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Alkoxymagnesium Iodide Complexes

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Dedicated to Professor Michael Hanack on the occasion of his 80th birthday

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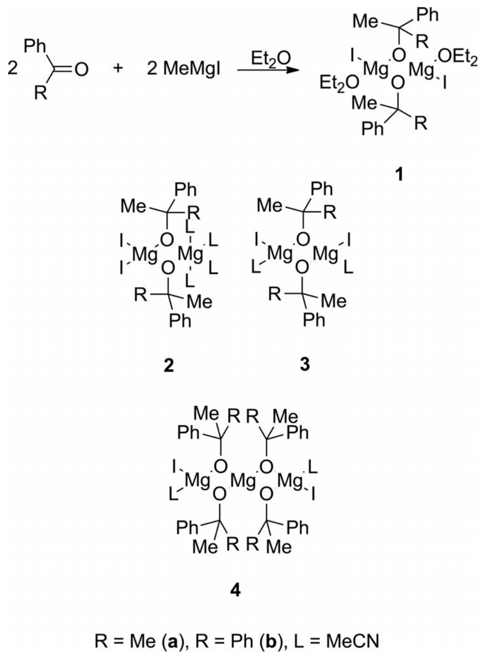
The complexes R(Ph)MeCOMg(Et_2O)I [**1**, R = Me (**a**), Ph (**b**)] were obtained by the reaction of R(Ph)C=O with MeMgI in diethyl ether in good yields. Crystallisation of **1** from acetonitrile resulted in single crystals of di- and trinuclear complexes $I_2(\mu\text{-OCPhMe}_2)_2Mg(MeCN)_4$ (**2**) and {2[I(MeCN)Mg(μ-$OCPh_2Me)_2$Mg(MeCN)I] (**3**) × [I(MeCN)Mg(μ-$OCPh_2Me)_2$Mg(μ-$OCPh_2Me)_2$Mg(MeCN)I] (**4**) × $2CH_2Cl_2$} in which the metal centres are linked by alkoxy substituents. The thermal decomposition of the complexes **1** was studied by successive detection of the EI mass spectra of diethyl ether, the olefins **5**, the tertiary alcohols **6**, and the formal olefin dimers **7**.

Introduction

There has been considerable interest in metal alkoxides and their derivatives in the past decades concerning their structural chemistry and application.[1] The polymeric structures of $Mg(OR)_2$ compounds[2] are broken by co-ligands, preferentially containing nitrogen or oxygen donor functions, and numerous crystal-structure investigations have been reported thereon.[3,4] Though the Grignard analogous alkoxymagnesium halides,[5] as well as their organometallic neighbours,[6] play an important role in organic synthesis, structures of the parent type RO–Mg–X stabilized by solvent molecules are almost completely absent from the literature.[7] We have therefore been interested in the structural chemistry and thermal properties of alkoxymagnesium iodide complexes.

Results and Discussion

The reaction of acetophenone and benzophenone with CH_3MgI in diethyl ether precipitates the alkoxides as solvent adducts R^1(Ph)MeCOMg(Et_2O)I [**1**; R^1 = Me (**a**), Ph (**b**)] in almost quantitative yields.[8] NMR spectroscopic data from $CDCl_3$ solutions show a duplicate set of signals for **1a** (Me) and **1b** (Ph), which indicates a rigid structure presumably as dimers with *trans* orientation of the terminal substituents owing to the prochiral nature of the organic substituent R^1(Ph)MeC.[9] Unfortunately, single crystals of **1** could not be obtained as a consequence from their limited stability in dichloromethane and chloroform (Scheme 1).



Scheme 1.

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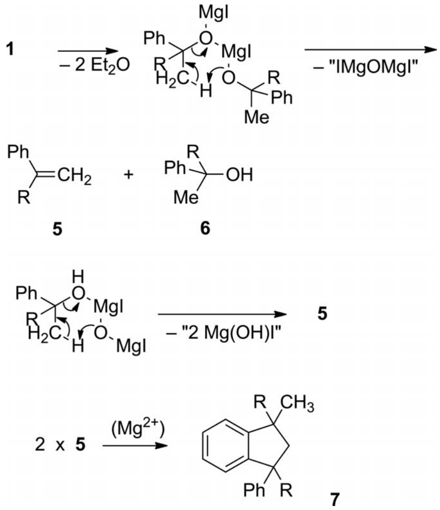
The thermal decomposition of magnesium alkoxides has been used as a technical route to obtain pure MgO.[10] Analogously, we obtained the corresponding olefins in addition to their formal dimers on heating the diethyl ether complexes **1** up to 150 °C in vacuo.[11,12] Introduction of the complexes **1** in the high vacuum of the EI source of a mass spectrometer and stepwise heating of the direct insertion probe (35 up to 150 °C) resulted in the time-dependent formation of decomposition products (Scheme 2). The complexes **1**, after removal of the diethyl ether ligands, decompose into the olefins **5** and the tertiary alcohols **6**. With increasing temperature, the alcohols yield additional amounts of the olefins **5**. By further rise of the temperature, the mass spectra of the olefins diminish and are replaced by those of the dimeric products **7**.



Scheme 2.

From acetonitrile solutions of **1**, products of varying compositions [R(Ph)MeCOMg(MeCN)$_x$I (x = 1–3)] were obtained, which could not be purified by recrystallisation from dichloromethane or acetonitrile on a preparative scale. However, small amounts of single crystals could be isolated. Their crystal structure analyses now reveal the presence of di- and trinuclear complexes in which the metal atoms are linked by alkoxy bridges exclusively (Figures 1, 2, and 3).[13] Whereas **1a** forms a dimer of the composition $I_2Mg(\mu\text{-}OCPhMe_2)_2Mg(MeCN)_4$ with "unsymmetrical" coordination spheres around the metal centres (**2**), the unit cell of the crystals obtained from **1b** contains both 2 equiv. of a dimer $[I(MeCN)Mg(\mu\text{-}OCPh_2Me)_2Mg(MeCN)I]$ of the *cis* type (**3**) and a trinuclear complex $[I(MeCN)Mg(\mu\text{-}OCPh_2Me)_2Mg(\mu\text{-}OCPh_2Me)_2Mg(MeCN)I]$ (**4**)[14] in which the central magnesium atom Mg(50) lies on a twofold crystallographic rotation axis and is linked to its metal neighbours by alkoxy bridges including additional 2 equiv. of dichloromethane. Thus, overall the crystal has the composition $(Ph_2MeOC)_8Mg_7I_6(MeCN)_6\cdot 2CH_2Cl_2$. All bond lengths and angles inside the alkoxy substituents are in the expected range.[15] For individual bond lengths and angles around the metal centres see Figures 1, 2, and 3.

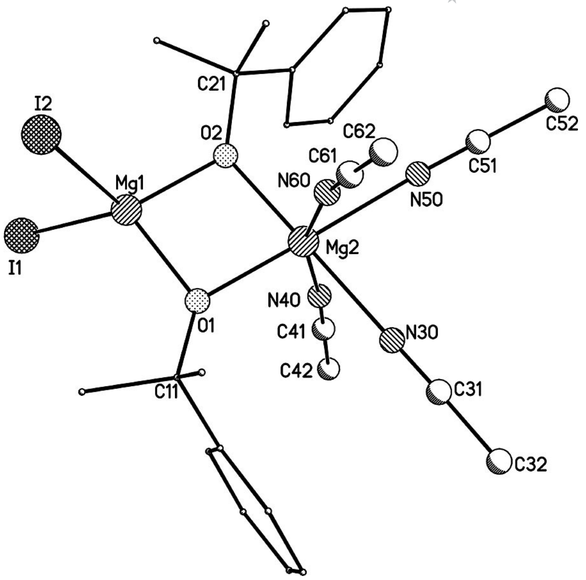


Figure 1. View of the molecule $C_{26}H_{34}I_2Mg_2N_4O_2$ (**2**) (hydrogen atoms omitted for clarity) in the crystal. Selected bond lengths [Å] and angles [°]: Mg(1)–O(1) 1.9382(19), Mg(1)–O(2) 1.9388(19), Mg(1)–I(1) 2.7396(9), Mg(1)–I(2) 2.7724(9), Mg(2)–N(30) 2.226(3), Mg(2)–N(40) 2.207(3), Mg(2)–N(50) 2.236(3), Mg(2)–N(60) 2.231(3), O(1)–C(11) 1.425(3), O(2)–C(21) 1.423(3), Mg(1)···Mg(2) 2.9478(12); O(1)–Mg(1)–O(2) 85.24(8), O(1)–Mg(2)–O(2) 81.36(7), Mg(1)–O(1)–Mg(2) 96.46(8), O(1)–Mg(2)–O(2) 96.43(8); interplanar angles [°]: Mg(1)O(1)Mg(2)//Mg(1)O(2)Mg(2) 8.2, O(1)Mg(1)O(2)//O(1)Mg(2)O(2) 7.3, O(1)Mg(1)O(2)//I(1)Mg(1)I(2) 90.7.

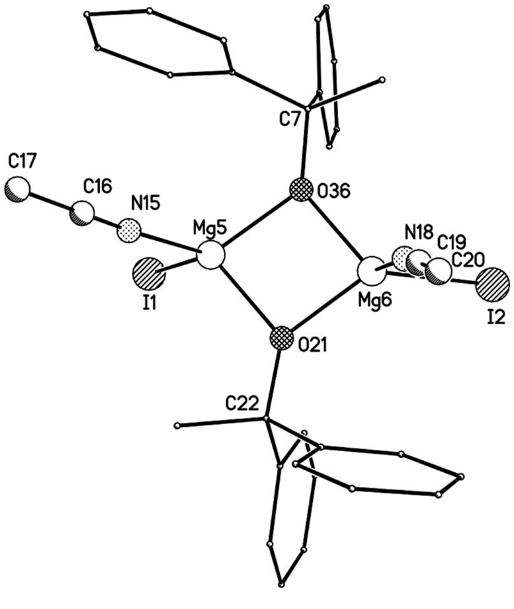


Figure 2. View of the molecule $C_{32}H_{32}I_2Mg_2N_2O_2$ (**3**) in the crystal of $2\mathbf{3}\cdot\mathbf{4}\cdot 2CH_2Cl_2$ (hydrogen atoms and solvent molecules omitted for clarity). Selected bond lengths [Å] and angles [°]: Mg(5)–O(21) 1.956(6), Mg(5)–O(36) 1.947(6), Mg(6)–O(21) 1.942(6), Mg(6)–O(36) 1.946(6), Mg(5)–I(1) 2.665(3), Mg(6)–I(2) 2.657(3), Mg(5)–N(15) 2.086(8), Mg(6)–N(18) 2.081(9), O(21)–C(22) 1.425(10), O(36)–C(7) 1.417(11), Mg(5)···Mg(6) 2.885(4); O(21)–Mg(5)–O(36) 84.1(2), O(21)–Mg(6)–O(36) 84.5(2), Mg(5)–O(21)–Mg(6) 95.5(3), Mg(5)–O(36)–Mg(6) 95.6(3); interplanar angles [°]: Mg(5)O(21)Mg(6)//Mg(5)O(36)Mg(6) 5.0, O(21)Mg(5)O(36)//O(21)Mg(6)O(36) 4.5.

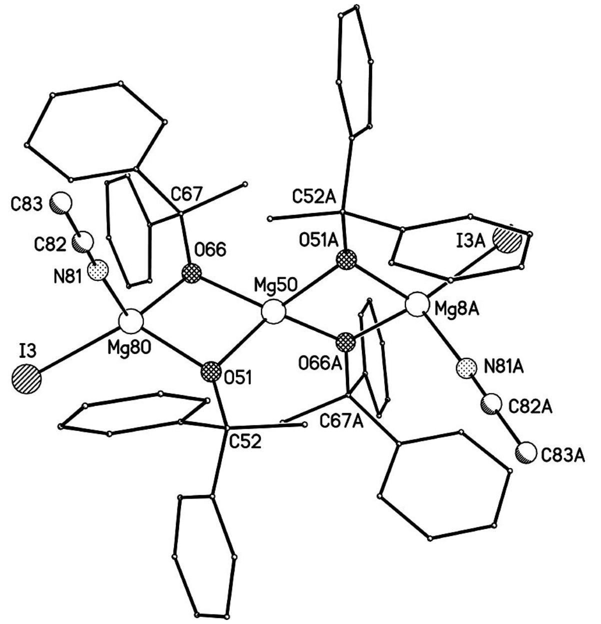
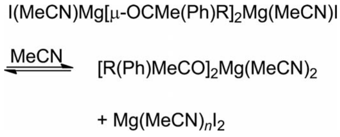


Figure 3. View of the molecule $C_{60}H_{58}I_2Mg_3N_2O_4$ (**4**) in the crystal of $C_{126}H_{126}Cl_4I_6Mg_7N_6O_8$ (**2**3·**4**·2CH$_2$Cl$_2$) (hydrogen atoms and solvent molecules omitted for clarity). Selected bond lengths [Å] and angles [°]: Mg{(RO)$_2$MgI(MeCN)}$_2$: Mg(50)–O(51) 2.001(5), Mg(50)–O(66) 1.972(6), Mg(80)–O(51) 1.952(6), Mg(80)–O(66) 1.959(6), Mg(80)–I(3) 2.709(3), Mg(80)–N(81) 2.100(10), O(51)–C(52) 1.445(10), O(66)–C(67) 1.434(11), Mg(50)···Mg(80) 2.936(3); O(51)–Mg(50)–O(66) 82.2(2), O(51)–Mg(50)–O(51A) 122.3(3), O(66)–Mg(50)–O(66A) 127.5(4), O(51)–Mg(50)–O(66A) 124.2(2), O(51)–Mg(80)–O(66) 96.6(3), Mg(50)–O(51)–Mg(80) 95.9(3), Mg(50)–O(66)–Mg(80) 96.6(3); interplanar angles [°]: O(51)Mg(50)O(66)//O(51A)Mg(50)O(66A) 90.5, O(51)Mg(50)O(66)//O(51)Mg(80)O(66) 11.9, Mg(50)O(51)Mg(80)//Mg(50)O(66)Mg(80) 13.3, O(51)Mg(80)O(66)//I(3)Mg(80)N(81) 96.5.

About 80 years ago, Schlenk proposed his famous equilibrium to explain the properties of Grignard reagents.[16] Later on, his idea was confirmed by ^{25}Mg NMR spectroscopy[17] and by ^{28}Mg isotope experiments.[18] From the composition of the single crystals mentioned above, the presence of a Schlenk-type equilibrium of alkoxymagnesium iodides in acetonitrile, which includes solvated magnesium iodide and alkoxide, may be suggested. The structures of **2**, **3** and **4** demonstrate the presence of oligonuclear species in which the metal centres are linked by alkoxy bridges. Thus, equilibria can explain both the results of solution and solid-state characterisation of the acetonitrile complexes. Therefore, we investigated solutions of **1** by ^{25}Mg NMR spectroscopy. In [D$_2$]dichloromethane, broad signals at $\delta \approx$ 40 ppm [vs. $Mg(H_2O)_6^{2+}$] were detected, whereas in [D$_3$]-acetonitrile broad signals at $\delta \approx 0$ ppm appeared in addition to a sharp signal at $\delta = -17$ ppm, which could be assigned to the $Mg(MeCN)_6^{2+}$ dication. Very similar spectra were obtained from mixtures of MgI$_2$ and Mg[OCR(Me)Ph]$_2$ in acetonitrile, which implies decomposition of the complexes **1** in donor solvents possibly due to equilibria of the Schlenk type (Scheme 3), though we could not prove their presence by temperature-dependent NMR spectroscopy.



Scheme 3.

Conclusions

Our results confirm the strong tendency of alkoxymagnesium derivatives to form oxygen-bridged oligomers even in the presence of halide substituents. Excess of donor solvent molecules, however, can split the Mg$_2$O$_2$ units as figured by the presence of solvated magnesium iodide, and novel – in part trinuclear – magnesium alkoxide derivatives in which the oxygen bridges are reformed. Though a definite proof is not present, our results are best interpreted in terms of a Schlenk-type equilibrium including oligomeric alkoxides and monomeric dihalides.

Thermal decomposition of alkoxymagnesium iodides, monitored by EI mass spectrometry, proves these complexes to be a valuable tool for the construction of organic moieties derived from the alkoxide substituents. We are continuing our investigations in this direction and will report on our results in due course.

Experimental Section

Synthesis: [Mg(MeCN)$_6$]I$_2$ was obtained from iodine and excess magnesium in acetonitrile. The filtered solution was used without further workup. Mg[OCMe(Ph)R]$_2$ was prepared from stoichiometric amounts of Mg(*n*Bu)$_2$ and the corresponding alcohol in *n*-heptane. The complexes **1** were prepared in almost quantitative yields from the reaction of the corresponding ketone with 2 equiv. of MeMgI in diethyl ether (12 h, room temp.) followed by washing of the resulting precipitate with diethyl ether. Crystals of **2** and **2**3·**4**·2CH$_2$Cl$_2$ were obtained by slow diffusion of diethyl ether into dichloromethane/acetonitrile (1:10) solutions of **1a** and **1b**. **1a:** ^{1}H NMR (CDCl$_3$): δ = 0.88 (t, ^3J = 7 Hz, CH$_2$*Me*), 1.51, 1.58 (2 s, PhC*Me*$_2$), 3.43 (q, C*H*$_2$Me), 6.88–7.12 (m, Ph) ppm. ^{13}C NMR (CDCl$_3$): δ = 13.9 (CH$_2$*Me*), 33.7, 34.7 (PhC*Me*$_2$), 65.6 (*C*H$_2$CH$_3$), 71.9 (Ph*C*Me$_2$), 125.6, 126.8, 128.4, 149.9 (Ph) ppm. $C_{13}H_{21}IMgO_2$ (360.52): calcd. I 35.20, Mg 6.74; found I 35.32, Mg 6.78. **1b:** ^{1}H NMR (CDCl$_3$): δ = 0.72 (t, ^3J = 7 Hz, CH$_2$*Me*), 2.01 (s, Ph$_2$C*Me*), 3.3 (q, C*H*$_2$Me), 6.97–7.38 (m, Ph) ppm. ^{13}C NMR (CDCl$_3$): δ = 13.9 (CH$_2$*Me*), 33.7, 34.7 (Ph$_2$C*Me*), 65.6 (*C*H$_2$Me), 71.9 (Ph$_2$*C*Me), 125.6, 126.8, 128.4, 149.9 (Ph) ppm. $C_{18}H_{23}IMgO_2$ (422.59): calcd. I 30.03, Mg 5.75; found I 30.00, Mg 6.19.

Crystallography: Single-crystal data for $C_{26}H_{34}I_2Mg_2N_4O_2$ (**2**): M = 737, monoclinic space group $P2_1/c$, a = 14.407(1), b = 11.459(1), c = 20.623(1) Å, β = 107.01(1)°, V = 3255.7(4) Å^3, Z = 4, $D_{\text{calcd.}}$ = 1.504 g cm^{-3}, μ = 1.997 mm^{-1}, Mo-K_α, λ = 0.71073, T = 173(2) K, $R(F^2 > 2\sigma)$ = 0.0317, $R(F^2$, all data) = 0.0599, goodness-of-fit = 1.166 for all 6646 unique data (45648 measured, 5863 refined, R$_{\text{int}}$ = 0.09030, 2Θ < 52.74°). Single-crystal data for $C_{126}H_{126}Cl_4I_6Mg_7N_6O_8$ (**2**3·**4**·2CH$_2$Cl$_2$): M = 2928, monoclinic space group $C2/c$, a = 23.179(1), b = 21.205(1), c = 28.970(2) Å, β = 112.16(1)°, V = 13187(1) Å^3, Z = 4, $D_{\text{calcd.}}$ = 1.471 g cm^{-3}, μ = 1.582 mm^{-1}, Mo-K_α, λ = 0.71073, T = 173(2) K, $R(F^2 > 2\sigma)$ =

0.0832, $R(F^2$, all data) = 0.1405, goodness-of-fit = 1.145 for all 10614 unique data (69326 measured, 7118 refined, R_{int} = 0.1980, $2\Theta < 48.82°$). CCDC-788536 (**2**), CCDC -788535 (**23·4**·2CH$_2$Cl$_2$) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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