



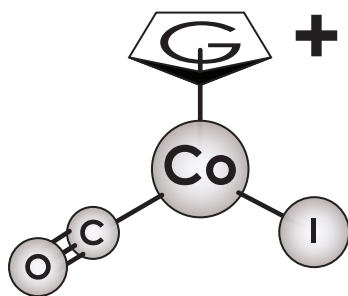
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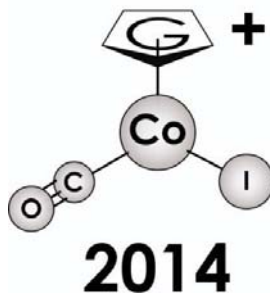
XI Congresso del Gruppo
Interdivisionale di Chimica

Organometallica

24-27 June, 2014

Milano

Abstract Book



Co.G.I.C.O. 2014

XI Congresso del Gruppo Interdivisionale di Chimica Organometallica

24 – 27 June 2014

Milano

ORGANIZED BY

Department of Chemistry

University of Milan

Abstract Book

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Welcome to Co.G.I.C.O. 2014

Welcome to the XI Conference of the Interdivisional Group of Organometallic Chemistry (Co.G.I.C.O.) of the Italian Chemical Society (SCI) which this year will take place at the University of Milan. The Conference has reached its eleventh edition demonstrating that the idea to establish an Interdivisional Group of Organometallic Chemistry (G.I.C.O), since 1991, had a solid scientific basis of common interdisciplinary interests between inorganic and organic chemists. This is also confirmed by the fact that the G.I.C.O., with about 120 members, is one of the largest Interdivisional Groups of the Italian Chemical Society (SCI), even larger than several divisions.

The project of joining in a common scientific activity chemists with a different cultural background has proven to be a winning idea and certainly many scientific collaborations have originated thanks to G.I.C.O. meetings, with a large benefit to the organometallic chemistry community.

Over the years, the accumulation of new and important information on to the chemistry of metals and their potential applications in different fields has led to a noteworthy expansion of the traditional research fields in which organometallic chemistry originated and developed. Indeed, new applications of organometallic compounds have allowed the development of fields such as Bioorganometallic Chemistry, Material Science, Nanotechnology, and Energy

The G.I.C.O. Conference, which takes place every two years, aims to be an opportunity for all researchers working in the field of organometallic chemistry to spread across the scientific community their most recent results, favoring the exchange of ideas, experience and collaboration with other colleagues.

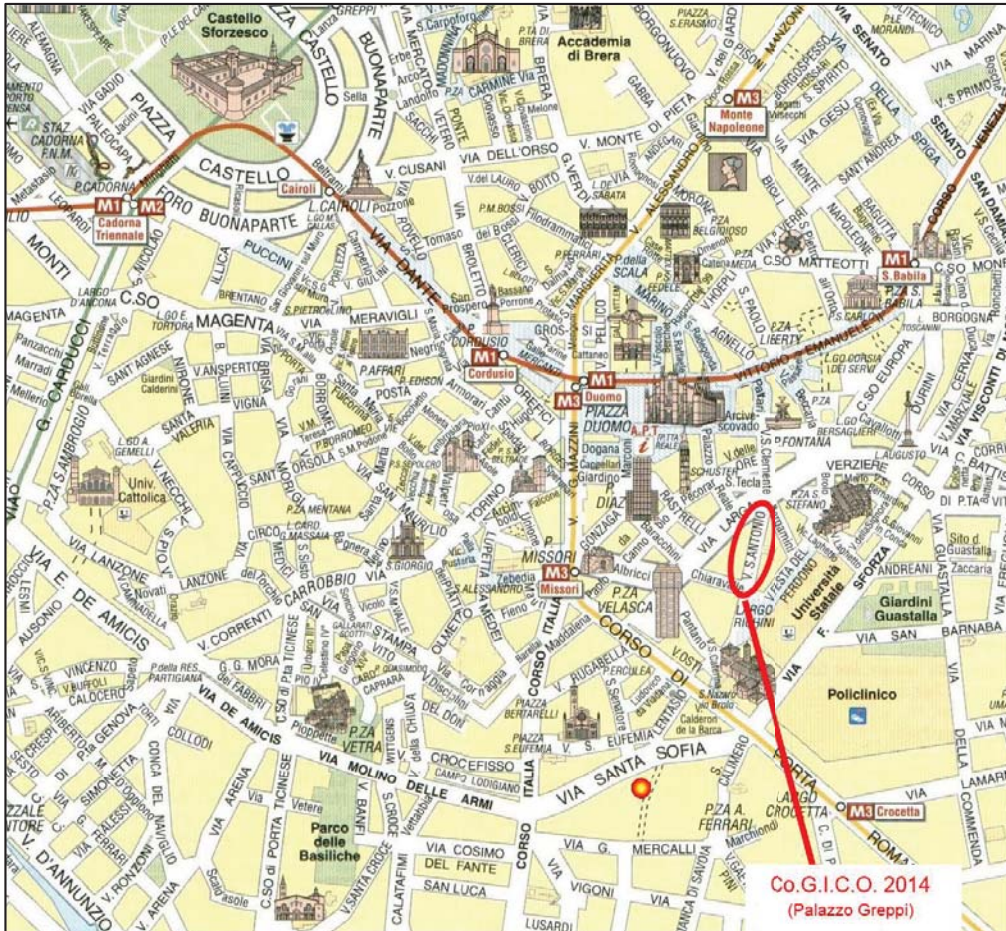
The Co.G.I.C.O. event in Milan is also the occasion to celebrate two different important anniversaries: 90 years since the foundation of the Milan University and 50 years since the graduation course in Chemistry was first established. Indeed, before 1964 only the graduation course in Industrial Chemistry existed, since the foundation of the University.

Benvenuti a Milano !

Emanuela Licandro and Fabio Ragaini

Co.G.I.C.O. 2014 Chairpersons

Map of Milan City Center



General Information

LOCATION

The conference will take place at University of Milan, at Palazzo Greppi, Sala Napoleonica, via S. Antonio 10, located in the city centre of Milan. The University is a five-minute walk from the underground stations of Missori (M3, yellow line) and Duomo (M2/M3, green and yellow lines).

ORAL AND FLASH COMMUNICATIONS

The lecture hall is equipped with a projector and Windows computers. Microsoft Power Point facilities will be available. Memory key is preferred instead of a personal laptop computer. All speakers are kindly invited to contact the conference desk before their presentation.

POSTER PRESENTATIONS

The poster section will take place on Wednesday 25th and Thursday 26th in the Richini open gallery in via Festa del Perdono 7, at a few-minutes walk from the conference room.

The poster dimensions should not exceed 90 cm (w) x 120 cm (h).

A number has been assigned to each poster and will appear on the allotted poster place.

Authors are kindly requested to affix their posters from Wednesday morning.

All posters will be on view throughout the conference.

AWARDS

The Bonati Award (junior) and G.I.C.O. Award (senior) of the SCI will be given during the conference.

The three best posters will receive a "Dalton Transaction Award" consisting in a book provided by RSC.

SOCIAL EVENTS

Welcome Reception will take place on Tuesday 24th at 7.30 pm at *Loggiato d'Onore*, at the first floor of the central courtyard of University of Milan, via Festa del Perdono 7.

The Social Dinner will take place on Thursday 26th at 8.30 pm in the central courtyard of University of Milan, via Festa del Perdono 7.

SCIENTIFIC PROGRAMME

Tuesday, 24th June

12.00 - 15.00 Registration

15.00 - 15.50 Opening Ceremony

Chairman: Luca Banfi

15.50 - 16.40 **PL01 Julio PEREZ** - University of Oviedo
Ligand deprotonation surprises

16.40 - 17.00 **OC01 G. MANCA:** *Electronic aspects of the phosphine oxide/phosphinous acid tautomerism and the assisting role of transition metals*

17.00 - 17.30 *Coffee break*

Chairman: Alceo Macchioni

17.30 - 18.00 **KN01 Valerio ZANOTTI** - University of Bologna
Bond forming reactions at diiron complexes

18.00 - 18.20 **OC02 R. MANSUETO:** *Regioselective desymmetrization of diaryltetrahydro furans via directed ortho-lithiation: building new bridges between polar organometallic chemistry and green chemistry*

18.20 - 18.40 **OC03 R. ARÉVALO:** *Deprotonation of CH₃ groups in coordinated sulfides and phosphines: C-C coupling with diimine coligands*

18.40 - 19.10 **KN02 Claudio PETTINARI** - University of Camerino
Biological and catalytic applications of metal complexes based on scorpionate-type ligands

19.30 **Welcome Reception**

Wednesday, 25th June

Chairman: Fabio Ragaini

- 09.00 - 09.50 **PL02 Matthias BELLER** - University of Rostock
Development of benign catalysts for the pharmaceutical and chemical industry
- 09.50 - 10.10 **OC04 C. NERVI**: *Organometallic complexes for photo and electro-catalytic Reduction of CO₂*
- 10.10 -10.30 **OC05 A. MACCHIONI**: *Activity of pyridine-carbene iridium water oxidation catalysts: methyl, butyl, octyl not futile*
- 10.30 - 11.00 *Coffee break*

Chairman: Giorgio Abbiati

- 11.00 - 11.30 **KN03 Bartolo GABRIELE** - University of Calabria
New catalytic routes to heterocycles
- 11.30 - 11.50 **OC06 L. BANFI**: *Synthesis of complex heterocyclic scaffolds through cascade processes based on multicomponent reactions followed by palladium mediated S_N2' cyclizations*
- 11.50 - 12.10 **OC07 N. DELLA CÀ**: *One-pot Pd/norbornene-catalyzed synthesis of dibenz[*c,e*]oxepin derivatives*
- 12.10 - 12.30 **OC08 F. CONDELLO**: *Selective anticancer ruthenium(II) arene RAPTA type complexes containing curcuminoids*
- 12.30 - 12.50 **OC09 A. BUCCI**: *An iridium catalyst as functional mimic of hydrogenase*
- 12.50 - 15.00 *Lunch*

Chairman: Emanuela Licandro

- 15.00 - 15.50 **PL03 Bernhard K. KEPPLER** - University of Wien
Metal complexes and organometallic compounds in anticancer drug development
- 15.50 - 16.20 **KN04 Angelo NACCI** - University of Bari
Metal nanostructured catalysts for green synthesis
- 16.20 - 17.00 **Poster Flash Communications**
- 17.00 - 17.00 *Coffee break*
- 17.30 – 18.20 **Poster session**
- 18.30 – 20.00 *Assemblea GICO*

Thursday, 26th June

Chairman: Alessandro Mordini

- 09.00 - 09.50 **PL04 Marco BANDINI** - University of Bologna
Stereoselective gold catalysis: keeping complexity in organic synthesis simple
- 09.50 - 10.10 **OC10 A. BIFFIS:** *N-phosphanyl-azolyliidene ligands: coordination chemistry and catalysis*
- 10.10 - 10.30 **OC11 R. MAZZONI:** *Sterically driven synthesis of novel mononuclear Ru and dinuclear Ru-Ag N-heterocyclic carbene complexes*
- 10.30 - 11.00 *Coffee break*

Chairman: Angelo Nacci

- 11.00 - 11.30 **KN05 Alfonso GRASSI** - University of Salerno
Organic transformations catalyzed by gold nanoparticles embedded in polymer matrices
- 11.30 - 11.50 **OC12 V. PIROVANO:** *C-3 functionalization of indoles with methyl 2-acetamidoacrylate under gold(I), silver or Brønsted acids catalysis*
- 11.50 - 12.10 **OC13 R. RUBBIANI:** *Anticancer profile of a novel photo-uncageable rhenium complex*
- 12.10 - 12.30 **OC14 T. PEDRAZZINI:** *Application in asymmetric cyclopropanation of new chiral macrocycles*
- 12.30 - 12.50 **OC15 M. JIA:** *Gold catalyzed enantioselective dearomative [2+2] reaction of indoles with allenamides*
- 12.50 - 15.00 *Lunch*

Chairman: Silvia Bordoni

- 15.00 - 15.50 **PL05 Silvia CAUTERUCCIO** - University of Milan (**Bonati Award**)
From the direct C-H arylation of azoles to the synthesis of chiral helical phosphorus ligands: a journey through the eclectic world of the organo metallic catalysis
- 15.50 - 16.20 **KN06 Giorgio ABBIATI** - University of Milan
The neglected brother: silver catalyzed domino reactions involving alkynes
- 16.20 - 17.00 **Poster Flash Presentations**
- 17.00 - 17.00 *Coffee break*
- 17.30 - 18.20 **Poster session**
- 20.30 *Social Dinner*

Friday, 27th June

Chairman: Antonella Dalla Cort

09.20 - 10.10 **PL06 Marta CATELLANI** - University of Parma (**GICO Senior Award**)
Palladium/norbornene catalysis in organic synthesis

10.10 – 10.30 **OC16 F. FERRETTI:** *Novel palladium-Ar-BIAN multinuclear complexes*

10.30 - 11.00 *Coffee break*

Chairman: Valerio Zanotti

11.00 - 11.20 **OC17 L. VERONESE:** *First dye-sensitized solar cells based on rhenium complexes as photosensitizers*

11.20 - 11.40 **OC18 A. BONETTI:** *Unusual chemoselective Rh(II)-catalysed transformations of α -diazocarbonyl-piperidine cores*

11.40 - 12.30 **PLO7 Carlo MEALLI** - CNR - ICCOM Firenze
Theoretical interpretations of catalytic profiles: radical C-H/olefin activations promoted by metal intersystem crossing

12.30 – 12.50 **Closing remarks**

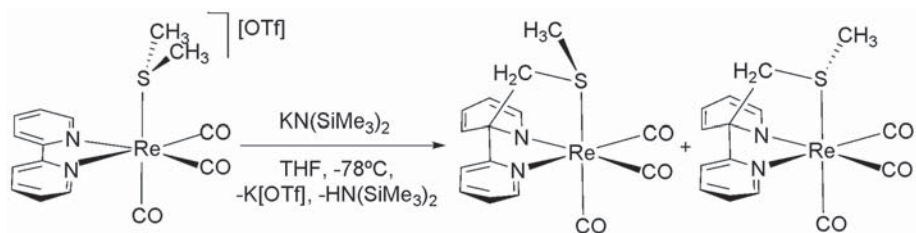
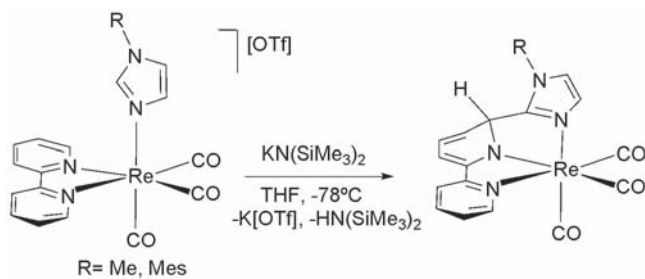
PLENARY LECTURES

Ligand Deprotonation Surprises

Julio Perez^{a,b}, Lucia Riera^b^aUniversidad de Oviedo, Oviedo, Spain.^bCINN-CSIC, Llanera, Spain.

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Coordination to $\text{Re}(\text{CO})_3$ fragments facilitates the deprotonation of endocyclic CH groups of imidazoles and pyridines, and of methyl substituents in imidazoles, pyridines, sulfides and phosphines, and their selective coupling under mild conditions to *cis* co-ligands such as imidazoles,¹ pyridines,² bipy, nitriles and isonitriles.



References

- Huertos, M. A.; Perez, J.; Riera, L.; Diaz, J.; Lopez, R. *Chem. Eur. J.* **2010**, *16*, 8495-8507.
- Espinal Viguri, M.; Perez, J.; Riera, L. *Chem. Eur. J.* **2014**, *20*, 5732-5740.

Acknowledgements: This work was funded by Ministerio de Economía y Competitividad

PL02

Development of Benign Catalysts for the Pharmaceutical and Chemical Industry

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Despite numerous important methodological advancements in all areas of chemistry, still most organic synthesis as well as the industrial production of chemicals can be improved. Currently, more than 80% of all products of the chemical industry are made via catalysis. In this regard, the development of new and more efficient catalysts constitutes a key factor for achieving a sustainable production of all kinds of chemicals today and in the future. Here, several major challenges will be presented in the talk; e.g. the use of mixtures for the synthesis of bulk chemicals. Furthermore, it will be shown that recently developed molecular-defined as well as nano-structured cobalt and iron catalysts enable us to perform catalytic hydrogenation processes with high yields and unprecedented selectivity. Specific examples which demonstrate the potential of catalytic processes with bio-relevant metal complexes compared to more traditional catalytic reactions will include hydrogenations and dehydrogenations as well as applications in the energy sector. In the future, also for industrial processes improved economics based on the presented novel catalysts might be expected.

References

1. S. Das, B. Wendt, K. Möller, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2012**, *51*, 1662.
2. F. Westerhaus, R. Jagadeesh, G. Wienhöfer, M.-M. Pohl, J. Radnik, A.-E. Surkus, K. Junge, H. Junge, M. Beller, *Nature Chem.* **2013**, *5*, 607-612.
3. M. Nielsen, E. Alberico, W. Baumann, H.-J. Drexler, H. Junge, S. Gladiali, M. Beller, *Nature* **2013**, *494*, 85-89.
4. A. Boddien, C. Federsel, P. Sponholz, R. Jackstell, H. Junge, G. Laurency, M. Beller, *Chem. Envir. Sci.* **2012**, *5*, **8907-8911**.
5. A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurency, R. Ludwig, M. Beller, *Science* **2011**, *333*, 1733-1736.

Metal Complexes and Organometallic Compounds in Anticancer Drug Development

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Even in the era of targeted therapies, efforts to develop metal compounds for cancer therapy are continuing. Advances are being made in all stages, from synthesis of innovative classes of compounds to clinical evaluation of investigational new drugs. Particularly remarkable results have been reported for the ruthenium(III) complex NKP-1339 from a clinical trial by Von Hoff and co-workers.¹ Anticancer activity was observed at well tolerable doses in heavily pretreated patients with various solid tumors, among them, most notably, gastro-intestinal neuroendocrine tumors which are poorly responsive to established medicinal treatments.

An example for compounds in advanced preclinical development is the class of methyl-substituted oxaliplatin derivatives, for which a synthetic route to enantiomerically pure compounds could be established. Some of these derivatives are superior to the parent drug in terms of both activity and tolerability in murine tumor models.² Remarkably, these minor structural changes are associated with major pharmacological changes, such as a reduced dependence on immunogenic cell death induction and reduced signs of the dose-limiting neuropathy as compared to oxaliplatin.³

Classes of organometallic compounds containing ruthenium, osmium or rhodium have recently been synthesized mainly with biologically active ligands with the intention to make use of possible synergies between the cytotoxicities of both the metal-containing scaffold and the respective class of ligands. Envisaged activities are, among others, topoisomerase inhibition, induction of oxidative stress and perturbation of cell cycle regulation. Candidate compounds for drug development still have to be identified and selected.

References

1. Dickson, N. R., Jones, S. F., Burris, H. A., Ramanathan, R. K., Weiss, G. J., Infante, J. R., Bendell, J. C., McCulloch, W., Von Hoff, D. D. *ASCO Annual Meeting* **2011**, abstract #2607.
2. Abramkin, S. A., Jungwirth, U., Valiahdi, S. M., Dvorak, C., Habala, L., Meelich, K., Berger, W., Jakupec, M. A., Hartinger, C. G., Nazarov, A. A., Galanski, M., Keppler, B. K. *J. Med. Chem.* **2010**, *53*, 7356-7364.
3. Jungwirth, U., Xanthos, D. N., Gojo, J., Bytzek, A. K., Körner, W., Heffeter, P., Abramkin, S. A., Jakupec, M. A., Hartinger, C. G., Windberger, U., Galanski, M., Keppler, B. K., Berger, W. *Mol. Pharmacol.* **2012**, *81*, 719-728.

Stereoselective Gold Catalysis: Keeping Complexity in Organic Synthesis Simple

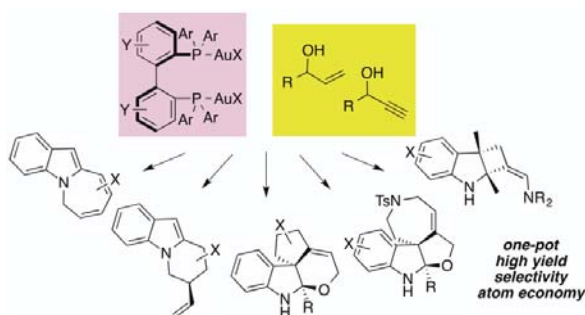
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Approaching chemical complexity in a sustainable manner is a mandatory issue in the modern organic synthesis. In this direction, chemical methodology is featuring an astonishing growth in terms of readily available/not hazardous starting materials, waste production and minimization of process costing. **Indole**-based alkaloids are an inspiring platform to test new chemical catalytic systems due to their not trivial molecular architectures combining saturated as well as unsaturated polycyclic fused structures with multiple stereogenic centers in stereochemically defined manner. In this context, dealing with densely functionalized compounds, the use of site selective transformations/catalysts is required.

Asymmetric gold(I) catalysis is rapidly become a mature reality in the asymmetric synthetic scenario due to the possibility to engage unactivated unsaturated hydrocarbons in single-step or cascade transformations. In this communication, the latest findings towards the realization of densely functionalized polycyclic indolyl cores (*i.e.* azepino-indoles, oxazino-indoles)¹ and dearomatized indoline/indolenine frameworks, under the assistance of chiral gold(I) complexes are presented. In addition, the use readily available environmentally friendly π -activated **alcohols** as acyclic precursors will be highlighted.



References

1. a) Cera, G.; Piscitelli, S.; Chiarucci, M.; Fabrizi, G.; Goggiamani, A.; Ramòn, R. S.; Nolan, S. P.; Bandini, M. *Angew. Chem., Int. Ed. Engl.* **2012**, *51*, 9891-9895. b) Chiarucci, M.; Mocci, R.; Syntrivanis, L. D.; Cera, G.; Mazzanti, A.; Bandini, M. *Angew. Chem., Int. Ed. Engl.* **2013**, *52*, 10850-10853.

Acknowledgements: This work was funded by Progetto FIRB – Futuro in Ricerca (2008) and University of Bologna.

From the Direct C-H Arylation of Azoles to the Synthesis of Chiral Helical Phosphorus Ligands: a Journey through the Eclectic World of the Organometallic Catalysis

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Regio and stereoselective synthesis using organometallic catalysts is currently one of the most active areas of research in organic chemistry. A rapid progress in the study of organometallic and coordination compounds has led to the development and successful industrial application of a number of catalytic processes based on use of these compounds as catalysts. The major advantage of organometallic catalysis is selectivity, and the ability to produce pure products in high yield.

Two different topics in the field of the transition metal complex catalyzed regio and stereoselective organic transformations will be addressed. The first topic will concern the regioselective palladium- and/or copper-mediated direct C-H arylation of π -electron-rich heteroarenes with (hetero)aryl halides. Recently, the transition metal-catalyzed direct arylation of heteroaromatic compounds has emerged as an attractive strategy for the effective construction of aryl-aryl bonds which, unlike the traditional metal-catalyzed cross-coupling strategies involving preformed organometallic reagents, enables direct elaboration of heterocyclic cores without the use of preactivated coupling partners.¹ In the second issue, the study of a new class of thiahelixene-based phosphanes as potential innovative chiral ligands in asymmetric organometallic catalysis will be discussed, especially in the homogenous rhodium(I)-catalyzed hydrogenation reactions, and gold(I)-catalyzed cycloisomerizations. Although helixenes displaying phosphorus functions represent promising scaffolds for applications in enantioselective organometallic catalysis,² To date their use in this field is still in its infancy, especially in terms of number of compounds as well as structural diversity.

References

1. Alberico, D.; Scott, M. E.; Lautens, M. *Chem. Rev.* **2007**, *107*, 174-238.
2. Narcis, M. J.; Takenaka, N. *Eur. J. Org. Chem.* **2014**, 21-34.

PL06

Palladium/norbornene Catalysis in Organic Synthesis

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Synthetic perspectives will be discussed of a methodology for selective functionalization of arenes. A catalytic system containing both an inorganic and organic component, such as palladium and norbornene, enabled us to obtain the selective incorporation of a series of different molecules and groups into a complex structure. Mechanistic studies of the organometallic system responsible for this reactivity allowed the identification and isolation of relevant intermediates.

The key for the success of this methodology is the temporary construction of a palladacycle able to direct the reaction steps with a precise chemo-, regio- and stereochemistry. Palladium and norbornene act in a concerted way to form a metallacycle by olefin insertion into an aryl-palladium bond and subsequent cyclization. The resulting species further reacts with organic compounds through a palladium(IV) complex. Reductive elimination brings back a palladium(II) intermediate which allows norbornene expulsion. Subsequent steps lead to termination of the process with liberation of the organic product together with palladium(0).

Several classes of compounds of interest to pharmaceutical industry and not easily accessible by conventional ways can thus be prepared by very simple and efficient synthetic procedures under mild conditions.

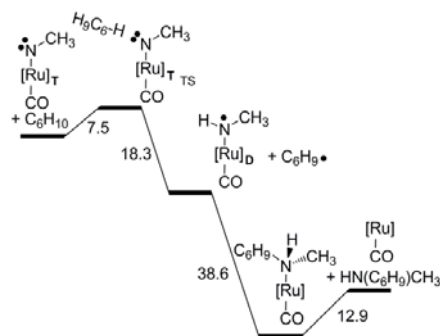
Theoretical Interpretations of Catalytic Profiles: Radical C-H/Olefin Activations Promoted by Metal Intersystem Crossing

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Since my early years in research, I tried to interpret chemical bonding and reactivity (especially of TM compounds) based on X-ray structures. Also, I used MO methods (the EHMO one, when *ab-initio* was still inadequate) and perturbation theory (PT) to describe electrons in molecules and their rearrangement upon reactivity. Today, the PT concepts are still a guideline, although the DFT calculations indicate the key intermediates in a reaction and provide reliable energy profiles. Based on these underpinnings, numerous catalytic processes were examined.¹⁻⁴

Here, I present the computational analysis of the catalytic amination promoted by the Ru-porphyrin ([Ru]) moieties developed by E. Gallo and her group. In the chemistry, the radical mechanism plays a key role. Provided a metal vacant position (the CO ligand removal is carefully examined), the initial diamagnetic system activates one or two RN₃ azide molecules with the eco-friendly N₂ release and the *in-situ* formation of imido ligand(s). The resulting mono- or bis-imido species promote distinct, yet comparable, catalytic cycles, where a C-H bond of an organic R'-H substrate (*e.g.*, cyclohexene, C₆H₁₀) is homolytically activated to afford different amine products and by-products. The presence of radicals, undefined in the experiments, can be theoretically corroborated. Indeed, an imido diradical is accessed through metal intersystem crossing (singlet→triplet), while NR is still bound to the metal. Spin unpairing is endergonic for the mono-imido complex, whereas the energy cost is not prohibitive for the diimido one. In the latter case, the spin delocalization extends over the N-Ru-N axis, ensuring diradical character to both the N atoms with singly populated orthogonal orbitals. The points emerge from wavefunctions, spin density plots and scans to evaluate the Minimum Energy Crossing Point (MECP). The diradical RN character is exerted toward a R'-H organic substrate, with the H atom first anchoring to N (see Figure) and followed by the •R' release. Provided a sufficient stability, the latter radical either approaches the just



formed amido-type ligand in the same molecule (*i.e.*, the monoradical •H-N-R) or its equivalent in a different one. These possibilities are in agreement with various amino products forming through the “rebound mechanism”, already proposed for comparable oxo species but unknown for N analogues. In the talk, the formation of several by-products, detected in the experiments (even a bimetallic species), are rationalized. The mentioned study has just appeared in the literature,⁵ but the easily accessed triplet state of the catalyst(s) suggests other extensions, such as a radical activation of an olefin C=C bond to give aziridine (study in progress).

References: 1) Perez-Carreño E.; Paoli, P.; Ienco A.; Mealli C. *Eur. J. Inorg. Chem.* **1999**, 1315. 2) Catellani M.; Mealli C.; Motti E.; Paoli P.; Perez-Carreño E.; Pregosin P. *J. Am. Chem. Soc.* **2002**, *124*, 4336. 3) Monnier F.; Vovard-Le Bray C.; Castillo D.; Aubert V.; Dérien S.; Dixneuf P. H.; Toupet L.; Ienco A.; Mealli C. *J. Am. Chem. Soc.*, **2007**, *129*, 6037. 4) Baratta W.; Baldino S.; Calhorda M.J.; Costa P.J.; Esposito G.; Herdtweck E.; Magnolia S.; Mealli C.; Messaoudi A.; Mason, S.; Veiros L. *Chem. Eur. J.* **2014**, *accepted*. 5) Manca G.; Gallo E.; Intriери D.; Mealli C. *ACS Catal.* **2014**, *4*, 823.

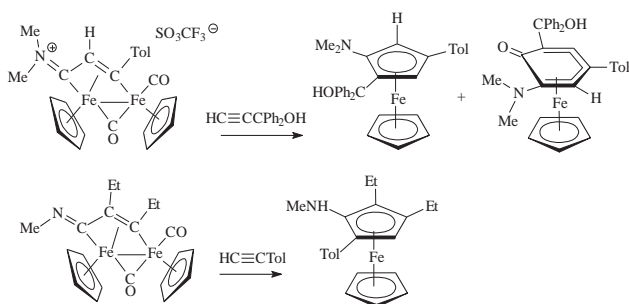
KEYNOTE LECTURES

Bond Forming Reactions at Diiron Complexes

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Increasing attention to sustainability and the need for new catalysts based on more cost-effective and benign transition metal compounds has produced an exponentially grown interest toward iron mediated bond formation. In this field, diiron complexes can play a distinctive role in that they combine advantages associated to iron with those due to the presence of two adjacent metal centres.¹ We have previously reported on C-C and C-heteroatom bond formation occurring at bridging hydrocarbyl ligands L (L = carbyne, vinylalkylidene, vinyliminium etc.) in complexes of the type $[\text{Fe}_2(\mu\text{-X})(\mu\text{-CO})(\text{CO})_n\text{Cp}_2]$ ($n = 1, 2$).² Here we focus on the [3+2] cycloaddition of bridging C3 ligands with alkynes, to form polysubstituted ferrocenes. The reaction has a general character, in that different $\mu\text{-C3}$ ligands can be involved (e.g. vinyliminium, vinylalkylidene, bis-alkylidenes and enimes) and provides a synthetic route to ferrocenes in which only one of the cyclopentadienyl ring contains different substituents and functional groups. Two examples are reported in the following scheme.



A second point concerns the use of diiron complexes the type $[\text{Fe}_2(\mu\text{-L})(\mu\text{-CO})(\text{Cp}2)(\text{CO})(\text{L}')]$ containing bridging hydrocarbyl ligands (L), as hydrogen-producing electrocatalysts. We have found that, in a few cases, they can act as valuable electrocatalysts, in spite of the fact they do not contain $\mu\text{-thiolate}$ ligands, and, therefore, do not closely resemble the diiron unit of the $[\text{FeFe}]$ hydrogenase.

References

1. Mazzoni, M.; Salmi, M.; Zanotti, V. *Angew. Chem., Eur. J.* **2012**, *18*, 10174-10194.
2. Zanotti, V. *Pure and Appl. Chem.* **2010**, *82*, 1555-1568.

Biological and Catalytic Applications of Metal Complexes Based on Scorpionate-type Ligands

Dedicated to Daniela Pucci

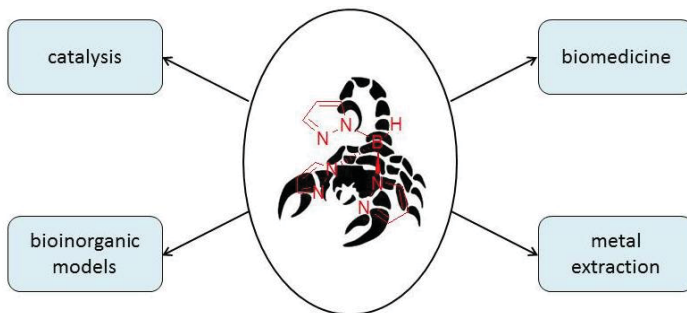
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Since poly(pyrazolyl)borates were first synthesized by Trofimenko in the late 1960s,¹ numerous papers have been published describing these ligands. Poly(pyrazolyl)borates and their analogues are also known as scorpionate ligands and, apart from Trofimenko himself,² several authors have reviewed their coordination chemistry and applications in catalysis, bioinorganic model systems, metal extraction, and biomedicine. A useful property of this N₃-donor tripodal ligands is the ability to tune both their electronic and steric properties by adding the desired R substituents to control steric bulk and donating ability. We report here the chemistry of a number of scorpionate ligands (Tp^x, Tpms, bpza, H_{4-n}C(pz^x)_n) with different transition metal ions of group 8-12 elements, of diverse electronic and stereochemical predilections, together with X-ray structure determinations of their metal complexes, in order to better define the role and extent of the substituent in the heterocyclic rings in determining the coordination behaviour.



References

1. (a) Trofimenko, S. *J. Am. Chem. Soc.* **1966**, *88*, 1842–1844; (b) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170–3177. Surname, M. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 322–325.
2. (a) Trofimenko, S., *Chem. Rev.* **1993**, *93*, 943–980; (b) Trofimenko, S. *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*; Imperial College Press: London, **1999**; (c) Trofimenko, S. *Polyhedron* **2004**, *23*, 197–203.

Acknowledgements: This work was funded by University of Camerino

KN03

New Catalytic Routes to Heterocycles

Bartolo Gabriele

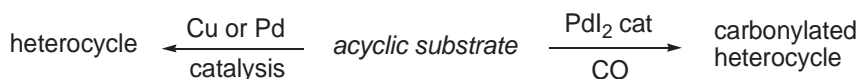
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In this lecture, some novel catalytic approaches, recently developed in our laboratories, to the synthesis of heterocyclic derivatives starting from readily available acyclic substrates will be described.¹

The presentation will be divided in two parts: in the first part, palladium- and copper-catalyzed annulation processes will be discussed, while the second part will focus on PdI₂-catalyzed carbonylative heterocyclizations.



References

1. Reviews: (a) Gabriele, B.; Mancuso, R.; Salerno, G. *Eur. J. Org. Chem.* **2012**, 6825-6839; (b) Gabriele, B.; Salerno, G.; Costa, M. *Top. Organomet. Chem.* **2006**, 18, 239-272; (c) Gabriele, B.; Salerno, G.; Costa, M. *Synlett* **2005**, 2468-2483; (d) Gabriele, B.; Salerno, G.; Costa, M.; Chiusoli, G. P. *Curr. Org. Chem.* **2004**, 8, 919-946.

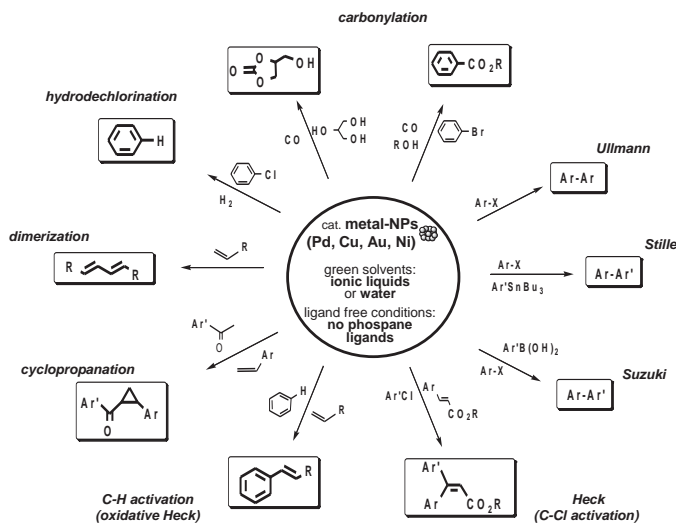
Metal Nanostructured Catalysts for Green Synthesis

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Transition-metal nanoparticles (NPs) are attracting a great deal of attention in almost any scientific and technological field, including catalysis, where nanoscale materials are becoming more prevalent in a wide range of applications such as fuel conversion, pollution abatement and fine chemical production.¹ An increasing interest is also devoted nowadays to properly exploit the high activity and selectivity of nanocatalysts in order to develop greener and waste-minimized processes. From the Green Chemistry standpoint, new nanocatalysts must be designed to operate under environmentally friendly (for instance phosphine-free) conditions or in neoteric green solvents (e.g. ionic liquids, supercritical fluids, water and so on).² In this context, during the last decade, we exploited the use of nanostructured metal catalysts based on Pd, Cu, Au, and Ni to perform a wide range of C-C bond forming reactions (like Heck, Suzuki, Stille, carbonylations and Ullmann couplings) using tetraalkylammonium ionic liquids and water as green reaction media.³



This lecture deals with our recent advances in controlling the catalyst performances by choosing properly the nature of the ionic liquid or the aqueous medium.

1. Astruc, D.; Lu, F.; Aranzas J. R.. *Angew. Chem.* **2005**, 117, 8062-8083; *Angew. Chem. Int. Ed.* **2005**, 44, 7852-7872. 2. Pârvulescu, V. I.; Hardacre, C.; *Chem. Rev.* **2007**, 107, 2615-2665. 3. a) Calò, V.; Nacci, A.; Monopoli, A.; Cotugno, P. *Angew. Chem. Int. Ed.* **2009**, 48, 6101-6103; b) A Monopoli, P Cotugno, G Palazzo, N Ditaranto, B Mariano, N Cioffi, F. Ciminale, A. Nacci *Adv. Synth. & Catal.* **2012** 354 (14-15), 2777-2788.

Organic Transformations Catalyzed by Gold Nanoparticles Embedded in Polymer Matrices

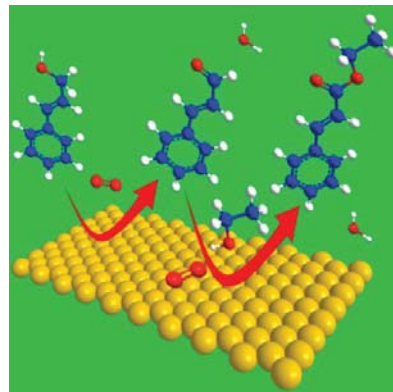
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Gold nanoparticles (AuNPs) with narrow dimensional distribution were successfully incarcerated in a semicrystalline nanoporous polymer matrix based on syndiotactic polystyrene. This catalyst was found highly active in the aerobic oxidation of a variety of allyl and benzyl alcohols to yield the corresponding aldehydes under mild conditions using oxygen as oxidant and water as solvent.¹ The direct oxidative coupling of these alcohols with alkyl alcohols led to a cascade of oxidation reactions that produces, one pot, the corresponding alkyl esters. E.g. alkyl cinnamates of commercial interest were obtained in the oxidation of cinnamyl alcohol in the presence of methanol or *n*-butanol.² Kinetic investigation of these reactions allowed to assess the rate determining steps and the role of the host polymer matrix in determining the high catalytic efficiency and selectivity of the incarcerated AuNPs. Similar results were obtained with AuNPs embedded in a commercial nanoporous polymer matrix, namely polyphenylenoxide (PPO). A comparison of the performances of the two catalysts will be discussed.

Under appropriate reaction conditions the course of the oxidation reactions radically changed leading to unexpected products. Pieces of experimental evidences suggest a radical pathway in some of the investigated reactions.



References

1. Buonerba, A.; Cuomo, C.; Ortega Sánchez, S.; Canton, P.; Grassi, A. *Chem. Eur. J.* **2012**, 18, (2), 709-715.
2. Buonerba, A.; Noschese, A.; Grassi, A. *Chem. Eur. J.* **2014**, 20, (18), 5478-5486.

Acknowledgements: This work was funded by Ministero dell'Istruzione dell'Università e della Ricerca (MIUR) (FARB-2013) and POR Campania FSE 2007-2013, "Sviluppo di reti di eccellenza tra Università – Centri di Ricerca -Imprese", Asse IV, "Materiali e strutture intelligenti" (MASTRI).

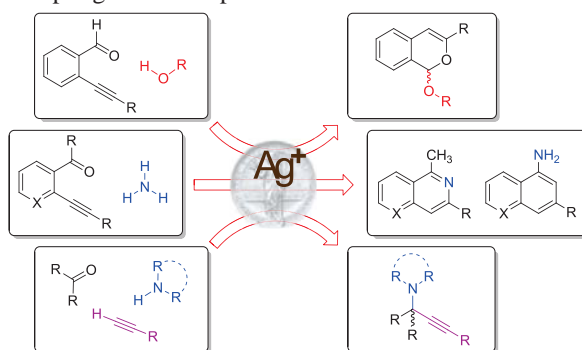
The Neglected Brother: Silver Catalyzed Domino Reactions Involving Alkynes

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Among the noble metals used in homogeneous catalysis, silver is the most neglected one, and only with the new millennium it has been rediscovered as suitable catalyst for a number of different organic transformations¹ including the synthesis of heterocycles.² Beside the versatility of copper catalysts and the much-in-vogue gold catalysis, silver salts and complexes demonstrated to be able to promote a number of reactions involving both σ and π activation. Its ability to act as Lewis acid as well as transition metal can be profitably used to promote domino and multicomponent³ transformations involving multiple bonds and heteroatoms. A certain number of examples in which silver catalysts effectively replaced copper ones or displayed an activity comparable – or higher – than more expensive gold catalysts have been reported. Here, our recent findings on silver catalyzed domino and multicomponent reactions involving alkynes will be disclosed. In particular, this talk will be focused both on domino addition/annulation reactions of 2-alkynylacetophenone derivatives with ammonia by means of simple silver salts catalysts⁴ and on the activity of some original pyridine-containing tetra-aza macrocyclic silver complexes, called [Ag(I)(Pc-L)],⁵ in two different transformations: the regioselective domino addition/cycloisomerization reaction of 2-alkynylbenzaldehydes with alcohols⁶ and the A³-coupling⁷ multicomponent reaction.



References

- 1) *Silver in Organic Chemistry* (Ed. M. Harmata), John Wiley and Sons, Inc., Hoboken, 2010.
- 2) Álvarez-Corral, M.; Munõz-Dorado, M.; Rodríguez-García, I. *Chem. Rev.* **2008**, *108*, 3174–3198.
- 3) Abbiati, G.; Rossi, E. *Beilstein J. Org. Chem.* **2014**, *10*, 481–513.
- 4) Dell'Acqua, M.; Abbiati, G.; Arcadi, A.; Rossi, E. *Org. Biomol. Chem.* **2011**, 7836–7848.
- 5) Castano, B.; Guidone, S.; Gallo, E.; Ragaini, F.; Casati, N.; Macchi, P.; Sisti, M.; Caselli, A. *Dalton Trans.* **2013**, *42*, 2451–2562.
- 6) Dell'Acqua, M.; Castano, B.; Cecchini, C.; Pedrazzini, T.; Pirovano, V.; Rossi, E.; Caselli, A.; Abbiati, G. *J. Org. Chem.* **2014**, *79*, 3494–3505.
- 7) Trose, M.; Dell'Acqua, M.; Pedrazzini, T.; Pirovano, V.; Gallo, E.; Rossi, E.; Caselli, A.; Abbiati, G. *submitted*.

ORAL COMMUNICATIONS

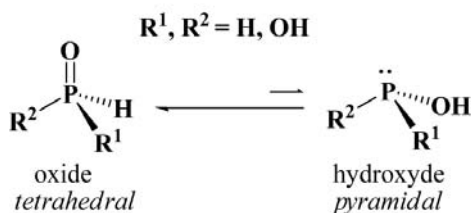
Electronic Aspects of the Phosphine Oxide \rightarrow Phosphinous Acid Tautomerism and the Assisting Role of Transition Metals

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The $\text{H}_3\text{P}(\text{O}) \rightarrow \text{H}_2\text{P}(\text{OH})$ tautomerism is addressed through experimental and DFT approaches.^{1,2} The process, which is energetically difficult for the free molecule, is easier over a metal fragment of the type $\{\text{CpL}_2\text{Ru}^{\text{III}}\}^n$ (L = uncharged or anionic phosphine ligand), because of the much lower barrier. The free $\text{H}_3\text{P}(\text{O})$ molecule is a very weak acid and hardly a proton may intramolecularly migrate toward the oxygen atom, as expected for a classic acid-base reaction.



Actually, a portion of the P-H bonding electron density remains associated to the transferring hydrogen up to the TS, whose high barrier is originated by the electronic repulsion of the electron moving toward one oxygen. After TS, a proton is actually formed, allowing O-H bond formation, while the translated electron density localizes again as a lone pair of the P atom. By monitoring the wavefunctions along the

pathway, the assisting role of a metal in reducing the barrier has been estimated. The promptly optimized intermediate $[\text{CpRu}(\text{PR}_3)_2(\text{H})(\text{H}_2\text{PO})]^n$ (undetected by experiments) indicates how the strong P-H bond is favorably cleaved in an oxidative addition process. Therefore much of the energy necessary for the free molecules is unneeded and the H transfer requires four-times less energy. Nonetheless, there remains a barrier of about 15 kcal mol^{-1} due to the residual electron repulsion. Analogous behaviors are found for all the molecules $\text{H}_n\text{R}_{3-n}\text{P}(\text{O})$ ($n = 3, 2, 1$; R = OH) and their metal derivatives, except for the Ru complex with two TPPMS phosphines [TPPMS = $\text{PPh}_2(m\text{-C}_6\text{H}_4\text{SO}_3^-)$], selected for allowing the chemistry in water. The following unexpected behaviors are observed: i) the reaction with $\text{H}_3\text{P}(\text{O})$ yields two isomeric products with formula $[\text{CpRu}(\text{TPPMS})_2\{\text{H}_2\text{P}(\text{OH})\}]^n$; ii) the tautomerization of $\text{H}(\text{OH})_2\text{P}(\text{O})$ is uniquely inhibited. Specific DFT calculations with full TPPMS models highlight the important effects played by the phosphine SO_3^- substituent in forming H-bonding networks with OH groups of the reactant or products. Important indications on the electronic rearrangements, which involve a redox behavior of some sort and the implications for the variable P oxidation states will be underlined.

References

1. Yakhvarov, D.; Caporali, M.; Gonsalvi, L.; Latypov, S.; Mirabello, V.; Rizvanov, I.; Schipper, W.; Sinyashin, O.; Stoppioni, P.; Peruzzini, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 5370-5373
2. Manca, G.; Caporali, M.; Ienco, A.; Peruzzini, M.; Mealli, C. *J. Organomet. Chem.* **2014**, *760*, 177-185.

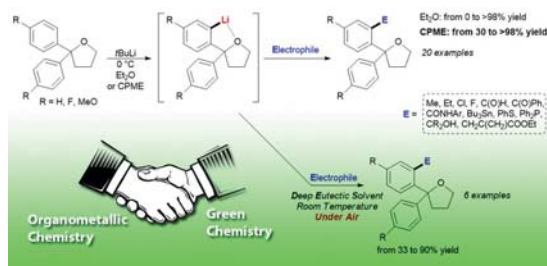
Regioselective Desymmetrization of Diaryltetrahydrofurans via Directed *ortho*-Lithiation: Building New Bridges between Polar Organometallic Chemistry and Green Chemistry

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Among saturated oxygen heterocycles, substituted tetrahydrofuran (THF) derivatives are important scaffold encountered in many synthetic and natural products with wide-ranging biological activity.¹ Their lack of reactivity, however, has discouraged their use as starting material in organic synthesis, which remains a challenging task. In this communication, we report the first successful use of tetrahydrofuran as a direct metalation group in the regioselective desymmetrization/ functionalization of diaryltetrahydrofurans. By replacing Et₂O with a "greener" solvent such as Cyclopentyl Methyl Ether (CPME), better yields and selectivities were obtained. In addition, we noticed that the trapping reactions of the *ortho*-lithiated intermediate with electrophiles could also be successfully carried out at *room temperature* and *under open air conditions* in Deep Eutectic Solvents² as new eco-friendly reaction media for organolithium compounds. Protic eutectic mixtures of choline chloride and donor molecules such as glycerol and urea proved to be especially efficient.³



References

1. (a) Wolfe, J. P.; Hay, M. B. *Tetrahedron* **2007**, *63*, 261; (b) Lorente, A.; Lamariano-Merketegi, J.; Albericio, F.; Alvarez, M. *Chem. Rev.* **2013**, *113*, 4567.
2. M. Francisco, A. van den Bruinhorst, M. C. Kroon *Angew. Chem. Int. Ed.* **2013**, *52*, 3074.
3. Mallardo, V.; Rizzi, R.; Sassone, F.; Mansueto, R.; Perna, F. M.; Salomone, A.; Capriati, V. submitted

Deprotonation of CH₃ Groups in Coordinated Sulfides and Phosphines: C-C Coupling with Diimine Coligands

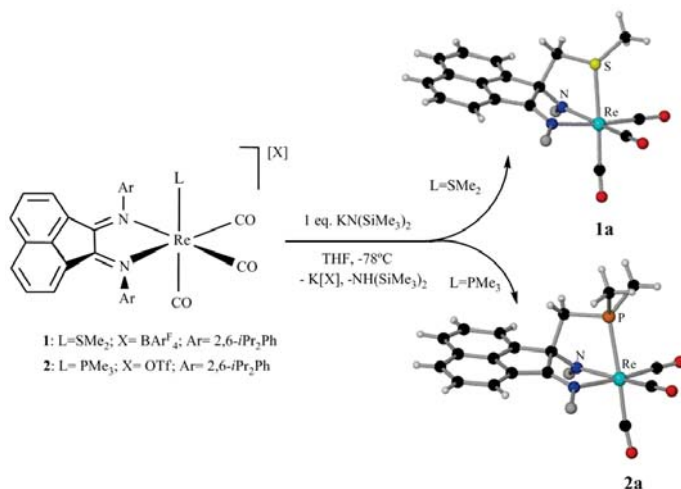
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Reaction of compounds [Re(N-N)(CO)₃L][X] (N-N= 2,2'-bipyridine, 2,6-*i*Pr₂BIAN, *p*-MeBIAN; L= SMe₂, SMePh, PMe₃, PMe₂Ph, PMePh₂; X= OTf, BAR^F₄) with KN(SiMe₃)₂ led to deprotonation of one of the sulfide or phosphine methyl groups and C-C coupling between the resulting CH₂ and an imine carbon of N-N.¹ Neither CH₃ group deprotonation nor nucleophilic attack on bipyridine are conventional reactions.



References

1. Arévalo, R., Pérez, J., Riera, L. *Inorg. Chem.* **2013**, 52, 6785-6787.

Acknowledgements: This work was funded by Ministerio de Economía y Competitividad and Ministerio de Educación Cultura y Deporte (Spanish Government)

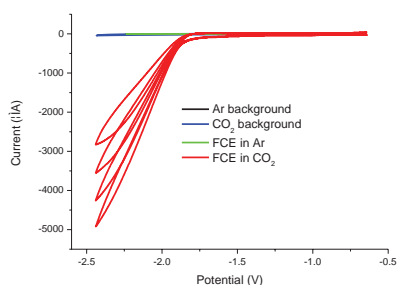
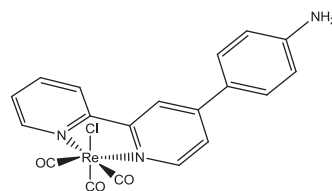
Organometallic Complexes for Photo and Electro-Catalytic Reduction of CO₂

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The reduction of CO₂ emissions and the quest for sustainable energy are top priorities on the world's strategic research agenda.¹ Conversion of sunlight directly into electricity suffers of few drawbacks, like discontinuity and the less convenient nature of electricity for energy storage. An efficient and suitable approach is to store solar energy in chemicals, possibly by using CO₂ in order to mimic the natural photosynthesis and at the same time take the advantage to reduce the amount of CO₂ in the atmosphere.¹ Photochemical activation followed by reductive quenching is a process very close to the electrochemical one² (in both cases the active specie is the 1e reduced molecule), thus this complex reaction mechanism can be explored by studying separately the two processes/steps: a) the light-harvesting antenna, and b) the system of the real catalyst. This makes the electrochemical reduction of CO₂ mediated by redox catalyst a very interesting, convenient and clean way to test catalysts for CO₂ reduction without the need to have the antenna system and avoiding the use (and the interference) of sacrificial reagents.



In this contribution we report the photochemical and electrochemical reduction of CO₂ by means of selected organometallic rhenium complexes both in homogeneous solution and chemically bonded to the electrode surface (FCE). We extended our previous experience in functionalizing intact Ru and Ir organometallic molecules to carbon electrode surface by means of electrochemical techniques³ to some rhenium organometallic complexes bearing a pendent amino group.

References

1. Rongé, J.; Bosserez, T.; Martel, D.; Nervi, C.; Boarino, L.; Taulelle, F.; Decher, G.; Bordiga, S.; Martens, J. A. *Chem.Soc.Rev* **2014**, doi: 10.1039/c3cs60424a
2. Zanello, P.; Nervi, C.; Fabrizi De Biani, F. *Inorganic Electrochemistry. Theory, Practice and Application*; RSC, Cambridge, **2011**.
3. Sandroni, M.; Volpi, G.; Fiedler, J.; Buscaino, R.; Viscardi, G.; Milone, L.; Gobetto, R.; Nervi, C. *Catal.Today* **2010**, *158*, 22-28.

Acknowledgements: This work has been funded by the PHOTORECARB project (Compagnia di San Paolo and University of Turin).

Activity of Pyridine-Carbene Iridium Water Oxidation Catalysts: Methyl, Butyl, Octyl *not* Futile

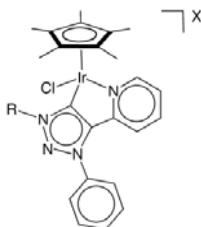
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The realization of an efficient apparatus for artificial photosynthesis, aimed at producing solar fuels, is strongly hampered by the difficulty of oxidizing water. Several transition metal complexes demonstrated to be competent catalysts for water oxidation,¹ including those based on pyridine triazolyl-carbene N,C-ligand²⁻⁴ reported by some of us. It starts to be evident that the catalytic activity may strongly depend on a small modification of the “ancillary” ligands.



In this respect, herein we show that changing R group from methyl (**1**) to octyl (**2**) (Figure), causes a dramatic alteration of the catalyst performance when water oxidation is driven by CAN (cerium ammonium nitrate). Particularly, the maximum TOF measured for **2** is remarkable (168 min⁻¹) and about one order of magnitude higher than that of **1** (16 min⁻¹). With the aim of shedding some light on catalyst transformation under oxidative stress and possibly disclose the reasons of the above-mentioned difference in activity, we performed a series of detailed *in situ* NMR studies. The latter indicate that the degradation of catalyst involves firstly the Cp* functionalization, as previously found for other catalysts.⁵ On the contrary, the N,C-ligand remains coordinated at iridium and forms a likely paramagnetic and molecular species with a higher nuclearity, as deduced by diffusion NMR experiments.

References

1. McDaniel, N. D. *et al. J. Am. Chem. Soc.* **2008**, *130*, 210. Hull, J. F. *et al. J. Am. Chem. Soc.* **2009**, *131*, 8730. Blakemore, J. D. *et al. J. Am. Chem. Soc.* **2010**, *132*, 16017. Savini, A. *et al. Chem. Commun.* **2010**, 46, 9218. Dzik, W. I. *et al. Organometallics* **2011**, *30*, 372. Bucci A. *et al. Organometallics*, **2012**, *31*, 8071.
2. Lalrempuia R. *et al. Angew. Chem. Int. Ed.* **2010**, *49*, 9765.
3. Petronilho A. *et al. Dalton Trans.* **2012**, *41*, 13074.
4. Petronilho A. *et al. Eur. J. Inorg. Chem.* **2014**, 708.
5. Zuccaccia C. *et al. Chem. Eur. J.* **2014**, *20*, 3446 and references therein.

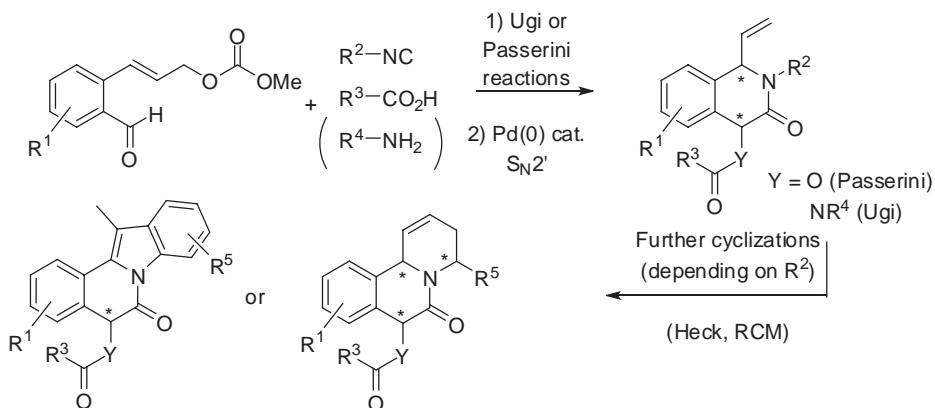
Synthesis of Complex Heterocyclic Scaffolds through Cascade Processes Based on Multicomponent Reactions Followed by Palladium Mediated S_N2' Cyclizations

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The strategy that combine classical isocyanide-based multicomponent reactions followed by subsequent cyclizations has proved to be one the most effective methods for the diversity-oriented obtainment in few steps (typically 1-3) of a variety of drug-like or natural-like heterocyclic scaffolds.^{1,2} We envisioned that a 2-step protocol involving an Ugi reaction followed by Pd(0) mediated S_N2' cyclization could have a great potential: this latter reaction leaves a terminal double bond that can be involved in a third organometal catalysed step leading to complex polycyclic heterocycles. We already previously demonstrated this principle using a custom-made isocyanide containing an allyl carbonate.³ Now we have decided to access a different type of alkaloid-like systems, by incorporating the allyl carbonate in the aldehyde component instead. We have carried out a series of Passerini and Ugi reactions followed by the S_N2' cyclization, where the isocyanide derived NH group acts as nucleophile. Finally the terminal double bond has been used for further cyclizations based on the Heck reaction or on Ring Closing Metathesis. In this way 4 different scaffolds could be accesses. The successes and failures of this approach will be discussed, also with emphasis on the stereochemical aspects.



References

1. Banfi, L.; Basso, A.; Riva, R. *Top. Heterocycl. Chem.* **2010**, *23*, 1.
2. Banfi, L.; Riva, R.; Basso, A. *Synlett* **2010**, 23.
3. Riva, R.; Banfi, L.; Basso, A.; Cerulli, V.; Guanti, G.; Pani, M. *J. Org. Chem.* **2010**, *75*, 5134.

One-pot Pd/Norbornene-Catalyzed Synthesis of Dibenz[c,e]Oxepin Derivatives

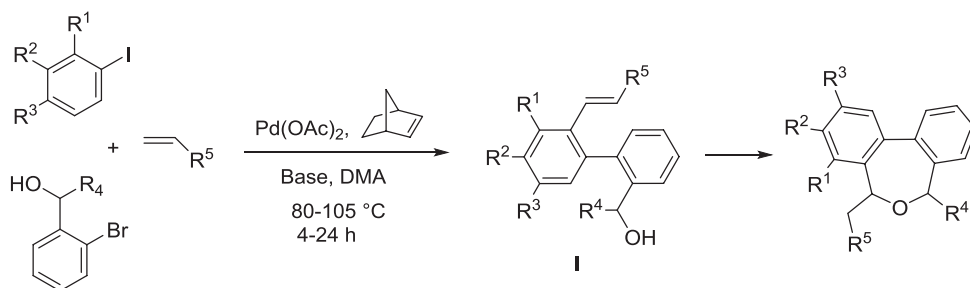
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We have recently reported the sequential Pd/norbornene catalyzed process leading to dibenzopyran derivatives starting from *o*-aryl iodides and *o*-bromobenzyl alcohols.¹ An activated olefin added to the same reagents gives rise to seven-membered heterocycles belonging to the oxepin class. The equation below shows the reaction of an *ortho*-substituted aryl iodide with a secondary *o*-bromobenzyl alcohol and an electron-poor terminal olefin, i.e. an acrylate ester, that gives compound **I**, which undergoes an intra oxa-Michael reaction leading to dibenz[c,e]oxepin derivatives as a mixture of two diastereoisomers.



References

1. Motti, E; Della Ca', N.; Xu, D.; Piersimoni, A.; Bedogni, E.; Zhou, Z.-M.; Catellani, M. *Org. Lett.* **2012**, *14*, 5792-5795.

Acknowledgements: This work was funded by University of Parma. D.Xu is a recipient of a fellowship from the Beijing Institute of Technology, Beijing, PR China.

Selective Anticancer Ruthenium(II) Arene RAPTA Type Complexes Containing Curcuminoids

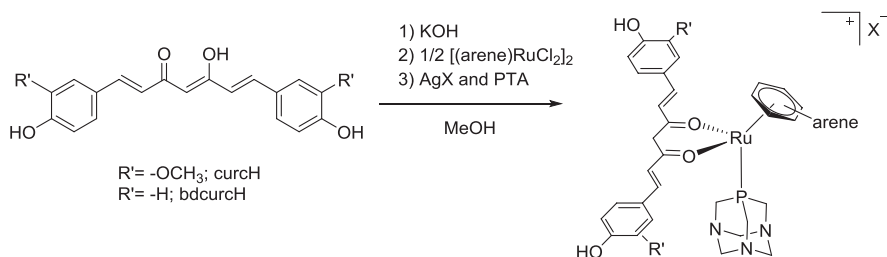
Francesca Condello^a, S. Orbisaglia^a, J. Palmucci^b, A. Petrini^a, R. Pettinari^a, F. Marchetti^b, C. Pettinari^a, P. J. Dyson^c

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Ruthenium-arene complexes are considered valid alternatives to platinum drugs, owing to their lower toxicity and stronger selectivity.¹ Since curcumin possesses anti-inflammatory, antioxidant and antitumoral effects, it has been extensively studied as a chemo preventive agent in some cancer models.²

As continuation of our previous work,³ a series of novel Ru^{II} arene RAPTA type derivatives (arene = cymene and hexamethylbenzene) containing curcumin-based ligands (curcH = curcumin, bdcurcH = bisdemethoxycurcumin) and PTA (1,3,5-triaza-7-phosphaadamantane) has been synthesized and fully characterized. The antitumor activity of the complexes has been evaluated *in vitro* against human ovarian carcinoma cells, A2780 and A2780cisR, as well as against non-tumorous Human Embryonic Kidney (HEK293) cells.



References

- Harteringer, C. G.; Metzler-Nolte N.; Dyson, P. J. *Organometallics* **2012**, *31*, 5677–5685.
- Aggarwal, B. B.; Sundaram, C.; Malani, N.; Ichikawa H. *Curcumin: The Indian solid gold*. 2007, New York: Springer.
- Caruso F., Rossi M., Benson A., Opazo C., Freedman D., Monti E., Gariboldi M. B., Shaulky J., Marchetti F., Pettinari R., Pettinari C. *J. Med. Chem.* **2012**, *55*, 1072-1081.

Acknowledgements: This work was funded by University of Camerino and École Polytechnique Fédérale de Lausanne.

An Iridium Catalyst as Functional Mimic of Hydrogenase

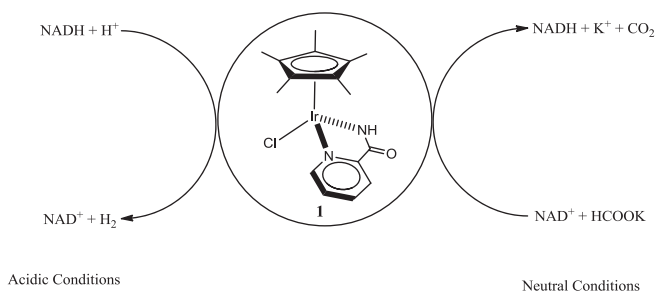
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The replacement of fossil fuels with renewable and sustainable energy sources is the most important challenge of our century [1]. Solar energy seems to be an attractive alternative to fossil fuels because it is green, abundant, low cost and potentially convertible into chemical energy through the artificial photosynthesis of solar fuels. Among the latter, H₂ has attracted a lot of interest but its utilization is hampered by its explosiveness and low volumetric energy density [2]. For these reasons, it would be extremely important to realize an efficient system capable to perform catalytic reversible hydrogenation and dehydrogenation reactions, in order to transform hydrogen in a safer and easier to handle product.

Although many organometallic complexes are capable to carry on reversible hydrogenation of a large variety of inorganic or organic substrates [3], only few of them efficiently interconvert the NAD⁺/NADH redox couple [4]. The latter is a fundamental process catalyzed in Nature by hydrogenase [5]. Herein we show that the iridium organometallic compound **1** (Figure) is a competent catalyst both for the hydrogenation reaction of NAD⁺ and for dehydrogenation reaction of NADH. UV-Vis measurements indicate that catalyst (**1**) has a remarkable TOF value (4 min⁻¹) for the dehydrogenation reaction of NADH and a TOF of 2 min⁻¹ for the hydrogenation reaction of NAD⁺.



References

- Balzani, V. *et al. ChemSusChem*, **2008**, *1*, 26-58.
- Fukuzumi, S. *et al. Dalton Trans.*, **2013**, *42*, 18-28.
- Fukuzumi, S. *et al. Energy Environ. Sci.*, **2012**, *5*, 5356–5363.
- a) Fukuzumi, S. *et al. J. Am. Chem. Soc.*, **2012**, *134*, 367-374; b) Sadler, P.J. *et al. Angew. Chem.*, **2012**, *124*, 3963-3966; c) Sadler, P.J. *et al. Organometallics*, **2012**, *31*, 5958-5967
- a) Hammarström, L. *et al. Acc. Chem. Res.*, **2009**, *42*, 1899–1909 b) Maness, P.C. *et al. Chem. Soc. Rev.*, **2009**, *38*, 52–61. c) Adams, M.W.W. *et al. J. Bacteriol.*, **2009**, *191*, 4451–4457

Acknowledgements: This work was funded by POR-UMBRIA FSE

N-Phosphanyl-Azolylidene Ligands: Coordination Chemistry and Catalysis

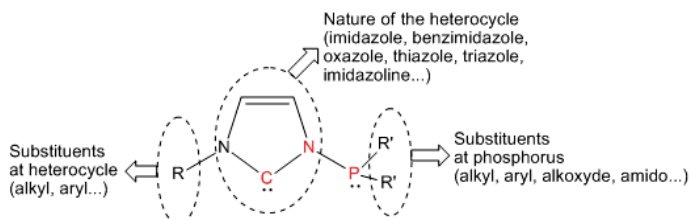
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N-phosphorylated azolylidenes represent a novel class of N-heterocyclic carbenes featured by a direct N-P bond between one of the heterocyclic nitrogens and an exocyclic phosphorus-containing group. Such compounds may serve as tunable bidentate ligands for transition metal complexes with a broad spectrum of potential applications. In the last few years, several original synthetic approaches to such compounds have been developed, and the first examples of their mono-, di- and polynuclear complexes with transition metals have very recently appeared in the literature.[1,2]



In the present contribution, we wish to report on our continuing research efforts towards the synthesis, characterization and application of late transition metal complexes of such ligands. In particular, we have targeted the development of methods for the preparation of dinuclear gold(I) complexes with different stoichiometries, potentially amenable to technological applications as catalysts, luminescent moieties or bioactive compounds. Preliminary results involving the catalytic potential of mononuclear palladium(II) complexes with these ligands in cross-coupling reactions will be also presented.

References

1. a) Marchenko, A. P.; Koidan, H. N.; Zarudnitskii, E. V.; Hurieva, A. N.; Kirilchuk, A. A.; Yurchenko, A. A.; Biffis, A.; Kostyuk, A. N. *Organometallics* **2012**, *31*, 8257; b) Marchenko, A. P.; Koidan, H. N.; Hurieva, A. N.; Gutov, O. V.; Kostyuk, A. N.; Tubaro, C.; Lollo, S.; Lanza, A.; Nestola, F.; Biffis, A. *Organometallics* **2013**, *32*, 718.
2. a) Kühnel, E.; Shishkov, I. V.; Rominger, F.; Oeser, T.; Hofmann, P. *Organometallics* **2012**, *31*, 8000; b) Nägele, P.; Herrlich (née Blumbach), U.; Rominger, F.; Hofmann, P. *Organometallics* **2013**, *32*, 181; c) Ai, P.; Danopoulos, A. A.; Braunstein, P.; Monakhov, K. Y. *Chem. Commun.* **2014**, *50*, 103.

Sterically Driven Synthesis of Novel Mononuclear Ru and Dinuclear Ru-Ag N-Heterocyclic Carbene Complexes.

1

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N-heterocyclic carbenes (NHC) are efficient ancillary ligands because of their strong coordination ability and their tuneable character which allows the control of the steric and electronic properties of the metal centre.¹ Herein we report the synthesis and characterization of new carbonylic ruthenium complexes that combine tetraphenylcyclopentadienone ligands and N-heterocyclic carbenes (NHC). Coordination of less bulky carbenes occurred through a straightforward transmetallation from the corresponding silver carbene intermediate to the dinuclear complex, dicarbonyl(η^4 -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) ruthenium dimer, leading to the formation of a series of mononuclear complexes of type **1** (Figure 1). Conversely, sterically demanding imidazolium salts yielded the dinuclear Ru-Ag complexes of type **2**, in which the carbene remains coordinated to silver (Figure 1). New complexes have been characterized by spectroscopy (NMR, IR, ESI-MS) and X-ray diffraction studies.

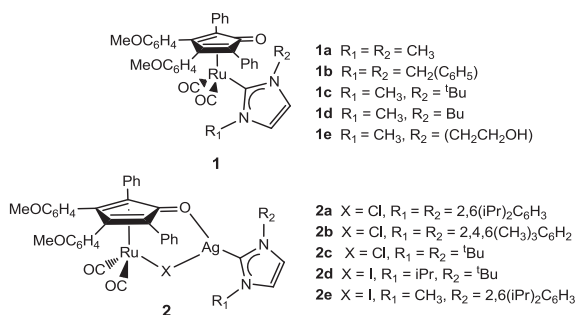


Figure 1. Carbonylic ruthenium complexes of type **1** and **2**.

Preliminary results on the direct reactivity between dicarbonyl(η^4 -3,4-bis(4-methoxyphenyl)-2,5-diphenylcyclopenta-2,4-dienone) ruthenium dimer and imidazolium salts will be also presented and discussed.

References

1. L. A. Schaper, S.J. Hock, W. A. Hermann, F. E. Kuhn, *Angew. Chem., Int. Ed.*, **2013**, *52*, 270; L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Lamponnaz, V. Cesar, *Chem. Rev.*, **2011**, *111*, 2705; L. Mercs, M. Albrecht, *Chem. Soc. Rev.*, **2010**, *39*, 1903; S. Diez-Gonzales, N. Marion, S. P. Nolan, *Chem. Rev.*, **2009**, *109*, 3612.

Acknowledgements: This work was funded by the Ministero dell'Università e della Ricerca (MIUR) (project: "Designing metal containing molecular fragments for advanced chemical applications").

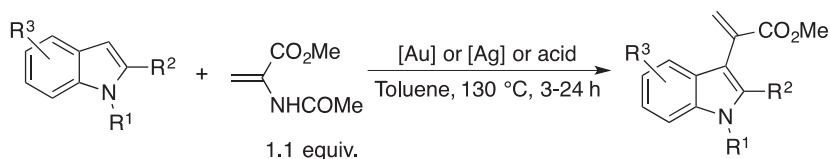
C-3 Functionalization of Indoles with Methyl 2-Acetamidoacrylate under Gold(I), Silver or Brønsted Acids Catalysis

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The chemical modification of indoles through direct functionalization of their C–H bonds constitute a widespread research area of continuous interest for organic synthesis since this scaffold is present in a huge variety of natural product families, medicines or drug candidates, among others.¹ In particular, the formation of a new C–C bond by means of innovative catalytic systems represents an alternative to traditional Friedel-Crafts reactions and allows the use of less toxic reagents and to operate in milder conditions. Among metals, gold catalysts have been employed to this scope in the last years.² In our research group, in particular, we get interested in investigating the reactivity of indoles towards α -amidoacrylates, as specific class of enones, in the presence of gold or silver catalysts. Thus, under the optimized reactions conditions we were able to synthesize a series of α -indolylacrilates in high yields.⁴ Furthermore an acid-catalyzed version of this reaction was also explored achieving similar results.



References:

1. a) R. J. Sundberg, *Indoles*, Academic Press, London, **1996**; b) R. K. Brown, *Indoles* (Ed.: W. J. Houlihan), Wiley-Interscience, New York, **1972**; c) B. A. Trofimov, N. A. Nedolya, *Comprehensive Heterocyclic Chemistry*; (Eds.: G. Jones, C. A. Ramsden), Elsevier, Oxford, **2008**, vol. 3, pp. 88-168; d) J. Alvarez-Builla, J. J. Vaquero, J. Barluenga, *Modern Heterocyclic Chemistry*, Wiley-VCH, Weinheim, **2011**, p. 377.
2. M. Dell'Acqua, D. Facoetti, V. Pirovano, G. Abbiati, E. Rossi, *Targets in Heterocyclic Systems* **2011**, *15*, 86-139.
3. For an example on the use of α -amidoacrylates in the presence of Lewis acids see: E. Angelini, C. Balsamini, F. Bartoccini, S. Lucarini, G. Piersanti, *J. Org. Chem.* **2008**, *73*, 5654-5657.
4. V. Pirovano, D. Facoetti, M. Dell'Acqua, E. Della Fontana, G. Abbiati, E. Rossi, *Org. Lett.* **2013**, *15*, 3812-3815.

Anticancer Profile of a Novel Photo-Uncageable Rhenium Complex

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R. K. O. Sigel^a, S. Ferrari^b, G. Gasser^a**

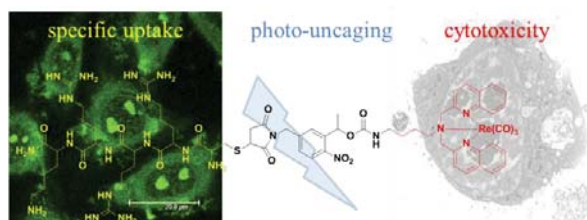
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To enhance the therapeutic profile of a drug, the use of external triggers (e.g. light, ultra-sound, temperature) or the coupling with a targeting vector showed to be very promising and successful strategies.¹ In this work, we envisioned to combine these two methods to an organometallic compound. A Re(I) tricarbonyl *N,N*-bis(quinolinoyl) complex (**Re-NH₂**) was caged with a photolabile protecting group (**PLPG**) and further coupled to a nuclear localization sequence (**NLS**) peptide to achieve bioactivity control and organelle/cellular specificity, respectively.² Of high interest, the obtained **Re-PLPG-NLS** showed toxicity comparable to that of cisplatin on cervical cancer cells (HeLa) more marked upon light irradiation. Its cell death mechanism associated to its photo-release was explored using different techniques including fluorescence microscopy, ICP-MS, gel electrophoresis, flow cytometry and transmission electron microscopy (TEM). It could be demonstrated that HeLa cells treated with **Re-PLPG-NLS** in the dark and upon irradiation showed severe cell stress (nucleolar segregation, pyknosis, vacuolation). Due its specific nuclear/nucleolar accumulation, **Re-PLPG-NLS** efficiently cleaved RNA and photo-cleaved DNA. This severe onset led to cell death with features ascribable to late apoptosis and necrosis.



References

1. Hamblin M. R., Huang Y.-Y., *Handbook of Photomedicine*, 2014, edited by Taylor and Francis group, ISBN: 978-1-4398-8469-0.
2. Leonidova A., Pierroz V., Rubbiani R., Lan Y., Schmitz A. Kaech A., G., Sigel R. K. O., Ferrari S., Gasser G., 2014, *submitted*

Acknowledgements: This work was funded by Swiss National Scientific Foundation, Novartis Jubilee Foundation, Stiftung für Wissenschaftliche Forschung, Stiftung zur Krebsbekämpfung, Huggenberger Bischoff Stiftung, European Research Council, COST Action CM1105, State Secretariat for Education, Research and Innovation, University Zurich Priority Program, Center for Microscopy and Image Analysis and University of Zurich.

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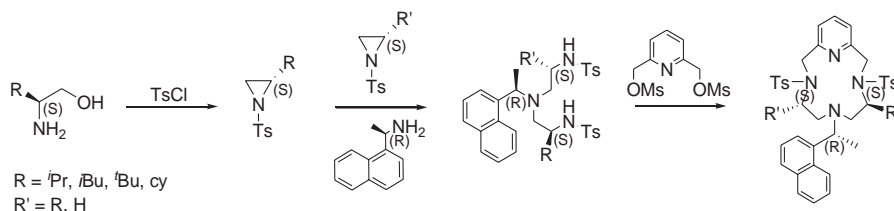
Application in Asymmetric Cyclopropanation of New Chiral Macrocyclic Ligands

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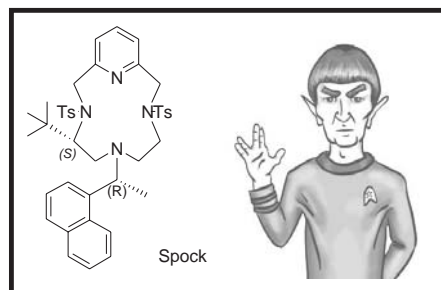
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Our group has been focusing for years on the synthesis and on the study of chiral macrocyclic ligand. Their complexes with metal ions – specially copper(I) and silver(I) – are competent catalysts in various organic reactions.¹⁻³ The synthesis of this class of compounds is simple and fast (Scheme 1). It does not involve either complex procedures nor expensive reagents, since the macrocycles can be obtained from enantiomerically pure and naturally available aminoacids in good yields (overall 40-50%).



Scheme 1

In this presentation, we reported the synthesis of three new chiral ligands bearing different chiral arms on the macrocyclic backbone. We also report the studies of complexation of these ligands by Ag(I) and Cu(I) ions and the good applicative results of the latter complexes as catalysts for the cyclopropanation reaction of α -methylstyrene. The best ligand – friendly called Spock – was used to scope the reaction by employing different substrates, with interesting results in terms of yields and enantioselectivities.



1. Castano, B.; Guidone, S.; Gallo, E.; Ragaini, F.; Casati, N.; Macchi, P.; Sisti, M.; Caselli, A. *Dalton Trans.* **2013**, 2451-2462
2. Castano, B.; Pedrazzini, T.; Sisti, M.; Gallo, E.; Ragaini, F.; Casati, N.; Caselli, A. *Appl. Organometal. Chem.* **2011**, 25, 824–829
3. Dell'Acqua, M.; Castano, B.; Cecchini, C.; Pedrazzini, T.; Pirovano, V.; Rossi, E.; Caselli, A.; Abbiati, G. *J. Org. Chem.* **2014**, 79, 3494-3505

Gold Catalyzed Enantioselective Dearomative [2+2] Reaction of Indoles with Allenamides

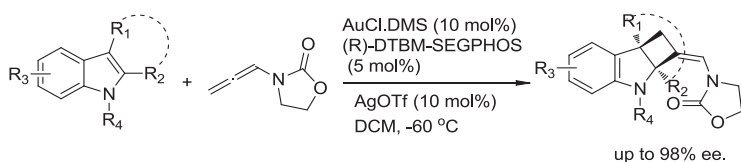
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Dearomatization of indole has been a powerful method to access to polycyclic C2,C3-fused indoline motifs.¹ Consequently, various kinds of methodologies have been developed to construct this kind of structures, in which annulation of indole with cycloaddition reaction gained much more attention, because of its high efficiency and readily available indole feedstocks.² Many types of cycloaddition reactions have been reported, such as [4+2], [3+2], [3+3], [1+2] reactions. However, very rare examples of the dearomative [2+2] reaction of indoles have been reported.³

As our on-going research program focused on gold catalysis to construct polycyclic indole structures,⁴ we envisaged that gold activated allenamide would be suitable for the dearomatization of indole via an intermolecular [2+2]-cycloaddition reaction. After an extensive survey of reaction conditions, we found out that 2,3-cyclobutyl-indolines can be obtained in high enantioselectivity by running the reaction at low temperature in the presence of chiral gold(I) complexes (Scheme 1).



Scheme 1

References

- (a) Roche, S. P.; Porco Jr., J. A. *Angew. Chem. Int. Ed.* **2011**, *50*, 4068-4093. (b) Zhuo, C.-X.; Zhang, W.; You, S.-L. *Angew. Chem. Int. Ed.* **2012**, *51*, 12662-12686.
- Li, H.; Hughes, R. P.; Wu, J. *J. Am. Chem. Soc.* **2014**, *136*, 6288-6296.
- For an intramolecular example: Zhang, L. *J. Am. Chem. Soc.* **2005**, *127*, 16804-16805.
- (a) Cera, G.; Chiarucci, M.; Mazzanti, A.; Mancinelli, M.; Bandini, M. *Org. Lett.* **2012**, *14*, 1350-1353. (b) Chiarucci, M.; Mocci, R.; Syntrivanis, L.-D.; Cera, G.; Mazzanti, A.; Bandini, M. *Angew. Chem. Int. Ed.* **2013**, *52*, 10850-10853.

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Novel Palladium-Ar-BIAN Multinuclear Complexes

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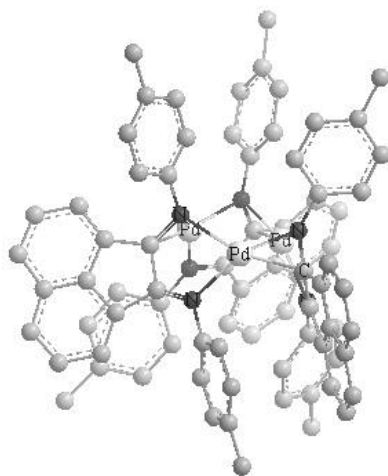
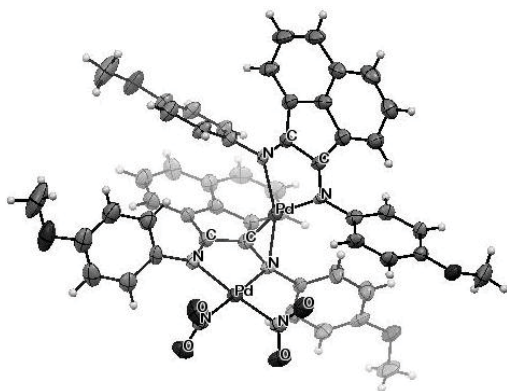
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Zerovalent palladium complexes of 1,2-bis(arylimino)acenaphthenes (Ar-BIAN), in particular complexes with the formula $[\text{Pd}(\text{Ar-BIAN})(\eta^2\text{-olefin})]$, **1**, play an important role in several catalytic reactions. However their synthesis is limited to complexes with electron poor alkenes. We developed a new synthetic strategy to this kind of complexes using a reduced form of Ar-BIAN (Ar-BIANH_2)¹ and a palladium (II) precursor, thus obtaining the complexation of the chelating diimine, the reduction of the metal center and the coordination of the olefin at the same time.

While trying to synthesize the tricoordinated complex **1** using electron rich olefins, we discovered that a new palladium (0) complex in which no coordinated olefin is



present, forms instead. An X-ray characterization showed it to be a cyclic Pd/Ar-BIAN trimer in which each $\text{Pd}(\text{Ar-BIAN})$ fragment is linked to the other by a peculiar η^2 coordination of one $\text{C}=\text{N}$ bond of another unit.

In one of the attempts to synthesize **1** we were also able to isolate a mixed valence dinuclear Pd complex in which a $[\text{Pd}(\text{Ar-BIAN})]^0$ fragment is connected to a $[\text{Pd}(\text{Ar-BIAN})(\text{NO}_2)_2]$ by a similar bridging η^2 coordination of the iminic bond.

References

1. M. Viganò, F. Ferretti, A. Caselli, F. Ragaini, M. Rossi, P. Mussini, P. Macchi, *submitted*

First Dye Sensitized Solar Cells based on Rhenium Complexes as Photosensitizers

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The dye sensitized solar cell (DSSC) is considered the most promising new-generation alternative to conventional solar energy harvesting devices.¹ Many different photosensitizers, including metal complexes, porphyrins, phthalocyanines and metal-free organic dyes, have been designed and applied to DSSCs in the past two decades.² The use of rhenium complexes as sensitizers in dye-sensitized solar cells has been here investigated for the first time. These new complexes (see Figure 1) are characterized by two rhenium(I) tricarbonyl units connected by a properly functionalized diazine ligand and two anionic ligands.³ Notably, one of them can be a bridging hydride, without any detrimental effect on the stability of the sensitizer in the operating conditions. The design concept of these dyes to improve light-to-electricity conversion will be discussed in terms of absorption, electron injection, dye regeneration and recombination. The cell performances of the investigated rhenium-based dyes will be compared. Results show an improvement of photocurrent generation and power conversion efficiency up to 1% obtained with the dye containing the TPA moiety as electron acceptor unit.

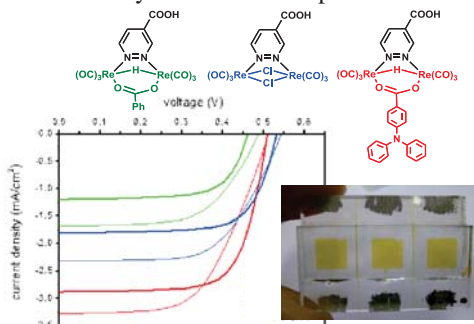


Fig. 1: Current density–voltage characteristics of the photovoltaic cells containing the three different dyes

References

1. Yella, A. Lee, H. W., Tsao, H. N., Yi, C., Chandiran, A. K., Nazeeruddin, M. K., Diao, E. W. G., Yeh, C. Y., Zakeeruddin S. M., Gratzel, M. *Science*, **2011**, *334*, 629–634.
2. Polo, A. S.; Itokazu, M. K.; Iha, N. Y. M., *Coord. Chem. Rev.* **2004**, *248*, 1343-1361. Hagfeldt, A., Boschloo, G., Sun, L., Kloo, L., Pettersson, H., *Chem. Rev.*, **2010**, *110*, 6595–6663.
3. Panigati, M. Mauro, M. Donghi, D. Mercandelli, P. Mussini, P., De Cola, L., D'Alfonso, G. *Coord. Chem. Rev.* **2012**, *256*, 1621-1643

Unusual Chemoselective Rh(II)-Catalysed Transformations of α -Diazocarbonylpiperidine Cores.

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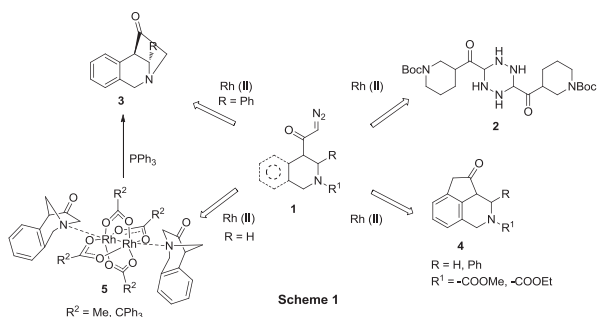
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α -Diazocarbonyl-derivatives are characterized by a quite exceptional flexibility in synthesis,¹ reacting catalytically with numerous transition metals and their salts forming reactive intermediates. Here we report on a study on different piperidine systems of general formula **1**, showing an increased complexity and substitution pattern, using the very interesting chemistry that combines the use of α -diazocarbonyl compounds and rhodium(II) catalysts. Three different classes of α -diazocarbonyl piperidine compounds were prepared. Both CH-insertion and the Büchner reaction^{1b,2a-d} could be expected when the aromatic moiety is present. Furthermore, nitrogen atom on the ring could be another center of carbene insertion. Our challenge has been to compare the different behavior of the starting reagents and to find the optimal reaction conditions and catalyst to direct the chemoselectivity of the reaction.

It was found that the structure of the starting reagent is of relevance for the synthetic results. An unexpected dimerization process took place starting from the simple piperidine scaffold giving the hexahydro-tetrazine ring **2**³. Instead, both products of *NH*- (1,2,3,3a-tetrahydrocyclopenta[*de*]isoquinolin-4(5*H*)-one ring) **3** and *CH*-insertion



(1,3,4,5-tetrahydro-2,5-methanobenzo[*c*]azepine **4**) were obtained from tetrahydroisoquinoline derivatives (Scheme 1). Depending on the starting reagent, the Rh(II) catalyst and the reaction conditions, the chemoselectivity of the reaction can be controlled. Finally, it was found that the azepino derivative is able to coordinate the catalyst affording new Rh(II)-complexes **5**⁴.

References

- (a) Ye, T.; McKervey M. A. *Chem. Rev.* **1994**, *94*, 1091-1160. (b) Zhang, Z.; Wang, J. *Tetrahedron* **2008**, *64*, 6577-6605. 2. (a) Gois, P. M. P.; Afonso, C. A. M. *Eur. J. Org. Chem.* **2004**, 3773-3788. (b) Doyle, M. P.; McKervey, M. A.; Ye, T. in *Modern Catalytic Methods for Organic Synthesis With Diazo Compounds*, Wiley-Interscience, New York, **1998**. (c) Wyatt, E. E.; Galloway, W. R. J. D.; Spring, D. R. *Synlett*. **2011**, *10*, 1449-1453. (d) Maguire, A. R.; O'Leary, P.; Harrington, F.; Lawrence, S. E.; Blake, A. J. *J. Org. Chem.* **2001**, *66*, 7166-7177 and references cited therein. 3. Atesr P.; Giles G. F., Farnum Nd D. G. *Can. J. Chem.* **1969**, 3997-4003. 4. Florian P.; Francis R.; Yves J.; and Suzanne J.; *Inorg. Chem.* **1996**, *35*, 4261-4263

POSTERS

Activity Study of Mn(Salen) Catalysts in Sulfides Oxidation by Hydrogen Peroxide

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Organic sulfoxides are valuable synthetic intermediates employed in the production of a range of chemically and biologically active molecules. The catalytic oxidation of sulfides promoted by Mn(salen) complexes¹ provides a straightforward synthetic approach for preparing sulfoxides. Among the oxidants, hydrogen peroxide is considered as an ideal "green" one, due to the absence of any toxic byproduct. These complexes have shown remarkably high activities, which haven't yet been investigated in such environment.

On these basis, starting from thioanisole, we have investigated the catalytic system shown in figure 1, elucidating the dependence of activity on several variables^{2a,b} which can influence the reaction environment such as solvent, additives, counterion, etc.

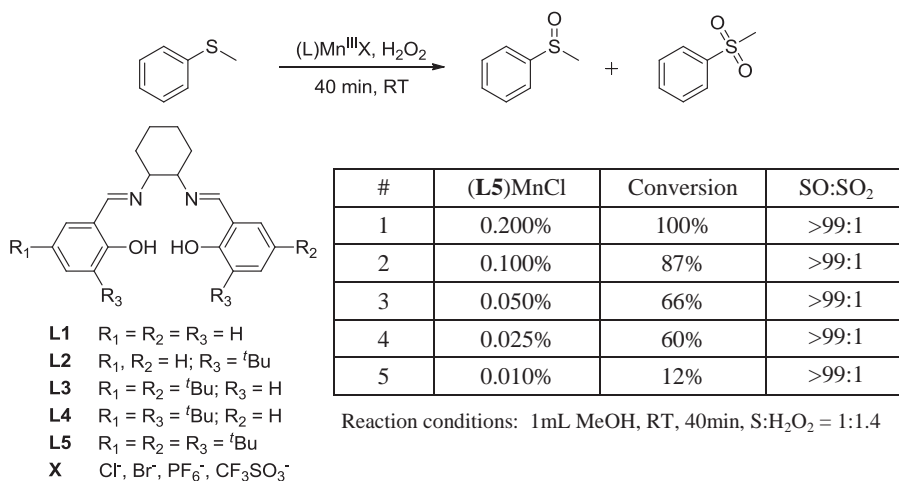


Figure 1

Further details will be reported in the poster.

References

1. Katsuki, T. *Coord. Chem. Rev.* **1995**, *140*, 189-214.
2. (a) Xie, F. *et al. J. Mol. Catal. A* **2009**, *307*, 93-97; (b) Xia, C. *et al. Angew. Chem. Int. Ed.* **2003**, *34*, 1042-1044.

Rhodium(III)-Catalyzed Synthesis of Heterocyclic Systems Via Amination Reactions

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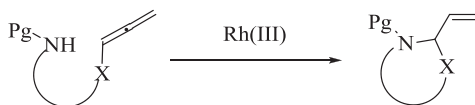
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Transition-metal-catalyzed directing-group-assisted C-H activation has emerged as a sustainable and intriguing protocol for the formation of C-C, C-N and C-O bonds.^[1] In this context, rhodium(III)-mediated reactions have proven valuable as key steps for the synthesis of various complex heterocyclic molecules.^[2]

As part of our ongoing interest in transition metal mediated heterocyclization reactions,^[3] involving the addition of a X-H group to multiple bonds, we have investigated a new Rh(III)-based approach to the synthesis of vinyl-substituted heterocycles via formal hydroamination reaction of amino allenes.

In many cases, these reactions lead to the formation of a new stereocenter, whose configuration can, in principle, be controlled. To achieve stereoselective transformations we have studied the synthesis of new Rh(III) chiral complexes bearing polydentate oxygen-, nitrogen-, and phosphorus-based ligands. Their reactivity and selectivity is now under investigation.



References

1. a) Ackermann, L., Vicente, R., Kapdi, A. R. *Angew. Chem. Int. Ed.* **2009**, *48*, 9792-9826; b) Chen, X., Engle, K. M., Wang, D. H., Yu, J. Q. *Angew. Chem.* **2009**, *121*, 5196-5217; c) Wencel-Delord, J., Droge, T., Liu, F., Glorius, F. *Chem. Soc. Rev.* **2011**, *40*, 4740-4761.
2. a) Colby, D. A., Bergman, R. G., Ellman, J. A. *Chem. Rev.* **2010**, *110*, 624-655; b) Song, G., Wang, F., Li, X. *Chem. Soc. Rev.* **2012**, *41*, 3651-3678.
3. Borsini, E., Broggini, G., Fasana, A., Galli, S., Khansaa, M., Piarulli, U., Rigamonti, M. *Adv. Synth. Catal.* **2011**, *353*, 985-994.

New [Pt((N[^]C[^]N)Cl)] (N[^]C[^]N= 1,3-di(2-pyridyl)benzene) Complexes with Interesting Luminescent Properties.

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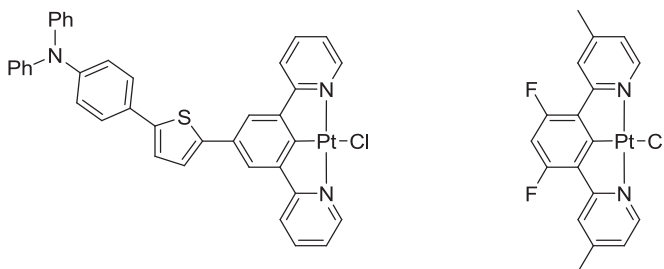
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There has been a growing interest in the design of luminescent transition metal complexes as phosphors for Organic Light Emitting Devices (OLEDs) over the past decade^{1,2}. Though the field has to date been dominated by iridium(III) complexes, platinum(II) complexes attract nowadays increasing interest. Pt(II) complexes with terdentate ligands based on cyclometallated 1,3-di(2-pyridyl)benzene (dpyb), which offer the metal ion an N[^]C[^]N coordination environment, are amongst the brightest Pt-based emitters in solution at room temperature³. Remarkably, the emission color of OLEDs based on these complexes can be easily tuned changing the substituents on the terdentate ligand³. Recently some of us have described the effect of the incorporation of ArC=C- and ArC≡C- substituents at the central 5-position of the phenyl ring of dpyb⁴. Now, we report new Pt(II) terdentate complexes with different π -delocalized ligands at the central 5-position of the phenyl ring of dpyb, such as reported in Figure, with interesting luminescent properties.



References

- Baldo, M.A., O'Brien, D.F., You, Y., Shoustikov, A., Sibley, S., Thompson, M.E., Forest, S.R. *Nature* **1998**, 395, 151-154.
- Chou, P.-T., Chi, Y., Chung, M.-W., Lin, C.-C. *Coord. Chem. Rev.*, **2011**, 255, 2653-2665.
- Williams, J. A. G. *Chem. Soc. Rev.*, **2009**, 38, 1783-1801.
- Nisic, F., Colombo, A., Dragonetti, C., Roberto, D., Valore, A., Malicka, J.M., Cocchi, M., Freeman, G.R., Williams, J.A.G. *J. Mat. Chem. C*, **2014**, 2, 1791-1800.

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Development of New Amphiphilic Systems Based on Metal-Salophen Schiff-Base Complexes for the Recognition of Anions In Water

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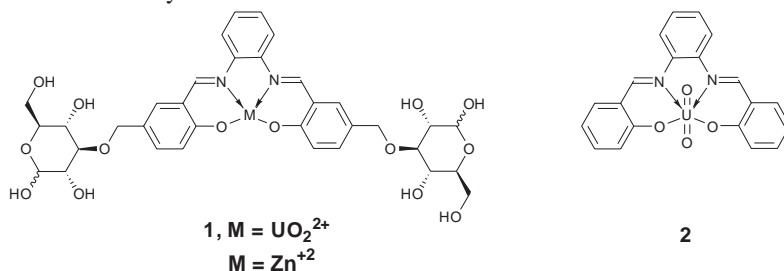
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The design and synthesis of water soluble receptors for selective and sensitive quantification of biologically and environmentally important ion species is a field of increasing interest.

Salophens are a quite popular class of Schiff base ligands. They are obtained by the condensation of 1,2-phenylenediamine with two equivalents of salicylaldehyde. The two starting building blocks can be easily functionalized and this gives access to a large variety of ligands with subtle variations in steric and electronic configuration. The resulting coordination site, an N_2O_2 binding pocket, is capable of bonding to a series of metals in a tetradentate fashion. Such derivatives are Lewis acids able to coordinate anions.¹

Here we report that metal-salophen based receptors can be protagonists in the field of anion recognition in water. Different strategies have been pursued in order to achieve the goal. The introduction on the salophen skeleton of neutral hydrophilic groups such as glucose, **1**, or oligosaccharides leads to water soluble, efficient receptors for carboxylates ($M = Zn^{2+}$) and hydrogen phosphate ($M = UO_2^{2+}$).² In alternative, the use of micelles (CTABr, CTACl) to solubilize the lipophilic receptor **2** provides supramolecular systems that bind fluoride in water with remarkable sensitivity.³



References

1. Dalla Cort, A.; De Bernardin, P.; Forte, G.; Yafteh Mihan, F. *Chem. Soc. Rev.*, **2010**, *39*, 3863-3874.
2. Bedini, E.; Forte, G.; De Castro, C.; Parrilli, M.; Dalla Cort, A. *J. Org. Chem.*, **2013**, *78*, 7962-7969.
3. Keymeulen, F.; De Bernardin, P.; Dalla Cort, A.; Bartik, K. *J. Phys. Chem. B* **2013**, *117*, 11654-11659.

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Well-Defined [Ag(I)(Pc-L)] Complexes: Suitable Catalysts for the Synthesis of 1-Alkoxy-Isocromenes

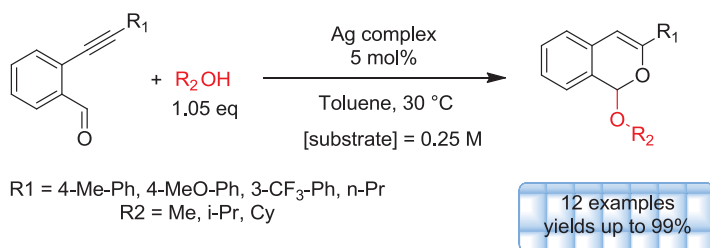
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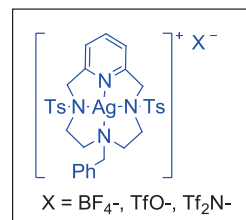
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The [Ag(I)(Pc-L)] complexes¹ – new silver(I) complex with an original macrocyclic pyridine-containing ligand (Pc-L) – demonstrated to be suitable catalysts for the synthesis of 1-alkoxyisocromenes² starting from various 2-alkynylbenzaldehydes³ and different primary and secondary alcohols.⁴ Best results were obtained with BF₄⁻ complex. The approach is characterised by absolute regioselectivity, mild reaction condition, good to excellent reaction yields, cleanness of the reaction and reduced purification steps. The reaction mechanism was investigated by in depth NMR studies and an aimed intramolecular “trapping” experiment to point out the possible involvement of an isochromenilium intermediate. In an enantioselective development perspective, some preliminary tests with Ag(I) complexes of previously synthesised chiral pyridine-containing ligands^{1b} were performed.



[Ag(I)(Pc-L)] complexes



References

- (a) Castano, B.; Pedrazzini, T.; Sisti, M.; Gallo, E.; Ragaini, F.; Casati, N.; Caselli, A. *Appl. Organometal. Chem.* **2011**, *25*, 824–829. (b) Castano, B.; Guidone, S.; Gallo, E.; Ragaini, F.; Casati, N.; Macchi, P.; Sisti, M.; Caselli, A. *Dalton Trans.* **2013**, *42*, 2451–2562.
- Belmont, P. in *Silver in Organic Chemistry* (Ed. M. Harmata), John Wiley and Sons, Inc., Hoboken, 2010, pp 143–165; Chapter 5.
- Dell'Acqua, M.; Facoetti, D.; Abbiati, G.; Rossi, E. *Synthesis* **2010**, 2367–2378.
- Dell'Acqua, M.; Castano, B.; Cecchini, C.; Pedrazzini, T.; Pirovano, V.; Rossi, E.; Caselli, A.; Abbiati G. *J. Org. Chem* **2014**, *79*, 3494–3505.

Ag₄(NHC)₄(NO₃)₄: a Tetrameric Silver (I) Complex with Bridging N-Heterocyclic Carbene Ligands[#]

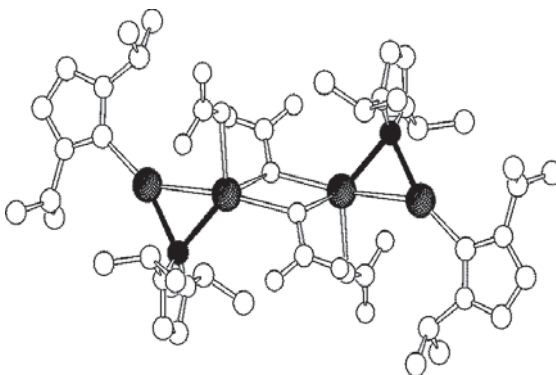
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In recent years the coordination chemistry of N-heterocyclic carbenes showed a boosting increment, since these new type of ligands have many valuable properties in terms of stability, versatility, possibility to introduce new functionalities.¹ Silver complexes are among the most widely studied since they have been used for several applications, including pharmaceutical, photophysical and catalytic.² In such a large number of characterized compounds, only two examples of bridging coordination of the NHC groups have been reported, one for a copper complex,³ and the other (with silver) assisted through symmetric pendant donor groups.⁴ Looking for new neutral silver complexes, we explored the reaction between Ag(cod)NO₃ and [Ag(*IPrIm*)Cl]₂, in CH₂Cl₂. The product was crystallized by diffusion of heptane, and the final yield was about 50 %. IR, elemental analyses and X-ray diffraction concurred to establish the actual formula of the compound as (HNC-Ag-NO₃)₄. In the solid state, the compound is composed by tetrameric unit with two short and one long Ag-Ag contacts. The short ones are bridged by the N-heterocyclic carbenes, and the long one by monodentate nitrate anions. According to DFT calculations, the tetramer can exist in two isomers and the one with terminal-only carbene ligands should be slightly more stable. Conversely, with other anions such as halide, only the isomer with terminal carbene ligands can be formed.



[#] Dedicated to the memory of Mario Manassero

1. Special issues on metal-carbene complexes: a) *Dalton. Trans.*, **2013**, *42*, 7245-7432; b) *Dalton. Trans.*, **2009**, 6873-7316; c) *Coord. Chem. Rev.*, **2007**, *251*, 595-896 d) *Chem. Rev.*, **2009**, *109*, 3209-3884; e) Jones, W.D.; *J. Am. Chem. Soc.*, **2009**, *131*, 15075-15077 f) *J. Organomet. Chem.*, **2005**, *690*, 5397-6252
2. Garrison, J.C.; Youngs, W.J.; *Chem. Rev.*, **2005**, *105*, 3978-4008.
3. Han, X.; Koh, L.-L.; Liu, Z.-P.; Weng, Z.; Hor, T.S.A.; *Organometallics*, **2010**, *29*, 2403-2405
4. Garrison, J. C.; Simons, R. S.; Kofron, W. G.; Tessier, C. A.; Youngs, W. J. *Chem. Commun.* **2001**, 1780-1781.-

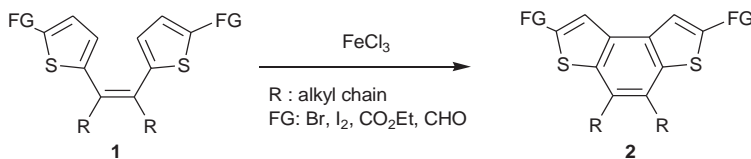
Non-Photochemical Synthesis of Functionalized Benzo[1,2-*B*:4,3-*B'*]Dithiophene Derivatives

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Thiophene-containing fused, aromatic compounds represent an interesting class of π -conjugated systems in functional organic materials. A role of increasing importance is going to be acquired by benzo[1,2-*b*:4,3-*b'*]dithiophene (BDT) which have been studied as units in mono and polydisperse oligomers in field of the materials science, and, more recently, as π -spacers in push-pull organic chromophores for photovoltaic applications¹. Moreover, BDT represents a key intermediate in the synthesis of inherently chiral helical systems such as tetrathia[7]helicenes². Within this context, and in view of potential wider and industrial applications, simple, reliable, reproducible and economic syntheses of BDTs, which avoid the use of photochemical pathway are highly desirable. Herein, we report the first results of our investigations on the FeCl₃-mediated cyclization of α,α' -disubstituted *Z*-alkenes **1** as a general and non-photochemical synthesis of BDT derivatives **2**.³



The influence of the temperature and the nature of the substituents, in determining the scope and limitations of this methodology have been also explored.

References

1. Longhi, E.; Bossi, A.; Di Carlo, G.; Maiorana, S.; De Angelis, F.; Salvatori, P.; Petrozza, A.; Binda, M.; Roiati, V.; Mussini, P. R.; Baldoli, C.; Licandro, E. *Eur. J. Org. Chem.*, **2013**, 84.
2. Licandro, E.; Rigamonti, C.; Ticozzelli, M. T.; Monteforte, M.; Baldoli, C.; Giannini, C.; Maiorana, S. *Synthesis*, **2006**, 3670.
3. Caeteruccio, S.; Dova, D.; Graiff, C.; Carrara, C.; Doulcet, J.; Stephenson, G. R.; Licandro, E. *New J. Chem.*, **2014**, 38, 2241.

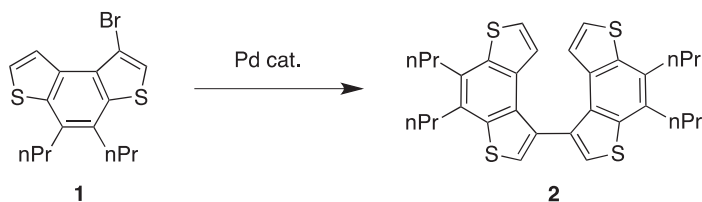
Synthesis of Axially Chiral Thiophene-Based Systems through Pd-Catalyzed Cross Coupling Reactions

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The biaryl motif occupies an iconic role in chemistry, being a key structural feature of natural products, biologically active molecules, drugs, agrochemicals, and other novel optical and mechanical materials. Furthermore, the stereogenic axes provide rigid molecular frameworks for highly efficient tools in asymmetric synthesis.¹ Exploiting the experience acquired in our laboratories on the synthesis of compounds based on alternating thiophene and benzene rings², we have started the study of a simple and efficient synthetic route to prepare bis(benzodithiophenes) system **2**, through Pd-catalysed cross coupling reactions, starting from bromide **1**.



This strategy provides a convenient approach to an interesting class of chiral atropisomeric biaryl derivatives with C_2 -symmetry, which are expected to have broad applications in asymmetric reactions, including the enantioselective synthesis of tetrathiahelicene derivatives.

References

1. Leroux, F. R.; Berthelot, A.; Bonnafoux, L.; Panossian, A.; F. Colobert F.; *Chem. Eur. J.* **2012**, *18*, 14232.
2. a) Licandro, E.; Rigamonti, C.; Ticozzelli, M. T.; Monteforte, M.; Baldoli, C.; Giannini, C.; Maiorana, S. *Synthesis*, **2006**, 3670. b) Cauteruccio, S.; Dova, D.; Graiff, C.; Carrara, C.; Doulcet, J.; Stephenson, G. R.; Licandro, E. *New J. Chem.*, **2014**, *38*, 2241.

Tuning The Dipolar Second-Order Nonlinear Optical Properties of Novel Cyclometalated Platinum(II) Complexes.

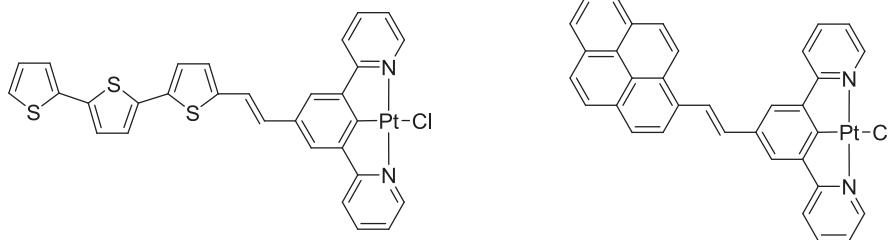
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Organometallic complexes with second-order nonlinear optical (NLO) properties are important as molecular building block materials for the exciting field of molecular photonics¹. It was reported² that a series of terpyridine and cyclometalated dipyritylbenzene Pt(II) complexes, display large quadratic hyperpolarizabilities, measured by the hyper-Rayleigh scattering technique (HRS). The N^{^C^N}-coordinated cyclometalated dipyritylbenzene Pt complexes are characterized by an enhanced NLO efficiency with respect to related N^{^N^N}-coordinated terpyridine complexes². These results prompted us to carry out an in-depth investigation of the tuning of the second-order NLO properties of variously substituted 1,3-di(2-pyridyl)benzene Pt(II) complexes³, measured with the electric-field-induced second-harmonic (EFISH) technique. We report here the syntheses of new Pt(II) terdentate complexes with different π -delocalized ligands at the central 5-position of the phenyl ring of the N^{^C^N} ligand (see Figure for selected examples) and the study of their appealing second order NLO response, measured with the EFISH technique.



References

1. Di Bella, S., Dragonetti, C., Pizzotti, M., Roberto, D., Tessore, F., Ugo, R. *Top. Organomet. Chem.* **2010**, 28, 1-55.
2. Scarpaci, A., Monnerau, C., Hergué, N., Blart, E., Legoupy, S., Odobel, F., Gorfo, A., Pérez-Moreno, J., Clays, K., Asselberghs, I. *Dalton Trans.* **2009**, 4538-4546.
3. Rossi, E., Colombo, A., Dragonetti, C., Righetto, S., Roberto, D., Ugo, R., Valore, A., Williams, J.A.G., Lobello, M.G., De Angelis, F., Fantacci, S., Ledoux-Rak, I., Singh, A., Zyss, J. *Chem. A European. J.* **2013**, 19, 9875-9883.

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Synthesis of Fused Bicyclic Heterocycles by Intramolecular Reductive Cyclization of Nitro-Olefins, Catalyzed by Palladium Complexes and with Carbon Monoxide as the Reductant.

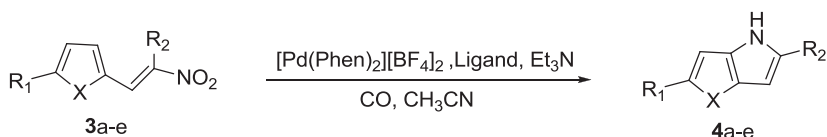
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Research in our unit recently showed that reductive cyclization of β -nitrostyrenes catalyzed by palladium/phenanthroline complexes and with CO as a reductant affords indoles in good yields.¹ The reaction proceeds by the activation of an aryl C-H bond. We decided to extend such cyclization reaction to other heterocyclic systems, although it is known that the activation of a C-H bond of electron-rich five member heterocycles is a more difficult reaction. Nitro olefins attached to 5-membered heterocyclic compounds **2a-e** were prepared by the Henry reaction and fully characterized by ¹H-NMR, ¹³C-NMR and elemental and mass analyses. Subsequent reductive cyclization catalyzed by palladium-phenanthroline complexes under CO pressure afforded A10 π aromatic compounds, isoelectronic with pentalenyl dianion, and containing a pyrrole ring fused to another 5-membered heterocyclic compound (**3a-e**). Compound **2c** was chosen as a model compound for the optimization of the experimental conditions. Among many tested ligands 4,7-dimethoxyphenanthroline showed good results for both conversion and selectivity. The optimization of temperature, CO pressure, nature of the base, type of ligand, reaction time and solvent are in progress.



- a, X = O, R₁ = CH₃, R₂ = CH₃
 b, X = S, R₁ = H, R₂ = CH₃
 c, X = NCH₃, R = H, R₂ = CH₃
 d, X = NAc, R = H, R₂ = CH₃
 e, X = S, R₁ = H, R₂ = COOEt

Reference

1. Ferretti, F.; Muto, S.; Hagar, M.; Gallo, E.; Ragaini, F. *manuscript in preparation*.

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8-Amino-5,6,7,8-Tetrahydroquinolines as Ligands in Iridium(III) Catalysts for the Reduction of Aryl Ketones by Asymmetric Transfer Hydrogenation (ATH)

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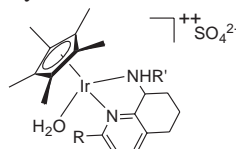
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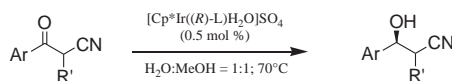
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Recently, it has been demonstrated the possibility to use iridium complexes as a valid alternative to the use of classical ruthenium systems.¹ Aqua iridium(III) complexes with 8-amino-5,6,7,8-tetrahydroquinolines, CAMPY L1 and its derivatives as chiral ligands proved to be very efficient catalysts in the reduction of a wide range of prochiral aryl ketones, revealing a variety of behaviours in terms of reaction rate and stereoselectivity.

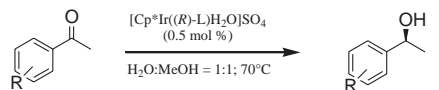
L1 R = R' = H; CAMPY
L2 R = CH₃; R' = H; Me-CAMPY
L3 R = H; R' = CH₃; CAMPY-NHMe
L4 R = R' = CH₃; Me-CAMPY-NHMe



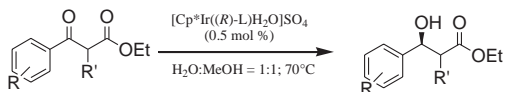
Screening was carried out for the reduction of different types of aryl ketones and three hydrogen donors were evaluated: HCOOH or HCOONa in a mixture solution 1:2=H₂O:MeOH or azeotropic mixture HCOOH/TEA = 5/2 in neat. A deep variety of behaviours emerged by changing reaction conditions, stressing the matching between the substrates and the ligands used in the metal complexes. In particular the presence of HCOOH as hydrogen donor played an important role on the stereoselectivity of the catalysts. ATH reactions on β -lactam precursors led to interesting results achieving very high e.e..



Ar = Ph, thienyl, furyl; R' = H, CH₂CH₃



R = H, o-CH₃, p-CF₃, R = m-OCH₃



R = H, p-OCH₃, p-CF₃; R' = H, -CH₂NHCOPh

References:

1. a) H. Vázquez-Villa, S. Reber, M. A. Ariger, E. M. Carreira, *Angew. Chem., Int. Ed.* **2011**, 50, 8979-8981; b) M. A. Ariger, E. M. Carreira, *Org. Lett.* **2012**, 14, 4522-4524.

Pd-Catalysed Allylic Substitution Reactions with Chiral Phthalaphos Ligands: Enantioselective Synthesis of 1-Vinyltetrahydroisoquinolines and 4-Vinyltetrahydrocarbazoles

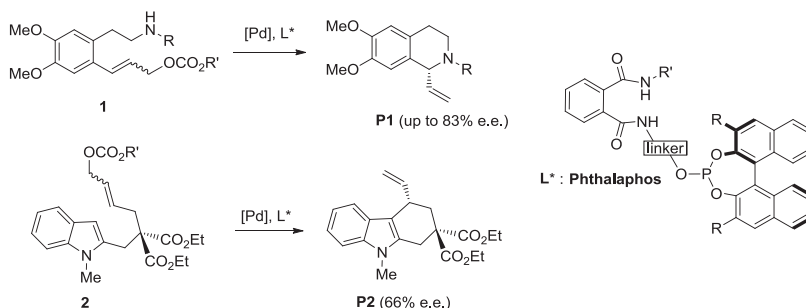
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Phthalaphos ligands, a new class of chiral BINOL monophosphites endowed with a phthalamide group, have been recently used in rhodium-catalysed hydrogenation of olefins with high level of enantioselectivity.¹ The catalytic potential of these ligands was further explored in palladium-catalysed C-C and C-N bond forming allylic substitution reactions² affording chiral isoquinoline^{3a} and carbazole^{3b} derivatives **P1** and **P2**. Under optimized conditions (ligand, solvent, temperature), carbonates **1** and **2** led to the desired products with up to 83% e.e.. The experimental data suggest that the ligands' phthalamide moiety plays a role in determining enantiocontrol, guiding the approach of the substrate towards the metal through hydrogen bonding.



References

1. (a) Pignataro, L.; Carboni, S.; Civera, M.; Colombo, R.; Piarulli, U.; Gennari, C. *Angew. Chem. Int. Ed.* **2010**, *49*, 6633 - 6637. (b) Pignataro, L.; Boghi, M.; Civera, M.; Carboni, S.; Piarulli, U.; Gennari, C. *Chem. Eur. J.* **2012**, *18*, 1383 - 1400.
2. For a recent review, see: Trost, B. M.; Zhang, T.; Sieber, J. D. *Chem. Sci.* **2010**, *1*, 427-440.
3. For relevant reviews, see: (a) Chrzanowska, M.; Rozwadowska, M. D. *Chem. Rev.* **2004**, *104*, 3341 - 3370. (b) Knoelker, H. J.; Reddy, K. R. *Chem. Rev.* **2002**, *102*, 4303 - 4428.

Acknowledgements: This work was funded by the European Commission [EID-ITN Network 'REDUCTO', contract n. PITN-GA-2012-316371] and Consiglio Nazionale delle Ricerche (CNR). L. Pignataro thanks the Dipartimento di Chimica, Università di Milano, for financial support (Piano di sviluppo dell'Ateneo – anno 2014 – Linea B.1 - grants for young researchers).

Ferrocene Meets Porphyrin: Consequences of a “Fusion”

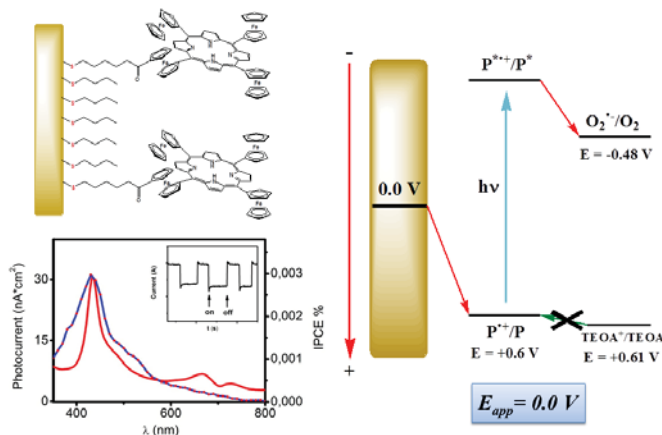
Barbara Floris^a, V. Conte^a, P. Galloni, M. Tiravia^a, A. Vecchi^a, V. N Nemykin^b

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Organometallic substituted porphyrinoids are a variegated class of compounds of general interest, both from the fundamental and from an applicative point of view¹. The extent to which the organometallic fragments affect the macrocycle properties are strictly related to the position where they are appended. In particular, *meso*-tetraferrocenylporphyrins (TFcPs)¹ was the object of a number of investigations, in view of applications, such as the construction of molecular electronic devices. The molecule and its metal complexes exhibit intense electronic communication among metal centres, resulting in multiredox processes and formation of mixed-valence species. Important consequences of the ferrocene-to-porphyrin linkage will be discussed, in particular with unsymmetrically substituted TFcPs attached to surfaces (gold or ITO).



Different surface functionalizations were performed, with resulting SAMs of different robustness. In all the examined cases photon-to-current experiments evidenced that the porphyrin is the photo-active species of the film, with a behaviour strongly influenced by ferrocenyl groups.

References

1. Vecchi, A.; Galloni, P.; Floris, B.; Nemykin, V. N. *J. Porphyrins Phthalocyanines* **2013**, *17*, 166.
2. Nemykin, V. N.; Rohde, G. T.; Barrett, C. D.; Hadt, R. G.; Bizzarri, C.; Galloni, P.; Floris, B.; Nowik, I.; Herber, R. H.; Marrani, A. G.; Zanoni, R.; Loim, N. M.; *J. Am. Chem. Soc.* **2009**, *131*, 14969.

Acknowledgements: This work was funded by PRIN 2010-11

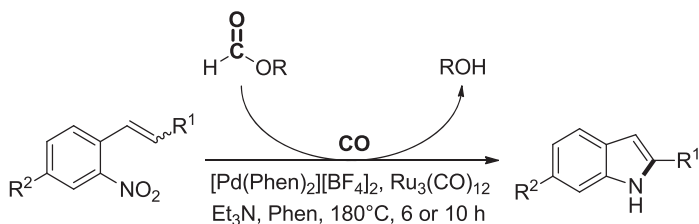
Formate Esters as CO Sources: Synthesis of Indoles by Reductive Cyclization of *ortho*-Nitrostyrenes

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The transition metal catalyzed synthesis of nitrogen-containing heterocycles has become a powerful tool in organic chemistry. In particular, the catalytic reductive cyclization of *ortho*-nitrostyrenes by palladium complexes using gaseous CO as the reductant, is a powerful method for the synthesis of substituted indoles.¹ From a laboratory scale point of view, the use of CO is often complicated and inconvenient. In fact its employment implies the installation of expensive safety measures and often the use of high-pressure reactors. A way to overcome this issue involves the use of organic molecules capable of releasing carbon monoxide *in situ*. In this perspective formate esters are considered promising alternatives to carbon monoxide. Ru₃(CO)₁₂ is able to act as catalyst for the decarbonylation of butyl and methyl formate to give CO and the corresponding alcohols.² [Pd(Phen)₂][BF₄]₂ has been used as catalyst in the nitrostyrenes cyclization using gaseous CO as the reductant for many years.³ Herein we report our results on the use of a bimetallic catalytic system based on [Pd(Phen)₂][BF₄]₂ and Ru₃(CO)₁₂ for the synthesis of substituted indoles from *ortho*-nitrostyrenes using formate esters (both butyl and methyl) as CO sources. All the reactions were performed in an economical pressure tube. The reactions were optimized using methyl 2-nitrocinnamate and 2-nitrostyrene and the substrate scope was extended for the synthesis of various 2,6-substituted indoles.



References

1. Ragaini, F.; Cenini, S.; Gallo, E.; Caselli, A.; Fantauzzi, S., *Curr. Org. Chem.* **2006**, *10*, 1479-1510.
2. Jenner, G.; Nahmed, E. M.; Leismann, H., *Tetrahedron Lett.* **1989**, *30*, 6501-6502.
3. Ragaini, F.; Rapetti, A.; Visentin, E.; Monzani, M.; Caselli, A.; Cenini, S., *J. Org. Chem.* **2006**, *71*, 3748-3753.

Synthesis and Characterization of New D- π -A Organic Photosensitizers for DSSCs.

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^a *Università degli Studi di Firenze, Dip. di Chimica "Ugo Schiff", V. della Lastruccia 13, 50019 Sesto Fiorentino, Italy;*

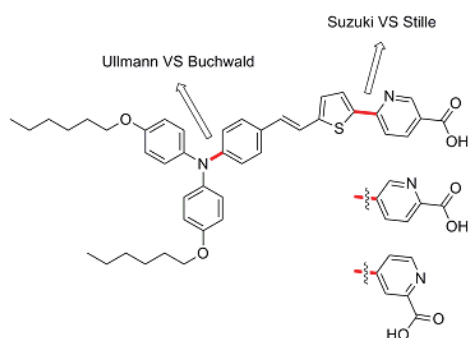
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Dye-sensitizer Solar Cells (DSSC) are innovative devices that allow photon-to-electron conversion without using silicon. The aim of this study is to design, synthesize and characterize a small library of new dyes to be used as sensitizers for TiO₂ in DSSCs. The efforts have been focused on purely organic compounds and, since most of the organic dyes reported in the literature have a D- π -A architecture, we decided to concentrate on such structures, aiming to improve the anchoring moiety first.



The main reaction steps to build a common D- π scaffold and to link new anchoring functions, have been performed through palladium-catalyzed cross-coupling reactions. The most efficient protocols have been assessed comparing different procedures such as Ullmann-type and Buchwald-Hartwig reactions to build new carbon-nitrogen bond; Suzuki and Stille coupling for the carbon-carbon bond formation. Further studies concerning the

use of specific legends, microwave-assisted heating, and the use of additives have been done to establish the most advantageous setup of reaction with our specific substrates. Such screening have allowed us to prepare the target molecules with new acceptors based on carboxypyridine containing electron-withdrawing substituents. Small test devices have been prepared with those new dyes as sensitizers: good conversion efficiencies and superior chemical and physical stability under DSSC's working condition have been noticed proving the efficiency of the new anchoring systems. An article concerning this work has already been submitted.

Towards a New Class of Chiral Fe-Catalysts for the Enantioselective Hydrogenation of Ketones

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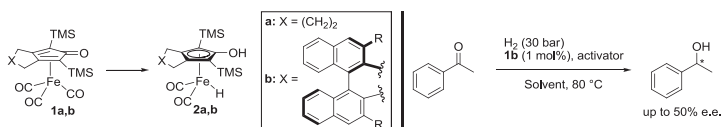
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Asymmetric catalysis is the most efficient strategy for producing enantiopure compounds, and the enantioselective reduction of double bonds (hydrogenation in particular) is one of its most well-developed applications. Compared to other transition metals, Fe is significantly less exploited for the homogeneous catalysis of double bond reductions. However, given the far lower cost and greater abundance of Fe over the more precious metals, in recent years there has been a growing interest for developing efficient and selective homogeneous Fe-catalysts.¹ Despite these efforts, only a few efficient enantioselective reduction methodologies based on Fe-catalysis have been developed so far. To fill this gap, we are developing new chiral catalysts for the enantioselective hydrogenation of ketones. We took inspiration from the Knölker-Casey catalyst **2a**,² an achiral Cp-Fe(II) hydride that can be generated *in situ* from the air-stable Fe(0)-cyclopentadienone precursor **1a**.³ Catalyst **2a** can promote the hydrogenation of ketones and imines with very high efficiency (up to 3,800 TON). Chiral cyclopentadienone complexes **1b** were obtained by replacing the six-membered fused ring of **1a** with a BINOL-derived chiral moiety.



Complexes **2b**, formed *in situ* from **1b** using known procedures,³ showed ability to promote the hydrogenation of acetophenone with good conversions and promising enantioselectivity (up to 50% e.e.). The synthesis of improved, second-generation catalysts is currently underway.

References

1. M. Darwish, M. Wills, *Catal. Sci. Technol.* **2012**, 2, 243-255.
2. A. Quintard, J. Rodriguez, *Angew. Chem. Int. Ed.* **2014**, 53, 4044-4055.
3. S. Fleischer, S. Zhou, K. Junge, M. Beller, *Angew. Chem. Int. Ed.* **2013**, 52, 5120-5124.

Acknowledgements: This work was funded by the European Commission [EID-ITN Network 'REDUCTO', contract n. PITN-GA-2012-316371] and Consiglio Nazionale delle Ricerche (CNR). L.P. thanks the Dipartimento di Chimica, Università di Milano, for financial support (Piano di sviluppo dell'Ateneo—anno 2014—Linea B.1—grants for young researchers).

Photo- and Electro-Chemical Reduction of CO₂ by Re(CO)₃ Carbonyl Complexes Containing Fluorescent 4-Piperidinyl-1,8-Naphthalimide

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The effect of the highly fluorescent PNI (4-piperidinyl-1,8-naphthalimide) chromophore on the CO₂ reduction catalytic properties of Rhenium based catalysts was investigated. In particular, the electro- and photocatalytic CO₂ reduction properties of Re(CO)₃(2,2'-bipyridine)Cl were compared with the activity of Re(CO)₃(phen-PNI)Cl, already known in the literature for its long-lived excited state lifetime. Moreover two novel Re complexes, namely Re(CO)₃(bpy-Ph-NH₂)Cl and Re(CO)₃(bpy-Ph-PNI)Cl were synthesized and tested as electro- and photocatalysts. The catalytic properties of the selected compounds were studied by means of electrochemical (cyclic voltammetry and controlled-potential electrolysis) and photophysical measurements, together with DFT calculations. Bulk electrolysis experiments revealed that, among the complexes under investigation, Re(CO)₃(bpy-Ph-PNI)Cl showed good electrocatalytic efficiency toward selective CO₂ reduction to CO, as reported below (Fig. 1). In particular, this novel organometallic sample revealed to have longer activity over electrolysis time than the reference compound, reaching a Turnover Number of about 50 after 8 hours of experiments, in the presence of 0.5 M CH₃OH as external proton source.

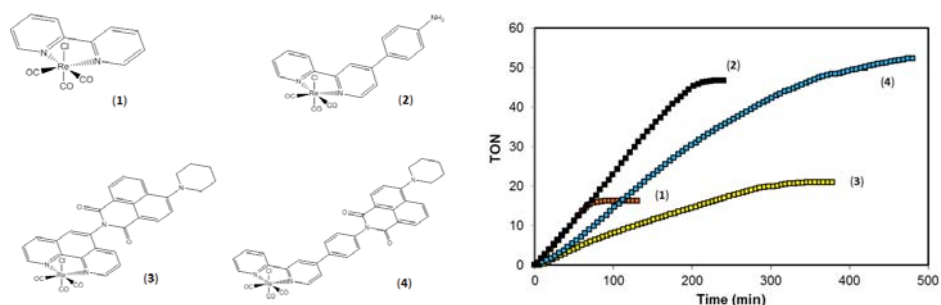


Fig. 1. Activities, in terms of Turnover Number (TON) over electrolysis time, for the compounds **1** (orange), **2** (black), **3** (yellow) and **4** (blue).

Acknowledgements: This work has been funded by the PHOTORECARB project (Compagnia di San Paolo and University of Turin).

Luminescent Poly(amidoamine)-Iridium Complex as New Singlet Oxygen Sensitizer for Photodynamic Therapy

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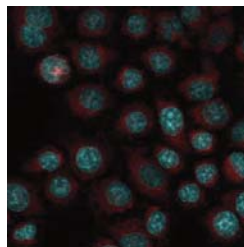
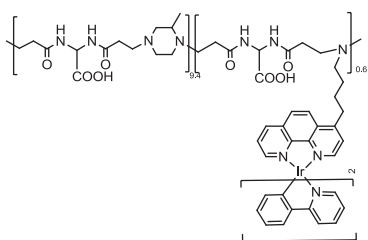
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Photodynamic therapy (PDT) has attracted much attention as a promising cancer therapy. Singlet oxygen ($^1\text{O}_2$) is one of the reactive oxygen species, and it is believed to act as a major cytotoxic agent that damages cancer tissues in PDT.

In order to obtain a new stealth and biocompatible PDT sensitizer, we have conjugated a metallorganic 'Ir(ppy)' fragment to a linear poly(amidoamine) copolymer (dubbed PhenISA)¹, exploiting a phenanthroline pendant present in the minor part of the copolymer (ca. 6 %, Scheme 1). In this way a luminescent $^3\text{MLCT}$ emitter able to photogenerate $^1\text{O}_2$ has been synthesized. In physiological conditions it self assembles to give nanoparticles with a hydrodynamic diameter of 15-20 nm.

A preliminary investigation of internalization in Hela cells, by means of fluorescence confocal microscopy, showed that Ir-PhenISA enters cells and homogeneously diffuse within the cytoplasm (Figure 1), without any cell damage, showing that the metallorganic fragment bonded to the poly(amidoamine) does not affect its biocompatible properties. Measures of $^1\text{O}_2$ production in culture cells and its effect on their viability are nowadays under investigation.



Scheme 1. Sketch of the Ir-PhenISA polymer complex. **Figure 1.** Fluorescence confocal microscopy image of Hela cells incubated with Ir-PhenISA 5 μM .

References

1. Maggioni D., Fenili F., D'Alfonso L., Donghi D., Panigati M., Zanoni I., Marzi R., Manfredi A., Ferruti P., D'Alfonso G., Ranucci E., *Inorg. Chem.* **2012**, *51*, 12776.

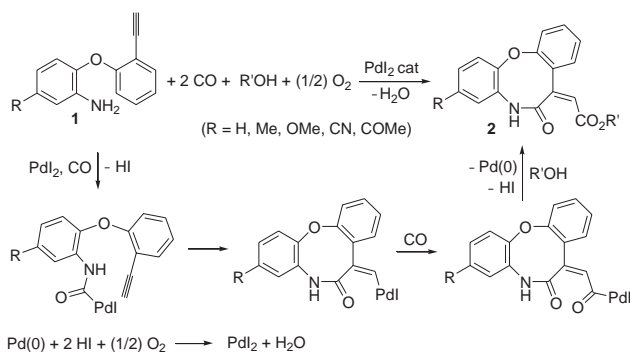
Synthesis of a Novel Class of 12-Oxa-5-azadibenzo[*a,d*]cycloocten-6-one Derivatives by PdI₂-Catalyzed Oxidative Cyclocarbonylation-Alkoxy carbonylation of 2-(2-Ethynylphenoxy)Anilines

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An expedient approach to 12-oxa-5-azadibenzo[*a,d*]cycloocten-6-one derivatives **2** starting from 2-(2-ethynylphenoxy)anilines **1** is reported. Under suitable oxidative carbonylation conditions, in the presence of the PdI₂/KI catalytic system,¹ substrates **1** undergo a remarkable cyclocarbonylation process, with closure of an 8-member ring followed by alkoxy carbonylation to give the final product (Scheme 1). The structure of products **2** has been confirmed by X-ray crystallographic analysis, as shown in Figure 1 for (*Z*)-7-(ethoxycarbonyl)methylene-5*H*,7*H*-12-oxa-5-azadibenzo[*a,d*]cycloocten-6-one (R = H, R' = Et).



Scheme 1

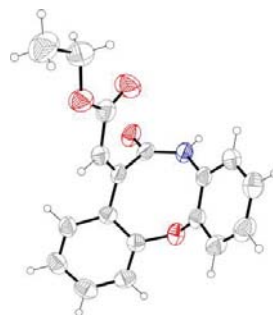


Figure 1

Reactions are carried out in alcoholic solvents (R'OH, R = Me, Et) under relatively mild conditions (at 100°C and 40 atm of a 4:1 mixture of CO-air for 24 h), using 2 mol% of PdI₂, in conjunction with 20 mol % of KI, to give **2** in moderately good yields (50-55%).

Reference

1. Gabriele B.; Mancuso, R.; Salerno, G., M. *Eur. J. Org. Chem.* **2012**, 6825-6839 (microreview).

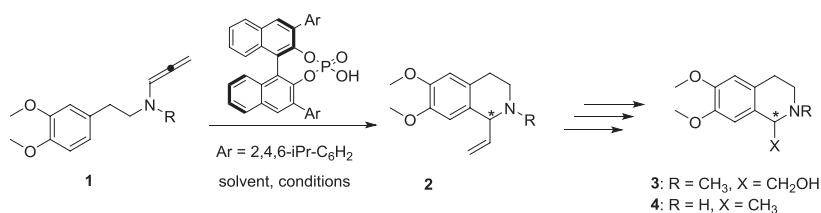
Stereoselective Catalytic Synthesis of Isoquinoline Alkaloids by Chiral Brønsted Acids

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In literature several examples of allenamide activation by Lewis and Brønsted acids are reported. In 2007 Navarro reported an intramolecular cyclization reaction of allenamide activated by TFA in which the nucleophile was an electron-rich aromatic ring.¹ In 2013 Terada presented a synthetic protocol for tetrahydroisoquinoline derivatives by a Pictet-Spengler reaction catalyzed by chiral phosphoric acids, that gave quite moderate results.² In order to improve the enantiomeric excess and the reaction scope obtained by Terada, in this paper we disclose our preliminary results concerning an intramolecular cyclization reaction of allenamides catalyzed by chiral Brønsted acid, delivering versatile molecular motifs for a range of naturally occurring compounds. This methodology is tolerant to several *N*-protecting groups and uses commercially available TRIP ((*R*)-3,3'-Bis(2,4,6-triisopropylphenyl)-1,1'-binaphthyl-2,2'-diyl hydrogenphosphate) as the catalyst.



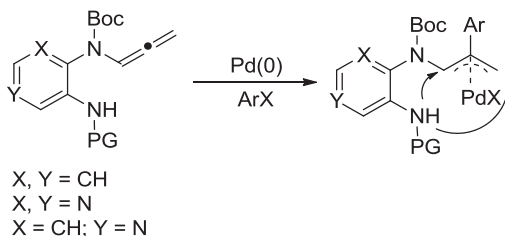
References

1. A. Navarro-Vázquez, D. Rodríguez, M.F. Martínez-Esperón, A. García, C. Saá, D. Domínguez *Tetrahedron Lett.*, **2007**, *48*, 2741-2743.
2. Y. Toda, M. Terada *Synlett*, **2013**, *24*, 752-756.

Pd-Catalyzed Reactivity of *N*-Allenyl Amino(hetero)arenes**Alberto Mazza, E. M. Beccalli***DISFARM, Sez. Chimica Generale e Organica "A. Marchesini", Università degli Studi di Milano, Via Venezian 21, 20133 Milano - Italy*

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The use of transition-metals catalyzed reactions, among them palladium catalysts, permits the formation of polyheterocyclic systems endowed with different kind of properties.¹ In this contest reactions involving C-N bond formation on easily available substrates containing C-C multiple bonds represent fruitful methodology to achieve nitrogenated cyclic structures, useful intermediates for natural and pharmaceutical products synthesis.² Allenic amines tethered to aryl or heteroaryl nucleus bearing a nucleophilic substituent represent a suitable substrates for intramolecular reactions such as amination or hydroamination.³ A successful method of hydroamination of allenes has been recently developed in our laboratories following a convenient procedure using mild conditions under microwave irradiation.⁴ In the present work we reported the different cyclization paths observed depending on the aryl or heteroaryl scaffold. Moreover domino reactions as carboaminations are reported as advantageous processes to afford polyfunctionalized molecules.

**References**

1. Li, J. J.; Gribble, G. W. *Palladium in Heterocyclic Chemistry: A Guide for the Synthetic Chemist*, Pergamon, New York, **2000**.
2. Beccalli, E. M.; Brogгинi, G.; Fasana, A.; Rigamonti, M. *J. Organomet. Chem.* **2011**, 696, 277.
3. Zimmer R., Dinesh R., Nandan R., and Khan F.A. *Chem Rev* **2000**, 100, 3067; Bates R.W. and Vachiraporn Satcharoen V. *Chem Soc Rev.* **2002**, 31, 12; Ma S. *Pure Appl. Chem.* **2006**, 78, 197.
4. Beccalli, E. M., Bernasconi, A., Borsini, E., Brogгинi, G. Rigamonti, M., Zecchi, G. *J. Org. Chem.* **2010**, 75, 6923

Palladium/Copper-Catalysed Cross-Coupling of Styrenes with Arylmethyl Ketones in Ionic Liquids: a Straight Route to Cyclopropanes

**Angelo Nacci,^{a,b} P. Cotugno,^a A. Monopoli,^a F. Lozito,^a M. Casiello,^a F. Iannone,^a
A. Rella,^a and F. Ciminale^a**

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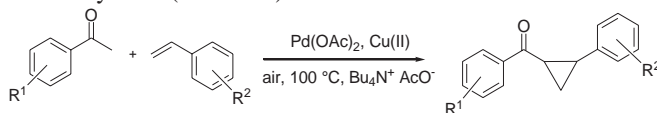
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Cyclopropanes are important subunits of many natural compounds and a large number of synthetic products carrying a cyclopropane unit possess biological properties. As a consequence, great efforts have been made to develop efficient methods for the synthesis of these small ring motifs and for their incorporation into pharmacologically active ingredients.¹

The most important strategies for constructing three member ring starts from olefins and involve the Simmons–Smith reaction,² the transition-metal-catalyzed decomposition of diazocompounds,³ and the MIRC approach (Michael-Initiated Ring Closure).⁴ The first two strategies are based on special reagents like the halomethyl-zinc carbenoids or the highly reactive metal carbenes. The third methodology concerns the nucleophilic addition-ring closure sequence and requires the presence of both electron-withdrawing and leaving groups on the reaction partners. Nevertheless, the synthesis of three-membered rings remains a considerable challenge. In this context, the search for new methylene sources that are easier to handle and more stable than currently used reagents, and the development of safer and greener methods are the major issues to be addressed.

In pursuing these objectives, we exploited our previous findings on palladium chemistry in ionic liquids (ILs),⁵ trying to develop a green and simple catalytic cyclopropanation that circumvents the need for carbene (or carbenoids) reagents by using large available starting materials. During our investigation on Pd-catalysed Fujwara-Moritani (oxidative Heck) coupling carried out in ILs with copper(II) salts as the re-oxidant, we found unexpectedly that quaternary ammonium ILs can promote, under aerobic conditions, an unusual cyclopropanation reaction between arylmethyl ketones and styrenes (scheme 1).



This process, which is unprecedented in the literature, can be seen as a dehydrogenative cyclizing coupling involving the formal double C–H activation to the α -position of ketone promoted by the Pd(II)/Cu(II)/air catalyst system with the assistance of the ionic liquid. This communication deals with the optimization of the reaction conditions and the study of the reaction mechanism.

References

1. Lebel, H.; Marcoux, J.-F.; Molinaro, C.; Charette, A.B. *Chem. Rev.* **2003**, *103*, 977-1050.
2. Charette, A. B.; Beauchemin, A. *Org. React.* **2001**, *58*, 1-395.
3. Davies, H. M.; Antoulinakis, L. E. G. *Org. React.* **2001**, *57*, 1-326.
4. Johansson, C. C. C.; Bremeyer, N.; Ley, S. V.; Owen, D. R.; Smith, S. C.; Gaunt, M. J. *Angew. Chem.* **2006**, *118*, 6170-6175; *Angew. Chem. Int. Ed.* **2006**, *45*, 6024 – 6028.
5. Mastroiilli, P.; Monopoli, A.; Dell'Anna, M. M.; Latronico, M.; Cotugno, P.; Nacci, A. in *Top. Organomet. Chem.*

New Half-Sandwich Ruthenium(II) Complexes bearing Hydrazone Ligands: Organometallic Chemistry and Bioactivity

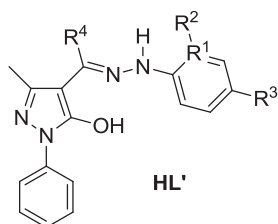
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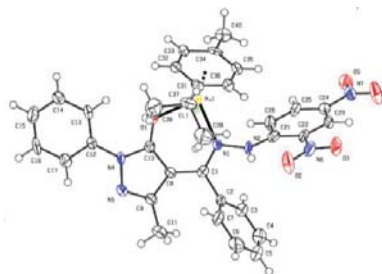
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The organometallic chemistry of half-sandwich η^6 -arene-ruthenium(II) complexes has been widely developed in the last few years, due to their wide range of potential applications as catalysts,¹ as well as for their potent antibacterial and anticancer activity.² As an extension of our previous work on the coordination chemistry of ruthenium arene fragments with 4-acyl-5-pyrazolone³ and β -ketoamine ligands,⁴ here we report the synthesis and full characterization (IR, ¹H NMR, ¹³C NMR, ESI-MS, Elem. Anal. and X-ray diffraction studies) of novel η^6 -arene Ru^{II} complexes (arene = benzene, *p*-cymene or hexamethylbenzene) containing new hydrazone ligands with general structure HL'. Preliminary results on their biological activity will be reported.



HL'

HL': R¹ = N or C; R² = H or NO₂;
R³ = H or NO₂; R⁴ = Ph or Bz



References

- Pettinari, C.; Marchetti, F.; Cerquetella, A.; Pettinari, R.; Monari, M.; Mac Leod, T. C. O.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Organometallics* **2011**, *30*, 1616-1626.
- Süss-Fink, G. *Dalton Trans.* **2010**, *39*, 1673-1688.
- Marchetti, F.; Pettinari, C.; Pettinari, R.; Cerquetella, A.; Cingolani, A.; Chan, E. J.; Kozawa, K.; Skelton, B. W.; White, A. H.; Wanke, R.; Kuznetsov, M. L.; Martins, L. M. D. R. S.; Pombeiro, A. J. L. *Inorg. Chem.* **2007**, *46*, 8245-8257.
- Pettinari, R.; Pettinari, C.; Marchetti, F.; Clavel, C. M.; Scopelliti, R.; Dyson, P. J. *Organometallics* **2013**, *32*, 309-316.

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Novel Composite Plastics Containing Silver(I) Acylpyrazolonate Additives Display Potent Antimicrobial Activity

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Plastics, due to their low cost, good mechanical properties and easy-high temperature processability, are widely used to prepare biomedical devices and food packaging.¹ However, typically they do not have inherent antibacterial properties, an important feature in prevention of infection in humans by microorganisms like bacteria, molds, yeasts.² Therefore, many efforts have been made in the last decades using novel nanotechnology and nanoscience knowledge in order to obtain nanomaterials with determined functionality. Among the wide range of antimicrobial plastics, metal-polymer nanocomposite and particularly silver-polymer are the subject of increased interest.³

Following our previous research on this topic,⁴ here we report some novel composite plastics, using polyethylene as polymer matrix, containing Silver(I) Acylpyrazolonate additives. They have undergone on specific tests such as antimicrobial activity against suspensions of *E. coli*, *P. aeruginosa* and *S. aureus*, test by contact, release test in according to EU Legislation and Acute Toxicity test using *D. Magna*.

References

1. Llorens, A.; Lloret, E.; Picouet, P. A.; Trbojevich, R.; *Trends in Food Sci. & Technol.* **2012**, *24*, 9–29.
2. Marini, M.; De Niederhausern, S.; Iseppi, R.; Bondi, M.; Sabia, C.; Toselli, M.; Pilati, F. *Biomacromol.* **2007**, *8*, 1246–54.
3. D. Crespy, K. Landfester, *Polymer* **2009**, *50*, 1616
4. Tăbăcaru, A.; Pettinari, C.; Marchetti, F.; Di Nicola, C.; Domasevitch, K. V.; Galli, S.; Masciocchi, N.; Scuri, S.; Grappasonni, I.; Cocchioni, M. *Inorg. Chem.* **2012**, *51*, 9775–9788.

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Asymmetric Imine Reductase based on Human Carbonic Anhydrase II as Host Protein

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In the context of dative anchoring strategies,^{1,5} hCAII is an attractive protein scaffold for the creation of artificial metalloenzymes for the asymmetric transfer hydrogenation of imines, using aryl-sulfonamide-bearing IrCp* pianostool complexes^{6,7}.

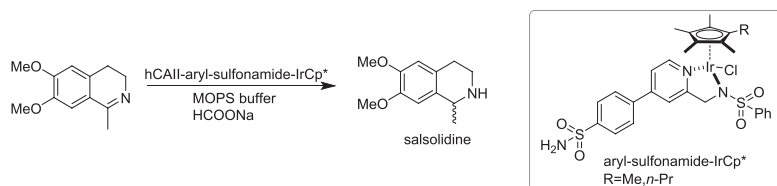


Fig.1 Artificial transfer hydrogenase for imine reduction and iridium cofactors used in the study.

Guided by the X-ray structure of complex $[(\eta^5\text{-Cp}^*)\text{Ir} \subset \text{WT hCA II}]$ (PDB ID 3ZP9)⁷, a chemogenetic optimization strategy was used to improve activity and selectivity of the ATHase. Mutations around the putative catalytic site were introduced based on design models generated by means of the Rosetta design suite. This *in silico* screening identified 8 mutations (L60V-A65T-N67W-E69Y-Q92F-L140M-L197M-C205S) which were combined to afford a total of 50 hCA II mutants. The resulting ATHases showed significantly improved performance both in terms of activity and of selectivity: up to *ee* 90 (*S*) and TON up to 50.

References

1. Ward, T.R. *Acc. Chem. Res.* **2011**, *44*, 47–57.
2. Rosati, F.; Roelfes, G. *ChemCatChem.* **2010**, *2*, 916-927.
3. Deuss, P. J.; denHeeten, R.; Laan, W.; Kamer, P. C. J. *Chem.–Eur. J.* **2011**, *17*, 4680-4698.
4. M. Ohashi, M.; Koshiyama, T.; Ueno, T.; Yanase, M.; Fujii, H.; Watanabe, Y. *Angew. Chem., Int. Ed.* **2003**, *42*, 1005-1008.
5. Krishnamurthy, V. M.; Kaufman, G. K.; Urbach, A. R.; Gitlin, I.; Gudiksen, K. L.; Weibel, D. B.; Whitesides, G. M. *Chem. Rev.* **2008**, *108*, 946-1051.
6. Can, D.; Spingler, B.; Schmutz, P.; Mendes, F.; Raposo, P.; Fernandes, C.; Carta, F.; Innocenti, A.; Santos, I.; Supuran, T. C.; Alberto, R. *Angew. Chem. Int. Ed.* **2012**, *51*, 3354-3357.
7. Monnard, F.W.; Nogueira, E.S.; Heinisch, T.; Schirmer, T.; Ward, T.R. *Chem. Sci* **2013**, *4*, 3269-3274.

Synthesis, Structure and Antiproliferative Activity of Novel Ru(II)-Arene Complexes with N,O-Chelating β -Ketoamine Ligands

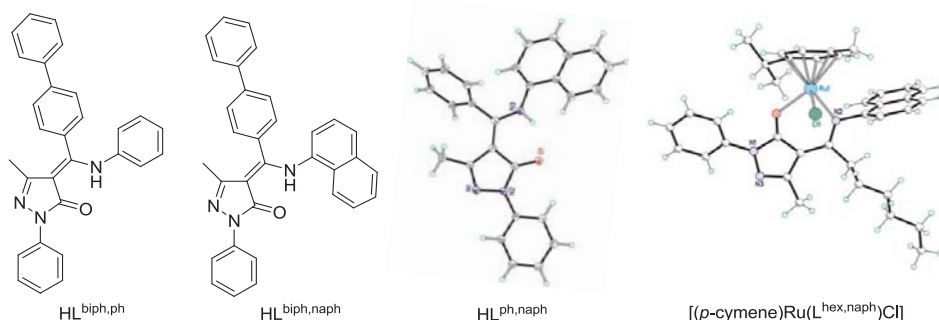
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Organometallic compounds are attracting a considerable interest in medicinal chemistry, especially as putative anticancer compounds.^{1,2} Of particular interest are ruthenium-arene complexes which have been extensively studied and modified to obtain compounds with various therapeutic effects. Ruthenium arene complexes with β -ketoamine ligands derived from 4-acyl-5-pyrazolones possess relevant anticancer properties in vitro.³ It was found that minor changes to the β -ketoamine ligand lead to considerable changes in cytotoxicity and, consequently, a series of novel Ru(II)-arene derivatives containing β -ketoamine ligands L' (HL' in general, HL^{biph,ph}, HL^{biph,naph}, HL^{ph,naph}, HL^{hex,naph}) has been synthesized and fully characterized by spectroscopy and single-crystal X-ray diffraction. The ligands in the anionic form coordinate to the ruthenium ion in a chelating κ^2 N,O-bidentate mode, affording 1:1 derivatives of the formula [(arene)Ru(L')Cl]. The in vitro anticancer activity of both the ligands and complexes has been evaluated against the human ovarian carcinoma cell line A2780 and its cisplatin-resistant equivalent A2780R.



References

1. Noffke A. L.; Habtemariam, A.; Pizarro A. M.; Sadler, P. J. *Chem. Commun.* **2012**, 48, 5219-546.
2. Coogan, M. P.; Dyson, P. J.; Bochmann, M. *Organometallics* **2012**, 31, 5671-5672.
3. Pettinari, R.; Pettinari, C.; Marchetti, F.; Clavel, C. M.; Scopelliti, R.; Dyson, P. J. *Organometallics* **2013**, 32, 309-316.

Acknowledgements: This work was funded by University of Camerino and École Polytechnique Fédérale de Lausanne.

Synthesis of Novel Push-Pull β -substituted Zn^{II} -Porphyrinates by a Microwave Assisted Sonogashira Coupling Approach

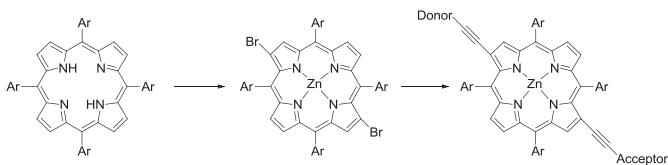
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Inspired by the process of solar energy collection by photosynthetic cores of bacteria and plants, involving a porphyrinic centre as light harvesting chromophore, porphyrinic structures have been considered as interesting dyes so that some of them have been synthesized and investigated for applications in Dye Sensitized Solar Cells (DSSCs).¹ Even though *meso* disubstituted push-pull Zn^{II} -porphyrinates are featured by interesting light conversion efficiencies, their synthesis required multi-step procedures. Conversely, β -substituted tetraaryl Zn^{II} -porphyrinates, which involve a tetraaryl porphyrinic core as starting material, are synthetically more attractive,² since this core can be easily obtained by means of a one-pot reaction between pyrrole and the appropriate aryl aldehyde. The more sterically hindered architecture of the tetraaryl porphyrinic core guarantees a decrease of π -stacking aggregation of the dye when adsorbed on TiO_2 photoanode, and further promotes a superior passivation of the surface against charge recombination with the oxidized specie (I_3^-) of the electrolyte.³ Hence these evidences, together with the promising light conversion efficiencies for DSSCs, have encouraged us to develop a facile synthetic pathway to obtain in good yield a series of β -substituted [tetrakis-(3,5-di-*tert*-butylphenyl)porphyrinates] Zn^{II} .^{2,4} Here, we report the optimized conditions to functionalize the porphyrinic core in β -pyrrolic position by using a light-induced bromination procedure. Subsequently a microwave enhanced Sonogashira coupling is exploited to circumvent the low reactivity of such brominated derivatives successfully providing both mono and, for the first time, disubstituted push-pull Zn^{II} -porphyrinates bearing a variety of substituents.



References

- Li, L.L.; Diau, E. W.-G. *Chem. Soc. Rev.* **2013**, *42* (1), 291-304.
- Di Carlo, G.; Orbelli Biroli, A.; Pizzotti, M.; Tessore, F.; Trifiletti, V.; Ruffo, R.; Abbotto, A.; Amat, A.; De Angelis, F.; Mussini, P. R. *Chem. Eur. J.* **2013**, *19*, 10723-10740.
- Di Carlo, G.; Caramori, S.; Trifiletti, V.; Pizzotti, M.; Orbelli Biroli, A.; Tessore, F.; Argazzi, R.; Bignozzi, C.A. *submitted*.
- Di Carlo, G.; Orbelli Biroli, A.; Tessore, F.; Pizzotti, M.; Mussini, P. R.; Amat, A.; De Angelis, F.; Abbotto, A.; Trifiletti, V.; Ruffo, R. *J. Phys. Chem. C* **2014**, *118*, 7307-7320

Bis-Cyclometalated Pt(II) Schiff Base Complexes: Unexpected *cis/trans* Isomery and Structure-Property Correlations

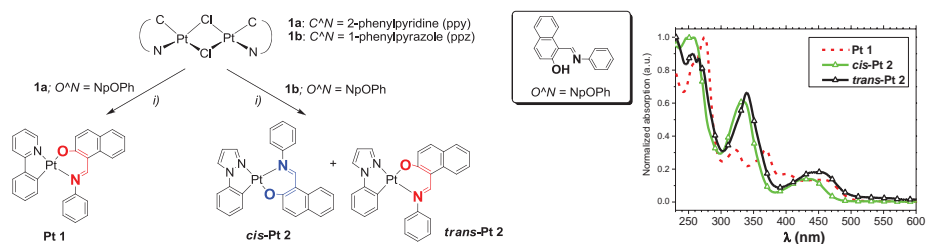
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Phosphorescent d^6 and d^8 metal complexes containing p-conjugated ligands with N and/or C donor atoms have attracted widespread research interest due to their excellent emission properties and potential applications in fields such as optoelectronic devices, chemo-/biosensors, bioimaging and medicinal chemistry. On the contrary transition-metal Schiff base complexes are less developed, even though Schiff base ligands are easily prepared and structurally modified, and have been demonstrated utility in several fields. In this communication we present the synthesis of two novel neutral square planar Pt(II) complexes, **Pt-1** and **Pt-2**, characterized by the presence of both a $C^{\wedge}N$ (ppy or ppz) cyclometalated ligand and a $O^{\wedge}N$ ancillary Schiff base ligand. The complexes have been synthesized as depicted in scheme 1 reacting the platinum chloro intermediate **1a,b** with the $O^{\wedge}N$ ligand. Reacting the intermediate **1a** with NpOPh Schiff base ligand, we obtained a single compound whose structure is indicated as **Pt 1** (Scheme 1).¹ On the contrary, the reaction of **1b**, carrying $C^{\wedge}N = ppz$ ligand, with the same NpOPh ligand provided a mixture of two products, which were easily purified by chromatography and structurally characterized by HPLC-MS, NMR analysis and X-Ray diffraction, proving to be the geometrical isomers *cis*-**Pt 2** and *trans*-**Pt 2** reported in scheme 1. To the best of our knowledge this is the first example of *cis/trans* isomer formation in neutral Pt(II) complexes carrying two different chelating ligands. **Pt 1** and **Pt 2** isomers properties were further investigated by means of UV-Vis, PL emission, cyclovoltammetry and IR techniques.



Scheme 1. Left panel: synthetic route for the preparation of **Pt 1** and **Pt 2** complexes. *i*) Na_2CO_3 , 2-ethoxyethanol, 100-140°C, Ar. Right panel: normalized absorptions in DCM.

Reference

1. S. Liu, H. Sun, Y. Ma, S. Ye, X. Liu, X. Zhou, X. Mou, L. Wang, Q. Zhao and W. Huang, *J. Mater. Chem.* **2012**, *22*, 22167-22173

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Re-Mediated C-C Coupling of Pyridines and Imidazoles

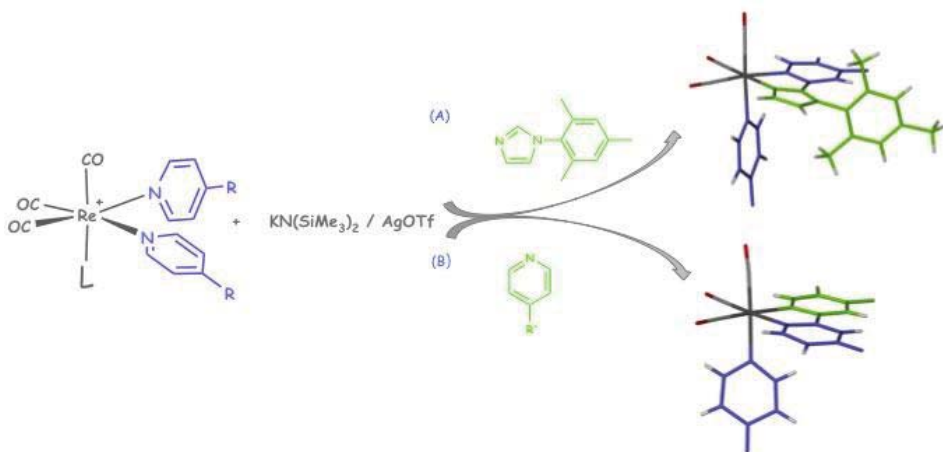
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Unprecedented intramolecular C-C coupling via deprotonation/oxidation sequences allowed the synthesis of complexes of pyridylimidazole chelates from complexes containing monodentate, non-functionalized pyridine and imidazole ligands (see Scheme A). Extension of this methodology to tris(pyridine) species afforded complexes bearing 2,2'-bipyridine ligands. In the particular case of combining two different types of pyridine ligands at the cationic *fac*-{Re(CO)₃} complexes, only the cross-coupling products displaying asymmetric 2,2'-bipyridines are obtained, the homocoupling products not being observed (see Scheme B).^{1,2}



References

1. Espinal Viguri, M.; Huertos, M. A.; Pérez, J.; Riera, L.; Ara, I. *J. Am. Chem. Soc.* **2012**, *134*, 20326-20329.
2. Espinal Viguri, M.; Pérez, J.; Riera, L. *Chem. Eur. J.* **2014**, DOI: 10.1002/chem.201400155.

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Synthesis of Magnetic Nanoparticles Functionalized with Transition Metals: Surface Effects on Coordination Geometry

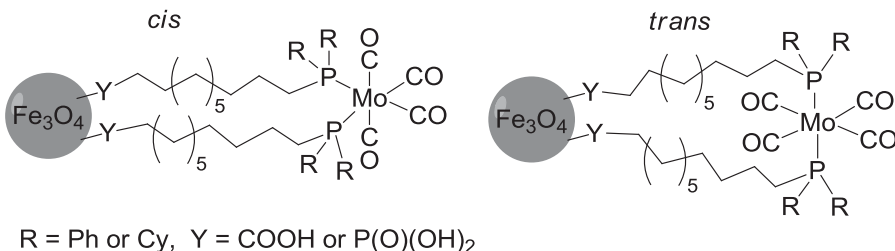
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In recent years, our group has investigated the synthesis of magnetic ferrite nanoparticles functionalized with a carboxylic or phosphonic acid bearing in the ω position a group (such as a halogen) able to be further modified. By this strategy, we synthesized several phosphine-functionalized ferrite nanoparticles. In order to confirm the presence of the phosphine group, we reacted the nanoparticles with different metal carbonyl complexes. Among them, we investigated in detail *cis*-Mo(CO)₄(pip)₂ (pip = piperidine). This complex is known to react at RT with phosphines, even sterically encumbered ones, to give exclusively the *cis bis*-phosphine complex. Only by heating at 110 °C isomerization to the more stable *trans* isomer observed.

Treating nanoparticles respectively functionalized with $-(\text{CH}_2)_{10}\text{-PPh}_2$ and $-(\text{CH}_2)_{10}\text{-PCy}_2$ groups with *cis*-Mo(CO)₄(pip)₂ at RT, we observed an unexpected result. Comparison of the recorded IR spectra with those of all possible reference compounds (including previously unreported mono-phosphine derivatives) evidenced that in neither case the observed spectra exactly match those expected for the *cis* or *trans* species. However, in the case of the diphenylphosphino derivative, the IR spectrum is closer to that of the *cis*-derivative and in the case of the dicyclohexyl derivative it is closer to the *trans* one. There are also minor differences between the spectra of nanoparticles in which the aliphatic chain is anchored to the ferrite through a carboxylic group and those having the same phosphine moiety, but in which the aliphatic chain is bound to ferrite through a phosphonic group.



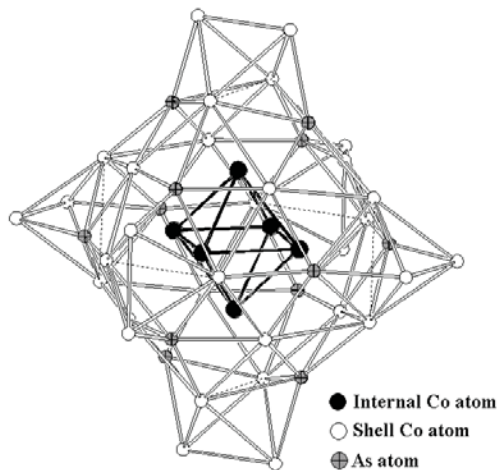
These results evidences that the surface organization of the phosphine groups, due to the ferrite structure and to packing effects of the long aliphatic chains influences the coordination sphere around the metal, affording geometries that cannot be observed in the homogeneous phase. This effect is clearly relevant to the photophysical and catalytic properties of the anchored complexes. Such effects are surely present even for other types of anchored complexes, such as those anchored on silica, despite not having been considered before.

Alloying Co and As at a Molecular Level

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Some elements belonging to the 14-16 groups of the Periodic Table are remarkably able to promote the aggregation of metallic carbonyl fragments and the consequent constitution of the so-called interstitial clusters. These structures, displaying both M-M and M-E bonds, represent a middle ground between solid state binary phases and actual molecular compounds; they could arise a deal of interest as electron sinks, or as catalyst and magnetic nanoparticle precursors. Since many medium-high nuclearity cobalt carbonyl clusters with nitrogen (1) and phosphorus (2) encapsulated atoms were successfully synthesized and characterized in the last decades, we have tried to isolate analogous systems with arsenic, considering that Co and As are often combined in natural minerals, such as smaltite and cobaltite. The reaction between Na[Co(CO)₄] and As₂O₅·xH₂O (1:0.4 molar ratio) in THF at room temperature followed by the addition of PPh₄Cl has led to the isolation of PPh₄[Co₆As(CO)₁₆]. Its structure, determined by single-crystal X-ray diffraction, is made of four adjoining metallic triangles that surround the heteroatom whose relatively big dimensions prevent it from being enclosed in a trigonal prism (unlike nitrogen). We investigated this cluster's thermal decomposition then, aiming at the synthesis of higher nuclearity species: indeed two other anionic carbonyl clusters have been isolated and structurally characterized, [Co₁₀As(CO)₂₂]³⁻ and [Co₃₈As₁₂(CO)₅₀]⁴⁻. Whereas the former is strictly related to the phosphorus containing species, in the latter an almost regular cobalt octahedron is surrounded by a shell made of 20 cobalt atoms and 12 arsenic atoms, constituting an irregular deltahedron (see figure). It is the largest known cobalt carbonyl cluster isolated in the solid state so far.



References

1. S. Martinengo *et al.*, *J. Am. Chem. Soc.*, **1979**, 101, 7095; S. Martinengo *et al.*, *J. Organomet. Chem.*, **1988**, 358, C23; A. Fumagalli *et al.*, *Inorg. Chem.*, **1998**, 37, 2826
2. P. Chini *et al.*, *J. Chem. Soc. Chem. Commun.*, **1979**, 188; G. Ciani *et al.*, *Inorg. Chem.*, **2001**, 40, 3905; C.S. Hong *et al.*, *Dalton Trans.*, **2003**, 2119

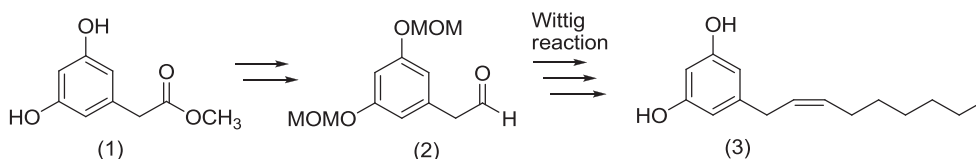
The Cerium(III) as Efficient Promoter in the Diastereoselective Synthesis of (Z)-Alkenes by means of the Wittig Olefination

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In recent years, scientific research has focused on the development of new synthetic methodologies for the efficient and selective synthesis of small molecules that have specific biological activities.¹ The olefinic moieties are present in a large number of biologically active molecules, and are involved in a large number of biological processes.² Many alkenes exist as either the (E) or the higher-energy (Z)-stereoisomer. The later isomer has been shown in many examples more active, and the Wittig reaction represents one of the most attractive approaches to stereoselective preparation of the desired functionality with the correct stereochemistry. The development of new methodologies for the diastereoselective synthesis of (Z)-isomer by Wittig reaction mediated by metal cations demonstrates the utility of the strategy in organic chemistry. We thought of evaluating the ability of cerium (III) to promote the diastereoselective synthesis of (Z)-climacostol (3), an important toxin belonging to the class of 5-alkenylresorcinols.³ The synthetic route that we propose includes the use of CeCl₃, which coordinates the carbonyl oxygen of aldehyde (2) for giving (Z)-configuration of the alkenyl chain of the molecule target (3).⁴



References

1. Veber, D. F.; Johnson, S. R.; Cheng, H. Y.; Smith, B. R.; Ward K. W.; Keople, K. D. *J. Med. Chem.* **2002**, *45*, 2615.
2. Meek, S. J.; O'Brien, R. V.; Liaverio, J.; Schrock, R. R.; Hoveyde, A. H. *Nature* **2011**, *471*,461.
3. Quassinti, L.; Ortenzi, F.; Marcantoni, E.; Ricciutelli, M.; Lupidi, G.; Ortenzi, C.; Buonomo, F.; Bramucci, M.; *Chem. Biol. Interact* **2013**, *206*, 109.
4. Fiorini D.; Giuli S.; Marcantoni, E.; Quassinti, L.; Bramucci, M.; Amantini C.; Santoni, G; Buonomo, F.; Ortenzi, C. *Synthesis* **2010**, *9*, 1550.

Synthesis of New Glicoporphyrin Ligands for Homogeneous Catalysis

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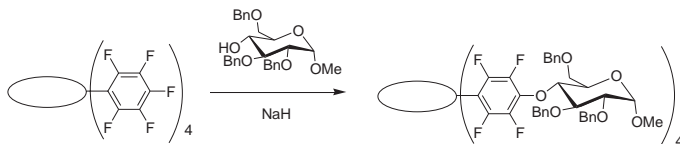
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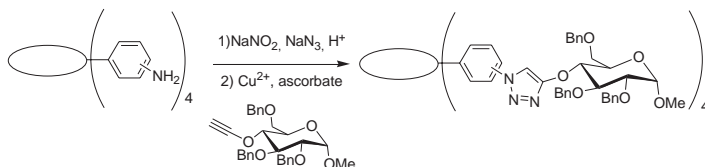
Glycoporphyrins are generated by the conjugation of saccharide units with a porphyrin molecule. These compounds have several biological applications due to the good activity of carbohydrates in ligand-acceptor interaction and recognition, and also because the porphyrin ligand is a biocompatible scaffold¹. Since metallo-porphyrins are active in promoting nitrene and carbene transfer reactions², glycoporphyrin complexes can be a new class of catalysts. Taking advantage of the chiral and hydrophilic nature of saccharide units, this class of compounds can be used either for asymmetric synthesis or to develop new sustainable water-soluble catalysts.

We synthesised glycoporphyrin derivatives following two synthetic strategies (**Scheme 1**):

a) Aromatic nucleophilic substitution using F₂₀-TPPH₂ (tetra-(pentafluoro)phenyl-porphyrin) and a sugar carrying an unprotected OH group.



b) Copper catalyzed azide-alkyne cycloaddition (CuAAC), starting from TAPPH₂ (tetra-(amino)phenyl-porphyrin) and a sugar functionalised with a propargyl moiety.



Scheme 1

We were able to synthesise the corresponding iron(III), cobalt (II) and ruthenium(II)-carbonyl complexes of the obtained glycoporphyrins. A preliminary study concerning the photochemical properties of the free-base compounds and the catalytic activity of the metal complexes was performed.

References:

1. *Top. Heterocycl. Chem.* **2007**, *7*, 179-248.
2. a) S. Fantauzzi, A. Caselli, E. Gallo, *Dalton Trans.* **2009**, *28*, 5434. b) D. Intriери, A. Caselli A, E. Gallo , *Eur. J. Inorg. Chem.*, **2011**, *33*, 5071-5081.

Synthesis and Characterization of Some Schiff Base Metal Complexes and the Investigation of their Biological Activity

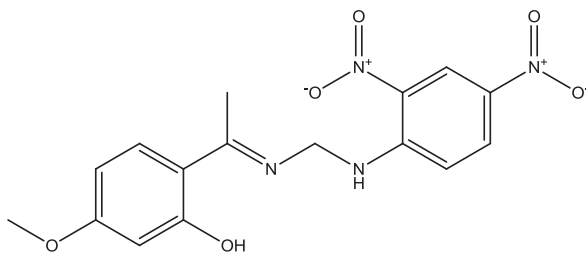
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Cu(II), Ni(II), Fe(III), Zn(II) and Mn(II) complexes of 2-(1-(((2,4-dinitrophenyl)amino)methyl)imino)ethyl)-5-methoxyphenol, H₂L, have been prepared and characterized. The proposed structures are consistent with the IR, UV-Vis as well as conductivity and magnetic moment measurements. The ligand behaved either as square planar or octahedral ligand. The antibacterial and antifungal activities of the compounds showed that, the complexes show more reactivity than the ligand. Metal complexes exhibited lower inhibitory effect than standard drugs as tetracycline (bacteria) and Amphotericin B (fungi) but were more reactive than the parent ligand and the corresponding metal ion.



2-(1-(((2,4-dinitrophenyl)amino)methyl)imino)ethyl)-5-methoxyphenol

References

- 1- Fernandez-G., J.M.; Tepal-Sanchez, P.; Hernandez-Ortega, S. J. Mol. Struct. 2006, 787, 1-7.
2. Majumder, A.; Rosair, G.M.; Mallick, A.; Chattopadhyay, N.; Mitra, S. Polyhedron 2006, 25, 1753-1762.
3. Nakamoto, K. Infrared and Raman spectra of inorganic and coordination compounds. Wiley Interscience, New York (1986).

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		SUN C.	OC04, P18

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	Tuesday, 24 th June	Wednesday, 25 th June	Thursday, 26 th June	Friday, 27 th June	
9:00-9:20		PL2 Matthias BELLER	PL4 Marco BANDINI		
9:20-9:50		OC4 Carlo NERVI	OC10 Andrea BIFFIS	PL6 Marta CATELLANI (GICO Senior Award)	
9:50-10:10		OC5 Alceo MACCHIONI	OC11 Rita MAZZONI	OC16 Francesco FERRETTI	
10:10-10:30		<i>Coffee Break</i>	<i>Coffee Break</i>	<i>Coffee Break</i>	
10:30-11:00		KN3 Bartolo GABRIELE	KN5 Alfonso GRASSI	OC17 Lorenzo VERONESE	
11:00-11:20		OC6 Luca BANFI	OC12 Valentina PIROVANO	OC18 Andrea BONETTI	
11:20-11:30		OC7 Nicola DELLA CA'	OC13 Riccardo RUBBIANI		
11:30-11:40		OC8 Francesca CONDELLO	OC14 Tommaso PEDRAZZINI	PL7 Carlo MEALLI	
11:40-11:50		OC9 Alberto BUCCI	OC15 Minqiang JIA		
11:50-12:10		<i>Lunch Break</i>	<i>Lunch Break</i>		
12:10-12:30	Registration				
12:30-12:50					
12:50-15:00					Closing Remarks
15:00-15:30	Opening	PL3 Bernhard K. KEPPLER	PL5 Silvia CAUTERUCCIO (Bonati Award)		
15:30-15:50		KN4 Angelo NACCI	KN6 Giorgio ABBIATI		
15:50-16:20	PL1 Julio PEREZ	Flash Presentations	Flash Presentations		
16:20-16:40					
16:40-17:00	OC1 Gabriele MANCA	<i>Coffee Break</i>	<i>Coffee Break</i>		
17:00-17:30	<i>Coffee Break</i>	Poster Session	Poster Session		
17:30-18:00	KN1 Valerio ZANOTTI	Assemblea GICO			
18:00-18:20	OC2 Rosmara MANSUETO				
18:20-18:40	OC3 Rebeca AREVALO				
18:40-19:10	KN2 Claudio PETTINARI				
19:30	Welcome Reception				
20:30			Social Dinner		