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Preliminary communication

ALKYL ACETATES BY STOICHIOMETRIC REACTION OF ALCOHOLS WITH THE METHYLENE BRIDGED COMPLEX $[Fe_2(\mu\text{-}CH_2)(CO)_8]$

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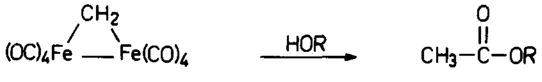
Summary

The stoichiometric reaction of the methylene-bridged complex $[Fe_2(\mu\text{-}CH_2)(CO)_8]$ with methanol and ethanol gives methyl and ethyl acetate, respectively, in high yields. Labelling studies with CH_3OD and CD_3OD provide insight in the reaction steps involved.

The synthesis and reactions of methylene-bridged transition metal complexes have recently attracted much interest because they are regarded as model compounds of the Fischer—Tropsch reaction [1—3]. Thus, the complex $[Fe_2(\mu\text{-}CH_2)(CO)_8]$ reacts with CO/H_2 to give methane and traces of acetaldehyde [4].

Methylene-bridged compounds can also be postulated as intermediates in the homologation of methanol to ethanol. To investigate this possibility we are studying the reaction of methylene-bridged multimetallic complexes with alcohols, which have not, to our knowledge been studied before.

The stoichiometric reaction of $[Fe_2(\mu\text{-}CH_2)(CO)_8]$ with methanol or ethanol was found to give methyl acetate or ethyl acetate, respectively (eq. 1).



(1)

I

II, R = Me III, R = Et

Typically, 1 mmol of I was treated with 4 g of methanol at 60°C for 14 h. The volatile products were distilled off in vacuum and analyzed by GLC using isobutanol as internal standard. Yields of II were 65—75%. The temperature can vary between 20 and 150°C, and the best yield of methyl acetate was observed at 105°C. The reaction was carried out at 30 bar of nitrogen or 30 bar of carbon monoxide. In both cases roughly the same amount of methyl acetate was formed with high selectivity. The carbonyl $Fe(CO)_5$ was observed as a by-product, especially under carbon monoxide pressure. No ethanol or ethyl methyl ether was detected.

However, at 150°C substantial amounts of methyl formate are also formed as a result of the reaction of $Fe(CO)_5$ with methanol, as confirmed by a separate experiment.

At 20°C the reaction is significantly enhanced by addition of monodentate phosphorus ligands as shown in Table 1. The reaction shows little dependence on the electronic and steric properties of the ligands, and yields of 63—79% are achieved.

TABLE 1

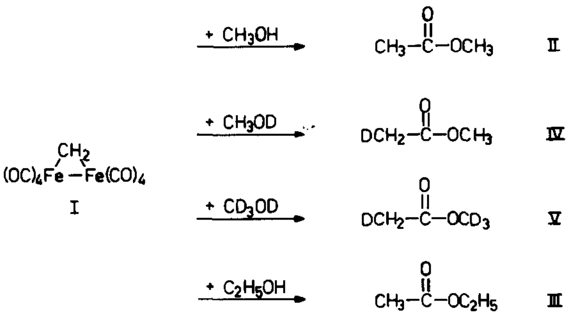
INFLUENCE OF PHOSPHORUS LIGANDS[a]

Ligand	Yield of methylacetate (%)
—	52
Ph_3P	79
$(EtO)_3P$	76
$(i\text{-}Pr)_3P$	72
$(t\text{-}Bu)_3P$	63

[a] Reaction conditions: 1 mmol I; P/Fe = 1; 4 g MeOH; 14 h; 20°C; atmospheric pressure of argon.

Following the work of Shriver [5], who observed the acceleration of CO insertion upon addition of Lewis acids such as $AlBr_3$, a suspension of I in toluene was treated at 0°C in a CO atmosphere with an equimolar amount of $AlBr_3$ in toluene. A deep red solution was immediately formed, which in contrast to I, was air sensitive. Addition of methanol to this solution gave after 2 minutes a 17% yield of methyl acetate, whereas in the absence of $AlBr_3$ no detectable amounts of methyl acetate were formed under identical conditions.

To obtain further information about the reaction mechanism, experiments with deuterated methanol were carried out. Reactions of I with CH_3OD or CD_3OD proceed according to Scheme 1 giving IV and V in yields of 70%. In both cases a monodeuterated acetyl group is exclusively formed. Since the re-



Scheme 1. Reaction of $[Fe_2(\mu\text{-}CH_2)(CO)_8]$ with methanol, deuterium labelled methanol and ethanol.

action also proceeds in the absence of carbon monoxide, the acetyl function is formed from the bridging methylene group, the acidic hydrogen of the alcohol, and CO from I. The structures of IV and V were confirmed by mass spectrometry. The molecular ions $m/e = 75$ ($DCH_2COOCH_3^{+\cdot}$) and $m/e = 78$ ($DCH_2COOCD_3^{+\cdot}$) as well as the key fragments $M^{+\cdot} - 16$ ($DCH_2\cdot$), $M^{+\cdot} - 31$ ($CH_3O\cdot$), $M^{+\cdot} - 34$ ($CD_3O\cdot$), and $m/e = 44$ (DCH_2CO^+, base peak) were observed.

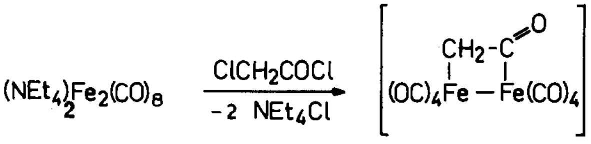
Ethyl acetate III was formed in 69% yield upon addition of ethanol to I. No ethyl propionate, propanol or propyl ethyl ether were detected.

Methyl acetate and ethyl propionate might in principle be formed by carbonylation of the corresponding alcohols, but the experiments with deuterated methanol and the absence of ethyl propionate rule this out.

The absence of ethanol or ethyl methyl ether (in the reaction of I with methanol) and the absence of propanol or propyl ethyl ether (in the reaction of I with ethanol) also exclude a reaction path such as that shown in eq. 2.

$$\mathrm{I} + \mathrm{ROH} \longrightarrow \mathrm{R{-}CH_2{-}OH} \qquad \textbf{(2)}$$

Besides this $(NEt_4)_2Fe_2(CO)_8$ was treated with $ClCH_2COCl$ in expectation of the reaction shown in eq. 3.



(3)

VI

Although VI could not be isolated, the addition of methanol to the deep red solution gave methyl acetate in 32% yield, indicating the formation of VI in the initial reaction.

A plausible explanation for the formation of the products II—V can be based on assumption of intermediates similar to VI, in which a ketene type precursor exists. Herrmann and Meyer [6] observed the elimination of the ketene fragment from the complex $[Rh_2(\mu\text{-}CH_2)(CO)_2Cp_2]$ by mass spectrometry. Our measurements with I at 70 eV and 0.3 mA gave a ketene base peak at $m/e = 42$ ($CH_2CO^{+\cdot}$). Messerle et al. [7] describe the formation of diphenylketene upon reaction of $[Cp_2Mo_2(CO)_4(CPh_2)]$ with CO. Furthermore, carbonylation of a manganese diphenylcarbene complex gave a η^2-diphenylketene complex, which was isolated and characterized by Herrmann et al. [8].

Our results add to the evidence for the remarkable reactivity of methylene-bridged complexes, which open the way to unusual reactions. Further work is in progress, aimed at the isolation of intermediates and trapping of ketene or its derivatives.

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