ture, the combination of Cu and Ba allows the conduction band to have a large oxygen component with strong coupling between metal *d* electrons and oxygen displacement[17]. Since the fluorine atom has lower $2p$ level in energy, it deteriorates the conduction band due to weaker overlap between Cu *d* orbital and F $2p$ orbitals. Therefore, Tc decreases with the substitution of fluorine.

In summary, the incorporation of fluorine atom into $HoBa_2Cu_3O_{7-x}$ results in the increase of the (001) peaks in the XRD spectra of which the reason is not clarified, the decrease of the unit cell volume, the increase of the grain size, and the decrease of Tc due to the perturbation of electron.

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Oxidative Addition Reaction of Mono(ary)cyanoplatinum(II) Complex with Two Amino Ligands with the Dihalogens

Jaejung Ko*, **Moonsik Kim**, **Seho Kim**, and **Yookil Shin**

Department of Chemical Education, Korea National University of Education, Chungbuk 363-791

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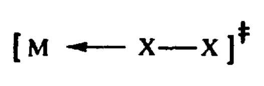
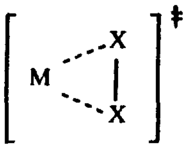
The mono(aryl)cyanoplatinum(II) complex $[Pt(CN)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ reacts with the dihalogens to yield the mono (aryl)cyanoplatinum complexes $[PtX_2(CN)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (X=Cl, Br, I). The structural configuration of the two halogen atoms for a square planar platinum complex was studied by ^{1}H-NMR spectroscopy and led to a mixture of *trans* and *cis* orientation. The *trans* orientation was found to be more stable in energy (1.33 kcal/mol) than the *cis* orientation by means of Extended Hückel calculations. On the base of a combination of the analysis of ^{1}H-NMR, ^{13}C-NMR spectra and computational calculations it is assumed that the intermediate consists of an initial attack in the linear transition state, leading to the S_N2 type mechanism.

Introduction

Oxidative addition reaction is of remarkable importance, since nearly all catalytic and many useful stoichiometric processes involve oxidative addition reation[1]. Recently, Rund and coworkers[2] reported the oxidative addition reaction of dihalogens to $(TBA)_2Pt(CN)_4$, leading to *trans* $(TBA)_2Pt(CN)_4X_2$ products. They suggested that the oxidative addition reactions presumably proceed with linear transition state (a) rather than three centered transition state (b), as shown below, leading to *trans*-X_2 arrangements in the product. In recent years, Koten and coworkers[3] also reported the oxidative addition reactions of dihalogens to square planar platinum (II) complexes. They also concluded that when steric factors preve-



(a)



(b)

nted this configuration or when the trans-X_2 product was thermodynamically unstable, *cis*-X_2 products were found. In connection with the oxidative addition reaction, we[4] carried out computational calculations for the oxidative addition reaction of Cl_2 to a square planar compound $(TBA)_2Pt(CN)_4$ in order to clarifty likely mechanisms. The calculation shows us that the energy differnece between linear transition state (a) and three centered transitions state (b) is 6.99 kcal/mol, the linear transitions state being more stable than three centered transition state. In order to test above observations and the calculations, we have the impetus to synthesize model complex and carry out the oxidative addition reactions. We chose $[Pt(CN)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)](I)$ as the model complex because the complex I is square planar, sterically small, and has a cyano group which is quite sensitive for the substituents.

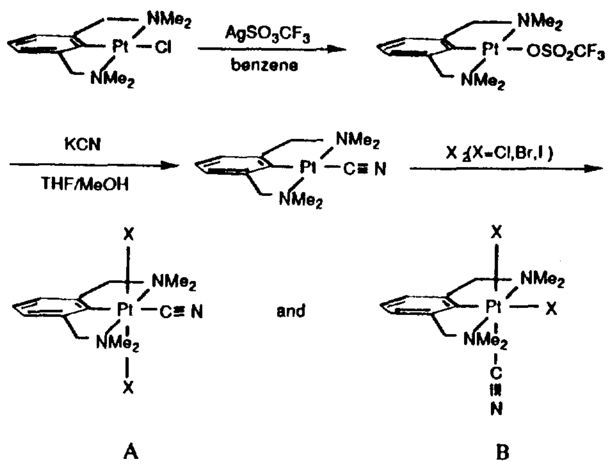
In this paper, we describe the oxidative addition reactions of the platinum compound $[Pt(CN)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ with the dihalogens as well as computational calculations of the resulting two isomers.

Experimental

All reaction were performed in dry, oxygen- free solvents in atmospheres of N_2 and Ar. The proton NMR and ^{13}C-NMR spectra were recorded on Bruker WM-250 spectrometer. IR spectra were obtained by using a Perkin-Elmer 1310 instrument. Elemental analyses were carried out at the Basic Science Research Center. Compound of the formula $[PtCN(C_6H_3\{CH_2NMe_2\}_2\text{-o-o'})]$ was prepared as previously described[5]. AgOTf and KCN were commercially available. Starting halogen compounds Cl_2, Br_2 and I_2 were purchased from Aldrich.

Preparation of $[Pt(CN)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)](I)$. To a stirred solution of $[PtCN(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.84 g, 1.99 mmol) in 10 m*l* of benzene was added $AgSO_3CF_3$ (2.3 mmol) dropwise. The solution was stirred at room temperature for 2 hr. The solution was filtered off. To the filtrate, after concentration to 5 m*l*, was added hexane (10 m*l*). The resulting white compound $[Pt(OTf)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ was dissolved in THF (5 m*l*). To this solution was added potassium cyanide (2.42 mmol) in MeOH (5 m*l*) dropwise. The solution was stirred for 10 hr. The solvent was removed under vacuum and the residue was extracted with 40 m*l* of benzene. The white powder was recrystallized from 50 : 50 methylenedichloride/hexane. The yield was 0.42 g (49%), mp. 168-173℃. Anal. Calcd for $PtC_{13}H_{19}N_3$: C, 37.88; H, 4.65. Found: C, 37.76; H, 4.20.

Preparation of $[PtCl_2(CN)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (II). A stream of dichlorine was bubbled through a solution $[Pt(CN)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.1 g) in benzene during 3 min. After the resultant mixture was stirred for 20 min, the yellowish orange precipitate was filtered off and washed with benzene (10 m*l*) and pentane (2×5 m*l*) and dried *in vacuo*. The yield of II was 85%. mp. 116-121℃. Anal. Calcd for $PtC_{13}H_{19}N_3Cl_2$: C, 32.31; H, 3.96. Found: C, 32.65; H, 3.85.



Scheme 1

Preparation of $[PtBr_2(CN)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)](III)$. A dark red solution of bromine (0.0387 g) in benzene (5 m*l*) was added dropwise to a stirred solution of $[Pt(CN)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.1 g) in benzene (5 m*l*). After the resultant dark red mixture was stirred for 2 hr, the orange precipitate was filtered off and washed with benzene (10 m*l*) and pentane (2×5 m*l*) and dried *in vacuo*. The yield of III was 92%. mp. 162-166℃. Anal. Calcd for $PtC_{13}H_{19}N_3Br_2$: C, 27.30; H, 3.35. Found: C, 26.80; H, 3.63.

Preparation of $[PtI_2(CN)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)](IV)$. The compound $[Pt(CN)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$ (0.1 g) was dissolved in benzene (15 m*l*). To this stirred solution was added dropwise a pink solution of iodine (0.062 g) in benzene (3 m*l*). An immediated red precipitate was developed. The reaction was stirred for 1 hr. The red precipitate was filtered off and washed with benzene (10 m*l*) and pentane (2×5 m*l*) and dried in vacuo. The yield of IV was 82%. mp. 168-174℃. Anal. Calcd for $PtC_{13}H_{19}N_3I_2$: C, 23.44; H, 2.88. Found: C, 24.02; H, 2.53.

Results

The reaction of [PtCl(NCN)], $(NCN{=}C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)$, with the potassium cyanide in a molar ratio of 1 : 1.5 in THF and MeOH solution did not proceed to give that cyanoplatinum complex [PtCN(NCN)]. It was thought that the ligand Cl was strongly bound to the platinum. Therefore, we changed the ligand Cl into a weakly bound ligand OSO_2CF_3 (see Scheme 1). Reaction of the organoplatinum compound [PtCl (NCN)] with silver triflate is benzene resulted in elimination of AgCl and formation of organoplatinum triflate compound.

The hygroscopic triflate compund was obtained as the water adduct. The platinum compound has been identified by ^1H-NMR spectrum (Table 1).

The *trans* (N) configuration and inert Pt-N coordination have been retained, as deduced from the observation of platinum coupling with the CH_2NMe_2H atom[6]. A terdentate bonding mode is inferred from the difference of 210 cm^{-1} between $\nu(OSO)_{asym}$ and $\nu(OSO)_{sym}$[7]. Thus a square planar geometry around platinum will be valid for this platinum triflate. The reaction of the platinum triflate in THF with potassium cyanide gave the formation of platinum cyanide.

Table 1. ^{1}H-NMR and IR Data for the Product

Compound	ppm^a		cm^{-1}
	δCH_2 (J_{PtH})	δCH_3 (J_{PtH})	$\nu(C\equiv N)^d$
$[PtCl(C_6H_3\{CH_2NMe_2\}\text{-}2,6)]^b$	4.00(46)	3.07(38)	
$[Pt(H_2O)(C_6H_3\{CH_2NMe_2\}\text{-}2,6)]SO_3CF_3{}^b$	3.94(44)	3.14(36)	
$[Pt(CN)(C_6H_3\{CH_2NMe_2\}\text{-}2,6)]^b$	4.10(41)	3.20(37)	2095
$[Pt(CN)Cl_2(C_6H_3\{CH_2NMe_2\}\text{-}2,6)]^c$	4.44(40), 4.37(40)	3.31(36), 3.10(36)	2180, 2165
$[Pt(CN)Br_2(C_6H_3\{CH_2NMe_2\}\text{-}2,6)]^c$	4.71(38), 4.62(38)	3.70(35), 3.40(33)	2172, 2157
$[Pt(CN)I_2(C_6H_3\{CH_2NMe_2\}\text{-}2,6)]^c$	4.82(41), 4.73(41)	3.83(37), 3.54(33)	2135, 2120

^{a}Chemical shifts are relative to Me_4Si and coupling constants are in Hz; $J(^{195}Pt\text{-}H)$ values are in parantheses. ^{b}In $CDCl_3$. ^{c}In DMSO-d_6. ^{d}On pellet.

The platinum cyanide complex(I) is readily soluble in benzene, dichloromethane and chloroform. The IR spectrum of this complex showed strong absorptions at 2095 cm^{-1}, which is assigned as $\nu(C\equiv N)$ stretching mode[8] and at 2920 cm^{-1}, which is attibutable to the aliphatic C-H stretching mode. The IR spectrum also showed strong characteristic absorptions at 1502 cm^{-1}, 1460 cm^{-1}, and 1350 cm^{-1}, which are probably due to the terdentate ligand $[C_6H_3\{CH_2NMe_2\}_2\text{-}2,6]$.

The ^{1}H-NMR spectrum (250 MHz) of the terdentate NCN ligand of I shows for the aryl protons at 7.02 and 6.89 ppm with relative intensity ratio 1 : 2, which is a typical AB_2 pattern. The spectrum shows singlets at 4.12 and 3.20 ppm for the CH_2 and NMe_2 proton with sharp ^{195}Pt (I=1/2, 34% abundance) satellites of magnitude 37-41 Hz. The platinum-hydrogen coupling constants (CH_2 : J(Pt−H)=41 Hz; NMe_2 : J(Pt−H)=37 Hz) are in accordance with other planar-coordinated platinum(II) compounds[9,10] in which the N atoms are mutually *trans* bonded. From the absorption resonances it may be concluded that the two NMe_2 groups and the two CH_2 groups are enantiotopic, indicating that a mirror plane through Pt and the central axis of the terdentate ligand exists.

The cyanoplatinum(II) complex [Pt(CN)(NCN)] reacts with dihalogens to give the formation of the stable cyanoplatinum (IV) complex $[PtX_2(CN)(NCN)]$ (X=Cl, Br, I) according to Eq. (1).

$$[Pt(CN)(NCN)] \xrightarrow{X_2} [PtX_2(CN)(NCN)] \qquad (1)$$

The orange-red products are air-stable and soluble in CH_2Cl_2, slightly soluble in $CHCl_3$. The complexes have been identified by elemental analyses, IR spectroscopy, and ^{1}H-NMR spectroscopy. The spectroscopic data for the new complexes, II, III, and IV are summarized in Table 1.

The ^{1}H-NMR spectral data for all the cyanoplatinum(IV) complexes are collected in Table 1. From the ^{1}H-NMR spectra it is clear that each compound exists in two isomeric forms, according to Scheme 1. For instance, in the bromoplatinum(IV) complex $[PtBr_2(CN)(NCN)]$ the resonance pattern for the hydrogen atoms CH_2 and NMe_2 gives a very convincing evidence for the two isomeric forms. These hydrogen atoms couple with platinum as has been deduced from the observation of a singlet flanked by doublet satellites. The doublet splitting is due to coupling with platinum. The satellites, which have a 1 : 4 intensity ratio with respect to the central doublet, arise from coupling with ^{195}Pt (I=1/2, 34%: CH_2, J=38 Hz; NMe_2, J=35 Hz). For the NMe_2 hydrogen, there are two singlets at 3.45 and 3.75 ppm flanked by doublet satellites, whose ratio is 6 : 4. Similarly, for the CH_2 hydrogen, there are two singlets at 4.62 and 4.71 ppm with doublet satellites (see Figure 1).

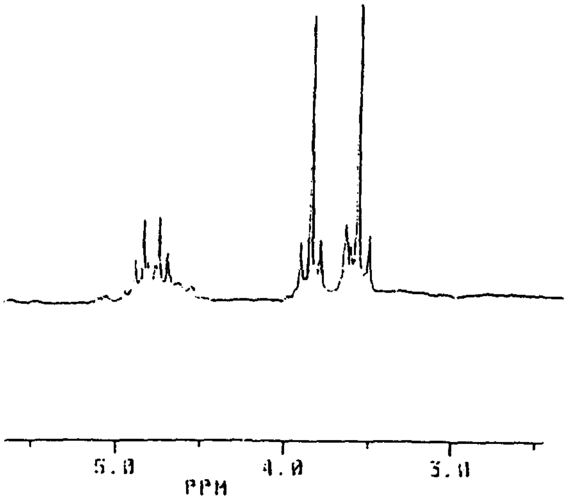


Figure 1. ^{1}H-NMR spectrum of the complex $[PtI_2(CN)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6)]$.

For the assignment of this observation, it may be assumed that two isomeric forms exist in the product. Two isomers (*trans* or *cis* configuration) for the complex can be expected to result from different orientation, as shown in Scheme 1. Although we can not exactly tell which isomeric form can be assignable for the two singlets at 3.45 and 3.75 ppm among two configurations (A or B), we tentatively assign that the singlet at 4.62 ppm may be attributable to the *trans* configuration in terms of the computational calculations. The calculation shows us that the *trans* configuration is more stable in energy (1.33 kcal/mol) than that of the *cis* form. For the three products the ratio of isomer of the trans configuration versus the *cis* one is 5.5 : 4.5 for Cl, 6 : 4 for Br, and 5.8 : 4.2 for I, respectively. For the chloroplatinum complex $[PtCl_2(CN)(NCN)]$(II) and the bromoplatinum(IV) complex $[PtBr_2(CN)(NCN)]$(IV), the pattern of the ^{1}H-NMR spectra is quite similar to that of the iodoplatinum complex(III) besides the chemical shift. In order to conform the presence of two isomeric forms, we synthesized the labelled [Pt(*CN)(NCN)] V with use of K*CN. Addition of K*CN in MeOH to a stirred THF solution of $[Pt(OTf)(C_6H_3\{CH_2NMe_2\}_2\text{-}2,6]$

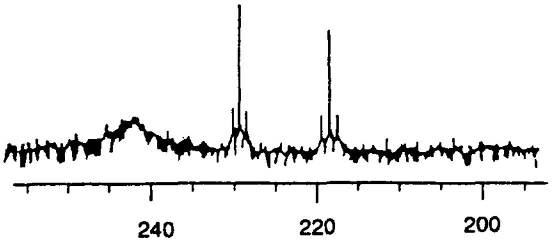


Figure 2. ^{13}C-NMR spectrum of the complex [PtI_2(*CN)(C_6H_3{CH_2NMe_2}$_2$-2,6)].

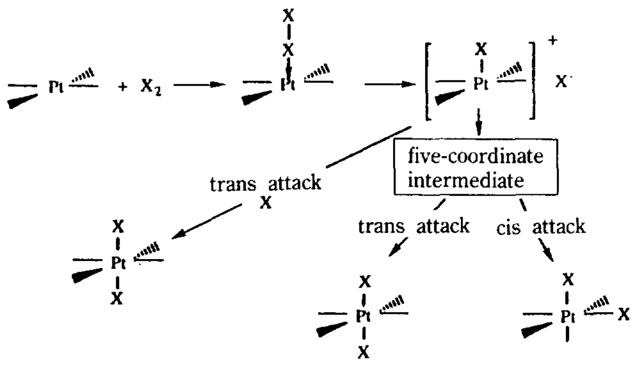
affords the stable, white cyanoplatinum(II) complex V. The complex V reacts with iodine to give the stable, red cyanoplatinum(IV) complex [PtI_2(*CN)(NCN)] VI. The ^{13}C-NMR spectrum of the labelled cyanoplatinum(IV) complex VI gave us a more conclusive result for the two isomeric forms. The cyano region of the ^{13}C-NMR spectrum of VI is shown in Figure 2. As Figure 2 shows, there are two singlets at 218.12 and 229.05 ppm flanked by doublet statellites ($J_{Pt\text{-}C}$=137.72 Hz for *trans*, $J_{Pt\text{-}C}$=158.02 Hz for *cis*). We tentatively assign that the singlet at 229.05 ppm may be attributable to the *trans* configuration. It is interesting to note that there is a substantial downfield shift of the cyano region for VI in comparison to V (198.32 ppm).

All the cyanoplantinum(IV) complexes displany single C≡N stretching mode in their IR spectra that fall within the range, *i.e.*, 2050-2250 cm^{-1}. The most interesting feature of the IR spectra of the complexes [PtX_2(CN)(NCN)] are that their CN stretching modes always occur at a higher wavenumber than the ν_{CN} exhibited by its starting material. For instance, the C≡N stretching modes observed at 2162 and 2180 cm^{-1} in the IR spectrum of [$PtCl_2$(CN)(NCN)] are higher in energy than the ν_{CN} at 2095 cm^{-1} exhibited by [Pt(CN)(NCN)]. The single ν_{CN} band of [Pt(CN)(NCN)] at 2095 cm^{-1} is replaced in IX by two bands at 2162 and 2180 cm^{-1}, shifted by 75 cm^{-1} relative to [Pt(CN)(NCN)], able assign to the cyanide vibration of *trans* configuration and the band at 2162 cm^{-1} assigned to that of *cis* configuration. This observation indicates that there is less electron density available on the metal centers for π-back-bonding to the antibonding orbitals on the cyanide ligand. It is also interesting to note that the CN stretching modes of [$PtCl_2$(CN)(NCN)] are higher in wavenumber than those exhibited by the complexes [$PtBr_2$(CN)(NCN)] and [PtI_2(CN)(NCN)]. These observations could be understood that it was attributable to the difference in electronegativity. Such a trend is in accordance with the result exhibited for the complexes $(TBA)_2PtX_2(CN)_4$ (X=Cl, Br, I)[2]. The IR spectra of these complexes also showed strong absorptions at 2900-2950 cm^{-1}, attributable to the aliphatic C-H stretching mode and characteristic absorptions at 1300-1550 cm^{-1}, which is attributable to the terdentate ligand. Although all the spectral data demonstrate the presence of two isomeric configuration, we attempted to separate the two isomers into each component with use of chromatography. However, the attempts failed due probably to the difficulty to find eluant and the low solubility. We have therefore undertaken the reaction of complex I and iodine at different temperature. For example, the reaction of complex I and iodine at 0℃ immediately occurred to give the red complex. The ^{1}H-NMR spectrum of the complex of the complex is essentially similar to that of complex IV. Therefore, it is likely that the oxidative addition reaction proceeds *via* a kinetic-controlled.

Discussion

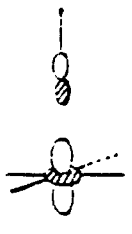
Addition of dichlorine, dibromine, and diiodine to the square-planar Pt(II) complex [Pt(CN)(NCN)] affords the stable, monomeric Pt(IV) complexes [PtX_2(CN)(NCN)] (X=Cl, Br, I). We chose the platinum complex as a model complex because the terdentate ligand (NCN=C_6H_3{CH_2NMe_2}$_2$-2,6) restricts the available coordination sites. This ligand is bonded to the platinum metal *via* a Pt-C bond and the two hard N donor atoms in a fixed *trans* position. Introduction of a cyano ligand to a Pt moiety gives an interesing system as a model complex because the C≡N stretching mode in the IR spectrum is quite sensitive for an oxidation state and substituents. Previously, Koten and coworkers[3] chose the mono(aryl)platinum complexe [PtX(CN)(NCN)] (X=Cl, Br) as model complexes for an oxidative addition reaction. They suggest that two halide atoms have *trans* configuration via a S_N2 type mechanism. This suggestion remains open to discussion because we can not tell where the two *trans* halide atoms come from, namely, the addendum or the ligand on the platinum complex. Many experimental evidences[11] are that oxidative addition reactions of dihalogens to square-planar complexes usually yield *trans*-X_2 products. On the other hand, the reaction of steric bulky organoplatinum complexes [PtR(NCN)] (R=phenyl, 4-tolyl) with I_2 provides only [$PtRI_2$(NCN)] products with *cis*-I_2 stereochemistry. However, our finding is that the oxidative addition reaction of [Pt(CN)(NCN)] with dihalogens gives a mixtrure of two configurations. In order to find the difference in energy for both configuration (A or B), we now turn to the computational calculation. This unusual observation reserve a comment for a mechanistic proposal. Accordingly, Extended Hückel calculations were carried out on the complex *trans*-$Pt(CH_3)(NH_3)_2(CN)Cl_2$ and *cis*-$Pt(CH_3)(CN)Cl_2$. The structure of the *trans*-$Pt(CH_3)(NH_3)_2(CN)Cl_2$ was found to be 1.33 kcal/mol lower in energy than that of the *cis*-$Pt(CH_3)(NH_3)_2(CN)Cl_2$. Although the calculation shows us the difference in energy for both configurations the problem sill remains as to which mechanistic pathway lead to the products. In order to obtain an idea on the mechanistic pathway, let us bring into focus on the starting complex [Pt(CN)(NCN)]. The CN stretching frequency of tree CN^- is 2080 cm^{-1}. The CN^- ion acts as a σ-donor by donating to the metal and also as a π-acceptor by accepting electrons from the metal. When π-back-bonding is dominating, the CN-stretching frequency will be decreased because the electrons enter into the antibonding $2p\pi^*$ orbital. Viewed from this fact, the CN stretching frequency of [Pt(CN)(NCN)] at 2095 cm^{-1} demonstrates that π-back-bonding occurs to give a quite strong Pt-C bond. The strong Pt-C bond of the starting material tells us that it is quite rigid for an addedum.

In the previous work, computational calculations were carried out on the linear and three-centered transition state. The energy difference between two states is 6.99 kcal/mol, the linear transition state being more stable than three cen-

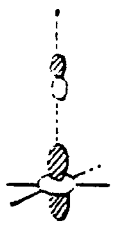


Scheme 2

tered transition state. The calculation shows us that as soon as the halogen atoms approach to a platinum metal in a bonding distance, the antibonding character between two chloride atoms is developed, the Pt-Cl antibonding orbital $2a_1$ and $4a_1$ being stabilized, as shown below.



$2a_1$



$4a_1$

In conformity to our calculation, computational studies[12] reveal that the $3\sigma_v$ orbital of I_2 is the LUMO which actually makes initial η^1-coordination of the I_2 to the d^8 metal more likely than the η^2-coordination for the concerted process. Based on these calculations, it may be assumed that the oxidative addition reactions proceed according to the Scheme 2.

The next step is the attack of the generated halide X to an intermediate. As explained previously, if the Pt-C bond is strong enough to resist any distortion, the generated halide X^- has one possibility, *i.e., trans* attack. However, if the Pt-C bond is weak enough to permit any distortion, the intermediate will be transformed into a trigonal bipyramidal or square pyramidal. The generated halide X^- has two possibility (*trans* attack or *cis* attack). It is noteworthy to note that the CN stretching mode are governed by (1) the electronegativity, (2) the oxidation state, and (3) the coordination number of the metal. Accordingly, it may be assumed that the Pt-C bond, an intermediate once formed, be weakened. If our assumption is correct, as seen in Scheme 2, the theoretical ratio for two configurations is 3 : 1. The experimental observation of product is that the the ratio of *trans* configuration to *cis* configuration is 6 : 4.

Although the theoretical and experimental ratio for both configurations is still in dispute, it is reasonable to assume that the mechanism of the oxidative addition reactions proceed as a Scheme 2.

Appendix

The Pt-C and Pt-N distances are based on the paper[13]. The extended Hückel calculations used a modified Wolfsberg-Helmholz formula. Orbital exponents and Hii's for Pt was obtained from previous work[14].

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