

**Preliminary communication**

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**CATALYTIC FIXATION OF CARBON DIOXIDE UNDER MILD CONDITIONS IN THE SYSTEM:  $\text{TiCl}_4 + \text{Mg} + \text{H}_2$  IN TETRAHYDROFURAN**

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**Summary**

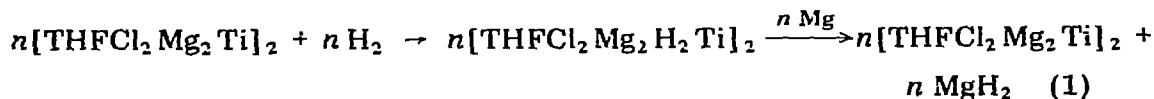
Catalytic fixation of  $\text{H}_2$  and  $\text{CO}_2$  was carried out in the system  $\text{TiCl}_4 \cdot 2\text{THF} + \text{Mg} + \text{THF}$  and as the result magnesium formate was obtained.

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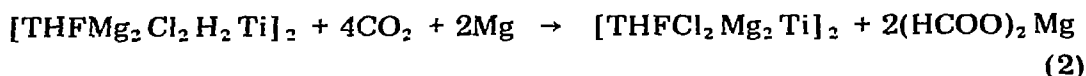
We have previously [1] reported the formation of the complex  $[\text{THFMg}_2\text{Cl}_2\text{Ti}]_2$  (I) in the system  $\text{TiCl}_4 \cdot 2\text{THF} + \text{Mg} + \text{THF}$  under an argon atmosphere. The complex in this system combines with two moles of carbon dioxide, yielding the complex  $[\text{THFTi}(\text{OOCH})_2\text{MgCl}_{1.5}]$  (II) which reacts with  $\text{C}_2\text{H}_5\text{I}$  to give the ester  $\text{HCOOC}_2\text{H}_5$ , and on hydrolysis  $\text{HCCOH}$ .

Now we have succeeded for the first time to catalytically synthesise magnesium formate directly from hydrogen, carbon dioxide and metallic magnesium under mild conditions. Catalytic fixation of  $\text{H}_2$  and  $\text{CO}_2$  was carried out in the system  $\text{TiCl}_4 \cdot 2\text{THF} + \text{Mg} + \text{THF}$  (A);  $\text{TiCl}_4 \cdot 2\text{THF}$  in a solution of tetrahydrofuran (THF) when treated with excess metallic magnesium. The solution changes colour from yellow via green to black. 20 h after the reaction was started argon was replaced by hydrogen. The fixation of  $\text{H}_2$  is catalytically possible only when free metallic magnesium is present in the system. In 24 h at a molar ratio  $\text{TiCl}_4/\text{Mg}$  1/20, 3 moles  $\text{H}_2$  per mole titanium are fixed. If the system  $\text{TiCl}_4 \cdot 2\text{THF} + \text{Mg} + \text{THF} + \text{H}_2$  (B) with fixed hydrogen was used and carbon dioxide was introduced, the  $\text{CO}_2$  fixation was achieved catalytically. The amount of fixed carbon dioxide depends on the amount of fixed hydrogen before introduction of  $\text{CO}_2$  to the system, fixed  $\text{H}_2/\text{CO}_2 \approx 0.5$ . At repeated introduction of hydrogen and carbon dioxide to the system with fixed carbon dioxide, the reaction continued. By alternate introduction of  $\text{CO}_2$  and  $\text{H}_2$  to the system we succeeded in fixation of some 15 moles of carbon dioxide per mole titanium at 50fold magnesium excess. If the catalytic products of  $\text{H}_2$  and  $\text{CO}_2$  fixation after evaporation of tetrahydrofuran under vacuum were treated with  $\text{C}_2\text{H}_5\text{I}$ , all the fixed  $\text{CO}_2$  converted into ethyl formate, and the reaction with dilute sulphuric acid yielded formic acid.

If, after reduction of the system  $\text{TiCl}_4 \cdot 2\text{THF} + \text{Mg} + \text{THF}$  under argon atmosphere the  $\text{H}_2$  and  $\text{CO}_2$  mixture was introduced, only  $\text{CO}_2$  was fixed, the compound  $[\text{THFTi}(\text{OOCH})_2 \text{MgCl}_{1.5}]$  was formed, and the reaction was not catalytic. This fact indicates the hydrogen transfer to magnesium only occurs when titanium in the active complex I has an empty coordination site. Hence it could be expected that the catalytic fixation process of  $\text{H}_2$  and  $\text{CO}_2$  should be as follows: complex I formed under argon atmosphere reacts with  $\text{H}_2$  giving rise to the intermediate compound III, which in reaction with metallic magnesium yields magnesium hydride.



It is most likely that catalytic fixation of carbon dioxide follows via the intermediate compound III and via  $\text{MgH}_2$ .



This reaction is possible as long as  $\text{MgH}_2$  is present in that system. The repeated introduction of  $\text{H}_2$  and  $\text{CO}_2$  to the system with magnesium excess alters the course of reactions 1, 2 and 3.

The reaction in the system  $\text{TiCl}_4 \cdot 2\text{THF} + \text{Mg} + \text{THF}$  does not occur at all, at attempts to carry out the reaction under  $\text{CO}_2$ , or  $\text{H}_2$  and  $\text{CO}_2$  atmosphere failed. The most likely cause is deactivation of the metallic magnesium by carbon dioxide. In such conditions  $\text{Ti}^{\text{IV}}$  cannot be reduced and complex I can not be formed.

## Reference

- 1 B. Jeżowska-Trzebiatowska and P. Sobota, *J. Organometal. Chem.*, 76 (1974) 43.