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FULL PAPER

Synthesis and characterisation of magnesium methyl complexes with monoanionic chelating nitrogen donor ligands and their reaction with dioxygen

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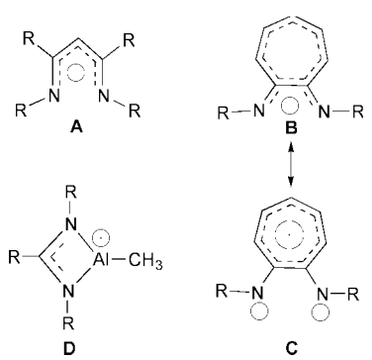
Treatment of the Grignard reagent MeMgCl with the lithiates Li[L–X] (Li[L–X] = lithium β-diketiminate [HC{C(Me)=NAr′}$_2$Li] (Ar′ = 2,6-diisopropylphenyl) or lithium *N*,*N*′-diisopropylaminotroponiminate, Li[(^{i}Pr$_2$)ATI]) in THF provided four-co-ordinate methylmagnesium complexes [Mg(η^2-L–X)Me(THF)]. The β-diketiminate complex has been characterised by X-ray crystallography, however the aminotroponiminate complex is an oil. Both complexes readily react with oxygen to provide methoxide-bridged dimeric complexes [Mg(μ-OMe)(η^2-L–X)]$_2$ and the complex [Mg(μ-OMe){η^2-(^{i}Pr$_2$)ATI}]$_2$ has structurally been characterised. The methyl-bridged dimeric complex [Mg(μ-Me){HC[C(Me)NAr′]}$_2$]$_2$ may be obtained by removal of THF from the adduct under vacuum at 150 °C or by treatment of the β-diketimine (L–XH) with dimethylmagnesium in toluene with elimination of methane, and has also been characterised crystallographically. In contrast to this, treatment of MgMe$_2$ with the aminotriponimine H[(^{i}Pr$_2$)ATI] provides only the bis-chelate complex [Mg{(^{i}Pr$_2$)ATI}$_2$] which has also been characterised structurally. However the methyl bridged dimer [Mg(μ-Me){η^2-(^{i}Pr$_2$)ATI}]$_2$ may be formed by removal of THF from [MgMe{η^2-(^{i}Pr$_2$)ATI}(THF)] at 110 °C under vacuum.

Introduction

The anionic chelating nitrogen donor diketiminato **A** and *N*,*N*′-dialkylaminotroponiminato (**B**, **C**) ligands have widely been employed in transition metal chemistry where the steric flexibility afforded by variation of the donor nitrogen substituents has extensively been exploited.[1,2] However, the co-ordination chemistry of these ligands with main group metals has less extensively been explored. Given their extensive use as reagents in both organic and organometallic synthesis, the chemistry of organometallic derivatives of the s-block metals has a special significance, however the complexity of their solution chemistry often hinders investigation of their mode of action.[3] The complexation of the organomagnesium species with polydentate nitrogen donor ligands has been a recurring theme in this area and has led to a number of advances in understanding of the structure, bonding and reactivity of the Mg–C bond.[4–8] The additional stability conferred by chelation provides a relatively less labile, well defined, system whose identity in solution may more confidently be equated to information obtained from solid state structural studies, thus allowing the development of structure–reactivity correlations. Furthermore, the electronic and steric properties of the ligand system may be tailored to modify the processes occurring at the metal centre and prevent unwanted reactions such as complex dimerisation or bis-ligand complex formation, thus potentially allowing the development of new modes of reactivity. These considerations have elegantly been demonstrated in p-block organometallic chemistry over recent years in the modification of the well known ethene oligomerisation (*aufbau*) activity of trialkylaluminium species AlR$_3$. Following Jordan's report of the ability of cationic, three-co-ordinate methylaluminium amidinato complexes (**D**) to polymerise ethene,[9] the first example of such activity for a main group metal complex, a number of groups have reported their characterisation of dimethylaluminium diketiminato,[10,11] *N*,*N*′-dialkylaminotroponiminato[12,13] and iminoamide[14] complexes and their cationic monomethyl derivatives. Although the activities of these systems fall far short of those of the most active transition metal catalysts,[15] they illustrate the potential of main group metal systems in a field previously considered to fall entirely within the realm of d- and f-block metal chemistry. Given these developments in aluminium chemistry, we have recently initiated a project to investigate the chemistry of nitrogen ligated organomagnesium species and we report here our studies on diketiminato and *N*,*N*′-dialkylaminotroponiminato complexes derived from Grignard reagents and dimethylmagnesium, and their reactivity with oxygen to provide methoxide species.



Experimental

General procedures

2-(2,6-Diisopropylphenylamino)-4-(2,6-diisopropylphenylimino)-2-pentene,[1] Ar′N=C(Me)C(H)=C(Me)NHAr′, and *N*-isopropyl-2-(isopropylamino)troponimine[12] [2-(isopropylamino)-1-isopropyliminocyclohepta-2,4,6-triene] H[(^{i}Pr)$_2$-ATI] were prepared according to the literature methods. Methylmagnesium chloride (3 M solution in THF), n-butyl

lithium (1.6 M solution in hexanes) and deuteriated NMR solvents were purchased from Aldrich and used as received. All reactions and manipulations were undertaken under an atmosphere of purified nitrogen in standard Schlenk apparatus or inside a Saffron Scientific glove-box unless otherwise stated. Diethyl ether and hydrocarbon solvents were distilled from sodium–benzophenone under an atmosphere of nitrogen immediately prior to use. Chlorinated solvents were distilled from CaH_2. All NMR spectra were recorded on a Bruker AC 250 spectrometer. Dimethylmagnesium was prepared by adding 1 equivalent of MeLi in ether to a THF solution of MeMgCl at room temperature. After removing THF under reduced pressure, the product was extracted from LiCl with ether. Ether was removed under vacuum and the residue dried for 5 hours at 150 °C under vacuum. The product was isolated as a white solid in 60% yield and analysed for chloride gravimetrically by hydrolysis and treatment with silver nitrate. Typically the chloride content was found to be in the region of 5% by weight.

Preparations

[MgMe{HC[C(Me)NAr′]$_2$}(THF)] 1 (Ar′ = 2,6-diisopropylphenyl). The compound n-BuLi (7.4 cm^3, 1.6 M in hexane, 11.9 mmol) was added dropwise *via* syringe to a stirred solution of Ar′N=C(Me)C(H)=C(Me)NHAr′ (5 g, 11.9 mmol) in 100 cm^3 of THF at −70 °C. The mixture was allowed to warm to room temperature and stirred for 30 min. A THF solution of MeMgCl (3.9 cm^3, 3 M in THF, 11.9 mmol) was added dropwise at room temperature. The resulting mixture was stirred at room temperature for 1 hour, the volatiles were removed under vacuum and the product was extracted from the LiCl with 100 cm^3 of hexane. White crystals of compound **1** deposited overnight at −20 °C and were collected by filtration (4.9 g, 78%). ^{1}H NMR ($CDCl_3$): δ −2.00 (s, 3 H, CH_3), 1.10 (d, 24 H, CH_3, $^3J_{H\text{-}H}$ = 6.0), 1.6 (s, 6 H, CH_3), 1.82 (t, 4 H, CH_2), 3.11 (spt, 4 H, CH, $^3J_{H\text{-}H}$ = 7.0 Hz), 3.71 (t, 4 H, CH_2), 4.71 (s, 1 H, CH) and 6.8–7.2 (m, 6 H, CH arom.). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ −19.8 (CH_3), 23.8 (CH_3), 24.0 and 24.8 (CH_3), 28.1 (CH_2), 27.6 (CH), 69.4 (CH_2), 93.7 (C_β), 123.1 (C_m), 124.2 (C_p), 142.1 (C_o), 145.3 (C_{ipso}) and167.6 (C_α). Calc. for $C_{34}H_{52}MgN_2O$: C, 77.18; H, 9.90; N, 5.29. Found: C, 77.24; H, 10.16; N, 5.09%.

[MgMe{η^2-(*i*Pr)$_2$ATI}(THF)] 2. The compound n-BuLi (1.5 cm^3, 1.6 M in hexane, 2.4 mmol) was added dropwise *via* syringe to a stirred solution of H[(*i*Pr)$_2$ATI] (0.5 g, 2.4 mmol) in THF at 0 °C. After stirring for 30 min, the mixture was allowed to warm to room temperature and stirred for 30 min. A THF solution of MeMgCl (0.8 cm^3, 3 M in THF, 2.4 mmol) was added dropwise at room temperature and the resulting mixture stirred for 30 min. The volatiles were removed under vacuum and the product was extracted from the LiCl with 20 cm^3 of hexane. Hexane was removed under vacuum, yielding the crude product as an orange oil in 98% yield (0.74 g). ^{1}H NMR (C_6D_6): δ −0.95 (s, 3 H, CH_3), 0.99 (t, 4 H, CH_2), 1.09 (d, 12 H, CH_3, $^3J_{H\text{-}H}$ = 6.0), 3.16 (t, 4 H, CH_2), 3.65 (spt, 2 H, CH, $^3J_{H\text{-}H}$ = 6.4), 6.1 (t, 1 H, H^4, $^3J_{H\text{-}H}$ = 9.0), 6.35 (d, 2 H, H^{2,6}, $^3J_{H\text{-}H}$ = 11) and 6.82 (dd, 2 H, H^{3,5}, $^3J_{H\text{-}H}$ = 10, $^3J_{H\text{-}H}$ = 11 Hz). ^{13}C-{^{1}H} NMR (C_6D_6): δ −14.2 (CH_3), 23.9 (CH_3), 25.1 (CH_2), 47.9 (CH), 68.6 (CH_2), 110.7 (C^{2,6}), 114.5 (C^4), 134.4 (C^{3,5}) and 162.4 (C^{1,7}). Calc. for $C_{18}H_{30}MgN_2O$: C, 68.69; H, 9.60; N, 8.89. Found: C, 67.86; H, 9.79; N, 8.99%.

[(Mg(OMe){η^2-(*i*Pr)$_2$ATI}]$_2$ 3. A stirred solution of [MgMe{η^2-(*i*Pr)$_2$ATI}(THF)] **2** (0.75 g, 2.4 mmol) in 20 cm^3 of hexane was treated with pure O_2 by bubbling the gas through it for 5 min. A yellow solid was obtained in suspension which was isolated by filtration and dried under vacuum (0.33 g, 53%). Suitable crystals for X-ray diffraction analysis were obtained from a saturated hexane solution of compound **2** in the presence of traces of air at −20 °C. ^{1}H NMR (C_6D_6): δ 1.32 (d, 24 H, CH_3, $^3J_{H\text{-}H}$ = 6.0), 3.24 (s, 6 H, CH_3), 3.82 (spt, 4 H, CH, $^3J_{H\text{-}H}$ = 6.0), 6.27 (t, 2 H, H^4, $^3J_{H\text{-}H}$ = 10.0), 6.56 (d, 4 H, H^{2,6}, $^3J_{H\text{-}H}$ = 12.0) and 6.98 (dd, 4 H, H^{3,5}, $^3J_{H\text{-}H}$ = 10.0 Hz). ^{13}C-{^{1}H} NMR (C_6D_6): δ 24.0 (CH_3), 47.9 (CH), 50.4 (CH_3), 111.7 (C^4), 115.3 (C^{2,6}), 134.6 (C^{3,5}), 162.6 (C^{1,7}). Calc. for $C_{14}H_{22}MgN_2O$: C, 65.01; H, 8.57; N, 10.82. Found: C, 64.94; H, 7.73; N, 10.88%.

[Mg(μ-Me){HC[C(Me)NAr′]$_2$}]$_2$ 4 (Ar′ = 2,6-diisopropylphenyl). *Method a.* To a stirred suspension of Me_2Mg (0.38 g, 7.1 mmol) in 50 cm^3 of toluene was added Ar′N=C(Me)C(H)=C(Me)NHAr′ (3 g, 7.1 mmol). The mixture was stirred for 2 days at room temperature. During this period $MgMe_2$ was slowly dissolved and reacted with the ligand. The product, insoluble in toluene, was isolated by filtration as a white solid in a 60% yield. A few X-ray quality crystals were obtained by standing the product overnight in suspension in toluene.

Method b. White crystals of [MgMe{HC[C(Me)NAr′]$_2$}(THF)] **1** (1.05 g, 2.0 mmol) were heated under vacuum at 150 °C for 1 hour to afford compound **4** as a white solid in quantitative yield (0.91 g, 1.0 mmol). ^{1}H NMR (THF-d$_8$): δ −2.00 (s, 3 H, CH_3), 1.15 (d, 24 H, CH_3, $^3J_{H\text{-}H}$ = 6.0), 1.6 (s, 6 H, CH_3), 1.70 (m, 4 H, CH_2), 3.20 (spt, 4 H, CH, $^3J_{H\text{-}H}$ = 7.0 Hz), 3.71 (t, 4 H, CH_2), 4.70 (s, 1 H, CH) and 6.9–7.1 (m, 6 H, CH arom.). ^{13}C-{^{1}H} NMR (THF-d$_8$): δ −20.5 (CH_3), 23.1 (CH_3), 22.3 and 24.3 (CH_3), 24.1 (CH_2), 27.4 (CH), 66.2 (CH_2), 93.7 (C_β), 122.8 (C_m), 124.0 (C_p), 141.8 (C_o), 145.3 (C_{ipso}) and 167.2 (C_α). Calc. for $C_{30}H_{44}Mg_2N_2$: C, 78.84; H, 9.70; N, 6.12. Found : C, 77.64; H, 9.52; N, 6.10%.

[Mg{η^2-(*i*Pr)$_2$ATI}]$_2$ 5. To a stirred suspension of $MgMe_2$ (0.13 g, 2.4 mmol) in 20 cm^3 of toluene was added H[(*i*Pr)$_2$ATI] (0.5 g, 2.4 mmol). The mixture was stirred for 12 h. The toluene was removed under vacuum and the product extracted from the excess of $MgMe_2$ with 20 cm^3 of hexane. The extract was evaporated to dryness under vacuum yielding [Mg{η^2-(*i*Pr)$_2$ATI}$_2$] as a yellow solid in 98% yield (0.5 g) based upon H[(*i*Pr)$_2$ATI] added. Suitable crystals for X-ray diffraction analysis were obtained from a saturated hexane solution at −20 °C. ^{1}H NMR (C_6D_6): δ 0.89 (d, 12 H, CH_3, $^3J_{H\text{-}H}$ = 6.4), 0.90 (d, 12 H, CH_3, $^3J_{H\text{-}H}$ = 6.2), 3.47 (spt, 4 H, CH, $^3J_{H\text{-}H}$ = 6.0), 5.97 (t, 2 H, H^4, $^3J_{H\text{-}H}$ = 8.8), 6.26 (d, 4 H, H^{2,6}, $^3J_{H\text{-}H}$ = 10.6) and 6.66 (dd, 4 H, H^{3,5}, $^3J_{H\text{-}H}$ = 10.8 Hz). ^{13}C-{^{1}H} NMR (C_6D_6): δ 24.1 (CH_3) 48.3 (CH), 113.1 (C^{2,6}), 116.1 (C^4), 135.0 (C^{3,5}) and 162.9 (C^{1,7}). Calc. for $C_{26}H_{38}MgN_4$: C, 72.47; H, 8.88; N, 12.99. Found: C, 72.18; H, 8.98; N, 12.61%.

[MgMe({η^2-(*i*Pr)$_2$ATI}]$_2$ 6. The orange oil [MgMe{η^2-(*i*Pr)$_2$ATI}(THF)] **2** (0.60 g, 1.91 mmol) was heated under vacuum at 110 °C for 1 hour to afford compound **6** as an orange powder in quantitative yield (0.46 g, 0.95 mmol). ^{1}H NMR (C_6D_6): δ −0.61 (s, 3 H, CH_3), 1.14 (d, 12 H, CH_3, $^3J_{H\text{-}H}$ = 6.0), 3.71 (spt, 2 H, CH, $^3J_{H\text{-}H}$ = 6.0), 6.23 (t, 1 H, H^4, $^3J_{H\text{-}H}$ = 9.0), 6.50 (d, 2 H, H^{2,6}, $^3J_{H\text{-}H}$ = 11) and 6.90 (dd, 2 H, H^{3,5}, $^3J_{H\text{-}H}$ = 10, 11 Hz). ^{13}C-{^{1}H} NMR (C_6D_6): δ −11.2 (CH_3), 23.9 (CH_3), 48.0 (CH), 112.9 (C^{2,6}), 115.9 (C^4), 134.8 (C^{3,5}) and 162.7 (C^{1,7}).

Crystal structure solution and refinement for compounds 1, 3, 4 and 5

All data sets were collected at 220 K using Cu-Kα radiation on a Stoe Stadi-4 diffractometer equipped with an Oxford Cryosystems low-temperature device. Absorption corrections were performed using ψ-scan data for compounds **1** and **3**; corrections for **4** and **5** were carried out using Gaussian integration following refinement of the crystal face indices and dimensions against a set of ψ scans (Stoe X-Shape).[16] The structures were solved by direct methods (SHELX 97 or SIR 92)[17] and refined against F^2 using SHELX 97.[17] Hydrogen atoms were placed in calculated positions. In **1** the THF is disordered in the ratio 50:50 over two conformations with a common oxygen-position; the hexane of solvation is also disordered over

Table 1 Crystal data and results of the structure analyses of compounds **1**, **3**, **4** and **5**

	1	**3**	**4**	**5**
Crystal description	Colourless plate	Orange block	Colourless block	Yellow block
Empirical formula	$C_{37}H_{59}MgN_2O$ [Mg(L–X)Me(THF)]·0.5C_6H_{14}	$C_{28}H_{44}Mg_2N_4O_2$ $[Mg(L–X)(OMe)]_2$	$C_{60}H_{88}Mg_2N_4$ $[Mg_2(L–X)_2(\mu\text{-}Me)_2]$	$C_{26}H_{38}MgN_4$ $[Mg(L–X)_2]$
M_w	572.17	517.29	913.96	430.91
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	*Pbca*	$P2_1/n$	$P2_1/n$
a/Å	9.136(3)	15.560(11)	14.068(5)	9.5281(6)
b/Å	12.690(5)	8.838(7)	14.903(7)	18.3692(13)
c/Å	16.004(6)	22.162(16)	14.110(5)	14.2891(10)
α/°	99.00(3)			
β/°	96.17(3)		108.02(3)	93.154(7)
γ/°	95.19(2)			
V/Å^3	1811.2(11)	3048(4)	2813(2)	2497.1(3)
Z	2	4	2	4
μ(Cu-Kα)/mm^{-1}	0.621	0.927	0.666	0.747
Independent reflections	5022	2715	4807	4652
Data with $I > 2\sigma(I)$	2393	1631	3228	4010
*R*1	0.0840	0.0582	0.0720	0.0346
*wR*2	0.2445	0.1871	0.2189	0.0931

Table 2 Selected bond distances (Å) and angles(°) for compounds **1**, **3**, **4** and **5**

1		**3** (# = $-x+2, -y+1, -z+1$)		**4** (# = $-x+1, -y, -z$)		**5**	
Mg–N(1)	2.061(5)	Mg–N(1)	2.034(3)	Mg–N(1)	2.075(3)	Mg–N(1A)	2.0528(11)
Mg–N(5)	2.063(5)	Mg–N(2)	2.046(3)	Mg–N(5)	2.076(3)	Mg–N(1B)	2.0502(11)
Mg–O(1T)	2.066(4)	Mg–O(1M)	1.941(3)	Mg–C(1M)	2.296(3)	Mg–N(2A)	2.0461(12)
Mg–C(1M)	2.107(6)	Mg–O(1M)#	1.932(3)	Mg–C(1M)#	2.259(3)	Mg–N(2B)	2.0420(12)
N(1)–C(2)	1.344(6)	N(1)–C(11)	1.516(6)	N(1)–C(2)	1.315(5)	N(1A)–C(1A)	1.3294(17)
C(2)–C(3)	1.396(7)	N(2)–C(2)	1.321(4)	C(2)–C(3)	1.410(5)	N(2A)–C(2A)	1.3268(17)
C(3)–C(4)	1.410(7)	C(1)–C(2)	1.506(5)	C(3)–C(4)	1.397(4)	N(1B)–C(1B)	1.3276(17)
C(4)–N(5)	1.341(6)	C(2)–C(3)	1.401(4)	C(4)–N(5)	1.332(4)	N(2B)–C(2B)	1.3325(17)
C(1M)–Mg–O(1T)	107.3(2)	C(3)–C(4)	1.373(5)	N(1)–Mg–N(5)	92.39(10)	C(1A)–C(2A)	1.4997(18)
N(1)–Mg–O(1T)	105.12(16)	C(4)–C(5)	1.373(6)	C(1M)–Mg–C(1M)#	102.80(11)	C(2A)–C(3A)	1.4176(19)
N(5)–Mg–O(1T)	104.74(16)	C(5)–C(6)	1.373(6)	Mg#–C(1M)–Mg	77.20(11)	C(3A)–C(4A)	1.386(2)
N(1)–Mg–C(1M)	124.7(2)	C(6)–C(7)	1.385(5)	Mg–N(1)–C(2)	121.3(2)	C(4A)–C(5A)	1.367(3)
N(5)–Mg–N(1M)	119.5(2)	N(1)–Mg–N(2)	78.94(12)	Mg–N(1)–C(11)	123.3(2)	C(5A)–C(6A)	1.382(3)
N(1)–Mg–N(5)	93.09(18)	O(1M)#–Mg–O(1M)	81.88(12)	C(2)–N(1)–C(11)	115.4(3)	C(6A)–C(7A)	1.378(2)
Mg–N(1)–C(2)	121.1(3)	O(1M)#–Mg–N(1)	126.92(13)	Mg–N(5)–C(4)	120.5(2)	C(1B)–C(2B)	1.5002(18)
Mg–N(1)–C(1A)	121.1(3)	O(1M)–Mg–N(1)	122.90(14)	Mg–N(5)–C(51)	123.1(2)	C(2B)–C(3B)	1.4175(19)
C(1A)–N(1)–C(2)	117.7(4)	O(1M)#–Mg–N(2)	131.26(13)	C(4)–N(5)–C(51)	116.4(3)	C(3B)–C(4B)	1.379(2)
Mg–N(5)–C(4)	121.8(3)	O(1M)–Mg–N(2)	121.15(12)			C(4B)–C(5B)	1.371(2)
Mg–N(5)–C(1B)	118.6(3)	Mg–N(1)–C(1)	116.0(2)			C(5B)–C(6B)	1.370(2)
C(1B)–N(5)–C(4)	119.6(4)	Mg–N(1)–C(11)	124.9(2)			C(6B)–C(7B)	1.381(2)
		C(1)–N(1)–C(11)	118.1(3)			N(1A)–Mg–N(2A)	79.02(4)
		Mg–N(2)–C(2)	115.4(2)			N(1B)–Mg–N(2B)	79.37(4)
		Mg–N(2)–C(21)	123.5(2)				
		C(2)–N(2)–C(21)	121.0(3)				

two conformations about a crystallographic inversion centre. Similarity restraints were applied to chemically equivalent bond lengths and angles involving partial-weight atoms. All full-weight non-H atoms were refined with anisotropic displacement parameters (adps) with similarity restraints applied globally for light atoms. In **3** one ^{i}Pr group is orientationally disordered in the ratio 75:25; similarity restraints were again applied to bond lengths and angles in the disordered region. All non-H atoms except those of the minor disorder component were refined with adps. In **4** the whole complex appears to be disordered over two orientations in the ratio 93:7 (this ratio was refined as part of the model). It is clear from the cell dimensions that this structure could be twinned *via* a twofold rotation about [101], but an attempt to refine it as a twin yielded a twin-component scale factor of 0.01, suggesting that this was not the source of the apparent disorder. The real source of this image remains unclear and we speculate that it may be due to the presence of a supercell (although we have no evidence of this from the initial reflection search); for the purposes of determining connectivity though it is sufficient to treat this effect as disorder. During refinement the minor component was constrained to be a rigid body with the same geometry as the major component; it was possible to refine isotropic displacement parameters for all atoms. The major component was refined normally with adps for all atoms. Refinement of **5** presented no problems, and all non-H atoms were refined with adps.

Crystallographic details are provided in Table 1 and selected bond distances and angles in Table 2.

CCDC reference number 186/1919.

See http://www.rsc.org/suppdata/dt/b0/b001316l/ for crystallographic files in .cif format.

Results and discussion

Treatment of the lithium β-diketiminate [HC{C(CH$_3$)=NAr′}$_2$-Li] (Ar′ = 2,6-diisopropylphenyl)[1,10] with MeMgCl in THF provides the THF solvated methyl magnesium complex [MgMe{HC[C(Me)NAr′]$_2$}(THF)] **1** which may be isolated as colourless crystals from hexane solution in 78% yield (Scheme 1). The ^{1}H NMR spectrum of **1** in $CDCl_3$ shows a characteristic signal at δ −2.0 attributable to the magnesium bound methyl and a corresponding signal at −19.8 in the ^{13}C NMR spectrum is also observed. The occurrence of only one set of signals due to the nitrogen substituents in both ^{1}H

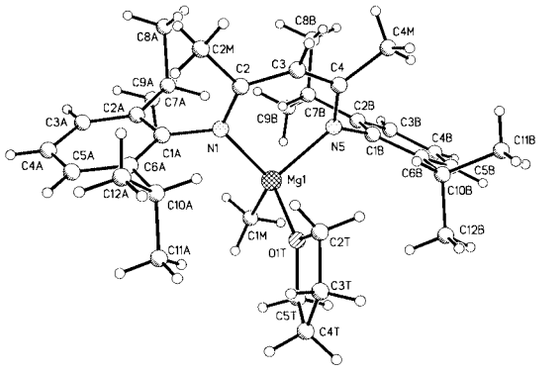
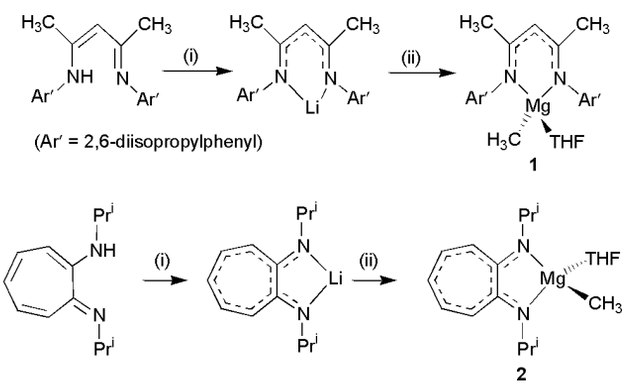


Fig. 1 Molecular structure of [MgMe{η²-HC[C(Me)NAr′]₂}(THF)] **1** (Ar′ = 2,6-diisopropylphenyl).



Scheme 1 Synthesis of complexes **1** and **2**. *Reagents and conditions*: (i) n-BuLi, THF, −78 °C, 1 h; (ii) MeMgCl, THF, 25 °C, 30 min.

and ^{13}C NMR spectra indicates the operation of a dynamic process; this is likely to be the reversible dissociation of the THF molecule rather than rotation about the C–N bonds given the steric congestion provided by the 2,6-diisopropylphenyl groups. Such a process is consistent with the observation that the THF may be removed from **1** under vacuum, as discussed below, indicating a relatively labile Mg–O bond. The crystal structure of **1** (Fig. 1) shows the complex to adopt a distorted tetrahedral co-ordination geometry around magnesium. The N–Mg–N chelate bite angle is 93.09(18)° and the six-membered chelate ring deviates from planarity to a considerable degree. This ring is best described as a distorted cyclohexane boat structure in which the magnesium and central carbon (C3) atoms lie 0.1256(27) and 0.2675(60) Å above the least squares plane, while N1 and N5 lie 0.1370(27) and 0.1225(27) Å below. This contrasts with the structure of the Me_2Al complex of the same ligand in which the N–Al–N angle is 96.18° and the five ligand atoms are essentially coplanar; the aluminium atom is displaced by 0.72 Å from this plane.[10] The differing sizes of Mg and Al are reflected in the metal–carbon bond distance of 2.107(6) Å in **1** which compares with 1.958(3) and 1.970(3) Å in the aluminium complex. A number of other nitrogen ligated methyl magnesium complexes have been structurally characterised and these include [$MgMe_2(Me_2NCH_2CH_2NMe_2)$] (Mg–C 2.166(6) Å),[5] [$MgMe\{Me_2N(CH_2)_2NMe\}]_2$ (Mg–C 2.100(4) Å),[6] [$MgMe_2(C_7H_{13}N)_2$] (Mg–C 2.163(9) and 2.224(8) Å; $C_7H_{13}N$ = quinuclidine),[7] and [$MgMe\{HB(pz)_3\}$] (Mg–C 2.118(11) Å).[8] The only other structurally characterised magnesium β-diketiminato complex is the bis-chelate [$Mg\{\eta^2$-$HC(CPhNSiMe_3)_2\}_2$] which also displays distorted tetrahedral co-ordination geometry around magnesium with N–Mg–N angles of 99.7(3) and 114.3(3)°.[18] Interestingly, although the Mg–N bond distances do not differ significantly from those in **1**, the six membered chelate rings are found to be planar in this structure.

Treatment of lithium *N*,*N*′-diisopropylaminotroponiminate, Li[(^{i}Pr$_2$)ATI],[12] with MeMgCl in THF provides [$MgMe\{\eta^2$-(^{i}Pr$_2$)ATI}(THF)] **2** as an orange oil in quantitative yield after extraction from LiCl into hexane (Scheme 1). In C_6D_6 solution the methyl ligand in this complex gives rise to signals at δ −0.95 and −14.2 in the ^{1}H and ^{13}C NMR spectra respectively, and signals for co-ordinated THF are also clearly observed. The corresponding dimethylaluminium complex of this ligand has also previously been characterised,[12] although, as far as we are aware, this is the first example of a magnesium *N*,*N*′-dialkyltroponiminato complex. Attempted crystallisation of **2** from hexane provided an orange crystal, however X-ray analysis showed this not to be the methyl complex, but rather the methoxy-bridged dimer [$Mg(\mu$-$OMe)\{\eta^2$-(^{i}Pr$_2$)ATI}]$_2$ **3** (Fig. 2). The Mg–O bond distances in the centrosymmetric dimer do not differ significantly and the nitrogen and ring atoms are coplanar indicating effective delocalisation in this system. The smaller bite angle of this five membered chelate ring is clearly evident in the narrow N–Mg–N angle of 78.94(12)°. It is interesting that, despite this, the Mg–N distances [2.034(3) and 2.046(3) Å] are slightly shorter than those in **1** possibly indicating the increased donor properties of the (^{i}Pr$_2$)ATI ligand attributable to the potential for a tropylium/diamide type charge separation in this ligand (**C**), although structural comparison with **2** would be necessary for firm conclusions to be drawn. Unfortunately we have so far been unsuccessful in obtaining crystals of **2**. However, the observation of similar differences in metal–nitrogen bond distances for the dimethylaluminium complexes of these two ligands supports this hypothesis.[10,12]

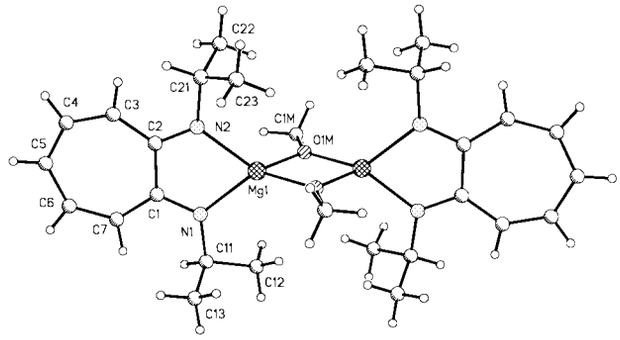
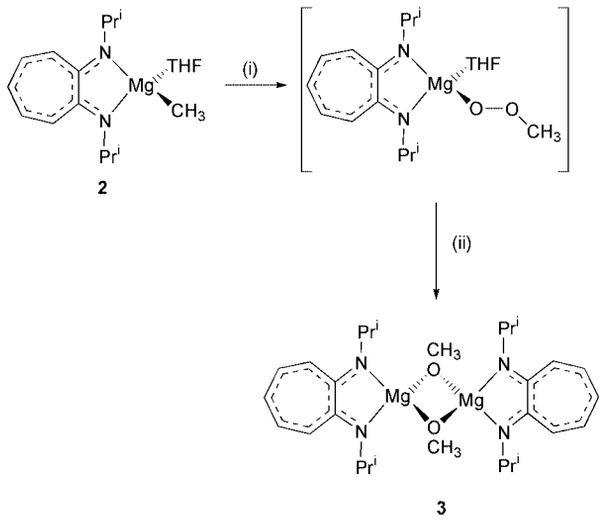


Fig. 2 Molecular structure of [$Mg(\mu$-$OMe)\{\eta^2$-(^{i}Pr$_2$)ATI}]$_2$ **3**.

Our initial concern that the conversion of compound **2** into **3** had resulted from contamination with methanol during crystallisation was ruled out when it was observed that controlled exposure of **2** in d_8-THF solution to dry air or pure oxygen led to the disappearance of the methyl ligand ^{1}H NMR signal at δ −0.95 and the appearance of the methoxide signal of **3** at δ 3.24. The intermediacy of a further species in this reaction, which we tentatively assign as a methyl peroxide complex, may be inferred from the initial rapid transformation to a species with a ^{1}H NMR signal at δ 3.40 on treatment of **2** with O_2, followed by the slower (*ca.* 5 min) decay of this signal concomitant with the growth of that due to the methoxide (Scheme 2). The nature of this intermediate, its molecularity and the co-ordination mode of the methyl peroxide is of course open to speculation as the structural characterisation of an alkyl peroxide complex of magnesium has never been reported. The complex **3** could be isolated in 53% yield as an orange powder from this reaction with oxygen. Following this observation we found that similar treatment of **1** also provides a methoxide complex, as indicated by a similar replacement of the methyl ligand signal with one due to methoxide at δ 3.21, although in this case the conversion is more rapid and no intermediate species could be observed. However, in this case we have been unable to isolate the methoxide complex as the oxidation appears to proceed beyond this stage for **1** and only a mixture of decomposition products has been obtained. This behavior is in contrast to that of the corresponding dimethylaluminium

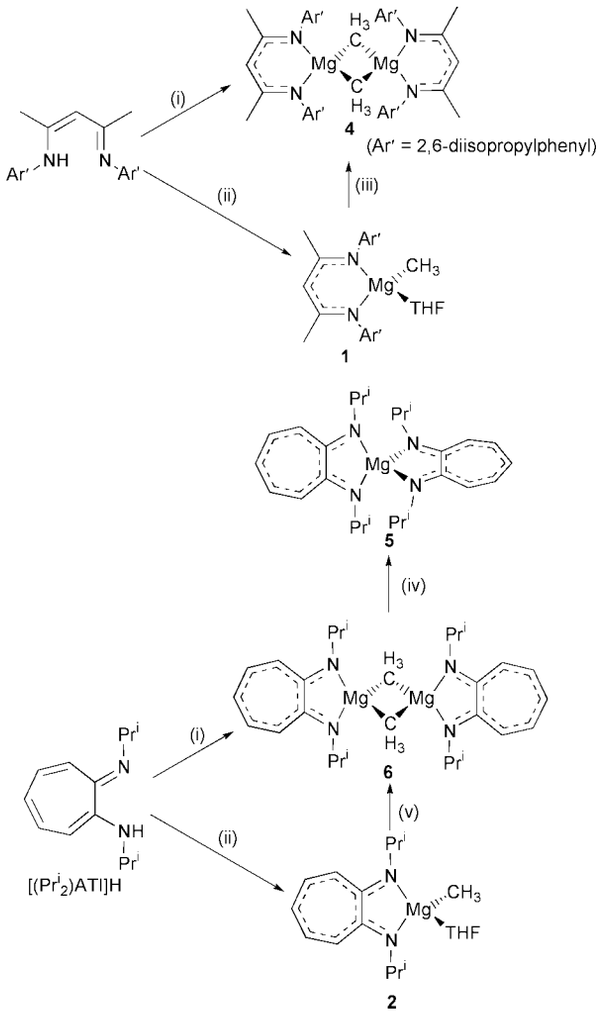


Scheme 2 Reaction of compound **2** with oxygen. *Reagents and conditions*: (i) O_2 gas, d_8-THF, <1 min; (ii) second mol of **2**, *ca.* 5 min.

complex which '*can be handled in air without decomposition*',[10] but is consistent with the observed formation of alkyl peroxide complexes on reaction of hydrotris(pyrazolyl)boratomagnesium alkyl complexes with oxygen.[19] The reaction of Grignard reagents with oxygen has long been known as a route to hydroperoxides and alcohols,[20] and there is both direct and indirect evidence that the reaction proceeds *via* a radical mechanism.[21] The only previously reported example of a structurally characterised magnesium alkoxide complex formed by oxygen insertion into a Mg–C bond is one derived from the heterometallic system $[\{Me_2Al(\mu\text{-}^iPr_2N)_2Mg(\mu\text{-}Me)\}_4]$ which provides a dimeric methoxide bridged system analogous to **3** but with $[\eta^2\text{-}Me_2Al(N^iPr_2)_2]^-$ ligands.[22] The structures of cyclic oxo- and peroxo-centred heterometallic Li/Mg and Na/Mg amides derived by exposure of the precursors to oxygen have also recently been reported.[23]

One of our aims in developing this chemistry is the formation of three-co-ordinate magnesium methyl complexes; neutral analogs of the ethene polymerisation active, cationic aluminium amidinate species produced by Jordan (**D**).[9] In order to allow access to the catalytic site by the incoming ethene, the co-ordination environment of the metal in such three-co-ordinate species is required to be somewhat open, and the metal may be regarded as possessing a vacant site. In the active aluminium amidinate species this site has been shown to be weakly ligated by the methyl adduct of the Lewis acid used to activate the precatalyst, and such weak associations have now been established crystallographically in many active, single site catalyst species.[24] For our target neutral magnesium species, such Lewis acid activation would be unnecessary and consequently, without the specific introduction of a weakly co-ordinating agent, none is available to occupy the vacancy. Strongly co-ordinating solvents, and in particular ethers, occupy the vacant site to provide complexes of the type **1** and **2** which would not be expected to show activity towards ethene. We have consequently sought to produce ether free species and have found that, contrary to expectation, it is possible to remove the co-ordinated THF from complex **1** by heating to 150 °C under vacuum (Scheme 3). The resulting methyl bridged dimer $[Mg(\mu\text{-}Me)\{HC[C(Me)NAr']_2\}]_2$ **4** shows only minimum solubility in hydrocarbon (hexane, toluene, benzene) solvents and NMR spectra were therefore unobtainable, however crystals suitable for X-ray analysis were obtained by allowing a suspension of **4** in toluene to stand overnight. The NMR spectra in d_8-THF indicate that the dimer is cleaved by this solvent to provide d_8-THF–**1**.

The molecular structure of compound **4** is shown in Fig. 3. Although the dimerisation of the three-co-ordinate $[(\eta^2\text{-L–X})MgMe]$ *via* the formation of methyl bridges creates a highly crowded molecule, it is clear that the 2,6-diisopropylphenyl ligand substituents are insufficiently bulky to prevent this from occurring. The crystal structure of **4** shows the complex to be centrosymmetric with the four-co-ordinate magnesium ions in a distorted tetrahedral environment imposed by the narrow ligand chelate (N–Mg–N) angle of 92.39(10)°, a feature also noted in the structure of **1**. The Ar′N=C(Me)-C(H)=C(Me)-NAr′ backbone of the diketiminato ligand is not planar but adopts a boat conformation similar to that observed for **1**. The



Scheme 3 Synthesis of complexes **4**, **5** and **6**. *Reagents and conditions:* (i) $MgMe_2$, toluene, $-CH_4$; (ii) $MgMe_2$, THF, $-CH_4$; (iii) 150 °C, vacuum; (iv) $H[(^iPr_2)ATI]$, $-CH_4$; (v) 110 °C, vacuum.

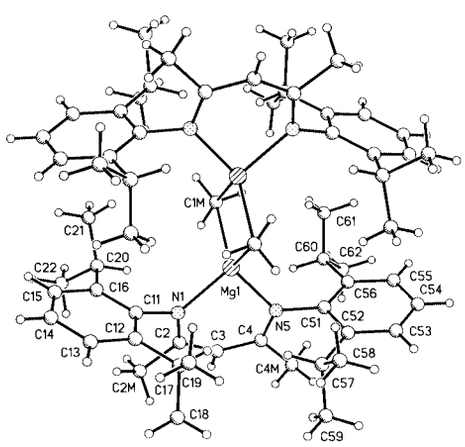


Fig. 3 Molecular structure of $[Mg(\mu\text{-}Me)\{HC[C(CH_3)NAr']_2\}]_2$ **4** (Ar′ = 2,6-diisopropylphenyl).

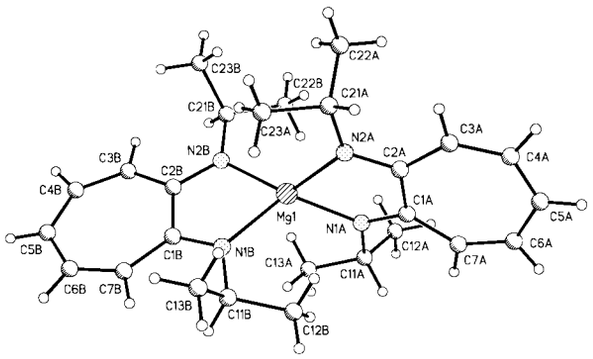


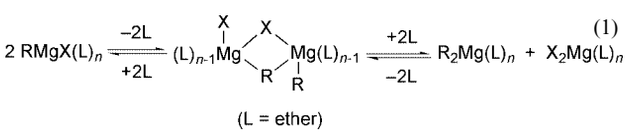
Fig. 4 Molecular structure of $[Mg\{\eta^2\text{-}(^iPr_2)ATI\}_2]$ **5**.

N–C and C–C bond lengths lie between those for single and double N–C and C–C bonds indicating a degree of π delocalisation. The Mg–Me distances in **4** [2.259(3) and 2.296(3) Å] are longer than that found in **1** [2.107(6) Å] as would be anticipated for a comparison of terminal and μ-co-ordinated methyl ligands. However, despite the apparent steric crowding resulting from the formation of the dimer, these Mg–C distances lie in the range found in the three other neutral $Mg(\mu\text{-}Me)_2Mg$ systems which have been structurally characterised to date. Thus, Mg–C distances of 2.243/2.297, 2.270/2.284 and 2.200/2.277 Å are found in the centrosymmetric systems $[\{\eta^2\text{-}Me_2Al(Et_2N)\text{-}Mg(\mu\text{-}Me)\}_2]$,[25] $[\{Cp'(THF)Mg(\mu\text{-}Me)\}_2]$[26] ($Cp' = C_5Me_4Et$) and $[MeSi(^tBuNAlMe_2)(^tBuNH)\{(^tBuNMg(\mu\text{-}Me)\}]_2$[27] respectively.

An alternative synthesis of compound **4** involves treatment of the β-diketimine, which exists as the iminoamine tautomer Ar′N=C(Me)C(H)=C(Me)NHAr′, with one molar equivalent of dimethylmagnesium in toluene, providing **4** in 60% yield with liberation of methane (Scheme 3). The formation of **4** by this route appears to be aided by its insolubility, and this is illustrated by the exclusive formation of the toluene soluble bis-chelate complex $[Mg\{\eta^2\text{-}(^iPr_2)ATI\}_2]$, **5** in 98% yield when the analogous reaction with the aminotroponimine is carried out. The formation of **5** in this reaction can be accounted for by both the greater toluene solubility, and therefore reactivity, of the initially formed $[Mg(\mu\text{-}Me)\{\eta^2\text{-}(^iPr_2)ATI\}]_2$ **6**, which we assume also to be a dimer, and the greater basicity of the methyl ligands in this species than those in $MgMe_2$. Thus, following initial formation of **6** in solution, a rapid reaction with a second aminotroponimine molecule ensues and all ligand is therefore consumed by one half of the essentially insoluble $MgMe_2$. Although disproportionation of **6** into **5** and $MgMe_2$ is a possible alternative explanation, we discount this on the grounds that such a process has not been observed for the β-diketiminate complexes **1** and **4** and the ligand exchange involved should be disfavored by the chelate effect. In THF, in which $MgMe_2$ is soluble, the anticipated formation of the THF adducts **1** and **2** take place (Scheme 3).

X-Ray quality crystals of compound **5** were grown from hexane solution at −20 °C and the resulting crystallographic analysis (Fig. 4) shows the magnesium atom to be in a distorted tetrahedral environment dictated by the narrow 79° N–Mg–N angle in the 5-membered chelate rings. However, the bulk of the ^{i}Pr substituents ensures that the two N–Mg–N planes are orthogonal, intersecting at an angle of 92.7°. On comparing the structure of **5** with that of the aluminium complex $[AlMe_2\{(^iPr_2)ATI\}]$,[12] a number of differences are apparent. The heterobicyclic ring system containing the 7-membered ring, the two nitrogen atoms and the metal is planar in the aluminium complex, but in **5** there is significant distortion with the N–Mg–N and N–C–C–N planes intersecting at 15.6 and 3.2° for ligands A and B respectively. Whether this difference is steric or electronic in origin is a moot point, however as the comparison is between $[LAlMe_2]$ and $[L_2Mg]$ complexes a steric origin cannot be ruled out. The N–Mg–N angles in **5** [79.37(4) and 79.02(4)°] are narrower than those observed in $[AlMe_2\{(^iPr_2)ATI\}]$ (83.3°), and the four Mg–N bond lengths [2.0528(11), 2.0461(12), 2.0420(14) and 2.0502(11) Å] are longer than in the $AlMe_2$ complex as would be anticipated for the larger metal. The N–C [range 1.3268(17) to 1.3325(17) Å] and C–C [range 1.367(3) to 1.386(2) Å] bond lengths lie between those for single and double N–C and C–C bonds which shows that there is a degree of π delocalisation as with complexes **1** and **3**. The observation of two doublets for the ^{i}Pr groups at δ 0.89 and 0.90 in the ^{1}H NMR spectrum of **5** indicates the congestion which the crowding of four ^{i}Pr groups around the metal creates in the molecule, and suggests that the inequivalence of the ligands observed crystallographically persists in solution.

Following the observation that THF could be removed from $[MgMe\{HC[C(Me)NAr']_2\}(THF)]$ **1** to provide the methyl bridged dimer **4** by heating under vacuum, we found that the putative dimer $[Mg(\mu\text{-}Me)\{(^iPr_2)ATI\}]_2$ **6** could also be formed as an orange powder by similar treatment of the orange oil $[MgMe\{(^iPr_2)ATI\}(THF)]$ **2** at 110 °C (Scheme 3). The NMR spectra of **6** indicate that all THF has been removed by the thermolysis treatment, and the methyl ligand signal appears at δ −0.61 and −11.2 in the ^{1}H and ^{13}C spectra respectively (*cf.* −0.95 and −14.2 for the monomeric THF complex **2**). On the basis that **4**, which has more sterically demanding nitrogen substituents, exists as a methyl bridged dimer, we assign a similar structure to **6**, although in the absence of a structural characterisation this cannot be conclusively proved. The relatively facile removal of THF from these complexes indicates a surprising level of lability, however this is not inconsistent with the well established Schlenk equilibrium[28] in which co-ordinated ether must be displaced in the formation of alkyl bridged intermediates which facilitate transfer of alkyl groups between magnesium ions to form dialkylmagnesium species in ether solutions, eqn. (1).



Conclusion

It is clear that the ligand steric properties required to provide a three-co-ordinate methylmagnesium species and prevent dimer formation are subtle, as has previously been indicated for aluminium by Jordan and co-workers.[9] Whether such species prove to be active for alkene polymerisation remains to be seen, but they remain our target as potential first generation magnesium based catalysts. Further studies will be directed at modification of the ligand and magnesium co-ordinated alkyl group properties to achieve this aim. Our investigations into the reactivity of compounds **1**, **2**, **4** and **6** with other small molecules are currently underway.

Acknowledgements

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