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Transient Amino-Hydrazino-Carbenes: A Radical Pathway for Intramolecular 1,2-Migration Reactions

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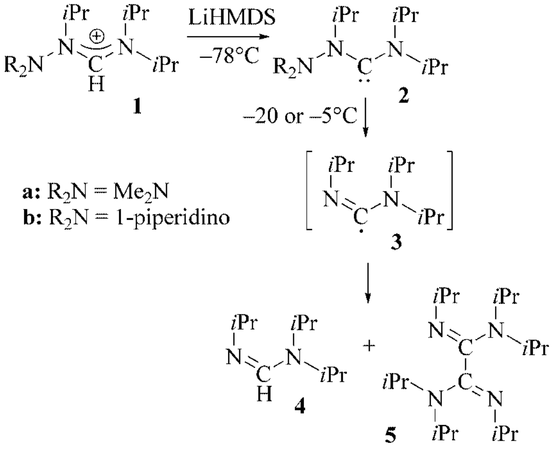
The transient amino-hydrazino-carbenes **2c**–**e** are reported to undergo intramolecular 1,2-migration reactions that proceed through a radical pathway according to DFT calculations.

Introduction

The last 15 years have seen tremendous advances in carbene chemistry that have shifted these electron-deficient reactive intermediates[1] into the realm of isolable compounds.[2] In particular, the use of N-heterocyclic carbenes as ancillary ligands for transition-metal catalysts[3] and as organocatalysts in their own right[4,5] has proven very fruitful. The availability of a variety of stable singlet carbenes[6] has also provided more insight into typical carbene reactivity, including dimerization,[7] cyclopropanation,[8] C–H insertion reactions,[9] 1,2-[10] and 1,3-[11] migration reactions. We have even recently reported experimental and theoretical evidence for radical fragmentation reactions.[12] Indeed, we have shown that deprotonation of the formamidinium salts **1a**,**b** afforded the carbenes **2a**,**b** that could be spectroscopically characterized at –30 °C, but that rearranged upon warming, into the formamidine **4** and the oxamidine **5** through the transient aminoimidoyl radical **3** (Scheme 1).



Scheme 1.

In extension of this work, we report here that the substitution pattern of the hydrazino group dramatically influences the lifetime of carbenes of type **2**,[13] and that such transient amino-hydrazino-carbenes are prone to undergo intramolecular 1,2-migration reactions that also proceed through a radical pathway according to DFT calculations.

Results and Discussion

The comparison of the lifetime of **2a** ($t_{1/2} \approx 20$ min at –22 °C) and **2b** ($t_{1/2} \approx 2.5$ h at –5 °C)[12] suggests that the substitution pattern of the N_β atom, and especially the number of labile hydrogen atoms, has a strong influence on the stability of amino-hydrazino-carbenes. This prompted us to investigate the related derivatives **2c**,**d** featuring pyrrole and diphenylamino groups, respectively. The required formamidinium precursors **1c**,**d** were synthesized by condensation of the corresponding silylhydrazines **7c**,**d** with chloro-*N*,*N*-diisopropylformamidinium chloride. Lastly, anion exchange with $NaBPh_4$ was performed in order to increase the solubility of the salts in tetrahydrofuran at low temperature (Scheme 2). The ^1H and ^{13}C NMR spectro-

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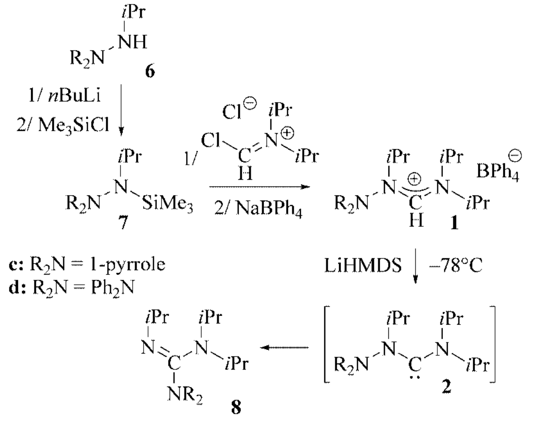
scopic data unambiguously support the structure of the salts **1c**,**d** and an X-ray diffraction study carried out on **1d** (Figure 1) revealed the *syn* relationship between the NPh_2 and $NiPr_2$ groups in the solid state. Deprotonation of **1c** and **1d** by lithium hexamethyldisilazide (LiHMDS) was carried out in deuterated tetrahydrofuran at –78 °C. The direct analysis of the reaction mixture by NMR at –80 °C revealed that deprotonation had completely and cleanly occurred, but surprisingly, the resulting products **8c**,**d** were apparently not the expected carbenes **2c**,**d**, as indicated by the absence of the characteristic low-field signals in the ^{13}C NMR spectra. Mass spectrometry analyses suggested that **8c**,**d** were isomers of their corresponding carbene species, and the signals observed at δ = 161 (**8c**) and 147 ppm (**8d**) in their ^{13}C NMR spectra supported their formulation as guanidines. Therefore, in marked contrast with **2a**,**b**, the amino-hydrazino-carbenes **2c**,**d** are only transient species that spontaneously undergo 1,2-migration reactions even at low temperature.



Scheme 2.

1,2-Migrations are well-established reactions for singlet carbenes, typically proceeding through an unimolecular concerted mechanism.[14] However, such a pathway has been predicted to be strongly disfavoured for diaminocarbenes. Accordingly, the 1,2-hydrogen migration from the parent imidazol-2-ylidene was predicted to be exothermic (by about 25–30 kcal mol^{-1}), but kinetically unfavourable (with an activation barrier of about 40 kcal mol^{-1}).[15] In line with these considerations, 1,2-migration reactions have rarely been observed for transient diaminocarbenes,[16] and the only mechanistic study conducted so far has evidenced (in the case of transient triazolylidenes) an intermolecular mechanism involving the electrophilic precursor.[10]

Despite the weakness of N–N single bonds (40 kcal mol^{-1} for hydrazines), the apparent ease of 1,2-migration reactions from the amino-hydrazino-carbenes **2c**,**d** is quite puzzling, and raises the question of their mechanism. In order to discriminate between inter- and intramolecular pathways, we prepared the related formamidinium salt **1e** featuring a 2-phenylpyrazolidine substituent, and studied its deprotonation under the same conditions. Accordingly, the guanidine **8e**, unambiguously characterized by X-ray diffraction analysis of its methylated salt **9e** (Figure 1), was formed as the only product at low temperature (Scheme 3). This result strongly supports an intramolecular mechanism for these 1,2-migration reactions because intermolecular processes would have led to oligomeric guanidines.

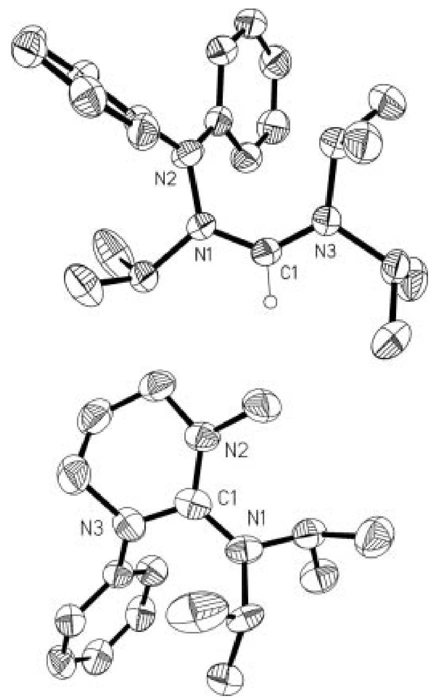
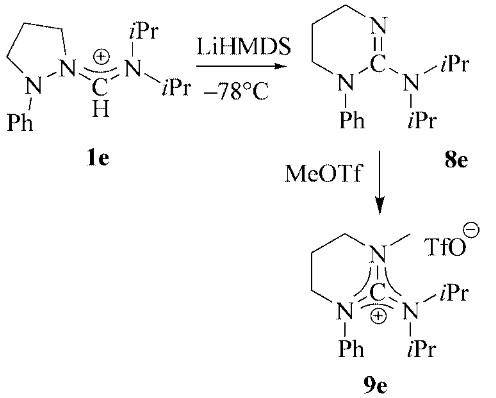


Figure 1. Thermal ellipsoid diagrams (50% probability) of **1d** (top) and **9e** (bottom); only the cationic part is represented for clarity.



Scheme 3.

To gain more insight into the mechanism of these intramolecular 1,2-migration reactions, DFT calculations were carried out on the model carbene **2c*** at the B3LYP/6-31G** level of theory. Accordingly, two close minima were found on the singlet potential energy surface, **2c*-S1** being more stable than **2c*-S2** by 3.4 kcal mol^{-1} (Figure 2). The 1,2-migration of the pyrrole moiety leading to the guanidine **8c*** was predicted to be highly exothermic (–50.8 kcal mol^{-1} from the most stable conformer **2c*-S1**), and a cyclic transition state $\mathbf{TS_{mig}}$ could be located on the closed-shell surface 60.4 kcal mol^{-1} higher in energy than **2c*-S1** (Figure 3). This activation barrier is even higher than that predicted for the 1,2-hydrogen migration from the parent imidazolylidene,[15] and therefore such a pathway cannot account for our experimental observations. The unimolecular concerted mechanism usually operating for transient carbenes could thus be ruled out.

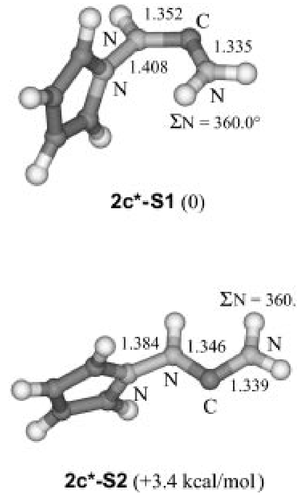


Figure 2. Optimized structures of the model singlet amino-hydrazino-carbene **2c*** at the B3LYP/6-31G** level.

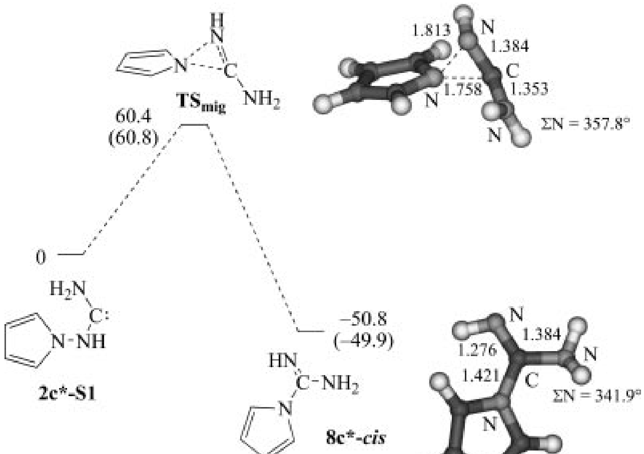
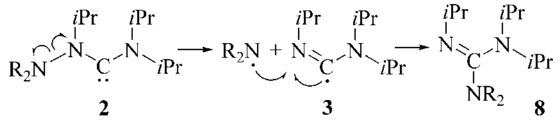


Figure 3. Closed-shell surface of the model amino-hydrazino-carbene **2c*** computed at the B3LYP/6-31G** level (total enthalpies *H* relative to the carbene **2c*** including ZPE correction are expressed in kilocalories per mol, distances given in Å). The corresponding free energies at 25 °C are given in brackets.

In line with the radical fragmentation[17] of amino-hydrazino-carbenes previously reported[12] for **2a**,**b**, the formation of the 1,2-migration products **8** can be envisaged by homolytic cleavage of the weak N–N bond of **2**, followed by C–N hetero-coupling of the resulting aminyl and aminoimidoyl radicals,[18] **10** and **3**, respectively (Scheme 4).[19] To confirm the feasibility of such a radical pathway for the fragmentation of **2c***, the pyrrolyl radical and parent aminoimidoyl radical **3*** were optimized at the UB3LYP/6-31G** level of theory, and the N–N bond energy for carbene **2c*** (ΔH) was thereby estimated to be 26.1 kcal mol^{-1} (from the most stable conformer **2c*-S1**). To a first approximation, this value can be considered as the energy required for homolytic fragmentation of **2c***.[20] Because of favourable entropic factors, the corresponding free enthalpy of dissociation was calculated to be only 12.5 kcal mol^{-1} at 25 °C. This activation barrier is much lower than that predicted for the formation of **8c*** through a concerted process ($\Delta G^{\neq}$ = 60.8 kcal mol^{-1} at 25 °C), and is in good agreement with the transient character of carbenes **2c**–**e** and their spontaneous rearrangement at low temperature. Given this data, the intramolecular nature of the rearrangement most probably results from fast recombination of the two radicals within the solvent cage.



Scheme 4.

Conclusions

The substitution pattern of amino-hydrazino-carbenes has been shown to dramatically influence their stability. Introduction of pyrrole or diphenylamino moieties at the N_β atom does not allow anymore the spectroscopic characterization of carbenes **2c**–**e** because clean 1,2-migration reactions occurred even at low temperature. The intramolecular nature of these rearrangements, supported experimentally using cyclic formamidinium salt precursors, is in marked contrast with the intermolecular pathway evidenced for transient triazolylidenes. DFT calculations on model compounds rule out the concerted pathway normally encountered with transient singlet carbenes, but strongly support a dissociative radical mechanism involving the homolytic cleavage of the weak N–N bond followed by C–N hetero-coupling of the resulting aminyl and aminoimidoyl radicals.[21–23]

Experimental Section

General Procedures: All manipulations were performed under argon using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^{1}H, ^{13}C, ^{19}F NMR spectra were recorded with Bruker AC200, WM250, Avance 300, Varian Inova 300 or Inova 500 spectrometers. ^{1}H and ^{13}C chemical shifts are reported in ppm relative to Me_4Si as external standard, and ^{19}F chemical shifts are reported in ppm relative to CF_3COOH as external standard. *N*-Aminopyrrole,[24] *N'*-isopropyl-*N*,*N*-diphenylhydrazine,[25] *N*-phenylpyrazolidine,[26] chloro-*N*,*N*-diisopropylformamidinium chloride[27] were prepared according to literature procedures.

Synthesis of the *N*-(Isopropylamino)pyrrole 6c: A solution of *N*-aminopyrrole (15 mmol) in acetone (100 mL) was refluxed in the presence of magnesium sulfate for 72 h. After filtration and concentration, a yellowish oil was obtained (1.61 g, 88 %). ^{1}H NMR (80 MHz, 298 K, $CDCl_3$): δ = 1.93 (s, 3 H, CH_3), 2.17 (s, 3 H, CH_3), 6.13 (t, $^3J_{HH}$ = 2 Hz, 2 H, CH_{pyr}), 6.78 (t, $^3J_{HH}$ = 2 Hz, 2 H, CH_{pyr}) ppm. This residue was then dissolved in 50 mL of acetonitrile, 0.60 g of sodium cyanoborohydride (16 mmol) was added portionwise over a period of 30 min, and the mixture was stirred for 45 min. Glacial acetic acid (2.7 mL) was then added, and the mixture was stirred for 6 h. Concentrated hydrochloric acid (6 mL, 37%w) was added. The solution was concentrated, then a 10% NaOH solution in water was carefully added until pH > 12. The mixture was extracted with diethyl ether, and the organic phase was washed with water, brine, then dried with sodium sulfate. After concentration, *N*-(isopropylamino)pyrrole was obtained as a yellowish oil (0.80 g, 49%). ^{1}H NMR (250 MHz, 298 K, $CDCl_3$): δ = 1.07 (d, $^{3}J_{HH}$ = 7.0 Hz, 6 H, CH_3), 3.45 (sept, $^{3}J_{HH}$ = 7.0 Hz, 1 H, NCH), 5.8 (br., 1 H, NH), 6.08 (t, $^{3}J_{HH}$ = 2.1 Hz, 2 H, CH_{pyr}), 6.78 (t, $^{3}J_{HH}$ = 2.1 Hz, 2 H, CH_{pyr}) ppm. ^{13}C NMR (63 MHz, 298 K, $CDCl_3$): δ = 21.0 (CH_3), 53.9 (NCH), 106.9 (CH_{pyr}), 121.0 (CH_{pyr}) ppm.

Synthesis of 1c: A solution of *N*-(isopropylamino)pyrrole (5.0 mmol) in tetrahydrofuran (10 mL) was cooled to –78 °C, then 2.0 mL of a 2.5 M solution of *n*-butyllithium in hexanes (5.0 mmol) was added. The solution was warmed to room temperature and stirred for half an hour, then cooled to –78 °C, and chlorotrimethylsilane (0.7 mL, 5.5 mmol) was added. After warming to room temperature, the solution was concentrated, and the residue was extracted with pentane (3 × 5 mL). The filtrate was concentrated to yield the silylhydrazine **7c** as a pale yellow oil. It was dissolved in 10 mL of dichloromethane, and added onto a suspension of chloro-*N*,*N*-diisopropylformamidinium chloride (0.55 g, 3.0 mmol) in dichloromethane at –50 °C. The mixture was then warmed to room temperature and stirred overnight. The solution was concentrated, and the residue was washed with pentane (3 × 10 mL), then dried. The formamidinium chloride was obtained as a white powder (0.46 g, 56%). ^{1}H NMR (300 MHz, 298 K, CD_3CN): δ = 1.02 [d, $^{3}J_{HH}$ = 6.5 Hz, 6 H, $NCH(CH_3)_2$], 1.25 [d, $^{3}J_{HH}$ = 6.5 Hz, 6 H, $NCH(CH_3)_2$], 1.40 [d, $^{3}J_{HH}$ = 6.8 Hz, 6 H, $NCH(CH_3)_2$], 2.33 [sept, $^{3}J_{HH}$ = 6.5 Hz, 1 H, $NCH(CH_3)_2$], 3.92 [sept, $^{3}J_{HH}$ = 6.8 Hz, 1 H, $NCH(CH_3)_2$], 4.62 [sept, $^{3}J_{HH}$ = 6.5 Hz, 1 H, $NCH(CH_3)_2$], 6.26 (t, $^{3}J_{HH}$ = 2.2 Hz, 2 H, CH_{pyr}), 6.93 (t, $^{3}J_{HH}$ = 2.2 Hz, 2 H, CH_{pyr}), 9.08 (s, 1 H, NCHN) ppm. ^{13}C NMR (75 MHz, 298 K, CD_3CN): δ = 19.1 [$NCH(CH_3)_2$], 20.0 [$NCH(CH_3)_2$], 22.8 [$NCH(CH_3)_2$], 49.7 [$NCH(CH_3)_2$], 51.2 [$NCH(CH_3)_2$], 62.4 [$NCH(CH_3)_2$], 109.1 (CH_{pyr}), 122.5 (CH_{pyr}), 152.0 (NCHN) ppm. The formamidinium chloride (2.0 mmol) was then dissolved in 10 mL of acetonitrile and sodium tetraphenylborate (0.70 g, 2.0 mmol) was added. After 2 h of stirring, the mixture was allowed to settle, and was filtered. The filtrate was concentrated and the solid was recrystallized from dichloromethane, yielding the formamidinium tetraphenylborate **1c** (0.82 g, 74%).

Synthesis of 1d: *N*′-Isopropyl-*N*,*N*-diphenylhydrazine was converted into the corresponding silylhydrazine **7d** using a procedure similar to that described for **1c**, but refluxing the reaction mixture for 1 h after the addition of *n*-butyllithium. The formamidinium chloride was obtained in 66% yield (0.74 g) as a brown powder. ^{1}H NMR (300 MHz, 298 K, CD_3CN): δ = 0.85 (d, $^{3}J_{HH}$ = 6.9 Hz, 6 H, CH_3), 1.31 (d, $^{3}J_{HH}$ = 6.9 Hz, 6 H, CH_3), 1.49 (d, $^{3}J_{HH}$ = 6.9 Hz, 6 H, CH_3), 3.93 (sept, $^{3}J_{HH}$ = 6.9 Hz, 1 H, NCH), 4.87 (sept, $^{3}J_{HH}$ = 6.9 Hz, 2 H, NCH), 7.1–7.3 (m, 6 H, CH_{Ar}), 7.4 (m, 4 H, CH_{Ar}), 8.58 (s, 1 H, NCHN) ppm. ^{13}C NMR (125 MHz, 298 K, CD_3CN): δ = 20.6 (CH_3), 22.2 (CH_3), 24.0 (CH_3), 52.0 (N*C*H), 52.4 (N*C*H), 63.4 (N*C*H), 120.1 (CH_{Ar}), 130.0 (CH_{Ar}), 130.9 (CH_{Ar}), 142.8 (Cq_{Ar}), 153.7 (NCHN) ppm. The solid was converted into the tetraphenylborate salt as for **1c** (1.04 g, 80%). Single crystals of **1d** were obtained by cooling a saturated solution in a mixture of dichloromethane and diethyl ether to –30 °C. ^{1}H NMR (300 MHz, 298 K, CD_3CN): δ = 0.87 (d, $^{3}J_{HH}$ = 6.7 Hz, 6 H, CH_3), 1.33 (d, $^{3}J_{HH}$ = 6.7 Hz, 6 H, CH_3), 1.39 (d, $^{3}J_{HH}$ = 6.7 Hz, 6 H, CH_3), 3.96 (sept, $^{3}J_{HH}$ = 6.7 Hz, 1 H, NC*H*), 4.28 (sept, $^{3}J_{HH}$ = 6.7 Hz, 1 H, NC*H*), 4.94 (sept, $^{3}J_{HH}$ = 6.7 Hz, 1 H, NC*H*), 6.8 (m, 4 H, BPh_4), 7.0 (m, 8 H, BPh_4), 7.2 (m, 14 H, BPh_4 and CH_{Ar}), 7.4 (m, 4 H, CH_{Ar}), 7.74 (s, 1 H, NCHN) ppm. M.p. 169 °C.

Synthesis of 1e: Following the same procedure as described for **1c**, the formamidinium chloride **1e** was synthesized in 49% yield (0.43 g) as yellowish crystals. ^{1}H NMR (300 MHz, 298 K, CD_3CN): δ = 0.6 (br., 3 H, CH_3), 1.1 (br., 3 H, CH_3), 1.4 (br., 6 H, CH_3), 2.1 (br., 1 H, NCH), 3.5 (br., 2 H, CH_2), 3.7 (br., 2 H, CH_2), 4.0 (br., 2 H, CH_2), 5.3 (br., 1 H, NC*H*), 6.9 (br., 2 H, CH_{Ar}), 7.0 (br., 1 H, CH_{Ar}), 7.3 (br., 2 H, CH_{Ar}), 7.8 (br., 1 H, NCHN) ppm. ^{13}C NMR (75 MHz, 298 K, CD_3CN): δ = 19.0 (CH_3), 19.6 (CH_3), 22.3 (CH_2); 22.5 (CH_3), 22.7 (CH_3), 49.5 (NCH), 50.2 (NCH), 52.0 (CH_2), 56.8 (CH_2), 116.5 (CH_{Ar}), 124.2 (CH_{Ar}), 129.9 (CH_{Ar}), 147.9 (C_{ipso}), 148.7 (NCHN) ppm. After anion exchange, the corresponding tetraphenylborate salt was then obtained in 77% yield (0.66 g).

General Procedure for the Deprotonation of the Formamidinium Salts: A solution of 27 mg of $LiHMDS.OEt_2$ (0.12 mmol) in 0.4 mL of $[D_8]$THF was added at –78 °C to a solution of the formamidinium tetraphenylborate (0.10 mmol) in 0.3 mL of $[D_8]$THF placed in an NMR tube. The tube was shaken, and directly submitted to NMR analysis at –80 °C.

Guanidine 6c: ^{1}H NMR (250 MHz, 298 K, $[D_8]$THF): δ = 0.95 (d, $^{3}J_{HH}$ = 6.0 Hz, 6 H, CH_3), 1.23 (d, $^{3}J_{HH}$ = 6.7 Hz, 12 H, CH_3), 2.89 (sept, $^{3}J_{HH}$ = 6.0 Hz, 1 H, NCH), 3.22 (sept, $^{3}J_{HH}$ = 6.7 Hz, 2 H, NCH), 6.11 (t, $^{3}J_{HH}$ = 2.1 Hz, 2 H, CH_{pyr}), 6.60 (t, $^{3}J_{HH}$ = 2.1 Hz, 2 H, CH_{pyr}) ppm. ^{13}C NMR (75 MHz, 298 K, $[D_8]$THF): δ = 18.6 (CH_3), 22.9 (CH_3), 45.0 (NCH), 46.9 (NCH), 106.9 (CH_{pyr}), 117.8 (CH_{py}), 161.4 (NCNN) ppm. MS (IE): *m*/*z* = 235 [M^+].

Guanidine 6d: Isolated in 80% yield (27 mg) after evaporation of the tetrahydrofuran, extraction with diethyl ether, filtration and concentration. The guanidine was purified by sublimation under vacuum. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ = 0.68 (br., 6 H, CH_3), 1.09 (d, $^{3}J_{HH}$ = 6.0 Hz, 6 H, CH_3), 1.69 (br., 6 H, CH_3), 3.16 (br., 1 H, NC*H*), 3.78 (sept, $^{3}J_{HH}$ = 6.0 Hz, 1 H, NC*H*), 3.88 (br., 1 H, NCH), 6.8–6.9 (m, 2 H, CH_{Ar}), 7.0–7.2 (m, 8 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ = 21.0 (CH_3), 21.6 (CH_3), 25.5 (CH_3), 46.0 (NCH), 48.9 (NCH), 49.7 (NCH), 120.9 (CH_{Ar}), 122.6 (CH_{Ar}), 129.8 (CH_{Ar}), 145.3 (C_{ipso}), 146.4 (NNCN) ppm. MS (CI, NH_3): *m*/*z* = 338 [MH^+].

Guanidine 6e: Isolated as a yellowish oil in 85% yield (22 mg) after evaporation of the tetrahydrofuran, extraction with diethyl ether, filtration and concentration. ^{1}H NMR (300 MHz, 298 K, C_6D_6): δ = 1.10 (d, $^{3}J_{HH}$ = 6.5 Hz, 12 H, CH_3), 1.35 (quint, $^{3}J_{HH}$ = 6.1 Hz, 2 H, CH_2), 3.10 (t, $^{3}J_{HH}$ = 6.1 Hz, 2 H, CH_2), 3.45 (t, $^{3}J_{HH}$ = 6.1 Hz, 2 H, CH_2), 3.54 (sept, $^{3}J_{HH}$ = 6.5 Hz, 2 H, NCH), 6.9–7.0 (m, 3 H, CH_{Ar}), 7.1–7.2 (m, 2 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, 298 K, C_6D_6): δ = 21.1 (CH_3), 21.2 (CH_2), 44.7 (CH_2), 46.7 (NCH), 49.8 (CH_2), 122.7 (CH_{Ar}), 123.6 (CH_{Ar}), 128.8 (CH_{Ar}), 149.2 (C_{ipso}), 153.1 (NNCN) ppm. MS (IE): *m*/*z* = 259 [M^+].

Guanidinium Salt 7e: Methyl trifluoromethanesulfonate MeOTf (0.22 mL, 1.9 mmol) was added at –50 °C to the guanidine **6e** (0.45 g, 1.8 mmol) in 1 mL of dichloromethane. The solution was warmed to room temperature, then stirred for half an hour. It was then concentrated, and the residue was washed with diethyl ether, and dried. Single crystals suitable for an X-ray analysis were obtained by cooling a saturated solution in THF/pentane to –30 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 0.83 (d, $^{3}J_{HH}$ = 7.0 Hz, 6 H, $CHCH_3$), 1.25 (d, $^{3}J_{HH}$ = 7.0 Hz, 6 H, $CHCH_3$), 2.21 (quint, $^{3}J_{HH}$

= 6.1 Hz, 2 H, CH_2), 3.25 (s, 3 H, NCH_3), 3.63 (t, $^3J_{HH}$ = 6.1 Hz, 2 H, CH_2), 3.7–3.8 (m, 4 H, CH_2 and NCH), 7.2–7.4 (m, 5 H, CH_{Ar}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH*C*H_3), 23.2 (CH*C*H_3), 23.3 (CH_2), 41.8 (NCH_3), 49.7 (CH_2), 51.6 (CH_2), 52.8 (NCH), 120.4 (q, $^1J_{CF}$ = 320 Hz, $CF_3SO_3^-$), 126.5 (CH_{Ar}), 128.4 (CH_{Ar}), 130.0 (CH_{Ar}), 143.4 (C_{ipso}), 163.1 (NNCN) ppm. ^{19}F NMR (188 MHz, $CDCl_3$): δ = –3.6 ($CF_3SO_3^-$) ppm. M.p. 46 °C.

Computational Details: Calculations were performed with the Gaussian 98 program[28,29] using the Density Functional Theory method.[30] The various structures were fully optimized at B3LYP level.[31] This functional is built with Becke's three parameter exchange functional[31a] and the Lee–Yang–Parr correlation functional.[31c] The 6-31G(d,p) basis set was used. All atoms were augmented with a single set of polarization functions. The second derivatives were calculated in order to determine if a minimum or a transition state (one negative eigenvalue) existed for the resulting geometry. The connection between the transition states $\mathbf{TS_{mig}}$ and the corresponding minima was confirmed by IRC calculations. All total energies have been zero-point energy (ZPE) and temperature corrected using unscaled density functional frequencies.

X-ray Crystallography: Data for **1d** and **9e** were collected at low temperatures using an oil-coated shock-cooled crystal with a Bruker-AXS CCD 1000 diffractometer with graphite-monochromated Mo-K_α (λ = 0.71073 Å) radiation. The structure was solved by direct methods using SHELXS-97[32] and refined with all data on F^2 using SHELXL-97.[33] All non-hydrogen atoms were treated anisotropically. The hydrogen atoms were geometrically idealized and refined using a riding model.

1d: Monoclinic, space group $P2_1/n$; T = 223 K; a = 19.421(4) Å, b = 10.132(2) Å, c = 20.888(4) Å; β = 111.766(2)°; V = 3817.2(12) Å^3; Z = 4; R [$I > 2\sigma(I)$] = 0.0415, wR_2 (all data) = 0.1150 for 7802 unique reflections, 509 parameters, GooF = 1.085.

9e: Monoclinic, space group $P2_1/n$; T = 193 K; a = 9.1693(1) Å, b = 13.2254(19) Å, c = 21.287(3) Å; β = 96.488(3)°; V = 2564.9(7) Å^3; Z = 4; R [$I > 2\sigma(I)$] = 0.0464, wR_2(all data) = 0.1148 for 3638 unique reflections, 379 parameters, GooF = 1.002.

CCDC-623872 (for **1d**) and -623873 (for **9e**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Z-matrix and energies (ua) for all of the optimized model compounds.

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