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Determining the Ligand Properties of N-Heterocyclic Carbenes from ⁷⁷Se NMR Parameters

Kathrin Verlinden,^[a] Hannes Buhl,^[a] Walter Frank,^[a] and Christian Ganter^{*[a]}

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The $^1\!J_{\rm CSe}$ coupling constants for a range of NHC–selenium adducts have been measured and used to establish a correlation with the σ -donor strength of the respective carbenes. For the subclass of amido-carbenes, the $^1J_{\rm CSe}$ values revealed a high donor capacity, very much in contrast to what the DFT-calculated HOMO energies suggest. The $^1J_{\rm CH}$ coupling constants for the C-2 atoms in azolium-type NHC precursors

Introduction

Since Arduengo et al.^[1] discovered the first isolable Nheterocyclic carbene more than 20 years ago, a wide range of sterically and electronically diverse carbenes have been reported.^[2] Owing to their strong σ -donor character, NHCs are suitable as ligands for transition-metal complexes and are increasingly employed in homogeneous catalysis, rivalling the ubiquitous phosphorus ligands in organometallic chemistry.^[3] The potential π -back-bonding exerted by NHCs has been the subject for debate for a long time. Meanwhile, theoretical and experimental studies have provided clear evidence that the acceptor character of NHCs can significantly contribute to the metal–NHC bonding interaction, and a couple of strongly π -acidic NHCs have been prepared.^[4]

To select a carbene for a specific application, detailed knowledge of its properties is of crucial importance. In particular, a couple of methods have been developed over the past years to assess the electronic properties of ligands.^[5] For example, the Tolman electronic parameter (TEP) relies on the measurement of the CO stretching frequencies in complexes of the type [(NHC)Ni(CO)₃] or [*cis*-(CO)₂-(NHC)MCl] (M = Rh or Ir);^[6] thus, the electron density on the metal as a result of donor and acceptor contributions of the ligand is measured. Originally developed for phosphorus ligands, the TEP has become the most frequently used parameter to assess the ligand properties of NHCs.

 [a] Institut für Anorganische Chemie und Strukturchemie, Heinrich-Heine-Universität, 40225 Düsseldorf, Germany E-mail: christian.ganter@hhu.de

http://www.metallorganik.hhu.de/

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were more readily obtained and show the same trend as the $^{1}J_{\rm CSe}$ coupling constants. In addition, the use of $^{77}{\rm Se}$ chemical shifts to determine $\pi\text{-acidity}$ has been extended to a broader range of derivatives, namely 1·Se–22·Se. The superior resolution of the $\delta(^{77}{\rm Se})$ method in comparison with the Tolman electronic parameters derived from IR spectroscopy is demonstrated for the caffeine-derived bis-carbene 19.

However, as the TEP reflects the overall ligand properties, it does not provide an insight into the relative importance of the σ -donor and π -acceptor properties of a particular NHC. In contrast, NMR methods have recently been reported that allow the determination of only the π -acceptor strength of NHCs. While Bertrand^[7] and Hudnall^[8] and their co-workers measured the ³¹P NMR chemical shifts of NHC-phosphinidene adducts, we utilized the ⁷⁷Se NMR chemical shifts of easily available NHC-Se adducts to determine the π -acceptor strengths of the NHCs within the adducts.^[9] This method has lately been applied to a broader range of NHCs by Nolan and co-workers.^[10] Both the phosphinidene and selenium adducts can be represented by two limiting canonical structures, a neutral hetero-olefin (B) and a polarized structure (A) with a C-P/Se single bond (for representations of these structures for the NHC-Se adducts, see Scheme 1). The ³¹P and ⁷⁷Se NMR chemical shifts are very sensitive to the relative position of a given adduct within the two limiting structures: π -acidic NHCs feature a higher degree of C-P/Se double-bond character leading to NMR signals shifted to lower field in comparison with less π -acidic NHCs.^[11]



Scheme 1. Canonical structures of selenium-NHC adducts.

It is well known that the coupling constants between directly bonded atoms arise mainly from the Fermi contact between nuclear magnetic moments and the electron spins in s orbitals.^[12] Several groups have shown that the ${}^{1}J_{PSe}$

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coupling constants of phosphane–selenides are correlated to the basicity of the corresponding phosphanes, increasing basicity being associated with decreasing coupling constants.^[13,14] According to Bent's rule,^[15] the coupling constant increases as the s character of the phosphorus orbital involved in bonding to the selenium atom increases as a consequence of more electron-withdrawing substituents on phosphorus. This effect is also observed for other NMRactive nuclei such as ¹¹B or ¹⁹⁵Pt.^[13,16]

Herein we report our attempts to determine the σ -donor character of NHCs by measuring the ${}^{1}J_{CSe}$ coupling constants of their corresponding selenium adducts. In addition, to assess the π -acceptor properties, 77 Se chemical shift data for a range of new NHC–Se adducts are presented and compared with the corresponding 31 P NMR spectroscopic data of related PhP–NHC adducts. Also, the resolution limit of the $\delta({}^{77}$ Se) method is compared with that of the TEP method.

Results and Discussion

While the ⁷⁷Se chemical shifts of easily available NHC-Se adducts have already been used to assess π -acidity, we wondered whether the ${}^{1}J_{CSe}$ coupling constants of these derivatives might provide a quantitative measure of the σ -donor strength of the respective NHCs. Therefore we attempted to obtain the ${}^{1}J_{CSe}$ coupling constants from the selenium satellites in the ${}^{13}C{}^{1}H$ NMR spectra, however, this proved to be difficult for two reasons. On one hand, the relative abundances of ^{13}C and ^{77}Se are 1.1 and 7.5%, respectively, which means that there is a probability of 0.08% that a ¹³C atom is adjacent to a ⁷⁷Se atom. On the other hand, the signal of the carbone carbon has a very low intensity as a consequence of a long relaxation time T_1 , which demands a long relaxation delay between pulses. This obstacle could be partly alleviated by the use of $[Cr(acac)_3]$ as a relaxation enhancing reagent and by increasing the

Table 1. NMR spectroscopic data and TEP values for the compounds considered in this study.

		Carbene Se ^[a]	Carbene H ^{+[b]}	Carbene·PPh				Carbene Se ^[a]	Carbene H ^{+[b]}	Carbene·PPh	
	Carbene	δ^{77} Se (ppm) $^{1}J_{CSe}$ (Hz)	δ ¹³ C (ppm) ¹ J _{CH} (Hz)	δ^{31} P (ppm)	TEP (cm ⁻¹)		Carbene	δ^{77} Se (ppm) $^{1}J_{CSe}$ (Hz)	δ ¹³ C (ppm) ¹ J _{CH} (Hz)	δ^{31} P (ppm)	TEP (cm ⁻¹)
1	ⁱ Pr~N~ ⁱ Pr	-3 -		-61.2 ^[7]	2052 ^{[17a][c]}	12	Np N+ Np	245 ^[e] _			2067 ^[4q]
2		3		-53.5 ^[7]	2052 ^{[17a][c]}	13	Mes Nes	271	155.6 200	14.8 ^{[7][f]}	2044 ^{[4g],[f]}
3	Mes-N_Mes	35 231	139.9 ^[d] 225	-23.0 ^[7]	2050 ^[17b]	14	Mes N-Mes	184 228			2058 ^[17d]
4	Pr N Pr	67 228	140.4 218	-34.6 ^[7]	2054 ^[4p]	15	Pr N Pr	364 -			2057 ^[17e]
5		87 -	139.4 224	-18.9 ^[7]	2052 ^[17b]	16	S N Dipp	396 <i>233</i>	158.5 218	57.0 ^[7]	2054 ^{[17f],[g]}
6	Mes~N~Mes	116 219	160.2 206	-10.4 ^[7]	2052 ^[17b]	17		437	146.3 218		2058 ^[17g]
7		174 ^[10b] 239	138.4 229		2055 ^[6e]	18	Mes Mes	472	160.4 ^[d] 206	37.7 ^[8]	2050 ^[17h]
8	FPh~N_N_PhF	178				19		516, 113 ^[d] _	155.4, 144.4 218, 230		2063
9		181		-10.2 ^[7]	2052 ^[17b]	20	^{ipr} N ^{ipr} Pr Pr	593 -		69.5 ^[7]	
10	Np Np Np	183			2055 ^[4q]	21	Mes N Mes	847 217		83.0 ^[8]	2057 ^[4i]
11		196 214	154.2 200		2052 ^[17c]	22	Mes N Mes	856 221		78.6 ^[8]	2068 ^[4n]

[a] ⁷⁷Se NMR spectra recorded in $[D_6]$ acetone, ¹J_{CSe} coupling constants determined in CDCl₃. [b] ¹³C NMR spectra recorded in $[D_6]$ DMSO. [c] Calculated by DFT methods. [d] Obtained in CDCl₃. [e] Calculated as described below. [f] Dipp (2,6-diisopropylphenyl) instead of Mes (mesityl). [g] Mes instead of Dipp.

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number of scans. Thus, the ${}^{13}C{}^{1}H$ NMR spectra of nearly saturated solutions of the selenium adducts in a 0.1 mol/L solution of [Cr(acac)₃] in CDCl₃ were recorded with around 70000 scans (2.5 d) on a 200 MHz (${}^{1}H$) NMR spectrometer. The use of a 600 MHz spectrometer allowed data acquisition within 24 h, as demonstrated for one example.

The NHC-selenium adducts 3·Se, 4·Se, 6·Se, 7·Se, 11·Se, 14·Se, 16·Se, 21·Se, and 22·Se were synthesized and their ${}^{1}J_{CSe}$ coupling constants determined (Table 1) by the procedure outlined above. The ${}^{1}J_{CSe}$ values cover a range of 25 Hz with the largest coupling constant of 239 Hz being observed for the selenium adduct 7·Se, which suggests that the NHC 7 should be the weakest σ -donor. This is in accord with the strong –I effect exerted by the electronegative chlorine atoms at the 4- and 5-positions. According to the $\delta(^{77}Se)$ value of 174 ppm for 7·Se, NHC 7 is only weakly π acidic. Thus, the TEP value of 2055 cm⁻¹ for 7, indicative of an overall quite poor donor ligand, is mainly due to its poor σ -basicity.

According to its ${}^{1}J_{CSe}$ value of 214 Hz, the saturated sixmembered-ring NHC 11 is the best σ -donor, whereas the saturated five-membered-ring carbene SIMes 6 is also a good σ -donor. However, some of the findings were quite surprising, in particular, the trend observed for the amido carbenes does not follow chemical intuition. According to the coupling constants, the donor strength seems to increase significantly by the successive introduction of carbonyl groups, whereas the opposite trend would be expected on the basis of the –I effect exerted by the electronegative oxygen atoms. The coupling constants suggest that the sixmembered-ring diamido carbene 21 is almost as good a σ donor as the best donor of the series, NHC 11. The high TEP values of the amido carbenes 14, 21, and 22, which indicate that these ligands are quite poor overall donors, are thus a result of their high π -acceptor character, which is evident from the ⁷⁷Se NMR chemical shifts. This is in particular the case for the oxalamide NHC 22, which has by far the highest TEP value of all the carbenes included in the present study. Because the ${}^{1}J_{CSe}$ coupling constants decrease for the series of selenium adducts $3 \cdot \text{Se} > 14 \cdot \text{Se} >$ **22**·Se, the σ -donor and π -acceptor strengths would seem to increase with the introduction of carbonyl groups into the backbone.

Surprisingly, carbenes **3** and **4** are characterized as being worse σ -donors than the amido carbenes. However, they are also the poorest π -acceptors in the series, which collectively leads to TEP values at the lower end of the range. With a coupling constant of 233 Hz, the thiazolylidene **16** is a little less σ -donating than IMes **3**. The higher TEP value of the former (2054 vs. 2050 cm⁻¹ for **3**) can be explained by the increased π -acceptor character of NHC **16**, as reflected by the ⁷⁷Se NMR shifts of 396 (**16**·Se) and 35 ppm (**3**·Se).

At a later stage of our investigations, we noticed that the ${}^{1}J_{\rm CH}$ coupling constants for the C-2 atom in the cationic carbene precursors show the same trend as the ${}^{1}J_{\rm CSe}$ coupling constants of the selenoureas (Table 1), covering the range of 200–229 Hz. Indeed, plotting the $J_{\rm CH}$ versus $J_{\rm CSe}$ coupling constants of related compounds resulted in a cor-

relation of $R^2 = 0.935$ for seven pairs of compounds for which both sets of data are available.

With potential scales for both the σ -donor as well as the π -acceptor strengths of carbenes in hand, it was tempting to combine these measures to arrive at a calculated TEP value that gives an indication of the overall ligand properties. Thus, we proposed Equation (1).

$$\text{TEP} = a\delta(^{77}\text{Se}) + b^1 J_{\text{CSe}} + c \tag{1}$$

Optimization of the weighting factors a, b, and c against the experimental values of the NHCs 3, 4, 7, 11, 14, 16, and 22 revealed $R^2 = 0.833$ for the correlation between the calculated and experimental TEP values. Apart from the amido carbenes 14, 21, and 22, all the NHCs examined have TEP values within a range of 5 cm⁻¹ and a maximum difference of 4 cm⁻¹ was observed between the calculated and experimental TEP values. Thus, although the correlation is not high enough to allow for a quantitative rationalization of the TEP values on the basis of the NMR spectroscopic data, the ⁷⁷Se NMR chemical shifts and ${}^{1}J_{CSe}$ coupling constants are suitable for giving qualitative insights into the σ -donor and π -acceptor abilities of NHCs. However, with regard to the donor capabilities, we will focus on the ${}^{1}J_{CH}$ coupling constants in future work because they are much more conveniently obtained from the proton-coupled ¹³C NMR spectra of the carbene precursors.

The selenium adducts 1·Se–3·Se, 7·Se, 8·Se, 10·Se–12·Se, 14·Se–17·Se, 19·Se₂, and 21·Se were additionally characterized by ⁷⁷Se NMR spectroscopy to probe the π -acceptor character of the NHCs within the adduct, thus extending the range of compounds reported in our previous study.^[9] The NMR data of all the compounds are compiled in Table 1. Thirteen analogous NHC–phosphinidene adducts have previously been characterized by ³¹P NMR spectroscopy by Bertrand and Hudnall and their co-workers.^[7,8] Plotting the ³¹P versus ⁷⁷Se chemical shifts of the related NHC adducts (Figure 1) confirmed the previously observed linear correlation of both scales with a correlation coefficient of $R^2 = 0.905$, which is only slightly worse than the correlation obtained before for five pairs of related adducts



Figure 1. Plot of ³¹P NMR chemical shifts against observed ⁷⁷Se NMR chemical shifts.

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 $(R^2 = 0.955)$. The linear Equation (2) of the correlation enables the determination of the selenium and phosphorus chemical shifts from each other.

$$\delta(^{31}\text{P}) = 0.1563\delta(^{77}\text{Se}) - 37.1 \text{ ppm}$$
(2)

The selenium adducts $1 \cdot \text{Se}-22 \cdot \text{Se}$ show the expected trends in π acidity and are in accord with the observations made by Bertrand and co-workers.^[7] Thus, unsaturated fivemembered-ring diamino carbenes $1 \cdot \text{Se}-5 \cdot \text{Se}$ are the poorest π -acceptors with the highest-field resonances (i.e., <100 ppm). A couple of chemical modifications that lead to increased π -acceptor strength can be deduced from the data in Table 1: Saturation of the backbone (8, 9), annulation to aromatic rings (4, 10, 15), increase of the NCN angle (11, 13, 15, 20, 21), replacement of nitrogen by the weaker σ -donor sulfur (16), and introduction of electron-withdrawing groups into the backbone (7, 14, 17–19, 21, 22).

Evidently, the introduction of carbonyl groups adjacent to the nitrogen atoms has the most pronounced effect, the amide resonance involving the nitrogen lone pair at the expense of decreased stabilization of the carbene center, which becomes a better acceptor. Thus, the monoamido (14, 17–19) and especially the diamido carbenes (21, 22) are the strongest π -acceptors in the series, resonating in the low-field region at up to 860 ppm.

Another interesting aspect was the investigation of the influence of cationic charge on the π -acceptor character. Recently we reported the preparation of cationic NHCs by the η^6 coordination of a $[(C_5Me_5)Ru]^+$ fragment to the aromatic rings of carbenes 4 and 15.^[40,17e] Unfortunately, the synthesis of the corresponding selenium adducts of the cationic carbenes was not successful. Moreover, the coordination of the cationic fragment to the selenium adducts 4·Se and 15·Se did not yield the desired compounds either.

As an alternative, alkylation of the pyridine nitrogen atom of the 1,3-dineopentyl-4-azabenzimidazolylidene **10** was carried out to give the cationic carbene **12**,^[4q] but the synthesis of its selenium adduct **12**·Se was again not successful. Therefore methylation of compound **10**·Se with Me-OTf was attempted to assess the π -acceptor character of carbene **12**. However, the selenium atom appeared to be more nucleophilic than the pyridine nitrogen atom in the backbone and the Me–Se compound **10**·Se–Me was obtained that displayed a ⁷⁷Se NMR signal at δ = 158 ppm, thus being shifted to a higher field by 25 ppm than that of **10**·Se (Scheme 2).

On the other hand, exposure of compound 10·Se to methyl trifluoromethanesulfonate under more forcing conditions (microwave irradiation) resulted in the double methylation of the selenium and pyridine nitrogen atom leading to the dicationic derivative 12·Se–Me, which has a ⁷⁷Se chemical shift of 220 ppm. To derive a rough estimate of the chemical shift of the monocationic derivative 12·Se, 25 ppm were added to the value for 12·Se–Me, assuming that the effect of the additional methyl group bonded to selenium was the same for both 10·Se–Me and 12·Se–Me (Scheme 2).



Scheme 2. Synthesis of 10-Se–Me and 12-Se–Me and estimation of the ⁷⁷Se NMR chemical shift of 12-Se.

Thus, the chemical shift for the cationic selenium adduct **12**·Se was estimated by this procedure to be 245 ppm, which is shifted to lower field by around 60 ppm compared with the neutral relative **10**·Se, thus indicating the superior π -acidity of the cationic species.

As is clear from the data compiled in Table 1, the ⁷⁷Se NMR chemical shifts of the carbenes discussed in this study cover a wide range of around 850 ppm, whereas their TEP values lie within a much narrower range of roughly 24 cm⁻¹ (or even only 19 cm⁻¹ if compound **22** is disregarded). Thus, the selenium NMR data clearly provide a much better resolution, which should allow the identification of two different carbenic centers within one molecule. This was demonstrated for the caffeine-derived bis-carbene **19**. To obtain its corresponding carbonyl complex, the dication **19**·[HOTf]₂ was deprotonated with NaHMDS and then allowed to react with [Rh(cod)Cl]₂ (Scheme 3). The molecular structure of the resulting complex **19**·[Rh(cod)Cl]₂ (**23**) was confirmed by X-ray diffraction (Figure 2).

However, although the positions of the two Rh(cod)Cl fragments are well defined, the bridging bis-carbene ligand appeared to be disordered by a superposition of two orientations, thus preventing the diamino and the amino-amido carbene moieties from being distinguished.^[18] Complex 23 was subsequently converted into the bis(dicarbonyl) complex 19-[Rh(CO)₂Cl]₂ (24) by exposure of a dichloromethane solution of 23 to gaseous CO (Scheme 3). Although the NMR spectra indicate a clean conversion to complex 24, the IR spectrum shows only two strong CO stretching vibrations at 2015 and 2091 cm⁻¹ from which a TEP value of 2063 cm⁻¹ was calculated (Figure 3). Thus, IR spectroscopy does not allow differentiation between the electronic properties of the two carbene centers within the molecule. One possibility for solving this problem could be the synthesis of the mixed iridium/rhodium bis(dicarbonyl) complex [Ir(CO)₂Cl]19[Rh(CO)₂Cl] as the CO stretching vibrations for the Rh and Ir dicarbonyl complexes for a given NHC usually differ by around 15 cm⁻¹.^[2d] This difference should



Scheme 3. Synthesis of compounds 23 and 24. Reagents and conditions: (a) NaHMDS, $[Rh(cod)Cl]_2$, thf, 5 h, -80 °C to room temp.; (b) CO, CH_2Cl_2 , 45 min, room temp.



Figure 2. Molecular structure of complex 23. The ellipsoids are drawn at the 25% probability level. Hydrogen atoms and solvent molecules have been omitted for clarity. Only one of the two disordered positions of the bridging ligand is shown.

be sufficient to resolve the two carbene moieties. However, the synthesis of the mixed complexes was not as trivial as had been initially expected and all the attempts to synthesize this complex carried out in our laboratory have so far been unsuccessful.



Figure 3. IR spectrum of complex 24 in CH_2Cl_2 .

Fortunately, the characters of the two carbene centers in the bis-adduct $19 \cdot (\text{Se})_2$ were easily discerned in the ⁷⁷Se NMR spectrum. Two well-separated signals were detected in CDCl₃ solution at $\delta = 516$ and 113 ppm (Figure 4). Owing to the electron-withdrawing amido group and the larger NCN angle, the carbene center of the six-membered ring can be assigned to the lower-field signal. This high value indicates significantly increased π -back-bonding. On the other hand, the carbene center of the five-membered ring is in the range of other imidazolylidenes with little π -acceptor character. Collectively, ⁷⁷Se NMR spectroscopy provides a much higher resolution than the TEP scale based on IR spectroscopy.



Figure 4. 77 Se NMR spectrum of $19 \cdot (Se)_2$ in CDCl₃ with KSeCN in D₂O as external standard.

With the aim of rationalizing the observed trends of the ⁷⁷Se NMR chemical shifts and the ${}^{1}J_{CSe}$ coupling constants, the HOMO and LUMO energies of a representative range of carbenes were computed by DFT methods (B3LYP/def2-TZVP). All the nitrogen substituents were replaced by methyl groups to speed up the calculations. The results are depicted in Figures 5 and 6. The order of δ (⁷⁷Se) values is qualitatively well reproduced by the calculated LUMO energies ($R^2 = 0.8969$), which thus warrants a correlation between chemical shifts and π -acceptor character with the amido carbenes being the strongest acceptors.^[19] On the other hand, the HOMO energies should reflect the σ -donor properties of the carbenes. Indeed, with the exception of the amido carbenes, the calculated HOMO energies parallel the experimentally derived coupling constants ($R^2 = 0.9101$). Although according to their HOMO energies, the amido derivatives 14, 21, and 22 are characterized as being poor σ -donors, the coupling constants suggest a much higher donor character. At this stage we do not have a convincing explanation for this contradictive finding. However, it should be noted that the HOMO energies span a range of only 1.6 eV, whereas the LUMO energies cover a much broader range of 4.2 eV. Thus, structural modifications of the basic NHC motif affect the acceptor character to a much higher extent than the donor properties.

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Figure 5. Plot of calculated LUMO energies vs. observed ⁷⁷Se NMR chemical shifts. [a] LUMO+1 due to the required π symmetry. [b] LUMO+2 due to the required π symmetry.



Figure 6. Plot of calculated HOMO energies vs. observed ${}^{1}J_{CSe}$ coupling constants.

Crystals of 2·Se, 9·Se, 10·Se, 16·Se, and 12·Se–Me suitable for X-ray diffraction analysis were obtained by solvent diffusion methods. The molecular structures of the compounds are depicted in Figures 7 and 8. The five-membered rings in all the derivatives are entirely flat within the limit of accuracy. For the selenoureas 2·Se, 9·Se, 10·Se, and 16·Se, interatomic distances are observed within the usual narrow ranges of 135-137 pm for the N-C(carbene) bonds and 182-184 pm for the C-Se bonds.^[10a,20-22] It should be noted that the Se adducts of strongly π -acidic diamido NHCs feature significantly shorter C-Se bonds of around 178 pm.^[4n,23] The most significant deviations from the idealized five-membered-ring geometry are observed for the thiazolylidene derivative 16.Se; as is usually observed, the S atom prefers a small intra-ring angle of 93.18(7)°, which leads to an increase in the SCN angle to 108.5(1)°, whereas slightly smaller NCN angles in the range of 104-107° are observed for the imidazole-derived compounds 2.Se and 10.Se. Compared with the neutral 10.Se, the doubly methylated dicationic derivative 12. Se-Me features a significantly elongated C(carbene)-Se bond of 190.31(15) pm, thus approaching the value for a Se-C single bond,^[24] and the Se-Me bond has a length of 195.9(2) pm. These values are close to those observed for a neutral 2-(methylselenyl)imidazole.^[25] Selenoureas are known to form adducts with iodine or to react to form Se-Se-bonded dicationic dimers stabilized by interaction with triiodide anions.^[26] Likewise, a closely related compound, 2-(cyanoselenyl)imidazolium iodide, forms dimeric aggregates in which two iodide anions form bridges between the selenium atoms of two cations.^[27] A related aggregation is observed in the structure of 12·Se-Me, with the oxygen atoms of two triflate anions in bridging positions between the Se atoms of two dicationic moieties



Figure 8. Left: Molecular structure of 12·Se–Me. Right: Dimeric aggregate of two molecules of 12·Se–Me and two triflates. The ellipsoids are drawn at the 50% probability level. Hydrogen atoms and OTf⁻ counter ions have been omitted for clarity.



Figure 7. Molecular structures of 2·Se, 9·Se, 10·Se, and 16·Se. The ellipsoids are drawn at the 25 (9·Se) and 35% (2·Se, 10·Se, 16·Se) probability levels. Hydrogen atoms have been omitted for clarity.

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(Figure 8). In the centrosymmetric four-membered rings, each Se atom has one short [290(1) pm] and one long contact [483(1) pm] to the triflate oxygens. The arrangement is almost rectangular with angles slightly larger than 90° at the oxygen atoms (95°) and slightly smaller at the selenium atoms (85°).

Conclusions

NHC–selenium adducts have been characterized by ⁷⁷Se NMR chemical shifts and, for the first time, by ${}^{1}J_{CSe}$ coupling constants. The NMR parameters as well as DFT-derived HOMO and LUMO energies were correlated to the σ -donor and π -acceptor properties of the carbenes, respectively. It has been found that the NMR parameters offer a much better resolution to distinguish carbene centers than the widely used TEP parameters, which rely on IR measurements. The ${}^{1}J_{CH}$ coupling constants for the C-2 atom in the cationic NHC precursors are straightforwardly available and show the same trend as the ${}^{1}J_{CSe}$ coupling constants of the NHC–Se adducts.

Experimental Section

General: Unless otherwise noted, all operations were carried out under precautions to exclude air and moisture. Glassware was dried at 120 °C in an oven for at least 12 h. All solvents were dried rigorously, freshly distilled prior to use, and stored under nitrogen (diethyl ether and tetrahydrofuran over Na/benzophenone, dichloromethane over CaH₂, and *n*-hexane over Na). Acetone and acetonitrile were obtained from a solvent purification system (Braun). Alumina was heated at 200 °C for at least 12 h, cooled under high vacuum, and deactivated with water (5% by weight). ${}^{1}H$, ${}^{13}C{}^{1}H$, ¹⁹F, and ⁷⁷Se NMR spectra were recorded with a Bruker Avance III 600 spectrometer. The ${}^{1}J_{CSe}$ coupling constants were recorded with a Bruker Avance 200 spectrometer. Chemical shifts (δ) are reported in parts per million (ppm) downfield from tetramethylsilane using the solvent as internal standard. The ⁷⁷Se NMR spectra were referenced to external KSeCN in D₂O at a specific concentration with a chemical shift of -316.5 ppm (4.0 mol/L) or -329.0 ppm (0.25 mol/L). Coupling constants are given in Hz. A Shimadzu IR Affinity-1 spectrometer was used to record IR spectra. Mass spectra were recorded with a Finnigan LCO Deca Thermo Quest (ESI), Bruker Ultrafex TOF (MALDI), Finnigan TSO 7000 (EI), Thermo Finnigan Trace DSQ (GC-MS), or a UHR-QTOF maXis 4G Bruker Daltonics (HRMS-ESI) spectrometer. A vario MICRO cube was used for elemental analysis.

Sodium bis(trimethylsilyl)amide (2 M in thf; Acros Organics, CAS: 1070-89-9), selenium powder (Strem Chemicals, 99.5%; CAS: 7782-49-2), and methyl trifluoromethanesulfonate (Acros Organics, CAS: 333-27-7) were purchased and used as received. Compounds **4**·Se, **5**·Se, **9**·Se, **13**·Se, **18**·Se, **20**·Se, **22**·Se,^[9] **7**·Se,^[10b] **11**·Se,^[17c] **15**·Se,^[17c] **17**·Se, and **19**·Se^[17g] are known in the literature. *N*,*N*′-1,4-Bis(4-fluorophenyl)-1,4-diaza-1,3-butadiene,^[28] **1**·HBr, **4**·HBr,^[29] **2**·HI,^[30] **3**·HCl, **5**·HCl,^[31] **6**·HCl,^[32] **7**·HCl,^[33] **10**·HPF₆,^[34] **11**·HBr,^[17c] **13**·HBr,^[35] 1,3-dimesityl-4-hydroxyimidazolium chloride,^[36] **16**·HClO₄,^[17f] **17**·HNO₃, **19**·(HOTf)₂,^[17g] **18**·HCl,^[17h] and **21**·HOTf^[4i] were prepared according to the literature.

General Preparation of Carbene Selenium Adducts: The desired NHC precursor was suspended in thf with an excess selenium powder. Sodium bis(trimethylsilyl)amide (NaHMDS, 2м in thf, 1.2 equiv.) was diluted with thf (5 mL) and added dropwise to the suspension at -78 °C. After stirring for 30 min at -78 °C, the mixture was allowed to warm up to room temperature, while stirring was continued overnight. The solvent was removed under high vacuum and the crude product was dissolved in dichloromethane. After slow filtration through Celite the solution was either dried in vacuo to obtain the product as a powdery solid (method a) or concentrated under high vacuum and n-hexane was added, which caused precipitation of a powdery solid, which was isolated by filtration, washed with *n*-hexane, and dried under high vacuum for several hours (method b) or the oily residue obtained by evaporation of the filtrate was dissolved in diethyl ether and evaporated under high vacuum to obtain the product as a powdery solid (method c).

1,3-Diisopropylimidazole-2-selenone (1·Se): Reagents: 1,3-diisopropylimidazolium bromide (0.50 g, 2.14 mmol), NaHMDS (1.18 mL, 2.36 mmol), selenium (0.51 g, 6.5 mmol). Purification method a, yield 37% (0.18 g, 0.79 mmol), white powder. ¹H NMR (600 MHz, CDCl₃): $\delta = 6.89$ (br. s, 2 H, CH), 5.24 [sept, ³J_{HH} = 6.8 Hz, 2 H, CH(CH₃)₂], 1.35 [d, ³J_{HH} = 6.8 Hz, 12 H, CH(CH₃)₂] ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃): $\delta = 153.2$ (s, CSe), 115.3 (s, CH), 50.5 [s, CH(CH₃)₂], 22.1 [s, CH(CH₃)₂] ppm. ⁷⁷Se NMR (114 MHz, [D₆]acetone): $\delta = -3$ (s, CSe) ppm. MS (EI): m/z = 232 [M]⁺, 190 [M - *i*Pr]⁺, 148 [M - 2 *i*Pr]⁺. C₉H₁₆N₂Se (231.20): calcd. C 46.76, H 6.98, N 12.12; found C 46.62, H 6.70, N 12.12.

1,3,4,5-Tetramethylimidazole-2-selenone (2·Se): Reagents: 1,3,4,5-tetramethylimidazolium iodide (0.34 g, 1.40 mmol), NaHMDS (0.77 mL, 1.54 mmol), selenium (0.17 g, 2.10 mmol). Purification method b, yield 42% (0.12 g, 0.59 mmol), brown powder. ¹H NMR (600 MHz, CDCl₃): δ = 3.64 (s, 6 H, CH₃), 2.11 (s, 6 H, CH₃) ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 153.8 (s, CSe), 123.1 (s, C_q), 34.2 (s, CH₃), 9.6 (s, CH₃) ppm. ⁷⁷Se NMR (114 MHz, [D₆]-acetone): δ = 3 (s, CSe) ppm. MS (EI): *m*/*z* = 204 [M]⁺, 189 [M – CH₃]⁺, 123 [M – Se]⁺. C₇H₁₂N₂Se (203.15): calcd. C 41.39, H 5.95, N 13.79; found C 41.18, H 5.88, N 13.52.

1,3-Dimesitylimidazole-2-selenone (**3·Se**): Reagents: 1,3-dimesitylimidazolium chloride (0.50 g, 1.46 mmol), NaHMDS (0.80 mL, 1.6 mmol), selenium (0.17 g, 2.20 mmol). Purification method b, yield 40% (0.23 g, 0.59 mmol), beige powder. ¹H NMR (600 MHz, CDCl₃): δ = 7.02 (s, 4 H, CH_{Mes}), 6.96 (s, 2 H, CH), 2.34 (s, 6 H, CH₃), 2.13 (s, 12 H, CH₃) ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 157.81 (s, CSe), 139.58 (s, C_{Mes}), 135.57 (s, C_{Mes}), 134.40 (s, C_{Mes}), 129.46 (CH_{Mes}), 120.30 (s, C-4, C-5), 21.38 (s, CH₃), 18.21 (s, CH₃) ppm. ⁷⁷Se NMR (114 MHz, [D₆]acetone): δ = 35 (s, CSe) ppm. MS (EI): *m/z* = 384 [M]⁺, 303 [M – Se]⁺, 185 [M – Se – Mes]⁺, 119 [Mes]⁺. C₂₁H₂₄N₂Se (383.39): calcd. C 65.79, H 6.31, N 7.31; found C 65.69, H 6.01, N 7.27.

1,3-Dimesitylimidazolidine-2-selenone (6·Se): Reagents: 1,3-dimesitylimidazolidinium chloride (1.00 g, 2.92 mmol), NaHMDS (1.89 mL, 3.8 mmol), selenium (0.35 g, 4.38 mmol). Purification method a, yield 45% (0.50 g, 1.30 mmol), white powder. ¹H NMR (600 MHz, CDCl₃): δ = 6.98 (s, 4 H, CH_{Mes}), 4.00 (s, 4 H, CH₂), 2.32 (s, 12 H, CH₃), 2.32 (s, 6 H, CH₃) ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 180.2 (s, CSe), 138.5 (s, C_{Mes}), 136.4 (s, C_{Mes}), 135.1 (s, C_{Mes}), 129.6 (s, CH_{Mes}), 48.8 (s, C-4, C-5), 21.3 (s, CH₃), 18.0 (s, CH₃) ppm. ⁷⁷Se NMR (114 MHz, CDCl₃): δ = 111 (s, CSe) ppm. ⁷⁷Se NMR (114 MHz, [D₆]acetone): δ = 116 ppm. MS (EI): *m/z* = 386 [M]⁺, 371 [M – CH₃]⁺, 305 [M – Se]⁺, 267



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 $[M - Mes]^+$, 119 $[Mes]^+$. C₂₁H₂₆N₂Se (385.41): calcd. C 65.44, H 6.80, N 7.27; found C 65.15, H 6.86, N 7.10.

1,3-Bis(4-fluorophenyl)imidazolidinium Hexafluorophosphate (8·HPF₆): Sodium borohydride (1.40 g, 36.01 mmol) in portions of 0.2 g was added to a solution of N,N'-1,4-bis(4-fluorophenyl)-1,4diaza-1,3-butadiene (2.20 g, 9.00 mmol) in thf (40 mL) at 0 °C over a period of 30 min. The mixture was warmed to room temperature, stirred for 18 h, and subsequently heated at reflux for 2 h. Ice-water (100 mL) was added to this reaction mixture over 30 min followed by the cautious addition of 1 M hydrochloric acid (20 mL). A colorless solid precipitated, which was collected by filtration and dried in vacuo. The resulting N, N'-bis(4-fluorophenyl)ethane-1,2-diamine was used in the next step without any purification. The diamine (1.00 g, 4.03 mmol) was heated at reflux over 15 h with sodium hexafluorophosphate (0.69 g, 4.20 mmol) in triethyl orthoformate (30 mL). A colorless solid precipitated that was collected by filtration, washed several times with *n*-hexane (20 mL), and dried in vacuo, yield 24% (0.86 g, 2.20 mmol). ¹H NMR (300 MHz, [D₆]-DMSO): $\delta = 9.87$ (s, 1 H, CH), 7.72–7.64 (m, 4 H, CH_{phenvl}), 7.50– 7.40 (m, 4 H, CH_{phenvl}), 4.58 (s, 4 H, CH₂) ppm. ¹³C{¹H} NMR (75 MHz, [D₆]DMSO): δ = 160.5 (d, ¹J_{CF} = 244.6 Hz, CF), 152.3 (s, C-2), 132.6 (s, ${}^{4}J_{CF} = 2.7$ Hz, CN), 120.8 (s, ${}^{3}J_{CF} = 8.5$ Hz, CH), 116.4 (s, ${}^{2}J_{CF}$ = 23.2 Hz, CH), 49.0 (s, CH₂) ppm. ¹⁹F NMR (282 MHz, [D₆]DMSO): $\delta = -70.16$ (d, ${}^{1}J_{\text{FP}} = 711.2$ Hz, 6 F, PF₆), -114.86 (s, 3 F, F_{phenyl}) ppm. MS (ESI): m/z = 259 [M]⁺. C₁₅H₁₃F₈N₂P (404.24): calcd. C 44.57, H 3.24, N 6.93; found C 44.60, H 3.36, N 6.93.

1,3-Bis(4-fluorophenyl)imidazolidene-2-selenone (8·Se): Reagents: 1,3-bis(4-fluorophenyl)imidazolidinium hexafluorophosphate (0.25 g, 0.85 mmol), NaHMDS (0.5 mL, 1.00 mmol), selenium (0.170 g, 2.14 mmol). Purification method b, yield 64% (0.18 g, 0.54 mmol), orange powder. ¹H NMR (600 MHz, CDCl₃): δ = 7.53–7.49 (m, 4 H, CH), 7.16–7.11 (m, 4 H, CH), 4.15 (s, 4 H, CH₂) ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 182.1 (s, CSe), 161.6 (d, ¹*J*_{CF} = 248 Hz, CF), 137.4 (s, ⁴*J*_{CF} = 3.2 Hz, CN), 128.6 (s, ³*J*_{CF} = 8.5 Hz, CH), 116.2 (s, ²*J*_{CF} = 22.8 Hz, CH), 51.3 (s, CH₂) ppm. ¹⁹F NMR (564 MHz, CDCl₃): δ = -113.52 (s, F_{phenyl}) ppm. ⁷⁷Se NMR (114 MHz, [D₆]acetone): δ = 178 (s, CSe) ppm. MS (EI): *m*/*z* = 338 [M]⁺⁺, 257 [M - Se]⁺⁺. C₁₅H₁₂F₂N₂Se·1/6Se: calcd. C 51.42, H 3.45, N 7.99; found C 51.56, H 3.53, N 7.86.

1,3-Dineopentylimidazo[4,5-b]pyridine-2-selenone (10.Se): Reagents: 1,3-dineopentylimidazolium[4,5-b]pyridine hexafluorophosphate (0.50 g, 1.20 mmol), NaHMDS (0.70 mL, 1.40 mmol), selenium (0.27 g, 3.45 mmol). Purification method c, yield 59% (0.24 g, 0.71 mmol), white powder. ¹H NMR (600 MHz, CDCl₃): δ = 8.24 (dd, ${}^{3}J_{HH} = 4.9$, ${}^{4}J_{HH} = 1.3$ Hz, 1 H, 7-H), 7.52 (dd, ${}^{3}J_{HH} = 8.1$, ${}^{4}J_{\rm HH} = 1.3$ Hz, 1 H, 5-H), 7.12 (dd, ${}^{3}J_{\rm HH} = 8.0$, ${}^{3}J_{\rm HH} = 4.9$ Hz, ¹H, 6-H), 4.50 (s, 2 H, CH₂), 4.39 (s, 2 H, CH₂), 1.11 [s, 9 H, C(CH₃)₃], 1.11 [s, 9 H, (CH₃)₃] ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 173.6 (s, CSe), 147.2 (s, C_q), 143.1 (s, C-7), 127.5 (s, Cq), 118.2 (s, C-6), 117.4 (s, C-5), 56.9 (s, N-CH₂), 55.6 (s, N-CH₂), 35.7 [s, C(CH₃)₃], 35.5 [s, C(CH₃)₃], 29.4 [s, C(CH₃)₃], 29.4 [s, C(CH₃)₃] ppm. ⁷⁷Se NMR (114 MHz, [D₆]acetone): δ = 183 (s, CSe) ppm. MS (EI): $m/z = 339 [M]^{+}$, 258 $[M - Se]^{+}$, 188 $[M - Se - Se]^{+}$ Np]⁺. C₁₆H₂₅N₃Se (338.35): calcd. C 56.80, H 7.45, N 12.42; found C 56.73, H 7.32, N 12.30.

2-Methylselanyl-1,3-dineopentylimidazolium[4,5-*b*]pyridine Trifluoromethanesulfonate (10·Se–Me): 1,3-Dineopentylimidazo-[4,5-*b*]pyridine-2-selenone (0.10 g, 0.30 mmol) was dissolved in dichloromethane (7 mL). Methyl trifluoromethanesulfonate (40 μ L, 0.33 mmol) was added dropwise and the mixture was stirred overnight. The solvent was removed under high vacuum to give a beige powder, which was washed several times with diethyl ether, yield 67% (0.10 g, 0.20 mmol). ¹H NMR (600 MHz, [D₆]acetone): δ = 8.82 (dd, ${}^{3}J_{HH}$ = 4.6, ${}^{4}J_{HH}$ = 1.4 Hz, 1 H, CH), 8.69 $(dd, {}^{3}J_{HH} = 8.5, {}^{4}J_{HH} = 1.4 \text{ Hz}, 1 \text{ H}, \text{ CH}), 7.80 (dd, {}^{3}J_{HH} = 8.5,$ ${}^{3}J_{\text{HH}} = 4.6 \text{ Hz}, 1 \text{ H}, \text{ CH}), 4.83 \text{ (s, 2 H, N-CH}_2), 4.77 \text{ (s, 2 H, N-CH}_2)$ CH₂), 2.78 (s, 3 H, Se-CH₃), 1.16 [s, 9 H, C(CH₃)₃], 1.14 [s, (CH₃) ₃] ppm. ¹³C{¹H} NMR (150 MHz, [D₆]acetone): δ = 210.0 (s, CSe), 149.7 (s, CH), 146.1 (s, C_q), 128.4 (s, C_q), 125.1 (s, CH), 123.6 (s, CH), 59.4 (s, CH₂), 57.8 (s, CH₂), 35.7 [s, C(CH₃)₃], 35.5 [s, C(CH₃) ₃], 28.8 [s, C(CH₃)₃], 28.5 [s, C(CH₃)₃], 12.5 (s, Se-CH₃) ppm. ¹⁹F NMR (282 MHz, [D₆]acetone): $\delta = -78.84$ (s, CF₃) ppm. ⁷⁷Se NMR (114 MHz, [D₆]acetone): $\delta = 158$ (s, CSe) ppm. MS (ESI): $m/z = 354 \, [M]^+, 260 \, [M - SeMe]^+. C_{18}H_{28}F_3N_3O_3SSe (502.45):$ calcd. C 43.03, H 5.62, N 8.36, S 6.38; found C 42.79, H 5.37, N 8.29, S 6.22.

4-Methyl-2-methylselanyl-1,3-dineopentylimidazolium[4,5-b]pyridine Trifluoromethanesulfonate (12:Se-Me): In a microwave tube 1,3-dineopentylimidazo[4,5-b]pyridine-2-selenone (0.10 g, 0.27 mmol) was suspended in methyl trifluoromethanesulfonate (1.2 mL, 10 mmol). The mixture was stirred in the microwave oven at 100 °C for 5 min, shaken, and then again stirred in the microwave oven at 100 °C for 5 min. The resulting clear red solution was suspended in diethyl ether (20 mL) and the mixture stirred for 30 min. After this time the resulting beige precipitate was filtered off, washed with thf (10 mL), and dried in vacuo, yield 46% (0.09 g, 0.14 mmol). ¹H NMR (600 MHz, [D₆]acetone): δ = 9.55 (dd, ³J_{HH} = 8.7 Hz, 1 H, CH), 9.37 (d, ${}^{3}J_{HH} = 6.1$ Hz, 1 H, CH), 8.46 (dd, ${}^{3}J_{HH} = 8.7$, ${}^{3}J_{HH}$ = 6.1 Hz, 1 H, CH), 5.41 (s, 1 H, N-CH₂), 5.20 (s, 1 H, N-CH₂), 5.08 (s, 3 H, NCH₃), 5.03 (s, 1 H, N-CH₂), 4.95 (s, 1 H, N-CH₂), 2.93 (s, 3 H, Se-CH₃), 1.23 [s, 9 H, C(CH₃)₃], 1.20 [s, (CH₃)₃] ppm. ¹³C{¹H} NMR (150 MHz, [D₆]acetone): δ = 210.0 (s, CSe), 149.0 (s, CH), 140.4 (s, C_q), 135.2 (s, CH), 134.9 (s, C_q), 125.2 (s, CH), 121.9 (q, ${}^{1}J_{CF}$ = 321.3 Hz, CF₃), 62.1 (s, CH₂), 61.3 (s, CH₂), 48.6 (s, N-CH₃), 36.2 [s, C(CH₃)₃], 35.9 [s, C(CH₃)₃], 28.3 [s, C(CH₃) ₃], 28.2[s, C(CH₃)₃], 14.8(s, Se-CH₃) ppm. ⁷⁷Se NMR (114 MHz, [D₆]acetone): $\delta = 220$ (CSe) ppm. MS (ESI): m/z = 370 [M]⁺, 355 [M – $Me]^{\cdot +},\,298\;[M-Np]^{\cdot +}.\;C_{20}H_{31}F_6N_3O_6S_2Se\;(666.55)\text{: calcd. C 36.04},$ H 4.69, N 6.30, S 9.62; found C 35.78, H 4.61, N 6.27, S 9.72.

1,3-Dimesityl-4-oxoimidazole-2-selenone (14·Se): 1,3-Dimesityl-4hydroxyimidazolium chloride (0.50 g, 1.40 mmol) and selenium powder (0.13 g, 1.68 mmol) were suspended in thf (50 mL) and cooled to 0 °C. NaHMDS (1.6 mL, 3.20 mmol) was added dropwise. After stirring for 20 min at 0 °C the mixture was warmed to room temperature and stirring was continued for another 3 h. HCl (3 M, 0.75 mL, 2.24 mmol, in MeOH) was added dropwise to the resulting intense green solution at 0 °C. After stirring for 2 h at room temperature, the solvent was evaporated in vacuo and the black residue suspended in dichloromethane (20 mL). After filtration through Celite the solution was dried in vacuo to obtain the product as a grey powder, yield 54% (0.30 g, 0.75 mmol). ¹H NMR (600 MHz, CDCl₃): δ = 7.03 (s, 2 H, CH_{Mes}), 7.02 (s, 2 H, CH_{Mes}), 4.22 (s, 2 H, CH₂), 2.34 (s, 3 H, CH₃), 2.34 (s, 3 H, CH₃), 2.27 (s, 6 H, CH₃), 2.22 (s, 6 H, CH₃) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, CDCl₃): δ = 184.7 (s, CSe), 170.3 (s, CO), 140.1 (s, $C_{Mes}),\ 139.8$ (s, $C_{Mes}),\ 136.1$ (s, $C_{Mes}),\ 135.6$ (s, $C_{Mes}),\ 133.3$ (s, $C_{Mes}),\;130.0$ (s, $CH_{Mes}),\;129.6$ (s, $CH_{Mes}),\;54.4$ (s, $CH_2),\;21.4$ (s, CH₃), 21.3 (s, CH₃), 18.0 (s, CH₃), 17.9 (s, CH₃) ppm. ⁷⁷Se NMR (114 MHz, [D₆]acetone): δ = 295 (s, CSe) ppm. MS (EI): m/z = 400 $[M]^{+}$, 385 $[M - O]^{+}$, 319 $[M - Se]^{+}$. C₂₁H₂₄N₂OSe (399.39): calcd. C 63.15, H 6.06, N 7.01; found C 62.90, H 5.86, N 6.91.

3-(2,6-Diisopropylphenyl)-4,5,6,7-tetrahydrobenzo[*d*]thiazole-2-selenone (16·Se): Reagents: 3-(2,6-Diisopropylphenyl)-4,5,6,7-tetra-

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(378.43): calcd. C 60.30, H 6.66, N 3.70, S 8.47; found C 60.19, H

6.45, N 3.79, S 8.69. 19-[Rh(cod)Cl]₂ (23): 1,3,7,9-Tetramethyl-6-oxopurinediium bis(trifluoromethanesulfonate) (0.40 g, 0.81 mmol) and [Rh(cod)Cl]₂ (0.40 g, 0.81 mmol) were suspended in thf (30 mL) and cooled to -78 °C. NaHMDS (1.05 mL, 2.10 mmol) was then added dropwise. After stirring for 30 min at low temperature, the mixture was warmed to room temperature and stirred for another 5 h. The solvent was removed in vacuo and the product purified by column chromatography over alumina using dichloromethane/thf (3:1) as eluent, yield 32% (0.18 g, 0.26 mmol). ¹H NMR (600 MHz, CDCl₃): δ = 5.17–5.07 (m, 4 H, CH_{cod}), 5.06 (s, 3 H, N-CH₃), 4.64 (s, 3 H, N-CH₃), 4.50 (s, 3 H, N-CH₃), 4.39 (s, 3 H, N-CH₃), 3.36-3.22 (m, 4 H, CH_{cod}), 2.49-2.33 (m, 8 H, CH_{2,cod}), 2.06-1.94 (m, 8 H, CH_{2,cod}) ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 215.7 (d, ${}^{1}J_{CRh}$ = 50.8 Hz, CRh), 194.7 (d, ${}^{1}J_{CRh}$ = 50.8 Hz, CRh), 151.1 (s, CO), 140.4 (s, C_q), 114.9 (s, C_q), 101.5 (d, ${}^{1}J_{CRh} = 6.5$ Hz, C_{cod}), 101.2 (d, ${}^{1}J_{CRh}$ = 6.5 Hz, C_{cod}), 100.4 (d, ${}^{1}J_{CRh}$ = 6.5 Hz, C_{cod}), 100.2 (d, ${}^{1}J_{CRh}$ = 6.5 Hz, C_{cod}), 71.2 (d, ${}^{1}J_{CRh}$ = 14.4 Hz, C_{cod}), 70.8 (d, ${}^{1}J_{CRh}$ = 14.4 Hz, C_{cod}), 69.5 (d, ${}^{1}J_{CRh}$ = 14.4 Hz, C_{cod}), 69.4 (d, ${}^{1}J_{CRh}$ = 14.4 Hz, C_{cod}), 44.5 (s, CH₃), 39.8 (s, CH₃), 39.4 (s, CH₃), 37.5 (s, CH₃), 33.1 (s, CH_{2,cod}), 32.8 (s, CH_{2,cod}), 32.6 (s, CH₂), 32.2 (s, CH₂), 29.0 (s, CH₂), 28.9 (s, CH₂), 28.7 (s, CH₂) ppm. MS (MALDI-TOF): $m/z = 649 [M - Cl]^{+}$. $C_{25}H_{36}Cl_2N_4ORh_2$ (685.30): calcd. C 43.82, H 5.30, N 8.18; found C 44.12, H 5.30, N 7.88

 $19 \cdot [Rh(CO)_2 Cl]_2$ (24): The complex $19 [Rh(cod)Cl]_2$ (70 mg, 0.102 mmol) was dissolved in dichloromethane. A stream of CO was bubbled through the solution whilst stirring for 45 min. During this time, the bright-yellow solution became bleached, which indicates complete conversion. The IR spectrum of the resulting bisdicarbonyl-NHC compound was recorded from the reaction mixture. The solution was concentrated under high vacuum and nhexane was added, which caused precipitation of a powdery solid. This solid was isolated by filtration, washed with *n*-hexane, and dried under high vacuum for several hours. The liberated cyclooctadiene could not be completely removed, yield 73% (44 mg, 0.075 mmol). ¹H NMR (600 MHz, CDCl₃): δ = 4.75 (s, 3 H, CH₃), 4.46 (s, 3 H, CH₃), 4.30 (s, 3 H, CH₃), 4.19 (s, 3 H, CH₃) ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 205.8 (d, ¹*J*_{CRh} = 43.9 Hz, CRh), 186.9 (d, ${}^{1}J_{CRh}$ = 45.6 Hz, CRh), 184.8 (d, ${}^{1}J_{CRh}$ = 55.8 Hz, CO_{trans}), 184.4 (d, ${}^{1}J_{CRh}$ = 55.8 Hz, CO_{trans}), 181.4 (d, ${}^{1}J_{CRh}$ = 55.8 Hz, CO_{cis}), 181.0 (d, ${}^{1}J_{CRh}$ = 55.8 Hz, CO_{cis}), 151.0 (s, CO), 140.0 (s, Cq), 115.8 (s, Cq), 45.7 (s, CH₃), 40.7 (s, CH₃), 40.3 (s, CH₃), 38.3 (s, CH₃) ppm. IR (CH₂Cl₂): $\tilde{v} = 2091$ (vs, v_{CO}), 2015 (vs, v_{CO}] cm⁻¹. (C₁₃H₁₂Cl₂N₄O₅Rh₂)(C₈H₁₂)_{0.21} (603.7): calcd. C 29.19, H 2.42, N 9.28; found C 29.40, H 2.35, N 9.62.

1,3-Dimesityl-5,5-dimethyl-4,6-dioxopyrimidine-2-selenone (21·Se): Reagents: 1,3-Dimesityl-5,5-dimethyl-4,6-dioxopyrimidinium triflate (0.50 g, 0.95 mmol), NaHMDS (0.57 mL, 1.14 mmol), selenium (0.11 g, 1.43 mmol). Purification method a, yield 60% (0.26 g, 0.58 mmol), pink powder. ¹H NMR (600 MHz, CDCl₃): $\delta = 6.97$ (s, 4 H, CH_{Mes}), 2.33 (s, 6 H, CH_{3,Mes}), 2.14 (s, 12 H, CH_{3,Mes}), 1.78 [s, 6 H, C(CH₃)₂] ppm. ¹³C{¹H} NMR (150 MHz, CDCl₃): δ = 182.8 (s, CSe), 169.8 (s, CO), 139.1 (s, C_{Mes}), 136.1 (s, C_{Mes}), 134.7 (s, C_{Mes}), 129.8 (s, C_{Mes}), 49.3 [s, C(CH₃)₂], 24.9 [s, C(CH₃) ₂], 21.4 (s, CH₃), 17.9 (s, CH₃) ppm. ⁷⁷Se NMR (114 MHz, [D₆]acetone): δ = 847 (s, CSe) ppm. MS (EI): *m/z* = 456 [M]⁺⁺, 441 [M – Me]⁺⁺, 375 [M – Se]⁺⁺. HRMS (ESI+, CH₃CN/H₂O): calcd. for C₂₄H₂₉N₂O₂Se 456.4665 [M + H]⁺; found 457.1390.

Crystal Structure Determinations: Details concerning the X-ray structure determinations can be found in the Supporting Information.

CCDC-1042142 (for 2·Se), -1042143 (for 9·Se), -1042144 (for 10·Se), -1042145 (for 16·Se), -1042146 (12·Se–Me), and -1042128 (for 23) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif.

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N-Heterocyclic Carbenes

K. Verlinden, H. Buhl, W. Frank,

C. Ganter* 1–11

Determining the Ligand Properties of N-Heterocyclic Carbenes from ⁷⁷Se NMR Parameters

Keywords: Nitrogen heterocycles / Carbenes / Ligand properties / Rhodium / Selenium / NMR spectroscopy



⁷⁷Se NMR chemical shift

The electronic properties of a range of Nheterocyclic carbenes have been evaluated by using the ⁷⁷Se NMR chemical shifts of NHC–Se adducts, to map the π -acceptor character, and ${}^{1}J_{CSe}$ coupling constants,

which provide insights into the σ -donor ability of the respective carbene. DFT calculations were conducted to rationalize the data. The NMR-derived parameters have been compared with TEP values.