Novel aspects of η'-diiodine coordination and diiodine oxidative addition to platinum(II) and halide transfer oxidation reactions of organo-platinum(II) with Cu^{II}X$_2$

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Abstract - Reactions of mono- and bis-orthochelated diorganoplatinum(II) species [Pt(1-naphthyl-8-NMe$_2$)$_2$], [Pt(C$_6$H$_4$\{CH$_2$NMe$_2$\}-2)$_2$], and [Pt(R)(C$_6$H$_3$\{CH$_2$NMe$_2$\}$_2$-2,6)] with the electrophiles dihalogen and copper(II) halides are discussed. η'-Diiodine coordination *vs.* diiodine oxidative addition has been observed in reactions of bis-orthochelated platinum(II) compounds [Pt(R)(C$_6$H$_3$\{CH$_2$NMe$_2$\}$_2$-2,6)] with diiodine. When R = I the reaction stops at the stage of the stable η'-I$_2$ complex whereas when R = 4-tolyl the Pt^{IV} oxidative addition product is obtained. On the bases of these novel findings a mechanism for the reactions of dihalogens with d^8 metal complexes is proposed. Reactions of diorganoplatinum compounds with Cu^{II}X$_2$ provide the platinum(IV) oxidative addition products rather than products originating from Pt^{II}-C bond cleavage reactions. A new mechanism is proposed for these reactions involving the formation of various types (depending on the type of chelated ligand) of encounter complexes of the organoplatinum(II) substrates with either the Cu^{II} or the X (terminal or bridging) centres of a polynuclear (Cu^{II}X$_2$)$_n$ species.

INTRODUCTION

One of the most fundamental reactions in inorganic and organometallic chemistry is oxidative addition, a collective term used to describe various means of electron transfer from a metal centre to a substrate. Conceptually, it is a simple process in which a reagent, XY, reacts with a metal centre, M^{n+} to form a M$^{(n+2)+}$ species with new M-X and M-Y σ-bonds (Scheme 1). Although this process and its reverse (reductive elimination) have been studied, in particular for metal-d^8 complexes, there is still an extensive discussion regarding the question whether - in a given system - oxidative addition occurs as a concerted two-electron transfer process involving a three-centre M(XY) transition state or whether it involves two separate (non-concerted) one-electron transfer processes. In the latter case, the involvement of radical species is to be expected, and with metal-d^8 substrates this should then result in the concomitant formation of paramagnetic species.
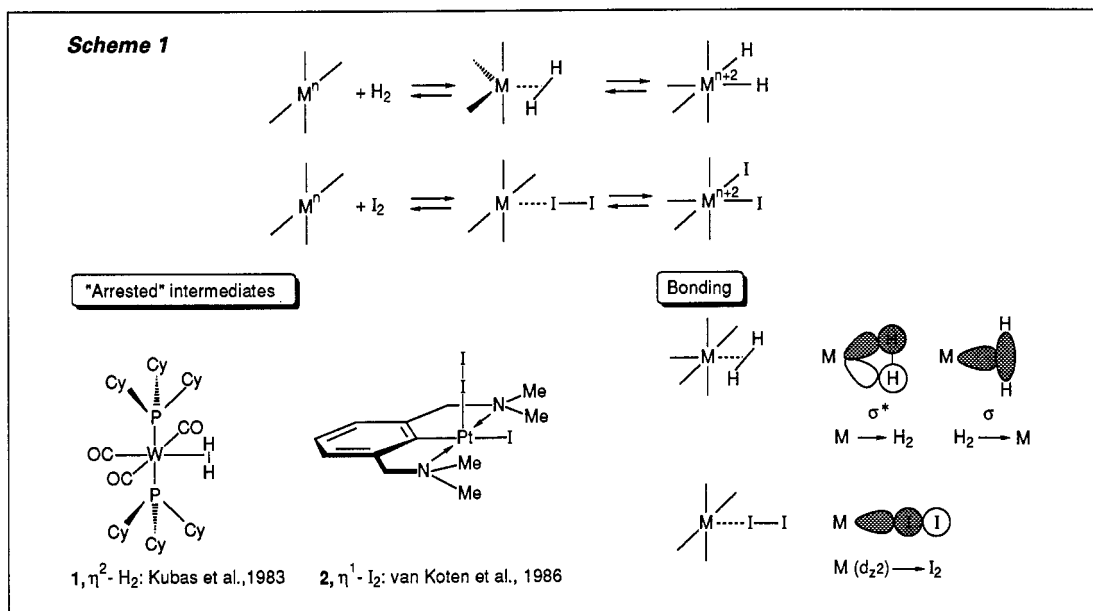
With metal-d^8 complexes the addition mechanisms of dihydrogen, silanes, hydrogen halides and alkyl halides have been extensively studied (ref. 1), but those of dihalogens and metal halides less so. It has been shown that for dihydrogen and silanes, concerted *cis*-addition takes place, while for the other cases, several mechanisms that all involve electrophilic attack of the substrate and the nucleophilic metal centre, have been proposed.

Striking examples that demonstrate the nature of the metal complex on dihydrogen and dihalogen complexation to a metal centre are the complexes [W(CO)$_3$(PCy$_3$)$_2$(η^2-H$_2$)], 1 (ref. 1) and [PtI(C$_6$H$_3$\{CH$_2$NMe$_2$\}$_2$-2,6)(η^1-I$_2$)], 2, (ref. 2) respectively. Both complexes can be seen as 'arrested' intermediates along the oxidative addition reaction co-ordinates, see Scheme 1. In the case of η^2-H$_2$ complexation, ample evidence has been obtained that an η^2-H$_2$ complex can exist in equilibrium with its dihydride tautomer (ref. 1). Each of the compounds 1and 2 is a unique example of the two limiting situations that can be theoretically expected for the binding of X$_2$ molecules to a metal centre, i.e. side-on X$_2$-M bonding involving σ(X$_2$)-to-M donation and M-to-σ*(X$_2$) back-bonding as is the case in 1, and end-on (X$_2$)-M bonding involving M-to-σ*(X$_2$) donation, found in 2.

In these X$_2$-metal complexes, the electronic and steric properties of the so-called 'spectator' ligands may also affect the oxidative addition process. In the case of H$_2$-complexation, it has been shown that a higher basicity of the metal centre leads to H-H bond cleavage as a result of the enhanced M-to-σ*(X$_2$) back-donation. In contrast, low metal basicity, the presence of stabilizing electron acceptors, and a positive charge, are all factors that favour H$_2$-complexation over H-H bond cleavage (ref. 1). In the case of end-on I$_2$ complexation our insight into the exact nature of the factors that determine I$_2$-complexation *versus* I-I bond cleavage, *i.e.* oxidative addition is just beginning to develop (ref. 2). Our discovery of the first example of dihalogen metal-complexation is connected to our interest in the reactivity of metal-d^8 centres that are caught in a rigid and sterically well-defined ligand system (ref. 3). A nice example of this is the bis-orthochelating CH$_2$NMe$_2$-substituted aryl ligand, called pincer, in

compound 2 (see Scheme 1). It is this spectator ligand for which metal-d^8 dihalogen bonding has first been discovered. Properties of this ligand in conjunction with its binding to Pt^{II}, that could contribute to the stability of the Pt-η'-I_2 interaction bonding are:
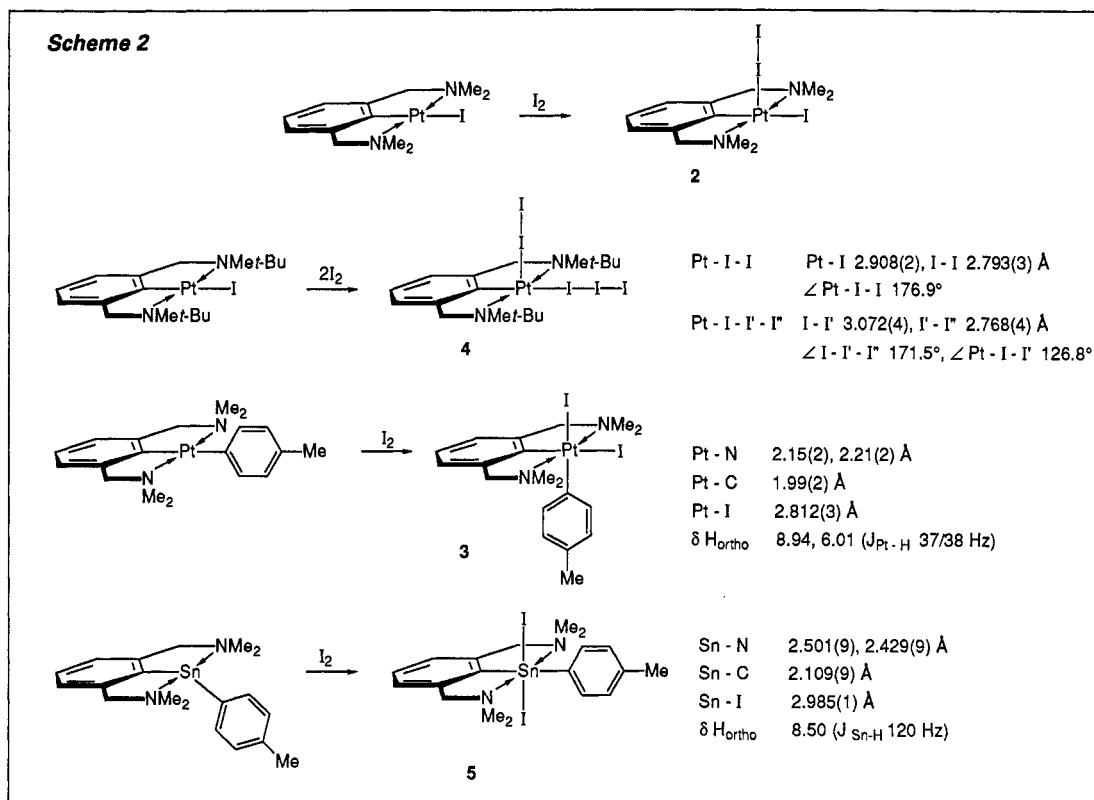
a) the presence of σ-donating amine ligands in *trans*-positions, which enhances the nucleophilicity of the Pt^{II} centre: *i.e.* of the d_{z^2} orbital;

b) the fact that in $[PtX(C_6H_3\{CH_2NMe_2\}_2-2,6)]$ the plane of the aryl ring coincides with the co-ordination plane: *i.e.* overlap between σ* and π* ring orbitals and suitable Pt d_{zx} and d_{zy} orbitals is feasible;

c) the steric constraints of the *trans* -N-spanning pincer ligand that stabilizes the η'-I_2 coordination product with respect to the possible oxidative addition product $[Pt(I)_3(C_6H_3\{CH_2NMe_2\}_2-2,6)]$ where three iodine atoms are bonded to Pt^{IV}.


Scheme 1

"Arrested" intermediates   Bonding

1, η^2- H_2: Kubas et al.,1983   2, η^1- I_2: van Koten et al., 1986 $M(d_{z^2}) \longrightarrow I_2$

Interestingly, $[Pt(I)(C_6H_3\{CH_2NMe(t\text{-}Bu)\}_2-2,6)]$ binds two molecules of diiodine: $[Pt(I_3)(C_6H_3\{CH_2NMe(t\text{-}Bu)\}_2-2,6)(\eta'\text{-}I_2)]$, 4 contains one I_2 η'-bonded to Pt^{II} as in 2 and a second I_2 bonded to the iodide ligand forming a triiodide, see Scheme 2. The binding of this second I_2 molecule may be due to the higher basicity of a NMe(t-Bu) fragment as compared with the NMe_2 grouping in 2 thereby enhancing the electron density on the iodide ligand in 4 relative to 2.

The fact that the reaction of $[Pt(4\text{-tolyl})(C_6H_3\{CH_2NMe_2\}_2-2,6)]$ with I_2 does result in the formation of the oxidative addition product $[Pt(4\text{-tolyl})(I)_2(C_6H_3\{CH_2NMe_2\}_2-2,6)]$, 3, seems to corroborate, in particular, point c (ref. 2). The orientation of the 4-tolyl ring in 3, as shown in Scheme 2, is sterically less demanding than a third iodine atom would be at this position. Illustrative for the restricted amount of space in the sixth coordination side is the observation that in the oxidative addition product $[Pt(4\text{-tolyl})(I)_2(C_6H_3\{CH_2NMe_2\}_2-2,6)]$ the 4-tolyl ring cannot rotate around its C1-C4 axis, and it is precisely this orientation that is found both in the solid state and in solution (cf. δH_2 6.01 and δH_6 8.94 ppm). Recently, we also found an interesting addition reaction of $[Sn^{II}(4\text{-}$ tolyl$)(C_6H_3\{CH_2NMe_2\}_2-2,6)]$, 5, with I_2 that gives rise to the formation of $[Sn^{IV}(4\text{-tolyl})(I)_2\text{-}$ $(C_6H_3\{CH_2NMe_2\}_2-2,6)]$, in which both I atoms are now mutually *trans* and *cis* to C(ipso) of the pincer ligand (ref. 4).

Actually the arrangement of C and I ligands in 3 and 5 is as would be expected on the bases of the respective *trans*-influences of the ligands. Moreover the *trans*-C-Sn-C stereochemistry in 5 is in line with the preference of diorganotin(IV) entities to adopt a linear rather than a perpendicular C-Sn-C arrangement. This suggests that 3 and 5 are thermodynamic rather than kinetic products. The pincer-M bonding in 3 and 5 shows some striking differences (see Scheme 2) indicating that the pincer ligand has a surprising flexibility to open up (*i.e.* elongate its M-C and M-N bonds) to the extent observed in 5. This may imply that the *trans*-I-M-I arrangement found in 5 is only possible because of the larger amount of space available for six ligands around a Sn^{IV} centre as compared to that of a Pt^{II} centre.

Scheme 2

Pt - I - I	Pt - I 2.908(2), I - I 2.793(3) Å
	∠ Pt - I - I 176.9°
Pt - I - I' - I"	I - I' 3.072(4), I' - I" 2.768(4) Å
	∠ I - I' - I" 171.5°, ∠ Pt - I - I' 126.8°

Pt - N	2.15(2), 2.21(2) Å
Pt - C	1.99(2) Å
Pt - I	2.812(3) Å
δ H$_{ortho}$	8.94, 6.01 (J$_{Pt-H}$ 37/38 Hz)

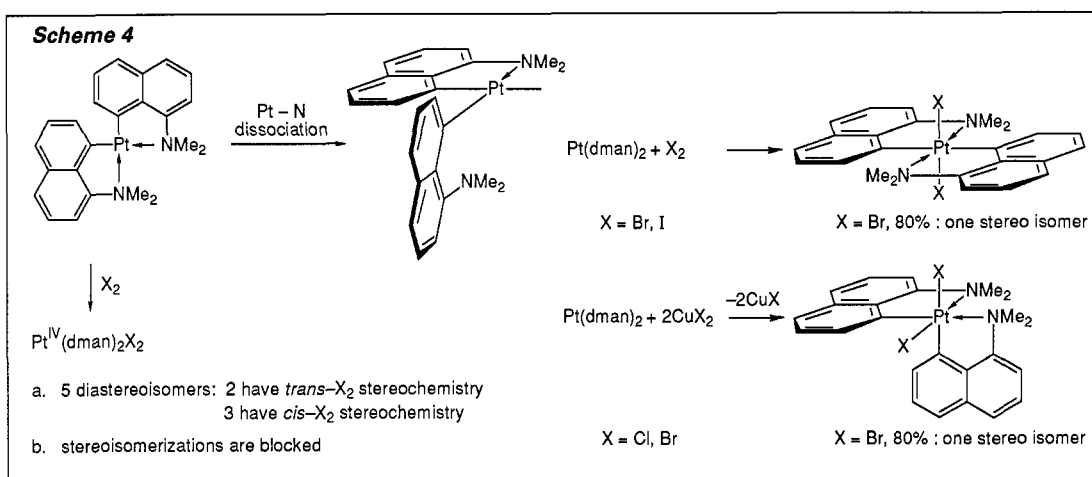| Sn - N	2.501(9), 2.429(9) Å
Sn - C	2.109(9) Å
Sn - I	2.985(1) Å
δ H$_{ortho}$	8.50 (J$_{Sn-H}$ 120 Hz)

On the bases of these and other observations we propose for the formation of **3** a mechanism (see Scheme 3) involving a S$_N$2 type of reaction sequence with initial η^1-diiodine coordination followed by or with concomitant two electron transfer and formation of I$^-$ and a cationic platinum(IV) intermediate. In particular the equilibrium between the η^1-diiodine-platinum(II) and the platinum(IV)-iodide cation in Scheme 3 is of interest because it represents actually an equilibrium that bears analogy to the η^2-H$_2$/dihydride equilibrium in Scheme 1: *i.e.* for R = I this equilibrium lies completely to the side of the η^1-diiodine platinum(II) complex, while for R = 4-tolyl it lies to the side of the oxidative addition product. Finally, the process shown in Scheme 3 is a concerted process involving the oxidation of platinum(II) to platinum(IV). Accordingly, the platinum(III) stage in this process is transient and undetectable. This situation contrasts with the formation of a stable arylnickel(III) compound in the reaction of the corresponding nickel(II) compound with diiodine, see Scheme 3. The formation of this Ni^{III} d^7-species points to
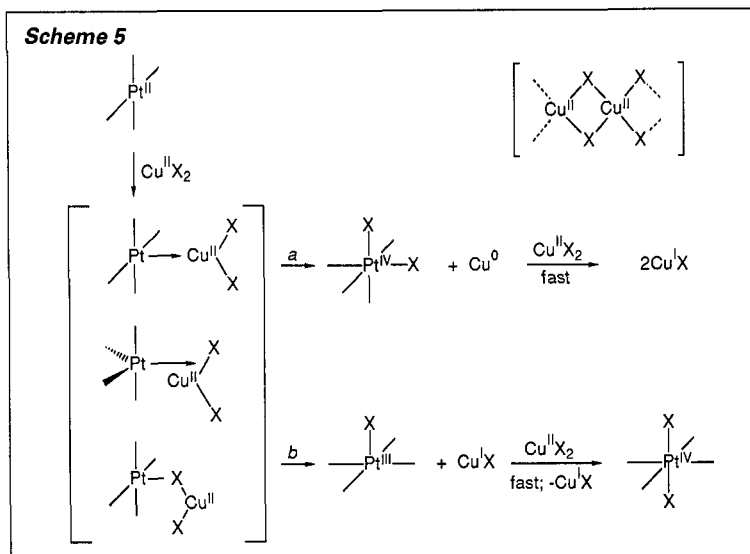
Scheme 3
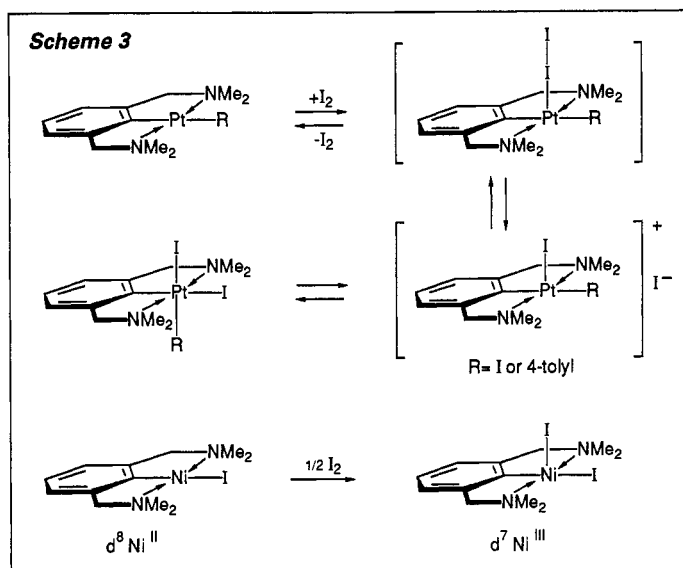
the occurrence of a one-electron ligand transfer oxidation. However, the yield (> 90%) and the absence of products originating from free radical reactions strongly suggests that the Ni^{II}-to-Ni^{III} oxidation occurs in an innersphere activated complex involving prior η^1-diiodine coordination to Ni^{II} as well as the participation at a latter stage in the process of a second Ni^{II} centre (ref. 5).

The second electrophile that is of interest to us are the copper(II) salts $CuCl_2$ and $CuBr_2$. In many Pd catalysed processes (*e.g.* the Wacker process), a Cu^{II}/O_2 cocatalyst is used for reoxidation of the low valent metal centres formed in the final stages of the catalytic cycle. It is surprising that organopalladium intermediates in, for example, the Wacker process would be unreactive towards the copper(II) salts in solution. Therefore, we studied the interaction of these inorganic electrophiles with the organoplatinum compound $[PtX(C_6H_3\{CH_2NMe_2\}_2-2,6)]$ (X = Cl or Br and 4-tolyl) as well as with *cis*-$[Pt(C_{10}H_6NMe_2-8)_2]$ (abbreviated as $[Pt(dman)_2]$, **6** as model compounds. The dman ligand has as a special feature its extremely rigid skeleton and therefore a rigid Pt and NMe_2 orientation which does not allow the N-donor site (i.e. the N lone pair) to turn away from the Pt coordination sphere even not when the Pt-N bond has dissociated (see Scheme 4).

Scheme 4

$Pt(dman)_2 + X_2 \longrightarrow$ X = Br, I   X = Br, 80% : one stereo isomer

$Pt(dman)_2 + 2CuX_2 \xrightarrow{-2CuX}$ X = Cl, Br   X = Br, 80% : one stereo isomer

a. 5 diastereoisomers: 2 have *trans*-X_2 stereochemistry
                       3 have *cis*-X_2 stereochemistry
b. stereoisomerizations are blocked

$[PtX(C_6H_3\{CH_2NMe_2\}_2-2,6)]$ (X = Cl or Br) reacts with CuX_2 to give in a ligand transfer oxidation process the corresponding platinum(IV) compounds (X = Cl 50% and Br 80%) while products from Pt-C bond cleavage could not be detected (refs. 2, 3, 6). In Scheme 5 possible reaction intermediates are shown, which form the present working hypothesis for our research in this field. Three possible initial stages for the encounter of the Pt substrate and Cu electrophile can be envisaged: i. Cu^{II}-Pt^{II} complexation in which the platinum(II) centre coordinates *via* its filled d_{z^2} orbital in an empty orbital of CuX_2; ii. side on coordination of a CuX_2 molecule *via* its Cu^{II}-X bond to Pt^{II} involving donation of its filled d_{xy} or d_{yz} in the σ^* of Cu^{II}-X and iii. formation of a five coordinated Pt^{II}

Scheme 5

intermediate through a Cu^{II}-X-Pt^{II} bridge. We anticipate that the "spectator" ligands play an important role which encounter is relevant for the forward reaction: *i.e.* the Pt^{II}-Ag^I complex in Scheme 6 is an excellent model for the Cu^{II}-Pt^{II} intermediate with the terdentate bonded pincer ligand whereas the Ir^I complex (ref. 7) with the side-on η^2-bonded Br-$SnMe_2Br$ group (ref. 8) demonstrates the influence of an aryl ligand with just one bidentate bonded ortho-CH_2NMe_2 aryl chelate. We propose that, instead of reactions <u>a</u> and <u>b</u> (Scheme 5) which both involve mononuclear CuX_2 species, these reactions preferably occur with a polynuclear $(CuX_2)_n$ species which would imply that the copper(II) halide species has to have at least a dinuclear structure. The overall Pt^{II} to Pt^{IV} oxidation requires two equivalents of $Cu^{II}X_2$ (ref. 6). In this polynuclear species the formation of various types of encounter complexes of the Pt^{II} substrates with either the Cu^{II} or the X (terminal or bridging) centres can be envisaged while the polynuclear Cu_nX_{2n} unit in the forward reaction can function as two electron sink. In particular, the results of the reactions with [Pt(dman)$_2$] (see Scheme 4) and less rigid *cis*-[Pt(C_6H_4{CH_2NMe_2}-2)$_2$] with X_2 and CuX_2, seems in bearing with the outlined reaction sequence (ref. 2). It is of interest to note that the bis- chelated aryl-nickel(II) compound [NiBr(C_6H_3{CH_2NMe_2}$_2$-2,6)] reacts with $CuBr_2$ *via* a one-electron transfer oxidation to [Ni(Br)$_2$(C_6H_3{CH_2NMe_2}$_2$-2,6)] with a nickel(III) d^7-centre (cf. the one electron I_2 oxidation shown in Scheme 3, ref.5).
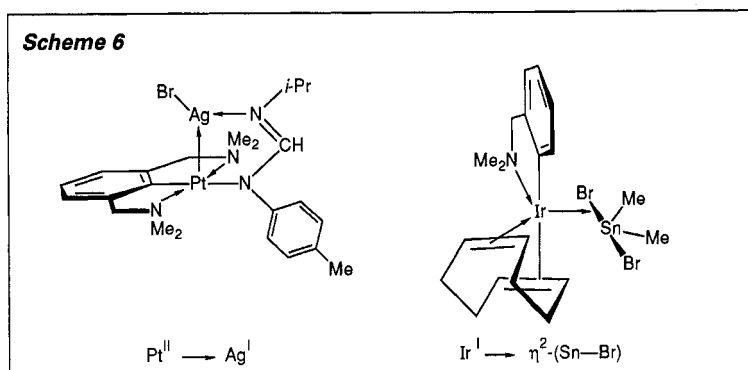
Scheme 6

$Pt^{II} \longrightarrow Ag^I$ $Ir^I \longrightarrow \eta^2$-(Sn—Br)

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