Syntheses and structures of a class of bridged bis(amidinate)s and derivatives

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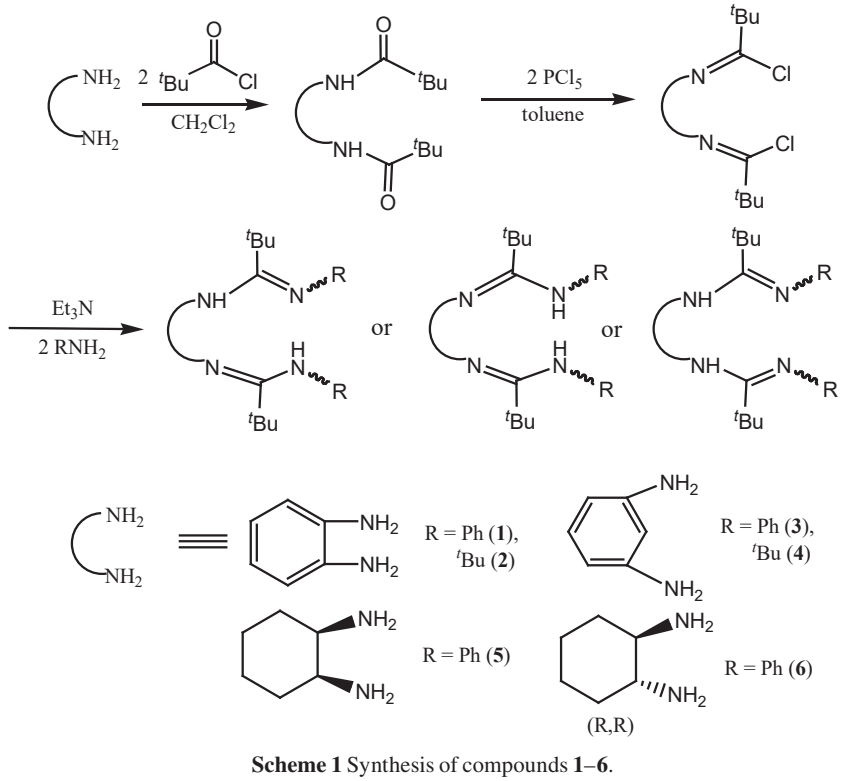
A series of different types of 'bridge' linked bis(amidinate)s have been prepared. Reactions of a variety of linked diamines with pivaloyl chloride yielded the corresponding diamides in very high yields. Conversion of the diamides to the diimine chloride is achieved with PCl_5 in CH_2Cl_2. Reactions of the diimine chloride with aniline or *t*-butyl amine yielded the bis(amidinate)s in good yields, while reaction with pyrrolyl sodium or 2,5-dimethyl pyrrolyl potassium afforded the corresponding derivatives. Their structures were characterised by NMR and HRMS, and some products were further characterised by X-ray crystal structure analysis. It was found that the locations of the hydrogen atoms within the two amidine fragments vary. The structures showed that in the phenylene-linked bis(amidinate)s, the hydrogen atoms were attached to different nitrogen atoms in the amidine groups, and in the cyclohexylene-linked bis(amidinate)s or their derivatives, the C=N of the amidine groups were conjugated with the aromatic rings.

Keywords: bridged bis(amidinate)s, phenylene linker, cyclohexylene linker

Amidinates are versatile ligands used in the fields of coordination and organometallic chemistry because their steric and electronic properties can be easily modulated by varying the substituents on the C and N atoms.[1] Bridged bis(amidinate)s as a special branch of amidinates have proven to be very versatile as they permit changes to the 'bridge' and the substituents of the amidine groups.[2–5] The frameworks have a rigid coordination sphere and provide a control over the geometry of the active metal centre. For example, the phenylene bridged ligands $[1,4\text{-}C_6H_4C(NR)_2\}_2]^{2-}$ (R = cyclohexyl, ^{i}Pr, $SiMe_3$)[6] and the oxalic amidinates[7] have been used to form bimetallic complexes. *o*-Phenylene-,[8,9] naphthalene-,[10,11] and propane-[12]linked bis(amidinate) complexes have been chelated to a monometal. Silyl-[13–15] and cyclohexyl-[16–18] bridged bis(amidinate)s lead to different configurations by variation of the terminal substituents on the framework. The reported examples of bridged bis(amidinate)s are mainly divided into two types: the traditional silylated and robust nonsilylated amidinates. This study details our efforts to extend the range of nonsilylated amidinates and derivatives with a variety of 'bridges' and *N*-aryl substituents. Here we report the synthesis and structures of a class of bridged bis(amidinate)s and their derivatives containing pyrrole rings.

Results and discussion

The linked bis(amidinate)s of **1**–**6** were synthesised by similar methods to those described in the literature.[19] Reactions of bridged diamines with pivaloyl chloride yielded the corresponding diamides. Then conversion of the diamides to the diimine chlorides was achieved by treatment with PCl_5. Reactions of the diimine chlorides with aniline or *t*-butyl amine yielded the bis(amidinate)s. All the reactions proceeded easily with high yields, providing facile variation of the 'bridge' and *N*-substituents (Scheme 1).



Scheme 1 Synthesis of compounds **1**–**6**.

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Attempted synthesis of compound **7**, using a diimine chloride and reaction with pyrrole or pyrrolyl lithium, gave no product. This may be attributed to the large steric hindrance of pyrrole. Therefore, the stronger nucleophile pyrrolyl sodium was needed (Scheme 2). In the synthesis of **8**, the pyrrolyl potassium salt had to be used instead of the sodium salt. This may be attributed to the larger steric hindrance of 2,5-dimethyl pyrrole; hence, a stronger nucleophile was needed (Scheme 3).

The crystal structures of compounds **1**, **5** and **7** were determined. The details of the structure refinement for the compounds are listed in Table 1. Selected bond lengths and bond angles are given in Table 2.

X-ray analysis showed that compound **1** crystallises in the monoclinic crystal system, $P2_1/n$ space group, and the molecular structure is shown in Fig. 1. In compound **1**, unlike in previously reported linked bis(amidinate) groups,[19] the hydrogen atoms in the amidine groups were attached to different nitrogen atoms. This fact was evident from analysis of the intramolecular N···H hydrogen bonds. The distance of N(3)···H(1) is 2.329 Å, which corresponds to that reported for naphthalene-linked bis(amidine)s.[12]

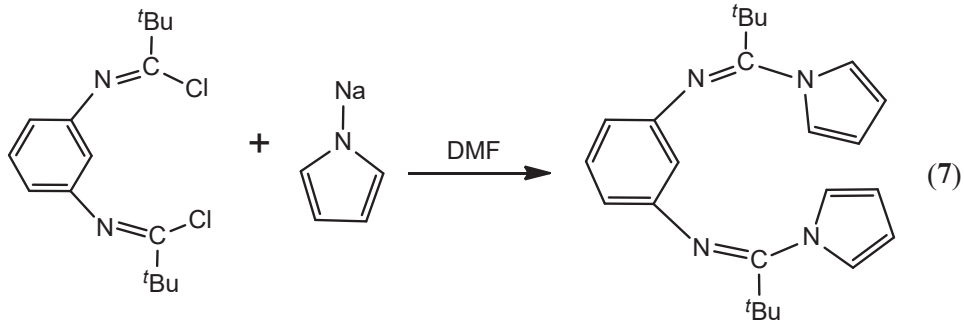
Compound **5** crystallises in the monoclinic crystal system, $P2_1/n$ space group, and the molecular structure is shown in Fig. 2. For compound **5**, the structure features the cyclohexyl backbone in its more stabilised chair form with one of the amidine groups in an equatorial position and the other in

Table 1 Crystal and structure refinement data for compounds **1**, **5** and **7**

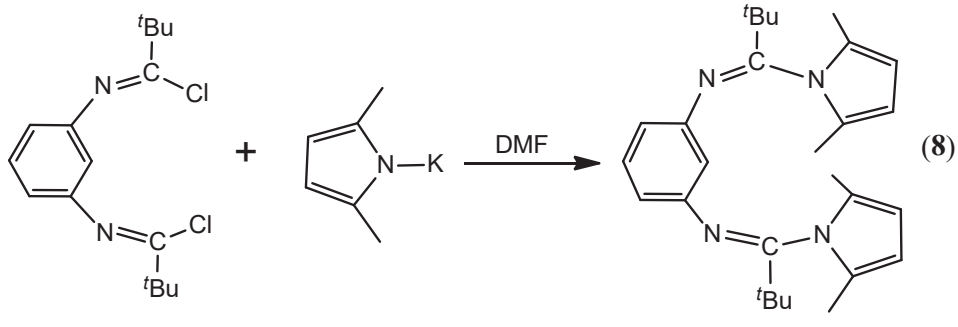
Crystal data	**1**	**5**	**7**
Empirical formula	$C_{28}H_{34}N_4$	$C_{28}H_{40}N_4$	$C_{24}H_{30}N_4$
Formula weight	426.59	432.64	374.52
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$
a (Å)	10.0943(7)	9.2163(9)	11.8992(14)
b (Å)	20.1523(12)	23.394(2)	8.1080(10)
c (Å)	11.9989(7)	12.4499(13)	23.811(3)
α (°)	90	90.00	90.00
β (°)	91.420(2)	93.755(2)	97.822(2)
γ (°)	90	90.00	90.00
V (Å^3)	2440.1(3)	2678.5(5)	2275.9(5)
T (K)	296.15	293(2)	293(2)
D_{calc} (g cm^{-3})	1.161	1.174	1.093
μ (mm^{-1})	0.069	0.064	0.066
Z	4	4	4
F(0 0 0)	920	944	808
Reflections (collected/unique)	21186/5657	23319/4981	22231/4189
R (int)	0.0493	0.0513	0.0393
Completeness to θ (%)	99.9	99.8	99.2
λ (Mo Kα radiation) (Å)	0.71073	0.71073	0.71073
θ range (°)	2.021–27.601	1.741–25.334	1.73–25.44
GOF	1.015	1.039	1.002
R_1, wR_2 [$I > 2\sigma(I)$]	0.0546, 0.1199	0.0741, 0.2033	0.0562, 0.1585
R_1, wR_2 (all data)	0.0866, 0.1334	0.1100, 0.2306	0.0963, 0.1888
Largest diff. peak and hole (e Å^{-3})	0.278 and −0.270	0.430 and −0.349	0.501 and −0.307

Table 2 Selected bond lengths and bond angles for compounds **1**, **5** and **7**

1		**5**		**7**	
Bond length (Å)					
C1–N1	1.408(2)	C1–N1	1.473(4)	C10–N2	1.419(3)
C7–N1	1.378(2)	C7–N1	1.355(4)	C5–N2	1.261(3)
C7–N2	1.275(2)	C7–N2	1.267(5)	C5–N1	1.432(3)
C6–N3	1.416(2)	C6–N3	1.459(4)	C14–N3	1.422(3)
C18–N4	1.381(2)	C18–N4	1284(5)	C16–N3	1.260(3)
C18–N3	1.283(2)	C18–N3	1.364(4)	C16–N4	1.426(3)
Bond angle (°)					
C1–N1–C7	128.78(14)	C1–N1–C7	130.3(3)	C10–N2–C5	122.61(19)
N1–C7–N2	117.51(15)	N1–C7–N2	128.1(3)	N2–C5–N1	121.99(19)
C6–N3–C18	121.52(13)	C6–N3–C18	128.8(3)	C14–N3–C16	123.4(2)
N3–C18–N4	125.49(15)	N3–C18–N4	127.2(3)	N3–C16–N4	122.3(2)



Scheme 2 Synthesis of compound **7**.



Scheme 3 Synthesis of compound **8**.

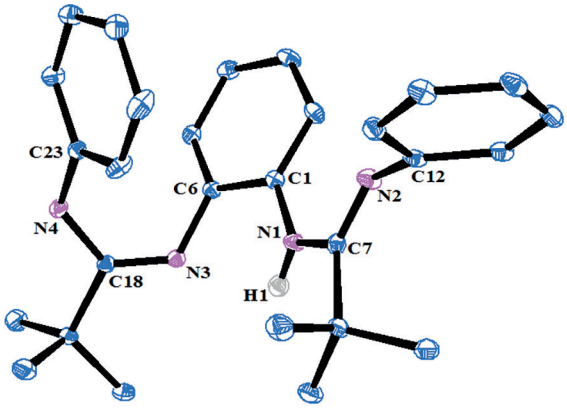


Fig. 1 Molecular structure of compound **1**.

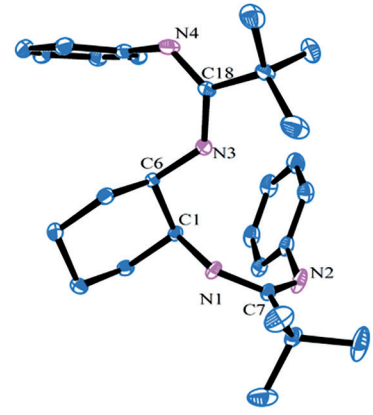


Fig. 2 Molecular structure of compound **5**.

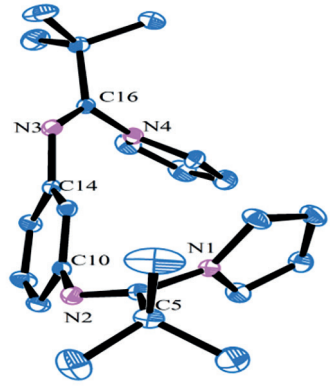


Fig. 3 Molecular structure of compound **7**.

an axial position. The C=N of the amidine group is in a *ZZ* configuration with the large *t*-butyl group on the opposite side of the aryl group. The bond lengths of N(1)–C(7) 1.355(4) Å and N(3)–C(18) 1.364(4) Å, are close to those found in other related structures.[18] In addition, the C(7)–N(2) and C(18)–N(4) bond lengths of 1.267(6) Å and 1.284(6) Å, respectively, are in the range of normal C=N double bonds. The N(1)–C(7)–N(2) and N(3)–C(18)–N(4) bond angles are 128.1(3)° and 127.2(3)°, respectively.

For compound **7**, the spatial structure is similar to that of compound **5**. The molecular structure is shown in Fig. 3. The solid-state structure of **7** features both C=N bonds in their *Z-syn* forms due to steric repulsion between the large *t*-butyl and the neutral pyrrolyl groups. In compound **7**, the bond length of N(3)–C(16) is 1.260(3) Å and that of N(2)–C(5) is 1.261(3) Å; the N(3)–C(16)–N(4) and N(2)–C(5)–N(1) bond angles are 122.3(3) and 121.99(3)°, respectively. The bond angle of N–C=N is approximately 5° smaller than in **5** with a more crowded pyrrolyl ring.

Conclusion

A class of new linked bis(amidinate)s have been designed and synthesised with high yields. Typical products were characterised by X-ray crystal structure analysis. It is revealed that with the *o*-phenylene-linked bis(amidinate)s, the hydrogen atoms between the amidine groups were attached to different nitrogen atoms owing to intramolecular hydrogen bonds. While with the cyclohexylene-linked bis(amidinate)s and the bis(amidinate) derivatives, the C=N of the amidine groups were symmetrical and conjugated with the aromatic rings in *ZZ* configurations. A chiral compound based on *R,R*-1,2-diaminocyclohexyl-linked bis(amidinate)s may be a useful ligand in the construction of chiral structures and materials, and this is being explored in our group.

Experimental

Materials and general methods

All commercial reagents were used as received without further purification. Toluene was distilled from sodium under nitrogen before use. CH_2Cl_2 was distilled from CaH_2 under nitrogen before use. A series of diimine chlorides were prepared under nitrogen in an oxygen-free atmosphere using standard Schlenk techniques and a glove box. Pyrrolyl sodium was prepared by deprotonation of pyrrole by NaH.[20] 2,5-Dimethyl pyrrolyl potassium was synthesised from 2,5-dimethyl pyrrole and KH.[21] Column chromatography was performed on silica gel 300–400 mesh. Melting points were measured on an XT-4 micromelting apparatus and are uncorrected. Optical rotations were recorded using a standard cell with a 10 cm pass on a Shanghai-Shenguang WZZ-1 polarimeter. ^{1}H NMR and ^{13}C NMR spectra for analyses of compounds were recorded on a Bruker AV-300 NMR spectrometer (300 MHz for ^{1}H; 75 MHz for ^{13}C) or Bruker AV-500 NMR spectrometer (500 MHz for ^{1}H; 125 MHz for ^{13}C). Chemical shifts (δ) are reported in ppm. *J* values are reported in Hz. HRMS measurements were conducted with an Agilent model G6220 APCI-TOF mass spectrometer.

Structure determination for compounds **1**, **5** *and* **7**

Colourless single crystals of compounds **1**, **5** and **7** were selected for X-ray diffraction analysis. Diffraction was performed on a Burker SMART CCD area detector diffractometer using graphite-monochromated Mo-*K*α radiation (λ = 0.71073 Å). An empirical absorption correction was applied using the SADABS program.[22] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses and refined anisotropically for all non-

hydrogen atoms by full-matrix least-squares calculations on F^2 using the SHELXTL program package.[23] CCDC numbers are 1836316 (**1**), 1569196 (**5**) and 1568147 (**7**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of linked diamides; general procedure

Pivaloyl chloride (2 equiv.) was added dropwise to a solution of Et_3N (2 equiv.) and linked diamines (1 equiv.) in CH_2Cl_2 to form a white precipitate. The mixture was heated under reflux for 3 h, then the solution was cooled to room temperature and diluted with CH_2Cl_2, which caused all of the precipitate to dissolve. The organic layer was added to water, separated, washed with water (3 × 100 mL) and dried over $MgSO_4$ before removal of the solvent under reduced pressure to yield a colourless crystalline solid.

Conversion of diamides to diimine chlorides; general procedure

Under N_2, PCl_5 was added in portions to the diamides in toluene giving a transparent light yellow solution, which was stirred for 3 d. Most of the solvent was removed under reduced pressure, and then the remaining solution was transferred by cannula filtration. Removal of volatiles under reduced pressure yielded a moisture-sensitive yellow oil.

Synthesis of linked bis(amidinate)s (**1**–**6**)*; general procedure*

To a solution of the yellow oil (1 equiv.) in toluene, the aniline (pyrrolyl sodium or pyrrolyl potassium, 2 equiv.) was added, forming a white precipitate. The reaction mixture was heated under reflux for 3 d, after which removal of the solvent yielded a light brown solid. Et_2O and saturated Na_2CO_3 solution was added. The solid dissolved upon 30 min stirring and the organic layer was separated, washed with water and dried over $MgSO_4$. Evaporation of the solvent under reduced pressure yielded the bis(amidinate)s or derivatives, which were recrystallised or purified by column chromatography.

C_6H_4-1,2-[NC(^{t}Bu)N(C_6H_5)H]$_2$ (**1**): Colourless crystals; yield 65% (after column chromatography using petroleum ether/ethyl acetate (10:1) as eluent); m.p. 101–102 °C; ^{1}H NMR (300 M, $CDCl_3$): δ 6.96–6.79 (m, Ph–*H*), 6.65–6.21 (m, Ph–*H*), 1.37 (s, ^{t}Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.0, 151.1, 139.3, 128.8, 121.2, 40.9, 39.7, 30.0, 29.6. HRMS (ESI) calcd for $C_{28}H_{35}N_4$ [M + H$^+$]: 427.2856; found: 427.2856.

C_6H_4-1,2-[NC(^{t}Bu)NH ^{t}Bu]$_2$ (**2**): Colourless crystals; yield 72% (after column chromatography using petroleum ether/ethyl acetate (10:1) as eluent); m.p. 84–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.46–6.44 (m, Ph–*H*), 4.11 (s, br, N–*H*), 1.34 (s, ^{t}Bu), 1.10 (s, ^{t}Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.6, 143.4, 119.5, 119.4, 50.4, 39.7, 29.6, 28.9. HRMS (ESI) calcd for $C_{24}H_{43}N_4$ [M + H$^+$]: 387.3482; found: 387.3486.

C_6H_4-1,3-[NC(^{t}Bu)N(C_6H_5)H]$_2$ (**3**): Colourless crystals; yield 78% (after recrystallisation from ethyl acetate); m.p. 98–99 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.98–6.84 (m, Ph–*H*), 6.65–6.58 (m, Ph–*H*), 6.21–5.93 (m, Ph–*H*), 3.71 (s, br, N–*H*), 1.33 (s, ^{t}Bu), 1.30 (s, ^{t}Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.9, 148.6, 129.0, 121.5, 115.3, 112.7, 108.7, 40.7, 28.8. HRMS (ESI) calcd for $C_{28}H_{35}N_4$ [M + H$^+$]: 427.2856; found: 427.2849.

C_6H_4-1,3-[NC(^{t}Bu)NH^{t}Bu]$_2$ (**4**): Colourless crystals; yield 68% (after recrystallisation from ethyl acetate); m.p. 97–99 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.93–6.90 (m, Ph–*H*), 6.10–6.00 (m, Ph–*H*), 4.18 (s, br, N–*H*), 1.34 (s, C–^{t}Bu), 1.13 (s, N–^{t}Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.1, 152.2, 128.2, 112.3, 112.0, 51.1, 40.7, 30.5, 29.1. HRMS (ESI) calcd for $C_{24}H_{43}N_4$ [M + H$^+$]: 387.3482; found: 387.3486.

*{(*cis*-C_6H_{12})-1,2-[NC(^{t}Bu)N(C_6H_5)H]$_2$}* (**5**): Colourless crystals; yield 90% (after recrystallisation from ethyl acetate); m.p. 72–74 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18–7.13 (m, 2H, Ph–*H*), 6.88–6.84 (m, Ph–*H*), 6.69–6.66 (m, Ph–*H*), 4.69 (s, br, N–*H*), 3.27 (s, br, N–*H*), 1.61 (bm, cyclohexyl), 1.25 (s, ^{t}Bu), 0.99 (bm, cyclohexyl); ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.0, 151.3, 128.6, 120.8, 120.5, 50.2, 39.0, 29.4, 28.7, 21.8. HRMS (ESI) calcd for $C_{28}H_{41}N_4$ [M + H$^+$]: 433.3326; found: 433.3321.

For compound **6**, a commercially available mixture of *cis*- and *trans*-1,2-diaminocyclohexane was transformed by the reported procedure to give (1*R*, 2*R*)-diaminocyclohexane.[24] The rest of the synthesis was in accordance with the general procedure. 1,2-Diaminocyclohexane were used in place of linked diamines in the general procedure.

{[(*R*, *R*)-C_6H_{12}]-1,2-[NC(^{t}Bu)N(C_6H_5)H]$_2$} (**6**): Colourless crystals; yield 87% (after recrystallisation from ethyl acetate); m.p. 98–99 °C; $[\alpha]_D^{20}$= 27.3° (*c* = 1 g per 100 mL MeOH); ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.23–7.18 (m, Ph–*H*), 6.87–6.72 (m, Ph–*H*), 4.33 (br, N–*H*), 2.67 (s, br, N–*H*), 1.78–159 (m, cyclohexyl), 1.37 (bm, cyclohexyl), 1.23 (s, ^{t}Bu), 0.63 (m, cyclohexyl); ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.7, 152.4, 129.0, 121.1, 120.8, 55.7, 39.1, 33.4, 29.7, 24.6. HRMS (ESI): calcd for $C_{28}H_{41}N_4$ [M + H$^+$]: 433.3326; found: 433.3330.

Synthesis of C_6H_4-1,3-[NC(^{t}Bu)NH(C_4H_4N)]$_2$ (**7**)

Under N_2, NaH (1.44 g, 60 %, 60 mmol) was suspended in DMF (20 mL), and a solution of pyrrole (2.01 g, 30 mmol) in DMF (10 mL) was added dropwise at 0 °C. The reaction mixture was stirred for 1 h at room temperature, then a diimine chloride (4.69 g, 15 mmol) dissolved in DMF (20 mL) was slowly added dropwise at room temperature giving an exothermic reaction (see Scheme 2). The reaction mixture was stirred for 24 h. After completion, water (50 mL) was added and the solution was extracted with ethyl acetate (2 × 50 mL), and washed with water (3 × 20 mL). After drying over $MgSO_4$, the ethyl acetate was removed under reduced pressure to yield a yellow solid. The crude product was purified by column chromatography on silica gel using ethyl acetate/petroleum ether (1/20, V/V) as eluent to give compound **7** as: Colourless crystals; yield 63% (3.53 g); m.p. 68–70 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85–6.82 (m, Ph), 6.39 (d, *J* = 2.0 Hz, Py–*H*), 6.14–6.12 (m, Ph–*H*), 6.05–6.02 (m, Ph–*H*), 6.01 (d, *J* = 2.0 Hz, Py–*H*), 1.32 (s, ^{t}Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ 162.5, 148.2, 128.6, 121.1, 114.9, 112.4, 108.3, 40.3, 28.4. HRMS (ESI): calcd for $C_{24}H_{31}N_4$ [M + H$^+$]: 375.2543; found: 375.2540.

Synthesis of C_6H_4-1,3-[NC(^{t}Bu)NH(2,5-Me_2-C_4H_2N)]$_2$ (**8**)

The synthesis of **8** was carried out in the same way as that for the synthesis of **7**, except 2,5-dimethyl pyrrolyl potassium was used. Compound **8** was obtained as: Colourless crystals; yield 48% (after recrystallisation from hexane/ethyl acetate (1:1)); m.p. 95–97 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.93–6.88 (m, Ph), 6.25–6.16 (m, Ph–*H*), 5.67 (s, Py–*H*), 2.01 (s, PyMe–*H*), 1.28(s, ^{t}Bu); ^{13}C NMR (125 MHz, $CDCl_3$): δ 163.0, 146.9, 128.7, 126.2, 116.8, 116.1, 106.9, 41.0, 29.5, 13.7. HRMS (ESI) calcd for $C_{28}H_{39}N_4$ [M + H$^+$]: 431.3175; found: 431.3171.

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Electronic Supplementary Information

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http://ingentaconnect.com/content/stl/jcr/2018/00000042/00000005/art00003

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