General Experimental Procedures

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 were collected on a Bruker AV300 spectrometer operating at 75.5 MHz ($^{13}$C), 96.3 MHz ($^{11}$B). Variable temperature $^1$H NMR data were recorded on a Bruker AV400 spectrometer. 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.

Synthesis of compound 1

[CH{C(Me)NDipp}$_2$H] (Dipp = 2,6-di-iso-propylphenyl) (2 mmol, 840 mg) was dissolved in a mixture of pyridine (2 mmol, 160 μL) and hexanes (c.a. 5 mL) then treated with one equivalent of $^6$Bu$_2$Mg (2 mL of 1M soln in heptanes). The resulting mixture was heated to 60°C for 1 hour, by which time a white precipitate had formed. This was isolated by filtration, washed with hexane, dried under vacuum and transferred to a glovebox for subsequent analyses. Crystals suitable for X-ray studies were grown from a saturated benzene solution. Yield: 870 mg, 75 %. Despite repeated attempts this highly reactive compound did not yield satisfactory elemental analyses. $^1$H NMR (C$_6$D$_6$, 300.22 MHz) δ (ppm): -0.18 (2H, t, CH$_2$, nBu), 0.40 (6H, bs, CH$_3$, iPr), 0.94 (3H, t, CH$_3$, nBu), 1.17 (12H, bs, CH$_3$, iPr), 1.49 (2H, m, CH$_2$, iPr), 1.54 (6H, bs, CH$_3$, iPr, overlapped with $^6$Bu signals), 1.75 (6H, s, CH$_3$), 2.76 (2H, bs, CH, iPr), 3.60 (2H, bs, CH, iPr), 4.94 (1H, s, CH(CNAr)$_2$), 6.50 (m, 2H, m-H pyridine), 6.83 (m, 1H, p-H pyridine), 7.13 (6H, s, Ar), 8.70 (d, 2H, o-H pyridine). $^{13}$C NMR (C$_6$D$_6$, 75.49 MHz) δ (ppm): 168.59, 149.92, 146.33, 142.71, 139.11, 128.35, 125.45, 124.68, 124.04, 94.43, 33.31, 32.42, 28.94, 24.97, 24.51, 14.87, 5.92.

Synthesis of compound 3

[CH{C(Me)NDipp}$_2$H] (1 mmol, 420 mg) was dissolved in toluene (c.a. 5 mL) then treated with $^6$Bu$_2$Mg (1 mL of 1M soln in heptanes), and heated to 60°C for 1 hour. After cooling to room temperature the resulting pale yellow solution was treated with two equivalents of pyridine (2 mmol, 160 μL) and one equivalent of phenylsilane (1 mmol, 123 μL) to give a clear orange solution. A mixture of 1,2- and 1,4-isomers is obtained on crystallisation at this point. Further heating (60°C for two days) leads to the isolation of exclusively the 1,4 isomer. Yield: 270 mg, 45 % ( Yield not optimised, further crystallisation is possible after concentration of filtrate). Anal calcd. for
C_{39}H_{52}MgN_{4}: C, 77.92; H, 8.72; N, 9.32. Found: C, 77.86; H, 8.78; N, 9.22. \(^1\)H NMR (D\textsubscript{8}-toluene, 300.22 MHz) \(\delta\) (ppm): 0.28 (6H, d, \(^3\)J\textsubscript{HH} 6.9 Hz, CH\textsubscript{3} \textsuperscript{i}Pr), 1.05 (6H, d, \(^3\)J\textsubscript{HH} 6.6 Hz, CH\textsubscript{3} \textsuperscript{i}Pr), 1.28 (6H, d, \(^3\)J\textsubscript{HH} 6.9 Hz, CH\textsubscript{3} \textsuperscript{i}Pr), 1.68 (6H, d, \(^3\)J\textsubscript{HH} 6.6 Hz, CH\textsubscript{3} \textsuperscript{i}Pr), 1.71 (6H, s, CH\textsubscript{3}CNAr), 2.73 (2H, sept, \(^3\)J\textsubscript{HH} 6.9 Hz, CH \textsuperscript{1}Pr), 3.55 (2H, CH\textsubscript{2}CNAr), 3.59 (2H, overlapping sept, \(^3\)J\textsubscript{HH} 6.6 Hz, CH \textsuperscript{1}Pr), 4.08 (2H, m, N(CH\textsubscript{2}CH\textsubscript{2})), 4.86 (1H, s, N(CNAr)\textsubscript{2}CH\textsubscript{2}), 5.40 (2H, d, \(^3\)J\textsubscript{HH} 7.8 Hz, N(CH\textsubscript{2}CH\textsubscript{2}), 6.43 (2H, t, \(^3\)J\textsubscript{HH} 6.75 Hz, m-H pyridine), 6.82 (1H, t, \(^3\)J\textsubscript{HH} 7.8 Hz, p-H pyridine), 6.96 (2H, m, m-H Ar), 7.09 (2H, m, m-H Ar), 7.23 (2H, m, p-H Ar), 8.42 (2H, bd, \(^3\)J\textsubscript{HH} 3.9 Hz, o-H pyridine). \(^{13}\)C NMR (D\textsubscript{8}-toluene, 75.49 MHz) \(\delta\) (ppm): 169.18, 149.56, 144.84, 143.27, 141.75, 139.33, 138.24, 137.45, 125.66, 124.84, 124.49, 123.48, 94.10, 93.62, 29.21, 28.07, 25.43, 24.93, 24.43, 24.19, 23.95, 23.88.

The \(^1\)H NMR spectrum (D\textsubscript{8}-toluene, 300.22 MHz) of a mixture containing both 1,2-(2) and 1,4-dihydropyridide (4) isomers shows two overlapping \(\beta\)-diketiminate environments, a broadening of the pyridine environments and two distinct sets of signals for the dihydropyridide fragments; Resonances assigned to compound 2: \(\delta\) (ppm): 3.35 (2H, d, \(^3\)J\textsubscript{HH} 4.2 Hz, NCH\textsubscript{2}CH), 4.37 (1H, m, NCH\textsubscript{2}CHCH), 5.03 (1H, t, \(^3\)J\textsubscript{HH} 5.7 Hz, NCHCHCH), 6.02 (1H, d, \(^3\)J\textsubscript{HH} 5.7 Hz, NCH\textsubscript{2}CHCHCH); Resonances assigned to compound 3: \(\delta\) (ppm): 3.55 (2H, m, N(CH\textsubscript{2}CH\textsubscript{2})), 4.08 (2H, m, N(CH\textsubscript{2}CH\textsubscript{2}), 5.40 (2H, d, \(^3\)J\textsubscript{HH} 7.8 Hz, N(CH\textsubscript{2}CH\textsubscript{2}), 6.43 (2H, t, \(^3\)J\textsubscript{HH} 6.75 Hz, m-H pyridine).
Figure S1: $^1$H NMR spectrum of a pure sample of compound 3.
Figure S2: $^1$H NMR spectrum of an approximate 50:50 mixture of compounds 2 and 3.
Crystallographic data
Data for 1, 2 and 3 were collected at 150 K on a Nonius Kappa CCD diffractometer equipped with a low temperature device, using graphite monochromated MoKα radiation (\( \lambda = 0.71073 \) Å). Data were processed using the Nonius Software.\(^1\) Structure solution, followed by full-matrix least squares refinement was performed using the programme suite X-SEED throughout.\(^2\)

The asymmetric unit of compound 1 consists of \( \frac{1}{2} \) of a molecule, with the magnesium, nitrogen, carbons 18-23 (plus associated hydrogens) located on a mirror plane implicit in the space group. Hydrogens 3, 16, 17, 18a and 18b were all evident in the penultimate difference Fourier map, but ultimately included at calculated positions. The methyl protons attached to C1 are modeled as being disordered over 2 sites.

The asymmetric unit of compound 2 consists of half of a molecule. Atoms Mg1, N2, C18 and C3 are located on a mirror plane – intrinsic to the space group symmetry. The combination of symmetry within the molecule, and possible disorder, meant that treatment of the dearomatised pyridine provided the challenges in this structure.
However, there is ample crystallographic evidence for the dearomatisation. Larger than normal ADPs are recorded for C16-18 – a combination of asymmetry with the ring based on N3, and some disorder. The hydrogens on C16 were readily located, and have been refined at 0.98Å from the parent atom. It was evident that one of these hydrogens is present at full occupancy, and one at half-occupancy. The full occupancy candidate (H16B) presents at an average position for an aromatic CH, or one hydrogen of a CH₂ pair. The half occupancy H16A is clearly only present half of the time – i.e. only one half of the pyridine ring has been reduced. H16a-H16b are closer to each other than one would expect for a CH₂ group – however, this is reasonable considering the comments herein. No additional attempts were made to restrain the H…H distance in this moiety.

Figure S4: ORTEP representation (50%) of compound 2

References
