OXIDATION OF ORGANOPALLADIUM AND PLATINUM COMPOUNDS: ROLE OF IRON (III) PORPHYRINS IN CHANGING SELECTIVITY

By

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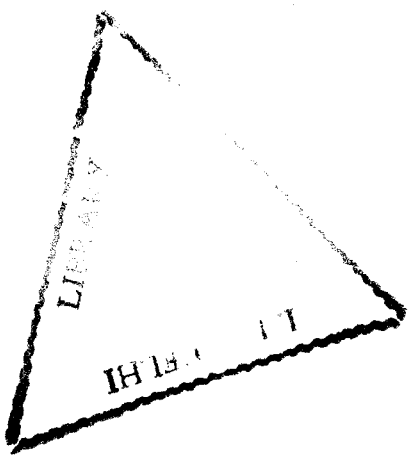

Dedicated

to my

Father

CERTIFICATE

This is to certify that the thesis entitled, "**OXIDATION OF ORGANO-PALLADIUM AND PLATINUM COMPOUNDS: ROLE OF IRON (III) PORPHYRINS IN CHANGING SELECTIVITY**", being submitted by **Mr. K. Kamaraj** to the Indian Institute of Technology, Delhi for the award of the degree of **Doctor of Philosophy** in **Chemistry** is a record of bonafide research work carried out by him. Mr. K. Kamaraj has worked under my guidance and supervision, and has fulfilled the requirements for the submission of this thesis which, to my knowledge has reached the requisite standard.

The results contained in this dissertation have not been submitted in part or full to any other University or Institute for the award of any degree or diploma.

Date: 24th Dec. '98

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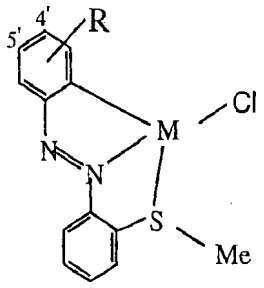
ABSTRACT

The organopalladium and platinum compounds **1a-d**, **2a-e**, **3a-d**, have been synthesized in high yields by the reaction of corresponding ligands with the metal salts. Pentafluoroiodosylbenzene (C_6F_5IO) selectively oxygenates C-Pd bond in **1a-c** to **2a-c**. The kinetics of one representative compound **1a** has been studied in detail to understand the mechanism of the reaction. Large negative value of entropy of activation supports an associative mechanism and smooth reaction in polar solvent supports polar intermediate structure. Involvement of oxopalladium (IV) has been proposed as a crucial step prior to C-Pd bond oxidation. Plausible mechanism for the smooth oxidation of Pd-C bond has been discussed.

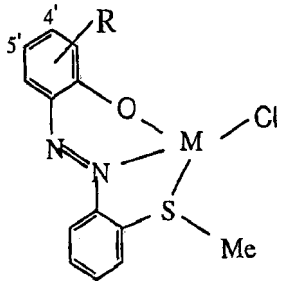
Methods of high yield selective oxidation of 1 to 2 are discussed. Thus it has been observed that almost quantitative oxidation of **1a** to **2a** has been achieved by t-BuOO$^{\bullet}$ radical and the same oxidation in very high yields (~94%) has been achieved by MCPBA in presence of a highly electronegative iron porphyrin catalyst (F_{20}TPPFe(III)Cl) in toluene medium, where involvement of catalyst-oxidant adduct as the active oxidant in this efficient C-Pd bond oxidation has been proposed.

The oxidation of **1** to **3** on the other hand has been achieved very successfully by oxoiron (IV) porphyrin cation radical (oxene). Oxoiron(IV) porphyrin on the other hand does not show any detectable reactivity with **1a-c** compounds. The above reactivity pattern of cyclopalladates has been well utilized in the identification of oxene and t-BuOO$^{\bullet}$ radical species in solution .Thus an artificial reaction medium having both oxene and t-BuOO$^{\bullet}$ radical has been generated and it is observed that **1a** gives both **2a** and **3a**. This unique feature of **1a** has been utilized in resolving an important issue in hydroperoxide oxidations catalyzed by iron(III)porphyrins. From product profile analysis of a reaction medium

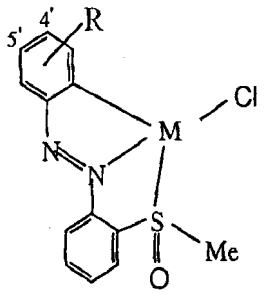
comprising **1a**, PFe(III)Cl, and t-BuOOH, it has been clearly demonstrated that in this oxidizing system oxene is not at all important reactive intermediate to consider.



1a : R= 4'-Me; M = Pd
1b : R= 5'-Me; M = Pd
1c : R= H ; M = Pd
1d : R= 4'-Me; M = Pt
1e : R= 5'-Me; M = Pt
1f : R= H ; M = Pt



2a : R= 4'-Me; M = Pd
2b : R= 5'-Me; M = Pd
2c : R= H ; M = Pd
2e : R= 5'-Me; M = Pt



3a : R= 4'-Me; M = Pd
3b : R= 5'-Me; M = Pd
3c : R= H ; M = Pd
3d : R= 4'-Me; M = Pt

In this oxidation of **1a** by F_{20}TPPFe(III)Cl + t-BuOOH oxidising system one remarkable observation is that this reaction does not proceed in neat dichloromethane while smooth reaction proceeds in 33-37% of methanol in dichloromethane. Pure methanol again is also not good for this reaction to proceed. The necessity of this peculiar solvent composition has also been observed in the oxidation of 2,4,6-tri-*tert*-butylphenol to the corresponding phenoxy radical. Thus maximum yield of phenoxy radical has been successfully achieved from 33-37% of methanol in dichloromethane by F_{20}TPPFe(III)Cl + t-BuOOH oxidizing system. It has been established that in this oxidising system dissociation of iron(III) bound chloride from the F_{20}TPPFe(III)Cl by methanolic solvent is very important which completes essentially in 33-37% of methanol and excess of methanol is not good in the sense that it acts as a substrate too.

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