

IN THE NAME OF GOD

OXIDATIVE ADDITION OF DIFFERENT REAGENTS TO
ORGANOPLATINEUM(II) COMPLEXES

BY:

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*To all my teachers
&
My family*



Y V K F O

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ABSTRACT

Oxidative Addition of Different Reagents to Organoplatinum(II) Complexes

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The complexes $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{NN})]$ ($\text{NN}=\text{bpy}$, I_a and $\text{NN}=\text{phen}$, I_b) are electron rich and are particularly reactive to oxidative addition. They reacted cleanly with excess of some primary alkyl halides, RX ($\text{R}=\text{}^n\text{Pr}$, $\text{}^n\text{Bu}$, $\text{X}=\text{I}$, Br), in benzene or in acetone to give new platina(IV)cyclopentane complexes with general formula $[\text{PtX}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)\text{R}(\text{NN})]$. The platinum(IV) products were fully characterized by ^1H and ^{13}C NMR spectroscopy and microanalysis. The kinetics of the reactions were studied using UV-Vis spectroscopy. Except for $\text{}^n\text{PrBr}$ in benzene, the reactions followed good second order kinetics in acetone and in benzene, first order in each reagent, and an $\text{S}_{\text{N}}2$ mechanism was suggested for them. The reaction of $\text{}^n\text{PrBr}$ with I_a and I_b and also with the dimethyl analogue $[\text{PtMe}_2(\text{bpy})]$, II_a , in benzene behaved more complex and it was tentatively suggested that the reactions reached equilibrium.

In a comparative kinetic study, the oxidative addition of EtI to I_a and II_a was studied. An $\text{S}_{\text{N}}2$ 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 $(\text{CH}_2)_4$ ligand compared to CH_3 ligands in platinum(II) complexes.

The reactions of I_a , I_b and II_a complexes with some oxiranes, $\overline{CH_2CH_2OR}$ ($R=CH_2OPh$, Ph , Me), in the presence of CO_2 were proceeded and stable metallacyclocarbonate complexes, as the first examples of tris-chelate organoplatinum compounds, were isolated and were characterized by 1H and ^{13}C 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 CO_2 . 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 H_2O_2) to I_a and I_b led to *trans* isomers of platinum (IV) adducts with the general formula $[Pt(CH_2CH_2CH_2CH_2)(RE)_2(NN)]$, $E=S, O$ and $R=Me, H$, as the main products. The reaction of $MeSSMe$ with an aryl complex of platinum $[Pt(4-OMeC_6H_4)_2(bpy)]$ was also studied. The product was characterized by 1H and ^{13}C NMR spectroscopy as $[Pt(4-OMeC_6H_4)_2(SMe)_2(bpy)]$.

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 $[Pt(CH_2CH_2CH_2CH_2)(dppm)]$, was performed and using H/C HETCOR experiments, the α - CH_2 and β - CH_2 protons were assigned.

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