C-H ACTIVATION AND MULTI-FUNCTIONALIZATION OF CARBOCYCLIC RINGS BOUND TO THE SANDWICH COMPOUND, $(\eta^5\text{-RCp})Co(\eta^4\text{-}C_4Ph_3R')$

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by

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Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the

INDIAN INSTITUTE OF TECHNOLOGY DELHI

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Dedicated

to

My Parents and Teachers

CERTIFICATE

This is to certify that the thesis entitled "***C-H activation and multi-functionalization of carbocyclic rings bound to the sandwich compound, (η^5-RCp)Co(η^4-C_4Ph_3R')***", being submitted by Mr. **Jatinder Singh** to **Indian Institute of Technology Delhi** for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him. Mr. **Jatinder Singh** has worked under my supervision and guidance and has fulfilled all the requirements for the submission of a Ph.D. thesis, which to my knowledge has reached the requisite standard and is worthy of consideration for the award of Ph.D. degree.

The work embodied in this thesis has not been submitted, in part or full, to other university or institute for the award of any degree or diploma.

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ABSTRACT

The thesis entitled "*C-H activation and multi-functionalization of carbocyclic rings bound to the sandwich compound, (η^5-RCp)Co(η^4-C_4Ph_3R')*" presents the results obtained from the research work carried out on the synthesis, characterization and exploration of the chemistry of cobalt sandwich compounds of the type (η^5-RCp)Co(η^4-C_4R_4'). The accompanied research work has been divided into the seven chapters.

Chapter 1 gives a general introduction to organometallic sandwich compounds and their applications. A general introduction on the synthesis, reactions and applications of (η^5-Cp)Co(η^4-C_4Ph_4) and related molecules is provided. As the work described in the thesis also encompass chemistry of various types of chiral oxazoline ligands, the literature on the chemistry of these compounds have also been covered in this chapter. Since fourth and fifth chapters of this thesis include work on transition metal and directing group assisted C-H activation and functionalization of aryl carboxamides, literature related to this topic is discussed in this chapter. The last chapter of this thesis include work on the olefination reaction of carbonyl compounds with Petasis reagent, Cp_2TiMe_2, and a brief introduction to this topic is also provided in this chapter. The chapter ends with scope of the present work carried out and reported in the thesis.

Chapter 2 describes the general experimental procedures adopted in the synthesis of new compounds and details of characterization techniques utilized. Specific synthetic details of the starting materials used in the thesis are also presented.

Chapter 3 describes the synthesis and characterization of a new type of [(η^5-RCp)Co(η^4-C_4Ph_3R')] type bisoxazoline compound having chiral oxazolinyl units on both the cyclobutadiene and cyclopentadienyl rings of the cobalt sandwich compound. We have

also observed the formation of a palladacycle resulting from the cyclopalladation of one of the cyclobutadiene bound phenyl groups of the cobalt sandwich compound. In addition, we report the synthesis of monooxazoline derived CpCoCb type compounds having the chiral oxazoline unit bound only to the cyclobutadiene ring and show their differences in palladacycle formation in comparison to the bisoxazoline derived sandwich compounds.

Chapter 4 describes the synthesis of the first 8-aminoquinoline derivative of $[\eta^5\text{-}C_5H_4(COOH)]Co(\eta^4\text{-}C_4Ph_4)$ and its reaction with palladium acetate to realize a novel palladacycle. An analogous ferrocene-derived palladacycle has also been synthesized. Such palladacycles have been described as intermediates in the reaction mechanisms proposed for C−H activation involving arylcarboxamides. We have also carried out reactions of these palladacycles exploring their utility and selectivity for α-alkylation of metal sandwich carboxylic amides.

Chapter 5 describes the synthesis and characterization of compounds having two 8-aminoquinoline moieties on the cyclopentadienyl ring alone as well on both the cyclopentadienyl and cyclobutadiene rings. We have used the 1, 3-$\{\eta^5\text{-}[HOC(O)]_2C_5H_3\}Co(\eta^4\text{-}C_4Ph_4)]$ and $(\eta^5\text{-}RCp)Co(\eta^4\text{-}C_4Ph_3R')$ (R=R'=COOH), derivatives of cobalt sandwich compound for attempting multiple C-H activation and functionalization.

Chapter 6 begins with the first reactions of Cp_2TiMe_2 with organometallic sandwich based carbonyl compounds. However, reactions of Cp_2TiMe_2, with the ester derivatives of organometallic sandwich compounds $(\eta^5\text{-}RC_5H_4)Fe(\eta^5\text{-}C_5H_5)$ and $(\eta^5\text{-}RC_5H_4)Co(\eta^4\text{-}C_4Ph_4)$ (R=ester groups) gave products having $R=C(CH_2)Me$, instead of the expected

vinyl ethers indicating conversion of the ester units by Cp_2TiMe_2 to methyl ketones followed by methylenation. The study has also been successfully extended to metal sandwich derived amides, thio and seleno esters. By controlling the amount of Cp_2TiMe_2, the reactions were also stopped at the methyl ketone stage and the methyl ketones were isolated in good yields and characterized. The method provides an easy and direct access to convert organometallic sandwich derived esters and related compounds to 1-methylvinyl derived products.

सारांश (Abstract)

"सैंडविच यौगिकों (sandwich compounds), (η^5-Cp)Co(η^4-C_4Ph_3R') से जुड़ी कार्बोसाइकलिक छल्लों (carbocyclic rings) के C-H सक्रियण और बहु-कार्यात्मकरण" शोध प्रबन्ध शीर्षक से प्राप्त सिद्धांत, संश्लेषण, लक्षण वर्णन और अन्वेषण पर किए गए अनुसंधान कार्य से प्राप्त परिणामों कोबाल्ट सैंडविच यौगिकों के रसायन (η^5-RCp)Co(η^4-C_4R_4') को प्रस्तुत करता है।

अनुसंधान कार्यों को निम्नलिखित सात अध्यायों में विभाजित किया गया है।

अध्याय 1 कार्बोधात्विक सैंडविच यौगिकों (organometallic sandwich compounds) और उनके अनुप्रयोगों के लिए सामान्य परिचय देता है। संश्लेषण, प्रतिक्रियाओं और अनुप्रयोगों (η^5-Cp)Co(η^4-C_4Ph_4) और संबंधित अणुओं पर एक सामान्य परिचय प्रदान किया गया है। जैसा की शोध प्रबन्ध में वर्णित काम में विभिन्न प्रकार के अनुकृति ऑक्साज़ोलिन संलग्नी (chiral oxazoline ligands) के रसायन शामिल हैं, इन यौगिकों के रसायन विज्ञान पर साहित्य भी इस अध्याय में शामिल किया गया है। चूंकि इस शोध प्रबन्ध के चौथे और पांचवें अध्यायों में संक्रमण धातु पर काम करना शामिल है और समूह सहायता प्रदान करने वाली C-H सक्रियण और एरिल-कार्बोक्सामाइड्स (aryl-carboxamides) के कार्यात्मककरण को निर्देशित करना है, इस विषय से संबंधित साहित्य इस अध्याय में चर्चा की गई है। इस शोध प्रबन्ध के आखिरी अध्याय में पेटीसिस अभिकर्मक (Petasis Reagent), Cp_2TiMe_2 के साथ कार्बोनिल यौगिकों (carbonyl compounds) के ओलेफ़िनेशन रिएक्शन (olefination reaction) पर काम करना शामिल है, और इस अध्याय में इस विषय का एक संक्षिप्त परिचय भी प्रदान किया गया है। अध्याय वर्तमान काम के दायरे के साथ समाप्त होता है और शोध प्रबन्ध में रिपोर्ट किया जाता है।

अध्याय 2 नए यौगिकों के संश्लेषण में अपनाई गई सामान्य प्रयोगात्मक प्रक्रियाओं और उपयोग की जाने वाली तकनीकों का वर्णन करता है । शोध प्रबन्ध में उपयोग की जाने वाली प्रारंभिक सामग्री के विशिष्ट कृत्रिम विवरण भी प्रस्तुत किए जाते हैं।

अध्याय 3 कोबाल्ट सैंडविच यौगिकों के साइक्लोब्युटडाइन (cyclobutadiene) और साइक्लोपेंटाडाइनाइल (cyclopentadienyl) छल्ले दोनों पर अनुकृति ऑक्साज़ोलिन

(chiral bisoxazoline) इकाइयों वाला एक बीसऑक्साज़ोलिन (bisoxazoline) सहित नए प्रकार के [(η^5-RCp) Co (η^4-C_4Ph_3R')] यौगिकों का संश्लेषण और लक्ष्छड़ों का वर्णन करता है। और हमने कोबाल्ट सैंडविच यौगिकों के साइक्लोबूटडाडिनी (cyclobutadiene) बंधन वाले फेनिल समूहों (phenyl groups) में से एक cyclopalladation के परिणामस्वरूप एक पैलाडासीकल (palladacycle) के संगठन भी देखा है । इसके अलावा, हम मोनोऑक्साज़ोलिन (mono-oxazoline) व्युत्पन्न CpCoCb प्रकार के यौगिकों के संश्लेषण का रिपोर्ट करते हैं जो अनुकृति ऑक्साज़ोलिन (chiral bisoxazoline) यूनिट को साइक्लोबूटडाडिनी छल्ले (cyclobutadiene ring) तक ही सीमित कर देते हैं और बिसऑक्साज़ोलिन (bisoxazoline) व्युत्पन्न सैंडविच यौगिकों की तुलना में पैलाडेसीक्लिक संरचना (palladacyclic structure) में उनके अंतर दिखाते हैं।

अध्याय 4 वर्णित है कि [η^5-C_5H_4(COOH)]Co(η^4-C_4Ph_4) सहित 8-एमिनोक्विनोलिन (8-aminoquinoline) व्युत्पन्न के संश्लेषण और पैलेडियम एसीटेट [$Pd(OAc)_2$] के साथ इसकी प्रतिक्रिया एक आदर्श पैलाडासीकल (palladacycle) का एहसास और एक समान फेरोसीन (ferrocene) व्युत्पन्न पैलाडेसीकल (palladacycle) को भी संश्लेषित किया गया है। इस तरह के पैलाडासीकल (palladacycle) को एरिल-कार्बोक्सामाइड्स (aryl-carboxamides) से जुड़े C-H सक्रियण के लिए प्रस्तावित प्रतिक्रिया तंत्र में मध्यवर्ती के रूप में वर्णित किया गया है। हमने इन पैलाडेसीकलों (palladacycles) की प्रतिक्रियाओं को भी अपनाया है और धातु सैंडविच कार्बोक्जिलिक एमाइड्स (carboxylic amides) के अल्फा-अल्किलिशन (α-alkylation) के लिए उनकी उपयोगिता और चयनात्मकता की खोज की है।

अध्याय 5 अकेले साइक्लोपेंटाडाइनाइल (cyclopentadienyl) या दोनों छल्लों (rings) साइक्लोपेंटाडाइनाइल (cyclopentadienyl) और साइक्लोब्युटडाइन (cyclobutadiene) पर भी दो 8-एमिनोक्विनोलिन (8-aminoquinoline) अंश वाले यौगिकों के संश्लेषण और लक्षणों का वर्णन करता है। हमने व्युत्पन्न एकाधिक C-H सक्रियण और कार्यात्मककरण के प्रयास के लिए कोबाल्ट सैंडविच यौगिकों 1, 3- {η^5- [HOC (O)]$_2$$C_5H_3$}$C_O$($\eta^4$-$C_4Ph_4$)] और ($\eta^5$-RCp)Co($\eta^4$-$C_4Ph_3R'$) (R=R'=COOH) का उपयोग किया है,

अध्याय 6 Cp_2TiMe_2 की पहली प्रतिक्रियाओं से शुरू होता है जिसमें कार्बोधात्विक सैंडविच (organometallic sandwich) आधारित कार्बोनिल यौगिकों (carbonyl compounds) के साथ होता है। हालांकि, Cp_2TiMe_2 की

प्रतिक्रियाएं, कार्बोधात्विक सैंडविच यौगिकों (organometallical sandwich compounds) (η^5-RC_5H_4)Fe(η^5-C_5H_5) और (η^5-RC_5H_4)Co(η4-C_4Ph_4) (R=ester groups) के एस्टर डेरिवेटिव के साथ, (R=$C(CH_2)Me$) दिया, उम्मीद की गई विनाइल ईथर (vinyl ethers) के बजाय Cp_2TiMe_2 द्वारा एस्टर (ester) इकाइयों के रूपांतरण को मिथाइल केटोन्स (methyl ketones) के संकेत देते हैं और इसके बाद मेथिलिनेशन (methylenation)। अध्ययन को सफलतापूर्वक धातु सैंडविच व्युत्पन्न एमाइड्स (amides), थियो (thio) और सेलेन (Seleno) एस्टर (esters) तक बढ़ाया गया है। Cp_2TiMe_2 की मात्रा को नियंत्रित करके, मिथाइल केटोन चरण में भी प्रतिक्रियाएं बंद कर दी गईं और मिथाइल केटोन्स अच्छी पैदावार में अलग-थलग हो गए थी। यह विधि 1-मेथिलविनाइल व्युत्पन्न (1-methylvinyl derivatives) उत्पादों के लिए ऑर्निमेटैमलिक सैंडविच युक्त एस्टर और संबंधित यौगिकों को कनवर्ट करने के लिए एक आसान और सीधी पहुंच प्रदान करता है।

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LIST OF ABBREVIATIONS USED

Calcd.	Calculated
Cp	Cyclopentadienyl
Cb	Cyclobutadiene
Me	Methyl
Et	Ethyl
*i*Pr	Isopropyl
Ph	Phenyl
Fc	Ferrocene
Mp	Melting point
r. t.	Room Temperature
h	Hour(s)
min	Minutes
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
IR	Infrared spectroscopy
NMR	Nuclear Magnetic Resonance Spectroscopy
HRMS	High Resolution Mass Spectroscopy
HPLC	High Performance Liquid Chromatography
Py	Pyridine
AQ	8-aminoquinoline
DG	Directing group