

Notes

Selective Hydrogenation of 2-Cyclohexen-1-One with Ruthenium(II) and Osmium(II) Complexes

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Sanchez-Delgado *et al.* have reported selective hydrogenation of 2-cyclohexen-1-one with $\text{OsHBr}(\text{CO})(\text{PPh}_3)_3$, in which cyclohexanone was obtained as a product after 24 hrs of hydrogenation reaction at 100 °C and 1 atm of H_2 , but 69% cyclohexanone and 31% cyclohexanol were obtained after 2 hrs of hydrogenation reaction at 150 °C and 5 atm of H_2 .¹ They have also reported hydrogenation of bezothiophene and quinoline with $\text{MHCl}(\text{CO})(\text{PPh}_3)_3$ ($\text{M}=\text{Ru}, \text{Os}$).² We have previously reported the synthesis and catalytic activities of the ruthenium and osmium complexes containing arsine ligands for the hydrogenation of propionaldehyde, which showed somewhat higher catalytic activities than their analogous phosphine derivatives.³⁻⁵ In our recent work we have also found the effectiveness of the ruthenium(II) complexes containing the chelating bidentate diphosphine ligands in the homogeneous hydrogenation of cyclohexene.⁶ As a continuation of this research we now report the catalytic activities for the selective hydrogenation of 2-cyclohexen-1-one to cyclohexanone and cyclohexanol with previously prepared ruthenium(II) complexes, $\text{RuHCl}(\text{CO})(\text{PPh}_3)(\text{L-L})$ [$\text{L-L}=\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$, $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$] and newly prepared $\text{OsHCl}(\text{CO})(\text{PPh}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ under moderate conditions. The results were compared to that of well known $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$.

Experimental

Preparations of the $\text{RuHCl}(\text{CO})(\text{PPh}_3)(\text{L-L})$ complexes [$\text{L-L}=\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$, $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$] were described previously.⁵ The complex, $\text{OsHCl}(\text{CO})(\text{PPh}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$, was prepared according to the same method as the corresponding ruthenium complex. Found; C, 60.4; H, 4.3. Calcd. for $\text{OsC}_{45}\text{H}_{40}\text{OClP}_3$: C, 59.0; H, 4.4. IR (KBr disc, cm^{-1}): $\nu(\text{CO})$ 1915 (vs), $\nu(\text{Os-P})$ 517 (m). $\nu(\text{Os-H})$ could not be observed. ^1H NMR (CDCl_3 , 25 °C): $-\text{6.0}$ ppm [dq, $^2J(\text{H-P}_{\text{trans}})=93.2$ Hz, $^2J(\text{H-P}_{\text{cis}})=11.7, 16.5$ Hz]

Hydrogenation of 2-cyclohexen-1-one. A toluene (5.5 mL) solution containing catalyst (0.01 mmole), 2-cyclohexen-1-one (1 mmole) and internal standard (*n*-heptane, ca. 0.1 mL) was introduced into a Parr Series 4702 bench top mini reactor (Parr Instrument, 22 mL) with a gas inlet valve and a sampling valve. The system was purged twice with

nitrogen and then once with hydrogen to 3 atm at room temperature to remove air in the vessel. The reactor was introduced rapidly to 150 °C silicone oil bath. As soon as the temperature of the reactor maintained constant, the hydrogen pressure was fitted to 5 atm and stirring was started. This point was regarded as zero time and sampling was performed intermittently using a needle attached to the sampling valve. The temperature was maintained constant throughout the reaction. The extracted sample was immediately analysed by GC.

Results and Discussion

The catalytic activity of each of the ruthenium and osmium complexes containing bidentate ligands, $\text{RuHCl}(\text{CO})(\text{PPh}_3)(\text{L-L})$ [$\text{L-L}=\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, (1) $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{PPh}_2$ (2), $\text{Ph}_2\text{AsCH}_2\text{CH}_2\text{AsPh}_2$ (3)] and $\text{OsHCl}(\text{CO})(\text{PPh}_3)(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$ (4), has been investigated and also compared to that of well known $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ complex (5) in the hydrogenation of 2-cyclohexen-1-one to cyclohexanone and cyclohexanol conducted at 150 °C and hydrogen pressure of 5 atm. All the compounds tested have shown good catalytic activity under such reaction condition.³ More than 90% of mass balance have been observed and most of cyclohexen-1-one have been converted to cyclohexanone and cyclohexanol. All the hydrogenation reactions catalyzed by these complexes obey the pseudo-first order rate law. The observed rate constant, k_{obsd} , was obtained from the equation $-\text{d}[2\text{-cyclohexen-1-one}]/\text{dt} = k_{\text{obsd}}[2\text{-cyclohexen-1-one}]$ and the slope of the straight line in the graph of $\ln[2\text{-cyclohexen-1-one}]$ vs time (min).

The catalytic activities decrease in the order $1 > 5 > 2 > 4 > 3$ as shown in Table 1. Only the complex 1 shows a higher activity than 5. In the case of bidentate complexes 1-4, the reaction rate increases as the complex has more phosphines than arsines. This is the same results as we observed with the complexes 1-3 for the hydrogenation of propionaldehyde to propanol.⁵ The catalytic activities for the hydrogenation of 2-cyclohexen-1-one with complexes 1-5 are larger by 7-10 times than for the hydrogenation of cyclohexene carried out under the same condition. In addition, all the complexes show much higher selectivities for the C=C bond than the C=O bond in the 2-cyclohexen-1-one. (Table 2)

Table 1. Hydrogenation of 2-cyclohexen-1-one with 1-5^a

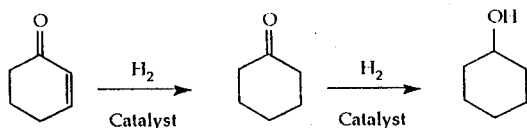
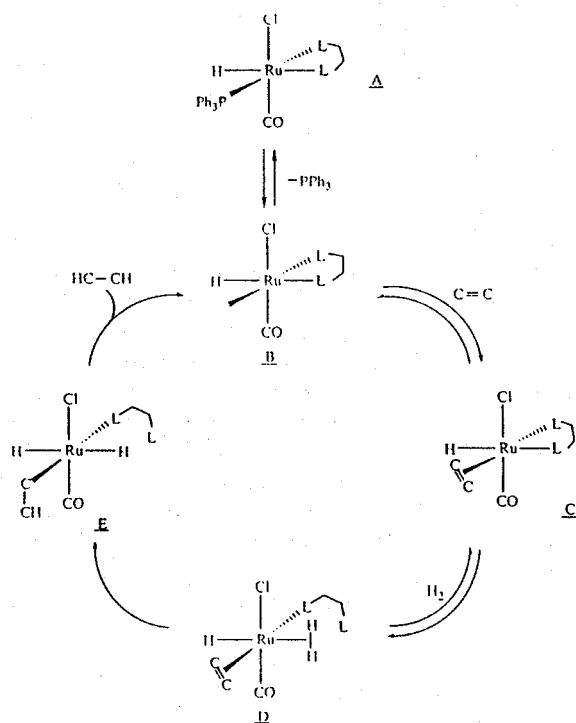
Complex	$r^a \times 10^3$	$k_{\text{obsd}}^b \times 10^3$ (min^{-1})	relative activity ^c	$k_{\text{obsd, 2-cyclohex-1-one}}/$ $k_{\text{obsd, cyclohexene}}$
1	479 ± 11	15.5 ± 1.2	1.68	7.4
2	394 ± 12	7.0 ± 0.4	0.81	7.4
3	260 ± 15	4.2 ± 0.1	0.43	10.7
4	389 ± 7	5.3 ± 0.2	0.65	—
5	523 ± 20	13.4 ± 0.9	1.00	8.6

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^aInitial rate constant at turnover number vs time. ^b $-\text{d}[2\text{-cyclohexen-1-one}]/\text{dt} = k_{\text{obsd}}[2\text{-cyclohexen-1-one}]$. ^c $k_{\text{obsd}}/k_{\text{obsd}}$ for complex 5.

Table 2. Product distribution (%) of 2-cyclohexen-1-one with 1-5

Compds	1 hr			2 hrs			3 hrs		
	S	P ₁	P ₂	S	P ₁	P ₂	S	P ₁	P ₂
1	57.6	42.4	15.1	17.5	14.0	68.5	6.0	4.9	89.1
2	56.1	34.4	9.5	32.9	46.1	21.0	18.8	53.0	28.2
3	73.0	24.0	3.0	56.7	40.0	3.3	42.4	54.1	3.5
4	69.4	30.6	0.0	47.4	46.6	6.1	10.0	70.1	19.9
5	49.5	49.2	1.3	20.5	70.8	8.7	8.8	75.8	15.4

S: substrate. P₁: cyclohexanone. P₂: cyclohexanol**Scheme 1.** Hydrogenation of 2-cyclohexen-1-one.**Scheme 2.**

The reaction mechanism on the hydrogenation of olefine has been widely studied.⁷⁻¹⁰ In the case with $\text{RhCl}(\text{PPh}_3)_3$, the rate determining step is the formation of a hydride alkyl complex by the attack of hydride to olefin. Although the hydride has a strong trans effect so that the ligand trans to the hydride is easily dissociated,¹¹ it is also reported

that the dissociation of the monodentate phosphine increases entropy in Rh and Ir complexes containing both chelate ring and monodentate phosphine.¹² Now we propose a possible mechanism for the hydrogenation of olefin with bidentate chelate complexes in Scheme 2. Due to a large basicity of the phosphines than that of the arsine, substitution by phosphine ligand proceeds more rapidly than by the arsine in step from E to B in Scheme 2. Our result is strongly supported by the fact that the increment of basicity activates the heterolytic cleavage of the dihydrogen complexes.¹³⁻¹⁵ Therefore, in the case of the bidentate complexes 1-4, the reaction rate increases as the complex has more phosphines than arsines.

When an electron withdrawing group is attached to the C=C bond as in 2-cyclohex-1-one, the electron density in the double bond is diminished so that the migration of hydride to olefin becomes easier (D→E), thus the catalytic activity for the hydrogenation of 2-cyclohexen-1-one with complexes 1-5 are larger than for the hydrogenation of cyclohexene carried out under the same condition.

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