Electronic Supplementary Information for Dalton Transactions
This journal is © The Royal Society of Chemistry 2009

Electronic Supplementary Information

N-heterocyclic Carbenes bearing two, one and no nitrogen atoms at the ylidene carbon: insight from theoretical calculations.

Aleksandr A. Tukov[a], Adrien T. Normand[b*], Mikhail S. Nechaev[a,c,*]

[a] Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory 1/3, Moscow, 119991, Russian Federation
[b] Department of Chemistry and Center for Catalysis Research and Innovation, University of Ottawa, 10 Marie Curie Street, Ottawa K1N 6H5, ON, Canada
[c] A. V. Topchiev Institute of Petrochemical Synthesis, RAS, Leninsky Prosp., 29, Moscow 119991, Russian Federation

* Corresponding authors. Address: A.T.N.: Department of Chemistry and Center for Catalysis Research and Innovation, University of Ottawa, 10 Marie Curie Street, Ottawa K1N 6H5, ON, Canada. M.S.N.: Department of Chemistry, M. V. Lomonosov Moscow State University, Leninskie Gory 1/3, Moscow, 119991, Russian Federation.
Tel./fax: +7 495 9392677.
E-mail address: nechaev@nmr.chem.msu.ru (M.S.N). anormand@uottawa.ca (A.T.N.)

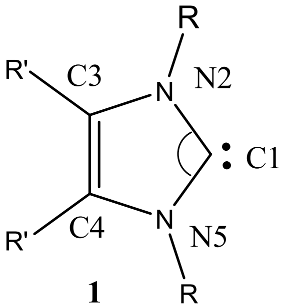
Contents

Free NHCs

Structures

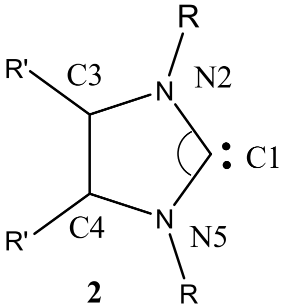
Table S1.

Experimental and calculated structures of carbenes (distances in Å, valence angles in degrees; data obtained in present work are in bold).



1

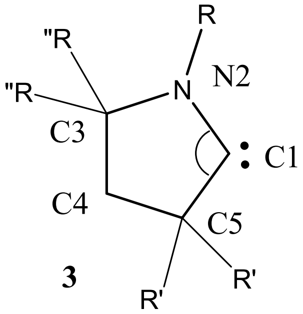
Method / Substitutes	C_1-$N_{2(5)}$	$C_{3(4)}$-$N_{2(5)}$	C_3-C_4)	N_2-C_1-N_5
X-ray (R=Ad, R'=H), [1]	1.373 / 1.367	1.386 / 1.382	1.338	102.2
X-ray (R=Mes, R'=H), [2]	1.365 / 1.371	1.381 / 1.378	1.333	101.4
X-ray (R=Me, R'=Me), [2]	1.363	1.394	1.352	101.5
MP2/6-31G(d), R=Me, R'=H [3]	1.373	1.382	1.366	100.9
MP2/6-31G(d), R=R'=H [3]	1.371	1.384	1.364	99.4
BPW91/I, R=Me, R'=H [4]	1.382	1.397	1.372	101.4
PBE/TZ2P-SBK, R=Me, R'=H	**1.376**	**1.393**	**1.366**	**101.6**



2

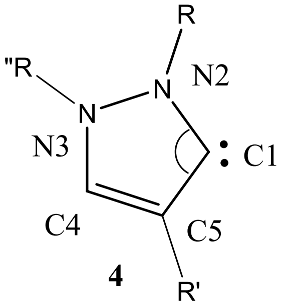
Method / Substitutes	C_1-$N_{2(5)}$	$C_{3(4)}$-$N_{2(5)}$	C_3-C_4	N_2-C_1-N_5
X-ray, R=Mes, R'=H [5]	1.352 / 1.345	1.475 / 1.487	1.505	104.7
MP2/6-31G(d), R=R'=H [3]	1.356	1.471	1.529	103.4

B3LYP/6-31G*, R=Me, R'=H [6]	1.352	-	-	105.2
PBE/TZ2p-SBK, R=Me, R'=H	**1.353**	**1.484**	**1.536**	**105.7**



3

Method / Substitutes	C_1-N_2	C_1-C_5	N_2-C_1-C_5
X-ray, R = (i-Pr)$_2$Ph, 2R'= Cy*, R"= Me [7]	1.315	1.516	106.5
PBE/TZ2p-SBK, R=R'=Me, R"=H	**1.313**	**1.531**	**105.7**



4

Method / Substitutes	C_1-N_2	C_1-C_5	N_3-C_4	C_4-C_5	N_2-N_3	N_2-C_1-C_5
R=R"=Me, R'=H. BPW91/I [4]	1.355	1.423	1.368	1.390	1.444	102.3
R=R'=R"=Me. PBE/TZ2p-SBK	1.346	1.416	1.370	1.386	1.444	103.2

1. *J. Am. Chem. Soc.* 1991, **113**, 361-363.
2. *J. Am. Chem. Soc.* 1992, **114**, 5530-5534.
3. *J. Am. Chem. Soc.* 1996, **118**, 2039-2046.
4. *J. Am. Chem. Soc.* 2002, **124**, 5865-5880.
5. *J. Am. Chem. Soc.* 1995, **117**, 11027-11028.
6. *Chem. Phys. Lett.* 2001, **349**, 477-482.
7. *Angew. Chem.* Int. Ed. 2005, **44**, 5705-5709.

AIM

The bonding situation was studied using AIM approach founded by Bader.[T5] The AIM method, based on the topological analysis of the electron density $\rho(r)$, allows a classification of interatomic interactions and quantitative analysis of characteristics of the bonds. In order to accomplish this, the gradient of ρ ($\nabla\rho$), the Hessian matrix (the collection of second derivatives of ρ), and the Laplacian of ρ ($\nabla^2\rho$) should be analyzed. The points where $\nabla\rho = 0$ are called critical points (CPs). They are labeled by their rank, the number of non-zero eigenvalues (denoted λ_1, λ_2, λ_3) of the Hessian matrix, and signature σ, the sum of their algebraic signs. There are four possible types of CPs of rank three: maxima (3,-3), minima (3,+3), and saddles (3,-1) and (3,+1). Considerable attention is usually focused on the (3,-1) CPs, since they are found between every bonded pair of nuclei. The existence of such a critical point and its associated atomic interaction line is a necessary condition for the presence of chemical bond. [T5] The value of $\rho(r_c)$, its Laplacian $\nabla^2\rho(r_c)$ (defined as the sum of the eigenvalues of the Hessian of the electron density, $\nabla^2\rho = \lambda_1 + \lambda_2 + \lambda_3$) in such points (usually called bond critical points BCPs) allow the classification of bonds as shared or closed-shell interactions. Usually, in contrast to the shared interaction (covalent or polar bonds), rather low values of $\rho(r_c)$ (of the order of 10^{-2} a.u.), $\nabla^2\rho(r_c) > 0$ are evident signs of the closed-shell interaction (e.g., ionic or hydrogen bonds, van der Waals interactions). The eigenvector associated with λ_3 is parallel to the bond path (the gradient line connecting the nuclei where (3,-3) CPs are located), whereas the eigenvectors associated with λ_1 and λ_2 are perpendicular to the bond path. For the closed-shell interaction the ratio $|\lambda_1|/\lambda_3$ is expected to be less than 1 whereas for shared interaction the value is more than 1. However, intermediate values may be ascribed to a mixed character of the bond.[T5] The ellipticity ε (defined as $\varepsilon = \lambda_1/\lambda_2 - 1$) at the BCP gives some additional information about the bond or the bond critical point. This can be interpreted as an indicator of the structural stability of the bond in a situation when the ring critical point (RCP, point (3,+1)) is located close to the BCP. Ellipticity ε can be also interpreted as a quantitative index of the π-character of the bond.[T5]

T5. Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: New York, 1990.

Table S2.

Bond critical points within cycles in molecules **1 – 6** ($\rho(r_{cp})$, $\nabla^2\rho(r_{cp})$, λ_1, λ_2, λ_3 in a.u.).

Molecule	Bond	$\rho(r_{cp})$	$\nabla^2\rho(r_{cp})$	λ_1	λ_2	λ_3	$\lvert\lambda_1\rvert/\lambda_3$	ε
1	**N-C:**	0.292	-0.522	-0.533	-0.501	0.513	1.04	0.06
	=C-N	0.288	-0.551	-0.473	-0.422	0.344	1.38	0.12
	C=C	0.325	-0.937	-0.687	-0.530	0.280	2.45	0.29
2	**N-C:**	0.307	-0.591	-0.607	-0.535	0.551	1.10	0.13
	C-N	0.244	-0.431	-0.442	-0.423	0.435	1.02	0.05
	C-C	0.235	-0.419	-0.433	-0.428	0.443	0.98	0.01
3	**N-C:**	0.328	-0.449	-0.705	-0.555	0.812	0.87	0.27
	Me_2C-C:	0.237	-0.373	-0.440	-0.417	0.484	0.91	0.05
	C-N	0.235	-0.386	-0.421	-0.403	0.438	0.96	0.04
	C-C	0.235	-0.425	-0.431	-0.422	0.427	1.01	0.02
	C-$C(Me)_2$	0.218	-0.334	-0.390	-0.380	0.436	0.89	0.03
4	**N-C:**	0.296	-0.207	-0.566	-0.415	0.774	0.73	0.36
	C-C:	0.276	-0.561	-0.510	-0.494	0.443	1.15	0.03
	N-N	0.306	-0.185	-0.720	-0.601	1.136	0.63	0.20
	N-C	0.296	-0.353	-0.493	-0.443	0.582	0.85	0.11
	C=C	0.308	-0.843	-0.621	-0.497	0.274	2.26	0.25
5	**C3-C:**	0.284	-0.646	-0.547	-0.526	0.426	1.28	0.04
	N-C:	0.283	-0.312	-0.540	-0.382	0.611	0.88	0.41
	C5-C6	0.319	-0.934	-0.666	-0.543	0.275	2.42	0.23
	C3-C4	0.307	-0.838	-0.627	-0.526	0.315	1.99	0.19
	C6-N	0.302	-0.599	-0.542	-0.491	0.434	1.25	0.11
	C4-C5	0.298	-0.797	-0.607	-0.525	0.335	1.81	0.16
6	**C-C:**	0.283	-0.643	-0.523	-0.514	0.394	1.33	0.02
	C-N	0.299	-0.384	-0.529	-0.478	0.623	0.85	0.11
	C=C	0.308	-0.864	-0.627	-0.522	0.285	2.20	0.20

NBO

Table S3.

Selected NBO orbitals of free carbenes **1** – **6**.

Molecule	Orbital	Symmetry	Occupation (e)	Bond polarization (%)	Hybridization
1	BD C1-N2	π	1.85	C, 20.75; N, 79.25	C, p; N, p
	BD C3-C4	π	1.89	C, 50.00; C, 50.00	C, p; C, p
	LP C1	σ	1.91	-	$sp^{1.10}$
	LP N5	π	1.55	-	p
2	BD C1-N2	π	1.92	C, 17.40; N, 82.60	C, p; N, p
	LP C1	σ	1.87	-	$sp^{1.34}$
	LP N5	π	1.64	-	p
3	BD C1-N2	π	1.94	C, 22.26; N, 77.74	C, p; N, p
	LP C1	σ	1.87	-	$sp^{1.38}$
4	BD C1-N2	π	1.90	C, 21.45; N, 78.55	C, p; N, p
	BD C4-C5	π	1.80	C, 48.19; C, 51.81	C, p; C, p
	LP C1	σ	1.85	-	$sp^{1.47}$
	LP N3	π	1.62	-	p
5	BD C1-N2	π	1.78	C, 21.45; N, 78.55	C, p; N, p
	BD C3-C4	π	1.74	C, 48.78; C, 51.22	C, p; C, p
	BD C5-C6	π	1.68	C, 49.45; C, 50.55	C, p; C, p
	LP C1	σ	1.88	-	$sp^{1.58}$
6	BD C2-C3	π	1.69	C, 49.58; C, 50.42	C, p; C, p
	BD C5-C6	π	1.69	C, 49.58; C, 50.42	C, p; C, p
	LP C1	σ	1.84	-	$sp^{1.95}$
	LP* C1	π	0.59	-	p
	LP N4	π	1.49	-	p

Table S4.

Selected MP2 orbital interactions in free carbenes **1** – **6** ($\Delta E^{(2)}_{i\rightarrow j*}$ in kcal/mol).

Molecule	Donor		Acceptor	$\Delta E^{(2)}_{i\rightarrow j*}$
1	LP N(5)	→	BD*(π) C(1)-N(2)	45.4
	LP N(5)	→	BD*(π) C(3)-C(4)	27.6
	BD(π) C(1)-N(2)	→	BD*(π) C(3)-C(4)	17.6
	BD(π) C(3)-C(4)	→	BD*(π) C(1)-N(2)	7.9
2	LP N(5)	→	BD*(π) C(1)-N(2))	53.7
4	LP N(3)	→	BD*(π) C(4)-C(5)	24.6
	BD(π) C(4)-C(5)	→	BD*(π) C(1)-N(2)	19.3
	LP N(3)	→	BD*(π) C(1)-N(2)	9.4
5	BD*(π) C(3)-C(4)	→	BD*(π) C(1)-N(2)	65.8
	BD*(π) C(3)-C(4)	→	BD*(π) C(5)-C(6)	60.9
	BD(π) C(5)-C(6)	→	BD*(π) C(1)-N(2)	19.5
	BD(π) C(1)-N(2)	→	BD*(π) C(3)-C(4)	18.7
	BD(π) C(5)-C(6)	→	BD*(π) C(3)-C(4)	14.8
	BD(π) C(3)-C(4)	→	BD*(π) C(5)-C(6)	13.0
6	LP* C(1)	→	BD*(π) C(2)-C(3)	124.3
	LP* C(1)	→	BD*(π) C(5)-C(6)	124.1
	LP N(5)	→	BD*(π) C(2)-C(3)	27.9
	LP N(5)	→	BD*(π) C(5)-C(6)	27.9
	BD(π) C(2)-C(3)	→	LP* C(1)	26.6
	BD(π) C(5)-C(6)	→	LP* C(1)	26.6

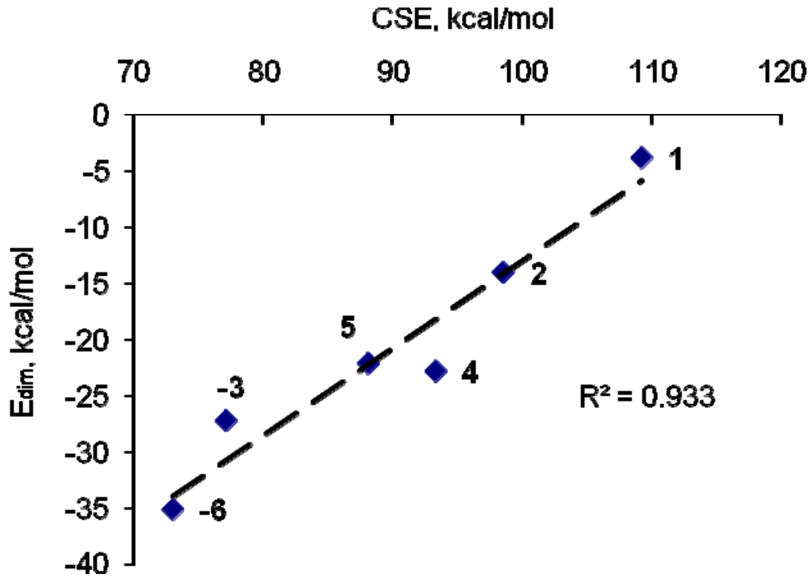
In carbenes **1**, **2** and **4** the highest non-Lewis corrections correspond to donation from nitrogen lone electron pairs LP N to antibonding orbitals BD*(π) C=N (**1** and **2**) and BD*(π) C=C (**4**). In **5** the highest correction corresponds to donation from antibonding BD*(π) C3=C4 to antibonding BD*(π) C1=N2. In **6** the highest correction corresponds to donation from vacant orbital LP* C1 to antibonding BD*(π) C=C. Donation of electron density from antibonding orbitals is due to their significant non-zero population and proximity in energy to accepting orbitals. In carbenes **1**, **4** and **5** corrections corresponding to donation from bonding π-orbitals BD(π) to π-antibonding orbitals BD*(π) of multiple C=C and C=N bonds are also significant. In **6** the noticeable corrections are:

donation from the nitrogen lone pair LP N to the two π-antibonding BD*(π) of C=C, and donation from BD(π) of C=C to the vacant orbital of the ylidene carbon LP* C1.

Carbene stability

Scheme S1.

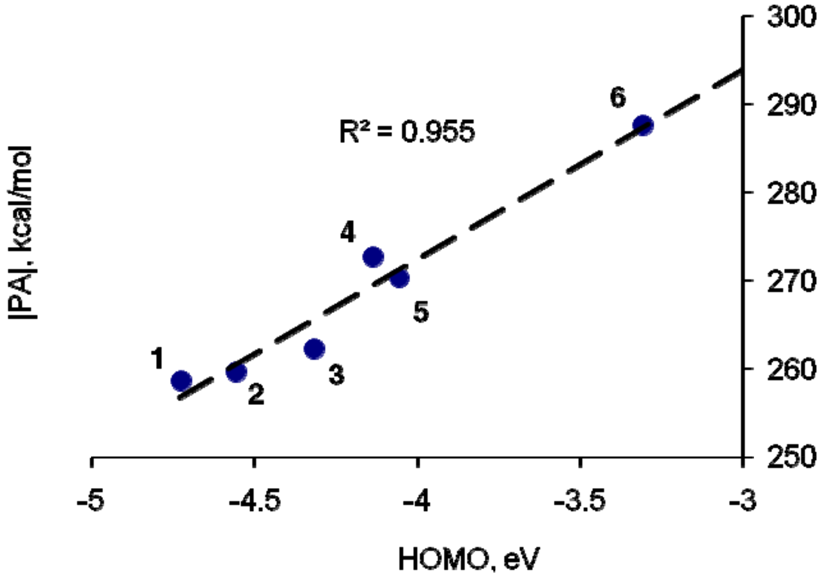
Correlation of calculated CSE and E_{dim} (kcal/mol) of free carbenes **1** – **6**.



PA

Scheme S2.

Correlation of calculated proton affinities PA (kcal/mol) and HOMO energies E_{HOMO} (eV) of free carbenes **1** – **6**.

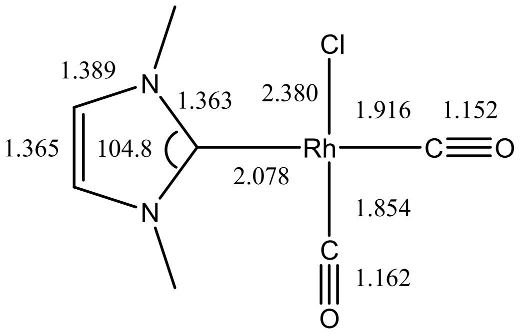


NHCs as ligands

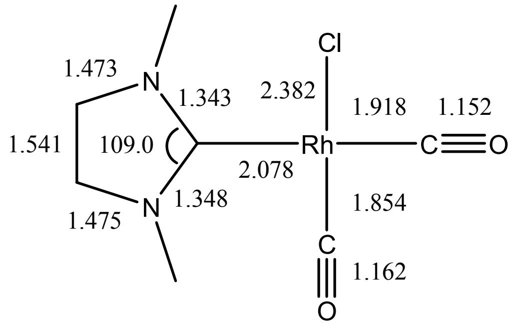
Structures

Scheme S3.

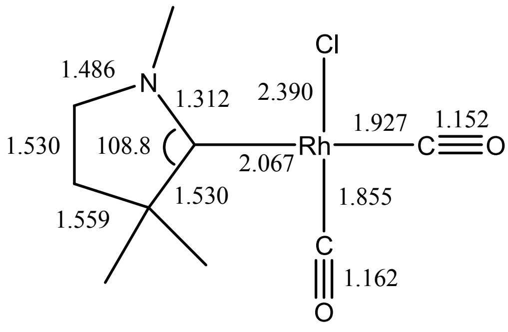
Selected structural parameters of the complexes (NHC)Rh(CO)$_2$Cl (**1a** – **6a**; interatomic distances in Å, valence angles in degrees).



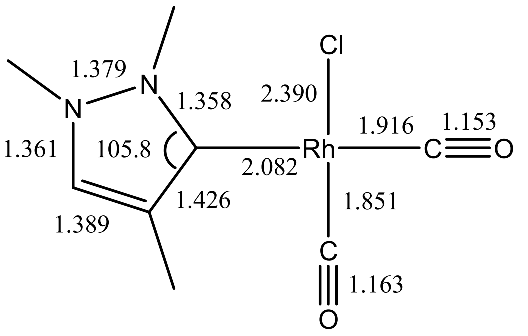
1a



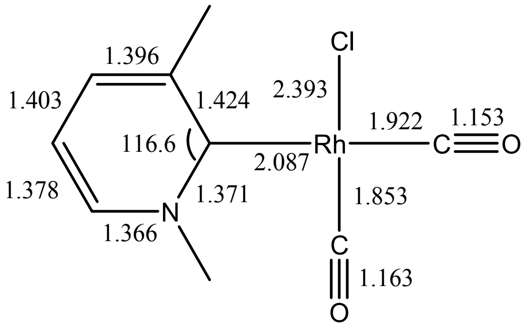
2a



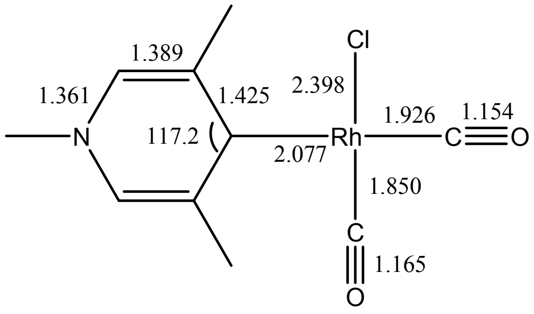
3a



4a



5a



6a

Table SXX.

Correlation of calculated parameters. R^2 higher than 0.95 are marked.

	E_{HOMO}	E_{ST}	E_{dim}	CSE	ASE	PA	HLG	X-C-X	LP_{C1} sp^x	IP	NICS-1	η	ν_s(CO)	D	ΔN
E_{HOMO}	■	0.878	0.774	0.640	0.855	0.955	0.898	0.652	0.966	0.997	0.438	0.971	0.884	0.988	0.975
E_{ST}		■	0.883	0.808	0.625	0.751	0.945	0.730	0.883	0.895	0.167	0.913	0.616	0.860	0.818
E_{dim}			■	0.933	0.672	0.631	0.713	0.479	0.778	0.807	0.274	0.721	0.474	0.972	0.805
CSE				■	0.778	0.452	0.619	0.481	0.648	0.680	0.319	0.599	0.331	0.664	0.681
ASE					■	0.836	0.645	0.521	0.798	0.847	0.754	0.771	0.944	0.877	0.897
PA						■	0.826	0.514	0.888	0.935	0.486	0.920	0.963	0.949	0.919
HLG							■	0.768	0.875	0.895	0.170	0.969	0.741	0.868	0.795
X-C-X								■	0.755	0.667	0.088	0.754	0.449	0.565	0.559
LP_{C1} sp^x									■	0.975	0.340	0.952	0.785	0.921	0.938
IP										■	0.422	0.966	0.852	0.984	0.978
NICS-1											■	0.296	0.667	0.504	0.550
η												■	0.847	0.939	0.896
ν_s(CO)													■	0.886	0.848
D														■	0.980
ΔN															■