

## Contents

### Special Issue: 40th Anniversary Issue Dedicated to Professor Colin Eaborn

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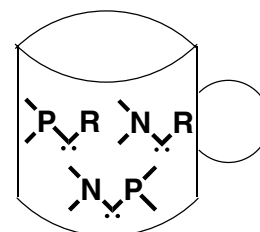
### Papers

**Yves Canac, Michele Soleilhavoup,  
Salvador Conejero, Guy Bertrand**

*J. Organomet. Chem.* 689 (2004) 3857

Stable non-N-heterocyclic carbenes (non-NHC): recent progress

This account summarizes the results that have been obtained by our group since 2000 in the area of stable singlet acyclic carbenes. It includes aryl- and alkyl-(phosphino)-carbenes, aryl(amino)carbenes, and (amino)-(phosphino)carbenes. Our most recent achievements, the transformation of stable carbenes into other stable carbenes are also discussed, along with preliminary results concerning the ligand properties of these species.

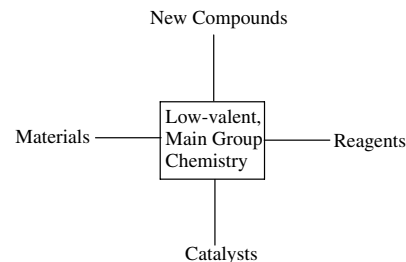


**Alan H. Cowley**

*J. Organomet. Chem.* 689 (2004) 3866

Some past achievements and future perspectives in main group chemistry

A survey of selected examples of current and past developments in low-valent, main group chemistry of the group 13, 14, and 15 elements is presented. Some future challenges in this area of chemistry are identified.

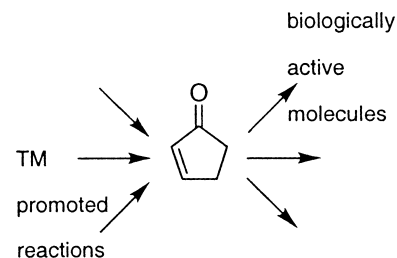


**Susan E. Gibson, Sara E. Lewis,  
Nello Mainolfi**

*J. Organomet. Chem.* 689 (2004) 3873

Transition metal-mediated routes to cyclopentenones

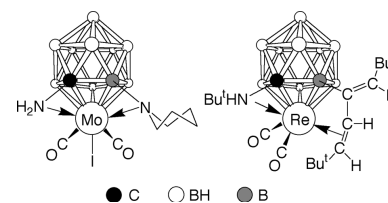
Cyclopentenones are not only key building blocks for organic synthesis but many possess interesting biological properties in their own right. This review provides an overview of the many transition-metal promoted methods of synthesising cyclopentenones developed in the last forty years.



**Thomas D. McGrath, F. Gordon A. Stone***J. Organomet. Chem.* 689 (2004) 3891

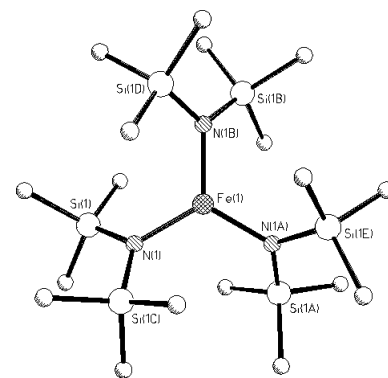
Metal complexes of monocarbon carboranes bearing C-amine or -amino substituents

The extensive chemistry of complexes between transition metals and monocarbollide {*nido*-CB<sub>10</sub>} ligands that carry an *exo*-polyhedral -NR<sub>3</sub> or -NR<sub>2</sub> group is illustrated. Many novel structures and unusual bonding modes are encountered, as in the compounds shown.

**Philip P. Power***J. Organomet. Chem.* 689 (2004) 3904

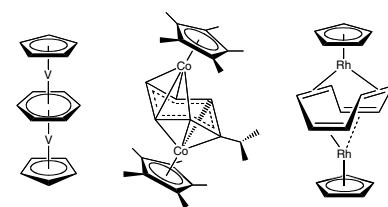
Some highlights from the development and use of bulky monodentate ligands

A brief review of the development of monodentate oxygen, nitrogen or carbon ligands (and their heavier congeners) bearing bulky organic substituents is given. It is shown that these versatile ligands have made an immense contribution to the development of modern inorganic and organometallic chemistry.

**Victoria Beck, Dermot O'Hare***J. Organomet. Chem.* 689 (2004) 3920

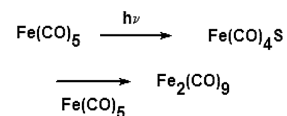
Triple-decker transition metal complexes bridged by a single carbocyclic ring

This paper reviews the synthesis and characterisation of triple-decker complexes with carbocyclic middle decks. The complexes are mainly of the transition metals, with some main group examples where appropriate. Only those triple-deckers with monocyclic middle ligands are considered. Studies of the complexes' properties are described where applicable.

**Thomas E. Bitterwolf***J. Organomet. Chem.* 689 (2004) 3939

Organometallic photochemistry at the end of its first century

A review of 100 years of organometallic photochemistry from Dewar's synthesis of Fe<sub>2</sub>(CO)<sub>9</sub> to modern fs spectroscopy.

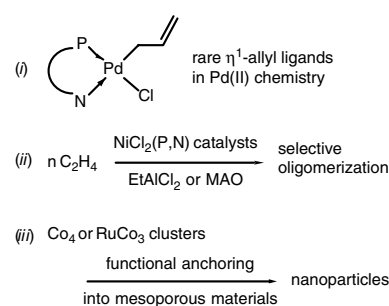


**Pierre Braunstein***J. Organomet. Chem.* 689 (2004) 3953

Functional ligands and complexes for new structures, homogeneous catalysts and nanomaterials

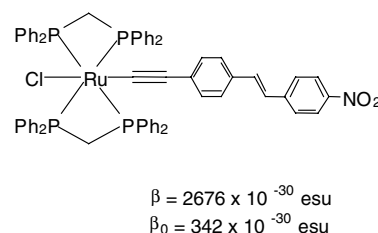
In this account, we focus on results from our laboratory to illustrate recent developments in various fields of organometallic chemistry: (i) studies on hemilabile P,N donor ligands and on the ion-pair behaviour of cationic Pd(II) complexes have led to the full characterization of still rare

complexes with  $\eta^1$ -allyl ligands of enhanced reactivity compared to the related  $\eta^3$ -allyl complexes; (ii) new homogeneous catalysts for the selective dimerization and oligomerization of ethylene are based on Ni(II) complexes with new chelating P,N ligands (P = phosphine, phosphinite or phosphonite donor group; N = pyridine or oxazoline moiety), and (iii) bottom-up approaches to the formation of new nanomaterials of magnetic or catalytic interest involve covalent anchoring of metal complexes and clusters into mesoporous materials using functional phosphine or alkyne ligands containing an alkoxy-silyl group.

**Marie P. Cifuentes, Mark G. Humphrey***J. Organomet. Chem.* 689 (2004) 3968

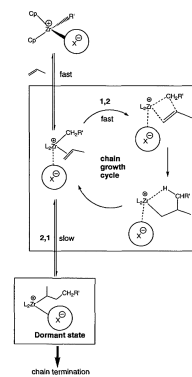
Alkynyl compounds and nonlinear optics

The syntheses and nonlinear optical (NLO) properties of metal alkynyl complexes prepared at ANU are summarized, including development of structure–NLO property relationships, and attempts to “switch” optical nonlinearities.

**Manfred Bochmann***J. Organomet. Chem.* 689 (2004) 3982

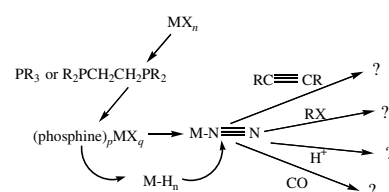
Kinetic and mechanistic aspects of metallocene polymerisation catalysts

For over 40 years metallocene complexes of titanium, zirconium and hafnium have been studied as catalysts in olefin polymerisations and are now of major industrial importance. This review summarises recent advances in mechanistic understanding of well defined metallocene catalysts based on ion pairs  $[\text{L}_2\text{ZrR}^+\cdots\text{X}^-]$ . The interplay of ligand structure and nature of the counteranions demonstrates a fascinating subtlety that continually challenges our ability to rationalise and predict catalyst performance.

**G.J. Leigh***J. Organomet. Chem.* 689 (2004) 3999

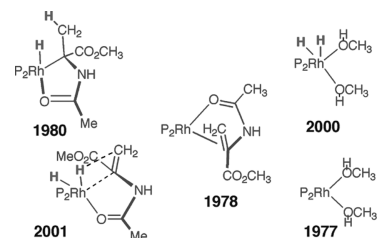
A personal account of some dinitrogen and organometallic chemistry research at the University of Sussex

This review describes the development of dinitrogen and related chemistry as seen by one participant in the story. M = Re, Os, Mo, W, or Fe; X = Cl or Br; R = H, alkyl or aryl.



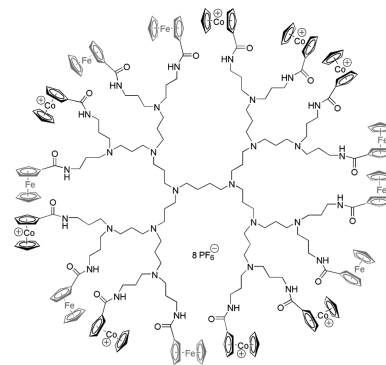
**John M. Brown***J. Organomet. Chem.* 689 (2004) 4006

Mechanism in homogeneous catalysis; NMR as a prime mover

NMR observed cationic intermediates in RhP<sub>2</sub> catalysed asymmetric hydrogenation of enamides [Year of characterisation].**Preston A. Chase,  
Robertus J.M. Klein Gebbink,  
Gerard van Koten***J. Organomet. Chem.* 689 (2004) 4016

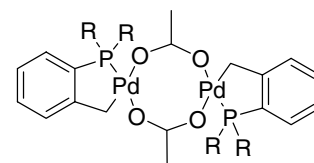
Where organometallics and dendrimers merge: the incorporation of organometallic species into dendritic molecules

This review describes the recent efforts to incorporate organometallic fragments into the framework of dendrimers. While purely dendritic organic molecules are well known, species incorporating organometallic moieties potentially offer many benefits that are not available to only organic containing dendrimers. Selected examples are presented to detail novel synthetic methodologies, interesting practical applications or address specific problems associated with organometallic dendrimers.

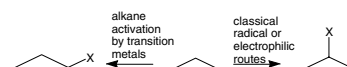
**Irina P. Beletskaya, Andrei V. Cheprakov***J. Organomet. Chem.* 689 (2004) 4055

Palladacycles in catalysis – a critical survey

The application of palladacycles as catalysts for cross-coupling and similar reactions is reviewed. In the majority of cases palladacycles are likely to serve as a source of highly active but unstable zero-valent palladium species. In this respect the palladacycles resemble the so-called phosphine-free catalysts. The advantages and limitations of palladacycle catalysts are discussed.

**Robert H. Crabtree***J. Organomet. Chem.* 689 (2004) 4083

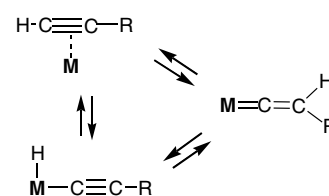
Organometallic alkane CH activation

The title topic is reviewed with emphasis on catalysis and on recent advances. Alkane  $\sigma$  complexes, Shilov chemistry and oxidative addition routes are covered. Attention is also given to  $\sigma$  bond metathesis, surface-bound organometallics and CH activation involving carbene complexes. Closely related reactions of non-alkane substrates such as the Murai reaction are also discussed.

**Yasuo Wakatsuki***J. Organomet. Chem.* 689 (2004) 4092

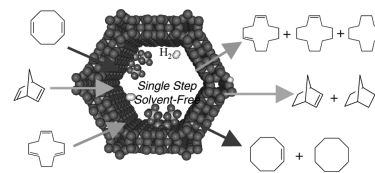
Mechanistic aspects regarding the formation of metal vinylidenes from alkynes and related reactions

This review focuses on the tautomerization mechanism between alkynes and vinylidene units taking place in the coordination sphere of transition metal fragments. Reactions of vinylidene complexes as well as catalytic reactions involving a metal-vinylidene intermediate are also reviewed from the mechanistic point of view.

**John Meurig Thomas, Robert Raja***J. Organomet. Chem.* 689 (2004) 4110

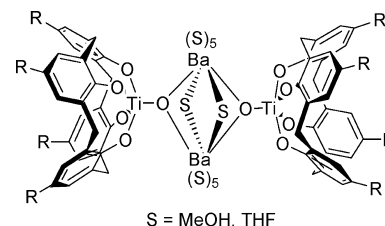
Catalytic significance of organometallic compounds immobilized on mesoporous silica: economically and environmentally important examples

The catalytic significance of immobilized, single-site,  $\text{Ti}^{\text{IV}}$ -centered epoxidation catalysts, anchored, asymmetric, organometallic chiral diamino catalysts, encapsulated "ship-in-bottle" and bimetallic nanoparticle catalysts, has been highlighted for a number of industrially significant and economically viable catalytic reactions ranging from the epoxidation of fatty acid methyl esters, asymmetric hydrogenation of keto-carboxylic esters, oxidation of methane, oxyhalogenation of aromatics and single-step, solvent-free hydrogenation of polyenes.

**Antonella J. Petrella, Colin L. Raston***J. Organomet. Chem.* 689 (2004) 4125

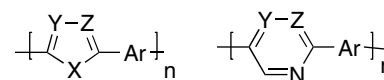
Calixarenes as platforms for the construction of multimetallic complexes

The use of calix[*n*]arenes ( $n = 4-6$ ) in building up multi-metal species based on group 1 or 2 ions and early transition metal ions, through synergistic metal-O and metal- $\pi$  interactions, is reviewed, along with recent advances on metal alkyl/cyclopentadienyl complexes and future prospects on the use of calixarenes in general in building up multi-metal complexes in a controlled way.

**Yen-Ju Cheng, Tien-Yau Luh***J. Organomet. Chem.* 689 (2004) 4137

Synthesizing optoelectronic heteroaromatic conjugated polymers by cross-coupling reactions

Heteroaromatics-containing polymers comprise a huge class of materials that have received considerable attention due to their interesting electrical, electrochemical, and optical properties. In this review, the recent advances on the use of organometallic cross-coupling reactions for the synthesis of heteroaromatic conjugated polymers for the optoelectronic interests and applications are summarised.



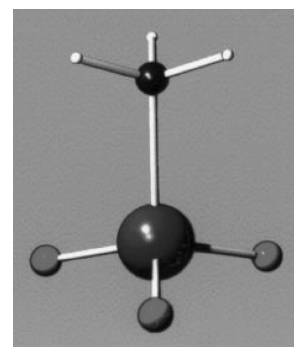
X = O, S, NR,  $\text{SiR}_2$ , Se  
 Y, Z = N or CH  
 Ar = aromatic or heteroaromatic or arylene-vinylene

**Fritz E. Kühn, Andrea Scherbaum,  
Wolfgang A. Herrmann**

*J. Organomet. Chem.* 689 (2004) 4149

Methyltrioxorhenium and its applications in olefin oxidation, metathesis and aldehyde olefination

MTO is nowadays available by several straightforward synthetic procedures and found even applications in material sciences, forming the first known polymeric organometallic oxide. In this review, the applications of MTO in oxidation catalysis, olefin metathesis and aldehyde olefination are summarized and conclusions concerning possible future applications of organorhenium oxides and related complexes are drawn.

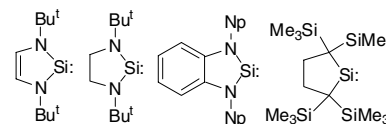


**Nicholas J. Hill, Robert West**

*J. Organomet. Chem.* 689 (2004) 4165

Recent developments in the chemistry of stable silylenes

Recent developments in the synthesis, spectroscopy and structure, theory, and chemical reactivity of thermally stable silylenes are reviewed.

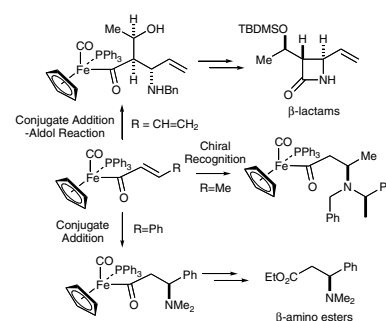


**Stephen G. Davies, Jairton Dupont,  
Robert J. C. Easton, Osamu Ichihara,  
Jeffrey M. McKenna, Andrew D. Smith,  
José A. A. de Sousa**

*J. Organomet. Chem.* 689 (2004) 4184

Stereoselective conjugate addition reactions of lithium amides to  $\alpha,\beta$ -unsaturated chiral iron acyl complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCH}=\text{CHR})]$

The conjugate additions of a range of achiral and homochiral lithium amides derived from primary and secondary amines to  $\alpha,\beta$ -unsaturated chiral iron acyl complexes  $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{COCH}=\text{CHR})]$  have been studied to determine the extent of enantioselectivity in these reactions, and for the asymmetric synthesis of  $\beta$ -amino acids and  $\beta$ -lactams.

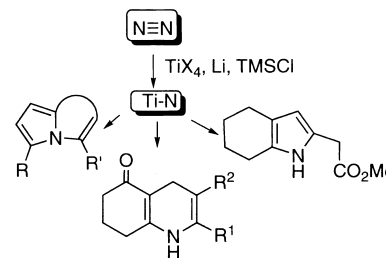


**Miwako Mori**

*J. Organomet. Chem.* 689 (2004) 4210

Activation of nitrogen for organic synthesis

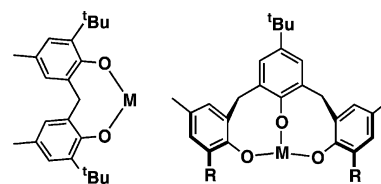
Various nitrogen-heterocycles could be synthesized using titanium–nitrogen complexes prepared from nitrogen gas (1 atm)  $\text{TiX}_4$ , Li and  $\text{TMSCl}$ . Using transmetalation of nitrogen on titanium–nitrogen complexes to palladium complex, aniline, benzamide, allylamide, and allylamine derivatives could be synthesized.



**Hiroyuki Kawaguchi, Tsukasa Matsuo***J. Organomet. Chem.* 689 (2004) 4228

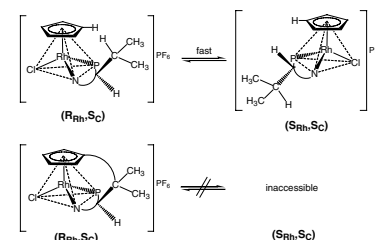
Aryloxy-based multidentate ligands for early transition metals and f-element metals

This article presents an overview of the chemistry of early transition metal and f-element complexes stabilized by aryloxy-based multidentate ligands. The presence of the bridging units in this ligand system imposes a strong geometry constraint to the aryloxy groups, which leads the way to novel patterns of structure and reactivity.

**Henri Brunner, Andreas Köllnberger, Arshad Mehmood, Takashi Tsuno, Manfred Zabel***J. Organomet. Chem.* 689 (2004) 4244

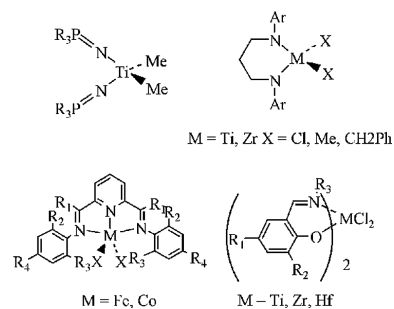
Stabilization of the labile metal configuration in halfsandwich complexes [CpRh(PN)Hal]X

In contrast to bidentate ligands, e.g. PN, tripod ligands CpPN<sup>-</sup> predetermine a single metal configuration preventing formation of the opposite metal configurations.

**Sungjin Park, Yonggyu Han, Seong Kyun Kim, Junseong Lee, Hwa Kyu Kim, Youngkyu Do***J. Organomet. Chem.* 689 (2004) 4263

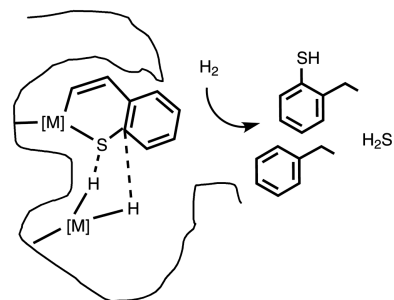
Non-Cp type homogeneous catalytic systems for olefin polymerization

In this review, state-of-the-art non-Cp type olefin polymerization catalysts is described from the coordination number as well as the ligand type points of view to emphasize their structural characteristics.

**Claudio Bianchini, Andrea Meli, Francesco Vizza***J. Organomet. Chem.* 689 (2004) 4277

Role of single-site catalysts in the hydrogenation of thiophenes: from model systems to effective HDS catalysts

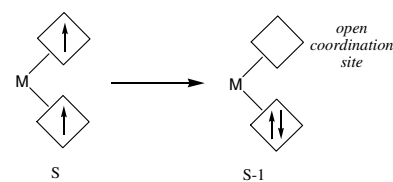
The desulfurization of benzo[*b*]thiophene by a polystyrene-tethered rhodium(I) catalyst might involve the interaction of contiguous metal sites.



**Rinaldo Poli***J. Organomet. Chem.* 689 (2004) 4291

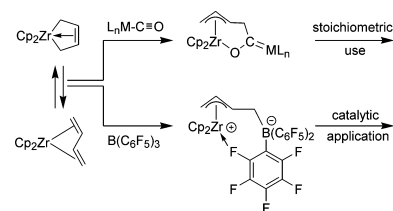
Open shell organometallics: a general analysis of their electronic structure and reactivity

The rationalization of the stability, physical properties, and chemical reactivity of open-shell organometallic compounds has witnessed tremendous progress in recent years. Effects associated to spin state changes are particularly relevant for reaction rates and selectivities. The synergy of experimentations and high-level computations have resulted in a much higher level of understanding.

**Gerhard Erker, Gerald Kehr, Roland Fröhlich***J. Organomet. Chem.* 689 (2004) 4305

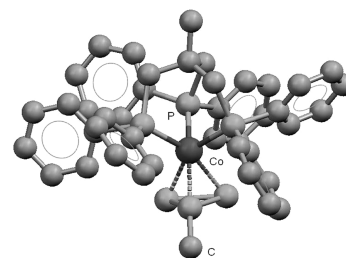
Some selected chapters from the (butadiene)-zirconocene story

The (butadiene)zirconocene system is characterized by the occurrence of two isomers, (*s-cis*-) and (*s-trans*- $\eta^4$ -C<sub>4</sub>H<sub>6</sub>-)ZrCp<sub>2</sub>. Out of this equilibrium, (butadiene)zirconocene has successfully been employed as a stoichiometric reagent in organic and organometallic synthesis and as a precursor for the generation of active homogeneous Ziegler–Natta catalyst systems.

**Maurizio Peruzzini, Rumia R. Abdreimova, Yulia Budnikova, Antonio Romerosa, Otto J. Scherer, Helmut Sitzmann***J. Organomet. Chem.* 689 (2004) 4319

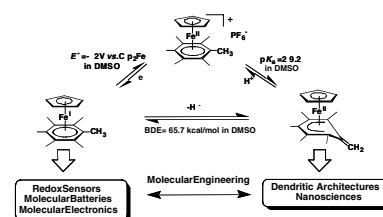
Functionalization of white phosphorus in the coordination sphere of transition metal complexes

This review highlights the stoichiometric functionalization of both white phosphorus and naked P<sub>n</sub> fragments derived from the metal-mediated demolition of the P<sub>4</sub> tetrahedron.

**Didier Astruc***J. Organomet. Chem.* 689 (2004) 4332

Organoiron activation combined with electron- and proton transfer: implications in biology, organic synthesis, catalysis and nanosciences

This Account reflects some key examples of our research on organoiron chemistry in the last 25 years from the design and functions of electron-reservoir complexes to nano-organometallic chemistry and its perspectives of applications. For instance, simple proton-reservoir properties led to giant dendrimer construction while combined electron transfer and iron coordination produced a variety of activation modes.



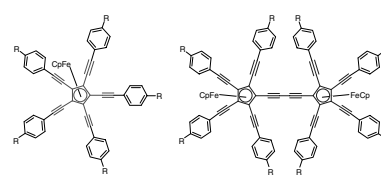


Winfried Steffen, Matthew Laskoski,  
Jason G.M. Morton, Uwe H.F. Bunz

*J. Organomet. Chem.* 689 (2004) 4345

Synthesis of the first pentaethynylferrocene derivatives

The synthesis of novel pentaethynylated ferrocene derivatives by a combination of consecutive lithiation and functionalization steps is reported. The repetitive functionalization scheme involves the *ortho* metalation of an acetal functionalized ferrocene followed by reaction with *N*-formylpiperidine and alkylation utilizing a diazophosphonate reagent.

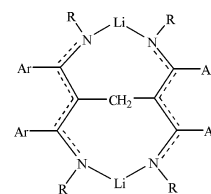


Laurence Bourget-Merle, Peter B. Hitchcock,  
Michael F. Lappert

*J. Organomet. Chem.* 689 (2004) 4357

Metal  $\beta$ -diketimines revisited: *ansa*-CH<sub>2</sub>-bridged bis( $\beta$ -diketiminate)s of lithium and aluminium having diverse structures

Synthesis of the  $\beta$ -diketimines H[ $\{N(R)C(Ar)\}_2CH$ ] [R = SiMe<sub>3</sub> and Ar = Ph (**1**) or C<sub>6</sub>H<sub>4</sub>Me-4 (**2**)] and the *ansa*-CH<sub>2</sub>-bridged bis( $\beta$ -diketimines)s [H $\{N(R)C(Ar)\}_2C\}_2CH_2$ ] [Ar = Ph (**3**), C<sub>6</sub>H<sub>4</sub>Me-4 (**4**)] is described. From 2 LiBu<sup>n</sup> and **3** or **4** the product was the dilithio compound **5** or **6**; whereas from **4** and 2 AlMe<sub>3</sub> **7** was obtained, also prepared from **6** and 2 Al(Cl)Me<sub>2</sub>. The X-ray structures of the known compounds **2** and **3** and of **5**, **6** and **7** are presented.



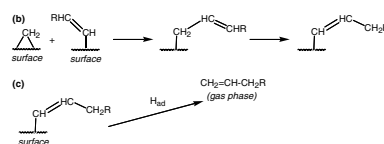
Peter M. Maitlis

*J. Organomet. Chem.* 689 (2004) 4366

Fischer–Tropsch, organometallics, and other friends

Based upon data from (i) a variety of labeling and spectroscopic studies of Fischer–Tropsch reactions, (ii) model stoichiometric reactions of organometallic complexes, and (iii) some theoretical and computational data, the mechanism for the formation of

1-alkenes from CO + H<sub>2</sub> over Fe, Co, Ru, or Rh catalysts is proposed to involve (a) initiation by deoxygenation of coordinated CO and the formation of a C<sub>2</sub> based surface species, probably a vinyl {CH<sub>2</sub>=CH<sub>(ad)</sub>}; (b) propagation involving reaction of surface methylene {CH<sub>2(ad)</sub>} with surface vinyl or alkenyl {RCH=CH<sub>(ad)</sub>} to give a surface allyl {RCH=CHCH<sub>2(ad)</sub>}, followed by a 1,3-H shift to generate a new surface alkenyl {RCH<sub>2</sub>CH=CH<sub>(ad)</sub>}; and (c) termination by hydride-mediated removal of the alkenyl chain from the catalyst giving the 1-alkene, RCH<sub>2</sub>CH=CH<sub>2</sub>, directly.

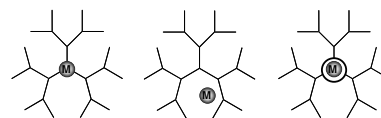


Paola Ceroni, Veronica Vicinelli,  
Mauro Maestri, Vincenzo Balzani,  
Sang-kyu Lee, Jeroen van Heyst,  
Marius Gorka, Fritz Vögtle

*J. Organomet. Chem.* 689 (2004) 4375

Luminescent dendrimers as ligands for metal ions

The design of dendrimers capable of playing the role of ligands for metal ions can lead to novel classes of metal complexes where the properties of the dendrimer and metal ion moieties can be profitably combined to obtain interesting and useful light-related functions.

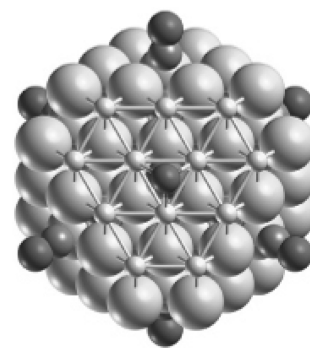


**Konstantin M. Neyman, Georgi N. Vayssilov, Notker Rösch**

*J. Organomet. Chem.* 689 (2004) 4384

Transition metal clusters and supported species with metal–carbon bonds from first-principles quantum chemistry

The impact of density functional calculations for understanding the organometallic chemistry of transition metal surface complexes and clusters, relevant mainly to heterogeneous catalysis, is illustrated by case studies of supported carbonyl complexes and clusters exhibiting chemical bonds with CO or atomic carbon.

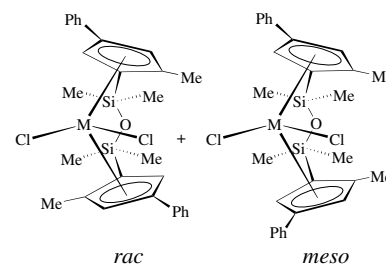


**Gema Martínez, Pascual Royo, Marta E.G. Mosquera**

*J. Organomet. Chem.* 689 (2004) 4395

Group 4 metallocene complexes with non-bridged and tetramethyldisiloxane-bridged methyl-phenyl-cyclopentadienyl ligands: synthesis, characterization and olefin polymerization studies

*meso*- and *rac*-Diastereomers of the Me-Ph-cyclopentadienyl-disubstituted zirconocene and tetramethyldisiloxane-bridged *ansa*-metallocene dichlorides (M = Zr, Hf) have been isolated by transmetalation of their lithium salts to  $MCl_4$  and characterized by NMR spectroscopy and X-ray diffraction methods. The zirconocene dichlorides activated with MAO are active catalysts for ethene and propene polymerization.

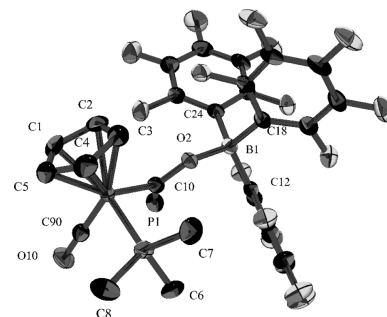


**Grant D.W. Anderson, Oliver J. Boys, Andrew R. Cowley, Jennifer C. Green, Malcolm L.H. Green, Simon A. Llewellyn, Carlo Maresca von Beckh, Sofia I. Pascu, Ino C. Vei**

*J. Organomet. Chem.* 689 (2004) 4407

Structural investigations on new iron-acyl derivatives of  $B(C_6F_5)_3$

$B(C_6F_5)_3$  adducts of the iron-acyl complexes  $[Fe(\eta-C_5H_5)(COCH_3)(CO)(L)]$  (where L =  $PPh_3$  (1),  $PMe_3$  (2),  $PPhMe_2$  (3),  $PCy_3$  (4), CO (5)) have been prepared and investigated. Studies using density function theorem, DFT, of several model compounds containing the systems  $[Fe-acyl]$  and  $[Fe-acyl-BF_3]$  provide into their electronic structure.

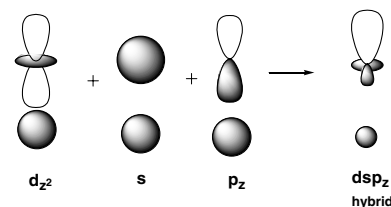


**D. Michael P. Mingos**

*J. Organomet. Chem.* 689 (2004) 4420

Complementary spherical electron density model and its implications for the 18 electron rule

The Complementary Spherical Electron Density Model developed by Mingos and Hawes in 1985 is reviewed and its implications to 18 electron complexes and co-ordinatively unsaturated complexes are developed.

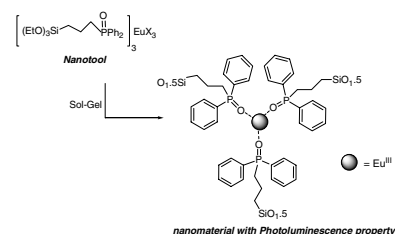


**Robert Corriu, Ahmad Mehdi,  
Catherine Reyé**

*J. Organomet. Chem.* 689 (2004) 4437

Nanoporous materials: a good opportunity  
for nanosciences

Different ways to build nanomaterials starting from nanotools (bottom-up way) are described. Nanotools are the elementary bricks of the future materials. They can be clusters, metallic nanoparticles, or molecules with a specific property (optic, magnetic, electric, chemical, mechanical). This article emphasizes the importance of the chemistry in this approach bottom-up for nanomaterials.

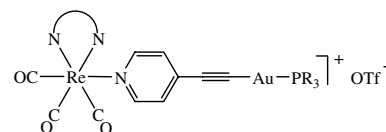


**Kai-Leung Cheung, Sung-Kong Yip,  
Vivian Wing-Wah Yam**

*J. Organomet. Chem.* 689 (2004) 4451

Synthesis, characterization, electrochemistry  
and luminescence studies of heterometallic  
gold(I)–rhenium(I) alkynyl complexes

The present work provides a brief summary review of the chemistry of luminescent gold(I) alkynyls and their ability to form heterometallic complexes. A series of luminescent heterometallic gold(I)–rhenium(I) alkynyl complexes has been synthesized and characterized. Their electrochemical and photophysical properties have been studied and their emission origins elucidated.

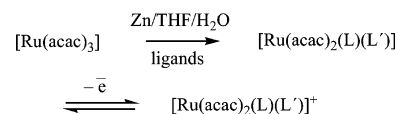


**Martin A. Bennett, Matthew J. Byrnes,  
Ivan Kováčik**

*J. Organomet. Chem.* 689 (2004) 4463

The fragment bis(acetylacetonato) ruthenium:  
a meeting-point of coordination and organo-  
metallic chemistry

The classical coordination compound tris-(acetylacetonato)ruthenium(III), Ru(acac)<sub>3</sub>, is a useful precursor to a range of coordination and organometallic complexes containing the fragment Ru(acac)<sub>2</sub> in which the metal atom displays the oxidation states +2 and +3. The review summarizes work on the alkene and alkyne complexes, in particular, the behaviour of the ruthenium(III) compounds towards nucleophiles.

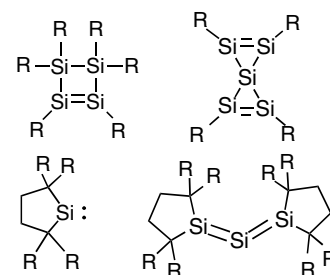


**Mitsuo Kira**

*J. Organomet. Chem.* 689 (2004) 4475

Isolable silylene, disilenes, trisilaallene, and  
related compounds

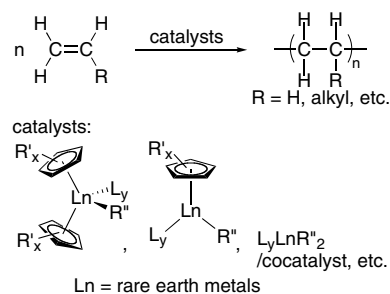
Recent studies on the synthesis, structures, and properties of stable unsaturated silicon compounds such as a dialkylsilylene, acyclic and cyclic disilenes, and a trisilaallene, and related germanium and tin compounds are summarized with the author's personal reminiscences during the research.



**Yuushou Nakayama, Hajime Yasuda***J. Organomet. Chem.* 689 (2004) 4489

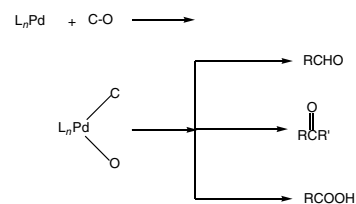
Developments of rare earth metal catalysts for olefin polymerization

This review article describes recent developments in rare earth metal complexes as polymerization catalysts, focusing on the polymerization of ethylene and  $\alpha$ -olefins. Most of this kind of catalysts had been based on metallocene type complexes, and their catalytic behaviors are surveyed. Advanced series of half-metallocene and non-Cp type catalysts systems are also summarized.

**Akio Yamamoto***J. Organomet. Chem.* 689 (2004) 4499

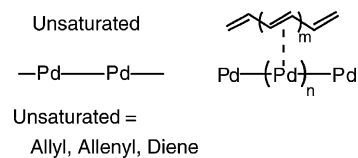
Design of catalytic processes based on studies of elementary processes

The reminiscences of the author's experiences in the period of rapid development of organometallic chemistry are given with some of the recent development of synthetic methods based on the studies of elementary processes involving Pd-promoted C–O bond cleavage to yield aldehydes, ketones, and carboxylic acids are described.

**Hideo Kurosawa***J. Organomet. Chem.* 689 (2004) 4511

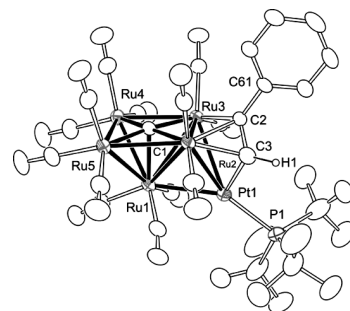
From mononuclear to multinuclear complexes of palladium containing unsaturated hydrocarbon ligands

New structure and reactivity trends in the multipalladium complexes with bridging allyl and allenyl/propargyl ligands, as well as bridging conjugated polyene molecules, are discussed in terms of some unique bonding features of these complexes.

**Richard D. Adams, Burjor Captain***J. Organomet. Chem.* 689 (2004) 4521

Bimetallic cluster complexes: synthesis, structures and applications to catalysis

A brief history of the seminal discoveries in the field of bimetallic cluster complexes with discussion of their structures is presented. A review of some recent studies of palladium and platinum–ruthenium cluster complexes is included with a discussion of applications of these complexes in the area of homogeneous hydrogenation catalysis of alkynes.

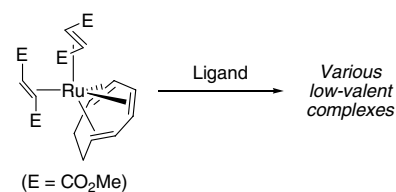


**Take-aki Mitsudo, Yasuyuki Ura,  
Teruyuki Kondo**

*J. Organomet. Chem.* 689 (2004) 4530

$\text{Ru}(\eta^6\text{-1,3,5-cyclooctatriene})(\eta^2\text{-dimethyl fumarate})_2$ : a novel, versatile zerovalent ruthenium complex with electron-deficient olefinic ligands

The reactions of a novel zerovalent ruthenium complex,  $\text{Ru}(\eta^6\text{-1,3,5-cyclooctatriene})(\eta^2\text{-dimethyl fumarate})_2$ , which has high catalytic activity for a carbon-carbon bond forming reaction, with various ligands such as phosphines, amines, arenes and *p*-quinones were reviewed.

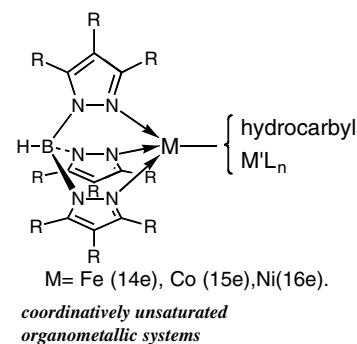


**Munetaka Akita**

*J. Organomet. Chem.* 689 (2004) 4540

Coordinatively unsaturated organometallic system based on Tp ligand: tetrahedral  $\text{Tp}^{\text{R}}\text{M-R}'$  and  $\text{Tp}^{\text{R}}\text{M-M}'\text{L}_n$  species

Chemistry of the highly coordinatively unsaturated, tetrahedral hydrocarbyl and dinuclear complexes bearing a hydrotris(pyrazolyl)borate ( $\text{Tp}^{\text{R}}$ ) ligand,  $\text{Tp}^{\text{R}}\text{M-R}'$  and  $\text{Tp}^{\text{R}}\text{M-M}'\text{L}_n$ , is reviewed. The  $\text{Tp}^{\text{R}}$  ligand works as a tetrahedral enforcer to afford high spin species with 14 (Fe), 15 (Co) and 16 (Ni) valence electrons.

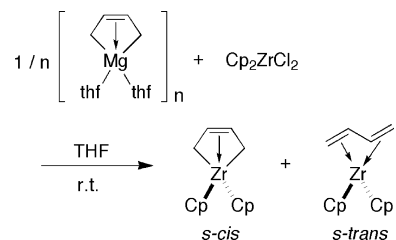


**Akira Nakamura, Kazushi Mashima**

*J. Organomet. Chem.* 689 (2004) 4552

Diene complexes of early transition metals: ideas and progresses at Osaka University

Historical perspectives for the chemistry of diene complexes of early transition metals developed at Osaka University in the period after 1970s were reviewed briefly and personally.

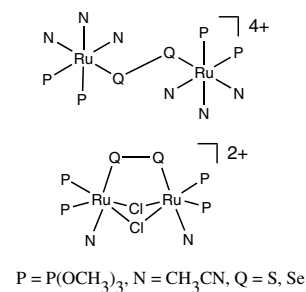


**Kazuko Matsumoto, Hiroyasu Sugiyama**

*J. Organomet. Chem.* 689 (2004) 4564

Novel C-H activation and C-S formation reactions on disulfide and diselenide ligands in dinuclear ruthenium complexes

The C-S bond formation reactions of the transition metal sulfides with organic molecules are collected and reviewed to understand the reactivity of the sulfide ligands supported by the transition metals. As an example of the role of the sulfide, the C-H bond activation is focused and discussed.

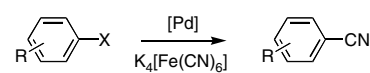


**Thomas Schareina, Alexander Zapf, Matthias Beller**

*J. Organomet. Chem.* 689 (2004) 4576

Improving palladium-catalyzed cyanation of aryl halides: development of a state-of-the-art methodology using potassium hexacyanoferrate(II) as cyanating agent

Benzonitriles are easily accessible via palladium-catalyzed cyanation of aryl halides using potassium hexacyanoferrate(II) as cyanide source. This method is applicable on both activated and deactivated aryl and heteroaryl bromides and activated chlorides giving the corresponding benzonitriles in good to excellent yield. Advantageously, the used cyanating agent is non-toxic and cheap. The presented catalyst system is rather simple and it is not necessary to add expensive phosphines, making the novel method also attractive for industrial applications.

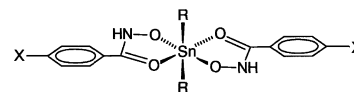


**Qingshan Li, M. Fátima C. Guedes da Silva, Zhao Jinghua, Armando J.L. Pombeiro**

*J. Organomet. Chem.* 689 (2004) 4584

Diorganotin(IV) derivatives of arylhydroxamic acids: synthesis, properties and antitumor activity

Series of diorganotin(IV) complexes of *para*-substituted benzohydroxamic acid,  $[R_2SnL_2]$  and  $[R_2Sn(L)_2O]$ , have been prepared and characterized. Their *in vitro* antitumor activity against a series of human tumor cell lines was tested and, in a few of them, is identical to, or higher than, that of cisplatin.

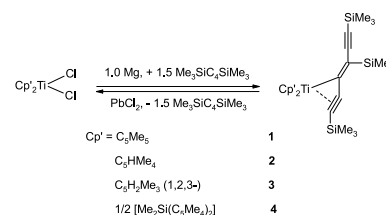


**Michal Horáček, Ivana Císařová, Jiří Kubišta, Anke Spannenberg, Kai Dallmann, Uwe Rosenthal, Karel Mach**

*J. Organomet. Chem.* 689 (2004) 4592

Titanocene – 1,4,6-tris(trimethylsilyl)hex-3-ene-1,5-diyne-3-yl complexes – crystal structures and their retro reaction

The formation of the  $\pi$ -coordinated 1,4,6-tris(trimethylsilyl)hex-3-ene-1,5-diyne-3-yl ligand at the  $(Ti^{III})$  atom is a general reaction for highly methyl-substituted titanocenes. The retroreaction to 1,4-bis(trimethylsilyl)buta-1,3-diyne is induced by oxidation with  $PbCl_2$ .

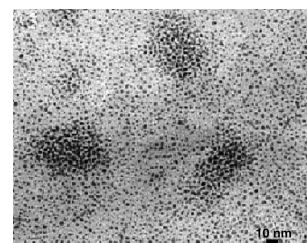


**Esther Ramirez, Susanna Jansat, Karine Philippot, Pierre Lecante, Montserrat Gomez, Anna M. Masdeu-Bultó, Bruno Chaudret**

*J. Organomet. Chem.* 689 (2004) 4601

Influence of organic ligands on the stabilization of palladium nanoparticles

The synthesis of palladium nanoparticles is performed by hydrogenation of an organometallic precursor,  $Pd_2(dba)_3$  (**1**). In the presence of polyphosphines as stabilizers, complex (**1**) leads to stable spherical nanoparticles of small size (2 nm) while hexadecylamine (HDA; weakly coordinating ligand) undergoes different results depending on the HDA amount, as a result of equilibrium present at the particles surface.

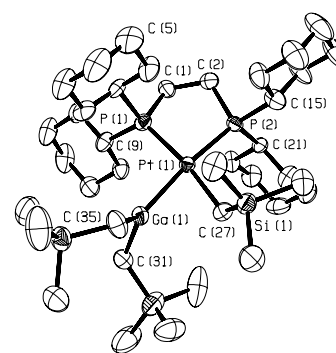


**Roland A. Fischer, Dana Wei,  
Manuela Winter, Iris Müller,  
Herbert D. Kaesz, Nikolaus Fröhlich,  
Gernot Frenking**

*J. Organomet. Chem.* 689 (2004) 4611

The reaction of the group-13 alkyls  $ER_3$  ( $E = Al, Ga, In$ ;  $R = CH_2t\text{-Bu}, CH_2SiMe_3$ ) with the platinum complex  $[(dcpe)Pt(H)(CH_2t\text{-Bu})]$  were re-investigated, leading to the bimetallic compounds  $[(dcpe)Pt(ER_2)(R)]$  with direct  $\sigma(Pt-E)$  bonds by oxidative addition an  $E-C$  bond to the coordinatively unsaturated fragment  $[(dcpe)Pt]$ .

The reactions of sterically demanding group-13 alkyls  $ER_3$  ( $E = Al, Ga, In$ ;  $R = CH_2t\text{-Bu}, CH_2SiMe_3$ ) with the platinum complex  $[(dcpe)Pt(H)(CH_2t\text{-Bu})]$  were re-investigated, leading to the bimetallic compounds  $[(dcpe)Pt(ER_2)(R)]$  with direct  $\sigma(Pt-E)$  bonds by oxidative addition an  $E-C$  bond to the coordinatively unsaturated fragment  $[(dcpe)Pt]$ .

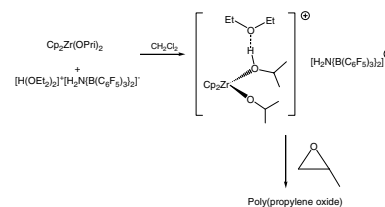


**Elaine Farrow, Yann Sarazin,  
David L. Hughes, Manfred Bochmann**

*J. Organomet. Chem.* 689 (2004) 4624

Synthesis and structure of  $[Cp_2Zr(OPr^f)(HOPr^f)]^+$  and its activity in the polymerisation of propene oxide

The reaction of  $Cp_2Zr(OPr^f)_2$  with  $[H(OEt_2)_2][H_2N\{B(C_6F_5)_3\}_2]$  in gives  $[Cp_2Zr(OPr^f)(HOPr^f)]^+[H_2N\{B(C_6F_5)_3\}_2]^- \cdot Et_2O$  in high yield. The complex initiates the polymerisation of propylene oxide, most probably via a cationic mechanism.

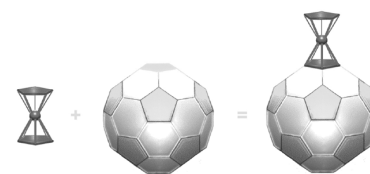


**Eiichi Nakamura**

*J. Organomet. Chem.* 689 (2004) 4630

Bucky ferrocene and ruthenocene: serendipity and discoveries

An idea of making a ferrocene/fullerene hybrid, “bucky ferrocene”, has intrigued chemists for some time, but the compounds remained to be hypothetical. The synthesis of such hybrid molecules as  $Fe(C_{60}Me_5)Cp$ ,  $Ru(C_{60}Me_5)Cp$  and  $Fe(C_{70}Me_3)Cp$  as well as their functionalized derivatives from [60] and [70]fullerenes has been achieved in recent years. With their esthetically pleasing structures and the dual character of metallocene and graphite, these molecules may stimulate the interest of both chemists and non-chemists.

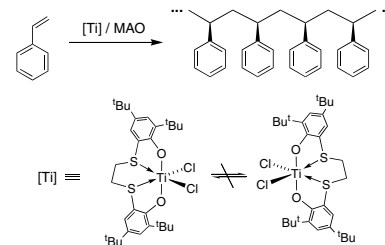


**Klaus Beckerle, Carmine Capacchione,  
Henner Ebeling, R. Manivannan,  
Rolf Mülhaupt, Antonio Proto,  
Thomas P. Spaniol, Jun Okuda**

*J. Organomet. Chem.* 689 (2004) 4636

Stereospecific post-metallocene polymerization catalysts: the example of isospecific styrene polymerization

In the context of developing single-site stereoselective post-metallocene catalysts, the case for isospecific styrene polymerization catalysts based on methylaluminoxane-activated group 4 metal bis(phenolato) complexes is summarized.

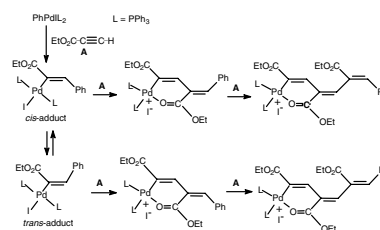


**Christian Amatore, Samia Bensalem,  
Said Ghalem, Anny Jutand**

*J. Organomet. Chem.* 689 (2004) 4642

Mechanism of the carbopalladation of  
alkynes by aryl-palladium complexes

The carbopalladation between  $\text{PhPdI}(\text{PPh}_3)_2$  and  $\text{EtO}_2\text{C}-\text{C}\equiv\text{CH}$  gives  $\text{EtO}_2\text{C}-\text{C}(\text{PdIL}_2)=\text{CHPh}$  **1**, the *trans*-adduct as the major complex formed by isomerization of the primary *cis*-adduct  $\text{EtO}_2\text{C}-\text{C}(\text{PdIL}_2)=\text{CHPh}$  **2**. A multicarbopalladation is also observed.

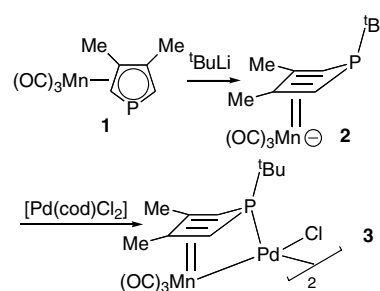


**Bernard Deschamps, Louis Ricard,  
Franois Mathey**

*J. Organomet. Chem.* 689 (2004) 4647

$\eta^4$ -Phosphole tricarbonylmanganates: a new  
type of chelating ligands for transition metals

The nucleophilic attack of phosphacyman-  
trene **1** by *tert*-butyllithium leads to a  $\eta^4$ -  
phospholemanganate **2** which can act as a  
*P,Mn*-chelating ligand toward Pd(II).



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