

**CHEMISTRY OF METAL SANDWICH COMPOUNDS:
STUDIES ON C-H FUNCTIONALIZATIONS, DESIGN OF
NOVEL LIGANDS AND USE AS CATALYSTS**

MAYUKH DEB



**DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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STUDIES ON C-H FUNCTIONALIZATIONS, DESIGN OF
NOVEL LIGANDS AND USE AS CATALYSTS**

by

MAYUKH DEB

Department of Chemistry

Submitted

in fulfillment of the requirements of the degree of Doctor of Philosophy

to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI INDIA

OCTOBER 2018

Dedicated

to

My Family and Teachers

CERTIFICATE

This is to certify that the thesis entitled “*Chemistry of metal sandwich compounds: Studies on C-H functionalization, design of novel ligands and use as catalysts*”, being submitted by Mr. **Mayukh Deb** 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. **Mayukh Deb** 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 universities or institutes for the award of any degree or diploma.

Dr. Anil J. Elias

Research Supervisor,

Professor (HAG),

Department of Chemistry

Indian Institute of Technology Delhi

Hauz Khas, New Delhi-110016, India.

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Mayukh Deb

ABSTRACT

The thesis entitled “*Chemistry of metal sandwich compounds: Studies on C-H functionalization, design of novel ligands and use as catalysts.*” presents the results obtained from the research work carried out on the synthesis, characterization and exploration of the chemistry of ferrocene and cobalt sandwich compounds. The accompanied research work has been divided into the seven chapters.

Chapter 1 is a general introduction providing the background and literature required for the understanding of the actual experiments carried out and presented in the subsequent chapters. As the work described in this thesis has mainly been focused on the metal sandwich compounds, this chapter includes types and applications of ferrocene and cobalt sandwich compounds of the type $(\eta^5\text{-C}_5\text{H}_5)\text{Co}(\eta^4\text{-C}_4\text{Ph}_4)$. This chapter also deals with a brief discussion on the literature around C-H functionalization: through chelation and short contacts. Under the chelation mediated C-H activation, different monodentate, bidentate, traceless and transient directing group assisted C-H bond functionalization has been briefly described. Under short contact driven C-H activation, template assisted remote/distal C-H bond functionalization has been discussed in brief. A detailed discussion on the transition metal mediated C-H bond activation of metal sandwich substrates has also been provided. In the last section of this chapter, a brief background for the oxidation of benzyl amines and use of metal sandwich compounds in organic transformations has been portrayed. Necessity of oxidizing benzyl amines using atmospheric air and water as the solvent using a ferrocene/ferrocenium redox catalyst has been addressed and existing challenges have been identified. The chapter ends with the scope of the present of 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 described in the thesis are also presented.

Chapter 3 describes the unprecedented isolation of Cu(I) complexes as product in a Sonogashira coupling wherein the coupled product holds CuX (X= I, Br) as a "classical side-on" type complex which has been found to be highly air and moisture stable. The use of cuprous acetylide of ethynyl ferrocene yielded the same product and this observation indirectly proves that cuprous acetylide is formed in the copper cycle of the Sonogashira coupling mechanism. The spatial arrangement provided by the coupled product is sufficient for one monomeric Cu-X fragment to be present in it. Treatment of the above monomeric copper complexes with aq. ammonia in DMF yielded the metal free Cu(I) specific ligands in quantitative yields. This metal free compound could bind recyclably to Cu(I)X salts almost quantitatively and within 1 minute time, even from a suspension of mixture of various metal salts.

Chapter 4 describes the bidentate directing group assisted C-H bond functionalization of the ferrocene and cobalt sandwich substrates. Carbon-boron, carbon-silicon and carbon-selenium bond formations have been achieved using bis(pinacolato)diboron, hexamethyldisilane and diphenyl diselenide as the reactive species, respectively. A catalytic C-H borylation reaction was achieved using pyridine-*N*-oxide as the directing group. A stoichiometric borylation was also attained using 2-(methylthio)phenyl as the directing group. Identities of some of the palladacycle intermediates were confirmed by single crystal XRD studies. Palladium catalyzed C-H silylation was achieved using 2-(methylthio)phenyl directing group using hexamethyldisilane as the silylating agent, on

cobalt sandwich substrates. Palladium catalyzed C-H selenation was successfully achieved using 8-aminoquinoline as the directing group on palladacycles of both ferrocene and cobalt sandwich compounds.

Chapter 5 describes the synthesis of multi-aryl derivatives of ferrocene using palladium catalyst and oxime-ether as a directing group. The reactions were carried out under air and aldehydes were used as the acylating agents, under the influence of aqueous *tert*-butyl hydroperoxide (TBHP) as the oxidant. The multi-aryl derivatives obtained following this method is difficult to synthesize in traditional methods. A detailed optimization of the mentioned method has been discussed in the thesis. Substrate scope of the aldehydes and benzyl alcohols were investigated and the mechanism of the reaction was proposed by taking in account the literature reports and control experiments. Straightforward deprotection of the oxime directing group was possible using acidic hydrolysis. The rate and order of the initiation reaction was also determined by kinetic experiments.

Chapter 6 deals with the oxidation of benzylamines to the corresponding imines in purely aqueous medium. A ferrocenium based catalyst was used for this transformation. Iron being the second most abundant metal on the earth's crust and atmospheric air being the most inexpensive and safest oxidant, this method has a considerable scope in the imine chemistry. The substrate scope showed the applicability of this reaction in presence of electron-donating as well as electron withdrawing substrates. Mixture of two amines gave the cross-coupled imine products in low to moderate yields. Different literature reports and control experiments enabled us to propose the mechanism of the oxidation

reaction. A ferrocenium salt played a dual role as a catalyst and initiator for chain reaction in the above reaction.

Chapter 7 gives the overall conclusions of the entire work carried out in the present study.

सार

थीसिस "केमिस्ट्री ऑफ़ मेटल सैंडविच कंपाउंड्स: स्टडीज ऑन सी-एच फंक्शनलीजेसान, डिज़ाइन ऑफ़ नावेल लिगंड्स एंड यूज़ अस काटलिस्ट्स" संश्लेषण, विशेषता और फेरोसीन और कोबाल्ट सैंडविच यौगिकों की रसायन शास्त्र के अन्वेषण की खोज पर किए गए शोध कार्यों से प्राप्त परिणाम प्रस्तुत करता है। शोध कार्य सात अध्यायों में बांटा गया है।

अध्याय १ एक सामान्य परिचय है जो बाद के अध्यायों में किए गए वास्तविक प्रयोगों की समझ के लिए आवश्यक पृष्ठभूमि और साहित्य प्रदान करता है। चूंकि इस थीसिस में वर्णित कार्य मुख्य रूप से धातु सैंडविच यौगिकों पर केंद्रित है, इस अध्याय में $(\eta^5-C_5H_5)Co(\eta^4-C_4Ph_4)$ प्रकार के फेरोसीन और कोबाल्ट सैंडविच यौगिकों के प्रकार और अनुप्रयोग शामिल हैं। यह अध्याय चेलेशन और छोटे संपर्कों के माध्यम से सी-एच कार्यान्वयन के आसपास साहित्य पर एक संक्षिप्त चर्चा से संबंधित है। चेलेशन मध्यस्थ सी-एच सक्रियण के तहत, अलग-अलग मोनोडेंटेट, बिडेण्टेट, ट्रेसलेस् और क्षणिक निर्देश समूह की सहायता से सी-एच बंधन कार्यान्वयन संक्षेप में वर्णित किया गया है। संक्षिप्त संपर्क संचालित सी-एच सक्रियण के तहत, टेम्पलेट सहायता दूरस्थ / दूरस्थ सी-एच बॉन्ड कार्यान्वयन पर चर्चा की गई है। धातु सैंडविच सबस्ट्रेट्स के संक्रमण धातु मध्यस्थ सी-एच बॉन्ड सक्रियण पर एक विस्तृत चर्चा भी प्रदान की गई है। इस अध्याय के अंतिम खंड में, बेंजाइल अमाइन के ऑक्सीकरण और कार्बनिक परिवर्तनों में धातु सैंडविच यौगिकों के उपयोग के लिए एक संक्षिप्त पृष्ठभूमि चित्रित की गई है। बेंजाइल अमाइनों को वायुमंडलीय वायु, पानी का विलायक के रूप में और एक फेरोसिन / फेरोसेनियम रेडॉक्स उत्प्रेरक का उपयोग करके ऑक्सीकरण करने की आवश्यकता को संबोधित किया गया है और मौजूदा चुनौतियों की पहचान की गई है। थीसिस में किए गए कार्यों के वर्तमान दायरे के साथ अध्याय समाप्त होता है।

अध्याय २ में नए यौगिकों के संश्लेषण और उपयोग की गई विशेषता तकनीकों के विवरण में अपनाई गई सामान्य प्रयोगात्मक प्रक्रियाओं का वर्णन किया गया है। थीसिस में वर्णित प्रारंभिक सामग्री के विशिष्ट सिंथेटिक विवरण भी प्रस्तुत किए जाते हैं।

अध्याय ३ में $Cu(I)$ परिसरों के अभूतपूर्व अलगाव का वर्णन सोनोगिशिरा युग्मन में उत्पाद के रूप में किया गया है जिसमें युग्मित उत्पाद में "क्लासिकल साइड-ऑन" प्रकार परिसर के रूप में CuX ($X = I, Br$) होता है जो अत्यधिक हवा और नमी स्थिर पाया जाता है। एथनील फेरोसिन के कपस एसिटाइलाइड के उपयोग ने वही उत्पाद पैदा किया और यह अवलोकन अप्रत्यक्ष रूप से साबित करता है कि सोनोगिशिरा युग्मन तंत्र के तांबा चक्र में कपूर एसिटाइड का गठन होता है। युग्मित उत्पाद द्वारा प्रदान की गई स्थानिक व्यवस्था एक मोनोमेरिक क्यू-एक्स खंड में मौजूद होने के लिए पर्याप्त है। उपरोक्त मोनोमेरिक तांबा परिसरों के डीएमएफ में जलीय अमोनिया से उपचार ने मात्रात्मक उपज में धातु मुक्त $Cu(I)$ विशिष्ट लिगेण्डों को जन्म दिया। यह धातु मुक्त यौगिक $Cu(I)$ एक्स लवण को लगभग मात्रात्मक रूप से और १ मिनट के भीतर पुनर्नवीनीकरण कर सकता है, यहां तक कि विभिन्न धातु नमक के मिश्रण के निलंबन से भी।

अध्याय ४ निर्देशक समूह सी-एच बॉन्ड फक्शनलाइजेशन की सहायता से फेरोसीन और कोबाल्ट सैंडविच सबस्ट्रेट्स का वर्णन करता है। कार्बन-बोरॉन, कार्बन-सिलिकॉन और कार्बन-सेलेनियम बंधन संरचना क्रमशः प्रतिक्रियाशील प्रजातियों के रूप में बीस (पिनकोलाटो) डिबोरॉन, हेक्सामेथिलिडसिलन और डिफेनिल डिसेलेनाइड का उपयोग करके हासिल की गई हैं। निर्देशक समूह के रूप में पाइरीडिन-एन-ऑक्साइड का उपयोग करके उत्प्रेरक सी-एच बोरीलेशन प्रतिक्रिया प्राप्त की गई। निर्देशक समूह के रूप में 2- (मेथिलथियो) फेनिल का उपयोग करके एक स्टॉइचियोमेट्रिक बोरीलेशन भी प्राप्त किया गया। कुछ पल्लाडैसीकल इंटरमीडिएट्स की पहचान एकल क्रिस्टल एक्स आर डी अध्ययनों द्वारा पुष्टि की गई थी। पैलेडियम उत्प्रेरित सी-एच सिलाईलेशन को कोबाल्ट सैंडविच सबस्ट्रेट्स पर, सिलेलाइडिंग एजेंट के रूप में हेक्सामेथिलिडसिलन का उपयोग करके 2- (मेथिलथियो) फेनिल निर्देशन समूह का उपयोग करके हासिल किया गया था। पैलेडियम उत्प्रेरित सी-एच सेलेनेशन को 8-एमिनोक्विनोलिन का फेरोसीन और कोबाल्ट सैंडविच यौगिकों के पैलाडैसीकल पर निर्देशक समूह के रूप में का उपयोग करके सफलतापूर्वक हासिल किया गया था।

अध्याय ५ में निर्देशक समूह के रूप में पैलेडियम उत्प्रेरक और ऑक्सीम-ईथर का उपयोग करके फेरोसिन के बहु-एरोइल डेरिवेटिव के संश्लेषण का वर्णन किया गया है। ऑक्सीडेंट के रूप में जलीय टर्ट-ब्यूटिल हाइड्रोप्रोक्साइड (टीबीएचपी) के प्रभाव में, हवा के तहत प्रतिक्रियाएं की जाती थीं और एल्डेहाइडिस को एसीलेटिंग एजेंट के रूप में उपयोग किया जाता था। इस विधि के बाद प्राप्त बहु-एरोइल डेरिवेटिव पारंपरिक तरीकों से संश्लेषित करना मुश्किल है। थीसिस में उल्लिखित विधि का एक विस्तृत अनुकूलन पर चर्चा की गई है। एल्डेहाइड और बेंजाइल अल्कोहल के सबस्ट्रेट गुंजाइश की जांच की गई और साहित्य की रिपोर्ट और नियंत्रण प्रयोगों को ध्यान में रखते हुए प्रतिक्रिया का तंत्र प्रस्तावित किया गया। ऑक्सीम डायरेक्ट्रोलिंग समूह का सीधा डिफ्रेंस अम्लीय हाइड्रोलिसिस का उपयोग करके संभव था। दीक्षा प्रतिक्रिया की दर और क्रम भी गतिशील प्रयोगों द्वारा निर्धारित किया गया था।

अध्याय ६ पूरी तरह से जलीय माध्यम में बेंजाइलामाइनस के संबंधित इमाइनों में ऑक्सीकरण से संबंधित है। इस परिवर्तन के लिए एक फेरोसेनियम आधारित उत्प्रेरक का उपयोग किया गया था। पृथ्वी की परत पर लौह दूसरा सबसे प्रचुर मात्रा में धातु है और वायुमंडलीय हवा सबसे सस्ती और सुरक्षित ऑक्सीडेंट है, इस विधि की इमाइन रसायन शास्त्र में काफी गुंजाइश है। सबस्ट्रेट स्कोप ने इलेक्ट्रान-दान करने के साथ-साथ इलेक्ट्रॉन को सबस्ट्रेट को वापस लेने की उपस्थिति में इस प्रतिक्रिया की प्रयोज्यता दिखाई। दो अमीन्स के मिश्रण ने क्रॉस-युग्मित इमेइन उत्पादों को कम से कम पैदावार में दिया। विभिन्न साहित्य रिपोर्टों और नियंत्रण प्रयोगों ने हमें ऑक्सीकरण प्रतिक्रिया के तंत्र का प्रस्ताव देने में सक्षम बनाया। एक फेरोसेनियम नमक ने उपरोक्त प्रतिक्रिया में चेन प्रतिक्रिया के लिए उत्प्रेरक और शुरुआतकर्ता के रूप में दोहरी भूमिका निभाई।

अध्याय ७ वर्तमान अध्ययन में किए गए पूरे काम के समग्र निष्कर्ष देता है।

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List of Abbreviations Used

Anal.	Analysis
<i>i</i> Pr	Isopropyl
Calcd.	Calculated
Cp	Cyclopentadienyl
Cb	Cyclobutadiene
Me	Methyl
Et	Ethyl
Ph	Phenyl
Fc	Ferrocene
Mp	Melting point
RT	Room Temperature
h	Hour(s)
min	Minutes
THF	Tetrahydrofuran
UV	Ultraviolet Spectroscopy
TLC	Thin Layer Chromatography
NMR	Nuclear Magnetic Resonance Spectroscopy
HRMS	High Resolution Mass Spectroscopy
PyO	Pyridine- <i>N</i> -oxide
NOESY	Nuclear Overhauser effect spectroscopy
BHT	Butylated hydroxytoluene
TEMPO	(2, 2, 6, 6-tetramethylpiperidin-1-yl)oxyl

TMEDA	Tetramethylethylenediamine
TDG	Transient directing group
DG	Directing group
DMSO	Dimethyl sulfoxide
SCXRD	Single crystal X-ray diffraction
DCM	Dichloromethane
DMF	<i>N, N</i> -dimethyl formamide
Aq.	Aqueous
TON	Turn Over Number
DCE	1, 2-dichloroethane
NHPI	<i>N</i> -hydroxy phthalimide
DDQ	2, 3-dichloro-5,6-dicyanobenzoquinone
TBHP	<i>tert</i> -Butyl hydroperoxide
TBPB	<i>tert</i> -Butyl peroxybenzoate
GC-MS	Gas Chromatography Mass Spectrometry