

## HOMOGENEOUS HYDROGENATION OF CYCLIC OLEFINS CATALYSED BY NITROSYLCATECHOLATOIRIDIUM COMPLEXES

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### Summary

The catalytic activity of the nitrosylcatecholato complexes  $\text{Ir}(\text{NO})(1,2\text{-O}_2\text{C}_6\text{Br}_4)(\text{PPh}_3)$  and  $\text{Ir}(\text{NO})(1,2\text{-O}_2\text{C}_6\text{H}_4)(\text{PPh}_3)$  in homogeneous hydrogenation of cyclic olefins, dienes and trienes has been studied. The activities of the catalysts are related to the electron density on the central metal.

### Introduction

There is much interest in hydrogenation catalysed by soluble transition metal complexes [1]. In general, complexes of the heavier transition metals of Group VIII are good catalysts for these type of reactions [2]. The influences on the catalytic activity of ligands able to stabilize low oxidation states, such as phosphine, carbonyl, and various good  $\pi$ -acceptor ligands has been much studied [3]. There is very little information, however, about the influence on the catalytic activity of the ligands which are capable of assuming different oxidation states and coordinating in various modes, and possibly of changing their electronic configuration and the coordination mode during the catalytic reaction. Examples of this class of ligands are nitrosyl group and the quinonoid species. It is known that the nitrosyl ligand can be formally considered to be coordinated as linear  $\text{NO}^+$  (MNO angle  $180^\circ$ ) [4] or bent  $\text{NO}^-$  (MNO angle  $120^\circ$ ) [4], that the two coordination modes can undergo interconversion [5], and that intermediate angles are possible [4]. Three different coordination modes are possible for *o*-benzoquinone ligands, differing in the formal oxidation state of the ligand on going from unreduced quinone coordination, to semiquinone coordination, and finally to catecholato coordination [6]. The three coordination modes can in principle be interconverted during the catalytic reaction. Very few cases of hydrogenation reactions by transition metal nitrosyl complexes are known, and of these none is catalyzed by a nitrosyl complex of a third row transition metal [7]. While polyquinone complexes are known to catalyze

heterogeneously dehydrogenation of saturated hydrocarbons [8], only a few quinone complexes are known to act as homogeneous catalyst for the hydrogenation of organic unsaturated substrates [9]. Because the chemical and the structural features of homogeneous catalyst systems depend on the nature of the coordinated ligands, it should be possible to achieve a high degree of selectivity and catalytic activity when varying the ligand properties. Thus the simultaneous presence in the metal coordination sphere of two ligands such as nitrosyl and the *o*-quinonoid group makes it possible for the metal to adapt various coordination states by a simple intramolecular redox reaction. Consequently, we thought that it might be interesting to study the catalytic behaviour of this type of complex in homogeneous hydrogenation.

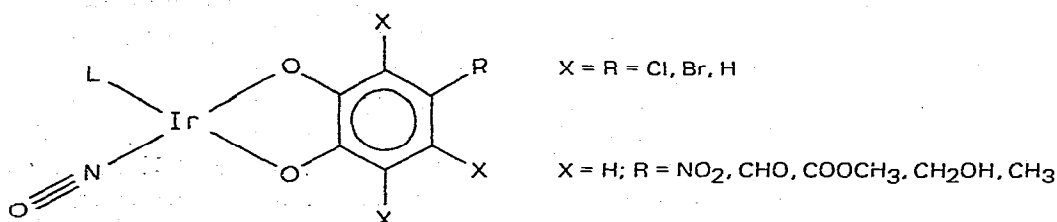
## Experimental

The catalysts  $\text{Ir}(\text{NO})(1,2\text{-O}_2\text{C}_6\text{Br}_4)(\text{PPh}_3)$  and  $\text{Ir}(\text{NO})(1,2\text{-O}_2\text{C}_6\text{H}_4)(\text{PPh}_3)$  were prepared by published methods [6,10]. The THF was freshly distilled from  $\text{LiAlH}_4$  under nitrogen. All liquid olefins (Fluka or Aldrich products) were passed through a Woelm neutral alumina column before use, and then stored for only short periods of time under nitrogen. Norbornene and norbornane were Aldrich reagent grade products.

The hydrogenations were carried out in Fisher-Porter pressure vessels at  $30 \pm 1^\circ\text{C}$  under 3 atm of  $\text{H}_2$ . The catalyst concentration was 3.35 mM (0.05 mmol in 15 ml of THF). The molar ratio of catalyst to olefin for each run is shown in Tables 1 and 2. Reaction products were analyzed quantitatively on a Hewlett-Packard 5750 dual column research gas chromatograph equipped with a thermal conductivity detector and connected to a Hewlett-Packard 3380A integrator for the measurement of the product composition. The following columns and phases (Carlo Erba) were used: 3 m  $\times$  1/8 in. 10% DMS on CWS and 3 m  $\times$  1/8 m 10% UCCW-982 on CWS.

## Results and discussion

We previously described the syntheses and characterisation of nitrosylcatecholatoiridium complexes of the type [10]:



We now report on the catalytic activity of the tetrabromo-*o*-catecholato- $\text{Ir}(\text{NO})(1,2\text{-O}_2\text{C}_6\text{Br}_4)(\text{PPh}_3)$  and catecholato- $\text{Ir}(\text{NO})(1,2\text{-O}_2\text{C}_6\text{H}_4)(\text{PPh}_3)$  complexes in the homogeneous hydrogenation of cyclic olefins, dienes and trienes. The complexes are moderately active homogeneous catalysts at  $30^\circ\text{C}$  and 3 atm of  $\text{H}_2$  in THF solution. Under such conditions the nitrosylcatecholatoiridium complexes are very stable, and can be easily recovered from the reaction mix-

TABLE 1

DETAILS OF OLEFIN HYDROGENATION REACTIONS WITH THE CATALYST  $\text{Ir}(\text{NO})(1,2\text{-O}_2\text{C}_6\text{Br}_4)(\text{PPh}_3)$ <sup>a</sup>

Olefin <sup>b</sup>	Conversion (%) <sup>c</sup> at time <i>t</i> (h) (Catalyst/Olefin)	Products (Yield (%)) <sup>d</sup>
1,3-CED	86, 48 (1/300)	CEE (100)
1,3-CED	100, 42 (1/150)	CEE (99), CEA (1)
1,3-CED	100, 24 (1/75)	CEE (96), CEA (4)
1,4-CED	19, 48 (1/150)	CEE (96), CEA (4)
CEE	12, 48 (1/300)	CEA (100)
CEE	21, 48 (1/75)	CEA (100)
NBD	11, 48 (1/300)	NBE (100)
NBD	58, 48 (1/75)	NBE (87), NBA (13)
NBE	34, 48 (1/300)	NBA (100)
NBE	97, 48 (1/75)	NBA (100)
1,3-CHD	19, 48 (1/300)	CHE (84), CHA (16)
1,3-CHD	44, 48 (1/75)	CHE (87), CHA (13)
CHE	42, 48 (1/300)	CHA (100)
CHE	48, 48 (1/75)	CHA (100)
CHT	—, 48 (1/300)	—
CHT	31, 48 (1/75)	CHD (100)
COE	24, 48 (1/300)	COA (100)
COE	35, 48 (1/75)	COA (100)
BEN	—, 48 (1/75)	—

<sup>a</sup> In THF at  $30 \pm 1^\circ\text{C}$  ( $p(\text{H}_2)$  3 atm). <sup>b</sup> CED = Cyclohexadiene; CEE = Cyclohexene; CEA = Cyclohexane; NBD = Norbornadiene; NBE = Norbornene; NBA = Norbornane; CHD = Cycloheptadiene; CHE = Cycloheptene; CHA = Cycloheptane; CHT = Cycloheptatriene; COE = Cyclooctene; COA = Cyclooctane; BEN = Benzene. <sup>c</sup> Determined by GLC (based on olefin consumption). <sup>d</sup> Relative ratio determined by GLC.

ture. The recovered catalysts have the same catalytic activity as freshly prepared samples. The results for the tetrabromocatechol complex are shown in Table 1, which also gives the catalyst/substrate ratios.

The results clearly show that 1,3-cyclohexadiene is selectively reduced to cyclohexene in 86% yield in 48 h with a catalyst/substrate ratio of 1/300. With a higher catalyst/diene ratio a faster and complete diene conversion was obtained, and small amounts of cyclohexane were detected in the products. In the case of the non-conjugated 1,4-cyclohexadiene the hydrogenation reaction proceeds very slowly compared with that for the conjugated 1,3-isomer. The reduction of cyclohexene to the corresponding saturated compound is slower than that of the conjugated 1,3-diene to monoene, but the rates of hydrogenation of cyclohexene and 1,4-cyclohexadiene are comparable. The monoene species are hydrogenated in good yield in the case of norbornene and cycloheptene. In hydrogenation of norbornadiene and 1,3-cycloheptadiene the corresponding saturated compound is always formed in detectable amounts. 1,3,5-Cycloheptatriene is selectively hydrogenated at a moderate rate to 1,3-cycloheptadiene. Cyclooctene is easily reduced to cyclooctane. Aromatic hydrocarbons such as benzene are not hydrogenated under our conditions.

The above results show that the complex  $\text{Ir}(\text{NO})(1,2\text{-O}_2\text{C}_6\text{Br}_4)(\text{PPh}_3)$  catalyzes the hydrogenation of cyclic olefins, dienes and trienes and the reductions usually go at satisfactory rates. The complex is a selective catalyst for the hydrogenation of 1,3-cyclohexadiene to cyclohexene and 1,3,5-cycloheptatriene

TABLE 2

DETAILS OF OLEFIN HYDROGENATION WITH THE CATALYST  $\text{Ir}(\text{NO})(1,2\text{-O}_2\text{C}_6\text{H}_4)(\text{PPh}_3)^a$ 

Olefin <sup>b</sup>	Conversion (%) <sup>c</sup> at time <i>t</i> (h) (Catalyst/Olefin)	Products (yield (%) <sup>a</sup> )
1,3-CED	2, 48 (1/300)	CEE (100)
1,3-CED	3, 48 (1/150)	CEE (100)
1,3-CED	6, 48 (1/75)	CEE (100)
1,4-CED	—, 48 (1/150)	—
CEE	—, 48 (1/75)	—
NBD	—, 48 (1/75)	—
NBE	20, 48 (1/75)	NBA (100)
1,3-CHD	38, 48 (1/75)	CHE (73), CHA (27)
CHE	28, 48 (1/75)	CHA (100)
CET	—, 48 (1/75)	—
COE	11, 48 (1/75)	COA (100)

<sup>a, b, c, d</sup> See Table 1.

to cycloheptadiene. Studies of the mechanism are in progress in our laboratories.

It is known that the activity of a homogeneous catalyst depends on several factors, such as ease of electron transfer, bond strengths, availability of coordination sites, and electron configuration. They vary from species to species, and so comparisons can be made only between complexes in homogeneous series. It is thus noteworthy that the series of nitrosylcatecholatoiridium complexes comprises several isostructural and isoelectronic tetracoordinate complexes differing only in the catecholato ring substituents. For a comparison, we have examined the catalytic activity of the complex  $\text{Ir}(\text{NO})(1,2\text{-O}_2\text{C}_6\text{H}_4)(\text{PPh}_3)$  containing a different catecholato ligand. The results are shown in Table 2 and a comparison with Table 1 shows that the olefin conversions are in general much smaller at a given time and catalyst/substrate ratio. Thus the complex  $\text{Ir}(\text{NO})(1,2\text{-O}_2\text{C}_6\text{H}_4)(\text{PPh}_3)$  only weakly catalyzes the hydrogenation of 1,3-cyclohexadiene to cyclohexene, while the 1,4-diene does not react. Cyclohexene, norbornadiene and cycloheptatriene are not reduced. Norbornene, cycloheptene and cyclooctene are hydrogenated to the corresponding saturated species. 1,3-Cycloheptadiene is slowly hydrogenated, and the ratio between cycloheptene and cycloheptane products differs from that with the tetrabromocatecholato catalyst, the proportion of saturated product being higher. Thus it appears that replacement on the catecholato ring of four electron withdrawing bromine atoms by four hydrogen atoms lowers the catalytic activity, and thus the catalyst activity is higher the lower the electron density on the central metal.

### Acknowledgement

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