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Graphical Abstract

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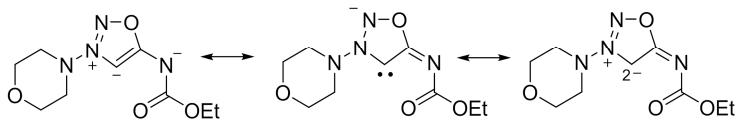

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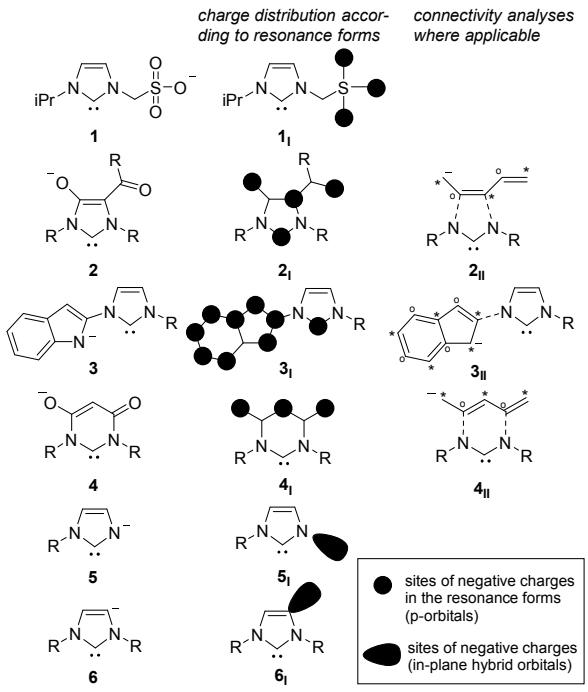
ABSTRACT

The sydnone imines Molsidomine and 5-(benzoylimino)-3-(2-methoxyphenyl)-1,2,3-oxadiazolium-2-ide gave anionic N-heterocyclic carbenes on deprotonation at C4 which were trapped as methylated selenium adducts, gold complexes (X-ray analysis) as well as palladium complexes (X-ray analysis). The ^{13}C NMR resonance frequencies of the carbene carbon atom are extremely shifted upfield and appear at δ = 142.1 ppm (Molsidomine carbene) and δ = 159.8 ppm (sydnone imine carbene). The Pd complexes were applied as catalysts in Suzuki-Miyaura and Sonogashira-Hagihara cross-coupling reactions.

1. Introduction

Currently, the design and the syntheses of anionic N-heterocyclic carbenes[1] including ditopic carbanionic N-heterocyclic carbenes[2] and anionic dicarbenes[3-5] constitute an important topic in structural, complex, synthetic and catalytic chemistry. To date, anionic NHCs have been generated by deprotonation of neutral N-heterocycles,[6-10] by incorporation of anionic groups into the NHC backbone,[11-15] or by reduction of an NHC in the presence of a metal.[16-18] Consequently, several types of anionic N-heterocyclic carbenes have been prepared which can be differentiated *i.a.* by the π-electronic influence of the negatively charged partial structure on the carbene carbon atom. Some selected examples are presented in Scheme 1. In the anionic N-heterocyclic carbene **1** the carbene carbon atom of the imidazol-2-ylidene ring is isolated by σ-bonds from the sulfonate group (*cf.* $\mathbf{1_I}$).[19] By contrast, the anionic carbenes **2**[20] and **3**[21-23] are examples of anionic N-heterocyclic carbenes which are π-conjugated as they originate from conjugated mesomeric betaines. As shown by $\mathbf{2_I}$ and $\mathbf{3_I}$, the negative charge is delocalized within the π-conjugated system which includes the carbene carbon atom. Consequently, the carbene carbon atom possesses coefficients of the highest occupied molecular orbitals (HOMO) which were calculated to be π-orbitals, respectively. In general π-electrons can be fed into the imidazol-2-ylidene moiety by substituents which are attached to C4/5 as in carbene **2** or to one of the nitrogen atoms as in carbene **3**. Other examples of conjugated systems with related structures have been described as well.[24-32]

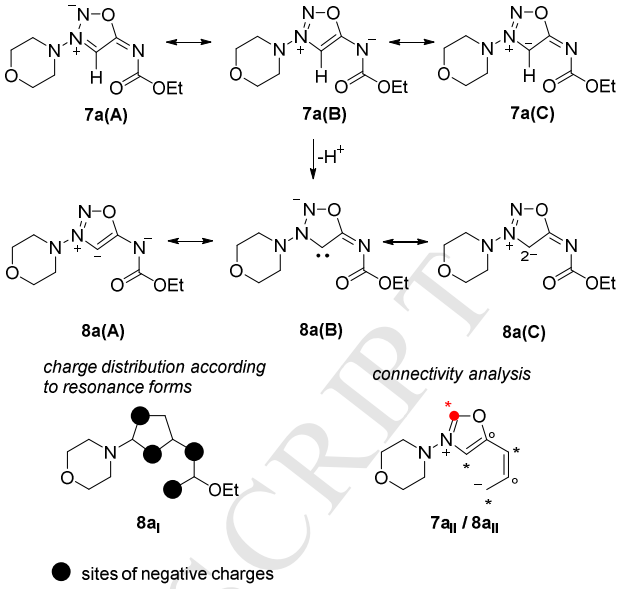


Scheme 1. *Comparison of anionic N-heterocyclic carbenes*

The relationship between heterocyclic mesomeric betaines isoconjugate with hydrocarbon dianions and pairs of alternant hydrocarbon fragments has been studied by Ramsden.[33-35] The interactions of alternant hydrocarbon fragments with pairs of associated 2p heteroatoms (NR, O, S) is the base for an understanding of chemical and physical properties of mesomeric betaines and structures derived thereof. If we translate this theory into the structural design of anionic N-heterocyclic carbenes we have to realize that in the carbenes **2** and **3** one heteroatom is connected to a starred position of the alternant hydrocarbon fragment as shown by $\mathbf{2_{II}}$ and $\mathbf{3_{II}}$, respectively. This is a legacy of their origin, as they are deprotonated conjugated heterocyclic mesomeric betaines. By contrast, the pyrimidine derivative **4**[36-39] was generated from a cross-conjugated mesomeric betaine. Consequently, the negative charge is exclusively delocalized in the 3-oxobut-1-en-1-olate partial structure without mesomeric charge distribution into the diaminocarbene moiety (c.f. $\mathbf{4_I}$). The π-electronic charge separation sets molecule **4** apart from the other N-heterocyclic carbenes presented in Scheme 1; the connectivity between the two partial structures is exclusively via unstarred positions (c.f. $\mathbf{4_{II}}$). The relationship between the distinct classes of mesomeric betaines and N-heterocyclic carbenes has been reviewed recently.[40] Neither the negative charge of the anionic N-heterocyclic carbene **5** (R = tBu_2P)[41] nor of dicarbene **6** are delocalized in terms of resonance. Consequently, a lithium cation was found to bind to the nitrogen atom of **5** and dicarbene **6** has been described as adducts and complexes (e.g. BF_3 at C2 and Ag/Ru at C4[42] or Li, V, Pd at C2 and BF_3 at C4[43,44]). In continuation of our interest in sydnone derived carbenes[45] we report here on N-heterocyclic carbenes of two sydnone imines, among those the carbene of Molsidomine. This orally active vasodilating drug for the prevention of angina pectoris attacks[47] is the subject of intense ongoing pharmacological research,[48-52] however, during the last decade not much effort has been directed toward its chemical properties. We present some surprising results in the light of the relationship between mesomeric betaines and N-heterocyclic carbenes.

2. Results and Discussion

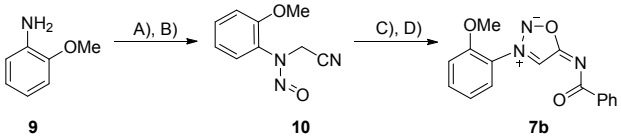
Molsidomine **7a** is a sydnone imine[53-57] belonging to the class of mesoionic compounds[58,59] and conjugated heterocyclic mesomeric betaines (CMB) of class 1B[33] (Scheme 2). It can exclusively be described by a number of dipolar or tetrapolar resonance forms such as **7a(A)**, **7a(B)** and **7a(C)** from which **7a(A)** is in better agreement with bond lengths (c.f. Supporting Information) and the imine stretching frequencies of the exocyclic imine bond. In continuation of our interest in the chemistry of N-heterocyclic carbenes,[60] mesomeric betaines[61,62] and the intersection between these two substance classes we aimed at studying the deprotonation of Molsidomine and of another model sydnone imine at C4 for comparison, which resulted in the formation of unique anionic N-heterocyclic carbenes. The anion of Molsidomine **7a** can be formulated as anionic abnormal NHC **8a(A)** and as anionic normal NHCs **8a(B)**. According to the rules of resonance it can even be described by structure **8a(C)** which displays two negative charges on the carbene carbon atom, one of which is delocalized within the π-electron system, and the other is located in the in-plane sp^2 hybrid orbital. The distinct resonance forms of **8a** are reflected in representation $\mathbf{8a_I}$. The anionic N-heterocyclic carbene **8a** differs from the examples presented in Scheme 1 in such a way, that the carbene carbon atom is a starred position of the alternant hydrocarbon fragment itself as shown by a connectivity analysis according to Ramsden´s classification[33] (c.f. $\mathbf{8a_{II}}$).



Scheme 2. *Resonance forms of Molsidomine* **7a** *and of its anion* **8a**. *π-Electronic charge distribution according to the resonance rules. Connectivity analysis.*

According to a DFT calculation at the B3LYP/6-31G(d,p) level the highest occupied molecular orbital (HOMO) of the Molsidomine anion **8a** is a π-orbital which includes a large coefficient of the p-orbital of C-4, whereas the HOMO-1 corresponds to the characteristic σ-orbital of NHCs. Thus HOMO and HOMO-1 are switched in comparison to the parent 1,3-dimethylimidazol-2-ylidene **Im** (Figure 1).[63] In addition, the E_σ level changes considerably in comparison to the parent carbene (ΔE_σ(HOMO for **Im** – HOMO-1 for **8a**) = +3.75 eV). The lowest unoccupied molecular orbital (LUMO) of carbene **8a** is essentially located in the 1,2,3-oxadiazole ring as well as in the conjugated side chain. Its energy is by 1.65 eV higher than that of the parent carbene **Im** and it also possesses a large coefficient on the carbene carbon atom. These calculations hint at considerably changed π-accepting properties of sydnone imine carbenes.

To enable comparisons, a sydnone imine was prepared by a modified HCN-free synthesis according to modified literature procedures[64,65] starting from 2-methoxyaniline **9** (Scheme 3). Nucleophilic substitution with bromoacetonitrile followed by N-nitrosation gave nitroso compound **10** which cyclized by gaseous HCl to form a sydnone imine hydrochloride in quantitative yields. Deprotonation followed by benzoylation gave the sydnone imine **7b** as brownish stable solid. A single crystal analysis of **7b**, obtained by slow evaporation from small amounts of DCM, confirmed structure and exocyclic imine bond (Fig. 2).



Reaction conditions: A) $BrCH_2CN$, NaOAc, EtOH, reflux (83%); B) $NaNO_2$, HCl, 0 °C (92%); C) HCl(g), Et_2O, 20 °C (99%); D) PhCOCl, CH_2Cl_2, -10 °C, then NEt_3 (80%).

Scheme 3. *Syntheses of sydnone imine* **7b**.

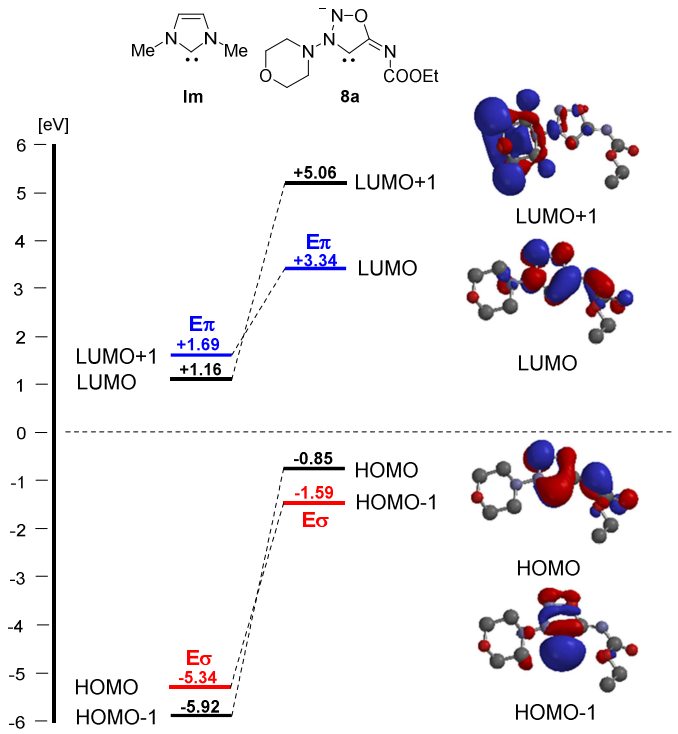


Fig. 1. *Frontier orbital energies of 1,3-dimethylimidazol-2-ylidene* **Im** *in comparison to Molsidomine carbene* **8a**.

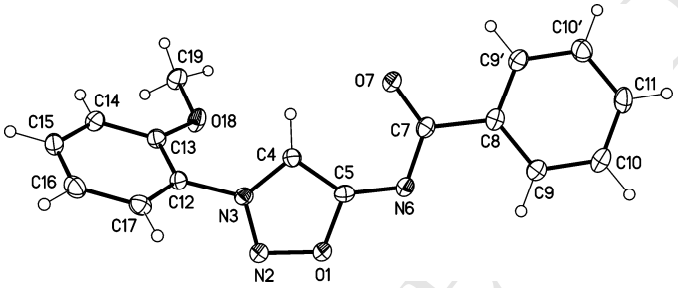
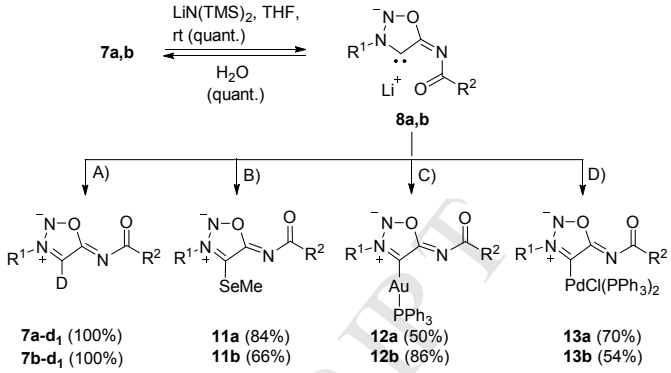


Fig. 2. *Molecular drawing of sydnone imine* **7b** *(displacement parameters are drawn at 50% probability level). Selected bond lengths [pm] (crystallographic numbering): N3-C4: 134.40(13), C4-C5: 138.65(14), C5-N6: 132.09(13), N6-C7: 137.18(13), C7-O7: 123.58(13) pm.*

To generate and examine anionic N-heterocyclic carbenes of **7a,b** we performed a base screening to circumvent difficulties caused by the known photochemical and thermal sensitivity of sydnone imines[66,67] as well as their tendency to undergo ring cleavages[55] or ring transformations.[68,69] The base nBuLi initiated several electrophilic attacks despite of a restricted nucleophilicity of C4 in accordance with some literature data,[70] however, rapid decomposition at elevated temperatures occurred.[71,72] We finally found that quantitative deprotonation of Molsidomine **7a** and sydnone imine **7b** to give the carbenes **8a,b** can be achieved on addition of 1M lithium bis(trimethylsilyl)amide in THF at rt (Scheme 4).



A) MeCN-d_3, rt B) 1. Se, THF, 0 °C, 1 h; 2. MeI, rt, 2h; C) 1. $(PPh_3)AuCl$, THF, -50 °C, 1 h; 2. Stirring, rt, 2 h; D) 1. $PdCl_2(PPh_3)_2$, THF, -50 °C, 1 h; 2. stirring, rt, 2 h.

Scheme 4. *Carbene generation and trapping reactions.*

Surprisingly the anionic carbenes **8a,b** proved to be stable at rt in solution under an inert atmosphere over a period of several weeks. According to the DFT calculation the lithium cation is located between the oxygen of the carbonyl group and the carbene carbon atom, and the bond distances were calculated to be 199.8 (C4-Li) and 176.8 pm (C=O-Li). Traces of water protonated the carbenes **8a,b** spontaneously to give the starting materials without any traces of decomposition products. Performing the reaction in MeCN-d_3 gave the C4-deuterated sydnone imines **7a-d$_1$** and **7b-d$_1$** in quantitative yields, respectively, which are not formed starting from **7a,b** without base even after 24 h upon warming to 50 °C under identical conditions (Scheme 4). Replacement of the lithium of the resulting anionic NHC **8a,b** to potassium by addition of KOtBu induced a spontaneous decomposition, and the same is true for deprotonations of **7a,b** by addition of 1M potassium bis(trimethylsilyl)amide in THF. The carbene carbon atoms of **8a,b** are extremely shielded, and resonance frequencies at δ = 142.1 ppm and 159.8 ppm for **8a** and **8b** were measured, respectively. These resonance frequencies set the carbenes **8a,b** apart from other π-conjugated and π-cross-conjugated NHCs and anionic NHCs mentioned before. The sydnone imine carbenes **8a,b** were then trapped by selenium followed by methylation to give the first selenium derivatives of sydnone imines **11a,b** in good yields. The chemical shifts of the C4 carbon atom were detected between δ = 98.4 ppm (**11a**) and 107.1 ppm (**11b**) in the ^{13}C NMR spectra, while ^{77}Se chemical shifts were found between δ = 97.2 ppm (**11a**) and 106.9 ppm (**11b**). Unambiguous structure elucidation was accomplished by ^{1}H,^{77}Se-HMBC measurements to exclude isomers. The sydnone imine carbenes **8a,b** were also trapped as gold complexes **12a,b** by $(PPh_3)AuCl$. The chemical shifts of the C4 carbon atom were detected between δ = 145.2 ppm (**12a**) and 156.0 ppm (**12b**) in the ^{13}C NMR spectra. The C4 ^{13}C NMR chemical shifts of the gold complexes are closely comparable to its preceding carbenes **8a,b**, however, large coupling constants for the C4 atom were observed. Thus, $^{2}J_{C4,P}$ of **12a** was measured to be 125.5 Hz. Single crystals of **12b** have been subjected to an X-ray crystal structure analysis (Fig. 3). To the best of our knowledge, gold complexes of 1,2,3-oxadiazoles have been unknown to date.

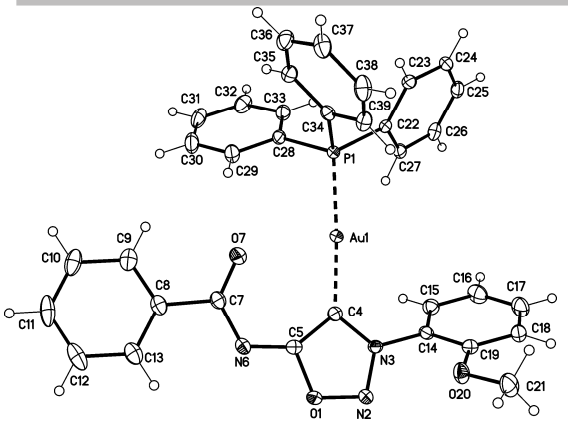


Fig. 3. *Molecular drawing of gold complex* **12b** *(displacement parameters are drawn at 50% probability level). Selected bond lengths [pm] (crystallographic numberings): O1-N2: 136.4(2), N2-N3: 132.0(2), N3-C4: 136.7(3), C4-C5: 140.3(3), C5-O1: 139.3(2), C5-N6: 132.6(3), N6-C7: 135.8(3), C7-O7: 123.4(3), Au1-C4: 203.3(2) pm.*

The sydnone imine carbenes **8a,b** were also trapped with $Pd(II)Cl_2(PPh_3)_2$ to give the trans-palladium complexes **13a,b** in moderate yields (Scheme 4). The chemical shifts of the C4 carbon atom were detected at δ = 118.0 ppm (**13a**) and 128.6 ppm (**13b**) in the ^{13}C NMR spectra. To the best of our knowledge, these are first examples of sydnone imine carbene Pd complexes. Single crystals of **13b** have been subjected to an X-ray analysis and the molecular drawing is shown in Fig. 4. In comparison to the mesomeric betaine **7b** a shortening of the N6-C7 bond (crystallographic numbering) by 4.9 pm and a prolongation of the carbonyl bond C7-O7 bond by 1.7 pm are observed.

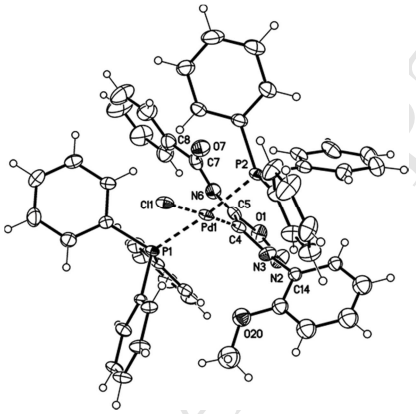
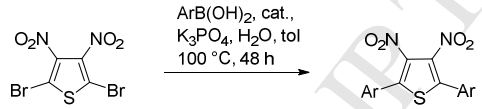


Fig. 4. *Molecular drawing of palladium complex* **13b** *(solvent and minor disordered part of the o-methoxyphenyl substituent omitted for clarity, displacement parameters are drawn at 50% probability level). Selected bond lengths [pm] (crystallographic numberings): O1-N2: 135.8(5), N2-N3: 132.4(5), N3-C4: 136.1(5), C4-C5: 140.3(5), C5-O1: 137.3(5), C5-N6: 131.7(5), N6-C7: 132.3(6), C7-O7: 125.3(5), Pd1-C4: 201.5(4) pm.*

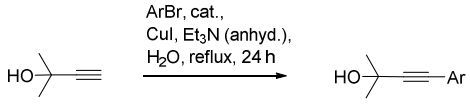
We then tested the Pd complexes **13a,b** as catalysts in Suzuki-Miyaura and Sonogashira-Hagihara cross-couplings. For the former reaction, we chose 2,5-dibromo-3,4-dinitrothiophene as starting material and performed coupling reactions with phenylboronic acid, 1-naphthylboronic acid and 2-thiophenylboronic acid (Scheme 5). Compound **14a** has been prepared before in 37% yield on employing tetrakis(triphenylphosphine) palladium(0) as the catalyst.[73] The compound **14b** has been prepared before in 80% by using N-phenylsydnone-palladium complexes as catalysts.[45,46] The yields of compound **14c** are comparable to those which are described in the literature which were achieved with bis(triphenylphosphine)-palladium(II)dichloride in THF as the solvent.[74]



14a: Ar = Ph (cat. **13a**: 77%; cat. **13b**: 62%)
14b: Ar = 1-naphth (cat. **13a**: 68%; cat. **13b**: 50%)
14c: Ar = 2-thiophen (cat **13a**: 67%; cat **13b**: 52%)

Scheme 5. *Sydnone imine Pd complexes as catalysts in Suzuki-Miyaura reactions.*

The Sonogahira-Hagihara reactions were performed starting from 2-methyl-3-butyn-2-ol which was coupled with bromobenzene, 1-bromonaphthalene and 3-bromothiophene, respectively (Scheme 6). The yields of **15a** are comparable to those described in the literature which were achieved with bis(triphenylphosphine)-palladium(II)dichloride in the presence of ammonium chloride.[75] The yields of the acetylenes **15b** were much better than in the literature,[76] although longer reaction times were required. Compound **15c** has been prepared before in 45% yield on employing bis(acetonitrile)dichloropalladium(II) as the catalyst.[77]



15a: Ar = Ph (cat **13a**: 87%; cat **13b**: 83%)
15b: Ar = 1-naphth (cat **13a**: 63%; cat **13b**: 51%)
15c: Ar = 3-thiophen (cat **13a**: 78%; cat **13b**: 69%)

Scheme 6. *Sydnone imine Pd complexes as catalysts in Sonogashira-Hagihara reactions*.

3. Conclusion

In conclusion, Molsidomine as well as the model sydnone imine form anionic N-heterocyclic carbenes on deprotonation, the ^{13}C NMR resonance frequencies of which appear at unusually high field, *i.e.* at δ = 142.1 ppm and 159.8 ppm, respectively. The carbenes gave selenium adducts, gold complexes as well as palladium complexes. The latter proved to be active as catalysts in Suzuki-Miyaura and Sonogashira-Hagihara couplings. These results supplement our knowledge on sydnones[78] and their relationship to the substance class of N-heterocyclic carbenes.[40]

Acknowledgement

Dr. Gerald Dräger, university of Hannover (Germany), is greatfully acknowledged for measuring the HR-ESI-MS spectra. The Deutsche Forschungsgemeinschaft (DFG) is gratefully acknowledged for financial support.

4. Experimental Section

General considerations. Flash-chromatography was performed with silica gel 60 (0.040-0.063 mm). Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker Avance 400 and Bruker Avance III 600 MHz. ^{1}H NMR spectra were recorded at 400 MHz or 600 MHz and ^{13}C NMR spectra were measured at 100 MHz or 150 MHz, with the solvent peak or tetramethylsilane used as the internal reference. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. Signal orientations in DEPT experiments were described as follows: o = no signal; + = up (CH, CH_3); - = down (CH_2). The numbering of the compounds is not always in accordance with IUPAC rules to allow comparisons ("spectroscopic numbering"). FT-IR spectra were obtained on a Bruker Vector 22 in the range of 400 to 4000 cm^{-1}. Melting points were measured by differential scanning calorimetry (DSC) using a DSC 6 apparatus (Perkin Elmer). The electrospray ionization mass spectra (ESIMS) were taken with an Agilent LCMSD series HP 1100 with APIES at a fragmentor voltage of 30 V unless otherwise noted. Samples were dissolved in MeOH and sprayed from MeCN at 4000 V capillary voltage. The HR-MS spectra were measured on a Bruker Daltonik Tesla-Fourier transform - ion cyclotron resonance mass spectrometer with electrospray ionisation. Yields are not optimized.

Crystal Structure Determinations. The single-crystal X-ray diffraction study was carried out on a Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Cu-Kα radiation (λ = 1.54178 Å) (**7b**) or Mo-Kα radiation (λ = 0.71073 Å) (**12b**, **13b**). Direct Methods (**7b**) or Patterson Methods (**12b**, **13b**) (SHELXS-97)[79] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2).[80] Hydrogen atoms were localized by difference electron density determination and refined using a riding. Semi-empirical absorption corrections and extinction correction were applied. In **13b** the *o*-methoxyphenyl substituent is disordered (see cif-file for details).

7b: yellow crystals, $C_{16}H_{13}N_3O_3$, M = 295.29, crystal size 0.45 × 0.35 × 0.30 mm, orthorhombic, space group Pbca (no. 61), a = 11.4610 (3) Å, b = 11.3954 (3) Å, c = 21.6786 (6) Å, V = 2831.28 (13) Å^3, Z = 8, ρ(calc) = 1.386 Mg m^{-3}, F(000) = 1232, μ(MoKα) = 0.81 mm^{-1}, 20087 reflections (θ_{max} = 72.2°), 2781 unique [R_{int} = 0.024], 201 parameters, R1 (for 2668 I > 2σ(I)) = 0.032, wR2 (all data) = 0.081, S = 1.05, largest diff. peak and hole 0.23 and -0.20 e Å^{-3}.
12b: colorless crystals, $C_{34}H_{27}AuN_3O_3P$, M = 753.52, crystal size 0.28 × 0.22 × 0.18 mm, monoclinic, space group P21/n (no. 14), a = 13.2351 (6) Å, b = 14.9811 (7) Å, c = 15.3479 (8) Å, β = 106.184 (2)°, V = 2922.5 (2) Å^3, Z = 4, ρ(calc) = 1.713 Mg m^{-3}, F(000) = 1480, μ(MoKα) = 5.13 mm^{-1}, 65092 reflections (θ_{max} = 27.5°), 6714 unique [R_{int} = 0.029], 381 parameters, R1 (for 6191 I > 2σ(I)) = 0.017, wR2 (all data) = 0.039, S = 1.19, largest diff. peak and hole 1.21 and -0.64 e Å^{-3}.
13b: yellow crystals, $C_{52}H_{42}ClN_3O_3P_2Pd\cdot CH_2Cl_2$, M = 1045.60, crystal size 0.20 × 0.14 × 0.08 mm, monoclinic, space group P21/c (no. 14), a = 17.0717 (7) Å, b = 13.6507 (6) Å, c = 21.5274 (8) Å, β = 108.203 (1)°, V = 4765.7 (3) Å^3, Z = 4, ρ(calc) = 1.457 Mg m^{-3}, F(000) = 2136, μ(CuKα) = 0.67 mm^{-1}, 135804 reflections (θ_{max} = 27.6°), 10975 unique [R_{int} = 0.066], 550 parameters, 22 restraint, R1 (for 8653 I > 2σ(I)) = 0.055, wR2 (all data) = 0.137, S = 1.06, largest diff. peak and hole 1.95 and -1.55 e Å^{-3}.
CCDC 1541425 (**7b**), CCDC 1541426 (**12b**), and CCDC 1541427 (**14b**) 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.

Calculations. All density-functional theory (DFT)-calculations were carried out by using the current Spartan Software (Spartan'16, Wavefunction, Inc., Irvine, CA. Available from: http://www.wavefun.com) running on an Intel® CoreTM i7-6950X deca-core system equipped with 64 GB RAM main memory and sufficient solid-state disc space. MMFF optimized structures were used as starting geometries. Then, the B3LYP density functional and the 6-31G(d,p) basis set was used in order to allow for comparison with previous results.[63] All final structures were proven to be true minima by the absence of imaginary frequencies or transition states by the occurrence of a negative frequency.

Synthesis of sydnone imine 7b.

N-(o-Methoxyphenyl)-aminoacetonitrile. 2-Methoxyaniline (5.00 g, 40.6 mmol), bromoacetonitrile (5.84 g, 48.7 mmol), sodium acetate trihydrate (6.63 g, 48.7 mmol) and 30 mL of EtOH were mixed in a 100 mL flask equipped with a reflux condenser. The mixture was heated to 80 °C and stirred for 24 h. Afterwards the cooled mixture was poured into 250 mL of iced water. The aqueous phase was extracted three times with DCM. Then the combined organic phases were dried over $MgSO_4$ and the solvent was evaporated *in vacuo*. The product was purified by recrystallization from EtOH. Yield: 5.46 (83 %) of a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.93-6.97 (m, 1H, 3-H), 6.83-6.85 (m, 2H, 4/5-H), 6.70-6.72 (m, 1H, 2-H), 4.57 (br. s, 1H, 9-H), 4.15 (d, 2H, $^{3}J_{H,H}$ = 7.0 Hz, 10-H), 3.86 (s, 3H, 8-H) ppm. Spectroscopic data are in agreement with those reported in the literature.[81]

N-(o-Methoxyphenyl)-N-nitrosoaminoacetonitrile (**10**). Into a 250 mL flask N-(o-methoxyphenyl)-aminoacetonitrile (10.60 g, 65.4 mmol) and 50 mL of hydrochloric acid (12.5 %) were given and cooled to 0 °C. To this suspension a solution of sodium nitrite (6.76 g, 98.0 mmol) in 10 mL water was added slowly. After 30 min of stirring at 0°C 50 mL of Et_2O were added and the mixture was stirred for an additional 1.5 h at that temperature. After warming to rt, additional 50 mL of Et_2O were added. The two phases were separated and the aqueous layer was extracted three times with DCM. The combined organic phases were dried over $MgSO_4$, the solvent was evaporated *in vacuo* and the resulting solid was purified by recrystallization from EtOH. Yield: 11.51 g (92 %) of a brown solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45-7.53 (m, 2H, 3/5-H), 7.08-7.14 (m, 2H, 2/4-H), 4.66 (s, 2H, 10-H), 3.93 (s, 3H, 8-H) ppm. The compound is known from the literature (without comparable NMR-spectra).[64]

N-(o-Methoxyphenyl)-sydnonimine hydrochloride. Into a suspension of N-(o-methoxyphenyl)-N-nitrosoaminoacetonitrile (4.73 g, 24.7 mmol) in 30 mL Et_2O (abs.) in a two-necked flask, gaseous hydrochloric acid was passed for 3 h. The reaction temperature was held at 20 °C. At the bottom layer of the flask the formation of black oil was observed. After separation of the layers, the black oil was washed three times with Et_2O and dried *in vacuo*. A solid could only be obtained after several hours of drying *in vacuo*. Adding any solvent other then Et_2O immediately resulted in the formation of an oily compound again. Therefore further purification was not possible. Yield: 5.580 (99 %, crude product) of a dark brown solid. ^{1}H NMR (400 MHz, DMSO-d_6): δ = 10.15 (s, 2H, 6-H), 8.38 (s, 1H, 4-H), 7.73-7.80 (m, 2H, 10/12-H), 7.45-7.49 (m, 1H, 9-H), 7.21-7.25 (m, 1H, 11-H), 3.91 (s, 3H, 14-H) ppm. The compound is known from the literature (without comparable NMR-spectra).[64]

N3-(o-Methoxyphenyl)-N6-benzoylsydnone imine (7b). Benzoyl chloride (1.10 mL, 9.49 mmol) was added to a solution of N-(o-methoxyphenyl)-sydnonimine hydrochloride (1.80 g, 7.91 mmol) in 15 mL of DCM (abs.) in a 50 mL flask. The solution was cooled to -10 °C and triethylamine (2.65 mL, 18.98 mmol) in 5 mL DCM (abs.) was added dropwise. The mixture was stirred for 1 h at the same temperature, then warmed to rt and stirred for another 16 h. Afterwards 100 mL of water were added. The aqueous layer was extracted three times with DCM. The combined organic layers were dried over $MgSO_4$ and the solvent was evaporated *in vacuo*. Purification was achieved by column chromatography (silica gel, DCM : MeOH = 40 : 1). Yield: 1.86 g (80 %) of a brown solid, mp: 199 °C (decomposition). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.54 (s, 1H, 4-H), 8.30-8.32 (m, 2H, 9/9'-H), 7.63-7.69 (m, 2H, 15/17-H), 7.47-7.51 (m, 1H, 11-H), 7.42-7.45 (m, 2H, 10/10'-H), 7.16-7.21 (m, 2H, 14/16-H), 3.97 (s, 3H, 19-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.3 (o, C5), 174.1 (o, C7), 152.3 (o, C13), 137.2 (o, C8), 134.1 (+, C15), 131.4 (+, C11), 129.4 (+, C9/C9'), 128.0 (+, C10/C10'), 125.6 (+, C17), 122.7 (o, C12), 121.3 (+, C16), 113.0 (+, C14), 108.9 (+, C4), 56.4 (+, C19) ppm; ^{15}N NMR (60 MHz, CDCl3): δ = -29.6 (N6), -104.7 (N3), -202.7 (N2) ppm; IR (ATR): 3151, 3054, 2838, 1613, 1577, 1548, 1501, 1354, 1318, 1286, 1262, 1211, 1165, 1022, 957, 929, 858, 750, 707, 674 cm^{-1}; MS (ESI 30 V) *m/z* (%) = 296.0 (80) [M+H$^+$], 318.1 (100) [M+Na$^+$], 613.2 (79) [2M+Na$^+$]. HR-ESI-MS: calcd for $C_{16}H_{14}N_3O_3^+$ 296.1035. Found 296.1032 (100%).

4-Lithiomolsidomine (8a). In an NMR tube a dry sample of Molsidomine (0.022 g, 0.091 mmol) was dissolved in 0.4 mL of anhydrous THF-d_8 under an inert atmosphere. Then a 1M solution of LHMDS in THF (0.109 mL, 0.109 mmol) was added to give the lithium adduct in quantitative yields. ^{1}H NMR (600 MHz, THF-d_8): δ = 4.07 (q, $J_{H,H}$ = 7.1 Hz, 2H, 9-H), 3.78 (t, $J_{H,H}$ = 4.6 Hz, 4H, 13/13'-H), 3.37 (t, $J_{H,H}$ = 4.6 Hz, 4H, 12/12'-H), 1.17 (t, $J_{H,H}$ = 7.1 Hz, 3H, 10-H) ppm; ^{13}C NMR (150 MHz, THF-d_8): δ = 185.4 (o, C5), 162.9 (o, C7), 142.1 (o, C4), 66.7 (- , C13/C13'), 61.5 (-, C9), 56.2 (-, C12/C12'), 15.3 (+, C10) ppm.

4-Lithio-N3-(o-methoxyphenyl)-N6-benzoylsydnonimine (8b). In an NMR tube a dry sample of N3-(o-methoxyphenyl)-N6-benzoylsydnonimine (0.022 g, 0.075 mmol) was dissolved in 0.4 mL of anhydrous THF-d_8 under an inert atmosphere. Then a 1M solution of LHMDS in THF (0.089 mL, 0.089 mmol) was added to give the lithium adduct in quantitative yields. ^{1}H NMR (600 MHz, THF-d_8): δ = 8.25-8.24 (m, 2H, 9/9'-H), 7.48-7.51 (m, 1H, 15-H), 7.46-7.47 (m, 1H, 17-H), 7.22-7.25 (m, 1H, 11-H), 7.19-7.20 (m, 1H, 14-H), 7.13-7.16 (m, 2H, 10/10'-H), 7.05-7.07 (m, 1H, 16-H), 3.73 (s, 3H, 19-H) ppm. ^{13}C NMR (150 MHz, THF-d_8): δ = 185.4 (o, C5), 170.4 (o, C7), 159.8 (o, C4), 154.9 (o, C13), 140.8 (o, C8), 131.8 (+, C15), 130.8 (o, C12), 130.1 (+, C11), 129.8 (+, C9/C9'), 128.2 (+, C17), 127.9 (+, C10/C10'), 121.0 (+, C16), 113.4 (+, C14), 56.1 (+, C19) ppm.

4-(Methylseleno)-molsidomine (11a). Under an inert atmosphere Molsidomine (0.24 g, 1.00 mmol) was dissolved in 15 mL of THF (abs.). Then a 1M solution of LHMDS in THF (1.20 mL, 1.20 mmol) was added and the mixture was cooled to 0 °C. Selenium (0.10 g, 1.20 mmol) was added and the mixture was stirred for 0.5 h. Then iodomethane (0.08 mL, 1.20 mmol) was added. The mixture was stirred for an additional 0.5 h at 0 °C, then slowly warmed to rt and stirred for another 2 h. Afterwards the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (DCM:MeOH 25:1). Yield: 0.282 g (84 %) of a brownish solid, mp: 212 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.17 (q, $J_{H,H}$ = 7.1 Hz, 2H, 9-H), 3.94 (t, $J_{H,H}$ = 4.5 Hz, 4H, 13/13'-H), 3.49 (t, $J_{H,H}$ = 4.5 Hz, 4H, 12/12'-H), 2.39 (s, 16-H), 1.29 (t, $J_{H,H}$ = 7.1 Hz, 3H, 10-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 186.6 (o, C5), 159.5 (o, C7), 98.4 (o, C4), 66.0 (- , C13/C13'), 61.3 (-, C9), 55.3 (-, C12/C12'), 14.5 (+, C10), 7.9 (+, C16) ppm; ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 97.2 (s) ppm; IR (ATR): 2972, 2932, 2900, 2858, 1662, 1592, 1405, 1371, 1198, 1146, 1100, 1056, 1042, 1024, 934, 882, 791 cm-1; MS (ESI 10 V) *m/z* (%) = 337.0 (100) [M+H$^+$], 359.0 (40) [M+Na$^+$], 695.0 (100) [2M+Na$^+$]. HR-ESI-MS: calcd for $C_{10}H_{17}N_4O_4Se^+$ 337.0415. Found 337.0414.

4-(Methylseleno)-N3-(o-methoxyphenyl)-N6-benzoylsydnonimine (11b). Under an inert atmosphere N3-(o-methoxyphenyl)-N6-benzoylsydnonimine (0.30 g, 1.00 mmol) was dissolved in 15 mL of THF (abs.). Then a 1M solution of LHMDS in THF (1.20 mL, 1.20 mmol) was added and the mixture was cooled to 0 °C. Selenium (0.10 g, 1.20 mmol) was added and the mixture was stirred for 0.5 h. Then iodomethane (0.08 mL, 1.20 mmol) was added. The mixture was stirred for an additional 0.5 h at 0 °C, then slowly warmed to rt and stirred for another 2 h. Afterwards the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (DCM:MeOH 40:1). Yield: 0.255 g (66 %) of a brownish solid, mp: 240 °C (decomposition); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.32-8.35 (m, 2H, 9/9'-H), 7.64-7.69 (m, 1H, 15-H), 7.47-7.51 (m, 1H, 11-H), 7.41-7.45 (m, 3H, 10/10'/17-H), 7.17-7.21 (m, 1H, 16-H), 7.15-7.17 (m, 1H, 14-H), 3.90 (s, 3H, 19-H), 2.38 (s, 3H, 21-H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 172.8 (o, C7), 168.8 (o, C5), 153.3 (o, C13), 137.5 (o, C8), 134.0 (+, C15), 131.3 (+, C11), 129.6 (+, C9/C9'), 127.9 (+, C10/C10'), 127.0 (+, C17), 122.5 (o, C12), 121.1 (+, C16), 112.5 (+, C14), 107.1 (+, C4), 56.1 (+, C19), 7.4 (+, C21) ppm; ^{77}Se NMR (114 MHz, $CDCl_3$): δ = 106.9 (s) ppm; IR (ATR): 3056, 2930, 2841, 1553, 1498, 1339, 1311, 1284, 1254, 1207, 1160, 1014, 978, 753, 704, 684 cm^{-1}; MS (ESI 30 V) *m/z* (%) = 390.0 (100) [M+H$^+$], 799.2 (40) [2M+Na$^+$]; HR-ESI-MS: calcd for $C_{17}H_{16}N_3O_3Se^+$ 390.0356. Found 390.0357.

(N3-Morpholinyl-N6-ethoxycarbonyl-sydnonimine-4-yl)-(triphenylphosphine)-gold(I) (12a). Under an inert atmosphere Molsidomine (0.028 g, 0.118 mmol) was dissolved in 10 mL of THF (abs.). Then a 1M solution of LHMDS in THF (0.141 mL, 0.141 mmol) was added and the mixture was cooled to -50 °C. After adding chloro(triphenylphosphine)gold(I) (0.064 g, 0.129 mmol) the mixture was stirred for 1 h, then slowly warmed to rt and stirred for another 2 h. Afterwards the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (EE:PE 3:1). Yield: 0.041 g (50 %) of a colorless solid, mp: 244 °C (decomposition); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62-7.66 (m, 3x2H, 16/16'-H), 7.52-7.55 (m, 3x1H, 18-H), 7.47-7.50 (m, 3x2H, 17/17'-H), 4.14 (q, $J_{H,H}$ = 7.1 Hz, 2H, 9-H), 3.83 (t, $J_{H,H}$ = 4.5 Hz, 4H, 13/13'-H), 4.64 (t, $J_{H,H}$ = 4.5 Hz, 4H, 12/12'-H), 1.27 (t, $J_{H,H}$ = 7.1 Hz, 3H, 10-H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 180.8 (o, d, $^3J_{C,P}$ = 4.0 Hz, C5), 160.9 (o, C7), 145.2 (o, d, $^2J_{C,P}$ = 125.5 Hz, C4), 134.3 (+, d, $^2J_{C,P}$ = 14.0 Hz, C16/C16'), 130.6 (+, C18), 129.8 (o, d, $^1J_{C,P}$ = 56.0 Hz, C15), 129.1 (+, d, $^3J_{C,P}$ = 11.5 Hz, C17/C17'), 66.3 (-, C13/C13'), 60.4 (-, C9), 55.8 (-, C12/C12'), 14.7 (+, C10) ppm; ^{31}P NMR (243 MHz, $CDCl_3$): δ = 40.4 (s) ppm; IR (ATR): 2972, 2922, 2894, 2855, 1631, 1553, 1435, 1283, 1247, 1193, 1100, 1062, 1039, 893, 751, 692, 536, 504 cm^{-1}; MS (ESI 10 V) *m/z* (%) = 701.2 (100) [M+H+]; HR-ESI-MS: calcd for $C_{27}H_{29}N_4O_4PAu^+$ 701.1592. Found 701.1592.

(N3-(o-Methoxyphenyl)-N6-benzoylsydnonimine-4-yl)-(triphenylphosphine)-gold(I) (12b). Under an inert atmosphere N3-(o-methoxyphenyl)-N6-benzoylsydnonimine (0.054 g, 0.184 mmol) was dissolved in 10 mL of THF (abs.). Then a 1M solution of LHMDS in THF (0.22 mL, 0.221 mmol) was added and the mixture was cooled to -50 °C. After adding chloro(triphenylphosphine)gold(I) (0.100 g, 0.202 mmol) the mixture was stirred for 1 h, then slowly warmed to rt and stirred for another 2 h. Afterwards the solvent was evaporated *in vacuo*. The crude product is purified by column chromatography (EE:PE = 3:1). Yield: 0.119 g (86 %) of a yellow solid, mp: 248 °C (decomposition); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.35-8.37 (m, 2H, 9/9'-H), 7.57-7.58 (m, 1H, 17-H), 7.45-7.53 (m, 3x2H+3x1H+1H, 21/21'/23/15-H), 7.34-7.37 (m, 2H, 10/10'-H), 7.38-7.43 (m, 3x2H+2H+1H, 22/22'/10/10'/11-H), 7.04-7.07 (m, 1H, 16-H), 7.00-7.01 (m, 1H, 14-H), 3.70 (s, 3H, 19-H) ppm; ^{13}C NMR (150 MHz, $CDCl_3$): δ = 180.0 (o, d, $^3J_{C,P}$ = 7.6 Hz, C5), 172.0 (o, C7), 156.0 (o, d, $^2J_{C,P}$ = 126.5 Hz, C4), 153.8 (o, C13), 139.4 (o, C8), 134.3 (+, d, $^2J_{C,P}$ = 14.2 Hz, C21/C21'), 132.1 (+, C15), 131.3 (+, C23), 130.2 (+, C11), 130.1 (o, d, $^1J_{C,P}$ = 55.6 Hz, C20), 129.2 (+, C9/C9'), 128.9 (+, d, $^3J_{C,P}$ = 11.3 Hz, C22/C22'), 127.9 (o, C12), 127.8 (+, C17), 127.6 (+, C10/C10'), 120.2 (+, C16), 112.3 (+, C14), 55.9 (+, C19) ppm; ^{31}P NMR (243 MHz, $CDCl_3$): δ = 40.1 (s) ppm; IR (ATR): 3051, 3018, 2963, 2839, 1596, 1563, 1498, 1435, 1335, 1282, 1254, 1099, 1022, 847, 746, 709, 690, 675, 536, 500 cm^{-1}; MS (ESI 10 V) *m/z* (%) = 754.2 (100) [M+H+]; HR-ESI-MS: calcd for $C_{34}H_{28}N_3O_3PAu^+$ 754.1534. Found 754.1533.

trans-Chloro-(N3-morpholinyl-N6-ethylester-sydnonimine-4-yl)-bis-(triphenylphosphine)-palladium(II) (13a). Under an inert atmosphere Molsidomine (0.08 g, 0.33 mmol) was dissolved in 10 mL of THF (abs.). Then a 1M solution of LHMDS in THF (0.40 mL, 0.40 mmol) was added and the mixture was cooled to -50 °C. After adding bis(triphenylphosphine)palladium(II) dichloride (0.26 g, 0.36 mmol) the mixture was stirred for 1 h, then slowly warmed to rt and stirred for another 2 h. Afterwards the solvent was evaporated in vacuo. The crude product was purified by column chromatography (1. EE:PE = 3:1, 2. DCM:MeOH = 15:1). Yield: 0.211 g (70 %) of a yellow solid, mp: 197 °C (decomposition); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.62-7.65 (m, 6x2H, 15/15'-H), 7.40-7.43 (m, 6x1H, 17-H), 7.33-7.36 (m, 6x2H, 16/16'-H), 3.95 (q, $J_{H,H}$ = 7.1 Hz, 2H, 9-H), 3.69 (t, $J_{H,H}$ = 4.5 Hz, 4H, 13/13'-H), 2.76 (t, $J_{H,H}$ = 4.5 Hz, 4H, 12/12'-H), 1.18 (t, $J_{H,H}$ = 7.1 Hz, 3H, 10-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 174.8 (o, C5), 159.5 (o, C7), 134.7 (+, t, $^2J_{C,P}$ = 6.0 Hz, C15/C15'), 130.6 (+, C17), 130.2 (o, t, $^1J_{C,P}$ = 24.0 Hz, C14), 128.0 (+, t, $^3J_{C,P}$ = 5.3 Hz, C16/C16'), 118.0 (o, t, $^2J_{C,P}$ = 8.2 Hz, C4), 65.9 (-, C13/C13'), 60.2 (-, C9), 55.1 (-, C12/C12'), 14.8 (+, C10) ppm. ^{31}P NMR (243 MHz, $CDCl_3$): δ = 21.0 (s, trans) ppm; traces of solvent are visible in the spectra. IR (ATR): 3053, 2969, 2859, 1631, 1541, 1481, 1434, 1280, 1237, 1176, 1094, 1061, 1040, 887, 743, 690, 509 cm^{-1}; MS (ESI 0 V) *m/z* (%) = 907.3 (100) [M+H$^+$]. HR-ESI-MS: calcd for $C_{45}H_{44}N_4O_4P_2PdCl^+$ 907.1561. Found 907.1559.

trans-Chloro-(N3-(o-methoxyphenyl)-N6-benzoylsydnonimine-4-yl)-bis-(triphenylphosphine)-palladium(II) (14b). Under an inert atmosphere N3-(o-methoxyphenyl)-N6-benzoylsydnonimine (0.08 g, 0.28 mmol) was dissolved in 10 mL of THF (abs.). Then a 1M solution of LHMDS in THF (0.33 mL, 0.33 mmol) was added and the mixture was cooled to -50 °C. After adding bis(triphenylphosphine)palladium(II) dichloride (0.21 g, 0.31 mmol) the mixture was stirred for 1 h, then slowly warmed to rt and stirred for another 2 h. Afterwards the solvent was evaporated *in vacuo*. The crude product was purified by column chromatography (EE:PE = 3:1). Yield: 0.143 g (54%) of a yellow solid, mp: 212 °C (decomposition); ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.07-8.09 (m, 2H, 9/9'-H), 7.55-7.52 (m, 1H, 15-H), 7.46-7.49 (m, 6x2H, 21/21'-H), 7.40-7.42 (m, 6x1H+1x2H, 23/11-H), 7.34-7.37 (m, 2H, 10/10'-H), 7.26-7.29 (m, 6x2H, 22/22'-H), 6.98-7.00 (m, 1H, 14-H), 6.75-6.78 (m, 1H, 16-H), 6.24-6.26 (m, 1H, 17-H), 3.13 (s, 3H, 19-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 173.2 (o, t, $^3J_{C,P}$ = 3.3 Hz, C5), 170.7 (o, C7), 153.8 (o, C13), 139.5 (o, C8), 134.4 (+, t, $^2J_{C,P}$ = 6.3 Hz, C21/C21'), 132.2 (+, C15), 130.5 (+, C23), 130.0 (o, t, 1JC,P = 24.5 Hz, C20), 129.8 (+, C11), 128.6 (+, C9/C9'), 128.6 (o, t, $^2J_{C,P}$ = 7.8 Hz, C4), 128.4 (+, C17), 128.2 (+, t, $^3J_{C,P}$ = 5.0 Hz, C22/C22'), 127.3 (+, C10/C10') 125.8 (o, C12), 120.2 (+, C16), 112.4 (+, C14), 55.5 (+, C19) ppm; ^{31}P NMR (243 MHz, $CDCl_3$): δ = 20.8 (s, trans) ppm; traces of solvents are visible in the spectra. IR (ATR): 3052, 2962, 1597, 1537, 1501, 1433, 1334, 1259, 1093, 1013, 798, 744, 690, 518 cm^{-1}; MS (ESI 0 V) *m/z* (%) = 662.0 (100) [M-PPh$_3$-Cl$^-$], 960.2 (30) [M+H$^+$]. HR-ESI-MS: calcd for $C_{52}H_{43}N_3O_3P_2PdCl^+$ 960.1503. Found 960.1503.

General procedure for the preparation of the compounds 14a-c.

Under a nitrogen atmosphere a sample of 2,5-dibromo-3,4-dinitrothiophene (0.075 g, 0.2 mmol) was dissolved in 8 mL of anhydrous toluene and treated with 10 mol% of the catalyst (complexes **13a,b**). The mixture was then

subjected to ultrasound irradiation for 5 min and then stirred at room temperature for additional 25 min. Then, two equivalents of the corresponding boronic acid, potassium phosphate (0.318 g, 1.5 mmol) and 2 mL of water were added. The mixture was heated under reflux at 100 °C for 48 h. After cooling at room temperature, the mixture was dried over magnesium sulfate. The resulting crude products were purified by column chromatography over silica gel using a PE:DCM (1:3) mixture as eluent.

2,5-Diphenyl-3,4-dinitrothiophene (14a). A sample phenylboronic acid (0.110 g, 0.1 mmol) was used. The product was isolated as a yellowish solid. Yield 0.057 g (77%) by using complex **13a** and 0.046 g (62%) by using complex **13b** as the catalyst. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.52-7.60 (m, 10H) ppm. Spectroscopic data are in agreement with those reported in the literature.[82]

2,5-Bis(naphthalen-1-yl)-3,4-dinitrothiophene (14b). A sample 1-naphthylboronic acid (0.102 g, 0.1 mmol) was used. The product was isolated as a yellowish solid. Yield 0.065 g (68%) by using complex **13a** and 0.048 g (50%) by using complex **13b** as the catalyst. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.48-7.55 (m, 6H), 7.59-7.61 (d, $J_{H,H}$ = 7.8 Hz, 2H), 7.73-7.75 (m, 2H), 7.88-7.90 (m, 2H), 7.96-7.98 (d, J = 7.8 Hz, 2H) ppm. Spectroscopic data are in agreement with those reported in the literature.[45]

3',4'-Dinitro-2,2':5',2''-terthiophene (14c). A sample 3-thiophenylboronic acid (0.115 g, 0.1 mmol) was used. The product was isolated as a yellowish solid. Yield 0.051 g (67%) by using complex **13a** and 0.040 g (52%) by using complex **13b** as the catalyst. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18 (dd, J = 3.6, 5.2 Hz, 2H), 7.55 (dd, $J_{H,H}$ = 1.2, 3.6 Hz, 2H), 7.61 (dd, $J_{H,H}$ = 1.2, 5.2 Hz, 2H) ppm. Spectroscopic data are in agreement with those reported in the literature.[45]

General procedure for the preparation of the compounds 15a-c.

Under a nitrogen atmosphere 2.5 mmol of the arylhalogenides were dissolved in 15 mL of anhydrous triethylamine and treated with 1 mol% of the catalyst (complexes **13a,b**) and copper-(I)-iodide (0.015 g, 0.07 mmol). After the addition of the catalysts, 1.2 eq of 2-methyl-3-butyn-2-ol (0.25 g, 3 mmol) were slowly added dropwise. Then the reaction mixture was stirred under reflux for 48 h. After cooling down at room temperature, water was added. The mixture was extracted with dichloromethane and dried over magnesium sulfate. The resulting crude products were purified by column chromatography over silica gel (40-60 mesh) using PE:EE (2:1) mixture as eluent.

2-Methyl-4-phenylbut-3-yn-2-ol (15a). A sample of bromobenzene (0.393 g, 2.5 mmol) was used. The product was isolated as a brown solid. Yield 0.414 g (87%) by using complex **13a** and 0.395 g (83%) by using complex **13b** as the catalyst. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.62 (s, 6H), 1.99 (s, 1H, OH), 7.29-7.32 (m, 3H), 7.40-7.43 (m, 1H) ppm. Spectroscopic data are in agreement with those reported in the literature.[83]

2-Methyl-4-(naphthylen-1-yl)but-3-yn-2-ol (15b). A sample of 1-bromonaphthalene (0.517 g, 2.5 mmol) was used. The product was isolated as a brown solid. Yield of 0.393 g (63%) by using complex **13a** and 0.318 g (51%) by using complex **13b** as the catalyst. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.71 (s, 6H), 2.72 (s, 1H, OH), 7.33-7.36 (m, 1H), 7.44-7.48 (m, 1H), 7.52-7.55 (m, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.74-7.80 (m, 2H), 8.28 (d, J = 7.8 Hz, 1H) ppm. Spectroscopic data are in agreement with those reported in the literature.[84]

2-Methyl-4-(thiophen-3-yl)but-3-yn-2-ol (15c). A sample of of 3-bromothiophene (0.408 g, 2.5 mmol) was used. The product was isolated as a brown solid. Yield 0.385 g (78%) by using complex **13a** and 0.341 g (69%) by using complex **13b** as the catalyst. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.53 (s, 6H), 2.19 (s, 1H, OH), 7.01 (d, $J_{H,H}$ = 7.8 Hz, 1H), 7.15-7.18 (m, 1H), 7.33 (d, $J_{H,H}$ = 7.8 Hz, 1H) ppm. Spectroscopic data are in agreement with those reported in the literature.[85]

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