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KINETICS OF THE HOMOGENEOUS HYDROGENATION OF CYCLOHEXENE CATALYZED BY HYDRIDOCOBALT COMPLEXES FORMED IN SITU FROM $CoH(N_2)(PPh_3)_3$

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Summary

A study has been made of the kinetics of homogeneous hydrogenation of cyclohexene catalyzed by hydridocobalt complexes formed in situ from $CoH(N_2)(PPh_3)_3$ at room temperature under dihydrogen at atmospheric pressure, and has revealed that under certain conditions the following rate equation is approached:

Rate = $k_{obs} \cdot [H_2] \cdot [\text{olefin}] \cdot [Co] \cdot [PPh_3]^{-1}$ where [olefin], $[H_2]$, [Co] and $[PPh_3]$ are the concentrations of cyclohexene, dihydrogen, catalyst and free phosphine. The mechanism of the reaction is discussed.

Introduction

Cobalt dinitrogen complexes are known to catalyze several homogeneous reactions such as the isomerization of alkenes[1,2], the dimerization of ethylene[3] and propylene[4,5] and the hydrogenation[6] of olefins. A large number of investigations[7,8] have been performed in recent years to clarify the mechanism of homogeneous hydrogenation.

Our kinetic studies were carried out with the aim of throwing further light on the mechanism of hydrogenation and extending the knowledge of homogeneous hydrogenation processes in general. Cyclohexene was chosen as substrate in order to avoid double bond isomerization as a side reaction.

Experimental

$CoH(N_2)(PPh_3)_3$ was prepared by the published procedure[1]. The benzene used as solvent was distilled over sodium—potassium alloy under dinitrogen. Cyclohexene was purified from peroxides by ferrous sulfate, boiled over sodium—potassium alloy, and distilled under dinitrogen immediately before use. Commercial dihydrogen was purified with diethyl aluminium ethoxide after drying over silica gel and P_2O_5.

Experiments were performed in a water-thermostatted 100 ml reaction vessel connected to a thermostatted gas buret. Cyclohexene and benzene were placed into the reaction vessel under dihydrogen. After addition of the catalyst, the evolved dinitrogen was pumped off and the vessel filled with the dihydrogen. The consumption of dihydrogen was measured by volume.

Results

Experiments were carried out in benzene solution at temperatures between 15° and 30° and pressures between 400 - 1000 mmHg. A range of concentrations of cyclohexene, cobalt catalyst, dihydrogen and free phosphine was examined, and the initial rates were used to determine the rate equation. This procedure avoids any interference from slow side-reactions of the substrate or of the catalyst.

Dihydrogen uptake experiments

Dihydrogen uptake was followed volumetrically using a thermostatted gas buret. In Fig. 1 the amount of dihydrogen consumed is plotted against time. It can be seen that the initial rate is fairly constant in the presence of excess cyclohexene. The experiments were reproducible to within ± 5%, and the rates were obtained from the slopes of plots such as that shown in Fig. 1.

Clear solutions were always obtained after completion of the reaction showing that no heterogeneous catalyst such as metallic cobalt was formed during the reaction.

Dependence on cobalt concentration

The experimental data are shown in Fig. 2. The linear trend obtained with cobalt concentrations lower than 1.5×10^{-2} $\text{mol} \cdot l^{-1}$ suggests a first-order

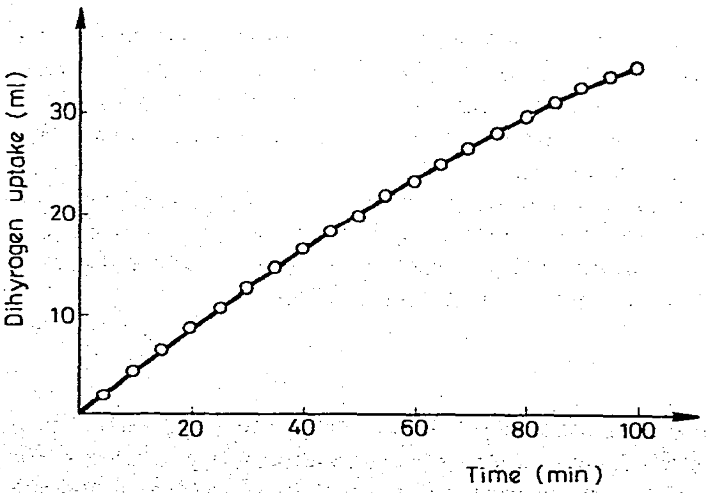


Fig. 1. Typical hydrogenation of cyclohexene using $CoH(N_2)(PPh_3)_3$. Solvent benzene; olefin concn. 3.26 $\text{mol} \cdot l^{-1}$; catalyst concn. 1.61×10^{-2} $\text{mol} \cdot l^{-1}$; temp. 20°C; dihydrogen pressure 1 atm.

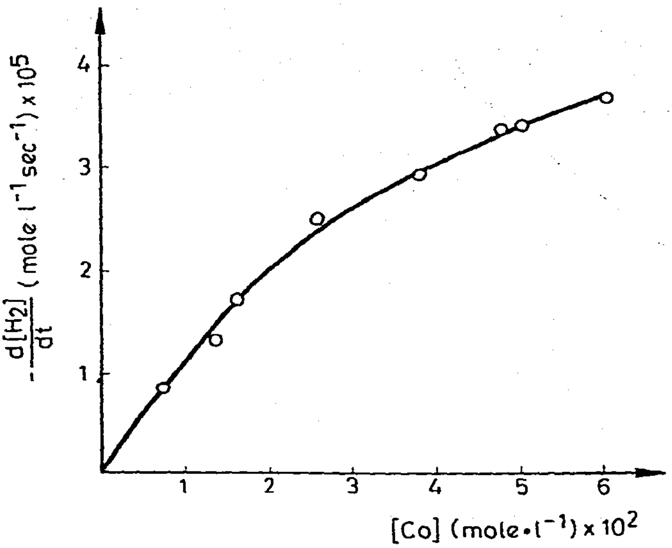


Fig. 2. Rate of hydrogenation of cyclohexene as a function of cobalt concentration. Solvent benzene; olefin concn. 3.26 mol•l^{-1} ; temp. 20°C; dihydrogen pressure 1 atm.

dependence which goes over to a lower reaction order at higher catalyst concentrations. In Fig. 3 the reaction rate is plotted against the square root of cobalt concentration. At concentrations higher than 2.0×10^{-2} mol•l^{-1} a straight line is obtained, indicating a half-order dependence. At smaller concentrations the deviations from the straight line clearly suggest an increase in order with respect to the cobalt concentration. Similar observations were reported by other authors[9,10], who proposed a two-step dissociation of the phosphine ligands bound to the catalyst to form two coordinatively unsaturated species, with the second step taking place only in dilute solutions.

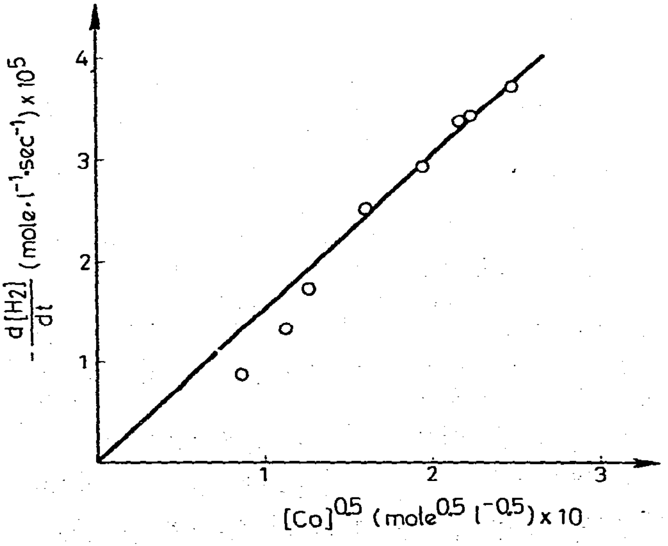


Fig. 3. Rate of hydrogenation of cyclohexene as a function of the square root of cobalt concentration. Solvent benzene; olefin concn. 3.26 mol•l^{-1} ; dihydrogen pressure 1 atm; temp. 20°C.

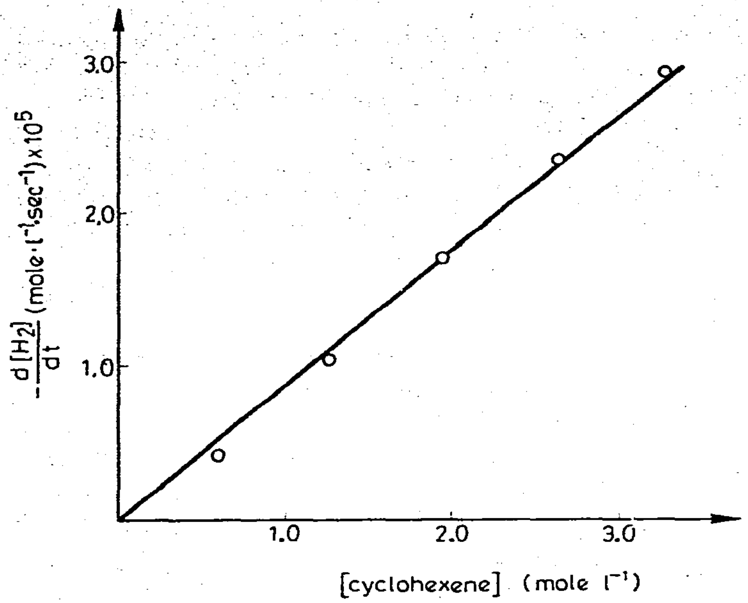


Fig. 4. Rate of hydrogenation of cyclohexene as a function of olefin concentration. Solvent benzene; catalyst concn. 3.87 X 10^{-2}mol·l^{-1}; dihydrogen pressure 1 atm; temp. 20°C.

Dependence on cyclohexene concentration

Hydrogenations were carried out with different initial olefin concentrations and the initial rate of hydrogenation was measured as described above. The experimental data are shown in Fig. 4. The linear relationship suggests a first-order dependence.

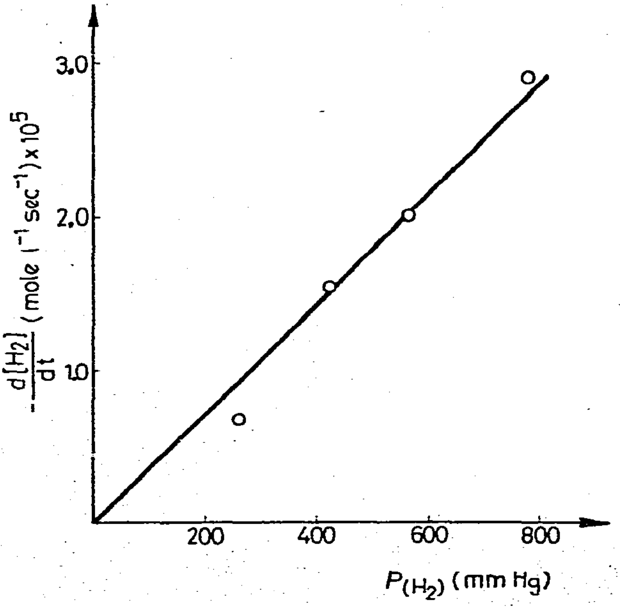


Fig. 5. Rate of hydrogenation of cyclohexene as a function of dihydrogen pressure. Solvent benzene; olefin concn. 3.26 mol·l^{-1}; cobalt concn. 3.87 X 10^{-2}mol · l^{-1}; temp. 20°C.

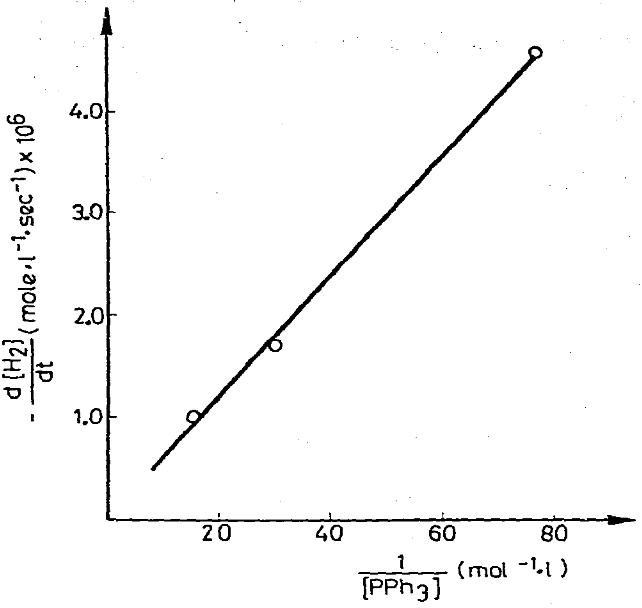


Fig. 6. Rate of hydrogenation of cyclohexene as a function of the reciprocal of the phosphine concentration. Solvent benzene; catalyst concn. 3.83 × 10^{-2}mol·l^{-1} ; olefin concn. 3.26 mol·l^{-1} dihydrogen pressure 1 atm.

Influence of dihydrogen pressure

For hydrogenations under standard conditions and at various dihydrogen pressures a linear plot of the reaction rate against dihydrogen pressure was obtained (Fig. 5).

Effect of phosphine concentration

Excess of free phosphine reduces the hydrogenation rate. In Fig. 6 the hydrogenation rate is plotted against the reciprocal of the added free phosphine concentrations. It can be seen that even a relatively small addition of free phosphine has a large effect. As already suggested by many authors[9,10,11] this effect must be ascribed to the suppression of the dissociation of phosphine from complexes in the catalytic cycle to form vacant coordination sites.

Dependence on temperature

The effect of temperature can be seen in Fig. 7 and Table 1. The results give a linear Arrhenius plot. The activation parameters are ΔE_a = 28.9 kcal·mol^{-1}, $\Delta H^{\ddagger}$ = 28.3 kcal·mol^{-1} and $\Delta S^{\ddagger}$ = 30.3 cal·mol^{-1}·K^{-1}. It should be noted that these values were calculated from k_{obs}, and thus contain the contributions of the preequilibria K_2 and K_5. Any comparison with related data from the literature[9,12] is therefore of little value.

Kinetic isotope effect

The rate of deuteration is very similar to that of hydrogenation; the ratio k_H/k_D was found to be 0.9 - 1.3, showing that primary isotope effect is absent. In other hydrogenation reactions involving $RhCl(PPh_3)_3$ [9], $RhH(CO)_2$-

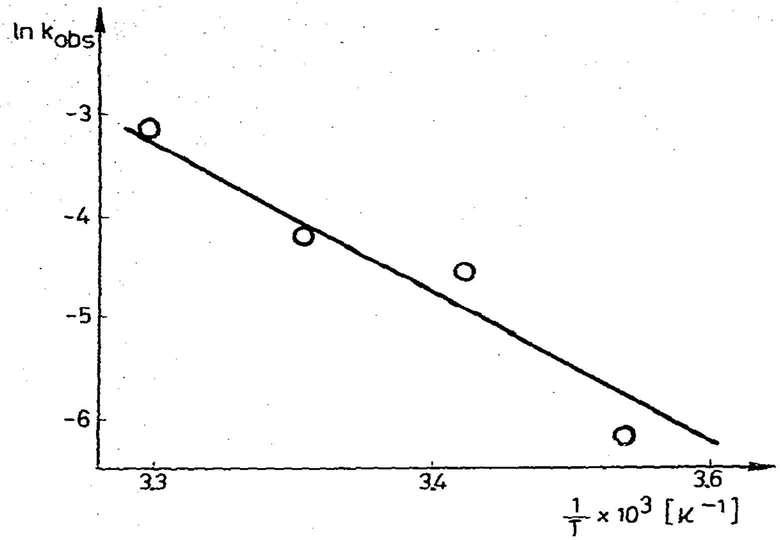


Fig. 7. Arrhenius plot of ln k_{obs} against $1/T \times 10^3$.

$(PPh_3)_2$ [11] and $CoH(CO)_2[P(n\text{-}Bu)_3]_2$[12], k_H/k_D ratios between 0.9 and 1.47 have been reported.

Discussion

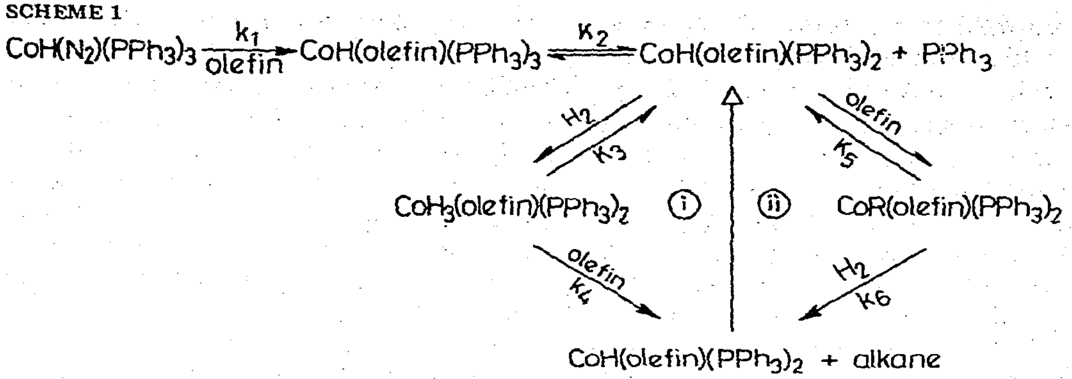
Upon addition of the olefin to a solution of $CoH(N_2)(PPh_3)_3$, dinitrogen is evolved almost quantitatively and the colour of the mixture changes to deep reddish brown. In keeping with this observation, no absorption in the infrared spectrum attributable to $\nu(N_2)$ can be seen. The NMR spectrum of this solution shows a quartet at τ 21.7 ppm, indicating the absence of the dinitrogen complex and suggesting a $CoH(L)(PPh_3)_3$ type species in which L could be H_2 or cyclohexene. The reddish colour of the solution and evolution of dinitrogen without the absorption of an equivalent amount of dihydrogen suggests the formation of the cyclohexene complex in which the Co—H bond is probably *trans* to the coordinated cyclohexene. This species is formed from the dinitrogen complex in an irreversible reaction, and practically all the cobalt added to the reaction mixture is present in this form. It should be mentioned that Deeming et al. [13] recently succeeded in isolating the analogous complex *trans*-$[PtH(C_2H_4)(PEt_3)_2]BPh_4$.

TABLE 1

THE REACTION RATE CONSTANTS k_{obs} AT VARIOUS TEMPERATURES, THE EQUILIBRIUM CONSTANT K_2 AND THE DEGREE OF DISSOCIATION AT 20°

Temperature (°C)	$k_{obs} \times 10^4$ ($mol^{1.5} l^{1.5} \cdot sec^{-1}$)	$K_2 \times 10^4$ ($mol \cdot l^{-1}$)	Degree of dissociation (%)
15	0.20		
20	1.08	1.2	5.4
25	1.49		
30	4.31		

SCHEME 1



The kinetic data reported in this paper may be interpreted in terms of Scheme 1. The reaction of $CoH(N_2)(PPh_3)_3$ with olefin is irreversible and fast. The value of K_2 can be determined from the experiments involving added free phosphine. Equation (1) must apply, and if K_2 is small and a large amount of free phosphine $[L]_{add}$ is added, the amount of the phosphine dissociating from the complex $[L]_{diss}$ may be neglected. Using the value of C thus obtained, the concentration of the dissociated phosphine when no added phosphine is present may be calculated. K_2 was found by this method to be 1.2×10^{-4} mol·l^{-1} at 20°. At the usual concentration of 2.0×10^{-2} mol·l^{-1} [Co] this means that $\approx$ 5% of the cobalt is present as the catalytically active species.

$$([L]_{diss} + [L]_{add}) \times \text{Rate} = C \text{ (constant)} \tag{1}$$

There are two kinetically indistinguishable alternative paths *(i)* and *(ii)* *for the catalytic cycle* as shown in Scheme 1. Ferrari et al. [12] have found that the structurally analogous $CoH(CO)_2[P(nBu)_3]_2$ catalyses H_2—D_2 exchange to form HD at a much lower rate than the hydrogenation of olefin. If this is also the case for the $CoH(N_2)(PPh_3)_3$ reaction, cycle (*i*) is too slow to be considered.

From Scheme 1, the reaction rate can be expressed by equation (2).

$$r = -\frac{d[\text{olefin}]}{dt} = \frac{d[\text{alkane}]}{dt} = k_6 \cdot [\text{CoR(olefin)(PPh}_3)_2] \cdot [H_2] \tag{2}$$

Incorporation of the two pre-equilibria, (3) and (4) gives the rate equation (5).

$$K_2 = \frac{[\text{CoH(olefin)(PPh}_3)_2] \cdot [\text{PPh}_3]}{[\text{CoH(olefin)(PPh}_3)_3]} \tag{3}$$

$$K_5 = \frac{[\text{CoR(olefin)(PPh}_3)_2]}{[\text{CoH(olefin)(PPh}_3)_2] \cdot [\text{olefin}]} \tag{4}$$

$$r = k_6 \cdot K_2 \cdot K_5 \cdot [H_2] \cdot [\text{olefin}] \cdot [\text{CoH(olefin)(PPh}_3)_3] \cdot [\text{PPh}_3]^{-1} \tag{5}$$

According to equation (5) the reaction rate is generally not linear with respect to added cobalt, [Co], since [$CoH(olefin)(PPh_3)_3$] is a complicated function of the total cobalt concentration. A linear relationship should be approximately realized in very dilute solutions in which $CoH(olefin)(PPh_3)_3$ is dissociated to a large extent and practically all the [Co] is transformed into $CoH(olefin)(PPh_3)_2$. Actually at cobalt concentrations below $\approx 1.5 \times 10^{-2}$ mol·l^{-1} an approximate first-order dependence on the catalyst concentration was found. A linear relationship is also to be expected if a large excess of free phosphine is added since [PPh_3] is practically independent of [Co] and most of the [Co] is in the form of $CoH(olefin)(PPh_3)_3$.

At catalyst concentrations above $\approx 2.0 \times 10^{-2}$ mol·l^{-1} we have found an approximately half-order partial rate law with cobalt added. In this case the dependence of [L] on [Co], again practically equal to $CoH(olefin)(PPh_3)_3$, has to be taken into account. Since without added phosphine [PPh_3] = [$CoH(olefin)(PPh_3)_2$] we get the expression (6) for K_2, and with [$CoH(olefin)(PPh_3)_3$] ≈ [Co] this leads to the rate law expressed in eqn. (7).

$$K_2 = \frac{[\mathrm{CoH(olefin)(PPh_3)_2}]^2}{[\mathrm{CoH(olefin)(PPh_3)_3}]} \tag{6}$$

$$r = k_6 \cdot K_2^{0.5} \cdot K_5 \cdot [\mathrm{H_2}] \cdot [\mathrm{olefin}] \cdot [\mathrm{Co}]^{0.5} \tag{7}$$

(where [Co] is the total cobalt concentration)

All the above reasoning is based on the assumption that the preequilibrium K_5 is fast and has a very small value, which we regard as reasonable. Which of the two olefins is transformed to the alkyl group in this step can not be decided on the basis of the available data. Apparently the formation of an alkyl group by olefin insertion into the Co—H bond is brought about by the second olefin molecule, and in this connection it may be further of interest to note that a similar phenomenon may be the cause for a second-order dependence on olefin concentration observed in the case of vinyl—bicycloheptene isomerization with the same catalyst [14]. Complexes such as $CoR(olefin)(PPh_3)_2$ may be the intermediates in the olefin dimerizations already mentioned [3,4,5]. This latter route may be supressed in the present case, however, by the structure of the olefin and the presence of dihydrogen.

References

1 A. Yamamoto, S. Kitazume, L.S. Pu and S. Ikeda, J. Amer. Chem. Soc., 93 (1971) 371.
2 J. Kovács, G. Speier and L. Markó, Inorg. Chim. Acta, 4 (1970) 412.
3 G. Speier and L. Markó, Proceedings of the XIIIth ICCC, Vol. 2, 1970, p. 27.
4 L.S. Pu, A. Yamamoto and S. Ikeda, J. Amer. Chem. Soc., 90 (1968) 7170.
5 G. Speier and L. Markó, unpublished results.
6 M. Hidai, T. Kuse, T. Hikita, Y. Uchida and A. Misono, Tetrahedron Lett., (1970) 1715.
7 R.S. Coffey, in R. Ugo (ed.), Aspects of Homogeneous Catalysis, Vol.1, Manfredi, Milano, 1970, p. 3.
8 A. Andreetta, F. Conti and G.F. Ferrari, in R. Ugo (ed.), Aspects of Homogeneous Catalysis, Vol.1, Manfredi, Milano, 1970, p. 203.
9 J.A. Osborne, F.H. Jardine, J.F. Young and G. Wilkinson, J. Chem. Soc. A., (1966) 1711.
10 C. O'Connor and G. Wilkinson, J. Chem. Soc. A, (1968) 2665.
11 B.R. James and N.A. Memon, Can. J. Chem., 46 (1968) 217.
12 G.F. Ferrari, A. Andreetta and G.F. Pregaglia, J. Organometal. Chem., 43 (1972) 213.
13 A.J. Deeming, B.F.G. Johnson and J. Lewis, Chem. Commun., (1970) 598.
14 J. Kovács, Thesis, University of Chemical Engineering, Veszprém, 1970.