Novel reactions catalyzed by iridium pentahydride complex

Xiyan Lu, Yingrui Lin and Dawei Ma

Shanghai Institute of Organic Chemistry, Academia Sinica,
345 Lingling Lu, Shanghai 200032, China

Abstract- Several novel reactions catalyzed by iridium penta-
hydride complex(1) are described. Complex 1 can catalyze the
hydrogen transfer reaction normally and can catalyze the
dehydrogenation of secondary alcohols in the absence of a
hydrogen acceptor to give ketones in high yield. Pinane is
converted to β-pinene catalyzed by complex 1 as a first trial
to obtain the useful organic compound by the activation and
functionalization of a saturated hydrocarbon. The iridium
pentahydride complex catalyzed formation of C-C bond by C-H
bond activation followed by olefin insertion is observed for
the first time.

INTRODUCTION

The chemistry of transition metal polyhydride complexes is an area of
current interest. In general, these polyhydride complexes are not especially
reactive or useful as organometallic reagents or catalysts (ref. 1). The
recent developments in the coordination chemistry of molecular hydrogen
opens a new epoch in this field (ref. 2). It was observed that there is an
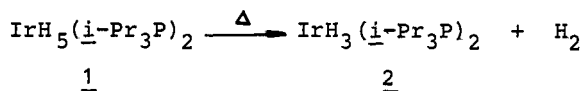equilibrium between the metal-dihydrogen and -hydride species (ref. 3,4).

$$\underset{\text{M-H}_2}{\overset{\text{H}}{}} \rightleftharpoons \underset{\text{M}}{\overset{\text{H} \quad \text{H}}{}}\text{H}$$
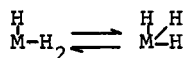
Crabtree has pointed out that there is an analogy between these two binding
modes for H_2 and the agostic (C-H···M) and (C-M-H) forms known in the case of
C-H binding to metal complexes (ref. 4). In this paper, we wish to review
several novel reactions catalyzed by iridium pentahydride complex
$IrH_5(\underline{i}\text{-}Pr_3P)_2$ (1) based on these interesting chemistry.

REACTION OF IRIDIUM PENTAHYDRIDE COMPLEX WITH ALCOHOLS

Isomerization of unsaturated alcohols

The isomerization of allylic alcohols catalyzed by transition metal complexes
yields, after tautomerization, an aldehyde or ketone. Many catalyst systems
have been studied for this reaction, which can be regarded as an intra-
molecular hydrogen transfer reaction (ref. 5,6). We found that complex 1 can
smoothly catalyze the reaction of transforming allylic secondary alcohols
into ketones (ref. 7). The results are shown in Table 1.

The plausible mechanism of the reaction is as follows. First, complex 1 loses
one molecule of hydrogen on heating to form the active species 2 (ref. 8):

$$IrH_5(\underline{i}\text{-}Pr_3P)_2 \xrightarrow{\Delta} IrH_3(\underline{i}\text{-}Pr_3P)_2 + H_2$$

$$\underset{1}{\qquad\qquad} \underset{2}{\qquad\qquad}$$

Complex 2 coordinates with the olefin to form complex 3, followed by olefin
insertion into the Ir-H bond to form 4 and β-elimination to yield 6 and 2.
Compound 6 can tautomerize to form the saturated ketone.

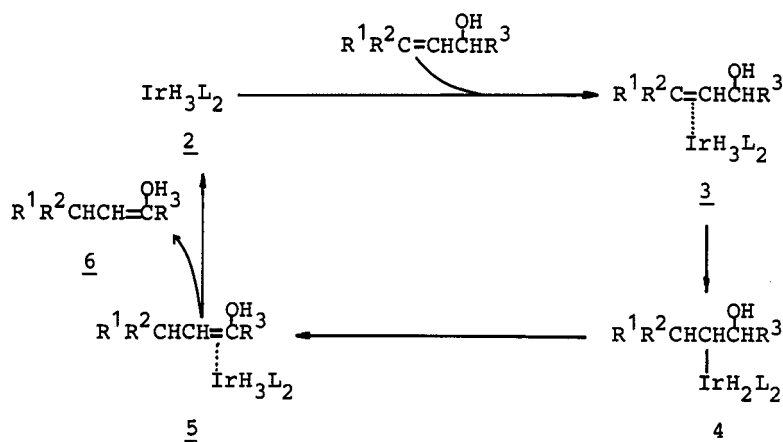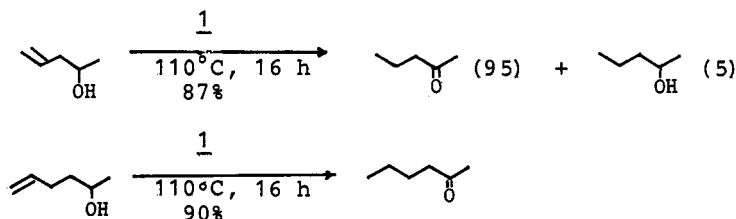$$R^1R^2C=CHCHR^3 \text{ with } OH$$

$$IrH_3L_2 \quad \underline{2} \longrightarrow R^1R^2C\!\!=\!\!CHCHR^3 \text{ (OH)}, \quad IrH_3L_2 \quad \underline{3}$$

$$R^1R^2CHCH=CR^3 \text{ (OH}_3) \quad \underline{6}$$

$$R^1R^2CHCH=CR^3 \text{ (OH}_3), \quad IrH_3L_2 \quad \underline{5} \longleftarrow R^1R^2CHCHCHR^3 \text{ (OH)}, \quad IrH_2L_2 \quad \underline{4}$$

TABLE 1. Hydrogen transfer reaction of unsaturated secondary alcohols[a]

Unsaturated alcohol	Temp. (°C)	Time (h)	Yield (%)	Products				
(allylic alcohol)	100	12	88	(ketone)	(91)	(alcohol)	(9)	
(alcohol)	110	12	88	(ketone)	(94)	(alcohol)	(6)	
(alcohol)	110	12	89	(ketone)	(100)			
(cyclohexenol)	120	16	89	(cyclohexanone)	(95)	(cyclohexanol)	(5)	
(alcohol)	110	16	92	(ketone)	(100)			

a: 0.01 mmol IrH₅(i-Pr₃P)₂ and 5 mmol unsaturated alcohol were used.

From Table 1, it is shown that besides the saturated ketone, saturated alcohols are also formed. This may be resulted from the intermolecular hydrogen transfer reaction. It is worth noting that the β,γ- or γ,δ-unsaturated alcohol also yields the saturated ketones in high yield.

$$\text{(unsaturated alcohol)} \xrightarrow[\substack{110°C,\ 16\ h \\ 87\%}]{\underline{1}} \text{(ketone)} (95) + \text{(alcohol)} (5)$$

$$\text{(unsaturated alcohol)} \xrightarrow[\substack{110°C,\ 16\ h \\ 90\%}]{\underline{1}} \text{(ketone)}$$

A mechanism of multistep isomerization of double bond may be suggested for these reactions.

**Dehydrogenation of secondary alcohols in the absence of hydrogen acceptor**

The reaction of saturated alcohols with 1 is different from that of the unsaturated alcohols. From saturated alcohols, the dehydrogenation reaction occur under the catalysis of 1 to give saturated ketones.

The catalytic dehydrogenation of saturated compounds is more difficult than its reversed reaction---hydrogenation of unsaturated compounds, since the thermodynamic factor favours the saturated species. A number of catalytic

dehydrogenation of alcohols rely for their effectiveness on the continual
removal of hydrogen by a hydrogen acceptor or on providing high energy by
photochemical method. The most widely studied reaction is the dehydrogenation
of secondary alcohols to ketones using ketone or olefin as the hydrogen
acceptor. However, the homogeneous systems capable of catalyzing dehydroge-
nation of alcohols without a hydrogen acceptor are rare. Homogeneous cata-
lytic systems such as $Rh(III)-SnCl_2/HCl$ (ref. 9), $Ru(OOCCF_3)_2(CO)(PR_3)_2/$
CF_3COOH (ref. 10) and $Rh_2(OAc)_4/PR_3$ (ref. 11) have been found to dehydroge-
nate the secondary alcohols into the ketones accompanied with the evolution
of hydrogen without an external hydrogen acceptor, but they do require H^+ as
a hydride ion acceptor. In addition, conversion of primary alcohols to esters
is achieved in the presence of $RuH_2(Ph_3P)_4$ (ref. 12). The reaction involves
two steps: first, alcohol is dehydrogenated to aldehyde and then the reaction
product of aldehyde and alcohol is dehydrogenated to form the ester. The
latter step would make the reaction thermodynamically favourable. On studying
the reaction of 1 with saturated alcohols, we found that complex 1 can cata-
lyze the dehydrogenation of secondary alcohols to ketones even in the absence
of a hydrogen acceptor (ref. 13).

The reaction is carried out under mild conditions. Neither external hydrogen
acceptor nor H^+ as hydride ion acceptor is required. When saturated secondary
alcohols and 1-2 mole% of 1 are refluxed in hexamethyldisiloxane under
nitrogen for 24 h, 90-100% of the saturated ketones are obtained accompanied
with the evolution of hydrogen. The catalytic turnover number reached 150 for
the dehydrogenation of the cyclohexanol using 1 as the catalyst. The results
of dehydrogenation of various alcohols are shown in Table 2.

TABLE 2. Dehydrogenation of saturated secondary alcohols in
$(Me_3Si)_2O$ at 100°C under nitrogen

Alcohol	1 (mole %)	Time (h)	Product	Yield (%)
	1	24		100
	1	24		100
	2	28		90
	1	28		91
	1	28		100
	1	34		100
	2	24		50

In contrast to the intramolecular hydrogen transfer reaction of unsaturated
alcohols promoted by 1 to give the saturated ketones (ref. 7), the steroidal
alcohols with hindered double bond are mainly dehydrogenated to yield the
unsaturated ketones. When cholest-5-en-3ol (7) is heated in the presence of
a hydrogen acceptor, 3,3-dimethylbutene (8), with 2 mol% of 1, 92% of
cholest-4-en-3-one (9) is isolated and none of 10 is detected.
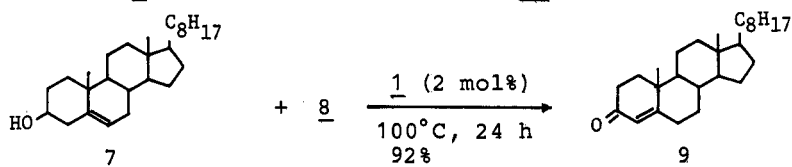
However, when 7 and 2 mol% of 1 are heated in the absence of a hydrogen
acceptor in hexamethyldisiloxane in a sealed tube at 100°C for 30 h, 55% of
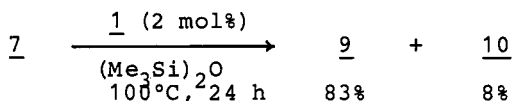9 and 13% of cholestan-3-one (10) are obtained:

$$7 \quad \xrightarrow[\substack{(Me_3Si)_2O \\ sealed\ tube \\ 100°C,\ 30\ h}]{1\ (2\ mol\%)} \quad 9 \quad + \quad 10$$
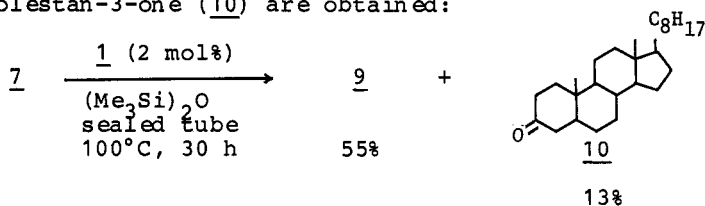
If the above reaction is carried out under nitrogen in an open system which
would favour the evolution of hydrogen, 83% of 9 and 8% of 10 are formed even
without a hydrogen acceptor.

$$7 \quad \xrightarrow[\substack{(Me_3Si)_2O \\ 100°C,\ 24\ h}]{1\ (2\ mol\%)} \quad 9 \quad + \quad 10$$
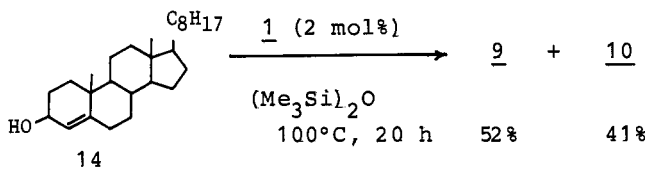$$\qquad\qquad\qquad\qquad\quad 83\% \qquad 8\%$$

The preferential formation of 9 to 10 indicates that the dehydrogenation
reaction is easier to occur than the hydrogen transfer reaction in these
cases. This may be due to the preferential coordination of the oxygen atom
of the hydroxy group to the metal center than the hindered double bond in 7,
which results in affording the dehydrogenated product, whereas cholest-1,4-
dien-3-ol (11) still undergoes the hydrogen transfer reaction normally to
give the ketone 9 owing to the facility of the coordination of double bond at
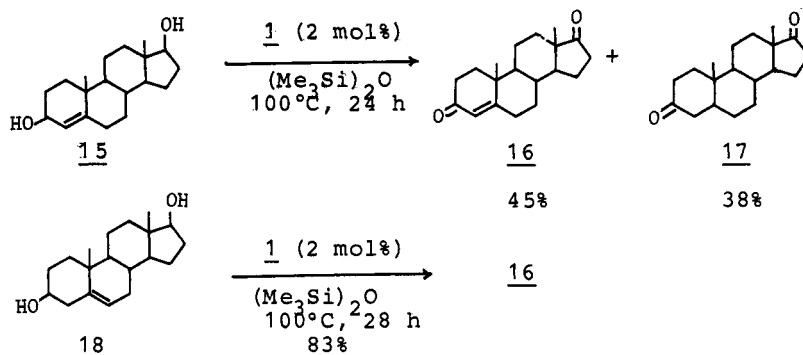the 1-position to the metal center.

$$11 \quad \xrightarrow[\substack{(Me_3Si)_2O \\ 100°C,\ 12\ h \\ 90\%}]{1\ (2\ mol\%)} \quad 9$$
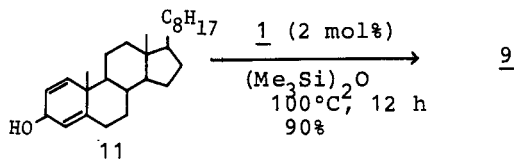
When 12 is reacted under the same condition, both hydroxy groups are dehydro-
genated to give 13:

$$12 \quad \xrightarrow[\substack{(Me_3Si)_2O \\ 100°C,\ 33\ h \\ 81\%}]{1\ (2\ mol\%)} \quad 13$$
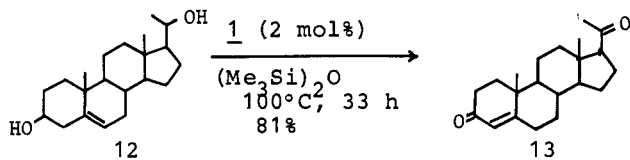
For the allylic steroidal alcohols 14 and 15, intramolecular hydrogen
transfer reactions also occur and more saturated ketones 10 and 17 are
formed as compared to the homoallylic alcohols 7 and 18. In the case of 7
and 18, the dehydrogenation reaction seems to be faster than the hydrogen
transfer reaction because in these cases, the coordination of double
bond with the metal would be rather difficult (ref. 14). The different results
obtained either from 7 and 14 as well as from 15 and 18 implies that the
dehydrogenation reaction may occur before the isomerization of the double
bond in 7 or 18. Otherwise, the same intermediate formed in these reactions
would give the same ratio of products.

$$14 \quad \xrightarrow[\substack{(Me_3Si)_2O \\ 100°C,\ 20\ h}]{1\ (2\ mol\%)} \quad 9 \quad + \quad 10$$
$$\qquad\qquad\qquad\qquad\quad 52\% \qquad 41\%$$

It was reported recently that the hydrogen ligands of many known polyhydride complexes were proved to be associated with molecular hydrogen ligands in solution, at least to an extent of equilibrium between the dihydride and η^2-dihydrogen ligands (ref. 4,15,16). This dynamic equilibrium process probably leads to the continuous evolution of dihydrogen in our catalytic cycle. From the mechanistic point of view, this may be the main difference between this new dehydrogenation reaction using polyhydride system and the dehydrogenation of alcohol in the presence of hydride acceptor. The mechanism of the dehydrogenation of the alcohols catalyzed by 1 is proposed as follows:
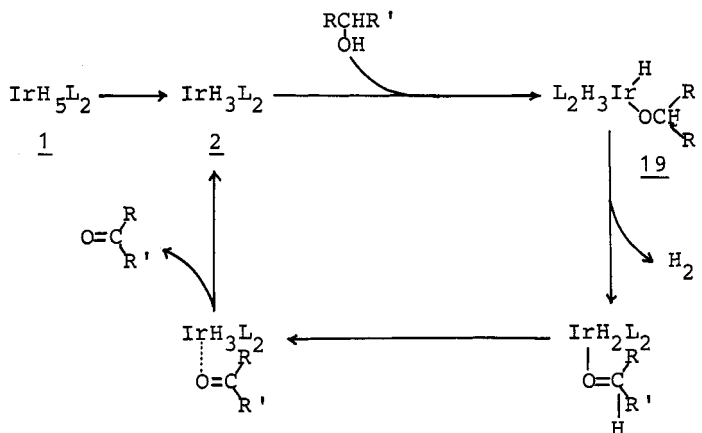
For saturated alcohols and unsaturated alcohols with a hindered double bond, the oxidative addition of hydroxy group with 1 to form 19 is preferable to the coordination of the double bond with the metal center. After hydrogen evolution and β-hydrogen abstraction, 2 and ketone are formed to complete the catalytic cycle.

The catalytic dehydrogenation of alcohols in the absence of a hydrogen acceptor is not only useful in organic synthesis owing to its simplicity and convenience, but also very important in the future. This reaction can be regarded as the catalytic production of hydrogen from alcohols which has been the subject of substantial research interest in recent years since it offers a means of obtaining a useful fuel from industrial waste alcohol, or of producing hydrogen from biomass-derived materials (ref. 17).

REACTION OF IRIDIUM PENTAHYDRIDE COMPLEX WITH C–H BOND

Alkane activation is an area of great current interest (ref. 18); selective catalytic functionalization of alkanes is one important goal in this area (ref. 19). Considerable attention has been increasingly devoted to the study of chemistry subsequent to the activation of carbon-hydrogen bond

(ref. 20,21). 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 (ref. 22) and Felkin (ref. 23) represents the success of the second route. Felkin et al. (ref. 24) recently reported that the selective catalytic conversion of methylcyclohexane into methylenecyclohexane has been effected using complex 1 as the catalyst and an olefin 8 as the hydrogen acceptor. This catalytic selective reaction, which has been proved preferentially to attack the methyl group in saturated hydrocarbons, might have some useful applications in the selective functionalization of methyl group in special organic compounds.

Selective conversion of pinane into β-pinene

As an example of the application of Felkin's work (ref. 24), the selective catalytic conversion of pinane (20) into β-pinene (21) by means of 1 in the presence of 8 was tried (ref. 25). When pinane, which is easily obtained from α-pinene (22) by hydrogenation, was treated with 1 at 100-110°C in the presence of 8, the products obtained are shown as follows:
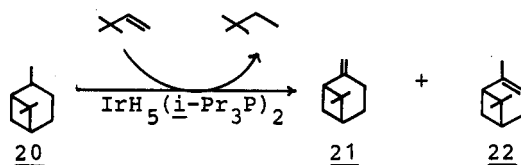
Conditions	Catalytic turnovers	Mole %	
100°C, 10 min	8.5	97.6	2.4
30 min	10.0	93.8	6.2
1 h	12.0	89.7	10.3
4 h	11.8	77.2	22.8

The dehydrogenation of pinane is rapid and almost completed within one hour under the above condition. At the initial 10 min., 4.0 mol% of β-pinene and 0.1 mol% of α-pinene compared to pinane were formed (8.5 catalytic turnovers) with high regioselectivity of β-pinene(>95%). After 1 h, the mixture of products formed contained 5.2 mole% of β-pinene (12.0 catalytic turnovers) and 0.6 mol% of α-pinene. The latter was formed from the isomerization of β-pinene in the same catalytic system and proved by a control experiment. No ring-opened product was detected, even though the reaction was carried out in the presence of a small amount of acid.

It is suggested that the catalytic dehydrogenation may proceed through the mechanism proposed by Felkin (ref. 8) in which the key step involves the insertion of a ligand-deficient intermediate into a C-H bond of methyl group of pinane. Radical and carbocationic intermediates are excluded because neither reing opened product nor Wagner-Meerwein rearrangement product is detected.
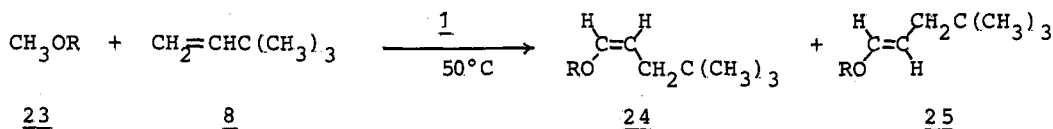
The dehydrogenation of pinane could also carried out in suitable solvents like hexamethyldisiloxane to give the β-pinene with lower conversion (2-3 turnovers). Unlike the iridium system, the selective conversion to β-pinene is not effected by other transition metal systems. Nearly no reaction takes place using $RhH(Ph_3P)_4$, $ReH_7(Ph_3P)_2$ and $ReH_7(i-Pr_3P)_2$ as the catalyst.

To our knowledge, the conversion of pinane to β-pinene by soluble transition metal catalyst is the first trial to obtain the useful organic compounds by the activation and functionalization of a saturated hydrocarbon. Although the number of catalytic turnover is not large enough, the reaction does show the potentiality of the application of the activation and functionalization of the C-H bond in saturated hydrocarbons in the future.

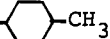### Formation of C–C bond by C–H bond activation followed by olefin insertion

On studying the substituent effect of the dehydrogenation reaction of the substituted methylcyclohexanes, we observed the complex 1 catalyzed carbon-carbon bond formation by first carbon-hydrogen bond activation followed by olefin insertion into the carbon-metal bond (ref. 26), which may be regarded as the third route of the reaction pathway of an alkyl metal hydride complex formed from the activation of carbon-hydrogen bond.
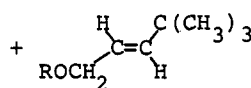
When 1 (0.035 mmol) was heated with methyl ethers (23) (9.63 mmol) at 50°C in the presence of 8 (7.76 mmol), the products 24, 25 and 26 are obtained as shown below:

$$CH_3OR + CH_2=CHC(CH_3)_3 \xrightarrow[50°C]{1}$$

24   25

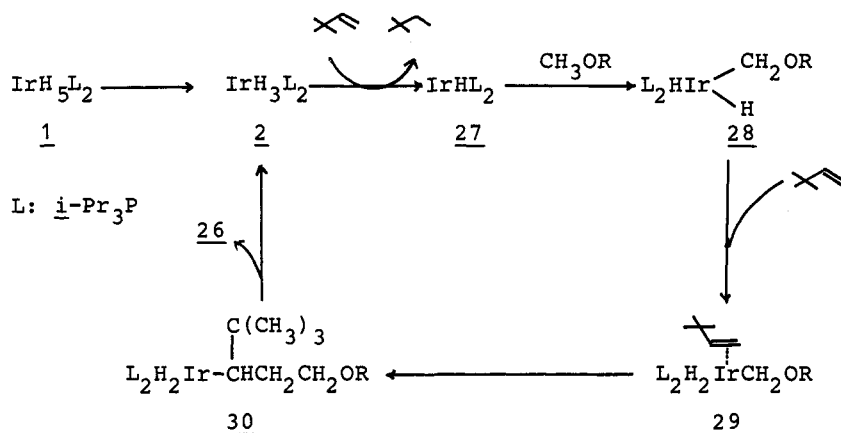a: R: -CH$_2$CH$_2$OCH$_3$

b: R: (cyclohexyl)

c: R: (cyclohexyl)-CH$_3$

26

Heating the reaction mixture for 30 min., the mixture of olefins formed from 23a and 8 contains cis-olefin 24a(31%), trans-olefin 25a(54%) and trans-olefin 26a(15%) in turnover number of 7. After 24 h, the maximum turnover number reaches 12, and the final constitution of the products is 24a 45%, 25a 44% and 26a 11%. The turnover numbers of the products from 23b and 23c are nearly the same with that of 23a. The product analysis disclosed the preferential insertion of 1 on C–H bonds of the methoxy group over other C–H bonds.

The mechanism of the catalytic dehydrogenation of alkane using transition metal polyhydride has been suggested by Felkin (ref. 8) to proceed through the highly unsaturated fourteen-electron species, after oxidative addition, 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:

$$IrH_5L_2 \longrightarrow IrH_3L_2 \longrightarrow IrHL_2 \xrightarrow{CH_3OR} L_2HIr$$

1   2   27   28

L: i-Pr$_3$P

26

$$L_2H_2Ir-CHCH_2CH_2OR \longleftarrow L_2H_2IrCH_2OR$$

30   29

In case of lacking a β-hydrogen atom, the sixteen electron species 28 formed by the oxidative addition of carbon-hydrogen bond can further coordinate with the olefin 8 to yield 29. Then, the insertion of the olefin into the carbon-metal bond followed by the β-hydrogen elimination of 30 leads to the formation of the trans-olefin 26. The migration of the double bond and cis/trans isomerization of alkene occur in the same catalytic system. Thus, 26 is rapidly isomerized to the enol ethers 24 and 25, and only about 10% or a very small

amount of olefin 26 remains unchanged. 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.

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 sp^3 carbon-hydrogen bond.

REFERENCES

1. J. P. Collman and L. S. Hegedus, Principles and Application of Organo-transition Metal Chemistry, p. 63, University Science Books, Mill Valley (1980).
2. G. J. Kubas, J. Chem. Soc., Chem. Commun., 61-62 (1980); G. J. Kubas, R. R. Ryan, B. I. Swanson, P. J. Vergamini and H. J. Waserman, J. Am. Chem. Soc., 106, 451-452 (1984).
3. R. H. Morris, J. F. Sawyer, M. Shiralian and J. D. Zubkowski, J. Am. Chem. Soc., 107, 5581-5582 (1985).
4. R. H. Crabtree and M. Lavin, J. Chem. Soc., Chem. Commun., 794-795 (1985). R. H. Crabtree, M. Lavin and L. Bonnviot, J. Am. Chem. Soc., 108, 4032-4037 (1986).
5. P. A. Chaloner, Handbook of Coordination Catalysis in Organic Chemistry, Butterworth, London (1986).
6. G. Brieger and T. T. Nestrick, Chem. Rev., 74,567-580 (1974); R. A. W. Johnstone, A. H. Wilby and I. D. Entwistle, Chem. Rev., 85,129-170 (1985).
7. Y. Lin, D. Ma and X. Lu, Acta Chimica Sinica, in the press.
8. H. Felkin, T. Fillebeen-Khan, Y. Gault, R. Holmes-Smith and J. Zakrzewski, Tetrahedron Lett., 25, 1279-1282 (1984).
9. H. B. Charman, J. Chem. Soc. B 629-632 (1967); 584-587 (1970).
10. A. Dobson and S. D. Robinson, Inorg. Chem., 16, 137-142 (1977).
11. S. Shinoda, T. Kojima and Y. Saito, J. Mol. Cat., 18, 99-104 (1983).
12. S. Murahashi, K. Ito, T. Naota and Y. Maeda, Tetrahedron Lett., 22, 5327-5330 (1981).
13. Y. Lin, D. Ma and X. Lu, Tetrahedron Lett., 28, 3115-3118 (1987).
14. J. W. Suggs, S. D. Cox, R. H. Crabtree and J. M. Quirk, Tetrahedron Lett., 22, 303-306 (1981).
15. J. W. Bruno, J. C. Huffman and K. G. Caulton, J. Am. Chem. Soc., 106, 1663-1669 (1984).
16. G. J. Kubas, C. J. Unkefer, B. I. Swanson and E. Fukushima, J. Am. Chem. Soc., 108, 7000-7009 (1986).
17. E. M. Goodger, Alternative Fuels, Chemical Energy Resources, McMillan, London, 1980.
18. A. E. Shilov, Activation of Saturated Hydrocarbons by Transition Metal Complexes, D. Riedel Publishing Co., Dordrecht, 1984; H. Crabtree, Chem. Rev., 85, 245-269 (1985); A. H. Janowicz and R. G. Bergman, J. Am. Chem. Soc., 104, 352-354 (1982); 105, 3929-3939 (1983); J. K. Hoyano and W. A. G. Graham, J. Am. Chem. Soc., 104, 3723-3725 (1982); W. D. Jones and F. J. Feher, J. Am. Chem. Soc., 104, 4240-4242 (1982); 106, 1650-1663 (1984).
19. M. Ephritikhine, Nouv. J. Chem., 10, 9-15 (1986).
20. L. N. Lewis and J. F. Smith, J. Am. Chem. Soc., 108, 2728-2735 (1986).
21. W. D. Jones and W. P. Kosar, J. Am. Chem. Soc., 108, 5640-5641 (1986).
22. R. H. Crabtree, J. M. Mihelcic and J. M. Quirk, J. Am. Chem. Soc., 101, 7738-7740 (1979); R. H. Crabtree, M. F. Mellea, J. M. Mihelcic and J. M. Quirk, J. Am. Chem. Soc., 104, 107-113 (1982).
23. D. Baudry, M. Ephritikhine and H. Felkin, J. Chem. Soc., Chem. Commun., 1243-1244 (1980); 606-607 (1982).
24. H. Felkin, T. Fillebeen-Khan, R. Holmes-Smith and Lin Yingrui, Tetrahedron Lett., 26, 1999-2000 (1985).
25. Y. Lin, D. Ma and X. Lu, J. Organometal. Chem., 323, 407-409 (1987).
26. Y. Lin, D. Ma and X. Lu, Tetrahedron Lett., in the press.