PLATINUM(II) COMPLEXES OF PYRIDINES. A REVIEW

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The chemistry of platinum(II) complexes of pyridine and related compounds is reviewed. Also the oxidative addition reaction to platinum(II) complexes of pyridines, as a method of conversion of Pt(II) into Pt(IV) species is described. A review with 90 references.

Key words: Platinum complexes; Pyridines; Pyridine complexes; Terpyridine complexes; Bipyridine complexes; Oxidative addition.

1. INTRODUCTION

Platinum complexes of pyridines deserve much attention, they are a topic of intense investigation[1–8].

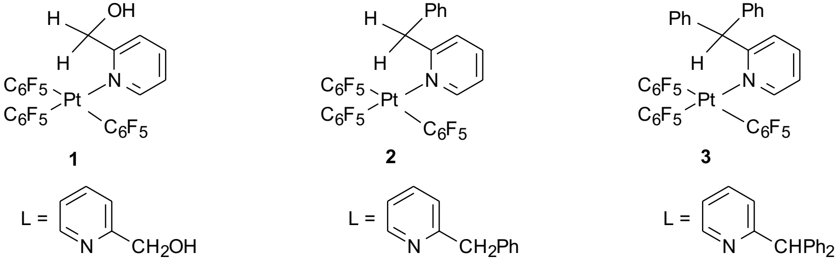
In continuation of our articles concerning transition metal complexes of azaaromatics[9–11] and treatment with metallofullerenes[12], as well as of our study of complexes of benzonaphthyridines[13], this paper reviews the chemistry of platinum(II) complexes of pyridine and related compounds. Many works concern platinum complexes of azaaromatics[14–17], these species being interesting in the context of their applications as intercalators of nucleic acids[18], catalysts[19], *etc*. Fascinating oligomeric species such as platinum molecular squares[20,21] and dendrimers[22,23] are attracting now a growing attention.

Platinum(II) complexes of pyridines have been studied in the aspect of kinetics of their syntheses[24,25] and reactivity[26–29]; their spectroelectrochemical[30–32] and dynamic NMR (refs[33,34]) results are also reported.

We present here Pt(II) complexes of pyridines along with the oxidative addition to platinum(II) complexes serving for conversion of Pt(II) into Pt(IV) species.

2. PLATINUM(II) COMPLEXES

In the study of platinum(II) complexes where pyridines serve as ligands, anionic species **1**–**3** have been synthesized by the cleavage of the pentafluorophenyl bridging system in $(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]$ (**4**) with L (Scheme 1, ref.[35]).

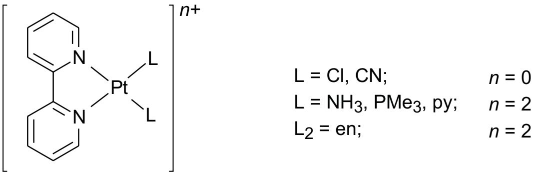


$$\underset{\mathbf{4}}{(NBu_4)_2[Pt_2(\mu\text{-}C_6F_5)_2(C_6F_5)_4]} \xrightarrow[CH_2Cl_2]{L} 2(NBu_4)[Pt(C_6F_5)_3L]$$

SCHEME 1

Complexes **1**–**3** contain ligands L with a substituent in the position 2 bearing a hydrogen atom capable of a Pt···H interaction. In contrast to quinoline complexes[36], such interactions have not been found in **1**–**3**; this difference is due to a lower rigidity of **1**–**3** as compared with that of quinoline complexes.

Electrochemical and spectroelectrochemical properties of complexes **5** have been studied (Scheme 2). In these investigations, UV/VIS/NIR spectra of the one-electron reduction products were consistent with coordinated bipyridine anion-radical species rather than d^9 metal centres[37].



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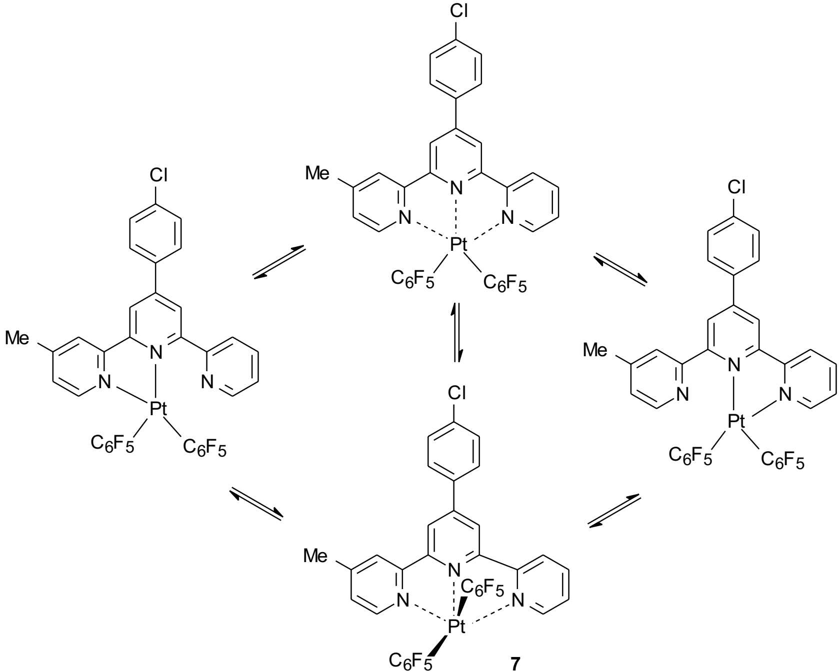
SCHEME 2

The complex [$PtLCl_2$] (**6**) (L = 4,4′-dinitro-2,2′-bipyridine) has been prepared by the following reaction.

$$K_2PtCl_4 \xrightarrow[H_2O,\ reflux]{L} [PtLCl_2]$$

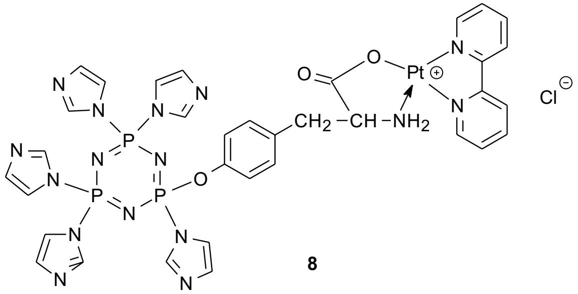
It was found that complex **6** undergoes four consecutive one-electron reductions with a small $E_1 - E_2$ separation of 180 mV. The first two are fully reversible, the third and fourth are quasi-reversible and reversible, respectively. The single and double reduction products can be electrochemically generated with formation of EPR active solutions; it may be suggested that **6** has a nearly degenerate pair of predominantly ligand-based π^* orbitals[38]. The ^{14}N coupling to the nitro group nitrogen nuclei was assigned using extended Hückel molecular orbital calculations[38].

The associative mechanism of 1,4-metallotropic shifts in the complex of substituted 2,2′:6,2″-terpyridine **7** has been revealed by $^1H/^{19}F$ NMR two-dimensional exchange spectroscopy (EXSY); the 1,4-metallotropic shifts proceed *via* five-coordinate species, as shown below (Scheme 3, refs[39,40]).



SCHEME 3

In the search for platinum(II) complexes possessing anticancer activity[41,42] complex **8** has been obtained (Scheme 4, ref.[43]).



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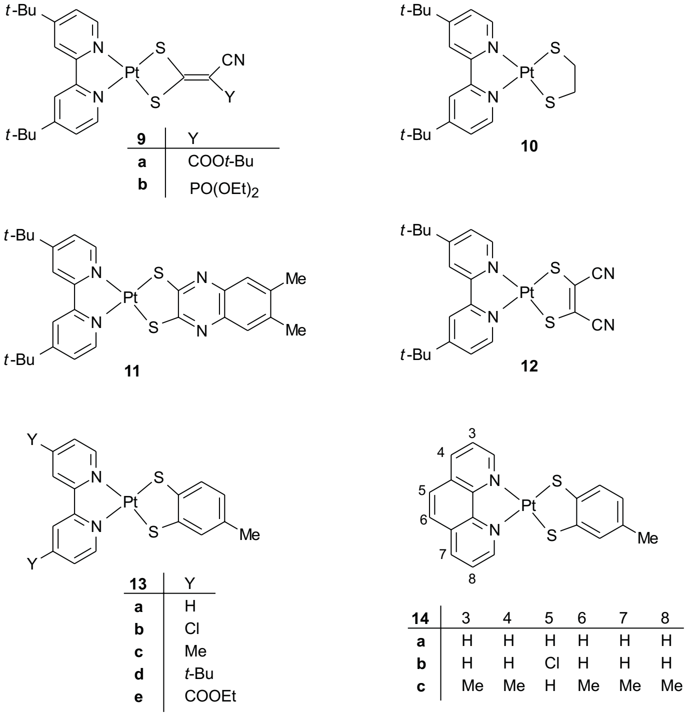
SCHEME 4

Numerous papers deal with platinum(II) diimine dithiolate complexes; some examples will be described here. In order to investigate photoluminescent properties of platinum(II) diimine dithiolate complexes, compounds **9–14** were synthesized and the influence of their molecular structure on the excited-state behaviour was examined (Scheme 5, ref.[44]).



9	Y
a	COO*t*-Bu
b	PO(OEt)$_2$

10

11

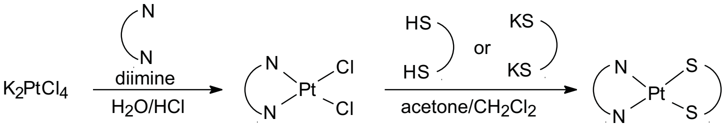
12

13	Y
a	H
b	Cl
c	Me
d	*t*-Bu
e	COOEt

14	3	4	5	6	7	8
a	H	H	H	H	H	H
b	H	H	Cl	H	H	H
c	Me	Me	H	Me	Me	Me

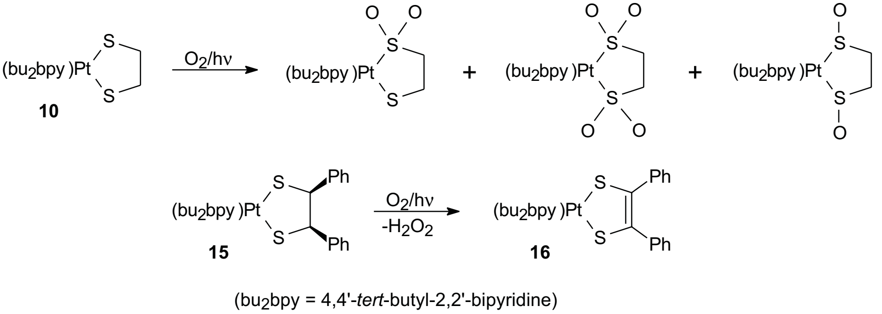
SCHEME 5

General synthetic procedure involves the treatment of K_2PtCl_4 with diimine followed by the displacement of chlorine atoms of the resulting $[Pt(diimine)Cl_2]$ with the dithiolate ligand (Scheme 6).



SCHEME 6

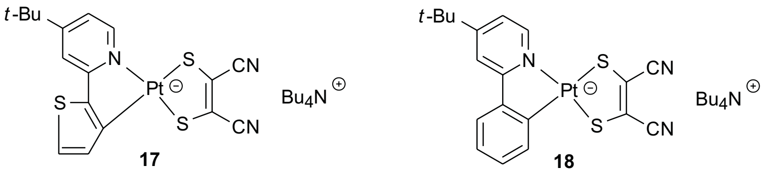
It was established that variations of the electron-donor and electron-acceptor character of ligands allow to tune important excited-state properties of **9**–**14**. All complexes exhibit solvatochromic absorption bands and solution luminescence, attributed to transition from a common MLCT to the diimine excited state. The nonradiative and radiative decay rate constants have been calculated. Based on spectroscopic and electrochemical data, the excited-state redox potentials of **9**–**14** have been estimated. The photooxidation of complexes **10** and **15** has been investigated (Scheme 7).



SCHEME 7

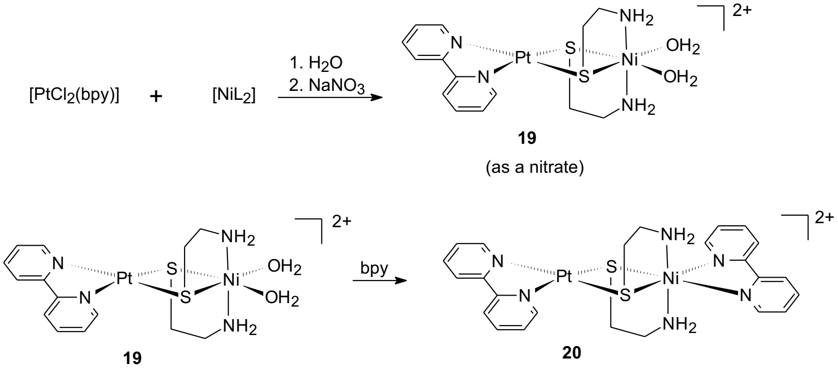
The reaction involves $^1O_2$ as the active oxidizing agent. $^1O_2$ is formed by energy transfer from the luminescent charge transfer to diimine excited state of the [diimine)(dithiolate)Pt(II)] complexes. It was established that the photooxidation of **10** leads to the *S*-oxygenated complexes, while in the case of **15**, the dehydrogenation product **16** is formed[45].

One should mention here also investigation of spectroscopic and electrochemical properties of complexes **17** and **18** (Scheme 8). The results show that **17** is luminescent in solutions while **18** exhibits luminescence only in the solid state at room temperature[46,47].



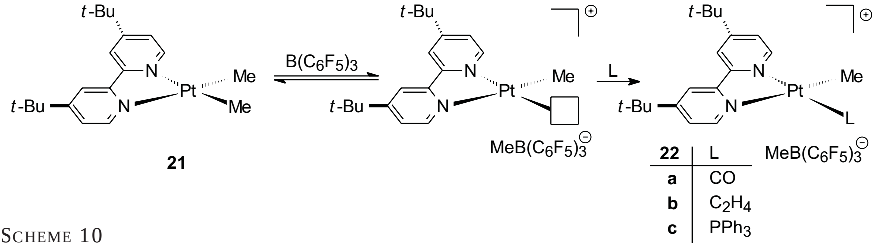
Scheme 8

In the study of dinuclear complexes, the reaction of $[PtCl_2(bpy)]$ with $[NiL_2]$ (L = 2-aminoethanethiolate) was performed (Scheme 9). In the obtained *S*-bridged Pt(II)–Ni(II) complex, $[Pt(bpy)\{NiL_2(H_2O)_2\}]^{2+}$ (**19**), the Ni(II) ion has an octahedral and not a square-planar geometry. The treatment of **19** with 2,2′-bipyridine results in the formation of the complex **20** (Scheme 9, ref.[48]).



Scheme 9

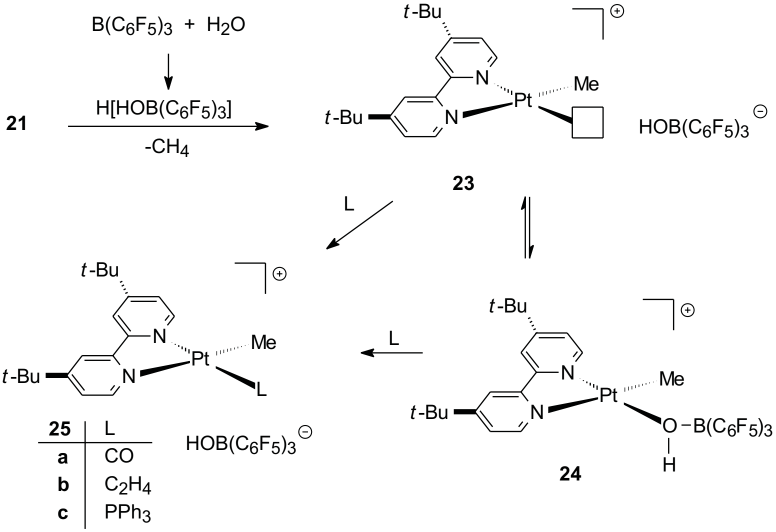
In investigation of methylplatinum complexes it was observed that the interaction of $[PtMe_2(bu_2bpy)]$ (**21**) with $B(C_6F_5)_3$ in the presence of ligand L = CO, C_2H_4, PPh_3, occurring under anhydrous conditions, affords **22a**–**22c**, respectively (Scheme 10, refs[49,50]).



Scheme 10

However, in the presence of water, $B(C_6F_5)_3$ does not directly attack the Pt–Me bond of **21** but forms an adduct $[H_2O{\cdot}B(C_6F_5)_3]$ which acts as a strong acid $H[HOB(C_6F_5)_3]$.

The rapid protonation of the Pt–Me bond in $[PtMe_2(bu_2bpy)]$ (**21**) by this acid leads to the cationic intermediate $[PtMe(bu_2bpy)]^+[HOB(C_6F_5)_3]^-$ (**23**) under the loss of CH_4. The complex **23** in the absence of L forms $[Pt\{HOB(C_6F_5)_3\}Me(bu_2bpy)]$ (**24**) while in the presence of L, complexes $[PtMeL(bu_2bpy)][HOB(C_6F_5)_3]$ (**25a**–**25c**) result (Scheme 11).

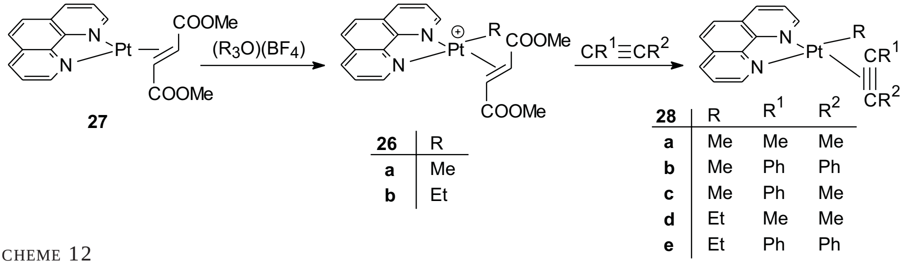


SCHEME 11

Thus, when no ligand is present, the low-temperature reaction of $[PtMe_2(bu_2bpy)]$ (**21**) with $B(C_6F_5)_3$ and water affords **24** and CH_4. It should be noted that **24** is an interesting example of a transition-metal complex containing the coordinated $[HOB(C_6F_5)]^-$ ligand. The $[HOB(C_6F_5)_3]^-$ ligand in **24** is only weakly bound to platinum; the reaction of **24** with CO, C_2H_4 and PPh_3 affords complexes **25a**–**25c**, respectively[49,51].

Square-planar cationic Pt(II) complexes containing methyl and an alkene in *cis*-position deserve a special interest; an example is *cis*-$[PtR(\eta^2\text{-}E\text{-}MeOOCCH{=}CHCOOMe)(phen)]^+(BF_4)^-$ (**26a**, **26b**) formed *in situ* by treatment of the three-coordinated complex **27** with $(R_3O)^+(BF_4)^-$ (R = Me, Et) (refs[52,53]).

The fumarate is weakly bound to platinum and can be easily replaced by alkynes. The formed **28a**–**28e** are stable and can be isolated when the disubstituted electron rich alkyne is used (Scheme 12).

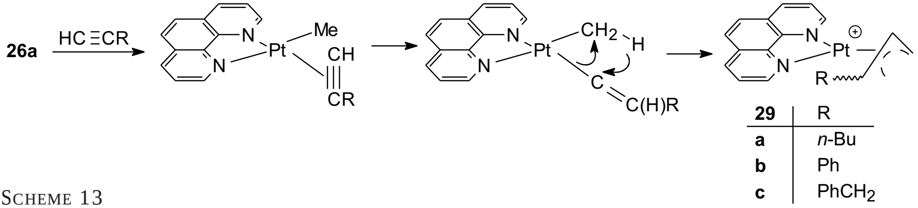


26	R
a	Me
b	Et

28	R	R^1	R^2
a	Me	Me	Me
b	Me	Ph	Ph
c	Me	Ph	Me
d	Et	Me	Me
e	Et	Ph	Ph

SCHEME 12

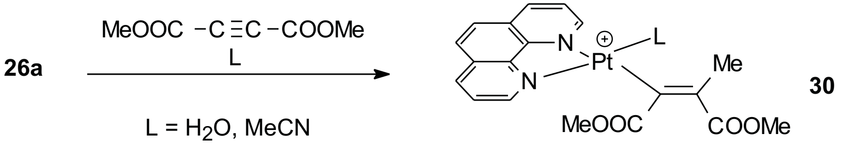
When complex **26a** was treated with terminal electron-rich alkynes, stable η^3-allyl species **29a**–**29c** were rapidly formed; the proposed mechanism involves the hydride shift (Scheme 13). This interesting rearrangement provides a new approach to η^3-allyl derivatives.



29	R
a	*n*-Bu
b	Ph
c	PhCH$_2$

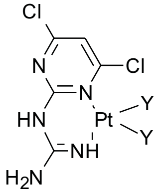
SCHEME 13

However, when complex **26a** is treated with disubstituted electron-poor alkyne, *e.g.* dimethyl acetylenedicarboxylate, its *cis*-insertion into the Pt–R bond occurs, the resulting empty coordination site being occupied by a weak donor present in solution, *e.g.* H$_2$O or MeCN to give the σ-vinyl derivative **30** (Scheme 14).



SCHEME 14

Much attention is paid to DNA intercalators[2]; for this purpose, many platinum complexes have been synthesized[54–57]. Having in view the interesting biological activities of guanidinopyrimidines, complexes **31** have been prepared and their IR and UV/VIS spectra discussed (Scheme 15, refs[58,59]).

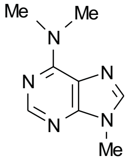


Y = Cl, Br, I, NO_3, NCS

31

Scheme 15

In the study of Pt(II) complexes of methylated adenines[60] it was found that in trimethylated adenine **32**, positions 1 and 7 are sterically blocked, which makes the metal coordination impossible; therefore the binding of *trans*-$[Pt(NH_3)_2Cl_2]$ or of Pt(dien) moieties (dien = diethylenetriamine) resulting in **33** or **34**, respectively, occurs through N3. However, the presence of only one methyl at NH_2 group, as in dimethyladenine **35** allows the binding of Pt to N7, since the N6 methyl group may adopt an *anti*-orientation with respect to 7 position (Scheme 16, refs[60,61]).



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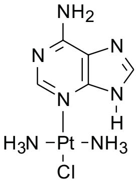

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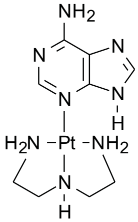

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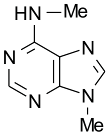
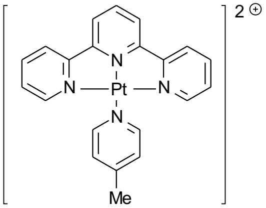


35

Scheme 16

It is known that cation **36** is an effective intercalator of poly(dA-T)$_2$, better than cation **37** (Scheme 17).



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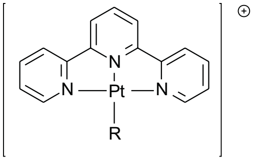
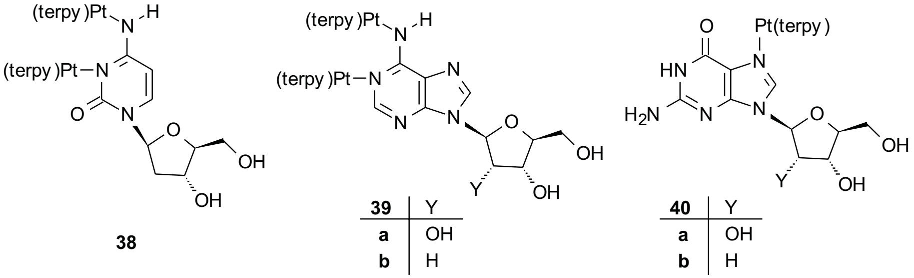


37

R = Cl, SCH_2CH_2OH

Scheme 17

The picoline ligand undergoes a displacement by nucleosides 2′-deoxycytidine, adenosine, 2′-deoxyadenosine, guanosine and 2′-deoxyguanosine acting as nucleophiles[18,62]. The reaction of cation **36** with 2-deoxycytidine gives compound **38** diplatinated at N1 and N6; with adenosine and 2′-deoxyadenosine, compounds diplatinated at N1 and N6, **39a** and **39b**, respectively, are formed. On the other hand, in the case of guanosine and 2′-deoxyguanosine, compounds monoplatinated at N7, **40a** and **40b**, respectively, have been obtained (Scheme 18).



38

39	Y
a	OH
b	H

40	Y
a	OH
b	H

SCHEME 18

The interaction between $[Pt(bpy)_2L_2]^{2+}$ (**41**) (L = 2-Rpy, 4-Rpy; R = H, Cl, CN, NH_2, Me, Ph) and calf-thymus DNA was studied. Complexes $[Pt(bpy)_2L_2](PF_6)_2$ were prepared by the reaction of $[Pt(bpy)Cl_2]$ with corresponding pyridine derivatives (Scheme 19).

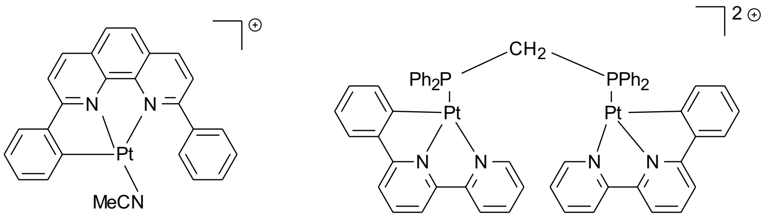
$$[Pt(bpy)Cl_2] \xrightarrow[]{\substack{1.\ L/H_2O \\ 2.\ NH_4PF_6}} \underset{\mathbf{41}}{[Pt(bpy)_2L_2](PF_6)_2}$$

SCHEME 19

The results show that the binding affinity of **41** for DNA increases with the increase of the pK_a of the coordinated pyridine (the only exception is 2-methylpyridine, due to steric reasons)[63]. The intercalation takes place through stacking of the bipyridyl moieties; no insertion of pyridine rings, oriented out of plane was detected[63].

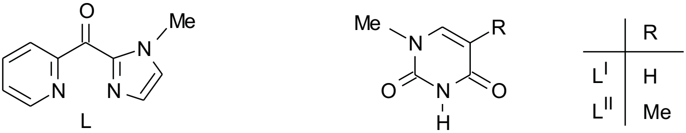
Intercalation of cyclometallated platinum(II) complexes **42** and **43** (Scheme 20) into calf-thymus DNA causes a considerable enhancement of photoluminescence, allowing their application as luminescent switches[64,65].

In the absence of calf-thymus DNA, **42** and **43** exhibit a relatively weak photoluminescence. An addition of DNA to **42** leads to the red shift of the emission maxima, and that to **43** , to the blue shift. It was established that the binding of **42** with calf-thymus DNA is stronger than that of **43**.



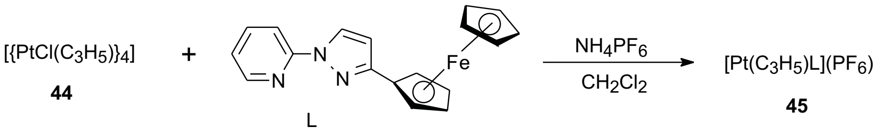
SCHEME 20 **42** **43**

In the study of platinum complexes as antitumour species, it was found that the reaction of $[PtL(H_2O)_2](NO_3)_2$ with 1-methyluracil HL' and 1-methylthymine HL'' affords dinuclear complexes $[Pt_2L_2L'](ClO_4)_2$ and $[Pt_2L_2L''](ClO_4)_2$, respectively, along with the side product $[PtL_2](ClO_4)_2$ formed by a ligand exchange (Scheme 21, ref.[66]).



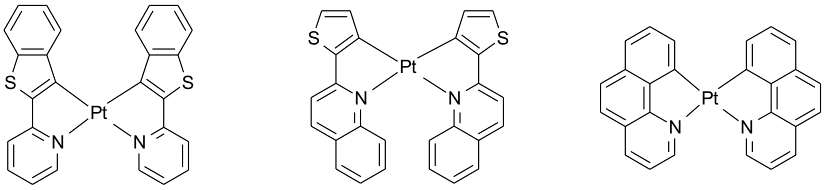
SCHEME 21

An example of the ligand bearing a ferrocene system is the didentate compound L in Scheme 22 (ref.[67]). The reaction of the allylplatinum complex **44** with L and NH_4PF_6 gives $[Pt(C_3H_5)L](PF_6)$ (**45**).



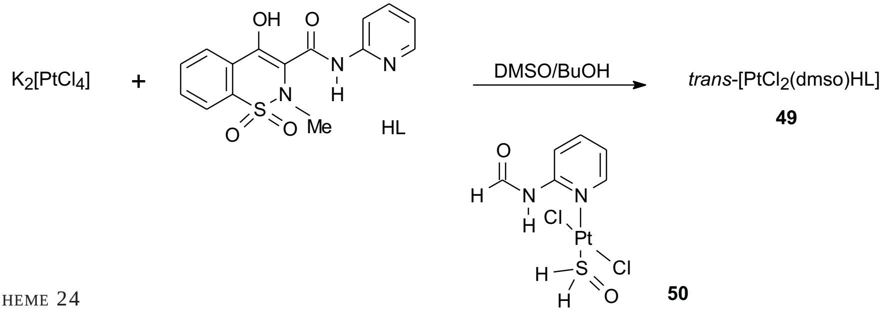
SCHEME 22

Platinum (II) *cis*-bishomoleptic complexes **46**–**48** (Scheme 23) have been obtained by metal exchange of $[Pt(Et_2S)_2]Cl_2$ with lithiated ligands; the mechanism of the process is proposed[68].



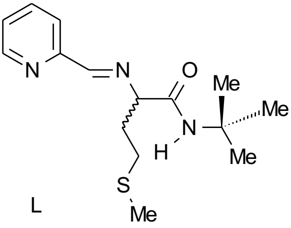
SCHEME 23 **46** **47** **48**

It was found that $K_2[PtCl_4]$ reacts with the antiinflammatory drug piroxicam HL to give the complex **49** (Scheme 24, refs[69,70]). The investigation of crystal and molecular structure of **49** shows that the pyridyl nitrogen atom is the preferred donor, and not the hydroxy or amide oxygen or benzothiazine nitrogen atom. In the extended Hückel molecular orbital analysis of an analog **49**, *trans*-$[PtCl_2(H_2SO)\{NC_5H_4(NHCOH)\text{-}2\}]$ (**50**) was investigated as a model molecule (Scheme 24).



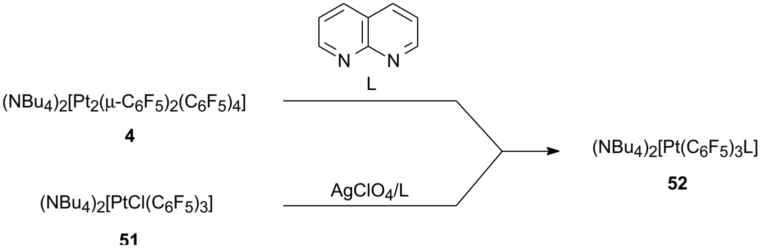
SCHEME 24

The reaction of $[PtI_2(cod)]$ with a tridentate ligand L affords [PtI(L)]I (cod = cyclo-1,5-octadiene) (Scheme 25, ref.[71]).



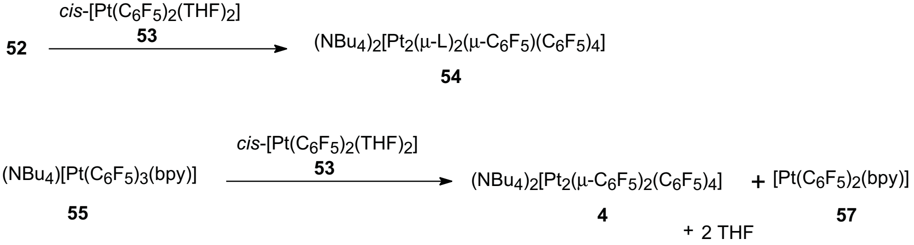
SCHEME 25

Homo- and heterodinuclear complexes of platinum are known; some examples will be described here. The reactions of Pt complexes **4** and **51** with 1,8-naphthyridine L used as a didentate ligand lead to **52** (Scheme 26).



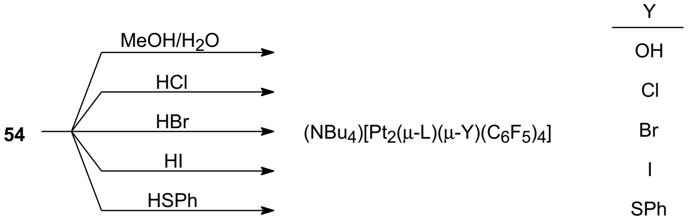
SCHEME 26

The treatment of **52** with *cis*-[Pt(C_6F_5)$_2$(THF)$_2$] (**53**) affords the dinuclear complex **54**. It should be noted that similar reaction of **55** with **53** does not give the dinuclear derivative; instead **4** and **57** are formed because bpy acts here as a chelating agent and not as a bridging one (Scheme 27).



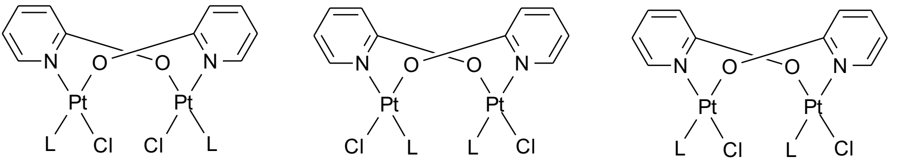
SCHEME 27

The substitution of the bridging C_6F_5 in **54** with Y = OH, Cl, Br, I, SPh proceeds as shown below (Scheme 28, ref.[72]).



SCHEME 28

Dinuclear platinum complexes of the type [Pt_2Cl_2(μ-Opy)$_2$$L_2$] (Opy = pyridin-2-olate ion; L = PEt_3, PBu_3, PMe_2Ph, $PMePh_2$) have been synthesized and characterized. These species are obtained by treatment of a CH_2Cl_2 solution of [$PtCl_2$(μ-Cl)$_2$$L_2$] with solid AgOpy (ref.[73]). Three isomeric complexes **58**–**60** are possible (Scheme 29). The isomerization of **58**, **59** and **60**



58
L *trans* to O

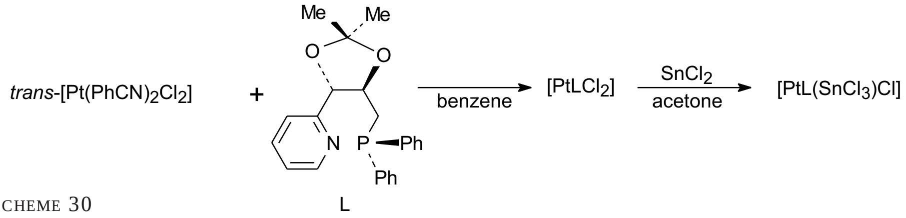
59
L *trans* to N

60
cis
(one L *trans* to O
and the other *trans* to N)

SCHEME 29

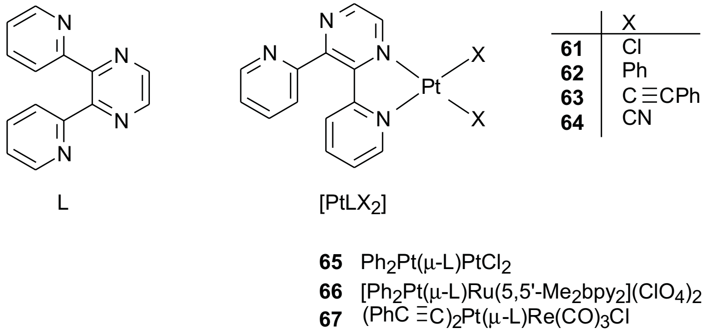
occurs when the compounds are left for several days or heated for a few minutes. The population of the isomers depends on reaction conditions; when $[Pt_2Cl_2(\mu\text{-}Cl)_2(PEt_3)_2]$ reacted with AgOpy in refluxing benzene, **58** was formed exclusively[73].

In the study of didentate compounds containing both N and Pt centers in the ligand molecule, square-planar platinum(II) complexes $[PtLCl_2]$ and $[PtL(SnCl_3)Cl]$ where L is a chiral pyridyl phosphine hybrid ligand, have been obtained (Scheme 30, ref.[74]).



SCHEME 30

Platinum complexes **61**–**67** with 2,3-bis(2-pyridyl)pyrazine L used as a ligand, have been synthesized and their spectroscopic properties investigated (Scheme 31).



	X
61	Cl
62	Ph
63	C≡CPh
64	CN

65 $Ph_2Pt(\mu\text{-}L)PtCl_2$
66 $[Ph_2Pt(\mu\text{-}L)Ru(5,5'\text{-}Me_2bpy_2](ClO_4)_2$
67 $(PhC{\equiv}C)_2Pt(\mu\text{-}L)Re(CO)_3Cl$

SCHEME 31

Complexes **61**–**64** and dinuclear compounds **65**–**67** were prepared in the following way (Scheme 32).

Complexes **61**–**64** show luminescence in the solid state, while **63** and **64** are also emissive in solution at room temperature. The heterodinuclear complexes **66** and **67** are emissive both in the solid state and in solution. These properties are interesting for the use of the above complexes as photocatalysts[19].

$$[Pt(MeCN)_2Cl_2] \xrightarrow[\text{MeCN}]{L} \mathbf{61}$$

$$[Pt(cod)Ph_2] \xrightarrow[\text{benzene}]{L} \mathbf{62}$$

$$[Pt(cod)(C{\equiv}CPh)_2] \xrightarrow[\text{MeCN}]{L} \mathbf{63}$$

$$Pt(CN)_2 \, . \, xH_2O \xrightarrow[\text{DMF}]{L} \mathbf{64}$$

$$[PtLPh_2] \xrightarrow[\text{MeCN}]{[Pt(MeCN)_2Cl_2]} \mathbf{65}$$

$$[PtLPh_2] \xrightarrow[Me_2CO]{[Ru(5,5'Me_2bpy)_2(H_2O)_2](ClO_4)} \mathbf{66}$$

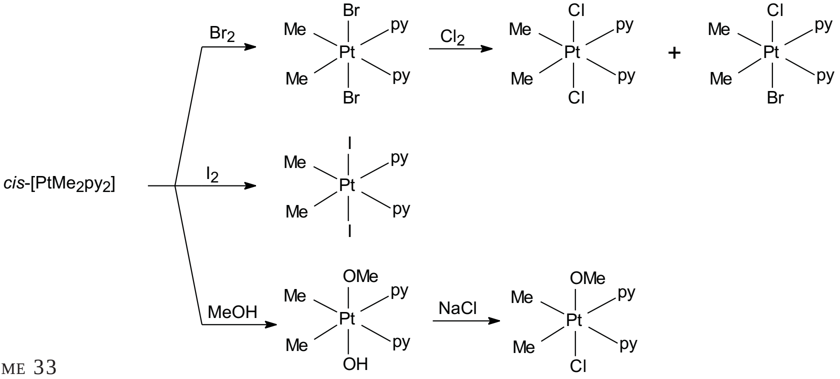
$$[PtL(C{\equiv}CPh)_2] \xrightarrow[\text{MeCN}]{[Re(CO)_3Cl(MeCN)_2]} \mathbf{67}$$

SCHEME 32

3. OXIDATIVE ADDITION TO Pt(II) COMPLEXES

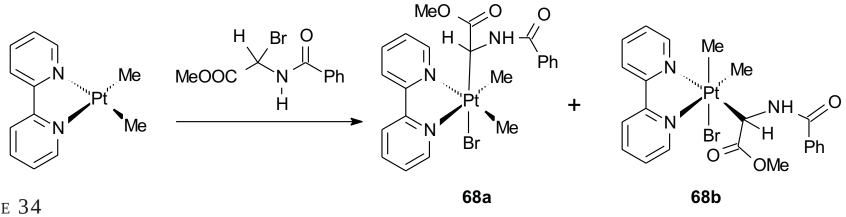
Platinum(II) complexes of pyridines may be converted into platinum(IV) complexes[75]. A synthetic approach to platinum(IV) complexes $[PtA_2BB'L_2]$ is the oxidative addition of a halogeno derivative BB′ to *cis*-$[PtA_2L_2]$ (L = monodentate azaaromatic, such as pyridine, or L_2 = didentate azaaromatic, such as 2,2′-bipyridine); some examples of these reactions will be presented[76].

Synthetic procedures for dimethylplatinum(IV) compounds of the type $[PtMe_2X_2py_2]$ and $[PtMe_2XYpy_2]$ (X, Y = anionic ligands) have been reported (Scheme 33, ref.[77]).



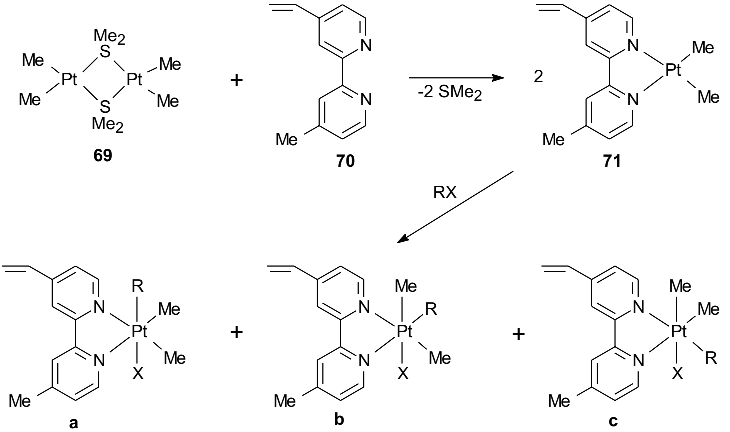
SCHEME 33

The oxidative addition of methyl (benzoylamino)bromoacetate to [$PtMe_2$(bpy)] leads to [(bpy)Me_2(Br)PtC(BzNHCHCOOMe)] (**68**) as a mixture of *cis*- and *trans*-isomers **68a** and **68b** (Scheme 34). It was established that **68a** is thermodynamically preferred. After 12 h at –76 °C the ratio **68a**/**68b** is 1 : 5; for the shorter reaction time (2 h), it is 1 : 2 (refs[23,78,79]).



SCHEME 34

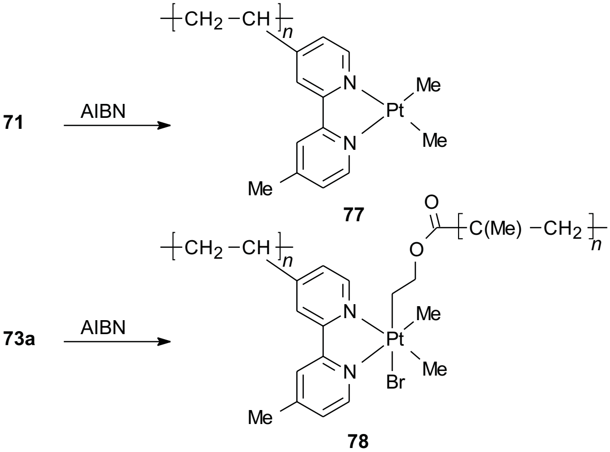
For the study of polymers containing Pt(II) complexes, the monomers possessing two polymerizable vinyl groups were obtained. The reaction of [$Pt_2Me_4(\mu\text{-}SMe_2)_2$] (**69**) with bipyridine **70** bearing one vinyl group (v-bpy) involves the displacement of the weakly bound Me_2S ligands by the bipyridine leading to [$PtMe_2$(v-bpy)] (**71**). The oxidative addition of vinyl-functionalized organic halide to **71** gives products **72**–**76** containing two vinyl groups. In the case of **72**–**74**, three isomers are formed, while **75** and **76** are obtained exclusively as **75a** and **76a** (Scheme 35, ref.[78]).



	R	X
72abc	$CH_2COOCH{=}CH_2$	Br
73abc	$CH_2CH_2OOC\text{-}C(Me){=}CH_2$	Br
74abc	$C({=}O)\text{-}CH{=}CH_2$	Cl
75a	$3\text{-}CH_2\text{-}C_6H_4\text{-}CH{=}CH_2$	Cl
76a	$4\text{-}CH_2\text{-}C_6H_4\text{-}CH{=}CH_2$	Cl

SCHEME 35

Polymerization of **71** and **73a** affords polymers **77** and **78** (AIBN = 2,2′-azobisisobutyronitrile) (Scheme 36).



SCHEME 36

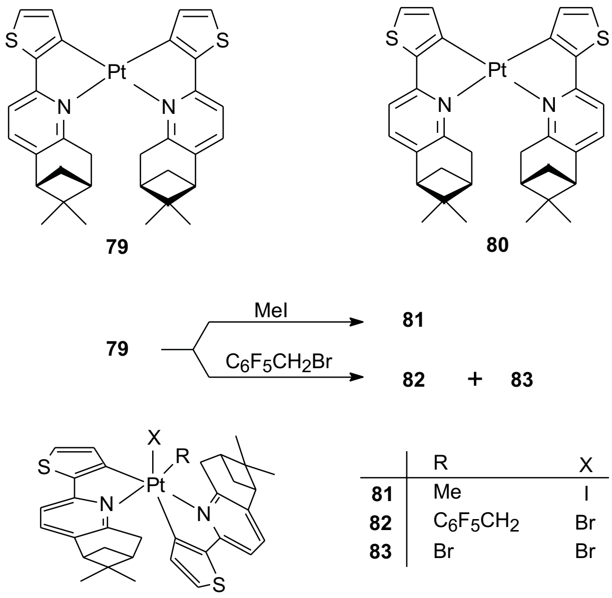
Kinetics of the oxidative additions of MeI and EtI to [PtMe$_2$(bpy)] has been studied; in order to accelerate the process, the pressure of the range 0–200 MPa was used (Scheme 37). The stopped-flow spectrophotometry results indicate the pseudo-first order rate of these reactions[80]. Such processes provide new routes to organometallic polymers[80].

$$[Me_2Pt(bpy)] \xrightarrow[R = Me, Et]{RI} [RMe_2Pt(bpy)]^{\oplus} + I^{\ominus} \longrightarrow [RMe_2Pt(bpy)I]$$

SCHEME 37

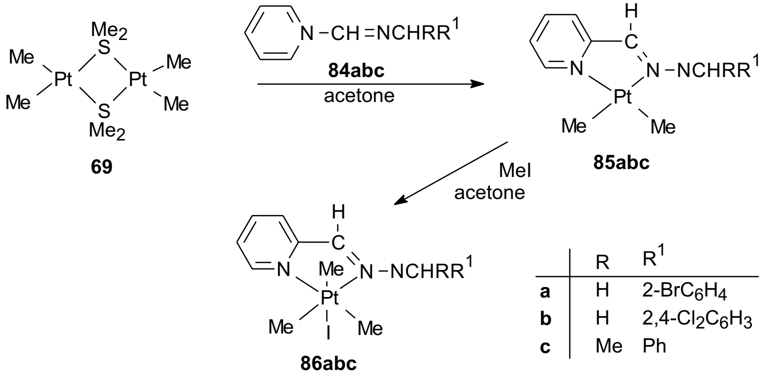
cis-Homoleptic platinum(II) complexes **79** and **80** rank among Pt(II) complexes with strongly sterically interacting ligands. They possess helical chirality. Thermal oxidative addition of MeI to **79** leads to one isomer **81**; similar reaction with the use of $C_6F_5CH_2Br$ gives one isomer **82** along with the unexpected dibromo derivative **83** (Scheme 38). On the other hand, the thermal oxidative addition of $C_6H_5CH_2Br$ to **80** under the same conditions affords three isomeric products[81].

The reaction of [Pt$_2$Me$_4$(μ-SMe$_2$)$_2$] (**69**) with aldimines **84a**–**84c** leads to **85a**–**85c** which were subjected to the oxidative addition of MeI, resulting in platinum(IV) complexes **86a**–**86c** (Scheme 39). It should be noted, that ligand **84c** is optically active, therefore platinum(IV) compound **86c** is a mixture of two diastereoisomers[82].



	R	X
81	Me	I
82	$C_6F_5CH_2$	Br
83	Br	Br

SCHEME 38



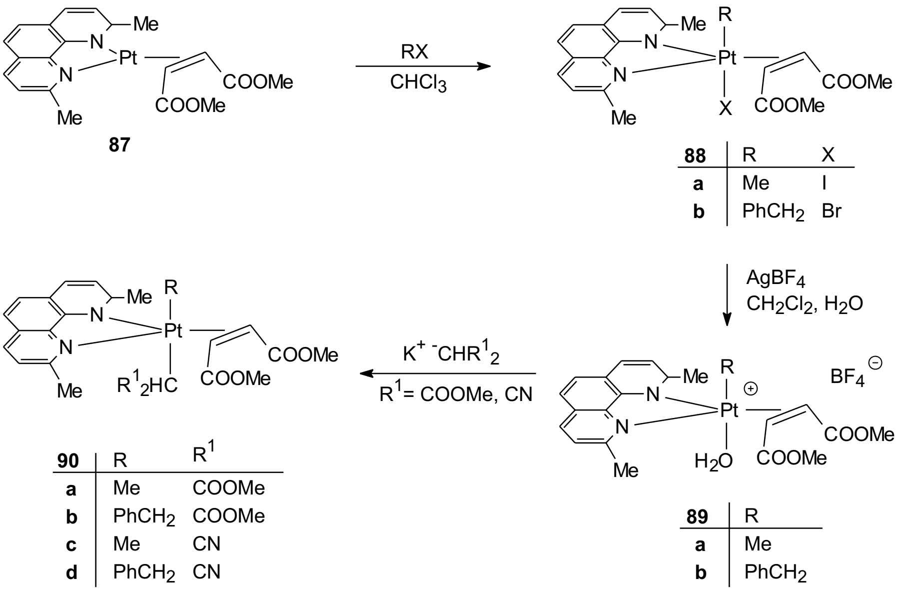
	R	R^1
a	H	$2\text{-}BrC_6H_4$
b	H	$2,4\text{-}Cl_2C_6H_3$
c	Me	Ph

SCHEME 39

In order to obtain trigonal bipyramidal Pt(II) complexes containing two axial groups bonded through σ-carbon bond, the following reactions of the three-coordinate platinum complex **87** have been performed (Scheme 40).

Complexes **88** abstract halide in the presence of $AgBF_4$ to give corresponding cationic species **89**. The neutral axial donor of complexes **89**, H_2O

molecule undergoes a displacement by treatment with a carbon nucleophile $R^1_2CH^-$ affording **90a**–**90d** (refs[83,84]).



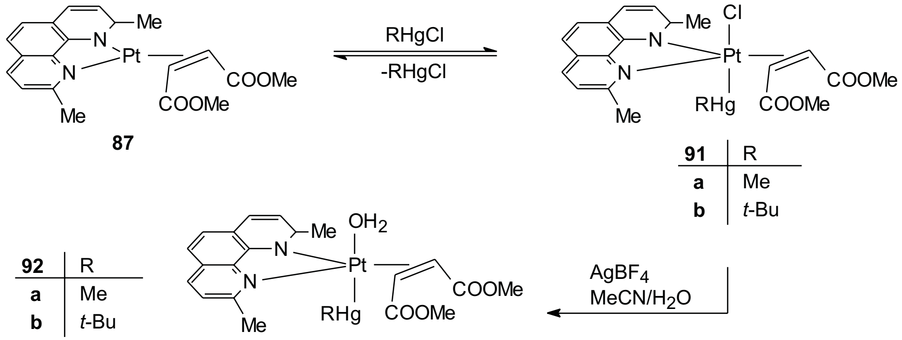
88	R	X
a	Me	I
b	$PhCH_2$	Br

89	R
a	Me
b	$PhCH_2$

90	R	R^1
a	Me	COOMe
b	$PhCH_2$	COOMe
c	Me	CN
d	$PhCH_2$	CN

SCHEME 40

The oxidative addition of RHgCl to complex **87** leads to **91a**, **91b** which, in the presence of $AgBF_4$ and $MeCN/H_2O$, afford **92a**, **92b** (Scheme 41).

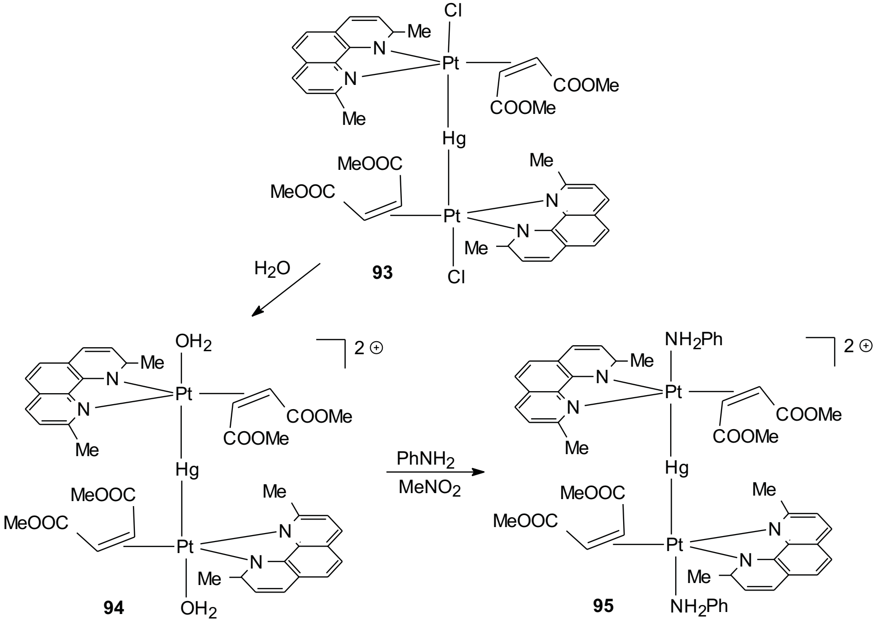


91	R
a	Me
b	*t*-Bu

92	R
a	Me
b	*t*-Bu

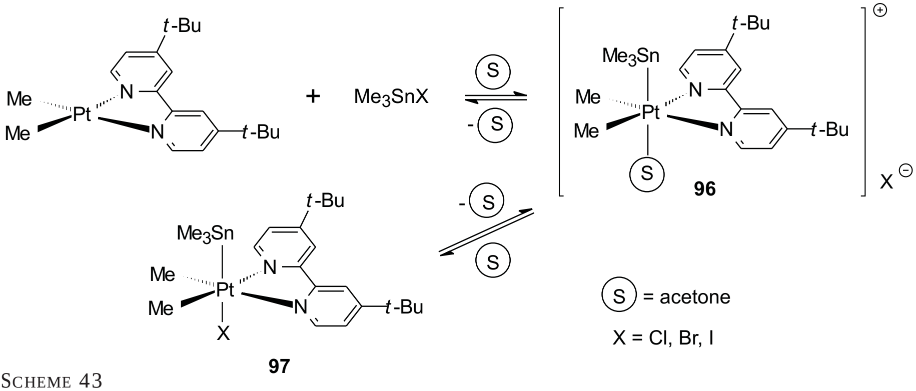
SCHEME 41

If R = Cl, then **93** results[85–87]. In **93**, the chloride atom is easily substituted by a water molecule to give the cationic species **94** converted by treatment with aniline into the cationic cluster **95** (Scheme 42).



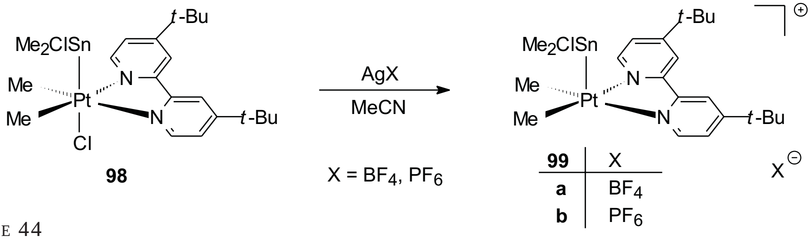
SCHEME 42

The reversible oxidative addition of Me_3SnCl to $[PtMe_2(bu_2bpy)]$ proceeding *via* a thermodynamically stable cationic intermediate **96** leads to **97** (Scheme 43, ref.[88]).



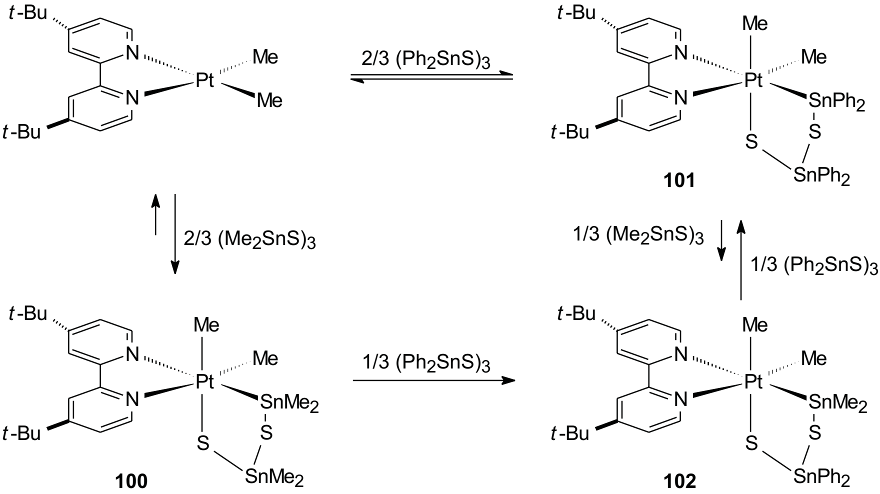
SCHEME 43

It was established that silver salts abstract halide from [PtClMe$_2$(Me$_2$SnCl)(bu$_2$bpy)] (**98**) to give cationic platinum(IV) complexes **99a**,**99b** (Scheme 44, ref.[88]). Analogous cationic silylplatinum(IV) complexes are less stable than **99**.



SCHEME 44

Strongly luminescent **100**–**102** are examples of complexes containing five-membered Pt–Sn–S–Sn–S rings. These species are obtained by the following reactions (Scheme 45, refs[89,90]).



SCHEME 45

Complex **102** is also formed by a redistribution process between **100** and **101** (ref.[89]).

4. CONCLUSION

Reactions described in the first part of the above review deal with syntheses of platinum(II) complexes of pyridines and their chemical properties. The recently reported examples of oxidative addition, given in the second part, show a convenient approach to Pt(IV) complexes.

So platinum(II) as platinum(IV) complexes of azaaromatics are of interest from the theoretical and practical viewpoints – here their applications as DNA intercalators, redox systems, luminescent switches and catalysts should be mentioned; an attempt has been made, in this paper, to present a concise account of this rapidly developing research area.

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