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Modelling catalytic intermediates with organoplatinum complexes

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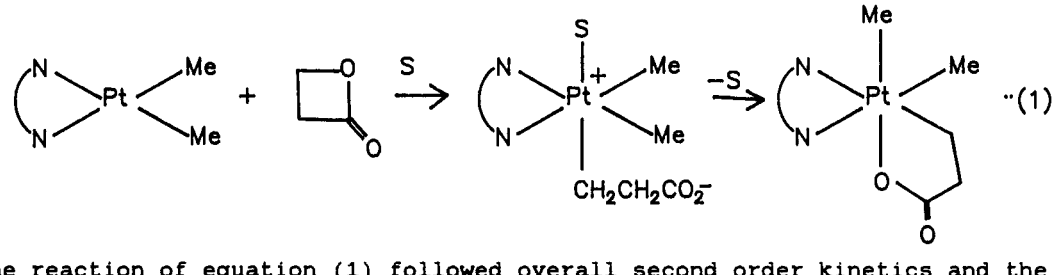
Abstract - The oxidative addition to organoplatinum complexes of some normally unreactive bonds can be achieved using enhanced reactivity due to ring strain, intramolecular activation or the cooperative effects of two or three metal atoms. As examples, the oxidative addition of the C-O bond of β-lactones or oxiranes to $[PtMe_2(NN)]$, where NN = 2,2'-bipyridine or 1,10-phenanthroline, is aided by ring strain, the oxidative addition of the aryl-halogen bond in $[PtMe_2(Me_2NCH_2CH_2N{=}CH\text{-}2\text{-}C_6H_4X)]$ or $[PtMe_2(Me_2NCH_2CH_2N{=}CHC_6F_5)]$ is facilitated by intramolecular activation, and the activation of the C=S bond of CS_2, COS or RNCS to binuclear or trinuclear complexes such as $[Pt_2(\mu\text{-dppm})_3]$ or $[Pt_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$, dppm = $Ph_2PCH_2PPh_2$, involves cooperative effects between two or three metal centers.

INTRODUCTION

Many small molecules can be activated by oxidative addition to transition metal complexes and so oxidative addition and reductive elimination are vital steps of many catalytic reactions. Some difficult bonds to activate by oxidative addition are the C-O bonds of esters and ethers, aryl-halogen bonds, especially C-F bonds, and multiple bonds. This paper describes some recent work on the oxidative addition of such bonds to organoplatinum complexes, with emphasis on the factors which influence reactivity and mechanism.

ACTIVATION USING RING STRAIN

Esters are usually unreactive in oxidative addition, except in those cases where there is a particularly good leaving group such as triflate.[1] For example, methyl acetate fails to react with the complexes $[PtMe_2(NN)]$, **1a**, NN = 2,2'-bipyridene; **1b**, NN = 1,10-phenanthroline. The ring strain present in β-propiolactone is therefore probably responsible for its greater reactivity towards **1** and the products are shown in equation (1).[2]



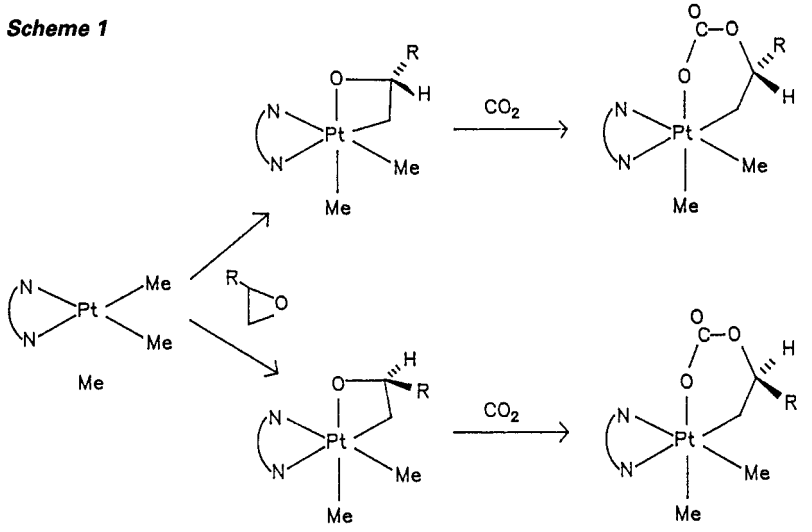
(1)

The reaction of equation (1) followed overall second order kinetics and the activation parameters in acetone were E_a = 46(±2) kJ mol^{-1} and $\Delta S^{\ddagger}$ = -142 JK^{-1} mol^{-1}. The large negative value of $\Delta S^{\ddagger}$ is suggestive of an S_N2 mechanism in which the platinum nucleophile attacks the CH_2-O methylene group to give a dipolar intermediate $[Pt^{+}Me_2(CH_2CH_2CO_2^{-})(S)(NN)]$, S = solvent. The Pt-O bond of the product **2** is labile and the metallalactone can be further derivatized by reactions with methyl iodide or hydrogen chloride.

To activate ethers by oxidative addition is particularly difficult and only reactions of the three-membered strained ring oxiranes have been successful.[3] The reaction in which the proposed platinaoxacyclobutane product is trapped by reaction with carbon dioxide is shown in Scheme 1. The kinetics are first order in platinum(II) complex and in epoxide but zero order in CO_2 and, when R = Ph, the activation parameters in acetone solution

are $\Delta G^{\dagger}$ = 33 kJ mol^{-1} and $\Delta S^{\dagger}$ = -207 JK^{-1} mol^{-1}. The large negative value of $\Delta S^{\dagger}$ is indicative of an S_N2 mechanism involving a dipolar intermediate $[Pt^{+}Me_2(NN)CH_2CHRO^{-}]$, NN = bipy or phen. In the absence of CO_2, oligomerization of the epoxide appears to occur.

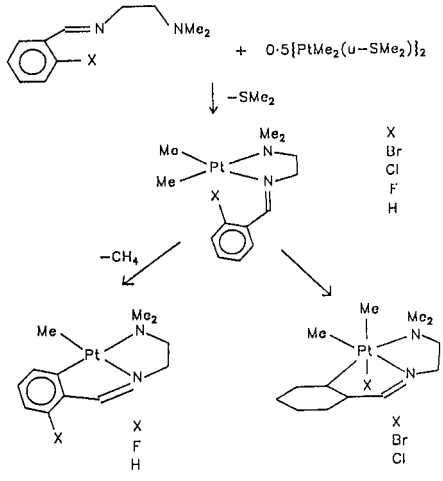
Scheme 1



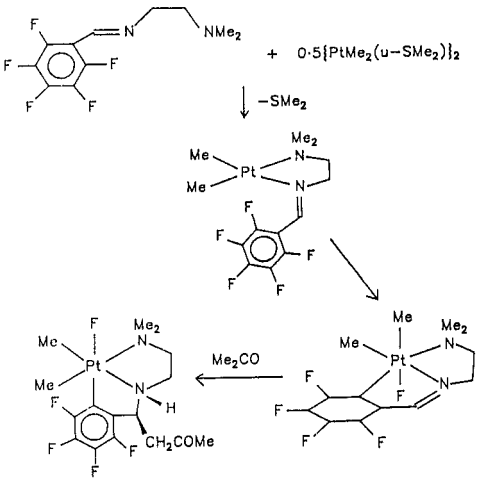
INTRAMOLECULAR ACTIVATION

Simple aryl halides fail to react with $[PtMe_2(bipy)]$ and so to study aryl-halogen oxidative addition it was necessary to use intramolecular activation as shown in Scheme 2.[4] The C-Br and C-Cl derivatives underwent oxidative addition but the C-H and C-F derivatives reacted by orthometallation. From kinetic studies of the oxidative addition step and from the intramolecular competition between C-X and C-H bond activation, the order of reactivity C-Br > C-Cl > C-H > C-F was obtained and this is also the order of increasing C-X bond energies. In this case $\Delta S^{\dagger}$ is almost zero for the C-Br and C-Cl oxidative additions and this is inconsistent with a polar transition state. A concerted mechanism of oxidative addition is therefore indicated, as proposed already for C-H bond activation.

Scheme 2



Scheme 3



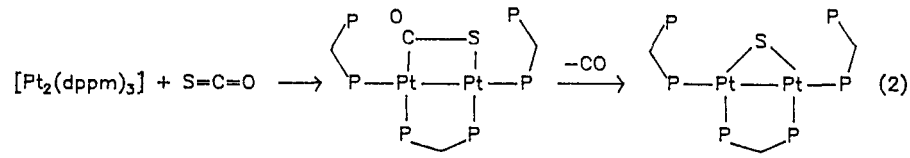
In order to activate the C-F bond of an aryl halide, the pentafluorophenyl derivative was needed as shown in Scheme 3. Obviously, C-H activation is no longer possible and the reaction is also favoured by the presence of electronegative fluorine substituents which activate the ring to nucleophilic attack. This is therefore a facile reaction, complicated in acetone solution

by the addition of a C-H bond of acetone across the imine bond of the initial platinum(IV) product. This product, which forms a hydrogen-bonded dimer, has been characterized crystallographically.[4]

Finally, it is not necessary or perhaps even desirable to have the aryl-halogen bond appended to a chelate ligand since the derivatives PhN=CH-2-C_6H_4X or PhN=CHC_6F_5 give very similar reactions.

ACTIVATION BY COOPERATIVE EFFECTS BETWEEN METAL CENTRES

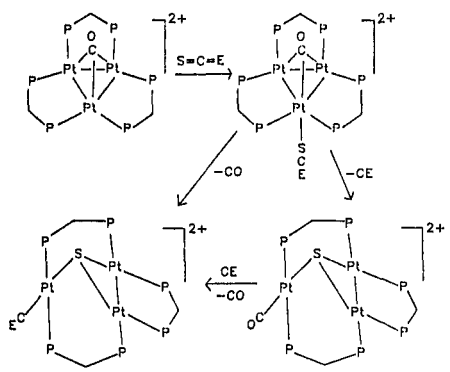
The C=S bond has been activated by mononuclear complexes but activation by binuclear or trinuclear complexes is much easier. For example, CSE (E = O or S) reacts with platinum(O) complexes to give $[PtL_2(\eta^2\text{-CSE})]$ and this reacts with more platinum(O) complex to give $[Pt_2L_4(\mu\text{-}\eta^2\text{-CSE})]$ and then $[Pt_2L_3(\mu\text{-S})(CE)]$. This reaction occurs much more easily with binuclear platinum(O) complexes, as shown in equation (2), the reaction being rapid at -40°C.[5]



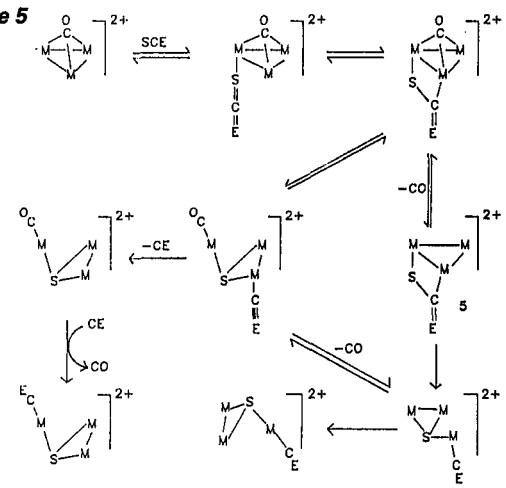
(2)

A similar bond activation occurs with SCN^-, CS_2, COS or RNCS with the coordinatively unsaturated cluster complexes $[M_3(\mu_3\text{-CO})(\mu\text{-dppm})_3]^{2+}$, M = Pd or Pt, as shown in Scheme 4.[6,7] For the reagents CS_2 and SCN^-, no intermediates other than the initial coordination compounds are observed and kinetic studies show that the reactions are retarded in the presence of free CO. However, with RNCS (R = Me, Ph, t-Bu), the intermediate $[Pt_3(\mu_3\text{-S})(CO)(\mu\text{-dppm})_3]^{2+}$ was detected, thus implicating loss of RNC at an intermediate stage followed more slowly by displacement of CO by the better ligand RNC. Similarly, with COS, labelling studies showed that the major product $[Pt_3(\mu_3\text{-S})(CO)(\mu\text{-dppm})_3]^{2+}$ contains the carbonyl which was initially present as the $Pt_3(\mu_3\text{-CO})$ group, implying loss of CO from COS.

Scheme 4



Scheme 5



Based on the above results, we suggest that two mechanisms may operate as shown in Scheme 5. After formation of the initial coordination complex, which can be detected by NMR in all cases, we suggest that rearrangement to a μ-CSE form and then cleavage of the C=S bond occurs. This might occur more readily after loss of CO, thus rationalizing the retarding effect of free CO, and inversion at sulfur could give the product. This accounts for the observations when the reagent is SCN^- or CS_2. However, for RNCS and COS it seems that loss of RNC or CO respectively occurs from the intermediate to give $[Pt_3(\mu_3\text{-S})(CO)(\mu\text{-dppm})_3]^{2+}$, followed at least when CE = RNC by substitution of CE for CO. The different behaviour can be rationalized in terms of the stability of CE, since formation of free CS or CN^- would be a high energy process.

CONCLUSIONS

Oxidative addition can be enhanced in a number of ways, and the mechanisms by which oxidative addition can be enhanced in binuclear and trinuclear complexes are complex but are now beginning to be elucidated.

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