Structural and EPR characterisation of single electron and alkyl transfer products from reaction of dimethyl magnesium with bulky α-diimine ligands†‡

Philip J. Bailey,* Robert A. Coxall, Caroline M. Dick, Sylvie Fabre, Simon Parsons and Lesley J. Yellowlees

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Treatment of dimethylmagnesium with bulky α-diimine ligands provides either the biradical methyl-bridged complexes [(α-diimine$^{-\bullet}$)Mg$^+$(μ-CH$_3$)]$_2$ *via* single electron transfer (SET), or the product of methyl transfer to an imine carbon atom depending upon conditions.

Chelating ligands containing the α-diimine unit [RN=C(R)C(R)=NR], of the polypyridine (*e.g.* 2,2′-bipyridine, 1,10-phenanthroline)[1] and 1,4-diazabutadiene[2] form, are among the most widely employed nitrogen donor ligands in coordination chemistry. Their σ-donor characteristics coupled with the accessibility and symmetry properties of the π* molecular orbitals result in their compatibility with both main group and transition metals in a quite surprising range of oxidation states. This π-acid character may alternatively be viewed as non-innocent behaviour involving the reduced ligand mono- and di-anions, the former being a radical species.[3] The formation of highly coloured solutions by reaction of Grignard reagents with bipy and phen has been known since the 1960s, however the formation of radical species in such reactions was not appreciated at this time.[4] More recent investigations have shown that initial coordination of α-diimine ligands to alkyls and hydrides of Mg, Zn, Al and other metals may be followed by a variety of reaction pathways.[5] These secondary reactions include single electron transfer (SET) to the ligand concomitant with loss of an alkyl or H radical, and alkyl radical transfer to a ligand imine carbon or nitrogen atom following the SET process. For magnesium the predominant pathway is the formation of a stable radical complex, however, such [(α-diimine)MgR] species have not been structurally characterised, and we report here for the first time the structure of a complex of this type. The first isolation of a product of alkyl transfer from magnesium to a coordinated diimine ligand is also reported.

The reaction of diisopropylphenylbis(imino)-acenaphthene [(2,6-^{i}Pr$_2$Ph)BIAN] (**1**) with MgMe$_2$ in Et$_2$O at room temperature produces a deep red solution from which crystals can be obtained by concentration and layering with hexane. An X-ray crystal structure analysis§ revealed the product to be the methyl-bridged dimeric complex [Mg{(2,6-^{i}Pr$_2$Ph)BIAN}(μ-Me)]$_2$ (**2**) which represents the first structural characterisation of a paramagnetic magnesium alkyl complex of this type. There are two independent molecules in the unit cell which each lie about an inversion centre, and the molecule containing Mg1 is depicted in Fig. 1. The magnesium centres are significantly distorted from ideal tetrahedral geometry induced by the narrow bite angle of the chelating ligand. The bond lengths in the NCCN part of the ligand backbone are intermediate between those of double and single bonds found in the free diimine ligand [1.25 Å, 1.295 Å (C–N) and 1.528 Å (C–C)],[6] supporting the view of the ligand as a radical anion. The dimeric nature of this species implies the presence of a diradical system and is supported by the observation of an EPR spectrum (Fig. 2).

Treatment of the ligand diacetal-bis(2,6-diisopropylphenylimine) (**3**) with MgMe$_2$ under similar conditions also provides a red paramagnetic species (**4**) which we were unable to isolate, however, its EPR spectrum indicates the presence of the radical anion ligand. The solution EPR spectra of both **2** and **4** in Et$_2$O are shown in Fig. 2.¶ For **2** hyperfine coupling to two equivalent N atoms provides a 5-line signal, and simulation provides a value of 4.6 G for coupling to the nitrogen atoms (a^N). The additional coupling to two equivalent ligand methyl groups in **4** results in an 11-line signal for this species. Simulation of this spectrum provides a line width of 4.0 G which does not allow the values of a^N and a^H to be distinguished within the resolution achieved. The *g* values of *ca.* 2.012 for both **2** and **4** suggest that the electrons are highly

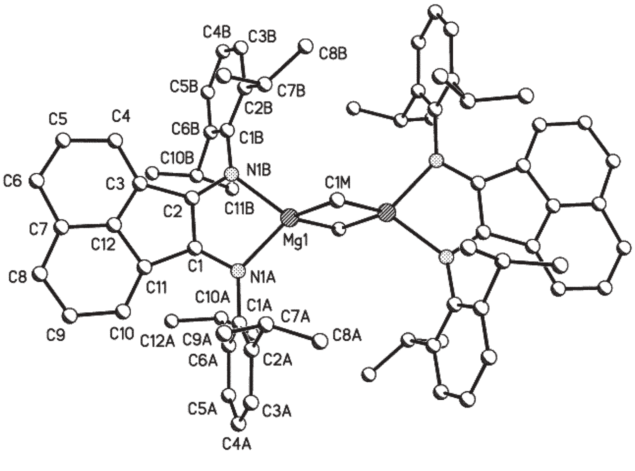


Fig. 1 Molecular structure of **2**. Selected bond distances (Å) and angles (°): Mg1–C1M 2.263(5), Mg1–N1A 2.066(5), Mg1–N1B 2.065(4), C1–C2 1.422(7), C1–N1A 1.345(6), C2–N1B 1.333(6) N1A–Mg1–N1B 84.54(17), N1A–Mg1–C1M 113.9(2), N1B–Mg1–C1M 116.4(2).

Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ. E-mail: Philip.Bailey@ed.ac.uk

† Electronic supplementary information (ESI) available: Experimental details and characterisation of **2**, **4** and **5**; details of EPR analyses of **2** and **4**. See http://dx.doi.org/10.1039/b505697g

‡ Dedicated to Prof. Brian F. G. Johnson on the occasion of his retirement.

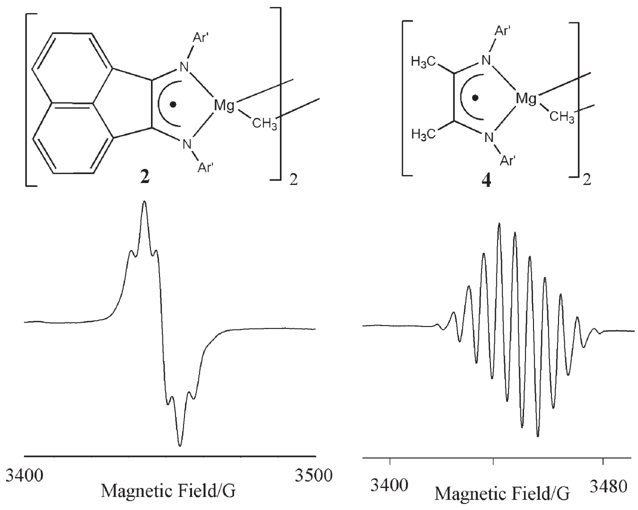


Fig. 2 Room temperature EPR spectra of **2** and **4** in Et_2O solution.¶

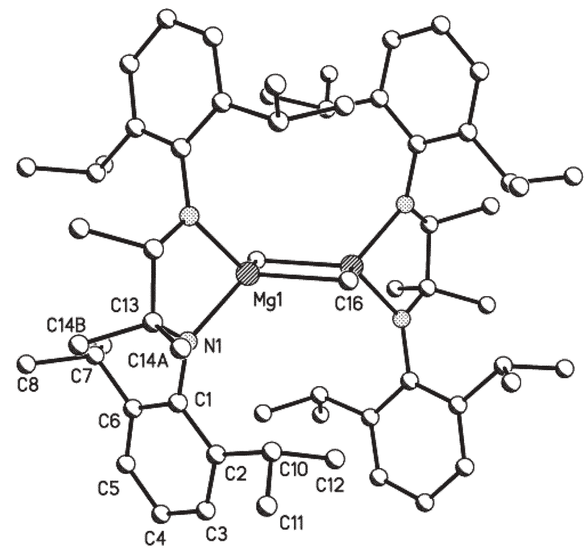
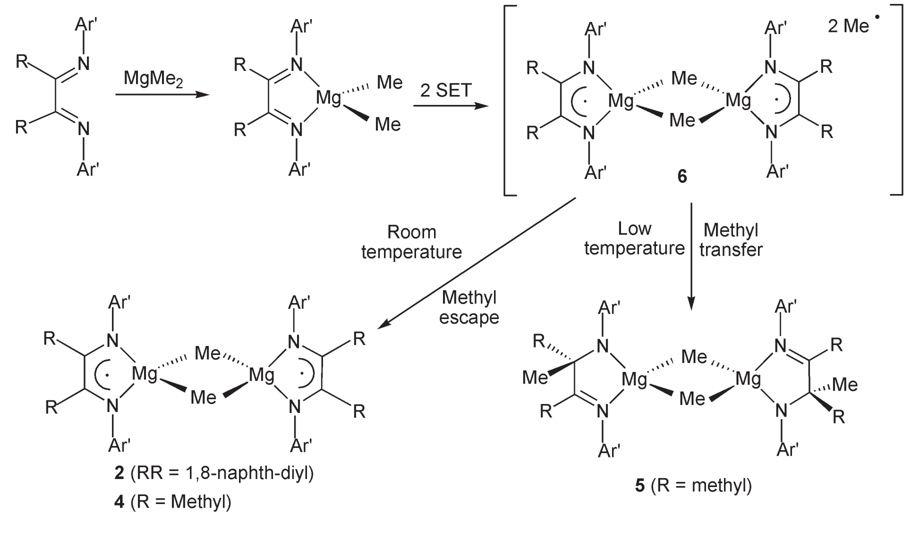


Fig. 3 Molecular structure of **5** derived from the disordered crystal structure. Selected bond distances (Å) and angles (°): Mg1–C16 2.2499(25), Mg1–N1 2.0422(14), C13–C13 1.505(4), N1–C13 1.370(2), N1–Mg1–N1 81.08(8).

delocalised. Coupling to the two ligand CH_3 groups in **4**, and the lack of coupling to the naphthyl protons in **2**, indicate its location within the NCCN unit. Spectra of both **2** and **4** were also recorded at 77 K in an attempt to observe the half field ($\Delta M_s = 2$) transitions characteristic of the $S = 1$ state. However, no signals could be observed in the low field region characteristic for such transitions, which is probably due to a very small zero field splitting, and these species therefore appear to act as two non-interacting doublets.

The reaction of **3** with $MgMe_2$ at low temperature was achieved by freezing a toluene–THF (10 : 1) solution of $MgMe_2$ in liquid nitrogen. A similarly cooled, but not frozen, solution of **3** was then added by cannula and the mixture allowed to slowly warm to room temperature. Under these conditions the reaction provides not the paramagnetic **4**, but rather an orange solution from which $[Mg\{(2,6\text{-}^iPr_2Ph)NC(Me)_2C(Me)N(2,6\text{-}^iPr_2Ph)\}(\mu_2\text{-}Me)]_2$ (**5**) could be obtained in low yield by storage at −20 °C. This complex is the result of methyl transfer to an imine carbon atom. X-Ray crystallography|| showed the structure to be disordered due to space group imposed 2/*m* symmetry; in part one of the data both carbon atoms in the ligand NCCN unit bear two methyl groups, while in part two there is only one methyl per carbon atom. Modelling of the disorder as a 1 : 1 combination of these two proved satisfactory and the resulting structure of **5** is shown in Fig. 3. As a result of the disorder the bond lengths related by the mirror plane containing the Mg–C–Mg–C unit are averaged and N1–C13 cannot be distinguished from its symmetry related partner for example. It is also not possible to determine whether the dimeric structure has a centre of inversion or if both methylated carbon atoms are on the same side of the molecule as is shown in Fig. 3.

The different outcome of the low temperature reaction demonstrates that the escape of the methyl radicals liberated by the SET process can be suppressed and their transfer to the diimine ligand favoured by reducing the reaction temperature. This is demonstrated by the isolation of the product of methyl transfer (**5**),



Scheme 1 Formation of radical and methyl transfer products *via* competing processes from the intermediate **6**.

the first time such a product has been isolated from reaction of a magnesium alkyl. The reactions of ZnR_2 and AlR_3 with α-diimines have been more extensively studied[5,7] and for these metals the products of alkyl transfer to both C and N atoms of the coordinated diimine appear to be equally common. Transfer to C in the present case may reflect the presence of the bulky 2,6-diisopropylphenyl nitrogen substituents in the ligands studied. The temperature dependence of the reaction pathway supports the existence of an intermediate (**6**, Scheme 1) of the type previously observed by EPR in frozen solutions[5b,7a] in which the initial products of the SET process are confined in close proximity within a solvent cage. The two reaction products may then be seen as the outcome of the competitive processes of methyl radical escape and transfer to the ligand.

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Notes and references

§ Crystal data for **2**: $C_{8150}H_{103.50}Mg_2N_4$ $[Mg_2Me_2L_2]1.25(C_6H_{14})$, M = 1187.80, triclinic, a = 14.513(9), b = 14.781(9), c = 18.381(9) Å, U = 3688(3) $Å^3$, T = 150(2) K, space group $P\bar{1}$, Z = 2, μ(Mo-Kα) = 0.613 mm^{-1}, 9159 reflections measured, 9159 unique (R_{int} = 0.000) which were used in all calculations. The SQUEEZE routine[8] was applied to remove contributions from disordered solvent. $R_1[F > 4\sigma(F)] = 0.0970$, wR_2(all data) = 0.2867. CCDC 270216. See http://dx.doi.org/10.1039/b505697g for crystallographic data in CIF or other electronic format.

¶ Simulation of the EPR spectra using "WINepr" provided the following parameters: **2** g = 2.0117, a^N = 4.6 G, Lorentzian line width 4.7 G.; **4** g = 2.0123, a^N = 5.554 G, a^H = 5.554 G, Lorentzian line width 4.0 G. Full details in ESI.†

‖ Crystal data for **5**: $C_{71}H_{108}Mg_2N_4O$ $[\{MgMeL\}_2]\cdot C_7H_8\cdot C_4H_8O$, M = 1082.23, monoclinic, a = 18.459(3), b = 18.337(3), c = 12.190(2) Å, U = 3301.6(10) $Å^3$, T = 150(2) K, space group $C2/m$, Z = 2, μ(Mo-Kα) = 0.080 mm^{-1}, 9392 reflections measured, 3459 unique (R_{int} = 0.0373) which were used in all calculations. The SQUEEZE routine[8] was applied to remove contributions from disordered solvent. $R_1[F > 4\sigma(F)] = 0.526$, wR_2(all data) = 0.1454. CCDC 270217. See http://dx.doi.org/10.1039/b505697g for crystallographic data in CIF or other electronic format.

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