films will be presented, as well as our work towards expanding this system to other metals.

References

1. Dumée, L.D.; He, L.; Lin, B.; Ailloux, F-M.; Lemoine, J-B.; Velleman, L.; She, F.; Duke, M.C.; Orbell, J.D.; Erskine, G.; Hodgson, P.D.; Gray, S.; Kong, L. *J. Mater. Chem. A*, 1, 15185-15206, **2013**.
2. Guterman, R.; Hesari, M.; Ragogna, P.J.; Workentin, M.S. *Langmuir*, 29, 6460-6466, **2013**.
3. Colombo, P. *J. Am. Ceram. Soc.* 93, 1805-1837, **2010**.
4. Thomas, J. C.; Peters, J. C. *Inorg. Chem.* **2003**, 42, 5055-5073.

Notes

07 Ketone Asymmetric Hydrogenation Catalyzed by P-NH-P' Pincer Iron Catalysts: an Experimental and Computational Study

Kai Yang Wan, Jessica F. Sonnenberg, Peter E. Sues and Robert H. Morris

University of Toronto, City of Toronto, ON M5S 3H6, kwan@chem.utoronto.ca

Recently our group reported the development of iron carbonyl catalysts bearing chiral tridentate P-N-P' ligands for the asymmetric hydrogenation of prochiral ketones in THF. An NMR study into the activation process identified the amine hydride alkoxide complexes $\text{Fe}(\text{P-NH-P}')(\text{CO})(\text{H})(\text{OR}^4)$ with $\text{R}^4 = \text{Me, tBu or tAmyl}$ and $\text{P-NH-P}' = \text{PPh}_2\text{CHR}^3\text{CHR}^2\text{NHCH}_2\text{CH}_2\text{PR}^1_2$ with $\text{R}^1 = \text{iPr or Cy}$, R^2 and $\text{R}^3 = \text{H}$; or (*S,S*)-P-NH-P' with $\text{R}^1 = \text{Cy}$, $\text{R}^2 = \text{Me}$, $\text{R}^3 = \text{Ph}$. These still required treatment with excess KOtBu and H_2 (g) to be catalytically active in THF. We use experiment and Density Functional Theory (DFT) calculations to show that this treatment leads to the hydride amide $\text{Fe}(\text{PPh}_2\text{CHR}^3\text{CHR}^2\text{NCH}_2\text{CH}_2\text{PR}^1_2)(\text{CO})(\text{H})$ which reacts with dihydrogen to form cis and trans dihydride complexes $\text{Fe}(\text{P-NH-P}')(\text{CO})(\text{H})_2$, identified by NMR for $\text{R}^1 = \text{iPr}$ and for (*S,S*)-P-NH-P'. In the presence of KOtBu, NaOtBu or KOtBu/2,2,2-cryptand and H_2 (g), these species are active for the catalytic hydrogenation of acetophenone, while in the absence of H_2 (g), Fe(0) complexes form. Ketone hydrogenation is proposed to occur in an outer sphere stepwise process and this enantiodetermining step has been modeled by DFT. The calculations suggest that the energy barriers for hydride attack on the ketone and dihydrogen splitting at the amido complex are similar and that either step could be turn-over limiting depending of the size of the ketone.

Reference:

- (1) P. O. Lagaditis, P. E. Sues, J. F. Sonnenberg, K. Y. Wan, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.*, **2014**, *136* (4), pp 1367–1380. (2) Jessica F. Sonnenberg, Kai Yang Wan, Peter E. Sues and Robert H. Morris, *submitted*.

Notes

O8

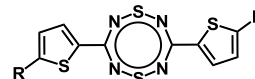
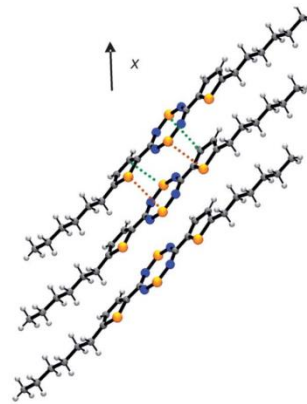
Synthesis and Characterization of Thiophene Functionalized Dithiatetrazocines

François Magnan, Soofieh S. Afjeh, Alicea Leitch, Iliia Korobkov, Jaclyn Brusso*

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Organic semiconductors (OSCs) are attractive materials for electronic and photonic devices, in large part thanks to their tunable photophysical and electrochemical properties. Competitive device efficiency, however, remains an ongoing challenge and is often attributed to the poor intermolecular charge transport commonly observed in organic materials. Since charge transport is dependant on the molecular packing, engineering OSC molecules to self-assemble in a π -stack structure with maximum overlap in the solid-state is one approach to enhance device efficiency.

Furthermore, sulfur- and nitrogen-containing heterocycles are attractive electron-transporting semiconductors due to the lowering of the HOMO-LUMO energies as a result of the heteroatoms' higher electronegativities, as well as their potential to enhance electronic communication through sulfur's more diffuse orbitals. To that end, this presentation will focus on a family of thiophene functionalized dithiatetrazocines (DTTA), a relatively unexplored eight-membered ring system for use as an active material in device applications. More specifically, the synthesis of several halogenated and alkylated thiophene-functionalized DTTAs, as well as their characterization by optical, electrochemical and computational methods, will be presented.



R = H, Hex, Br, CH(OCH₂CH₂O), CHO

Top – Packing motif of a

hexylthiophene-functionalized DTTA.

Bottom – Structural framework of thiophene-functionalized DTTA.

Notes

O9

Emission Properties of Three Coordinated Organoboron Compounds Containing B=N

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We recently reported¹ the synthesis of several 2,2-disubstituted benzothiazoline-BMes₂ (Mes = mesityl) compounds containing a B=N bond. Unexpectedly, these compounds were found to display dual emission which was assigned to monomer and excimer fluorescence of the molecules respectively. Furthermore, the excimer emission maxima of each compound was found to be sensitive to temperature. This presentation will focus on the unusual photophysical properties of these compounds as well as attempt to rationalize their origin.



Figure 1. The proposed mechanism of excimer emission and its shift with decreasing temperature

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Notes

O10 Activation of Robust Bonds by Aluminum(I)

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Activation of robust bonds (H–X, C–X, P–P, S–S) has historically been the domain of transition metal complexes.^[1] However, recent work has demonstrated the ability of low valent main group complexes to mimic the ability of transition metal complexes to cleave enthalpically strong single bonds.^[2]

Recently, we have demonstrated the facile activation of H–X bonds (where X = H, B, C, Si, N, P, O) by the β -diketoiminato stabilized complex of aluminum in the +1 oxidation state, **1**.^[3] We have since extended the scope of bond activation to other single bonds including carbon–oxygen, carbon–halide, carbon–sulfide, disulfides, and diphosphides. In particular, complex **1** is able to oxidatively add very robust alkyl and aryl fluoride bonds across the low valent aluminum centre. The synthesis and characterization of these novel products will be presented.

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- [2] Asay, M.; Jones, C.; Driess, M. *Chem. Rev.* **2011**, *111*, 354.
- [3] Chu, T.; Korobkov, I.; Nikonov, G. I. *J. Amer. Chem. Soc.* **2014**, *136*, 9195.

Notes

O11 **Tuning Luminescence Properties of Au(I) Compounds through Au(I)-Au(I) Interactions: Application of Pressure-Dependent Spectroscopy to Dithiocarbamates**

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Dithiocarbamate gold(I) compounds often form linear polymeric chains in the solid state which show interesting luminescence properties¹. Their luminescence properties strongly depend on intramolecular and intermolecular aurophilic interactions. Several dithiocarbamate gold(I) compounds were synthesized and exhibit linear and kinked chains in the solid-state with significantly different luminescence properties². We gain insight on the origin of those different properties through different techniques: Crystallography^{2,3}, Theoretical Calculations (Molecular Orbitals)^{2,4} and Pressure-dependent luminescence spectroscopy².

1. Azani et al., Chem. Eur. J., **2012**, 18, 9965
2. Roberts, Bélanger-Desmarais, Reber, Leznoff, Chem. Comm., **2014**, 50, 3148
3. Paliwoda, Wawrzyniak, Katrusiak, J. Phys. Chem. Lett., **2014**, 5, 2182
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Notes

O12

Reaction and Coordination Chemistry of Poly-(Chalcogenotrimethylsilanes)

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Silylated chalcogen reagents of the type RESiMe₃ (R = an organic group, E = S, Se) have been shown to be a convenient source of organo-chalcogenide (RE⁻) in metal chalcogen bond formation reactions.ⁱ Their potential in coordination chemistry has been confirmed for the assembly of polynuclear metal-chalcogen (cluster) architectures as well as in single metal coordination complexes.ⁱⁱ

As part of our continued interest in developing the chemistry of poly metal chalcogenolates via organochalcogenotrimethylsilane reagents, we probed the coordination chemistry of Ar(CH₂ESiMe₃)_nⁱⁱⁱ (E = S, Se) in two different systems.

Here the reaction of [(dppp)PdCl₂], (1,3-bis(diphenylphosphino)propane)palladium(II), with Ar(CH₂ESiMe₃)_n when n = 2 (ortho) or 4 (1,2,4,5) provide a single or a double butterfly shaped Pd₂E₂ cluster on the aromatic spacer, respectively: n = 2 (ortho); [(dppp)₂Pd₂-μ-κ²E-{1,2-(ECH₂)₂C₆H₄}]²⁺, n = 4; [(dppp)₄Pd₄-μ-κ⁴E-{1,2,4,5-(ECH₂)₄C₆H₂}]⁴⁺. The structures were determined by single crystal X-ray diffraction analysis. A variety of NMR experiments including two-dimensional homonuclear and heteronuclear correlated spectra were used to probe the solution behaviour of the dinuclear palladium complexes, [(dppp)₂Pd₂-μ-κ²E-{1,2-(ECH₂)₂C₆H₄}]²⁺, in more detail.

Furthermore, the silylated reagents Ar(CH₂ESiMe₃)_n (n = 2 (para), 3 (1,3,5)) form a series of multinuclear carbene-copper chalcogenolates complexes, Ar(CH₂ECuIPr)_n (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) via reaction with IPr-Cu(OAc). The synthesis, structures and spectroscopic properties of Ar(CH₂ECuIPr)_n (E = S, Se; n = 2, 3) will be described.

ⁱ MacDonald D. G.; Corrigan J. F., *Philos. Trans. A Math. Phys. Eng. Sci.* **2010**, *368*, 1455-1472.

ⁱⁱ MacDonald, D. G.; Eichhöfer, A.; Campana, C.F.; Corrigan, J. F., *Chem. Eur. J.* **2011**, *17*, 5890-5902.

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Notes

O13 On the Coordination Chemistry of *N,N'*-Disubstituted Amidine-*N*-oxides

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The coordination chemistry of *N,N'*-disubstituted amidine-*N*-oxides (AMOXs) with late first row transition metals is explored. The synthesis of the ligands and their metallic complexes is presented. Structural analysis, spectroscopic methods and DFT calculations are used to study the influence of the metal-ligand interaction on the structure and properties of the compounds.

The cobalt(II) homoleptic AMOX complexes are square-planar (low spin) in the solid state, according to XDR and magnetic measurements ($\mu_{\text{eff}} = 1.8$ to $2.1 \mu_{\text{B}}$), and show square-planar (low spin) to tetrahedral (high-spin – $\mu_{\text{eff}} = 1.8$ to $2.1 \mu_{\text{B}}$) isomerization in solution of non-coordination solvents.^{1,2} The thermodynamic parameters for the isomerization equilibrium were determined, suggesting a major influence of the ligand substitution pattern. The zinc(II) bis-chelates present tetrahedral geometry, as expected for d^{10} metal complexes, and exhibit solution and solid state luminescence.

¹Hanan *et al.*, *Dalton Trans.*, **2011**, 40, 1038

²Hanan *et al.*, *Eur. J. Inorg. Chem.*, accepted for publication

Notes

**O14 Creating Phosphine Based Polymer Networks Using
Air-Stable Primary Phosphines**

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New developments in polymer science can often be traced to research in fundamental synthetic chemistry. All polymer science relies on a bedrock of a select few chemical transformations that are both high yielding and tolerant over a wide range of conditions. While organic chemistry has typically been the major inspiration for such developments, inorganic chemistry has witnessed fewer advances in transitioning between small molecule to polymer chemistry. One of the key features to enable this evolution lies in satisfying the requirements for a practical polymerization reaction. In this context, our interest in the fundamental chemistry of phosphorus, specifically the P-H bond has allowed us to generate a completely new class of polymer network systems. Our P-H containing monomers are synthesized readily, are uniquely air stable, and the polymerization reactions are high yielding, fast, and tunable. These features combined allow us to tune the mechanical, thermal, and chemical nature of the polymer by simply varying monomer structure and stoichiometry. We have begun exploring the utility of our new materials as oxygen and metal scavengers, and as a solid support for a variety of organophosphorus transformations that would otherwise be impossible to perform.

Notes

O15

Pure hydrogen evolution from small organic molecules using iron photocatalysts

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The two largest problems with the advent of a renewable hydrogen economy are hydrogen production and storage.^{1,2} Recently, many researchers have focused using small organic liquids as renewable sources of hydrogen. Photocatalytic, electrochemical and thermal dehydrogenation reactions using methanol, formic acid and formaldehyde to produce H₂ and CO₂ have been explored extensively in recent years.³ A dehydrogenation catalyst which can selectively oxidize small organic molecules into formate, without producing CO₂, will effectively bypass the difficult CO₂ reduction step. To our knowledge, no photo-, thermo-, or electrocatalyst has been reported to selectively dehydrogenate any small organic molecule to produce pure H₂ and avoid the formation of either CO₂ or CO₃²⁻.

Herein, we report the use of inexpensive iron photocatalysts for the selective dehydrogenation of small organic molecules into pure H₂ and formate. The best catalyst is capable of turnover numbers exceeding 4500 and is effective at ambient temperature and atmosphere, and resilient in both river and seawater, only requiring visible light to initiate the reaction.

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Notes

O16

**The Highly Lewis Acidic Dicationic Phosphonium Salt:
[(SIMes)PFPh₂][B(C₆F₅)₄]₂**

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Phosphorus compounds have been traditionally thought of as Lewis donor ligands used in transition metal and organometallic chemistry. Such ancillary roles have been critical to a number of landmark advances in catalysis. However, phosphorous based Lewis acids have been studied to a less extent.¹ Previously, the Stephan Group reported the preparation and Lewis acidity of the fluorophosphonium cations [(C₆F₅)₂PhPF]⁺ and [(C₆F₅)₃PF]⁺ and the application of these species in the hydrodefluorination of fluoroalkanes, the isomerization of terminal olefins and the hydrosilylation of alkenes and alkynes.² This reactivity has been attributed to their energetically accessible $\sigma^*(\text{P-F})$ acceptor orbitals. This original system requires strongly electron-withdrawing substituents, thus limiting potential structural variations. This work focuses on avoiding perfluoroarenes to enhance the Lewis acidity of the fluorophosphonium. In this presentation, the preparation of the dicationic phosphonium salt [(SIMes)PFPh₂][B(C₆F₅)₄]₂ will be discussed.³ This system exhibited remarkable Lewis acidity in stoichiometric reactions and acted as an effective Lewis acid catalyst for the hydrodefluorination of fluoroalkanes³, hydrosilylation of olefins³, deoxygenation of ketones and etherification of aldehydes.

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2. (a) M. Perez, L. J. Hounjet, C. B. Caputo, R. Dobrovetsky, D. W. Stephan, *J. Am. Chem. Soc.* **2013**, *135*, 18308–18310; (b) C. B. Caputo, L. J. Hounjet, R. Dobrovetsky, D. W. Stephan, *Science* **2013**, *341*, 1374–1377; (c) L. J. Hounjet, C. B. Caputo, D. W. Stephan, *Dalton Trans.* **2013**, *42*, 2629–2635.
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Notes

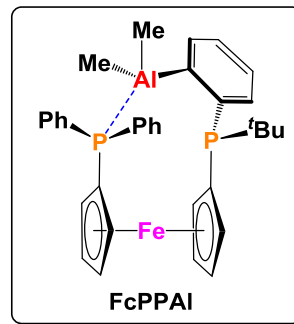
O17

Platinum Complexes of an Alane-Appended Analogue of 1,1'-Bis(diphenylphosphino)ferrocene

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The reaction of a new ferrocene based alane-containing ambiphilic ligand, FcPPAI (see Figure), with $[\text{Pt}(\text{nb})_3]$ (nb = norbornene) yielded $[\text{Pt}(\eta^2\text{-nb})(\text{FcPPAI})]$, which features bisphosphine coordination of the 1,1'-disubstituted ferrocene backbone to the metal centre, and η^1 -coordination of the pendant alane to platinum. Reaction of $[\text{Pt}(\eta^2\text{-nb})(\text{FcPPAI})]$ with C_2H_4 , C_2Ph_2 or H_2 results in the formation of $[\text{Pt}(\eta^2\text{-L})(\text{FcPPAI})]$ ($\text{L} = \text{C}_2\text{H}_4, \text{C}_2\text{Ph}_2$) and $[\text{PtH}_2(\text{FcPPAI})]$, respectively; all three complexes adopt distorted square-pyramidal geometry with the pendant alane η^1 -coordinated to the metal centre in the axial position. In addition, $[\text{Pt}(\eta^2\text{-nb})(\text{FcPPAI})]$ reacts with CO to afford $[\text{Pt}(\text{CO})(\text{FcPPAI})]$, and co-ligand free $[\text{Pt}(\text{FcPPAI})]$ may be obtained by heating a benzene solution of $[\text{Pt}(\eta^2\text{-nb})(\text{FcPPAI})]$ to 70°C overnight, resulting in the precipitation of $[\text{Pt}(\text{FcPPAI})]_2$; these complexes adopt distorted square planar and T-shaped geometries, respectively, and also feature η^1 -coordination of aluminum to platinum. X-ray crystallographic, NMR and IR spectroscopic data, along with a discussion of the remarkable coordination geometries observed for the formally Pt(0)- and Pt(II)-FcPPAI complexes will be presented here-in.



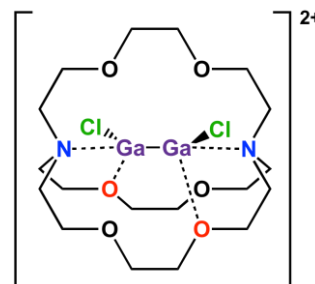
Notes

O18 Synthesis and Reactivity of Novel Low Valent Cationic Gallium Complexes

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Low valent gallium compounds are of particular interest, not only due to their unique structural and electronic properties, but also for recent developments in their reactivity with small molecules,^{1,2} as well as their use as alternative catalysts for industrially significant transformations.^{3,4} Previous work in our group has utilized macrocyclic ethers to stabilize reactive germanium(II) dications,⁵ however, only a few examples incorporating gallium into macrocyclic ethers have been reported.⁶ Herein, we describe the synthesis and spectroscopic characterization of low valent cationic cryptand-222 complexes of gallium from readily available low valent gallium sources. The bonding in these novel complexes has been examined through X-ray crystallography and computational methods.



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Notes

O19 Coordination of phosphido-boratabenzene ligands to transition metals to obtain zwitterionic complexes

Viridiana Perez, Wenhua Bi, and Frédéric-G. Fontaine*

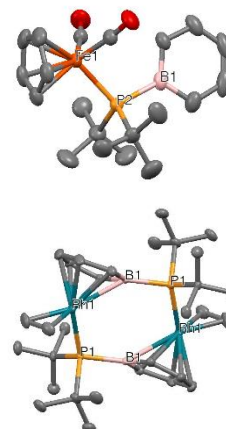
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Amongst the wide variety of metal complexes used as catalysts, zwitterionic complexes are of particular interest due to their increased catalytic activity that often surpasses that of their cationic parent complexes.[1] A zwitterionic complex is a neutral metal-ligand fragment where the positive charge is localized over the metal center and the negative charge is delocalized over the ligands.[2]

In order to generate new zwitterionic complexes, we are looking at the coordination chemistry of anionic phosphine ligands bearing boratabenzene functionalities. Boratabenzene is a six-membered heterocycle where one of the C-H fragment is replaced by a negatively charged B-X fragment.[3,4] The ability of these anionic phosphine to bind to a metal center by the phosphorous lone pair is due to the nature of the P-B interaction, which disfavors orbital overlap between the lone pair of electrons on phosphorous and the empty *p* orbital on boron.

The properties of phosphido-boratabenzene as a highly donating and bulky ligand had been explored.[5] New insights into the coordination modes of phosphido-boratabenzene and the strength of the P-B interaction will be discussed as well as catalytic applications.

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Notes

O20

Facile 1,1-carboboration of mono- and bis(alkynyl)tellurides

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The 1,1-carboboration of alkynes using strongly Lewis acidic boranes of the type $\text{RB}(\text{C}_6\text{F}_5)_2$ (R=alkyl or aryl groups) has allowed for the facile synthesis of otherwise difficult to access heterocycles such as boroles¹ and phospholes². Herein we investigated the extension of this work to the 1,1-carboboration of mono- and bis(alkynyl)tellurides, as the interest in tellurium-containing heterocycles increased dramatically in recent years due to their potential as new optoelectronic materials³. The reaction between the alkynyltelluride $\text{Ph}(\text{CH}_2)_2\text{TeCCPh}$ and a series of electrophilic boranes $\text{RB}(\text{C}_6\text{F}_5)_2$ (R=Me, Ph, C_6F_5) proceeded cleanly at room temperature to give borylated vinyl tellurides $\text{Ph}(\text{CH}_2)_2\text{TeC}(\text{Ph})\text{CRB}(\text{C}_6\text{F}_5)_2$. The reactivity of these compounds will be discussed in the context of frustrated Lewis pair (FLP) chemistry, where the tellurium centre acts as the Lewis base and the boron centre acts as the Lewis acid. By contrast, the reaction between bis(alkynyl)telluride, $\text{Te}(\text{CCPh})_2$, and the same series of boranes led to two distinct products depending on the R substituent on the borane. Both products are unique heterocycles containing boron and tellurium in either 6-membered or 5-membered rings. The influence of the R-substituent of boron on the reaction outcome and the solid-state structures of these products will be discussed in detail.

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Notes

O21

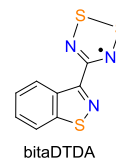
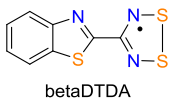
New Designs for 1,2,3,5- dithiadiazolyl Radical Ligands

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Our group specializes in creating molecular materials based on thiazyl radicals as ligands. These spin bearing ligands are used to mediate magnetic coupling between paramagnetic metal centers.^{[1][4]} The resulting complexes have exhibited various novel and interesting magnetic properties.^{[2][3]} Our work makes a unique contribution to the field of molecular magnetic materials.^[4]

Thiazyl heterocycles contain primarily sulfur and nitrogen atoms.^[4] The radicals presented here are new 1,2,3,5-dithiadiazolyls (DTDAs) referred to as bitaDTDA and betaDTDA. These are the first DTDA radicals that contain a sulfur atom outside the heterocyclic ring. This sulfur atom promotes extensive networks of intermolecular contacts in the crystal structure. These new radical ligands have been coordinated to paramagnetic metals. Here we will examine the magnetometry and crystal structures of several lanthanide and metal complexes with bita and betaDTDA ligands.



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O22

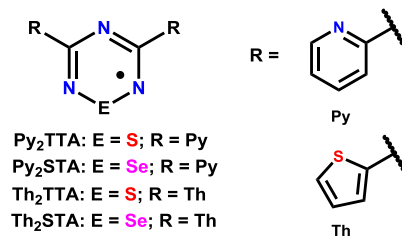
Synthesis of 1,2,4,6-Thiatriazinyl and 1,2,4,6-Selenatriazinyl π -Radicals for Molecular Electronics

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Thiazyl-based neutral radicals have been seen as attractive candidates for molecular conductors and magnets. These radicals have the potential to be used as multifunctional materials where their applications can be extended towards spin-bearing ligands, magnetic switches, or liquid crystalline radicals. The 1,2,4,6-thiatriazinyl (**TTA**) radical has been considered for these applications; however, only a few derivatives are known.

Substitution at the R positions of these radicals ultimately changes the properties and the end applications of these systems. To this end, the 3,5-bis(2-pyridinyl)-1,2,4,6-thiatriazinyl (**Py₂TTA**) and the 3,5-bis(2-pyridinyl)-1,2,4,6-thiatriazinyl (**Th₂TTA**) have been viewed as interesting derivatives. **Py₂TTA** has been seen as a spin-bearing ligand with a binding motif structurally similar to terpyridine, whereas **Th₂TTA** exhibits facile functionalization on the thienyl substituents giving rise for the potential of liquid crystalline radicals. This presentation will focus on the development of these radicals in regards to their synthesis, characterization, and crystal structures and their applications towards molecular electronics. Furthermore, replacement of sulfur for its heavier chalcogen, selenium, in the **TTA** ring will be discussed in efforts to pursue 1,2,4,6-selenatriazinyl (**STA**) radicals.



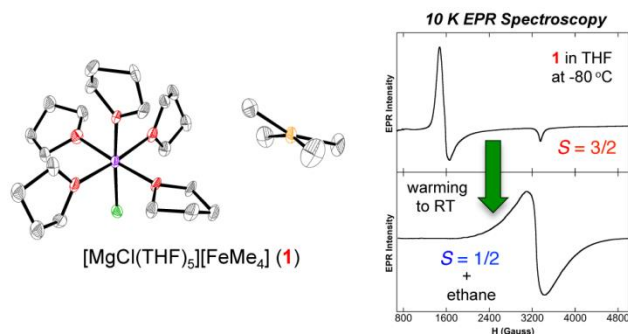
Notes

O23 Isolation and Characterization of a Tetramethyliron(III) Ferrate: An Intermediate in the Reduction of Ferric Salts with MeMgBr

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While iron-catalyzed Kumada cross-coupling reactions with simple iron salts have been known since the early 1970s, the nature of the in-situ formed iron species remains elusive. Herein, we report the synthesis of the homoleptic tetraalkyliron(III) ferrate complex, $[\text{MgCl}(\text{THF})_5][\text{FeMe}_4]$ from the reaction of FeCl_3 with MeMgBr in THF. Upon warming, this distorted square-planar $S = 3/2$ species converts to the $S = 1/2$ species originally observed by Kochi and co-workers with concomitant formation of ethane, consistent with its intermediacy in the reduction pathway of FeCl_3 to generate the reduced iron species involved in C-C cross-coupling catalysis.



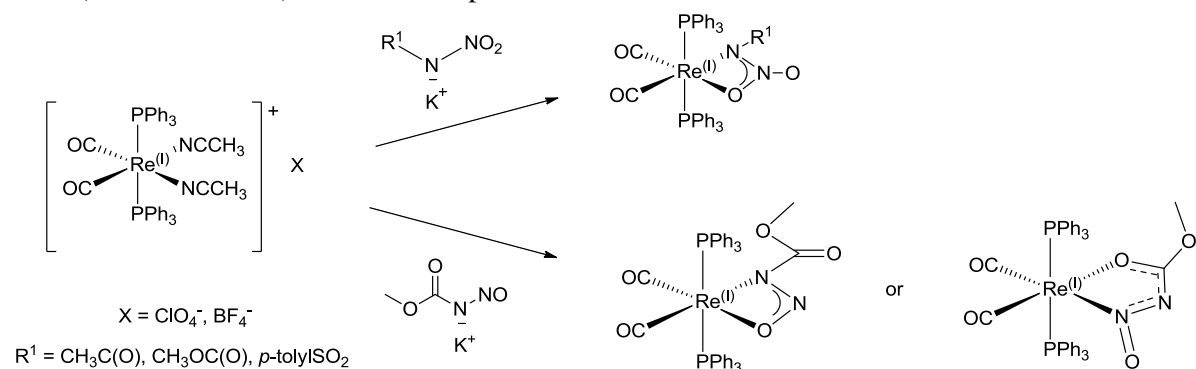
Notes

O24 Rhenium Complexes of Carboxamides Acids

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The synthesis of novel acidic carboxamides with nitro groups and their coordination chemistry with a Re complex have been reported.¹ The coordination chemistry of the conjugate anion of the carboxamide acids (nitro and nitroso) with a Re complex will be discussed.



1. (a) D. S. Bohle, Z. Chua, *Inorg. Chem.*, **2011**, *50*, 3135, (b) D. S. Bohle, Z. Chua, *Inorg. Chem.*, **2014**, *53*, 11160.

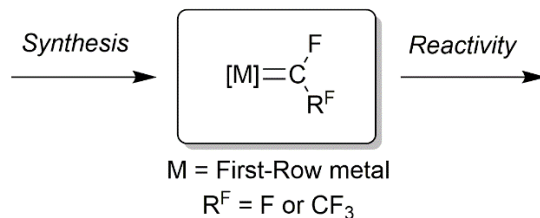
Notes

O25 **Synthesis and Reactivity of Metal Fluorocarbene Complexes**

Graham M. Lee, Matthew C. Leclerc, Daniel J. Harrison, and R. Tom Baker*

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Organometallic complexes with fluorinated organic ligands have received widespread attention in recent years for their role in new synthetic methodologies for the production of fluorinated products.¹ While metal-fluoroalkyl compounds (M-CF₃ in particular) and metal-fluorides have been studied extensively, metal fluorocarbenes (M=CF₂, M=CF(CF₃), etc.), particularly those based on first-row metals, have been studied much less by comparison. Herein, the synthesis² of novel cobalt and nickel fluorocarbene complexes are described, and their reactions with various small molecules are discussed in detail.³ The potential role of fluorocarbene complexes in catalysis is also considered.



(1)Kirsch, P. *Modern Fluoroorganic Chemistry*, **2004**, WILEY-CVH Verlag BmbH & Co. K GaA, Weinheim.

(2)Lee, G. M.; Harrison, D. J.; Korobkov, I.; Baker, R. T. *Chem. Commun.* **2014**, 50, 1128.

(3)Harrison, D. J.; Lee, G. M.; Leclerc, M. C.; Korobkov, I.; Baker, R. T. *J. Am. Chem. Soc.* **2013**, 135, 18396.

Notes

O26 The First Family of Lanthanide Molecule-Based Magnets Assembled from Crown Ether Ligands

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Many lanthanide ions display great potential in the field of molecular magnetism due to their high intrinsic anisotropies, which can be enhanced by an appropriate coordination environment. However, many of the ligand systems employed to date require multi-step syntheses and result in complexes which are unstable to air or moisture. Our approach has been to make use of the inherently oxophilic nature of lanthanide ions and employ oxygen-rich ligands, such as crown ethers. Given that the radii of the Ln^{III} ions (Ln = Tb, Dy, Ho, Er) are approximately 1 Å, the smaller commercially-available crown ethers 12-crown-4 and 15-crown-5 (cavity sizes of 1.1-2.1 Å) were chosen for study.



By employing a range of stoichiometric ratios and experimental conditions, a novel family of half-sandwich and sandwich-like complexes have been synthesized. Several of the resulting complexes exhibit slow relaxation of magnetization (**a** and **b**, above), representing the first examples of the exploitation of crown ethers as ligands for the formation of mononuclear single molecule magnets (SMMs).

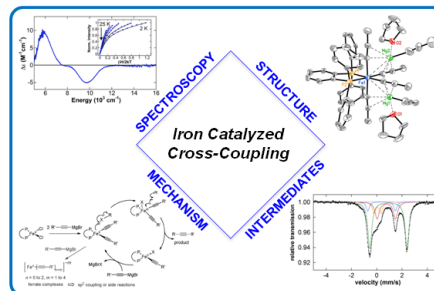
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O27 Elucidating effects of nucleophile variation in (SciOPP)FeX₂ catalyzed Kumada cross-coupling reactions: the case of alkyl-alkynyl couplings

Jared L. Kneebone and Michael L. Neidig*

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The field of iron catalyzed cross-coupling has experienced a renaissance of activity over the last two decades. Significant focus has recently been given to developing methodologies employing bisphosphines as additives in catalysis or incorporating these molecules as ligands in well-defined ferrous precatalysts. The effective usage of such reagents has been documented in a number of Suzuki-Miyaura,¹ Kumada,² and Negishi³ couplings, and studies have examined reactivity trends among bisphosphine additives/supporting ligands. Despite this progress, thorough examinations of the consequences that result *in situ* from varying the nature of the nucleophilic coupling partner have not yet been undertaken. Through the application of a rigorous multi-technique approach involving inorganic spectroscopic methods such as electron paramagnetic resonance, magnetic circular dichroism, and ⁵⁷Fe Mössbauer spectroscopy, molecular-level insight into the nature of the iron-based species and intermediates that form in solution under catalytically relevant reaction conditions can be obtained. A very striking observation is how *in situ* speciation and reactivity can differ greatly between systems that use nucleophiles bearing no β-hydrogens. An expansion upon the methodology used along with interesting consequences accompanying the variation of nucleophile from aryl to alkynyl within (SciOPP)FeX₂ catalyzed Kumada couplings will be discussed.



References: (1) Hatakeyama, T.; Nakamura, M.; et al. *J. Am. Chem. Soc.* **2010**, *132*, 10674. (2) Hatakeyama, T.; Nakamura, M.; et al. *Chem. Lett.* 2011, *40*, 1030. (3) Adams, C.J.; Bedford, R.B.; et al. *J. Am. Chem. Soc.* **2012**, *134*, 10333.

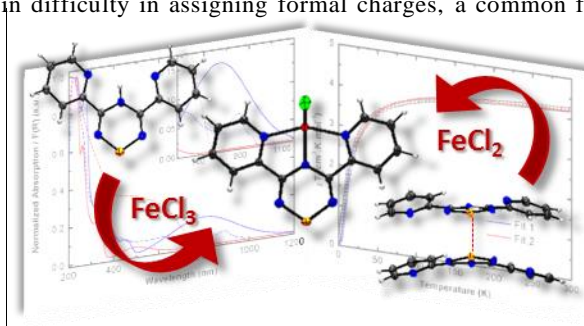
Notes

O28 A strategy to create a class III mixed-valence complex via a non-innocent terpyridine structural mimic

Katie L. M. Harriman, Alicea A. Leitch, Fatemah Habib, Jaclyn L. Brusso,* and Muralee Murugesu*

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A mixed-valence complex exhibiting class III delocalization was prepared from 3,5-bis(2-pyridyl)-1,2,4,6-thiatriazinyl (**Py₂TTA**[•]), an inherently redox active pincer-type ligand, coordinated to iron (**Fe(Py₂TTA)Cl₂** (**1**)). Complex **1** can be prepared *via* two routes, either from the reaction of the neutral radical with FeCl₂ or by treatment of the anionic ligand (**Py₂TTA**⁻) with FeCl₃, demonstrating its unique redox behaviour. Electrochemical studies, solution absorption and solid state diffuse reflectance measurements, X-ray crystallography, and magnetic measurements provide evidence for a **Py₂TTA** neutral radical coordinated Fe (II) complex; however, strong electronic interactions between the redox active ligand and metal leads to delocalization of electron density between the redox active centres. This is supported by DFT calculations, X-ray crystallography, and Mössbauer spectroscopy, and results in difficulty in assigning formal charges, a common feature in class III mixed-valence compounds.



Notes

O29

Titanocene-based Catalysts for the Dehydrocoupling/Dehydrogenation of Amine-Boranes

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Catalytic dehydrocoupling/dehydrogenation of amine-boranes has become a field of intense interest and rapid growth; largely driven by potential applications in hydrogen storage, transfer hydrogenations, and synthesis of novel inorganic polymers. Consequently, a wide variety of catalysts systems have been developed to promote this reaction, with the majority based on late transition metals. Our group has previously reported that first-row Group 4 metallocene [Cp₂Ti] is an efficient homogeneous catalyst for the dehydrogenation of secondary amine-borane adduct Me₂NH•BH₃. Prior mechanistic understanding of this reaction centered around the interplay of Ti intermediates in the +2 and +4 oxidation states.

Our group had previously reported the isolation of several analogous paramagnetic Ti^{III} species as potential intermediates in the catalytic dehydrogenation process. We report the synthesis of several new Ti^{III} species, and report their catalytic activity for the dehydrocoupling of Me₂NH•BH₃ and dehydrogenation of *i*Pr₂NH•BH₃. Our results reinforce that paramagnetic Ti^{III} species play a key catalytic role in the dehydrogenation chemistry. Moreover, we have recently found that modifications to the ligand framework can have drastic effects on catalyst performance. For example, several new variants of our titanocene-based catalysts display not only a ten-fold increase in activity for the dehydrocoupling of secondary amine-boranes, but are also highly active as dehydropolymerization catalysts for primary amine-boranes; the first example of early transition metal amine-borane polymerization catalysts.

Notes

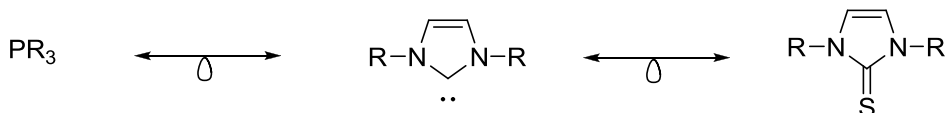
O30

Synthesis and characterization of new half sandwich ruthenium silyl complexes

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Recently, we discovered unusual chemoselective hydrosilylation of nitriles and pyridines catalysed by the half sandwich complex of ruthenium, $[\text{Cp}(\text{iPr}_3\text{P})\text{Ru}(\text{NCCH}_3)_2]^+$ [1,2]. Given the isolobal analogy between N-heterocyclic carbene (NHC), phosphine, and thiourea-based ligands (Scheme 1), we became interested in investigating the chemistry of isolobal analogues of complex $[\text{Cp}(\text{iPr}_3\text{P})\text{Ru}(\text{NCCH}_3)_2]^+$ supported by NHC and ligands. Here we report the syntheses and characterization of a series of silyl and silane complexes of ruthenium supported by these ligands platforms and the comparison with their phosphine-supported analogues



Scheme 1

References: [1] Nikonov G.I., et al, *Angew. Chem. Int. Ed.* **2010**, *49*, 7553. [2] Nikonov G.I. et al, *J. Am. Chem. Soc.* **2010**, *132*, 5950.

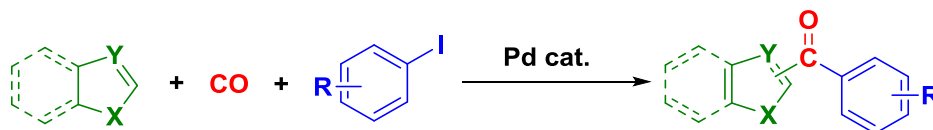
Notes

O31 Palladium-Catalyzed Carbonylative C-H Functionalization of Heterocycles

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The palladium catalyzed C-H functionalization of arenes has become an important new approach in synthetic chemistry. Relative to classical cross coupling reactions, the direct functionalization of C-H bonds does not require stoichiometric organometallic reagents and/or pre-activated compounds, leading to greater efficiency, atom economy, and minimizing waste. While many transition metal catalyzed C-H arylation, alkylation, alkynylation, alkenylation reactions of arenes and heteroarenes have been developed, transition metal catalyzed carbonylative C-H functionalizations have not been extensively studied, presumably due to the inhibitory effect of CO on C-H activation. We describe here how the influence of ligands can be exploited to develop a general approach to carbonylative C-H functionalization, and allow, overall, palladium catalyzed carbonylative coupling of various aryl halides and heterocycles. The details of this reaction, catalyst development, mechanism and substrate scope will be discussed.



Notes

O32

The Destructive Interaction of Dirhodium (II) Tetraacetate and Human Metallothionein

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Organometallic drugs are widely used in treatments against cancer and other diseases. Because human physiological chemistry is quite adept at detoxifying metals, treatment with metal-based complexes can be ineffective, leading to drug resistance. Metallothioneins (MT) are a ubiquitous class of cysteine-rich proteins which primarily store Zn^{2+} and detoxify Cd^{2+} , but are also known to bind a wide variety of other metals. As a heavy metal scavenger and reliever of oxidative stress particularly through toxic metal effects, metallothioneins bind many multivalent metals indiscriminately by forming cysteine thiolate-metal (RSH-M) bonds. The facility of metallothioneins to casually scavenge metals ions will affect the desired metabolic interactions of such metallodrugs. This presentation outlines data from electrospray ionization mass spectrometry that indicates evidence that MT interacts with rhodium-based tetracarboxylates $[(RCOO)_4L_2Rh_2(II)]$, a potential anti-tumour compound.

Notes

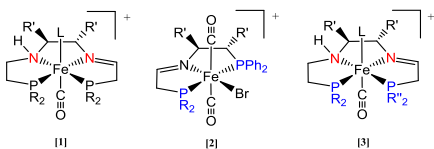
O33

Reduction of Ketones using Fe(II)(P-NH-N-P') Catalysts

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samanthaam.smith@mail.utoronto.ca

The catalytic asymmetric hydrogenation (AH) of unsaturated substrates is a challenging transformation in homogeneous. Usually catalysts based on ruthenium, rhodium, iridium and palladium with expensive chiral ligands are used to provide valuable enantiomerically pure products for use in the pharmaceutical, fragrance and flavor industries.ⁱ It is highly desirable to develop efficient, inexpensive, and non-toxic catalysts for this reaction and it is a long-standing goal in industry and the scientific community to use non-precious, abundant metals such as iron to achieve this.



Our third generation iron catalyst [1] has unsymmetrical amine(imine) moieties (P-NH-N-P) and shows high stereoselectivity and activity surpassing that of precious metal catalysts.ⁱⁱ Very recently, we reported the synthesis of an Fe(II)(P-N-P') catalyst [2] for the AH of ketones, and found that the most active system had a pincer ligand with unsymmetrical phosphines.ⁱⁱⁱ These results indicate that catalyst improvement can be achieved by making small

modifications to the ligand. Given our success using unsymmetrical amines and phosphines in these iron catalysts, we incorporated both into a tetradentate P-NH-N-P' system [3]. This was achieved by using a modular metal-assisted template approach developed in our lab. New complexes have been synthesized with varying steric and electronic properties, one of which gives higher %ee for the reduction of acetophenone to 1-phenylethanol than our previous catalysts.

References: ⁱ R. H. Morris, *Chem. Soc. Rev.* **2009**, 8, 2282-2291; ⁱⁱ W. Zuo, A. J. Lough, Y. F. Li, R. H. Morris, *Science* **2013**, 342, 1080-1083; ⁱⁱⁱ P. O. Lagaditis, P. E. Sues, J. F. Sonnenberg, K. Y. Wan, A. J. Lough, R. H. Morris, *J. Am. Chem. Soc.* **2014**, 136, 1367-1380

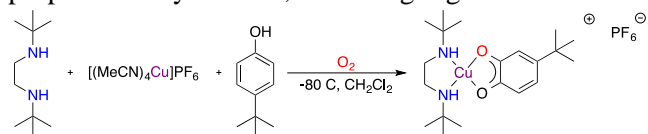
Notes

O34 Mechanism of a Cu-Catalyzed Phenolic Oxygenation

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The copper-catalyzed aerobic oxygenation of phenols into *ortho*-quinones is a powerful synthetic method that mimics the oxygenation of tyrosine by the Cu-containing enzyme tyrosinase in the first step of melanogenesis (formation of melanin pigments in many biological systems). Despite 50 years of research, a truly catalytic system was reported only in 2014 by our collaborator JP Lumb [1]. The efficiency of this reaction allows for an in-depth study of the mechanism of O₂ activation and oxygen-atom-transfer. We have identified a Cu(II)-semiquinone intermediate and here report a mechanistic study of its formation using low-temperature stopped-flow kinetics and control experiments. Our mechanistic proposal accounts for the selectivity towards *ortho*-oxygenation during turnover and is similar to the one proposed for tyrosinase, which highlights the biomimetic nature of this reaction.



DBED

[1] Esguerra, K. V. N.; Fall, Y.; and Lumb, J. P. *Angew. Chem., Int. Ed.* **2014**, 53, 5877.

Notes

O35 What causes isomerization during olefin metathesis?

Carolyn S. Higman, Anabel Lanterna, M. Luisa Marin, Juan C. Scaiano and, Deryn E. Fogg*

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Isomerization is a common, unwanted side-reaction in olefin metathesis [1], attributed to catalyst degradation products. NMR analysis of metathesis reactions promoted by **GII** (Chart 1) have revealed formation of ruthenium hydrides, including **Ru-1** and **Ru-2** (Chart 1). While the latter complexes have been widely regarded as probable culprits [2-3], we recently demonstrated [4] that neither is kinetically competent to account for the levels of isomerization observed. Importantly, however, most studies to date have relied solely on NMR analysis to identify the ruthenium decomposition products. We hypothesized that NMR-silent impurities might be significant contributors to catalyst decomposition, and to unintended isomerization pathways. Here we demonstrate that such contaminants are indeed present. We show that they are formed both during catalyst synthesis, and metathesis. The nature of these species will be discussed, as well as their impact on isomerization during metathesis reactions.

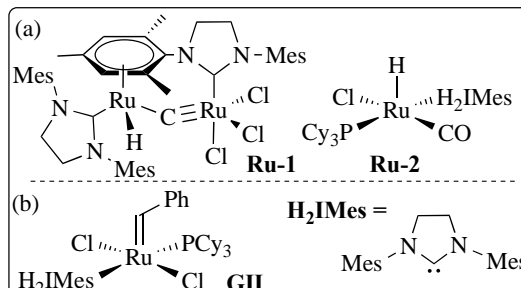


Chart 1. (a) Hydrides from decomposition. (b) Second-generation Grubbs catalyst (GII).

[1] B.J. van Lierop, J.A.M. Lummiss, D.E. Fogg, Ring-Closing Metathesis: A How-To Guide. In “Olefin Metathesis: Theory and Practice”; Grela, K., Ed.; Wiley: Hoboken, NJ, 2014; pp 85–152. [2] S. H. Hong, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2004**, *126*, 7414–7415. [3] J. R. Clark, J. R. Griffiths, S. T. Diver, *J. Am. Chem. Soc.* **2013**, *135*, 3327–3330. [4] C.S Higman, L. Plais, and D.E. Fogg, *ChemCatChem* **2013**, *5*, 3548–3551.

Notes

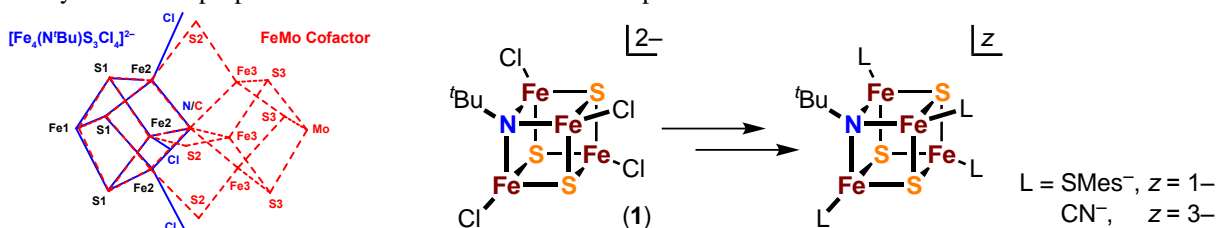
O36

Ligand and Redox Derivatives of a Core Heteroligated Analogue of the Nitrogenase Cofactor

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The cubane cluster $[\text{Fe}_4(\text{N}^t\text{Bu})\text{S}_3\text{Cl}_4]^{2-}$ (**1**) affords a synthetic representation of the $[\text{Fe}_4(\text{C})\text{S}_3]$ subunit of the nitrogenase FeMo cofactor¹, and the study of **1** offers potential opportunities to gain insight into the nature of the biometallocluster.² Toward this end, we have explored the chemistry of the $[\text{Fe}_4(\text{N}^t\text{Bu})\text{S}_3]^{2+}$ core to define general chemical and physical properties of this system and access alternate redox states for comparative spectroscopic study. The oxidized $[\text{Fe}_4(\text{N}^t\text{Bu})\text{S}_3]^{3+}$ core has been stabilized via thiolate-ligated derivatives. The reduced $[\text{Fe}_4(\text{N}^t\text{Bu})\text{S}_3]^+$ core, however, proved chemically inaccessible with the same ligand set despite promising electrochemical behavior, and terminal cyanide ligation was necessary to attain an isolable form of this redox state. The synthesis and properties of these new clusters and their precursors will be discussed.



References: 1. (a) Lee et al., *J. Am. Chem. Soc.* **2010**, *132*, 15884. (b) Lee et al., *Inorg. Chem.* **2012**, *51*, 12891. 2. (a) Lee, Lo, Holm, *Chem. Rev.*, **2014**, *114*, 3579. (b) Lee, DeBeer et al., *Inorg. Chem.* **2014**, *53*, 2591.

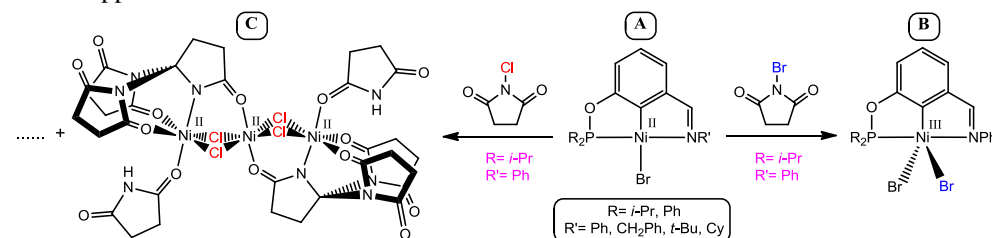
Notes

P1 Synthesis and Oxidation of New POCN_{imine}-Type Pincer Complexes of Nickel

Berline Mougang-Soumé, Francine Belanger-Gariépy and Davit Zargarian*

Department of Chemistry, Université de Montréal, Montréal, Québec, Canada, djanbe@yahoo.fr

Direct, C-H nickelation of the unsymmetrical pincer-type ligands, R-POCN^HN_{imine}R', gave the corresponding Ni(II) complexes (R-POCN_{imine}R')NiBr, **A**. Treating these compounds with various oxidants gave very different results depending on the nature of R and oxidant. For instance, reaction of (*i*-Pr-POCN_{imine}Ph)NiBr with Br₂ or *N*-bromosuccinimide (NBS) gave the desired 17-electron trivalent complex (*i*-Pr-POCN_{imine}Ph)NiBr₂, **B**, whereas oxidation attempts using *N*-chlorosuccinimide gave a complex mixture from which was isolated an unusual trinuclear compound, **C**. Oxidation of (Ph-POCN_{imine}R')NiBr appeared to bring about the desired one-electron oxidation of the Ni(II) center, but the putative trivalent species decompose over time and could not be isolated. This presentation will discuss the characterization of the target complexes and various by-products obtained to illustrate the complexities that appear to be inherent in these oxidation reactions.



P2 N-heterocyclic Carbenes Activation by Triarylborane-phosphonium compound

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N-heterocyclic carbenes (NHCs) are known as robust ligands. The activation NHCs by main group elements with insertion into a C-N bond has been reported recently.¹ Here we report the unusual reactivity of an NHC with a stable triarylborane phosphonium compound under mild condition. The unique reactivity provides a new pathway for NHCs activation. Investigation on the reactivity of NHC adducts with related borane-phosphine compounds has also been examined and the details will be presented.

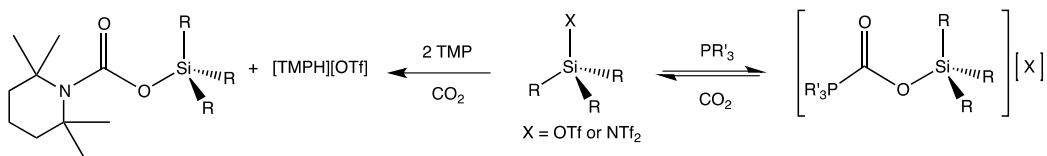
(1) (a) Arrowsmith, M.; Hill, M. S.; Kociok-Köhn, G.; MacDougall, D. J.; Mahon, M. F. *Angew. Chem., Int. Ed.* 2012, *51*, 2098. (b) Schmidt, D.; Berthel, J. H. J.; Pietsch, S.; Radius, U. *Angew. Chem., Int. Ed.* 2012, *51*, 8881. (c) Al-Rafia, S. M. I.; McDonald, R.; Ferguson, M. J.; Rivard, E. *Chem. Eur. J.* 2012, *18*, 13810. (d) Wang, T.; Stephan, D. W. *Chem. Eur. J.* 2014, *20*, 3036.

P3 Four Coordinate Silicon Lewis Acids in the Frustrated Lewis Pair Sequestration of Carbon Dioxide

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Since the industrial revolution, increasing atmospheric carbon dioxide (CO₂) concentrations due to fossil fuel combustion have been a strong contributor to global climate change. As a consequence, research into systems that can sequester or chemically transform CO₂ into value-added species is currently of high interest. Frustrated Lewis Pairs (FLPs) have been shown to capture CO₂¹ and, in some cases, allow for its stoichiometric² or catalytic reduction.³ Although these systems have typically utilized group 13 Lewis acids, there is interest in exploring if similar reactivity can be observed with other main group Lewis acids. Herein, we describe the FLP-type sequestration of CO₂ using four coordinate silicon Lewis acids in the form of R_{4-n}Si(OTf)_n (n= 1, 2) and R₃SiNTf₂. These species are shown to capture CO₂ when paired with trialkyl phosphines, with the strength of binding being dependent on the substituents of the Lewis acid. Different reactivity is observed when a secondary amine, tetramethylpiperidine (TMP), is used as the base, resulting in the irreversible formation of silyl carbamates.



1) C. M. Mömming, E. Otten, G. Kehr, R. Fröhlich, S. Grimme, D. W. Stephan, G. Erker *Angew. Chem. Int. Ed.* **2009**, *48*, 1.

2) G. Ménard, D. W. Stephan, *J. Am. Chem. Soc.* **2010**, *132*, 1796.

3) M.-A. Courtemanche, M.-A. Légaré, L. Maron, F.-G. Fontaine, *J. Am. Chem. Soc.* **2013**, *135*, 9326.

P4 New Green and Blue Phosphorescent Pt(II) Compounds with Improved Thermal Stability

Xiang Wang and Suning Wang

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A new class of brightly phosphorescent Pt(II) compounds that contain an N[^]C-chelate phenyl-1,2,3-triazolyl ligand (ptrz) and an N[^]C-chelate pyridyl-1,2,4-triazolyl ligand (pytrz) in the central core have been achieved. The impact of various substituent groups on phosphorescence of this class of molecules has been examined. These molecules are highly robust and display exceptionally high thermal stability. Bright electrophosphorescent devices with external quantum efficiencies as high as 15.9% have been fabricated.

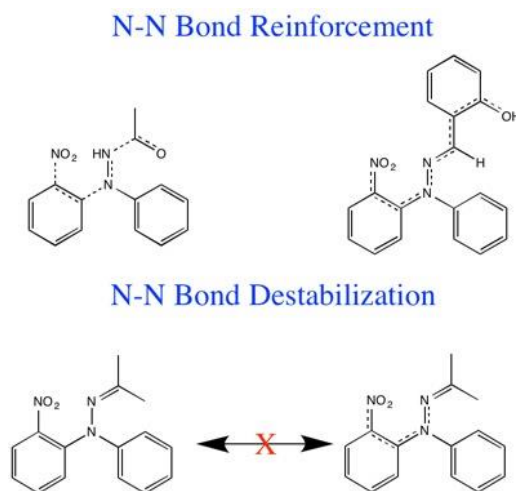
P5

Inductive Effects in Schiff Bases of 1-(2-nitrophenyl)-1-phenyl hydrazine

Joël Poisson, Ian S. Butler, and D. Scott Bohle*

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N,N-diphenylhydrazine derivatives have been used in photovoltaics and as analytical reagents. They are also known to exhibit unique reactivity and certain derivatives have generated some questions in the literature with regard to their conductivity. Due to the lack of their synthetic availability, N,N-diphenylhydrazines containing electron-withdrawing substituents such as –nitro groups remain unexplored. Several derivatives of 1-(2-nitrophenyl)-1-phenylhydrazine with known diphenyl analogues have been prepared and characterized by NMR, IR, ESI-MS and UV-Visible spectroscopy as well as X-ray diffraction. A stabilization of the N-N bond is seen in the solid-state structure of derivatives that allow for π -delocalisation of electron density, whereas electron donating substituents cause an out-of-plane rotation, making π -electron delocalization impossible.



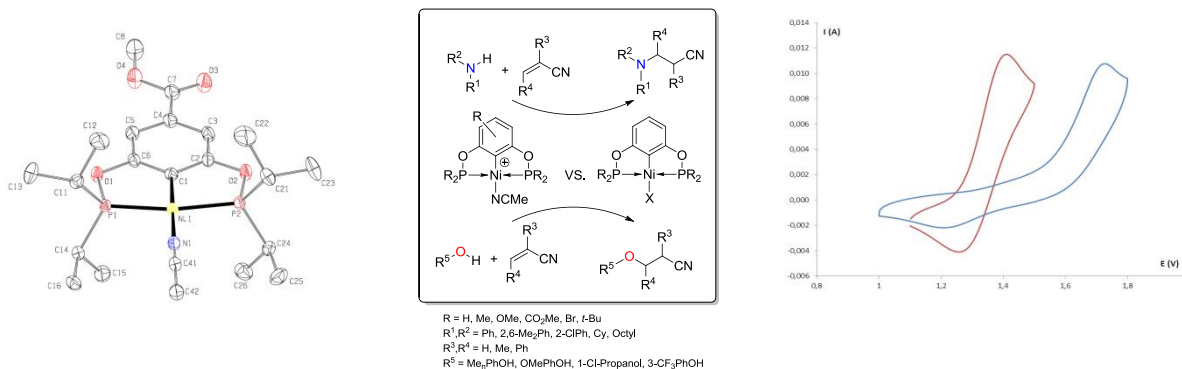
P6

Cationic POCOP nickel complexes: Synthetic, catalytic and mechanistic studies

Sébastien Lapointe, Boris Vabre, and Davit Zargarian*

Université de Montréal, Montréal, QC H3C 3J7, sebastien.lapointe@umontreal.ca

We have prepared a new series of **POCOP-type ligands** and used them to synthesize the cationic nickel complexes $[(R\text{-POCOP}^R)\text{Ni}^{\text{II}}\text{NMe}]^+$. Analysis of these complexes by cyclic voltammetry, IR, UV and NMR spectroscopy, and X-Ray crystallography has allowed us to probe how the Ni(II) center is affected by the electronic and steric effects of the various backbone substituents of the ligand. Furthermore, their catalytic activities toward hydroamination reactions has been studied, and different aspects of the catalytic cycle have been addressed.



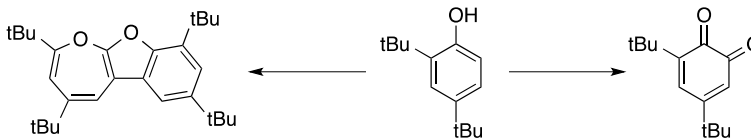
P7

Controlling Selectivity in Catalytic Aerobic Oxygenations of Disubstituted Phenols

Yuxuan Li, Mohammad S. Askari, Xavier Ottenwaelde*

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The aerobic oxidation of phenols into *ortho*-quinones is often accompanied by C-C coupling side-products due to the formation of phenoxy radicals. Metalloenzymes and in particular tyrosinase avoid the formation of side products by confining the oxygen-atom-transfer in the first coordination sphere. Only recently a fully selective oxygenation of disubstituted phenols using a Cu catalyst was reported [1]. Depending on the type of the ligand used, two possible products were observed: *ortho*-quinone or benzoxepine, when the ligand is triethylamine or the bidentate *N,N'*-di-*tert*-butylethylenediamine, respectively (scheme). The purpose of this study, done in collaboration with the Lumb lab at McGill, is to understand the mechanism of oxygenation of 2,4-di-*tert*-butylphenol by identifying intermediates involved in the reaction by UV-Vis spectroscopy and control experiments. We are here presenting our preliminary results.



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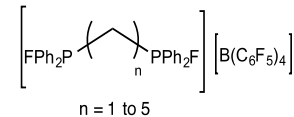
P8

Cooperative Catalysis Using Bifunctional Phosphonium Systems

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Phosphorus is most commonly thought of in its III oxidation state, typically forming Lewis bases. Nevertheless, P(V) compounds, particularly phosphonium cations, are capable of displaying Lewis acidic character. It was recently shown by our group that phosphonium systems, either containing electron withdrawing pentafluorophenyl substituents, $[\text{PF}(\text{C}_6\text{F}_5)_3][\text{B}(\text{C}_6\text{F}_5)_4]$,¹ or possessing dicationic charge, $[(\text{SIMes})\text{PFPh}_2][\text{B}(\text{C}_6\text{F}_5)_4]_2$,² displayed significant Lewis acidity and were capable of catalyzing numerous reactions, such as dehydrocoupling and hydrosilylation.^{1,2,3,4} Herein, we describe the facile synthesis of linked diphosphonium systems. It was observed that by modifying the length of the carbon chain between the phosphonium centers, the Lewis acidity of the system could be tuned to afford different reactivity. The species with shorter carbon linkers displayed greater Lewis acidity and catalyzed various reactions, including hydrodefluorination, ketone reduction, hydrosilylation and dehydrocoupling.



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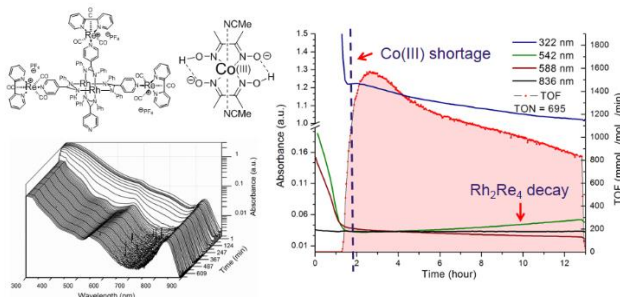
P9

Fate of Rhenium-Rhodium Chromophore Assemblies During Hydrogen Photocatalysis

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In our general objective of forming discrete assemblies of multi-chromophoric units for homogenous solution photocatalysis studies, we use stable rhodium amidinate dimers as structural backbone for polynuclear assemblies.^{1,2} Using this approach, we were able to prepare assemblies of one to four rhenium chromophores. These were tested for hydrogen photocatalysis with a cobalt catalyst. By studying their turn-over rates over time and their spectral signature by UV-vis spectroscopy, various additional observations were made: stability over time, active species implied and possible degradation pathways.



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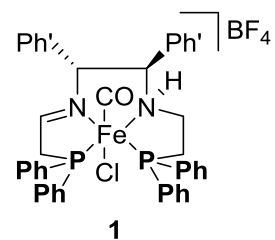
P10

Iron (II) P-NH-N-P Transfer Hydrogenation in Water

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Iron is a cheap and abundant metal which has been shown to be catalytically active for the transfer hydrogenation of ketones and imines in an enantioselective manner when combined with suitably designed ligands (see complex **1**).¹ These iron catalysts can be used as a substitute for rare and expensive late-transition metals such as rhodium and ruthenium currently used by the pharmaceutical, fragrance, and flavour industries.² In our current batch reaction process performed in isopropanol, equilibrium between the ketone and product alcohol is quickly reached at 80% conversion. This project investigates the catalyst's reactivity using more economic and green reaction conditions, employing water as the solvent and sodium formate as the hydride source. During transfer hydrogenation, the sodium formate converts into carbon dioxide which is removed from the reaction flask due to the incoming argon. This shifts the equilibrium to allow a more complete conversion to the desired alcohol.³ After the optimization of the reaction conditions including temperature, stirring rate, substrate:catalyst ratio, sodium formate:catalyst ratio, as well as the effects of various phase-transfer catalysts, the activity of this system will be compared to the activity of the current isopropanol batch reaction with various ketone substrates.



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P11 XAS and Optical Study of an Interfacial Al₂O₃ Coating: Enhancement of Refractive Index Sensitivity in Optical Fibers for CVD Monitoring

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Tilted fiber Bragg gratings (TFBGs) are refractometry-based sensor platforms that have been employed herein as devices for the real-time monitoring of chemical vapour deposition (CVD) in the near-infrared range (NIR). The core-guided light launched within the TFBG core is back-reflected off a gold mirror sputtered onto the fiber-end and is scattered out into the cladding where it can interact with a nucleating thin film. Evanescent fields of the growing gold nanostructures behave differently depending on the polarization state of the core-guided light interrogating the growing film, therefore the resulting spectral profile is typically decomposed into two separate peak families for the orthogonal S- and P-polarizations. Wavelength shifts and attenuation profiles generated from gold films in the thickness regime of 5-100 nm are typically degenerate for deposition directly onto the TFBG. However, a polarization-dependence can be imposed by adding a thin dielectric pre-coating onto the TFBG prior to using the device for CVD monitoring of the ultrathin gold films. It is found that addition of this Al₂O₃ interface enhances the sensitivity of the S-polarized (i.e. the in-plane polarization component) peak family in the NIR range to the deposition of ultrathin gold films and renders the films optically anisotropic. It is shown herein that addition of the metal oxide coating can increase the peak-to-peak wavelength separation ($\Delta\lambda_{S-P}$) between orthogonal polarization modes as well as allow for easy resonance tracking during deposition. This is also the first reporting of anisotropic gold films generated from this particular gold(I) iminopyrrolidinate precursor and CVD process. Using a battery of x-ray techniques, the local fine structure of the gold films deposited directly on the TFBG is compared to gold films of similar thicknesses deposited onto the Al₂O₃ pre-coated TFBG and Si(100) witness slides.

P12 Aerobic Oxidations Mediated by Ni(NHC) Complexes: Investigating the Role of a Pendant H-bonding Group

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Molecular oxygen (O₂) represents the most ideal "green" oxidant for the large-scale oxidation of organic compounds, due to its inexpensive and environmentally benign characteristics.¹ However, a number of challenges remain for its use in the fine chemical and pharmaceutical industry, including the development of highly selective transformations. NiCl(allyl)(NHC) complexes have been shown to react with O₂ to promote the oxidation of the allylic ligand.² However, due to poor selectivity between the ketone and aldehyde products, and the process being non-catalytic, this system is not ideal. Several recent reports show that a H-bond donor in the second-coordination sphere can stabilize reactive O₂-derived intermediates. This can lead to high selectivity in oxidation reactions.³ We have targeted a NiCl(allyl)(NHC) complex containing a pendant 2° amine arm on the NHC ligand to act as a H-bond donor group. Preliminary reactivity studies indicate that the complexes are active for aerobic oxidation, and product distribution is different than that of previous systems.

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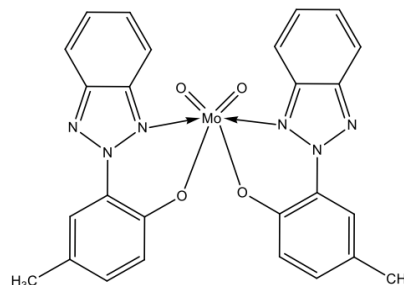
P13

Synthesis and Anticancer Activity of a Family of 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole-based Metal Complexes (Pt, Pd, Ru, Rh, Ag, Mo, Zn)

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New complexes based on the 2-(2'-hydroxy-5'-methylphenyl)-benzotriazole (Hhmbt) ligand, notably [Zn(hmbt)₂(H₂O)₂], [Zn(hmbt)(OAc)(H₂O)₂], [Pd(hmbt)(H₂O)Cl], [Pd(hmbt)₂], [M(PPh₃)(hmbt)Cl], [M(L)(hmbt)]Cl (M(II) = Pd, Pt; L = bpy, phen), [Ag₂(hmbt)₂], [Ag(phen)(hmbt)], [Ag(PPh₃)(hmbt)], [Rh(hmbt)₂(H₂O)₂]Cl, [Ru(hmbt)₂(H₂O)₂], [Ru(PPh₃)(hmbt)₂]Cl and *cis*-[MoO₂(hmbt)₂] were synthesized. They were structurally and spectroscopically characterized on the basis of elemental analyses, IR, NMR (¹H, ¹³C{¹H}, ³¹P{¹H}), UV-Vis, ESI-MS, as well as thermal and molar conductivity measurements. 2-(2'-



Hydroxy-5'-methylphenyl)-benzotriazole behaves as a monoanionic bidentate ligand through the deprotonated of phenolic oxygen and imine nitrogen atoms. The cytotoxicity of Hhmbt and some complexes was tested against human breast cancer (MDA-MB231) and human ovarian cancer (OVCAR-8) cell lines. [Ag(hmpbt)(PPh₃)], [Rh(hmbt)₂(H₂O)₂]Cl, [Pt(phen)(hmbt)]Cl and [Pd(phen)(hmbt)]Cl were found to exhibit the highest cancer cell growth inhibitory activity with mean IC₅₀ values of 1.37, 7.52, 5.24 and 4.85 μM (MDA-MB231) and 1.75, 8.50, 3.00 and 2.99 μM (OVACAR-8), respectively. This study revealed that hmbt-based metal complexes hold promise for the development of novel anticancer therapeutics.

P14

Azadipyrrromethene Cyclometallation on Ru^{II} Complexes: Sensitizers with Extended NIR Absorption for Solar Energy Conversion Applications

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As analogues of porphyrinoids and dipyrromethene families of dye, aza-dipyrrromethene (ADPM) derivatives exhibit exciting photophysical properties. Their high absorbance (ϵ up to 100 000 M⁻¹cm⁻¹) and strong near-IR (NIR) luminescence are especially interesting in the context of designing new light-harvesting materials.¹⁻⁵ In the present study, we introduce the first examples of ADPM cyclometallation on neutral ruthenium complexes bearing either bipyridine, phenanthroline or terpyridine and demonstrate the latter support further chemical modifications toward the achievement of new photosensitizers for dye-sensitized solar cells (DSSC). Photophysical characterization and modelization studies will be presented to assess the origin of the bathochromic shift in the NIR region observed in the absorption spectra. Electrochemistry of the complexes will also be discussed in the perspective of optimization toward the specific energetic levels required for photovoltaic applications such as DSSC and OPV.

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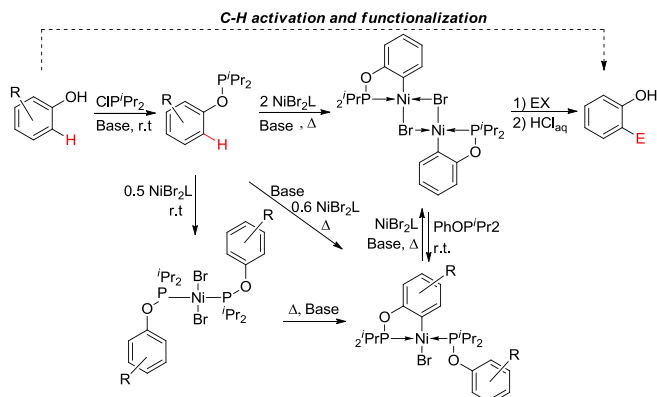
P15

Ortho-Derivatization of Phenols Through C-H Nickelation via New Orthonickelated Complexes

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Cyclometallated complexes have attracted much interest because of their remarkable activities in a wide range of catalytic processes,^[1] including C-H functionalization chemistry.^[2] Curiously, few examples exist of cyclometallated nickel compounds even though such species should have great potential in catalysis owing to the established reactivities and abundance of nickel.



This presentation will report the synthesis and characterization of new Ni(II)-phospinite compounds featuring a cyclometallated moiety. We will discuss the mechanism of C-H nickelation step and the subsequent reaction of the cyclonickelated complex with electrophiles. The latter reactions result in the formation of C_{sp2}-C_{sp3}, C_{sp2}-C(O)Me and C_{sp2}-Si bonds, thus providing an efficient methodology for functionalization of phenols.

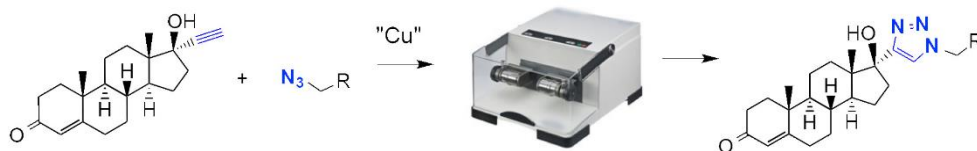
P16

Cu-Catalyzed Alkyne Azide Click Mechanochemistry: Liquid-Assisted Solid-State Reactions in a Ball Mill

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Although liquid-phase Cu-catalyzed alkyne azide cycloaddition (CuAAC) click reactions have been thoroughly examined, solid-phase CuAAC reactions have not yet been widely explored. In this presentation, we report CuAAC mechanochemical reactions (CuAACM) that are performed between solid-state alkynes and azides in a ball mill. In such systems, high conversions of the reactants into the products can be achieved after short grinding times, using a Cu catalyst and small amounts of base and solvent (liquid-assisted grinding, LAG). CuAACM reactions are promising for large-scale applications due to their short reaction times and their minimal usage of solvent or facilitating reagent. While it is known that a great amount of large substrates used in CuAAC reactions are not soluble in environmental-friendly solvents, and that complex molecules sometimes require long reaction times or tedious purification steps, ball milling appears to be a method of choice for the synthesis of pharmaceuticals and other biologically relevant molecules from solid-state substrates.



P17 X-ray single crystal structure of *mono*- and *ortho*- Bi(OH)CrO₄, synthesis and thermal behavior towards reverse combustion

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A great variety of metal mixed oxides and molecular compounds have been prepared and studied towards photochemical reactions for water splitting in mild conditions.¹ In this work we prepared and characterized by x-ray single crystal (Figure 1), TGA, FTIR and EA two forms of Bi(OH)CrO₄. Their activity at different pH on reverse combustion was evaluated. The structural differences of the bismuth environment cause an unusual thermal stability in *mono*- specie and an interesting lability in the *ortho*- isomer. In both cases upon heating, molecular oxygen is generated but only the *ortho*- isomer can be recovered under hydrothermal treatment in good yield.

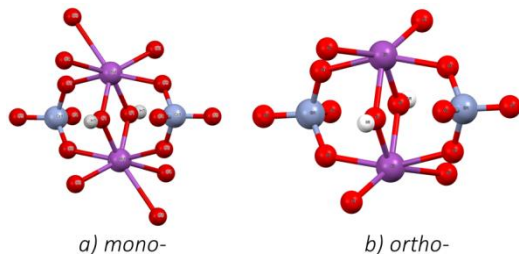


Figure 1. Crystal structures of Bi(OH)CrO₄

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P18 Supramolecular chemistry of iso-tellurazole N-oxides

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Lucia M. Lee, Ignacio Vargas-Baca*

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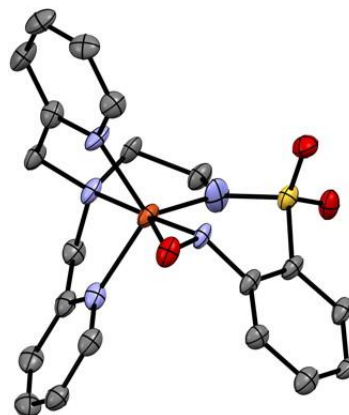
Molecules of the title compounds readily aggregate through strong Te-O secondary bonding interactions. In this way, a variety of supramolecular structures have been isolated and characterized by single-crystal X-ray diffraction, including polymers and macrocyclic tetra- and hexamers. Spectroscopic studies have demonstrated the existence of the cyclic structures in solution. These self-assembled macrocyclic super-molecules can act as ligands in coordination complexes and as fullerene receptors.

P19 Redox Chemistry of Nitrogen-Containing Functional Groups Near a Copper Centre

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We are studying how a metal ion influences the conversion between NH₂, NHOH, NO and NO₂ moieties. The onus is that these transformations involve oxygen-atom transfers (e.g. NH₂ to NHOH or NO to NO₂), a reaction of tremendous importance but that is not yet fully understood. In the present work, complexation of a Cu(II) source with tetradentate ligand having a pendant NHOH group results in the formation of a neutral 5-coordinated Cu-nitroso complex. X-ray crystallography supports a Cu(I)-(arylnitroso) assignment. However, NMR is consistent with a Cu(II)-(arylnitrosyl anion) formulation. This valence isomerism is indicative of the propensity of a metal ion to influence the NO bond and thus its reactivity. We will present our discussion on this intriguing species as well as its role in oxygen-atom transfer reactions.



P20 Supramolecular Photo-chemistry : Ru photo-sensitizers and Co evolving hydrogen catalyst

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In the field of molecular artificial photosynthesis, absorption and emission of light, energy transfer, charge separation, electronic transfer, electrochemical potentials, and catalytic activity can be tuned by the chemical and structural composition of the molecules. In 1983, the reduction part of water splitting was illustrated by Lehn: in DMF, a system with a sacrificial electron donor such as triethanolamine, a photosensitizer Ru(bipy)₃²⁺ and 'cobaloxime' catalyst produces some hydrogen under blue light irradiation (450 nm) [1]. The function of the oxime is known to mediate protons to the Co catalyst [2]. In this following work, new heteroleptic and homoleptic photosensitizers [Ru(L)_x(bipy)_{3-x}]²⁺ (L=diphenyl-[2,2'-bipyridine]-4,4'-dicarboxamide) are investigated in different conditions (various wavelengths of irradiation, various concentrations, organic or aqueous media). Additionally, the activity of new cobalt complexes with different functions as imine, oxime, hydrazone is studied for hydrogen evolving capacity. The choice of various substituents on the ligand affords steric and electronic tunability. The monitoring of activity by U.V - visible absorption and gas chromatography displays the evolution of molecular species, rate of mechanism and the stability of the systems.

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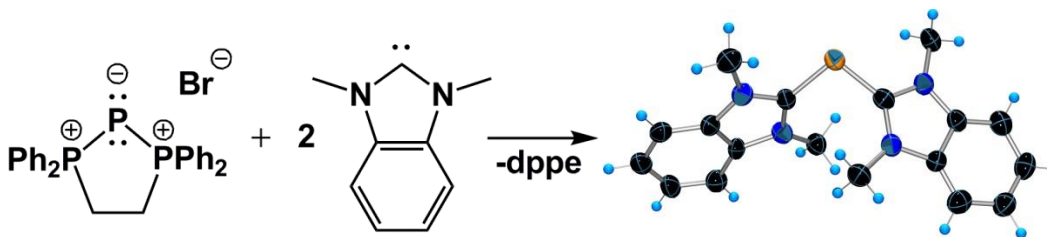
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P21 **N-Heterocyclic Carbene Adducts of P(I) Cations: Synthesis, Properties and Reactivity**

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The discovery of phosphamethine cyanine dyes was a landmark for main group and phosphorus chemistry in that they were among the first cases of molecules containing dicoordinate phosphorus centers and they were the first salts in which P-C π bonding had been observed at ambient temperature.¹ Recently, our group has discovered a new route to this class of compounds through a more convenient synthetic pathway: the reaction of carbenes with readily prepared triphosphenium precursors.² This procedure has been successful for a variety of carbenes and has granted access to further chemistry involving these heavy allene analogues.³ This poster presents the synthesis, reactivity and the spectroscopic, electronic and structural properties of a series of these dyes and their coordination and oxidation products.

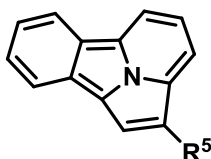


P22 **Synthesis and Properties of Highly Fluorescent Mes₂B-Funtionlized Indolizino[3,4,5-ab]isoindoles**

Dengtao Yang,¹ Kang Yang¹ and Suning Wang*¹

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Triarylboranes have recently emerged as an important class of molecules with many applications in materials sciences. The empty p_π orbital on the boron center makes these compounds excellent electron acceptors, which enables their use in such diverse fields as nonlinear optics, anion sensing, hydrogen activation and storage, and as emitters and electron transport materials in organic light-emitting diodes (OLEDs).^{1,2} Recently our group has discovered several highly blue and green fluorescent boron-containing pyrrolopyridazines, which are expected to be good chromophores for highly efficient OLEDs.



**R⁵ = Dimesitylboron,
o-dimesitylboronphenyl,
p-dimesitylboronphenyl**

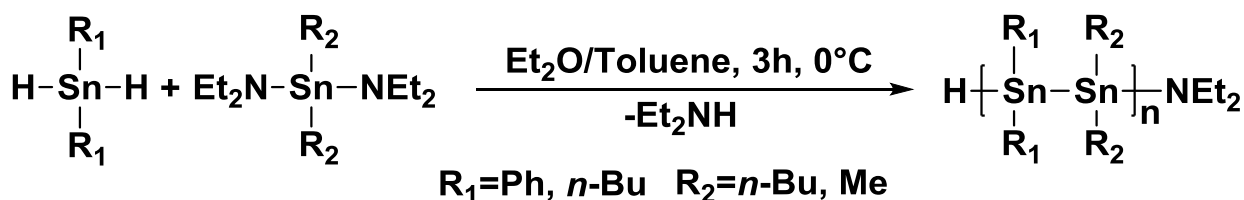
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P23 Preparation of Alternating Polystannanes

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Polystannanes have been synthesized by a multitude of reductive coupling routes; however for the most part these polymers have been limited to dialkyl and diaryl homopolymers. Our interest with polystannanes is to utilize condensation polymerization to synthesize alternating polymers where each neighbouring tin center has different R groups. With this in mind, we first synthesized alternating trimers that act as model systems for the larger alternating polymers. This established observable trends in structure, chemical shift information and spectrochemical trends. This approach allows for mix and match of polymers types and control of side group functionality. In this manner, we were able to add solubilizing side groups with less soluble substituents and electron donating functionality beside electron withdrawing ones. We characterized these new polymers and trimers using NMR (¹H, ¹¹⁹Sn and ¹³C), UV-Vis, GPC, DSC, MS, DFT and EA.



P24 Chemical Vapour Deposition of Gold: Morphology Control from Ligand Design

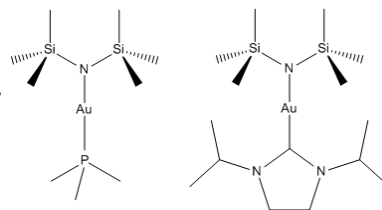
Matthew B. E. Griffiths¹, Sara E. Koponen¹, Jennifer F. McLeod¹, David J. Mandia¹, Jason P. Coyle¹, Javier B. Giorgi², and Seàn T. Barry¹

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Chemical vapour deposition (CVD) is a widely used process for thin film deposition of many different materials. Applications in microelectronics have curbed research and development of CVD towards uniform, conformal, and continuous films when considering conductors or insulators. However, it is possible to target different film morphologies depending on the material to be deposited. The addition of catalytic metals and molecular chemisorption initiators can alter the method of chemisorption and specify the shape of the growing film. VLS-type growth has been employed in numerous systems for the growth of nanowires, rods, and more complex structures thereof.

It is also possible to control surface chemistry via design of the chemical precursor, for example by incorporating surface-reactive ligands. Hexamethyldisilazane (HMDS) is well-known to passivate silanol surface species as a free amine. Similar passivating reactivity has been observed in an [Au(HMDS)]₄ species upon reaction with high-surface area silica in a solution-phase synthesis of Si-supported gold nanoparticles.

Synthesis of two gold(I) species each bearing an HMDS ligand resulted in volatile compounds suitable for CVD studies. The HMDS ligand, as well as the coordinative ligand in each case is observed to influence the morphology, crystallinity, and coverage of the deposited gold films. The first compound, bearing a tertiary phosphine ligand, deposits only sub-20nm diameter nanoparticles, which appear to saturate in size, regardless of total precursor flux. The second compound, bearing an NHC ligand, deposits gold crystallites in three morphologies: nanoparticles, nanowires, and microflakes. The NHC ligand is thought to play the role of surfactant during this process.



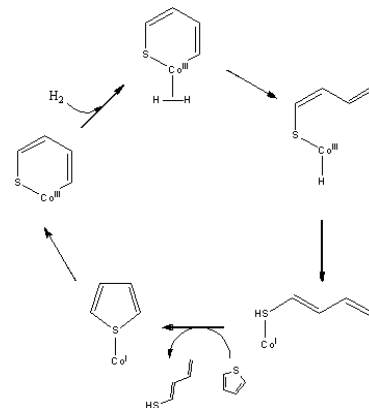
P25

A Cobalt(I) Half-Sandwich Pincer Complex for Homogeneous Hydrodesulfurization

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Hydrodesulfurization (HDS) is a process which allows for the catalytic removal of organosulfur compounds using hydrogen as a feedstock. This process is critical to the oil and gas industry, as sulfur-containing compounds are undesirable. When burned, they produce SO₂, a toxic gas which is a primary contributor to acid rain. Lower grade deposits of crude oil which are becoming more extensively used contain higher concentrations of refractory aromatic sulfur heterocycles (thiophenes). Such compounds are significantly more difficult to remove via hydrodesulfurization, making new techniques for "deep" hydrodesulfurization necessary.^[1,2] The most common industrial method for HDS involves the use of heterogeneous MoS₂ based catalysts doped with cobalt under high pressure and temperature conditions, but the activities of these catalysts are limited to the more easily desulfurized (non-aromatic) substrates.^[3] Small molecule catalysts based on inexpensive first row transition metals like cobalt could provide low cost alternatives with greater deep HDS activity. DFT and preliminary experimental evidence suggest that a cobalt(I) half-sandwich complex has the potential to act as a highly efficient homogeneous catalyst for the HDS process.



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P26

Dynamics of Optical Self-trapping in Polymeric Matrices Containing Tris(2,2'-bipyridine)ruthenium(II)

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The photophysical properties of tris(2,2'-bipyridine)ruthenium(II), [Ru(bpy)₃]²⁺, complexes have shown considerable promise in applications ranging from light harvesting to optical modulation. These luminescent complexes can also serve as photocatalysts due to the redox properties of their excited states. Here, we report that photochemical systems based on [Ru(bpy)₃]²⁺ can elicit the self-trapping of laser light, which results in the self-inscription of cylindrical waveguides.

Our experiments consisted of launching a continuous-wave, visible laser beam ($\lambda = 532$ nm) in two (separate) photochemical systems based on [Ru(bpy)₃]²⁺ dispersed in a Pluronic F-127 hydrogel. Careful monitoring of the spatial intensity profile of the optical field revealed that the natural divergence of the beam was strongly suppressed due to an increase in the refractive index along its propagation path. The result was a tightly trapped beam, which propagated over long distances (\gg Rayleigh range) without broadening or losing intensity. The refractive index increase in the first photochemical system originated from the photochemical oxidation of iodide, which was deliberately introduced in the system. We found that self-trapping occurred, albeit more slowly, even in the absence of iodide. Here, the mechanism can be attributed to singlet oxygen-induced photo-oxidation and cross-linking of the polymer network. The critical role of [Ru(bpy)₃]²⁺ in eliciting and governing the dynamics of self-trapping was confirmed by contrasting the Stern-Volmer plots obtained from both the self-trapping experiments and measurements of fluorescence in the presence of methyl viologen quencher.

P27 On the use of molecular radial architectures for the design of magnetic and photophysical devices

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Dendrimeric architectures allow a fine topological control of functional molecular structures. Dendrimers based on the coordination of metallic centers enable a fine-tuning of the properties by carefully choosing the monometallic complexes. The aim of this work is to evaluate the advantages of a radial structure compared to the building blocks themselves. Two main fields are concerned for this work:

- *Magnetism*: by increasing the generation number of spin carriers, the total spin of the molecule increases exponentially. If the assembly presents a high anisotropy, Single Molecule Magnet properties may be observed. In addition, having an isotropic or weakly anisotropic architecture might lead to important magneto-caloric effects.

- *Artificial Photosynthesis*: A combination of photochromic complexes absorbing at different wavelengths and capable of energy transfer are able to mimic the antenna effect of natural systems. Transferring electrons from the photosensitizer to a catalyst enables water splitting and hydrogen formation. The radial architecture allows all of the actors to be in close proximity on the same molecule thus enabling higher efficiency in energy and electron transfer reactions.

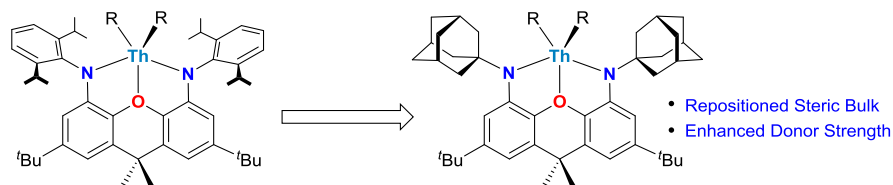
To conclude, perspectives on multi functional materials will also be discussed.

P28 Thermally Robust Organothorium(IV) Complexes of a Rigid NON-Donor Pincer Ligand

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The newly flourishing field of non-carbocyclic organoactinide chemistry is being driven forward through the development of new ligand systems of enormous structural and electronic variety. As a result, exciting and highly sought-after molecular species have become accessible, and new chemical transformations are steadily being uncovered. Our group has developed extremely rigid, tridentate NON- and NSN-pincer ligands for the support of thermally robust organothorium(IV) species, as well as uranium chloro complexes in various oxidation states, and uranium(IV) alkyl complexes. The modularity of our ligand construction has facilitated our interest in exploring modified NON-donor ligands, and recently we have prepared a 4,5-bis(1-adamantylamido)xanthene derivative to probe the effect of enhanced donor-ability and repositioned steric bulk on the corresponding organothorium(IV) chemistry. This contribution will aim to highlight recent developments in this area including halide, alkyl, and allyl complex synthesis, and spectroscopic and crystallographic characterization.



P29 Saturated vs. Aromatic N-Heterocyclic Carbenes in Olefin Metathesis

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The dominant catalysts in current use for olefin metathesis are the so-called “second-generation” ruthenium catalysts bearing an *N*-heterocyclic carbene (NHC) ligand.¹ By far most widely used are the Grubbs and Hoveyda catalysts in which the NHC ligand is H₂IMes (Chart 1), although the unsaturated IMes analogues are also used. Scattered reports in the literature show no consistent performance differences for the two NHCs, although the H₂IMes ligand has been suggested to confer greater activity.^{2,3} Here we report a systematic comparison of catalysis by the H₂IMes and IMes analogues. Specifically, we examine the impact of varying conditions (temperature, solvent, rigour of air-exclusion) on catalyst productivity; i.e. total turnover numbers. Based on these results, we put forward a rationale that accounts for the lack of consensus in the current literature. These findings will provide a road map for the synthetic organic community in matching catalysts to conditions.

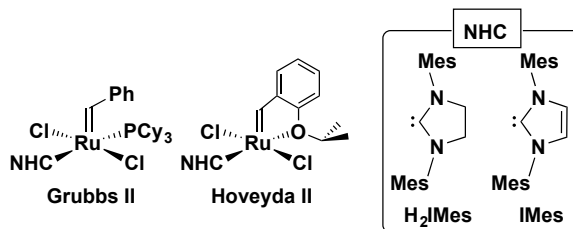


Chart 1. The dominant metathesis catalysts

Based on these results, we put forward a rationale that accounts for the lack of consensus in the current literature. These findings will provide a road map for the synthetic organic community in matching catalysts to conditions.

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P30 A simple [4x1] directional bonding strategy for the synthesis of discrete Re(I) assemblies

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Over the past few decades, self-assembly of simple components has led to the synthesis of remarkable materials such as molecular cages, macrocycles, helices, grids, and MOFs.¹ Although there are several ways to build complex assemblies, the directional bonding approach is quite straightforward and probably the most useful for the construction of rigid assemblies.² However, it usually requires two separate entities, an organic donor ligand and a metallic acceptor, reacting together in perfect symbiosis in order to arrive at the final assembly.

In our ongoing project, the discrete self-assembly of two Re(I) squares was achieved by a simple and efficient [4x1] strategy where the complexes, [Re(4-pytpy-κ²N)(CO)₃Br] and [Re(4-pytpy-κ³N)(CO)₂Br], act as their own ligands. The photophysical and electrochemical properties of the assemblies and their precursors will be presented along with solid-state X-ray diffraction studies.³

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P31

Expanding the Horizons of Amido-Based Organoactinide Chemistry

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The organometallic chemistry of actinide metals is dominated by the use of cyclopentadienyl (Cp) ligands. However, recent years have seen significant development of non-Cp containing actinide complexes in an effort to develop a better understanding of the chemistry available to f-block metals and the important role of f-electrons. Actinide research in the Leznoff group uses diamido-based ligands with several frameworks: a silylether ligand $\{[RNSiMe_2]_2O\}^{2-}$, an alkylether ligand $\{[RN(CH_2)_2]_2O\}^{2-}$ and an amido-siloxo-amino ligand $\{[RNSiMe_2]NR[SiMe_2O]\}^{2-}$ (R = various aryl, alkyl).

This presentation will focus on the preparation of a series of amido-actinide (Th(IV) and U(IV)) dialkyl complexes and the discussion of their reactivity patterns in catalysis. A number of these complexes have been established as active catalysts for ethylene polymerization, propylene oligomerization, intramolecular hydroamination and are active initiators for the ring-opening polymerization of *rac*- and L-lactide. The results described herein will place particular focus on the difference in activity between choice of actinide metal and choice of diamido ligand as a means of answering the question: *Are actinide metals capable of acting like d-block transition metals?* Furthermore, a brief introduction into the unique oxidation chemistry of amido-based uranium(IV) complexes will also be described.

P32 N,O-donor ligands for cobalt-ion coordination

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Complexes of cobalt(II) are promising catalysts for hydrogen production in homogeneous photocatalytic systems.¹ Therefore, we are interested in synthesizing new cobalt(II) complexes based on *N*-acylamidines, bis-(*N*-acylamidines) and *N*-acyl-guanidines ligands, and test their performance in this type of system. Herein, the synthesis and characterization of the ligands are showed. Amidines precursor is used for preparing *N*-acylamidines(1). Generally, the amidines are prepared in good yields (60-90%) from carboxylic acids and anilines, using polyphosphoric acid trimethylsilyl ester (PPSE).² The bis-(*N*-acylamidines)(2) ligands were described by Würthwein group³. The ligands were synthesized starting from diamine reacting with acyl halides, and linked through the amino group by a PPSE reaction.^{2,3} The *N*-acyl-guanidines(3)⁴ are synthesized from 1,5,7-triazabicyclo (4.4.0) dec-5-ene (TBD) and acyl chlorides. The guanidines are obtained by the reaction of guanidine salts reacting with *N*'-(3aminopropyl)propane-1,3diamine.⁵ The desired ligands are subsequently obtained, Figure 1, by *N*-acylation of the ligands.^{6,7} The ligands were characterized by NMR spectroscopy and mass spectrometry and their reaction with Co(II) will be discussed.

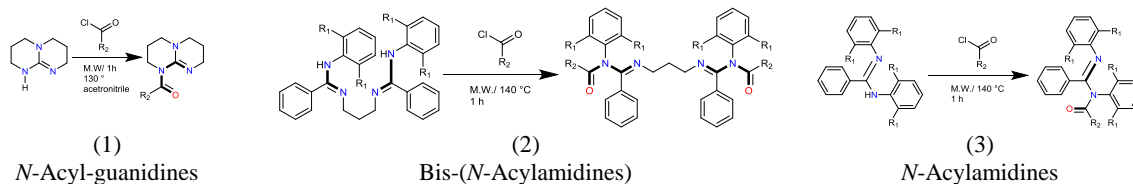


Figure 1 - *N*-Acylation reaction

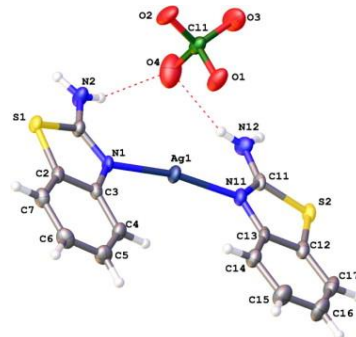
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P33 Synthesis, Characterization, Anticancer Activity and DNA Interaction Studies of Various 2-aminobenzothiazole Metallic Complexes

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The synthesis of various metallic complexes of 2-aminobenzothiazole (Habt), [M(Habt)₃Cl]Cl, [M(L)(abt)]Cl (M(II) = Pd, Pt; L = bpy, phen), [Ir(Habt)₃(H₂O)Cl₂]Cl, [Ru(Habt)₃(H₂O)Cl₂], [Rh(Habt)₃Cl₃], [OsO₂(Habt)₂(OH)₂], [Zn(bpy)(Habt)Cl]Cl, [Zn(PPh₃)(Habt)₂Cl]Cl, [Ag(Habt)₂]ClO₄, [Ag(L)(Habt)]ClO₄ (L = bpy, phen, PPh₃) and [Au(Habt)₃Cl]Cl₂ is reported. Their characterization was achieved by means of IR, Raman, UV-Vis, NMR, MS, elemental analysis, as well as molar conductivity and thermal degradation measurements. The X-ray crystal structure and the DFT conformational analysis of the complex, [Ag(Habt)₂]ClO₄ were undertaken. The *in vitro* anticancer activity of Habt and some of its complexes was evaluated against human breast cancer (MDA-MB231) and human ovarian cancer (OVCAR-8) cell lines. [Ag(Habt)(PPh₃)]ClO₄, [Ag(phen)(Habt)]ClO₄, [Pt(Habt)₃Cl]Cl and [Pd(abt)(phen)]Cl, were found to be more cytotoxic than cisplatin to these cell lines, with mean IC₅₀ values of 1.38, 1.78, 4.15 and 5.06 (MDA-MB231), and 1.26, 1.45, 4.04 and 5.20 (OVCAR-8) μM, respectively. DNA-binding properties of some of the complexes were studied using circular dichroism (CD) spectroscopy, and the results indicate that the complexes may have intercalative CT-DNA binding capabilities.

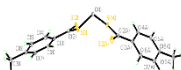


P34 Transition Metal Thiols and the Reactivity of Sulfur-rich Chelates

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Considerable interest has risen in recent years in studying transition metal thiolates and other sulfur derivatives due to their use in biological, synthetic and environmental applications.¹ There is much precedence for the theory that sulfur groups become potent nucleophiles once coordinated to metal centers and these allow for enhanced sulfur nucleophilicity. Our current study focuses on generating such complexes, particularly stable, four- to six-coordinate complexes which still exhibit high reactivity. Many of these types of complexes have the ability to reversibly bind other small molecules ability to reversibly bind other small molecules through oxidative addition though the reactivity of these complexes bear a strong ligand-dependence.² Sulfur-rich complexes, specifically those of sulfur chelates, also have the ability to undergo oxidation to yield disulfides and tend to be more relatively stable than other oxygenated-derivatives, allowing for better analysis of organic compounds.



Recently there has been many cases of sulfur-containing heterocycles being able to reversibly add and eliminate sulfur atoms, permitting better investigation into the dynamics of the ring-opening mechanism as well as the kinetic dynamics that drive such reactions.³ Due to the continually growing trends in examining sulfur-containing complexes it was the purpose of this study to investigate the coordination spheres of these types of complexes as well as analyze the reactivity of some of these thiol groups by transition metal anomeric effects.

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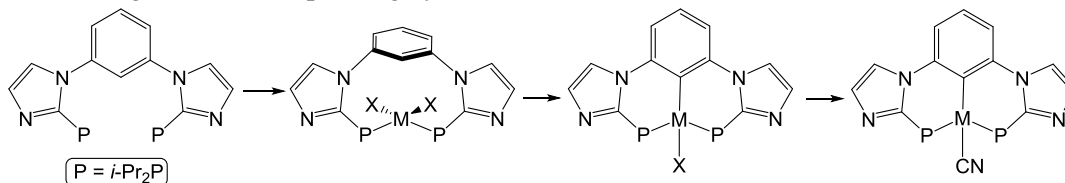
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P35 Synthesis and characterisation of the first PimCimP-type and NCimP-type pincer complexes of nickel

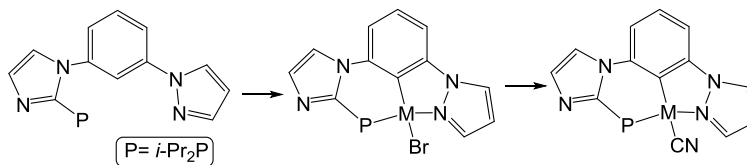
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Chelation of a symmetrical, meta-phenylene-based pincer ligand featuring imidazolophosphine functionalities gives the corresponding complexes ($\kappa^P, \kappa^{P'}$ -PimC(H)imP)MX₂ (M = Ni, Pd). Metalation of these complexes gives the corresponding pincer complexes (PimCimP)MX, and salt metathesis of the latter with KCN gave the corresponding cyano derivatives.



We have also investigated the chelation/metalation of a closely related but unsymmetrical ligand NCimP featuring imidazolophosphine and pyrazole moieties. Treating with MX₂ gave the complexes (NCimP)MBr (M = Ni, Pd), which have been characterized and converted to their cyano derivatives.



P36 Reinvestigating the Structural and Magnetic properties of a Dy^{III} Calixa[4]arene Cluster

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Single molecule magnets (SMMs) have a broad range of potential applications that include information storage, spintronics and magnetic refrigeration. Employing ligands with the ability to control or determine the composition of the metal ions in an SMM is particularly advantageous as it allows for the rational design of molecules with specific magnetic properties. Methylene bridged C[4] calixarenes have been previously explored for the self-assembly of lanthanide-based SMMs and have afforded Ln^{III}₆ clusters where the metals are arranged at the vertices of an octahedron, Fig.1.^{1,2} In this context, the first study was reported by Brechin *et al.* in 2012¹. In recent months, we have developed a synthetic strategy for the crystallization of Ln^{III}₆ clusters assembled from *p-tert*-butylcalix[4]arenes and report herein detailed structural and magnetic studies of the Dy^{III} cluster.

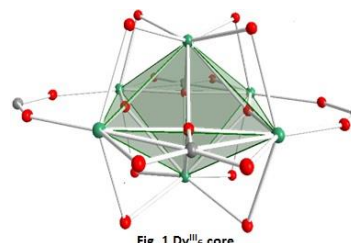


Fig. 1 Dy^{III}₆ core.

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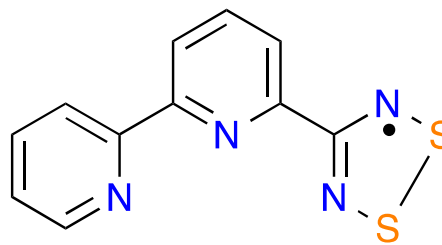
P37

Paramagnetic thiazyl ligands for the design and synthesis of molecular materials displaying

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The design and synthesis of thiazyl radical ligands can be tailored in order to create molecular materials with desired properties. The incorporation of an aromatic system, such as bipyridine, to the thiazyl radical heterocycle could afford a compound possessing interesting luminescent behavior. By combining the luminescence of bipyridine, with the reversible monomer-dimer equilibrium characteristic of thiazyls¹, one could in theory generate a luminescent switch. Others have demonstrated that paramagnetic nitroxide radical derivatives show significantly diminished quantum yields and shorter fluorescent lifetimes than their diamagnetic counterparts². Because pancake-bonded dimers of DTDA radicals are typically diamagnetic, and the monomer-dimer equilibrium observed in solution can be manipulated by altering specific conditions, dimerization of the thiazyl bipyridine can be controlled, turning on and off the luminescence. We have recently observed the rupture of a [DTDA]₂ dimer in the solid state for a related species, suggesting that similar manipulations may be possible in solids as well as solutions. Synthesis of bipyridine DTDA and several of its lanthanide coordination complexes will be presented.



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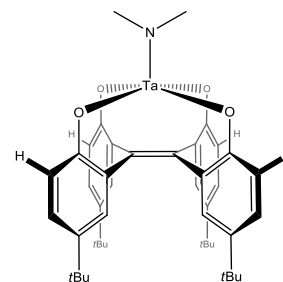
P38

Synthesis and Reactivity Studies of Square Pyramidal Tantalum Complexes

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The synthesis of new tantalum pseudo-square pyramidal complexes bearing the *tert*-butyl-substituted (ethenediylidene)tetrakis[phenol] “TPO” ligand system and their reactivity is herein described. The tantalum ethoxide and dimethylamide complexes were prepared and structurally characterized, giving valuable insight into the interactions between the metal centre and the axial ligand. The solid-state structures confirmed the targeted geometry of both complexes, with the TPO ligand coordinating to tantalum and forming the base of the pseudo-square pyramidal structure, with the ethoxide and dimethylamide ligands occupying the axial position (formally along the z-axis). The bond lengths and angles from the structure show clear evidence of significant π -electron density donation from the heteroatom of the axial ligand into the empty $d\pi$ orbitals on the metal (d_{xz} and d_{yz}), a key feature for activation of small molecules, such as molecular nitrogen. Reaction of (TPO)Ta(OEt) with trimethylaluminum cleanly gave the methyl complex. Further reactivity studies will be presented, including protonolysis by strong and weak acids.

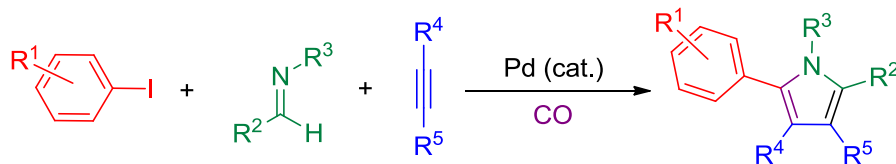


P39 Palladium catalyzed multicomponent synthesis of substituted pyrroles

Gerardo Martin Torres, and Bruce A. Arndtsen*

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Pyrroles have found use in a broad variety of areas, ranging from components in biologically relevant compounds, to materials science and polymers. Nevertheless, approaches to construct pyrroles, especially highly substituted variants typically require multistep synthesis. These can be time consuming, create significant waste with each step, and make the generation and tuning of pyrroles an involved, iterative process. In recent years, multicomponent synthesis has arisen as an attractive route to prepare complex products from simple building blocks. In this work, a palladium catalyzed multicomponent synthesis of pyrroles is presented. The building blocks in this reaction are all simple: imines, aryl iodides, alkynes and CO, and are coupled together in a one pot, palladium catalyzed cascade. The mechanism of this transformation, catalyst design, reaction intermediates, and the diversity of pyrrole products available, will each be discussed.

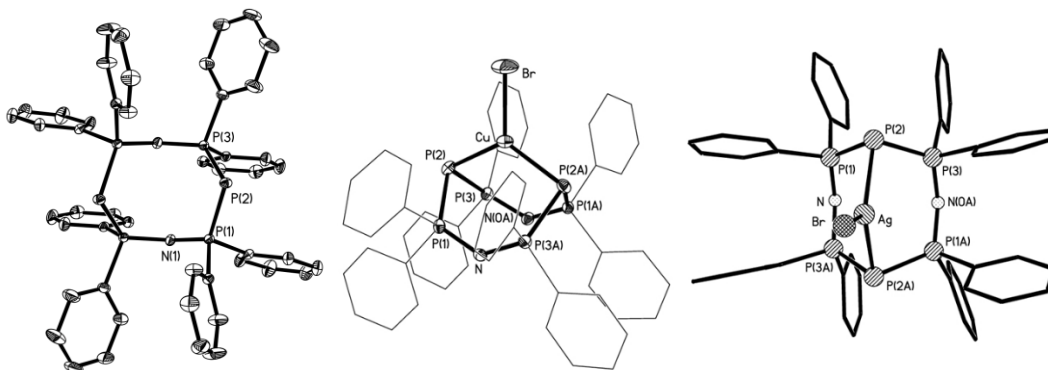


P40 The Reactivity of Low Valent Phosphorus Heterocycles

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Polyphosphazenes have been extensively investigated and used industrially for a variety of applications. The isovalent phosphorus-rich analogues of phosphazenes are of interest to our group as they feature low valent phosphorus centres linked by (bis)-anionic phosphine fragments, to generate unique heterocycles in which four or more potential donor sites may be accessed. Herein, we present a convenient methodology to obtain these heterocycles, as well as reactivity studies including the coordination of coinage metal to the low valent P^I centres. In this study, NMR spectroscopy and X-ray diffraction have been utilized to probe these molecules and other related systems.

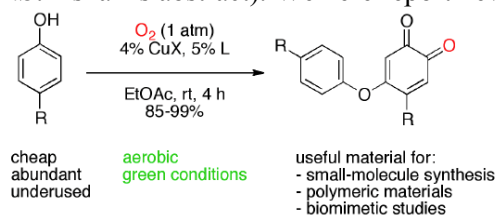


P41 Catalytic Aerobic Phenol Functionalization with Cu(II) Complexes

Laura A. Rodríguez-Solano, M.S. Askari, A. Proppe, B. McAllister, X. Ottenwaelder*

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The catalytic aerobic oxidation of phenols defines many biological processes in life, however under laboratory conditions these reactions are difficult to control. Recently, work carried out in the Lumb lab (McGill) led to the development of the first copper-catalyzed process that cleanly controls aerobic oxidation of phenols to selectively generate o-quinones or catechols in 85-99% yields (scheme) [1]. The reaction conditions require a copper(I) salt, CuX, which is not easy to handle due to oxidation in air. In collaboration with the Lumb group, we have been studying the mechanism of this reaction, which provided some insight into the catalytic intermediates (see M.S. Askari's abstract). We here report new sets of conditions that employ air-stable copper(II) precatalysts for the phenol oxygenation. The Cu(II) complexes provide high yield of the coupled quinone while eliminating the need for inert atmosphere during reaction set-up.



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P42 Regioselective synthesis of six-membered cyclometalated complexes

Craig M. Anderson^a, Matthew Greenberg^a, Asad Hasim^a, Leila Duman^a, Tedros A. Balema^a, Leah Ladner^a, Kyan Jain^a, Paul Lawrence, and Joseph M. Tanski^b

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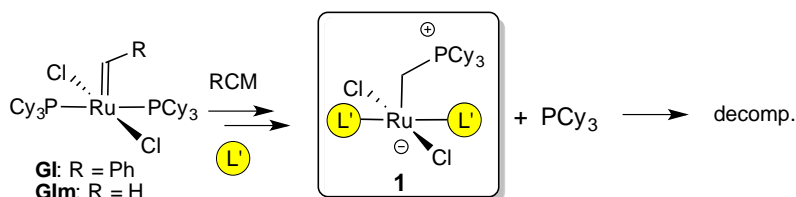
Cyclometalated platinum and palladium complexes have been synthesized with tridentate C^NN and bidentate C^N-type ligands, characterized by NMR spectroscopy, and several using X-ray diffraction (XRD). Exclusively six-membered (more rare than five-membered) cyclometalated rings are initially formed in many cases. As expected, the C^NN ligand adopts the *mer* configuration while the three carbon donors adopt the *fac* geometry. Regarding the regioselectivity, C-X is activated exclusively over C-H and sp² C-H bonds exclusively over sp³ C-H bonds. The complexes with C^N naphthyl-derived ligands were heated to study the possible reductive elimination reactions and any subsequent reactions. In some cases, C-C couplings occurred with subsequent C-H oxidative addition resulting in new cyclometalated rings, some with seven-membered rings.

P43 Donor-Induced Decomposition of Grubbs Catalysts: A Threat Assessment

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As industrial applications of ruthenium metathesis catalysts begin to emerge,¹ understanding their decomposition pathways is increasingly important. By focusing on the slower-reacting first-generation catalyst **GI**, we were recently able to intercept a key intermediate, σ -alkyl species **1** (Scheme 1). Complex **1** is formed in near-quantitative yields by ligand exchange of **GI** with pyridine, and attack of liberated PCy₃ at the methylenide site. Here we examine the tendency of other donors to trigger this deactivation pathway. An ascending state of reactivity is presented, which shows some unexpected trends in terms of functional group tolerance.



Scheme 1. Donor-induced decomposition of the first-generation Grubbs catalyst.

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P44 Mechanistic Investigations of the Concerted Metallation-Deprotonation Reaction with [Cp*₂RhCl₂]₂

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C-H activation provides a unique and efficient method for the functionalization of, otherwise, featureless and un-activated organic compounds.^[1] Work done by Fagnou^[2] and Davies invoke an intermediary cyclometallated species which can then insert molecules into the metal-carbon bond forming a new metal-carbon or metal-heteroatom bond. These cyclometallated species can be synthesized and studied independently to, then, develop a better understanding of a presumed reaction manifold.^[4] Herein we describe the kinetics of an acetate assisted cyclometallation of 2-(*p*-methoxyphenyl) pyridine with [Cp*₂RhCl₂]₂ with a range of substituted acetates to probe the effect of *p*K_a on the observed rate. In general as the *p*K_a increases up to a *p*K_a of 4.7 then after decreases possibly due to steric bulk associated with the substituted carboxylate. Under stoichiometric conditions the reaction proceeds smoothly via first-order kinetics based on the active Cp*₂RhCl(κ^2 -OAc) specie and a second-order dependence on the concentration of phenyl pyridine only when in excess.^[5] This observation may be attributed to a secondary process with excess phenyl pyridine that creates a rhodium species with two *N*-bound phenyl pyridines and one acetate that's *faster* leading to a linear increase in observed rate.

References:

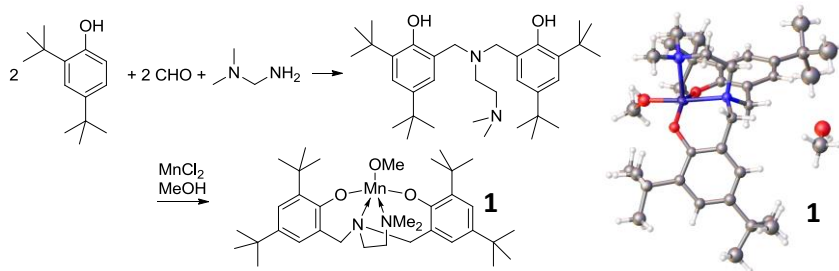
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P45 Lactide polymerization with manganese complexes

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Polyesters are attractive targets for biodegradable plastics since bacteria can hydrolyse the ester bond, under the right conditions, thus breaking down the polymeric material. While research into catalysts for cyclic ester polymerization has increased dramatically (particularly in lactide polymerization), most of the reported catalysts are unsuitable for industrial application, which require high thermal stability (> 150 °C) and robustness to water. Tetradentate diphenol ligands were used to prepare Mn(III) complexes of type **1**, which are stable in ambient atmosphere. The complexes proved to be moderately active (full conversion in 4 h) for lactide polymerization under industrial conditions. More importantly, the catalysts retain most of their activity even when polymerization is performed under ambient atmosphere and using non-purified lactide monomer. While activities and polydispersities are comparable to better than the tin octoate industry standard, further catalyst optimization is required to enable this catalyst to be competitive with the current industrial process.

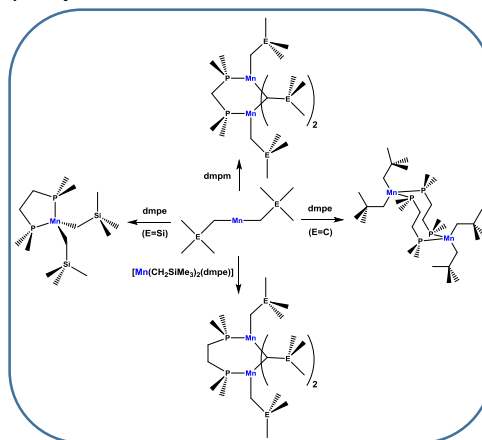


P46 Bis(phosphine) Adducts of Dialkyl Manganese(II) Complexes

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As with many transition metals, manganese complexes of acyclic hydrocarbonyl ligands typically have much higher thermal stability when the metal coordination sphere contains at least one cyclopentadienyl or other non-hydrocarbonyl anionic supporting ligands. Consequently, there are very few examples of thermally robust manganese(II) complexes bearing alkyl and/or allyl ligands as the only anionic donors. However, complexes of this type are of interest due to their high reactivity and potential for use as precursors in Chemical Vapor Deposition (CVD) or Atomic Layer Deposition (ALD) of thin metal-containing films. Here, we will present structural characterization of the bis(dimethylphosphino)ethane (dmpe) and bis(dimethylphosphino)methane (dmpm) adducts of $[\text{Mn}(\text{CH}_2\text{EMe}_3)_2]$ (E=C, Si). Control over reaction stoichiometry has been shown to permit diphosphine ligands to act as either bridging or chelating ligands, producing three distinct structures types. Reactivity and physical properties of these complexes were examined for comparison to phosphine-free analogues.

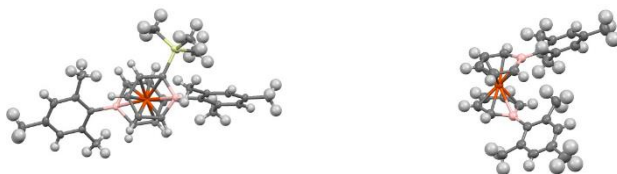


P47 **Synthesis and reactivity of a novel mesityl boratabenzene ligand and its coordination to transition metals**

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The borabenzene ring has been a subject of considerable recent interest because of the flexibility of its coordination modes, its potential in catalytic reactions and in the generation of optoelectronic materials. Our group is interested in studying the reactivity and coordination chemistry boratabenzene ligand. We have synthesized and characterized a new bulky 1-mesityl-4-isopropyl-boratabenzene ligand. The potential precursor for this ligand has been isolated in two isomeric forms 1-mesityl-2-trimethylsilyl-4-isopropylboracyclohexa-2,5-diene and 3,5-diene. They have been selective hydrolyzed to remove trimethylsilyl group thereby providing the first water stable 1-mesityl-4-isopropyl-boracyclohexa-3,5-diene. This selective hydrolysis of trimethylsilyl group has also been observed in the iron sandwich of this ligand.



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P48 **Bis Benzoselendiazolium Dications**

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Secondary bonding interactions (SBIs) centred on heavy main-group elements constitute an appealing alternative to hydrogen bonding and the coordination of metal ions for the construction of supramolecular structures. Heterocycles such as the 1,2,5-chalcogenadiazole readily assemble the [E-N]₂ (E=S, Se, Te) *supramolecular synthon*, a virtual four-membered ring that features two antiparallel E—N SBIs.¹ The tellurium derivatives form the strongest links within the family but their moisture sensitivity restricts the widespread application.¹ The selenium analogues associate in a similar fashion but with weaker SBIs. However, N-alkylation of the heterocycle greatly strengthens the Se-N links.² We have extended this concept by developing bridged dication species capable to infinite catenation.

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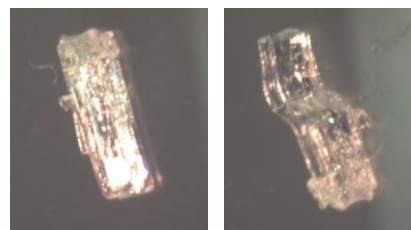
P49

Bending Crystals of 2-cyano-4,6-dimethylpyrimidine

Adam C. Maahs, Dmitriy Soldatov, and Kathryn E. Preuss*

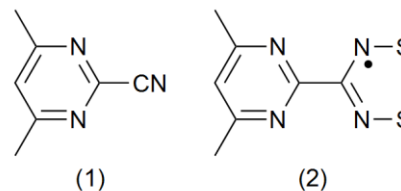
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Breakage is a typical response when mechanical stress is applied to a crystal. However, when strong intermolecular interactions are perpendicular to much weaker interactions, bending can occur.¹ The structural origin of the plastic bending phenomenon was first rationalized for hexachlorobenzene,² in which molecules crystal pack in 2D sheets, defined by weak intermolecular by Cl...Cl contacts, stacked along a short crystallographic axis with comparatively stronger π - π interactions. The criterion of possessing perpendicular strong and weak interactions is a reliable predictor of bending behaviour.³ The crystal structure of 2-cyano-4,6-dimethylpyrimidine, **1**, is characterized by a short axis (~4Å) along which π stacks are formed [100], while the {100} planes have no contacts within the sum of van der Waals radii. As a result of its solid state structure, **1** is observed to bend without breaking when pressure is applied perpendicular to [100]. **1** was prepared as a synthetic intermediate in the design of a stable radical ligand, (**2**), intended for coordination to transition metal and lanthanide ions.



Single crystal of (**1**) before and after bending

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P50

Interpreting effects of structure variations induced by temperature and pressure on luminescence spectra of square-planar Pt(II) and Pd(II) complexes

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Luminescence properties of several square-planar complexes of platinum(II) and palladium(II) with a d^8 electron configuration are investigated. First, structural modifications are studied through increasing pressure, which causes a blue shift in luminescence spectra for most of complexes. Increasing pressure cause a weakening of intermolecular interaction in a platinum(II) complex, inducing a more pronounced blue shift of the maxima. Increasing pressure cause a weak intermolecular interaction in a palladium(II) complex, inducing a red shift of the maxima. DFT calculations show the molecular orbitals involved in the interactions for the palladium(II) complex. Secondly, structural modifications are investigated through temperature variation. Luminescence spectroscopy allows distinguishing vibronic and structural contributions with variation of temperature. Most square-planar luminescence spectra exhibit only the vibronic effet, causing a blue shift with increase of temperature for platinum(II) complexes and a red shift for iso-structural palladium(II) complexes. A rare case of a platinum(II) complex is presented, where the structural effect is clearly present in temperature-dependent luminescence spectra.

P51

Building blocks for supramolecular assemblies : New AMOX based Coordination Polymers

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N,N'-Disubstituted hydroxyamidines, also known as α -aminonitrones (AMOXs), display high steric and electronic modularity, as a wide range of substituents can be introduced on the α -carbon and/or on the nitrogen atoms. Hence, they afford precise electronic tunability, facilitated by the delocalization on the amidine backbone. They are excellent bidentate ligands that form stable 5-membered rings with metal ions. In our research, we exploit these properties by investigating their incorporation into supramolecular assemblies, based on coordination chemistry and/or hydrogen bonding, by introducing a bridging substituent on the α -carbon and/or on the nitrogen, which opens a second coordination site on the ligand. The properties of the metals used will dictate the function of the final assembly (eq.: light-harvesting properties with Ru, Re, Ir or magnetic properties with Co, Fe or Mn). The type of assembly is induced by the coordination geometry of the metal ion, in combination with the coordination vectors of the ligand (e.g.: tetrahedral metal + parallel coordination vectors = grid type assembly). Herein, we present the synthesis and characterization of bis-AMOX ligands (Figure 1), and their precursors.

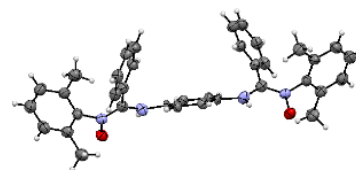


Figure 1. Solid-state structure of an *N*-bridged bis-AMOX ligand.

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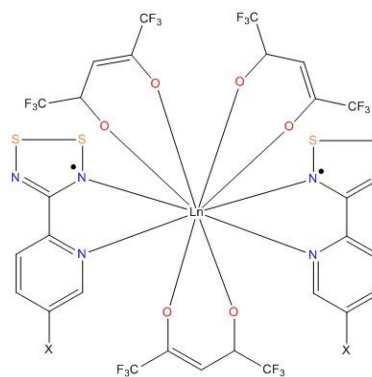
P52

Chemical Tuning of Lanthanide Complex Re-entrant Phase Transition by Alteration of the 4-(2'-pyridyl)-1, 2, 3, 5-Dithiadiazolyl Radical Ligand

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Previous work in the Preuss group has revealed that $\text{Ln}(\text{1,1,1,5,5,5-hexafluoroacetylacetonato})_3[4-(2'\text{-pyridyl})-1,2,3,5\text{-dithiadiazolyl}]_2$ exhibits a re-entrant phase transition: $\text{Ln} = \text{La, Ce, Pr, Nd}$. The study presented herein attempts to further investigate this phenomenon incorporating various functional groups to the 4-(2'-pyridyl)-1,2,3,5-dithiadiazolyl ligands in order to modify the electron properties and the crystal packing of the molecular species. The functionalized ligands and their lanthanide coordination complexes are new species. Initial work toward the synthesis of the complexes- illustrated in figure (X=F, Cl, Br) is presented.

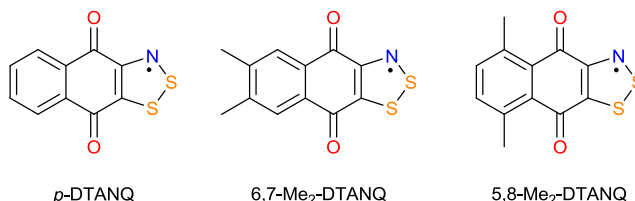


P53 Determination of Ferromagnetic Impurities in 1,2,3-DTA-Napthoquinone Radical Ligands

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The development of 1,2,3-dithiazolyl (DTA) radical ligands is a relatively new venture in the design of interesting molecular materials. A class of DTA radical ligand, 1,2,3-dithiazolyl-naphthoquinones (DTANQs), has been developed and is being explored by the Preuss group. These radical ligands have shown promising results with the publication of the first DTA coordination complex in 2012^[1]. One of the issues discovered with this class of ligand is the presence of a ferromagnetic (FM) impurity in many of the final products, both in the purified radical ligands and their metal complexes. The goal of this poster is to present a method of identifying the nature and origin of this FM impurity and eliminating it from the radical ligands and their complexes. A combination of inductively coupled plasma optical emission spectrometry (ICP-OES) and field dependent magnetization measurements is proposed to identify trace metals responsible for the FM impurities. The results will be used to determine the efficacy of purification methods. Once the FM impurity issue is resolved, a complete series of DTANQ-metal complexes will be synthesized and their magnetic properties measured in confidence.



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P54 Discrete supramolecular assemblies based on polypyridyl functionalized polyoxometalates

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Polyoxometalates (POMs) are nanoscale molecular oxide based on early transition metals (Mo, W or V). They find application in various areas ranging from medicine to catalysis and materials science. A lot of research focus on the elaboration of organic-inorganic hybrid materials via organic moieties covalently grafted on the POM.^[1] In our group, we focus on the covalent grafting of poly-pyridyl moieties in order to prepare new light harvesting devices (LHDs) taking advantage of the POMs ability to behave as electron reservoir^[2]. We've been able to complex different transition metals on the poly-pyridyl ligand, leading to multi-component systems that feature the combined intrinsic properties of each component as well as new properties originating from the combination of these components. We're presenting discrete supramolecular assemblies obtained through the self-assembly of these platform with Pd²⁺, Re⁺ and Ru³⁺ complexes.^[2,3,4]

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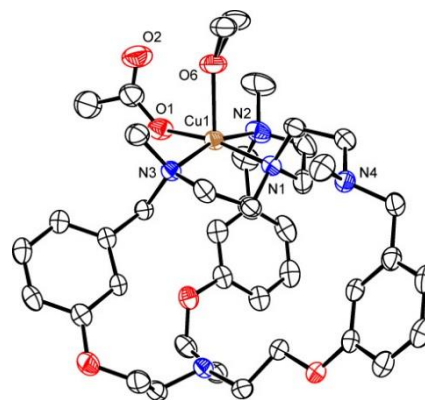
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P55 Oxidation Chemistry with Bioinspired Cryptates

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Understanding C–H bond hydroxylation mechanisms that mimic those of monooxygenase enzymes can lead to new synthetic methods for C–H bond oxidations. They would involve standard oxidants like O₂ or H₂O₂, produce water as the only byproduct, and employ the less toxic copper or iron metal catalysts. Here, we report on the formation of a Cu(II)-hydroperoxo species with a biomimetic coordinating cryptand and its hydroxylation behaviour. A combination of mass spectrometry, EPR, low-temperature stopped-flow experiments and kinetic studies provided evidence for the hydroxylation mechanism and how it is influenced by second coordination sphere features [1,2].



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P56 Deactivation during acrylate cross-metathesis

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Acrylate cross-metathesis, as a technology enabling direct access to α,β -unsaturated esters, has enormous potential in renewable synthesis.¹ Recent advances in this area have been achieved largely through use of the Hoveyda catalyst, **HII** (Chart 1).² In numerous reports, **HII** has been shown to tremendously outperform **GII** in acrylate cross-metathesis reactions.³ Importantly, this disparity does not hold true for olefin substrates in general, suggesting that the observed deactivation may be particular to the electron-deficient catalytic intermediates formed during the metathesis cycle.

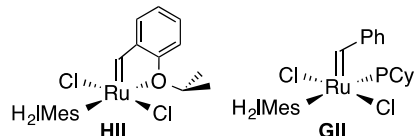


Chart 1. Grubbs and Hoveyda olefin metathesis precatalysts. H₂IMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene.

Mechanistic understanding of this deactivation is important in light of improving turnover through intelligent catalyst design, and to inform on choice of catalyst for implementation of metathesis reactions in industry. Here we present the results of mechanistic studies aimed at understanding the conspicuous superiority of the **HII** over **GII** in acrylate cross-metathesis reactions.

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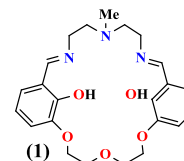
P57

Exploitation of an Asymmetric Compartmental Macrocycle for the Preparation of SMMs

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Single Molecule Magnets (SMMs) are traditionally polynuclear clusters comprised of transition metal ions that display superparamagnetic behavior at low temperature.¹ In recent years the large magnetic anisotropy associated with Ln^{III} ions has led to the observation of SMM behaviour in mononuclear complexes.² The geometric requirements for slow relaxation in Ln^{III}-based complexes are specific to each ion, but the most common geometry observed is square-antiprismatic (pseudo-D_{4d}).³ In contrast, mononuclear SMMs assembled from heptacoordinate D_{5h} complexes are rare. Our approach is to employ macrocyclic ligands for the preparation of Ln^{III} complexes with pseudo-D_{5h} geometries. Following this strategy we successfully prepared the first penta-aza Dy^{III} mononuclear complex displaying slow relaxation of magnetization.³ We present herein our recent progress in exploiting a second class of macrocyclic ligand, **(1)** for the preparation of Ln^{III}-based SMMs.



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P58

Bismuth Compounds as Photocatalysts

Laura E. Hull, Nick P. Alderman, Camilo J. Viasus, Jacob M. Sommers, and Sandro Gambarotta*

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BiVO₄ has been shown in several instances to be an effective photocatalyst. In various cases it was shown to facilitate water splitting,¹ reduction of CO₂ into ethanol² and methanol³, and decomposition of organic dyes.⁴ BiVO₄ is well-suited as an ultraviolet/visible light photocatalyst, but has some drawbacks, especially regarding yield.

With this in mind, other bismuth complexes were explored for their photocatalytic potential. BiTaO₄ in particular was investigated in a number of areas, such as whether it is able to convert CO₂ into alcohols such as ethanol or methanol, as well as other potentially interesting applications such as formic acid into formaldehyde.

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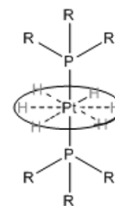
P59 A Platinum *trans*-Dihydride Complex as a Potential Molecular Rotor

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The development of synthetic rotors on the molecular scale represents a significant challenge in science and requires an intimate understanding of the relationship between structure and dynamics. If molecular or supramolecular motion can be achieved in a controlled fashion, molecular rotors have great potential for information storage technology.

The single crystal X-ray structure (including crystallographically located hydride positions) and solid state NMR (SSNMR) data for *trans*-H₂/D₂-Pt(P^tBu₃)₂ as a potential molecular rotor are presented. Based on X-ray and ¹⁹⁵Pt SSNMR the *trans*-hydrides appear to be oriented axially to the P-Pt-P axis. This apparent axial symmetry along with a quadrupolar coupling constant (*Q_c*) of 40 KHz from ²D SSNMR of the *trans*-deuteride complex implies that the hydrides are orbiting in a plane perpendicular to the P-Pt-P axis. Progress in assessing the rotational dynamics of the hydrides will also be presented.



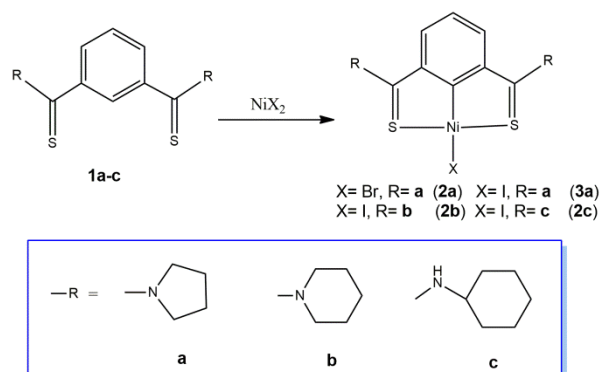
P60 Ni(II) complexes with thioamide pincer ligands: An interesting electrochemical behavior of secondary thioamide unit

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Four new nickel(II) complexes, [Ni(SCS)X] having SCS pincer ligands with two thioamide units have been synthesized and fully characterized by NMR spectroscopy and X-ray crystallography. The crystal

structures of all complexes hint at significant delocalization of bonding in the ($\text{-N}=\overset{\text{S}}{\text{C}}\text{-}$) units. In addition, cyclic voltammetry measurements of **2c** indicate that the secondary thioamide moiety is easily deprotonated to produce its thionate anionic form.



P61

The $Ba_{1-x}Sn_xCl_{1-y}F_{1-y}$ doubly disordered solid solution: instability of preparation and unit-cell parameters

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The reaction of barium chloride and tin(II) fluoride in aqueous solution at high barium chloride content results in the precipitation of a $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ solid solution, with $0 \leq x \leq 0.15$ and $0 \leq y \leq 0.15$. For slightly lower barium content, a mixture of another new compound, stoichiometric $BaSnClF_{3.0.8}H_2O$ is obtained, mixed with the $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ solid solution. Large instability regarding the product obtained is observed around the composition of the reaction mixture where the change of product takes place. X-ray powder diffraction shows that the $Ba_{1-x}Sn_xCl_{1+y}F_{1-y}$ solid solution has the structure of $BaClF$ ($PbClF$ type), with no superstructure or lattice distortion. This implies that Ba and Sn are disordered on the Ba site. Elemental analysis shows that, in addition to the metal non-stoichiometry, there is also anionic non-stoichiometry. It was found that up to 15% of the fluoride ions can be replaced by chloride ions. This appears surprising since the reason for the tetragonal distortion of the $PbClF$ type relative to cubic MF_2 fluorite type resides in the large difference of size between the chloride and fluoride ions. Tin-119 Mössbauer spectroscopy shows that, against all expectations for a chloride fluoride, tin(II) is in the form of the Sn^{2+} stannous ion with a unhybridized non-stereoactive lone pairs, similar to the case of $SnCl_2$, while covalently bonded tin(II) with a hybridized stereoactive lone pair is usually observed when tin is bonded to fluorine and/or chlorine. The products obtained will be discussed using analytical, crystallographic and Mössbauer spectroscopy

P62

Synthesis and crystal structure of bis 4-aminobenzoic acid, bis nickel nitrate dihydrate

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In the course of the systematic investigation of complexes of transition metals with bidentate ligands, bis 4-aminobenzoic acid, bis nickel nitrate dehydrate, $C_{14}H_{18}N_4O_{12}Ni$, was prepared and its crystal structure solved. The preparation was carried out according to the method described by Middleton et al., (1958)^[1], and yielded green colored crystals. The compound crystallizes in the $P2_1/c$ monoclinic space group. The unit-cell parameters are the following: $a = 11.2950 \text{ \AA}$, $b = 12.4970 \text{ \AA}$, $c = 6.6740 \text{ \AA}$, $\beta = 97.72^\circ$. The structural data were collected on a CAPPa CCD diffractometer^[2]. After the final refinements, the residuals were $R[F^2 > 2\sigma(F^2)] = 0.0251$ and $wR(F^2) = 0.1003$ with an estimated variance of 1.19. Examination of the geometry of the structure shows that the molecule takes the Trans S-Cis conformation. This conformation is stabilized by O...H attractions that are 2.88 \AA long, i.e quite close to the literature value of 2.60 \AA ^[3]. The C-C bond lengths are also in excellent agreement with literature values (1.380 \AA ^[4]). The stacking of the molecules in the crystal is close to make sheets parallel to (a,b) plane. Superimposing these sheets create channels parallel to the a axis that run through the apices and the center of the unit-cell.

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P63

Synthesis and structural study of bis N-diethyl-P-phenylenediamine nitrate

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Several synthetic procedures of compounds similar to the title compound have been proposed in the literature, however little interest seems to have been focused on the parameters that control the outcome of the synthesis. This work proposes to make up for this oversight in order to be able to have a better control of the structure and properties of the compounds obtained. This presentation is concerned with the synthesis of bis N-diethyl-P-phenylenediamine nitrate, using nickel(II) nitrate hexahydrate and N-diethyl-P-phenylenediamine N-sulfate in the 1:1 stoichiometry. Brown single crystals were obtained. The crystal structure of the compound was obtained by single crystal diffraction. It crystallizes in the Fdd2 orthorhombic space group, with the following unit-cell parameters: $a = 20.8997 \text{ \AA}$, $b = 38.8214 \text{ \AA}$ et $c = 7.1720 \text{ \AA}$. Data collection was carried out on a CAPPa CCD diffractometer. After the final refinements, the residuals were $R[F^2 > 2\sigma(F^2)] = 0.0652$ and $wR(F^2) = 0.0499$ with an estimated variance of 1.05. The structure of the compound is ionic, $[L]^{2+} 2[NO_3]^-$, related to the AB₂ type, with two polyatomic ions, the nitrate anions $[NO_3]^-$, and a polyatomic organic cation $[L]^{2+}$. The ions are held together by ionic bonding. All bond lengths are comparable to literature values. These units generate by symmetry corrugated sheets along the b axis, parallel to the (a,b) plane. Hydrogen bonding ensures the cohesion of the structure.

P64

Site distortions created by the stereoactive lone pair of tin(II) in highly symmetric structures

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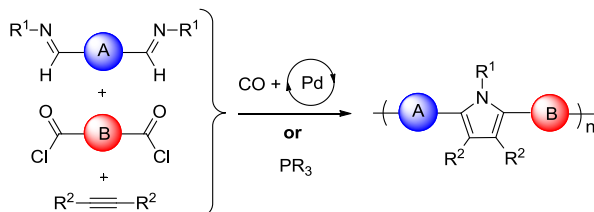
We have shown that tin(II) that has a stereoactive lone pair cannot be located in sites of high symmetry, particularly if the point symmetry of the site contains an inversion center or a mirror plane, otherwise the lone pair would be duplicated by the site symmetry, and tin does not have enough electrons to have more than one lone pair. However, several tin(II)-containing fluoride phases that have a cubic unit-cell have been obtained in our laboratory. These phases are the following: $PbSn_4F_{10}$, γ - $PbSnF_4$, $\mu\gamma$ - $PbSnF_4$, and the $M_{1-x}Sn_xF_2$ ($x = Ca$ and Pb). All these phases have a cubic unit-cell with the fluorite (CaF_2) type. Since no lattice distortion or superlattice is observed, the two metals, Sn and M, must be disordered on the metal site of the fluorite site. However, this site has the cubic symmetry (point group $m\bar{3}m - O_h$), which contains an inversion center and several mirrors. It results that tin(II) in this site should be ionic, i.e. in the form of the Sn^{2+} stannous ion. In Sn^{2+} , the tin orbitals are not hybridized, therefore the lone pair is on the spherical $5s$ orbital compatible with the high symmetry of the site. However, ¹¹⁹Sn Mössbauer spectroscopy shows that the lone pair is stereoactive, therefore in contradiction with the site symmetry. The presentation will show that tin is displaced from the site along all equivalent directions, in this case, towards the six faces of the cubic unit-cell. This avoids favoring one direction and preserves the cubic symmetry of the unit-cell. A judicious combination of X-ray powder diffraction and Mössbauer spectroscopy was required to solve this problem.

P65 Multicomponent Synthesis of Conjugated Polymers

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Conjugated polymers have emerged as an interesting class of organic semiconductors with potential applications as sensors, transistors, light-emitting diodes, and in photovoltaics. However, their multistep synthesis is often a limitation for accessing tunable properties and a large-scale production. To address these challenges, we have developed a palladium-catalyzed, multicomponent polymerization platform, and a complementary reaction mediated by simple phosphines. These approaches use simple starting materials (bis-imines, bis-acid chlorides, alkynes, alkenes) to generate conjugated polymers with complex repeat units in one-pot. Families of conjugated polymers with tunable properties can be easily accessed by changing each of the monomers. The development of this methodology, the libraries of polymers that can be generated, and their optical and electronic properties will be presented. This new approach allows for the modular and efficient generation of new classes of conjugated polymers from available substrates.



P66 Development of the solid amphiphilic systems, containing coexisting Lewis acid-base pairs

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Interest in bifunctional systems has been growing recently. Particularly of interest are nanomaterials having two antagonist functions, such as acids and bases. These materials are attracting great attention since acid–base bifunctionalized heterogeneous materials may be capable of exhibiting reactivity not achievable in homogeneous conditions. Previous work on bifunctional solid-catalyst largely involves the use Brønsted acid-base pairs, such as organic amines (base) immobilized together with thiols [1] and sulfonic acid [2] functional groups. However the implementation of the Lewis acid-base pairs still remains a great challenge. Inspired by the elegant concept of frustrated Lewis pairs, describing the Lewis acid and base pair, which are sterically precluded to form an adduct, first proposed by Stephan and Erker [3], our work aims to extend the possibilities of bifunctionalization using periodic mesoporous organosilicas, such as SBA-15, MCM-41, KIT-6 with Lewis acid-base pairs to form Lewis amphiphilic systems. Transition metals (Ti, Zr, etc.) covalently attached to the silica framework were proposed as water tolerant Lewis acids. Acidity was adjusted by the variation of the metal nature as well as metal content. Bulky phosphines and amines were used as Lewis bases. In this case, molecular hindrance and electronic density on the heteroatom was one of the principal factors. The grafting of acidic and basic components on silica porous framework resulted in solid Lewis amphiphilic system. Various characterization techniques were used to monitor the acidic and basic properties of the final system.

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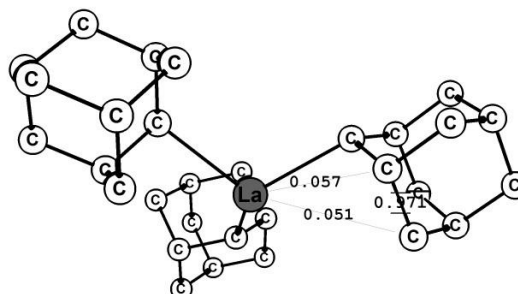
P67

Li, Ca, and Transition Metal Adamantyls - Synthesis and Reactivity

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While the chemistry of adamantane has been known for decades, developments into the synthesis of higher diamondoids (diamantane, triamantane, etc.) have progressed slowly and the basis of reactions involving adamantane is still very limited.^{1,2} The current scope of transformations that can be performed on adamantane are largely limited to oxidations and brominations, and the subsequent substitution reactions that can be carried out. Within these known transformations, the bulk of them are directed at the bridge-head position of the cage, as the bridge-head bromination of adamantane is a straight-forward reaction to perform.³ Adamantane, due to its unique structure and stability, has the potential to be used in a number of applications ranging from advanced materials, to ligands for transition metal catalysts, to scaffolds for drug molecules, and more. By expanding the scope of transformations that can be performed on adamantane, the usefulness of diamondoid chemistry could be vastly increased. Our research focuses on the synthesis and reactivity of organometallic adamantyl complexes, and the reactivity that can be exploited with these species.



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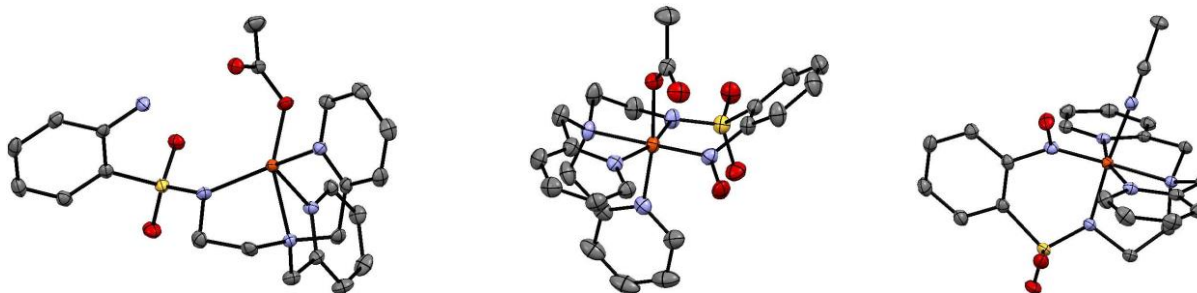
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P68 Reactions on Discrete Iron-Arylnitroso Complexes

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We are studying the redox conversion between nitrogen-based groups in the vicinity of iron as a means to understand the influence of a metal centre on oxygen-atom transfer reactions ($\text{NH}_2 \rightarrow \text{NHOH}$ or $\text{NO} \rightarrow \text{NO}_2$). Thus, the reaction of iron(II) salts with a polydentate ligand containing a hydroxylamine (NHOH) appendice leads to disproportionation of the ligand to make the amine (NH_2) and nitroso (NO) complexes. We present reactions of these complexes with oxygen abstracting reagents, which potentially generate a nitrene intermediate, and oxygen donors (oxidants), to study oxygen-atom transfers.



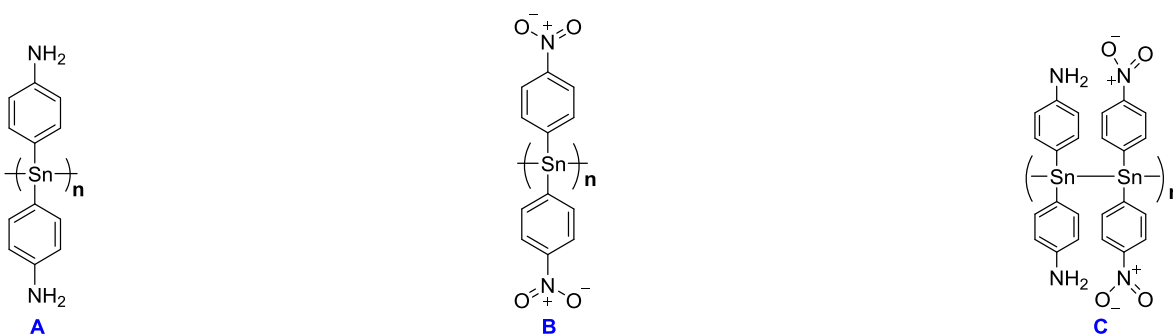
P69

Preparation of a Push-pull Polystannane

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Polystannanes, conjugated polymers consisting entirely of a backbone of Sn atoms, are very susceptible when exposed to light or moisture. Currently, several efforts in our laboratory are directed to identifying ways to increase the stability of these products, including the introduction of new structural features. This approach utilizes electron donating and withdrawing ligands (*p*-aniline and *p*-nitrobenzene, respectfully) attached to the Sn centers that could offer unique photo-physical behaviours including red or blue shifted UV absorbance and photoluminescence. Specifically, this research focuses on creating novel donor and acceptor homo-polymers (**A** and **B**, respectively) by dehydrocoupling routes and an alternating donor-acceptor polystannane (**C**) via a condensation polymerization route. Our target is to enhance the stability of polystannanes.



P70

The Solid State Syntheses of MOFs: A Green and Scalable Method

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In recent years, MOFs have emerged as promising materials for a wide variety of applications ranging from gas storage to sensors¹. A major barrier towards commercialization of these materials is their expensive and energy intensive solvothermal synthesis². Solid-state techniques, such as the ageing and milling of abundant and inexpensive metal oxides with MOF linkers, provide environmentally friendly and cost effective alternatives which avoid the use of bulk solvents and reduce the energy cost³. In this work, MOF-74, a known porous metal organic framework topology which has demonstrated selective gas absorption, separation, and catalysis was synthesized in the solid-state with very high yields. The versatility and selectivity of milling reactions is highlighted.

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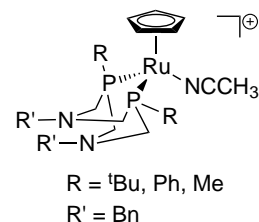
P71

Investigations into the Cooperative Nature of [CpRu(P^R₂N^{R'}₂)(NCMe)]⁺ Complexes

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Cooperative catalysts have expanded our scope for performing difficult transformations. Cooperative interactions between the metal and ligand are critical to facilitate processes such as transfer hydrogenation. Typically cooperative catalysts have an acid/base site on the ligand to facilitate proton transfer steps.¹ Studies that investigate the systematic tuning of these functional sites on the ligand are limited. A class of ligands known as P^R₂N^{R'}₂ ligands can be sterically and electronically altered by varying the R and R'.² In addition to the known complex [CpRu(P^{tBu}₂N^{Bn}₂)(NCMe)]PF₆,³ two new [CpRu(P^R₂N^{Bn}₂)(NCMe)]PF₆ (R = Ph, Me) complexes have been synthesized and characterized. Preliminary reactivity studies towards hydration, and transfer hydrogenation of alcohols and amines will be discussed.



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P72

Formation of a solid solution of LiFePO₄ (Li_{0.6}(Fe²⁺_{0.6}Fe³⁺_{0.4})PO₄)

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The development of electric cars is promoted by companies as they believed to represent the future of transport. Battery materials have been studied in recent years to achieve higher performance and a longer battery life. One of the widely studied materials is LiFePO₄. Several factors make LiFePO₄ interesting as positive electrode but the electronic conductivity is low in the absence of conductive coating. The oxidation of this compound leads to a phase separation between LiFePO₄ and FePO₄ which can be observed by X-ray diffraction. By suppressing this phase separation a semiconducting solid solution is formed that has higher electron conductivity than the separate phases.¹

Four steps are necessary to achieve the formation of the solid solution. First step is a delithiation of carbon-coated LiFePO₄. Atomic emission lithium analysis confirms the formation of FePO₄. Then the samples are heated in a flow of compressed air to remove then carbon coating. Elemental combustion analysis shows the complete elimination. The lithium is re-inserted with lithium iodide³ to produce Li_{0.6}FePO₄ which is confirmed by lithium atomic emission. Finally, the solid solution is formed by heating at elevated temperatures under nitrogen atmosphere followed by a quench at room temperature¹. The product is characterized by three techniques: infrared spectroscopy, UV-visible reflectance and the X-ray diffraction.

P73

Self-Assembled Square-lattice IDA-Copper Sheets; A Comparison of (Alkyl)-IDA-Copper Complexes

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Transition metal complexes have a number of important applications; catalysis and guest exchange, gas storage/separation, and even applications in the field of molecular-based magnets. The ability to adjust the properties of a complex by varying the ligand, its substituents, or the metal center, makes them invaluable. (Alkyl)-IDA-Cu(II) complexes can be formed by the reaction of (Alkyl)-Iminodiacetate with Copper(II) Nitrate; a tridentate ligand coordinating in a *mer* fashion, resulting in carboxylate-bridged, $[(\text{CuIDA})_4]_\infty$ complexes self-assembled into infinite 2x2 sheets. The complexes have been formed with alkyl chains of varying length (C₀, C₁, C₁₀, C₁₂, C₁₆); maintaining the infinite 2x2 sheets. Through comparison of the varying chain length on the ligand, it can be shown that the inter-planar distance is linearly proportional to the length of the alkyl chain present on the amino group. The coordination geometry of the Cu(II) metal ions is that of severely distorted square pyramidal. The Cu(II) metal centers are coordinated by one amino group and four carboxylate groups, two of which coordinate from adjacent complexes in a *syn-anti* fashion forming a square grid. The magnetic interactions depend on the ligand. The longer (alkyl) chain complexes only experience inter-sheet antiferromagnetic coupling and are thus antiferromagnetic as a whole. In contrast the shorter chain complexes experience both inter/intra-sheet antiferromagnetic/ferromagnetic interactions and overall display weak ferromagnetic coupling. These self-assembled (Alkyl)-IDA-Cu(II) complexes stand to serve many unique applications due to their adjustable inter-planar distance and ferromagnetic/antiferromagnetic properties.

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