

# Synthesis of a Pyrazol-3-ylidene Palladium Complex, Pyrazolium Salts and Mesomeric Betaines of Pyrazole as *N*-Heterocyclic Carbene Precursors

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The synthesis of a pyrazol-3-ylidene palladium complex is described, and results of a single-crystal X-ray diffraction study are presented. The properties of pyrazolium salts as well as of two types of heterocyclic mesomeric betaines, the pseudo-cross-conjugated mesomeric betaine pyrazolium-3-carboxylate and its cross-conjugated analog pyrazolium-4-carboxylate, are compared.

**Key words:** NHC, Pyrazol-4-ylidene, NHC Complex, Decarboxylation, X-Ray Structure, CCMB, PCCMB

## Introduction

The iminium as well as the iminium-2-carboxylate partial structures **I** and **II** of heterocycles and heteroaromatics can serve as *N*-heterocyclic carbene precursors, when deprotonation of **I** or decarboxylation of **II** are performed, respectively (Fig. 1). Thus, imidazolium- [1–4], pyridinium- [5, 6], quinolinium- [7, 8], pyrazolium- [9–12], indazolium- [12–15], and other hetarenium-carboxylates undergo decarboxylation to *N*-heterocyclic carbenes which can be trapped *in situ* or examined spectroscopically. Conversely, it is well-known that NHCs can be trapped with heterocumul-

enes such as carbon dioxide [16–18]. By contrast, the prop-2-en-1-iminium moiety **III** and the 2-(iminomethyl)acrylate partial structure **IV** are building blocks of precursors of remote *N*-heterocyclic carbenes (*r*NHC) [19–21] which are set apart from the class of abnormal *N*-heterocyclic carbenes (*a*NHC) [22–24]. Deprotonations and decarboxylations from partial structures **III** and **IV**, however, are seemingly limited to a quite small number of suited substrates. Thus, only few examples of deprotonations of substituted pyrazolium salts have been reported to date [25]. Imidazol-4-ylidenes, members of the class of abnormal NHCs, have been obtained by decarboxylation of imidazolium-4-carboxylates [3].

*N*-Heterocyclic carbenes of pyrazole and of its relative, indazole, have so far stood in the shadow of the impressive development of pyrazole [26, 27] and indazole chemistry [28] taking place during the last decade. However, some very interesting structures and applications have been published recently. As outlined in Fig. 2, two types of *N*-heterocyclic carbenes of pyrazole can be differentiated, the NHC pyrazol-3-ylidene **V** – which can be represented by a zwitterionic canonical formula and by an electron sextet structure –

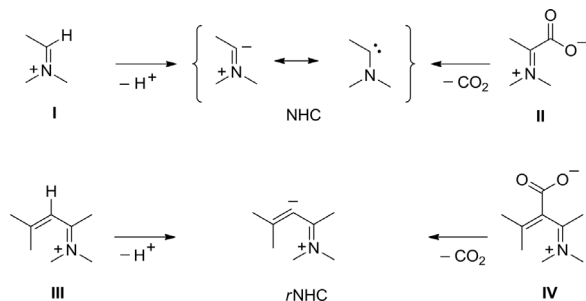


Fig. 1.

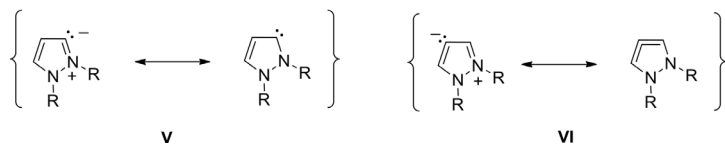


Fig. 2.

and pyrazol-4-ylidene **VI**. The carbenoid C atom of the latter is not adjacent to the N atoms, and it cannot be represented by electron sextet structures. Therefore, it has been referred to as remote *N*-heterocyclic carbene (*r*NHC) [22–24], cyclic bent allene [25], or aromatic zwitterion [29].

Several pyrazol-3-ylidene complexes have been described, the structures of which are summarized in a recent review on pyrazole chemistry [27]. Palladium pyrazol-3-ylidene complexes have been obtained by oxidative addition of 3-chlorotetramethylpyrazolium chloride and 3-chloro-1,5-dimethyl-2,4-diphenylpyrazolium chloride to a palladium(0) complex [30]. Likewise, oxidative addition of suited ligand precursors to  $[\text{Pd}_2(\text{dba})_3]/\text{PPh}_3$  led to  $\text{Pd}^{\text{II}}$ (pyrazol-4-ylidene) complexes [24, 31]. The ligand donor strength of pyrazol-3-ylidene and pyrazol-4-ylidene has been determined by  $^{13}\text{C}$  NMR spectroscopy [32]. In continuation of our studies of heterocyclic mesomeric betaines [33, 34], zwitterions [35, 36], *N*-heterocyclic carbenes [37–39], and the chemistry of organic polycations [40], we describe here the synthesis of a new pyrazol-3-ylidene palladium complex, as well as new aspects of the syntheses and properties of pyrazolium salts and pyrazolium-3- and -4-carboxylates as potential *N*-heterocyclic carbene precursors.

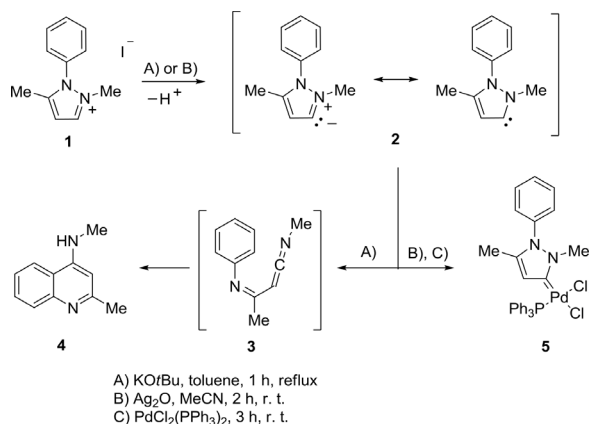
## Results and Discussion

Deprotonation of the pyrazolium salt **1**, obtained by methylation of pyrazole with methyl iodide in THF according to known procedures [41, 42], gives the *N*-heterocyclic carbene pyrazol-3-ylidene **2** *in situ* (Scheme 1). This NHC can be detected as the sodium adduct in electrospray ionization mass spectrometric measurements at  $m/z = 195.1$ ,  $[\text{M}+\text{Na}]^+$  [11, 12]. When  $\text{KO}t\text{Bu}$  is employed as base, and toluene is used as the solvent to remove the stabilizing water of crystallization by azeotropic distillation, a sequence of ring cleavage,  $6\pi$ -electrocyclization of **3** and subsequent tautomerization occurs to result in the formation of 4-aminoquinoline **4** [10]. As already shown, this reaction is applicable to a broad variety of pyrazolium salts to accomplish syntheses of new substituted quinolines [11]. When the salt was dissolved in anhydrous acetonitrile and treated with silver oxide at 20 °C, followed by the addition of bis(triphenylphosphine)palladium(II) chloride, the palladium complex **5** was isolated in 51 % yield. The carbene carbon atom appears at  $\delta = 165.6$  ppm in the  $^{13}\text{C}$  NMR spectrum, slightly more downfield than that of the com-

Table 1. Crystal structure data for the Pd complex **5** ·  $\text{CHCl}_3$  ·  $1/6 \text{H}_2\text{O}$ .

Formula	$\text{C}_{29}\text{H}_{27}\text{Cl}_2\text{N}_2\text{PPd} \cdot \text{CHCl}_3 \cdot 1/6 \text{H}_2\text{O}$
$M_r$	734.17
Crystal size, $\text{mm}^3$	$0.24 \times 0.16 \times 0.08$
$T$ , K	123(2)
Crystal system	trigonal
Space group	$R\bar{3}$ (no. 148)
$a = b$ , Å	38.704(3)
$c$ , Å	10.732(1)
$V$ , Å <sup>3</sup>	13923(2)
$Z$	18
$D_{\text{calc}}$ , $\text{g cm}^{-3}$	1.58
$\mu(\text{MoK}\alpha)$ , $\text{mm}^{-1}$	1.1
$F(000)$ , e	6654
$hkl$ range	$\pm 50, \pm 50, \pm 13$
$2\theta_{\text{max}}$ , deg.	55
Refl. measured / unique / $R_{\text{int}}$	70724 / 7086 / 0.032
Param. refined	356
$R(F)$ (for $I \geq 2\sigma(I)$ ) / $wR(F^2)$ (all refl.) <sup>a,b</sup>	0.051 / 0.141
GoF ( $F^2$ ) <sup>c</sup>	1.122
$\Delta\rho_{\text{fin}}$ (max / min), $\text{e Å}^{-3}$	1.983 (near Pd1) / $-1.073$

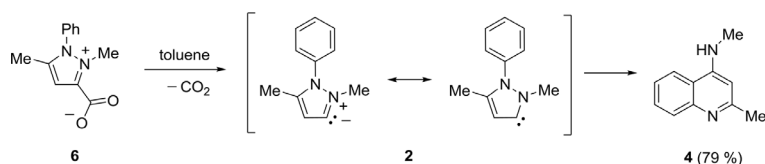
<sup>a</sup>  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ; <sup>b</sup>  $wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ,  $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$ , where  $P = (\text{Max}(F_o^2, 0) + 2F_c^2) / 3$ ; <sup>c</sup>  $\text{GoF} = [\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$ .



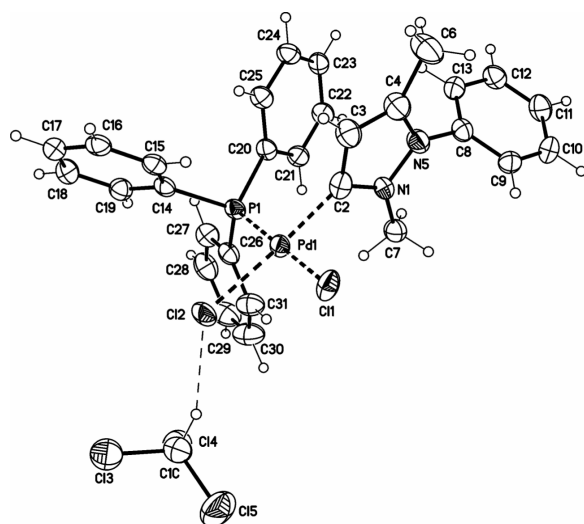
Scheme 1. Carbene generation from a pyrazolium salt with an acidic proton in position 3, followed by rearrangement or complex formation.

plexes of 1,4-diphenyl-2,3-dimethyl-pyrazol-5-ylidene and its 1,2,3,4-tetramethyl derivative [30]. Spraying a sample of **5** from methanol gives a base peak at  $m/z = 576.7$  in the electrospray ionization mass spectrum which can be assigned to the complex minus one chloride.

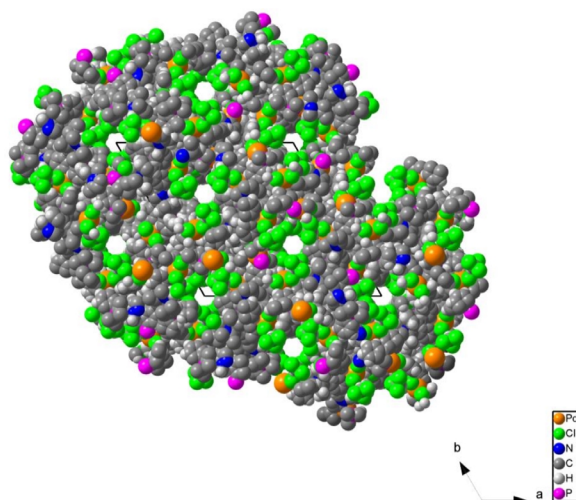
Single crystals of the palladium complex **5** were obtained by slow evaporation of a concentrated solution of the complex in chloroform and analyzed by X-ray diffraction. The complex crystallizes as the sol-

Scheme 2. Decarboxylation of pyrazolium-3-carboxylate **6**.Table 2. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for the palladium complex **5** with estimated standard deviations in parentheses.

Pd1–Cl1	2.3621(1)	Pd1–Cl2	2.3523(1)
N1–N2	1.3457(1)	N1–N5	1.3726(1)
C2–C3	1.3913(1)	C3–C4	1.3687(1)
N1–C7	1.4381(1)	C4–C6	1.4989(1)
P1–C14	1.8237(1)		
C2–N1–Pd1	123.057(5)	C2–C3–Pd1	130.562(5)
P1–C20–Pd1	115.966(4)	P1–C26–Pd1	115.817(4)
Pd1–C2–Cl1	87.469(3)	Pd1–C2–Cl2	175.839(4)
Pd1–Cl2–Cl1	91.821(3)	Pd1–P1–Cl1	176.794(4)
Pd1–P1–Cl2	87.799(3)		
Cl1–Pd1–C2–C3	–77.4(4)	Cl1–Pd1–C2–N1	101.7(3)
Cl1–Pd1–P1–Cl14	–24.6(8)	Cl1–Pd1–P1–C20	93.7(7)
Cl1–Pd1–P1–C26	–146.2(7)	Cl2–Pd1–P1–C26	–62.9(2)
Cl2–Pd1–P1–C20	176.9(2)	Cl2–Pd1–P1–C14	58.71(14)
P1–Pd1–C2–N1	–81.5(3)		

Fig. 3. Molecular structure of the palladium complex **5** in the crystal including the co-crystallized chloroform molecule. The displacement ellipsoids are drawn at the 50 % probability level.

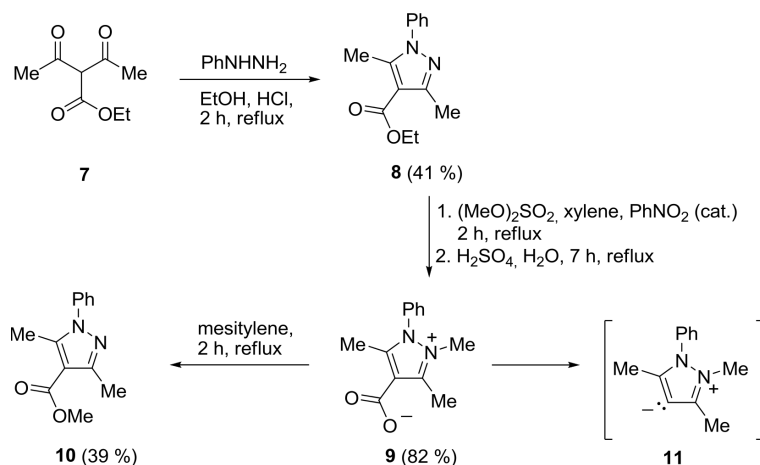
vate **5** · CHCl<sub>3</sub> · 1/6 H<sub>2</sub>O. Results are given in Table 1 and are shown in Figs. 3 and 4; selected bond lengths, bond angles and torsion angles are presented in Table 2. The complex crystallizes in the trigonal space group *R* $\bar{3}$  with *Z* = 18 and exhibits a *cis* configuration of the chlorine ligands in an essentially square-

Fig. 4 (color online). Projection of the crystal structure of **5** · CHCl<sub>3</sub> · 1/6 H<sub>2</sub>O as viewed down the *z* axis showing the hydrophilic channels running parallel to the *z* axis. The disordered water molecules are located in these channels.

planar geometry around the palladium center. The carbene ring plane is twisted by approximately 10° from a perpendicular geometry to the PdCCl<sub>2</sub>P coordination plane. The Pd–C(carbene) bond length was determined to be 199.30(1) pm and is comparable with those reported for other standard NHC–Pd complexes [30] as well as pyrazole-based *r*NHC–Pd complexes [24, 31]. The Pd–P bond has a length of 224.76(1) pm and is slightly shorter than in the aforementioned NHC [30] and *r*NHC complexes [24, 31].

The pyrazol-3-ylidene **2** can also be generated by decarboxylation of the pyrazolium-3-carboxylate **6** to induce aldol additions, Knoevenagel reactions, and redox esterifications (Scheme 2) [9]. In addition, this compound as well as its derivatives undergoes a similar sequence of reactions yielding 4-aminoquinolines as mentioned before. According to a DFT calculation, the decarboxylation of **6** to **2** requires an activation energy of 80 kJ mol<sup>–1</sup>.

For comparison, we prepared a cross-conjugated analog of **6**, the pyrazolium-4-carboxylate **9**, which possesses the partial structure **IV** (Fig. 1). We started by condensation of phenylhydrazine with ethyl 2-acet-



Scheme 3. Preparation of pyrazolium-4-carboxylate **9**.

yl-3-oxobutanoate **7** to the pyrazole ester **8**, which was first methylated with dimethyl sulfate in the presence of catalytic amounts of nitrobenzene and then saponified under acidic conditions to yield the target betaine **9** in good overall yield (Scheme 3). The thermal behavior of this pyrazolium-4-carboxylate is different from that of the pyrazolium-3-carboxylate, as heating in mesitylene at reflux temperature yielded the pyrazole ester **10** as result of an *N*-demethylation/*O*-methylation sequence. Betaine **9** gives the base peak of the electrospray ionization mass spectrum at  $m/z = 253.1$ ,  $[\text{M}+\text{Na}]^+$ , measured from methanol as solvent and spraying the sample at 0 V fragmentor voltage. At 100 V, the corresponding pyrazolium salt, formed on decarboxylation of the betaine **9** to the carbene **11** followed by protonation of the carbene by the solvent can be detected as a prominent peak at  $m/z = 187.1$ ,  $[\text{11}+\text{H}]^+$ . At vigorous measurement conditions (250 V), the corresponding *remote N*-heterocyclic carbene can be detected at  $m/z = 209.1$  as the sodium adduct  $[\text{11}+\text{Na}]^+$ , and, in the presence of lithium carbonate, at  $m/z = 193.1$ ,  $[\text{11}+\text{Li}]^+$ . These results are in agreement with calculations which predict a much higher energy barrier ( $120 \text{ kJ mol}^{-1}$ ) for the decarboxylation of **9** to **11** in comparison to the decarboxylation of **6** to **2**.

The betaines **6** and **9** belong to two distinct types of heterocyclic mesomeric betaines. Pyrazolium-3-carboxylate possesses partial structure **II** (Fig. 1) and is a member of the class of pseudo-cross-conjugated heterocyclic mesomeric betaines (PCCMB). This class of compounds can be recognized by a closer inspection of the mesomeric structures. Positive as well as negative charges are distributed in common areas of

the  $\pi$  electron system, when electron sextet structures are involved as shown (Fig. 5). In addition, this class of compounds can be identified by characteristic dipole types, as realized by Ollis, Stanforth and Ramsden [43]. Dipoles of PCCMB can be used in cycloadditions [44]. By contrast, pyrazolium-4-carboxylates belong to the class of cross-conjugated heterocyclic mesomeric betaines (CCMB). According to the mesomeric structures, the charges are strictly delocalized in separated parts of the molecule. Characteristic dipole types can also be dissected from this class of compounds.

Fig. 6 displays the frontier orbital profile of both types of mesomeric betaines. Characteristically for both of them, the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecular orbitals (LUMOs) are located in separated parts of the common  $\pi$  electron system. As already recognized by Potts, in both types of conjugation the anionic part is bound by a union bond through a nodal position of the HOMO to the cationic part of the molecule [45, 46].

The salt which possesses partial structure **III** (Fig. 1) was finally prepared starting from 1,2-diphenylhydrazine and 4-chloropentenone in chlorobenzene, followed by precipitation as perchlorate (Scheme 4). Attempts to convert this salt into the ester by deprotonation with *n*BuLi, followed by the addition of  $(\text{MeO})_2\text{CO}$  failed, presumably due to the low acidity of 4-*H* of the pyrazolium salt. It is also known from the literature, that the *in situ* deprotonation of 1,2,3,5-tetrasubstituted pyrazolium salts with basic metal precursors such as  $\text{Pd}(\text{OAc})_2$  or  $\text{Ag}_2\text{O}$  was unsuccessful [28, 35]. In agreement with these observations, the *remote N*-heterocyclic carbene **14** could not be de-

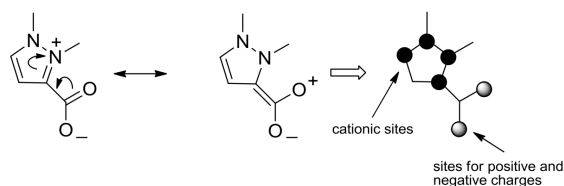
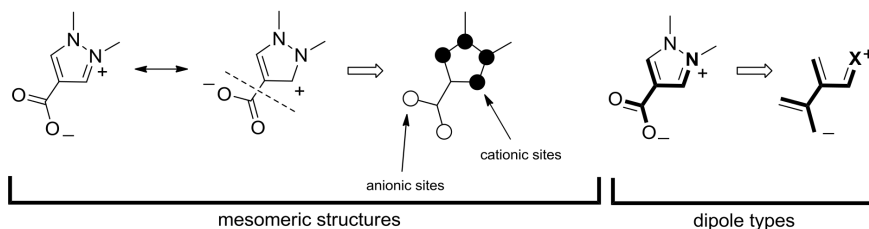
**PCCMB:****CCMB:**

Fig. 5. Characteristic features of PCCMB and CCMB.

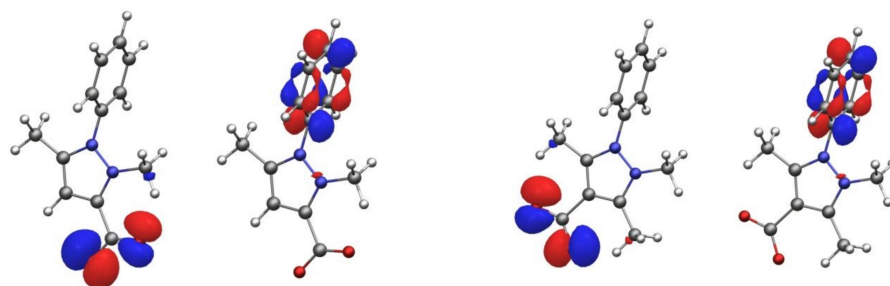
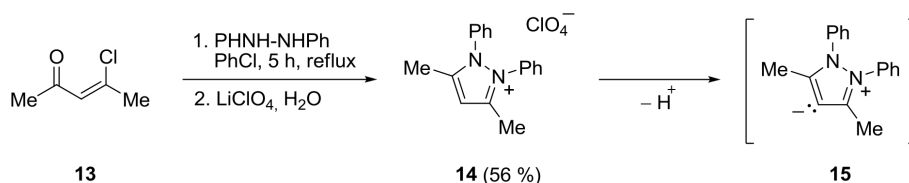


Fig. 6 (color online). From left to right: HOMO (6), LUMO (6), HOMO (9), and LUMO (9).



Scheme 4. Preparation of a pyrazolium salt with an acidic proton in position 4.

tected in electrospray ionization mass spectrometry, even under more vigorous reactions conditions as applied before, such as 250 V fragmentor voltage and the presence of lithium carbonate in the solution.

According to a DFT calculation, the deprotonation of the pyrazolium salt **1** to the *N*-heterocyclic carbene **2** by methoxide under formation of methanol is by 86.8 kJ mol<sup>-1</sup> more favorable than the analogous deprotonation of **14** to the *remote N*-heterocyclic carbene **15**.

In summary, the pseudo-cross-conjugated heterocyclic mesomeric betaine (PCCMB) pyrazolium-3-carboxylate **6** is a suitable precursor for *N*-heterocyclic carbenes (NHC), and so are pyrazolium salts such as **1** which possess a proton in position 3. Pyrazolium salt **1** was used to prepare a pyrazol-3-ylidene palladium complex. The decarboxylation of the cross-conjugated

heterocyclic mesomeric betaine (CCMB) pyrazolium-4-carboxylate **9** to the remote *N*-heterocyclic carbene (*r*NHC) pyrazol-4-ylidene requires considerably more energy in comparison to **6**.

## Experimental Section

Flash chromatography was performed with silica gel 60 (0.040–0.063 mm). Nuclear magnetic resonance (NMR) spectra were obtained with a Bruker Avance III (600 MHz) and a Bruker Avance (400 MHz) spectrometer. Spectra were recorded with the solvent peak or tetramethylsilane as the internal reference. Chemical shifts are given in ppm. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, and m = multiplet. FT-IR spectra were obtained on a Bruker Vector 22 instrument in the range of 400 to 4000 cm<sup>-1</sup>. All substances were measured as pellets (2.5 %) in KBr. The

mass spectra were measured with a Varian 320 MS Triple Quad GC/MS/MS coupled with a Varian 450-GC. The ESI mass spectra were measured with an Agilent LCMSD Series HP1100 with APIES. Samples were sprayed from methanol. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). All yields are isolated yields. They are not optimized.

*Complex of bis(triphenylphosphine)palladium(II) chloride and 2,5-dimethyl-1-phenylpyrazol-3-ylidene (5)*

A sample of 0.447 g (1.49 mmol) of 2,5-dimethyl-1-phenylpyrazolium iodide (**1**) was dissolved in 20 mL of anhydrous MeCN. Then, 0.345 g (1.49 mmol) of silver(I) oxide was added. The mixture was stirred for 2 h at r.t. and then filtered through a plug of celite. The filtrate was then treated with 0.526 g (0.75 mmol) of bis(triphenylphosphine)palladium(II) chloride and stirred for additional 3 h. After filtration through celite, the solvent was distilled off *in vacuo*, and the residue was subjected to chromatography (acetone-CH<sub>2</sub>Cl<sub>2</sub> = 1 : 2). Complex **5** was isolated as a pale-yellow solid (51 %), m.p. 180–183 °C. – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.72–7.77 (m, 6 H, PPh<sub>3</sub>-H), 7.53–7.61 (m, 3 H, Ph-H), 7.45–7.49 (m, 3 H, PPh<sub>3</sub>-H), 7.36–7.40 (m, 6 H, PPh<sub>3</sub>-H), 7.18 (d, 1 H, Ph-H, *J* = 6.8 Hz), 6.73 (d, 1 H, Ph-H, *J* = 6.8 Hz), 5.97 (s, 1 H, 4-H), 3.69 (s, 3 H, 2-CH<sub>3</sub>), 1.79 (s, 3 H, 5-CH<sub>3</sub>). – <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = 165.6, 144.1, 134.6 (d, *J*<sub>CP</sub> = 11.1 Hz), 132.4, 131.8, 130.9 (d, *J*<sub>CP</sub> = 2.4 Hz), 130.8, 130.6 (d, *J*<sub>CP</sub> = 53.3 Hz), 130.4, 128.4, 128.3 (d, *J*<sub>CP</sub> = 11.0 Hz), 127.7, 114.2, 39.3, 12.0. – IR (KBr): ν = 3464, 3052, 1589, 1529, 1497, 1435, 1349, 1223, 1096, 788, 748, 695, 535, 513 cm<sup>-1</sup>. – MS ((+)-ESI): *m/z* (%) = 576.7 (100) [M–Cl]<sup>+</sup>.

*Ethyl 3,5-dimethyl-1-phenyl-1H-pyrazole-4-carboxylate (8)*

A sample of 1.0 g (5.81 mmol) of ethyl diacetoacetate **7** in 10 mL of ethanol was treated with 0.628 g (5.81 mmol) of phenylhydrazine and 1 mL of concentrated hydrochloric acid. The mixture was heated at reflux for 2 h. After cooling, the solution was neutralized with aqueous NaOH and evaporated to dryness *in vacuo*. The residue was then subjected to chromatography (petroleum ether-EtOAc = 5 : 1). The ester **8** was obtained in 41 % yield. – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.38–7.50 (m, 5 H, Ar-H), 4.33 (q, 2 H, CH<sub>3</sub>CH<sub>2</sub>O, *J* = 7.1 Hz), 2.52 (s, 3 H, CH<sub>3</sub>), 2.50 (s, 3 H, CH<sub>3</sub>), 1.38 (t, 3 H, CH<sub>3</sub>CH<sub>2</sub>O, *J* = 7.1 Hz). – All spectroscopic data are in agreement with those reported in the literature [47].

*2,3,5-Trimethyl-1-phenylpyrazolium-4-carboxylate (9)*

A sample of 0.366 g (1.5 mmol) of ethyl 3,5-dimethyl-1-phenylpyrazol-4-carboxylate (**8**) in 10 mL of xylene containing one drop of nitrobenzene was treated with 0.14 mL

(1.5 mmol) of dimethyl sulfate. The mixture was heated to reflux temperature for 2 h. After cooling, the solvent was distilled off *in vacuo*, and the residue was treated with 15 mL of 18 % hydrochloric acid. Then, the mixture was heated for 7 h at reflux temperature. After neutralization with aqueous sodium hydroxide, the water was distilled off, and the residue was extracted six times with portions of 10 mL of ethanol. After distilling off the solvent, the resulting residue was subjected to chromatography (MeOH). The mesomeric betaine **9** was isolated as a colorless solid in 82 % yield, dec. 240 °C. – <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD): δ = 7.74–7.83 (m, 3 H, Ar-H), 7.61–7.64 (m, 2 H, Ar-H), 3.66 (s, 3 H, 2-CH<sub>3</sub>), 2.77 (s, 3 H, 5-CH<sub>3</sub> oder 3-CH<sub>3</sub>), 2.44 (s, 3 H, 5-CH<sub>3</sub> oder 3-CH<sub>3</sub>). – <sup>13</sup>C NMR (100 MHz, 21 °C, CD<sub>3</sub>OD): δ = 167.8, 149.8, 149.4, 133.9, 132.7, 132.0, 130.1, 120.4, 34.7, 12.4, 11.7. – IR (KBr): ν = 3441, 1601, 1381, 1322, 1192, 809, 782, 705 cm<sup>-1</sup>. – MS ((+)-ESI): *m/z* = 231.1 (100) [M+H]<sup>+</sup>. – HRMS ((+)-ESI): *m/z* = 231.1134 (calcd. 231.1134 for C<sub>13</sub>H<sub>15</sub>N<sub>2</sub>O<sub>2</sub>, [M+H]<sup>+</sup>).

*Methyl 3,5-dimethyl-1-phenylpyrazol-4-carboxylate (10)*

A sample of 58 mg (0.25 mmol) of 2,3,5-trimethyl-1-phenylpyrazolium-4-carboxylate **9** was suspended in 2 mL of mesitylene and heated under reflux over a period of 2 h. After cooling, the solvent was distilled off *in vacuo*, and the residue was subjected to chromatography (petroleum ether-EtOAc = 5 : 1). The ester was isolated in 39 % yield. – <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ = 7.38–7.50 (m, 5 H, Ph-H), 3.86 (s, 3 H, O-CH<sub>3</sub>), 2.52 (s, 3 H, 5-CH<sub>3</sub> oder 3-CH<sub>3</sub>), 2.50 (s, 3 H, 5-CH<sub>3</sub> oder 3-CH<sub>3</sub>). – All spectroscopic data are in agreement with those reported in the literature [47].

*3,5-Dimethyl-1,2-diphenylpyrazolium perchlorate (14)*

A solution of 20.1 g (0.2 mol) of acetylacetone in 200 mL of anhydrous diethyl ether was treated with 41.7 g (0.2 mol) of PCl<sub>5</sub>. The reaction mixture was stirred at r.t. for 1 h and then poured into 300 mL of water and ice. The organic phase was separated and then treated with a slurry of 9.0 g (0.09 mol) of calcium carbonate in 100 mL of water. After stirring at r.t. over a period of 14 h, the organic layer was concentrated and finally distilled *in vacuo* [48]. The resulting 4-chloropent-3-en-2-one (**13**) was isolated in 81 % yield. A sample of 0.652 g (5.5 mmol) of **13** in 50 mL of chlorobenzene was then treated with 0.921 g (5.0 mmol) of hydrazobenzene. After heating to reflux temperature for 5 h the solution was concentrated *in vacuo* to approximately 80 % of its original volume. After cooling to r.t., 100 mL of water was added, and the resulting mixture was extracted three times with 50 mL of diethyl ether. Finally, a saturated solution of LiClO<sub>4</sub> was added to precipitate the compound as the perchlorate, which was filtered off and dried on air. The salt **14** was obtained as a

pale-brownish solid in 56 % yield, m.p. 182–183 °C. –  $^1\text{H}$  NMR (400 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 7.58–7.60 (m, 4 H, Ph-*H*), 7.46–7.53 (m, 6 H, Ph-*H*), 7.06 (s, 1 H, 4-*H*), 2.32 (s, 6 H, 3- $\text{CH}_3$  und 5- $\text{CH}_3$ ). –  $^{13}\text{C}$  NMR (100 MHz,  $[\text{D}_6]\text{DMSO}$ ):  $\delta$  = 148.2, 131.8, 131.5, 129.8, 129.1, 108.1, 12.0. – IR (KBr):  $\nu$  = 1556, 1497, 1415, 1088, 778, 695, 623  $\text{cm}^{-1}$ . – MS ((+)-ESI):  $m/z$  (%) = 249.1 (100). – HRMS ((+)-ESI):  $m/z$  = 249.1390 (calcd. 249.1392 for  $\text{C}_{17}\text{H}_{17}\text{N}_2$ ,  $[\text{M}+\text{H}]^+$ ).

### Calculations

All density-functional theory (DFT) calculations were carried out by using the JAGUAR 7.7.107 software running on Linux 2.6.18-238.el5 SMP (x86\_64) on two AMD Phenom II X6 1090T processor workstations (Beowulf-cluster) parallelized with OpenMPI 1.3.4. MM2-optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented LACVP\* basis set (Hay-Wadt effective core potential (ECP) basis on heavy atoms, N31G6\* for all other atoms) and with the

B3LYP density functional. All calculated structures were proven to be true minima by the absence of imaginary frequencies. Plots were obtained using MAESTRO 9.1.207, the graphical interface of JAGUAR.

### X-Ray structure determination

Data of **5** were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda$  = 0.71073 Å) at  $T$  = –150 °C, and the structure was solved by Patterson methods and refined by full-matrix least-squares on  $F^2$  [49]. A semi-empirical absorption correction was applied. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located from difference Fourier maps and refined at idealized positions using a riding model. One water molecule is disordered about the 3-fold axis (in 0, 0,  $z$ ).

CCDC 855158 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre (CCDC) via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

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- [1] A. M. Voutchkova, L. N. Appelhans, A. R. Chianese, R. H. Crabtree, *J. Am. Chem. Soc.* **2005**, *127*, 17624–17625.
- [2] A. Tudose, L. Delaude, B. André, A. Demonceau, *Tetrahedron Lett.* **2006**, *47*, 8529–8533.
- [3] A. Schmidt, A. Beutler, M. Albrecht, B. Snovydyovych, F. J. Ramírez, *Org. Biomol. Chem.* **2008**, *6*, 287–295.
- [4] I. Tommasi, F. Sorrentino, *Tetrahedron Lett.* **2005**, *46*, 2141–2145.
- [5] A. R. Katritzky, R. Awartani, R. C. Patel, *J. Org. Chem.* **1982**, *47*, 498–502.
- [6] A. R. Katritzky, H. M. Faid-Allah, *Synthesis* **1983**, 149–150.
- [7] H. Quast, E. Schmitt, *Justus Liebigs Ann. Chem.* **1970**, *732*, 43–63.
- [8] H. Quast, E. Schmitt, *Justus Liebigs Ann. Chem.* **1970**, *732*, 64–69.
- [9] A. Schmidt, T. Habeck, *Lett. Org. Chem.* **2005**, *2*, 297–307.
- [10] A. Dreger, R. Cisneros Camuña, N. Münster, T. A. Rokob, I. Pápai, A. Schmidt, *Eur. J. Org. Chem.* **2010**, 4296–4305.
- [11] A. Schmidt, N. Münster, A. Dreger, *Angew. Chem.* **2010**, *122*, 2851–2854; *Angew. Chem. Int. Ed.* **2010**, *49*, 2790–2793.
- [12] A. Schmidt, T. Habeck, L. Merkel, M. Mäkinen, P. Vainiotalo, *Rapid Comm. Mass Spectrom.* **2005**, *19*, 2211–2216.
- [13] A. Schmidt, L. Merkel, W. Eisfeld, *Eur. J. Org. Chem.* **2005**, 2124–2130.
- [14] A. Schmidt, A. Beutler, T. Habeck, T. Mordhorst, B. Snovydyovych, *Synthesis* **2006**, 1882–1894.
- [15] A. Schmidt, B. Snovydyovych, T. Habeck, P. Dröttboom, M. Gjika, A. Adam, *Eur. J. Org. Chem.* **2007**, 4909–4916.
- [16] L. Delaude, *Eur. J. Inorg. Chem.* **2009**, 1681–1699.
- [17] N. Kuhn, M. Steinmann, G. Weyers, *Z. Naturforsch.* **1998**, *54b*, 427–433.
- [18] N. Kuhn, E. Niquet, M. Steinmann, I. Walker, *Z. Naturforsch.* **1999**, *54b*, 1181–1187.
- [19] S. K. Schneider, P. Roembke, G. R. Julius, C. Loschen, H. G. Raubenheimer, G. Frenking, W. A. Herrmann, *Eur. J. Inorg. Chem.* **2005**, 2973–2977.
- [20] Y. Han, L. J. Lee, H. V. Huynh, *Organometallics* **2009**, *28*, 2778–2786.
- [21] Y. Han, H. V. Huynh, G. K. Tan, *Organometallics* **2007**, *26*, 6581–6585.
- [22] M. Albrecht, *Chem. Commun.* **2008**, 3601–3610.
- [23] D. Holschumacher, T. Bannenberg, C. G. Hrib, P. G. Jones, M. Tamm, *Angew. Chem.* **2008**, *120*, 7538–7542; *Angew. Chem. Int. Ed.* **2008**, *47*, 7428–7432.
- [24] S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller, R. H. Crabtree, *J. Am. Chem. Soc.* **2002**, *124*, 10473–10481.
- [25] V. Lavallo, C. A. Dyker, B. Donnadiou, G. Bertrand, *Angew. Chem.* **2008**, *120*, 5491–5494; *Angew. Chem. Int. Ed.* **2008**, *47*, 5411–5414.
- [26] A. Schmidt, A. Dreger, *Curr. Org. Chem.* **2011**, *15*, 1423–1463.
- [27] A. Schmidt, A. Dreger, *Curr. Org. Chem.* **2011**, *15*, 2897–2970.



- [28] A. Schmidt, A. Beutler, B. Snovydyovych, *Eur. J. Org. Chem.* **2008**, 4073–4095.
- [29] M. Christl, B. Engels, *Angew. Chem.* **2009**, *121*, 1566–1567; *Angew. Chem. Int. Ed.* **2009**, *48*, 1538–1539.
- [30] J. Schütz, E. Herdtweck, W. A. Herrmann, *Organometallics* **2004**, *23*, 6084–6086.
- [31] Y. Han, H. V. Huynh, *Chem. Commun.* **2007**, 1089–1091.
- [32] H. V. Huynh, Y. Han, R. Jothibas, J. A. Yang, *Organometallics* **2009**, *28*, 5395–5404.
- [33] A. Schmidt, *J. Heterocycl. Chem.* **2002**, *39*, 949–956.
- [34] A. Schmidt, M. Nieger, *Heterocycles* **1999**, *51*, 2119–2126.
- [35] H. Wamhoff, A. Schmidt, M. Nieger, *Tetrahedron Lett.* **1991**, *26*, 4473–4476.
- [36] H. Wamhoff, A. Schmidt, *Heterocycles* **1993**, *35*, 1055–1066.
- [37] A. Rahimi, J. C. Namyslo, M. Drafz, J. Halm, E. Hübner, M. Nieger, N. Rautzenberg, A. Schmidt, *J. Org. Chem.* **2011**, *76*, 7316–7325.
- [38] A. Rahimi, A. Schmidt, *Synthesis* **2010**, 2621–2625.
- [39] A. Schmidt, A. Rahimi, *Chem. Commun.* **2010**, 2995–2998.
- [40] A. Schmidt, T. Mordhorst, *Synthesis* **2005**, 781–786.
- [41] A. de la Hoz, E. Díez-Barra, M. C. Pardo, J. P. Declercq, G. Germain, M. Van Meerssche, J. Elguero, *Tetrahedron* **1983**, *39*, 2193–2200.
- [42] A. de la Hoz, M. C. Pardo, J. Elguero, A. Fruchier, *Magn. Reson. Chem.* **1989**, *27*, 603–609.
- [43] W. D. Ollis, S. P. Stanforth, C. A. Ramsden, *Tetrahedron* **1985**, *41*, 2239–2329.
- [44] A. Schmidt, T. Habeck, A. S. Lindner, B. Snovydyovych, J. C. Namyslo, A. Adam, M. Gjikaj, *J. Org. Chem.* **2007**, *72*, 2236–2239.
- [45] K. T. Potts, P. M. Murphy, W. R. Kuehnling, *J. Org. Chem.* **1988**, *53*, 2889–2898.
- [46] K. T. Potts, P. M. Murphy, M. R. DeLuca, W. R. Kuehnling, *J. Org. Chem.* **1988**, *53*, 2898–2910.
- [47] J. J. Neumann, M. Suri, F. Glorius, *Angew. Chem.* **2010**, *122*, 7957–7961; *Angew. Chem. Int. Ed.* **2010**, *49*, 7790–7794.
- [48] A. G. M. Barrett, T. M. Morris, D. H. R. Barton, *J. Chem. Soc., Perkin Trans. 1* **1980**, 2272–2277.
- [49] G. M. Sheldrick, *Acta Crystallogr.* **2008**, *A64*, 112–122.