

## КРАТКИЕ СООБЩЕНИЯ

UDC

CHEMICAL BONDING AND PROPERTIES IN [Ni(N-HETEROCYCLIC CARBENE)(NO)(R)]  
(R = H, Me, HC=CH<sub>2</sub>, AND C≡CH) COMPLEXES: THEORETICAL INSIGHTS

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A series of N-heterocyclic carbene nickel complexes of the type [Ni(N-heterocyclic carbene)(NO)(R)] (R = H, Me, HC=CH<sub>2</sub>, and C≡CH) are examined to study the influence of a substituent on the molecular structure and bonding of these complexes. Geometrical and AIM analyses of the interaction between Ni and the carbene fragment reveal that for the metal-carbene bond donation is more important than back-donation. The NICS values suggest that aromaticity in the heterocyclic ring is less than in the free heterocycle.

**Key words:** N-heterocyclic carbene nickel complexes, density functional theory (DFT), nucleus-independent chemical shift (NICS), natural bonding orbital (NBO), Atoms in Molecules (AIM) analysis.

N-Heterocyclic carbene (NHC) ligands have involved much attention due to their strong  $\sigma$ -donating ability to stabilize complexes and have been used as ligands for a range of catalytic reactions to achieve better catalytic activities [ 1—3 ]. Also, N-heterocyclic carbenes can be used for a large variety of reactions of high synthetic interest, such as 1,2-migration reactions, dimerization and cycloaddition reactions.

Unlike typical Fischer type carbenes, imidazol-2-ylidene (**1**) apparently binds only through  $R_2C \rightarrow ML_n$   $\sigma$  donation, while  $R_2C \leftarrow ML_n$   $\pi$  back donation is negligible. The metal-ligand bonding in the complexes of N-heterocyclic carbenes has been investigated [ 4—8 ].

M.S. Varonka et al. have synthesized a series of low-coordinate nickel nitrosyl complexes, in which N-heterocyclic carbene serves as a supporting ligand [ 9 ]. The aim of the present study is to provide answers to the changes in the nature of the N-carbene bond after the modification of carbene substituent in these complexes.

**Computational method.** All calculations were carried out with the Gaussian 03 suite of programs [ 10 ]. The calculations of systems containing C, H, N, O are performed with the standard 6-31G(*d*) basis set [ 11—13 ]. For the Ni element the standard LANL2DZ basis set is used [ 14—16 ] and Ni is described by an effective core potential (ECP) of Wadt and Hay's pseudopotential [ 17 ] with double- $\xi$  valence using LANL2DZ. Geometry optimization was performed with Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP) [ 18, 19 ]. A vibrational analysis was performed at each stationary point found, which confirms its identity as an energy minimum.

The nature of the metal-ligand bonding has been investigated by the natural bond orbital (NBO) analysis [ 20 ]. We have previously shown that the results from NBO calculations can provide a detailed insight into the electronic structure of molecules [ 21—23 ].

The nucleus-independent chemical shift (NICS) is defined as the absolute magnetic shielding computed at the center of a ring in a molecule [ 24, 25 ]. NICS(0), NICS(0.5), NICS(1.0), and NICS(1.5) are calculated at the center and 0.5, 1.0, and 1.5 Å above the ring respectively.

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Table 1

Energy (Hartree), stretching frequency of NO and NICS values of the heterocycle in [Ni(N-heterocyclic carbene)(NO)(R)] (R = H, Me, HC=CH<sub>2</sub>, and C≡CH)

	E(Hartree)	$\nu(\text{NO})$	NICS(0.0)	NICS(0.5)	NICS(1.0)	NICS(1.5)	NICS(2.0)
C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	-226.166693	—	-14.13	-13.85	-10.82	-6.64	-3.70
H	-526.0099042	1568.38	-13.54	-13.06	-9.91	-6.01	-3.40
Me	-565.3284633	1567.32	-12.36	-12.22	-9.54	-5.83	-3.29
HC=CH <sub>2</sub>	-603.4112398	1578.7	-12.19	-12.23	-9.53	-5.77	-3.21
C≡CH	-602.1838328	1602.93	-12.13	-12.16	-9.57	-5.83	-3.24

Table 2

Structural parameters in [Ni(N-heterocyclic carbene)(NO)(R)] (R = H, Me, HC=CH<sub>2</sub>, and C≡CH)

	$r(\text{Ni}-\text{C})$	$r(\text{Ni}-\text{N})$	C—N <sub>a</sub>	N <sub>a</sub> —C <sub>a</sub>	C <sub>a</sub> —C <sub>b</sub>	C <sub>b</sub> —N <sub>b</sub>	N <sub>b</sub> —C	$\angle\text{N}-\text{Ni}-\text{C}$	$\angle\text{N}-\text{C}-\text{N}$
C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	—	—	1.372	1.393	1.356	1.393	1.372	—	99.854
H	1.868	1.821	1.355	1.384	1.360	1.388	1.360	109.446	103.115
Me	1.872	1.817	1.355	1.385	1.360	1.388	1.360	105.517	103.067
HC=CH <sub>2</sub>	1.876	1.811	1.352	1.383	1.361	1.388	1.360	157.060	103.445
C≡CH	1.883	1.775	1.351	1.382	1.361	1.388	1.357	102.866	103.747

The AIM2000 program was used for the topological analysis of the electron density. The following characteristics of ring critical points (RCPs) are taken into account: density at RCP ( $\rho(r_c)$ ), its Laplacian ( $\nabla^2(r_c)$ ), and ellipticity ( $\epsilon$ ) [26].

**Results and Discussion. Geometries.** The values of the Ni—C<sub>carbene</sub> bond distance in Table 1 clearly indicate that  $\pi$ -donor substituents are shorter. This bond length increases in the following order: C≡CH > HC=CH<sub>2</sub> > Me > H. This trend reveals that donation is more important than back-donation for the metal-carbene bond. On the other hand, imidazol-2-ylidene binds through R<sub>2</sub>C → ML<sub>n</sub>  $\sigma$  donation, while R<sub>2</sub>C ← ML<sub>n</sub>  $\pi$  back donation is negligible. The reverse trend is observed for the Ni—N bond. Therefore, back bonding increases in the Ni—N bond in the following order: C≡CH > HC=CH<sub>2</sub> > Me > H.

The structure of the carbene ring changes to some extent in the complexes (Table 2). The bonding angle at the C<sub>carbene</sub> atom widens by 2.5—3.9°, and the C<sub>carbene</sub>—N and C(C=C)—N bond lengths shorten by 0.02 Å and 0.1 Å respectively. The C=C bond distance remains unchanged. This is in agreement with the experimental observations for metal complexes of this type of carbene.

**Electrophilicity.** To evaluate the electrophilicity of these complexes, we have calculated the electrophilicity index  $\omega$  for each complex measured, according to Parr, Szentpaly, and Liu [27], using the expression

$$\omega = \frac{\mu^2}{2\eta},$$

where  $\mu$  is the chemical potential (the negative of the electronegativity), and  $\eta$  is the hardness [28, 29]. These values can be calculated from the HOMO and UMO orbital energies using the following approximate expression:

$$\mu = (\epsilon_{\text{HOMO}} + \epsilon_{\text{LUMO}}) / 2,$$

$$\eta = \epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}}.$$

The values of the electrophilicity index in Table 3 indicate that the complex with R = H has a weaker electrophilic character. On the other hand, the R=C≡CH complex has the largest electrophilicity, compatible with the acceptor character of the C≡CH group [30, 31].

Table 3

*HOMO, LUMO orbital energies, chemical potential, hardness, and electrophilicity of [Ni(N-heterocyclic carbene)(NO)(R)] (R = H, Me, HC=CH<sub>2</sub>, and C≡CH)*

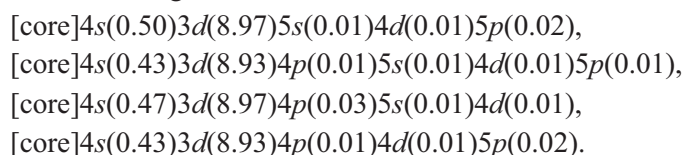
	HOMO	LUMO	$\mu$	$\eta$	$\omega$		HOMO	LUMO	$\mu$	$\eta$	$\omega$
H	-0.197	-0.087	-3.86	2.99	2.49	C <sub>2</sub> H <sub>4</sub>	-0.196	-0.088	-3.86	2.94	2.54
Me	-0.186	-0.080	-3.62	2.88	2.27	C <sub>2</sub> H <sub>2</sub>	-0.217	-0.098	-4.29	3.24	2.84

Table 4

*Atomic Charges obtained by NBO Analysis, electron density, and electron density Laplacian of the heterocycle in [Ni(N-heterocyclic carbene)(NO)(R)] (R = H, Me, HC=CH<sub>2</sub>, and C≡CH)*

	Ni	N	O	C <sub>carbene</sub>	X	$\rho(3,+1)$	$\nabla^2\rho(3,+1)$
C <sub>3</sub> H <sub>4</sub> N <sub>2</sub>	—	—	—	0.1138	—	0.0507	0.4317
H	0.5053	-0.0273	-0.3000	0.1468	-0.4374	0.0506	0.4334
Me	0.6108	-0.0341	-0.3142	0.1372	-1.1456	0.0506	0.4338
HC=CH <sub>2</sub>	0.6009	-0.0127	-0.3030	0.1413	-0.6085	0.0508	0.4343
C≡CH	0.6225	0.0222	-0.2880	0.1389	-0.4809	0.0509	0.4345

**NBO analysis.** The Natural Bond Orbital (NBO) analysis of [Ni(N-heterocyclic carbene)(NO)(R)] (R = H, Me, HC=CH<sub>2</sub>, and C≡CH) has provided a detailed insight into the nature of electronic conjugation between the bonds in these molecules. Table 4 collects the natural charges on atoms. According to the NBO results, the electron configurations of Ni are



Thus, 18 core electrons, 9.47(X=H), 9.36(X=Me), 9.44 (X=HC=CH<sub>2</sub>), and 9.36 (X=C≡CH) valence electrons (on 4s and 3d atomic orbitals) and 0.03 Rydberg electrons (mainly on 4d and 5p orbitals for X=H, Me, C≡CH and 4d and 5s for X=HC=CH<sub>2</sub>) give the total of 27.50 (X=H), 27.39 (X=Me), 27.47 (X=HC=CH<sub>2</sub>), and 27.39 (X=C≡CH) electrons. This is consistent with the calculated natural charge on the Ni atom: +0.5(X=H), +0.61(X=Me), +0.53(X=HC=CH<sub>2</sub>), and +0.61e (X=C≡CH).

The results of the NBO analysis of the complexes, which are given in Table 4, nicely show that the donor carbon atom of NHC ligand, which carries a slightly positive charge of 0.114 e in the free ligand NHC, receives an electronic charge although the NHC ligand is an overall donor in X=HC=CH<sub>2</sub>, while the ligand (C) atoms, which are positively charged in NHC, release an electronic charge. This shows that donation is more important than back-donation for the metal-carbene bond. As illustrated in the NBO analysis, the  $\sigma$  bonds of Ni—C(carbene) bonds of the complexes are composed of the *sd* hybrid orbital of iron and the *sp*<sup>2</sup> hybrid orbital of carbene carbon. The natural bond orbital energies of the  $\sigma$  bonds are also shown in Table 5.

**AIM analysis.** The calculated values of the energy density at the bond critical points for the Ni—N bonds are less in X=H (Table 6). The H<sub>c</sub> values for these bonds are less than those for X=H. Therefore, there is a considerable decrease in the covalent character of the Ni—N bond in X=H.

A similar investigation of the N—O bond character indicate that  $\rho$  and H<sub>c</sub> values of this is less in X=H. Consequently, the covalent character of this bond is less in X=H.

On the other hand, the calculations exhibit that Ni—C bonds have larger  $\rho$  and H<sub>c</sub> values in X=H. So, the Ni—C bond has the more covalent character in X=H.

Table 5

Occupancy, hybridization, orbital energy of the Ni—C<sub>carbene</sub> bond in  
[Ni(N-heterocyclic carbene)(NO)(R)] (R = H, Me, HC=CH<sub>2</sub>, and C≡CH)

	Occupancy	Ni—C	%(sp) <sub>C</sub>	%(sd) <sub>Ni</sub>	Orbital energy
H	1.94346	0.8774 (sp <sup>1.59</sup> ) <sub>C</sub> + 0.4797 (sp <sup>0.01</sup> d <sup>1.22</sup> ) <sub>Ni</sub>	76.99	23.01	-0.43769
Me	1.93520	0.8819 (sp <sup>1.61</sup> ) <sub>C</sub> + 0.4714 (sd <sup>1.04</sup> ) <sub>Ni</sub>	77.78	22.22	-0.43009
HC=CH <sub>2</sub>	1.93258	0.8776 (sp <sup>1.65</sup> ) <sub>C</sub> + 0.4794 (sd <sup>1.07</sup> ) <sub>Ni</sub>	77.02	22.98	-0.43038
C≡CH	1.89546	0.8918 (sp <sup>1.71</sup> ) <sub>C</sub> + 0.4524 (sp <sup>0.01</sup> d <sup>0.60</sup> ) <sub>Ni</sub>	79.53	20.47	-0.42297

The bond ellipticity is defined as  $\varepsilon = (\lambda_1/\lambda_2) - 1$ , where,  $|\lambda_1| \geq |\lambda_2|$  and provides a quantitative measure of the  $\pi$  character of the bond. The plane of the  $\pi$  distribution is uniquely specified by the direction of the axis associated with the curvature of the smallest magnitude  $\lambda_2$ . The  $\varepsilon$  values of various bonds show that the Ni—N bond in X = H, Me species has the most pronounced  $\pi$  character, while in X=HC=CH<sub>2</sub>, C≡CH, the Ni—C bond has most pronounced  $\pi$  character (Table 7). Therefore, donation for the metal-carbene bond is more important than back-donation.

**Nucleus-independent chemical shift (NICS).** As an effort to discuss the use of NICS as a measure of aromaticity for the N-heterocycle, we have calculated NICS values along the  $z$  axis to the ring plane beginning in the center of the ring up to 2.0 Å. These calculations show that the shape of the NICS profile with respect to the distance from the ring center is similar. In addition, for all species, we have localized the NICS maxima and minima and determined the distances to the center of the ring at

Table 6

Bond Critical Point Properties Obtained by AIM analysis for [Ni(N-heterocyclic carbene)(NO)(R)] (R = H, Me, HC=CH<sub>2</sub>, and C≡CH)

	$\rho$	$\nabla^2\rho$	H
X=H			
Ni—N	0.1338	0.6146	0.0521
N—O	0.1338	0.6146	0.0521
Ni—C	0.1247	0.4256	0.0468
Ni—X	0.1018	0.2211	0.0280
X=Me			
Ni—N	0.1369	0.6045	0.0558
N—O	0.4937	-1.2677	0.7251
Ni—C	0.1231	0.4327	0.0448
Ni—X	0.1091	0.2701	0.0333
X=HC=CH <sub>2</sub>			
Ni—N	0.1391	0.5984	0.0586
N—O	0.4975	-1.2925	0.7361
Ni—C	0.1224	0.4207	0.0440
Ni—X	0.1144	0.3173	0.0379
X=C≡CH			
Ni—N	0.1544	0.5800	0.0772
N—O	0.5052	-1.3415	0.7565
Ni—C	0.1206	0.4123	0.0422
Ni—X	0.1115	0.3876	0.0366

Table 7

Hessian matrix values and ellipticity obtained by AIM analysis for [Ni(N-heterocyclic carbene)(NO)(R)] (R = H, Me, HC=CH<sub>2</sub>, and C≡CH)

	$\lambda_1$	$\lambda_2$	$\lambda_3$	$\varepsilon$
X=H				
Ni—N	-0.2340	-0.2169	1.0656	0.0788
Ni—C	-0.1634	-0.1626	0.7516	0.0052
Ni—X	-0.1651	-0.1559	0.5422	0.0590
X=Me				
Ni—N	-0.2415	-0.2207	1.0667	0.0942
Ni—C	-0.1601	-0.1598	0.7526	0.0022
Ni—X	-0.1434	-0.1353	0.5487	0.0602
X=HC=CH <sub>2</sub>				
Ni—N	-0.2460	-0.2260	1.0704	0.0888
Ni—C	-0.1610	-0.1597	0.7414	0.0078
Ni—X	-0.1552	-0.1414	0.6140	0.0978
X=C≡CH				
Ni—N	-0.2843	-0.2573	1.1216	0.1049
Ni—C	-0.1575	-0.1569	0.7268	0.0038
Ni—X	-0.1461	-0.1303	0.6640	0.1216

which they occur (Table 1). For all complexes, the highest absolute value of NICS is close to the center of the ring. It is possible that induced magnetic fields generated by  $\sigma$  aromaticity are particularly large in the center of the ring, but systems with  $\pi$  aromaticity have minimum NICS at a certain distance from the center of the ring. Also, these values indicate a decrease in the aromaticity of the complexes compared to  $C_3H_4N_2$ .

**Conclusions.** In this paper, we have carried out a DFT study of a series of heterocyclic carbene nickel complexes of the type  $[Ni(N\text{-heterocyclic carbene})(NO)(R)]$  ( $R = H, Me, HC=CH_2, \text{ and } C\equiv CH$ ) to investigate the influence of carbene substituents on their molecular and electronic properties. We have examined the geometries, electronic structures, frontier orbitals (HOMO and LUMO), and aromaticity of these complexes. Calculation results confirm that the metal-carbene bond donation is more important than back-donation in the interaction between Ni and the carbene fragment. The NICS values suggest that aromaticity decreases in the heterocyclic ring in the complexes.

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