The Function of Magnesium(II) *N,N'*-Dicyclohexylamidinide Complexes as a Carbon Dioxide Carrier

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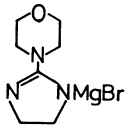
Synopsis. It is found that magnesium(II) *N,N'*-dicyclohexylamidinide complexes are useful reagents for the fixation of carbon dioxide and the transfer of the captured carbon dioxide moiety to active methylene compounds.

A carbon dioxide carrier,[1] which performs its function in the fixation of carbon dioxide and transcarboxylation, is of interest in connection with a biological biotin-dependent carboxylation[2] and in applications to organic syntheses. Recently we have reported that 2-morpholino-4,5-dihydro-1-imidazolylmagnesium complex (**1**) acts effectively as a carbon dioxide carrier in the carboxylation of active methylene compounds under mild conditions.[3] In our continuing investigation of carbon dioxide carrier, we have studied the transcarboxylating function of magnesium(II) complexes **2a**—**d** having an amidinide-type ligand which is derived readily from available dicyclohexylcarbodiimide (DCC). Herein, we wish to report that complexes **2a** and **2b** are the useful carbon dioxide carriers and that the C=N bond, the substituent Y of the amidinide type ligand and the magnesium(II) ion play an important role in the transcarboxylation process.



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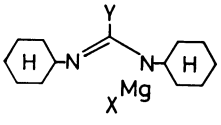
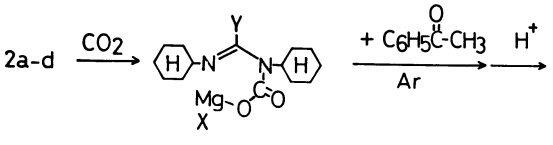


2

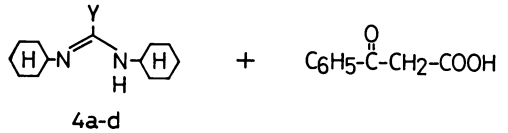
a: Y=C_6H_5, X=Br
b: Y=n-C_4H_9, X=Br
c: Y=CH_3O, X=CH_3O
d: Y=  , X=Br

The transcarboxylating ability of complexes **3a**—**d**, prepared by the reactions of **2a**—**d** with carbon dioxide, was investigated using acetophenone as the substrate. The reaction afforded benzoylacetic acid and **4a**—**d** as the products. The yield of benzoylacetic acid shown in Table 1 indicated that complexes **3a** and **3b** exhibit activity for the transfer of their carbon dioxide moiety to acetophenone, but complexes **3c** and **3d** are much less active. Thus, contrary to complex **1**, the morpholino group of complex **3d** was undesirable for the activation of the carbon dioxide moiety.

Next, the transcarboxylating activity of complex **3b** was compared with that of the lithium–carboxylato complex (**5**). It was observed that acetophenone is carboxylated by **5** in only 10% yield. The fact that the magnesium(II) complex is much more effective than the lithium complex was the same as that in the case of the imidazolinide complex **1** described previously.[3]



3a-d



4a-d

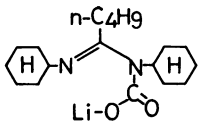
TABLE 1. THE YIELD OF BENZOYLACETIC ACID IN THE REACTION OF ACETOPHENONE WITH COMPLEXES **3a**—**d**

Complex	Yield/%[b]
3a	44
3b	45
3c	Trace
3d	8

a) Solvent; DMF. Temperature; r. t. Reaction time; 40 h.
b) Besed on acetophenone.

In order to investigate whether the C=N bond of the *N,N'*-dicyclohexylamidinide ligand is required for the transcarboxylating function or not, we carried out the carboxylation of acetophenone using complex **6** under the similar conditions. The complex **6** absorbed an equimolar amount of carbon dioxide, but the resulting magnesium(II)–carboxylato complex was found not to transfer the carbon dioxide moiety to acetophenone at all. This fact demonstrates that the C=N bond is necessary for transcarboxylation.

Other active methylene compounds described in Table 2 also were carboxylated by the magnesium(II)–carboxylato complex **3a**. It is interesting that *S*-benzyl thioacetate is carboxylated though in a low yield, since it may be related to CH_3CO–CoA in a biological system.



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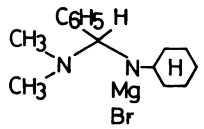


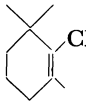
6

Experimental

Materials. Active methylene compounds were distilled or recrystallized prior to use. Tetrahydrofuran (THF) was refluxed over $LiAlH_4$, distilled and stored in argon atmosphere.

Carboxylation of Active Methylene Compounds with 2a—d. A typical experiment was as follows: a solution of phenylmagnesium bromide, butylmagnesium bromide, magnesium dimethoxide, or morpholinomagnesium bromide (8.16 mmol) in THF (10 cm^3) was under argon added to a solution of DCC (6.81 mmol) in THF (10 cm^3) and the solution was stirred for 1 h. After removal of the solvent, the residue was dissolved in 25 cm^3 of *N,N*-dimethylformamide (DMF) by bubbling

Table 2. Carboxylations of active methylene compounds with complex **3a** under argon[a)]

R_1-CO-CH_2-R_2		Yield[b)] of R_1-CO-CH(-R_2)-COOH
R_1	R_2	
p-NO_2-C_6H_4	H	74
p-CH_3O-C_6H_4	H	14
C_6H_5-CH=CH	H	50
	H	68
$C_6H_5CH_2S$	H	24
C_6H_5	CH_3	32
n-C_4H_9	H	8
-$(CH_2)_4$-		25
H	$C_6H_5CH_2$	35

a) Solvent; DMF. Temperature; r. t. Reaction time; 40 h. b) Based on the substrate.

carbon dioxide and the solution was stirred at room temperature for 1 h. The solvent was evaporated *in vacuo* at room temperature and the residue was dried *in vacuo* at 40 °C. The resulting white solid, which contains complex **3**, was allowed immediately to react under argon with active methylene compounds (1.7 mmol) in dry DMF (35 cm^3) at room temperature for 40 h. The formation of complex **3** was confirmed by the method described previously:[3)] complex **3a** was confirmed by the facts that the IR spectrum of the solid has the carbonyl absorption at 1665 cm^{-1} and that complex **2a** absorbs an equimolar amount of carbon dioxide and the fixed carbon dioxide is released quantitatively by treatment with a dilute sulfuric acid solution. The reaction was stopped by adding water. The carboxylation products and **4a**—**d** were isolated in the usual manner and were identified by a comparison of their melting points, IR, ^1H NMR, and mass spectra, and elemental analyses with those of the respective authentic specimens.

*Compounds **4a**—**d***: HCl salt of **4a**: mp 264—265 °C (decomp); IR (KBr) 3420 (NH), 1630 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) 0.5—3.0 (m, 24H, NH+aliphatic) 6.9—7.7 (m, 5H, aromatic). Found: C, 71.11; H, 9.11; N, 8.73%. Calcd for $C_{19}H_{29}N_2Cl$: C, 70.98; H, 8.91; N, 8.54%. **4b**: bp 161—162 °C/7 mmHg; IR (film) 3350 (NH), 1640 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) 0.5—2.5 (m, 29H, aliphatic), 2.5—3.2 (m, 3H, NH+NCH_2); MS *m/e* 264 (M^+), 235, 222, 153, 140, 101, 84, 83. Found: C, 76.95; H, 12.38; N, 10.53%. Calcd for $C_{17}H_{32}N_2$: C, 77.21; H, 12.20; N, 10.59%. **4c**: bp 118—120 °C/2 mmHg; IR (film) 3440 (NH), 1660 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) 0.7—3.4 (m, 23H, aliphatic), 3.5 (s, 3H, OCH_3); MS *m/e* 238 (M^+), 206, 165, 164, 83, 82, 81. Found: C, 70.53; H, 11.24; N, 11.60%. Calcd for $C_{14}H_{26}N_2O$: C, 70.54; H, 10.99; N, 11.75%. **4d**: mp 99—101 °C; IR (KBr) 3380 (NH), 1630 cm^{-1} (C=N); ^1H NMR ($CDCl_3$) 1.0—2.2 (m, 22H, aliphatic), 2.2—3.9 (m, 9H, NH+morpholino). Found: C, 69.58; H, 10.65; N, 14.32%. Calcd for $C_{17}H_{31}N_3O$: C, 69.86; H, 10.92; N, 14.34%.

*The Reaction of Acetophenone with Complex **6**.* A solution of phenylmagnesium bromide (6.81 mmol) in 10 cm^3 of THF was added under argon, drop by drop, to a solution of N^2-cyclohexyl-N^1,N^1-dimethylformamidine (6.81 mmol), which was prepared by the method described in the literature,[4)] in 10 cm^3 of THF at room temperature. The mixture was magnetically stirred at this temperature for 1 h. After removal of the solvent in vacuo, the residue was dissolved in 25 cm^3 of DMF under bubbling carbon dioxide and the solution was stirred under bubbling carbon dioxide at room temperature for 1 h. The solvent was evaporated *in vacuo* at room temperature and the residue was dried *in vacuo* at 40 °C. The resulting white solid, which contains complex **6**, was allowed immediately to react under argon with acetophenone. The reaction mixture was treated by the method being similar to that in the cases of **2a**—**d**. Acetophenone and benzaldehyde were obtained in good yields, but benzoylacetic acid was not detected at all.

References

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