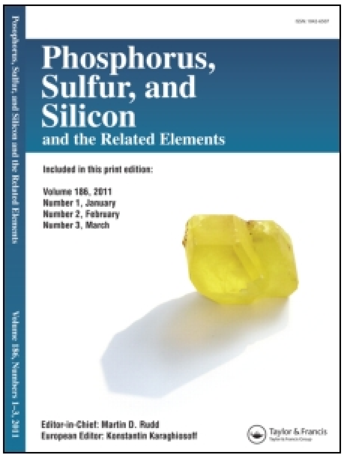

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THE ACTIVATION OF C-H BOND CATALYZED BY ORGANOTRANSITION-METAL COMPLEXES CONTAINING DIPHOSPHINE CHELATE LIGAND

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Abstract The syntheses of new organotransition-metal complexes containing diphosphine chelate ligand and the function of these complexes for the activation of C-H bond are investigated.

INTRODUCTION

Owing to the strong interaction between d-orbital of transition-metal and unoccupied π^*-orbital of diphosphine ligand,it can be applied to stabilize the organotransition-metal complexes of low-valent state and electron-rich center,which is necessary for the activation of C-H bond.[1] We report here the syntheses of new organotransition-metal complexes containing diphosphine ligand and the function of these complexes for the activation of C-H bond and insertion reaction.

RESULTS AND DISCUSSIONS

Synthesis of 1,2-Bis(dichlorophosphino)ethane

In the presence of yellow phosphorus and iron filings, 1,2-Bis(dichlorophosphino)ethane is prepared from ethylene and phosphorus trichloride under 20 atm. and 260-280^{0}C conditions. We suggest that the forming $FeCl_3$ during the process is served as a catalyst to accelerate the reaction.

Synthesis of Diphosphine

Diphosphine chelate ligand is prepared from 1,2-Bis(dichlorophosphino)ethane and Grignard reagent.[2] It is noted that the high reaction temperature and the rapid rate of feed will bring about the decomposition of products.

Syntheses of (M(COD)(diphos))Cl Complexes

In room temperature, the complexes (M(COD)(diphos))Cl (M=Rh,Ir; COD=1,5-cyclooctadiene) are prepared from $(M(COD)(\mu\text{-}Cl))_2$ and diphosphine according to the following equation:[3]

$$(M(COD)(\mu\text{-}Cl))_2 + 2\text{diphos} \longrightarrow 2(M(COD)(\text{diphos}))Cl \qquad (1)$$

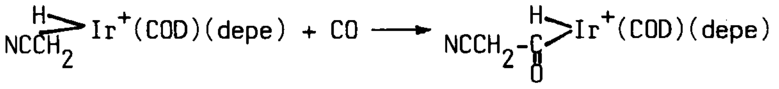
The structures of complexes are characterized by infrared spectra, proton nuclear magnetic resonance spectra, electric conductivity and elemental analysis.

Activation of C-H Bond and Insertion Reaction

In the absence of carbon monoxide the reaction of (M(COD)(diphos))Cl with acetonitrile is a reversible reaction, for example:

$$(Ir(COD)(depe))Cl + CH_3CN \rightleftharpoons (HIr(COD)(depe)(CH_2CN))Cl \qquad (2)$$

The product of the oxidative-addition reaction is only present in the acetonitrile solution: ^{1}H NMR, δ -22ppm(1H, triplet); IR(film), 2190(ν Ir-H), 2248(ν $C\equiv N$)cm^{-1}. While in the presence of CO, the reaction is shifted to the right:



$$\overset{H}{\underset{NCCH_2}{}}\!\!>Ir^+(COD)(depe) + CO \longrightarrow NCCH_2\text{-}\underset{\underset{O}{\|}}{C}\!\overset{H}{>}Ir^+(COD)(depe) \qquad (3)$$

The reaction product is an orange red solid. Comparing the infrared spectrum of reaction (3) with that of reaction (2), we foond the former has a novel additional peak, 1666(ν M-CO-R)cm^{-1}. This peak may refer to the carbonyl absorption in the acetyl metal complexes, which are formed by CO insertion into M-C bond.

In same conditions, if we use deuterioacetonitrile instead of acetonitrile as the substrate to perform same experiment, then the characteristic stretch frequency of infrared absorption 2190 cm^{-1} and proton chemical shift δ-22 ppm disappeared simultaneously. Thus it can be seen that the activation of acetonitrile C-H bond is a intermolecular oxidative-addition reaction.

Similerly, in the presence of carbon dioxide, the IR spectrum of the product appears two broad strong absorption bands at 1660, 1525 cm^{-1}, which are respectively symmetric and anti-symmetric stretch frequencies of carboxyl group in the carboxyl metal complexes formed by carbon dioxide into M-C bond.

Effect of Diphosphine Ligand on Activation and Insertion Reaction

We found experimentally the effect of diphosphine ligand on the proton chemical shift of =C-H group in (M(COD)(diphos))Cl and the insertion reaction of CO, CO_2 into M-C bond. The results are listed in Table I and II.

TABLE I Chemical shift of olefinic proton

Ligands	Complexes	=C-H, ppm
depe	(Ir(COD)(depe))Cl	2.9
dmpe	(Ir(COD)(dmpe))Cl	3.4
dppe	(Ir(COD)(dppe))Cl	4.0
μ-Cl	$(Ir(COD)(\mu\text{-}Cl))_2$	4.4

TABLE II Effect of diphosphine on C-H bond activation and insertion reaction

Diphos	t(hr)	T(^{o}C)	IR, cm^{-1}		
			Ir-H	$Ir\text{-}\underset{\underset{O}{\|}}{C}\text{-}R$	$Ir\text{-}O\text{-}\underset{\underset{O}{\|}}{C}\text{-}R$
depe	5	21	2190	1666	1660, 1525
dmpe	5	21	2180	1670	no
dppe	5	21	no	no	no

If the P^{Ka} value of diphosphine is defined as a measure of donation electron toward the central metal, the order obtained from P^{Ka} value is consistent with that obtained experimentally, that is depe$>$dmpe$>$dppe. Thus it can be seen that the higher electron density of the central metal is in favour of the oxidative-addition reaction and insertion reaction.

Cl/H Exchange Reaction

In the presence of carbon monoxide and (Rh(COD)(dppe))Cl complexes, the Cl/H exchange reaction between methane and o-dichlorobenzene is occured:

$$CH_4 + C_6H_4Cl_2 \xrightarrow[20\text{ atm., } 60\text{-}80^\circ C]{(Rh(COD)(dppe))Cl/CO} CH_2Cl_2 + C_6H_6$$

The products of reaction were identified by GC/MS method. The further investigation shows that the active species of the reaction is a carbonyl metal complex $(Rh(COD)(CO)_2)Cl$.

EXPERIMENTAL SECTION

The experimental operations were carried out under protetion of an atmosphere of argon. All solvents were dried and purified by means of standard techniques.

Syntheses of (M(COD)(diphos))Cl: To a stirred solution of $(M(COD)(\mu\text{-}Cl))_2$($1.17\times10^{-1}$mmol) in toluene(6ml) was added dropwise solution of diphosphine(1 mmol) in toluene. The mixture was stirred for 3 hours under room temperature, the yellow precipitate was isolated and filtered, then washed with toluene and pentane respectively, finally dried under vacuum (yield ca. 80%).

Activation of C-H Bond and Insertion Reaction: To acetonitrile solution of (Ir(COD)(diphos))Cl was leaded carbon monoxide or carbon dioxide, and was allowed to react for 3 hours under temperature 55°C. An orange red solution was obtained, which was then concentrated in vacuo to obtain an orange red solid, which was washed with CH_3CN and n-C_5H_{12} respectively.

Cl/H Exchange Reaction: The solution of (Rh(COD)(dppe))Cl in o-dichlorobenzene(0.03 mol, 7 ml) was poured into 0.1 L-autoclave, which was flushed with pure methane. The methane and carbon monoxide were pressed to 20 atm.($P(CH_4):P(CO) = 4:1$). The pressure of the reaction mixture was reduced to 15 atm. after 4 hours reacted under 60°C.

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