A Library of Peralkylated Bis-guanidine Ligands for Use in Biomimetic Coordination Chemistry

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Dedicated to Professor Bernt Krebs

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A series of bis-guanidine ligands designed for use in biomimetic coordination chemistry has been extended to a library matrix combining unprecedented substitutional flexibility within the guanidyl residues with a wide range of aliphatic and aromatic spacers connecting these functionalities. The underlying protocol can be used with predefined ureas as well as secondary amines to build up these units by reaction with phosgene if the ureas are otherwise unavailable. In the latter case, the resulting urea intermediates do not have to be isolated as the reaction proceeds further with additional phosgene to yield a chloroformamidinium chloride which is transformed into the bis-guanidine functionality by subsequent reaction with a suitable primary diamine in the presence of triethylamine as an auxiliary base. This concept has been used to synthesise and characterise more then two dozen different bis-guanidines based on 12 discrete monoguanidine units and seven different spacers. These spacers have been chosen such that the most important phenotypes have been dealt with and which range from rigid to more flexible scaffolds. In addition to spacers with no metal-binding capabilities, other species containing further donor functions such as *N*-methyldiphenyleneamine or pyridine-2,6-diyl have also been used. The substitution patterns of the guanidine residues can be classified into acyclic and cyclic types. Among the cyclic types, one subset is characterised by five- or six-membered heterocycles containing both the amino nitrogen atoms and another one by individual N-heterocyclic systems for each amino nitrogen. Structurally characterised examples are 2-{2-[2-(tetramethylguanidino)-ethoxy]ethoxy}-1-(tetramethylguanidino)ethane (TMG_2doo) in its diprotonated form and 2,2′-bis[2*N*-(1,1′,3,3′-tetramethylguanidine)]diphenyleneamine (TMG_2PA) as well as N^1,N^3-bis(dimorpholinomethylene)propane-1,3-diamine ($DMorphG_2$p) as free bases. For the permethylated bis-guanidine derivatives, the barrier to rotation around the $(C{=}N)_{guanidine}$ bond has been determined by means of temperature-dependent EXSY ^{1}H NMR spectroscopy to range between 54 and 79 kJ mol^{-1} depending on the type of spacer. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2005)

Introduction

Guanidines are emerging as a potentially useful class of ligand owing to their versatile coordination chemistry. Neutral guanidines $[(R_2N)_2C{=}NR]$, guanidinates(1–) $[(RN)_2CNR_2]^-$ and guanidinates(2–) $[(RN)_2C{=}NR]^{2-}$ are capable of exhibiting a variety of coordination modes and a range of donor properties and thus are compatible with a remarkably wide range of metal-ion requirements from all parts of the periodic table.[1–4] Furthermore, numerous complexes have been reported in which guanidinium cations are present but these are not located within the coordination sphere of the metal ion and consequently merely represent counterions.[5,6] Whilst the application of negatively charged guanidinates has become more widespread in coordination chemistry, the use of neutral guanidines has not, to date, received similar attention.[1] Bailey et al. have investigated the behaviour of monodentate guanidine ligands,[7] whereas Coles and co-workers introduced bicyclic guanidine systems into coordination chemistry.[2] These systems are mostly not peralkylated, but meanwhile, peralkylated phosphorus-[8] or silicon-bridged[9] bis-guanidine systems have been developed. Pruszynski[10] Pohl[11] and Sundermeyer[12] and their co-workers have investigated peralkylated guanidine systems with organic bridges. Furthermore, Kuhn et al.[13] have developed imidazoline-based systems that belong to the bis-guanidine class of ligand.

In guanidine complexes, coordination occurs almost exclusively through the donation of the lone-pair electrons of

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the N^{imine} atom to the appropriate acceptor orbitals of the metal. Such ligands have been successfully used in the stabilisation of different coordination geometries, including linear,[7,14] trigonal-planar,[2a,c,11] tetrahedral[2c,7,11] and trigonal-bipyramidal[15] species.

In our search for bifunctional nitrogen donor ligands able to stabilise unusually high metal oxidation states, we became interested in peralkylated guanidyl-type systems. Bis(tetramethylguanidino)propylene (btmgp) was synthesised as the first member of a series of bifunctional peralkylated guanidine ligands designed for use in biomimetic coordination chemistry.[11,14–20] A great advantage of guanidine ligands lies in their stability towards fragmentation reactions. We have shown that btmgp-containing copper–dioxygen complexes react only with the peripheral substituents with conservation of the guanidine scaffold[20] in contrast to other systems in which dealkylation reactions are observed.[21] Attempts to modify the guanidine moieties resulted in the successful preparation of bis(dimethylpropyleneguanidino)propylene ($DMPG_2p$), bis(dipiperidylguanidino)propylene ($DPipG_2p$)[17] and bis(dimethylethyleneguanidino)propylene ($DMEG_2p$).[14] We have recently shown that copper(I) complexes containing these ligands are able to react with molecular oxygen under formation of a heterocyclic Cu_2O_2 core at low temperatures.[14,15,20]

By suitable modification of the guanidine substitution patterns in such complexes, our intention was to redirect their hydroxylation potential from the ligand to external substrates such as 2,4-di-*tert*-butylphenol or methylated aniline derivatives. As the ligands are bidentate, the reaction centre should be easily accessible by external substrates and well suited to substrate pre-coordination. In addition, the oxygen atom is protected against too fast a reaction with these substrates by the spatially demanding guanidine moieties resulting in enhanced oxidation selectivities. At this stage, efficient use of this potential is restricted owing to a lack of accessible ligands demonstrating that a synthetic protocol that supports our objectives has to be developed.

For this purpose, we have developed a modular approach to bis-guanidine compounds that provides a library of biomimetic ligands. This library contains compounds with complete flexibility in the spacers connecting the guanidine functionalities as well as in the substitution patterns of the guanidine moieties. Modification of the spacer allows the denticity, the bite angle and the coordination geometry to be varied, whereas modification of the guanidine moieties allows us to influence directly the σ-donating and π-accepting properties of the N^{imine} atom.[14]

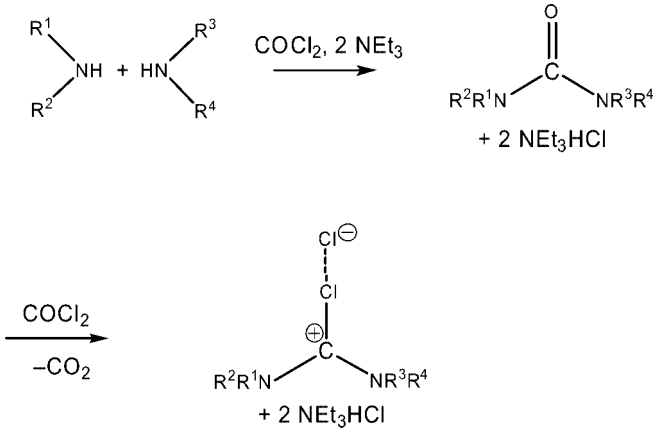
In order to increase the steric demand of the guanidine moieties and thus the oxygen-shielding effect in their complexes, we have prepared a series of chloroformamidinium chlorides from secondary amines containing the required bulky substituents. By this method, the transformation of almost every aliphatic secondary amine into the corresponding chloroformamidinium chloride should be possible. In this paper, we report the synthesis and the characterisation of 25 bis-guanidine ligands for the first time and describe a new concept in guanidine ligand design.

Results and Discussion

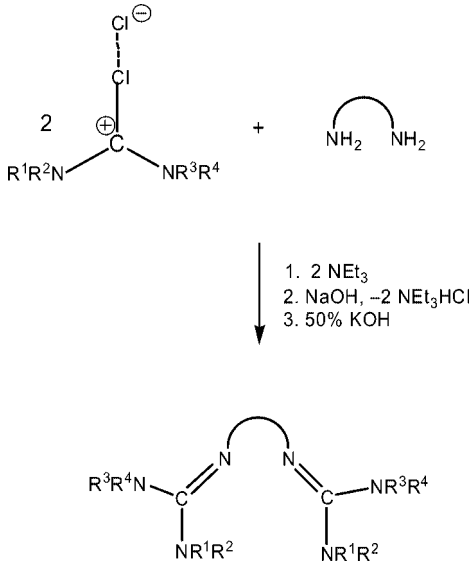
Ligand Synthesis

The ligands were synthesised following a general procedure that allows the condensation of almost every aliphatic urea with almost every primary amine to form a guanidine compound. This condensation reaction proceeds by the transformation of the urea component into its corresponding chloroformamidinium chloride, which is sometimes referred to as a Vilsmeier salt.[17e,18]

Conventional chloroformamidinium chlorides can be obtained in good yields by the reaction of specific peralkylated ureas with phosgene in toluene or acetonitrile.[18] The biomimetic approach requires spatially demanding substituents on the guanidine moieties because sterically hindered systems are expected to control the access of substrates to the oxygen atoms in the corresponding copper–dioxygen complexes. Therefore, a straightforward synthetic protocol starting with bulky secondary amines has been developed (Scheme 1).



Scheme 1. Generation of the chloroformamidinium chlorides.



Scheme 2. Reaction between the chloroformamidinium chloride and the diamine.

This one-pot synthesis involves the reaction of two equivalents of a secondary amine with two equivalents of phosgene in acetonitrile. In the first reaction step, the alkyl-substituted urea is formed and triethylamine acts as an auxiliary base by capturing the released HCl (Scheme 1). In the second step, a further equivalent of phosgene transforms this urea into the chloroformamidinium chloride.

Reaction of the mixture containing the chloroformamidinium chloride with a diamine in the presence of triethylamine as an auxiliary base leads to the bis-hydrochloride of the ligand. The by-product NEt_3·HCl was separated by adding 1 equiv. of NaOH per guanidine functionality and removing the resulting NEt_3 and the solvent under reduced pressure. The hydrochloride was not isolated but deprotonated by using the two-phase system of MeCN/50% aqueous KOH in order to obtain the pure free base which needs no further purification (Scheme 2).

Table 1. Overview of the chloroformamidinium chlorides R^1R^2N–CCl_2–NR^3R^4.[a]

Substituents R^1–R^4		Chloroformamidinium chloride
R^1, R^2, R^3, R^4: Me	*	V1[b]
R^1, R^2, R^3, R^4: Et	*	V2[c]
R^1, R^2, R^3, R^4: *i*Pr		V3[d]
R^1, R^4: Me; R^2–R^3: –$(CH_2)_2$–	*	V4[b]
R^1, R^4: Me; R^2–R^3: –$(CH_2)_3$–	*	V5[b]
R^1, R^4: *n*Pr; R^2–R^3: –$(CH_2)_3$–	*	V6[d]
R^1–R^2, R^3–R^4: –$(CH_2)_5$–	*	V7[e]
R^1–R^2, R^3–R^4: –CH(Me)$(CH_2)_3$CH(Me)–		V8[d]
R^1–R^2, R^3–R^4: –C$(Me)_2(CH_2)_3C(Me)_2$–		V9[d]
R^1–R^2, R^3–R^4: –CHNCHCH–	*	V10[d]
R^1–R^2, R^3–R^4: –$(CH_2)_2O(CH_2)_2$–		V11[d]
R^1–R^2, R^3–R^4: –$(CH_2)_2S(CH_2)_2$–		V12[d]

[a] Reactions starting from the urea are marked with an asterisk. [b] Ref.[12,14] [c] Ref.[17e] [d] This work. [e] Ref.[18]

Table 1 gives an overview of the chloroformamidinium chlorides prepared in this work. By using these chloroformamidinium chlorides, the guanidine moieties shown in Figure 1 could be synthesised, where **G*x*** denotes the guanidine moiety derived from the chloroformamidinium chloride **V*x*** and R_S indicates the connection with the spacer.

The spacers shown in Figure 2 have been used as constituents of the bis-guanidine ligands for several reasons: the propane-1,3-diyl (**p**) spacer is a typical aliphatic spacer with a suitable "bite" for 3d metal coordination,[11,14,16,20] the flexible 3,6-dioxaoctane-1,8-diyl (**doo**) spacer offers more donor functions for metal coordination, whereas the cyclohexane-1,3-diyl (**ch**) system is more rigid. The aromatic systems diphenyleneamine (**PA**), *N*-methyldiphenyleneamine (**MePA**) and pyridine-2,6-diyl (**py**) offer a further N-donor function whilst the *m*-xylene-α,α′-diyl (**mX**) unit has a great "bite" and more flexibility than the other spacers.

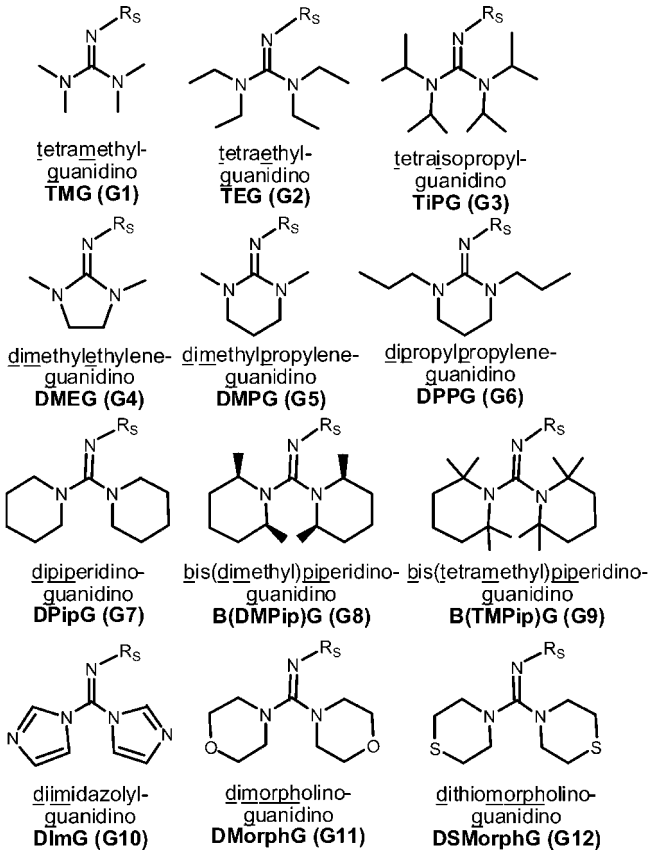


Figure 1. Guanidine portions of the bis-guanidine ligands.

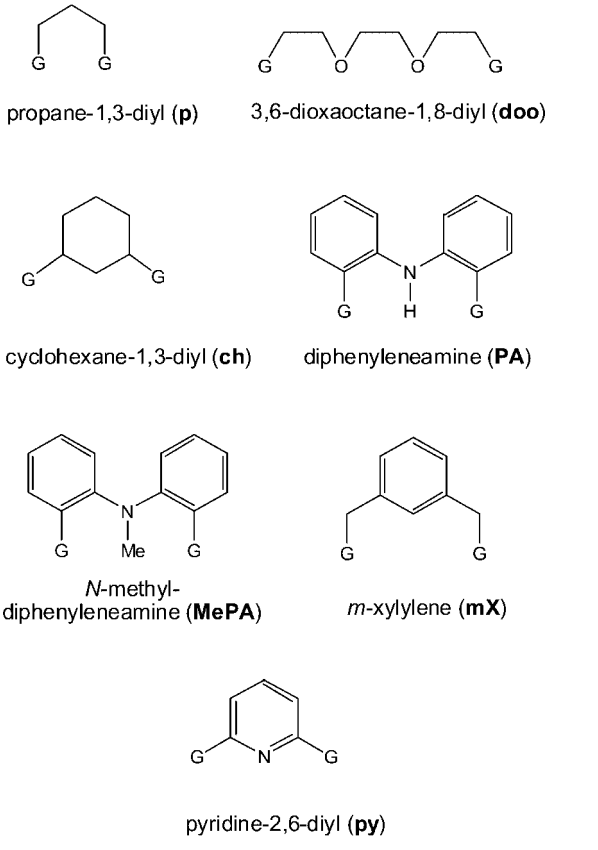


Figure 2. Spacer units of the bis-guanidine ligands (G indicates the position of the attached guanidine moiety).

Table 2. Overview of the synthesised ligands.

Guanidine moieties	Spacers						
	p	**doo**	**ch**	**PA**	**MePA**	**mX**	**py**
TMG (**G1**)	TMG_2p[a] (**L1–1**)	TMG_2doo (**L1–2**)	TMG_2ch (**L1–3**)	TMG_2PA (**L1–4**)	TMG_2MePA (**L1–5**)	TMG_2mX (**L1–6**)	TMG_2py (**L1–7**)
TEG (**G2**)	TEG_2p (**L2–1**)					TEG_2mX (**L2–6**)	TEG_2py (**L2–7**)
TiPG (**G3**)	$TiPG_2p$ (**L3–1**)						
DMEG (**G4**)	$DMEG_2p$[b] (**L4–1**)	$DMEG_2doo$ (**L4–2**)	$DMEG_2ch$ (**L4–3**)			$DMEG_2mX$ (**L4–6**)	$DMEG_2py$ (**L4–7**)
DMPG (**G5**)	$DMPG_2p$[c] (**L5–1**)	$DMPG_2doo$ (**L5–2**)			$DMPG_2MePA$ (**L5–5**)	$DMPG_2mX$ (**L5–6**)	$DMPG_2py$ (**L5–7**)
DPPG (**G6**)	$DPPG_2p$ (**L6–1**)						
DPipG (**G7**)	$DPipG_2p$[c] (**L7–1**)						
B(DMPip)G (**G8**)	$B(DMPip)G_2p$ (**L8–1**)						
B(TMPip)G (**G9**)	$B(TMPip)G_2p$ (**L9–1**)						
DImG (**G10**)	$DImG_2p$ (**L10–1**)						
DMorphG (**G11**)	$DMorphG_2p$ (**L11–1**)	$DMorphG_2doo$ (**L11–2**)					
DSMorphG (**G12**)	$DSMorphG_2p$ (**L12–1**)						

[a] Known in the literature as btmgp, see ref.[11,14,16,20] [b] Ref.[14] [c] Ref.[14,17a,17b]

The modular approach, which is illustrated in Figure 3, allows systematic tuning of the properties of polyguanidine ligands. By combining the different spacers and guanidine moieties, a library of bis-guanidine ligands could be built up (Table 2).

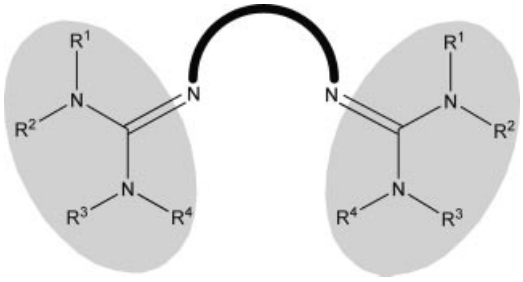


Figure 3. Schematic representation of the variable modules in the bis-guanidine ligands.

Crystal Structures

In order to discuss the structural features of this diverse series of ligands, we chose three crystal structures for a closer look: the structure of **L1–4** exhibits properties typical of aromatic bis-guanidine ligands whereas **L11–1** is a typical aliphatic bis-guanidine ligand. Compound [H_2**L1–2**]I_2·Et_2O contains a typical diprotonated bis-guanidine ligand.

Single crystals of [H_2**L1–2**]I_2·Et_2O were grown by slow diffusion of diethyl ether into an acetonitrile solution. Single crystals of **L1–4** were obtained by slow crystallisation at –25 °C whereas **L11–1** crystallised by slow evaporation of the acetonitrile solution. The results of the structure analyses are shown in Figures 4, 5 and 6, while selected bond lengths and angles are collected in Table 3, and parameters relating to data collection and refinement are listed in Table 6.

Table 3. Selected bond lengths and angles of the molecules in crystals of **L1–4**, **L11–1** and of the ligand cation in crystals of [H_2**L1–2**]I_2·Et_2O (average values).

	L1–4	**L11–1**	[H_2**L1–2**]I_2·Et_2O
Bond lengths [Å]			
N=C	1.282	1.273	1.349
C^{imine}–N^{amine}	1.365	1.402	1.336
Bond angles [°]			
N^{amine}–C–N^{amine}	113.6	112.0	120.1

Crystals of **L1–4** contain two crystallographically independent but otherwise identical molecules. One of them (A) is shown in Figure 4. The structural features of this aromatic guanidine ligand (N=C, 1.281 Å; C^{imine}–N^{amine}, 1.365 Å; N^{imine}–C^{arom}, 1.402 Å) are comparable to those reported for TMGN (N=C, 1.282 Å; C^{imine}–N^{amine}, 1.384 Å; N^{imine}–C^{arom}, 1.399 Å).[12c] The trigonal-planar environment of the nitrogen atom that connects the two phenyl rings is remarkable. The corresponding N–C bonds are drastically shortened to 1.400 Å which indicates delocalisation of the free amine electron-pair into the phenyl π system. The phenyl rings are twisted against each other by an angle of 36.7°. The angles between the CN_3-guanidine plane and the C^{imine}–N^{amine}–$(C^{alkyl})_2$-planes within the guanidine moieties have a mean value of 31.9° (individual values range from 22.2 to 38.6°). Furthermore, the N–H group forms a bifurcated hydrogen bridge to the imine nitrogen atoms (av. 2.235 Å, corrected for N–H, 1.080 Å).

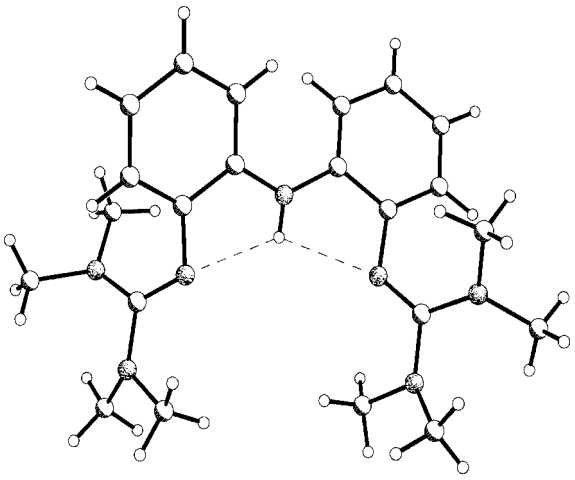


Figure 4. Molecular structure of compound **L1–4** (N: random dots; H···N hydrogen bonds: dashed line).

The molecular structure of **L11–1** is depicted in Figure 5. The molecule lies on a crystallographic two-fold axis that runs through the centre of the spacer. The geometric parameters of this ligand (N=C, 1.272 Å; C^{imine}–N^{amine}, 1.402 Å) are in good agreement with those of the aliphatic guanidine ligand $DPipG_2p$ (**L7–1**) (N=C, 1.276 Å; C^{imine}–N^{amine}, 1.399 Å). The guanidine moieties are planar as expected.[17a] The angles between the CN_3 guanidine plane and the C^{imine}–N^{amine}–$(C^{alkyl})_2$ planes are larger (on average 36.0°; individual values range from 29.0 to 42.9°) than those of **L1–4** as steric hindrance forces the NR_2 units to twist around the C^{imine}–N^{amine} axis.

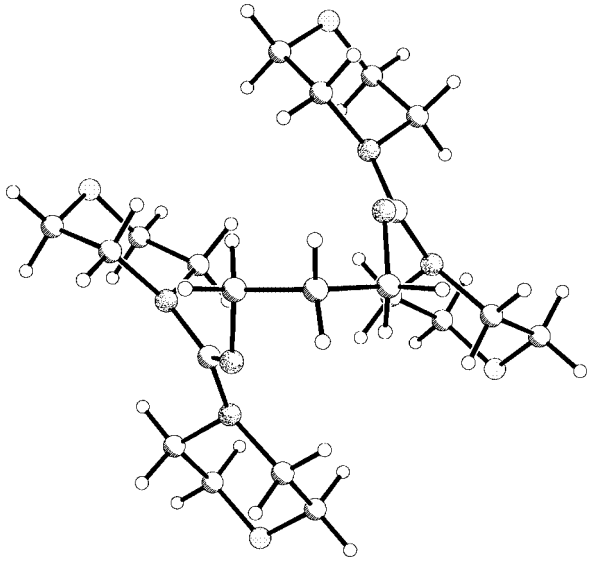


Figure 5. Molecular structure of compound **L11–1** (N: random dots; O: regular dot pattern).

The N=C double bonds of this ligand are clearly localised in contrast to the diprotonated form of **L1–2** in which the double bond is delocalised over the guanidine centre. Compound [H_2**L1–2**]I_2·Et_2O comprises the diprotonated form of TMG_2doo, two iodine anions and a diethyl ether molecule. The centroid of the cation lies on a crystallographic inversion centre (Figure 6). The bond lengths are typical of a protonated guanidine (C=NH^+, 1.349(3) Å; C^{imine}–N^{amine} av., 1.336 Å; these compare with C=NH^+, 1.334 Å and C^{imine}–N^{amine}, 1.341 Å for $[H_2btmgp]^{2+}$).[11a] The bond lengths in the guanidine centre are equal. Therefore, the conjugation is enhanced although the dihedral angles are diminished only to a small extent (on average 30.8°; individual values range from 29.8 to 31.8°). The iodide ions are stabilised by N–H···I hydrogen bonds with H···I distances of 2.768 Å.

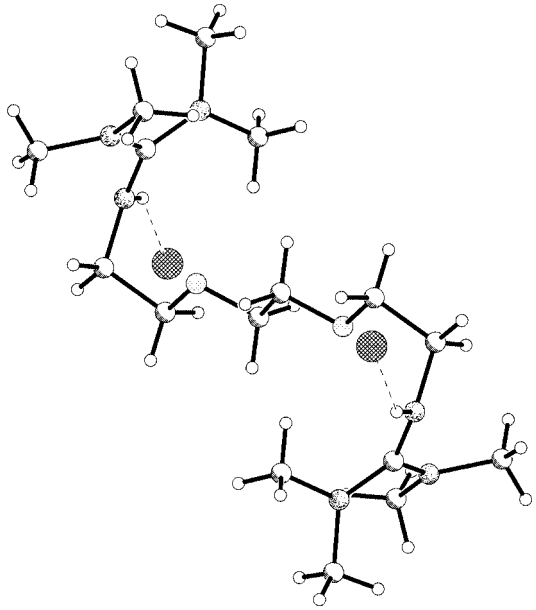


Figure 6. Molecular structure of $[H_2$**L1–2**$]^{2+}$ in crystals of [H_2**L1–2**]I_2·Et_2O (N: random dots; O: regular dot pattern; I: cross-hatched; H···I and H···N hydrogen bonds: dashed lines).

NMR Spectroscopy

The chemical shifts of the dimethylamino groups of the ligands containing the tetramethylguanidine moiety are listed in Table 4. The ^1H and ^{13}C NMR spectra of the guanidine ligands with aliphatic spacers exhibit two separate signals for the methyl groups. On heating, these two signals approach each other and coincide on reaching the coalescence temperature. Compared with the aliphatic systems described above, the aromatic systems exhibit only one signal for the methyl groups at room temperature. This signal splits into two resonances of equal intensity if the temperature is lowered.

This behaviour is caused by a *syn–anti* exchange typical of guanidines which has been discussed for selected TMG systems by Kessler and Leibfritz.[22a] In the case of pentasubstituted guanidines, rotation around the C–NR_2 single bonds as well as *syn–anti* isomerisation can take place (Figure 7). Rotation around a C–NR_2 single bond is too rapid on the NMR timescale to result in individual resonances even at low temperatures. This is not the case with the *syn–anti* exchange which can principally be caused by rotation around the C=N bond or by inversion.[22a]

Table 4. NMR spectroscopic shifts of the NMe_2 groups at 298 K.

	δ [ppm]	
	^1H	^{13}C
btmgp (**L1–1**)	2.56, 2.65	38.6, 39.4[a]
H_2btmgpCl_2 (H_2**L1–1**Cl_2)	2.94, 3.02	40.1, 40.5[a]
TMG_2doo (**L1–2**)	2.51, 2.60	38.6, 39.5
$H_2TMG_2dooI_2$ (H_2**L1–2**I_2)	2.95, 3.09	40.0, 40.4
TMG_2ch (**L1–3**)	2.42, 2.49	39.1, 39.6
TMG_2PA (**L1–4**)	2.68	38.6
TMG_2MePA (**L1–5**)	2.58	39.9
TMG_2mX (**L1–6**)	2.65	38.7
TMG_2py (**L1–7**)	2.73	39.9
TMGN	2.65[b]	39.4[b]
$H_2TMGN(PF_6)_2$	2.95[b]	41.6[b]

[a] Ref.[11a] [b] Ref.[12c]

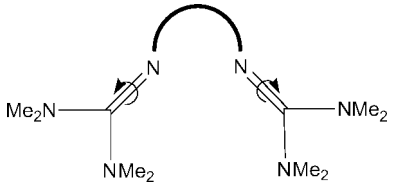


Figure 7. Rotation around the C=N double bond in tetramethylguanidino molecules.

The coalescence behaviour of selected guanidine ligands was investigated by EXSY ^1H NMR spectroscopy. The kinetic data were determined from the resulting Eyring plots (Figures 8 and 9 and Table 5).

Table 5 clearly shows that aromatic tetramethylguanidines have lower activation barriers for the *syn–anti* exchange than aliphatic ones. Our findings are thus in accordance with data for related systems reported in the literature.[12c,22a] In aromatic systems like TMG_2PA and TMGN, the C=N bond is weakened as a result of conjugation with the adjacent aromatic system resulting in lower energy barriers. In contrast, in aliphatic systems like btmgp, TMG_2doo or $[Bz_2TMG]^+$, which lack these effects, the free enthalpies of activation have to be considerably higher. The free enthalpies of activation of btmgp and TMG_2doo are in good agreement with the values reported for simple alkyl-substituted guanidines like pentamethylguanidine (TMG-CH_3) and tetramethyl-ethyl- or tetramethyl-propyl-guanidine (TMG-C_2H_5 and TMG-C_3H_7, respectively). In the case of btmgp and TMG_2doo, an inversion mechanism appears to be unlikely owing to the restrictions introduced by the second guanidyl function attached to the same linker. This means that rotation takes place that is facilitated if we go from smaller to larger alkyl chains. With this in mind and taking the data for comparable monoguanidine molecules into account, which are nearly identical,[22a] a unique rotational mechanism for all these systems can be postulated.

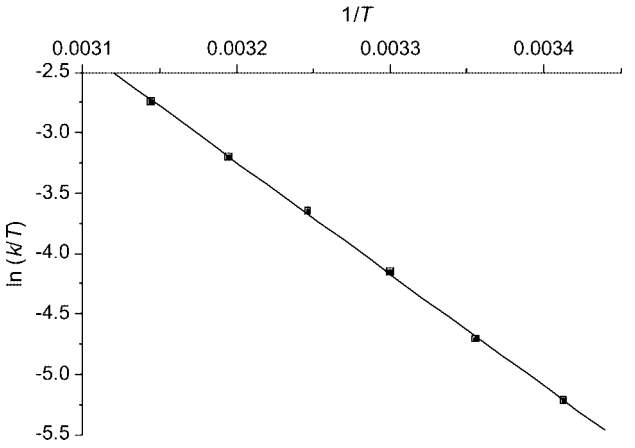


Figure 8. Eyring plot (293–318 K) for *syn–anti* exchange in TMG_2doo (**L1–2**).

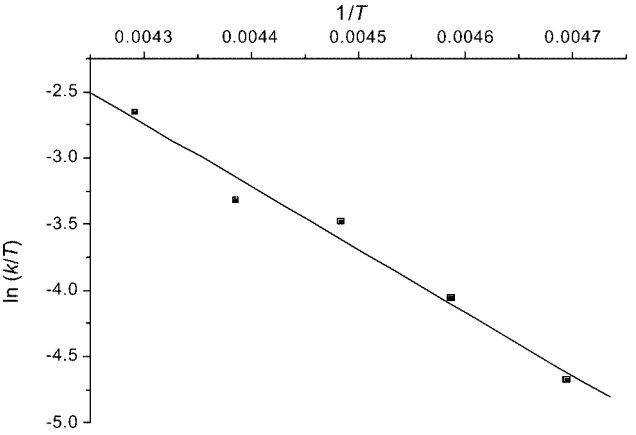


Figure 9. Eyring plot (213–233 K) for *syn–anti* exchange in TMG_2PA (**L1–4**).

Table 5. Coalescence parameters of *syn–anti* isomerisation.

	Solvent	T_c [K]	$\Delta H^{\ddagger}$ [kJ mol^{-1}]	$\Delta S^{\ddagger}$ [J mol^{-1} K^{-1}]	$\Delta G^{0\ddagger}$ [kJ mol^{-1}]
btmgp (**L1–1**)	[D_6]DMSO	375	92.4 ± 1.5	46.2 ± 0.8	78.6 ± 1.7
TMG_2doo (**L1–2**)	[D_6]DMSO	348	77.0 ± 0.8	21.8 ± 0.3	70.5 ± 0.9
TMG_2PA (**L1–4**)	CD_2Cl_2	267	41.5 ± 2.3	–40.9 ± 2.7	53.7 ± 3.0
TMG_2MePA (**L1–5**)	CD_2Cl_2	242			_[a]
TMG_2py (**L1–7**)	CD_2Cl_2	229			_[a]
TMGN	CD_2Cl_2	253[b]	53.4[b]		48.3[b]
TMGPh	$CDCl_3/CS_2$	238[c]			50.7[c]
$[Bz_2TMG]^+$	$CDCl_3$	276[d]			61.1[d]
TMG-CH_3	$CDCl_3$	346[c]			78.2[c]
TMG-C_2H_5	$CDCl_3$	338[c]			76.2[c]
TMG-C_3H_7	$CDCl_3$	326[c]			73.2[c]

[a] Temperature range limited by solvent (T_{min} = 183 K). [b] Ref.[12c] [c] Ref.[22a] [d] Ref.[22b]

The inductive effect of homoaromatic neighbourhoods can be enhanced by using a more electron-rich system like pyridine, as has been observed for TMG_2py (T_c = 229 K). The aromatic ligand TMG_2MePA exhibits coalescence of the methyl singlets at 242 K. A similar value was found for TMGPh (T_c = 238 K)[22a] whereas the methyl signal of the TMG_2PA molecule splits into two components below 267 K. This temperature is remarkably high in comparison with those reported for other aromatic systems like TMGN (253 K).[12c] Additionally, TMG_2PA has a negative activation entropy for the rotation around the C=N bond indicating that hydrogen bonds participate in the exchange mechanism (Figure 4). It is assumed that the bifurcated hydrogen bond between the amino hydrogen atom and the two guanidine nitrogen atoms stabilises the conformation observed in the crystal resulting in a raised activation barrier of rotation and thus in a higher coalescence temperature.

Conclusions

The assembly of bis-guanidine molecules starting from secondary amines and phosgene for use in biomimetic coordination chemistry, especially in the field of copper-controlled oxygen activation, has provided a set of bifunctional N-donor ligands. Each member of this series is expected to redefine the redox capabilities of its corresponding Cu^I complexes towards molecular oxygen in a specific fashion depending on the spatial demands of the guanidine functionalities as well as on the conformational freedom possible within the steric limits allowed by the spacer fragments connecting these units.

In contrast to established literature procedures, our method to arrive at bis-guanidine molecules is not dependent on predefined peralkylated urea precursors as we start from secondary amines as simple building blocks and thus define the urea intermediates by simply choosing suitably substituted starting materials. The synthetic protocol has been optimised to obtain overall yields in the range of 65–95%. This modular approach allows universal modification of the aliphatic guanidine substitution pattern as well as of the spacers with respect to rigidity, extension of the backbone and additional donor functions.

The bis-guanidine molecules described here are currently used as ligands with Cu^I with the aim being to activate molecular oxygen for the selective catalytic oxidation of organic substrates. The possibility of controlling oxidation selectivity by peripheral modifications is a particularly attractive feature of this ligand design. In general, such a matrix of bis-guanidine ligands can also be screened for their ability to stabilise complexes of other transition metals in unusually high oxidation states.

Experimental Section

Materials and Methods: All manipulations were performed under nitrogen (99,996%) dried with P_4O_{10} granulate using Schlenk techniques. Solvents were purified according to literature procedures and stored under nitrogen. Triethylamine and 1,3-diaminopropane were used as purchased from Fluka. The chloroformamidinium chlorides **V1**, **V2**, **V4**, **V5** and **V7** were prepared according to literature procedures.[12,14,17e,18]

Physical Measurements: Spectra were recorded with the following spectrometers: NMR: Bruker AMX 300 and Avance 500. The NMR signals were referenced to residual solvents measured relative to TMS. IR: Nicolet P510. UV: Perkin-Elmer Lambda 45. MS (EI, 70 eV): Saturn 2. Elemental analyses: Perkin-Elmer analysator Model 2400.

Crystal Structure Determinations: Data were collected with a Bruker AXS SMART APEX CCD diffractometer, Mo-K_α radiation with graphite monochromator at T = 120(2) K, absorption corrections by multiscans (SADABS[23]); structures were solved by direct methods[23] and subsequent Fourier difference maps. Full-matrix least-squares refinement on F^2[23] with all but hydrogen atoms refined anisotropically; hydrogen atoms were located from difference Fourier maps and refined at idealized positions assuming "riding" modes and U(H) = 1.2U_{iso}(C) or 1.5U_{iso}(C-methyl). Pertinent crystal and refinement data are given in Table 6.

CCDC-237479 (for **L1–4**), CCDC-275934 (for **L11–1**) and CCDC-275935 (for $[H_2$**L1–2**$]I_2 \cdot Et_2O$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

EXSY ^{1}H NMR Measurements: Variable-temperature EXSY spectra of compounds **L1–1**, **L1–2** and **L1–4** were recorded with the pulse program *noesygpph* from Bruker's pulse program library. The mixing time τ_m was optimised according to literature procedures[22c] and amounted to 200 ms. As the observed exchange process of the methyl groups is a simple two-side case with equal populations and uncoupled spins the exchange rate constant has been calculated[22c] from the integrals of the diagonal- and cross-peaks: $k = (\tau_m^{-1})\ln[(r + 1)/(r - 1)]$, where $r = (I_{D1} + I_{D2})/(I_{C1} + I_{C2})$ and I_{D1}, I_{D2} are the integrals of the diagonal-peaks and I_{C1}, I_{C2} are the integrals of the cross-peaks.

Preparation of Compounds: CAUTION! Phosgene is a severe toxic agent that can cause pulmonary embolism and in the case of heavy exposure may be lethal. Use only in a well-ventilated fume hood.

***N*,*N*,*N*′,*N*′-Tetraisopropylchloroformamidinium Chloride (V3):** In a Schlenk flask fitted with a condenser cooled to –40 °C, phosgene was passed through a solution of diisopropylamine (0.2 mol, 20.2 g, 14.5 mL) and NEt_3 (0.2 mol, 20.2 g, 27.9 mL) in dry MeCN (200 mL) at 0 °C (attention: highly exothermic) for 15 min. The urea was formed immediately, but the solution could not be stirred owing to its high viscosity. After 30 min, the reaction mixture was allowed to warm to room temperature and was stirred again. Then the mixture was heated at 40 °C for 40 h. After the mixture had cooled to room temperature, the solvent was evaporated under reduced pressure in order to obtain the product with $NEt_3 \cdot HCl$ as a by-product as a colourless wax; yield about 80% (22.6 g).

***N*,*N*′-Dipropyl-*N*,*N*′-propyleneurea:** Based on a literature procedure,[19] *N*,*N*′-trimethyleneurea (Fluka, 0.05 mol, 5 g) in freshly distilled dioxane (200 mL) was treated with NaH (0.11 mol, 2.64 g). The reaction mixture was refluxed for 16 h and then cooled to room temperature. After the addition of propyl iodide (0.2 mol, 34.0 g, 59.2 mL), the reaction mixture was refluxed for another 16 h and filtered to remove precipitated NaI. After evaporation of the solvent, vacuum distillation of the residual oil yielded the product as a yellow oil in a yield of about 60% (5.5 g). ^{1}H NMR (500 MHz,

Table 6. Crystallographic data for **L1–4**, **L11–1** and $[H_2$**L1–2**$]I_2 \cdot Et_2O$.

	L1–4	**L11–1**	$[H_2$**L1–2**$]I_2 \cdot Et_2O$
Empirical formula	$C_{22}H_{33}N_7$	$C_{21}H_{38}N_6O_4$	$C_{20}H_{48}I_2N_6O_3$
M_r	395.5	438.6	674.4
Crystal size [mm]	0.30 × 0.15 × 0.12	0.40 × 0.38 × 0.28	0.30 × 0.28 × 0.06
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/n$
a [Å]	18.577(4)	16.4003(11)	8.1966(4)
b [Å]	13.218(3)	8.2314(4)	14.0360(7)
c [Å]	20.144(4)	16.6413(9)	12.3715(6)
β [°]	113.24(3)	92.310(2)	93.983(1)
V [Å^3]	4545(2)	2244.7(2)	1419.9(1)
Z	8	4	2
$_{calcd.}$ [g cm^{-3}]	1.156	1.298	1.578
$F(000)$	1712	952	680
Θ range [°]	1.3–28.3	2.4–28.2	2.2–28.3
Reflections collected	24735	13601	12043
Reflections unique	10255	2771	3515
Variables	539	145	153
R_1 [$I > 2\sigma(I)$]	0.055	0.038	0.027
wR_2 (all data)	0.119	0.107	0.074
Min/max ΔF [e Å^{-3}]	–0.19/0.17	–0.18/0.34	–0.40/1.19

$CDCl_3$, 25 °C): δ = 0.83 (t, 6 H, CH_3), 1.50 (m, 4 H, CH_2), 1.89 (m, 2 H, CH_2), 3.23 (m, 8 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 11.2 (CH_3), 21.0 (CH_2), 22.5 (CH_2), 45.7 (CH_2), 49.7 (CH_2), 155.9 (C_{quat}) ppm.

***N,N′*-Dipropyl-*N,N′*-propylenechloroformamidinium Chloride (V6):** In a Schlenk flask fitted with a condenser cooled to –30 °C, phosgene was passed at 0 °C through a solution of *N,N′*-dipropyl-*N,N′*-propyleneurea (90 mmol, 16.6 g) in dry toluene (150 mL) for 20 min. The reaction mixture was stirred for 2 h at room temperature and for another 80 h at 40 °C. Afterwards the mixture was cooled to room temperature and the toluene was decanted. The residual orange oil was washed with dry diethyl ether and dried in vacuo; yield: 80% (17.2 g).

^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.86 (t, 6 H, CH_3), 1.65 (m, 4 H, CH_2), 2.19 (m, 2 H, CH_2), 3.62 (t, 4 H, CH_2), 3.87 (t, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 10.8 (CH_3), 19.6 (CH_2), 20.7 (CH_2), 49.5 (CH_2), 57.7 (CH_2), 151.1 (C_{quat}) ppm.

Chloroformamidinium Chloride V8: In a Schlenk flask fitted with a condenser cooled to –30 °C, phosgene was passed through a solution of *cis*-2,6-dimethylpiperidine (0.1 mol, 11.3 g, 9.3 mL) and NEt_3 (0.1 mol, 10.1 g, 14.0 mL) in dry MeCN (200 mL) at 0 °C for 15 min. After 30 min, the reaction mixture was allowed to warm to room temperature and heated at 40 °C for 36 h. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure in order to obtain the product as a colourless powder in a yield of about 65% (9.9 g) as well as $NEt_3 \cdot$HCl.

Chloroformamidinium Chloride V9: In a Schlenk flask fitted with a condenser cooled to –30 °C, phosgene was passed through a solution of 2,2,6,6-tetramethylpiperidine (0.1 mol, 14.1 g, 11.7 mL) and NEt_3 (0.1 mol, 10.1 g, 14.0 mL) in dry MeCN (200 mL) at 0 °C for 15 min. After 30 min, the reaction mixture was allowed to warm to room temperature and then heated at 40 °C for 50 h. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure in order to obtain the product as yellow powder in a yield of about 57% (10.3 g) as well as $NEt_3 \cdot$HCl.

Chloroformamidinium Chloride V10: In a Schlenk flask fitted with a condenser cooled to –30 °C, phosgene was passed at 0 °C through a solution of 1,1′-carbonyl-diimidazole (Fluka, 154 mmol, 25 g) in dry MeCN (300 mL) for 15 min. The reaction mixture was stirred for 2 h at room temperature and for another 30 h at 40 °C. The mixture was then cooled to room temperature and the excess phosgene and MeCN were evaporated under reduced pressure. The yellow residue was dried in vacuo; yield: 80% (26.7 g).

Chloroformamidinium Chloride V11: In a Schlenk flask fitted with a condenser cooled to –40 °C, phosgene was passed through a solution of morpholine (0.2 mol, 17.4 g, 17.5 mL) and NEt_3 (0.2 mol, 20.2 g, 27.9 mL) in dry MeCN (250 mL) at 0 °C (attention: highly exothermic) for 15 min. The urea was formed immediately, but the solution could not be stirred owing to its high viscosity. After 30 min, the reaction mixture was allowed to warm to room temperature and it was then stirred again. The mixture was heated at 40 °C for 50 h. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure in order to obtain the product as a yellow oil in a yield of about 70% (17.9 g) together with $NEt_3 \cdot$HCl as a by-product.

Chloroformamidinium Chloride V12: In a Schlenk flask fitted with a condenser cooled to –40 °C, phosgene was passed through a solution of thiomorpholine (0.049 mol, 5 g) and NEt_3 (0.097 mol, 9.7 g, 13.4 mL) in dry MeCN (150 mL) at 0 °C for 15 min. After 30 min, the reaction mixture was allowed to warm to room temperature and heated at 40 °C for 50 h. The mixture was then cooled to room temperature and the solvent was evaporated under reduced pressure in order to obtain the product as a yellow powder in a yield of about 45% (3.2 g) as well as $NEt_3 \cdot$HCl.

General Synthesis of Bis-guanidine Ligands from Chloroformamidinium Chlorides V1, V2, V4–V7 and V10: A solution of the chloroformamidinium chloride (40 mmol) in dry MeCN (60 mL) was added dropwise under vigorous stirring to an ice-cooled solution of a diamine (20 mmol) and triethylamine (5.57 mL, 4.04 g, 40 mmol) in dry MeCN (30 mL). After 3 h at reflux, a solution of NaOH (1.6 g, 40 mmol) in water was added. The solvent and NEt_3 were then evaporated under vacuum. In order to deprotonate the bis-hydrochloride, 50 wt.-% KOH (aq,, 25 mL) was added and the free base was extracted into the MeCN phase (3 × 25 mL). The organic phase was dried with Na_2SO_4 over charcoal. After filtration through Celite®, the solvent was evaporated under reduced pressure.

General Synthesis of Bis-guanidine Ligands from Chloroformamidinium Chlorides V3, V8, V9, V11, V12: The reaction mixture containing the chloroformamidinium chloride (40 mmol) in dry MeCN (60 mL) was added dropwise under vigorous stirring to an ice-cooled solution of a diamine (20 mmol) and triethylamine (5.57 mL, 4.04 g, 40 mmol) in dry MeCN (30 mL). After 3 h at reflux, a solution of NaOH (4.8 g, 120 mmol) in water was added. The solvent and NEt_3 were then evaporated under vacuum. In order to deprotonate the bis-hydrochloride, 50 wt.-% KOH (aq. 25 mL) was added and the free base was extracted into the MeCN phase (3 × 25 mL). The organic phase was dried with Na_2SO_4 over charcoal. After filtration through Celite®, the solvent was evaporated under reduced pressure.

1-(1,1,3,3-Tetramethylguanidino)-2-{2-[2-(1,1,3,3-tetramethylguanidino)ethoxy]ethoxy}ethane, TMG_2doo (L1–2): Colourless oil, yield: 96% (6.6 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.51 (s, 12 H, CH_3), 2.60 (s, 12 H, CH_3), 3.19 (t, ^3J = 6.9 Hz, 4 H, CH_2), 3.44 (t, ^3J = 6.9 Hz, 4 H, CH_2), 3.51 (s, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 38.6 (CH_3), 39.5 (CH_3), 49.4 (CH_2), 70.2 (CH_2), 73.3 (CH_2), 160.8 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ = 2995 (w), 2868 (vs), 2800 (w), 1619 (vs) (C=N), 1496 (m) (C=N), 1452 (m) (C=N), 1367 (vs), 1299 (w), 1236 (m), 1137 (s) (C–O–C), 1064 (m) (C–O–C), 991 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 344.4 (1) $[M]^+$, 300 (5) $[M - NMe_2]^+$, 230 (2) $[M - (NMe_2)_2CN]^+$, 186 (7) $[M - (NMe_2)_2CN(CH_2)_2O]^+$, 173 (8) $[M - NMe_2, NC(NMe_2)_2]^+$, 141 (71) $[M - (NMe_2)_2CN(CH_2)_2O]^+$, 129 (44) $[M - \{NMe_2NCH_3CN(CH_2)_2O(CH_2)_2\}]^+$, 114 (6) $[M - (NMe_2)_2CN(CH_2)_2O(CH_2)_2]^+$, 100 (17) $[M - (NMe_2)_2CN(CH_2)_2O(CH_2)_2N]^+$, 85 (100) $[M - (NMe_2)_2CN(CH_2)_2O(CH_2)_2N, CH_3]^+$, 71 (17) $[M - (NMe_2)_2CN(CH_2)_2O(CH_2)_2, NMe_2]^+$. Elemental analysis (*M* = 344.3 g mol^{-1}): calcd. for $C_{16}H_{36}N_6O_2$: C 55.77, H 10.54, N 24.40; found C 55.54, H 10.89, N 24.15.

[$H_2$$TMG_2$doo]$I_2$·$Et_2O$ ([H_2L1–2]I_2·Et_2O): Compound **L1–2** (688 mg, 2 mmol) was dissolved in THF (10 mL) and added to a suspension of ammonium iodide (576 mg, 4 mmol) in THF (10 mL). The reaction mixture was refluxed for 2 h and the solvent removed under reduced pressure. The resulting precipitate was dissolved in acetonitrile (15 mL) and filtered. Diethyl ether was added to the colourless filtrate by vapour diffusion to form [H_2**L1–2**]I_2·Et_2O as colourless needles; yield: 90% (1.08 g).

^{1}H NMR (500 MHz, CD_3CN, 25 °C): δ = 2.95 (s, 12 H, CH_3), 3.09 (s, 12 H, CH_3), 3.37 (t, ^3J = 5.2 Hz, 4 H, CH_2), 3.61 (s, 4 H, CH_2), 3.78 (t, ^3J = 5.2 Hz, 4 H, CH_2), 8.8 (v br.s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 40.0 (CH_3), 40.4 (CH_3), 45.3 (CH_2), 69.4 (CH_2), 70.4 (CH_2), 162.2 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3456 (m), 3178 (m), 2943 (w), 2858 (w), 1620 (vs) (C=N), 1584 (vs) (C=N), 1462 (m), 1450 (m), 1404 (s), 1315 (w), 1173 (w), 1135 (m), 1115 (m), 1092 (m), 889 (w) cm^{-1}. Elemental analysis (*M* = 600.1 g mol^{-1}, after drying in vacuo): calcd. for $C_{16}H_{38}N_6O_2I_2$: C 31.99, H 6.38, N 14.00; found C 32.19, H 6.23, N 13.93.

1,3-Bis(1,1,3,3-tetramethylguanidino)cyclohexane, TMG_2ch (L1–3): Colourless oil, yield: 95% (5.9 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.0–1.6 (m, 8 H, CH_2 from ring), 2.42 (s, 12 H, CH_3), 2.49 (s, 12 H, CH_3), 3.44 (m, 2 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 20.0 (CH_2), 32.6 (CH_2), 33.7 (CH_2), 39.1 (CH_3), 39.6 (CH_3), 50.7 (CH), 159.2 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ = 2993 (m), 2925 (m), 2856 (m), 1618 (vs) (C=N), 1496 (vs) (C=N), 1450 (s), 1402 (m), 1363 (m), 1236 (m), 1126 (s), 1056 (w), 1012 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 310.3 (49) $[M]^+$, 267 (11) $[M - N(CH_3)_2 + H]^+$, 212 (5), 195 (50), 151 (75), 100 (52), 85 (55), 71 (100), 57 (22). Elemental analysis (*M* = 310.3 g mol^{-1}): calcd. for $C_{16}H_{34}N_6$: C 61.88, H 11.04, N 27.08; found C 61.72, H 11.38, N 26.90.

Bis[2-(1,1,3,3-tetramethylguanidino)phenyl]amine, TMG_2PA (L1–4): Off-white powder, after recrystallisation colourless needles, yield: 81% (6.4 g), m.p. = 128 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.68 (s, 24 H, CH_3), 6.53 (dd, ^3J = 7.72, ^4J = 1.5 Hz, 2 H), 6.71 (dt, ^3J = 7.60, ^4J = 1.5 Hz, 2 H), 6.82 (dt, ^3J = 7.70, ^4J = 1.5 Hz, 2 H), 6.95 (s, 1 H, N–H), 7.37 (dd, ^3J = 7.70, ^4J = 1.6 Hz, 2 H) ppm. ^{1}H NMR (300 MHz, CD_3CN, 25 °C): δ = 2.64 (s, 24 H, CH_3), 6.44 (dd, ^3J = 7.6, ^4J = 1.3 Hz, 2 H), 6.67 (dt, ^3J = 7.60, ^4J = 1.3 Hz, 2 H), 6.77 (dt, ^3J = 7.60, ^4J = 1.3 Hz, 2 H), 7.24 (s, 1 H, N–H), 7.30 (dd, ^3J = 7.60, ^4J = 1.3 Hz, 2 H) ppm. ^{13}C NMR (75 MHz, CD_3CN, 25 °C): δ = 38.6 (CH_3), 112.8, 116.9, 119.9, 120.0, 135.5, 140.4, 159.4 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3302 (w) (N–H), 3062 (w), 3033 (w), 2993 (w), 2941 (m), 2916 (m), 2873 (m), 2841 (m), 2808 (w), 2789 (w), 1597 (vs) (C=N), 1591 (vs) (C=N), 1570 (vs) (C=N), 1565 (vs) (C=N), 1512 (vs) (C=N), 1508 (vs) (C=N), 1483 (s), 1437 (m), 1419 (s), 1379 (vs), 1338 (m), 1265 (m), 1230 (m), 1215 (m), 1140 (s), 1111 (m), 1062 (w), 1051 (w), 1034 (w), 1020 (s), 922 (w), 911 (w), 852 (w), 777 (m), 731 (s), 710 (w), 654 (w), 619 (w), 552 (w) cm^{-1}. UV/Vis {CH_2Cl_2, λ_{max} (ε/M^{-1} cm^{-1}): 242 (13900), 323 nm (10100). EI-MS [CH_2Cl_2]: *m*/*z* (%) = 350 (100) $[M - 45]^+$, 305 (10) $[M - 90]^+$, 58 (18) $[CH_2NMe_2]^+$. Elemental analysis (*M* = 395.3 g mol^{-1}): calcd. for $C_{22}H_{33}N_7$: C 66.80, H, 8.41, N 24.79; found C 66.45, H 8.74, N 24.40.

Methylbis[2-(1,1,3,3-tetramethylguanidino)phenyl]amine, TMG_2MePA (L1–5): Dark red-violet powder, yield: 76% (6.2 g), m.p. = 95 °C. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.58 (s, 24 H, CH_3), 3.38 (s, 3 H, N–CH_3), 6.45 (m, 2 H), 6.75–6.85 (m, 6 H) ppm. ^{13}C NMR (75 MHz, CD_3CN, 25 °C): δ = 39.9 (gua-CH_3), 68.3 (CH_3), 115.6, 117.8, 120.7, 122.8, 130.6, 131.6, 159.2 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3180 (vw), 2941 (w), 2870 (w), 2793 (w), 1626 (vs) (C=N), 1552 (vs) (C=N), 1504 (m), 1473 (m), 1458 (m), 1438 (m), 1414 (m), 1402 (m), 1308 (m), 1254 (w), 1227 (w), 1165 (m), 1127 (vs), 1065 (m), 1036 (m), 906 (w), 877 (w), 849 (w), 762 (m), 747 (m), 619 (m), 503 (w) cm^{-1}. UV/Vis (CH_2Cl_2) λ_{max} (ε/M^{-1} cm^{-1}): 260 (12900), 322 (4300), 517 nm (450). EI-MS [CH_2Cl_2]: *m*/*z* (%) = 409 (100) $[M]^+$, 364 (70) $[M - 45]^+$, 319 (52) $[M - 90]^+$, 58 (75) $[CH_2NMe_2]^+$, 44 (33) $[NMe_2]^+$. Elemental analysis (*M* = 409.3 g mol^{-1}): calcd. for $C_{23}H_{35}N_7$: C 67.45, H 8.61, N 21.94; found C 67.84, H 8.88, N 21.85.

α,α′-Bis(1,1,3,3-tetramethylguanidino)-*m*-xylene, TMG_2mX (L1–6): Colourless oil, yield: 96% (6.4 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.65 (s, 24 H, CH_3), 4.40 (s, 4 H, CH_2), 7.13 (m, 3 H, CH), 7.28 (s, 1 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 38.7 (CH_3), 52.9 (CH_2), 124.4 (CH), 125.7 (CH), 127.4 (CH), 143.0 (C_{quat}), 160.1 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ = 2996 (w), 2925 (m), 2884 (m), 2796 (w), 1554 (vs) (C=N), 1457 (m), 1423 (m), 1390 (s), 1346 (w), 1238 (w), 1155 (m), 1108 (w), 1062 (w), 1031 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 332.4 (42) $[M]^+$, 279 (11), 234 (12) $[M - C(NMe_2)_2 + 2H]^+$, 213 (28), 175 (18), 149 (42), 116 (31), 105 (68) $[CH_2–Ph–CH_2 + 1]^+$, 91 (13) $[C_7H_7]^+$, 85 (82), 72 (80), 57 (59). Elemental analysis (*M* = 332.3 g mol^{-1}): calcd. for $C_{18}H_{32}N_6$: C 65.01, H 9.71, N 25.29; found C 64.92, H 10.06, N 25.02.

2,6-Bis(1,1,3,3-tetramethylguanidino)pyridine, TMG_2py (L1–7): Colourless waxy solid, yield: 93% (5.7 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.73 (s, 24 H, CH_3), 6.30 (d, ^3J = 7.48 Hz, 2 H), 7.37 (t, ^3J = 7.48 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 39.9 (CH_3), 107.7 (CH), 138.4 (CH), 158.0 (C_{quat}), 161.4 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3062 (m), 2993 (m), 2937 (s), 2871 (s), 1604 s (C=N), 1552 (vs) (C=N), 1539 (vs) (C=N), 1411 (vs), 1389

(vs), 1225 (s), 1213 (s), 1132 (vs), 1058 (m), 1022 (s), 1003 (m), 912 (m), 812 (s), 739 (m), 614 (w), 555 (w), 514 (w), 441 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 305.3 (81) $[M]^+$, 290 (9) $[M - CH_3]^+$, 261 (11) $[M - NMe_2]^+$, 245 (15), 202 (48), 189 (22), 161 (12), 132 (31), 116 (49) $[H_2N{=}CN_2(CH_3)_4]^+$, 85 (50), 72(100). Elemental analysis (M = 305.3 $g\,mol^{-1}$): calcd. for $C_{15}H_{27}N_7$: C 58.97, H 8.91, N 32.11; found C 58.72, H 9.16, N 32.02.

1,3-Bis(1,1,3,3-tetraethylguanidino)propane, TEG_2p (L2–1): Colourless oil, yield: 97% (7.4 g). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.00 (s, 24 H, CH_3), 1.78 (m, 2 H, CH_2), 3.00 (q, 8 H, CH_2), 3.12 (q, 8 H, CH_2), 3.14 (t, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 12.9 (CH_3), 13.6 (CH_3), 35.9 (CH_2), 41.3 (CH_2CH_3), 42.5 (CH_2CH_3), 48.7 (CH_2), 158.0 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ = 2966 (m), 2929 (m), 2870 (m), 1610 (vs) (C=N), 1454 (w), 1400 (m), 1375 (m), 1336 (w), 1300 (w), 1261 (s), 1219 (w), 1134 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 382.4 (73) $[M]^+$, 353(19) $[M - Et]^+$, 310 (5) $[M - NEt_2]^+$, 228 (12) $[M - C(NEt_2)_2]^+$, 205 (62), 198 (57), 142 (51), 113 (100) $[CH_2N{=}C(NEt_2)_2]^+$, 85 (42), 72 (41) $[NEt_2]^+$. Elemental analysis (M = 382.4 $g\,mol^{-1}$): calcd. for $C_{21}H_{46}N_6$: C 65.90, H 12.12, N 21.97; found C 65.61, H 12.37, N 22.02.

α,α′-Bis(1,1,3,3-tetraethylguanidino)-*m*-xylene, TEG_2mX (L2–6): Colourless oil, yield: 95% (8.4 g). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.07 (s, 24 H, CH_3), 3.10 (q, 8 H, CH_2), 3.22 (q, 8 H, CH_2), 4.36 (s, 4 H, CH_2), 7.22 (m, 3 H, CH), 7.29 (s, 1 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 13.4 (CH_3), 41.4 (benzyl-CH_2), 42.7 (CH_2), 124.9 (CH), 126.5 (CH), 127.6 (CH), 143.3 (C_{quat}), 159.1 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ = 2968 (m), 2929 (m), 2870 (m), 1604 (vs) (C=N), 1450 (m), 1403 (m), 1375 (m), 1338 (w), 1302 (w), 1261 (s), 1203 (w), 1132 (w), 1068 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 444.4(70) $[M]^+$, 372 (22) $[M - NEt_2]^+$, 275 (75) $[M - HN{=}C(NEt_2)_2]^+$, 172 (39) $[H_2N{=}C(NEt_2)_2]^+$, 119 (31), 105 (75) $[CH_2{-}Ph{-}CH_2 + 1]^+$, 91 (11) $[C_7H_7]^+$, 72 (100) $[NEt_2]^+$. Elemental analysis (M = 444.4 $g\,mol^{-1}$): calcd. for $C_{26}H_{48}N_6$: C 70.21, H 10.89, N 18.91; found C 70.06, H 11.20, N 18.74.

2,6-Bis(1,1,3,3-tetraethylguanidino)pyridine, TEG_2py (L2–7): Colourless oil, yield: 95% (7.9 g). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.06 (m, 24 H, NCH_2CH_3), 3.07 (m, 16 H, NCH_2CH_3), 6.22 (d, ^3J = 7 Hz, 8 Hz, 2 H), 7.22 (t, ^3J = 7 Hz, 8 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 12.82 (CH_3), 42.66 (CH_2), 104.99 (CH), 138.48 (CH), 157.90 (C_{quat}), 159.37 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ = 3064 (vw), 2970 (s), 2931 (m), 2871 (m), 1556 (vs) $(C{=}N)_{Gua}$, 1531 (vs) $(C{=}N)_{Gua}$, 1483 (m), 1446 (vs), 1417 (vs) $(C{=}N)_{Pyridine}$, 1377 (s), 1356 (m), 1269 (vs), 1198 (m), 1136 (vs), 1057 (vs) cm^{-1}. EI-MS: *m*/*z* (%) =417 (8) $[M]^+$, 388 (2) $[M - Et]^+$, 345 (1) $[M - NEt_2]^+$, 274 (3) $[M - 2\,NEt_2 + H]^+$, 263 (52) $[M - C(NEt_2)_2 + 2H]^+$, 191 (49) $[M - C(NEt_2)_2 - NEt_2 + 2H]^+$, 172 (58) $[H_2N{=}C(NEt_2)_2]^+$, 163 (52) $[M - C(NEt_2)_2 - NEt_2 - Et + 3\,H]^+$, 100 (70) $[H_2N{=}C(NEt_2) - NEt_2]^+$, 72 (100) $[NEt_2]^+$, 29 (61) $[Et]^+$. Elemental analysis (M = 417.4 $g\,mol^{-1}$): calcd. for $C_{23}H_{43}N_7$: C 66.13, H 10.38, N 23.49; found C 65.81, H 10.55, N 23.64.

1,3-Bis(1,1,3,3-tetraisopropylguanidino)propane, $TiPG_2p$ (L3–1): Off-white powder, yield: 81% (8.0 g). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.23 (d, 24 H, CH_3), 1.46 (d, 24 H, CH_3), 1.59 (m, 2 H, CH_2), 3.31 (t, 4 H, CH_2), 3.40 (m, 4 H, CH), 3.82 (m, 4 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 19.2 (CH_3), 21.4 (CH_3), 31.6 (CH_2), 36.7 (CH_2), 45.2 (CH), 47.4 (CH), 157.7 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 2972 (s), 2845 (m), 2774 (m), 2721 (m), 1699 (s), 1622 (vs) (C=N), 1525 (vs), 1473 (s), 1451 (m), 1405 (m), 1309 (m), 1153 (m), 765 (w) cm^{-1}. EI-MS: *m*/*z* (%): = 494.4 (0.1) $[M]^+$, 459 (1) $[M - Me]^+$, 429 (5), 401 (1), 355 (8), 314 (13), 281 (5), 230 (90) $[(iPr_2N)_2C{=}NH_2 + 2H]^+$, 215 (19), 175 (9), 149 (11), 114 (20) $[(iPr_2N)_2CH_2]^+$, 112 (18) $[(iPr_2N)_2C]^+$, 86 (100) $[iPr{-}N{-}CH{-}CH_3 + H]^+$, 41 (76). Elemental analysis (M = 494.5 $g\,mol^{-1}$): calcd. for $C_{29}H_{62}N_6$: C 70.37, H 12.64, N 16.99; found C 70.16, H 12.90, N 16.95.

1-(1,3-Dimethylimidazolidin-2-ylideneamino)-2-{2-[2-(1,3-dimethylimidazolidin-2-ylideneamino)ethoxy]ethoxy}ethane, $DMEG_2doo$ (L4–2): Colourless oil, yield: 98% (6.6 g). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.77 (s, 6 H, CH_3), 2.79 (s, 6 H, CH_3), 3.15 (s, 8 H, CH_2), 3.59 (br., 8 H, CH_2), 3.66 (s, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 31.5 (CH_3), 36.3 (CH_3), 47.4 (CH_2), 49.4 (CH_2), 70.5 (CH_2), 73.7 (CH_2), 157.9 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ = 2915 (w), 2858 (m), 1666 (vs) (C=N), 1617 (vs) (C=N), 1483 (m), 1441 (m), 1383 (m), 1302 (w), 1122 (s) (C–O–C), 1023 (m) cm^{-1}. EI-MS: *m*/*z* (%) = 340.2 (1) $[M]^+$, 325 (1) $[M - CH_3]^+$, 184 (4), 140 (9) $[CH_2CH_2N{=}CN_2(CH_3)_2C_2H_4]^+$, 126 (100) $[CH_2N{=}CN_2(CH_3)_2C_2H_4]^+$, 112 (8), 85 (3). Elemental analysis (M = 340.3 $g\,mol^{-1}$): calcd. for $C_{16}H_{32}N_6O_2$: C 56.43, H 9.48, N 24.69; found C 56.21, H 9.76, N 24.81.

***N*¹,*N*³-Bis(1,3-dimethylimidazolidin-2-ylidene)cyclohexane-1,3-diamine, $DMEG_2ch$ (L4–3):** Colourless powder, yield: 93% (5.7 g). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.16–1.72 (m, 8 H, CH_2 from ring), 2.71 (s, 12 H, CH_3), 3.05 (m, 8 H, CH_2), 4.05 (m, 2 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 20.0 (CH_2), 25.6 (CH_2), 35.7 (CH_2), 45.1 (CH_2), 49.0 (CH_3), 53.2 (CH), 155.8 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ =: 2933 (s), 2852 (s), 1660 (vs) (C=N), 1637 (vs) (C=N), 1477 (m), 1442 (m), 1410 (m), 1379 (s), 1259 (s), 1226 (s), 1142 (w), 1119 (w), 1095 (w), 1065 (w), 1032 (s), 991 (m), 953 (s), 908 (m), 877 (m), 850 (m), 766 (w), 719 (m), 669 (w), 642 (m), 580 (m), 538 (w), 503 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 306.2 (11) $[M]^+$, 263 (19) $[M - NMe_2 + H]^+$, 193 (100) $[M - N{=}CN_2(C_2H_4)Me_2{-}H]^+$, 152 (35), 114 (32) $[H_2N{=}CN_2(C_2H_4)Me_2]^+$, 98 (29), 70 (23), 55 (15). Elemental analysis (M = 306.2 $g\,mol^{-1}$): calcd. for $C_{16}H_{30}N_6$: C 62.69, H 9.87, N 27.43; found C 62.41, H 10.03, N 27.56.

***N*¹,*N*³-Bis(1,3-dimethylimidazolidin-2-ylidene)-*m*-xylylene-α,α′-diamine, $DMEG_2mX$ (L4–6):** Colourless oil, yield: 96% (6.3 g). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.78 (s, 12 H, CH_3), 3.18 (t, 8 H, CH_2), 4.67 (s, 4 H, CH_2), 7.24 (m, 3 H, CH), 7.39 (s, 1 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 31.5 (CH_3), 45.06 (CH_2), 49.54 (CH_2), 50.89 (CH_2), 124.4 (CH), 125.4 (CH), 127.7 (CH), 143.2 (C_{quat}), 157.7 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ = 2935 (m), 2843 (m), 1655 (vs) (C=N), 1483 (m), 1437 (m), 1384 (m), 1350 (w), 1269 (s), 1230 (w), 1199 (w), 1065 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 328.3 (19) $[M]^+$, 313.2 (8) $[M - CH_3]^+$, 232.2 (78), 215 (26), 126 (56) $[CH_2N{=}C(CH_3)_2C_2H_4]^+$, 114 (100) $[H_2N{=}CN_2(CH_3)_2C_2H_4]^+$, 112 (60) $[N_3C_5H_{10}]^+$, 106 (81), 91.1 (40) $[C_7H_7]^+$. Elemental analysis (M = 328.3 $g\,mol^{-1}$): calcd. for $C_{18}H_{28}N_6$: C 65.81, H 8.60, N 25.60; found C 65.61, H 8.97, N 25.42.

***N*²,*N*⁶-Bis(1,3-dimethylimidazolidin-2-ylidene)pyridine-2,6-diamine, $DMEG_2py$ (L4–7):** Colourless waxy solid, yield: 92% (5.5 g). ^1H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.65 (s, 12 H, CH_3), 3.30 (s, 8 H, CH_2), 6.23 (d, ^3J = 7.7 Hz, 2 H), 7.23 (t, ^3J = 7.7 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 34.9 (CH_3), 48.2 (CH_2), 108.2 (CH), 138.6 (CH), 157.8 (C_{quat}), 160.9 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3161 (w), 3064 (w), 2919 (m), 2852 (m), 1616 (vs) (C=N), 1569 (s) (C=N), 1541 (vs) (C=N), 1429 (s), 1281 (s), 1236 (m), 1193 (w), 1144 (w), 1038 (m), 955 (m), 808 (m), 702 (w), 669 (w), 582 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 301.2 (89) $[M]^+$, 300 (100) $[M - H]^+$, 245 (9), 205 (39) $[M - CN_2(CH_3)_2C_2H_4 + 2H]^+$, 204 (58) $[M - CN_2(CH_3)_2C_2H_4 + H]^+$, 189 (9), 132 (7), 114 (11), 98 (8)

$[N{=}CN_2(CH_3)_2C_2H_4]^+$, 70 (29). Elemental analysis (M = 301.2 g mol^{-1}): calcd. for $C_{15}H_{23}N_7$: C 59.76, H 7.70, N 32.54; found C 59.49, H 7.91, N 32.60.

2-(2-{2-[Tetrahydro-1,3-dimethylpyrimidin-2(1*H*)-ylideneamino]-ethoxy}ethoxy)-*N*-[tetrahydro-1,3-dimethylpyrimidin-2(1*H*)-ylidene-amino]ethanamine, DMPG$_2$doo (L5–2): Colourless oil, yield: 93% (6.8 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.58 (m, 4 H, CH_2), 1.88 (m, 8 H, CH_2), 2.85 (s, 12 H, CH_3), 3.20 (t, 4 H, CH_2), 3.54 (br., 8 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 21.6 (CH_2), 38.4 (CH_3), 39.1 (CH_3), 48.1 (CH_2), 49.6 (CH_2), 70.5 (CH_2), 73.9 (CH_2), 160.1 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ = 2925 (w), 2865 (m), 1635 (vs) (C=N), 1620 (vs) (C=N), 1558 (m), 1541 (s), 1458 (m), 1386 (m), 1309 (w), 1261 (m), 1101 (s) (C–O–C), 1045 (m) (C–O–C), 850 (w), 742 (w), 627 (s) cm^{-1}. EI-MS: m/z (%) = 368.4 (1) $[M]^+$, 266 (21), 205 (8), 152 (9), 173 (8) [M – NMe_2, $NC\{N(CH_3)_2\}_2]^+$, 141 (65) [M – $\{N(CH_3)_2\}_2$-$CN(CH_2)_2O]^+$, 128 (100) $[H_2N{=}CN_2(CH_3)_2C_3H_6]^+$, 98 (34), 70 (48). Elemental analysis (M = 368.3 g mol^{-1}): calcd. for $C_{18}H_{36}N_6O_2$: C 58.65, H 9.85, N 22.81; found C 58.42, H 10.16, N 22.73.

***N*-Methyl-2,2′-bis[tetrahydro-1,3-dimethylpyrimidin-2(1*H*)-ylidene-amino]diphenyleneamine, DMPG$_2$MePA (L5–5):** Dark red-violet oil, yield: 68% (5.9 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 6.95 (m, 4 H, CH), 6.7 (m, 4 H, CH), 2.9 (s, 15 H, CH_3), 1.9 (m, 8 H, CH_2), 1.65 (m, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, CD_3CN, 25 °C): δ = 21.1 (CH_2), 38.0 (CH_3), 48.6 (CH_2), 69.1 (N–CH_3), 115.2, 117.6, 122.1, 124.6, 136.5 (C_{quat}), 142.1(C_{quat}), 153.3 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3065 (w), 3025 (w), 2940 (m), 2869 (m), 2345 (w), 1621 (vs) (C=N), 1563 (vs) (C=N), 1546 (vs) (C=N), 1452 (s), 1417 (s), 1317 (s), 1120 (m), 1052 (m), 746 (s) cm^{-1}. EI-MS $[CH_2Cl_2]$: m/z (%) = 433.6 (1) $[M]^+$, 419 (2) [M – 14]$^+$, 323 (5), 285 (3), 252 (100), 213 (98), 181 (33), 128 (30) $[H_2N{=}CN_2(CH_3)_2$-$C_3H_6]^+$, 112 (29), 69 (48), 58 (69). Elemental analysis (M = 433.3 g mol^{-1}): calcd. for $C_{25}H_{35}N_7$: C 69.24, H 8.14, N 22.62; found C 69.02, H 8.49, N 22.49.

***N*^{1},*N*^{3}-Bis[tetrahydro-1,3-dimethylpyrimidin-2(1*H*)-ylidene]-*m*-xylylene-α,α′-diamine, DMPG$_2$mX (L5–6):** Colourless oil, yield: 95% (6.8 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.83 (q, 4 H, CH_2), 2.86 (s, 12 H, CH_3), 3.07 (t, 8 H, CH_2), 4.36 (s, 4 H, CH_2), 7.21 (m, 3 H, CH), 7.33 (s, 1 H, CH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 20.5 (CH_2), 39.0 (CH_3), 48.3 (CH_2), 51.57 (CH_2), 124.9 (CH), 126.5 (CH), 127.9 (CH), 142.6 (C_{quat}), 157.6 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ = 2635 (m), 2843 (m), 1655 (vs) (C=N), 1483 (m), 1437 (m), 1402 (w), 1385 (m), 1350 (w), 1269 (s), 1231 (w), 1199 (w), 1065 (w) cm^{-1}. EI-MS: m/z (%) = 356.3 (20) $[M]^+$, 229 (15), 178 (5), 149 (7), 128 (100) $[H_2N{=}CN_2(CH_3)_2$-$C_3H_6]^+$, 99 (22), 57 (23). Elemental analysis (M = 356.3 g mol^{-1}): calcd. for $C_{20}H_{32}N_6$: C 67.36, H 9.05, N 23.58; found C 67.12, H 9.41, N 23.47.

***N*^{2},*N*^{6}-Bis[tetrahydro-1,3-dimethylpyrimidin-2(1*H*)-ylidene]pyridine-2,6-diamine, DMPG$_2$py (L5–7):** Colourless waxy solid, yield: 94% (6.2 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.90 (m, 4 H, CH_2), 2.78 (s, 6 H, CH_3), 2.84 (s, 6 H, CH_3), 3.17 (m, 8 H, CH_2), 5.74 (d, ^3J = 7.7 Hz, 1 H), 5.89 (d, ^3J = 7.7 Hz, 1 H), 7.10 (t, ^3J = 7.7 Hz, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 22.2 (CH_2), 35.6 (CH_3), 39.2 (CH_3), 47.8 (CH_2), 104.7 (CH), 138.5 (CH), 157.8 (C_{quat}), 161.9 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3010 (w), 2902 (w), 2856 (w), 1624 (vs) (C=N), 1529 (vs), 1448 (s), 1413 (s), 1317 (s), 1252 (m), 1221 (m), 1157 (w), 1109 (w), 1059 (m), 802 (w), 756 (w), 709 (w), 474 (w) cm^{-1}. EI-MS: m/z (%) = 329.2 (62) $[M]^+$, 314 (4) [M – CH_3]$^+$, 245 (33), 219 (100) [M – $CN_2(CH_3)_2$-C_3H_6 + 2 H]$^+$, 218 (48) [M – $CN_2(CH_3)_2C_3H_6$ + H]$^+$, 191 (9), 148 (28), 112 (25) $[N{=}CN_2(CH_3)_2C_3H_6]^+$, 109 (19), 70 (11). Elemental analysis (M = 329.2 g mol^{-1}): calcd. for $C_{17}H_{27}N_7$: C 61.96, H 8.27, N 29.77; found C 61.65, H 8.42, N 29.93.

***N*^{1},*N*^{3}-Bis[tetrahydro-1,3-dipropylpyrimidin-2(1*H*)-ylidene]propane-1,3-diamine, DPPG$_2$p (L6–1):** Yellowish oil, yield: 89% (7.2 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 0.83 (t, 12 H, CH_3), 1.44 (q, 2 H, CH_2), 1.56 (m, 8 H, CH_2), 1.91 (m, 4 H, CH_2), 3.19 (m, 20 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 11.6 (CH_3), 21.3 (CH_2), 22.7 (CH_2), 46.1 (CH_2), 49.9 (CH_2), 53.7 (CH_2), 158.0 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ = 2960 (s), 2931 (m), 2871 (m), 1633 (vs) (C=N), 1604 (vs) (C=N), 1500 (m), 1456 (m), 1363 (m), 1325 (w), 1296 (m), 1263 (w), 1207 (s), 1099 (m) cm^{-1}. EI-MS: m/z (%) = 406.4 (9) $[M]^+$, 391 (1) [M – Me]$^+$, 363 (1) [M – Pr]$^+$, 240 (10), 211 (15), 184 (28) $[H_2N{=}CN_2Pr_2C_3H_6]^+$, 155 (100), 113 (38), 70 (32), 98.1 (29), 70.0 (23), 55.1 (14.5). Elemental analysis (M = 406.4 g mol^{-1}): calcd. for $C_{23}H_{46}N_6$: C 67.92, H 11.41, N 20.67; found C 67.61, H 11.67, N 20.72.

***N*^{1},*N*^{3}-Bis[bis(2,6-dimethylpiperidin-1-yl)methylene]propane-1,3-diamine, B(DMPip)G$_2$p (L8–1):** Yellowish oil, yield: 76% (8.2 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.01 (d, 24 H, CH_3), 1.53 (m, 16 H, CH_2), 1.61 (m, 2 H, CH_2), 1.68 (m, 8 H, CH_2), 2.58 (m, 8 H, CH), 2.70 (t, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 21.5 (CH_2), 23.0 (CH_3), 24.9 (CH_2-Pip), 33.9 (CH_2-Pip), 39.8 (CH_2), 52.4 (CH), 157.0 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ =: 2958 (s), 2931 (s), 2871 (m), 1693 (vs) (C=N), 1651 (vs) (C=N), 1643 (vs) (C=N), 1537 (s), 1479 (m), 1415 (m), 1373 (w), 1311 (m), 1275 (w), 1236 (w), 1159 (m) cm^{-1}. EI-MS: m/z (%) = 542 (0.01) $[M]^+$, 430 (1) [M – $Me_2Pip]^+$, 292 (13) [M – $N{=}C(Me_2Pip)_2]^+$, 279 (14) [M – $CH_2N{=}C(Me_2Pip)_2$ + H]$^+$, 237 (9) $[(Me_2Pip)_2CH]^+$, 183 (22), 149 (48), 112 (43) $[Me_2Pip]^+$, 98 (100) $[CH_3CH(CH_2)_3CHCH_3]^+$, 56 (39). Elemental analysis (M = 542.5 g mol^{-1}): calcd. for $C_{33}H_{62}N_6$: C 72.99, H 11.52, N 15.49; found C 72.64, H 11.75, N 15.61.

***N*^{1},*N*^{3}-Bis[bis(2,2,6,6-tetramethylpiperidin-1-yl)methylene]propane-1,3-diamine, B(TMPip)G$_2$p (L9–1):** Yellow oil, yield: 72% (9.4 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.05 (s, 48 H, CH_3), 1.18 (m, 2 H, CH_2), 1.50 (m, 8 H, CH_2), 3.17 (t, 16 H, CH_2), 3.29 (t, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 13.2 (CH_3), 13.9 (CH_3), 16.3 (CH_2), 35.0 (CH_2), 40.4 (CH_2), 41.1 (CH_2), 42.2 (CH_2), 56.7 (C_{quat}), 156.4 (C_{gua}) ppm. IR (film between NaCl plates): $\tilde{\nu}$ = 2970 (s), 2935 (m), 2733 (w), 1645 (vs) (C=N), 1531 (vs) (C=N), 1454 (m), 1379 (s), 1351 (m), 1271 (s), 1223 (m), 1182 (w) cm^{-1}. EI-MS: m/z (%) = 654 (0.01) $[M]^+$, 408 (2), 340 (4), 308 (8) $[(Me_4Pip)_2C{=}NH_2]^+$, 268 (6), 240 (13), 184 (21), 157 (28), 140 (11) $[Me_4Pip]^+$, 126 (35) $[Me_4Pip\text{-}N]^+$, 109 (58), 84 (22) $[(CH_3)_2$-$C(CH_2)_3]^+$, 69 (37) $[CH_3C(CH_2)_3]^+$, 58 (100). Elemental analysis (M = 654.6 g mol^{-1}): calcd. for $C_{41}H_{78}N_6$: C 75.16, H 12.01, N 12.83; found C 74.91, H 12.37, N 12.72.

***N*^{1},*N*^{3}-Bis[di(1*H*-imidazol-1-yl)methylene]propane-1,3-diamine, DImG$_2$p (L10–1):** Yellow powder, yield: 58% (4.2 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.92 (m, 2 H, CH_2), 3.3 (m, 4 H, =N–CH_2-), 7.12 (s, 8 H, =N–CH=CH–N-), 7.71 (s, 4 H, -N–CH=N-) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 21.3 (CH_2), 40.0 (CH_2), 121.9 (CH=CH), 135.1 (CH), 155.2 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 3122 (m), 3035 (m), 2935 (m), 2843 (m), 2698 (m), 2607 (m), 1791 (m), 1689 (s), 1652 (vs) (C=N), 1533 (vs) (C=N), 1482 (s), 1442 (vs), 1373 (m), 1324 (s), 1257 (s), 1222 (w), 1197 (w), 1141 (m), 1095 (s), 1064 (s), 1035 m) cm^{-1}. EI-MS: m/z (%) = 362.3 (0.1) $[M]^+$, 212 (10), 179 (21), 151 (22), 123 (35), 116 (24), 68,0 (100) $[C_3H_4N_2]^+$. Elemental analysis (M = 362.2 g mol^{-1}): calcd. for $C_{17}H_{18}N_{10}$: C 56.33, H 5.01, N 38.66; found C 56.43, H 5.16, N 38.41.

N^1,N^3-Bis(dimorpholinomethylene)propane-1,3-diamine, DMorphG_2p (L11–1): White powder, after recrystallisation colourless needles, yield: 71% (6.2 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.75 (q, 2 H, CH_2), 3.02–3.38 (br., 18 H, CH_2), 3.64–6.76 (m, 14 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 25.58, 44.0, 47.2, 48.5, 157.3 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 2967 (m), 2898 (m), 2844 (m), 1633 (vs) (C=N), 1600 (vs) (C=N), 1436 (s), 1386 (m), 1357 (m), 1268 (vs), 1228 (m), 1114 (vs) (C–O–C), 1027 (m), 883 (s), 601 (m) cm^{-1}. EI-MS: *m*/*z* (%) = 438.3 (6) $[M]^+$, 408 (11) $[M - CH_2O]^+$, 393 (12) $[M - CH_3CH_2O]^+$, 363 (21) $[M - 2(CH_2O)–(CH_3CH_2O)]^+$, 283 (13) $[M - C_3H_6NC(Morph)]^+$, 254 (6) $[M - C_6H_6NC(Morph)\text{-}(CH_2O)]^+$, 226 (14) $[M - CH_2NC(Morph)_2]^+$, 196 (42) $[M - C_3H_6NC(Morph)_2]^+$, 171 (17) $[M - CNC_3H_6NC(Morph)_2]^+$, 127 (61) $[M - CNC_3H_6NC(Morph)_2\text{-}C_3H_6]^+$, 86 (37) $[Morph]^+$. Elemental analysis (M = 438.3 gmol^{-1}): calcd. for $C_{21}H_{38}N_6O_4$: C 57.50, H 8.74, N 19.17; found C 57.31, H 8.97, N 18.87.

2-{2-[2-(Dimorpholinomethyleneamino)ethoxy]ethoxy}-*N*-(diorpholinomethylene)ethanamine, DMorphG_2doo (L11–2): White powder, after recrystallisation colourless needles, yield: 65% (6.7 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 3.1–3.3 (br., 16 H, Morph-CH_2), 3.41 (t, 4 H, CH_2, 3.61 (t, 4 H, CH_2), 3.66 (s, 4 H, CH_2), 3.69 (m, 16 H, Morph-CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 47.2 (Morph-CH_2), 48.3, 66.8 (Morph-CH_2), 67.1, 70.5, 163.8 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 2972 (m), 2893 (s), 2856 (s), 1647 m (C=N), 1621 (vs) (C=N), 1458 (m), 1413 (s), 1390 (s), 1360 (m), 1300 (m), 1265 (vs), 1228 (m), 1115 (vs) (C–O–C), 1070 (m), 1032 (s), 991 (w), 966 (w), 881 (s), 833 (w), 611 (w) cm^{-1}. EI-MS: *m*/*z* (%) = 512.6 (0.1) $[M]^+$, 426 (4) $[M - Morph]^+$, 314 (5) $[M - NC(Morph)_2]^+$, 270 (19) $[M - NC(Morph)_2\text{-}(CH_2)_2O]^+$, 226 (18) $[M - NC(Morph)_2 - 2(CH_2)_2O]^+$, 200 (22) $[(Morph)_2CNH_2]^+$, 169 (52), 127 (100), 114 (69), 86 (37) $[Morph]^+$, 70 (69) $[Morph\text{-}O]^+$. Elemental analysis (M = 512.3 gmol^{-1}): calcd. for $C_{24}H_{44}N_6O_6$: C 56.21, H 8.66, N 16.40; found C 56.10, H 8.87, N 16.64.

N^1,N^3-Bis[bis(thiomorpholino)methylene]propane-1,3-diamine, DSMorphG_2p (L12–1): Yellowish powder, yield: 66% (6.6 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 1.25 (q, 2 H, CH_2), 2.65 (m, 16, CH_2), 3.2 (m, 16 H, CH_2), 3.4 (t, 4 H, CH_2) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 13.5 (CH_2), 27.0 (SMorph-CH_2), 42.3 (SMorph-CH_2), 46.6 (CH_2), 158.0 (C_{gua}) ppm. IR (KBr): $\tilde{\nu}$ = 2969 (m), 2911 (m), 1733 (m), 1621 (vs) (C=N), 1533 (s), 1405 (s), 1374 (m), 1292 (m), 1251 (m), 1205 (m), 1170 (m) cm^{-1}. EI-MS: *m*/*z* (%) = 502.1 (23) $[M]^+$, 487 (76), 469 (98) $[M - S]^+$, 443 (45) $[M - SEt]^+$, 400 (33) $[M - SMorph]^+$, 384 (34), 298 (9) $[M - 2SMorph]^+$, 196 (23) $[M - 3SMorph]^+$, 143 (100) $[HN{=}C–SMorph]^+$, 102 (44) $[SMorph]^+$, 87 (38), 69 (30). Elemental analysis (M = 502.2 gmol^{-1}): calcd. for $C_{21}H_{38}N_6S_4$: C 50.18, H 7.63, N 16.73; found C 50.02, H 7.41, N 16.45.

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