Synthesis of Nitrile Oligomers through Multiple Anion Capture Reactions of Allene Dianions

Peter Langer,*[a] Manfred Döring,[b] Dietmar Seyferth,[c] and Helmar Görls[d]

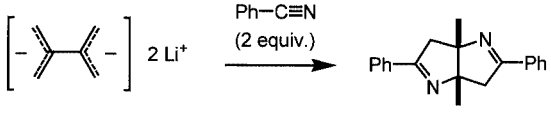
Keywords: Allenes / Anions / Cyclizations / Domino reactions / Nitriles

Domino reactions between 1,1-dilithio-3,3-diphenylallene and nitriles resulted in the formation of products containing up to four nitrile molecules, representing the highest number to date of nitrile molecules involved in the formation of unambiguously characterized oligomers. The unusual domino process reported constitutes a new method for the synthesis of imidazoles. The solid-state structures of the sterically encumbered products were studied by crystal structure analyses.

Introduction

Domino reactions have found widespread applications in organic synthesis.[1] Organolithium reagents have been used as key intermediates in domino processes. These reactions proceed by attack of the carbanion on a suitable relay species to form a reactive intermediate, which is subsequently trapped by an electrophile. Padwa et al. have reported reactions between carbon nucleophiles and allenes and subsequent cyclization with acrylates.[2] A domino process involving *N*-nucleophiles and isocyanates has been reported by Schaumann and Ketcham,[3] while Banert and co-workers have employed allenyl isothiocyanates as relay species in domino reactions.[4]

Nitriles represent versatile relay species in domino reactions. The base-catalysed polymerization of nitriles has been studied for a long time, and the mixtures obtained were among the first organic polymers. We have recently reported the one-pot synthesis of radialene-shaped pyrroles through the addition of *one* equivalent of a nitrile to a 1,3-dianion and subsequent cyclization by addition of an oxalic acid-bis(imidoyl)dichloride.[5] Only a few structurally characterized oligomers prepared by addition of more than one nitrile molecules to an organolithium compound have so far been reported.[6] Bates et al. have reported the cyclization of bislithiated 2,3-dimethylbutadiene (1 equiv.) with *two* equivalents of benzonitrile (Scheme 1).[7] In this reaction, each nucleophilic centre reacts with one nitrile molecule to give a 2:1-condensation product, which subsequently undergoes a cyclization. Related behaviour was observed for reactions between nitriles and (butadiene)zirconocene.[8] The base-induced oligomerization of glycolonitrile involved two nitrile molecules.[9] A domino reaction between Grignard reagents and a *tris*-nitrile has also been reported,[10] while we have recently reported that reactions between dilithiated allenes and benzonitrile resulted in the addition of up to *four* nitrile molecules.[11] This multiple anion-capture reaction involves the highest number so far of nitrile molecules added to an organolithium reagent to give an unambiguously characterized oligomer. Here we wish to report full details of this unusual reaction, which we believe also constitutes a new method for the synthesis of imidazoles. The solid-state structures of the products and the mechanism of the reaction are discussed.



Scheme 1. Double anion-capture reaction between dilithiated 2,3-dimethyl-1,3-butadiene and benzonitrile

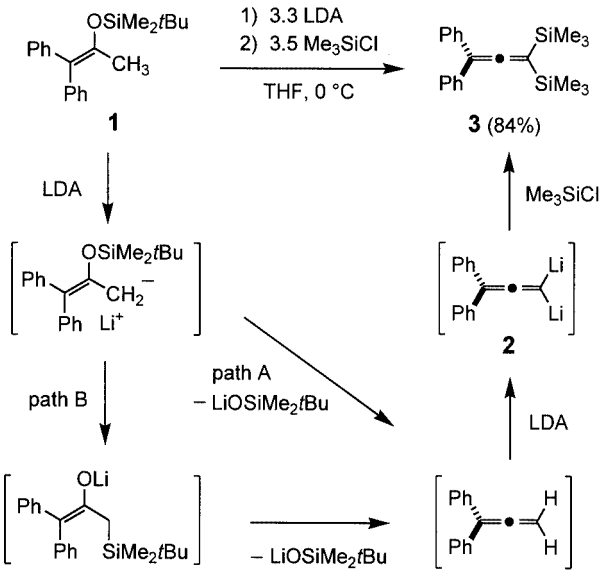
Results and Discussion

1,1-Diphenyl-3,3-dilithioallene (**2**) was generated by treatment of silyl enol ether **1** with LDA (3.3 equiv.) in a

[a] Institut für Chemie und Biochemie der Ernst-Moritz-Arndt Universität Greifswald,
Soldmannstrasse 16, 17487 Greifswald, Germany
E-mail: peter.langer@uni-greifswald.de
[b] Institut für Technische Chemie (ITC-CPV), Forschungszentrum Karlsruhe,
Postfach 3640, 76021 Karlsruhe, Germany
[c] Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139, USA
[d] Max-Planck-Arbeitsgruppe für CO_2-Chemie der Universität Jena,
Lessingstr. 12, 07743 Jena Germany

  DOI: 10.1002/ejoc.200200685

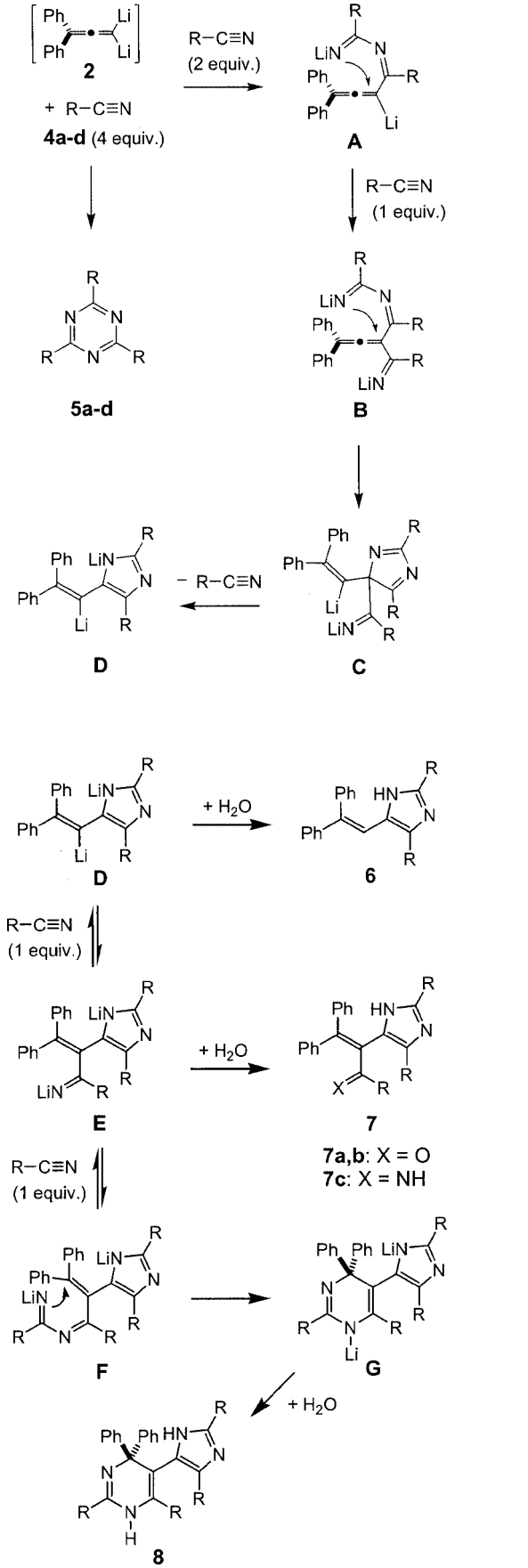
reaction recently developed by us.[11,12] This reaction proceeds by lithiation of the silyl enol ether, elimination of lithium silanolate and lithiation of 1,1-diphenylallene (Scheme 2). The elimination either occurs directly (path A) or proceeds through a O→C silyl migration/Peterson elimination sequence (path B). Addition of Me_3SiCl to **2** afforded bis-silylated allene **3**.



Scheme 2. Formation of 1,1-dilithio-3,3-diphenylallene

Treatment of nitriles with lithiated allenes was expected to result in the formation of iminoallenes, which should be interesting synthetic building blocks.[13] The reaction between 1,1-diphenyl-3,3-dilithioallene **2** and 2.2 molar equivalents of benzonitrile, however, resulted in formation of a complex mixture (Scheme 3), although two products − **7a** (9%) and **8a** (14%) − were isolated by column chromatography in low yield. Mass spectrometry (FAB) suggested that these products had originated from reactions between the allene and three and four nitriles, respectively. The yields of **7a** and **8a** were dramatically improved by employment of 4.5 molar equivalents of benzonitrile. The yellow imidazole **7a** and the colourless 5-(imidazol-4-yl)pyrimidine **8a** were isolated in 12% and 51% yields, respectively.

The formation of sterically encumbered imidazoles **7a** and **8a** can be explained by the mechanism depicted in Scheme 3, in which the terminal carbon atom of dilithiated allene **2** reacts with two or three equivalents of the nitrile (intermediates **A** and **B**). The terminal allene carbon atom is subsequently attacked by the lithiated amidine to give intermediate **C**, extrusion of a nitrile results in formation of lithiated imidazole **D**, and the vinylic carbanion reacts with the nitrile to give intermediate **E**. An additional nitrile molecule is then attacked to generate a lithiated amidine (intermediate **F**), and this attacks the carbon attached to the two allene-derived phenyl groups to give lithiated dihydropyrimidine **G**. The final products **8a** and **7a** are then formed by protonation of intermediates **G** and **E**, respectively, during aqueous workup.



Scheme 3. Reaction between 1,1-dilithio-3,3-diphenylallene and nitriles

Table 1. Products and yields

Entry	R	[%] (**5**)[a]	[%] (**6**)[a]	[%] (**7**)[a]	[%] (**8**)[a]
a	Ph	0	0	12	51
b	*t*Bu	0	0	66	0
c	4-Tol	0	0	28	0
d	3-Tol	28	40	0	traces

[a] Isolated yields.

The structures of **7a** and **8a** were confirmed by crystal structure analyses. Pyrimidine **8a** contains two directly linked heterocyclic systems (Figure 1). An interesting structural feature of **8a** is the intramolecular π-stacking interaction of two phenyl groups (distance: 4.08 Å), which is energetically favourable. In addition, the π-stacked conformation allows optimal conjugation of the phenyl and hetaryl groups; other conformations would result in orthogonal twisting of the π-systems. Atropic isomers are, in principle, possible for **8a**, due to restricted rotation of the single bond between the heterocyclic moieties. However, the enantiomers could not be separated by HPLC on a chiral stationary phase because of rapid racemization. Inspection of the crystal lattice (Figure 2) shows a weak intermolecular hydrogen bond [N(4B)−H···N(2A)]. The N···N distance is 3.056 Å.

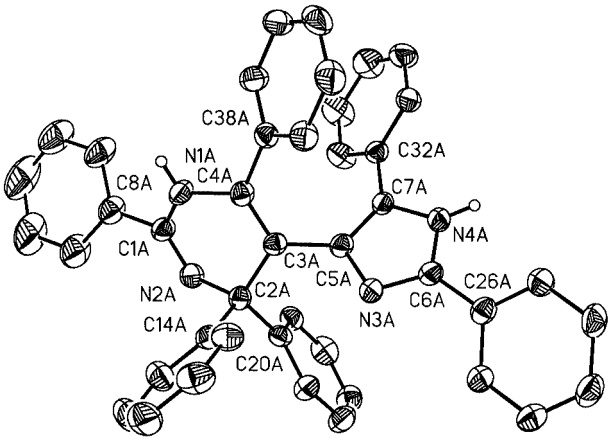


Figure 1. ORTEP plot of **8a**; thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms; selected bond lengths [A] and angles [°]: N1A−C1A 1.365(5), N2A−C1A 1.284(5), N3A−C6A 1.318(4), N4A−C6A 1.356(4), C1A−C8A 1.479(5), C3A−C4A 1.342(5), N1A−C4A 1.396(4), N2A−C2A 1.500(4), N3A−C5A 1.381(4), N4A−C7A 1.382(4), C2A−C3A 1.532(5), C3A−C5A 1.473(5), C5A−C7A 1.376(5); C1A−N1A−C4A 119.3(3), C6A−N3A−C5A 105.3(3), N2A−C1A−N1A 122.5(3), N1A−C1A−C8A 116.8(3), C1A−N2A−C2A 116.3(3), C6A−N4A−C7A 107.2(3), N2A−C2A−C3A 109.6(3), C4A−C3A−C2A 116.8(3), C3A−C4A−N1A 118.0(3)

The imino group of **7a** was hydrolysed during aqueous workup. The crystal structure analysis of **7a** also shows an intramolecular π-stacking interaction of two phenyl groups (Figure 3). The conjugation between the phenyl and imidazole rings is decreased by orthogonal twisting induced by steric interactions. The orange colour of **7a**, as compared to the colourless **8a**, can be explained by the fact that the

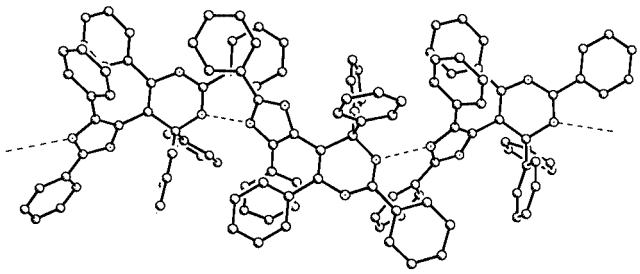


Figure 2. Crystal lattice of **8a**

conjugation between the two phenyl groups and the rest of the molecule is interrupted for **8a**, but not for **7a**. Imidazole **7a** has a dimeric structure in the crystal lattice (Figure 4). The intermolecular interaction is made up of two intermolecular hydrogen bonds (N2A−H···O1; N···O distance: 2.950 Å) and by the π-stacking interaction of two phenyl groups.

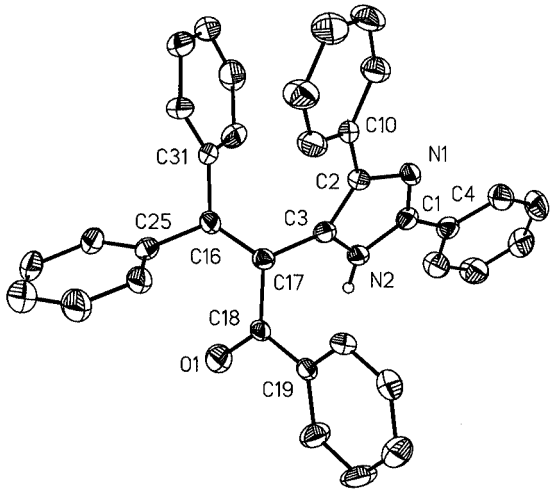


Figure 3. ORTEP plot of **7a**; thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms

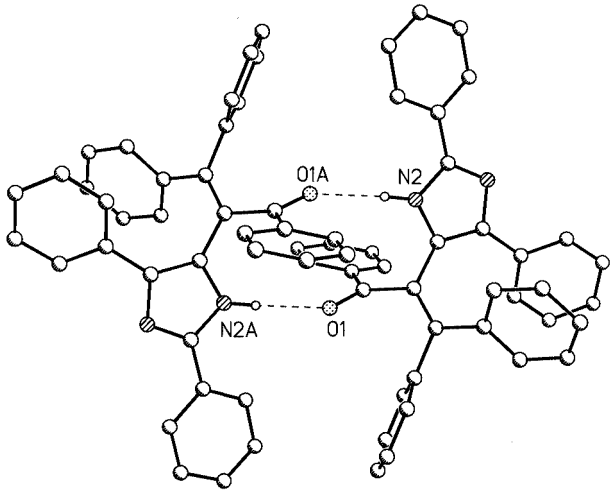


Figure 4. Dimeric structure of **7a**

The reaction between dilithioallene **2** and pivalonitrile afforded the colourless imidazole **7b** in 66% yield. Mass spec-

trometry (FAB) indicated the formation of a 3:1 cyclization product. The structure of **7b** was again elucidated by crystal structure analysis (Figure 5). As in the case of **7a**, the imino group was hydrolysed during aqueous workup. The phenyl groups, the imidazole ring, the carbon−carbon double bond and the carbonyl bond are twisted out of plane, due to the steric demand of the *tert*-butyl groups, so no intramolecular hydrogen bond (N−H···O) is observed. Inspection of the crystal lattice shows the presence of a dimeric structure (Figure 6). The carbonyl groups of two molecules **7b** are linked by hydrogen bonds (O−H···O) to a water molecule (O···O distance: 2.863 Å).

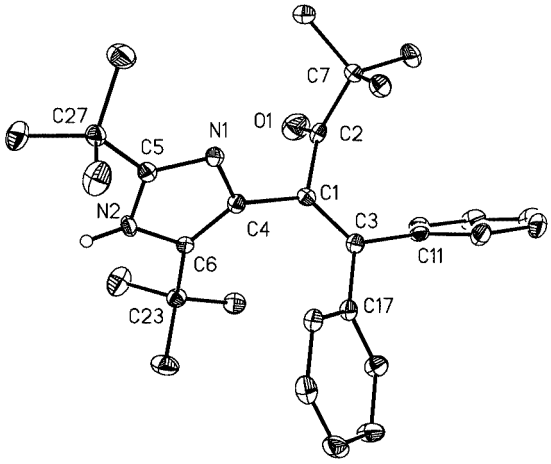


Figure 5. ORTEP plot of **7b**; thermal ellipsoids of 50% probability are shown for the non-hydrogen atoms; selected bond lengths [Å] and angles [°]: O1−C2 1.287(4), N1−C4 1.392(4), N2−C6 1.388(4), C1−C4 1.491(4), N1−C5 1.317(4), N2−C5 1.361(5), C1−C3 1.351(4), C1−C2 1.500(4), C4−C6 1.373(5); C5−N1−C4 105.6(3), C3−C1−C4 125.2(3), C4−C1−C2 113.4(3), O1−C2−C7 118.1(3), C6−C4−C1 132.0(3), N1−C5−N2 110.5(3), C5−N2−C6 109.2(3)

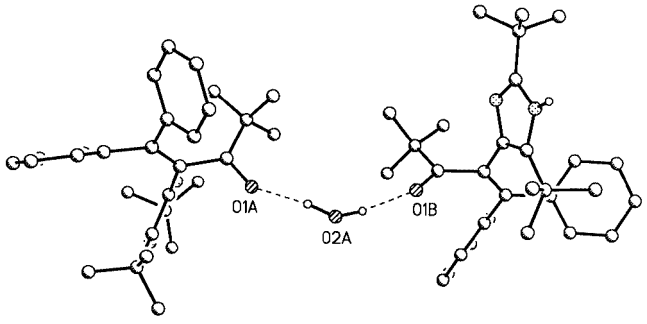


Figure 6. Dimeric structure of **7b**

The reaction between allene dianion **2** and *p*-tolunitrile gave the orange 3:1 cyclization product **7c**, which was characterized by spectroscopy (FAB-MS and NMR). The cyclization of **2** with *m*-tolunitrile afforded the colourless 2:1 cyclization product **6d** (40%) and the triazine **5d** (28%). The formation of **6d** can be explained by protonation of intermediate **D** during aqueous workup. Triazine **5d** was formed by trimerization of the nitrile.[14] Condensations between dilithiated allene **2** and other nitriles (such as 2-cyanonaphthalene or acetonitrile) proved unsuccessful, presumably due to steric hindrance and deprotonation of the nitrile, respectively.

Conclusions

It is noteworthy that the number of nitrile molecules added to **2** does not depend on the stoichiometric amount of nitrile employed. During the formation of oligonitrile **8a** all three carbon atoms of the allene are sequentially involved in the reaction. The mechanism can be explained by formation of a thermodynamically stable lithiated imidazole. In fact, the reported chemistry constitutes a new approach to sterically encumbered imidazoles. Steric hindrance seems to be the reason why no addition of a fourth nitrile molecule can take place with pivalo- and *p*-tolunitrile. In the case of *m*-tolunitrile the reaction stopped with formation of a 2:1 cyclization product.

The domino process reported here is interesting from a mechanistic viewpoint. Reactions between benzonitrile and other dianions, such as dilithiated 2-methylbenzimidazole or acetanilide, resulted in the formation of open-chained 1:1 condensation products rather than oligonitriles.[9] Related reactions[5,7,8] also involve addition of only one nitrile molecule to the carbanion. In all these reactions, lithiated imines were formed and underwent irreversible transformations into stable dianionic intermediates. In contrast, the formation of lithiated amidines by attack of an additional nitrile was not observed. To the best of our knowledge, there is only one reaction[10] (except for triazine formation) that involves attack of a lithiated imine onto a nitrile to give a lithiated amidine. In the third step of that domino reaction, the amidine was irreversibly transformed into a stable monoanionic intermediate. In our case, the formation of lithiated amidine **F** from lithiated imine **E** is presumably a reversible process (Scheme 3). It is interesting to note, for comparison, that elimination of a nitrile from a lithiated 1,3-diazadiene has been reported.[15] Intermediate **F** underwent an irreversible consecutive reaction to give the stable lithiated pyrimidine **G**.

Experimental Section

General: All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. Petroleum ether (PE, bp 40−70 °C) and diethyl ether (E) were distilled prior to use. IR: Perkin−Elmer 2000 FT-IR. NMR (Bruker AC 200 F): 200 MHz and 50 MHz (for, ^{1}H and ^{13}C, respectively), if not quoted otherwise. For ^{1}H NMR the solvents $CDCl_3$ and CD_2Cl_2 were used. Tetramethylsilane (TMS) was used as internal standard, [D_8]THF as solvent δ = 1.73, 3.58 ppm. For ^{13}C NMR, $CDCl_3$ and [D_8]THF were used (δ = 25.5, 67.7 ppm). The multiplicities of the carbon atoms were determined by the DEPT 135 technique and are quoted as CH_3, CH_2, CH, and C for primary, secondary, tertiary, and quaternary carbon atoms. Mass spectrometry: Finnigan Mat SSQ 710 spectrometer. Electronic ionization: EI, 70 eV. Chemical ionization with water: CI, H_2O. For preparative scale chromatography, silica gel (60−200 mesh) was used. Melting points

are uncorrected and were measured on a Büchi apparatus. Elemental analyses: Microanalytical laboratory of the University of Hannover.

General Procedure for the Generation of 1,1-Dilithio-3,3-diphenylallene (2) and Its Reaction with Nitriles: A THF solution of LDA, prepared by addition of *n*BuLi (1.6 M solution in hexane) to a THF solution (20 mL) of diisopropylamine (3.3 equiv.), was added at 0 °C to a THF solution (40 mL) of silyl enol ether **1** (1.80 g, 5.60 mmol). The solution was stirred at 20 °C for 6 h, during which it became deep red. A THF solution (10 mL) of benzonitrile (2.58 mL, 4.5 equiv.), pivalonitrile (1.61 g) or *p*-tolunitrile (2.26 g) was then added at 0 °C by syringe. After the mixture had been stirred for 10 h at 20 °C, water (20 mL) was added. The colour of the solution changed from deep purple to yellow. The reaction mixture was extracted (diethyl ether/THF, 1:1) and the combined organic layers were dried ($MgSO_4$) and filtered, and the solvent was removed in vacuo to give the crude product, which was purified as indicated.

5-(2,4-Diphenylimidazol-5-yl)-2,4,4,6-tetraphenyl-1,4-dihydropyrimidine (8a): From **1** (1.80 g, 5.60 mmol), **8a** was isolated by chromatography (silica gel, diethyl ether/petroleum ether, 1:1) as a colourless solid (1.73 g, 51%), m.p. 146−150 °C. Imidazole **7a** was isolated as a second product in 12% yield (spectroscopic data: see below). ^{1}H NMR ([D$_8$]THF, 200 MHz): δ = 6.75−8.20 ppm (m, 30 H, Ar), 8.75 (br., 1 H, NH), 10.68 (br., 1 H, NH). ^{13}C NMR ([D$_8$]THF, 50 MHz): δ_c = 107.20 ppm (C, *C*Ph$_2$), 125.27, 125.76, 125.87, 126.06, 126.26, 127.12, 127.30, 127.50, 128.02, 128.08, 128.17, 128.30, 128.68, 128.90, 129.21, 129.76 129.92, 130.86 (CH, Ph), 132.15, 132.19, 136.43, 136.73, 137.37, 138.19 (C, Ph, = *C*CPh$_2$), 145.67, 148.50, 148.78 (C, C=*C*N), 150.65, 150.78 (C, CN$_2$). IR (KBr): $\tilde{\nu}$ = 3495 cm^{-1} (br), 3395 (br), 3060 (m), 3029 (m), 2923 (w), 1640 (s), 1598 (m), 1578 (m), 1524 (s), 1496 (m), 1446 (m), 1395 (s), 1370 (m), 1178 (m), 1072 (m), 1028 (m), 697 (s). MS (FAB): *m*/*z* (%) = 605 [M + 1]$^+$ (100). $C_{43}H_{32}N_4$ (604.729): calcd. C 85.41, H 5.33, N 9.26; found calcd. C 85.17, H 5.61, N 9.62.

2-(2,4-Diphenylimidazol-5-yl)-1,3,3-triphenyl-2-propen-1-one (7a): From **1** (1.80 g, 5.60 mmol), **7a** was isolated by chromatography (silica gel, diethyl ether/petroleum ether, 3:1, more polar fraction) as an orange solid (337 mg, 12%), m.p. 160−163 °C. ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 6.80−7.70 ppm (m, 25 H, Ar), 9.10 (br., 1 H, NH), 9.30 (br., 1 H, NH). ^{13}C NMR (CDCl$_3$, 50 MHz): δ_c = 125.26 ppm, 125.32, 125.90, 126.83, 127.60, 127.62, 127.78, 128.06, 128.18, 128.38, 128.60, 128.99, 129.60, 130.02, 130.14 (CH, Ph), 132.00, 134.11, 137.40, 137.45, 138.22 (C, Ph, *C*=CPh$_2$), 141.51, 142.24, 146.81, 147.55 (C, Ph-C to CNH, C=*C*N, *C*Ph$_2$), 160.0 (C, CN$_2$), 177.11 (C, *C*=NH). IR (KBr): $\tilde{\nu}$ = 3430 cm^{-1} (m), 3133 (m), 3060 (s), 3029 (s), 2925 (m), 1593 (s), 1565 (s), 1494 (s), 1459 (s); 1446 (s), 1365 (s), 1190 (m), 1159 (m), 1073 (m), 1028 (m), 693 (s). MS (CI, H_2O): *m*/*z* (%) = 502 [M + 1]$^+$ (100).

1-(*tert*-Butyl)-2-[2,4-di(*tert*-butyl)imidazol-5-yl]-3,3-diphenyl-2-propen-1-one (7b): From **1** (1.80 g, 5.60 mmol), **7b** was isolated by crystallization of the crude product (from ether) and subsequent washing of the crystals (ether) as colourless crystals (1.63 g, 66%), m.p. 171−172 °C. ^{1}H NMR ([D$_8$]THF, 200 MHz): δ = 1.00 ppm (s, 9 H, CH$_3$), 1.05 (s, 9 H, CH$_3$), 1.36 (s, 9 H, CH$_3$), 7.01 (m, 3 H, Ph), 7.24 (m, 3 H, Ph), 9.65 (br., 1 H, NH). ^{13}C NMR ([D$_8$]THF, 50 MHz): δ_c = 126.93 ppm, 127.38, 127.72, 128.26, 131.86, 132.45 (CH, Ph), 132.93, 133.95, 137.64 (C, Ph, *C*=CPh$_2$), 140.29, 143.84, 144.28 (C, C=*C*N, *C*Ph$_2$), 154.21 (C, CN$_2$), 191.71 (C, *C*=O). IR (KBr): $\tilde{\nu}$ = 3455 cm^{-1} (m), 3060 (m), 3028 (m), 2959 (s), 2928 (m), 1695 (m), 1599 (m), 1494 (m), 1480 (m), 1443 (m), 1363 (m), 1203 (m), 1078 (w). MS (EI): *m*/*z* (%) = 442 [M$^+$] (14), 441 [M − 1]$^+$ (50), 440 [M − 2]$^+$ (100), 385 (76).

2-[2,4-Bis(4-methylphenyl)imidazol-5-yl]-1-(4-methylphenyl)-3,3-diphenylpropen-1-imine (7c): From **1** (1.80 g, 5.60 mmol), **7c** was isolated by column chromatography (silica gel, diethyl ether/petroleum ether, 3:1) as an orange solid (851 mg, 28%), m.p. 152−157 °C. ^{1}H NMR ([D$_8$]THF, 200 MHz): δ = 2.21 ppm, 2.28, 2.32 (s, 9 H, Tol-CH$_3$), 6.75−7.85 (m, 22 H, Ar), 11.20 (br., 1 H, NH). ^{13}C NMR ([D$_8$]THF, 50 MHz): δ_c = 125.89 ppm, 127.79, 128.25, 128.68, 128.91, 129.19, 129.27, 129.55, 129.89, 130.92, 131.01, 131.47 (CH, Ph, Tol), 132.57, 133.00, 134.90, 135.92, 136.81, 137.23, 138.23, 139.01 (C, Ph, Tol, *C*=CPh$_2$), 139.52, 142.11, 143.17, 144.50 (C, Tol-C to CNH, C=*C*N, *C*Ph$_2$), 162.82 (C, CN$_2$), 178.21 (C, *C*=NH). IR (KBr): $\tilde{\nu}$ = 3429 cm^{-1} (m), 3027 (m), 2921 (m), 1598 (m), 1558 (m), 1506 (s), 1444 (m); 1362 (m), 1183 (m), 1078 (w), 1033 (w), 823 (s), 698 (s). MS (CI, H_2O): *m*/*z* (%) = 544 [M + 1]$^+$ (100). $C_{39}H_{33}N_3$ (543.693): calcd. C 86.16, H 6.12, N 7.72; found C, 85.25, H 6.27, N 8.45.

5-(2′,2′-Diphenylethenyl)-2,4-bis(3-methylphenyl)imidazole (6d): From **1** (1.80 g, 5.60 mmol), **6d** was isolated by chromatography (silica gel, diethyl ether/petroleum ether, 3:1) as an orange solid (954 mg, 40%). In addition, **5d** was isolated as an orange solid (550 mg, 28%). ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 2.35 ppm, 2.48 (2 × s, 2 × 3 H, 2 × CH$_3$), 7.05−7.75 (m, 19 H, Ar, =CH−), 8.23 (br., 1 H, NH). ^{13}C NMR (CDCl$_3$, 75 MHz): δ_c = 21.22 ppm, 21.49 (CH$_3$), 114.61, 121.58 (CH), 125.49 (C), 125.60, 125.64, 126.67, 127.35, 128.05, 128.28, 128.30, 128.34, 128.55, 129.09 (CH), 129.24 (C), 129.43, 129.71, 129.90 (CH), 134.43, 137.86, 138.11, 138.38, 140.33, 141.21, 144.20, 145.64 (C). MS (EI): *m*/*z* (%) = 426 (100) [M$^+$], 349 (6).

1,3,5-Tris(3-methylphenyl)triazine (5d): Yield: 550 mg (28%). ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 2.60 ppm (s, 9 H, CH$_3$), 7.30−7.60 (m, 9 H, Ar), 8.58 (s, 3 H, Ar). ^{13}C NMR (CDCl$_3$, 75 MHz): δ_c = 42.30 ppm (CH$_3$), 126.14, 128.40, 129.29, 133.14 (CH), 136.16, 138.12 (C), 171.50 (CN$_2$). MS (EI): *m*/*z* (%) = 351 [M$^+$] (100), 119 (22). MS (CI, H_2O): *m*/*z* (%) = 703 [2M + 1]$^+$ (6), 352 [M + 1]$^+$ (100).

Crystal Structure Determinations: The intensity data for the compounds were collected on a Nonius CAD4 diffractometer (graphite-monochromated Mo-K_α radiation). Data were corrected for Lorentz and polarization effects, but not for absorption.[16] The structures were solved by direct methods (SHELXS)[17] and refined by full-matrix, least-squares techniques against F_o^2 (SHELXL-97).[18] For the imine nitrogen N2 and for the water-molecule of **7b** the hydrogen atoms were located by difference Fourier synthesis and refined isotropically. The other hydrogen atoms were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.[19] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 7a:[19] $C_{36}H_{24}N_2O{\cdot}H_2O$, *Mr* = 518.59 g·mol^{-1}, colourless prism, size 0.40 × 0.38 × 0.36 mm, triclinic, space group $P\bar{1}$, *a* = 11.415(2), *b* = 11.551(2), *c* = 11.655(2) Å, α = 72.77(3), β = 87.02(3), γ = 85.88(3)°, *V* = 1463.2(4) Å^3, *T* = 20 °C, *Z* = 2, $\rho_{calcd.}$ = 1.177 g·cm^{-3}, μ(Mo-K_α) = 0.73 cm^{-1}, *F*(000) = 544, 3660 reflections in *h*(−12/0), *k*(−12/12), *l*(−12/12), measured in the range 6.88° ≤ Θ ≤ 21.97°, completeness Θ $_{max}$ = 96.8%, 3457 independent reflections, R_{int} = 0.090, 2333 reflections with $F_o > 4\sigma(F_o)$, 357 parameters, 0 restraints.

Crystal Data for 8a:[19] $C_{43}H_{32}N_4$, *Mr* = 604.73 g·mol^{-1}, colourless prism, size 0.40 × 0.38 × 0.36 mm, triclinic, space group $P\bar{1}$, *a* =

12.256(2), b = 16.184(3), c = 19.538(4) Å, α = 81.23(3), β = 85.32(3), γ = 73.14(3)°, V = 3662.6(12) Å^3, T = 20 °C, Z = 4, $\rho_{calcd.}$ = 1.097 g·cm^{-3}, μ(Mo-K_α) = 0.65 cm^{-1}, F(000) = 1272, 10358 reflections in h(−13/13), k(−17/17), l(−21/0), measured in the range 8.18° ≤ Θ ≤ 23.26°, completeness Θ_{max} = 95.4%, 10037 independent reflections, R_{int} = 0.042, 5942 reflections with $F_o > 4\sigma(F_o)$, 864 parameters, 0 restraints, $R1_{obsd.}$ = 0.070, $wR^2_{obsd.}$ = 0.205, $R1_{all}$ = 0.147, wR^2_{all} = 0.2625, GOOF = 0.999, largest difference peak and hole: 0.488/−0.402 e·Å^{-3}.

Crystal Data for 7b:[19] $C_{30}H_{38}N_2O{\cdot}0.5H_2O$, Mr = 451.63 g·mol^{-1}, colourless prism, size 0.40 × 0.38 × 0.37 mm, orthorhombic, space group *Pbcn*, a = 22.900(5), b = 11.933(2), c = 19.754(4) Å, V = 5398(2) Å^3, T = −90 °C, Z = 8, $\rho_{calcd.}$ = 1.111 g·cm^{-3}, μ(Mo-K_α) = 0.68 cm^{-1}, F(000) = 1960, 2700 reflections in h(−23/0), k(0/11), l(0/20), measured in the range 2.67° ≤ Θ ≤ 21.64°, completeness Θ_{max} = 85.4%, 2700 independent reflections, 2078 reflections with $F_o > 4\sigma(F_o)$, 308 parameters, 0 restraints, $R1_{obsd.}$ = 0.048, $wR^2_{obsd.}$ = 0.124, $R1_{all}$ = 0.075, wR^2_{all} = 0.148, GOOF = 0.549, largest difference peak and hole: 0.575/−0.454 e·Å^{-3}.

Acknowledgments

Financial support from the Deutsche Forschungsgemeinschaft (Heisenberg scholarship to P. L. and Normalverfahren) is gratefully acknowledged.

[1] For reviews of domino reactions, see: [1a] L. F. Tietze, U. Beifuss, *Angew. Chem.* **1993**, *105*, 137; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 131. [1b] L. F. Tietze, *Chem. Rev.* **1996**, *96*, 115.
[2] A. Padwa, P. E. Yeske, *J. Am. Chem. Soc.* **1988**, *110*, 1617.
[3] I. Khattak, R. Ketcham, E. Schaumann, G. Adiwidjaja, *J. Org. Chem.* **1985**, *50*, 3431.
[4] K. Banert, H. Hückstädt, K. Vrobel, *Angew. Chem.* **1992**, *104*, 72; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 90.
[5] P. Langer, M. Döring, P. R. Schreiner, H. Görls, *Chem. Eur. J.* **2001**, *7*, 2617.
[6] For the palladium-catalysed oligomerization of six *isocyanide* molecules, see: T. Tanase, T. Ohizumi, K. Kobayashi, Y. Yamamoto, *J. Chem. Soc., Chem. Commun.* **1992**, 707.
[7] R. B. Bates, B. Gordon III, P. C. Keller, J. V. Rund, *J. Org. Chem.* **1980**, *45*, 168.
[8] [8a] G. Erker, M. Berlekamp, L. Lopez, M. Grehl, B. Schönecker, R. Krieg, *Synthesis* **1994**, 212. [8b] M. Riedel, G. Erker, *Synthesis* **1994**, 1039.
[9] G. Arrhenius, K. K. Baldridge, S. Richards-Gross, J. S. Siegel, *J. Org. Chem.* **1997**, *62*, 5522.
[10] [10a] S. Mathé, A. Rassat, *Tetrahedron Lett.* **1998**, *39*, 383. See also: [10b] L. N. Cherkasov, K. V. Balyan, *Z. Org. Chim.* **1965**, *1*, 1811.
[11] P. Langer, M. Döring, D. Seyferth, *Chem. Commun.* **1998**, 1927.
[12] [12a] D. Seyferth, P. Langer, M. Döring, *Organometallics* **1995**, *14*, 4457. [12b] P. Langer, M. Döring, D. Seyferth, H. Görls, *Chem. Eur. J.* **2001**, *7*, 573.
[13] M. S. Sigman, B. E. Eaton, *Tetrahedron Lett.* **1993**, 5367.
[14] Triazines have been previously obtained by base-induced cyclotrimerization of aryl nitriles, see: K. Schank, in: *Methoden Org. Chem.* (Houben-Weyl), 4th ed., vol. *E11/2*, **1985**, 1257.
[15] Open-chained oligonitriles have been prepared by a different way: M. Buhmann, M. H. Möller, U. Rodewald, E.-U. Würthwein, *Chem. Ber.* **1993**, *126*, 2467.
[16] *MOLEN*, An Interactive Structure Solution Procedure, Enraf−Nonius, Delft, The Netherlands, **1990**.
[17] G. M. Sheldrick, *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.
[18] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1997**.
[19] CCDC 198696 (**7b**), CCDC 198697 (**8a**), and CCDC 198698 (**7a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223/336-033; or deposit@ccdc.cam.ac.uk].

Received December 5, 2002

