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N-Heterocyclic-Carbene-Induced Monomerization of Sterically Encumbered Dialkylmagnesium and Dialkylmanganese Polymers

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The sterically encumbered polymeric dialkyl complexes $[M(CH_2SiMe_3)_2]_\infty$ [M = Mg, Mn^{II}] were deaggregated by the potent two-electron σ-donor, 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr), to yield the first examples of the monomeric three-coordinate $[M(CH_2SiMe_3)_2]$·donor complexes [M = Mg (**1**); Mn (**2**)]. Similarly, monomeric three-coordinate species $M[CH(SiMe_3)_2]_2$·IPr [M = Mg, (**3**); Mn, (**4**)] were obtained from the bulkier disilyl-substituted alkyl $[CH(SiMe_3)_2]$ congeners $M[CH(SiMe_3)_2]_2$·ether by displacement of the ether by IPr. Complexes **1**–**4**, which represent rare examples of N-heterocyclic-carbene-stabilized dialkylmagnesium and dialkylmanganese species, were crystallographically characterized; the diamagnetic magnesium complexes were also characterized in an arene solution by ^1H and ^{13}C NMR spectroscopy.

Introduction

The metal–carbon σ bond can trace its roots all the way back to 1849, when Frankland first identified the organozinc compound Et_2Zn.[1] Since that groundbreaking discovery, research into M–C bond-containing species has increased exponentially.[2] One of the main decomposition pathways for such compounds involves the well-established principle of beta-hydride elimination.[3] The trimethylsilylmethyl family of ligands, $[(Me_3Si)_{3-x}CH_x]^-$ ($x = 0, 1, 2$), have been exploited to great effect in organometallic synthetic chemistry by many chemists, most notably Lappert and Wilkinson, as they possess no β-hydrogen atoms and have considerable steric bulk. The Mg^{II} and Mn^{II} dialkyl species are of specific interest to us, as they are precursors to discrete heterometallic complexes that have a propensity for directly magnesiating[4] or manganating[5] a multitude of substrates, which include functionalized aromatic species at room temperature in nonpolar solvents. They also act as starting materials for the production of a class of compounds that has been labelled "inverse crowns" due to the antithetical nature of the Lewis acidic and basic sites with respect to a typical crown ether.[6] Part of our recent studies have involved the preparation of N-heterocyclic-carbene-stabilized alkyl/amido magnesium complexes, such as *n*BuMg(TMP)·IPr, *n*BuMg(HMDS)·IPr and $[nBu_2Mg]_4$·2IPr (TMP = 2,2,6,6-tetramethylpiperidide and HMDS = 1,1,1,3,3,3-hexamethyldisilazane).[7] We now extend this concept to bulky Mg and Mn dialkyl species and present herein the new complexes $[(Me_3Si)_{3-x}CH_x]_2M$·IPr [$x = 2$, M = Mg (**1**) and Mn (**2**); $x = 1$, M = Mg (**3**) and Mn (**4**); IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene], which are novel because they are monomeric and each contains a trigonal-planar three-coordinate MC_3 centre.

Results and Discussion

N-heterocyclic carbene chemistry has arguably been the most burgeoning branch of organometallic chemistry over the past 20 years, and virtually every metal in the periodic table possesses a known NHC adduct.[8] Nevertheless, magnesium and manganese NHC chemistry can be considered as under-represented in this domain.[9] For our synthetic work, the relevant metal alkyl reagent and IPr were stirred together in warm hexane according to Scheme 1. This was sufficient for complete dissolution in the case of M = Mn, but some toluene had to be added dropwise for M = Mg until a homogeneous solution was obtained. The slow cooling of these solutions to room temperature afforded X-ray-quality crystals, the yields of which were subsequently maximized by the further cooling of these solutions to –35 °C for 24 hours. Colourless crystals were obtained for all of the complexes with the exception of **2**, whose crystals were yellow.

A single-crystal-diffraction experiment was performed on each of the four new complexes to elucidate their molecular structures. Complexes **1** and **2**, as well as **3** and **4**, were demonstrated to be isostructural monomers, as shown in Figures 1 and 2. The N-heterocyclic carbene proved to be a sufficiently strong σ-donor to break up the $[M(CH_2SiMe_3)_2]_\infty$ polymer in the donor-ligand-free parent compounds in order to give **1** and **2**. For the bulkier disilyl-substituted alkyl complexes **3** and **4**, however, the carbene displaced the weaker donating ether molecule that was pres-

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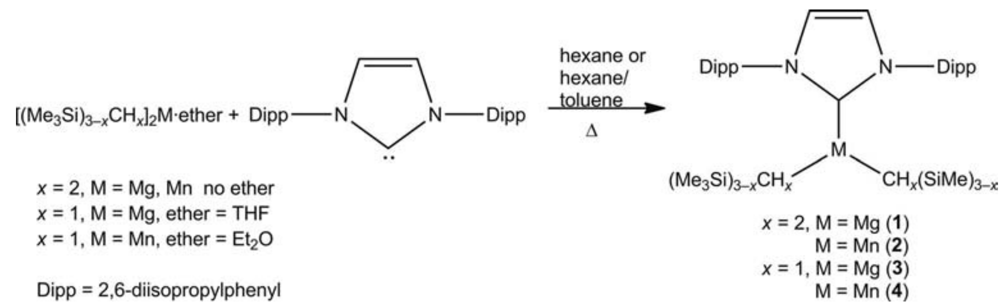

Scheme 1. Synthesis of complexes **1**–**4**.

ent. Pertinent bond parameters are presented in Table 1, and details of the crystallographic data are presented in Table 2.

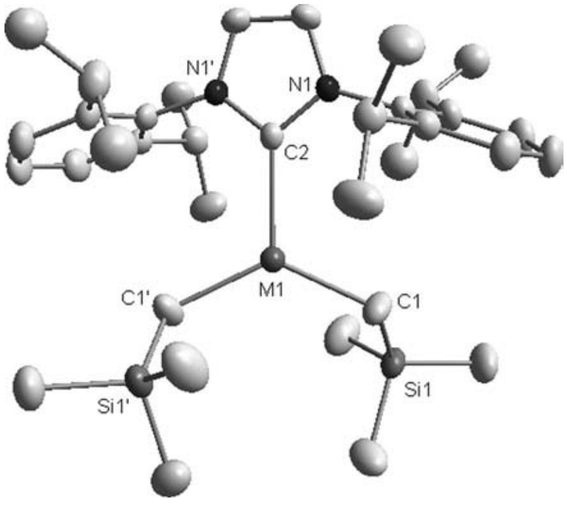

Figure 1. Molecular structure of monosilyl-substituted alkyl complex **1** (M = Mg) with selective atom labelling and thermal ellipsoids at the 50% probability level. Hydrogen atoms and the minor disordered component are omitted for clarity. Complex **2** (M = Mn) is isostructural with this compound **1**.

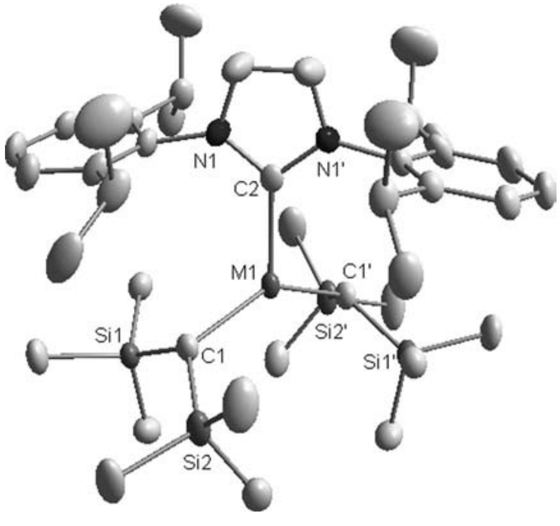

Figure 2. Molecular structure of disilyl-substituted alkyl complex **3** (M = Mg) with selective atom labelling and thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. The coordination geometry of complex **4** (M = Mn) is similar to that of **3**.

Table 1. Key bond lengths [Å] and angles [°] of complexes **1**–**4**.

	1 (M = Mg)	**2** (M = Mn)	**3** (M = Mg)	**4** (M = Mn)[a]
M1–C1	2.131(2)	2.129(1)	2.115(3)	2.154(2), [2.146(3)]
M1–C2	2.267(3)	2.236(2)	2.288(5)	2.277(4)
C1–Si1	1.831(2)	1.832(2)	1.840(4)	1.847(2), [1.845(2)]
C1–Si2	–	–	1.847(3)	1.850(2), [1.846(3)]
C1–M1–C2	115.44(6)	116.52(4)	111.33(9)	113.03(9), [109.76(9)]
C1–M1–C1′	129.11(8)	126.96(6)	137.33(14)	137.22(8)

[a] C1′ = C3, N1′ = N2. As a result of its reduced symmetry relative to that in the other complexes, there are additional bond parameters in **4**, which are presented in brackets.

Complexes **1**–**3** have a crystallographically imposed C_2 axis running through the plane of the M–C$_{carbene}$ bond. Although M(CH$_2$SiMe$_3$)$_2$ (M = Mg, Mn) have previously been characterized in the presence of donors, complexes **1** and **2** represent the first examples of monomeric three-coordinate Mg and Mn bis(trimethylsilyl)methyl complexes to be structurally authenticated. Indeed, to the best of our knowledge, complex **2** is the first N-heterocyclic carbene adduct of any dialkylmanganese compound. Monomeric silyl-substituted alkyl structures of Mg and Mn typically require a bidentate donor[10] or two monodentate donors[5c,10b] in addition to two anionic ligands (to complete a four-coordinate tetrahedral metal centre), while, in the presence of a single monodentate donor, dimerization frequently occurs with a CH$_2$SiMe$_3$ group functioning as an anionic bridge.[11] This is also true of simpler bulky dialkylorganomagnesium[12] and dialkylorganomanganese[13] complexes in general, which also require bis-solvation as a minimum. Clearly, in complexes **1** and **2** the NHC, in conjunction with the neopentyl-type anions, combines to provide enough steric protection for the metal centres without resorting to dimerization.

The Mg–C$_{carbene}$ distances of **1** [2.267(3) Å] and **3** [2.288(5) Å] are consistent with those previously reported for monomeric, three-coordinate alkylamido,[7] dialkyl[7,14] and diamido[15] Mg–NHC complexes (2.254–2.285 Å), while the Mn–C$_{carbene}$ distances of **2** [2.236(2) Å] and **4** [2.277(4) Å] are marginally longer than those of a series of

Table 2. Selected crystallographic data for complexes **1**–**4**.

	1	**2**	**3**	**4**
Empirical formula	$C_{35}H_{58}MgN_2Si_2$	$C_{35}H_{58}MnN_2Si_2$	$C_{41}H_{74}MgN_2Si_4$	$C_{41}H_{74}MnN_2Si_4$
M_r	587.32	617.95	731.69	762.32
Crystal system	monoclinic	monoclinic	monoclinic	triclinic
Space group	$C2/c$	$C2/c$	$C2/c$	$P\bar{1}$
a [Å]	10.8017(6)	10.7915(5)	24.595(2)	11.0527(7)
b [Å]	19.5372(12)	19.5112(10)	11.0511(13)	13.3668(8)
c [Å]	18.5351(10)	18.5120(10)	20.945(2)	18.4328(12)
α [°]	90	90	90	81.210(5)
β [°]	102.658(5)	102.888(5)	122.098(11)	74.171(6)
γ [°]	90	90	90	67.415(6)
V [Å^3]	3816.5(4)	3799.6(3)	4822.7(10)	2415.5(3)
Z	4	4	4	2
$\rho_{calcd.}$ [g cm^{-3}]	1.022	1.080	1.008	1.048
Reflections measured	13838	15485	10793	17021
Unique reflections	3252	5256	5261	17021
R_{int}	0.0417	0.0219	0.0462	n.a.
GooF	1.051	1.123	1.094	0.906
R [on F, observed reflections only]	0.0645	0.0345	0.0699	0.0478
wR [on F^2,all data]	0.1588	0.0980	0.1729	0.1011
Largest diff. peak/hole [e Å^{-3}]	0.506/–0.495	0.433/–0.275	0.467/–0.455	0.561/–0.428

manganocene NHC complexes[16] (2.214–2.227 Å) and $MnX_2 \cdot 2NHC$ (X = Cl, I) halide complexes[17] (2.204–2.219 Å). The metal–alkyl bond lengths concur with those of other terminal Mg/Mn-$CH_x(SiMe_3)_{3-x}$ complexes that have been crystallographically characterized. The typical bond length range is 2.111–2.170 Å,[5c,10–11] with only one anomalously low value of 2.06 Å that was seen in $Mn[CH(SiMe_3)_2]_2 \cdot thf$.[18] The mean bond length in polymeric $[Mn(CH_2SiMe_3)_2]_\infty$ is 2.204 Å,[10b] while those of the bridging alkyl groups fall in the range 2.199–2.388 Å.[11] Cámpora reported a terminal Mn^{III}-CH_2SiMe_3 fragment that displays an average Mn–alkyl bond length of 2.069 Å.[11e]

The coordination spheres of the metal centres are all clearly trigonal-planar ($\Sigma(\angle M)$ = 359.99, 360.00, 359.99 and 360.00° for **1**, **2**, **3** **4**, respectively). All complexes show a distortion from planarity with respect to the dihedral angle between the two planes defined by N–$C_{carbene}$–N and C_{alkyl}–M–C_{alkyl}, the less bulky alkyl groups of complexes **1** and **2** [16.64(6) and 16.15(4)° for **1** and **2**, respectively] almost certainly causing an appreciably lower movement away from planarity than the bulkier ligands in **3** and **4** [46.17(10) and 45.42(7)° for **3** and **4,** respectively].

In solution, only the diamagnetic magnesium complexes **1** and **3** could be studied by means of NMR spectroscopy, since the paramagnetic Mn^{II} (d^5) centre of complexes **2** and **4** compromised their spectra. The ^1H and ^{13}C NMR spectra of complexes **1** and **3** in C_6D_6 solution were entirely predictable: the expected resonances pertaining to the carbene were present (the chemical shifts were close, but not identical, to those of the free carbene,[19] which is consistent with the coordination of the carbene to an electron-deficient metal centre) and a pair of resonances representing the distinct M–CH_x and trimethylsilyl groups were observed. In both cases, the integration corresponded to a 2:1 alkyl ligand/carbene ratio, the metal-bound, highly shielded CH_x groups resonating at –1.59/–5.42 and –1.82/3.81 ppm ($^1H/^{13}C$) for **1** and **3**, respectively. The most indicative resonance of the carbene coordination was that of the highly deshielded carbene carbon at 188.6 and 185.9 ppm for **1** and **3**, respectively (the free IPr[19] shows the corresponding resonance at δ = 220.6 ppm).

Conclusions

The N-heterocyclic carbene bis(2,6-diisopropylphenyl)-imidazol-2-ylidene (IPr) has been shown to be an effective deaggregating agent, which breaks down polymeric magnesium and manganese trimethylsilylmethyl complexes into discrete monomeric complexes of the general formula $[(Me_3Si)_{3-x}CH_x]_2M \cdot IPr$, whose molecular structures have been crystallographically characterized. In each case, these rare examples of NHC-stabilized Mg and Mn species contain a three-coordinate, trigonal-planar metal centre (MC_3), in which the steric bulk of the constituents force the planar central carbene ring to tilt away from the CH_x–M–CH_x plane. This effect is clearly more pronounced in the presence of the bulkier disilyl-substituted $CH(SiMe_3)_2$ group. When $x = 2$ (that is, when only one trimethylsilyl group is bound to the metallated alkyl carbon atom), the structures represent the first monomeric examples that involve a single monodentate donor, as such donors typically provide insufficient steric protection for monomerization and hence the complexes usually dimerize through an anionic ligand bridge.

Experimental Section

General Remarks: All of the reactions and manipulations were carried out under an atmosphere of dry pure argon gas by using the standard Schlenk and glove box techniques. All of the solvents were freshly distilled from Na/benzophenone prior to use. $Mg(CH_2SiMe_3)_2$,[20] $Mn(CH_2SiMe_3)_2$,[21] $Mg[CH(SiMe_3)_2]_2 \cdot OEt_2$,[22]

$Mn[CH(SiMe_3)_2]_2·thf$[18] and IPr[19] were prepared according to the literature procedures. The elemental analyses were performed by the University of Strathclyde Elemental Analysis Service. NMR spectra were recorded with a Bruker AVANCE 400 NMR spectrometer, which was operated at 400.13 MHz for the ^1H NMR spectroscopy and at 100.62 MHz for the ^{13}C NMR spectroscopy.

$(Me_3SiCH_2)_2Mg·IPr$ (1): Equimolar amounts of $Mg(CH_2SiMe_3)_2$ (0.100 g, 0.5 mmol) and bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) (0.194 g, 0.5 mmol) were suspended in hexane (5 mL), and toluene was added dropwise with gentle heating until all of the visible solid had dissolved. Slow cooling of the resulting solution afforded X-ray-quality crystals. This mixture was then kept overnight at –34 °C to yield a crop of needlelike colourless crystals (0.15 g, 50%). ^1H NMR (C_6D_6): δ = 7.22 (t, 7.6 Hz, 2 H, aromatic *p*-CH), 7.09 (d, 4 H, aromatic *m*-CH), 6.39 (s, 2 H, olefin CH), 2.70 [sept., $^2J_{H,H}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$], 1.34 [d, $^2J_{H,H}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$], 0.97 [d, $^2J_{H,H}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$], 0.17 (s, 18 H, $SiMe_3$), –1.59 (s, 4 H, Mg-CH_2) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 188.6 (carbene C), 145.4 (aromatic *o*-C*i*Pr), 135.2 (aromatic *ipso*-C), 130.8 (aromatic *p*-CH), 124.6 (aromatic *m*-CH), 123.5 (olefin CH), 28.8 [$CH(CH_3)_2$], 25.2 [$CH(CH_3)_2$], 23.5 [$CH(CH_3)_2$], 4.7 ($SiMe_3$), –5.4 (Mg-CH_2) ppm. $C_{35}H_{58}MgN_2Si_2$ (587.32): calcd. C 71.57, H 9.95, N 4.77; found C 70.75, H 9.97, N 4.65.

$(Me_3SiCH_2)_2Mn·IPr$ (2): Equimolar amounts of $Mn(CH_2SiMe_3)_2$ (0.115 g, 0.5 mmol) and bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) (0.194 g, 0.5 mmol) were suspended in hexane (20 mL), and the mixture was heated gently until all of the visible solid had dissolved. Slow cooling of the resulting solution yielded X-ray-quality crystals. This mixture was then kept overnight at –34 °C to yield a crop of cubic yellow crystals (0.24 g, 77%). $C_{35}H_{58}MnN_2Si_2$ (617.96): calcd. C 68.03, H 9.46, N 4.53; found C 67.50, H 9.84, N 4.41.

$[(Me_3Si)_2CH]_2Mg·IPr$ (3): This magnesium complex was prepared in the same way as complex **1** by using $Mg[CH(SiMe_3)_2]_2·OEt_2$ (0.210 g, 0.5 mmol) to give colourless crystals (0.264 g, 67%). ^1H NMR (C_6D_6): δ = 7.22 (t, 6.8 Hz, 2 H, aromatic *p*-CH), 7.15 (d, 7.3 Hz, 4 H, aromatic *m*-CH), 6.37 (s, 2 H, olefin CH), 2.78 [sept., $^2J_{H,H}$ = 6.8 Hz, 4 H, $CH(CH_3)_2$], 1.42 [d, $^2J_{H,H}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$], 0.87 [d, $^2J_{H,H}$ = 6.8 Hz, 12 H, $CH(CH_3)_2$], 0.18 (s, 36 H, $SiMe_3$), –1.82 (s, 2 H, Mg-CH) ppm. $^{13}C\{^1H\}$ NMR (C_6D_6): δ = 186.0 (carbene C), 145.5 (aromatic *o*-C*i*Pr), 136.5 (aromatic *ipso*-C), 131.1 (aromatic *p*-CH), 125.4 (olefin CH), 125.0 (aromatic *m*-CH), 28.9 [$CH(CH_3)_2$], 26.4 [$CH(CH_3)_2$], 23.0 [$CH(CH_3)_2$], 5.9 ($SiMe_3$), 3.8 (Mg-CH) ppm. $C_{41}H_{74}MgN_2Si_4$ (731.69): calcd. C 67.30, H 10.19, N 3.83; found C 66.99, H 10.52, N 3.80.

$[(Me_3Si)_2CH]_2Mn·IPr$ (4): This manganese complex was prepared in the same way as complex **2** by using $Mn[CH(SiMe_3)_2]_2·thf$ (0.230 g, 0.5 mmol) to give colourless crystals (0.27 g, 71%). $C_{41}H_{74}MnN_2Si_4$ (762.32): calcd. C 64.60, H 9.78, N 3.68; found C 64.03, H 10.17, N 3.89.

X-ray Crystallographic Study: The crystallographic data were collected at 123(2) K with Oxford Diffraction diffractometers having Cu-K_α (λ = 1.5418 Å, **1**) or Mo-K_α (λ = 0.71073 Å, **2**–**4**) radiation. The structures were solved by using *SHELXS-97*[23] and were refined to convergence on F^2 against all of the independent reflections by the full-matrix least-squares method with the *SHELXL-97* program.[23] Structures **1** and **2** had an *i*Pr group whose position was rotationally disordered over two sites. Samples of **4** were found to be twinned, and so the data was processed by assuming a 180° rotation about reciprocal 2 1 1 to produce *SHELX hklf* 5 format reflection data. CCDC-827830, -827831, -827832 and -827833 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.

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