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Synthesis and reactivity of subvalent compounds[☆] Part 10. Fast deuterium labeling and the basicity of stable diamino carbenes (imidazole-2-ylidenes)

Michael K. Denk *, José M. Rodezno

Department of Chemistry, University of Toronto at Mississauga, Missussauga, Ontario L5L 1C6, Canada

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Abstract

The aromatic ring protons in imidazol-2-ylidenes (Arduengo carbenes) undergo rapid deuterium–hydrogen exchange in DMSO-d_6, CD_3OD and D_2O. © 2000 Published by Elsevier Science S.A.

Keywords: Carbenes; Imidazol-2-ylidenes; Hydrogen–deuterium exchange; Proton affinities; DFT calculations; Mechanism

1. Introduction

Since the description of stable carbenes by Bertrand [1] and Arduengo, [2] the exploration of their chemical reactivity has become a major area of current main group chemistry [1–3]. We have previously reported on the structure and synthesis of stable diamino carbenes **1** [4], silylenes [5], germylenes [6] and phosphenium cations [7] (Fig. 1) and are currently investigating the reactivity of these species with small molecules like oxygen, hydrogen and water.

In principle, *N*-heterocyclic carbenes like **1** and their isoelectronic analogs **1Si**, **1Ge** or **1P** should be powerful deoxygenating agents [8] but their reactivity towards oxygen donors seems to be kinetically slow. For example, stable diamino carbenes were obtained by Arduengo through the deprotonation of the respective imidazolium salts with NaH in tetrahydrofuran, using catalytic amounts of dimethyl sulfoxide [2a]. Under the reaction conditions (r.t.), DMSO is inert towards the diamino carbenes [2a]. By way of contrast, non-stabilized carbenes are known to react readily with DMSO to give the respective carbonyl compounds (ureas) and dimethyl sulfide [9].

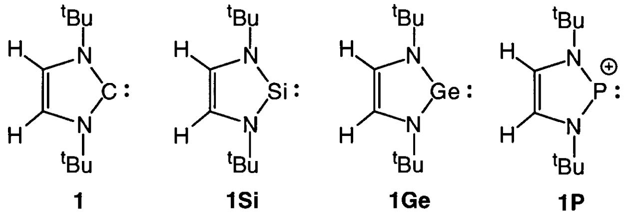

Fig. 1. Imidazol-2-ylidenes and isoelectronic silylenes, germylenes and phosphenium cations.

2. Results and discussion

We were interested in the synthetic potential of stable carbenes as deoxygenating agents [8] and have examined the reactivity of **1** towards DMSO with temperature-dependent ^{1}H-NMR spectroscopy in the temperature range of 25–145°C. While no oxygen transfer could be observed over the entire temperature range, we noticed that the NMR signal of the carbene ring protons vanished upon dissolution of **1** in DMSO-d_6.

The assumption, that **1** reacts rapidly with DMSO-d_6 to give selective H/D exchange of the ring protons was verified by the isolation and characterization of 1,3-di-*tert*-butyl-4,5-bis(deutero)-imidazol-2-ylidene (**1-D$_2$**). Pure **1-D$_2$** can be isolated from the DMSO solution by

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* Corresponding author.

E-mail address: mdenk@credit.erin.utoronto.ca (M.K. Denk).

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Table 1
Electronic energies and (in brackets) zero point vibrational energies in kcal mol^{-1} for imidazol-2-ylidene **1H** and the cations **2H**–**4H** at different levels of theory [a]

	E (kcal mol^{-1}) [b]			
	1H	**2H**	**3H**	**4H**
HF/6-31G*//HF/6-31G*	−141054.91 (48.36)	−141250.64 (56.39)	−141232.77 (56.08)	−141053.22 (57.69)
B3PW91/6-31G*//B3PW91/6-31G*	−141860.28 (45.06)	−142064.16 (52.26)	−142051.21 (52.67)	−142129.42 (53.81)
B3PW91/cc-pVDZ//B3PW91/cc-pVDZ	−141875.54 (44.87)	−142076.48 (51.78)	−142064.32 (52.15)	−142139.64 (53.53)
B3LYP/6-311+G(2d,p)//HF/6-31G*	−141961.87	−142160.11	−142149.11	−142221.17

[a] R = H.

[b] Converted from Hartrees: 1 Hartree = 627.5095 kcal mol^{-1}.

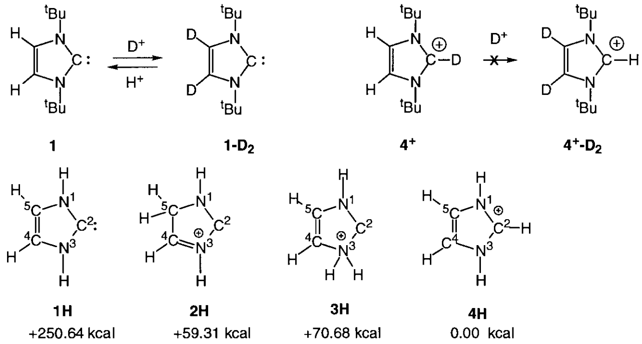
extraction with hexanes or other hydrocarbons that are imiscible with DMSO.

The degree of deuteration depends on the relative amount of **1** and DMSO-d_6. The position of the deuterium atoms is obvious from the ^{13}C-NMR spectrum of **1-D$_2$** which shows the characteristic 1:1:1 deuterium triplet (^1J(C,D) = 27.2 Hz) for the olefinic carbon atoms at 114.9 ppm (^3J(C,D) unresolved). The IR-spectrum of **1-D$_2$** shows two strong, partially overlapping IR bands at 2309 and 2318 cm^{-1}, which correspond to the anti-symmetric and symmetric C–D stretching frequency combinations. The EI–MS spectrum shows the expected mass and isotope pattern of the bis-deuteration product ($m/z = 182$, $[M]^{+\cdot}$). The deuteration of **1** is reversible: dissolution of the deuterated carbene **1-D$_2$** in DMSO leads to the reformation of **1**.

The formation of **1-D$_2$** from **1** suggests a reversible protonation/deuteration of **1** via a σ-complex **2** (Scheme 1). The formation of the σ-complex **2** is counter-intuitive. Protonation of the highly basic carbene carbon atom should be thermodynamically more favorable [10,11]. We have therefore investigated the relative thermodynamic stability of the different protonation products **2**–**4** through calculations of model compounds (**2H**–**4H**) at the B3LYP/6-311 + G(2d,p)//HF/6-31G(d) level [12].

The structures **2H**–**4H** are stationary points on the hypersurface. The geometrical parameters of the calculated structures **1H**–**4H** are listed in Table 2. The sequence of relative stabilities (Table 1, kcal mol^{-1}) is **4H** (= 0) > **2H** (+59.31) > **3H** (+70.7). This confirms, that the protonation of the carbene **1H** at the olefinic carbon (formation of **2H**) is indeed thermodynamically unfavorable versus the formation the imidazolium cation **4H**. The observed H/D exchange reaction would therefore be only kinetically favored with respect to protonation of the carbene carbon atom.

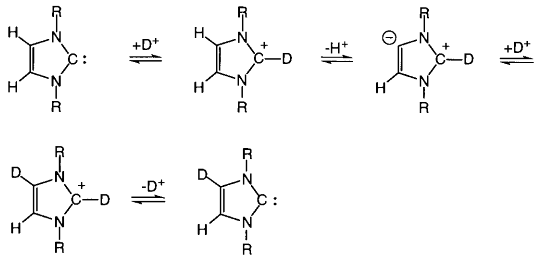
The H/D exchange reaction bears a formal analogy to the recently reported reaction of an imidazol-2-ylidene with CCl_4 which leads to the formation of the 4,5-dichloro-imidazol-2-ylidene [2d]. At first sight, the mechanism that was suggested for this reaction seems to be capable of explaining the observed H/D exchange reaction as well (Scheme 2). However, the mechanism



Scheme 1. Deuteration of **1**. Energies are at the at the B3LYP/6-311 + G(2d,p)//HF/6-31G* level, $T = 0$ K and are referenced to **4H** = 0.00. Zero point energies were obtained at the B3PW91/cc-pVDZ level and are unscaled.

Table 2
Bond distances (pm) and angles (°) for the carbene **1H** and the protonated carbenes **2H**–**4H** at the HF/6-31G* level

	1H	**2H**	**3H**	**4H**	**[4]Cl** [13]
N1–C2	131.3	130.3	131.6	131.3	133.2(7)
C2–N3	131.3	147.0	154.1	131.3	133.5(7)
N3–C4	138.2	127.3	146.8	138.2	137.2(7)
C4–C5	134.0	148.4	133.0	134.0	135.9(7)
C5–N1	138.2	144.9	142.2	138.2	137.7(7)
N1–C2–N3	107.9	100.4	98.7	108.0	108.6(4)
C2–N3–C4	113.7	114.4	109.4	109.5	108.3(8)
N3–C4–C5	105.8	108.5	105.8	106.5	107.1(5)
C4–C5–N1	105.8	99.2	108.2	106.5	108.6(4)
Point-group	C_{2v}	C_s	C_s	C_2	C_2



Scheme 2. H/D exchange of imidazol-2-ylidenes via imidazolium cations.

requires the deuteration of the carbenium cation **4**. This is in contrast to our experimental findings which show, that the carbenium salt **[4]Cl** [13] is not deuterated under the reaction conditions that lead to rapid H/D exchange for the carbene.

Although the H/D exchange of **1** may involve the participation of DMSO in the transition state of the reaction, replacement of DMSO-d_6 as deuterium source with D_2O or CD_3OD did likewise lead to the rapid formation of **1-D$_2$**. This makes a specific participation of the counterion (dimsyl, methoxy of hydroxy) unlikely.

Irrespective of the operating mechanism, the reaction is a convenient tool for the 4,5-bis-deuteration of **1** and, presumably, other imidazol-2-ylidenes as well.

3. Experimental

3.1. Synthesis of 1,3-di-tert-butyl-4,5-bis-deutero-imidazole-2-ylidene

The deuterium exchange reactions were studied through NMR scale reactions at room temperature. DMSO-d_6 (99.5 atom% D) was dried by sonication over CaH_2 followed by three freeze/pump/thaw cycles. Methanol-d_4 (99.8 atom% D, Merck-Frost) and D_2O (99.9 atom% D, Merck-Frost) were used as received. Carbene **1** was obtained from 1,3-di-*tert*-butyl-imidazolium chloride (**[4]Cl**) [13] according to published procedures [2a]. The deuterated carbene **1-D$_2$** can be isolated by sublimation at reduced pressure (1 Torr) after removal of the solvent (methanol-d_4) or by extraction from the solvent (DMSO-d_6) with pentane or hexane.

1,3-Di-*tert*-butyl-imidazol-2-ylidene (1.3 g) of is dissolved in 5 ml of DMSO-d_6 and stirred for 10 min. The solution is extracted with three 5 ml portions of dry pentane. The combined pentane phase is stirred with 5 ml of fresh DMSO-d_6, the solvent evaporated in vacuo and the crystalline white residue sublimed under reduced pressure (40°C/1 Torr), m.p. 60–61°C. Selected NMR data: ^{1}H (DMSO-d_6): δ 1.48 [s, $C(CH_3)_3$]; (C_6D_6): δ 1.51 [s, $C(CH_3)_3$]. $^{13}C\{^{1}H\}$ (DMSO-d_6): δ 30.95 [s, $C(CH_3)_3$], 55.16 [s, $C(CH_3)_3$], 115.44 [t, $CD{=}CD$, $^{1}J(C,D) = 27.5$ Hz], 208.7 [s br, N_2C:]. $^{13}C\{^{1}H\}$ (C_6D_6): δ 31.46 [s, $C(CH_3)_3$], 55.76 [s, $C(CH_3)_3$], 114.90 [t, $CD{=}CD$ $^{1}J(C,D) = 27.2$ Hz], 212.9 [s br, N_2C:]. EI–MS (70 eV): m/z (rel. int.%): 182 (21) $[M]^+$, 126 (36), 111 (17), 83 (12), 71 (100), 70 (76), 57 (64). IR (hexanes, CaF_2 cell, cm^{-1}): 2309 s, 2318 s.

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[13] The imidazolium salt $[\mathbf{4}]^+\mathbf{Cl}^-$ was prepared from *tert*-butyl amine, glyoxal, and formaldehyde following the procedure in Ref. [2a]. X-ray quality crystals of $[\mathbf{4}]^+\mathbf{Cl}^-$ were grown by slow evaporation of a concentrated aqueous solution. Monoclinic, space group $P2_1/n$, $a = 9.036(1)$, $b = 12.0229(1)$, $c = 11.341(1)$ Å; $\alpha = \gamma = 90$, $\beta = 95.78°$, volume = 1225.7(4) Å^3, $Z = 4$, $D_{\text{calc.}} = 1.175$ g cm^{-3}, $4.37 \leq \theta \leq 23.02°$, total reflections 6315, independent reflections 1695 ($R_{\text{int}} = 0.1140$), scaleback absorption correction, refinement full-matrix least squares on F^2, Goodness-of-fit = 1.057, $R_1 = 0.0697$, largest difference peak and hole $+0.360$ and -0.264 e Å^{-3}.