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The influence of C(sp³)H-Selenium Interactions on the ⁷⁷Se NMR Quantification of the π-Accepting Properties of Carbenes

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Abstract: Selenium NMR has become a standard tool for scaling the π-accepting character of carbenes. Herein, we highlight that non-classical hydrogen bonding (NCHB), likely resulting from hyperconjugation, can play a significant role in the carbene-selenium ⁷⁷Se NMR chemical shift, thus triggering a non-linear behaviour of the Se-Scale.

Since the isolation of a (phosphino)(silyl)carbene¹ and an N-heterocyclic carbene (NHC),² stable carbenes have become ubiquitous in chemical science.³ Nowadays, a variety of stable carbenes, featuring very diverse electronic and steric properties, are known.⁴ Accordingly, choosing the best carbene for a given application is not an easy task;⁵ it requires a thorough understanding of the carbene stereoelectronic properties.

To evaluate the electronic properties of carbenes, several techniques have been developed, including calorimetric measurements of ruthenium complexes,⁶ the ¹³C NMR chemical shifts of palladium complexes,⁷ the electrochemical E₀ value for the Ru(III)/Ru(II) redox couples,⁸ and the Tolman Electronic Parameter (TEP), which is the most popular.⁹ Although all of these techniques provide a convenient way to evaluate the overall donor abilities of carbenes, they fail to deconvolute the σ-donating and π-accepting properties. To determine their π-accepting character, the ³¹P{¹H} NMR¹⁰ and ⁷⁷Se{¹H} NMR¹¹ chemical shifts of phenylphosphinidene- and selenium-carbene-adducts, respectively, have been exploited. The latter, developed by Ganter, relies on the ability of carbenes to engage in backbonding with the selenium lone pair (Figure 1). The more π-accepting carbenes favor resonance form I, which results in a downfield ⁷⁷Se{¹H} NMR signal, whereas the less π-accepting ones favor resonance form II resulting in an upfield shift. Compared with the phosphinidene scale (~400 ppm),¹⁰ the selenium scale covers a wider spectral range (~1200 ppm) which should allow for a greater delineation of the π-accepting

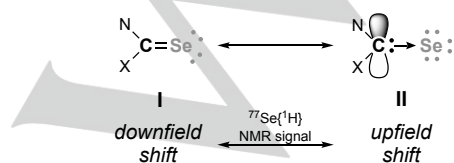


Figure 1. Canonical Structures of Carbene-Se adducts and their relation to ⁷⁷Se{¹H} NMR Spectroscopy.

properties of closely matching carbenes. Moreover, it benefits from a simple experimental protocol *i.e.* addition of elemental selenium to an *in-situ* generated free carbene. Despite the popularity of this method,¹² careful examination of the literature reveals several inconsistencies in ⁷⁷Se{¹H} NMR data. For example, it appears that the chemical shift for the selenium adduct of NHCs bearing tertiary N-alkyl substituents such as **IAd** (197 ppm) and **I^tBu** (183 ppm) display unexpectedly downfield signals with respect to secondary alkyl analogues such as **ICy** (-22 ppm) and **IⁱPrMe₂** (-18 ppm) (Figure 2).^{12m}

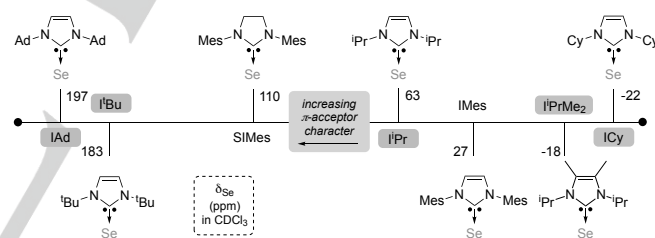


Figure 2. Non-linear behavior of the ⁷⁷Se{¹H} NMR chemical shifts in NHC-Se adducts

As mentioned by Cavallo, Nolan *et al.*,^{12m} such “difference amongst N,N-dialkylimidazol-2-ylidenes was very intriguing” since these data support, counterintuitively, a much stronger π-accepting character for tertiary N-alkyl substituted NHCs. Similar observations were recently highlighted by Huynh across several other carbenes families,¹³ stating caution should be taken when analyzing ⁷⁷Se{¹H} NMR data of carbene-selenium adducts. Rather short intramolecular Se–H distances, which are close to or within the sum of Van der Waals radii, were previously noted across several Se–NHC adducts by Cavallo and co-workers.^{12m} Herein, combining an experimental and theoretical approach, we demonstrate that non-classical hydrogen bonding (NCHB)¹⁴ interactions resulting from negative hyperconjugation trigger a non-linear behavior of the ⁷⁷Se{¹H} NMR scale in carbene-selenium adducts. NCHB is well established with O and S, but is less common for selenium, which is less electronegative.¹⁵ These interactions have been proposed with acidic protons in some oxazolidene-selenium adducts¹⁶ but are much more surprising with unactivated alkyl protons.

To begin our study, we first considered the five-membered cyclic (alkyl)(amino) carbenes (CAAC-5).¹⁷ We previously reported that the $^{77}\text{Se}\{^1\text{H}\}$ NMR signal of the selenium adduct of $^{\text{Et}}\text{CAAC-5}$ **1a** is at 481 ppm.^{12g} As observed with the NHC series, we found that the $^{77}\text{Se}\{^1\text{H}\}$ NMR chemical shift of the selenium adducts of the more sterically hindered $^{\text{Menth}}\text{CAAC-5}$ (635 ppm) **1b** and $^{\text{Ad}}\text{CAAC-5}$ (683 ppm) **1c** (Figure 3) appeared considerably downfield. Going further, we synthesized the adducts of six-membered cyclic (alkyl)(amino)carbenes (CAAC-6), which provide more steric crowding than CAAC-5s as a result of a larger C-C_{carb}-N angle.¹⁸ Here also, we observed marked differences in the chemical shift of the small $^{\text{Et}}\text{CAAC-6}$ (715 ppm) **2a** and the large $^{\text{Ad}}\text{CAAC-6}$ (863 ppm) **2b**. Altogether, these results suggest, counterintuitively, that the bulkier CAACs **1b,c** and **2b** could be more π -accepting than their smaller variants **1a** and **2a**, respectively. Intrigued by these results, we verified by DFT that within the same family, these carbenes have comparable HOMO-LUMO gap and should therefore display similar electronic properties (Figure 4).¹⁹ Furthermore, the X-ray crystallographic analysis showed short intramolecular Se \cdots H distances for the adamantyl variants **1c** and **2b** (Figure 5), which are not present in **1a**^{12g} and **2a**.^{18,20}

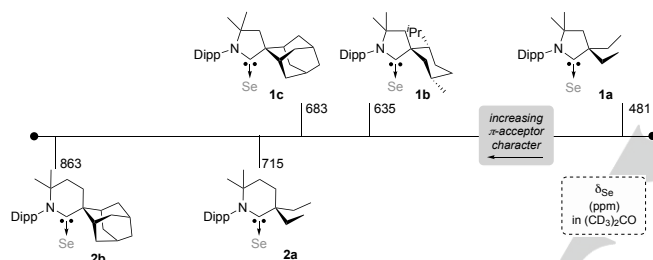


Figure 3. Non-linear behavior of the $^{77}\text{Se}\{^1\text{H}\}$ NMR chemical shifts in CAAC-Se adducts.

Free carbene	$^{\text{X}}\text{CAAC-5}$		$^{\text{X}}\text{CAAC-6}$	
	Et	Ad	Et	Ad
LUMO ^[a]	-0.44	-0.47	-0.41	-0.44
HOMO ^[a]	-5.26	-5.16	-4.85	-4.72

[a] values in eV

Figure 4. Differences in $^{77}\text{Se}\{^1\text{H}\}$ NMR chemical shifts of **1a,c** and **2a,b** are not expected since the carbene HOMO-LUMO gaps are similar within each CAAC family.

Thus, it appears, that the same phenomenon is present in both CAACs and NHCs, although the substituent involved is attached to nitrogen for NHCs and on carbon for CAACs. To make a direct comparison, N-alkyl substituted CAACs were desirable, but until now they were hardly available using current synthetic methodologies. We found that they are readily accessible upon using a monomethylated instead of a dimethylated backbone (Scheme 1). Several CAAC-6^{Me} iminium salts **3a-e** with various substituents on the nitrogen were prepared.²¹ Contrary to the well-known dimethylated CAAC derivatives, the corresponding free CAAC-6^{Me} **4a-e** are not stable at room temperature. However, using variable

temperature $^{13}\text{C}\{^1\text{H}\}$ NMR, we confirmed that they can be generated at $-80\text{ }^\circ\text{C}$ and are persistent until $-60\text{ }^\circ\text{C}$. Adducts **5a-e** were prepared by deprotonation of **3a-e** with KHMDS at $-78\text{ }^\circ\text{C}$ in the presence of excess elemental selenium.

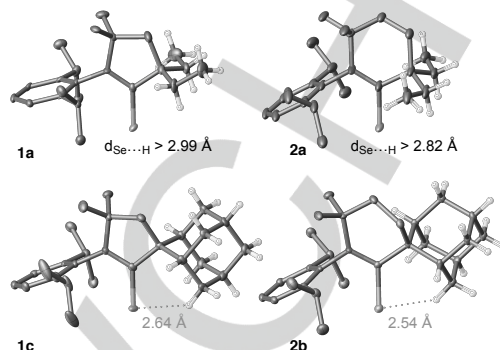
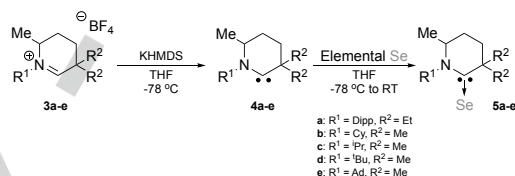


Figure 5. Short intramolecular Se-H distances are observed in **1c** and **2b** but not in **1a** and **2a**.



Scheme 1. Synthesis of CAAC-6 Se adducts **5a-e**.

The $^{77}\text{Se}\{^1\text{H}\}$ NMR chemical shifts for the room temperature stable **5a-e** were explored to confirm the substitution pattern that leads to NCHB (Figure 6). Compared to the N-aryl substituted **5a** (669 ppm), an upfield shift is observed for the N-alkyl substituted derivatives (**5b**: 521; **5c**: 526 ppm). This is in good agreement with alkyl substituents increasing electron density on the nitrogen, thus raising the LUMO and reducing the carbene π -acidity. This should also be the case with N -^tBu **5d** and N -Ad **5e** but their signals (777 and 789 ppm, respectively), were downshifted by over 268 ppm compared **5b,c**. As a reference, this range is larger than the difference between the DAC-Se adducts (846-856 ppm),^{12l} and Alder's acyclic diaminocarbene-Se (593 ppm),²² which are two very distinct families of carbenes. Interestingly, DFT predicted that the π -accepting properties of N-alkyl carbenes **4b-e** are within the same range, which conflicted with the ^{77}Se NMR data.¹⁹

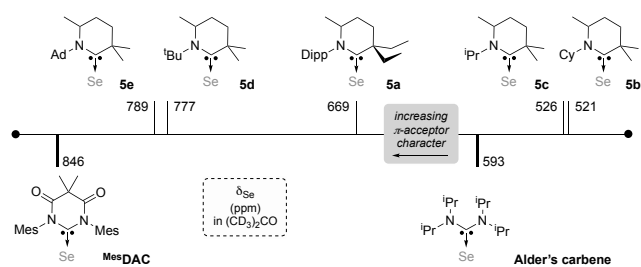


Figure 6. Non-linear behaviour of the $^{77}\text{Se}\{^1\text{H}\}$ NMR chemical shifts in CAAC-Se adducts. DAC- and Alder carbene-Se adducts included for comparison.

Upon comparing the ^1H NMR of aldiminium **3b** and carbene-selenium adduct **5b**, we noticed a marked downfield shift of the exocyclic N-C-H_a hydrogen from 3.75 ppm to 5.85 ppm (Figure 7). This is an additional indication of the participation of C(sp³)-H bonds in non-classical C-H...Se interactions. Note that recording the ^1H NMR of **5b** up to 100 °C did not show a coalescence of the signal suggesting the presence of a rather strong Se-H interaction.

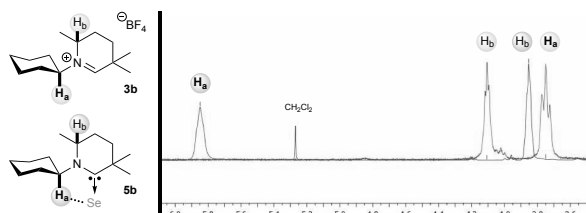


Figure 7. Comparison of the ^1H NMR of **3b** and **5b** highlights NCHB Se-H interactions.

The solid-state structures of compounds **5b-e** also display short intramolecular Se-H distances, which is not the case for **5a** (Figure 8).²⁰ Note, that these distances (2.46-2.66 Å) are well within the range of intramolecular hydrogen bonding in Silks' crystalline selenourea adduct [Se-H 2.51-2.60 Å], and in line with their proposed NCHB interactions.¹⁶ Following geometry optimizations of **5c** and **5d**, based on the X-ray crystal structure data,¹⁸ at the BP98/def2tzvpp level of theory,²³ and quantum theory of atoms in molecules (QTAIM) analysis we confirmed the existence of bond paths in both compounds (Figure 9).²⁴ Comparison of the electron density $\rho(r)$ at the Se-H bond path critical points (BCP) showed that NCHB interactions are stronger when involving a β -hydrogen (**5c**) than a γ -hydrogen to nitrogen (**5d**).²⁵ Thus, the strength of these interactions does not rationalize the observed upfield chemical shift of **5c** compared to **5d**.

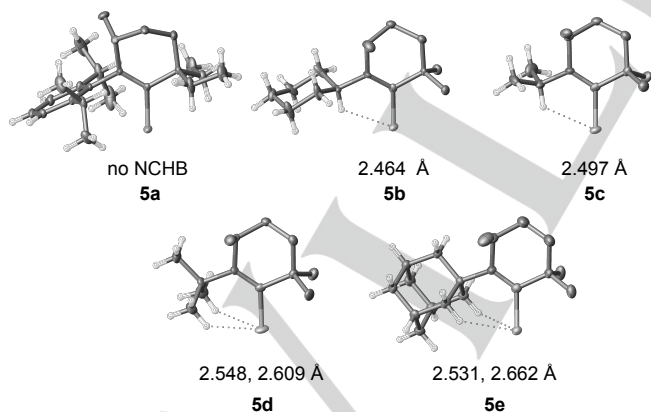


Figure 8. Solid state structures of selenoamides **5a-e** indicating NCHB Se-H interactions or absence thereof.

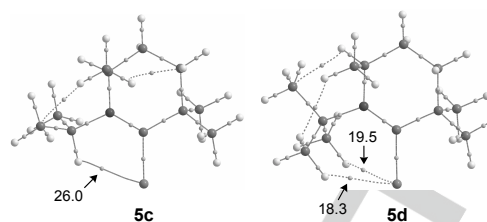


Figure 9. QTAIM analysis highlighting the Se-H bond paths and the electron density $\rho(r)$ at the bond path critical points (BCP) (values in 10^{-3} a.u.)

To investigate further, ^{77}Se NMR chemical shifts of **1c**, **2b** and **5b-e** were calculated by DFT (Figure 10). The experimental value was well reproduced in the case of the conformationally rigid **1c** and **2b**. For the N-alkyl substituted **5b-e**, which allow for a higher degree of rotation at nitrogen, calculations predicted upfield selenium NMR chemical shifts compared to those observed experimentally. We wondered, if in these cases, the accessibility of other conformational isomers, also stabilized through NCHB interactions, could explain the discrepancies. As an example, we considered **5c** and its conformer **5c'**. We confirmed that **5c'** is energetically accessible ($+2.3$ kcal.mol⁻¹) and more importantly predicts a significant downfield shift ($+74$ ppm) of the Se NMR signal. Consequently, we propose that the deshielding of the selenium atom in **5c'** is favored by the formation of a quasi-cyclic 6-membered conformation stabilized by NCHB C(sp³)-H-Se interaction. In this case, the NCHB is better described as a negative hyperconjugative interaction between the lone pair of the Se atom (H-bond acceptor) and the $\sigma_{\text{C-H}}^*$ orbital of the C(sp³)-H (H-bond donor); orbital overlap is maximized in a quasi 6-membered ring and facilitates electron transfer.^{26,27} Note that the directionality of this type of interaction has already been shown to be a critical parameter for maximizing orbital overlap.^{26,27} This effect is more pronounced in more constrained systems such as **5d-e**, which have a higher probability of such 6-membered ring conformations than **5b,c**. Moreover, it is particularly well exemplified in **1c** and **2b** in which the unusual distortion of the backbone, observed by X-ray, places the C-H bond in the right position with respect to the selenium atom (Figure 11).

		$^{77}\text{Se}\{^1\text{H}\}$ in ppm	
		(CAAC)Se Experimental	Predicted ^[c]
rigid	1c ^[a]	683	688
	2b ^[a]	863	883
flexible	5b ^[b]	521	425
	5c ^[a]	526	427
	5d ^[a]	777	688
	5e ^[a]	789	694

[a] CDCl₃. [b] (CD₃)₂CO. [c] Using X-ray data

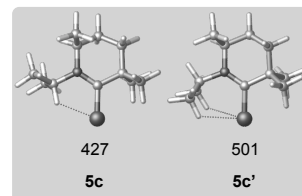


Figure 10. Experimental and predicted $^{77}\text{Se}\{^1\text{H}\}$ NMR chemical shift of **1c**, **2b** and **5b-e** (left). Significant downfield-shift of $^{77}\text{Se}\{^1\text{H}\}$ NMR signal caused by rotation of substituent and formation of quasi 6-membered ring (right).

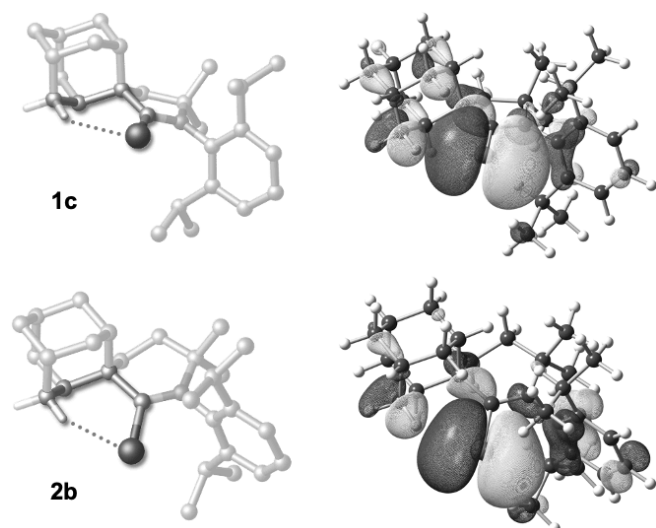


Figure 11. Quasi-cyclic 6-membered conformation stabilized by NCHB C(sp³)-H-Se interaction in **1c** and **2b** maximizes orbital overlap with a significant backbone distortion.

In conclusion, we have provided experimental and computational evidence for the existence of non-classical hydrogen bonding interactions in CAAC-selenium adducts, causing major deviations from the expected trend in ⁷⁷Se NMR chemical shifts. Since the same reasoning can also be applied to **1Bu** and **1Ad**, it is likely that this phenomenon is also found in other carbene motifs not considered in the present study. These findings encourage caution when probing π -accepting properties within a carbene family, especially when bulky substituents are in proximity to the carbene center. However, the easy access to carbene-selenium adducts, the abundance of the ⁷⁷Se nucleus, and the wide range of chemical shifts makes the use of ⁷⁷Se NMR spectroscopy a very powerful method to compare different types of carbenes.

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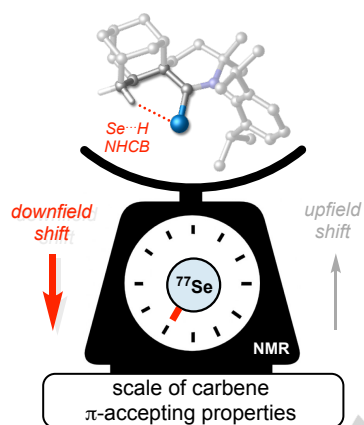
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Keywords: Selenium scale • carbenes • NHC • CAAC • Hydrogen bonding

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Non-classical hydrogen bonds (NCHB) in carbene-selenium adducts cause pronounced downfield shifts in ^{77}Se NMR spectra, perturbing the Se scale for probing π -accepting properties within a carbene family.