Steric Variations between the Synthesis of a Stable Chiral C_2-Symmetric Diimidazolidinylidene and an Electron-Rich Tetraazafulvalene

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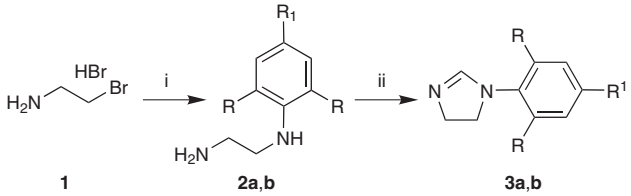
Abstract: C_2-Symmetric electron-rich olefin dimers and imidazolidinylidene ligands with a 2,2-dimethyl-1,3-dioxolane backbone were synthesised and characterised. The steric protection of the carbene dictates which product is obtained.

Key words: electron-rich olefin dimer, imidazolidinylidene, chiral, C_2-symmetric

In recent years, synthetic efforts towards transition-metal complexes containing *N*-heterocyclic carbene ligands (NHC) have been the subject of intense interest.[1] Major stimuli for the renewed appeal of these complexes lie in their use as catalysts, where they often display significant advantages over the analogous phosphine-containing compounds.[2] In catalytic systems, NHCs were shown to prevent the formation of elemental metal, a problem often associated with weak ligand–metal interactions.[3] Consequent stability towards heat, oxygen and moisture led to palladium, rhodium and ruthenium complexes of NHCs featuring prominently in catalytic reactions, for which these metals are already well known.[4]

The literature abounds with examples of chiral monodentate carbene complexes designed for asymmetric synthesis,[5] but, until recently, C_2-symmetric bidentate complexes were notable by their absence.[6] Mindful of this, we began the synthesis and isolation of stable free C_2-symmetric diimidazolidinylidenes bridged by a *trans*-2,2-dimethyl-1,3-dioxalane backbone to use as chiral ligands in catalytic asymmetric transformations.

It is well established that in order to isolate free imidazolidinylidenes the nitrogen substituents have to bear sufficient steric bulk to protect the carbene from dimerisation.[7] The key to the synthesis of these stable chiral dicarbenes involved the preparation of 1-arylimidazolidines with large bulky substituents. The groups selected were 2,4,6-trimethylphenyl and 2,6-diisopropylphenyl, as these substituents had been successfully used in order to isolate simple symmetrical *N*-heterocyclic carbenes.[8] Amination of commercially available 1-bromoethylamine hydrobromide (**1**) by refluxing excess arylamine in toluene gave access to the diamines **2a**,**b** in yields of 74–83%. Cyclisation of **2a**,**b** with triethyl orthoformate in the presence of *p*-toluenesulfonic acid gave the 1-arylimidazolidines **3a**,**b**

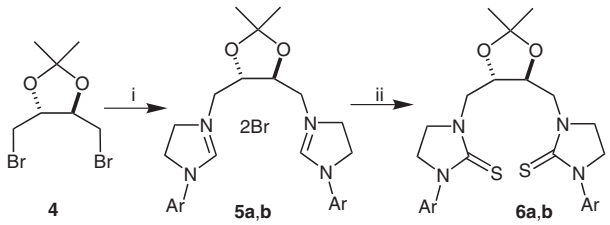


R = R^1= Me (**a**), R = *i*-Pr, R^1 = H (**b**)

Scheme 1 Synthesis of 1-arylimidazolidines **3**; i) $ArNH_2$, toluene; ii) $HC(OEt)_3$, TsOH.

in yields of 91–92% as colourless oils, which crystallised over time (Scheme 1).

Manipulation of commercially available enantiopure L-tartaric acid by conventional means[9] gave access to (4*S*,5*S*)-bis(bromomethyl)-2,2-dimethyl-1,3-dioxolane (**4**), which, when heated with 1-arylimidazolidines **3a**–**b**, produced almost quantitative yields of the salts **5a**,**b** as light yellow glassy solids.



Ar = 2,4,6-trimethylphenyl (a), 2,6-diisopropylphenyl (b)

Scheme 2 Synthesis of diimidazolidin-2-thiones **6a**,**b**; i) **3a**,**b**; ii) DBU, S, MeOH, pyridine

Modifying the methods set out by Karkhanis et al.[10] allowed access to the thiones **6a**,**b** in yields of 54–65% by deprotonation of the crude diimidazolidinium salts **5a**,**b** with DBU in the presence of sulfur (Scheme 2). The dithiones were characterised by HRMS and their typical C=S resonance in the ^{13}C NMR proved diagnostic. Suitable crystals for solid-state analysis of these colourless thiones were obtained from methanol for **6a** and diethyl ether–petroleum spirit (40–60 °C) (1:1) for **6b** (Figures 1 and 2).[11–12]

The structure determination of the solid dithione revealed that both molecules contained puckered 2,2-dimethyl-1,3-dioxolane and imidazolidin-2-thione rings. The carbon–

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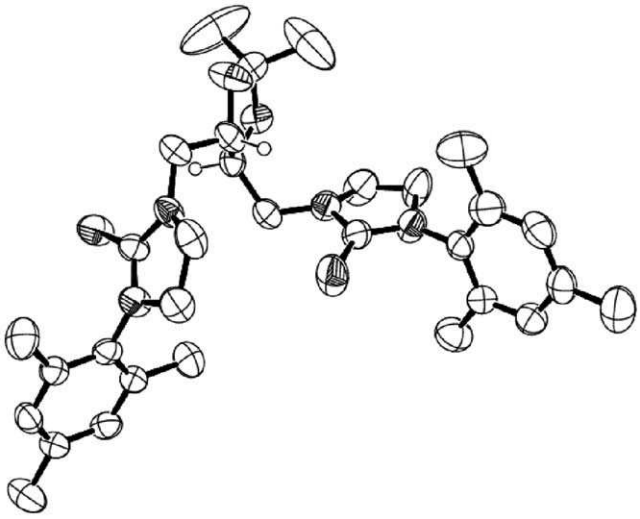


Figure 1 ORTEP diagram of the molecular structure of **6a**

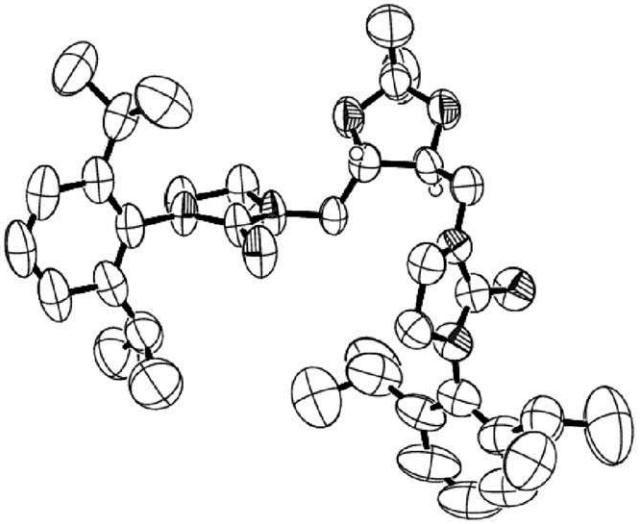
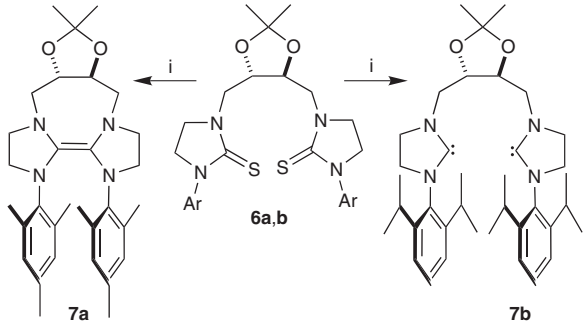


Figure 2 ORTEP diagram of the molecular structure of **6b**

sulfur bond lengths are consistent with literature imidazolidin-2-thiones.[13]

Reduction of the dithione **6a** by an alloy of potassium and sodium in hot toluene was monitored by TLC and revealed a clean reaction. After consumption of the thione, the metal sulfide by-product was filtered. Concentration of the solution deposited a light yellow solid, which was identified as the dimeric product **7a** by the characteristic carbon–carbon double bond at 122.4 ppm in the ^{13}C NMR (Scheme 3). No resonance for the free carbene was detected.

This indicated that the 2,4,6-trimethylphenyl groups on the imidazolidines did not carry enough steric bulk to protect the carbenes from dimerisation. Lappert devised a method of cleaving electron-rich olefin dimers to form NHC metal complexes. The formation of mono-, bis-, tris-



Scheme 3 Synthesis of bisimidazolidin-2-ylidene and electron-rich olefin dimer **7a**,**b**; i) Na/K, toluene

or tetrakis-carbene complexes was achieved by reaction of the dimers with bridged dinuclear or mononuclear organometallic systems. Carbene complexes of a vast array of metals, in various oxidation states, were obtained by this method.[14]

Employing the same reduction methodology with the bulkier **6b** and potassium/sodium resulted in the isolation of a viscous orange oil, which, when analysed by ^{13}C NMR, gave the typical downfield shift for the *N*-heterocyclic carbene at 242.2 ppm (Scheme 3). In view of this, the need for the larger 2,6-diisopropylphenyl over 2,4,6-trimethylphenyl groups proved necessary for the isolation of the free stable chiral dicarbene. The formation of NHC complexes of a vast array of metals, in various oxidation states, is well established by reacting free stable carbenes with a metal precursor.[15]

The synthesis and isolation of stable free C_2-symmetric diimidazolidinylidenes bridged by a *trans*-2,2-dimethyl-1,3-dioxalane backbone was achieved. Firstly, the synthesis of bulky 1-arylimidazolidines was accomplished by amination of 1-bromoethylamine hydrobromide followed by cyclisation of the resultant diamine. Quaternisaton of the imidazolidines with a C_2-symmetric dibromo backbone gave the crude diimidazolidinium salts, which were converted to their corresponding crystalline dithiones. Reduction of these chiral C_2-symmetric dithiones with bulky aryl groups on the imidazolidine was anticipated to allow isolation of the free dicarbenes. Interestingly, employing 2,4,6-trimethylphenyl groups, which were successful in the isolation of the simple symmetrical 1,3-(2,4,6-trimethylphenyl)imidazolidin-2-ylidene prepared by Arduengo et al.,[8] did not allow access to the free stable chiral dicarbene and resulted in the isolation of the electron-rich tetraazafulvalene. This unexpected result revealed that the steric protection was insufficient to prevent dimerisation. Conversely, when the steric bulk around the carbene was increased to 2,6-diisopropylphenyl groups, the free dicarbene was isolated giving the first stable dicarbene bridged by a chiral *trans*-2,2-dimethyl-1,3-dioxolane backbone. As NHC complexes found application in catalysis, com-

plexes containing these chiral ligands are anticipated to allow catalytic asymmetric transformations.

Starting materials were used as supplied by Lancaster synthesis and Aldrich Chemical Company without further purification. Reactions involving air-sensitive reagents were carried out in an atmosphere of nitrogen or argon using standard Schlenk techniques. Toluene was dried and distilled from sodium and benzophenone before use. NMR spectra were recorded using a Bruker AC 250 spectrometer. All ^{1}H and ^{13}C NMR spectra were obtained at 250 MHz and 62.9 MHz respectively. Chemical shifts are reported in ppm relative to TMS and were determined by reference to the residual ^{1}H or ^{13}C solvent peaks. Infrared spectra were recorded as KBr pellets or neat samples on NaCl plates using an ATI Mattson Genesis series FTIR instrument and are reported in cm^{-1}. The Butterworth Contract Analytical Chemistry and Microbiology Company provided elemental microanalysis. Mass spectrometry was recorded by the EPSRC National Mass Spectrometry Service Centre, University of Wales, Swansea. Melting point were determined using a Kofler hot-stage microscope and are uncorrected. Polarimetry was carried out on a Bellingham and Stanley P20 polarimeter and the values are given in 10^{-1} deg cm^2 g^{-1}.

_N_-2,4,6-Trimethylphenyl-(1,2-diaminoethane) (2a)
To a suspension of 2-bromoethylamine hydrobromide (**1**) (10.00 g, 48.80 mmol) and toluene (20 mL) was added 2,4,6-trimethylaniline (13.20 g, 97.61 mmol) and the mixture was heated at reflux for 18 h. The cooled solution was opened to H_2O (50 mL) and 2 M KOH soln (50 mL) was added. The aqueous layer was extracted with Et_2O (3 × 30 mL) and the extracts were washed with aq sat. NaCl soln (100 mL) and dried with Na_2SO_4, filtered and concentrated. The residual yellow oil was purified by column chromatography (EtOAc–MeOH–Et_3N, 17:2:1) to give the diamine (14.48 g, 83%) as a colourless oil.

IR (film): 3362, 2914, 1485, 1449, 1373 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.97 (br s, 3 H, NH), 2.24 (s, 3 H, CH_3), 2.29 (s, 6 H, CH_3), 2.90 (m, 2 H, NCH_2), 2.99 (m, 2 H, NCH_2), 6.83 (s, 2 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 18.4, 20.6, 42.6, 51.3, 129.5, 129.8, 131.2, 143.6.

ESI-MS: *m*/*z* (%) = 179.1 (100) $[M + H]^+$.

_N_-2,6-Diisopropylphenyl-(1,2-diaminoethane) (2b)
The procedure for the synthesis of **2a** was followed using 2-bromoethylamine hydrobromide (**1**) (10.00 g, 48.80 mmol), 2,6-diisopropylaniline (17.31 g, 97.62 mmol) and toluene (20 mL). The crude product was purified by column chromatography (MeOH–CH_2Cl_2, 3:7) to give a light yellow oil, which was distilled (144 °C/3 mmHg) to give the diamine (7.91 g, 74%) as a colourless oil.

IR (film): 3365, 2960, 2867, 1589, 1458, 1382, 1362, 939, 802, 754 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.20 (d, *J* = 6.8 Hz, 12 H, CH_3), 2.13 (br s, 3 H, NH), 2.96 (m, 4 H, NCH_2), 3.35 (sept, *J* = 6.8 Hz, 2 H, CH), 7.11 (m, 3 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.4, 27.6, 42.6, 54.4, 123.6, 123.8, 142.6, 143.4.

ESI-MS: *m*/*z* (%) = 221.3 (100) $[M + H]^+$.

1-(2,4,6-Trimethylphenyl)imidazolidine (3a)
A mixture of *N*-2,4,6-trimethylphenyl-1,2-diaminoethane (**2a**) (2.00 g, 11.2 mmol), triethyl orthoformate (6.65 g, 44.9 mmol) and PTSA (0.10 g, 0.58 mmol) was heated at reflux for 18 h. Once cooled to r.t., the suspension was dissolved in aq 5% NaOH soln (5 mL) and extracted with $CHCl_3$ (3 × 50 mL). The extracts were dried over $MgSO_4$, filtered and concentrated to give a brown oil. Distillation under reduced pressure gave the imidazolidine (1.90 g, 91%) as a colourless oil, which crystallised over time.

Bp 198 °C (3 mmHg); mp 66 °C.

IR (KBr): 2967, 2927, 2861, 1486, 1373 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.98 (s, 6 H, CH_3), 2.03 (s, 3 H, CH_3), 3.28 (t, *J* = 10.3 Hz, 2 H, NCH_2), 3.79 (t, *J* = 10.3 Hz, 2 H, NCH_2), 6.52 (s, 1 H, N_2CH), 6.64 (m, 2 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.9, 20.7, 48.6, 55.1, 129.2, 134.7, 136.5, 136.9, 155.5.

ESI-MS: *m*/*z* (%) = 189.1 (100) $[M + H]^+$.

1-(2,6-Diisopropylphenyl)imidazolidine (3b)
The procedure for **3a** was followed using *N*-2,6-diisopropylphenyl-1,2-diaminoethane (**2b**) (7.89 g, 36.0 mmol), triethyl orthoformate (21.34 g, 144.0 mmol) and PTSA (0.30 g, 1.7 mmol). Distillation under reduced pressure gave the imidazolidine (7.63 g, 92%) as a light yellow oil, which crystallised over time and was recrystallised from PE.

Bp 198 °C (3 mmHg); mp 74 °C.

IR (KBr) 3024, 2964, 2928, 2866, 1678, 1652, 1458, 1381 cm^{-1}.

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.18 (dd, *J* = 6.8, 5.3 Hz, 12 H, CH_3), 3.08 (sept, *J* = 6.8 Hz, 2 H, CH_3), 3.61 (t, *J* = 10.2 Hz, 2 H, NCH_2), 4.05 (t, *J* = 10.2 Hz, 2 H, NCH_2), 6.82 (s, 1 H, N_2CH), 7.17 (d, *J* = 8.0 Hz, 2 H, ArH), 7.29 (1 H, t, *J* = 8.3 Hz, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.9, 24.9, 28.2, 51.6, 54.9, 124.2, 128.7, 134.2, 148.9, 156.2.

ESI-MS: *m*/*z* (%) = 231.1 (100) $[M + H]^+$.

(4*S*,5*S*)-4,5-Bis[1-(2,4,6-trimethylphenyl)imidazolidinium-3-methyl]-2,2-dimethyl-1,3-dioxolane Dibromide (5a)
A mixture of (4*R*,5*R*)-4,5-bis(bromomethyl)-2,2-dimethyl-1,3-dioxolane (**4**) (0.38 g, 1.3 mmol) and 1-(2,4,6-trimethylphenyl)imidazolidine (**3a**) (0.50 g, 2.7 mmol) was heated at 100 °C under an atmosphere of Ar for 14 h to give the salt (0.88 g, 100%) as a light yellow glass.

^{1}H NMR (250 MHz, DMSO-d_6): δ = 1.18 (s, 6 H, CH_3), 1.91–2.01 (3 s, 18 H, $ArCH_3$), 3.25–3.42 (m, 2 H, OCH), 3.73–4.35 (m, 12 H, NCH_2), 6.59 (s, 4 H, ArH), 9.08 (s, 2 H, N_2CH).

^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 17.8, 18.0, 20.8, 27.1, 49.1, 51.3, 52.8, 76.1, 110.7, 129.3, 129.7, 130.5, 135.1, 139.8, 159.4.

(4*S*,5*S*)-4,5-Bis[1-(2,6-diisopropylphenyl)imidazolidinium-3-methyl]-2,2-dimethyl-1,3-dioxolane Dibromide (5b)
The procedure for **6a** was followed using (4*R*,5*R*)-4,5-bis(bromomethyl)-2,2-dimethyl-1,3-dioxolane (**4**) (0.45 g, 1.6 mmol) and 1-(2,6-diisopropylphenyl)imidazolidine (**3b**) (0.72 g, 3.1 mmol) to give the salt (1.17 g, 100%) as a light yellow glass.

^{1}H NMR (250 MHz, DMSO-d_6): δ = 1.23 (4 d, *J* = 8.5, 6.7 Hz, 24 H, CH_3), 1.38 (s, 6 H,CH_3), 2.91–2.99 (m, 4 H, CH), 3.29–3.47 (m, 2 H, OCH), 3.78–4.27 (m, 12 H, NCH_2), 7.38 (m, 4 H, ArH), 7.50 (t, *J* = 7.9 Hz, 2 H, ArH), 9.07 (s, 2 H, N_2CH).

^{13}C NMR (62.9 MHz, DMSO-d_6): δ = 24.0, 24.9, 27.2, 28.5, 49.1, 51.2, 53.7, 76.1, 111.0, 124.4, 124.6, 124.8, 129.7, 130.9, 146.0, 146.5, 159.1.

(4*S*,5*S*)-4,5-Bis[1-(2,4,6-trimethylphenyl)imidazolidin-2-thio-3-methyl]-2,2-dimethyl-1,3-dioxolane (6a)
A mixture of (4*S*,5*S*)-4,5-bis[1-(2,4,6-trimethylphenyl)imidazolidinium-3-methyl]-2,2-dimethyl-1,3-dioxolane dibromide (**5a**) (0.88 g, 1.3 mmol), MeOH (20 mL), pyridine (1.8 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (0.89 g, 5.9 mmol) and sulfur (0.13 g,

4.1 mmol) was heated at 65 °C for 18 h. Once cooled to r.t., the mixture was opened to H_2O (50 mL) and extracted with $CHCl_3$ (3 × 20 mL). The combined extracts were dried over $MgSO_4$, filtered and concentrated under reduced pressure to leave a brown residue. The residue was purified by column chromatography (EtOAc–PE, 1:1, loaded as a solution in CH_2Cl_2) to give the dithione (0.39 g, 54%) as a colourless solid, which can be recrystallised from MeOH to give colourless needles.

Mp 228–226 °C; $[\alpha]_D^{25}$ +42.3 (*c* 1.87, CH_2Cl_2).

IR (KBr) 2983, 2909, 1610, 1486, 1448, 1411, 1375, 1081 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.47 (s, 6 H,CH_3), 2.19 (s, 6 H, $ArCH_3$), 2.22 (s, 6 H, $ArCH_3$), 2.27 (s, 6 H, $ArCH_3$), 3.71–4.13 (m, 12 H, NCH_2), 4.45 (m, 2 H, OCH), 6.92 (s, 4 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 17.9, 18.0, 21.1, 27.0, 47.3, 49.2, 49.6, 77.3, 108.9, 129.5, 134.9, 136.4, 136.7, 138.2, 183.0.

ESI-MS: *m*/*z* (%) = 589.2 (95) $[M + Na]^+$, 567.2 (100) $[M + H]^+$.

HRMS–ESI: *m*/*z* $[M + H]^+$ calcd for $C_{31}H_{43}N_4O_2S_2$: 567.2827; found 567.2824.

Anal. Calcd for $C_{31}H_{42}N_4S_2O_2$: C, 65.69; H, 7.47; N, 9.88; S, 11.31. Found: C, 65.42; H, 7.11; N, 9.62; S, 11.25.

(4*S*,5*S*)-4,5-Bis[1-(2,6-diisopropylphenyl)imidazolidin-2-thio-3-methyl]-2,2-dimethyl-1,3-dioxolane (6b)

The procedure for **7a** was followed using (4*S*,5*S*)-4,5-bis[1-(2,6-diisopropylphenyl)imidazolidinium-2-methyl]-2,2-dimethyl-1,3-dioxolane dibromide (**5b**) (1.15 g, 1.54 mmol), MeOH (20 mL), pyridine (1.8 mL), 1,8-diazabicyclo[5.4.0]undec-7-ene (1.03 g, 6.76 mmol) and sulfur (0.15 g, 4.6 mmol). The crude product was purified by column chromatography (EtOAc–PE, 1: 2, loaded as a solution in CH_2Cl_2) to give the dithione (0.63 g, 63%).

Mp 188 °C (from Et_2O–PE, 1:2); $[\alpha]_D^{25}$ +50.3 (*c* 2.04, CH_2Cl_2).

IR (KBr): 2965, 2868, 1492, 1458, 1404, 1347, 1083 cm^{-1}.

^1H NMR (250 MHz, $CDCl_3$): δ = 1.20 (4 d, *J* = 6.5, 5.0 Hz, 24 H, CH_3), 1.49 (s, 6 H, CH_3), 2.88 (sept, *J* = 7.5 Hz, 2 H, CH), 3.02 (sept, *J* = 7.5 Hz, 2 H, CH), 3.99 (m, 12 H, NCH_2), 4.52 (app br t, 2 H, OCH), 7.21 (m, 4 H, ArH), 7.34 (t, *J* = 7.5 Hz, 2 H, ArH).

^{13}C NMR (62.9 MHz, $CDCl_3$): δ = 24.2, 24.4, 24.6, 24.7, 28.6, 28.7, 49.1, 49.3, 49.8, 77.4, 108.6, 124.4, 129.2, 135.1, 147.3, 147.7, 184.5.

ESI-MS: *m*/*z* (%) = 651.4 (100) $[M + H]^+$, 619.3 (15) $[M - S]^+$.

HRMS–ESI: *m*/*z* $[M + H]^+$ calcd for $C_{37}H_{55}N_4O_2S_2$: 651.3784; found: 651.3766.

Anal. Calcd for $C_{37}H_{54}N_4O_2S_2$: C, 68.2; H, 8.5; N, 8.4; S, 9.5. Found: C, 68.3; H, 8.4; N, 8.6; S, 9.9.

(4*S*,5*S*)-4,5-Bis[1-(2,4,6-trimethylphenyl)tetraazafulvalene]-2,2-dimethyl-1,3-dioxolane (7a)

To a mixture of sodium (0.05 g, 2.3 mmol) and potassium (0.18 g, 4.7 mmol) in toluene (20 mL) was added (4*S*,5*S*)-4,5-bis[1-(2,4,6-trimethylphenyl)imidazolidin-2-thio-3-methyl]-2,2-dimethyl-1,3-dioxolane (**6a**) (0.20 g, 0.35 mmol), and the mixture was heated to 50 °C for 18 h. After cooling to r.t., the toluene was separated from the suspension via cannular filtration and removed under reduced pressure to give the dimer of the desired product as a light yellow solid.

^1H NMR (250 MHz, C_6D_6): δ = 1.56 (s, 6 H, CH_3), 1.73 (s, 6 H, $ArCH_3$), 2.35 (s, 6 H, $ArCH_3$), 2.48 (s, 6 H, $ArCH_3$), 2.64–2.70 (m, 4 H, NCH_2), 3.02–3.11 (m, 4 H, NCH_2), 3.21–3.27 (dd, *J* = 7.0, 5.0 Hz, 2 H, NCH_2), 3.92–3.97 (dd, J = 7.0, 5.0 Hz, 2 H, NCH_2), 4.84 (app br t, 2 H, OCH), 6.77–6.80 (2 s, 4 H, ArH).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 18.6, 20.9, 21.3, 28.2, 52.0, 54.5, 55.5, 79.2, 109.2, 122.4, 129.7, 130.2, 133.2, 133.3, 136.4, 143.5.

(4*S*,5*S*)-4,5-Bis[1-(2,6-diisopropylphenyl)imidazolidin-2-ylidene-3-methyl]-2,2-dimethyl-1,3-dioxolane (7b)

The procedure for **8a** was followed using Na (0.05 g, 2.2 mmol), K (0.16 g, 4.2 mmol), toluene (20 mL) and (4*S*,5*S*)-4,5-bis[1-(2,6-diisopropylphenyl)imidazolidin-2-thio-3-methyl]-2,2-dimethyl-1,3-dioxolane (**6b**) (0.20 g, 0.31 mmol), which gave the diylidene as a viscous orange oil.

^1H NMR (250 MHz, C_6D_6): δ = 1.37 (m, 24 H, CH_3), 1.55 (s, 6 H, CH_3), 2.82 (m, 2 H, CH), 2.98 (m, 2 H, CH), 3.20–3.80 (m, 12 H, NCH_2), 4.78 (app br t, 2 H, OCH), 7.30 (m, 6 H, ArH).

^{13}C NMR (62.9 MHz, C_6D_6): δ = 24.5, 25.0, 25.8, 27.8, 28.5, 29.1, 51.4, 52.3, 54.8, 78.3, 108.7, 129.7, 139.9, 143.4, 147.7, 147.9, 242.2.

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(11) Crystallographic data (excluding structure factors) for the structure in this paper were deposited with the Cambridge Crystallographic Data Centre as supplementary publication

numbers CCDC 273128, 273129 and 273130. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif or on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Crystal Data for **6a** (CCDC 273128 and 273129): Empirical formula $C_{31}H_{42}N_4O_2S_2$, formula weight 566.81, temperature 296 (2) K, wavelength 0.71073 Å, monoclinic, space group $P2_1$. Unit cell dimensions a = 7.7147 (4) Å, b = 18.6723 (8) Å, c = 11.1002 (5) Å, β = 104.461 (2)°, V = 1548.34 (13) Å^3, Z = 2, D_c = 1.216 Mg m^{-3}, absorption coefficient 0.205 mm^{-1}, F(000) = 608, crystal size 0.30 × 0.08 × 0.05 mm. Theta range for data collection 1.89–24.99°, index ranges $-9 \le h \le 8$, $-18 \le k \le 22$, $-13 \le l \le 13$, reflections collected 10775, unique reflections 2812 [R_{int} = 0.0940], completeness to c_{max} (32.63°) = 99.9%, max. and min. transmission 0.9280 and 0.8000, refinement method full-matrix least-squares on F^2. **Ordered Model:** Data/restraints/parameters 2812/1/360, goodness-of-fit on F^2 = 0.811, final R indices [$I > 2\sigma(I)$], $R1$ = 0.0412, $wR2$ = 0.0624, R indices (all data), $R1$ = 0.0993, $wR2$ = 0.0727, absolute structure parameter 0.00(9), largest diff. peak and hole 0.207 and –0.169 e Å^{-3}. **Disordered Model:** Data/restraints/parameters 2812/1/381, goodness-of-fit on F^2 = 0.791, final R indices [$I > 2\sigma(I)$], $R1$ = 0.0372, $wR2$ = 0.0464, R indices (all data), $R1$ = 0.0956, $wR2$ = 0.0547, absolute structure parameter –0.02 (7), largest diff. peak and hole 0.132 and –0.137 e Å^{-3}. Two of the methyl groups (numbered C-16, C-17) were found to have very high U_{eq} values. These could be split to give disorder over the two sites. Whilst this significantly improved $wR2$, one of the methyl groups (C-16) still had high U_{eq} values and the data/parameter ratio was worsened. Both models, therefore, have their merits and data for both were deposited.

(12) Crystal data of compound **6b** (CCDC 273130): Empirical formula $C_{37}H_{54}N_4O_2S_2$, formula weight 650.96, temperature 295 (2) K, wavelength 0.71073 Å, monoclinic, space group $P2_1$. Unit cell dimensions a = 13.5162 (13) Å, b = 6.9703 (6) Å, c = 21.051 (2) Å, β = 102.897 (2)°, V = 1933.2 (3) Å^3, Z = 2, D_c = 1.118 Mg m^{-3}, absorption coefficient 0.172 mm^{-1}, F(000) = 704, crystal size 0.80 × 0.10 × 0.10 mm. Theta range for data collection 1.98–32.63°, index ranges $-10 \le h \le 20$, $-10 \le k \le 10$, $-31 \le l \le 29$, reflections collected 18951, unique reflections 7507 [R_{int} = 0.1700], completeness to c_{max} (32.63°) = 99.1%, max. and min. transmission 0.9830 and 0.8721, refinement method full-matrix least-squares on F^2, data/restraints/parameters 7507/1/416, goodness-of-fit on F^2 = 0.653, final R indices [$I > 2\sigma(I)$], $R1$ = 0.0487, $wR2$ = 0.0758, R indices (all data), $R1$ = 0.3135, $wR2$ = 0.1151, absolute structure parameter 0.12 (9), largest diff. peak and hole 0.155 and –0.163 e Å^{-3}.

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