IN THE NAME OF GOD

OXIDATIVE ADDITION OF DIFFERENT REAGENTS TO ORGANOPLATINEUM(II) COMPLEXES

BY:

NAHID SHAHABADI

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EVALUATED AND APPROVED BY THE THESIS COMMITTEE AS: EXCELLENT

M. Rashidi, Ph.D., Prof. of Chemistry.

(Chairman)

D. Mohajer, Ph.D. Assoc. Prof. of Chemistry.

A. Tarassoli, Ph.D., Prof. of Chemistry.

M. Asadi, Ph.D. Assoc. Prof. of

Chemistry.

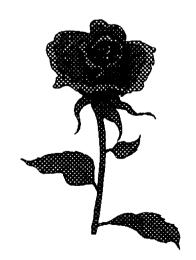
N. Irapnoor, Ph.D., Pfor. of Chemistry.

S. Tangestaninejad, Ph.D., Assis. Prof. of Chemistry.

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To all my teachers & My familly



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ABSTRACT

Oxidative Addition of Different Reagents to Organoplatinum(II) Complexes

By:

Nahid Shahabadi

The complexes [Pt(CH₂CH₂CH₂CH₂)(NN)] (NN=bpy, I_a, and NN=phen, I_b,) are electron rich and are particularly reactive to oxidative addition. They reacted cleanly with excess of some primary alkyl halides, RX (R=nPr, nBu, X=I, Br), in benzene or in acetone to give new platina(IV)cyclopentane complexes with general formula [PtX(CH₂CH₂CH₂CH₂)R(NN)]. The platinum(IV) products were fully characterized by ¹H and ¹³C NMR spectroscopy and microanalysis. The kinetics of the reactions were studied using UV-Vis spectroscopy. Except for PrBr in benzene, the reactions followed good second order kinetics in acetone and in benzene, first order in each reagent, and an S_N2 mechanism was suggested for them. The reaction of PrBr with I_a and I_b and also with the dimethyl analogue [PtMe2(bpy)], IIa, in benzene behaved more complex and it was tentatively suggested that the reactions reached equuilibrium.

In a comparative kinetic study, the oxidative addition of EtI to I_a and II_a was studied. An S_N2 mechanism was suggested and it was demonstrated that at different temperatures, EtI reacted 2.2-2.6 times faster with platina(II)cyclopentane complex I_a than with the dimethyl analogue II_a, which reflects higher donor ability of (CH₂)₄ ligand compared to CH₃ ligands in platinum(II) complexes.

The reactions of I_a, I_b and II_a complexes with some oxiranes, CH₂CH₂OR (R=CH₂OPh, Ph, Me), in the presence of CO₂ were proceeded and stable metallacyclocarbonate complexes, as the first examples of tris-chelate organoplatinum compounds, were isolated and were characterized by ¹H and ¹³C NMR spectroscopy and microanalysis. H/C HETCOR experiments were performed for the complexes to ascertain the assignments. The kinetics of the reactions with 2,3-epoxypropyl-phenyl ether were studied using UV-Vis spectroscopy. It was suggested that the reactions followed good second order kinetics, first order in Pt complex and also in oxirane, and the rates were unaffected by the presence of CO₂. Also, the metallacycle analogue I_a reacted 2.5 times faster than the dimethyl analogue II_a.

The oxidative addition of some reagents containing group 16 elements (MeSSMe and H₂O₂) to I_a and I_b led to *trans* isomers of platinum (IV) adducts with the general formula [Pt(CH₂CH₂CH₂CH₂)(RE) ₂ (NN)], E=S, O and R=Me, H, as the main products. The reaction of MeSSMe with an aryl complex of platinum [Pt(4-OMeC₆H₄)₂(bpy)] was also studied. The product was characterized by ¹H and ¹³C NMR spectroscopy as [Pt(4-OMeC₆H₄)₂(SMe)₂(bpy)].

A detailed multinucleare NMR investigation, including 13 C and 2D experiments, of a platina(II)cyclopentane complex containing bis(diphenyl phosphino)methane (dppm), i.e [Pt(CH₂CH₂CH₂CH₂) (dppm), was performed and using H/C HETCOR experiments, the α -CH₂ and β -CH₂ protons were assigned.

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