Coordination Chemistry Reviews, 133 (1994) 67–114

Five-coordinate alkene complexes of palladium(II) and platinum(II)

Vincenzo G. Albano
Dipartimento di Chimica "G. Ciamician," via Selmi 2, I-40126 Bologna (Italy)
Giovanni Natile
Dipartimento Farmaco-Chimico, via E. Orabona 4, I-70125 Bari (Italy)
Achille Panunzi
Dipartimento di Chimica, via Mezzocannone 4, I-80134 Napoli (Italy)

(Received 21 December 1992)

CONTENTS

Correspondence to: A. Panunzi, Dipartimento di Chimica, via Mezzocannone 4, I-80134 Naples, Italy.

0010-8545/94/$26.00
SSDI 0010-8545(93)00977-Z

ABSTRACT

The review is focused on five-coordinate Pd(II)– and Pt(II)–alkene complexes with a trigonal bipyramidal arrangement of the ligands. Synthetic methods are extensively described and the characterization procedures of 243 compounds are listed. Stereochemical and reactivity aspects are reported. A chart with the X-ray structural parameters of 19 complexes and a list of 76 references are included.

1. INTRODUCTION

In the past 20 years, several reports on five-coordinate platinum(II) complexes have appeared in the literature. Most of the compounds have the general formula [M(η^2-alkene)(N—N)XY] where N—N is a bidentate nitrogen donor ligand, X and Y are either two anions (type A) or one anion and one neutral ligand (type B). There are also cases in which the five-coordinate species contains, in addition to the alkene and one monodentate ligand, a tridentate nitrogen donor ligand (type C).

More recently, five-coordinate alkene complexes of palladium(II) have also been reported. These compounds are of type A and have ancestors in the complexes of formula [Pd(η^5-C_5H_5)L(alkene)]$^+$ described by Kurosawa in 1980 [1]. The five-coordinate species of palladium(II) are much fewer than those of platinum(II), but represent a relevant portion of the monoalkene complexes of palladium(II) so far reported, here including also those having a square planar geometry.

The five-coordinate complexes, although being coordinatively saturated, represent a novelty for platinum(II) and palladium(II), for which square planar coordination is commonly found. No quotation of five-coordinate species of platinum(II) or palladium(II) containing an alkene is found up to the end of the 1960s [2], although the first organometallic compound (Zeise's anion reported in 1825) was a platinum(II) complex containing an ethene and three chloride ions in a square planar arrangement.

The aim of this article is to give an overview of the five-coordinate alkene complexes of platinum(II) and palladium(II), describing their syntheses, characterization and some relevant aspects of their chemistry.

2. GENERAL SURVEY

In 1970, Theophanides and Kong reported on the preparation of a five-coordinate complex of platinum containing an alkyne ligand [3]. The synthesis, however, could not be extended to alkene complexes of similar geometry.

In the same year, a complex of formula $[Pt(\eta^2{-}C_2F_4)RX(N{-}N')]$ (R and X are carbon and halide ions, respectively) was reported by Clark and Puddephatt [4]. The trigonal bipyramidal structure was assigned on the ground of IR data and by comparison with the already known structure of the alkyne complexes. This complex was the first of a wide series of complexes synthesized by the group of Panunzi and co-workers from 1985 onward [5]. One of them represents the first example of a resolved stereogenic transition metal centre in a trigonal bipyramidal geometry [5].

Complexes similar to that reported by Clark and Puddephatt, but containing unsubstituted ethene and two halide ions, were reported by the group of Natile and co-workers since 1973 [6]. Their structure was assigned on the basis of NMR, IR and conductivity data and later fully confirmed by X-ray analysis [7]. These complexes are rather stable in the solid state, while in solution they decompose with loss of the ethene.

Another research group involved in this type of chemistry was that of van Koten and co-workers [8]. They generally used diimines as chelating N-donor ligands, which were invariably σ,σ-coordinated to the metal.

All neutral complexes containing a bidentate, generally N-donor, ligand, two anionic ligands and an alkene have been grouped in type A.

Complexes similar to those of type A, but in which one anionic ligand has been replaced by a neutral ligand, have also been isolated. These complexes have a net positive charge and have been grouped in type B.

Another relevant series of five-coordinate complexes is that having the formula $[Pt(\eta^2\text{-alkene})X(L)]$ where L spans three coordination sites. These were described by Clark and Manzer in 1973 and have been grouped in type C [9]. Cyclopentadienyl complexes can also be included in this group.

Finally, there are complexes in which the coordinated alkene moiety is part of a chelate ligand. These complexes have been grouped in type D.

The different types of complexes and ligands are summarized in Charts 1 and 2, respectively, and a list of the complexes is given in Table 1.

3. SYNTHETIC PROCEDURES: PLATINUM COMPLEXES

3.1 Type A complexes

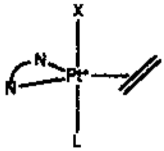
(1) Type A dihalide– [6–8,10–29] and halide–alkyl complexes [5,28,30–32] are prepared by reaction of a bidentate ligand, usually a N-donor ligand (N–N), with a four-coordinate complex containing the alkene. The starting complex can be mononuclear, such as the Zeise's anion (eqn. (1)) [10], or, alternatively, a binuclear alkene complex such as the Zeise's dimer (eqn. (2)) [9].

$$K[Pt(\eta^2{-}C_2H_4)Cl_3] + N{-}N = [Pt(\eta^2{-}C_2H_4)Cl_2(N{-}N)] + KCl \qquad (1)$$

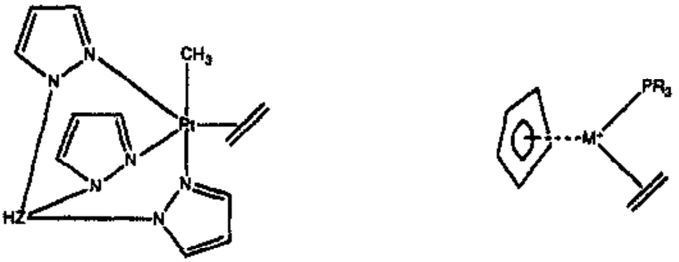
$$[Pt(\eta^2{-}C_2H_4)Cl_2]_2 + 2N{-}N = 2[Pt(\eta^2{-}C_2H_4)Cl_2(N{-}N)] \qquad (2)$$

TYPE A COMPLEXES

TYPE B COMPLEXES



TYPE C COMPLEXES

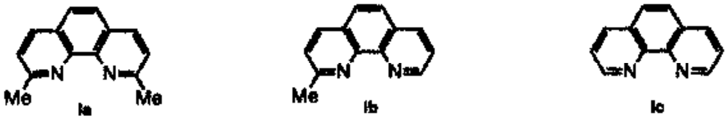


TYPE D COMPLEXES

R= hydrocarbyl group
X= halide or hydrocarbyl group
Y= halide
Z= carbon or boron
L= neutral ligand or donor group
M= Pd or Pt

Chart 1. Types of complexes.

TYPE I LIGANDS

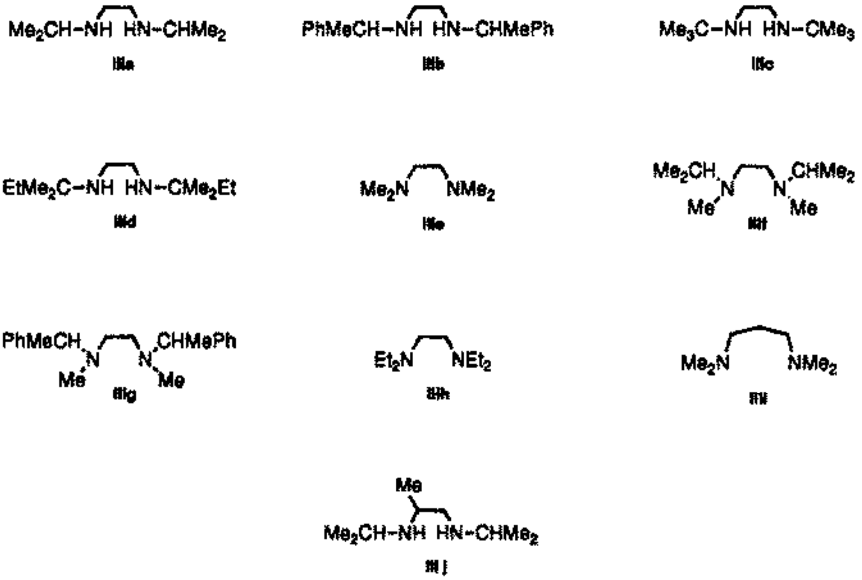


Ia Ib Ic

TYPE II LIGANDS

IIa IIb

TYPE III LIGANDS



IIIa IIIb IIIc IIId IIIe IIIf IIIg IIIh IIIi IIIj

Chart a.

TYPE IV LIGANDS

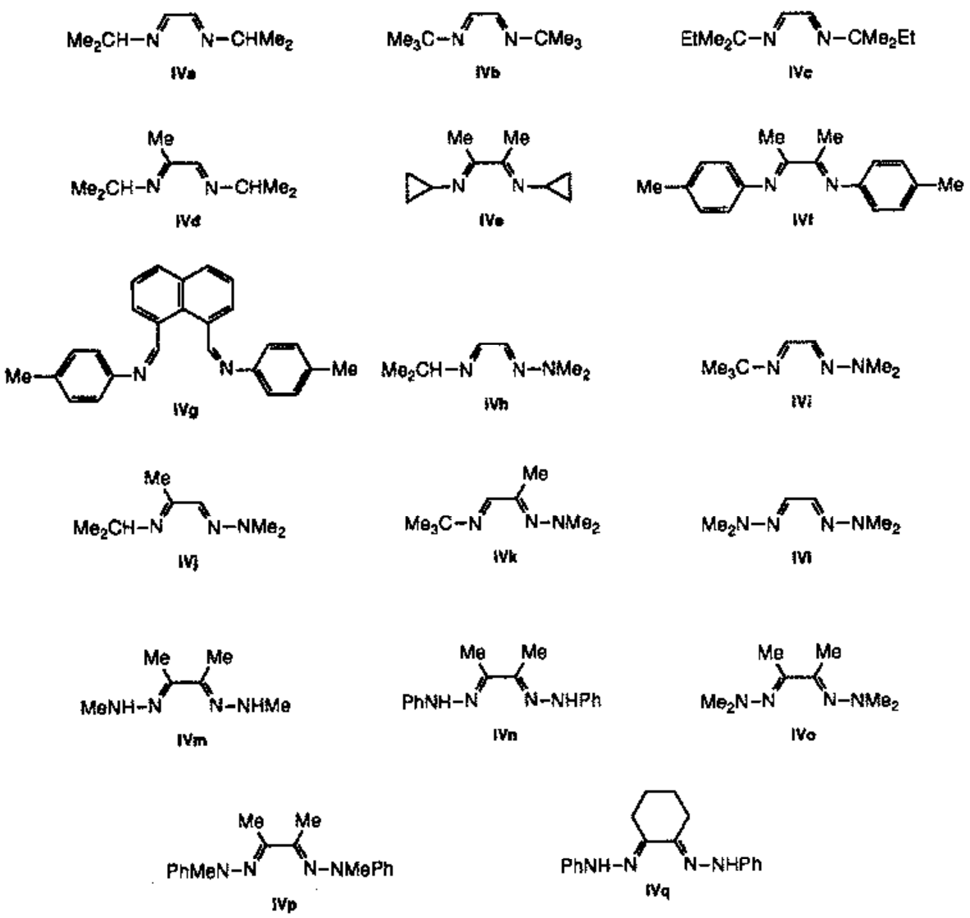
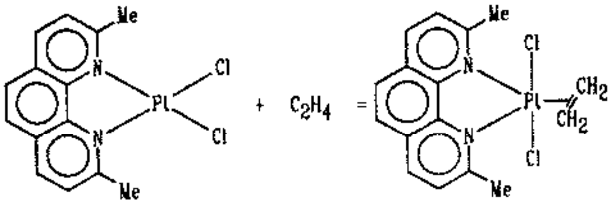
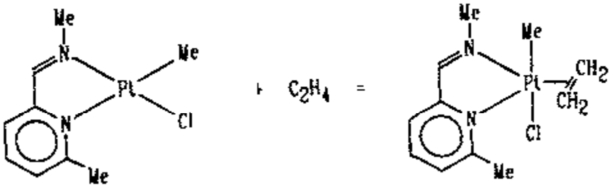


Chart 2 (continued).

(2) Another possible procedure for the preparation of this type of complex is the addition of the alkene to a four-coordinate species of formula [PtXY(N–N)]. This procedure can be used only in the cases in which the starting complex is strongly activated towards dissociation of one end of the diamine, e.g. eqns. (3) and (4) [29,30].

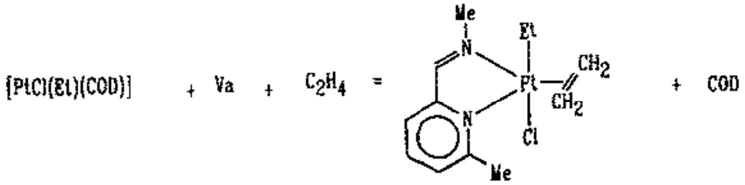


(3)



(4)

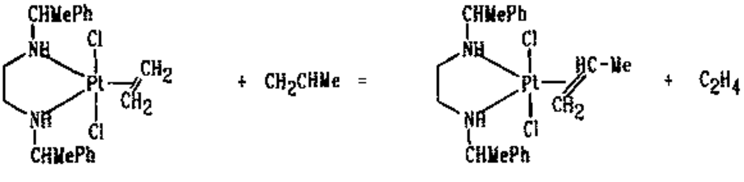
(3) A short-cut procedure leading directly to type A complexes is the simultaneous reaction of a labile four-coordinate complex with both the N–N and the alkene ligands (eqn. (5), COD = cycloocta-1,5-diene) [32].



(5)

(4) Another synthetic procedure which is largely feasible and, on some occasions, most convenient, is the ligand exchange reaction which transforms a five-coordinate species into another compound of the same type.

(4a) Alkene exchange. Equation (6) is an example of this procedure [11].



(6)

The substitution of an alkene by another alkene of comparable steric hindrance and bearing electron-withdrawing groups is thermodynamically favoured. The ancillary ligands can influence the reaction rate, e.g. the presence of a rigid and sterically demanding N–N ligand such as 2,9-dimethyl-1,10-phenanthroline causes a remarkable slow down of the exchange reaction.

(4b) Halide exchange. This reaction is very useful for the preparation of complexes containing halide ligands other than chloride, e.g. the diiodo derivative reported in eqn. (7) [16].

TYPE V LIGANDS

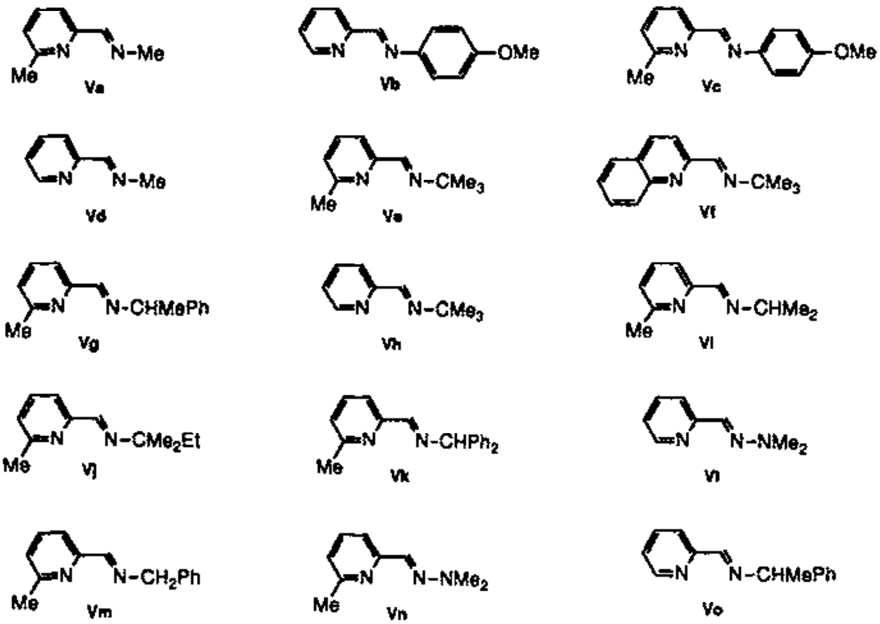
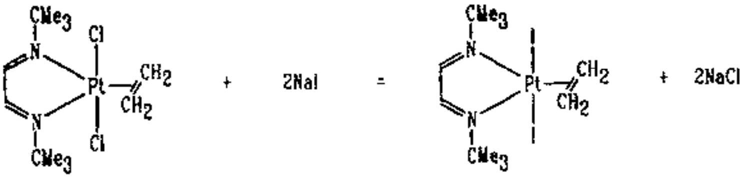
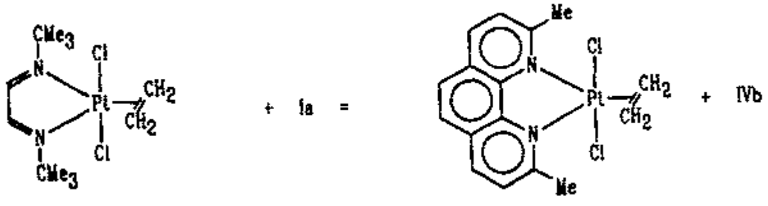


Chart 2 (continued).



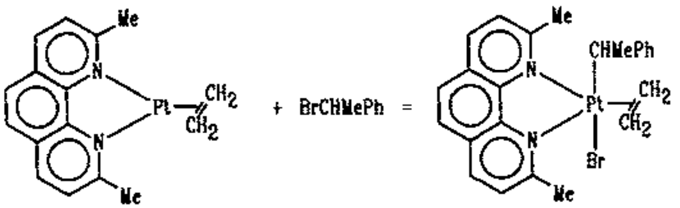
(7)

(4c) Exchange of the N–N chelate. To date, this reaction has only a limited synthetic utility (eqn. (8)) [16].



(8)

(5) Another synthetic route to type A complexes involves the oxidative addition of an electrophilic reagent to three-coordinate [Pt(alkene)(N–N)] species containing N–N ligands with great steric demand (eqn. (9)) [28].



(9)

This procedure is particularly useful for the synthesis of complexes with functionalized alkyl groups attached to platinum [33].

(6) A recent paper by Mink et al. describes the synthesis and characterization of a five-coordinate complex containing three C=C double bonds coordinated to platinum in the equatorial plane. This compound can be considered a type A complex

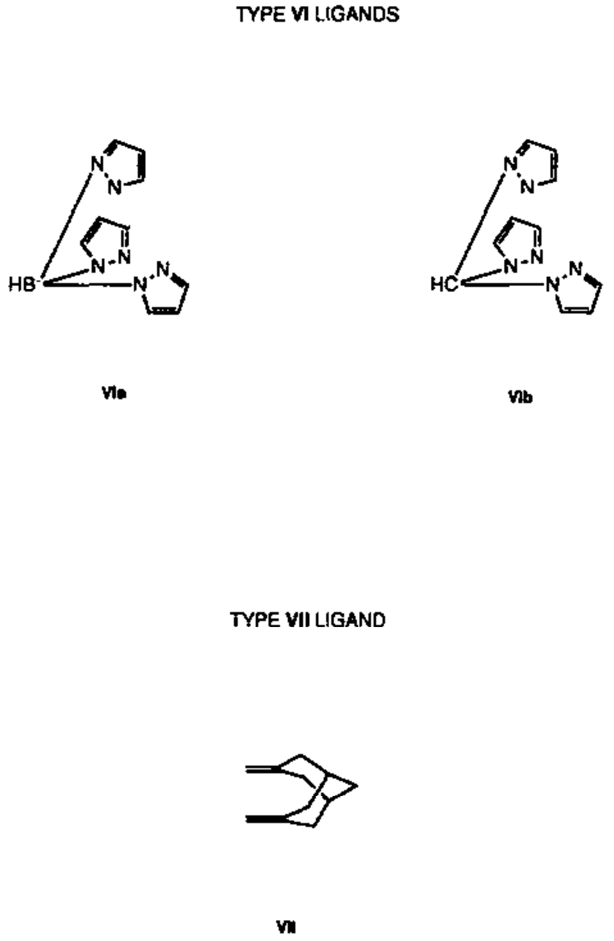


Chart 2 (continued). Types of chelate ligands.

TABLE 1

A. Type A complexes: [M(alkene)XY(N–N)]

Entry	M	X	Y	Alkene	N–N	
A_1	Pt	Cl	Cl	$CH_2{=}CH_2$	Ia	properties, synth., NMR, X-ray [29]
A_2	Pt	Cl	Br	$CH_2{=}CH_2$	Ia	properties, synth., NMR [29]
A_3	Pt	Br	Br	$CH_2{=}CH_2$	Ia	properties, synth., NMR [29]
A_4	Pt	I	I	$CH_2{=}CH_2$	Ia	properties, synth., NMR [29]
A_5	Pd	Cl	Cl	$CH_2{=}CH_2$	Ia	properties, synth., NMR [29]
A_6	Pd	Cl	Br	$CH_2{=}CH_2$	Ia	properties, synth., NMR [29]
A_7	Pd	Br	Br	$CH_2{=}CH_2$	Ia	properties, synth., NMR [29]
A_8	Pd	I	I	$CH_2{=}CH_2$	Ia	properties, synth., NMR [29]
A_9	Pt	Cl	Cl	$CH_2{=}CH_2$	Ic	properties, synth., NMR, IR [10]
A_{10}	Pt	Cl	Cl	$CH_2{=}CH_2$	IIa	synth., NMR, IR [10]; properties [44]
A_{11}	Pt	Cl	Cl	$CH_2{=}CH_2$	IIIa	properties [25]; synth., IR [19]; NMR [19,25]
A_{12}	Pt	Cl	Cl	$CH_2{=}CH_2$	IIIb	properties [25]; synth., IR [19]; NMR [19,25]; X-ray [25]
A_{13}	Pt	Cl	Cl	$CH_2{=}CH_2$	IIIc	properties, NMR [18,25]; synth., IR, Raman spect. [25]
A_{14}	Pt	Cl	Cl	$CH_2{=}CH_2$	IIIe	properties, synth., NMR [10,12]; IR [10]
A_{15}	Pt	Cl	Cl	$CH_2{=}CH_2$	IIIf	properties, synth., NMR, IR [19]
A_{16}	Pt	Cl	Cl	$CH_2{=}CH_2$	IIIg	properties [11,14]; synth. [11,19]; NMR, IR [11,14,19]; X-ray [14]
A_{17}	Pt	Cl	Cl	$CH_2{=}CH_2$	IIIh	properties, synth., NMR, IR [19]
A_{18}	Pt	Cl	Cl	$CH_2{=}CH_2$	IIIi	properties, synth., NMR [12]
A_{19}	Pt	Cl	Cl	$CH_2{=}CH_2$	IIIj	properties, synth., NMR, IR, Raman spect. [18]
A_{20}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVa	properties, synth., NMR, IR, Raman spect. [18]
A_{21}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVb	properties, synth., NMR [16,18]; IR, Raman spect. [18]
A_{22}	Pt	Br	Br	$CH_2{=}CH_2$	IVb	properties, synth., NMR [16,18]; IR, Raman spect. [18]
A_{23}	Pt	Cl	Br	$CH_2{=}CH_2$	IVb	properties, synth., NMR [16]
A_{24}	Pt	I	I	$CH_2{=}CH_2$	IVb	properties, synth., NMR [16]
A_{25}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVc	properties, synth., NMR [16,18]; IR, Raman spect. [18]

A_{26}	Pt	Br	Br	$CH_2{=}CH_2$	IVc	properties, synth., NMR [16]
A_{27}	Pt	I	I	$CH_2{=}CH_2$	IVc	properties, synth., NMR [16]
A_{28}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVd	properties, synth., NMR, IR, Raman spect. [18]
A_{29}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVe	properties, synth., NMR, IR [10]
A_{30}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVf	properties, synth., NMR, IR [10]
A_{31}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVg	properties, synth., NMR, IR [10]
A_{32}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVh	properties, synth., NMR, X-ray [21]
A_{33}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVi	properties, synth., NMR [21]
A_{34}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVj	properties, synth., NMR [21]
A_{35}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVk	properties, synth., NMR [21]
A_{36}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVl	properties, synth., NMR, IR [21]; X-ray [73]
A_{37}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVm	properties, synth., NMR, IR, X-ray [7]
A_{38}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVn	properties, synth., NMR, IR [7]
A_{39}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVo	properties, synth., NMR, IR [7]
A_{40}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVp	properties, synth., NMR, IR [6,7]
A_{41}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVq	properties, synth., NMR, IR [7]
A_{42}	Pt	Cl	Cl	$CH_2{=}CH_2$	Vg	properties, synth., NMR, IR, Raman spect. [17]
A_{43}	Pt	Cl	Cl	$CH_2{=}CH_2$	Vh	properties, synth., NMR, IR, Raman spect. [17]
A_{44}	Pt	Cl	Cl	$CH_2{=}CH_2$	IVk	properties, synth., NMR, IR, Raman spect. [17]
A_{45}	Pt	Cl	Cl	$CH_2{=}CH_2$	Vo	properties, synth., NMR, IR, Raman spect. [17]
A_{46}	Pt	Cl	Cl	$CH_2{=}CH_2$	VII	properties, synth., NMR, IR [34]
A_{47}	Pt	Br	Br	(*E*)-MeOOCCH=CHCOOMe	Ia	synth., NMR [27,28]
A_{48}	Pt	Cl	Cl	$CH_2{=}CHMe$	Ia	properties, synth., NMR [29]
A_{49}	Pt	Cl	Cl	$CH_2{=}CHEt$	Ia	properties, synth., NMR [29]
A_{50}	Pt	Cl	Cl	(*E*)-MeCH=CHMe	Ia	properties, synth., NMR [29]
A_{51}	Pt	Cl	Cl	(*Z*)-MeCH=CHMe	Ia	properties, synth., NMR [29]
A_{52}	Pt	Cl	Cl	$CH_2{=}CHPh$	Ia	properties, synth., NMR [29]
A_{53}	Pt	Br	Br	(*E*)-MeCH=CHMe	Ia	properties, synth., [29]
A_{54}	Pt	I	I	(*E*)-MeCH=CHMe	Ia	properties, synth., [29]
A_{55}	Pd	Cl	Cl	$CH_2{=}CHMe$	Ia	properties, synth., NMR [29]
A_{56}	Pd	Br	Br	$CH_2{=}CHMe$	Ia	properties, synth., NMR [29]
A_{57}	Pt	Cl	Cl	$CH_2{=}CHMe$	IIIb	properties, synth., NMR, IR [11]
A_{58}	Pt	Cl	Cl	$CH_2{=}CHPh$	IIId	properties, synth., NMR, IR, Raman spect. [18]

TABLE 1 *continued*

Entry	M	X	Y	Alkene	N–N	
A_{59}	Pt	Cl	Cl	CH_2=CHMe	IIIg	properties, synth., NMR, IR [11,20]; X-ray [20]
A_{60}	Pt	Cl	Cl	CH_2=CHEt	IIIg	properties, synth., NMR, IR [11]
A_{61}	Pt	Cl	Cl	(*Z*)-MeCH=CHMe	IIIg	properties, synth., NMR, IR [11]
A_{62}	Pt	Cl	Cl	(*E*)-MeCH=CHMe	IIIg	properties, synth., NMR, IR [11]
A_{63}	Pt	Cl	Cl	CH_2=CHPh	IIIg	properties, synth., NMR, IR [11]
A_{64}	Pt	Cl	Cl	CH_2=CHCHO	IIIg	properties [14,26]; synth., NMR, IR [14]
A_{65}	Pt	Cl	Cl	CH_2=CHCN	IIIg	properties [14,26]; synth., NMR, IR [14]
A_{66}	Pt	Cl	Cl	(*E*)-NCCH=CHCN	IIIg	properties [14,26]; synth., NMR, IR [14]; X-ray [26]
A_{67}	Pt	Cl	Cl	maleic anhydride	IIIg	properties, synth., NMR, IR [14]
A_{68}	Pt	Cl	Cl	maleimide	IIIg	properties, synth., NMR, IR [14]
A_{69}	Pt	Cl	Cl	CH_2=CHCOOMe	IIIg	properties, synth., NMR [26]
A_{70}	Pt	Cl	Cl	CH_2=CHPh	IVb	properties, synth. [8,18]; IR, NMR [18]; X-ray [8]
A_{71}	Pt	Cl	Cl	CH_2=CHCN	IVb	properties, synth., NMR [23]
A_{72}	Pt	Cl	Cl	Me_2C=C=CH_2	IVb	properties, synth., NMR [42]
A_{73}	Pt	Cl	Cl	(*E*)-MeCH=CHMe	IVh	properties, synth., NMR [21]
A_{74}	Pt	Cl	Cl	CH_2=CHEt	IVi	properties, synth., NMR [21]
A_{75}	Pt	Cl	Cl	(*E*)-MeCH=CHMe	IVi	properties, synth., NMR [21]
A_{76}	Pt	Cl	Cl	(*E*)-EtCH=CHEt	IVi	properties, synth., NMR [21]
A_{77}	Pt	Cl	Cl	(*E*)-cyclooctene	IVi	properties, synth., NMR [21]
A_{78}	Pt	Cl	Cl	(*E*)-MeCH=CHMe	IVj	properties, synth., NMR [21]
A_{79}	Pt	Cl	Cl	(*E*)-MeCH=CHMe	IVk	properties, synth., NMR [21]
A_{80}	Pt	Cl	Cl	CH_2=CHMe	IVk	properties, synth., NMR [21]
A_{81}	Pt	Cl	Cl	CH_2=CHMe	IVo	properties [13,21,23]; synth., NMR [13,21]
A_{82}	Pt	Cl	Cl	(*E*)-NCCH=CHCN	IVo	properties [20,23]; synth., NMR [23]
A_{83}	Pt	Cl	Cl	CH_2=CHCN	IVo	properties [20,23]; synth., NMR [23]
A_{84}	Pt	Cl	Cl	CH_2=CHCHO	IVo	properties [20,23]; synth., NMR [23]
A_{85}	Pt	Cl	Cl	(*E*)-MeCH=CHMe	IVo	properties [20,21,23]; synth., [21,22]; NMR [21]; X-ray [22]
A_{86}	Pt	Cl	Cl	CH_2=CHEt	IVo	properties, synth. [21,23]; NMR [21]

A_{87}	Pt	Cl	Cl	(*E*)-EtCH=CHEt	IVo	properties, synth. [21,23]; NMR [21]
A_{88}	Pt	Cl	Cl	(*E*)-cyclooctene	IVo	properties, synth. [21,23]; NMR [21]
A_{89}	Pt	Cl	Cl	$Me_2C=C=CH_2$	IVo	properties, synth., NMR [42]
A_{90}	Pt	Cl	Cl	$CH_2=CHMe$	Vh	properties, synth., NMR [21,23]
A_{91}	Pt	Cl	Cl	$CH_2=CHEt$	Vh	properties, synth., NMR [21,23]
A_{92}	Pt	Cl	Cl	(*E*)-MeCH=CHMe	Vh	properties, synth., NMR [21,23]
A_{93}	Pt	Cl	Cl	(*E*)-EtCH=CHEt	Vh	properties, synth., NMR [21,23]
A_{94}	Pt	Cl	Cl	(*E*)-cyclooctene	Vh	properties, synth., NMR [21,23]
A_{95}	Pt	Cl	Cl	$CH_2=CHCHO$	Vh	properties, synth., NMR [23]
A_{96}	Pt	Cl	Cl	(*E*)-NCCH=CHCN	Vh	properties, synth., NMR [23]
A_{97}	Pt	Cl	Cl	$CH_2=CHCN$	Vh	properties, synth., NMR [23]
A_{98}	Pt	Cl	Cl	$CH_2=CHPh$	Vi	properties, synth., NMR, IR [17]
A_{99}	Pt	Cl	Cl	$CH_2=CHPh$	Vj	properties, synth., NMR, IR [17]
A_{100}	Pt	Cl	Me	$CH_2=CH_2$	Ia	properties, synth., NMR [32]
A_{101}	Pt	I	Me	$CH_2=CH_2$	Ia	synth., NMR [28]
A_{102}	Pt	Cl	Et	$CH_2=CH_2$	Ia	properties, synth., NMR [32]
A_{103}	Pt	Br	Et	$CH_2=CH_2$	Ia	synth., NMR [28]
A_{104}	Pt	I	Ph	$CH_2=CH_2$	Ia	synth., NMR [28]
A_{105}	Pt	Br	CHMeCOOEt	$CH_2=CH_2$	Ia	synth., NMR [28]
A_{106}	Pt	Cl	CH_2Cl	$CH_2=CH_2$	Ia	synth., NMR [28]
A_{107}	Pd	Cl	Me	$CH_2=CH_2$	Ia	properties, synth., NMR [43,74]
A_{108}	Pt	Cl	Me	$CH_2=CH_2$	Ib	properties, synth., NMR [32]
A_{109}	Pt	Cl	Me	$CH_2=CH_2$	IIb	properties, synth., NMR [32]
A_{110}	Pt	Cl	Me	$CH_2=CH_2$	IIIa	properties, synth., NMR [32]
A_{111}	Pt	Cl	Me	$CH_2=CH_2$	IIIc	properties, synth., NMR [32]
A_{112}	Pt	Cl	Me	$CH_2=CH_2$	IIIe	properties, synth., NMR [30]
A_{113}	Pt	Cl	Me	$CH_2=CH_2$	IVb	properties, synth., NMR [30]
A_{114}	Pt	Cl	Me	$CH_2=CH_2$	IVo	properties, synth., NMR [5]
A_{115}	Pt	Cl	Me	$CH_2=CH_2$	Va	properties, synth., NMR [30]
A_{116}	Pt	Cl	Et	$CH_2=CH_2$	Va	properties, synth., NMR [32]
A_{117}	Pt	Cl	4-MeO-Ph	$CH_2=CH_2$	Va	properties, synth., NMR [32]
A_{118}	Pt	Cl	Me	$CH_2=CH_2$	Vb	properties, synth., NMR [32]
A_{119}	Pt	Cl	Me	$CH_2=CH_2$	Vc	properties, synth., NMR [32]

TABLE 1 *continued*

Entry	M	X	Y	Alkene	N–N	
A_{120}	Pt	Cl	C_6F_5	CH_2=CH_2	Vc	properties, synth., NMR [32]
A_{121}	Pt	Cl	2-Me-Ph	CH_2=CH_2	Vc	properties, synth., NMR [32]
A_{122}	Pt	Cl	Me	CH_2=CH_2	Ve	properties, synth., NMR [30]
A_{123}	Pt	Cl	Me	CH_2=CH_2	Vf	properties, synth., NMR [30]
A_{124}	Pt	Cl	Me	CH_2=CH_2	Vg	properties, synth., NMR [5,30,32]; X-ray [30]
A_{125}	Pt	Cl	Me	CH_2=CH_2	Vh	properties, synth., NMR [30]
A_{126}	Pt	Cl	Me	CH_2=CH_2	Vl	properties, synth., NMR [32]
A_{127}	Pt	Cl	Me	CH_2=CH_2	Vm	properties, synth., NMR [30]
A_{128}	Pt	Cl	Me	CH_2=CH_2	Vn	properties, synth., NMR [32]
A_{129}	Pd	Cl	Me	CH_2=CH_2	Vc	properties, synth., NMR [43]
A_{130}	Pd	Cl	Me	CH_2=CH_2	Ve	properties, synth., NMR [43]
A_{131}	Pd	Cl	Me	CH_2=CH_2	Vg	properties, synth., NMR [43]
A_{132}	Pt	I	Me	CH_2=CHMe	Ia	synth., NMR [28]
A_{133}	Pt	I	Me	(*E*)-MeOOCCH=CHCOOMe	Ia	synth., NMR [28]
A_{134}	Pt	Br	CHMePh	(*E*)-MeOOCCH=CHCOOMe	Ia	synth., NMR [28]
A_{135}	Pt	Br	Me	(*E*)-MeOOCCH=CHCOOMe	Ia	synth., NMR [28]
A_{136}	Pt	I	Et	(*E*)-MeOOCCH=CHCOOMe	Ia	synth., NMR [28]
A_{137}	Pt	I	CH_2Ph	(*E*)-MeOOCCH=CHCOOMe	Ia	synth., NMR [28]
A_{138}	Pt	Br	CH_2Ph	(*E*)-MeOOCCH=CHCOOMe	Ia	synth., NMR [28]
A_{139}	Pt	Cl	Me	CH_2=$CHCMe_3$	Ia	properties, synth., NMR [32]
A_{140}	Pt	Cl	Me	CH_2=CMe_2	Ia	properties, synth., NMR [32]
A_{141}	Pt	Cl	Me	(*E*)-MeCH=CHCMe	Ia	properties, synth., NMR [32]
A_{142}	Pd	Cl	Me	CH_2=CHMe	Ia	properties, synth., NMR [43,74]
A_{143}	Pd	Cl	Me	CH_2=CHO—*n*-Bu	Ia	properties, synth., NMR [43]
A_{144}	Pd	Cl	Me	CH_2=CHCOOMe	Ia	properties, synth., NMR [43]
A_{145}	Pd	Cl	Me	(*Z*)-$HOCH_2CH$=$CHCH_2OH$	Ia	properties, synth., NMR [43]
A_{146}	Pd	Cl	Me	CH_2=$CHCH_2OH$	Ia	properties, synth., NMR [43]
A_{147}	Pd	Cl	Me	CH_2=CHCHO	Ia	properties, synth., NMR [43,74]
A_{148}	Pd	Cl	Me	CH_2=CHCN	Ia	properties, synth., NMR [43]

A$_{149}$	Pd	Cl	Me	(*E*)-NCCH=CHCN	Ia	properties, synth., NMR [43]
A$_{150}$	Pd	Cl	Me	maleic anhydride	Ia	properties, synth., NMR, X-ray [43]
A$_{151}$	Pt	Cl	Me	maleic anhydride	IIa	properties, synth., NMR [32]
A$_{152}$	Pt	Cl	Me	maleimide	IIa	properties, synth., NMR [32]
A$_{153}$	Pt	Cl	Me	maleic anhydride	IVd	properties, synth., NMR [32]
A$_{154}$	Pt	Cl	Me	(*Z*)-COOHCH=CHCOOH	Va	properties, synth., NMR [24]
A$_{155}$	Pt	Cl	Me	CH$_2$=CHCN	Vb	properties, synth., NMR [32]
A$_{156}$	Pt	Cl	Me	(*E*)-NCCH=CHCN	Vb	properties, synth., NMR [32]
A$_{157}$	Pt	Cl	Me	CH$_2$=CHC(OH)(Me)$_2$	Vc	properties, synth., NMR [32]
A$_{158}$	Pt	Cl	Me	(*E*)-MeCH=CHMe	Vc	properties, synth., NMR [32]
A$_{159}$	Pt	Cl	Me	(*Z*)-MeCH=CHMe	Vc	properties, synth., NMR [32]
A$_{160}$	Pt	Cl	Me	CH$_2$=CHO–*n*-Bu	Vc	properties, synth., NMR [32]
A$_{161}$	Pt	Cl	Me	CH$_2$=CHC$_6$H$_5$	Vc	properties, synth., NMR [32]
A$_{162}$	Pt	Cl	Me	CH$_2$=CHC$_6$F$_5$	Vc	properties, synth., NMR [32]
A$_{163}$	Pt	Cl	Me	CH$_2$=CHEt	Vc	properties, synth., NMR [32]
A$_{164}$	Pt	Cl	Me	CH$_2$=CHCH$_2$OEt	Vc	properties, synth., NMR [32]
A$_{165}$	Pt	Cl	Me	CH$_2$=CHCH$_2$OH	Vc	properties, synth., NMR [32]
A$_{166}$	Pt	Cl	Me	(*E*)-ClCH=CHCl	Vc	properties, synth., NMR [32]
A$_{167}$	Pt	Cl	Me	CH$_2$=CHCOOMe	Vc	properties, synth., NMR [32]
A$_{168}$	Pt	Cl	Me	CH$_2$=CHCHO	Vc	properties, synth., NMR [32]
A$_{169}$	Pt	Cl	Me	CH$_2$=CHCN	Vc	properties, synth., NMR [32]
A$_{170}$	Pt	I	Me	(*E*)-MeOOCCH=CHCOOMe	Vc	synth., NMR [28]
A$_{171}$	Pt	Cl	Ph	CH$_2$=CHMe	Vc	properties, synth., NMR [32]
A$_{172}$	Pt	Cl	4-MeO-Ph	CH$_2$=CHMe	Vc	properties, synth., NMR [32]
A$_{173}$	Pt	Cl	4-CF$_3$O-Ph	CH$_2$=CHMe	Vc	properties, synth., NMR [32]
A$_{174}$	Pt	Cl	Me	CH$_2$=CHCN	Vd	properties, synth., NMR [32]
A$_{175}$	Pt	Cl	Me	maleic anhydride	Vd	properties, synth., NMR [32]
A$_{176}$	Pd	Cl	Me	(*E*)-NCCH=CHCN	Vc	properties, synth., NMR [43]
A$_{177}$	Pd	Cl	Me	CH$_2$=CHCN	Ve	properties, synth., NMR [43]
A$_{178}$	Pt	Cl	Cl	(*S*)-[CH$_2$=CH-CHMeEt]	IVo	properties, synth., NMR, X-ray [76]
A$_{179}$	Pt	Cl	Cl	(*R*,*S*)-[CH$_2$=CH-CHMeEt]	IVo	properties, synth., NMR [76]

TABLE 1 *continued*

B. Type B complexes: $[M(alkene)X(L)(N{-}N)]^+BF_4^-$

Entry	M	X	L	Alkene	N–N	
B_1	Pt	Me	MeCN	$CH_2{=}CH_2$	Ia	properties, synth., NMR [36]
B_2	Pt	Me	Me_3CCN	$CH_2{=}CH_2$	Ia	properties, synth., NMR [36]
B_3	Pt	Me	Me_2S	$CH_2{=}CH_2$	Ia	properties, synth., NMR [36]
B_4	Pt	Me	$MeNH_2$	$CH_2{=}CH_2$	Ia	properties, synth., NMR [36]
B_5	Pt	Me	pyridine	$CH_2{=}CH_2$	Ia	properties, synth., NMR [36]
B_6	Pt	Me	$PhNH_2$	$CH_2{=}CH_2$	Ia	properties, synth., NMR [36]
B_7	Pt	Me	MeCN	$CH_2{=}CH_2$	Vc	properties, synth., NMR [36]
B_8	Pt	Me	Me_3CCN	$CH_2{=}CH_2$	Vc	properties, synth., NMR [36]
B_9	Pt	Me	CF_3CN	$CH_2{=}CH_2$	Vc	properties, synth., NMR [36]
B_{10}	Pt	4-MeO-Ph	MeCN	$CH_2{=}CH_2$	Vc	properties, synth., NMR [36]
B_{11}	Pt	4-CF_3-Ph	MeCN	$CH_2{=}CH_2$	Vc	properties, synth., NMR [36]
B_{12}	Pt	Me	MeCN	$CH_2{=}CH_2$	Ve	properties, synth., NMR [36]
B_{13}	Pt	Me	MeCN	$CH_2{=}CH_2$	Vg	properties, synth., NMR [36]
B_{14}	Pt	Me	4-Me-$PhNH_2$	$CH_2{=}CH_2$	Vg	properties, synth., NMR [36]
B_{15}	Pt	Me	MeCN	$CH_2{=}CHMe$	Ia	properties, synth., NMR [36]
B_{16}	Pt	Me	MeCN	$CH_2{=}CHMe$	Vc	properties, synth., NMR [36]
B_{17}	Pt	Me	$PhNH_2$	$CH_2{=}CHCOOMe$	Vc	properties, synth., NMR [36]

C. Type C complexes: $[M(alkene)(PR_3)(Cp)]^+Y^-$

Entry	M	Y	PR_3	Alkene ($R-CH=CH_2$)	
C_1	Pt	ClO_4^-	PPh_3	R = H	properties, synth., NMR [1]
C_2	Pd	ClO_4^-	PPh_3	R = H	properties, synth., NMR [1]
C_3	Pd	ClO_4^-	PPh_3	R = Me	properties, synth., NMR [1]
C_4	Pd	ClO_4^-	PPh_3	R = Ph	properties, synth., NMR [1]
C_5	Pd	ClO_4^-	PPh_3	R = 4-Me–Ph	properties, synth. [1]
C_6	Pd	ClO_4^-	PPh_3	R = 4-Cl–Ph	properties, synth. [1]
C_7	Pd	ClO_4^-	PPh_3	R = 4-MeO–Ph	properties, synth. [1]
C_8	Pd	ClO_4^-	PPh_3	R = 4-NO_2–Ph	properties, synth., NMR [1]
C_9	Pd	ClO_4^-	PPh_3	R = 4-NMe_2–Ph	properties, synth., NMR [1]
C_{10}	Pd	ClO_4^-	$P(n\text{-}Bu)_3$	R = H	properties, synth., NMR [1]
C_{11}	Pd	ClO_4^-	$P(n\text{-}Bu)_3$	R = 4-NO_2–Ph	properties, synth., NMR [1]
C_{12}	Pd	ClO_4^-	$P(n\text{-}Bu)_3$	R = 4-MeCO–Ph	properties, synth. [1]
C_{13}	Pd	ClO_4^-	$P(n\text{-}Bu)_3$	R = 4-Cl–Ph	properties, synth., NMR [1]
C_{14}	Pd	ClO_4^-	$P(n\text{-}Bu)_3$	R = Ph	properties, synth., NMR [1]
C_{15}	Pd	ClO_4^-	$P(n\text{-}Bu)_3$	R = 4-Me–Ph	properties, synth., NMR [1]
C_{16}	Pd	ClO_4^-	$P(n\text{-}Bu)_3$	R = 4-MeO–Ph	properties, synth., NMR [1]
C_{17}	Pd	ClO_4^-	$P(n\text{-}Bu)_3$	R = 4-NMe_2–Ph	properties, synth., NMR [1]
C_{18}	Pd	BF_4^-	$P(n\text{-}Bu)_3$	R = 4-Cl–Ph	properties, synth. [1]
C_{19}	Pd	BF_4^-	$P(n\text{-}Bu)_3$	R = Ph	properties, synth. [1]
C_{20}	Pd	BF_4^-	$P(n\text{-}Bu)_3$	R = 4-MeO–Ph	properties, synth. [1]
C_{21}	Pd	ClO_4^-	PEt_3	R = Ph	properties, synth., NMR [1]
C_{22}	Pd	BF_4^-	PEt_3	R = Ph	synth., X-ray [75]

TABLE 1 *continued*

C′. Type C complexes: [M(alkene)X(L_3)]

Entry	M	X	Alkene	L_3	
C_{23}	Pt	Me	CH_2=CH_2	VIa	synth., NMR [38]
C_{24}	Pt	Me	maleic anhydride	VIa	properties [37]; synth. [41]; NMR [9,37,38]
C_{25}	Pt	Me	CH_2=C(CN)Me	VIa	properties [37]; synth. [37]; NMR [9,37]
C_{26}	Pt	Me	MeCH=CHCHO	VIa	properties [37]; synth. [37]; NMR [9,37]
C_{27}	Pt	Me	(*E*)-EtOOCCH=CHCOOEt	VIa	properties [37]; synth. [37]; NMR [9,37,38]
C_{28}	Pt	Me	*p*-benzoquinone	VIa	properties [37]; synth. [37]; NMR [9,37]
C_{29}	Pt	Me	CH_2=CHCOOMe	VIa	properties [37]; synth. [37]; NMR [9,37,38]
C_{30}	Pt	Me	CF_2=CF_2	VIa	properties [37]; synth. [37]; NMR [37,38]
C_{31}	Pt	Me	CH_2=CF_2	VIa	properties, synth., NMR [37]
C_{32}	Pt	Me	MeCH=C=CMe_2	VIa	properties, synth., NMR [37]
C_{33}	Pt	Me	CH_2=C(CF_3)CN	VIa	properties, synth., NMR [37]
C_{34}	Pt	Me	CH_2=CHCN	VIa	properties, synth. [37]; NMR [37,38]
C_{35}	Pt	Me	CF_2=CFH	VIa	properties, synth., NMR [37]
C_{36}	Pt	Me	CH_2=C=CHMe	VIa	properties, synth., NMR [37]
C_{37}	Pt	Me	(*E*)-NCCH=CHCN	VIa	synth., NMR [38]
C_{38}	Pt	Me	CH_2=CH_2	VIb	properties, synth., NMR [43]

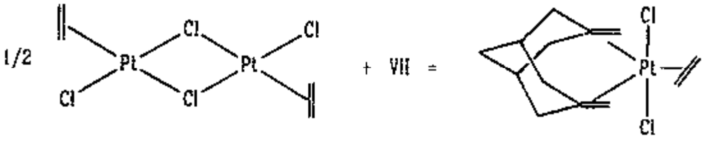
D. Type D complexes: [M(Y, alkene)X(N–N)]

Entry	M	X	Y, alkene	N–N	
D_1	Pt	Cl	$C_6H_{10}OMe$	Ia	properties, synth., NMR [41]
D_2	Pt	Cl	$C_8H_{12}OMe$	Ia	properties, synth., NMR, X-ray [41]
D_3	Pt	Cl	C_7H_8OMe	Ia	properties, synth., NMR [41]
D_4	Pd	Cl	$C_8H_{12}OMe$	Ia	properties, synth., NMR [41]
D_5	Pt	Cl	$C_6H_{10}OMe$	IVb	properties, synth., NMR [41]
D_6	Pt	Cl	$C_8H_{12}OMe$	IVb	properties, synth., NMR [41]
D_7	Pt	Cl	C_7H_8OMe	IVb	properties, synth., NMR [41]
D_8	Pt	Cl	$C_6H_{10}OMe$	IVl	properties, synth., NMR [41]
D_9	Pt	Cl	$C_8H_{12}OMe$	IVl	properties, synth., NMR [41]
D_{10}	Pt	Cl	C_7H_8OMe	IVl	properties, synth., NMR [41]

E. Type D complexes: $[M(dialkene)X(N–N)]^+BF_4^-$

Entry	M	X	Dialkene	N–N	
D_{11}	Pd	Me	C_8H_8	Ia	synth., NMR [43]
D_{12}	Pt	Me	C_8H_8	Ia	synth., NMR [35]

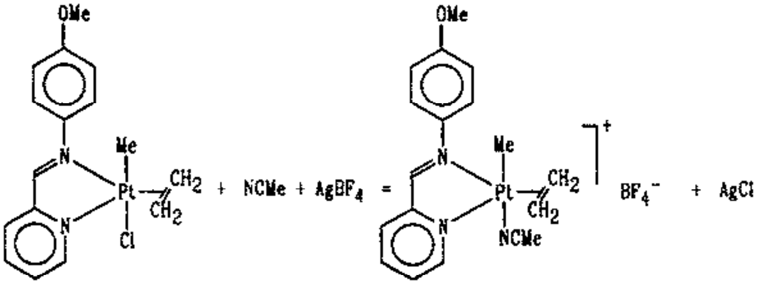
with a dialkene ligand taking the place of the bidentate N-donor ligand (eqn. (10)) [34].



(10)

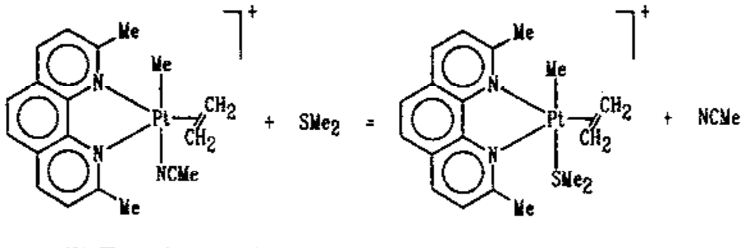
3.2 *Type B complexes*

(1) The general synthetic route to type B complexes involves the reaction of a type A complex with the silver salt of a poorly coordinating anion in the presence of a neutral ligand L (eqn. (11)) [35].



(11)

(2) Complexes of type B with a fairly labile L ligand can be used as precursors for the preparation of compounds of the same type but with a different L via an exchange reaction (eqn. (12)) [35].

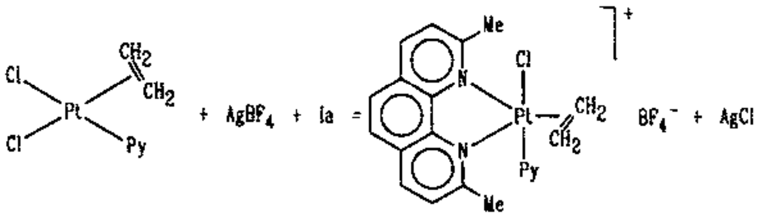


(12)

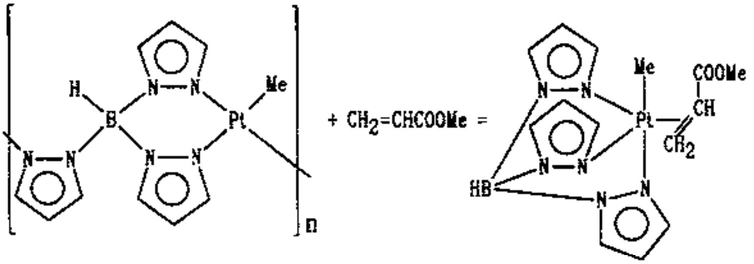
(3) Type B complexes can also be obtained from *cis*-[$PtCl_2$(alkene)(L)] species by treatment with a silver salt in the presence of an N—N ligand (eqn. (13)) [36].

3.3 *Type C complexes with ligands spanning three coordination sites*

(1) Five-coordinate complexes have been obtained by reaction with alkenes of the four-coordinate polymeric species containing the trispyrazolylborate anion as indicated in eqn. (14) [9,37,38].



(13)



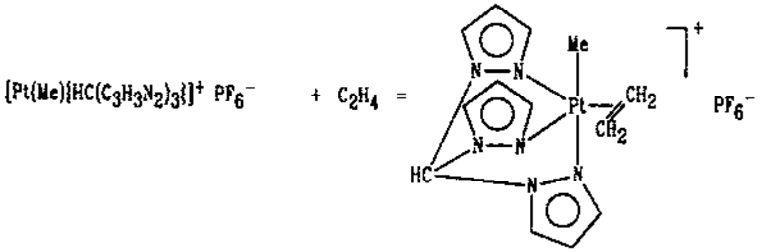
(14)

(2) Cationic complexes have been prepared by reaction of a square planar platinum–COD compound with tris-pyrazolylmethane and ethene (eqn. (15)) [39].

$[Pt(Me)Cl(COD)] + acetone + AgPF_6 = [Pt(Me)(COD)(acetone)]^+ PF_6^- + AgCl$

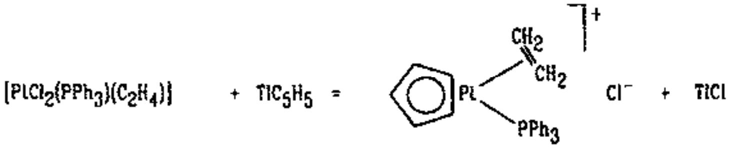
$[Pt(Me)(COD)(acetone)]^+ PF_6^- + VIb$

$= [Pt(Me)\{HC(C_3H_3N_2)_3\}]^+ PF_6^- + COD + acetone$



(15)

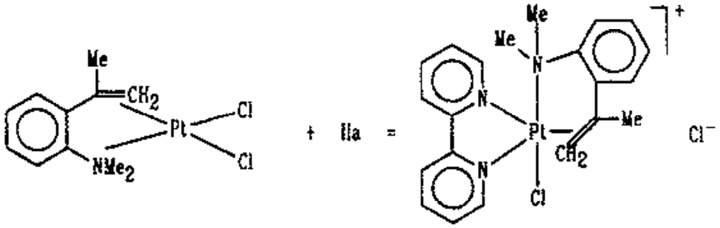
(3) Platinum complexes of formula $[Pt(\eta^5\text{–}C_5H_5)(PR_3)(alkene)]^+$ have also been prepared and characterized. These compounds can be included in class C if we consider the cyclopentadienyl ligand spanning three coordination positions (eqn. (16)) [1].



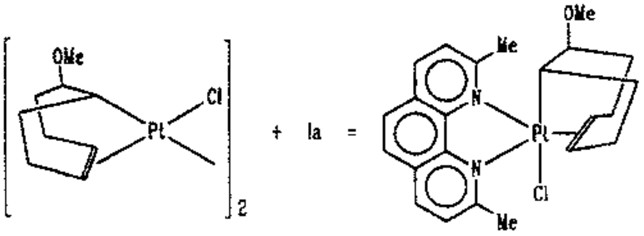
(16)

3.4 Type D complexes

(1) There are cases in which the alkene moiety is part of a chelate ligand. We shall call this class of compounds type D. The complexes can be either cationic [40] or neutral [41,42], depending upon the total charge of the chelating ligand containing the alkene (eqns. (17) and (18)).

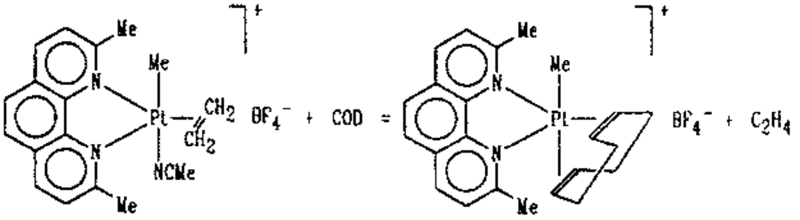


(17)



(18)

(2) In contrast with the behaviour of other dienes, which react with two metallic units to give binuclear complexes of type A [42], COD displays chelating ability toward platinum and gives five-coordinate species of type D (eqn. (19)) [35,43].



(19)

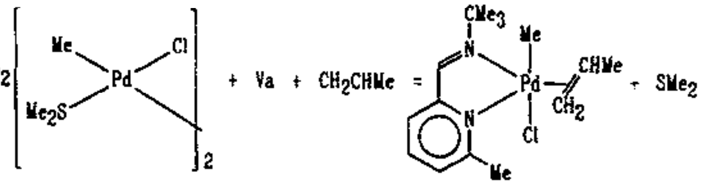
4. SYNTHETIC PROCEDURES: PALLADIUM COMPLEXES

4.1 Type A complexes

(1) Addition of the alkene to a suitable four-coordinate precursor is to date the most convenient procedure for the synthesis of palladium complexes of type A (eqn. (20)) [43].

$$[\mathrm{PdMeX(N{-}N)}] + \text{alkene} = [\mathrm{Pd}(\eta^2\text{-alkene})\mathrm{MeX(N{-}N)}] \tag{20}$$

(2) Type A complexes can also be prepared by reaction of a four-coordinate binuclear complex with an alkene and a bidentate N-donor ligand as shown in eqn. (21) [43].



(21)

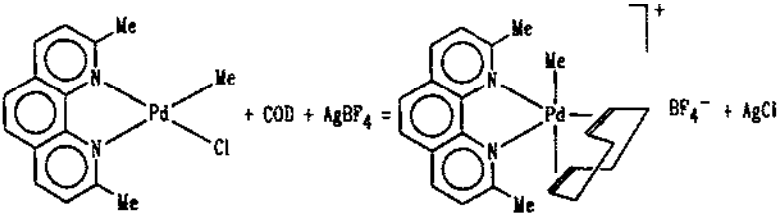
4.2 *Type C complexes*

Complexes of formula $[Pd(alkene)(\eta^5{-}C_5H_5)(PR_3)]^+$ [1] have also been prepared and characterized. These compounds can be included in class C if we consider the cyclopentadienyl ligand spanning three coordination positions (eqn. (22)).

$$[Pd(\eta^5{-}C_5H_5)(PR_3)Br] + CH_2{=}CHPh + AgClO_4 \tag{22}$$
$$= [Pd(alkene)(\eta^5{-}C_5H_5)(PR_3)](ClO_4) + AgBr$$

4.3 *Type D complexes*

A complex of type D can be obtained, as in the case of platinum, by reaction of a suitable palladium substrate with COD (eqn. (23)) [43].



(23)

5. STABILITY AND REACTIVITY

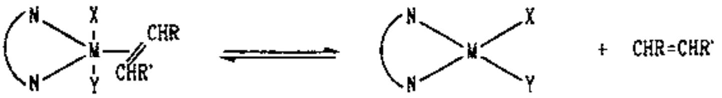
Five-coordinate species have been extensively investigated with respect to decomposition and ligand exchange reactions.

The decomposition patterns of the five-coordinate complexes include loss of the alkene, loss of an axial ligand, chelate ring opening, reductive elimination, and insertion of the unsaturated ligand into a σ bond.

5.1 Loss of the alkene

Five-coordinate complexes can have very different thermodynamic stabilities, ranging from cases in which the alkene is lost only at high temperature (close to the temperature of decomposition of the whole molecule) to cases in which the alkene is lost at rather low temperature and in the solid state.

The loss of the alkene is an irreversible process for many of the species described here; however, in some cases, an equilibrium has been observed (eqn. (24)). Some equilibrium constants are reported in Table 2.



(24)

Such an equilibrium is observed whenever there is a strong destabilization of the four-coordinate square planar geometry.

The steric requirements of the chelate ligand and, in particular, the in-plane bulk of the nitrogen substituents, appear to be the most important factor in determining such a destabilization. The relief of the interligand contacts which takes place on rearranging the molecular geometry from a square plane to a trigonal bipyramid results in an increased thermodynamic stability of the five-coordinate versus the four-coordinate species. This feature is well supported by the results obtained using 2,9-dimethyl-1,10-phenanthroline as a chelate in complexes of type A [32,34].

The electronic properties of the bidentate N donor ligand in positioning the equilibrium are definitely of minor importance with respect to the steric factors. This is clearly shown by the much greater stability of five-coordinate species containing 2,9-substituted-1,10-phenanthroline with respect to those containing phenanthrolines of similar basicity but with substituents in different ring positions.

The steric and electronic properties of the alkene also play an important role. Five-coordination is destabilized by the presence of bulky and electron-donating substituents on the alkene. Conversely, it is stabilized by the presence of electron-withdrawing substituents which strengthen the π back-donation from the metal to the alkene. The electronic effect can be balanced or even overcome by the steric factors [32].

The halide ligands in the apical positions of the trigonal bipyramid can also influence the stability of the five-coordinate species. The bulkier the anionic ligands, the more crowded becomes the four-coordinate species formed by alkene loss.

Steric factors also dominate in the stabilization of the five-coordinate geometry by an apical carbanion. Little difference is found in the pK_{diss} of a series of propene and ethene complexes of formula [Pt(alkene)Cl(C_6H_4R)(6-Me-pyridine-2-CH=N–C_6H_4OMe)], where R=CF_3 or OCH_3 (Table 2). On the other hand, the

TABLE 2

Alkene dissociation constants for [M(alkene)XY(N–N′)] complexes

M	X	Y	N–N′	Olefin	pK_{diss}
Pt	Cl	Cl	Ia	$CH_2{=}CH_2$	2.9
Pt	Cl	Cl	Ia	$CH_2{=}CHMe$	2.5
Pt	Cl	Cl	Ia	$CH_2{=}CHEt$	2.0
Pt	Cl	Cl	Ia	(*Z*)-MeCH=CHMe	1.0
Pt	Cl	Cl	Ia	$CH_2{=}CHPh$	0.7
Pt	Cl	Cl	Ia	(*E*)-MeCH=CHMe	0.2
Pt	Br	Br	Ia	(*E*)-MeCH=CHMe	1.2
Pt	I	I	Ia	(*E*)-MeCH=CHMe	2.7
Pt	Cl	Me	Ia	$CH_2{=}CHCMe_3$	0.4
Pt	Cl	Me	Ia	(*E*)-MeCH=CHMe	2.7
Pt	Cl	Me	Ib	$CH_2{=}CH_2$	2.3
Pt	Cl	Me	IIa	$O{=}\overline{CCH{=}CHC({=}O)O}$	0.6
Pt	Cl	Me	IIa	$O{=}\overline{CCH{=}CHC({=}O)N}H$	0.2
Pt	Cl	Me	IVo	$CH_2{=}CH_2$	4.2
Pt	Cl	Ph	Va	$CH_2{=}CH_2$	1.6
Pt	Cl	4-$MeOC_6H_4$	Va	$CH_2{=}CH_2$	1.5
Pt	Cl	Me	Va	$CH_2{=}CH_2$	1.8
Pt	Cl	Et	Va	$CH_2{=}CH_2$	2.3
Pt	Cl	Me	Vb	$CH_2{=}CH_2$	0.0
Pt	Cl	Me	Vb	$CH_2{=}CHCN$	1.2
Pt	Cl	Me	Vb	(*E*)-NCCH=CHCN	3.7
Pt	Cl	Me	Vc	$CH_2{=}CH_2$	3.7
Pt	Cl	Me	Vc	(*E*)-MeCH=CHMe	−0.6
Pt	Cl	Me	Vc	(*Z*)-MeCH=CHMe	0.2
Pt	Cl	Me	Vc	$CH_2{=}CHO$–*n*-Bu	0.5
Pt	Cl	Me	Vc	$CH_2{=}CHPh$	0.7
Pt	Cl	Me	Vc	$CH_2{=}CHC_6F_5$	1.2
Pt	Cl	Me	Vc	$CH_2{=}CHEt$	1.3
Pt	Cl	Me	Vc	$CH_2{=}CHC(OH)Me_2$	1.7
Pt	Cl	Me	Vc	$CH_2{=}CHCH_2OEt$	2.3
Pt	Cl	Me	Vc	$CH_2{=}CHCH_2OH$	2.8
Pt	Cl	Me	Vc	(*E*)-ClCH=CHCl	2.9
Pt	Cl	Me	Vc	$CH_2{=}CHCOOMe$	3.0
Pt	Cl	Me	Vc	$CH_2{=}CHCHO$	4.0
Pt	Cl	Me	Vc	$CH_2{=}CHCN$	5.0
Pt	Cl	Me	Vc	$CH_2{=}CHMe$	1.4
Pt	Cl	Ph	Vc	$CH_2{=}CHMe$	1.6
Pt	Cl	4-$MeOC_6H_4$	Vc	$CH_2{=}CHMe$	1.7
Pt	Cl	4-$CF_3C_6H_4$	Vc	$CH_2{=}CHMe$	1.5
Pt	Cl	2-MeC_6H_4	Vc	$CH_2{=}CH_2$	0.9
Pt	Cl	C_6F_5	Vc	$CH_2{=}CH_2$	0.7
Pt	Cl	Me	Vd	$O{=}\overline{CCH{=}CHC({=}O)O}$	0.7
Pt	Cl	Me	Vd	$CH_2{=}CHCN$	−0.8
Pt	Cl	Me	Vf	$CH_2{=}CH_2$	1.8
Pt	Cl	Me	Vg	$CH_2{=}CH_2$	3.1

TABLE 2 (*continued*)

M	X	Y	N–N'	Olefin	pK_{diss}
Pt	Cl	Me	Vh	$\mathrm{CH_2{=}CH_2}$	1.3
Pt	Cl	Me	Vm	$\mathrm{CH_2{=}CH_2}$	2.6
Pt	MeCN	Me	Vc	$\mathrm{CH_2{=}CHMe}$	0.9
Pt	MeCN	Me	Vc	$\mathrm{CH_2{=}CHCOOMe}$	1.7
Pt	py	Me	Vc	$\mathrm{CH_2{=}CHMe}$	−0.6
Pt	py	Me	Vc	$\mathrm{CH_2{=}CHCOOMe}$	0.5
Pt	$\mathrm{C_6H_5NH_2}$	Me	Vc	$\mathrm{CH_2{=}CHMe}$	1.6
Pt	$\mathrm{C_6H_5NH_2}$	Me	Vc	$\mathrm{CH_2{=}CHCOOMe}$	>3
Pt	Cl	$\mathrm{SnMe_2Cl}$	Ib	$\mathrm{CH_2{=}CH_2}$	2.5
Pd	Cl	Cl	Ia	$\mathrm{CH_2{=}CH_2}$	1.6
Pd	Cl	Cl	Ia	$\mathrm{CH_2{=}CHMe}$	−0.04
Pd	Br	Br	Ia	$\mathrm{CH_2{=}CHMe}$	0.6
Pd	Cl	Me	Ia	$\mathrm{CH_2{=}CH_2}$	2.5
Pd	Cl	Me	Ia	$\mathrm{CH_2{=}CHMe}$	0.4
Pd	Cl	Me	Ia	$\mathrm{CH_2{=}CHO{-}}n\mathrm{{-}Bu}$	−0.7
Pd	Cl	Me	Ia	$\mathrm{CH_2{=}CHCH_2OH}$	1.9
Pd	Cl	Me	Ia	$(Z)\mathrm{{-}HOCH_2CH{=}CHCH_2OH}$	1.0
Pd	Cl	Me	Ia	$\mathrm{CH_2{=}CHCOOMe}$	1.2
Pd	Cl	Me	Ia	$\mathrm{CH_2{=}CHCHO}$	2.3
Pd	Cl	Me	Ia	$\mathrm{CH_2{=}CHCN}$	2.6
Pd	Cl	Me	Vc	$\mathrm{CH_2{=}CH_2}$	0.2
Pd	Cl	Me	Vc	$(E)\mathrm{{-}NCCH{=}CHCN}$	0.4
Pd	Cl	Me	Vg	$\mathrm{CH_2{=}CH_2}$	−0.1

presence of a substituent in the ortho position of an apical phenyl group destabilizes considerably the five-coordinate geometry [32].

In general, five-coordinate complexes containing palladium(II) are less stable than the corresponding species containing platinum(II) and the formation constant for the trigonal bipyramidal species has been found to decrease by four orders of magnitude on going from Pt(II) to Pd(II) (Table 2).

5.2 Loss of an apical ligand

Another decomposition pattern for the five-coordinate trigonal bipyramidal species involves the loss of an apical anion and formation of a cationic complex still containing the alkene (eqn. (25)).

$$[\mathrm{Pt}(\eta^2\text{–alkene})\mathrm{Cl_2(N{-}N)}] = [\mathrm{Pt}(\eta^2\text{–alkene})\mathrm{Cl(N{-}N)}]^+ + \mathrm{Cl}^- \tag{25}$$

The released anion, in turn, can react with the cationic complex to displace the alkene (eqn. (26)).

$$[\mathrm{Pt}(\eta^2\text{–alkene})\mathrm{Cl(N{-}N)}]^+ + \mathrm{Cl}^- = [\mathrm{PtCl_2(N{-}N)}] + \text{alkene} \tag{26}$$

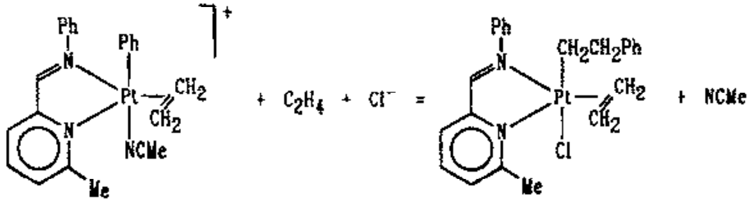
This mechanism has been demonstrated to dominate in the decomposition of $[Pt(\eta^2-C_2H_4)Cl_2(bipyridyl)]$ in methanol solution [44].

In some cases, the cationic substrate has been isolated and found to be very reactive towards nucleophiles [45–49].

5.3 Insertion of the alkene in a σ-bond

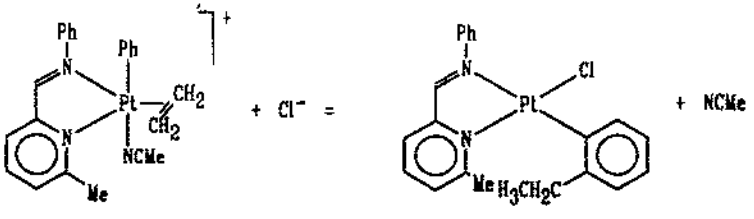
Complexes of type A can also evolve to a square planar geometry via insertion of the unsaturated ligand into a metal–carbon σ bond. This reaction pattern has been observed when the alkene carries electron-withdrawing substituents. A similar reaction has also been reported for analogous alkyne complexes.

The insertion of an alkene into a platinum–aryl σ bond has been observed, in chloroform solution and in the presence of free alkene, for type B complexes (eqn. (27)).



(27)

In the absence of free ethene, another reaction path, leading to the insertion of the alkene in a C—H bond, has been observed (eqn. (28)).



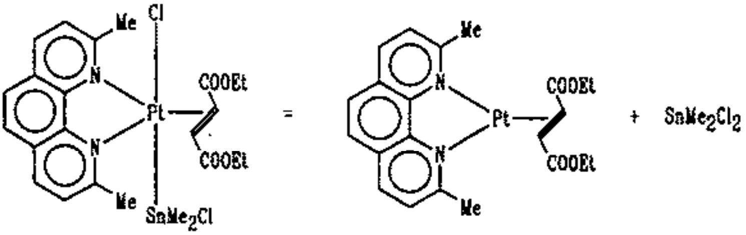
(28)

Insertion of the alkene ligand into an apical platinum iodide bond has also been reported [26].

5.4 Reductive elimination

Five-coordinate complexes containing an alkyl and a halide ion in axial positions can decompose to a trigonal species of zero-valent metal and alkyl halide (RX). This reaction pattern has also been observed in a few five-coordinate Ni(II) alkene complexes having a square pyramidal geometry [50].

An addition/elimination equilibrium has been observed for a type A complex bearing an $SnClMe_2$ group in apical position (eqn. (29)) [51].



(29)

5.5 *Ligand exchange*

The reactions of ligand exchange bring no variation into the stereochemistry of the complexes except for the possible change of the absolute configuration of the metallic centre, if stereogenic. These reactions can involve all the ligands present in the complex, i.e. the alkene, the apical ligands, and the N-donor chelate, and are useful tools for the preparation of new five-coordinate species.

The most likely mechanism, which applies to all ligand exchange reactions, implies the opening of the chelate ring and formation of a four-coordinate intermediate which undergoes ligand substitution reactions according to the usual associative mechanism operating in square-planar d^8 metal complexes. This step is followed by ring closing of the bidentate ligand (the same as before or the exchanged one) which restores the trigonal bipyramidal geometry.

6. STEREOCHEMICAL ASPECTS

Most of the five-coordinate complexes of platinum(II) and palladium(II) have general formula [M(alkene)(bidentate ligand)(monodentate ligand)$_2$] (type A and B) or [M(alkene)(tridentate ligand)(monodentate ligand)] (type C). The coordination polyhedron is always a trigonal bipyramid having the alkene and two ends of the polydentate ligand in the equatorial plane and two monodentate ligands (or one monodentate ligand and the third end of the polydentate ligand) in the axial positions.

6.1 *The alkene ligand*

(1) The hindered rotation of the alkene ligand originates two atropisomers if the alkene has a symmetry different from C_{2h} or D_{2h} and the axial ligands and/or the equatorial coordinated ends of the polydentate ligand are chemically different. The two rotamers are in enantiomeric relationship if the alkene has C_{2v} symmetry (e.g. *Z*-2-butene) and the C_2 axis is parallel to the line connecting either chemically equivalent axial ligands or equivalent ends of the equatorial chelate.

The ratio of the two stereoisomers can range from 1 : 1 to the almost exclusive formation of only one isomer [32,43].

(2) The coordination of a prochiral alkene affords two enantiomeric species. Chiroptical properties have been investigated with the aim of finding correlations between CD bands and the configuration of the coordinated prochiral alkene [23]. Data so far collected seem to indicate the presence of a positive dichroism in the region 28 000–30 000 cm^{-1} for the *R* configuration.

If the two axial ligands and the two ends of the equatorial chelate are chemically different, the metal centre is stereogenic and the coordination of a prochiral alkene affords two couples of enantiomers. In one case, namely A_{124} in Table 1, it was possible, through an asymmetric second-order transformation, to isolate a pure enantiomer [5] on which an X-ray analysis was performed [30]. A rapid epimerization ($t_{1/2} = 15$ min) to a 5 : 3 mixture of two diastereoisomers was observed in solution. Analogous behaviour was found for Pd(II) species.

The simultaneous occurrence of the two types of isomerism considered in paragraphs (1) and (2) increases the total number of isomers proportionally.

6.2 *The equatorial chelate*

Another type of isomerism can be born when the bidentate ligand is a prochiral diamine (e.g. a secondary diamine, $RHNCH_2CH_2NHR$) [25]. In this case, two enantiomers and a diastereoisomer are formed and they are generally indicated as trans (the two enantiomers) and cis (the diastereoisomer), depending upon the mutual orientation of the nitrogen substituents with respect to the plane of the chelate ring. The cis conformation has one of the N substituents in a quasi axial and the other in a quasi equatorial position; the trans conformations have both substituents in quasi equatorial positions.

Unlike four-coordinate complexes, the five-coordinate species have, at room temperature, changeable configuration at the nitrogens that "freezes out" as the temperature is lowered. The trans conformations (those in which the two nitrogens have equal absolute configuration, either *R*,*R* or *S*,*S*), appear to be preferred. One possible explanation is that the two apical ligands, in a trigonal–bipyramidal arrangement, compress the other three ligands in the equatorial plane, whereby the amine is forced to adopt the trans conformation with the N substituents in quasi equatorial positions.

The influence of a chiral N substituent on the configuration of the coordinating nitrogen has also been investigated for symmetrically substituted ethylenediamines such as *N*,*N'*-$(CHMePh)_2$-1,2-diaminoethane (IIIb in Chart 2).

For the reasons given above, at low temperature the bidentate ligand is forced to assume a trans conformation, therefore the effect of the asymmetric carbon on the configuration of the adjacent nitrogen can only result in the preference for one of the two possible trans conformations (either *R*,*R* or *S*,*S* absolute configurations at the nitrogen atoms). Experimental data have led to the conclusion that the preferred trans conformation of the bidentate ligand is that which allows the chiral alkyl substituents to direct the least bulky group toward the apical ligands and the one immediately bigger toward the equatorial alkene ligand. When the priority of the groups for the assignment of the absolute configuration parallels their bulk, this corresponds to equal configurations on adjacent C and N atoms.

7. NMR SPECTROSCOPY AND MOLECULAR DYNAMICS

NMR spectroscopy provided information on coordination number and geometry, conformation and configuration of the ligands, molecular dynamics, and fluxional processes. Also, ligand release and exchange processes and reaction kinetics were studied via NMR spectroscopy [29,30,32,35,43].

7.1 The alkene

A clear correlation between the alkene spectral parameters and the coordination number has been observed [18,21,29,32,35,43]. This correlation affords both a diagnostic criterion for the assignment of the coordination number and a reliable ground for inference on the nature of the metal–alkene bond.

The most significant feature of the NMR spectra of the five-coordinate complexes is the high field shift of the signals concerned with the alkene hydrogen and carbon nuclei. This coordination shift ($\Delta\delta$) is significantly higher than that observed in square-planar four-coordinate complexes. Typical ^{1}H values (δ) for ethene compounds are 5.4 (free); 4.8–4.4 (four-coordinate complexes); 3.7–3.0 (type A complexes); 3.4–1.7 (type B complexes). The corresponding ^{13}C values are 122.8 (free); 75–65 (four-coordinate complexes); 50–33 (type A complexes); 32–28 (type B complexes).

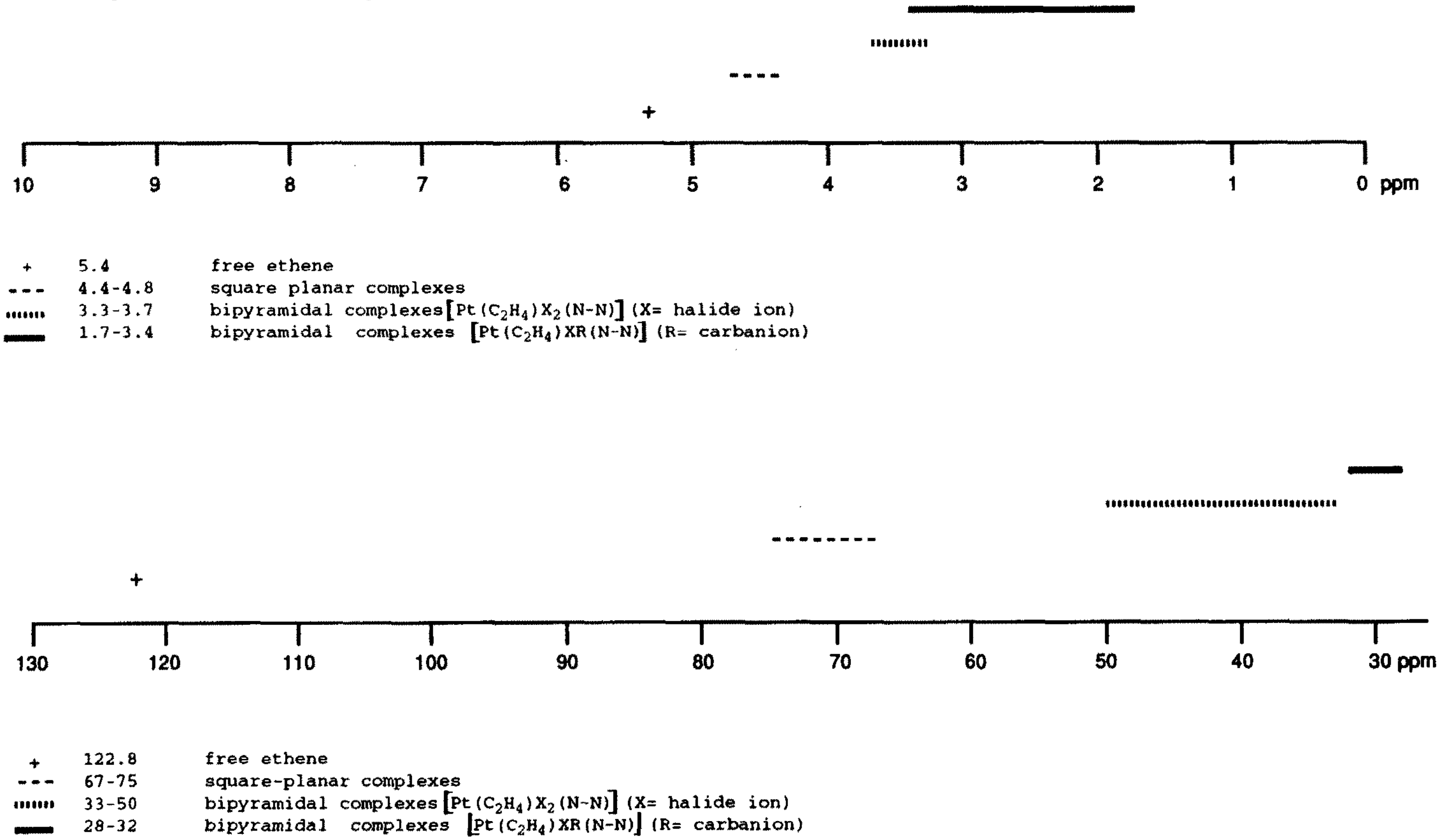
A schematic representation of the above cited ranges is given in Chart 3. Table 3 reports the ^{13}C coordination shifts $\Delta\delta$ and the corresponding ^{195}Pt coupling constants for some complexes having coordination numbers 3 (Pt(0)), 4 and 5 (Pt(II)).

A correlation between coordination shifts and π back-donation could be deduced [11,19,30,38]. For example, alkenes bearing electron-withdrawing substituents, which should favour metal-to-alkene π back-donation, give particularly stable complexes and show the greatest coordination shifts with respect to ethene.

The coordination shift of the alkene also appears to increase when an alkyl group is present in the axial position of the trigonal bipyramid. Indeed, the presence of a good electron donor such as the alkyl group could enforce π back-donation to the equatorial alkene.

It is to be noted that an increase of the ^{13}C coordination shift is not observed for a C=C bond coordinated in apical position. For example, in [Pt(COD)Me(2,9-Me$_2$-1,10-phenanthroline)]$^+$, the value of $\Delta\delta$ was 11 ppm for the COD moiety in axial position and 71 ppm for the COD moiety in the equatorial position [35]. This

Ranges of chemical shift for alkene hydrogen (upper) and carbon atoms (lower diagram) in platinum-ethene complexes.



+	5.4	free ethene
- - -	4.4-4.8	square planar complexes
┅┅	3.3-3.7	bipyramidal complexes $[Pt(C_2H_4)X_2(N\text{-}N)]$ (X= halide ion)
▬	1.7-3.4	bipyramidal complexes $[Pt(C_2H_4)XR(N\text{-}N)]$ (R= carbanion)

+	122.8	free ethene
- - -	67-75	square-planar complexes
┅┅	33-50	bipyramidal complexes $[Pt(C_2H_4)X_2(N\text{-}N)]$ (X= halide ion)
▬	28-32	bipyramidal complexes $[Pt(C_2H_4)XR(N\text{-}N)]$ (R= carbanion)

Chart 3. Schematic representation of ^1H and ^{13}C chemical shift ranges for coordinate alkenes.

TABLE 3

Up-field ^{13}C coordination shifts ($\Delta\delta$, ppm) and ^{195}Pt coupling constants (Hz) for some three-, four- and five-coordinate alkene complexes of platinum

Metal fragment	Alkene				
	CH_2=CH_2	CH_2=CH–Ph	*E*-Me–CH=CH–Me	CH_2=CH–COOMe	*E*-MeOOC–CH=CH–COOMe
$(PMe_3)(C_2H_4)Pt$	87.1 (146)				
(2,9-Me_2-phen)Pt					108.3 (442)
trans-$(Me_3Py)Cl_2Pt$	47.8 (166)	50.0 (166), 39.9 (140)	32.6 (155)		
(*t*-Bu–N=CHCH=N–Bu-*t*)Cl_2Pt	84.7 (297)	[71.5 (256), 71.5 (242)]	[33.0 (160)]		
(*t*-Bu–N=CHCH=N–Bu-*t*)MeClPt	91.6 (370)				
(2,9-Me_2-phen)MeClPt	87.5 (370)	92.9 (366), 84.2 (358)		96.6 (375), 96.4 (364)	101.5 (345)
{HB$(Pyraz)_3$}(Me)Pt	98.1 (384)			108.3 (377), 97.2 (356)	103.1 (350)

result indicates that no back-donation is involved in the bonding of an alkene in the axial sites of a trigonal bipyramid.

The coupling constant $^1J(^{13}C-^{195}Pt)$ for the alkene carbons is another parameter deeply influenced by the coordination number of the metal and by the presence of electron releasing axial alkyl groups. It is also observed that the presence of electron-withdrawing substituents on the alkene prompts an increase of the coupling constant. A direct correlation between $^1J(^{13}C-^{195}Pt)$ and the extent of π back-donation appears to exist.

Also, in the palladium complexes, a substantial up-field shift of the alkene signals in the five-coordinate complexes with respect to square planar species was observed [43]. Moreover, a difference in ^{13}C shift between apical and equatorial alkene was observed similar to that mentioned above for a platinum complex.

The energy of activation for the alkene rotation around the platinum–alkene bond was also investigated [18,52,53]. $\Delta G^{\neq}$ for five-coordinate complexes was found to be in the same range (10–16 kcal mol^{-1}) as those for four-coordinate Pt(II) and three coordinate Pt(0) species (Table 4). However, particularly high values of $\Delta G^{\neq}$, with a low-energy limit of 20 kcal mol^{-1}, were recently observed for a series of dihalide complexes of type A [29]. We wish to point out that in trigonal bipyramidal complexes it is not easy to discriminate between alkene rotation and N—N side exchange occurring through an intramolecular rearrangement. The simultaneous occurrence of both dynamic processes could lead, in some cases, to an underestimation of the rotational barrier for the alkene rotation.

The alkene substituents as well as the apical ligands can influence the barrier to rotation. The activation energy appears to increase if electron-withdrawing substituents are present on the alkene and, to a smaller extent, if the size of the apical ligands increases.

7.2 The equatorial chelate

In the case of prochiral N-donor chelate ligands, the two coordinated nitrogens can have either equal or opposite configuration, giving rise to the formation of the so-called trans and cis isomers, respectively (see Sect. 6) [11,14,25].

A thorough study [25] comprising low-temperature NMR measurements has shown that, in this type of complex, the diamine undergoes rapid inversion of configuration at nitrogens at room temperature. Spectroscopic and structural data indicated that both inversion of configuration and proton exchange at the nitrogen atoms involve release of the platinum–nitrogen bond. On lowering the temperature, the configuration at nitrogens could be frozen and the resulting stereochemical implications have already been discussed in the section on stereochemical aspects.

NMR data also revealed that an important feature in the stabilization of five-coordinate trigonal bipyramidal geometry is the bite angle of the nitrogen donor chelate. A theoretical study had envisaged how large bite angles should favour the

TABLE 4

Activation energies for alkene rotation in $[M(alkene)X_2(N{-}N)]$ complexes

N–N[a]	Olefin	X	ΔG (kcal mol^{-1})	Ref.
Platinum complexes				
R,S-IIIg	$CH_2{=}CH_2$	Cl	15.0[b]	[d]
R,S-IIIb	$CH_2{=}CH_2$	Cl	13.8	25
R,R-IIIg	$CH_2{=}CHCH_3$	Cl	14.9[b] 15.9[c]	[d]
	$CH_2{=}CHCHO$	Cl	>17[b]	[d]
	$O{=}\overline{CCH{=}CHC({=}O)O}$	Cl	>17.8[b]	[d]
IVo	$CH_2{=}CHCH_3$	Cl	16.7[b]	[d]
	$CH_2{=}CHCH_2CH_3$	Cl	16.6[b] 16.3[c]	[d] [d]
	$CH_2{=}CHCHO$	Cl	>18[c]	[d]
	$CH_2{=}CHCOOCH_3$	Cl	>18[c]	[d]
IVb	$CH_2{=}CHPh$	Cl	13.80[b] 14.09[c]	18
	$CH_2{=}CHCOOCH_3$	Cl	15.91[b] 15.82[c]	18
	$CH_2{=}CHPh$	Br	13.2[b]	18
Ia	$CH_2{=}CHCH_2CH_3$	Cl	20.6[b]	29
	$CH_2{=}CHCH_2CH_3$	Br	20.8[b]	29
	$CH_2{=}CHCH_2CH_3$	I	20.5[b]	29
Palladium complexes				
Ia	$CH_2{=}CHCH_2CH_3$	Cl	14.1[b]	29
	$CH_2{=}CHCH_2CH_3$	Br	13.6[b]	29

[a] See Chart 2.
[b] Determined by ^1H NMR.
[c] Determined by ^{13}C NMR.
[d] A. De Renzi, L. Paolillo and A. Vitagliano, unpublished results.

in-plane coordination of the ligand [54]. Experimental results, on the other hand, evidenced how the increase of the bite angle destabilizes the trigonal bipyramid which shifts to a square planar geometry by chelate ring opening. For instance, in a study concerned with the behaviour in solution of complexes of composition $[Pt(\eta^2{-}C_2H_4)Cl_2\{Me_2N(CH_2)_nNMe_2\}]$ ($n=2, 3, 4$), it was found that for $n=2$ the only species present (until the decomposition temperature was reached) had a five-coordinate geometry. When $n=3$, there was rapid interconversion between five- and four-coordination (the square planar species containing singly bonded diamine) and at lower temperatures, the equilibrium shifted in favour of the five-coordinate geometry. When $n=4$, the amine could act only as a monodentate ligand although the two ends of the diamine remained equivalent because of a fast head-to-tail rearrangement of the ligand.

8. X-RAY STRUCTURAL STUDIES

Less than a score of structures have been reported for Pt(II) and Pd(II) five-coordinate alkene-containing compounds. The relevant bond parameters pertinent to the coordination sphere are illustrated in Chart 4. The structural data are reported in diagrammatic form so that the degree of chemical equivalence of topologically corresponding interactions can be easily appreciated.

An analysis of the bond distances and angles shows that the estimated standard deviations involving light atoms are quite high, and, more than that, some values are surely unrealistic. This drawback is innate to X-ray diffraction experiments in which the overwhelming scattering power of platinum and the thermal motion make the accuracy of structural details involving light atoms quite poor. An additional inconvenience is that the detection of the hydrogen atoms is not only uncertain but often impossible. However, the location of the hydrogen atoms is essential for a correct positioning of the carbon atoms by least-squares calculations. If the position parameters of a carbon atom are refined, ignoring the scattering contribution of the attached hydrogens, the atom is displaced toward the centre of gravity of the CH_n electronic system, resulting in an artificially long carbon–carbon distance. For these reasons, comparisons should be made not only observing the quoted standard deviations of the compared values but also paying attention to how the hydrogen atoms were treated, i.e. experimentally located, added in calculated positions (an acceptable procedure), or even omitted (source of serious errors). Other sizeable disturbances are the deformations caused by the packing forces that affect the softer metal–ligand interactions more seriously than the intraligand bonds. This being the experimental situation, the analysis of the molecular geometries will be oriented towards the search for trends based on average values more than comparisons among individual values. (The mean values of bond distances cited in the following discussion have been calculated omitting those judged to be seriously in error because of poor experimental data or inadequate structure model.)

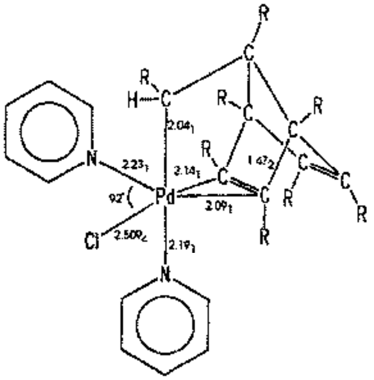
All the structures described in Chart 4 share the following features.

(a) The coordination geometries are invariably trigonal–bipyramidal when assuming the coordinated alkene to be monodentate.

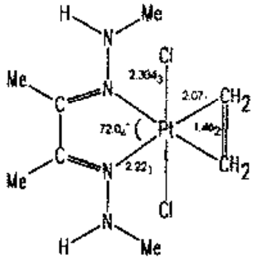
(b) The alkene ligand is always in the equatorial position and the coordinated carbon atoms lie in the equatorial plane. Therefore all the complexes in this family belong to class T according to the Hartley's classification [55].

(c) A chelate ring, either flat or puckered, produced by a bidentate dinitrogen ligand occupies the other equatorial sites.

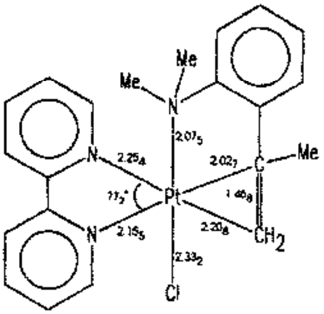
(d) Two monodentate ligands, mostly two chloride ions or one chloride and one alkyl group, define the axial sites.



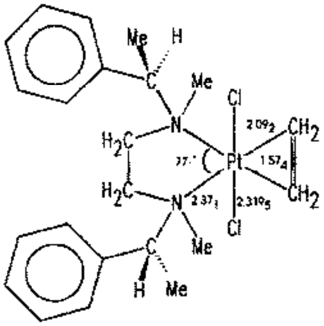
[Pd{HC$_8$(CO$_2$Me)$_8$}Cl(py)$_2$]
1, ref. 66



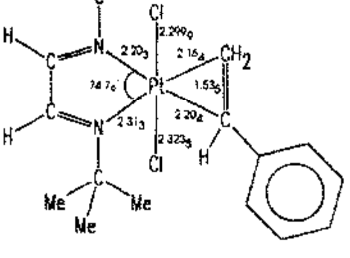
[Pt(C$_2$H$_4$)Cl$_2$(MeHNNCMeCMeNNHMe)]
2, ref. 7



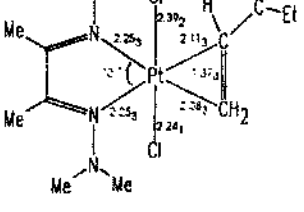
[Pt{Me$_2$N(C$_6$H$_4$)CMe=CH$_2$}Cl(bipy)]
3, ref. 40



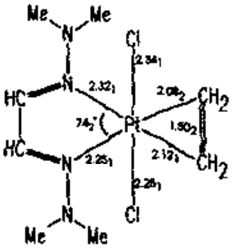
[Pt(C$_2$H$_4$)Cl$_2${*R*,*R*Me(PhMeHC)NCH$_2$-CH$_2$NMe(CHMePh)}] **4**, ref. 14



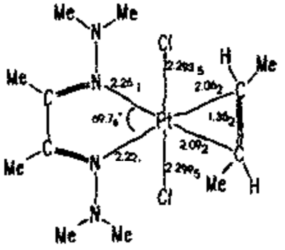
[Pt(CH$_2$CHPh)Cl$_2$(Bu^{t}NCHCHNBu^t)]
5, ref. 17



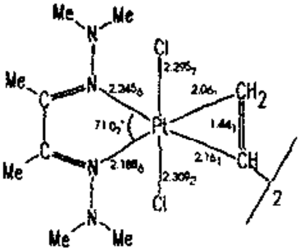
[Pt(CH$_2$=CHCHMeEt)Cl$_2$(Me$_2$NNCMeCMeNNMe$_2$)]
6, ref. 76



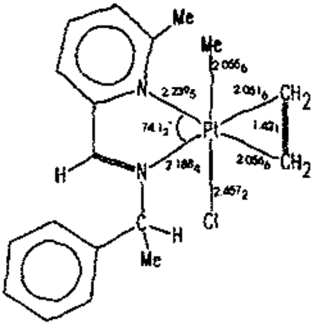
$[Pt(C_2H_4)Cl_2(Me_2NNCHCHNNMe_2)]$
7, ref. 73



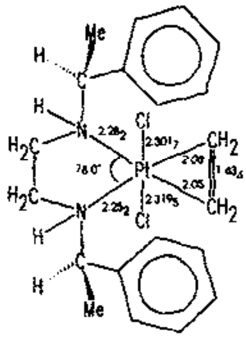
$[Pt(E\text{-}2\text{-}butene)Cl_2(Me_2NNCMeCMeNNMe_2)]$
8, ref. 22



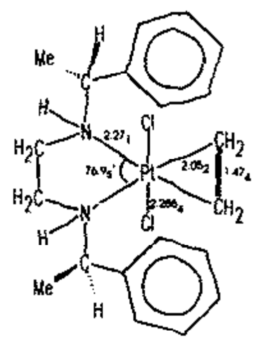
$[\{(Me_2NNCMeCMeNNMe_2)Cl_2Pt(CH_2{=}CH\text{-}\}_2]$
9, ref. 42



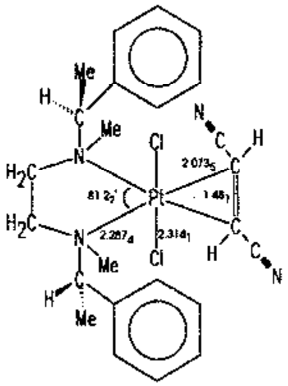
$[Pt(C_2H_4)ClMe\{6\text{-}Me\text{-}py\text{-}2\text{-}CHN(CHMePh)\}]$
10, ref. 30



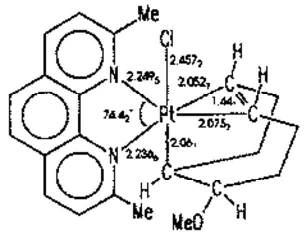
$[Pt(C_2H_4)Cl_2\{R,S\text{-}(PhMeHC)HNCH_2\text{-}CH_2NH(CHMePh)\}]$ **11**, ref. 25



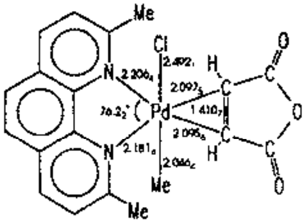
$[Pt(C_2H_4)Cl_2\{R,R\text{-}(PhMeHC)HNCH_2\text{-}CH_2NH(CHMePh)\}]$ **12**, ref. 25



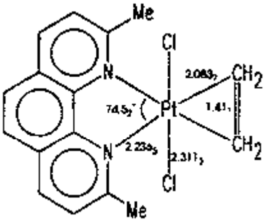
[Pt(*E*-NCCH=CHCNCl$_2${Me(PhMeHC) NCH$_2$CH$_2$NMe(CHMePh)}] **13**, ref. 26



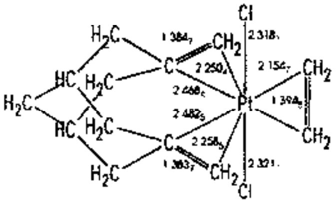
[Pt{CH(CH$_2$)$_2$CH=CH(CH$_2$)$_2$CH(OCH$_3$)} Cl(Me$_2$Phen)] **14**, ref. 41



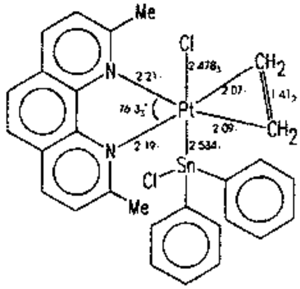
[Pd(C$_4$H$_2$O$_3$)ClMe(Me$_2$phen)] **15**, ref. 43



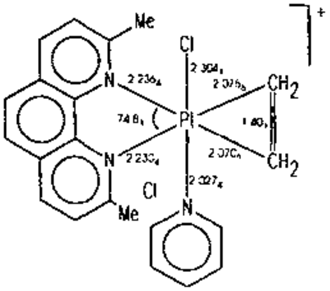
[Pt(C$_2$H$_4$)Cl$_2$(Me$_2$phen)] **16**, ref. 29



[Pt(C$_2$H$_4$)Cl$_2$(dialkene)] **17**, ref. 34



[Pt(C$_2$H$_4$)Cl(SnClPh$_2$)(Me$_2$phen)] **18**, ref. 63



$[Pt(C_2H_4)Cl(py)(Me_2phen)]^+$ **19**, ref. 36

Chart 4. Relevant bond parameters pertinent to the coordination sphere of five-coordinate complexes.

The Pt–ligand interactions are not found to be systematically different from the corresponding Pd–ligand values [43,56], therefore the two metals will not be treated separately and the average bond distances will be calculated over both metals, and considering the very limited number of structures reported for palladium.

8.1 The coordinated alkene

The geometrical modifications of an alkene molecule upon bonding in a five-coordinate Pt(II) or Pd(II) complex are similar to those observed in four- and three-coordinate species, i.e. bending away from the metal centre of the hydrogens or substituent groups. These effects are explained by the σ donation and π back-donation bonding model primarily put forward by Dewar [57], and Chatt and Duncanson [58]. Both components of the bond concur in strengthening the metal–alkene interaction and weakening the C=C bond. The out-of-plane displacement of the substituent groups is mainly ascribed to the π back-bonding [55,59] and is a good indicator of this component of the bond. Therefore the structural data should follow the following trend: the shorter the metal–carbon distances, the longer the carbon–carbon distance and the larger the deviation from planarity. Unfortunately, the data at hand are not so accurate as to show unambiguously the whole sequence of effects. The Pt–C distances are spread in the interval 2.05–2.16 Å (average 2.08 Å). The C=C values span the range 1.35–1.48 Å (average 1.43 Å). The average values are likely to be reliable estimates and can be assumed to be standard values for coordinated alkenes in five-coordinate complexes. They can be compared with the most accurate distances available for four-coordinate species determined by neutron diffraction for the Zeise's anion $[Pt(C_2H_4)Cl_3]^-$ [60] and the cation $[Pt(C_2H_4)Cl(Me_2NCH_2CH_2NMe_2)]^+$ [61]. In these species, the Pt–C and C=C values are 2.131(3), 2.175(5) and 1.375(4), 1.376(3) Å, respectively. Another important element of comparison is the carbon–carbon distance in the free ethene (1.337(2) Å [62]). These figures clearly indicate stronger metal–alkene interactions in five-coordinate complexes with respect to four-coordinate species. They are accounted for in terms of higher π contribution to the bond promoted by greater charge accumulation on five-coordinate metal atoms. Further information about the different balance between σ and π components of the bond in five- and four-coordinate compounds are contained in the deviation from planarity of the alkene. As already specified, the hydrogen atoms are not located with sufficient accuracy to give reliable information so that we have to rely on substituted alkenes such as E-2-butene. Two structures well suited for such a comparison are those of [Pt(E-MeHC=CHMe)Cl_2(Me_2NN=CMeCMe=NNMe_2)] (**8** in Chart 4) [22] and [Pt(E-MeHC=CHMe)Cl_2(Bu^tN=CHCH=NBu^t)] [21], the diimine acting as monodentate in the latter species. The Me–C=C–Me torsion angle is found to be 50(2) and 27(1)° in the five- and four-coordinate species, respectively. These angles are in keeping with the Pt–C average distances of 2.07(2) and 2.16(2) Å, respectively, and give firm evidence of greater π back-bonding in five-coordinate complexes.

Unfortunately, the C=C distances of 1.35(2) and 1.38(3) Å, respectively, are not sufficiently accurate for a meaningful comparison. Values in accord with the expected trend are exhibited by the fumarodinitrile in [PtCl_2(E-NCCH=CHCN){(PhMeHC)MeNCH_2CH_2NMe(CHMePh)}] (**13** in Chart 4) [26]: Pt–C, 2.073(5); C=C, 1.48 Å; NC–C=C–CN torsion angle, 40.0(4)°.

This analysis of the Pt–alkene interactions is in accord with that found in [Pt(C_2H_4)Cl_2(dialkene)] (**17** in Chart 4) in which three alkene double bonds are coordinated in the equatorial plane [34]. The bond values of the ethene in this molecule, with longer Pt–C (2.154(7) Å) and shorter C=C bonds (1.394(8) Å), clearly show the effects of three competing π acceptors.

8.2 The equatorial chelate

A key feature in the stabilization of the five-coordinate Pt(II) and Pd(II) complexes is the presence of a bidentate ligand, a dinitrogen donor in most of the species so far reported, forming a five-membered ring in the equatorial plane. The ring can be either puckered for the aliphatic diamines or flat for the aromatic diamines and imines. The stabilizing effect of the chelate rings is a combination of electronic and steric factors and it could be interesting to get them apart. The electronic contributions can be assessed in terms of stability of the Pt–N interactions as inferred from the bond distances.

In spite of the large spreading of values some differences can be appreciated. The sp^3 hybridized amine nitrogens exhibit average Pt–N distances of 2.31 Å. The Pt–N(aromatic) and Pt–N(imine) distances are not detectably different and their average value is 2.23 Å. The 0.08 Å difference between the above distances can be explained in terms of greater π contribution to the coordination interactions and lower radius of the sp^2 hybridized nitrogen atoms. Minor differences in bond strengths between sp^2-N(pyridine) and sp^2-N(imine) have been demonstrated with a sufficient level of confidence in the molecule [Pt(C_2H_4)ClMe(6-Me-pyridine-2-CH=N−CHMePh)] (**10** in Chart 4) [30], in which both kinds of nitrogen are present. The Pt–N(imine) and Pt–N(pyridine) distances are 2.188(4) and 2.239(5) Å, respectively.

The Pt–N distances are, on average, 0.20 Å longer in five-coordinate than in four-coordinate compounds. This effect can be better appreciated on comparing the bond distances for the same ligand in five- and four-coordinate molecules. Good examples are as follows: [Pt(C_2H_4)Cl_2(2,9-Me_2-1,10-phenanthroline)] (**16** in Chart 4) and [PtCl_2(2,9-Me_2-1,10-phenanthroline)], 2.236(5) and 2.045(8) Å [29]; [PtCl_2(C_2H_4){*R*,*S*-(PhMeHC)MeNCH_2CH_2NMe(CHMePh)}] (**11** in Chart 4) and [PtCl_2{*R*,*S*-(PhMeHC)MeNCH_2CH_2NMe(CHMePh)}], 2.265(11) and 2.044(11) Å [25], respectively. The elongation in five-coordinate species can be ascribed to the following factors:

(a) greater electronic saturation of the platinum atom in five-coordinate complexes that weakens the σ donation. This effect should be of importance, was it not offset by the π accepting power of the alkene; and

(b) less favourable overlap between donor orbitals and hybrid metal orbitals due to the acute bite angle imposed by the ring constraints (72–81°).

The importance of the last factor is demonstrated by an analysis of the bite angles, the more flexible diamine ligands exhibit an average value (78.3°) significantly wider than the more rigid aromatic diamines and imines (73.7°).

Most probably, the cooperation of both factors leads to the remarkable N−N bond lengthening. It should be noted that these factors appear to operate specifically in the equatorial plane and remarkable differences in length have been observed between equatorial and axial Pt–N bonds. The recently determined structure of the cation [Pt(C_2H_4)Cl(2,9-Me_2-1,10-phenanthroline)(pyridine)]$^+$ (**19** in Chart 4) [36] has shown that the equatorial and axial Pt–N distances are 2.233(4) and 2.027(4) Å, respectively, with a net difference of 0.2 Å.

The figures discussed above reveal that the donor abilities of the dinitrogen ligands are not determining in stabilizing the five-coordination and that the chelate rings are more stable in the square planar than in the trigonal-bipyramidal coordination.

Furthermore, some chelate ligands have been found to greatly stabilize the five-coordinate species. The stabilizing effect of these ligands can be understood in terms of non-bonded interactions, i.e. the possibility of building up the steric hindrance in the equatorial plane by suitable substituents in the vicinity of the donor atoms. The higher the atom crowding in the equatorial plane, the lower the tendency towards alkene dissociation (Table 2). That happens because bulky substituents hinder the full stabilization of an undistorted square-planar geometry after the alkene elimination. In other words, the enthalpic cost of the dissociation is greater because of retention of some potential energy (in the form of interligand repulsions and bond deformations) and the associated entropic gain does not afford sufficient motivation to the alkene dissociation. The geometric side of this thermodynamic effect is well documented in the dramatic deformations exhibited by two four-coordinate species containing 2,9-dimethyl-1,10-phenanthroline as chelating ligand, [$PtCl_2$(2,9-Me_2-1,10-phenanthroline)] [29] and [PdClMe(2,9-Me_2-1,10-phenanthroline)] [56] in which the phenanthroline plane is bent some 39° away from the coordination plane.

8.3 The axial ligands

The axial ligands are, in most cases, either two Cl^- or one Cl^- and one alkyl group. In molecules with two chloride ligands, the average Pt–Cl distance is 2.305 Å, most values being within ±0.02 Å of this value. In one case (**3** in Chart 4), an aminic nitrogen is present trans to the chloride and the Pt–Cl distance is slightly longer (2.33(2) Å [40]). Significantly longer distances are found when an alkyl group is the trans ligand (**10**, **14** and **15** in Chart 4), average value 2.47 Å [30,41,43]. The strong trans influence of the alkyl ligands is responsible for this elongation. The Pt–Cl average distances are strictly comparable with those found in four-coordinate species. See, for example, the values reported for the Zeise's anion [60] (2.302(2) and 2.340(2) Å, the latter value referring to the chloride trans to the ethene) and [$Pt(C_2H_4)Cl(Me_2NCH_2CH_2NMe_2)]^+$ [61] (2.304(2) Å, neutron diffraction studies).

Very recently, the structure of the tin derivative [$Pt(C_2H_4)Cl(SnPh_2Cl)$-(2,9-Me_2-1,10-phenanthroline)] (**18** in Chart 4) has been determined and the trans influence of Sn on the chloride ligand has been found to be comparable with that of the alkyl groups: Pt–Cl 2.478(3) Å [63].

The mean value of the Pt–C(alkyl) distance (2.05 Å) is almost equal to the corresponding value for four-coordinate complexes and only slightly shorter than the average Pt–C(alkene) distance (2.08 Å) in five-coordinate species. The latter figure indicates that the $\sigma+\pi$ Pt–C(alkene) bond is comparable in strength with the purely σ Pt–C(alkyl) interaction.

It is remarkable that, while the axial Pt–Cl and Pt–C(alkyl) average distances are quite unaffected by the change in coordination number, the equatorial Pt–N and Pt–(alkene) are significantly elongated and shortened, respectively, in five-coordinate complexes with respect to four-coordinate species. We have already discussed these effects, explaining the Pt–N elongation in terms of greater electron density on the metal atom and less favourable orbital overlap and the Pt–C(alkene) shortening in terms of stronger metal-to-ligand π back-donation.

These results are in complete agreement with the theoretical calculations carried out by Rossi and Hoffmann on [M(monodentate)$_5$] species which led to the conclusion that, for a trigonal-bipyramidal geometry of a d^8 metal ion, (a) when only σ bonds are considered the strongest σ donors prefer the axial sites, (b) for the same reason good π acceptors prefer the equatorial sites and (c) in the case of single-faced acceptors, as the alkene, the preferred orientation is that with the C=C double bond lying in the equatorial plane [64].

8.4 Trygonal-bipyramidal versus octahedral description of the complexes

The question whether a coordinated alkene is a truly monodentate ligand or can be considered bidentate is as old as the early bonding theories of π complexes. It has been demonstrated that there is no contradiction between the Dewar–Chatt–Duncanson model and the valence bond view in terms of cyclopropane ring [20,55]. The real situations are somewhere in between the two limiting cases of predominant σ donation (unidentate ligand) and predominant π back-donation (bidentate ligand forming a cyclopropane ring).

As already discussed, most five-coordinate species have a chelate ligand in the equatorial plane with N—Pt—N′ bite angles in the interval 72–81°. In two cases, the L—Pt—L equatorial angle could be measured in the absence of chelate ring constraints. In $[Pt(F_3CC{\equiv}CCF_3)ClMe(AsMe_3)_2]$ [65] (the arsine ligands and the alkyne molecule in the equatorial plane), the As—Pt—As angle was 104.2(2)°, and is probably influenced by methyl–methyl steric interferences. In $[Pd\{HC_8(CO_2Me)_8\}Cl(C_5H_5N)_2]$ (**1** in Chart 4) [66] (the equatorial sites occupied by a pyridine molecule, a chloride ion and an alkene), the Cl—Pd—N angle was 92°. These values of bond angles could be interpreted as evidence for a distorted octahedral coordination of the metal atoms (oxidation state +4) and a cyclopropane type description of the metal—alkene bond [the electron-attracting substituents could foster the metal-to-ligand back-donation].

The small N—Pt—N′ bite angle observed in most of the five-coordinate species described here will be discussed in the next section.

9. CONCLUDING REMARKS. REQUIREMENTS FOR A STABLE FIVE-COORDINATE COMPLEX

The results achieved in the last two decades allow a good rationalization of the four- versus five-coordination for d^8 metal ions. These are, among the transition metals, a special case [67,68]. Their preferred coordination number is four and there is a general agreement that the non-bonding d_{z^2} electron pair is responsible for the stabilization of the square planar geometry especially for the second and the third transition row.

The switch from four- to five-coordination can be described according to the initial step in the associative mechanism operating in the substitution reactions involving four-coordinate 16-electron transition metal complexes. The vacant p_z orbital of the metal, which is perpendicular to the molecular plane, can accept an electron pair from the entering ligand. As the reaction proceeds, the entering ligand and two trans ligands of the square plane move from a mutual T-shaped to a Y-shaped arrangement. These define the equatorial plane of the trigonal bipyramid in which the other two trans ligands of the former square planar complex occupy the apical positions. In the equatorial plane are also confined the two electron concentrations (filled d_{z^2} orbital), which in the square-planar precursor were located above and below the coordination plane.

This description of four- versus five-coordination can assist in enlightening the role of the alkene and of the bidentate ligand in stabilizing the five-coordination.

9.1 The alkene

A series of platinum(II) complexes of formula [Pt(L)X_2(2,9-Me_2-1,10-phenanthroline)], where L is either an alkene or a ligand with a C, N or P donor atom (L = C_2H_4, CO, PPh_3, ONPh), has been characterized crystallographically [69]. It has been found that, depending upon the nature of L, the phenanthroline shifts from a symmetrical doubly bonded to a non-symmetrical singly bonded situation (Chart 5). Ab initio molecular orbital calculations indicate that all L ligands are good σ donors (as expected from the 2+ oxidation state of the metal) but, in contrast, the π-accepting capability varies dramatically along the series $C_2H_4 > CO > PPh_3 > ONPh$. The most reasonable explanation for the observed trend is that, in the complexes containing L ligands other than alkene, the second end of the phenanthroline is not allowed to enter the coordination sphere of platinum because of the repulsion caused by the d_{z^2} electron concentrations located above and below the square coordination plane. On the other hand, when a strong π-

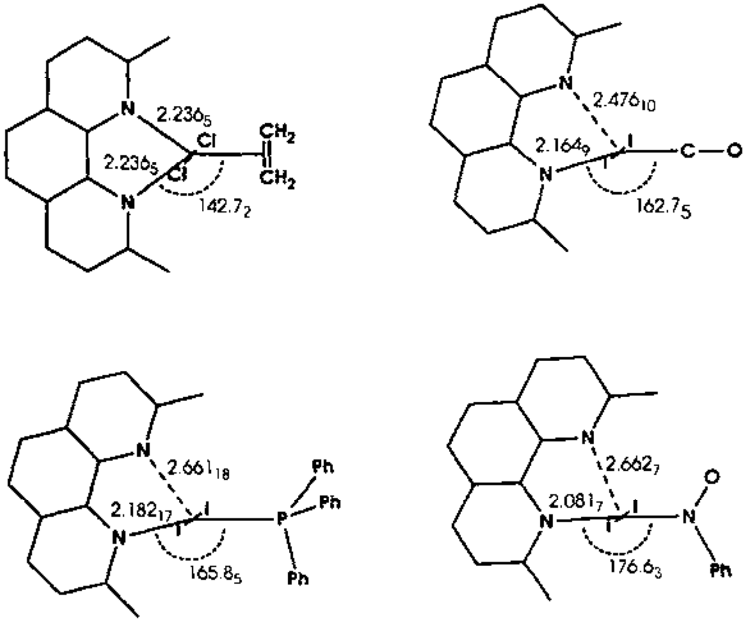


Chart 5. Relevant bond parameters pertinent to the coordination sphere of [Pt(L)X_2(2,9-Me_2-1,10-phenanthroline)] complexes.

acceptor ligand such as an alkene is present, these electron concentrations are reduced, allowing the second nitrogen of the diamine to donate its lone pair to the metal. The residual repulsion between the nitrogen lone pairs and the d_{z^2} electron clouds contributes to the destabilization of the two platinum nitrogen bonds.

9.2 The equatorial chelate

The presence of a chelate, with a variable degree of rigidity, is particularly relevant in order to isolate a five-coordinate complex. Two unidentate ligands, in place of one bidentate ligand are, instead, quite ineffective in stabilizing five-coordination and only in a few cases an equilibrium between the four-coordinate and the five-coordinate species has been evidenced at low temperature (−40°C) [70,71].

Theoretical calculations on the exchange process of the ammine ligand in *trans*-$[Pt(L)Cl_2(NH_3)]$ were performed by Lin and Hall [72]. It was found that, even in the most favourable case, i.e. when there is an alkene trans to the exchanging ammine, the trigonal bipyramidal activated complex is higher in energy than the reagents (the square planar complex and the free ammine). To reverse the relative stability of these two situations, along the reaction coordinate, it is necessary to circumvent the favourable entropic contribution of the two separate reagents which become bound together in the transition state. This can be achieved by linking together the two reagents and this is what is really done by employing a bidentate ligand.

In the paper of Lin and Hall quoted above, the optimum angle between the two metal ammine links, in the trigonal bipyramidal transition state, was calculated to be 85.5° for $[PtCl_2(NH_3)_2(C_2H_4)]$ with the NH_3 groups and C_2H_4 in the equatorial plane and Pt–N distances of 2.45 Å. Such a small angle originates from the presence, in the equatorial plane, not only of the entering and leaving ammine and the alkene ligand but also, as already pointed out, of the two electron concentrations (filled d_{z^2} orbital), which in the square planar precursor were located above and below the coordination plane. The molecular structures already discussed have shown that the bidentate ligand always exhibits an acute bite angle in the range of 72–81°, in good agreement with the value calculated by Lin and Hall. This answers the question why a small ligand bite, in contrast to what most people would have expected, could favour the formation of a five-coordinate species.

9.3 The steric constraints in trigonal versus square planes

For a given chelate, the steric constraints are bigger in a square-planar species than in the equatorial plane of a trigonal-bipyramidal complex, and the change in the relative stability as a function of the ligand hindrance is well evidenced whenever an equilibrium takes place between a five-coordinate species, [M(bidentate ligand) (unidentate ligand)$_3$], and a four-coordinate species, [M(bidentate ligand)(monodentate ligand)$_2$] (which can be either precursor or decomposition compound of the former). Steric factors can therefore destabilize the square-planar complex and not affect the stability of the five-coordinate species, apparently contradicting the widely accepted idea that an increase of bulkiness favours a lower coordination number. On this basis, several N-donor bidentate ligands, having the proper steric requirement, could be used to construct stable five-coordinate complexes.

ACKNOWLEDGEMENTS

This work was supported by the Ministero della Università e della Ricerca Scientifica e Tecnologica (MURST) and Consiglio Nazionale delle Ricerche (CNR). The contribution of A. De Renzi and A. Vitagliano (University of Naples), F. P. Fanizzi (University of Bari), and C. Castellari (University of Bologna) is gratefully acknowledged.

REFERENCES

1 H. Kurosawa, T. Majima and N. Asada, J. Am. Chem. Soc., 102 (1980) 6996.
2 M. Herberhold, Metal π-Complexes, Vol.2, Elsevier, Amsterdam, 1972.
3 T. Theophanides and P.C. Kong, Can. J. Chem., 48 (1970) 1084.
4 H.C. Clark and R.J. Puddephatt, Inorg. Chem., 9 (1970) 2670.
5 A. De Renzi, G. Morelli, A. Panunzi and A. Vitagliano, Gazz. Chim. Ital., 115 (1985) 247.
6 L. Cattalini, L. Maresca and G. Natile, J. Chem. Soc. Chem. Commun., (1973) 369.
7 L. Maresca, G. Natile, M. Calligaris, P. Delise and L. Randaccio, J. Chem. Soc. Dalton Trans., (1976) 2386.
8 H. Van der Poel, G. van Koten and K. Vrieze, J. Organomet. Chem., 175 (1979) C21.
9 H.C. Clark and L.E. Manzer, J. Am. Chem. Soc., 95 (1973) 3812.
10 L. Maresca, G. Natile and L. Cattalini, Inorg. Chim. Acta, 79 (1975) 14.
11 A. De Renzi, A. Panunzi, A. Saporito and A. Vitagliano, Gazz. Chim. Ital., 107 (1977) 549.
12 L. Maresca, G. Natile and L. Cattalini, J. Chem. Soc. Dalton Trans., (1979) 1140.
13 A. De Renzi, A. Panunzi, A. Saporito, M. Scalone and A. Vitagliano, Inorg. Nucl. Chem. Lett., 16 (1980) 535.
14 A. De Renzi, B. Di Blasio, A. Saporito, M. Scalone and A. Vitagliano, Inorg. Chem., 19 (1980) 960.
15 H. van der Poel and G. van Koten, J. Organomet. Chem., 187 (1980) C17.
16 H. van der Poel, G. van Koten and G.C. van Stein, J. Chem. Soc. Dalton Trans., (1981) 2164.
17 H. van der Poel, G. van Koten, M. Kokkes and C.H. Stam, Inorg. Chem., 20 (1981) 2941.
18 H. van der Poel and G. van Koten, Inorg. Chem., 20 (1981) 2950.
19 A. De Renzi, A. Panunzi and M. Scalone, Inorg. Synth., 21 (1982) 86.
20 A. De Renzi, G. Morelli, A. Panunzi and S. Wurzburger, Inorg. Chim. Acta, 76 (1983) L285.
21 V.G. Albano, F. Demartin, A. De Renzi, G. Morelli and A. Saporito, Inorg. Chem., 24 (1985) 2032.
22 V.G. Albano, F. Demartin, B. Di Blasio, G. Morelli and A. Panunzi, Gazz. Chim. Ital., 115 (1985) 361.
23 A. De Renzi, M. Funicello, G. Morelli, A. Panunzi and C. Pellecchia, J. Chem. Soc. Perkin Trans. 2, (1987) 427.

24 S. Bartolucci, M. Rossi, M. Estenoz, A. Panunzi and A. Vitagliano, Inorg. Chim. Acta, 137 (1987) 53.

25 F.P. Fanizzi, L. Maresca, G. Natile, M. Lanfranchi, A.M. Manotti-Lanfredi and A. Tiripicchio, Inorg. Chem., 27 (1988) 2422.

26 V.G. Albano, F. Demartin, A. De Renzi and G. Morelli, Inorg. Chim. Acta, 149 (1988) 253.

27 M.E. Cucciolito, A. Panunzi, F. Ruffo and V. De Felice, Gazz. Chim. Ital., 119 (1989) 461.

28 V. De Felice, M. Funicello, A. Panunzi and F. Ruffo, J. Organomet. Chem., 403 (1991) 243.

29 F.P. Fanizzi, F.P. Intini, L. Maresca, G. Natile, M. Lanfranchi and A. Tiripicchio, J. Chem. Soc. Dalton Trans., (1991) 1007.

30 V.G. Albano, D. Braga, V. De Felice, A. Panunzi and A. Vitagliano, Organometallics, 6 (1987) 517.

31 V. De Felice, P. Ganis, A. Vitagliano and G. Valle, Inorg. Chim. Acta, 144 (1988) 57.

32 M.E. Cucciolito, V. De Felice, A. Panunzi and A. Vitagliano, Organometallics, 8 (1989) 1182.

33 V. De Felice, B. Giovannitti, A. Panunzi, F. Ruffo and D. Tesauro, Gazz. Chim. Ital., 123 (1993) 65.

34 L. Mink, M.F. Rettig and R.M. Wing, J. Am. Chem. Soc., 113 (1991) 2065.

35 A. Sanchez, C. Castellari, A. Panunzi, A. Vitagliano and V. De Felice, J. Organomet. Chem., 388 (1990) 243.

36 V.G. Albano, C. Castellari, M. Monari, V. De Felice, A. Panunzi and F. Ruffo, Organometallics, 11 (1992) 3665.

37 H.C. Clark and L.E. Manzer, Inorg. Chem., 13 (1974) 1996.

38 L.E. Manzer, Inorg. Chem., 15 (1976) 2354.

39 H.C. Clark and M.A. Mesubi, J. Organomet. Chem., 215 (1981) 131.

40 M.K. Cooper, D.W. Yaniuk and M. McPartlin, J. Organomet. Chem., 166 (1979) 241.

41 V.G. Albano, C. Castellari, G. Morelli and A. Vitagliano, Gazz. Chim. Ital., 119 (1989) 235.

42 V.G. Albano, F. Demartin, V. De Felice, G. Morelli and A. Vitagliano, Gazz. Chim. Ital., 117 (1987) 437.

43 V.G. Albano, C. Castellari, M.E. Cucciolito, A. Panunzi and A. Vitagliano, Organometallics, 9 (1990) 1269.

44 G. Natile, L. Maresca, L. Cattalini, U. Belluco, P. Uguagliati and U. Croatto, Inorg. Chim. Acta, 20 (1976) 49.

45 L. Maresca, G. Natile, A.M. Manotti-Lanfredi and A. Tiripicchio, J. Am. Chem. Soc., 104 (1982) 7661.

46 L. Maresca and G. Natile, J. Chem. Soc. Chem. Commun., (1983) 40.

47 F.P. Fanizzi, F.P. Intini, L. Maresca, G. Natile and F. Gasparrini, J. Chem. Soc. Dalton Trans., (1990) 1019.

48 F.P. Fanizzi, F.P. Intini, L. Maresca and G. Natile, J. Chem. Soc. Dalton Trans., (1992) 309.

49 L. Maresca, G. Natile and F.P. Fanizzi, J. Chem. Soc. Dalton Trans. (1992) 1867.

50 T. Yamamoto, A. Yamamoto and S. Ikeda, J. Am. Chem. Soc., 93 (1971) 3350.

51 B. Åkermark, V. De Felice, A. Panunzi and F. Ruffo, Acta Chem. Scand., 46 (1992) 499.

52 J. Ashley-Smith, Z. Donek, B.F.G. Johnson and J. Lewis, J. Chem. Soc. Dalton Trans., (1974) 128.

53 N.C. Harrison, M. Murray, J.L. Spencer and F.G.A. Stone, J. Chem. Soc. Dalton Trans., (1978) 1337.

54 J.C. Dewan and D.L. Kepert, J. Chem. Soc. Dalton Trans., (1975) 959.

55 F.R. Hartley, Angew. Chem. Int. Ed. Engl., 11 (1972) 596.

56 V. De Felice, V.G. Albano, C. Castellari, M.E. Cucciolito and A. De Renzi, J. Organomet. Chem., 403 (1991) 269.

57 M.J.S. Dewar, Bull. Soc. Chim. Fr., 18 (1951) C79.
58 J. Chatt and L.A. Duncanson, J. Chem. Soc., (1953) 2959.
59 F.R. Hartley, J. Organomet. Chem., 216 (1981) 277.
60 R.A. Love, T.F. Koetzle, G.J.B. Williams, L.C. Andrews and R. Bau, Inorg. Chem., 14 (1975) 2653.
61 G. Gervasio, S.A. Mason, L. Maresca and G. Natile, Inorg. Chem., 25 (1986) 220.
62 L.S. Bartell, E.A. Roth, C.D. Hollowell, K. Kuchitou and J.E. Young, J. Chem. Phys., 42 (1965) 2683.
63 V.G. Albano, C. Castellari, V. De Felice, A. Panunzi and F. Ruffo, J. Organomet. Chem., 425 (1992) 177.
64 A.R. Rossi and R. Hoffmann, Inorg. Chem., 14 (1975) 365.
65 B.W. Davies, R.J. Puddephatt and N.C. Payne, Can. J. Chem., 50 (1972) 2276.
66 A. Konietzny, P.M. Bailey and P.M. Maitlis, J. Chem. Soc. Chem. Commun., (1975) 78.
67 M.C. Favas and D.L. Kepert, Prog. Inorg. Chem., 27 (1980) 325.
68 D.L. Kepert, Prog. Inorg. Chem., 23 (1977) 1.
69 F.P. Fanizzi, L. Maresca, G. Natile, M. Lanfranchi, A. Tiripicchio and G. Pacchioni, J. Chem. Soc. Chem. Commun., (1992) 333.
70 H.C. Clark and R.J. Puddephatt, Inorg. Chem., 10 (1971) 417.
71 D.J. Cookson, T.D. Smith, J.F. Boas, P.R. Hicks and J.R. Pilbrown, J. Chem. Soc., (1977) 212.
72 Z. Lin and M.B. Hall, Inorg. Chem., 30 (1991) 646.
73 A. Bavoso, M. Funicello, G. Morelli and V. Pavone, Acta Crystallogr. Sect. C, 40 (1984) 2035.
74 A. De Renzi, G. Morelli, A. Panunzi and A. Vitagliano, Gazz. Chim. Ital., 117 (1987) 445.
75 K. Miki, M. Yama, Y. Kai and N. Kasai, J. Organomet. Chem., 239 (1982) 417.
76 P. Ammendola, M.R. Ciajolo, A. Panunzi and A. Tuzi, J. Organomet. Chem., 254 (1983) 389.