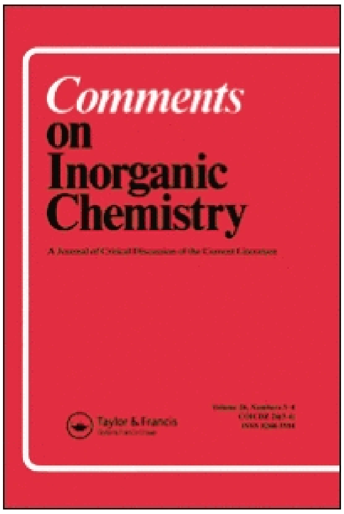
This article was downloaded by:
On: *15 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Comments on Inorganic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

Cationic Complexes of Platinum(l1) Containing Olefins: A Type of Highly Electrophilic Substrate

Luciana Maresca[a]; Giovanni Natile[a]
[a] Dipartimento Farmaco-Chimico, Bari, Italy

To cite this Article Maresca, Luciana and Natile, Giovanni(1994) 'Cationic Complexes of Platinum(l1) Containing Olefins: A Type of Highly Electrophilic Substrate', Comments on Inorganic Chemistry, 16: 1, 95 — 112

To link to this Article: DOI: 10.1080/02603599408035853

URL: http://dx.doi.org/10.1080/02603599408035853

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Cationic Complexes of Platinum(II) Containing Olefins: A Type of Highly Electrophilic Substrate

LUCIANA MARESCA and GIOVANNI NATILE
Dipartimento Farmaco-Chimico,
via E. Orabona 4,
I-70125, Bari, Italy

Received November 24, 1993

The topic discussed in this article is the synthesis of cationic complexes of platinum(II) containing η^2-olefins, their reaction with nucleophiles, and the cleavage, under acidic conditions, of the platinum–carbon bond of the addition products obtained therefrom. Some general features related to the electron distribution and bonding, the structural and conformational preferences, the reaction mechanisms and reactivity are discussed.

Key Words: *cationic alkene complexes, intramolecular* $\pi \rightarrow \sigma$ *rearrangement, nucleophilic addition, platinum(II)*

SYNTHESIS AND STABILITY OF CATIONIC η^2-OLEFIN COMPLEXES

The nature of the bond between olefins and transition metals is generally understood in terms of the description made by Dewar, Chatt and Duncanson in the early 1950's.[1] This bond can be safely described as a "continuum" between two limiting situations represented, respectively, by pure donation of π electrons of the olefin

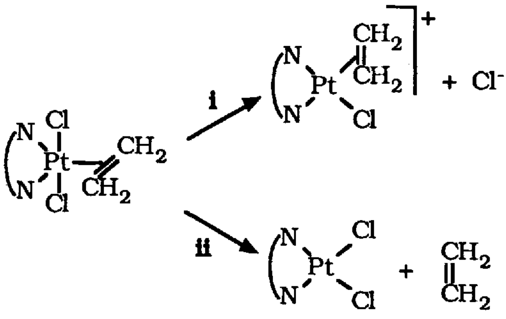
Comments Inorg. Chem.
1994, Vol. 16, Nos. 1 & 2, pp. 95–112
Reprints available directly from the publisher
Photocopying permitted by license only

into a vacant *dp* orbital of the metal and by back donation from a filled *dp* orbital of the metal into the vacant π^* orbital of the olefin.[2]

The relative importance of the π and σ components of this bond has long been discussed and debated. Up to the end of the 1970's several authors pointed out that the stability of the platinum(II) complexes decreases as the overall charge of the complex becomes more positive, thus reducing the extent of the metal π back donation.[3] This explanation was offered to account for the lability of cationic complexes such as *trans*-$[Pt(Me)(\eta^2\text{-olefin})(PMe_2Ph)_2](PF_6)$, preventing a thorough investigation of the reactivity of the coordinated olefin.[4] A more recent study by Chang and Zink,[5] based on the single-crystal polarized electronic absorption spectrum of Zeise's salt and its ligand field interpretation, concluded that ethylene as a σ-donor is better than ammonia, thus emphasizing the relevance of the σ-component in the metal–olefin bond.

Cationic olefin complexes of formula $[PtX(\eta^2\text{-olefin})(N{-}N)]^+$ (X = monodentate anion, N–N = bidentate N-donor ligand) could be obtained by spontaneous decomposition of five-coordinate platinum–olefin complexes of trigonal bipyramidal geometry prepared by reaction of Zeise's salt (or its dimer) with a bidentate N-donor ligand.[6] For a given type of N–N ligand (diamine, diimine, etc.) the stability of the five-coordinate species greatly depends upon the bulk of the substituents at the nitrogen atoms.[7] Five-coordinate complexes of low or moderate stability decay to a square-planar four-coordinate species either by loss of an axial ligand (generally a chloride ion) or of the olefin (paths **i** and **ii** in Scheme 1, respectively); the choice between the two reaction paths is influenced by the nature of the bidentate ligand and by the solvent.[8]

The cationic olefin complexes appear to be thermally stable as long as the labilizing effect of the olefin is balanced by the coordinating ability of the trans ligand. The nature of the diamine plays a critical role. For example, whereas N,N,N′,N′-tetramethylethylenediamine (tmen) leads to a very stable compound ($[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$, **1** throughout the text), the N,N,N′,N′-tetramethylpropanediamine (tmpn) and the unsubstituted ethylenediamine (en) ligands give, preferentially, complexes of the type $[Pt(\eta^2\text{-}C_2H_4)Cl_2(H\text{-diamine})]^+$, in which the diamine



SCHEME 1

is monocoordinated to platinum and protonated at the free end.[9] The greater coordinating ability of tmen as compared to tmpn ligand stems from a greater tendency to ring formation. It is known from kinetic studies performed on $[PtCl_3(Htmen)]$ and $[PtCl_3(H\text{-}tmpn)]$ complexes that the rate constant for the ring closing step is greater (by a factor of ca. 200) in the former complex than in the latter one.[10] Moreover, it has been found that the species of formula $[Pt(\eta^2\text{-}C_2H_4)Cl_2(Me_2N[CH_2]_nNMe_2)]$ have in solution a five-coordinate geometry (both ends of the diamine coordinated to platinum) only in the case of $n = 2$ (tmen ligand), while in the case of $n = 3$ (tmpn ligand) the coordination number is five only at −35°C and four at room temperature (with a fast head-to-tail rearrangement of the monocoordinated diamine) and, finally, in the case of $n = 4$ (tmbn ligand) the coordination number is always four, even at low temperature (with the diamine in fast head-to-tail rearrangement).[11]

Also the unsubstituted en ligand, which would be able to form a sterically favored five-membered chelate ring, failed to give a cationic species. This could be justified in terms of effect of the nitrogen substituents. It is well established, both in organic and organometallic chemistry, that cyclization reactions are favored by the presence of substituents on the ring forming atoms. This effect appears to be relevant mainly for two methyl groups attached to the same carbon or nitrogen atom and for this reason has been called the "gem dimethyl" effect or also the Thorpe–Ingold effect from the names of the discoverers.[12] Moreover, kinetic studies performed on four-coordinate platinum(II) substrates have shown that the rate of chelate ring formation for the tmen ligand is ca. 100 times greater than that for en.[10]

Stable cationic species are also obtainable when the diamine is N,N′-dimethyl-2,3-diaminobutane ($[Pt(\eta^2\text{-}C_2H_4)Cl(Me_2dab)]^+$, **2**). In this case the two methyl substituents, one on the nitrogen and the other on the adjacent carbon atom of the chelating chain, create the conditions for a Thorpe–Ingold effect. In compound **2** an asymmetric induction on the configuration of the coordinated nitrogens, promoted by the adjacent chiral carbons, has been observed.[13]

The cationic compounds **1** and **2** are stable indefinitely in the solid state and can be recrystallized from water or methanol, as long as nucleophiles are excluded.[14] Significant ^1H NMR and IR parameters of the cationic olefin complexes are collected in Table I, in which the data for neutral *trans*-$[Pt(\eta^2\text{-}C_2H_4)Cl_2(L)]$ (L = $Me\overline{NCH_2CH_2OCH_2C}H_2$ and $Me_2NCH_2CH_2Cl$)[14] and Zeise's anion are also included for comparison.[15] Moving from cationic to neutral and then to anionic species, a slight, but regular, upfield shift of the ethylene protons and an increase of their coupling constant with ^{195}Pt are observed; moreover, in the cationic complexes the platinum–carbon stretching frequencies are the lowest. These observations indicate that the platinum–olefin interaction becomes weaker when the complex carries a positive charge and the π component of the bond is reduced.

TABLE I

IR[a] and ^1H NMR[b] data for some cationic, neutral, and anionic η^2-ethylene complexes of platinum(II).

	ν(Pt–C)				
Compound	Asym.	Sym.	$\delta(C_2H_4)$	$J_{(PtH)}$	Ref.
$[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]ClO_4$ (**1**)	458	368	4.79	61.0	14
$[Pt(\eta^2\text{-}C_2H_4)Cl(R,S\text{-}Me_2dab)]ClO_4$ (**2**)	460	355	4.73	60.0	13
trans-$[Pt((\eta^2\text{-}C_2H_4)Cl_2(Me\overline{NCH_2CH_2OCH_2C}H_2)]$	490	392	4.63	63.0	14
trans-$[Pt(\eta^2\text{-}C_2H_4)Cl_2(Me_2NCH_2CH_2Cl)]$	488	392	4.58	63.4	14
$K[Pt(\eta^2\text{-}C_2H_4)Cl_3]$	492	404	4.39	65.1	15

[a] Infrared values ±3 cm^{-1}.

[b] All spectra were recorded in methanol-d_4 solutions, chemical shifts (δ) are in ppm from internal reference TMS, coupling constants (J) in Hz.

The bonding situation should also influence the geometry of the coordinated olefin. As the link between the metal and the olefin strengthens, the C=C distance should increase while the metal–carbon bonds should become shorter; the olefin should no longer be planar but show a bending back of the carbon substituents. These effects are ascribed to an increased electron population of the π^* orbital (as a consequence of the charge donation from the metal) which reduces the C=C double-bond order, strengthens the interaction with the central metal, and puts the olefin in a cis bent excited state.[16] A neutron diffraction analysis of $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)](ClO_4)$ (Fig. 1) has allowed a more precise determination of the light atom positions.[17] The results (Table II) have shown that the structural parameters of ethylene in the cationic substrate are very close to those found in Zeise's anion[18] and also in platinum(O) complexes which are also included for comparison.[19]

In conclusion, the platinum–olefin linkage does not appear to depend dramatically upon the total charge of the complex, and the stability of some positively charged substrates appears to reside on different factors such as the anchoring of the ligand trans to the olefin which prevents a dissociative pathway for the decomposition reaction.

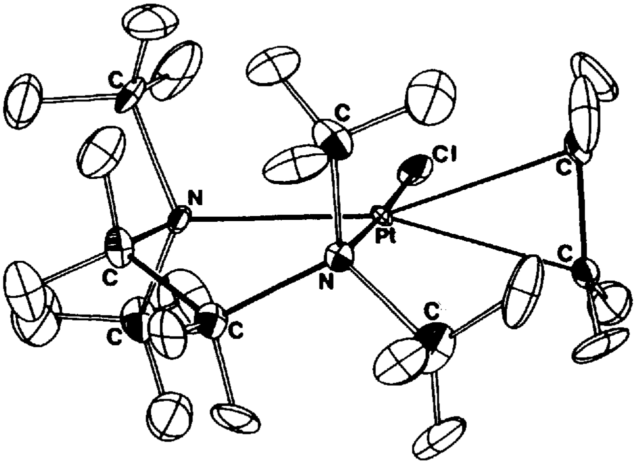


FIGURE 1 Molecular structure of the $[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$ cation.

TABLE II

Structural parameters involving the metal atom and the ethylene ligand for selected complexes.[a]

Compound	Pt–C (Å)	C–C (Å)	α (°)	β (°)	Ref.
$[Pt(\eta^2\text{-}C_2H_4)Cl_3]^-$	2.128 (3)	1.375 (4)	32	74	18
	2.135 (3)				
$[Pt(\eta^2\text{-}C_2H_4)_3]$	2.176 (2)	1.402 (7)	31	74	19
	2.191 (6)	1.365 (8)	32	74	
	2.272 (6)				
	2.195 (6)	1.378 (8)			
	2.258 (6)				
$[Pt(\eta^2\text{-}C_2H_4)Cl(tmen)]^+$	2.184 (5)	1.376 (3)	32	77	17
	2.166 (5)			71	

[a] α is the angle between the normals to the CH_2 planes; β is the angle between the normal to the CH_2 plane and the ethylene bond.

EFFECT OF SUBSTITUENTS ON THE OLEFIN. FORMATION OF HETEROMETALLACYCLES VIA INTRAMOLECULAR NUCLEOPHILIC ADDITION

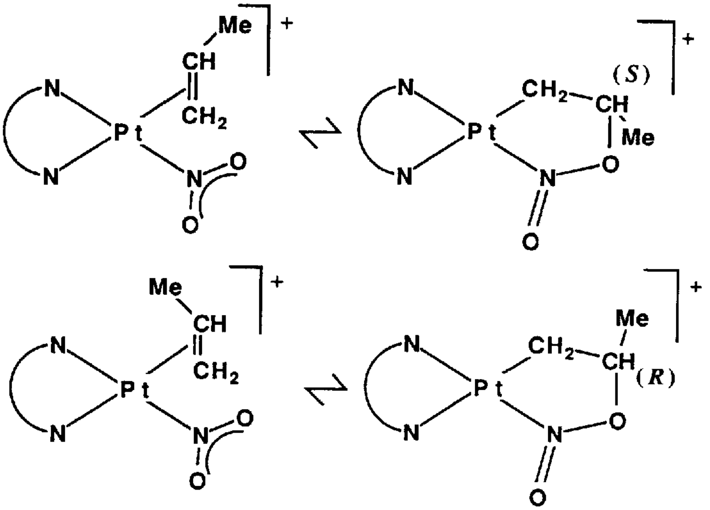
Cationic complexes with different olefins can be prepared by alkene metathesis. The chloro complex **1** reacts only with monosubstituted olefins (such as propene and styrene) while the corresponding complex in which a NO_2^- has been substituted for Cl^- ($[Pt(\eta^2\text{-}C_2H_4)(NO_2)(tmen)]^+$, **3**) reacts also with disubstituted olefins (such as *E*- and *Z*-2-butene).

The reason for the different reactivity of **1** and **3** could be either steric or electronic. The nitro group is rather small and flat and could allow easier access of the exchanging olefin; moreover, the Pt–olefin bond appears to be weaker in **3** with respect to **1** and this could also favor the exchange reaction.[20]

The nitro cationic complexes with propene and *E*-2-butene showed the existence in solution of a $\eta^2 \Leftrightarrow \eta^1$ rearrangement of the alkene caused by nucleophilic attack of one oxygen of the NO_2 group on the cis lying olefin. Evidence is based on NMR and IR data. The protons of a η^2 olefin in a square-planar geometry exhibit a $^2J_{Pt,H}$ not greater than 70 Hz. Moreover, when a methyl substituent is present, the $^3J_{Pt,H}$ is ca. 40 Hz. The complex $[Pt(E\text{-}2\text{-butene})(NO_2)(tmen)]^+$ (**4**), in CD_2Cl_2 solution, shows the presence of two isomeric species. One species has chemical shift (ppm) and J(PtH) (Hz, in parentheses) of 2.06(50) and 1.99(40) for the methyl protons of the olefin and of 5.46 (coupling not detectable for overlapping signals) and 4.98 (coupling not detectable for overlapping signals) for the vinyl protons. These data are in accord with a η^2 complex in conditions of slow rotation of the olefin.[21] The second species, which is ca. 60% of the total, shows two methyl signals at 1.69 and 1.10 ppm, only that at higher field being coupled with ^{195}Pt (40 Hz). Signals of vinyl protons were at 3.89 (negligible coupling) and 2.98 (coupling not detectable for overlapping signals) ppm, respectively. This is in accord with an η^1 complex in which only one end of the olefin is bound to platinum. A solution of the same complex, when examined in the infrared, showed two absorption bands at 1340 and 1400 cm^{-1}, characteristic of a nitro group (-NO_2), and another absorption at 1590 cm^{-1}, assignable to the N=O stretch of an alkylnitrito group (-NOOR). The analogous propene complex [Pt(propene)(NO_2)(tmen)]$^+$ (**5**), in the same solvent, has chemical shift (ppm) and J(Pt–H) (Hz, in parentheses) of 1.59(9) for the methyl protons and of 4.92 (negligible coupling), 3.23(85) and 2.9 (coupling not detectable for overlapping signals) for the vinyl protons. The ^{195}Pt coupling of 85 Hz is too big for an η^2 olefin and is close to that observed for protons on a carbon atom σ bound to platinum. The small coupling (9 Hz) of the methyl substituent indicates that this is on the β carbon (the same coupling was 40 Hz in the corresponding chloro species [Pt(η^2-propene)Cl(tmen)]). The IR spectrum in CD_2Cl_2 solution showed only a strong absorption at 1588 cm^{-1} (N=O stretch of an alkylnitrito group), while the pair at 1340 and 1400 cm^{-1} was practically absent (the latter absorptions are the strongest of the spectrum when a terminal -NO_2 is present).

These data are in accord with the formation of a metallacycle via nucleophilic addition of one oxygen of the nitro ligand onto the cis olefin. Since the addition occurs at the endo face of the olefin, only one couple of enantiomers is formed. In the case of propene the equilibrium is largely shifted to the right and only the Markovnikov type of compound is formed (Scheme 2).

A similar reaction was reported by Andrews *et al.*[22] for some palladium–nitro-alkene complexes. In that case, however, the nucleophilic attack of the oxygen of the nitro group onto the cis alkene (ethene or propene) led to a transient species which further



SCHEME 2

reacted, transferring the NO_2 moiety onto the olefin ligand. Only in the case of more complex alkenes, such as a substituted norbornene, did the complex containing the heterometallacycle become an isolable species.

ELECTROPHILICITY OF THE CATIONIC OLEFIN COMPLEXES

The cationic species under discussion are far more reactive towards nucleophiles as compared with neutral and anionic complexes, and behave like the cationic olefin complexes of other platinum group metals such as iron, ruthenium and rhodium.[23]

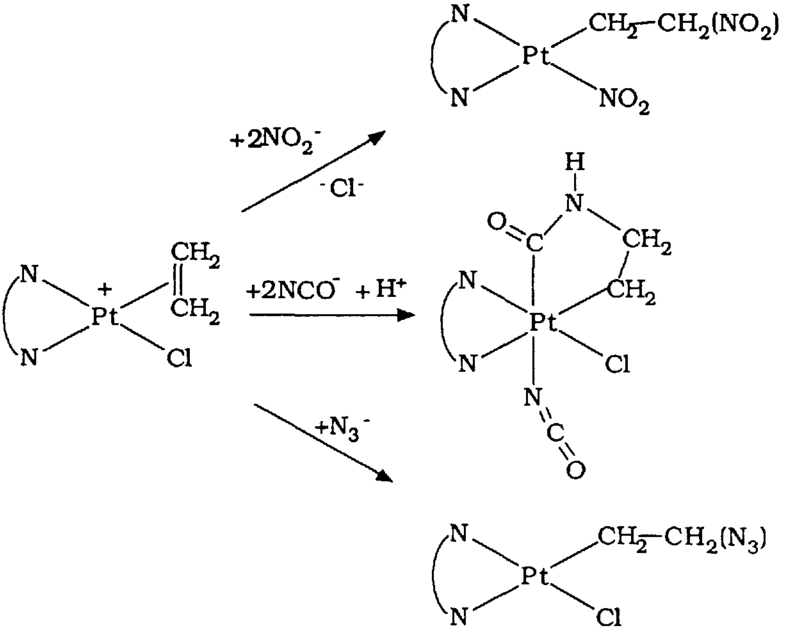
The reactivity towards amines and ammine is quite obvious, since these nucleophiles also add to olefins in neutral complexes of platinum(II).[24,25] The formation constant for the addition products is a function of the amine substituents and decreases as the number of substituents at the nitrogen atom increases.[25] The great reactivity of cationic compounds allows the formation of stable addition products even with tertiary amines, and in the particular case of tetramethylethylenediamine a dimeric complex in which two cationic units have added to the two ends of the diamine is formed. The latter species contains two quaternary ammonium groups adjacent to one another, and still it is rather stable.[26] By reaction with secondary and primary amines, and ammine, di-, tri-, and tetra-metallated ammonium ions of formula $[\{Pt(C_2H_4)Cl(tmen)\}_n(NR_{4-n})]^+$ (n = 2, 3, and 4, respectively) are formed.[27] These are the species postulated as intermediates in the reaction of polyalkylation of amines and ammine mediated by olefin complexes of transition metals.[28]

The greater stability of the Pt–C σ bond in the addition products derived from a cationic substrate could be the consequence of a more favorable electron distribution. When the nucleophile adds to a neutral substrate, the resulting addition product has a zwitterionic character, and a formal negative charge is localized on the metal. On the contrary, in the case of a cationic substrate the resulting addition product does not have any formal charge on platinum.[29]

Compound **1** also reacts with inorganic anions such as nitrite, cyanate, and azide (all of which are known to have good coordinating ability towards platinum) to give addition products as shown in Scheme 3.

It can be noted that the addition products with nitrite and cyanate ions contain two moles of nucleophile per mole of starting complex, and that these are the only products isolated irrespective to the ratio of reactants.[30]

The reaction with cyanate ion is particularly interesting, since the nucleophilic attack to the ethylene of the terminal nitrogen of the anion is followed (or accompanied) by the electrophilic addition of the central carbon to the metal, which therefore behaves as a Lewis base. The latter step is assisted by a second cyanate ion which enters the coordination sphere of platinum (formally in the oxidation state +4) and by a proton, abstracted from the solvent, which neutralizes the negative charge accumulated on the nitrogen atom (Fig. 2). This reaction shows the potential electrophilic character of the central carbon of the NCO^- anion, which is isoelectronic and isostructural with the CO_2 molecule. Reagents of this type should therefore be able to give bifunctional reactions with complexes containing an electron-rich transition metal and



SCHEME 3

an acidic center close together in the same molecule, a situation which is met in the cationic substrates that are presently discussed.

The addition product with cyanate ion undergoes a thermal rearrangement leading to the formation of mono-, di- and tri-(ethylplatina)isocyanurates [ethylplatina = $CH_2CH_2PtCl(tmen)$; isocyanuric acid = 1,3,5-triazacyclohexane-2,4,6-trione]. The same compound, under mass spectrometric conditions, exhibits two decomposition patterns corresponding to the loss of the N-ethylenecarbamoyl group, either alone or simultaneously with the cyanate ion. Therefore, both the thermal and MS experiments are consistent with a reaction pathway in which an intramolecular reductive elimination is the first step.[31]

Cationic complexes such as **1** can also add oxoanions like OH^-, RO^-, and $RCOO^-$.[32] Addition of CH_3O^- and $C_2H_5O^-$ can be performed in an undried alcoholic medium made basic for KOH. Addition of OH^- takes place in water at basic pH. In the latter

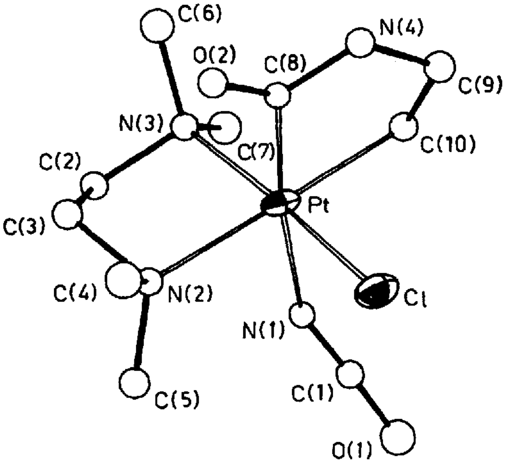


FIGURE 2 Molecular structure of the $[\overline{\mathrm{Pt}(\mathrm{CH_2CH_2NHC}}{=}\mathrm{O})\mathrm{Cl}(\mathrm{NCO})(\mathrm{tmen})]$ complex.

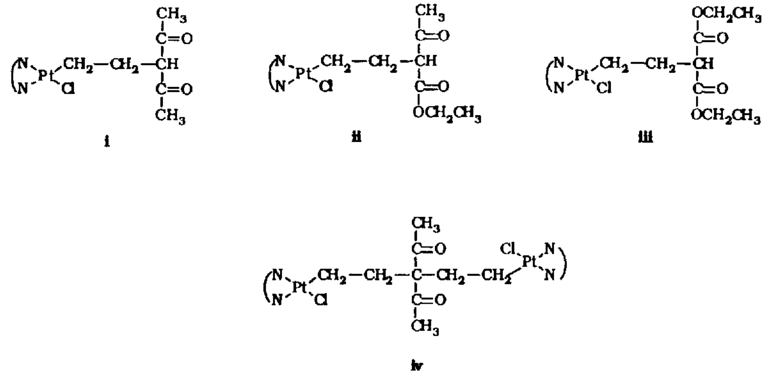
case the addition product, either in non-protic solvents or (more slowly) in the solid state, spontaneously undergoes a condensation reaction with formation of a dimeric species bearing an ether function. The latter species can be obtained directly by reaction of **1** dissolved in chlorinated solvents with powdered KOH.

Compound **1** also reacts with carboxylate anions in water solutions to give an addition compound containing an ester function. This compound is rather labile and in the solid state is reversed to the starting species (IR data). Aged samples, however, when dissolved in chlorinated solvents, restore the ester function (^{1}H NMR data).[32]

The most stable among oxo species appears to be that containing CH_3O^-; all other complexes when dissolved in methanol are transformed into the methoxo compound but not vice versa.

We wish to remark that neutral monoolefin complexes of platinum(II) react with oxoanions to give displacement instead of addition products.[33]

The cationic compounds also react with carbon nucleophiles (such as the anions of acetylacetone, ethylacetoacetate, and diethylmalonate) to give the addition products.[34] A list of isolated compounds is reported in Scheme 4. The addition compound with

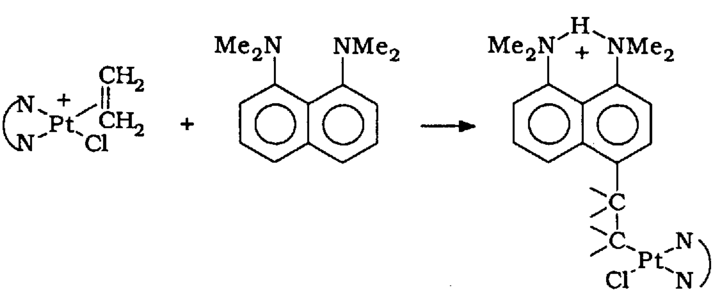


SCHEME 4

acetylacetonate (**i** in Scheme 4) exhibits a keto-enol tautomerism; the interconversion rate is quite slow and allows the separation of the pure forms. The same compound reacts further with a second molecule of the complex to give a disubstituted product (**iv** in Scheme 4) in which two ethylplatina units have taken the place of the two protons initially present on the nucleophilic carbon. Also, neutral diolefin complexes of platinum react with carbanions to give the addition product; the reaction, however, requires more severe experimental conditions and the addition product is more easily reversed to the starting reagents.[35]

The electrophilicity of a cationic complex such as **1** is further evidenced by the reaction with 1,8-bisdimethylaminonaphthalene (the so-called proton sponge) (Scheme 5).

The reaction can be described as an electrophilic substitution of an aromatic ring proton. Aromatic amines have a tendency to behave as weak carbon bases because of the strong resonance interaction between the aminic group and the aromatic ring system, but this type of effect should be considerably reduced in the proton sponge, owing to steric reasons (the dimethylamino groups cannot be brought into the plane of the aromatic rings). Nevertheless the reaction of the proton sponge with **1** may suggest that, at least in aprotic solvents, a zwitterionic form, having a proton shared by the two aminic functions and a naked carbanion in the *para* position, is present.[36]



SCHEME 5

The reactivity of cationic complexes with propene, styrene, and 2-butene is quite similar to that of the compounds with ethylene, the only difference being a reduced capability to react with weak nucleophiles.[20,36] The presence of substituents seems, however, to reduce the electrophilicity of the alkene, either for electronic or steric reasons.

In the case of monosubstituted olefins the addition reaction occurs with a high degree of regioselectivity according to Markovnikov's rule. Steric bulk, on the metal coordination sphere or on the entering nucleophile, increases the yield of the anti-Markovnikov type of adduct. Kinetic control of the addition reaction has been observed in some cases. Rearrangement of the initially formed anti-Markovnikov product into the thermodynamically more favored Markovnikov type of compound has also been observed.

The yield of the anti-Markovnikov addition product is considerably smaller in the case of the nitro complexes as compared with the chloro ones. This is in accord with a smaller crowding around the metal in the nitro complex as suggested previously.

The data presented here emphasize the great electrophilicity of the olefin in cationic substrates. This is in complete accord with the results of a theoretical investigation performed by Eisenstein and Hoffmann which has led to the following conclusions: (i) An electrostatic attraction between the organometallic complex and the nucleophile is an important factor in promoting the reaction. (ii) A smaller electron donation from the metal to the π^* orbital of the olefin leaves this orbital freer to accept an extra electron pair from the incoming nucleophile. (iii) Slippage of the metal fragment along the olefin axis, while the nucleophile is approaching, promotes the addition reaction which, otherwise, would be disfavored with respect to the uncomplexed olefin. In conclusion, the weaker the metal–olefin interaction in the symmetrical η^2 complex (this is the case of cationic complexes), the stronger it becomes in the η^1 slipped form.[37]

STRUCTURAL FEATURES OF THE ADDITION PRODUCTS

Proton NMR spectroscopy is very useful for elucidating structural details of platinum complexes, particularly the chemical shifts and ^{195}Pt coupling constants of protons which are in close proximity to the metal.

The protons of a methylene group in the α position with respect to platinum are always located between 1 and 2 ppm downfield TMS. The presence of a chiral center in the β position can cause a diastereotopic splitting of these protons as large as 1 ppm. If the chiral center is in the γ position with respect to the metal, the diastereotopic splitting of the methylene group in the α position can be greater than that of the methylene group in the β position although the latter is nearer to the chiral center.[32]

The coupling with ^{195}Pt nucleus of the α-methylene protons ($^2J_{PtH} \approx 90$ Hz) is greater than that observed for the protons of an η^2-coordinated olefin ($^2J_{PtH} \approx 60$ Hz).

The $^3J_{Pt,H}$ can range from a few up to 50 Hz. For a proton on the β carbon of the monohapto olefin the $^3J_{PtH}$ is usually small (10 Hz or less); on the contrary, for a proton of a methyl substituent on the α carbon the $^3J_{PtH}$ is rather large (up to 50 Hz). In the latter case a through-space interaction between the methyl and the metal could account for the greater coupling.

It is also worth noting that the NMe_2 groups of the tmen ligand in the compounds $[Pt(\eta^1\text{-}CH_2CH_2Nu)Cl(tmen)]$ show two very different values of $^3J_{PtH}$ (15 and 50 Hz, respectively). The smaller coupling is to be assigned to the NMe_2 group trans to the σ carbon (the trans-labilizing ability of an alkyl group, being greater than that of a chloride ligand, causes a weakening and lengthening of the Pt–N bond opposite to it and a reduction of the magnetic interaction of the methyl protons with the platinum nucleus). This type of effect is not observed in the compounds containing the η^2 olefin, $[Pt(\eta^2\text{-olefin})Cl(tmen)]^+$, where the values of $^3J_{PtH}$ of the NMe_2 groups of the diamine are not significantly different, although one is trans to the olefin and the other trans to a chloride ligand.

REACTION OF THE ADDITION PRODUCTS WITH ACIDS

Two reaction pathways are observed in the reaction of the addition products with acids: either the addition reaction is reversed (the nucleophile is protonated and the parent ionic complex is restored) or the platinum-to-carbon σ bond is cleaved (and the nucleophile is alkylated). In the latter case, depending upon the coordinating ability of the acid anion, the platinum is recovered either as a neutral complex (with a coordinated acid anion) or as a cationic species (with the acid anion as counter ion and the coordination sphere completed by dimerization or addition of a molecule of solvent).

When the nucleophile is an inorganic anion or an oxoanion, the reaction with acids always reverses the addition reaction. In the case of amines as nucleophiles, both reversal of the addition reaction and cleavage of the platinum–carbon bond are observed. Finally, in the case of carbon nucleophiles, the cleavage of the platinum–carbon bond is largely preferred.

The protolytic behavior of a series of platinum complexes obtained by reaction of **1** with ammonia, primary, secondary, and tertiary amines (these species all contained a quarternized nitrogen having one more metal residues than the number of hydrogen atoms in the starting amine) was studied.[38] It was found that on increasing the stability of the addition product, and hence the stability of the C–N bond, the cleavage of the Pt–C bond became more important. The C–N bond cleavage is an intramolecular process and it does not depend upon the concentration of acid or the shielding of the reaction center. In contrast, the Pt–C bond cleavage is an intermolecular process, and its rate is not only dependent upon the acid concentration but also very sensitive to the shielding of the reaction center.

In the addition compounds of **1** with carbon nucleophiles, the Pt–C cleavage is the unique reaction pattern. The yield of alkylated product becomes smaller in the case of complexes containing a substituted olefin in place of ethylene. Also, the substitution of a nitrite for chloride results in a lower yield of alkylated product.

CONCLUSIONS

The platinum–olefin bond can also be a stable interaction in the presence of a positive charge on the complex molecule. The cationic character of the complexed species confers an interesting reactivity on the coordinated alkene, and complexes of this type can be used for the functionalization by several nucleophiles. Some general features concerned with the electron distribution and bonding, the structural and conformational preferences, the reaction mechanisms and reactivity have been elucidated.

References

1. J. Chatt and L. A. Duncanson, J. Chem. Soc. 2939 (1953). M. J. S. Dewar, Bull. Soc. Chim. Franc. **18**, C71 (1951). M. J. S. Dewar, Annu. Rep. Prog. Chem. **48**, 112 (1951).
2. M. J. S. Dewar and G. P. Ford, J. Am. Chem. Soc. **101**, 783 (1979).
3. F. R. Hartley, Chem. Rev. **69**, 799 (1969).
4. M. H. Chisholm and H. C. Clark, Inorg. Chem. **12**, 991 (1973).
5. T.-H. Chang and J. I. Zink, J. Am. Chem. Soc. **106**, 287 (1984).
6. L. Cattalini, F. Gasparrini, L. Maresca and G. Natile, J. Chem. Soc., Chem. Commun. 369 (1973). L. Maresca, G. Natile and L. Cattalini, Inorg. Chim. Acta **14**, 79 (1975). L. Maresca, G. Natile, M. Calligaris, P. Delise and L. Randaccio, J. Chem. Soc., Dalton Trans. 2386 (1976).
7. F. P. Fanizzi, L. Maresca, G. Natile, M. Lanfranchi, A. M. Manotti-Lanfredi and A. Tiripicchio, Inorg. Chem. **27**, 2422 (1988). F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile, M. Lanfranchi and A. Tiripicchio, J. Chem. Soc., Dalton Trans. 1007 (1991). F. P. Fanizzi, L. Maresca, G. Natile, M. Lanfranchi, A. Tiripicchio and G. Pacchioni, J. Chem. Soc., Chem. Commun. 333 (1992).
8. G. Natile, L. Maresca, L. Cattalini, U. Belluco, P. Uguagliati and U. Croatto, Inorg. Chim. Acta **20**, 49 (1976).
9. C. Bisi-Castellani, L. Maresca and G. Natile, Inorg. Chim. Acta **89**, 157 (1984). L. Maresca, G. Natile and G. Rizzardi, Inorg. Chim. Acta **38**, 137 (1980).
10. G. Annibale, L. Maresca, L. Cattalini and G. Natile, J. Chem. Soc., Dalton Trans. 1 (1982).

11. L. Maresca, G. Natile and L. Cattalini, J. Chem. Soc., Dalton Trans. 1140 (1979).
12. L. E. Eliel, *Stereochemistry of Carbon Compounds* (McGraw-Hill, New York, 1962), pp. 197–202. L. E. Eliel, N. L. Allinger, S. J. Angyal and G. A. Morrison, *Conformational Analysis* (Interscience, New York, 1965).
13. L. Maresca and G. Natile, unpublished work.
14. L. Maresca, G. Natile and G. Rizzardi, Inorg. Chim. Acta **38**, 53 (1980). A. Tiripicchio, M. Tiripicchio-Camellini, L. Maresca, G. Natile and G. Rizzardi, Cryst. Struct. Comm. **8**, 689 (1979).
15. J. Hiraishi, Spectrochim. Acta **25A**, 749 (1969).
16. A. C. Blizzard and D. P. Santry, J. Am. Chem. Soc. **90**, 5749 (1968).
17. G. Gervasio, S. A. Mason, L. Maresca and G. Natile, Inorg. Chem. **25**, 2207 (1986).
18. R. A. Love, T. F. Koetzle, G. J. B. Williams, L. C. Andrews and R. Bau, Inorg. Chem. **14**, 2653 (1975).
19. J. A. K. Howard, J. L. Spencer and S. A. Mason, Proc. R. Soc. London, Ser. A **386**, 145 (1983).
20. F. P. Fanizzi, L. Maresca, G. Natile and C. Pacifico, Gazz. Chim. Ital., in press.
21. C. E. Holloway, G. Hulley, B. F. G. Johnson and J. Lewis, J. Chem. Soc. (A) 53 (1969).
22. M. A. Andrews, T. C.-T. Chang, C.-W. F. Cheng, T. J. Emge, K. P. Kelly and T. F. Koetzle, J. Am. Chem. Soc. **106**, 5913 (1984).
23. S. G. Davies, M. L. H. Green and D. M. P. Mingos, Tetrahedron **34**, 3047 (1978). T. C. T. Chang, T. S. Coolbaugh, B. M. Foxman, M. Rosenblum, N. Simms and C. Stockman, Organometallics **6**, 2394 (1987). P. J. Lennon, A. Rosan, M. Rosenblum, J. Tancrede and P. Waterman, J. Am. Chem. Soc. **102**, 7033 (1980). H. Werner, R. Feser and R. Werner, J. Organomet. Chem. **181**, C7 (1979).
24. P. D. Kaplan, P. Schmidt and M. Orchin, J. Am. Chem. Soc. **90**, 4175 (1968). R. Palumbo, A. De Renzi, A. Panunzi and G. Paiaro, J. Am. Chem. Soc. **91**, 3879 (1969). G. Natile, L. Maresca and L. Cattalini, J. Chem. Soc., Dalton Trans. 651 (1977).
25. D. Hollings, M. Green and D. V. Claridge, J. Organomet. Chem. **54**, 399 (1973).
26. L. Maresca, G. Natile, A. Tiripicchio, M. Tiripicchio-Camellini and G. Rizzardi, Inorg. Chim. Acta **37**, L545 (1979).
27. G. Annibale, L. Maresca, G. Natile, A. Tiripicchio and M. Tiripicchio-Camellini, J. Chem. Soc., Dalton Trans. 1587 (1982). M. Lanfranchi, A. Tiripicchio, L. Maresca and G. Natile, Cryst. Struct. Commun. **11**, 343 (1982).
28. A. De Renzi, G. Paiaro, A. Panunzi and L. Paolillo, Gazz. Chim. Ital. **102**, 281 (1972).
29. G. Natile, J. Chem. Soc., Chem. Commun. 654 (1978).
30. L. Maresca, G. Natile, A. M. Manotti-Lanfredi and A. Tiripicchio, J. Am. Chem. Soc. **104**, 7661 (1982). L. Maresca and G. Natile, J. Chem. Soc., Chem. Commun. 40 (1983).
31. L. Maresca, G. Natile, S. Pucci, B. Pelli and P. Traldi, Gazz. Chim. Ital. **119**, 301 (1989).
32. F. P. Fanizzi, F. P. Intini, L. Maresca, G. Natile and F. Gasparrini, J. Chem. Soc., Dalton Trans. 1019 (1990).
33. F. R. Hartley and J. J. Perié, Nature (London) **256**, 636 (1975).

34. F. P. Fanizzi, F. P. Intini, L. Maresca and G. Natile, J. Chem. Soc., Dalton Trans. 309 (1992).
35. H. Takahashi and J. Tsuji, J. Am. Chem. Soc. **90**, 2387 (1968). J. K. Stille and D. B. Fox, J. Am. Chem. Soc. **92**, 1274 (1970). B. F. G. Johnson, J. Lewis and D. A. White, J. Chem. Soc. (A) 1738 (1970).
36. L. Maresca, G. Natile and F. P. Fanizzi, J. Chem. Soc., Dalton Trans. 1867 (1992).
37. O. Eisenstein and R. Hoffmann, J. Am. Chem. Soc. **103**, 4308 (1981).
38. L. Maresca and G. Natile, J. Chem. Soc., Dalton Trans. 1903 (1982).