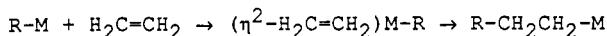


Specific reactions of organylmetal complexes with unsaturated hydrocarbons

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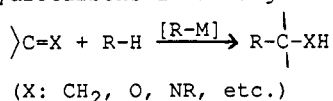
Abstract - Some η^2 -ethylene complexes of organyltransition metals R-M react by insertion of the coordinated C=C into the R-M bond:



Furthermore, it has been observed that some organyltransition metals R'-M of a similar type are able to cleave the H-C bonds of hydrocarbons R-H in a sigma bond metathesis reaction:



A suitable combination of both reactions would offer an approach to the selective functionalization of ethylene, alkenes or of heteroalkenes by hydrocarbons in an organometal mediated or catalyzed fashion:

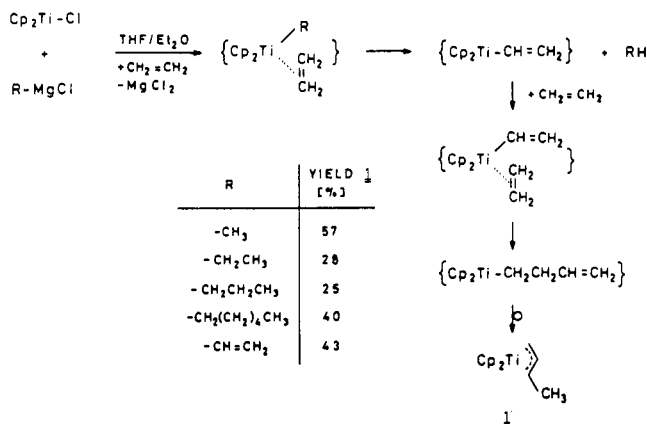


The chemical, kinetic and thermodynamic basis for some of these reactions have been investigated.

INTRODUCTION

Some time ago we became interested in the synthesis of the unknown η^2 -ethylene complexes of Cp₂Ti-alkyl by reacting titanocene monochloride with various alkyl-magnesium halides in the presence of excess ethylene. Independent of the nature of the alkyl substituent in the magnesium compound the Cp₂Ti(η^3 -crotyl) complex 1 was isolated as the only organotitanium product (ref. 1). In order to explain the formation of 1 we postulated a reaction sequence in which the initially formed alkyl(ethylene)titanium complex reacts with cleavage of one H-C bond of the coordinated ethylene to give Cp₂Ti-vinyl. Ethylene insertion into the vinyl-Ti bond and isomerization via β H-elimination would yield the crotyl complex 1 (Scheme 1).

Scheme 1



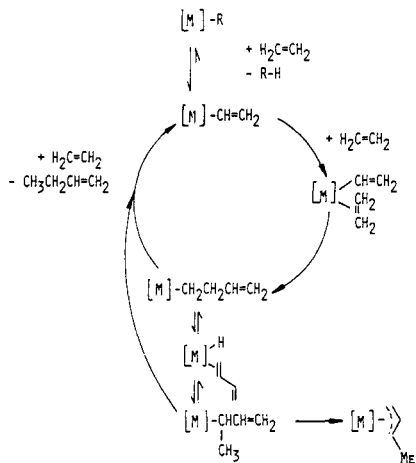
Scheme 1: Formation of Cp₂Ti- η^3 -crotyl from Cp₂TiCl, alkylmagnesium halide and ethylene.

R	YIELD $\frac{1}{2}$ [%]
-CH ₃	57
-CH ₂ CH ₃	28
-CH ₂ CH ₂ CH ₃	25
-CH ₂ (CH ₂) ₄ CH ₃	40
-CH=CH ₂	43

In the case of titanium, no intermediates could be identified in this reaction sequence and at that time no examples of similar reactions with complexes of other transition metals were known.

Starting from these observations we began to look for model reactions and complexes of this kind, especially, keeping in view to develop a catalytic process. If it were possible to repeat the sequence of H-C bond cleavage of ethylene by means of organo-metal species and ethylene insertion into the vinyl-metal bond to give a 3-butenyl metal intermediate, it should be possible to catalytically dimerize ethylene to 1-butene by a new type of reaction (Scheme 2).

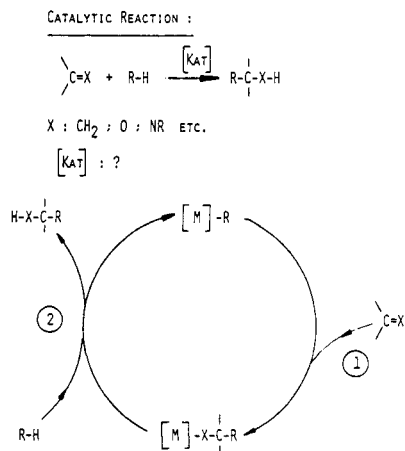
Scheme 2



Scheme 2: Catalytic cycle for ethylene dimerization via a vinylmetal intermediate.

Scheme 3 generalizes the ethylene dimerization shown in Scheme 2 to the reaction of ethylene or hetero alkenes >C=X (X: CH_2 , O, NR, etc.) with hydrocarbons R-H. In this case an analogous reaction sequence of insertion reaction and H-R bond cleavage would lead to the catalytic alkylation of a >C=X bond by the hydrocarbon (Scheme 3).

Scheme 3



Scheme 3: Catalytic cycle for the alkylation of unsaturated compounds with C=X bond by hydrocarbons RH.

REACTION SEQUENCE :

- ① INSERTION REACTION
- ② SUBSTITUTION REACTION BY H-C BOND CLEAVAGE IN R-H
 " SIGMA BOND METATHESIS REACTION "

Comparing the thermodynamic data for the reactions shown in Scheme 3, it can be seen that the alkylation of C=C bonds by hydrocarbons is thermodynamically more favourable than that of the corresponding C=O or C=NR bonds (Table 1).

THERMODYNAMICS OF THE REACTION

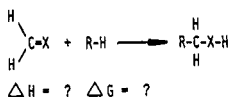


Table 1. Enthalpy and free energy changes for the reaction of ethylene or hetero alkenes with hydrocarbons (ethane).

C=X	$[D(\text{C}=\text{X}) - D(\text{C}-\text{X})]$	$D(\text{R}-\text{H})^*$	$D(\text{R}-\text{C})$	$D(\text{H}-\text{X})$	ΔH^{298} KCAL.MOLE ⁻¹	ΔG^{298} KCAL.MOLE ⁻¹
$\text{H}_2\text{C}=\text{CH}_2$	62 to 72	98	83 to 85	98	-23 to -11	-14 to -2
$\text{H}_2\text{C}=\text{O}$	82 to 96	98	83 to 85	104	-9 to +7	0 to +16
$\text{H}_2\text{C}=\text{NR}$	68 to 74	98	83 to 85	95	-14 to -4	-5 to +5

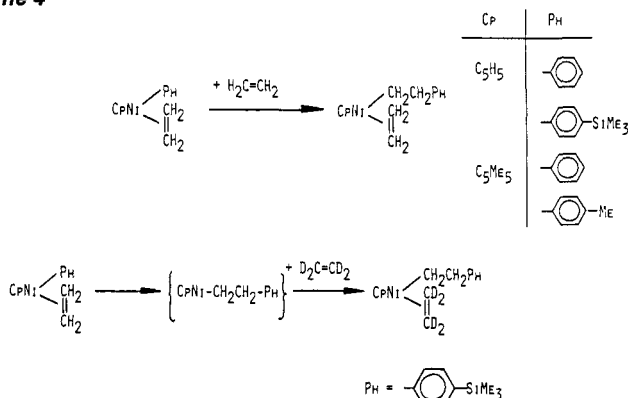
We, therefore, concentrated on two main aspects:

1. The synthesis of (η^2 -olefin)organylmetal complexes and their insertion reactions.
2. H-C bond cleavage reactions of hydrocarbons by organyl metal complexes.

ETHYLENE INSERTION REACTIONS OF $\text{Cp}(\text{C}_2\text{H}_4)\text{NiR}$

Recently, we developed a convenient synthesis for the preparation of new (η^2 -alkene)-(organyl)CpNi complexes with a variety of organyl groups and different types of alkenes (ref. 2-6). In these complexes the Ni atom has a trigonal planar coordination geometry with the C=C bond coordinated perpendicular to the trigonal plane (ref. 5,7). The ^1H NMR solution spectra are temperature dependent as the result of the rotation of the alkene around the coordination axis (ref. 2,3,7). The η^2 -ethylene complexes react by migratory insertion of the ethylene and the organyl ligand generating the prim. alkyl $-\text{CH}_2\text{CH}_2\text{R}$ unit which does not react further under these conditions, because the reactivity of the organyl-Ni bond decreases in the sequence vinyl \geq phenyl $>$ cyclopropyl $>$ methyl - ethyl $>$ propyl - butyl (ref. 2,4,5,7). The initial $16e^-$ insertion product can be stabilized by coordination to ethylene which should, therefore, be present in excess. Using $\text{Cp}(\eta^2-\text{C}_2\text{H}_4)\text{NiPhenyl}$ and C_2D_4 , it could be demonstrated by ^1H and ^{13}C NMR investigations that the coordinated C_2H_4 inserts into the Ph-Ni bond and that free C_2D_4 serves to stabilize the insertion product (ref. 5) (Scheme 4). An exchange between the coordinated C_2H_4 and the free C_2D_4 is not observed.

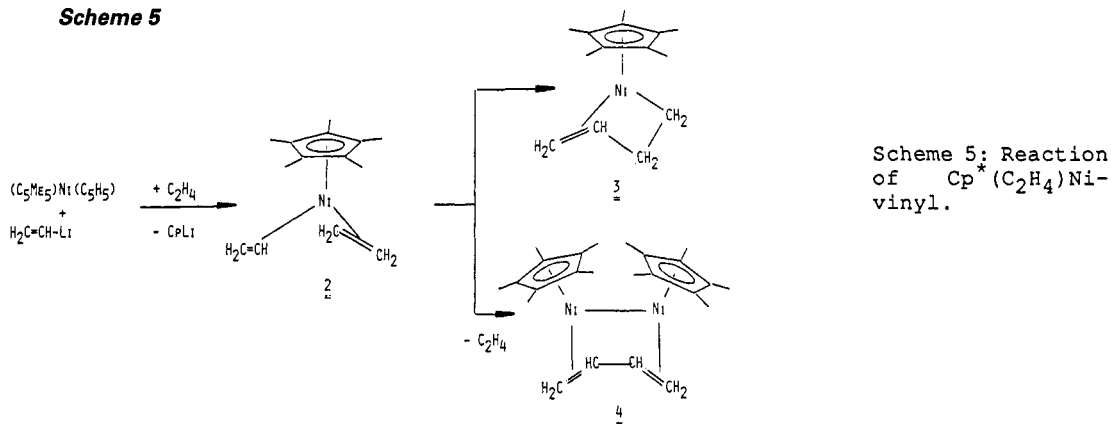
Scheme 4



Scheme 4: Ethylene insertion reactions with $\text{Cp}(\eta^2-\text{C}_2\text{H}_4)\text{Ni}$ -phenyl complexes

The ethylene complex of CpNi -vinyl is too reactive to be detected or isolated even at -80°C . The reactivity of comparable organylnickel complexes decreases on going from the $\eta^5-\text{C}_5\text{H}_5$ to the $\eta^5-\text{C}_5\text{Me}_5$ ligand. The η^2 -ethylene complex of $\text{C}_5\text{Me}_5\text{Ni}$ -vinyl **2** is isolable below -20°C . Above this temperature **2** reacts both by ethylene insertion to give the η^1, η^2 -3-butenylnickel complex **3** as well as by loss of the coordinated ethylene and coupling of two vinyl units to give the dinuclear (CpNi)₂-cluster **4** in which butadiene bridges the two metal atoms (ref. 6) (Scheme 5). Complex **3** is the sole product if the thermolysis of **2** is carried out in the presence of excess ethylene in order to suppress ethylene dissociation.

Scheme 5

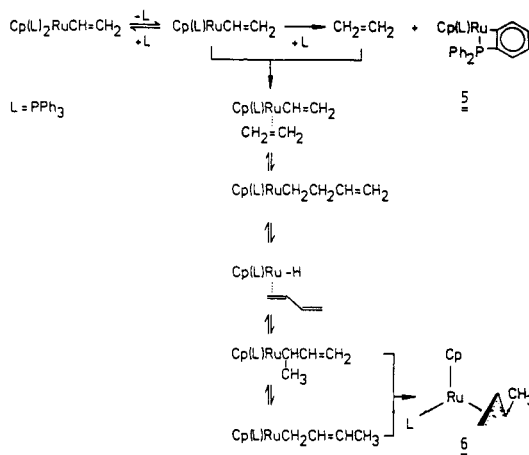


ORGANYLRUTHENIUM COMPLEXES AND H-C CLEAVAGE OF HYDROCARBONS

Organylruthenium compounds of the type $[\eta^5\text{-Cp}(\text{ligand})_2\text{RuR}]$ ($\text{Cp} = \text{C}_5\text{H}_5, \text{C}_5\text{Me}_5$; ligand = $\text{Ph}_3\text{P}, \text{Ph}_2\text{MeP}, \text{PhMe}_2\text{P}, \text{Me}_3\text{P}$; $\text{R} = \text{Et}, \text{Pr}, \text{Bu}, \text{CH}_2\text{CHMe}_2, \text{CH}_2\text{CH}_2\text{Ph}, \text{Ph}, \text{CH}_2\text{Ph}$) can be synthesized by metathesis reactions from the corresponding rutheniumchloride complex with organylmagnesium halides in benzene/ether mixtures (ref. 8-10). With sec. and tert. alkylmagnesium halides these reactions yield the rutheniumhydride complexes and free alkene (ref. 8).

The organylruthenium systems react on warming with dissociation of one phosphane ligand to give the transient coordinatively unsaturated $[\text{Cp}(\text{ligand})\text{RuR}]$, which is stabilized in the case of alkyl groups R having βH atoms by βH -elimination to give $[\text{Cp}(\text{ligand})(\eta^2\text{-alkene})\text{RuH}]$ (ref. 8), in the case of alkenyl ligands with βH atoms to give $[\text{Cp}(\text{ligand})(\eta^3\text{-allyl})\text{Ru}]$ complexes by isomerization or in the absence of available βH atoms to give Ru complexes with chelating η^1, η^2 -alkenyl ligands (ref. 11). The thermolysis of the vinylruthenium complex in which $\text{Cp} = \text{C}_5\text{H}_5$ and ligand = Ph_3P at 100°C results in the formation of a mixture of 5 and 6 (Scheme 6).

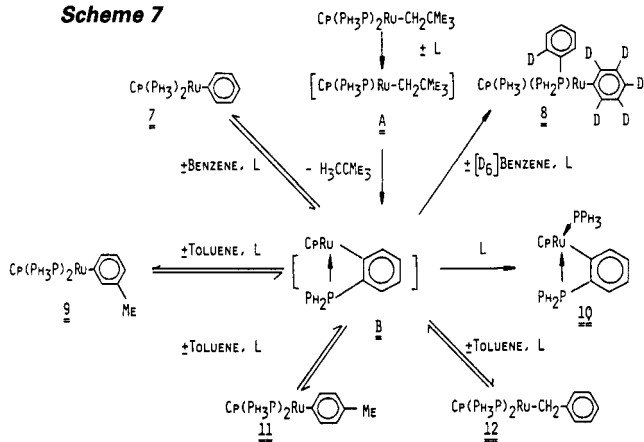
Scheme 6



5 together with ethylene are the products of an ortho-metallation of one phenyl unit in the Ph_3P ligand. The eliminated ethylene is suggested to insert into the vinyl-Ru bond to give after isomerization the $(\eta^3\text{-crotyl})\text{Ru}$ complex 6 (ref. 11). Thermolysis in the presence of an excess of ethylene gives 6 as the sole organoruthenium product.

The attempted synthesis of $\text{Cp}(\text{Ph}_3\text{P})_2\text{Ru}$ -neopentyl in benzene leads instead to the phenylRu complex 7. The initially formed neopentylRu presumably loses one Ph_3P ligand to give the $16e^-$ -intermediate A, which reacts further with cleavage of one ortho-H-C bond in one phenyl group of the remaining Ph_3P ligand to give B. In the absence of an aromatic hydrocarbon as substrate, B coordinates the free Ph_3P and forms the ortho-metallated complex 10. In the presence of benzene, B cleaves one H-C bond of benzene and the phenylRu complex 7 results while with toluene, a mixture of the meta- and para-tolylRu compounds 9 and 11 (ratio 70-80/30-20) is formed (ref. 10,12) (Scheme 7).

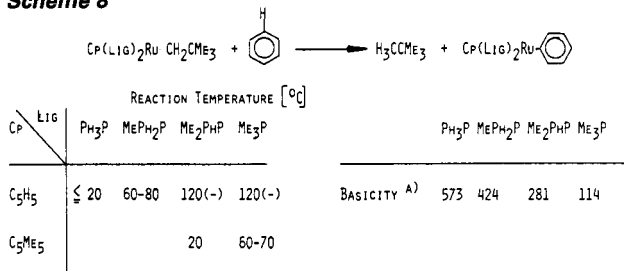
Scheme 7



Scheme 7: H-C bond cleavage reactions with neopentylruthenium

The reactivity of the neopentylRu complexes with respect to the H-C bond cleavage of aromatic hydrocarbons decrease on going from Ph_3P to the more basic phosphanes Ph_2MeP , PhMe_2P and Me_3P . However, if the $\eta^5\text{-C}_5\text{Me}_5$ -unit a surprising increase in reactivity is observed. In several cases ($\text{Cp} = \text{C}_5\text{H}_5$, ligand¹ = Ph_2MeP , PhMe_2P , Me_3P , ligand² = Me_3P , ligand³ = Ph_3P ; $\text{Cp} = \text{C}_5\text{Me}_5$, ligand¹ = Me_3P , ligand² = Ph_3P) the neopentyl-ruthenium complexes can be isolated, but they remain reactive enough to cleave H-C bonds of hydrocarbons upon warming (Scheme 8) (ref. 10).

Scheme 8



Scheme 8: Reactivity of neopentylRu complexes towards H-C bond cleavage of benzene

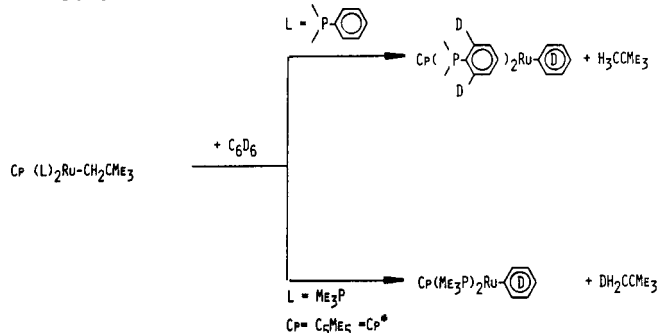
REACTIVITY TOWARDS BENZENE:
 $\text{C}_5\text{Me}_5 > \text{C}_5\text{H}_5$ COMPOUNDS
 $\text{Ph}_3\text{P} > \text{MePh}_2\text{P} > \text{Me}_2\text{PhP} > \text{Me}_3\text{P}$

A) Δ HNP : HALF-NEUTRALIZATION POTENTIAL.
 GREATER BASICITY IS INDICATED BY SMALLER VALUES.

(-) : NO REACTION OBSERVED

Starting with isolated neopentylRu compounds and using benzene- d_6 as the solvent, either nondeuterated or monodeuterated neopentane is formed depending upon the presence or the absence of at least one phenyl group in the phosphane ligand (ref. 10). In the case of phenyl containing ligands, H_3CCMe_3 is formed whereas neopentylRu complexes with Me_3P as the ligand give DH_2CCMe_3 by reaction with benzene- d_6 (Scheme 9).

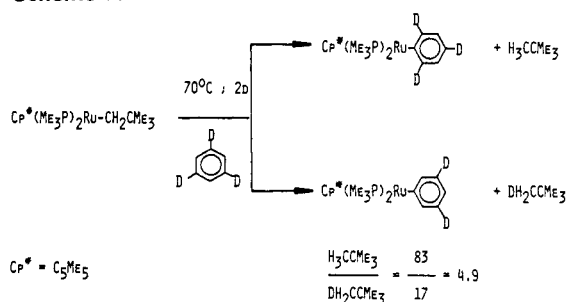
Scheme 9



Scheme 9: Reactions of neopentylruthenium complexes with benzene- d_6

These observations indicate that the two types of compounds react by different pathways. In the Me_3P complexes, dissociation of one phosphane ligand is followed by a direct attack of the coordinatively unsaturated intermediate - analogous to **A** in Scheme 7 - by the benzene- d_6 . With 1,3,5-benzene- d_3 a kinetic isotope effect of 4.9 is observed (Scheme 10).

Scheme 10



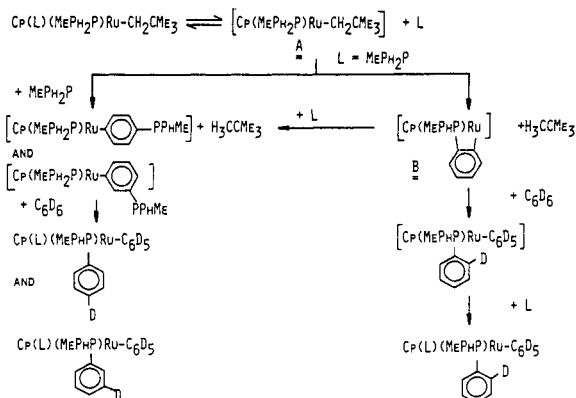
Scheme 10: Reaction of $\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuCH}_2\text{CMe}_3$ with 1,3,5-benzene- d_6

H. LEHMKUHL, M. BELLENBAUM (1988)

This relatively large isotope effect is consistent since there is an H-C or D-C bond breaking in the rate determining step. From this value the difference of the activation enthalpies for H-C or D-C bond cleavage can be calculated to be 1.08 kcal/mole, which is close to the zero point energy difference between H-X and D-X, which is 1.15 kcal/mole at 0°C.

In Ru complexes with phenyl containing phosphanes, dissociation is followed by ortho-metallation to give **B** and undeuterated neopentane is eliminated. The initial species **B** reacts with benzene- d_6 to give phenyl- d_5 -Ru with deuteration of one ortho position in one phenyl unit of the ligand. If these reactions of **B** are reversible then the entire ortho positions within the phenyl groups of the ligands should be exchanged with time. In reality, however, this mechanism must be more complex, since the meta and para positions of the phenyl groups in the ligands also exchange with deuterium. This fact suggests that either **A** or **B**, or both species together can react with the free phenylphosphane molecule by H-C bond cleavage in meta and para positions of the phenyl units (Scheme 11).

Scheme 11

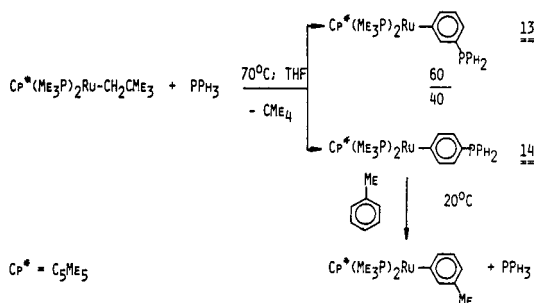


Scheme 11: Reaction pathways for H-C or D-C bond cleavage by neopentylRu complexes containing phenylphosphane ligands

H. LEHMKUHL, M. BELLENBAUM (1988)

This assumption has been proved by an independent synthesis of a mixture of the meta and para substituted triphenylphosphane derivatives **13** and **14** by a reaction of $\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuCH}_2\text{CMe}_3$ with Ph_3P (Scheme 12).

Scheme 12

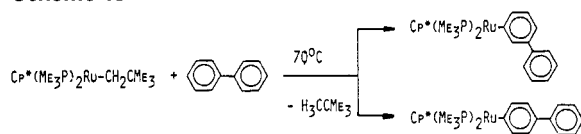


H. LEHMKUHL, M. BELLENBAUM (1988)

Scheme 12:
H-C bond cleavage in Ph_3P
by $\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuCH}_2\text{CMe}_3$

Mono substituted benzene derivatives (PhCH_3 , PhBr , PhCN) react with neopentylRu complexes either to give exclusively the meta metallated derivative or to give mixtures of the meta and para isomers (ref. 10). The reactivity of disubstituted benzenes with respect to the H-C bond cleavage by $\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuCH}_2\text{CMe}_3$ depends on the number of H atoms in meta positions within the benzene derivative, with xylene in the series 1,2- > 1,3-xylene. 1,4-xylene and mesitylene react with decomposition. In the biphenyl molecule the bond dissociation enthalpy of the H-C bond amounts to 12 kcal/mole higher than $\text{D}(\text{Ph}-\text{Ph})$, but nevertheless only H-C bond cleavage is observed (Scheme 13).

Scheme 13



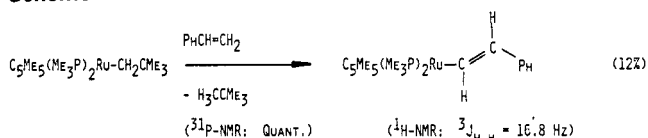
BIPHENYL: $\text{D}(\text{H}-\text{C}) : 110 \text{ KCAL/MOLE}$
 $\text{D}(\text{Ph}-\text{Ph}) : 98 \text{ KCAL/MOLE}$

H. LEHMKUHL, R. SCHWICKARDI (1989)

Scheme 13:
H-C bond cleavage of biphe-
nyl

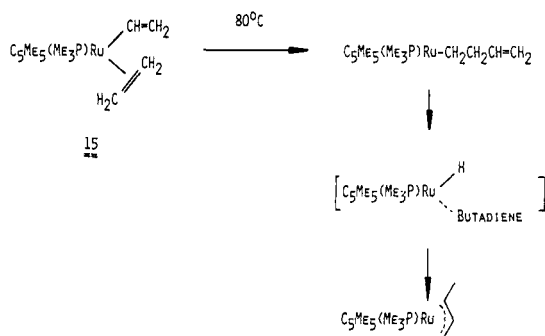
The H-C bond cleavage of styrene by neopentylRu is found to be chemo- and stereo-selective with a preference for activation of the vinylic H-C bond trans to the phenyl substituent of the βC atom. No cleavage of an H-phenyl bond is observed (Scheme 14) (ref. 10).

Scheme 14

Scheme 14:
Vinylic H-C bond cleavage in
styrene

Cleavage of a vinylic H-C bond is also observed with ethylene at 70°C. In addition, one Me_3P ligand is displaced by coordinating ethylene to give **15** (Scheme 15) (ref. 10). Upon warming **15** for a longer period of time, the coordinated ethylene inserts into the vinyl-Ru bond to give the η^3 -crotylRu complex after isomerization.

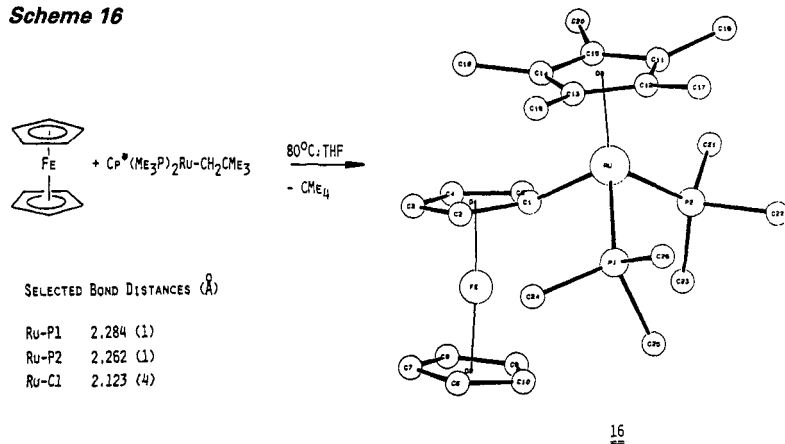
Scheme 15



Scheme 15:
Ethylene insertion in 15 to
give η^3 -crotylRu

The H-C bond cleavage reaction by ruthenium complexes is not limited to allylic and vinylic H-C bonds. Reacting neopentylRu with ferrocene at 80°C also leads to the elimination of neopentane and a stable crystalline ferrocenylruthenium complex 16 is formed (Scheme 16).

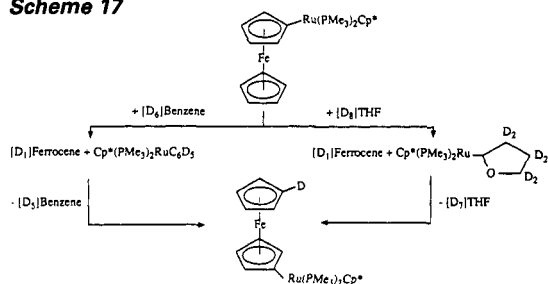
Scheme 16



Scheme 16: Formation and molecular structure of 16

The Ru atom in 16 has a distorted tetrahedral geometry, the planar Cp ligands in the ferrocenyl unit are eclipsed (ref. 13). Upon heating with benzene- d_6 to 70-100°C an H/D exchange is observed in the ferrocenyl part of 16 and after several days at 80°C, a complete exchange of the entire H atoms within the ferrocenyl unit with deuterium has occurred. At 100°C the formation of a small amount of phenyl- d_5 -Ru is detected by ^1H and ^{31}P NMR. On the basis of these observations the existence of an equilibrium between the ferrocenylRu complex/benzene and ferrocene/phenylRu is suggested. This equilibrium is situated to the left but enables successive H/D exchange in the ferrocenyl part of 16 to occur (Scheme 17) (ref. 13).

Scheme 17

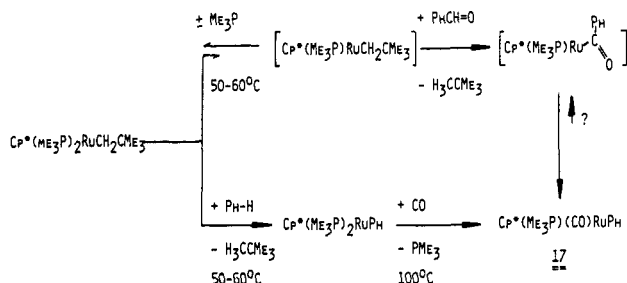


Scheme 17: H/D exchange between 16 and benzene- d_6 or THF- d_8

A catalytic H/D exchange between ferrocene and benzene- d_6 or THF- d_8 is effected by catalysts such as 16, $\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuCH}_2\text{CMe}_3$ or $\text{Cp}^*(\text{Me}_3\text{P})_2\text{RuH}$.

With benzaldehyde, neopentylRu cleaves the H-C bond at the carbonyl function to quantitatively give the monophosphane complex 17, in which the eliminated CO coordinates to the Ru atom. 17 is also synthesized by a displacement reaction of Me₃P with CO in the phenyl ruthenium complex (Scheme 18). Cleavage of one H-C bond in benzene by the CO insertion product of 17 to give phenylRu and benzaldehyde would complete a catalytic cycle for the synthesis of benzaldehyde starting from benzene and carbon monoxide assuming the favourable thermodynamics.

Scheme 18

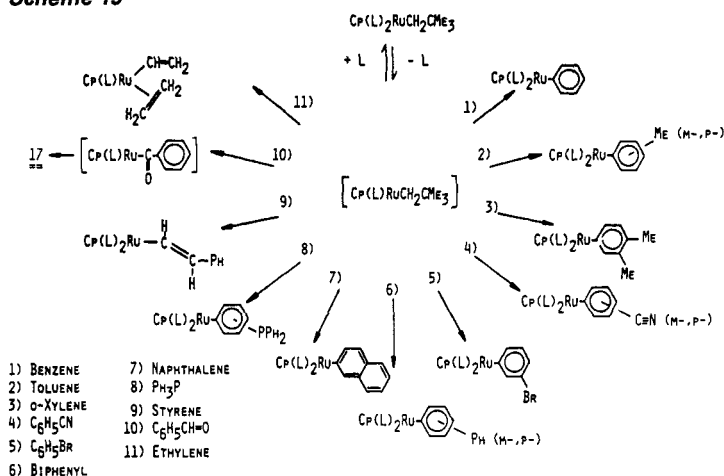
Scheme 18: Two synthetic routes for 17

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The free enthalpy for the carbonylation of benzene by carbonmonoxide has been determined to be $\Delta G^{298} = 2.06$ and $\Delta G^{373} = 4.35$ kcal/mole (ref. 14,15), indicating that this reaction can only occur with the assistance of complexation of the benzaldehyde to suitable lewis acids (ref. 15), which will make the free energy change more favourable.

In conclusion, Scheme 19 summarizes some of our results of the H-C cleavage reactions with organylruthenium complexes and indicates that this method has considerable potential for selective metallations of unsaturated hydrocarbons.

Scheme 19



Scheme 19: Sigma bond metathesis reactions of neopentylruthenium complexes with hydrocarbons

Acknowledgements

I have been fortunate to have a number of enthusiastic and qualified collaborators and colleagues working with me over the last few years and their names are mentioned in the references.

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