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Solvent effects and molecular rearrangements during the reaction of Hauser bases with enolisable ketones: structural characterization of [{$Bu^tC(=CH_2)OMgBr \cdot HMPA$}$_2$] and [$MgBr_2 \cdot (HMPA)_2$].

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Abstract

The Hauser base reagents Pr^i_2NMgCl **1** and Pr^i_2NMgBr **2** react with a variety of enolisable ketones to yield magnesium enolates. Attempts at isolation of these enolates when THF was present in the solvent media was unsuccessful, with the exclusive precipitation of the solvated dihalide salts ($MgX_2 \cdot S_x$, where X = Cl or Br and S = THF, TMEDA or HMPA). Using diethyl ether as solvent media and one molar equivalent of HMPA, the halomagnesium enolate compounds [{$Bu^tC(=CH_2)OMgBr \cdot HMPA$}$_2$] **3** and [$Me_2CHC(=CMe_2)OMgBr \cdot HMPA$] **5** were isolated and identified. Both **3** and **5** precipitate as mixtures with the dihalide salt [$MgBr_2 \cdot (HMPA)_2$] **4**. X-ray crystallographic studies reveal **3** to be dimeric utilizing enolate bridges, whereas **4** is a simple monomer. A molecular-orbital theoretical study (HF/6-31G*) was conducted to determine the relative bridging abilities of several model anions. The enolate anion $H(CH_2=)CO^-$ was determined to be a favoured bridge in preference to the halides F^-, Cl^- and Br^-, which is consistent with the X-ray evidence. The amido anions Me_2N^-, $(H_3Si)_2N^-$ and $(Me_3Si)_2N^-$ are also calculated to be favoured over the chloride anion in three-coordinate dimer systems. This is contrary to the known structure of [{$(Me_3Si)_2NMgCl \cdot (Et_2O)$}$_2$] **8** which bridges through the chloride atoms. The influence of solvent may be critical in determining which anion bridges. Solvent also plays a decisive role in the dismutation reaction of Hauser bases or halomagnesium enolates into their homoleptic components, similar to the Schlenk equilibrium for Grignard reagents.

Keywords: Magnesium enolate; MO calculations; Ab initio; Crystal structure; Magnesium halide; Solvent effects; Bridging ability; Equilibria

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1. Introduction

The reaction between compounds carrying a carbonyl group with an α-hydrogen, such as esters or ketones, with strong bases to form enolates has become one of the premier reactions in organic chemistry [1]. Over the past two decades, the method of choice for the preparation of enolates is via reaction with organometallic bases, such as lithium or magnesium amides. The most commonly used magnesium reagents for the preparation of enolates are halomagnesium amides (R_2NMgX), also known as Hauser bases [2], such as chloromagnesium diisopropylamide, Pr^i_2NMgCl **1**, and the bromo derivative Pr^i_2NMgBr **2** [3]. Although there is a great deal of information on the utility of these reagents, very little is known regarding the nature of the reacting species. We now outline an investigation of Hauser bases and their reactions with ketones.

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Table 1
Reactions of Pr^i_2NMgCl **1** with various ketones and donor solvents

Reaction number	Bulk solvent	Ketone	Added donor	Isolated product	Yield (%)
1	Et_2O	Bu^tCOMe	THF	$MgCl_2 \cdot (THF)_4$	62
2	Et_2O	Bu^tCOMe	TMEDA	$MgCl_2 \cdot TMEDA$	32
3	Et_2O	Bu^tCOMe	HMPA	$MgCl_2 \cdot (HMPA)_2$	46
4	THF	Bu^tCOMe	THF	$MgCl_2 \cdot (THF)_4$	44
5	THF	Bu^tCOMe	TMEDA	$MgCl_2 \cdot TMEDA$	20
6	THF	Bu^tCOMe	HMPA	$MgCl_2 \cdot (HMPA)_2$	36
7	Et_2O	Pr^i_2CO	THF	$MgCl_2 \cdot (THF)_4$	74
8	Et_2O	Pr^i_2CO	TMEDA	$MgCl_2 \cdot TMEDA$	14
9	Et_2O	Pr^i_2CO	HMPA	$MgCl_2 \cdot (HMPA)_2$	56
10	THF	Pr^i_2CO	THF	$MgCl_2 \cdot (THF)_4$	58
11	THF	Pr^i_2CO	TMEDA	$MgCl_2 \cdot TMEDA$	22
12	THF	Pr^i_2CO	HMPA	$MgCl_2 \cdot (HMPA)_2$	26

2. Results and discussion

2.1. Synthetic studies

We were interested in isolating halomagnesium enolate complexes to investigate their bonding and aggregation characteristics. This was initiated by following literature procedures for the preparation of enolates via the reaction of Hauser bases with ketones (Eq. (1)) [3].

$$R_2NH + EtMgX \longrightarrow R_2NMgX + EtH \xrightarrow{R'COCH_2R''} R'(R''CH{=})COMgX + R_2NH \quad (1)$$

The reagents and isolated solid products from the reactions of **1** and **2** with various ketones and donor solvents are listed in Tables 1 and 2. In brief, when the reactions are carried out using THF as solvent media, only the corresponding dihalide solvates are precipitated from solution. With diethyl ether as cosolvent and hexamethylphosphoramide (HMPA) as donor, the reaction of **2** with either pinacolone or diisopropyl ketone, yielded a mixture of solvated dihalide and bromomagnesium enolate. In the case of pinacolone, the complex $[\{Bu^tC(=CH_2)OMgBr \cdot HMPA\}_2]$ **3** was obtained as a mixture with $[MgBr_2 \cdot (HMPA)_2]$ **4**, and with diisopropyl ketone a mixture of **4** and $[Me_2CHC(=CMe_2)OMgBr \cdot HMPA]$ **5** was isolated. In all other reactions only the solvated dihalides were precipitated from solution. It appears that an equilibrium exists between the dienolate and the dihalide at the halomagnesium enolate stage. No dienolates were isolated as solids, presumably due to their high solubility. It is also probable that there is a similar equilibrium with the Hauser bases giving a much more complex reaction pathway than previously described (Scheme 1).

This view is supported by the recent identification of the novel bromomagnesium imide $[(Et_2OMg)_6 \cdot (NPh)_4 \cdot Br_4]$ **6** by Power, which was isolated from the reaction of aniline with EtMgBr in diethyl ether solution. Compound **6** results from the disproportionation reaction outlined in Eq. (2).

$$4PhN(MgX)_2 \longrightarrow Mg_6(NPh)_4X_4 + 2MgX_2 \quad (2)$$

The existence of equilibria is important when considering the influence of the organometallic intermediates on the regio- or stereochemistry of reactions. For example, if the equilibrium of the halomagnesium enolates lies in favour of the homoleptic complexes, then further reaction may proceed through a magnesium dienolate which will influence the reagent's reactivity and selectivity characteristics.

It has been known from some time that the Schlenk equilibrium for Grignard reagents tends towards dissociation into the homoleptic components with increasing solvent polarity [4]. This is consistent with the isolation of **3** from an ether solution and not the corresponding THF solution. In these reactions HMPA is present in a stoichiometric quantity. If excess HMPA was used only **4** was isolated from solution. A large excess of donor was required when THF or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) was used as ligand in order to solubilize the halomagnesium enolate solutions. It is therefore unsurprising that only the dihalides were isolated in these instances since the donor now acts as polar solvent media and consequently moves the equilibrium towards the homoleptic components.

Several batches of product from reaction 15 were isolated and the ratio of **3** to **4** varied between 3:1 to 4:1, as determined by integration of the two sets of HMPA signals seen in the ^{1}H-NMR spectra. The crystals could be separated by hand in an argon-filled glove box, since **3** grew as blocks and **4** as needles. In comparison, only microcrystalline precipitates could be isolated from reaction 20, and **5** was the minor component as a mixture with **4** (average ratio of 4:96 of solid produced in 46% yield).

Table 2
Reactions of Pr^i_2NMgBr **2** with various ketones and donor solvents

Reaction number	Bulk solvent	Ketone	Added donor	Isolated product	Yield (%)
13	Et_2O	Bu^tCOMe	THF	$MgBr_2 \cdot (THF)_4$	36
14	Et_2O	Bu^tCOMe	TMEDA	$MgBr_2 \cdot$ TMEDA	24
15	Et_2O	Bu^tCOMe	HMPA	$MgBr_2 \cdot (HMPA)_2$ and **3**	46[a]
16	THF	Bu^tCOMe	THF	$MgBr_2 \cdot (THF)_4$	36
17	THF	Bu^tCOMe	TMEDA	$MgBr_2 \cdot$ TMEDA	22
18	THF	Bu^tCOMe	HMPA	$MgBr_2 \cdot (HMPA)_2$	30
19	Et_2O	Pr^i_2CO	THF	$MgBr_2 \cdot (THF)_4$	52
20	Et_2O	Pr^i_2CO	TMEDA	$MgBr_2 \cdot$ TMEDA and **5**	46[a]
21	Et_2O	Pr^i_2CO	HMPA	$MgBr_2 \cdot (HMPA)_2$	56
22	THF	Pr^i_2CO	THF	$MgBr_2 \cdot (THF)_4$	38
23	THF	Pr^i_2CO	TMEDA	$MgBr_2 \cdot$ TMEDA	18
24	THF	Pr^i_2CO	HMPA	$MgBr_2 \cdot (HMPA)_2$	32

[a] Combined yield for the two complexes.

2.2. Crystallographic studies

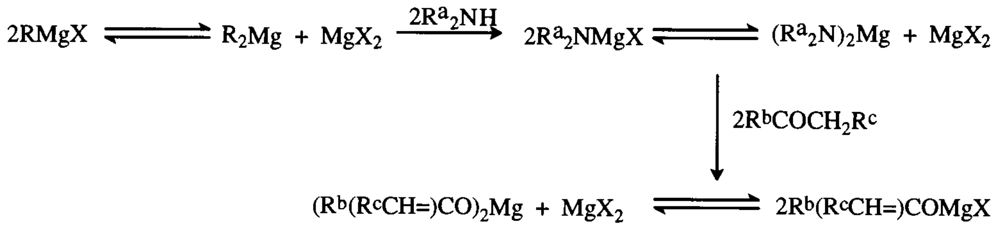
X-ray analyses determined **4** to be monomeric and **3** to be dimeric utilizing bridging enolate functions (Figs. 1 and 2; listings of bond distances and angles are given in Tables 3 and 4).

Rather surprisingly only two examples of bis-solvated, monomeric magnesium dibromide, namely $[MgBr_2 \cdot (OEt_2)_2]$ [5] and $[MgBr_2 \cdot (C_5H_4NCH_3)_2]$ [6], appear in the Cambridge Structural Database [7]. More commonly, tetrasolvated, six-coordinate magnesium complexes are found, such as $[MgBr_2 \cdot (THF)_4]$ and $[MgBr_2 \cdot (NC_5H_5)_4]$ [6,8]. Also known are chain structures of magnesium dibromides such as $[\{MgBr_2 \cdot (THF)_2\}_\infty]$ [9] and $[\{MgBr_2 \cdot (Et_2O)\}_\infty]$ [10] which utilize bridging bromines to polymerize. A combination of solvent stoichiometry and steric bulk determines the structural arrangement adopted [11]. In the case of **4**, the relatively bulky HMPA ligands reduces the possibility of higher aggregation. Comparison of bond lengths and angles between **4** and $[MgBr_2 \cdot (OEt_2)_2]$ is limited due to the low accuracy of the data collected for the etherate. Overall the dimensions and angles within **4** are in line with those expected for a tetracoordinated monomer of magnesium [12].

The characterization of **3** represents the first isolation and structural determination of a halomagnesium enolate under synthetic conditions normally applied to organic transformations. Compound **3** adopts a dimeric structure utilizing bridging enolate groups, with terminally bound bromide and HMPA units. Rather unusually, four independent dimers are present in the unit cell of **3**. Data for this crystal were collected on a Siemens SMART CCD area detector diffractometer and over 20000 reflections were recorded overnight. The dimers have similar geometric parameters and discussion of atomic dimensions will be for averaged values unless otherwise stated.

Previously, Williard prepared and crystallographically characterized the compound $[\{Bu^tC(=CHMe)OMgBr \cdot (Et_2O)\}_2]$ **7** by reaction of the α-bromoketone with magnesium metal in ether [13]. Gross structural features of **7** resemble those of **3**. Of note in **3** is the short Mg–O(HMPA) bond distance of 1.907(4) Å, compared to the Mg–O(ether) distance of 2.049(9) Å in **7**. In fact, the Mg–O(enolate) bonds of both **3** and **7** at 1.966(4) and 1.953(7) Å respectively, are also significantly longer than the Mg–O(HMPA) dative bonds. This is a consequence of the strong solvating ability of HMPA, which may be represented as the resonance structure $(Me_2N)_3P^+-O^-$. One distinction between the four dimers found for **3** are the P–O–Mg angles which were determined to be 159.2(2), 167.7(3), 171.2(3) and 171.9(3)°. For **4** the P–O–Mg angle is even smaller at 149.46(9)°. This range of angles illustrates the variable coordination mode of the HMPA ligand towards strongly Lewis acidic metal centres. We have previously intimated that the P–O–Mg angle adopted has little bearing on the resulting bond strength [14]. As expected, the four membered MgOMgO ring has smaller angles at the metal (84.3°) and larger angles at the oxygen (95.7°).

Recently Power has determined the crystal structure of the Hauser base $[\{(Me_3Si)_2NMgCl \cdot (Et_2O)\}_2]$ **8** [15]. Compound **8** is dimeric in the solid state utilizing bridging chlorides in favour of the amido units. The preference for bridging bromides instead of amides has also been demonstrated for the bromo derivative of **8** (P.G. Williard, Q.Y. Liu, personal communications). Therefore, on moving from a Hauser base to a halomagnesium enolate there is a molecular rearrangement, switching from bridging halogens to bridging enolates (Scheme 2). Reaction of heteroleptic dimers is feasible in ether solutions, since the position of the equilibria in these systems tends towards these species. However, it is also possible that this rearrangement takes place on the association of monomeric halomagnesium enolates in solution.

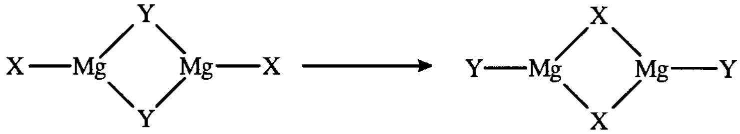


Scheme 1.

2.3. Theoretical calculations

A theoretical MO study of heteroleptic magnesium compounds using F^-, Cl^- and Br^- as halides, and $CH_3CH_2^-$, Me_2N^-, $(H_3Si)_2N^-$, $(Me_3Si)_2N^-$ and $CH_2{=}C(H)O^-$ as the alternative anions was undertaken to assess their relative bridging abilities. Data from this investigation could then be compared with the known structures.

For simplicity, three-coordinate dimers were used as model compounds [17]. The relative bridging ability of the anions was determined at the HF/6-31G* level (Table 5) using the general reaction shown in Eq. (3).



As expected, all of the halides are better bridging groups than an ethyl group. However, only fluoride is a better bridge than the dimethylamido anion. The enolate anion $CH_2{=}C(H)O^-$ was determined to be the best of the bridging agents. These results are in agreement with the crystal structures of **3** and **7**, where bridging enolate is preferred over bridging bromide. However, the calculations also predict that the amide Me_2N^- is a preferred bridge compared to chloride or bromide and this is not what is seen experimentally from the crystal structure evidence of **8**. One possibility for this discrepancy may be the influence of the bulky silyl groups. Calculations using the model anion $(H_3Si)_2N^-$ and chloride showed a preference for amido bridges by 9.9 kcal mol^{-1}. So although there was a significant energy drop on moving from Me_2N^- to $(H_3Si)_2N^-$, amide bridges are still calculated to be preferred over chloride bridges. Using $(Me_3Si)_2N^-$ anions only a 4.1 kcal mol^{-1} preference for bridging chlorides was found. It appears that increasing the steric bulk of the amide anion has the effect of significantly decreasing its bridging ability.

Calculations were performed to determine the influence of tetracoordination at the metal centres. Dimers utilizing H_2O as model donor ligand, chloride as halide and either Me_2N^- or $(H_3Si)_2N^-$ as counter anion were geometry optimized (Table 6) [18]. These calculations give pseudo-tetrahedral magnesium centres (Eq. (4)).

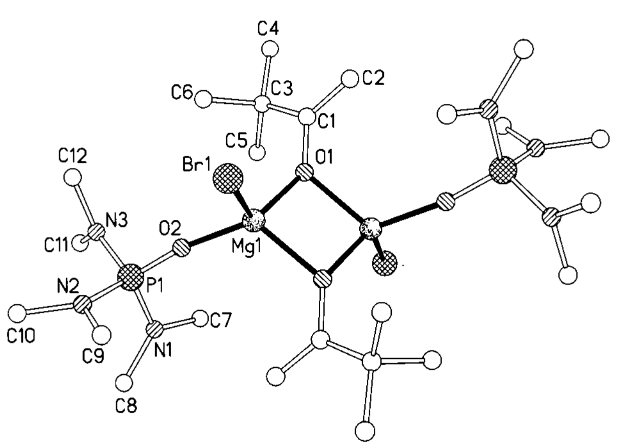


Fig. 1. One of the independent molecules of **3** without hydrogen atoms and with the unique atoms labelled.

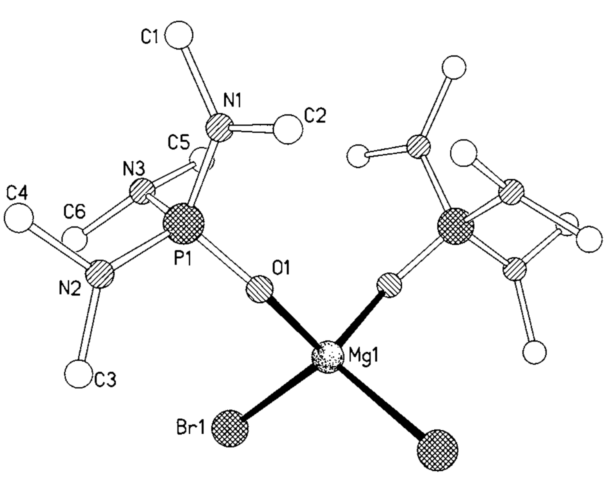
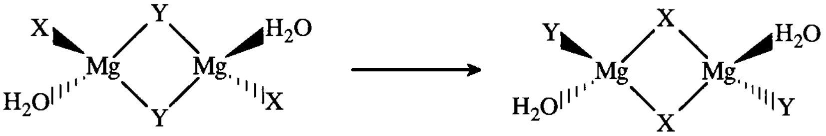


Fig. 2. The molecular structure of **4** without hydrogen atoms and with unique atoms labelled.



Although the introduction of water as donor had a dramatic effect on the geometry of the complex, it made no significant difference to the relative bridging abilities of the anions.

The inconsistency between the calculated preference for amido bridges and the X-ray data for **8**, which displays bridging chloride, may be accounted for by two scenarios. First, the calculations need to take into account the steric requirements of the whole system i.e. solvation by a bulky solvent such as diethyl ether may be sufficient to switch the preference for bridging to the halide. Such calculations require a large number of basis sets and degrees of freedom and are at present too time consuming to complete. A second possibility is the calculations are correct in predicting the theoretical preference for amide bridges but this is not observed due to the requirement of the complex to rearrange i.e. the kinetic product is obtained. Hauser bases are prepared from the Grignard reagents which will mostly consist of dimers bridged through halide in diethyl ether solvent. It is therefore possible that the terminal organyl groups of these dimers undergo replacement by amido anions on reaction of the Grignard and amine with retention of the dimeric structure. This will result in complexes with structures similar to those characterized in the solid state i.e. **8**. In order for the complex to rearrange to the 'energy minimum' conformation with bridging amides, the central MgClMgCl ring has to break (similar to the final step in Scheme 2). It may be that the activation barrier for this bond-breaking step is of sufficiently high energy to prevent rearrangement occurring.

3. Conclusions

In summary, Schlenk-type reactions have been shown to exist for halomagnesium enolates. This complicates any proposed reaction mechanisms involving these compounds. The nature of the solvent media appears to affect the position of the equilibrium, as is seen from the isolation of mixtures from reactions of $Pr^{i}_{2}NMgBr$ with pinacolone or diisopropyl ketone from ether solutions, but exclusively dihalides when THF was used as solvent media. Also, the nature of the halogen is important. No enolate complexes were obtained using chloride reagents. Lastly, the nature of the enolate is also significant, since changing from pinacolone to diisopropyl ketone results in different product ratios in reactions 15 and 20.

One of the driving forces for disproportionation in the reactions using THF as solvent media is an increase in coordination number at the metal. In heteroleptic dimers such as **3** and **7**, magnesium is four-coordinate and further solvation is precluded by steric interferences. However, the metals are six-coordinate in the THF solvates of the dihalides [19]. Using diethyl ether as donor, only tetracoordinated dihalides are possible due to the increased steric requirements of the ligands. This leads to a more balanced equilibrium between the homoleptic and heteroleptic complexes.

A structural determination of **3** found that bridging enolate anions are preferred over bridging bromides. Therefore transforming a Hauser base to a halomagnesium enolate must involve bond breaking of the bridging anions and rearrangement of the complex. Our calculations are consistent with the preference of enolate over either chloride or bromide bridges. However, the calculations also indicate that simple, sterically undemanding dialkylamido bridges are preferred over chloride or bromide bridges. As the steric bulk of the amido anion is increased its bridging ability decreases. Nevertheless, the hexamethyldisilazide anion, $(Me_3Si)_2N^-$, is still predicted to be favoured over bridging chloride in a three-coordinate dimer.

This study illustrates the care which must be taken when considering reaction mechanisms involving halide substituted magnesium compounds. Solvent effects influence: (i) the position of any dismutation equilibria, (ii) the aggregation state of the complexes and (iii) which anions will bridge in the complexes produced.

Table 3
Selected bond lengths (Å) and angles (°) for one of the four independent dimers of **3**

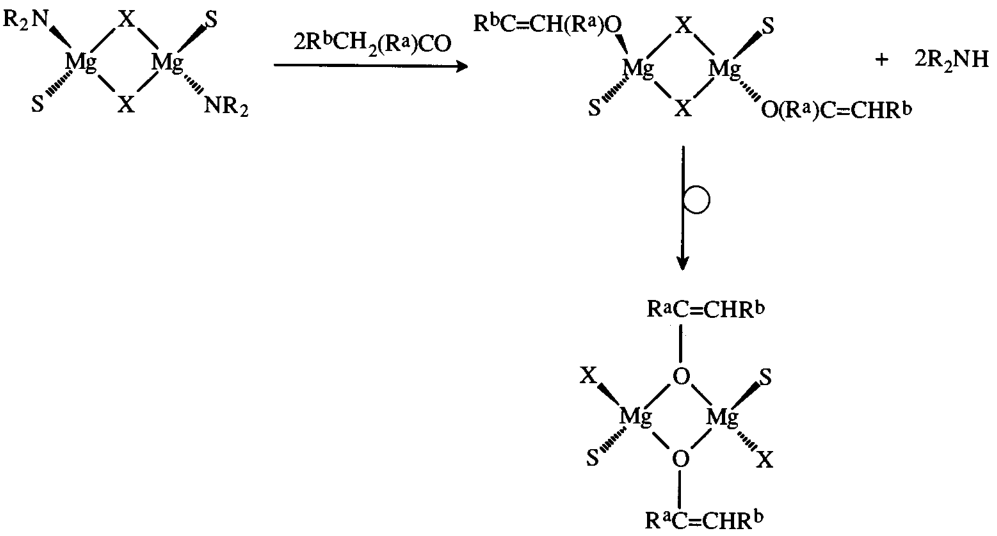
Mg1–O1	1.956(4)	Mg1–O1′	1.981(4)
Mg1–O2	1.910(4)	Mg1–Br1	2.442(2)
Mg1–O1–Mg1′	96.1(2)	Mg1–O1–C1	139.0(4)
Mg1′–O1–C1	123.7(3)	O1–Mg1–O1′	83.9(2)
O1–Mg1–O2	115.3(2)	O1′–Mg1–O2	115.1(2)
O2–Mg1–Br1	108.58(14)	O1–Mg1–Br1	117.64(13)
O1′–Mg1–Br1	114.84(12)	P1–O2–Mg1	171.2(3)

The prime indicates a symmetry-generated atom.

Table 4
Selected bond lengths (Å) and angles (°) of the monomer **4**

Mg1–Br1	2.4819(5)	Mg1–O1	1.9313(13)
P1–O1	1.4970(13)		
O1–Mg1–O1′	111.03(9)	O1–Mg1–Br1′	106.29(4)
O1–Mg1–Br1	107.52(4)	Br1–Mg1–Br1′	118.20(4)
Mg1–O1–P1	149.46(9)		

The prime indicates a symmetry-generated atom.



Scheme 2.

4. Experimental

4.1. Syntheses

All syntheses were conducted in Schlenk-type glassware under a blanket of argon gas [20]. The metallated compounds isolated are highly air- and moisture-sensitive, and were handled in an argon filled glove box fitted with a recirculating column. Donor ligands, amines and ketones were distilled over CaH_2 and stored over 4A molecular sieves before use. All solvents were distilled over sodium/benzophenone prior to use.

Preparation of the enolate mixtures were carried out in a similar manner. Diisopropylamine (10 mmol) was added dropwise to a 0°C chilled solution of Grignard reagent (10 mmol of a 2 M solution in either THF or ether) using 5 ml of hexane as cosolvent. The ketone (10 mmol) was then added dropwise by syringe to the mixture. A white suspension formed which could be dissolved on addition of the appropriate donor solvent. This was approximately one equivalent of HMPA, four equivalents of TMEDA or fifteen equivalents of THF. The clear solution was then placed at -20°C for precipitation of the product.

Table 5
Relative energies of the three-coordinate dimers

Dimer numbers	Anion X	Anion Y	Thermicity of reaction (kJ mol^{-1})
I/II	F^-	Et^-	-42.1
III/IV	Cl^-	Et^-	-13.2
V/VI	Br^-	Et^-	-9.3
VII/VIII	F^-	Me_2N^-	-3.3
IX/X	Cl^-	Me_2N^-	$+27.4$
XI/XII	Br^-	NMe_2	$+30.9$
XIII/XIV	F^-	$CH_2{=}C(H)O^-$	$+1.4$
XV/XVI	Cl^-	$CH_2{=}C(H)O^-$	$+32.7$
XVII/XVIII	Br^-	$CH_2{=}C(H)O^-$	$+35.9$
XIX/XX	Cl^-	$(H_3Si)_2N^-$	$+9.9$
XXI/XXII	Cl^-	$(Me_3Si)_2N^-$	$+4.1$

Thermicities are quoted on a per dimer basis.

4.2. ^1H-NMR spectra (Bruker AMX 400 MHz, 300 K, C_6D_6)

[$MgCl_2\cdot(THF)_4$]: THF (CH_2, 4H, m, δ 1.39; OCH_2, 4H, m, δ 3.64). [$MgBr_2\cdot(THF)_4$]: THF (CH_2, 4H, m, δ 1.40; OCH_2, 4H, m, δ 3.65). [$MgBr_2\cdot(HMPA)_2$] **4**: HMPA (CH_3, 18H, d, δ 2.37) [$MgBr_2\cdot TMEDA$]: TMEDA (CH_2, 4H, s, δ 2.14; CH_3, 12H, s, δ 2.28) **3**: HMPA (CH_3, 18H, d, δ 2.27) enolate (CH_3, 9H, s, δ 1.53; CH, 1H, s, δ 4.37; CH, 1H, s, δ 4.92). **5**: HMPA (CH_3, 18H, d, δ 2.34) enolate (CH_3, 6H, m, 0.89; CH_3, 6H, s, δ 1.54; OCH, 1H, δ 4.32).

4.2.1. ^1H-NMR spectra (bruker WM 250 MHz, 300 K, d_5-pyridine)

[$MgCl_2\cdot(HMPA)_2$]: HMPA (CH_3, 18H, d, δ 2.57) [$MgCl_2\cdot TMEDA$]: TMEDA (CH_2, 4H, s, δ 2.39; CH_3, 12H, s, δ 2.17)

4.2.2. X-ray crystallographic studies

Crystals of **3** and **4** were mounted onto glass fibres in an oil drop. Data were collected on a Siemens SMART

Table 6
Relative energies of the four-coordinate dimers

Dimer numbers	Anion X	Anion Y	Thermicity of reaction (kJ mol^{-1})
XXIII/XXIV	Cl^-	Me_2N^-	$+28.6$
XXV/XXVI	Cl^-	$(H_3Si)_2N^-$	$+10.2$

Thermicities are quoted on a per dimer basis.

CCD diffractometer and corrected semiempirically for absorption. The structure solutions were by direct methods with refinement on F^2 [21].

Crystal data for **3**: $C_{24}H_{58}Br_2Mg_2N_6O_4P_2$, $M = 765.1$, $T = 160$ K, triclinic, $P\bar{1}$, $a = 15.4729(10)$ Å, $b = 15.6631(10)$ Å, $c = 16.5376(11)$ Å, $\alpha = 102.496(2)°$, $\beta = 95.137(2)°$, $\gamma = 92.910(2)°$, $V = 3887.1(4)$ Å^3, $Z = 4$, $d_{calc} = 1.307$ Mg m^{-3}, $2\theta_{max} = 50°$, 20361 reflections collected, 13454 unique reflections, $R_{int} = 0.0956$, number of variables = 784, full-matrix least-squares refinement on F^2 converged to $wR = [w(F_o^2 - F_c^2)^2/w(F_o^2)^2]^{1/2} = 0.2020$ and $S = 1.111$ for all data, conventional $R = 0.0683$ for F values of 10759 reflections with $F_o^2 > 2\sigma(F_o^2)$, difference map extremes $+1.10$ and -1.32 eÅ^{-3}. Disorder was resolved and refined for some bromo and HMPA ligands.

Crystal data for **4**: $C_{12}H_{36}Br_2Mg_1N_6O_2P_2$, $M = 542.5$, $T = 160$ K, monoclinic, $I2/a$, $a = 15.6661(14)$ Å, $b = 8.1619(7)$ Å, $c = 18.573(2)$ Å, $b = 94.795(2)°$, $V = 2366.5(4)$ Å^3, $Z = 4$, $d_{calc} = 1.523$ Mg m^{-3}, $2\theta_{max} = 57°$, 7170 reflections collected, 2698 unique reflections, $R_{int} = 0.0471$, number of variables = 121, full-matrix least-squares refinement on F^2 converged to $wR = 0.0773$ and $S = 1.118$ for all data, conventional $R = 0.0280$ (2570 reflections), difference map extremes $+0.59$ and -0.87 eÅ^{-3}.

Atomic coordinates, bond lengths and angles, and displacement parameters have been deposited at the Cambridge Crystallographic Data Centre.

4.2.3. Theoretical calculations

The Gaussian 94 program, revision E.2, was used for the calculations [22]. Geometry optimization was carried out using the HF/6-31G basis set as an initial guess and then reoptimized at the higher 6-31G* level.

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