Room Temperature Photoluminescence Enhancement of Ag_{20} Nanoclusters

Carolina Vega Verduga[1], and Mark S. Workentin*[1]
[1]*University of Western Ontario, 1151 Richmond St, London, ON N6A 3K7*

E-mail of presenting author: cvega2@uwo.ca
E-mail of corresponding author: mworkent@uwo.ca

Photoluminescence properties of silver nanoclusters (Ag NCs) have enabled multiple biological and chemical sensing applications. Ag NCs with mixed-valence metals ($M^{(0)/(I)}$) exhibit remarkable and well-studied photophysical properties.[1] On the contrary Ag(I)-based NCs display PL emission at low temperatures at around 77K resulting from ligand to metal charge transfer.[2] This low emission of Ag(I)-NCs is attributed to the dominance of thermally activated non-radiative transitions, which are supresssed when the system is cooled with liquid nitrogen. Alternatives to enhance PL properties of Ag(I)-NCs at room temperature include core-shell architectural design, template nature and surface modifications.[3] In this work, the PL emission of Ag_{20} NC was modulated by adding rigidity to the Ag NC and selecting an emissive molecule as capping ligand. The effect of the capping ligand is demonstrated by the comparison of PL emission of previously reported Ag(I) NCs.[4] This approach allows us to maintain synthesis conditions and template, reducing the time in synthesis optimization of Ag NCs with different templates. The high yields, scalability and stable precursors of the Ag_{20} NC synthesis makes it a valuable system to explore room temperature luminescence properties of silver-templated nanoclusters.

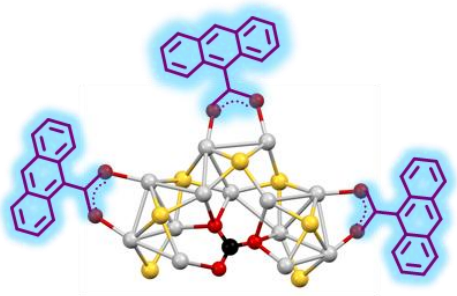


Figure 1. Graphical representation of luminescent Ag_{20} NC

References:

1) X. Liu, T. Ki, G. Deng, S. Yoo, K. Lee, B.-H. Lee, T. Hyeon, M. S. Bootharaju, *Nanoscale* **2024**, *16*, 12329.
2) A. H. Stöckli, J. A. de Jong, C. Vega Verduga, N. H. Vogeler, M. Hesari, P. D. Boyle, J. F. Corrigan, M. S. Workentin, *Small* **2024**, *n/a*, 2405727.
3) S. Biswas, A. K. Das, S. Mandal, *Acc Chem Res* **2023**, *56*, 1838.
4) C. Vega Verduga, Z. Wang, T.-K. Sham, J. F. Corrigan, M. S. Workentin, *Can J Chem* **2025**, DOI 10.1139/cjc-2025-0168.

Scalable, Distributed Quantum Computations on Spin-State Energetics of Strongly Correlated Iron Complexes

Daniel Gómez-Bustos, Rahul Koka, Hans-Arno Jacobsen and Ulrich Fekl*

University of Toronto, Toronto, ON, Canada (DGB, UF: Chemistry; RK: Physics; HAJ: EC Engineering)

E-mail of presenting author: daniel.gomezbustos@utoronto.ca
E-mail of corresponding authors: ulrich.fekl@utoronto.ca

Iron complexes are strongly correlated systems with complex spin-state energetics. Accurately determining the energy separation between different spin states is essential for understanding their reactivity as well as their magnetic and spectroscopic properties. However, simulating these systems remains a significant challenge: routine Density Functional Theory often fails to capture correlation effects, while configuration interaction methods are computationally prohibitive due to their exponential scaling. Quantum computers offer a promising alternative, enabling electronic structure calculations with polynomial scaling and potentially outperforming classical methods. However, near-term noisy quantum devices are limited by their small number of qubits, restricting direct calculations to very small systems.[1] To overcome these limitations, distributed quantum algorithms have been proposed to make quantum chemical calculations in real quantum devices possible. In this work, we present the distributed calculation of spin-energetics in a porphyrin-based iron complex using the Variational Quantum Eigensolver (VQE) framework. We employ a state-averaging approach combined with an orbital-optimization routine to calculate the wavefunction of several spin states and compare their energies.[2] Additionally, the computational workload is distributed using Density Matrix Embedding Theory (DMET),[3] which enables the fragmentation of the studied molecules into smaller subsystems, thus mitigating the current limitations of quantum hardware.
Our results demonstrate a scalable strategy for predicting the spin-energetics of strongly correlated molecular —such as first-row transition metal complexes—on near-term quantum hardware.

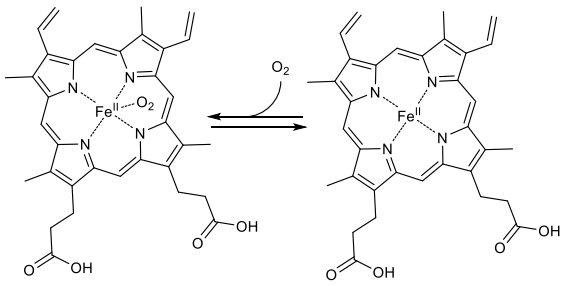


Figure 1. Iron porphyrin in heme b.

References:

1) Skosana, U.; Gumede, S.; Tame, M. **2025**, arXiv:2504.08494
2) Yalouz, S.; Senjean, B.; Günther, J.; Buda, F.; O'Brien T. E.; Visscher, L. Quantum Sci. Technol. **2021**, 6, 024004
3) Wouters, S.; Jiménez-Hoyos, C. A.; Sun, Q.; Chan, G. K.-L. J. Chem. Theory Comput. **2016**, 12, 6, 2706–2719

An Efficient 2,6-di(thiazol-2-yl)pyridine-based Chemosensor for Dual-response Fluorometric and Colorimetric Detection of Fe^{2+} and Cu^{2+}.

Cordelia Y. Adams[1], Yelyzaveta V. Antsybora[1], Alan J. Lough[2], Nisha R. Agarwal[1], and Olena V. Zenkina*[1]
[1]*Ontario Tech University, 2000 Simcoe Street N, City of Oshawa, ON L1G 0C5*
[2]*X-Ray Facility at University of Toronto, Department of Chemistry, Toronto, ON M5S 3H6*

E-mail of presenting author: cordelia.adams@ontariotechu.net
E-mail of corresponding author: olena.zenkina@ontariotechu.ca

We introduced a straightforward synthetic pathway for two novel, simple chemosensors based on 2,6-di(thiazol-2-yl)pyridine (**dthp**) -core ligands. The first chemosensor, 2,6-di(thiazol-2-yl)isonicotinic acid (**2**) is fully water soluble (up to 0.3 g/L (1.04 mmol/L) at ambient temperature). It can be utilized for sensing Fe^{2+} ions in an aqueous environment (aqueous phosphate buffer) by monitoring the absorption signal corresponding to the Metal-to-Ligand Charge Transfer (MLCT) band upon formation of the Fe^{2+} adduct with the receptor. Detection is rapid, and changes in the absorbance band are instantly observable. The limit of detection (LOD) of 0.68 ppm and a limit of quantification (LOQ) of 2.07 ppm at λabs = 560 were established. However, prolonged interaction of the chemosensor with Fe^{2+} ions results in some side reactions, such as the autooxidation of Fe^{2+} to Fe^{3+} by air in phosphate buffer and/or interactions with carboxylic groups, which hamper its application for prolonged measurements or analysis of complex matrices containing metal ions. The methylated analog, methyl 2,6-di(thiazol-2-yl)isonicotinate (**3**), is a dual-response chemosensor, which enables the sensitive and selective detection of Fe^{2+} and Cu^{2+} ions in organic media. Notably, this receptor can detect and differentiate between Fe^{2+} and Cu^{2+} metal ions in the presence of 18 different common competing ions. Chemosensor **3** allow for iron and copper speciation, in other words, can differentiate between Cu^{2+} and Cu^{+} as well as Fe^{2+} and $Fe^{3+}$and is capable of quantifying Fe^{2+} and Cu^{2+} ions at sub-ppm levels. Paper-based solid sensing strips coated with the chemosensor **3** were developed for practical, real-time detection of Fe^{2+} and Cu^{2+}, as well as for their discrimination from competing ions, including Fe^{3+} and Cu^{+}. Additionally, we will present an efficient fluorometric terpyridine-based sensor for Hg^{2+} and Au^{3+}.

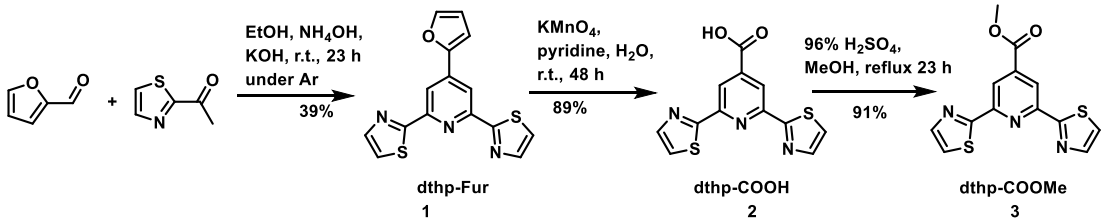


Figure 1. Synthetic route to chemosensors **2** and **3**.

References:

1) Maroń, A.; Kula, S.; Szlapa-Kula, A.; Świtlicka, A.; Machura, B.; Krompiec, S.; Małecki, J. G.; Kruszyński, R.; Chrobok, A.; Schab-Balcerzak, E.; Kotowicz, S.; Siwy, M.; Smolarek, K.; Maćkowski, S.; Janeczek, H.; Libera, M. *Eur. J. Org. Chem.* **2017,** *2017* (19), 2730-2745,
2) Bennett, M. J.; Donaldson, P. B. *J. Am. Chem. Soc.* **1971,** *93* (13), 3307-8
3) Shinpuku, Y.; Inui, F.; Nakai, M.; Nakabayashi, Y. *Journal of Photochemistry and Photobiology A: Chemistry* **2011,** *222* (1), 203-209

Technetium-Based TSPO Targeting Radiotracers for Imaging Inflammatory Neurodegenerative Diseases with SPECT

Ghazaleh Takalloobanafshi,[1,2] Leonard Luyt,[1,3] and Justin W. Hicks[1-3]

[1]Department of Chemistry, Western University, London, ON, Canada,[2]Cyclotron and Radiochemistry Facility, Lawson Research Institute, London, ON, Canada, [3]Department of Medical Biophysics, Western University, London, ON, Canada.

E-mail of presenting author: gtakallo@uwo.ca
E-mail of corresponding author: jhicks53@uwo.ca

The 18-kDa translocator protein (TSPO) is a promising target for imaging and therapy in neuroinflammatory diseases due to its high expression in activated microglia. It has been widely studied using PET with fluorine-18 and carbon-11 tracers such as [^{18}F]DPA-714, [^{11}C]PBR28, and [^{11}C]PK11195.[1] However, PET high operational cost limits accessibility compared to SPECT.[2] In 2014, Denora et al. developed an imidazo[1,2-*a*]pyridine–di(2-picolyl)amine scaffold suitable for technetium-99m (^{99m}Tc; E_γ = 141 keV, $t_{1/2}$ = 6.01 h).[3] Building on this, we designed a compact, neutral, and stable cytectrene-based system to replace the bis-pyridine unit and improve brain uptake.

The TSPO vector CB-3 was prepared according to literature procedures[3] and coupled with Boc-Gly-OH, Boc-β-Ala-OH, and Boc-GABA-OH. After deprotection, the intermediates were reacted with Cp-2 to form precursors for technetium labeling. Because technetium has no stable isotope, the corresponding rhenium analogues were synthesized for chemical characterization by reacting with Re-2. Cp-1, obtained via a 2+3 annulation,[4] was coordinated with $Re_2(CO)_{10}$, hydrolyzed to the carboxycyrhetrene derivative (80% yield), and coupled with TSPO vectors to yield Re-L1–Re-L3 in 30–66% yield and >95% purity.

These results confirm the successful synthesis and characterization of three TSPO-targeted metallodrugs as non-radioactive surrogates of their ^{99m}Tc analogues. In vitro binding studies are underway to support future $^{99m}Tc(H_2O)_3(CO)_3^+$ radiolabeling and imaging experiments.

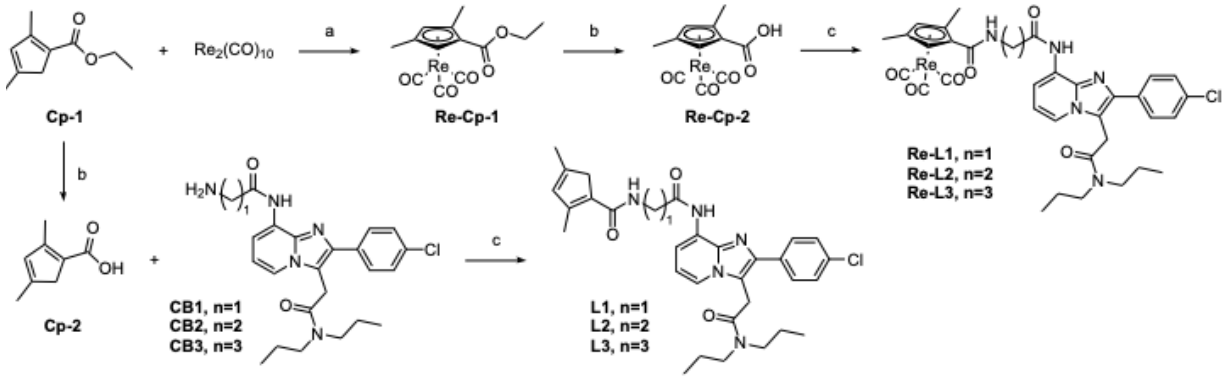


Figure 1. synthesis route of interest compounds of **Re-L1** to **Re-L3.** *a) O-xylene, 220℃, 15′. b) NaOH 1M, MeOH, 100℃, 5′. c) HCTU, DIPEA, DMF, rt, 24h.*

References:

1) Solingapuram Sai, K. K., et al., Sci. Pharm. 2015, 83 (3), 413–427.
2) Takalloobanafshi, G.; et al., Front. Nucl. Med. 2022, 2, 963698.
3) Denora, N., et al., ACS Med. Chem. Lett. 2014, 5 (6), 685–689.
4) Hatanaka, M., et al., J. Chem. Soc. Perkin 1 1993, No. 19, 2269–2274.

An Exploration into the Synthesis and Mechanism of an Unsymmetrical C_6F_5-Substituted 1-Boraindenes

Emily J. Addison[1], Joseph A. Zurakowski[1], David J. Nelson*[2], Marcus W. Drover*[1]
[1]Western University, 1151 Richmond St, London, ON, N6A 3K7, Canada
[2]University of Strathclyde 295 Cathedral Street, Glasgow, G1 1XL, United Kingdom

E-mail of presenting author: eaddiso@uwo.ca
E-mail of corresponding author: david.nelson@strath.ac.uk, marcus.drover@uwo.ca

Heterocycles are one of the largest and most varied families of organic compounds.[1] The introduction of a heteroatom into their cyclic core allows for compound tunability. Heterocycles containing a group 13 element provide a vacant *p*-orbital, extending π-conjugation and allowing for the alteration of molecular properties. Boroles, such as 1-boraindenes, are an example of a class of heterocycles that contain the group 13 element boron in the center of their six-five-six fused ring cycles, allowing for various Lewis acids to bind.[2] Previously, other boron-based heterocycles, such as borafluorenes, have been widely studied, but 1-boraindenes have received significantly less attention.[3–5] Here, we will discuss the synthesis and mechanistic studies of a unique 1-boraindene created through an unusual and complex route.

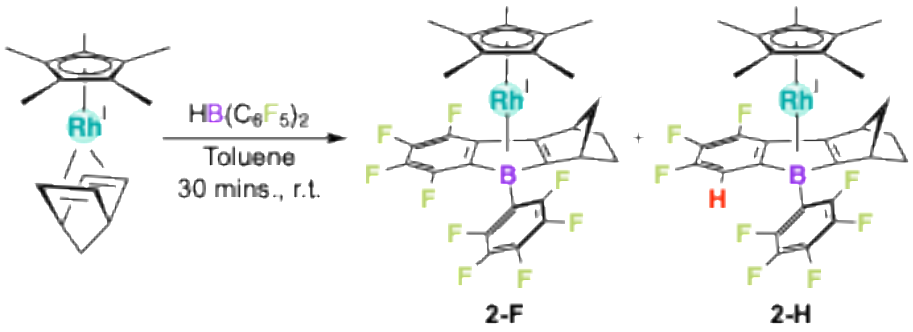


Figure 1. Synthesis of [Cp*Rh(1-boraindene-F)] and [Cp*Rh(1-boraindene-H)].

References:

1) Katritzky, A. R. *Chem. Rev.* **2004**, *104* (5), 2125–2126.
2) Wieprecht, N.; Krummenacher, I.; Wüst, L.; Michel, M.; Fuchs, S.; Nees, S.; Härterich, M.; Braunschweig, H. *Chem. Sci.* **2024**, *15* (31), 12496–12501.
3) Köster, R.; Benedikt, G. *Angew. Chem. Int. Ed. Engl.* **1963**, *2* (6), 323–324.
4) Chase, P. A.; Piers, W. E.; Patrick, B. O. *J. Am. Chem. Soc.* **2000**, *122* (51), 12911–12912.
5) Su, X.; Bartholome, T. A.; Tidwell, J. R.; Pujol, A.; Yruegas, S.; Martinez, J. J.; Martin, C. D. *Chem. Rev.* **2021**, *121* (7), 4147–4192.

Strategies in the Systematic Functionalization of Arenes

Jackie Wu[1], Marc-André Légaré*[1], and Jean-Philip Lumb*[1]
[1]*McGill University, 801 Sherbrooke St W, Montréal, QC H3A 3E8*

E-mail of presenting author: jackie.wu@mail.mcgill.ca
E-mail of corresponding author: ma.legare@mcgill.ca & jean-philip.lumb@mcgill.ca

Multi-functionalized arenes have been a long-standing synthetic challenge to achieve in organic chemistry. Current methods to synthesize highly complex benzenoid motifs in a combinatorial approach utilize systematic cross-coupling reactions.[1] However, the limitation of exploiting halogenated arenes as a cross-coupling partner poses issues with regioselectivity when halogens handles are installed (typically by electrophilic aromatic substitution)[2]. This is because S_EAr is often difficult to install meta-substituents as meta-directors are deactivating (making S_EAr difficult) and overcoming the constraints of *ortho*- and *para*-directors leads to unfavorable regio-isomers. Other methods such as cycloaddition[3] and utilizing benzyne intermediates[4] can also lead to the synthesis of poly-functionalized arenes, though again, not without the same issues of regio- and chemo-selectivity. Recently, the Lumb lab has made quinones an attractive building block for the functionalization of arenes. The hydroquinone, resulting from the reduction of para-quinone, can be used as a scaffold for a poly-arene. Suitable reagents react with quinones to undergo a reductive conjugate addition to append an additional functional handle to the hydroquinone product, providing an adduct for a redox neutral transformation.[5] This work describes the appendage of a main group-based functional handle to a quinone, allowing for a combinatorial approach to obtain poly-functionalized arenes.

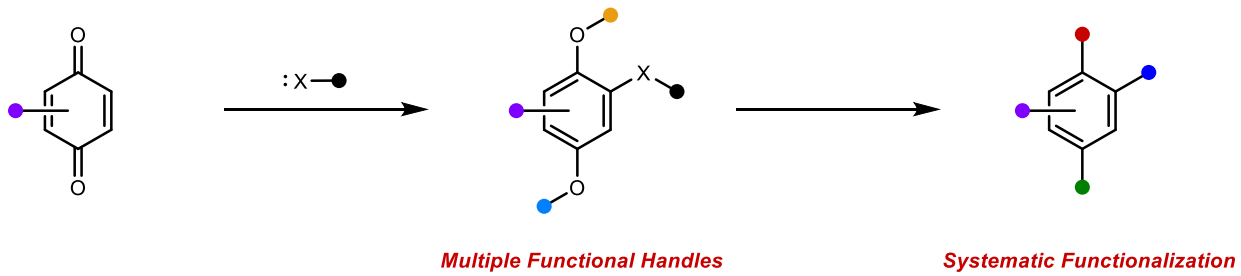


Figure 1. An approach to synthesize poly-substituted arenes from quinones and organophosphorus (III) reagents.

References:

1) Brown, D.G., Boström, J. *J. Med. Chem.* **2016**, *59*, 4443−4458.
2) March, J. Advanced Organic Chemistry: Reactions, Mechanisms, and Structure, 4th ed.; John Wiley & Sons: New York, 1992.
3) Pradhan, S., Mohammadi, F., Bouffard, J. *J. Am. Chem. Soc.* **2023**, *145*, 12214−12223.
4) Shi, J., Li, L., Shan, C., Chen, Z., Dai, L., Tan, D., Lan, Y., Li, Y. *J. Am. Chem. Soc.* **2021**, *143*, 10530−10536.
5) Ramierz, F., Dershowitz, S. *J. Am. Chem. Soc.* **1956**, *78*, 5614–5622.

Wittig Carbenation: From Degradation to a New Beginning in Olefin Metathesis

Samantha K. Cormier,[1] Harrison C. Max ,[1] Eliza-Jayne Y. Boisvert,[1] Michael J. Ferguson,[2] and Deryn E. Fogg*[1,3]

[1]Centre for Catalysis Research & Innovation and Department of Chemistry and Biomolecular Sciences, University of Ottawa, Ottawa, ON K1N 6N5, Canada. [2]X-ray Crystallography Laboratory, University of Alberta, 11227 Saskatchewan Dr., Edmonton, AB T6G 2G2, Canada.[3]Department of Chemistry, University of Bergen, Allégaten 41, N-5007, Bergen, Norway.

E-mail of presenting author: scorm016@uottawa.ca
E-mail of corresponding author: dfogg@uottawa.ca, deryn.fogg@uib.no

Stereoselective and stereoretentive olefin metathesis enabled by **Ru-1** (Figure 1) is opening new doors in materials science, natural products synthesis, and the discovery of new therapeutics for potential antiviral and oncology applications.[1][2] The cis-chelating dithiocatecholate ligand in **Ru-1** is key to stereocontrol. However, it also renders the catalyst extraordinarily oxygen-sensitive.[3] In sharp contrast with the air-stable, readily-handled Hoveyda-Grubbs dichloride catalysts, solutions of **Ru-1** are oxidized within minutes in air at room temperature, undergoing quantitative conversion to metathesis-inactive oxo complex **Ru-2**. Here we demonstrate that oxidation can be readily reversed via "Wittig carbenation": that is, reaction of **Ru-2** with phosphonium ylides, a reaction precluded for most transition metals by the strength of the metal-oxo bond. Further, we demonstrate that the stabilizing ether donor in **Ru-1** is extraneous. The bulk of the H_2IPr ligand is shown to stabilize the [Ru]=CHR intermediate against bimolecular decomposition, even in the absence of the chelating benzylidene ligand. This approach represents a significant advance over the original catalyst design. It offers direct, in situ access to a highly metathesis-active, well-defined alkylidene species from air-stable oxo complex **Ru-2**, eliminating the need for off-site production, shipping, or storage of extremely air-sensitive **Ru-1**. The resulting advances in reactivity, stability, and tractability are anticipated to create new opportunities for the widespread adoption of metathesis methodologies for the production of valuable, stereodefined olefins.

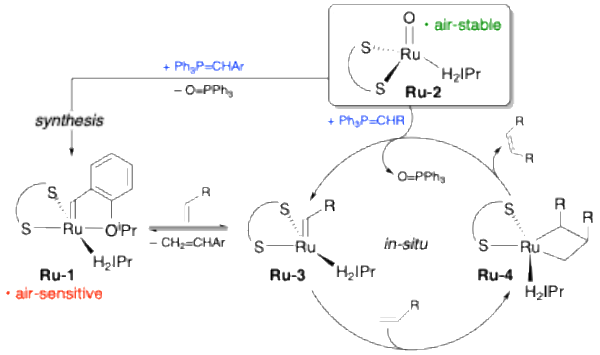


Figure 1. From degradation to catalysis via Wittig carbenation.

References:

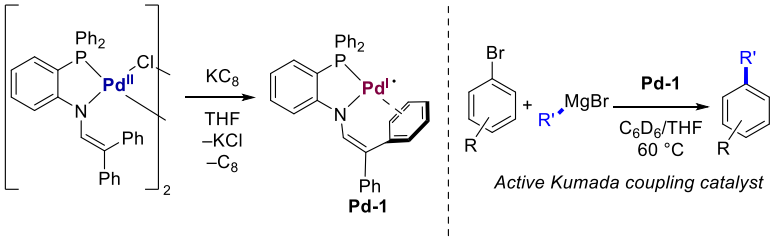
1) Jung, K.; Ahmed, T. S.; Lee, J.; Sung, J. C.; Keum, H.; Grubbs, R. H.; Choi, T. L.,. *Chem. Sci*. **2019**, 10, 8955–8963.
2) Grzesiński, Ł.; Nadirova, M.; Guschlbauer, J.; Brotons-Rufes, A.; Poater, A.; Kajetanowicz, A.; Grela, K., *Nat. Commun.* **2024**, *15*, 8981.
3) Boisvert, E. J.; Max, H.; Fogg, D. E., *ACS Catal.* **2023**, *13*, 2885−2891.

Phosphine-1-Azaallyl Ligand Enabled Mononuclear Pd(I) Catalysis

John S. Lee[1], Alliana L. Dimitrio[1] and Johanna M. Blacquiere*[1]
[1]*Western University, 1151 Western Rd, London, ON N6A 3K7*

E-mail of presenting author: jlee3865@uwo.ca
E-mail of corresponding author: johanna.blacquiere@uwo.ca

Palladium is a ubiquitous metal centre in the field of homogeneous catalysis and is widely used as mononuclear Pd(0) or Pd(II) compounds.[1] Compounds with the rarer Pd(I) oxidation state, specifically dinuclear Pd(I) species, exhibit unique reactivity compared to that of mononuclear Pd(0)/Pd(II) compounds, with greater selectivity and efficiency over traditional systems.[2] Mononuclear Pd(I) species on the other hand, are considerably more rare than even dinuclear Pd(I) compounds. The scarce examples of these compounds in the literature all contain sterically bulky ligands and demonstrates the importance of ligand design in the stabilization of the low oxidation state metal centre.[3,4] The only known examples of catalytic reactivity for these compounds to date are cross-coupling reactions between aryl antimony and aryl trifluoroborate compounds, and Kumada coupling reactions.[3,5] It is currently unclear what range of reactions are possible for mononuclear Pd(I) complexes; more work is required to fully realize their reactivity. Previously in our group, we have explored the chemistry of the dynamic phosphine 1-azaallyl (P^AzA) ligand family, showing how changes in ligand coordination mode can facilitate reactivity.[6] To this end, a new redesigned ligand was developed with phenyl substituents at the 3,3'-positions of the 1-azaallyl group, that impart additional steric bulk and electron delocalizing effects to support a mononuclear Pd(I) centre. Herein we present the synthesis, characterization and reactivity of mononuclear Pd(I) **Pd-1**, stabilized by a P^AzA ligand. The preliminary stoichiometric and catalytic reactivity will be discussed, including unprecedented Heck-type reactivity for mononuclear Pd(I). The results of radical trapping reactions, and its relevance to catalysis will also be discussed.



References:

1) Fricke, C.; Sperger, T.; Mendel, M.; Schoenebeck, F. *Angew. Chem. Int. Ed.* **2021**, 51, 5062-5085
2) Mendel, M.; Gnagi, L.; Dabranskaya, U.; Schoenebeck, F. *Angew. Chem. Int. Ed.* **2023**, 62, e202211167
3) Tran, G.N.; Bouley, B.S.; Mirica, L.M. *J. Am. Chem. Soc.* **2022**, 144, 20008-20015
4) Luo, J.; Tran, G.N.; Rath, N.P.; Mirica, L.M. *Inorg. Chem.* **2020**, 59, 15659-15669
5) Simpson. Q.; Sinclair, M.J.G.; Lupton, D.W.; Chaplin, A.B.; Hooper, J.F. *Org. Lett.* **1018**, 20, 5537-5540
6) Jackman, K.M.K.; Bridge, B.J.; Sauve, E.R.; Rowley, C.N.; Zheng, C.H.M.; Stubbs, J.M.; Boyle, P.D.; Blacquiere, J.M. *Organometallics* **2019**, 38, 1677-1681

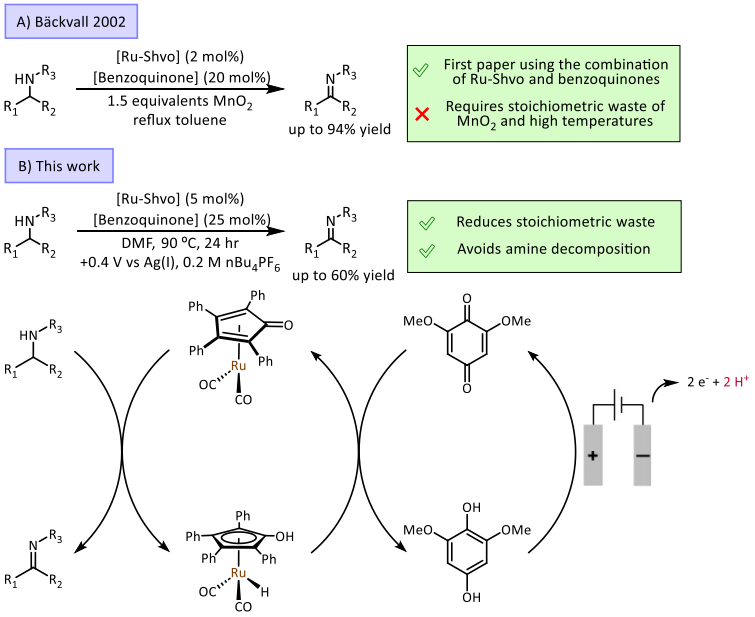
Ruthenium-Catalyzed, Benzoquinone- and Electrochemically-Assisted Amine Dehydrogenation

Ignacio Camarero Temiño[1], Mikhaila D. Ritz[1], William D. Jones*[1]

[1]*Department of Chemistry, University of Rochester, Rochester, NY 14627*

E-mail of presenting author: icamarer@chem.rochester.edu
E-mail of corresponding author: jones@chem.rochester.edu

The oxidation of alcohols and amines to ketones and imines, respectively, is a fundamental chemical transformation with significant industrial relevance, particularly in the synthesis of biologically active synthetic building blocks. Current dehydrogenation strategies either require the use of a stoichiometric amount of organic oxidants or a transition metal pre-catalyst with hydrogen acceptors, resulting in a considerable amount of chemical waste.[1] Traditionally, this transformation has relied on heterogeneous catalysis, primarily using metal oxides, and under high-temperature reaction conditions. In 2002, Bäckvall co-workers reported a ruthenium-catalyzed dehydrogenation of secondary amines using manganese oxide as the terminal oxidant.[2] Building on this work, our group developed an iron-catalyzed dehydrogenation of secondary alcohols, where a stoichiometric amount of manganese oxide was replaced with electrochemically regenerable benzoquinone mediators.[1] My primary objective was to apply this electrochemical strategy to the dehydrogenation of secondary amines. This talk aims to provide a complementary, atom-economical route to imine synthesis by minimizing the need for stoichiometric external oxidants.



Scheme 1. Electrochemical approach to amine dehydrogenation.

References:

1) Ritz, M. D.; Jones, W. D. *European J. Org. Chem.* **2022**, *2022.*
2) Éll, A. H.; Samec, J. S. M.; Brasse, C.; Bäckvall, J. E. *Chem. Comm.* **2002**, *10*, 1144–1145

From Phosphadiazonium Cations to Phosphorus-Nitrogen (PN) Heterocycles

Shrabani Khan[1], Shaun K. Milkovich[1], Paul D. Boyle[1], Joe B. Gilroy[*1]

[1]*Department of Chemistry, The University of Western Ontario, London, Ontario N6A 5B7, Canada*

E-mail of presenting author: skha222@uwo.ca
E-mail of corresponding author: joe.gilroy@uwo.ca

Compounds containing phosphorus-nitrogen (PN) bonds are relatively rare, despite their potential in optoelectronic materials, inorganic polymers, and for understanding structure/bonding and discovering new reactivity.[1] This rarity may stem from both elements being Group 15, and their compounds often acting as Lewis bases.[1] Phosphorus-containing heterocycles in industry typically feature P(V) due to the reactivity of P(III) with oxygen. However, the P(III) lone pair can be beneficial for reacting with metals or in catalysis. The main research gap in this area lies in stabilizing the P(III) center, which could advance phosphorus chemistry and unlock its practical uses. *N*-donor ligands are used for stabilizing low valent atoms, such as phosphadiazonium cations, due to their π-donor ability.[2] *N*-donor ligands are also prominent in optoelectronic materials such as boron difluoride dipyrromethenes (**1**) (BODIPY) and related compounds. While the coordination of heavier main group elements like phosphorus in ligand systems has seen limited exploration compared to lighter counterparts, it offers intriguing possibilities. Replacing boron with phosphorus (**2–4**) can impart desirable properties such as enhanced water solubility, simplified synthesis, and unique donor-acceptor characteristics as well as unique reactivity.[3-4] This presentation will discuss the chemistry of novel phosphorus-nitrogen frameworks (**5**,**6**).[2]

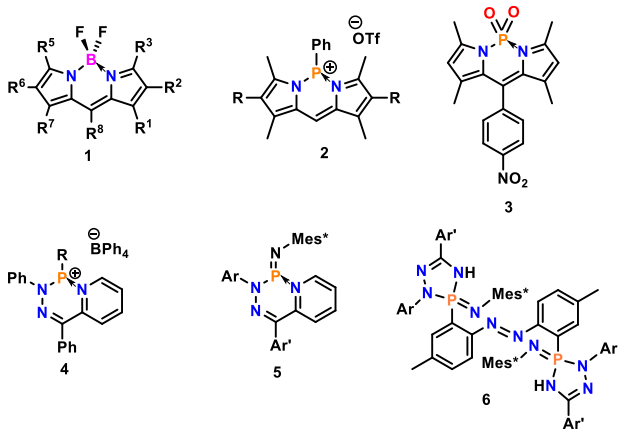


Figure 1. Examples of main group complexes of conjugated *N*-donor ligands.

References:

1) S. Khan, J. B. Gilroy, *Chem. Eur. J.* **2025**, *31*, e202404420.
2) S. K. Milkovich, F. L. Buguis, P. D. Boyle, J. B. Gilroy, *Chem. Eur. J.* **2024**, *30*, e202400569.
3) X.-D. Jiang, J. Zhao, D. Xi, H. Yu, J. Guan, S. Li, C.-L. Sun, L.-J. Xiao, *Chem. Eur. J.* **2015**, *21*, 6079−6082.
4) A. E. R. Watson, M. J. Grant, P. D. Boyle, P. J. Ragogna, J. B. Gilroy, *Inorg. Chem.* **2022**, *61*, 18719−18728

A T-shaped Phosphinidene

Elaina Bourque[1], Douglas Turnbull[1], Keyu Zhao[1], and Marc-Andre Legare*[1]
[1]McGill University, 801 Sherbrooke St W, Montreal, QC H3A 3E8

E-mail of presenting author: elaina.bourque@mail.mcgill.ca
E-mail of corresponding author: ma.legare@mcgill.ca

Organophosphinidenes (RP) constitute an elusive class of compound in which a phosphorus atom at the +1 oxidation state is substituted by a single organic residue.[1] These highly reactive, low-valent species could have intriguing applications in areas such as main-group catalysis if stabilised in a singlet ground state. They are potential ambiphiles due to their combination of nonbonding electron pairs and sub-octet electron configuration.[2] As such, organophosphinidenes are highly reactive molecules and generally exist momentarily as transient intermediates when generated.[1] We present work that shows a singlet organophosphinidene can be accessed by a ligand design that both destabilizes P(+3) states through lone pair repulsions and stabilises P(+1) through weak interactions. These weak interactions modulate the compound's reactivity and preclude decomposition of the molecule, while maintaining much of the organophosphinidene's reactive nature. This strategy allows the synthesis of organophosphinidenes while avoiding oligomerization, the need for redox non-innocent trapping agents, or extreme steric bulk.

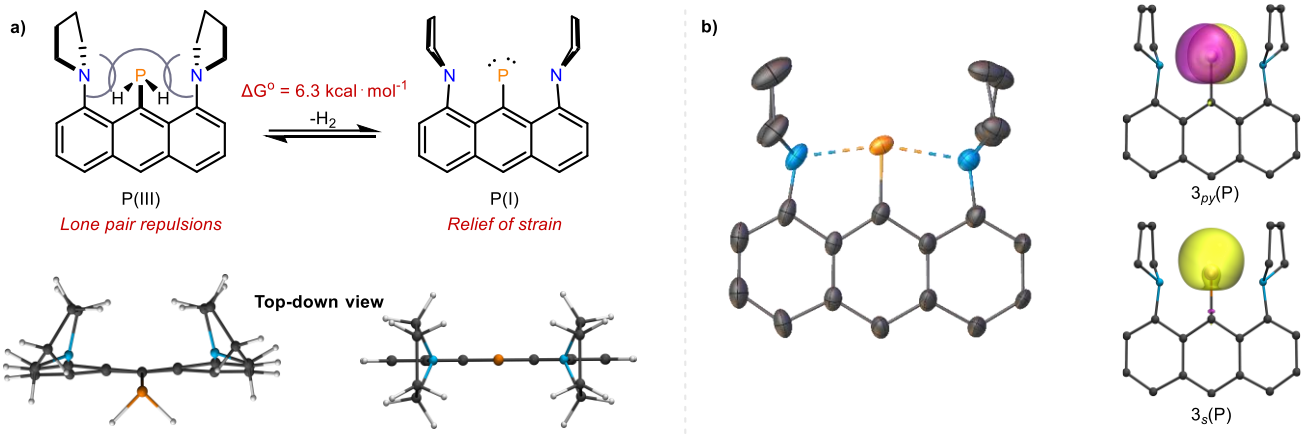


Figure 1. a) Computational analysis of the optimised energies of P(III) vs P(I) when phosphorus is bearing bis-1,8-pyrrolidinylanthracenyl ligand. b) Thermal ellipsoid plot of the organophosphinidene alongside two P-centered NBOs corresponding to the two lone pairs on the singlet organophosphinidene.

References:

1) Mitchell, E. C.; Wolf, M. E.; Turney, J. M.; Schaefer, H. F. Group 15 and 16 Nitrene-Like Pnictinidenes. *Chem. Eur. J.* **2021**, *27* (58), 14461–14471.
2) Lu, B.; Zeng, X. Phosphinidenes: Fundamental Properties and Reactivity. *Chem. Eur. J.* **2024**, *30* (15), e202303283.

Unsymmetrical Imidazopyrimidines: Ligand Design for Selective Multi-metallic Complexes

Ryan J. Scott[1], Mila Abaeva[1], Riley T. Woods[1], Jincheng Ren[1], and Derek J. Schipper*[1]
[1]*University of Waterloo, 200 University Ave, Waterloo, ON N2L 3G1*

E-mail of presenting author: r9scott@uwaterloo.ca
E-mail of corresponding author: derek.schipper@uwaterloo.ca

Bimetallic catalysis, a growing field in coordination chemistry, is dominated by homobimetallic systems over heterobimetallic.[1,2,3] Heteronuclear bimetallic catalyst systems have been shown to be more reactive and selective then monometallic counterparts.[1,3] However, the development of non-symmetric bimetallic catalysts is challenging to do the symmetric nature of many ligands.[1] Previous work in our group has addressed this shortcoming, through the incorporation of a central imidazopyrimidine ring system as a non-symmetric backbone for bimetallic binding.[4] We hereby describe a series of novel multi-nucleating ligands based on the imidazopyrimidine motif. These ligands enable the scalable synthesis of various classes of complexes, including those of copper, nickel, cobalt and palladium. Complexes of these ligands, specifically that of homometallic Copper or Nickel have also shown be promising catalysts in various metal catalyzed reactions. This work serves to diversify heterobimetallic catalysis through the development of a series of ligands with tunable electronic, geometric and steric properties.

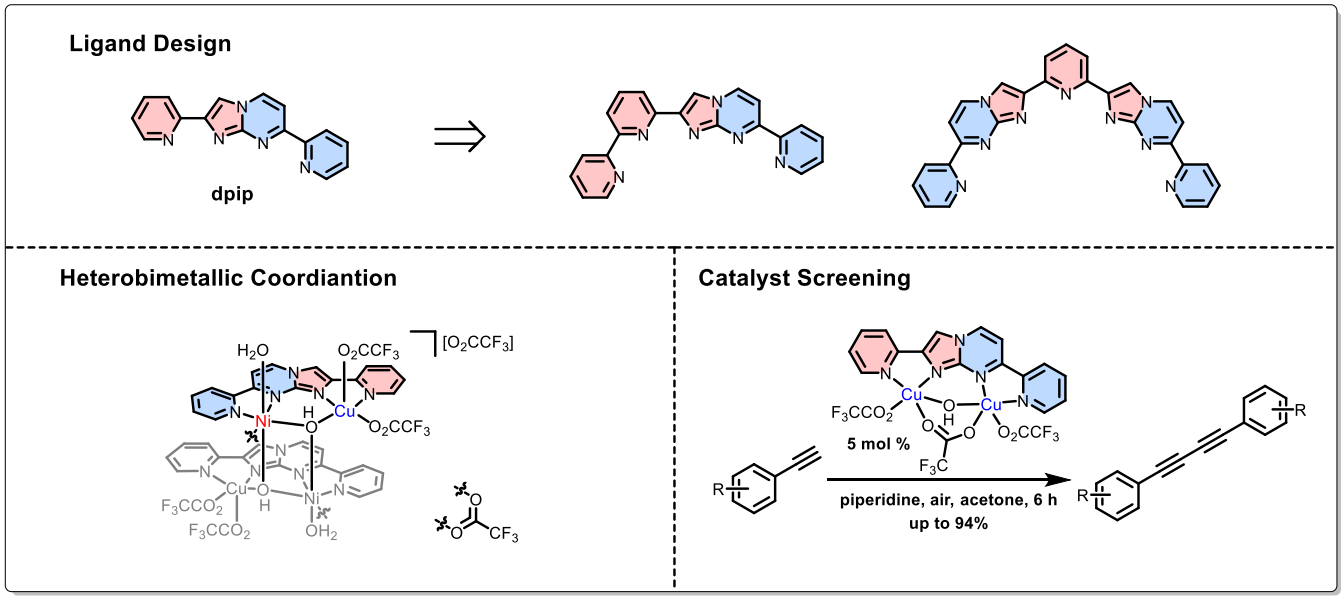


Figure 1. Design of imidazopyrimidine-based ligands, heterobimetallic coordination and catalytic activity of dpip complexes.

References:

1) Desnoyer, A. N.; Nicolay, A.; Ríos, P.; Ziegler, M. S.; T. Don Tilley. *Accounts of Chemical Research* **2020**, *53* (9), 1944–1956.
2) Nicolay, A.; T. Don Tilley. *Chemistry: A European Journal* **2018**, *24* (41), 10329–10333.
3) See, M. S.; Ríos, P.; Tilley, T. D. *Organometallics* **2024**, *43* (10), 1180–1189.
4) Abaeva, M.; Ieritano, C.; Hopkins, W. S.; Schipper, D. J. *Inorganic Chemistry* **2023**, *63* (2), 1010–1019.

Ligandless Iron-catalyzed C(sp^3)-H Bond Fluorination

Aiyireti (Dina) Dilinaer, Marcus Drover*
Western University, 1151 Richmond St, London, ON N6A 3K7

E-mail of presenting author: adilinae@uwo.ca
E-mail of corresponding author: marcus.drover@uwo.ca

Fluorination methods have become a burgeoning area of research following the emergence of increasing fluoro-pharmaceuticals, agrochemicals, and ^{18}F radioisotope-labelled medicines in recent years.[1,2] In the case of pharmaceuticals, fluorine incorporation has been found to increase metabolic stability, enhance membrane permeability, and strengthen binding affinity.[3] As a result, various organic fluorinating reagents have been developed over the past few decades.[4] While in some cases these reagents may be sufficient to achieve fluorination on their own, they are often paired with a transition metal catalyst for improved reactivity.[5]

Herein, we describe an $Fe(OTf)_2$ catalyzed strategy to perform directing group free C(sp^3)-H fluorination without the use of any ligand. This reaction employs mild conditions and low catalyst loading, using Selectfluor as the fluorine source. The reaction optimization, substrates scope, and functional group tolerance of this fluorination strategy will be discussed.

References:

1) R. Halder and T. Ritter, *J. Org. Chem.*, **2021**, *86*, 13873–13884.
2) Saghir Ali, Andrew A. Bolinger, and Jia Zhou, *Current Topics in Medicinal Chemistry*, **2024**, *24*, 843–849.
3) X. Li, X. Shi, X. Li and D. Shi, *Beilstein J. Org. Chem.*, **2019**, *15*, 2213–2270.
4) N. Rozatian and D. R. W. Hodgson, *Chem. Commun.*, **2021**, *57*, 683–712.
5) Purushotam, A. Bera and D. Banerjee, *Org. Biomol. Chem.*, **2023**, *21*, 9298–9315.