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SELECTIVE HYDROGENATION OF UNSATURATED KETONES BY RHODIUM(I) COMPLEXES CONTAINING 2,2'-BIPYRIDINE LIGAND

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Summary

The selective homogeneous reduction of C=O groups in the presence of C=C bonds with $[Rh(Bipy)S_2]^+$ or $[Rh(Bipy)_2]^+$ as catalyst was studied. Stereochemical features of the hydrogenation of substituted cyclohexanones with the two complexes are also reported.

Introduction

The known hydrogenation catalysts, either homogeneous [1—6] or heterogeneous [7], are usually very active for carbon—carbon multiple bonds, but less active for carbonyl groups. This feature, which is mainly due to the higher coordinating power of the olefins, allows saturated ketones to be made from unsaturated ketones with high selectivities [7,8]. In contrast, reduction of unsaturated ketones to unsaturated alcohols is difficult [9], and is usually effected with a stoicheiometric amount of sodium borohydride.

In previous papers [10—12] we reported that rhodium(I) complexes of the type $[Rh(Chel)Hx]^+$ and $[Rh(Bipy)_2Cl_2]Cl$ (Chel = 2,2'-bipyridine; 1,10-phenanthroline and its methyl derivatives; Hx = 1,5-hexadiene) are catalysts for hydrogenation of unsaturated organic substrates such as olefins and ketones. The rate of hydrogenation depends markedly on the Chel/Rh ratio, increasing with this ratio for ketones but decreasing for olefins. We have now found that $[Rh(Bipy)_2]^+$ shows a selectivity similar to that of sodium borohydride in the hydrogenation of unsaturated ketones. In this paper we compare the results for the catalytic hydrogenation of olefins, ketones and unsaturated ketones in systems in which the Bipy/Rh ratios are 1 and 2, and we propose a tentative mechanism to explain their contrasting behaviour.

Results

Catalytic activity of $[Rh(Bipy)S_2]^+$

The catalyst is obtained readily by hydrogenating an alkaline methanol solu-

TABLE 1

HYDROGEN UPTAKE (ml/min) BY UNSATURATED ORGANIC SUBSTRATES (2.5 g) WITH 1×10^{-4} mol CATALYST AT 30°C AND 1 atm

Substrate	$Rh(PPh_3)_3Cl$	$[Rh(Bipy)S_2]^+$	$[Rh(Bipy)_2]^+$
Methyl methacryiate	10	20	<1
1-Hexene		10	<1
Cyclopentene	20	19	<1
Norbornene	14	10	4
Cyclohexene	22	6	<1
Cyclohexanone	0	3	12
2-Cyclohexenone	20	30	<1
2-Methyl-2-cyclohexenone	0.1	12	12
2-Methyl-2-cyclohexenone	0	8	13
Carvone	1	12	27
Dihydrocarvone		6	3
2-Hexyne		18	1

tion of [Rh(Bipy)Hx]Cl. The $[Rh(Bipy)S_2]^+$ (S = solvent), which forms under these conditions, is a good hydrogenation catalyst for carbon—carbon multiple bonds, especially carbon—carbon double bonds activated by electron-withdrawing groups, as for example, those in α,β-unsaturated esters and ketones. Saturated ketones are hydrogenated at lower rates [12] (Table 1). In the case of α,β-unsaturated esters the hydrogen uptake ceases after absorption of one mol of gas per mol of substrate, and the corresponding saturated ester is obtained in 100% yield, as shown by GLC. In the case of ketones the uptake is usually higher than 1, because the hydrogenation of the C=C bond can be followed by the reduction of the carbonyl group. After absorption of one mol of hydrogen per mol of substrate, the yield in saturated ketones is $\geqslant$98% for the 2-cyclohexenone, but decreases to 90% for the 2-methyl- and to 70% for the 3-methyl-2-cyclohexenone, which suggests that in these derivatives the steric requirement of the methyl hinders the π-coordination of the substrate to the metal. Furthermore the different yield of methylcyclohexanones can be explained by assuming that in the 3-substituted derivative the methyl group, while hindering the C=C bond, allows a competitive reduction of the C=O group. Dihydrocarvone affords the corresponding saturated ketone selectively.

Catalytic activity of $[Rh(Bipy)_2]^+$

As previously reported [12] $[Rh(Bipy)_2]^+$ is obtained by reduction of $[Rh(Bipy)_2Cl_2]Cl$ [13] with molecular hydrogen in alkaline methanol. This reduction shows an induction period, which increases with the purity of the sample [14] and can be eliminated by adding a trace of sodium borohydride. The intense violet colour (λ_{max} 557 nm) of the $[Rh(Bipy)_2]^+$ solutions fades only partially in the hydrogen atmosphere, suggesting that the coordinatively saturated dihydridic species is formed with a low equilibrium constant.

(i) Hydrogenation of ketones. $[Rh(Bipy)_2]^+$ is very efficient for the reduction of ketones, as confirmed by the conversion yields, which are $\geqslant$98% for all the substrates listed in Table 2.

From a comparison of the data for acetone, methyl ethyl ketone and methyl isobutyl ketone and for acetophenone and propiophenone, it can be seen that

TABLE 2

HYDROGENATION OF KETONES AT 30°C AND 1 atm IN 20 ml 0.3 *N* METHANOLIC NaOH WITH 1×10^{-4} mol OF $[Rh(Bipy)_2Cl_2]Cl \cdot 2\,H_2O$

Substrate	Hydrogen uptake (ml/min)	Substrate/catalyst
Acetone	12	680
Methyl ethyl ketone	8	560
Methyl isobutyl ketone	3	400
Propiophenone [a]	11	188
Acetophenone [a]	14	214
p-Methylacetophenone [a]	13	188
p-Methoxoacetophenone [a]	10	166
Cyclopentanone [b]	6	565
Cyclohexanone [b]	14	482
2-Methylcyclohexanone [b]	10	410
3-Methylcyclohexanone [b]	11	410
4-Methylcyclohexanone [b]	12	410
4-t-Butylcyclohexanone [b]	10	324

[a] In 10 ml 0.3 *N* methanolic NaOH. [b] At 35°C.

steric effects lower the hydrogenation rate. Highly hindered ketones, such as camphor, do not undergo reduction. A small decrease in the rate is observed also in the series of the *para*-substituted acetophenones on increasing the electron-donating power of the substituent.

In the case of substituted cyclohexanones the resulting alcohols can exist as *cis*- or *trans*-isomers. To study the stereoselectivity of the reaction in the presence of $[Rh(Bipy)_2]^+$, the products were isolated and identified by NMR spectroscopy [15]. The quantitative determination of the isomers was effected by GLC. The results are summarized in Table 3 and compared with those obtained with $[Rh(Bipy)S_2]^+$. It follows that the stereoselectivity of $[Rh(Bipy)_2]^+$ increases on increasing the bulk of the substrate, always giving the thermodynamically less stable isomer in higher yield. It is noteworthy that a good yield is obtained for 2-methylcyclohexanone, even though the reaction is carried out in an alkaline medium. Recent reports [16,17] have shown that the stereoselectivity of the catalytic reduction of this compound with metallic rhodium is high in an acidic or neutral environment, but very low in a basic medium.

The hydrogenation of norcamphor to norbornenol, which can exist in *exo*

TABLE 3

YIELDS OF THE *cis*- OR *trans*-ALKYLCYCLOHEXANOL PREFERENTIALLY FORMED DURING THE HYDROGENATION OF ALKYLCYCLOHEXANONES

Alcohol	Catalyst	
	$[Rh(Bipy)S_2]^+$	$[Rh(Bipy)_2]^+$
2-Methylcyclohexanol	75% *cis*	>95% *cis*
3-Methylcyclohexanol	80% *trans*	80% *trans*
4-Methylcyclohexanol	75% *cis*	70% *cis*
4-t-Butylcyclohexanol	75% *cis*	77% *cis*

TABLE 4

SELECTIVE HYDROGENATION OF KETONES (2×10^{-2} mol) IN THE PRESENCE OF EQUIMOLECULAR AMOUNTS OF OLEFINS, WITH 2×10^{-4} mol OF $[Rh(Bipy)_2Cl_2]Cl \cdot 2\,H_2O$ IN 20 ml 0.3 *N* METHANOLIC NaOH AT 30°C AND 1 atm

Substrate	H_2 uptake (ml/min)	Alcohol (%)	Alkane (%)
Cycloheptene + cyclohexanone	17	98	2
Cyclohexene + cyclohexanone	17	98	2
Cyclopentene + cyclohexanone	3	98	5
Cyclopentene + acetophenone	3	98	5
Cyclopentene + cyclopentanone	2	70	20

and *endo* forms, gives 90% of the *endo*-isomer (CH—OH multiplet centered at δ 4.17 ppm [18]) with $[Rh(Bipy)_2]^+$.

(ii) Hydrogenation of carbon—carbon multiple bonds. The hydrogen uptakes observed at 30°C for the substrates used (methylmethacrylate, 1-hexene, cyclopentene, cyclohexene, norbornene and 2-hexyne) with 1×10^{-4} mol $[Rh(Bipy)_2]^+$ (Table 1), are less than 1 ml/min, except for norbornene (initial rate 4 ml/min). The low activity of the catalyst towards the olefins compared with its high activity towards the ketones, suggested the possibility of a selective hydrogenation of the carbonyl group in the presence of carbon—carbon double bonds.

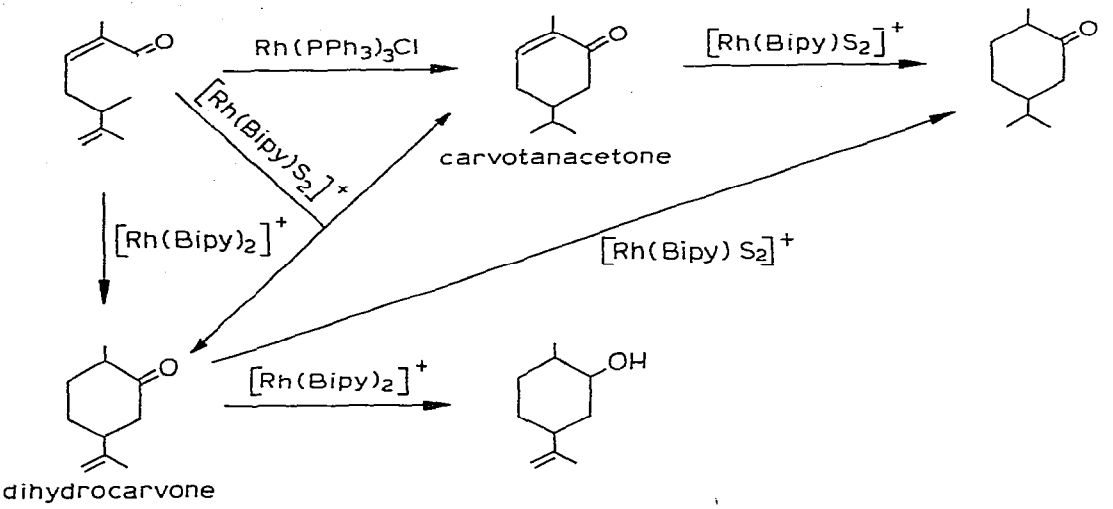
(iii) Hydrogenation of ketones in the presence of olefins. To confirm the above possibility, hydrogenated mixtures of equimolecular amounts of ketones and olefins, were allowed to react until uptake of 1 mol of gas per mol of substrate. Conversion percentages and initial uptake rates are given in Table 4. It can be seen from the results that the hydrogenation of ketones is practically complete in the presence of cyclohexene and cycloheptene, but that the selectivity decreases on increasing the coordinating power of the olefins. Increase in the temperature leads to a higher selectivity [12]. The reaction rates seem to be qualitatively related to the inhibitory action of the olefin on the catalyst.

(iiii) Hydrogenation of α,β-unsaturated ketones. Subsequently we examined the possibility of obtaining unsaturated alcohols from various types of unsaturated ketones (Table 1). The results show that $[Rh(Bipy)_2]^+$ is of low activity for 2-cyclohexenone, while the hydrogenation rate of its 2- and 3-methyl derivatives is comparable with that observed for the corresponding saturated ketones. The gas-chromatographic analysis of the products after uptake of one mol of hydrogen per mol of substrate revealed that the main product was, unexpectedly, the saturated ketone. The unsaturated alcohol is absent, while appreciable amounts of the starting compound and of the saturated alcohol are present. The results imply initial reduction of the conjugated C=C bond followed by hydrogenation of the saturated ketone. Similar behaviour is observed in the presence of $[Rh(Bipy)S_2]^+$, but with a higher selectivity.

We then examined dihydrocarvone, an unsaturated ketone with a terminal substituted carbon—carbon double bond. The unsaturated alcohol, dihydrocarveol, was selectively obtained, whereas as noted above, $[Rh(Bipy)S_2]^+$ gave the saturated ketone dihydrocarvotanacetone.

Afterwards we then looked at carvone, a compound with three potentially

SCHEME 1



reducible functions: one carbonyl group, one conjugated C=C bond, and one isolated C=C bond. The products obtained with various catalysts are shown in Scheme 1. They were identified by IR spectroscopy and gas chromatography. After uptake of one mol of hydrogen per mol of substrate, the carvone is selectively reduced to dihydrocarvone by $[Rh(Bipy)_2]^+$. In contrast, $Rh(PPh_3)_3Cl$ gives carvotanacetone [8], while $[Rh(Bipy)S_2]^+$ hydrogenates both double bonds at approximately the same rate. If the hydrogenation is continued dihydrocarveol is selectively formed with $[Rh(Bipy)_2]^+$, while dihydrocarvotanacetone is the final product with $[Rh(Bipy)S_2]^+$.

Discussion

The results show clearly the differing behaviour of the two catalysts. $[Rh(Bipy)S_2]^+$ is more active in hydrogenating carbon—carbon double bonds than CO groups, and the reaction occurs with a regioselectivity similar to that observed with Wilkinson's complex [8]. However the latter is more active in hydrogenating cyclohexene, while $[Rh(Bipy)S_2]^+$ is a better catalyst than $Rh(PPh_3)_3Cl$ in reduction of carbon—carbon double bonds activated by electron-withdrawing groups. Furthermore, comparison of the rates for various cyclohexenones suggests that the steric hindrance with $[Rh(Bipt)S_2]^+$ is less than that with Wilkinson's complex. On the other hand $[Rh(Bipy)_2]^+$ is a better hydrogenation catalyst for ketones, and can also selectively reduce unsaturated ketones (except the α,β-unsaturated ones) to saturated alcohols.

The hydrogenation in presence of $[Rh(Bipy)S_2]^+$ is probably similar in mechanism with that of $Rh(PPh_3)_3Cl$ [8] and $[Rh(PR_3)_2H_2S_2]^+$ [2,3,5]. The solvated rhodium(I) species may react with molecular hydrogen to give a cationic dihydridic derivative in equilibrium with a neutral hydridic rhodium(I) species. This reaction would be followed by π-coordination of the olefin or σ-coordination of the ketone (which could also coordinate as the enolate [19]). The hydrogenation rates for the various substrates and the regioselectivities

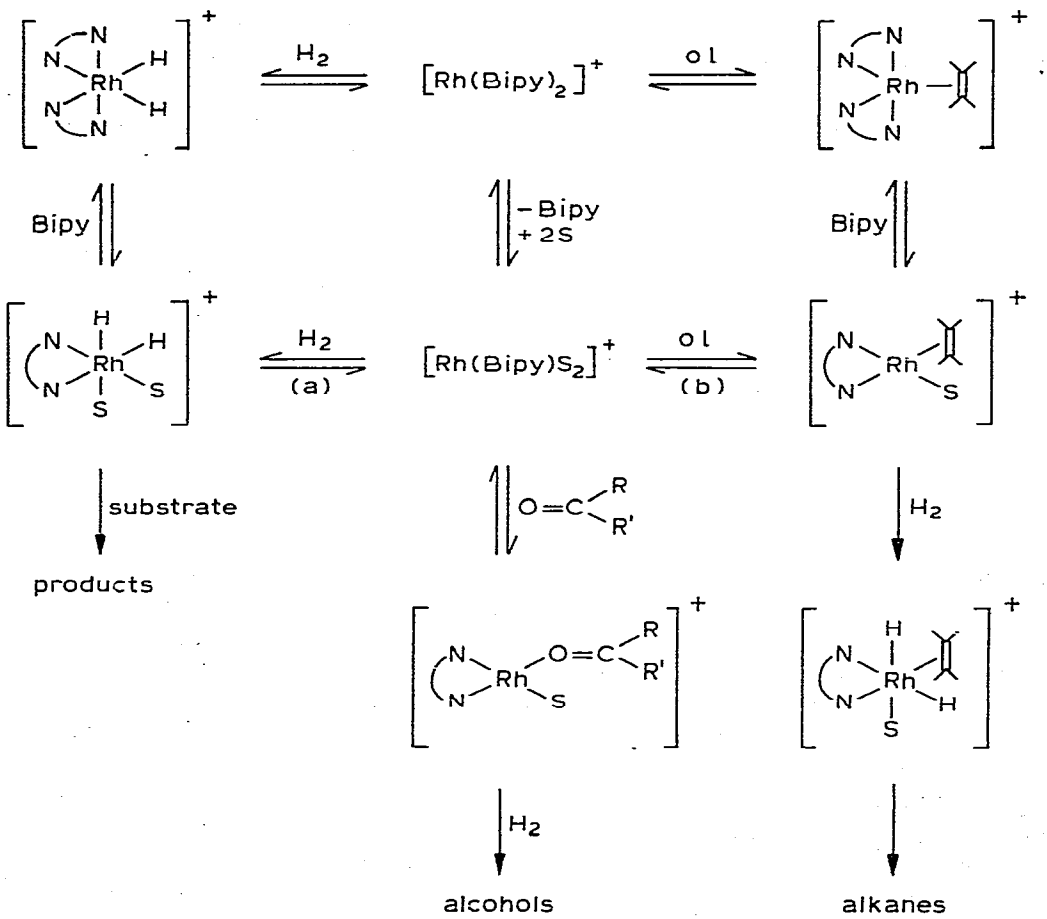
observed are in agreement with the proposed mechanism, the coordinating power of the substrates being in the order: activated olefins > olefins > ketones.

It is more difficult to propose a mechanism consistent with the selectivities found with $[Rh(Bipy)_2]^+$, in which the second molecule of bipyridine must act as a selective inhibitor for the hydrogenation of the olefinic bond.

In general the complexes with two molecules of Bipy have a non planar geometry, owing to the steric interactions between hydrogen atoms in 6 and 6′ positions [20]. While $[Co(Bipy)_2]^+$ has a tetrahedral configuration, $[Rh(Bipy)_2]^+$ probably shows only a small distortion from the square planar structure, as in $[Pd(Phen)_2]^{2+}$ [21] or in the isoelectronic $[Pd(Bipy)_2]^{2+}$ [22,23]. The square planar structure is found in the great majority of rhodium(I) complexes, and in any case would be favoured with this chelating ligand over a tetrahedral structure by the greater delocalization.

When $[Rh(Bipy)_2]^+$ reacts with molecules able to subtract charge from the metal (e.g. Cl_2, H_2, oxidative addition) or when an olefin coordinates to the metal (coordinative addition), bonding with one of the two orbitals engaged in

SCHEME 2



the delocalization, the Bipy moieties can reduce the steric interaction in the molecule by assuming a *cis*-position [24].

When the ligand is σ-coordinated (e.g. OH^-, Cl^-, H^+) the steric hindrance can be relieved by dissociation of a molecule of Chel from the complex *. Thus an equilibrium between $[Rh(Bipy)_2]^+$ and solvated $[Rh(Bipy)S_2]^+$ species is probably established in our system. A tentative mechanism is given in Scheme 2.

The low hydrogenation rates generally observed for the olefins are associated with the presence in the system of free Bipy derived from the above dissociation. In fact Bipy can easily react with the active species $[Rh(Bipy)H_2]^+$ (a, hydridic route) or $[Rh(Bipy)ol]^+$ (b, unsaturated route) formed from $[Rh(Bipy)S_2]^+$ affording the inactive species $[Rh(Bipy)_2H_2]^+$ and $[Rh(Bipy)_2ol]^+$. These are formed also from $[Rh(Bipy)_2]^+$, but, as mentioned above, with a low equilibrium constant. It must be noted also that the high delocalization of the chelating system is thermodynamically unfavourable for oxidative addition reactions. For instance, in the following series of iridium complexes $[Ir(Bipy)COD]^+$ (I); $[Ir(bAdH)COD]^+$ (II); $[Ir(DMG)(COD)]^+$ (III) (bAdH = diacetyldihydrazone; DMG = dimethylglyoxime) the low delocalization of the π-system of the ligands in II and III allows, almost quantitative, reversible addition of dihydrogen at room temperature and atmospheric pressure, while I gives essentially no reaction [12,25].

In the case of bulky olefins the stability of the inactive pentacoordinated species is decreased and the concentration of the less hindered coordinatively, unsaturated species and hence the hydrogenation rate is increased. This may explain why norbornene is hydrogenated more rapidly than cyclopentene, and why the rate sequences in the cyclohexenone series are the opposite of those observed with $[Rh(Bipy)S_2]^+$ or with the Wilkinson's catalyst (Table 1).

In the reaction with ketones, the reentry of the second Bipy molecule to form a planar complex is sterically more difficult and therefore the substrates can be hydrogenated rapidly.

Further experiments with other ligands are in progress. Preliminary results with 2,9-phenanthroline suggest that the hydrogenation rates can be improved by use of ligands having an electronic structure more delocalized than Bipy.

Experimental

Techniques

NMR spectra were recorded with a Jeol JNM-C-60HL Spectrometer at 60 MHz. Gas chromatograms were performed with a C. Erba Fractovap GT (2 m columns with 15% Carbowax 20M on Chromosorb W, 60/80 mesh, were used, except for the separation of the cyclohexanols when the active phase was 10% β,β′-oxydiproprionitrile).

The hydrogenations were carried out at atmospheric pressure with magnetic stirring in a thermostatted vessel connected to a gasometric burette. The substrates were added under hydrogen.

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* See for example the rapid reaction of $[Pd(Phen)_2]^{2+}$ with anionic species to give Pd(Phen)X, with displacement of a molecule of Phen. This dissociation should be favoured by an increase of the σ-donating power of the entering ligand.

Chemicals

The organic substrates used were commercially available, except for the 2-methyl-2-cyclohexenone; this was prepared by the method of Warnhoff et al. [26]. The compound was purified by fractional distillation with a spinning band column.

Preparation of the catalysts. $[Rh(Bipy)S_2]^+$: to a 40 ml of a 0.3 *N* NaOH methanolic solution containing 17 mg Bipy (1.09×10^{-4} mol) were added 20 mg of $[RhHxCl]_2$ (0.9×10^{-2} mol) [12], and the solution was hydrogenated for 30 min.

$[Rh(Bipy)_2]^+$: 55 mg of $[Rh(bipy)_2Cl_2]Cl \cdot 2\ H_2O$ (1×10^{-4} mol) [13] were added to 10—20 ml of a 0.3 *N* NaOH methanolic solution and the solution was hydrogenated for 1 h at 30°C.

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