CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.200901897

Structural Tracking of the Potassium-Mediated Magnesiation of Anisole

William Clegg,[b] Ben Conway,[a] Pablo García-Álvarez,[a] Alan R. Kennedy,[a] Robert E. Mulvey,*[a] Luca Russo,[b] Jörg Sassmannshausen,[a] and Tell Tuttle[a]

Magnesiation (metal–hydrogen exchange) is currently going through a period of remarkable reassessment with regard to its effectiveness—previously poor but presently exceptionally good—in directly metalating aromatic and heteroaromatic substrates.[1] Eaton's enterprising employment of $[Mg(tmp)_2]$ (TMP = 2,2,6,6-tetramethylpiperidide) for executing direct *ortho*-magnesiation of representative aromatic amides and esters marked an early pivotal development in this transformation.[2] TMP was also a key factor in our later 1999 report of the dimagnesiation of arenes achieved in situ with sodium–magnesium alkyl–TMP mixtures, which coincidentally opened up a new facet of inverse crown chemistry.[3] The seeds of these initial results have since grown into the idea of "alkali-metal-mediated magnesiation (AMMMg)" and blossomed further to other lowly electropositive metals such as zinc,[4] cadmium,[5] aluminium,[6] and manganese,[7] so prompting the general designation "alkali-metal-mediated metalation (AMMM)". Knochel and co-workers have demonstrated that TMP-driven magnesiation of, for example, chlorinated pyrimidines[8] can also be effected by using alkyl-free halide compositions, "turbo-Grignard reagents", such as "TMPMgCl·LiCl".[9]

To date, nearly all AMMMg chemistry has involved lithium or sodium exponents. Potassium, the common utility heavier alkali metal, has received only a modicum of attention, which is surprising given both its prominence in Lochmann–Schlosser mixed-metal superbase chemistry,[10] and especially since in 2000 it produced one of the most spectacular outcomes of AMMMg in the 24-atom inverse crown ring complexes $[(tmp)_{12}K_6Mg_6(C_6H_4R)_6]$ (R = H or CH_3).[11] This potassium-mediated magnesiation was accomplished through the action of in situ mixtures of *n*-butylpotassium, dibutylmagnesium, and the amine TMP(H) on the relevant arene (benzene or toluene). Therefore, in contrast to alkali-metal-mediated zincation (AMMZn), which through more extensive study has produced several examples of mixed alkyl-amido bases that have been prepared in solid form and structurally defined,[12] until the present work no potassium magnesiate base has been similarly prepared, characterized, or applied in metalation chemistry.

As the starting point in this study, we fill this gap in knowledge by introducing the first example of such a mixed alkyl–amido potassium magnesiate characterized spectroscopically and crystallographically. Furthermore, in a development without precedent across AMMMg or AMMM chemistry in general, we follow the reaction of this new base with the aromatic ether anisole (PhOMe)[13] in detailed structural terms, elaborating both kinetic and thermodynamic *ortho*-magnesiated products through a combination of X-ray crystallographic and time-dependent NMR spectroscopic studies.

Based on a simple co-complexation procedure used to good effect previously with potassium zincates,[12] the new potassium magnesiate base [(pmdeta)K(μ-tmp)(μ-R′)Mg-(tmp)] **1** (Figure 1) (PMDETA = *N,N,N′,N″,N″*-pentamethyldiethylenetriamine, R′ = CH_2SiMe_3) was prepared by simply mixing together (co-complexing) its component chemicals in hexane solution (see the Supporting Information). Made through a metathesis reaction from the lithium congener and potassium *tert*-butoxide, KR′,[12a][14] is a convenient, easy to manipulate potassium alkyl less susceptible to decomposition than its silicon-free counterparts (*n*-butyl, *n*-pentyl etc). The new base **1** can be isolated in colorless crystalline form in yields in excess of 50%. For the reactions with anisole it was more convenient to prepare **1** in situ before adding a molar equivalent of the ether. Depending on conditions, two distinct crystalline *ortho*-magnesiated anisole complexes were produced from these reactions, namely monoalkyl–monoamido [(pmdeta)K(μ-tmp)(*o*-C_6H_4OMe)Mg-

[a] B. Conway, Dr. P. García-Álvarez, Dr. A. R. Kennedy, Prof. R. E. Mulvey, Dr. J. Sassmannshausen, Dr. T. Tuttle
WestCHEM, Department of Pure and Applied Chemistry
University of Strathclyde, Glasgow, G1 1XL (UK)
Fax: (+44) 141-548-2093
E-mail: r.e.mulvey@strath.ac.uk

[b] Prof. W. Clegg, Dr. L. Russo
School of Chemistry, Newcastle University
Newcastle upon Tyne, NE1 7RU (UK)

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200901897.

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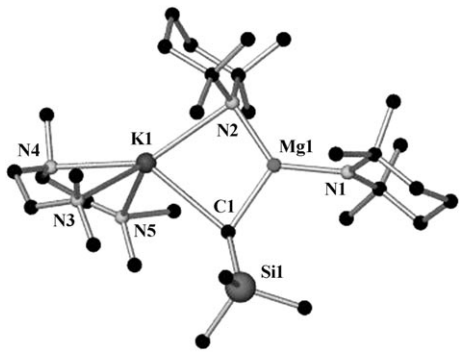


Figure 1. Molecular structure of base **1**. Disorder in the PMDETA ligand and hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: K1–N2 2.927(4), K1–C1 3.056(6), Mg1–N1 2.006(4), Mg1–N2 2.065(4), Mg1–C1 2.202(5), K1-N2-Mg1 90.5(1), N2-Mg1-C1 111.5(2), Mg1-C1-K1 84.6(2), C1-K1-N2 72.2(1).

(CH_2SiMe_3)], **2**, and bisamido [(pmdeta)K(μ-tmp)(*o*-C_6H_4OMe)Mg(tmp)], **3**. The kinetic product is **2** since it is the major product of reactions carried out over a shorter timescale (about 2 h), although small amounts of **3** are also detectable in the mixture. Over a longer timescale (4 days), **3** predominates, marking it as the thermodynamic product, while the amount of **2** present in the mixture is considerably diminished. With **1**, **2**, and **3** having distinct diagnostic resonances in their ^{1}H NMR spectra, these reactions can be followed easily by recording spectra at different time intervals (see Figure 2). Unusually for potassium organometallics,[15] compounds **1**–**3** are readily soluble in hydrocarbon solvents, thus enabling [D_{12}]cyclohexane to be used as the NMR solvent.

Reactions of 1:1 mixtures of the base and anisole (0.15 mmol of each) were performed in NMR tubes under inert atmospheres with spectra recorded after 5 min, then at periods of 1, 3, 7, and 22 h. After 5 min at ambient temperature, no reaction has taken place as best evidenced by resonances at $\delta = 7.12$ ppm (triplet of *meta*-H) and $\delta = -2.11$ ppm (singlet of CH_2SiMe_3) characteristic of unreacted anisole and base **1**, respectively. By the one-hour mark, some of these starting materials are still present but **2** has formed, as seen by the emergence of a singlet resonance at $\delta = -0.28$ ppm (associated with CH_2SiMe_3, see $\delta = 0.01$ ppm in **1**) and new anisole-derived aromatic resonances centered at $\delta = 7.53$, 6.94, 6.81, and 6.58 ppm. Concomitantly, characteristic resonances of free TMP(H), most prominently a singlet at $\delta = 1.06$ ppm denoting its CH_3 groups, also appears. This confirms the kinetic reaction is underway with base **1** magnesiating anisole to generate the alkyl-amido-arylmagnesiate product **2** and at the same time releasing the amine TMP(H). After 3 h have elapsed the relative proportions of **2** and TMP(H) grow substantially and at the same rate in comparison to the diminishing amount of **1** and anisole present. Reaching 7 h, **2** is joined by the bisamido-arylmagnesiate product **3** with a concomitant loss in the relative amount of TMP(H) and a concomitant appearance of tetramethylsilane (Me_4Si), the product of protonating the alkyl ligand $Me_3SiCH_2^-$. Recorded after 22 h, the final spectrum establishes the dominance of the thermodynamic reaction with the major aromatic anisole resonances centered at $\delta = 7.47$, 6.96, 6.81, and 6.52 ppm denoting a high proportion of **3** (accompanied by an increasing amount of Me_4Si), whereas there is a significantly reduced proportion of **2**. Scheme 1 summarizes this reaction sequence.

Crystallographic characterization of the base **1**, the kinetic intermediate **2**, and the thermodynamic final product **3** provides three still frames of the structural maneuvers accompanying the reactions taking place in solution. These molecular structures are shown in Figure 1, Figure 3, and Figure 4,

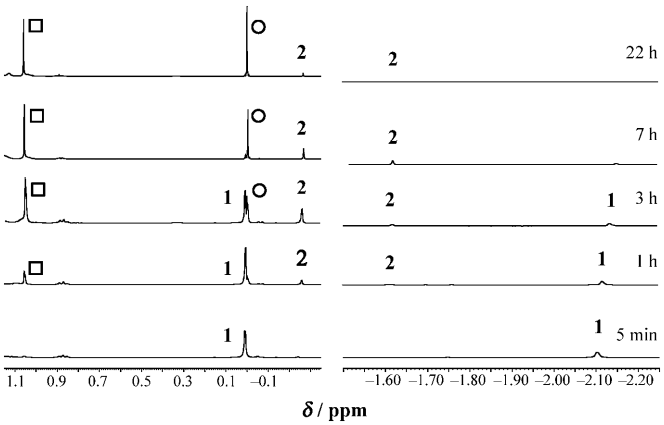
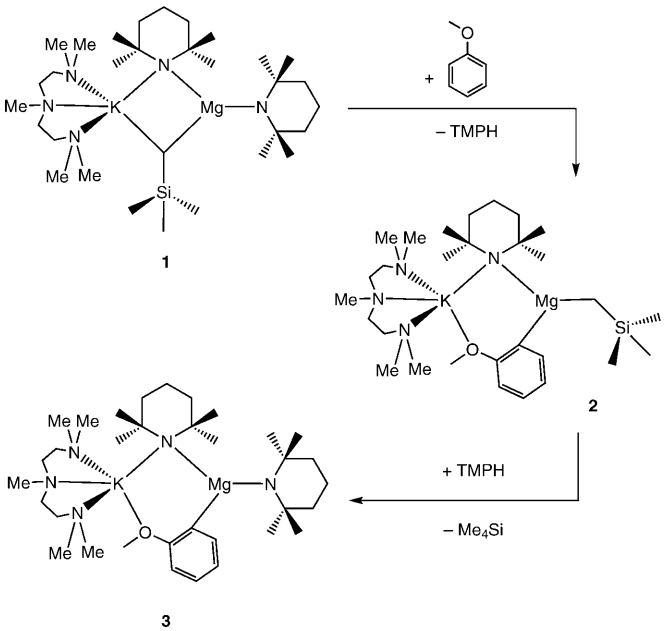


Figure 2. Tracking of the metal–$CH_2Si(CH_3)_3$ region of the ^{1}H NMR-tube reaction of base **1** with anisole. □ represents the free amine TMP(H) released on formation of **2** and ○ represents Me_4Si that is eliminated during the formation of **3**.



Scheme 1. Reaction sequence displaying the initial *ortho*-magnesiation of anisole by the TMP ligand in **1** followed by the reincorporation of TMP through protonation of the $Me_3SiCH_2^-$ group in **2** with the previously released free amine to yield **3**.

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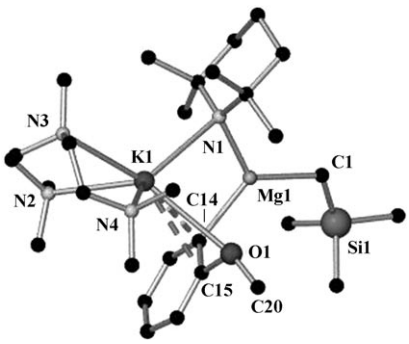

Figure 3. Molecular structure of **2**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: K1–N1 2.948(4), K1–C14 3.216(5), K1–C15 3.187(5), K1–O1 3.071(5), Mg1–N1 2.047(4), Mg1–C1 2.156(5), Mg1–C14 2.212(6), K1-N1-Mg1 88.70(14), N1-Mg1-C14 115.02(19), Mg1-C14-C15 111.7(4), C14-C15-O1 112.2(5), C15-O1 K1 81.5(3), O1-K1-N1 79.77(12).

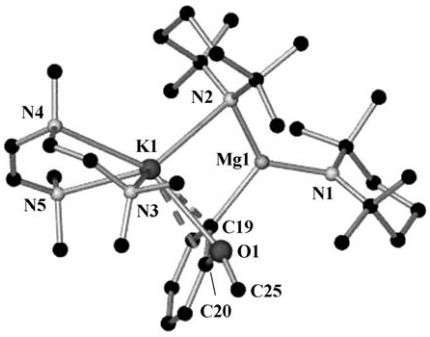

Figure 4. Molecular structure of one of the two independent molecules in the asymmetric unit of **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: K1–N2 3.005(6), K1–C19 3.162(8), K1–C20 3.190(8), K1–O1 2.843(6), Mg1–N1 1.998(6), Mg1–N2 2.040(7), Mg1–C19 2.185(8), K1-N2-Mg1 87.1(2), N2-Mg1-C19 116.0(3), Mg1-C19-C20 121.6(6), C19-C20-O1 115.5(7), C20-O1-K1 90.8(4), O1-K1-N2 90.03(17). The second molecule is essentially identical.

respectively, together with their key dimensions. There exists significant disorder in the PMDETA ligand within **1**, as such the structure of **1** was optimized computationally to clarify its connectivity. The RMSD of all atoms is 0.56 Å, relative to the crystal structure. The inflated RMSD value reflects the experimental disorder in the PMEDTA ligand of the crystal structure (RMSD excluding the PMEDTA ligand is only 0.18 Å). The BP86-D[16] optimized structure of **1** shows a slightly shorter C1–Mg bond relative to the crystal structure (2.19 Å). The optimized structure of **1** indicates that the silyl moiety also interacts with the K atom through an agostic interaction with the C1–H1a bond (d(K–H1) = 2.57 Å). This interaction has been confirmed by a Bader analysis[17] of the interaction, which shows a bond critical point (bcp1, Figure 5) and a bonding path between the two atoms ($\rho(r) = 0.0145$ and $\nabla^2\rho(r) = -=0.01463$). The strength of the interaction is 1.87 kcal mol^{-1}, as determined by the second order perturbation energy from an NBO[18] analysis of the system.

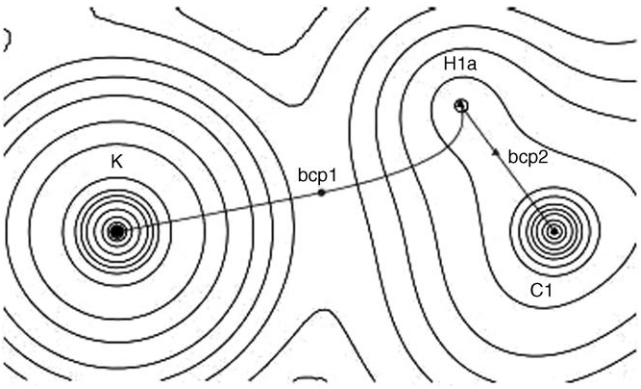

Figure 5. Electron density map of K–H1a agostic interaction in **1**.

Common to all three structures is a K-TMP-Mg backbone unit, chelated by PMDETA at the K terminus. Moving from **1** to **2**, the terminal site on Mg loses TMP [in the reaction released as TMP(H)] and gains an R′ ligand (switching from a bridging position), while the vacated bridging position is refilled by an *ortho*-deprotonated anisole ligand that binds in an ambidentate (C14 to Mg, O to K) arrangement. The central four-element (K-C-Mg-N) ring of **1** therefore expands to a six-atom, five-element (K-N-Mg-C-C-O) ring in **2**. Moving from **2** to **3**, the terminal site on Mg loses R′ (in the reaction released irreversibly as Me_4Si) and gains a TMP ligand, with retention of the remainder of the structure. A full structural picture of the two-step AMMMg process is thus unveiled with anisole *ortho*-magnesiated through amido activity, with a subsequent deprotonation of the generated amine through alkyl activity. This dual kinetic/thermodynamic behavior mimics that found in some AMMZn reactions.[19]

Mg adopts its usual (in the context of AMMMg bases and products) distorted trigonal-planar geometry within **1**–**3** and lies essentially coplanar with the aryl ring in the *ortho*-magnesiated anisole structures. In **2** and **3**, the mean Mg–*ortho*-C bond length (2.198 Å) lies at the top end of the range of corresponding bonds (2.132(6)–2.199(7) Å) in the unsymmetrical dimer $[Mg\{bis(ortho\text{-}anisyl)\}(thf)]_2$, the only previously reported C-magnesiated anisole structure—made not by direct magnesiation but through transmetalation from the mercury analogue.[20] Corresponding bonds involving K in **2** and **3** show little variation [e.g., d(K–N(TMP)) = 2.948(4) Å and 3.005(6) Å, respectively; mean d(K–N-(PMDETA)) = 2.907 Å and 2.893 Å, respectively] with the exception of the dative K–O bonds (d = 3.071(5) Å and 2.843(6) Å, respectively). Probably as an artifact of the making of these ring closing K–O bonds, close topological contacts exist between K and the *ipso*/*ortho*(-magnesiated) C atoms of the anisole ligands (d = 3.216(5)/3.187(5) Å for **2**; d = 3.162(8)/3.190(8) Å for **3**).

In summary, the potassium-mediated magnesiation of anisole by [(pmdeta)K(μ-tmp)(μ-R′)Mg(tmp)], **1**, has been tracked structurally by a combination of X-ray crystallographic and time-dependent NMR spectroscopic studies.

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This has established that the heteroleptic base reacts kinetically through its TMP component to generate the first *ortho*-magnesiated anisole product [(pmdeta)K(μ-tmp)(*o*-C_6H_4OMe)Mg(CH_2SiMe_3)], **2**, which, in turn, reacts through its alkyl component to yield the thermodynamic final *ortho*-magnesiated anisole product [(pmdeta)K(μ-tmp)(*o*-C_6H_4OMe)Mg(tmp)], **3**, and Me_4Si (R′H). This most complete study of any alkali-metal-mediated metalation to date has greatly improved our knowledge of how such reactions work and will help towards the rational design of new synthetic applications in the future. An important consideration that this study brings out is that the timing of any subsequent electrophilic quench of the base–substrate reaction mixture may be critical to the outcome given the presence of different *ortho*-magnesiated products, though both should yield the same functionalized anisole product on electrophilic quenching. Studies aimed at exploring this factor are currently in progress in our laboratory.

Experimental Section

Methods and materials: All reactions and manipulations were performed by using standard Schlenk techniques under argon gas. Products were isolated inside an argon-filled dry box. Solvents were freshly distilled from sodium/benzophenone prior to use. TMP(H) was obtained from Aldrich, distilled from CaH_2 and stored over 4 Å molecular sieves. All other chemicals were obtained from Aldrich and used as supplied. ^{1}H and ^{13}C NMR spectra were proton decoupled. Correlations between protons and carbon atoms were obtained through COSY and HSQC NMR spectroscopic methods. Single-crystal X-ray diffraction data were recorded on an Oxford Diffraction Gemini S and A Ultra diffractometers and a Nonius Kappa CCD diffractometer using $Mo_{K\alpha}$ ($\lambda = 0.71073$ Å) or $Cu_{K\alpha}$ ($\lambda = 1.54184$ Å) radiation.[21] The structures were solved by direct methods (SHELX program family or SIR) and refined on all unique F^2 values (SHELX).[22] CCDC-737822, CCDC-737823, and CCDC-737824 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of [(pmdeta)K(μ-tmp)(μ-CH_2SiMe_3)Mg(tmp)] (1): Hexane (10 mL) was added to an oven-dried Schlenk tube followed by 1 M nBu$_2$Mg (2 mL, 2 mmol) and TMP(H) (0.68 mL, 4 mmol). The reaction mixture was placed under reflux conditions for 5 h, and was then transferred, through a cannula, to a separate Schlenk tube containing KCH_2SiMe_3 (0.24 g, 2 mmol). Next PMDETA (0.42 mL, 2 mmol) was added to produce a clear yellow solution. The Schlenk tube was placed in the freezer (−28 °C) to yield colorless crystals (0.65 g, 54 % yield). ^{1}H NMR (400.13 MHz, C_6D_{12}): $\delta = 2.36$ (m, 8 H; 4 × CH_2 of PMDETA), 2.23 (s, 12 H; 4 × CH_3 of PMDETA), 2.22 (s, 3 H; CH_3), 1.72 (m, 4 H; 2 × γCH_2 of TMP), 1.25 (m, 24 H; 8 × CH_3 of TMP), 1.21 (t, 8 H, $J = 6.1$ Hz; 4 × βCH_2 of TMP), 0.01 (s, 9 H; 3 × CH_3 of Me_3Si), −2.11 ppm (s, 2 H; metal−CH_2−Si); ^{13}C NMR (100.63 MHz, C_6D_{12}): $\delta = 57.1$ (2 × CH_2 of PMDETA), 55.3 (2 × CH_2 of PMDETA), 52.1 (4 × αC of TMP), 45.0 (4 × CH_3 of PMDETA), 41.7 (CH_3 of PMDETA), 41.1 (4 × βC of TMP), 34.9 (8 × CH_3 of TMP), 19.9 (2 × γCH_2 of TMP), 4.1 (metal−CH_2−Si), 4.0 ppm (3 × CH_3 of Me_3Si).

Synthesis of [(pmdeta)K(μ-tmp)(*o*-C_6H_4OMe)Mg(CH_2SiMe_3)] (2): Hexane (10 mL) was added to an oven-dried Schlenk tube followed by 1 M nBu$_2$Mg (2 mL, 2 mmol) and TMP(H) (0.68 mL, 4 mmol). The reaction mixture was placed under reflux conditions for 5 h, and was then transferred, through a cannula, to a separate Schlenk tube containing KCH_2SiMe_3 (0.24 g, 2 mmol). Next PMDETA (0.42 mL, 2 mmol) was added to produce a clear yellow solution. Anisole (0.22 mL, 2 mmol) was added to the reaction mixture, which was stirred for 2 h. The Schlenk tube was then placed in the freezer (−28 °C) to yield colorless crystals (0.41 g). ^{1}H NMR (400.13 MHz, C_6D_{12}): $\delta = 7.53$ (d, 1 H; $J = 6.4$ Hz, H of anisole), 6.94 (t, 1 H, $J = 7.6$ Hz; H of anisole), 6.81 (t, 1 H; $J = 6.5$ Hz, H of anisole), 6.58 (d, $J = 8.0$ Hz 1 H; H of anisole), 3.72 (s, 3 H; OCH_3 of anisole), 2.23–2.27 (m, 8 H; 4 × CH_2 of PMDETA), 2.06 (s, 15 H; 5 × CH_3 of PMDETA), 1.72 (m, 2 H; γCH_2 of TMP), 1.35 (t, 4 H, $J = 6.0$ Hz; 2 × βCH_2 of TMP), 1.22 (s, 12 H; 4 × CH_3 of TMP), −0.28 (s, 9 H; 3 × CH_3 of Me_3Si), −1.60 ppm (s, 2 H; Mg−CH_2−Si); ^{13}C NMR (100.63 MHz, C_6D_{12}): $\delta = 163.0$ (ipso-C of anisole), 141.4 (aromatic C at $^H\delta = 7.53$), 126.8 (aromatic C at $^H\delta = 6.94$), 123.2 (aromatic C at $^H\delta = 6.81$), 109.7 (aromatic C at $^H\delta = 6.58$), 57.9 (2 × CH_2 of PMDETA), 56.5 (2 × CH_2 of PMDETA), 56.3 (CH_3 of anisole), 52.7 (2 × αC of TMP), 45.6 (4 × CH_3 of PMDETA), 42.2 (CH_3 of PMDETA), 41.4 (2 × βCH_2 of TMP), 35.3 (4 × CH_3 of TMP), 20.9 (γCH_2 of TMP), 4.3 (3 × CH_3 of Me_3Si), −3.8 ppm (Mg−CH_2−Si).

Synthesis of [(pmdeta)K(μ-tmp)(*o*-C_6H_4OMe)Mg(tmp)] (3): Hexane (10 mL) was added to an oven-dried Schlenk tube followed by 1 M nBu$_2$Mg (2 mL, 2 mmol) and TMP(H) (0.68 mL, 4 mmol). The reaction mixture was placed under reflux conditions for 5 h, and was then transferred, through a cannula, to a separate Schlenk tube containing KCH_2SiMe_3 (0.24 g, 2 mmol). Next PMDETA (0.42 mL, 2 mmol) was added to produce a clear yellow solution. Anisole (0.22 mL, 2 mmol) was added to the reaction mixture, which was stirred for 4 days. The Schlenk tube was then placed in the freezer (−28 °C) to yield colorless crystals (0.44 g). ^{1}H NMR (400.13 MHz, C_6D_{12}): $\delta = 7.47$ (br d, 1 H; H of anisole), 6.96 (t, 1 H, $J = 7.2$ Hz; H of anisole), 6.81 (t, 1 H, $J = 6.4$ Hz; H of anisole), 6.52 (d, 1 H, $J = 7.8$ Hz; H of anisole), 3.60 (s, 3 H; OCH_3 of anisole), 2.22–2.29 (m, 8 H; 4 × CH_2 of PMDETA), 2.09 (s, 3 H; CH_3 of PMDETA), 2.02 (s, 12 H; 4 × CH_3 of PMDETA), 1.67 (m, 4 H; 2 × γCH_2 of TMP), 1.24 (s, 24 H; 8 × CH_3 of TMP), 1.06 ppm (m, 8 H; 4 × βCH_2 of TMP); ^{13}C NMR (100.63 MHz, C_6D_{12}): $\delta = 139.7$ (aromatic C at $^H\delta = 7.47$), 126.1 (aromatic C at $^H\delta = 6.96$), 122.8 (aromatic C at $^H\delta = 6.81$), 109.1 (aromatic C at $^H\delta = 6.52$), 58.2 (2 × CH_2 of PMDETA), 56.9 (2 × CH_2 of PMDETA), 55.2 (CH_3 of anisole), 52.7 (4 × αC of TMP), 45.7 (4 × CH_3 of PMDETA), 42.7 (4 × βCH_2 of TMP), 42.5 (CH_3 of PMDETA), 36.0 (8 × CH_3 of TMP), 20.6 ppm (2 × γCH_2 of TMP).

Computational methods: The structure of **1** was obtained from the crystallographic coordinates and the dislocations in the PMDETA ligand were removed manually. The structure was optimized at the BP86-D/def2-TZVP level of theory by using TurboMole.[23] The converged wavefunction file from the optimized structure was used for the subsequent Bader and NBO analyses. The Bader analysis was performed with the AIM2000[24] program and the NBO perturbation study was carried out within the NBO5.0[18] program.

Acknowledgements

We thank the UK EPSRC for their generous sponsorship through grant awards EP/D076889/1 and EP/F03637X/1 and the Royal Society/Wolfson Foundation for a research merit award to R.E.M. This research was also supported by a Marie Curie Intra European Fellowship within the 7th European Community Framework Programme (for P.G.-A.). Our useful discussions with Dr. E. Hevia and Dr. C. O'Hara are also gratefully acknowledged.

Keywords: crystal structure · magnesiation · metalation · NMR spectroscopy · potassium

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Received: July 8, 2009
Published online: September 11, 2009

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