The First Structural Characterisation of a Group 2 Metal Alkylperoxide Complex: Comments on the Cleavage of Dioxygen by Magnesium Alkyl Complexes

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Abstract: A new high-yield synthesis of $[(PhCH_2)_2Mg(thf)_2]$ and $[\{(PhCH_2)CH_3Mg(thf)\}_2]$ via benzylpotassium has allowed a simple entry into benzylmagnesium coordination chemistry. The syntheses and X-ray crystal structures of both $[(\eta^2\text{-}Me_2NCH_2CH_2NMe_2)Mg(CH_2Ph)_2]$ and $[\eta^2\text{-}HC\{C(CH_3)NAr'\}_2Mg(CH_2Ph)(thf)]$ (Ar′ = 2,6-diisopropylphenyl) are reported. The latter β-diketiminate complex reacts with dioxygen to provide a 1:2 mixture of dimeric benzylperoxo and benzyloxo complexes. The benzylperoxo complex $[\{\eta^2\text{-}HC\{C(CH_3)NAr'\}_2Mg(\mu\text{-}\eta^2\text{:}\eta^1\text{-}OOCH_2Ph)\}_2]$ is the first example of a structurally characterised Group 2 metal–alkylperoxo complex and contains the benzylperoxo ligands in an unusual $\mu\text{-}\eta^2\text{:}\eta^1$-coordination mode, linking the two five-coordinate magnesium centres. The O–O separation in the benzylperoxo ligands is 1.44(2) Å. Reaction of the benzylperoxo/benzyloxo complex mixture with further $[\eta^2\text{-}HC\{C(CH_3)NAr'\}_2Mg(CH_2Ph)(thf)]$ results in complete conversion of the benzylperoxo species into the benzyloxo complex. This reaction, therefore, establishes the cleavage of dioxygen by this system as a two-step process that involves initial oxygen insertion into the Mg–CH_2Ph bond followed by O–O/Mg–C σ-bond metathesis of the resulting benzylperoxo ligand with a second Mg–CH_2Ph bond. The formation of a 1:2 mixture of the benzylperoxo and benzyloxo species indicates that the rate of the insertion is faster than that of the metathesis, and this is shown to be consistent with a radical mechanism for the insertion process.

Keywords: alkylperoxo ligand · magnesium · N ligands · oxygen

Introduction

The dioxygen oxidation of Grignard reagents to provide alcohols is a reaction that was established very soon after Grignard's initial report of his reagents.[1] The reaction was found to be less successful for phenols,[2] an observation attributed to the availability of alternative reaction pathways provided by the differing reactivity of aryl radicals thought to be intermediates.[3] As early as 1920, the mechanism was proposed to proceed through a two-step oxidation followed by metathesis process [Eqs. (1) and (2)] involving the intermediacy of an alkylperoxo species.[4] Both direct and indirect evidence has been provided for the involvement of radical species in the oxidation step,[3, 5, 6] but radicals are apparently not involved in the subsequent metathesis process.[6, 7] At low temperatures, the alkylperoxide intermediates may be intercepted by hydrolysis to provide a useful synthetic route to hydroperoxides in some cases.[8] However, the magnesium alkylperoxy species present in such systems have never been characterised. We report here for the first time the structural characterisation of alkylperoxide and alkoxide magnesium complexes derived by reaction of the corresponding alkyl complex with dioxygen, and provide evidence which strongly supports the mechanism represented by Equations (1) and (2).

$$RMgX + O_2 \rightarrow ROOMgX \quad (1)$$

$$ROOMgX + RMgX \rightarrow 2\,ROMgX \quad (2)$$

Transition-metal alkylperoxide species play an important role in oxidation reactions,[9] and the involvement of η^2-

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. Syntheses, spectroscopic data and molecular structures of $[(TEEDA)Mg(CH_2Ph)_2]$ and $[(PMDETA)Mg(CH_2Ph)_2]$. Carbon-13 NMR spectra of **5/6** and **6** derived by reaction of **5/6** with added **4**.

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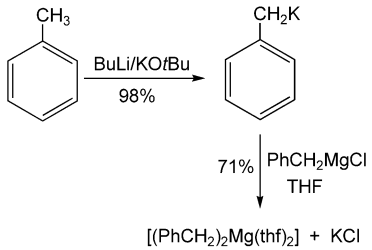
coordination of the ROO moiety is often discussed in this context. However, although numerous examples of η^1-coordination of these species have been structurally authenticated,[10] there are only two examples of η^2-coordination to transition metals thus for established.[11] For main-group metals the literature is similarly sparse, with just a single example of η^2-coordination of tBuOO$^-$ found in a lithium complex.[7] In fact the number of structurally characterised main-group metal alkyl peroxides is very limited, the only other examples displaying μ_2-η^1-coordination in $[(t\mathrm{Bu})_2\mathrm{M}(\mu\text{-}\mathrm{OO}t\mathrm{Bu})]_2$ (M = Ga, In)[12] and η^1-coordination in $[(t\mathrm{BuOO})_2(t\mathrm{BuO})(\mu\text{-}\mathrm{O}t\mathrm{Bu})_2\mathrm{Al}(\mathrm{mesal})_2]$ (mesalH = methylsalicylate).[13] These complexes are synthesised by treatment of the corresponding alkyl complex with dioxygen, and as such represent unusual examples of reactions that may be stopped at the oxygen insertion stage [Eq. (1)] without proceeding to O–O cleavage to form alkoxo species, which is more commonly found.[14] A few other examples of such isolation of alkylperoxo species are also known.[15, 16] There is, however, thus far, no structural data for a Group 2 metal complex, although the magnesium complexes [{η^3-HB(3-tBuPz)$_3$}MgOOR] (R = CH_3, CH_2CH_3, $CH(CH_3)_2$, $C(CH_3)_3$) and their ^{18}O isotopomers have been fully characterised by ^{17}O NMR and IR spectroscopies.[16]

Results and Discussion

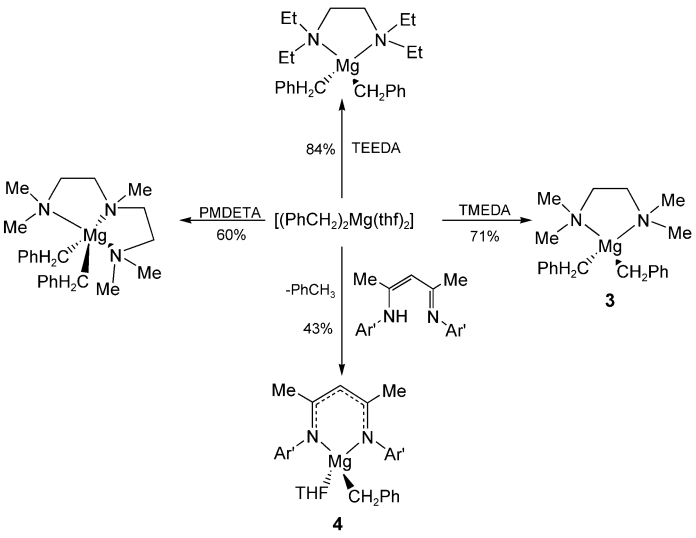
Existing synthetic routes to dibenzylmagnesium are based upon either the classical shifting of the Schlenk equilibrium, induced by complexation and precipitation of $MgCl_2$ by addition of dioxane or other ethers to benzylmagnesium chloride,[17] or transmetallation from dibenzylmercury.[18] The former route suffers from the practical difficulties associated with the removal of the precipitated $[MgCl_2(\mathrm{dioxane})_2]_\infty$, which is exceptionally fine and rapidly blocks any filter, thus necessitating centrifugation for effective separation. The best quoted yield of crude $[Mg(CH_2Ph)_2]$ from this preparation is 29%, from which crystalline $[Mg(CH_2Ph)_2(thf)_2]$ may be obtained in 55% yield by crystallisation from THF.[19] Further problems arise in the general applicability of this method in that, for complete precipitation of $[MgCl_2(\mathrm{dioxane})_2]_\infty$, a 5–10% excess of dioxane is required. This excess complexes with the dialkyl magnesium in solution and is difficult to remove from the solid material. Heating under vacuum to effect this is often complicated by competing alkene elimination and formation of MgH_2 for alkyls with β-hydrogen atoms. Although the transmetallation route provides halide-free magnesium dialkyls and reasonable yields, it involves an additional step in the synthesis of the mercury compound and the associated toxicity hazards. For the preparation of dimethylmagnesium we have previously followed Kaminski's route to avoid these problems.[20] Thus, treatment of MeMgCl with MeLi in THF, followed by solvent removal and extraction from LiCl into diethyl ether and subsequent removal of coordinated THF at 150 °C under vacuum, provides $MgMe_2$ in good yield. To apply this route to the preparation of dibenzylmagnesium, a source of benzyllithium is required. In the absence of additional donors, toluene is only lithiated by nBuLi to the extent of a few percent in THF.[21] Clean lithiation is possible in the presence of TMEDA or DABCO, but the presence of these additional donors limits the usefulness of the resulting complexes for subsequent synthesis.[22] Benzylpotassium may be prepared in almost quantitative yield as an orange microcrystalline precipitate by treatment of toluene with a 1:1 mixture of nBuLi and KOtBu, a so-called "super base".[23] The reaction of a suspension of KCH_2Ph in THF with benzylmagnesium chloride, followed by removal of the THF, extraction from KCl with diethyl ether and crystallisation, provides pure $[(PhCH_2)_2Mg(thf)_2]$ (**1**) in 71% yield (Scheme 1). NMR



Scheme 1. Synthesis of $[(PhCH_2)_2Mg(thf)_2]$.

spectra indicate that attempts at removal of THF by heating to between 50 and 150 °C under vacuum (10^{-2} Torr) resulted in only partial desolvation, and even melting at the higher temperatures proved ineffective. However, since our primary interest is in the preparation of benzylmagnesium complexes with chelating nitrogen donor ligands, the prior displacement of THF is not necessary. We have also prepared the mixed methyl/benzyl derivative from MeMgCl in 76% yield following the same procedure. The NMR spectra of this species in C_6D_6, however, suggest it to be a mono-THF adduct $[Me(CH_2Ph)Mg(thf)]$ for which we suggest a methyl-bridged structure $[\{(thf)(CH_2Ph)Mg(\mu\text{-}Me)\}_2]$ (**2**) in accord with the preference of methyl for bridging coordination. However, in diethyl ether solutions the structure is unlikely to be static.[24]

The reaction of **1** with 1,2-bis(dimethylamino)ethane (TMEDA) in diethyl ether leads to rapid displacement of coordinated THF and formation of $[(tmeda)Mg(CH_2Ph)_2]$ (**3**), which can be precipitated in 71% yield by addition of hexane (Scheme 2). The insolubility of **3** in hydrocarbon solvents required that NMR spectra were obtained in [D_8]THF; however, no displacement of the TMEDA ligand was evident. Crystals of **3** suitable for X-ray crystallography were obtained from a toluene/THF solvent mixture at −20 °C. The molecular structure of **3** is shown in Figure 1 and selected bond lengths and angles are presented in Table 1. The structures of both $[(tmeda)MgPh_2]$[25] and $[(tmeda)MgMe_2]$[26] have previously been determined and a comparison of the structure of **3** with these is instructive. In all three complexes the coordination geometry about the magnesium is distorted from tetrahedral, induced by the narrow bite angle of the TMEDA ligand (83.36(5)° in **3**) and the varying bulk of the carbon ligands. Thus in **3** the C(1A)-Mg-C(1B) angle is 117.12(7)°, whilst the corresponding angles in the diphenyl and dimethyl derivatives are 119.2(1) and 130.0(4)°, respectively. The



Scheme 2. Complexation of $[(PhCH_2)_2Mg(thf)_2]$ by chelating nitrogen donor ligands (Ar′ = 2,6-diisopropylphenyl).

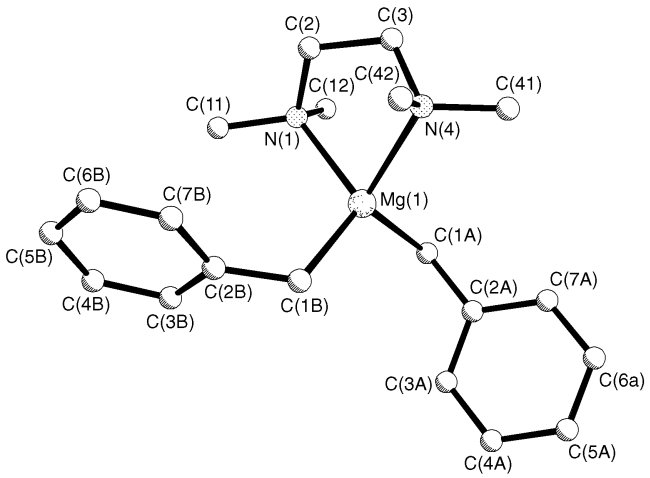


Figure 1. Molecular structure of $[(tmeda)Mg(CH_2Ph)_2]$ (**3**). Hydrogen atoms are omitted for clarity.

N-Mg-N and C-Mg-C planes are, however, almost perpendicular (88.06°). Perhaps somewhat surprisingly, the Mg–C bond lengths do not differ significantly for the three complexes (2.1697(7) Å for **3** and 2.167(3) and 2.166(6) Å for the Ph and Me derivatives respectively). A feature that is evident in the structures of both **3** and the diphenyl derivative is the distortion of the aromatic rings; this is best characterised by the deviation of the *ortho-ipso-ortho* angles from 120° (115.38(15) and 115.82(15)° for **3** vs. 113.9(3) and 114.8(3)° for the diphenyl derivative). There is, however, no evidence for allylic coordination of either of the benzyl ligands in **3**, as although the Mg-C-C angles about the methylene carbon atoms differ significantly (109.76(11) and 113.95(10)°), the Mg–C(*ipso*) (C2A: 3.0037(16) and C2B: 3.0715(15) Å) and Mg–C(*ortho*) (C3A: 3.6971(18), C3B: 3.7964(19), C7A: 3.8387(18) and C7B: 3.8889(18) Å) distances preclude any such interaction. We have also synthesised and structurally characterised complexes of dibenzylmagnesium with the *N*,*N*,*N*′,*N*′-tetraethylethylenediamine $[(teeda)Mg(CH_2Ph)_2]$, and the tridentate *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine ligands $[(pmdeta)Mg(CH_2Ph)_2]$ (Scheme 2), full details of which are provided in the Supporting Information.

The reaction of $[(PhCH_2)_2Mg(thf)_2]$ (**1**) with Ar′N=C(CH$_3$)C(H)=C(CH$_3$)NHAr′ (Ar′ = 2,6-diisopropylphenyl) in THF at 50 °C for one hour provides the β-diketiminate complex $[\eta^2$-HC{C(CH$_3$)NAr′}$_2$Mg(CH$_2$Ph)(thf)] (**4**) in 43 % yield after crystallisation from toluene (Scheme 2). The synthesis of **4** in 31 % yield by initial lithiation of Ar′N=C(CH$_3$)C(H)=C(CH$_3$)NHAr′ followed by treatment with $PhCH_2MgCl$ in THF was also achieved. The ^{1}H and ^{13}C{^{1}H} NMR spectra of **4** in C_6D_6 contain signals for the benzylmethylene group at 1.60 and 24.7 ppm, which compares with values of 1.90/22.8 and 1.33/21.0 ppm for the bis-THF (**1**) and TMEDA (**3**) dibenzyl complexes, respectively. The signals attributable to the β-diketiminate ligand are little changed from those in the corresponding methyl complex.[27] Crystals of **4** as its monotoluene solvate suitable for X-ray crystallography were grown from toluene; the

Table 1. Selected bond lengths [Å] and angles [°] for **3**, **4**, **5** and **6**.

Compound **3**							
Mg(1)–C(1A)	2.1697(17)	Mg(1)–C(1B)	2.1697(17)	Mg(1)–N(1)	2.1929(13)	Mg(1)–N(4)	2.2073(12)
C(1A)–C(2A)	1.470(2)	C(1B)–C(2B)	1.465(2)	Mg(1)–C(2A)	3.0037(16)	Mg(1)–C(2B)	3.0715(15)
C(1A)-Mg(1)-C(1B)	117.12(7)	N(1)-Mg(1)-N(4)	83.36(5)	Mg(1)-C(1A)-C(2A)	109.76(11)	Mg(1)-C(1B)-C(2B)	113.95(10)
C(3A)-C(2A)-C(7A)	115.82(15)	C(3B)-C(2B)-C(7B)	115.38(15)				
Compound **4**							
Mg(1)–C(1B)	2.1325(18)	Mg(1)–O(1T)	2.0333(13)	Mg(1)–N(1)	2.0575(15)	Mg(1)–N(5)	2.0484(15)
C(1B)–C(2B)	1.475(2)	N(1)–C(2)	1.333(2)	C(2)–C(3)	1.408(2)	C(3)–C(4)	1.402(2)
C(4)–N(5)	1.333(2)						
N(1)-Mg(1)-N(5)	93.29(6)	C(1B)-Mg(1)-O(1T)	111.24(7)	Mg(1)-C(1B)-C(2B)	121.02(12)	C(3B)-C(2B)-C(7B)	116.04(17)
Compound **5**							
Mg(1)–O(2)	2.168(12)	Mg(1)–O(3)	2.07(2)	Mg(1)–O(3A)	1.93(2)	O(2)–O(3)	1.44(2)
Mg(1)–N(1)	2.081(4)	Mg(1)–N(2)	2.012(4)	N(1)–C(2)	1.327(6)	C(2)–C(3)	1.405(7)
C(3)–C(4)	1.399(6)	C(4)–N(2)	1.339(6)	O(2)–C(30A)	1.51(3)		
N(1)-Mg(1)-N(2)	92.2(2)	O(2)-Mg(1)-O(3)	39.7(5)	O(3)-Mg(1)-O(3A)	81.5(8)	Mg(1)-O(3)-Mg(1A)	98.5(8)
Compound **6**							
Mg(1)–O(1)	1.998(6)	Mg(1)–O(1A)	2.033(7)	Mg(1)–N(1)	2.081(4)	Mg(1)–N(2)	2.012(4)
N(1)–C(2)	1.327(6)	C(2)–C(3)	1.405(7)	C(3)–C(4)	1.399(6)	C(4)–N(2)	1.339(6)
O(1)–C(30)	1.398(10)						
N(1)-Mg(1)-N(2)	92.2(2)	O(1)-Mg(1)-O(1A)	82.4(3)	Mg(1)-O(1)-Mg(1A)	97.6(3)		

molecular structure is shown in Figure 2 and selected bond lengths and angles are presented in Table 1. The coordination geometry about the Mg centre is distorted tetrahedral with

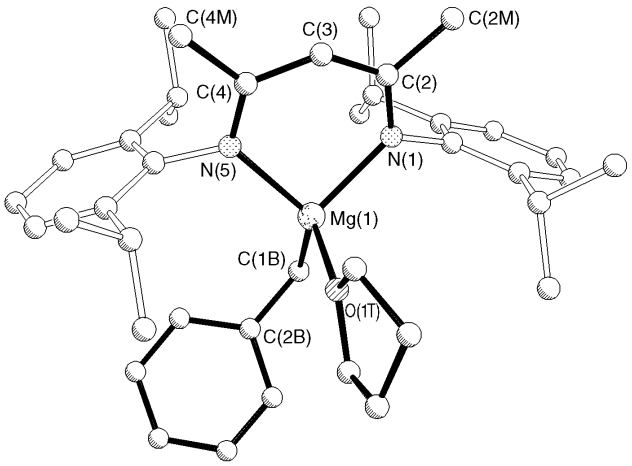


Figure 2. Molecular structure of $[\eta^2\text{-HC}\{C(CH_3)NAr'\}_2Mg(CH_2Ph)(thf)]$ (**4**) showing selected atom labels. Hydrogen atoms and toluene solvate molecule omitted for clarity.

the N-Mg-N chelate and C-Mg-O angles being 93.29 and 111.24°, respectively; these planes are almost perpendicular (88.92°). The six-membered chelate ring is non-planar and its conformation is best described as a distorted boat in which the magnesium and central carbon C(3) atoms lie 0.5 and 0.11 Å above the least-squares plane, respectively. The planes of the two 2,6-diisopropylphenyl rings are almost perpendicular to that of the chelate ring and, thus, shield the magnesium centre. A comparison of the angles around the magnesium centres in **4** and its methyl analogue[27] reveal differences consistent with the greater bulk of the benzyl ligand.

We have previously shown that $[(\eta^2\text{-L-X})MgMe(thf)]$ (L-X = $HC\{C(CH_3)NAr'\}_2$, or (*N*,*N*′-diisopropylamino)troponiminate) reacts with dioxygen to provide the dimeric μ-methoxide complexes $[\{(\eta^2\text{-L-X})Mg(\mu\text{-}OCH_3)\}_2]$ via an "intermediate" species that we tentatively identified as a methylperoxo complex from the NMR spectra of the reaction mixtures, but we were never able to isolate.[27] The reaction of the corresponding benzyl complex **4** with dioxygen was therefore examined in order to establish a similar reactivity for this system. Treatment of a solution of **4** in $[D_6]$benzene with an excess of dry oxygen gas provided a solution whose $^{13}C\{^1H\}$ NMR spectrum indicated the presence of a mixture of two species characterised by benzylmethylene signals at 67.1 and 53.2 ppm in an approximate ratio of 1:2.[28] The appearance of the methylene signals in this region indicate oxygen-bound benzyl groups in both species and should be compared with chemical shifts of 24.7 ppm for the Mg-bound benzyl CH_2 in **4** and 50.4 ppm for the OMe ligands in $[\{\{\eta^2\text{-(N,N′-diisopropylamino)troponiminate}\}Mg(\mu\text{-OMe})\}_2]$.[27] However, no further information about the identity of the two species could be deduced from the NMR spectra. Cooling of a similarly prepared hexane solution to 5 °C provided crystals which X-ray crystallography showed to contain a 1:2 mixture of dimeric benzylperoxo and benzyloxo complexes $[HC\{C(CH_3)NAr'\}_2Mg(\mu\text{-}\eta^2\text{:}\eta^1\text{-}OOCH_2Ph)]_2$ (**5**) and $[\{HC\{C(CH_3)NAr'\}_2Mg(\mu\text{-}OCH_2Ph)\}_2]$ (**6**). The respective occupancies of 1:2, as determined by X-ray crystallography, is consistent with the observation of two products in a 1:2 ratio in the $^{13}C\{^1H\}$NMR spectrum.[28] The molecular structures of **5** and **6** are shown in Figures 3 and 4, respectively, and selected bond lengths and angles are presented in Table 1. Unfortunately, the disorder present in the structure resulted in weak and poor quality diffraction data and the final *R* factor of

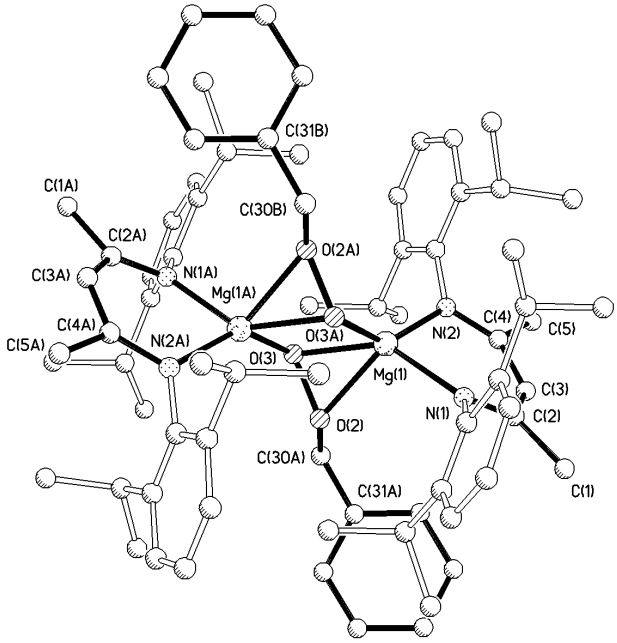


Figure 3. Molecular structure of $[\{\eta^2\text{-HC}\{C(CH_3)NAr'\}_2Mg(\mu\text{-}\eta^2\text{:}\eta^1\text{-}OOCH_2Ph)\}_2]$ (**5**) showing selected atom labels. Hydrogen atoms are omitted for clarity.

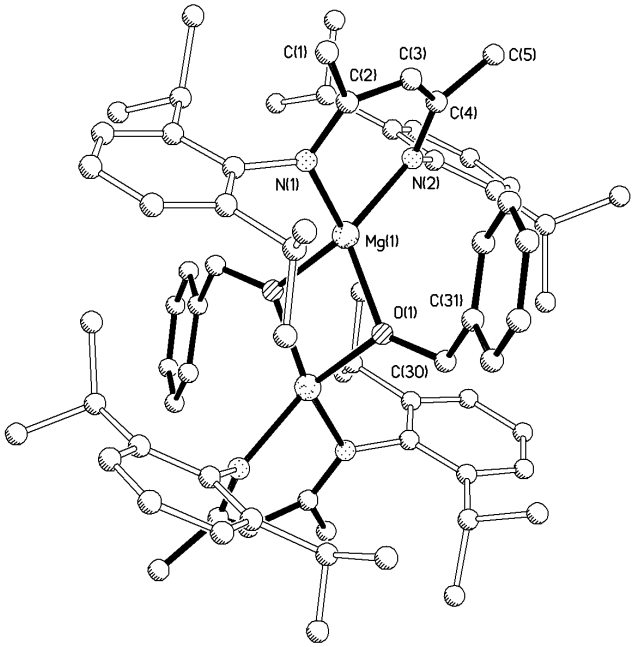


Figure 4. Molecular structure of $[\{\eta^2\text{-HC}\{C(CH_3)NAr'\}_2Mg_2(\mu\text{-}OCH_2Ph)\}_2]$ (**6**) showing selected atom labels. Hydrogen atoms are omitted for clarity. The structure of **6a** is essentially identical.

9.33% is undesirably high. However, structural and NMR characterisation of the benzyloxo complex [{HC{C-(CH$_3$)NAr′}$_2$Mg(μ-OCH$_2$Ph)}$_2$] (**6a**), prepared independently by treatment of the methyl complex [{HC{C-(CH$_3$)NAr′}$_2$MgMe}$_2$] with benzyl alcohol, confirms the structural data obtained for this species as its co-crystal with **5**.[29] Since the modelling of disorder in crystal structure analysis can be rather subjective, we performed a difference Fourier synthesis against the diffraction data derived from the disordered co-crystal **5**/**6** using the structure determined from the undisordered pure **6a** as a phasing model. The resulting map and the structure derived from it (Figure 5) can

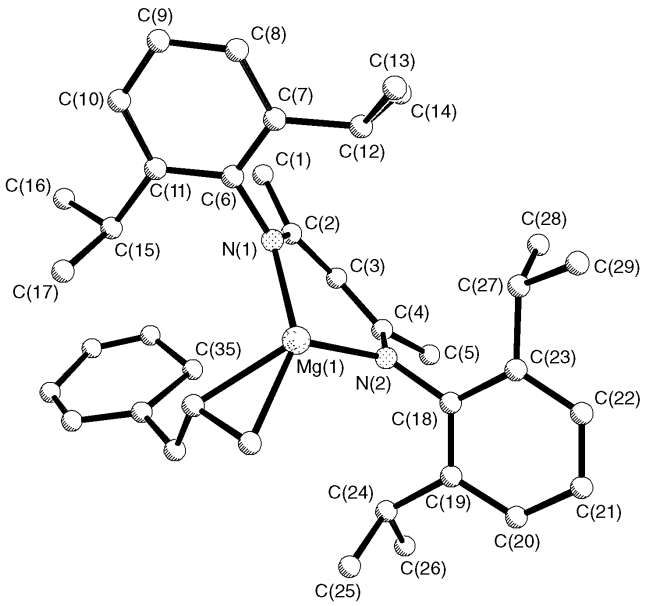


Figure 5. Illustration of the benzylperoxo fragment revealed from the difference map by refinement of the asymmetric unit of **6a** against the diffraction data of **5**/**6**. Atoms from the alkoxide fragment, except for the shared C(35) atom, are omitted for clarity.

unambiguously be assigned to be a benzylperoxo species in which one carbon atom (C(35)) is shared between the two part-weight ligands. This, taken together with the NMR data for this system discussed above and the observations made on its reactivity to be discussed below, confirms the identities of **5** and **6** as those deduced from the original X-ray data of the disordered co-crystal **5**/**6**.

The co-crystallisation of **5** and **6** is fortuitous, but inspection of the structures reveals that the steric bulk of the β-diketiminate ligand effectively encapsulates the central regions of the dimeric species in which the benzyl groups are located, and the exterior of both complexes are consequently sufficiently similar to allow their co-crystallisation. This is exemplified by the fact that the structure of **6a** can be superimposed on **6** from the disordered model with a root mean square deviation of less than 0.2 Å. However, it is pertinent to note that the **5**/**6** system is not isostructural with the pure sample of **6a**. Consequently, in **5**/**6** the benzylperoxo and benzyloxo dimers are randomly disordered over the same equivalent sites in the crystalline state, with the β-diketiminate ligands and magnesium centres sharing common positions.

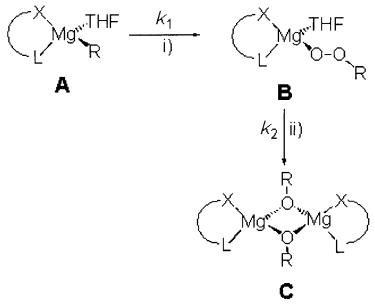
The benzylperoxo ligands in **5** link the centrosymmetric dimer and are coordinated to one Mg atom through the oxygen remote from the benzyl group (O(3)) and to the second Mg atom through both oxygen atoms (μ-η^2:η^1-), thus maximising the number of Mg–O bonds. The coordination sphere of each magnesium atom is completed by a *β*-diketiminate ligand, which results in each magnesium atom attaining a coordination number of five. The O(2)–O(3) separation of 1.44(2) Å is consistent with values of 1.475(3) and 1.477(3) Å found in [{LiOO*t*Bu}$_{12}$], in which the *tert*-butylperoxo ligands are found in a similar μ-η^2:η^1-coordination mode.[7] The poor quality of the diffraction data preclude a detailed discussion of the metrical parameters, but the coordination of the magnesium atom by the diketiminate ligand appears to be somewhat asymmetric with Mg–N bond lengths of 2.012(4) and 2.081(4) Å, a feature which may be attributed to the unsymmetrical coordination mode of the benzylperoxo ligands and the steric crowding induced by dimerisation. The angles around magnesium are dictated by the narrow chelate bite angle N(1)-Mg(1)-N(2) of 92.2(2)°, and the narrow O(2)-Mg(1)-O(3) bond angle of 39.7(5)°. In the structure of the dimeric benzyloxo complex **6** the centrosymmetric dimer is formed by two bridging μ-benzyloxo ligands. The importance of the narrow chelate bite angle (92.2(2)°) is apparent by the resulting compression of the O(1)-Mg(1)-O(1A) angle (82.4(3)°) and the consequent widening of the Mg(1)-O(1)-Mg(1A) angle (97.6(3)°).

Both IR and Raman spectra of the co-crystal **5**/**6** and pure **6a** were recorded in an attempt to identify an absorption associated with stretching vibration of the O–O bond. Unfortunately, a number of absorptions due to vibrations of the β-diketiminate ligand are present in the 800 – 1000 cm^{-1} region of the spectra where such an absorption would be anticipated to occur, and no band could conclusively be identified as being due to O–O vibration. No ^{18}O labelling studies were attempted.

The benzylperoxo complex **5** represents the first structurally characterised example of a Group 2 metal alkylperoxo species. Furthermore, the μ-η^2:η^1-coordination mode of the benzylperoxo ligand in **5** is highly unusual and has only previously been reported in the structure of [{LiOO*t*Bu}$_{12}$].[7] A large number of examples of transition-metal and main-group complexes containing alkylperoxo ligands in η^1-,[10, 13] η^2-,[11] μ-η^1-[12, 30] and μ-η^2-coordination[7] modes have, however, been structurally characterised. For the peroxo ligand [O$_2$]$^{2-}$, the μ-η^2:η^1-coordination mode is relatively common, having been characterised in complexes of W,[31] Mo,[32] V[33] and Rh,[34] for example. A μ-η^2:η^2-coordination mode has also been characterised for the peroxo ligand in three copper(II) complexes synthesised as models for the Cu$_2$(μ-η^2:η^2-O$_2$) centres in oxyhemocyanin and oxytyrosinase.[35] Barium[36] and magnesium[37] peroxo species have also been structurally characterised.

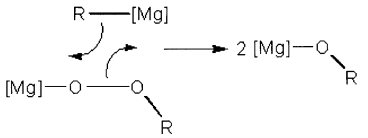
The observed formation of a 1:2 mixture of the benzylperoxo and benzyloxo complexes **5** and **6** from the reaction of the benzyl complex **4** with dioxygen provides mechanistic information about the O–O bond cleavage process. For the methyl

species [η^2-HC{C(CH_3)NAr′}$_2$MgMe(thf)] and [{η^2-(*N*,*N*′-diisopropylamino)troponiminate}MgMe(thf)] we have shown that reaction with oxygen provides methoxy complexes.[27] Our proposed mechanism for this process (Scheme 3) involves initial insertion of O_2 into the Mg–R bond of the



Scheme 3. Mechanism of O=O cleavage by magnesium alkyl complexes [(η^2-L-X)MgR]. i) O_2, benzene, 20 °C; ii) [(η^2-L-X)MgR], benzene, 20 °C.

starting complex **A** to provide the alkylperoxo species **B**; subsequent reaction of this with a further mole of **A** provides the alkoxo species **C** with cleavage of the O–O bond by means of a σ-bond metathesis and a 4-centre transition state (Scheme 4). For such a process to proceed to complete



Scheme 4. Cleavage of the O–O bond in magnesium alkylperoxo complexes [Mg]OOR by σ-bond metathesis with the Mg–C bond of [Mg]R, [Mg] = (η^2-L-X)Mg.

conversion to the alkoxo species, the rate of the O–O cleavage process (k_2) must equal or exceed that of the O_2 insertion process (k_1). This condition is clearly satisfied in the reaction of the methyl species discussed above as, although a species assigned to be an OOMe complex could be observed in the reaction of [{η^2-(*N*,*N*′-diisopropylamino)troponiminate}MgMe(thf)] with O_2 by NMR spectroscopy, this was completely consumed as the reaction proceeded to completion with formation of the methoxy product.[27] The corresponding reaction of [HC{C(CH_3)NAr′}$_2$MgMe(thf)] with O_2 proceeded more rapidly and, although NMR spectra could provide no evidence for a methylperoxo intermediate, a similar replacement of the Mg–Me signal by one attributable to a magnesium-bound methoxo ligand was observed.

The mechanism of O_2 insertion into the Mg–C bond [Eq. (1)], which represents the first step in the generally accepted insertion/metathesis mechanism for the oxidation of Grignard reagents to alcohols as discussed above, has been a matter of some debate. It may be argued that direct insertion of the triplet ground state of dioxygen into metal–carbon bonds is unlikely, and there is much evidence to suggest that the reaction proceeds via radical intermediates.[3, 5, 6, 7] In particular, the observation of the loss of stereochemistry in configurationally stable cyclopropyl compounds during the reaction of their Grignard reagents with O_2 to provide the corresponding alcohols is convincing evidence for the intermediacy of radical species, especially when contrasted with the retention of stereochemistry during the oxidation of the same Grignards with *t*BuOOLi.[5f] Radical chain mechanisms according to Equations (3)–(5) have therefore been suggested for the insertion process, and this may be followed by O–O cleavage by means of σ-bond metathesis in the presence of an excess of the alkyl complex [Eq. (6)].

$$L_nM\text{-}R + O_2 \rightarrow L_nM\text{-}OO^{\bullet} + R^{\bullet} \text{ (initiation)} \quad (3)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \quad (4)$$

$$L_nM\text{-}R + ROO^{\bullet} \rightarrow L_nM\text{-}OOR + R^{\bullet} \text{ (propagation)} \quad (5)$$

$$L_nM\text{-}OOR + L_nM\text{-}R \rightarrow 2\,L_nM\text{-}OR \quad (6)$$

Although we cannot be certain that such a mechanism is operating in the present case, it is consistent with certain of our observations. According to this mechanism, for a given metal–ligand fragment L_nM, the rate of formation of the alkylperoxide species L_nM-OOR (k_1 in Scheme 3) must be dependent upon the stability of the alkyl radical R•. A more stable radical will result in a more rapid initiation [Eq. (3)] and a faster liberation of R• in the propagation step [Eq. (5)]. The relative stability of methyl and benzyl radicals would therefore suggest that the rate of the O_2 insertion process (k_1 in Scheme 3) would be considerably faster for the benzyl complex. The observed progress of the reaction to yield exclusively the alkoxide when R = CH_3, but a mixture of alkylperoxide and alkoxide when R = benzyl, therefore, supports the radical mechanism illustrated by Scheme 1 and Equations (3)–(6). This is also consistent with the observation that, for the complexes [{η^3-HB(3-*t*BuPz)$_3$}MgR], the reaction with dioxygen could be monitored over a period of days at room temperature when R = CH_3, while the corresponding reactions in which R = CH_2CH_3, $CH(CH_3)_2$, and $C(CH_3)_3$ were too fast to be similarly monitored,[16] again illustrating a direct relationship between the rate of O_2 insertion and radical stability consistent with the proposed radical mechanism. The effect of the increased steric bulk of the benzyl ligand on the rate of the O–O cleavage process [Eq. (6), k_2 in Scheme 3] cannot, however, be ruled out as a contributory factor in reducing the value of k_2 below that of k_1. A similar steric hindrance argument was used to account for the slow O–O cleavage reaction of [{η^3-HB(3-*t*BuPz)$_3$}-MgOOCH(CH_3)$_2$] on reaction with the corresponding alkyl complex [{η^3-HB(3-*t*BuPz)$_3$}MgCH(CH_3)$_2$].[16]

Final confirmation of the two-step mechanism (Scheme 3) is provided by NMR monitoring of the addition of the benzyl complex **4** to the 1:2 mixture of **5** and **6** obtained by reaction of **4** with O_2 in [D_6]benzene. This shows complete consumption of the benzylperoxo complex **5** and its clean conversion to **6**; this is also further corroborated by comparison with the NMR spectra of pure **6a**.[28]

Conclusion

In summary, we have synthesised and characterised a series of new benzylmagnesium complexes based upon a new high

yielding synthesis of $[(PhCH_2)_2Mg(thf)_2]$. The reaction of the β-diketiminate complex $[\eta^2\text{-}HC\{C(CH_3)NAr'\}_2MgCH_2Ph\text{-}(thf)]$ with O_2 provides a 1:2 mixture of dimeric benzylperoxo and benzyloxo complexes **5** and **6**, consistent with a mechanism involving initial O_2 insertion into the Mg–C bond followed by O–O cleavage by means of σ-bond metathesis of the resulting benzylperoxo O–O bond with a further Mg–C bond. This reactivity contrasts with that previously established for the corresponding methyl complex, which is converted into the methoxy species only. The conclusion, therefore, is that for the methyl species $k_1 \leq k_2$, while for the benzyl complex $k_1 > k_2$ (Scheme 3). Given the large difference that must exist between the two reaction steps in terms of the steric congestion of their transition states and the strong affinity of magnesium for oxygen donor ligands, it is surprising that the rate of the reaction of Mg–R with O_2 is comparable with the subsequent O–O cleavage reaction in these systems, and indeed apparently slower for the methyl species. However, this apparent anomaly may be accounted for by proposing a radical mechanism for the initial O_2 insertion step [Eqs. (3)–(5)] and is consistent with the low stability of the methyl radical and the consequent slow rate of the O_2 insertion process in comparison to that involving the more stable benzyl radical.

Experimental Section

General procedures: The 2-(2,6-diisopropylphenylamino)-4-(2.6-diisopropylphenylimino)2-pentene,[38] Ar′N=C(CH$_3$)C(H)=C(CH$_3$)NHAr′ and benzylmagnesium chloride in THF[39] were prepared according to the literature methods. Methylmagnesium chloride (3 M solution in THF), *n*butyl lithium (2.5 M solution in hexanes), benzylalcohol (pre-dried) and potassium *tert*-butoxide were purchased from Aldrich and used as received unless stated otherwise. Deuterated NMR solvents and 1,2-bis(dimethylamino)ethane (TMEDA) were purchased from Aldrich and dried over activated 4 Å sieves. All reactions and manipulations were undertaken under an atmosphere of purified nitrogen in standard Schlenk apparatus or inside a Saffron Scientific glovebox unless otherwise stated. Diethyl ether and hydrocarbon solvents were distilled from sodium benzophenone ketyl radical under an atmosphere of nitrogen immediately prior to use. Dioxygen was purchased from BOC Gases and passed over a column of activated 4 Å sieves prior to use. All NMR spectra were recorded on a Bruker AC250 spectrometer.

$[(PhCH_2)_2Mg(thf)_2]$ (1): *n*BuLi (20 cm^3, 2.5 M in hexanes, 50 mmol) was added by syringe to a stirred suspension of KO*t*Bu (5.6 g, 50 mmol) in toluene (100 cm^3) at 0 °C. The mixture was warmed to room temperature and allowed to stir for an additional 30 min. The orange/red suspension was filtered, and the resulting solid was washed twice with toluene (50 cm^3) and once with hexane (20 cm^3). The volatiles were removed under vacuum to provide benzylpotassium as a free flowing orange solid (6.4 g, 49 mmol, 98 %). $PhCH_2MgCl$ in THF (0.71 M, 49 mmol) was added to a stirred suspension of $PhCH_2K$ (6.4 g, 49 mmol) in THF (30 cm^3) at −78 °C. The mixture was allowed to warm to room temperature and stirred over night. The volatiles were removed under vacuum and the product extracted from KCl into diethyl ether (100 cm^3). Diethyl ether was removed from the resulting solution under vacuum until precipitation began; at this point hexane (15 cm^3) was added and resulted in the deposition of microcrystalline $[(PhCH_2)_2Mg(thf)_2]$. The product was isolated by filtration, washed with hexane (15 cm^3) and dried under vacuum to yield **1** as a light yellow solid (12.2 g, 34.8 mmol, 71 %). ^{1}H NMR [D$_6$]benzene: $\delta =$ 1.28 (t, ^3J(H,H) = 6.45 Hz, 8H; THF), 1.9 (s, 4H; -CH_2), 3.34 (t, ^3J(H,H) = 6.30 Hz, 8H; THF), 6.83 (t, ^3J(H,H) = 7.03 Hz, 2H; *p*-C$_6H_5$), 7.18 (d, ^3J(H,H) = 7.10 Hz, 4H; *o*-C$_6H_5$), 7.25 ppm (t, ^3J(H,H) = 7.56 Hz, 4H; *m*-C$_6H_5$); ^{13}C{^{1}H} NMR [D$_6$]benzene: δ = 22.8 (-CH_2Ph), 25.8 (THF), 67.7 (THF), 115.4 (Ph), 123.2 (Ph), 127.7 (Ph), 157.2 ppm (*ipso*-Ph). Despite repeated attempts, and the lack of any impurities in the NMR spectra, it was not possible to obtain reliable microanalysis; we attribute this to the air- and moisture-sensitive nature of **1**.

$[\{(thf)(CH_2Ph)Mg(\mu\text{-}Me)\}_2]$ (2): This complex was prepared in a manner similar to the procedure outline for the preparation of **1** from $PhCH_2K$ (2.5 g, 19.2 mmol) and MeMgCl (6.4 cm^3, 3.0 M in THF, 19.2 mmol) to yield 3.0 g of **2** (76 %) as a light yellow powder. ^{1}H NMR [D$_6$]benzene: $\delta = -0.76$ (s, 3H; CH_3), 1.22 (t, ^3J(H,H) = 6.46 Hz, 4H; THF), 1.88 (s, 2H; -CH_2), 3.34 (t, ^3J(H,H) = 6.30 Hz, 4H; THF), 6.79 (t, ^3J(H,H) = 4.20 Hz, 1H; *p*-C$_6H_5$), 7.21 ppm (m, 4H; *o*-C$_6H_5$, *m*-C$_6H_5$; ^{13}C{^{1}H} NMR (C$_6$D$_6$): $\delta = -14.9$ (CH_3), 23.3 (-CH_2Ph), 25.3 (THF), 69.5 (THF), 116.9 (Ph), 124.1 (Ph), 128.6 (Ph), 156.4 ppm (*ipso*-Ph). Despite repeated attempts, and the lack of any impurities in the NMR spectra, it was not possible to obtain reliable microanalysis; we attribute this to the air- and moisture-sensitive nature of **2**.

$[(tmeda)Mg(CH_2Ph)_2]$ (3): TMEDA (0.30 cm^3, 2 mmol) was added by syringe to a stirred solution of $[(PhCH_2)_2Mg(thf)_2]$ (**1**) (700 mg, 2 mmol) in diethyl ether (20 cm^3) at room temperature. The mixture was allowed to stir over night and diethyl ether was then removed in vacuum until precipitation began, at which point hexane (5 cm^3) was added to complete precipitation. The resulting product was isolated as a white powder by filtration followed by washing with hexane (20 cm^3) and drying under vacuum (460 mg, 1.43 mmol, 71 %). ^{1}H NMR [D$_6$]benzene: δ = 1.33 (s, 4H; -CH_2), 2.15 (s, 12H; CH_3), 2.33 (s, 4H; $^-$CH_2CH_2-), 6.30 (t, ^3J(H,H) = 7.09 Hz, 2H; *p*-C$_6H_5$), 6.67 (d, ^3J(H,H) = 7.86 Hz, 4H; *o*-C$_6H_5$), 6.75 ppm (t, ^3J(H,H) = 7.60 Hz, 4H; *m*-C$_6H_5$); ^{13}C{^{1}H} NMR [D$_6$]benzene: δ = 21.0 (-CH_2Ph), 43.9 (-CH_3), 56.0(-CH_2CH_2-), 113.6 (Ph), 121.6 (Ph), 125.9 (Ph), 155.2 ppm (*ipso*-Ph). Despite repeated attempts, and the lack of any impurities in the NMR spectra, it was not possible to obtain reliable microanalysis; we attribute this to the air- and moisture-sensitive nature of **3**.

$[HC\{C(CH_3)NAr'\}_2Mg(CH_2Ph)(thf)]$ (Ar′ = 2,6-diisopropylphenyl) (4)

Method 1: $[(PhCH_2)_2Mg(thf)_2]$ (**1**) (1.05 g, 3.0 mmol) was added to Ar′N=C(CH$_3$)C(H)=C(CH$_3$)NHAr′ (1.26 g, 3.0 mmol) in THF (20 cm^3); the mixture warmed to 50 °C for 1 hour and then allowed to stir at room temperature over night. The volatiles were removed under vacuum and the resulting solid dissolved in toluene (20 cm^3). Storage of at −20 °C over night provided **4**·toluene as a colorless microcrystalline solid (0.90 g, 1.30 mmol, 43 %). Crystals suitable for X-ray crystallography were obtained by storage of a solution of 1.0 g of this solid in 10 cm^3 toluene at 7 °C over night.

Method 2: *n*BuLi (1.20 cm^3, 2.5 M in hexanes, 3.0 mmol) was added to a solution of Ar′N=C(CH$_3$)C(H)=C(CH$_3$)NHAr′ (1.26 g, 3.0 mmol) in THF (20 cm^3) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 1 hour. At room temperature $PhCH_2MgCl$ in THF (6.25 cm^3, 0.48 M, 3.0 mmol) was added to this solution and the mixture allowed to stir over night. The volatiles were removed under vacuum and the product extracted from LiCl into toluene (20 cm^3). From this solution microcrystalline **4**·toluene could be obtained (0.55 g) by cooling to −20 °C over night. A further 0.10 g of **4**·toluene could be obtained from the mother liquor by reducing the volume and recooling to −20 °C. Overall yield 0.65 g (31 %). ^{1}H NMR [D$_6$]benzene: δ = 1.34 (d, ^3J(H,H) = 6.86 Hz, 24H; CH(CH_3)$_2$), 1.6 (s, 4H; THF), 1.77 (s, 6H; CH_3), 2.24 (s, 3H; PhCH_3), 3.1–3.48 (m, 4H; CH(CH$_3$)$_2$), 3.66 (t, ^3J(H,H) = 6.72 Hz, 4H; THF), 4.90 (s, 1H; CH), 6.54 (d, ^3J(H,H) = 7.02 Hz, 2H; *o*-C$_6H_5$), 6.72 (t, ^3J(H,H) = 7.46 Hz, 1H; *p*-C$_6H_5$), 7.01 (t, ^3J(H,H) = 7.65 Hz, 2H; *m*-C$_6H_5$), 7.15–7.33 (m, 6H; -C$_6H_3$*i*Pr$_2$), 7.34 ppm (s, 5H; C$_6H_5$CH$_3$); ^{13}C{^{1}H} NMR [D$_6$]benzene: δ = 20.3 (THF), 24.3 (-CH_3), 24.7 (-CH_2Ph), 25.2, 25.6 (-CH_3), 28.4 (-CH(CH$_3$)$_2$), 70.1 (THF), 94.8 (-Cα), 117.0, 124.2, 124.7, 125.6, 128.3, 142.6, 145.9, 156.1 (Ar-CH), 168.6 ppm (-Cα); elemental analysis calcd (%) for $C_{40}H_{56}N_2OMg$: C 79.38, H 9.33, N 4.63; found: C 79.50, H 9.23, N 4.53.

$[\{HC\{C(CH_3)NAr'\}_2Mg(OOCH_2Ph)\}_2]$ (5) and $[\{HC\{C(CH_3)NAr'\}_2\text{-}Mg(OCH_2Ph)\}_2]$ (6) (Ar′ = 2,6-diisopropylphenyl): A solution of $[HC\{C(CH_3)NAr'\}_2Mg(CH_2Ph)(thf)]$ (Ar′ = 2,6-diisopropylphenyl) (**4**) (1.55 g, 2.22 mmol), prepared by Method 1, in toluene (30 cm^3) was bubbled with pre-dried oxygen for 1 minute (an excess of O_2) to afford an off-white precipitate. The precipitate was dissolved with gentle warming and the volatiles removed under vacuum. The resulting orange oil was extracted into *n*-hexane (10 cm^3). Concentration and storage at 5 °C for

3 days afforded colourless crystals of co-crystallised **5** and **6** in a 1:2 ratio as determined by X-ray crystallography (0.51 g, 0.46 mmol, 45%). ^{1}H NMR [D$_6$]benzene: $\delta =$ 1.32 (d, ^3J(H,H) = 6.85 Hz, 144H; CH(CH_3)$_2$), 1.79 (s, 36H; CH_3), 2.25 (s, 8H; O-CH_2Ph), 3.1–3.48 (m, 24H; CH(CH$_3$)$_2$), 3.49 (s, 4H; O$_2$-CH_2Ph), 4.75 (s, 6H; CH), 7.12–7.56 (m, 66H; Ar-CH); ^{13}C{^{1}H} NMR [D$_6$]benzene: δ = 20.7, 21.0 (-CH_3), 23.1, 23.6, 23.9, 24.7 (-CH_3), 28.5, 28.8 (-CH(CH$_3$)$_2$), 53.2 (O-CH_2Ph), 67.1 (O$_2$-CH_2Ph), 94.5, 97.8 (-Cα), 123.5, 123.8, 124.2, 124.3, 125.8, 126.1, 128.7, 129.5, 136.6, 136.8, 141.4, 142.9, 147.0, 147.6, 161.7, 164.5 (Ar-CH), 167.7, 170.2 (-Cα); elemental analysis calcd (%) for $C_{72}H_{96}N_4O_{2.63}Mg_2$ (**5/6**): C 78.03, H 8.73, N 5.06; found: C 78.23, H 8.79, N 5.07.

Reaction of [{HC{C(CH$_3$)NAr′}Mg(OOCH$_2$Ph)}$_2$] (5) and [{HC{C(CH$_3$)NAr′}Mg(OCH$_2$Ph)}$_2$] (6) with [HC{C(CH$_3$)NAr′}$_2$Mg-(CH$_2$Ph)(thf)] (4) (Ar′ = 2,6-diisopropylphenyl): Compound **4** (0.02 g, 0.03 mmol) in deuteriated benzene (0.2 cm^3) was added to a solution of (**5**) and (**6**) (0.11 g, 0.1 mmol) in deuteriated benzene (0.4 cm^3), prepared as above and contained in a 5 mm NMR tube. Monitoring of the mixture by ^{13}C NMR showed rapid consumption of **4** and **5** and formation of a clean solution of **6**.[28]

Independent synthesis of [{HC{C(CH$_3$)NAr′}$_2$Mg(OCH$_2$Ph)}$_2$] (6a) (Ar′ = 2,6-diisopropylphenyl): Benzylalcohol (0.45 cm^3, 4.34 mmol) was added by syringe to a slurry of [{HC{C(CH$_3$)NAr′}MgMe}$_2$] (1.98 g, 2.17 mmol)[27] in toluene (20 cm^3) affording rapid evolution of methane and yielding a yellow solution. Concentration and standing at room temperature overnight yielded colorless crystals of **6a** suitable for an X-ray crystallographic study (1.25 g, 1.32 mmol, 61%). ^{1}H NMR [D$_6$]benzene: $\delta =$ 1.32 (d, ^3J(H,H) = 6.88 Hz, 48H; CH(CH_3)$_2$), 1.78 (s, 12H; CH_3), 2.26 (s, 4H; O-CH_2Ph), 3.1–3.47 (m, 8H; CH(CH$_3$)$_2$), 4.74 (s, 2H; CH), 7.06 (d, ^3J(H,H) = 7.03 Hz, 4H; o-C$_6H_5$), 7.24 (t, ^3J(H,H) = 7.41 Hz, 2H; p-C$_6H_5$), 7.29 (t, 4H; p-C$_6H_3iPr_2$), 7.43 (t, ^3J(H,H) = 7.65 Hz, 4H; m-C$_6H_5$), 7.54 ppm (d, 8H; m-C$_6H_3iPr_2$); ^{13}C{^{1}H} NMR [D$_6$]benzene: δ = 20.9 (-CH_3), 23.6, 24.6 (-CH_3), 28.8 (-CH(CH$_3$)$_2$), 53.2 (O$_2$-CH_2Ph), 94.6 (-Cα), 123.7, 124.2, 125.8, 128.7, 136.6, 141.5, 146.9, 161.7 (Ar-CH), 167.7 ppm (-Cα); elemental analysis calcd (%) for $C_{72}H_{96}N_4O_2Mg_2$: C 78.75, H 8.81, N 5.10; found: C 78.86, H 8.81, N 5.05.

X-ray crystallography: Crystal samples were mounted using frozen oil drop techniques. Selected geometric parameters are given in Table 1, and crystal data and refinement parameters are listed in Table 2. All data sets were collected at 150 K using graphite-monochromated Mo$_{K\alpha}$ radiation ($\lambda =$ 0.71073 Å) on a Bruker AXS SMART APEX CCD area detector diffractometer equipped with an low-temperature device. Data were corrected semi-empirically for absorption. The structures were solved by direct methods (SHELX 97),[40] and refined by least-squares against F^2 with anisotropic non-hydrogen atoms using SHELX 97.[40] Hydrogen atoms were placed in geometrically calculated positions and refined isotropically. There were no significant features in the final difference maps.

In the co-crystal **5/6** the benzylperoxo and benzyloxo dimers are disordered over the same site in the ratio 31:69 (this ratio was refined as part of the model), sharing common positions for the diketiminate ligand and magnesium centre. All full weight atoms were refined with anisotropic displacement parameters. Similarity restraints for bond lengths and angles were required for the benzylperoxo component and it was necessary to refine some atoms isotropically. One *i*Pr group was orientationally disordered over two sites in the ratio 77:23; similarity restraints were again applied for the minor component.

Our interpretation of structure **5/6** in terms of a mixed alkylperoxo/alkoxide system was dependent upon the modelling of the disordered region in the crystal structure. In order to support our interpretation of the disorder, the structure of the pure alkoxide complex was taken from structure **6a**, and its orientation and position refined as a rigid body against the data set derived from the disordered crystal structure **5/6**. For the purpose of this refinement, the alkoxy ligand was assumed to have an occupancy of 50%. Isotropic thermal parameters were allowed to refine freely. The difference map calculated subsequently to this can be unambiguously interpreted as an alkylperoxo ligand, in which one atom (C(35)) was shared with the alkoxy ligand.

CCDC-208183 [(TEEDA)Mg(CH$_2$Ph)$_2$], CCDC-208184 [(PMDETA)Mg(CH$_2$Ph)$_2$], CCDC-208185 [Mg(CH$_2$Ph)$_2$(tmeda)] (**3**), CCDC-208186 [MgBz(MeNDiip)(thf)]·PhMe (**4**), CCDC-208187 [{CH(MeNDiip)$_2$MgO/O$_2$Bz}$_2$] (**5/6** co-crystal) and CCDC-208188 [{CH(MeNDiip)$_2$MgOBz}$_2$] (**6a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

Table 2. Crystal data for **3**, **4** and **5/6**.

	3	**4**	**5/6**
crystal	colourless block	colourless plate	colourless block
formula	$C_{20}H_{30}MgN_2$	$C_{47}H_{64}MgN_2O$	$C_{72}H_{96}Mg_2N_4O_{2.63}$
M_r	322.77	697.31	1108.23
T [K]	150(2)	150(2)	150(2)
crystal system	monoclinic	triclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$
a [Å]	7.9035(17)	8.978(2)	11.6115(15)
b [Å]	16.105(3)	12.159(3)	12.993(2)
c [Å]	15.882(3)	19.605(5)	13.176(2)
α [°]	90	81.698(4)	98.679(2)
β [°]	97.872(4)	80.072(4)	111.891(2)
γ [°]	90	85.621(4)	111.379(2)
V [Å^3]	2002.6(7)	2083.1(9)	1620.3(4)
Z	4	2	1
μ(Cu$_{K\alpha}$) [mm^{-1}]	0.090	0.078	0.085
independent reflections	4063	8409	4227
data with $I > 2\sigma(I)$	2719	5300	4227
transmission min/max[a]	0.676/0.928	0.845/1.000	0.708/1.000
$R1$[b]	0.0373	0.0471	0.0933
$wR2$[c]	0.0957	0.1191	0.2080

[a] Absorption correction: SADABS. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [for $I > 2\sigma(I)$]. [c] $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$ (all data).

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[1] a) L. Bouveault, *Bull. Soc. Chim.* **1903**, *29*, 1051; b) M. T. Goebel, C. S. Marvel, *J. Am. Chem. Soc.* **1933**, *55*, 1693.
[2] F. Bodroux, *C. R. Seances Acad. Sci. Ser. A* **1903**, *136*, 158.
[3] J. F. Garst, C. D. Smith, A. C. Farrar, *J. Am. Chem. Soc.* **1972**, *94*, 7707.
[4] a) C. W. Porter, C. J. Steel, *J. Am. Chem. Soc.* **1920**, *42*, 2650; b) H. Wuyts, *Bull. Soc. Chim. Belg.* **1927**, *36*, 222.
[5] a) R. C. Lamb, M. K. Toney, P. W. Ayers, J. F. Garst, *J. Am. Chem. Soc.* **1966**, *88*, 4261; b) A. G. Davies B. P. Roberts, *J. Chem. Soc. B* **1969**, 317; c) A. G. Davies, B. P. Roberts, *Acc. Chem. Res.* **1972**, *5*, 387; d) A. G. Davies, B. P. Roberts, *J. Chem. Soc. Dalton Trans.* **1968**, 1074; e) E. J.; Panek, G. M. Whiteside, *J. Am. Chem. Soc.* **1972**, *94*, 8764; f) M. Möller, M. Husemann, G. Boche, *J. Organometal. Chem.* **2001**, *624*, 47.
[6] C. Walling A. Cioffari, *J. Am. Chem. Soc.* **1970**, *92*, 6609.
[7] G.Boche, L. Möbus, K. Harms, J. C. W. Lohrenz, M. Marsch, *Chem. Eur. J.* **1996**, *2*, 604.
[8] a) M. S. Kharasch, O.Reinmuth, *Grignard Reactions of Nonmetallic Substances* pp. 1264–1274, Prentice Hall, Eaglewood Cliffs, NJ, **1954**; b) T. G. Brilkina, V. A. Shushunov, *Reactions of Organometallic Compounds with Oxygen and Peroxides*, CRC, Clevland, Ohio, **1969**.
[9] See, for example: a) E. N. Jacobsen, in *Comprehensive Organometallic Chemistry II*, *Vol. 12* (Eds.: E. W. Abel, F. G. A. Stone, G. Wilkinson), Pergamon, New York, **1995**, pp. 1097–1135; b) I. D. Williams, S. F.

Pederson, B. K. Sharpless, S. J. Lippard, *J. Am. Chem. Soc*. **1984**, *106*, 6430; c) R. M. Hanson, K. B. Sharpless, *J. Org. Chem*. **1986**, *51*, 1922; d) K. A. Jørgensen, *Chem. Rev.* **1989**, *89*, 431; e) M. Bonchio, S. Calloni, F. Di Furia, G. Licini, G. Modena, S. Moro, W. A Nugent, *J. Am. Chem. Soc*. **1997**, *119*, 6935; f) S.-I. Murasahi, Y. Oda, K. Naota, T. Kuwabara, *Tetrahedron Lett*. **1993**, *34*, 1299; g) J. Kim, R. G. Harrison, C. Kim, L. Que, Jr., *J. Am. Chem. Soc.* **1996**, *118*, 4373.

[10] a) G. Furguson, M. Parves, P. K. Monaghan, R. J. Puddephatt, *Chem. Commun.* **1983**, 267; b) N. Kitajima, T. Katayama, K. Fujisawa, Y. Iwata, Y. Moro-oka, *J. Am. Chem. Soc.* **1993**, *115*, 7872; c) L. Saussine, E. Brazi, A. Robine, H. Mimoun, J. Fischer, R. Weiss, *J. Am. Chem. Soc.* **1985**, *107*, 3534; d) A. van Asselt, B. D. Santarsiero, J. E. Bercaw, *J. Am. Chem. Soc.* **1986**, *108*, 8291; e) J. Lewinski, J. Zachara, E. Grabska, *J. Am. Chem. Soc.* **1996**, *117*, 6794; f) A. L. Balch, C. R. Cornman, M. M. Olmstead, *J. Am. Chem. Soc.* **1990**, *112*, 2963; g) C. Giannotti, C. Fontaine, A. Chiaroni, C. Riche, *J. Organomet. Chem.* **1976**, *113*, 57; h) H. Komatsuzaki, N. Sakamoto, M. Satoh, S. Hikichi, A. Akita, Y. Moro-oka, *Inorg. Chem.* **1998**, *37*, 6554; i) G. Strukul, R. A. Michelin, J. D. Orbell, L. Randaccio, *Inorg. Chem.* **1983**, *22*, 3706.

[11] a) H. Mimoun, P. Chaumette, M. Magnard, L. Saussine, J. Fischer, R. Weiss, *Nouv. J. Chim.* **1983**, *7*, 467; b) G. Boche, K. Möbus, K. Harms, M. Marsch, *J. Am. Chem. Soc.* **1996**, *118*, 2770.

[12] a) W. Cleaver, A. R. Barron, *J. Am. Chem. Soc.* **1989**, *111*, 8966; b) M. B. Power, W. M. Cleaver, A. W. Apblett, A. R. Barron, J. W. Ziller, *Polyhedron* **1992**, *11*, 477.

[13] a) J. Lewinski, J. Kachara, E. Grabska, *J. Am. Chem. Soc.* **1996**, *118*, 6794; b) J. Lewinski, J. Kachara, P. Gos, E. Grabska, I. M. Kopec, W. Marciniak, I. Prwotorow, *Chem. Eur. J.* **2000**, *6*, 3215.

[14] See, for example: a) A. Nishinaga, H. Tomita, H. Ohara, *Chem. Lett.* **1983**, 1751; b) T. V. Lubben, P. T. Wolczanski, *J. Am. Chem. Soc.* **1987**, *109*, 424; c) G. Parkin, W. P. Schaefer, R. E. Marsh, J. E. Bercaw, *Inorg. Chem.* **1988**, *27*, 3262; d) G. Parkin, J. E. Bercaw, *Polyhedron* **1988**, *7*, 2053; e) F. Bottomley, C. P. Magill, P. S. White, *J. Am. Chem. Soc.* **1989**, *111*, 3070.

[15] a) C. Fontaine, K. N. V. Duong, C. Merienne, A. Gaudemer, C. Gianotti, *J. Organomet. Chem.* **1972**, *38*, 167; b) F. R. Jensen, R. C. Kiskis, *J. Organomet. Chem.* **1973**. *47*, C46.

[16] R. Han, G. Parkin, *J. Am. Chem. Soc.* **1992**, *114*, 748.

[17] E. Weiss, *J. Organomet. Chem.* **1964**, *2*, 314.

[18] E. C. Ashby, R. C. Arnot, *J. Organomet. Chem.* **1968**, *14*, 1.

[19] R. R. Schrock, *J. Organomet. Chem.* **1976**, *122*, 209.

[20] a) C. W. Kaminski, J. F. Eastman, *J. Organomet. Chem.* **1967**, *8*, 542; b) C. W. Kaminski, J. F. Eastman, *J. Org. Chem.* **1969**. *34*, 1116.

[21] W. Zarges, M. Marsch, K. Harms, G. Boche, *Chem. Ber*. **1989**, *122*, 2303.

[22] B. J. Wakefield, *Organolithium Methods*, Academic Press, New York, **1988**, p. 38.

[23] M. Schlosser, J. Hartmann, *Angew. Chem.* **1973**, *85*, 544; *Angew. Chem. Int. Ed. Engl.* **1973**, *12*, 508.

[24] H. Viehbrock, D. Abeln, E. Weiss, *Z. Naturforsch. Teil B* **1994**, *49*, 89.

[25] D. Thoennes, E. Weiss, *Chem. Ber.* **1978**, *111*, 3381.

[26] T. Greiser, J. Kopf, D. Thoennes, E. Weiss, *J. Organomet. Chem.* **1980**, *191*, 1.

[27] P. J. Bailey, C. M. Dick, S. Fabre, S. Parsons, *J. Chem. Soc. Dalton Trans.* **2000**, 1655.

[28] The $^{13}C\{^{1}H\}$ NMR spectrum of the 2:1 mixture of **5** and **6** obtained by treatment of **4** with dry oxygen in [D_6]benzene is provided in the Supporting Information along with the spectrum of **6** obtained by addition of a further quantity of **4** to this mixture.

[29] Crystal data for $[\{HC\{C(CH_3)NAr'\}Mg(\mu\text{-}OCH_2Ph)\}_2]$ (**6a**): Space group $P2_1/n$, $a = 14.3543(14)$, $b = 11.4635(11)$, $c = 19.748(2)$, $\beta = 90.779(2)$, $R1 = 0.0487$ (CCDC-208188).

[30] a) H. Mimoun, R. Carpentier, A. Mischler, J. Fischer, R. Weiss, *J. Am. Chem. Soc.* **1980**, *102*, 1047; b) M. B. Power, J. W. Ziller, A. R. Barron, *Organometallics*, **1993**, *12*, 4908.

[31] a) C. Venturello, R. D'Aloisio, J. C. J. Bart, M. Ricci, *J. Mol. Catal.* **1985**, *32*, 107; b) J-Y. Piqiemal, C. Bois, J-M. Brégeault, *Chem. Commun.* **1997**, 437.

[32] a) N. M. Gresley, W. P. Griffith, B. C. Parkin, A. J. P. Whide, D. J. Williams, *J. Chem. Soc. Dalton Trans.* **1996**, 2039; b) L. Salles, C. Aubry, F. Robert, *New J. Chem.* **1993**, *17*, 367.

[33] a) A. E. Lapshin, Y. I. Smolin, Y. F. Sheplev, D. Gyepesova, P. Schwendt, *Acta Crystallogr. Sect. C* **1989**, *45*, 1477; b) V. Suchá, J. T. Tyršelová, J. Marek, *Polyhedron* **1997**, *16*, 2837.

[34] M. J. Bennett, P. B. Donaldson, *Inorg. Chem.* **1977**, *16*, 1585.

[35] a) N. Kitajima, K. Fujisawa, Y. Moro-oka, K. Toriumi, *J. Am. Chem. Soc*. **1989**, *111*, 8975; b) N.Kitajima, T. Koda, S. Hasimoto, T. Kitagawa, Y. Moro-oka, *J. Am. Chem. Soc*. **1991**, *113*, 5664; c) N. Kitajima, K. Fujisawa, C. Fujimoto, Y. Moro-oka, S. Hasimoto, T. Kitagawa, K. Toriumi, K. Tatsumi, A. Nakamura, *J. Am. Chem. Soc*. **1992**, *114*, 1277; d) K. D. Karlin, Z. Tyeklar, A. Farooq, M. S. Haka, P. W. Ghosh, R. Cruse, Y. Gultneh, J. C. Heys, P. Toscano, *Inorg. Chem*. **1992**, *31*, 1436; e) M. Kodera, K. Katayama, Y. Tachi, K. Kano, S.; Hirota, S. Fujinami, M. Suzuki, *J. Am. Chem. Soc*. **1999**, *121*, 11 006.

[36] a) N. Hovnanian, J. Galloy, P. Miele, *Polyhedron* **1995**, *14*, 297; b) A.Drozdov, S. Troyanov *Polyhedron*, **1996**, *15*, 1741.

[37] a) A. R. Kennedy, R. E. Mulvey, R. B Rowlings, *Angew. Chem.* **1998**, *110*, 3321; *Angew. Chem. Int. Ed.* **1998**, *37*, 3180; b) A. R. Kennedy, R. E. Mulvey, R. B. Rowlings, *J. Am. Chem. Soc.* **1998**, *120*, 7816; c) A. R. Kennedy, R. E. Mulvey, C. L. Raston, B. A. Roberts, R. B Rowlings, *Chem. Commun*. **1999**, 353.

[38] J. Feldman, S. J. McLain, A. Parthasarathy, W. J. Marshal, C. J. Calabrese, S. D. Arthur, *Organometallics* **1997**, *16*, 1514.

[39] K. V. Baker, J. M. Brown, N. Hughes, A. J. Sharnulis, A. Sexton, *J. Org. Chem.* **1991**, *56*, 698.

[40] G. M. Sheldrick, SHELX 97, University of Göttingen (Germany), **1997**.

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