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Synthesis of an Alkylmagnesium Amide and Interception of a Ring-opened Isomer of the Important Utility Amide 2,2,6,6-Tetramethylpiperidide (TMP)

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Abstract

Two new magnesium complexes containing the important utility amide 2,2,6,6-tetramethylpiperidide (TMP) have been synthesised. Treating the magnesium bis(alkyl) reagent $(\text{Me}_3\text{SiCH}_2)_2\text{Mg}$ with a molar equivalent of TMP(H) in hydrocarbon medium produces the dimeric alkylmagnesium amide complex $[(\text{Me}_3\text{SiCH}_2)\text{Mg}(\mu\text{-TMP})]_2$ **2**, which was isolated in high yield. X-ray crystallography revealed that **2** was an unsymmetrical dimer as unusually the two TMP ligands adopt different conformations – one a chair, the other a twisted boat. Solution studies (multinuclear NMR and DOSY NMR spectroscopies) show that **2** undergoes a monomerisation and Schlenk equilibrium in d_8 -THF. When $(\text{Me}_3\text{SiCH}_2)_2\text{Mg}$ was reacted with two molar equivalents of TMP(H) in hydrocarbon medium [in an effort to prepare $\text{Mg}(\text{TMP})_2$] a crystalline sample of a surprising product, a tetranuclear triheteroanionic amide-alkoxide-amidoalkene $[(\text{TMP})\text{Mg}(\mu\text{-TMP})\{\mu\text{-N}(\text{H})\text{C}(\text{Me})_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{Me})=\text{CH}_2\}\text{Mg}(\mu\text{-OCH}_2\text{SiMe}_3)]_2$ **3** was obtained. Complex **3** contains two unexpected anions, namely the alkoxide produced via oxygen insertion into a Mg-C bond, and the primary amidoalkene which is produced via ring opening of the TMP anion.

1. Introduction

Alongside diisopropylamide, 2,2,6,6-tetramethylpiperidide (TMP) is one of the most widely utilised amido ligands in synthetic chemistry. Long used in the form of its lithium salt,[1-4] the high steric demand and extremely strong Brønsted basicity of TMP means that it is often employed in deprotonative metallation reactions in place of an alkyllithium which can be more prone to inducing nucleophilic addition (or reduction) side reactions.[5] The synthetic and structural chemistry of alkali metal TMP reagents continues to be the focus of considerable attention particularly with respect to their incorporation in magnesiate and zincate systems.[6-31] In this paper we introduce novel TMP complexes of magnesium. The parent bis(amide) $\text{Mg}(\text{TMP})_2$ – a considerably weaker base than LiTMP – was first utilised by Eaton to selectively magnesiate aryl esters, amide-activated strained cyclopropanes and cubanes, and to even doubly deprotonate diamido arenes.[32] Despite almost 40 years of investigation,[1-4] the chemistry of TMP continues to surprise. For example, recently, we reported that the strongly basic TMP anion can itself be metallated (*i.e.*, forming a N^- , C^- dianion) and trapped within a potassium aluminate framework.[33] In our past research studies, $\text{Mg}(\text{TMP})_2$ was generally prepared by treating commercially-sourced $^{n,s}\text{Bu}_2\text{Mg}$ /heptane solution with two molar equivalents of $\text{TMP}(\text{H})$ in hexane solution. To ensure complete *bis*(amination) of the dialkylmagnesium, the mixture was heated to reflux for at least twelve hours. Recently, the process used to prepare commercial ‘ Bu_2Mg ’ has been altered, and the composition of the new solutions consists of approximately a 9:1 ratio of $^{n}\text{Bu}_2\text{Mg}:\text{Et}_3\text{Al}$ in heptane. The aluminium additive is needed to aid solubilisation of the magnesium reagent in the hydrocarbon medium. We have recently discovered that this additive can unexpectedly take part and alter the course of reactions.[34] To overcome this complication, we have introduced another magnesium reagent into our synthetic repertoire, namely $(\text{Me}_3\text{SiCH}_2)_2\text{Mg}$ **1**. [35-38] Prepared by taking advantage of the dioxane-driven Schlenk equilibrium (Scheme 1), **1** can be isolated, and purified, by sublimation in good yields. Shifting from Bu_2Mg to **1** can have a dramatic influence on the regioselectivity of specific reactions. For instance when toluene is reacted with ‘ $\text{NaMg}(\text{TMP})_2^{n}\text{Bu}$ ’ a regioselective 2,5-dimetallation (dimagnesiumation) of toluene occurs;[39] however, when ‘ $\text{NaMg}(\text{TMP})_2\text{CH}_2\text{SiMe}_3$ ’ is employed, regioselective dimagnesiumation again takes place, but this time at the 3- and 5-positions.[40] In this work, we have turned

our attention to two magnesium-only complexes of TMP where our magnesium source is $(\text{Me}_3\text{SiCH}_2)_2\text{Mg}$. One product is a dimeric alkylmagnesium amide and the other a tetranuclear triheteroanionic amide-alkoxide-amidoalkene, which has implications for the ring opening of TMP.

<<Scheme 1 HERE>>

Scheme 1. Synthesis of the silyl-stabilised (bis)alkylmagnesium $(\text{Me}_3\text{SiCH}_2)_2\text{Mg}$ **1**.

2. Results and Discussion

Using **1** in this work, we attempted to prepare some fundamental monometallic building blocks which are crucial in constructing a greater understanding of the role neutral magnesium reagents play in magnesiate systems[25, 27] and also in the chemistry of macrocyclic “inverse crown complexes”. [41] Firstly, by treating one molar equivalent of **1** with an equimolar quantity of TMP(H) in hexane solution, a large crop of crystals (93% yield) deposited upon cooling, which by X-ray crystallography and NMR spectroscopy were found to be the dimeric alkylmagnesium amide $[(\text{Me}_3\text{SiCH}_2)\text{Mg}(\mu\text{-TMP})]_2$ **2** (Fig. 1). While four-membered dimeric rings are common in *s*-block amide chemistry,[42, 43] that of **2** is interesting for displaying two distinctly different TMP bridging conformations,[44] which renders the structure non-centrosymmetric. One ligand prefers the common chair conformation (N1 ligand in Fig. 1), which is adopted in the vast majority of *s*-block homo- and heterometallic complexes; but, the second TMP ligand adopts a rarer, less thermodynamically-preferred twisted boat conformation[45] (N2 ligand in Fig. 1). This is perhaps indicative of the steric strain which this latter ligand is under in **2**'s sterically-congested architecture as this conformation has only previously been observed in other systems which encompass ligands of high steric demand [*e.g.*, in $[\text{tBuMg}(\mu\text{-TMP})]_2$ both TMP ligands adopt boat forms[45] and in $[\text{tBuMg}(\mu\text{-TMP})]_2$ [46]]. The two crystallographically distinct Mg centres in **2** adopt severely distorted trigonal planar environments [range of angles around Mg, $95.36(8) - 138.85(4)^\circ$] where the narrowest angles belong to the N-Mg-N due to the constraints of forming the central four-membered Mg_2N_2 ring. There is little discrimination between the four Mg-N bond distances in **2** [2.121(2) – 2.144(2) Å].

<<Figure 1 HERE>>

Figure 1. Molecular structure of **2**. Key bond distances (Å) and angles (°): Mg1-N1, 2.144(2); Mg1-N2, 2.129(2); Mg1-C1, 2.108(3); Mg2-N1, 2.121(2); Mg2-N2, 2.125(2); Mg2-C5, 2.113(3); N1-Mg1-N2, 95.36(8); N1-Mg1-C1, 135.57(10); N2-Mg1-C1, 127.82(10); N1-Mg2-N2, 96.13(8); N1-Mg2-C5, 124.37(11); N2-Mg2-C5, 138.85(11); Mg1-N1-Mg2, 84.00(8); Mg1-N2-Mg2, 84.27(8).

Turning to the solution behaviour of **2**, in C₆D₆ solution at 300 K, only one set of TMP resonances is observed despite there being two chemically-distinct TMP ligands in its solid state structure. This is not too surprising as Collum has shown that the TMP anion is “conformationally mobile” in solution.[47] In d₈-THF solution, the chemistry of **2** is rather more complex. The logical scenario when a donor solvent is utilised is that dimeric **2** is broken down to donor-solvated monomers. This was indeed observed and corroborated by DOSY NMR studies,[48] which give a predicted molecular weight (MW) of 335 g mol⁻¹ intermediate between the expected values of an unsolvated (252 g mol⁻¹) and bis-THF solvated monomer (396 g mol⁻¹); perhaps suggesting the formation of a mono-THF monomer (324 g mol⁻¹). The predicted MW is far removed from the dimeric species characterised in the solid state (504 g mol⁻¹). In addition, a Schlenk-type equilibrium must also be operative as significant (equimolar) quantities of Mg(CH₂SiMe₃)₂ and Mg(TMP)₂ were also observed (Scheme 2). The ratio of these homoleptic products to “monomeric-**2**” can be altered depending on the concentration of the d₈-THF solution. Full details of these NMR data can be found in the Supporting Information†.

<<Scheme 2 HERE>>

Scheme 2. Monomerisation of **2** in d₈-THF and subsequent Schlenk equilibrium to produce homoanionic magnesium reagents.

The next monometallic building block we turned to was Mg(TMP)₂. As alluded to earlier, this reagent is generally prepared *in-situ* by heating a mixture of dialkylmagnesium with two molar equivalents of TMP(H), and is then used in further reactions.[49] Here, as we are using a ‘cleaner’ magnesium reagent, we attempted to grow crystals as the solid state structure of Mg(TMP)₂ has remained elusive. When **1** was treated with two molar equivalents of TMP(H) in hexane, heated to reflux for 12

hours and subsequently left at -28°C for two weeks, a small batch of X-ray quality crystals deposited from the hydrocarbon solution. By X-ray crystallographic analysis it was discovered that the crystalline material was not representative of the simple formulation $\text{Mg}(\text{TMP})_2$; but surprisingly was the tetranuclear triheteroanionic amide-alkoxide-amidoalkene $[(\text{TMP})\text{Mg}(\mu\text{-TMP})\{\mu\text{-N}(\text{H})\text{C}(\text{Me})_2\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{Me})=\text{CH}_2\}\text{Mg}(\mu\text{-OCH}_2\text{SiMe}_3)]_2$ **3** (Figs. 2 and 3).

<<Figure 2 HERE>>

Figure 2. Molecular structure of centrosymmetric and dimeric **3** with selective atom labelling. For clarity all H atoms have been omitted except those present on the amidoalkene ligands. Key bond distances (\AA) and angles ($^{\circ}$): Mg-N1, 2.1502(18); Mg1-N2, 1.9796(18); Mg1-N3, 2.0661(17); Mg2-O1, 1.9982(14); Mg2-O1*, 1.9908(15); Mg2-N1, 2.1974(16); Mg2-N3, 2.1017(18); N1-Mg1-N2, 137.56(7); N1-Mg1-N3, 91.41(7); N2-Mg1-N3, 129.45(8); O1-Mg2-O1*, 83.49(6); O1-Mg2-N1, 124.07(7); O1-Mg2-N3, 114.08(7); O1*-Mg2-N1, 126.04(7); O1*-Mg2-N3, 123.57(7); N1-Mg2-N3, 89.16(7).

<<Figure 3 HERE>>

Figure 3. ChemDraw[®] representation of heterotri-anionic **3**.

With complex **3** containing only one intact TMP ligand per Mg centre when two were expected, the reaction had clearly taken an unexpected course in generating two surprising anions. The first is a primary amidoalkene, which could be explained by a ring opening of a TMP anion. This reaction – perhaps a first step in the thermal degradation of TMP – is similar to that observed in the ring-opening/cleavage of cyclic ethers to produce enolates.[50-52] To the best of our knowledge, this represents the first time that a ring-opened derivative of TMP has been captured within an organometallic product. Berg and Cowling[53] reported that when $\text{TMP}(\text{H})$ is reacted with carbonyl dichloride or acetic anhydride, a mixture of isomeric isocyanates (6-isocyanato-2,6-dimethylhept-1-ene and 6-isocyanato-2,6-dimethylhept-2-ene) and a mixture of isomeric acetamides [N -(2,6-dimethylhept-6-en-2-yl)acetamide and N -(2,6-dimethylhept-5-en-2-yl)acetamide] respectively is produced; hence, providing

indirect evidence of ring-fissure of TMP(H). Ring-opening in our case is probably sterically driven by the congestion about the Mg centres and is induced thermally. Inevitably when TMP is contained within a Mg compound, the metal adopts a three-coordinate, trigonal planar arrangement (akin to the outer Mg1 atoms in **3**). However, due to the fortuitous inclusion of oxygen in **3**, the second unexpected anion to form, the alkoxide imparts less steric hindrance (and electronically provides an excellent bridge) at the inner Mg sites (Mg2) allowing coordination expansion (to four-coordinate distorted tetrahedral geometry) at these Mg centres. If ring-opening did not occur then it is envisaged that Mg1 would be surrounded by three sterically demanding cyclic TMP anions, although of course, the oxidation of the carbanions to the alkoxide may not drive the ring-opening but merely facilitate crystal formation. A magnesium centre surrounded by three TMP ligands has only been observed once before[54] [in the solvent-separated mononuclear *tris*(TMP) anion, $\text{Mg}(\text{TMP})_3^-$] and is not likely to reoccur with the geometric constraints which are applied in a neutral polynuclear complex; hence, to release steric strain, one could envisage that a H-shift from a CH_3 group to the amido N occurs followed by ring opening to form the less sterically demanding, unsaturated, linear, primary amide ligand [pathway a) in Scheme 3]. As mentioned earlier, we have recently documented that the TMP anion can itself be deprotonated at a methyl group, to produce a TMP dianion which is trapped and presumably stabilised within a mixed metal potassium aluminate framework.[33] In addition, Strohmman has shown that *N,N,N',N'*-tetraethylethylenediamine (TEEDA) can undergo β -deprotonation followed by ethene elimination to transform di-tertiary amine TEEDA into a tertiary amine-secondary amide.[55] Therefore a further potential pathway which could account for the ring-opening of TMP^- , is that sterically-driven self-deprotonation of the amide takes place, followed by alkene formation, ring opening and reprotonation of the imido N atom [pathway b) in Scheme 3].

<<Scheme 3 HERE>>

Scheme 3. Possible pathways for the generation of the acyclic amidoalkene ligand from its isomeric cyclic TMP anion.

The synthesis of an oxide-free analogue of **3** was attempted by treating two molar

equivalents of $\text{Mg}(\text{CH}_2\text{SiMe}_3)_2$ with three molar equivalents of $\text{TMP}(\text{H})$ in hexane. However, the only isolable product obtained from this reaction was the previously discussed alkylmagnesium amide dimer **2**. Despite our best efforts, it has proven difficult to reproduce **3**. We have attempted to prepare **3** rationally by systematically studying a number of routes including: combining genuine, pre-prepared samples of $\text{Mg}(\text{TMP})_2$ and $(\text{Me}_3\text{SiCH}_2\text{O})\text{Mg}(\text{TMP})$; reacting 2:3 mixtures of **1** and $\text{TMP}(\text{H})$ with dried air; and, oxygen-free **2** with $\text{Mg}(\text{TMP})_2$ in the presence of dried air, but none of these have been successful thus far. Returning to the solid-state structure of **2**, the presence of a TMP ligand adopting a less thermodynamically stable boat configuration may have a role to play in the generation of a ring-opened form of the TMP anion. Future studies will therefore focus on other sterically encumbered alkylmagnesium amides [*e.g.*, ${}^t\text{BuMg}(\text{TMP})$][45]] to ascertain whether species akin to **3** can be isolated.

4. Conclusions

To conclude, we have prepared a new alkylmagnesium amide and synthesised a highly unusual tetranuclear triheteroanionic amide-alkoxide-amidoalkene which appears to contain a ring-opened isomer of the TMP anion. This latter result shows one possible decomposition pathway when metal TMP solutions are heated strongly. Thermal decompositions of this type may be synthetically useful provided refined, reproducible ways of generating primary amidoalkenes can be found.

5. Experimental Section

All reactions were performed under an inert argon atmosphere using standard Schlenk techniques. Hexane was dried by refluxing over Na metal and benzophenone and distilled before use. NMR spectra were recorded on a Bruker DPX 400MHz spectrometer operating at 400.13 MHz for ${}^1\text{H}$ and 100.62 MHz for ${}^{13}\text{C}$. X-ray measurements were made with Oxford Diffraction instruments at 123 K using MoK_α $\lambda = 0.71073\text{\AA}$ radiation. Both structures are refined to convergence against F^2 with SHELX-97.[56] *Crystal Data* for **2**: $\text{C}_{26}\text{H}_{58}\text{Mg}_2\text{N}_2\text{Si}_2$; A colourless needle of approximate dimensions 0.20 x 0.04 x 0.02 mm gave a monoclinic space group $\text{P}2_1/c$, $a = 19.9838(14)$ $b = 13.0725(10)$ $c = 24.1832(11)$ \AA , $\beta = 94.452(1)^\circ$ $V = 6298.5(7)$ \AA^3 ,

$Z = 8$, $\rho_{calc} = 1.062 \text{ Mg m}^{-3}$, $2\theta_{max} = 54.0^\circ$. $R1 = 0.0690$ (for 9145 reflections with $I > 2\sigma(I)$) $wR2 = 0.1366$ and $S = 1.076$ for 648 parameters and 13737 unique reflections. Minimum/maximum residual electron density $-0.256/0.394 \text{ e}\text{\AA}^{-3}$.

Crystal Data for 3: $\text{C}_{62}\text{H}_{130}\text{Mg}_4\text{N}_6\text{O}_2\text{Si}_2$; A colourless block of approximate dimensions $0.20 \times 0.12 \times 0.10 \text{ mm}$ gave a monoclinic space group $\text{P}2_1/\text{n}$, $a = 11.6060(6)$ $b = 23.3204(10)$ $c = 13.5540(6) \text{ \AA}$, $\beta = 107.695(5)^\circ$, $V = 3494.9(3) \text{ \AA}^3$, $Z = 2$, $\rho_{calc} = 1.088 \text{ Mg m}^{-3}$, $2\theta_{max} = 56.0^\circ$. $R1 = 0.0592$ (for 5614 reflections with $I > 2\sigma(I)$) $wR2 = 0.1389$ and $S = 1.040$ for 368 parameters and 8338 unique reflections. Minimum/maximum residual electron density $-0.251/0.390 \text{ e}\text{\AA}^{-3}$.

Synthesis of $[(\text{Me}_3\text{SiCH}_2)\text{Mg}(\mu\text{-TMP})]_2$ (**2**): Dialkylmagnesium $(\text{Me}_3\text{SiCH}_2)_2\text{Mg}$ **1** was prepared as described in a previous publication.[40] A Schlenk tube was charged with 0.40g (2 mmol) of **1** and 8 mL of hexane. The resultant suspension was agitated in an ultrasonic bath for 15 minutes. An equimolar quantity of TMP(H) (0.34 mL, 2 mmol) was added and the solution was heated to reflux for 12 hours. The pale yellow solution was allowed to cool to ambient temperature, then placed in a freezer operating at -28°C . After approximately 72 hours, a large crop (0.47 g, 93%) of colourless needle-like crystals of **2** deposited from solution. ^1H NMR (400.03 MHz, 300 K, C_6D_6): δ 1.52 (4H, m, TMP $\gamma\text{-CH}_2$), 1.33 (8H, m, TMP $\beta\text{-CH}_2$), 1.30 (24H, s, TMP CH_3), 0.35 [18H, s, $\text{CH}_2\text{Si}(\text{CH}_3)_3$], -1.09 [4H, s, $\text{CH}_2\text{Si}(\text{CH}_3)_3$]. ^{13}C NMR (100.59 MHz, 300 K, C_6D_6): δ 53.0 (TMP $\alpha\text{-C}$), 38.3 (TMP $\beta\text{-CH}_2$), 36.0 (TMP CH_3), 17.2 (TMP $\gamma\text{-CH}_2$), 4.5 [$\text{CH}_2\text{Si}(\text{CH}_3)_3$], -1.4 [$\text{CH}_2\text{Si}(\text{CH}_3)_3$].

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Appendix A. Supplementary Information.

Full experimental details, X-ray data, NMR spectra. CCDC 873706 and 873707 (for **2** and **3** respectively). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/

References

- [1] R.A. Olofson, C.M. Dougherty, *J. Am. Chem. Soc.*, 95 (1973) 582.
- [2] R.A. Olofson, C.M. Dougherty, *J. Am. Chem. Soc.*, 95 (1973) 581.
- [3] M.W. Rathke, R. Kow, *J. Am. Chem. Soc.*, 94 (1972) 6854.
- [4] C.L. Kissel, B. Rickborn, *J. Org. Chem.*, 37 (1972) 2060.
- [5] M. Campbell, V. Snieckus, *Encyclopedia of Reagents for Organic Synthesis*, Vol. 5, Wiley, Chichester, 1995.
- [6] D.R. Armstrong, L. Balloch, J.J. Crawford, B.J. Fleming, L.M. Hogg, A.R. Kennedy, J. Klett, R.E. Mulvey, C.T. O'Hara, S.A. Orr, S.D. Robertson, *Chem. Commun.*, 48 (2012) 1541-1543.
- [7] S.E. Baillie, V.L. Blair, D.C. Blakemore, D. Hay, A.R. Kennedy, D.C. Pryde, E. Hevia, *Chem. Commun.*, 48 (2012) 1985-1987.
- [8] B.J. Fleming, P. García-Álvarez, E. Keating, A.R. Kennedy, C.T. O'Hara, *Inorg. Chim. Acta*, 384 (2012) 154-157.
- [9] B. Haag, M. Mosrin, H. Ila, V. Malakhov, P. Knochel, *Angew. Chem., Int. Ed.*, 50 (2011) 9794.
- [10] D.R. Armstrong, P. García-Álvarez, A.R. Kennedy, R.E. Mulvey, S.D. Robertson, *Chem. Eur. J.*, 17 (2011) 6725-6730.
- [11] D.R. Armstrong, L. Balloch, E. Hevia, A.R. Kennedy, R.E. Mulvey, C.T. O'Hara, S.D. Robertson, *Beilstein J. Org. Chem.*, 7 (2011) 1234-1248.
- [12] V.L. Blair, D.C. Blakemore, D. Hay, E. Hevia, D.C. Pryde, *Tetrahedron Lett.*, 52 (2011) 4590-4594.
- [13] L. Balloch, A.R. Kennedy, R.E. Mulvey, T. Rantanen, S.D. Robertson, V. Snieckus, *Organometallics*, 30 (2011) 145-152.
- [14] J.J. Crawford, B.J. Fleming, A.R. Kennedy, J. Klett, C.T. O'Hara, S.A. Orr, *Chem. Commun.*, 47 (2011) 3772-3774.
- [15] P. García-Álvarez, R.E. Mulvey, J.A. Parkinson, *Angew. Chem., Int. Ed.*, 50 (2011) 9668-9671.
- [16] R.E. Mulvey, D.R. Armstrong, B. Conway, E. Crosbie, A.R. Kennedy, S.D. Robertson, *Inorg. Chem.*, 50 (2011) 12241-12251.
- [17] D.R. Armstrong, V.L. Blair, W. Clegg, S.H. Dale, J. García-Álvarez, G.W. Honeyman, E. Hevia, R.E. Mulvey, L. Russo, *J. Am. Chem. Soc.*, 132 (2010) 9480-9487.
- [18] D.R. Armstrong, P. García-Álvarez, A.R. Kennedy, R.E. Mulvey, J.A. Parkinson, *Angew. Chem., Int. Ed.*, 49 (2010) 3185-3188.
- [19] L. Balloch, A.R. Kennedy, J. Klett, R.E. Mulvey, C.T. O'Hara, *Chem. Commun.*, 46 (2010) 2319-2321.
- [20] R.E. Mulvey, V.L. Blair, W. Clegg, A.R. Kennedy, J. Klett, L. Russo, *Nature Chem.*, 2 (2010) 588-591.

- [21] G. Bentabed-Ababsa, F. Blanco, A. Derdour, F. Mongin, F. Trécourt, G. Quéguiner, R. Ballesteros, B. Abarca, *J. Org. Chem.*, 74 (2009) 163.
- [22] K. Snegaroff, J.M. L'Helgoual'ch, C. Bentabed-Ababsa, T.T. Nguyen, F. Chevallier, M. Yonehara, M. Uchiyama, A. Derdour, F. Mongin, *Chem. Eur. J.*, 15 (2009) 10280-10290.
- [23] F. Garcia, M. McPartlin, J.V. Morey, D. Nobuto, Y. Kondo, H. Naka, M. Uchiyama, A.E.H. Wheatley, *Eur. J. Org. Chem.*, (2008) 644-647.
- [24] Y. Kondo, J.V. Morey, J.C. Morgan, H. Naka, D. Nobuto, P.R. Raithby, M. Uchiyama, A.E.H. Wheatley, *J. Am. Chem. Soc.*, 129 (2007) 12734-12738.
- [25] R.E. Mulvey, F. Mongin, M. Uchiyama, Y. Kondo, *Angew. Chem., Int. Ed.*, 46 (2007) 3802.
- [26] H. Naka, M. Uchiyama, Y. Matsumoto, A.E.H. Wheatley, M. McPartlin, J.V. Morey, Y. Kondo, *J. Am. Chem. Soc.*, 129 (2007) 1921-1930.
- [27] R.E. Mulvey, *Organometallics*, 25 (2006) 1060.
- [28] O. Bayh, H. Awad, F. Mongin, C. Hoarau, L. Bischoff, F. Trécourt, G. Quéguiner, F. Marsais, F. Blanco, B. Abarca, R. Ballesteros, *J. Org. Chem.*, 70 (2005) 5190-5196.
- [29] O. Bayh, H. Awad, F. Mongin, C. Hoarau, F. Trécourt, G. Quéguiner, F. Marsais, F. Blanco, B. Abarca, R. Ballesteros, *Tetrahedron*, 61 (2005) 4779-4784.
- [30] F. Mongin, A. Bucher, J.P. Bazureau, O. Bayh, H. Awad, F. Trécourt, *Tetrahedron Lett.*, 46 (2005) 7989-7992.
- [31] H. Awad, F. Mongin, F. Trécourt, G. Quéguiner, F. Marsais, *Tetrahedron Lett.*, 45 (2004) 7873-7877.
- [32] P.E. Eaton, C.-H. Lee, Y. Xiong, *J. Am. Chem. Soc.*, 111 (1989) 8016-8018.
- [33] B. Conway, A.R. Kennedy, R.E. Mulvey, S.D. Robertson, J. García-Álvarez, *Angew. Chem., Int. Ed.*, 49 (2010) 3182.
- [34] A.R. Kennedy, R.E. Mulvey, S.D. Robertson, *Dalton Trans.*, 39 (2010) 9091-9099.
- [35] V.L. Blair, A.R. Kennedy, J. Klett, R.E. Mulvey, *Chem. Commun.*, (2008) 5426.
- [36] W. Clegg, B. Conway, P. García-Álvarez, A.R. Kennedy, R.E. Mulvey, L. Russo, J. Sassmannshausen, T. Tuttle, *Chem. - Eur. J.*, 15 (2009) 10702.
- [37] R. Forret, A.R. Kennedy, J. Klett, R.E. Mulvey, S.D. Robertson, *Organometallics*, 29 (2010) 1436.
- [38] S.E. Baillie, W. Clegg, P. García-Álvarez, E. Hevia, A.R. Kennedy, J. Klett, L. Russo, *Chem. Commun.*, 47 (2011) 388.
- [39] D.R. Armstrong, A.R. Kennedy, R.E. Mulvey, R.B. Rowlings, *Angew. Chem., Int. Ed. Engl.*, 38 (1999) 131-133.
- [40] V.L. Blair, L.M. Carrella, W. Clegg, B. Conway, R.W. Harrington, L.M. Hogg, J. Klett, R.E. Mulvey, E. Rentschler, L. Russo, *Angew. Chem., Int. Ed. Engl.*, 47 (2008) 6208-6211.
- [41] R.E. Mulvey, *Chem. Commun.*, (2001) 1049.
- [42] R.E. Mulvey, *Chem. Soc. Rev.*, 20 (1991) 167.
- [43] J. Barker, D. Barr, N.D.R. Barnett, W. Clegg, I. Cragg-Hine, M.G. Davidson, R.P. Davies, S.M. Hodgson, J.A.K. Howard, M. Kilner, C.W. Lehmann, I. Lopez-Solera, R.E. Mulvey, P.R. Raithby, R. Snaith, *J. Chem. Soc., Dalton Trans.*, (1997) 951-955.
- [44] A.M. Belostotskii, H.E. Gottlieb, P. Aped, A. Hassner, *Chem. - Eur. J.*, 5 (1999) 449.
- [45] B. Conway, E. Hevia, A.R. Kennedy, R.E. Mulvey, S. Weatherstone, *Dalton Trans.*, (2005) 1532.

- [46] E. Hevia, A.R. Kennedy, R.E. Mulvey, S. Weatherstone, *Angew. Chem., Int. Ed.*, 43 (2004) 1709.
- [47] B.L. Lucht, D.B. Collum, *J. Am. Chem. Soc.*, 116 (1994) 7949.
- [48] D. Li, I. Keresztes, R. Hopson, P.G. Williard, *Acc. Chem. Res.*, 42 (2009) 270.
- [49] Preparation of magnesium bis(2,2,6,6-tetramethylpiperidide): Under an argon atmosphere, a Schlenk tube was charged with 1 mmol (1 mL of 1 M hexane solution) of di-*n*-butylmagnesium. To this solution, 5 mL of hexane were added, followed by 2 mmol (0.34 mL) of 2,2,6,6-tetramethylpiperidine. The mixture was heated to reflux for 24 hours, then all volatiles were removed *in-vacuo* to leave the product as an oil. ¹H NMR (400 MHz, 300 K, *cyc*-C₆D₁₂): δ 1.67 (C_γ-H, m, 4H), 1.33 (C_β-H, m, 8H), 1.21 (CH₃, br s, 24H).
- [50] J. Clayden, S.A. Yasin, *New J. Chem.*, 26 (2002) 191.
- [51] A. Maercker, *Angew. Chem., Int. Ed. Engl.*, 1987 (1987) 972.
- [52] R.B. Bates, L.M. Kroposki, D.E. Potter, *J. Org. Chem.*, 37 (1972) 560.
- [53] S.S. Berg, D.T. Cowling, *J. Chem. Soc. (C)*, (1971) 1653.
- [54] D.V. Graham, E. Hevia, A.R. Kennedy, R.E. Mulvey, C.T. O'Hara, C. Talmard, *Chem. Commun.*, (2006) 417.
- [55] V.H. Gessner, C. Strohmman, *J. Am. Chem. Soc.*, 130 (2008) 14412.
- [56] G. Sheldrick, *Acta Crystallogr.*, 64 (2008) A112.