Structural and theoretical investigation of 2-iminoimidazolines – carbene analogues of iminophosphoranes†

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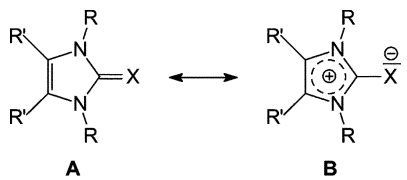
Received 24th October 2006, Accepted 1st December 2006
First published as an Advance Article on the web 4th January 2007
DOI: 10.1039/b615418b

The preparation of 2-iminoimidazolines **3a**–**3f** has been accomplished by the Staudinger reaction of the carbenes 1,3-di-*tert*-butylimidazolin-2-ylidene (**1a**), 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene (**1b**), 1,3-diisopropylimidazolin-2-ylidene (**1c**), 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (**1d**), 1,3-bis(2,6-diisopropylphenylimidazolin-2-ylidene (**1e**) and 1,3,4,5-tetramethylimidazolin-2-ylidene (**1f**) with trimethylsilyl azide (Me_3SiN_3) followed by desilylation of the resulting 2-trimethylsilylimino-imidazolines **2a**–**2e**. The X-ray crystal structures of **2d** and **2e** have been established, revealing C1–N1–Si1 angles that are more obtuse than the corresponding P–N–Si angles observed in related trimethylsilyl iminophosphoranes. Together with **2c**, the disilylated side product 1,3-diisopropyl-2-(trimethylsilylimino)-4-trimethylsilylimidazoline (**4**) has been isolated and structurally characterized. Cleavage of the N–Si bonds in **2a**–**2f** and formation of **3a**–**3f** is easily achieved by stirring in methanol. The molecular structures of the 2-iminoimidazolines **2a**–**2c** are reported, indicating that the structural parameters are best described by non-ylidic resonance structures and that electron delocalization within the imidazole heterocycle does not play a crucial role in these imine systems. Compound **2a** forms a head-to-head dimer in the solid state *via* weak intermolecular N–H · · · N contacts, which have additionally been characterized by means of compliance constants. To further analyze the electronic structure of these imines in comparison to related guanidine ligands, the proton affinities (PAs) of the model compounds 2-imino-1,3-dimethylimidazoline (**5**), 2-imino-1,3-dimethylimidazolidine (**6**) and tetramethylguanidine (**7**) have been calculated by means of density functional theory. Finally, the charge distribution in **5**–**7** and the relative contribution of relevant resonance structures have been determined using natural bond orbitals (NBO) and natural resonance theory (NRT).

Introduction

Ligands derived from the 1*H*-imidazole heterocycle currently play a major role in organotransition metal and coordination chemistry. In particular, *N*-heterocyclic carbenes of the imidazolin-2-ylidene type[1] are nowadays ubiquitous and indispensable to the development of diverse research areas such as homogeneous catalysis,[2] materials science[3] and medicinal chemistry.[4] The stability of these carbenes can be attributed *inter alia* to the capability of the imidazolium ring to effectively stabilize a positive charge leading to strongly basic and highly nucleophilic ligands. This behaviour can be transferred to an exocyclic moiety X at the 2-position of the *N*-heterocycle, so that for species such as 2-methylen-, 2-imino- and 2-oxo-imidazolines (X = CH_2, NH, O) a strong contribution from the ylidic mesomeric structure **B** (Scheme 1) must be considered.[5,6] The resulting build-up of negative charge at X affords compounds with considerably enhanced basicity and nucleophilicity. Accordingly, the heavier 2-chalcogenoimidazolines (X = S, Se, Te) have been regarded as neutral analogues of thiolate, selenolate and tellurolate ligands, respectively[7] and, as a further example, the extensive use of the tripodal ligand hydrotris(methimazolyl)borate is based on the excellent electron-donating ability of the exocyclic sulfur atoms.[8,9]



Scheme 1 Mesomeric structures of imidazole-based ligands.

We have exploited this concept in the synthesis of various novel 2-trimethylsilyliminoimidazolines (X = $NSiMe_3$) and have shown that these are suitable precursors for the synthesis of transition metal complexes incorporating ancillary imidazolin-2-iminato ligands (X = N^-).[10] Since these ligands can act as 2σ,4π-electron donors in a similar fashion to that described for related phosphoraneimides, R_3PN^-,[11] they can be regarded as monodentate analogues of cyclopentadienides, $C_5R_5^-$. With this contribution, we now wish to give a full account of the synthesis and structural

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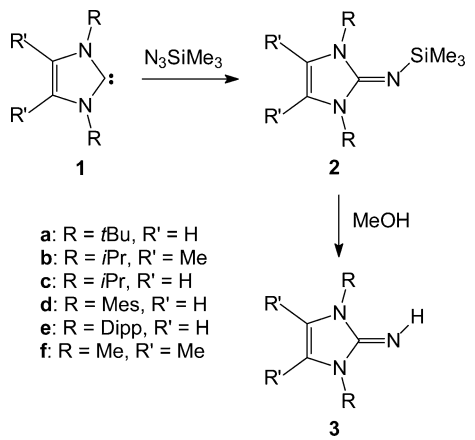
† Electronic supplementary information (ESI) available: Cartesian coordinates of the atomic positions for all calculated structures and the most important resonance structures obtained for **5**–**7** by NRT (natural resonance theory) analysis. See DOI: 10.1039/b615418b

characterization of several 2-trimethylsilyliminoimidazolines (X = $NSiMe_3$) and their resulting 2-iminoimidazolines (X = NH), which are useful building blocks for the preparation of poly(imidazoline-2-imine) ligands currently under investigation in our laboratory.[12] In addition, we report a comparative theoretical study of the electronic structure of these imines and some related guanidine systems.

Results and discussion

Preparation and characterization of *N*-silylated 2-iminoimidazolines

Silylated iminophosphoranes have been widely used for complexation reactions with various metal halides or oxides to yield phosphoraneiminato complexes by the elimination of trialkylsilyl halides or hexaalkyldisiloxanes, respectively.[11] Therefore, the syntheses of analogous *N*-silylated 2-iminoimidazolines **2** are of great interest in view of the possibility of generating novel transition metal complexes *via* the cleavage of the N–Si bond. We have previously reported a general high-yield synthesis of the 2-(trimethylsilylimino)imidazolines **2**;[10] the reaction between readily available stable carbenes **1** and trimethylsilyl azide (TMS-N_3) in boiling toluene furnishes the *N*-silylated 2-iminoimidazolines **2** in a similar way to that described for the preparation of silylated phosphoraneimines (Scheme 2).[11d,13] It is reasonable to assume that this conversion also follows the mechanism of the Staudinger reaction,[14] which would involve nucleophilic attack of the carbene on the terminal azide nitrogen atom and intermediate triazene formation followed by N_2 dissociation.[15] This mechanism is supported by the observation that stable triazenes can be isolated by treatment of imidazolin-2-ylidenes with alkyl and aryl azides.[16]



Scheme 2 Preparation of 2-iminoimidazolines **3**.

Compounds **2a** (R = *t*Bu, R′ = H), **2d** (R = Mes, R^1 = H), **2e** (R = Dipp, R′ = H) and **2f** (R = Me, R′ = Me) are obtained as colourless solids. In contrast, the *N*-silylated 2-iminoimidazolines **2b** (R = *i*Pr, R′ = Me) and **2c** (R = *i*Pr, R′ = H) are isolated as brownish oils, which can be purified by bulb-to-bulb distillation at 180 °C/9 mbar affording colourless liquids. The conversion of the carbenes bearing 4,5-hydrogen atoms (**1a**, **1c**, **1d**, **1e**) can easily be followed by ^{1}H NMR spectroscopy, as pronounced high-field shifts of about −0.70 ppm are observed for the resonances of the NCH hydrogen atoms upon formation of the corresponding imines. In the case of **2b**, silylation leads to a marked low-field shift of the septet C*H* resonance from 3.95–4.61 ppm. The resonances of the trimethylsilyl protons of the compounds **2a**–**2c** and **2f** appear in the range of 0.47–0.53 ppm, whereas in the case of the aryl-substituted imines **2d** and **2e** the corresponding signals appear at −0.10 and −0.16 ppm, respectively. In the ^{13}C NMR spectra of all silylated imines **2**, the resonances of the former carbene carbon atoms are found between 139 and 154 ppm, which is a shift of approximately 80 ppm up-field from the related resonances in the free carbenes **1**. According to their ^{1}H and ^{13}C NMR spectra, the silylated imines **2** exhibit pseudo-C_{2v} symmetry in solution, implying either that the N1–C1–Si axis is linear or that rotation around the N1–C1 axis is fast on the NMR time scale. In fact, the C1–N1–Si angle in **2a** was found to be close to linearity [169.3(2)°].[10a]

To study the effect of different substituents on the nitrogen atoms, we have established the molecular structures of **2d** (Fig. 1) and **2e** (Fig. 2) by means of X-ray diffraction analysis, revealing significantly smaller angles of 147.2(1)° in **2d** and 155.4(1) and 157.8(1)° for the two independent molecules in **2e** (Table 1). [A least-squares fit of the central parts of the molecules (five-membered ring plus NSi and *ipso* C atoms) gave an r.m.s. deviation of 0.05 Å; the interplanar angles of the aryl groups to the central ring of 78.5 and 78.5° for molecule 1, and 81.6 and 89.0° for molecule 2 show, however, that the molecular conformations are somewhat different.] Although electronic factors might also account for these differences,[10a,b] the observed trend follows the increased steric requirements of the *N*-substituents [*t*Bu (**2a**) >Dipp (**2e**) >Mes (**2d**)]. This implies that the potential energy surface is quite shallow with respect to the C–N–Si angle, as has been previously demonstrated for phosphoraneiminato transition metal complexes.[17] On average, these angles are more obtuse than the corresponding P–N–Si angles observed in trimethylsilyl iminophosphoranes such as $Ph_3PNSiMe_3$ [140.2(2)°] and

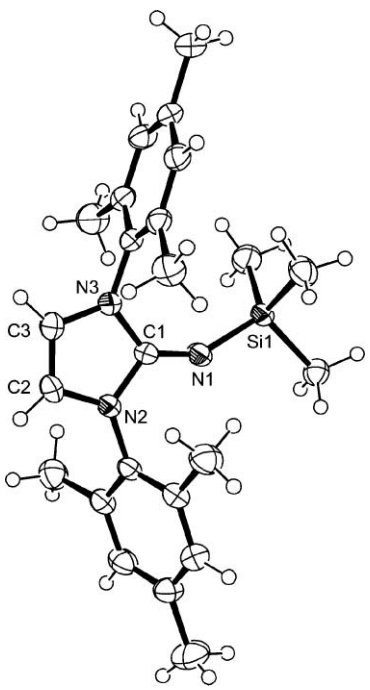


Fig. 1 ORTEP drawing of **2d** with thermal displacement parameters drawn at 50% probability.

Table 1 Selected bond distances (Å) and angles (°) for **2d**, **2e**, **3a**–**3c** and **4**

	2d	2e	3a	3b	3c	4
C1–N1	1.267(2)	1.264(2)/1.265(2)	1.295(2)	1.294(3)	1.298(1)	1.274(4)
C1–N2	1.394(2)	1.400(2)/1.397(2)	1.390(2)	1.386(3)	1.384(1)	1.386(3)
C1–N3	1.391(2)	1.399(2)/1.397(2)	1.395(2)	1.389(3)	1.383(1)	1.392(3)
N1–Si	1.687(1)	1.677(2)/1.677(2)				1.665(2)
C1–N1–Si	147.2(1)	155.4(1)/157.8(1)				150.9(2)
N1–C1–N2	125.0(1)	131.6(2)/131.4(2)	123.5(1)	124.1(2)	127.1(1)	126.5(2)
N1–C1–N3	131.6(1)	125.6(2)/125.6(2)	131.2(1)	130.9(2)	127.9(1)	129.7(2)
N2–C1–N3	103.4(1)	102.9(2)/103.0(2)	105.3(1)	105.1(2)	105.0(1)	103.9(2)

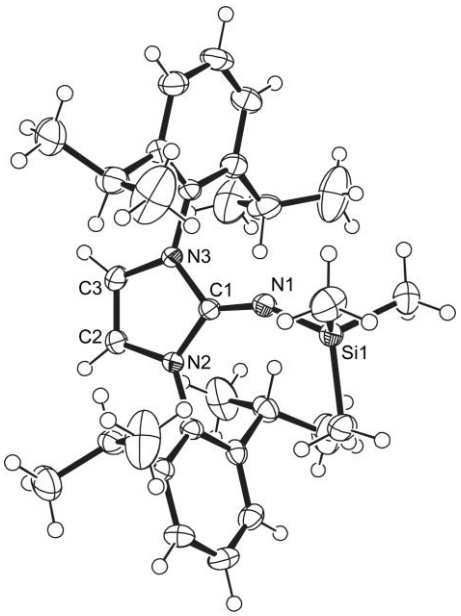
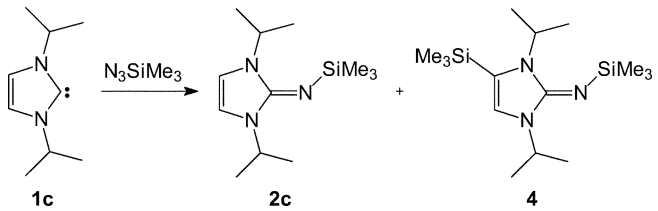


Fig. 2 ORTEP drawing of **2e** (one of two independent molecules) with thermal displacement parameters drawn at 50% probability.



Scheme 3 Formation of the imines **2c** (65%) and **4** (15%).

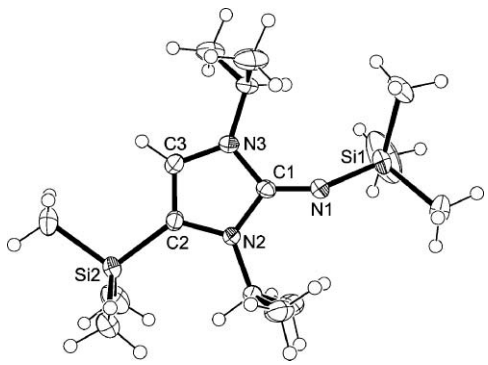


Fig. 3 ORTEP drawing of **4** with thermal displacement parameters drawn at 50% probability.

$Cy_3PNSiMe_3$ [149.8(2)°] (Cy = *cyclo*-C_6H_{11}).[18,19] Whereas the exocyclic C1–N1 bond distances found in **2d** [1.267(2) Å] and **2e** [1.263(3), 1.265(3) Å] are the same as in **2a** [1.275(3) Å] within experimental error, slightly longer N–Si distances are observed [1.687(1) Å (**2d**) and 1.677(2), 1.677(2) Å (**2e**) *versus* 1.655(3) Å (**2a**)]. For comparison, the N–Si bonds in phosphoraneimines fall in the same range [1.686(2) Å ($Ph_3PNSiMe_3$), 1.656(4) Å ($Cy_3PNSiMe_3$)]. A more detailed evaluation and discussion of these structural aspects will be given below in connection with the structures of the desilylated 2-iminoimidazolines **3**.

It should be noted that the conversion of **1c** into **2c** was accompanied by the formation of noticeable amounts (15%) of the compound 1,3-diisopropyl-2-(trimethylsilylimino)-4-trimethylsilylimidazoline (**4**) (Scheme 3). Imine **2c** can be separated by bulb-to-bulb distillation, and sublimation of the residue affords the disilylated **4** as a crystalline solid, which was subjected to a single-crystal X-ray structure analysis. The molecular structure is presented in Fig. 3, unequivocally proving that the second trimethylsilyl substituent has been incorporated into the molecule in the 4-position of the *N*-heterocycle. The additional silyl substituent does not alter the metric parameters significantly, and the C1–N1–Si1 angle [150.9(2)°] and the C1–N1 [1.274(4) Å] and N1–Si1 distances [1.665(2) Å] fall in the expected ranges (*vide supra*). Finally, it should be emphasized that the activation and silylation of the 4-position in **2c** is in line with previous recent reports on the 'abnormal' binding of *N*-heterocyclic carbenes in transition metal complexes by activation of the HC=CH imidazole fragment.[20]

Preparation and characterization of 2-iminoimidazolines

The *N*-silylated imines **2** are useful compounds, not only because of their application in the synthesis of transition metal complexes,[5b,10,21] but also because of the possibility of producing 2-iminoimidazolines **3** by desilylation and cleavage of the N–Si bond. These compounds and their corresponding bases, the imidazolin-2-imides, can serve not only as valuable ligands, but also as building blocks for the preparation of poly(imidazoline-2-imine) ligands.[5b,12,22] Prior to this work, the 2-imino-1,3-dimethylimidazoline reported by Kuhn *et al.* was the only well documented 2-iminomidazoline derivative, and its synthesis was achieved by a multi-step protocol from 2-aminoimidazole.[23] In contrast, our novel procedure for the preparation of 2-trimethylsilyliminoimidazolines **2** (*vide supra*) now allows convenient access to 2-iminoimidazolines **3** with a variable substitution pattern by

desilylation in methanol at ambient temperatures (Scheme 2). The reaction is complete within two hours, and the formation of the 2-iminoimidazolines **3** can be easily followed by ^{1}H NMR spectroscopy with a singlet resonance for the imine proton (N*H*) emerging in the range between 4.20 and 4.77 ppm. In addition, the desilylation is accompanied by a marked low-field shift of the N*C*N ^{13}C NMR resonance, which can be observed in the range from 159.5 to 153.0 ppm, by about 10 ppm.

Sublimation of compounds **3** affords crystalline solids, which proved suitable for X-ray crystal structure determination in the cases of **3a** (Fig. 4), **3b** (Fig. 5) and **3c** (Fig. 6). Most noticeably, the C1–N1 bond distance in all imines **3** is increased with respect to the corresponding distance in the silyl derivatives **2** [1.295(2) (**3a**), 1.294(3) (**3b**) and 1.298(1) Å (**3c**) *versus* 1.275(3) (**2a**), 1.267(2) Å (**2d**) and 1.263(3)/1.265(3) Å (**2e**)], indicating that the imines **3** might exhibit a slightly stronger ylidic behaviour than their silyl congeners **2**. In contrast, all other structural parameters remain almost completely unaffected by the variation of the substitution pattern. Consequently, the previously structurally characterized 2-imino-1,3-dimethylimidazoline also exhibits similar distances and angles, *e.g.* *d*(C1–N1) = 1.296(2) Å.[23] All C1–N1 distances observed so far clearly fall in the range expected for a C(sp^2)–N(sp^2) double bond (1.28 Å),[24] suggesting that the solid-state structures of the imines **2** and **3** are in good agreement with the non-ylidic mesomeric structure **A** shown in Scheme 1. This

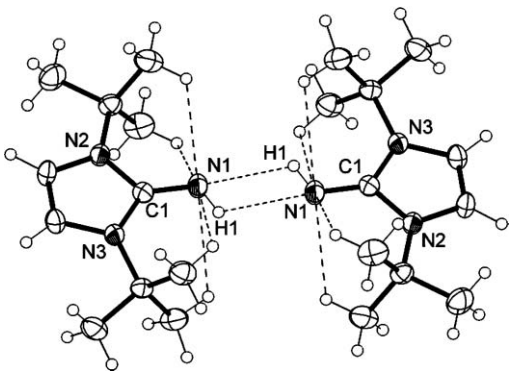


Fig. 4 DIAMOND drawing of a hydrogen-bonded dimer of **3a** showing weak inter- and intra-molecular non-covalent contacts with thermal displacement parameters drawn at 50% probability.

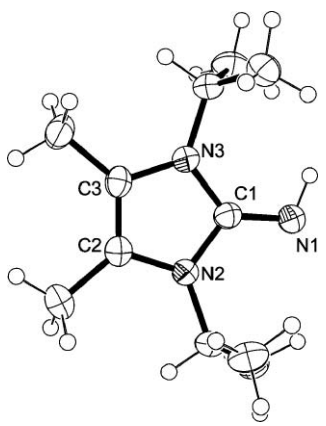


Fig. 5 ORTEP drawing of **3b** with thermal displacement parameters drawn at 50% probability.

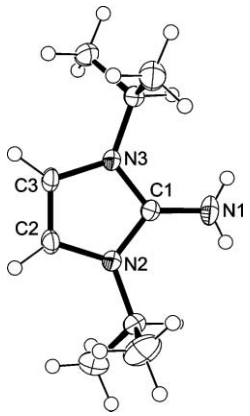


Fig. 6 ORTEP drawing of **3c** with thermal displacement parameters drawn at 50% probability; the position of the N1–H hydrogen atom is disordered.

is also supported by the fact that the imidazole heterocycles in all compounds **2** and **3** show consistent differences from the structures of imidazolium ions, which have N–C–N angles in the range 108.3–109.7° and C1–N2(3) bonds ranging from 1.315 to 1.335 Å.[25] For **2d** and **2e**, the N2–C1–N3 angles of 103.4(1)° and of 102.9(2) and 103.0(2)°, respectively, are close to the corresponding angles observed for free imidazolin-2-ylidenes (101.2–102.2°),[1,25,26] whereas the angles in **3a**–**3c** of 105.3(1), 105.1(2) and 105.0(1)° adopt an intermediate position between the values found in imidazolium ions and imidazolin-2-ylidenes. Finally, the internal C1–N2 and C1–N3 distances of about 1.39 Å (Table 1) in both the imines **2** and **3** are significantly longer than the corresponding bonds in imidazolium ions (*vide supra*) and also in imidazolin-2-ylidenes (1.363–1.373 Å), indicating that from a structural point of view electron delocalization within the heterocycle does not play a crucial role in these imine systems.

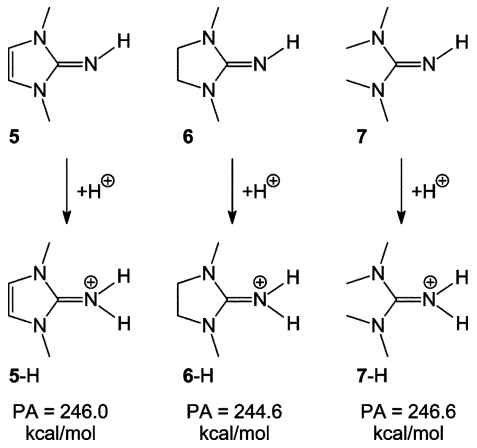
Investigation of the crystal packing in **3a**–**3c** does not reveal the formation of strong intermolecular N–H···N hydrogen bonds, which one might have anticipated from the basicity of the exocyclic nitrogen atoms (*vide infra*). Only **3a** exhibits N1–H1···N1 contacts below 2.75 Å, which qualify for hydrogen bonding according to the van der Waals cut-off criterion [r_{vdW}(N) = 1.55 Å, r_{vdW}(H) = 1.20 Å].[27] Two molecules **3a** adopt a head-to-head arrangement with the two imine groups forming a four-membered NHNH parallelogram (Fig. 4). The position of the exocyclic imine hydrogen atom could be refined with individual isotropic displacement parameters producing N–H distances of 0.87(2) and 2.57(2) Å and N1–H1···N1 and H1–N1···H1 angles of 125(1) and 55(1)°, respectively. These geometric parameters, specifically the comparatively long non-covalent N1···H1 contact and the small N1–H1···N1 angle, indicate the weakness of the hydrogen bonds.[28] In addition, intramolecular C–H···N1 contacts can be identified with the *tert*-butyl groups acting as weak hydrogen donors towards the imine nitrogen atom.[29,30] As a consequence, the methyl groups adopt a staggered conformation with respect to the N1–H1 bond, and the shortest N1···H distances to each of the four methyl groups below and above the N1–H1 moiety are 2.41 and 2.50, and 2.58 and 2.79 Å, respectively. The two shortest contacts are those to the *tert*-butyl group attached to N2, and the imine group is clearly bending over towards this alkyl substituent, since a significantly smaller N2–C1–N1 angle of

123.5(1)° is observed in comparison with the adjacent N3–C1–N1 angle of 131.2(1)°.

To investigate the relative strength of these intra- and intermolecular hydrogen bonds, we performed DFT (density functional theory) calculations on a dimeric unit of **3a** using an augmented triple zeta basis set. Further details are given in the following section. The fully optimized gas phase structure of the dimer is similar to the solid-state structure, and the head-to-head hydrogen bond arrangement is retained, while the non-covalent N1 · · · H1 distance of 2.644 Å is now slightly elongated. Because geometrical parameters are not always ideal interaction strength descriptors,[29] we additionally computed generalized compliance constants as a second order property.[31] The results indeed point to a very weak non-covalent N1 · · · H1 interaction, which is reflected by the high value of 24.40 Å mdyn^{-1}. In comparison, strong N–H · · · N interactions such as in the adenine–thymine or guanine–cytosine base pairs are indicated by short contacts with d(N · · · H) < 2 Å and compliance constants of 4.50 and 2.28 Å mdyn^{-1}, respectively.[32] The intramolecular C–H · · · N1 contacts mentioned above are also reproduced by our gas phase calculation with distances ranging from 2.42 to 2.72 Å. The associated compliance constants amount to 8.71–9.31 mdyn Å^{-1}, indicating that the intramolecular non-covalent interactions are significantly stronger than the intermolecular ones. Accordingly, we suggest that these C–H · · · N contacts are responsible for the reduced tendency of the notably polarized imine moiety to aggregate *via* strong N–H · · · N hydrogen bonds and that the negative charge on the exocyclic nitrogen atom (*vide infra*) is consequently tempered by delocalization. The other structures discussed here have not been theoretically analysed in such detail. The structures as determined do not display significant N–H · · · N contacts, and the intra- and inter-molecular C–H · · · N contacts are in general appreciably longer than in **3a** (*e.g.* intramolecular C_{methyl}–H · · · N of 2.53 Å in **3b**, or intermolecular C3–H · · · N of 2.66 Å in **3c**).

Comparative calculations of ligand properties

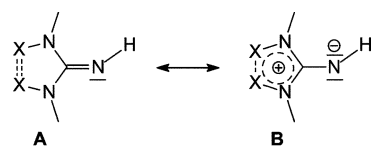
Since 2-iminoimidazolines represent interesting ligands in their own right and can also serve as valuable building blocks for the preparation of poly(imidazoline-2-imine) ligands,[5b,12,22] we became interested in further investigation of their electronic structure in comparison with related guanidine-type ligands.[33] Thus, we have performed extensive and systematic DFT calculations on the model systems **5**–**7** (Scheme 4). All computations were performed using the hybrid density functional method B3LYP implemented in the Gaussian03 program[34] in combination with a triple zeta basis set augmented with polarization functions on hydrogen and all heavy atoms [6-311++G(d,p)]. Since the ligand basicity can be regarded as a key feature in terms of their reactivity towards transition metals, we calculated the proton affinities (PAs) of 2-imino-1,3-dimethylimidazoline (**5**), 2-imino-1,3-dimethylimidazolidine (**6**) and tetramethylguanidine (**7**). The computed values are given in Scheme 4. In contrast to earlier calculations employing a reduced basis set [6-31+G(d,p)], we could not reproduce the exceptionally high proton affinity of 253.4 kcal mol^{-1} reported for **5**.[5b] Our calculations reveal only slight differences in the proton affinities obtained for **5**–**7** with the highest value observed for tetramethylguanidine (**7**) (246.6 kcal mol^{-1}) followed by **5**



Scheme 4 Calculated proton affinities (PAs) of guanidine model systems **5**–**7**.

(246.0 kcal mol^{-1}) and **6** (244.6 kcal mol^{-1}). This trend is in agreement with recent calculations on **6** and **7**.[35,36]

Since proton affinities should not be regarded as the one and only descriptor for ligand Lewis basicity, we have additionally computed the NBO (natural bond orbital) charges for the exocyclic nitrogen atoms. In contrast to the trend in the PAs, a pronounced difference is found between **5** (−0.822), its saturated analogue **6** (−0.781) and acyclic **7** (−0.755). In order to explain these results further in terms of resonance structures, all possible contributions to the total electronic wave function have been determined by means of natural resonance theory (NRT).[37,38] Evaluation of the relative contribution of all ylidic resonance structures of type **B** for compounds **5**–**7** reveals (Scheme 5) an increase of the zwitterionic nature for the guanidine **7** (to 14.1%), the saturated ligand **6** (to 16.7%) and the 2-iminoimidazoline system **5** (to 20.6%). A complete list of the most important NRT structures is given in the ESI.† This trend is consistent with the stronger capability of the imidazole ring in **5** to stabilize a positive charge in comparison with the NCN moieties in **6** and **7**. Accordingly, 2-iminoidazolines should be particularly well suited for the complexation of Lewis-acidic transition metal complex fragments and for the stabilization of electron deficient transition metal complexes.



Scheme 5 Relative contributions from the ylidic mesomeric structures **B** and NBO charges of the exocyclic nitrogen atom for the guanidine model systems **5**–**7**.

Conclusions

With this contribution, we have presented a convenient and flexible route for the preparation of various 2-iminoimidazolines. Our results suggest that the basic and nucleophilic properties of the

imidazolin-2-ylidenes are transferred to the exocyclic nitrogen atom. As a result, these imines are strong bases that are likely to exhibit even stronger nucleophilic properties than related guanidine-type systems and might therefore serve as valuable ligands in their own right, and also as important building blocks for the design and preparation of novel multidentate poly(2-iminoimidazoline) ligands. In addition, applications in organic synthesis such as the aza-Wittig reaction can be envisaged.[14c,39]

Experimental

All operations were performed in an atmosphere of dry argon by using Schlenk and vacuum techniques. All solvents were purified by standard methods and distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded on JEOL-GX 400 (400 MHz), JEOL-GX 270 (270 MHz), Bruker AC 200, Bruker DPX 200, Bruker AV 300 and Bruker DPX 400 devices. The chemical shifts are given in ppm relative to TMS. The spin coupling patterns are indicated as s (singlet), d (doublet), m (multiplet), sept (septet) and br (broad, for unresolved signals). Elemental analysis (C, H, N) succeeded by combustion and gas chromatographical analysis with a Vario EL III CHNS, Carlo Erba Mod. 1106 and a Vario Micro Cube. Trimethylsilyl azide was received from Aldrich and dried over molecular sieve (4 Å). The imidazolin-2-ylidenes **1a**–**1f**[40–42] and the 2-(trimethylsilylimino)imidazolines **2a**–**2e**[10] were prepared according to literature procedures.

1,3,4,5-Tetramethyl-2-(trimethylsilylimino)imidazoline (2f)

A solution of 1,3,4,5-tetramethylimidazolin-2-ylidene (**1f**) (1.242 g, 10 mmol) in toluene (20 mL) was treated dropwise with trimethylsilyl azide (14 mmol) at ambient temperature, and the resulting reaction mixture was subsequently heated in boiling toluene for 24 h. Filtration and evaporation of the solvent afforded the desired product as a yellowish solid, which can be further purified by sublimation (yield: 1.416 g, 67%). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 2.80 (s, 6 H, NCH_3), 1.45 (s, 6 H, CCH_3), 0.53 (s, 12 H, $SiCH_3$) ppm. ^{13}C NMR (50.32 MHz, C_6D_6): δ 152.9 (NCN), 113.1 (N*C*Me), 28.4 (*C*HMe), 8.6 (NC*C*H$_3$), 5.1 ($SiCH_3$) ppm.

General procedure for the preparation of 2-iminoimidazolines 3

2-(Trimethylsilylimino)imidazolines **2** (1 equiv.) were treated with an excess of CH_3OH (15 equiv.) at ambient temperature for 2 h. The solvent was then removed *in vacuo* and the product extracted with *n*-hexane. Filtration and evaporation of *n*-hexane afforded the imines as colourless solids (**3a**, **3c**, **3d** and **3e**) or as brownish oils (**3b** and **3f**), respectively, of which the latter can be purified by bulb-to-bulb distillation at 70 °C/0.1 mbar.

Compound 3a. Yield: 96%. Found: C, 67.39; H, 11.01; N, 21.27%. Calc. for $C_{11}H_{21}N_3$: C, 67.65; H, 10.84; N, 21.51%; ^{1}H NMR (270 MHz, C_6D_6, 25 °C): δ 5.94 (s, 2 H, NCH), 1.39 (s, 18 H, CCH_3) ppm. ^{13}C NMR (100.52 MHz, C_6D_6): δ 153.1 (NCN), 107.0 (NCH), 53.8 (N*C*Me), 27.7 (C*C*H$_3$) ppm.

Compound 3b. Yield: 97%. Found: C, 67.29; H, 11.15; N, 21.45%. Calc. for $C_{11}H_{21}N_3$: C, 67.65; H, 10.84; N, 21.51%; ^{1}H NMR (270 MHz, C_6D_6, 25 °C): δ 4.31 (s, 1 H, NH), 4.17 (sept., $^3J_{H,H}$ = 6.8 Hz, 2 H, C*H*Me), 1.63 (s, 6 H, CH_3), 1.37 (d, $^3J_{H,H}$ = 7.2 Hz, 12 H, CH_3) ppm. ^{13}C NMR (100.52 MHz, C_6D_6): δ 153.4 (NCN), 113.3 (N*C*Me), 44.8 (*C*HMe), 20.4 (CH*C*H$_3$), 9.6 (NC*C*H$_3$) ppm.

Compound 3c. Yield: 91%. Found: C, 64.59; H, 10.71; N, 25.13%. Calc. for $C_9H_{17}N_3$: C, 64.63; H, 10.24; N, 25.12%; ^{1}H NMR (270 MHz, C_6D_6, 25 °C): δ 5.81 (s, 2 H, NCH), 4.25 (s, 1 H, NH), 4.13 (br., 2 H, CHMe), 0.96 (d, $^3J_{H,H}$ = 6.7 Hz, 12 H, CH_3) ppm. ^{13}C NMR (67.93 MHz, C_6D_6): δ 153.0 (NCN), 106.4 (N*C*Me), 44.2 (*C*HMe), 21.1 (CH*C*H$_3$) ppm.

Compound 3d. Yield: 95%. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 6.76 (s, 4 H, *m*-H), 5.71 (s, 2 H, NCH), 4.28 (s, 1 H, NH), 2.23 (s, 12 H, *o*-CH_3), 2.11 (s, 6 H, *p*-CH_3) ppm. ^{13}C NMR (100.52 MHz, C_6D_6): δ 151.7 (NCN), 137.7 (*ipso*-*C*), 137.2 (*p*-*C*Me), 134.3 (*o*-*C*Me), 129.2 (*m*-*C*H), 112.0 (*C*H), 20.8 (*p*-C*C*H$_3$), 17.9 (*o*-C*C*H$_3$) ppm.

Compound 3e. Yield: 97%. Found: C, 80.27; H, 9.02; N, 10.26%. Calc. for $C_{27}H_{37}N_3$: C, 80.35; H, 9.24; N, 10.41%; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.22 (m, 4 H, *m*-H), 7.14 (s, 2 H, *p*-H), 5.87 (s, 2 H, NCH), 4.21 (br., 1 H, NH), 3.22 (sept., 4 H, C*H*Me), 1.35 (d, 12 H, CH_3), 1.22 (d, 12 H, CH_3) ppm. ^{13}C NMR (100.52 MHz, C_6D_6): δ 159.5 (N*C*N), 154.6 (*ipso*-*C*), 148.6 (*o*-*C*), 129.6 (*p*-*C*H), 124.3 (*m*-*C*H), 113.6 (*C*H), 29.0 (*C*HMe), 24.1 (CH*C*H$_3$), 24.0 (CH*C*H$_3$) ppm.

Compound 3f. Yield: 97%. Found: C, 60.63; H, 9.53; N, 29.83%. Calc. for $C_7H_{13}N_3$: C, 60.40; H, 9.41; N, 30.19%; ^{1}H NMR (200.13 MHz, C_6D_6, 25 °C): δ 4.20 (s, 1 H, NH), 2.75 (s, 6 H, NCH_3), 1.48 (s, 6 H, CCH_3) ppm. ^{13}C NMR (50.32 MHz, C_6D_6): δ 155.4 (NCN), 113.0 (N*C*Me), 44.8 (*C*HMe), 27.7 (CH*C*H$_3$), 8.4 (NC*C*H$_3$) ppm.

1,3-Diisopropyl-2-(trimethylsilylimino)-4-trimethylsilylimidazoline (4)

A solution of the 1,3-diisopropyl-4,5-dimethylimidazolin-2-ylidene (**1c**) (1.522 g, 10 mmol) in toluene (20 mL) was treated dropwise with trimethylsilyl azide (20 mmol) at ambient temperature, and the resulting reaction mixture was subsequently heated in boiling toluene for 24 h. Filtration and evaporation of the solvent afforded the mixture of the mono- and di-silylated product in the ratio 5 : 1 according to the integration of the ^{1}H NMR peaks. The monosilylated product was distilled off by bulb-to-bulb distillation at 180 °C/9 mbar, and the disilylated product was sublimed from the residue to give a white solid (yield: 0.498 g, 16%). Found: C, 57.83; H, 10.26; N, 13.85%. Calc. for $C_{15}H_{33}N_3Si_2$: C, 57.82; H, 10.67; N, 13.48%; ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 6.19 (s, 1 H, NCH), 4.27 (sept., 1 H, C*H*Me), 3.94 (sept., 1 H, C*H*Me), 1.54 (d, 6 H, CCH_3), 0.95 (d, 6 H, CCH_3), 0.48 (s, 9 H, $SiCH_3$) and 0.14 (s, 9 H, $SiCH_3$) ppm. ^{13}C NMR (100.52 MHz, C_6D_6): 143.8 (NCN), 121.8 (N*C*H), 115.2 (N*C*Si), 50.5 (*C*HMe), 43.9 (*C*HMe), 22.0 (CH*C*H$_3$), 19.9 (CH*C*H$_3$), 4.4 ($NSiCH_3$), −0.6 (CSi*C*H$_3$) ppm.

Single-crystal X-ray crystal structure determinations

Compounds 2d, 3a, 3b. Data were recorded at −100 °C on an area detector (NONIUS, MACH3, κ-CCD) at the window of a rotating anode (NONIUS, FR591) using MoKα radiation (λ = 0.71073 Å). Absorption corrections were applied during the scaling procedure. Structures were refined on F^2 using the program system SHELXL-97 (G. M. Sheldrick, University of Göttingen,

Germany). All other calculations were performed with the STRUX-V system, including the programs PLATON (A. L. Spek, University of Utrecht, Netherlands), SIR92 (C. Giacovazzo, University of Bari, Italy). All hydrogen atom positions were found in difference maps. The hydrogen positions were refined with individual isotropic displacement parameters. *Exceptions/special features*: for **3a**, hydrogen atoms were included using rigid methyl groups allowed to rotate but not tip, or a riding model; for **3b**, in the absence of significant anomalous scattering, no Friedel opposite reflections were registered.

Crystal data for **2d**: $C_{24}H_{33}N_3Si$, triclinic, space group $P\bar{1}$, a = 8.4729(1), b = 8.9346(1), c = 15.8498(3) Å, α = 88.5376(6), β = 80.8585(6), γ = 83.8057(6)°, Z = 2. A yellow irregular fragment 0.40 × 0.35 × 0.35 mm was used to record a total of 8419 reflections to $2\theta_{max}$ 50.7°, of which 4282 were unique. The structure was refined to wR_2 = 0.104 (all reflections), R_1 = 0.0374 [$I > 2\sigma(I)$] for 385 parameters; S = 1.03, max. $\Delta\rho$ 0.24 e Å^{-3}.

Crystal data for **3a**: $C_{11}H_{21}N_3$, monoclinic, space group $P2_1/c$, a = 9.8042(1), b = 11.0624(2), c = 11.6724(2) Å, β = 112.3293(7)°, Z = 4. A colourless fragment 0.3 × 0.15 × 0.13 mm was used to record a total of 4140 reflections to $2\theta_{max}$ 50.7°, of which 2137 were unique. The structure was refined to wR_2 = 0.0981 (all reflections), R_1 = 0.038 [$I > 2\sigma(I)$] for 137 parameters; S = 1.04, max. $\Delta\rho$ 0.16 e Å^{-3}.

Crystal data for **3b**: $C_{11}H_{21}N_3$, monoclinic, space group Cc, a = 7.5606(2), b = 16.9628(4), c = 9.1745(2) Å, β = 92.2557(8)°, Z = 4. A colourless fragment 0.36 × 0.18 × 0.15 mm was used to record a total of 1080 reflections to $2\theta_{max}$ 50.8°, of which 1080 were unique. The structure was refined to wR_2 = 0.0673 (all reflections), R_1 = 0.0296 [$I > 2\sigma(I)$] for 211 parameters; S = 1.10, max. $\Delta\rho$ 0.09 e Å^{-3}.

CCDC reference numbers 618030 (**2d**), 618032 (**3a**), 618033 (**3b**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615418b.

Compounds 2e, 3c, 4. Data were recorded at −140 °C on a Bruker SMART 1000 CCD diffractometer (MoKα radiation, λ = 0.71073 Å). No absorption corrections were applied. Structures were refined on F^2 using the program system SHELXL-97 (G. M. Sheldrick, University of Göttingen, Germany). Hydrogen atoms were included using rigid methyl groups allowed to rotate but not tip, or a riding model. *Exceptions/special features*: for **3c**, the hydrogen atom of the NH group was disordered over two positions, which were refined with half occupancy and an N–H distance restraint.

Crystal data for **2e**: $C_{30}H_{45}N_3Si$, triclinic, space group $P\bar{1}$, a = 9.6170(8), b = 12.4620(10), c = 25.214(2) Å, α = 88.322(2), β = 84.261(2), γ = 79.785(2)°, Z = 4. A colourless irregular fragment 0.40 × 0.35 × 0.3 mm was used to record a total of 20 896 reflections to $2\theta_{max}$ 56.6°, of which 14 394 were unique. The structure was refined to wR_2 = 0.127 (all reflections), R_1 = 0.055 [$I > 2\sigma(I)$] for 635 parameters; S = 0.90, max. $\Delta\rho$ 0.42 e Å^{-3}.

Crystal data for **3c**: $C_9H_{17}N_3$, monoclinic, space group $P2_1/c$, a = 10.3194(11), b = 8.4799(9), c = 12.1497(13) Å, β = 106.293(2)°, Z = 4. A colourless tablet 0.3 × 0.3 × 0.1 mm was used to record a total of 11 493 reflections to $2\theta_{max}$ 61°, of which 3121 were unique. The structure was refined to wR_2 = 0.128 (all reflections), R_1 = 0.050 [$I > 2\sigma(I)$] for 120 parameters and 1 restraint; S = 1.03, max. $\Delta\rho$ 0.31 e Å^{-3}.

Crystal data for **4**: $C_{15}H_{33}N_3Si_2$, monoclinic, space group $P2_1/n$, a = 11.259(2), b = 9.8467(18), c = 18.752(3) Å, β = 103.035(6)°, Z = 4. A colourless prism 0.5 × 0.15 × 0.1 mm was used to record a total of 17 512 reflections to $2\theta_{max}$ 53.7°, of which 4145 were unique. The structure was refined to wR_2 = 0.158 (all reflections), R_1 = 0.063 [$I > 2\sigma(I)$] for 191 parameters; S = 1.13, max. $\Delta\rho$ 0.39 e Å^{-3}.

CCDC reference numbers 618031 (**2e**), 618034 (**3c**), 618035 (**4**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615418b.

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft (DFG Ta 189-6/1). D. P. thanks the Bavarian Science Foundation (Bayerische Forschungsstiftung) for a scholarship (2003–2006).

References

1 M. Regitz, *Angew. Chem.*, 1996, **108**, 791–794; M. Regitz, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 725–728; W. A. Herrmann and C. Köcher, *Angew. Chem.*, 1997, **109**, 2256–2282; W. A. Herrmann and C. Köcher, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2162–2187; A. J. Arduengo, III and R. Krafczyk, *Chem. Unserer Zeit*, 1998, **32**, 6–14; Anthony J. Arduengo, III, *Acc. Chem. Res.*, 1999, **32**, 913–921; D. Bourissou, O. Guerret, F. P. Gabbaï and G. Bertrand, *Chem. Rev.*, 2000, **100**, 39–91; C. Wentrup, *Science*, 2001, **292**, 1846–1847; V. Nair, S. Bindu and V. Sreekumar, *Angew. Chem.*, 2004, **116**, 5240–5245; V. Nair, S. Bindu and V. Sreekumar, *Angew. Chem., Int. Ed.*, 2004, **43**, 5130–5135; F. E. Hahn, *Angew. Chem.*, 2006, **118**, 1374–1378; F. E. Hahn, *Angew. Chem., Int. Ed.*, 2006, **45**, 1348–1352.

2 L. Jafarpour and S. P. Nolan, *Adv. Organomet. Chem.*, 2000, **46**, 181–222; T. Weskamp, V. P. W. Böhm and W. A. Herrmann, *J. Organomet. Chem.*, 2000, **600**, 12–22; W. A. Herrmann, T. Weskamp and V. P. W. Böhm, *Adv. Organomet. Chem.*, 2001, **48**, 1–69; L. Jafarpour and S. P. Nolan, *J. Organomet. Chem.*, 2001, **617–618**, 17–27; D. Enders and H. Gielen, *J. Organomet. Chem.*, 2001, **617–618**, 70–80; W. A. Herrmann, *Angew. Chem.*, 2002, **114**, 1342–1363; W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1290–1309; A. C. Hillier, G. A. Grasa, M. S. Viciu, H. M. Lee, C. Yang and S. P. Nolan, *J. Organomet. Chem.*, 2002, **653**, 69–82; D. Enders and T. Balensiefer, *Acc. Chem. Res.*, 2004, **37**, 534–541; V. Cesar, S. Bellemin-Laponnaz and L. H. Gade, *Chem. Soc. Rev.*, 2004, **33**, 619–636; E. Peris and R. H. Crabtree, *Coord. Chem. Rev.*, 2004, **248**, 2239–2246; V. Nair, R. S. Menon and V. Sreekumar, *Pure Appl. Chem.*, 2005, **77**, 1191–1198.

3 A. J. Boydston, K. A. Williams and C. W. Bielawski, *J. Am. Chem. Soc.*, 2005, **127**, 12496–12497; M. Egen, K. Kahle, M. Bold, T. Gessner, C. Lennartz, S. Nord, H.-W. Schmidt, M. Thelakkat, M. Bäte, C. Neuber, W. Kowalsky, C. Schildknecht and H.-H. Johannes, (BASF AG), WO 2006056418, 2006; M. Bold, C. Lennartz, M. Prinz, H.-W. Schmidt, M. Thelakkat, M. Bäte, C. Neuber, W. Kowalsky, C. Schildknecht and H.-H. Johannes, (BASF AG), WO 2005019373, 2005.

4 J. C. Garrison and W. C. Youngs, *Chem. Rev.*, 2005, **105**, 3978–4008.

5 (*a*) N. Kuhn, M. Göhner, G. Frenking and Y. Chen, in *Unusual Structures and Physical Properties in Organometallic Chemistry*, ed. M. Gielen, R. Willem and B. Wrackmeyer, John Wiley & Sons, The Atrium, West Sussex (UK), 2002, pp. 337–386; (*b*) N. Kuhn, M. Göhner, M. Grathwohl, J. Wiehoff, G. Frenking and Y. Chen, *Z. Anorg. Allg. Chem.*, 2003, **629**, 793–802.

6 C. J. Carmalt and A. H. Cowley, *Adv. Inorg. Chem.*, 2000, **50**, 1–32; N. Kuhn and A. Al-Sheikh, *Coord. Chem. Rev.*, 2005, **249**, 829–857.

7 N. Kuhn, K. Kotowski, T. Kratz and G. Henkel, *Phosphorus, Sulfur Silicon Relat. Elem.*, 1998, **136–138**, 517–520.

8 M. Garner, J. Reglinski, I. Cassidy, M. D. Spicer and A. R. Kennedy, *Chem. Commun.*, 1996, 1975–1976.

9 Selected recent publications: V. K. Landry, J. G. Melnick, D. Buccella, K. Pang, J. Ulichny and G. Parkin, *Inorg. Chem.*, 2006, **45**, 2588–2597; J. G. Melnick, G. Zhu, D. Buccella and G. Parkin, *J. Inorg. Biochem.*,

2006, **100**, 1147–1154; M. Rombach, J. Seebacher, M. Ji, G. Zhang, G. He, M. M. Ibrahim, B. Benkmil and H. Vahrenkamp, *Inorg. Chem.*, 2006, **45**, 4571–4575; C. A. Dodds, M. Garner, J. Reglinski and M. D. Spicer, *Inorg. Chem.*, 2006, **45**, 2733–2741; A. Cetin and C. J. Ziegler, *Dalton Trans.*, 2006, 1006–1008; S. L. Kuan, W. K. Leong, L. Y. Goh and R. D. Webster, *J. Organomet. Chem.*, 2006, **691**, 907–915; C. A. Dodds, J. Reglinski and M. D. Spicer, *Chem.–Eur. J.*, 2006, **12**, 931–939; I. R. Crossley, A. F. Hill and A. C. Willis, *Organometallics*, 2006, **25**, 289–299.

10 (*a*) M. Tamm, S. Randoll, T. Bannenberg and E. Herdtweck, *Chem. Commun.*, 2004, 876–877; (*b*) M. Tamm, S. Beer and E. Herdtweck, *Z. Naturforsch., B: Chem. Sci.*, 2004, **59**, 1497–1504; (*c*) M. Tamm, S. Randoll, E. Herdtweck, N. Kleigrewe, G. Kehr, G. Erker and B. Rieger, *Dalton Trans.*, 2006, 459–467.

11 (*a*) D. W. Stephan, *Organometallics*, 2005, **24**, 2548–2560; (*b*) K. Dehnicke and A. Greiner, *Angew. Chem.*, 2003, **115**, 1378–1392; K. Dehnicke and A. Greiner, *Angew. Chem., Int. Ed.*, 2003, **42**, 1340–1354; (*c*) K. Dehnicke, M. Krieger and W. Massa, *Coord. Chem. Rev.*, 1999, **182**, 19–65; (*d*) K. Dehnicke and F. Weller, *Coord. Chem. Rev.*, 1997, **158**, 103–168; (*e*) K. Dehnicke and J. Strähle, *Polyhedron*, 1989, **6**, 707–726.

12 M. Tamm, D. Petrovic, S. Beer, S. Randoll, S. Filimon and T. Glöge, unpublished results.

13 A similar reaction resulting directly in the formation of 1,3-dimesityl-2-iminoimidazoline in low yield has been reported previously, see: J. M. Hopkins, M. Bowdridge, K. N. Robertson, T. S. Cameron, H. A. Jenkins and J. A. C. Clyburne, *J. Org. Chem.*, 2001, **66**, 5713–5716; in a similar fashion, the reaction of stable *N*-heterocyclic silylenes with covalent azidosilanes leads to the intermediate formation silaimines, which undergo further nucleophilic addition or cycloaddition reactions, see: M. Denk, R. K. Hayashi and R. West, *J. Am. Chem. Soc.*, 1994, **116**, 10813–10814; N. J. Hill, D. F. Moser, I. A. Guzei and R. West, *Organometallics*, 2005, **24**, 3346–3349.

14 (*a*) H. Staudinger and J. Meyer, *Helv. Chim. Acta*, 1919, **2**, 635–646; (*b*) Y. G. Gololobov, I. N. Zhmurova and L. F. Kasukhin, *Tetrahedron*, 1981, **37**, 437–472; (*c*) S. Bräse, C. Gil, K. Knepper and V. Zimmermann, *Angew. Chem.*, 2005, **117**, 5320–5374; S. Bräse, C. Gil, K. Knepper and V. Zimmermann, *Angew. Chem., Int. Ed.*, 2005, **44**, 5188–5240.

15 W. Q. Tian and Y. A. Wang, *J. Org. Chem.*, 2004, **69**, 4299–4308.

16 D. M. Khramov and C. W. Bielawski, *Chem. Commun.*, 2005, 4958–4960.

17 A. Diefenbach and F. M. Bickelhaupt, *Z. Anorg. Allg. Chem.*, 1999, **625**, 892–900.

18 F. Weller, H.-C. Kang, W. Massa, T. Rübenstahl, F. Kunkel and K. Dehnicke, *Z. Naturforsch., B: Chem. Sci.*, 1995, **50**, 1050–1054.

19 A. Müller, M. Möhlen, B. Neumüller, N. Faza, W. Massa and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1999, **625**, 1748–1751.

20 D. Bacciu, K. J. Cavell, I. A. Fallis and L.-l. Ooi, *Angew. Chem.*, 2005, **117**, 5416–5418; D. Bacciu, K. J. Cavell, I. A. Fallis and L.-l. Ooi, *Angew. Chem., Int. Ed.*, 2005, **44**, 5282–5284; H. Lebel, M. K. Janes, A. B. Charette and S. P. Nolan, *J. Am. Chem. Soc.*, 2004, **126**, 5046–5047; A. R. Chianese, A. Kovacevic, B. M. Zeglis, J. W. Faller and R. H. Crabtree, *Organometallics*, 2004, **23**, 2461–2468; S. Gründemann, A. Kovacevic, M. Albrecht, J. W. Faller and R. H. Crabtree, *J. Am. Chem. Soc.*, 2002, **124**, 10473–10481.

21 N. Kuhn, R. Fawzi, M. Steimann and J. Wiethoff, *Z. Anorg. Allg. Chem.*, 1997, **623**, 769–774; N. Kuhn, R. Fawzi, M. Steimann and J. Wiethoff, *Z. Anorg. Allg. Chem.*, 1997, **623**, 554–560.

22 N. Kuhn, M. Grathwohl, M. Steimann and G. Henkel, *Z. Naturforsch., B: Chem. Sci.*, 1998, **53**, 997–1003; N. Kuhn, M. Grathwohl, C. Nachtigal and M. Steimann, *Z. Naturforsch., B: Chem. Sci.*, 2001, **56**, 704–710.

23 N. Kuhn, R. Fawzi, M. Steimann, J. Wiethoff, D. Bläser and R. Boese, *Z. Naturforsch., B: Chem. Sci.*, 1995, **50**, 1779–1784 and refs cited therein.

24 J. March, *Advanced Organic Chemistry*, John Wiley & Sons, Inc., New York, 4th edn, 1992, p. 21.

25 A. J. Arduengo, III, H. V. Rasika Dias, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1992, **114**, 5530–5534.

26 A. J. Arduengo, III, R. L. Harlow and M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361–363; A. J. Arduengo, III, H. V. Rasika Dias, D. A. Dixon, R. L. Harlow, W. T. Klooster and T. F. Koetzle, *J. Am. Chem. Soc.*, 1994, **116**, 6812–6822.

27 A. Bondi, *J. Phys. Chem.*, 1964, **68**, 441–451; R. S. Rowland and R. Taylor, *J. Phys. Chem.*, 1996, **100**, 7384–7391.

28 G. A. Jeffrey, *An Introduction to Hydrogen Bonding*, Oxford University Press, Oxford, 1997.

29 T. Steiner, *Angew. Chem.*, 2002, **114**, 50–80; T. Steiner, *Angew. Chem., Int. Ed.*, 2002, **41**, 48–76; G. R. Desiraju and T. Steiner, *The Weak Hydrogen Bond in Structural Chemistry and Biology*, Oxford University Press, Oxford, 1999.

30 G. R. Desiraju, *Chem. Commun.*, 2005, 2995–3001.

31 Compliance constants, whether recorded experimentally or computed theoretically, measure the displacement of a single internal coordinate due to an external force. For details, see: J. Grunenberg and N. Goldberg, *J. Am. Chem. Soc.*, 2000, **122**, 6045–6047; G. Frantzius, R. Streubel, K. Brandhorst and J. Grunenberg, *Organometallics*, 2006, **25**, 118–121; L. H. Jones and B. I. Swanson, *Acc. Chem. Res.*, 1976, **9**, 128–134.

32 J. Grunenberg, *J. Am. Chem. Soc.*, 2004, **126**, 16310–16311.

33 C. Würtele, E. Gaoutchenova, K. Harms, M. C. Holthausen, J. Sundermeyer and S. Schindler, *Angew. Chem.*, 2006, **118**, 3951–3954; C. Würtele, E. Gaoutchenova, K. Harms, M. C. Holthausen, J. Sundermeyer and S. Schindler, *Angew. Chem., Int. Ed.*, 2006, **45**, 3867–3869; S. Herres-Pawlis, U. Flörke and G. Henkel, *Eur. J. Inorg. Chem.*, 2005, 3815–3824; M. Schatz, V. Raab, S. P. Foxon, G. Brehm, S. Schneider, M. Reiher, M. C. Holthausen, J. Sundermeyer and S. Schindler, *Angew. Chem.*, 2004, **116**, 4460–4464; M. Schatz, V. Raab, S. P. Foxon, G. Brehm, S. Schneider, M. Reiher, M. C. Holthausen, J. Sundermeyer and S. Schindler, *Angew. Chem., Int. Ed.*, 2004, **43**, 4360–4363; S. Herres, A. J. Heuwing, U. Flörke, J. Schneider and G. Henkel, *Inorg. Chim. Acta*, 2005, **358**, 1089–1095; H. Wittmann, V. Raab, A. Schorm, J. Plackmeyer and J. Sundermeyer, *Eur. J. Inorg. Chem.*, 2001, 1937–1948; V. Raab, J. Kipke, O. Burghaus and J. Sundermeyer, *Inorg. Chem.*, 2001, **40**, 6964–6971; S. H. Oakley, M. P. Coles and P. B. Hitchcock, *Inorg. Chem.*, 2004, **43**, 5168–5172; S. Pohl, M. Harmjanz, J. Schneider, W. Saak and G. Henkel, *J. Chem. Soc., Dalton Trans.*, 2000, 3473–3479; H. Wittmann, A. Schorm and J. Sundermeyer, *Z. Anorg. Allg. Chem.*, 2000, **626**, 1583–1590.

34 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford, CT, 2004.

35 A. A. Kolomeitsev, I. A. Koppel, T. Rodima, J. Barten, E. Lork, G.-V. Röschenthaler, I. Kaljurand, A. Kütt, I. Koppel, V. Mäements and I. Leito, *J. Am. Chem. Soc.*, 2005, **127**, 17656–17666.

36 I. A. Koppel, R. Schwesinger, T. Breuer, P. Burk, K. Herodes, I. Koppel, I. Leito and M. Mishima, *J. Phys. Chem. A*, 2001, **105**, 9575–9586.

37 E. D. Glendening and F. Weinhold, *J. Comput. Chem.*, 1998, **19**, 593.

38 The NRT analysis was done using the NBO 5.0 G program extension for Gaussian; E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales and F. Weinhold, Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2001.

39 S. Shah and J. D. Protasiewicz, *Coord. Chem. Rev.*, 2000, **210**, 181–201; F. P. Cossío, C. Alonso, B. Lecea, M. Ayerbe, G. Rubiales and F. Palacios, *J. Org. Chem.*, 2006, **71**, 2839–2847.

40 A. J. Arduengo, H. Bock, H. Chen, M. Denk, D. A. Dixon, J. C. Green, W. A. Herrmann, N. L. Jones, M. Wagner and R. West, *J. Am. Chem. Soc.*, 1994, **116**, 6641–6649.

41 A. J. Arduengo, R. Krafczyk, R. Schmutzler, H. A. Craig, J. R. Goerlich, W. J. Marshall and M. Unverzagt, *Tetrahedron*, 1999, **55**, 14523–14534.

42 N. Kuhn and T. Kratz, *Synthesis*, 1993, 561–562.

