

Determining the π -Acceptor Properties of N-Heterocyclic Carbenes by Measuring the ^{77}Se NMR Chemical Shifts of Their Selenium Adducts

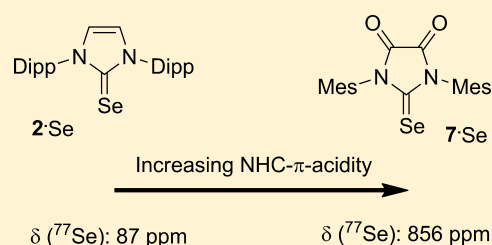
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S Supporting Information

ABSTRACT: A new method for the assessment of the π -acceptor strength of N-heterocyclic carbenes is presented. The ^{77}Se chemical shifts of the easily available selenium carbene adducts 1–Se–7–Se correlate with the π -acceptor character of the respective carbenes. The observed $\delta(^{77}\text{Se})$ values cover a range of almost 800 ppm, with increasing π -acidity leading to a downfield shift of the signal.

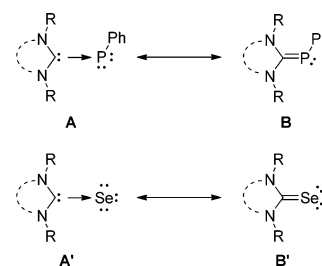


On the basis of the first reports that carbenes can exist as isolable species,¹ especially N-heterocyclic carbenes (NHCs) have attracted tremendous attention within the last 20 years. Meanwhile, NHCs constitute a well-established class of ligands for transition-metal complexes that have been increasingly applied in homogeneous catalysis, thus rivaling the ubiquitous phosphorus ligands in organometallic chemistry.² A wide range of electronically and sterically diverse NHCs have been reported to date.³ A thorough knowledge of the electronic nature of a ligand is a prerequisite for the design of a suitable catalyst. The question if NHCs may comprise a significant level of π -acceptor character on coordination to a metal center has been a point of controversy. Although NHCs were originally regarded basically as pure σ -donors, more recent work, both theoretical and experimental, has revealed that π -back-donation may indeed contribute significantly to the metal–carbene bonding and a couple of strongly π -acidic NHCs have been prepared.⁴ Separating these σ -donor and π -acceptor components on the basis of experimental data is not an easy task, because most methods for the assessment of ligand properties measure the overall effect.⁵ For example, the Tolman electronic parameter (TEP)⁶ relies on the measurement of the CO stretching frequencies in complexes of the type NHC-Ni(CO)_3 and $\text{cis-(CO)}_2(\text{NHC})\text{MCl}$ complexes ($\text{M} = \text{Rh, Ir}$), which are much more convenient to handle. The TEP gives an estimate to which extent an NHC ligand influences the electron density at the metal as a result of donor and acceptor contributions. However, the TEP seems to be the most frequently applied probe to assess the ligand properties of NHCs, especially in comparison to phosphorus-based ligands, for which the scale was originally devised.

Recently, Bertrand reported a new powerful experimental method based on ^{31}P NMR spectroscopy that allows the

determination of the π -accepting properties of NHCs.⁷ Phosphinidene adducts of NHCs can be represented by the two limiting canonical structures of a neutral phosphalkene and a polarized structure with a P–C single bond (A and B; Chart 1). The ^{31}P chemical shift is very sensitive to the relative

Chart 1. Canonical Structures of Phenylphosphinidene– and Selenium–NHC Adducts



contributions of these limiting structures to the true nature of such a phosphinidene adduct.⁸ Bertrand was able to demonstrate that increasing π -acceptor character of the NHC leads to a stronger contribution of formula B, shifting the ^{31}P resonance to lower field. The method has been adopted for the evaluation of a series of amido-NHCs by Hudnall.⁹

Inspired by Bertrand's method, we wondered if the ^{77}Se resonances of NHC–Se adducts would also correlate with the π -accepting character of the particular NHC, as two analogous canonical structures can be formulated for these compounds. It

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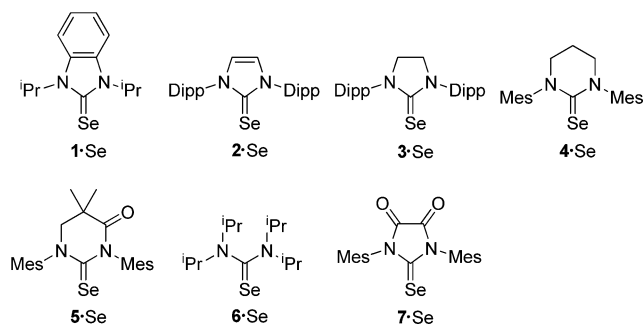


is known from the literature that ^{77}Se NMR chemical shifts of selenoureas appear over a wide range of 320 ppm.¹⁰

For a purely donating NHC, Lewis structure A' is supposed to prevail, leading to a highly shielded selenium atom with a high-field resonance. In contrast, for a π -acidic NHC a resonance shifted to lower field would be expected as a consequence of the less shielded Se atom in formula B'. Consequently, the NHC π -acceptor property should correlate with the chemical shift of the selenium atom just as the ^{31}P resonance does in the case of the phosphinidene adducts.

In order to get a first impression whether these considerations are warranted, the selenium adducts 1·Se–7·Se were synthesized (Chart 2) according to a modified literature

Chart 2. NHC–Selenium Adducts 1·Se–7·Se



procedure.¹¹ In comparison to the phosphinidene adducts the advantage is that the selenium compounds can be straightforwardly obtained in one step by deprotonation of a suitable NHC precursor in the presence of elemental selenium in THF at low temperature. As this protocol does not require the existence of the free carbene under ambient conditions, it can also be applied to NHCs which exist only as intermediate species of limited lifetime at low temperature, as for example the oxalamide-based diamidocarbene 7. Thus, the adduct 7·Se was chosen as an example for a very strong π -accepting NHC. On the other hand, 2·Se features a well-documented electron-rich, strongly σ -donating NHC, while 3·Se–6·Se represent compounds with gradually increasing π -acceptor character. ^{77}Se NMR spectra were recorded in acetone- d_6 solution with KSeCN in D_2O as the external standard. It should be noted that the relative receptivity of ^{77}Se ($I = 1/2$, 7.5% natural abundance) is roughly 3 times that of ^{13}C at natural abundance, so that spectra with acceptable signal-to-noise ratios can be acquired within reasonable time (30–60 min). Care has to be taken in order to maintain constant conditions for the NMR measurements, because ^{77}Se NMR chemical shifts are known to be sensitive to concentration, temperature, pH, and the solvent.¹² Table 1 shows that the ^{77}Se NMR chemical shifts cover a wide range of about 800 ppm, with the signals for 1·Se (67 ppm) and 7·Se (856 ppm) being located at the highest and lowest field, respectively. 3·Se (181 ppm) and 4·Se (271 ppm) feature intermediate values and are located in the lower third of the range. The increasing π -acidity of the carbenes contained in the adducts 5·Se (472 ppm) and 6·Se (593 ppm) is due to the presence of an electron-withdrawing carbonyl group in the former and the acyclic nature of the carbene in the latter, leading to an enhanced conformational flexibility and reduced interaction of the nitrogen lone pair with the vacant p orbital on the carbene C atom.^{7,13}

Table 1. Selected NMR Data and TEP Values for the Compounds Discussed in This Contribution

carbene	carbene–Se adduct		carbene TEP (cm^{-1})	carbene–PPh adduct $\delta(^{31}\text{P})$ (ppm)
	$\delta(^{77}\text{Se})$ (ppm) ^a	$\delta(^{13}\text{C})$ (ppm) ^b		
1	67	164.9	2054	–34.6 ⁷
2	87	162.3	2052 ¹⁴	–18.9 ⁷
3	181	184.3	2052 ¹⁴	–10.2 ⁷
4	271	177.3	2044 ^c	14.8 ⁷
5	472	182.3	2050 ¹⁵	39.7 ⁷
6	593	201.7		69.5 ⁷
7	856	182.3	2068 ⁴ⁿ	78.6 ⁹

^aObtained in acetone- d_6 . ^bObtained in CDCl_3 . ^cDipp instead of Mes.^{4g}

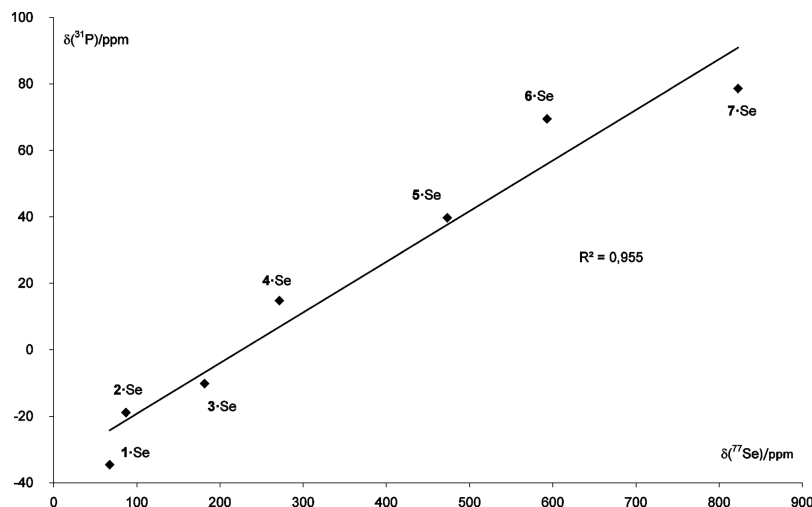
The signal for the saturated NHC adduct 3·Se is located 94 ppm downfield in comparison to the unsaturated 2·Se, indicating an increased π -acceptor character which is in accord with the literature.¹⁶ The six-membered compound 4·Se is shifted for another 90 ppm to lower field. Due to the wider NCN angle the vacant p orbital of the carbene carbon atom is lowered in energy, which promotes π -back-bonding from the selenium atom.¹⁷ In addition, the greater conformational flexibility of the six-membered ring leads to a less efficient stabilization of the carbene C atom by the nitrogen lone pair (vide supra). The diamidocarbene 7 is known as a very electron poor carbene with a strong π -acceptor character,^{4m,n} and it consequently appears at the lowest field. However, the extreme downfield position of 7·Se is noteworthy.

While the results are in good qualitative agreement with the literature, we were interested to see if a correlation exists between the ^{77}Se data and the ^{31}P chemical shifts reported by Bertrand⁷ and Hudnall,⁹ respectively, and the corresponding data were plotted against each other (Chart 3). Gratifyingly, a correlation coefficient of 0.955 was calculated, suggesting that the ^{77}Se chemical shifts may provide an equally well suited tool for the assessment of the π -acidity of NHCs in comparison to the phosphinidene approach.

The advantages of ^{77}Se NMR already became evident in this early stage of the investigation: the preparation of the selenium adducts is an easy-to-run one-pot procedure which can be applied also to NHCs that are not stable under ambient conditions. Moreover, as the selenium lacks an additional substituent apart from the NHC, the Se resonances are not affected by conformational effects in the case of unsymmetrical carbenes such as (alkyl)(amino)carbenes. On the other hand, measurements of the barrier of rotation around the C–Se bond by ^1H or ^{13}C NMR spectroscopy in order to confirm the double-bond character of this bond is obviously not possible for the Se adducts and this additional piece of information can be obtained only from the phosphinidene adducts.

As was already noted by Bertrand, the ^{31}P chemical shifts of the phosphinidene derivatives do not correlate with the TEP of the corresponding carbenes, and the same is of course true for the ^{77}Se values. This is a consequence of the fact that a π -acidic carbene might feature either a good or poor σ -donor character and both effects add together concomitantly in determining the overall ligand property that is finally reflected in the TEP.

Notably, no obvious correlation between the ^{77}Se and ^{13}C resonances of the Se adducts can be delineated from the data in Table 1, whereas Bertrand found a linear correlation between the ^{31}P NMR chemical shifts and the ^{13}C NMR chemical shifts of his carbene phosphinidene adducts.⁷

Chart 3. Plots of ^{31}P NMR Chemical Shifts against Observed ^{77}Se NMR Chemical Shifts

We are currently synthesizing additional NHC–selenium adducts in order to further corroborate the $^{31}\text{P}/^{77}\text{Se}$ NMR correlation. Additional DFT studies are also in progress aiming at a description of the C–Se bonding on a theoretical basis.

■ ASSOCIATED CONTENT

■ Supporting Information

Text and figures giving experimental details for the preparation and analytical data of the NHC selenium adducts 1-Se–7-Se. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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(11) General procedure for the synthesis of the selenium adducts: the desired NHC precursor and red selenium powder were suspended in THF and cooled to -78°C . Sodium bis(trimethylsilyl)amide (NaHMDS, 2 M in THF) was diluted with THF and added dropwise to the suspension at -78°C . After it was stirred for 20 min at low temperature, the mixture was warmed to room temperature while stirring was continued overnight. The solvent was removed under vacuum, and the product was dissolved in dichloromethane. After filtration over Celite the solution was concentrated under reduced pressure and *n*-hexane was added, which caused precipitation of a powdery solid. After the mixture was stirred for a few minutes, the product was filtered, washed with *n*-hexane, and dried under high vacuum for several hours. 1-Se: 88% yield; ^1H NMR (600 MHz, CDCl_3): δ 7.51–7.55 (m, 2H, CH_{Ph}), 7.19–7.23 (m, 2H, CH_{Ph}), 5.96 (br s, 2H, $\text{CH}(\text{CH}_3)_2$), 1.61 (d, 12H, $^3J_{\text{HH}} = 7.1$ Hz, $\text{CH}(\text{CH}_3)_2$). 2-Se: 60% yield; ^1H NMR (600 MHz, CDCl_3): δ 7.47 (t, $^3J_{\text{HH}} = 7.8$ Hz, 2H, CH_{para}), 7.30 (d, $^3J_{\text{HH}} = 7.8$ Hz, 4H, CH_{meta}), 7.00 (s, 2H, CH), 2.69 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.34 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.20 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). 3-Se: 29% yield; ^1H NMR: δ 7.40 (t, $^3J_{\text{HH}} = 7.7$ Hz, 2H, CH_{para}), 7.25 (d, $^3J_{\text{HH}} = 7.7$ Hz, 4H, CH_{meta}), 4.03 (s, 4H, CH_2), 3.06 (sept, $^3J_{\text{HH}} = 6.9$ Hz, 4H, $\text{CH}(\text{CH}_3)_2$), 1.38 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$), 1.31 (d, $^3J_{\text{HH}} = 6.9$ Hz, 12H, $\text{CH}(\text{CH}_3)_2$). 4-Se: 17% yield; ^1H NMR: δ 6.92 (s, 4H, CH_{Mes}), 3.57 (m, 4H, NCH_2), 2.37 (m, 2H, CH_2), 2.30 (s, 12H, CH_3_{Mes}), 2.29 (s, 6H, CH_3_{Mes}). 5-Se: 63% yield; ^1H NMR (600 MHz, CDCl_3): δ 6.96 (s, 2H, CH_{Mes}), 6.94 (s, 2H, CH_{Mes}), 3.58 (s, 2H, NCH_2), 2.33 (s, 6H, CH_3_{Mes}), 2.30 (s, 6H, CH_3_{Mes}), 2.15 (s, 6H, CH_3_{Mes}), 1.51 (s, 6H, $\text{C}(\text{CH}_3)_2$). 6-Se: 75% yield; ^1H NMR (600 MHz, CDCl_3): δ 4.31 (sept, 4H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$), 1.38 (d, 24H, $^3J_{\text{HH}} = 6.8$ Hz, $\text{CH}(\text{CH}_3)_2$). 7-Se: 80% yield; ^1H NMR δ 7.04 (s, 4H, CH), 2.35 (s, 6H, CH_3), 2.18 (s, 12H, CH_3). See the Supporting Information for more details.

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