

Fixation of Carbon Dioxide by Oxalic Amidinato Magnesium Complexes: Structures and Reactions of Trimetallic Magnesium Carbamato and Related Complexes

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Dedicated to Professor Heinrich Vahrenkamp on the occasion of his 60th birthday

Keywords: Carbon dioxide fixation / Magnesium / N ligands / C–C coupling

The reaction of oxalic amidines $R^1-N=C(NHR^2)-C(NHR^2)=N-R^1$ with CH_3MgX followed by uptake of CO_2 results in the formation of the trimeric carbamato complexes $[R^1-N=C(NR^2-COO)-C(NR^2COO)=N-R^1]_3Mg_3(THF)_6$ (**2a**: $R^1 = R^2 = Ph$; **2b**: $R^1 = R^2 = p\text{-tolyl}$) as the thermodynamically stable final products of the reaction. Their X-ray crystal structures show that the three metal centres are in a linear arrangement. The central magnesium ion is octahedrally surrounded by six O-donor atoms of the μ_2 -carbamato bridges, while both peripheral magnesium ions are facially coordinated by three O-donor atoms of the carbamato groups and three THF

molecules. This coordination sphere can be considered as a structural model for the active centre in the ribulose-1,5-bisphosphate carboxylase/oxygenase enzyme. Compound **2a** reacts with $ZnCl_2$ or $CoBr_2$, with CO_2 elimination, to form dimeric complexes of the type $[X_2M(oxalamidinato)MX_2][Mg(DMF)_6]$ ($M = Zn, Co$; $X = Cl, Br$). X-ray crystal structure analyses show that the d-metals are tetrahedrally coordinated. The magnesium-bromide-containing intermediates in the formation of **2a** and **2b** are able to transfer CO_2 to acetophenone, thus simulating the CO_2 activation step in enzymatic biotin-dependent carboxylation reactions.

Introduction

Biological transformation reactions of carbon dioxide into organic material by C–C linkage are either activated by biotin-depending enzymes (Acetyl CoA carboxylase) in the fatty acids synthesis, or catalysed by Rubisco in the dark reaction of natural photosynthesis. In both enzymes carbamato magnesium complexes seems to play an essential role. In biotin-containing systems the carbamato magnesium complexes are carriers of “active CO_2 ” which can be transferred to C–H bonds to form the C–COOH group. However, neither the structure of the carbamato complex nor the mechanism of the CO_2 activation reaction have yet been established.^[1–8]

In contrast, in Rubisco the carbamato group does not act as a CO_2 source, but is proposed to serve as proton relay which abstracts the C3 proton from ribulose-1,5-bisphosphate. The resulting enol reacts with carbon dioxide in the coordination sphere of the magnesium centre to form a new C–C bond (for reviews see refs.^[9–11]). The structure of various forms of Rubisco have been elucidated by X-ray crystallography.^[9] In the substrate-free complex the Mg^{II} centre is

octahedrally surrounded by a monodentate carbamato group, two carboxylato ligands and three water molecules.^[12]

It is noteworthy that, so far, the chemistry of abiotic carbamato magnesium complexes is poorly developed, especially with respect to the understanding of their reactivity as CO_2 -transfer reagents.^[13–19] Furthermore, structurally elucidated complexes which might act as structural or functional models for the above-mentioned enzymes are very rare. Only one organometallic mixed Al–Mg alkyl compound has been structurally characterised.^[20a] Recently the X-ray structure of an oligomer consisting of six diethylcarbamato–Mg units has also been reported.^[20b]

We describe here the synthesis, structure, and reactivity of a variety of new magnesium carbamato complexes which may act as models for the above-mentioned CO_2 -transforming systems. The complexes were synthesised from magnesium oxalic amidinates or from the di(isopropyl)amido magnesium complex and carbon dioxide.

Results and Discussion

Synthesis and Structure of Carbamato Mg Complexes

The reaction of tetraphenylloxalic amidine **H₂A** (2.56 mmol, Figure 1) with two equivalents of CH_3MgBr in 50 mL of THF resulted in the deprotonation of the ligand and formation of methane. Subsequent reaction with CO_2 at $-20^\circ C$ afforded a white precipitate (**1a**, 60%). According to the elemental analyses it was contaminated with ca. 10% of complex **2a** which was formed by elimination of $MgBr_2$

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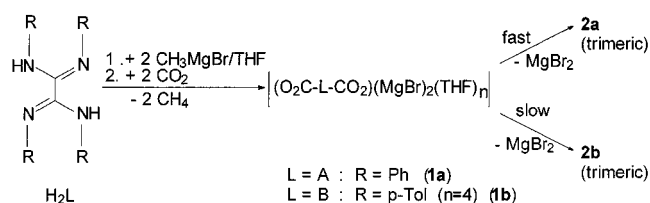
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Figure 1. Pathway of the formation of **2a** and **2b**

from **1a**. Colourless crystals of pure **2a** could be obtained from the filtrate in 30% yield.

When the synthesis was carried out in dilute solution (90 mL of THF) only pure **2a** was isolated in 80% yield. In contrast, the product of the analogous reaction with tetra-*p*-tolylloxalic amidine was analytically pure **1b** (Figure 1).

The IR spectrum of **2a** exhibits two bands in the region of the C=O and C=N valence frequencies at 1630 (less intense) and 1656 cm^{-1} (more intense). This suggests that both C=N and carbamato groups are present in the molecule.

Elemental analysis of **2a** showed that there was no bromide in the CO_2 insertion product and pointed to the analytical composition of $[\text{Mg}(\text{CO}_2)_2(\text{A})(\text{THF})_2]_n$. A spectroscopically identical product was obtained by using dried air for the CO_2 insertion.

Single crystals of **2a** were grown from a dilute THF solution. The X-ray crystal structure revealed a trimeric structure of the product in which three magnesium centres are connected by six μ_2 -carbamato bridges according to the above-mentioned analytical composition $[\text{Mg}(\text{CO}_2)_2(\text{A})(\text{THF})_2]_3$. Figure 2 shows the molecular structure of the

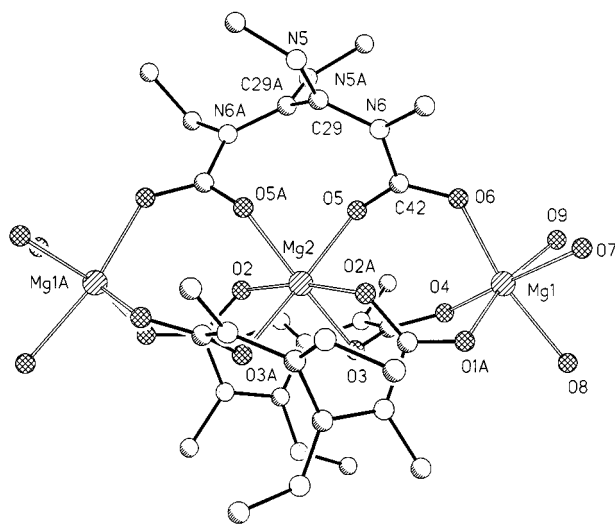
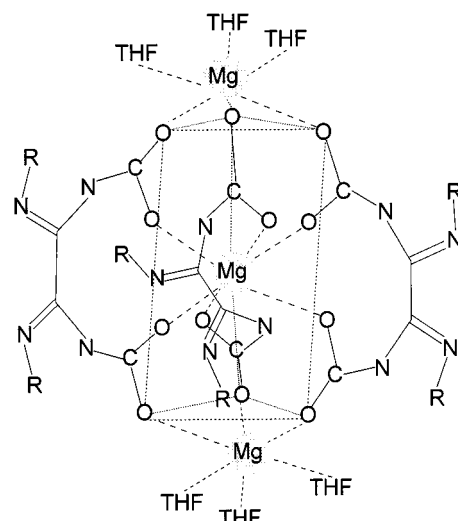


Figure 2. View of the inner sphere of complex **2a** with selected bond lengths [Å] and bond angles [°]: Mg1–O1A 2.021(6), Mg1–O4 2.026(5), Mg1–O6 2.016(6), Mg1–O7 2.169(6), Mg1–O8 2.144(6), Mg1–O9 2.110(7), Mg2–O2 2.075(4), Mg2–O3 2.089(6), Mg2–O5 2.076(6), C42–O5 1.239(8), C42–O6 1.263(9), N6–C29 1.377(10), N6–C42 1.420(10), N5–C29 1.271(10), C29–C29A 1.54(2); O1A–Mg1–O4 97.0(2), O1A–Mg1–O6 98.7(3), O1A–Mg1–O7 89.5(2), O1A–Mg1–O8 85.7(3), O1A–Mg1–O9 168.4(3), O2–Mg2–O2A 170.6(3), O2–Mg2–O3 84.9(2), O2–Mg2–O3A 88.8(2), O2–Mg2–O5 96.3(2), O2–Mg2–O5A 90.6(2), O5–C42–O6 127.6(7), N5–C29–N6 120.3(7); symmetry transformation used to generate equivalent atoms A: $-x - 1, -y, z$

Figure 3. Coordination of the three carbamate strains in **2a** around the Mg centres

molecule and Figure 3 the inner part of **2a**. Relevant bond lengths and angles are also summarised in Figure 2.

The shape of the molecule resembles a straight prism ($h = 6.4 \text{ Å}$) with two eclipsed (by 17°) triangles ($3 \times 3 \times 3 \text{ Å}$) (Figure 3). The three magnesium atoms are exactly linear (the Mg–Mg–Mg angle is 180°) and lie within a distance of $d_{\text{Mg}} = 4.211(6) \text{ Å}$. The central magnesium ion is surrounded by six O-donor atoms of the μ_2 -carbamato bridges in an octahedral fashion, while the two peripheral magnesium ions are facially coordinated by three O-donor atoms of the carbamato groups and three THF molecules. The six negatively charged carbamato groups in **2a** have almost identical C–O distances [$1.25(1) \text{ Å}$] and O–C–O angles [$127.0(4) - 127.6(4)^\circ$]. Three strongly twisted oxalamidine groups are located above the edges of the prism, with the 1,2-diimine units directed outwards, with a torsion angle for the N=C–C=N groups of 122.3° .

Thus, the molecule exhibits three soft Lewis base centres (the uncoordinated 1,2-diimine units) above the edges of the prism and two (potentially hard) Lewis centres (the peripheral magnesium atoms) above the basic triangles of the same prism. Because of the energetically unfavourable “hard-soft” combination the Lewis acid and base centres do not proceed to polymers. However, the free 1,2-diimine units can react with further metal centres (vide infra).

The ^{13}C -NMR spectrum of **2a** in $[\text{D}_6]\text{DMSO}$ has only twelve resonances which correspond to the carboxylated oxalic amidinato ligands. The very strong carbamate signal appears at $\delta = 159.5$ and the signals for THF at $\delta = 67.9$ and 26.3 . This simple pattern clearly shows that the highly symmetrical trimeric structure found by X-ray diffraction remains intact in solution.

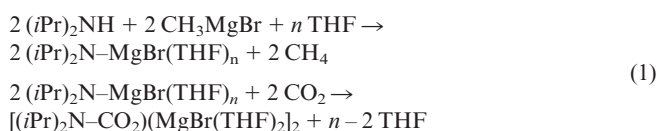
The coordination of the peripheral magnesium atoms resembles the coordination of the magnesium ion in the substrate-free Rubisco enzyme^[4] in which the magnesium centre also has an octahedral environment formed by three facially coordinated COO groups (one from a carbamato ligand and two from carboxylato groups) and three coord-

inated solvent molecules (water). However, the Mg–O(carbamato) distances in **2a** [$d_{\text{Mg-O}} = 2.016(6)–2.169(6)$ Å] are significantly shorter than in the enzyme crystal ($d_{\text{Mg-O}} = 2.31$ Å).

In contrast to the above-described reaction with tetraphenylloxalic amidine, the reaction of tetra-*p*-tolylloxalic amidine **H₂B** with CH_3MgBr , followed by treatment with carbon dioxide, resulted in the pure bromo magnesium complex **1b** with the analytical composition $[(\text{MgBr})_2(\text{CO}_2)_2 \cdot (\text{B})(\text{THF})_4]_n$, which was isolated as a microcrystalline solid. In this reaction the subsequent elimination of MgBr_2 proceeded very slowly (Figure 1). Nevertheless, some crystals of bromide-free carbamato complex **2b** could be obtained from the reaction mixture after some weeks. Compound **2b** was found to be isostructural with **2a** by an X-ray structural analysis.

The ^{13}C -NMR investigations of **1b** pointed to a molecule with only low symmetry; the signal of the carbamato group was found at $\delta = 161.7$. The IR spectrum showed a strong band at 1639 cm^{-1} which may be assigned to the carbonyl group of the carbamato ligand. Since single crystals of **1b** could not be isolated, the structure of this compound remains unknown.

To gain further insight into the coordination sphere in MgBr -containing carbamato complexes, we have also synthesised complex **3** by deprotonation of $(\text{isopropyl})_2\text{NH}$ with one equivalent MeMgBr and subsequent reaction with CO_2 to form a white, crystalline product with the analytical composition $[(i\text{Pr})_2\text{N-CO}_2\text{-MgBr}(\text{THF})_2]_2$ in high yield (95%) (Equation 1).



The ^1H -NMR spectrum of **3** ($[\text{D}_6]\text{DMSO}$, 20°C) shows only the resonances for the protons of the isopropyl group ($\delta = 1.17, 1.20$, and 3.28) and the protons of THF ($\delta = 1.73, 3.57$). However, no signal for the N–H proton was found. Furthermore, the ^{13}C -NMR spectrum exhibits only one, weak carbamate signal at $\delta = 166.39$ in $[\text{D}_7]\text{DMF}$. In addition, the IR spectrum showed no band for the N–H stretching frequency in the 3300 cm^{-1} region. An X-ray crystal structure determination showed the dimeric structure of **3**, which is shown in Figure 4 along with relevant bond lengths and angles. The coordination sphere around the magnesium ions consists of three oxygen donor atoms of the bridging carbamato groups, two axially coordinated THF molecules and one monodentate bromide anion, and can be described as a distorted octahedron. Two of the carbamato oxygens are bonded at a distance of $1.963(2)$ Å, while the third one is more weakly bound with a bond length of $2.358(2)$ Å. Both carbamato groups act as tridentate bridging ligands and form, together with the two Mg ions, a planar eight-membered ring with a Mg–Mg distance of $3.277(2)$ Å.

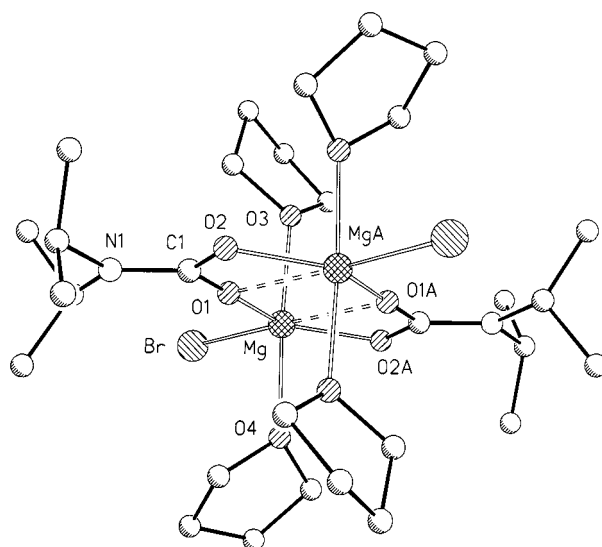


Figure 4. Molecular structure of the dimeric complex **3** with selected bond lengths [Å] and bond angles [$^\circ$]: Mg–Br $2.572(1)$, Mg–O1 $1.963(2)$, Mg–O2A $2.042(2)$, Mg–O1A $2.358(2)$, Mg–O3 $2.117(2)$, Mg–O4 $2.119(2)$, C1–O1 $1.286(3)$, C1–O2 $1.262(4)$, C1–N1 $1.348(4)$, Br–Mg–O1 $108.88(7)$, Br–Mg–O1A $168.95(7)$, Br–Mg–O2A $110.06(7)$, Br–Mg–O3 $89.92(7)$, Br–Mg–O4 $91.49(7)$, O1–C1–O2 $118.8(3)$, N1–C1–O1 $120.5(3)$, N1–C1–O2 $120.7(3)$; symmetry transformation used to generate equivalent atoms A: $-x+2, -y+2, -z+2$

Reactions of the Carbamato Complexes With Metal Halides

The reaction of **2a** with ZnCl_2 in DMF gave the yellow, sparingly soluble complex $[\text{Cl}_2\text{Zn}(\text{A})\text{ZnCl}_2][\text{Mg}(\text{DMF})_6]^{2+}$ (**4**) in 80% yield (with respect to ZnCl_2) even when the starting materials were reacted in the molar ratio 1:1. Using an excess of ZnCl_2 (6:1) resulted in higher yields of **4** (Figure 5)

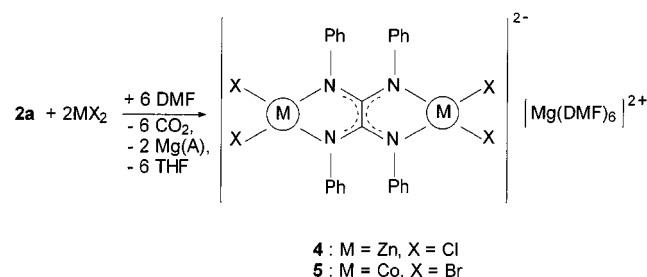


Figure 5. Formation reaction of the dimeric complexes **4** and **5**

An X-ray crystal structure determination (Figure 6) and FAB-MS showed a complex anion with two tetrahedrally coordinated zinc ions bridged by the deprotonated oxalamidine ligand. The electrostatic charge is counterbalanced by a magnesium ion which is surrounded by six DMF molecules. No CO_2 is present in the complex. This structure seems to indicate that coordination of metal fragments at the peripheral 1,2-diimine units of the trimeric complex **2a** causes steric strain in the inner part of the trimer leading to a complete rearrangement of the molecule with elimination of CO_2 and formation of the dimer **4**.

The same reaction was observed when CoBr_2 was treated with **2a** (Figure 5). Single crystals of the resulting green Co complex **5** were obtained from THF. According to the X-

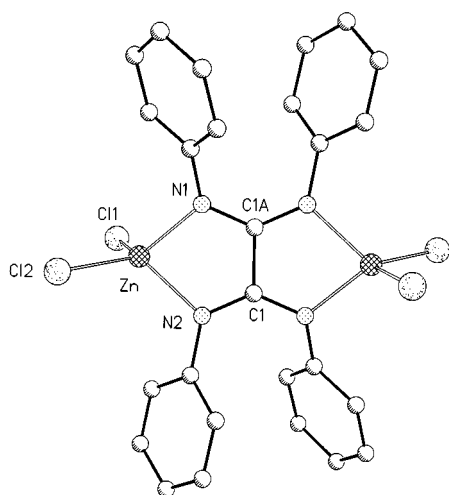


Figure 6. Molecular structure of **4** with selected bond lengths [Å] and bond angles [°] (the cation $[\text{Mg}(\text{DMF})_6]^{2+}$ is omitted for clarity): Zn–Cl1 2.296(1), Zn–Cl2 2.278(1), Zn–N1 2.016(5), Zn–N2 2.020(5), N1–C1A 1.338(7), N2–C1 1.320(7), C1–C1A 1.565(11); Cl1–Zn–Cl2 113.10(7), Cl1–Zn–N1 114.7(1), Cl1–Zn–N2 111.1(1), N1–C1A–N2A 131.9(5), N2–C1–C1A 114.4(6); symmetry transformation used to generate equivalent atoms A: $-x + 2, -y + 2, -z + 1$.

ray structural analysis, compound **5** exhibits the same dimeric structure as found for the Zn complex **4**. The bond lengths and angles in the bridging oxalic amidinate, and between the tetrahedral Co^{II} centres and the nitrogen donor atoms, are also similar (Figure 7).

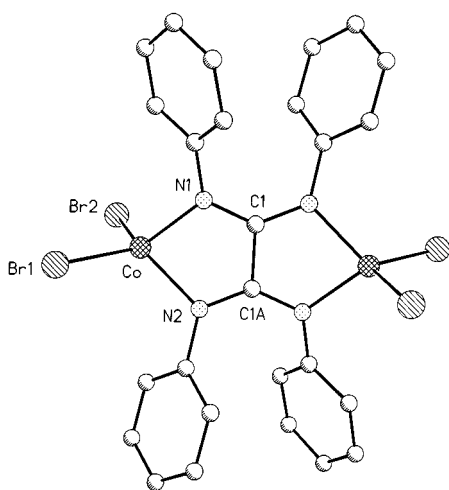


Figure 7. Molecular structure of **5** with selected bond lengths [Å] and bond angles [°] (the cation $[\text{Mg}(\text{DMF})_6]^{2+}$ is omitted for clarity): Co–Br1 2.375(1), Co–Br2 2.375(1), Co–N1 1.986(6), Co–N2 1.999(6), N1–C1 1.340(9), N2–C1A 1.328(9), C1–C1A 1.555(13); Br1–Co–Br2 112.30(6), Br1–Co–N1 115.6(1), Br1–Co–N2 115.0(1), N1–C1–N2A 132.7(6), N1–C1–C1A 113.2(8); symmetry transformation used to generate equivalent atoms A: $-x + 1, -y + 1, -z + 2$.

Carboxylation of Acetophenone

Acetophenone was used as the substrate for CO_2 transfer reactions because it contains the $\text{CH}_3\text{CO-R}$ group which is carboxylated in biotin-dependent reactions as well. The reaction of acetophenone with the carbamate complexes **1b** or **1a** (contaminated with ca. 10% of the inactive trimer **2a**) either in THF at 70 °C or in DMF at room temperature,

followed by hydrolysis, resulted in the formation of the carboxylation product benzoic acid. The free carboxylic acid could either be determined by NMR spectroscopy or by HPLC determination. Although the yields of this C–C-linkage reaction were low (10%), the reaction may be considered as a model step for the CO_2 transfer reaction of carboxybiotin in biological reactions which proceed with acetylCoA to form the carboxylated product $\text{HOOC-CH}_2\text{-CO-CoA}$. In contrast, **2a**, **2b**, and **3** do not contain “activated” CO_2 . This suggests that the coordination environment of the metal centre essentially influences the reactivity of the carbamato–Mg group.

Conclusions

In the present paper we have shown that carbamate magnesium complexes can be synthesised by treating oxalic amidines or di(isopropyl)amine with CH_3MgBr , followed by uptake of CO_2 . The complexes **2a**, **2b**, and **3** represent structurally elucidated carbamate magnesium complexes which are of interest with respect to the magnesium containing active centres of biotin-dependent enzymes and Rubisco. The reaction of ZnCl_2 or CoBr_2 with the free diimine groups of **2a** results in the complete elimination of CO_2 and a rearrangement of the system to form the dinuclear complexes **4** and **5**.

Whereas **2a**, **2b**, and **3** are not able to transfer CO_2 to compounds with C–H-acidic bonds, both the carbamate complexes **1b** and **1a** (containing ca. 10% of the inactive trimer **2a**) react with acetophenone to form benzoic acid upon hydrolysis, simulating the C–C linking step in biotin-dependent CO_2 transfer reactions.

Experimental Section

General: The oxalic amidine ligands were prepared according to literature procedures.^[21] CH_3MgBr and CH_3MgCl (3 M in diethyl ether), purchased from Aldrich, and pure CO_2 (4.8) from Linde AG, were used without additional purification.

All reactions were carried out under argon with standard Schlenk techniques and all solvents dried and distilled before use.

$^1\text{H-NMR}$ spectra were obtained with a Bruker AC 200 MHz spectrometer and all spectra were referenced to TMS or deuterated solvent as an internal standard. FAB mass spectra were obtained with a Finnigan MAT SSQ 710 spectrometer (2,4-dimethoxybenzyl alcohol as matrix). IR measurements were carried out with a Perkin–Elmer System 2000 FT-IR. Analytical HPLC experiments were carried out using a water HPLC system, consisting of a Knauer HPLC pump 64, a Rheodyne 7125 5 μL injector loop, a Merck Li Chrophor RP 18 (5 μm) column and a Knauer variable wavelength detector at $\lambda = 295 \text{ nm}$. The system was controlled by Knauer HPLC 2.21a software. The mobile phase used was 50:50 $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ containing 0.01 M KH_2PO_4 and adjusted to pH = 2. Elemental analyses were carried out at the Microanalytical Laboratory of the Friedrich Schiller University, Jena. Metals were determined by complexometric titration of an aqueous solution, obtained by reaction of the complex with dilute H_2SO_4 , followed by extraction

of the organic products with diethyl ether and subsequent addition of ammonia. Halogen was determined by titration with silver nitrate.

[Mg(CO₂)₂(A)(THF)₂]₃ (2a): One equivalent (per N–H group) of CH₃MgBr (3 M in diethyl ether) was added slowly to a stirred solution of ligand H₂A (1 g, 2.56 mmol) in 50 mL of anhydrous THF until the gas evolution was finished. Then the yellowish solution was cooled to –20 °C and CO₂ was bubbled through the solution for some minutes. The resulting solution was shaken at room temperature for 1 h. After 24 h, a white precipitate of product **1a** (containing ca. 10% **2a** as calculated from the elemental analysis) was isolated by filtration, washed three times with diethyl ether and subsequently dried in vacuo. Yield: 60%. Additionally, pure complex **2a** crystallised from the mother liquor after standing overnight. Yield: 30% of pure **2a**.

When the reaction was carried out in 90 mL of THF as solvent and a CH₃MgBr solution in toluene was used, only pure crystalline **2a** was isolated in 80% yield.

Single crystals of **2a** were obtained by reducing the remaining THF solution to half volume and allowing to crystallise at room temperature, or by recrystallisation of the isolated crude product **1a** from THF. Longer reaction times and higher temperatures resulted in the formation of **2a** in higher yields by accomplished MgBr₂ extrusion.

2a: C₁₀₈H₁₀₈Mg₃N₁₂O₁₈ (1935.03); calcd. C 67.0, H 5.6, Mg 3.8, N 8.7; found C 66.3, H 5.8, Mg 3.7, N 8.7. – ¹H NMR ([D₆]DMSO, 20 °C): δ = 6.63–7.28 (m, arom.). – ¹³C NMR ([D₆]DMSO, 20 °C): δ = 25.2, 67.1 (THF), 120.4, 121.6, 122.0, 124.4, 127.2, 128.2, (arom., phenyl), 143.3 (*ipso*-C-amine), 149.3 (N=C–N), 150.4 (*ipso*-C-imine), 159.5 (carbamate). – IR (nujol): ν̃ = 1592 (C=C_{arom}), 1630, 1656, (N–COO, C=N) cm^{–1}.

Mixture 1a/2a: (90:10) {**1a**: [Mg₂Br₂(CO₂)₂(A)(THF)₄]_n}; calcd. C 56.6, H 4.9, Br 13.4 Mg 5.0, N 6.3; found C 55.4, H 5.3, Br 13.4, Mg 5.0, N 5.8.

[Mg₂Br₂(CO₂)₂(B)(THF)₄]_n (1b): The reaction was carried out as described above for **2a**. The main product in this reaction was **1b**. Yield 92%. – C₄₈H₆₀Br₂Mg₂N₄O₈ (1029.5); calcd. C 56.0, H 5.9, Br 15.4, Mg 4.7, N 5.4; found C 55.0, H 6.1, Br 14.1, Mg 4.5, N 5.3. – ¹H NMR ([D₆]DMSO, 20 °C): δ = 1.73 (dd, 16 H, CH₂), 2.13, 2.26 (2 × s, 12 H, CH₃), 3.57 (dd, 16 H, CH₂), 7.27–6.62 (m, 20 H, arom.). – ¹³C NMR ([D₆]DMSO, 20 °C): δ = 20.8, 20.9, (CH₃), 25.2, 67.0 (CH₂, THF), 120.0, 121.7, 122.3, 128.8, 129.2, 130.8, 131.7, 134.9 (arom. tolyl), 141.6 (*ipso*-C-amine), 148.1 (N=C–N), 151.0 (*ipso*-C-imine), 161.7 (carbamate). – IR (Nujol): ν̃ = 1592 (C=C_{arom}), 1630, 1639 (N–COO, C=N) cm^{–1}.

Single crystals of **2b** were isolated from the mother liquor after storage at –20 °C for some weeks. Yield: 5%. Characterization by X-ray analysis.

[(iPr)₂NCO₂MgBr(THF)₂]₂ (3): The reaction was analogously carried out as described for **2a**. Yield 95%. – C₃₀H₆₀Br₂Mg₂N₂O₈ (785.2); calcd. C 45.9, H 7.7, Br 20.4, N 3.6; found: C 44.6, H 8.2, Br 24.1, N 3.6. – ¹H NMR ([D₆]DMSO, 20 °C): δ = 1.17 (s, 6 H, CH₃), 1.20 (s, 6 H, CH₃), 1.73 (dd, 8 H, CH₂, THF), 3.28 (m, 2 H, CH), 3.57 (dd, 8 H, O–CH₂, THF). – ¹³C NMR ([D₆]DMSO, 20 °C): δ = 19.9 (CH₃), 28.8 (CH₂, THF), 34.2 (C–H), 67.8 (O–CH₂, THF), 166.3 (carbamate). – IR (Nujol): ν̃ = 1578 cm^{–1} (carbamate).

[Mg(DMF)₆][Zn₂(A)Cl₄] (4): Compound **2a** (100 mg, 5.2·10^{–5} mol) was dissolved in 1 mL of anhydrous DMF and ZnCl₂ (42 mg,

31.2·10^{–5} mol), dissolved in 1 mL of DMF, was added. After a few minutes of stirring, a yellow solid precipitated. The solid was filtered off, washed with THF and dried in vacuo. Single crystals were grown from the mother liquor at room temperature. Yield: 152 mg (87%). – C₄₄H₆₂Cl₂MgN₁₀O₆Zn₂ (1123.9); calcd. C 47.0, H 5.5, Cl 12.6, N 12.5; found C 42.7, H 5.1, Cl 12.6, N 11.2. – ¹H NMR ([D₆]DMSO, 20 °C) δ = 2.72 (s, CH₃, 18 H, DMF), 2.88 (s, CH₃, 18 H, DMF), 6.55–6.82 (m, 20 H, arom.), 7.94 (s, 6 H, CH, DMF). – IR (nujol): ν̃ = 1591 (C=C_{arom}), 1659 (C=O, DMF) cm^{–1}. – FAB-MS [DMBA]: *m/z* = 945 [M⁺ – 2 DMF – Cl + 2 H], 622 [M⁺ – 6 DMF – Mg – Cl + 2 H].

[Mg(DMF)₆][Co₂(A)Br₄] (5): This compound was prepared in a similar manner to **4**. Single crystals of the green compound were grown from a solution of the redissolved product in DMF at –20 °C. IR (nujol): ν̃ = 1659 (C=O, DMF), 1591 (C=C_{arom}) cm^{–1}. – FAB-MS [DMBA]: *m/z* = 1288 [M⁺], 838 [M⁺ – 2 DMF – Cl + 2 H – 2 DMF + 2 H⁺], 602 [ACoBr(DMF) + 2 H⁺], 528 [ACoBr + 2 H⁺].

Carboxylation of Acetophenone: Compound **1b** (1.35 mol), dissolved in 70 mL, of anhydrous DMF was treated with 1.2 mL of acetophenone and the resulting solution was stirred for 12 h at room temperature. The resulting benzoyl acetic acid was determined either by aqueous work up or by HPLC.

By Wet Workup: After removal of the DMF in vacuo, the remaining residue was hydrolysed with 50 mL of 25% HCl and the water phase extracted three times with diethyl ether. The organic phase was washed with a 10% solution of Na₂CO₃ and the separated water phase was acidified carefully until pH = 5 and subsequently extracted with diethyl ether. The diethyl ether phase was dried with solid Na₂SO₄ and the solvent removed in vacuo to give benzoyl acetic acid as a white solid. Yield 5–10%. – ¹H NMR ([D₆]acetone, 20 °C): δ = 4.02 (–CH₂–).

By HPLC: Benzoyl acetic acid was determined by comparison with an authentic sample of benzoic acid. Yield: 6–10%.

The reaction product **1a/2a** (90:10) reacts analogously to form 6–10% benzoic acid.

Crystal Structure Determinations: The intensity data for the compounds **2a** and **3** were collected with a Nonius CAD4 diffractometer and for the other compounds with a Nonius Kappa CCD diffractometer, using graphite-monochromated Mo-*K*_α radiation. Data were corrected for Lorentz and polarization effects. Only the compounds **3** and **5** were corrected for absorption effects.^[22,23]

The structures were solved by direct methods (SHELXS^[24]) and refined by full-matrix least-squares techniques against *F*_o² (SHELXL-97^[25]). For compound **4** the hydrogen atoms were located by difference Fourier synthesis and refined isotropically; the hydrogen atoms of the other compounds were included at calculated positions with fixed thermal parameters. All non-hydrogen atoms were refined anisotropically.^[25] XP (SIEMENS Analytical X-ray Instruments, Inc.) was used for structure representations.

Crystal Data for 2a:^[26] C₁₀₈H₁₀₈Mg₃N₁₂O₁₈ · 1.5 C₄H₈O, *M*_r = 2043.15 g mol^{–1}, colourless prism, size 0.40 × 0.38 × 0.36 mm, orthorhombic, space group *Aba*2, crystal is a racemic twin, *a* = 17.978(2), *b* = 23.753(3), *c* = 28.248(3) Å, *V* = 12063 (1) Å³, *T* = –90 °C, *Z* = 4, ρ_{calcd.} = 1.125 g cm^{–3}, μ (Mo-*K*_α) = 0.91 cm^{–1}, *F*(000) = 4320, 6269 reflections in *h*(0/22), *k*(0/29), *l*(0/35), measured in the range 2.27° ≤ Θ ≤ 26.33°, 6269 independent reflections, 3659 reflections with *F*_o > 4 σ(*F*_o), 620 parameters, 1 restraint, *R*_{1obs} = 0.086, *wR*_{2obs} = 0.218, *R*_{1all} = 0.177, *wR*_{2all} = 0.274,

GOOF = 1.765, largest difference peak and hole: 0.862/−0.332 e Å^{−3}.

Crystal Data for 2b: C₁₄₆H₁₈₀Mg₃N₁₂O₂₄, M_r = 2559.95 g mol^{−1}, colourless prism, size 0.40 × 0.35 × 0.30 mm, monoclinic, space group *P*2₁/*c*, a = 24.085(2), b = 18.1640(10), c = 30.297(3) Å, β = 91.274(4)°, V = 13251.1(19) Å³, T = −90 °C, Z = 4, $\rho_{\text{calcd.}}$ = 1.283 g cm^{−3}, μ (Mo- K_α) = 1 cm^{−1}, $F(000)$ = 5472, 30541 reflections in $h(-25/25)$, $k(0/20)$, $l(-30/32)$, measured in the range $2.44^\circ \leq \Theta \leq 23.28^\circ$, completeness Θ_{max} = 97.2%, 17884 independent reflections, R_{int} = 0.099, 10749 reflections with $F_o > 4 \sigma(F_o)$, 1438 parameters, 0 restraints, $R1_{\text{obs}}$ = 0.225, $wR2_{\text{obs}}$ = 0.542, $R1_{\text{all}}$ = 0.281, $wR2_{\text{all}}$ = 0.580, GOOF = 1.255, largest difference peak and hole: 1.063/−0.694 e Å^{−3}.

Crystal Data for 3:^[26] C₃₀H₆₀Br₂Mg₂N₂O₈, M_r = 785.24 g mol^{−1}, colourless prism, size 0.40 × 0.35 × 0.35 mm, monoclinic, space group *P*2₁/*n*, a = 11.062(3), b = 11.743(2), c = 15.184(3) Å, β = 101.38(2)°, V = 1933.6(7) Å³, T = −90 °C, Z = 2, $\rho_{\text{calcd.}}$ = 1.349 g cm^{−3}, μ (Mo- K_α) = 21.73 cm^{−1}, ψ scan, $\text{trans}_{\text{min.}}$: 0.117, $\text{trans}_{\text{max.}}$: 0.279, $F(000)$ = 824, 3762 reflections in $h(0/13)$, $k(-14/0)$, $l(-18/17)$, measured in the range $2.21^\circ \leq \Theta \leq 26.30^\circ$, 3579 independent reflections, R_{int} = 0.028, 2440 reflections with $F_o > 4 \sigma(F_o)$, 319 parameters, 0 restraints, $R1_{\text{obs}}$ = 0.035, $wR2_{\text{obs}}$ = 0.075, $R1_{\text{all}}$ = 0.084, $wR2_{\text{all}}$ = 0.091, GOOF = 1.080, largest difference peak and hole: 0.305/−0.504 e Å^{−3}.

Crystal Data for 4:^[26] [C₁₈H₄₂MgN₆O₆]⁺[C₂₆H₂₀Cl₄N₄Zn₂][−], M_r = 1123.9 g mol^{−1}, colourless prism, size 0.32 × 0.30 × 0.28 mm, triclinic, space group *P*−1, a = 9.6879(4), b = 10.9384(4), c = 13.9082(4) Å, α = 78.401(2), β = 71.791(2), γ = 78.934(2)°, V = 1358.19(8) Å³, T = −90 °C, Z = 1, $\rho_{\text{calcd.}}$ = 1.367 g cm^{−3}, μ (Mo- K_α) = 11.43 cm^{−1}, $F(000)$ = 578, 12317 reflections in $h(0/12)$, $k(-13/13)$, $l(-16/17)$, measured in the range $3.12^\circ \leq \Theta \leq 26.35^\circ$, completeness Θ_{max} = 99.2%, 5496 independent reflections, R_{int} = 0.036, 4374 reflections with $F_o > 4 \sigma(F_o)$, 304 parameters, 0 restraints, $R1_{\text{obs}}$ = 0.083, $wR2_{\text{obs}}$ = 0.210, $R1_{\text{all}}$ = 0.104, $wR2_{\text{all}}$ = 0.228, GOOF = 1.004, largest difference peak and hole: 1.419/−1.350 e Å^{−3}.

Crystal Data for 5:^[26] [C₁₈H₄₂MgN₆O₆]⁺[C₂₆H₂₀Co₂Br₄N₄][−], M_r = 1282.80 g mol^{−1}, colourless prism, size 0.28 × 0.22 × 0.11 mm, triclinic, space group *P*−1, a = 9.8104(6), b = 11.0742(5), c = 14.0020(9) Å, α = 76.997(3), β = 71.602(2), γ = 78.400(3)°, V = 1392.46(14) Å³, T = −90 °C, Z = 1, $\rho_{\text{calcd.}}$ = 1.530 g cm^{−3}, μ (Mo- K_α) = 35.27 cm^{−1}, semi-empirical, $\text{trans}_{\text{min.}}$: 0.432, $\text{trans}_{\text{max.}}$: 0.776, $F(000)$ = 644, 9237 reflections in $h(0/12)$, $k(-13/13)$, $l(-16/17)$, measured in the range $3.04^\circ \leq \Theta \leq 26.49^\circ$, completeness Θ_{max} = 98.5%, 5693 independent reflections, R_{int} = 0.085, 3271 reflections with $F_o > 4 \sigma(F_o)$, 304 parameters, 0 restraints, $R1_{\text{obs}}$ = 0.078, $wR2_{\text{obs}}$ = 0.178, $R1_{\text{all}}$ = 0.1527, $wR2_{\text{all}}$ = 0.2164, GOOF = 0.986, largest difference peak and hole: 0.706/−1.020 e Å^{−3}.

Acknowledgments

Financial support for this work from the Deutsche Forschungsgemeinschaft (SFB 436), the VW-Stiftung and the Fonds der Chem-

ischen Industrie is gratefully acknowledged. M. R. wishes to thank the Studienstiftung des Deutschen Volkes for a grant.

- [1] S. D. Taylor, R. Kluger, *J. Am. Chem. Soc.* **1993**, *115*, 867–871.
- [2] D. J. Kuo, I. A. Rose, *J. Am. Chem. Soc.* **1993**, *115*, 387–390.
- [3] H. Martini, J. Retey, *Angew. Chem.* **1993**, *105*, 287–289; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 278–280.
- [4] F. Lynen, J. Knappe, E. Lorch, G. Jütting, E. Ringelmann, *Angew. Chem.* **1959**, *71*, 481–486.
- [5] F. Lynen, J. Knappe, E. Lorch, G. Jütting, E. Ringelmann, J. P. Lachance, *Biochem. Z.* **1961**, *335*, 123–167.
- [6] S. Berger, A. Braune, W. Buckel, U. Härtel, M.-L. Lee, *Angew. Chem.* **1996**, *108*, 2259–2261; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2132–2133.
- [7] Y. Musashi, T. Hamada, S. Sakaki, *J. Am. Chem. Soc.* **1995**, *117*, 11320–11326.
- [8] T. J. Andrews, G. H. Lorimer, N. E. Tolbert, *Biochem.* **1973**, *12*, 11–17.
- [9] W. W. Cleland, T. J. Andrews, S. Gutteridge, F. C. Hartman, G. H. Lorimer, *Chem. Rev.* **1998**, *98*, 549–561.
- [10] W. A. King, J. E. Gready, T. J. Andrews, *Biochem.* **1998**, *37*, 15414–15422.
- [11] I. Anderson, S. Knight, Y. Lindqvist, T. Lundqvist, C.-I. Bränden, G. H. Lorimer, *Nature* **1989**, *337*, 229–234.
- [12] T. C. Taylor, I. Anderson, *Nat. Struct. Biol.* **1996**, *3*, 95–101.
- [13] A. S. Mildvan, D. C. Fry, E. H. Serpersu, in: *Enzymatic and Model Carboxylation and Reduction Reactions for Carbon Dioxide Utilization* (Eds.: M. Aresta, J. V. Schloss), Kluwer Academic Publishers, Dordrecht, The Netherlands, **1990**, p. 321–345.
- [14] D. Walther, U. Ritter, R. Kempe, J. Sieler, B. Undeutsch, *Chem. Ber.* **1992**, *125*, 1529–1536.
- [15] R. E. Tirpak, R. S. Olsen, M. W. Rathke, *J. Org. Chem.* **1985**, *50*, 4877–4879.
- [16] N. Matsamura, N. Asai, S. Yoneda, *J. Chem. Soc., Chem. Commun.* **1983**, 1487–1488.
- [17] N. Matsamura, T. Ohba, S. Yoneda, *Chem. Lett.* **1983**, 317–318.
- [18] N. Matsamura, T. Ohba, H. Inoue, *Bull. Chem. Soc.* **1982**, *55*, 3949–3950.
- [19] D. Walther, M. Ruben, S. Rau, *Coord. Chem. Rev.* **1999**, *182*, 68–100.
- [20] [20a] C. C. Chang, B. Srinivas, M. L. Wu, W. H. Chiang, M. Y. Chiang, C. S. Hsiung, *Organometallics* **1995**, *14*, 5150–5159. – [20b] C. C. Chang, M. S. Ameerunisha, *Coord. Chem. Rev.* **1999**, *189*, 199–278 and references therein.
- [21] A. Bauer, *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 2650–2662.
- [22] *MOLEN, An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, The Netherlands, **1990**.
- [23] Z. Otwinowski, W. Minor, “Processing of X-ray Diffraction Data Collected in Oscillation Mode”, in: *Methods in Enzymology*, vol. 276, “Macromolecular Crystallography”, Part A (Eds.: C.W. Carter, R.M. Sweet), Academic Press, **1997**, pp. 307–326.
- [24] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **1990**, *46*, 467–473.
- [25] G. M. Sheldrick, *SHELXL-97*, University of Göttingen, Germany, **1993**.
- [26] Crystallographic data (excluding structure factors) for the structures included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-407983 (**2a**), -135156 (**2b**), -135157 (**3**), -135158 (**4**), -135159 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Received July 13, 1999
[199373]