

## Preliminary communication

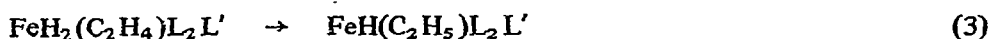
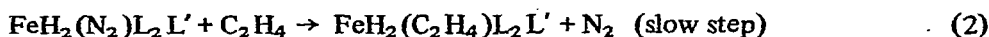
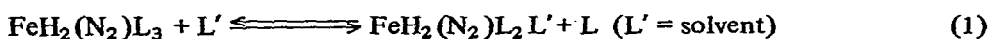
### Reaction of ethylene with a dihydridodinitrogen complex of iron(II)

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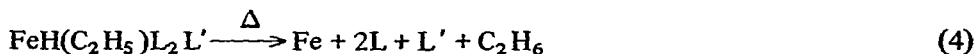
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We recently reported the insertion of  $\text{CO}_2$  into the Fe-H bond of the complex  $\text{FeH}_2\text{N}_2\text{L}_3$  (I) ( $\text{L} = \text{PEtPh}_2$ )<sup>1</sup>. We have investigated now the reaction of the above complex with ethylene in order to determine whether it can act as a polymerization or hydrogenation catalyst toward olefins. The reaction was followed by means of gas-volumetric, chromatographic (GLC) and spectroscopic (IR and NMR) techniques. (NMR was not in fact very helpful because of the formation of paramagnetic iron by decomposition of the reaction product at temperatures near room temperature, coupled with the low solubility of the starting material at lower temperatures.) When the solid, powdered dihydridodinitrogen iron(II) complex (I) was kept under ethylene (1 atm) at room temperature, no uptake of olefin was detected after two days. However, when the complex was dissolved in benzene (or toluene, or THF) a reaction did take place in which the olefin concentration and the temperature exercised important influences. At lower temperatures (near 0°) and with a partial pressure of ethylene of 1 atm, the reaction occurred very slowly ethylene being taken up and nitrogen evolved (one mole per mole), but no insertion of the olefin into the Fe-H bond was observed. On raising the temperature the reaction took place more rapidly, but at the same time the decomposition of the reaction product became significant. At temperatures of about 25–30° the reaction was immediate but the product decomposed spontaneously to give metallic iron, phosphine, and ethane (one mole per mole). The best working temperature was in the range 5–10°, since while the reaction was rather slow, little or no decomposition of the product occurred. From the reaction in this temperature range we have detected in solution a reaction product which we formulate as  $\text{FeH}(\text{C}_2\text{H}_5)\text{L}_2\text{L}'$  (II) ( $\text{L}' = \text{solvent or L}$ ) on the basis of its IR spectrum (in solution), which shows no coordinated nitrogen, but in which a broad band at  $1820\text{ cm}^{-1}$ , attributable to Fe-H stretching, is present, and in accordance with the following scheme:



Warming the solution to 30° caused decomposition of the complex, one mole of ethane per

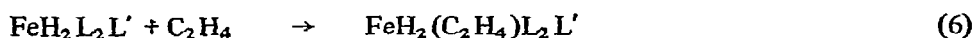
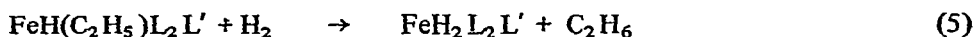
mole of complex being evolved and metallic iron and free phosphine formed according to the reaction:



The evolution of ethane confirms that one hydrogen atom is still bound to the metal in the ethyl complex.

All attempts to isolate the complex in the crystalline state failed owing to its ready decomposition. When the solution of the hydrido-ethyl iron complex (II) was exposed to ethylene at various temperatures, no further uptake of olefin was detected, no decrease in the intensity of the Fe-H stretching band was observed in the IR spectrum, and no dimerization or polymerization products were revealed by GLC after decomposition of the complex.

When a solution of complex (II) was exposed to hydrogen, ethane was produced, and the resulting solution was still able to take up ethylene. The following reaction scheme is proposed:



Likewise, ethane was produced when a solution of complex (I) was exposed to an ethylene-hydrogen atmosphere, the life of the catalyst depending upon the partial pressure of the olefin in the gas mixture; the best results were obtained when an inert gas was used as eluent, and a partial pressure of olefin of only 100 mmHg. On the basis of the results we can affirm that  $\text{FeH}_2(\text{N}_2)\text{L}_3$  is an hydrogenation catalyst, and that the hydrido-alkyl-iron(II) complex  $[\text{FeH}(\text{C}_2\text{H}_5)\text{L}_2\text{L}']$  is the effective intermediate species. Extensions of this investigation to other olefinic systems such as propene, butene, styrene, substituted ethylene, methylmethacrylate etc., are in progress in order to study the influence of the basicity of the olefin on the ability of complex (I) to act as polymerization catalyst. This influence should be related to the stability of the complex of the type  $\text{FeH}(\text{R})\text{L}_2\text{L}'$ , and to the ability of the complex to coordinate a further mole of olefin to give a complex of the type  $\text{FeH}(\text{R})(\text{olefin})\text{L}_2$ . The reactivity of complex (II) toward  $\text{CO}_2$  has been briefly examined, and the first results indicate that at room temperature no insertion of  $\text{CO}_2$  into the Fe-C bond occurs, because of the thermal instability of the alkyl complex. No ester was obtained when a solution of complex (II) was kept under an atmosphere of carbon dioxide for some time and the treated with ethyl bromide, but ethane was again evolved in this reaction.

#### ACKNOWLEDGMENT

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#### REFERENCE

- 1 V.D. Bianco, S. Doronzo and M. Rossi, *J. Organometal Chem.*, 35 (1972) 337.  
*J. Organometal Chem.*, 42 (1972)