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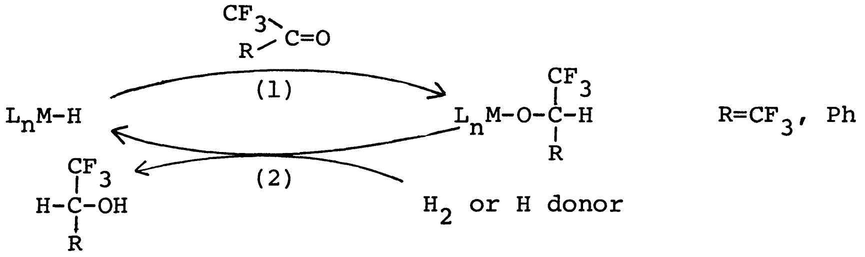
PREPARATION AND PROPERTIES OF GROUP 8 TRANSITION METAL ALKOXIDES RELEVANT TO CATALYTIC HYDROGENATION OF KETONES TO ALCOHOLS

Yoshinori HAYASHI, Sanshiro KOMIYA,† Takakazu YAMAMOTO,* and Akio YAMAMOTO*
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku Yokohama 227
†Department of Applied Chemistry for Resources, Tokyo University of Agriculture and Technology, 2-24-16 Nakamachi, Koganei, Tokyo 184

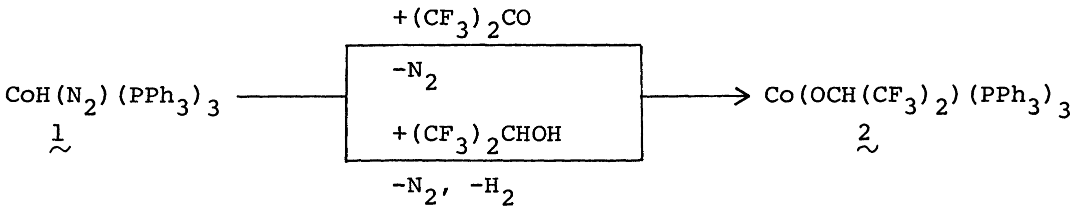
Alkoxo complexes, $M(OR)L_n$ and $MH(OR)L_n$ ($M=Co$, Rh, Ru; $L=PPh_3$; $R=CH(CF_3)_2$, $CHPh(CF_3)$)), have beeen prepared by insertion of fluoroketones into M-H bonds in $CoH(N_2)L_3$, $RhHL_4$, and RuH_2L_4. Hydrogenolysis of the Ru- and Rh-alkoxo complexes with H_2 or ethanol liberates corresponding fluoroalcohols in good yields. Catalytic activity in hydrogenation of ketones is correlated with the ease of hydrogenolysis of the alkoxo complexes.

Group 8 transition metal complexes having tertiary phosphines are known to catalyze hydrogenation of ketones with hydrogen donors (so-called transfer hydrogenation)$^{1)}$ or H_2.$^{2)}$ The catalytic process is considered to involve insertion of ketones into metal-hydride bonds (step 1 in Scheme 1) to give metal alkoxides as the key intermediates. The subsequent reaction of the alkoxides with H_2 or hydrogen donors (step 2) would constitute the next essential step to promote the catalytic hydrogenation. Reported examples of isolated, well characterized group 8 transition metal alkoxides are surprisingly rare$^{3)}$ and very few studies have been made regarding the reactivities of these metal alkoxides. We have found that stable alkoxides of cobalt, ruthenium, and rhodium can be prepared by introducing electron-withdrawing CF_3 group to the alkoxo group. Some of these alkoxides not only serve as model compounds relevant to catalytic hydrogenation of ketones, but also act as the actual hydrogenation catalysts of ketones.



Scheme 1. Possible reaction scheme for direct and transfer hydrogenations of ketones catalyzed by transition metal hydrides.

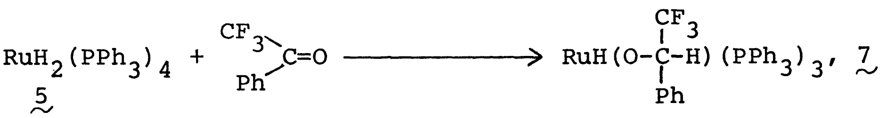
$CoH(N_2)(PPh_3)_3$ **1** reacts with perfluoroacetone, $(CF_3)_2CO$, at room temperature with liberation of N_2 to give a new alkoxo complex $Co(OCH(CF_3)_2)(PPh_3)_3$ **2** by insertion of the ketone into the Co-H bond. Complex **2** was also obtained by alcoholysis of **1** with $(CF_3)_2CHOH$ at 20 °C accompanied by evolution of H_2 and N_2.



$$\underset{\mathbf{1}}{CoH(N_2)(PPh_3)_3} \xrightarrow[\substack{+(CF_3)_2CHOH \\ -N_2,\ -H_2}]{\substack{+(CF_3)_2CO \\ -N_2}} \underset{\mathbf{2}}{Co(OCH(CF_3)_2)(PPh_3)_3}$$

The alkoxo cobalt complex **2** is thermally stable, but decomposes slowly in air. A similar reaction of **1** with trifluoromethyl phenyl ketone gave an insertion product, $Co(OCH(CF_3)Ph)(PPh_3)_3$, **3**. These alkoxo compounds were recrystallized from mixtures of benzene-hexane and characterized by elemental analysis, IR spectroscopy as well as by chemical reactions. The IR spectrum of complex **2** shows characteristic ν(C-O) and ν(C-F) bands at 1090 and 1200 cm^{-1}, respectively. Observed magnetic susceptibility of 3.0 BM for **2** suggests a tetrahedral structure. Acidolysis of **2** with dry HCl in Et_2O readily liberated hexafluoro-2-propanol quantitatively, supporting the composition of **2**. $CoCH_3(PPh_3)_3$ also reacted with $(CF_3)_2CO$ at 0 °C to give an insertion product $Co(OC(CH_3)(CF_3)_2)(PPh_3)_3$, **4**.

Although the second row transition metal hydrides such as $RuH_2(PPh_3)_4$, **5**, and $RhH(PPh_3)_4$, **6**, did not react with these fluoro ketones under ambient conditions, reactions performed for longer period at higher temperatures gave similar alkoxo complexes $RuH(OCH(CF_3)Ph)(PPh_3)_3$ **7** and $Rh(OCH(CF_3)_2)(PPh_3)_3$ **8**. In the reaction of $RuH_2(PPh_3)_4$, **5**, with trifluoromethyl phenyl ketone at 60 °C, the C=O bond insertion into one of the Ru-H bond takes place to afford a violet hydrido alkoxo complex $RuH(OCH(CF_3)Ph)(PPh_3)_3$, **7**.



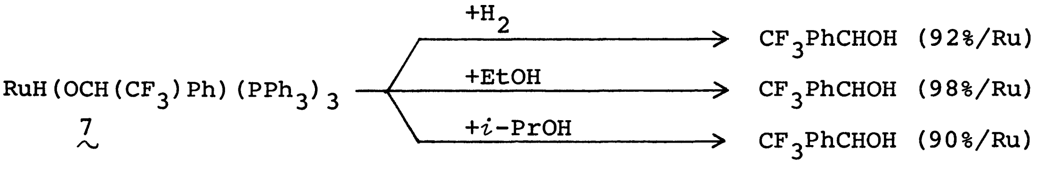
$$\underset{\mathbf{5}}{RuH_2(PPh_3)_4} + (CF_3)(Ph)C{=}O \longrightarrow RuH(O\text{-}\overset{CF_3}{\underset{Ph}{C}}\text{-}H)(PPh_3)_3,\ \mathbf{7}$$

IR spectrum of **7** shows characteristic ν(Ru-H), ν(C-F), and ν(C-O) at 1930, 1200, and 1010 cm^{-1}, respectively. ^1H-NMR of **7** at room temperature shows a broad peak at 5.0 ppm for $OC\underline{H}(CF_3)Ph$ and a quartet at -19.3 ppm assignable to Ru-H coupled with three magnetically equivalent phophorus nuclei (J(P-H)=29.2 Hz). $^{31}P\{^1H\}$-NMR spectrum of **7** at -78 °C in toluene shows typical ABX pattern suggesting a square pyramidal structure: δ: 93.4 (t), 53.7 (dd), 31.8 (dd) from external PPh_3, $J_{AX}=J_{BX}=27.3$ Hz, $J_{AB}=26.9$ Hz. Isolation of a similar alkoxo complex from insertion reaction of $(CF_3)_2CO$ into Rh-H bond of **6** was unsuccessful and an uncharacterized Rh-carbonyl complex was obtained. However, treatment of **6** with a large excess of hexafluoro-2-propanol in toluene at 80 °C for 3 d afforded an orange complex, $Rh(OCH(CF_3)_2)(PPh_3)_3$, **8**, with liberation of a quantitative amount of hydrogen.

$$\underset{\mathbf{6}}{RhH(PPh_3)_4} + (CF_3)_2CHOH \longrightarrow H_2 + \underset{\mathbf{8}}{Rh(OCH(CF_3)_2)(PPh_3)_3}$$

The IR spectrum of **8** shows ν(C-F) and ν(C-O) bands at 1200 and 1090 cm^{-1}, respectively. ^{1}H-NMR of **8** at room temperature in toluene shows a septet at 4.6 ppm assignable to $OC\underline{H}(CF_3)_2$ coupled with six fluorine nuclei (J(H-F)=7.0 Hz). $^{31}P\{^{1}H\}$-NMR of **8** at -20 °C shows a typical AX_2 pattern suggesting a square planer structure: 56.4 ppm (from external PPh_3, dt, J_{P-P}=43.0 Hz, J_{P-Rh}=173.8 Hz, 1P), 29.7 (dd, J_{P-Rh}=158.2 Hz, 2P). Acidolysis of **7** and **8** with dry HCl in Et_2O liberated quantitative amounts of the corresponding alcohols, supporting their compositions.

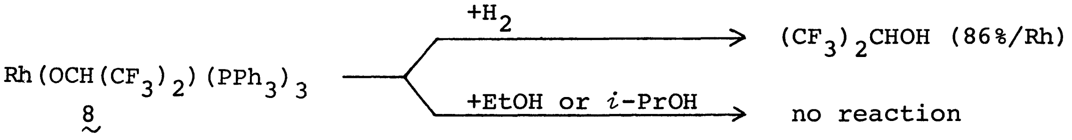
Reactivities of the isolated alkoxo complexes toward hydrogen donors such as H_2 and alcohols were examined. The ruthenium alkoxo complex, **7**, smoothly liberated 1 equivalent each of $CF_3PhCHOH$ on interaction with H_2, ethanol, and 2-propanol in toluene at room temperature. $RuH_4(PPh_3)_3$ was recovered in the hydrogenolysis of **7** with H_2 in benzene, whereas $RuH_2(PPh_3)_4$, **5**, was obtained on treatment of **7** with ethanol in the presence of free PPh_3. The latter reaction was accompanied by formation of ethyl acetate (50 mol%/Ru), a dimer of acetaldehyde.



$RuH_2(PPh_3)_4$ and ethyl acetate are considered to be formed by β-hydrogen elimination from $RuH(OC_2H_5)(PPh_3)_3$ formed by alkoxy group exchange reaction of **7**. RuH_2L_4 is known to catalyze dimerization of CH_3CHO into ethyl acetate.[4)] When phenol was employed in the alcoholysis, an intermediate hydrido phenoxo complex $RuH(OPh)(PPh_3)_2$,[5)] **9**, was isolated with concomitant formation of 1-phenyl-2-trifluoroethanol.

$$\underset{\mathbf{7}}{RuH(OCH(CF_3)Ph)(PPh_3)_3} + PhOH \longrightarrow \underset{\mathbf{9}}{RuH(OPh)(PPh_3)_2} + CF_3PhCHOH$$

The rhodium complex **8** also reacted with H_2 to liberate the corresponding alcohol quantitatively, but it was unreactive toward alcohols.



In contrast to the high reactivities of the alkoxo complexes of Ru and Rh, the cobalt analogue **2** showed no reactivity toward hydrogen and alcohol.

Results of catalytic hydrogenation and transfer hydrogenation of CF_3COPh with **1**, **5**, and **6** are shown in Table 1. Ruthenium dihydride **5** was found to be the most efficient catalyst for the hydrogenation and transfer hydrogenation of ketone. Rhodium hydride **6** catalyzes hydrogenation of CF_3COPh, but it did not catalyze the transfer hydrogenation. Cobalt hydride **1** showed no catalytic activity for the hydrogenation and transfer hydrogenation of ketone. The present catalytic behavior is clearly parallel to the ease of hydrogenolysis of the isolated alkoxo metal intermediates, suggesting the hydrogenolysis is the most important rate limiting step in the catalytic hydrogenation of ketones.

Table 1. Catalytic Hydrogenation of CF_3COPh

Catalyst		Hydrogen donor	Temp/ °C	Conversion/%
Co	**1**	H_2 (1 atm)	20	0
	1	H_2 (50 atm)	100	0
	1	EtOH	20	0
	1	EtOH	100	0
Ru	**5**	H_2 (1 atm)	100	100
	5	*i*-PrOH	60	75
	5	EtOH	100	95
Rh	**6**	H_2 (50 atm)	100	97
	6	H_2 (1 atm)	100	55
	6	*i*-PrOH	100	0
	6	EtOH	100	0

Conditions: in toluene (5 ml) for 2 d; CF_3COPh=3.6 mmol; catalyst=0.005 mmol.

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