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Rh(I) COMPLEXES CONTAINING FULLY ALKYLATED MONO- AND DIPHOSPHINE LIGANDS AS HIGHLY ACTIVE HYDROGENATION CATALYSTS FOR CARBONYL COMPOUNDS

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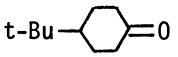
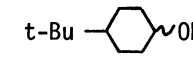
Our search for highly active hydrogenation catalysts for carbonyl compounds, starting with neutral Rh(I) hydride complexes, $[RhH(PR_3)_n]$ (R=i-Pr, n=3; R=Cy, n=2), has led to the discovery of cationic Rh(I) complexes with fully alkylated diphosphine ligands, $[Rh\{(i\text{-}Pr)_2P(CH_2)_nP(i\text{-}Pr)_2\}(NBD)]ClO_4$ (n=3,4). These compounds prove to be versatile and efficient for hydrogenation of a variety of carbonyl compounds, including aldehydes.

A number of rhodium complexes, e.g., neutral rhodium(I) complexes of Wilkinson type, $[RhXL_3]$ (L=triarylphosphines) and cationic rhodium(I) complexes containing an aryl-substituted diphosphines, were found to be active catalysts for olefin hydrogenation.[1] These metal complexes, however, are not very active for ketone hydrogenation.[1] An enhancement of the activity of rhodium complex catalysts was observed on the addition of strong alkali, i.e., $[RhCl(C_8H_{12})(PPh_3)]$–$NaBH_4$–KOH[2a] or $[RhCl_2(bpy)_2]Cl$–NaOH.[2b] In this paper we wish to report that the catalytic activity of rhodium(I) species for hydrogenation of carbonyl compounds can be markedly improved with electron-donating fully alkylated phosphines.

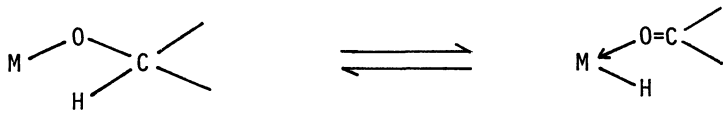
Our principal strategy was to increase the electron density of the metal center by utilizing the electron-donating trialkylphosphines together with a hydrido ligand. Since $[RhH\{P(i\text{-}Pr)_3\}_3]$ and $[RhH(PCy_3)_2]_2(\mu\text{-}N_2)$[3a] {a precursor of $[RhH(PCy_3)_2]$[3b] (Cy=cyclohexyl)} were then available, their activity was tested for several ketones (Table 1). The results were encouraging. $[RhH(PCy_3)_2]$ was even active for PhCOPh which could not readily be hydrogenated by Osborn's system, $[Rh(PPhMe_2)H_2(S)_2]^+$–H_2O (S=solvent), under ambient conditions.[4] This is rather remarkable since the Rh(I) hydride containing triarylphosphine, e.g., $[RhH(DBP)_4]$ (DBP=5-phenyl-5H-dibenzophosphole) is known to be totally inactive as a hydrogenation catalyst for ketones.[5]

Table 1 also includes results of transfer hydrogenation of some ketones effected with $[RhH(PCy_3)_2]_2(\mu\text{-}N_2)$ employing isopropanol as the hydrogen source. The product from 4-tert-butylcyclohexanone is mainly (94%) trans-4-tert-butylcyclohexanol in contrast to the predominant formation of the cis-product effected by $IrCl_6^{2-}$–$P(OMe)_3$ in acidic medium.[6] In the latter case an incipient protonation of the carbonyl oxygen atom may probably be involved, followed by the hydride transfer to the less hindered carbonyl face. The predominant formation of trans-alcohol in the present case suggests an extensive thermodynamic control which in turn implies a rapid reverse reaction, β-hydrogen elimination from the alcoholato complex intermediate. If this is the case, the overall catalytic rate with Rh(I) complexes of monodentate trialkylphosphines should have been impaired by rapid dehydrogenation of the product alcohol.

Table 1. Reduction of Ketones with $[RhH(PCy_3)_2]_2(\mu\text{-}N_2)$[a]

Entry	Substrate	H-source	Product(yield %)
1	cyclohexanone	H_2	cyclohexanol (93)
2	"	i-PrOH	" (99)
3	"	"	" (99)[b]
4	$PhCOCH_3$	i-PrOH	$PhCH(OH)CH_3$ (77)
5	PhCOPh	H_2	PhCH(OH)Ph (88)
6	"	i-PrOH	" (87)
7		i-PrOH	 (73)[c]
8	$CH_3COCOCH_3$	H_2	$CH_3CH(OH)COCH_3$ (89)[d]
9	"	i-PrOH	" (35)[e]

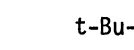
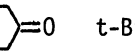
a) [Rh]=10mM, [S]/[Rh]=100 in abs. THF at 25°C, 1atm H_2, 20h. For transfer hydrogenation an excess of i-PrOH([i-PrOH]/[S]=10) was employed. b) Catalyst: $[RhH\{P(i\text{-}Pr)_3\}_3]$. c) trans/cis=94/6. d) H_2(100kg/cm^2) was employed; under ambient pressure no hydrogenation was occurred. e) $CH_3CH(OH)CH(OH)CH_3$ was also obtained in 7% yield.



The next problem is to discover how one can retard the reverse reaction. The use of a large amount of an alcohol should retard the dehydrogenation of the product alcohol. Contrary to our expectation, the qualitative experiment using i-PrOH as the solvent, which also functions as the hydrogen source, did not improve the rate (Table 1). Apparently we must seek the solution in the coordination structure of the catalyst complex. A dramatic effect of chelating ligands was found. A cationic Rh(I) complex of monodentate phosphine, $[Rh\{P(i\text{-}Pr)_3\}_2(NBD)]ClO_4$ (NBD=norbornadiene) was prepared in situ from $[Rh\{P(i\text{-}Pr)_3\}(NBD)]ClO_4$[7] and 1 mole of $P(i\text{-}Pr)_3$. This complex exhibited a much lower activity for hydrogenation of cyclohexanone and was practically inactive for 4-tert-butylcyclohexanone under ambient conditions (entry 1, Table 2). In contrast, cationic Rh(I) complexes of chelating diphosphines, $[Rh(L\text{-}L)(NBD)]^+$ [L-L=$(i\text{-}Pr)_2P(CH_2)_nP(i\text{-}Pr)_2$; n=3,4] showed a remarkable catalytic activity for hydrogenation of 4-tert-butylcyclohexanone (entry 2 and 3, Table 2). Notably, an analogous complex of aryldiphosphine, $[Rh\{Ph_2P(CH_2)_4PPh_2\}(COD)]ClO_4$ (COD=1,5-cyclooctadiene), shows only a poor activity for the cyclohexanone derivative, producing byproducts such as 4-tert-butyl-1-cyclohexenylmethyl ether and 4-tert-butyl-1,1-dimethoxycyclohexane (entry 4, Table 2). This result is a clear demonstration of the electronic effect of substituents on the phosphorous atoms.

The remarkable rate enhancement achieved by Rh(I) complexes of fully alkylated diphosphines deserves comment. The predominant formation of trans-4-tert-butylcyclohexanol from the cyclohexanone appears to be derived by a kinetic control since the reverse reaction is slow as confirmed by the following experiment. Thus, a mixture of cis- and trans-tert-butylcyclohexanol (33:67) was treated with hydrogen (25°C, 20h) in the presence of $[Rh(dipp)(NBD)]ClO_4$ [dipp=$(i\text{-}Pr)_2P(CH_2)_3$-

Table 2. Effect of Phosphine Ligand on Hydrogenation of Ketones with $[Rh(L\text{-}L)(NBD)]ClO_4$ [a]

Entry	L-L	Substrate	Product	$t_{1/2}$(min) [b]	Remarks
1	$2P(i\text{-}Pr)_3$			24h /1% [e]	
2	$(i\text{-}Pr)_2P(CH_2)_3P(i\text{-}Pr)_2$	"	"	7	trans/cis=89/11
3	$(i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2$	"	"	2.7	trans/cis=88/12
4	$Ph_2P(CH_2)_4PPh_2$ [c]	"	"	14h /38% [e]	trans/cis=99/1 [f]
5	$(i\text{-}Pr)_2P(CH_2)_3P(i\text{-}Pr)_2$ [d]	PhCOCOPh	PhCH(OH)CH(OH)Ph	7(15)	meso/dl=88/16
6	$(i\text{-}Pr)_2P(CH_2)_4P(i\text{-}Pr)_2$ [d]	"	"	9(20)	meso/dl=90/10

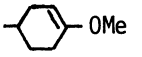
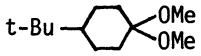
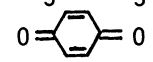
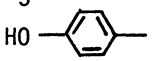
a) [Rh]=2.5mM, [S]/[Rh]=200 in abs. MeOH, 25°C, 1 atm H_2. b) Time required for 50% conversion of mono-ketone. The value in parentheses shows time required for 50% conversion of diketone. The yields were quantitative otherwise mentioned. c) COD was used instead of NBD. d) [Rh]=2mM, [S]/[Rh]=120. e) Time required for the given yield of alcohol. f)  (21%) and  (35%) were obtained as byproducts.

Table 3. Scope of Carbonyl Compounds for Hydrogenation with $[Rh(dipp)(NBD)]ClO_4$ [a]

Entry	Substrate	Product	$t_{1/2}$(min) [b]	Remarks
1	$CH_3COC_2H_5$	$CH_3CH(OH)C_2H_5$	70	
2	$PhCOCH_3$	$PhCH(OH)CH_3$	81	
3	PhCOPh	PhCH(OH)Ph	25h /70% [d]	
4	$CH_3COCOCH_3$	$CH_3CH(OH)CH(OH)CH_3$	10(24)	meso/dl=56/44
5			6	
6	PhCHO [c]	$PhCH_2OH$	5.5	
7	C_3H_7CHO [c]	C_4H_9OH	4	

a) [Rh]=2mM, [S]/[Rh]=120 in abs. MeOH, 25°C, 1 atm H_2. dipp=$(i\text{-}Pr)_2P(CH_2)_3P(i\text{-}Pr)_2$. b) Time required for 50% conversion of mono-ketone. The value in parentheses shows time required for 50% conversion of diketone. The yields were quantitative otherwise mentioned. c) [Rh]=2.5mM, [S]/[Rh]=200. d) Time required for the given yield of alcohol.

$P(i\text{-}Pr)_2$], only to recover the alcohol mixture of the same ratio (33:67). This demonstrates an effective suppression of the reverse reaction by the ligand chelation.

The bite angle of bidentate ligands (L-L) affects the coordination strength of the coplanar ligands A in square planar d^8 complexes $M(L\text{-}L)A_2$.[8] The effect of a change in the number of methylene groups between n=3 and 4 is small, for the catalytic rate varies only slightly depending on the carbonyl substrates (compare entry 2 and 3 or entry 5 and 6, Table 2). The stereoelectronic effects of chelating ligands are intricate in these cases.

Our successful strategy combining chelation and electronic effects of the ligands for Rh(I) ion led us to expand the substrate scope. In addition to the substrates already shown in Table 2, $[Rh(dipp)(NBD)]ClO_4$ is active for a variety of carbonyl compounds including benzoquinone and aldehydes as shown in Table 3. The monodentate phosphine complex, $[Rh\{P(i\text{-}Pr)_3\}_2(NBD)]ClO_4$, was totally inactive for hydrogenation of α-diketones and aldehydes. Neutral Rh(I) complexes of Wilkinson type are known to be effective decarbonylation agents for acyl halides[9] and aldehydes.[10] Cationic Rh(I) complexes, $[Rh\{P(i\text{-}Pr)_3\}_2(NBD)_2]ClO_4$, gave, upon treatment with benzaldehyde in methanol at ambient temperature, a carbonyl Rh(I) complex[11] and the hydrogenation did not proceed. The decarbonylation trend of Rh(I) species is apparently suppressed by the chelating diphosphine.

An understanding in depth of the marked enhancement of catalytic rates by the present cis-chelate diphosphine systems requires further research, and the mechanistic aspects will be the subject of future publications.

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6) H. B. Henbest and T. R. B. Mitchell, J. Chem. Soc., C. 1970, 785.

7) Orange crystals, mp 147.5-148.5°C(under vacuum), obtained from the reaction of $[Rh(NBD)Cl]_2$ and $P(i\text{-}Pr)_3$ in the presence of $AgClO_4$. Anal., Found: C, 42.35; H, 6.33%. Calcd for $C_{16}H_{29}ClO_4PRh$: C, 42.26; H, 6.43%. ^{1}H-NMR($CDCl_3$):δ 1.30 (q, J_{PH}=13 Hz, J_{HH}=7 Hz, 18H, $CHCH_3$), 1.88 (septet, J_{HH}=7 Hz, 3H, PCH), 3.75 (br s, 2H, CH=), 3.88 (br s, 2H, >CH), and 5.44 (br s, 2H, CH=). The $-CH_2-$ signal of NBD was overlapped with the large methyl signal of isopropyl group. IR(nujol): 1145 (br) and 1009 cm^{-1}(νClO_4).

8) T. Yoshida, K. Tatsumi, and S. Otsuka, Pure Appl. Chem., 52, 713 (1980).

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10) J. Tsuji and K. Ohno, Tetrahedron Lett., 1965, 3969.

11) The complex was recovered from the reaction mixture, pale yellow powder which showed an IR band at 1960 cm^{-1} for the terminal carbonyl groups.

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