

Nucleophilic Heterocyclic Carbenes and Related Species

a-NHC

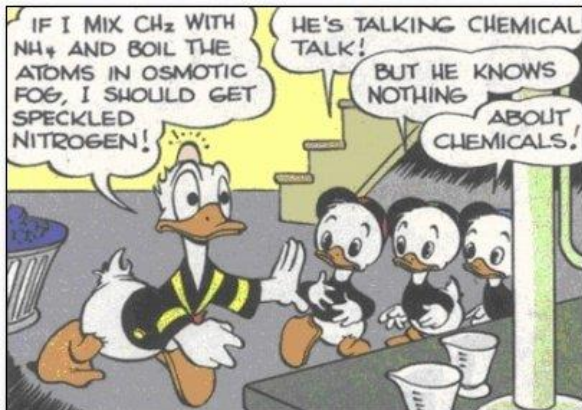
n-NHC

MIC

r-NHC

CBA

CAAC



Historical Overview

1944 Donald Duck

1957 Breslow

1961 Wanzlick

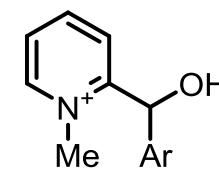
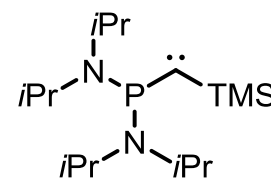
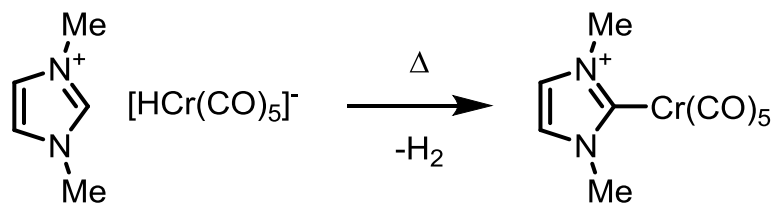
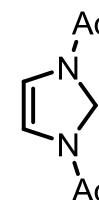
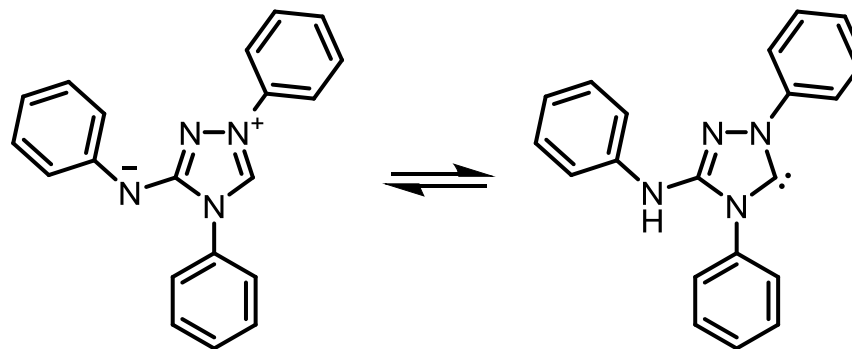
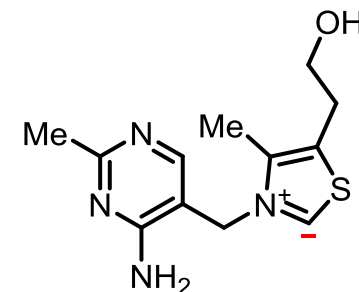
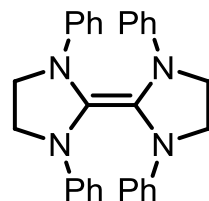
1968 Öfele

1983 Katrizky

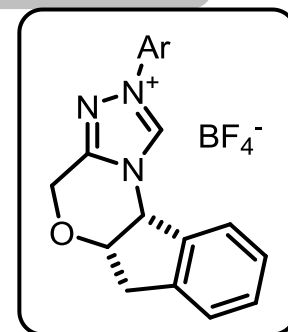
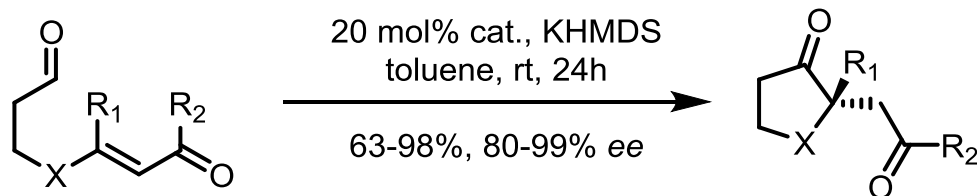
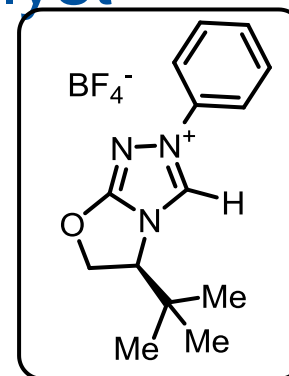
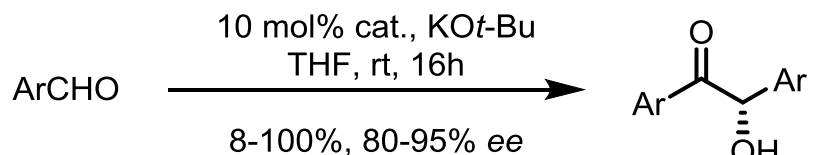
1988 Bertrand

1991 Arduengo

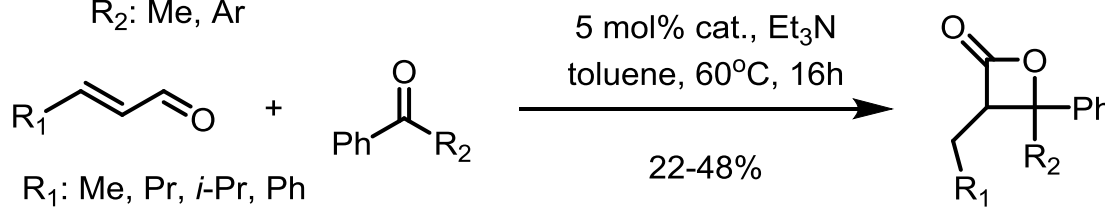
2012 Siemeling



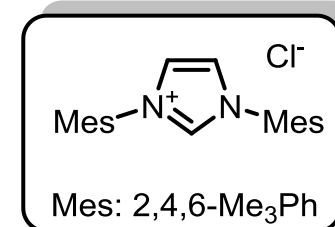
NHCs in Organocatalyst



x: CH₂, SO₂, NAc
R₁: Me, *n*-Pr, *n*-Bu
R₂: Me, Ar

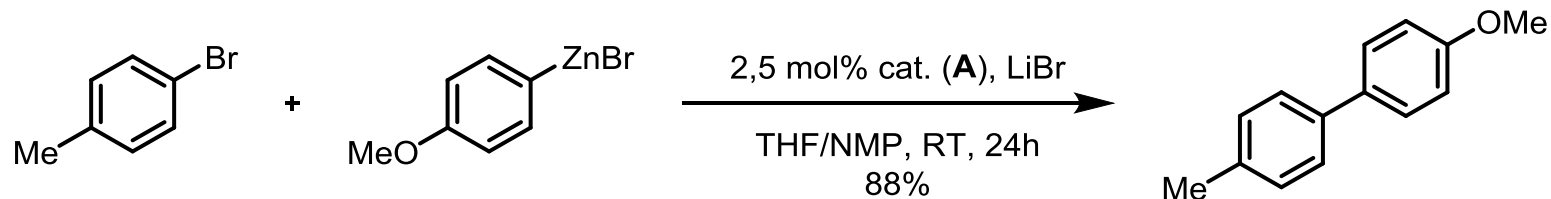
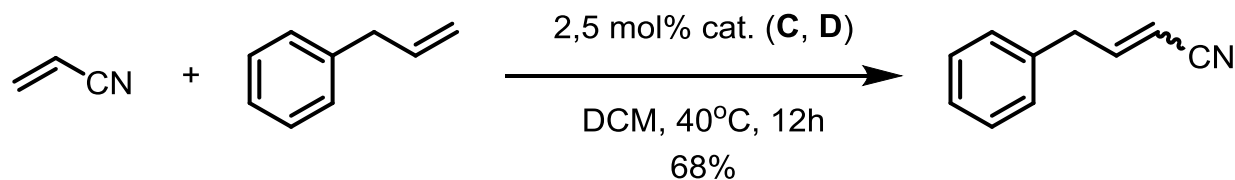
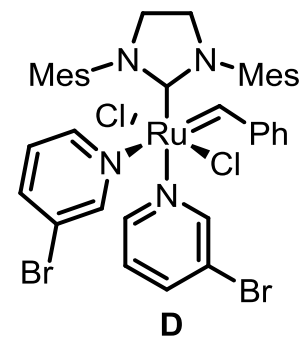
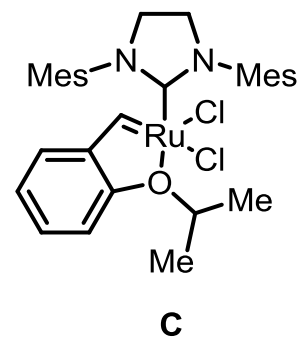
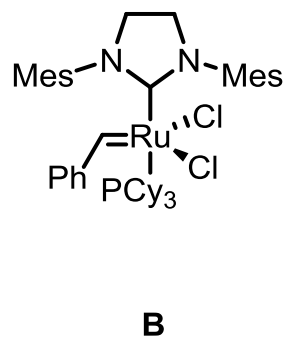
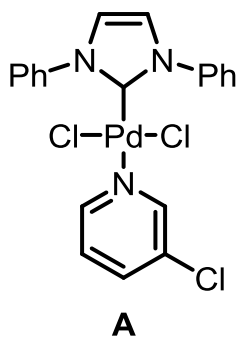


R₁: Me, Pr, *i*-Pr, Ph
R₂: CF₃, CO₂Me



D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, 107, 5606.

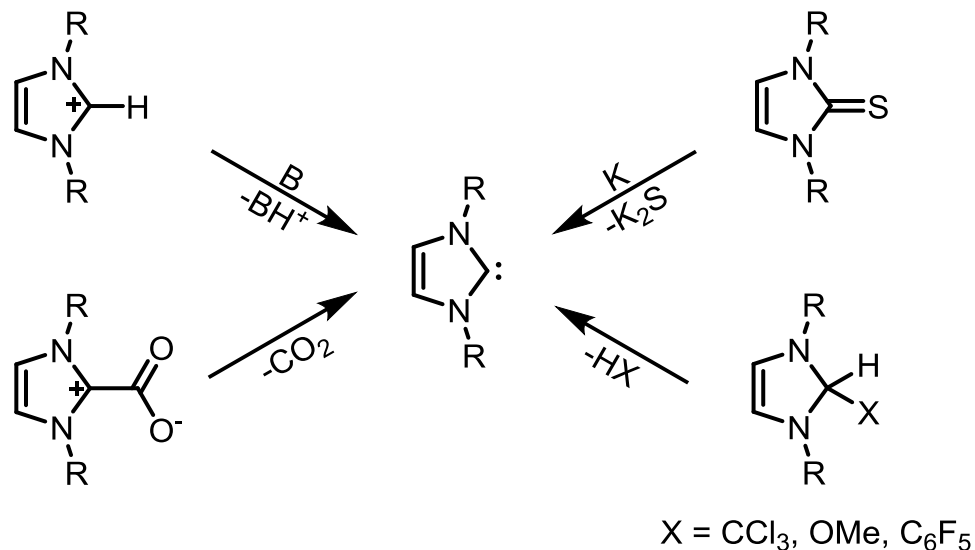
NHCs as Ligands



J. a Love, J. P. Morgan, T. M. Trnka, R. H. Grubbs, *Angew. Chem. Int. Ed.* **2002**, 41, 4035.

M. G. Organ, S. Avola, I. Dubovyk, N. Hadei, E. A. B. Kantchev, C. J. O'Brien, C. Valente, *Chemistry* **2006**, 12, 4749.

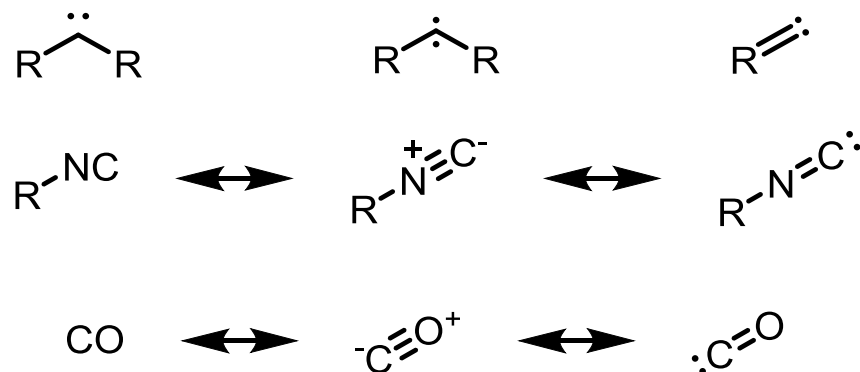
Synthesis



- A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, 113, 361.
A. Schmidt, A. Beutler, M. Albrecht, B. Snovydovych, F. J. Ramirez, *Org. Biomol. Chem.* **2008**, 6, 287.
L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Lapponnaz, V. Cesar, *Chem. Rev.* **2011**, 111, 2705.
N. Kuhn, T. Kratz, *Synthesis* **1993**, 561.
A. R. Katritzky, H. M. Faid-Allah, *Synthesis* **1983**, 149.
A. M. Voutchkova, M. Feliz, E. Clot, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **2007**, 129, 12834.
D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel, S. Brode, *Angew. Chem., Int. Ed.* **1995**, 34, 1021.
R. Savka, *Synlett* **2013**, 24, 1735.
H.-W. Wanzlick, E. Schikora, *Chem. Ber.* **1961**, 94, 2389.

Definition

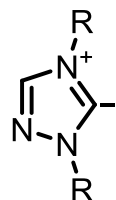
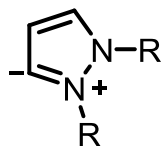
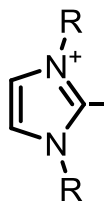
Carbenes are the electrically neutral species $\text{H}_2\text{C}:$ and its derivatives, in which the carbon is covalently bonded to two univalent groups of any kind or a divalent group and bears two nonbonding electrons, which may be spin-paired (singlet state) or spin-non-paired (triplet state).



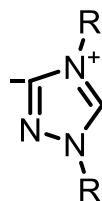
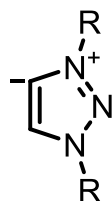
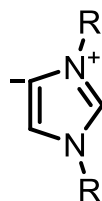
IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML online corrected version: <http://goldbook.iupac.org> (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8. doi:10.1351/goldbook.

Classification

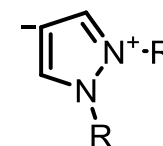
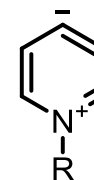
n-NHC (normal)



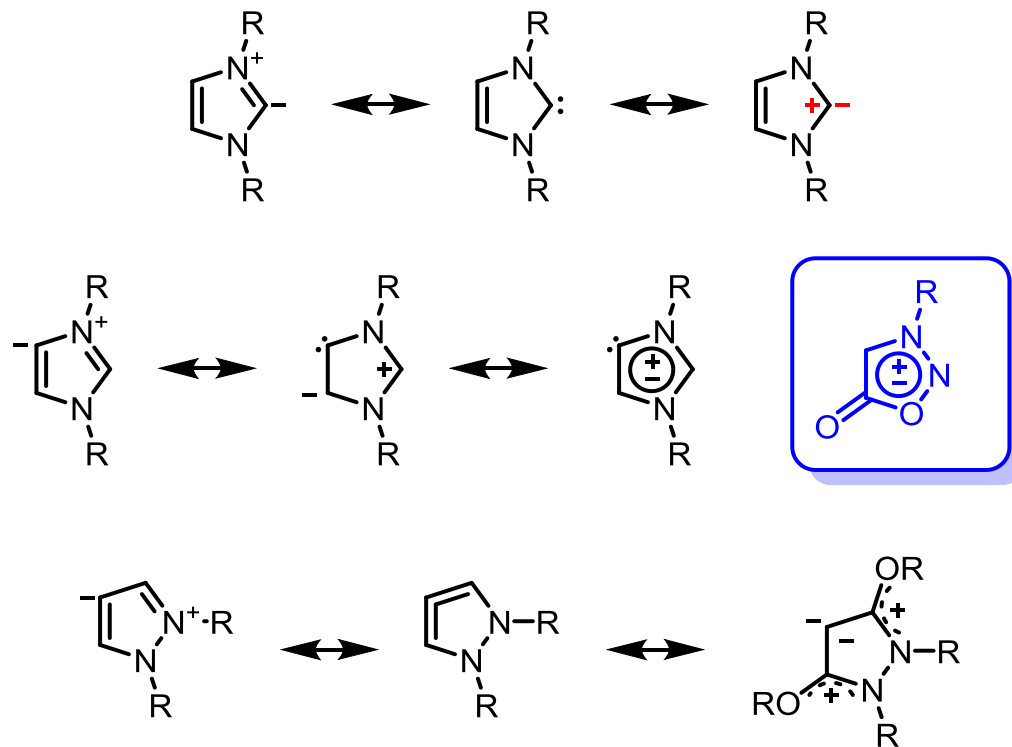
a-NHC (abnormal)



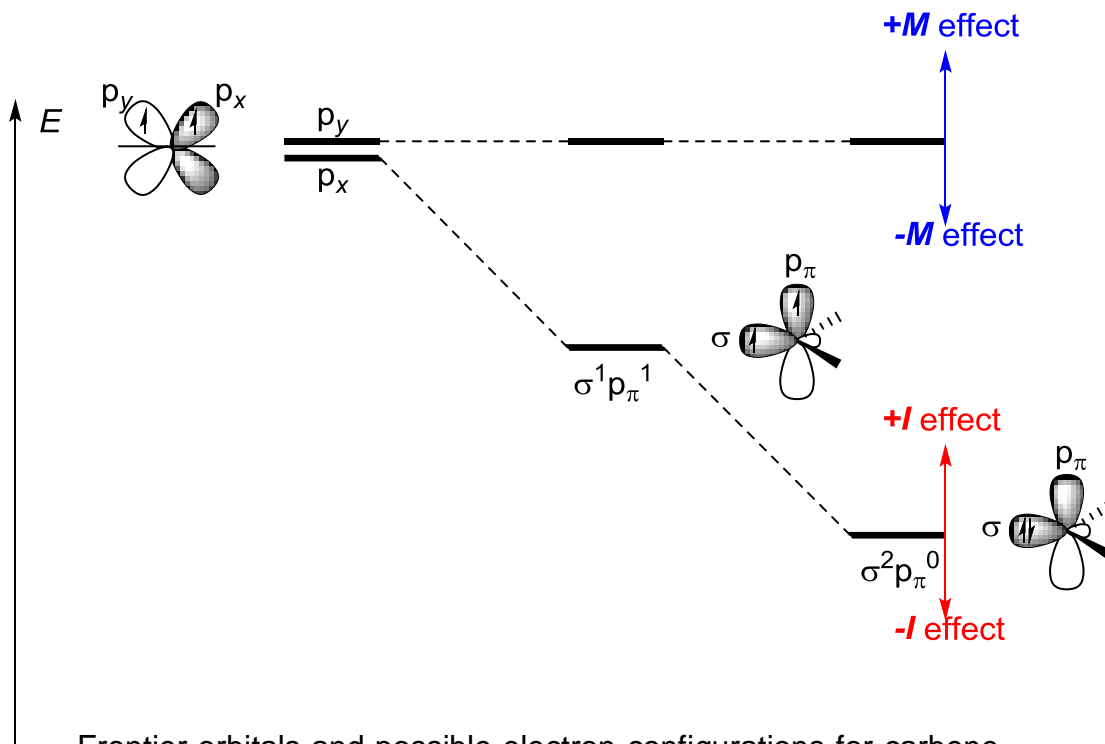
r-NHC (remote)



Classification



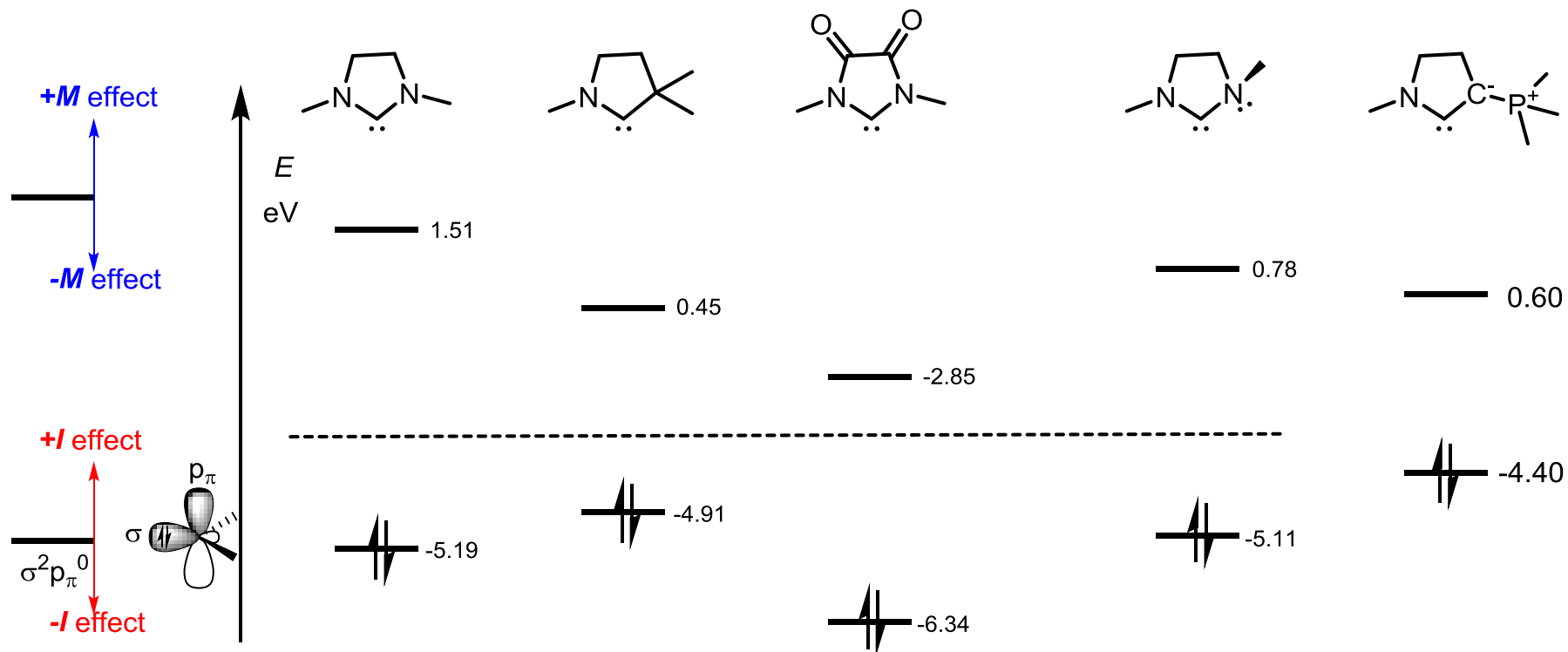
Geometry and Ground State



Frontier orbitals and possible electron configurations for carbene carbon atoms.

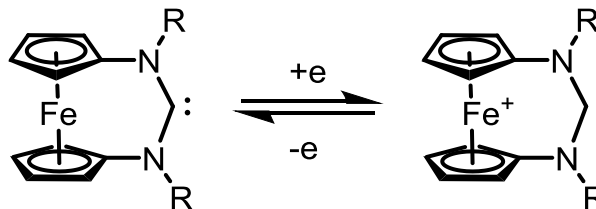
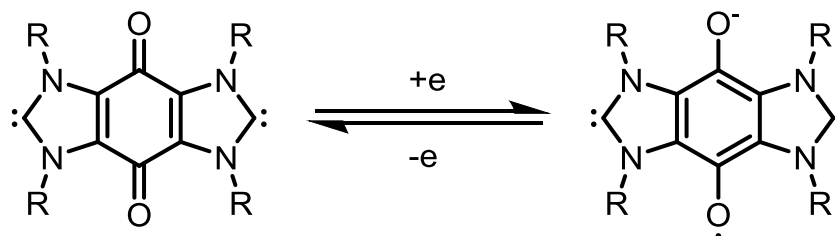
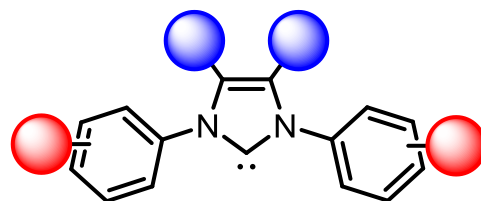
$$1 \text{ eV} = 23 \text{ kcal/mol} = 96 \text{ kJ/mol}$$

HOMO-LUMO



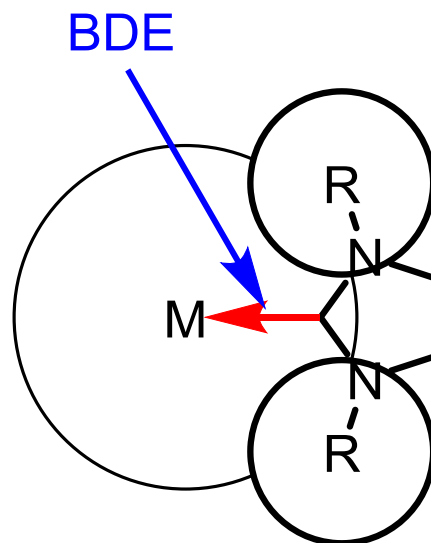
D. Martin, N. Lassauque, B. Donnadiou, G. Bertrand, *Angew. Chem. Int. Ed.* **2012**, 51, 6172.
 A. Fürstner, M. Alcarazo, K. Radkowski, C. W. Lehmann, *Angew. Chem. Int. Ed.* **2008**, 47, 8302.
 M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, 49, 8810.

Modulation of Electronic Properties



T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.* **2010**, *49*, 6940.

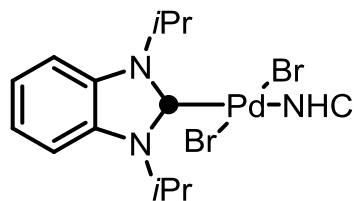
Properties of Metal Complexes



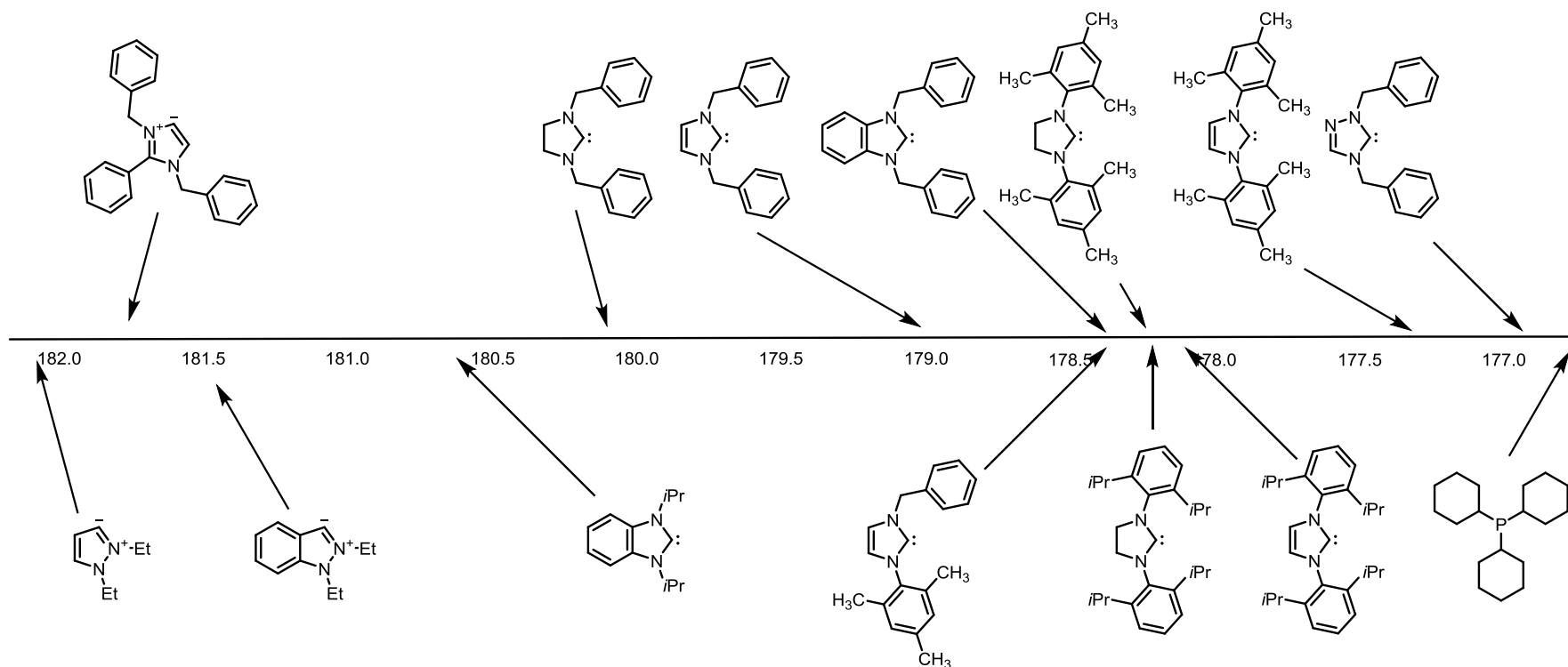
σ -Donation

^{13}C NMR Carbene's Donor Parameter (HUYNH)

Tolman's Electronic Parameter (TEP)

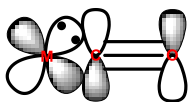
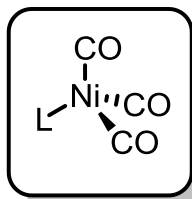


HUYNH Method

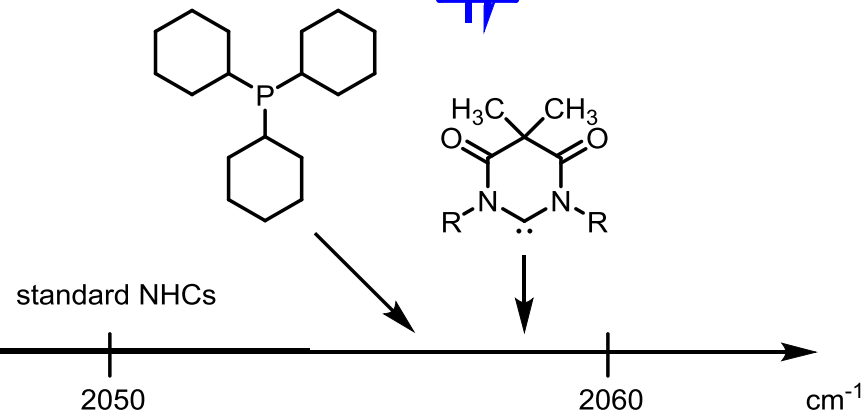
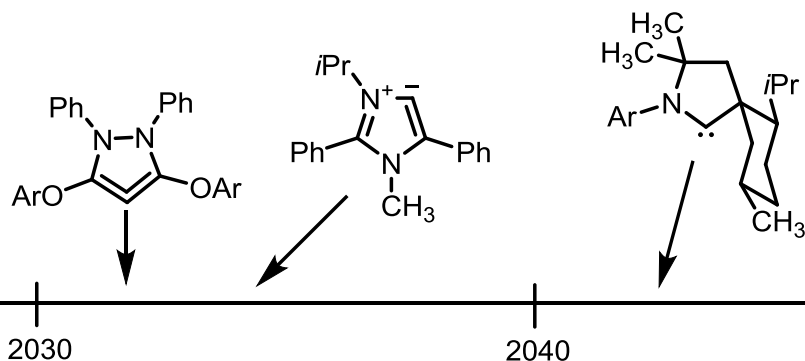
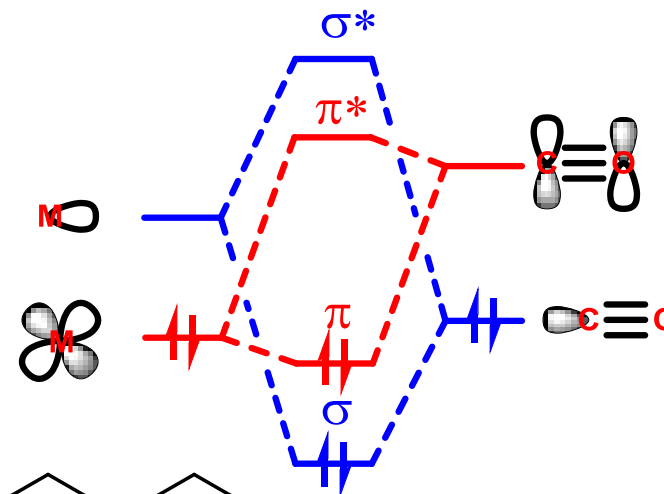


H. V. Huynh, Y. Han, R. Jothibasu, J. A. Yang, *Organometallics* **2009**, *28*, 5395.

TEP

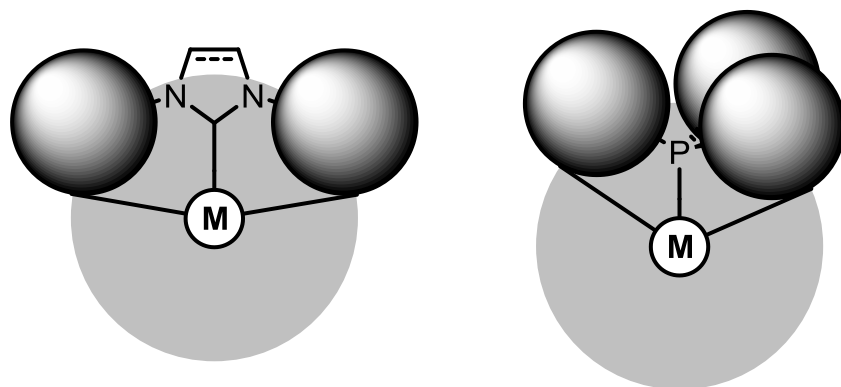


$$\begin{aligned} \nu_{\text{CO}}^{\text{Ni}} &= 0.8475\nu_{\text{CO}}^{\text{Ir}} + 336.2 \text{ [cm}^{-1}\text{]} \\ \nu_{\text{CO}}^{\text{Ir}} &= 0.9441\nu_{\text{CO}}^{\text{Rh}} + 98.9 \text{ [cm}^{-1}\text{]} \\ \nu_{\text{CO}}^{\text{Rh}} &= 0.8475\nu_{\text{CO}}^{\text{Ir}} - 56.9 \text{ [cm}^{-1}\text{]} \\ \nu_{\text{CO}}^{\text{Ni}} &= 0.8001\nu_{\text{CO}}^{\text{Rh}} + 420.0 \text{ [cm}^{-1}\text{]} \end{aligned}$$



C. A. Tolman, *Chem. Rev.* **1977**, 77, 313.
 T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.* **2010**, 49, 6940.
 L. Perrin, E. Clot, O. Eisenstein, J. Loch, R. H. Crabtree, *Inorg. Chem.* **2001**, 40, 5806.
 D. G. Gusev, *Organometallics* **2009**, 28, 6458.
 L. Mercks, G. Labat, A. Neels, A. Ehlers, M. Albrecht, *Organometallics* **2006**, 25, 5648.
 T. Dröge, F. Glorius, *Angew. Chem. Int. Ed. Engl.* **2010**, 49, 6940.

Steric Effects



$$E_{\text{Fit}} = a + b\%V_{\text{Bur}} + cE_{\text{ST}}$$

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Insert your input file

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c3d1 - Chem3D Cartesian 1 format

Keine Datei ausgewählt.

Parameters

Index of the atom coordinated at the center of the sphere

Number of atoms for axis definition

Atom indexes (space separated list)

Sphere radius

Distance from the center of the sphere

Mesh spacing

Include H atoms

Choose radii

Bondi radii

Bondi radii scaled by 1.17

Old set of radii, to be used for backward compatibility

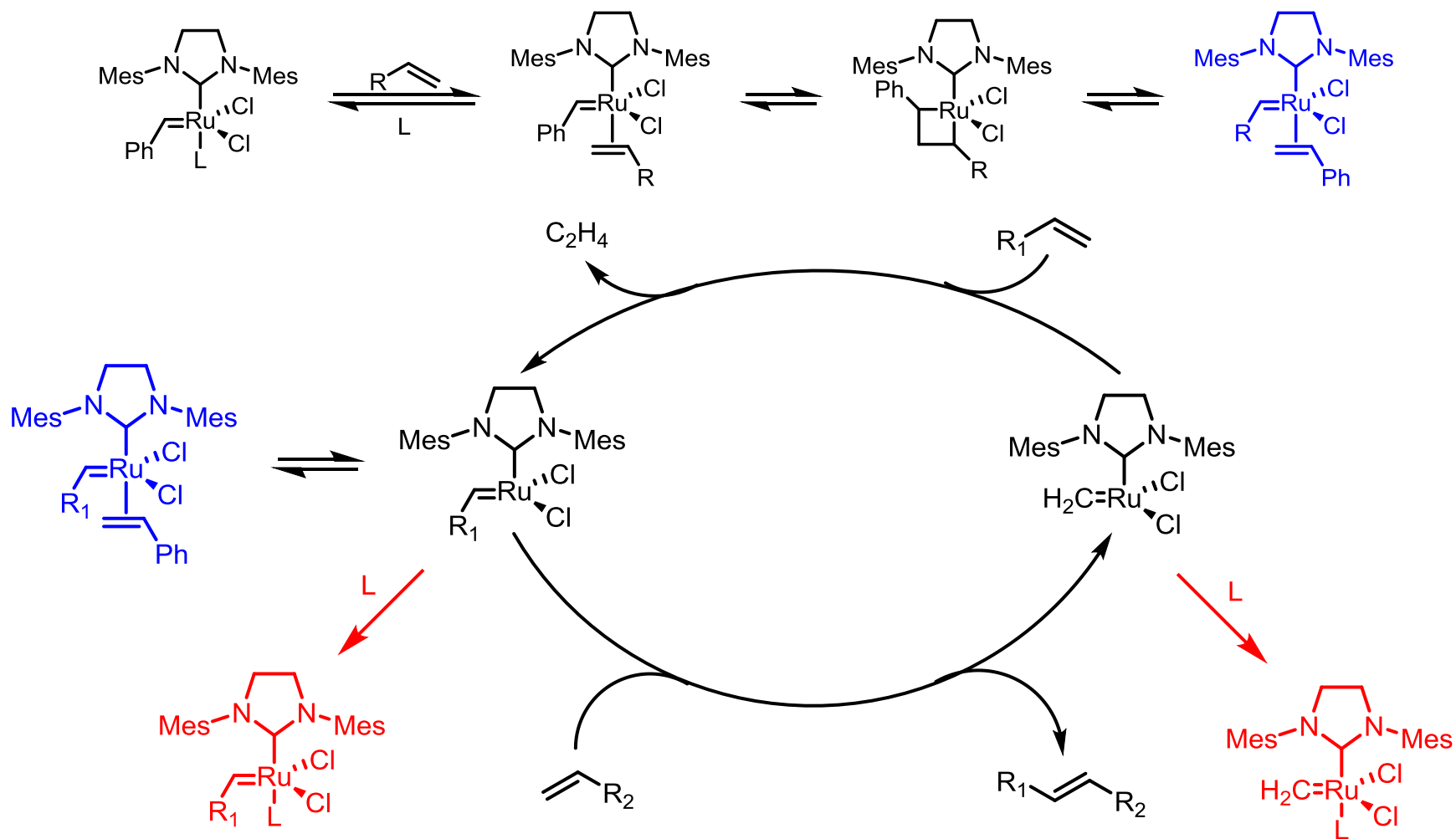
user defined radii

<https://www.molnac.unisa.it/OMtools/sambvca.php>

H. Clavier, S. P. Nolan, *Chem. Commun.* **2010**, 46, 841.

A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, *Eur. J. Inorg. Chem.* **2009**, 2009, 1759.

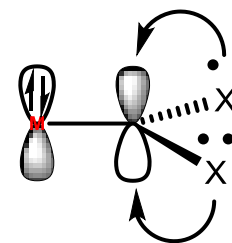
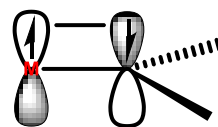
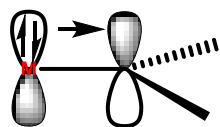
Grubbs Reaction Mechanism



T. Vorfalt, K.-J. Wannowius, H. Plenio, *Angew. Chem. Int. Ed.* **2010**, 49, 5533.

π Backbonding

Metal Complexes



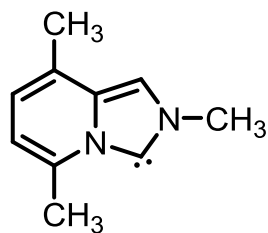
Fischer

Schrock

NHC

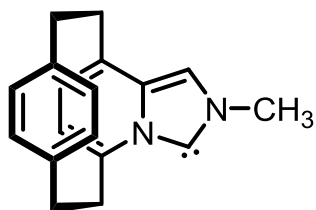
HOMO

LUMO



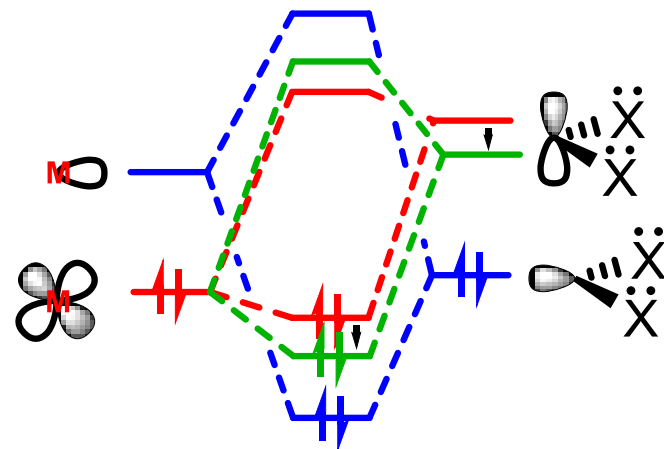
-4.97

-0.63



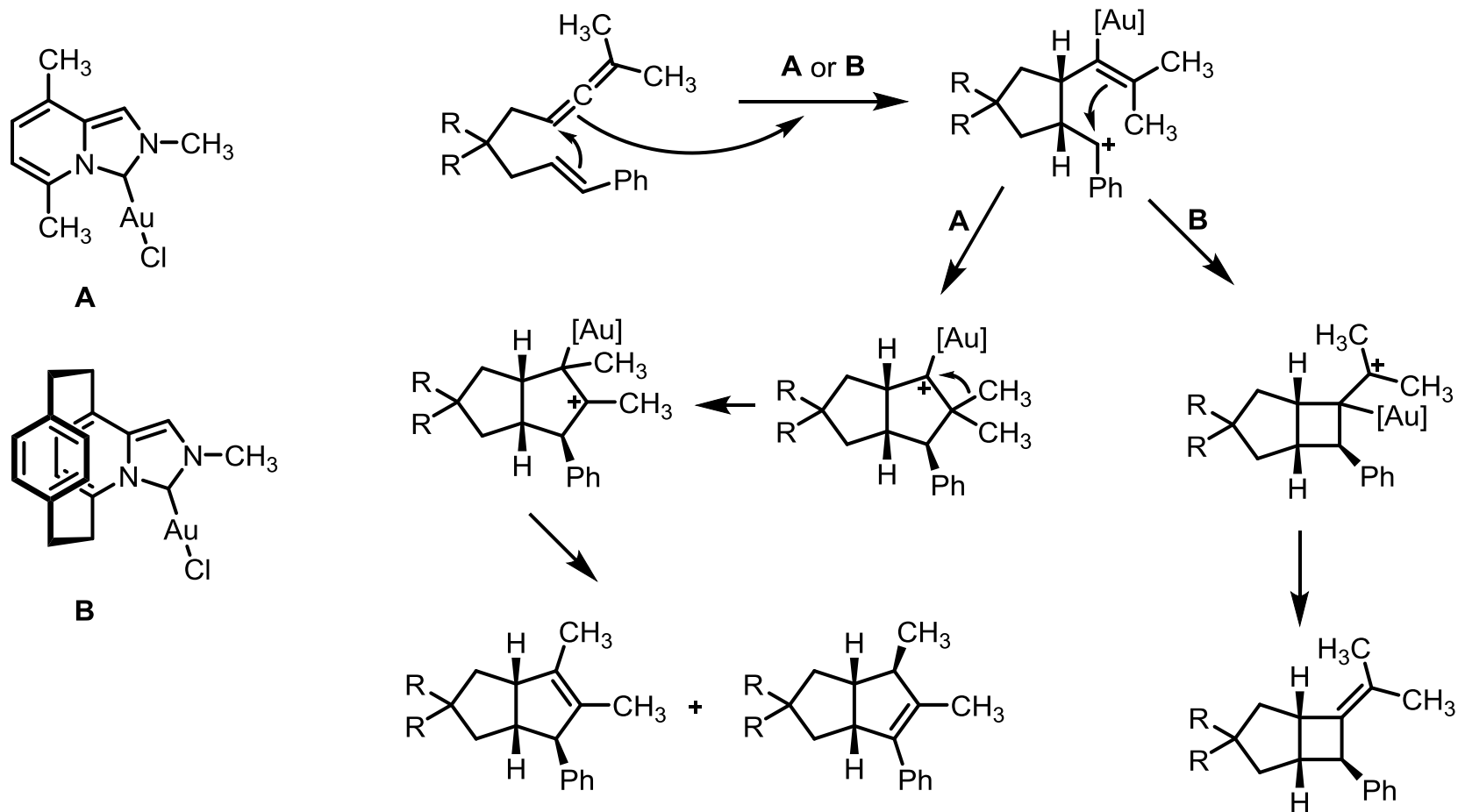
-5.00

-1.14



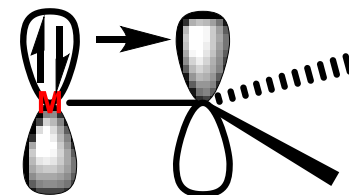
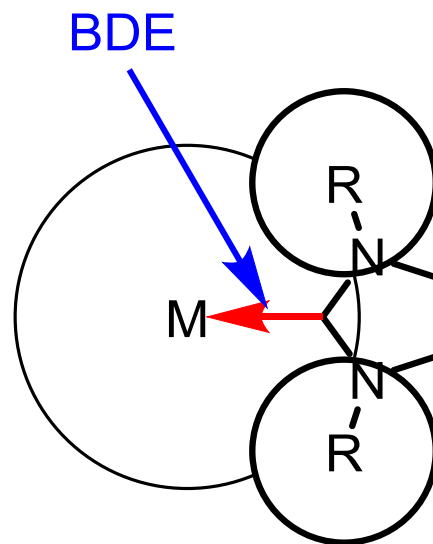
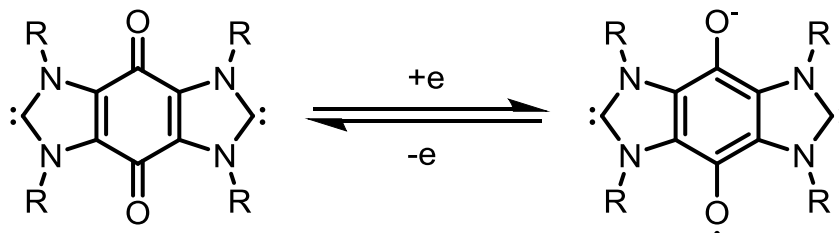
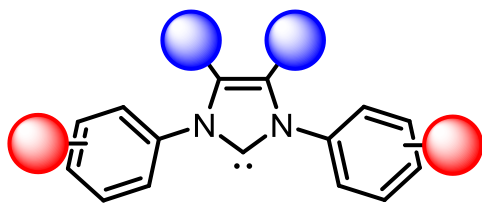
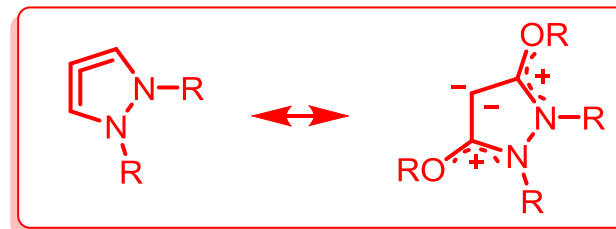
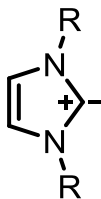
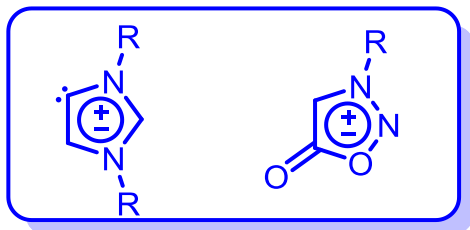
M. Alcarazo, T. Stork, A. Anoop, W. Thiel, A. Fürstner, *Angew. Chem. Int. Ed.* **2010**, 49, 2542.

π Backbonding



M. Alcarazo, T. Stork, A. Anoop, W. Thiel, A. Fürstner, *Angew. Chem. Int. Ed.* **2010**, 49, 2542.

Summary



M. Alcarazo, T. Stork, A. Anoop, W. Thiel, A. Fürstner, *Angew. Chem. Int. Ed.* **2010**, 49, 2542.

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- D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.

Thank You for Your Attention