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Special Issue: Carbene Chemistry

Preface 5397

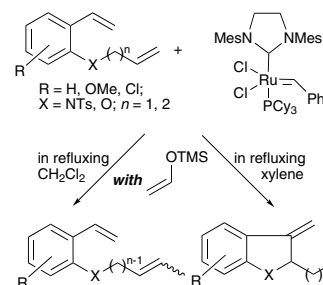
Reviews

**Mitsuhiro Arisawa, Yukiyo Terada,
Chumpol Theeraladanon, Kazuyuki Takahashi,
Masako Nakagawa, Atsushi Nishida**

J. Organomet. Chem. 690 (2005) 5398

Development of novel reactions using ruthenium carbene catalyst and its application to novel methods for preparing nitrogen-containing heterocycles

Second generation Grubbs ruthenium carbene catalyst, which is highly effective for ring-closing metathesis (RCM), reacts with an electron-rich terminal olefin selectively, and another ruthenium species, which effectively catalyzes the isomerization of terminal olefin and cycloisomerization of alpha, omega-diene, is generated.

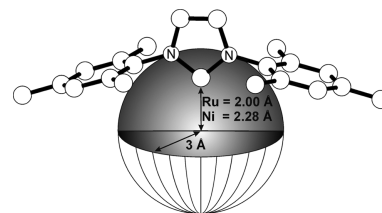


**Luigi Cavallo, Andrea Correa,
Chiara Costabile, Heiko Jacobsen**

J. Organomet. Chem. 690 (2005) 5407

Steric and electronic effects in the bonding of N-heterocyclic ligands to transition metals

Steric and electronic effects contribute to the strength of the bond that it is established between N-heterocyclic (NHC) ligands and transition metals. Using a computational approach we examined the nature of the Mt-NHC bond in a series of Ni, Ru and Ir complexes. Our analysis indicates that NHC are very flexible ligands both in terms of steric and electronic properties. An attempt is made to separate and quantify these effects.

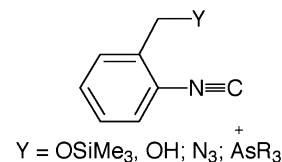


**Marino Basato, Rino A. Michelin,
Mirto Mozzon, Paolo Sgarbossa,
Augusto Tassan**

J. Organomet. Chem. 690 (2005) 5414

N-heterocyclic carbenes from transition metal coordinated functional isocyanides of the type o -(CH₂Y)C₆H₄N≡C (Y = OSiMe₃, OH; N₃; AsR₃⁺)

Recent results on the synthesis and the organometallic chemistry of the functional isocyanides o -(CH₂Y)C₆H₄N≡C (Y = OSiMe₃, OH; N₃; AsR₃⁺) specifically addressed to the formation of N-heterocyclic aminocarbene transition metal complexes are described.

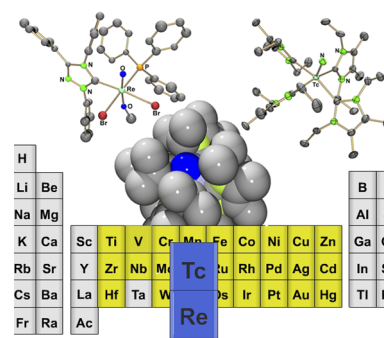


**Henrik Braband, Theresa I. Kückmann,
Ulrich Abram**

J. Organomet. Chem. 690 (2005) 5421

Rhenium and technetium complexes with N-heterocyclic carbenes – A review

The coordination chemistry of technetium and rhenium with N-heterocyclic carbenes of the dimethylimidazol-2-ylidene and 1,2,4-triazol-5-ylidene types is reviewed. General trends and differences in the chemical behaviour of the complexes, particularly between the different metal cores (oxo, nitrido, imido) of Tc(V) and Re(V) compounds, are discussed.

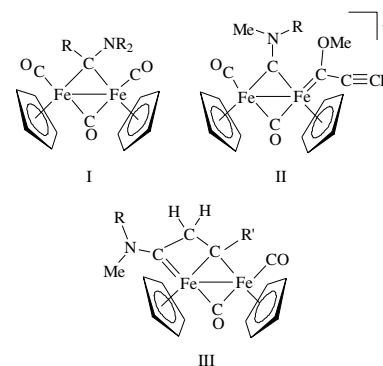


Luigi Busetto, Valerio Zanotti

J. Organomet. Chem. 690 (2005) 5430

Carbene ligands in diiron complexes

The diiron frame $\text{Fe}_2\text{Cp}_2(\text{CO})_2$ provides an efficient support for the coordination a variety of heteroatom substituted carbene ligands, both bridging (e.g., **I**) and terminal (e.g., **II**). These have been obtained from diiron μ -carbyne precursors. Insertion reactions, nucleophilic additions, and intramolecular couplings of coordinated ligands in these diiron complexes afford new multidentate ligands displaying carbene character (e.g., **III**).

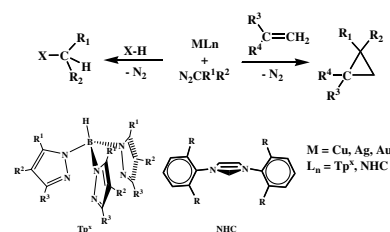


M. Mar Díaz-Requejo, Pedro J. Pérez

J. Organomet. Chem. 690 (2005) 5441

Copper, silver and gold-based catalysts for carbene addition or insertion reactions

Two families of catalysts containing trispyrazolylborate (Tp^n) or N-heterocyclic carbenes (NHC) with the group 11 metals have proven useful for several reactions involving the transfer of the $:\text{CHCO}_2\text{Et}$ group from ethyl diazoacetate to saturated and unsaturated substrates

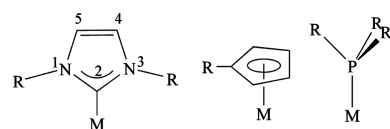


Robert H. Crabtree

J. Organomet. Chem. 690 (2005) 5451

NHC ligands versus cyclopentadienyls and phosphines as spectator ligands in organometallic catalysis

N-heterocyclic carbenes are compared with cyclopentadienyls and phosphines as ligands for transition metals, emphasizing bonding and reactivity aspects.

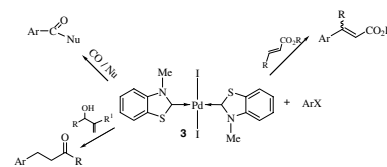


Vincenzo Calò, Angelo Nacci,
Antonio Monopoli

J. Organomet. Chem. 690 (2005) 5458

Pd–benzothiazol-2-ylidene complex in ionic liquids: Efficient catalyst for carbon–carbon coupling reactions

Pd–benzothiazol-2-ylidene complex **3** does catalyze, in tetrabutylammonium bromide melt as solvent, very fast and efficient both the Heck and the carbonylation reactions of aryl halides. In the Heck reaction of the aryl halides with cinnamates, the addition of tetrabutylammonium acetate as base, in order to control the stereospecificity of this process, leads to the decomposition of **3** affording Pd-nanoclusters that efficiently catalyze a stereospecific synthesis of β -aryl cinnamates.

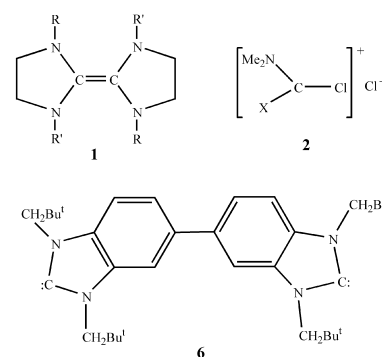


Michael F. Lappert

J. Organomet. Chem. 690 (2005) 5467

Contributions to the chemistry of carbene-metal chemistry

Our researches on carbenemetal chemistry have employed as carbenoids electron-rich olefins (EROs) such as **1**, salts such as **2**, or unsaturated carbenes including **6**. The work has been published in about 60 papers and has dealt with more than 500 carbene complexes of 16 transition metals in various oxidation states; topics included synthesis, structure and reactivity.

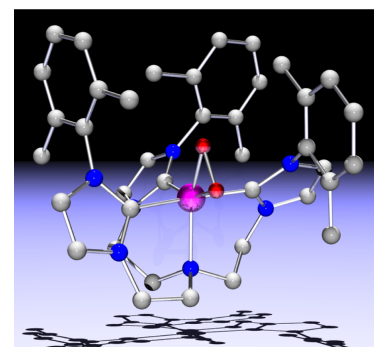


Xile Hu, Karsten Meyer

J. Organomet. Chem. 690 (2005) 5474

New tripodal N-heterocyclic carbene chelators for small molecule activation

Tripodal N-heterocyclic carbene (NHC) ligands for small molecule activation at electron-rich metal ions were synthesized. While the nitrogen-anchored tris(carbene) ligands bind to low-valent metal ions in 1:1 stoichiometry, the C-anchored version provided access to D_3 symmetrical trinuclear species. In-depth electronic structure studies revealed significant π -backbonding in electron-rich metal NHC complexes.

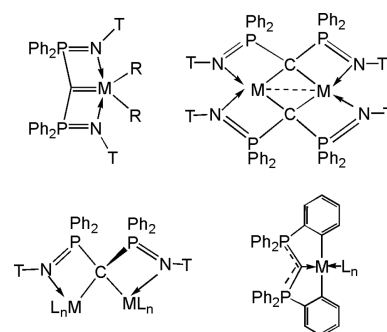


Nathan D. Jones, Ronald G. Cavell

J. Organomet. Chem. 690 (2005) 5485

Phosphorus-substituted carbene complexes: Chelates, pincers and spirocycles

Recent developments in carbene “pincer” complexes of the bis(phosphanimine)methandiide and carbodiphosphorane systems are summarised along with developments in related bridged carbene complexes of the imine system.



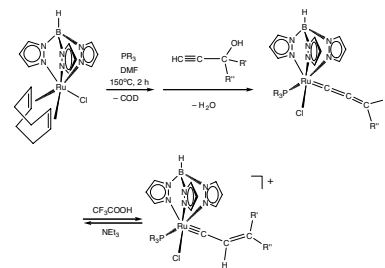
Regular Papers

Sonja Pavlik, Kurt Mereiter,
Michael Puchberger, Karl Kirchner

J. Organomet. Chem. 690 (2005) 5497

Reaction of the RuTp(PR₃)Cl fragment with alkynols: Formation of carbene, vinylidene, allenylidene, and carbyne complexes

The reaction of RuTp(COD)Cl with PR₃ = PPh₂Pr, PⁱPr₃, PPh₃ and alkynols HC≡CCR'₂OH affords neutral allenylidene complexes RuTp(PR₃)(=C=C=CR'₂)Cl. Addition of acid to a solution of these complexes leads to reversible formation of novel carbyne complexes of the type [RuTp(PR₃)(≡C-CHCR'₂)Cl]⁺.

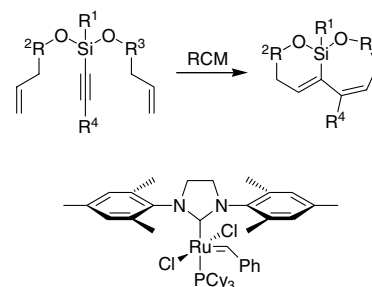


Jonathan B. Grimm, Ryan D. Otte,
Daesung Lee

J. Organomet. Chem. 690 (2005) 5508

Tandem dienyne ring-closing metathesis of alkynyl silaketals for the formation of bicyclic siloxanes

The tandem dienyne ring-closing metathesis of alkynyl silaketals containing two tethered olefins was achieved with second generation Grubbs NHC-ruthenium carbene complex to provide bicyclic siloxanes. Removal of the silicon tether was achieved through protodesilylation with fluoride to afford stereochemically defined (1*E*,3*Z*)-dienes.

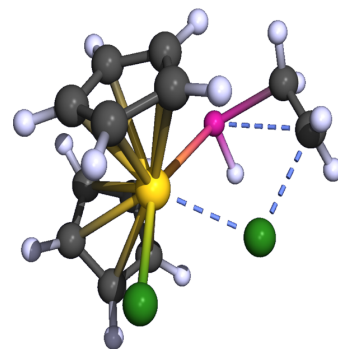


T.P.M. Goumans, Andreas W. Ehlers,
Koop Lammertsma

J. Organomet. Chem. 690 (2005) 5517

Toward the catalytic synthesis of phosphiranes. A computational study

The formation and reactivity of a zirconocene phosphinidene is investigated to explore its potential as a catalyst in the synthesis of phosphiranes.

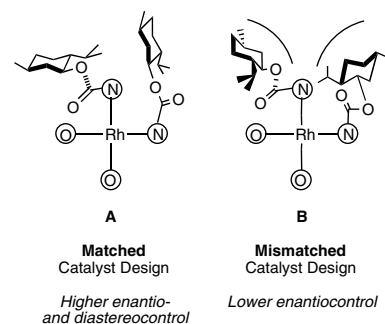


Michael P. Doyle, John P. Morgan,
John T. Colyer

J. Organomet. Chem. 690 (2005) 5525

Stereoselectivity in metal carbene and Lewis acid-catalyzed reactions from diastereomeric dirhodium(II) carboxamidates: Menthyl *N*-acetyl-2-oxoimidazolidine-4(*S*)-carboxylates

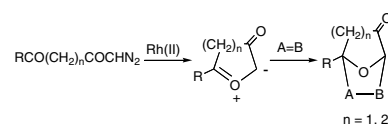
The influence of a chiral menthyl group as the pendant ester substituent on the *N*-acetyl-2-oxoimidazolidine-4*S*-carboxylate ligands in chiral dirhodium(II) imidazolidinone catalysts has been examined. Significant match/mismatch influences are evident in the observed stereocontrol for carbon-hydrogen insertion reactions with diazoacetates.



Albert Padwa*J. Organomet. Chem.* 690 (2005) 5533

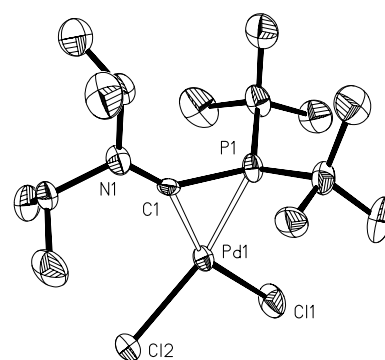
The interaction of rhodium carbenoids with carbonyl compounds as a method for the synthesis of tetrahydrofurans

This mini-review article emphasizes some of the more recent synthetic applications of the tandem *rhodium carbenoid cyclization/cycloaddition cascade* for natural product synthesis. Discussion centers on the chemical behavior of the rhodium metal carbenoid complex that is often affected by the nature of the ligand groups attached to the metal center.


**Emmanuelle Teuma, Céline Lyon-Saunier,
Heinz Gornitzka, Gérard Mignani,
Antoine Baceiredo, Guy Bertrand**
J. Organomet. Chem. 690 (2005) 5541

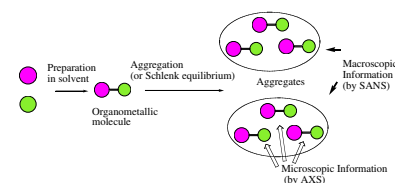
A stable (amino)(phosphino)carbene as bidentate ligand for palladium and nickel complexes: Synthesis, structure, and catalytic activity

Two original Pd and Ni complexes featuring an (amino)(phosphino)carbene η^2 -bonded to the metal have been prepared and the catalytic activity of the palladium complex was evaluated for aryl-amination reactions.


**Seijiro Matsubara, Hideaki Yoshino,
Yuhei Yamamoto, Koichiro Oshima,
Hideki Matsuoka, Koza Matsumoto,
Kazuhiko Ishikawa, Eiichiro Matsubara**
J. Organomet. Chem. 690 (2005) 5546

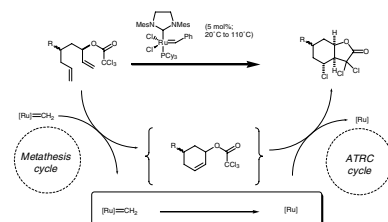
Structure and reactivity of bis(iodozincio)-methane solution

The structural information about bis(iodozincio)methane as THF solution was corrected by small angle neutron scattering and by anomalous X-ray scattering. Those scattering experiments implied that the prepared bis(iodozincio)methane exists without forming any oligomer or aggregate.

**Bernd Schmidt, Michael Pohler***J. Organomet. Chem.* 690 (2005) 5552

Ruthenium-catalyzed tandem ring closing metathesis (RCM) – atom transfer radical cyclization (ATRC) sequences

A sequential ring closing metathesis-radical cyclization reaction is described that proceeds in one pot using only one precatalyst.

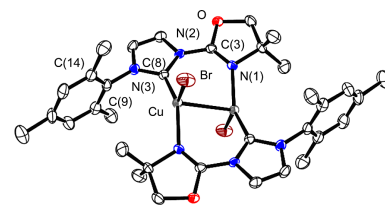


**Nathanaële Schneider, Vincent César,
Stéphane Bellemin-Laponnaz, Lutz H. Gade**

J. Organomet. Chem. 690 (2005) 5556

Synthesis and structural chemistry of oxazoliny-carbene copper(I) complexes

Reaction of a series of directly connected oxazoline-imidazolium salts with potassium *tert*-butoxide and in the presence of $\text{CuBr} \cdot \text{SMe}_2$ at -78°C cleanly gave the corresponding 2-oxazoliny-*N*-mesitylimidazolide-copper(I) complexes which are monomeric in solution but aggregate in the solid state.

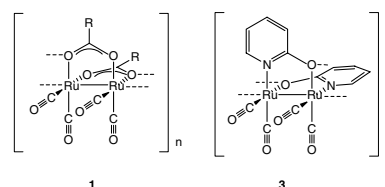


Thorsten Werle, Lutz Schäffler, Gerhard Maas

J. Organomet. Chem. 690 (2005) 5562

Dinuclear ruthenium(I) complexes of the type $[\text{Ru}_2(\text{CO})_4\text{L}_2]$ with carboxylate or 2-pyridonate ligands: Evaluation as catalysts for olefin cyclopropanation with diazoacetates

Dinuclear Ru(I,I) complexes $[\text{Ru}_2(\text{CO})_4(\mu\text{-OOCR})_2]_n$ ($\text{R} = \text{CH}_3, \text{C}_3\text{H}_7, \text{H}, \text{CF}_3$) (**1**) and $[\text{Ru}_2(\text{CO})_4(\mu\text{-pyridin-2-olato})_2]_n$ (**3**) are efficient and effective catalysts for cyclopropanation of nucleophilic alkenes with methyl diazoacetate. The influence of these catalysts and related ones with 6-halopyridin-2-olate ligands is investigated.

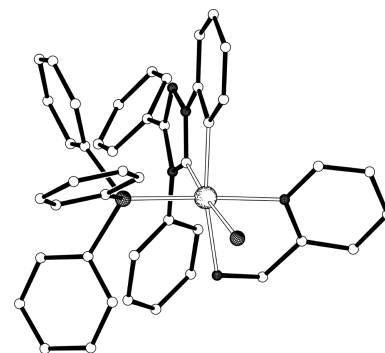


**Walter Baratta, Jan Schütz,
Eberhardt Herdtweck, Wolfgang A. Herrmann,
Pierluigi Rigo**

J. Organomet. Chem. 690 (2005) 5570

Fast transfer hydrogenation using a highly active orthometalated heterocyclic carbene ruthenium catalyst

The synthesis and X-ray characterization of the orthometalated *N*-heterocyclic carbene ruthenium complex **1** bearing 2-(aminomethyl)pyridine have been reported. This compound in presence of NaOH shows very high activity for the transfer hydrogenation of ketones with TOFs up to $120,000 \text{ h}^{-1}$.

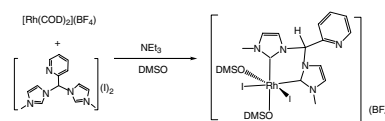


**Elena Mas-Marzá, Mercedes Sanaú,
Eduardo Peris**

J. Organomet. Chem. 690 (2005) 5576

A new pyridine-bis-*N*-heterocyclic carbene ligand and its coordination to Rh: Synthesis and characterization

The bis-imidazolylidene tripodal ligand precursor (2-pyridine)bis(3-methylimidazolium-1-yl)methane diiodide, $[\text{H}_2\text{PYBIM}^{\text{Me}}]_2\text{I}_2$, reacted with $[\text{Rh}(\text{cod})_2](\text{BF}_4)$ providing a Rh(III) complex with very low solubility in most solvents, which we attributed to the polymeric nature of the species. Solution of this polymer in DMSO provided a biscarbene Rh(III) complex in which the pyridine fragment remained unbound.

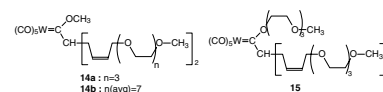


Debasis Samanta, Sudeshna Sawoo, Subrata Patra, Manju Ray, Michèle Salmain, Amitabha Sarkar

J. Organomet. Chem. 690 (2005) 5581

Synthesis of hydrophilic Fischer carbene complexes as organometallic marker and PEGylating agent for proteins

Syntheses of Fischer carbene complexes with various hydrophilic tethers are described. A water-soluble carbene complex was used to label and PEGylate bovine serum albumin (BSA) without affecting its conformation.

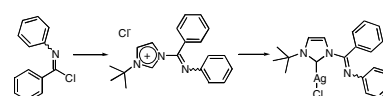


Karl S. Coleman, Sarim Dastgir, Guy Barnett, Maria J.P. Alvite, Andrew R. Cowley, Malcolm L.H. Green

J. Organomet. Chem. 690 (2005) 5591

A nonenolizable imino-*N*-heterocyclic carbene ligand and corresponding silver (I) metal complex

The nonenolizable imino-*N*-heterocyclic carbene ligand precursor [1-*t*-butylimidazolium-3- $\{C(Ph)=N(Ph)\}$] chloride and the corresponding silver (I) complex Ag(C^imine)Cl; where C^imine = [1-*t*-butylimidazolium-2-ylidene-3- $\{C(Ph)=N(Ph)\}$], have been prepared and structurally characterized by single crystal X-ray diffraction.

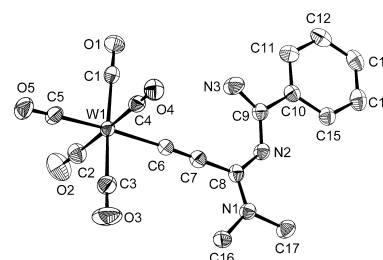


Normen Szesni, Matthias Drexler, Bernhard Weibert, Helmut Fischer

J. Organomet. Chem. 690 (2005) 5597

A convenient route to six-membered heterocyclic carbene complexes: Reactions of aminoallenylidene complexes with 1,3-bidentate nucleophiles

Complexes containing a heterocyclic carbene ligand such as pyrimidinylidene, pyrazolo[1,5-*a*]pyrimidinylidene, and thiazinylidene complexes are conveniently accessible by reaction of pentacarbonyl dimethylaminoallenylidene chromium complexes, $[(CO)_5Cr=C=C=C(R)OMe]$ (R = OMe, Ph) with 1,3-bidentate nucleophiles like amidines, guanidine, amino-5-methylpyrazole, or thioacetamide.

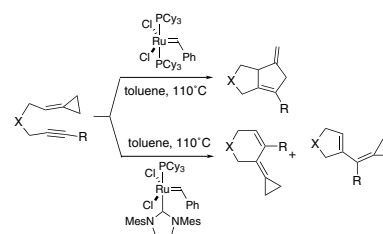


Beatriz Trillo, Moisés Gulías, Fernando López, Luis Castedo, José L. Mascareñas

J. Organomet. Chem. 690 (2005) 5609

Divergent reactivity of alk-5-ynylidenecyclopropanes in the presence of the 1st or the 2nd generation Grubbs' catalysts

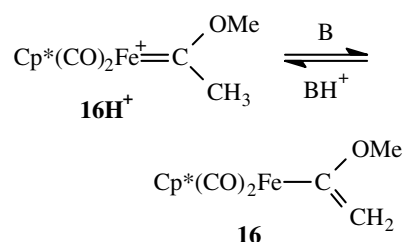
Alk-5-ynylidenecyclopropanes can be divergently elaborated into bicyclo[3.3.0]octenes or exocyclopropylidenecycloalkenes depending on whether they react with the first or the second generation Grubbs' ruthenium carbenes. The highly reactive second generation system catalyses the formation of ring-closing metathesis products, the first generation carbene promotes an intramolecular [3 + 2] cycloaddition.



Claude F. Bernasconi, Mark L. Ragains*J. Organomet. Chem.* 690 (2005) 5616

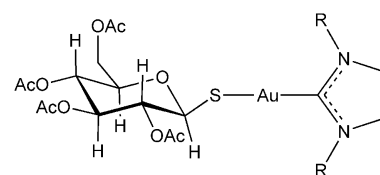
Factors that affect the kinetic and thermodynamic acidities of Fischer carbene complexes: New insights from the study of the cationic (methoxymethylcarbene)dicarbonylpentamethylcyclopentadienyl iron ($[\text{Cp}^*(\text{CO})_2\text{Fe}=\text{C}(\text{OMe})\text{Me}]^+$) in aqueous acetonitrile

The thermodynamic and kinetic acidities of Fischer carbene complexes depend on many structural features but there is no significant correlation between $\text{p}K_{\text{a}}$ values and intrinsic rate constants. The determination of the kinetic and thermodynamic acidities of 16H^+ reported in this paper provides new insights into how structural features affect both.


**Murray V. Baker, Peter J. Barnard,
Susan J. Berners-Price, Simon K. Brayshaw,
James L. Hickey, Brian W. Skelton,
Allan H. White**
J. Organomet. Chem. 690 (2005) 5625

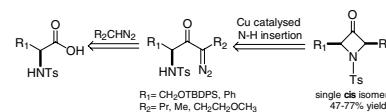
Synthesis and structural characterisation of linear Au(I) N-heterocyclic carbene complexes: New analogues of the Au(I) phosphine drug Auranofin

The synthesis and structural characterisation of a series of neutral Au(I) N-heterocyclic carbene complexes $[(\text{NHC})\text{AuX}]$ ($\text{X} = \text{Cl}$ and 2',3',4',6'-tetra-*O*-acetyl- β -D-glucopyranosyl-1-thiolato) are reported. These compounds are of interest as potential new antitumour drugs.


**Antonio Carlos B. Burtoloso,
Carlos Roque D. Correia**
J. Organomet. Chem. 690 (2005) 5636

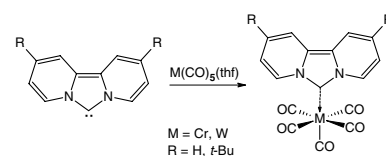
Asymmetric synthesis of *cis*-2,4-disubstituted azetidin-3-ones from metal carbene chemistry

Several chiral *cis*-2,4-disubstituted azetidin-3-ones were prepared as single diastereoisomers from *N*-protected amino acids, employing a highly stereoselective copper carbenoid N-H insertion reaction of diazoketones.


**Michael Nonnenmacher, Doris Kunz,
Frank Rominger, Thomas Oeser**
J. Organomet. Chem. 690 (2005) 5647

First examples of dipyrido[1,2-*c*:2',1'-*e*]imidazolin-7-ylidenes serving as NHC-ligands: Synthesis, properties and structural features of their chromium and tungsten pentacarbonyl complexes

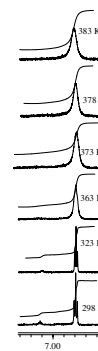
In situ generation of dipyridoimidazolinyldenes from the corresponding imidazolium salts and subsequent reaction with $\text{M}(\text{CO})_5(\text{thf})$ ($\text{M} = \text{Cr}, \text{W}$) leads to the first examples of complexes bearing this type of carbene ligands.



**Enrique Díez-Barra, Javier Guerra,
Valentín Hornillos, Sonia Merino, Juan Tejada**
J. Organomet. Chem. 690 (2005) 5654

Synthesis of palladium–biscarbene complexes derived from 1,1'-methylenebis(1,2,4-triazole) functionalized in the methylene bridge

Palladium–biscarbene complexes derived from *N,N'*-bis(1,2,4-triazol-1-yl)methane containing an alkyl chain functionalized with hydroxyl group have been synthesized. Each compound was obtained as a non-equimolar mixture of two conformers. The hydroxyl group has been changed to methanesulphonate or bromide and two new mixtures of conformers were obtained.

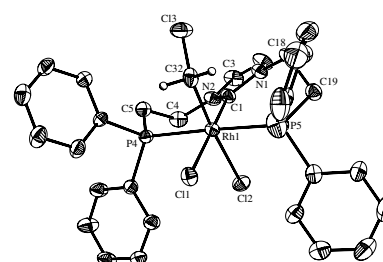


**Jing Yao Zeng, Meng-Hua Hsieh,
Hon Man Lee**

J. Organomet. Chem. 690 (2005) 5662

Rhodium complexes of PC^{NHC}P: Oxidative addition of dichloromethane and catalytic hydrosilylation of alkynes affording (*E*)-alkenylsilanes

Three new rhodium complexes of PC^{NHC}P have been synthesized by using the silver transfer reagent, [Ag₃(μ-Cl)(PC^{NHC}P)₂]Cl₂. The *cis,mer*-Rh^{III}(PC^{NHC}P)(CH₂Cl)Cl₂ complex is formed via the oxidative addition of dichloromethane to the Rh^I(PC^{NHC}P)Cl intermediate. All the complexes are catalyst precursors for efficient, chemoselective hydrosilylation of alkynes.

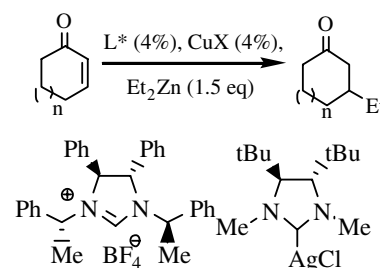


**Caroline L. Winn, Frédéric Guillen,
Julien Pytkowicz, Sylvain Roland,
Pierre Mangeney, Alexandre Alexakis**

J. Organomet. Chem. 690 (2005) 5672

Enantioselective copper catalysed 1,4-conjugate addition reactions using chiral *N*-heterocyclic carbenes

Chiral *N*-heterocyclic carbenes have been shown to be excellent ligands for the copper catalysed conjugate addition of dialkyl zinc reagents to various Michael acceptors. Up to 93% enantiomeric excess has been achieved for the addition of diethyl zinc to cycloheptenone using as little as 4 mol% of catalyst.

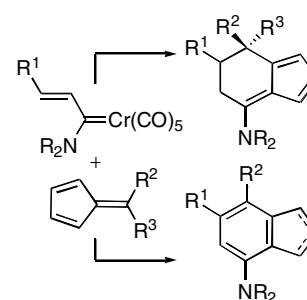


**José Barluenga, Silvia Martínez,
Angel L. Suárez-Sobriño, Miguel Tomás**

J. Organomet. Chem. 690 (2005) 5696

[6 + 3] Cycloaddition of Fischer aminocarbene complexes: An efficient annulation of fulvenes to indene derivatives

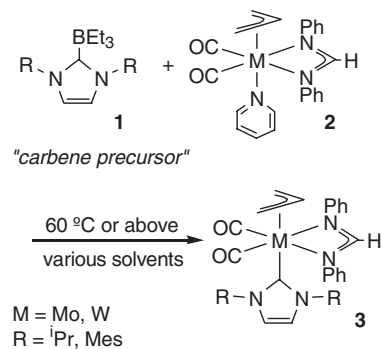
Fischer alkenyl aminocarbene complexes smoothly undergo a [6 + 3] cyclization reaction to fulvenes. This process allows to access 6,7-dihydro-4-amino-5H-indene and 7-amino-1H-indene derivatives.



**Kenichi Ogata, Yoshitaka Yamaguchi,
Taigo Kashiwabara, Takashi Ito**

J. Organomet. Chem. 690 (2005) 5701

The reaction of amidinato(pyridine) complexes of molybdenum and tungsten with triethylborane adduct of *N*-heterocyclic carbene (NHC · BEt₃, **1**) as a carbene precursor toward transition-metal complexes was investigated. The reaction of **1** with amidinato(pyridine) complex **2** under toluene-refluxing conditions afforded NHC complex **3**. The detailed reaction conditions of the utilization of **1** as NHC precursor are described.

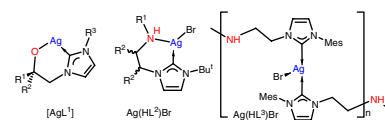


**Ian S. Edworthy, Mark Rodden,
Shaheed A. Mungur, Kate M. Davis,
Alexander J. Blake, Claire Wilson,
Martin Schröder, Polly L. Arnold**

J. Organomet. Chem. 690 (2005) 5710

Silver alkoxide and amino *N*-heterocyclic carbenes; syntheses and crystal structures

Complexes of Ag(I) with pendant arm *N*-heterocyclic carbenes have been prepared via reaction of silver(I) oxide with the corresponding imidazolium precursors.

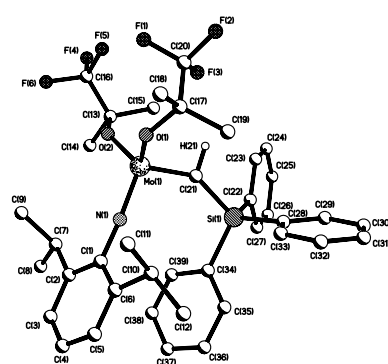


**Leonid N. Bochkarev, Yulia E. Begantsova,
Vladislav I. Shcherbakov,
Natalia E. Stolyarova, Irina K. Grigorieva,
Irina P. Malysheva, Galina V. Basova,
Andrey L. Bochkarev, Yulia P. Barinova,
Georgii K. Fukin, Evgenii V. Baranov,
Yurii A. Kurskii, Gleb A. Abakumov**

J. Organomet. Chem. 690 (2005) 5720

Synthesis and some properties of 14 group element-containing alkyldiene complexes of molybdenum and tungsten

The silicon-containing alkyldiene complex of molybdenum Ph₃Si-CH=Mo(NAr)(OCMe₂CF₃)₂ (Ar = 2,6-Pr₂C₆H₃) has been synthesized and structurally characterized. The formation of tungsten carbene complexes in low yield was observed by ¹H NMR spectroscopy in the reactions of (ArN)₂W(CH₂EMe₃)₂ (E = Si, Ge, Sn) with hydrogen chloride in THF-*d*₈. Catalytic activities of heteroelement-containing alkyldiene complexes of molybdenum R₃E-CH=Mo(NAr)(OCMe₂CF₃)₂ (E = Si, Ge; R = Me, Ph) and also hydrocarbon analogs Alkyl-CH=Mo(NAr)(OCMe₂CF₃)₂ (Alkyl = Bu^t, PhMe₂C) in metathesis of 1-hexene were determined.

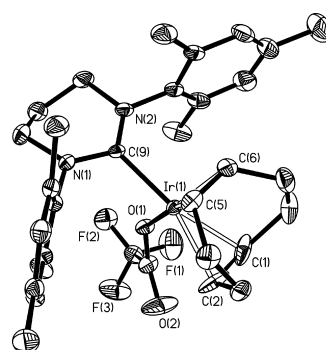


**Yan Zhang, Dongren Wang,
Klaus Wurst, Michael R. Buchmeiser**

J. Organomet. Chem. 690 (2005) 5728

Polymerization of phenylacetylene by novel Rh (I)-, Ir (I)- and Ru (IV) 1,3-R₂-3,4,5,6-tetrahydropyrimidin-2-ylidenes (R = mesityl, 2-propyl): Influence of structure on activity and polymer structure

Novel Rh (I)- and Ir (I)-1,3-R₂-tetrahydropyrimidin-2-ylidenes were synthesized. Together with existing Rh (I)-, Ir (I)- and Ru (IV)-1,3-R₂-tetrahydropyrimidin-2-ylidenes (R = mesityl, 2-propyl), they were used for the polymerization of phenylacetylene. Depending on the complex used, either pure *cis*- or *trans*-poly(phenylacetylene) was obtained.

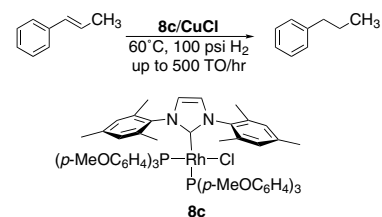


**Daryl P. Allen, Cathleen M. Crudden,
Larry A. Calhoun, Ruiyao Wang,
Andreas Decken**

J. Organomet. Chem. 690 (2005) 5736

Rhodium *N*-heterocyclic carbene complexes:
Synthesis, structure, NMR studies and
catalytic activity

The solid state structure, phosphine dissociation rates and catalytic activity of several Rh-*N*-heterocyclic carbene complexes were studied. Catalytic activity for the hydrogenation of β -methylstyrene was improved by up to two orders of magnitude upon the addition of copper chloride. The catalyst with the highest inherent activity was found to be [Rh(IMes)(P-*p*-FC₆H₄)₃], although the *p*-methoxy derivative benefited the most from the addition of CuCl, giving turnover numbers of over 400 h⁻¹.

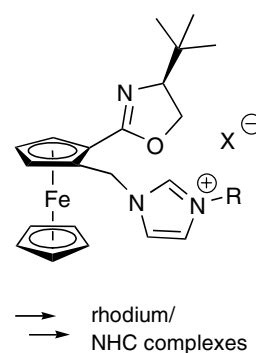


Yu Yuan, Gerhard Raabe, Carsten Bolm

J. Organomet. Chem. 690 (2005) 5747

Novel rhodium complexes with ferrocene-based *N*-heterocyclic carbenes: Synthesis, structure and catalysis

The synthesis of a chiral *N*-heterocyclic carbene (NHC) with an oxazolanyl ferrocenyl substituent is reported. Catalysis studies demonstrate the capability of the rhodium complexes to catalyze hydrosilylations of ketones, and an X-ray crystal structure reveals the chelating properties of the ligand.



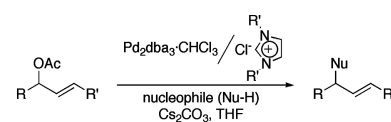
Yoshihiro Sato, Taro Yoshino, Miwako Mori

J. Organomet. Chem. 690 (2005) 5753

N-Heterocyclic carbenes as ligands in palladium-catalyzed Tsuji–Trost allylic substitution

A Pd(0)-catalyzed allylic substitution (i.e., Tsuji–Trost reaction) of various allylic acetates, lactone, and carbonate using *N*-heterocyclic carbene as a ligand was investigated. Allylic substitution using a Pd–NHC complex differed from that using a

Pd–phosphine complex as follows: (1) the reaction using a Pd–NHC complex required elevated temperature (50 °C or reflux in THF), (2) allylic carbonates were inert to a Pd–NHC complex, and (3) nitrogen nucleophiles such as sulfonamide and amine did not react with allylic acetate. It was also found that allylic substitution with a soft nucleophile using a Pd–NHC catalyst proceeds via overall retention of configuration to give the product in a stereospecific manner, the stereochemical reaction course obviously being the same as that of the reaction using a Pd–phosphine complex.

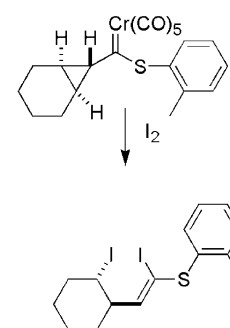


**Margaret D. Reid, Liz Tirado, Jianwei Zhang,
Nwamara Dike, James W. Herndon**

J. Organomet. Chem. 690 (2005) 5759

Reaction of cyclopropylcarbene–metal complexes with nucleophiles, halogens and HX

The reaction of halogens, pseudohalogens, and HX with cyclopropyl(phenylthio)carbene–chromium complexes leads to the formation of 1,4-dihalo-1-thiophenyl-1-butene systems with a moderate-high degree of stereocontrol in the formation of the alkene. A mechanism involving electrophilic activation of the carbene complex followed by nucleophilic attack at the cyclopropane carbon has been proposed and evaluated.

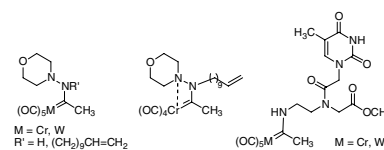


**Clara Baldoli, Paolangelo Cerea,
Luigi Falciola, Clelia Giannini,
Emanuela Licandro, Stefano Maiorana,
Patrizia Mussini, Dario Perdicchia**

J. Organomet. Chem. 690 (2005) 5777

The electrochemical activity of heteroatom-stabilized Fischer-type carbene complexes

The cyclic voltammetry study of some alkoxy, amino and hydrazino carbene complexes of chromium and tungsten is reported. This study represents a completely new behavior of Fischer-type carbene complexes. Two sets of carbene complexes, namely chromium and tungsten carbenes, have been studied, in order to verify the influence of the two different metals on the electrochemical results. The finding reported in the manuscript testify that Fischer carbenes are a class of compounds of significant and widely modulable electrochemical activity.

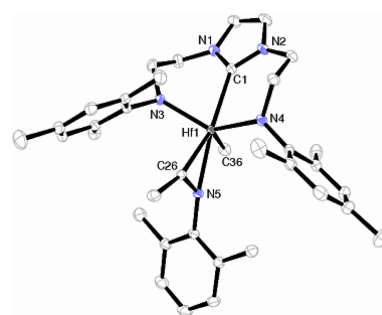


Liam P. Spencer, Michael D. Fryzuk

J. Organomet. Chem. 690 (2005) 5788

Synthesis and reactivity of zirconium and hafnium complexes incorporating chelating diamido-N-heterocyclic-carbene ligands

Zirconium and hafnium transition metal complexes employing a diamido N-heterocyclic carbene (NHC) ligand set (denoted [NCN]) have been synthesized. Activation of $\text{Mes}[\text{NCN}]\text{M}(\text{CH}_3)_2$ with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ yields $\{\text{Mes}[\text{NCN}]\text{MCH}_3\}\{\text{B}(\text{C}_6\text{F}_5)_4\}$, which is moderately active in polymerization of ethylene. The hafnium dialkyl complexes also insert carbon monoxide and substituted isocyanides to yield η^2 -acyls and η^2 -iminoacyls, respectively. In some circumstances, further C–C bond coupling occurs to yield enediolates and eneamidolate metallocycles.



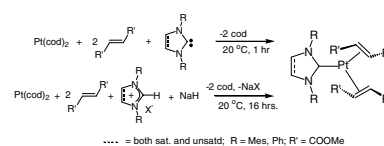
**Marcel A. Duin, Martin Lutz,
Anthony L. Spek, Cornelis J. Elsevier**

J. Organomet. Chem. 690 (2005) 5804

Synthesis of electron-rich platinum centers: Platinum⁰(carbene)(alkene)₂ complexes

Several zero-valent platinum-mono-carbene complexes $[\text{Pt}^0(\text{NHC})(\text{dimethyl fumarate})_2]$ (NHC = 1,3-dimesityl-imidazol-2-ylidene; 1,3-dimesityl-dihydroimidazol-2-ylidene; 1,3-di-

phenyl-dihydroimidazol-2-ylidene) have been synthesized by reaction of platinum(0)-bis(cycloocta-1,5-diene) with the appropriate isolated carbene, or the in situ generated carbene ligand. The synthesis of (1,3-diphenyl-dihydroimidazol-2-ylidene)-bis(η^2 -dimethyl fumarate) platinum(0) (**2b**) could be effected from the appropriate *Wanzlick* dimer. NMR characteristics of the new compounds and their reactions with 1,2,3-trimethylimidazolium iodide, with H₂ and subsequent insertions and C–H activations are presented.

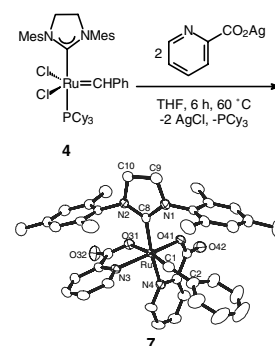


**F. Ekkehardt Hahn, Martin Paas,
Roland Fröhlich**

J. Organomet. Chem. 690 (2005) 5816

Synthesis, characterization, and catalytic activity of a ruthenium carbene complex coordinated with bidentate 2-pyridine-carboxylato ligands

The new halide and phosphine free complex $[(\text{sImes})(\text{C}_5\text{H}_4\text{NCO}_2)_2\text{Ru}=\text{CHPh}]$ (**7**) containing two bidentate pyridine-2-carboxylato ligands was synthesized from $[(\text{sImes})(\text{PCy}_3)(\text{Cl})_2\text{Ru}=\text{CHPh}]$ (**4**) and silver pyridine-2-carboxylate. The air-stable precatalyst **7** exhibits activity in ring-closing metathesis reactions (RCM) in both CH_2Cl_2 and methanol after activation with the cocatalyst HCl.

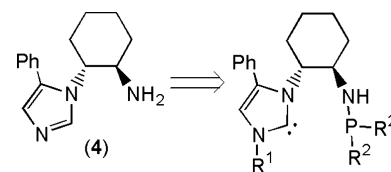


Richard Hodgson, Richard E. Douthwaite

J. Organomet. Chem. 690 (2005) 5822

Synthesis and asymmetric catalytic application of chiral imidazolium–phosphines derived from (1*R*,2*R*)-*trans*-diaminocyclohexane

Reaction between the imidazole amine **4** and chlorophosphines gives imidazole–phosphines that serve as precursors to chiral *N*-heterocyclic carbene (NHC)-phosphine derivatives. The NHC–P compounds have been applied as ancillary ligands to two transition metal catalysed asymmetric reactions.

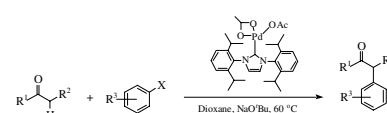


Rohit Singh, Steven P. Nolan

J. Organomet. Chem. 690 (2005) 5832

An efficient and mild protocol for the α -arylation of ketones mediated by an (imidazol-2-ylidene)palladium(acetate) system

The activity of well-defined *N*-heterocyclic carbene (NHC)-palladium acetate complexes has been studied in the α -arylation of ketones. Catalytic results indicate a high activity. The use of hindered substrates provide an avenue for convenient synthesis of various ketone derivatives. The first examples of α -arylation of ketones at room temperature mediated by an NHC-bearing catalyst are also presented.

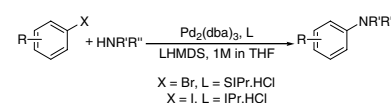


Israel Conesa Lerma, Mark J. Cawley, F. Geoffrey N. Cloke, Katherine Arentsen, James S. Scott, Stuart E. Pearson, John Hayler, Stephen Caddick

J. Organomet. Chem. 690 (2005) 5841

Studies on Pd/imidazolium salt protocols for aminations of aryl bromides and iodides using lithium hexamethyldisilazide (LHMDS)

The reactions of a range of secondary amines with aryl bromides and iodides have been performed using an in situ protocol involving palladium and imidazolium salts. Many of these reactions proceed at room temperature, providing a mild protocol for aminations of aryl iodides and bromides. Key to the success of this procedure is the use of lithium hexamethyldisilazide (LHMDS) as base.

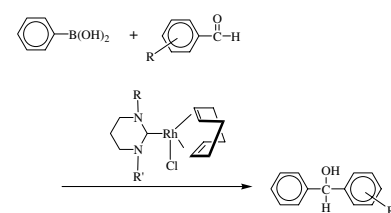


Ismail Özdemir, Serpil Demir, Bekir Çetinkaya, Engin Çetinkaya

J. Organomet. Chem. 690 (2005) 5849

Novel rhodium-1,3-dialkyl-3,4,5,6-tetrahydropyrimidin-2-ylidene complexes as catalysts for arylation of aromatic aldehydes

Novel Complexes of rhodium(I) based on 1,3-dialkyl-3,4,5,6-tetrahydropyrimidin-2-ylidenes give good yields for the addition of phenylboronic acid to aldehydes.

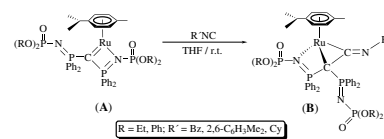


**Victorio Cadierno, Joaquín García-Álvarez,
José Gimeno, Javier Rubio-García**

J. Organomet. Chem. 690 (2005) 5856

Reaction of isocyanides with iminophosphorane-based carbene ligands: Synthesis of unprecedented ketenimine–ruthenium complexes

The first examples of ketenimine–ruthenium complexes, namely $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\kappa^3\text{-}C, C, N\text{-}C(\text{C}=\text{NR}')\{\text{P}\{=\text{N}(\text{P}(\text{OR})_2)\text{Ph}_2\}_2\})_2]$ (B), have been prepared by reacting the bis(iminophosphorano)methandiide-based ruthenium(II) carbenes $[\text{Ru}(\eta^6\text{-}p\text{-cymene})(\kappa^2\text{-}C, N\text{-}C\{\text{P}\{=\text{N}(\text{P}(\text{OR})_2)\text{Ph}_2\}_2\})]$ (A) with isocyanides.

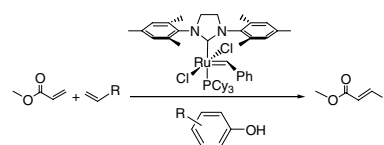


Grant S. Forman, Robert P. Tooze

J. Organomet. Chem. 690 (2005) 5863

Improved cross-metathesis of acrylate esters catalyzed by 2nd generation ruthenium carbene complexes

The performance of cross-metathesis reactions between acrylate esters and olefins catalyzed by Grubbs catalysts have been enhanced by the simple addition of *p*-cresol. For example, the efficiency of the cross metathesis reaction between methyl acrylate and 1-decene catalyzed by **2** was significantly increased by addition of *p*-cresol to the reaction mixture, resulting in increased product yields and *E/Z* ratios.

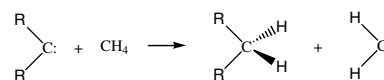


**Chun-Liang Lai, Wen-Hsin Guo,
Ming-Tsung Lee, Ching-Han Hu**

J. Organomet. Chem. 690 (2005) 5867

Ligand properties of *N*-heterocyclic and Bertrand carbenes: A density functional study

Density functional theory (DFT) shows that the carbene stabilization energy (CSE) computed using the energy of reaction of *N*-heterocyclic carbene (NHC) are significantly larger than those of Bertrand-type carbenes. The carbene–metal bonds of imidazol-2-ylidenes, imidazolin-2-ylidenes, thiazo-2-ylidenes, and triazo-5-ylidenes are stronger than those of Bertrand-type carbenes. Bertrand-type carbenes are more nucleophilic, and are softer ligands compared with NHCs. The force constants of C–O in $\text{Cr}(\text{CO})_5\text{L}$ and $\text{Ni}(\text{CO})_3\text{L}$ are related to the property of isolated carbenes such as PA, electronegativity (χ), and charge transfer (ΔN).

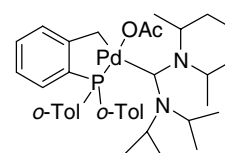


Guido D. Frey, Wolfgang A. Herrmann

J. Organomet. Chem. 690 (2005) 5876

Novel acyclic carbene-substituted phosphapalladacycles

Synthesis of a phosphapalladacycle substituted with acyclic carbenes, to form metastable η^1 -carbene complexes, which can be converted to zero valent palladium complexes.

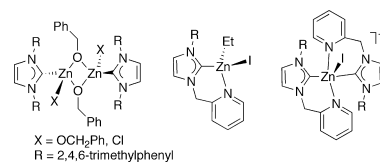


**Tryg R. Jensen, Chris P. Schaller,
Marc A. Hillmyer, William B. Tolman**

J. Organomet. Chem. 690 (2005) 5881

Zinc *N*-heterocyclic carbene complexes and their polymerization of D,L-lactide

A series of zinc complexes of monodentate *N*-heterocyclic carbenes (NHCs) and a new sterically bulky bidentate pyridyl-NHC ligand have been synthesized, characterized, and demonstrated to be initiators for the polymerization of D,L-lactide.

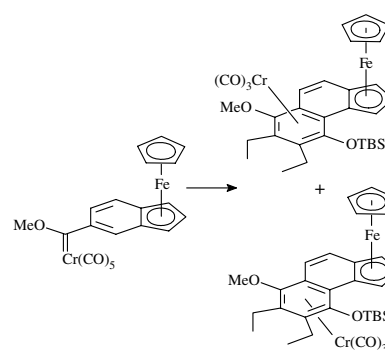


**Jan Bennowitz, Martin Nieger,
Burhanshah Lewall, Karl Heinz Dötz**

J. Organomet. Chem. 690 (2005) 5892

Reactions of complex ligands part 106. Heterobimetallic fused arenes: Chromium-templated benzannulation of a ferrocene-type metal carbene

The chromium-templated benzannulation of iron cyclopentadienyl(indenyl)carbene chromium with 3-hexyne affords *syn*- and *anti*-diastereomers of heterobimetallic hydroquinoid arene Cr(CO)₃ complexes which are characterized by X-ray, spectroscopic and electrochemical means.



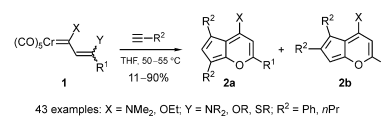
**Yao-Ting Wu, Takuya Kurahashi,
Armin de Meijere**

J. Organomet. Chem. 690 (2005) 5900

Some recent applications of Fischer carbene-metal complexes in organic synthesis

{[2-(Dialkylamino)ethenyl]ethoxycarbene}chromium complexes **1** (X = NMe₂) have been made available from lithiated terminal alkynes, hexacarbonylchromium, triethyl-oxonium tetrafluoroborate and secondary amines in a one-pot operation, in good to

excellent yields. Reactions of these complexes with alkynes can afford 5-dialkylamino-3-ethoxycyclopentadienes, and from these angular and linear triquinanes, di- and triannelated benzene derivatives, steroid-like skeletons, and hexacycles can be obtained with great facility. In addition, otherwise not easily accessible cyclopenta[*b*]pyrans **2a/2b** and novel spiro[4.4]nonatrienes can be prepared in single operational steps from complexes **1** and terminal alkynes via [3+2+2+1] and [3+2+2+2] cocyclizations incorporating two and three alkyne units, respectively.

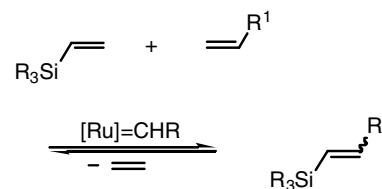


**Cezary Pietraszuk, Helmut Fischer,
Szymon Rogalski, Bogdan Marciniak**

J. Organomet. Chem. 690 (2005) 5912

The effect of substituents at silicon on the cross-metathesis of trisubstituted vinylsilanes with olefins

Efficient and selective cross-metathesis of vinylsilanes, carrying a large spectrum of different substituents at silicon, with various olefins in the presence of the first and second generation Grubbs catalyst and Hoveyda-Grubbs catalyst is described. Pronounced influence of the properties of substituents at silicon on the reactivity of vinylsilanes was demonstrated.

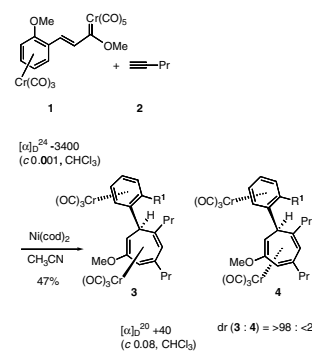


**Ken Kamikawa, Yasunori Shimizu,
Hiroyuki Matsuzaka, Motokazu Uemura**

J. Organomet. Chem. 690 (2005) 5922

Stereoselective [3+2+2] cycloaddition utilizing optically active binuclear Fischer carbene complexes with alkynes

Stereoselective [3+2+2] cycloaddition reaction of optically active binuclear α,β -unsaturated Fischer carbene complexes with alkynes via nickel carbene complexes gave planar chiral cycloheptatriene chromium complexes with high diastereoselectivity. The chromium-coordinated both rings of the product were stereo- and chemoselectively functionalized by utilizing distinct properties of the chromium complex.

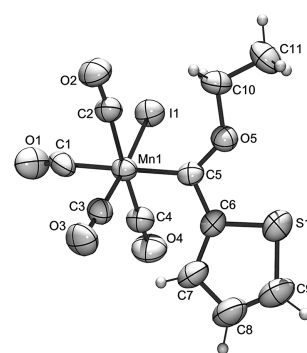


**Simon Lotz, Marilé Landman,
Daniela I. Bezuidenhout, Andrew J. Olivier,
David C. Liles, Petrus H. van Rooyen**

J. Organomet. Chem. 690 (2005) 5929

Metal–metal bond cleavage of carbene complexes by halogens: The crystal and molecular structures of *ax*- $[\text{Mn}_2(\text{CO})_9\{\text{C}(\text{OEt})_2\text{-thienyl}\}]$, $[\text{Mn}(\text{CO})_4(\text{I})\{\text{C}(\text{OEt})_2\text{-thienyl}\}]$ and *eq*- $[\text{Mn}_2(\text{CO})_9\{\text{C}(\text{NH}_2)_2\text{-thienyl}\}]$

The metal–metal bond in $[\text{M}_2(\text{CO})_9\{\text{C}(\text{OEt})\text{R}\}]$ ($\text{M} = \text{Mn}, \text{Re}$, $\text{R} = 2\text{-thienyl}, 2\text{-bithienyl}$) is readily cleaved with halogens to afford *cis*- $[\text{M}(\text{CO})_4(\text{X})\{\text{C}(\text{OEt})\text{R}\}]$ ($\text{M} = \text{Mn}$, $\text{X} = \text{I}$; $\text{M} = \text{Re}$, $\text{X} = \text{Br}$). In the binuclear manganese complex, the carbene ligand is found in an axial position, whereas the electronically favoured equatorial position is found for the carbene ligands in the corresponding rhenium complex.

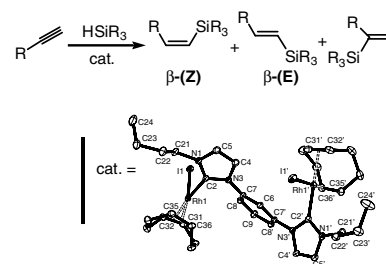


**Gurusamy Thangavelu Senthil Andavan,
Eike B. Bauer, Christopher S. Letko,
T. Keith Hollis, Fook S. Tham**

J. Organomet. Chem. 690 (2005) 5938

Synthesis and characterization of a free phenylene bis(*N*-heterocyclic carbene) and its di-Rh complex: Catalytic activity of the di-Rh and CCC–NHC Rh pincer complexes in intermolecular hydrosilylation of alkynes

A new di-Rh bis-carbene complex was found to be an efficient catalyst for hydrosilylation of alkynes without exclusion of air or water. Its catalytic effectiveness was compared to a CCC–NHC Rh pincer congener.

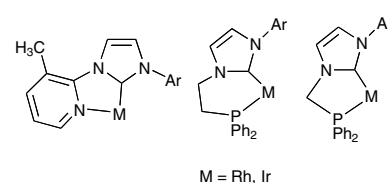


**Neoklis Stylianides, Andreas A. Danopoulos,
Nikolaos Tsoureas**

J. Organomet. Chem. 690 (2005) 5948

¹Pyridine and phosphine functionalised *N*-heterocyclic carbene complexes of rhodium and iridium

New, C–H activation stabilised, pyridine functionalised *N*-heterocyclic carbene complexes of Rh(I) and Ir(I) have been synthesised. Attempts to prepare phosphine functionalised –NHC complexes of rhodium and iridium gave well-defined species only in a few cases.

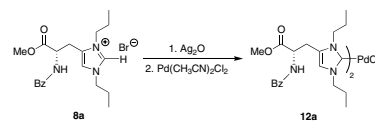


Frithjof Hannig, Gerald Kehr, Roland Fröhlich, Gerhard Erker

J. Organomet. Chem. 690 (2005) 5959

Formation of chiral ionic liquids and imidazol-2-ylidene metal complexes from the proteinogenic amino acid L-histidine

The readily available histidinium salt [Bz-His(*n*-propyl)₂-OMe⁺Br⁻] (**8a**), mp 39 °C, may serve as a useful chiral ionic liquid. Its subsequent treatment with silver oxide followed by transmetalation gave chiral L-histidine-derived N-heterocyclic carbene metal complexes.

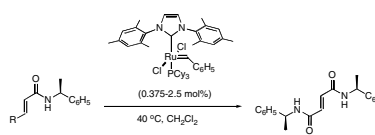


Jan Streuff, Kilian Muñiz

J. Organomet. Chem. 690 (2005) 5973

Efficient synthesis of fumaric amides through cross-metathesis of acrylic amides with the NHC Grubbs ruthenium catalyst

Application of the second generation Grubbs metathesis catalyst for the homo-cross-metathesis of acroyl amides from chiral amines is reported. This efficient and high-yielding reaction provides a side-product free synthesis of fumaric acid diamides which are formed with complete (*E*)-selectivity under the reaction conditions.

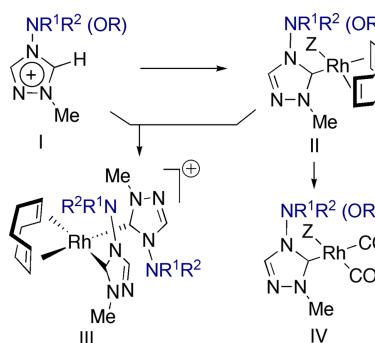


Manuel Alcarazo, Rosario Fernández, Eleuterio Álvarez, José M. Lassaletta

J. Organomet. Chem. 690 (2005) 5979

Synthesis, structure and electronic properties of *N*-dialkylamino- and *N*-alkoxy-1,2,4-triazol-3-ylidene ligands

A synthesis of 4-amino- or alkoxy-1,2,4-triazolium salts **I** has been key for the obtention of 1,2,4-triazol-3-ylidene derivatives such as neutral RhCl(carbene)(COD) **II** and cationic Rh(carbene)₂(COD) **III** complexes. The effect of the amino- and alkoxy groups in the σ -donor ability of these carbenes has been comparatively evaluated from the $\nu(\text{CO})$ stretching frequencies of RhCl(carbene)(CO)₂ complexes **IV**.

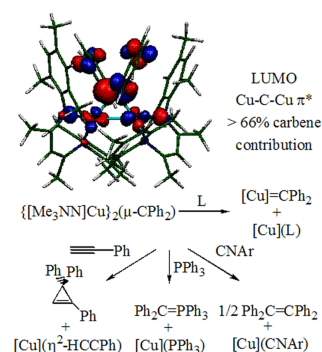


Yosra M. Badiei, Timothy H. Warren

J. Organomet. Chem. 690 (2005) 5989

Electronic structure and electrophilic reactivity of discrete copper diphenylcarbenes

The synthesis and X-ray structure of the β -diketiminato dicopper carbene $\{[\text{Me}_3\text{NN}]\text{Cu}\}_2(\mu\text{-CPh}_2)$ (**4**) are presented. DFT calculations indicate electrophilic character at the carbene C atom, borne out in group transfer reactions to phenylacetylene and triphenylphosphine. In contrast, loss of $\text{Ph}_2\text{C}=\text{CPh}_2$ is induced by isonitrile coordination while reaction with O_2 yields benzophenone.

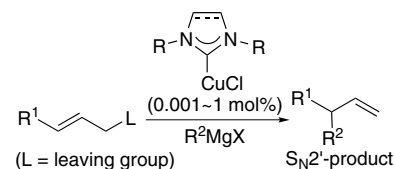


**Sentaro Okamoto, Satoshi Tominaga,
Naoko Saino, Kouki Kase, Kentaro Shimoda**

J. Organomet. Chem. 690 (2005) 6001

Allylic substitution reactions with Grignard reagents catalyzed by imidazolium and 4,5-dihydroimidazolium carbene–CuCl complexes

The ate-type complex(es) such as [(imidazolium carbene)-CuR₂][−](MgX)⁺ was postulated as an active species.

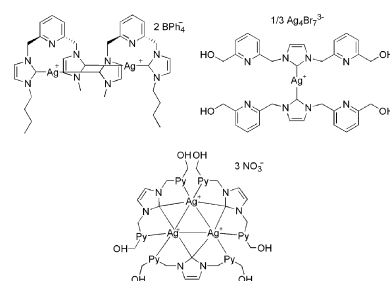


**Jered C. Garrison, Claire A. Tessier,
Wiley J. Youngs**

J. Organomet. Chem. 690 (2005) 6008

Synthesis and crystallographic characterization of multi-donor *N*-heterocyclic carbene chelating ligands and their silver complexes: Potential use in pharmaceuticals

Synthesis and structural characterization of two multi-donor NHC precursors and their silver complexes: Investigation of the potential use of NHCs in targeted pharmaceuticals.

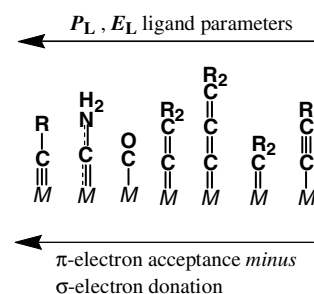


Armando J.L. Pombeiro

J. Organomet. Chem. 690 (2005) 6021

Electron-donor/acceptor properties of carbynes, carbenes, vinylidenes, allenylidenes and alkynyls as measured by electrochemical ligand parameters

Electrochemical Pickett's P_L and Lever's E_L ligand parameters are estimated for a high number of carbyne, carbene, vinylidene, allenylidene and alkenyl ligands which can then be ordered according to their net π -electron acceptor minus σ -donor character.

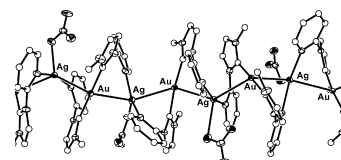


Vincent J. Catalano, Anthony O. Etogo

J. Organomet. Chem. 690 (2005) 6041

Luminescent coordination polymers with extended Au(I)–Ag(I) interactions supported by a pyridyl-substituted NHC ligand

One-dimensional, mixed-metal Ag(I)–Au(I) coordination polymers are prepared by treating the homoleptic [Au(CH₃impy)₂]⁺ complex with AgBF₄ or AgNO₃ in the presence of nitrile solvent. The X-ray structures of four polymers reveals short Ag–Au separations. These materials are intensely luminescent the solid state but dissociate into their monomers in solution.



Horst Kunkely, Arnd Vogler*J. Organomet. Chem. 690 (2005) 6051*

Excited state properties of $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ with NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene and quinone = 1,4-naphthoquinone

The carbene complex $[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$ with NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene and quinone = 1,4-naphthoquinone shows two wavelength absorptions at 312 and 399 nm which are assigned to (NHC \rightarrow quinone) LLCT and ($\text{Pd}^0 \rightarrow$ quinone) MLCT transitions. The MLCT state is not reactive, but emissive ($\lambda_{\text{max}} = 564$ nm at 77 K). At r.t. the complex undergoes a photoredox decomposition which is initiated by the LLCT state.

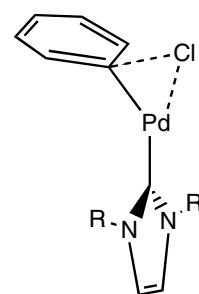
$[\text{Pd}^0(\text{NHC})(\text{quinone})]_2$
 NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
 quinone = 1,4-naphthoquinone

- LLCT** (NHC \rightarrow quinone) excitation: photoredox decomposition
- MLCT** ($\text{Pd}^0 \rightarrow$ quinone) excitation: phosphorescence at 77 K

Jennifer C. Green, Benjamin J. Herbert, Richard Lonsdale*J. Organomet. Chem. 690 (2005) 6054*

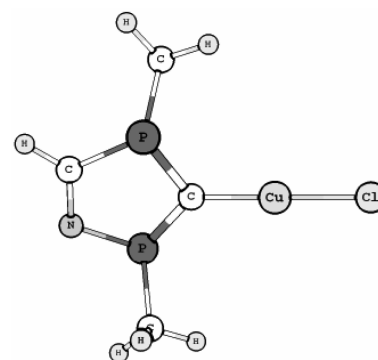
Oxidative addition of aryl chlorides to palladium N-heterocyclic carbene complexes and their role in catalytic arylation

The catalytic cycle for aryl amination has been investigated and the oxidative addition shown to be the rate determining step; the most likely transition state has been established as a $\text{PdL}(\text{arylchloride})$ species, with just one carbene ligand coordinated to the palladium.

**Heiko Jacobsen***J. Organomet. Chem. 690 (2005) 6068*

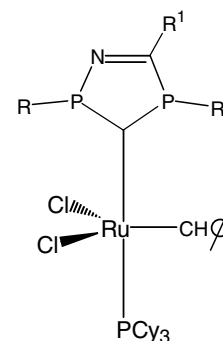
Bonding aspects of P-heterocyclic carbene transition metal complexes. A computational assessment

P-heterocyclic carbenes compete with N-heterocyclic carbenes as ligands for transition-metal-based catalysts in terms of metal-to-ligand bond strength, as well as complement NHC in terms of the nature of the metal–ligand bond.

**Wolfgang W. Schoeller, Daniela Schroeder, A.B. Rozhenko***J. Organomet. Chem. 690 (2005) 6079*

On the ligand properties of the P- versus the N-heterocyclic carbene for a Grubbs catalyst in olefin metathesis

The properties of various di-phosphorus substituted five-membered ring carbene ligands for the metathesis reaction are evaluated by density functional calculations.

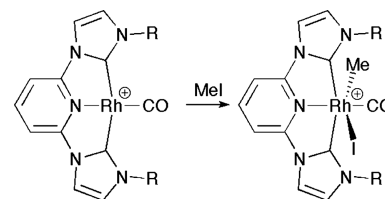


**John M. Wilson, Glenn J. Sunley,
Harry Adams, Anthony Haynes**

J. Organomet. Chem. 690 (2005) 6089

Oxidative addition of MeI to cationic Rh(I) carbonyl complexes with pyridyl bis(carbene) ligands

A series of cationic Rh(I) carbonyl complexes have been prepared by the reactions of $[\text{Rh}(\text{CO})_2(\text{OAc})_2]$ with diimidazolium pyridine salts in the presence of NEt_3 . The complexes have $\nu(\text{CO})$ values which indicate high electron density on the Rh(I) centres, and kinetic measurements on the oxidative addition of MeI show that the complexes have remarkably high nucleophilicity for cationic species.

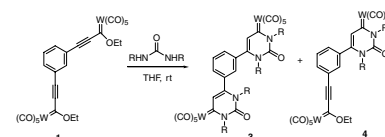


**Anna Llordes, Miguel A. Sierra,
Maria P. Lopez-Alberca, Elies Molins,
Susagna Ricart**

J. Organomet. Chem. 690 (2005) 6096

Synthesis of new polymetallic carbene complexes: Uracil analogs

The easy cycloaddition of ureas with the alkynyl alkoxy biscarbene complexes afforded, in fairly good yields, new biscarbene uracil analogs. X-ray structural data is reported for the dimethyluracil biscarbene complex. By changing the reaction conditions, a new non symmetric complex was obtained whose reaction with ethylenediamine afforded a new tetrakis amino carbene complex.

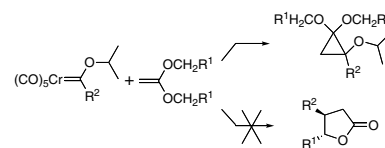


**Siu Ling B. Wang, Daniel R. Goldberg,
Xuejun Liu, Jing Su, Qi-Huang Zheng,
Vincent Liptak, William D. Wulff**

J. Organomet. Chem. 690 (2005) 6101

The first synthesis of cyclopropanone acetals from the reaction of Fischer carbene complexes with ketene acetals

Analysis of the mechanism previously proposed to account for the formation of butyrolactone products from the reaction of Fischer carbene complexes with ketene acetals led to the correction prediction that larger groups on the oxygen heteroatom substituent of the carbene complex would shift the reaction flux to the previously unobserved cyclopropanone acetals.

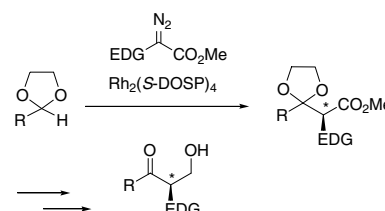


**Huw M.L. Davies, Jaemoon Yang,
Joachim Nikolai**

J. Organomet. Chem. 690 (2005) 6111

Asymmetric C–H insertion of Rh(II) stabilized carbenoids into acetals: A C–H activation protocol as a Claisen condensation equivalent

Diazoacetates substituted with an electron donor group (EDG) decompose in the presence of dirhodium tetraproline, $\text{Rh}_2(\text{S-DOSP})_4$, to give carbenoids which undergo regio- and stereoselective functionalizations of C–H bonds. The C–H activation of tertiary sites in acetals leads to ketals which are precursors to 1,3-keto esters, classically synthesized by a Claisen condensation.

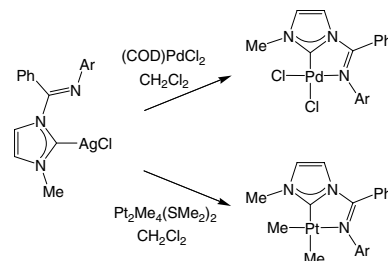


**Morten Frøseth, Kjetil Andreas Netland,
Christian Rømming, Mats Tilset**

J. Organomet. Chem. 690 (2005) 6125

Synthesis and characterization of novel Pd(II) and Pt(II) complexes with 5-ring chelating iminoylcarbene ligands

Pd and Pt complexes bearing a novel 5-membered iminoylcarbene chelate ring system have been prepared by carbene transfer from an Ag carbene precursor; the Ag and Pt complexes have been crystallographically characterized.

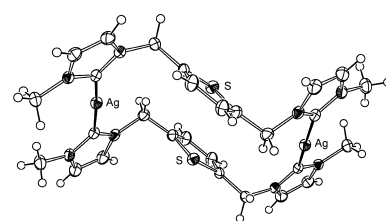


**David J. Nielsen, Kingsley J. Cavell,
Mihai S. Viciu, Steven P. Nolan,
Brian W. Skelton, Allan H. White**

J. Organomet. Chem. 690 (2005) 6133

Furan- and thiophene-functionalised bis-carbene ligands: Synthesis, silver(I) complexes, and catalysis

Silver(I) complexes of functionalised NHCs were prepared from novel furan- and thiophene-functionalised bis-imidazolium salts. The Ag(NHC) complexes adopt dinuclear formulations with X-ray studies revealing discrete twenty-membered $[Ag_2L_2]^{2+}$ dimetal-lacycles. The bis-imidazolium salts were tested as in situ additives for Pd(0)-catalysed aryl amination, with the *N*-*t*-Bu and *N*-mesityl examples showing greater activity than the *N*-methyl analogues.

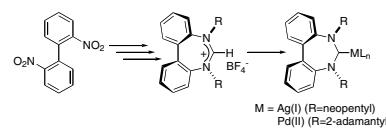


**Christopher C. Scarborough, Brian V. Popp,
Ilia A. Guzei, Shannon S. Stahl**

J. Organomet. Chem. 690 (2005) 6143

Development of 7-membered N-heterocyclic carbene ligands for transition metals

The syntheses of metal complexes bearing seven-membered N-heterocyclic carbenes are described, including X-ray characterization of one amidinium salt carbene precursor, one silver(I)-carbene complex, and two palladium(II)-carbene complexes. Computational analyses reveal a Möbius aromatic stabilization of the formally antiaromatic seven-membered framework.

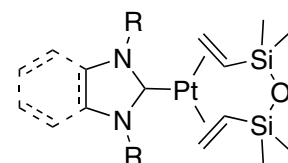


**Guillaume Berthon-Gelloz, Olivier Buisine,
Jean-François Brière, Guillaume Michaud,
Sébastien Stérin, Gérard Mignani,
Bernard Tinant, Jean-Paul Declercq,
David Chapon, István E. Markó**

J. Organomet. Chem. 690 (2005) 6156

Synthetic and structural studies of NHC-Pt(dvtms) complexes and their application as alkene hydrosilylation catalysts (NHC = N-heterocyclic carbene, dvtms = divinyltetramethylsiloxane)

The synthesis and structural properties of an extended family of N-heterocyclic carbene Pt(0) complexes are described. The structural information gained is used to rationalize their catalytic activity in the hydrosilylation of alkenes.



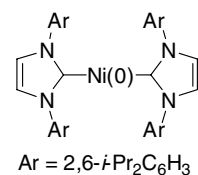
R = Me, Cy, *t*Bu, Mes, ...

Sébastien Kuhl, Yves Fort, Raphaël Schneider

J. Organomet. Chem. 690 (2005) 6169

Nickel(0)/*N*-heterocyclic carbene complexes catalysed arylation of aromatic diamines

The Ni(0) · 2IPr (IPr = *N,N'*-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) complex associated to *t*-BuONa allows either selective *N*-mono or *N,N'*-diarylation of aromatic diamines in high yields. A two-step procedure for the synthesis of unsymmetrical *N,N'*-diaryl aromatic diamines is also described.

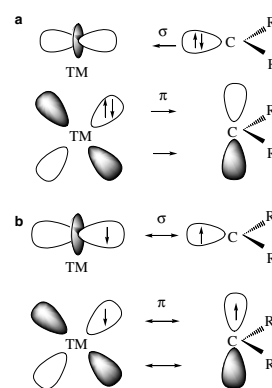


Gernot Frenking, Miquel Solà, Sergei F. Vyboishchikov

J. Organomet. Chem. 690 (2005) 6178

Chemical bonding in transition metal carbene complexes

The nature of the chemical bonding in Fischer- and Schrock-type carbene complexes as well as in complexes with *N,N*-heterocyclic carbene ligands has been analyzed with charge- and energy-partitioning methods.

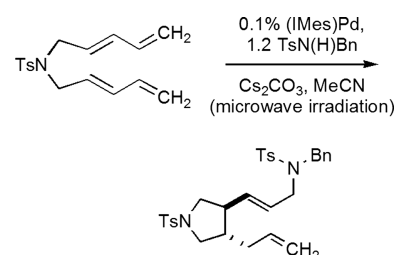


James M. Takacs, Somasundaram Venkataraman, Ross N. Andrews, Libbie S.W. Pelter

J. Organomet. Chem. 690 (2005) 6205

N-heterocyclic carbene-palladium catalysts for the bisdiene cyclization-trapping reaction with sulfonamides under thermal and microwave conditions

Simple (NHC)Pd catalysts effect the efficient cyclization-trapping of bisdienes with sulfonamides. For example, the (IMes)Pd-catalyzed (0.1%, generated in situ) cyclization-trapping of a simple bisdiene with TsN(H)CH₂Ph proceeds in 86% yield upon microwave heating at 75 °C (<250 W, 2.5 h).

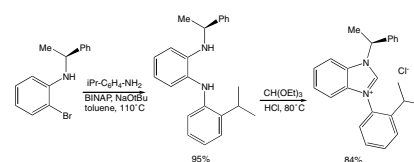


Philip C. Bulman Page, Benjamin R. Buckley, Steven D.R. Christie, Mark Edgar, Andrew M. Poulton, Mark R.J. Elsegood, Vickie McKee

J. Organomet. Chem. 690 (2005) 6210

A new paradigm in *N*-heterocyclic carbenoid ligands

A new type of *N*-heterocyclic carbene ligand that contains two different kinds of chirality, an asymmetric centre and an atropisomeric axis, has been prepared. A significant barrier to rotation results in two diastereoisomeric forms being produced, and this is carried forward into resulting metal complexes.

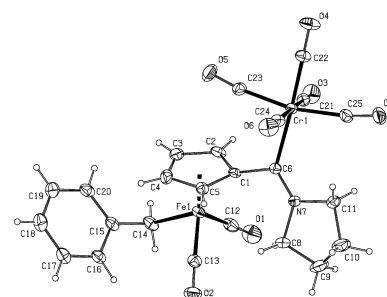


**Markus Schwarz, Rudolf Wartchow,
Holger Butenschön**

J. Organomet. Chem. 690 (2005) 6217

New metal aminocarbene-substituted cyclopentadienyliron half sandwich complexes

Some new half sandwich cyclopentadienyl aminocarbene complexes are reported, which were prepared by treatment of the corresponding alkoxycarbene complexes with primary and secondary amines including enantiopure chiral aminoalcohols and amines with acetyl, phosphine, alkene, and alkyne functionalities. Crystal structures of two representatives indicate no conjugation of the carbene double bond and the cyclopentadienyl π -system in the solid state.



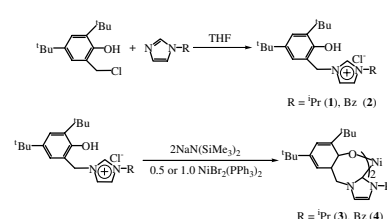
**Wan-Fei Li, Hong-Mei Sun, Zhi-Guo Wang,
Mu-Zi Chen, Qi Shen, Yong Zhang**

J. Organomet. Chem. 690 (2005) 6227

Synthesis and structural characterization of aryloxo-functionalized N-heterocyclic carbene complexes of nickel(II)

The reaction of $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ with two equivalents of anionic aryloxo-functionalized N-heterocyclic carbene $[\text{NaO}-4,6\text{-di-}^i\text{Bu}-\text{C}_6\text{H}_2-2\text{-CH}_2\{\text{C}(\text{NCHCHNR})\}]$ ($\text{R} = ^i\text{Pr}, \text{NaL}^1$; $\text{R} = \text{Bz}, \text{NaL}^2$), which are generated in situ by the

reaction of the corresponding salt $\text{H}_2\text{L}^n\text{Cl}$ ($n = 1$ or 2) with two equivalents of $\text{NaN}(\text{SiMe}_3)_2$, affords bis-ligand complexes of L_2^1Ni (**3**) and L_2^2Ni (**4**) in good yield, respectively. It is interesting to note that still the bis-ligand one not the mono-ligand Ni(II) halide is obtained, even the molar ratio of $\text{NaL}^1(\text{NaL}^2)$ to $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ is changed to 1:1. Complexes of **3** and **4** have been fully characterized including the X-ray structure determination. The structural analysis shows that each nickel atom in **3** or **4** is bonded to two bidentate ligands L^1 or L^2 , respectively, in a *cis* arrangement.

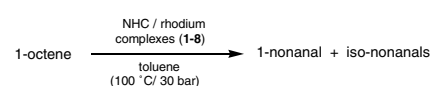


**Martin Bortenschlager, Jan Schütz,
Denise von Preysing, Oskar Nuyken,
Wolfgang A. Herrmann, Ralf Weberskirch**

J. Organomet. Chem. 690 (2005) 6233

Rhodium–NHC-complexes as potent catalysts in the hydroformylation of 1-octene

Application of NHC/rhodium complexes in the hydroformylation of 1-octene is described. Eight NHC/rhodium catalysts with differences in the electronic as well as steric properties of the NHC ligand have been studied in the homogeneous hydroformylation of 1-octene. While catalytic activity can be increased from electron-rich NHC-ligands to electron-poor ones selectivity was not affected.

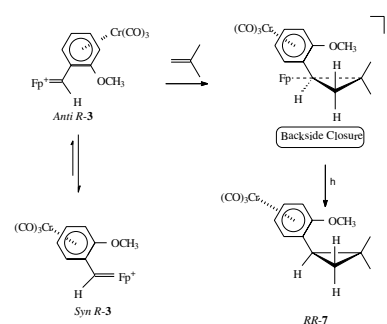


**Qinwei Wang, F. Holger Försterling,
M. Mahmud Hossain**

J. Organomet. Chem. 690 (2005) 6238

Study of the origin of enantioselectivity in cyclopropanation reactions using the chiral iron carbene complex $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CH}[(\eta^6\text{-}o\text{-MeOC}_6\text{H}_4)\text{Cr}(\text{CO})_3]]^+$

The iron carbene complexes $[(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}=\text{CH}[(\eta^6\text{-RC}_6\text{H}_4)\text{Cr}(\text{CO})_3]]^+$ ($\text{R} = \text{OMe}, \text{Me}$) exists as *syn* and *anti* isomers. The *anti* isomer is more reactive towards olefins and forms asymmetric cyclopropanes through backside ringclosure in high enantioselectivity.



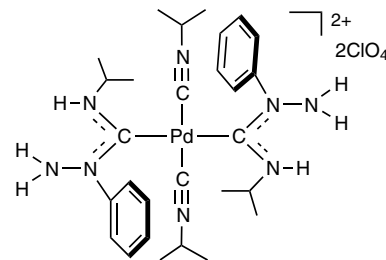
Communication

**Adriana I. Moncada, Joseph M. Tanski,
LeGrande M. Slaughter**

J. Organomet. Chem. 690 (2005) 6247

Sterically controlled formation of monodentate versus chelating carbene ligands from phenylhydrazine

The addition of phenylhydrazine to $[\text{Pd}(\text{CNR})_4]^{2+}$ results in a chelating dicarbene ligand in the case of methylisocyanide, whereas the use of isopropylisocyanide affords an unprecedented complex with monodentate aminohydrazinocarbene ligands that represent intermediates in chelating dicarbene ligand formation.



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