# Halogenation of Alkenes in Five-Coordinate Platinum(II) Complexes – A Route to Stable (β-Haloalkyl)platinum(IV) Species

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Five-coordinate complexes $[PtX_2(olefin)(2,9\text{-}Me_2\text{-}phen)]$ (**1**; 2,9-$Me_2$-phen = 2,9-dimethyl-1,10-phenanthroline; olefin = ethene denoted by **a**, propene by **b**, 1-butene by **c**; X = Cl denoted by **x**, Br by **y**) undergo photoactivated reactions with $Cl_2$ and $Br_2$ to give the (β-haloalkyl)platinum(IV) complexes $[Pt(CH_2CHRX)(2,9\text{-}Me_2\text{-}phen)X_3]$ (**2**). Bromination of the chloro species **1ax** leads to the formation of the $Pt^{IV}$ species **2axy** containing the bromide, the bromoalkyl, and the phenanthroline ligands in the equatorial plane and two chloride ions in axial positions. The iodo complexes **1**(**a**–**c**)**z** are not oxidized by iodine even under UV irradiation but react readily with $Cl_2$ or $Br_2$ to give **2**(**a**–**c**)**x** and **2**(**a**–**c**)**y**. The structure of **2ay**, the first structurally characterized (β-haloalkyl)platinum complex, has been determined by X-ray diffraction methods. The stereochemistry of the (β-haloalkyl)platinum(IV) complexes is in accord with a simultaneous addition of two halogen atoms to the coordinated olefin and to the metal center.

## Introduction

Although free olefins are very easily halogenated, only few reports have dealt with the halogenation of olefins coordinated to a metal center.[1] In the particular case of (olefin)platinum(II) complexes, reaction with $X_2$ generally leads to oxidation of the metal center and release of the π-olefin ligand to form $Pt^{IV}$ species. In some cases the reaction also involves the π-coordinated olefin, giving rise to the formation of an organic fragment which is retained by the metal center.[2] For instance the chelate *o*-styryldimethylarsane complex $\{PtBr_2[o\text{-}(AsMe_2)C_6H_4CH{=}CH_2]\}$ reacts with bromine to give a $Pt^{IV}$ product containing a metal−carbon σ bond, $\{PtBr_3[o\text{-}(AsMe_2)C_6H_4CHBrCH_2]\}_2$.[3] Similarly, the Zeise salt $K[PtCl_3(C_2H_4)]$ reacts with chlorine gas in water to give $[Pt(CH_2CH_2Cl)Cl_5]^{2-}$ together with some $[Pt(CH_2CH_2OH)Cl_5]^{2-}$.[4] The latter products have been extensively investigated as model compounds for the functionalization of alkanes mediated by platinum salts.[5] To the best of the authors knowledge $[Pt(CH_2CH_2Cl)Cl_5]^{2-}$ is the only example of a (β-haloalkyl)platinum complex so far reported.

The reason for which β-haloalkyl complexes are extremely rare in transition metal chemistry is to be found in the propensity of these species to undergo β-elimination reactions.[6] An alternative route to the synthesis of haloalkyl compounds is the oxidative addition of terminal dihaloalkanes $[X(CH_2)_nX]$ to transition metal complexes to yield $\{ML_m[(CH_2)_nX]\}$ compounds, which can be used as building blocks for the synthesis of homo- and heterometallic polymethylene-bridged dendritic macromolecules.[7] Again the isolation of the ω-haloalkyl complexes $\{ML_m[(CH_2)_nX]\}$ is easily accomplished when $n = 1$ or $n > 2$, whereas for $n = 2$ the β-haloalkyl species is much more difficult to prepare. As an example the oxidative addition of 1,2-diiodoethane to the $[PtMe_2(phen)]$ complex results in the formation of $[PtMe_2(phen)X_2]$ and the evolution of ethylene gas together with dimethylene-bridged dimeric or polymeric species.[8] Having investigated the reactivity of olefins in 4-coordinate platinum(II) complexes[9] attention was directed to the reactivity of olefins in five-coordinate substrates and, in particular, their reaction with halogens. These species were considered to be appealing substrates[10] because of: i) their thermodynamic stability, ii) their coordination geometry (the saturated coordination sphere should prevent direct attack of the halide on the metal center), and iii) the increased electronic charge on the olefinic carbon atoms (due to the efficient π-back donation from filled platinum d orbitals) which could render the alkene prone to the attack by electrophiles. Here the halogenation of the five-coordinate trigonal bipyramidal Pt compounds $[PtX_2(olefin)(2,9\text{-}Me_2phen)]$ (**1**) (2,9-$Me_2$-phen = 2,9-dimethyl-1,10-phenanthroline; olefin = ethene denoted by **a**, propene by **b**, 1-butene by **c**; X = Cl denoted by **x**, Br by **y**) to give the (β-haloalkyl)platinum(IV) complexes $[Pt(CH_2CHRX)(2,9\text{-}Me_2\text{-}phen)X_3]$ (**2**) (Scheme 1) is reported, together with the X-ray structure of **2ay** [the first for a (β-haloalkyl)platinum complex].

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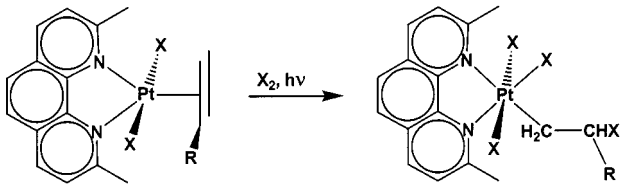



X = Cl, R = H, 1ax; Me, 1bx; Et, 1cx
X = Br, R = H, 1ay; Me, 1by; Et, 1cy

X = Cl, R = H, 2ax; Me, 2bx; Et, 2cx
X = Br, R = H, 2ay; Me, 2by; Et, 2cy

Scheme 1

## Results and Discussion

### The Five-Coordinate Precursor

Five-coordinate trigonal bipiramydal $Pt^{II}$ complexes [Pt(N−N)(olefin)XY] (X=halide, Y= halide or hydrocarbyl group; N−N = bidentate nitrogen ligand) represent a well-characterized class of platinum compounds.[10] The presence on the trigonal plane of a π-acceptor olefin ligand which draws electron charge from the metal center, so favouring the coordination of both ends of the bidentate nitrogen donor, plays a crucial role in stabilizing the five-coordinate geometry in these species.[11][12]

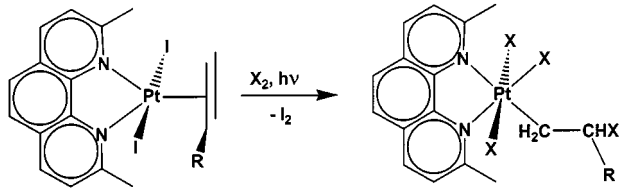
When N−N = 2,9-$Me_2$-1,10-phenanthroline the five-coordinate complexes are particularly stable if compared to analogous species with other bidentate nitrogen ligands.[10] Such a stabilization stems from the release, in the five-coordinate species, of the steric interaction between the *ortho*-methyl substituents of the phenanthroline and the *cis*-halogen ligands built up in square planar [$Pt^{II}X_2$(2,9-$Me_2$-phen)][13] and octahedral [$Pt^{IV}X_4$(2,9-$Me_2$-phen)][14] complexes.

Due to the steric strain the [$PtX_2$(2,9-$Me_2$-phen)] complexes easily dissociate one end of the phenanthroline chelate to form a T-shaped, coordinatively unsaturated, platinum species which is highly susceptible to addition reactions.[13][15] The addition product, [$Pt^{II}X_2$(2,9-$Me_2$-phen)(L)], can be either a square-planar species [L = CO, $PPh_3$, $Me_2SO$, $Me_2S$, PhNO, Py, $NH_2(CH_2)_2CH_3$], with the phenanthroline ligand monocoordinate to the platinum center (and exchanging in solution the donor nitrogen atoms at the coordination site) or, in the case of L = alkene[11] and alkyne,[16] a five-coordinate trigonal-bipyramidal (tbp) species with the halogen ions in the axial positions and the phenanthroline ligand acting as chelate and lying, together with the L ligand, in the trigonal plane.

Octahedral [$PtX_4$(2,9-$Me_2$-phen)] complexes also react with excess $C_2H_4$ to give reductive elimination of halogen (which, in turn, reacts with excess $C_2H_4$ to give 1,2-dihaloethane) and formation of the five-coordinate $Pt^{II}$ species [$PtX_2(C_2H_4)$(2,9-$Me_2$-phen)].[14]

### The Halogenation Reaction

In $CHCl_3$ solution and in the presence of light the five-coordinate complexes [$PtX_2$(olefin)(2,9-$Me_2$-phen)] (**1**) (olefin = ethene denoted by **a**, propene by **b**; 1-butene by **c**; X = Cl denoted by **x**, Br by **y**) react with $Cl_2$ and $Br_2$ to give the β-haloalkyl complexes [$Pt^{IV}(CH_2CHRX)$(2,9-$Me_2$-phen)$X_3$] (**2**) (see Scheme 1). The reaction requires photoactivation which is not required in the case of oxidative addition of $X_2$ to either the square-planar species [Pt(2,9-$Me_2$-phen)$X_2$][14] or to the free olefins. The iodo complexes **1(a−c)z** are not oxidized by iodine even under UV irradiation, while they react readily with $Cl_2$ or $Br_2$ to give **2(a−c)x** and **2(a−c)y**, respectively (see Scheme 2).

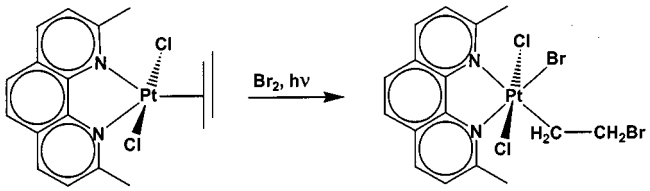



R = H, 1az; Me, 1bz; Et, 1cz

X = Cl, R = H, 2ax; Me, 2bx; Et, 2cx
X = Br, R = H, 2ay; Me, 2by; Et, 2cy

Scheme 2

The bromination of the chloro species **1ax** leads to the formation of a $Pt^{IV}$ species **2axy** containing, besides the phenanthroline and the two chloride ligands, one bromide and a bromoalkyl ligand (see Scheme 3). Comparison of the $^1$H-NMR spectra of the mixed halide complex with those of the chloro and bromo complexes **2ax** and **2ay** (Figure 1) led to the conclusion that the bromide, the bromoalkyl, and the phenanthroline ligands occupy equatorial positions while the two chloride ions occupy axial sites. The presence of a single sharp IR absorption (330 $cm^{-1}$) typical of two chloride ions mutually *trans* in an octahedral environment is in accord with this conclusion.[17]




1ax 2axy

Scheme 3

The use of $PhICl_2$, instead of chlorine gas, in the halogenation of **1ax**, did not eliminate the need for photoactivation, indicating that the reactive species is the $Cl_2$ released from the iodobenzene complex. Moreover, as observed for other photochlorination reactions,[18] the rate of halogenation of **1ax** by $Cl_2$ or $PhICl_2$ is strongly reduced if the reaction is carried out in benzene instead of chloroform. On the other hand the reaction of **1ax** with *N*-chlorosuccinimide (as substituted for the halogen) in the absence or presence of a radical initiator (benzoyl peroxide) did not give a significant amount of **2ax**.

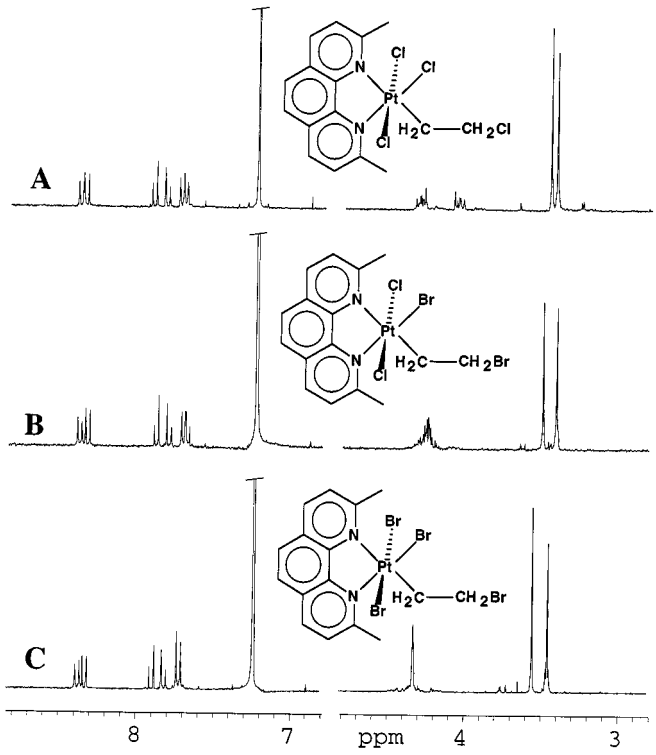
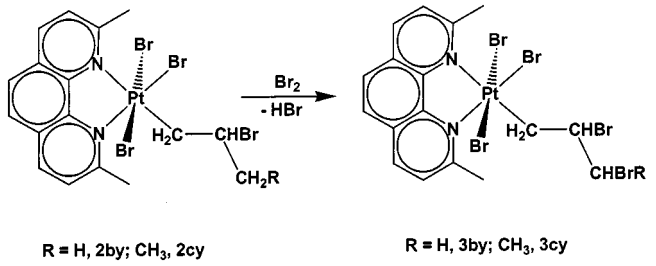



Figure 1. Comparison of the $^1$H-NMR spectra for **2ax** (**A**), **2axy** (**B**), and **2ay** (**C**) complexes

The haloethyl complexes **2a**(**x**, **y**) are stable for days in chloroform solution and, if kept in the dark, can also withstand an excess of halogen. For prolonged reaction time with excess bromine the complexes **2**(**b**, **c**)**y** undergo substitution at the γ-carbon atom with formation of the β,γ-dihaloalkyl species [Pt($CH_2CHBrCH_2Br$)(2,9-$Me_2$-phen)$Br_3$] (**3by**) and [Pt($CH_2CHBrCHBrMe$)(2,9-$Me_2$-phen)$Br_3$] (**3cy**), respectively (see Scheme 4). This γ-halogenation reaction is much faster for **2cy** than for **2by** and does not take place, under similar conditions, for the chloro species **2**(**b**, **c**)**x**. Analogous effects of substituents (activation by alkyl radicals and deactivation by halogens, with Cl stronger deactivator than Br) are observed in the halogenation of alkanes.[19] It should be noted that in the case of **3cy** the presence of two chiral centres at the β- and γ-carbon atoms leads to the formation of two diastereoisomers. Interestingly $^1$H-NMR experiments show a kinetic preference for one of the two diastereoisomers (ratio of major, **M** to minor, **m**, isomer of 80:20) (Figure 2).




Scheme 4

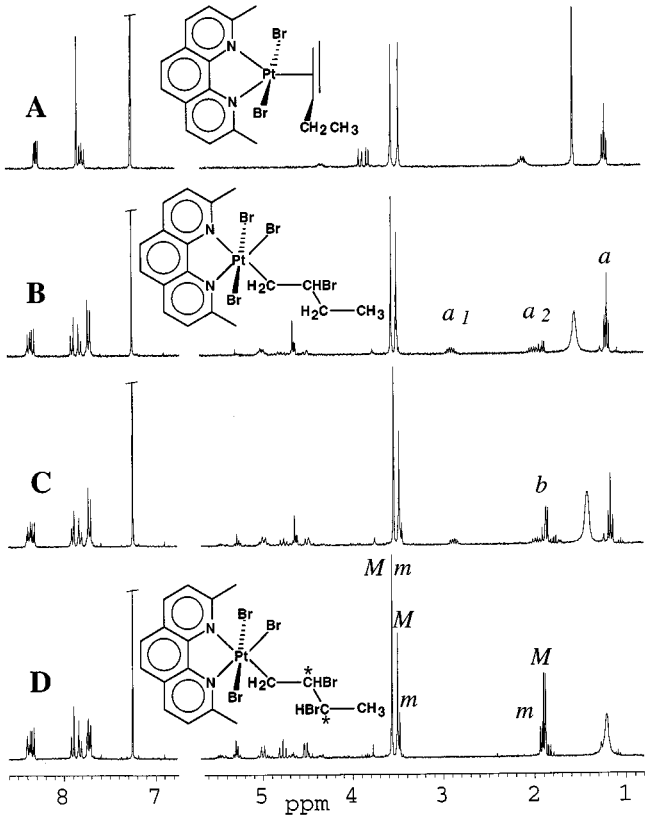



Figure 2. $^1$H-NMR spectra recorded during the reaction of **1cy** (**A**) with $Br_2$; the initially formed **2cy** species (**B**), characterized by the terminal $CH_3$ (a) and the two diastereotopic $CH_2$ protons (a1 and a2) reacts further (spectra **C** and **D**) to give two new species in which the terminal $CH_3$ is a doublet (only one proton in γ position) and correspond to different isomers (major and minor) of **3cy**; spectra were taken: (**B**) 8 min after $Br_2$ addition under neon light irradiation, (**C**) and (**D**) after 20 and 60 min incubation in the dark, respectively

## Stereochemistry of the β-Haloalkyl Complexes

$^1$H-NMR spectra of the new $Pt^{IV}$ complexes are reported in Table 1. The protons of one half of the coordinated phenanthroline ligand do not show measurable coupling with $^{195}$Pt as a consequence of the weakening of the Pt−N bond *trans* to the haloalkyl ligand.

In the case of the ethene (**a**) precursor the α- and β-$CH_2$ protons give rise to an AA′XX′ spin system of various complexity. Both the $C_α$-$H_2$ and $C_β$-$H_2$ protons show $^{195}$Pt coupling, however only in the case of **2ax** could both α-$H_2$ and β-$H_2$ values be given, in all other cases only the values for $C_α$-$H_2$ were measured.

In the case of 1-propene and 1-butene complexes halogenation occurs specifically at the alkyl-substituted carbon atom in accord with the preference expected for an electrophilic attack. In the β-halopropyl complexes **2bx** and **2by** the $C_α$-$H_2$ protons exhibit two different $^3J$(H−H) couplings (ca. 10 and 2 Hz, respectively) indicating that one is *anti* and the other *gauche* to $C_β$-H. (Figure 3). A connectivity ($^1$H NOESY experiments) between the β-Me group and only one of the $C_α$-H protons suggests that the Me group is *gauche* and the halide ion *anti* to the platinum center. The

Table 1. $^1$H-NMR data (δ, downfield from $SiMe_4$; $CDCl_3$ solvent) for (β-haloalkyl)- and (β,γ-dihaloalkyl)(phenanthroline)platinum(IV) complexes

| Compound | Phen[a] Me(2,9) | H(3,8) | H(4,7) | H(5,6) |
|---|---|---|---|---|
| **2ax** | 3.42[6] | 7.71d(8)[12] | 8.36d(8) | 7.83d(8) |
| | 3.46 | 7.74d(8) | 8.39d(8)[6] | 7.92d(8) |
| **2axy** | 3.43[6] | 7.70d(8)[12] | 8.35d(8) | 7.82d(8) |
| | 3.52 | 7.72d(8) | 8.40d(8)[6] | 7.90d(8) |
| **2ay** | 3.44[6] | 7.72d(8)[12] | 8.33d(8) | 7.82d(8) |
| | 3.54 | 7.72d(8) | 8.38d(8)[6] | 7.90d(8) |
| **2bx** | 3.44[6] | 7.70d(8)[12] | 8.35d(8) | 7.82d(8) |
| | 3.46 | 7.73d(8) | 8.38d(8)[6] | 7.91d(8) |
| **2by** | 3.48[6] | 7.71d(8)[12] | 8.32d(8) | 7.81d(8) |
| | 3.54 | 7.71d(8) | 8.37d(8)[6] | 7.89d(8) |
| **3by** | 3.45[6] | 7.72d(8)[12] | 8.35d(8) | 7.83d(8) |
| | 3.55 | 7.73d(8) | 8.40d(8)[6] | 7.91d(8) |
| **2cx** | 3.45[6] | 7.70d(8)[12] | 8.35d(8) | 7.82d(8) |
| | 3.46 | 7.73d(8) | 8.38d(8)[6] | 7.90d(8) |
| **2cy** | 3.48[6] | 7.71d(8)[12] | 8.32d(8) | 7.81d(8) |
| | 3.54 | 7.71d(8) | 8.37d(8)[6] | 7.90d(8) |
| **3cyM** | 3.48[6] | 7.72d(8)[12] | 8.34d(8) | 7.82d(8) |
| | 3.54 | 7.73d(8) | 8.39d(8)[6] | 7.91d(8) |
| **3cym** | 3.46[6] | 7.74d(8)[12] | 8.35d(8) | 7.83d(8) |
| | 3.54 | 7.74d(8) | 8.40d(8)[6] | 7.92d(8) |

| Compound | Haloalkyl[a] α-$CH_2$- | β-CH(R)X | R |
|---|---|---|---|
| **2ax** | 4.06 m[79]{2} | 4.30 m[18]{2} | – |
| **2axy** | 4.25 m[79]{2} | 4.28m{2} | |
| **2ay** | 4.31 m[84]{2} | 4.33m{2} | |
| **2bx** | 4.10dd(10,10)[72]{1} | 4.92dqd(10,7,2)[18]{1} | 1.95d(7){3} |
| | 4.35dd(10,2)[93]{1} | – | – |
| **2by** | 4.56dd(11,10)[72]{1} | 5.19dqd(11,7,2)[18]{1} | 2.22d(7){3} |
| | 4.64dd(10,2)[102]{1} | – | – |
| **3by** | 4.55dd(11,11)[54]{1} | 5.12dddd(11,8,3,2)[18]{1} | 3.84dd(11,8){1} |
| | 4.62dd(11,3)[105]{1} | – | 4.91dd(11,2){1} |
| **2cx** | 4.18dd(10,10)[69]{1} | 4.69dddd(10,9,3,2)[18]{1} | 1.13t(7){3} |
| | 4.32dd(10,2)[96]{1} | – | 1.88ddq(15,9,7){1} |
| | – | – | 2.70ddq(15,3,7){1} |
| **2cy** | 4.63 m[88]{2} | 4.99m{1} | 1.15t(7){3} |
| | – | – | 1.95ddq(15,9,7){1} |
| | – | – | 2.88ddq(15,3,7){1} |
| **3cyM** | 4.50dd(11,2)[104]{1} | 4.46ddd(11,2,1)[18]{1} | 1.86d(6){3} |
| | 4.76dd(11,11)[70]{1} | – | 5.27qd(6,1){1} |
| **3cym** | 4.43dd(11,11)[70]{1} | 5.42ddd(11,2,2)[18]{1} | 1.90d(6){3} |
| | 4.51dd(11,2)[105]{1} | – | 5.44qd(6,2){1} |

[a] Values of $J_{H-H}$ (in parentheses) and $J_{Pt-H}$ [in brackets] are given when assignable. Integral values are given in braces.

Me substituent of the phenanthroline ligand *cis* to the β-haloalkyl group (easily distinguishable from that *trans* to the β-haloalkyl group because of its coupling with $^{195}$Pt) has a cross peak [NOESY spectrum of **2b**(**x**, **y**)] with the $C_\alpha$-H weakly coupled with the $C_\beta$-H (2 Hz) indicating that this $C_\alpha$-H is *anti* to the β-Me group. The resulting preferred conformation of the β-haloalkyl group is that shown in the formula of Figure 3. The different couplings of the two $C_\alpha$-H protons with the platinum center [$^2J(Pt-H) \approx 100$ and 70 Hz, respectively], and the relatively small value of the $^3J(Pt-C_\beta-H)$ coupling (18 Hz), are also in accord with this conformation of the β-haloalkyl group.

In the β-halo-*n*-buthyl complexes **2c**(**x**, **y**) the α-$CH_2$ signals are quite similar to those found for **2b**(**x**, **y**). Moreover two multiplets (ca. 0.9 ppm apart from each other) are observed for the diastereotopic γ-$CH_2$ protons, and a triplet for the terminal $CH_3$.

## X-ray Structure of 2ay

The X-ray structure of [Pt($CH_2CH_2Br$)(2,9-$Me_2$-phen)$Br_3$] (**2ay**) is shown in Figure 4 together with the atomic labeling scheme; relevant bond lengths and angles are reported in Table 2. The octahedral complex adopts a *mer* configuration with the two N(1) and N(2) atoms from the 2,9-$Me_2$-phen chelating ligand and the σ-bonded C(15) atom of the β-bromoethyl group lying in the same plane.

The three Pt−Br bonds have nearly equal length, whereas the Pt−N(2) bond [2.217(10) Å] is much longer than the Pt−N(1) bond [2.110(10) Å] reflecting the much greater *trans* influence of the haloalkyl group with respect to the bromide ion. The Pt and Br(4) atoms are, as expected, in *anti* positions [Pt−C(15)−C(16)−Br(4) torsion angle of −170.8(6)°]. Due to the lengthening of the Pt−N(2) bond the clash between the methyl substituent C(14) of the phen

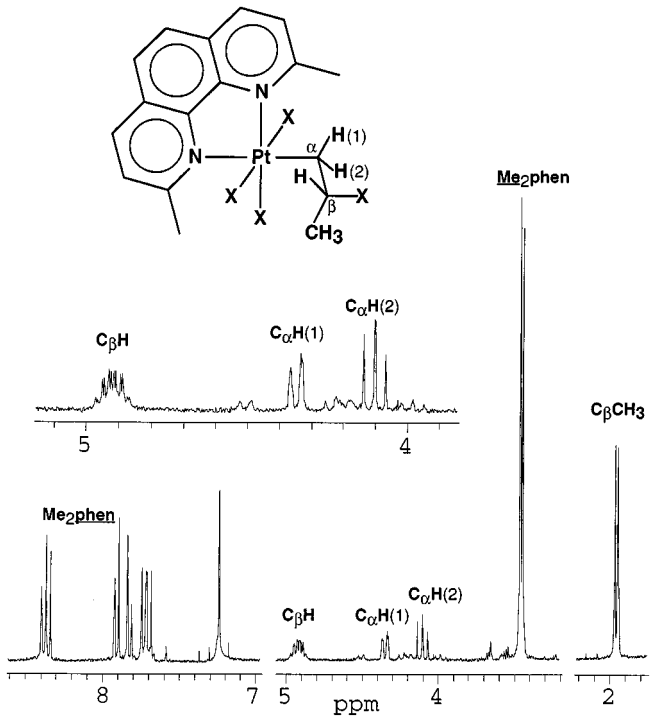



Figure 3. $^1$H-NMR spectrum of **2bx** showing that $J_{HH}$ and $J_{PtH}$ for the α and β protons of the haloalkyl group are in accord with a preferred conformer having the Me and halide substituents on the β-carbon atom, respectively, *gauche* and *anti* to the Pt atom

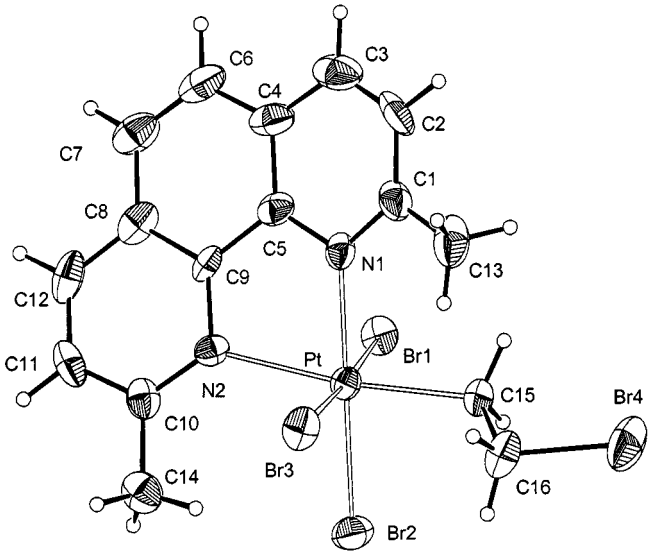



Figure 4. View of the complex molecule [Pt($CH_2CH_2Br$)(2,9-$Me_2$-phen)$Br_3$] (**2ay**) with the atomic numbering scheme (30% probability ellipsoids)

ligand and the Br(2) atom is smaller than that between the second methyl group of phen C(13) and the α-carbon atom C(15) of the bromoethyl group [the Pt−N(2)−C(10)−C(14) and Pt−N(1)−C(1)−C(13) torsion angles are 18(2)° and −27(2)° respectively].

The steric interaction between the 2,9-methyl substituents of phen and other ligands in the coordination sphere causes

Table 2. Selected bond lengths [Å] and angles [°] for **2ay**

| | | | |
|---|---|---|---|
| Pt−Br(1) | 2.469(2) | C(1)−C(13) | 1.49(2) |
| Pt−Br(2) | 2.446(2) | C(4)−C(5) | 1.39(2) |
| Pt−Br(3) | 2.460(2) | C(4)−C(6) | 1.41(2) |
| Pt−N(1) | 2.110(10) | C(5)−C(9) | 1.45(2) |
| Pt−N(2) | 2.217(10) | C(6)−C(7) | 1.38(3) |
| Pt−C(15) | 2.121(12) | C(7)−C(8) | 1.40(2) |
| N(1)−C(1) | 1.36(2) | C(8)−C(9) | 1.40(2) |
| N(1)−C(5) | 1.40(2) | C(8)−C(12) | 1.40(2) |
| N(2)−C(10) | 1.34(2) | C(10)−C(11) | 1.41(2) |
| N(2)−C(9) | 1.36(1) | C(10)−C(14) | 1.48(2) |
| C(1)−C(2) | 1.35(2) | C(11)−C(12) | 1.37(2) |
| C(2)−C(3) | 1.35(3) | C(15)−C(16) | 1.50(2) |
| C(3)−C(4) | 1.42(3) | Br(4)−C(16) | 1.96(2) |
| | | | |
| N(1)−Pt−C(15) | 96.6(5) | N(2)−Pt−Br(1) | 87.3(2) |
| N(1)−Pt−N(2) | 77.6(4) | Br(2)−Pt−Br(1) | 88.3(1) |
| C(15)−Pt−N(2) | 171.7(4) | Br(3)−Pt−Br(1) | 175.9(1) |
| N(1)−Pt−Br(2) | 175.9(3) | C(1)−N(1)−C(5) | 117.2(12) |
| C(15)−Pt−Br(2) | 83.8(4) | C(1)−N(1)−Pt | 131.2(9) |
| N(2)−Pt−Br(2) | 101.6(2) | C(5)−N(1)−Pt | 110.7(8) |
| N(1)−Pt−Br(3) | 91.7(3) | C(10)−N(2)−C(9) | 118.1(11) |
| C(15)−Pt−Br(3) | 97.6(4) | C(10)−N(2)−Pt | 132.7(9) |
| N(2)−Pt−Br(3) | 88.6(2) | C(9)−N(2)−Pt | 108.2(8) |
| Br(2)−Pt−Br(3) | 92.3(1) | C(16)−C(15)−Pt | 114.4(9) |
| N(1)−Pt−Br(1) | 87.6(3) | C(15)−C(16)−Br(4) | 107.7(10) |
| C(15)−Pt−Br(1) | 86.5(4) | | |

the same type of distortion already observed for (2,9-dimethylphenanthroline)platinum(II)[13] and -platinum(IV)[14] complexes: a) tilting of the plane of the chelating moiety (N−C−C−N) with respect to the equatorial coordination plane [dihedral angle between N(1)−C(5)−C(9)−N(2) and Br(2)−Pt−C(15) planes of 32.9(5)°]; b) narrowing of the angle between the *cis* ligands coplanar with $Me_2$-phen [Br(2)−Pt−C(15) = 83.8(4)°]; c) bowlike distortion of the phen ligand [dihedral angle between the outer rings of the phen ligand of 15.0(5)°]. It is to be noted that the presence of the two axial ligands reduces the tilting of the phen ligand with respect to the equatorial coordination plane which is smaller than that found in [$PtBr_2$(2,9-$Me_2$-phen)][13] [angles between the N−C−C−N and Br−Pt−Br planes of 41.9(4)°]. A decrease in the tilting angle of the phenanthroline on going from square planar $Pt^{II}$ to octahedral $Pt^{IV}$ species has already been observed in the case of [$PtI_2$(2,9-$Me_2$-4,7-$Ph_2$phen)] and [$PtI_4$(2,9-$Me_2$-4,7-$Ph_2$-phen)] complexes.[14]

## Insight Into the Halogenation Mechanism

The experimental results of the present investigation strongly suggest that the radical species $X^\bullet$ is responsible for the attack on the coordinated olefin. In accord with this hypothesis are: i) The scarce reactivity of our substrates with iodine (halogenation of olefins by a radical mechanism requires a much higher activation energy in the case of iodine with respect to chlorine and bromine).[20] ii) The use of $PhICl_2$ (instead of $Cl_2$) which could act as an ion source ($Cl^+$) does not eliminate the need for photoactivation. iii)

The reduced reactivity of chlorine in benzene due to the formation of chlorine atom−benzene π complexes.[18]

It is noteworthy that the bromination of **1ax** leads to the formation of the mixed-halide $Pt^{IV}$ species **2axy**, which contains the phenanthroline, the bromide, and the bromoalkyl ligand in equatorial positions and the two chloride ions in axial positions. This stereochemistry gives an indication of a nearly simultaneous addition of the halogen atoms to the olefin and to the metal center, preventing a possible scrambling of ligands in the five-coordinate intermediate formed after the addition of one halogen atom to the π-olefin. Also the observation that *N*-chlorosuccinimide (as substitute of the halogen) under radical conditions (presence of benzoyl peroxide) does not react with the five-coordinate olefin complexes to yield the β-haloalkyl species, can be taken as evidence that the photoactivation of the halogen must take place while the halogen molecule is already close to the platinum center and to the olefin ligand.

In spite of the several investigations concerned with the oxidative addition of halogens to square-planar platinum complexes,[21] only in a few cases were (olefin)platinum complexes involved, and the reaction very rarely gave products which retained the organic fragment bound to the platinum center. Oxidative addition of halogen or alkyl halide to three-coordinate $Pt^0$ species [Pt(2,9-$Me_2$-phen)(olefin)] results in an electrophilic attack to the metal center and formation of the five-coordinate trigonal-bipyramidal $Pt^{II}$ complexes [Pt(olefin)(2,9-$Me_2$-phen)XY] (X = halide Y = hydrocarbyl or halide).[22] Only in one case was evidence found of a further oxidation reaction involving the five-coordinate species, but no attempt was made to characterize the products.[22] Successful halogenation of the coordinate olefin has been reported, so far, for the bromination of [$PtBr_2${*o*-($Me_2As$)$C_6H_4$CH=$CH_2$}][3] and the chlorination of Zeise′s salt in water.[4] In the former case the reaction with bromine led to a $Pt^{IV}$ dimer, {$PtBr_3$[*o*-($Me_2As$)$C_6H_4$CHBr$CH_2$]}$_2$, in which the olefin of the chelate dimethyl(*o*-styryl)arsane ligand was converted into a β-haloalkyl group σ-bonded to the metal center. A synchronous *cis* addition of a polarized bromine molecule with the negative end attacking the platinum center and the positive end attacking the double bond was suggested.

In the reaction of Zeise′s salt with chlorine, $[Pt(CH_2CH_2Cl)Cl_5]^{2+}$, together with some $[[Pt(CH_2CH_2OH)Cl_5]^{2+}$, was formed and the reaction mechanism was assumed to imply external attack of halogen to ethene subsequent to oxidation of platinum(II) to platinum(IV) as observed for olefin complexes of palladium.[23] The oxidation of Zeise′s salt in water with $[PtCl_6]^{2-}$ produces only $[Pt(CH_2CH_2OH)Cl_5]^{2+}$, and in the latter case the reverse sequence of reactions, that is nucleophilic attack of the solvent on the coordinated ethylene ligand followed by oxidation of the (β-hydroxyalkyl)platinum(II) species just formed was suggested.[24] A cross oxidation involving simultaneously the metal center and the olefin ligand can be envisaged in this case, where the coordinatively saturated trigonal-bipyramidal platinum(II) species does not allow an attack on the metal center as first step.

## Conclusions

The five-coordinate complexes [$PtX_2$(olefin)(2,9-$Me_2$-phen)] react in the presence of light with $Cl_2$ and $Br_2$ to give the β-haloalkyl complexes [$Pt^{IV}$($CH_2$CHRX)(2,9-$Me_2$-phen)$X_3$]. The reaction requires photoactivation which is not required in the oxidative addition of $X_2$ to either the square-planar species [Pt(2,9-$Me_2$-phen)$X_2$] or to the free olefins. Experimental data suggest that the radical species $X^{\cdot}$ is responsible for attack on the coordinated olefin ligand in the five-coordinate platinum(II) species, by a cross oxidation which involves also the metal center. Such a reaction is completely different from other reported halogenation reactions of square-planar $Pt^{II}$ complexes for which the oxidation to $Pt^{IV}$ precedes the attack on the coordinated olefin ligand. Further work is in progress to elucidate the mechanism of the halogenation reaction in coordinatively saturated five-coordinate (olefin)platinum(II) complexes.

## Experimental Section

**General:** Commercial reagent-grade chemicals, ethylene, propene, 1-butene, chlorine (Matheson); bromine, iodine, *N*-chlorosuccinimide (NCS), and benzoyl peroxide (Aldrich) were used without further purification. $PhICl_2$ was prepared according to a literature method.[25] Starting complexes [$PtX_2$(2,9-$Me_2$-phen)] (**1**) (2,9-$Me_2$-phen = 2,9-dimethyl-1,10-phenanthroline; X = Cl, **x**; Br, **y**; I, **z**) were prepared as already described.[11] − $^1$H NMR: Bruker AM 300 instrument. COSY and NOESY spectra were recorded by using the automated Bruker microprograms, a mixing time of 1 s was used in the NOESY experiments. − IR: KBr pellets with Perkin−Elmer 283 and FT 1600 spectrophotometers. − Microanalyses: Dipartimento Farmaco-chimico Microanalytical Service (Bari University) with a Carlo Erba 1106 Elemental Analyzer.

**Synthesis of the Five-Coordinate Complexes:** [$PtX_2$(olefin)(2,9-$Me_2$-phen)] (olefin = ethylene, **a**; propene, **b**; 1-butene, **c**; X = Cl, **x**; Br, **y**; I, **z**) were prepared from the corresponding square-planar species **1**(**x**−**z**) by direct uptake of the olefin.[11]

**Synthesis of the (β-Haloalkyl)platinum(IV) Complexes:** [Pt($CH_2$CHRX)(2,9-$Me_2$-phen)$X_3$] (**2**); X= Cl (**x**) or Br (**y**); R= H (**a**), Me (**b**) or Et (**c**). The five-coordinate olefin complex [$PtX_2$(olefin)(2,9-$Me_2$-phen)] (0.2 mmol) was dissolved in chloroform (10 mL) and treated with excess halide (chlorine gas was bubbled for 5 min through the solution while bromine was added as pure liquid (0.4 mL). The solution was left under neon light (two OSRAM L36 W/10 Daylight tubes) for 5 min (**1cy**) or 10 min (all other complexes), then the (β-chloroalkyl)- (yellow) or (β-bromoalkyl)platinum(IV) complexes (orange) were precipitated by addition of *n*-pentane to the filtered solution. The solid was collected, washed with *n*-pentane and dried in air. The oxidation of the chloro complex **1ax** with bromine gave the mixed $Pt^{IV}$ halide complex [Pt($CH_2CH_2$Br)(2,9-$Me_2$-phen)$Cl_2$Br] (**2axy**). Yields of the isolated products were always above 80%. − $C_{16}H_{16}Cl_4N_2Pt$ (**2ax**; 573.2): calcd. C 33.5, H 2.8, N 4.9; found C 33.3, H 2.7, N 4.7. − $C_{16}H_{16}Br_2Cl_2N_2Pt$ (**2axy**; 662.1): calcd. C 29.0, H 2.4, N 4.2; found C 28.9, H 2.5, N 4.1. − $C_{16}H_{16}Br_4N_2Pt$ (**2ay**; 751.0): calcd. C 25.6, H 2.1, N 3.7; found C 25.7, H 2.0, N 3.5. − $C_{17}H_{18}Cl_4N_2Pt$ (**2bx**; 587.2): calcd. C 34.8, H 3.1, N 4.8; found C 34.6, H 3.2, N 4.7. − $C_{17}H_{18}Br_4N_2Pt$ (**2by**; 765.0): calcd. C 26.7, H 2.4, N 3.7; found C 26.6, H 2.3, N 3.5. − $C_{18}H_{20}Cl_4N_2Pt$ (**2cx**; 601.3): calcd. C 36.0, H 3.4, N 4.7; found C 35.8, H 3.2, N 4.5. − $C_{18}H_{20}Br_4N_2Pt$ (**2cy**; 779.1): calcd. C 27.8,

H 2.6, N 3.6; found C 27.6, H 2.5, N 3.4. − The reaction of the iodo complexes **1az** with excess $I_2$ (1:10 molar ratio) was performed in an NMR tube (ca. $5\cdot10^{-3}$ M in $CDCl_3$) and monitored by $^1H$ NMR. No oxidation of the starting complex was detected after several h even after prolonged UV irradiation. The analogous reactions of **1az** with excess $Cl_2$ (bubbled for 5 min trough the solution) or $Br_2$, monitored by $^1H$ NMR, showed, after exposure to a neon light for 10 min, the formation of **2ax** or **2ay,** respectively. − The oxidation of **1ax** with excess $PhICl_2$ was also performed in an NMR tube exposed to neon light (ca. $2\cdot10^{-3}$ M in $CDCl_3$; 1:5 complex/oxidant molar ratio) and monitored by $^1H$ NMR. When the solvent was $CDCl_3$, complete conversion of **1ax** into **2ax** was observed within 2 h of light exposure. In contrast, when the solvent was $C_6D_6$ only 5% conversion was observed after 2 h of light exposure. − Reactions of **1ax** with *N*-chlorosuccinimide (1:10, complex/oxidant molar ratio), in the absence and presence of a radical promoter (1:1, oxidant/benzoyl peroxide molar ratio) were also performed (complex concentration ca. $5\cdot10^{-3}$ M in $CDCl_3$) in an NMR tube exposed to neon light. In both cases no conversion of **1ax** into **2ax** was observed after 24 h ($^1H$ NMR).

**Synthesis of the (β,γ-Dibromoalkyl)platinum(IV) Complexes [Pt($CH_2CHBrCH_2Br$)(2,9-$Me_2$-phen)$Br_3$] (3by) and [Pt($CH_2CHBrCHBrMe$)(2,9-$Me_2$-phen)$Br_3$] (3cy):** Besides the β-haloalkyl complexes described above the reaction of the five-coordinate complexes **1by** and **1cy** with excess $Br_2$ can also afford products of further halogenation. The reactants were placed in an NMR tube (complex concentration ca. $5\cdot10^{-3}$ M, $Br_2$ concentration ca. $10^{-1}$ M, in $CDCl_3$), exposed for 10 min to neon light irradiation, and than post-incubated in the dark (1 h in the case of **1by**; 12 h in the case of **1cy**). Quantitative formation of new species was detected by $^1H$ NMR. The new species could be isolated as orange solids by addition of pentane to the filtered solution and were identified, on the basis of their $^1H$-NMR spectra and microanalytical data, as the β,γ-dihaloalkyl complexes [Pt($CH_2CHBrCH_2Br$)(2,9-$Me_2$-phen)$Br_3$] (**3by**) and [Pt($CH_2CHBrCHMeBr$)(2,9-$Me_2$-phen)$Br_3$] (**3cy**), respectively. The latter compound is found in two diastereoisomeric forms (major and minor, 80:20 molar ratio), due to the presence of two chiral centers. Yields of the isolated products **3by** and **3cy** were above 70%. − $C_{17}H_{17}Br_5N_2Pt$ (**3by**; 843.9): calcd. C 24.2, H 2.0, N 3.3; found C 24.0, H 1.9, N 3.1. − $C_{18}H_{19}Br_5N_2Pt$ (**3cy**; 858.0): calcd. C 25.2, H 2.2, N 3.3; found C 25.1, H 2.2, N 3.2.

**X-ray Data Collection, Structure Determination, and Refinement of Complex 2ay:** Crystals of **2ay** were obtained from $CH_2Cl_2/Et_2O$ solution. The crystallographic data are summarized in Table 3. Accurate unit-cell parameters were determined by least-squares refinement of the setting angles of 30 randomly distributed and carefully centered reflections with θ in the range 24−44°. The data collection was performed at 293 K with a Siemens AED diffractometer by using the θ/2θ scan mode. One standard reflection was monitored every 100 measurements, no significant decay was noticed over the time of data collection. The structure was solved by direct methods (SIR92[26]) and refined by full-matrix least squares based on $F_o^2$ using the SHELXL-97 program,[27] first with isotropic then with anisotropic thermal parameters for all the non-hydrogen atoms. All the hydrogen atoms were placed at their geometrically calculated positions and refined "riding" on their parent carbon atoms. The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (0.1028P)^2 + 11.5518P]$ where $P = (F_o^2 + 2F_c^2)/3$. All calculations were carried out with the ENCORE 91 of the "Centro di Studio per la Strutturistica Diffrattometrica" del CNR, Parma. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic data Centre, registration number CCDC-111824. Copies of the data may be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 3. Crystal data and structure refinement for **2ay**

| | |
|---|---|
| Formula | $C_{16}H_{16}Br_4N_2Pt$ |
| Molecular weight | 751.04 |
| Temperature [K] | 273(2) |
| Wavelength | 1.54184 Å |
| Crystal system, space group | monoclinic, $P2_1/n$ |
| Cell constants | |
| $a$ [Å] | 11.084(5) |
| $b$ [Å] | 14.729(6) |
| $c$ [Å] | 12.236(5) |
| β [°] | 109.23(2) |
| $V$ [Å$^3$] | 1886.1(14) |
| $Z$, calculated density | 4, 2.645 Mg/m$^3$ |
| Absorption coefficient | 23.836 mm$^{-1}$ |
| $F$(000) | 1376 |
| Crystal size | 0.28 × 0.18 × 0.12 mm |
| θ range [°] | 4.86−69.93 |
| Index ranges | $-13 \le h \le 12$, $-17 \le k \le 7$, $-13 \le l \le 14$ |
| Reflections collected/unique | 3735/3574 [$R$(int) = 0.0672] |
| Completeness to 2Θ = 69.93° | 95.6% |
| Max. and min. transmission | 1.000 and 0.450 |
| Refinement method | Full-matrix least squares on $F^2$ |
| Data/restraints/parameters | 3574:0:211 |
| Goodness-of-fit on $F^2$ | 1.124 |
| Final $R$ indices [$I > 2\sigma(I)$] | $R1$ = 0.0630, $wR2$ = 0.1643 |
| $R$ indices (all data) | $R1$ = 0.0748, $wR2$ = 0.1807 |
| Largest diff. peak and hole | 2.073 and −1.771 e·Å$^{-3}$ |

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