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Three-Coordinate [Pt(*N*,*N′*-chelate)(η^2-olefin)] Complexes: Synthesis, Properties and Reactions with Electrophiles

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Dedicated to Prof. Achille Panunzi on the occasion of his retirement

Keywords: Platinum / N ligands / Chelates / Olefin complexes / Oxidation

This review provides a survey of the key-class of Pt^0 complexes of general formula [Pt(*N*,*N′*-chelate)(η^2-olefin)]. The main spectroscopic, structural and chemical features are discussed, in terms of electronic and steric properties of the ancillary ligands. The versatile reactivity towards electrophiles is described as a very useful entry to Pt^{II} compounds with a wide assortment of ligands, such as halido, hydrido, hydrocarbyl, organometal, organoelement and carbene fragments, in some cases stabilised for the first time by the careful choice of the *N*,*N′*-ligand. Remarkably, the reactions can be an equilibrium, and their relevant thermodynamic parameters have also been collected, thus allowing a thorough discussion of the electronic and steric factors which affect its position.

Introduction

Within the rich chemistry of Group 10 metals a prominent role is played by molecular compounds in which the metal oxidation state is zero.[1] Complexes of Ni^0 and Pd^0 are especially appreciated as precursors or active species in relevant catalytic processes, given their distinct reactivity and the immediate availability of the higher oxidation state (II). On the contrary, the corresponding Pt^0 derivatives stand out for a superior stability and the consequent option to be decorated with a wider selection of ancillary ligands.

These complementary behaviours offer a comprehensive scenario, because Ni^0 and Pd^0 species can be preferred for synthetic purposes, while the more versatile Pt^0 derivatives allow a better comprehension of bonding properties and give insight into mechanistic details.

In all cases good π-acceptor ligands[2] are required for stabilising the low oxidation state. Beside the established and traditional phosphanes, over the years unsaturated molecules (principally alkenes or alkynes) and heterodonor bidentate ligands have been alternatively favoured, due to their precise features which in several occasions can be more suited than those of phosphanes.[3]

Within this fruitful context, trigonal Pt^0 complexes of general formula [Pt(*N*,*N′*-chelate)(η^2-olefin)] (**III**) have been widely investigated, because this combination of ligands provides highly flexible compounds along with a tuneable control of several physical and chemical properties.

Aim of this review is to furnish a complete survey of the complexes of type **III** prepared so far, with a description of their essential spectroscopic and structural features, and of their reactivity. This latter analysis will disclose the peculiar ability of the compounds to undergo oxidative addition, giving access to hundreds of five-coordinate Pt^{II} compounds (**V**) with a wide assortment of ligands. In very few and remarkable occasions, this reaction was found to be an equilibrium, and its occurrence allowed the disclosure of relevant trends and the evaluation of fundamental thermodynamic parameters.

Furthermore, the coordinative saturation of type-**V** products, prompted by the accurate choice of the *N*,*N′*-ligand, revealed to be essential for the stabilisation of previously unknown fragments, such as Pt–HgR (R = simple alkyl) and Pt–PbR_2Cl (R = Me and Ph), usually involved in fast decomposition processes.

Finally, the availability of strictly related compounds made a consistent assessment of the coordinating properties of several ligands possible, and the compilation of a homogeneous sequence of their *trans*-influence.

Synthesis of Three-Coordinate [Pt(*N*,*N′*-chelate)(η^2-olefin)] Complexes (III)

The three-coordinate complexes of type **III** prepared so far are reported in Table 1 along with references for their synthesis, spectroscopic or structural characterisation.

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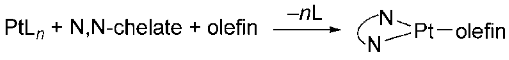
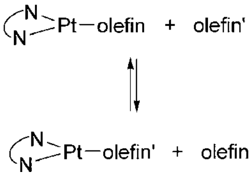
The complexes are usually obtained by reacting suitable Pt^0 precursors, such as Pt(dibenzylideneacetone)$_2$, Pt(1,5-cyclooctadiene)$_2$ or Pt(norbornene)$_3$ in the presence of the alkene and the *N,N′*-ligand (Scheme 1).



III

Scheme 1. Synthesis of complexes of type **III**.

An alternative procedure involves exchange of the alkene from another complex of type **III** (Scheme 2), which can be usefully adopted when the incoming olefin is more electron-poor of the leaving olefin (see below for a rationalisation of this behaviour).



Scheme 2. Alternative synthesis of complexes of type **III**.

In most cases, type-**III** complexes are air-stable and readily soluble in chlorinated solvents. Remarkable exceptions are propylene and ethylene derivatives, which promptly react with chlorinated solvents, and must be either used in situ or stored in the cold for preventing fast deposit of Pt black. In other cases, the appropriate choice of hydrophilic *N,N′*-chelates (**20**–**24**, **37**) prompts solubility in water.

Spectroscopic and Structural Features of [Pt(*N,N′*-chelate)(η^2-olefin)] Complexes (III)

The common feature of all the *N,N′*-ligands used for the synthesis of type-**III** complexes (phenanthrolines, bipyridyls or imines) is the presence of two sp^2-hybridized nitrogen atoms, apt to form a five-member cyclometallate ring upon chelation. This requirement plausibly reflects the ability of heteroaromatic rings to establish a definite contribution of π-backdonation with metals in low oxidation states.[26] However, the most distinctive structural feature of complexes of type **III** is the presence of the η^2-bonded alkene. The entire bouquet covers a wide range of olefins, from strongly electron-poor (e.g. tetracyanoethylene) to electron-rich donor systems (propylene). According to the Chatt–Dewar–Duncanson model of bonding,[2] linkage to the metal can be interpreted by invoking the synergic contributions of σ-donation and π-backdonation. In the Pt^0 compounds, the latter component is enhanced by the high charge density of the d^{10} metal centre, and is significantly reinforced by the good donor properties of the chelating nitrogen ligands, which pump electrons towards the alkene carbon atoms.

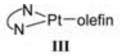
Maria Elena Cucciolito graduated in Industrial Chemistry from the University of Napoli "Federico II" in 1987 and received his PhD in 1992 with Prof. Achille Panunzi. The activity of Dr. Cucciolito is mainly in the field of organometallic chemistry, with particular interest towards the following subfields: 1) five-coordinate olefin complexes of Pt^{II} and Pd^{II}; 2) reactivity and stereochemitry of allylic complexes of Pt^{II} and Pd^{II}; 3) reactivity of alkenes coordinated to highly electrophilic dicationic complexes of Pt^{II} and Pd^{II}.

Vincenzo De Felice graduated in Industrial Chemistry from the University of Napoli "Federico II" in 1983 and received his PhD in 1989 with Prof. Achille Panunzi. He was guest at the KTH of Stockholm under the supervision of Prof. B. Åkermark (July to November 1991). The scientific activity of Prof. De Felice is mainly in the field of organometallic chemistry, with particular interest toward the following subfields: i) synthesis, characterization, reactivity of Pt and Pd complexes; ii) study of the mechanism of insertion of unsaturated molecules into metal-carbon bonds. Currently his research interest include studies on bis-chelating ligands based on bipyridine or bis-isoquinoline moieties and in the field of Groundwater research.

Giuseppina Roviello graduated in Chemistry from the University of Napoli Federico II in 2000 and received her Ph. D. in Chemical Sciences in 2003, with Prof. Achille Panunzi. The scientific activity of Dr. Roviello is mainly in the field of organometallic chemistry, with particular interest toward the following subfields: i) synthesis, characterization, reactivity of platinum complexes: oxidative addition reaction; ii) study of the mechanism of insertion of unsaturated molecules into s metal–carbon bonds; iii) synthesis and use in asymmetric catalysis of metal complexes containing new chiral ligands derived from carbohydrates; iv) study of the structural characteristics of organometallic complexes through RX diffractometric analysis.

Francesco Ruffo graduated in Industrial Chemistry from the University of Napoli "Federico II" in 1990 and received his PhD in 1994 with Prof. Achille Panunzi. He was guest at the KTH of Stockholm under the supervision of Prof. B. Åkermark (July 1992 and May to September 1997) and at the University of Göttingen (May to September 1993) under the supervision of Prof. A. de Mejere. The activity of Prof. Ruffo is mainly in the field of organometallic chemistry, with particular interest towards the following sub-fields: 1) Pt and Pd complexes in low oxidation states; 2) asymmetric catalysis promoted by metal complexes containing new chiral ligands derived from carbohydrates; 3) study of cationic hydrocarbyl/olefin complexes of Pt^{II} and Pd^{II}.

Table 1. Complexes of type **III** and their synthetic/spectroscopic references.



III

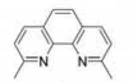
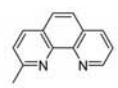
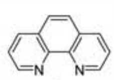
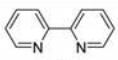
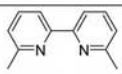
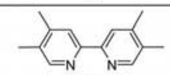
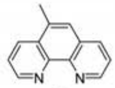
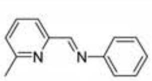
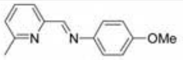
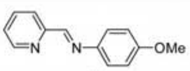
N,N'-Ligands	Olefins and labels of the complexes	Ref.
 **1**	CH$_2$=CHMe (**III-1a**)	4
	CH$_2$=CH$_2$ (**III-1b**)	5, 6
	CH$_2$=CHCO$_2$Me (**III-1c**)	5, 6
	CH$_2$=CHCN (**III-1d**)	7, 6
	(*Z*)-ClCH=CHCl (**III-1e**)	7
	(*E*)-ClCH=CHCl (**III-1f**)	7
	(*E*)-PhC(O)CH=CHC(O)Ph (**III-1g**)	8
	(*Z*)-MeO$_2$CCH=CHCO$_2$Me (**III-1h**)	4, 6
	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-1i**)	6,8,9
	(*Z*)-EtO$_2$CCH=CHCO$_2$Et (**III-1j**)	10
	(*E*)-EtO$_2$CCH=CHCO$_2$Et (**III-1k**)	11
	(*E*)-(*i*Pr)O$_2$CCH=CHCO$_2$(*i*Pr) (**III-1l**)	8
	(*Z*)-(*t*Bu)O$_2$CCH=CHCO$_2$(*t*Bu) (**III-1m**)	10
	(*E*)-(*t*Bu)O$_2$CCH=CHCO$_2$(*t*Bu) (**III-1n**)	8
	(*E*)-(*p*-Tol)O$_2$CCH=CHCO$_2$(*p*-Tol) (**III-1o**)	8
	(*E*)-PhO$_2$CCH=CHCO$_2$Ph (**III-1p**)	8
	(*E*)-(*p*-Cl-C$_6$H$_4$)O$_2$CCH=CHCO$_2$(*p*-Cl-C$_6$H$_4$) (**III-1q**)	8
	(*E*)-NCCH=CHCN (**III-1r**)	12
	maleic anhydride (**III-1s**)	13
 **2**	CH$_2$=CH$_2$ (**III-2b**)	5
	CH$_2$=CHCO$_2$Me (**III-2c**)	7
	CH$_2$=CHCN (**III-2d**)	7
	(*Z*)-ClCH=CHCl (**III-2e**)	7
	(*E*)-ClCH=CHCl (**III-2f**)	7
	(*Z*)-MeO$_2$CCH=CHCO$_2$Me (**III-2h**)	7
	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-2i**)	5
 **3**	CH$_2$=CHCO$_2$Me (**III-3c**)	6
	CH$_2$=CHCN (**III-3d**)	6
	(*Z*)-MeO$_2$CCH=CHCO$_2$Me (**III-3h**)	7
	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-3i**)	7
	p-benzoquinone (**III-3t**)	14
	naphthoquinone (**III-3u**)	14
	F$_2$C=CF$_2$ (**III-3v**)	15
 **4**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-4i**)	16
	(*E*)-NCCH=CHCN (**III-4r**)	16
	(NC)$_2$C=C(CN)$_2$ (**III-4x**)	16
 **5**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-5i**)	16
	p-benzoquinone (**III-5t**)	14
	naphthoquinone (**III-5u**)	14
	F$_2$C=CF$_2$ (**III-5x**)	15
 **6**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-6i**)	17
 **7**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-7i**)	16
 **8**	F$_2$C=CF$_2$ (**III-8v**)	15
 **9**	(*Z*)-MeO$_2$CCH=CHCO$_2$Me (**III-9h**)	7
	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-9i**)	8
	(*E*)-EtO$_2$CCH=CHCO$_2$Et (**III-9k**)	8
	(*E*)-(*i*Pr)O$_2$CCH=CHCO$_2$(*i*Pr) (**III-9l**)	8
	(*E*)-(*t*Bu)O$_2$CCH=CHCO$_2$(*t*Bu) (**III-9n**)	8
 **10**	(*Z*)-MeO$_2$CCH=CHCO$_2$Me (**III-10h**)	13
	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-10i**)	5
 **11**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-11i**)	5,18
	(*E*)-NCCH=CHCN (**III-11r**)	18
	maleic anhydride (**III-11s**)	18
	naphthoquinone (**III-11u**)	18
	(MeO$_2$C)$_2$C=C(CO$_2$Me)$_2$ (**III-11w**)	18

Table 1. *(Continued)*.

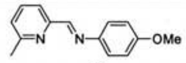
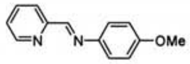
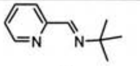
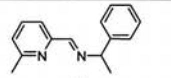
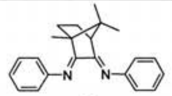
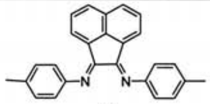
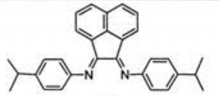
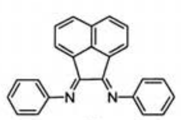
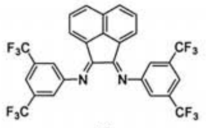
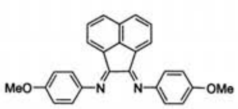
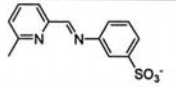
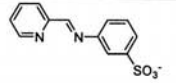
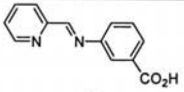
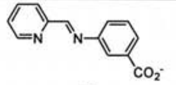
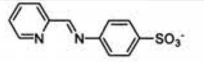
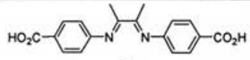
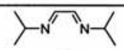
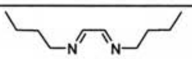
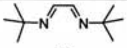
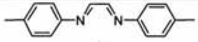
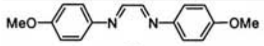
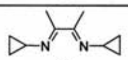
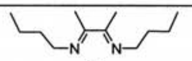
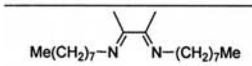
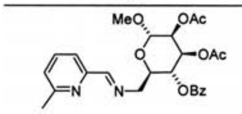
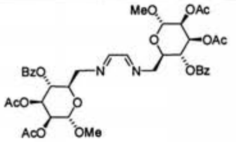
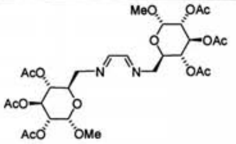
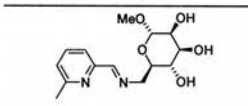
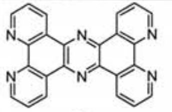
N,N'-Ligands	Olefins and labels of the complexes	Ref.
 **10**	(*Z*)-MeO$_2$CCH=CHCO$_2$Me (**III-10h**)	13
	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-10i**)	5
 **11**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-11i**)	5,18
	(*E*)-NCCH=CHCN (**III-11r**)	18
	maleic anhydride (**III-11s**)	18
	naphthoquinone (**III-11u**)	18
	(MeO$_2$C)$_2$C=C(CO$_2$Me)$_2$ (**III-11w**)	18
 **12**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-12i**)	18
	(*E*)-NCCH=CHCN (**III-12r**)	18
	maleic anhydride (**III-12s**)	18
	naphthoquinone (**III-12u**)	18
 **13**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-13i**)	5
	(*E*)-NCCH=CHCN (**III-13r**)	5
	maleic anhydride (**III-13s**)	5
 **14**	(*E*)-NCCH=CHCN (**III-14r**)	19
	maleic anhydride (**III-14s**)	19
 **15**	(*E*)-NCCH=CHCN (**III-15r**)	19
	maleic anhydride (**III-15s**)	19
	(NC)$_2$C=C(CN)$_2$ (**III-15x**)	19
 **16**	(*E*)-NCCH=CHCN (**III-16r**)	19
	maleic anhydride (**III-16s**)	19
 **17**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-17i**)	20
 **18**	maleic anhydride (**III-18s**)	20
	(NC)$_2$C=C(CN)$_2$ (**III-18x**)	20
 **19**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-19i**)	20
	maleic anhydride (**III-19s**)	20
 **20**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-20i**)	21
	(*E*)-NCCH=CHCN (**III-20r**)	21
 **21**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-21i**)	21
	(*E*)-NCCH=CHCN (**III-21r**)	21
	maleic anhydride (**III-21s**)	21
 **22**	(*E*)-NCCH=CHCN (**III-22r**)	21
 **23**	(*E*)-NCCH=CHCN (**III-23r**)	21

Table 1. *(Continued)*.

N,N'-Ligands	Olefins and labels of the complexes	Ref.
 **24**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-24i**) (*E*)-NCCH=CHCN (**III-24r**)	21 21
 **25**	(*E*)-NCCH=CHCN (**III-25r**)	21
 **26**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-26i**) maleic anhydride (**III-26s**)	22 22
 **27**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-27i**)	22
 **28**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-28i**)	22
 **29**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-29i**) (*E*)-NCCH=CHCN (**III-29r**)	22 22
 **30**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-30i**)	22
 **31**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-31i**)	22
 **32**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-32i**)	22
 **33**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-33i**) maleic anhydride (**III-33s**)	22
 **34**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-34i**) (*E*)-NCCH=CHCN (**III-34r**) maleic anhydride (**III-34s**)	23 23 23
 **35**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-35i**) (*E*)-PhO$_2$CCH=CHCO$_2$Ph (**III-100p**) (*E*)-NCCH=CHCN (**III-35r**) maleic anhydride (**III-35s**)	23 23 23 23
 **36**	(*E*)-NCCH=CHCN (**III-36r**) (NC)$_2$C=C(CN)$_2$ (**III-36x**)	24 24
 **37**	(*E*)-MeO$_2$CCH=CHCO$_2$Me (**III-37i**) (*E*)-NCCH=CHCN (**III-37r**) maleic anhydride (**III-37s**)	23 23 23
 **38**	(*E*)-NCCH=CHCN (**III-38r**)[a]	25

[a] This complex is binuclear.

For this reason, the stability of the complexes is improved by the presence of electron-poor alkenes, which prompt the most effective π-backdonation, and stabilise the low oxidation state. In other words, the stability of the complexes increases with the electron-withdrawing properties of the olefin substituents, according to the following order of general stability: propylene < ethylene < acrylic esters < acrylonitrile < maleic esters < fumaric esters < fumarodinitrile ≈ maleic anhydride.

The consequent introduction of electrons in the *anti*-bonding alkene orbital has the effect of introducing significant sp^3 character in the coordinated alkene carbons. This clearly reflects on spectroscopic and structural parameters, and, therefore, proton and carbon NMR spectroscopy are the most important techniques used so far for investigating the general properties of type-**III** compounds. In fact, NMR spectra provide useful information for the structural assignment, the interpretation of the metal olefin bond, stereoisomerism and dynamic of the complexes. In some cases this method has been supported by X-ray diffractometric investigation of a single crystal.

The most evident NMR feature is the high-field coordination shift of both olefin protons and carbons, whose extent is a reliable measure of the degree of π-backdonation. Table 2 reports the proton Δ*δ*'s values for selected complexes of ligand **1**, which are larger than those regularly observed for the corresponding Pt^{II} complexes, independent of the geometry of coordination.[27,28]

Table 2. Coordination shift for the olefin protons in selected complexes of type **III** (in CDCl$_3$ at room temperature).

Type-**III** complex	Δ*δ*
III-1b [Pt(**1**)(CH$_2$=CH$_2$)]	3.21
III-1c [Pt(**1**)(CH$_2$=CHCO$_2$Me)]	2.94, 3.75, 3.45
III-1d [Pt(**1**)(CH$_2$=CHCN)]	3.40, 3.33, 3.10
III-1i [Pt(**1**){(*E*)-MeO$_2$CCH=CHCO$_2$Me}]	3.02
III-1r [Pt(**1**){(*E*)-NCCH=CHCN}]	3.40

In a few cases, the significant amount of π-backdonation has been disclosed by solving the X-ray structure of representative complexes, i.e. **III-1i**, **III-13i**, **III-13r**, **III-13s** and **III-36r**. Worth of notice is the significant C=C bond length [respectively, 1.42(3), 1.46(1), 1.43(2), 1.45(1), 1.51(5) Å]. The lengthening the C=C distance can be usefully revealed by comparison with that of the free olefins: dimethyl fumarate, 1.318 Å[29] and fumarodinitrile 1.249 Å.[30] Of further interest is the bending back of the alkene carbon chain in **III-1i** and **III-36r** [C–C=C–C torsion angles of 50(2)° and 38(3)°, respectively for **III-1i** and **III-36r**], which emphasizes the partial rehybridization sp$^2 \rightarrow$ sp^3 of the olefin carbon atoms.

NMR spectra can be usefully employed for studying stereoisomerism and dynamic phenomena involving the alkene, such as its rotation around the platinum–alkene bond.

Stereoisomerism depends on the geometrical features of both the chelate and the olefin (Figure 1).

i) in the presence of ligands with a mirror plane bisecting the two halves (**1**, **3**–**7**, **15**–**19**, **25**–**33**, **38**), ethylene and *cis*-

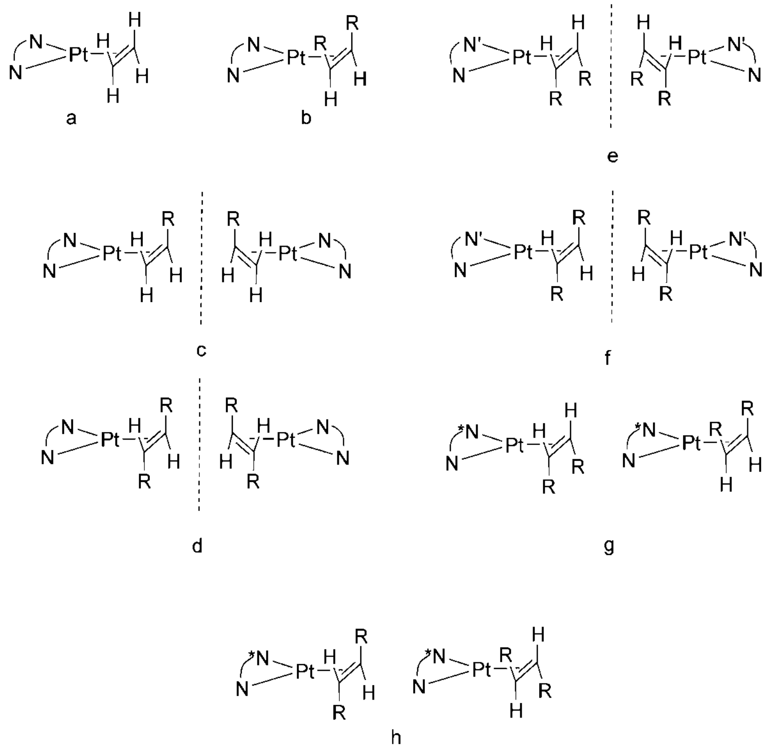


Figure 1. Possible isomers of complexes of type **III**.

alkenes afford only one isomer (Figure 1, a and b). Instead, prochiral alkenes, e.g. propylene, acrylic or fumaric esters afford a couple of enantiomers (see figure parts c and d, respectively), obviously not distinguishable through NMR spectroscopy. In a, b and d, the olefin protons are related by symmetry, and resonate as singlets with ^{195}Pt satellites.

ii) in the presence of achiral ligands lacking of a mirror plane (**2**, **8**–**12**, **20**–**24**), both *cis*- and *trans*-alkenes afford enantiomeric couples (Figure 1, e and f). In this case the olefin protons are not equivalent. Resolved NMR signals of the corresponding protons (which also couple to ^{195}Pt) indicate slow alkene rotation.

iii) Diastereomers can be instead detected when chirality is introduced in the chelate backbone, as in derivatives of **13** and **14** and **34**–**37**. *cis*-Alkenes afford a couple of isomers (Figure 1, g) which can interconvert through simple olefin rotation, while *trans*-alkenes give rise to diastereomers which can interconvert only through olefin dissociation and re-association with the opposite enantioface (h). In most cases, the complexes crystallize as pure diastereomers, as revealed by the spectrum of their freshly prepared solution. Upon standing, an equilibrium mixture is reached within a few hours, and the corresponding diastereomeric ratios are reported in Table 3. It is particularly remarkable that **36**, based on D-glucose, is able to recognise selectively one enantioface of fumarodinitrile in the trigonal Pt environment of **III-36r**. NMR and X-ray studies[24] disclosed that this outstanding selectivity originates from the aptitude of the ligand to create a chiral pocket of C_2 symmetry, which is retained both in solution and in the solid state.

Table 3. Equilibrium ratios between diastereomeric complexes of type **III** (at 298 K in $CDCl_3$).

Type-**III** complex	Ratio
III-13i [Pt(**13**){(E)-$MeO_2CCH{=}CHCO_2Me$}]	1:1[a]
III-13r [Pt(**13**){(E)-NCCH=CHCN}]	2:1[a]
III-14r [Pt(**14**){(E)-NCCH=CHCN}]	1.2:1
III-34i [Pt(**34**){(E)-$MeO_2CCH{=}CHCO_2Me$}]	1.3:1[a]
III-34r [Pt(**34**){(E)-NCCCH=CHCN}]	1.2:1[a]
III-35i [Pt(**35**){(E)-$MeO_2CCH{=}CHCO_2Me$}]	6:1[a]
III-35p [Pt(**35**){(E)-$PhO_2CCH{=}CHCO_2Ph$}]	1:2.7[a]
III-35r [Pt(**35**){(E)-NCCCH=CHCN}]	1:2.5[a]
III-36r [Pt(**36**){(E)-NCCH=CHCN}]	>99:1[a]
III-37i [Pt(**37**){(E)-$MeO_2CCH{=}CHCO_2Me$}][b]	1.3:1[a]
III-37r [Pt(**37**){(E)-NCCH=CHCN}][b]	1.2:1[a]

[a] The first number refers to the isomer isolated in the solid state, obtained through a second order transformation. [b] At 298 K in D_2O.

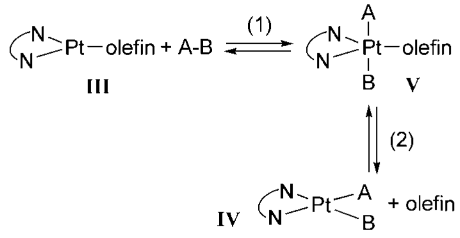
As mentioned above, at room temperature olefin rotation is slow on the NMR time scale. A few studies[19] were addressed to evaluate the rotation barrier, which was estimated to be higher than 72 kJ/mol for **III-14s**, **III-16r** and **III-16s**. This value is larger than those typically found for Pt^{II} complexes, both in square-planar and trigonal bipyramidal environment, and again this was ascribed to the relevant contribution of π-backdonation to the platinum–alkene bond.[19]

General Reactivity of Three-Coordinate [Pt(*N*,*N′*-chelate)(η^2-olefin)] Complexes (III)

The simplest reaction of type-**III** compounds is the olefin exchange described by Scheme 2. Although this reaction is useful for synthetic purposes, only one accurate study[18] demonstrated that the process proceeds via an associative mechanism. The olefin exchange rates were determined along the series **III-11i** through **III-12u**, and the reactivity order of the entering olefin was found to be: maleic anhydride > fumarodinitrile ≈ naphthoquinone >> tetramethyl ethylenetetracarboxylate.

However, the most versatile reaction of three-coordinate complexes of type **III** is the oxidative addition. Their aptitude to react reflects the basic properties conferred by the electronic characteristics of the alkene, which exactly follow the general trend of stability mentioned in the previous section: fumarodinitrile ≈ maleic anhydride < fumaric esters < maleic esters < acrylonitrile < acrylic esters < ethylene < propylene.

The general reaction pattern is described by Scheme 3, and the distribution of products principally depends on the nature of the chelate, the alkene and the electrophile. In general, reaction (1) is totally shifted either towards the reactants ($K_{eq1} = 0$) or the platinum(II) product **V** (complete conversion). Only in very few and remarkable occasions, this reaction is an equilibrium (see below), and its occurrence has allowed the disclosure of relevant trends and the evaluation of fundamental thermodynamic parameters.



Scheme 3. General reaction pattern of complexes of type **III**.

The five-coordinate platinum(II) product is stable ($K_{eq2} = 0$) only when the *N*,*N′*-ligand is hindered in the coordination plane (i.e. **1**).[31] Gradual reduction of in-plane hindrance shifts equilibrium 2 towards the square-planar Pt^{II} species (**IV**), which becomes the unique product if the ligand is completely unhindered in the coordination plane (e.g. **3**).

The product of type **V** adopt the typical geometry[31] for five-coordinate olefin complexes of Pt^{II}, that is the *N*,*N′*-chelate and the alkene define the equatorial plane, while the anionic ligands occupy the axial position of the coordination polyhedron.

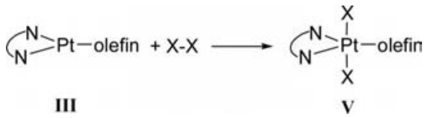
The possibility to stabilise the five-coordinate products is relevant not only for the atypical coordination number, but also because the coordinative saturation has allowed the stabilisation of previously unknown ligand fragments (see below). On the other hand, the presence of poorly hindered ligands, such as the simple **3**, inevitably leads to the square-planar product **IV** resulting from olefin loss, which can be more or less stable towards further rearrangements.

The reactions are presented in sections, according to the nature of the electrophile. In all cases, the complete list of reactants and products are given in Tables along with the appropriate references.

Reactions with Halogens and Pseudo-Halogens

Oxidative addition of Cl_2, Br_2, I_2, $(SCN)_2$ and $(CN)_2$ to the three coordinate complexes rapidly leads to the isolation of the corresponding five-coordinate species of type **V** (Table 4). In no cases, the addition reaction was found to be an equilibrium. Complex **V-2**, obtained upon addition of thiocyanogen to **III-1h**, displays both the –SCN anionic ligands coordinated through the sulfur atom.

Table 4. Oxidative addition of halides and pseudo-halides to the three-coordinate complexes.

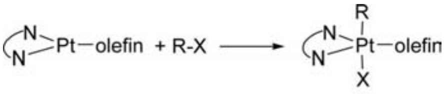


Type-**III** complex	X–X electrophile and labels of the type-**V** products	Ref.
III-1b	NC–CN (**V-1**)	[32]
III-1h	NCS–SCN (**V-2**)	[32]
III-1i	Cl–Cl (**V-3**)	[5]
	Br–Br (**V-4**)	[9]
	I–I (**V-5**)	[5]

Reactions with Alkyl and Aryl Halides

Reaction of type-**III** complexes with alkyl halides revealed to be a straightforward method for the introduction of a wide range of hydrocarbyl fragments in the coordination sphere of Pt^{II} (Table 5). These groups span from simple alkyl chains or aryl rings to severely functionalised moieties, e.g. containing halogenated, acylic, formyl, carbonyl, nitrilo, nitro, ester, alcoholic and amino functions. The extraordinary reactivity of ethylene or propene compounds **III-1a** and **III-1b** also allowed the rare activation of the C–Cl bond of chlorinated solvents, such as chloroform or dichloromethane. As an example, **III-1b** reacts within a few seconds at room temperature even with $Cl–CH_2Cl$, affording the five-coordinate product **V-7** with a chloro and a chloromethyl axial ligands. Moreover, the ethylene precursor was able to activate iodobenzene, while more electron-poor substrates did not afford appreciable amounts of addition products in the same conditions.

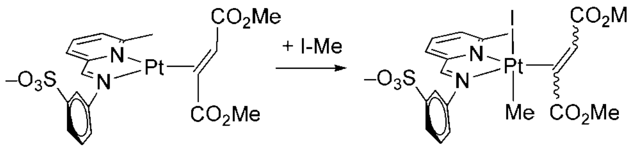
Table 5. Oxidative addition of alkyl and aryl halides to the three-coordinate complexes.



III **V**

Type-**III** complex	R–X electrophile and labels of the type-**V** products	Ref.
III-1a	I–Me (**V-6**)	[5]
III-1b	Cl–CH$_2$Cl (**V-7**)	[5]
	Cl–CO$_2$Et (**V-8**)	[34]
	Br–Et (**V-9**)	[5]
	Br–CH(CO$_2$Et)Me (**V-10**)	[5]
	Br–CH$_2$CH$_2$OH (**V-11**)	[34]
	Br–CH$_2$OC(O)Ph (**V-12**)	[34]
	Br–CH$_2$CHO (**V-13**)	[34]
	Br–CH$_2$CO$_2$Et (**V-14**)	[34]
	I–Me (**V-15**)	[5]
	I–Ph (**V-16**)	[5]
	I–CH$_2$CH$_2$OH (**V-17**)	[34]
III-1h	Cl–CH$_2$CO$_2$Et (**V-18**)	[32]
	Cl–CH$_2$CO$_2$CH=CH$_2$ (**V-19**)	[32]
	Cl–CO$_2$Me (**V-20**)	[32]
	Cl–CO$_2$CH=CH$_2$ (**V-21**)	[32]
III-1i	Cl–COMe (**V-22**)	[34]
	Cl–COCH$_2$Cl (**V-23**)	[34]
	Cl–COPh (**V-24**)	[34]
	Br–Me (**V-25**)	[5]
	Br–CH$_2$Ph (**V-26**)	[5]
	Br–CH(Me)Ph (**V-27**)	[5]
	Br–COCH$_2$Br (**V-28**)	[34]
	Br–CH$_2$CN (**V-29**)	[34]
	Br–CH$_2$NO$_2$ (**V-30**)	[34]
	I–Me (**V-31**)	[5]
	I–Et (**V-32**)	[5]
	I–CH$_2$Ph (**V-33**)	[5]
	I–CH$_2$I (**V-34**)	[34]
	I–CF$_3$ (**V-35**)	[34]
	I–CH$_2$CO$_2$Et (**V-36**)	[34]
	I–CH$_2$CONH$_2$ (**V-37**)	[34]
	I–CN (**V-38**)	[34]
	I–CH$_2$CN (**V-39**)	[34]
III-20i	I–Me (**V-40**)	[21]

The addition of iodomethane was also performed on a hydrophilic three-coordinate complex (**III-20i**) as depicted in Scheme 4. The corresponding diastereomeric product **V-40** showed solubility in water.



III-20i **V-40**

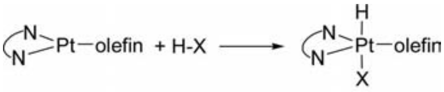
Scheme 4. Reaction of **III-20i** with Me–I.

As expected, when iodomethane was reacted[5] with a three-coordinate complex containing a poorly crowded ligand, i.e. **III-11i**, the only product was the corresponding square-planar Pt^{II} species [PtMe(I)(**11**)] (**IV-1**).

Reactions with Protic Acids

The extension of the addition to acids allowed the rare stabilisation of a platinum–hydrogen bond in five-coordinate complexes containing an olefin. The oxidative addition of H–Cl, H–Br or H–I was performed on three-coordinate substrates with maleic or fumaric esters, methyl acrylate, acrylonitrile, *trans*- or *cis*-dichloroethylene and ethylene (Table 6). Bidentate chelates with different steric hindrance in the coordination plane were used (i.e., **1**, **2** and **3**).

Table 6. Oxidative addition of protic acids to the three-coordinate complexes.



III **V**

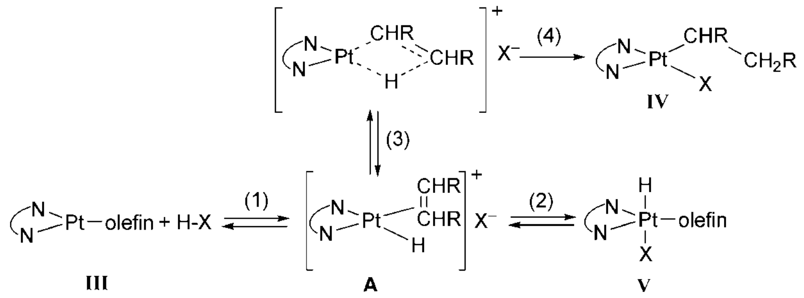
Type-**III** complex	X–Y electrophile and labels of the type-**V** products	Ref.
III-1b	H–Cl (**V-41**)[a]	[7]
III-1c	H–Cl (**V-42**)[a]	[7]
III-1d	H–Cl (**V-43**)[a]	[7]
III-1e	H–Cl (**V-44**)[a]	[7]
III-1f	H–Cl (**V-45**)[a]	[7]
III-1h	H–Cl (**V-46**)	[35]
	H–Br (**V-47**)	[35]
	H–I (**V-48**)	[35]
III-1i	H–Cl (**V-49**)	[35]
	H–Br (**V-50**)	[35]
III-1m	H–Cl (**V-51**)	[35]

[a] The complex was observed in CDCl$_3$ solution and was not isolated.

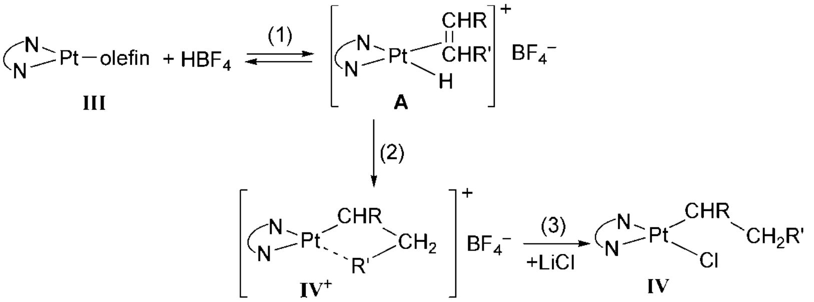
Starting from **III**, in all cases the attack of the proton is fast (see step 1 in Scheme 5), and plausibly leads to a square-planar intermediate with the olefin and the hydride in *cis* position (**A**). The fate of intermediate **A** depends on the feature of the *N,N′*-chelate. In the presence of **1**, the first products are the five-coordinate hydrido species **V-41** to **V-51**, which are stable and isolable only with maleic or fumaric esters (**V-46** to **V-51**). If the alkene has reduced electron withdrawing properties, the five-coordinate products can be observed by NMR spectroscopy only in the early stages of the reaction, since they are successively involved in the insertion of the alkene into the Pt–H bond with formation of the corresponding alkyl complex through steps (2)–(3)–(4).

The importance of the steric properties of the bidentate ligand in the stabilisation of the five-coordinate product could also be easily confirmed.[7] When the attack was performed on complexes of the poorly crowded **2** or **3**, the five-coordinate hydrido complexes were not detectable, since proton attack (1) was followed by fast insertion (3)–(4), and the five-coordinate adduct could not be observed.

Some experiments on fumarate or maleate complexes were performed by using HBF$_4$, an acid with a non-coordinating anion (Scheme 6). In all cases, regardless of the *N,N′*-ligand, rapid olefin insertion (steps 1 and 2) into the Pt–H bond leads to the square-planar insertion products (**IV$^+$**), stabilised by coordination of the carbonyl contained



Scheme 5. Reactions of complexes of type-**III** complexes with H–X.

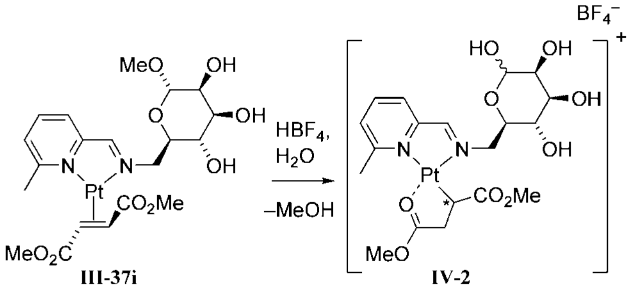


Scheme 6. Reactions of complexes of type-**III** complexes with H–BF_4.

in the olefin. Addition of Cl^- (step 3) may lead to the corresponding neutral species **IV**.

In a similar way, the tetrafluoroethene compound **III-3v** was reported to react with CF_3CO_2H to give the corresponding tetrafluoroethyl complex [Pt(CF_3CO_2)(CF_2CF_2H) (**3**)].[15b]

Remarkably, the hydrophilic complex **III-37i** underwent[23] a stereoselective attack of HBF_4 in water affording formation of the stereogenic σ-bound carbon atom (indicated with an asterisk in Scheme 7) with a significant degree of enantioselectivity (diastereomeric ratio 6:1).



Scheme 7. Reaction of HBF_4 with complex **III-37i**.

Reactions with Organometal Halides X–MR_nX_{3-n} (M = Ge, Sn, Pb: *n* = 1–3) and X–HgR

The three-coordinate olefin complexes react with organogermanium, organotin, organolead and organomercury halides affording type-**V** products with a Pt–metal bond in axial position (Tables 7 and 8).

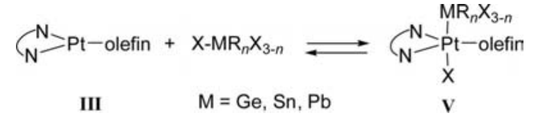
The germanium derivatives **V-54** to **V-57** represented the first class of five-coordinate platinum(II) species containing a Pt–Ge bond. Furthermore, the first example of metal activation of Cl–$GeMe_3$ bond was reported. Given the low reactivity of organogermanium species, the addition were carried out only on the ethylene precursor **III-1b**, and could not be extended to the less reactive Pt^0 species containing electron-poor olefins. For example, even the highly reactive Cl–$GeMeCl_2$ did not add to **III-1h** in dry toluene. Alternatively, in wet solvents, the product of the reaction was the known hydrido species **V-46**, which formed upon attack of H–Cl deriving from hydrolysis of the Ge–Cl bond.

On the contrary, organotin and organolead halides easily added to the three-coordinate precursors, affording the most representative class of five-coordinate complexes containing a Pt–Sn or a Pt–Pb bond. Type-**V** products were obtained with a wide range of alkenes and electrophiles X–MR_nCl_{3-n} (differing in the nature of X, R and in the value of n), as crystalline solids, which could be stored in the solid state without appreciable decomposition.

The organomercury halides afforded isolable products only with type-**III** complexes of dialkylmaleates, due to a reduced or more complicated reactivity of the X–HgR species towards Pt^0 compounds containing other alkenes. Remarkable exception to the typical course of the addition reaction was observed when Cl–HgPh was used as electrophile. In fact, in this case the attack led to the trinuclear cluster **V-104** (Scheme 8) containing the sequence Pt–Hg–Pt, while half equivalent of Hg was recovered as $HgPh_2$.

The crucial role played by the coordinative saturation around Pt in the stabilisation of otherwise reactive fragments was verified within these studies. For instance, when

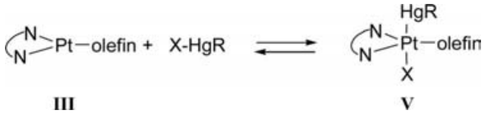
Table 7. Oxidative addition of organogermanium, organotin and organolead halides to the three-coordinate complexes.



Type-**III** complex	X–ER$_n$X$_{3-n}$ electrophile and labels of the type-**V** products	–pK_{add} (298 K)	Ref.
III-1a	Cl–SnPh$_3$ (**V-52**)	[a]	[4]
	Cl–SnMe$_2$Cl (**V-53**)	[a]	[4]
III-1b	Cl–GeMe$_3$ (**V-54**)	[a]	[36]
	Cl–GeMe$_2$Cl (**V-55**)	[a]	[36]
	Cl–GePh$_2$Cl (**V-56**)	[a]	[36]
	Cl–GeMeCl$_2$ (**V-57**)	[a]	[36]
	Cl–SnMe$_3$ (**V-58**)	[a]	[4]
	Cl–SnPh$_3$ (**V-59**)	[a]	[4]
	Cl–SnMe$_2$Cl (**V-60**)	[a]	[4]
	Cl–SnPh$_2$Cl (**V-61**)	[a]	[4]
	Cl–SnMeCl$_2$ (**V-62**)	[a]	[4]
	Br–SnMe$_3$ (**V-63**)	[a]	[4]
	Cl–PbPh$_2$Cl (**V-64**)	[a]	[37]
III-1c	Cl–SnMe$_2$Cl (**V-65**)	[a]	[8]
	Cl–PbMe$_2$Cl (**V-66**)	[a]	[37]
	Cl–PbPh$_2$Cl (**V-67**)	[a]	[37]
III-1d	Cl–SnMe$_2$Cl (**V-68**)	[a]	[8]
	Br–SnMe$_3$ (**V-69**)	1.1	[8]
	I–SnMe$_3$ (**V-70**)	3.4	[8]
	Cl–PbPh$_2$Cl (**V-71**)	[a]	[37]
III-1f	Cl–SnMe$_2$Cl (**V-72**)	3.3	[8]
III-1g	Cl–SnMe$_2$Cl (**V-73**)	3.8	[8]
	Cl–SnPh$_2$Cl (**V-74**)	[a]	[8]
III-1h	Cl–SnMe$_2$Cl (**V-75**)	[a]	[4]
	Cl–SnPh$_2$Cl (**V-76**)	[a]	[4]
	Cl–SnMeCl$_2$ (**V-77**)	[a]	[4]
	Cl–PbMe$_2$Cl (**V-78**)	[a]	[37]
	Cl–PbPh$_2$Cl (**V-79**)	[a]	[37]
	Cl–PbPhCl$_3$ (**V-80**)	[a]	[37]
III-1i	Cl–SnMe$_2$Cl (**V-81**)	2.9[b]	[4]
	Cl–SnMe(Ph)Cl (**V-82**)	3.7	[8]
	Cl–SnPh$_2$Cl (**V-83**)	[a]	[4]
	Cl–SnMeCl$_2$ (**V-84**)	[a]	[4]
	Cl–PbPh$_2$Cl (**V-85**)	[a]	[37]
III-1k	Cl–SnMe$_2$Cl (**V-86**)	3.2[c]	[11]
	Cl–SnMe(Ph)Cl (**V-87**)	4.0	[8]
III-1l	Cl–SnMe$_2$Cl (**V-88**)	3.8	[8]
	Cl–SnMe(Ph)Cl (**V-89**)	>4.1	[8]
III-1m	Cl–SnMe$_2$Cl (**V-90**)	[a]	[8]
III-1n	Cl–SnMe$_2$Cl (**V-91**)	[a]	[8]
III-1o	Cl–SnMe$_2$Cl (**V-92**)	1.6	[8]
III-1p	Cl–SnMe$_2$Cl (**V-93**)	1.4	[8]
III-1q	Cl–SnMe$_2$Cl (**V-94**)	1.2	[8]
III-2i	Cl–SnMe$_2$Cl (**V-95**)	2.8	[8]
III-9h	Cl–PbMe$_2$Cl (**V-96**)	[a]	[37]
	Cl–PbPh$_2$Cl (**V-97**)	[a]	[37]
III-9i	Cl–SnMe$_2$Cl (**V-98**)	3.4	[8]
	Cl–PbPh$_2$Cl (**V-99**)	[a]	[37]
III-9k	Cl–SnMe$_2$Cl (**V-100**)	3.7	[8]
III-9l	Cl–SnMe$_2$Cl (**V-101**)	3.8	[8]
III-9n	Cl–SnMe$_2$Cl (**V-102**)	[a]	[8]

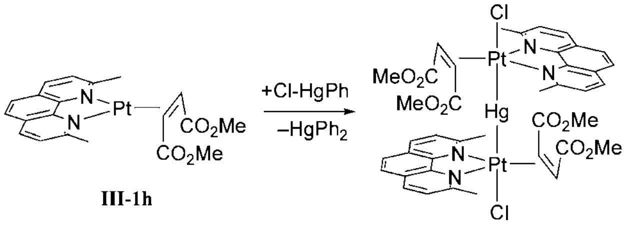
[a] Complete conversion. [b] $\Delta H = -12 \pm 1$ kcal mol^{-1}; $\Delta S = -26 \pm 4$ cal mol^{-1} K^{-1}. [c] $\Delta H = -11 \pm 1$ kcal mol^{-1}; $\Delta S = -23 \pm 3$ cal mol^{-1} K^{-1}.

Table 8. Oxidative addition of organomercury halides to the three-coordinate complexes.



Type-**III** complex	X–HgR electrophile and labels of the type-**V** products	–pK_{add} (248 K)	Ref.
III-1h	Cl–HgMe (**V-103**)	1.8	[10]
	Cl–HgPh (**V-104**)[a]	[b]	[10]
	Cl–HgCF$_3$ (**V-105**)	[b]	[8]
	Br–HgMe (**V-106**)	2.9	[8]
	I–HgMe (**V-107**)	2.4	[8]
III-1j	Cl–HgMe (**V-108**)	[b]	[10]
III-1m	Cl–HgMe (**V-109**)	[b]	[10]
	Cl–HgEt (**V-110**)	[b]	[10]
	Cl–Hg(*t*Bu) (**V-111**)	[b]	[10]

[a] The product is a trinuclear species, see Scheme 8. [b] Complete conversion.



V-104

Scheme 8. Addition of Cl–HgPh to **III-1h**.

the addition of Cl–PbPh$_2$Cl was performed on three-coordinate derivatives containing **2** or **3**, the reaction only afforded the mononuclear Pt^{II} complexes [PtCl(Ph)(*N*,*N*′-chelate)], while Pb separated as an insoluble material. It is conceivable that the early binuclear product [PtCl(PbPh$_2$Cl)(*N*,*N*′-chelate)(olefin)] is not stable towards olefin loss (see reaction 2 in Scheme 3), and the resulting four-coordinate [PtCl(PbPh$_2$Cl)(*N*,*N*′-chelate)] compound undergoes fast deplumbation as described for similar species.[38] Analogues stabilising effects were operating for the organomercury fragments bound to Pt, which in four-coordinate compounds are reported to be very unstable, unless the hydrocarbyl group on Hg does not meet strict steric or electronic requirements.[39,40]

Notably, the addition of organotin and organomercury halides revealed to be an *equilibrium*, i.e. a very rare case (probably observed for the first time) in which it was possible to observe and measure similar concentrations of both different metal states at equilibrium. The occurrence of this phenomena allowed a thorough NMR study[8] aimed at disclosing the effects of the electronic and the steric features of the ligands (Tables 7 and 8 also report the pK_{add} for selected reactions). The most prominent findings can be summarised as follows. The addition is favoured by:

– an increase of the electron-donor properties of the olefin substituents, which plausibly enhance the basicity of the metal centre. This emerges very clearly by comparing the results of the addition of the same organotin halide, Cl–SnMeCl$_2$, to the three-coordinate precursors along the series **III-1a** to **III-1r**. Complete addition is observed with ethylene, propene, methyl acrylate or acrylonitrile. The addition is an equilibrium if two electron withdrawing substituents are present on the olefin carbons (i.e. Cl, COPh, or CO_2R). Instead, no appreciable reaction was observed with the fumarodinitrile precursor **III-1r**.

– an increase of the bulkiness of the olefin substituents. For instance, the addition of Cl–$SnMe_2Cl$ to the (*E*)-$RO_2CCH{=}CHCO_2R$ precursors **III-1i**, **1k**, **1l**, **1n** gradually becomes more favoured according to the trend: R = Me < Et < *i*Pr < *t*Bu. This result was interpreted by assuming that an increase of the steric hindrance of the CO_2R groups progressively lowers the conformational freedom of these groups around C–C and C–O bonds in three-coordinate species but has little effect on the corresponding adducts. This may happen because the axial ligands are very effective in restricting the intramolecular mobility, possibly also through carbonyl–tin and carbonyl–mercury interactions, and the additional constraints of bulkier R groups do not increase the molecular rigidity any further.[41]

– an increase of the electron-withdrawing properties of the substituents on tin or mercury, which favours the formal reduction $Sn^{IV} \rightarrow Sn^{II}$ or $Hg^{II} \rightarrow Hg^0$ that follows the reaction. For instance, the addition of Cl–$SnMeCl_2$ to **III-1i** is quantitative, the addition of Cl–$SnMe_2Cl$ is an equilibrium, while Cl–$SnMe_3$ does not appreciably react with the same precursor.

– an decrease of the steric hindrance of the substituents on tin and mercury, e.g. Cl–Sn(*t*Bu)$_2$Cl does not appreciably reacts with **III-1i**, while an equilibrium establishes in solution when Cl–$SnMe_2Cl$ is added to the same three-coordinate compound.

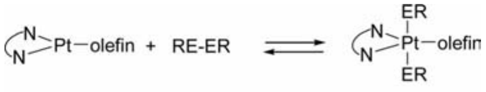
Finally, the addition of organotin and organomercury halides display opposite behaviour according to the nature of the adding halide. Thus the pK_{add} values respectively grow along the two series: Cl–$SnMe_3$ < Br–$SnMe_3$ < I–$SnMe_3$ and I–HgMe < Br–HgMe < Cl–HgMe. Very remarkably, this behaviour was found in agreement with the HSAB principle, which dictates the following order of hardness for the involved metal centres: $Hg^{II} < Pt^{II} < Sn^{IV}$. Thus, as the hardness of the halide ion increases (I < Br < Cl), the Sn^{II}–X bond becomes more favoured with respect to the corresponding contender Pt^{II}–X bond. This effect is obviously reversed when the Pt^{II}/Hg^{II} is considered.

Reactions with Dichalcogenides and Phenyl Selenyl Halides

The olefin complexes react with dichalcogenides RE-ER (E = O, S, Se, Te) and phenyl selenyl halides (PhSe–X) as reported in Table 9 and Table 10. In this way, a wide number of Pt^{II} complexes with Pt–O, Pt–S, Pt–Se and Pt–Te was isolated and characterised, both in solution and in the solid state.

The addition of dichalcogenides (Table 9) proceeded with symmetrical cleavage of the E–E bond, affording type-**V** product with Pt–ER fragments in axial position. The only exception was observed by using dibenzoyl peroxide, PhC(O)O–OC(O)Ph, which unexpectedly led to the attainment of the five-coordinate complex [Pt(OH)-$(PhCO_2)$(**1**){(*E*)-$MeO_2CCH{=}CHCO_2Me$}] (**V-121**) in which

Table 9. Oxidative addition of dichalcogenides.

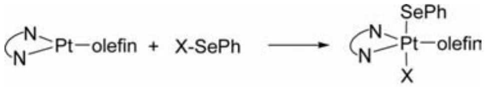


III **V**

Type-**III** complex	RE–ER electrophile and labels of the type-**V** products	–pK_{add} (298 K)	Ref.
III-1h	HO–OH (**V-112**)	[a]	[43]
	AcO–OAc (**V-113**)	[a]	[43]
	PhS–SPh (**V-114**)	[a]	[43]
	MeS–SMe (**V-115**)	[a]	[43]
	MeSe–SeMe (**V-116**)	[a]	[43]
	PhSe–SePh (**V-117**)	[a]	[43]
	PhTe–TePh (**V-118**)	[a]	[43]
III-1i	HO–OH (**V-119**)	[a]	[43]
	AcO–OAc (**V-120**)	[a]	[43]
	PhC(O)O–OC(O)Ph[b] (**V-121**)	[a]	[43]
	MeS–SMe (**V-122**)	[a]	[43]
	PhS–SPh (**V-123**)	[a]	[43]
	MeSe–SeMe (**V-124**)	3.0[c]	[44]
	PhSe–SePh (**V-125**)	[a]	[44]
	PhTe–TePh (**V-126**)	[a]	[43]
III-1k	MeSe–SeMe (**V-127**)	3.3[d]	[44]
III-1l	MeSe–SeMe (**V-128**)	3.4[e]	[44]
III-1o	MeSe–SeMe (**V-129**)	2.8	[44]
III-1p	MeS–SMe (**V-130**)	[a]	[43]
	MeSe–SeMe (**V-131**)	2.7	[44]
III-1q	MeSe–SeMe (**V-132**)	2.5	[44]
	PhSe–SePh (**V-133**)	[a]	[44]
III-3i	MeSe–SeMe (**V-134**)	[a]	[43]
	PhSe–SePh (**V-135**)	[a]	[43]

[a] Complete conversion. [b] The isolated product is the five-coordinate complex [Pt(OH)(OBz)(**1**){(*E*)-$MeO_2CCH{=}CHCO_2Me$}]. [c] $\Delta H = -13.5 \pm 0.6$ kcal mol^{-1}; $\Delta S = -31 \pm 2$ cal mol^{-1} K^{-1}. [d] $\Delta H = -15.5 \pm 0.6$ kcal mol^{-1}; $\Delta S = -38 \pm 2$ cal mol^{-1} K^{-1}. [e] $\Delta H = -15.0 \pm 0.3$ kcal mol^{-1}; $\Delta S = -36 \pm 1$ cal mol^{-1} K^{-1}.

Table 10. Oxidative addition of selenyl phenyl halides.



III **V**

Type-**III** complex	PhSe–X electrophile and labels of the type-**V** products	Ref.
III-1b	PhSe–Cl (**V-136**)	[45]
III-1c	PhSe–Cl (**V-137**)	[45]
	PhSe–Br (**V-138**)	[45]
III-1h	PhSe–Cl (**V-139**)	[45]
	PhSe–Br (**V-140**)	[45]
III-1i	PhSe–Cl (**V-141**)	[45]
	PhSe–Br (**V-142**)	[45]
	PhSe–I (**V-143**)	[45]
III-1p	PhSe–Cl (**V-144**)	[45]
	PhSe–Br (**V-145**)	[45]
III-1r	PhSe–Cl (**V-146**)	[45]
	PhSe–Br (**V-147**)	[45]

one benzoate was substituted for a hydroxy group. Another exception was experimented by performing the addition of diselenides on a three-coordinate precursor containing a sterically unhindered chelates, i.e. **III-3i**. Contrary to the general trend depicted in Scheme 2, stable five-coordinate compounds (**V-135** and **V-136**) could be isolated. These species did not undergo the expected olefin loss, but slowly decomposed in solution in a non-chemoselective way.

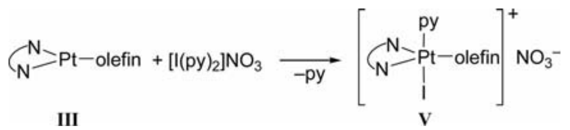
Analogously to organotin and organomercury derivatives (see previous section), type-**V** compounds containing MeSe– axial ligands equilibrated in solution with the corresponding three-coordinate precursors and MeSe–SeMe. This prominent and salient behaviour, unprecedented for diselenides, was again usefully employed for revealing clean relationship between the extent of addition and the electronic and steric properties of the alkene. Furthermore, the ΔH_{add}'s values were used to estimate the Pt–Se bond energy, which was found to be 33 kcal mol^{-1}.

As expected, the addition of phenyl selenyl halides X–SePh involved the activation of the selenium-halogen bond (Table 10).

Reactions with Iodonium and Trialkyloxonium Salts

The three-coordinate olefin complexes promptly reacted with formally charged electrophiles affording corresponding cationic complexes. Thus, the {I$^+$} ion, in the form of [I(py)$_2$]NO$_3$, gave rise to five-coordinate compounds with Pt–I and Pt–py bonds in axial position (Table 11).

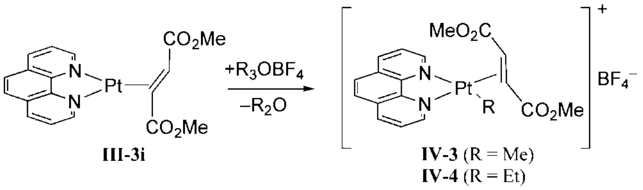
Table 11. Oxidative addition of [I(py)$_2$]NO$_3$.



Type-**III** complex	Labels of the type-**V** products	Ref.
III-1c	**V-148**	[14]
III-1g	**V-149**	[14]
III-1h	**V-150**	[14]
III-1i	**V-151**	[14]
III-1j	**V-152**	[14]
III-1k	**V-153**	[14]
III-1s	**V-154**	[14]
III-9i	**V-155**	[14]
III-10h	**V-156**	[14]

The most important feature of these **V** products is the high solubility in water, which was employed for assessing the cytotoxic activity of **V-148** with very promising results.

The addition was also extended to methyl and ethyl cations stabilized as the corresponding oxonium salts (R$_3$O$^+$)(BF$_4^-$).[46] This reaction was found to be very useful for the isolation of very rare examples of square-planar compounds containing an electron-poor alkene, according to Scheme 9.



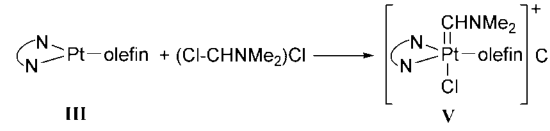
Scheme 9. Addition of R$_3$OBF$_4$ to **III-3i**.

Complexes **IV-3** and **IV-4** belong to a larger class of related compounds whose spectroscopic and bonding properties have been the object of thorough studies.[28]

Reactions with a Carbene Precursor

Within a wider study concerning the feasibility of five-coordinate Pt^{II} complexes bearing carbene ligands in axial position, some three-coordinate compounds were treated with the carbene precursor (ClCH=NMe$_2$)Cl (Table 12). This approach revealed successful and the corresponding cationic products of type **V** showed, in axial positions, the desired carbene ligand fragment **:**CH=NMe$_2$ and a chloride.

Table 12. Oxidative addition of carbene precursors to the three-coordinate complexes.



Type-**III** complex	Labels of the type-**V** products	Ref.
III-1h	**V-157**	[17]
III-1i	**V-158**	[17]
III-1r	**V-159**	[17]
III-6i	**V-160**	[17]

The compounds of type **V** were thoroughly characterised, and the molecular structure of **V-157** was solved along with that of a corresponding by-product [PtCl(H$_2$O)(**1**)(*Z*-MeO$_2$CCH=CHCO$_2$Me)] (**V-161**), which displays water in place of the axial carbene ligand.

Other Reactions

As mentioned in the Introduction, complexes of type **III** are especially appreciated for their stability and the consequent opportunity to carry out thorough characterization studies. In some remarkable occasions,[20] the complexes (from **III-17i** to **III-19s**) have been used in catalysis, i.e. styrene hydrosilylation, and their activity homogeneously compared. In general, the ligands which stabilise the platinum complexes result in a reduced catalytic activity. For example, the fumarate species **III-19i** is intrinsically more stable than the corresponding maleic anhydride complex **III-19s**, but the latter one is a more active catalyst.

Conclusions

This review offers a complete survey of the Pt^0 compounds of general formula [Pt(N,N'-ligand)(olefin)] (**III**), along with a description of their essential spectroscopic and structural features.

The reactivity of type-**III** complexes towards X–Y electrophiles has also been evaluated, with particular emphasis towards the factors which affect both the equilibrium position and the stability of the corresponding five-coordinate compounds [PtX(Y)(N,N'-ligand)(olefin)] (**V**). In this way, fundamental thermodynamic parameters have been assessed, and relevant trends have been disclosed.

The availability of strictly related compounds has also allowed a consistent assessment of the coordinating properties of several ligand fragments. Thus, by simply comparing the distances of the Pt–Cl axial bonds within a homogeneous series of type-**V** complexes, it is possible to suggest a reliable trend for the *trans*-influence for several ligands (Table 13).

Table 13. *trans*-Influence of ligand fragments according to the elongation of Pt–Cl bonds.

Type-**V** complex	Ligand fragment	Pt–Cl distance [Å]	Ref.
V-161	–OH_2	2.269(2)	[17]
V-157	=$CHNMe_2$	2.389(2)	[17]
V-79	–$PbPh_2Cl$	2.447(6)	[37]
V-56	–$GePh_2Cl$	2.452(4)	[36]
V-46	–H	2.464(3)	[35]
V-81	–$SnMe_2Cl$	2.476(2)	[8]
V-61	–$SnPh_2Cl$	2.478(3)	[4]
V-103	–HgMe	2.558(1)	[10]

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[41] Alternatively, larger substituents on the olefin surely result in longer Pt–olefin bonds. Since olefins with electron-withdrawing groups stabilize the Pt^0 complex by decreasing the electron density on the metal, a longer Pt olefin bond results in a less effective backdonation and, as a consequence, a more electron-rich platinum centre. This in turn would favor formation of the Pt^{II}

type-**V** complex, in which charge removal plays a much less important role.[42]

[42] We thank a referee for this suggestion.

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