Efficient Catalytic C–H Activation of Alkanes: Regioselective Carbonylation of the Terminal Methyl Group of n-Pentane by $RhCl(CO)(PMe_3)_2$

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The terminal methyl group of n-pentane was regioselectively carbonylated to give n-hexanal under mild conditions (1 atm pressure of CO, room temperature) by photocatalysis in the presence of $RhCl(CO)(PMe_3)_2$.

C–H bond activation of hydrocarbons by transition metal complexes is a subject of current interest.[1] In particular, the regioselective functionalization of the terminal methyl group of alkanes is the ultimate goal. Conventional functionalization methods available for alkanes *via* cationic or radical reactions such as acid-catalysed carbonylation,[2] halogenation with various reagents,[3] and biomimetic hydroxylation catalysed by metalloporphyrins,[4] are not terminal-selective. On the other hand, functionalization through transition metal complex-assisted C–H bond activation is believed to have considerable potential, as judged from the selective attack at the primary C–H bond.[5] However, there have been few catalytic reactions which involve C–H bond activation. Although preferential formation of hex-1-ene was observed at the very early stage of the transfer hydrogenation reaction of neohexene with n-hexane in the presence of an iridium polyhydride, internal alkenes were the final main products because of a rapid isomerization.[6] In the previous paper, we reported efficient carbonylation of benzene by photocatalysis in the presence of $RhCl(CO)(PMe_3)_2$.[7] We report herein that alkanes can be catalytically carbonylated and that the reaction is highly regioselective toward primary C–H bonds.

When cyclohexane under atmospheric pressure of carbon monoxide was irradiated for 16.5 h in the presence of $RhCl(CO)(PMe_3)_2$, cyclohexanecarboxaldehyde, cyclohexanemethanol, and cyclohexanecarboxylic acid were obtained in yields of 206, 172, and 82%/Rh, respectively.† The alcohol and the carboxylic acid seemed to be secondary products from the aldehyde.[7a] This provides the first example of the catalytic carbonylation of alkane C–H bonds assisted by transition metal complexes. As the reaction progressed, the activity diminished with the concomitant decrease in the i.r. absorption band of the catalyst (ν_{CO} 1966 cm^{-1}) present in the

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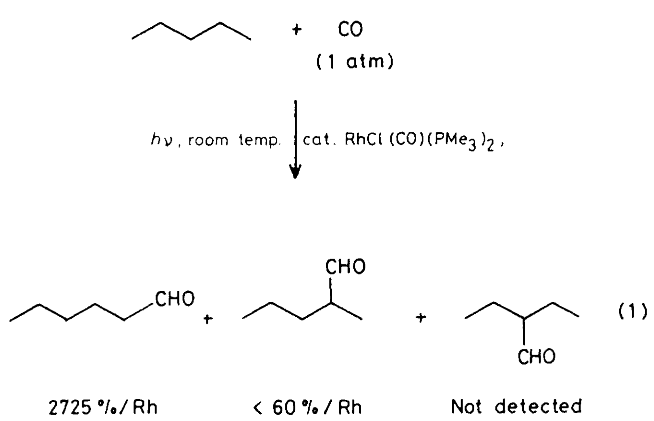
† A typical reaction procedure was as follows; 0.7 mM solution of the catalyst [$RhCl(CO)(PMe_3)_2$ 6.7 mg (0.021 mmol) in cyclohexane as a solvent (30 ml)] placed in a Pyrex flask was irradiated by a 100 W high pressure mercury lamp (UVL-100H, Riko Corp.) at room temperature under an atmospheric pressure of CO (balloon). The products were characterized by g.c. retention time and g.c.–mass spectrometry.



reaction mixture. The yields of the products obtained above were only 193, 245, and 149%/Rh, respectively, even after a prolonged irradiation time of 26.5 h.

When the same procedure was applied to the carbonylation of a non-cyclic alkane, the reaction was much more efficient than for cyclohexane and extremely regioselective. Thus, n-pentane afforded n-hexanal in a yield of 2725%/Rh after 16.5 h, while the yield of 2-methylpentanal was less than 60%/Rh and 2-ethylbutanal was not detected [equation (1)].[‡] The higher reactivity of primary C–H bonds as compared with secondary ones is probably due to steric reasons because the bond energy of the former is larger than the latter.[8]

The active species is presumably $RhCl(PMe_3)_2$ which is in equilibrium with $RhCl(CO)(PMe_3)_2$, since it has been reported that flash photolysis of $RhCl(CO)(PPh_3)_2$ with light >315 nm revealed the formation of $RhCl(PPh_3)_2$.[9][§] A tentative catalytic cycle is summarized as follows, *e.g.* for n-pentane: (i) oxidative addition of n-pentane to $RhCl(PMe_3)_2$ to afford $(n\text{-}C_5H_{11})(H)RhCl(PMe_3)_2$ is followed by (ii) CO insertion to result in $(n\text{-}C_5H_{11}CO)(H)RhCl(PMe_3)_2$, and (iii) reductive elimination leading to the formation of n-hexanal and regeneration of $RhCl(PMe_3)_2$. The diminishing catalytic activity is possibly due to the formation of $[RhCl(PMe_3)_2]_2$.[9]

In summary, this reaction offers a novel procedure for catalytic carbonylation of alkanes leading to aldehydes. In relation to the hydroformylation reaction of alkenes, an important class of industrial processes, the new procedure will have considerable potential in view of the mild reaction conditions and remarkably high terminal selectivity, as well as the abundance of the raw materials.

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[‡] A benzene reaction under the same conditions gave benzaldehyde, benzyl alcohol, and benzoic acid, in yields of 5729, 1278, and 149%/Rh, respectively.

[§] It is interesting to note that the wavelength of the most intense emission from a high pressure mercury lamp (365 nm) coincides with the absorption maximum of $RhCl(CO)(Pme_3)_2$ ($\lambda_{max.}$ 360nm) which is assigned to the metal-to-ligand charge-transfer band.[10]