Oxidative Addition Reactions of Organoplatinum(II) Complexes with Nitrogen-Donor Ligands

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Contents

I. Introduction

The oxidative addition reaction represents one of the most fundamental processes in transition metal chemistry,[1–3] and it plays an invaluable role in many synthetic and catalytic reactions, particularly in organic synthesis. Ever since the preparation of $K[Pt(C_2H_4)Cl_3]\cdot H_2O$ by Zeise in 1827,[4] organoplatinum chemistry has been of major interest to chemists because platinum forms a wide range of complexes that are stable enough to allow their solution chemistry to be studied in great detail. Furthermore, two-electron oxidation and reduction reactions between three oxidation states (0, +2, and +4) are an integral part of the chemistry of platinum, with the oxidative addition process dominating the reactions of the metal in its lower oxidation states.[5]

Oxidative addition of the substrate X−Y to a metal center (M) leads to an increase in the coordination number of the complex due to the formation of two new bonds, M−X and M−Y, upon complete dissociation of the X−Y bond (Scheme 1). Both one- and two-electron oxidative addition reactions are known, but the process itself does not imply any mechanism. Most importantly, the oxidation state assigned to the metal is a strict formalism and *there is no obligatory association between formal oxidation state and electron density at the metal center*.

Goddard and Low[6–8] have reported an elegant *ab initio* model for the oxidative addition process which primarily depends on the electronic structure of the metal atom. Electronic promotion rather than ionization ("oxidation") is the basis of understanding the

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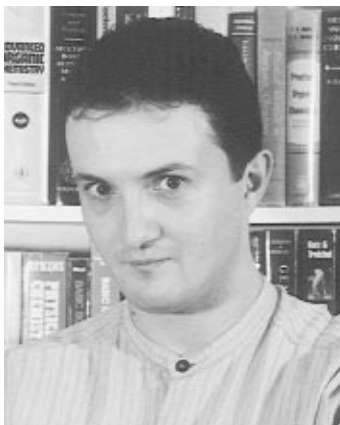
Louis M. Rendina received his B. Sc. with First-Class Honours in Chemistry from the Australian National University in 1988. From 1988–1991 he was the recipient of a Commonwealth Postgraduate Research Award, and he obtained his Ph.D. in Bio-inorganic Chemistry (with Dr. John A. Broomhead) in 1991. He was then awarded an ANU-IAS Postdoctoral Fellowship to work with Prof. Martin A. Bennett, FRS, at the Research School of Chemistry, Institute of Advanced Studies, ANU. In 1993 he was awarded a prestigious NSERC Canada International Fellowship to work with Prof. Richard J. Puddephatt at the University of Western Ontario, Canada. In October 1995 he returned to the Australian National University as a Visiting Fellow, and in February 1996 he was appointed lecturer at the University of Adelaide, Australia. His current research interests lie in the area of bio-inorganic chemistry, with a particular emphasis on metal-DNA chemistry.

Richard J. Puddephatt was educated at University College, London, graduating with a B. Sc. in Chemistry in 1965 and Ph.D. in 1968 for research in organotin and organolead chemistry carried out with A. G. Davies and R. J. H. Clark. After two years as a postdoctoral fellow with Prof. H. C. Clark at the University of Western Ontario, Canada, he was appointed lecturer at the University of Liverpool, UK. He returned to the University of Western Ontario as professor in 1978. His research interests are in organometallic and coordination chemistry of the late transition elements, with relevance to applications in catalysis and materials science. In catalysis, he has contributed to mechanistic studies of bond activation by oxidative addition and the modelling of surface reactivity by coordinatively unsaturated clusters, while in materials chemistry his research ranges from chemical vapor deposition to the synthesis of organometallic polymers and dendrimers. He was elected Fellow of the Royal Society of Canada in 1991, and he is the recipient of a Royal Society Award for Chemistry of the Noble Metals and their Compounds. He is the Royal Society of Chemistry Nyholm Lecturer for 1997-98. He has published two books and over 400 articles in the field of organometallic chemistry.

reactivity of coordinatively unsaturated complexes such as those of platinum(II). The authors state that platinum(II) should be considered as a neutral atom with a d^9s^1 electronic configuration. Two singly occupied orbitals (*s* and *d*) are combined into *sd* hybrids which overlap with the singly occupied ligand (e.g., Me) orbitals resulting in the formation of a

Scheme 1

$$M^{(n)} + X–Y \longrightarrow M^{(n+2)} \begin{smallmatrix} \diagup X \\ \diagdown Y \end{smallmatrix}$$
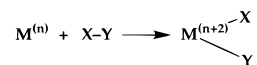
covalent bond pair. Related bonding arguments have also been made for platinum(IV), where the neutral platinum atom is promoted to the d^8s^2 configuration. If one considers a concerted interaction, for example, between a substrate X–Y bond and a platinum(II) center, then the Goddard and Low model clearly demonstrates that a significant distortion of ligands from the square-planar geometry is a necessary requirement at the transition state to allow the electronic promotion required for the formation of two, new covalent bonds (Pt–X and Pt–Y) in the six-coordinate platinum(IV) product. In summary, the platinum(II) and platinum(IV) oxidation state formalisms indicate the electronic configuration of the neutral atoms which are capable of forming *two* and *four* covalent bonds, respectively, i.e., the formalisms should be looked at in terms of maximum covalency and *not* to the degree of oxidation.

The first well-defined σ-alkyl complex of platinum(II), *trans*-[PtIMe(P^{n}Pr$_3$)$_2$], was first prepared in 1952 by Foss in collaboration with Chatt and Shaw.[9] Foss studied the reaction of *trans*-[PtIMe(P^{n}Pr$_3$)$_2$] with MeI to give the organoplatinum(IV) derivative [PtI$_2$Me$_2$(P^{n}Pr$_3$)$_2$], but soon after the work was abandoned until it was continued by Chatt and Shaw in 1959. Ever since, coordinatively unsaturated 16-electron organoplatinum(II) complexes have proved highly amenable for the study of the oxidative addition process. Indeed, valuable insights into the mechanistic details of these reactions have been elucidated, including both the thermodynamic and kinetic aspects, in part due to the high stability and inertness of the final coordinatively saturated, 18-electron organoplatinum(IV) products.

Ever since the report of the oxidative addition of MeI to *cis*-[Pt(*o*-tolyl)$_2$(py)$_2$] by Doyle *et al.*[10] in 1963, the versatility of nitrogen-donor ligands, especially diimines, in stabilizing the platinum(IV) products has been shown to be far greater than the ubiquitous tertiary phosphine and arsine ligands. This is most probably due to the favorable electronic (strong σ-donor/weak π-acceptor) and steric properties of the nitrogen-donors. Furthermore, the "hard" nature of nitrogen enhances the nucleophilicity of the platinum(II) center, an important feature in S$_N$2-type reactions where electron-rich metal centers (i.e., those possessing high-energy HOMOs with substantial nonbonding character) are required to activate the substrate. Indeed, the great interest in the use of nitrogen-donor ligands, in both group 10 metal synthesis and homogeneous catalysis, has been the subject of recent reviews.[11–15]

Section II of this review will outline the various mechanisms by which oxidative addition reactions with organoplatinum(II) complexes can occur, with key examples of each type of mechanism presented in this section. Section III will comprehensively review the many chemical bonds that have been broken by oxidative addition to organoplatinum(II) complexes with nitrogen-donor ligands.

II. Mechanisms of Oxidative Addition[1−3]

Several types of mechanisms are proposed for the oxidative addition reaction. Minor changes in the nature of the metal, substrate, and ligands can often dramatically alter the pathway for the addition process. Substrates for oxidative addition are classified into three different categories. Class A substrates are nonpolar or of low polarity (e.g., H_2, R_3Si-H, and R−H), class B reagents are electrophilic (e.g., H−X, X_2, and R−X), and class C substrates retain bonding between the two added fragments (e.g., O_2, cyclopropane, and epoxides). A brief discussion of the types of oxidative addition mechanism for each of the three classes of substrate follows, with more detail given when examples for oxidative addition to organoplatinum(II) complexes are known.
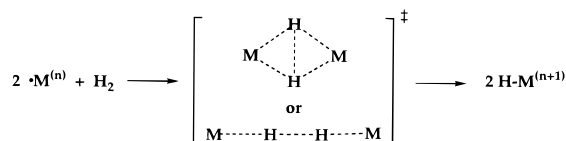
A. Class A Substrates

There are three distinct mechanisms that are proposed for class A substrate activation, two of these being *cis* oxidative addition (concerted) and homolytic bond activation. The former is the dominant pathway for class A substrates such as H_2 (Scheme 2). In contrast, the latter is less common and utilizes two metal centers, each undergoing a formal one-electron oxidation (Scheme 3). The third available pathway is heterolytic activation and it is not classed as an oxidative addition reaction.
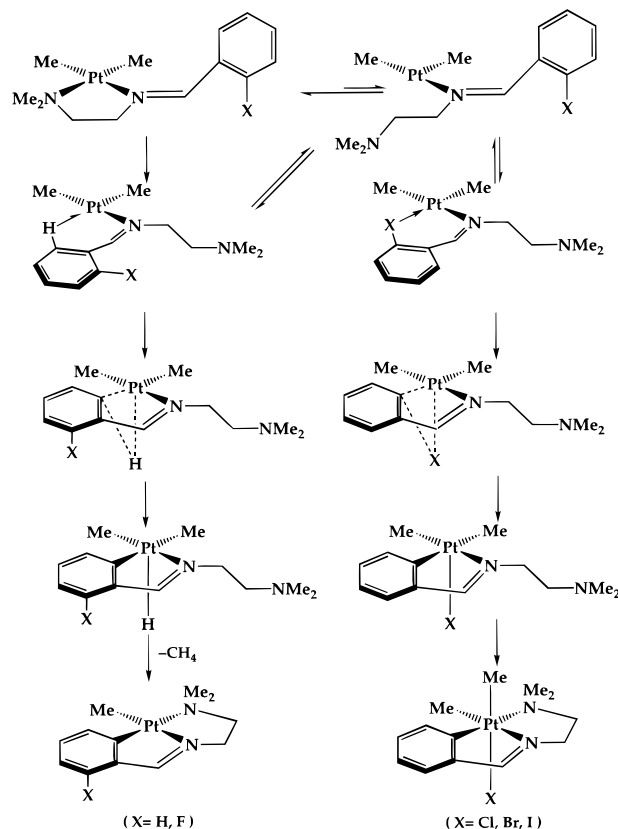
Scheme 2
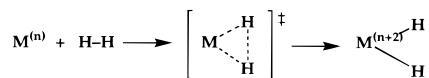
Scheme 3

1. Reaction of Class A Substrates with Platinum(II) Complexes

There are very few examples of the oxidative addition of class A substrates to platinum(II) centers because these substrates are often exceedingly difficult to activate. Even so, concerted intramolecular C−H oxidative additions are known for organoplatinum(II) complexes. Through the use of ligand design, *ortho*-metalation can occur in diimine complexes of the type [PtMe₂{PhCH=N(CH₂)₂NMe₂}] (Scheme 4).[16,17] The reaction follows first-order kinetics, and the authors propose that it proceeds by a concerted C−H oxidative addition followed by reductive elimination of CH₄. It is possible that the NMe₂ group dissociates prior to oxidative addition, and its ease of dissociation was demonstrated by addition of monodentate ligands such as PPh₃ or SMe₂ to the reaction mixture. Such ligands coordinate to the site formerly occupied by the NMe₂ group, consistent with the proposal that concerted oxidative addition probably requires preliminary ligand dissociation to generate a five-coordinate platinum(IV) intermediate. This is rationalized on the basis of the principle of microscopic reversibility, since it has been shown that

Scheme 4

(X= H, F)   (X= Cl, Br, I)

Scheme 5
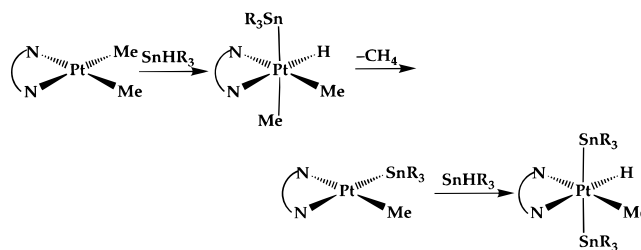
concerted reductive elimination from coordinatively saturated platinum(IV) centers requires a vacant coordination site created by ligand dissociation.[1,2]

The oxidative addition of the class A substrate R₃Sn−H (R = Ph, *o*-tolyl, *p*-tolyl) with [PtMe₂(bpy)] has been investigated.[18] Reaction gives *cis,trans*-[PtH(Me)(SnR₃)₂(bpy)], with vigorous evolution of CH₄ (Scheme 5). A mixture of Ph₃SnH and [PtMe₂(bpy)] homogeneously catalyzes the formation of the dimer Sn₂Ph₆. No reaction was observed with Sn−Sn or Sn−Ar bonds of various substrates, in contrast to the reactivity of platinum(0) species.[19−21]

The oxidative addition of compounds with group 16−group 16 bonds (e.g., PhSe−SePh) to [PtMe₂-(phen)] has been reported.[22] The observation of exclusively *trans* oxidative addition is not consistent with a concerted mechanism, but rapid isomerization of the *cis* complex to the thermodynamic *trans* isomer cannot be ruled out. A radical chain mechanism may be involved, as observed for certain class B substrates, although no free radicals were detected in this system.

B. Class B Substrates

Oxidative additions of electrophilic X−Y reagents usually proceed in a straightforward manner, but

sometimes these reactions are complicated by many competing mechanisms. The known reaction pathways are classed as those involving formal one- or two-electron oxidation.

1. Formal One-Electron Mechanisms for the Oxidative Addition of X–Y Bonds[1,3,23–26]

a. Free-Radical–Nonchain (Inner-Sphere Electron-Transfer/Caged Radical-Pair) Mechanism. A free-radical nonchain mechanism usually involves alkyl halides (R–X) as the substrate (Scheme 6, ref 1).
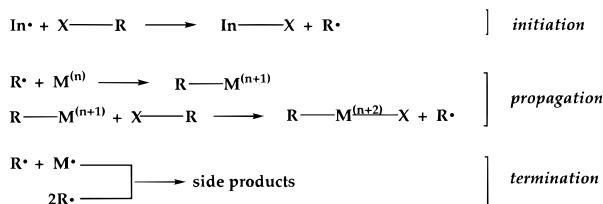
Scheme 6
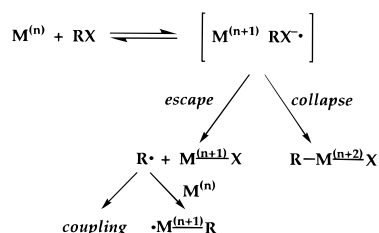
Coordination of R–X to the metal center is followed by electron transfer from the metal to afford a solvent-caged radical pair. The caged radical pair may then react further by one of two possible pathways. The radical pair can collapse to give the final product of oxidative addition. Otherwise, escape of the radical pair affords the free radicals R•, which can react further to give side products. In contrast to the S_N2-type pathway described in the next section, racemization instead of inversion is found at the chiral carbon of the substrate, otherwise the principal oxidative addition products of the two pathways are identical.

Characteristic features for a free-radical nonchain reaction include a bond reactivity order of R–I > R–Br > R–Cl, which reflects the ability of R–X to be reduced by the metal; indeed, the rate of the oxidative addition of Ar–X bonds to nickel(0) complexes correlates with the reduction potential of the aryl halide.[27] The reaction is very slow or inhibited when X is a good leaving group, e.g., tosylate, in contrast to the S_N2-type mechanism, and the reactivity order for the R group is tertiary > secondary > primary > Me, a trend which reflects the relative stability of the radical.

b. Free-Radical–Chain Mechanism. The radical–chain mechanism usually has an induction period, a number of atom-abstraction steps, and a source of initiator radicals. A metal-centered radical abstracts X• from the halide to form the chain carrier R• which can react with itself to terminate the chain (Scheme 7, ref 1). Evidence for this type of mechanism includes the racemization at a chiral carbon of the substrate. In contrast to the radical–nonchain process, however, radical–chain reactions are consider-

ably slowed or completely inhibited by the presence of radical inhibitors due to quenching of the chain carrier.

2. Formal Two-Electron Mechanisms for the Oxidative Addition of X–Y Bonds[1–3]

a. Three-Center Cis Addition. This mechanism is established for class A substrates such as R–H, but it is also frequently proposed for more polar reagents (Scheme 8). A necessary requirement of the *cis*
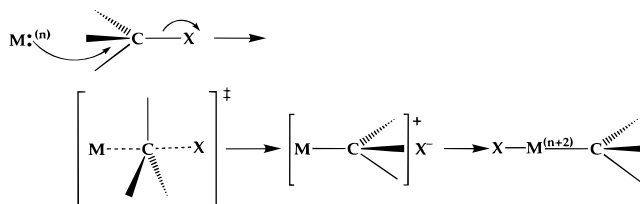
Scheme 8
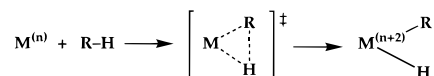
addition process is coordinative unsaturation at the metal center, and the reaction proceeds with retention of configuration at a chiral carbon in the substrate. This type of mechanism has yet to be supported by conclusive experimental evidence.

b. Bimolecular (S_N2-type) Oxidative Addition. The metal center acts as a nucleophile in the S_N2-type mechanism, and a characteristic feature of this process is the formation of a cationic intermediate (Scheme 9, ref 1). A few S_N2-type oxidative addition

Scheme 9

reactions require coordination of an anion to the metal center to generate a highly nucleophilic complex (Scheme 10, ref 1). Other features that are

Scheme 10
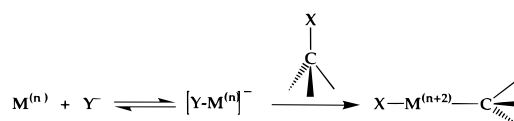
typical of classical organic S_N2 reactions are also evident, including inversion of configuration at a chiral carbon of the substrate, the classical structure/ activity pattern for the substrate (i.e., Me > primary > secondary >> tertiary, and I > Br > Cl >> F), increased reaction rates in more polar solvents, and a (usually) large negative entropy of activation ($\Delta S^{\ddagger}$) consistent with a polar transition state. The *trans* stereochemistry of oxidative addition is consistent with, but does not necessarily prove, the S_N2-type mechanism owing to possible isomerization processes.

3. Reaction of Class B Substrates with Platinum(II) Complexes

a. Formal One-Electron Oxidative Addition Mechanisms. **i. Free-Radical–Nonchain (Inner-Sphere Electron Transfer/Caged Radical-Pair) Mechanism.** Even though the complex [PtCl$_2$(bpy)] does not meet the requirement of being organometallic for the purposes of this review, its photochemical (280

Scheme 7

Scheme 11

$$[Pt^{II}Cl_2(bpy)] + CHCl_3 \xrightarrow{h\nu} [Pt^{III}Cl_3(bpy)] + \cdot CHCl_2$$

$$[Pt^{III}Cl_3(bpy)] + \cdot CHCl_2 \longrightarrow [Pt^{IV}Cl_3(bpy)]^+ + CHCl_2^-$$

$$[Pt^{IV}Cl_3(bpy)]^+ + CHCl_2^- \longrightarrow [Pt^{IV}Cl_4(bpy)] + :CHCl$$
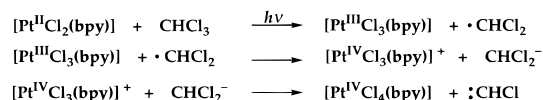
$< \lambda < 300$ nm) reaction with $CHCl_3$ to generate $[PtCl_4(bpy)]$ is particularly instructive as it is an example of a one-electron, inner-sphere oxidation of a platinum(II) center (Scheme 11).[28] Radical intermediates were not detected by ESR spectroscopy at 77 K or in the presence of spin traps at room temperature, thus showing that a caged radical species with an extremely short lifetime is the most likely intermediate. The carbene byproduct was trapped by reaction with $CHCl_3$ to afford $Cl_2HCCHCl_2$, thus further supporting the proposed mechanism. An inner-sphere mechanism has also been suggested for the oxidative addition of $[AuCl_4]^-$ to $[PtCl_2(phen)]$.[29]
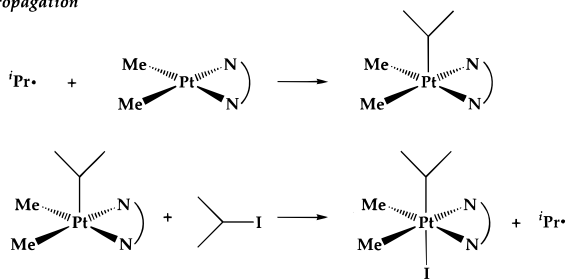
ii. Free-Radical–Chain Mechanism. A comprehensive kinetic study of the photochemically initiated oxidative addition of ^iPrI to $[PtMe_2(phen)]$ has been reported.[30] A radical–chain mechanism is proposed with the $^iPr^\bullet$ radicals acting as chain carriers (Scheme 12). The chain is initiated by a
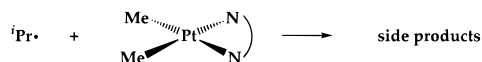
Scheme 12

Initiation
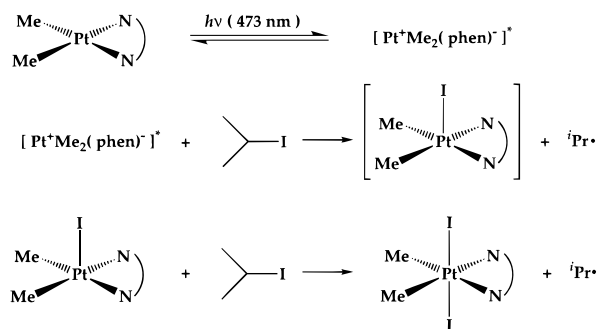
Propagation

Termination

photochemical ^3MLCT that leads to abstraction of an iodine atom from the organic substrate; the chain length is 1700 ± 700 molecules. The $^iPr^\bullet$ radicals are rapidly captured by the $[PtMe_2(phen)]$ with a rate constant of 10^7 M^{-1} s^{-1}, close to the rate of a diffusion-controlled process (*ca.* 10^9 M^{-1} s^{-1}). The proposed termination step for the mechanism is the formation of nonradical products by the reaction of $^iPr^\bullet$ radicals with the phen or Me ligands of the complex. Thermal addition of ^iPrI to $[PtMe_2(phen)]$ largely follows a free-radical mechanism, albeit at a much slower rate

than the photochemical route, but there is also a minor contribution of the S_N2-type pathway.

It has been demonstrated that the oxidative addition of ^iPrI or ^tBuI to $[PtMe_2(phen)]$ in the presence of $CH_2=CHX$ (X = CN, CHO, C(O)Me), which capture radical intermediates in the chain, gives the platinum(IV) complexes $[PtIMe_2(CHXCH_2R)(phen)]$ (R = ^iPr, ^tBu) in good yield (Scheme 13).[31,32] Similarly,

Scheme 13
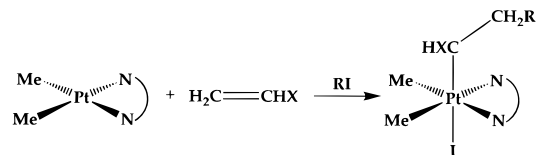
reaction of the platinum(II) precursor in the presence of O_2 gives a stable alkylperoxoplatinum(IV) species (**1**) and is a useful test for a free-radical mechanism

(1)
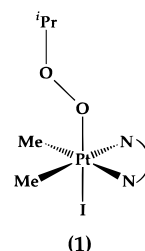
of oxidative addition, where the complexes are inert to O_2 and where the final peroxo complexes are thermally stable.[33,34] Such reactions are the first reported examples of the synthesis of high-yielding organometallic products that are obtained from the oxidative addition of tertiary alkyl halides.

An inefficient radical–chain mechanism for the reaction of CH_2I_2 with $[PtMe_2(phen)]$ is proposed.[35] A radical–chain pathway is also favored for the reaction of 1,2-diiodoethane, but $I(CH_2)_nI$ ($n = 3-5$) reacts by a S_N2 mechanism (Scheme 14). Indeed, the

Scheme 14
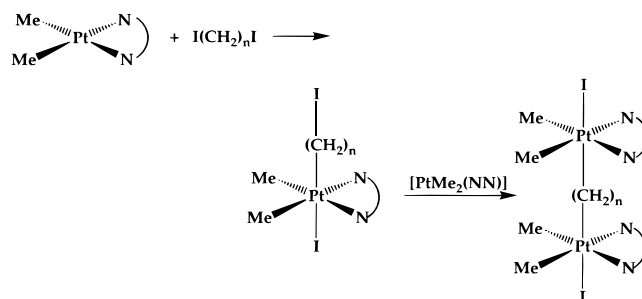
close relationship that exists between the radical–chain and S_N2 mechanisms is clearly demonstrated by these studies, and in cases where one is disfavored, the other may become more competitive.

b. Formal Two-Electron Oxidative Addition Mechanisms. **i. Three-Center *Cis* Addition.** The intermolecular oxidative addition of aryl halides to platinum(II) centers has not been observed, although intramolecular addition is realized with electron-rich complexes and by ligand design. In the first example of aryl–halogen bond activation by platinum(II), complexes of the type $[PtMe_2\{2\text{-}XC_6H_4CH=N\text{-}$

Table 1. Second-Order Rate Data for the Reaction of Organoplatinum(II) Complexes with N-Donor Ligands and Electrophilic Substrates (X−Y)

complex	substrate	X−Y	solvent	T (K)	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	k_2 (L mol^{-1} s^{-1})	ref
[PtMe$_2$(^{t}Bu$_2$bpy)]	Me$_3$SnCl	Sn−Cl	CD$_2$Cl$_2$	298	-100 ± 10	$1.86 \pm 0.04 \times 10^6$	40
			acetone-d_6		-62 ± 8	$0.94 \pm 0.07 \times 10^6$	
			CD$_3$CN		-77 ± 9	$1.96 \pm 0.05 \times 10^6$	
	Me$_3$SnBr	Sn−Br	CD$_2$Cl$_2$		-124 ± 7	$3.10 \pm 0.08 \times 10^6$	
	Me$_3$SnI	Sn−I	CD$_2$Cl$_2$		-80 ± 20	$39 \pm 2 \times 10^6$	
			CD$_3$CN			$2.2 \pm 0.2 \times 10^8$	
cis-[Pt(thpy)$_2$]	PhCH$_2$Br	C−Br	CH$_3$CN			6.507×10^{-2}	81
			acetone			9.204×10^{-3}	
			ethyl acetate			5.182×10^{-4}	
[PtMe$_2$(bpy)]	β-propiolactone	C−O	toluene		-129	2.8×10^{-3}	41
			ethyl acetate			2.4×10^{-3}	
			CH$_2$Cl$_2$			1.3×10^{-2}	
			acetone		-142	2.2×10^{-3}	
			CH$_3$CN			8.5×10^{-3}	
			^{t}BuOH			1.1×10^{-1}	
			^{i}PrOH			1.0×10^{-1}	
			MeOH		-151	8.7×10^{-2}	
[PtMe$_2$(phen)]	β-propiolactone	C−O	C$_6$H$_6$	300		5.4×10^{-4}	41
			acetone			1.3×10^{-3}	
			MeOH			1.5×10^{-1}	
[PtMe$_2$(bpy)]	2-(phenoxymethyl)-oxirane	C−O	acetone	298	-160 ± 15	9.2×10^{-5}	42
[PtPh$_2$(bpy)]	MeI	C−I	C$_6$H$_6$	313		1.1×10^{-1}	36
			ethyl acetate			1.9×10^{-1}	
			CH$_2$Cl$_2$			3.5×10^{-1}	
			acetone			6.75×10^{-1}	
			CH$_3$NO$_2$			1.48	
[PtMe$_2$(bipym)]	1,2-C$_6$H$_4$(CH$_2$Br)$_2$	C−Br	acetone	298		2.75	98
	1,4-C$_6$H$_4$(CH$_2$Br)$_2$					17.5	
[Me$_2$Pt(μ-pyen)PtMe$_2$]	1,2-C$_6$H$_4$(CH$_2$Br)$_2$	C−Br	acetone			2.08	98
	1,4-C$_6$H$_4$(CH$_2$Br)$_2$					18.1	
	I(CH$_2$)$_3$I	C−I	acetone			3.2×10^{-2}	
	I(CH$_2$)$_4$I					2.0×10^{-2}	
	I(CH$_2$)$_5$I					2.0×10^{-2}	
	I(CH$_2$)$_6$I					2.2×10^{-2}	
[PtR$_2$(bpy)]	MeI	C−I	acetone	303			37
R = Me						46.8	
R = p-MeOC$_6$H$_4$					-100	1.4	
R = p-MeC$_6$H$_4$					-111	8.3×10^{-1}	
R = Ph					-114	3.7×10^{-1}	
R = p-FC$_6$H$_4$						8×10^{-2}	
R = p-ClC$_6$H$_4$						7×10^{-2}	
R = m-MeOC$_6$H$_4$						4.1×10^{-1}	
R = m-FC$_6$H$_4$						4×10^{-2}	
[PtMe$_2$(phen)]	EtI	C−I	acetone	298		$6.9 \pm 0.5 \times 10^{-2}$	96, 35
	^{n}PrI					$3.4 \pm 0.2 \times 10^{-2}$	
	^{n}BuI					$3.9 \pm 0.2 \times 10^{-2}$	
	I(CH$_2$)$_3$I					$1.3 \pm 0.1 \times 10^{-1}$	
	I(CH$_2$)$_4$I					$1.0 \pm 0.1 \times 10^{-1}$	
	I(CH$_2$)$_5$I					$8.4 \pm 0.4 \times 10^{-2}$	
	CH$_3$(CH$_2$)$_4$I					$4.4 \pm 0.3 \times 10^{-2}$	
	MeI					69 ± 5	
[PtMe$_2$(bipym)]	MeI	C−I	acetone	298		9.7	100
[PtMe$_2$(μ-bipym)PtIMe$_3$]						1.4	
[PtMe$_2$(μ-bipym)PtBrMe$_3$]						1.5	
[PtMe$_2$(μ-bipym)PtClMe$_3$]						1.65	
[PtMe$_2$(μ-bipym)PtI(^{i}Pr)Me$_2$]						1.1	
[PtMe$_2$(μ-bipym)PtMe$_4$]						2.0	
[PtMe$_2$(pypz)]						8.4	
			toluene			1.7	
[PtMe$_2$(μ-pypz)PtMe$_2$]			acetone			4.9	
			toluene			0.76	
[PtMe$_2$(μ-pypz)PtMe$_4$]			acetone			5.15	
[PtMe$_2$(μ-pypz)PtIMe$_3$]						2.9	
[PtMe$_2$(pyen)]						21	
[PtMe$_2$(μ-pyen)PtMe$_2$]						8.2	
[PtMe$_2$(phen)]						69	
[PtMe$_2$(bpy)]	MeI	C−I	acetone	265.5		14 ± 1	78
				276.6		22 ± 1	
				293	-129 ± 1	40 ± 1	

Table 1 (Continued)

complex	substrate	X–Y	solvent	T (K)	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	k_2 (L mol^{-1} s^{-1})	ref
[PtMe$_2$(phen)]	MeI	C–I	acetone	293	-48 ± 7	87 ± 1	71
				288		61.3	
				283		48.95	
				277		27.3	
	PhCH$_2$Br	C–Br	acetone	293	-135 ± 1	18.3 ± 2	
				283		12.68 ± 0.2	
				277		9.42 ± 0.2	
[PtMe$_2$(bpy)]	PhCH$_2$Br	C–Br	acetone	293	-110 ± 4	11.0 ± 0.1	
				283		7.14 ± 0.1	
				278		4.83 ± 0.1	
[PtMe$_2$(bpy)]	PhCH$_2$Cl	C–Cl	acetone	298		0.051	79
	[Au(CH$_2$Cl)(PPh$_3$)]				-144	0.41	
	Hg(CH$_2$Cl)$_2$				-145	3.46	

(CH$_2$)$_2$NMe$_2$}] (X = F, Cl, Br) undergo oxidative addition of the C–X bond to give the platinum(IV) product [PtXMe$_2${C$_6$H$_4$CH=N(CH$_2$)$_2$NMe$_2$}] (Scheme 4).[16,17] The reaction exhibits first-order kinetics, and the authors propose that oxidative addition of the C–X bond occurs by a concerted mechanism. The overall reactivity pattern follows the order C–Br > C–Cl > C–F, consistent with increasing C–X bond energies. It is of interest that competitive C–H oxidative addition is also observed in this system, a class A substrate that reacts in a concerted manner.

ii. Bimolecular (S$_N$2-type) Oxidative Addition. Kinetic data for S$_N$2-type reactions of organoplatinum(II) complexes with nitrogen-donor ligands and various electrophiles are summarized in Table 1. From the data it is clear that the second-order rate constants for this type of reaction vary by several orders of magnitude ($k_2 = 9.2 \times 10^{-5}$ to 2.2×10^8 L mol^{-1} s^{-1}) and, as expected, a large negative $\Delta S^{\ddagger}$ is found in all cases.

Mechanistic studies of the reaction of MeI with organoplatinum(II) complexes with nitrogen-donor ligands were first reported for the complex [PtPh$_2$(bpy)] by Jawad *et al.*[36] The sensitivity of this reaction to various electronic, steric, and solvent effects was established. The rate constant for the reaction is second order, first order in each of the reagents, and an increase in the rate of the reaction was found in more polar solvents, as would be expected for a polar transition state. The kinetic data are consistent with a S$_N$2-type mechanism, whereby the metal center acts as a nucleophile and attacks the carbon atom of the substrate to afford the transient cationic intermediate [PtMePh$_2$(bpy)]I that subsequently rearranges to give the final product [PtIMePh$_2$(bpy)] (Scheme 15).

A direct correlation between the energy of the lowest energy MLCT [5d$_\pi$ (Pt) $\rightarrow$ π^* (bpy)] band with the rate of reaction in a polar solvent such as acetone was observed, with the faster reactions occurring with electron-donating substituents on the phenyl ligands due to an increased basicity of the metal center. This correlation strongly implies that the energy of the filled d orbitals of the platinum(II) center primarily determines the reactivity of the complex. The reactions are bimolecular in nature and show large negative entropies of activation ($\Delta S^{\ddagger}$ = -100 to -160 J K^{-1} mol^{-1}). The effect of the reaction medium on the rate is highly dependent on

Scheme 15
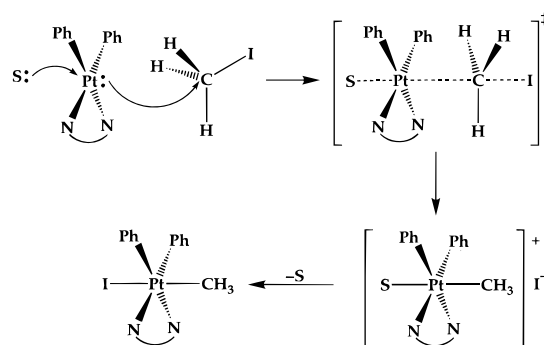
the $\Delta S^{\ddagger}$ term, as expected for reactions that proceed via a polar transition state. The rate of the reaction is also dependent on the steric bulk of the ligands. For example, phenyl ligands containing *ortho* substituents hinder the approach of MeI due to the blocking of the sites above and below the coordination plane, and thus inhibit the reaction.[37] Indeed, it has been demonstrated that a 10^3-fold decrease in the rate occurs for the S$_N$2-type oxidative addition of EtI to [PtMe$_2$(phen)] as compared to MeI.[34]

Direct evidence for a S$_N$2-type mechanism would be the unambiguous characterization of cationic intermediates and, in some cases, these have been observed at low-temperatures by using ^{1}H NMR spectroscopy.[38,39] For example, in the reaction of MeI with [PtMe$_2$(bpy)], cationic species were observed in polar solvents such as CD$_3$CN and acetone-d_6 (Scheme 16). The experiments that were conducted in CD$_3$CN

Scheme 16
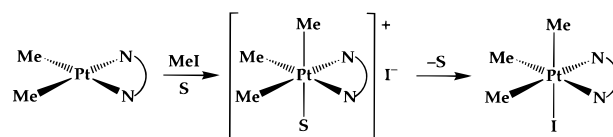
led to unambiguous observations of the cationic intermediate, most probably due to the ability of the solvent to stabilize the cationic platinum(IV) center by coordination. The authors concluded that the oxidative addition step occurs simultaneously with solvent coordination, thus contributing to the large $-\Delta S^{\ddagger}$ term and reducing incipient positive charge buildup at the metal center. Entry of the anion into the coordination sphere to displace the solvent proceeds very rapidly due to the large *trans* effect of the
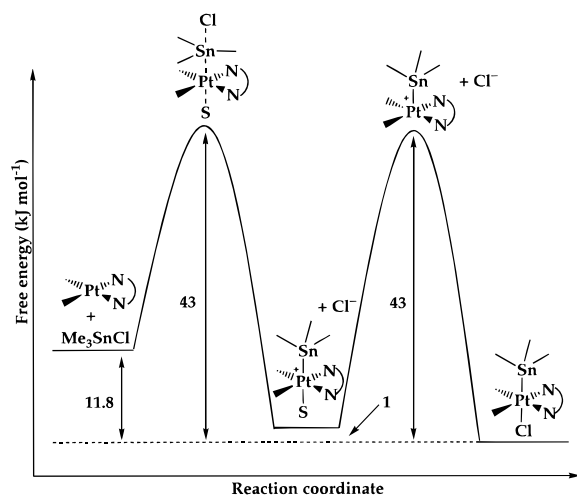
Figure 1. A plot of free energy versus reaction coordinate for the reaction of [PtMe$_2$(^{t}Bu$_2$bpy)] with Me$_3$SnCl. (Reproduced with permission from ref 40. Copyright 1995 The Royal Society of Chemistry.)

methyl ligand and the superior Lewis basicity of the anion over the solvent.

Oxidative addition of Me$_3$SnCl to [PtMe$_2$(^{t}Bu$_2$bpy)] occurs both rapidly and reversibly to afford [PtClMe$_2$(SnMe$_3$)(^{t}Bu$_2$bpy)], and a detailed thermodynamic and kinetic analysis of the reaction has been described recently.[40] A particularly detailed structure for the transition state was elucidated from the activation energies for the process, and the energy profile for the proposed S$_N$2-type mechanism was determined (Figure 1). From this profile, it is notable that the relative free energies of the transition-state species in both the oxidative addition step and halide (Cl$^-$) for solvent (acetone) exchange step are identical within experimental error ($\Delta G^{\ddagger}$ = 43 kJ mol^{-1}). Although this result may be coincidental, it is more likely that the energies are identical because the structures of the two species are similar. Indeed, the structure of the transition-state species is expected to be closely related to that of the five-coordinate complex [PtMe$_2$(SnMe$_3$)(^{t}Bu$_2$bpy)]$^+$, as would be expected for the cationic intermediate formed by a S$_N$2-type pathway.

C. Class C Substrates

In principle, class C substrates can undergo formal one- or two-electron oxidative addition to coordinatively unsaturated metal centers, and the possible mechanisms of reaction are very similar to those described for Class B reagents. Nonpolar substrates such as O$_2$, alkenes and alkynes react with metal centers to give metallacycles if the reaction is viewed as an oxidative addition, otherwise it is simple coordination to the metal with no change in its oxidation state. In most cases the exact nature of the bonding lies in between these two extremes, and its description essentially becomes an exercise in semantics because the bonding is strictly dependent on the molecular orbital scheme and on differing degrees of electron transfer. Therefore, only polar class C reagents will be included in this review.

1. Reaction of Polar Class C Substrates with Platinum(II) Complexes

Ring strain can enhance the reactivity of certain bonds and facilitate the oxidative addition reaction. For example, the C–O bond of certain oxiranes and β-lactones is activated by ring strain to oxidatively add to diimine complexes of the type [PtMe$_2$(NN)].[41,42] Thus, β-propiolactone oxidatively adds to the platinum(II) center with overall second-order kinetics and $\Delta S^{\ddagger}$ = −129 to −151 J K^{-1} mol^{-1}, both consistent with a polar S$_N$2-type pathway (Scheme 17).[41]

Scheme 17
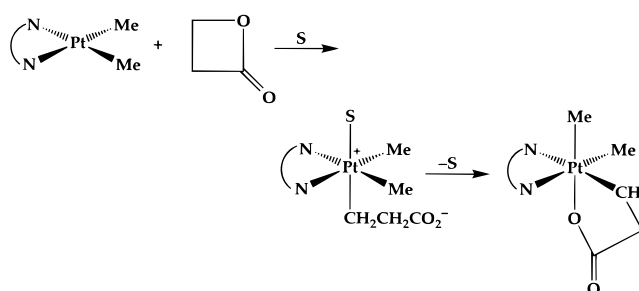
The coupling of three-membered ring ethers (oxiranes) with CO$_2$ to give cyclic carbonates is an important reaction in organic synthesis, and the use of transition metal catalysis is often necessary.[43–45] Ring strain aids the reaction of oxiranes such as 2-(phenoxymethyl)oxirane with certain platinum(II) centers to give a platinaoxacyclobutane complex,[41] a model for one of the key intermediates in the catalytic synthesis of cyclic carbonates (Scheme 18). The

Scheme 18

(R = H, Ph, CH$_2$OPh)
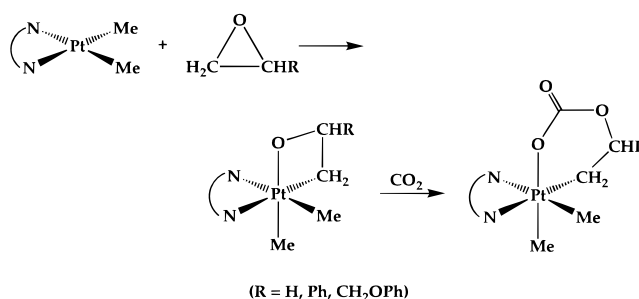
product is trapped with CO$_2$ to afford the corresponding platinacarbonate complex; absence of this reagent leads to oligomerization of the oxirane. The kinetics for the reaction in acetone solution are zero order in CO$_2$ and first-order in both the platinum(II) complex and the oxirane. The large negative $\Delta S^{\ddagger}$ (−160 ± 15 J K^{-1} mol^{-1} at 298 K) for the reaction is consistent with a S$_N$2-type mechanism with a dipolar intermediate.

III. Oxidative Addition of X–X or X–Y Bonds to Organoplatinum(II) Complexes

The discussion that follows will be arranged in order of group number for the X–X or X–Y bonds of the substrate. For X–Y bonds, the discussion will be found in most cases under the group number for the element with the *higher* atomic mass. An excep-

tion to this will be made in the case of systematic studies within a particular group (e.g., O, S, Se), where the discussion for all related substrates will be combined where appropriate.

A. Group 17

1. Halogen–Hydrogen

The cleavage of metal–carbon σ bonds by electrophiles such as protic acids is of fundamental importance in organometallic chemistry, and the mechanism of this process has been the subject of several studies (Scheme 19).[46–55] Detection of the alkyl(hy-

Scheme 19
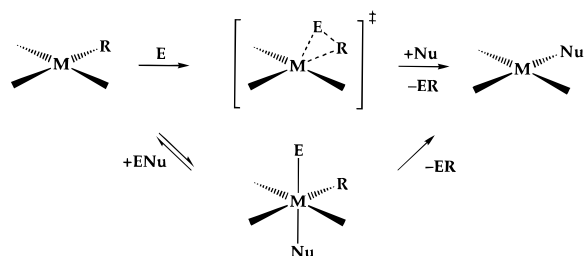
drido)platinum(IV) intermediate would provide definitive evidence for an oxidative addition pathway in the protonolysis of Pt–C bonds, although it is difficult to achieve owing to the facile reductive elimination of the alkane. Recently, a few groups have reported the detection and, in some cases, isolation of alkyl(hydrido)platinum(IV) complexes by protonation of the corresponding alkylplatinum(II) complex with HX.

Reaction of [PtR$_2$(dmphen)] (R = Me, p-MeOC$_6$H$_5$) with Me$_3$SiX in the presence of H$_2$O (to generate HX *in situ*) leads to the rapid formation of [Pt(H)-XR$_2$(dmphen)] which possesses *cis* stereochemistry of the H and X ligands about the metal center.[56] This geometry is most probably a consequence of the bulky methyl groups in the dmphen ligand as similar experiments with other nitrogen-donor ligands such as bpy or ^{t}Bu$_2$bpy give the analogous *trans* isomer. The complexes with R = Me are stable in the solid state, but readily lose CH$_4$ in CHCl$_3$ solution. With R = p-MeOC$_6$H$_5$, the platinum(IV) complex is stable only in the solid state with rapid decomposition in solution, thus precluding its characterization.

Very recently, Canty et al.[57] and Templeton et al.[58] prepared and characterized remarkably stable dimethyl(hydrido)platinum(IV) complexes with the hydrotris(1-pyrazolyl)borate and hydrotris(3,5-dimethyl-1-pyrazolyl)borate ligands by formal oxidation of the platinum(II) precursor [PtMe$_2$\{(pz*)$_3$BH\}]$^-$ (pz* = 1-pyrazolyl, 3,5-dimethyl-1-pyrazolyl) with HX (X = Cl, BF$_4$, phenolate), (**2**). The tris(1-pyrazolyl)borate complex, for example, is stable to reductive elimination of CH$_4$ up to 140 °C.
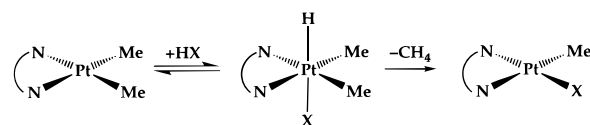
Hill et al.[59] investigated the *trans* oxidative addition of HX (X = Cl, Br, I, O$_2$CCF$_3$, SO$_3$CF$_3$) with [PtMe$_2$(NN)] (NN = bpy and ^{t}Bu$_2$bpy) (Scheme 20). In most cases, the unstable hydridoplatinum(IV) intermediate was detected at low temperature (−78 °C) by ^{1}H NMR spectroscopy, but the products were not isolated, owing to rapid reductive elimination of
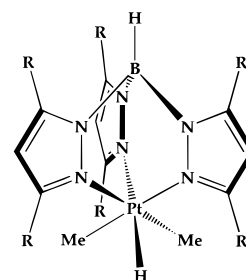
(R = H, Me)

(2)

Scheme 20

CH$_4$. The thermal stability of the platinum(IV) intermediate follows the sequence X = Cl > Br > I > O$_2$CCF$_3$ > SO$_3$CF$_3$. Indeed, attempts to detect the intermediate in cases where X$^-$ is a poor ligand for platinum, i.e. where X = SO$_3$CF$_3$ or O$_2$CCF$_3$, proved unsuccessful even at −90 °C.

Bercaw et al.[60] conducted quantitative studies of the protonation reaction of [PtCl(CH$_2$Ph)(tmeda)] with HCl at low temperatures (Scheme 21). Isotope

Scheme 21
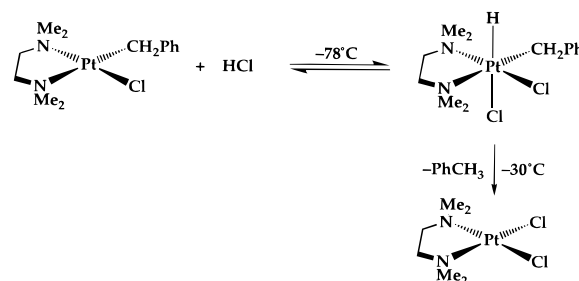
effects (equilibrium and kinetic) were determined for the formation of the alkyl(hydrido)platinum(IV) species ($K_H/K_D = 0.51 \pm 0.05$ at −28 °C; $k_H/k_D = 1.55 \pm 0.10$ at 0 °C and −28 °C in CD$_2$Cl$_2$/Et$_2$O-d_{10}).

Very recently, Hill and Puddephatt reported that certain methyl(hydrido)platinum(IV) complexes are resistant to the reductive elimination reaction.[61] Treatment of *fac*-[PtMe$_3$(SO$_3$CF$_3$)(^{t}Bu$_2$bpy)], prepared by oxidative addition of MeOTf to [PtMe$_2$(^{t}Bu$_2$bpy)], with NaBH$_4$ yields the unique cationic, (μ-hydrido)-diplatinum(IV) complex [Pt$_2$(μ-H)Me$_6$(^{t}Bu$_2$bpy)$_2$]$^+$ which, along with the corresponding mononuclear species *fac*-[PtHMe$_3$(^{t}Bu$_2$bpy)], are stable with respect to reductive elimination of CH$_4$, and to isotopic H–D exchange between the hydride and methyl ligands (Scheme 22). The unusual thermal stability of these complexes is most probably due to the absence of labile ligands and, in the case of the dimer, steric protection of the hydride ligand and its diminished hydridic nature compared to the mononuclear complex.

Scheme 22
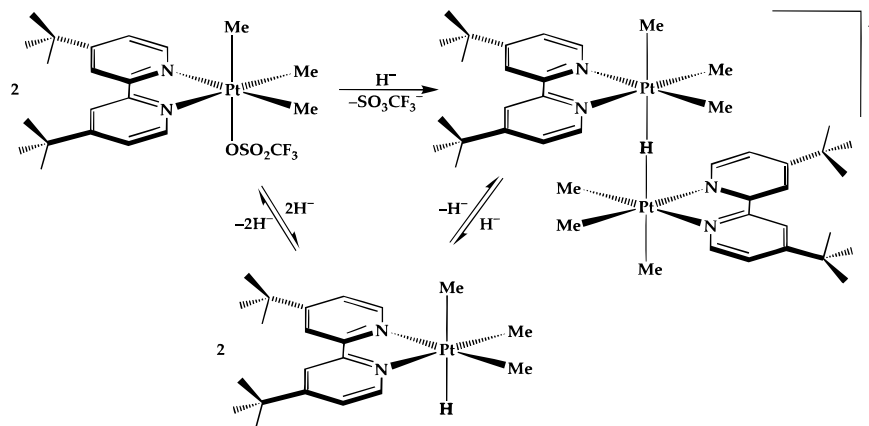
2. Halogen–Nonaromatic Carbon

The great majority of oxidative addition reactions that have been reported to date have focused on the preparation of platinum(IV) complexes with nitrogen-donor ligands by the oxidation of the corresponding platinum(II) precursors with organohalides. More recent work has encompassed not only synthesis but also the more subtle aspects of inter- and intramolecular mechanism and reactivity, both thermally and photochemically. Section II of this review detailed a number of important examples involving organohalides for most of the known mechanisms of oxidative addition.

Cis-alkyl and -arylplatinum(II) complexes with nitrogen-donor ligands such as the bidentate diimines (e.g., 2,2'-bipyridine and 1,10-phenanthroline) react with a variety of organohalides[62–80] such as alkyl, allyl, sulfonium salts, and acid halides to usually give the products of *trans* oxidative addition. Sometimes, the *cis* isomer is formed by a competitive *cis* oxidative addition pathway, or it may be formed by *trans* oxidative addition with subsequent isomerization of the platinum(IV) product to the thermodynamically more stable *cis* isomer. As described in section II, primary alkyl halides such as MeI react in a S_N2-type manner, with a highly polar transition state, whereas bulkier analogues such as ^iPrI react thermally by radical chain pathways or sometimes by a mixture of both. In photochemical reactions of alkyl halides with certain cyclometalated complexes of platinum(II),[81–87] where a radical chain mechanism is thought to operate, only *cis* oxidative addition occurs (Scheme 23),

Scheme 23
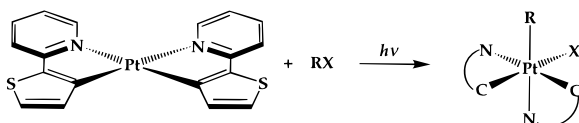
although *trans* addition occurs with a few substrates. In contrast, anaerobic photochemical oxidation of [PtMe₂(phen)] with ^iPrI gives the *trans* addition product [PtIMe₂(^iPr)(phen)] and small amounts of [PtI₂Me₂(phen)] by a free-radical mechanism.[32]

Van Koten *et al.*[14] have shown that platinum(II) complexes containing the anionic, *ortho*-chelating tridentate ligand, 2,6-bis[(dimethylamino)methyl]phenyl, are very useful in studies of the mechanism of the

oxidative addition process by, for example, alkyl halides. The "hard" nature of the N- and C-donor atoms of this ligand make the resulting complexes very susceptible to S_N2-type reactivity due to the highly nucleophilic nature of the metal center. In addition, the highly rigid nature of the ligands stabilize the platinum(IV) species with respect to reductive elimination, a feature that is also found in other rigid nitrogen-donor ligands such as bis(arylimino)acenaphthene and bis(phenylimino)camphane (**3a** and **3b**), respectively.[88]

(3a)   (3b)
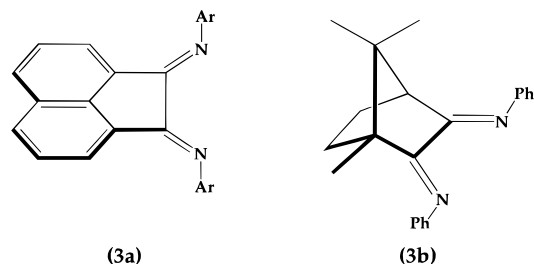
Addition of MeI to the cationic aqua complex [Pt{C₆H₃(CH₂NMe₂)₂-*o,o'*}(H₂O)]BF₄ leads to the formation of an unusual cationic arenonium (Wheland-type) species [PtI{MeC₆H₃(CH₂NMe₂)₂-*o,o'*}]BF₄, where the methyl group becomes bonded to the C-donor (C_{ipso}) atom of the ligand (Scheme 24).[89] The reaction most likely proceeds in a S_N2-type manner via a five-coordinate methylplatinum(IV) intermediate, whereby the substrate MeI acts as an electrophile. The filled d_{z^2}-orbital of platinum(II) overlaps with the LUMO of MeI, an interaction that is supported by elegant theoretical studies that show an initial Pt–I interaction by approach of the MeI along the axis perpendicular to the coordination plane (Scheme 25).[90] The resulting cationic, five-coordinate platinum(IV) species is unstable and attempts to reductively eliminate the Me ligand. A (reversible) 1,2-methyl shift occurs along the Pt–C_{ipso} bond to give the final arenonium species, which is trapped owing to the steric constraints imposed by the rigid, *ortho*-chelating ligand. Similar reactions occur when complexes of the type [PtX{C₆H₃(CH₂NMe₂)₂-*o,o'*}] (X = Cl, Br, I) are treated with MeOTf to afford the related arenonium species [PtX{MeC₆H₃(CH₂NMe₂)₂-*o,o'*}]OTf. With MeI, only for X = *o*-tolyl does one observe the species [Pt(*o*-tolyl){MeC₆H₃(CH₂NMe₂)₂-*o,o'*}]I, otherwise overall substitution of the halide ensues (e.g., when X = Br).
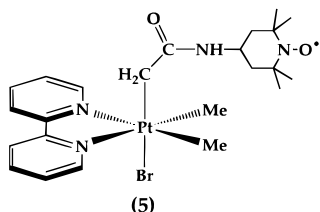
Scheme 24
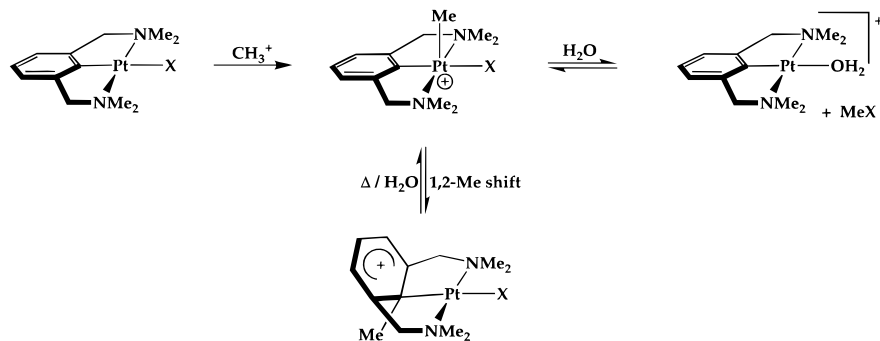
Scheme 25
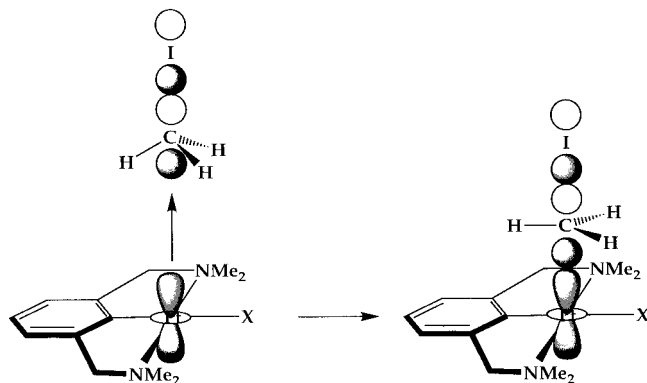
Heteronuclear complexes with bridging methylene groups have been prepared by the reaction of [PtMe$_2$(bpy)] with [Hg(CH$_2$Cl)Cl] or [Au(CH$_2$Cl)(PR$_3$)] (R = Ph, Et, OPh) to afford [PtClMe$_2$(CH$_2$Y)(bpy)] (Y = Au(PR$_3$), HgCl).[79] The presence of the metal substituent activates the C$-$Cl bond toward oxidative addition by a factor of 10^3 to 10^4. Mixed-metal complexes have also been synthesized by treatment of [PdMe$_2$(bpy)] with α,α'-dibromo-m-xylene, followed by oxidative addition of [PtMe$_2$(bpy)], to afford novel, dinuclear palladium(IV)$-$platinum(IV) species.[91,92]

Other interesting examples of C$-$X bond cleavage by oxidative addition to organoplatinum(II) complexes include the preparation of cationic, aminocarbene platinum(IV) complexes from chloroiminium (Vilsmeier) salts (**4**);[93] stable, organoplatinum(IV)

(4)
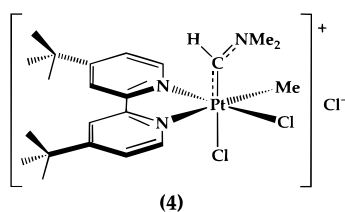
complexes with pendant free-radical nitroxides such as proxyl and tempo (**5**);[94] and the synthesis of a

(5)

highly fluorescent platinum complex with a coumarin ligand (**6**).[95]

(6)
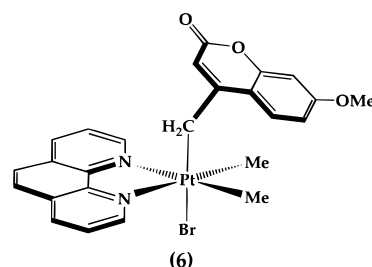
The oxidative addition reactions of C$-$X bonds to mononuclear platinum(II) complexes can be used to prepare the corresponding dimeric (Scheme 14),[34,96$-$100] trimeric,[101] and tetrameric[98,102] platinum(IV) complexes such as **7**, and mixed oxidation-state species, e.g., **8** and **9**.[98,101] More recently, platinum-containing

(7)

(8)

(9)
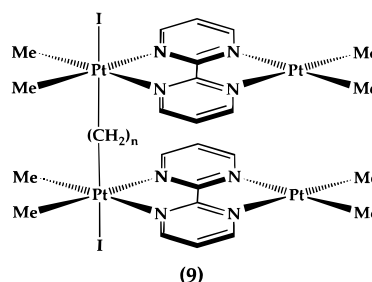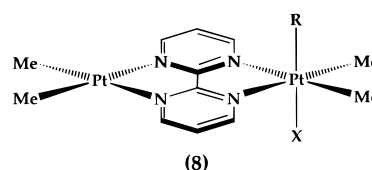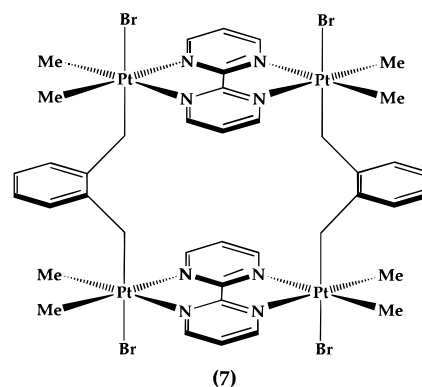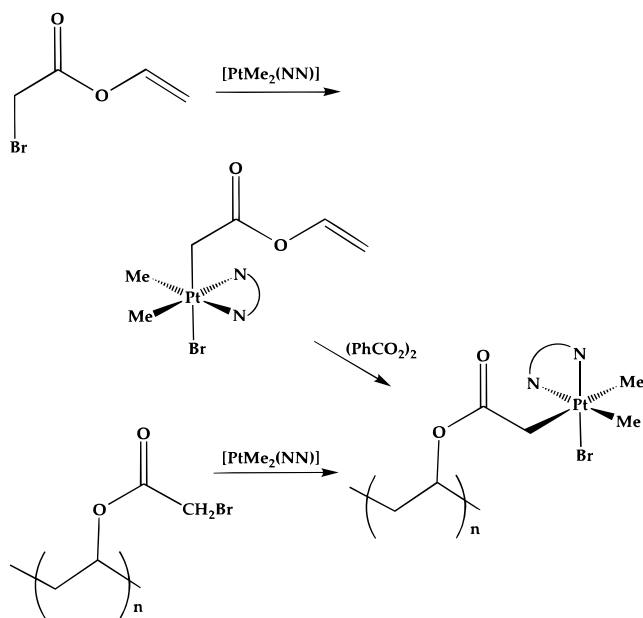
Scheme 26

Scheme 27

oligomers, polymers, and highly branched (dendritic) polymers known as dendrimers have also been prepared by the oxidative addition method.[101,103−109]

Scheme 28

Free-radical polymerization of the vinylplatinum-(IV) monomer, prepared by oxidative addition of BrCH$_2$C(O)OCH=CH$_2$ to [PtMe$_2$(′Bu$_2$bpy)], with the initiator dibenzoyl peroxide g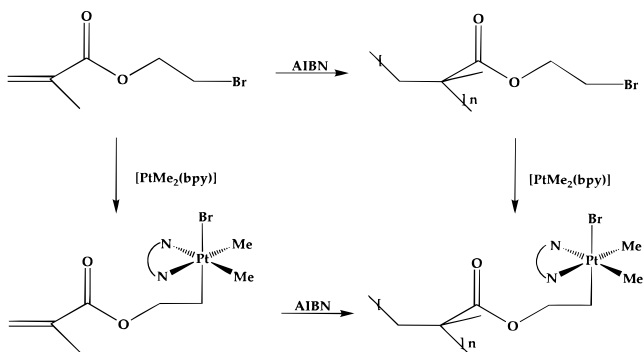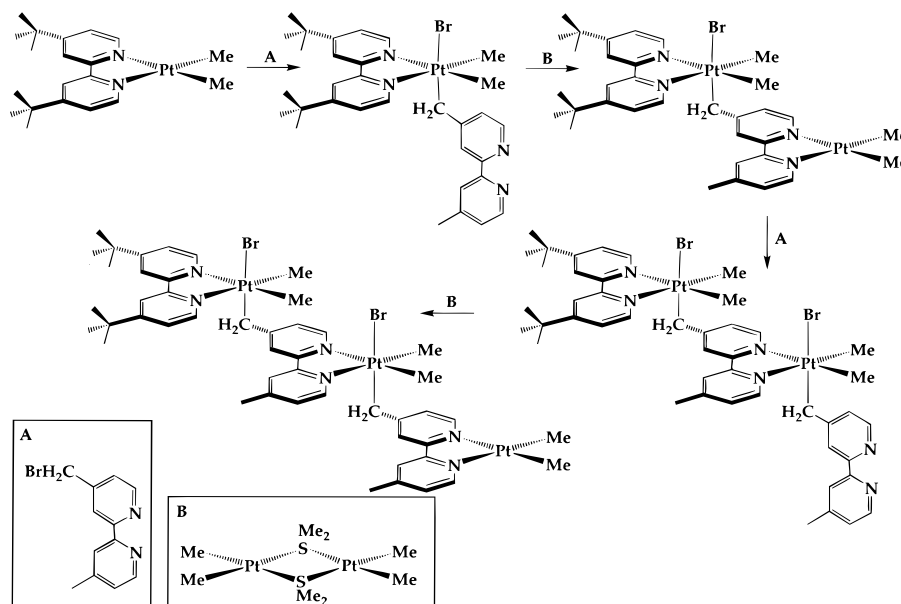ives a polymeric species with organoplatinum moieties attached to the acetate groups of the poly(vinyl acetate) chain (Scheme 26).[104] Alternatively, poly(vinyl bromoacetate) reacts with [PtMe$_2$(′Bu$_2$bpy)] to generate the same polymer in one step. The compounds are reported to show high thermal stability, although no melting transitions were observed by differential scanning calorimetry (DSC). Some of the platinum(IV) centers arise from *cis* rather than *trans* oxidative addition of the C−Br bond, and the resulting products are not stereoregular. Cross-linked vinyl polymers of platinum have been prepared by polymerization of alkylplatinum-(IV) complexes containing two vinyl groups.[105] The monomers are prepared by oxidative addition of vinyl derivatives of alkyl or acyl halides to the vinyl-containing monomer [PtMe$_2$(vbpy)].

Oxidative addition of 2-bromoethyl methacrylate to [PtMe$_2$(bpy)], followed by free-radical polymerization with the initiator AIBN gives an insoluble organoplatinum(IV) polymer (Scheme 27).[106] Other vinyl monomers also undergo this type of reaction. Readily available organic polymers with electrophilic substituents can also be used. For example, oxidative addition of the C−Br bonds of poly(2-bromoethyl methacrylate) to platinum(II) precursors occurs with ~80% incorporation of the metal. The cross-linked styrene(chloromethyl)styrene copolymer known as Merrifield's resin also undergoes an oxidative addition reaction with platinum(II) precursors to give a sparingly soluble polymer with almost complete platinum incorporation.

The oxidative addition methodology has also been used in the preparation of linear oligomers and polymers by incorporation of a bromomethyl substituent onto the nitrogen-donor (bpy) ligand.[107] One

Scheme 29
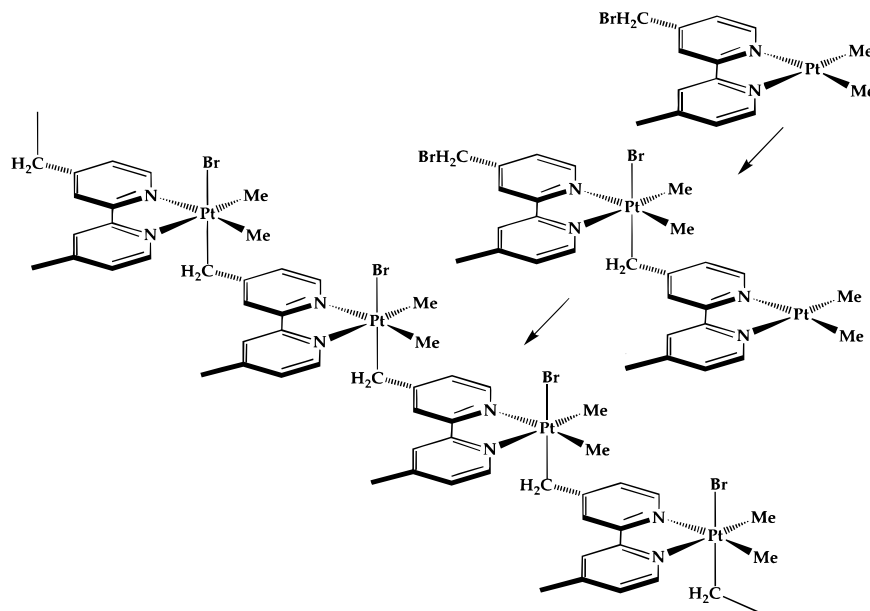
Scheme 30
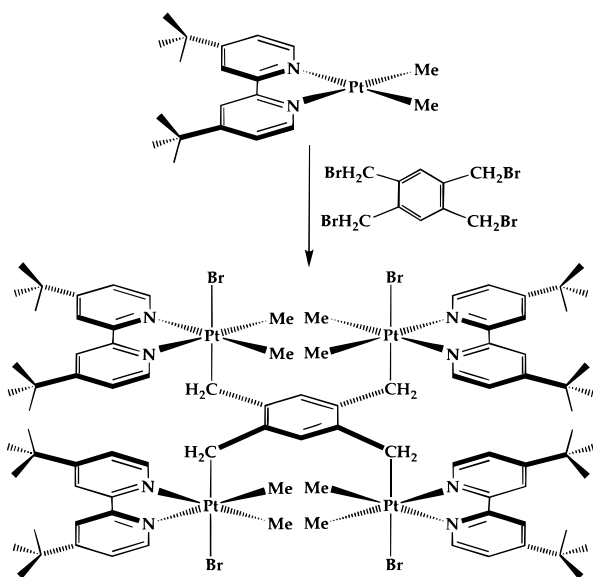
method involves the reaction of the "initiator" [PtMe₂('Bu₂bpy)] species with the functionalized bpy ligand by oxidative addition of the C−Br bond. This
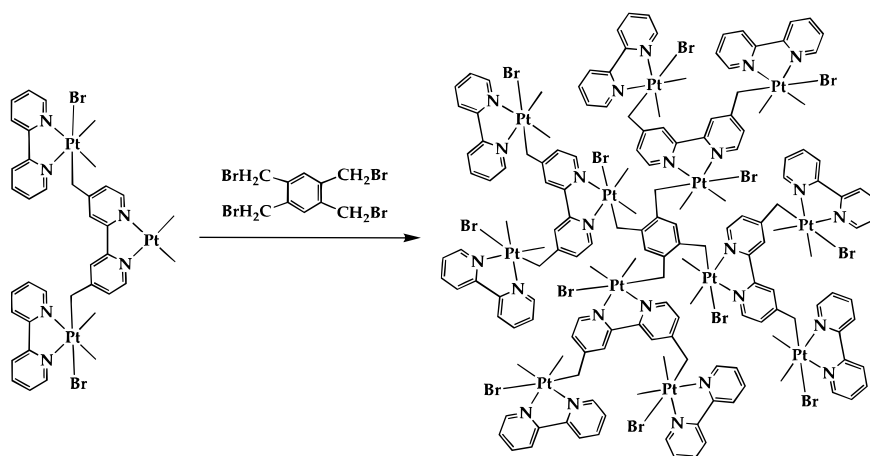
is followed by reaction of the tethered diimine with the platinum(II) precursor and, finally, by further oxidative addition of the C−Br bond of another functionalized ligand to the new platinum(II) center (Scheme 28). The oligomeric chain can be lengthened in a stepwise manner by simple repetition of the cycle. Alternatively, the functionalized platinum(II) species acts as the "initiator" complex which can undergo a series of oxidative addition reactions with other functionalized platinum(II) complexes to give the final polymer (Scheme 29). Finally, use of the "core" aromatic electrophile with four bromomethyl substituents, 1,2,4,5-tetrakis(bromomethyl)benzene, four simultaneous oxidative addition reactions have been accomplished to give novel, star-shaped (branched) oligomers which show greater solubility than the linear polymers due to an increase in branching (Scheme 30). The final methodology was exploited to give large organoplatinum dendrimers by a convergent synthesis (Scheme 31).[101,103,108] One such product **10**, contains 28 platinum atoms and is one of the largest transition metal dendrimers reported to date.[108]

Scheme 31

(10)
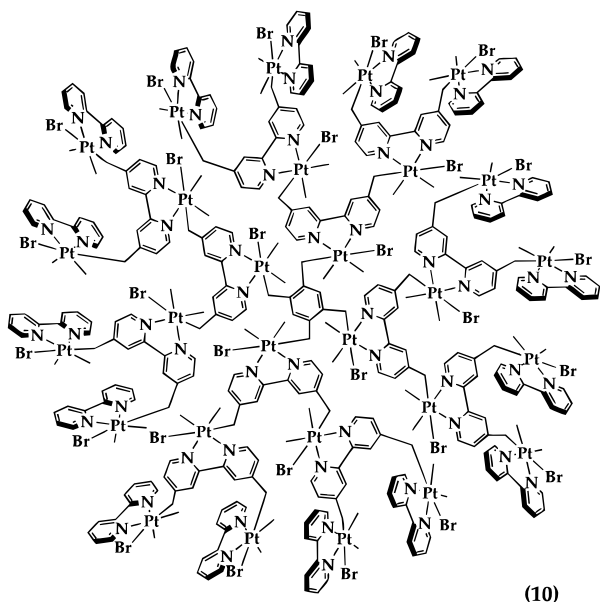
3. Halogen–Aromatic Carbon

Very few examples of oxidative addition reactions of aryl halides with square-planar d[8] complexes, such as those of platinum(II), are known. By the use of ligand design, the oxidative addition of aryl halides to platinum(II) was first reported by Anderson *et al.*[16,17] The complexes [PtMe$_2$\{2-XC$_6$H$_4$CH=N-(CH$_2$)$_2$NMe$_2$\}] (X = F, Cl, Br) oxidatively add to the C−X bond in an intramolecular manner to give the corresponding platinum(IV) product. Even the particularly strong C−F bond is reactive under these conditions. The pattern of reactivity is correlated with C−X bond energies, with C−Br > C−Cl > C−F. The reactions proceed with first-order kinetics and small values of $\Delta S^\ddagger$, as expected for a concerted addition process. Similar results have been reported for related systems.[110] For the bifunctional imine ligand (C$_6$F$_5$)CH=NCH$_2$(2-XC$_6$H$_4$) (X = H, Cl, Br), selective cleavage of the C−F bond by oxidative addition to platinum(II) is found, even in the presence of the weaker Ar−X bonds (Scheme 32).[111] The

Scheme 32

(X = H, Cl, Br)
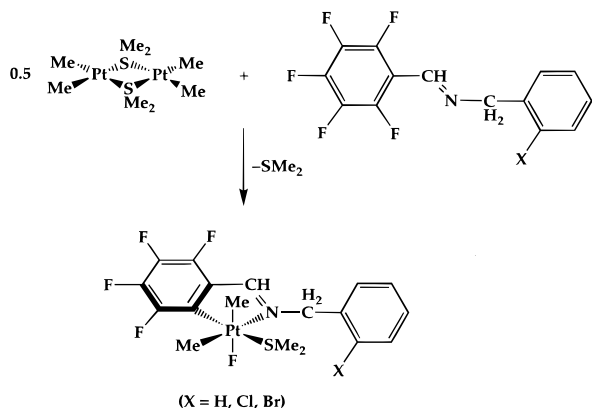
reaction follows second-order kinetics with a large negative $\Delta S^\ddagger$. These results are consistent with a S$_N$2-type rather than a concerted mechanism, although electron transfer from the metal center to the pentafluorophenyl group cannot be discounted.

Canty *et al.*[112] also have oxidatively added an aryl−bromide bond to a platinum(II) center in an intramolecular manner. Reaction of [PtMe$_2$(μ-SEt$_2$)]$_2$ with the nitrogen-donor ligand 2,6-(pzCH$_2$)$_2$C$_6$H$_3$Br leads to facile replacement of the thioether ligands by the bidentate nitrogen-donor (Scheme 33). The close

Scheme 33
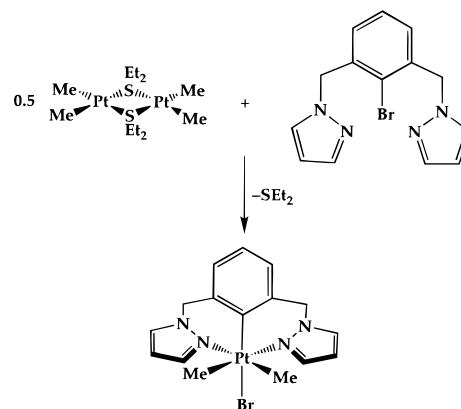
proximity of the C−Br bond to the platinum(II) center results in subsequent oxidative addition to afford the final platinum(IV) product [PtBrMe$_2$\{2,6-(pzCH$_2$)$_2$C$_6$H$_3$-*N,N',C'*\}]. The kinetics for this reaction were not reported, but presumably the oxidative addition proceeds by a similar concerted mechanism to that described above.

4. Halogen–Halogen

The addition of halogens to organoplatinum(II) complexes is of historical significance,[113–115] and the fundamental mechanisms of halogen interaction with the platinum(II) center have been elucidated for complexes with nitrogen-donor ligands.[116–121] Halogens commonly react with platinum(II) complexes with N-, P-, and As-donor ligands by *trans* oxidative addition. Subsequent isomerization of the platinum(IV) product to the thermodynamically stable *cis* isomer occurs in some cases.

Van Koten *et al.*[122–125] extensively studied the interaction of halogens with organoplatinum(II) complexes containing rigid *ortho*-chelating ligands. Stable organoplatinum(IV) complexes are formed by *trans* oxidative addition of halogens X$_2$ (X = Cl, Br) to [PtY(C$_6$H$_3$\{CH$_2$NMe$_2$\}$_2$-2,6)] (Y = Cl, Br) to afford [PtX$_2$Y(C$_6$H$_3$\{CH$_2$NMe$_2$\}$_2$-2,6)]. With Y = phenyl and *p*-tolyl, exclusive *cis* addition of X$_2$ (X = Br, I) occurs due to rearrangement of the product to the thermodynamically stable isomer. Interestingly, the reaction of I$_2$ with [PtY(C$_6$H$_3$\{CH$_2$NMe$_2$\}$_2$-2,6)] (Y = *p*-tolyl, I) proceeds to give the expected platinum(IV) product when Y = *p*-tolyl, but a stable η^1-I$_2$ platinum(II) adduct is formed when Y = I (Scheme 34).[124]

Scheme 34
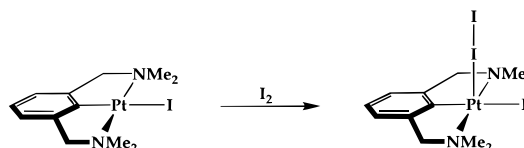
Initial η^1-I$_2$ coordination to the metal center is effected by overlap of the d$_{z^2}$ orbital of platinum(II)

and the vacant σ^* orbital (LUMO) of I_2, with the oxidation state of the platinum remaining unchanged.[126] The steric constraints of the *trans* spanning nitrogen-donor ligand stabilise the η^1-I_2 adduct with respect to further reaction to give the expected platinum(IV) product. The η^2-I_2 intermediate required for a concerted process is never observed and, indeed, theoretical studies show this bonding arrangement is less likely to occur than η^1 coordination.[127]

The isolation of the unusual η^1-I_2 adduct serves as a useful model for the initial stage in the oxidation of organoplatinum(II) complexes by halogens. Such a reaction invariably follows a S_N2-type pathway via a cationic, five-coordinate intermediate; the stereochemistry of the final platinum(IV) product is determined by thermodynamic factors alone. This conclusion is supported by related work involving the oxidation of *cis*-[PtL$_2$] (L = 2-[(dimethylamino)methyl]phenyl; 8-(dimethylamino)-1-naphthyl) by Br_2 and I_2, for example, to give stable *trans*-dihaloplatinum-(IV) products.[128] Furthermore, the kinetics for the oxidation of [Pt(CN)$_4$]$^{2-}$ in aqueous solution by Cl_2 and Br_2 are consistent with a S_N2-type pathway.[129]

B. Group 16

1. Oxygen–Hydrogen

Treatment of [PtMe$_2$(NN)] with H_2O, MeOH, or EtOH at room temperature gives products of the type [PtMe$_2$(OR)(OH$_2$)(NN)](OH) (R = H, Me, Et) (**11**).[130,131]

(11)
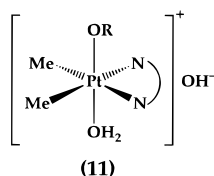
Such complexes are particularly robust with respect to further hydrolysis. No evidence for the formation of Pt–H bonds was reported, probably due to their instability in a protic solvent, and indeed H_2 is liberated during the reaction. The OR ligand is inert to solvolysis by alcohols, water, and dilute HClO$_4$; an extremely unusual property for a metal alkoxide that presumably reflects the kinetic inertness of platinum-(IV). Oxidative addition of water or alcohols to *cis*-[PtMe$_2$(py)$_2$] yields [PtMe$_2$(py)$_2$(OR)(OH)] (R = H, Me, Et).[132] For R = Me, addition of acid results in elimination of the pyridine ligand *trans* to the methyl group to afford [PtMe$_2$(OMe)(H$_2$O)$_3$]$^+$, which is indefinitely stable in aqueous acid.

Canty *et al.*[133] have also found that water oxidizes [PtMe$_2${pz$_3$BH}]$^-$ to give the stable hydroxoplatinum-(IV) product [Pt(OH)Me$_2${(pz)$_3$BH}]. A similar reaction utilizing [PtPh$_2${(py)$_3$COH}] yields [PtPh$_2$-{(py)$_3$COH}(OH)]OH·nH$_2$O ($n \approx 1$).[134] The hydroxo ligand is readily protonated by protic acids such as CF_3CO_2H to afford the corresponding aqua complex.

2. Oxygen–Carbon

As described in section II.C, ring strain promotes the C–O bond cleavage of certain oxiranes and β-lactones by oxidative addition to [PtMe$_2$(NN)] complexes.[41,42,135] For β-propiolactone, the reaction proceeds by a polar S_N2-type pathway (Scheme 17).[41] Similar reaction chemistry was observed with oxiranes such as ethylene oxide and styrene oxide.[42,135] The kinetic parameters are consistent with a S_N2-type mechanism, with the reaction first order in both platinum complex and oxirane reagent. Interestingly, the rate of reaction does not correlate with solvent polarity, although the reaction is faster in hydroxylic solvents. The presence of CO_2 during the course of the reaction leads to the formation of a stable metallacarbonate complex (Scheme 18).

With styrene oxide, retention of configuration at the chiral carbon is observed on oxidative addition of the C–O bond, as determined crystallographically.[135] In solution, the complex interconverts between Δ and Λ forms (**12a** and **12b**), respectively, presumably by dissociation of the labile Pt–O bond followed by pseudorotation and recoordination. A S_N2-type mechanism of oxidative addition where the metal center attacks the less sterically hindered carbon atom is inferred here.

R-Δ R-Λ
(12a) **(12b)**
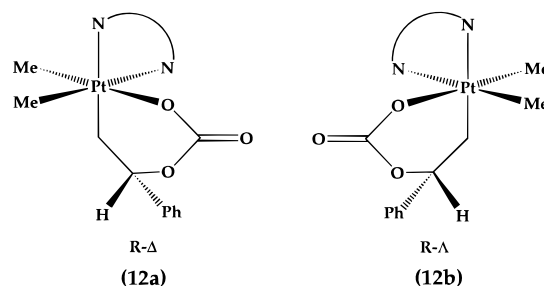
3. Group 16–Group 16

In a comparative study of the oxidative addition of group 16 E–E bonds, Aye *et al.*[22] treated RE–ER (ER = OH; OC(=O)Ph; SMe; SPh; SePh) with [PtMe$_2$(phen)] to give [PtMe$_2$(ER)$_2$(phen)], with the major isomer having ER ligands mutually located *trans* to each other; for E = Se, the *trans* isomer is formed exclusively. The kinetics of the reaction with PhSSPh are complicated and were difficult to reproduce. A free-radical chain reaction might be involved, although no free radicals were detected in this system.

Recently, Deacon *et al.*[136] reported the synthesis of the stable pentafluorophenyl complex [Pt(OH)$_2$-(C$_6$F$_5$)$_2$(en)] by *trans* oxidative addition of H_2O_2 to [Pt(C$_6$F$_5$)$_2$(en)]. The oxidation reaction was also attempted with water, but it did not proceed to completion.

C. Group 14

1. Group 14–Hydrogen

As described in section II, certain dimethylplatinum(II) complexes containing diimine ligands with pendant aromatic groups react to give a transient alkyl(hydrido)platinum(IV) complex, most probably by a concerted, intramolecular oxidative addition of a C–H bond.[16,17] This intermediate was never detected and is thermodynamically unstable with respect to reductive elimination of CH_4 to afford an *ortho*-metalated platinum(II) species. For the aromatic halide derivatives, one observes competition

between the *ortho*-metalation and intramolecular oxidative addition reactions of the C–X bond (X = F, Cl, Br), with *ortho*-metalation occurring when X = F. Oxidative addition of the C–X bond is favored when X = Cl and Br, thus establishing a qualitative reactivity series that follows the inverse of aromatic–X bond energies (i.e., C–Br > C–Cl > C–H > C–F).

Very few cases of the oxidative addition reaction of group 14-hydride substrates to platinum(II) complexes with nitrogen-donor ligands are known. Pidcock *et al.*[18] have investigated the reaction of R_3SnH (R = Ph, *o*-tolyl, *p*-tolyl) with [PtMe$_2$(bpy)] (Scheme 5). A vigorous reaction occurs to give a transient platinum(IV) species by *cis* oxidative addition of the Sn–H bond, followed by reductive elimination of CH_4. Further reaction of the substrate with the intermediate platinum(II) species [PtMe(SnR$_3$)(bpy)] affords the final, stable platinum(IV) species *cis,trans*-[PtH(Me)(SnR$_3$)$_2$(bpy)].

2. Group 14–Halogen

One rarely observes the oxidative addition of heavier group 14–halide bonds to coordinatively unsaturated metal complexes because the addition of group 14–hydride, –carbon, and –group 14 bonds is usually preferred. However, Levy *et al.*[40,137–139] recently demonstrated that there is a clear thermodynamic "halogen effect" in the oxidation reactions of tin– and silicon–halide bonds with various [PtMe$_2$(NN)] complexes to afford the corresponding platinum(IV) species [PtXMe$_2$(MMe$_3$)(NN)] (M = Si, Sn; X = Cl, Br, I) (Scheme 35). These bonds become

Scheme 35

(M = Si, Sn)
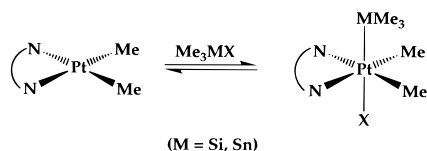
considerably weaker with the heavier halides and, as a result, the oxidative addition reaction is more favored. Indeed, the ease of oxidation follows the order X = I ≫ Br > Cl.

Kuyper[140,141] has reported the reaction of various group 14–halide bonds in compounds of the type R_nMX_{4-n} (M = C, Si, Ge, Sn, Pb; X = Cl, Br; R = Me, Ph; n = 0–3), to the electron-rich [PtMe$_2$(NN)] complexes. These studies showed that several group 14–halide bonds readily undergo the oxidation reaction to afford stable platinum(IV) products of the type [PtXMe$_2$(R$_n$MX$_{3-n}$)(NN)], but Si–Cl addition is not observed. For M = Sn, a more electron-deficient tin center results in the formation of a more stable platinum(IV) complex; the order of stability for the addition of R_nSnCl_{4-n} (n = 1–3) being PhSnCl$_3$ > MeSnCl$_3$ > Ph$_2$SnCl$_2$ > Me$_2$SnCl$_2$ > Me$_3$SnCl. The resulting platinum(IV) products [PtClMe$_2$(R$_n$SnCl$_{3-n}$)(NN)] are quite stable with respect to hydrolysis, but the corresponding germanium complexes [PtClMe$_2$(R$_n$GeCl$_{3-n}$)(NN)] are exceedingly unstable in the presence of moisture.[138]

For the addition of a Sn–Cl bond by R_nSnCl_{4-n} substrates (n = 2, 3), an equilibrium exists between [PtMe$_2$(NN)] and [PtClMe$_2$(R$_n$SnCl$_{3-n}$)(NN)].[138] The relative position of the equilibrium is greatly dependent on the nature of the tin substrate. For Me$_3$SnCl, for example, the equilibrium lies toward the platinum(II) precursor, and the corresponding platinum(IV) species [PtClMe$_2$(SnMe$_3$)(NN)] is isolated only in the presence of excess tin reagent. In contrast, with Me$_2$SnCl$_2$ the equilibrium is shifted toward the platinum(IV) product [PtClMe$_2$(Me$_2$SnCl)(NN)]. Qualitatively, Kuyper[140] determined the rates of reaction to be Me$_3$SnCl ≫ Me$_2$SnCl$_2$ > Ph$_3$SnCl. With $RSnCl_3$ (R = Me, Ph) and Ph$_2$SnCl$_2$ the reactions were found to be extremely rapid. For the analogous germanium substrates,[138] an equilibrium between the platinum(IV) product [PtClMe$_2$(GeMe$_3$)(NN)] and the platinum(II) species was only observed for Me$_3$GeCl, although small amounts of platinum(II) precursor were also observed for Me$_3$GeBr.

The reaction of Me$_3$Sn–X (X = Cl, Br, I) with [PtMe$_2$(NN)] occurs quite readily and reversibly to allow both thermodynamic and kinetic data to be obtained, and this system has been studied in great detail by means of variable-temperature NMR spectroscopy (Scheme 36).[40,137] All the reactions proceed

Scheme 36
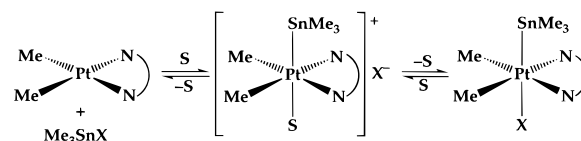
by a polar S_N2-type mechanism. The addition of Me$_3$Sn–I to [PtMe$_2$(^{t}Bu$_2$bpy)] is exceedingly rapid (k_2 = {2.2 ± 0.2} × 10^8 L mol^{-1} s^{-1}) in CD$_3$CN solution at 20 °C. This value is very close to the limit of diffusion control (~10^9 L mol^{-1} s^{-1}), and it is easily the fastest rate ever measured for any thermal oxidative addition system. As described earlier, a particularly detailed energy profile for the oxidative addition of Me$_3$Sn–Cl to [PtMe$_2$(^{t}Bu$_2$bpy)] was also determined, and both the nature and energy of the transition state was elucidated for this particular reaction (Figure 1).[40]

Treatment of the cyclometalated complex *cis*-[PtL$_2$] (L = 8-(dimethylamino)-1-naphthyl) with Me$_2$SnX$_2$ (X = Cl, Br) affords the first examples of isolable arylplatinum(IV) hydrides by an unusual intramolecular H-atom abstraction from the Me$_2$Sn ligand of an intermediate platinum(IV) species [PtX(Me$_2$SnX)L$_2$] (Scheme 37).[142–145] For X = Br, the intermediate [PtBr(Me$_2$SnBr)L$_2$] was detected by ^{1}H NMR spectroscopy. When Ph$_2$SnCl$_2$ is used in place of Me$_2$SnX$_2$, the product of Sn–Cl oxidative addition is formed exclusively, with no evidence of the hydridoplatinum(IV) complex. In the presence of methanol, treatment of the platinum(II) complex with Me$_2$SnBr$_2$ initially affords the hydridoplatinum(IV) species, but this rapidly tautomerizes to an unusual zwitterionic platinum(II) species with an agostic interaction between a protonated amine group and the metal center (Scheme 37).

Scheme 37

Scheme 38
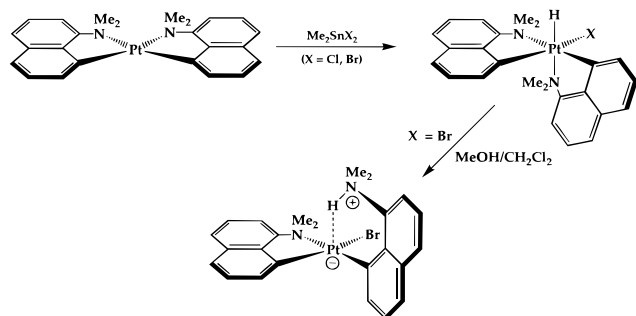
3. Tin–Sulfur

In the first examples of oxidative addition of Sn−S bonds to a transition metal complex, the ring compounds $(R_2SnS)_3$ (R = Me, Ph) react with [PtMe$_2$-(^{t}Bu$_2$bpy)] to give the luminescent organoplatinum-(IV) metallacycles [PtMe$_2$(R$_2$SnS)$_2$(^{t}Bu$_2$bpy)] (R = Me and Ph) which contain a 5-membered PtSnSSnS ring (**13**).[146] Interestingly, only two of the three R$_2$SnS units present in (R$_2$SnS)$_3$ are incorporated into the final products.

(13)
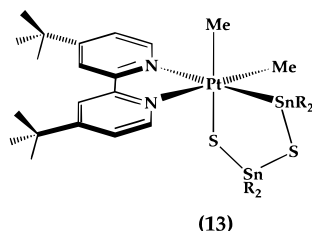
4. Lead–Carbon and Lead–Chlorine

The complex [PtMe$_2$(bpy)] reacts with Me$_3$PbCl and Me$_4$Pb to afford two different oxidative addition products, *fa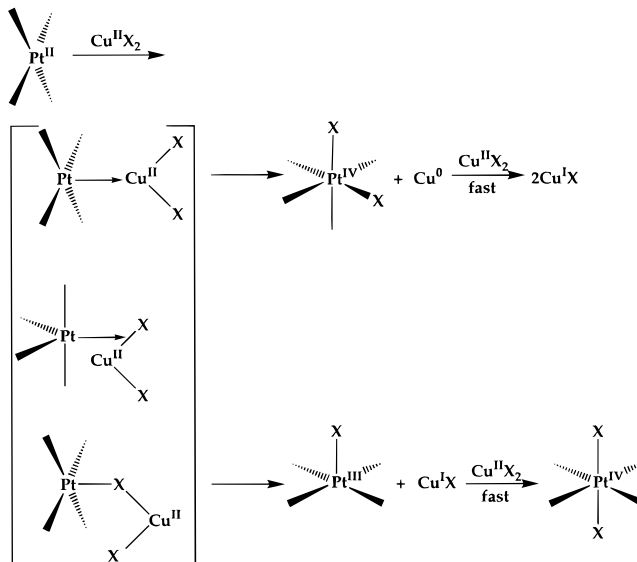c*-[PtMe$_3$Cl(bpy)] and [PtMe$_4$(bpy)], respectively, along with metallic lead.[147] The reactions are quite complicated, and several uncharacterized intermediate species were detected by UV/visible and NMR spectroscopy.

D. Metal Compounds

Oxidative addition of CuCl$_2$ and CuBr$_2$ salts to the organoplatinum(II) complexes with rigid nitrogen-donor ligands, notably [PtR(C$_6$H$_3${CH$_2$NMe$_2$}$_2$-2,6)] (R = Cl, Br, *p*-tolyl) and *cis*-[Pt(C$_{10}$H$_6$NMe$_2$-8)$_2$], have been studied by Van Koten *et al.*[14,122,123,125,128] The oxidation proceeds to give the *cis*-dihaloplatinum(IV) species as the major product in many cases. The process most likely involves an initial interaction of the filled platinum(II) d$_{z^2}$ orbital with a vacant orbital of copper(II), followed by an inner-sphere redox process to yield the final platinum(IV) product and CuX (Scheme 38, ref 128). Products arising from Pt−C bond cleavage are never detected. Other possible mechanisms are also proposed, including side-on coordination of a Cu−X bond to the platinum(II) center by donation of the filled platinum d$_{xy}$ (d$_{yz}$) orbital to the empty σ^* orbital of the Cu−X bond. A five-coordinate intermediate involving a bridging halide, i.e. Pt^{II}−X−Cu^{II}, might also be involved. In order to account for 2 equiv of CuX$_2$ salt being required for the formal oxidative addition, the au-

thors favor a mechanism for the oxidation reaction which involves a polynuclear (CuX$_2$)$_n$ species. The possible mechanisms outlined above are also feasible here, with the polynuclear copper(II) species acting as a two-electron acceptor.

The reactions of mercury(II) compounds with organoplatinum(II) complexes with nitrogen-donor ligands proceed by *trans*-metalation or oxidative addition to afford Hg metal and either the dinuclear organoplatinum(III) species or mononuclear organoplatinum(IV) compounds. Dinuclear Pt−Hg species probably act as key intermediates in such reactions.

Cis oxidative addition of stoichiometric amounts of HgX$_2$ to [PtMe$_2$(NN)] complexes affords [PtMe$_2$X-(HgX)(NN)] (NN = Ph$_2$Me$_2$phen; X = Cl, Br, I, O$_2$CMe, O$_2$CCF$_3$; NN = bpy; X = O$_2$CMe; O$_2$CCF$_3$).[148] Higher nuclearity complexes, such as the trinuclear [Pt$_2$Me$_4$(O$_2$CCF$_3$)(HgO$_2$CCF$_3$)(bpy)$_2$] and the penta-nuclear species [Pt$_4$Me$_8$(O$_2$CCF$_3$)(HgO$_2$CCF$_3$)(bpy)$_4$] (**14**) are formed by simply modifying the stoichiom-

(14)
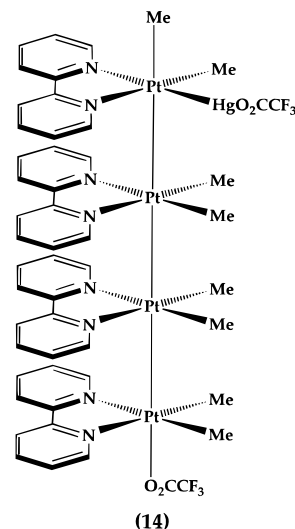
etry of the reaction. The oxidation reactions of bis-aryl cyclometalated platinum(II) complexes with mercury(II) carboxylates have also been studied.[149,150] For example, reaction of *cis*-[Pt(o-Me$_2$NCH$_2$C$_6$H$_4$)$_2$]

with $Hg(O_2CMe)_2$ affords the cyclometalated, di-nuclear Pt−Hg complex $[PtHg(O_2CMe)(\mu\text{-}MeCO_2)(\sigma\text{-}Me_2NCH_2C_6H_4)_2]$ by *cis* oxidative addition. A similar reaction with the isomeric *trans* platinum(II) precursor complex proceeds via the unstable Pt−Hg intermediate species $[(\sigma\text{-}Me_2NCH_2C_6H_4)_2Pt\text{−}Hg(O_2CMe)_2]$, followed by elimination of Hg metal and $[Pt(O_2CMe)_2(\sigma\text{-}Me_2NCH_2C_6H_4)_2]$. Related work employing thallium(III) carboxylates $Tl(O_2CR)_3$ (R = Me, ^iPr) and *trans*-$[Pt(\sigma\text{-}Me_2NCH_2C_6H_4)_2]$ gives $Tl(O_2CR)$ and the platinum(IV) species $[Pt(O_2CR)_2(\sigma\text{-}Me_2NCH_2C_6H_4)_2]$.[151] Furthermore, for the reaction of $Tl(O_2CR)_3$ with $[PtBr\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}]$ both *cis* oxidative addition and halide metathesis reactions were reported. In contrast to the Hg results, no Pt−Tl intermediates were detected for any of these reactions, and the authors propose an inner-sphere redox reaction involving the thallium(III) carboxylate.

Jawad *et al.*[147] demonstrated that the reaction of $[PtMe_2(bpy)]$ with $HgCl_2$ gives the complex formulated as $[PtMe_2Cl(HgCl)(bpy)]$ by the oxidative addition of the Hg−Cl bond, whereas reaction with $MeHgCl$ results in the formation of *fac*-$[PtMe_3Cl(bpy)]$ and Hg metal.

Addition of $[Au(PPh_3)]X$ (X = NO_3^-, BF_4^-, PF_6^-) or $[Ag(PPh_3)]BF_4$ to $[PtMe_2(bpy)]$ affords the cationic adducts $[Me_2(bpy)Pt\text{−}M(PPh_3)]X$ (M = Au, Ag) (Scheme 39),[152] the isolobal analogues of the unstable

Scheme 39
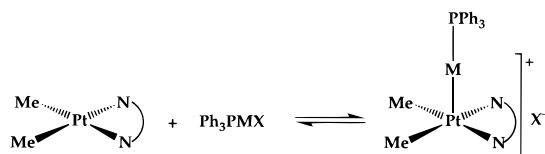
$[PtMe_2HL_2]^+$ species which are proposed as key intermediates in the protonolysis of Pt−C bonds in *cis*-$[PtMe_2L_2]$ complexes. The dinuclear adducts can be regarded as the products of a formal oxidative addition of the electrophilic silver or gold fragments to the electron-rich platinum(II) precursor. Presumably, such species are formed by overlap of the filled d_{z^2} orbital of platinum(II) with the vacant *sp* hybrid orbital on silver(I) or gold(I). Rehybridization of platinum then accompanies Pt−M bond formation.

IV. Conclusions

A variety of chemical bonds in many types of group 14, 16 and 17 substrates are cleaved both thermally and photochemically by oxidative addition to organoplatinum(II) complexes with nitrogen-donor ligands, and major insights into the various possible mechanisms of the oxidative addition reaction have been elucidated. The reactivity of these complexes is attributed to favorable electronic and steric features of the nitrogen-donor ligands which not only enhance the reactivity of the platinum(II) complex but also stabilize the resulting platinum(IV) product. Factors such as ring strain or intramolecular activation can enhance reactivity and facilitate the oxidative addition of certain bonds.

Studies of the oxidative addition reaction have resulted in the preparation of novel polymers, metallacycles, and molecules with luminescent properties.

Furthermore, the intermediates in some important catalytic cycles have been modeled with organoplatinum complexes. Indeed, the role of nitrogen-donor ligands in homogeneous catalysis, especially in asymmetric synthesis, is an area of increasing importance.[15] Platinum(II) complexes can be used to model the intermediates in reactions involving oxidative addition reactions with the more labile palladium(II) species, for example, and allow the derivation of both kinetic and thermodynamic data for these reactions. Finally, the use of the oxidative addition methodology for the construction of platinum-containing molecular superstructures, such as dendrimers, with potential applications in advanced materials is made feasible by the simplicity of the addition reaction coupled with the high yield of desired products.

The paucity of oxidative addition reactions of organoplatinum(II) complexes with groups 13 and 15 substrates shows that there exists a substantial area of research that has yet to be explored. For example, recent work has shown that the hydroboration of alkenes with boranes such as catecholborane can be made catalytic by the use of certain rhodium(I) and iridium(I) complexes,[153] but studies with platinum(II) are lacking. The catalytic amination of alkenes is another area of great topical interest,[154] and the oxidative addition of N−H bonds to a transition metal center could be a key step in such a process. Future studies of the oxidative addition reaction with organoplatinum(II) complexes containing nitrogen-donor ligands in these, and other systems of interest, are clearly warranted.

V. Abbreviations

AIBN	azobis(isobutyronitrile)
Ar	aryl
bipym	2,2′-bipyrimidine
bpy	2,2′-bipyridine
^tBu	*tert*-butyl
dmphen	2,9-dimethyl-1,10-phenanthroline
E	electrophile
en	ethylenediamine
Et	ethyl
In	initiator
L	ligand
M	metal
Me	methyl
MLCT	metal-to-ligand charge transfer
NN	diimine ligand
Nu	nucleophile
OTf	triflate (trifluoromethanesulfonate)
^iPr	*iso*propyl
^nPr	*n*-propyl
Ph	phenyl
Ph_2Me_2phen	2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
phen	1,10-phenanthroline
py	pyridine
pyen	bis(2-pyridinal)ethylenediimine
pypz	2,3-bis(2-pyridyl)pyrazine
pz	1-pyrazolyl
S	solvent
$^tBu_2bpy$	4,4-di-*tert*-butyl-2,2′-bipyridine
thpy	2-(2′-thienyl)pyridine
tmeda	*N,N,N′,N′*-tetramethylethylenediamine
vbpy	4-methyl-4′-vinyl-2,2′-bipyridine
X	halide

VI. Acknowledgments

VII. References

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CR9704671