ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 617–618 (2001) 242–253

Journal of Organo metallic Chemistry

Synthesis and reactivity of subvalent compounds☆ Part 11. Oxidation, hydrogenation and hydrolysis of stable diamino carbenes

Michael K. Denk *, José M. Rodezno, Shilpi Gupta, Alan J. Lough

Department of Chemistry, Erindale College, University of Toronto, 3359 Mississauga Road, Mississauga, Ontario, Canada L5L 1C6

Received 26 May 2000; accepted 2 August 2000

Abstract

The reactivities of the two stable diamino carbenes 1,3-di-*tert*-butylimidazol-2-ylidene (**1**) and 1,3-di-*tert*-butylimidazolin-2-ylidene (**2**) toward hydrogen, oxygen, water and carbon monoxide were investigated. The carbenes do not react with O_2 or CO but are attacked by water to give the respective hydrolysis products ^{t}Bu–N=CHCH$_2$–N(CHO)^{t}Bu (**7**) and ^{t}Bu–NH–CH$_2$CH$_2$–N(CHO)^{t}Bu (**8**). While **2** is hydrolyzed instantaneously, the aromatically stabilized **1** reacts only very slowly and can be handled in air for brief periods of time. The carbenes **1** and **2** are unreactive towards H_2 alone but can be catalytically hydrogenated to the respective aminals 2,3-dihydro-1,3-di-*tert*-butylimidazole (**5**) and 1,3-di-*tert*-butylimidazolidine (**6**). The reaction products were characterized by single crystal X-ray crystallography, multinuclear NMR spectroscopy (^{1}H, ^{13}C, ^{17}O), IR spectroscopy and DFT methods. The extent of aromatic delocalization in **1** was investigated through isodesmic hydrogenation reactions at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level. At this level of theory, the 'carbene oxide' (2,3-dihydro-imidazol-2-one) retains ca. 50% of the aromatic delocalization energy of the carbene. The oxidation of the diamino carbenes to the 'carbene oxides' (ureas) is calculated to be exothermic by -79.1 kcal mol^{-1} (**1**) and -86.4 kcal mol^{-1} (**2**). The oxygen affinity of the carbenes resembles that of trimethylphosphine (-79.7 kcal mol^{-1}) and triethyl phosphite (-88.6 kcal mol^{-1}) and is significantly higher than that of CO (-67.6 kcal mol^{-1}). The aminals **5** and **6** are structurally related to Thauer's hydrogenase (**TH$_2$/TH$^+$**) but do not show hydrogenase activity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Carbenes; Deoxygenation; DFT calculations; Thermochemistry; Oxygen; Hydrogenase; Aminal; Urea; Hydrogenation; Hydrolysis

---

1. Introduction

The structurally characterized imidazol-2-ylidenes reported by Arduengo et al. [1,2] constitute the first [3] stable carbenes. They are stabilized electronically by an aromatic sextet [1–5] and, unlike the more recently obtained carbenes **2**, [6,7] do not require additional steric stabilization through bulky substituents on nitrogen (Scheme 1) [7].

Derivatives of **1** like the benzoanellated benzimidazol-2-ylidenes [8] and the 4-aza-imidazol-2-ylidene [9], and even the open-chain diamino carbene (^{i}Pr$_2$N)$_2$C: [10] have been described as stable, colorless solids. Stable aminooxy- and aminothio carbenes have been described by Alder et al. [11]. With one notable exception [1h], all stable carbenes have been described as air sensitive but the precise reason for this behavior has remained unclear.

2. Results and discussion

2.1. Reactivity

In our previous studies on the synthesis, structure and bonding of carbenes **1** and **2** [4,7] and the isostructural silylenes [4,12], germylenes [4,13], and phosphenium cations [14] the compounds were handled with inert gas techniques due to their apparent air sensitiv-

---

☆ This paper was presented at the Canadian Society for Chemistry Conference, May 27–May 31, 2000, Calgary, Alberta. Part 10, see Ref. [34].

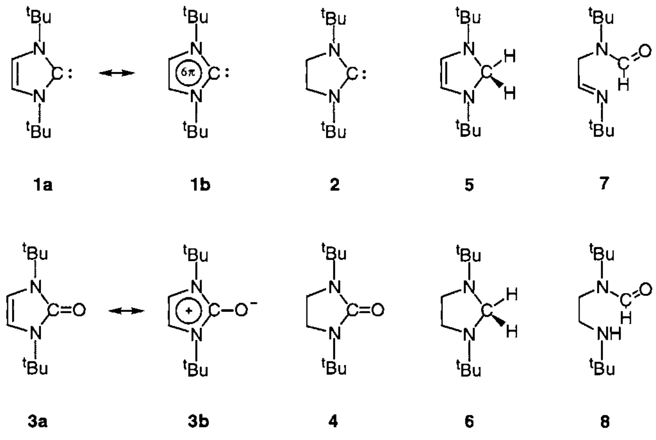
* Corresponding author. Tel.: + 1-905-8285335.

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

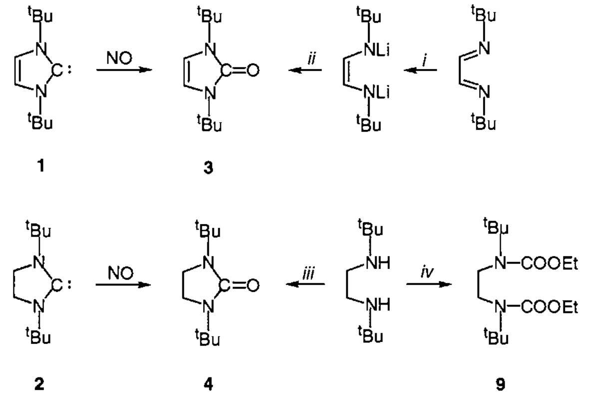
0022-328X/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0022-328X(00)00551-9

ity. It seemed obvious to assume that these subvalent compounds will readily be oxidized by O_2 or other oxidizing agents. An investigation of the stable carbenes **1** and **2** has presented us with a different picture.

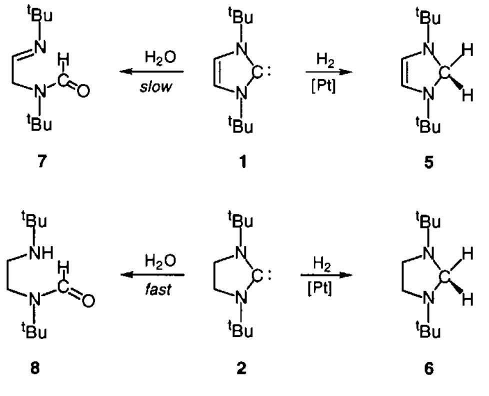
We found, much to our surprise, that the carbenes **1** and **2** are inert towards oxygen. The stable carbenes **1** and **2** are not only inert towards oxygen [15] but are also unreactive towards other oxidizing agents. They do not react with CuO, Cu_2O or HgO, even after prolonged heating. Clean oxidation to the respective ureas **3** and **4** was observed with NO (Scheme 2).



Scheme 1. Stable carbenes (**1**, **2**) and their reaction products (**3**–**8**).



Scheme 2. Synthesis of **3** and **4**. (i) 2.2 equivalents Li, THF; (ii) one equivalent Cl–COOEt, THF, –LiOEt; (iii) two equivalents *n*-BuLi, 2.2 equivalents Cl–COOEt, *n*-hexane, –LiOEt; (iv) two equivalents Cl–COOMe, *n*-hexane.



Scheme 3. Hydrolysis and hydrogenation of stable carbenes **1** and **2**.

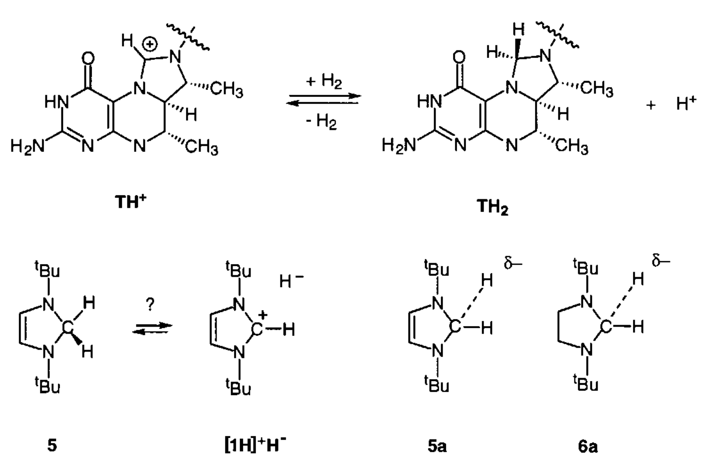
The ‘air sensitivity’ of **1** and **2** is due to the attack of water, which leads to ring opening to give the formamides **7** and **8**. While **2** is instantly hydrolyzed by moist THF or by brief exposure to air, hydrolysis of the aromatically stabilized carbene **1** requires days to become noticeable and months to be completed. As a result of this difference in reactivity, carbene **1** can be handled in air for brief periods of time, while **2** requires the usual inert gas techniques.

The hydrolysis of **1** and **2** can, in principle, proceed through a polar, stepwise mechanism (attack of H^+ or OH^- as initial step) or as insertion of the carbene into H_2O. In the case of the conveniently slow hydrolysis of **1**, the reaction rate was not affected by the addition of catalytic amounts of HCl or NH_3. Addition of HCl merely leads to the formation of the imidazolium salt **[1H]$^+$Cl$^-$** which is entirely inert towards hydrolysis under ambient reaction conditions. In the light of these results, it is unlikely that protonation of the carbene or nucleophilic attack by OH^- are rate determining steps of the hydrolysis. Most likely, the reaction with water proceeds via an insertion mechanism.

Conflicting results have been reported for the reactivity of imidazol-2-ylidenes towards carbon monoxide [16]. While Lyashchuk et al. have reported the isolation of the corresponding diamino-ketene **1**=C=O from mixtures of **1** and CO [16b], Arduengo et al. have ruled out the formation of this compound as a result of ab initio calculations [16a]. In agreement with Arduengo’s findings, we were unable to observe the formation of any reaction products in mixtures of **1** and CO. Carbene **2**, which should be more likely to undergo reaction with CO as a result of its lack of aromatic stabilization, was also found to be inert towards CO.

Hydrogenation energies obtained from DFT calculations (see below) indicate that the insertion of carbenes **1** and **2** into H_2 should be exothermic (Scheme 6). In the absence of a catalyst, both carbenes are inert towards hydrogen but addition of catalytic amounts of palladium or platinum leads to slow hydrogen uptake and to the clean formation of the 1,1-addition products, the aminals **5** and **6** (Scheme 3). The CC-double bond present in **1** is unreactive under these conditions (1 atm H_2, room temperature).

The aminals **5** and **6** show surprisingly different chemical reactivity. While **6** is not attacked by air or moisture under ambient conditions, **5** is decomposed even by trace amounts of oxygen to give a resinous, insoluble material. Under strict exclusion of air, **5** is thermally stable and can be stored indefinitely. This leads us to conclude that **5** is catalytically polymerized by traces of oxygen. It is interesting to note that the



Scheme 4. Hydrogenation products (**5**, **6**) of stable carbenes (**1**, **2**) and their relationship to Thauer's hydrogenase (TH^+/TH_2).

closely related compound **3** which contains the same 1,2-diamino-ethene unit but is stabilized by the amide resonance and aromatic delocalization, is air stable. The high reactivity of **5** must thus be linked to the presence of the *unstabilized*, electron rich 1,2-diamino-olefin moiety.

The aminals **5** and **6** are not only of interest in their relationship to the carbenes **1** and **2**, but are also structurally related to Thauer's metal-free hydrogenase (**TH^+/TH_2**) [17]. This remarkable, naturally occurring aminal reacts with protons in a fashion that is reminiscent of the behavior of compounds with negatively polarized 'hydridic' hydrogen like silanes and boranes. This reactivity leads to the intriguing question whether **TH_2**, the hydrogenated form of Thauer's hydrogenase, and related aminals like **5** or **6** do in fact have hydridic structures **5a** ($[1H]^+H^-$) or **6a** ($[2H]^+H^-$). Precedence for these structures are the ionic imidazolium chlorides $[1H]^+Cl^-$ and $[2H]^+Cl^-$ (Scheme 4).

The NMR data of **5** and **6** do not offer any evidence for the presence of the ionic or crypto-ionic structures but are in good agreement with covalent bonding. The computationally obtained structures of **5H** and **6H** are likewise covalent and give no indication for ionic structures **5a** or **6a**.

While the possibility of a hydridic structure can thus be ruled out, **5** or **6** may still resemble Thauer's hydrogenase in their reactivity in acting as hydride donors. The possible hydrogenase type reactivity of **5** and **6** was examined by reacting the respective carbenium salts **$[1H]^+Cl^-$** [18] and **$[2H]^+Cl^-$**, [19] which correspond to **TH^+**, with H_2. Both salts were found to be completely inert under 1 atm of H_2 even after the addition of pyridine or 4-dimethylaminopyridine as auxiliary bases (no formation of **5** or **6**). The ability of Thauer's hydrogenase **TH_2/TH^+** to reversibly transfer hydride ions is thus not a function of the aminal skeleton per se, but is the result of the rather specific steric and electronic fine tuning of TH_2 and TH^+. These experimental observations confirm earlier predictions derived from the computational investigation of simplified models of **TH_2** and **TH^+** [17c,d].

2.2. Synthesis

Carbene **2** was obtained from the corresponding thiourea by reduction with potassium in THF [7a], carbene **1** from the imidazolium salt $[1H]^+Cl^-$ through deprotonation [18]. The imidazol-2-one **3** has been previously obtained by carbonylation of 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene with $Fe(CO)_5$ or $Fe_2(CO)_9$ [20]. The reaction has been reported to give a rather complex product mixture from which **3** could only be obtained after chromatographic separation in unspecified yield. Vrieze and Staal obtained **3** in an analogous fashion by using only catalytic amounts of $Fe_2(CO)_9$ and high pressures of CO, but isolation of **3** still required HPLC separation [21].

We were interested in a high yield synthesis of **3** that would avoid lengthy separation procedures and found that reduction of the easily accessible 1,4-di-*tert*-butyl-1,4-diaza-1,3-butadiene with two equivalents of lithium and subsequent reaction with ethyl chloroformate affords **3** in good yield as the only product (Scheme 2).

The saturated imidazolidine-2-one **4** was obtained via the dilithio salt of *N*,*N*′-di-*tert*-butylethylenediamine and ethyl chloroformate. Use of the dilithio salt is necessary, because the reaction of the free amine with chloroformate leads to the biscarbamic acid ester **9**. The imidazolidines **5** and **6** are accessible through catalytic hydrogenation of the respective carbenes **1** and **2** (Pd, 1 atm H_2). Alternative routes that do not require the carbenes as starting materials are the condensation reaction of *N*,*N*′-di-*tert*-butylethylenediamine with formaldehyde (formation of **6**) and the reduction of the imidazolium chloride $[1H]^+Cl^-$ [18] with $LiAlH_4$. (formation of **5**).

2.3. Structure and bonding

Compounds **1**, **3**, **4** and **8** were studied through single crystal X-ray crystallography [22,23]. The structure of **2** has been previously reported [7a]. Figs. 1–4 show ORTEP [23] presentations for the molecules, experimental details of the structure determination are listed in the supplementary material. The similarity of the π-systems in the carbenes **1** and **2** and their 'oxides' **3** and **4** is reflected by the similarity of the respective bond distances and bond angles. For a discussion of the NMR data and for ab initio calculations [24,25] see below.

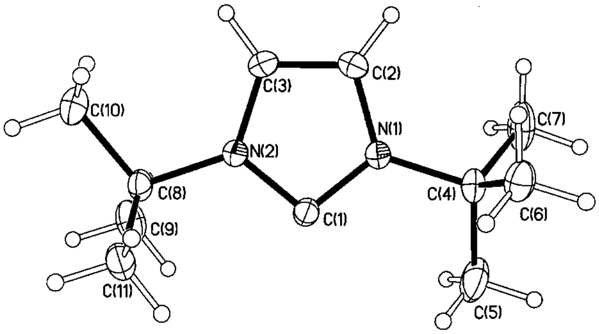


Fig. 1. Molecular structure of (^{t}BuNCH=CHN^{t}Bu)C (**1**) in the solid state. ORTEP [23] view, thermal ellipsoids are at the 50% probability level. Selected bond distances [pm] and bond angles [°]: C(1)–N(1) 136.6(2), C(1)–N(2) 136.6(2), N(1)–C(2) 138.0(2), N(2)–C(3) 138.0(2), N(1)–C(4) 148.9(2), N(1)–C(4) 149.2(3), C(2)–C(3) 134.1(2), N(1)–C(1)–N(2) 102.19(12), C(1)–N(1)–C(2) 112.57(12), C(1)–N(2)–C(3) 112.20(12), N(1)–C(2)–C(3) 106.23(14), N(2)–C(3)–C(2) 106.81(14), C(4)–N(1)–C(2) 123.53(13), C(8)–N(2)–C(3) 125.74(12), C(4)–N(1)–C(1) 123.74(12), C(8)–N(2)–C(1) 122.04(13).

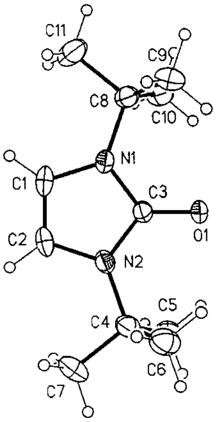


Fig. 2. Molecular structure of (^{t}BuNCH=CHN^{t}Bu)C=O (**3**) in the solid state. ORTEP [23] view, thermal ellipsoids are at the 50% probability level. Selected bond distances [pm] and bond angles [°]: O(1)–C(3) 123.7(3), C(3)–N(1) 138.1(3), C(3)–N(2) 137.5(3), N(1)–C(1) 139.1(3), N(2)–C(2) 139.1(3), C(1)–C(2) 133.4(3), N(2)–C(4) 148.7(3), N(1)–C(8) 148.6(3), N(1)–C(3)–N(2) 106.0(2), C(3)–N(1)–C(1) 108.9(2), C(3)–N(2)–C(2) 108.8(2), N(2)–C(2)–C(1) 108.4(2), N(1)–C(1)–C(2) 107.9(2), C(2)–N(2)–C(4) 127.5(2), C(1)–N(1)–C(8) 127.2(2), C(3)–N(1)–C(8) 123.9(2), C(3)–N(2)–C(4) 123.7(2).

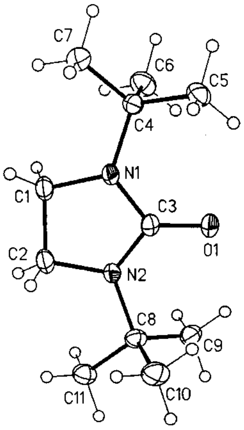


Fig. 3. Molecular structure of (^{t}BuNCH$_2$–CH$_2$N^{t}Bu)C=O (**4**) in the solid state. ORTEP [23] view, thermal ellipsoids are at the 50% probability level. Selected bond distances [pm] and bond angles [°]: O(1)–C(3) 122.7(2), C(3)–N(1) 138.3(2), C(3)–N(2) 137.7(2), N(2)–C(8) 148.9(2), N(2)–C(2) 145.8(2), N(1)–C(1) 146.2(2), N(1)–C(4) 148.6(2), C(1)–C(2) 150.7(2), O(1)–C(3)–N(1) 125.57(14), O(1)–C(3)–N(2) 125.35(14), C(3)–N(2)–C(8) 122.47(12), C(3)–N(1)–C(4) 122.42(12) C(3)–N(1)–C(1) 108.38(12) C(3)–N(2)–C(2) 108.98(12), N(1)–C(1)–C(2) 102.59(12), N(2)–C(2)–C(1) 102.10(12).

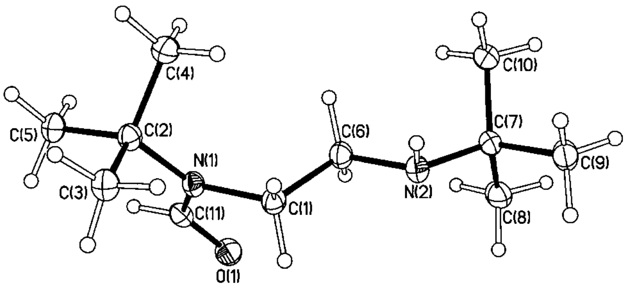


Fig. 4. Molecular structure of ^{t}BuN(CH=O)CH$_2$–CH$_2$NH^{t}Bu (**8**) in the solid state. ORTEP view, thermal ellipsoids are at the 50% probability level. Selected bond distances [pm] and bond angles [°]: O(1)–C(11) 123.63(17), C(11)–N(1) 134.14(18), C(1)–N(1) 147.29(17), N(1)–C(2) 149.38(18), C(1)–C(6) 152.5(2), C(6)–N(2) 145.86(18, N(2)–C(7) 148.27(18), O(1)–C(11)–N(1) 123.98(14), C(11)–N(1)–C(2) 124.51(12), C(11)–N(1)–C(1) 116.65(12), N(1)–C(1)–C(6) 114.15(12), C(6)–N(2)–C(7) 117.45(12).

Consistent with aromatic delocalization, **1** and **3** have planar ring geometries whereas **2** and **4** are puckered, with slightly pyramidal geometries at the nitrogen atoms (Table 1). The carbenes are characterized by small N–C–N bond angles. The short C(II)–N bond distances imply significant double bond character. The C–O bond distance in **3** appears slightly elongated versus **4** (123.7 versus 122.7 pm). While consistent with the contribution of mesomeric structure **3b** (compare spectroscopic differences below) the difference is small compared with the standard deviations.

2.4. Infrared and nuclear magnetic resonance spectra

The polarization of the CO double bond by the aromatic π-system in **3** is reflected by the IR and NMR data of **3** and **4**. The C=O stretching frequency of **3** (1685 cm^{-1}) is significantly lowered versus **4** (1705 cm^{-1}) [26,27]. The ^{13}C and ^{17}O-NMR shifts of the carbonyl groups (Table 2) in **3** and **4** also show significant differences. Compound **3** shows an additional shielding of the carbonyl carbon atom ($\Delta\delta = 8.9$ ppm in C_6D_6, 9.5 ppm in CD_3CN) due to the aromatic stabilization of the partial positive charge in mesomeric structure **3b**. The ^{17}O-NMR spectrum of **3** shows a strong shielding of the oxygen atom relative to **4** ($\Delta\delta =$ 35 ppm in C_6D_6, 38 ppm in CD_3CN). The polarization of the carbonyl group by the aromatic sextet is also noticeable from the melting points of the two compounds (**3**: 117°C, **4** 64°C). A co-sublimation experiment showed that **3** is significantly less volatile than **4**. The chemical shifts of the ring protons reflect the fact that **1** is more aromatic than the urea **3**.

3. Computational studies

The structures (Table 2) and energies (Table 3) of the model compounds **1H**–**6H** were calculated [24] at the B3LYP/6-31G(d) level. The final energies were corrected by the addition of zero point energies (ZPE) and, where indicated, thermal energies (298.15 K). The vibratory energies were scaled by 0.9804, the scaling factor recommended for B3LYP/6-31G(d) calculations [25].

The structures of **1H**–**4H** are in good agreement with the experimental structures of **1**–**4**. The equilibrium geometries of **1H**–**4H** show planar (**1H**, **3H**, **4H**) or close to planar (**2H**) ring geometries. Compounds **5H** and **6H** have strongly pyramidalized nitrogen atoms which gives rise to a series of isomers that are characterized by *syn*- or *anti*- orientation of the NH bonds (Scheme 7).

The isomers were studied individually by choosing starting geometries with the H–N–N–H dihedral angles frozen at 0° or 180°. The restriction was then lifted

Table 1
Selected spectroscopic data of stable carbenes (**1**, **2**) and the respective ureas (**3**, **4**)

	Chemical shift (ppm)	**1** C_6D_6	**3** C_6D_6	**3** CD_3CN	**2** C_6D_6	**4** C_6D_6	**4** CD_3CN
^1H	N–CH=	6.79	5.96	6.34			
	$N–CH_2$				3.04	2.67	3.14
	$C(CH_3)_3$	1.51	1.42	1.46	1.36	1.32	1.27
^{13}C	$>C:/>C=O$	212.9	152.7	153.3	238.3	161.6	162.8
^{17}O	$>C=O$		215	209		250	247

Table 2
Experimental (**1–4**) and calculated (**1H–6H**) structures of heterocycles $(CH)_2(NR_2)E$ and $(CH_2)_2(NR_2)E$ at the B3LYP/6-31G(d) level; $R = {}^tBu$ (**1–4**), H (1H–6H); $E = CH_2$ (**5**, **5H**, **6**, **6H**), >C: (**1**, **1H**, **2**, **2H**) or C=O (**3**, **3H**, **4**, **4H**)

	1H	**1**	**3H**	**3**	*syn*-**5H**	*anti*-**5H**	**2H**	**2** [7a]	**4H**	**4**	*anti*-**6H**	*syn*-**6H**
N–E	137.2	136.6(2) 136.6(2)	139.3	138.1(3) 137.5(3)	147.1	148.4 147.3	135.4	134.83(13) 143.73(13)	139.4	138.3(2) 137.7(2)	148.17 148.15	147.1
N–C(IV)	139.3	138.0(2) 138.0(2)	139.5	139.1(3) 139.1(3)	147.7	142.1 144.5	147.8	147.64(14) 147.54(14)	145.8	146.2(2) 145.8(2)	147.31 147.31	147.7
C–C	135.6	134.1(2)	135.2	133.4(3)	157.4	133.8	154.2	151.2(12)	154.4	150.7(2)	153.90	157.4
E=X			122.2	123.7(3)					121.7	122.7(2)		
N–E–N	99.9	102.19(12)	102.8	106.0(2)	108.6	105.6	103.9	106.44(9)	106.4	109.07(12)	108.74	108.6
N–C–C	105.5	106.23(14)	107.2	107.9(2) 108.4(2)	106.0	110.9 110.6	100.9	101.34(9) 100.96(9)	100.9	102.59(12) 102.10(12)	103.81 103.81	106.0
R–N–C	123.9	123.53(13) 125.74(12)	127.0	127.2(2) 127.5(2)	108.2	109.8 113.8	121.2	120.53(8) 120.53(8)	120.8	120.90(12) 118.86(12)	108.12 108.12	108.2
E–N–C	114.6	112.57(12) 112.20(12)	111.4	108.9(2) 108.8(2)	103.2	103.2 103.2	116.0	112.51(8) 112.91(8)	110.6	108.38(12) 108.98(12)	105.63 105.63	103.2
E–N–R	121.5	125.74(12) 123.53(12)	121.6	123.7(2) 123.9(2)	107.7	112.6 109.9	120.8	123.10(8) 123.37(9)	116.1	122.42(12) 122.47(12)	108.38 108.38	107.7
Point group	C_{2v}	C_2	C_{2v}	C_2	C_1	C_1	C_2	C_2	C_2	C_2	C_1	C_s

Table 3

Energies (in kcal mol^{-1}) of the model compounds **1H–6H** at the B3LYP/6-31G(d)//B3LYP/6-31G(d) level, converted to kcal mol^{-1} with 1 Hartree = 627.51 kcal; zero point energies (ZPE*) were multiplied with a scaling factor of 0.9804 [25] (ZPE* = 0.9804•ZPE)

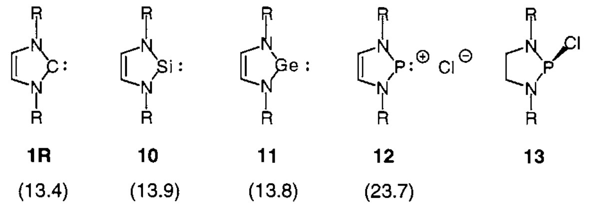
	E_{el}	ZPE	E_{th} (298.15 K)	E_0 (E_{el}+ZPE*)	$E_{298.15}$ ($E_{el}+E_{th}$)
1H	−141921.86	44.75	47.16	−141877.99	−141875.62
2H	−142678.02	59.05	62.02	−142620.13	−142617.22
3H	−189165.95	47.44	50.58	−189119.43	−189116.36
4H	−189930.51	63.18	66.38	−189868.57	−189865.43
anti-5H	−142682.78	59.27	62.01	−142624.67	−142621.99
syn-5H	−142682.19	59.12	61.91	−142624.23	−142621.49
anti-6H	−143454.35	74.83	77.84	−143380.99	−143378.03
syn-6H	−143452.43	74.93	77.89	−143378.97	−143376.07
H_2C:	−24551.80	10.42	12.20	−24541.88	−24539.84
$H_2C{=}O$	−71829.55	16.83	18.63	−71813.05	−71811.29
F_2C:	−149143.19	4.36	6.24	−149139.41	−149137.07
$F_2C{=}O$	−196403.10	8.87	10.94	−196394.41	−196392.37
H_2	−737.63	6.37	7.85	−731.38	−729.93
CO	−71102.82	3.16	4.64	−71099.72	−71098.27
CO_2	−118336.43	7.27	8.94	−118329.30	−118327.66

and the geometries were fully optimized without symmetry restrictions at the B3LYP/6-31G(d) level. Both isomers of **5H** and **6H** represent local minima.

3.1. Aromatic stabilization energies and hydrogenation energies

Evidence for the extent of aromatic stabilization in carbenes **1** and related species has been obtained from spectroscopic [4] and computational [5] investigations. However, the effect of aromatic delocalization can also manifest itself in significant structural changes. For the isoelectronic phosphenium cations **12** [14] and **13** [14], the additional aromatic delocalization operating in **12** is strong enough to change the overall bonding situation. While **13** exists as a covalent chlorophosphane, **12** is an ionic phosphenium chloride (Scheme 5) [14].

We have previously used *ab initio* calculations to quantify the extent of aromatic stabilization through isodesmic hydrogenation reactions and have obtained aromatic stabilization energies (ASEs) for the hetero-analogs of **1**, the silylenes [12], germylenes [13a], and phosphenium cations [14] (Scheme 5). We now use the same approach to study the oxygen affinity of the carbenes **1** and **2** and the extent of aromatic delocalization operating in **1** and **3** (Schemes 6 and 8).



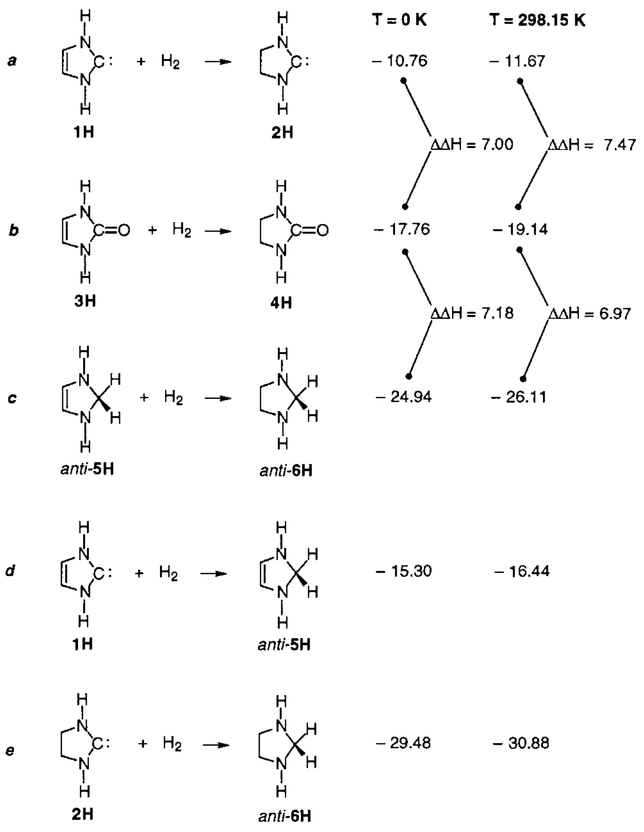
Scheme 5. Aromatic stabilization energies (in kcal mol^{-1}) derived from isodesmic hydrogenation reactions for diamino carbenes **1** and isoelectronic species **10**–**13**.

The aromatic stabilization energies (ASEs) of compounds **1H** and **3H** are derived from the hydrogenation reactions **a**–**c**. Comparison of equations **a** and **c** shows a significant aromatic stabilization of the carbene **1H** ($ASE_{289.15} = |\mathbf{a} - \mathbf{c}| = 14.44$ kcal mol^{-1}). As expected, the delocalization energy of the carbene **1H** is diminished by the introduction of the exocyclic CO double but the urea **3H** still retains a significant aromatic delocalization energy ($ASE_{289.15} = |\mathbf{b} - \mathbf{c}| = 6.97$ kcal mol^{-1}).

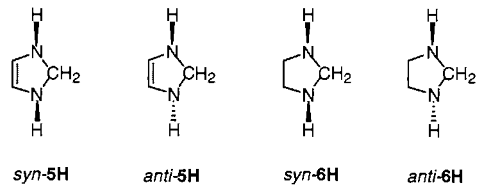
The hydrogenation reactions of carbenes **1H** and **2H** to the respective aminals **5H** and **6H** are both exothermic (Scheme 7). This rules out the synthesis of carbenes through the 1,1-elimination of H_2 from aminals, but the magnitude of the reaction energies suggests that the reaction might become feasible as a transfer hydrogenation process with a suitable hydrogen acceptor.

3.2. Oxophilicity of diamino carbenes

In principle, stable carbenes like **1** or **2** should be powerful deoxygenating agents with significant synthetic potential. Transient carbenes have been shown to act as potent deoxygenating agents towards oxiranes [28], and ureas [29] in recent studies by Warkentin and Lusztyk [28] and by Jackson [29]. Particularly noteworthy is the deoxygenation of ureas by fluorene-9-ylidene reported by Jackson et al. [29] because it constitutes the first example of an oxygen transfer reaction from a stabilized carbene to an unstabilized carbene. The rapid reaction of unstabilized carbenes with oxygen in cryogenic matrices has been studied by Sander et al. [30]. The reluctance of carbenes **1** and **2** to react with oxygen is surprising in this context and leads to the question about the thermodynamic potential of carbenes to act as deoxygenating agents.



Scheme 6. Aromatic stabilization energies (in kcal mol^{-1}) derived from isodesmic hydrogenation reactions for diamino carbenes **1** and ureas **3**; B3LYP/6-31G(d)//B3LYP/6-31G(d) level [24,25].



Scheme 7. Geometrical isomers of 5H and 6H. Relative energies at 0 K (298.15 K) in kcal mol^{-1}: *syn*-5H = 0 (0), *anti*-5H = 0.44 (+0.50); *syn*-6H = +2.02 (+1.96), *anti*-6H 0 (0).

The thermodynamic ability of subvalent compounds to act as deoxygenating agents has been reviewed by Holm and Donahue [31] who have tabulated experimental heats of formation to establish a thermodynamic scale of increasing oxygen affinity (Eq. (1), Table 4). For covalent compounds, the extremes of the oxophilicity scale are defined by the pairs O_2/O_3 ($\Delta H_{298.15} = +34$ kcal mol^{-1}) [31] and $Me_3Si{-}SiMe_3$/$Me_3Si{-}O{-}SiMe_3$ ($\Delta H_{298.15} = -99.0$ kcal mol^{-1}) [31]. Compared to hexamethyldisilane, carbon monoxide, the only divalent carbon compound listed, is only a moderately strong deoxygenating agent ($\Delta H_{298.15} = -67.6$ 34 kcal mol^{-1}) [31]. We were interested to compare the oxophilicity of the carbenes **1** and **2** with that of other subvalent compounds like CO, phosphines, etc.

$$f \qquad X + 1/2\,O_2 \longrightarrow X{=}O \tag{1}$$

The oxophilicity of the carbenes **1** and **2** is defined through the reactions $\mathbf{1H} + 0.5O_2 \rightarrow \mathbf{3H}$ and $\mathbf{2H} + 0.5O_2 \rightarrow \mathbf{4H}$ (Scheme 8). To avoid the inaccuracies that result from the comparison of open shell systems (triplet oxygen) with closed shell systems (**1H**, **2H**), the oxophilicities of **1H** and **2H** were not derived directly from reactions of the singlet carbenes **1H** and **2H** with triplet oxygen but rather from the reactions of **1H** and **2H** with CO_2 (formation of CO). The reaction energies for the oxidation of the carbenes with triplet oxygen were obtained by adding the reaction equation $CO + 0.5\ O_2 \rightarrow CO_2$ and its experimentally determined reaction enthalpy [31,32].

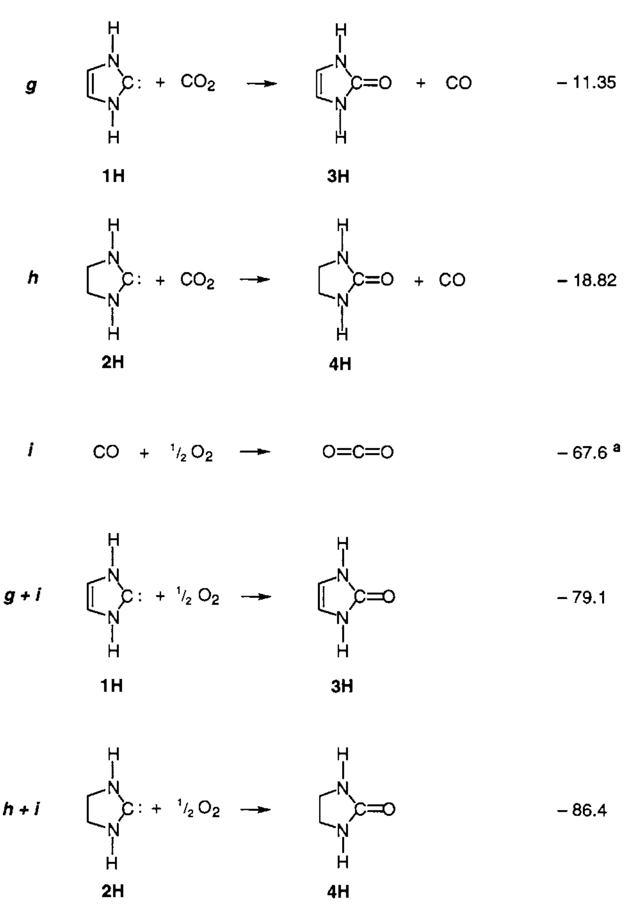
The calculations show that the reactions of the carbenes **1H** and **2H** with O_2 to give the respective ureas **3H** and **4H** are both strongly exothermic. The lack of reactivity of **1** and **2** towards O_2 must therefore have kinetic reasons [15].

The computational reaction energies show, that the carbenes **1H** and **2H** are stronger deoxygenating agents than carbon monoxide and should accordingly be able to reduce CO_2 to CO. The oxophilicity of the aromatically stabilized carbene **1H** (−79.1 kcal mol^{-1}) closely resembles that of trimethylphosphine ($E = -79.7$ kcal mol^{-1}) [26,27], while carbene **2H** which lacks aromatic stabilization shows a reaction energy of −86.4 kcal mol^{-1}. This makes **2H** as oxophilic as triethyl phosphite, $(EtO)_3P$: ($E = -88.6$ kcal mol^{-1}). The oxygen affinity of the carbenes $\mathbf{H_2C}$: and $\mathbf{F_2C}$: was calculated in the same manner. Both carbenes are more oxophilic than the highly stabilized carbenes **1H** and **2H** (Table

Table 4
Selected experimental [31] and computational (**1H**, **2H**, $\mathbf{H_2C}$:, $\mathbf{F_2C}$:) enthalpies of oxygen transfer reactions

X	XO	$\Delta H_{298.15}$
O_2	O_3	+34.1
C_5H_5N	C_5H_5NO	−12.6
NO	NO_2	−13.6
Me_2S	$Me_2S{=}O$	−27.1
CO	CO_2	−67.6
$[CN]^-$	$[OCN]^-$	−70.9 [a]
Me_3P	$Me_3P{=}O$	−79.7
1H	**3H**	−79.1 [b]
2H	**4H**	−86.4 [b]
$(EtO)_3P$	$(EtO)_3P{=}O$	−88.6
F_2C:	$F_2C{=}O$	−93.0 [b]
Si_2Me_6	$(Me_3Si)_2O$	−99.0
H_2C:	$H_2C{=}O$	−109.5 [b]
Mg	MgO	−144 [c]
Ca	CaO	−152 [c]

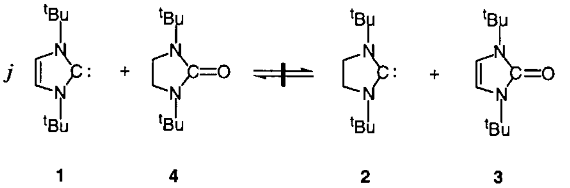
[a] In aqueous solution.
[b] This study.
[c] Solid phase.



Scheme 8. Reaction energies (in kcal mol^{-1}) for oxygen transfer reactions of stable carbenes and CO. ^{a}Experimental value [31].

4). As would be expected, singlet methylene, which lacks inductively or mesomerically stabilizing substituents, is the carbene with the highest oxygen affinity and indeed the highest oxygen affinity of all molecular deoxygenation agents listed in Table 4. The oxygen affinity of singlet methylene is only surpassed by that of metals like magnesium or calcium. The data suggest that it should be possible to reduce ureas like **3** or **4** to the respective carbenes with molecular deoxygenating agents like hexamethyldisilane ($E_{ox} = -99$ kcal mol^{-1}) and niobium trichloride ($E_{ox} = -93.8$ kcal mol^{-1}) but that the reduction of formaldehyde to methylene is only possible with strongly oxophilic metals like magnesium or calcium.

The reduction of ureas by carbenes has recently been previously observed by Jackson et al. [29] with photochemically generated fluorene-9-ylidene as oxygen acceptor. Our attempts to obtain the respective carbenes **1** or **2** from the ureas **3** and **4** and reducing metals like magnesium, potassium or sodium [7a], in analogy to the successful reduction of thioureas, have so far been unsuccessful [33]. We were also unable to observe the thermodynamically possible oxygen exchange reaction between **1** and **4** (Eq. (2)). Heating mixtures of **1**/**4** or **2**/**3** did not produce any cross-over products even after five months of heating at 150°C.



(2)

4. Conclusion

In the absence of catalysts, the carbenes **1** and **2** are inert towards triplet oxygen but can be oxidized to the corresponding ureas **3** and **4** in the presence of catalytic amounts of CuCl or with NO. At the B3LYP/6-31G(d) level, the oxidation of **1** and **2** is strongly exothermic: the oxygen affinity of the carbenes **1** and **2** is comparable to that of phosphines and phosphites and is substantially higher than that of CO. The air sensitivity of the stable diamino carbenes **1** and **2** is due to hydrolysis. At room temperature, the aromatically stabilized carbene **1** hydrolyzes only very slowly (weeks); the non-aromatic carbene **2** hydrolyzes instantaneously. The hydrolysis reactions are not catalyzed by acids or bases. Both carbenes give 1,1-hydrogenation products (aminals) with H_2 in the presence of platinum as catalyst.

5. Experimental

Melting points were recorded in sealed capillaries and are uncorrected. EI mass spectra were determined at an ionizing voltage of 40 eV or 70 eV as indicated. NMR-spectra were recorded on a Varian Gemini 200 (^{1}H), a Bruker 500 MHz (^{13}C) or a Varian 400 MHz (^{17}O) NMR spectrometer at room temperature. The spectra are referenced versus TMS (^{1}H and ^{13}C, internal), H_2O (^{17}O, external) or $CH_3{-}NO_2$ (^{15}N, external). IR spectra were recorded on a Nicolet FT-IR spectrometer. *N*,*N*′-di-*tert*-Butyl-diazabutadiene [20,21], 1,3-di-*tert*-butylimidazolin-2-ylidene (**2**) [7a] and **[1H]$^{+}$Cl^{-}** [18] were obtained by published procedures. Lithium (1% Na), *N*,*N*′-di-*tert*-butylethylenediamine and *n*-BuLi were obtained from Aldrich and used as received. For details on the single crystal X-ray structure determinations see supplementary material. All operations were carried out under inert gas unless indicated otherwise.

5.1. *1,3-di-tert-Butylimidazol-2-ylidene (**1**)*

The synthesis uses *n*-butyllithium instead of ^{t}BuOK as previously reported [4a]. For NMR data in THF-d_8 see Ref. [4a]. In a 100 ml Schlenk flask, 1,3-di-*tert*-

butylimidazolium chloride [18] (2.0 g, 9.3 mmol, one equivalent) is suspended in 15 ml dry THF. A 1.6 M solution of *n*-butyllithium in *n*-hexane (5.8 ml, 9.3 mmol, one equivalent) is added dropwise over a period of 30 min. The reaction mixture warms up and is stirred until the gas evolution ceases. The crude reaction mixture is transferred to a sublimation flask and the solvent evaporated in vacuo. The carbene is isolated by sublimation at 40–50°C/1 Torr (oil bath temperature) in the form of large colorless prisms. Yield 1.34 g (80%). ^{1}H-NMR (C_6D_6): δ 1.51 [s, CH_3], 6.79 [s, NCH]; ^{13}C-NMR (C_6D_6): δ 31.5 [q, CH_3, $^{1}J(C,H) = 126.6$ Hz, $^{3}J(C,H) = 4.4$ Hz], 55.8 [s, $C(CH_3)_3$, $^{2}J(C,H) = 12.1$ Hz, $^{3}J(C,H) = 3.6$ Hz], 115.0 [d, NCH, $^{1}J(C,H) = 185.3$ Hz, $^{2}J(C,H) = 13.2$ Hz], 212.9 [s, N_2C]; ^{15}N-NMR (C_6D_6) δ −167.6; EI-MS (70 eV, pos. ions): *m*/*z* (rel. int.%): 181 (48) $[M]^{+\cdot}$, 125 (13), 111 (10), 95 (10), 82 (3), 69 (100), 57 (32), 41 (20); IR (Nujol, KBr) ν (cm^{-1}): 3107 w, 3072 w, 1547 w, 1384 m, 1321 m, 1279 w, 1237 vs, 1181 m, 1136 m, 1103 m, 1033 w, 984 w, 966 m, 850 w, 829 m, 720 vs, 697 m, 632 s.

5.2. 1,3-di-*tert*-Butylimidazol-2-one (**3**)

N,*N*′-di-*tert*-Butyldiazabutadiene [31,32] (5.05 g, 30 mmol) dissolved in 30 ml of anhydrous THF is stirred with 2.2 equivalents of finely cut lithium wire (1% Na, 66 mmol, 46 mg) for 8 h. If the deep red color of the diazadiene dianion is not observed within minutes after the addition of the lithium, the reaction can be started by brief sonication. The resulting dark red solution is cooled to −30°C (formation of colorless precipitate) and one equivalent of ethyl chloroformate (3.26 g, 2.87 ml, 30 mmol) dissolved in 10 ml of THF is added over a period of 5 min (heat evolution). The resulting yellow–orange solution is diluted with 50 ml of toluene and filtered under exclusion of air and moisture. After removal of the solvents the residue is sublimed at 130°C oil bath/0.1 Torr to give 65% (3.8 g) of pure **3**. ^{1}H-NMR (C_6D_6): δ 1.42 (s, 18 H, CH_3), 5.96 (s, 2 H, ${=}CH$); ^{1}H-NMR (CD_3CN): δ 1.46 (s, 18 H, CH_3), 6.34 (s, 1 H, NCH); ^{13}C-NMR (C_6D_6): δ 28.2 (q, $^{1}J = 125.7$ Hz, CH_3), 54.3 (s, $C(CH_3)_3$), 106.4 (dd, $^{1}J = 192.1$ Hz, $^{3}J = 9.0$ Hz, NCH), 152.7 (s, $C{=}O$); ^{13}C-NMR (CD_3CN): δ 28.3 (q, $^{1}J = 125.7$ Hz, CH_3), 55.1 (s, $C(CH_3)_3$), 107.6 (dd, $^{1}J = 192.1$ Hz, $^{2}J = 9.0$ Hz, NCH), 153.3 (s, $C{=}O$); ^{17}O-NMR (C_6D_6): δ +215; ^{17}O-NMR (CD_3CN): δ +209; EI-MS (70 eV, pos. ions) *m*/*z* (rel. int.%): 196 (25) $[M]^{+\bullet}$, 140 (24), 125 (4), 84 (100), 57 (20); HR-MS: obs. 196.1580, calc. 196.1576, fit = 2.4 ppm; m.p. 117°C; FT-IR (Nujol, CsI) ν (cm^{-1}): 1685 s, 1366 s, 1306 w, 1261 m, 1231 m, 1163 w, 1097 m, 1022 m, 801 m, 722 w, 662 w, 631 w.

5.3. 1,3-di-*tert*-Butylimidazolidine-2-one (**4**)

To a stirred solution of *N*,*N*′-di-*tert*-butylethylenediamine (5.0 ml, 24 mmol) in 100 ml of *n*-hexane are added two equivalents of 2.5 molar *n*-BuLi in *n*-hexane. The reaction mixture is boiled to reflux until the evolution of *n*-butane ceases. The solution turns yellow and a white solid precipitates. The reaction mixture is cooled to −20°C and one equivalent of ethyl chloroformate (2.61 g, 2.30 ml, 24 mmol) dissolved in 10 ml of *n*-hexane is added dropwise under stirring. The reaction mixture is boiled for 2 h, cooled to room temperature and filtered through a medium porosity glass frit. The filtrate is evaporated in vacuo and the residue purified by sublimation (100°C oil bath/0.1 Torr) to afford 3.6 g (75%) of pure **4**. Colorless crystals, m.p. 64°C. ^{1}H-NMR (C_6D_6): δ 1.32 (s, 18 H, CH_3), 2.67 (s, 4 H, NCH_2); ^{1}H-NMR (CD_3CN): δ 1.27 (s, 18 H, CH_3), 3.14 (s, 4 H, NCH_2); ^{13}C-NMR (C_6D_6): δ 27.4 (q, $^{1}J = 125.7$ Hz, CH_3), 40.4 (t, $^{1}J = 141.8$ Hz, NCH_2), 52.8 (s, $C(CH_3)_3$), 161.6 (s, $C{=}O$); ^{13}C-NMR (CD_3CN): δ 27.6 (q, $^{1}J = 125.7$ Hz, CH_3), 41.1 (t, $^{1}J = 141.8$ Hz, NCH_2), 53.4 (s, $C(CH_3)_3$), 162.8 (s, $C{=}O$); ^{17}O-NMR (C_6D_6): δ +250; ^{17}O-NMR (CD_3CN): δ +247; EI-MS (70 eV, pos. ions) *m*/*z* (rel. int.%): 198 (9) $[M]^{+\bullet}$, 183 (55), 142 (3), 127 (100), 86 (10), 70 (8), 57 (19); HR-MS: obs. 198.1729, calc. = 198.1732, fit = −1.7 ppm; FT-IR (KBr) ν (cm^{-1}): 2751 s, 2729 s, 2667 s, 1710 s, 1699 s, 1402 m, 1271 s, 1244 s, 1104 w, 1096 w, 1030 w, 946 w, 802 m, 739 m; FT-IR (Nujol, NaCl) ν (cm^{-1}): 1710 s, 1699 s, 1271 s, 1244 s, 1225 s, 1104 w, 1097 w, 1030 w, 946 w, 802 m, 770 m, 740 w, 722 s.

5.4. 1,3-di-*tert*-Butyl-4,5-dehydro-imidazolidine (**5**)

1,3-di-*tert*-Butyl-2,3-dihydro-imidazolium chloride **[1H]Cl** [18] (2.38 g, 10.98 mmol, one equivalent) is suspended in 12 ml THF and 3 ml of a freshly prepared solution of $LiAlH_4$ (0.21 g, 5.49 mmol, 0.5 equivalent) in 12 ml THF is added dropwise under constant stirring (gas evolution). After 5 min, the solution is decanted from the insoluble material with a syringe and the solvent evaporated in vacuo. The crude product (0.27 g) is spectroscopically pure $L'CH_2$. Attempts to distill the compound lead to a non-volatile, greyish solid that is insoluble in common solvents. ^{1}H-NMR (C_6D_6): δ 1.00 ppm [s, CH_3], 4.26 [s, NCH_2N], 5.49 [s, NCH]; ^{13}C-NMR (C_6D_6): δ 27.0 ppm [q, $^{1}J(C,H) = 125.2$ Hz, $^{3}J(C,H) = 4.3$ Hz, CH_3], 52.8 [s, $C(CH_3)_3$], 66.5 [t, $^{1}J(C,H) = 145.0$ Hz, NCH_2N], 116.3 [d, $^{1}J(C,H) = 181.7$ Hz, $^{2}J(C,H) = 11.0$ Hz, NCH]; FT-IR (Nujol, NaCl) ν (cm^{-1}): 1652 w, 1616 m, 1553 w, 1539 w, 1370 m, 1286 w, 1258 m, 1202 s, 1173 w, 1152 w, 1124 m, 1096 w, 1026 w, 871 vw, 808 w, 723 w, 639 m.

5.5. *1,3-di-tert-Butylimidazolidine* (***6***)

Paraformaldehyde (6.76 g, 225 mmol) is added to *N*,*N*′-di-*tert*-butylethylenediamine (38.69 g, 225 mmol) under water cooling. The reaction mixture is stirred until all the paraformaldehyde is consumed. The crude reaction product is dissolved in 20 ml of dry diethyl ether, dried over $MgSO_4$ and isolated after filtration and removal of the solvent in vacuo as a colorless oil (36.9 g, 89%). ^{1}H-NMR (C_6D_6): δ 1.09 ppm [s, 18H, CH_3], 2.75 [s, 4H, NCH_2C], 3.67 [s, 2H, NCH_2N]; ^{1}H-NMR ($CDCl_3$): δ 1.07 [s, 18H, CH_3], 2.83 [s, 4H, NCH_2C], 3.56 ppm [s, 2H, NCH_2N]; ^{13}C-NMR (C_6D_6): δ 26.1 ppm [CH_3], 46.0 [NCH_2C], 52.0 [$C(CH_3)_3$], 63.3 [NCH_2N]; FT-IR (neat, NaCl) ν (cm^{-1}): 2968 s, 2872 s, 2822 s, 1654 w, 1473 m, 1463 m, 1392s, 1360 s, 1275 s, 1251 s, 1225 s, 1211 s, 1158 m, 1104 w, 1086 w, 1037 m, 922 w, 861 w, 820 m, 743 w; EI-MS (70 eV, pos. ions) *m*/*z* (rel. int.%): 184 (15) $[M]^{+\bullet}$, 183 (97), 127 (30), 113 (100), 98 (8), 84 (30), 71 (89), 57 (28).

5.6. *1,4-di(tert-Butyl)-4-formyl-1,4-diaza-but-1-ene* (***7***)

In a 50 ml Schlenk flask, degassed water (23 μl, 23 mg, 0.13 mmol) is added to a solution of 1,3-di-*tert*-butylimidazol-2-ylidene (**1**, 230 mg, 0.13 mmol) dissolved in 10 ml of THF. The color of the solution changes from colorless to yellow over a period of 1–2 h but NMR spectra (^{1}H, C_6D_6) of the reaction mixture taken after 24 h showed only signals for the unreacted carbene. The mixture was monitored for 3 months, at which point the 1,3-di-*tert*-butylimidazol-2-ylidene had been completely hydrolyzed to **7**. ^{1}H-NMR ($CDCl_3$): δ 1.16 ppm [s, 9H, CH_3], 1.36 [s, 9H, CH_3], 4.15 [d, NCH_2], 7.44 [t, $HC{=}N$], 8.53 [s, $HC=O$]; ^{1}H-NMR (C_6D_6): δ 0.88 [s, 9H, CH_3], 1.08 [s, CH_3], 4.16 [d, CH_2], 7.53 [t, $N{=}CH$], 8.44 [s, $O=CH$]; ^{13}C-NMR (C_6D_6): δ 29.4 ppm [s, CH_3], 29.5 [s, CH_3], 45.9 [s, CH_2], 54.9 [s, $C(CH_3)_3$], 56.7 [s, $C(CH_3)_3$], 155.8 [s, $C{=}N$], 161.0 [s, $C{=}O$]; FT-IR (neat, NaCl): ν (cm^{-1}) 2969 br, 1736 m, 1651 br, 1473 br, 1425 br, 1378 br, 1274 s, 1207 br, 1064 m, 1031 m, 996 m, 937 m, 872 m, 829 w, 810 w, 752 w, 702 w; EI-MS (70 eV): *m*/*z* (rel. int.%): 198 (10) $[M]^{+\bullet}$, 141 (8), 127 (21), 115 (41), 99 (23), 97 (24), 85(14), 69 (24), 59 (72), 57 (100).

5.7. *N-Formyl-N,N′-di-tert-butylethylenediamine* (***8***)

43 μl of distilled water (43 mg, 2.4 mmol) was added to a solution of 1,3-di-*tert*-butyl-4,5-dihydro-imidazol-2-ylidene (**2**, 0.43 mg, 2.4 mmol) dissolved in 6 ml of THF, the mixing was accompanied by heat evolution. The solution was stirred for 30 min and the solvent removed in vacuo. The white crystalline residue is sublimed at 60°C/1 Torr. ^{1}H-NMR (C_6D_6): δ 0.85 [s, 9H, $NH{-}C(CH_3)_3$], 1.02 [s, 9H, $O{=}CH{-}N{-}C(CH_3)_3$], 2.74 [t, 2H, $NHCH_2$], 3.33 [t, 2H, $CH_2N(CHO)$], 8.41 [s, 1H, HCO]; ^{13}C-NMR (C_6D_6): δ 29.2 [$HNC(CH_3)_3$], 29.4 [$O{=}CH{-}N{-}C(CH_3)_3$], 42.3 [$NHCH_2$], 43.1 [$CH_2N(CHO)$], 50.0 [$HNC(CH_3)_3$], 54.2 [$O{=}CH{-}N{-}C(CH_3)_3$], 161.1 [HCO]; ^{15}N{^{1}H}-NMR (C_6D_6): δ −243.8 [$N(CHO)$], −314.4 [$NC(CH_3)_3$]; FT-IR (nujol, NaCl) ν (cm^{-1}): 1643 s, 1563 w, 1516 br w, 1364 sh s, 1311 m, 1297 sh w, 1284 w, 1264 w, 1231 m, 1211 m, 1198 s, 1138 m, 1098 m, 1052 m, 1032 m, 1018 m; CI-MS (*i*-butane, pos. ions) *m*/*z* (rel. int.%): 282 (2), 201 (100), 183 (9), 173 (2), 145 (10), 128 (20), 111 (4), 99 (19), 86 (23), 69 (13); EI-MS (70 eV, pos. ions) *m*/*z* (rel. int.%): 201 (50), 185 (1), 128 (11), 100 (1), 86 (6), 72 (9), 57 (13), 42 (18), 31 (100).

5.8. *N,N′-bis-tert-Butyl-N,N′-di(carbomethoxy)-ethylenediamine* (***9***)

N,*N*′-di-*tert*-butylethylenediamine (6.39 g, 37.1 mmol) and triethylamine (5.13 ml) are dissolved in 100 ml of *n*-hexane. Methyl chloroformate (2.86 ml, 37.1 mmol) is added at room temperature and the mixture boiled to reflux for 2 h. The crude reaction mixture consists of unreacted *N*,*N*′-di-*tert*-butylethylenediamine and **9** (1:1 ratio by ^{1}H-NMR). Filtration of the solution, evaporation of the solvent and sublimation affords pure **9**. 42% yield; m.p. 79°C; ^{1}H-NMR (C_6D_6): δ 1.41 (s, 18H, CH_3), 3.29 (s, 4H, NCH_2), 3.43 (s, 6H, OCH_3); ^{13}C-NMR (C_6D_6): δ 29.3 (q, $^1J = 126.3$ Hz, CH_3), 45.1 (t, $^1J = 140.0$ Hz, NCH_2), 51.5 (q, $^1J = 145.4$ Hz, OCH_3), 56.1 (s, $C(CH_3)_3$), 156.2 (s, $C{=}O$).

6. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 140765 for compound **1**, 140766 for compound **3**, 141246 for compound **4** and 141247 for compound **8**. Copies of this information may be obtained free of charge from The Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for support of this work through an operating grant. We thank Professor R. West and Dr S. Powell for the crystallographic investigation of **3** and **4** in the University of Wisconsin Crystallography Laboratory (supported by the National Science Foundation (NSF) through grant CHE-9105497).

References

[1] (a) A.J. Arduengo, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361. (b) D.A. Dixon, A.J. Arduengo, J. Phys. Chem. 95 (1991) 4180. (c) A.J. Arduengo, H.V.R. Dias, J.C. Calabrese, F. Davidson, J. Am. Chem. Soc. 114 (1992) 9724. (d) A.J. Arduengo, H.V.R. Dias, J.C. Calabrese, F. Davidson, Inorg. Chem. 32 (1993) 1541. (e) A.J. Arduengo, H.V.R. Dias, R.L. Harlow, M. Kline, J. Am. Chem. Soc. 114 (1992) 5530. (f) A.J. Arduengo, H.V.R. Dias, D.A. Dixon, R.L. Harlow, W.T. Klooster, T.F. Koetzle, J. Am. Chem. Soc. 116 (1994) 6812. (g) A.J. Arduengo, D.A. Dixon, K.K. Kumashiro, C. Lee, W.P. Power, K.W. Zilm, J. Am. Chem. Soc. 116 (1994) 6361. (h) A.J. Arduengo, F. Davidson, H.V.R. Dias, J.R. Goerlich, D. Khasnis, W.J. Marshall, T.K. Prakasha, J. Am. Chem. Soc. 119 (1997) 12742.

[2] For reviews on the subject see: (a) M. Regitz, Angew. Chem. 108 (1996) 791; Angew. Chem. Int. Ed. Engl. 35 (1996) 725. (b) W.A. Herrmann, C. Köcher, Angew. Chem. Int. Ed. Engl. 36 (1997) 2163. (c) A.J. Arduengo, R. Krafczyk, Chem. Z. 32 (1998) 6. (d) A.J. Arduengo, Acc. Chem. Res. 32 (1999) 913. (e) D. Bourissou, O. Guerret, F.P. Gabbai, G. Bertrand, Chem. Rev. 100 (2000) 39. (f) C. Buron, H. Gornitzka, V. Romanenko, G. Bertrand, Science 288 (2000) 834.

[3] A stable λ^5-phospha-acetylene with carbenoid reactivity has been reported: (a) A. Igau, H. Grützmacher, A. Baceiredo, G. Bertrand, J. Am. Chem. Soc. 110 (1988) 6463. (b) L. Nyulaszi, D. Szieberth, J. Reffy, T. Veszpremi, Theochem. J. Mol. Struct. 453 (1998) 91. See also the comments in Ref. [2d].

[4] (a) A.J. Arduengo, H. Bock, H. Chen, M. Denk, D.A. Dixon, J.C. Green, W.A. Herrmann, N.L. Jones, M. Wagner, R. West, J. Am. Chem. Soc. 116 (1994) 6641. (b) J.F. Lehmann, S.G. Urquhart, L.E. Ennis, A.P. Hitchcock, K. Hatano, S. Gupta, M.K. Denk, Organometallics 18 (1999) 1862. (c) H.M. Muchall, N.H. Werstiuk, B. Choudhury, Can. J. Chem. 76 (1998) 221.

[5] (a) C. Boehme, G. Frenking, J. Am. Chem. Soc. 118 (1996) 2039. (b) C. Heinemann, T. Müller, Y. Apeloig, H. Schwartz, J. Am. Chem. Soc. 118 (1996) 2023. (c) M.-D. Su, S.-Y. Chu, Chem. Phys. Lett. 308 (1999) 283. (d) C. Heinemann, W. Thiel, Chem. Phys. Lett. 217 (1994) 11. J. Cioslowski, Int. J. Quantum Chem.: Quantum Chem. Symp. 27 (1993) 309.

[6] A.J. Arduengo, R. Goerlich, W.J. Marshall, J. Am. Chem. Soc. 117 (1995) 11027.

[7] (a) M.K. Denk, A. Thadani, K. Hatano, A.J. Lough, Angew. Chem. Int. Ed. Engl. 36 (1997) 2607; Angew. Chem. 109 (1997) 2719. (b) M.K. Denk, K. Hatano, M.J. Ma, Tetrahedron Lett. 40 (1999) 2057.

[8] (a) F.E. Hahn, L. Wittenbecher, D. Le Van, R. Fröhlich, Angew. Chem. Int. Ed. Engl. 39 (2000) 541. (b) F.E. Hahn, L. Wittenbecher, R. Boese, D. Bläser, Chem. Eur. J. 5 (1999) 1931. (c) F.E. Hahn, M. Foth, J. Organomet. Chem. 585 (1999) 241.

[9] (a) D. Enders, K. Breuer, J. Runsink, J.H. Teles, Liebigs Ann. Chem. (1996) 2019. (b) D. Enders, K. Breuer, J.H. Teles, K. Ebel, J. Prakt. Chem. 339 (1997) 397. (c) D. Enders, K. Breuer, G. Raabe, J. Simonet, A. Ghanimi, H.B. Stegmann, J.H. Teles, Tetrahedron Lett. 38 (1997) 2833.

[10] (a) R.W. Alder, P.R. Allen, M. Murray, A.G. Orpen, Angew. Chem. 108 (1996) 1211; Angew. Chem. Int. Ed. Engl. 35 (1996) 1121. (b) R.W. Alder, M.E. Blake, J. Chem. Soc. Chem. Commun. (1997) 1513.

[11] (a) R.W. Alder, C.P. Butts, A.G. Orpen, J. Am. Chem. Soc. 120 (1998) 11526. (b) R.W. Alder, M.E. Blake, C. Bortolotti, S. Bufali, C.P. Butts, E. Linehan, J.M. Oliva, A.G. Orpen, M.J. Quayle, J. Chem. Soc. Chem. Commun. (1999) 241.

[12] (a) S. Urquhart, A.P. Hitchcock, M.K. Denk, Organometallics 17 (1998) 2352. (b) M.K. Denk, K. Hatano, A.J. Lough, Eur. J. Inorg. Chem. (1998) 1067. (c) N. Metzler, M.K. Denk, J. Chem. Soc. Chem. Commun. (1996) 2657. (d) R. West, M. Denk, Pure Appl. Chem. 68 (1996) 785. (f) M. Denk, J.C. Green, N. Metzler, M. Wagner, J. Chem. Soc. Dalton Trans. (1994) 2405. (e) M. Denk, R. Lennon, R. Hayashi, R. West, A.V. Belyakov, H.P. Verne, A. Haaland, M. Wagner, N. Metzler, J. Am. Chem. Soc. 116 (1994) 2691. (f) M. Denk, R.K. Hayashi, R. West, J. Am. Chem. Soc. 116 (1994) 10813. (g) M. Denk, R.K. Hayashi, R. West, J. Chem. Soc. Chem. Commun. (1994) 33.

[13] W.A. Herrmann, M. Denk, J. Behm, W. Scherer, F.-R. Klingan, H. Bock, M. Solouki, M. Wagner, Angew. Chem. 104 (1992) 1489.

[14] (a) M.K. Denk, S. Gupta, R. Ramachandran, Eur. J. Inorg. Chem. (1999) 41. (b) M.K. Denk, S. Gupta, R. Ramachandran, Tetrahedron Lett. 37 (1996) 9025.

[15] Note added in proof: the oxidation of carbenes **1** and **2** by O_2 to give **3** and **4** can be catalyzed by CuCl.

[16] (a) A.J. Arduengo, D.A. Dixon, K.D. Dobbs, Tetrahedron Lett. 36 (1995) 645. (b) S.N. Lyashchuk, Y.G. Skrypnik, Tetrahedron Lett. 35 (1994) 5271. (c) For reactions of transient carbenes with CO in frozen matrices see: P. Visser, R. Zuhse, M.W. Wong, C. Wentrup, J. Am. Chem. Soc. 118 (1996) 12598.

[17] (a) C. Zirngibl, R. Heddrich, R.K. Thauer, FEBS Lett. 261 (1990) 112. (b) C. Zirngibl, W. van Dongen, B. Schwörer, R. von Bünau, M. Richter, M. Klein, R.K. Thauer, Eur. J. Biochem. 208 (1992) 511. (c) J. Cioslowski, G. Boche, Angew. Chem. Int. Ed. Engl. 36 (1997) 107. (d) J.H. Teles, S. Brode, A. Berkessel, J. Am. Chem. Soc. 120 (1998) 1345.

[18] (a) A.J. Arduengo, US Pat. 5077414, Wilmington, DE, 1991. (b) B.L. Benac, E.M. Burgess, A.J. Arduengo, Org. Synth. 64 (1986) 92.

[19] Obtained from **2** and one equivalent of HCl in Et_2O at room temperature after filtration.

[20] H.-W. Frühauf, A. Landers, R. Goddard, C. Krüger, Angew. Chem. Int. Ed. Engl. 17 (1978) 64.

[21] L.H. Staal, L.H. Polm, K. Vrieze, Inorg. Chim. Acta 40 (1980) 165.

[22] G.M. Sheldrick, version 4.2, Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1990.

[23] C.K. Johnson, ORTEP, FORTRAN Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, National Laboratories, Oak Ridge, TN, USA, 1965.

[24] The calculations reported in this paper were carried out with the Spartan 5.02 and Gaussian 94 suite of programs: M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, Gaussian 94, Revision D.4, Gaussian, Inc., Pittsburgh, PA, 1995.

[25] (a) J.B. Foresman, A. Frisch, Exploring Chemistry with Electronic Structure Methods, Gaussian Inc., Pittsburgh, PA, 2nd Edn., 1996. (b) I. Bytheway, M.W. Wong, Chem. Phys. Lett. 282 (1998) 219. (c) A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502. (d) A.P. Scott, B.T. Golding, L. Radom, New. J. Chem. (1998) 1171. (e) A.D. Becke, Phys. Rev. A 38 (1988) 3098. (f) C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785. (g) A.D. Becke, J. Chem. Phys. 98 (1993) 5648. (h) W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257.

[26] For **4**, the IR band of CO appears as a doublet, while a single line is observed for **3**. This split can be ascribed to Fermi resonance ($CH_2/C{=}O$) and has been previously observed in the case of the closely related ethylene carbonates, for which the assignment was verified by deuteration (no splitting observed for the D_4-ethylenecarbonate) [27]. The splitting of the CO band is also commonly observed for cyclopentanones, unsaturated cyclic lactones and conjugated cyclic ketones [27].

[27] H.N. Al-Jallo, F.N. Al-Azawi, Spectrochim. Acta 34A (1978) 819.

[28] (a) J.P. Pezacki, P.D. Wood, T.A. Gadosy, J. Lusztyk, J. Warkentin, J. Am. Chem. Soc. 120 (1998) 8681. (b) M.D. Su, S.Y. Chu, Chem. Phys. Lett. 320 (2000) 475.

[29] D. Kovacs, M.S. Lee, D. Olson, J.E. Jackson, J. Am. Chem. Soc. 118 (1996) 8144.

[30] W. Sander, Angew. Chem. Int. Ed. Engl. 29 (1990) 344.

[31] R.H. Holm, J.P. Donahue, Polyhedron 45 (1993) 571 Polyhedron Special Report 12.

[32] For the isodesmic equations, the differences in enthalpies $\Delta\Delta H$ and energies $\Delta\Delta E$ can be substituted for each other because the because the terms RT in $H = E + RT$ cancel. It is thus possible to compare the isodesmic reaction energies directly with the tabulated [31] enthalpies.

[33] M.K. Denk, unpublished results.

[34] M.K. Denk, J. Rodezno, J. Organomet. Chem. 608 (2000) 122.