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6-Aminofulvene-2-aldimine, a novel class of ambidentate cyclopentadienyl/diimine ligand: synthesis and characterisation of magnesium complexes

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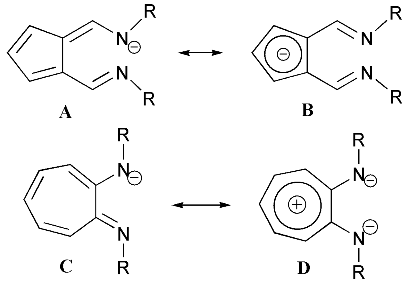
Two magnesium complexes of the 6-aminofulvene-2-aldimine (AFA) system bearing cyclohexyl groups on the donor nitrogen atoms have been synthesised; in the first the ligand is coordinated *via* the two nitrogen donors while in the second it is found to ligate magnesium *via* the cyclopentadienyl and the imine donors.

The search for new ancillary ligands to support the metal centre in homogeneous catalysts is driven by a desire to precisely tune the steric and/or electronic properties of the active site in order to maximise selectivity and productivity. Our earlier studies of the potential of nitrogen donor stabilised magnesium alkyls as alkene polymerisation catalysts[1] have led to an investigation of ligands which provide neutral but zwitterionic complexes with negative charge localised in the ligand and a positive metal centre. Although the 6-aminofulvene-2-aldimine system (H**A**) was first prepared in 1963,[2] until recently it remained a curiosity of interest by virtue of the unusual nature of its tautomerism and intramolecular hydrogen bonding.[3] With respect to charge separation this ligand is the antithesis of the better known α-aminotroponiminate system (**C**)[4] in that the predominant tautomer, as shown by dipole moment studies, contains a negative charge localised in the aromatic ring (**B**) creating a neutral diimine donor set contrasting with the preferred tropylium-diamide tautomer of the α-amino-troponiminate system (**D**). The discovery of a new synthesis of the C-phenyl derivative $C_5H_3\{1,2\text{-}C(Ph)NH\}_2H$ based upon the reaction of benzonitrile with magnesocene has led to recent reports of Mg,[4] Al,[5] Ga[5] and Zr[4] complexes of this derivative. However, the applicability of this system with H atoms on the nitrogen donors as an ancillary ligand in catalysis is likely to be limited. We have revisited the original synthesis of the 6-aminofulvene-2-aldimine system which provides a flexible entry into this chemistry allowing preparation of the ligand with a broad range of nitrogen substituents, and even those with different groups on the two nitrogen atoms.[2] We report here two magnesium complexes of the dicyclohexyl derivative (Cy_2AFA), one of which demonstrates the potential ambidentate nature of this system as a ligand.



A **B**

C **D**

Treatment of N,N′-dicyclohexyl-6-aminofulvene-2-aldimine (HCy_2AFA)† with methyllithium followed by methylmagnesium bromide in toluene provides the methyl magnesium complex $[(Cy_2AFA)Mg(CH_3)THF]$ (**1**). The ^1H nmr spectrum of **1**‡ contains a signal at −0.98 ppm for the Mg bound methyl ligand. Other characteristic signals are a pentuplet at 1.91 ppm for the cyclohexyl NCH protons and a singlet at 7.89 ppm for the imine N=CH protons. The ^{13}C nmr spectrum shows the expected number of signals for a pseudo C_s-symmetric species. The X-ray crystal structure of this species§ (Fig. 1) shows the coordination geometry of the magnesium to be approximately tetrahedral. The cyclopentadienyl and imine portions of the Cy_2AFA ligand are coplanar but the Mg centre is located around 0.64 Å out of this plane. Molecular models of the structure and the 3-coordinate species formed by removal of THF,¶ in which Mg is coplanar with the ligand, indicate that this distortion may be a result of the bulk of the THF ligand. The Mg–C distance of 2.116(2) Å compares with values of 2.107(6) and 2.189(4) Å for the β-diketiminate complexes $[HC(RCNAr')_2Mg(Me)THF]$ (Ar = 2,6-diisopropyl) where R = Me and ^{t}Bu respectively.[1a, 1b] The C–N and C–C bond lengths within the ligand may be used to provide some information about the electronic structure of the π-system and thus the tautomeric form of the ligand (**A** *vs.* **B**). The C–N distances are found to be indistinguishable at 1.29 Å. This is significantly shorter than in either the β-diketiminate complex $[HC(MeCNAr')_2Mg(CH_3)THF]$ (C–N = 1.34 Å) or the bis-chelate [N,N′-diisopropyl-α-aminotroponiminate)$_2$Mg] (C–N = 1.33 Å)[1a] thus indicating significant double bond character. Similarly, the ring C–imine C distances are indistinguishable (1.42 Å) and consistent with single bonds. Together these data provide a consistent picture of the coordinated ligand as a cyclopentadienyldiimine (**B**) rather than an amidofulvenealdimine (**A**). The variation of the C–C– bond lengths within the C_5 ring are consistent with the negative charge being localised in an allyl system spanning the C3–C4–C5 unit, with the C–C distances being significantly shorter in this part of the ring.

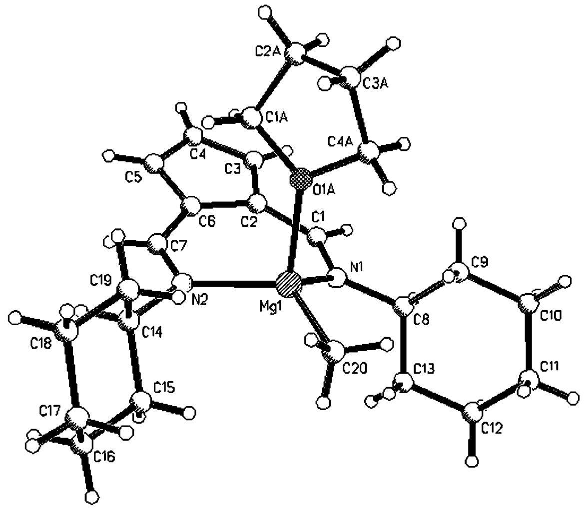


Fig. 1 Molecular structure of $[(Cy_2AFA)Mg(CH_3)THF]$ (**1**). Selected bond distances (Å) and angles (°): Mg–C20 2.116(2), Mg–N1 2.0882(16), Mg–N2 2.0821(15), Mg–O1A 2.0526(15), N1–Mg–N2 103.96(6), N1–C1 1.294(2), C1–C2 1.422(3), C2–C3 1.412(3), C3–C4 1.378(3), C4–C5 1.389(3), C5–C6 1.411(3), C2–C6 1.447(3), C6–C7 1.424(3), N2–C7 1.292(2).

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The direct reaction of HCy$_2$AFA with methylmagnesium bromide without prior lithiation liberates methane and provides a species (**2**) whose ^{1}H nmr spectrum is significantly more complex than that for **1** indicating the presence of two Cy$_2$AFA ligands in different environments.‖ The X-ray crystal structure** of **2** reveals an asymmetric dimeric structure (Fig. 2) in which one of the Cy$_2$AFA ligands is found in essentially the same environment as that in **1**, chelating one Mg ion through its two nitrogen donors. The coordination sphere of this magnesium centre is completed by the symmetrical η^5-coordination of the cyclopentadienyl ring of a second Cy$_2$AFA ligand and a bromide ligand which bridges the two Mg centres in the molecule. The nitrogen atoms of this second ligand are also coordinated to Mg(1) whose fourth coordination site is occupied by a terminal bromide ligand. The symmetrical coordination of the C$_5$ ring to Mg(2) [Mg–C range = 2.526(3)–2.570(3) Å] and the C–C bond lengths supports an aromatic rather than a fulvene picture of the electronic structure, and thus the location of the negative charge within the C$_5$ ring, this being consistent with a cyclopentadienyldiimine (**B**) description of the ligand rather than an amidofulvenealdimine (**A**).

Magnesium cyclopentadienyl complexes are relatively common, but the structure most closely related to **2** is that obtained from the reaction of magnesocene with benzonitrile discussed above.[4] This provides the complex $[(\eta^5\text{-}C_5H_5)Mg\{\eta^2\text{-}(NHCPh)_2C_5H_3\}NCPh]$ in which the C$_5$ ring of the AFA ligand remains uncoordinated and the Mg coordination sphere is completed by η^5-Cp and benzonitrile ligands. The zwitterionic nature of complexes of AFA type ligands has previously been recognised,[4] and the localisation of negative charge in the cyclopentadienyl ring of the ligand would be anticipated to favour metal coordination, however **2** is the first example of a complex in which coordination of this portion of the ligand has been observed. This therefore gives us confidence that nitrogen coordination is the favoured mode of metal attachment for this ligand system as required for our intended application in the formation of zwitterionic transition and main group metal alkyl complexes for alkene polymerisation. Our exploration of the properties conferred by this ligand system and its derivatives upon a range of both main group and transition metal complexes is underway.

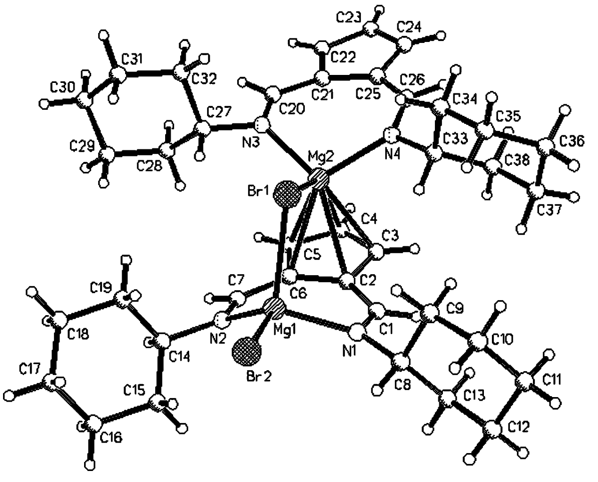

Fig. 2 Molecular structure of [(Cy$_2$AFA)$_2$MgBr$_2$] (**2**). Selected bond distances (Å) and angles (°): Mg1–N1 2.061(2) Mg1–N2 2.066(3), N1–Mg1–N2 105.12(10), Mg2–N3 2.038(2), Mg2–N4 2.035(3), N3–Mg2–N4 106.26(10), N1–C1 1.282(3), C1–C2 1.442(4), C2–C3 1.410(4), C3–C4 1.398(4), C4–C5 1.393(4), C5–C6 1.413(4), C2–C6 1.451(4), C6–C7 1.439(4), N2–C7 1.280(3), N3–C20 1.297(3), C20–C21 1.413(4), C21–C22 1.402(4), C22–C23 1.385(4), C23–C24 1.386(4), C24–C25 1.404(4), C21–C25 1.463(4), C25–C26 1.412(4), N4–C26 1.296(4).

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Notes and references

† We have determined the X-ray crystal structure of N,N′-dicyclohexyl-6-aminofulvene-2-aldimine (HCy$_2$AFA) and found the essential features to be similar to that of the diphenyl derivative.[6] CCDC 205721.

‡ *Spectroscopic data* for **1**: ^{1}H nmr (d_8-toluene): δ −0.98 (s, 3H, CH$_3$), 0.93 (m, 4H, THF), 1–1.8 (m, 20H, Cy CH$_2$), 1.91 (pent., 2H, Cy CH), 3.18 (m, 4H, THF), 6.45 (t, J = 3.5 Hz, 1H, Cp CH), 6.66 (d, 3.5 Hz, 2H, Cp CH), 7.89 (s, 2H, N=CH); ^{13}C nmr (d_8-toluene): δ −10.6 (CH$_3$), 23.9 (CH$_2$), 24.3 (CH$_2$), 24.9 (CH$_2$), 33.1 (CH$_2$), 67.5 (CH$_2$), 69.1 (NCH), 113.8 (C), 115.9 (CH), 133.0 (CH), 162.8(N=CH). Satisfactory elemental analysis for **2** could not be obtained which we attribute to its air-sensitive nature.

§ *Crystal data* for **1**: C$_{24}$H$_{38}$MgN$_2$O, *F*w = 394.87, space group orthorhombic *Pbca*, a = 11.3464(9), b = 15.2076(13), c = 27.249(2) Å, $\alpha = \beta = \gamma$ = 90°, U = 4701.9(7) Å^3, Z = 8, l = 0.71073 Å, D_{calc} = 1.116 Mg m^{-3}, μ(Mo-Kα) = 0.091 mm^{-1}. Data were collected on a Bruker SMART APEX diffractometer[7] equipped with an Oxford Cryosystems low-temperature device at 150 K and using a colourless rod oil-coated crystal[8] of dimension 0.38 × 0.36 × 0.10 mm using the θ/ω method ($2.98 \leq 2\theta \leq 58.12°$). Of a total of 28371 reflections collected 5846 were independent. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1$ = 0.0652 (for 5846 data with $F > 4sF$) and $wR2$ = 0.1578 (all data) [$R1 = \Sigma|F_o - F_c|/\Sigma|F_o|$, $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2/3)$]. Goodness of fit on F^2 = 1.078, 271 parameters. Largest difference between peak and hole in the final difference map, 0.540 and −0.373 e Å^{-3}. CCDC 205884.

¶ Molecular modelling was conducted using the mm2 forcefield employed by CACHe software.

‖ Spectroscopic data for **2**: ^{1}H nmr (d_8-toluene): δ 0.7–1.7 (m, 20H, Cy CH$_2$), 1.85 (pent. J = 2.2 Hz, 2H, Cy CH), 6.40 (t, J = 3.6 Hz, 1H, Cp CH), 6.71 (d, J = 3.6 Hz, 2H, Cp CH), 6.74 (t, J = 1.1 Hz, 1H, Cp CH), 6.86 (d, J = 1.1 Hz, 2H, Cp CH), 7.32 (s, 2H, N=CH), 7.34 (s, 2H, N=CH) ^{13}C nmr (d_8-toluene): δ 28.1 (CH$_2$), 28.7 (CH$_2$), 38.1 (CH$_2$), 66.7 (CH), 121.0, CH), 124.2 (CH), 133.9 (CH), 157.2 (CH). Satisfactory elemental analysis for **2** could not be obtained which we attribute to its air-sensitive nature.

** Crystal data for **2**: C$_{38}$H$_{54}$Br$_2$Mg$_2$N$_4$, *F*w = 775.27, space group monoclinic $P2_1/c$, a = 11.354(5), b = 26.306(5), c = 12.779(5) Å, α = 90, β = 100.925(5), γ = 90°, U = 3748(2) Å^3, Z = 4, l = 0.71073 Å, D_{calc} = 1.374 Mg m^{-3}, μ(Mo–Kα) = 2.229 mm^{-1}. Data were collected on a a Bruker SMART APEX diffractometer[7] equipped with an Oxford Cryosystems low-temperature device at 150 K and using a colourless plate oil-coated crystal[8] of dimension 0.30 × 0.25 × 0.10 mm using the θ/ω method ($3.10 \leq 2\theta \leq 58.06°$). Of a total of 33990 reflections collected 10006 were independent. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 to final values of $R1$ = 0.0491 (for 10006 data with $F > 4sF$) and $wR2$ = 0.1092 (all data) [$R1 = \Sigma|F_o - F_c|/\Sigma|F_o|$, $wR2 = \{[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma wF_o^4\}^{0.5}$, $w = 1/[\sigma^2(F_o^2) + (xP)^2 + yP]$, $P = (F_o^2 + 2F_c^2/3)$]. Goodness of fit on F^2 = 1.024, 415 parameters. Largest difference between peak and hole in the final difference map, 0.674 and −0.490 eÅ^{-3}. CCDC 205885. See http://www.rsc.org/suppdata/cc/b3/b303540a/ for crystallographic data in .cif or other electronic format.

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