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THE INFLUENCE OF SOME LEWIS ACIDS ON HOMOGENEOUS OLEFIN HYDROGENATION BY METAL COMPLEXES

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Summary

The rate of hydrogenation of cyclohexene catalyzed by $RhCl(PPh_3)_3$ was studied in the presence of BCl_3, $B(CH_3)_3$, $Eu(fod)_3$ (fod = 6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octadione anion), $AlCl_3$, $AlBr_3$ and $Al(i\text{-}C_4H_9)_3$. Only $AlBr_3$ effected a large increase in rate, which is attributed to the formation of the more active catalyst $RhBr(PPh_3)_3$ by a simple metathesis. A very significant rate enhancement was found for the hydrogenation of ethylene by $RhCl(PPh_3)_3$ when $Al(i\text{-}C_4H_9)_3$ was added to the system. It is postulated that $RhH(PPh_3)_3$ formation is responsible for this rate increase. The rate of 1-hexene hydrogenation catalyzed by $RuCl_2(PPh_3)_3$ is increased by the presence of aluminum alkyls, and the origin of this rate increase is elucidated. In the course of this work the compound $RuCl(CH_3)(PPh_3)_3$ was isolated and characterized. This compound is closely related to alkyl complexes which have been postulated as intermediates in olefin hydrogenation catalysis by $RuClH(PPh_3)_3$.

Introduction

Ligand dissociation is an important step in the mechanisms which have been presented for many homogenous catalyzed olefin hydrogenations [1-4]. For example the currently accepted mechanism of catalysis by $RhCl(PPh_3)_3$ involves phosphine dissociation as the first step, eqn. 1, in the catalytic cycles [3,4].

$$RhCl(PPh_3)_3 \rightleftharpoons RhCl(PPh_3)_2 + PPh_3 \qquad (1)$$

This dissociation produces a coordinatively unsaturated and therefore highly reactive species, $RhCl(PPh_3)_2$, which readily enters into other reactions of the catalytic cycle. The present work was motivated by the idea that an added Lewis acid might complex ligands such as PPh_3 in reaction 1 and therefore promote the formation of coordinatively unsaturated species. There is to our knowledge only one report on the Lewis acid promotion of metal catalyzed homogenous hydrogenation of olefins, in which the apparent role of the Lewis acid is ligand abstraction [5].

However the above postulated effect of a Lewis acid on the delicately balanced homogenous hydrogenation reactions is only one of a large number of possibilities. For example Lewis acids are known to add to coordinated ligands [6, 7] add to central metals [7, 8], and to undergo metathetical reactions [9, 10].

Results and discussion

$RhCl(PPh_3)_3$

The rate data which are summarized in Table 1 demonstrate that the influence of various Lewis acids is highly specific. Under the conditions which we employed boron trichloride inhibited olefin hydrogenation, aluminum trichloride, trimethylboron and $Eu(fod)_3$ had little effect, and two Lewis acids, aluminum tribromide and triisobutylaluminum, increased the rate.

Boron trichloride slows hydrogenation at a 1/1 $RhCl(PPh_3)_3/BCl_3$ ratio, and totally blocks catalysis at a 1/2 ratio. This result correlates with the known tendency of $RhCl(PPh_3)_3$ to form a 1/2 adduct with BCl_3 [7], which apparently is devoid of catalytic activity. Both a Lewis acid of comparable strength, $AlCl_3$, and two weaker acids, $B(CH_3)_3$ and $Eu(fod)_3$, have little influence on the rate, so the blocking of catalysis is not related in a simple fashion to the Lewis acidity. The increase in rate which was observed with $AlBr_3$ probably arises from a metathesis reaction to produce $RhBr(PPh_3)_3$ which is known to be a better catalyst than its chloride analog [1].

TABLE 1

RATES OF HYDROGENATION BY $RhCl(PPh_3)_3$ AND LEWIS ACIDS [a]

Co-catalyst [b]	Initial rates (mol/min)
Olefin: cyclo-C_6H_{10}	
None	$66 \pm 1 \times 10^{-6}$
BCl_3 (1/1)	14×10^{-6} [c]
BCl_3 (1/2)	0
$B(CH_3)_3$ (1/1)	$66 \pm 7 \times 10^{-6}$
$B(CH_3)_3$ (1/2)	$64 \pm 1 \times 10^{-6}$
$Eu(fod)_3$ (1/1) [d]	52×10^{-6}
$AlBr_3$ (1/1)	134×10^{-6}
$AlCl_3$ (1/1)	54×10^{-6}
$Al(i\text{-}Bu)_3$ (3/1)	$54 \pm 6 \times 10^{-6}$
$Al(i\text{-}Bu)_3$ (3/1)	82×10^{-6} [e]
Olefin: C_2H_4 [f]	
None	ca. 3×10^{-6}
$Al(i\text{-}Bu)_3$ (3/1)	ca. 26×10^{-6}

[a] $RhCl(PPh_3)_3$: 1.0×10^{-5} mol; initial C_6H_{10}: 4.9×10^{-3} mol and 4 ml C_6H_6 at 25 ± 0.1° and 760 Torr H_2. [b] Ratio of $RhCl(PPh_3)_3$ to Lewis acid is given in parenthesis. [c] Rate obtained after an 8.0 min induction period. [d] Fod = 6,6,7,7,8,8-heptafluoro-2,2-dimethyl-3,5-octadione anion. [e] Catalyst and $Al(i\text{-}Bu)_3$ premixed 1 h before olefin addition. [f] Solvent: 4 ml C_6H_6; $RhCl(PPh_3)_3$: 1.0×10^{-5} mol; initial C_2H_4 pressure: 300 mm; initial hydrogen pressure: 300 mm; temperature: ca. 25°.

The most interesting results were obtained with $Al(i\text{-}Bu)_3$ for which premixing of the aluminum alkyl and the rhodium complex was necessary to produce a modest rate enhancement for hydrogenation of cyclohexene. With ethylene a large rate enhancement was observed. The initial reaction between triisobutylaluminum and the rhodium complex which occurs during the premixing period probably involves alkylation (eqn. 2) followed by β-elimination (eqn. 3) to yield $RhH(PPh_3)_3$ in a manner similar to that reported by Keim [10].

$$3\,RhCl(PPh_3)_3 + Al(i\text{-}C_4H_9)_3 \rightarrow 3Rh(i\text{-}C_4H_9)(PPh_3)_3 + AlCl_3 \tag{2}$$

$$Rh(i\text{-}C_4H_9)(PPh_3)_3 \rightarrow RhH(PPh_3)_3 + C_4H_8 \tag{3}$$

From the rate data it appears that $RhH(PPh_3)_3$ displays more comparable rates in the hydrogenation of ethylene vs. cyclohexene than does $RhCl(PPh_3)_3$. The low rate of reaction of the latter catalyst with ethylene is attributed to the formation of a stable complex $RhCl(C_2H_4)(PPh_3)_2$ which does not react with H_2 at an appreciable rate [1, 11]. With other olefins the stability of the olefin complex is much less and as a result the metal complex can readily reenter the catalytic cycle via olefin dissociation. However, in the presence of $Al(i\text{-}Bu)_3$ the generation of $RhH(PPh_3)_3$ appears to create alternative pathways for the reaction of the ethylene complex. There are at least two reasonable possibilities: *(1)*, the olefin complex $RhH(C_2H_4)(PPh_3)_3$ is less stable and readily loses C_2H_4 thus avoiding the trapping of the catalyst or *(2)*, the presence of a metal hydride bond opens a new reaction pathway, involving C_2H_4 insertion via eqn. 4 or closely related alternatives, followed by hydrogenation of the alkyl complex,

$$RhH(PPh_3)_2 + C_2H_4 \rightleftharpoons Rh(C_2H_5)(PPh_3)_2 \tag{4}$$

$$Rh(C_2H_5)(PPh_3)_2 + H_2 \rightarrow RhH_2(C_2H_5)(PPh_3)_2 \tag{5}$$

$$RhH_2(C_2H_5)(PPh_3)_2 \rightarrow RhH(PPh_3)_2 + C_2H_6 \tag{6}$$

eqn. 5, and hydride transfer with alkane elimination, eqn. 6.

$RuCl_2P(Ph_3)_3$

The hydrogenation rate data given in Table 2 demonstrates that BCl_3, in a 1/1 mole ratio to the ruthenium complex, stops all catalytic activity, however a modest rate enhancement is observed upon addition of aluminum alkyls to the catalytic system. It is possible to explain this rate increase by a small perturbation of the proposed mechanism for olefin hydrogenation in the absence of acids, Fig. 1. According to this mechanism $RuCl_2L_3$ is only a precursor to the ruthenium containing species in the main catalytic cycle [12]. The transformation of $RuCl_2L_3$ to $RuClHL_2$ via reaction a and b (Fig. 1) is thus a key feature of the mechanism. It is well known for example, that addition of base promotes the formation of $RuHL_2$ by scavenging the HCl in equilibrium b.

To determine whether the aluminum alkyl was influencing reactions in the catalytic cycle (reactions c-e of Fig. 1) or those out of the cycle (a and b), we studied the influence of aluminum alkyls upon the rate of hydrogenation by one of the complexes in the main catalytic loop. As can be seen from Table 3

TABLE 2

RATES OF HYDROGENATION BY $RuCl_2(PPh_3)_3$ PLUS LEWIS ACIDS [a]

Co-catalyst [b]	Induction period (min)	Initial rate (mol/min)
Olefin: 1-hexene		
None	1.0	28×10^{-6}
BCl_3 (1/1)		0
Al(i-Bu)$_3$ (3/1)	<1.0	53×10^{-6}
None		2×10^{-6}
$Al(CH_3)_3$ (1/1)	<1.0	32×10^{-6} [c]
$Al(CH_3)_3$ (1/1)	<1.0	50×10^{-6} [d]
$Al(CH_3)_3$ (1/1)	<1.0	56×10^{-6} [d]
Olefin: 1-hexene plus 2 hexene [e]		
None	19	1×10^{-6}
Al(i-Bu)$_3$ (1/1)	5	14×10^{-6}
Al(i-Bu)$_3$ (3/1)	5.1	11×10^{-6}
$Al(CH_3)_3$ (3/1)	7.0	5×10^{-6}
$Al(CH_3)_3$ (3/1)	8.0	9×10^{-6} [f]

[a] $RuCl_2(PPh_3)_3$: 1.0×10^{-5} mol; initial C_6H_{12}: 3.9×10^{-3} mol and 4 ml C_6H_6 at 25 ± 0.1° and 760 Torr H_2. [b] The mole ratio of $RuCl_2(PPh_3)_3$ to Lewis acid is given in parenthesis. [c] Aluminum alkyl added to previous reaction mixture. [d] Consecutive to the previous reaction with olefin replenished. [e] 1-Hexene, 40%; *cis-* and *trans-*2-hexene, 60%. [f] Olefin added immediately after $Al(CH_3)_3$ no premixing.

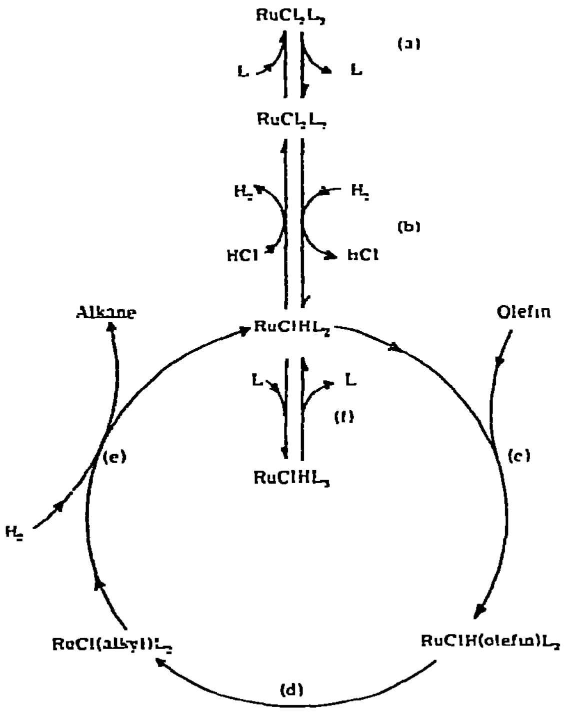

Fig. 1. Proposed mechanism for the catalytic hydrogenation of olefins by $RuCl_2(PPh_3)_3$.

TABLE 3

RATES OF HYDROGENATION OF 1-HEXENE BY $RuClH(PPh_3)_3$ PLUS LEWIS ACIDS[a]

Co-catalyst[b]	Induction period (min)	Initial rates (mol/min)
None	<1.0	230×10^{-6}
$Al(i\text{-}Bu)_3$ (1/1)	<1.0	230×10^{-6}[c]
None	<1.0	350×10^{-6}
$Al(CH_3)_3$ (1/1)	<1.0	340×10^{-6}[c]

[a] $RuClH(PPh_3)_3$: 1.0×10^{-5} mol; initial C_6H_{12}: 3.9×10^{-3} mol and 4 ml C_6H_6 at $25 \pm 0.1°$ and 760 Torr H_2. [b] Ratio of $RuClH(PPh_3)_2$ to Lewis acid given in parenthesis. [c] Performed as a successive experiment in which the olefin was replenished when AlR_3 was added.

the aluminum alkyls had a negligible influence upon the catalytic activity of $RuClH(PPh_3)_2$. Furthermore we found from independent spectrophotometric and NMR experiments that $RuClH(PPh_3)_3$ is produced from $RuCl_2(PPh_3)_3$ and AlR_3 in the presence of H_2. Therefore it seems highly unlikely that the main features of the mechanism (reactions c through e in Fig. 1) are altered by the presence of aluminum alkyls, but instead the function of the aluminum alkyl is to afford more rapid generation of $RuClH(PPh_3)_2$ or $RuClH(PPh_3)_3$.

There are at least three reaction sequences which are promising candidates for the rate enhancement by aluminum alkyls.

(1). Rapid Cl—alkyl interchange followed by β-alimination analogous to reactions 2 and 3 could yield $RuClHL_2$.

(2). Chlorine alkyl interchange (eqn. 7) followed by hydrogen uptake and alkane elimination (eqn. 8) could be faster than reactions a and b of Fig. 1, and thus promote the formation of $RuClHL_2$; i.e., reactions 7 and 8:

$$RuCl_2(PPh_3)_3 + AlR_3 \rightleftharpoons RuClR(PPh_3)_3 + AlClR_2 \tag{7}$$

$$RuClR(PPh_3)_3 + H_2 \rightarrow RuClH(PPh_3)_3 + RH \tag{8}$$

(3). The aluminum alkyl might scavenge HCl and thereby promote the formation $RuClH(PPh_3)_3$ via reactions 9 and 10:

$$RuCl_2(PPh_3)_2 + H_2 \rightarrow RuClH(PPh_3)_3 + HCl \tag{9}$$

$$HCl + AlR_3 \rightarrow AlClR_2 + RH \tag{10}$$

The first and second of the above possibilities were rendered possible by the detection of $RuClR(PPh_3)_3$ species in mixtures of $RuCl_2(PPh_3)_3$ and AlR_3. For R = methyl this compound was isolated and characterized as described in the experimental section. For R = isobutyl the compound appeared to be isolable but of insufficient stability for elemental analysis by an outside laboratory. To determine which of the three possiblities is the most likely, the reactions, $RuCl_2(PPh_3)_3 + Al(CH_3)_3$, $RuCl_2(PPh_3)_3 + H_2$, and $RuCl_2(PPh_3)_3 + Al(CH_3)_3 + H_2$, were followed spectrophotometrically. At 25° and with concentrations close to those used in the catalytic studies the first two reactions did not proceed to an appreciable extent in the course of an hour but the third was ca. 50% complete, $RhClH(PPh_3)_3$ being the product. It therefore appears that the primary influence of aluminum alkyls is to scavenge HCl via reaction 9 and thus increase the equilibrium concentrations of $RuClH(PPh_3)_3$ and $RuClH(PPh_3)_2$ in the catalytic reaction mixture.

In summary, Lewis acids were found to exert a variety of influences on some metal complex catalyzed, olefin hydrogenation reactions. Apparently none of the cases we studied involved rate enhancement via Lewis acid promoted ligand dissociation. However, it is likely that the systems reported by Hughes [5] do involve ligand removal by the Lewis acid and further search for similar systems is warranted.

Experimental

All reactions and syntheses were carried out by inert atmospheric and vacuum line techniques using oxygen-free solvents [13]. The catalysts $RhCl(PPh_3)_3$ and $RuCl_2(PPh_3)_3$ were obtained from Strem Chemical Co. and also synthesized by published methods [1, 14]. $RuClH(PPh_3)_3$ was synthesized from $RuCl_2(PPh_3)_3$ with H_2 and $N(C_2H_5)_3$ [15].

$RuCl(CH_3)(PPh_3)_3$ was prepared by the reaction of 2.0 g of $RuCl_2(PPh_3)_3$ with 0.3 ml $Al(CH_3)_3$ in 150 ml of dry, air-free benzene. The reaction mixture was stirred for two hours after which the yellow solid which formed was filtered, washed with n-hexane, and dried in vacuum. A CH_3 group analysis was performed by reaction of the product with HCl and collection of the evolved gas with a Toepler pump. (Found: Ru, 10.50; Cl, 3.77%; CH_3, 1.99. $RuC_{55}H_{48}P_3Cl$ calcd.: Ru, 10.77; Cl, 3.78%; CH_3, 1.61.)

BCl_3, $B(CH_3)_3$, $AlCl_3$ and $AlBr_3$ were purified by trap-to-trap distillation or sublimation. The $Eu(fod)_3$ (Pierce Chemical) was dried over P_2O_3. The aluminum alkyls (Texas Alkyls) were used as received.

With the exception, noted below, rate data were collected on a previously described isobaric hydrogenation apparatus [16, 17]. Considerable variation in rate was observed for runs in which $RuCl_2(PPh_3)_3$ was used without added Lewis acids. These erratic rates may arise from variable traces of base either in the complex or on the glass surface. Ethylene hydrogenation was followed by pressure change in a simple manometer system. Owing to the lack of vigorous stirring of the solution and lack of provision for gas circulation the actual rates are probably greater than those observed for the ethylene hydrogenation.

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