Supporting Information for:

Synthesis and Characterisation of Magnesium Complexes Containing Sterically Demanding *N,N′*-Bis(aryl)amidinate Ligands

Graeme J. Moxey,*‡ Fabrizio Ortu, Leon Goldney Sidley, Helen N. Strandberg, Alexander J. Blake, William Lewis and Deborah L. Kays*

School of Chemistry, University of Nottingham, University Park, Nottingham, NG7 2RD, United Kingdom

‡ Current address: Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia.

Contents

Characterisation data for amidines L^2H and L^4H

Data for DippN{C(Cy)}N(H)Dipp (L^2H)

^{1}H NMR (CDCl$_3$, 298 K, 300 MHz): δ 0.99 (d, 6H, CH(CH_3)$_2$, J = 6.9Hz), 1.21 (d, 6H, CH(CH_3)$_2$, J = 6.7Hz), 1.27 (d, 6H, CH(CH_3)$_2$, J = 7.0Hz), 1.31 (d, 6H, CH(CH_3)$_2$, J = 7.0Hz), 1.55-1.64 (m, 4H, Cy-CH_2), 1.71-1.83 (m, 6H, Cy-CH_2), 1.98-2.02 (m, 1H, Cy-CHN), 3.13 (sept, 2H, CH(CH$_3$)$_2$, J = 6.9Hz), 3.21 (sept, 2H, CH(CH$_3$)$_2$, J = 6.9Hz), 5.21 (s, 1H, NH), 7.00-7.03 (m, 1H, ArH), 7.11-7.15 (m, 4H, ArH), 7.23-7.26 (m, 1H, ArH). ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K, 100 MHz): δ 22.4 (CH(CH$_3$)$_2$), 22.8 (CH(CH$_3$)$_2$), 24.1 (CH(CH$_3$)$_2$), 25.4 (CH(CH$_3$)$_2$), 25.8 (Cy-CH$_2$), 26.1 (Cy-CH$_2$), 28.0 (CH(CH$_3$)$_2$), 28.3 (CH(CH$_3$)$_2$), 30.9 (Cy-CH$_2$), 39.0 (Cy-HCN), 122.6 (ArCH), 122.9 (ArCH), 123.5 (ArCH), 127.9 (ArCH), 133.1 (ArC), 139.0 (ArC), 144.2 (ArC), 147.1 (ArC), 159.0 (CN$_2$). Elemental analysis: calcd for C$_{31}$H$_{46}$N$_2$: C 83.35, H 10.38, N 6.27; found C 83.27, H 10.23, N 6.17. High res. mass spec. (ESI): calcd for C$_{31}$H$_{47}$N$_2$ [M + H]$^+$: 447.3734; measd 447.3745; calcd for C$_{31}$H$_{46}$N$_2$Na [M + Na]$^+$: 469.3553; measd 469.3557. IR (Nujol): v = 3374 (m, NH), 1950 (w), 1634 (s, C=N), 1587 (s), 1360 (w), 1324 (m), 1268 (s), 1225 (w), 1190 (m), 1159 (w), 1137 (w), 1110 (s), 1044 (s), 936 (s), 893 (m), 843 (m), 821 (m), 802 (s), 777 (s), 673 (m) cm^{-1}.

Data for DippN{C(Ph)}N(H)Dipp (L^4H)

^{1}H NMR (CDCl$_3$, 298 K, 300 MHz): δ 0.92 (d, 6H, CH(CH_3)$_2$, J = 6.8Hz), 1.02 (d, 6H, CH(CH_3)$_2$, J = 6.9Hz), 1.28 (d, 6H, CH(CH_3)$_2$, J = 6.7Hz), 1.39 (d, 6H, CH(CH_3)$_2$, J = 7.0Hz), 3.20 (sept, 2H, CH(CH$_3$)$_2$, J = 6.9Hz), 3.27 (sept, 2H, CH(CH$_3$)$_2$, J = 6.6Hz), 5.74 (s, 1H, NH), 7.01-7.03 (m, 2H, ArH), 7.07-7.32 (m, 7H, ArH), 7.41-7.44 (m, 2H, ArH). ^{13}C{^{1}H} NMR (CDCl$_3$, 298 K, 75 MHz): δ 22.3 (CH(CH$_3$)$_2$), 22.5 (CH(CH$_3$)$_2$), 24.4 (CH(CH$_3$)$_2$), 25.2 (CH(CH$_3$)$_2$), 28.4 (CH(CH$_3$)$_2$), 28.6 (CH(CH$_3$)$_2$), 123.3 (ArCH), 123.4 (ArCH), 123.6 (ArCH), 127.5 (ArCH), 127.7 (ArCH), 128.8 (ArCH), 129.2 (ArCH), 133.9 (ArC), 134.9 (ArC), 139.3 (ArC), 143.7 (ArC), 145.1 (ArC), 153.6 (CN$_2$). Elemental analysis: Calcd for C$_{31}$H$_{40}$N$_2$: C 84.49, H 9.15, N 6.36; found C 84.38, H 9.24, N 6.43. Accurate mass (ESI): Calcd for C$_{31}$H$_{41}$N$_2$ [M + H]$^+$: 441.3264; measd 441.3269; calcd for C$_{31}$H$_{40}$N$_2$Na [M + Na]$^+$: 463.3084; measd 463.3078. IR (Nujol): v = 3361 (m, NH), 1611 (s, C=N), 1586 (w), 1571 (s), 1352 (s), 1322 (m), 1255 (m), 1189 (m), 1092 (s), 1058 (w), 933 (w), 834 (m), 802 (m), 772 (s), 760 (s), 736 (m), 697 (s) cm^{-1}.
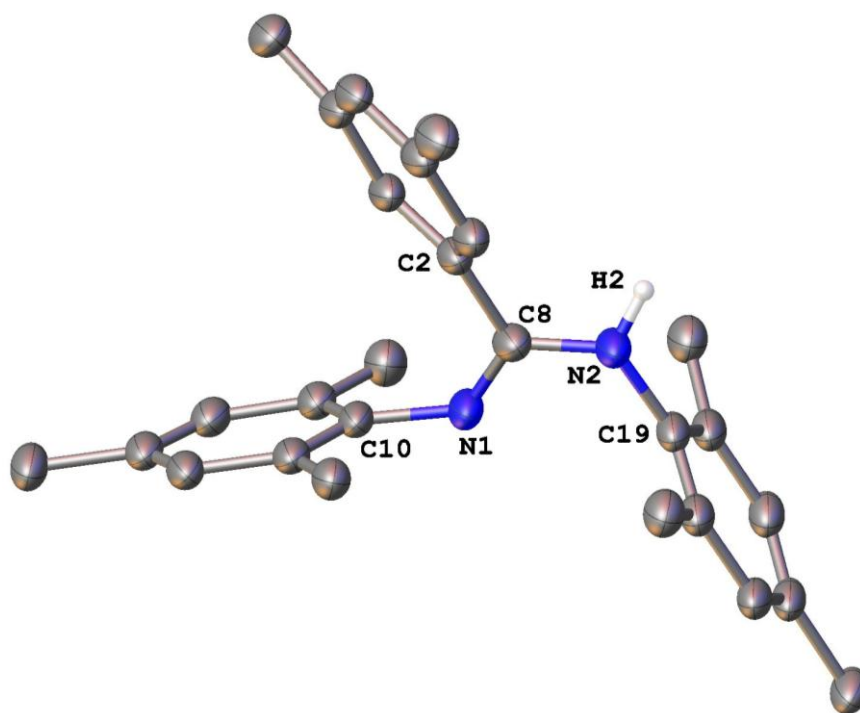
Figure S1: Crystal structure of MesN{C(Dmp)}N(H)Mes **L**^{5}H with displacement ellipsoids set at 40% probability. The NH hydrogen atom is disordered over two positions, N(1)–H(1) and N(2)–H(2); these hydrogen atoms are each half occupied, giving Z_{anti} and E_{syn} tautomers. Only the E_{syn} tautomer is displayed. Hydrogen atoms (apart from N(2)–H(2)) are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(8) 1.320(3), N(2)–C(8) 1.332(3), N(1)–C(10) 1.430(3), N(2)–C(19) 1.432(3), N(2)–H(2) 0.87(4), N(1)–H(1) 0.88(5), N(1)–C(8)–N(2) 121.7(2), C(8)–N(1)–C(10) 125.97(19), C(8)–N(2)–C(19) 119.52(19), N(1)–C(8)–C(2) 122.8(2), N(2)–C(8)–C(2) 115.5(2).
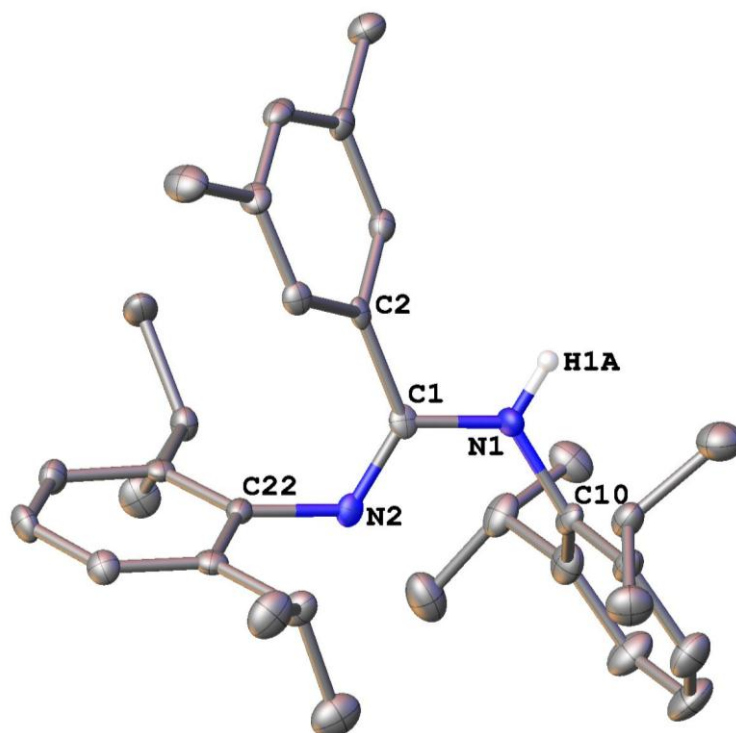
Figure S2: Crystal structure of DippN{C(Dmp)}N(H)Dipp **L^6**H with displacement ellipsoids set at 40% probability. Hydrogen atoms (apart from N–H) are omitted for clarity. Selected bond lengths (Å) and angles (°): N(1)–C(1) 1.370(5), N(2)–C(1) 1.293(5), N(1)–C(10) 1.437(5), N(2)–C(22) 1.412(5), N(1)–H(1A) 0.90(4), N(1)–C(1)–N(2) 119.3(4), C(1)–N(1)–C(10) 123.1(4), C(1)–N(2)–C(22) 120.1(4), N(1)–C(1)–C(2) 114.4(4), N(2)–C(1)–C(2) 126.3(4).

Crystal structures of L^5H and L^6H

In the crystal structure of $\mathbf{L^5H}$, the hydrogen atom is disordered over two positions, each with 50% occupancy, a result of two tautomers (Z_{anti} and E_{syn}) of $\mathbf{L^5H}$ co-existing in the crystal. A further consequence of this is that the C=N bond is disordered, giving near identical C–N distances [1.320(3) Å and 1.332(3) Å]. Similar behaviour has been reported in the crystal structure of DippN{C(*p*-Tol)}N(H)Dipp (*p*-Tol = 4-methylphenyl);[S1] the authors report two tautomers Z_{anti} (72% occupancy) and E_{syn} (28% occupancy) and similar C–N distances [1.344(3) Å and 1.317(3) Å]. Similar Z_{anti} and E_{syn} disorder was reported in the structure of DippN{C(*p*-^{t}BuPh)}N(H)Dipp.[S2] Surprisingly, the closely related amidine DippN{C(*p*-MeOPh)}N(H)Dipp (*p*-MeOPh = 4-methoxyphenyl)[S1] crystallises solely in a Z_{anti} structure, with well defined C–N [1.3633(17) Å] and C=N [1.3066(17) Å] bonds. Evidently, small changes in the amidine backbone substituents can have a marked effect on the solid-state structure. The N–C–N angle in $\mathbf{L^5H}$ [121.7(2)°] is comparable with that in DippN{C(*p*-Tol)}N(H)Dipp [120.4(2)°][S1] and DippN{C(^{t}Bu)}N(H)Dipp [119.1(2)°].[S3]

In contrast to $\mathbf{L^5H}$, $\mathbf{L^6H}$ crystallises solely in an E_{syn} structure, with disparate C–N [1.370(5) Å] and C=N [1.293(5) Å] bonds. These bond distances are in good agreement with related amidines, such as MesN{C(^{t}Bu)}N(H)Mes [C–N 1.375(3) Å, C=N 1.280(2) Å].[S3] The N–C–N angle in $\mathbf{L^6H}$ [119.3(4) °] is within the range of the reported values for DippN{C(*p*-Tol)}N(H)Dipp [121.38(12)°][S1] and MesN{C(^{t}Bu)}N(H)Mes [116.0(2) °].[S3]

Calculation of the Δ_{CN} parameter for complexes 1-3, 5, 6, $\mathbf{L^5H}$ and $\mathbf{L^6H}$

In amidinate and guanidinate chemistry, the Δ_{CN} parameter is defined as the difference between the amine (C–N) and imine (C=N) bond lengths $[\Delta_{CN} = d(C–N) – d(C=N)]$,[S4] and is a useful method for quantifying the degree of delocalisation in the N–C–N component of amidines. Table S2 presents calculated Δ_{CN} values, in addition to the N–C–N angles, for amidines $\mathbf{L^5H}$ and $\mathbf{L^6H}$, and amidinate ligands in **1**-**3**, **5** and **6**. In the case of $\mathbf{L^5H}$, it should be noted that the presence of two tautomeric forms within the crystal precludes an accurate determination of Δ_{CN}. For **1**-**3**, **5** and **6**, the magnitude of Δ_{CN} is reported for each amidinate ligand.

Table S1: Calculated Δ_{CN} values (Å) and N–C–N angles (°) for amidinate ligands in **1**-**3**, **5** and **6**, and amidines $\mathbf{L^5H}$ and $\mathbf{L^6H}$.

	1	2	3	5	6	$\mathbf{L^5H}$	$\mathbf{L^6H}$
Δ_{CN} N(1,2)	0.016(6)	0.014(6)	0.004(3)	0.007(4)	0.003(9)	0.012(6)	0.077(10)
Δ_{CN} N(3,4)	0.021(6)	0.008(6)	0.005(3)	0.001(4)	0.011(9)		
N(1)-C-N(2)	112.6(2)	112.60(18)	114.67(10)	113.88(14)	114.1(3)	121.7(2)	119.3(4)
N(3)-C-N(4)	112.46(19)	112.90(17)	114.51(10)	114.06(14)	114.3(3)		

Δ_{CN} N(1,2) $= d(C–N) – d(C=N)$ for $\mathbf{L^5H}$ and $\mathbf{L^6H}$
Δ_{CN} N(1,2) $= | d[C\text{-----}N(2)] – d[C\text{-----}N(1)] |$ for **1**-**3**, **5** and **6**
Δ_{CN} N(3,4) $= | d[C\text{-----}N(4)] – d[C\text{-----}N(3)] |$ for **1**-**3**, **5** and **6**

Comparing the data of $\mathbf{L^6H}$ and **6**, it is evident that on deprotonation of the amidine and coordination to the magnesium centre, the Δ_{CN} values decrease, indicating delocalisation of the anionic charge across the amidinate backbone. Delocalisation of the anionic charge is also observed in **1**-**3** and **5**. Furthermore, on chelation of the amidinate to the magnesium centre, the N–C–N angle becomes more acute.

References

S1. R. T. Boeré, V. Klassen and G. Wolmershäuser, *J. Chem. Soc., Dalton Trans.,* 1998, 4147.

S2. C. Jones, S.J. Bonyhady, N. Holzmann, G. Frenking and A. Stasch, *Inorg. Chem.,* 2011, **50**, 12315.

S3. A. Xia, H.M. El-Kaderi, M.J. Heeg and C.H. Winter, *J. Organomet. Chem.,* 2003, **682**, 224.

S4. G. Häfelinger and F. K.H. Kuske, in *The Chemistry of the Amidines and Imidates,* eds. S. Patai and Z. Rappoport, Wiley, Chichester, 1991, vol. 2, ch. 1, p. 1.