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First N-Heterocyclic Carbenes Relying on the Triazolone Structural Motif: Syntheses, Modifications and Reactivity

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Abstract: 4-Phenylsemicarbazide and 1,5-diphenylcarbazide are suitable starting materials for the syntheses of N-heterocyclic carbene (NHC) compounds with new backbone structures. In the first case, cyclisation and subsequent methylation leads to a cationic precursor whose deprotonation affords the triazolon-ylidene **2**, which was converted to the corresponding sulfur and selenium adducts and a range of metal complexes. In contrast, cyclisation of diphenylcarbazide affords a neutral betain-type NHC-precursor **7**, which is not in equilibrium with its carbene tautomer **7a**. Precursor **7** can either be deprotonated to give the anionic NHC **8** or methylated at the N or O atom of the backbone resulting in two isomeric cationic species **16** and **20**. Deprotonation of the latter two provides neutral NHC compounds with a carboxamide or carboximidate backbone, respectively. The ligand properties of the new NHC compounds were evaluated by IR and ^{77}Se NMR spectroscopy. Tolman electronic parameter (TEP) values range from 2050 to 2063 cm^{-1} with the anionic NHC **8** being the best overall donor.

Introduction

Commencing with the first isolated derivative reported by Arduengo and co-workers in 1991,[1] most of the stable N-heterocyclic carbenes (NHCs) are still based on the unsaturated imidazole-2-ylidene.[2] However, in the meantime a variety of related NHCs have been prepared, ranging from three-membered up to seven-membered heterocycles. Triazole-based NHCs have also attracted considerable attention (Figure 1). The first

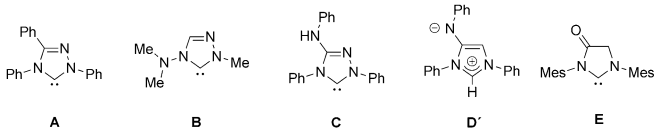

Figure 1. Selected examples of carbenes or crypto-carbenes relevant to the present study.

triazolylidene **A** was synthesized by Enders et al. in 1995[3] and a number of differently modified 1,2,4-triazolylidenes have subsequently been reported.[4] Biscarbenes relying on the 1,2,4-triazole core have been reported by the groups of Bertrand[5] and Peris.[6] 4-Amino-substituted triazolylidenes **B** were investigated by Schottenberger and co-workers[7] and Lassaletta,[8] while Siemeling and co-workers[9] demonstrated that Nitron, a commercially available triazole-based zwitterionic compound bearing an amido group at C3, provides access to carbene **C** by a tautomeric proton shift. Likewise, the carbon analogue of Nitron, **D′**, reported by César, Lavigne et al.,[10] also represents a "crypto-NHC", as it features the reactivity of its carbene tautomer. Triazolylidenes are particularly successful as organocatalysts,[11] while when coordinated as ligands to metal fragments they are less donating than structurally related imidazolylidenes.[2e]

In continuation of our previous work directed towards the syntheses and reactivity studies of amido[12] or mixed amino-amido[13] NHCs based on the imidazoline or triazine framework, we became interested in new backbone structures. We wondered if commercially available 4-phenylsemicarbazide and 1,5-diphenylcarbazide could be suitable starting materials for the preparation of new amido-functionalized triazole-based NHCs. Our first results concerning these investigations are reported herein.

Results and Discussion

Semicarbazide-based NHCs

For the synthesis of triazolonium salt **1·BF$_4$**, 4-phenylsemicarbazide was cyclized with formamidinium acetate in DMF according to a procedure recently reported by Zhang and Yao.[14] The resulting neutral triazole was alkylated in two steps; first it was treated with iodomethane in the presence of potassium carbonate to give the methylated amide backbone intermediate,[15] which was then further methylated using trimethyloxonium tetrafluoroborate to afford the amidinium cation (**1·BF$_4$**) in 74% yield (Scheme 1). **1·BF$_4$** was fully characterized by mass spectrometry, elemental analysis, ^{1}H and ^{13}C{^{1}H} NMR spectros-

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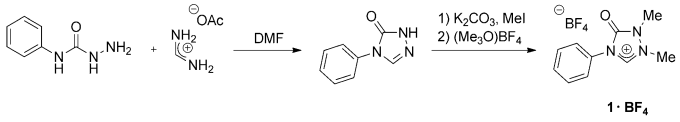
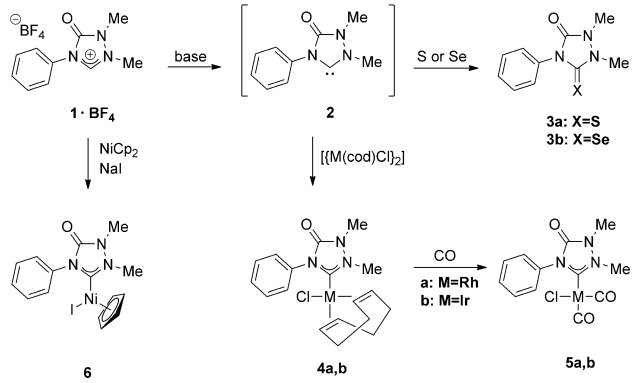


Scheme 1. Preparation of triazolonium salt **1·BF$_4$**.

copy. Notably, a $^4J_{HH}$ coupling between the amidinium proton and the methyl group was observed as evidenced by the appearance of a quartet and a doublet, respectively, in the ^{1}H NMR spectrum with $^4J_{HH} = 0.9$ Hz.

Deprotonation of precursor **1·BF$_4$** with bases such as sodium bis(trimethylsilyl)amide (NaHMDS) or potassium *tert*-butoxide generated in situ the carbene **2**. While all attempts to isolate the free carbene failed, its intermediate existence was proven by trapping reactions with sulfur and selenium leading to thiourea **3a**[16] and selenide **3b** in 70 and 46% yield, respectively (Scheme 2). Slow diffusion of *n*-hexane into a dichloromethane solution of **3a** led to crystals suitable for X-ray diffraction stud-



Scheme 2. Deprotonation of the triazolonium salt **1·BF$_4$**.

ies. The molecular structure is depicted in Figure 2. As expected, the carbon–oxygen bond (121.4(2) pm) is much shorter than the carbon–sulfur bond (165.8(2) pm). Both distances fall in the range usually observed for related compounds. The heterocycle is essentially flat and forms an interplanar angle of 66.6(1)° with the phenyl ring plane.

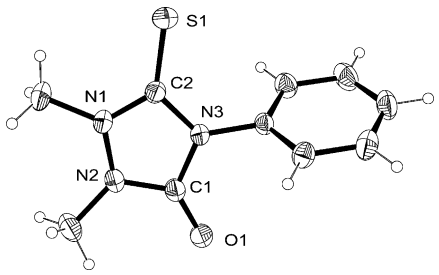


Figure 2. Molecular structure of **3a** in the solid state. Thermal ellipsoids are drawn at the 35% probability level. Selected interatomic distances [Å] and bond angles [°]: S1–C2 1.6578(18), O1–C1 1.214(2), N2–C1 1.361(2), N1–C2 1.326(2), N2–N1 1.392(2), N3–C2 1.382(2), N3–C1 1.382(2); N1-C2-N3 104.97(14), N2-C1-N3 104.18(14).

A variety of metal complexes of NHC **2** could be obtained starting from the triazolonium precursor **1**. For example, refluxing a THF solution of **1·BF$_4$** with nickelocene in the presence of sodium iodide afforded the nickel half-sandwich complex **6** in 51% yield. In this reaction, one of the cyclopentadienyl ligands of the nickelocene acts as a base for precursor deprotonation and sodium iodide is added to saturate the coordination sphere of the nickel atom. The molecular structure of complex **6** is depicted in Figure 3. The geometrical parameters are within the range typically observed for CpNi half-sandwich complexes with other NHC ligands.[17]

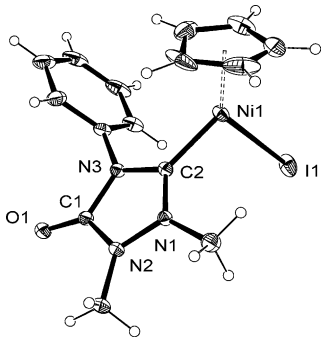


Figure 3. Molecular structure of complex **6** in the solid state. Thermal ellipsoids are drawn at the 35% probability level. Selected interatomic distances [Å] and bond angles [°]: Ni1–I1 2.5072(6), Ni1–C2 1.8539(17), N1–C2 1.325(2), N3–C2 1.371(2); N1-C2-N3 104.6(2).

Furthermore, precursor **1** was also deprotonated with potassium *tert*-butoxide in the presence of [{M(cod)Cl}$_2$] to yield the corresponding rhodium and iridium complexes [M(cod)(**2**)Cl] (M = Rh, Ir) **4a,b**. A convenient measure for the overall ligand properties of NHCs is the Tolman electronic parameter (TEP), which can be easily obtained by IR spectroscopy of carbonyl complexes containing the respective ligands. Therefore, dichloromethane solutions of the cod complexes were stirred while a slow stream of carbon monoxide was bubbled through the solutions for several minutes resulting in a complete cod → CO exchange. The IR spectra of both dicarbonyl derivatives (**5a,b**) feature the typical symmetrical and anti-symmetrical CO stretching vibrations, which were converted using well established relations[2c,18] to a TEP value of 2060 cm^{-1} for ligand **2**, which is slightly higher than for other triazole-based NHCs.[2e,6,9,19] A specific measure of the π-acceptor character of an NHC is provided by the chemical shift of its phosphinidene or selenium adduct in the ^{31}P or ^{77}Se NMR spectrum, respectively.[20,21] The ^{77}Se NMR spectrum of the corresponding selenide **3b** was recorded and revealed a resonance at $\delta = 137$ ppm, suggesting that the π-acidity of **2** is comparable to that of the saturated five-membered ring NHC 1,3-di-(mesityl)imidiazolidin-2-ylidene (SIMes, $\delta = 116$ ppm). However, triazolylidene **2** is significantly less π-acidic than the five-membered ring monoamido carbene 1,3-di(mesityl)imidiazolidin-4-one-2-ylidene (**E**) with $\delta(^{77}Se) = 295$ ppm.[22] In this compound, the carbonyl group withdraws electron density only from the N atom adjacent to the carbene-C atom, while in the triazole

derivative **2** the electron-withdrawing effect of the carbonyl group is attenuated by the presence of the additional N atom remote to the carbene-C atom. In addition to being less π-acidic than **E**, the slightly higher TEP value of **2** (2060 cm^{-1}) in comparison to that of **E** (2058 cm^{-1}) suggests that **2** should also be a weaker σ-donor.

The molecular structures of the cod–iridium complex **4b** and the dicarbonyl complexes **5a** and **5b** were determined by X-ray diffraction and their perspective drawings are depicted in Figure 4.

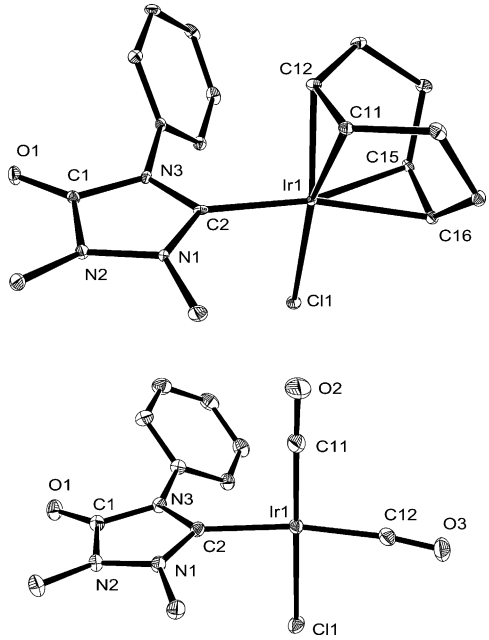


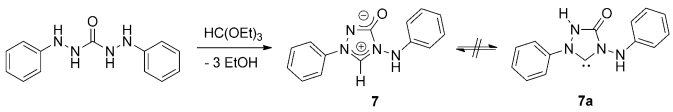
Figure 4. Molecular structures of Ir complexes **4b** (top) and **5b** (bottom) in the solid state. Thermal ellipsoids are drawn at the 35% probability level. H atoms have been omitted for clarity. Selected interatomic distances [Å] and bond angles [°]: **4b**: Ir1–C2 2.028(3), Ir1–C11 2.114(3), Ir1–C12 2.116(3), Ir1–C16 2.178(3), Ir1–C15 2.200(3), Ir1–Cl1 2.3696(8), C1–O1 1.227(4), N1–C2 1.322(4), C2–N3 1.374(4), C1–N2 1.359(4); N1-C2-N3 105.5(3); **5b**: Ir1–C11 1.8336(16), Ir1–C12 1.8896(13), Ir1–C2 2.0657(11), Ir1–Cl1 2.3591(5), O1–C1 1.2181(15), N1–C2 1.3271(16), C2–N3 1.3682(15), O2–C11 1.145(2), O3–C12 1.1364(17); N1-C2-N3 105.28(10).

All structures feature slightly distorted square–planar metal environments. The NHC ligand is oriented almost perpendicularly to the coordination plane with interplanar angles in the range of 80–86°. As is usually observed, the geometric parameters regarding the bonding of the two olefin moieties in the cod complex **4b** are quite different: the Ir–C distances to the C15–C16 double bond *trans* to the NHC are significantly longer (av. 219 pm) than those *trans* to the chloride ligand (C11–C12, av. 212 pm), indicating that the latter enforces stronger backbonding to the *trans*-olefin than the NHC. Accordingly, the C11–C12 double bond appears longer (142.3(4) pm) than C15–C16 (138.8(4) pm). Compound **4b** crystallizes with two independent molecules in the asymmetric unit that do not differ significantly regarding their geometrical data. The structural parameters of complex **4b** agree well with those reported for closely related complexes.[9,19,23]

Replacement of the cod ligand in **4b** by two CO molecules leads to the typical geometrical features of a dicarbonyl complex in **5b**. While the cod ligand renders the metal fragment in **4b** electron rich and capable of significant back bonding to the NHC, the strongly π-acidic CO group diminishes the π-component in the NHC–Ir bond in complex **5b**. Thus, a longer C2–Ir1 bond (206.6(1) pm) is observed in **5b**, compared with that in the cod derivative **4b** (202.8(3) pm). Again, chloride is the better donor than the NHC, leading to increased backbonding to the *trans*-CO, and as a result the Ir1–C11 bond is shorter (183.4(2) pm) than the Ir1–C12 bond *trans* to the NHC (189.0(1) pm). The analogous Rh compound **5a** is isostructural to complex **5b** with only marginally different geometrical parameters.

Carbazide-based NHCs

In the presence of acetic acid, 1,5-diphenylcarbazide undergoes a cyclisation reaction in refluxing triethyl orthoformate, leading to the formation of betaine **7** in 71% isolated yield under concomitant release of three equivalents of ethanol (Scheme 3). The five-membered ring is formed exclusively, in which one amide-nitrogen atom and one aniline-nitrogen



Scheme 3. Formation of betaine **7**.

atom are connected to the CH fragment delivered by the orthoformate. Betaine **7** is an air-stable white solid, which was characterized by X-ray diffraction, and various spectroscopic and analytical methods; its molecular structure is depicted in Figure 5. Betaine **7** features a delocalized negative charge in

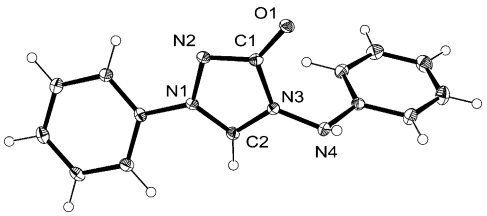
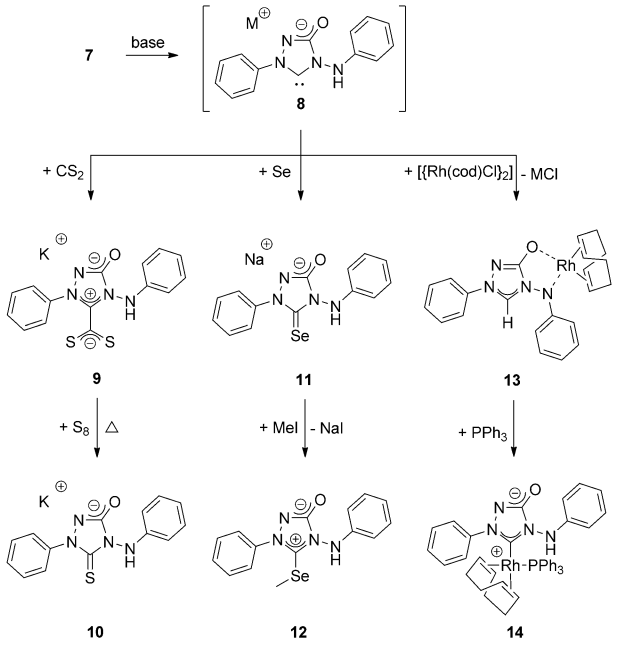


Figure 5. Molecular structure of betaine **7** in the solid state. Thermal ellipsoids are drawn at the 30%. probability level. The co-crystallized DMSO molecule has been omitted for clarity. Selected interatomic distances [Å] and bond angles [°]: N1–C2 1.3169(15), N1–N2 1.3893(13), C1–O1 1.2443(13), C1–N2 1.3450(14), C1–N3 1.4195(15), C2–N3 1.3386(14), N4–N3 1.3947(13), N1-C2-N3 106.09(10).

the amide backbone and a delocalized positive charge in the formamidinium fragment (Scheme 3).

In the ^{1}H NMR spectrum of **7**, the signals for C2–H and N4–H were detected at $\delta = 10.2$ ppm and 9.3 ppm, respectively. We found no indication that betaine **7** is in a tautomeric equilibrium with its neutral carbene tautomer **7a**, as no reac-

tion occurred with **7** in the presence of sulfur, selenium or carbon disulfide. This is in marked contrast to Siemeling's nitron[9] and the mesoionic 4-amido-imidazolium cation reported by César and Lavigne,[10] which were both found to exhibit the reactivity of the corresponding free carbenes. The mesoionic structures were shown to be thermodynamically more stable, but still served as sources for the carbenes in low concentration. Probably, in the case of **7**, due to the delocalization of the negative charge the basicity is not sufficient to allow for the existence of the neutral carbene tautomer even in trace amounts. However, deprotonation at C2 is easily accomplished by addition of an external base such as KO*t*Bu or NaHMDS yielding the negatively charged NHC **8** with potassium or sodium as a counter ion depending on the base used (Scheme 4). In the presence of carbon disulfide or selenium,



Scheme 4. Reactions of the anionic NHC **8**.

the in situ generated carbene **8** reacted cleanly to give the dithiocarboxylate **9** or the selenide **11**. A high-field signal at $\delta =$ 91 ppm was recorded in the ^{77}Se NMR spectrum of compound **11**, which indicated that compared to other NHCs,[21] carbene **8** has only a weak acceptor character, in accord with its negatively charged backbone (compare selenide **3b** at $\delta = 137$ ppm, vide supra). Interestingly, treatment of **11** with methyl iodide resulted in the selective alkylation at the selenium atom to afford the neutral mesoionic selenoether **12**. The selenium satellites in the ^{1}H NMR spectrum of **12** ($^2J_{HSe} = 12$ Hz) prove that the alkylation occurred at selenium and not at the nitrogen or oxygen sites in the backbone. The selenium methylation resulted in a downfield shift of 90 ppm and a resonance at $\delta =$ 181 ppm was detected in the ^{77}Se NMR spectrum of selenoether **12**. The identity of the CS_2-adduct **9** was deduced by mass spectrometry, ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The signal for the N_2-*C*-CS_2 atom is located at $\delta = 217.2$ ppm, comparable with the dithiocarboxylate of **C** ($\delta = 219.9$ ppm).[9] In contrast to other dithiocarboxylates, compound **9** shows only a limited stability,[24] which is already apparent from the ESI mass spectrum; besides a peak for **9** centered at *m/z* 327, a peak for **8** at *m/z* 251 is observed as well. The weak carbene–CS_2 bond is also reflected by the reactivity of **9**, which can serve as a source of free NHC. Thus, refluxing of **9** in the presence of sulfur provided the corresponding thiourea **10** in 76% yield. Unfortunately, apart from the reaction with sulfur, all other attempts to use **9** as a source for **8** met with failure.

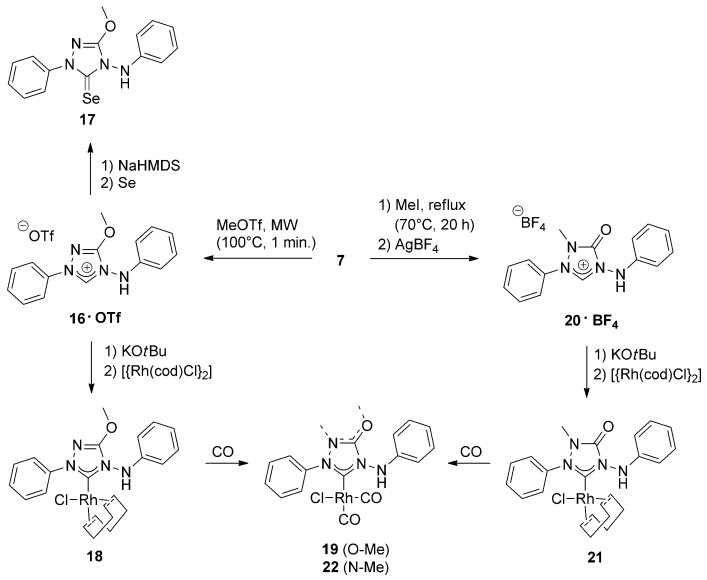
Next, we turned our attention to the coordination chemistry of **8**. Deprotonation of **7** with potassium *tert*-butoxide in the presence of [{Rh(cod)Cl}$_2$] afforded the neutral rhodium complex **13** in 64% yield under elimination of potassium chloride. Initially, we assumed that the anionic ligand would coordinate to the Rh atom through the carbene-C atom, analogous to the behaviour of another anionic NHC reported by César and Lavigne.[25] However, NMR investigations revealed that the coordination had instead occurred in a N,O-chelating manner, whereas the formamidinium fragment was still present, featuring a resonance at $\delta = 8.68$ ppm in the ^{1}H NMR spectrum. Accordingly, the corresponding formamidinium carbon resonance appeared as a doublet at $\delta = 124.1$ ppm in the proton-coupled ^{13}C NMR spectrum with a $^1J_{CH}$ coupling constant of 218 Hz. The coordination of the hard N- and O-atoms in a chelating manner leading to a square–planar (cod)Rh complex is preferred compared to the monodentate coordination through the soft C atom of the carbene tautomer. This observation leads to the question whether betaine **7** might initially be deprotonated at the secondary NH function before it eventually undergoes a tautomeric proton shift leading to **8**. Such a behaviour was observed for the mesoionic 4-amido-imidazolium cation reported by César and Lavigne.[10] Further investigations concerning this question are currently in progress.

The above-mentioned tautomerism was also observed when one equivalent of PPh_3 was added to the N,O-chelate complex **13**, which resulted in the formation of the neutral rhodium carbene complex **14** under concomitant proton shift. The coordination of the phosphine was confirmed by ^{31}P{^{1}H} NMR spectroscopy, where a doublet was detected at $\delta = 24$ ppm with a $^1J_{PRh}$ coupling constant of 157 Hz. Furthermore, the ^{13}C{^{1}H} NMR spectrum delivered a doublet of doublets for the carbene atom due to a $^1J_{CRh}$ coupling constant of 47 Hz in combination with a $^2J_{CP}$ coupling constant of 12 Hz. Likewise, addition of NBu_4Cl to the cod–complex **13** was sufficient to induce the tautomeric rearrangement of the ligand, leading to the anionic complex [(**8**)Rh(cod)Cl]$^-$. While this species could not be isolated in a pure form, its ^{13}C{^{1}H} NMR spectrum featured a doublet for the Rh-bound carbene-C atom with a typical $^1J_{CRh}$ coupling constant of 47 Hz.

The corresponding dicarbonyl complex [(**8**)RhCl(CO)$_2$]$^-$ (**15**) was generated in situ from the cod complex **13** by treatment with CO in CH_2Cl_2 solution and in the presence of NBu_4Cl as a chloride source. The chloride ion coordinates to the rhodium and initiates the internal amide-to-carbene rearrangement reaction. Unfortunately, complex **15** could not be isolated in a pure form but was characterized by two strong CO stretch-

ing bands in the IR spectrum, leading to a TEP value of 2050 cm^{-1}.

Due to the delocalized negative charge on the backbone of **7**, the nitrogen and the oxygen atoms are potential sites for attack by electrophiles. Both positions could be addressed depending on the reaction conditions leading to positively charged NHC precursors, which were subsequently converted to the respective NHCs (Scheme 5). Under relatively mild conditions (oil bath, reflux) and with the weak alkylating agent methyl iodide, the nitrogen atom was alkylated to afford the



Scheme 5. Selective alkylation of the anionic backbone in betaine **7**.

triazolonium salt **20·I** (**20·BF_4** after anion exchange) with an amide backbone. On the other hand, the oxygen atom was selectively methylated to give the methoxytriazolium salt **16·OTf** with a carboximidate backbone under more forcing conditions (MW, 100 °C) and with the more powerful alkylating agent methyl trifluoromethansulfonate. The reaction with other electrophiles like trimethylsilyl chloride was unsuccessful. Both triazolium salts were characterized by spectroscopic and analytical methods and the molecular structures were elucidated for both compounds by X-ray diffraction analysis (Figure 6 and Figure 7). The most significant structural differences are found in the backbones and are in accord with the chemical intuition (Table 1): a long N2–C1 and a short C1–O1 bond length is found for the urea fragment in the N–Me compound **20**, while the opposite is true for the O–Me derivative **16** with a C1–N2 double and a C1–O1 single bond, respectively. Intermediate values for **7** nicely reflect the delocalized nature of the betaine compound **7**. Analogously, the C2–N distances within the amidinium moieties in compounds **7**, **16** and **20** are found within a narrow range of 131 and 134 pm, intermediate between the typical values for single and double bonds. In all three structures the C2–N1 bond is consistently shorter than the C2–N3 bond. Analogous structural trends have been observed by Lavigne and César for a pair of compounds related to **7** and **16** based on a 4-amino/amido-substituted imidazolium cation.[10]

Both cationic species could be successfully converted to the respective neutral NHCs by deprotonation with sterically demanding strong bases (Scheme 5). Thus, treatment of the O-methylated derivative **16** with NaHMDS in the presence of selenium afforded the neutral selenide **17** which was purified by column chromatography with diethyl ether as eluent. The compound has a very good solubility in solvents of different polarity from methanol to *n*-hexane. Its resonance at $\delta =$ 119 ppm in the ^{77}Se NMR spectrum is intermediate between those of the neutral **3b** ($\delta = 137$ ppm) and the anionic derivative **11** ($\delta = 91$ ppm). Thus, carbene **8** is the weakest π-acceptor due to the anionic nature of the backbone. On the other hand, O-methylation of the anionic backbone to afford the neutral carboximidate unit in **17** enhances the acceptor character, while it is even more pronounced in derivative **3b** with the carboxamide functional group. Unfortunately, the corresponding Se-adduct of the N-methylated precursor **20** could not be prepared.

In order to gauge the overall ligand properties of the NHCs obtained from the isomeric precursors **16** and **20**, the $Rh(CO)_2$ complexes **19** and **22** were prepared by routine procedures, involving deprotonation of the cations in the presence of $[\{Rh(cod)Cl\}_2]$ at low temperature. The (cod)Rh complexes **18** and **21** thus obtained were then exposed to CO in dichloromethane solution, and IR spectra were recorded for the resulting carbonyl derivatives **19** and **22**. TEP values of 2058 and 2063 cm^{-1} were calculated for the NHCs **16**$-H^+$ and **20**$-H^+$, respectively. Thus, the relative order of π-acceptor strength suggested above

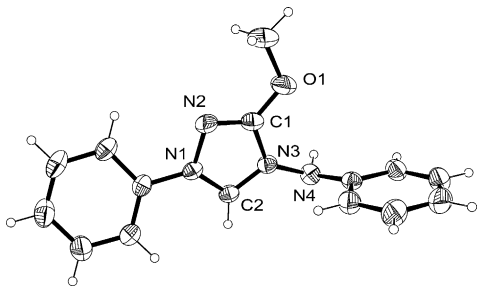


Figure 6. Molecular structure of triazolium salt **16·OTf** in the solid state. Thermal ellipsoids are drawn at the 35% probability level. The anion has been omitted for clarity. Selected geometrical parameters are compiled in Table 1.

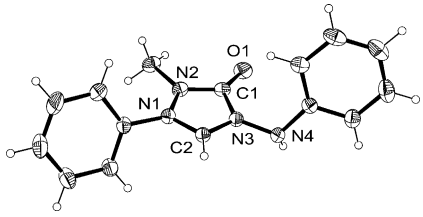
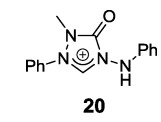
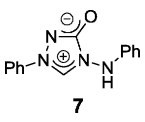
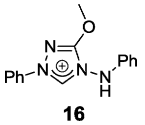


Figure 7. Molecular structure of triazolonium salt **20·I** in the solid state. Thermal ellipsoids are drawn at the 35% probability level. The anion has been omitted for clarity. Selected geometrical parameters are compiled in Table 1.

Table 1. Selected interatomic distances and bond angles of **7**, **16** and **20**.

	 **20**	 **7**	 **16**
N_2–C_1 [Å]	1.362(3)	1.3450(14)	1.294(4)
C_1–O_1 [Å]	1.204(3)	1.2443(13)	1.316(3)
N_1–C_2 [Å]	1.307(3)	1.3169(15)	1.311(3)
N_3–C_2 [Å]	1.331(3)	1.3386(14)	1.344(3)
N_3–C_1 [Å]	1.415(3)	1.4195(15)	1.380(3)
N_3-C_2-N_1 [°]	108.3(2)	106.1(1)	107.4(2)

on the basis of the ^{77}Se NMR data is well reflected by the overall ligand properties as indicated by the TEP values. An analogous sequence of values was established by César and Lavigne for a related series of compounds (see Figure 8 for a compilation of relevant data).[22]

Interestingly, while a CD_2Cl_2 solution of **16·OTf** showed no changes in the ^{1}H NMR spectrum within a couple of days, a new signal set started to appear overnight when the compound was dissolved in [D_6]DMSO. The spectra indicated that the newly formed species was the betaine **7** formed by formal loss of a methyl cation from **16**, which was subsequently transferred to the nucleophilic DMSO molecule resulting in the formation of the well-known cation $Me(CD_3)_2SO^+$. A related slow demethylation was also observed by Hudnall and co-workers for their amino–acrylamido carbene precursor.[26] Thus, the triazolium salt **16** is obviously a good electrophilic methylating agent. To confirm this, **16** was treated with a series of N-nucleophiles such as triethylamine, methylimidazole, pyridine and DABCO, which were all cleanly converted to the corresponding N-methylated cationic derivatives (dicationic in the case of DABCO) while **16** was converted back to **7**. However, we never observed a methyl transfer from O to the N-atom resulting in the formation of cation **20**. Furthermore, it should be noted that this N-methyl derivative **20** did not show any alkylating reactivity at all.

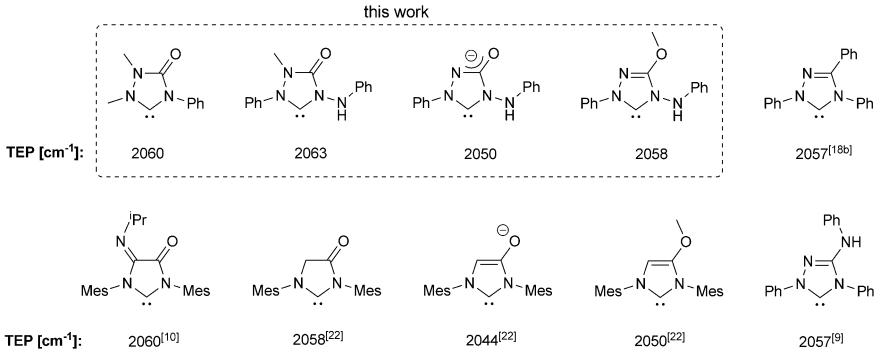


Figure 8. Comparison of TEP values of the compounds synthesized with those reported in the literature.

Conclusion

A series of new NHCs with O-functionalized triazole backbones could be prepared from cheap starting materials. 4-Phenylsemicarbazide was cleanly converted to the neutral triazolon-ylidene **2**, which could be incorporated into metal complexes of Ni, Rh and Ir. Its ligand properties as determined by the TEP value of 2060 cm^{-1} are in accord with the presence of the electron-withdrawing amido group in the backbone. On the other hand, 1,5-diphenylcarbazide turned out to be an even more versatile starting material. Its cyclisation afforded betaine **7**, in which a cationic amidinium fragment is connected to an anionic imidate moiety. The betaine is however not in equilibrium with its carbene tautomer **7a**. Deprotonation of betaine **7** and subsequent treatment with electrophilic trapping reagents leads to derivatives of the corresponding anionic NHC **8** or to the exceptional formation of the anionic N,O-coordinated chelate complex **13**. Furthermore, betaine **7** can be selectively methylated at the N- or O-atom of the backbone depending on the reaction conditions. The resulting cationic species **16** and **20** allow access to the isomeric neutral NHCs with an iminoether or carboxamide function, respectively. The range of TEP values obtained from the $(CO)_2ClRh$–NHC complexes indicates that the anionic NHC **8** is the best overall donor in this series of ligands (2050 cm^{-1}), while the donating ability is significantly diminished for the O–Me derivative (2058 cm^{-1}) and even more attenuated for the N–Me functionalized NHC (2063 cm^{-1}). Thus, by simple chemical modifications of the basic structural motif the electronic properties of the corresponding NHCs can be varied considerably, leading to a spread of TEP values of 13 wavenumbers.

Experimental Section

General information: All reactions were performed in an oxygen-free, dry nitrogen atmosphere using standard Schlenk techniques. The microwave-assisted reactions were carried out in a CEM-Discover-System microwave. Diethyl ether and THF were dried and distilled over sodium/benzophenone, dichloromethane over CaH_2 and *n*-hexane over sodium. The NMR spectra were recorded on a Bruker Avance DRX 200, a Bruker Avance DRX 500, a Bruker Avance III 300 or a Bruker Avance III 600. All ^{1}H and ^{13}C{^{1}H} NMR spectra are referenced to the chemical shifts of residual undeuterated solvent signals. ^{77}Se NMR spectra were referenced to external KSeCN in D_2O with specific concentration and a chemical shift of $\delta = -316.5$ ppm (4.0 mol L^{-1}) or -329.0 ppm (0.25 mol L^{-1}). Mass spectra were recorded on a UHR-QTOF maxis 4G (HR-ESI), a GC/MS-System Finnigan Trace DSQ, a MALDI-TOF Ultraflex or a Triple-

Quadrupol-mass spectrometer TSQ 7000 (EI-MS). Elemental analyses were recorded on an Elementar vario Micro cube. X-ray crystal structure data were collected on a Bruker Apex Duo. IR spectra were obtained with a Shimadzu IR Affinity-1 spectrometer. Reagents such as potassium *tert*-butoxide and NaHMDS (2 M in THF) were purchased from Acros Organics or Sigma Aldrich and used as received. $[\{Rh(cod)Cl\}_2]$ and $[\{Ir(cod)Cl\}_2]$ were synthesized according to a literature procedure.[27]

Synthesis of triazolonium salt 1·BF$_4$: A 100 mL Schlenk flask was charged with 1-methyl-4-phenyl-1,2,4-triazol-5-one (3.0 g, 17.1 mmol) and trimethyloxonium tetrafluoroborate (2.6 g, 17.9 mmol). After addition of acetonitrile (30 mL) the solution was stirred for 12 h at room temperature. The solvent was reduced in vacuo and the product was precipitated by addition of diethyl ether (80 mL). After filtration the pale yellow solid was dried in vacuo to afford compound **1** in 87% yield (4.2 g, 15.0 mmol). ^{1}H NMR (200 MHz, CD_3CN): $\delta = 9.07$ (q, $^4J(H,H) = 0.94$ Hz, 1H; NCHN), 7.69–7.50 (m, 5H; Ph–H), 3.94 (d, $^4J(H,H) = 0.94$ Hz, 3H; N–Me), 3.59 ppm (s, 3H; N–Me); $^{13}C\{^1H\}$ NMR (126 MHz, CD_3CN): $\delta =$ 149.2 (s; C=O), 139.3 (s; NCHN), 132.4 (s; Ph–C), 131.7 (s; Ph–C), 131.4 (s; Ph–C), 125.4 (s; Ph–C), 37.5 (s; N–Me), 31.0 ppm (s; N–Me); MS (MALDI): *m/z* 189.6 $[M]^+$; elemental analysis calcd (%) for $C_{10}H_{12}N_3OBF_4$: C 43.36, H 4.37, N 15.17; found: C 43.11, H 4.24, N 15.05.

Synthesis of thiourea 3a and selenide 3b: *General procedure*: A mixture of precursor **1·BF$_4$**, S_8 (or Se) and potassium *tert*-butoxide was cooled to −80 °C. After 10 min THF (30 mL) was added and the resulting suspension was stirred for 12 h. The mixture was allowed to warm up to room temperature. The solvent was removed in vacuo and the crude product was dissolved in dichloromethane. After filtration over Celite, the clear solution was reduced in vacuo and precipitated by addition of *n*-hexane to give compound **3a** as a pale yellow and compound **3b** as a white solid. Diffusion of *n*-hexane into a THF solution of **3a** delivered suitable crystals for X-ray diffraction studies.

Compound 3a: The deprotonation of **1·BF$_4$** (200 mg, 0.72 mmol) with potassium *tert*-butoxide (82 mg, 0.73 mmol) in the presence of S_8 (26 mg, 0.81 mmol) led to **3a** (70%, 112 mg, 0.51 mmol). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.56$–7.37 (m, 5H; Ph–H), 3.72 (s, 3H; N–Me), 3.44 ppm (s, 3H; N–Me); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta =$ 170.1 (s; C=O), 152.4 (s; NCN), 133.0 (s; Ph–C), 129.5 (s; Ph–C), 129.4 (s; Ph–C), 128.0 (s; Ph–C), 33.9 (s; N–Me), 32.1 ppm (s; N–Me); MS (GC-MS): *m/z* 221 $[M]^+$; elemental analysis calcd (%) for $C_{10}H_{11}N_3OS$: C 54.28, H 5.01, N 18.99, S 14.49; found: C 54.22, H 5.11, N 19.06, S 14.30.

Compound 3b: The deprotonation of **1·BF$_4$** (100 mg, 0.36 mmol) with potassium *tert*-butoxide (45 mg, 0.40 mmol) in the presence of selenium (32 mg, 0.41 mmol) led to **3b** (46%, 45 mg, 0.17 mmol). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.58$–7.38 (m, 5H; Ph–H), 3.88 (s, 3H; N–Me), 3.51 ppm (s, 3H, N–Me); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 166.5$ (s; C=O), 151.9 (s; NCN), 133.8 (s; Ph–C), 129.8 (s; Ph–C), 129.5 (s; Ph–C), 128.3 (s; Ph–C), 35.2 (s; N–Me), 31.9 ppm (s; N–Me); ^{77}Se NMR (115 MHz, [D$_6$]Acetone): $\delta = 137$ ppm (s; C=Se); MS (EI): *m/z* 269 $[M]^+$; elemental analysis calcd (%) for $C_{10}H_{11}N_3OSe$: C 44.79, H 4.13, N 15.67; found: C 44.92, H 4.09, N 15.67.

Synthesis of rhodium complex 4a and iridium complex 4b: *General procedure*: Precursor **1·BF$_4$**, potassium *tert*-butoxide and $[\{M(cod)Cl\}_2]$ (M = Rh or Ir) were charged into a 100 mL Schlenk flask and cooled to −80 °C. After a few minutes THF (30 mL) was added and the solution was stirred overnight. Afterwards the solvent was evaporated in vacuo. The rhodium complex **4a** was purified by flash chromatography on aluminium oxide with dichloromethane as eluent. In the case of the iridium complex **4b**, the crude product was dissolved in dichloromethane and filtered over Celite. The clear solution was reduced in vacuo and precipitated by addition of *n*-hexane. The resulting yellow solid was washed a few times with *n*-hexane and dried in vacuo.

Compound 4a: Deprotonation of **1·BF$_4$** (114 mg, 0.41 mmol) with potassium *tert*-butoxide (53 mg, 0.47 mmol) in the presence of $[\{Rh(cod)Cl\}_2]$ (100 mg, 0.20 mmol) led to **4a** (50%, 85 mg, 0.20 mmol) as a yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.10$–8.03 (m, 2H; Ph–H), 7.61–7.41 (m, 3H; Ph–H), 5.20–5.07 (m, 1H; $cod_{olef.}$), 5.06–4.93 (m, 1H; $cod_{olef.}$), 4.21 (s, 3H; N–Me), 3.48 (s, 3H; N–Me), 3.42–3.31 (m, 1H; $cod_{olef.}$), 2.71–2.58 (m, 1H; $cod_{olef.}$), 2.45–2.18 (m, 2H; $cod_{aliph.}$), 2.11–1.72 (m, 4H; $cod_{aliph.}$), 1.59–1.40 ppm (m, 2H; $cod_{aliph.}$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = 189.4$ (d, $^1J(Rh,C) =$ 51 Hz; NCN), 151.5 (s; C=O), 135.5 (s; Ph–C), 129.0 (s; Ph–C), 128.7 (s; Ph–C), 126.7 (s; Ph–C), 100.4 (d, $^1J(Rh,C) = 7$ Hz; $cod_{olef.}$), 100.2 (d, $^1J(Rh,C) = 7$ Hz; $cod_{olef.}$), 69.6 (d, $^1J(Rh,C) = 14$ Hz; $cod_{olef.}$), 69.4 (d, $^1J(Rh,C) = 14$ Hz; $cod_{olef.}$), 37.3 (s; N–Me), 33.6 (s; $cod_{aliph.}$), 31.7 (s; $cod_{aliph.}$), 30.4 (s; N–Me), 29.0 (s; $cod_{aliph.}$), 28.5 ppm (s; $cod_{aliph.}$); MS (MALDI): *m/z* 399.9 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{18}H_{23}N_3ORhCl$: C 49.61, H 5.32, N 9.64; found: C 49.75, H 5.43, N 9.67.

Compound 4b: Deprotonation of **1·BF$_4$** (164 mg, 0.59 mmol) with potassium *tert*-butoxide (68 mg, 0.61 mmol) in the presence of $[Ir(cod)Cl]_2$ (199 mg, 0.3 mmol) led to **4b** (57%, 177 mg, 0.34 mmol) as a yellow solid. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.93$–7.86 (m, 2H; Ph–H), 7.54–7.41 (m, 3H; Ph–H), 4.82–4.70 (m, 1H; $cod_{olef.}$), 4.68–4.56 (m, 1H; $cod_{olef.}$), 4.09 (s, 3H; N–Me), 3.52 (s, 3H; N–Me), 2.99–2.89 (m, 1H; $cod_{olef.}$), 2.39–2.28 (m, 1H; $cod_{olef.}$), 2.23–2.05 (m, 2H; $cod_{aliph.}$), 1.87–1.49 (m, 4H; $cod_{aliph.}$), 1.36–1.23 ppm (m, 2H; $cod_{aliph.}$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = 185.2$ (s; NCN), 151.8 (s; C=O), 135.1 (s; Ph–C), 128.8 (s; Ph–C), 128.7 (s; Ph–C), 127.1 (s; Ph–C), 88.0 (s; $cod_{olef.}$), 87.5 (s; $cod_{olef.}$), 53.3 (s; $cod_{olef.}$), 53.2 (s; $cod_{olef.}$), 36.8 (s; N–Me), 34.0 (s; $cod_{aliph.}$), 32.6 (s; $cod_{aliph.}$), 30.5 (s; N–Me), 29.4 (s; $cod_{aliph.}$), 29.2 ppm (s; $cod_{aliph.}$); MS (MALDI): *m/z* 525.1 $[M]^+$; elemental analysis calcd (%) for $C_{18}H_{23}N_3OIrCl$: C 41.17, H 4.42, N 8.00; found: C 40.95, H 4.25, N 7.84.

Synthesis of dicarbonyl complexes 5a and 5b: *General procedure*: Carbon monoxide was bubbled through a solution of **4a** (**4b**) in dichloromethane for 10 min. The solvent was evaporated in vacuo.

Compound 5a: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.69$–7.62 (m, 2H; Ph–H), 7.55–7.46 (m, 3H; Ph–H), 4.04 (s, 3H; N–Me), 3.56 ppm (s, 3H; N–Me); $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta = 184.7$ (d, $^1J(Rh,C) =$ 56 Hz; Rh–CO), 181.3 (d, $^1J(Rh,C) = 73$ Hz; Rh–CO), 179.9 (d, $^1J(Rh,C) = 45$ Hz; NCN), 150.8 (s; C=O), 134.6 (s; Ph–C), 129.6 (s; Ph–C), 129.5 (s; Ph–C), 127.0 (s; Ph–C), 38.0 (s; N–Me), 30.4 ppm (s; N–Me); MS (MALDI): *m/z* 348.0 $[M-Cl]^+$; IR (CH_2Cl_2): $\tilde{\nu} = 2089$ (Rh–CO), 2011 (Rh–CO), 1746 cm^{-1} (amide–CO); elemental analysis calcd (%) for $C_{12}H_{11}N_3O_3RhCl$: C 37.57, H 2.89, N 10.95; found: C 37.28, H 2.89, N 10.68.

Compound 5b: ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.57$–7.49 (m, 2H; Ph–H), 7.47–7.42 (m, 3H; Ph–H), 3.97 (s, 3H; N–Me), 3.54 ppm (s, 3H; N–Me); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = 179.72$ (s; Ir–CO), 177.5 (s; Ir–CO), 166.8 (s; NCN), 150.9 (s; C=O), 134.2 (s; Ph–C), 129.8 (s; Ph–C), 129.5 (s; Ph–C), 127.5 (s; Ph–C), 37.7 (s; N–Me), 30.4 ppm (s; N–Me); MS (MALDI): *m/z* (%): 438.2 $[M-Cl]^+$; IR (CH_2Cl_2): $\tilde{\nu} = 2076$ (Ir–CO), 1994 (Ir–CO), 1749 cm^{-1} (amide–CO); elemental analysis calcd (%) for $C_{12}H_{11}N_3O_3IrCl$: C 30.48, H 2.34, N 8.89; found: C 30.26, H 2.24, N 8.79.

Synthesis of nickel complex 6: A mixture of precursor **1·BF$_4$** (202 mg, 0.73 mmol), sodium iodide (253 mg, 1.69 mmol) and nick-

elocene (138 mg, 0.73 mmol) was refluxed in THF (35 mL) for 4 h. All volatiles of the resulting red solution were removed in vacuo. The residue was dissolved in dichloromethane and filtered over Celite. The solvent was reduced in vacuo and the product was precipitated by addition of *n*-hexane (35 mL) as a red solid (162 mg, 0.37 mmol, 51%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 7.92–7.83$ (m, 2H; Ph–H), 7.65–7.51 (m, 3H; Ph–H), 4.92 (s, 5H; Ni–Cp), 4.32 (s, 3H; N–Me), 3.53 ppm (s, 3H; N–Me); ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$): $\delta =$ 179.5 (s; NCN), 151.7 (s; C=O), 135.9 (s; Ph–C), 129.4 (s; Ph–C), 129.3 (s; Ph–C), 127.9 (s; Ph–C), 92.8 (s; Ni–Cp), 39.3 (s; N–Me), 30.8 ppm (s; N–Me); MS (MALDI): *m/z* 439.0 $[M]^+$; HRMS (ESI): *m/z* calcd for $C_{15}H_{16}N_3NiO$: 312.0641; found: 312.0640.

Synthesis of betaine 7: A 250 mL Schlenk flask was charged with 1,5-diphenylcarbazide (5.0 g, 20.6 mmol) and triethylorthoformate (50 mL). After addition of acetic acid (0.1 mL), the suspension was refluxed for 3 h while a white solid precipitated from the solution. The product was filtered and washed with diethyl ether (3x20 mL). After drying in vacuo the betaine **7** was obtained analytical pure in 71% yield (3.7 g, 14.7 mmol). ^{1}H NMR (200 MHz, [D$_6$]DMSO): $\delta =$ 10.17 (s, 1H; NCHN), 9.31 (s, 1H; NH–Ph), 7.91–7.79 (m, 2H; Ph–H_{ortho}), 7.63–7.53 (m, 2H; Ph–H_{meta}), 7.50–7.40 (m, 1H; Ph–H_{para}), 7.30–7.18 (m, 2H; NHPh–H_{meta}), 6.94–6.84 (m, 1H; NHPh–H_{para}), 6.80–6.70 ppm (m, 2H; NHPh–H_{ortho}); ^{13}C{^{1}H} NMR (126 MHz, [D$_6$]DMSO): $\delta = 157.4$ (s; C–O$^-$), 146.7 (s; NHPh–$C_{quart.}$), 136.5 (s; NCHN), 135.9 (s; Ph–$C_{quart.}$), 129.6 (s; Ph–C_{meta}), 129.1 (s; NHPh–C_{meta}), 128.4 (s; Ph–C_{para}), 120.8 (s; NHPh–C_{para}), 118.9 (s; Ph–C_{ortho}), 113.2 ppm (s; NHPh–C_{ortho}); MS (MALDI): *m/z* 252.7 $[M]^+$; elemental analysis calcd (%) for $C_{14}H_{12}N_4O$: C 66.65, H 4.79, N 22.21; found: C 66.43, H 4.54, N 22.29.

Synthesis of dithiocarboxylate 9: The betaine **7** (102 mg, 0.40 mmol) and potassium *tert*-butoxide (46 mg, 0.41 mmol) were charged in a 100 mL Schlenk flask and cooled to −80 °C. After a few minutes THF (20 mL) was added and the suspension was stirred while the colour changed to bright green. After 10 min carbon disulfide (50 μL, 0.83 mmol) was added and the reaction mixture was stirred for a further six hours while the mixture was allowed to warm up to room temperature. The precipitated off-white solid was filtered and washed first with THF and then *n*-hexane. The product was obtained in 68% yield (100 mg, 0.27 mmol). ^{1}H NMR (200 MHz, [D$_6$]DMSO): $\delta = 10.41$ (s, 1H; NH–Ph), 7.83–7.75 (m, 2H; Ph–H), 7.66–7.52 (m, 4H; Ph–H), 7.46–7.39 (m, 1H; Ph–H), 7.37–7.27 (m, 2H; Ph–H), 7.26–7.17 ppm (m, 1H; Ph–H); ^{13}C{^{1}H} NMR (125 MHz, [D$_6$]DMSO): $\delta = 217.2$ (s; NCN), 156.6 (s; CS_2^-), 145.5 (s; CO^-), 136.4 (s; Ph–C), 136.2 (s; Ph–C), 129 (s; Ph–C), 129.6 (s; Ph–C), 128.7 (s; Ph–C), 128.1 (s; Ph–C), 126.6 (s; Ph–C), 118.4 ppm (s; Ph–C); MS (ESI): *m/z* 327 $[M]^-$; HRMS (ESI): *m/z* calcd. for $C_{15}H_{11}N_4OS_2^-$: *m/z* 327.0380; found: 327.0376.

Synthesis of thiourea 10: A 100 mL Schlenk flask was charged with the dithiocarboxylate **9** (200 mg, 0.55 mmol) and S_8 (32 mg, 1.00 mmol). After addition of THF (25 mL), the reaction mixture was refluxed for 3 h. The solution was cooled to room temperature, filtrated over Celite and then reduced in vacuo. After addition of *n*-hexane (40 mL), the product precipitated in 76% yield (134 mg, 0.42 mmol). ^{1}H NMR (200 MHz, [D$_6$]DMSO): $\delta = 8.30$ (m, 2H; Ph–H), 8.26 (s, 1H; NH–Ph), 7.37 (m, 2H; Ph–H), 7.14 (m, 3H; Ph–H), 6.71 (m, 1H; Ph–H), 6.59 ppm (m, 2H; Ph–H); ^{13}C{^{1}H} NMR (76 MHz, [D$_6$]DMSO): $\delta = 161.2$ (s; C–O$^-$), 157.2 (s; NCN), 148.0 (s; Ph–C), 140.3 (s; Ph–C), 128.4 (s; Ph–C), 127.7 (s; Ph–C), 124.5 (s; Ph–C), 122.1 (s; Ph–C), 118.5 (s; Ph–C), 112.6 ppm (s; Ph–C); HRMS [ESI]: *m/z* calcd for $C_{14}H_{11}N_4OS^-$: *m/z* 383.0659; found: 383.0657.

Synthesis of selenide 11: A suspension of **7** (199 mg, 0.79 mmol) and selenium (128 mg, 1.62 mmol) in THF (35 mL) was cooled to −80 °C. After a few minutes, sodium bis(trimethylsilyl)amide (0.5 mL, 1 mmol, 2M in THF) was diluted in THF (5 mL), and added drop wise to the reaction mixture and stirred for 17 h. The solvent was removed and the residue dissolved in dichloromethane. After filtration over Celite, the solvent was removed and the product was obtained in 68% yield (189 mg, 0.53 mmol). ^{1}H NMR (200 MHz, [D$_6$]DMSO): $\delta = 8.32$ (s, 1H; NH–Ph), 8.27–8.19 (m, 2H; Ph–H), 7.44–7.34 (m, 2H; Ph–H), 7.28–7.19 (m, 1H; Ph–H), 7.18–7.08 (m, 2H; Ph–H), 6.78–6.68 (m, 1H; Ph–H), 6.65–6.55 ppm (m, 2H; Ph–H); ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]DMSO): $\delta = 158.5$ (s; C–O$^-$), 154.2 (s; NCN), 147.8 (s; Ph–C), 140.6 (s; Ph–C), 128.4 (s; Ph–C), 127.8 (s; Ph–C), 125.5 (s; Ph–C), 123.4 (s; Ph–C), 118.8 (s; Ph–C), 113.0 ppm (s; Ph–C); ^{77}Se NMR (115 MHz, [D$_6$]acetone): $\delta = 91$ ppm (s; C=Se); MS (MALDI): *m/z* 330.8 $[M-Na]^-$; elemental analysis calcd (%) for $C_{14}H_{11}N_4OSeNa$: C 47.61, H 3.14, N 16.86; found: C 47.21, H 3.54, N 16.46.

Synthesis of selenoether: **12**: Selenide **11** (113 mg, 0.33 mmol) was dissolved in a 100 mL Schlenk flask with dichloromethane (20 mL). Methyl iodide (80 μL, 1.29 mmol) was added to the clear solution. After a few minutes a white solid precipitated from the solution. After 5 h the suspension was filtered over Celite, the solvent reduced in vacuo and the product precipitated with *n*-hexane. The selenoether **12** was obtained in 56% yield (61 mg, 0.18 mmol). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 9.25$ (s, 1H; NH–Ph), 7.75–7.68 (m, 2H; Ph–H), 7.63–7.54 (m, 3H; Ph–H), 7.28–7.18 (m, 2H; Ph–H), 6.92–6.83 (m, 1H; Ph–H), 6.80–6.72 (m, 2H; Ph–H), 2.26 ppm (s, 3H; Se–Me); ^{13}C{^{1}H} NMR (75 MHz, [D$_6$]DMSO): $\delta =$ 158.1 (s; C–O$^-$), 146.4 (s; NHPh–C_{quart}), 137.6 (s; NCN), 137.3 (s; Ph–C_{quart}), 129.6 (s; Ph–C_{para}), 129.1 (s; Ph–C_{meta}), 129.0 (s; NHPh–C_{meta}), 125.7 (s; Ph–C_{ortho}), 120.4 (s; NHPh–C_{para}), 113.0 (s; NHPh–C_{ortho}), 9.7 ppm (s; Se–Me); ^{77}Se NMR (114 MHz, [D$_6$]acetone): $\delta = 181$ ppm (s; C–Se–Me); HRMS (ESI): *m/z* calcd for $C_{15}H_{15}N_4OSe^+$: 347.0406; found: 347.0410.

Synthesis of rhodium complex 13: A mixture of betaine **7** (201 mg, 0.8 mmol), potassium *tert*-butoxide (91 mg, 0.81 mmol) and [{Rh(cod)Cl}$_2$] (200 mg, 0.4 mmol) was charged in a 100 mL Schlenk flask and precooled to −80 °C. After addition of THF (25 mL) the reaction mixture was allowed to warm up to room temperature, while stirring was continued for 15 h. All volatiles were removed in vacuo, the residue dissolved in dichloromethane and filtered over Celite. The clear yellow solution was reduced in vacuo and the product precipitated after addition of *n*-hexane. The product was filtered off and washed with *n*-hexane (3×20 mL). The solid was dried in vacuo to yield the rhodium complex **13** (64%, 237 mg, 0.51 mmol). ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.68$ (s, 1H; NCHN), 7.53–7.38 (m, 4H; Ph–H), 7.36–7.21 (m, 3H; Ph–H), 6.98–6.84 (m, 3H; Ph–H), 4.26–4.08 (m, 2H; $cod_{olef.}$), 3.62–3.45 (m, 2H; $cod_{olef.}$), 2.48–2.29 (m, 4H; $cod_{aliph.}$), 1.83–1.65 ppm (m, 4H; $cod_{aliph.}$); ^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2): $\delta = 165.1$ (s; C–O$^-$), 152.7 (d, ^2J(C,Rh) = 2 Hz; N–N$^-$–$Ph_{quart.}$), 137.6 (s; N–$Ph_{quart.}$), 130.2 (s; Ph–C), 130.1 (s; Ph–C), 128.2 (s; Ph–C), 124.1 (s; NCHN), 122.3 (s; Ph–C), 120.7 (s; Ph–C), 118.8 (s; Ph–C), 77.0 (d, ^1J(C,Rh) = 13 Hz; $cod_{olef.}$), 74.5 (d, ^1J(C,Rh) = 15 Hz; $cod_{olef.}$), 31.6 (s; $cod_{aliph.}$), 30.2 ppm (s; $cod_{aliph.}$); MS (EI): *m/z* 462 $[M]^+$; elemental analysis calcd (%) for $C_{22}H_{23}N_4ORh$: C 57.15, H 5.01, N 12.12; found: C 57.10, H 5.05, N 11.93.

Synthesis of rhodium complex 14: Rhodium complex **13** (150 mg, 0.32 mmol) and triphenyl phosphine (91 mg, 0.35 mmol) were charged in a 100 mL Schlenk flask. After addition of dichloromethane (20 mL) the solution was stirred for 5 h. The solvent was reduced in vacuo and the target compound was precipitated by addition of *n*-hexane (40 mL). After filtration the yellow solid was washed with *n*-hexane and **14** was obtained (63%, 146 mg, 0.20 mmol). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 8.70–8.59$ (m, 2H; Ph–H),

7.50–7.29 (m, 17H; Ph–H), 7.26–7.15 (m, 3H; Ph–H), 6.94–6.85 (m, 1H; Ph–H), 6.80–6.70 (m, 2H; Ph–H), 6.26 (bs, 1H; NH–Ph), 5.27–5.04 (m, 1H; $cod_{olef.}$), 4.74–4.51 (m, 1H; $cod_{olef.}$), 4.13–3.88 (m, 2H; $cod_{olef.}$), 2.42–1.86 ppm (m, 8H; $cod_{aliph.}$); $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2): $\delta = 176.9$ (dd, $^1J(C,Rh) = 48$ Hz, $^2J(C,P) = 12$ Hz; NCN), 160.9 (s; C–O$^-$), 147.6 (s; Ph–C), 141.2 (s; Ph–C), 134.2 (d, $^2J(C,P) = 12$ Hz; PPh_3–C_{ortho}), 132.2 (d, $^1J(C,P) = 40$ Hz; PPh_3–C_{quart}), 130.9 (d, $^4J(C,P) = 2$ Hz; PPh_3–C_{para}), 129.5 (s; Ph–C), 129.0 (d, $^3J(C,P) = 9.7$ Hz; PPh_3–C_{meta}), 128.7 (s; Ph–C), 126.3 (s; Ph–C), 121.5 (s; Ph–C), 120.3 (s, Ph–C), 114.2 (s, Ph–C), 98.1 (m, cod_{olef}), 93.4 (m; cod_{olef}), 92.1 (m; cod_{olef}), 90.6 (m; cod_{olef}), 31.3 (s; cod_{aliph}), 30.8 (s, cod_{aliph}), 30.7 (s, cod_{aliph}), 30.6 ppm (s, cod_{aliph}); ^{31}P NMR (121 MHz, CD_2Cl_2): $\delta =$ 23.98 ppm (d, $^1J(P,Rh) = 159$ Hz; PPh_3); MS (MALDI): *m/z* 724.5 $[M]^+$.

Synthesis of triazolium salt 16·OTf: A microwave tube was charged with betaine **7** (304 mg, 1.21 mmol) and methyl trifluoromethansulfonate (2 mL, 18.2 mmol). The reaction mixture was heated at 100 °C for one minute under microwave irradiation (200 W). From the resulting brown clear solution the product was precipitated by addition of diethyl ether (30 mL) and the suspension was stirred for 1 h. The grey precipitate was filtered off and washed with diethyl ether (20 mL) to give **16·OTf** in 67% yield (339 mg, 0.81 mmol). ^1H NMR (200 MHz, $[D_6]$DMSO): $\delta = 11.10$ (s, 1H; NCHN), 10.02 (s, 1H; NH–Ph), 8.01–7.91 (m, 2H; Ph–H), 7.78–7.61 (m, 3H; Ph–H), 7.37–7.26 (m, 2H; Ph–H), 7.08–6.96 (m, 3H; Ph–H), 4.27 ppm (s, 3H; O–Me); $^{13}C\{^1H\}$ NMR (75 MHz, $[D_6]$DMSO): $\delta = 157.2$ (s; C–OMe), 144.5 (s; NCHN), 142.6 (s; Ph–C), 135.1 (s; Ph–C), 130.4 (s; Ph–C), 130.0 (s; Ph–C), 129.4 (s; Ph–C), 122.4 (s; Ph–C), 120.2 (s; Ph–C), 113.7 (s; Ph–C), 60.9 ppm (s; O–Me); MS (MALDI): *m/z* 267.0 $[M]^+$; elemental analysis calcd (%) for $C_{16}H_{15}F_3N_4O_4S$: C 46.15, H 3.63, N 13.46, S 7.70; found: C 46.17, H 3.93, N 13.45, S 8.00.

Synthesis of selenide 17: The precursor **16·OTf** (239 mg, 0.57 mmol) and selenium (79 mg, 1.00 mmol) were added in THF (25 mL) and cooled to −80 °C. Sodium bis(trimethylsilyl)amide (0.3 mL, 0.60 mmol, 2 M in THF) was diluted in THF (5 mL) and added drop wise to the cooled reaction mixture. The reaction mixture was stirred for 16 h and then allowed to warm up to room temperature. After evaporation to dryness the crude product was purified by flash chromatography on alumina with diethyl ether. The product was obtained as a brown solid in 62% yield (122 mg, 0.35 mmol). ^1H NMR (200 MHz, $[D_6]$DMSO): $\delta = 9.24$ (s, 1H; NH–Ph), 8.10–8.02 (m, 2H; Ph–H), 7.59–7.46 (m, 3H; Ph–H), 7.28–7.19 (m, 2H; Ph–H), 6.91–6.83 (m, 1H; Ph–H), 6.72–6.65 (m, 2H; Ph–H), 4.11 ppm (s, 3H; O–Me); $^{13}C\{^1H\}$ NMR (75 MHz, $[D_6]$DMSO): $\delta =$ 161.5 (s; C–OMe), 157.1 (s; NCN), 145.3 (s; Ph–C), 138.6 (s; Ph–C), 129.0 (s; Ph–C), 128.7 (s; Ph–C), 128.2 (s; Ph–C), 124.4 (s; Ph–C), 120.5 (s; Ph–C), 112.8 (s; Ph–C), 58.7 ppm (s; O–Me); ^{77}Se NMR (115 MHz, $[D_6]$Acetone): $\delta = 119$ ppm (s; C=Se); MS (MALDI): *m/z* 347.1 $[M+H]^+$; elemental analysis calcd (%) for $C_{15}H_{14}N_4SeO$: C 52.18, H 4.09, N 16.23; found: C 52.27, H 4.32, N 16.11.

Synthesis of rhodium complex 18: A 100 mL Schlenk flask was charged with the triazolium salt **16·OTf** (144 mg, 0.35 mmol), $[\{Rh(cod)Cl\}_2]$ (85 mg, 0.17 mmol) and potassium *tert*-butoxide (43 mg, 0.38 mmol). The mixture was cooled to −80 °C. After 10 min THF (20 mL) was added and the solution was stirred for 20 h. The solvent was evaporated in vacuo and the residue dissolved in dichloromethane. After filtration over Celite, the solvent was evaporated and the resulting yellow solid was washed with *n*-hexane (2×20 mL). The rhodium complex **18** was obtained in 47% yield (82 mg, 0.16 mmol). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 8.49$–8.39 (m, 2H; Ph–H), 8.34 (bs, 1H; NH–Ph), 7.57–7.49 (m, 2H; Ph–H), 7.48–7.42 (m, 1H; Ph–H), 7.41–7.32 (m, 2H; Ph–H), 7.14–7.05 (m, 1H; Ph–H), 7.04–6.96 (m, 2H; Ph–H), 5.09–4.97 (m, 2H; $cod_{olef.}$), 4.18 (s, 3H; O–Me), 2.87–2.76 (m, 1H; $cod_{olef.}$), 2.68–2.57 (m, 1H; $cod_{olef.}$), 1.81–1.06 ppm (m, 8H; $cod_{aliph.}$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = 187.6$ (d, $^1J(Rh,C) = 51$ Hz; NCN), 159.6 (s; C–OMe), 147.1 (s; Ph–C), 140.0 (s; Ph–C), 129.6 (s; Ph–C), 128.8 (s; Ph–C), 128.6 (s; Ph–C), 123.6 (s; Ph–C), 122.9 (s; Ph–C), 116.0 (s; Ph–C), 100.6 (d, $^1J(Rh,C) = 7$ Hz; $cod_{olef.}$), 98.6 (d, $^1J(Rh,C) = 7$ Hz; $cod_{olef.}$), 71.6 (d, $^1J(Rh,C) = 14$ Hz; $cod_{olef.}$), 70.6 (d, $^1J(Rh,C) = 14$ Hz; $cod_{olef.}$), 59.3 (s; O–Me), 32.2 (s; $cod_{aliph.}$), 31.9 (s; $cod_{aliph.}$), 28.9 (s; $cod_{aliph.}$), 28.3 ppm (s; $cod_{aliph.}$); HRMS (ESI): calcd for $C_{23}H_{26}N_4ORh^+$: *m/z* 477.1156; found: 477.1153.

Synthesis of triazolonium salt 20·I: Betaine **7** (1.47 g, 5.8 mmol) and methyl iodide (1.5 mL, 24.1 mmol) were stirred together at 70 °C in DMF (20 mL). After 23 h the solvent was removed in vacuo and the residue was dissolved in dichloromethane (5 mL). The product was precipitated completely by addition of *n*-hexane (70 mL). The white solid was filtered off and washed first with dichloromethane (10 mL) and then with diethyl ether (50 mL). The product was dried in vacuo to give the triazolonium salt in 78% yield (1.8 g, 4.6 mmol). Suitable crystals for X-ray diffraction studies were obtained by slow diffusion of diethyl ether in an acetonitrile solution of **20·I**. ^1H NMR (200 MHz, $[D_6]$DMSO): $\delta = 10.70$ (s, 1H; NCHN), 9.74 (s, 1H; NH–Ph), 7.98–7.88 (m, 2H; Ph–H), 7.85–7.74 (m, 3H; Ph–H), 7.38–7.28 (m, 2H; Ph–H), 7.14–7.06 (m, 2H; Ph–H), 7.05–6.96 (m, 1H; Ph–H), 3.39 ppm (s, 3H; N–Me); $^{13}C\{^1H\}$ NMR (75 MHz, $[D_6]$DMSO): δ 147.9 (s; C=O), 144.8 (s; NHPh–C_{quart}), 143.6 (s; NCN), 132.8 (s; Ph–C_{quart}), 130.3 (s; Ph–C_{meta}), 129.8 (s; Ph–C_{para}), 129.1 (s; NHPh–C_{meta}), 127.3 (s; Ph–C_{ortho}), 121.9 (s; NHPh–C_{para}), 113.8 (s; NHPh–C_{ortho}), 31.6 ppm (s; N–Me); MS (MALDI): *m/z* 267.1 $[M]^+$; elemental analysis calcd (%) for $C_{15}H_{15}IN_4O$: C 45.70, H 3.84, N 14.21; found: C 45.58, H 3.81, N 14.06.

Synthesis of triazolonium salt 20·BF_4: The triazolonium salt **20·I** (200 mg, 0.51 mmol) and silver tetrafluoroborate (100 mg, 0.51 mmol) were stirred at room temperature in acetonitrile (20 mL). After 3 h the precipitated solid was filtered off and the resulting clear colourless solution was reduced in vacuo. The addition of diethyl ether led to precipitation of the target compound in 89% yield (161 mg, 0.46 mmol). ^1H NMR (200 MHz, $[D_6]$DMSO): $\delta = 10.66$ (s, 1H; NCHN), 9.75 (s, 1H; NH–Ph), 7.94–7.85 (m, 2H; Ph–H), 7.83–7.75 (m, 3H; Ph–H), 7.39–7.27 (m, 2H; Ph–H), 7.11–6.95 (m, 3H; Ph–H), 3.38 ppm (s, 3H; N–Me); $^{13}C\{^1H\}$ NMR (75 MHz, $[D_6]$DMSO): $\delta = 147.9$ (s; C=O), 144.8 (s; Ph–C), 143.6 (s; NCN), 132.8 (s; Ph–C), 130.3 (s; Ph–C), 129.9 (s; Ph–C), 129.2 (s; Ph–C), 127.2 (s; Ph–C), 122.0 (s; Ph–C), 113.8 (s; Ph–C), 31.5 ppm (s; N–Me); MS (MALDI): *m/z* 266.9 $[M]^+$; elemental analysis calcd (%) for $C_{15}H_{15}N_4OBF_4$: C 50.88, H 4.27, N 15.82; found: C 50.72, H 4.50, N 16.09.

Synthesis of rhodium complex 21: The triazolonium salt **20·BF_4** (142 mg, 0.40 mmol), $[\{Rh(cod)Cl\}_2]$ (100 mg, 0.20 mmol) and potassium *tert*-butoxide (45 mg, 0.40 mmol) were cooled to −80 °C. THF (20 mL) was added and the solution was stirred for 18 h. After evaporation of the solvent in vacuo, the residue was dissolved in dichloromethane and filtered over Celite. The solvent was reduced in vacuo and after addition of *n*-hexane (40 mL) the product precipitated as a yellow solid. After filtration the rhodium complex was obtained in 40% yield (83 mg, 0.16 mmol). ^1H NMR (200 MHz, $CDCl_3$): $\delta = 7.96$–7.86 (m, 2H; Ph–H), 7.83 (s, 1H; NH–Ph), 7.69–7.56 (m, 3H; Ph–H), 7.40–7.29 (m, 2H; Ph–H), 7.10–7.00 (m, 3H; Ph–H), 5.09–4.90 (m, 2H; $cod_{olef.}$), 3.32 (s, 3H; N–Me), 2.89–2.77 (m, 1H; $cod_{olef.}$), 2.48–2.36 (m, 1H; $cod_{olef.}$), 2.04–1.84 (m, 2H; $cod_{aliph.}$), 1.72–1.55 (m, 2H; $cod_{aliph.}$), 1.50–1.14 ppm (m, 4H; $cod_{aliph.}$); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): $\delta = 194.6$ (d, $^1J(Rh,C) = 51$ Hz; NCN), 153.2 (s; C=O), 147.3 (s; Ph–C), 135.0 (s; Ph–C), 130.7 (s; Ph–C), 129.8 (s; Ph–C), 129.5 (s; Ph–C), 127.5 (s; Ph–C), 122.7 (s; Ph–C), 116.1 (s;

Ph–C), 101.6 (d, ^1J(Rh,C) = 7 Hz; $cod_{olef.}$), 100.1 (d, ^1J(Rh,C) = 7 Hz; $cod_{olef.}$), 71.4 (d, ^1J(Rh,C) = 14 Hz; $cod_{olef.}$), 70.8 (d, ^1J(Rh,C) = 14 Hz; $cod_{olef.}$), 32.8 (s; N–Me), 32.3 (s; $cod_{aliph.}$), 31.9 (s; $cod_{aliph.}$), 28.5 (s; $cod_{aliph.}$), 28.2 ppm (s; $cod_{aliph.}$); MS (MALDI): *m/z* 477.1 $[M-Cl]^+$; elemental analysis calcd (%) for $C_{23}H_{26}ClN_4ORh$: C 53.87, H 5.11, N 10.92; found: C 53.68, H 4.97, N 10.83.

Synthesis of dicarbonyl complexes 19 and 22: *General procedure*: The rhodium complex **18 or 21** was dissolved in dichloromethane and stirred for 10 min while carbon monoxide was bubbled through the solution. The solvent was evaporated in vacuo.

Dicarbonyl complex 19: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 8.11 (m, 3H; Ph–H), 7.54–7.47 (m, 2H; Ph–H), 7.52 (bs, 1H; NH–Ph), 7.33 (m, 2H; Ph–H), 7.07 (m, 1H; Ph–H), 6.80 (m, 2H; Ph–H), 4.24 ppm (s, 3H; O–CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 184.9 (d, ^1J(Rh,C) = 56 Hz; NCN or Rh–CO), 179.5 (d, ^1J(Rh,C) = 44 Hz; NCN or Rh–CO), 159.5 (s; CO–Me), 145.6 (s; Ph–C), 139.5 (s; Ph–C), 129.6 (s; Ph–C), 129.5 (s; Ph–C), 129.2 (s; Ph–C), 128.8 (s; Ph–C), 123.5 (s; Ph–C), 115.9 (s; Ph–C), 66.0 (s; O–CH_3); IR (CH_2Cl_2): $\tilde{\nu}$ = 2089 cm^{-1} (strong; Rh–CO), 2014 cm^{-1} (strong; Rh–CO).

Dicarbonyl complex 22: ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.65 (m, 5H; Ph–H), 7.55 (bs, 1H; NH–Ph), 7.36–7.29 (m, 2H; Ph–H), 7.09–7.01 (m, 1H; Ph–H), 6.94–6.89 (m, 2H; Ph–H), 3.37 ppm (s, 3H; N–CH_3); $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$): δ = 151.5 (s; C=O), 145.6 (s; Ph–C), 134.3 (s; Ph–C), 131.8 (s; Ph–C), 130.4 (s; Ph–C), 129.5 (s; Ph–C), 127.9 (s; Ph–C), 123.3 (s; Ph–C), 116.1 (s; Ph–C), 32.4 ppm (s; N–CH_3). MS (MALDI): *m/z* 396.9 $[M$-CO-Cl$]^+$; IR (CH_2Cl_2): $\tilde{\nu}$ = 2092 (strong; Rh–CO), 2015 (strong; Rh–CO), 1761 cm^{-1} (strong; amide–CO).

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[1] A. J. Arduengo III, R. J. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361 – 363.

[2] a) D. Bourissou, O. Guerret, F. P. Gabbai, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39 – 91; b) F. E. Hahn, M. C. Jahnke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3122 – 3172; *Angew. Chem.* **2008**, *120*, 3166 – 3216; c) T. Dröge, F. Glorius, *Angew. Chem. Int. Ed.* **2010**, *49*, 6940 – 6952; *Angew. Chem.* **2010**, *122*, 7094 – 7107; d) L. Benhamou, E. Chardon, G. Lavigne, S. Bellemin-Laponnaz, V. César, *Chem. Rev.* **2011**, *111*, 2705 – 2733; e) D. J. Nelson, S. P. Nolan, *Chem. Soc. Rev.* **2013**, *42*, 6723 – 6753; f) M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810 – 8849; *Angew. Chem.* **2010**, *122*, 8992 – 9032; g) D. Martin, M. Melaimi, M. Soleilhavoup, G. Bertrand, *Organometallics* **2011**, *30*, 5304 – 5313; h) M. N. Hopkinson, C. Richter, M. Schedler, F. Glorius, *Nature* **2014**, *510*, 485 – 496.

[3] D. Enders, K. Breuer, G. Raabe, J. Runsink, J. H. Teles, J.-P. Melder, K. Ebel, S. Brode, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1021 – 1023; *Angew. Chem.* **1995**, *107*, 1119 – 1122.

[4] For recent reports concerning electron-poor triazolylidene see: a) T. Sato, Y. Hirose, D. Yoshioka, T. Shimojo, S. Oi, *Chem. Eur. J.* **2013**, *19*, 15710 – 15718; b) T. Sato, D. Yoshioka, Y. Hirose, S. Oi, *Chem. Lett.* **2014**, *43*, 325 – 327.

[5] O. Guerret, S. Solé, H. Gornitzka, M. Teichert, G. Trinquier, G. Bertrand, *J. Am. Chem. Soc.* **1997**, *119*, 6668 – 6669.

[6] E. Mas-Marzá, J. A. Mata, E. Peris, *Angw. Chem.* **2007**, *119*, 3803 – 3805; *Angew. Chem. Int. Ed.* **2007**, *46*, 3729 – 3731. .

[7] A. Schwärzler, G. Laus, V. Kahlenberg, K. Wurst, T. Gelbrich, C. Kreutz, H. Kopacka, G. Bonn, H. Z. Schottenberger, *Z. Naturforsch. Sect. B* **2009**, *64*, 603 – 616.

[8] M. Alcarazo, R. Fernández, E. Álvarez, J. M. Lassaletta, *J. Organomet. Chem.* **2005**, *690*, 5979 – 5988.

[9] C. Färber, M. Leibold, C. Bruhn, M. Maurer, U. Siemeling, *Chem. Commun.* **2012**, *48*, 227 – 229.

[10] V. César, J.-C. Tourneaux, N. Vujkovic, R. Brousses, N. Lugan, G. Lavigne, *Chem. Commun.* **2012**, *48*, 2349 – 2351.

[11] D. Enders, O. Niemeier, A. Henseler, *Chem. Rev.* **2007**, *107*, 5606 – 5655.

[12] a) M. Braun, W. Frank, G. J. Reiss, C. Ganter, *Organometallics* **2010**, *29*, 4418 – 4420; M. Braun, W. Frank, C. Ganter, *Organometallics* **2012**, *31*, 1927 – 1934.

[13] a) A. Makhloufi, W. Frank, C. Ganter, *Organometallics* **2012**, *31*, 2001 – 2008; b) A. Makhloufi, W. Frank, C. Ganter, *Organometallics* **2012**, *31*, 7272 – 7277; c) A. Makhloufi, M. Wahl, W. Frank, C. Ganter, *Organometallics* **2013**, *32*, 854 – 861.

[14] C. Sheng, X. Che, W. Wang, S. Wang, Y. Cao, Z. Miao, J. Yao, W. Zhang, *Eur. J. Med. Chem.* **2011**, *46*, 5276 – 5282.

[15] G. Fairley, C. Hall, R. Greenwood, *Synlett* **2013**, *24*, 570 – 574.

[16] For older synthetic routes to thiourea **3a** see: a) H. Buchwald, K. Rühlmann, *Zeitschr. Chem.* **1978**, *18*, 336 – 337; b) US Pat. 4276420 (1981).

[17] V. Ritleng, C. Barth, E. Brenner, S. Milosevic, M. J. Chetcuti, *Organometallics* **2008**, *27*, 4223 – 4228.

[18] a) S. Wolf, H. Plenio, *J. Organomet. Chem.* **2009**, *694*, 1487 – 1492; b) R. A. Kelly III, H. Clavier, S. Giudice, N. M. Scott, E. D. Stevens, J. Bordner, I. Samardjiev, C. D. Hoff, L. Cavallo, S. P. Nolan, *Organometallics* **2008**, *27*, 202 – 210.

[19] W. A. Herrmann, G. Schütz, G. D. Frey, E. Herdtweck, *Organometallics* **2006**, *25*, 2437 – 2448.

[20] O. Back, M. Henry-Ellinger, C. D. Martin, D. Martin, G. Bertrand, *Angew. Chem. Int. Ed.* **2013**, *52*, 2939 – 2943; *Angew. Chem.* **2013**, *125*, 3011 – 3015.

[21] a) A. Liske, K. Verlinden, H. Buhl, K. Schaper, C. Ganter, *Organometallics* **2013**, *32*, 5269 – 5272; b) K. Verlinden, H. Buhl, W. Frank, C. Ganter, *Eur. J. Inorg. Chem.* **2015**, 2416 – 2425; c) S. V. C. Vummaleti, D. J. Nelson, A. Poater, A. Gómez-Suárez, D. B. Cordes, A. M. Z. Slawin, S. P. Nolan, L. Cavallo, *Chem. Sci.* **2015**, *6*, 1895 – 1904.

[22] L. Benhamou, N. Vujkovic, V. César, H. Gornitzka, N. Lugan, G. Lavigne, *Organometallics* **2010**, *29*, 2616 – 2630.

[23] G. S. Nichol, D. P. Walton, L. J. Anna, E. Rajaseelan, *Acta Crystallogr. Sect. E* **2012**, *68*, m158 – m159.

[24] L. Delaude, *Eur. J. Inorg. Chem.* **2009**, 1681 – 1699.

[25] V. César, N. Lugan, G. Lavigne, *J. Am. Chem. Soc.* **2008**, *130*, 11286 – 11287.

[26] R. M. Mushinski, B. M. Squires, K. A. Sincerbox, T. W. Hudnall, *Organometallics* **2012**, *31*, 4862 – 4870.

[27] a) G. Giordiano, R. H. Crabtree, R. M. Heintz, D. Forster, D. E. Morris, *Inorg. Synth.* **1990**, *28*, 88 – 90; b) J. Choudhury, S. Podder, S. Roy, *J. Am. Chem. Soc.* **2005**, *127*, 6162 – 6163.

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