Journal of Organometallic Chemistry, 341 (1988) 549–557
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Theoretical study of the catalytic activity of platinum(II) and palladium(II) complexes in *cis–trans* isomerisations of alkenes *

Robert Ponec and Roman Řeřicha*
Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, CS-165 02 Prague 6-Suchdol (Czechoslovakia)

(Received September 15th, 1987)

Abstract

On the basis of an EHT model study of Pt^{II} and Pd^{II} complexes, it has been shown that the coordination of ethene to the MCl_3^- species results in a lowering of the C=C torsional barrier by 9% in Pt^{II} complexes and 31% in Pd^{II} complexes, in comparison with free C_2H_4 molecule. The larger decrease of this barrier for palladium suggests that Pd^{II} acts as a more efficient "C=C bond softening agent" than Pt^{II}. This conclusion is consistent with the observed *cis–trans* isomerisation activity of Li_2PdCl_4 in acidified solutions of *cis*- or *trans*-2-butene.

Introduction

It is known that K_2PtCl_4 in aqueous solutions at room temperature reacts with internal alkenes to form stable Zeise salt or neutral Zeise dimer complexes with retention of the original *cis* or *trans* configuration of the alkene [1,2]. The *cis–trans* isomerisations in this case require more drastic reaction conditions [3].

On the other hand, for the analogous Pd^{II} compounds the isomerisation reactions predominate over the formation of stable alkenic complexes [3,4]. From a catalysis viewpoint, there is remarkable difference between Pt^{II} and Pd^{II} complexes despite the fact that in both cases the transition element ion is characterised by the same low-spin d^8 configuration of the valence electrons.

Free alkene *cis–trans* isomerisations can be brought about by thermal initiation [5], pressure shock waves [6], and photosensitisation by UV [7] or IR [8] radiation. The *cis–trans* isomerisation of free alkene is governed by the height and the shape of the barrier for C=C torsion [7]. For simple alkenes such as 1,2-dideuteroethene or

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* Dedicated to Professor C. Eaborn on the occasion of his 65th birthday.

0022-328X/88/$03.50

2-butenes, this barrier is [9] roughly 60–65 kcal/mol which makes thermal isomerisation difficult.

This isomerisation is facilitated after photoexcitation of the molecule, in which the removal of one electron from the π orbital destroys the planarity of the π system of the C=C bond and so rotation of the terminal groups becomes less hindered [7]. Because of remarkable similarities which are frequently observed between electronic excitation and catalytic action of transition elements [10], it is probable that the C=C torsional barrier in some alkenic complexes may be analogously lowered by the so-called chemical pseudoexcitation [11]. The corresponding complexes may then display some catalytic activity in *cis-trans* isomerisations of alkenes.

The aim of this study is to estimate, on the basis of simple quantum chemical calculations, the magnitude of the change of the C=C torsional barrier in Zeise anion alkenic complexes of Pt^{II} and Pd^{II} and further to elucidate the observed difference in the catalytic activity of Pt^{II} and Pd^{II} complexes.

Calculations

All calculations were carried out by use of the standard EHT method [12] (program ICON 8) using a double zeta basis for *d* orbitals of the transition elements. The necessary parameters, taken from refs. [13,14], are collected in Table 1. Calculated energies of all considered molecular species are given in Table 2. Because the geometrical structure of the complexes, except for the stable Zeise salts and the $PtCl_4^{2-}$, $PdCl_4^{2-}$ ions, is not known with certainty, we attempted to estimate it as realistically as possible on the basis of quantum chemical calculations. In carrying out these calculations, we did not use complete optimisation of geometry because of the well-known failure of the EHT method to incorporate the stretching of the bonds, which would have led to unrealistic geometries. Instead, we used a maximal combination of the results of the existing model EHT study on the Zeise

Table 1

Parameters used in EHT calculations

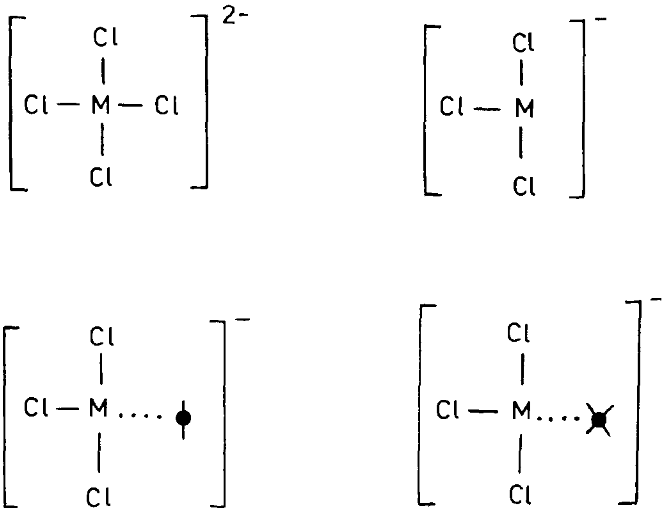
Atom	Orbital	H_{ii} (eV)	ξ_1	(ξ_2)	C_1	C_2
Pt	5*d*	−12.59	6.013	(2.696)	0.6634	0.5513
	6*s*	−9.077	2.554			
	6*p*	−5.575	2.554			
Pd	4*d*	−12.020	5.983	(2.613)	0.5535	0.6701
	5*s*	−7.32	2.190			
	5*p*	−3.45	2.152			
Cl	3*s*	−26.30	2.033			
	3*p*	−14.20	2.033			
C	2*s*	−21.40	1.625			
	2*p*	−11.40	1.625			
H	1*s*	−13.6	1.3			

Table 2

Calculated total EHT energies

Molecule	E (eV)	Note
C_2H_4 (planar)	−212.88	denoted ♦
C_2H_4 (perpendicularly twisted)	−209.19	denoted ✕.
$PtCl_4^{2-}$ (square planar)	−704.33	
$PdCl_4^{2-}$ (square planar)	−698.04	
Cl^- (isolated ion)	−150.00	
$PtCl_3^-$ (planar)	−553.75	
$PdCl_3^-$ (planar)	−547.80	
$PtCl_3 \cdots$ ethene (planar)	−767.52	$r_{M \cdots \mathrm{ethene}}$ 200 pm[a]
$PdCl_3 \cdots$ ethene (planar)	−762.24	$r_{M \cdots \mathrm{ethene}}$ 150 pm[a]
$PtCl_3 \cdots$ ethene (twisted)	−764.16	$r_{M \cdots \mathrm{ethene}}$ 200 pm
$PdCl_3 \cdots$ ethene (twisted)	−759.63	$r_{M \cdots \mathrm{ethene}}$ 175 pm

[a] For comparison, the experimental [16,17] Pt ··· ethene distance is 202 pm whereas the ab-initio calculations gave 211 pm for Pt ··· ethene and 225 pm for Pd ··· ethene [19].



Scheme 1

Table 3

Geometrical parameters used for idealised molecular structures

Parameter	Idealised value
r(Pt–Cl)	230 pm
r(Pd–Cl)	230 pm
r(C=C)	134 pm
r(C–H)	108 pm
< H–C–H	120 °
< Cl–M–Cl	90 °

anion complexes [13–15], and the available experimental data [16–18]. Using such an approach, we have limited our calculations to optimisation of the ethene-to-central ion distance, and thereby simultaneously fixed the structure of the MCl_3^- fragment and of the coordinated ethene.

For simplicity, the small deviations from the ideal perpendicular orientation of the coordinated ethene with respect to the MCl_3 plane [16] and the minor differences in lengths of individual C–H and M–Cl bonds revealed by X-ray crystallography [17] have been neglected. The corresponding idealised structures together with the necessary geometrical parameters are depicted in Scheme 1 and Table 3.

Results and discussion

It is known that the introduction of an alkene into an acidified solution of K_2PtCl_4 results in the formation of the stable complex K[(alkene)$PtCl_3$], Zeise salt or its analogues. On the other hand, in the case of Pd^{II} the situation is more complicated. Stability of the analogous alkenic complex is so low that it has been assumed to exist as only a hypothetical intermediate undergoing a number of rapid consecutive transformations which are dependent on reaction conditions [3]. Of these the most usual is the hydrolysis leading to the hydroxo complex K[(alkene)$PdCl_2$(OH)] which plays a crucial role in the industrially important Wacker process [19–23]. Suppressing these hydrolytic reactions by appropriate reaction conditions, transformation of the primary Pd Zeise's salt analogue leads either to the formation of binuclear Zeise dimer complexes, or in an excess of Cl^- ions to the *cis–trans* isomerisation of alkenes. Since there is up to now no experimental information about the details of the mechanism of these transformations, any attempt to rationalise these must be restricted to different, more or less hypothetical, models. Such theoretical insight into the observed differences in the behaviour of the structurally related Pt^{II} and Pd^{II} complexes, especially from the point of view of their catalytic activity in *cis–trans* isomerisations, is a subject of the present paper.

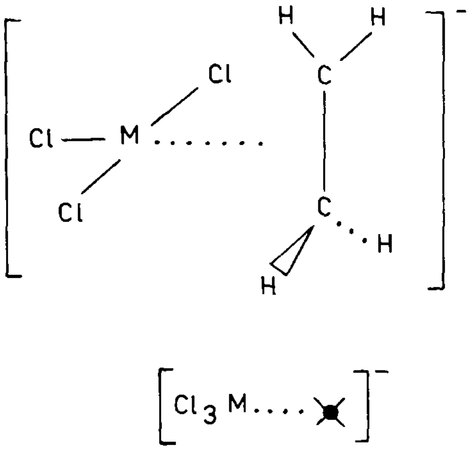
Among the many alternatives considered for the mechanism of *cis–trans* isomerisation, the most likely is that originating from the expected analogous behaviour of Pt^{II} and Pd^{II} complexes and requiring the isomerisation to proceed via the primary formation of the Zeise anion complexes.

$$[MCl_4]^{2-} + \textit{cis}\text{-alkene} \rightleftharpoons \underset{(I)}{[(\textit{cis}\text{-alkene})MCl_3]^-} + Cl^-$$

$$\rightleftharpoons \underset{(II)}{[(\textit{trans}\text{-alkene})MCl_3]^-} + Cl^- \rightleftharpoons [MCl_4]^{2-} + \textit{trans}\text{-alkene}$$

Scheme 2

This mechanism can be described as a hypothetical reaction (Scheme 2), the key step of which is the isomerization of the complexes I $\rightleftharpoons$ II. The readiness with which this isomerization takes place, and consequently the difference in the chemistries of the corresponding Pt^{II} and Pd^{II} complexes, is then governed to a considerable extent



(III)

Scheme 3

by their stabilities. Whereas in the case of Pt^{II} the reaction stops at the Zeise's anion stage, the isomerization of the alkene ligand in the Pd^{II} analogue takes place under conditions which suppress the above-mentioned complicating side reactions, if the corresponding C=C torsional barrier is sufficiently lowered. The height of this barrier is given by the energetic difference between that of structure I or II and that of structure III which plays the role of the corresponding transition state. For example, ethene is coordinated to the transition element species in a perpendicularly twisted form with the local point symmetry D_{2d} (Scheme 3).

Quantum chemical determination of the energies of these important structures thus opens up the possibility of theoretical analysis of the factors causing the observed differences in the properties and the catalytic activity of alkenic complexes of Pt^{II} and Pd^{II}.

In light of the above discussion, the most important features that offer a certain measure of the reliability of the proposed reaction scheme (Scheme 2), is the relative stability of the Pt^{II} and Pd^{II} complexes of the type I or II. Within the framework of our model, this stability can be simply estimated as the energetic difference ΔE between the corresponding complex and the starting reactants (eq. 1):

$$\Delta E = E(\mathrm{MCl_3} \cdots \mathrm{ethene})^- + E(\mathrm{Cl^-}) - E(\mathrm{MCl_4}^{2-}) - E(\mathrm{ethene}) \qquad (1)$$

In contrast to the observed differences in the chemistry of alkenic complexes of Pt^{II} and Pd^{II}, the values of ΔE calculated with the aid of total energies collected in Table 2, surprisingly suggest a greater stability of Pd^{II} compared with Pt^{II} complexes. As can be seen from Fig. 1, this difference is due to the greater stability of the Pd complex with respect to the hypothetical dissociation to give MCl_3 anion and the free alkene. Irrespective of the simplicity of our model, which does not include the solvating influence of the reaction medium and does not take into account the fact that the geometries used probably do not correspond to the true equilibrium geometries, we believe that the apparent discrepancy of the calculated and experimental results does not imply complete failure of the EHT method but

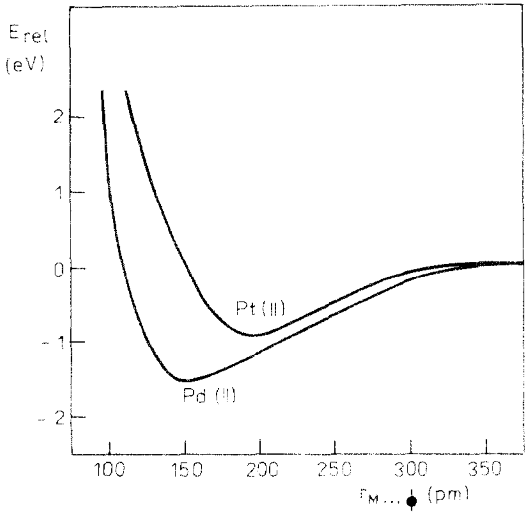
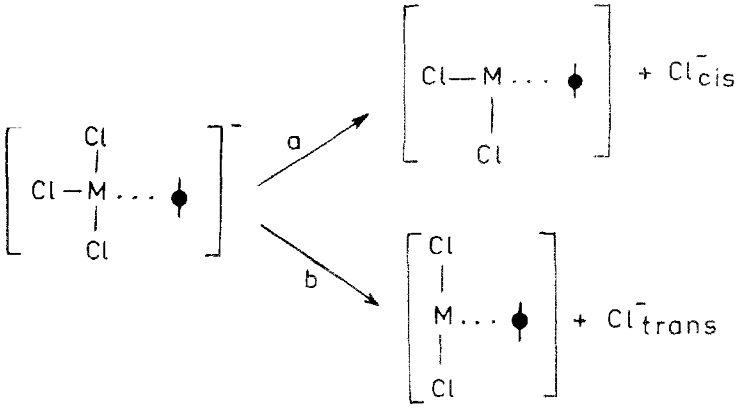


Fig. 1. The calculated potential curves of [Cl$_3$M ··· ethene]$^-$ anions, M = Pd^{II} or Pt^{II}, for planar C$_2$H$_4$ which is perpendicular to the MCl$_3$ plane.

rather it suggests that our original picture of the stability problem was probably oversimplified. It appears, that the adequate discussion of the stability problem cannot be based only on the ΔE values without considering some additional factors. The most important of these seems to be the tendency of chloride ligands to dissociate from the original Zeise anion complexes. This was clearly confirmed by the calculations. Calculated values of the corresponding "dissociation energies" for the hypothetical process outlined in Scheme 4 are given in Table 4. The tendency to dissociation in the case of palladium is so remarkable that under the hypothetical conditions of gas-phase reaction, the *cis*-chloride ligand would dissociate spontaneously. In real situations this dissociating ability will certainly be influenced by the solvating effect of the reaction medium but we believe that this change does not distort too much the qualitative picture suggested by our simple EHT model. In



Scheme 4

Table 4

Calculated EHT "Dissociation energies" of *cis*- or *trans*-chloride ligands in $(C_2H_4)MCl_3^-$ anions

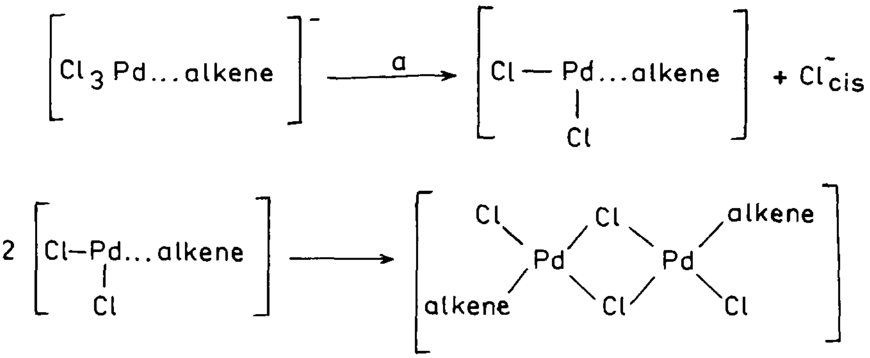
Molecule	ΔE (eV)	Note (see Scheme 4)
$PdCl_3 \cdots$ ethene [a]	−0.431	process a (*cis*)
$PdCl_3 \cdots$ ethene [a]	+0.090	process b (*trans*)
$PtCl_3 \cdots$ ethene [a]	+0.494	process a (*cis*)
$PtCl_3 \cdots$ ethene [a]	+0.332	process b (*trans*)

[a] Always planar C_2H_4 ligand.

other words, we believe that the precision of the model can manifest itself in terms of more or less additive shifts of the absolute values of the corresponding dissociation energies without altering their relative order. Justification for this intuitive belief is given by the fact that the conclusions of the simple EHT model can be naturally incorporated into the context of known experimental facts about the chemistry of the alkenic complexes of Pt^{II} and Pd^{II}.

Thus the formation of binuclear Pd^{II} complexes of the Zeise type dimers can be simply elucidated as a consecutive process which stabilises the two monomeric fragments primarily formed by the dissociation of *cis*-chloride ligands from the original complex (Scheme 5). Similarly, the easier dissociation of *trans*-chloride ligand from the Pd analogue of the Zeise anion (Table 4) could account for the tendency to undergo the (S_N1) hydrolysis leading to the hydroxo complex $[(alkene)PdCl_2(OH)]^-$ in the Wacker process. The instability of the Zeise anion Pd analogue with respect to the dissociation of chloride ligands is moreover consistent with the fact, that for *cis–trans* isomerisation to occur it is necessary to work with solutions containing an excess of Cl^- ions. Their action, consisting in shifting the above dissociation equilibrium, thus formally closes the reaction channels leading to the formation of dimers or to hydrolysis, which leaves only the *cis–trans* isomerisation of the coordinated alkene (Fig. 2).

If such a picture of the mechanism of the *cis–trans* isomerisation is correct, the higher catalytic activity of the Pd^{II} complex should be reflected in the level of calculated energy values by the more important decrease of the barrier for the C=C bond torsion than in the case of Pt^{II}. The height of this barrier can, in the sense of



Scheme 5

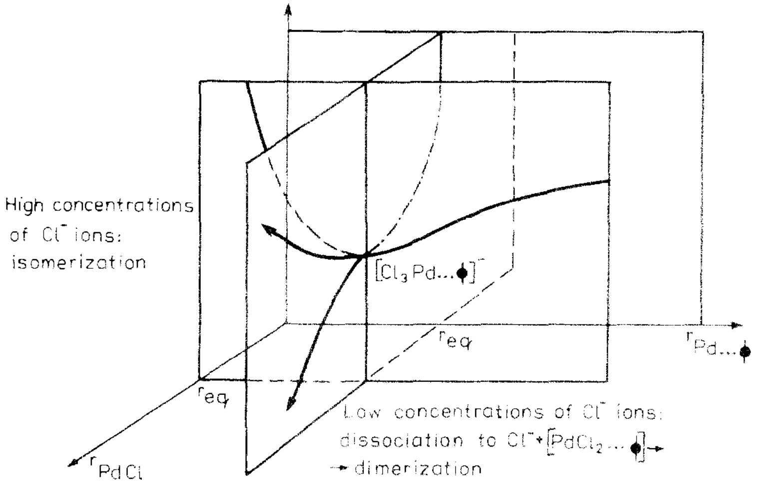


Fig. 2. Radial slices through the potential surface of the $[\mathrm{Cl} \cdots \mathrm{PdCl}_2 \cdots \mathrm{C}_2\mathrm{H}_4]^-$ anion.

the above discussion, be approximated to the energetic difference between structure I or II and the corresponding transition state III in which the alkene is coordinated in the perpendicularly twisted form. Keeping in mind the fact that in the framework of EHT method used, even complete optimisation of geometry probably would not lead to sufficiently reliable structures, in the estimation the energies of this hypothetical structure we have restricted ourselves again only to the determination of the (alkene ··· central ion) distance, i.e. with the remaining geometrical degrees of freedom fixed. In using this simplified model, we believe that even if such procedure overestimates the values of the corresponding torsional barriers, the validity of qualitative conclusions – based on the comparison of the relative changes against the molecule of free alkene – remains practically unchanged.

The calculated values of the C=C torsional barriers collected in Table 5 thus confirm the validity of the above theoretical considerations in that there was a more remarkable decrease in the barrier for $\mathrm{Pd^{II}}$ analogue (more than 30%) than for the original Zeise anion (about 9%). This result consistently complements the mosaic of known experimental facts about the chemistry of alkenic complexes of $\mathrm{Pt^{II}}$ and $\mathrm{Pd^{II}}$. It naturally accounts for the observed difference in the catalytic activity of both transition elements through the so-called C=C bond softening [24,25] or through the mutual chemical pseudoexcitation of the alkenic ligand and the transition element species due to the multiple coordination bond between them.

Table 5

Calculated EHT C=C torsional barriers for free and coordinated ethene in Zeise anion type complexes

Molecule	ΔE (eV)	%
Free ethene	3.69	100
$[\mathrm{PtCl}_3 \cdots \phi]^-$	3.36	91
$[\mathrm{PdCl}_3 \cdots \phi]^-$	2.61	69

Acknowledgement

The authors thank Dr. Z. Havlas (Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague) for providing them with a copy of the original program from the laboratory of Prof. R. Hoffmann (Cornell University).

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