

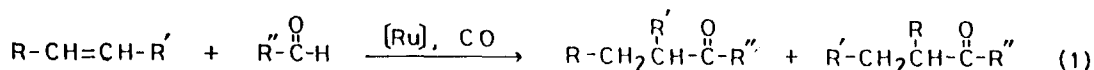
RUTHENIUM COMPLEX CATALYZED INTERMOLECULAR HYDROACYLATION OF OLEFINS

Teruyuki Kondo, Yasushi Tsuji, and Yoshihisa Watanabe*

Department of Hydrocarbon Chemistry, Faculty of Engineering,
 Kyoto University, Sakyo-ku, Kyoto 606, Japan

Summary: Dodecacarbonyltriruthenium ($\text{Ru}_3(\text{CO})_{12}$) and (η^4 -1,5-cyclooctadiene)(η^6 -1,3,5-cyclooctatriene)ruthenium ($\text{Ru}(\text{COD})(\text{COT})$) catalyzed the hydroacylation of olefins with aldehydes at 180 - 200 °C for 48 h under 20 kgcm⁻² of carbon monoxide to give unsymmetric ketones in good yields.

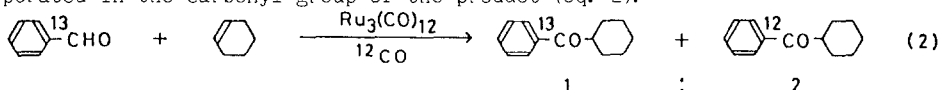
Although a number of examples of transition-metal complexes catalyzed activation of aldehydes leading to decarbonylation have been reported,¹⁾ little is known about catalytic addition of aldehydes to olefins via activation of the C-H bond. It has been reported that a rhodium complex catalyzes intramolecular hydroacylation of ω -unsaturated aldehydes²⁾ and the mechanistic studies are well performed.³⁾ However, there are still only a few methods for intermolecular hydroacylation reaction and the substrates are strictly limited.⁴⁾ In the course of our study on ruthenium complex catalysts,⁵⁾ we found that zero-valent ruthenium complexes catalyze intermolecular hydroacylation of olefins with aldehydes to give unsymmetric ketones in good yields (eq. 1), the preliminary results of which we now report.



In a typical procedure, a mixture of cyclohexene (4.05 ml, 40 mmol), benzaldehyde (530 mg, 5 mmol) and $\text{Ru}_3(\text{CO})_{12}$ (32 mg, 0.05 mmol) was heated in a 50 ml stainless steel autoclave with stirring at 200 °C for 48 h under 20 kgcm⁻² of carbon monoxide. Careful vacuum distillation of the reaction mixture afforded 414 mg (yield 44 %) of 1. Other reactions were performed in a similar manner except for paraformaldehyde (see Table). All products were characterized spectroscopically and satisfactory analytical data were obtained.




















Representative results are summarized in Table. In the presence of a catalytic amount of the ruthenium complex, the addition of benzaldehyde and its derivatives to olefins gave the adducts in 40 - 54 % yield (Runs 1-5, 7). For the reaction of 4-chlorobenzaldehyde with cyclohexene, the adduct 2 was obtained in 51 % yield (Run 2), together with chlorobenzene (44 % yield). This result indicates that the present reaction was competed with decarbonylation of aldehydes.⁶⁾ From terminal olefin, both straight and branched adducts were obtained in ca. 2.9/1 ratio (Run 5). When cyclohexene was treated with paraformaldehyde under the same reaction conditions, firstly generated aldehyde 4 was converted to ester 5 via Tishchenko-type transformation (Run 6). Only when the reaction was carried out in benzene, 4 and alcohol 6 which is a reduced product of aldehyde, were obtained (Run 7).

In the present reaction, carbon monoxide pressure is essential for the catalytic activity. Under an argon atmosphere, benzaldehyde was converted to various products and the adduct **1** was obtained in only 5 %, while $\text{Ru}_3(\text{CO})_{12}$ was decomposed to Ru metal. When the reaction was carried out under 20 kgcm^{-2} of carbon monoxide, $\text{Ru}_3(\text{CO})_{12}$ was recovered in 60 %. $\text{Ru}(\text{COD})(\text{COT})$ showed the comparable catalytic activity (Run 4) but it was completely converted to $\text{Ru}_3(\text{CO})_{12}$. These results indicate that carbon monoxide stabilizes active catalyst species such as $\text{Ru}(\text{CO})_5$ and $\text{Ru}_3(\text{CO})_{12}$, which were identified by FT-IR absorption, and suppresses decarbonylation of aldehydes. The reaction using ^{13}C -enriched benzaldehyde with cyclohexene revealed that the scramble occurred to some extent and external carbon monoxide was also incorporated in the carbonyl group of the product (eq. 2).



In summary, this reaction offers a novel procedure for the synthesis of unsymmetric ketones via hydroacylation. Application of the present reaction is now in progress.

Table. Ruthenium Complex Catalyzed Intermolecular Hydroacylation of Olefins^a

Run	Aldehyde	Olefin	Products (%) ^b	Run	Aldehyde	Olefin	Products (%) ^b
1			 50 (44) 1	5		$n\text{-C}_4\text{H}_9\text{CH=CH}_2$	 35 $n\text{-C}_6\text{H}_{13}\text{CO-}$
2	Cl- 		Cl-  51 (48) 2	6	$(\text{HCHO})_n$		 12 $n\text{-C}_4\text{H}_9\text{CH-CO-}$
3	$\text{CH}_3\text{-}$ 		$\text{CH}_3\text{-}$  54 (50) 3	7 ^d	$(\text{HCHO})_n$		 15 5 CH_3 CH-CO-
4 ^c			1 40				 4 15  5 30 CH_2OH

^a Aldehyde (5 mmol), olefin (40 mmol), $\text{Ru}_3(\text{CO})_{12}$ (0.05 mmol) at 200 °C for 48 h under 20 kgcm⁻² of CO.

^b Determined by GLC and figures in parentheses were isolated yields. ^c Ru(COD)(COT) (0.15 mmol) was used.

^d (HCHO)_n (15 mmol), cyclohexene (5 mmol), Ru₃(CO)₁₂ (0.05 mmol), benzene (3.5 ml) at 200 °C for 24 h under 20 kgcm⁻² of CO.

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