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IRIDIUM PENTAHYDRIDE COMPLEX CATALYZED FORMATION OF C-C BOND BY C-H BOND ACTIVATION FOLLOWED BY OLEFIN INSERTION

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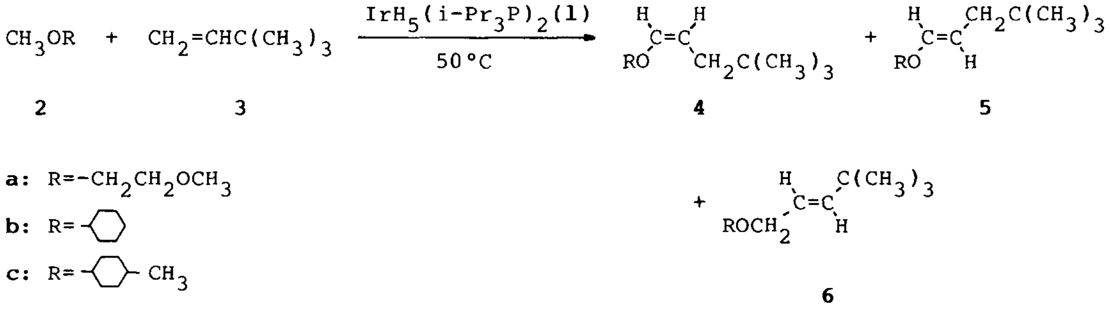
Abstract: The formation of carbon-carbon bond was found to occur by first carbon-hydrogen bond activation followed by olefin insertion under the catalysi of an iridium pentahydride complex.

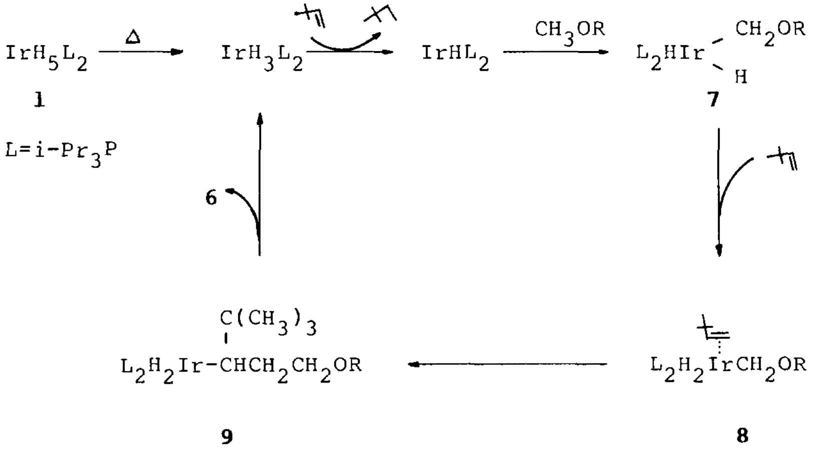
Soluble transition metal complexes have been found to activate carbon-hydrogen bond in saturated hydrocarbons by intermolecular oxidative addition[1]. Considerable attention has been increasingly devoted to the study of chemistry subsequent to the activation of carbon-hydrogen bond[2,3]. The fate of an alkyl metal hydride complex resulting from the oxidative addition of carbon-hydrogen bond to transition metal complexes involves, in principle, three possible pathways: (1) the reductive elimination of the alkyl metal hydride, (2) the β-hydrogen elimination of the alkyl group and (3) the insertion of an olefin or other small molecules. The first pathway is the reverse process of the oxidative addition of the carbon-hydrogen bond. The conversion of alkanes into alkenes by Crabtree[4] and Felkin[5] represents the success of the second route. Here, we wish to report the iridium pentahydride complex catalyzed carbon-carbon bond formation by first carbon-hydrogen bond activation followed by olefin insertion into the carbon-metal bond. To the best of our knowledge, this seems to be the first example of the insertion of an olefin into carbon-metal bond formed in situ by the intermolecular activation of sp3 carbon-hydrogen bond.

When bis(triisopropylphosphine)iridium pentahydride(**1**)(0.035 mmol) was heated with methyl ethers(**2**)(9.63 mmol) at 50°C in the presence of 3,3-dimethyl butene-1(**3**)(7.76 mmol), the products **4**, **5** and **6** were obtained as shown below:



Thus, heating the reaction mixture for 30 min., the mixture of olefins formed from **2a** and **3** contains cis-olefin **4a**(31%), trans-olefin **5a**(54%), and trans-olefin **6a**(15%) in turnover number of 7. After 24 h, the maximum turnover number reaches 12, and the final constitution of the products is **4a** 45%, **5a** 44% and **6a** 11%. The turnover numbers of the products from **2b** and **2c** are nearly the same with that of **2a**. The isomerization of **6** to **4** and **5** was found more facile in the case of **2b** and **2c**, therefore, after distillation, **2b** or **2c** gave mainly **4** and **5** in 1:1 ratio. The product analysis disclosed the preferential insertion of **1** on C-H bonds of the methoxyl group over other C-H bonds. This order of reactivity is in consistent with the work reported by Felkin[6].

The mechanism of the catalytic dehydrogenation of alkane using transition metal polyhydride has been suggested by Felkin[7] to proceed through the highly unsaturated fourteen-electron species, from which the alkyl metal hydride undergoes β-hydrogen elimination to give the corresponding olefin. However, for the alkyl metal species without a β-hydrogen atom, the olefin insertion reaction occurs instead. Thus, the possible pathway is shown below:



In case of lacking a β-hydrogen atom, the sixteen electron-species **7** formed by the oxidative addition of carbon-hydrogen bond can further coordinate with the olefin **3** to yield **8**. Then, the insertion of the olefin into the carbon-metal bond followed by the β-hydrogen elimination leads to the formation of the trans-olefin **6**. The migration of the double bond and cis/trans isomerization of alkene occur in the same catalytic system. Thus, **6** is rapidly isomerized to the enol ethers **4** and **5**, and only about 10% or a very small amount of olefin **6** remains unchanged. The ratio of **4** to **5** is changed from 1:2 at the initial stage of the reaction to the equilibrium value of 1:1. When the reaction of **2** and **3** was carried out in a sealed tube at 150°C, the cis-olefin **4a** was increased to 52%. For comparison, the isomerization of propen-2-yl butyl ether

(**10**) and (E)-buten-2-yl butyl ether (**11**) has been carried out. The ratio of cis and trans isomers of both propen-1-yl butyl ether and buten-1-yl butyl ether was found to be 1:1 when **10** and **11** were heated at 50°C in the presence of **1**.

With regard to the regioselectivity of the olefin insertion, it is found that the ROCH$_2$ group adds exclusively to the least substituted carbon atom of the double bond. Neither terminal olefin nor its isomeric product was detected.

This insertion reaction could also be carried out in suitable solvents, such as ethylene dichloride and hexamethyldisiloxane, to give the same products with lower yield (turnover numbers of 2-3). If the rhenium polyhydride, ReH$_7$(i-Pr$_3$P)$_2$ is used instead of the iridium complex **1**, the turnover number is lower, but less isomerization of the double bond was observed.

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8. **4a**: GC-IR: 768, 1119(s), 1362, 1393, 1663(s), 3043; ^{1}H NMR(CDCl$_3$,200 MHz): 0.88(s, 9H), 1.98(dd, 2H, J=8 Hz,2 Hz), 3.40(s,3H), 3.56(s, 4H), 4.40(dt, 1H, J=6 Hz,8 Hz), 6.03(dt, 1H, J=6 Hz, 2 Hz); MS: 172(M$^+$), 115, 59.
   5a: GC-IR: 930, 1130(s), 1370,1397, 1655(s), 1670,3063; ^{1}H NMR(CDCl$_3$,200 MHz): 0.90(s, 9H), 1.78(dd, 2H, J=8 Hz,2 Hz), 3.40(s,3H), 3.56(s, 4H), 4.81(dt,1H, J=14 Hz,8 Hz), 6.22(dt, 1H, J=14 Hz,2 Hz); MS: 172(M$^+$), 115, 59.
   6a: GC-IR: 972, 1123(s), 1357; ^{1}H NMR(CDCl$_3$, 200 MHz): 1.02(s,9H), 3.40(s,

3H), 3.56(s, 4H), 3.99(dd, 2H, J=6 Hz,2 Hz), 5.49(dt, 1H, J=16 Hz, 6 Hz), 5.71(dt, 1H, J=16 Hz,2 Hz); MS: 115, 97, 59, 55.

4b: GC-IR: 767, 1111(s),1369(s), 1396, 1662(s), 3043; ^{1}H NMR: (C_6D_6, 400 MHz): 0.97(s, 9H), 1.00-1.85(m, 10H), 2.25(dd, 2H, J=8 Hz,1.2 Hz), 3.30 (m, 1H), 4.47(dt, 1H, J=6 Hz,8 Hz), 5.98(dt, 1H, J=6 Hz,12 Hz). MS: 196 (M$^+$), 139, 114, 83, 57.

5b: GC-IR: 926, 1145(s), 1373, 1651, 1670(s), 3065; ^{1}H NMR(C_6D_6, 400 MHz): 0.94(s,9H), 1.00-1.85(m, 10H), 1.81(dd, 2H, J=8 Hz, 12 Hz), 3.47(m, 1H), 5.11(dt, 1H, J=12 Hz,8 Hz), 6.04(dt, 1H, J=12 Hz, 1.2 Hz); MS: 196(M$^+$), 139, 114, 83, 57.

6b: GC-IR 978, 1111(s), 1361; GC-MS: 138, 114, 97, 83, 57.

4c: GC-IR: 770, 1107(s), 1370, 1659(s), 3043; ^{1}H NMR(C_6D_6, 200 MHz): 0.77 (s, 3H), 0.92(s, 9H), 1.08-2.06(m, 9H), 2.23(dd, 2H, J=8 Hz, 2 Hz), 3.41 (m, 1H), 4.47(dt, 1H, J=6 Hz, 8 Hz), 5.99(dt, 1H, J=6 Hz,2 Hz); MS:210 (M$^+$), 153, 114, 97, 55.

5c: GC-IR: 926, 1145, 1370, 1667, 3043; ^{1}H NMR(C_6D_6, 200 MHZ): 0.80(s,3H), 1.00(s, 9H), 1.08-2.06(m, 9H), 1.98(dd, 2H, J=8 Hz,2 Hz),3.53(m, 1H),5.1 (dt, 1H, J=12 Hz,8 Hz), 6.06(dt, 1H, J=12 Hz,2 Hz); MS: 210(M$^+$), 153,114, 97, 55.

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