Poly{guanidinium} salts: application in the preparation of a coordinatively saturated aluminium cation

Pedro J. Aragón Sáez,[a] Sarah H. Oakley,[b] Martyn P. Coles*[b] and Peter B. Hitchcock[b]

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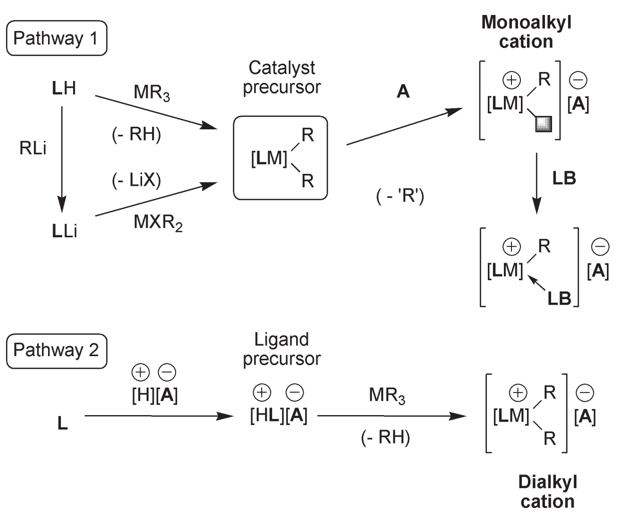
Protonation of the linked bis(guanidine), $H_2C\{hpp\}_2$, affords isolated guanidinium salts that have been used to prepare a coordinatively saturated aluminium cation.

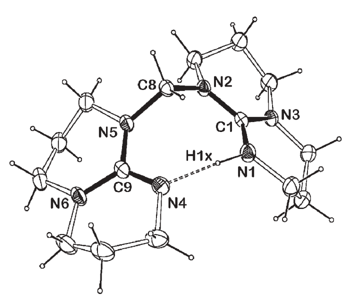
The chemistry of the main group metals has been undergoing somewhat of a renaissance in the last decade, fuelled in part by the realization that complexes of these elements are capable of catalyzing a range of chemical transformations previously thought to lie exclusively within the remit of the transition and lanthanide metals. In these metal-mediated processes, a basic requirement of the ancillary ligand set is that a balance between (i) offering sufficient steric support to prevent rearrangement and/or decomposition and (ii) allowing access of the substrate to the metal centre, be maintained throughout the catalytic cycle. For catalysis purported to proceed *via* a positively charged metal centre, the 'play-off' between (i) and (ii) becomes even more critical as the process whereby the cation is generated typically involves the removal of a ligand from a neutral 'pre-catalytic' state. This necessarily reduces the steric environment at the metal (Pathway 1, Scheme 1) thereby making it more susceptible to decomposition or formation of catalytically inert Lewis base adducts. In the context of the work reported herein, this is perhaps best illustrated by the activation of dialkyl aluminium amidinate compounds using ammonium borate salts, $[HNR_3][B(C_6F_5)_4]$, where formation of stable amine adducts result.[1] In this contribution, we describe a fundamentally different approach to the generation of cationic main group compounds *via* the reaction of a protonated ligand precursor with a neutral metal alkyl reagent (Pathway 2, Scheme 1). Using this protocol, the cationic charge is generated at the same time that the neutral ligand-set is introduced, and the resultant metal species has a higher intrinsic degree of coordinative saturation than the corresponding cation generated in Pathway 1.



Scheme 1 Synthetic routes to cationic main group alkyl complexes, illustrated for a group 13 element (M) supported by ligand set (**L**), in the presence of Lewis base (**LB**).

Reaction of the linked bis(guanidine), $H_2C\{hpp\}_2$ (**1**,[2] (hppH = 1,3,4,6,7,8-hexahydro-2*H*pyrimido[1,2-*a*]pyrimidine) with triethylamine hydrochloride afforded the guanidinium salt, $[H_2C\{hpp\}\{hppH\}][Cl]$ (**2a**). The low solubility of **2a** in hydrocarbon solvents limited its use as a reagent, and hence anion metathesis was conducted with $NaBPh_4$ to afford the tetraphenylborate reagent, $[H_2C\{hpp\}\{hppH\}][BPh_4]$ (**2b**). The IR spectrum of **2b** (Nujol mull) shows an N–H stretch at 3384 cm^{-1}, with a shift of υ(C=N) from 1611 cm^{-1} in **1** to a broad absorption centred at 1584 cm^{-1} in the protonated species. Key features of the ^{1}H NMR spectrum† include a highly deshielded N*H* resonance at 14.00 ppm and a broad peak centred at ~4.5 ppm for the *exo*cyclic bridging methylene group. Upon cooling to 203 K, this latter resonance is resolved into an AB pattern‡ (δ 5.44 and 3.64, $^2J_{HH}$ = 15.3 Hz), although only one set of resonances for the corresponding methylene protons of each hpp group is observed over this temperature range, suggesting rapid exchange of the N*H* proton between the guanidine and guanidinium components.

Single crystal X-ray diffraction§ (Fig. 1) confirmed the formation of the mono-protonated guanidinium salt, consisting of isolated $[H_2C\{hpp\}\{hppH\}]^+$ cations and non-coordinating $[BPh_4]^-$ anions. Both 'hpp' groups in the cation are aligned, with



Key bond lengths (Å)

C1–N1	1.326(2)	C9–N4	1.300(2)
C1–N2	1.357(2)	C9–N5	1.384(2)
C1–N3	1.341(2)	C9–N6	1.362(2)
N2–C8	1.463(2)	N5–C8	1.451(2)

Fig. 1 ORTEP of the cationic component of **2b** (ellipsoids drawn at 30%).

[a]*Departamento de Química Inorgánica, Orgánica y Bioquímica, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Avenida Camilo José Cela, 10 CP 13071, Ciudad Real, Spain. E-mail: PedroJose.Aragon@uclm.es; Fax: +34 926 295318; Tel: +34 926 295300*
[b]*Department of Chemistry, University of Sussex, Falmer, Brighton, BN1 9QJ, UK. E-mail: m.p.coles@sussex.ac.uk; Fax: +44 (0)1273 677196; Tel: +44 (0)1273 877339*

the *exo*cyclic methylene group located above the plane defined by N1/2/4/5. The hydrogen on N1 was located and refined, showing that it is associated within an asymmetric $[N–H\cdots N]^+$ intramolecular hydrogen bridge (IHB).[3,4] This structural motif has been observed in related bis{guanidine} systems in which the two nitrogen atoms involved are constrained in the 1,8-positions of di-substituted naphthalene, resulting in non-linear bridges with angles of 152 and 142°. In **2b**, the higher degree of flexibility inherent in the methylene bridge allows a considerably more linear IHB of 167° to be adopted.

The similar ρ values¶ for the guanidinium and guanidine components of **2b** (0.98 and 0.95, respectively) indicate 'partial protonation'[5] of the neutral moiety *via* the proton bridge,[4] in agreement with the equivalent ^1H NMR resonances for the two hpp groups. Further examination of the carbon-nitrogen distances, however, show significant differences between the two components. For example, the Δ_{CN} value¶ for the protonated guanidine is 0.03 Å, whilst within the formally neutral hpp-unit, a larger difference between the C–N single and C=N double bonds of 0.08 Å is noted.[6] There is also a significant reduction in the C(1)–N(3) distance [1.341(2) Å] compared with the corresponding value in the neutral guanidine [1.362(2) Å], indicating a greater delocalization of the N_{amide} lone pair into the sp^2 carbon of the framework for the protonated guanidine. Considering the different resonance forms possible within a protonated hpp moiety, this is consistent with a large contribution from resonance form **B**, Fig. 2.

Using the same synthetic methodology, we have demonstrated that **1** can also be doubly protonated to afford the bis{guanidinium} dication. Exchanging one of the chloride anions for $[BPh_4]^-$ allowed isolation of the mixed anion salt, $[H_2C\{hppH\}_2][BPh_4][Cl]$ (**3b**). The IR spectrum (Nujol mull) shows a broad absorption at 2296 cm^{-1}, in the region associated with υ(NH) for weakly hydrogen bonded systems,[7] as indicated in the crystal structure (*vide infra*). The ^1H NMR spectrum† in CD_3CN displays a single sharp resonance for the bridging methylene protons at δ 5.07, with a broad peak at δ 8.43 for N*H* suggesting a symmetric structure in solution. The X-ray crystal structure of **3b**§ (two independent molecules) shows that the two guanidinium components within the dication $[H_2C\{hppH\}_2]^{2+}$ are positioned with the N–H moieties spatially removed from one another (Fig. 3a), rationalized in terms of electrostatic repulsion between the two positively charged centres. The distribution of C–N distances differs substantially from that in **2a**, with ρ values of 0.99 and shorter bonds to both the protonated [N2/N5: 1.328(3) and 1.329(3) Å] and the amide [N3/N6: 1.329(3) and 1.332(3) Å] nitrogen atoms. This suggests an almost equal contribution from resonance forms **A** and **B** in the guanidinium components of **3b**. Hydrogen bonding between the N*H* and the chloride anion is observed in the solid-state [H···Cl distances in the range 2.27–2.36 Å] generating a dimeric

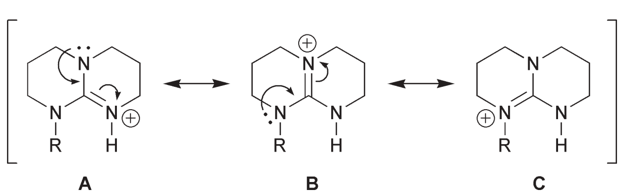


Fig. 2 Resonance contributions to the bicyclic guanidinium cation, $[hppRH]^+$.

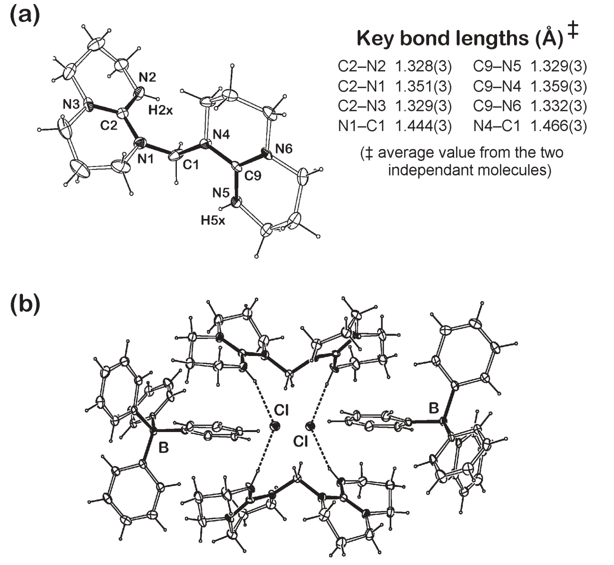


Fig. 3 (a) ORTEP of one of the cationic components of **3b** (ellipsoids drawn at 30%). (b) Dimeric arrangement of $[H_2C\{hppH\}_2][Cl][BPh_4]$ showing N*H*···Cl hydrogen bonds.

arrangement of cations bridged by two N*H*···Cl···*H*N bridges, with angles of 118.6 and 101.1° at the chloride (Fig. 3b).

Reaction of **2b** with one equivalent of $AlMe_3$ proceeded smoothly with evolution of methane and generation of a colourless crystalline solid that was purified by crystallization from THF. ^1H NMR and elemental analysis† were consistent with formation of the cationic aluminium alkyl, $[H_2C\{hpp\}_2AlMe_2][BPh_4]$ (**4b**), with the predicted high field ^1H NMR resonance for the two equivalent $AlMe_2$ groups at −0.86 ppm. The signal for the protons of the bridging methylene group is broad, suggestive of conformational changes within the eight-membered C_3N_4Al metallacycle.

The crystal structure§ of **4b** (Fig. 4) consists of two molecules in the unit cell that differ slightly in their bond lengths and angles; there are also two molecules of THF within the lattice. The cation

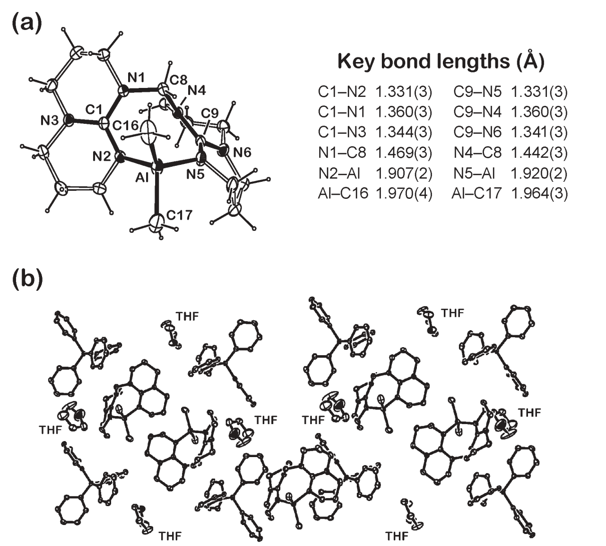


Fig. 4 (a) ORTEP of one of the independent molecules of **4b** (ellipsoids drawn at 30%). (b) Crystal packing for **4b** showing the presence of non-coordinated THF molecules within the lattice.

consists of a distorted tetrahedral aluminium dimethyl centre supported by two donor nitrogen atoms from the $H_2C\{hpp\}_2$ ligand, forming an eight-membered metallacycle in a distorted 'twist-boat' configuration. The Al–N distances [1.907(2) Å–1.922(2) Å] are relatively short compared to other Al–N_{imine} bonds,[8] and a contraction of the Al–Me bond lengths from 1.985(2) Å/1.993(2) Å in the related $[Al\{hpp\}Me_2]_2$ dimer[9] to 1.964(3) Å–1.976(3) Å in **4b** is commensurate with a positive charge located at the metal. However, whilst formally neutral, the C–N bond lengths within the guanidine components are not localised into single and double bonds to a great extent (Δ_{CN} = 0.03 Å), suggesting the charge is shared between the metal and the ligand. It is of interest to note that there are no close contacts between the THF molecules and the metal centre within the unit cell of **4b**, suggesting a crowded environment at aluminium. The effects of this steric protection on potential catalytic applications form part of an ongoing study into the chemistry of this system.[10]

In summary we have synthesized and characterized mono- and di-protonated guanidium salts of the linked bis(guanidine) precursor, $H_2C\{hpp\}_2$. The application of the former as a reagent for the direct synthesis of cationic main group complexes has been illustrated for the dialkyl aluminium system, affording the stable cation, $[H_2C\{hpp\}_2AlMe_2][BPh_4]$. Unfortunately, limited solubility of the product species has, to date, hampered extension of this work using compound **3b** as a method of potentially generating dicationic metal complexes.

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Notes and references

† Selected analytical data: *$[H_2C\{hpp\}\{hppH\}][BPh_4]$ (**2b**)*: Anal. calc. for $C_{39}H_{47}BN_6$: C 76.71, H 7.76, N 13.76%. Found: C 76.71, H 7.64, N 13.89%. ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K): δ 14.00 (s, 1H, N*H*), 7.32 (m, 8H, *m*-C_6H_5), 7.03 (t, *J* = 7.4, 8H, *o*-C_6H_5), 6.89 (m, 4H, *p*-C_6H_5), 4.54 (br s, 2H, $H_2C\{hpp\}\{hppH\}$), 3.25 (m, 4H, hpp-CH_2), 3.17 (m, 4H, hpp-CH_2), 3.11 (m, 4H, hpp-CH_2), 3.05 (m, 4H, hpp-CH_2), 1.86 (m, 4H, hpp-CH_2), 1.82 (m, 4H, hpp-CH_2). $^{13}C\{^1H\}$ NMR (125 MHz, CD_2Cl_2, 298 K): δ 164.3 (q, *J* = 49, *i*-C_6H_5), 151.7 (CN_3), 136.3 (*m*-C_6H_5), 125.9 (q, *J* = 3, *o*-C_6H_5), 122.1 (*p*-C_6H_5), 66.8 ($H_2C\{hpp\}\{hppH\}$), 48.1 (hpp-CH_2), 47.7 (hpp-CH_2), 47.6 (hpp-CH_2), 40.9 (hpp-CH_2), 22.3 (hpp-CH_2), 21.9 (hpp-CH_2). ^{11}B NMR (160 MHz, CD_2Cl_2, 298 K): δ 12.2 (m). *$[H_2C\{hppH\}_2][Cl][BPh_4]$ (**3b**)*: Anal. calc. for $C_{39}H_{48}BClN_6$: C 72.39, H 7.48, N 12.99%. Found: C 72.45, H 7.49, N 12.81%. ^{1}H NMR (300 MHz, CD_3CN, 298 K): δ 8.43 (br s, 2H, N*H*), 7.13 (m, 8H, *m*-C_6H_5), 6.86 (t, *J* = 7.4, 8H, *o*-C_6H_5), 6.71 (t, *J* = 7.2, 4H, *p*-C_6H_5), 5.07 (s, 2H, $H_2C\{hppH\}_2$), 3.14 (m, 12H, hpp-CH_2), 1.81 (m, 12H, hpp-CH_2). $^{13}C\{^1H\}$ NMR (75 MHz, CD_3CN, 353 K): δ 165.2 (q, *J* = 49, *i*-C_6H_5), 152.8 (CN_3), 137.0 (*m*-C_6H_5), 126.7 (q, *J* = 3, *o*-C_6H_5), 122.9 (*p*-C_6H_5), 64.6 ($H_2C\{hppH\}_2$), 49.3 (hpp-CH_2), 48.6 (hpp-CH_2), 46.6 (hpp-CH_2), 39.7 (hpp-CH_2), 21.9 (hpp-CH_2), 21.5 (hpp-CH_2). *$[H_2C\{hpp\}_2AlMe_2][BPh_4]$ (**4b**)*: Anal. Calc. for $C_{41}H_{52}AlBN_6$ (C_4H_8O): C 73.16, H 8.19, N 11.38%. Found: C 73.80, H 7.97, N, 12.51%. ^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.33 (m, 8H, *m*-C_6H_5), 7.05 (t, *J* = 7.4, 8H, *o*-C_6H_5), 6.90 (t, *J* = 7.2, 4H, *p*-C_6H_5), 4.65 (br s, 2H, $H_2C\{hpp\}_2$), 3.15 (m, 8H, hpp-CH_2), 3.06 (m, 4H, hpp-CH_2), 2.96 (m, 4H, hpp-CH_2), 1.84 (m, 8H, hpp-CH_2), −0.86 (s, 6H, $AlMe_2$). $^{13}C\{^1H\}$NMR (75 MHz, CD_2Cl_2, 298 K): δ 164.3 (q, *J* = 49, *i*-C_6H_5), 158.4 (CN_3), 136.2, (*m*-C_6H_5), 125.9 (q, *J* = 3, *o*-C_6H_5), 122.1 (*p*-C_6H_5), 70.0 ($H_2C\{hpp\}_2$), 48.5 (hpp-CH_2) 47.8 (hpp-CH_2), 47.0 (hpp-CH_2), 41.9 (hpp-CH_2), 23.6 (hpp-CH_2), 22.4 (hpp-CH_2), −9.4 (br, $AlMe_2$).

‡ The Gibbs free energy associated with this process is calculated at 51.4 kJ mol^{-1}, according to the equation: $\Delta G^{\ddagger} = [22.96 + \ln (T_c/\Delta\upsilon)]$.

§ Crystallographic **2b**: $C_{39}H_{47}BN_6$, *M* = 610.64, *T* = 173(2) K, triclinic, space group $P\bar{1}$ (no. 2), *a* = 10.2719(3), *b* = 12.4868(3), *c* = 14.3087(5) Å, α = 109.992(2), β = 99.770(1), γ = 100.197(2)°, *U* = 1644.02(8) $Å^3$, *Z* = 2, D_c = 1.234 Mg m^{-3}, μ (Mo-Kα) = 0.073 mm^{-1}, independent reflections = 5727 [R_{int} = 0.051], R_1 [for 4569 reflections with $I > 2\sigma(I)$] = 0.046, wR_2 (all data) = 0.115. **3b** $C_{39}H_{48}BClN_6$, *M* = 647.09, *T* = 173(2) K, triclinic, space group $P\bar{1}$ (No.2), *a* = 13.8838(3), *b* = 16.0260(3), *c* = 17.2417(4) Å, α = 114.885(1), β = 93.524(1), γ = 91.947(1), *U* = 3466.80(13) $Å^3$, *Z* = 4, D_c = 1.24 Mg m^{-3}, μ (Mo-Kα) = 0.15 mm^{-1}, independent reflections = 13606 [R_{int} = 0.059], R_1 [for 9575 reflections with $I > 2\sigma(I)$] = 0.056, wR_2 (all data) = 0.140. **4b** $C_{41}H_{52}AlBN_6\cdot(C_4H_8O)$, *M* = 738.78, *T* = 173(2) K, triclinic, space group $P\bar{1}$ (no. 2), *a* = 10.8106(2), *b* = 19.9865(4), *c* = 21.7023(3) Å, α = 66.307(1), β = 87.632(1), γ = 74.326(1), *U* = 4122.18(13) $Å^3$, *Z* = 4, D_c = 1.19 Mg m^{-3}, μ (Mo-Kα) = 0.09 mm^{-1}, independent reflections = 16005 [R_{int} = 0.055], R_1 [for 11181 reflections with $I > 2\sigma(I)$] = 0.061, wR_2 (all data) = 0.167. CCDC 617259–617261. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b611343e

¶ The ρ value is defined as the ratio of the doubled C=N distance (*a*) and C–NR_2 distances (*b*, *c*): $\rho = 2a/(b + c)$, and has been used as a measure of the degree of protonation of a guanidine. See ref. 4 and 5. The Δ_{CN} value is defined as the difference between the formally C=N double and C–N single bonds within the amidine unit: $\Delta_{CN} = d(C–N) - d(C=N)$. See ref. 6.

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10 Preliminary studies have indicated that cation **4b** is remarkably stable, showing no reactivity with olefins (1-hexene) or weak acids (phenyl-acetylene). P. J. Aragón Sáez and M. P. Coles, unpublished results.

