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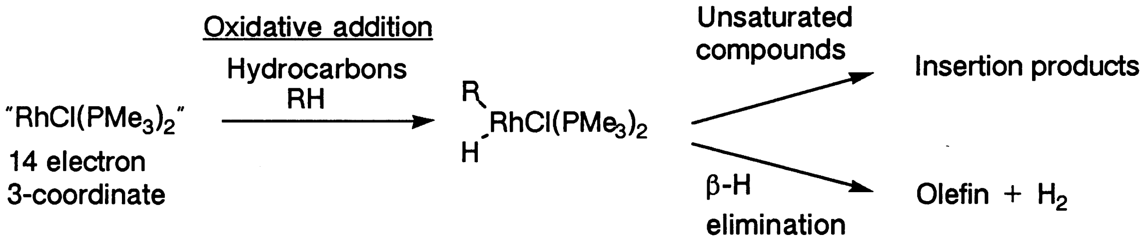
Thermal C-H Activation Catalyzed by $RhCl(CH_2=CH_2)(PMe_3)_2$. Hydrogen Transfer from Cycloalkanes to Ethylene and Ethylene Insertion into Cycloalkanes

Toshiyasu SAKAKURA, Fujio ABE, and Masato TANAKA*
National Chemical Laboratory for Industry, Tsukuba, Ibaraki 305

Dehydrogenation of cycloalkanes to cycloalkenes is catalyzed by $RhCl(CH_2=CH_2)(PMe_3)_2$ under ethylene pressure at a high temperature over 170 °C. Ethylene insertion into sp^3 C-H bond of cycloalkanes occurs at 230 °C to afford ethylcycloalkanes.

Recently we have demonstrated that the $RhCl(CO)(PMe_3)_2$ (**1**)-hν catalytic system efficiently functionalizes C-H bonds of hydrocarbons.$^{1)}$ A problem of this system is the necessity of constant UV irradiation. Here, we wish to report thermal C-H activation of alkanes with the ethylene analogue of **1**.$^{2)}$

In the $RhCl(CO)(PMe_3)_2$-hν system, $RhCl(PMe_3)_2$ was postulated as a key intermediate (Eq. 1).$^{1,3)}$ Hence, we investigated the reactivity of



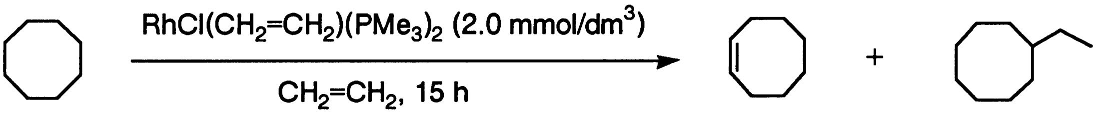
(1)

$RhCl(PMe_3)_2$ equivalents. A chlorine-bridged dimer, $[RhCl(PMe_3)_2]_2$$^{4)}$ (**2**) is an easily accessible equivalent to "$RhCl(PMe_3)_2$". Although cyclooctene (1 to 100 equivalent) did not form any adduct with **2**, ethylene easily reacted with **2** to give the four-coordinate complex, $RhCl(CH_2=CH_2)(PMe_3)_2$ (**3**). The trans configuration of the two phosphine ligands can be assigned by the relatively small rhodium-phosphorus coupling (J_{Rh-P} = 120 Hz) in ^{31}P-NMR.$^{5)}$

Since the ethylene complex **3** easily decomposes in the absence of excess ethylene at room temperature (Eq. 2),$^{5)}$ we investigated the

$$RhCl(CH_2{=}CH_2)(PMe_3)_2 \rightleftharpoons \{RhCl(PMe_3)_2\}_2 + CH_2{=}CH_2 \qquad (2)$$

utilization of a thermally generated "$RhCl(PMe_3)_2$" in catalytic C-H bond activation. When a cyclooctane solution of **3** (0.010 mmol in 5 cm^3) was heated at 120 °C under ethylene (50 atm), no reaction occurred. However, severer conditions (170 °C, 56 atm) resulted in catalytic cyclooctene formation (Eq. 3). It is noteworthy here that the ethylene complex remained undeteriorated after the reaction as judged from the UV absorption. The dihydrogen abstracted from cyclooctane seems to have been transferred to give ethane;6) no dihydrogen was detected in the gas phase. Although transfer hydrogenation-type dehydrogenation of alkanes has been well investigated by Crabtree and Felkin, the capable hydrogen acceptor has been limited to *t*-butylethylene.7) Thus, the present procedure to use ethylene is much more preferable from an economical view point. The pentahydrido-iridium complex, $IrH_5[P(i\text{-}Pr)_3]_2$, which was reported to be a very effective catalyst by Felkin,7b) exhibited only a low catalytic activity under ethylene; turnover of cyclooctane dehydrogenation was 0.32 after 15 h at 170 °C under 58 atm of ethylene.

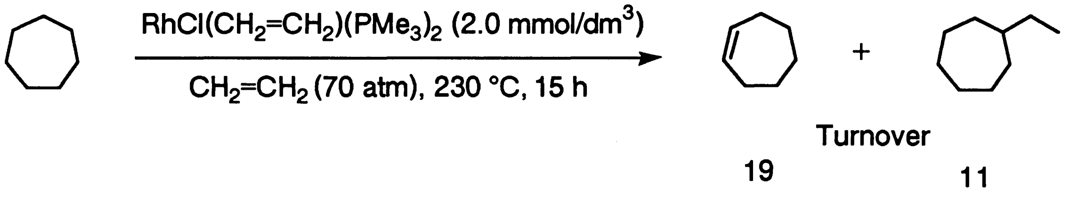


Temp /°C	Press. /atm	Turnover	
170	11	3.0	0.0
170	56	9.2	0.2
230	30	32	7.2
230	70	11	14

(3)

The reaction under a lower ethylene pressure (11 atm at 170 °C) resulted in partial decomposition of the complex; absorbance at 416 nm decreased to 62% of the starting solution. On the other hand, the reactions at 230 °C led to the complete disappearance of the absorption band at 416 nm and a new band appeared at 361 nm with some deposit of the metal. Interestingly, the reaction at 230 °C , especially under a higher ethylene pressure, afforded ethylcyclooctane8,9) besides cyclooctene. Examples of addition of aliphatic hydrocarbons to olefinic compounds10) are rare as compared with addition of arenes to C=C bond.11) Butenes were also formed in a considerable amount at 230 °C (turnover 12 after 15 h under 30 atm, 1- : 2-trans : 2-cis = 5 : 3 : 2).12)

Cycloheptane reacted similarly to give cycloheptene and ethylcycloheptane (Eq. 4).[8,9] Since cyclooctene and ethylcyclooctane were not detected at all in the reaction of Eq. 4, the formation of these products in Eq. 3 cannot be ascribed to ethylene oligomerization.



(4)

In summary, thermal C-H activation of alkanes proceeded catalytically with RhCl(CH$_2$=CH$_2$)(PMe$_3$)$_2$. Improvement of the catalytic activity and utilization of other unsaturated compounds in place of ethylene will be coming topics.

References

1) a) M. Tanaka and T. Sakakura, *Pure Appl. Chem.*, **62**, 1147 (1990); b) T. Sakakura, T. Sodeyama, K. Sasaki, K. Wada, and M. Tanaka, *J. Am. Chem. Soc.*, **112**, 7221 (1990); c) T. Sakakura, T. Sodeyama, and M. Tanaka, *New J. Chem.*, **13**, 737 (1989) and references cited therein.

2) We have reported some rhodium(I) complexes thermally promote the dehydrogenation of cyclooctane.[1c] Recently, Saito et al. have demonstrated the turnover number could exceed the unity when the reaction was carried out at higher temperatures. See T. Fujii and Y. Saito, *J. Chem. Soc., Chem. Commun.*, **1990**, 757.

3) C. T. Spillet and P. C. Ford, *J. Am. Chem. Soc.*, **111**, 1932 (1989); J. A. Maguire, W. T. Boese, and A. S. Goldman, *ibid.*, **111**, 7088 (1989); D. B. Pourreau, T. L. Netzel, and W. F. Humer, 7th International Symposium on Homogeneous Catalysis, Abstracts P-28, Lyon (1990).

4) H. Werner and R. Feser, *Z. Naturforsch., B*, **35**, 689 (1980); the complex can be recrystallized from toluene at a low temperature. ^{31}P-NMR (C$_6$D$_6$) δ 2.7 (d, $J_{\mathrm{Rh-P}}$ = 193 Hz).

5) Spectral data of **3**. ^{1}H-NMR (C$_6$D$_6$) δ 0.93 (t, J = 2.8 Hz, PMe$_3$), 3.99 (br. s, CH$_2$=CH$_2$). ^{31}P-NMR (C$_6$D$_6$) δ -10.4 (d, $J_{\mathrm{Rh-P}}$ = 120 Hz). UV-VIS (benzene) 413 nm (ε 2.0 x 10^3). Cooling of a toluene solution of **3** under ethylene atmosphere gave bright yellow crystals. However, the filtrated complex rapidly decomposed when brought to dryness under vacuum at room temperature. Hence, the complex was used for catalysis as prepared *in situ*. [RhCl(PMe$_3$)$_2$]$_2$ also reacts with various compounds

such as diphenylacetylene, carbon monoxide, trimethylphosphine, hydrosilane, dihydrogen, aldehyde, *etc*. Detailed results of stoichiometric reactions of **2** with these compounds will be published separately.

6) A larger amount of ethane than cyclooctene was detected (≈ 180%/cyclooctene). The disagreement may be due to various byproducts formed especially at high temperatures.

7) a) R. H. Crabtree, *Chem. Rev.*, **85**, 245 (1985); b) H. Felkin, T. Fillebeen-Khan, Y. Gault, R. Holmes-Smith, and J. Zakrzewski, *Tetrahedron Lett.*, **25**, 1279 (1984).

8) Ethylcyclooctane was identified by the comparison of the GC retention time (capillary column) and fragmentation pattern of GC-MS with an authentic sample prepared according to the literature: N. Hagihara, *Nippon Kagaku Zasshi*, **73**, 373 (1952). GC-MS spectra of ethylcyclooctane in Eq. 3: m/e 140 (M^+, 0.7), 111 (100, cyclooctyl), 69 (87), 55 (45), 41 (33). HI-MS: obsbd 140.1577; calcd 140.1565. The structure of ethylcycloheptane was determined by MS fragmentation and high resolution mass spectrometry.

9) Besides ethylcyclooctane (Eq. 3) and ethylcycloheptane (Eq. 4), their analogues with two less hydrogens were detected in small amounts (about 20% of the ethylcycloalkanes). These are presumably vinylcyclooctane and vinylcycloheptane or their isomers with different C=C double bond position. The structure of these products were assigned by MS fragmentations and high resolution mass spectrometry.

10) Y. Lin, D. Ma, and X. Lu, *Tetrahedron Lett.*, **28**, 3249 (1987).

11) Y. Fujiwara, I. Moritani, S. Danno, S. Asano, and S. Teranishi, *J. Am. Chem. Soc.*, **91**, 7166 (1969); P. Hong and H. Yamazaki, *J. Mol. Catal.*, **26**, 297 (1984); R. F. Jordan and D. F. Taylor, *J. Am. Chem. Soc.*, **111**, 778 (1989).

12) For ethylene dimerization with rhodium catalysts, see R. Cramer, *Acc. Chem. Res.*, **1**, 186 (1968).

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