HETEROCYCLES, Vol. 96, No. 7, 2018, pp. 1203 - 1215. © 2018 The Japan Institute of Heterocyclic Chemistry
Received, 7th May, 2018, Accepted, 12th June, 2018, Published online, 26th June, 2018
DOI: 10.3987/COM-18-13916

DEPROTONATION OF 4-ETHYNYLPYRAZOLIUM SALTS

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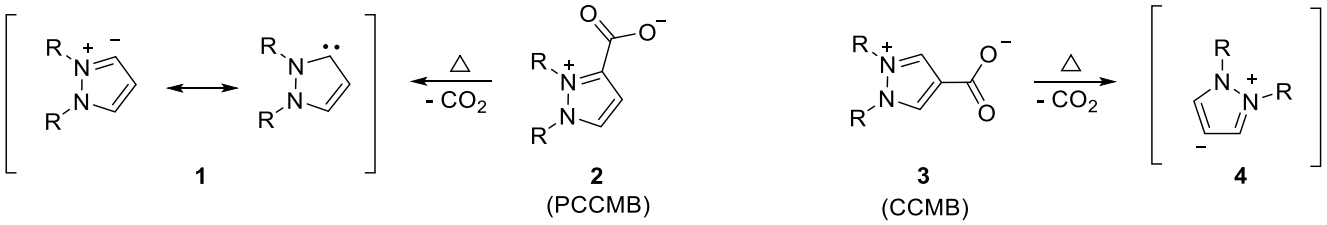
Abstract – 4-Ethynyl-1,2-dimethylpyrazolium salts were prepared by methylation of the corresponding 4-ethynyl-1-methylpyrazoles with trimethyloxonium tetrafluoroborate and were deprotonated to give the corresponding pyrazolium-4-acetylenides, which are mesomeric betaines. These can be represented as alkynyl- or mesoionic allenylidene-type resonance forms. Calculations and spectroscopic investigations were performed to determine the contribution of each canonical form to the overall structure. Ylides and N-heterocyclic carbenes are tautomers of the betaines. Their relative stabilities have been compared.

INTRODUCTION

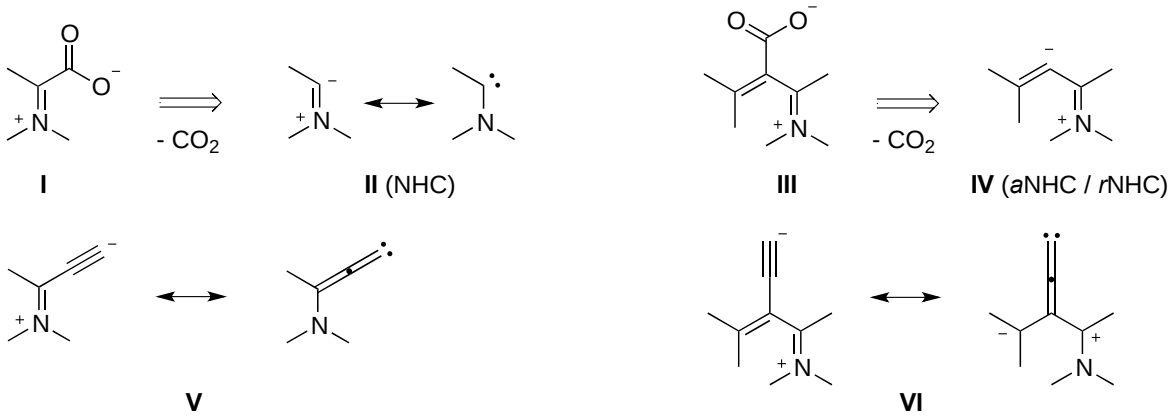
Numerous synthetic biologically active compounds[1-4] as well as natural products[1,5,6] are based on the pyrazole nucleus, and the COX-2 enzyme inhibitor celecoxib, the analgesic and anti-inflammatory agent difenamizole as well as the alkaloid withasomnine[7] from *Withania somnifera* and other plants are just three examples. Moreover, pyrazole proved to be a versatile starting material for complex chemistry and heterocycle synthesis via their N-heterocyclic carbenes.[8] Thus, pyrazol-3-ylidene **1** forms complexes with chromium,[9] iron,[9] rhodium,[10] palladium[11] and other metals, and it can be used for the synthesis of quinolines[12,13] by rearrangements. Pyrazolium-3-carboxylates **2** are pseudo-cross-conjugated heterocyclic mesomeric betaines (PCCMB) and masked N-heterocyclic carbenes (NHC) which are suited to generate pyrazol-3-ylidenes in-situ. In general, PCCMBs decarboxylate thermally under relatively mild conditions to form the corresponding N-heterocyclic carbenes (Scheme 1). By contrast, the decarboxylation of pyrazolium-4-carboxylates **3**, which are members of the class of cross-conjugated heterocyclic mesomeric betaines (CCMB), requires harsh reaction conditions, and the corresponding pyrazol-4-ylidene **4** has only been detected mass spectrometrically under these conditions.[14] Its synthesis can better be accomplished

by deprotonation of suitable pyrazolium salts.[15] Complexes were prepared.[16,17]



Scheme 1

In general, pseudo-cross-conjugated mesomeric betaines which possess iminium-2-carboxylate partial structures **I** give normal N-heterocyclic carbenes **II** by decarboxylation, whereas cross-conjugated iminium-3-carboxylates **III** give abnormal or remote N-heterocyclic carbenes **IV** (Scheme 2). A review deals with the intersection between the substance classes of mesomeric betaines (MB) and N-heterocyclic carbenes (NHC).[18] Formal replacement of the carboxylate group by the ethynyl group opens new perspectives, as resonance forms of neutral allenylidenes **V** or mesoionic allenylidene resonance forms **VI** can be formulated depending on the site of attachment of the ethynyl group. Ethynyl substituted pyridinium salts,[19-23] quinolinium salts[24] and imidazolium salts[25] have been reported and their betaines have been mentioned. In most cases, the latter are sensitive molecules which tend to decompose or polymerize.

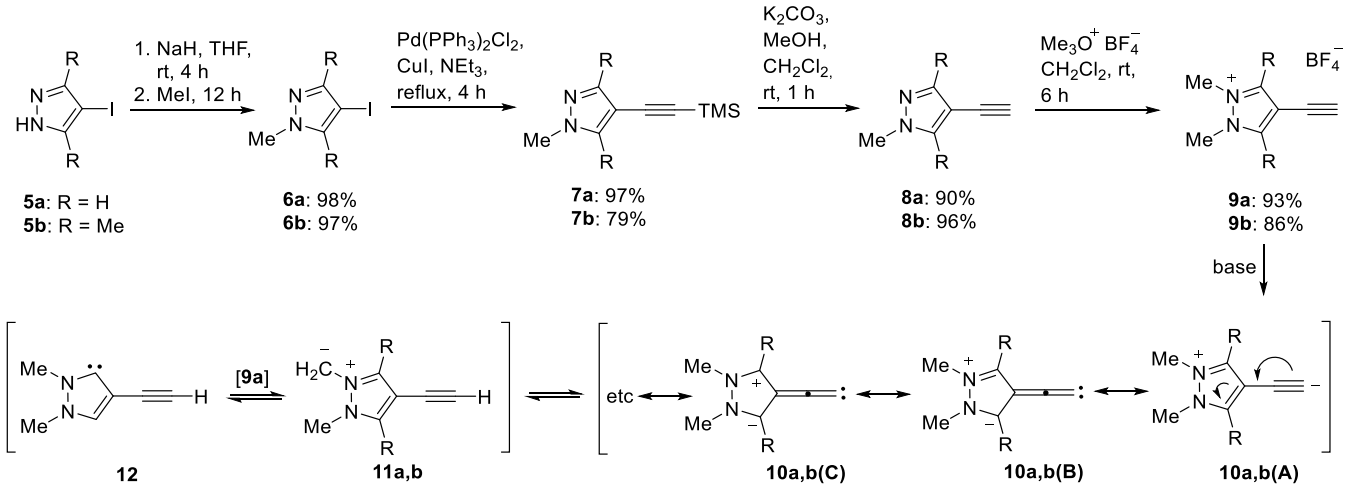


Scheme 2

In continuation of our interest in new types of mesomeric betaines[26,27] and N-heterocyclic carbenes[28] we describe here the syntheses of 4-ethynylpyrazolium salts and our results of experiments to convert them into mesomeric betaines (MB), ylides, or N-heterocyclic carbenes (NHC) by deprotonation. Spectroscopic investigations as well as DFT-calculations have been performed in order to elucidate the site of deprotonation and the alkynyl vs. allenylidene character of the pyrazolium-4-acetylenides.

RESULTS AND DISCUSSION

We started the synthesis of the title compounds by an iodination of pyrazole and 3,5-dimethylpyrazole with iodine in the presence of ceric ammonium nitrate in anhyd. acetonitrile according to literature-known procedures, respectively, which resulted in the formation of **5a**,**b** in excellent yields[29] (Scheme 3). Methylation was best accomplished with an excess of sodium hydride and methyl iodide under careful exclusion of moisture to give **6a**,**b**. A Sonogashira-Hagihara coupling employing ethynyltrimethylsilane in the presence of one equivalent of dichlorobis(triphenylphosphine)palladium and 0.03 equivalents of copper(I) iodide in anhyd. triethylamine resulted in the formation of the corresponding 4-ethynylpyrazoles **7a**,**b**. The deprotection of the triple bonds to give **8a**,**b** was then accomplished with potassium carbonate at temperatures below 40 °C. Various reagents and reaction conditions were tried to methylate **8a**,**b** to prepare the title compounds **9a**,**b**. Methyl triflate failed, even if reaction times of more than 72 h at elevated temperatures were applied, and only yet unidentified decomposition products were obtained. Likewise, treatment of **8a**,**b** with dimethyl sulfate in toluene in the presence of catalytic amounts of nitrobenzene – as successfully applied earlier[12] – also resulted in the decomposition of the starting material. Finally trimethyloxonium tetrafluoroborate gave good yields of the desired 4-ethynylpyrazolium salts **9a**,**b**, if the reaction temperature was kept below 30 °C, followed by cooling to -78 °C to induce crystallization under inert conditions.



Scheme 3

The detection of the NMR resonance frequencies especially of the terminal alkyne carbon required changed measurement parameters. In addition to standard HSQC NMR measurements with an assumed value of 145 Hz for averaged $^{1}J_{CH}$ coupling constants, in case of the terminal alkyne a further HSQC experiment was tuned to 245 Hz in order to unambiguously assign the terminal alkynyl carbon. Thus, the ^{13}C NMR signals of **9b** in pyridine-d_5 were detected at δ = 104.24 ppm (*C*4-C≡C-H), 69.70 ppm

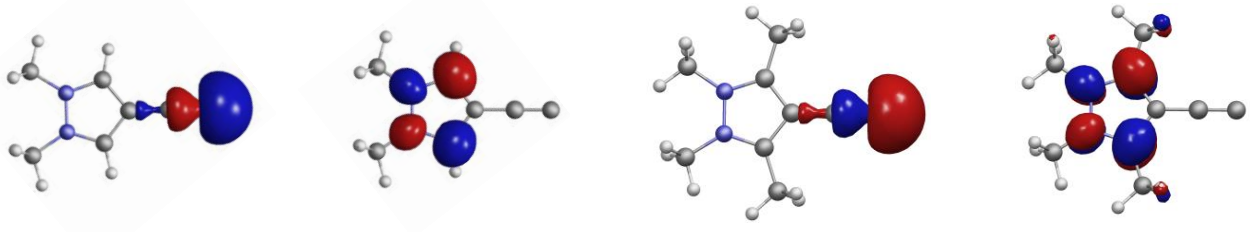
(C4-*C*≡C-H), and 86.44 ppm (C4-C≡*C*-H), respectively, and the hydrogen atom (C4-C≡C-*H*) resonated at δ = 4.46 ppm under these conditions. A priori, three different C-H acidic positions can be identified in 4-ethynylpyrazolium salt **9a** which are located in the terminal position of the ethynyl group, in the methyl groups as well as in the positions 3/5 of the pyrazolium ring. Deprotonation of the ethynyl group resulted in the formation of the mesomeric betaine **10a(A)** which can also be represented by mesoionic allenylidene resonance forms such as **10a(B)** and **10a(C)** (Scheme 3). The ylide **11a** and the N-heterocyclic carbene **12** are tautomers of **10a** and resulted from deprotonation of one of the methyl group or position 3/5 of **9a**, respectively. Due to limited solubilities we had to choose different solvents for the following studies. On treatment of **9a** with *n*BuLi in THF at -78 °C, an extremely moisture sensitive solid precipitated. Quenching the solution with D_2O resulted in the formation of the 3,5-dideuterio-4-ethynylpyrazolium salt of **9a** which possessed a 50% deuterated -C≡C-H/D group. The anion of acetonitrile-d_3, formed in-situ on treatment of MeCN-d_3 with *n*BuLi at -78 °C,[18] gave 4:1 and 3:2 H/D ratios at the position 3/5 and the terminal ethynyl group, respectively. Under analogous conditions without base, no deuteration of **9a** took place. In agreement with these results an electrospray ionization mass spectrometric measurement of the deprotonated species showed intact starting material due to re-protonation under the measurement conditions. When a solution of **9b**, which possesses a priori two different acidic positions, was treated with the anion of MeCN-d_3 under analogous conditions, the integral of the resonance frequency of the -C≡C-*H* proton at δ = 3.74 ppm decreased considerably after stirring for 15 min at that temperature, whereas attempts to deprotonate **9b** with *n*BuLi in benzene at 0 °C failed completely and resulted in decomposition of the starting material. Addition of D_2O resulted in the spontaneous formation of the deuterated salt of **9b** possessing a -C≡C-D group. The system consisting of pyridine-d_5 and one eq. of lithium bis(trimethylsilyl)amide (HMDS), however, caused an immediate quenching of the ^{1}H NMR resonance frequency at δ = 4.54 ppm of the -C≡C-*H* proton. The signals of the resulting -C≡C-Li group appeared at δ = 60.6 ppm (-*C*≡C-Li) and 70.8 ppm (-C≡*C*-Li) in ^{13}C NMR spectroscopy. When the salt **9b** was treated with *n*BuLi at -35 °C prior to the ^{7}Li NMR measurement, the corresponding ^{7}Li NMR resonance frequency could be detected at δ = 2.33 ppm. The ^{1}H NMR resonance frequencies of the methyl groups shifted upfield from 4.08 ppm and 2.31 ppm in the salt **9b** in pyridine-d_5 to 3.61 ppm and 1.60 ppm in the betaine **10b** which proved to be stable in solution, but it decomposed on warming and on trying to remove the solvent. Due to this sensitivity we were prevented from attempts to trap the ylide tautomer by Michael additions[30,31] or cycloadditions[32-36] with DMAD, and the NHC tautomer by reaction with sulfur or selenium. DFT calculations supported the experimental observations. According to the calculations the NHC tautomer **12** is energetically favorable in the gas phase. Polar solvents favor the more polar structure of the mesomeric betaine **10a** in which charge separation occurs. Increasing solvent polarity (dielectric constants: THF: 7.4, MeCN: 37.5, DMSO: 48.9) is reflected by an

increasing preference of the mesomeric betaine, although the energy differences between the NHC and the MB are small in all solvents. Neglecting possible stabilizing influences from counter ions and metal coordination, equilibria may be expected. The ylide tautomer is disfavored in comparison to the MB and NHC tautomer according to the calculations. Correspondingly, the betaine tautomer **10b** is clearly favored in comparison to its ylide tautomer **11b** in polar solvents.

Table 1. Results of DFT calculations. Relative stabilities.

			MBs 10 [E_h]	ylides 11 [E_h]	nNHC 12 [E_h]	ΔE MB - ylide [kJ/mol]	ΔE nNHC - ylide [kJ/mol]	ΔE nNHC - MB [kJ/mol]
a	stabilities	gas phase	-380.83875	-380.87180	**-380.87639**	86.76	-12.05	-98.82
		THF	-380.89501	-380.88110	**-380.89716**	-36.52	-42.16	-5.64
		MeCN	**-380.90521**	-380.88324	-380.90391	-57.68	-54.27	3.42
		DMSO	**-380.90527**	-380.88328	-380.90386	-57.71	-54.01	3.70
b	stabilities	gas phase	-459.48305	-459.51548		85.15		
		THF	-459.53219	-459.52602		-16.19		
		MeCN	-459.54196	-459.52841		-35.58		
		DMSO	-459.54164	-459.52839		-34.79		

The highest occupied molecular orbitals (HOMO) of the mesomeric betaines **10a**,**b** are shown in Figure 1. They are σ lone pairs located at the terminal carbon atoms of the triple bonds with additional coefficients on the triple bond's carbon atoms. As expected the lowest unoccupied molecular orbitals (LUMO) are π orbitals located in the pyrazolium ring. These results resemble those of pyridinium- and quinolinium-acetylenides which we described earlier.[19,24]



HOMO (**10a**) LUMO (**10a**) HOMO (**10b**) LUMO (**10b**)

Figure 1

According to DFT calculations the σ-bond which connects the pyrazolium rings with the triple bond are slightly shortened to 139.0 pm (**10a**) and 139.5 pm (**10b**) *in vacuo* in comparison to vinylacetylene (143 pm).[37] Furthermore the bond lengths of the triple bonds, calculated to be 125.7 pm and 125.8 pm *in vacuo*,

are longer than in acetylene (118 pm),[38] in phenylacetylene (120.8 ppm),[39] in the ylides (**11a**: 121.0 ppm; **11b**: 121.2 ppm) as well as in the NHC tautomer **12** (121.1 ppm) *in vacuo*. They are indicative of a very small contribution of an allenylidene-typ resonance form to the overall structures *in vacuo*, as observed earlier for related systems.[19,24] As shown in Table 2, the bond lengths are slightly solvent-dependent in such a way, that the small allenylidene contribution of the betaines is diminished in polar solvents. Moreover, according to calculations, the negative charge is predominantly located on the α-carbon atom in betaine **10a** in solutions of THF and DMSO. The aforementioned ^{7}Li NMR data were compared with resonance frequencies of the lithium adduct of ethynylbenzene which was prepared under identical conditions which show a difference of only +0.45 ppm [^{7}Li NMR (Ph-C≡C-Li) = 2.78 ppm]. This finding also supports the predominant alkynyl-type character of the betaine **10b**.

Table 2. Results of DFT calculations. Bond lengths.

		Triple bond	C_{sp}-C_{sp^2}
10a	gas phase	125.7	139.0
	THF	125.0	142.3
	MeCN	125.0	142.8
	DMSO	124.9	142.8
10b	gas phase	125.8	139.5
	THF	125.3	142.4
	MeCN	125.2	142.9
	DMSO	125.2	142.9

CONCLUSION

In view of NMR investigation and DFT calculations of bond lengths and frontier orbital profiles of the anions of 4-ethynylpyrazolium salts the structure of the instable betaines can best be described as an alkynyl-type structure with possible small influences of an allenylidene-type structure *in vacuo*. The tautomers of the pyrazolium-4-acetylenides, ylides and the N-heterocyclic carbene, are disfavored according to the calculation.

EXPERIMENTAL

General considerations. Flash-chromatography was performed using silica gel 60 (0.040–0.063 mm). Nuclear magnetic resonance (NMR) spectra were obtained using Bruker Avance 400 and Bruker Avance III 600 MHz instruments. ^{1}H NMR spectra were recorded at 400.18 MHz or 600.35 MHz. ^{13}C NMR spectra were recorded at 100.63 MHz or 150.96 MHz, with the solvent peak or tetramethylsilane used as

the internal reference. ^{7}Li NMR spectra were recorded at 233.32 MHz. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet. FT-IR spectra were recorded on a Bruker Vector 22 in the range of 400 to 4000 cm^{-1}. ATR-IR spectra were recorded on a Bruker Alpha in the range of 400 to 4000 cm^{-1}. The mass spectra were measured with a Varian 320 MS Triple Quad GC/MS/MS with a Varian 450-GC. The electrospray ionization mass spectra (ESIMS) were measured with an Agilent LCMSD series HP 1100 with APIES. Melting points are uncorrected and were determined in an apparatus according to Dr. Tottoli (Büchi). Yields are not optimized. Compounds **5a** and **5b** were prepared according to literature procedures.[29]

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 five AMD Phenom II X6 1090T processor workstations (Beowulf-cluster) parallelized with OpenMPI.[40] MM2 optimized structures were used as starting geometries. Complete geometry optimizations were carried out on the implemented LACVP* (Hay-Wadt effective core potential (ECP) basis on heavy atoms, N31G6* for all other atoms) basis set and with the B3LYP density functional. Solvent effects were estimated by help of the Poisson Boltzmann Finite element method implemented in Jaguar. Plots were obtained using Maestro 9.1.207, the graphical interface of Jaguar. Partial charges were obtained with NBO 6.0 from the results of the DFT calculations.[41]

4-Iodo-1-methyl-1*H*-pyrazole 6a.

Under an atmosphere of nitrogen a solution of 4-iodo-1*H*-pyrazole (1.58 g; 8.0 mmol) in anhyd. THF was added dropwise to a freshly prepared suspension of sodium hydride (0.21 g; 8.7 mmol). The reaction mixture was stirred for 3 h and then 1.0 mL of methyl iodide (2.24 g; 15.8 mmol) was added dropwise. The mixture was stirred for additional 12 h and quenched by adding approximately 50 mL of water. The crude product was extracted with Et_2O and dried over sodium sulfate. After evaporation of the solvent the product was obtained as a yellowish solid. Yield: 1.64 g (98%), Mp 68-69 °C. **^{1}H NMR ($CDCl_3$):** δ = 3.85 (s, 3H, Me), 7.33 (s, 1H, 3-H), 7.42 (s, 1H, 5-H) ppm. **^{13}C NMR ($CDCl_3$):** δ = 39.3 (+, Me), 55.9 (o, C-4), 134.3 (+, C-5), 144.4 (+, C-3) ppm. **IR (ATR):** ν = 3117, 3103, 2939, 1601, 1542, 1365, 1296, 942, 801, 605 cm^{-1}. **MS (EI, DEP, 70 eV):** *m/z* 207.6 [M^{+}].

4-Iodo-1,3,5-trimethyl-1*H*-pyrazole 6b.

Under an atmosphere of nitrogen a solution of 4-iodo-3,5-dimethyl-1*H*-pyrazole (8.95 g; 40.0 mmol) in anhyd. THF was added dropwise to a freshly prepared suspension of sodium hydride (1.06 g; 44.0 mmol). The reaction mixture was stirred for 3 h and then 5.0 mL of methyl iodide (11.94 g; 88.0 mmol) were

added dropwise. The mixture was stirred for additional 12 h and then quenched by adding approximately 50 mL of water. The crude product was extracted with Et_2O and dried over sodium sulfate. After evaporation of the solvent the product was obtained as a yellowish solid. Yield: 9.18 g (97%), Mp 77-78 °C. **^{1}H NMR** ($CDCl_3$): δ = 2.13 (s, 3H, 3-Me), 2.19 (s, 3H, 5-Me), 3.72 (s, 3H, N-Me) ppm. **^{13}C NMR** ($CDCl_3$): δ = 10.9 (+, 3-Me), 12.9 (+, 5-Me), 36.0 (+, N-Me), 61.1 (o, C-I), 139.6 (+, C-5), 150.0 (+, C-3) ppm. **IR (ATR):** ν = 2983, 2969, 2935, 2921, 2189, 2020, 1531, 1417, 1407, 1374, 1279, 1063, 1032, 824, 661, 590 cm^{-1}. **MS (EI, DEP, 70 eV):** *m/z* = 236.1 [M^+].

1-Methyl-4-[(trimethylsilyl)ethynyl]]-1*H*-pyrazole 7a.

Under nitrogen, a suspension of 0.919 g (4.42 mmol) of 4-iodo-1-methylpyrazole, 0.102 g (0.13 mmol) of $Pd(PPh_3)_2Cl_2$ and 0.025 g (0.133 mmol) of CuI in 50 mL of anhyd. NEt_3 was treated dropwise with 0.937 mL (0.651 g; 6.628 mmol) of trimethylsilylacetylene. After heating the mixture for 4 h under reflux, the suspension was cooled to rt and the solvent was distilled off *in vacuo*. The residue was dissolved in EtOAc and filtered through celite. Column chromatography (silica gel, petroleum ether / EtOAc = 5/4) gave the product as colorless crystalline solid. Yield: 0.763 g (97%), Mp 78-79 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): *δ* = 0.00 (s, 9H; TMS), 3.64 (s, 3H; Me), 7.05 (s, 1H; H-5), 7.35 (s, 1H; H-3) ppm. **^{13}C NMR** ($CDCl_3$, 150 MHz): *δ* = 0.0 (+, 3C; TMS), 39.0 (+, 1C; Me), 94.9 (o, 1C; -C≡*C*-TMS), 96.2 (o, 1C; -*C*≡C-TMS), 103.4 (o, 1C; C-4), 133.1 (+, 1C; C-5), 142.3 (+, 1C; C-3) ppm. All spectroscopic data are in agreement with literature values.[42,43]

1,3,5-Trimethyl-4-[(trimethylsilyl)ethynyl]-1*H*-pyrazole 7b.

Under nitrogen, a suspension of 2.078 g (8.803 mmol) of 4-iodo-1,3,5-trimethylpyrazole, 0.124 g (0.176 mmol) of $Pd(PPh_3)_2Cl_2$ and 0.050 g (0.264 mmol) of CuI in 50 mL of anhyd. NEt_3 was treated dropwise with 1.866 mL (1.297 g; 13.205 mmol) of trimethylsilylacetylene. After heating the mixture for 4 h under reflux, the suspension was cooled to rt and the solvent was distilled off *in vacuo*. The residue was dissolved in EtOAc and filtered through celite. Column chromatography (silica gel, petroleum ether / EtOAc = 5/4) gave the product as colorless crystalline solid. Yield: 1.435 g (6.966 mmol, 79%), Mp 93-94 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): *δ* = 0.23 (s, 9H; TMS), 2.25 (s, 3H; 3-Me), 2.28 (s, 3H; 5-Me), 3.69 (s, 3H; N-Me) ppm. **^{13}C NMR** ($CDCl_3$, 150 MHz): *δ* = 0.0 (+, 3C; TMS), 10.4 (+, 1C; 5-Me), 12.3 (+, 1C; 3-Me), 36.0 (+, 1C; N-Me), 97.2 (o, 1C; -C≡*C*-TMS), 97.4 (o, 1C; -*C*≡C-TMS), 101.9 (o, 1C; C-4), 142.4 (o, 1C; C-5), 149.8 (o, 1C; C-3) ppm. **IR (ATR)**: $\tilde{\nu}$ = 2965 (Me), 2151 ($\nu_{C\equiv C}$), 1242, 840, 762, 651 cm^{-1}. **MS (ESI-MS):** *m/z* = **[**MH^+] 207.1. **HRMS (ESI, LCT):** [$C_{11}H_{18}N_2Si+Na^+$] required 229.1131. Found 229.1119. [$C_{11}H_{18}N_2Si+H^+$] required: 207.1312. Found: 207.1299.

4-Ethynyl-1-methyl-1*H*-pyrazole 8a.

A sample of 1-methyl-4-[(trimethylsilyl)ethynyl]-1*H*-pyrazole (2.00 g, 11.0 mmol) was dissolved in 27.5 mL of anhyd. CH_2Cl_2. Then, 2 eq. of K_2CO_3 and 5 mL of anhyd. MeOH were added. The suspension was stirred for 1 h and then the solvent was distilled off *in vacuo*. The residue was dissolved in EtOAc and washed three times with water. The organic layer was dried over $MgSO_4$ and then the solvent was distilled off. The resulting crude reaction product was subjected to column chromatography (petroleum ether / EtOAc = 3/2). Yield: 1.071 g (90%), Mp 44 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 3.01 (s, 1H; C≡C-H), 3.88 (s, 3H; N-Me), 7.52 (s, 1H; 3-H), 7.60 (s, 1H; 5-H) ppm. All spectroscopic data are in agreement with literature values.[42]

4-Ethynyl-1,3,5-trimethyl-1*H*-pyrazole 8b.

Under a nitrogen atmosphere 1.403 g (6.797 mmol) of 1,3,5-trimethyl-4-[(trimethylsilyl)ethynyl]-1*H*-pyrazole were suspended in approximately 4 mL of anhyd. CH_2Cl_2 with 1.879 g (13.595 mmol) of K_2CO_3 in approximately 15 mL of anhyd. MeOH. The mixture was stirred for 1 h and the solvents are distilled off *in vacuo*. The organic phase was dissolved in EtOAc and washed twice with 20 mL of water. The organic phase was then dried over sodium sulfate and finally the solvent was distilled off *in vacuo*. The resulting crude reaction product was subjected to column chromatography (petroleum ether / EtOAc = 3/2). Yield: 0.741 g (91%), Mp 93-94 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ = 2.00 (s, 3H; 3-Me), 2.03 (s, 3H; 5-Me), 3.21 (s, 1H; -C≡C-*H*), 3.42 (s, 3H; N-Me) ppm. **^{13}C NMR** ($CDCl_3$, 150 MHz): δ = 10.8 (+, 1C; 5-Me), 12.8 (+, 1C; 3-Me), 37.0 (+, 1C; N-Me), 77.5 (o, 1C; -*C*≡C-H), 82.3 (o, 1C; -C≡*C*-H), 101.2 (o, 1C; C-4), 144.2 (o, 1C; C-5), 150.2 (o, 1C; C-3) ppm. All spectroscopic data are in agreement with literature values.[44]

4-Ethynyl-1,2-dimethyl-1*H*-pyrazolium tetrafluoroborate 9a.

Under nitrogen, a solution of 4-ethynyl-1-methyl-1*H*-pyrazole (0.872 g; 8.2 mmol) in 3 mL of anhyd. CH_2Cl_2 was added dropwise to a freshly prepared suspension of trimethyloxonium tetrafluoroborate (1.46 g; 9.9 mmol) in 4 mL of anhyd. CH_2Cl_2. The mixture was stirred for 6 h at rt and then approximately 50 mL of cold Et_2O were added. The mixture was then cooled to -78 °C for additional 1.5 h and then filtered. The crude product was washed with small amounts of cold Et_2O, acetone and petroleum ether. Yield: (93%). Mp 320 °C (decomp). For the deuteration, we treated a solution of **9a** (0.1 g, 0.48 mmol) in anhyd. MeCN under nitrogen at -78 °C dropwise with 0.033 g of *n*BuLi (0.52 mmol, 0.33 mL). The mixture was stirred for 15 min and then was allowed to warm to rt. Then, 0.05 mL of D_2O were added. **^{1}H NMR** (DMSO-d_6, 400 MHz): δ = 3.08 (s, 6H; Me), 3.45 (s, 1H; -C≡C-*H*), 7.77 (s, 2H; H-3, H-5) ppm. **^{1}H NMR** after deuteration (CD_3CN, 600 MHz): δ = 4.00 (s, 6H; Me), 4.05 (s, 0.6H, -C≡C-*H*), 8.24 (s, 0.4 H; H-3,

H-5) ppm. **^{13}C NMR** (DMSO-d_6, 150 MHz): δ = 36.9 (+, Me), 71.0 (0, 1C; -*C*≡C-H), 84.4 (+, 1C; -C≡*C*-H), 102.1 (0, 1C; C-4), 139.5 (+, 2C, C-3; C-5) ppm. **^{13}C NMR** after deuteration (CD_3CN, 100 MHz): δ = 27.4 (+, 2C; N-Me), 83.3 (+,1C; -C≡C-D/H), 117.4 (o, 1C; C-4), 140.5 (+, 2C; C-3, C-5) ppm. The signal of -C≡C-H could not be detected under these measurement conditions. **IR (ATR):** $\tilde{\nu}$ = 3132, 1447, 1334, 1241, 1033, 605 cm^{-1}. **ESI-MS:** *m/z* = 121.0 (100%). **HRMS (ESI, LCT&Q-Tof Premier UPLC):** $C_7H_9N_2^+$ required: 121.0760. Found: 121.0763.

4-Ethynyl-1,2,3,5-tetramethyl-1*H*-pyrazolium tetrafluoroborate 9b.

Under nitrogen, a solution of 4-ethynyl-1,3,5-trimethyl-1*H*-pyrazole (3.25 g; 24.0 mmol) in 3 mL of anhyd. CH_2Cl_2 was added dropwise to a freshly prepared suspension of trimethyloxonium tetrafluoroborate (4.30 g; 29.0 mmol) in 4 mL of anhyd. CH_2Cl_2. The mixture was stirred for 6 h at rt and then approximately 50 mL of cold Et_2O were added. The mixture was then cooled to -78 °C for additional 1.5 h and filtered. The crude product was washed with small amounts of cold Et_2O, acetone and petroleum ether. The product was obtained as yellowish solid. Yield: 4.89 g (86%), Mp 154-155 °C (decomp). **^{1}H NMR** (CD_3CN, 600 MHz): δ = 2.44 (s, 6H; 3-Me, 5-Me), 3.74 (s, 1H; -C≡C-*H*), 3.83 (s, 6H; N-Me) ppm. **^{13}C NMR** (CD_3CN, 150 MHz): δ = 11.5 (+, 2C; 3-Me, 5-Me), 35.3 (+, 2C; N-Me), 71.4 (o, 1C; -*C*≡C-H), 86.3 (o, 1C; -C≡*C*-H), 104.3 (o, 1C; C-4), 149.6 (o, 2C; C-3, C-5) ppm. **MS (ESI-MS):** *m/z* = 149.1 **[**M]$^+$, 385.1 [MBF_4]$^+$. **IR (ATR):** $\tilde{\nu}$ = 3259, 2031, 2160 ($\nu_{C\equiv C}$), 1461, 1333, 1022, 915, 744, 521 cm^{-1}. **HRMS (ESI, LCT):** [$C_9H_{13}N_2^+$] required: 149.1073. Found: 149.1079. [$(C_9H_{13}N_2)_2BF_4$]$^+$ required: 385.2182. Found: 385.2164.

(1,2,3,5-Tetramethyl-1*H*-pyrazolium-4-yl)ethyn-1-ide 10b.

Under nitrogen, 0.020 g (0.0847 mmol) of 4-ethynyl-1,2,3,5-tetramethyl-1*H*-pyrazolium tetrafluoroborate were dissolved in 0.5 mL of anhyd. pyridine. A sample of 0.014 g (0.0847 mmol) of lithium bis(trimethylsilyl)amide solution (1 M in THF) was added carefully. Decomposition occurred on attempting to isolate the product by removing the solvent. For the ^{7}Li NMR measurement, we treated 0.100 g (0.424 mmol) of tetramethyl-1*H*-pyrazolium tetrafluoroborate in 1.0 mL of anhyd. pyridine-d_5 under nitrogen with 0.027 g (0.424 mmol, 0.27 mL) of *n*BuLi solution (1.6 M in hexane). **^{1}H NMR** (pyridine-d_5, 600 MHz): δ = 1.60 (s, 6H; 3-Me, 5-Me), 3.61 (s, 6H; N-Me) ppm. **^{13}C NMR** (pyridine-d_5, 150 MHz): δ = 14.5 (+, 2C; 3-Me, 5-Me), 39.3 (+, 2C; N-Me), 60.6 (o, 1C; -*C*≡C$^-$), 70.8 (o, 1C; -C≡*C*$^-$), 104.5 (o, 1C; C-4), 153.3 (o, 2C; C-3, C-5) ppm. **^{7}Li NMR** (pyridine-d_5, 233 MHz): δ = 2.33 ppm.

ACKNOWLEDGEMENTS

Dr. Gerald Dräger, university of Hannover (Germany), is gratefully acknowledged for measuring the HRESIMS spectra.

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