Rh(I)-S-triazene complexes as effective homogeneous recyclable catalyst for catalytic hydrogenation of organic substrates

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ABSTRACT

Rh(I) complexes of S-triazines were found very efficient towards the catalytic hydrogenation of alkenes, alkynes at normal pressure and at room temperature. Reduction of aromatic nitrocompounds, benzaldehyde and benzil were observed in appreciable amount only at high pressure and at high temperature. No diminished catalytic activity was observed even after 6-8 repeated catalytic runs. Profound effect was observed on the rate of reduction in presence of extra ligand without affecting the nature of yield, both under normal and high pressure conditions.

Key words: Rh(I) Complexes; NitrocompouCnds; Alkenes; Alkynes; Catalytic hydrogenation.

INTRODUCTION

Catalytic hydrogenation is undoubtly the most useful and widely applicable method for the reduction of chemical substances. For instance it has been estimated that between 10-20% of synthetic chemical reactions in a typical pharmaceutical company are carried out by catalytic hydrogenation (1). Catalytic hydrogenation of organic nitro compounds often lead to valuable compounds such as amine, azo, azoxy etc. These compounds are frequently used in dye industries[2]. Similarly selective hydrogenation of dienes and trienes to mono-olefines has several useful applications in food industries more particularly in vegetable oil industries[3]. Transition metal complexes have long been used as catalysts for the dihydrogen reduction of organic nitrocompounds[4-16], alkenes[17-24], alkynes[24-29], aldehydes[30-33], ketones[32-35], shiff-bases[36], nitriles[37]. Among the numerous homogeneous catalysts used for the dihydrogen reduction of various unsaturated organic compounds[4-6,18,25,36-41)] only few were found stable enough to reduce nitrocompounds, ketones and nitriles[42-45], and in most of the cases the reduction

mechanism could not be well established[6,46,47]. A good number of Rh (I) non-orthometallated and orthometallated complexes have also been found to exhibit excellent catalytic activity towards dihydrogen reduction of wide variety of unsaturated organic compounds. Catalyst decomposition and poor reproducibility at the time of its repeated use was major disadvantage associated with these catalytic systems.

In our previous communication we have studied the catalytic activity of Pd (II) and Rh(I) complexes towards various unsaturated organic substrates[48,49]. The present paper reports the successful use of homogeneous Rh(I) complexes of S-triazene derivatives for the catalytic hydrogenation of a wide variety of unsaturated organic substrates.

EXPERIMENTAL

Materials and Equipments

Analytical grade chemicals, dry and ultra pure quality of N_2, Ar and H_2 were always used. AR grade solvents and liquid substrates were purified

by distillation and dried on molecular sieves (4A). Solid substrates were always recrystallized before use. S-triazines[1] OEt-TH, DEt-ATH$_3$, DEt-ATH were prepared and purified using literature methods[50, 51]. RhCl$_3$.3H$_2$O of Arora-Matthey Ltd. was used without further purification. Catalytic hydrogenation were carried out by using J.T.Baker (U.S.A.) analyzed DMF.

Carbon, Hydrogen and nitrogen of the complexes were recorded on Perkin Elemer 2400 CHN Elemental Analyser. Rhodium was not estimated rather it was calculated by difference. Molecular weight of the complexes was determined by using KNAUER, DAMPEFDRUCK-Osmometer. UV/Vis., IR and NMR spectra were recorded on Pyeunicam PU8600, Pyeunicam SP3-300, Brucker AC-300F Spectrophotometer respectively. The product mixture were analyzed by TLC on silica gel coated plastic sheets (Merck Silica gel F$_{254}$) and by GLC (5700 Nucon gas chromatograph) using Apiezon.L, Carbowax 20M, SE-30 columns.

Catalyst Preparation
Preparation of Dicarbonyl(S-triazino)Rhodium(I) [Rh(OEt-T)(CO)$_2$] 1

RhCl$_3$.3H$_2$O (0.26 g; 1.242mmol) in deoxygenated DMF (10ml) was stirred with S-triazine (0.313 g; 1.355mmol) in dinitrogen atmosphere for half an hour. The solution was then refluxed under dinitrogen atmosphere for 2h in oil bath. During the first 10 min. the solution changed its colour from dark red to yellow. The solution was cooled to room temperature and diluted with deoxygenated water (35 ml). A yellow precipitate appeared. The reaction mixture was kept at 5^{0}C for 1h and then filtered under dinitrogen atmosphere. The Precipitate was washed with deoxygenated water and acetone successively and dried in vacuum. The other two Rhodium(S-triazine) complexes i.e. [Rh(DEt-ATH$_2$)(CO)$_2$] 2, [Rh(DEt-AT)(CO)$_2$] 3 were prepared following the above procedure. Yield: 1 – 70%, 2 – 68%, 3 –65%

m.p.: 170^{0}C. Anal.Data found: N,14.40 ; C,40.08 ; H,2.80 [Rh(OEt-T)(CO)$_2$] 1 Calcd: N,14.36 ; C,40.02 ; H,2.84. IR(KBr): nNH/NH$_2$ 3390-3300 cm^{-1}; n-CO 2200-2000 cm^{-1} ; n-CO(phenol) 1545 cm^{-1} ; nNH$_2$ 1615 cm^{-1} . UV/Vis(DMF) : 22472 cm^{-1}(d-d transition).

m.p.: 175^{0}C. Anal.Data found: N,16.55; C,42.95 ; H,4.30 [Rh(DEt-ATH$_2$)(CO)$_2$] 2 Calcd: N,18.70 ; C,42.97 ; H,4.33. IR(KBr) : nNH/NH$_2$ 3455-3220 cm^{-1}; n-CO 2085-2010 cm^{-1} ; n-CO(phenol) 1535 cm^{-1} ; nNH$_2$ 1615 cm^{-1} . UV/Vis(DMF) : 21978cm^{-1}(d-d transition).

m.p. :180^{0}C. Anal.Data found: N,16.75; C,43.00 ; H,3.85 [Rh(DEt-AT)(CO)$_2$] 3 Calcd: N,16.78 ; C,43.18 ; H,3.86. IR(KBr): nNH/NH$_2$ 3395-3230 cm^{-1} ; n-CO 2080-2019 cm^{-1} ; n-CO(phenol) 1545 cm^{-1} ; nNH$_2$ 1615 cm^{-1} . UV/Vis(DMF) : 22358cm^{-1}(d-d transition).

Hydrogenation Procedure

Catalytic hydrogenation reactions were carried out in normal pressure as well as in high pressure of hydrogen. Normal pressure hydrogenations were carried out in normal pressure hydrogenation assembly. The reduction of substrates such as nitroaromatics, benzaldehyde and benzil which could not be done in normal pressure conditions, were studied in high pressure conditions. High pressure hydrogenation is carried out in non-magnetic stainless steel high pressure autoclave. The reaction procedure was used as per literature method (48). The products were identified by their boiling point/melting points and finally by GLC using Apiezon.L, Carbowax 20M, SE-30 columns.

RESULTS AND DISCUSSION

Rh(I) complexes of S-triazine derivatives were found catalytically active for dihydrogen reduction of alkenes and alkynes under normal pressure. Rhodium complexes were synthesized by Refluxing RhCl$_3$.3H$_2$O with S-triazene derivatives in DMF medium under dry and pure argon atmosphere respectively. DMF at its boiling temperature decomposed to CO and generated the reducing atmosphere for Rh(III) and at the same time acted as a source of CO. Rhodium complexes were found sparingly soluble in alcohol and benzene and highly soluble in DMF and DMSO. In soluble phase the Rh(I) complexes were found susceptible to aerobic oxidation leading to Rh(III) species. However, the DMF solution of the rhodium complexes could be stored under N$_2$/Ar atmosphere at least for several months.

[Rh(OEt-T)(CO)$_2$] was found highly but not equally active as compared to other Rh(I) complexes. The relative activity of all the Rh(I) complexes are shown in Table 1 The complexes may be placed in the following order according to their catalytic activities -
[Rh(OEt-T)(CO)$_2$] > [Rh(DEt-AT)(CO)$_2$] > [Rh(DEt-ATH$_2$)(CO)$_2$]

The nature of products obtained for a particular substrates using different complexes as catalyst were almost same but the yield of different products was found to depend on the nature of the catalyst. The rate of hydrogenation, turn over number, nature and % of yield of various products using [Rh(OEt-T)(CO)$_2$] has been presented in Table 2 DMF medium was found the best solvent for catalytic hydrogenation. On the basis of reduction rates, the substrates may be arranged in the following order-

Styrene > acrlyonitrile > pent-1-ene > hex-1-ene > hept-1-ene > ù-nitrostyrene > cyclohexene > maleic acid > fumaric acid
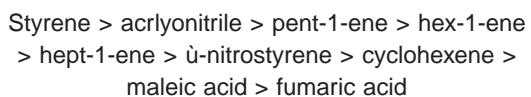
The reduction of alk-1-ene was always accomplished by isomerization. Isomerized product were mainly the corresponding alk-2-ene and to

Table 1: Relative activities of the Rhodium (I) complexes as homogeneous hydrogenation catalyst

Catalyst	Initial rate of H$_2$ absorption (ml/min.)	Initial turn over no. (min^{-1})	Product with % of yield
[Rh(OEt-T)(CO)$_2$]	7.42	27	Ethylbenzene-98
[Rh(DEt-AT)(CO)$_2$]	6.91	25	Ethylbenzene-96
[Rh(DEt-ATH$_2$)(CO)$_2$]	6.12	22	Ethylbenzene-95

Medium-DMF, Styrene-0.29mol/lit, [Cat] – 6.83 x 10^{-4} mol/lit, Total volume- 15 ml., P$_{H2}$-1atm., Temp.- 25^{0}C

**Table 2: Optimum conditions and yields of main products at 1 atm. pressure of hydrogen and 25^{0}C using [Rh(OEt-T)(CO)$_2$] as catalyst**

Substrate	[Cat]x10^4 (mol/lit)	Initial rate of H$_2$ absorption (ml/min.)	Initial turn over number (min^{-1})	Products with % of yield
Styrene	6.83	7.42	27	Ethylbenzene-98
Acrylonitrile	7.0	6.43	24	Ethylcynide-97
Pent-1-ene	7.13	5.64	21	Pentane-55, Pent-2-ene-42
Hex-1-ene	7.33	4.45	20	Hexane-70 Hex-2-ene-28
Hept-1-ene	7.46	3.86	14	Heptane-58, Hept-2-ene-39
ω -Nitrostyrene	7.66	2.77	11	ω -Nitroethyl benzene-98
Cyclohexene	8.0	2.77	10	Cyclohexane-97
Maleic acid	8.0	2.47	8.0	Succinic acid-95
Fumaric acid	8.0	1.48	5.0	Succinic acid-96
Phenylacetylene	6.83	8.9	17	Ethylbenzene-95
Diphenylacetylene	6.83	6.43	13	Diphenylethane-96

Medium = DMF, [Subs] = 0.32 mol/lit, Total Vol. = 15 ml.

some extent alk-3-ene. From the order of the rate of the reduction of the substrates, it appeared that the double bonds which were the part of the delocalized system were reduced more quickly than the localized one. Again any electron attracting group attached to the carbon atom of the double bond decreased the rate of reduction of the double bond. ù-nitrostyrene , maleic acid and fumaric acid were reduced more slowly than styrene. This might be due to decrease electron density on the double bond. Again steric factor influenced the reduction rate to a great extent. Cyclohexene or alk-2-enes were reduced too much slower rate than hex-1-ene. Sequential hydrogenations were observed in case of diphenylacetylene. Diphenylacetylene first reduced to Cis-stilbene and than to 1,2-diphenylethane (Fig.-1). Preferential hydrogenations were also observed in case of phenylacetylene in presence of hex-1-ene (Fig.-2).

Dihydrogen reduction of organic nitrocompounds, benzaldehyde and benzil were generally observed only at high pressure and high temperature conditions. Optimum conditions and yield of main product at 60⁰C and high pressure of hydrogen using [Rh(OEt-T)(CO)₂] as catalyst has

been presented in Table 3 In accordance to their initial rate of reduction various nitroaromatics may be arranged as follows-

$C_6H_5NO_2$ > p-$CH_3C_6H_4NO_2$ > m-$(NO_2)_2C_6H_4$ > p-$ClC_6H_4NO_2$> p-$NH_2C_6H_4NO_2$ > m-$ClC_6H_4NO_2$ > m-$NO_2C_6H_4NH_2$ > o-nitronaphthalene > o-$NO_2C_6H_4CH_3$ > o-$NO_2C_6H_4Cl$ > p-$NO_2C_6H_4OH$
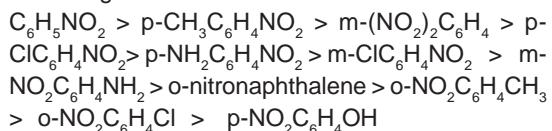
In high pressure conditions m-dinitrobenzene was sequentially reduced first to m-nitroaniline and then to m-phenylenediamine (Fig.-3). Nitrobenzene was reduced to aniline, to the extent of 85% before the reduction of nitromethane when both of them are present together. No preferential hydrogenation was observed in any other cases.

It has been mentioned that under normal pressure the light brown DMF solution of [Rh(OEt-T)(CO)₂] changed to deep brown on stirring under hydrogen for nearly 15 minutes. Addition of Styrene to this deep brown solution started hydrogen absorption at very slow rate. The rate of hydrogen absorption was increased slowly and reached to its maximum value within 15 minutes. This indicated that the resulting solution became catalytically most

Table 3: Optimum conditions and yields of main products at High pressure of hydrogen and 60⁰C using [Rh(OEt-T)(CO)₂] as catalyst

| Substrate(mol/lit)	H₂ pressure (in 10^{-3} KNm⁻²)	Reaction Time (h)	[Cat / subs ratio]x10³	Products with % yield
Nitrobenzene(0.32)	2.07	2.0	1.5	Aniline-95
p-Chloronitrobenzene-(0.25)	2.07	3.5	2.44	p-Chloroaniline(88)
o-Chloronitrobenzene-(0.25)	2.76	4.5	2.44	o-Chloroaniline(90)
p-Nitrotoluene(0.32)	2.41	2.0	1.5	p-Toludine-(90)
o-Nitrotoluene(0.32)	2.76	5.0	1.5	o-Toludine-(85)
p-Nitro aniline(0.25)	2.41	4.0	2.44	p-phenylene-diamine(90)
m-Dinitrobenzene(0.25)	2.76	8.5	2.44	m-phenylene-diamine(92)
Nitromethane 0.30)	3.45	9.0	1.66	Methylamine-(95)
Nitroethane (0.30)	3.45	9.0	1.66	Ethylamine(92)
Nitroprpoane(0.32)	3.45	10.0	1.68	Propylamine-(90)
Benzaldehyde(0.25)	2.76	3.5	1.5	Benzylalcohol(95)
Benzil (0.25)	2.76	5.5	2.44	1,2-Diphenyl-ethylglycol(92)

Medium = DMF, Total Vol. = 15 ml
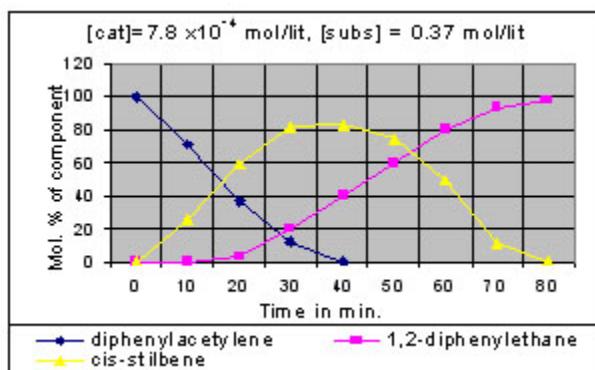
**Fig.1: Sequential hydrogenations of diphenylacetylene with
[Rh(OEt-T)(CO)$_2$] in DMF at 25^0 C and 1 atm. Pressure of hydrogen**
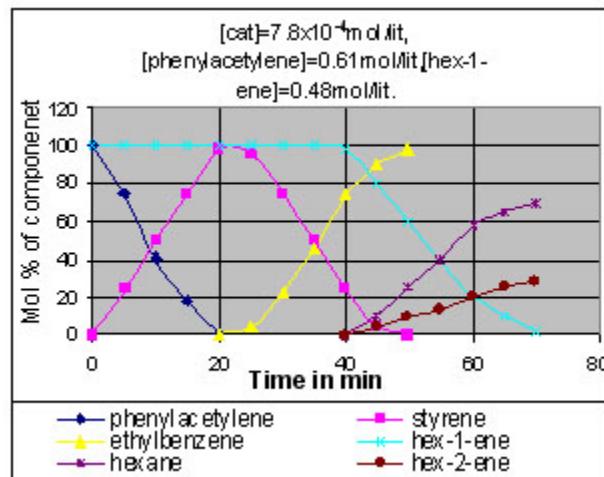
**Fig. 2: Preferential hydrogenation of phenylacetylene in presence of hex-1-ene
with [Rh(OEt-T)(CO)$_2$] in DMF at 25^0 C and 1 atm. Pressure of hydrogen**
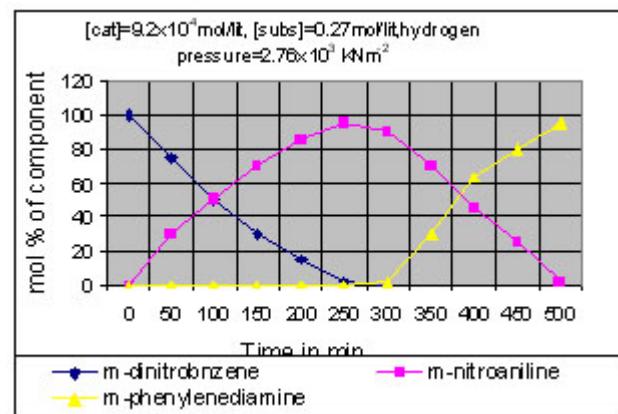
**Fig. 3: Sequential reduction of m-dinitrobenzene with [Rh(OEt-T)
(CO)$_2$] in DMF at 600C and 2.76 x 10^3 KNm^{-2} pressure of hydrogen**

active. The deep brown compound [Rh(OEt-T)(CO)(DMF)] isolated from the final solution at the end of styrene reduction. The highest rate of hydrogen absorption was observed whenever the solution of [Rh(OEt-T)(CO)(DMF)] was in contact with both, hydrogen and styrene and was independent of the order of addition of styrene and the hydrogen to the catalyst solution. These facts lead us to suggest that the brown solution contain both the species [Rh(OEt-T)(CO)$_2$] and [Rh(OEt-T)(CO)(DMF)] along with some other intermediates. An equilibrium involving [Rh(OEt-T)(CO)$_2$], [Rh(OEt-T)(CO)(DMF)] and probably other species were attained during first 15 minutes of stirring of the solution under hydrogen atmosphere. The most active catalytic species was either [Rh(OEt-T)(CO)(DMF)] or some other species to which it might immediately be converted in presence of

hydrogen and C=C. On the basis of above observation the following Scheme-1 has been proposed for this reduction process.

Effect of solvent

Among different organic solvents DMF was found to be the best medium for these hydrogenation processes. The reduction rate was decreased both in stronger coordinating solvents like THF and DMSO and in non coordinating solvents like C$_6$H$_6$ and C$_6$H$_5$CH$_3$ etc. This is probably due to the decomposition or lower solubility of complexes in them. It appeared that some type of interaction between the complexes and the solvent molecule required for the complexes to become catalytic active.

$$Rh(L_1)(L_2)_2 \xrightarrow[\text{-(L}_2)]{\text{+(S)}} Rh(L_1)(L_2)(S)$$
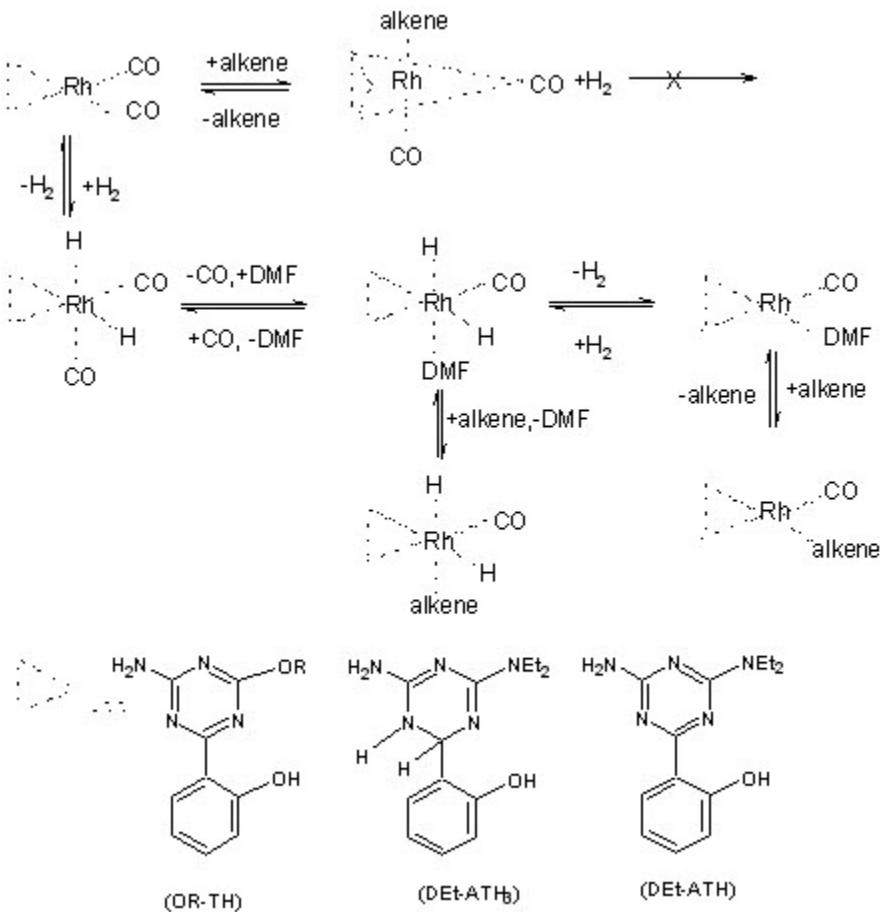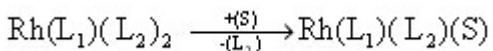
Scheme 1.

Where, S is the solvent molecule. Moderately strong coordinating solvents might be sufficient for this purpose.

Effect of acid, base and extra ligand

The rate of hydrogenation, nature and yield of products remain unchanged in presence of small amount of acid and alkali (10^{-2} mol/lit). Initial addition of extra ligand such as PPh_3, $P(OEt_3)$, pyridine and quinoline etc. decreased the rate of hydrogenation greatly without affecting the nature and yield of products both under normal and high pressure conditions.

Isolation of intermediate complexes

It has already mentioned that the light brown DMF solution of Rh-S-triazene complexes changed to deep brown in presence of hydrogen within 15 minutes. At the end of catalytic run the deep brown compounds were isolated from each of this solution by distilling out the volatile matters under vacuum. The residue was stirred with CCl_4, finally filtered, washed several times CCl_4 and dried in vacuum.

m.p.-108^0C (decomposition temperature). Anal.Data found: N,16.11 ; C,41.28 ; H,3.45. [Rh(OEt-T)(CO)(DMF)]. Calcd: N,16.13 ; C,41.49 ; H,3.94 . IR(KBr) n-CO 2045 cm^{-1} ; n-CO(DMF) 1640 cm^{-1} ; UV/Vis(DMF) $18320cm^{-1}$(d-d transition)

Recycle of the catalyst

At the end of catalytic run the addition of fresh substrate to the final reaction mixture resumed the hydrogen absorption with almost initial rate of the complexes. The compound [Rh(OEt-T)(CO)(DMF)] isolated from the final solution of catalytic run, could be used repeatedly without any diminished catalytic activity.

CONCLUSION

Rh(I) complexes of S-triazene derivatives could be used as active catalysts for the dihydrogen reduction of a number of organic substrates. Among [Rh(OEt-T)(CO)$_2$], [Rh(DEt-AT)(CO)$_2$] and [Rh(DEt-ATH$_2$)(CO)$_2$] the first two were found most efficient. The rate of reduction of substrates was found to depend both on steric and electronic factors. No diminished catalytic activity was observed even after 6-8 repeated catalytic runs. DMF was found best solvent for these catalytic systems.

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