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HOMOGENEOUS TRANSFER HYDROGENATION OF KETONES CATALYZED BY MOLYBDENUM COMPLEXES

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Phosphine complexes of molybdenum, especially bisdinitrogenbis[1,2-bis(diphenylphosphino)ethane]molybdenum and tetrahydridobis-[1,2-bis(diphenylphosphino)ethane]molybdenum promote transfer hydrogenation of ketones by hydrogen donors, amongst which secondary alcohols are most effective.

We have recently reported the reaction of trans-$Mo(N_2)_2(DPE)_2$ [DPE = 1,2-bis-(diphenylphosphino)ethane] (I) with organic hydrogen donors [$D(H_n)$] to yield $MoH_4(DPE)_2$ (II) (eq.1).$^{1)}$ Since the chemistry of the molybdenum hydride of the

$$\underset{(I)}{\text{trans-}Mo(N_2)_2(DPE)_2} + m\ D(H_n) \longrightarrow \underset{(II)}{MoH_4(DPE)_2} + m\ D(H_{n-4/m})^{2)} + 2\ N_2 \quad (1)$$

type MoH_4L_4 (L = tertiary phosphine) has not been extensively investigated, we have examined the reaction of (II) with several unsaturated substrates. The hydride (II) has been found to react readily with ketones to give the corresponding alcohols

$$\underset{(II)}{MoH_4(DPE)_2} + 2\ RR'C{=}O \longrightarrow \text{"Mo complex"} + 2\ RR'CH\text{-}OH \quad (2)$$

(eq. 2). Combined equations 1 and 2 had led to the speculation that by using the complex (I), hydrogen atoms should be transferred from an organic hydrogen donor [$D(H_n)$] to a ketone to yield the corresponding dehydrogenated product [$D(H_{n-4/m})$] and alcohol. We now wish to report that such transferhydrogenation occurs in the presence of (I) and (II) as a catalyst (eq. 3). Although a number of group VIII metal catalysts are known to be active in the homogeneous hydrogenation of ketones by both molecular hydrogen$^{3)}$ and hydrogen donors, $^{4)}$ this is the first observation of the homogeneous group VI metal catalyst capable of hydrogenating ketones.

$$m\ D(H_n) + 2\ RR'CH{=}O \xrightarrow[\text{Mo complex}]{} m\ D(H_{n-4/m}) + 2\ RR'CH\text{-}OH \quad (3)$$

The reaction of (II) (0.1 mmol) with cyclohexanone (3 mmol) in benzene (4 ml) at reflux for 1 hr afforded cyclohexanol (0.14 mmol) and a green complex whose structure is yet uncertain. The hydride (II) can be prepared from (I) and 1-phenylethanol in good yield. Thus the transfer hydrogenation of cyclohexanone using 1-phenylethanol as a hydrogen donor has been expected to occur with the complex (I) as a catalyst. Cyclohexanone (3 mmol) has been allowed to react with 1-phenylethanol (3 mmol) in benzene (4 ml) at reflux in the presence of (I) (0.01 mmol). After 1 hr, cyclohexanol is obtained in 93 % yield.

To determine the effectiveness as a hydrogen donor, several compounds have been examined (Table 1). Although secondary alcohols such as 2-propanol are also effective, primary alcohols such as ethanol, benzyl alcohol, and methanol are less effective. It is noteworthy that both ethanol and benzyl alcohol, with which (I) gave no (II)1), show moderate hydrogen donating abilities. As a dehydrogenation product, the corresponding ketones and aldehydes are obtained from secondary and primary alcohols, respectively. These transfer hydrogenation reactions seem to be selective, since the following stoichiometries hold; e.g., when 1-phenylethanol is a donor, I) the amount of the acetophenone formed is equal to that of the cyclohexanol formed, II) the total amount of the acetophenone and the unchanged 1-phenylethanol is equal to that of the charged alcohol, and III) the total amount of the cyclohexanol and the unchanged cyclohexanone is equal to that of the charged ketone. Hydroaromatic compounds, such as tetrahydrofuran, pyrrolidine, and indoline which were found capable of affording the hydride (II),1) are not so effective. Acetone and diethyl ketone are also reducible by this catalyst system.

In the evaluation of other molybdenum complexes as a catalyst of hydrogen transfer from 2-propanol to cyclohexanone, it has been found that (II) is also a satisfactory catalyst (Table 2). Although moderate activity is exhibited with $Mo(C_2H_4)(DPE)_2$ (III)5) and trans-$Mo(CO)(N_2)(DPE)_2$ (IV)6), cis-$Mo(CO)_2(DPE)_2$ (V) proved to be inactive. The effectiveness of the complex (I), (III), (IV), and (V) as catalysts may be elucidated in terms of the degree of ligand dissociation. In fact, when (I) is used as a catalyst precursor, the resulting complex has lost two dinitrogen ligands. When (III) and (IV) are used, they can be recovered after the reaction. The color of the reaction mixture using (IV), however, changed from orange to dark brown at reflux, suggesting the formation of the five-coordinate

Table 1. Transfer Hydrogenation of Cyclohexanone Catalyzed by (I)[a]

Hydrogen donor	(mmol)	Yield of cyclohexanol, (%)	Dehydrogenation product
1-phenylethanol	3	93	acetophenone
1-phenylethanol[b]	20	77	acetophenone
2-propanol	3	81	acetone
2-propanol[b]	20	75	acetone
ethanol	3	17	acetaldehyde
benzyl alcohol	3	43	benzaldehyde
methanol	3	1	—[c]
tetrahydrofuran	4	4	—[c]
2,5-dihydrofuran	4	4	—[c]
pyrrolidine	4	14	—[c]
indoline	15	6	indole

a) solvent: benzene = 4 ml, reaction time 1 hr. Unless otherwise noted, (I) = 0.1 mmol and cyclohexanone = 3 mmol

b) (I) = 0.05 mmol , cyclohexanone = 5 mmol

c) The dehydrogenation product was not identified.

Table 2. Effect of the Ligands[a]

Mo complex	Yield of cyclohexanol , (%)
trans-$Mo(N_2)_2(DPE)_2$ (I)	81
$MoH_4(DPE)_2$ (II)	88
$Mo(C_2H_4)(DPE)_2$ (III)	69
trans-$Mo(CO)(N_2)(DPE)_2$ (IV)	43
cis-$Mo(CO)_2(DPE)_2$ (V)	0

a) solvent: benzene = 4 ml, reaction time: 1 hr, Mo complex = 0.1 mmol , cyclohexanone = 3 mmol , 2-propanol = 3 mmol

$Mo(CO)(DPE)_2$ species[7)] analogous to (III). The inactivity of (V) may be ascribable to the stability of the six-coordinate species due to the strong coordination ability of the carbonyl ligands. When the hydride (II) is used as a catalyst, (II) is recovered in nearly quantitative yield.

Since (II) can be also prepared by the reaction of (I) with molecular hydrogen,[8)] ketone reduction by H_2 has been attempted. H_2 gas has been bubbled into a benzene solution (10 ml) of cyclohexanone (2 mmol) and (I) (0.1 mmol) at reflux. After 2 hr, 0.21 mmol of cyclohexanone has been obtained, thereby indicating that, in this condition, molecular hydrogen is less active for the ketone reduction.

A close mechanistic study is now in progress.

References and Note

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