

Some mono- and binuclear platinacyclopentane complexes: a comparative kinetic study of reaction of ethyl iodide with platina(II)cyclopentane and dimethylplatinum(II) complexes

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Received 9 February 1998

Abstract

The reaction of $\text{Li}(\text{CH}_2)_4\text{Li}$ with $[\text{PtCl}_2(\text{SEt}_2)_2]$ yielded an unstable complex, probably $[\{\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\mu\text{-SEt}_2)\}_2]$, **1**. Complex **1** reacts with bis(diphenylphosphino)methane, dppm, and forms $[\{\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\mu\text{-dppm})\}_2]$, **2**. Complex **2** has been fully characterized using multinuclear NMR and FAB mass spectroscopies and shown to be fluxional in solution. The bright red platinacyclopentane complex $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{bpy})]$, **3**, in which $\text{bpy} = 2,2'$ bipyridyl, has been prepared by reaction of **1** with bpy. In a comparative kinetic study, it was demonstrated that at different temperatures, EtI reacted 2.2–2.6 times faster with the platina(II)cyclopentane complex **3** than with the dimethyl analogue $[\text{PtMe}_2(\text{bpy})]$. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Platinum; Metallacycle

1. Introduction

Metallacycles are of particular interest because of their possible role in catalysis [1,2]. The binuclear complexes $[\text{Pt}_2\text{Me}_4(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)_2]$, in which $\text{R} = \text{Me}$, Ph , or Et , have been synthesized and characterized [3], and it has been shown that the bulk of the substituents R in the bidentate ligands has a significant effect on the stability of mononuclear $[\text{PtMe}_2(\text{R}_2\text{PCH}_2\text{PR}_2)]$ vs dinuclear $[\text{Pt}_2\text{Me}_4(\mu\text{-R}_2\text{PCH}_2\text{PR}_2)_2]$. Thus, for $\text{R} = \text{Ph}$, both complexes could be isolated, although the mononuclear form was more stable [3].

The monomeric platinacyclopentane analogue with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, dppm, i.e. $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dppm})]$, has been prepared by treatment of $[\text{PtCl}_2(\text{dppm})]$ with 1,4 dilithiobutane [4]. In this article a

presumed dimeric platinacycle complex, $[\{\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\mu\text{-SEt}_2)\}_2]$, **1**, is synthesized and used as precursor to prepare the corresponding dimeric analogue $[\{\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\mu\text{-dppm})\}_2]$, **2**, and also the monomeric complex $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{bpy})]$, **3**, in which bpy is 2,2'-bipyridyl.

In a direct comparison, the chelating $(\text{CH}_2)_4$ ligand in some platinacyclopentane complexes has been shown to exert a significantly higher *trans*-influence than the methyl ligand [5,6]. This has been suggested to reflect the stronger donor ability of the $(\text{CH}_2)_4$ group compared to the CH_3 group [6]. In order to confirm this suggestion, we have undertaken a comparative kinetic study of the oxidative addition reaction of EtI with $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{bpy})]$, and $[\text{PtMe}_2(\text{bpy})]$. We report the result of this kinetic study as well as the synthesis and characterization of the resulting platina(IV)cyclopentane.

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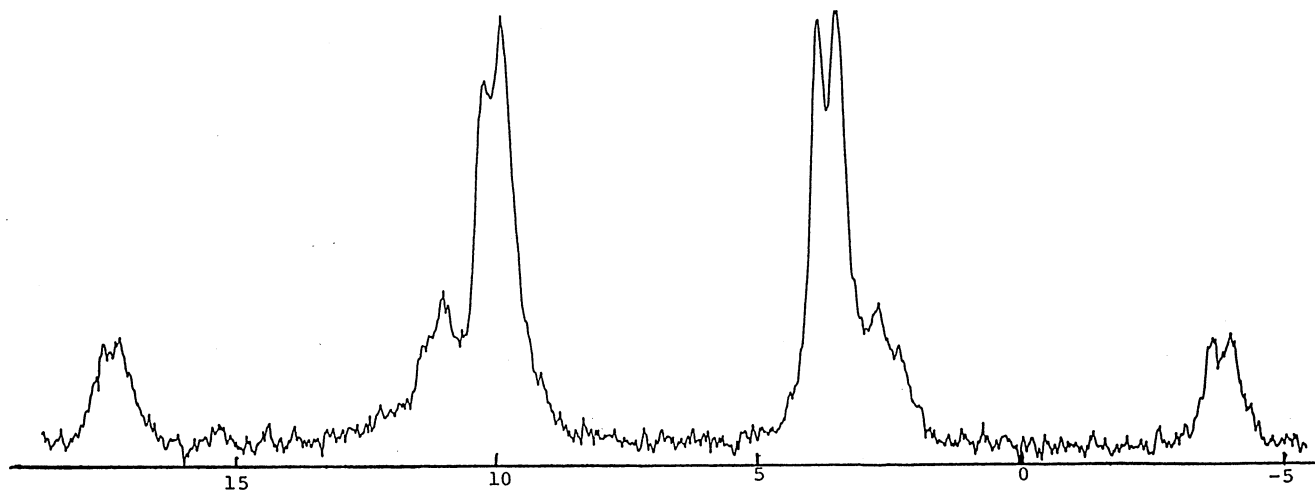
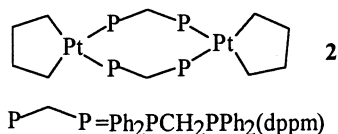


Fig. 1. ^{31}P -NMR spectrum (121 MHz) of $[\{\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\mu\text{-dppm})\}_2]$, **2**.

2. Results and discussion

2.1. Synthesis and characterization of the dimeric platinacyclopentane complexes

The complex $[\text{PtCl}_2(\text{SEt}_2)_2]$, as a mixture of *cis*- and *trans*-isomers, was prepared by the reaction of $(\text{NH}_4)_2\text{PtCl}_6$ and SEt_2 . Reaction of this complex with 1,4 dilithiobutane gave an oily residue which is believed to have a dimeric structure $[\{\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\mu\text{-SEt}_2)\}_2]$, **1**. This complex is not stable and so it was used without further purification soon after the preparation. In the ^1H -NMR spectrum, this complex showed three broad signals which were assigned to CH_2 and CH_3 groups of SEt_2 and CH_2 groups of metallacycle (see the experimental section). The dimeric nature of complex **1** was confirmed by its reaction with dppm (compare the reaction of $[\text{Pt}_2\text{Me}_4(\mu\text{-SMe}_2)_2]$ with dppm which yields the dimer $[\text{PtMe}_4(\mu\text{-dppm})_2]$ [3]). Thus, the reaction of complex **1** with dppm gave the dimeric complex $[\{\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\mu\text{-dppm})\}_2]$, **2**.



Complex **2** was fully characterized using multinuclear NMR spectroscopy, FAB mass spectroscopy, and elemental analysis. Complete NMR data are given in the experimental section. In the ^{31}P -NMR spectrum (Fig. 1), complex **2** gave two doublet resonances for two non-equivalent phosphorus atoms, each with $^2J(\text{PP}) = 42$ Hz and each with satellites due to coupling to the directly attached ^{195}Pt with values of $^1J(\text{PtP}) = 1795$ and 1784 Hz which are similar to the values obtained from the ^{31}P -NMR spectrum of the dimeric complex $[\text{Pt}_2\text{Me}_4(\mu\text{-dppm})_2]$ at -50°C [3]. Note that the long

range coupling of ^{31}P atoms to ^{195}Pt , $^3J(\text{PtP})$, were not resolved. Also the ^{31}P chemical shifts were characteristic of bridging dppm [3]. In benzene solution at room temperature the non-equivalent phosphorus atoms appeared at $\delta = 7.4$ and 13.5 in the ^{31}P -NMR spectrum. However, at 50°C a broad peak centred around $\delta = 11$ was observed. As expected in the light of the above data, the ^{195}Pt -NMR spectrum contained a triplet, with the $^1J(\text{PtP})$ value 1800 Hz close to the $^1J(\text{PtP})$ couplings obtained from the ^{31}P spectrum.

In the ^1H -NMR spectrum of complex **2**, two broad multiplets were observed for the CH_2P_2 protons in contrast to one signal observed at $\delta = 4.37$ ppm in the ^1H -NMR spectrum of the mononuclear $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{dppm})]$ [4]. The ring protons appeared as a broad signal.

The ^{13}C -NMR spectrum of complex **2** at room temperature and at -50°C (Fig. 2) were also useful for structure determination. At room temperature the CH_2Pt groups of the ring appeared as a doublet of doublets at $\delta = 40.60$, $^2J(\text{PC trans}) = 89.4$ Hz, $^2J(\text{PC cis}) = 5.5$ Hz, $^1J(\text{PtC}) = 660$ Hz. Two broad signals at $\delta = 36.6$ and 37.6 are assigned to the $\beta\text{-CH}_2$ groups of the metallacycles. At -50°C , the signal due to the CH_2Pt groups split into two signals at $\delta = 40.22$ and 40.49 for two non-equivalent α -carbon atoms. The signals due to $\beta\text{-CH}_2$ groups of the metallacycles were sharper at low temperature.

Based on the above NMR data, it is suggested that the eight-membered $\text{Pt}_2\text{P}_4\text{C}_2$ dimetallacycle in the static solution structure has the S_4 twist-boat conformation with C_2 symmetry. The variable-temperature ^{31}P and ^{13}C -NMR spectra indicate that fluxionality occurs in solution. As originally proposed for $[\text{Pt}_2\text{Me}_4(\mu\text{-dppm})_2]$, a simple twisting motion going through a boat-boat (saddle) intermediate, as shown in equation 1 (Newman projection down PtPt axis, a and b represent non-equiv-

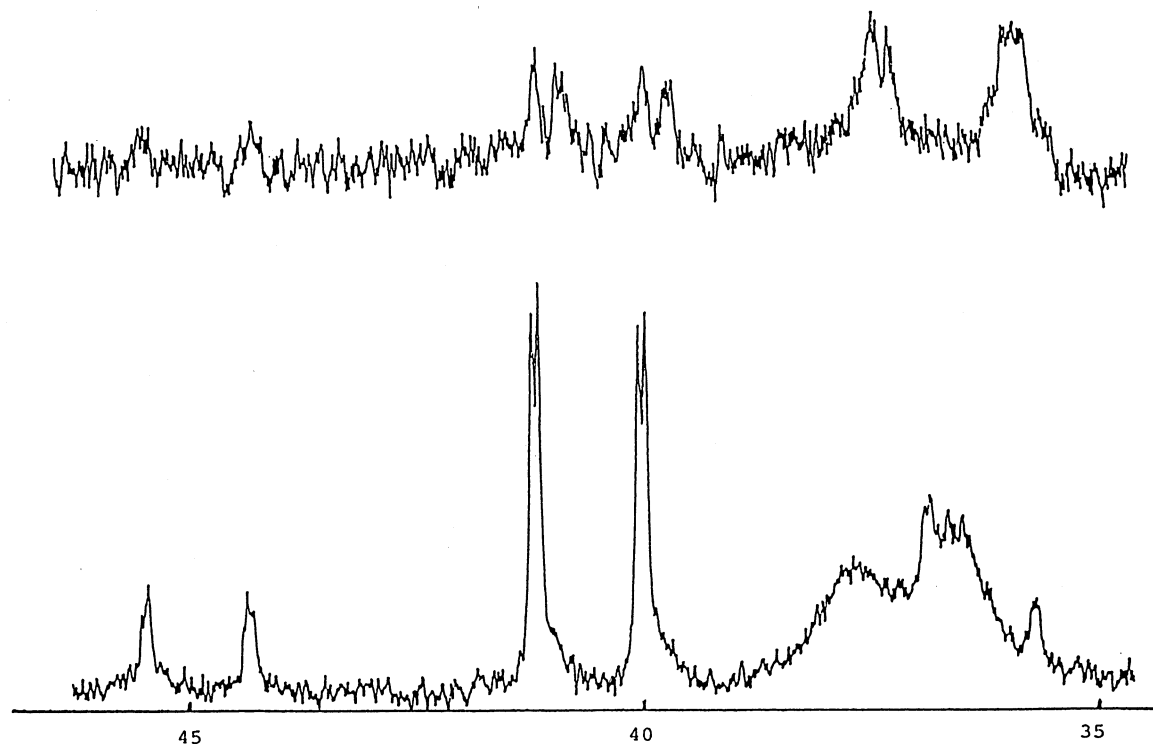
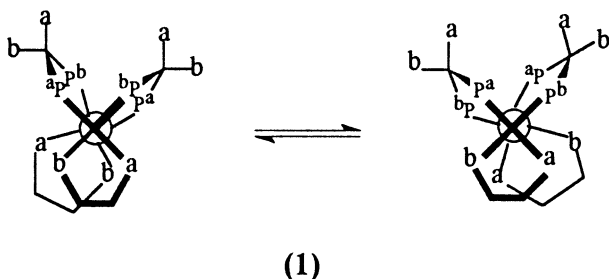


Fig. 2. The ^{13}C -NMR spectra (75.4 MHz) of $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\mu\text{-dppm})]_2$, **2**: (above) -50°C ; (below) 20°C .

alent atoms), can account for the features observed in the variable temperature NMR spectra. The activation energy for the fluxional process of equation 1 is estimated to be $\Delta G^\ddagger = 60.5 \pm 0.5 \text{ kJ mol}^{-1}$, somewhat higher than the value of $\Delta G^\ddagger = 56 \text{ kJ mol}^{-1}$ for $[\text{Pt}_2\text{Me}_4(\mu\text{-dppm})_2]$ [3].



The mass spectrum of complex **2** gives a cluster of peaks centred at m/e 1270 for the parent ion, with an isotopic abundance pattern similar to that for the ion $[\text{Pt}_2(\text{dppm})_2]^+$ observed at m/e 1158 as the most intense signal. The pattern observed is in good agreement with that calculated for the $[\text{Pt}_2(\text{dppm})_2]^+$ ion. The smaller mass fragment observed at m/e 1214 corresponds to loss of one $(\text{CH}_2)_4$ ligand from complex **2**.

A sample of **2** in benzene- d_6 or in the presence of SMe_2 or dppm did not change as monitored by ^{31}P -NMR spectroscopy, even on heating to 50°C for 36 h. After heating in toluene- d_8 for 15 min at 100°C , significant decomposition did occur.

For the dimeric complex $[\text{Pt}_2\text{Me}_4(\mu\text{-dppm})_2]$ and the corresponding monomer $[\text{PtMe}_2(\text{dppm})]$, it was shown that the monomer is thermodynamically stable form and the dimer is formed by kinetic control. Thus, free SMe_2 or dppm can attack the dimer and convert it to the monomeric form [3]. It is probable that free SMe_2 or dppm can not attack the dimeric complex **2**, and so it is not possible to convert it to the monomeric form, which is likely to be thermodynamically more stable.

2.2. Synthesis and characterization of the monomeric platinumacyclopentane complexes

Our attempts to prepare $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{COD})]$, in which $\text{COD} = 1,5$ cyclooctadiene, by the published method [7] in order to prepare $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{bpy})]$, **3**, by displacement of COD with bpy [8] was unsuccessful. However, the SEt_2 containing platinumacyclopentane complex **1**, proved to be a suitable starting material. Thus, complex **1** reacted with bpy to give **3**.

The ^1H -NMR spectrum of **3** (Fig. 3) contained (see Section 3) two signals at $\delta = 3.37 (J(\text{PtH}) = 100\text{ Hz})$ and $\delta = 2.23 (J(\text{PtH}) = 89 \text{ Hz})$ which were assigned to $\alpha\text{-CH}_2$ and $\beta\text{-CH}_2$ protons of the metallacycle.

The bright red color of **3** was ascribed to a transition from a platinum 5d-orbital to the lowest π^* orbital of the aromatic ligand [9].

This MLCT band was at 514 nm (shoulder at 486 nm) in benzene solution.

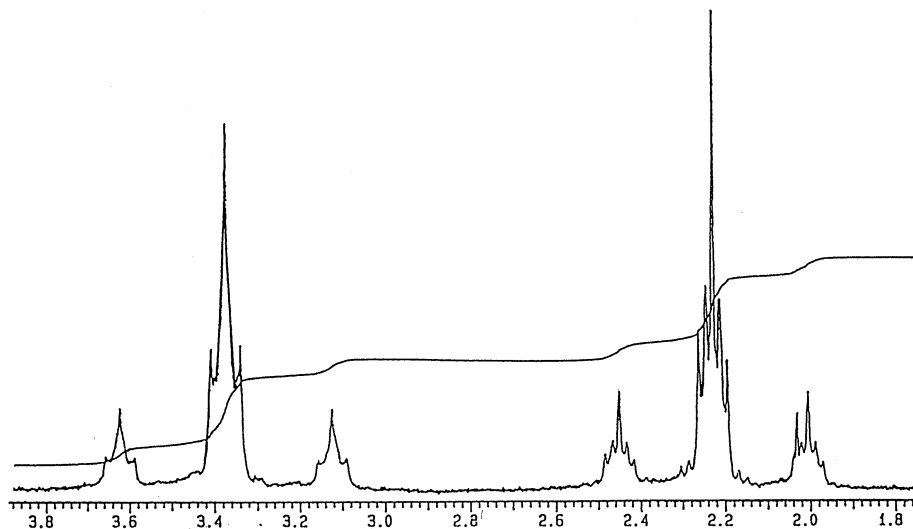
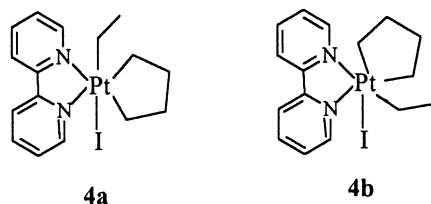


Fig. 3. The ^1H -NMR spectrum (200 MHz) of $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{bpy})]$, **3**, in the methylene region.

Oxidative addition of EtI to **3** gave $[\text{PtEtI}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{bpy})]$, **4**, as an approximately 2:1 mixture of two isomers, **4a** and **4b**. The isomers could not be separated and were characterised as a mixture.



In the ^1H -NMR spectrum, the more symmetrical isomer **4a** gave a triplet at $\delta = 0.2$ due to the CH_3 group of Et ligand with $^3J(\text{HH}) = 7.6$ Hz, and with satellites due to coupling to ^{195}Pt with $^3J(\text{PtH}) = 66.7$ Hz. The $\alpha\text{-CH}_2$ protons appeared as two multiplets at $\delta = 3.9$ and 2.03 with satellites due to coupling to ^{195}Pt with $^2J(\text{PtH}) = 92$ Hz and $^2J(\text{PtH}) = 58$ Hz, respectively [10]. The $\beta\text{-CH}_2$ and also the CH_2 group of the Et ligand appeared as overlapping multiplets around $\delta = 1.2\text{--}1.9$.

The less symmetrical isomer **4b** gave a triplet at $\delta = 0.06$ for the CH_3 group of Et with $^3J(\text{HH}) = 7.6$ Hz, and $^3J(\text{PtH}) = 74.1$ Hz. Two multiplets at $\delta = 3.28$ and 2.93 with $^2J(\text{PtH}) = 112$ Hz and $^2J(\text{PtH}) = 108$ Hz, respectively, were assigned to $\alpha\text{-CH}_2$ protons of ring. The $\beta\text{-CH}_2$ and CH_2 group of Et ligand were located around $\delta = 1.2\text{--}1.9$.

For comparison, the known complex $[\text{PtMeI}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{bpy})]$ [7] was prepared from the oxidative addition of MeI to **3**. As expected this complex gave a mixture of two isomers in which the methyl group is either *trans* to halogen (more symmetrical isomer) or to bpy (less symmetrical isomer), with an approximate ratio 2.5:1, respectively.

In the ^1H -NMR (see Section 3 for complete data), two multiplets at $\delta = 3.42$ ($^2J(\text{PtH}) = 106$ Hz) and $\delta = 2.15$ ($^2J(\text{PtH}) = 60$ Hz) were similarly assigned to the $\alpha\text{-CH}_2$ protons of the metallacycle in the more symmetrical isomer. For the less symmetrical isomer, these appeared as two multiplets at $\delta = 2.7$ ($^2J(\text{PtH}) = 116$ Hz) and $\delta = 2.52$ ($^2J(\text{PtH}) = 104$ Hz).

2.3. The kinetic study

The kinetics of oxidative addition of EtI to $[\text{PtMe}_2(\text{bpy})]$, **5**, and $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{bpy})]$, **3**, in benzene was studied by using UV–Vis spectroscopy. In each case, excess EtI was used and the disappearance of the MLCT bands at 509 or 518 nm for complexes **5** or **3**, respectively, were used to monitor the reaction. The reactions followed good first order kinetics (Fig. 4). Graphs of these first order rate constants against the concentration of EtI showed linear correlations with zero intercepts, showing a first order dependence of the rate on the concentration of EtI (Fig. 5). Thus, the overall second order rate constants were determined. The activation parameters were also determined from measurement at different temperatures, and the data are given in Table 1. The observation of good second order kinetics strongly suggests an $\text{S}_{\text{N}}2$ mechanism for oxidative addition of EtI to the Pt(II) complexes [11]. Also, the large negative values of $\Delta S^\ddagger$ are typical of oxidative addition by a common $\text{S}_{\text{N}}2$ mechanism which involves a polar transition state.

For the reactions of complexes **3** and **5** with EtI at different temperatures, the metallacycle complex **3** reacted 2.2–2.6 times faster than the dimethyl analogue complex **5** and this is attributed to the stronger donor ability of the $(\text{CH}_2)_4$ group compare to that of the CH_3 groups. Thus, the platinacycle complex **3** is more elec-

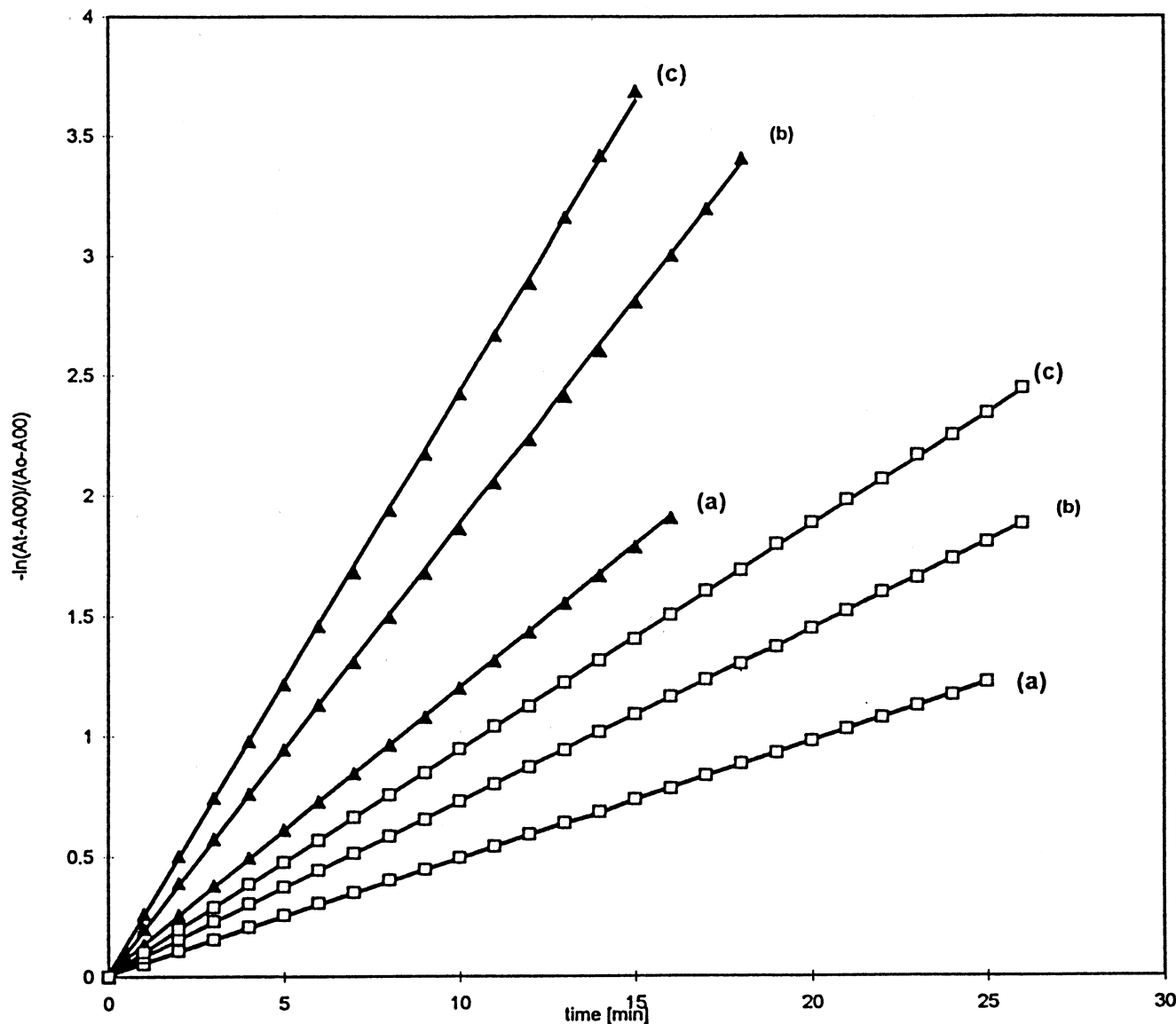


Fig. 4. First order plots for the reactions of complex $[\text{PtMe}_2(\text{bpy})]$, $\square$, and $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{bpy})]$, $\blacktriangle$, with EtI in benzene at 20°C . (a) $[\text{EtI}] = 0.82 \times 10^{-1}$; (b) $[\text{EtI}] = 1.23 \times 10^{-1}$; (c) $[\text{EtI}] = 1.64 \times 10^{-1} \text{ mol dm}^{-3}$

tron rich than the dimethyl complex **5** towards oxidative addition reactions. The complex **5** itself is among the most active of noble-metal complexes in oxidative addition reactions [11–13].

3. Experimental details

^1H -NMR spectra were recorded either on a Varian XL-200 or a Bruker Avance DPX 250 MHz spectrometer. Where indicated, some ^1H -NMR spectra were obtained using a Hitachi Perkin Elmer 60 MHz spectrometer. ^{31}P -, ^{195}Pt -, and ^{13}C -NMR spectra were recorded on a Varian XL-300 NMR spectrometer. Ref-

erences were TMS (^1H and ^{13}C), H_3PO_4 (^{31}P) and aqueous $\text{K}_2[\text{PtCl}_4]$ (^{195}Pt). All the chemical shifts and coupling constants are in ppm and Hz, respectively. FAB Mass spectra were obtained using a Finnigan Mat 8230 Mass spectrometer. Kinetic studies were carried out by using a Philips PU 8675 VIS spectrophotometer, with temperature control using a poly sciences 900 constant temperature bath. The starting materials were made by literature methods: $\text{Li}(\text{CH}_2)_4\text{Li}$ [14], $[\text{PtMe}_2(\text{bpy})]$ [13].

3.1. $[\text{PtCl}_2(\text{SEt}_2)_2]$

Diethyl sulfide (5 ml) was added to a suspension of

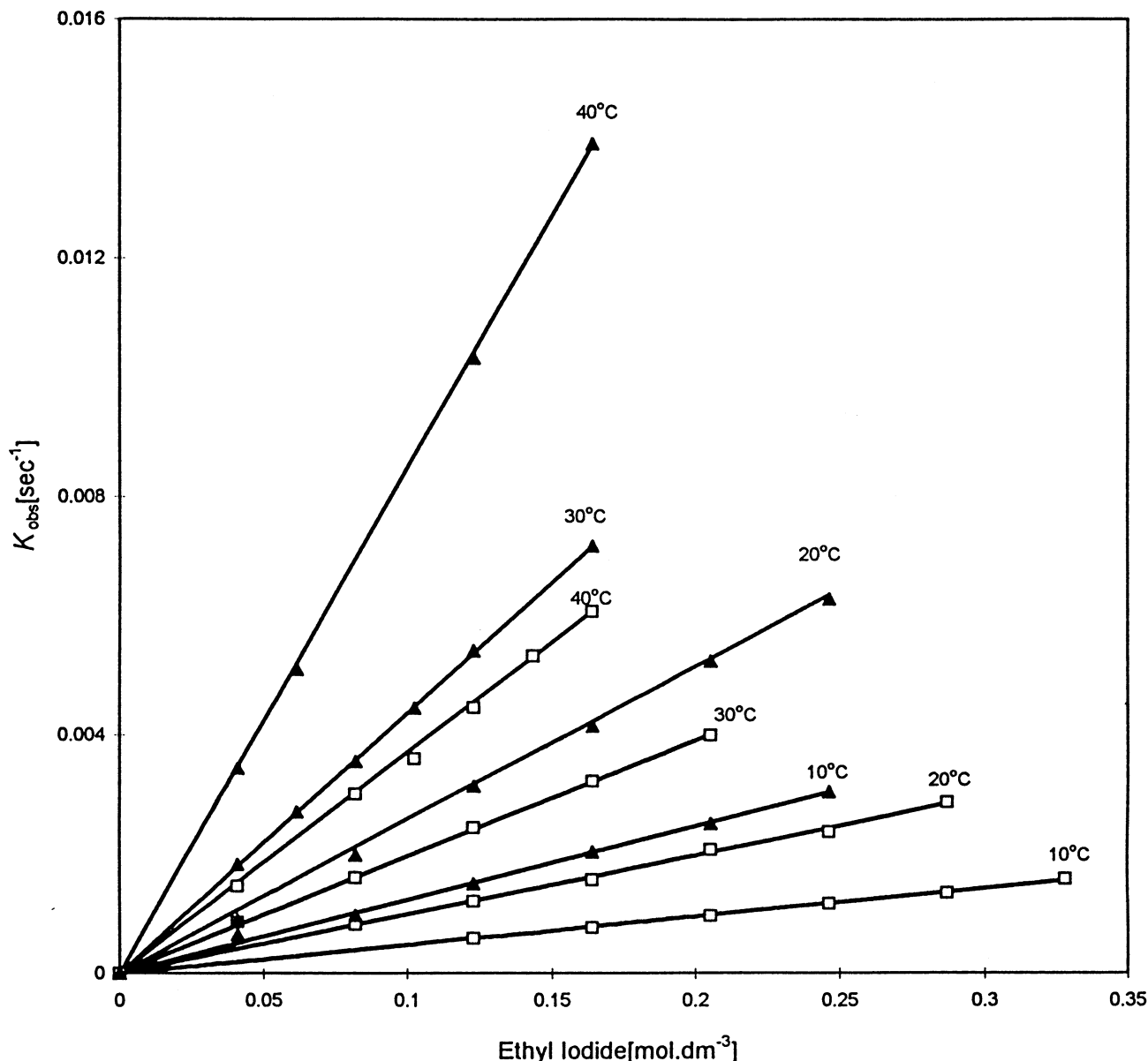


Fig. 5. Plots of first order rate constants ($k_{\text{obs}}/\text{s}^{-1}$) for the reaction of $[\text{PtMe}_2(\text{bpy})]$, $\square$, or $[\text{Pt}(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)(\text{bpy})]$, $\blacktriangle$, with EtI in benzene at different temperatures vs concentration of EtI.

$[\text{NH}_4]_2\text{PtCl}_6$ (4.5 g) in H_2O (100 ml) through a water condenser. The reaction mixture was stirred for 30 min at room temperature and then heated to 80°C . A bulky precipitate was formed. A solution of Na_2SO_3 (2.1 g) in water (20 ml) was added slowly through the condenser. The orange solid dissolved to give a colourless solution. The reaction mixture was stirred for a further 1 h at room temperature and then concentrated HCl (20 ml) was added slowly. The mixture was then boiled for 30 min to drive off excess SEt_2 , SO_2 and HCl . The solvent was removed and the residue extracted with CH_2Cl_2 (40 ml) and dried over MgSO_4 . The solvent was removed and the resulting orange oil was solidified with diethyl ether. The orange solid was dried in vacuo. Yield 92%.

The product was identified as a mixture (approximately 2:1) of *cis*- and *trans*- $[\text{PtCl}_2(\text{SEt}_2)_2]$. {Found: C, 20.8; H, 4.3. Calc. for $\text{C}_8\text{H}_{20}\text{S}_2\text{Cl}_2\text{Pt}$: C, 21.5; H, 4.5%}. NMR data in CDCl_3 : ^{13}C , major isomer: $\delta = 12.44[\text{s}, {}^3J(\text{Cpt}) = 22.54 \text{ Hz, 2C of methyl groups}]$; $29.77[\text{s}, {}^3J(\text{Cpt}) = 22.5 \text{ Hz, 2C of methylene groups}]$; minor isomer: $12.57[\text{s}, {}^3J(\text{Cpt}) = 22.5 \text{ Hz, 2C of methyl groups}]$; $31.62[\text{s}, {}^3J(\text{Cpt}) = 36 \text{ Hz, 8H of methylene groups}]$; ^1H , major isomer: $\delta = 1.36[\text{t}, {}^3J(\text{HH}) = 7.37 \text{ Hz, 12H of methyl groups}]$; $2.83[\text{q}, {}^3J(\text{HH}) = 7.5 \text{ Hz, } {}^3J(\text{HPt}) = 36 \text{ Hz, 8H of methylene groups}]$; minor isomer: $\delta = 1.32[\text{t}, {}^3J(\text{HH}) = 7.65 \text{ Hz, 12H of methyl groups}]$; $3.15[\text{q}, {}^3J(\text{HH}) = 7.8 \text{ Hz, 8H of methylene groups}]$. The data for the methylene groups were obtained from 60 MHz NMR spectrum.

Table 1
Second-order rate constants^a and activation parameters^b for oxidative addition of Ethyl iodide to [PtMe₂(bpy)], **5**, and [Pt(CH₂CH₂CH₂CH₂)(bpy)], **3**, in benzene

Complex	<i>T</i> (°C)	10 ³ <i>k</i> ₂ (dm ³ mol ^{−1} s ^{−1})	Δ <i>H</i> [‡] (kJ mol ^{−1})	Δ <i>S</i> [‡] (20°C) ^c (JK ^{−1} mol ^{−1})
5	10	4.76 ± 0.06	47.9 ± 0.1	−120 ± 1
	20	9.87 ± 0.17		
	30	19.5 ± 0.19		
	40	37.03 ± 0.31		
3	10	12.33 ± 0.14	44 ± 2	−126 ± 6
	20	25.83 ± 0.29		
	30	43.63 ± 0.32		
	40	84.36 ± 0.53		

^a The ratio *k*₂ for complex **3**/*k*₂ for complex **5**: at 10°C, 2.6; at 20°C, 2.6; at 30°C, 2.2; at 40°C, 2.3.

^b Values given based on 95% confidence limits from least squares regression analysis.

^c Obtained from the Arrhenius equation.

3.2. [*Pt*(CH₂CH₂CH₂CH₂)(μ-SEt₂)₂]

A freshly prepared solution of 1,4 dilithiobutane in dry ether (4.2 ml, 0.8 mmol) was added to a stirred, cold solution of [PtCl₂(SEt₂)₂](0.39 g, 0.67 mmol) in benzene (50 ml). The brownish solution was allowed to slowly warm up to room temperature during 45 min. The reaction mixture was then stirred at 0°C under an atmosphere of air for 20 min to decompose any excess dilithiobutane. This was then filtered and the solvent was removed from the filtrate under reduced pressure. The resulting oil was exposed to the air for 30 min. Benzene (20 ml) was added and the solution was filtered. Removal of the solvent under vacuum gave a brownish oil which is proposed to be [*Pt*(CH₂CH₂CH₂CH₂)(μ-SEt₂)₂]. The compound is not stable and was used without further purification soon after it was prepared. Yield is about 70%. ¹H-NMR in C₆D₆: δ = 2.7[br.m, CH₂ of SEt₂]; 1.1[br.m, CH₃ of SEt₂]; 0.55–2.75[br., CH₂ groups of platinacycle].

3.3. [*Pt*(CH₂CH₂CH₂CH₂)(μ-dppm)₂]

A solution of dppm (0.207 g, 0.54 mmol) in benzene (10 ml) was added to a solution of [*Pt*(CH₂CH₂CH₂CH₂)(μ-SEt₂)₂](0.19 g, 0.28 mmol) in benzene (15 ml) and the mixture swirled and then set aside for 12 h at room temperature. The solvent was removed under reduced pressure and the residue triturated with ether to give a creamy powder. The powder was dissolved in CH₂Cl₂ (3 ml) and carefully layered with n-pentane. Long colourless crystals formed that were separated and dried in vacuo. Yield 0.184 g (52%), m.p. 215–218°C. {Found: C, 54.22; H, 4.68. Calc. for C₂₉H₃₀P₂Pt: C, 54.77; H, 4.72%}. NMR data in CDCl₃: ¹H, δ = 0.5–2.3[br., (CH₂)₄]; 2.75[br., 1H of dppm]; 4.2[m, 1H of dppm]; ³¹P, δ = 6.65(7.4 in benzene)[d, ²*J*(P^aP^b) = 42 Hz, ¹*J*(P^aPt) = 1795 Hz, 2P^a of dppm lig-

and]; 12.96 (13.5 in benzene)[d, ²*J*(P^bP^a) = 42 Hz, ¹*J*(P^bPt) = 1784 Hz, 2P^b of dppm ligand]; ¹⁹⁵Pt, δ = −4141[t, ¹*J*(PtP) = 1800 Hz]; δ (³¹P) in benzene at +50°C = 11; ¹³C-NMR data in CD₂Cl₂: At room temperature, δ = 28.40[t, ¹*J*(PC) = 11.0 Hz, CH₂ of dppm ligands]; 36.6[br., 1C^β of (CH₂)₄]; 37.6[br., 1C^β of (CH₂)₄]; 40.60 [dd, ²*J*(PC *trans*) = 89.4 Hz, ²*J*(PC *cis*) = 5.5 Hz, ¹*J*(PtC) = 660 Hz, 2C^α of (CH₂)₄]; At −50°C, δ = 26.2[m, CH₂ of dppm]; 35.8[m, 1C^β of (CH₂)₄]; 37.2[m, 1C^β of (CH₂)₄]; 40.22[dd, ²*J*(PC *trans*) = 90.73 Hz, ²*J*(PC *cis*) = 5.84 Hz, ¹*J*(PtC) = 660 Hz, 1C^α of (CH₂)₄]; 40.49[d, ²*J*(PC *trans*) = 88.54 Hz, ²*J*(PC *cis*) = not resolved, ¹*J*(PtC) = 660 Hz, 1C^α of (CH₂)₄]. FAB mass (*m/e*): 1270, 1214, 1158. Calc. for [Pt(dppm)(CH₂)₄]₂, [Pt₂(dppm)₂(CH₂)₄] and [Pt₂(dppm)₂]: 1270, 1214 and 1158, respectively.

3.4. Heating of [*Pt*(CH₂CH₂CH₂CH₂)(μ-dppm)₂] in benzene or toluene.

Small sample (ca. 6 mg) of [*Pt*(CH₂CH₂CH₂CH₂)(μ-dppm)₂] was dissolved in C₆D₆ (0.3 ml) in a sealed NMR tube. After being heated for 15 h at 50°C, the sample gave an unchanged ³¹P spectrum. The procedure was repeated with samples to which a relatively large excess of (i) SME₂ and (ii) dppm was added. In each case, no change was observed in the ³¹P-NMR spectrum after 36 h. In a similar procedure in toluene-d₆, decomposition to some unidentified products took place to a large extent after the sample was heated for 15 min at 100°C.

3.5. [*Pt*(CH₂CH₂CH₂CH₂)(bpy)]

A solution of 2,2'-bipyridyl (0.1 g, 0.64 mmol) in benzene (10 ml) was added to a solution of [*Pt*(CH₂CH₂CH₂CH₂)(μ-SEt₂)₂] (0.212 g, 0.34 mmol)

in benzene (20 ml). The mixture was stored at ambient temperature in the absence of light. Over a period of 4 h the solution gradually turned deep red and a small amount of a brown solid separated. After filtration, the solvent was evaporated under reduced pressure without heating. The red residue was washed with n-hexane and then dissolved in a hot 1:1 mixture of ethanol-acetone and filtered. The filtrate was cooled to ambient temperature and the solvent was evaporated by a stream of nitrogen to obtain the product as red solid. Yield 55%. {Found: C, 40.45; H, 3.80; N, 6.39. Calc. for $C_{14}H_{16}N_2Pt$: C, 41.27; H, 3.96; N, 6.88%}. 1H -NMR in C_6D_6 : $\delta = 2.23$ [m, $J(PtH) = 89$ Hz, 4H of ring]; 3.37 [m, $J(PtH) = 100$ Hz, 4H of ring]; 9.09 [m, $^3J(PtH^o) = 22$ Hz, $^3J(H^mH^o) = 5.38$ Hz, $2H^o$ of bpy]; 6.35 [m, $^3J(H^oH^m) = 5.40$ Hz, $^3J(H^pH^m) = 5.47$ Hz, $^4J(H^mH^m) = 1.41$ Hz, $2H^m$ of bpy]; 6.78 [d, $^3J(H^pH^m) = 8.12$ Hz, $2H^m$ of bpy], 6.98 [m, $^3J(H^mH^p) = 7.78$, $^4J(H^oH^p) = 1.46$, $2H^p$ of bpy].

3.6. $[PtEtI(CH_2CH_2CH_2CH_2)(bpy)]$

A solution of $[Pt(CH_2CH_2CH_2CH_2)(bpy)]$ (30 mg) in benzene (15 ml) was treated with an excess of EtI (1 ml). After 15 min, the solvent was removed at reduced pressure, leaving a yellow solid. This was recrystallized from CH_2Cl_2 /pentane and dried in vacuo. Yield 50%, m.p. 120–125°C (decomp). {Found: C, 34.87; H, 4.01; N, 5.01. Calc. for $C_6H_{21}IN_2Pt$: C, 34.10; H, 3.73; N, 4.97%}. 1H -NMR in $CDCl_3$; major isomer **4a**; $\delta = 3.90$ [m, $^2J(PtH) = 92$ Hz, $2H^x$ of ring], 2.03 [m, $^2J(PtH) = 58$ Hz, $2H^x$ of ring], 0.2 [t, $^3J(HH) = 7.6$ Hz, $^3J(PtH) = 66.7$ Hz, 3H, CH_3 group], 1.2 – 1.9 [β - CH_2 groups of ring and CH_2 of Et group]; minor isomer **4b**; $\delta = 3.28$ [m, $^2J(PtH) = 112$ Hz, $2H^x$ of ring]; 2.93 [m, $^2J(PtH) = 108$ Hz, $2H^x$ of ring]; 0.06 [t, $^3J(HH) = 7.6$ Hz, $^3J(PtH) = 74.1$ Hz, 3H, CH_3 group], 1.2 – 1.9 [β - CH_2 group of ring and CH_2 of Et group]; The bpy protons for the two isomers: $\delta = 8.78$ – 8.90 (H^o); 7.54 – 7.66 (H^m); 8.14 – 8.28 (H^m); 7.96 – 8.10 (H^p).

3.7. $[PtMeI(CH_2CH_2CH_2CH_2)(bpy)]$

$[PtMeI(CH_2CH_2CH_2CH_2)(bpy)]$, was prepared similarly using MeI. Yield 78%. {Found: C, 32.42; H, 3.68; N, 5.35. Calc. for $C_{15}H_{19}IN_2Pt$: C, 32.80; H, 3.46; N, 5.10%}. 1H -NMR data in $CDCl_3$: major isomer, $\delta = 3.42$ [m, $^2J(PtH) = 106$ Hz, $2H^x$ of ring]; 2.15 [m, $^2J(PtH) = 60$ Hz, $2H^x$ of ring]; 0.73 [s, $^2J(PtH) = 75.14$ Hz, 3H of CH_3]; minor isomer; $\delta = 2.7$ [m, $^2J(PtH) = 116$ Hz, $2H^x$ of ring]; 2.52 [m, $^2J(PtH) = 104$ Hz, $2H^x$ of ring]; 1.54 [s, $^2J(PtH) = 72.00$ Hz, 3H of CH_3]; 1.2 – 1.8 [br., H^x atoms of ring for both isomers]. The bpy protons for the two isomers: $\delta = 8.80$ – 8.92 (H^o);

7.50 – 7.64 (H^m); 8.14 – 8.26 (H^m); 7.93 – 8.08 (H^p).

3.8. $[PtEtI Me_2(bpy)]$

A solution of $[PtMe_2(bpy)]$ (50 mg) in benzene (20 ml) was treated with an excess of EtI (1 ml). After 20 min, the solvent was removed at reduced pressure, leaving a yellow solid. This was recrystallized from CH_2Cl_2 /ether and dried in vacuo. Yield 72%, m.p. 174–176°C (decomp). {Found: C, 30.82; H, 3.41; N, 5.02. Calc. for $C_{14}H_{19}IN_2Pt$: C, 31.28; H, 3.51; N, 5.21}. 1H -NMR in $CDCl_3$: $\delta = -0.03$ [t, $^3J(HH) = 7.6$ Hz, $^3J(PtH) = 76.2$ Hz, 3H, CH_3 group of Et], 1.41 [m, $^2J(HH) = 7.56$ Hz, 2H, CH_2 group of Et], 1.47 [s, $^2J(PtH) = 82.7$ Hz, 6H of CH_3 ligands]; The bpy protons: $\delta = 7.59$ (H^m), 8.03 (H^p), 8.19 (H^m), 8.95 (H^o).

3.9. Kinetic studies of oxidative addition by UV-visible spectroscopy

A solution of $[Pt(CH_2CH_2CH_2CH_2)(bpy)]$ in benzene (3 ml, 2.5×10^{-4} M) in a cuvette was thermostated at 20°C, and a known excess of EtI was added by using a microsyringe. After rapid stirring, absorbance values at $\lambda = 518$ nm were collected at 0.1-min intervals for 20–40 min, at which time the reaction was complete.

Computer treatment of data showed good first order kinetics (see Fig. 4) from which the observed first order rate constants and standard deviations were obtained. A plot of k_{obs} vs $[EtI]$ was linear (Fig. 5), and the slope gave the second-order rate constant. The same method was used at other temperatures, and the activation parameters were obtained from the Arrhenius equation.

The oxidative addition of EtI to $[PtMe_2(bpy)]$ was monitored in a similar way but with $\lambda = 509$ nm.

Acknowledgements

We thank the Shiraz University Research Council, Iran (Grant No. 75-SC-946-555) and NSERC (Canada) for financial support.

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