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Preliminary communication

REACTION OF CYCLOHEXENE WITH A DIHYDRIDO—DINITROGEN COMPLEX OF IRON(II) AND A TETRAHYDRIDO COMPLEX OF IRON(IV)

V.D. BIANCO*, S. DORONZO and N. GALLO
Istituto di Chimica Generale ed Inorganica, Università di Bari, Bari (Italy)
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Summary

The reaction of cyclohexene with $FeH_2N_2L_3$ and FeH_4L_3 ($L = PEtPh_2$) to give the cyclohexyl derivative $FeH(C_6H_{11})L_2L'$ (L' = solvent) is described, and a possible mechanism suggested.

We have previously described the insertion of CO_2 into the Fe—H bond of the complex $FeH_2N_2L_3$ (I) ($L = PEtPh_2$) [1], and also the reaction of that complex with ethylene [2]. We now consider the insertion of cyclohexene into the Fe—H bond of the dihydridodinitrogen complex (I) and of the tetrahydrido complex FeH_4L_3 (II) ($L = PEtPh_2$). The reaction was followed by means of gas-volumetric, chromatographic (GLC) and spectroscopic (IR) techniques. When the reaction was performed in the absence of solvent, the addition of cyclohexene to the solid, powdered dihydridodinitrogen iron(II) complex (I) at room temperature caused rapid evolution of nitrogen, but the product decomposed. When the complex was dissolved in tetrahydrofuran under nitrogen at room temperature, the nitrogen was eliminated slowly, as shown by the gradual disappearance of the strong band ν(N—N) of the dinitrogen complex (I) at 2060 cm^{-1}. At lower temperatures (near 0°C) the reaction was very slow. Free phosphine was detected by washing with n-pentane, but all attempts to isolate the complex in the crystalline state failed, because of its instability. Probably only one of the Fe—H bonds is involved in the reaction, since the bands ν(Fe—H) did not disappear completely at any of the examined concentrations of the hydride solution, but a short, broad band at 1865 cm^{-1} (in solution) was still present in the IR spectrum:

$$FeH_2N_2L_3 + C_6H_{10} \underset{}{\overset{N_2}{\rightleftharpoons}} FeH(C_6H_{11})L_2L' + N_2 + L \quad (L' = \text{solvent}) \qquad (1)$$

The reaction of complex I with cyclohexene, in the solid or in THF solution, was performed under nitrogen and under argon but the nitrogen of the complex was irreversibly released only when the reaction was performed under argon:

$$\mathrm{FeH_2N_2L_3 + C_6H_{10} \xrightarrow{Ar} FeH(C_6H_{11})L_2L' + N_2 + L} \quad (2)$$

The elimination of the nitrogen was also complete when working with a molar ratio Fe : C_6H_{10} of 1 : 1, since the strong ν(N—N) band at 2060 cm^{-1} of the original dinitrogen complex disappeared completely.

A possible mechanism is one in which a molecule of solvent (L′) first coordinates to the complex with loss of a molecule of phosphine. Subsequently, nitrogen is released and a molecule of cyclohexene attaches to the metal to give a π-cyclohexenyl compound, which in turn is rapidly converted into a cyclohexyl derivative, in accordance with the following scheme:

$$\mathrm{FeH_2(N_2)L_3 + L' \rightleftarrows FeH_2(N_2)L_2L' + L} \quad (3)$$

$$\mathrm{FeH_2(N_2)L_2L' + C_6H_{10} \rightleftarrows FeH_2(C_6H_{10})L_2L' + N_2} \quad \text{(slow step)} \quad (4)$$

$$\mathrm{FeH_2(C_6H_{10})L_2L' \rightleftarrows FeH(C_6H_{11})L_2L'} \quad (5)$$

The tetrahydrido complex FeH_4L_3 in THF, at room temperature and 0°C, also reacted with cyclohexene with evolution of hydrogen and displacement of phosphine, to give the cyclohexyl derivative $FeH(C_6H_{11})L_2L'$, identified by its IR spectrum (in solution). When the reaction was performed under nitrogen, in the first step hydrogen was replaced by nitrogen [3] and the dihydridodinitrogen complex (I) was formed. This then reacted with cyclohexene as in the scheme above. Under argon the dihydrido complex FeH_2L_3 was first formed from the corresponding tetrahydrido complex [3], and insertion of cyclohexene then took place:

$$\mathrm{FeH_2L_3 + C_6H_{10} \rightleftarrows FeH(C_6H_{11})L_2L' + L} \quad (6)$$

Further investigations on the insertion of olefins into the M—H bonds are in progress.

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References

1 V.D. Bianco, S. Doronzo and M. Rossi, J. Organometal. Chem., 35 (1972) 337.
2 V.D. Bianco, S. Doronzo and M. Aresta, J. Organometal. Chem., 42 (1972) C63.
3 M. Aresta, P. Giannoccaro, M. Rossi and A. Sacco, Inorg. Chim. Acta, 5 (1971) 115.