Magnesium Hydrides and the Dearomatisation of Pyridine and Quinoline Derivatives

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Abstract

Reactions of the β-diketiminato n-butyl magnesium complex, [HC{(Me)CN(2,6\textsuperscript{-}iPr\textsubscript{2}C\textsubscript{6}H\textsubscript{3})\textsubscript{2}}\textsubscript{2}Mg\textsuperscript{\textregistered}Bu], with a range of substituted pyridines and fused-ring quinolines in the presence of PhSiH\textsubscript{3} has been found to result in dearomatisation of the N-heterocyclic compounds. This reaction is proposed to occur through the formation of an unobserved N-heterocycle-coordinated magnesium hydride and subsequent hydride transfer via the C2-position of the heterocycle prior to hydride transfer to the C4-position and formation of thermodynamically-favoured magnesium 1,4-dihydropyridides. This reaction is kinetically suppressed for 2,6-dimethylpyridine while the kinetic product, the 1,2-dihydropyridide derivative, was isolated through reaction with 4-methylpyridine (4-methylpyridine) in which case the formation of the 1,4-dihydropyridide is prevented by the presence of the 4-methyl substituent. X-ray structures of the products of these reactions with 4-methylpyridine, 3,5-dimethylpyridine and iso-quinoline comprise a pseudo-tetrahedral magnesium centre while the regiochemistry of the particular dearomatisation reaction is determined by the substitution pattern of the N-heterocycle under observation. The compounds are
all air-sensitive and exposure of the magnesium derivatives of dearomatised pyridine and 4-dimethylaminopyridine (DMAP) to air resulted in ligand rearomatisation and the formation of dimeric $\mu^2$-$\eta^2$-$\eta^2$-peroxomagnesium compounds which have also been subject to analysis by single crystal X-ray diffraction analysis. An unsuccessful extension of this chemistry to N-heterocycle hydrosilylation is suggested to be a consequence of the low basicity of the silane reagent in comparison to the pyridine substrates which effectively impedes any further interaction with the magnesium centres.

Introduction

While recent interest in the dearomatisation and hydrogenation of aromatic nitrogen heterocycles (pyridines, quinolines) has been driven by the prevalence of these functions in many natural products and pharmaceuticals, a number of reductive and group 1 and group 13-based dearomatisation strategies have been known for some time. Lansbury’s reagent, [Li{Al(1,4-dihydropyrid-1-yl)$_4$}], for example, is generated by reaction of LiAlH$_4$ and pyridine and has been known to effect the selective reduction of ketones in the presence of carboxylic and ester groups for some fifty years. Applications of these types of reagents in further syntheses where the reduced N-heterocyclic core is retained are, however, relatively limited. More attractive, therefore, is the development of milder, more conveniently employed and, ideally, catalytic reagents suitable for the conversion of a wide range of N-heterocyclic substrates to isolable dearomatised derivatives which are then available for use as synthons in subsequent multi-step syntheses. Although preceded by several heterogeneous processes, the initial report of homogeneous pyridine hydrosilylation was only described in 1998. In this case a [Cp$_2$TiMe$_2$]/PhMeSiH$_2$ system was reported
to effect the transformation of a variety of 3- and 4-substituted and 3,5-disubstituted pyridines to the N-silylated 1,2- and 1,4-dihydropyridines or, dependent upon substitution patterns, the corresponding tetrahydropyridine products. This process was reasoned to proceed via a Ti-H pyridine coordination/insertion and silane metathesis mechanism (Scheme 1) and an inability to dearomatise pyridines with 2- or 6-substitution patterns was attributed to the substrate steric demands. Although similar limitations have been observed in very recent work described by Nikonov and co-workers, in this case the catalytic ability of the cationic ruthenium complex \([\text{Cp}^*(\text{Pr}_3\text{P})\text{Ru(NCCH}_3)]\text{PF}_6\) to effect hydrosilylation of 3- and 5-substituted pyridines to the dihydropyridines was not compromised by the concomitant reduction of these products to tetrahydropyridines. In further related work Crabtree and co-workers have developed a reduction of quinolines by silanes in the presence of rhodium or iridium catalysts and a very recent report has described an extension of this chemistry to effect a palladium-catalysed silaboration of a variety of pyridines.

Scheme 1: Proposed mechanism for the titanocene-catalysed hydrosilylation of pyridine.

Our own interest in this area derives from our attempts to develop a catalytic and stoichiometric reaction chemistry for the abundant and environmentally benign group 2 elements heavier than beryllium that takes them beyond their traditional applications.
as, for example, Grignard reagents or Hauser bases. Much of this initial work has explored the reactivity of the redox-inactive divalent cations of these elements by analogy with chemical behaviour previously observed for similarly d⁰ complexes of early transition elements or lanthanides in their highest and trivalent oxidation states respectively. In this regard, Diaconescu and co-workers have recently shown that both N-heterocycle dearomatisation and C-H activation may be combined into an elegant group 3-centred scheme which results in C-C coupling reactivity between the two relevant heterocycles (Scheme 2). In earlier work Kiplinger and co-workers had also shown that dearomatisation of terpyridines may be readily induced through reaction with lanthanide alkyls.

Although a somewhat ‘lanthanide mimetic’ reactivity has emerged from our studies of the group 2-catalysed hydroelementation of C=E multiple bonds (E = CR₂, NR, O), and examples of N-heterocycle dearomatisation are well precedent in the chemistry of groups 1 and 13, examples of well-defined behaviour comparable to the second reaction step depicted in Scheme 2 are relatively unexplored for group 2-based systems. On the basis of a series of detailed NMR spectroscopic investigations, van der Kerk and Budzelaar deduced that the outcome of the room temperature reaction between MgH₂ and pyridine was exclusively the magnesium bis(1,4-dihydropyridide) isomer, which formed via the intermediacy of short-lived but observable 1,2-dihydropyridide species. In support of these observations we have recently reported that reaction of the well-defined β-diketiminato-supported n-butylmagnesium complex, [HC{(Me)CN(2,6-Pr₂C₆H₃)}₂Mg^nBu], I, with pyridine in the presence of PhSiH₃ results in heterocycle dearomatisation by a hydride transfer which occurs with the formation of isolable magnesium compounds containing 1,2- and 1,4-dihydropyridide anions as the respective kinetic and thermodynamic
products. In this contribution we describe extensions of this behaviour to a range of substituted pyridine and quinoline substrates and outline attempts to establish a catalytic variant of this reactivity which is reminiscent of the titanocene-based system illustrated in Scheme 1.

Scheme 2: Group 3-catalysed pyridine ortho-CH activation and dearomatisation/coupling.

Results and Discussion

We have previously reported that addition of pyridine to a toluene solution of compound I results in the rapid and clean formation of the \(n\)-butylmagnesium pyridine adduct, compound 1 (Scheme 3). A series of NMR scale reactions demonstrated that this process occurs for every monocyclic and fused ring pyridine investigated in this study and no evidence for magnesium \(n\)-butyl-induced substrate dearomatisation was observed even under forcing conditions. This observation contrasts markedly with those of Okuda of the reactivity of pyridine with more reactive calcium bis-allyl species and our own observations of the reactivity of heavier group 2 bis(trimethylsilyl)methanides, \([M\{CH(SiMe_3)_2\}_2(THF)_2]\) (\(M = \text{Ca, Sr, Ba}\)) with bis(imino)pyrines in which case rapid formation of the respective allylated and alkylated pyridine was observed upon combination of the reagents. As the
reactivity with compound I was assessed to be straightforward and unambiguous, only the reaction utilising one equivalent of 2-methylpyridine was repeated on a preparative scale resulting in the isolation of pale yellow crystals of compound 2 which were suitable for an X-ray diffraction analysis. The single crystal X-ray structure of the Mg(2)-containing molecule (there are two unique molecules in the unit cell) of compound 2 is illustrated in Figure 1 while selected bond length and angle data and details of the crystallographic analysis are provided in Tables 1, 2 and 3 respectively. Like compound 1, compound 2 is a four-coordinate pseudo-tetrahedral magnesium complex in which the coordination sphere of the Mg atoms is provided by the bidentate β-diketiminate ligand and the n-butyl and 2-methylpyridine ligands. The bond lengths and angles are perturbed only very slightly from those observed in compound 1 and the structure is otherwise unremarkable and will not, therefore, be discussed further here.\textsuperscript{13}

\begin{center}
\textbf{Figure 1:} ORTEP representation (25\% probability ellipsoids) of the X-ray structure of compound 2. Hydrogen atoms and iso-propyl methyl groups are deleted for clarity.
\end{center}
Following the procedure of Jones and Stasch for magnesium hydride generation from compound I,\(^{16}\) we have previously reported that addition of PhSiH\(_3\) to a solution of compound 1 or to I in the presence of pyridine results in the formation of magnesium compounds containing 1,2- and 1,4-dihydropyridide (identified as compound 3 in this submission) anions as the respective kinetic and thermodynamic products. Accordingly a series of preparative scale reactions were undertaken through addition of two molar equivalents of the relevant pyridine or quinoline derivative to a toluene solution of compound I. For monocyclic pyridine derivatives this gave a yellowing of the solution whereas for bicyclic quinoline derivatives a red solution formed. A further molar equivalent of phenylsilane was then added and the reactions heated at 60 °C for 48 hours. Crystalline samples of compounds 4 – 10 were then isolated by slow cooling and crystallisation from the saturated reaction solutions (Schemes 3 and 4).

\[ \text{Scheme 3} \]

\[
\begin{array}{c}
\text{Ar} = 2,6-	ext{di-iso-proplyphenyl} \\
\text{I} \quad \xrightarrow{\text{Mg}} \quad \text{Ar} \\
\end{array}
\]

\[
\begin{array}{c}
3: R, R' = H \\
4: R = 2-\text{Me}, R' = 4-\text{H} \\
5: R = 3-\text{Me}, R' = 4-\text{H} \\
7: R = 3,5-\text{Me}_2, R' = 4-\text{H} \\
8: R = H, R' = 4-\text{NMe}_2 \\
6
\end{array}
\]

**Scheme 3**: Dearomatisation of pyridine derivatives by I and PhSiH\(_3\).
The products of 2-methylpyridine (4), 3-methylpyridine (5) and 3,5-lutidine, (7) dearomatisation under these conditions were identified as the respective 1,4-dihydropyridide derivatives by a combination of $^1$H (COSY) and $^{13}$C NMR spectroscopy. In line with the previously reported data of Budzelaar and co-workers,\textsuperscript{12a,b} in all cases the new sp\(^3\) CH\(_2\) protons were found to resonate between $\delta$ 3.30 and $\delta$ 4.00 ppm while the alkenic components of the newly formed dihydropyridide substituent were observed as a series of multiplets at chemical shifts upfield from the aromatic region; ortho-protons were found within $\delta$ 5.4 to $\delta$ 6.3 ppm and meta-protons shifted to between $\delta$ 4.2 to $\delta$ 5.0 ppm. In contrast to this behaviour, no reaction was observed with 2,6-lutidine, while 4-methylpyridine was converted selectively to the 1,2-dihydropyridide derivative, compound 6. Consistent with our previous proposal, we interpret these latter observations to indicate that hydride transfer generally occurs via an initially formed 1,2-dihydropyridide derivative. In the case of 2,6-lutidine this process is completely suppressed by the presence of the two methyl groups positioned adjacent to the lutidine nitrogen centre. Similarly, for compound 6 the initial 1,2-dihydropyridide is formed but can not then convert to the 1,4-dihydropyridide observed for compounds 3, 4, 5, 7 or 8.

In contrast to the reactivity observed when a methyl group occupies the 4-position of the pyridine substrate, treatment of 4-dimethylaminopyridine (DMAP) under analogous conditions was found to result in the production of a mixture of the 1,2- and 1,4-hydride transfer products in a 3:1 ratio, which could be converted completely to the product of hydride transfer to the 4-position to form compound 8 by heating at 60 °C in toluene for a further 96 hours. This latter transformation contrasts markedly with the previous observation of Jones and Stasch of the similarly four-coordinate magnesium hydride species, [HC\((^{t}{\text{Bu}}CN(2,6-^{1}{\text{Pr}}_{2}{\text{C}}_{6}{\text{H}}_{3}))_{2}\text{Mg(H)(DMAP)}\)]
in which the hydride maintains its integrity as a terminally-bonded ligand.\textsuperscript{16} The observation of both potential isomers during the early stages of the reaction implies that the ultimate conversion to the symmetrical 1,4-dihydropyridide-containing isomer, compound, 8, again occurs under overall thermodynamic control. This observation was borne out by calculations performed on model complexes of compound 8, its 1,2-dihydropyridide isomer and a DMAP-coordinated magnesium hydride species in which the complete β-diketiminate ligand was replaced by [HC{(H)CN(Me)}]\textsuperscript{+} in the interests of computational expense. Despite this simplification, geometry optimisations performed at the B3LYP density functional theory with LAN2DZ pseudopotentials (and basis set) implemented in the Gaussian03 suite of programmes provided a good approximation of the local bond lengths and angles about each Mg atom in comparison to the crystallographically deduced structures (vide infra).\textsuperscript{17} Consistent with the experimentally observed transformation into compound 8 the isomer containing the 1,4-dihydropyridide anion was calculated to be marginally lower (1.02 kcal mol\textsuperscript{-1}) in total energy than its 1,2-dihydropyridide isomer, while both species were more significantly lower (1,2-isomer, 9.01 kcal mol\textsuperscript{-1}; 1,4-isomer 10.02 kcal mol\textsuperscript{-1}) than the alternative pyridine-adducted magnesium hydride formulation, [HC{(H)CN(Me)}Mg(H)-κ\textsuperscript{1}-NC\textsubscript{5}H\textsubscript{4}-4-NMe\textsubscript{2}]. C\textsubscript{5}H\textsubscript{4}N-4-NMe\textsubscript{2}. These data reflect our previous DFT examination of the dearomatisation of pyridine and earlier MNDO calculations which assessed the heats of formation, ΔH\textsubscript{f}, of the various potential isomers of pyridine reduction, albeit with less thermodynamic discrimination between the alternative isomeric forms.\textsuperscript{13,18} While the reaction to produce compound 8 is effectively identical to that employed by Jones and Stasch to synthesise [HC{(tBu)CN(2,6-\textsuperscript{2}Pr\textsubscript{2}C\textsubscript{6}H\textsubscript{3})}\textsubscript{2}Mg(H)(DMAP)],\textsuperscript{16} the outcome of the two reactions is quite different. The dearomatisation-based syntheses reported herein generally
required elevated temperatures to occur and, thus, this latter compound may again be assigned as a kinetic reaction product, which may display some enhanced kinetic stability resulting from the increased steric demands of the tert-butyl-substituted β-diketiminate ligand employed in the earlier study. Analogous calculations performed upon model complexes containing dearomatised 4-methylpyridine revealed a similar thermodynamic preference of 1.55 kcal mol\(^{-1}\) for the formation of the 1,4-dihydropyridide isomer over the corresponding 1,2-dihydropyridide isomer. We thus tentatively ascribe the formation of compound 6 to occur under overall kinetic rather than thermodynamic control.

The fused ring substrates quinoline and isoquinoline underwent clean dearomatisation to form compounds 9 and 10. In the case of compound 9 complete conversion to the 1,4-dihydroquinolide product was observed while for the isomeric derivative, compound 10, selective hydride transfer occurred to the 2-carbon centre adjacent to the isoquinoline nitrogen. In this latter case the reaction is necessarily unambiguous as the 4-position of the heterocyclic ring is blocked by the fused aromatic system (Scheme 4).

![Scheme 4](image)

**Scheme 4**: Dearomatisation of quinoline derivatives by 1 and PhSiH\(_3\).

Representative crystal structures of the dearomatised pyridine derivatives were acquired after slow crystallisation from toluene at room temperature for the 1,4-
dihydropyridide derivative of 3,5-lutidine, compound 7, the 1,2-dihydropyridide derivative of 4-methylpyridine, compound 6, and the iso-quinoline derivative, compound 10. The results of these analyses are presented in Figures 2 – 4, while selected bond length and angle data and details of the X-ray experiments are provided in Tables 1, 2 and 3 respectively. In a manner similar to the previously described 1,2-dihydropyridide complex of pyridine itself, the methylene hydrogen atoms were disordered between the 2-carbon and/or 6-carbon centres (C30 and C34) of the reduced methylpyridine moiety of compound 6. These were, thus, omitted from the refinement because of the inability to determine precisely which of these best represents a CH₂ moiety.

Each of the three structures feature a pseudo-tetrahedral magnesium atom in which the coordination sphere is provided by the bidentate β-diketiminate ligand and single equivalents of the relevant dearomatised and non-dearomatised pyridine derivative. While the magnesium-bound dihydropyridide N(3) centres are not significantly pyramidalised [Σbond angles = 6: 359.1°; 7: 359.2°; 10: 355.3°], the pyridine and dihydropyridide donors are readily discriminated by the alternation of double and single bonds about the dearomatised ligand as well as the non-planarity of the heterocycle introduced upon incorporation of the saturated methylene carbon centre. The differing bonding modes (covalent/electrostatic versus dative covalent) are also reflected in the respective Mg(1)-N(3) [6: 1.993(3); 7: 1.9827(13); 10: 1.9926(16) Å] and Mg(1)-N(4) [6: 2.140(3); 7: 2.1282(13); 10: 2.1301(15) Å] distances linking the Mg centre to the two heterocycles with the latter distances effectively identical to the Mg-NDMAP distance [2.135(3) Å] within the similarly four-coordinate magnesium hydride species, [HC(ʻBu)CN(2,6-Pr₂C₆H₃)]₂Mg(H)(DMAP)], in which the hydride maintains its integrity as a terminally-bonded ligand.¹⁶
Figure 2: ORTEP representation (25% probability ellipsoids) of the X-ray structure of compound 7. Hydrogen atoms except those attached to C(32) and iso-propyl methyl groups are deleted for clarity.

Figure 3: ORTEP representation (25% probability ellipsoids) of the X-ray structure of compound 6. Hydrogen atoms and iso-propyl methyl groups are deleted for clarity.
Figure 4: ORTEP representation (25% probability ellipsoids) of the X-ray structure of compound 10. Hydrogen atoms except those attached to C(30) and iso-propyl methyl groups are deleted for clarity.

The aluminate derivative, Lansbury’s reagent, and previously reported dihydropyridine derivatives of magnesium and zinc have been reported as air-sensitive and to behave as selective reducing agents for a variety of organic substrates. Although none of this latter reactivity will be reported in this submission, all of the compounds 3 – 10, were found to display a marked sensitivity toward molecular and/or atmospheric oxygen. Exposure of reaction solutions or solutions of the isolated compounds to the open atmosphere was observed to result in rapid decolourisation of the distinctive (red or orange) colours attributed to the formation of the dearomatised pyridine species. In two cases, the previously reported 1,4-dihydropyrididine derivative, 3, and the product of DMAP dearomatization, compound 8, serendipitous reactions with atmospheric O₂ were found to result in the
formation of isolable quantities of the well-defined dimeric magnesium peroxide species, compounds 11 and 12. The compounds were characterised by $^1$H and $^{13}$C NMR spectroscopy and, in the case of 11, by CHN microanalysis. X-ray diffraction analyses were performed on both compounds after crystallisation from saturated solutions in toluene at room temperature. The molecular structures of compounds 11 and 12 are shown in Figures 5 and 6, while selected bond length and angle data and details of the X-ray analyses are provided in Tables 1, 2 and 3 respectively. The structures of both compounds were found to be centrosymmetric and to contain five-coordinate Mg centres in which the coordination sphere of each group 2 atom is provided by a single bidentate $\beta$-diketiminate ligand, a molecule of the relevant pyridine donor (11, pyridine; 12, DMAP) and a side-on $\mu$-$\eta^2$-$\eta^2$-O$_2$ peroxide dianion which bridges symmetrically between the two magnesium atoms. Although two peroxo-centred mixed metal magnesium/alkali metal ‘inverse crown’ structures, [{{(Me$_3$Si)$_2$N)$_4$M$_2$Mg$_2$(O$_2$)}$_\infty$}] (M = K or Li) have been reported previously, $^{20}$ compounds 11 and 12 appear to be the first examples of monometallic magnesium peroxo species. The Mg-O bond lengths within the structures of compounds 11 (1.9583(12), 1.9716 Å) and 12 (1.969(3), 1.972(3) Å) are shorter than those observed in the potassium ‘inverse crown’ species (2.010(2), 2.015(1) Å), $^{20b}$ while the O-O separation of the peroxide units of the pyridine coordinated compounds (11, 1.625(5); 12, 1.638(5) Å) is somewhat longer than in both of the previously reported [{{(Me$_3$Si)$_2$N)$_4$M$_2$Mg$_2$(O$_2$)}$_\infty$}] systems (M = K, 1.583; M = Li, 1.551 Å). While these latter measurements for compounds 11 and 12 are undoubtedly long, they are not unprecedented and similar distances have been observed in several high oxidation state early metal derivatives such as tetrafluoro(2-methylpyridine-N-oxide)peroxotantalate(V) (1.67(5) Å) $^{21}$ and in a dimeric tetraaryl porphyrin
hafnium(IV) complex (1.618 Å). We are satisfied to discount the possibility that compounds 11 and 12 are \( \mu \)-hydroxo species through comparison with the previously reported THF-solvated complex \([\text{HC}((\text{Me})\text{CN}(2,6-'\text{Pr}_2\text{C}_6\text{H}_3))_2\text{Mg(OH)(THF)})_2,\) which bears the same \( \beta \)-diketiminate ligand. In this case the O-O separation is elongated to more than 2.46 Å and the relevant O-Mg-O’ bond angles are consequently considerably more obtuse (76.78° versus 48.8° for 11 and 49.14(13)° for 12).

**Figure 5:** ORTEP representation (25% probability ellipsoids) of the X-ray structure of compound 11. Hydrogen atoms and \textit{iso}-propyl methyl groups are deleted for clarity. Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z+2.
The possibility of a magnesium-catalysed hydrosilylation/dearomatisation procedure reminiscent of the titanium-catalysed process illustrated in Scheme 1 is dependent upon consecutive magnesium hydride-induced dearomatisation and subsequent Si-H/Mg-N metathesis steps (Scheme 5). The viability of the first of these processes for a variety of pyridine derivatives is clearly demonstrated by the isolation of compounds 3 – 10, while we have previously employed the latter metathesis reactivity between [Mg{N(SiMe$_3$)$_2$}]$_2$] and PhSiH$_3$ to synthesise a high nuclearity magnesium hydride species.$^{24}$ Reactions between the pyridine derivative, 3, and the quinoline and \textit{iso}-quinoline complexes, compounds 9 and 10, with an excess of PhSiH$_3$ were, thus, studied on an NMR scale. Monitoring of reactions in d$_8$-toluene performed at 60 °C for a period of one week evidenced no conversion of the pyridine starting materials, while heating to 90 °C caused the \(\beta\)-diketiminato magnesium
complexes to begin to decompose with the liberation of the free di-imine ligand. Similarly, attempted catalytic reactions of 10 mol% of the magnesium $n$-butyl complex, I, with pyridine and PhSiH$_3$ at 60 °C provided ca. 10% consumption of the pyridine and silane reagents and stoichiometric formation of compound 3 based upon the starting quantity of compound I employed. It appears, therefore, that the silane reagent employed as a potential source of hydride is insufficiently reactive to engage in any further metathesis reactivity with the magnesium dihydropyridide species. We believe that this lack of reactivity is due to the low Lewis basicity of the silane in comparison to the pyridine substrates and a consequent inability to engage the Mg-N bond in an appropriate metathesis transition state (inset, Scheme 5).

Scheme 5: Proposed mechanism for the magnesium-catalysed hydrosilylation of pyridine derivatives.

In summary, we have observed that reactions of *in situ* generated magnesium hydrides and aromatic pyridine derivatives result in $N$-heterocycle dearomatization which generally results in the formation of well-defined 1,4-dihydropyridide derivatives as the thermodynamic reaction products. We are continuing to study the reductive reactivity of these well defined species and to elaborate their reactions with more potent hydride sources in attempts to achieve some level of catalytic pyridine
heterofunctionalisation with this abundant and benign element and its heavier group 2 congeners. This work will be reported in subsequent publications.

Experimental Section

All manipulations were carried out using standard Schlenk line and glovebox techniques under an inert atmosphere of either nitrogen or argon. NMR experiments were conducted in Youngs tap NMR tubes made up and sealed in a Glovebox. NMR data were collected on a Bruker AV300 spectrometer operating at 75.5 MHz ($^{13}$C). Solvents (Toluene, THF, hexane) were dried by passage through a commercially available (Innovative Technologies) solvent purification system, under nitrogen and stored in ampoules over molecular sieves. C$_6$D$_6$ and d$_8$-toluene were purchased from Goss Scientific Instruments Ltd. and dried over molten potassium before distilling under nitrogen and storing over molecular sieves. Compounds 1 and 3 were synthesised by literature procedures and all silanes and pyridine substrates were purchased from Sigma-Aldrich.$^{25}$ CHN microanalysis was performed by Mr Stephen Boyer of London Metropolitan University. In NMR assignments Dipp = 2,6-di-iso-propylphenyl.

Synthesis of Compound 2

Compound I (0.75 g, 1.51 mmol) was dissolved in toluene (10 mL) and a solution of 2-methylpyridine (0.14g, 1.72 mmol) in toluene (2 mL) was added at room temperature. The resulting pale yellow solution was stirred for one hour. The solution was concentrated and 2 was isolated as pale crystals after storage at $-30^\circ$C. (0.67 g, 75%). $^1$H NMR (300 MHz, C$_6$D$_6$, 300 K) $\delta_H$ (ppm): 1.40 (24H, d, $J_{HH}$ = 6.9 Hz, CH(CH$_3$)$_2$), 1.95 (6H, s, NC(CH$_3$), 3.45 (2H, m, CH(CH$_3$)$_2$), 5.21 (1H, s,
NC(CH$_3$)C), 6.68 (2H, s, NCHCH), 6.70 (2H, s, NC(CH$_3$)CH), 7.07 (2H, t, J$_{HH}$ = 7.8 Hz, NCHCHCH), 7.35 (6H, s, Ar-H), 9.02 (2H, s, NCH).

$^{13}$C NMR (75.5 MHz, C$_6$D$_6$, 300 K) $\delta$ (ppm): 168.44 (s, NCH), 159.71 (s, NCH(CH$_3$)), 150.71 (s, NCH(Ar)), 146.64 (s, NCHCHC), 142.92 (s, p-C$_6$H$_3$), 138.27 (s, NCH(CH$_3$)), 125.51 (s, NC(CH$_3$)C), 124.15 (s, m-C$_6$H$_3$), 121.59 (s, NCHCH), 95.20 (s, NC(CH$_3$)CH), 32.75 (s, CH(CH$_3$)$_2$), 32.31 (s, CH(CH$_3$)$_2$), 28.74 (s, NC(CH$_3$)), 24.82 (s, NC(CH$_3$)), 24.63 (s, CH(CH$_3$)$_2$), 24.45 (s, CH(CH$_3$)$_2$).

Elemental analysis (%) for C$_{39}$H$_{57}$MgN$_3$ (found): C 79.09 (78.91); H 9.72 (9.60); N 7.10 (7.00).

**General procedure for dearomatisation reactions**

Compound I (1 mmol, 500 mg) was dissolved in toluene (ca. 5 mL) followed by the addition of 1 equivalent of the relevant pyridine or quinoline derivative. The reactions were then stirred at room temperature overnight before further equivalents of the N-heterocycle and phenyl silane were added. The reactions were then heated to 60 $^\circ$C for 48 hrs, before cooling and concentration of the solution provided crystalline products suitable for isolation by filtration in ca. 50 – 60% yield.

**Compound 4 (dearomatisation of 2-methylpyridine)**

$^1$H NMR (300MHz, C$_6$D$_6$, 300K) $\delta$H (ppm): 0.72 (6H, d, J$_{HH}$ = 9 Hz, CH(CH$_3$)$_2$), 0.87 (6H, d, J$_{HH}$ = 6 Hz, CH(CH$_3$)$_2$), 1.50 (6H, d, J$_{HH}$ = 6 Hz, CH(CH$_3$)$_2$), 1.76 (6H, d, J$_{HH}$ = 6 Hz, CH(CH$_3$)$_2$), 2.10 (3H, s, NC(CH$_3$)CHCH$_2$), 2.13 (9H, br.s, NC(CH$_3$)), 2.98 (2H, m, CH(CH$_3$)$_2$), 3.29 (2H, m, CH(CH$_3$)$_2$), 4.05 (2H, s, NCHCHCH$_2$), 4.59 (1H, m, NC(CH$_3$)CHCH$_2$), 4.74 (1H, m, NCHCHCH$_2$), 5.44 (1H, s, (NC(CH$_3$))$_2$CH), 5.82 (1H, d, J$_{HH}$ = 6 Hz, NCHCHCH$_2$), 6.79 (2H, m, m-Pyr), 7.16 (1H, m, p-Pyr), 7.45 – 7.66 (6H, m, Ar), 9.37 (1H, m, o-Pyr). $^{13}$C NMR (75.5 MHz, C$_6$D$_6$, 300 K) $\delta$ (ppm):
169.59 (o-Pyr), 139.39 (m-Pyr), 139.08 (m-Pyr), 126.11, 125.20, 123.99, 95.76 (NC(CH₃))₂CH), 93.33 (NC(CH₃)CHCH₂), 92.49 (NCHCHCH₂), 29.33 (NCHCHCH₂), 28.30 (CH(CH₃)₂), 25.26 (NC(CH₃)-Pyr), 25.15 (NC(CH₃)CHCH₂), 25.02 (CH(CH₃)₂), 24.72 (CH(CH₃)₂). Elemental analysis (%) for C₄₁H₅₆MgN₄ (found); C 78.31 (78.09); H 8.95 (8.84); N 8.67 (8.80).

**Compound 5 (dearomatisation of 3-methylpyridine)**

¹H NMR (300 MHz, C₆D₆, 300 K) δ_H (ppm): 0.35 (6H, d, J_HH = 6Hz, (CH₃)₂CH), 1.08 (6H, d, J_HH = 6Hz, (CH₃)₂CH), 1.30 (6H, d, J_HH = 6Hz, (CH₃)₂CH), 1.51 (3H, s, NCHC(CH₃)CH₂), 1.54 (3H, s, NCHC(CH₃)(CH₃)), 1.68 (6H, d, J_HH = 9Hz, (CH₃)₂CH), 1.75 (6H, s, NC(CH₃)CH), 2.82 (2H, m, (CH₃)₂CH), 3.53 (2H, m, NCHC(CH₃)CH₂(CH)₂), 3.64 (2H, m, (CH₃)₂CH), 4.30 (1H, m, NCHCHCH₂), 4.92 (1H, s, NC(CH₃)CH), 5.29 (1H, s, NCHC(CH₃)), 5.65 (1H, d, J_HH = 6Hz, NCHCHCH₂), 6.36 (1H, m, m-Pyr), 6.67 (1H, d, J_HH = 6Hz, p-Pyr), 7.03 (2H, m, m-Ar(Diip)), 7.17 (2H, m, p-Ar(Dipp)), 7.28 (2H, m, m-Ar(Dipp)), 8.25 (2H, m, o-Pyr).

¹³C NMR (75.5 MHz, C₆D₆, 300 K) δ_C (ppm): 169.48 (o-Pyr), 145.42, 143.76, 142.23, 138.16 (NCHCH₂), 133.54 (NCHC(CH₃)), 125.88, 124.87, 123.90, 100.41 (NC(CH₃)CH), 94.40 (NCHC(CH₃)), 92.51 (NCHCH), 31.80 (NCHCHCH₂), 29.52 (CH(CH₃)₂), 28.43 (CH(CH₃)₂), 25.35 (CH(CH₃)₂), 24.77(CH(CH₃)₂), 24.56 (CH(CH₃)₂), 24.47 (CH(CH₃)₂), 24.35 (NC(CH₃)₂), 22.96 (CH₃- 3Pic), 18.00 (NCHC(CH₃)CH₂). Elemental analysis (%) for C₄₁H₅₆MgN₄ (found); C 78.26 (78.09); H 8.97 (8.84); N 8.90 (8.80).
Compound 6 (dearomatisation of 4-methylpyridine)

$^1$H NMR (300 MHz, C$_6$D$_6$, 300 K) $\delta_H$ (ppm): 0.38 (6H, d, $J_{HH} = 6$Hz, (CH$_3$)$_2$CH), 1.10 (6H, d, $J_{HH} = 6$Hz, (CH$_3$)$_2$CH), 1.29 (6H, d, $J_{HH} = 6$Hz, (CH$_3$)$_2$CH), 1.55 (3H, s, Pyr-CH$_3$), 1.57 (6H, d, $J_{HH} = 6$Hz, (CH$_3$)$_2$CH), 1.76 (6H, s, NC(CH$_3$)CH), 1.95 (3H, s, NCH$_2$CHC(CH$_3$)), 2.82 (2H, m, (CH$_3$)$_2$CH), 3.58 (2H, d, $J_{HH} = 3$Hz, NC(H)$_2$), 3.64 (2H, m, (CH$_3$)$_2$CH), 4.32 (1H, m, NCH$_2$CHC(CH$_3$)), 4.94 (1H, s, NC(CH$_3$)CH), 4.99 (1H, m, NCH$_2$CH), 6.17 (1H, d, $J_{HH} = 6$Hz, NCH), 6.32 (2H, d, $J_{HH} = 6$Hz, m-Pyr), 7.04 (2H, m, m-Ar(Dipp)), 7.16 (2H, m, p-Ar(Dipp)), 7.25 (2H, m, m-Ar(Dipp)), 8.42 (2H, d, $J_{HH} = 6$Hz, o-Pyr). $^{13}$C NMR (75.5 MHz, C$_6$D$_6$, 300 K) $\delta_c$ (ppm): 169.59 (o-Pyr), 148.77, 145.37, 143.49, 142.28, 135.81 (NCH), 126.02, 124.82, 124.00, 98.03 (NC(CH$_3$)CH), 94.48 (NCH$_2$CH), 94.42 (NCH$_2$CH), 48.71 (NCH$_2$CH), 29.49 (CH(CH$_3$)$_2$), 28.43 (CH(CH$_3$)$_2$), 25.22 (CH(CH$_3$)$_2$), 24.82 (CH(CH$_3$)$_2$), 24.37 (NC(CH$_3$)$_2$), 24.33 (CH(CH$_3$)$_2$), 21.59 (CH$_3$- 4-Pic), 20.96 (NCH$_2$CHC(CH$_3$)). No meaningful microanalytical data could be obtained for this compound.

Compound 7 (dearomatisation of 3,5-lutidine)

$^1$H NMR (300 MHz, C$_6$D$_6$, 300 K) $\delta_H$ (ppm): 0.41 (6H, d, $J_{HH} = 6$Hz, (CH$_3$)$_2$CH), 1.09 (6H, d, $J_{HH} = 6$Hz, (CH$_3$)$_2$CH), 1.29 (6H, d, $J_{HH} = 6$Hz, (CH$_3$)$_2$CH), 1.58 (6H, d, $J_{HH} = 6$Hz, (CH$_3$)$_2$CH), 1.61 (6H, s, N(CHC(CH$_3$)$_2$CH)$_2$), 1.62 (6H, s, N(CHC(CH$_3$)$_2$CH)$_2$), 1.77 (6H, s, NC(CH$_3$)), 2.87 (2H, m, (CH$_3$)$_2$CH), 3.33 (2H, s, N(CHC(CH$_3$)$_2$CH)$_2$), 3.64 (2H, m, (CH$_3$)$_2$CH), 4.93 (1H, s, NC(CH$_3$)CH), 5.42 (2H, s, NCH), 6.56 (1H, s, p-Pyr), 7.04 (2H, m, m-Ar(Dipp)), 7.19 (2H, p-Ar(Dipp)), 7.28 (2H, m, m-Ar(Dipp)), 8.03 (2H, s, o-Pyr). $^{13}$C NMR (75.5 MHz, C$_6$D$_6$, 300 K) $\delta_c$ (ppm): 169.41 (o-Pyr), 147.17, 145.69, 143.98, 142.28, 140.95, 135.08, 133.17 (NCHC(CH$_3$)CH)$_2$, 125.78, 124.91, 123.82, 98.88 (NC(CH$_3$)CH), 94.33
(NCHC(CH$_3$)$_2$), 37.79 (NCHC(CH$_3$)$_2$), 29.46 (CH(CH$_3$)$_2$), 28.49 (CH(CH$_3$)$_2$), 25.36 (CH(CH$_3$)$_2$), 24.62 (CH(CH$_3$)$_2$), 24.52 (CH(CH$_3$)$_2$), 24.38 (NC(CH$_3$)), 22.72 (CH$_3$- 3,5Lut), 17.93 (NCHC(CH$_3$)CH$_2$). Elemental analysis (%) for C$_{43}$H$_{60}$MgN$_4$ (found); C 78.58 (78.10); H 9.20 (8.77); N 8.52 (8.14).

**Compound 8** (dearomatisation of 4-dimethylaminopyridine)

$^1$H NMR (300 MHz, C$_6$D$_6$, 300 K) $\delta$ (ppm): 0.80 (6H, d, $J_{HH} = 9$ Hz, CH(CH$_3$)), 1.33 (6H, d, $J_{HH} = 6$ Hz, CH(CH$_3$)), 1.49 (6H, d, $J_{HH} = 6$ Hz, CH(CH$_3$)), 1.77 (6H, d, $J_{HH} = 9$ Hz, CH(CH$_3$)), 1.97 (NC(CH$_3$)), 2.16 (6H, s, HN(CH$_3$)$_2$), 2.80 (6H, s, N(CH$_3$)$_2$), 3.20 (2H, m, CH(CH$_3$)), 3.77 (1H, m, C$_2$H(N(CH$_3$)$_2$)), 3.88 (2H, m, CH(CH$_3$)), 3.91 (2H, m, NCHC(CH$_3$)$_2$)), 5.15 (1H, s, NC(CH$_3$)), 5.86 (NC), 6.43 (1H, t, $J_{HH} = 6$ Hz, NCHCH(N(CH$_3$)$_2$)), 7.23 – 7.49 (8H, m, Ar), 8.32 (2H, m, o-Pyr). $^{13}$C NMR (75.5 MHz, C$_6$D$_6$, 300 K) $\delta$ (ppm): 169.87 (o-Pyr), 146.63, 143.62, 142.19, 138.57, 135.89, 130.21, 126.43, 126.12, 125.16, 124.01 (NCHC(H)(NMe$_2$)), 122.13, 118.71, 117.67, 94.95 ((NC(CH$_3$)$_2$)CH), 92.37 (NCHCH(NMe$_2$)), 29.38 (NCHC(N(CH$_3$)$_2$)), 27.87 (NCHCH(N(CH$_3$)$_2$)), 25.21 (CH(CH$_3$)$_2$), 25.12 (CH(CH$_3$)$_2$), 24.35 (CH(CH$_3$)$_2$), 23.55 (CH(CH$_3$)$_2$). Elemental analysis (%) for C$_{43}$H$_{32}$MgN$_4$ (found); C 75.14 (75.26); H 9.09 (8.97); N 12.23 (12.18).

**Compound 9** (dearomatisation of quinoline)

$^1$H NMR (300 MHz, C$_6$D$_6$, 300 K) $\delta$ (ppm): -0.06 (6H, d, $J_{HH} = 6$ Hz, (CH$_3$)$_2$CH), 0.79 (6H, d, $J_{HH} = 6$ Hz, (CH$_3$)$_2$CH), 1.25 (6H, d, $J_{HH} = 6$ Hz, (CH$_3$)$_2$CH), 1.34 (6H, d, $J_{HH} = 6$ Hz, (CH$_3$)$_2$CH), 1.77 (6H, s, NC(CH$_3$)), 2.73 (2H, m, (CH$_3$)$_2$CH), 3.61 (2H, m, (CH$_3$)$_2$CH), 3.94 (2H, m, NCHCHCH$_2$), 4.24 (1H, m, NCH(CH$_3$)), 5.26 (1H, NC(CH$_3$)CH), 5.41 (1H, m, NCH), 5.44 (1H, m, NCH), 6.20 (1H, m, 3-H-Quin),
6.34 (1H, m, NC(CH)₂CH), 6.60 (1H, m, NCCHCH), 6.89 (1H, m, N(CH)₂CH₂CCH),
6.91 – 7.28 (9H, m, Ar), 7.57 (1H, m, 7-Quin), 8.67 (1H, d, J₆₇ = 6Hz, 8-Quin),
9.08 (1H, s, 2-Quin). ¹³C NMR (75.5 MHz, C₆D₆, 300 K) δc (ppm): 169.87 (NC),
169.71 (NCH), 155.60, 150.70, 146.67, 146.38, 143.74, 143.62, 142.19, 138.57,
135.89, 130.21, 126.43, 125.14, 124.01 (NCHCH₂), 122.13, 118.71, 117.67, 94.95
(NC(CH₃)CH), 92.37 (NCHCH₂), 29.58 (CH(CH₃)₂), 29.38 (NCHCH₂), 27.87
(CH(CH₃)₂), 25.21(CH(CH₃)₂), 25.00 (CH(CH₃)₂), 24.75
(CH(CH₃)₂), 24.35 (NC(CH₃)), 23.55 (CH(CH₃)₂). Elemental analysis (%) for
C₄₇H₅₆Mg₄ (found); C 80.50 (80.38), H 8.05 (8.08); N 7.99 (7.92).

**Compound 10 (dearomatisation of iso-quinoline)**

¹H NMR (300 MHz, C₆D₆, 300 K) δH (ppm): 0.08 (6H, d, J₆₇ = 9Hz, (CH₃)₂CH), 0.98
(6H, d, J₆₇ = 6Hz, (CH₃)₂CH), 1.27 (6H, d, J₆₇ = 6Hz, (CH₃)₂CH), 1.48 (6H, d, J₆₇ =
9Hz, (CH₃)₂CH), 1.78 (6H, s, NC(CH₃)), 2.82 (2H, m, (CH₃)₂CH), 3.63 (2H, m,
(CH₃)₂CH), 3.94 (2H, s, NCH₂), 5.00 (1H, s, NC(CH₃)CH), 5.54 (1H, d, J₆₇ = 6Hz,
NCHCH), 6.31 (1H, d, J₆₇ = 6Hz, NCH), 6.64 (1H, d, J₆₇ = 6Hz, NCH₂CCH), 6.92 –
7.25 (14H, m, Ar-H), 8.33 (1H, s, 2-Quin), 8.69 (1H, s, 8-Quin). ¹³C NMR
(75.5 MHz, C₆D₆, 300 K) δc (ppm): 169.79 (NCH), 145.20, 142.49, 136.80, 133.26,
129.67, 128.80, 126.08, 124.86, 124.17, 121.72, 119.64 (NCHCH), 94.55
(NC(CH₃)CH), 52.82 (NCH₂), 29.47 (CH(CH₃)₂), 28.32 (CH(CH₃)₂), 25.25
(CH(CH₃)₂), 24.87 (CH(CH₃)₂), 24.50 (CH(CH₃)₂), 24.38 (NC(CH₃)). Elemental
analysis (%) for C₄₇H₅₆Mg₄ (found); C 80.50 (80.38); H 8.05 (7.91); N 7.99 (7.83).
**Compound 11**

$^1$H NMR (300 MHz, C$_6$D$_6$, 300 K) $\delta_H$ (ppm): 0.65 (12H, d, $J_{HH} = 6$ Hz, CH(CH$_3$)$_2$), 1.15 (12H, d, $J_{HH} = 9$ Hz, CH(CH$_3$)$_2$), 1.66 (12H, s, NC(CH$_3$)), 3.05 (8H, m, CH(CH$_3$)$_2$), 4.97 (2H, s, NC(CH$_3$)CH), 6.79 (4H, m, NCH$_2$CH$_2$), 6.99-7.15 (14H, m, Ar), 8.61 (4H, s, NCH$_2$). $^{13}$C NMR (75.5 MHz, C$_6$D$_6$, 300 K) $\delta_c$ (ppm): 168.59 (s, NCH$_2$), 148.68 (s, N(CH$_2$)$_2$C), 142.65 (s, NCH$_2$CH$_2$), 129.66 (s, CCH$_2$), 126.03, 124.65, 123.96, 64.64 (s, NC(CH$_3$)CH), 28.61, 25.88, 25.31, 24.59, 21.76. Elemental analysis (%) for C$_{68}$H$_{92}$N$_6$Mg$_2$O$_2$ (found): C 76.04 (75.93); H 8.63 (8.52); N 7.82 (7.84).

**Compound 12**

$^1$H NMR (300 MHz, C$_6$D$_6$, 300 K) $\delta_H$ (ppm): 0.80 (12H, d, $J_{HH} = 9$ Hz, CH(CH$_3$)), 1.33 (12H, d, $J_{HH} = 6$ Hz, CH(CH$_3$)), 1.97 (12H, s, NC(CH$_3$)), 2.80 (6H, s, N(CH$_3$)$_2$), 3.20 (4H, m, CH(CH$_3$)), 5.15 (2H, s, NC(CH$_3$)CH), 7.23 – 7.49 (16H, m, Ar), 8.32 (4H, m, o-Pyr). $^{13}$C NMR (75.5 MHz, C$_6$D$_6$, 300 K) $\delta_c$ (ppm): 169.87 (o-Pyr), 146.63, 143.62, 142.19, 138.57, 135.89, 130.21, 126.43, 126.12, 125.16, 122.13, 118.71, 117.67, 94.95 ((NC(CH$_3$))$_2$CH), 29.38 (NCHCH(N(CH$_3$)$_2$), 27.87 (NCHCHCH(N(CH$_3$)$_2$), 25.21 (CH(CH$_3$)$_2$), 25.12 (CH(CH$_3$)$_2$) 24.35 (CH(CH$_3$)$_2$), 23.55 (CH(CH$_3$)$_2$). No meaningful microanalytical data could be obtained for this compound.

**X-ray Crystallography**

Data for 2, 6, 7, 10, 11 and 12 were collected at 150 K on a Nonius Kappa CCD diffractometer equipped with an Oxford Cryosystem low temperature device, using graphite monochromated MoKα radiation ($\lambda = 0.71073$ Å). Data were processed using
the Nonius Software. Structure solution, followed by full-matrix least squares refinement was performed using the programme suite X-SEED for compounds for 2, 6, 7, 10 and 11 while WINGX-1.70 was used for compound 12. Noteworthy points related to the structure determinations follow.

The asymmetric unit of 2 consisted of 2 molecules. Disorder was modeled as follows: the ligand based on N(3) was modeled over 2 positions in a 50:50 ratio, while that based on N(6) in addition to the butyl group based on C(30) were modeled over 2 sites in a 70:30 split. Disordered aromatic groups were treated as rigid hexagons in the refinement and only partial atoms with 50% occupancy or above were refined anisotropically. For 6 data were truncated to a Bragg angle of 25° due to a decline of diffraction intensity beyond this point. This is most likely to be related to the small crystal dimension. The electron density in the reduced methylpyridine moiety based on N(3) was quite smeared, and suggested that this functionality may be disordered. However, ardent efforts to model the same over two sites did not improve convergence. The hydrogens attached to C(30) and C(34) have been omitted from the refinement because of an inability to determine precisely which of these best represents a CH$_2$ moiety. For 10 the asymmetric unit comprised half of a dimer molecule plus a small region of disordered solvent. Both fragments straddled inversion centres. The solvent bore a resemblance to toluene, but because of the symmetry imposed disorder and its diffuse nature, it could not be modeled in any logical way. Hence PLATON SQUEEZE was employed, and allowance has been made herein for the presence of one molecule of toluene per unit cell based on the results from using this algorithm.29
Electronic Supplementary Information (ESI) available: CCDC 831736 – 831741 contain the supplementary crystallographic data for this paper.

References


Table 1. Selected bond lengths (Å) for compounds 2, 6, 7, 10, 11 and 12

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$^a$ Mg(2)-N(4) 2.073(2); $^b$ Mg(2)-N(5) 2.081(2); $^c$ Mg(2)-N(6) 2.2058; $^d$ Mg(1)-C(30); $^e$ Mg(2)-C(69) 2.118(3); $^f$ Mg(1)-O(1); $^g$ Mg(1)-O(1)'.
Table 3: Selected bond angles (°) for compounds 2, 6, 7, 10, 11 and 12

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a N(1)-Mg(1)-C(30); b N(2)-Mg(1)-C(30); c N(1)-Mg(1)-O(1); d N(2)-Mg(1)-O(1); e N(1)-Mg(1)-O(1)'; N(2)-Mg(1)-O(1)'; O(1)-Mg(1)-O(1)'.

- 31 -
Table 1. Crystallographic data for compounds 2, 6, 7, 10, 11 and 12

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<td>C₇₂H₁₀₂Mg₂N₈O₂</td>
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<td>Formula weight (g mol⁻¹)</td>
<td>592.19</td>
<td>629.21</td>
<td>657.26</td>
<td>701.27</td>
<td>1120.16</td>
<td>1160.24</td>
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<td>Crystal system</td>
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<td>monoclinic</td>
<td>orthorhombic</td>
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<td>Space group</td>
<td>P2₁/c</td>
<td>C2/c</td>
<td>P₂₁,₂₁,₂₁</td>
<td>P2/a</td>
<td>P₂₁/n</td>
<td>P₂₁/n</td>
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<tr>
<td>a (Å)</td>
<td>15.8710(2)</td>
<td>35.9897(12)</td>
<td>10.5988(1)</td>
<td>18.3245(2)</td>
<td>13.0079(1)</td>
<td>13.0079(1)</td>
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<tr>
<td>b (Å)</td>
<td>24.1760(4)</td>
<td>15.3126(3)</td>
<td>18.1105(2)</td>
<td>10.8579(1)</td>
<td>14.3714(2)</td>
<td>14.3714(2)</td>
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<td>c (Å)</td>
<td>19.3490(3)</td>
<td>14.6944(5)</td>
<td>21.0057(2)</td>
<td>22.0748(3)</td>
<td>18.6803(3)</td>
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<tr>
<td>α (deg)</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>90</td>
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<tr>
<td>β (deg)</td>
<td>98.312(1)</td>
<td>105.416(1)</td>
<td>90</td>
<td>108.966(1)</td>
<td>94.299(1)</td>
<td>95.414(3)</td>
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<tr>
<td>γ (deg)</td>
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<td>V (Å³)</td>
<td>7346.17(19)</td>
<td>7806.7(4)</td>
<td>4032.04(7)</td>
<td>4153.68(8)</td>
<td>3482.22(9)</td>
<td>3465.9(3)</td>
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<td>Z</td>
<td>8</td>
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<td>4</td>
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<tr>
<td>μ (mm⁻¹)</td>
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<td>0.077</td>
<td>0.079</td>
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<td>ρ (g cm⁻³)</td>
<td>1.071</td>
<td>1.071</td>
<td>1.083</td>
<td>1.121</td>
<td>1.068</td>
<td>1.112</td>
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<td>θ range (°)</td>
<td>4.27 to 27.48</td>
<td>4.04 to 25.02</td>
<td>3.54 to 27.52</td>
<td>3.98 to 27.48</td>
<td>3.53 to 27.48</td>
<td>4.68 to 25.15</td>
</tr>
<tr>
<td>R₁, wR₂ [I &gt; 2σ(I)]</td>
<td>0.0663, 0.1442</td>
<td>0.0663, 0.1561</td>
<td>0.0384, 0.0980</td>
<td>0.0523, 0.1217</td>
<td>0.0723, 0.2008</td>
<td>0.0845, 0.2027</td>
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<tr>
<td>R₁, wR₂ (all data)</td>
<td>0.1506, 0.1919</td>
<td>0.1199, 0.1913</td>
<td>0.0426, 0.1014</td>
<td>0.0812, 0.1403</td>
<td>0.0909, 0.2128</td>
<td>0.1291, 0.2394</td>
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<tr>
<td>Measured/independent reflections/ R₁th</td>
<td>133599 / 16753 /</td>
<td>55881 / 6839 /</td>
<td>55112 / 9226 /</td>
<td>61721 / 9439 /</td>
<td>55826 / 7938 /</td>
<td>24351 / 6008 /</td>
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<tr>
<td>reflections/ R₁th</td>
<td>0.1155</td>
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<td>0.0481</td>
<td>0.0599</td>
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<td>0.1851</td>
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Magnesium Hydrides and the Dearomatisation of Pyridine and Quinoline Derivatives

Michael S. Hill,* Gabriele Kociok-Köhn, Dugald J. MacDougall, Mary F. Mahon and Catherine Weetman

Reaction of $N$-heterocycles with magnesium hydride species generated by reaction of a magnesium $n$-butyl precursor with phenyl silane results in heterocycle dearomatisation by a hydride transfer which occurs with the formation of magnesium compounds containing dearomatised dihydropyridide anions.