Preliminary communication

HYDROGENATION OF ALKENES CATALYZED BY DINUCLEAR THIOLATO BRIDGED RHODIUM(I) COMPLEXES

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Summary

The catalytic activities of the complexes $[Rh_2(\mu\text{-}SR)_2(CO)_2L_2]$ for the hydrogenation of 1-hexene or cyclohexene have been examined at low pressure; the best yields were observed for L = phosphite. The tetrasubstituted complexes $[Rh_2(\mu\text{-}SR)_2(P(OR')_3)_4]$ were found to be very active catalysts for the same reaction; turnover rates as high as 15 min^{-1} were observed at 20°C and 1 atm of H_2.

There have been many studies of the homogeneous hydrogenation of alkenes catalyzed by transition metal complexes [1—3], especially by Wilkinson's catalyst $[RhCl(PPh_3)_3]$, [4] and more recently $[Rh(COD)(PR_3)_2]^+$ [5] and $[Ir(COD)(PR_3)_2]^+$ [6] where COD is cyclooctadiene. In a key step of the catalytic cycle, the presence of the alkene and hydride ligands on a single metal center in order to obtain the alkane by two successive hydrogen atom transfers involves a subtle balance between the electron density on the metal under the influence of the chloro and phosphine ligands and the steric hindrance of the various ligands. The electron density on the metal is particularly important since a high density prevents the coordination of the alkene while the activation of hydrogen is favoured by electron donating ligands.

Continuing our investigations on the dinuclear bridged d^8 metal complexes [7], we assumed that in a dinuclear entity in which the two metals are held close together by bridging ligands, activation of hydrogen might be realized on one

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metal center while the alkene was coordinated to the other metal atom. This idea was suggested by spectroscopic evidence for the existence of [$H_2(PPh_3)_2Rh(\mu$-Cl$)_2Rh(PPh_3)_2$] [8] and by our isolation of a Rh^I—Rh^{III} complex [9] arising from the oxidative addition of one mol of CH_3I on [$Rh_2(\mu$-S-t-Bu$)_2(CO)_2(PMe_2Ph)_2$]*. Against that background, this communication deals with examination of the homogeneous hydrogenation of cyclohexene or 1-hexene by various dinuclear bridged rhodium(I) complexes as precursors.

Using the complexes [$Rh_2(\mu$-S-t-Bu$)_2(CO)_2(PR_3)_2$] [11] moderate yields were obtained whatever the basicity of the phosphine. However, the complex [$Rh_2(\mu$-S-t-Bu$)_2(P(OMe)_3)_4$], prepared from [$Rh_2(\mu$-Cl$)_2(P(OMe)_3)_4$] [12] by metathesis of the chlorobridges by t-BuSLi [11] or from [$Rh_2(\mu$-S-t-Bu$)_2(COD)_2$] by addition of four moles of ligands [13], showed an interesting catalytic activity. Thus a yield of 70% of cyclohexane was obtained in 2 h for a [complex] to [cyclohexane] ratio of 3.1×10^{-4} (Table 1). Similarly, we prepared the complexes of general formula [$Rh_2(\mu$-S-t-Bu$)_2L_4$], where L is a phosphite ligand. The experiments were performed in batches in a 500 ml stainless steel autoclave, generally at an initial hydrogen pressure of 4 atm. The reaction mixtures were analyzed by GLC and in some case also by ^{1}H NMR. In Table 1 are listed the results obtained for the complexes in which L is trimethyl-, triphenyl- or trilauryl-phosphite. While the nature of the phosphite does not affect significantly the yield, the latter is sensitive to the nature of the alkene, cyclohexene being less readily hydrogenated than 1-hexene.

Using various mercaptans to prepare the RSLi reagent we were able to synthesize the complexes [$Rh_2(\mu$-SR$)(\mu$-SR$')(P(OMe)_3)_4$]. Table 2 shows the yield obtained for the hydrogenation of cyclohexene when the R and R' groups

TABLE 1

HYDROGENATION OF 1-HEXENE OR CYCLOHEXENE CATALYZED BY [$Rh_2(\mu$-S-t-Bu$)_2L_4$] PRECURSORS (AT 40°C)

Complex	substrate	$\dfrac{[\text{complex}]}{[\text{substrate}]}$	initial pH_2 (atm)	time (h)	yield (%)
L = P(OMe)$_3$	cyclohexene	3.1×10^{-4}	4	2	70
L = P(OMe)$_3$	1-hexene	2.8×10^{-4}	1.5	3	100
L = P(OPh)$_3$	1-hexene	5×10^{-3}	4	8	99
L = P(OC$_{12}$H$_{25}$)$_3$	1-hexene	2.5×10^{-3}	4	7	88
L = P(OC$_{12}$H$_{25}$)$_3$	cyclohexene	10^{-3}	4	7	55

TABLE 2

HYDROGENATION OF CYCLOHEXENE CATALYZED BY [$Rh_2(\mu$-SR$)(\mu$-SR$')(P(OMe)_3)_4$] PRECURSORS (AT 40°C AND INITIAL PRESSURE OF 4 atm)

Complex	$\dfrac{[\text{complex}]}{[\text{substrate}]}$	time (h)	yield (%)
R = R' = t-Bu	3×10^{-4}	1.5	59
R = R' = Ph	3.2×10^{-4}	8	20
R = R' = Et	2.4×10^{-4}	9	16
R = t-Bu R' = CH$_2$Ph	10^{-3}	8	67

*While this work was in progress a paper appeared describing the catalytic activity of [$Rh_2(\mu$-H$)_2(P(O$-i-Pr$)_3)_4$] [10] for the hydrogenation of alkenes.
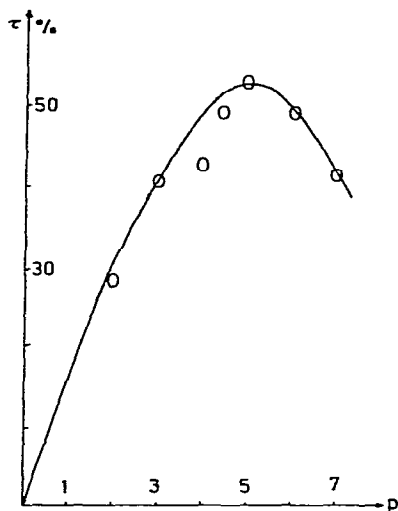
Fig. 1. Yield τ after 30 min of reaction as function of the pressure (atm) for the hydrogenation of cyclohexane catalyzed by $[Rh_2(\mu\text{-S-t-Bu})_2(P(OMe)_3)_4]$.

were varied. Tert-butyl groups appear to favour higher yields. The use of the complex $[Rh_2(\mu\text{-S-t-Bu})_2(P(OMe)_3)_4]$ is particularly attractive owing to its easy preparation and crystallization and to its good solubility in all organic solvents, alkanes included. This latter complex was used for hydrogenations at constant pressure in a stainless steel autoclave. The preliminary experiments show a first-order catalyst concentration rate dependence. However the effect of the pressure on the rate seems particularly troublesome (Fig. 1). Thus a plot of the yield of cyclohexane after 30 min as a function of the pressure shows a maximum at about 5 atm. Such a maximum was also observed when the complexes $[Rh_2(\mu\text{-S-t-Bu})_2(P(OPh)_3)_4]$ and $[Rh_2(\mu\text{-S-t-Bu})_2(P(OC_{12}H_{25})_3)_4]$ were used. Furthermore, the alkene exhibits a slight inhibiting effect on the rate.

In addition we performed some experiments in a glass vessel at 1 atm and the uptake of hydrogen was measured. Thus a solution containing 10 ml of benzene, 10 ml of 1-hexene (0.078 mmol) and 0.265 g of $[Rh_2(\mu\text{-S-t-Bu})_2(P(OMe)_3)_4]$ (3×10^{-4} mole) was introduced into the vessel. An induction period of 4 min was observed during which the brown-yellow solution turned red. The initial hydrogen consumption was 58 ml min^{-1}, i.e. a turn over rate of 9 min^{-1}. After 1 h no further uptake occurred and the GLC measurements revealed that complete hydrogenation of the 1-hexene had taken place. No isomerisation to 2- or 3-hexene was detected. A further addition of 10 ml of 1-hexene gave, without any induction period, an initial turn over rate of 15 min^{-1}. ^{1}H NMR spectra after the reaction were not very informative, since we detected new t-Bu and P(OMe)$_3$ signals but no hydrido signals. Attempts to crystallize the red complex failed.

Further work to elucidate some of these points is in progress.

Acknowledgement

C12

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