Bicyclic-guanidines, -guanidinates and -guanidinium salts: wide ranging applications from a simple family of molecules†

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Bicyclic guanidines have physical, electronic and chemical properties that differentiate them from their acyclic counterparts, with many of these characteristics directly imposed by the rigid framework. These distinctive features have led to this class of molecule finding practical applications in many areas of chemistry, including organocatalysis and as ligands in coordination compounds. In addition to the neutral molecules, the corresponding cationic (guanidinium) and anionic (guanidinate) species have also been widely studied. Applications of these ions range from anion recognition and supramolecular arrays involving guanidinium salts, to the utilization of bicyclic guanidinate anions as ligands for metal compounds and clusters. This article reviews the chemistry of these compounds in light of recent advances in the synthesis of new derivatives, highlighting the potential for cross-stimulation of different areas.

Introduction

Substituted guanidines, in which the carbon of the central CN_3 unit is incorporated into a bicyclic framework fused along one C–N bond (**1**, Fig. 1), display physical, electronic and chemical characteristics that distinguish them from their acyclic analogues. As a consequence, compounds conforming to these general criteria have been employed in many fields of chemistry, and interest in their application in new areas continues to emerge. The systematic naming schemes for non-substituted bicyclic guanidines are presented in Table 1,‡ incorporating both the von Baeyer[1] and the IUPAC nomenclatures;[2] we also find it convenient to describe these compounds as {*m*,*n*}-bicyclic guanidines (**1**), defining the size of the component heterocyclic rings (where $m > n$).

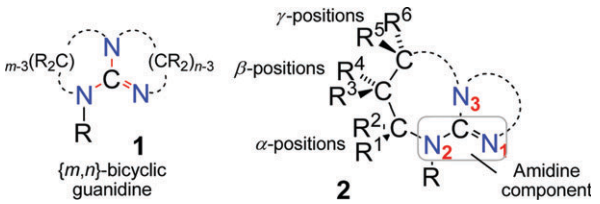

Fig. 1 Generic bicyclic guanidines defining parameters in this article.

This class of compound has several common structural features, illustrated for the generic example, **2**. The amidine component, consisting of the localized ''N(2)–C=N(1)' fragment in neutral guanidines, is the position at which most chemistry exhibited by these molecules occurs, although the tertiary nitrogen, N(3), plays an important role in defining the electronic and physical attributes of the guanidines. In this article we have restricted our discussion to molecules in which the remaining constituent atoms of each ring are sp^3-carbon atoms, differentiating these compounds from related nitrogen ligand systems.[3] We describe the carbon atoms adjacent to the amidine nitrogens within each ring as the α- and α′-positions, respectively, with the sequence β-/β′-, γ-/γ′- used sequentially for larger rings (**2**).

Consequences of the bicyclic framework

The influence that the bicyclic framework exerts over the steric and electronic properties of the guanidines can be summarized in three main areas:

• A defining characteristic of guanidines is their ability to effectively distribute charge throughout the molecule, either

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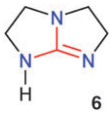
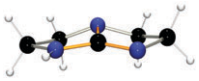
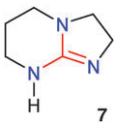
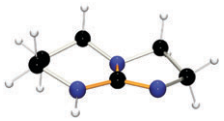
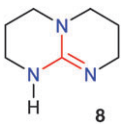
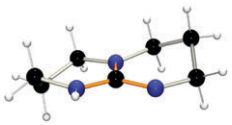
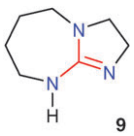
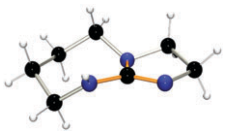
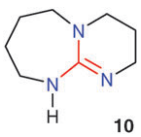
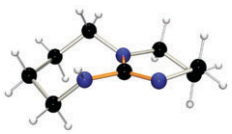
† Electronic supplementary information (ESI) available: von Baeyer nomenclature for bicyclic guanidines. See DOI: 10.1039/b901940e

‡ Some ambiguity over the correct von Baeyer nomenclature for the bicyclic guanidines exists in the literature, and this article seems an appropriate vehicle for clearing up any confusion. A short document has therefore been included as ESI describing the correct convention for the naming of these compounds.

Martyn Coles

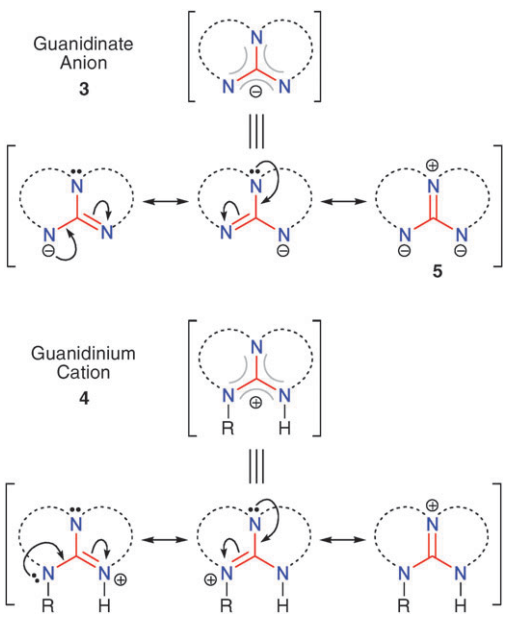
Martyn Coles received his BSc from the University of Durham in 1992. After completing his PhD with Prof. Vernon C. Gibson at the same institution, he travelled to the US for post-doctoral work with Prof. Richard F. Jordan and Prof. T. Don Tilley. In 1999 he returned to the UK to a faculty position at the University of Sussex, where he is currently a senior lecturer. His research interests lie primarily in the development of novel ligand systems for a range of applications. He has been involved with the chemistry of bicyclic guanidines since the beginning of his independent research career and continues to exploit their unique properties in his work.

Table 1 Structure and naming schemes for the non-substituted bicyclic {*m*,*n*}-guanidines, and X-ray structural projection illustrating steric profile

Chemical structure	von Baeyer name	IUPAC name	Abbreviation	X-Ray projection	{*m*,*n*}-	Ref.
 **6**	1,4,6-Triaza-bicyclo-[3.3.0]oct-4-ene	2,3,5,6-Tetrahydro-1*H*-imidazo[1,2-*a*]imidazole	H-tbo		{5,5}-	4
 **7**	1,5,7-Triaza-bicyclo-[4.3.0]non-6-ene[b]	2,3,5,6,7,8-Hexahydroimidazo[1,2-*a*]pyrimidine	H-tbn		{6,5}-	4
 **8**	1,5,7-Triaza-bicyclo-[4.4.0]dec-5-ene	1,3,4,6,7,8-Hexahydro-2*H*-pyrimido[1,2-*a*]pyrimidine	H-hpp[a]		{6,6}-	5
 **9**	1,6,8-Triaza-bicyclo-[5.3.0]dec-7-ene[c]	2,5,6,7,8,9-Hexahydro-3*H*-imidazo[1,2-*a*][1,3]diazepine	H-tbd		{7,5}-	6
 **10**	1,6,8-Triaza-bicyclo-[5.4.0]undec-7-ene[d]	2,3,4,6,7,8,9,10-Octahydropyrimido[1,2-*a*]-[1,3]diazepine	H-tbu		{7,6}-	6

[a] In this article, the abbreviation adopted for the {6,6}-bicyclic derivative (H-hpp) is taken from the IUPAC, rather than the von Baeyer naming scheme, which avoids confusion with the isomeric {7,5}-derivative, for which the van Baeyer abbreviation, H-tbd, is used. [b] Incorrectly referred to as 1,4,6-triazabicyclo[3.4.0]non-4-ene in the original reference. [c] Incorrectly referred to as 1,4,6-triazabicyclo[3.5.0]dec-4-ene in the original reference. [d] Incorrectly referred to as 1,5,6-triazabicyclo[3.5.0]undec-5-ene in the original reference.

negative for guanidinate anions **3**, or positive for guanidinium cations **4** (Scheme 1). From a simple orbital description, this is determined by the extent of overlap between the nitrogen lone-pairs and the empty p-orbital of the sp^2-carbon within the CN_3 unit. Constraining the substituents of the non-amidine nitrogen atom N(3) into the ring system generates a favourable alignment for the lone-pair of this atom to be included in the delocalization scheme. This contrasts with acyclic guanidines where steric interactions play a dominant role, often favoring an orthogonal displacement of the N(3) substituents with respect to the CN_2 amidine unit (**11**).



Scheme 1 Localized and delocalized forms of the guanidinate anion (**3**) and the guanidinium cation (**4**).

- Constraining the nitrogen substituents into the ring system generates a rigid framework with reduced rotational freedom about the C–N bonds, and no possible isomerization of the C=N double bond. For tetra-substituted derivatives this effectively locks the substituents in the E_{anti} conformation

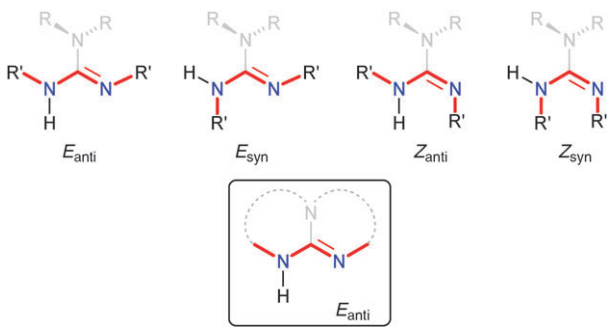


Fig. 2 Different orientations of nitrogen substituents in tetra-substituted guanidines, including a generic bicyclic example.

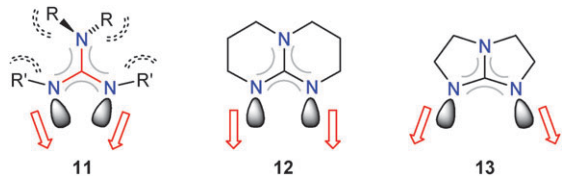


Fig. 3 Projection of frontier orbitals for acyclic guanidines compared with the {6,6}- and {5,5}-bicyclic derivatives.

(Fig. 2), defining a specific orientation of the N–H bond. The rigid framework has also been exploited in the preparation of chiral variants of these molecules for catalytic applications with selective incorporation of substituents at the annular C-atoms, in particular the α- and α′-positions.

• Defining the size of the rings imposes a further geometric constraint on the molecule, which dictates the projection of the frontier orbitals of the amidine nitrogen atoms (Fig. 3). For guanidinate anions this has an important bearing on coordination at metals and for neutral guanidines and guanidinium cations it will influence the direction of any NH···X hydrogen-bonding interactions. This is in contrast with acyclic guanidines, where the bulk of the nitrogen substituents most strongly influences the direction of orbital projection, often favoring a confluence at the 'mouth' of the amidine (**11**). Table 1 includes the molecular structures of unsubstituted bicyclic guanidines viewed from slightly above the C–N(3) vector. Acknowledging that these projections are generated from solid-state structures, it is clear that different size rings have different spatial requirements even before substitution of the annular carbons, which will influence their interactions with other chemicals.

Naturally occurring bicyclic guanidines

The majority of compounds described in this article are the product of research into a specific area of chemistry. However, it is noted that a selection of naturally occurring molecules incorporate bicyclic (and tricyclic) guanidine frameworks.[7] Examples include the relatively simple {5,5}-based system (±)-isoalchorneine (**14**), an alkaloid isolated from the South African plant *Alchornea hirtella*,[8] and several more exotic families of biomolecules including crambescidins (cytotoxic/anti-viral)[9] and batzelladines (anti-HIV),[10] shown to be metabolites from the parent alkaloid, ptilomycalin A (**15**), Fig. 4.[11] The total synthesis of these compounds has been the driving force behind some of the major advances made in the synthesis of bicyclic guanidines.

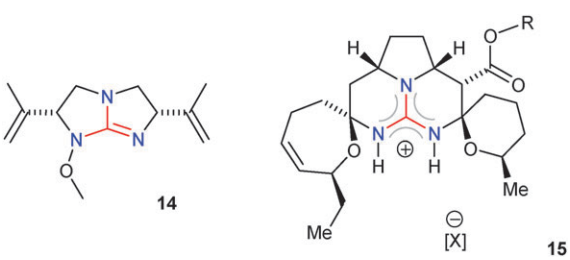


Fig. 4 Natural products containing cyclic guanidine components (**15**, R = $-(CH_2)_{15}C(O)N\{(CH_2)_4NH_2\}\{(CH_2)_3NH_2\}$).

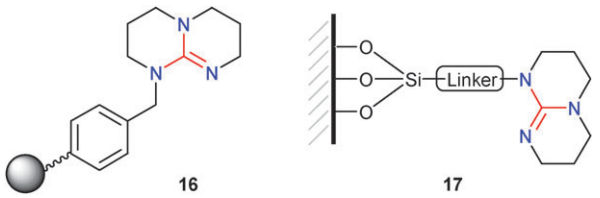


Fig. 5 Bicyclic guanidines on solid-supports: **16** polystyryl supported; **17** silica (*e.g.* MCM 41) supported.

Supported bicyclic guanidines

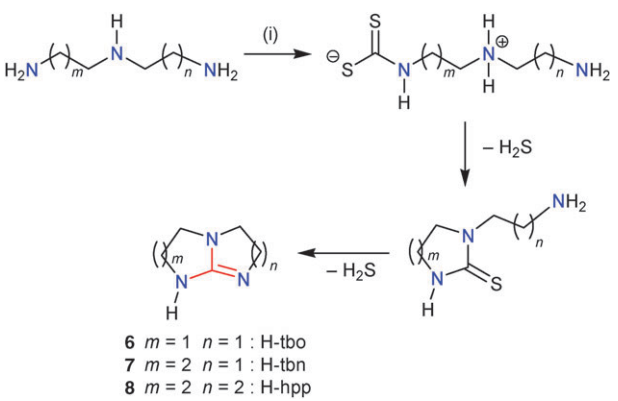
A potentially useful development in the chemistry of bicyclic guanidines is the attachment of the molecule to a solid-support at the N(2) position. Examples employing both organic (**16**) and inorganic (**17**) supports are known and selected materials are commercially available, although to date these compounds are restricted to the {6,6}-bicyclic skeleton (Fig. 5). The application of these reagents in organocatalysis is described in more detail below.

Neutral guanidines

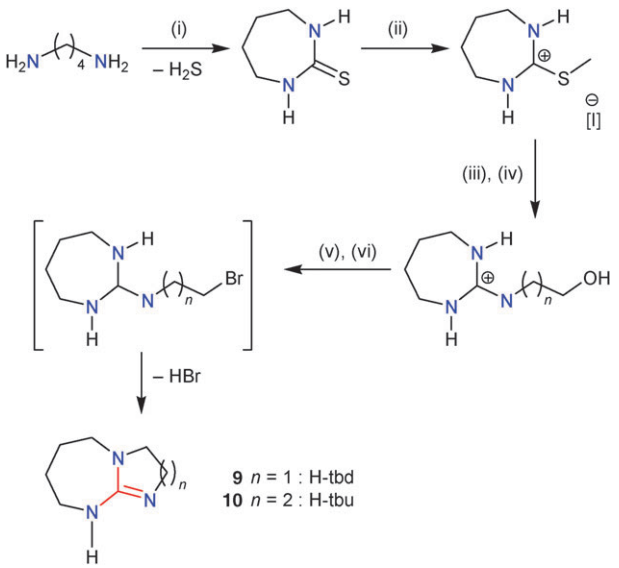
Synthesis of non-substituted derivatives

Initial publications detailing the syntheses of non-functionalized bicyclic guanidines involved either multi-step procedures,[12] or the use of expensive starting reagents,[13] and as such these molecule remained an academic curiosity for a number of years. However, a simple one-pot procedure to the {6,6}- and {5,5}-guanidines, H-hpp (**8**) and H-tbo (**6**), which lead to the commercial availability of the former compound, was published in the patent literature in 1990 (Scheme 2),[5] driven by an interest in the application of these compounds in organocatalysis.[14] Extension of this synthetic procedure to the non-symmetric {6,5}-bicyclic example, H-tbn (**7**), has recently been presented, from the reaction of CS_2 with *N*-(2-aminoethyl)-1,3-propanediamine.[4]

A multi-step procedure for the synthesis of non-functionalized guanidines incorporating seven-membered rings, {7,*n*}-guanidines (n = 5 and 6), has been reported (Scheme 3).[6] The larger ring is synthesized in the first stage from CS_2 and 1,4-diaminobutane, and formation of the second ring occurs through a series of reactions in which the C=S group is initially converted to the more reactive methylmercapto group. The size of the second



Scheme 2 (i) CS_2, *p*-xylene, reflux.



Scheme 3 (i) CS_2, EtOH–H_2O, reflux; (ii) MeI, EtOH, reflux; (iii) $H_2N(CH_2)_nOH$, EtOH, reflux; (iv) KOH, reflux; (v) PBr_3, $CHCl_3$, reflux; (vi) KOH, MeOH, reflux.

ring is determined by the chain length of the amino alcohol, with the second cyclization sequence proceeding *via* bromination and dehydrohalogenation with KOH.

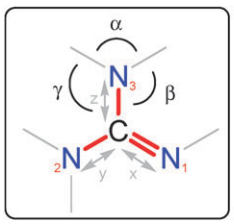
Structure of non-substituted derivatives

The availability of X-ray diffraction data for the complete series of {*m*,*n*}-bicyclic guanidines enables comparison of key structural features (Table 2). The parameters are defined in Fig. 6 and are described in more detail elsewhere.[15–17] For each molecule, a similar distribution of carbon–nitrogen bond distances is observed in the amidine component, with clearly defined C=N(1) and C–N(2) bonds. However, a significant range of values for the degree of pyramidalization (DP%) is noted for N(3), which effects the Δ'_{CN} value (used as a measure of the contribution of the N(3) lone-pair to the delocalization scheme). The presence of the five-membered ring in H-tbo, H-tbn and H-tbd (n = 5) prevents tertiary nitrogen N(3) from attaining a planar configuration (higher DP% values), consistent with retention of electron density at this position. This reduces any delocalization throughout the CN_3 core of these neutral compounds, resulting in the larger Δ'_{CN} values. The synthetic routes to these derivatives have only recently been published,[4,6] and the consequences of these differences in delocalization have yet to be explored. It will, however, clearly

Table 2 Summary of structural parameters for non-substituted bicyclic guanidines (as defined in Fig. 6)

Abbreviation	{*m*,*n*}-	Δ_{CN}/Å	Δ'_{CN}/Å	DP% N(3)
H-tbo **6**	{5,5}-	0.048	0.070	26.58
H-tbn **7**	{6,5}-	0.057	0.065	18.19
H-hpp **8**	{6,6}-	[a]	0.038	0.11
H-tbd **9**	{7,5}-	0.062	0.069	20.74
H-tbu **10**	{7,6}-	0.090	0.034	4.20

[a] Disorder in the N*H* position precludes meaningful discussion of carbon–nitrogen bond distances in the amidine component of H-hpp.



$$\Delta_{CN}\,/\,\text{Å} = y - x$$

$$\Delta'_{CN}\,/\,\text{Å} = z - [\{x + y\}\,/\,2]$$

$$\text{DP}\,\% = [360 - (\alpha + \beta + \gamma)]\,/\,0.9$$

Fig. 6 Definition of parameters used in the comparison of structural data taken from bicyclic guanidines.

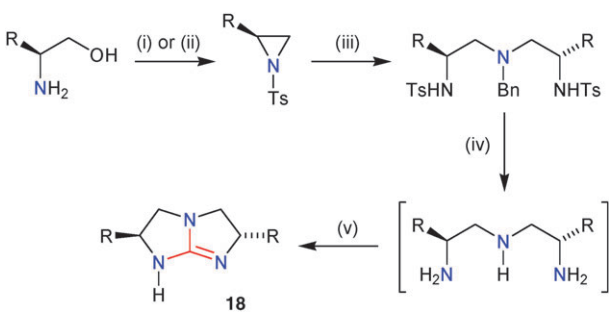
impact not only the neutral forms of these compounds but also their positive and negative ions (Scheme 1), predicted to result in differences in chemical behaviour.

Synthesis of substituted derivatives

Many applications of bicyclic guanidines rely on additional substituents decorating the carbon skeleton, and often the synthetic goal is to introduce chirality *via* asymmetric substitution of the annular methylene groups. To attain enantiomerically pure products, elaborate syntheses have been developed, primarily involving the use of chiral synthons in the construction of the target molecules. As the chemistry associated with these compounds occurs mainly through the amidine nitrogen atoms, the main synthetic targets are the α,α′-di-substituted derivatives.

The first general synthetic route to chiral C_2-symmetric bicyclic guanidines was published by Corey and Ohtani in 1989,[18] which described the synthesis of the {5,5}-derivative (**18**, R = Cy) using D-(−)-α-phenylglycine methyl ester as the chiral source. This procedure was modified ten years later to give the α,α′-diphenyl derivative (**18**, R = Ph) in a nine-step synthesis.[19] More recently an efficient five-step route involving stereoselective ring-opening of azirdines has been developed (Scheme 4), affording α,α′-di-substituted examples in yields up to 71%.

Synthetic protocols to yield {5,5}-derivatives with different substitution patterns have also been developed. For example, the tri-substituted α,α′,β- and N(2),β,α′-bicyclics, **19** and **20**, were investigated as potential (chiral) superbases, Fig. 7.[20] The synthesis of these derivatives proceeded *via* a thiourea intermediate that was reacted with 2-chloro-1,3-dimethylimidazolium chloride in a stepwise cyclization sequence. Using



Scheme 4 (i) R = Bn, ^{i}Pr: TsCl, NEt_3, MeCN; (ii) R = ^{t}Bu: TsCl, NEt_3, MeCN, 4 Å mol. sieves, 0 °C, then MsCl, NEt_3, DMAP, CH_2Cl_2; (iii) BnOH, MeOH, 60 °C; (iv) (a) Na/NH_3(l), THF, (b) H_2, Pd/C, MeOH; (v) $(MeS)_2C{=}S$, then MeI–AcOH, $MeNO_2$, reflux.

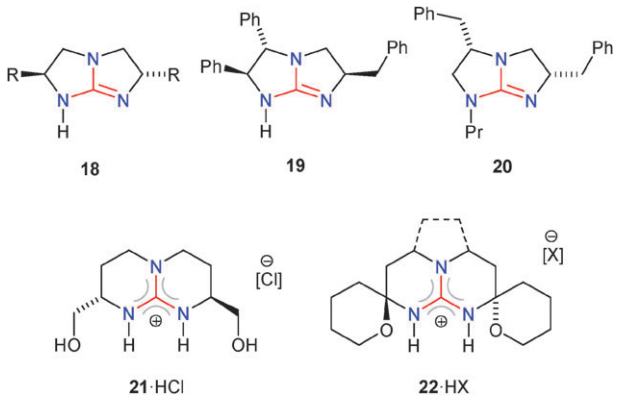


Fig. 7 Examples of chiral bicyclic guanidines based on the {5,5}- and {6,6}-frameworks. Dotted lines in **22**·HX represent extension to the pentacyclic derivative.

a resin-bound approach, reduction of *N*-acylated dipeptides to generate the corresponding triamines, and their subsequent cyclization provided a route to N(2),α,β′-substituted {5,5}-derivatives.[21] Using this methodology individual compound and mixture-based combinatorial libraries of more than 100 000 compounds were reported.

In 1988 a multi-step synthesis of bicyclic guanidines based on the {6,6}-framework (**21**) was reported.[22] Although an overall yield of only 5.1% was reported, the use of asparagine represented an economical and efficient method of introducing the chiral centre without the need for resolution of the final product. Furthermore, the presence of the benzyl alcohol groups in the α-positions enabled further functionalization of this molecule, affording many examples with different substituents chosen to fulfil particular chemical requirements (*vide infra*).

A different class of chiral {6,6}-derivative that originated from work towards the total synthesis of ptilomycalin A (**15**) is tetra-substituted in the α-positions, with spirocyclic carbon atoms linking to tetrahydropyran rings (**22**). The tetracyclic derivative was initially reported from the conjugate addition of guanidine to a vinyl ketone,[36] with subsequent modifications to the synthesis, affording substituted examples.[37] Related optically active pentacyclic derivatives have also been developed for organocatalysis, in which the final cyclization sequence involved double *N*,*O*-acetalization of a guanylated dihydroxy–diketone intermediate.[38,39]

Coordination chemistry

Coordination chemistry of neutral bicyclic compounds has been almost exclusively restricted to the parent {6,6}-derivative, H-hpp.[40] Bonding occurs *via* donation of the N_{imine} lone-pair to an electronically unsaturated centre, supporting a range of different coordination geometries (Table 3). Most synthetic routes involve the direct combination of the neutral guanidine with a suitable metal precursor, which may proceed *via* displacement of an existing ligand at the metal (*e.g.* $PdCl_2(COD)$, $Mo(CO)_6$) indicating a strong coordination of the guanidine.

An important consequence of the rigid E_{anti} conformation in tetra-substituted bicyclics (Fig. 2) is the position of the N*H* atom relative to other atoms in the coordination sphere of the metal. In this configuration, stabilization of the guanidine adduct may occur through intramolecular hydrogen bonding to additional ligands (Fig. 8), which has been demonstrated structurally for halide,[23] alkoxide,[28] and guanidinate[17,30] co-ligands. The ability of {*m*,*n*}-ligands other than H-hpp to participate in this 'synergic' type of bonding has not been investigated, but will be dependent on the projection of the N–H bond relative to potential donor X-atoms. Despite this additional interaction, such complexes may still be fluxional in solution, as observed from VT NMR data for the copper adduct $CuCl(H\text{-hpp})_2$.[23]

The influence of this intramolecular hydrogen bond on the molecular structure of the compound was probed in a series of Cu(I) complexes containing the N(2)-substituted {6,6}-derivatives Me-hpp and Me_3Si-hpp.[24] Whereas H-hpp gave the bis-adducts $CuX(H\text{-hpp})_2$,[23] the *N*-methyl derivative resulted in either the ionized species $[Cu(Me\text{-hpp})_2][CuCl_2]$ or the mono-adduct $[CuI(Me\text{-hpp})]_2$, indicating that the halide also plays a role in the structural type adopted. Increasing the bulk of the *N*-substituent to a trimethylsilyl group prevented two

Table 3 Summary of metal complexes containing neutral R-hpp ligands (R = H, Me, $SiMe_3$) that have been characterized crystallographically

Geometry	Metal	Formula	Ref.
Linear	Cu(I)	$[Cu(H\text{-hpp})_2][I]$[a]	23
	Cu(I)	$[Cu(Me\text{-hpp})_2][CuCl_2]$	24
	Cu(I)	$CuCl(Me_3Si\text{-hpp})$	24
Trigonal planar	Cu(I)	$[Cu(CN)(H\text{-hpp})]_\infty$	25
	Cu(I)	$CuX(H\text{-hpp})_2$ (X = Cl, Br, I[a])	23
	Cu(I)	$[CuI(Me\text{-hpp})]_2$	24
	Cu(I)	$CuCl(H\text{-hpp})(PPh_3)$	26
	Ag(I)	$AgCl(H\text{-hpp})_2$	26
Tetrahedral	Cu(I)	$CuX(H\text{-hpp})(PPh_3)$ (X = Br, I)	26
	Cu(II)	$L_2(H\text{-hpp})Cu(\mu\text{-}CN)Cu(CN)L_2$[b]	25
	Fe(II)	$FeCl_2(H\text{-hpp})_2$	27, 28
	Mn(II)	$MnCl_2(H\text{-hpp})_2$	28
	Ni(II)	$NiCl_2(H\text{-hpp})_2$	28
	Zn(II)	$ZnBr_2(H\text{-hpp})_2$	28
	Co(II)	$CoCl_2(H\text{-hpp})_2$	28, 29
	Li(I)	$[LiCl(H\text{-hpp})]_2$	26
		$[Li(hpp)(H\text{-hpp})]_2$	30
		$[Li(OSiPh_3)(H\text{-hpp})(THF)]_2$	28
Square planar	Pd(II)	$PdCl_2(H\text{-hpp})_2$	27
	Pt(II)	$PtCl_2(H\text{-hpp})_2$	31
	Pt(II)	$[PtCl(H\text{-hpp})_3][Cl]$	31
Octahedral	Mo(0)	$Mo(H\text{-hpp})_3(CO)_3$	32
	M(0)	$M(H\text{-hpp})_2(CO)_4$ (M = W, Mo)	33
	Rh(II)	$Rh_2(O_2CMe)_4(H\text{-hpp})_2$	34
	Pt(IV)	$Pt(hpp)(NHC(O)Me)Cl_2(H\text{-hpp})$	35

[a] $CuI(H\text{-hpp})_2$ crystallized with eight molecules in the unit cell, three containing trigonal copper (*i.e.* $CuI(H\text{-hpp})_2$) and the remaining five in the ionized form (*i.e.* $[Cu(H\text{-hpp})_2][I]$) with a linear coordination geometry at copper. [b] L = PPh_3.

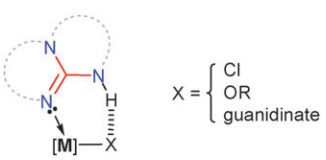
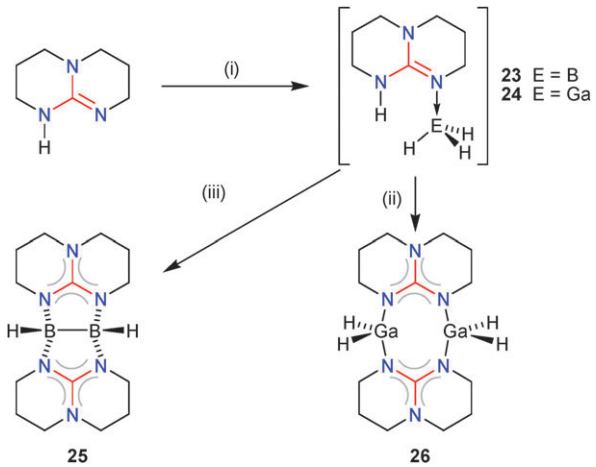


Fig. 8 Intramolecular hydrogen bonding observed in coordinated guanidines.



Scheme 5 (i) $H_3E{\cdot}NMe_3$, Et_2O, −78 °C; (ii) E = Ga, room temperature (decomposition); (iii) reflux, toluene, 20 h.

guanidines from bonding to the copper, affording the monomer, CuCl(Me$_3$Si-hpp).

Many H-hpp adducts were originally targeted as precursors to complexes containing metal–metal bonds (*vide infra*) in an analogous route to that successfully demonstrated for amidine containing compounds.[41] Conversion to the guanidinate anion could be achieved by reaction with lithium alkyls, although formation of metal–metal bonds using this approach was shown to be highly dependent on reaction conditions.[29]

Himmel and co-workers have recently reported the H-hpp adducts of group 13 hydrides, H-hpp·EH$_3$, accessed by displacement of trimethylamine from $H_3E{\cdot}NMe_3$ (Scheme 5).[42,43] Formation of boron adduct **23** involved prolonged heating to 60 °C, and structural analysis of the crystalline product revealed both intra- and intermolecular H···H contacts. In contrast the proposed gallane adduct, $H_3Ga{\cdot}$(H-hpp) **24**, is thought to decompose directly to afford the dinuclear compound [H_2Ga(μ-hpp)]$_2$ (**26**).[43,44] Computer modelling has been used in conjunction with the synthetic studies, showing that the position of the N*H* atom is important in determining the energy barrier to hydrogen elimination, and that intramolecular H···H contacts play a crucial role in this reactivity.[45]

We have recently reported the first examples of complexes in which the neutral {5,5}-guanidine functions as a ligand.[17] The mixed lithium imidazolinethionate–guanidinate salt [{Li$_2$(tbo)(**L**)(H-tbo)}$_2$]$_\infty$ (**27**, H–**L** = 1-(2-aminoethyl)-2-imadazolidinethione) forms a polymeric chain in the solid-state whilst the molecular complex Li$_6$(tbo)$_6$(H-tbo), **28**, contains a 'folded-ladder' structure of six lithium atoms held together by the [tbo]$^-$ guanidinate anions (Fig. 9). Comparing bond parameters within the H-tbo ligand with the corresponding values for structurally characterized H-hpp complexes suggested a significant reduction in electron delocalization within the CN$_3$-core of the guanidine. This is most clearly shown by large DP% values for N(3) in **27** and **28** (typically: 0–2° for H-hpp; 25–30° for H-tbo) and has been examined by natural bond orbital (NBO) analysis using density functional theory (DFT). Further work is required to fully assess the effect that the different electronic structure of H-tbo has on its

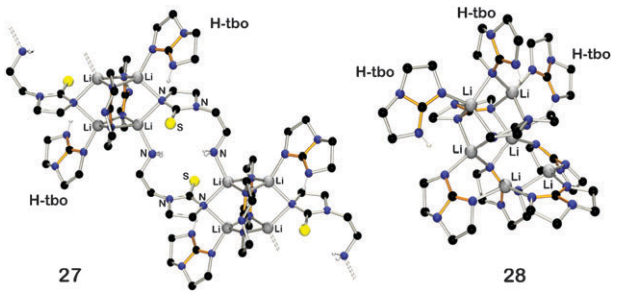


Fig. 9 Crystal structure of lithium salts containing the neutral {5,5}-guanidine as a ligand.

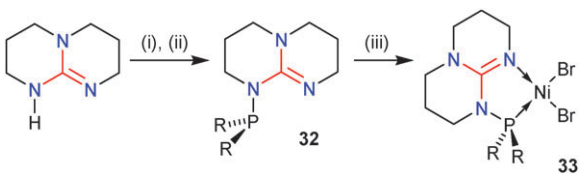
coordinating ability, and the behaviour of the other members of the series of bicyclic guanidines (**6–10**) in this context remains to be determined.

Bridged systems incorporating neutral bicyclic guanidines

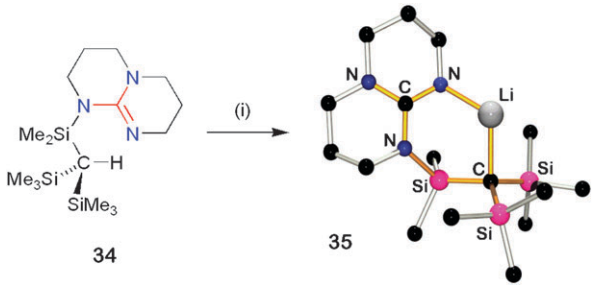
We recently targeted compounds incorporating more than one bicyclic guanidine, in which the integrity of the imine groups was retained for subsequent coordination to metal fragments. Building on work by Kummer *et al.*, in which they investigated the reactivity of Me$_3$Si-hpp,[46] a general synthetic procedure was developed in which the [hpp]$^-$ anion was quenched by a halide containing reagent that would form the constituent atom of the bridging group. Initial work with silicon-bridged systems demonstrated that the bis{guanidyl} compound Me$_2$Si{hpp}$_2$ (**29**) was a suitable precursor to a chelating ligand at copper, whereas the tris{guanidyl} compound did not afford a clean coordination compound.[47] Spectroscopic studies of bis{guanidyl} **29** and its copper complex, CuCl(Me$_2$Si{hpp}$_2$) **30**, indicated fluxional systems whereby the two six-membered rings of the hpp-framework were equivalent by ^{1}H NMR spectroscopy. The methylene-bridged compound H$_2$C{hpp}$_2$ **31** was, however, non-labile in solution, and was shown to coordinate to trigonal planar [Cu(I)], tetrahedral [Fe(II)] and square planar [Pd(II)] metal centres.[27] Coordination at a cationic aluminium centre has also been reported,[48] although a different synthetic strategy was employed in the synthesis of this compound (*vide infra*).

A series of compounds that combine the {6,6}-bicyclic guanidine with an N-bound phosphine donor to afford κ*P*,κ*N*-ligands have been recently reported (**32**, Scheme 6).[49] The R$_2$P-hpp ligands were complexed at nickel and the resultant compounds (**33**) were investigated as precatalysts for the oligomerization of ethylene, with the derivative containing ^{i}Pr$_2$N-substituents at phosphorus showing reasonable selectivity to C$_4$ products.

We have also developed a bulky heteroditopic mono-anionic ligand system with hpp replacing one of the methyl



Scheme 6 (i) ^{n}BuLi, Et_2O, −78 °C; (ii) R_2PCl, Et_2O, −78 °C; (iii) $NiBr_2$(DME), CH_2Cl_2, reflux.



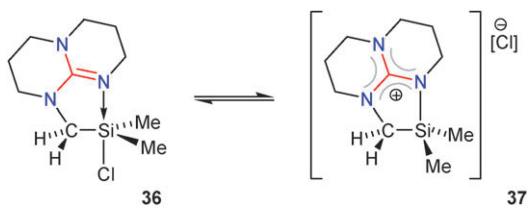
Scheme 7 (i) MeLi, hexanes.

groups in tris(trimethylsilyl)methane (**34**).[50] Deprotonation of the central carbon in the absence of donor solvent molecules affords the organolithium **35**, which crystallizes as the base-free compound containing an unusual two-coordinate lithium (Scheme 7). This compound has been successfully used in the synthesis of a range of organometallic complexes which, on the basis of a short N_{imine} to metal bond, indicate a strongly bound guanidine moiety in the chelating κ*C*,κ*N*-ligand.[51] The ligand forms a six-membered metallacycle that is sterically more bulky than related $-NMe_2$[52] and 2-pyridyl[53] derivatives, allowing access to novel organometallic compounds, such as the recently reported zinc hydride cluster, $R_4Zn_5(H)_6$ (RH = **34**).[51]

Nucleophilic chemistry of bicyclic guanidines

Despite the basic behaviour of bicyclic guanidines dominating their chemistry, on occasion nucleophilic reactivity has also been observed.[54] Early work involving the reaction of X-hpp (X = $SiMe_3$, Me) with a series of chlorosilanes noted a pentacoordinate silicon in the structurally characterized compound chloro-dimethyl-(3,4,7,8-tetrahydro-2*H*,6*H*-pyrimido-[1,2-*a*]pyrimidin-1-yl-methyl-C^1,N^9)-silicon (**36**). However, the four-coordinate silicon species (**37**) was identified in solution, resulting from ionization of an Si–Cl bond (Scheme 8).[46]

We have recently noted that $H_2C\{hpp\}_2$ (**31**) reacted with a range of alkyl halides to afford the corresponding dication, $[H_2C\{hppR\}_2]^{2+}$.[55] The product from the reaction with dichloromethane was structurally determined as the unusual C_4N_4-heterocycle, $[H_2C\{hpp\}_2CH_2]^{2+}$, **38**. This compound crystallizes as a *pseudo*-chair (Fig. 10), although other conformations for the eight-membered ring were identified in solution and by computational analysis. Extension of this reactivity to phosphorus halide substrates afforded the corresponding *P*-heterocycle, $[H_2C\{hpp\}_2PPh]^{2+}$ (**39**), which, despite the formal dipositive charge at phosphorus, was shown to coordinate to platinum.[56] The scope of this reactivity has yet to be fully explored, but given the ability of the guanidyl groups to temper the reactivity by 'absorbing' the positive



Scheme 8 Nucleophilic attack of the hpp-unit at silicon.

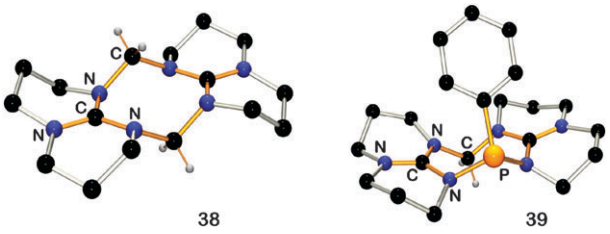


Fig. 10 Dicationic heterocycles resulting from nucleophilic attack of an hpp-unit at CH_2Cl_2 (**38**) or $PhPCl_2$ (**39**).

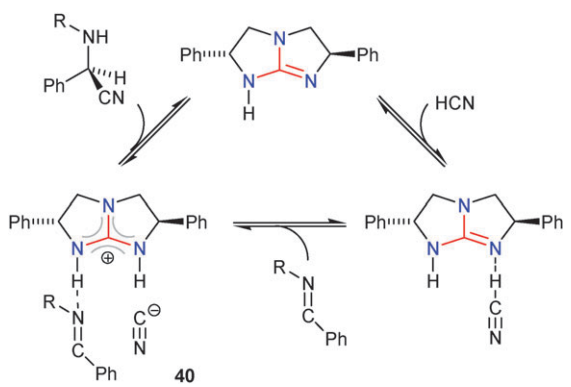
charge of the bridging cationic atom, further applications are likely to be forthcoming.

Organocatalysis

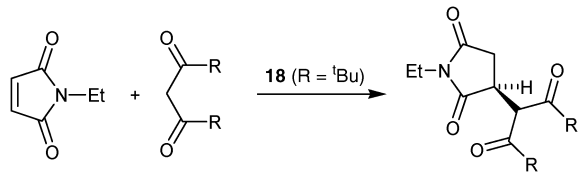
One of the primary forces motivating research into the chemistry of bicyclic guanidines has been their application as organocatalysts, primarily utilizing their high basicity in addition reactions or for kinetic resolution.[57] Advantages over more widely used ionic bases include ease of handling and mildness of reaction conditions. To date their efficacy has been demonstrated in many transformations, and examples of new reactions in which this class of compound plays a catalytic role continue to be reported in the current literature. Early work demonstrated that the chiral {5,5}-derivative **18** (R = Ph) was effective in the enantioselective Strecker synthesis of chiral α-amino nitriles.[19] A bifunctional mechanism was evoked involving a single pre-transition-state assembly **40**, consisting of the guanidine, HCN and the aldimine (Scheme 9). This mechanism was later investigated computationally, ruling out the possibility of aminoisoacetonitrile formation.[58]

Shortly after this report appeared in the literature, it was shown that unsubstituted H-hpp and Me-hpp were active in the nitroaldol (Henry) reaction.[59] Tetracyclic guanidines **22** were also shown to catalyze this reaction,[37] although only low (~20%) ee's were obtained. More recently H-hpp and Me-hpp have been developed for the aza-Henry reaction of ketimines, where it was shown that the *N*-diphenylphosphinoyl protecting groups were necessary to furnish the desired product.[60]

The use of H-hpp and Me-hpp as catalysts in the direct Michael addition or Michael-type conjugate reaction was investigated as recently as 2005,[61] although previous reports



Scheme 9 Synthesis of chiral α-amino nitriles catalyzed by an α,α′-di-substituted {5,5}-bicyclic guanidine.



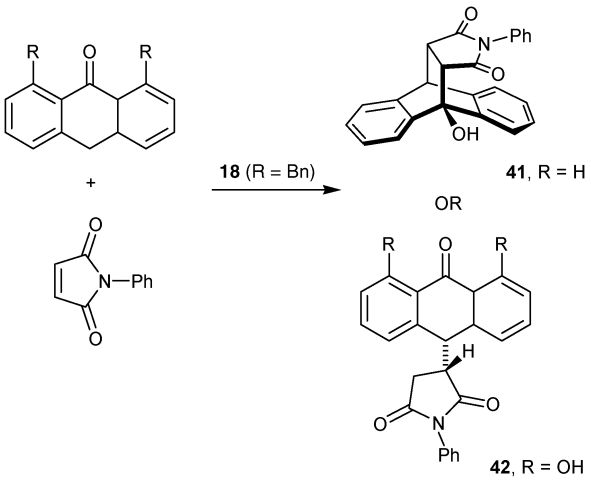
Scheme 10 R = S′Bu: 10 mol% cat., −50 °C, 6 h, 98% yield, 95% ee; R = Ph: 20 mol% cat., −50 °C, 60 h, 99% yield, 92% ee.

of the hetero-Michael reaction involving conjugate addition of pyrrolidine to unsaturated lactones catalyzed by **22** appeared in earlier reports.[36,39] Recent work has focussed on the use of chiral {5,5}-derivatives.[62] By avoiding the use of organometallic catalysts which would be poisoned by these reagents, high enantioselectivity has been achieved in the Michael reactions of dithiomalonates and β-keto thioesters (Scheme 10). Using non-sulfur containing β-keto esters slowed the reaction considerably, although good yields and ee's were also recorded.

The catalytic formation of P–C bonds is of synthetic interest and the direct addition of P(O)–H bonds to activated alkenes has been shown to be catalyzed by H-hpp.[63] During this study a one-pot, three component reaction involving diphenylphosphinite, malononitrile and an aldehyde was catalyzed effectively by H-hpp, affording the corresponding tri-substituted phosphine oxide in yields of up to 97%. Using the chiral {5,5}-bicyclic **18** (R = ^{t}Bu) as catalyst, phospha-Michael reactions of diaryl phosphine oxide and nitroalkenes afforded chiral α-substituted β-aminophosphine oxides and β-aminophosphines with excellent ee's.[64] Further work involving phosphorus reagents has shown that H-hpp and Me-hpp promote the Wittig reaction, providing a practical alternative to ionic base-promoted procedures.[65]

Green aspects of guanidine-promoted chemistry have been explored by examining the potential for catalysis under solvent-free conditions (SFC). H-hpp was shown to be a suitable base-catalyst for the synthesis of symmetric *N*,*N*′-substituted ureas under SFC,[66] and is also an active catalyst for the aminolysis of esters in the presence of various amines.[67] The utilization of CO_2 as a carbon resource also represents an important target for chemists, and a recent report has demonstrated that H-hpp is active as a catalyst for the synthesis of propylene carbonate (PC) from propylene glycol and carbon dioxide.[68] In this case acetonitrile solvent was important for the removal of the water side product, and it was shown that addition of ammonium carbonate as the coupling reagent optimized conditions giving an overall yield of 15.3% PC with 100% selectivity. It is also noted that the {6,5}-bicyclic guanidine, H-tbn, reacts with atmospheric water and CO_2 to afford the structurally characterized bicarbonate salt, [H-tbnH][HCO_3].[4]

Other areas in which bicyclic guanidines have been utilized include asymmetric silylation of secondary alcohols using {5,5}-derivatives **19**,[69] and the direct 5- and 6-*enolexo* aldolization of ketoaldehydes promoted by R-hpp (R = H, Me).[70] The Brønsted base-catalyzed Diels–Alder reaction between anthrones and various dienophiles was demonstrated for the first time using **18** (R = Bn) as catalyst.[71] Examples of both Diels–Alder (**41**) and Michael

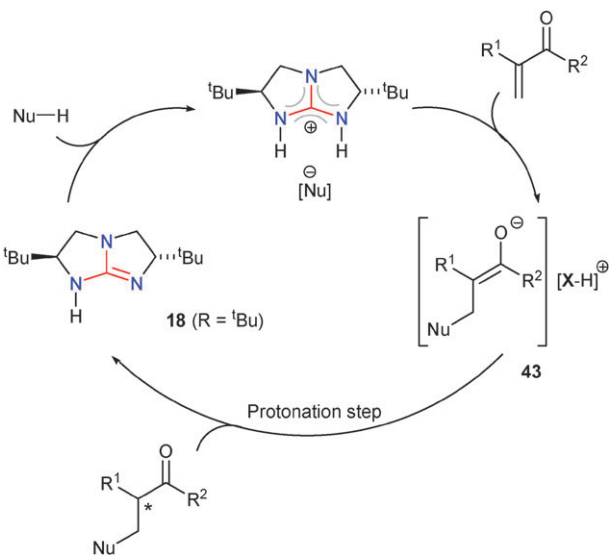


Scheme 11 Diels–Alder and Michael products from the α,α′-disubstituted {5,5}-guanidine catalyzed reaction of anthrones with *N*-phenylmaleimide.

(**42**) adducts were obtained with high regio- and enantioselectivities (Scheme 11).

The lability of the N*H* atom of H-hpp has been exploited in an isotope exchange reaction.[72] Using 4′-methoxyacetophenone as a test substrate and a catalyst loading of 30% at room temperature, the total incorporation yield for H-hpp was 92% after 0.5 h, with a slower rate observed for Me-hpp.

Enantioselective protonation using **18** (R = ^{t}Bu) as the catalyst has recently been demonstrated (Scheme 12).[73] The mechanism proceeds *via* the transient enolate **43**, followed by protonation by the guanidinium cation [**X**-H]$^+$. Both linear and cyclic substrates reacted with a rapid, selective and irreversible protonation step. The scope of this reaction is under investigation, but it represents an important advance in the preparation of carbonyl compounds with α-stereogenic centres.



Scheme 12 Enantioselective protonation promoted by a chiral {5,5}-bicylic guanidine.

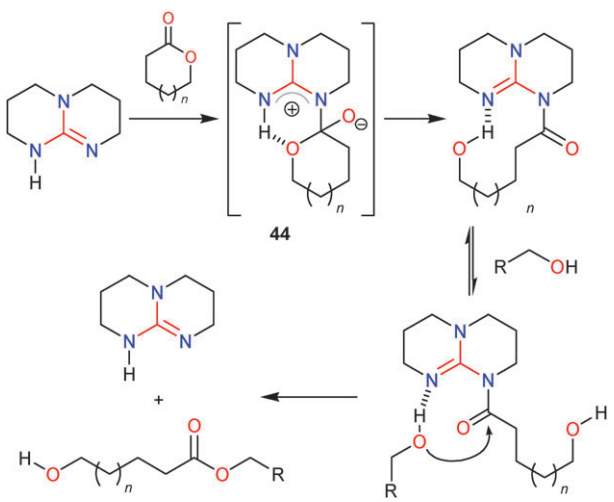
Ring-opening polymerization (ROP) catalysis

Bicyclic guanidines have recently been used as organocatalysts for ring-opening polymerization (ROP) catalysis.[74] Examples have so far been restricted to the unadorned {6,6}-bicyclic framework; the ability to control the tacticity of polymers containing chiral groups (*e.g.* lactide) using optically active guanidines has not yet been explored.

Reports on dual component H-hpp–ROH mixtures as an initiator system for the polymerization of caprolactone under solvent-free conditions first appeared in 2004.[75] It was proposed that H-hpp was behaving purely as a strong base to activate the alcohol and that polymerization proceeded by a (pseudo) anionic mechanism. Work by Waymouth and co-workers demonstrated that a combination of H-hpp–ROH was also active for polymerization in solution.[76] They proposed a bifunctional nucleophilic mechanism (Scheme 13) that proceeds *via* intermediate **44**. This activates the incoming alcohol by hydrogen bonding to facilitate esterification.[77]

An alternative mechanism has been investigated computationally,[78] based on observations from a bifunctional thiourea amine system.[79] In this pathway, dual activation of the monomer and alcohol occurs *only* through hydrogen bonding to the guanidine, giving intermediates **45** and **46** (Fig. 11). This was energetically preferred over the acetyl transfer pathway, and the theoretical results were consistent with experimental data.

Extension to other monomer systems has been established, including the polymerization of cyclic carbosiloxanes,[80] trimethylene carbonate,[81] and other substituted cyclic carbonate monomers.[82] The formation of organic–inorganic hybrid materials involving the graft polymerization of ε-caprolactone onto a polysilsesquioxane demonstrates the flexibility of this organocatalytic system.[83] During this process, the potential problem of incorporating guanidine end-groups on the grafted polymer chains was avoided by using urea-based initiators PhNHC(O)-hpp and $H_2C{=}CHCH_2NHC(O)$-hpp, accessed from the reaction of H-hpp with the corresponding isocyanate.



Scheme 13 Initially proposed mechanism by which H-hpp catalyzes ring-opening polymerization of lactide.

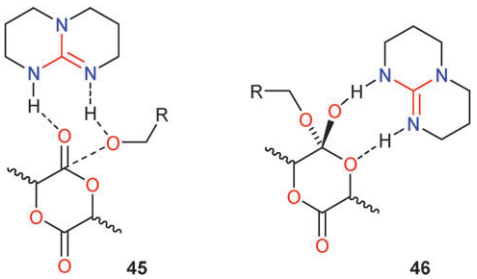


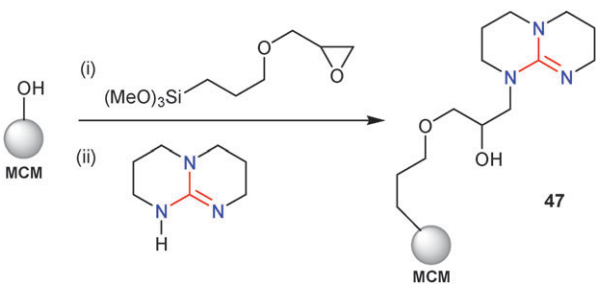
Fig. 11 Hydrogen bonded intermediates predicted by computational analysis.

Supported organocatalysis[84]

Incorporating catalytically active species on inert supports frequently offers significant advantages over their homogeneous counterparts, including ease of separation, recyclability and in certain favourable cases enhanced selectivity. In recent years these features have been put to use in the synthesis of extensive combinatorial libraries of organic compounds. Relatively early in the development of bicyclic guanidines as organocatalysts it was shown that the polystyryl (PS)-supported {6,6}-compound **16** was an efficient promoter for the addition of nucleophiles to unsaturated substrates,[59] including the synthesis of a library of substituted benzofurans.[85] Following these reports, micelle-templated silicas (MTS) functionalized by hpp were produced and their application in transesterification catalysis was studied.[86]

Inorganic–organic hybrid catalysts substituted by hpp have also been studied; in this case the inorganic support was the all-silica mesoporous material MCM-41, and the organic linker group was derived from 3-trimethylsilyl propoxy methylene oxirane (**47**, Scheme 14).[87] A range of catalytic transformations have been investigated using this material, including Michael additions,[87] Knoevenagel condensations,[88] preparation of carbamates from diethyl carbonate,[89] and the synthesis of thioureas from carbon disulfide and primary amines.[90] Generally, enhanced thermal and mechanical stability was observed compared to resin-bound examples, potentially important for transformations requiring harsher conditions.

Further examples of the application of anchored bicyclic guanidines and the development of new support materials (*e.g.* hpp-functionalized SBA-15[91]) have been recently reported, demonstrating that this area continues to elicit interest. Once again addressing environmental issues, it has been demonstrated that the polystyrene-supported derivative



Scheme 14 Synthetic route to the hpp group supported on inorganic–organic hybrid materials.

16 can be used under solvent-free conditions for a number of organic transformations including 1,2-epoxide ring-opening, aldol-type condensation and Michael additions.[92] In fact it was noted that SFC greatly *increased* the efficiency of **16** for the nucleophilic ring-opening of oxiranes by thiols.[93] As for the unsupported guanidines,[68] silica-supported hpp has also been shown to catalyze the chemical coupling of CO_2 with propylene carbonate.[94] In a novel biocatalytic application, PS-supported hpp has been used in tandem with *Candida rugosa* lipases immobilized on polypropylene powders for the production of (*S*)-naproxen from (*R*,*S*)-naproxen 2,2,2-trifluoroethyl ester.[95] In this system, the lipase enzyme catalyzed the enantioselective hydrolysis of the ester, with the polymer-bound guanidine serving as an *in situ* racemization catalyst for the remaining (*R*)-ester by a dynamic kinetic resolution.

Cationic guanidinium salts

Introduction

Nature regularly utilizes the guanidinium group in the side-chain of the amino acid arginine in the formation of hydrogen-bonding and electrostatic interactions for a number of important biological processes. These interactions frequently involve bonding to oxoanions (*e.g.* carboxylates, phosphates, sulfonates) that are present in enzymes and antibodies and also occur internally in proteins to stabilize tertiary structure.[96] For many years chemists have exploited this model in the development of guanidinium derivatives for application in anion recognition chemistry.[97]

The high basicity of bicyclic guanidines ensures that formation of the corresponding guanidinium salt is facile and the opportunity for resonance stabilization generates a very stable cationic species (**4**, Scheme 1). The experimentally determined absolute pK_a values of the conjugate acids $[H\text{-hppH}]^+$ and $[Me\text{-hppH}]^+$ in acetonitrile are 26.03 and 25.49, respectively,[98] and the neutral guanidines are therefore often referred to as 'superbases'. No work has yet been carried out on the basic properties of the new {*m*,*n*}-bicyclic guanidines, although the subtle differences in structure for the $n = 5$ members may attenuate the strength of the base by reducing the extent of delocalization.

Synthesis and structure

The formation of the $[H\text{-hppH}]^+$ and $[Me\text{-hppH}]^+$ cations, their structure and how they interact with different anions have been comprehensively studied using a combination of spectroscopy (NMR, UV-vis and vibrational analysis), calorimetry and conductivity;[99–101] in recent years these studies have been complemented by computational work.[102] Many examples have also been structurally characterized showing extensive variety in both short and long range order in the solid-state. Pertinent examples include metal-oxide (**48**)[103] and -halide (**49**)[104,105] species, oxoanions based on nitrogen (**50–52**),[106] sulfur (**54** and **55**),[101,107] and carbon (**53**)[108] functionalities, and several aryloxide derivatives (**56** and **57**)[100] (Fig. 12).

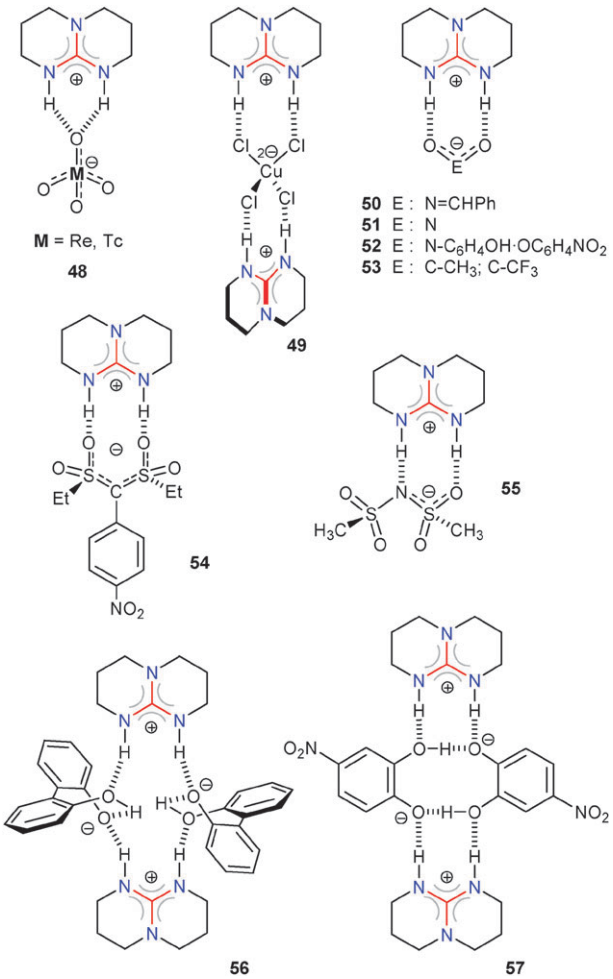


Fig. 12 Structurally characterized examples of guanidinium salts involving the cation $[H\text{-hppH}]^+$.

NMR and crystal structure data of the hydrohalide derivatives [H-hppH][X] (X = Cl and Br) have recently been compared with the corresponding $[BPh_4]^-$ salt, to assess the role of hydrogen bonding in both solution and the solid-state.[31,109] Evidence suggested that the ^{13}C NMR chemical shift for the tertiary CN_3 (δ_{CN3}) is sensitive to the presence of hydrogen bonding (*e.g.* δ_{CN3} 153.0 X = Cl; δ_{CN3} 165.3 X = BPh_4) and may serve as a useful tool in evaluating the strength of cation···anion interactions in solution. The crystal structure of the {5,5}-hydrochloride salt [H-tboH][Cl] was reported as a part of this study,[109] confirming that an increased angle between the projection of the hydrogen bonds (**13**) leads to formation of extended structures in the solid-state (Fig. 13).

Applications in synthesis

We have recently shown that $[H_2C\{hpp\}\{hppH\}]^+$ (**58**), synthesized by mono-protonation of the linked bis{guanidyl} compound **31**, can be used to generate the formally cationic aluminocenium complex **59** *via* protonolysis of an Al–Me bond (Scheme 15).[48] The resultant species is coordinatively saturated at the metal, and bond length analysis suggests that the positive

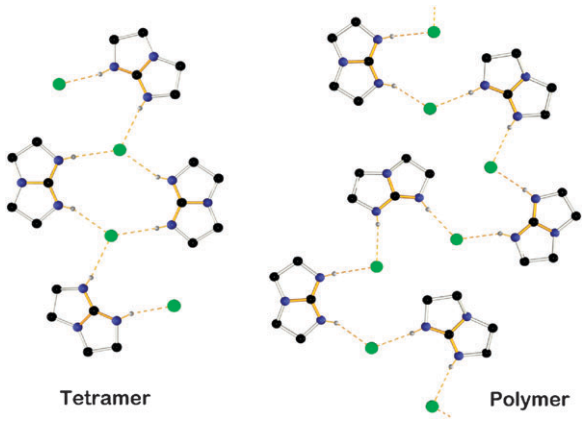
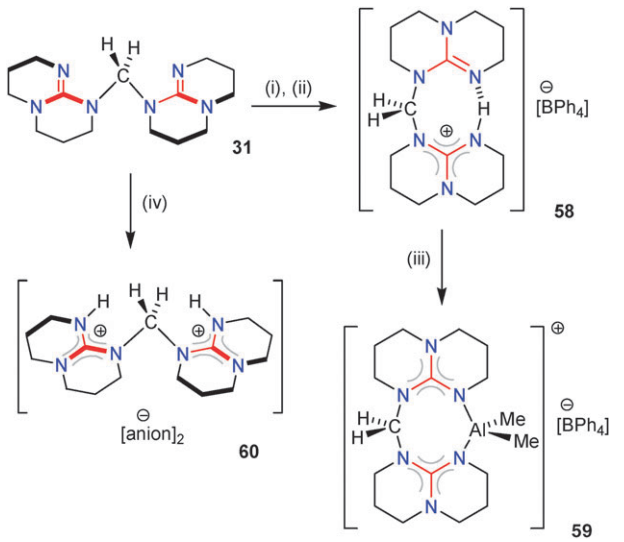


Fig. 13 Intermolecular hydrogen-bonding networks for the hydrochloride salt of the {5,5}-bicyclic guanidine.

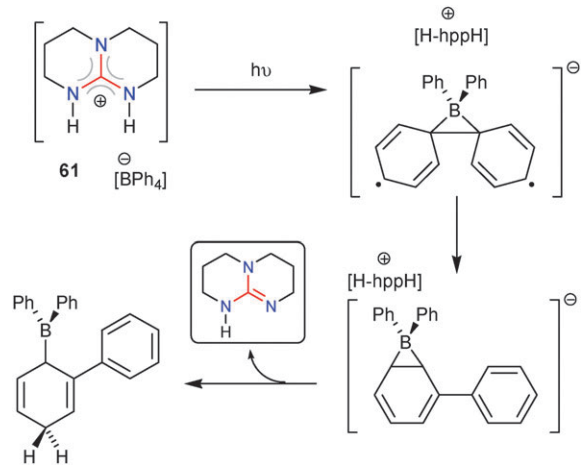


Scheme 15 (i) $[HNEt_3][Cl]$, THF; (ii) $NaBPh_4$, H_2O; (iii) $AlMe_3$, toluene; (iv) 2 $[HNEt_3][Cl]$, CH_2Cl_2, 2 Na[anion] (anion = $[BPh_4]^-$, $[OTf]^-$).

charge is sequestered within the guanidyl-components of the ligand. It is hoped that these features will moderate the high reactivity normally associated with these types of cation, leading to wider applications in catalysis. Dicationic guanidinium salts (**60**) can be made by a similar route.

Applications in catalysis

The water solubility of many guanidinium salts has enabled them to be investigated as phase-transfer catalysts (PTCs) for organic transformations. Derivatives of the chiral pentacyclic derivative (**22**·HCl) show high asymmetric induction for the enantioselective alkylation of a glycinate benzophenone Schiff's base under phase-transfer conditions.[110] Related PTCs have also been used in epoxidation of chalcones, giving ee's of up to 93%.[37] Other alkoxide and siloxide derived examples have been used for the phase transfer of the pertechnetate anion.[111] Extraction profiles were compared with ammonium,



Scheme 16 [H-hppH][BPh_4] as a photobase generator (PBG) for polymerization catalysis.

phosphonium and arsonium salts, concluding that the enhanced lipophilicity of the guanidinium derivatives was the cause of the high efficiency and selectivity for $[TcO_4]^-$ in this process.

The tetraphenylborate salt [H-hppH][BPh_4] (**61**) has recently been employed as a photobase generator (PBG) for the anionic ring-opening of cyclic esters and the photo-cross-linking of polymers containing hydroxyl-ester groups.[112] The mechanism was studied by UV-vis spectroscopy, and strongly suggests that photolysis under short-wave UV-radiation proceeds *via* the excited $[BPh_4]^-$ anion, which rearranges and abstracts a proton from the $[H\text{-hppH}]^+$ cation (Scheme 16). The H-hpp that is released proceeds to act as an organocatalyst, as described previously.

Applications in anion recognition

By far the most widely utilized application for guanidinium cations is as sensors for anion recognition.[97] The domination of the {6,6}-framework in this area is a combination of the historical development and the favourable alignment of the hydrogen-bonding N*H* groups enabling multiple interactions with a substrate/anion (**12**). Much of the early work was directed at the synthesis of cation hosts specific to a particular substrate, and as such many elaborate derivatives have been developed.[113] Key to the advancement of this area was the synthesis of chiral derivative, **21**,[22] enabling additional functionalization through derivatization at the pendant hydroxide groups.

Work towards understanding the exceptionally high affinity that guanidinium salts show towards oxoanions continues apace. Recently, calorimetric analysis revealed the importance of entropic factors when considering enhanced binding properties,[114] leading to the development of new α,α,α′,α′-tetra(*sec*-carboxyamido) derivatives **62** (Fig. 14).[115] The nature of the host–guest interactions were studied in polar and protic solvents, confirming that enhanced binding results from more positive association entropies rather than the formation of stronger hydrogen bonds.

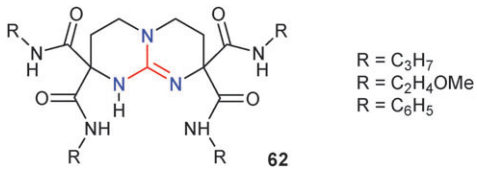


Fig. 14 α,α,α′,α′-Tetra(carboxyamido) derived {6,6}-guanidine developed for the calorimetric study of guest binding.

Anionic guanidinate salts

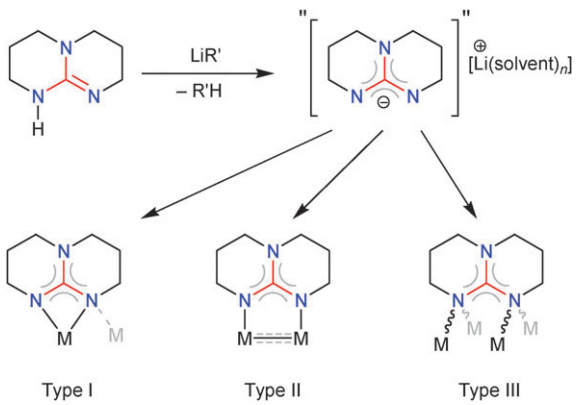
Introduction

Conversion of neutral, tetra-substituted guanidines to the corresponding anionic guanidinate *via* loss of the N*H* proton is a facile process, routinely achieved using organolithium reagents.[116] Whilst it is possible to isolate examples of lithium guanidinate salts, the anions are commonly generated *in situ* for further reactivity, with the most widely studied reaction being salt metathesis with additional metal-halide substrates. For the purposes of this article, the coordination chemistry of bicyclic guanidinate anions has been divided into three sub-categories (Scheme 17):

- compounds in which the guanidinate is principally involved in bonding to a single metal, including dimers thereof (molecular species—Type I)
- compounds containing only two metal atoms that exhibit some degree of bonding to one another (also referred to as 'paddlewheel' or 'lantern' compounds—Type II)
- compounds containing greater than two metal atoms held in place by bridging guanidinate anions (cluster species—Type III).

Previous reviews in the area[116] have included reference to examples of these compounds in the broader context of the general coordination of guanidinates; this discussion focuses on the novel aspects that are derived from the bicyclic framework.

As for neutral and cationic systems, the majority of work to date has been concerned with chemistry derived from H-hpp. Incorporating the $N_{amidine}$ substituents into the six-membered rings effectively 'ties them back', generating a sterically non-demanding guanidinate ligand, which, in combination with the parallel projection of the nitrogen frontier orbitals



Scheme 17 Different sub-categories of complex described in this article.

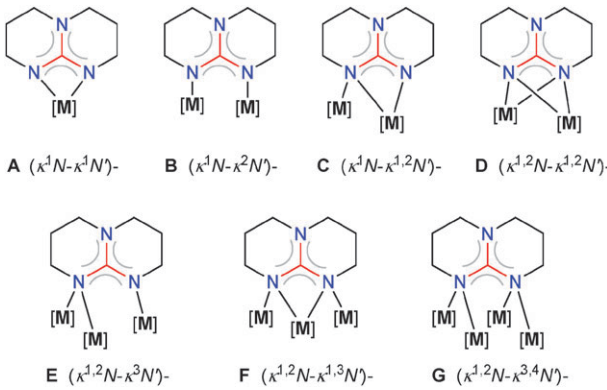


Fig. 15 Different structurally characterized bonding modes for the $[hpp]^-$ anion.

(**12**), favours a bridging coordination mode. Fig. 15 summarizes the bonding modes (**A** to **G**) that have been observed for the $[hpp]^-$ anion; for reference, no structurally characterized examples of **F**- or **G**-type bonding have been reported for acyclic guanidinates.

Somewhat surprisingly, there are very few metal complexes incorporating anions derived from substituted hpp-derivatives. Given the proven track record for the appropriately substituted neutral guanidines to promote asymmetric reactions and the ability of these anions to serve as ancillary ligands in metal-mediated catalysis, one can assume that it is only a matter of time before these two areas are brought together with substituted bicyclic guanidinate compounds being employed in asymmetric transformations.

Molecular compounds (Type I)

Most studies of $[hpp]^-$ as a ligand for molecular species occurred between 1998 and 2005 (Table 4). Important comparisons between the bonding for these compounds and their acyclic analogues were made, concluding that the anion behaved as an "electron-rich" variant due to a large contribution from zwitterionic resonance form **5** (Scheme 1).[16,117] Despite

Table 4 Molecular compounds (Type I) involving bicyclic guanidinates

Metal	Formula	Ref.
Li	$[Li(hpp)(H\text{-}hpp)]_2$	30
Ln	$Cp^*_2Ln(hpp)$ [Ln = Y, Ce, Sm]	120
Ti	$Ti(hpp)_2Cl_2$; $[Ti(hpp)Cl_3]_2$; $Ti(hpp)_2(CH_2Ph)_2$; $[Ti(hpp)Cl(\mu\text{-}N^tBu)]_2$; $[Ti(hpp)(N^tBu)(\mu\text{-}hpp)]_2$	16, 118
Nb	$Nb(hpp)Cl_4$; $Nb(hpp)Cl_4{\cdot}MeCN$; $Nb(hpp)_2Cl_3$	117
Ta	$[Ta(hpp)_4][TaCl_6]$	105
	$[Ta(hpp)_4][Ta(CO)_6]$	121
Mn	$[CpMn(hpp)]_2$	122
Pt	$Pt(hpp)(NHC(O)CH_3)Cl_2(hppH)$	35
Cu	$[Cu(hpp)]_2$	123
Ag	$[Ag(hpp)]_4$	124
Au	$[Au(hpp)Cl]_2$; $[Au(hpp)]_4$; $[Au(tbo)]_4$	124, 125
Zn	$[Zn(hpp)(N\{SiMe_3\}_2)]_2$	119
Al	$[Al(hpp)Me_2]_2$; $[Al(tbo)Me_2]_2$	17, 126
Ga	$[Ga(hpp)(H)Cl]_2$	43
Si	$[Si(hpp)Me_2][Cl]_2$; $Si(hpp)Ph_2Cl$; $Si(hpp)\{CH_2\}_4Cl$	127
Sn	$Sn(hpp)_2$; $[Sn(hpp)Cl]_2$; $Sn(hpp)_2Cl_2$	128

the relatively small size, the robust character of the hydrocarbon skeleton and strong binding of the hpp ligand enable it to maintain a stable metal environment, as demonstrated through its application as an ancillary ligand in catalysis. Examples of both olefin polymerization at titanium[118] and ROP of lactide at zinc[119] have been presented, although in the former case, transfer of the $[hpp]^-$ anion from the group 4 metal to the aluminium component of the co-catalyst was observed belying its innocent behaviour.

Recently reported compounds incorporating $[hpp]^-$ have built on the results from these fundamental studies, making it the guanidinate of choice to stabilize electron deficient metal centres, or in the preparation of compounds in which a bridging guanidinate is desirable. For example, the ability of $[hpp]^-$ to stabilize metals in high oxidation states has been investigated for platinum(IV).[35] Oxidation of $PtCl_2$(H-hpp)$_2$ using H_2O_2 was performed in acetonitrile, affording the octahedral Pt^{IV} complex Pt(hpp)(NHC(O)CH_3)Cl_2(hppH). Both anionic and neutral forms of the guanidine are present in the product, with the acetamido ligand generated from the reaction of acetonitrile solvent with a transient platinum hydroxide species.

Whilst Type I compounds of both main group and transition metals are known, until recently the only known example of the $[hpp]^-$ at a lanthanide centre was in the oxide containing tetrametallic (Type III) cluster, $Y_4(hpp)_8(O)Cl_2$.[129] The ability to support molecular lanthanide complexes has, however, lately been demonstrated by Evans *et al*. who report Cp^*_2Ln(hpp) (Ln = Y, Ce, Sm).[120] The ligand was symmetrically chelated in all cases, with sufficient space at samarium to allow incorporation of MeCN without changing the coordination mode of the guanidinate.

We have recently studied the {5,5}-bicyclic anion, $[tbo]^-$, as a ligand, focussing initially on compounds for which the $[hpp]^-$ analogue was known. The crystallographically characterized aluminium dimer [Al(tbo)Me_2]$_2$ (**63**) has been synthesized,[17] and structural parameters have been compared with [Al(hpp)Me_2]$_2$ (**64**).[126] The major difference is the 'boat' conformation of the $Al_2N_4C_2$-metallacycle in **63** compared with the sterically less encumbered 'chair' in **64**, although the AlMe_2 groups in **63** are equivalent by NMR spectroscopy in solution suggesting that this is a solid-state (packing) effect. More significantly, perhaps, the non-bonding nitrogen atom possesses greater lone-pair character in **63**, manifest in longer Δ'_{CN} values and a higher degree of pyramidalization at N(3).

Bridged metal···metal compounds (Type II)[130]

The original application of $[hpp]^-$ as a ligand arose as an extension of the work by Cotton and co-workers with dinuclear 'paddlewheel' complexes,[131] where a more robust ligand than the widely applied amidinates was desirable. The ligand has been used to great effect in this area with many examples now known (Table 5), and has enabled access to many derivatives not previously available with other bridging ligand systems. For example, the first compound with a Nb≡Nb triple bond,[132] the first dinuclear Pd^{III} compound,[133] and the first structurally characterized paddlewheel compound with an M_2^{7+} core[134] all owe their existence to the ability of the $[hpp]^-$ anion to support the M_2^{n+} core.

Table 5 Bridged metal···metal compounds (Type II) involving bicyclic guanidinates

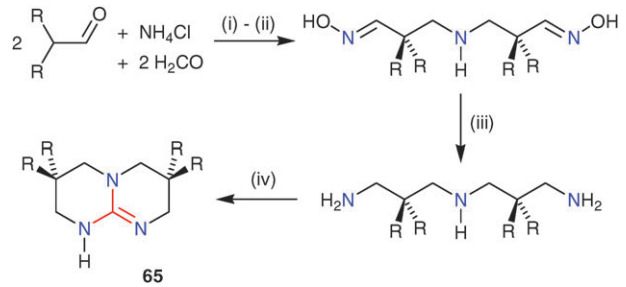
Metal	Formula	Ref.
Ti	$Ti_2(\mu\text{-hpp})_2(\eta^2\text{-hpp})_2Cl_2$	141
V	$V_2(hpp)_4$	108
V	$[(\mathbf{L})Li(\mu\text{-Cp})Li(\mu\text{-Cp})Li(L)]^+$ $[(\eta\text{-Cp})Li(\mu\text{-Cp})Li(\eta\text{-Cp})]^-$ ($\mathbf{L}$ = $[V_2(hpp)_4]$)	142
Nb	$Nb_2(hpp)_4$; $[Nb_2(\mu\text{-hpp})(\eta^2\text{-hpp})_2][PF_6]$	132, 141, 143
Cr	$Cr_2(hpp)_4$	108, 135
Mo	$Mo_2(hpp)_4$; $Mo(hpp)_4Cl$; $Mo(hpp)_4Cl{\cdot}2CH_2Cl_2$; $Mo(hpp)_4Cl_2$[a] $[Mo(hpp)_4Cl][BF_4]$; $[Mo_2(hpp)_4][BF_4]_2$	108, 135, 144, 145
Mo	$Mo_2(tbd)_4$; $Mo_2(tbd)_4Cl$; $Mo_2(tbd)_4Cl_2$	6
Mo	$Mo_2(tbu)_4$; $Mo_2(tbu)_4Cl$; $[Mo_2(tbu)_4][B(Ar_F)_4]_2$[a]	6
Mo	$Mo_2(tbo)_4$; $Mo_2(tbo)_4Cl$	4
Mo	$Mo_2(tbn)_4$; $[Mo_2(tbn)_4][PF_6]$; $Mo_2(tbn)_4Cl_2$	4
Mo	Mo_2(TM-hpp)$_4$[c]; Mo_2(TE-hpp)$_4$[c]; $[Mo_2(TM\text{-hpp})_4][B(Ar_F)_4]_n$[ac] ($n$ = 1, 2); $[Mo_2(TE\text{-hpp})_4][B(Ar_F)_4]_n$[ac] ($n$ = 1, 2)	139
W	$W_2(hpp)_4Cl_2$[b]; $W_2(hpp)_4$; $W_2(hpp)_4Cl_2{\cdot}4CH_2Cl_2$; $W_2(hpp)_4Cl$; $W_2(hpp)_4{\cdot}2NaHBEt_3$; $W_2(\mu\text{-hpp})_2(\eta^2\text{-hpp})_2(\mu\text{-CO})_2$; $[W_2(\mu\text{-hpp})_2(\eta^2\text{-hpp})_2(\mu\text{-CO})_2][PF_6]$; $[W_2(hpp)_4][X]_2$ [X] = $[PF_6]$; $[B(Ar_F)_4]$[a]	33, 144, 146, 147
Re	$Re_2(hpp)_4Cl_2$[b]; $Re(hpp)_3Cl_3$; $[Re_2(hpp)_4Cl_2][PF_6]$; $Re_2(hpp)_4(OTf)_2$; $Re_2(hpp)_4(O_2CCF_3)_2$; $Re(hpp)_4F_2$; $[Re_2(hpp)_4F][B(Ar_F)_4]_2$[a]	148
Ru	$Ru_2(hpp)_4Cl_2$[b]; $Ru_2(hpp)_4(OTf)_2$	149
Os	$Os_2(hpp)_4Cl_2$[b]; $[Os_2(hpp)_4Cl_2][PF_6]$	134, 146
Rh	$Rh_2(hpp)_4Br$	34
Rh	$Rh_2(hpp)(O_2CMe)_3{\cdot}([H\text{-hppH}][O_2CMe])_2$	34
Ir	$Ir_2(hpp)_4Cl_2$[b]	150
Pd	$Pd_2(hpp)_4$; $Pd_2(hpp)_2Cl_2$[b]	133
Pt	$Pt_2(hpp)_4Cl_2$[b]	146
B	$B_2(hpp)_2H_2$; $[B_2(hpp)_2(NHMe_2)_2][Cl]_2$	42, 151

[a] Ar_F = 3,5-{CF_3}$_2C_6H_3$. [b] The structures of these compounds were also analyzed for conformational ambiguities.[152] [c] TM-hpp = β,β,β′,β′-Me_4-hpp; TE-hpp = β,β,β′,β′-Et_4-hpp.

Amongst the most significant discoveries in this area was the observation that the closed-shell species $W_2(hpp)_4$ had a gas-phase ionization enthalpy lower than that of caesium.[135,136] DFT calculations showed that this was due to loss of an electron from the δ-bonding orbital of the tungsten–tungsten quadruple bond, and that a strong interaction of this orbital with a filled orbital on the $[hpp]^-$ ligands facilitated this progress. Subsequent work showed that this compound was an excellent reducing agent, with CH_2Cl_2, C_{60} and TCNQ all of which are rapidly reduced in solution.[137]

A potential problem with the practical application of $M_2(hpp)_4$ species as reducing agents in homogeneous systems is their limited solubility in common organic solvents. This led to the development of β,β,β′,β′-tetra alkyl substituted {6,6}-guanidines (Scheme 18: **65**, R = Me, Et),[138] and synthesis of the corresponding molybdenum paddlewheel compounds.[139] The authors noted that, in contrast to the synthesis of unsubstituted $Mo_2(hpp)_4$,[108] no precipitate was formed when the lithium guanidinates were reacted with $Mo_2(O_2CCF_3)_4$, indicating that a more soluble product was forming.

Recent developments in this area have driven the development of new (*m*,*n*)-bicyclic ring systems described in Table 1. For comparative purposes, the series $Mo_2(L)_4$ has been prepared and the electrochemical properties have been investigated. In



Scheme 18 (i) Reflux; (ii) $NH_2OH{\cdot}HCl$, NaOH; (iii) H_2, RANEY® Ni, 100 °C, 100 atm; (iv) CS_2, *p*-xylene, reflux.

all cases differential pulse voltammograms (DVPs) indicated two successive one-electron processes comparable to that previously observed in $Mo_2(L)_4$ species. It is noteworthy that the {5,5}-derivative, $Mo_2(tbo)_4$, differs from other compounds in the series as the Mo_2^{6+}/Mo_2^{5+} couple is non-reversible.[4] This is consistent with a smaller interaction between $[tbo]^-$ and the δ-electrons of the Mo_2-unit, a likely consequence of the retention of electron density at N(3), as noted elsewhere in this manuscript.

Most recently, group 4 metal paddlewheel compounds containing $[hpp]^-$ have been targeted, encouraged by reports of amidinate derivatives containing a Ti–Ti bonded core.[140] Reduction of $Ti(hpp)_2Cl_2$[118] with potassium graphite afforded a compound that analyzed as $Ti_2(hpp)_4Cl_2$.[141] However, X-ray analysis indicated that only two $[hpp]^-$ anions were bridging and that, rather than the expected κ^1N,κ^2N'-mode (**B**, Fig. 15), they were orientated perpendicular to the Ti–Ti bond with $\kappa^{1,2}N,\kappa^{1,2}N'$-bonding (**D**, Fig. 15 and **66**, Fig. 16). This report noted a similar complex involving an Nb_2^{5+} unit, (**67**), isolated during attempts to oxidize triply bonded $Nb_2(hpp)_4$.

In an unrelated area, scientists from Cambridge were investigating the chemistry of $[Cp_2V]$ with a view to extend the known ionic chemistry of the main group cyclopentadienyls to transition metals.[142] Reaction between vanadocene and Li-hpp resulted in ligand exchange, affording the complex salt $[(\mathbf{L})Li(\mu\text{-}Cp)Li(\mu\text{-}Cp)Li(\mathbf{L})][(\eta\text{-}Cp)Li(\mu\text{-}Cp)Li(\eta\text{-}Cp)]$ ($\mathbf{L} = [V_2(hpp)_4]$, **68**, Fig. 17). This is of interest as the neutral $V_2(hpp)_4$ units effectively disrupt the lattice of $[LiCp]_\infty$, dividing the polymer into 'Li_3Cp_2' cations and 'Li_2Cp_3' anions.

Whilst not a bridged M···M compound *per se*, Himmel and co-workers have shown that borane adduct $H_3B{\cdot}$(H-hpp) (**23**) eliminates two equivalents of dihydrogen upon heating to 110 °C, to afford the bridged boron(II) species, $[HB(\mu\text{-}hpp)]_2$

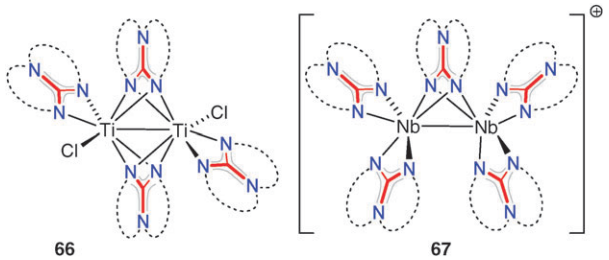


Fig. 16 Recent examples of early transition metal Type II compounds supported by the $[hpp]^-$ ligand.

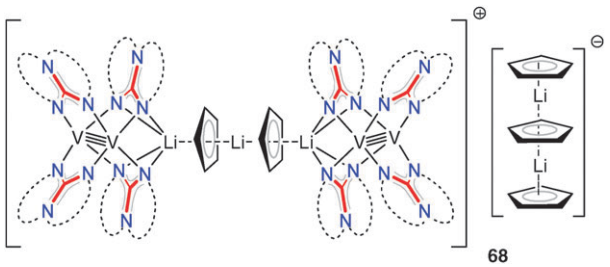


Fig. 17 Structure of $[LiCp]_\infty$ which has been disrupted by $V_2(hpp)_4$ groups.

(**25**).[42] This compound has been structurally characterized and shown to contain a boron–boron bond (B–B = 1.772(3) Å) and a κ^1N,κ^2N'-bridging $[hpp]^-$ anion. Further work showed that related di- and monocationic B^{II} compounds containing the '$B_2(\mu\text{-}hpp)_2$' core are also accessible, with shorter B–B distances of 1.746(2) Å and 1.753(4) Å in the doubly and singly charged species, $[B_2(hpp)_2(NHMe_2)][Cl]_2$ and $[B_2(hpp)_2(NMe_2)(NHMe_2)][Cl]$, respectively.[151,153]

Cluster species (Type III)

The bridging tendency of the $[hpp]^-$ anion has been exploited in polyhedral cluster species, comprising multiple metals spanned by guanidinates that typically present **E**-, **F**- or **G**-type bonding (Fig. 15 and Table 6). This has been most intensively studied for alkali-metal clusters,[154] many of which contain interstitial ions. Early work demonstrated that hydride ions were incorporated in cationic clusters (*i.e.* $[Li_8(hpp)_6(H)]^+$),[155] with a recent mechanistic study indicating that the likely source of hydride is the ^{t}BuLi reagent.[156] The dicationic $[Li_8(hpp)_6]^{2+}$ ion, which contains an interstitial void, was also isolated during this study, comprising a slightly larger cage due to no attenuation of the electrostatic $Li^+\cdots Li^+$ repulsions from a centrally located hydride anion. In both clusters a cubic array of eight lithium atoms is present, with each face capped by $[hpp]^-$ in ($\kappa^{1,2}N\text{-}\kappa^{3,4}N'$)-bonding mode (**G**, Fig. 15).

Incorporation of larger anions in clusters of this type relies on an expanded cage-structure, illustrated in the nine-vertex mono-capped cube, $Li_9(hpp)_7(O_2)(THF)_n$ ($n = 0, 1$), containing an encapsulated peroxide dianion.[30] In this structure five anions adopt **G**-type bonding, with the remaining two present as **F**-type to the face-capping lithium. A subsequent theoretical study confirmed the presence of a single bond between the oxygen atoms within the $[O_2]^{2-}$ dianion.[157]

Other combinations of bonding modes for $[hpp]^-$ have been observed. For example, Cotton *et al.* noted the trimetallic $M_3(hpp)_4Cl_2$ (M = Fe, Co) clusters containing both **B**- and **E**- type bonding in 1999.[29] This structural core was also identified in $Zn_3(hpp)_4Me_2$ (**69**),[158] and was shown to be robust in the presence of dimesitylborinic acid, affording the boroxide, $Zn_3(hpp)_4(OB\{mes\}_2)_2$. The direct analogue of (**69**) incorporating the {5,5}-derivative, $Zn_3(tbo)_4Me_2$ (**70**), has also been structurally characterized.[17] Comparison of the Zn···Zn distances once again reflects the wider angle between the donor orbitals of the {5,5}-bicyclic anion compared with the {6,6}-analogue (Fig. 18).

Table 6 Cluster compounds (Type III) involving bicyclic guanidinates

Metal	Formula	Ref.
Li	$Li_9(hpp)_7(O_2)(THF)_n$ (n = 0, 1)	30
	$[Li_8(hpp)_6(H)][Zn^tBu_3]$	
	$[Li_8(hpp)_6][Li(Me_2Al^tBu_2)_2]_2$	155
	$[Li_8(hpp)_6(H)][^tBuBEt_3]$	
	$[Li_8(hpp)_6(H)][HBEt_3]$	
	$[Li_8(hpp)_6(H)][H(BEt_3)_2]$	156
	$[\{Li(tbo)(L)(H\text{-}tbo)\}_2]_\infty$ (LH = 1-(2-aminoethyl)-2-imidazolidinethione)	17
	$Li_6(tbo)_6(H\text{-}tbo)_3$	
	$Zn_3(tbo)_3Me_2$	
Li/Mn	$Li_2Mn_2(hpp)_6$	122
Y	$Y_4(hpp)_8(O)Cl_2$	129
Ti/Al	$Ti(Me_2Al\{hpp\}_2)Cl_2{\cdot}AlMe_3$	16, 118
Fe	$Fe_3(hpp)_4Cl_2$	29
Co	$Co_3(hpp)_4Cl_2$	29
Zn	$Zn_3(hpp)_4X_2$ (X = Me, OB{mes}$_2$)	158

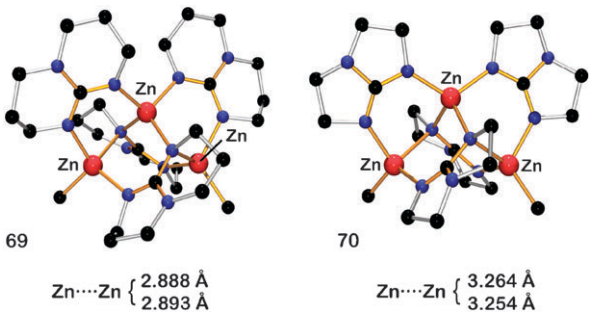


Fig. 18 ZnL_4Me_2 (L = $[hpp]^-$, $[tbo]^-$) comparing intermetallic distances.

The first example of a heterometallic cluster supported by bicyclic guanidinate anions has recently been published, consisting of a combination of lithium and manganese in the compound $Li_2Mn_2(hpp)_6$.[122] The structure comprised a butterfly-shaped core of metals with four guanidinates present with (κ^1N-κ^2N')-bonding (**B**-type) along the M···M edges, and the remaining ligands orientated orthogonally to one another above and below the M_4-cluster with **G**-type bonding.

Conclusions

When preparing this manuscript it quickly became apparent that researchers in many diverse branches of chemistry successfully utilize compounds based on essentially the same basic framework in their work, namely the bicyclic guanidines. However, overlap between different interest groups has, to date, remained superficial at best: organic chemists have concentrated on chiral derivatives of neutral compounds, supramolecular chemists have focussed on cationic salts incorporating additional functionality to aid in substrate binding and inorganic chemists have barely scratched the surface with by far the majority of work revolving around a single, non-substituted example. Recent developments in the synthesis of these compounds should facilitate researchers employing examples from other areas in their own work, and it is hoped that this article will help to stimulate research across these boundaries involving this highly versatile family of compounds.

Acknowledgements

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Notes and references

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