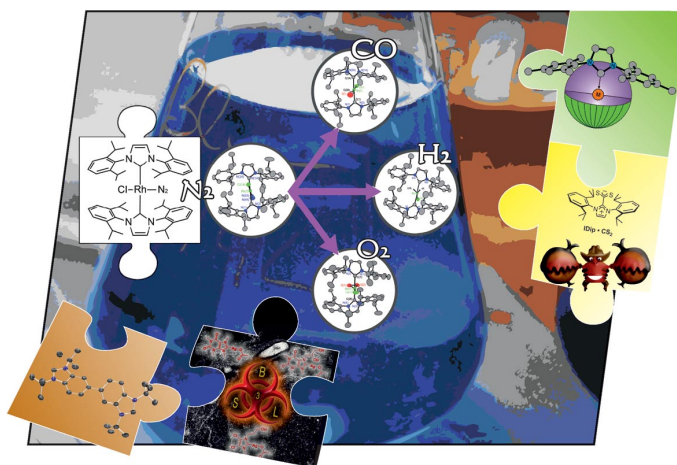


A union formed by chemical societies in Europe (ChemPubSoc Europe) has taken the significant step into the future by merging their traditional journals, to form two leading chemistry journals, the *European Journal of Inorganic Chemistry* and the *European Journal of Organic Chemistry*. Three further members of ChemPubSoc Europe (Austria, Czech Republic and Sweden) are Associates of the two journals.

## COVER PICTURE

The cover picture is a composite design depicting the variety in NHC complex chemistry. Like pieces in a puzzle, all details contribute to our growing knowledge of these compounds. The first puzzle piece in the bottom left corner represents the carbene precursors, essential in all synthesis design (C. W. Bielawski et al.; p. 1729ff). The background reflects the importance of these complexes, here in the homogeneous catalytic chemistry of gaseous molecules (C. M. Crudden et al.; p. 1746ff), while the diverse structural types are highlighted by the zwitterionic “crabenes” mid right (L. Delaude; p. 1681ff). Related aspects such as the physical chemistry or biological relevance are not forgotten: the sketch of the buried volume of an NHC ligand symbolizes the former (L. Cavallo et al.; p. 1759ff), and the antimicrobial activity of silver–NHC complexes against biosafety level 3 bacteria typifies the latter (W. J. Youngs et al.; p. 1739ff). Mr. François Nicks is acknowledged for drawing the “crabene”. The editorial office thanks all authors for their excellent contributions to this cover picture puzzle. Finally, there are many gaps. EurJIC hopes that this issue will stimulate you to discover another fragment that will complete the picture.



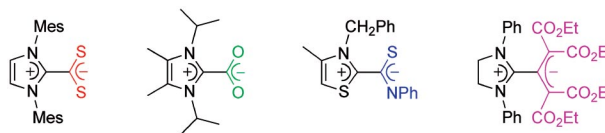
## MICROREVIEWS

### NHC Betaines

L. Delaude\* ..... 1681–1699

Betaine Adducts of N-Heterocyclic Carbenes: Synthesis, Properties, and Reactivity

**Keywords:** Betaines / Carbene ligands / N-Heterocyclic carbenes / Homogeneous catalysis / Nitrogen heterocycles / Zwitterions



N-Heterocyclic carbenes (NHCs) form stable betaines with a range of heteroallenes, ketenes, and allenes. The synthesis, properties, and reactivity of these zwitterions are reviewed. The NHCs under con-

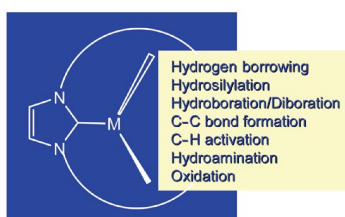
sideration are those derived from (benz)imidazole, thiazole, or triazole, and the heteroallenes investigated are CO<sub>2</sub>, CS<sub>2</sub>, isocyanates, isothiocyanates, and their selenium analogues.

### NHC Complexes in Catalysis

R. Corberán, E. Mas-Marzá,  
E. Peris\* ..... 1700–1716

Mono-, Bi- and Tridentate N-Heterocyclic Carbene Ligands for the Preparation of Transition-Metal-Based Homogeneous Catalysts

**Keywords:** Carbenes / Chelates / Homogeneous catalysis / C–H activation / C–C coupling



The current status of the design of mono-, bi- and tridentate NHC ligands is reviewed. The catalytic applications of such complexes include hydrogen-borrowing, C–C coupling, reduction of double bonds and C–H activation reactions.

## SHORT COMMUNICATIONS

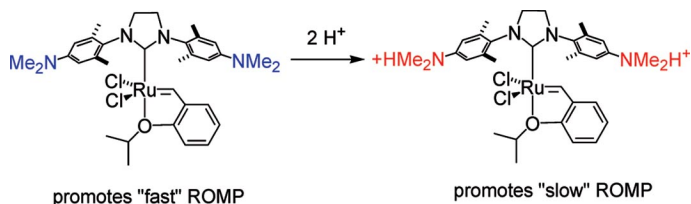
### pH-Responsive Catalysts

S. L. Balof, B. Yu, A. B. Lowe, Y. Ling,  
Y. Zhang, H.-J. Schanz\* ..... 1717–1722



Ru-Based Olefin Metathesis Catalysts Bearing pH-Responsive N-Heterocyclic Carbene (NHC) Ligands: Activity Control via Degree of Protonation

**Keywords:** Ruthenium / Metathesis / Ring-opening polymerization / Carbene ligands / N-Heterocyclic carbenes / Density functional calculations



The ROMP activity of two Ru-based olefin metathesis catalysts was moderated by gradual addition of acid. Experimental and

computational investigations confirm that acid addition predominantly reduces their propagation rates.

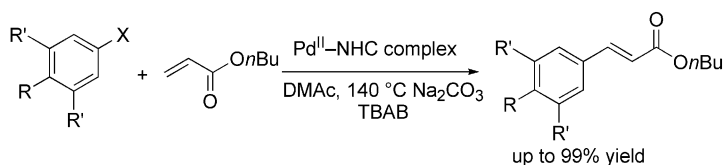
### NHC–Metal Complexes

L.-j. Liu, F. Wang,\*  
M. Shi\* ..... 1723–1728



Elimination of an Alkyl Group from Imidazolium Salts: Imidazole-Coordinated Dinuclear Monodentate NHC–Palladium Complexes Driven by Self-Assembly and Their Application in the Heck Reaction

**Keywords:** Heck reaction / Carbene ligands / Palladium / Self-assembly / NHCs (N-Heterocyclic carbenes)



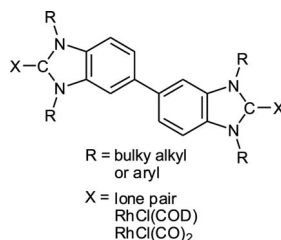
A new vision for NHC–metal complexes: Imidazolium salts can be converted into imidazole and an N-heterocyclic carbenes (NHC) in the presence of a base that will promote the development of a new

family of imidazole-coordinated monodentate NHC–metal complexes driven by self-assembly. Catalysts **9** and **10** showed excellent catalytic activities (up to 99% yield) in the Heck reaction.

## FULL PAPERS

### N-Heterocyclic Carbenes

Bis(carbene)s featuring two N-heterocyclic carbenes annulated to a common biphenyl linker have been synthesized and characterized. A variety of bimetallic Rh complexes were prepared with these ligands and the degree of communication between the two metal centers was evaluated electrochemically and spectroscopically, and compared with a series of monometallic analogues.



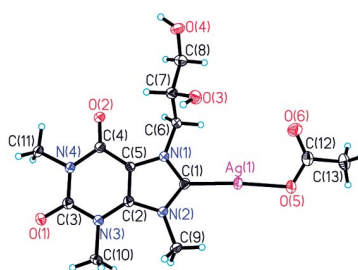
**J. A. V. Er, A. G. Tennyson,  
 J. W. Kamplain, V. M. Lynch,  
 C. W. Bielawski\*** ..... 1729–1738

Synthesis and Study of 5,5'-Bibenzimidazolylidenes and Their Bimetallic Complexes

**Keywords:** Nitrogen heterocycles / Carbenes / Benzimidazolium salts / Bimetallics / Rhodium / Polychlorinated biphenyls

### Silver Carbene Antimicrobials

A series of silver N-heterocyclic carbene complexes were tested to determine their antimicrobial efficacy on biosafety level 3 bacteria. These complexes were found to be effective in vitro at single-digit  $\mu\text{g/mL}$  concentrations against *Burkholderia pseudomallei*, *Burkholderia mallei*, *Bacillus anthracis*, MRSA, and *Yersinia pestis*.



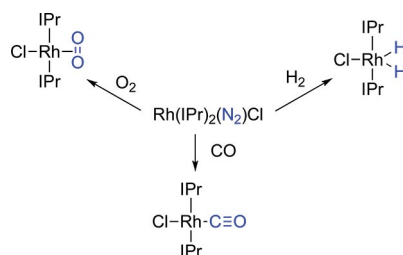
**M. J. Panzner, A. Deeraksa, A. Smith,  
 B. D. Wright, K. M. Hindi,  
 A. Kascatan-Nebioglu, A. G. Torres,  
 B. M. Judy, C. E. Hovis, J. K. Hilliard,  
 R. J. Mallett, E. Cope, D. M. Estes,\*  
 C. L. Cannon,\* J. G. Leid,\*  
 W. J. Youngs\*** ..... 1739–1745

Synthesis and in vitro Efficacy Studies of Silver Carbene Complexes on Biosafety Level 3 Bacteria

**Keywords:** Silver / Carbenes / N-Heterocyclic carbenes / *Burkholderia* / Antibiotics / Nitrogen heterocycles

### Dinitrogen Complexes

A rhodium N-heterocyclic carbene complex featuring coordination of molecular nitrogen has been synthesized and characterized. The lability of the nitrogen ligand in solution has been exploited to afford various complexes of the formula  $[\text{Rh}(\text{IPr})_2(\text{XY})\text{Cl}]$ .

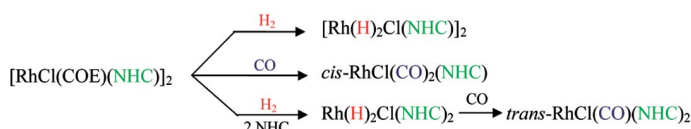


**J. M. Praetorius, R. Wang,  
 C. M. Crudden\*** ..... 1746–1751

Structure and Reactivity of Dinitrogen Rhodium Complexes Containing N-Heterocyclic Carbene Ligands

**Keywords:** Carbene ligands / Rhodium / Metal hydride / N-Heterocyclic carbenes / Dihydride / N ligands

### Rhodium Carbenes



The  $\text{NHC-Rh}^{\text{I}}$  complexes  $[\text{RhCl}(\text{COE})(\text{NHC})]_2$  are used to synthesize  $[\text{Rh}(\text{H})_2\text{Cl}(\text{NHC})]_2$ , and  $\text{Rh}(\text{H})_2\text{Cl}(\text{IPr})_2$  reacts reversibly with  $\text{D}_2$  to give the dideuteride, and with  $\text{O}_2$  to form  $\text{Rh}(\text{O}_2)\text{Cl}(\text{IPr})_2$ .

plexes with CO give  $\text{RhCl}(\text{CO})_2(\text{NHC})$  or  $\text{RhCl}(\text{CO})(\text{NHC})_2$ ;  $\text{Rh}(\text{H})_2\text{Cl}(\text{IPr})_2$  reacts reversibly with  $\text{D}_2$  to give the dideuteride, and with  $\text{O}_2$  to form  $\text{Rh}(\text{O}_2)\text{Cl}(\text{IPr})_2$ .

**X.-Y. Yu, H. Sun, B. O. Patrick,  
 B. R. James\*** ..... 1752–1758

N-Heterocyclic Carbene Rhodium Complexes and Their Reactions with  $\text{H}_2$  and with CO

**Keywords:** Carbene ligands / Carbonyl ligands / Rhodium / Hydrogenation / Hydrides

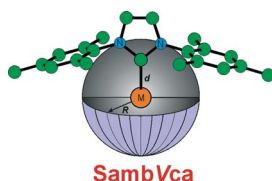
# CONTENTS

## N-Heterocyclic Carbenes

A. Poater, B. Cosenza, A. Correa,  
S. Giudice, F. Ragone, V. Scarano,  
L. Cavallo\* ..... 1759–1766

SambVca: A Web Application for the  
Calculation of the Buried Volume of N-  
Heterocyclic Carbene Ligands

**Keywords:** Density functional calculations /  
Homogeneous catalysis / N-Heterocyclic  
carbenes / Carbene ligands / Buried vol-  
umes / Ligand effects / Steric hindrance



SambVca, a free web application for calcu-  
lation of the buried volume (%  $V_{\text{Bur}}$ ) of  
NHC ligands, is described.

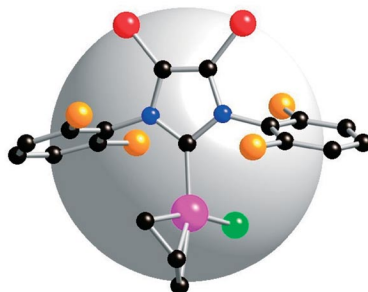
## N-Heterocyclic Carbene Sterics

H. Clavier,\* A. Correa,  
L. Cavallo, E. C. Escudero-Adán,  
J. Benet-Buchholz, A. M. Z. Slawin,  
S. P. Nolan\* ..... 1767–1773



[Pd(NHC)(allyl)Cl] Complexes: Synthesis  
and Determination of the NHC Percent  
Buried Volume (%  $V_{\text{bur}}$ ) Steric Parameter

**Keywords:** Ligand effects / Carbenes / Pal-  
ladium / Steric hindrance



The synthesis and characterization of  
[Pd(NHC)(allyl)Cl] complexes were  
achieved by using various NHC ligands.  
The percent buried volume (steric param-  
eter) of these NHCs was determined as a  
function of the NHC backbone by using  
X-ray diffraction data.

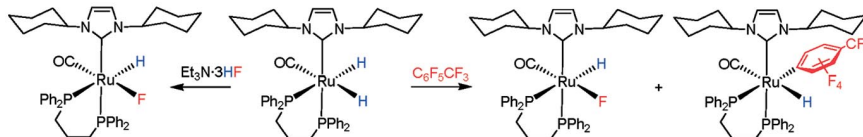
## Metal Fluorido Complexes

S. P. Reade, A. L. Acton,  
M. F. Mahon, T. A. Martin,  
M. K. Whittlesey\* ..... 1774–1785



Synthesis and Reactivity of Ru(NHC)-  
(dppp)(CO)H<sub>2</sub> and Ru(NHC)(dppp)(CO)-  
HF Complexes: C–H and C–F Activation

**Keywords:** Carbene ligands / Ruthenium  
complexes / Hydrido ligands / Fluorido li-  
gands / C–H activation / C–F activation /  
Nitrogen heterocycles / Cleavage reactions



The hydrido fluorido complexes  
[Ru(NHC)(dppp)(CO)HF] are formed by  
reaction of the free carbene (for NHC =  
IMes) with [Ru(PPh<sub>3</sub>)(dppp)(CO)HF], or  
by addition of Et<sub>3</sub>N·3HF to [Ru(NHC)-  
(dppp)(CO)H<sub>2</sub>] for NHC = IMes and ICy.

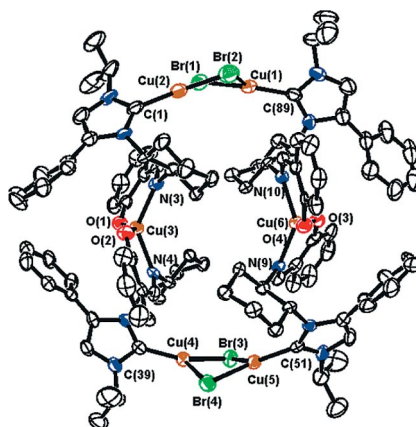
C–F bond activation of C<sub>6</sub>F<sub>6</sub>, C<sub>6</sub>F<sub>5</sub>CF<sub>3</sub>  
and C<sub>5</sub>F<sub>5</sub>N takes place upon reaction with  
[Ru(ICy)(dppp)(CO)H<sub>2</sub>] to give a mixture  
of [Ru(ICy)(dppp)(CO)HF] and the fluoro-  
aryl hydrido species.

## Carbene Copper Clusters

S. Simonovic, A. C. Whitwood, W. Clegg,  
R. W. Harrington, M. B. Hursthouse,  
L. Male, R. E. Douthwaite\* .... 1786–1795

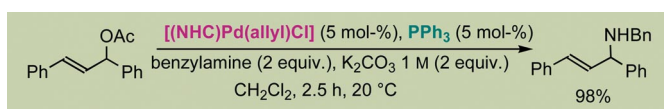
Synthesis of Copper(I) Complexes of  
N-Heterocyclic Carbene–Phenoxyimine/  
amine Ligands: Structures of Mononuclear  
Copper(II), Mixed-Valence Copper(I)/(II),  
and Copper(II) Cluster Complexes

**Keywords:** Carbene ligands / Copper /  
Homogeneous catalysis / Mixed-valence  
compounds / Cluster compounds



Mononuclear and mixed-valence Cu<sup>I</sup>/Cu<sup>II</sup>  
complexes of N-heterocyclic carbene–  
phenolimine ligands have been structurally  
characterised, including a unique Cu<sub>6</sub>  
cluster. Additionally, analogous NHC–  
phenolamine complexes have been pre-  
pared and the catalytic activity of both  
complex classes studied for 1,4-conjugate  
addition to enones and aziridination of  
alkenes.





An efficient procedure for the allylic amination reaction is developed which makes use of [(NHC)Pd(allyl)Cl] complexes and PPh<sub>3</sub> under biphasic conditions. The reaction conditions are optimized and the

influence of the NHC and allyl ligands of the pre-catalyst studied. The scope of the reaction is examined with several different nitrogen nucleophiles and allylic acetates.

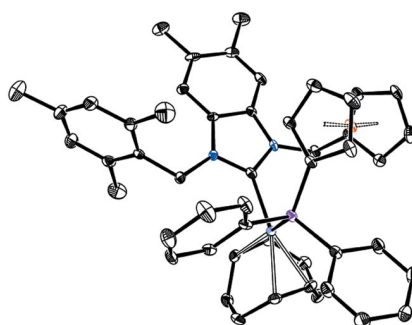
S. Roland,\* W. Cotet,  
P. Mangeney ..... 1796–1805

Allylic Amination Using Well-Defined [(NHC)Pd(η<sup>3</sup>-allyl)Cl] Complexes and PPh<sub>3</sub>

**Keywords:** Carbene ligands / Phosphanes / P ligands / Allylic amination / Palladium / Biphasic catalysis

## Chelating Effects in Catalysis

Precursors of new ferrocenylphosphane-benzimidazol-2-ylidene bifunctional ligands and monodentate ferrocenyl benzimidazol-2-ylidene ligands have been prepared. The cationic and neutral rhodium(I) complexes showed good activities for the catalytic hydrosilylation of ketones. The use of bidentate ligands proved to be essential for obtaining good selectivities of the desired alcohol.



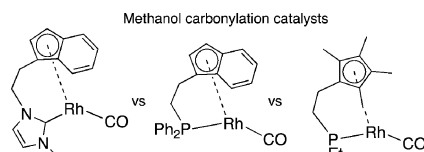
S. Gülcemal, A. Labande,\* J.-C. Daran,  
B. Çetinkaya, R. Poli ..... 1806–1815

Rhodium(I) Complexes of New Ferrocenyl Benzimidazol-2-ylidene Ligands: The Importance of the Chelating Effect for Ketone Hydrosilylation Catalysis

**Keywords:** Carbenes / P ligands / Ferrocenes / Rhodium / Hydrosilylation

## Rh and Ir Carbene Complexes

Indenyl- and fluorenyl-functionalized NHC complexes of Rh<sup>I</sup> and Ir<sup>I</sup> were prepared and tested as catalysts for alkene hydroformylation and methanol carbonylation reactions.



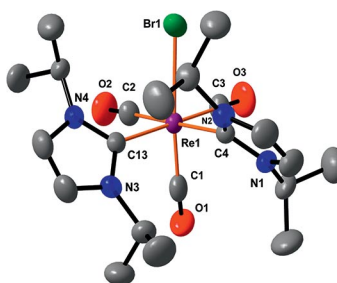
S. P. Downing, P. J. Pogorzelec,  
A. A. Danopoulos,\*  
D. J. Cole-Hamilton\* ..... 1816–1824

Indenyl- and Fluorenyl-Functionalized N-Heterocyclic Carbene Complexes of Rhodium and Iridium – Synthetic, Structural and Catalytic Studies

**Keywords:** N-Heterocyclic carbenes / Carbenes / Carbene ligands / Rhodium / Iridium / Carbonylation / Cyclopentadienyl complexes

## Nonbridged Biscarbene Complexes

*fac*-Bromidotricarbonylbis(1,3-diisopropylimidazoline-2-ylidene)rhenium(I) and *fac*-bromidotricarbonylbis(1,3-dicyclohexylimidazoline-2-ylidene)rhenium(I) with two coordinated 1,3-dialkyl-substituted imidazole-2-ylidenes were prepared and structurally characterized by NMR, IR, and X-ray.



O. Hiltner, E. Herdtweck, M. Drees,  
W. A. Herrmann,\*  
F. E. Kühn\* ..... 1825–1831

Synthesis and Characterization of Two New *fac*-Tricarbonylrhenium(I) Biscarbene Complexes

**Keywords:** Carbonyl ligands / Imidazole / Carbenes / N-Heterocyclic carbenes / Rhenium

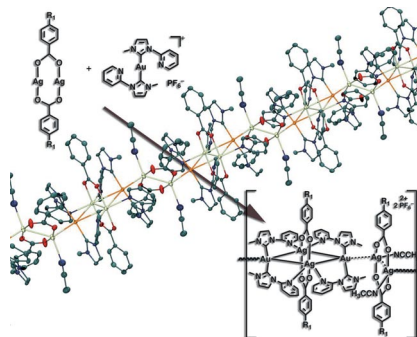
# CONTENTS

## Auophilic Attractions

A. K. Ghosh,  
V. J. Catalano\* ..... 1832–1843

Synthesis and Characterization of a Series of New Luminescent NHC-Coordinated  $\text{Au}^{\text{I}}$ – $\text{Ag}^{\text{I}}$  Tetra- and Polymetallic Complexes Containing Benzoate-Bridged  $\text{Ag}_2$  Dimers

**Keywords:** Gold / Silver / Auophilicity / N-Heterocyclic carbenes / Coordination polymers



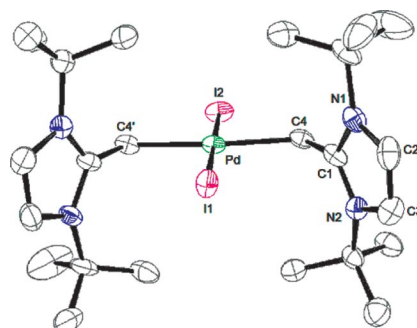
A series of tetra- and polymetallic  $\text{Au}^{\text{I}}$ – $\text{Ag}^{\text{I}}$  N-heterocyclic carbene complexes are reported where the simple substitution of halides on the auxiliary benzoate backbone ligands leads to subtle changes in the emission maxima and metal–metal separations.

## Zwitterionic Palladium Complexes

O. Esposito, D. E. Roberts,  
F. G. N. Cloke,\* S. Caddick,\*  
J. C. Green,\* N. Hazari,  
P. B. Hitchcock ..... 1844–1850

Carbon–Silicon Bond Activation by  $[\text{Pd}(\text{IrBu})_2]$  – the Molecular Structures of  $[\text{Pd}(\text{Me}_3\text{Si})(\text{IrBu})(\mu\text{-I})_2]$  and  $[\text{Pd}(\text{CH}_2\text{IrBu})\text{I}_2]$

**Keywords:** Palladium / N-heterocyclic carbenes / Oxidation / Zwitterions / Density functional calculations



The reaction of  $\text{Me}_3\text{SiCH}_2\text{I}$  with the  $\text{Pd}^0$  NHC complex  $[\text{Pd}(\text{IrBu})_2]$  results in unexpected carbon–silicon bond activation and the formation of  $[\text{Pd}(\text{Me}_3\text{Si})(\text{IrBu})(\mu\text{-I})_2]$  and the zwitterionic complex  $[\text{Pd}(\text{CH}_2\text{IrBu})\text{I}_2]$  (see graphic). The former has also been synthesised by the direct oxidative addition of  $\text{Me}_3\text{SiI}$  to  $[\text{Pd}(\text{IrBu})_2]$ .

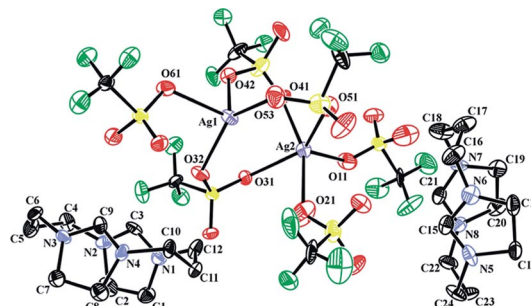
## Super-Electron-Rich Olefins

M. F. Lappert,\* S. Álvarez, G. Aullón,  
R. Fandos, A. Otero, A. Rodríguez,  
S. Rojas, P. Terreros\* ..... 1851–1860



Reactivity of a Super-Electron-Rich Olefin Derived from Cyclam

**Keywords:** Nitrogen heterocycles / Alkenes / Density functional calculations / Imidazolium compounds / Silver triflate



A series of new compounds, such as a *syn*-bis(urea), an *anti*-bis(thiourea), a bis(imidazolium) triflate and a monoprotonated imidazolium tetraphenylborate, has been synthesised from an electron-rich olefin

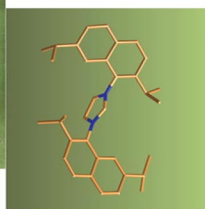
derived from cyclam. Upon treatment with silver oxide, the bis(imidazolium) triflate affords the di- and monoprotonated cationic salts, depending upon the nature of the solvent.

## Saturated Carbenes

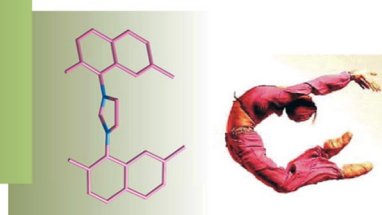
L. Vieille-Petit, X. Luan, R. Mariz,  
S. Blumentritt, A. Linden,  
R. Dorta\* ..... 1861–1870

A New Class of Stable, Saturated N-Heterocyclic Carbenes with *N*-Naphthyl Substituents: Synthesis, Dynamic Behavior, and Catalytic Potential

**Keywords:** Carbenes / Atropisomerism / Interconversion / Amination / Carbenoids



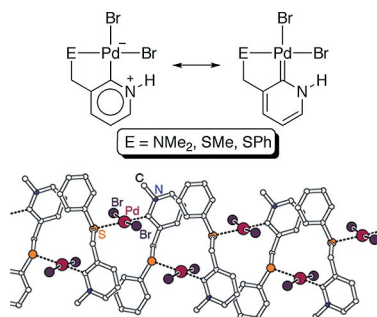
*Dancing NHCs*



A new family of saturated N-heterocyclic carbenes (NHCs) has been synthesized, fully characterized, and used as ligands in palladium-catalyzed Buchwald–Hartwig amination reactions. These carbenes represent

rare examples of stable, saturated NHCs. The incorporation of naphthyl side chains leads to atropisomeric mixtures comprising  $C_2$ -symmetric (*anti*) and  $C_s$ -symmetric (*syn*) conformers.

Palladium complexes with pyridinium-derived carbene ligands containing a chelating donor group have been prepared by oxidative addition. These complexes have been studied structurally and also in Mizoroki–Heck-type cross-coupling. Evidence is provided for a heterogeneous catalytic system when using such pyridylidene palladium catalyst precursors.

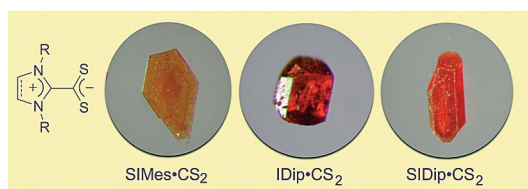


**A. Poulain, A. Neels,  
M. Albrecht\*** ..... 1871–1881

Palladium Complexes Containing Potentially Chelating Pyridylidene-Type Carbene Ligands

**Keywords:** Palladium / Carbene ligands / Metallacycles / Heterogeneous catalysis / Cross-coupling

## Carbene Adducts



Five imidazol(in)ium-2-dithiocarboxylates were prepared from the corresponding N-heterocyclic carbenes (NHCs) by reaction with carbon disulfide. Because of their out-

standing ability to crystallize, these stable adducts are promising candidates to probe the steric parameters of NHC ligands via XRD analysis.

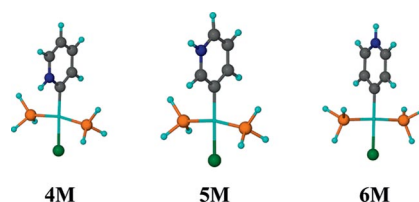
**L. Delaude,\* A. Démonceau,  
J. Wouters** ..... 1882–1891

Assessing the Potential of Zwitterionic NHC·CS<sub>2</sub> Adducts for Probing the Stereo-electronic Parameters of N-Heterocyclic Carbenes

**Keywords:** Betaines / Carbenes / Ligand effects / Nitrogen heterocycles / Zwitterions

## Remote N-Heterocyclic Carbenes

The nature of the metal–ligand interactions with N-heterocyclic pyridyl, pyridylidene, quinolydene or isoquinolydene ligands wherein the nitrogen atom is either adjacent to the carbene carbon atom or in a remote (*meta* or *para*, or in the adjacent ring) position is investigated by energy decomposition analysis.



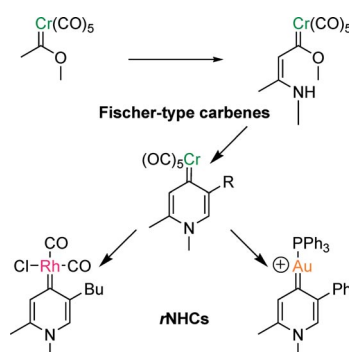
**G. Heydenrych, M. von Hopffgarten,  
E. Stander, O. Schuster,  
H. G. Raubenheimer,\*  
G. Frenking\*** ..... 1892–1904

The Nature of the Metal–Carbene Bond in Normal and Abnormal Pyridylidene, Quinolydene and Isoquinolydene Complexes

**Keywords:** Density functional calculations / Carbenes / Carbene homologs / Carbene ligands / Nitrogen heterocycles / Pyridylidene / Quinolydene / Pyridyl complexes / Metal–carbon bonds / Energy-decomposition analysis

## Carbene Transfer

The first examples of rhodium and gold *r*NHC complexes, obtained from well-known acyclic group-6 metal Fischer-type carbene complexes, are reported.



**C. E. Strasser, E. Stander-Grobler,  
O. Schuster, S. Cronje,  
H. G. Raubenheimer\*** ..... 1905–1912

Preparation of *Remote* NHC Complexes of Rhodium(I) and Gold(I) by Ligand Transfer

**Keywords:** Carbene ligands / N-Heterocyclic carbenes / Gold / Rhodium / Group-6 metals

# CONTENTS

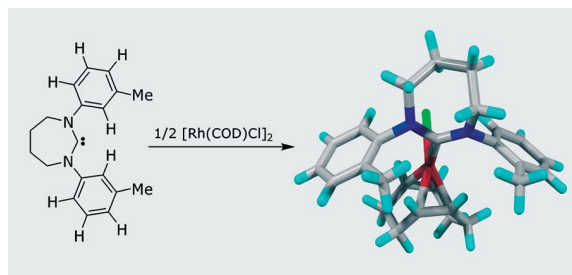
## Expanded N-Heterocyclic Carbenes

M. Iglesias, D. J. Beetstra, B. Kariuki,  
K. J. Cavell,\* A. Dervisi,\*  
I. A. Fallis\* ..... 1913–1919



Synthesis and Structural Features of Rhodium Complexes of Expanded Ring N-Heterocyclic Carbenes

**Keywords:** Carbene ligands / Rhodium / Carbonyl ligands / Electronic structure



Sterically crowded rhodium complexes of seven-membered N-heterocyclic carbenes with aromatic N-substituents have been formed. By varying the degree of substi-

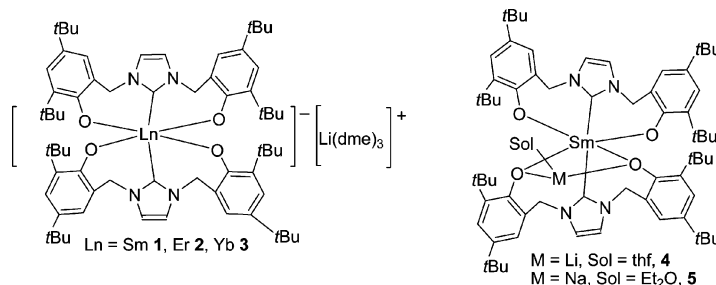
tution on the N-aromatic rings, the stability of these complexes can be influenced directly. Their donor ability is compared with that of smaller ring size NHCs.

## Bis(phenoxy)-NHC Complexes

H. Yao, Y. Zhang, H. Sun,  
Q. Shen\* ..... 1920–1925

Anionic Lanthanide Complexes Bearing a Bis(phenoxy)-Functionalized N-Heterocyclic Carbene Ligand: Syntheses and Molecular Structures

**Keywords:** Synthesis design / Carbene ligands / N-Heterocyclic carbenes / Lanthanides



Five lanthanide complexes supported by bis(phenoxy)-functionalized N-heterocyclic carbene ligands were synthesized and structurally characterized. Complexes 1–3 have the discrete ion-pair structures [L<sub>2</sub>Ln][Li-

(dme)<sub>3</sub>] (Ln = Sm 1, Er 2, Yb 3), while complexes [(thf)Li(μ-L)SmL] (4) and [(Et<sub>2</sub>O)Na(μ-L)SmL] (5) have “ate” structures.

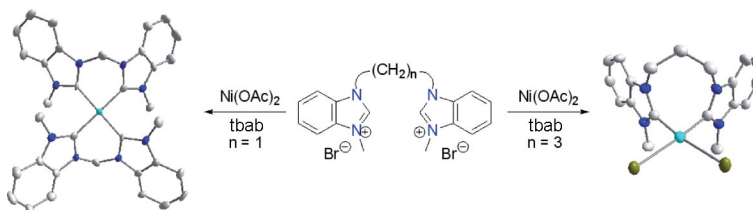
## Nickel(II) Carbenes

H. Vinh Huynh,\*  
R. Jothibasu ..... 1926–1931



Formation of Homoleptic Tetracarbene versus *cis*-Chelating Dicarbene Complexes of Nickel(II) and Applications in Kumada–Corriu Couplings

**Keywords:** Nickel / Carbene ligands / Autoionization / Cross-coupling / Chelates



The formation of mono- versus bis(chelate) NHC complexes of nickel(II) is influenced by the bridging unit of the dicarbene ligand. A methylene spacer leads to a bis-(chelate) complex, whereas a propylene

bridge affords the monochelate complex, which slowly autoionizes. Comparative studies show that the monochelate complex is catalytically more active than the bis-(chelate) complex.

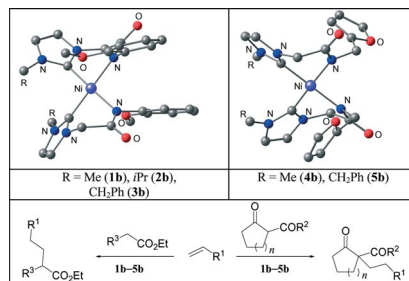
## Base-Free Michael Reaction

S. Ray, M. M. Shaikh,  
P. Ghosh\* ..... 1932–1941



Nickel Complexes of *N/O*-Functionalized N-Heterocyclic Carbenes as Precatalysts for Michael Reactions in Air at Room Temperature Under the Much Preferred Base-Free Conditions

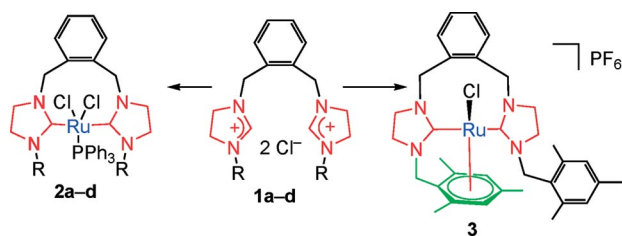
**Keywords:** Nickel / N-heterocyclic carbene / Michael addition / Base-free / Density functional calculations



A series of nickel precatalysts of *N/O*-functionalized N-heterocyclic carbenes efficiently carried out highly desirable base-free Michael reactions of β-dicarbonyl compounds with α,β-unsaturated carbonyl compounds in air at ambient temperature.



## Chelating N-Heterocyclic Carbenes



Four novel RuCl<sub>2</sub>(dicarbene)(PPh<sub>3</sub>) complexes and the unprecedented [RuCl(η<sup>1</sup>-carbene-η<sup>1</sup>-carbene-η<sup>6</sup>-arene)]PF<sub>6</sub> complex have been prepared and characterized. The

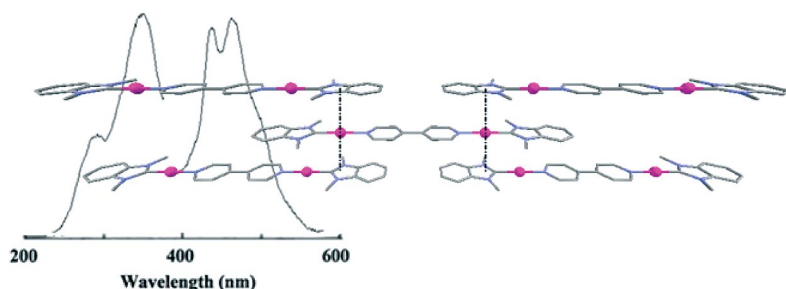
RuCl<sub>2</sub>(dicarbene)(PPh<sub>3</sub>) complexes with coordinating bases act as catalyst precursors for the bis-*ortho*-arylation of 2-phenylpyridine with aryl chlorides.

İ. Özdemir,\* S. Demir, N. Gürbüz,  
B. Çetinkaya, L. Toupet, C. Bruneau,\*  
P. H. Dixneuf ..... 1942–1949

Synthesis, Characterization and Catalytic Activity of New N-Heterocyclic Bis(carbene)ruthenium Complexes

**Keywords:** Ruthenium / Carbenes / Bis-(imidazolinium) salts / N ligands / C–H activation

## NHC–Au–Pyridine



[Au(NHC)(pyridine)][PF<sub>6</sub>]-type complexes exhibit secondary Au···Au, Au···π, or π···π interactions and are luminescent in the solid state. The HOMO is mainly associated

with pyridine ligands and the LUMO is predominantly auophilic. Oxidation of benzyl alcohol to aldehyde can be catalyzed by these compounds.

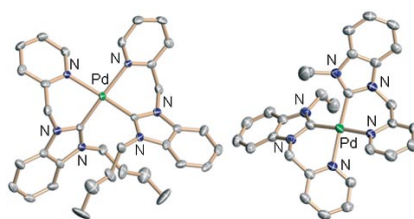
J. Y. Z. Chiou, S. C. Luo, W. C. You,  
A. Bhattacharyya, C. S. Vasam,  
C. H. Huang, I. J. B. Lin\* ..... 1950–1959

Gold(I) Complexes of N-Heterocyclic Carbenes and Pyridines

**Keywords:** Carbenes / Gold / Pyridine / Homogeneous catalysis / Luminescence / Oxidation

## Picolyl-Substituted NHC Ligands

Picoline-functionalized benzimidazolium salts react with suitable palladium precursors to yield palladium carbene complexes. These complexes have been characterized by NMR spectroscopy and X-ray diffraction studies. They were used as precatalysts in Heck-type C–C coupling reactions.



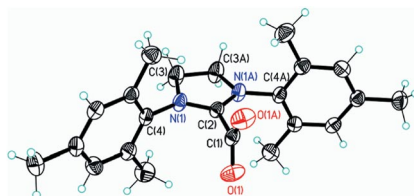
M. C. Jahnke, T. Pape,  
F. E. Hahn\* ..... 1960–1969

Synthesis and Catalytic Application of Palladium Complexes with Picoline-Functionalized Benzimidazolin-2-ylidene Ligands

**Keywords:** Carbenes / Palladium / C–C coupling

## Catalysts for PUR Synthesis

Novel CO<sub>2</sub>, Mg<sup>II</sup>, Al<sup>III</sup>, and Zn<sup>II</sup>-protected NHCs were synthesized and used as catalysts and latent catalysts in polyurethane synthesis. All CO<sub>2</sub>, Mg<sup>II</sup>, and Zn<sup>II</sup>-protected NHCs displayed significant catalytic activity; moreover, selected CO<sub>2</sub>-protected imidazolium-derived NHCs as well as di-μ-chlorido bis[ZnCl(1,3-dimesitylimidazol-2-ylidene)] displayed pronounced latent behavior.



B. Bantu, G. Manohar Pawar, K. Wurst,  
U. Decker, A. M. Schmidt,  
M. R. Buchmeiser\* ..... 1970–1976

CO<sub>2</sub>, Magnesium, Aluminum, and Zinc Adducts of N-Heterocyclic Carbenes as (Latent) Catalysts for Polyurethane Synthesis

**Keywords:** Carbenes / Magnesium / Aluminum / Zinc / Polyurethane

# CONTENTS

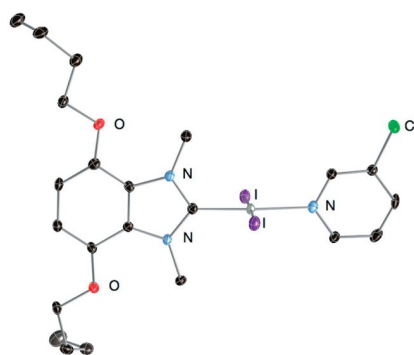
## Pd Benzimidazolin-2-ylidene Catalysts

M. V. Baker,\* D. H. Brown,\*  
P. V. Simpson, B. W. Skelton,  
A. H. White ..... 1977–1988



Synthesis and Characterisation of (Alkoxybenzimidazolin-2-ylidene)palladium Complexes: The Effect of Ancillary Ligands on the Behaviour of Precatalysts

**Keywords:** N-Heterocyclic carbenes / Palladium / Benzimidazole / Homogeneous catalysis / Nitrogen heterocycles / Ligand effects



N-Heterocyclic carbene (NHC)–palladium(II) complexes bearing electron-rich benzimidazolin-2-ylidene ligands are described. These complexes bear butoxy groups and a range of ancillary ligands (iodide, PPh<sub>3</sub>, 3-chloropyridine). The effect of varying the ancillary ligands on the activity of the complexes as precatalysts is investigated.

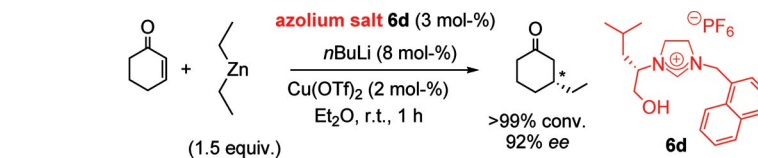
## Chiral NHCs

D. Rix, S. Labat, L. Toupet, C. Crévisy,\*  
M. Mauduit\* ..... 1989–1999



Design of Chiral Hydroxyalkyl- and Hydroxyarylazolinium Salts as New Chelating Diaminocarbene Ligand Precursors Devoted to Asymmetric Copper-Catalyzed Conjugate Addition

**Keywords:** Asymmetric catalysis / Diaminocarbene / Carbene ligands / Ligand design / Conjugate addition / Atropisomerism



A set of new chiral hydroxyalkyl- and hydroxyaryl-chelating diaminocarbene ligands has been synthesized and evaluated towards Cu-catalyzed asymmetric conjugate addition (ACA). These studies show

the importance of the scaffold design around the NHC unit in obtaining a high enantioselectivity. The highest selectivity (up to 92%) is reached with NHC precursor salt **6d** (see Scheme).

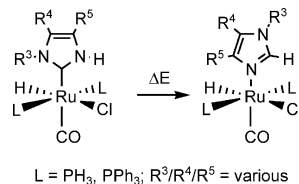
## Tautomerism in NHC Complexes

L. J. L. Häller,  
S. A. Macgregor\* ..... 2000–2006



Computational Study of the C- and N-Bound Tautomers of [Ru(Cl)(H)(CO)-(PPh<sub>3</sub>)<sub>2</sub>](LiPrMe<sub>2</sub>)] (LiPrMe<sub>2</sub> = 3-Isopropyl-4,5-dimethylimidazol-2-ylidene)

**Keywords:** N-Heterocyclic carbenes / Carbene ligands / Tautomerism / Ruthenium / Density functional calculations



Density functional theory calculations show a *trans*-CO ligand dictates the greater stability of the N-bound tautomer of the title compound. C-Bound analogues are favoured by bulky substituents at C5 and smaller groups at N3 and C4. Five-coordinate species with a vacant site *trans* to the C/N binding site are computed to be more stable as the C-bound form.

# CORRECTION

H. Clavier,\* A. Correa, L. Cavallo,  
E. C. Escudero-Adán, J. Benet-Buchholz,  
A. M. Z. Slawin, S. P. Nolan\* ..... 2007

[Pd(NHC)(allyl)Cl] Complexes: Synthesis and Determination of the NHC Percent Buried Volume (%V<sub>bur</sub>) Steric Parameter

**Keywords:** Ligand effects / Carbenes / Palladium / Steric hindrance

\* Author to whom correspondence should be addressed.

Supporting information on the WWW (see article for access details).

If not otherwise indicated in the article, papers in issue 12 were published online on April 8, 2009