*Contribution from the Research Center Montecatini-Edison S.p.A., Bollate (Milan) and *from the Istituto di Chimica Generale C.N.R. Laboratory, Milan University, Milan, Italy*

Hydrogen Transfer Reaction from Alcohols Catalysed by Rhodium Carbonyl Phosphine Complexes

G. Gregorio, G. Pregaglia, and R. Ugo*

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The hydrogen transfer from alcohols or alkoxides to olefins is catalysed by the $RhCl_3$-tertiary phosphines system. The complexes formed by reduction of $Rh(CO)Cl(PR_3)_2$ with alkali alkoxides in mild conditions have been investigated as well as the nature of catalytic hydrogenating species. The changes in the catalytic activity with the nature of the phosphines have been correlated with the ability of Rh^0 phosphine complexes to abstract hydrogen from alkoxides.

Introduction

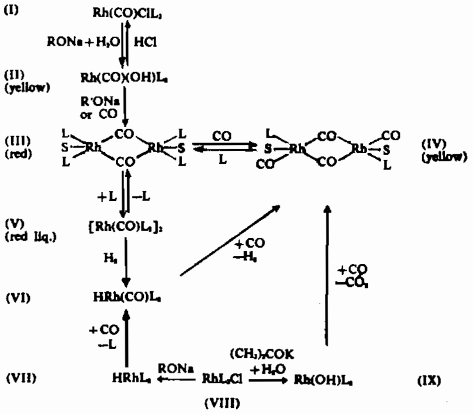
During our studies of hydrogen transfer from alcohols catalysed by tertiary phosphine-transition metal complexes,[1] which will be reported elsewhere, we realized that our experimental results could be justified by assuming a general pattern such as:

$$ML_x \xrightarrow{RCH_2OH} HML_x$$

where the metal M could be Rh, Pt, Ir, Ru and Os. The catalytic activity of $RhCl_3$ − aliphatic phosphines system has been found to be of particular interest. An approach to the comprehension of the mechanism was the comparison between the behaviour of aliphatic and aromatic phosphines towards rhodium chloride. Indeed, even if the $RhCl_3$ - triphenylphopshine system is not active from the catalytic point of view, the nature and the chemical properties of the complexes which can be isolated in an easier way, are of help in the interpretation of the mechanism of the catalysis.

It is well known[2] that the first step in the reduction of Rh^{III}-phosphine complexes by alcohols in alkaline solution (either by addition of alkali or alkaline ethoxides) is the formation of Rh^I compounds of the type $Rh(CO)Cl(PR_3)_2$. We have however observed that the reduction may proceed further giving place to zerovalent or hydrido compounds.

Here we report some data about the rhodium-phosphine complexes **(scheme 1) and the preliminary results concerning the hydrogen transfer from alcohols to olefinic compounds.



Scheme 1 - S = Solvent. L = PR_3; if L = $PMePh_2$, PEt_2Ph or PEt_3, (V) and (VI) are directly formed in presence of sodium alkoxides.

Experimental Section

Elementary analyses have been carried out in the analytical laboratory of the Research Center Montecatini-Edison S.p.A., Bollate (Milan).

Infrared spectra have been taken on a Perkin-Elmer 225, grating spectrophotometer and n.m.r. spectra on a Varian HA 100 using tetramethylsilane as internal standard.

Hydroxocarbonylbis(triphenylphosphine)rhodium(I) 685 mg (1 mmole) of chlorocarbonylbis(triphenylphosphine)rhodium(I) are suspended in 15 ml of benzene under inert atmosphere. By addition of three mmoles of sodium methoxyethoxide, dissolved in 2 ml of methoxyethanol, a clear solution is obtained. After 8 hours 5 ml of water are added and the benzene layer is separated and cooled at 0°C.

By addition of an excess of hexane yellow crystals are collected and washed with methanol and ether. 530 mg (80% yield) of a yellow diamagnetic material are finally obtained, m.p. 176-178°C.

Anal. calcd. for $Rh(CO)(OH)\{P(C_6H_5)_3\}_2$: C, 65.8; H, 4.8; O, 4.8; Rh, 15.3; CO 4.15. Found: C, 66.8; H, 4.9; O, 4.8; Rh, 14.5; CO 3.8.

(**) When this work was in progress two papers appeared in which some of the compounds here described were reported.[3,4]

(1) Italian Patent n. 783795 (dep. 21-7-1966). G. Pregaglia, G. Gregorio, F. Conti (Montecatini Edison S.p.A.).

(2) J. Chatt and B. L. Shaw: *J. Chem. Soc.* (A), 1437 (1966).

(3) D. Evans, G. Yagupsky and G. Wilkinson: *J. Chem. Soc.* (A) 2660 (1968).

(4) K. C. Dewhirst, W. Keim and C. A. Reilly: *Inorg. Chem.* 7, 546 (1968).

This compound, also in benzene solution, is stable under inert atmosphere. By reaction with HCl at room temperature in methanol, chlorocarbonylbis(triphenylphosphine)rhodium(I) is formed; by reaction at 50°C in acetone with LiI iodocarbonylbis(triphenylphosphine)rhodium(I) is obtained.

Anal. Calcd. C, 56.9; H, 3.85; I, 16.2; Rh, 13.1. Found: C, 57.0; H, 3.5; I, 14.8; Rh, 14.2.

Hydroxocarbonylbis (triisopropylphosphine) rhodium(I). 480 mg (1 mmole) of chlorocarbonylbis(triisopropylphosphine)rhodium(I) (prepared from $[Rh(CO)_2Cl]_2$ and phosphine in n-hexane. *Anal.* Calcd. C, 46.8; H, 8.6; Cl, 7.3; Rh, 20.9. Found: C, 47.6; H, 8.9; Cl, 7.2; Rh, 21.2, are dissolved in 20 ml of benzene containing a slight excess of free phosphine and reacted at room temperature with 3 mmoles of sodium n-propoxide dissolved in 2 ml of n-propanol.

After 8 hours the solution is washed with water, concentrated under vacuum and diluted with n-pentane at –40°C. 220 mg of a pale yellow powder are filtered and dried.

Anal. Calcd. for $Rh(CO)(OH)\{P(C_3H_7)_3\}_2$: C, 48.8; H, 9.2; Rh, 21.5. Found: C, 48.1; H, 8.9; Rh, 22.5.

This compound is stable in an inert atmosphere; by reaction with HCl in methanol at room temperature it transforms again into chlorocarbonylbis(triisopropylphosphine)rhodium(I) without gas evolution.

Tetracarbonylbis(triphenylphosphine)dirhodium(0)-bisbenzene. a) 685 mg (1 mmole) of chlorocarbonylbis(triphenylphosphine)rhodium(I) are dissolved under carbon monoxide atmosphere in 25 ml of benzene in the presence of slight excess of free phosphine. 3 mmoles of sodium propoxide, dissolved in 2 ml of n-propanol, are added.

After nearly one hour the solution is washed with water, the organic layer is concentrated with a stream of carbon monoxide and diluted with n-hexane. The yellow crystals separated are filtered off and dried. The compound is diamagnegtic.

b) 650 mg (1 mmole) of hydroxocarbonylbis(triphenylphosphine)rhodium(I) are suspended in 15 ml of benzene under nitrogen atmosphere. The slurry is stirred and small portions of carbon monoxide are introduced with a hypodermic syringe. The solid slowly dissolves and, when 0.5 mmoles of carbon monoxide are added, a red solution is obtained while CO_2 is detected in the gas phase.

By addition of an excess of carbon monoxide the colour of the solution turns yellow and by dilution with n-hexane, by bubbling carbon monoxide, a yellow diamagnetic compound, similar to that above reported, is obtained.

Anal. calcd. for $Rh(CO)_2 P(C_6H_5)_3 C_6H_6$: C 62.5%, H 4.2%, P 6.2%, Rh 20.3%, CO 11.2%. Found: a) C 62.2%, H 4.1%, P 6.1%, Rh 20.1%, CO 9.9%; b) C 61.7%, H 4.3%, Rh 18.8%, CO 9.6%.

The compound is stable in carbon monoxide atmosphere but it transforms to brown-red species just with a stream of nitrogen.

Dicarbonyltetrakis(triphenylphosphine)dirhodium(0) bisbenzene. 500 mg (1 mmole) of tetracarbonylbis(triphenylphosphine)dirhodium(0)bisbenzene are suspended in 20 ml of benzene containing 2 mmoles of triphenylphosphine. By maintaining the system under vacuum, carbon monoxide is evolved and the colour of the solution turns red. After few minutes the solvent is evaporated to half the initial volume and by addition of n-hexane at 0° C a dark-red crystalline compound separates. It is filtered off, washed with n-hexane and dried.

The crystalline compound is diamagnetic and stable in inert atmosphere.

Anal. Calcd. for $Rh(CO)\{P(C_6H_5)_3\}_2 C_6H_6$ C 67.2%, H 4.5%, Rh 15.4%, CO 3.8%; Found. C 66.5%, H 4.7%, Rh 15.8%, CO 3.6%.

The compound is not very soluble in benzene, but it dissolves easier by addition of free phosphine. Evaporating the benzene a viscous red oil is obtained which shows only one carbon monoxide stretching at 1965 cm^{-1}.

By addition of n-hexane the starting material is again obtained. The same oil is obtained from $[Rh(CO)_2P(C_6H_5)_3C_6H_6]_2$ in the presence of an excess of $P(C_6H_5)_3$, with a stream of an inert gas or from benzene solution of $Rh(CO)Cl\{P(C_6H_5)_3\}_2$ with sodium alkoxides, in the presence of carbon monoxide and triphenylphosphine, by removing the excess of carbon monoxide under vacuum.

The oil is easily oxidised by air to a yellow species which turns again red by reduction with carbon monoxide (carbon dioxide is formed). The cycle can be repeated many times.

Hydridocarbonyltris(triphenylphosphine)rhodium(I). 400 mg of chlorocarbonylbis(triphenylphosphine)rhodium(I) are dissolved in 30 ml of benzene in which 2 mmoles of triphenylphosphine were previously dissolved. 2 mmoles of sodium propoxide are added under a carbon monoxide atmosphere. After 6 hours sodium chloride is filtered off, the benzene solution is washed with water and maintained under vacuum until turned to a deep red colour. By treating this red solution with hydrogen, the colour turns yellow and the hydrido compound already described by Bath and Vaska[5] (form α) is obtained by concentration. If hydrogen reacts directly with the red oil obtained by evaporating the benzene the absorption is slow and a solid crystalline compound is obtained.

The compound (form β) is purified by washing with ethanol and ether.

Anal. Calcd. for $HRh(CO)\{C_6H_5)_3\}_3$: C 71.9%, H 5.1%, Rh 11.2%. Found: C 71.7%, H 5.2%, Rh 11.5%.

The latter form is more soluble in benzene but it changes in solution into the first one. In both cases the solution shows the same n.m.r. signal at τ 19.2 and the form α is always obtained from the solution.

Hydridotetrakis(triphenylphosphine)rodium(I). 925 mg (1 mmole) of chlorotris(triphenylphosphine)rhodium(I) are suspended under inert atmosphere in 15 ml of benzene containing 2 mmoles of triphenylphosphine. By adding 3 mmoles of sodium propoxide, dissolved in 2 ml of n-propanol, a clear solution is

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(5) S. S. Bath and L. Vaska: *J. Am. Chem. Soc. 85*, 3500 (1963).

Table I.

Compound	m.p.°C ^{a}	ν(CO) cm^{-1} ^{b}	ν(Rh—H) cm^{-1} ^{b}	τ ^{c}	J_{P-H} c.p.s.
$Rh(CO)I(PPh_3)_2$	235-240	1982			
$Rh(CO)(OH)(PPh_3)_2$	176-178	1948			
$Rh(CO)Cl(P(i{-}C_3H_7)_3)_2$	223-224	1940			
$Rh(CO)(OH)(P(i{-}C_3H_7)_3)_2$	154-158	1920			
$Rh(OH)(PPh_3)_3$	221-222				
$HRh(PPh_3)_4$	178-181		2140 (m)	18.55 ^{f}	13 ^{g}
$[Rh(CO)_2(PPh_3)C_6H_6]_2$	108-112	1797 (m) 1772 2020 (m) 1985			
$[Rh(CO)(PPh_3)_2C_6H_6]_2$	167-170	1732			
$HRh(CO)(PPh_3)_3$ $^{\alpha}$	166-167	1920	2035 (m)	19.2	—
$HRh(CO)(PPh_3)_3$ $^{\beta}$	138-140	2012	1917 (m)	19.2	—
$HRh(CO)(PPh_2Me)_3$ ^{e}		1968	1913 (m)	19.9	13 ^{d}
$HRh(CO)(PPhEt_2)_3$ ^{e}		1970	1915 (m)	20.7	17 ^{d}
$[Rh(CO)(PPhEt_2)_3]_2$ ^{e}		1955			
$[Rh(CO)(PPh_3)_3]_2$ ^{e}		1965			
$HRh(CO)(PEt_3)_3$		1952	1880	21.3	17 ^{d}
$HRh(CO)(Pn{-}but_3)_3$ ^{e}		1960	1890	21.2	17

^{a} All the melting points are uncorrected. Most of the compounds decompose on melting. ^{b} All the infrared spectra have been obtained in nujol mull for solids and in thin film for liquids; the bands are strong unless otherwise stated. ^{c} in benzene solution, T.M.S. as internal standard. ^{d} $J_{Rh-H} \simeq 4$ c.p.s. ^{e} Characterized only by n.m.r. in solution or by infrared of not completely purified liquid samples. ^{f} In tetrahydrofurane, T.M.S. as internal standard. ^{g} doublet corresponding to the species $HRh(PPh_3)_3$ exchanging with free PPh_3.

obtained; after 3 hours a yellow-orange compound separates. It is filtered, washed with ethanol and ether and dried with a stream of nitrogen. Yield 90%.

Anal. Calcd. for $HRh\{P(C_6H_5)_3\}_4$ C 73.5%, H 5.2%, Rh 8.8%; Found: C 75.2%, H 5.2%, Rh 8.5%.

Hydroxotris(triphenylphosphine)rhodium(I). 925 mg (1 mmole) of chlorotris(triphenylphosphine)rhodium(I) are suspended, under inert atmosphere, in 20 ml of benzene containing a slight excess of triphenylphosphine.

2 mmoles of potassium ter. butoxide dissolved in 5 ml of ter.butanol, are then added. After 3 hours a clear orange solution is obtained and the solution is washed with water. The organic layer is concentrated to small volume and, by addition of n-hexane, 650 mg of a crystalline compound are obtained.

Anal. Calcd. for $Rh(OH)\{P(C_6H_5)_3\}_3$ (IX): C 71.5%, H 5.1%, Rh 11.4%. Found: C 69.8%, H 5.0%, Rh 11.0%.

450 mg of this compound dissolved in benzene react with carbon monoxide. 0.25 mmoles of carbon dioxide are detected in the effluent gas by absorption in $Ba(OH)_2$ and tetracarbonylbis(triphenylphosphine)-dirhodium(0)bisbenzene is recovered.

Hydridocarbonyltris(diphenylmethylphosphine)rhodium(I). A benzene solution of 1 mmole of chlorocarbonylbis(diphenylmethylphosphine)rhodium(I) to which 1 mmole of diphenylmethylphosphine has been previously added, is treated under nitrogen atmosphere with sodium propoxide. The colour turns brown-red. After 3 hours the solution is washed with water and evaporated under vacuum; a viscous liquid is obtained; the hydride so obtained was characterized by its infrared and n.m.r. spectra (see Table I).

Hydridocarbonyltris(diethylphenylphosphine)rhodium(I). A benzene solution of 1 mmole of chlorocarbonylbis(diethylphenylphosphine)rhodium(I), to which 1 mmole of diethylphenylphosphine has been previously added, is treated under nitrogen with sodium propoxide. After 3 hours the solution is washed with water and benzene is evaporated under vacuum. A red viscous liquid, which contains about 0,9 moles of CO per atom of rhodium, is obtained. By reaction with hydrogen the hydrido compound is obtained as a liquid.

The compound was characterized by its infrared and n.m.r. spectra (see Table I).

Preparation of catalysts for hydrogen transfer reactions. The triethyl and tri(n-butyl)phosphine zerovalent complexes were obtained according to the reduction method with sodium propoxide above described. These compounds were always impure for traces of the hydrido species (detected by n.m.r.) which greatly increased by reaction with hydrogen.

The reactions of hydrogen transfer from alcohols to n-octene have been carried out under nitrogen in benzyl alcohol at 130°C in the presence of sodium benzylate. By excluding the alkoxide the hydrogenation is rather limited (with the triethylphosphine complex 9% against nearly 40%). The results are reported in Table II.

Table II. Activity of some rhodium-phosphine catalysts in the hydrogen transfer from benzyl alcohol to 1-octene (benzyl alcohol 0.06 moles; 1-octene 0.035 moles; potassium benzylate 0.006 moles; catalyst 0.0003 moles; temperature 130°C; time 4 hrs).

Catalyst	Convertion of benzylate to benzoate	Convertion of 1-octene to octane ^{a}
$HRh(CO)(PEt_3)_3$	50%	35%
$HRh(CO)(PBut_3)_3$	25%	6%
$HRh(CO)(PEt_2Ph)_3$	15%	3%
$HRh(CO)(PMePh_2)_3$	2%	traces
$HRh(CO)(PEt_3)_3$	4%	6% ^{b}

^{a} The recovered olefin was mainly trans-2 octene. ^{b} Cyclohexene was used as hydrogen acceptor.

Results and Discussion

In order to isolate all the possible intermediates, whose nature depends on the phosphine and on the reaction conditions, the reduction of $Rh(CO)Cl(PR_3)_2$ compounds was carried out in very mild conditions, more precisely in benzene with sodium alkoxides at room temperature. Starting from the triphenylphosphine complex a yellow compound of formula $Rh(CO)(OH)(PPh_3)_2$ is formed, probably by hydrolysis of an alkoxy derivative. The formulation of this compound is based on the analysis, on the formation of water by pyrolysis (the water has been identified by mass spectrometry), on the easy reformation of the starting complex (I) by action of HCl and on the reaction to $Rh(CO)I(PPh_3)_2$ by action of LiI. Also in the case of triisopropylphosphine as ligand a similar compound was obtained which turned out to be monomeric.

The triphenylphosphine compound is easily reduced at room temperature by carbon monoxide to a stable yellow diamagnetic compound of probable dimeric formula $[Rh(CO)_2(PPh_3)S]_2$ (IV) where S is the solvent (in our case benzene). The presence of benzene was confirmed by infra-red spectroscopy (band at 685 cm^{-1}), vapour phase cromatography and analysis.

The reduction proceeds via a red intermediate as becomes evident by adding only 0,5 moles of carbon monoxide which is oxidised to carbon dioxide in agreement with the proposed oxidation state of the metal in (II). Only on addition of excess of carbon monoxide does the solution turn yellow and (IV) as crystalline diamagnetic species separates out. Its analysis and the reaction to form the red compound (III) in the presence of PPh_3 support this formulation. In fact, a red solution is obtained after evaporation of some solvent in the presence of triphenylphosphine and (III) precipitates by addition of n-hexane. The red solution is easily oxidised even when the oxygen is in very small concentration giving place to a yellow, not yet identified, product, probably a Rh^I species; this yellow compound can be again reduced by carbon monoxide allowing the catalytic oxidation of carbon monoxide with oxygen at room temperature.

It is interesting to note that while (III) has only bridging carbonyl groups (see Table I) the yellow compound (IV) has both terminal and bridging carbonyl groups. Both compounds can interchange easily with excess of carbon monoxide or with excess of phosphine. We suppose that the compound of formula $[Rh(CO)_2(PPh_3)_2]_2$ isolated by Wilkinson and coworkers[3] may be an intermediate of this transformation. Both (III) and (IV) can react in solution in the presence of an excess of triphenylphosphine forming a red species which shows one terminal carbonyl group (ν (C=O) at 1965 cm^{-1}).

This compound was obtained as a red diamagnetic unstable liquid of possible formula $[Rh(CO)(PPh_3)_3]_2$ (V) impure of free triphenylphosphine: by trying to isolate it in crystalline form with solvents like n-hexane it transforms again into (III).

The interesting point is that the liquid species (V) activates molecular hydrogen. Indeed by addition of hydrogen to the red liquid the well known hydrido compound $HRh(CO)(PPh_3)_3$ (VI)[5] was obtained. As observed by Malatesta and coworkers[6] on the parent compound $HIr(CO)(PPh_3)_3$, we obtained this hydride in two different crystalline forms depending on reaction conditions: the former one (α) already described by Bath and Vaska[5] and the second (β) different by solubility, melting point, and I.R. spectrum (see Table I). In solution only one structure appears, in agreement with the N.M.R. spectrum which is consistent with the trigonal bipyramid of Vaska's hydride[5] complex. As it has been pointed out by many authors,[7,10] the compound (VI) hydrogenates terminal olefins very readily.

It is worth remarking that while the reaction of (I) with alkali gives place to hydroxo rhodium compounds, red solutions containing (V) and (VI) species were directly obtained in the case of $Rh(CO)Cl(PPh_2Me)_2$ and $Rh(CO)Cl(PPhEt_2)_2$. The amount of the hydrido species was dependent from the nature of the phosphine.

The hydrogen abstraction by metal complexes from alkoxides giving place to hydrides is a well known reaction.[8] In the case of the rhodium complexes of the type Rh L_2L^*Cl (were L* may be CO or a tertiary phosphine) it seems that the ability of the metal to abstract hydrogen from the alkoxides is directly related to its electronic density. In the case of triphenylphosphine such a reaction takes place easily only when three triphenylphosphines are bound to the rhodium atom: indeed $Rh(PPh_3)_3Cl$ gave place to the known hydride $HRh(PPh_3)_4$ by excess of sodium alkoxide while $Rh(CO)Cl(PPh_3)_2$ was transformed into the stable hydroxo compound (see scheme 1). As above reported, by using phosphines containing just one alkyl group, such as PPh_2Me, we observed the formation of hydrido species also in the case of the carbonyl complex (I). In any case, with more basic phosphines (L = $PMePh_2$, PEt_2Ph, PEt_3, $P(n\text{-}But)_3$) substantial amounts of zerovalent species were directly obtained by reduction of the carbonyl complexes of type (I) with sodium alkoxides. The reaction of the hydride on the alkoxide intermediate could be responsible for such compounds. The only peculiar exception concerns the triisopropylphosphine complex which is not reduced by alkoxides and behaves like the triphenylphosphine complex.

An interesting point is that, in any case, the reduction of RhL_2L^*Cl species proceeds via the formation of the $RhL_2L^*(OH)$ precursor. In some cases like with $Rh(PPh_3)_3Cl$ it was impossible to isolate the hydroxo intermediate because its precursor was reduced too easily. By reaction with a non reducing alkoxide such as $(CH_3)_3COK$ the $Rh(PPh_3)_3OH$ (IX) species was obtained (see scheme 1). The reduction of this compound could be completed by a reducing alkoxide to $HRh(PPh_3)_4$ or by carbon monoxide to $[Rh(CO)_2(PPh_3)S]_2$.

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(6) L. Malatesta, G. Caglio and M. Angoletta: *J. Chem. Soc.* 6974 (1965).
(7) L. Vaska: *Inorg. Nuclear Chem. Letters 1*, 89 (1965).
(8) J. Chatt and B. L. Shaw: *J. Chem. Soc.* 5075 (1962).
(9) S. Montelatici, A. Van Der Ent, J. A. Osborn and G. Wilkinson: *J. Chem. Soc. (A)* 1054 (1968).
(10) Charmian O' Connor and G. Wilkinson: *J. Chem. Soc. (A)* 2665 (1968).

All the zerovalent red species activate molecular hydrogen with the formation of hydrides extremely active as catalysts in the hydrogenation of terminal olefins. In fact the catalytically important dissociation:

$$HRh(CO)(PR_3)_3 + S \rightleftharpoons HRh(CO)(PR_3)_2S + PR_3$$

was facile also with more basic phosphine as is showed by the N.M.R. signal of hydridic hydrogen which splits into a quartet (see experimental) only at temperatures below 5-0°C. In contrast with this remark, it is worth noting that the RhH_2ClL_3 species dissociate easily when $L = PPh_3$, but only to a little extent when L is a more basic phosphine.[9]

The different behaviour of the zerovalent complexes according to the type of phosphine, may explain why the $RhCl_3$-PPh_3 system is inactive in the transfer of hydrogen from alcohols. Only more basic phosphines make easier hydrogen abstraction from alkoxides as source of hydrogen for $Rh^0 \rightarrow Rh^I$ oxidation.

Comparative experiments have been carried out with different hydrides (see table 2). The source of hydrogen to reduce 1-octene was potassium benzylate, which was converted mainly to benzoate with small amounts of esters. In all cases the recovered olefin was isomerised substantially to *trans*-2-octene.

All the catalytic systems are deactivated in carbon monoxide atmosphere; in particular the yellow $[Rh(CO)_2(PR_3)S]_2$ species are formed with hydrogen evolution as pointed out by Wilkinson and coworkers[3] (see scheme 1).