

N-Heterocyclic Carbenes

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MacMillan Group Meeting
August 19, 2003

N-Heterocyclic Carbenes

Outline

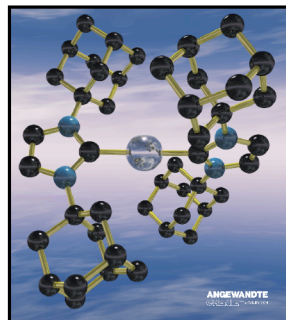
■ Introduction

- Historical Background
- Syntheses of NHCs

■ Carbene Stability and Electronic Structure

■ Structural Versatility

- Chelation
- Functionalization
- Immobilization
- Chirality
- Ionic Liquids

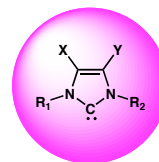


Relevant and Comprehensive Reviews:

- Herrmann, W.A.; Kocher, C. "N-Heterocyclic Carbenes." *Angew. Chem. Int. Ed.* **1997**, *36*, 2162.
- Bertrand, G. et al. "Stable Carbenes." *Chem. Rev.* **2000**, *100*, 39.
- Herrmann, W.A. "N-Heterocyclic Carbenes: A New Concept in Organometallic Catalysis." *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
- Arduengo, A.J. III. "Looking for Stable Carbenes: The Difficulty in Starting Anew." *Acc. Chem. Res.* **1999**, *32*(11), 913.
- Herrmann, W.A.; Weskamp, T.; Bohm, V.P.W. "Metal Complexes of Stable Carbenes." *Adv. Organomet. Chem.* **2001**, *48*, 1.
- Jafarpour, L.; Nolan, S.P. "Transition-Metal Systems Bearing a Nucleophilic Carbene Ancillary Ligand: from Thermochemistry to Catalysis." *Adv. Organomet. Chem.* **2001**, *46*, 181.

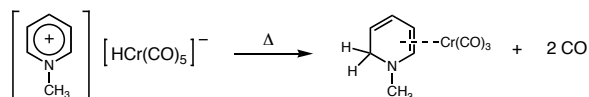
N-Heterocyclic Carbenes Introduction

- Diaminocarbenes (NHCs) are strong σ -donors, have reactivities like other classical $2 e^-$ donors: phosphines, amines, ethers
- NHCs have come to replace phosphines in many organometallic and organic reactions for several reasons
 - have mostly comparable or superior activity to phosphines
 - NHCs are easy to make on a large scale
 - the salts of the carbenes are stable without decomposition in air
 - phosphines degrade at higher temperatures and oxidize upon exposure to air
- NHCs can complex with low valent and high valent transition metals, alkaline earth metals, and lanthanides (Yt and Sc)
- Exceptionally stable Metal-Carbene bonds give high thermal and hydrolytic durability
 - long-shelf life
 - resistant to oxidation
- No need for excess NHC ligand in reactions
- Structural Versatility
 - chirality
 - functionalization
 - immobilization
 - water solubility
 - chelate effects

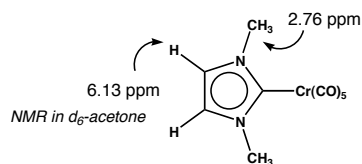
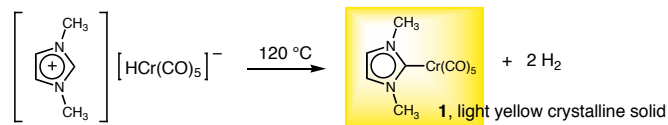


Ofele's Carbene Discovery : 1968 Back to the Beginning

- Ofele was trying to obtain dihydro-complexes from heterocyclic salts



- When using imidazolium salts, Ofele noted a "Verlauf" - a side reaction.



- 1 sublimates at 80 °C, decomposes to $Cr(CO)_6$ over 175 °C
- CO stretches of 2057 and 1927 cm^{-1} , UV absorbances at 351 nm and 253 nm.
- 1 is soluble in petroleum ether, CCl_4 , alcohol, ether
- 1 is insoluble in H_2O

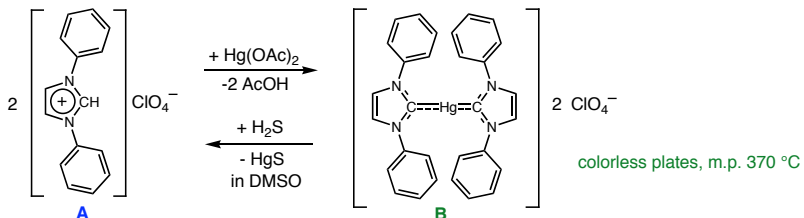
Ofele, K. *J. Organomet. Chem.* **1968**, P42.

Wanzlick's Carbene Discovery : 1968

Same Year, 550 kilometers away

Wanzlick was directly synthesizing from nucleophilic carbenes (W. Kirmse. *Carbene Chemistry*. Acad. Press. 1964)

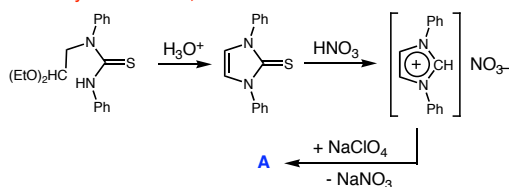
- Fischer carbenes are obtained indirectly
- Nucleophilic carbenes should be similar to isocyanides and do direct displacements on TM



1-H NMR proves the structure of B

ppm	H(2)	H(4), H(5)	H(phenyl)
A	-0.29 (t) J = 1.5	1.47 (t) J = 1.5	1.95-2.5 (m)
B	---	1.71 (s)	2.2-2.7 (m)

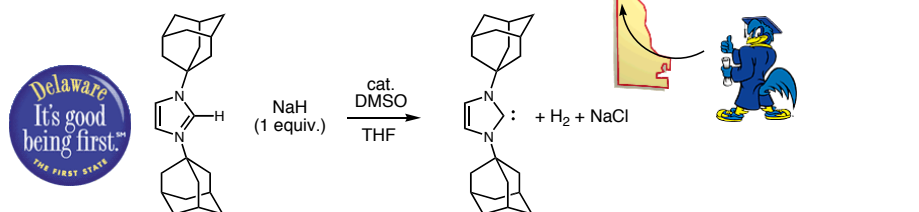
Synthesis of A, no intermediate isolations



Wanzlick, H.-W.; Schonherr, H.-J. *Angew. Chem. Int. Ed.* **1968**, 7(2), 141.

Arduengo Reports the First Stable Crystalline Carbene

After 21 reports by Wanzlick that Attempt to Isolate a Carbene



Structural X-Ray Data

bond length (pm)		bond angle (deg)	
C ₂ -N ₁	136.7	N ₁ -C ₂ -N ₃	102.2
C ₂ -N ₃	137.3	C ₅ -N ₁ -C ₂	112.1
C ₄ -C ₅	133.8	C ₄ -N ₃ -C ₂	112.3
N ₁ -C ₅	138.2	N ₁ -C ₅ -C ₄	107.2
N ₃ -C ₄	138.6	N ₃ -C ₄ -C ₅	106.2

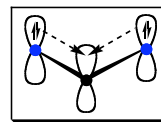
- imidazolium salt has typical angle of 108.5 - 109.7°

- C₂ - N₁₍₃₎ has typical value of 132 pm in salt

changes indicate a diminished π -delocalization in free carbene

A combination of steric and electronic effects contribute to the iAd carbene stability

- π donation into the carbene out of plane p orbital from N, α -electronegativity effect = "push-pull" mechanism
- extra stabilization by electron-rich π -system
- electronic factors alone were not enough to isolate carbenes
- steric bulk allowed for less chemical reactions to take place



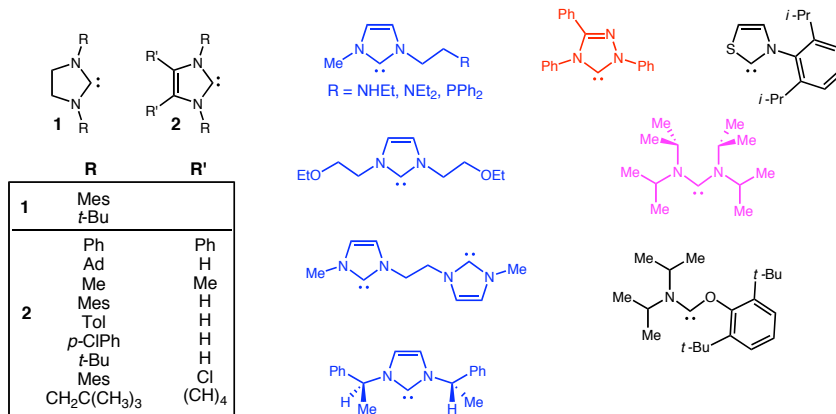
Arduengo, A.J. III; Harlow, R.L.; Kline, M. *J. Am. Chem. Soc.* **1991**, 113, 361.

An Explosion of Free Carbene Isolations

Herrmann's New Prep is Money!

■ Deprotonation with NaH or KNH₂ is achieved in liquid ammonia

- new homogenous method provided carbenes that were not previously accessible oxygen-, nitrogen-, and diarylalkylphosphino-functionalized or chiral carbenes



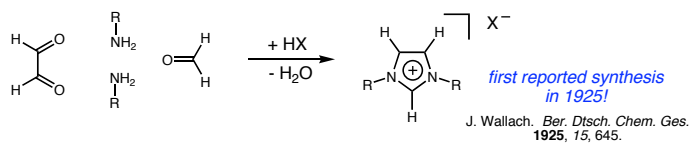
Stability of the carbenes can be attributed more to electronic factors than sterics!

Herrmann, W. A. et al. *Chem. Eur. J.* **1996**, *2*, 1627 and 1627.
 Enders, D. et al. *Angew. Chem. Int. Ed.* **1995**, *34*, 1021.
 Alder, R. W. et al. *Angew. Chem. Int. Ed.* **1998**, *35*, 1121.
 Bertrand, G. et al. *Chem. Rev.* **2000**, *100*, 39.

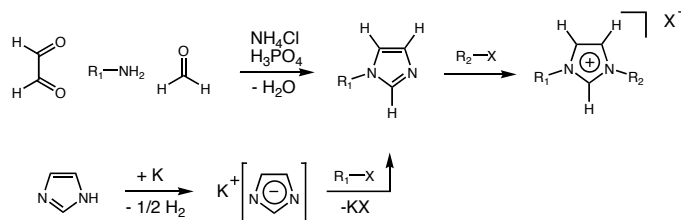
Synthesis of N-Heterocyclic Carbenes

Convenient Routes to Imidazolium Salts and Derived Imidazolin(2)-ylidenes

■ Symmetric N-Substitution



■ Unsymmetric N-Substitution (if necessary)

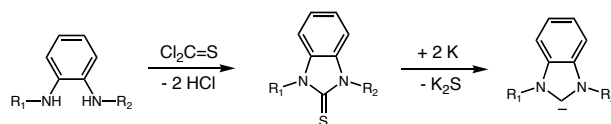


A. J. Arduengo III (E.I. DuPont de Nemours & Company) US 5,077,414 A2, **1992**.
 A. A. Gridnev, I. M. Mihaliseva. *Synth. Commun.* **1994**, *24*, 1547.

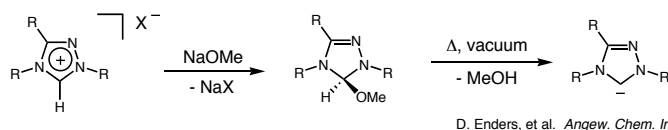
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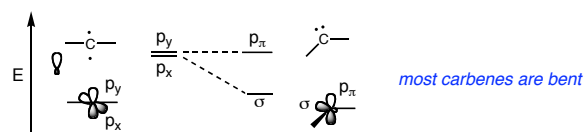
F. E. Hahn, L. Wittenbacher, D. L. Van, R. Frolich. *Angew. Chem. Int. Ed.* **2000**, *39*, 541.



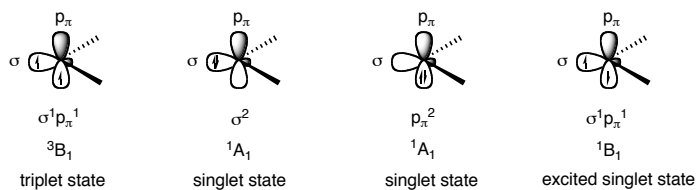
Carbene Stability

Introduction

■ The hybridization breaks the degeneracy of the carbene's p orbitals



■ Triplet versus Singlet carbenes - Ground State Spin Multiplicity



singlet state occupying σ is generally more stable

■ Ground-state spin multiplicity dictates a carbene's reactivity.

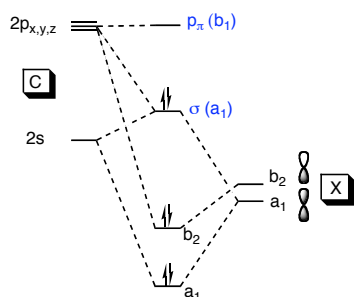
- singlet carbenes have a filled and vacant orbital \Rightarrow possess ambiphilic character
- triplet carbenes can be regarded as diradicals
- Hoffmann determined $>2\text{eV}$ is needed to impose a singlet ground state, $<1.5\text{eV}$ leads to a triplet state
- Influence of substituents on the carbene will have large effects - **electronics and sterics!**

Gleiter, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475.
Bertrand, G. et al. *Chem. Rev.* **2000**, *100*, 39.

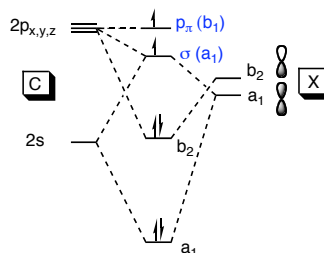
Carbene Stability Electronic Effects

■ Inductive Effects

- σ -electron-withdrawing substituents favor the singlet state over the triplet state
- can be rationalized by perturbation orbital diagrams of C_{2v} symmetry



σ-electron-withdrawing substituents



σ-electron-donating substituents

- σ -electron-withdrawing substituents inductively stabilize the σ nonbonding orbital by increasing its character and leaving the p_π orbital unchanged
- σ -electron-donating substituents induce a smaller s- p_π gap, favoring a triplet state.

Bertrand, G. et al. *Chem. Rev.* **2000**, *100*, 39.

Carbene Stability Electronic Effects

■ Mesomeric Effects - considers π effects more important

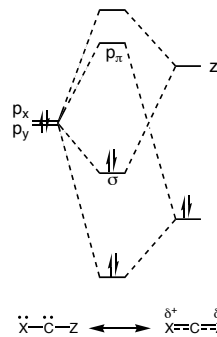
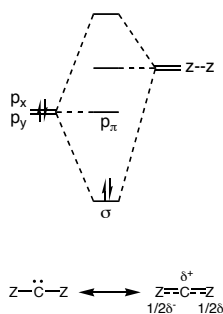
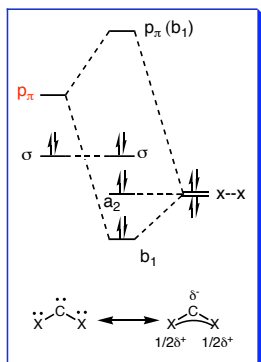
- π -electron-donating substituents (X)

-F, -Cl, -Br, -I, -NR₂, -PR₂, -SR, -SR₃, ...

- π -electron-withdrawing substituents (Z)

-COR, -CN, -CF₃, BR₂, -SiR₃, -PR₃⁺, ...

- Mesomeric effects consist of the interaction of the carbon orbitals (s, p_π or p_x, p_y) and the p or π orbitals of the carbene substituents

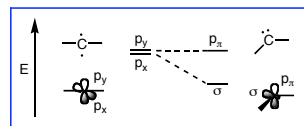


- The energy of the vacant p_π orbital is increased by the interaction with the symmetric combination of the substituent lone pairs (b_1). Since the σ orbital does not change, the σ - p_π gap increases.

Bertrand, G. et al. *Chem. Rev.* **2000**, *100*, 39.

Carbene Stability

Steric Effects - the Bigger the Better



■ Bulky substituents kinetically stabilize all types of carbenes.

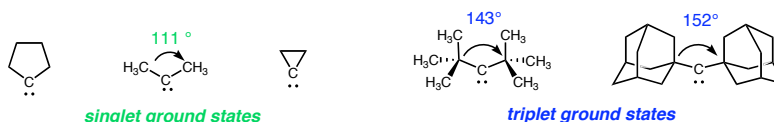
■ If electronic effects are insignificant, sterics can dictate the ground-state spin multiplicity.

- a linear geometry favors the triplet state, a bent geometry favors the singlet state



>90° the energy of the triplet state becomes less than that of the singlet state

- increasing the steric bulk of the carbene substituents broadens the bond angle = triplet state



Bertrand, G. et al. *Chem. Rev.* **2000**, *100*, 39.
 Gilbert, B. C.; Griller, D.; Nazran, A. S. *J. Org. Chem.* **1985**, *50*, 4738.
 Richards, C.A.; Kim, S.J.; Yamaguchi, Y.; Schaefer, H. F. III. *J. Am. Chem. Soc.* **1995**, *117*, 10104.
 Platz, M. S. et al. *J. Am. Chem. Soc.* **1986**, *108*, 4232.

Carbene Coordination to Metals

A Further Loss in Electron Delocalization

■ "...in general [NHCs] behave as better donors than the best phosphane donor ligands with the exception of the sterically demanding (adamantyl) carbene." - S. P. Nolan

- NHCs behave like classical 2 e⁻ donors ligands like amines, ethers and phosphanes

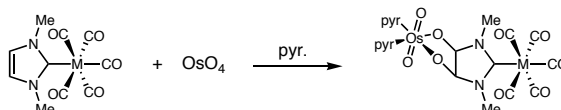


■ M - NHC bonds are longer (>210 pm) than Fischer- and Schrock-type carbenes (<200 pm)

- NHCs exhibit little to no π -backbonding
- in particular bonding situations, nucleophilic NHCs can rotate around the metal - carbon bond

■ Little to no π -aromaticity in the imidazol-2-ylidene

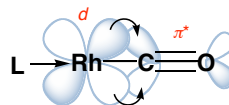
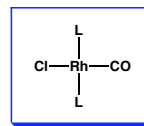
- consistent with charge-density studies



Huang, I.; Schanz, H.-C.; Stevens, E.D.; Nolan, S.P. *Organometallics*. **1999**, *18*, 2370.
 Herrmann, W.A.; Roesky, P.W.; Elison, M.; Artus, G.R.J.; Ofele, K. *Organometallics*. **1995**, *14*, 1085.
 Herrmann, W.A. *Angew. hem. Int. Ed.* **2002**, *41*, 1290.

Carbonyl Stretching Frequencies

L	ν (cm ⁻¹)
	1924
	1929
PCy ₃	1939
PMe ₃	1957
PPh ₃	1983
	2003
P(OPh) ₃	2018

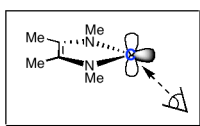


more electron density on the metal
 ↓
 more pi-backbonding on CO
 ↓
 longer CO bond
 ↓
 shorter CO stretching frequency

Kocher, C.; Herrmann, W. A. *J. Organomet. Chem.* **1997**, 532, 261.

Electronic Properties of NHCs

The Carbene has a Large Density of Negative Charge



Deformation Density Plot

■ Electron density in the plane of the carbene carbon

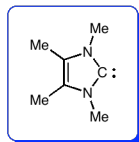
- the carbene lone pair density is located to the right of the carbon and the p density lies above and below the C
- there is a concentration of electron density in the direction of the lone pair around the spherically symmetric carbon
- there is a negative electron density in the p direction, as indicated by the pink/red.
- the deformation density profile is another way of analyzing the same information of the carbene center.

Arduengo, A. J. III *Accs. Chem. Res.* **1999**, 32, 913.

Electronic Properties of NHCs

The Carbene has Little π Electron Density

70pm above



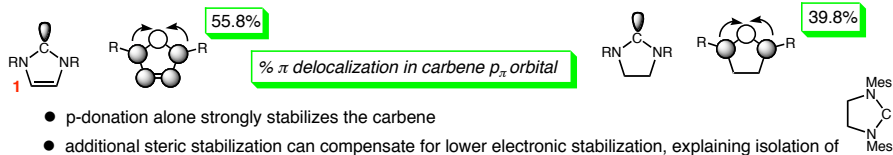
- In-plane network of electron density from 70 pm above shows a prominent electron density on the N and the π component of the C₄-C₅ π bond.
- The σ -framework is evident in picture (c), this time with an even more prominent view of the electron density on the nitrogens.

Arduengo, A. J. III *Accts. Chem. Res.* **1999**, 32, 913.

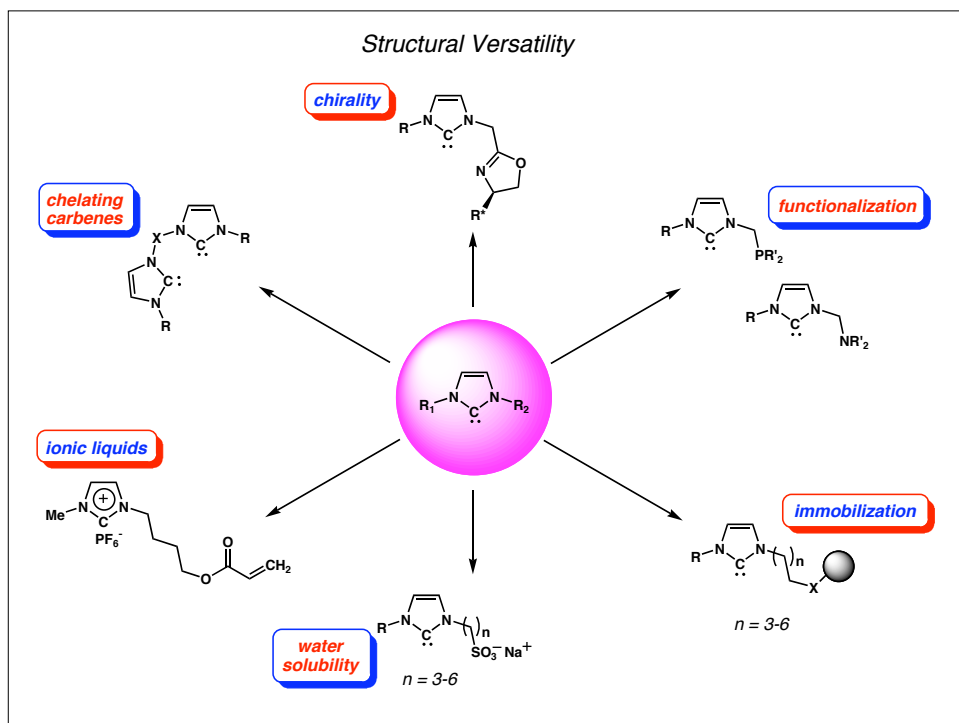
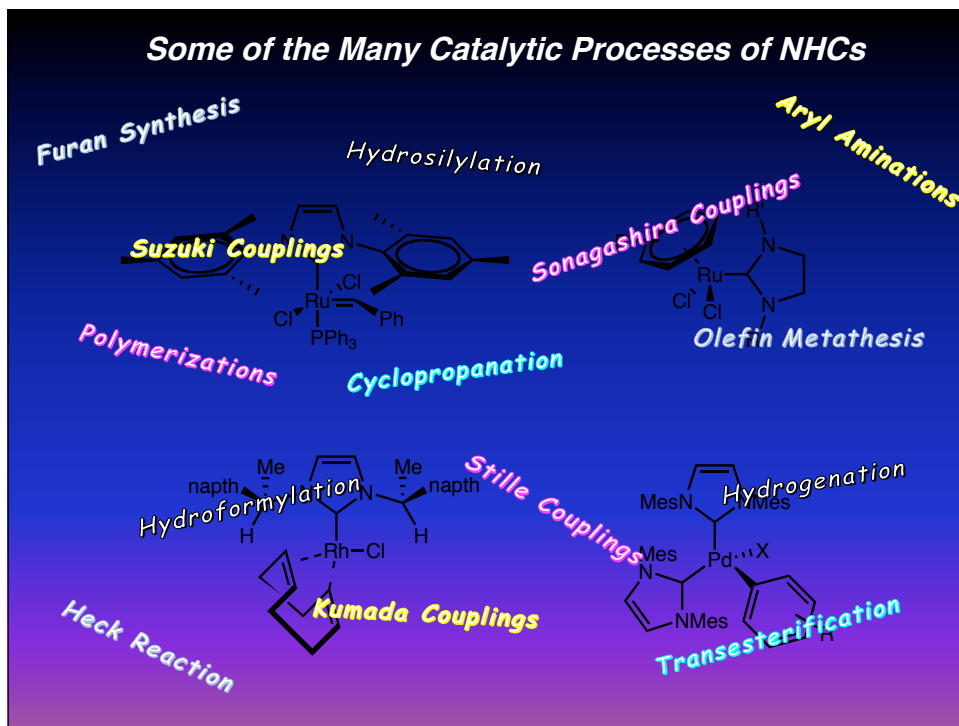
Carbene Stability - from π Donation or σ -charge transfer?

Frenking and Heinemann Independently Argue for π Donation Stability

- Stability arises from π -donation by the ion pairs of the N atoms into the empty p_{π} orbital of the carbene
 - Cyclic electron delocalization in imidazol-2-ylidenes is significant and displays some aromatic character
 - Heinemann's further studies supported this
- Heinemann's studies used thermodynamic, structural, and magnetic criteria, the properties of charge distributions, and low energy ionization processes to analyze the role of π -donation stability
 - Planar amino substituents stabilize carbenes significantly and added unsaturation adds 25 kcal/mol stabilization
 - Structural differences between the saturated, unsaturated, and acyclic NHCs are consistent with bond length compensation due to cyclic electron delocalization
 - the cyclic electron delocalization is 60% of the ED of benzene
- The higher stability of unsaturated NHCs as compared to the saturated analog is caused by the enhanced p_{π} - p_{π} delocalization of **1**, which gives rise to a significant electronic charge in the formally empty p_{π} orbital of the carbene.

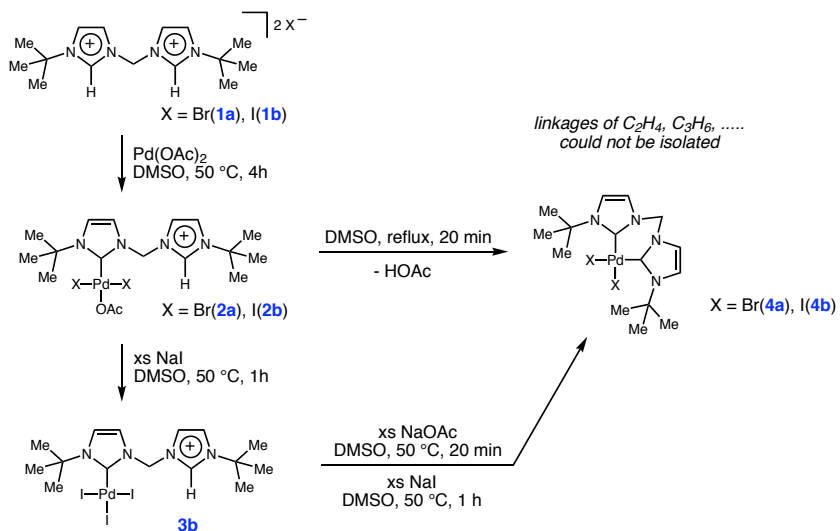


Boehme, C.; Frenking, G. *J. Am. Chem. Soc.* **1996**, 118, 2039.
 Heinemann, C.; Muller, T.; Apeloig, Y.; Schwarz, H. *J. Am. Chem. Soc.* **1996**, 118, 2023.



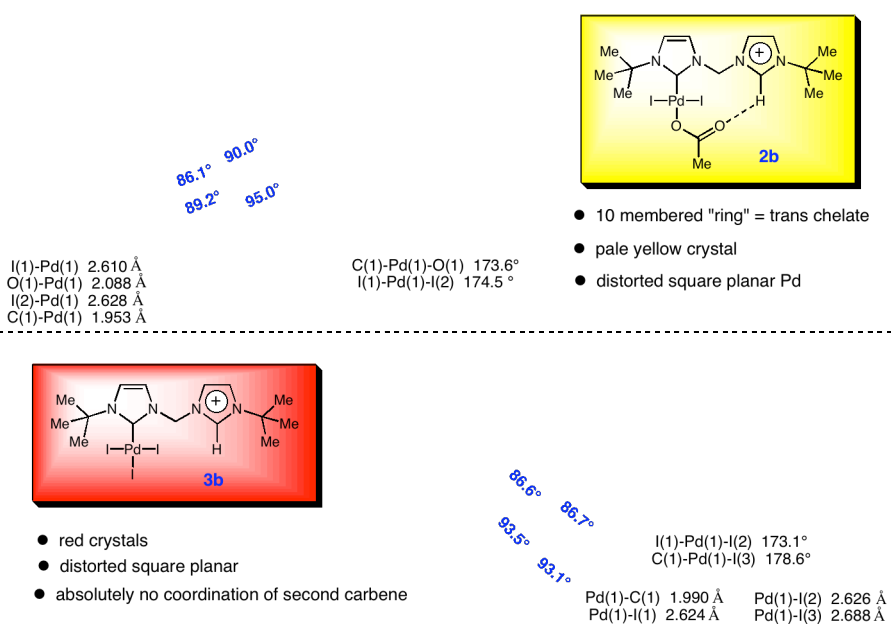
Chelating Bis-Carbenes with a Methylene Linker The Product is Always Cis

- Bis-Carbenes on Palladium are made stepwise and characterized by X-ray analysis



Herrmann, W. A.; et al. *Organometallics*. 1999, 18, 4082.

Chelating Bis-Carbenes with a Methylene Linker X-Ray Structures

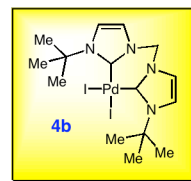


Chelating Bis-Carbenes with a Methylene Linker X-Ray Structures

83.3
91.6 91.6
90.1°

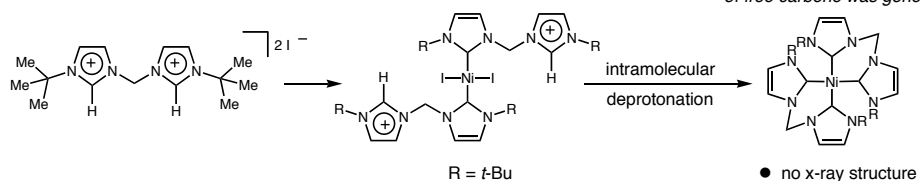
C(1)-Pd(1)-I(1) 167.3°

Pd-C(1) 2.004 Å
Pd-I(1) 2.669 Å



- C₂-symmetric complexes
- solely cis-substituted on Pd
- pale yellow crystals

■ Bis-Carbenes on Nickel

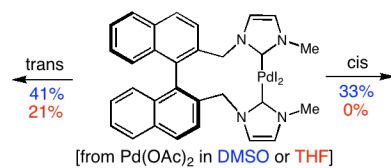


- no x-ray structure
- no prep found

Herrmann, W. A., et al. *Organometallics*. 1999, 18, 4082.

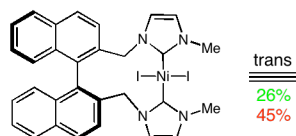
Larger Bite Angle Gives Trans-Substitution on Metal Trans-Chelation Substances are Rare

■ 11-membered chelate prepared and put on Pd and Ni



C₂-symmetric

Pd complexes to Heck reactions with ethyl acrylate and iodo- and bromobenzene



trans
26%
45%

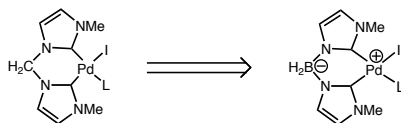
from Ni(acac)₂ in NMP at 200°C
from (PPh₃)₂NiCl₂ in THF at RT

stable to chromatography
C₂-symmetric
first trans-bis-carbene on Ni

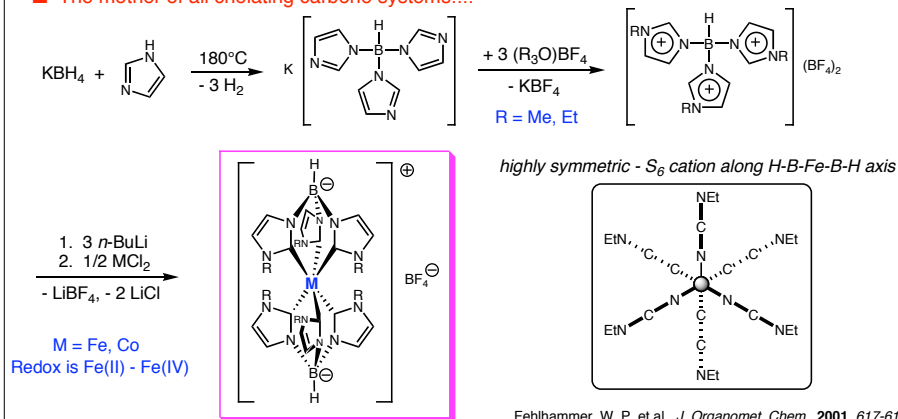
RajanBabu, T. V. et al. *Org. Lett.* 2000, 8, 1125.

Changing Backbone Changes the Charge of the System
From CH₂ to BH₂

- Changing the bridging group changes the charge on the metal

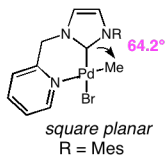


- The mother of all chelating carbene systems!!!!



Functionalized NHCs
Hemilabile Groups Attached to the NHC

- Highly active palladium catalysts are obtained by using hemilabile carbene complexes



Selected Bond Lengths (Å) and Bond Angles (°)

Pd - C1	1.964(4)
Pd - C10	2.147(3)
Pd - N3	2.183(3)
Pd - Br	2.4969(6)
Br-Pd-C1	177.5(1)
Br-Pd-C10	90.51(8)
Br-Pd-N3	92.59(8)

- Abstraction of the halide with AgOTf gives a free coordination site, hemilabile pyridine swings off to form stable tetramers (triflate occupies extra coordination site)

- active species in solution is probably the monomer

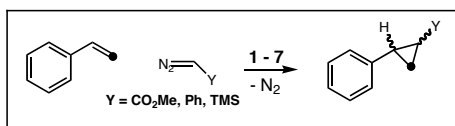
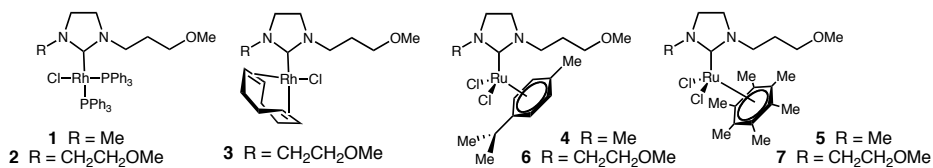
- Competitive with best systems for aryl halide Heck reactions into acrylates

- yields over 90%, 2.86 x 10⁶ TON for catalyst
- aryl bromides suffer from loss in reactivity

Danopoulos, A. A.; Hursthouse, M. B. *Chem. Comm.* **2000**, 1247.

Functionalized NHC Complexes of Rhodium (I) and Ruthenium (I)
Applications for Cyclopropanations

■ "...heterofunctional ligands...have been found to confer interesting properties to their metal complexes, such as dynamic behavior via reversible dissociation of the weaker metal-ligand bond resulting in unique catalytic properties."



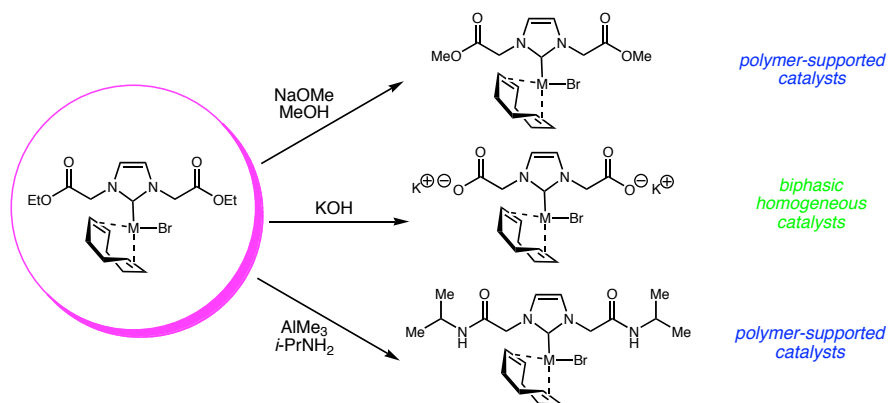
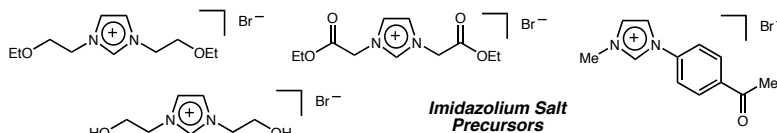
- one-arm catalysts 4 and 5 appear less efficient than two-arm catalysts 6 and 7 at 80°C
- Rh catalysts 1, 2, 3 are better than Ru catalysts 6, 7
- for Ru, the catalyst with the more electron donating substituent (hexamethylbenzene) has better activity
- the Rh catalysts are the most electron rich = best activity (cyclic voltammetry)

Cetinkaya, B. et al. *J. Organomet. Chem.* **1997**, 534, 153.

Y	Catalyst	T (°C)	Time (h)	Yield (%)	Cis/Trans
CO ₂ Et	1	80	4	71	25/75
	2	80	4	69	25/75
	3	80	4	91	24/76
	4	80	4	26	24/76
	5	80	4	44	24/76
	6	80	4	52	18/82
	7	60	4	34	33/67
Ph	7	80	4	54	25/75
	7	100	4	59	23/77
	7	80	2	39	51/49
TMS	3	80	2	37	48/52
	7	80	2	39	51/49
TMS	7	80	2	6	

Functionalized NHC Complexes of Rhodium and Palladium
Herrmann is at it again!!!!

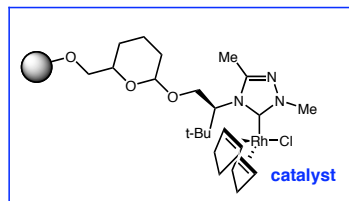
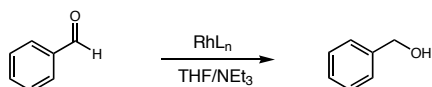
■ Herrmann and co-workers synthesized a bunch of functionalized Rh and Pd complexes



Herrmann, W. A.; Gooßen, L. J.; Spiegler, M. *J. Organomet. Chem.* **1997**, 547, 357.

Catalysts on Solid Support
The First Reaction Catalyzed by Immobile NHCs

■ Hydrosilylation of Acetophenone

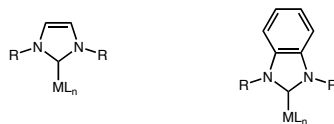


- reaction with non-resin-linked catalyst gives 19% e.e.
- reaction with the Merrifield polystyrene-linked resin **catalyst** gives 24% e.e. and 80% yield

■ Recycling was shown to be possible

■ Leaching was not quantified

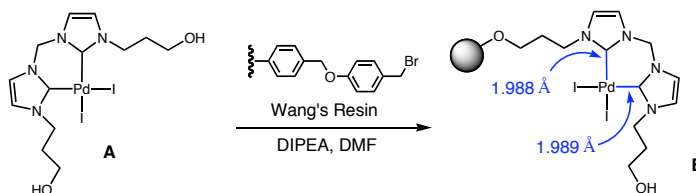
■ Immobilized imidazolin-2-ylidene and benzimidazolin-2-ylidene complexes have been used as well.



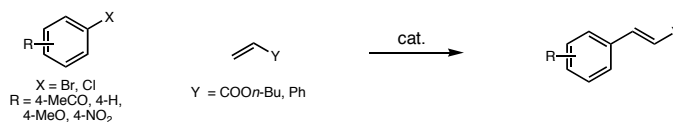
Enders, D.; Gielen, H.; Breuer, K. *Mol. Online*. **1998**, *2*, 105.
Herrmann, W. A.; Weskamp, T.; Bohm, V. P. W. *Adv. Organomet. Chem.* **2002**, *48*, 1.

Catalysts on Solid Support
Palladium Catalysts for the Heck Reaction

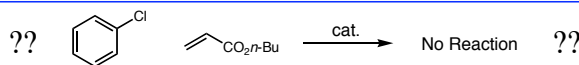
■ NHCs were chosen for solid support catalysis because of the strong M-C bond = less leaching



■ Heck Reaction Results - Homogenous Catalysis with A



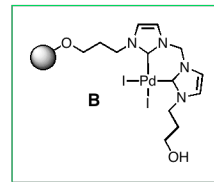
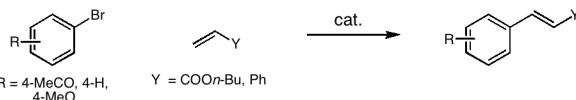
X	Catalyst (mol %)	time (h)	yields (%)	turnovers
Br	0.02 - 0.15 %	0.17 - 60 h	72% (MeO) - >99%	480 - 4800
Cl	1.0 %	72 h	59% (MeO) - 99% (NO ₂)	59 - 99



Herrmann, W. A. et al. *Chem. Eur. J.* **2000**, *6*, 1773.

Catalysts on Solid Support Palladium Catalysts for the Heck Reaction

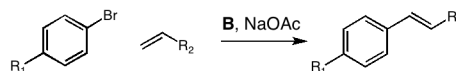
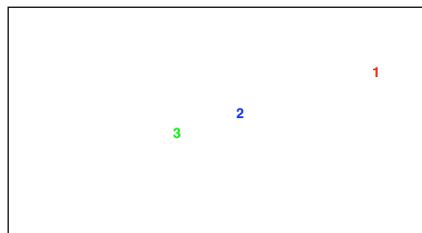
Heck Reaction Results - Heterogenous Catalysis with B



Catalyst (mol %)	time (h)	yields (%)	turnovers
0.02 %	12h (MeCO) - 60 h	42 - >99%	4000 - 21000!

Reaction results drastically vary: 42 or 100% conversion for same reaction

Effects of Leaching



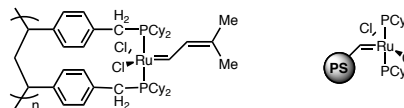
- 1 R₁=COMe, R₂=Ph, 15h, 150 °C, 0.15 mol%
- 2 R₁=COMe, R₂=CO₂*n*-Bu, 12h, 160 °C, 0.02 mol%
- 3 R₁=H, R₂=CO₂*n*-Bu, 36h, 160 °C, 0.02 mol%

Heterogenous catalyst **B** has high activity, easy accessibility, exceptional stability, high activity after recycling, and the lowest leaching levels for any heterogeneous Pd systems.

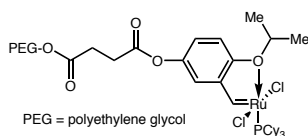
Herrmann, W. A. et al. *Chem. Eur. J.* **2000**, *6*, 1773.

Catalysts on Solid Support Olefin Metathesis Catalysts for Immobilized Support

Early Attempts to Immobilize Grubbs Catalyst were met with decreased activity in recycling.



Yao decided to take advantage of the chelating phosphine catalysts of Hoveyda and Snapper



cycle	1	2	3	4	5	6	7	8
conversion (%)	98	97.5	96.5	95	95	93	93	92

Reaction conditions: 5 mol % cat., CH₂Cl₂ (0.05M), reflux, 2h

		2.5 mol % 12 h, RT	> 99% conv
		2.5 mol % 2 h, reflux	90% conv
		2.5 mol % 2 h, reflux	96% conv
		2.5 mol % 3 h, reflux	>98% conv

limited solubility will require future aqueous application = industries happy!!

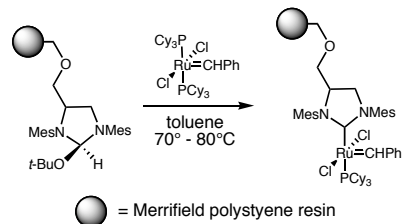
Yao, Q. *Angew. Chem. Int. Ed.* **2000**, *39*, 3896.

Catalysts on Solid Support

Back-to-Back Reports on Immobilized Metathesis Catalysts

■ Recovery of the ruthenium catalyst has become a subject of interest.

■ Construct NHC on resin then add etal

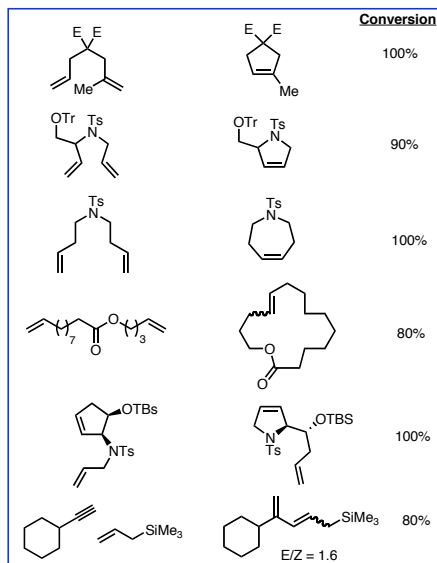


■ Recycling value varied

- some reactions held for over 5 runs without decrease in activity
- others lost significant reactivity after one run

■ Filtration is the only purification step = useful for combinatorial work

■ Recycling potential, long-term catalytic activity, and metal leaching still need to be studied in this system

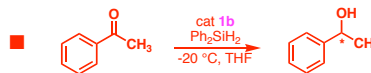
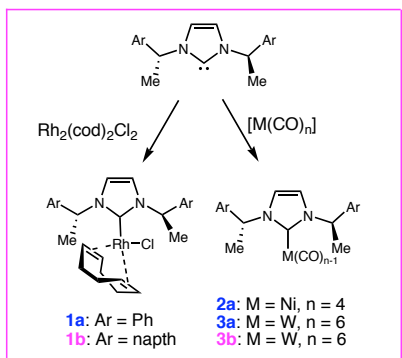
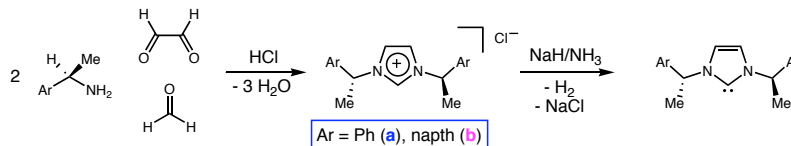


Schurer, S. C.; Gessler, S.; Buschmann, N.; Blechert, .. *Angew. Chem. Int. Ed.* **2000**, *39*, 3898.

Chiral NHCs for Enantioselective Catalysts

Lack of Success and Lack of Examples

■ Putting Chirality on the N of the NHC



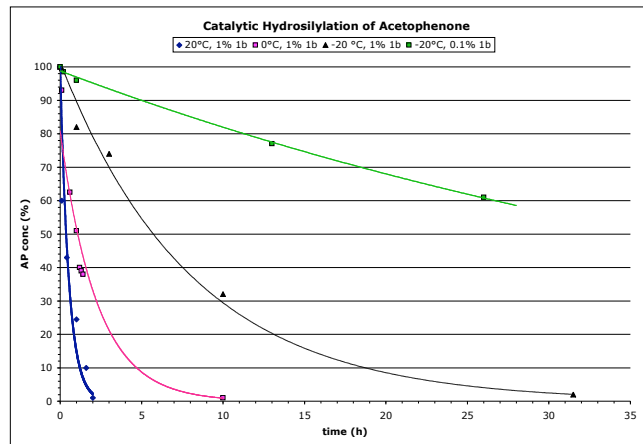
Cat (%)	T(°C)	time	Conv (%)	ee (%)	TON
1	-20	1 d	90	26	90
0.2	-20	6 d	90	26	450
0.1	-20	12 d	90	26	900
1	-34	2 d	90	32	90
1	0	4 h	90	12	90
1	20	1 h	90	<5	90
1 [a]	-20	1 d	90	26	90
0.1 [b]	-20	6 d	90	24	900
1	-20	7 d	60	26	60
1 [c]	-20	1 d	60	27	60

[a] Addition of 3 equiv carbene. [b] Containing 5% Rh₂(cod)₂Cl₂. [c] Methyl naphthyl ketone instead of acetophenone

Herrmann, W. A. et al. *Angew. Chem. Int. Ed.* **1996**, *35*, 2805.

Chiral NHCs for Enantioselective Hydrosilylation Low e.e.'s are Independent of Reaction Conditions

■ Optimization with Catalyst 1b

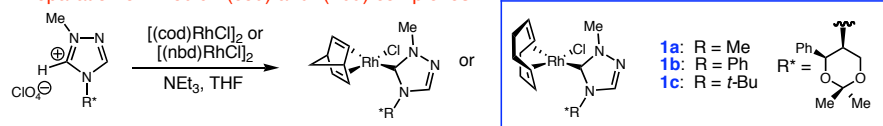


- both complexes **1a**, **1b** are active in the hydrosilylation without an inductive period, even at lower temperatures
- e.e.'s are independent of the catalyst concentration and the degree of conversion
- the NHC remains bound to the metal center - the dissociated ligand would not be stable under reaction conditions

Herrmann, W. A. et al. *Angew. Chem. Int. Ed.* **1996**, *35*, 2805.

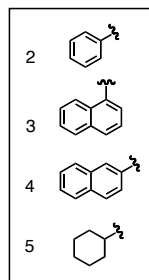
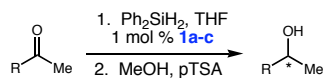
Chiral (Triazolinylidene)rhodium Complexes Another Example for Hydrosilylation

■ Preparation of Rhodium(cod) and -(nbd) complexes



- COD complexes give better e.e.'s than NBD because COD is bigger and restricts rotation around the Rh - carbene bond

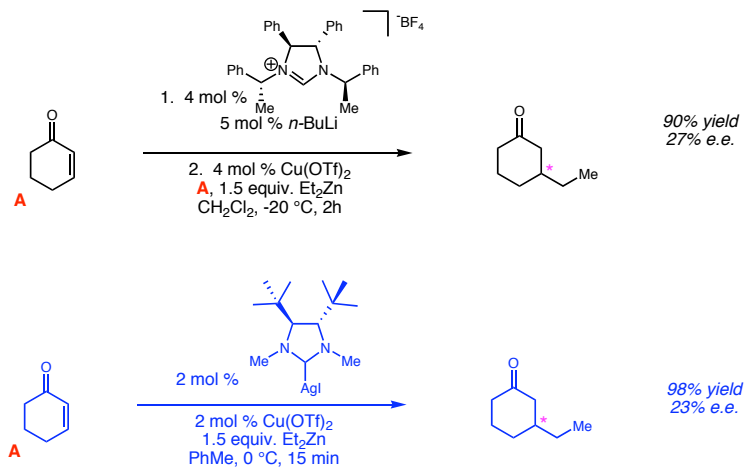
■ Hydrosilylation with Catalysts 1



Catalyst	Ketone	T (°C)	Time	Yield (%)	ee (%)
4a	9	22	4 h	90	20 (<i>S</i>)
4c	9	11	6 d	60	40 (<i>R</i>)
4a	10	42	4 h	80	37 (<i>R</i>)
4b	10	2	10 d	40	32 (<i>R</i>)
4a	11	2	5 d	90	19 (<i>S</i>)
4c	11	22	16 h	40	24 (<i>R</i>)
4a	12	-10	6 d	75	44 (<i>S</i>)
4b	12	2	4 d	80	43 (<i>S</i>)
4c	12	22	3 d	70	43 (<i>R</i>)

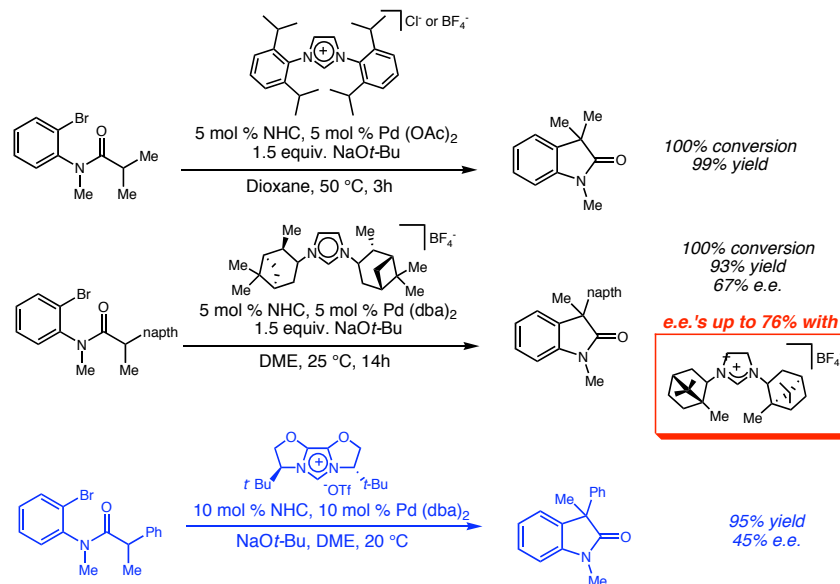
Enders, D. A.; Gielen, H.; Breuer, K. *Tetrahedron: Asymmetry*. **1997**, *21*, 3571.
Enders, D. A. et al. *Eur. J. Inorg. Chem.* **1998**, 913.

Enantioselective 1,4-Additions with Copper Systems



Guillen, F.; Winn, C. L.; Alexakis, A. *Tetrahedron: Asymmetry*. **2001**, *12*, 2083.
 Pytkowicz, J.; Roland, S.; Mangeney, P. *Tetrahedron: Asymmetry*. **2001**, *12*, 2087.

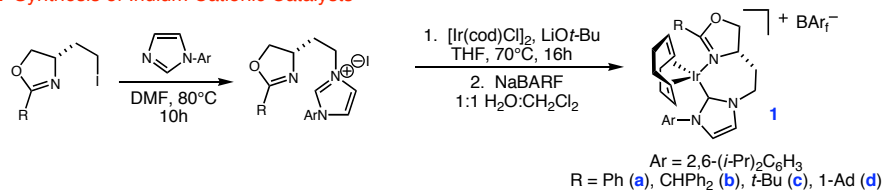
Chiral Catalysts for Syntheses of Oxindoles by α -Aryl Amination



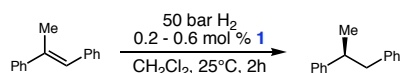
Lee, S.; Hartwig, J. F. *J. Org. Chem.* **2001**, *66*, 3402.
 Glorius, F.; Altenhoff, G.; Goddard, R.; Lehmann, C. *Chem. Commun.* **2002**, 2704.

Chiral Imidazolylidene Ligands for Asymmetric Hydrogenation First Examples of Practical Enantioselectivities with NHCs

Synthesis of Iridium Cationic Catalysts

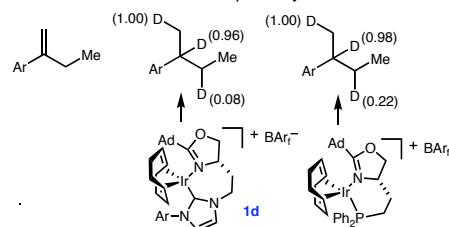


Hydrogenation with Catalysts 1a-d



3	e.e. (%)	yield (%)
a	13	25
b	25	12
c	40	33
d	98	66

- limited to tri-substituted (*E*)-aryl alkenes
- the marked differences in enantioselectivities when comparing complexes **1c** and **1d** is surprising
- direct hydrogenation, offers advantages over phosphines which have other mechanistic pathways



Burgess, K. et al. *J. Am. Chem. Soc.* **2001**, 123, 8878.

Chiral Imidazolylidene Ligands for Asymmetric Hydrogenation Scope and Limitations

Limited Scope but Useful E.e.'s

	1.0 mol% 3d	99 % Yield	93% e.e. (<i>R</i>)
	0.6 mol %	99%	97% (<i>S</i>)
	0.6 mol %	94%	84%
	1.0 mol %	99%	93%
	0.6 mol %	99%	91% (<i>S</i>)
	1.0 mol %	95%	78% (<i>R</i>)
	0.3 mol %	91%	31% (<i>R</i>)

- first example of chiral imidazolylidene complexes that induces high enantioselectivities
- *Z*- and 1,1-disubstituted alkenes gave lower e.e.'s
- ease of synthesizing carbene ligands over phosphine ligands

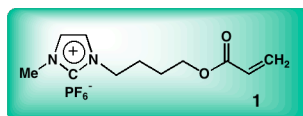
Powell, M. T.; Hou, D.-R.; Perry, M. C.; Cui, X.; Burgess, K. *J. Am. Chem. Soc.* **2001**, 123, 8878.

Molecular Ordering of SWNT by NHC Ionic Liquids

■ Regular Single-Walled NanoTubes (SWNT) ground up in ethanol tend to give suspensions of highly tangled materials, "bucky gels"

■ NHCs untangle the bucky gels to give much finer bundles

- physically cross-link due to cation- π interactions between the imidazolium ions of the ionic liquids and the carbon nanotube surface.
- ionic liquids are non-volatile = bucky gels are thermally stable and do not shrivel under vacuum



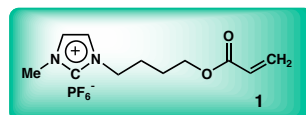
■ Preparation

- nanotube suspension + AIBN + **1** $\xrightarrow[10\text{ h}]{1\text{ hr}, \Delta}$ homogenous black polymer

Aida, T.; Fukushima, T. *Science*. 2003, 300, 2072. *C&EN*. June 30, 2003. 7.

Molecular Ordering of SWNT by NHC Ionic Liquids

■ What's the point?? Some important new properties.....



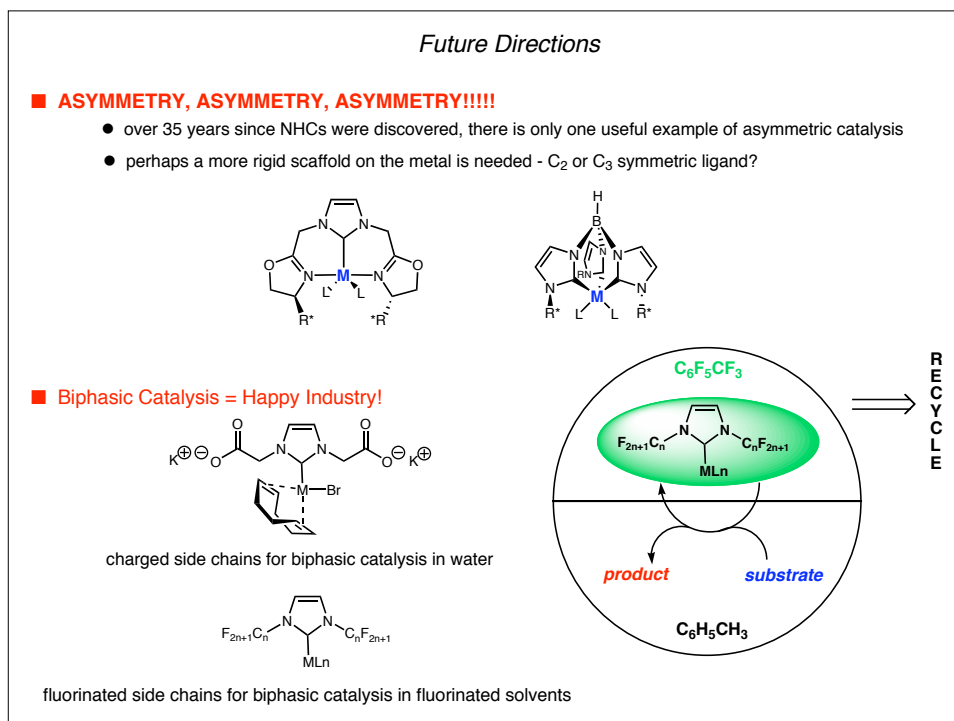
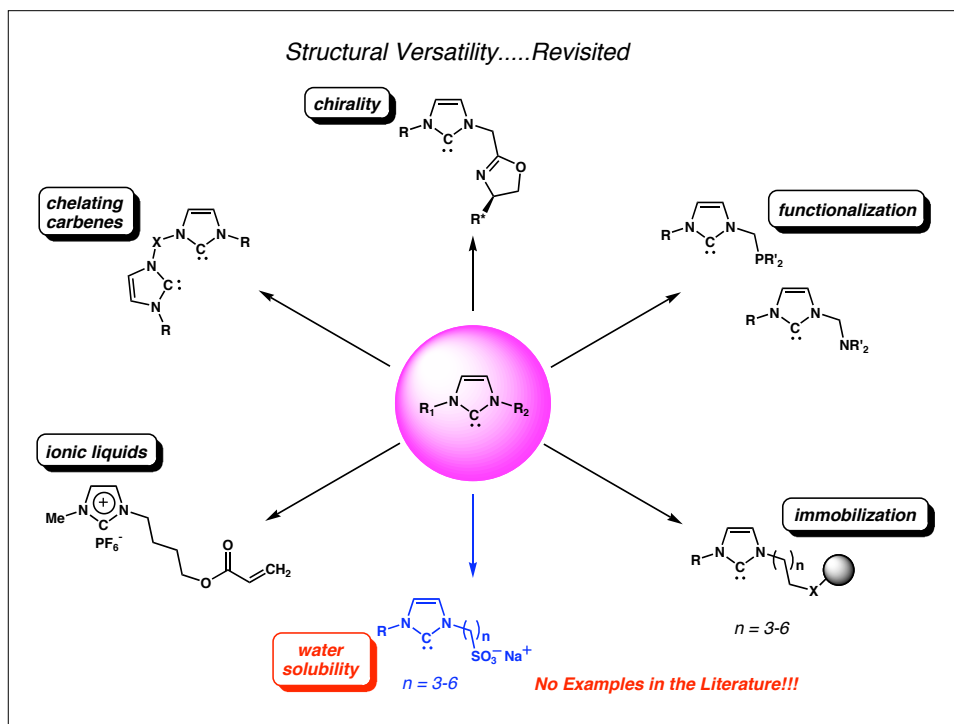
- SWNT were expected to be used as reinforcing polymers, but results thus far have been poor due to the poor adhesion at the polymer/SWNT surface
- bucky-gel-based polymer takes advantage of the strong affinity of NHC ion towards π -electronic surface of the SWNT
- hardness enhanced by 400% because of the strong interfacial interaction between the nanotubes and polymer of **1**
- the polymer/SWNT composite is highly electroconductive, whereas a polymer of **1** alone is essentially an insulator

3.8 weight % of SWNT gives a conductance of 0.56 S/cm

■ These properties have potential utility in:

- novel electronic devices
- coating materials
- antistatic materials

Aida, T.; Fukushima, T. *Science*. 2003, 300, 2072. *C&EN*. June 30, 2003. 7.



Conclusions

- N-Heterocyclic carbenes are an emerging class of transition metal ligands for organometallic catalysis.
- NHCs are easier to make and store than their phosphine counterparts.
- NHCs are stronger σ -donors than the most electron rich phosphine - less likely to dissociate from the metal during the reaction
- As the NHC goes from salt to free carbene to bound carbene, it loses π delocalization.
- NHCs show a range of versatility as ligands.
- Although many chiral imidazolylidene metal complexes exist, only one example of useful asymmetric catalysis has been shown thus far.
 - for a review of the chiral complexes made, see:
Perry, M. C.; Burgess, K. *Tetrahedron: Asymmetry*. **2003**, *14*, 951
- The area of N-heterocyclic carbenes has only partially been explored - there is a need for more ideas and work given the versatility for functionalization these ligands have.