Hydrogenation of alkenes and ketones catalyzed by rhodium(I) complexes containing thiophosphine ligands

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Abstract

Rhodium(I) complexes containing hybrid 'hemilabile' ligands of general formula $[Rh(NBD)(PSR)]^+$ and $[Rh(PSR)_2]^+$ (R = Me, Et, Ph) were checked as hydrogenation catalysts of terminal olefins to alkanes and of ketones to the corresponding alcohols. The profiles of the hydrogen uptake were determined for the above complexes.

Introduction

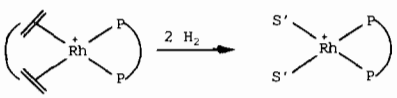
We recently reported [1] on the synthesis and multinuclear NMR characterization of cationic rhodium complexes of general formula $[Rh(diene)(PSR)]^+$ or $[Rh(PSR)_2]^+$, where diene is cycloocta-1,5-diene (COD) or bicyclo-hepta-1,5-diene (NBD) and PSR are various thiophosphine ligands of composition $Ph_2P(CH_2)_nSR$ ($n = 1$, R = Ph: PSPh-C_1; $n = 2$, R = Ph: PSPh-C_2; $n = 2$, R = Me: PSMe-C_2; $n = 2$, R = Et: PSEt-C_2; $n = 3$, R = Ph: PSPh-C_3). These complexes have been previously found to be effective catalysts for the O_2-oxidation of terminal olefins to methylketones [2]. On the other hand, it is well known that the closely related rhodium(I) complexes with diphosphine ligands are among the most popular catalysts for the hydrogenation of various substrates, such as olefins and ketones, the source of hydrogen being H_2 or isopropanol, respectively [3, 4].

With the aim of checking the effectiveness of the thiophosphine complexes in the hydrogenation of olefins and ketones, we report here some results obtained using $[Rh(NBD)(PSR)]^+$ or $[Rh(PSR)_2]^+$ complexes as catalysts.

Results

Catalytic hydrogenation of alkenes

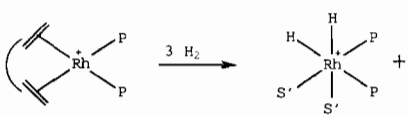
Methanol solutions of the $[Rh(NBD)(PSR)]BF_4$ complexes rapidly absorb molecular hydrogen at atmospheric pressure and 25 °C. The various complexes behave differently and the amount of absorbed hydrogen ranges between 92% for $[Rh(NBD)(PSPh\text{-}C_1)]^+$ and 52% for $[Rh(NBD)(PSPh\text{-}C_3)]^+$, of the theoretical values, calculated for the absorption of 3 mol of H_2 per mole of complex (see eqn. (2)). The complexes containing the PSR-C_2 ligands give intermediate results, being influenced by the nature of the organic substituents at the sulfur atom. The time course of H_2 absorption is given in Fig. 1. The amounts of absorbed hydrogen after 30 min are listed in Table 1. The general behaviour of the above complexes does not agree with that of the parent $[Rh(NBD)(diphos)]^+$ derivatives, which are reported to react with exactly 2 mol of H_2 per mole of complex, following eqn. (1) [5].



(1)

S' = solvent

The $[Rh(NBD)(PSR)]^+$ complexes are instead more strongly related to the monophosphino complexes $[Rh(NBD)(PR_3)_2]^+$ [3], which take up 3 mol of H_2 per mole of complex, leading to the formation of the corresponding dihydride derivatives (eqn. (2)).



(2)

S' = solvent

The different reactivity towards molecular hydrogen exhibited by $[Rh(NBD)(PSR)]^+$ and

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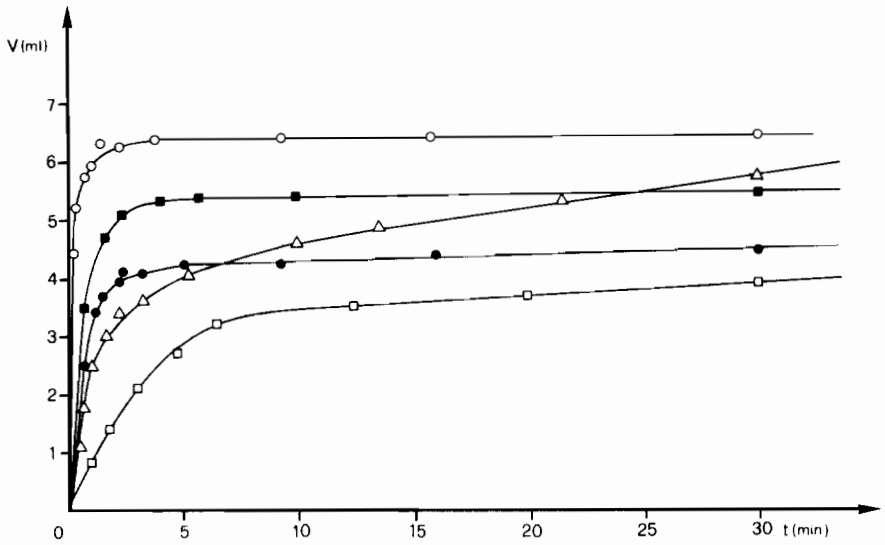


Fig. 1. Absorption curves of H_2 in methanol (20 ml) at 1 atm. and 25 °C for the complexes: △, [Rh(NBD)(PSPh-C_1)]BF_4 (0.0806 mmol); ○, [Rh(NBD)(PSMe-C_2)]BF_4 (0.0842 mmol); ■, [Rh(NBD)(PSEt-C_2)]BF_4 (0.0755 mmol); ●, [Rh(NBD)(PSPh-C_2)]BF_4 (0.0792 mmol); □, [Rh(NBD)(PSPh-C_3)]BF_4 (0.0830 mmol).

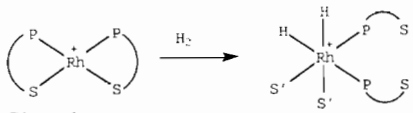
TABLE 1. Absorption of H_2 by rhodium(I) complexes[a]

Complex	H_2/catalyst[b]	H_2 absorbed (%)
[Rh(NBD)(PSPh-C_1)]BF_4	3	92
[Rh(NBD)(PSMe-C_2)]BF_4	3	90
[Rh(NBD)(PSEt-C_2)]BF_4	3	85
[Rh(NBD)(PSPh-C_2)]BF_4	3	67
[Rh(NBD)(PSPh-C_3)]BF_4	3	52
[Rh(PSPh-C_1)$_2$]BF_4	1	97
[Rh(PSPh-C_2)$_2$]BF_4	1	10
[Rh(PSPh-C_3)$_2$]BF_4	1	61

[a]Methanol solution, at 1 atm. and 25 °C after 30 min. [b]Theoretical molar ratio.

$[Rh(NBD)(diphos)]^+$ could be explained on the basis of a more or less quantitative formation of dihydride species, likely containing the thiophosphinic ligands acting as bridging bidentate ligands between two rhodium atoms. Significantly, the complex containing the PSPh-C_1 ligand, which gives rise to a very constrained four-membered metallocycle, gives the maximum extent of H_2 absorption (92%). Metal–sulfur bond cleavage in thiophosphine chelates is a rather common feature and has been repeatedly observed [6].

The rhodium(I) bis-thiophosphine derivatives $[Rh(PSPh\text{-}C_1)_2]^+$, $[Rh(PSPh\text{-}C_2]_2]^+$ and $[Rh(PSPh\text{-}C_3)_2]^+$ also react with molecular hydrogen in methanol solution, at 25 °C and atmospheric pressure. The absorption profiles and the amount of H_2 absorbed after 30 min are shown in Fig. 2 and in Table 1, respectively. Again, the observed reactivity markedly contrasts with the well-known lack of reactivity toward hydrogen exhibited by the parent diphosphine complexes $[Rh(diphos)_2]^+$ (diphos = 1,2-bis(diphenylphosphino)ethane or bis(diphenylphosphino)methane) [3]. Also in the present case, as in the $[Rh(NBD)(PSR)]^+$ complexes discussed above, dihydride derivatives are likely formed, possessing two monodentate PSR ligands, via Rh–S bond cleavage (eqn. (3)). Again, the complex containing the strained PSPh-C_1 ligands is, by and large, the most reactive (92% of absorbed hydrogen).



(3)

S′ = solvent

Our attempts to investigate directly the nature of the species arising from hydrogen addition to the rhodium(I) complexes were however unsuccessful. In fact, although a rapid change is observed in the $^{31}P\{^1H\}$ NMR spectra, when acetone-d_6 solutions of $[Rh(NBD)(PSR)]^+$ are kept under an hydrogen atmosphere, the distinctive doublets of the starting complexes are invariably replaced by a very complex pattern of signals, likely due to the presence of a variety of hydride species. Accordingly, ^1H NMR spectra were poorly resolved and exhibited only weak unstructured signals in the rhodium–hydride region.

The $[Rh(NBD)(PSR)]^+$ and $[Rh(PSR)_2]^+$ complexes in methanol solution have been checked as catalysts for the homogeneous hydrogenation of 1-hexene, at 25 °C and atmospheric pressure, but only

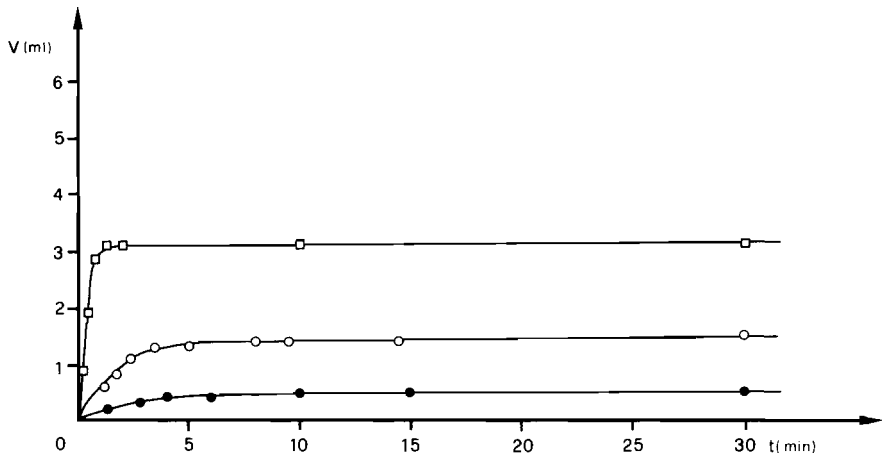
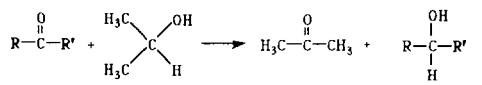


Fig. 2. Absorption curves of H_2 in methanol (20 ml) at 1 atm. and 25 °C for the complexes: □, $[Rh(PSPh\text{-}C_1)_2]BF_4$ (0.1144 mmol); ●, $[Rh(PSPh\text{-}C_2)_2]BF_4$ (0.1723 mmol); ○, $[Rh(PSPh\text{-}C_3)_2]BF_4$ (0.0790 mmol).

$[Rh(NBD)(PSPh\text{-}C_1)]BF_4$ showed a significant, although slight, catalytic activity. A 6% conversion in hexane was achieved after 75 min of reaction (gas-chromatographic measurements), with scarce isomerization of 1-hexene. It is to be noted that in the same reaction conditions, $[Rh(NBD)(diphos)]^+$ catalyzes an 18% conversion of 1-hexene to hexane with massive isomerization of 1-hexene to *cis*- and *trans*-2-hexene (15 and 60%, respectively) [7].

Catalytic reduction of ketones

Cationic complexes of rhodium(I) are known to effectively catalyze the reduction of ketones to the corresponding alcohols via hydrogen transfer reactions (eqn. (4)). The reaction occurs with rather good yields when isopropanol is used as a reducing agent at reflux temperature [8].



(4)

We have tested the catalytic activity of some of the $[Rh(NBD)(PSR)]^+$ complexes in the reduction of acetophenone and cyclohexanone to the corresponding alcohols. The thiophosphine complexes, like the corresponding diphosphino ones, need to be 'activated' by briefly (30 min) refluxing their isopropanol solutions in the presence of a large excess of KOH. During this time the colour of the solutions changes from orange to dark red, with the concomitant formation of the active catalytic species, which is commonly believed to be a hydride cluster of rhodium [9]. From Table 2, in which the conversions of acetophenone after 24 h reaction are listed, it can be seen that the best results (about 50% of conversion) are obtained with the $[Rh(NBD)(PSPh\text{-}C_2)]BF_4$ derivative. Data of Table 3, which summarizes the results obtained for various ketones using $[Rh(NBD)(PSPh\text{-}C_2)]BF_4$ as catalyst, confirm that also in the present case the aliphatic ketones appear to be particularly reluctant to the reduction [8]. Finally the best conversion to alcohol in the reduction of acetophenone with $[Rh(NBD)(PSPh\text{-}C_2)]BF_4$, was obtained with a [KOH]/[catalyst] = 50 molar ratio.

TABLE 2. Hydrogenation of acetophenone by hydrogen transfer from isopropanol[a]

Complex	Conversion (%)
$[Rh(NBD)(PSPh\text{-}C_1)]BF_4$	8
$[Rh(NBD)(PSEt\text{-}C_2)]BF_4$	8[b]
$[Rh(NBD)(PSPh\text{-}C_2)]BF_4$	49
$[Rh(NBD)(PSPh\text{-}C_3)]BF_4$	11

[a]In isopropanol at reflux, substrate/catalyst = 500 and KOH/catalyst = 50, after 24 h. [b]After 4 h.

TABLE 3. Catalytic activity of $[Rh(NBD)(PSPh\text{-}C_2)]BF_4$ on the hydrogenation of ketones by hydrogen transfer from isopropanol[a]

Substrate	Conversion (%)
Acetophenone	49
2-Octanone	1
2-Butanone	<1
Cyclohexanone	61

[a]In isopropanol at reflux, substrate/catalyst = 500 and KOH/catalyst = 50, after 24 h.

Discussion

Our data, although allowing only partial conclusions, are sufficient to describe a general behaviour. In fact, the catalytic activity of thiophosphine rhodium(I) complexes $[Rh(NBD)(LL)]^+$ in the hydrogenation of olefins and ketones appears to be definitely lower than those exhibited by the corresponding diphosphine complexes [4, 7]. Significantly, the most active catalyst for the hydrogenation of olefins is the complex $[Rh(NBD)(PSPh\text{-}C_1)]^+$, in which the bidentate ligand gives rise to a relatively unstable four-membered chelate ring. The results apparently contrast with those obtained in the O_2-oxidation [2] of 1-alkenes to methylketones, where the thiophosphine complexes are more active than those containing the corresponding diphosphines. However, since the mechanism of the two reactions are profoundly different, it is likely that the nature of the rhodium species during the two reactions might also be very different.

The lack of catalytic activity of many of the complexes under investigation in the hydrogenation reaction under the mild conditions used, may be due to a poisoning effect of the sulfur moiety. It should be noted that metal-coordinated PSR ligands often undergo spontaneous dealkylation, with formation of phosphino–thiolato derivatives [10]. Indeed, although it has been recently reported [11] that rhodium(I) complexes supported on silica-gel functionalized with –SH groups exhibit good catalytic activity in the oxidation of 1-alkenes to methylketones, it is well established that the presence of thiolic RSH ligands, either monomer [12] or polymer [13], strongly inhibits the catalytic activity of a variety of rhodium(I) complexes in the hydrogenation of 1-alkenes.

Experimental

Materials and instrumentation

1-Hexene was purified by chromatography on alumina and stored at −20 °C. All the complexes and ligands were prepared as previously reported [1, 2]. Organic analyses were carried out with a DANI 3800 gas chromatograph equipped with FID using a 4 m dimethylsulfolane on Chromosorb W/HP column (for the hydrogenation of olefins) and a 4 m Carbowax 20 M 10% on Chromosorb W column (for the hydrogenation of ketones). NMR spectra were recorded with a Jeol FX 90Q FT spectrometer. Gas absorption was performed on a standard gas burette thermostatted at 25 °C and were reproducible to within 10%.

Procedure of catalytic experiment

Hydrogenation of 1-hexene

A total of *c.* 20 mg of catalyst was dissolved in 20 ml of a 1 M solution of 1-hexene in methanol and the solution stirred under hydrogen (1 atm.) at 25 °C.

Hydrogenation of ketones

A total of *c.* 40 mg of catalyst was refluxed, under nitrogen, in 50 ml of isopropanol. After complete dissolution (30 min) KOH (KOH/catalyst = 50 molar ratio) and the ketone (1 M) were added and the solution refluxed under nitrogen. GLC analyses were performed on aliquots withdrawn periodically by microsyringe.

Acknowledgements

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References

1 C. Bonuzzi, M. Bressan, F. Morandini and A. Morvillo, *Inorg. Chim. Acta, 154* (1988) 41.
2 (a) M. Bressan, F. Morandini and P. Rigo, *Inorg. Chim. Acta, 77* (1988) L139; (b) M. Bressan, F. Morandini, A. Morvillo, P. Rigo, *J. Organomet. Chem., 280* (1985) 139.
3 L. H. Pignolet, *Homogeneous Catalysis with Metal Phosphine Complexes,* Plenum, New York, 1983.
4 G. Mestroni, G. Zassinovich, A. Camus and F. Martinelli, *J. Organomet. Chem., 198* (1980) 87.
5 J. Halpern, D. P. Riley, A. S. C. Chan and J. J. Pluth, *J. Am. Chem. Soc., 99* (1978) 8055.
6 A. Del Zotto, A. Mezzetti, P. Rigo, M. Bressan, F. Morandini and A. Morvillo, *Inorg. Chim. Acta, 158* (1989) 151.
7 K. Neuberg, *Ph.D. Thesis,* Stanford University, 1978.
8 R. Spogliarich, G. Zassinovich, G. Mestroni and M. Graziani, *J. Organomet. Chem., 198* (1980) 81.
9 R. Spogliarich, J. Kaspar, M. Graziani, F. Morandini and O. Piccolo, *J. Catal., 94* (1985) 292.
10 M. Bressan, L. Dal Mas, F. Morandini and B. Prozzo, *J. Organomet. Chem., 287* (1985) 275.
11 E. D. Nyberg, D. C. Pribich and R. S. Drago, *J. Am. Chem. Soc., 105* (1983) 3538.
12 J. A. Osborn, F. H. Jardine, J. F. Young and G. Wilkinson, *J. Chem. Soc. A,* (1966) 1711.
13 J. P. Collman, K. M. Kosydar, M. Bressan, W. Lamanna and T. Garrett, *J. Am. Chem. Soc., 106* (1984) 2569.