Pergamon

Tetrahedron 55 (1999) 14523–14534

TETRAHEDRON

Imidazolylidenes, Imidazolinylidenes and Imidazolidines

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Received 27 August 1999; revised 28 September 1999; accepted 14 October 1999

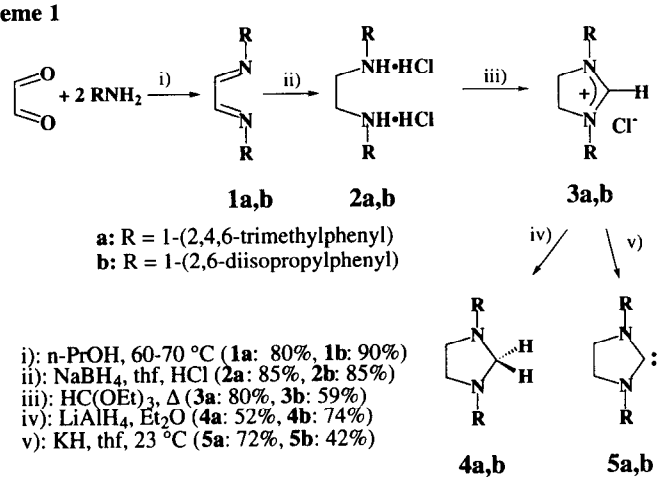
Abstract: Starting from glyoxal, 1,3-diarylimidazolinium chlorides **3** were obtained in a three-step sequence *via* the diimines (**1**) and ethylene diamine dihydrochlorides (**2**). Reduction of 1,3-diarylimidazolinium chlorides (**3**) with lithium alumnium hydride furnished the 1,3-diarylimidazolidines (**4**) while their deprotonation with potassium hydride in thf gave access to stable carbenes (1,3-diarylimidazolin-2-ylidenes, **5**). Similarly substituted imidazol-2-ylidenes are described for comparison.

Keywords: carbenes, imidazoles, imidazolines, imidazolidines

INTRODUCTION

The synthesis and isolation of stable imidazolin-2-ylidenes has been previously described.[1,2] While the related unsaturated imidazol-2-ylidenes bearing small groups (*e.g.* methyls) at the ring nitrogen atoms are stable at least for hours at room temperature,[3,4] sterically demanding substituents at the ring nitrogen atoms are essential in the imidazolin-2-ylidene series to prevent dimerization with formation of electron rich olefins.[1,2,5-12] Since deprotonation of suitable salts was proved to be a method of broad application for the generation of various types of carbenes.[1-15] General syntheses of imidazolinium salts as precursors of imidazolin-2-ylidenes are therefore of substantial interest.

Scheme 1



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0040-4020/99/$ - see front matter
PII: S0040-4020(99)00927-8

RESULTS AND DISCUSSION

Following established procedures,[16] the glyoxal diimines **1a,b** (**1a**: R = 1-(2,4,6-trimethylphenyl), **1b**: R = 1-(2,6-diisopropylphenyl)) were obtained as yellow solids from the condensation of glyoxal with two equivalents 2,4,6-trimethylphenylamine, or 2,6-diisopropylphenylamine, respectively (Scheme 1). As shown for **1a,b**, treatment of these diimines with sodium borohydride in tetrahydrofuran (thf) provides a convenient access to diamines bearing sterically encumbering substituents at the nitrogen atoms. The method described herein provides higher yields than those reported earlier.[17] The addition of hydrochloric acid to the reaction mixture led to the precipitation of the diamines dihydrochlorides **2a,b** in high yield. When **2a,b** were treated at elevated temperatures with triethyl orthoformate (as C_1-building block), cyclization occurred with formation of the imidazolinium salts **3a,b** as high melting colorless solids.[18] While a wide range of 1,3-diarylimidazolidines was obtained from the corresponding N-aryl-substituted ethylene diamines upon treatment with formaldehyde,[19,20] this reaction fails or affords only small yields when the aryl groups bear alkyl substituents in the *ortho*-positions as in the case of **2a,b**.[21] Reduction of **3a,b** with lithium aluminum hydride gave access to the desired imidazolidines **4a,b** under mild conditions. As reported earlier, deprotonation of the imidazolinium salts **3a,b** with potassium hydride in thf led to the corresponding imidazolin-2-ylidenes **5a,b**.[1] Other than in the case of imidazol-2-ylidenes, neither potassium *tert.*-butylate[3] can be used as base nor can ammonia or amines can be used as solvents[22,23] in this reaction. Both *tert.*-butanol and amines form adducts with imidazolin-2-ylidenes.[24,25] The carbenes **5a,b** are colorless solids and melt without decomposition. They are readily soluble in polar and nonpolar organic solvents like aliphatic and aromatic hydrocarbons, ethers, and remarkably are also stable for days in methylene chloride at room temperature.[26]

Changes in the electronic structure of the imidazoline ring system can easily be detected by means of ^1H and ^{13}C NMR spectroscopy. The chemical shift of $H^{4,5}$ and especially of C^2 reflect the differences between 1,3-imidazolinium chlorides **3**, 1,3-imidazolidines **4**, and 1,3-imidazolin-2-ylidenes **5**. Upon an increase of electron density in the ring δ_H of 4,5-H is shifted to higher field, *e. g.* for R = Mes: 4.48 (**3a**), 3.52 (**4a**), 3.26 (**5a**). In accordance with expectations[27] a strong downfield shift of *ca.* 80 ppm was observed for C^2 in **5a,b** (δ 243.77, δ 244.01, resp.) compared to the corresponding imidazolinium salts **3a,b**. Complete saturation of the C^2 center causes a marked upfield shift for the $^{13}C^2$ resonance; **4a,b** show C^2 resonances of δ 69.30 and δ 68.94, respectively. For **4a,b** and **5a,b** it is possible to detect their molecular ions with considerable intensity under EI conditions by mass spectrometry.

Since the molecular structures of **3a** and **5a** are already known from crystal structure determinations,[1] we were interested in the geometric consequences of saturation at C^2. The crystal structure of the imidazolidine **4a** was therefore determined. The unit cell of **4a** contains two unique molecules in the asymmetric unit. Both molecules are similar in structure but vary slightly in specific bond lengths and angles. The average variation in the bond lengths within the 5-membered ring is 1.6 pm). The average C^2–$N^{1(3)}$ bond distance in **4a** is 145 pm compared to 135 pm in **5a**. This lengthening of the nitrogen bonds to the C^2 center is consistent with the saturation at C^2 and the change from an approximate sp^2 geometry to a tetrahedral sp^3 geometry at carbon. The nitrogens are considerably more pyramidal in **4a** than **5a** with the nitrogens being on average 22.6 pm and 6.7 pm respectively out of the planes of the three substituent carbon atoms. This geometry for the saturated ring of **4a** is illustrated by the KANVAS[28] drawing for one of the crystallographically unique molecules in Figure 1.

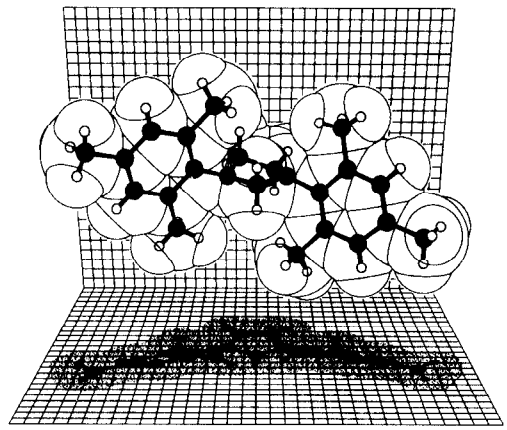
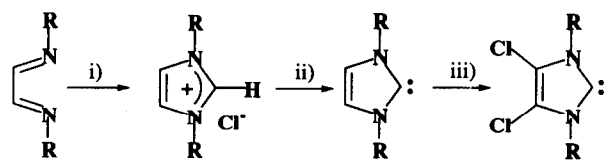


Figure 1. KANVAS drawing of the fully reduced imidazolidine **4a**.

The imidazolin-2-ylidenes **5a,b** and their related unsaturated analog, 1,3-dimesitylimidazol-2-ylidene (**7a**), have proven to be very useful ligands for various transition metal-centered catalyst designs.[29-32] It would be desirable to add the bis(2,6-diisopropylphenyl) substituted analog in the imidazol-2-ylidene (**7b**) to this palette of ligands. The original synthesis[33] that was devised for the precursor imidazolium ions (**6a,b**) performs well for the mesityl derivative **6a** but tends to give very low yields for the corresponding diisopropylphenyl substituted analog. Additionally, although these older imidazolium ion syntheses work well on a large scale, there is a highly colored ionomer byproduct that is a nuisance to separate from the desired imidazolium ion (particularly for a small-scale laboratory synthesis). The purity of the penultimate imidazolium ions is very important for clean deprotonation reactions to give the imidazol-2-ylidenes. An alternate imidazolium ion synthesis that can be more conveniently performed on a smaller scale and provide clean access to more hindered imidazolium ions like **6b** is thus needed.

Scheme 2.



a: R = 1-(2,4,6-trimethylphenyl)
b: R = 1-(2,6-diisopropylphenyl)

i) $ClCH_2OEt$, thf, 20-40 °C (**6a**: 40%, **6b**: 47%)
ii) KO-*t*-Bu, thf, 23 °C, (**7a**: 96%, **7b**: 80%)
iii) CCl_4, thf, 23 °C, (**8a**: 85%, **8b**: 77%)

As illustrated in Scheme 2, the same diimine intermediates (**1a,b**) that are used in the syntheses of **4a,b** and **5a,b** can also be used as precursors to the imidazol-2-ylidenes. The cyclization reactions with chloromethylethyl ether provide direct convenient access to the imidazolium ions on a small scale. Although the yield of **6a** is not as high as can be obtained from the earlier condensation route,[33] the crude reaction products (both **6a** and **6b**) are sufficiently pure to be used in subsequent deprotonation reactions without the need for additional recrystallization or purification.

The new imidazolium ion **6b** exhibits similar nmr spectroscopic properties to other 1,3-disubstituted imidazolium ions. The acidic proton at C^2 resonates at δ 10.16 in dmso-d_6. The protons on the other two imidazole rings carbons ($C^{4,5}$) resonate at δ 8.56. The diastereotopic methyl groups of the isopropyl substituents show well-resolved resonances at δ 1.15 and δ 1.25 with 3-bond couplings to the methine proton of 6.9 and 6.6 Hz respectively. The methine protons a broad septet pattern (individual $^3J_{HH}$ couplings are not resolved). This spectral pattern for the diisopropylphenyl groups is also evident in the spectra of the derivatives **3b** and **5b**.

Crystals of **6b** suitable for X-ray crystallographic structure determination were grown from a saturated thf solution by cooling to –25 °C. The structure of this imidazolium ion is comparable to the structure reported for the methanol solvate of **6a**.[34] The average C–N distance at the C^2 center is 134 pm. The N–C–N angle is 107.6°. The mean planes of the diisopropylphenyl groups are twisted 73° and 80° with respect to the central imidazole ring. These data suggest that the imidazole ring is not unusually stressed by the large diisopropylphenyl substituents. As is typical for other 2-protio-azolium halides,[1,3,14,26,34] there is a Cl–H–C hydrogen bond in the solid state structure of **6b**. This Cl–H–C interaction is clearly evident in the KANVAS drawing in Figure 2. The Cl–H–C angle is 172° and the H–C and H–Cl distances are 93 and 236 pm respectively.

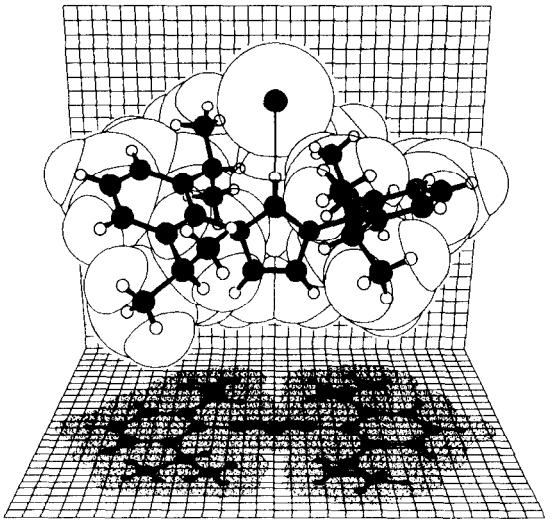


Figure 2. KANVAS drawing of imidazolium chloride **6b**.

The deprotonation of **6a** to form the corresponding carbene **7b** is easily accomplished with potassium *tert.*-butylate. The imidazol-2-ylidene **7b** is a colorless crystalline solid melting at 216-7 °C (about 50 °C higher than observed for **7a**).[3] The ^{13}C nmr spectrum (C_6D_6) shows a singlet at δ 220.6 for the carbene center that is very similar to the analogous resonance in **7a** (δ 219.7).[3] The isopropyl moieties continue to show two resolved resonances for the diasterotopic methyl groups as was apparent for **6b**. Crystals of **7b** were grown by cooling a saturated toluene solution to –20 °C. The solid state structure of **7b** is illustrated by the KANVAS drawing in Figure 3. The imidazole geometry in **7b** very similar to that observed for **7a** and the N–C–N angles in the two carbenes are identical (101.4°). The diisopropylphenyl substituents in **7b** are twisted 78° and 65° with respect to the central imidazole ring. On average these twists are slightly less than those observed for **7a** (80° and 71°) and may reflect a slight steric interaction across the imidazole ring, but no obvious non-bonding interaction is evident from the space-filling model (Figure 3).

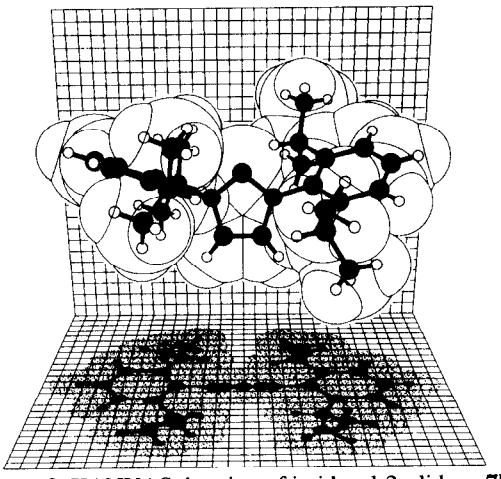


Figure 3. KANVAS drawing of imidazol-2-ylidene **7b**.

One final variation on imidazol-2-ylidenes that leads to exceptionally stable structures is the chlorination of the 4- and 5–positions of the imidazole rings. This chlorination reaction for carbenes like **7a,b** can be easily achieved by treating the imidazol-2-ylidene with carbon tetrachloride (**Scheme 2**).

Dichloroimidazolylidene **8b** is a colorless crystalline solid melting at 138–9 °C (*cf.* **8a** mp 180–2 °C).[26] As with **8a**, **8b** can be handled with short exposures to moist air without ill-effects. The carbene center in **8b** shows a ^{13}C nmr signal at δ 220.6 (*cf.* **7a**: δ 219.7; **7b**: δ 220.6; **8a**: δ 219.9). In the ^{1}H nmr spectrum **8b** also exhibits the resolved pattern for the diastereotopic methyl groups that was evident for **7b**, **6b**, **5b** and **3b**. Crystals of **8b** suitable for X-ray crystallographic structure determination were grown by cooling a saturated acetonitrile solution. Both **8a** and **8b** crystallize in the C2/c space group but the two structures are not isomorphoric and **8b** does not reside on the crystallographic 2-fold axis as was the case for **8a**.[26] Nonetheless these two dichloroimidazol-2-ylidenes exhibit very similar structures. The diisopropylphenyl substituents in **8b** are nearly orthogonal to the central imidazole ring (89° and 85° twists). This degree of twisting is greater than that observed for **8a** (81°). The steric interaction between the nitrogen aryl–substituents and the adjacent chlorines is most likely responsible for the higher degree on inclination of the aryl rings with respect to the central imidazole in **8a,b** compared to the other related structures (**7a,b**; **6a,b**; **5a,b** and **3a**). The solid state structure of **8b** is illustrated by the KANVAS representation in Figure 4.

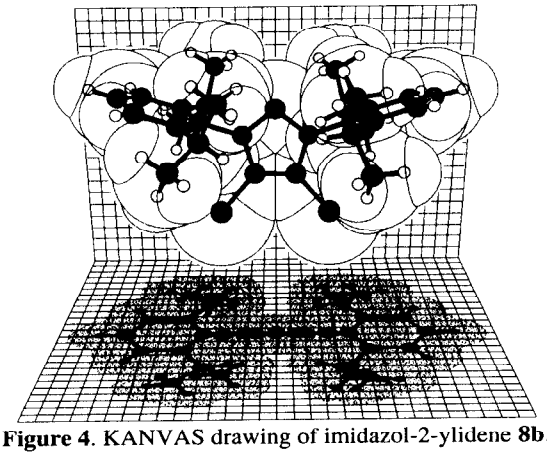


Figure 4. KANVAS drawing of imidazol-2-ylidene **8b**.

Table 1. Selected Bond Lengths (pm) and Angles (°) in **4a** and **6-8**.

Property	4a	6a[34]	7a[5]	8a[26]	6b	7b	8b
$\bar{r}$ (C^2–$N^{1(3)}$)	144.7	132.6	136.8	136.4	134.0	136.7	137.3
$\bar{r}$ ($N^{1(3)}$–$C^{5(4)}$)	143.0	138.4	138.0	138.0	139.2	139.4	138.2
$\bar{r}$ (C^4–C^5)	150.4	135.3	133.1	133.0	134.3	133.5	132.7
$\bar{\theta}$ (N^1–C^2–N^3)	102.8	108.7	101.4	101.9	107.6	101.4	101.2
$\bar{\theta}$ (C^2–$N^{1(3)}$–$C^{5(4)}$)	111.3	108.9	112.8	112.5	109.1	113.0	112.7
$\bar{\theta}$ ($N^{1(3)}$–$C^{5(4)}$–$C^{4(5)}$)	103.1	106.8	106.5	106.6	107.2	106.3	106.7

Average values for selected unique bond lengths and angles in **4a** and **6-8b** are presented in Table 1 along with related compounds whose structures have been determined previously (**6-8a**) for comparison.

CONCLUSION

A stepwise series of condensation reactions can be employed to produce imidazolin-2-ylidenes, imidazolindines, and imidazol-2-ylidenes. Divergent reaction schemes allow construction of related carbenes from a common, readily accessible, diimine (**1a,b**) starting material. This reaction sequence provides convenient access to imidazol-2-ylidenes bearing sterically demanding residues on the imidazole nitrogens.

EXPERIMENTAL

Reactions and manipulations were carried out under an atmosphere of dry nitrogen, either in a Vacuum Atmospheres dry box or using standard Schlenk techniques. Solvents were dried (using standard procedures),[35] distilled, and deoxygenated prior to use, unless otherwise indicated. Glassware was oven-dried at 160 °C overnight. Proton NMR spectra were recorded on a General Electric QE-300 spectrometer. Carbon-13 spectra were recorded on a GE Omega 300WB spectrometer. NMR references are $(CH_3)_4Si$ (^1H, ^{13}C) and NH_4NO_3 (^{15}N). Melting points were obtained on a Thomas-Hoover capillary apparatus and were not corrected. Elemental analyses were performed by Micro-Analyses Inc., Wilmington, Delaware or Oneida Research Services, Whitesboro, NY.

Preparation of Glyoxal-bis-(2,4,6-trimethylphenyl)imine ***1a****.*

To a solution of 67.61 g (0.5 mol) of 2,4,6-trimethylphenylamine in 300 ml of n-propanol were added at 23 °C a mixture of 36.3 g of a 40% aqueous solution of glyoxal (corresponding to 0.25 mol of glyoxal), 100 ml of n-propanol and 50 ml of water. The mixture was stirred for 16 h at 23 °C and then for 4 h at 60 °C. Upon addition of 200 ml of water, a yellow solid precipitated which was collected by filtration and dried *in vacuo*. Yield: 116.2 g (80%); mp 157–8 °C. ^1H NMR ($CDCl_3$): δ 2.19 [s, 12 H, *ortho*-CH_3], 2.32 [s, 6 H, *para*-CH_3], 6.93 [s, 4 H, *meta*-CH], 8.13 [s, 2 H, CH]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 18.2 [s, *ortho*-CH_3], 20.7 [s, *para*-CH_3], 126.5 [s, *ortho*-C], 128.9 [s, *meta*-C], 134.1 [s, *para*-C], 147.4 [s, ipso-C], 163.0 [s, HC=N].

Preparation of Glyoxal-bis-(2,6-diisopropylphenyl)imine ***1b****.*

To a solution of 49.25 g (0.28 mol) of 2,6-diisopropylphenylamine in 200 ml of n-propanol were added at 23°C a mixture of 18.15 g of a 40% aqueous solution of glyoxal (corresponding to 0.125 mol of glyoxal), 20 ml of n-propanol and 50 ml of water. After 1 h stirring at 70 °C 200 ml of water were added. The resulting precipitate was collected by filtration and dried *in vacuo*. Yield: 42.29 g (90%); mp 71–3 °C. ^1H NMR ($CDCl_3$): δ 1.21 [d, 24 H, $CH(C\underline{H}_3)_2$, $^3J_{HH}$ = 6.9 Hz], 2.94 [sept, 4 H, $C\underline{H}(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz], 7.1 - 7.25 [m, 12 H, aryl-CH], 8.11 [s, 2 H, CH]. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 22.4 [s, $CH(\underline{C}H_3)_2$], 28.1 [s, $\underline{C}H(CH_3)_2$], 123.1 [s, *meta*-C], 125.1 [s, *para*-C], 136.6 [s, *ortho*-C], 148.0 [s, ipso-C], 163.0 [s, HC=N].

Preparation of N,N'-Bis-(2,4,6-trimethylphenylamino)ethane Dihydrochloride **2a**.

A suspension of 29.5 g (100 mmol) of the glyoxal-bis-(2,4,6-trimethylphenyl)imine **1a** in 400 ml of thf was treated at 0 °C with 16.0 g (410 mmol) of sodium borohydride in portions of 1 g over a period of 1 h. The mixture was stirred for 16 h at 23 °C and heated subsequently for 2 h under reflux. To the mixture were added 300 ml of ice-water and subsequently 300 ml of 3 M hydrochloric acid. A colorless solid precipitated and was collected by filtration and dried *in vacuo*. Yield: 31.55 g (85%); mp > 250 °C. ^{1}H NMR (dmso-d_6): δ 2.22 [s, 6 H, *para*-CH_3], 2.44 [s, 12 H, *ortho*-CH_3], 3.67 [s, 4 H, NCH_2], 6.96 [s, 4 H, *meta*-CH]. - ^{13}C{^{1}H} NMR (dmso-d_6): δ 18.3 [s, *ortho*-CH_3], 20.9 [s, *para*-CH_3], 50.7 [s, NCH_2], 129.4 [s, ipso-C] 131.4 [s, *meta*-C], 132.3 [s, *ortho*-C], 137.6 [s, *para*-C].

Preparation of N,N'-Bis-(2,6-diisopropylphenylamino)ethane Dihydrochloride **2b**.

To a solution of 18.88 g (50 mmol) of glyoxal-bis-(2,6-diisopropylphenyl)imine **1b** in 200 ml of thf were added at 0 °C 8.0 g (211 mmol) of sodium borohydride in portions of 1 g over a period of 40 min. The mixture was allowed to warm up to 23 °C, stirred for 16 h, and subsequently refluxed for 2 h. To the reaction mixture were first added 200 ml of ice-water over 0.5 h, and then cautiously 200 ml of 3 M hydrochloric acid. A colorless solid precipitated and was collected by filtration, and dried *in vacuo*. Yield: 19.2 g (85%); mp > 250 °C. ^{1}H NMR (dmso-d_6): δ 1.24 [d, 24 H, $CH(C\underline{H}_3)_2$, $^3J_{HH}$ = 6.6 Hz], 3.58 [sept, 4 H, $C\underline{H}(CH_3)_2$, $^3J_{HH}$ = 6.6 Hz], 3.72 [s, 4 H, NCH_2], 7.25 - 7.40 [m, 12 H, aryl-CH]. ^{13}C{^{1}H} NMR (dmso-d_6): δ 24.4 [s, $CH(\underline{C}H_3)_2$], 27.2 [s, $\underline{C}H(CH_3)_2$], 50.6 [s, NCH_2], 124.8 [s, *meta*-C], 127.1 [s, *para*-C], 142.7 [s, *ortho*-C], 151.0 [s, ipso-C].

Preparation of 1,3-Bis-(2,4,6-trimethylphenyl)imidazolinium Chloride **3a**.

A mixture of 11.21 g (30.3 mmol) of N,N'-bis-(2,4,6-trimethylphenylamino)ethane dihydrochloride **2a**, 100 ml of triethyl orthoformate, and two drops of 96% formic acid was heated in a distillation apparatus until the ethanol distillation ceased. The temperature of the reaction mixture reached 130 °C. Upon cooling to 23 °C a colorless solid precipitated which was collected by filtration, and dried *in vacuo*. Yield: 8.30 g (80%); mp > 250 °C. In some cases an imidazolinium salt/triethyl orthoformate adduct formed, and purification was achieved by repeated recrystallizations from acetonitrile/ether. ^{1}H NMR (dmso-d_6): δ 2.28 [s, 6 H, *para*-CH_3], 2.36 [s, 12 H, *ortho*-CH_3], 4.48 [s, 4 H, im-$H^{4,5}$], 7.08 [s, 4 H, *meta*-CH], 9.22 [s, 1 H, im-H^2]. ^{13}C{^{1}H} NMR (dmso-d_6): δ 17.2 [s, *ortho*-CH_3], 20.5 [s, *para*-CH_3], 50.9 [s, im-$C^{4,5}$], 129.3 [s, *meta*-C], 130.8 [s, ipso-C], 135.3 [s, *ortho*-C], 139.5 [s, *para*-C], 160.2 [s, im-C^2].

Preparation of 1,3-Bis-(2,6-diisopropylphenyl)imidazolinium Chloride **3b**.

A mixture of 8.00 g (19.2 mmol) of N,N'-bis-(2,6-diisopropylphenylamino)ethane dihydrochloride **2b**, 100 ml of triethyl orthoformate, and two drops of 96% formic acid was refluxed for 45 h. After cooling to 23 °C, a solid precipitated. The solid was collected by filtration and dried *in vacuo*. ^{1}H NMR indicated it to be an imidazolinium salt/triethyl orthoformate adduct. Purification was achieved by repeated recrystallizations from acetonitrile/ether. Yield: 4.82 g (59%); mp 237–40 °C. ^{1}H NMR (dmso-d_6): δ 1.25 [d, 12 H, $CH(C\underline{H}_3)_2$, $^3J_{HH}$ = 6.9 Hz], 1.36 [d, 12 H, $CH(C\underline{H}_3)_2$, $^3J_{HH}$ = 6.9 Hz], 3.09 [sept, 4 H, $C\underline{H}(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz], 4.41 [s, 4 H, im-$H^{4,5}$], 7.3 - 7.6 [m, 6 H, aryl-CH], 9.63 [s, 1 H, im-H^2]. ^{13}C{^{1}H} NMR (dmso-d_6): δ 23.3 [s, $CH(\underline{C}H_3)$], 25.0 [s, $CH(\underline{C}H_3)$], 28.3 [s, $\underline{C}H(CH_3)_2$], 53.7 [s, C-4,5], 124.70 [s, *meta*-C], 129.80 [s, *ipso*-C], 131.0 [s, *para*-C], 146.0 [s, *ortho*-C], 160.0 [s, im-C^2].

Preparation of 1,3-Bis-(2,4,6-trimethylphenyl)imidazolidine **4a**.

To 0.10 g (2.6 mmol) of lithium aluminium hydride suspended in 20 ml of ether at 23 °C was added a suspension of 0.69 g (2 mmol) of 1,3-bis-(2,4,6-trimethylphenyl)imidazolinium chloride **3a** in 20 ml of ether. The mixture was stirred for 2 h at 23 °C, filtered, and evaporated to give a colorless solid. The solid was

dissolved in 40 ml of toluene, filtered, and the filtrate was evaporated to give 0.32 g (52%) of **4a** as a colorless solid. mp 55–7 °C. ^{1}H NMR ($CDCl_3$): δ 2.25 [s, 6 H, *para*-CH_3], 2.40 [s, 12 H, *ortho*-CH_3], 3.48 [s, 4 H, im-$H^{4,5}$], 4.29 [s, 2 H, im-H^2], 6.93 [s, 4 H, *meta*-CH]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 18.7 [s, *ortho*-CH_3], 20.8 [s, *para*-CH_3], 50.8 [s, im-$C^{4,5}$], 69.3 [s, im-C^2)], 129.5 [s, *meta*-C], 135.2 [s, *para*-C], 138.4 [s, *ortho*-C], 140.9 [s, *ipso*-C]. - MS (70 eV); m/z (%): 308.2240 (70) [M^+, calc. $C_{21}H_{28}N_2$: 308.2252], 307.2173 (95) [M^+ - H, 307.2174], 162.1308 (100) [M^+ - $C_{10}H_{12}N$, 162.1283], 146.1020 (50) [M^+ - $C_{11}H_{16}N$, 146.0970].

*Preparation of 1,3-Bis-(2,6-diisopropylphenyl)imidazolidine **4b**.*

To 0.10 g (2.6 mmol) of lithium aluminium hydride suspended in 10 ml of ether at 23 °C was added a suspension of 0.43 g (1 mmol) of 1,3-bis-(2,6-diisopropylphenyl)-imidazolinium chloride **3b** in 10 ml of ether. The mixture was stirred for 2 h at 23 °C, filtered, and evaporated to give 0.29 g (74%) of **4b** as a colorless solid. Further purification was achieved by recrystallization from thf/toluene (1:10). ^{1}H NMR (C_6D_6): δ 1.29 [d, 24 H, $CH(C\underline{H}_3)_2$, $^3J_{HH}$ = 6.9 Hz], 3.52 [s, 4 H, im-$H^{4,5}$], 3.67 [sept, 4 H, $C\underline{H}(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz], 4.59 [s, 2 H, im-H^2], 6.95 - 7.25 [m, 6 H, aryl-CH]. ^{13}C{^{1}H} NMR ($CDCl_3$): δ 24.4 [s, $CH(\underline{C}H_3)_2$], 25.4 [s, $CH(\underline{C}H_3)_2$], 28.0 [s, $\underline{C}H(CH_3)_2$], 53.2 [s, C-4,5], 68.9 [s, im-C^2], 128.1 [s, *meta*-C], 128.9 [s, *ortho*-C], 140.7 [s, ipso-C], 150.0 [s, *para*-C]. - MS (70 eV); m/z (%): [M^+, calc. for $C_{27}H_{40}N_2$: 392.3191], 548.3026 (65) [M^+ - N_2 - CH_3, 548.3065], 403.2213 (40) [M^+ - N_2 - $C_{11}H_{14}N$, 403.2175], 306.1953 (50) [M^+ - N_2 - $C_{19}H_{15}N$, 305.2018].

*Preparation of 1,3-Bis-(2,4,6-trimethylphenyl)imidazolin-2-ylidene **5a**.*

To 0.150 g of a ca. 35% suspension of potassium hydride in mineral oil (corresponding to 1.3 mmol KH) was added at 23 °C a suspension of 0.381 g (1 mmol) of 1,3-bis-(2,4,6-tri-methylphenyl)imidazolinium chloride **3a** in 20 ml of thf. Immediately a moderate evolution of gas was observed. The mixture was stirred for 3 h at 23 °C until the evolution of gas had ceased, filtered through a frit covered with celite, and evaporated. Recrystallization from hexane at –25 °C gave **4a** as a colorless solid. Yield: 0.22 g (72%); mp 107–9 °C. ^{1}H NMR (C_6D_6): δ 2.16 [s, 6 H, *para*-CH_3], 2.29 [s, 12 H, *ortho*-CH_3], 3.26 [s, 4 H, im-$H^{4,5}$], 6.83 [s, 4 H, *meta*-CH]. ^{13}C{^{1}H} NMR (C_6D_6): δ 18.2 [s, *ortho*-CH_3], 21.0 [s, *para*-CH_3], 50.7 [s, im-$C^{4,5}$], 129.3 [s, *meta*-C], 136.2 [s, *para*-C], 136.3 [s, *ortho*-C], 139.68 [s, *ipso*-C], 243.8 [s, im-C^2]. - MS (70 eV); m/z (%): 306.2095 (30) [M^+, calc. for $C_{21}H_{26}N_2$: 306.2096], 305.2035 (65) [M^+ - H, 305.2017], 278.1750 (30) [M^+ - C_2H_4, 278.1783], 148.1109 (100) [M^+ - $C_{11}H_{12}N$, 148.1126].

*Preparation of 1,3-Bis-(2,6-diisopropylphenyl)imidazolin-2-ylidene **5b**.*

To a mixture of 0.520 g of a ca. 35% suspension of potassium hydride in mineral oil (corresponding to 4.5 mmol KH) were added at r.t. a suspension of 0.65 g (1.52 mmol) of 1,3-bis-(2,6-diisopropylphenyl)imidazolinium chloride **3b** in 20 ml of thf, and a crystal of dibenzo-18-crown-6. The mixture was stirred for 5 h at 23 °C until the evolution of hydrogen had ceased. Filtration of the mixture and evaporation of the filtrate gave **5b** as a light yellow material. Recrystallization of **5b** from thf/hexane (1:1) led to an amorphous colorless solid. Yield: 0.251 g (42%); mp 167–8 °C. ^{1}H NMR (C_6D_6): δ 1.29 [d, 12 H, $CH(C\underline{H}_3)_2$, $^3J_{HH}$ = 6.9 Hz], 1.31 [d, 12 H, $CH(C\underline{H}_3)_2$, $^3J_{HH}$ = 6.9 Hz], 3.28 [sept, 4 H, $C\underline{H}(CH_3)_2$, $^3J_{HH}$ = 6.9 Hz], 3.36 [s, 4 H, im-$H^{4,5}$], 7.14 - 7.30 [m, 6 H, aryl-CH]. ^{13}C{^{1}H} NMR (C_6D_6): δ 23.6 [s, $CH(\underline{C}H_3)_2$], 25.4 [s, $CH(\underline{C}H_3)_2$], 28.9 [s, $\underline{C}H(CH_3)_2$], 53.7 [s, im-$C^{4,5}$], 124.0 [s, *meta*-C], 128.3 [s, *ortho*-C], 139.4 [s, ipso-C], 147.4 [s, *para*-C], 244.0 [s, im-C^2]. - MS (70 eV); m/z (%): 390.3021 (20) [M^+, calc. for $C_{27}H_{38}N_2$: 390.3035], 389.2952 (35) [M^+ - H, 389.2957], 190.1589 (100) [M^+ - $C_{14}H_{18}N$, 190.1596].

*Preparation of 1,3-Bis-(2,4,6-trimethylphenyl)imidazolium chloride **6a** from diimine **1a**.*

A 200 mL single-necked flask with 4 inch extension was charged with 3.03 g (30.77 mmol) of chloromethylethyl ether (96%) in ~9 ml of thf. To this colorless solution was added a solution of 9 g (30.77

mmol) of **1a** in 105 mL of thf. A 15 x 50 mm extraction thimble was charged with 4Å molecular sieves and suspended in the extension above the solution by means of a copper wire through a septum in the top of the extension. The reaction mixture was stirred under a static nitrogen atmosphere at 23 °C . A solid began to precipitate after 20 m. Stirring was continued for 5 days. The precipitated solid was then collected by filtration. The colorless crude solid (6.128 g, 40%) was identified as **6a** by comparison with an authentic sample.[33] The crude solid gave: mp 350–2 °C. ^{1}H NMR (dmso-d_6) δ 2.11 [s, 12 H, *ortho*-C$\underline{H}_3$], 2.48 [s, 6 H, *para*-C$\underline{H}_3$], 7.19 [s, 4 H, *meta*-C$\underline{H}$], 8.28 [s, 2 H, im-H^{4,5}], 9.74 [s, 1 H, im-H^2]. ^{1}H NMR (CD_2Cl_2) δ 2.17 [s, 12 H, *ortho*-C$\underline{H}_3$], 2.37 [s, 6 H, *para*-C$\underline{H}_3$], 7.08 [s, 4 H, *meta*-C$\underline{H}$], 7.61 [s, 2 H, im-H^{4,5}], 11.05 [s, 1 H, im-H^2]. ^{15}N NMR (dmso-d_6) δ −191.99. This crude material was sufficiently pure for the subsequent deprotonation reaction.

*Preparation of 1,3-Bis-(2,6-diisopropylphenyl)imidazolium chloride **6b** from diimine **1b**.*

A 100 mL single-necked flask is charged with 1.82 g (18.30 mmol) of chloromethylethyl ether (95%) in 3 ml of thf. To this colorless solution is added a solution of 6.89 g (18.30 mmol) of **1b** in 40 ml of thf and 2 drops of water. The flask is sealed under nitrogen with a septum and the mixture is stirred at 40 °C. A solid began to appear after 1 h of stirring. Stirring at 40°C was continued for 16 hours and then the mixture was allowed to cool to 23 °C and the precipitated solids were collected by filtration. The colorless crude solid (2.33 g, 47%) was identified as **6b** by NMR spectra and X-ray structure analysis. The crude solid gave: mp > 255 °C. ^{1}H NMR (dmso-d_6) δ 1.15 [d, 12 H, CH(C$\underline{H}_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 1.25 [d, 12 H, CH(C$\underline{H}_3$)$_2$, $^3J_{HH}$ = 6.6 Hz], 2.34 [sept, 4 H, C$\underline{H}$(CH$_3$)$_2$, $^3J_{HH}$ ≈ 6.9 Hz], 7.53 [d, 4 H, *meta*-CH, $^3J_{HH}$ = 7.8 Hz], 7.68 [t, 2 H, *para*-CH, $^3J_{HH}$ = 7.7 Hz], 8.56 [s, 4 H, im-H^{4,5}], 10.16 [s, 1 H, im-H^2]. ^{1}H NMR ($CDCl_3$) δ 1.22 [d, 12 H, CH(C$\underline{H}_3$)$_2$, $^3J_{HH}$ ≈ 6.9 Hz], 1.26 [d, 12 H, CH(C$\underline{H}_3$)$_2$, $^3J_{HH}$ = 6.6 Hz], 2.42 [sept, 4 H, C$\underline{H}$(CH$_3$)$_2$, $^3J_{HH}$ ≈ 6.9 Hz], 7.32 [d, 4 H, *meta*-CH, $^3J_{HH}$ = 7.8 Hz], 7.55 [t, 2 H, *para*-CH, $^3J_{HH}$ = 7.7 Hz], 8.13 [s, 4 H, im-H^{4,5}], 10.08 [s, 1 H, im-H^2]. This crude material was sufficiently pure for the subsequent deprotonation reaction.

*Preparation of 1,3-Bis-(2,6-diisopropylphenyl)imidazol-2-ylidene **7b**.*

A 200 mL round-bottom flask was charged with 6.94 g (16.33 mmol) of 1,3-di(2,6-diisopropylphenyl)imidazolium chloride (**6a**) and 80 mL of thf. The resulting suspension was stirred for 15 m. Then solid potassium *tert.*-butoxide (1.94 g, 17.31 mmol) was added to the suspension at room temperature. An orange solution was obtained immediately. After stirring the mixture for 20 m, all volatiles were removed *in vacuo*. The residue was extracted into warm (60 °C) toluene (2 x 50 mL) and filtered through diatomaceous earth. The solvent volume was decreased *in vacuo* to one third, and carbene **7b** crystallized. Yield: 5.05 g (80%). mp: 216–7 °C ^{1}H NMR (C_6D_6): δ 1.18 [d, 12 H, CH(C$\underline{H}_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 1.28 [d, 12 H, CH(C$\underline{H}_3$)$_2$, $^3J_{HH}$ = 6.9 Hz], 2.96 [sept, 4 H, $^3J_{HH}$ = 6.9 Hz, C$\underline{H}$(CH$_3$)$_2$], 6.62 [s, 2 H, im-H^{4,5}], 7.18 [d, 4 H, $^3J_{HH}$ = 7.5 Hz, *meta*-C$\underline{H}$], 7.29 [t, 2H, $^3J_{HH}$= 7.5 Hz, *para*-C$\underline{H}$]. ^{13}C NMR (C_6D_6): δ 23.56 [qm, $^1J_{CH}$ = 126.0 Hz, C$\underline{H}_3$], 24.78 [qm, $^1J_{CH}$ = 126.0 Hz, C$\underline{H}_3$], 28.74 [d, $^1J_{CH}$ = 128.9 Hz, C$\underline{(CH_3)_2}$], 121.49 [d, $^1J_{CH}$ = 191.0 Hz, N$\underline{C}$H], 123.64 [dm, $^1J_{CH}$ = 160.2 Hz, *meta*-C$\underline{H}$], 128.97 [d, $^1J_{CH}$ = 158.3 Hz, *para*-C$\underline{H}$], 138.94 [s, *ipso*-$\underline{C}$], 146.23 [m, *ortho*-$\underline{C}$], 220.52 [s, im-$\underline{C}^2$]. ^{13}C{^{1}H} NMR (C_6D_6): δ 23.6 [s, C$\underline{H}_3$], 24.8 [s, C$\underline{H}_3$], 28.7 [s, C$\underline{(CH_3)_2}$], 121.5 [s, im-$\underline{C}^{4,5}$], 123.6 [s, *meta*-$\underline{C}$], 129.0 [s, *para*-$\underline{C}$], 139.0 [s, *ipso*-$\underline{C}$], 146.2 [s, *ortho*-$\underline{C}$], 220.6 [s, im-$\underline{C}^2$]. ^{15}N NMR (C_6D_6): δ −181.18 [s]. $C_{27}H_{36}N_2$ (388.60) Calcd: C 83.45, H 9.34, N 7.21%. Found: C 83.71, H 9.11, N 7.17%.

*Preparation of 1,3-Bis-(2,6-diisopropylphenyl)-4,5-dichloroimidazol-2-ylidene **8b**.*

To a solution of 512 mg (1.32 mmol) of **7b** in 10 mL of thf was added a solution of 405 mg (2.64 mmol) of carbon tetrachloride (CCl_4) in 2 mL of thf at room temperature. The solution was stirred for 30 m. Subsequent removal of all volatiles *in vacuo* left **8b** as a colorless solid that was recrystallized from

acetonitrile. Yield: 463 mg (77%). mp: 138–9 °C. ^{1}H NMR (C_6D_6): δ 1.19 [d, 12 H, $^3J_{HH}$ = 6.9 Hz, CH(C$\underline{H}_3$)$_2$], 1.24 [d, 12 H, $^3J_{HH}$ = 6.9 Hz, CH(C$\underline{H}_3$)$_2$], 2.89 [sept, 4 H, $^3J_{HH}$ = 6.9 Hz, C$\underline{H}$(CH$_3$)$_2$], 7.14 [d, 4 H, $^3J_{HH}$= 7.0 Hz, *meta*-C$\underline{H}$], 7.26 [t, 2 H, $^3J_{HH}$= 7.0 Hz, *para*-C$\underline{H}$]. ^{13}C{^{1}H} NMR (C_6D_6): δ 23.0 [s, $\underline{C}$H$_3$], 24.7 [s, $\underline{C}$H$_3$], 29.1 [s, $\underline{C}$(CH$_3$)$_2$], 117.0 [s, im-$\underline{C}^{4,5}$], 123.9 [s, *meta*-$\underline{C}$], 130.0 [s, *para*-$\underline{C}$], 135.2 [s, *ipso*-$\underline{C}$], 146.8 [s, *ortho*-$\underline{C}$], 220.6 [s, im-$\underline{C}^2$]. ^{15}N NMR (C_6D_6): δ –181.78 [s]. $C_{27}H_{34}N_2Cl_2$ (457.49). Calcd: C 70.89, H 7.49, N 6.12, Cl 15.50%. Found: C 70.98, H 7.26, N 6.02, Cl 15.34%.

X-ray Structure Determination of ***4a****:*

Crystals of **4a** were grown from a saturated solution in hexane at -25 °C. Crystal data for **4a** at -100 °C with Mo Kα radiation: a = 984.0 (1), b = 1103.5 (2), c = 1767.3 (3) pm, α = 100.43 (1)°, β = 99.31 (1)°, γ = 96.21 (1)°, triclinic, P$\bar{1}$, Z = 4, μ(Mo) = 0.60 cm^{-1}, 2450 unique reflections with I > 2.5σ(I). The structure was solved by direct methods (MULTAN) and refined by full-matrix least-squares on F. Carbon and nitrogen were refined with anisotropic thermal parameters. Hydrogens were modeled in fixed positions. The largest residual electron density in the final difference Fourier map was 0.25 e/Å^3. The data/parameter ratio was 5.90. The final R factors were R = 0.065 and R_w = 0.048. Crystallographic data for the structure of **4a** have been deposited with the Cambridge Crystallographic Data Centre (ref. Nr. 133743). Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: int. code + (1223)336–033; e-Mail: teched@chemcrys.cam.ac.uk).

X-ray Structure Determination of ***6b****:*

Crystals of **6b** were grown from a saturated solution in thf at –25 °C. Crystal data for **6b** at –95 °C with Mo Kα radiation: a = 1719.0 (1), b = 1740.2 (1), c = 1060.0 (1) pm, β = 110.04 (1)°, monoclinic, P2$_1$/n, Z = 4, μ(Mo) = 1.49 cm^{-1}, 2765 unique reflections with I > 3.0σ(I). The structure was solved by direct methods (teXan SIR-92) and refined by full-matrix least-squares on F. Chlorine, carbon, and nitrogen were refined with anisotropic thermal parameters. H2 was refined with an isotropic thermal parameter and the remaining hydrogens were modeled in fixed positions. The largest residual electron density in the final difference Fourier map was 0.58 e/Å^3. The data/parameter ratio was 8.64. The final R factors were R = 0.059 and R_w = 0.057. Crystallographic data for the structure of **6b** have been deposited with the Cambridge Crystallographic Data Centre (ref. Nr. 133744). Copies of the data can be obtained free of charge at the address under **4a**.

X-ray Structure Determination of ***7b****:*

Crystals of **7b** were grown from a saturated solution in toluene at –25 °C. Crystal data for **7b** at –95 °C with Mo Kα radiation: a = 2083.3 (2), b = 583.9 (1), c = 19.907 (3) pm, β = 92.68 (1)°, monoclinic, P2$_1$/c, Z = 4, μ(Mo) = 0.57 cm^{-1}, 2731 unique reflections with I > 3.0σ(I). The structure was solved by direct methods (teXan SIR-92) and refined by full-matrix least-squares on F. Carbon and nitrogen were refined with anisotropic thermal parameters. Hydrogens were modeled in fixed positions. The largest residual electron density in the final difference Fourier map was 0.69 e/Å^3. The data/parameter ratio was 10.42. The final R factors were R = 0.068 and R_w = 0.080. Crystallographic data for the structure of **7b** have been deposited with the Cambridge Crystallographic Data Centre (ref. Nr. 133745). Copies of the data can be obtained free of charge at the address under **4a**.

X-ray Structure Determination of ***8b****:*

Crystals of **8b** were grown from a saturated solution in acetonitrile at –25 °C. Crystal data for **8b** at –55 °C with Mo Kα radiation: a = 2211.0 (5), b = 1361.6 (3), c = 1800.8 (5) pm, β = 102.18 (2)°, monoclinic, C2/c, Z = 8, μ(Mo) = 2.59 cm^{-1}, 2123 unique reflections with I > 3.0σ(I). The structure was solved by direct methods (SHELXS) and refined by full-matrix least-squares on F. Chlorine, carbon and nitrogen were refined

with anisotropic thermal parameters. Hydrogens were modeled in fixed positions. The largest residual electron density in the final difference Fourier map was 0.22 e/Å^3. The data/parameter ratio was 7.57. The final R factors were R = 0.045 and R_w = 0.037. Crystallographic data for the structure of **8b** have been deposited with the Cambridge Crystallographic Data Centre (ref. Nr. 133746). Copies of the data can be obtained free of charge at the address under **4a**.

ACKNOWLEDGEMENT

AJA, RK, and MU thank the DuPont Company for their support of portions of this work (Contribution No. 7555). The DuPont Company also facilitated this work through a Visiting Research Scientist Fellowship to JRG (1996–7). RK gratefully acknowledges the support of DuPont and the Technische Universität Braunschweig that enabled a visit in the DuPont Experimental Station Laboratories. The generous support of the Alexander von Humboldt Stiftung provided a Senior Research Prize for AJA and a Feodor-Lynen Fellowship for MU. Finally, this work is dedicated to Professor Edward M. Burgess on the occasion of his retirement from the Georgia Institute of Technology.

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