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Estimation of σ-Donation and π-Backdonation of Cyclic Alkyl(amino) Carbene-Containing Compounds

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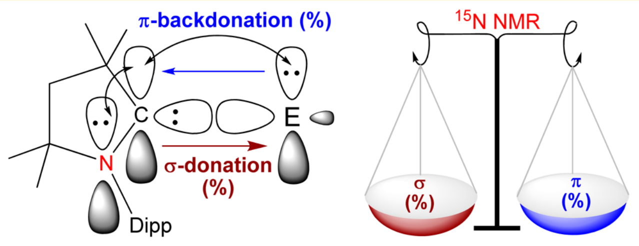
Supporting Information

ABSTRACT: Herein, we present a general method for a reliable estimation of the extent of π-backdonation ($C_{cAAC}\leftarrow E$) of the bonded element (E) to the carbene carbon atom and $C_{cAAC}\rightarrow E$ σ-donation. The $C_{cAAC}\leftarrow E$ π-backdonation has a significant effect on the electronic environments of the ^{15}N nucleus. The estimation of the π-backdonation has been achieved by recording the chemical shift values of the ^{15}N nuclei via two-dimensional heteronuclear multiple-bond correlation spectroscopy. The chemical shift values of the ^{15}N nuclei of several cAAC-containing compounds and/or complexes were recorded. The ^{15}N nuclear magnetic resonance chemical shift values are in the range from −130 to −315 ppm. When the cAAC forms a coordinate σ-bond ($C_{cAAC}\rightarrow E$), the chemical shift values of the ^{15}N nuclei are around −160 ppm. In case the cAAC is bound to a cationic species, the numerical chemical shift value of the ^{15}N nucleus is downfield-shifted (−130 to −148 ppm). The numerical values of the ^{15}N nuclei fall in the range from −170 to −200 ppm when σ-donation ($C_{cAAC}\rightarrow E$) of cAAC is stronger than $C_{cAAC}\leftarrow E$ π-backacceptance. The π-backacceptance of cAAC is stronger than σ-donation, when the chemical shift values of the ^{15}N nuclei are observed below −220 ppm. Electron density and charge transfer between C_{cAAC} and E are quantified using natural bonding orbital analysis and charge decomposition analysis techniques. The experimental results have been correlated with the theoretical calculations. They are in good agreement.



Over the past two and a half decades, stable singlet carbenes have been utilized as efficient ligands in different fields of chemistry.[1] Stable carbenes possess a divalent carbon atom that is bonded to at least one heteroatom (and to a maximum of two heteroatoms); otherwise, they cannot be isolated or stored under ambient conditions because of the electron deficiency at the carbene carbon center.[2] The heteroatom (such as N, P, S, or O) reduces the electron deficiency of the carbene carbon atom by sharing its lone pair of electrons.[2a] NHCs (NHC = N-heterocyclic carbene) generally stabilize chemical species via strong σ-donation from the carbene carbon atoms to the bonded elements ($C_{NHC}\rightarrow E$).[3] The role of carbenes as ligands for the stabilization of low-valent main group elements and transition metals in their low oxidation states has been demonstrated.[3] Moreover, carbenes have been shown to function as efficient ligands for transition metals in the field of catalysis.[1,4] The syntheses and characterizations of carbene-stabilized chemical species have an important influence on the rapidly growing areas of chemistry.[5] Initially, N-heterocyclic carbenes (NHCs) have been employed as strong σ-donating ligands.[1−3] Today, cyclic alkyl(amino) carbenes (cAACs) have been introduced as competing ligands (Figure 1).[6] In cAAC, the HOMO is slightly higher and the LUMO is slightly lower in energy when compared with those of NHC.[7] Consequently, the HOMO−LUMO energy gap is smaller in cAAC than in NHC, and this is the most crucial aspect of cAAC. A couple of years ago, the comparative σ-donation and π-acceptance properties of carbenes were studied in a series of carbene−phosphenidene adducts.[8] cAACs have been shown to be stronger σ-donors and better π-acceptors than NHCs,[9] making them more suitable[5−8] for the stabilization of chemical species that have not been isolated by employing NHCs as ligands. Recently, it was

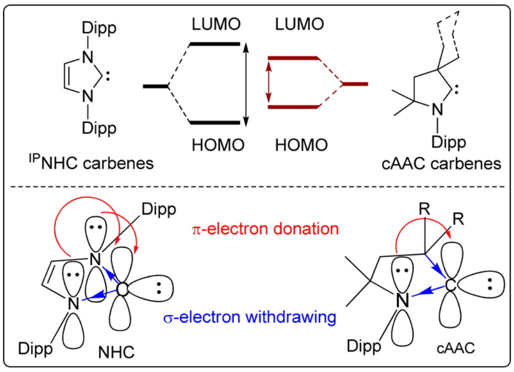


Figure 1. Comparison between NHC (left) and cAAC (right) carbenes.

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demonstrated that cAAC ligands have stabilized several monatomic first row transition metals (Zn−Mn) with coordination number two.[10] The cAAC-ligated diatomic molecules (Au_2 and Co_2)[11a,b] and the anionic Fe^- species[11c] have been reported. These systems (Au_2 and Co_2)[11a,b] are unique for the study of their metal−metal interactions. The strong π-accepting properties of cAACs induce diradicaloid character in silylones,[12a] germylones,[12b] and the carbon monoxide adduct.[12c] Over half of a decade, a large number of radicals and diradicals containing cAACs were isolated and studied by electron paramagnetic resonance (EPR) spectroscopy.[13]

The paramagnetic radicals are generally characterized by EPR measurements rather than by using nuclear magnetic resonance (NMR) spectroscopy. However, NMR spectroscopy is utilized as one of the very important tools for the characterization of diamagnetic cAAC-containing species. The chemical shift values of ^1H, ^{13}C, and ^{31}P NMR are among the most commonly recorded data for the characterization of these compounds. The most utilized carbenes contain nitrogen as heteroatoms. However, the ^{15}N ($I = {}^1/_2$) or ^{14}N ($I = 1$) NMR chemical shift values have seldom been recorded for the characterization of carbene-containing compounds. The ^{15}N NMR chemical shift values of free NHC and some NHC-containing complexes have been reported elsewhere.[14] Surprisingly, these values were not correlated with the π-backaccepting property of NHC ligands.

Experimental results suggest that the carbene carbon atom of cAAC polarizes the electron densities from the adjacent nitrogen atom to its vacant p_z orbital ($N \rightarrow C_{cAAC}$). This electron sharing depends on the electron density on the element (E) bound to the cAAC and their oxidation states.[10−13] Geometrically, this is reflected in the C−N bond distance that varies in the range of 1.28−1.46 Å.

The cAACs form stronger donor−acceptor bonds ($C_{cAAC} \rightarrow E$ and $C_{cAAC} \leftarrow E$), which are responsible for the better stability of the resulting products.[15,16] Structural bond parameters and theoretical investigations (NBO analysis) of cAAC-containing products often suggest that the π-backdonation from the bound element (E) to the carbene carbon atom ($C_{cAAC} \leftarrow E$) is stronger than the σ-donation from cAAC to the element E ($C_{cAAC} \rightarrow E$), which leads to a positive partial charge on E (E = main group element or metal).[10,11,12a,b] The cAAC favors a $C_{cAAC} \rightarrow E$ bond when E is higher-valent,[13a] while it prefers a combination of $C_{cAAC} \rightarrow E$ and $E \rightarrow C_{cAAC}$ when E is lower-valent.[15,16] Switching of the type of C_{cAAC}−E bond is achieved by oxidation or reduction of the E/EL_n part (L = halogen atoms).[13,15−17] Another type of C−E bond is observed in cAAC-containing radicals, in which the C_{cAAC} forms a covalent electron sharing single bond[13] with E along with one unshared electron (radical) on the C_{cAAC}. There is no such precedence of this type of bonding in case of NHC. The cAAC has the unique ability to control the distribution of electron densities around the bound element. Such a feature was not observed in NHC.

The significant π-accepting property makes cAAC in many ways different from NHC.[18] Herein, we report on the theoretical and experimental ^{15}N NMR spectroscopic studies (HMBC, three-bond coupling of ^1H−^{15}N) to estimate the amount of σ-donation and π-backacceptance of cAAC in some of the representative cAAC-containing compounds.

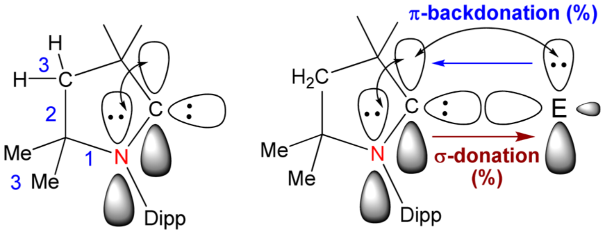


Figure 2. Three-bond ^1H−^{15}N coupling (left) and σ-donation of cAAC and π-backdonation from E (right).

cAAC has a singlet-spin ground state with a pair of electrons on the sp^2 orbital of the carbene carbon atom (C_{cAAC}) (Figure 2, left) and a vacant p-orbital on C_{cAAC}. The C_{cAAC}−N bond distance of a free cAAC is shorter (1.315 Å) than the normal C−N single bond due to the delocalization of the lone pair of electrons of the adjacent nitrogen atom to the p_z orbital of the carbene carbon atom ($N{:}\rightarrow C_{cAAC}$). As mentioned earlier, experimentally it has been observed that compounds containing cAAC as a ligand can have a wide range of bonding scenarios, e.g., coordinate σ-bond, donor−acceptor partial double bond, and covalent electron-sharing single bond. The C_{cAAC}−N bond distances are recorded within the range of 1.28−1.46 Å. The C_{cAAC}−N and C_{cAAC}−E bond distances often infer to the nature of the bond existing between C_{cAAC} and the acceptor atoms. However, there are exceptions. It has been reported in some cases that the C_{cAAC}−E bond distances are similar, although the natures of bonds between C_{cAAC} and E are completely different. For example, the monoradical $(cAAC^\bullet)SiCl_3$ has a bond distance (C_{cAAC}−Si) similar to that of $(cAAC)_2Si_2Cl_2$ (∼1.82 Å). However, the former contains an electron-sharing covalent C_{cAAC}−Si single bond between silicon and the carbene carbon atom, while the latter has a donor−acceptor type partial double ($C_{cAAC}{=}Si$) bond. The C_{cAAC}−N bond distances of $(cAAC^\bullet)SiCl_3$ and $(cAAC)_2Si_2Cl_2$ are slightly different. The difficulty in differentiating the nature of the C_{cAAC}−E bonds mentioned above has rarely[16] been experimentally addressed. Although, Bertrand et al. have experimentally observed a general trend of the π-accepting property of different carbenes in a series of carbene−phosphenidene adducts, a correlation between the nature of the chemical bond and an easily measurable observable is in general lacking.[8]

It is obvious that a change in the nature of the bonding should have an effect on the ^{14}N or ^{15}N nucleus. The former nucleus is more sensitive than the ^{15}N one. The NMR resonances are usually broadened by quadrupolar interactions, making the characterization via a high-resolution NMR spectrometer difficult. Therefore, two-dimensional heteronuclear multiple-bond correlation spectroscopy (^1H−^{15}N HMBC) has been employed to extract more information about the nature of the bond between C_{cAAC} and E (Figure 2, right). Using this method, chemical shift values of free cAAC and cAAC-containing compounds of main group elements (mostly silicon, E = Si) have been recorded.

The ^{15}N HMBC (three-bond correlation) measurement has been started with cAAC·LiOTf (**1**),[6] which shows a resonance at −159.0 ppm coupling with protons of the CH_2 unit of the five-membered carbene ring and methyl protons of the $NCMe_2$ group (as shown in Figure 2). The cAAC reacts with $SiCl_4$ to produce the $(cAAC)\rightarrow SiCl_4$ (**4**)[13a] adduct that shows a ^{15}N resonance at −164.1 ppm, suggesting the carbene carbon atom of cAAC forms a coordinate σ-bond with both LiOTf and $SiCl_4$ in **1** and **4**, respectively (Figure 3). The coordinate bond in **1** is very strong, and hence, it is very difficult to extract the free cAAC (Me_2-cAAC, Et_2-cAAC, and Cy-cAAC) by using

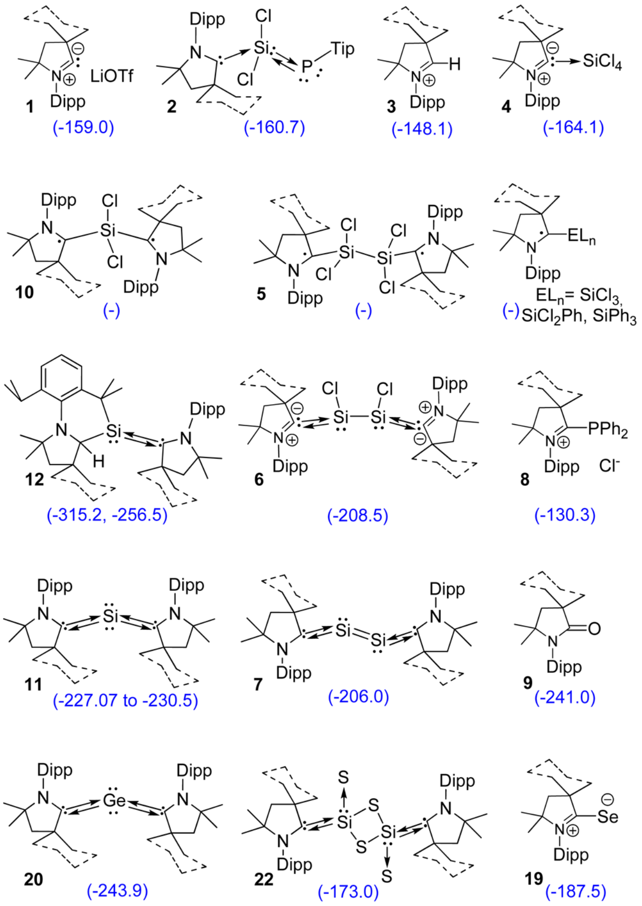


Figure 3. Representative cAAC-containing compounds with ^{15}N chemical shift values (δ) and their bonding characteristics.

nonpolar solvents such as *n*-hexane or toluene. Only bulky cAAC ligands can be extracted (free from LiOTf) with nonpolar solvents.[6] When cAAC forms a coordinate bond ($C_{cAAC}\rightarrow E$), the C_{cAAC}–N bond distance is close to 1.30 Å. Compound (cAAC)$\rightarrow$Si(Cl_2)$\rightarrow$P-Tip (**2**)[18c] shows a resonance at −160.7 ppm that is close to those of **1** and **4** (Figure 3), as expected. As a matter of fact, the carbon–silicon ($C_{cAAC}\rightarrow Si$) coordinate σ-bond distance is approximately ~1.94 Å, in **2** and **4**. The monoradical (cAAC$^{\bullet}$)$SiCl_3$ is produced when (cAAC)$\rightarrow SiCl_4$ (**4**) undergoes one-electron reduction.[13a] The bond between the carbene carbon atom and silicon atom results in a covalent electron-sharing single bond (C_{cAAC}–Si) leading to a shortening of the carbon–silicon bond distance by ~0.12 Å and lengthening of the C_{cAAC}–N bond by ~0.09 Å.[13a] A 1,4-singlet diradical (Cy-cAAC$^{\bullet}$) (Cl_2)Si–Si(Cl_2)($^{\bullet}$CAAc-Cy) (**5**) is formed when (cAAC$^{\bullet}$)$SiCl_3$ is further reduced with 1 equiv of KC_8.[13c] Singlet 1,3-diradical (cAAC$^{\bullet}$)$_2SiCl_2$ (**10**) is obtained via the metathesis of (^{IP}NHC)$\rightarrow SiCl_2$ with 3 equiv of cAAC.[13b] However, both monoradical (cAAC$^{\bullet}$)$SiCl_3$ and diradicals **5** and **10** are ^{15}N NMR silent because of the presence of the radical electron on the carbene carbon atoms.

Compounds with low-coordinate silicon, (cAAC)$\rightarrow$Si(Cl)–Si(Cl)$\leftarrow$(cAAC) (**6**)[15] and (Me_2-cAAC)$\rightarrow$Si=Si$\leftarrow$(CAAc-Me_2) (**7**),[16] are synthesized via the reduction of (cAAC)$\rightarrow SiCl_4$ (**4**) with 3 and 4 equiv of KC_8, respectively. The C–N bond distances are similar in both **6** and **7**, while the C_{cAAC}–Si bond distance is slightly shorter in **6**. Both **6** and **7** are theoretically suggested to possess donor–acceptor coordinate partial double bonds.[15,16] The ^{15}N NMR resonances are observed at −208.5 and −206.0 ppm for **6** and **7**, respectively, which are upfield-shifted when compared with that of precursor **4**, suggesting both $C_{cAAC}\rightarrow Si$ σ-donation and $C_{cAAC}\leftarrow Si$ π-backdonation in **6** and **7** (Figure 3). Replacement of Me_2-cAAC with Et_2-cAAC or Cy-cAAC has a negligible effect on the ^{15}N chemical shift values.

The ^{15}N chemical shift values of cAAC-containing cationic compounds are found to be downfield-shifted compared to those of cAAC$^{\bullet}$(LiOTf) (**1**). The $C_{cAAC}\leftarrow P$ π-backdonation becomes negligible in the cationic salt $[(cAAC)PPh_2]^+Cl^-$ (**8**).[13e] The cation PPh_2^+ is stabilized by the $C_{cAAC}\rightarrow P$ σ-donation, and the lone pair of electrons is tightly retained on the phosphorus atom, leading to a shorter C–N bond and a longer C–P bond. The ^{15}N resonance of **8** appears at −130.3 ppm, which is downfield-shifted with respect to that of **1** because of the cationic charge on the carbene carbon atom of $(cAAC)PPh_2^+$. The corresponding ^{15}N chemical shift value of the protonated carbene salt cAAC$^{\bullet}H^+$ OTf^- (**3**) is −148.1 ppm, which is upfield-shifted when compared with that of **8**. This might be due to the lower electronegativity of the hydrogen atom. The ^{15}N resonances of (cAAC)O (**9**),[19] (cAAC)S (**23**), and cAAC$\rightarrow$Se (**19**) are observed at −241.0, −199.8, and −187.5 ppm, respectively, suggesting a C=O/C=S double bond character in **9** and **23**, while the corresponding carbon–selenium bond is likely to be a $C_{cAAC}\rightarrow Se$ σ-bond in **19**. The accumulation of electronic charge on the selenium atom of cAAC$\rightarrow$Se is higher, and therefore, it is easily utilized by selenium to ionize iodine (I_2) to form the cAAC$\rightarrow$Se–I–I^+ I_3^- salt.[20]

When the 1,3-diradical (cAAC$^{\bullet}$)$_2SiCl_2$ (**10**) is completely dechlorinated with 2 equiv of KC_8, siladicarbene (cAAC)$_2$Si (**11**) is obtained.[12a] Theoretical calculations showed that the covalent C–Si single bond in **10** has transformed to a C–Si–C three-center, two-electron π-bond in **11**. The accumulation of positive charge on the central silicon atom of **11** suggests that the π-backdonation from silicon to the carbene carbon atom ($C_{cAAC}\leftarrow Si$) is greater than the $C_{cAAC}\rightarrow Si$ σ-donation.[12a] The ^{15}N chemical shift value of **11** is −230.5 ppm, which is more upfield-shifted compared with that of disiladicarbene (**7**)[16] but close to that of the analogous (cAAC)$_2$Ge (germylone)[12b] (−222.5 ppm). The electron-induced isomerization of **11** leads to the formation of compound (Cy-cAACH)Si(CMe_2)=(Cy-cAAC) (**12**),[13d] which is theoretically predicted to have a higher degree of donor–acceptor carbon–silicon double bond character because of the better $C_{cAAC}\leftarrow Si$ π-backdonation. The experimental chemical shift of **12** is further upfield-shifted (−256.5 ppm), as expected (Figure 3).

It is well-known that silicon is a metalloid, and hence, the silicon–carbon bond is expected to have covalent character greater than that of a metal–carbon bond.[10c,12a,d] The ^{15}N chemical shift values of some of the carbene–metal complexes (Figure 4) have been recorded to study the effect of σ-donation ($C_{cAAC}\rightarrow M$) of cAAC and π-backdonation ($C_{cAAC}\leftarrow M$) of the metal (M) and confirm the validity of the general trend. The bond between C_{cAAC} and nickel in the square planar complex (cAAC)$_2NiCl_2$ (**13**)[10c] is a $C_{cAAC}\rightarrow Ni$ coordinate σ-bond [C–N, 1.3154(18) Å; C–Ni, 1.9150(14) Å]. The ^{15}N chemical shift (−160.6, −161.0 ppm; two conformers) of **13** is close to the value of **1**. The theoretical calculations on (cAAC)$_2$Ni (**14**) [C–N, 1.3381(16)/1.3420(16) Å; C–Ni, 1.8448(14)/1.8419(13)][10c] showed the presence of significant π-backdonation ($C_{cAAC}\leftarrow Ni^0$). The electronegativities of Si and Ni are

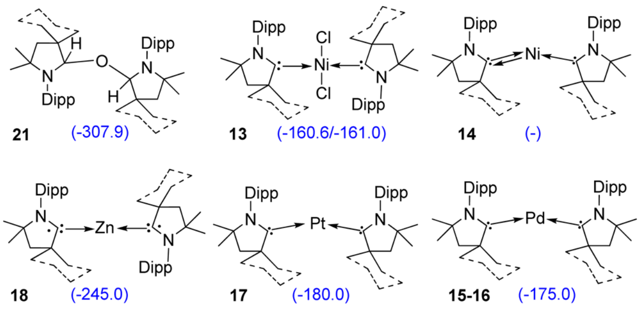


Figure 4. Representative diamagnetic cAAC compounds with ^{15}N chemical shift values (δ).

almost the same. Because the ionization potential of Si is slightly higher than that of Ni, the Si analogue is expected to exhibit greater covalent character. Earlier theoretical calculations[10c,12a,d] show that the π-backdonation from Si to C_{cAAC} is greater in $(cAAC)_2Si$ (**11**) than that of Ni in $(cAAC)_2Ni$ (**14**). This indicates greater covalent character for the C−Si bond. However, it is not reflected in the charge data (0.55 e for Si and 0.34 e for Ni). The extent of $C_{cAAC}{\leftarrow}M^0$ π-backdonation is similar in the palladium (**15**) (−175.0 ppm) and platinum (**16** and **17**) (−180.0 ppm) analogues.[21] However, the ^{15}N chemical shift of $(cAAC)_2Ni$ (**14**) is not obtained because of the broadening of ^1H NMR resonances. The π-backdonation is comparatively higher in the zinc analogue [singlet diradicaloid $(cAAC)_2Zn$ (**18**)[10a] complex] [δ (^{15}N) −245.0] than those of the corresponding Ni/Pd/Pt complexes (Figure 4). The chemical shift values of **12** and **21** are the most upfield-shifted [below −300 ppm (Figures 3 and 4)], when compared to those of the known compounds.

The ^{15}N NMR chemical shift values of some of the representative NHC-containing compounds have been recorded (Figure 5). The chemical shift in the ^{15}N NMR spectrum of the free ^{iPr}NHC (Figure 5)[14d] appears at −185.1 ppm, which is much more upfield-shifted than that of cAAC (−159.0 ppm). The corresponding chemical shift value of the protonated carbene salt ($^{iPr}NHC{\cdot}HCl$) is further upfield-shifted (−196.3 ppm). This trend of $^{iPr}NHC/^{iPr}NHC{\cdot}HCl$ is the opposite of those of cAAC/cAAC·HCl (Figure 3), which might be due to the polarization of electron density of the C═C bond toward the N atoms. Importantly, a similar C═C bond is absent within the cAAC molecule. The chemical shift values of $(^{iPr}NHC)SiCl_2$[22] and $(^{iPr}NHC)_2NiCl_2$[23] are −191.8 and −190.9 ppm, respectively, which are slightly upfield-shifted compared to that of free ^{iPr}NHC. These values are even slightly downfield-shifted when compared with that of $^{iPr}NHC{\cdot}HCl$. The chemical shift value of $(cAAC)_2NiCl_2$ (**13**) [−160.6/−161.0 ppm (Figure 4)] is far more downfield-shifted compared to that of the NHC analogue.[10c,23] $(^{iPr}NHC)_2Ni$ is obtained when $(^{iPr}NHC)_2NiCl_2$ is reduced with 2 equiv of KC_8 in a mixture (5:1) of solvents (toluene/THF). The ^{15}N NMR of $(^{iPr}NHC)_2Ni$ is observed at −197.5 ppm, which is close to the reported value of $(^{Mes}NHC)_2Ni$ (−193.9 ppm).[14f] The chemical shift values of NHC complexes given above are in line with the previously made[24] statement that NHC is a poor π-acceptor.

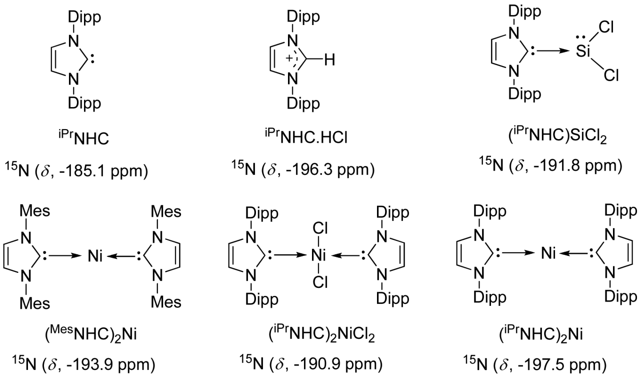


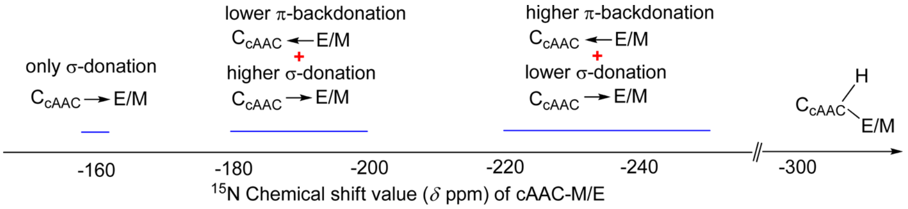
Figure 5. Representative diamagnetic NHC compounds with ^{15}N chemical shift values (δ).

The DFT calculations have been performed (for details, see Computational Details in the Supporting Information) on complexes **1**−**17**, **19**, **20**, and **22** to calculate theoretical ^{15}N chemical shift (δ) values, correlated with structural parameters. The calculated δ values at the R/U-B3LYP/def2-TZVP level of theory are very similar to the experimental findings (Table 1). The natural bond orbital (NBO) analysis that is implemented in Gaussian09 has been studied to gain insight into the electronic structure and bonding nature of C_{cAAC}−E and N−C_{cAAC} bonds. In most of the compounds, the C_{cAAC} is preferably connected to the E by σ-donation with concomitant π-acceptance to its vacant p-orbital to increase the stability.[15,16] The C_{cAAC} can also share the lone pair of electrons from the adjacent N atom to reduce its electron deficiency. Therefore, the electronic environment around the N atom is mainly regulated by the electron deficiency on the C_{cAAC}, which further depends upon the π-backdonation from the E atom.

To quantify the extent of $C_{cAAC}{\rightarrow}E$ σ-donation, $C_{cAAC}{\leftarrow}E$ π-backdonation, and $N{\rightarrow}C_{cAAC}$ π-donation, we performed natural localized molecular orbital (NLMO) analysis (Table 1). Unsurprisingly, the electron density of the C_{cAAC}−E σ-bond mostly resides on the carbene atom and the reverse is true for the C_{cAAC}−E π-bond. The delocalization of the lone pair electrons of the N atom toward C_{cAAC} ($N{\rightarrow}C_{cAAC}$) leads to another π-acceptance situation. Therefore, the extents of these two π-bonds ($C_{cAAC}{\leftarrow}E$ and $N{\rightarrow}C_{cAAC}$) are inversely related to each other. The natural bond order and Wiberg bond order of C_{cAAC}−E and N−C_{cAAC} bonds were calculated to evaluate the π-bond strength (Table S1). According to NBO results, there is no significant $C_{cAAC}{\leftarrow}E$ π-back-donation observed in compounds **1**−**5**, **8**, and **10** and the hydrogenated ($_{cAAC}H$) carbene part of **12**. In molecules **9**, both the σ- and π-bonding electrons are polarized toward the O atom because of the higher electronegativity indicating a higher degree of covalency. A similar type of covalency occurs in the C═Se bond of **19** and the C═Si part of **12**, which is obvious from the NLMO data (Table 1). Moreover, from Table 1, it is clear that in the C_{cAAC}−E donor−acceptor bond, C_{cAAC} shows greater σ-donation than π-acceptance, while an opposite result was found in the case of compound **11** where π-backdonation (31%) is predominant over σ-donation (23%), which is further supported by a previous report.[12a] The positive partial charges on the Si atoms in **7** ($q_{Si} = 0.109e$) and **11** ($q_{Si} = 0.546e$) also indicate that the $C_{cAAC}{\leftarrow}Si$ π-backdonation is stronger than the $C_{cAAC}{\rightarrow}Si$ σ-donation (Table 1 and Table S2). However, it is evident that the percentage of $N{\rightarrow}C_{cAAC}$ π-donation value is controlled by $C_{cAAC}{\leftarrow}E$ π-backdonation. There is no significant back-donation noticed in **13** because of the highly electronegative Cl atoms bonded with the Ni center.

The electronic scenario proposed using NLMO analysis were further studied by the CDA (charge decomposition analysis)

Table 1. ^{15}N Chemical Shift Values (recorded via 1,3-coupling of ^1H with ^{15}N)[a]



compound	no.	C_{cAAC}–N bond distance (Å)	^{15}N (δ)	^{15}N coupling with ^1H	calculated δ value	% of σ-donation	% of π-backdonation	% of N→C_{cAAC} π-donation
Cy-cAAC·LiOTf	1	1.315(3) (1.303)	−159.0	CH_2 and CMe_2	−150.1	6	–	23
(Cy-cAAC)Si(Cl_2)=P-Tip	2	1.301 (1.300)	−160.7	CMe_2	−152.9	23	–	28
Cy-cAACH$^+$OTf$^-$	3	1.290 (1.287)	−148.1	CH_2 and CMe_2	−167.3	35	–	27
(Me_2-cAAC)$SiCl_4$	4	1.303(2) (1.303)	−164.1	CH_2 and CMe_2	−172.2	24	<1	27
(Cy-cAAC$^\bullet$)(Cl_2)Si–Si(Cl_2)($^\bullet$CAAc-Cy)	5	1.376(6) (1.379)	no signal	–	−255.8	30	–	15
(Me_2-cAAC)(Cl)Si–Si(Cl)(CAAc-Me_2)	6	1.336(3)–1.337(2) (1.339)	−208.5	CH_2 and CMe_2	−197.7	30	27	20
(Me_2-cAAC)Si=Si(CAAc-Me_2)	7	1.342(5) (1.343)	−206.0	CH_2 and CMe_2	−200.9	22	13	24
[(Me_2-cAAC)PPh_2]$^+$Cl$^-$	8	1.302(18) (1.300)	−130.3	CH_2 and CMe_2	−126.0	35	–	32
(Me_2-cAAC)O	9	1.374(10) (1.365)	−241.0	CH_2 and CMe_2	−238.6	64	28	9
(Cy-cAAC$^\bullet$)$_2SiCl_2$	10	1.400(2)–1.403(2) (1.392)	no signal	–	−267.5	25	–	14
(Cy-cAAC)$_2$Si	11	1.382(16)–1.373(16) (1.368)	−230.5	CH_2 and CMe_2	−221.5	23	31	9.9
(Cy-cAACH)Si(CMe_2)=CAAc-Cy	12	1.461(3) (1.465)	−315.2	CH_2 and CMe_2	−310.6,	26	–	1
		1.383(3) (1.374)	−256.5		−248.2	28	49	6
(Me_2-cAAC)$_2NiCl_2$	13	1.3154(18)–1.3148(18) (1.307)	−160.6, −161.0	CH_2 and CMe_2	−152.7	20	<1	24
(Me_2-cAAC)$_2$Ni	14	1.3381(16)/1.3420(16) (1.332)	no signal	–	−197.6	16	5	21
(Cy-cAAC)$_2$Pd	15	1.3267(18) (1.314)	−175.0	CMe_2	−230.9	11	4	22
(Me_2-cAAC)$_2$Pt	16	1.3231(15) (1.324)	−180.1	CMe_2	−178.8	22	6	22
(Et_2-cAAC)$_2$Pt	17	1.3267(18) (1.325)	−180.0	CH_2, CMe_2	−183	20	–	21
(Me_2-cAAC)$_2$Zn	18	1.376(2)	−245.0	CH_2, CMe_2				
(Me_2-cAAC)Se	19	1.323(2) (1.337)	−187.5	CH_2, CMe_2	−185.1	38	30	19
(Me_2-cAAC)$_2$Ge	20	1.3666(19) (1.378)	−222.5	CH_2, CMe_2	−227.1	23	52	16
(Me_2-cAACH)$_2$O	21	1.4352(18)–1.4353(19)	−307.9	CH_2, CMe_2				
(Me_2-cAAC)$_2Si_2S_4$	22	1.308(5) (1.306)	−173.0	CH_2 and CMe_2	−176.7	22	–	26

[a] Calculated bond distances at the M06-2X/def2-SVP level are given in parentheses. Quantitative electron distributions of donor–acceptor bonds (C_{cAAC}→E σ-donation, C_{cAAC}←E π-backdonation, and N→C_{cAAC} π-donation) are taken from NLMO analysis. Here, C_{cAAC} is the carbene donor center of cAAC, E the element, and M the metal.

method developed by Dapprich and Frenking et al.,[25] implemented in AOMix-6.81. The CDA has been studied for carbene-stabilized silicon substituents and some metal compounds. The Mulliken charge (*e*) donation and backdonation between the carbene fragment (F_C) and the counterpart (F_E) and also the net charge donation from F_C to F_E are clearly displayed in Table 2. In some cases, the difference between the calculated amount of donation ($F_C \rightarrow F_E$) and backdonation ($F_C \leftarrow F_E$) is very different from the net charge donation between fragments [$\Delta q(F_C \rightarrow F_E)$]. This is because the terms donation and backdonation in the CDA include not only charge transfer interactions but also an overall reorganization of electron density, including both charge transfer and electron polarization between fragments. Very recently, Holzmann and Frenking et al. have performed detailed bonding analysis of $(L)_2Si_2$ and $(L)_2Si$ with the help of the EDA-NOCV method.[26] They have shown that the relative contributions of σ-donation to E_{orb} (orbital interaction) in $(cAAC)_2Si_2$ and $(cAAC)_2Si$ are greater (56.9 and 59.9%) than the respective π-backdonations (37.8 and 30.6%, respectively). Similar results have been obtained for compounds **7** and **11**; i.e., more donation occurs from F_C (0.277*e* and 0.467*e*) than backdonation from F_E (0.204*e* and 0.259*e*).

The N→C_{cAAC} π-electron delocalization is qualitatively correlated by pursuing in-depth analysis of the ^{15}N chemical shift tensor along the principle axis (Table S3). Ideally, if the lone pair of the N atom is shared with the vacant p-orbital of the C_{cAAC} center, the most deshielded direction will be

Table 2. Results of the CDA Analysis at the M06-2X/def2-TZVP Level of Theory[a]

	$F_C \rightarrow F_E$	$F_C \leftarrow F_E$	$\Delta q(F_C \rightarrow F_E)$	q_C	q_E
2	0.438	0.266	0.376	0.141	1.198
4	0.430	0.392	0.312	0.158	1.395
5	0.299	−0.061	−0.027	−0.249	1.091
6	0.426	0.263	0.247	−0.082	0.522
7	0.277	0.204	0.181	−0.052	0.109
8	0.429	0.205	0.577	0.279	0.846
9	−0.163	−0.602	0.387	0.722	−0.637
10	0.317	−0.021	−0.025	−0.289	1.580
11	0.467	0.259	0.212	−0.172	0.546
13	0.286	0.226	0.294	0.331	0.445
14	−17.191	−8.779	1.544	0.191	−0.367

[a] $F_C \rightarrow F_E$ and $F_C \leftarrow F_E$ represent charge donation and backdonation between carbene fragment (F_C) and E-counterpart (F_E), respectively. $\Delta q(F_C \rightarrow F_E)$ represents the net charge donation from F_C to F_E. q_C and q_E are the partial atomic charges (NPA) of C_{cAAC} and E atoms, respectively.

perpendicular to the $N-C_{cAAC}$ σ-bond. Herein, we observe that eigenvectors δ_{11} and δ_{22} show maximal deshielding for **8**, corresponding to the strongest $N \rightarrow C_{cAAC}$ π-donation and the opposite for **12**, having the weakest $N \rightarrow C_{cAAC}$ π-donation (Table S3).

In conclusion, the chemical shift values (δ) (^{15}N HMBC NMR) of some representative cAAC-containing compounds have been recorded via correlated three-bond nitrogen−proton coupling ($^1H/^{15}N$ HMBC). The accumulation of electron density on the carbene carbon (cAAC) is sensibly reflected in the chemical shift value of the ^{15}N nuclei. Our results show that the extent of donation (σ-donation $C_{cAAC} \rightarrow E$ or π-backdonation $C_{cAAC} \leftarrow E$) affects the electronic environment on the ^{15}N nuclei of cAAC-E compounds. The chemical shift values (-160 ppm $< \delta$) of cationic cAAC-containing compounds (**3** and **8**) are shifted to lower field when compared with that of cAAC. The chemical shift values have so far two border lines at around −160 ppm for strong $C_{cAAC} \rightarrow E/M$ σ-donation and below −200 ppm for σ-donation and very strong π-backdonation.

The chemical shift (δ) exhibits a value around −160 ppm for strong σ-donation $C_{cAAC} \rightarrow Si$ (coordinate single bond). The intermediate numerical values ($-160 > \delta > -210$ for E = Si; **2**, **4**, **6**, and **7**) of the ^{15}N nuclei infer that $C_{cAAC} \rightarrow E$ σ-donation is higher than $C_{cAAC} \leftarrow E$ π-backdonation. When the numerical value of δ is smaller than −220 (for E = Si), the $C_{cAAC} \leftarrow Si$ π-backdonation is stronger than $C_{cAAC} \rightarrow Si$ σ-donation, indicating a higher extent of donor−acceptor partial double bond ($C_{cAAC}{=}Si$) such as in silylone (**11**) and germylone (**20**) (Table 1). When the carbene bears a covalently bound hydrogen atom such as in **12** and **21**, the ^{15}N NMR values appear below −300 ppm. The theoretical NMR calculations strongly resemble the experimental values. The calculated data and the bonding analysis provide convincing evidence of the electron donation and backdonation from C_{cAAC} and E/M, respectively. These promising results might encourage the researchers working with cAAC carbenes to study their compounds by ^{15}N HMBC NMR spectroscopy and include additional ^{15}N HMBC NMR chemical shift values (δ) along with other characterization data to provide an estimation of σ-donation ($C_{cAAC} \rightarrow E/M$) and π-backdonation ($C_{cAAC} \leftarrow E/M$).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02055.

^{15}N HMBC NMR spectra of the representative compounds and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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