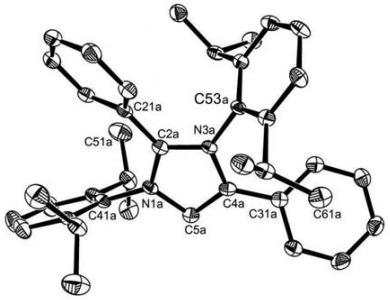
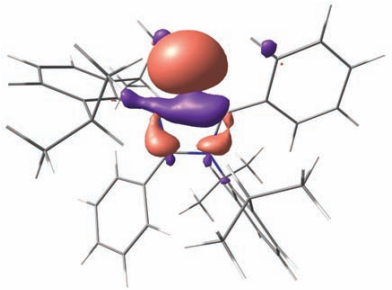
Beyond Conventional NHCs
-abnormal NHC-

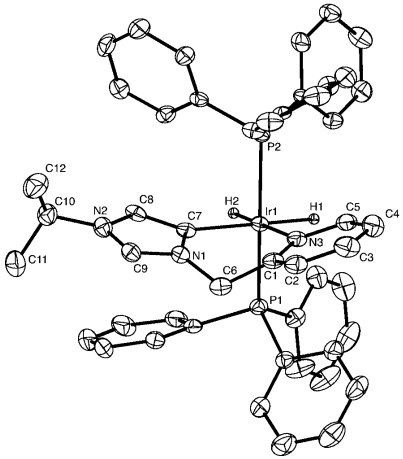
Sep. 29, 2012

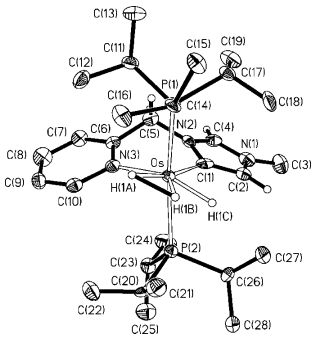
Kumiko Yamamoto

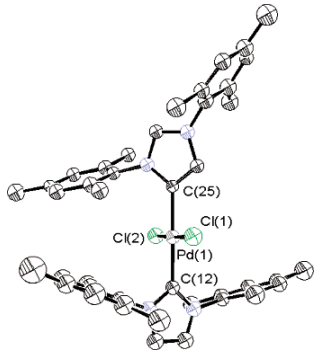
Contents











carbenes
The electrically neutral species H_2C: 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 Gold Book-carbenes (http://goldbook.iupac.org/C00806.html)

singlet vs triplet

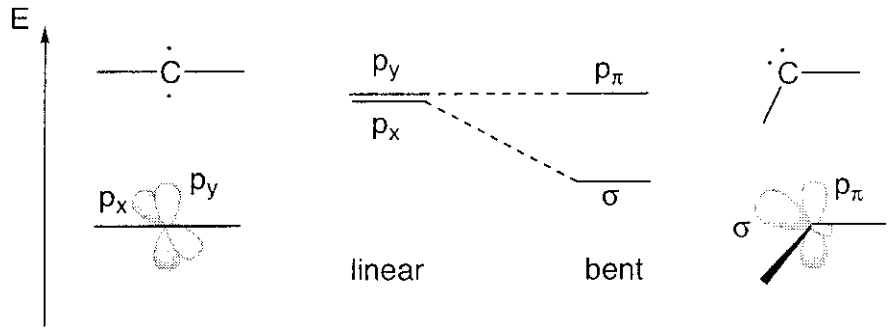


Figure 2. Relationship between the carbene bond angle and the nature of the frontier orbitals.

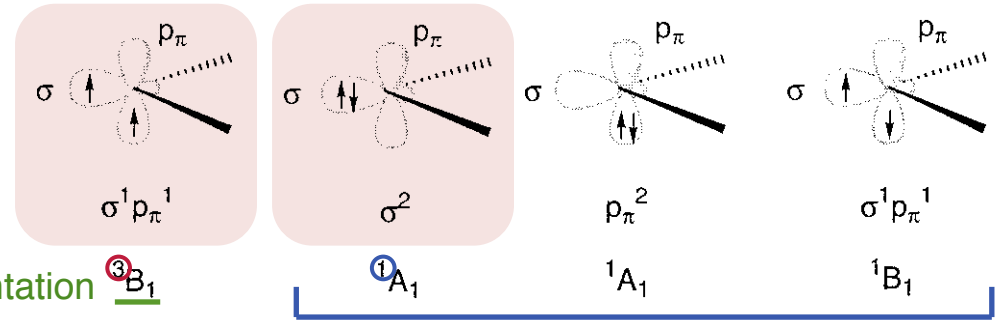


Figure 3. Electronic configurations of carbenes.

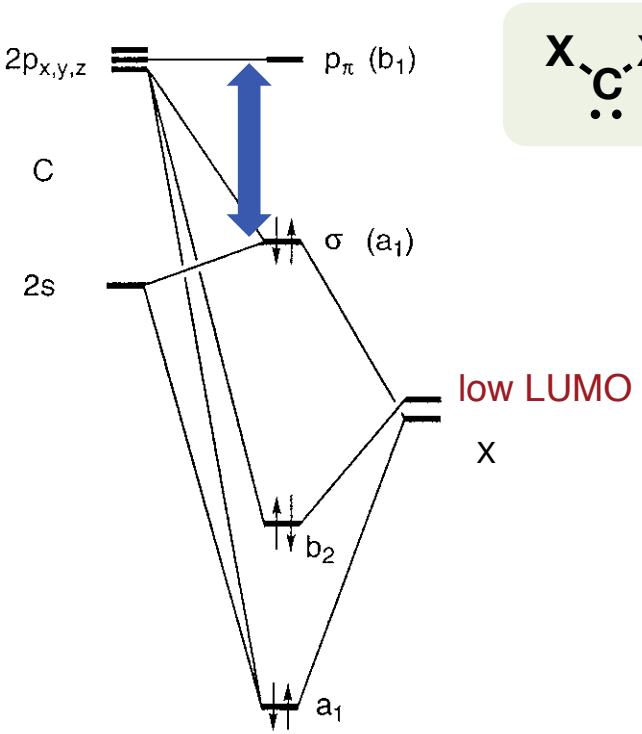
triplet state

singlet state

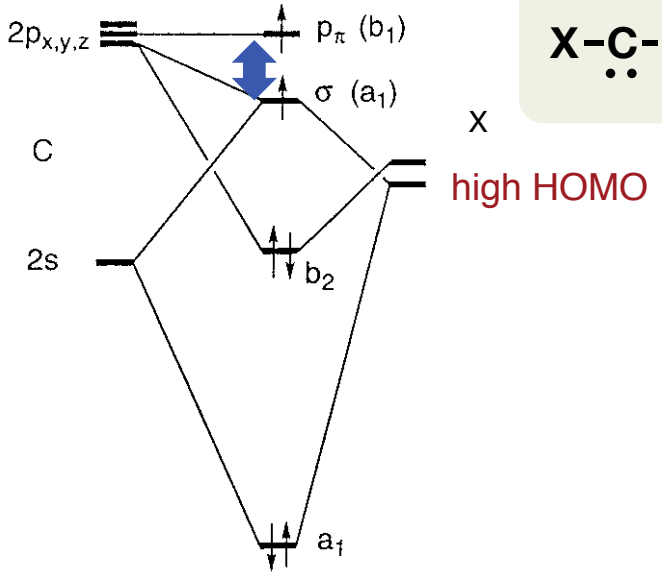
D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.

electronic effect -inductive effect-

σ-electron-withdrawing substituents



σ-electron-donating substituents

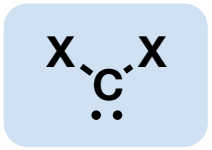


σ-electron withdrawing substituents favor the singlet state.

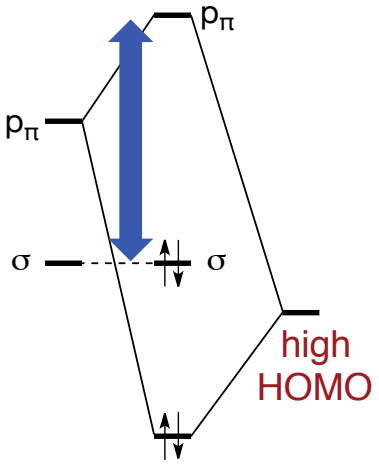
D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.

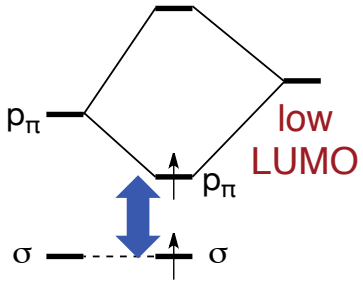
electronic effect -mesomeric effect-

X: π-electron-donating substituents
F, Cl, Br, I, NR_2, PR_2, OR, SR, SR_3, …



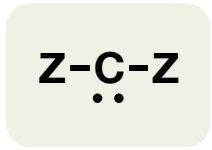
bent singlet carbene



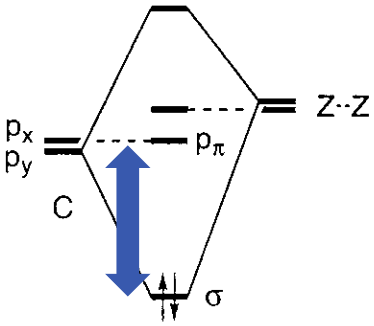


bent carbene
with π-EWG substituents

X: π-electron-withdrawing substituents
COR, CN, CF_3, BR_2, SiR_3, PR_3^+, …



linear singlet carbene



- mesomeric effects can play a more significant role.
- (X,X)-carbenes are predicted to be bent singlet carbenes.
- (Z,Z)-carbenes are predicted to be linear singlet carbenes.

D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39.
大学院講義, pp.284.

steric effect

- bulky substituents kinetically stabilize all types of carbenes
- if electronic effects are negligible…

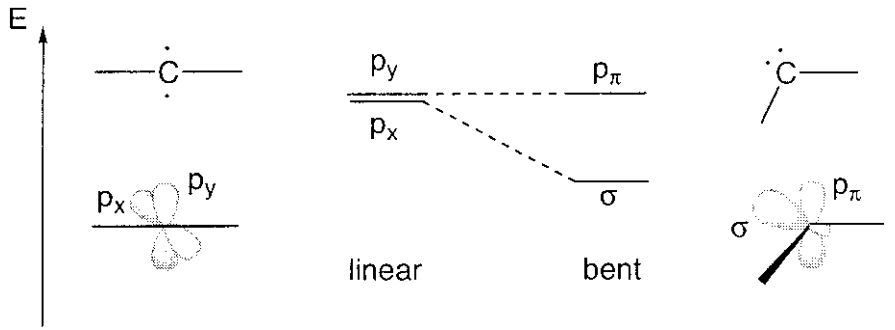
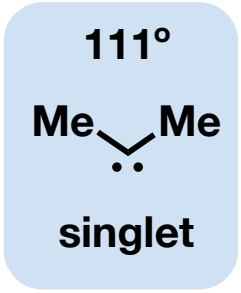
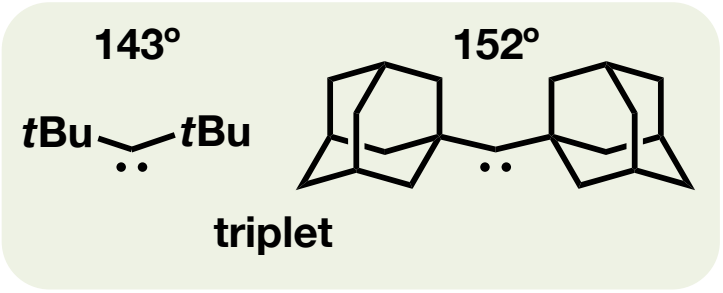


Figure 2. Relationship between the carbene bond angle and the nature of the frontier orbitals.

A linear geometry favors the triplet state.





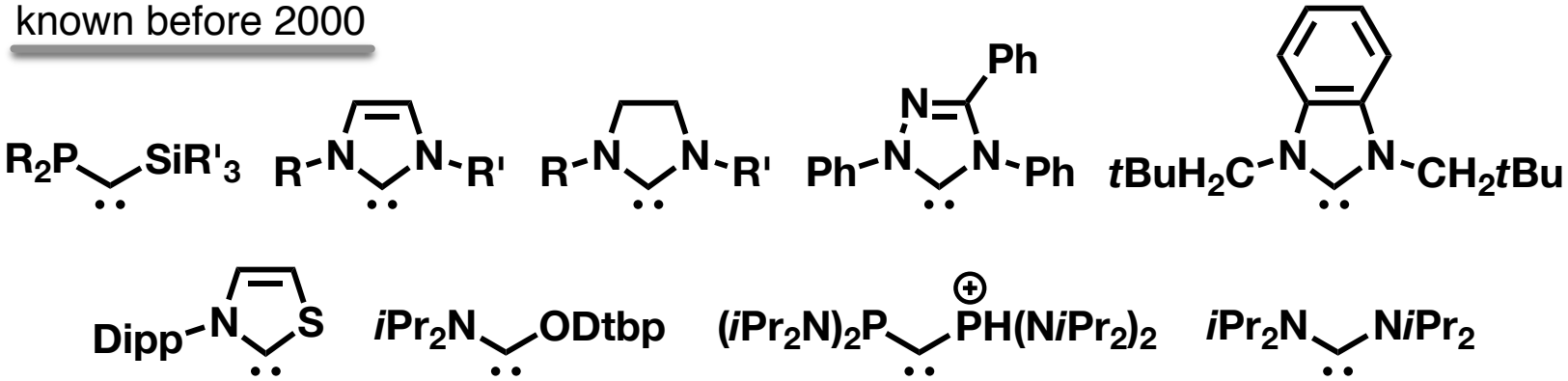
Bulky substituents favor the triplet state.

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

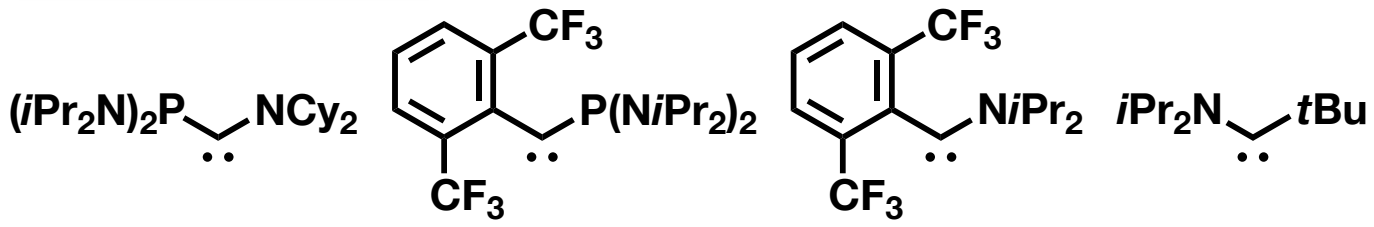
carbenes
The electrically neutral species H_2C: and its derivatives, in which the carbon is covalently bonded to two univalent groups of any kind or a divalent group and bears two nonbonding electrons, which may be spin-paired (singlet state) or spin-non-paired (triplet state).

IUPAC Gold Book-carbenes (http://goldbook.iupac.org/C00806.html)

known before 2000



discovered after 2000



and so on...

M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810.

Contents

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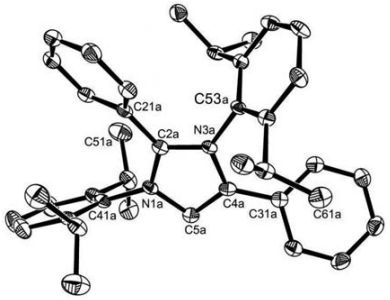
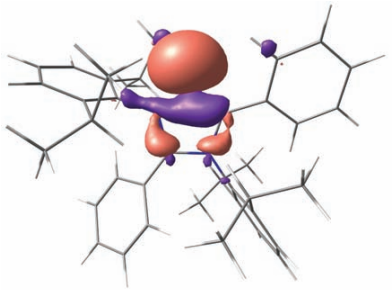
   first metal-NHC complex
   first free, isolable NHC
   NHCs as ligands for transition metals
   NHCs as organocatalysts

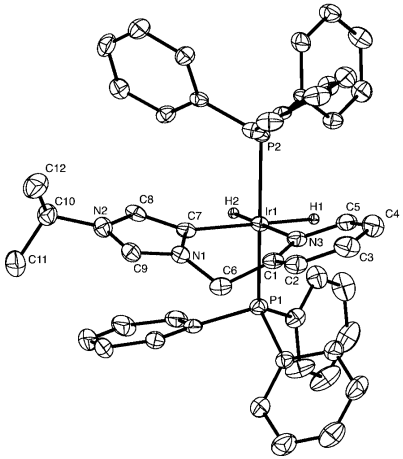
3. abnormal N-heterocyclic carbenes (aNHCs)

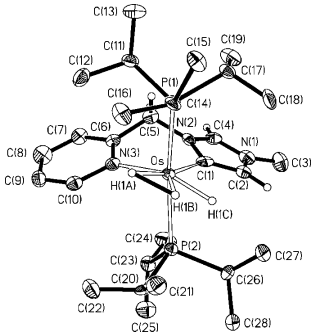
   first metal-aNHC complex
   first free aNHC
   C2- vs C4- bound carbene
   NHC vs aNHC
   application to catalysts

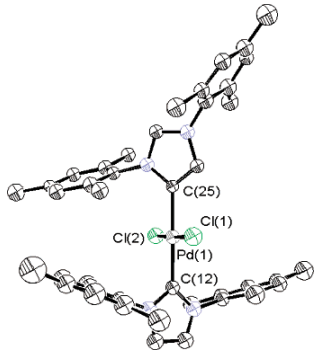
4. summary



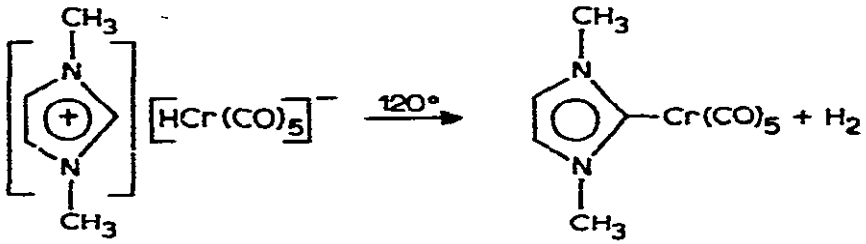






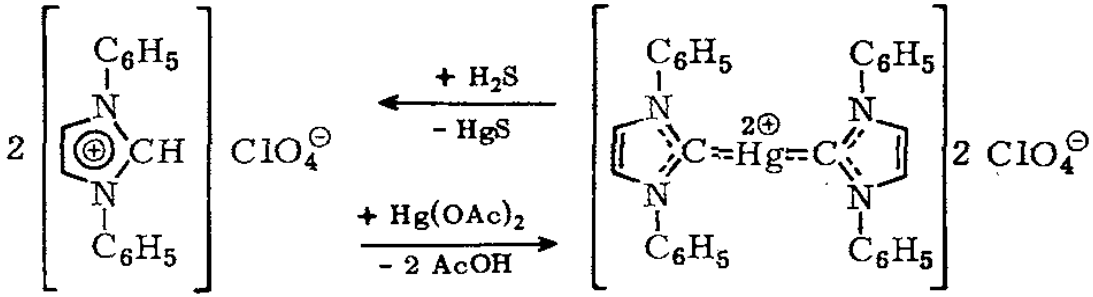


first metal-NHC complexes



pale yellow crystalline
air and thermally stable
mp. 100.5 °C
^{1}H NMR (d_6-acetone) δ = 7.24, 3.87 ppm

K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42.

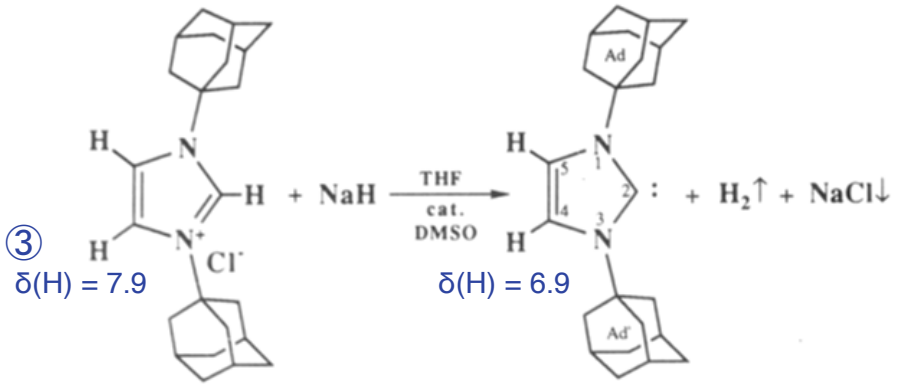


colorless rectangular plates
stable to acids
mp. ca. 370 °C (decomp.)

H.-W. Wanzlick, H.-J. Schönherr, *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141.

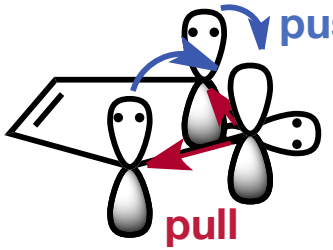
N-Heterocyclic Carbenes (NHCs)

first free, isolable NHC



colorless rectangular prism
stable in the absence of oxygen and moisture
mp. 240-241 °C

features of this NHC
① small N-C-N angle
② longer C-N bonds
③ diminished π-delocalization



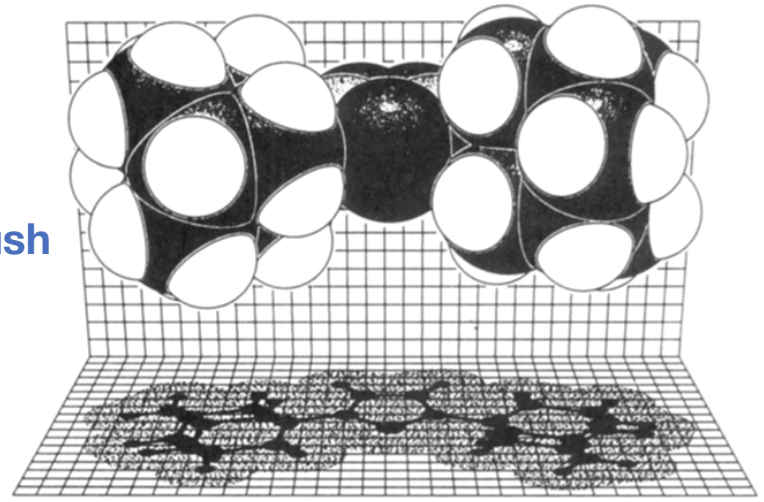


Figure 1. Space-filling KANVAS[1] drawing of the X-ray structure of **1**.

Table I. Selected Bond Lengths (pm) and Angles (deg) in **1**

	bond length		bond angle
② C_2-N_1	136.7 (2)	① $N_1-C_2-N_3$	102.2 (2)
C_2-N_3	137.3 (2)	$C_5-N_1-C_2$	112.1 (2)
C_4-C_5	133.8 (3)	$C_4-N_3-C_2$	112.3 (2)
N_1-C_5	138.2 (2)	$N_1-C_5-C_4$	107.2 (2)
N_3-C_4	138.6 (2)	$N_3-C_4-C_5$	106.2 (2)
$N_1-C_{1\text{-Ad}}$	148.2 (2)	$C_2-N_1-C_{1\text{-Ad}}$	123.4 (2)
$N_3-C_{1\text{-Ad}'}$	148.5 (2)	$C_2-N_3-C_{1\text{-Ad}'}$	122.1 (2)

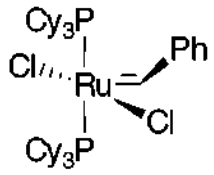
imidazolium salts 1.32 Å

imidazolium salts ca. 109°

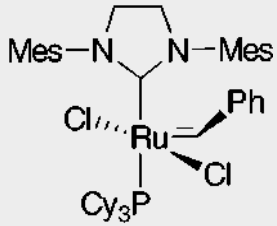
What made this NHC isolable?
▸ electronic stabilization
π-donation into the carbene p orbital
σ-electronegativity effects of the nitrogens
▸ steric stabilization

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

NHCs as ligands for transition metals



(1)
1st generation
Grubbs catalyst



(2)
2nd generation
Grubbs catalyst

strong σ-donation
→ enhance the dissociation of PCy_3
→ stabilize the 14-e intermedaite

steric bulk
→ stabilize the 14-e intermedaite

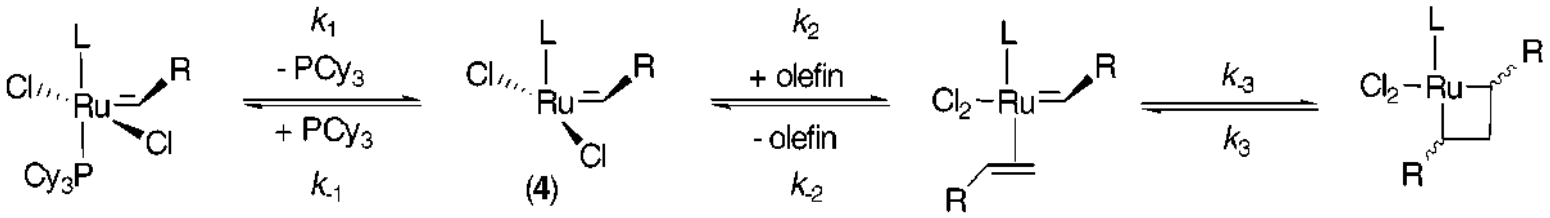


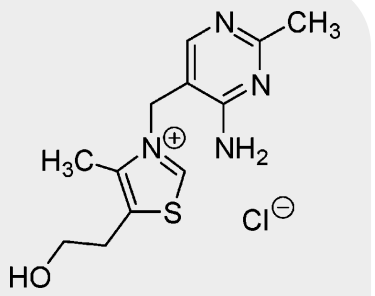
Table 2. Values for the k_{-1}/k_2 Ratio in Catalysts **1** and **2**

catalyst	T (°C)	k_1(intercept) (s^{-1})	k_B(predicted) (s^{-1})	k_{-1}/k_2
1	37	0.26	0.16	15300
2	50	0.0031	0.003	1.25

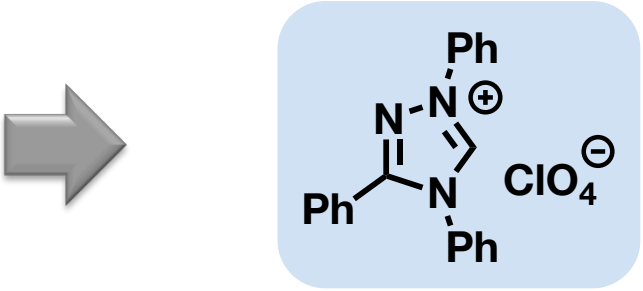
"the activity of catalyst **1** and **2** is not only related to the phosphine dissociation rate k_1, but also to the k_{-1}/k_2 ratio which determines whether the catalyst binds olefin or returns to its resting state"

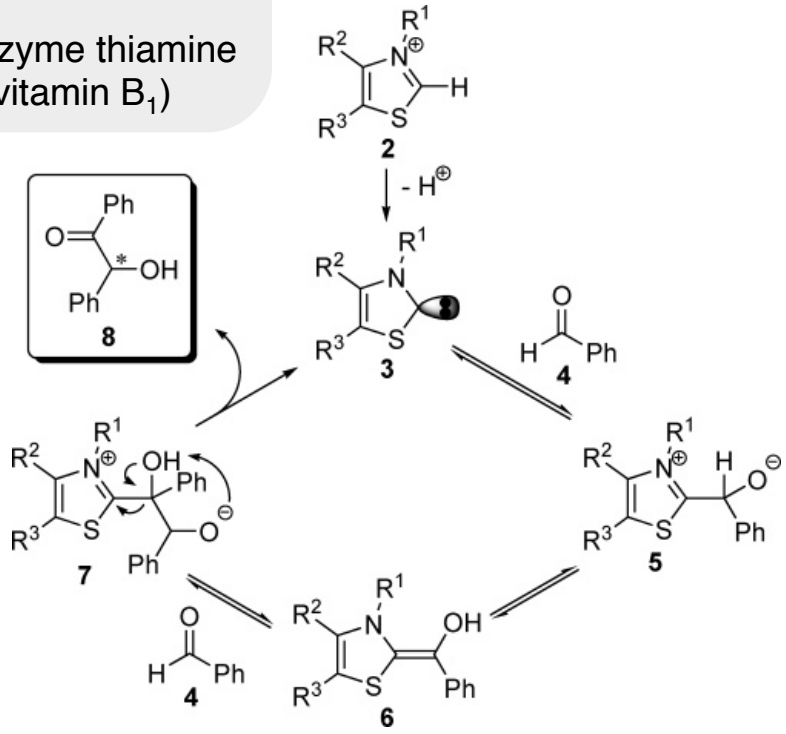
2nd generation Grubbs catalyst; M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953.
mechanistic study; M. S. Sanford, M. Ulman, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 749.
M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 6543.

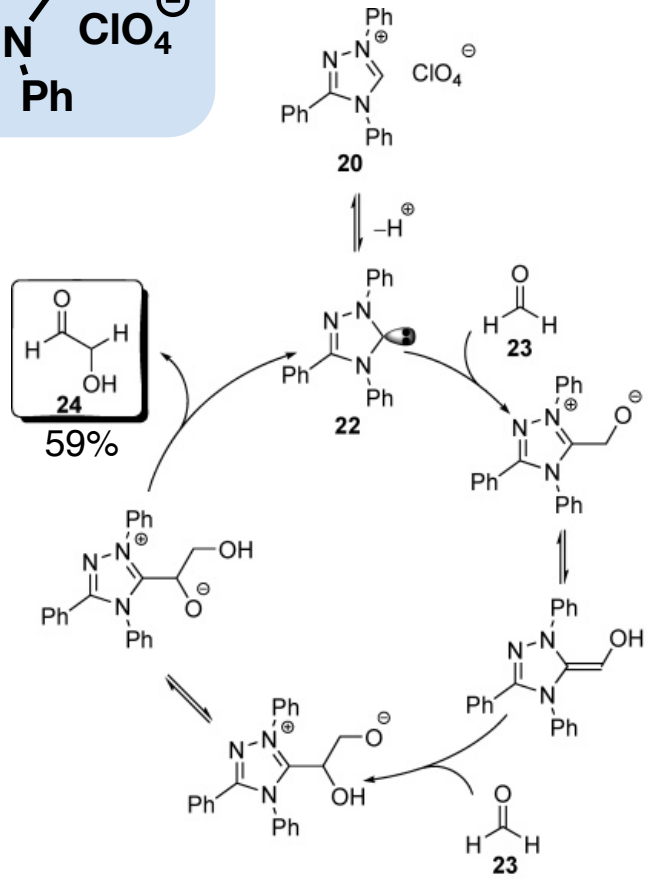
NHCs as organocatalysts



coenzyme thiamine
(vitamin B_1)







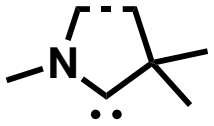
T. Ugai, S. Tanaka, S. Dokawa, *J. Pharm. Soc. Jpn.* **1943**, *63*, 296.
R. Breslow, *J. Am. Chem. Soc.* **1958**, *80*, 3719.
J. H. Teles, J.-P. Melder, K. Ebel, R. Schneider, E. Gehrer, W. Harder, S. Brode, D. Enders, K. Breuer, G. Raabe, *Helv. Chim. Acta.* **1996**, *79*, 61.

Cyclic Non-NHCs

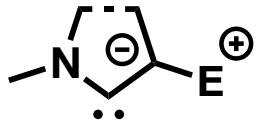
NHC

PHC
diphosphinocarbene

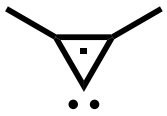
N-PHC
(amino)(phosphino)carbene



CAAC
(alkyl)(amino)carbene



N-YHC
(amino)(ylidic)carbene

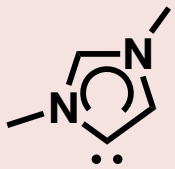


CP
cyclopropenylidene

CBA
cyclic bent allene

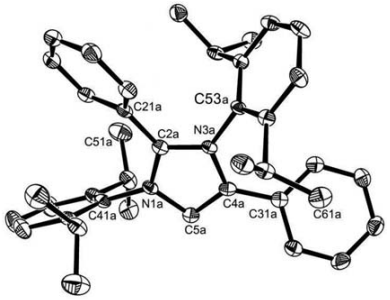
CCDP
cyclic carbodiphosphorane

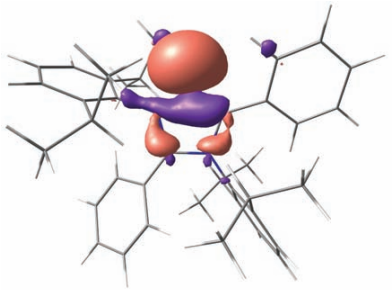
CVP
vinylidenephosphorane

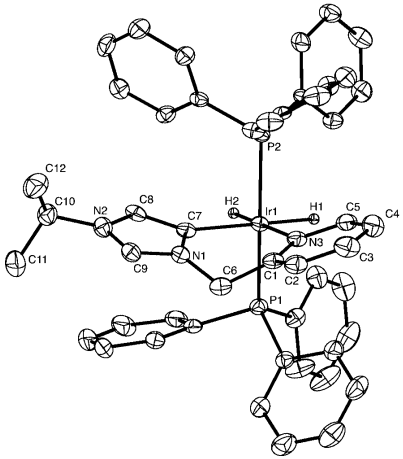


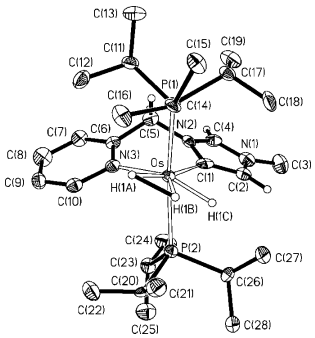
aNHC
abnormal-NHC

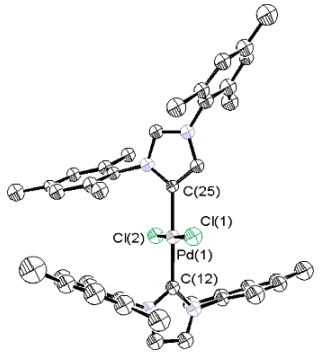
M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810.





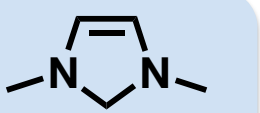






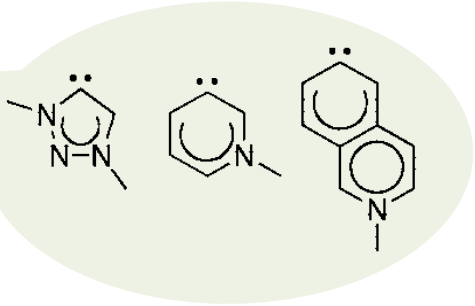
abnormal NHC (aNHC)
Those NHC ligands for which a canonical valence bond representation requires the introduction of additional formal charges on some nuclei.

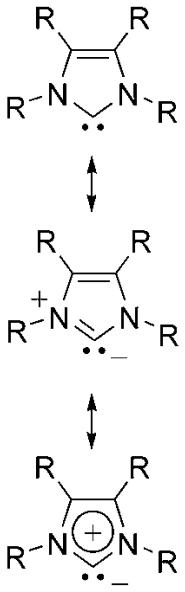
O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445.

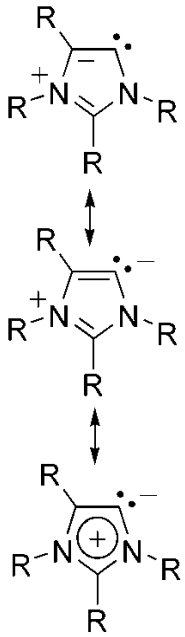


NHC

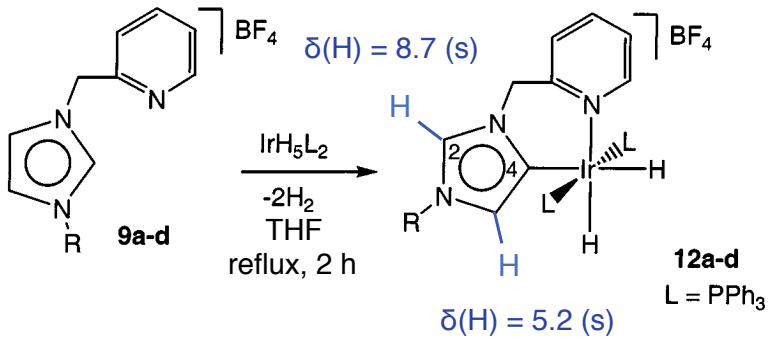
aNHC







First Example of Metal-aNHC Complex



colorless solid
stable toward air and moisture

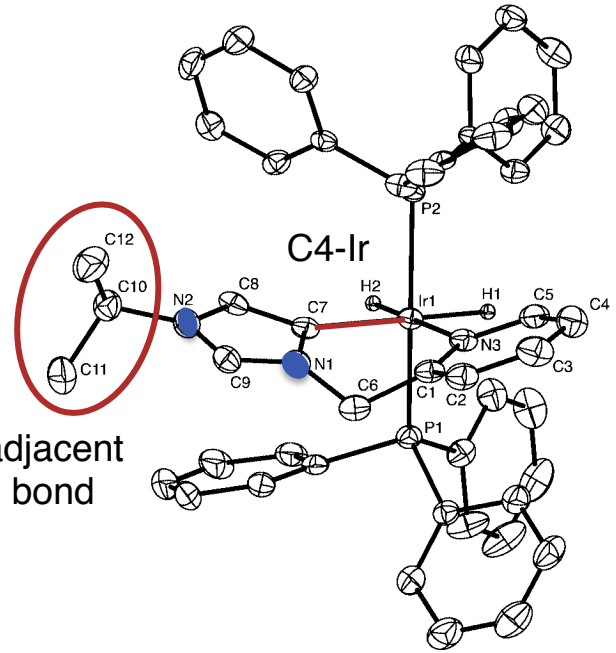
	R	yield (%)	mp. (°C)
12a	mesityl	79	255-257 (dec)
12b	*i*Pr	85	246-248 (dec)
12c	*n*Bu	68	229 (dec)
12d	Me	75 (C5/C2 = 1.2:1)	

①DMSO, 100 °C, 1 h
②DMSO, 160 °C

①no reaction
②gradual decomp.

①DMSO, 100 °C, several h
②DMSO, 100 °C, 3 d

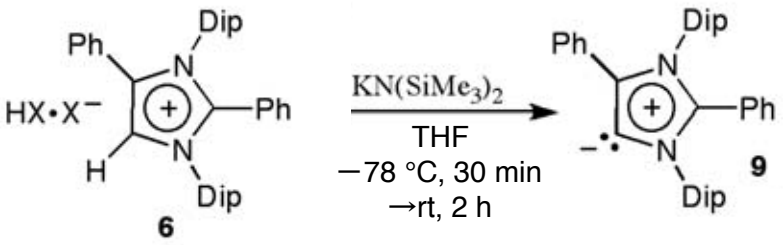
①C4/C2 = 1.2:1
②decomp.



*i*Pr is not adjacent
to the M-C bond

S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *Chem. Commun.* **2001**, 2274.
S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *J. Am. Chem. Soc.* **2002**, *124*, 10473.

First Example of Free aNHC



X = Cl, Br

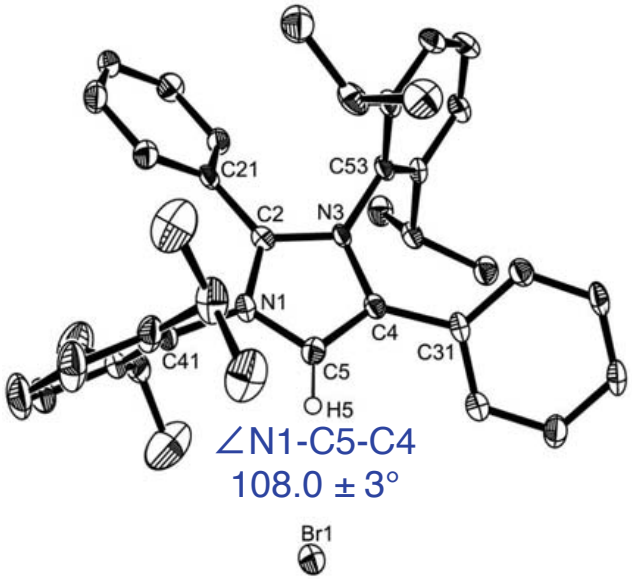
Dip: 2,6-di*iso*propylphenyl

yellow crystal
sensitive to air
stable at rt for a few days
mp. 65 °C (dec)

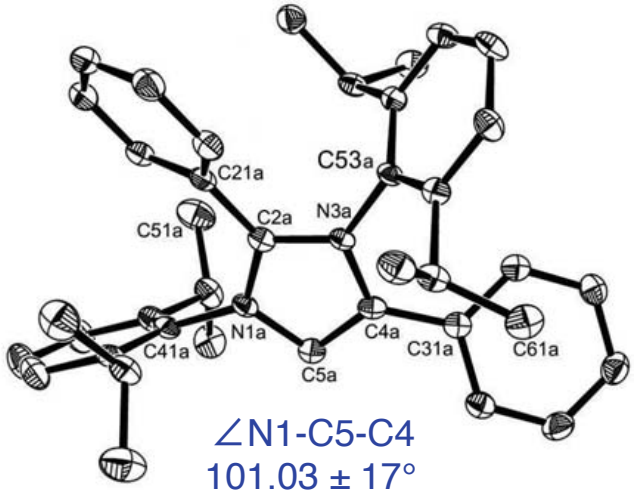
68% yield (X = Cl)
green powder

↓ recrystallization from Hex. at −78 °C

yellow crystal



∠N1-C5-C4
108.0 ± 3°

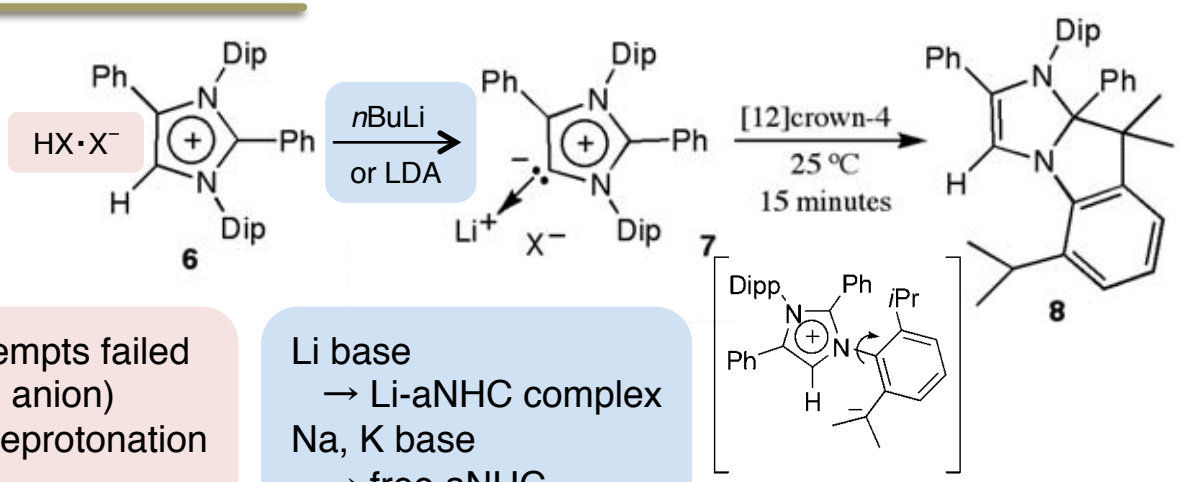


∠N1-C5-C4
101.03 ± 17°

E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science*, **2009**, *326*, 556.

First Example of Free aNHC

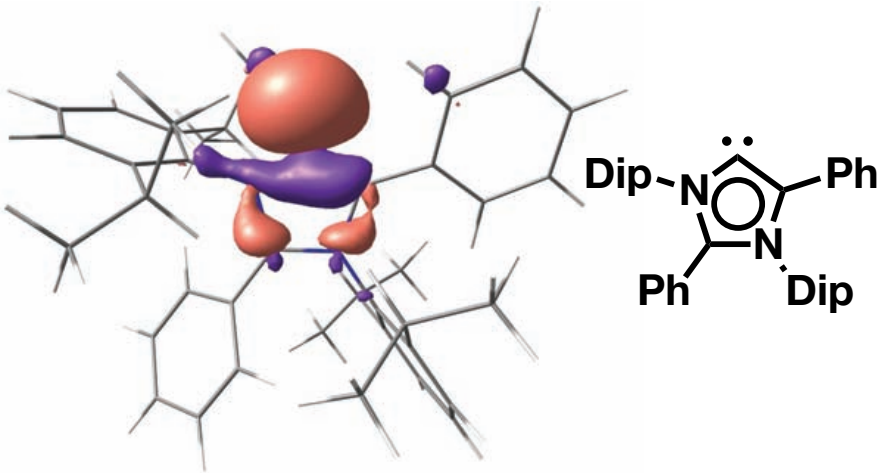
counter anion and base effects



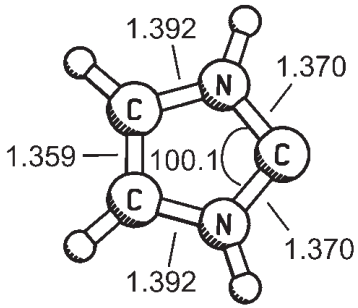
X = BF_4^- → all attempts failed
X = Cl^-, Br^- (small anion)
→ promote the deprotonation reaction at C5

Li base
→ Li-aNHC complex
Na, K base
→ free aNHC

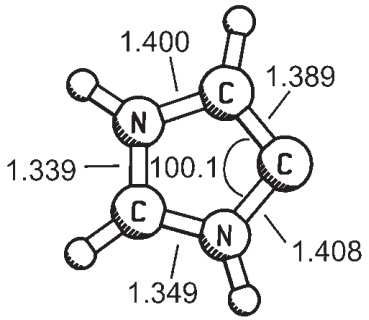
HOMO of aNHC



relative energy



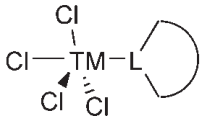
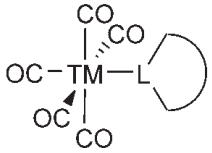
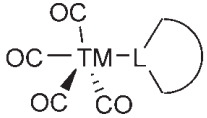
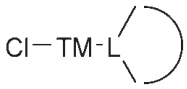
NHC (0.0 kcal/mol)



aNHC (17.4 kcal/mol)

R. Tonner, G. Heydenrych, G. Frenking, *Chem. Asian J.* **2007**, *2*, 1555.
E. Aldeco-Perez, A. J. Rosenthal, B. Donnadieu, P. Parameswaran, G. Frenking, G. Bertrand, *Science*, **2009**, *326*, 556.

kinetic vs thermodynamic -calculation-

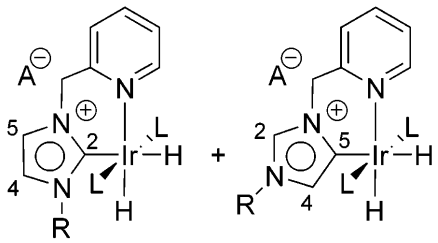
Descriptor	Complex[a]	Central atoms
1		Ti (**1Ti**) Zr (**1Zr**) Hf (**1Hf**)
2		Cr (**2Cr**) Mo (**2Mo**) W (**2W**)
3		Fe (**3Fe**) Ru (**3Ru**) Os (**3Os**)
4		Cu (**4Cu**) Ag (**4Ag**) Au (**4Au**)

nNHC(n)

aNHC(a)

L	nNHC E_{rel}	aNHC E_{rel} (kcal/mol)
Free L	0.0	17.4
1Ti	0.0	11.9
1Zr	0.0	11.7
1Hf	0.0	11.7
2Cr	0.0	13.7
2Mo	0.0	13.6
2W	0.0	13.5
3Fe	0.0	13.7
3Ru	0.0	13.4
3Os	0.0	13.2
4Cu	0.0	13.4
4Ag	0.0	12.8
4Au	0.0	13.2

R. Tonner, G. Heydenrych, G. Frenking, *Chem. Asian J.* **2007**, *2*, 1555.



2 **3**

	nNHC (**2**) *E* (kcal/mol)	aNHC (**3**) *E* (kcal/mol)
free	0	14.5
Ir	0	10.1

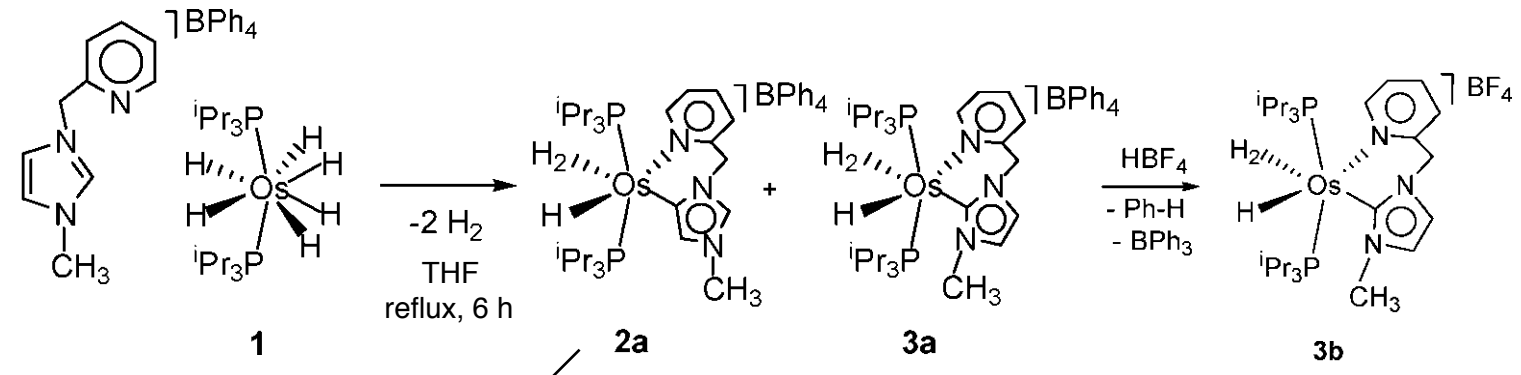
*didn't introduce anion effect.

L. N. Appelhans, D. Zuccaccia, A. Kovacevic, A. R. Chianese, J. R. Miecznikowski, A. Macchioni, E. Clot, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **2005**, *127*, 6299.

- C2 is more stable than C4
- the energy differences between M-NHC and M-aNHC are decreased relative to the free ligands.

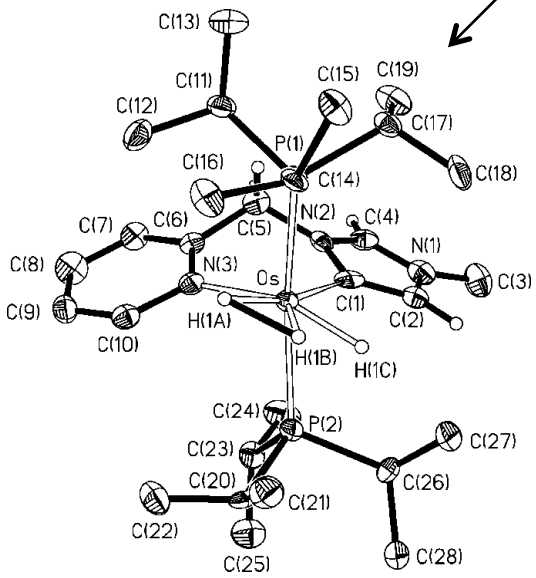
C2- vs C4-bound Carbene

kinetic vs thermodynamic -experimental-

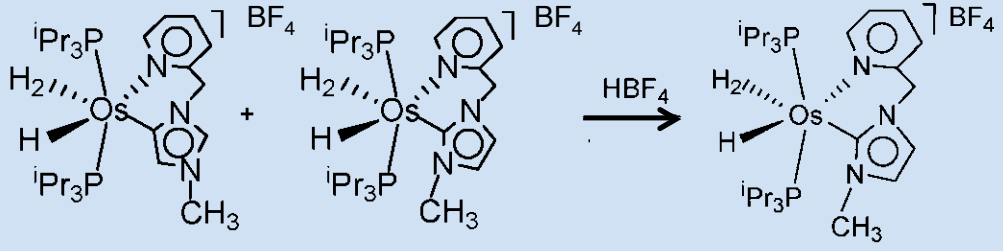


1 **2a** **3a** **3b**

63% (**2a**:**3a** = 5.3:1)



2a (yellow crystal)



2b **3b** **3b**

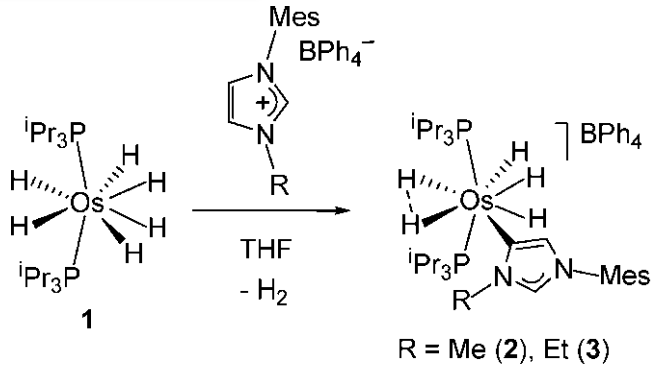
2b:**3b** = 1.3:1

C4-bound carbene isomerized to its thermodynamically favored C2-bound carbene in acidic condition.

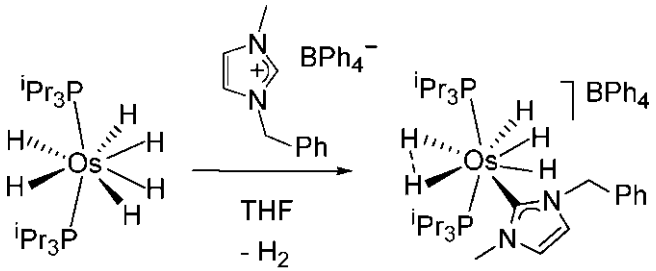
M. Baya, B. Eguillor, M. A. Esteruelas, M. Oliván, E. Qñate, *Organometallics*, **2007**, *26*, 6556.

C2- vs C4-bound Carbene

wingtip groups

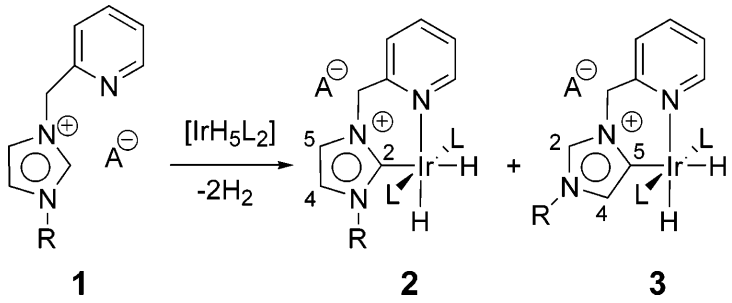


71% (**2**) abnormal
67% (**3**) abnormal



69% normal

B. Eguillor, M. A. Esteruelas, M. Oliván, M. Peurta, *Organometallics*, **2008**, *27*, 445.



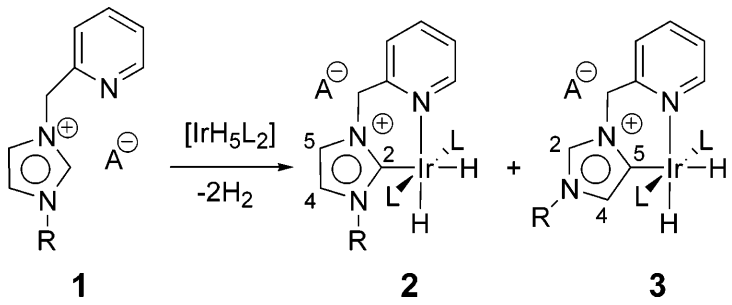
R	A	**2** (normal)	**3** (abnormal)
Me	Br	91	9
*i*Pr	Br	84	16
Me	BF_4	45	55
*i*Pr	BF_4	0	100

L. N. Appelhans, D. Zuccaccia, A. Kovacevic, A. R. Chianese, J. R. Miecznikowski, A. Macchioni, E. Clot, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **2005**, *127*, 6299.

Large wingtip groups favor C4-bound carbene.

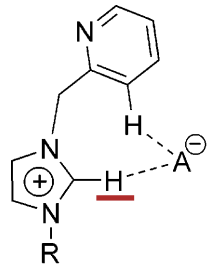
C2- vs C4-bound Carbene

counter anion effect



R	A	**2** (normal)	**3** (abnormal)
Me	Br	91	9
Me	OAc	80	20
Me	BF_4	45	55
Me	PF_6	50	50
Me	SbF_6	11	89

imidazolium **1** ion-pair solution structure

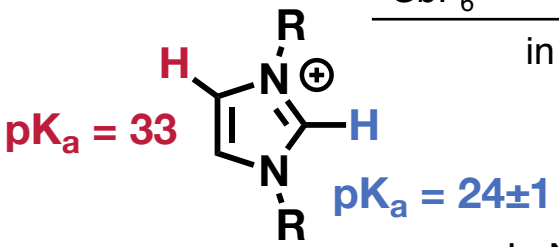


1

A	δ(H) (ppm)
Br	9.71
BF_4	8.66
PF_6	8.44
SbF_6	8.38

in $CDCl_3$

stronger H···A bond



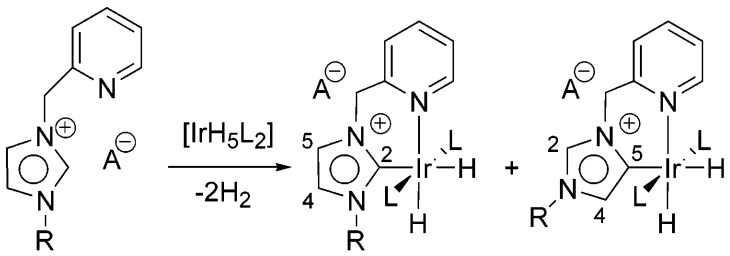
ion-pair energetics

anion	**2** *E* (kcal/mol)	**3** *E* (kcal/mol)
none	0	10.1
Br	0	3.8
OAc	0	0.9
BF_4	0	1.6

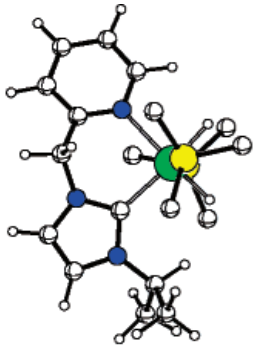
L. N. Appelhans, D. Zuccaccia, A. Kovacevic, A. R. Chianese, J. R. Miecznikowski, A. Macchioni, E. Clot, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **2005**, *127*, 6299.
O. Schuster, L. Yang. H. G. Raubenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445.

C2- vs C4-bound Carbene

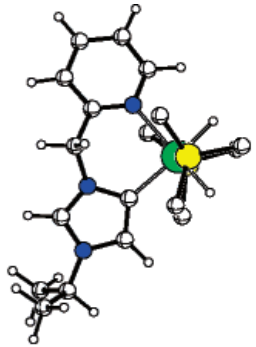
counter anion effect



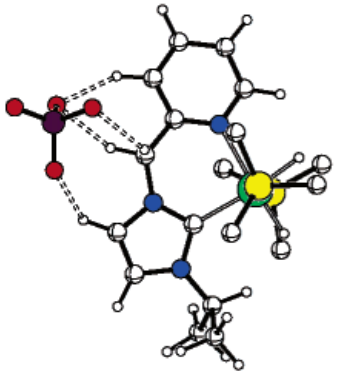
1 **2** **3**



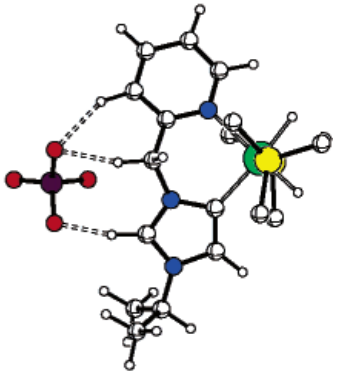
free 2 (R = *i*Pr)



free 3 (R = *i*Pr)



BF_4-2 (R = *i*Pr)



BF_4-3 (R = *i*Pr)

	free 2	BF_4-2	free 3	BF_4-3
Ir-H_c (Å)	1.600	1.608	1.623	1.630
Ir-C2	2.115	2.114	-	-
Ir-C5	-	-	2.098	2.107
C2-H	-	-	1.079	1.092
C5-H	1.079	1.082	-	-

aNHC vs NHC

- the higher electron-donating power of aNHC
  - →shorter Ir-C bond (2.098 vs 2.115)
  - →higher trans effect (1.623 vs 1.600)

counter anion effect

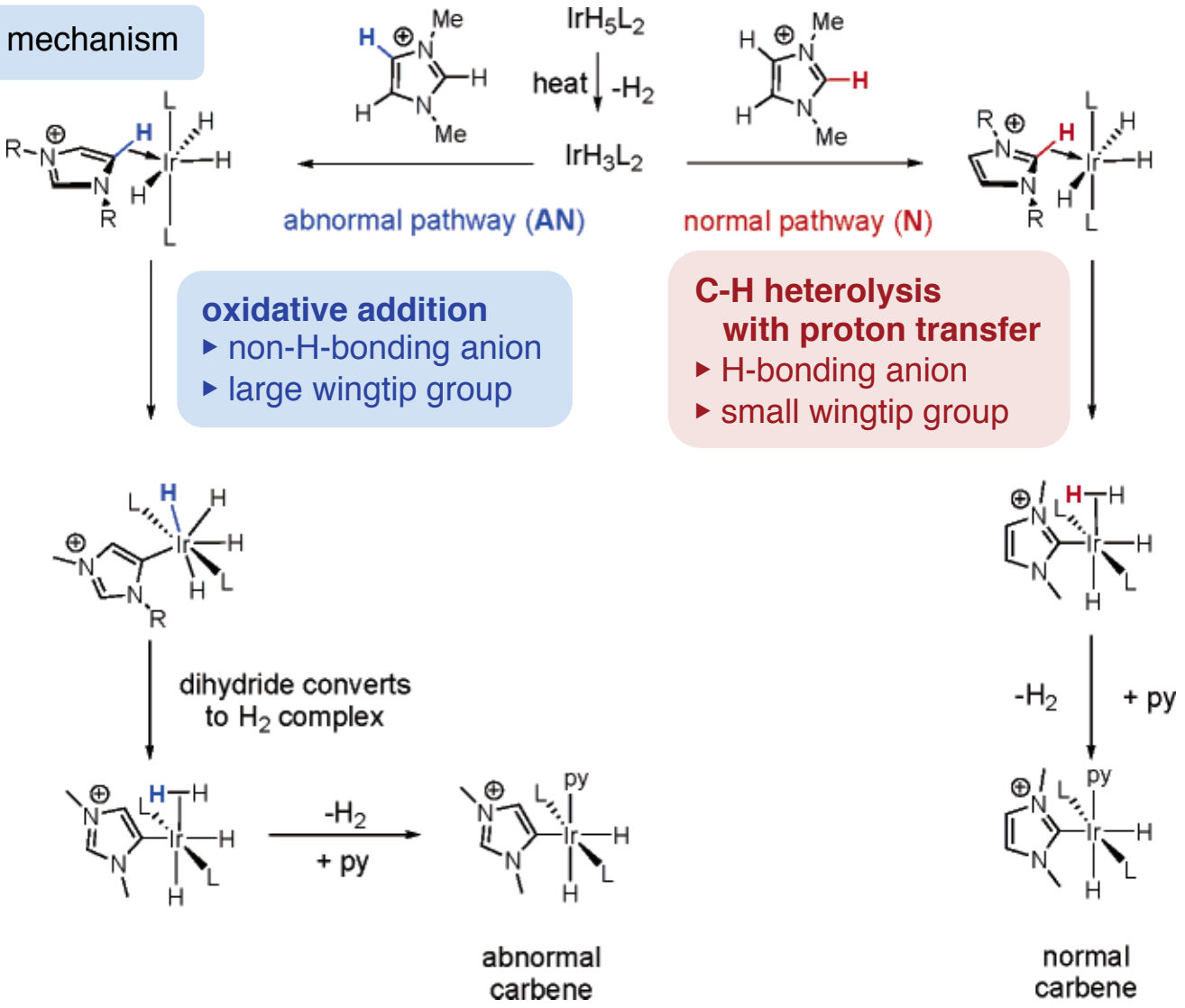
- the presence of H-bonding interactions
  - →longer C-H bond (1.082 vs 1.079 / 1.092 vs 1.079)

L. N. Appelhans, D. Zuccaccia, A. Kovacevic, A. R. Chianese, J. R. Miecznikowski, A. Macchioni, E. Clot, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **2005**, *127*, 6299.

C2- vs C4-bound Carbene

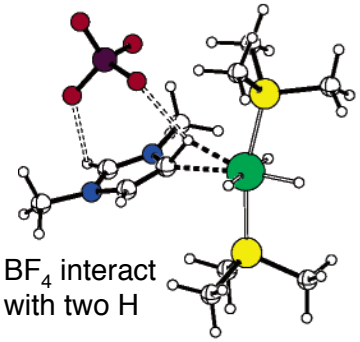
counter anion effect

proposed mechanism

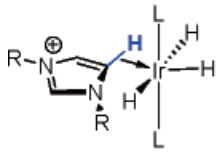


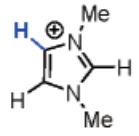
L. N. Appelhans, D. Zuccaccia, A. Kovacevic, A. R. Chianese, J. R. Miecznikowski, A. Macchioni, E. Clot, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **2005**, *127*, 6299.

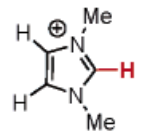
C2- vs C4-bound Carbene



BF_4 interact with two H







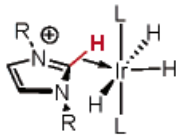
IrH_5L_2

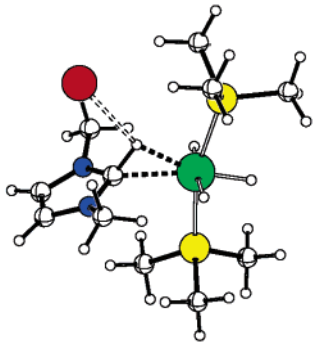
heat, $-H_2$

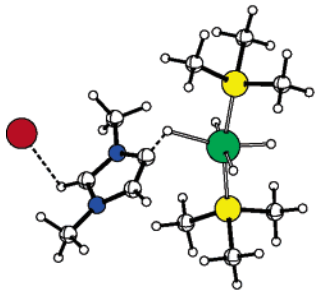
IrH_3L_2

abnormal pathway (**AN**)

normal pathway (**N**)



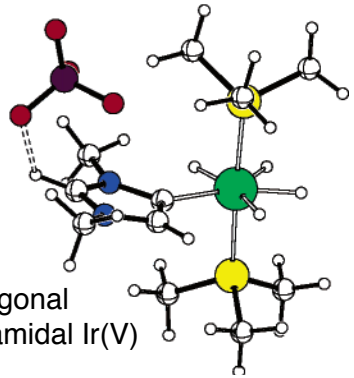




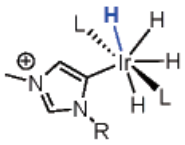
Br anion interact strongly with C2-**H**

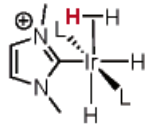
oxidative addition
- non-H-bonding anion
- large wingtip group

C-H heterolysis with proton transfer
- H-bonding anion
- small wingtip group

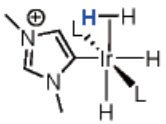


pentagonal bipyramidal Ir(V)



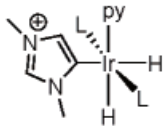


dihydride converts to H_2 complex



$-H_2$

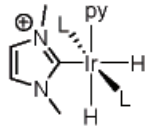
+ py



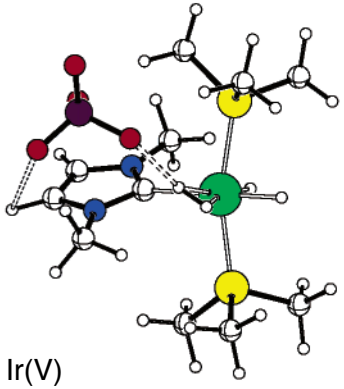
abnormal carbene

$-H_2$

+ py



normal carbene



not Ir(V)
but Ir(III) dihydrogen complex

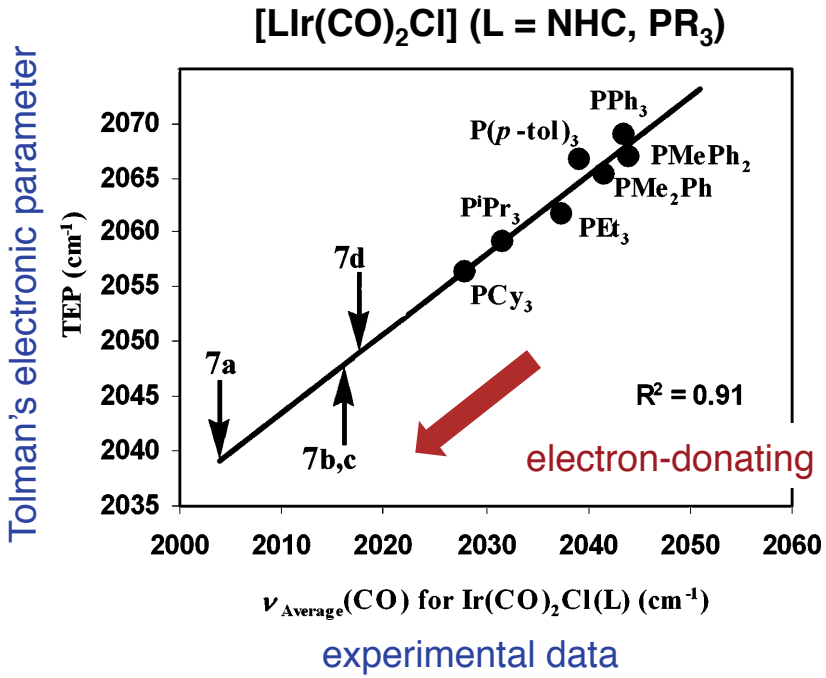
L. N. Appelhans, D. Zuccaccia, A. Kovacevic, A. R. Chianese, J. R. Miecznikowski, A. Macchioni, E. Clot, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **2005**, *127*, 6299.

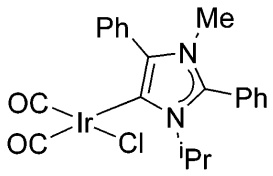
A Comparison of aNHCs with NHC

- aNHCs are stronger σ-electron donors than NHCs.
- aNHCs tend to cleave from the metal more easily than NHCs.

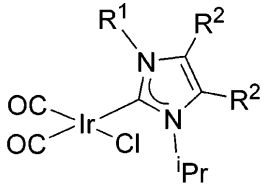
R. H. Crabtree, *J. Organomet. Chem.* **2005**, *690*, 5451.

electron-donating ability -experimental-





7a

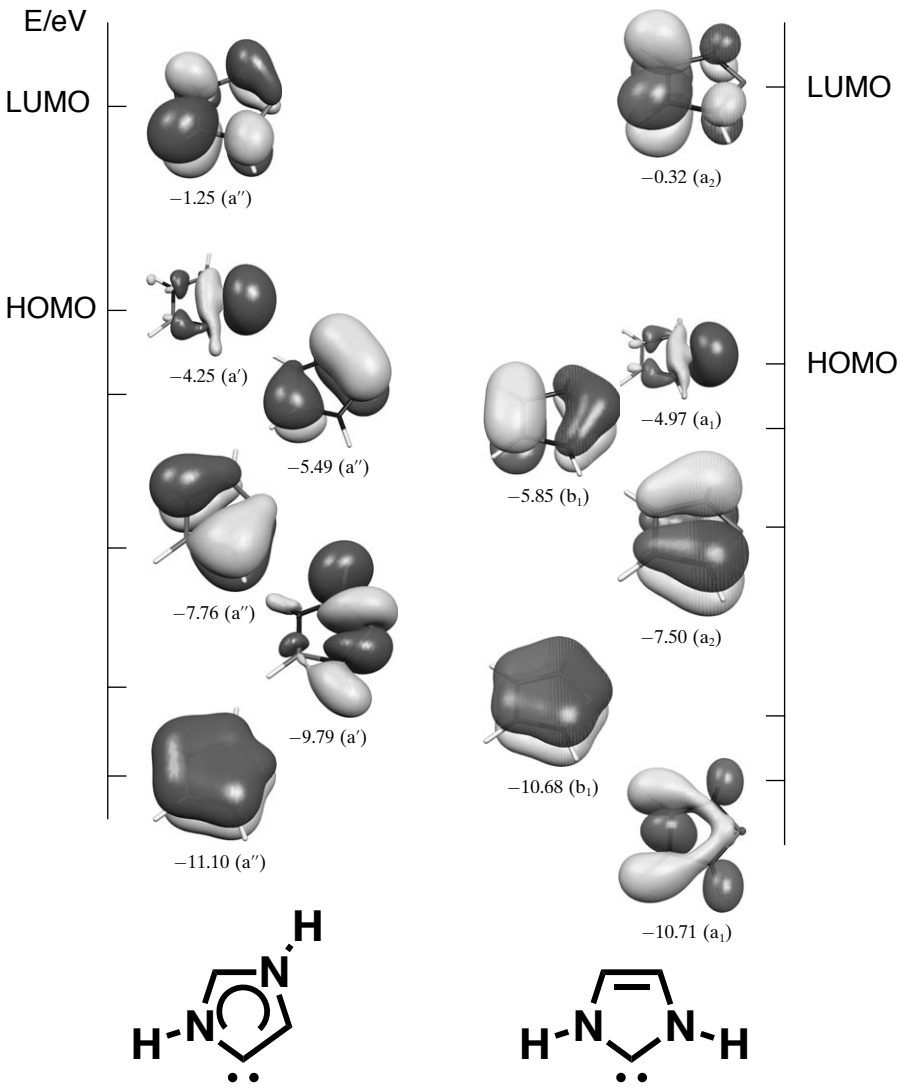


7b: R^1 = Me, R^2 = Ph
7c: R^1 = *i*Pr, R^2 = Ph
7d: R^1 = Ph, R^2 = H

A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller, R. H. Crabtree, *Organometallics*, **2004**, *23*, 2461.

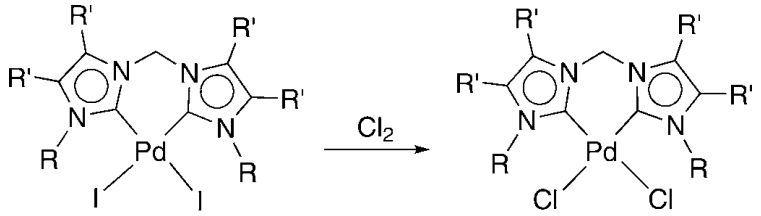
A Comparison of aNHCs with NHC

electron-donating ability -calculation-



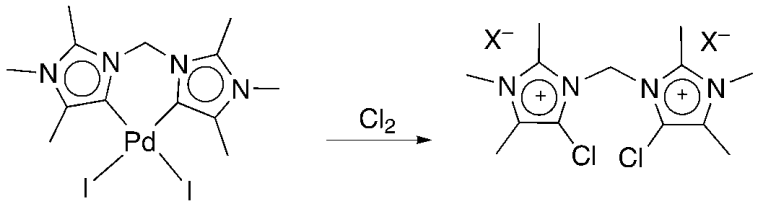
R. Tonner, G. Heydenrych, G. Frenking, *Chem. Asian. J.* **2007**, *2*, 1555.

cleavage from the metal



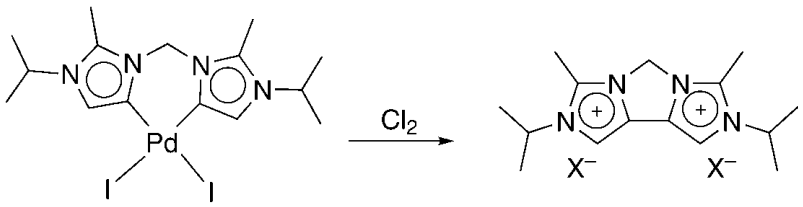
4b (R = R' = Me)
13b (R = *i*Pr, R' = H)

4a
13a (92%)



8b

14 (48%)



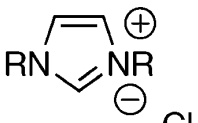
15

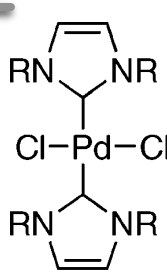
16 (50%)

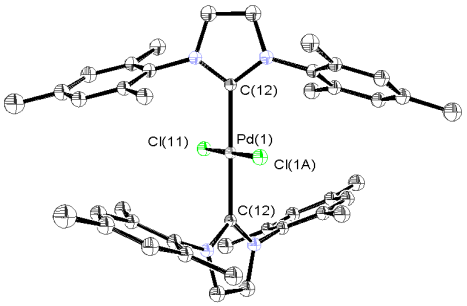
Scheme 4. Reactivity of abnormal dicarbene complexes towards molecular chlorine ($X^- = [PdCl_3(DMSO)]^-$ or $0.5\,[PdCl_4]^{2-}$).

N. Heckenroth, A. Neels, M. G. Garnier, P. Aebi, A. W. Ehlers, M. Albrecht, *Chem. Eur. J.* **2009**, *15*, 9375.

Suzuki–Miyaura coupling







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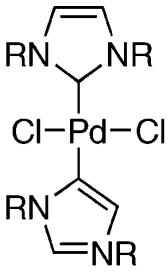
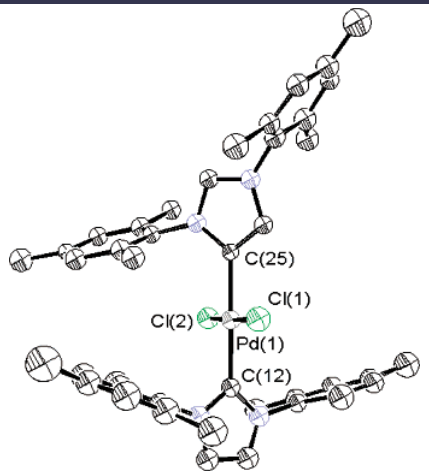
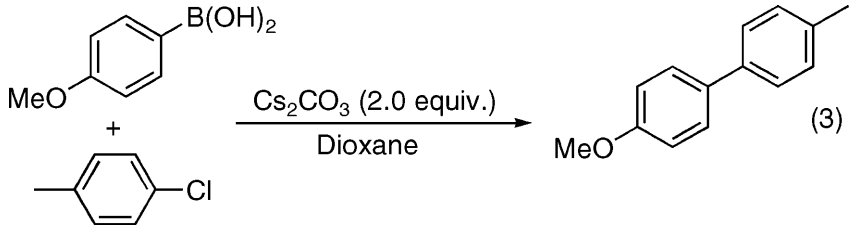




R = 2,4,6-trimethylphenyl (Mes)

	1	**2**
$Pd(OAc)_2$, Dioxane, 80 °C	<1%	74%
$Pd(Cl)_2$, Cs_2CO_3 Dioxane, 80 °C	68%	<1%



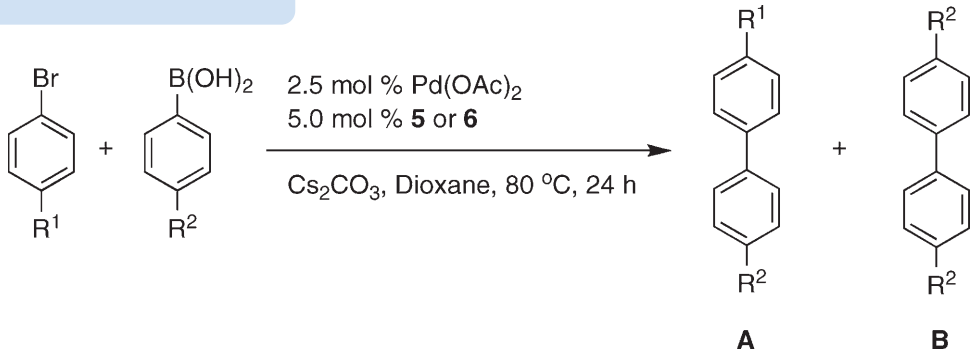
entry	catalyst (2 mol %)	temp (°C)	yield (%)
1	complex **1**	80	<5
2	complex **2**	80	44
3	IMes·HCl, $Pd(OAc)_2$ (2:1)	80	76
4	IMes·HCl, $Pd(OAc)_2$ (1:1)	80	28

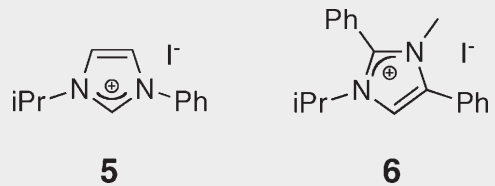
the first report of the catalytic activity of aNHC

H. Lebel, M. K. Janes, A. B. Charette, S. P. Nolan, *J. Am. Chem. Soc.* **2004**, *126*, 5046.

Suzuki–Miyaura coupling

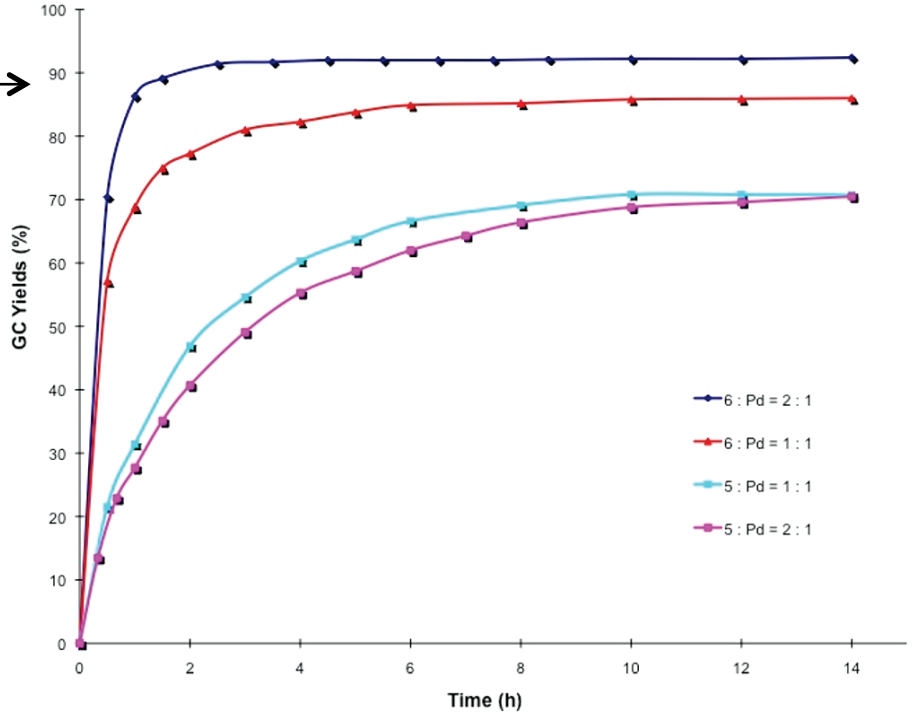
substrate scope





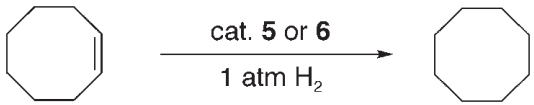
			5		6	
entry	R^1	R^2	A	B	A	B
1	OMe	Me	60 (57)	23	76 (73)	< 0.1
2	H	Me	79 (76)	14	90 (89)	< 0.1
3	F	Me	75 (72)	28	84 (76)	< 0.1
4	Me	OMe	41 (34)	10	64 (61)	< 0.1
5	Me	H	30 (25)	4	66 (62)	2
6	Me	F	6 (4)	4	29 (24)	1.3
7	H	OMe	67 (63)	7	78 (70)	< 0.1
8	H	F	30 (25)	3	50 (41)	< 0.1

[a] GC yields using dodecane as an internal standard; isolated yields are shown in parentheses, average of at least two runs.



X. Xu, B. Xu, Y. Li, S. H. Hong, *Organometallics*, **2010**, *29*, 6343.

hydrogenation



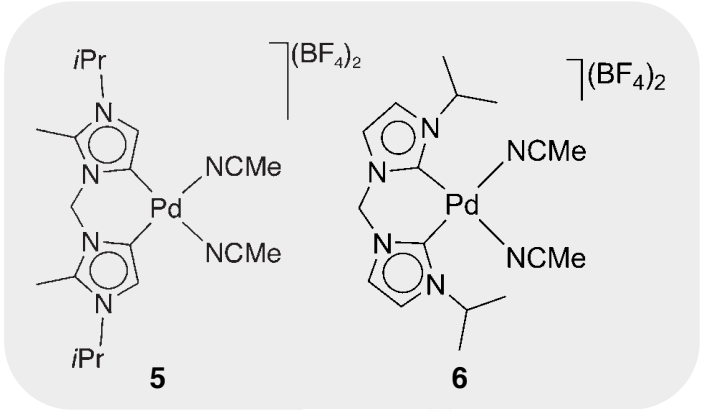
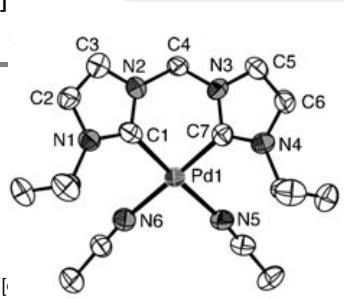
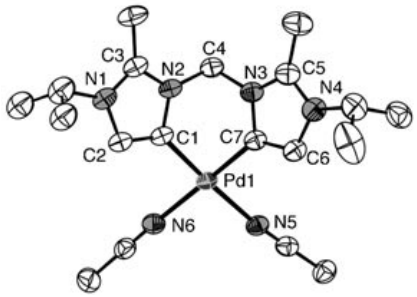


Table 1: Catalytic hydrogenation of cyclooctene with complexes **5** and **6**.[a]

Entry	Solvent	*t* [h]	cat. loading[b]	Conversion[c] [%]	
				5	**6**
1	MeOH	8 (24)	1%	78 (100)	24
2	EtOH	4.5	1%	100	19
3	THF	8 (24)	1%	50 (100)	9
4	CH_2Cl_2	8 (24)	1%	30 (100)	0
5	toluene	8 (24)	1%	0 (34)	0
6	EtOH	2.5	3%	100	n.d.[d]
7	EtOH	26	0.1%	66	n.d.
8	EtOH	72	0.01%	< 5	n.d.

[a] General conditions: cyclooctene (2.0 mmol), Pd complex (1 mol%), EtOH (6 mL), RT, 1 atm H_2; catalyst precursor **6** is the product from an $AgBF_4$-mediated halide abstraction from **3b** (Scheme 1, see also Ref. [12]). [b] In mol equiv relative to cyclooactene. [c] Determined by GC. [d] Not determined.





M. Heckenroth, E. Kluser, A. Neels, M. Albrecht, *Angew. Chem. Int. Ed.* **2007**, *46*, 6293.
M. Heckenroth, A. Neels, M. G. Garnier, P. Aebi, A. W. Ehlers, M. Albrecht, *Chem. Eur. J.* **2009**, *15*, 9375.

hydrogenation

about mechanism

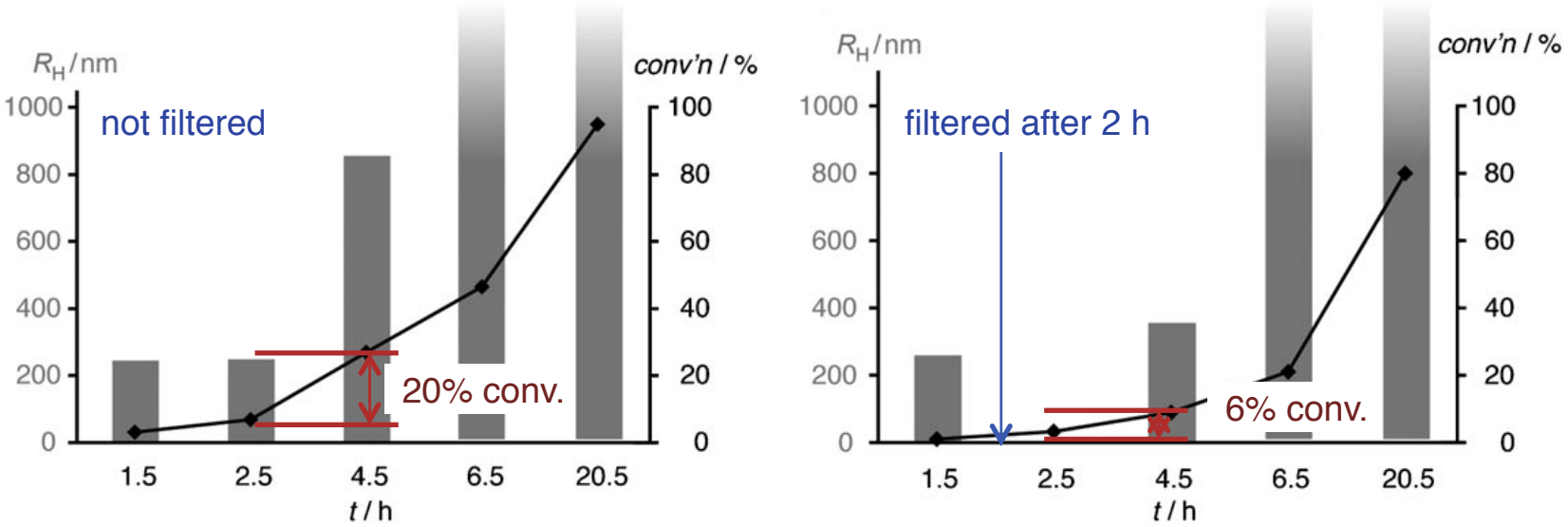


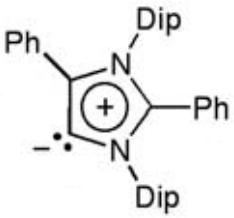
Figure 5. Correlation of particle size R_H (grey columns) and conversion (◆) for catalytic runs

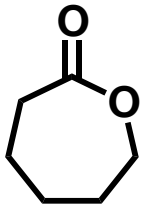
"formation of submicrometer size particles is essential for the catalytic activity, hence indicating a heterogeneous mechanism."

Pd-aNHC complex didn't activate H-H bond…

M. Heckenroth, V. Khlebnikov, A. Neels, P. Schurtenberger, M. Albrecht, *ChemCatChem,* **2011**, *3*, 167.

ring opening polymerization of cyclic esters

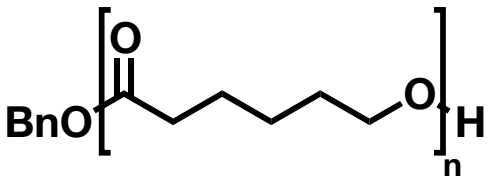




ε-caprolactone
(ε-CL)

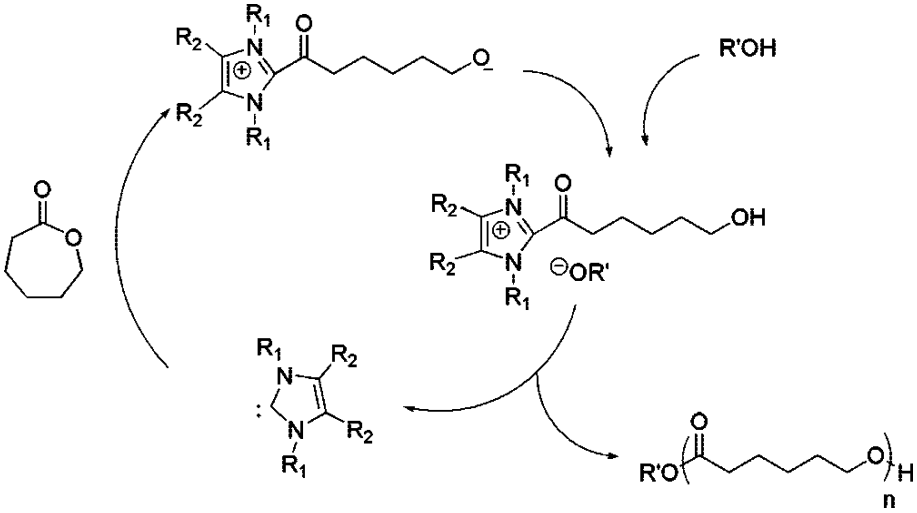
BnOH (initiator)

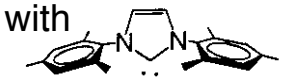
25 °C, 1 h



M	Solvent	$[M]_0/[1]/[BnOH]$	Conv.[a] (%)	M_n (NMR)[a]	M_n (theory)[b]	PDI
ε-CL	Toluene	100/1/1	99	10 500	11 400	1.09
ε-CL	THF	100/1/1	99	11 300	11 400	1.07
ε-CL	THF	100/1/2	95	5100	5500	1.12
ε-CL[c]	THF	500/1/1	55	23 200	31 500	1.11

[a] Determined by ^{1}H NMR spectroscopy. [b] Calculated from $MW_{monomer} \times (\%\ Conv.) \times ([M]_0/[BnOH]_0) + MW_{BnOH}$. [c] Reaction time 2 h instead of usual 1 h reaction time.



with 

24 h, rt

THF 120/1/2 99 1.30

T. K. Sen, S. C. Sau, A. Mukherjee, A. Modak, S. K. Mandal, *Chem. Commun.* **2010**, *47*, 11972.
E. F. Connor, G. W. Nyce, M. Myers, A. Möck, J. L. Hedrick, *J. Am. Chem. Soc.* **2002**, *124*, 914.

ring opening polymerization of cyclic esters

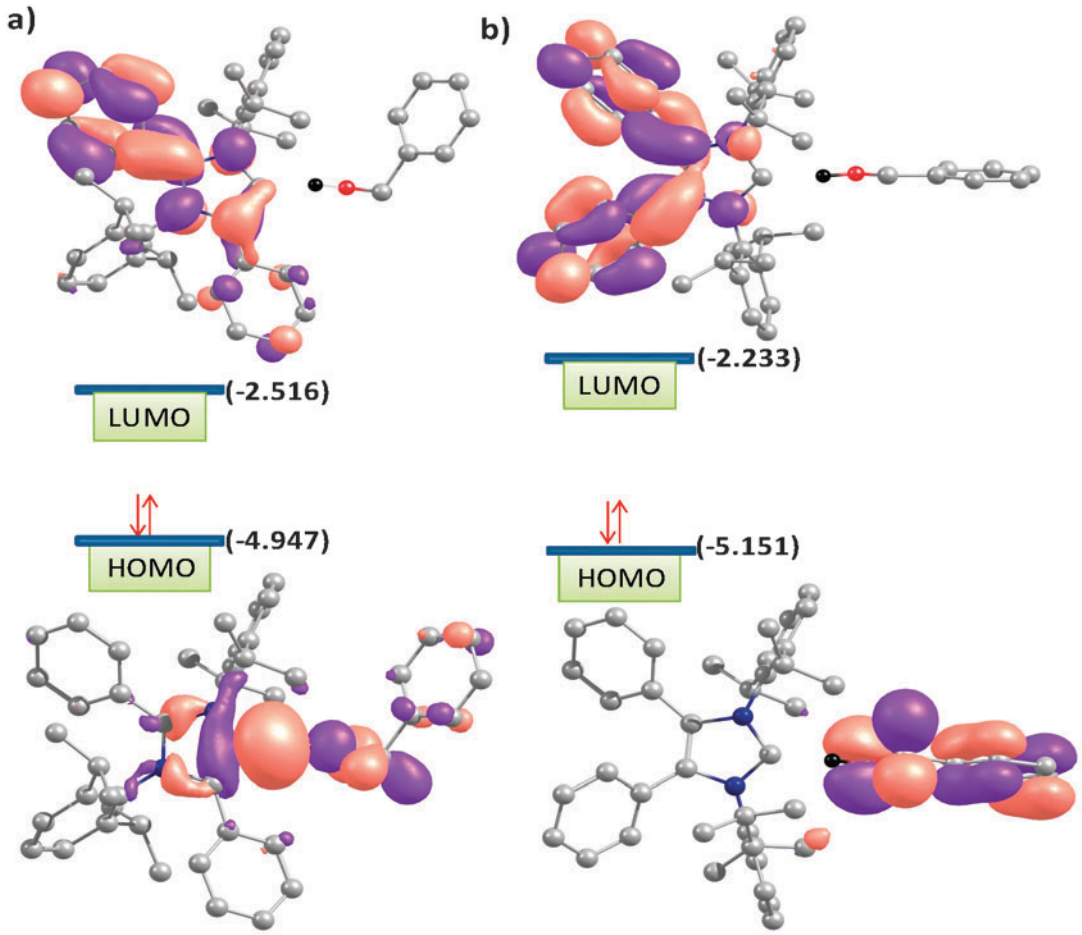
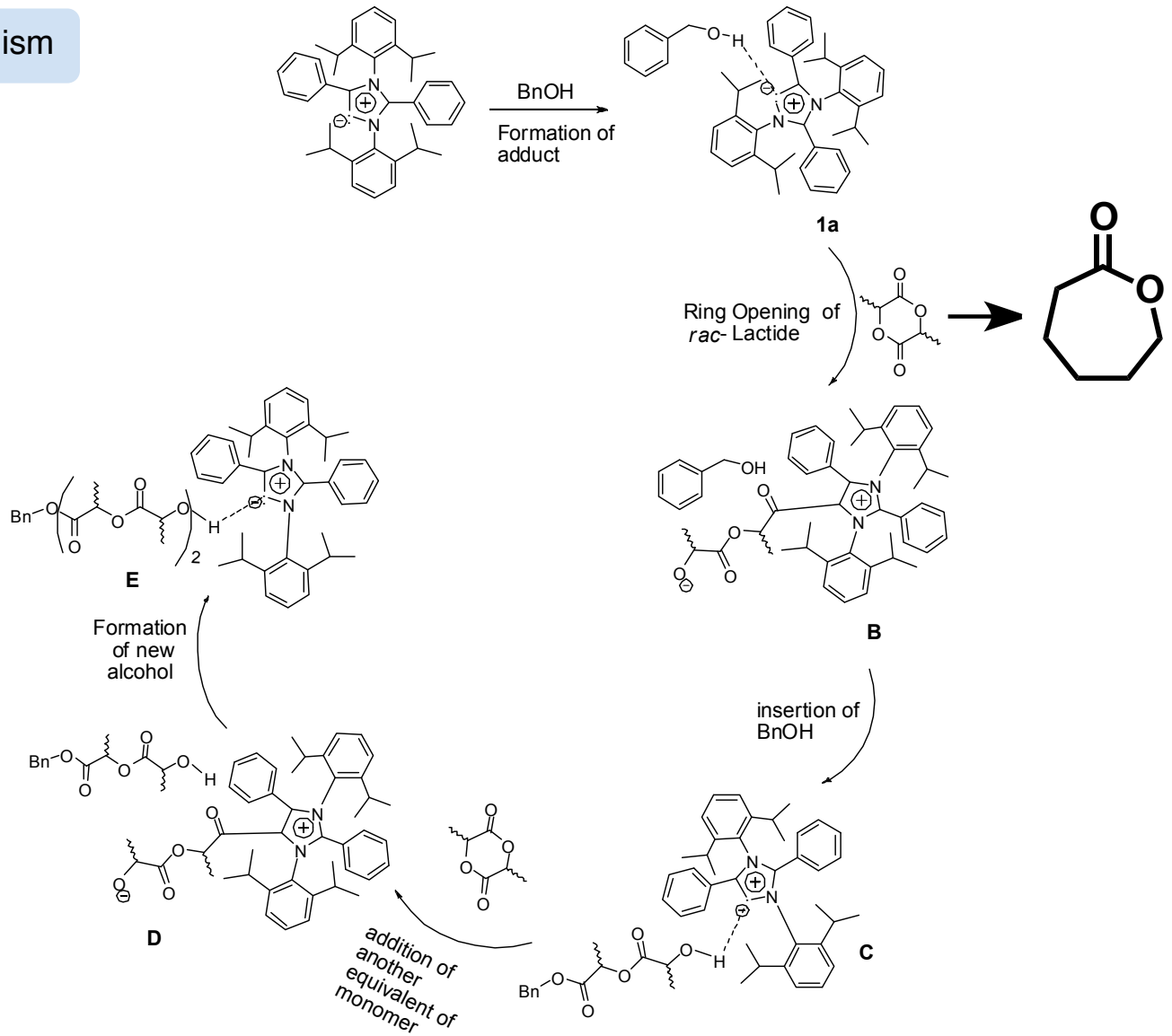


Fig. 2 Frontier KS-molecular orbitals for hydrogen bonded adducts with benzyl alcohol: (a) **1a** (*a*NHC···BnOH adduct) and (b) **2a** (*n*NHC···BnOH adduct). The orbital energies are in eVs.

T. K. Sen, S. C. Sau, A. Mukherjee, A. Modak, S. K. Mandal, *Chem. Commun.* **2010**, *47*, 11972.

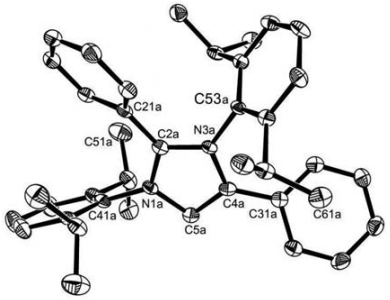
ring opening polymerization of cyclic esters

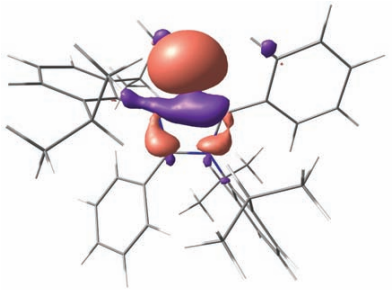
plausible mechanism

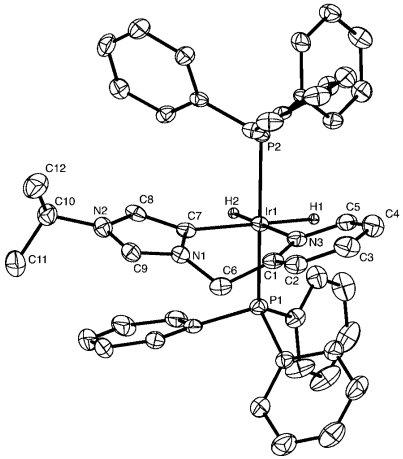


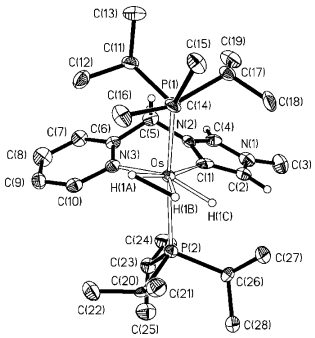
T. K. Sen, S. C. Sau, A. Mukherjee, A. Modak, S. K. Mandal, *Chem. Commun.* **2010**, *47*, 11972.

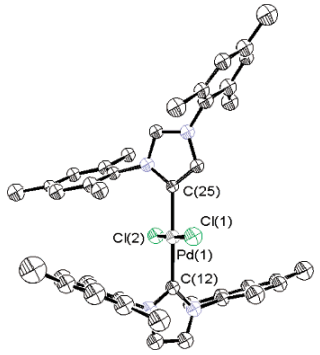
Contents











Summary

1. introduction

2. N-heterocyclic carbenes (NHCs)

   first metal-NHC complex
   first free, isolable NHC
   NHCs as ligands for transition metals
   NHCs as organocatalysts

3. abnormal N-heterocyclic carbenes (aNHCs)

   first metal-aNHC complex
   first free aNHC
   C2- vs C4- bound carbene
   NHC vs aNHC
   application to catalysts

- C4-carbenes are kinetically favored products.
- Large wingtip groups and non-H-bound anions favor C4-bound carbene.

- aNHCs are stronger σ-electron donors than NHCs.
- aNHCs tend to cleave from the metal more easily than NHCs. This may limit their utility in catalysis…

4. summary

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