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ω-Monobromoalkyl platina(IV)cyclopentane complexes: synthesis, characterization and kinetic studies of the formation

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Abstract

The complexes $[Pt(CH_2CH_2CH_2CH_2)(NN)]$, **1a** (NN = 2,2′-bipyridyl) and **1b** (NN = 1,10-phenanthroline), react with dibromoalkanes $Br(CH_2)_nBr$ ($n = 3$–6) to give new platina(IV)cyclopentane complexes fully characterized as $[PtBr(CH_2CH_2CH_2CH_2)\{(CH_2)_nBr\}(NN)]$. When $n = 2$, complexes **1** react with $Br(CH_2)_2Br$ to give binuclear complexes $[Pt_2Br_2(CH_2CH_2CH_2CH_2)_2\{\mu\text{-}(CH_2)_2\}(NN)_2]$. All the reactions proceed by the S_N2 mechanism and rates of reactions follow the sequence $n = 2 \gg 6 > 3 > 4 \cong 5$. The trend of reactivity is discussed in terms of chain lengths of dibromides and $^1J(Pt–C)$ values of bond between Pt and polymethylene chain in the platina(IV)cyclopentane complexes. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Platinum; Metallacycle; ω-Monobromoalkyl

1. Introduction

There is a considerable current interest in the synthesis of halogenoalkyl complexes of transition metals of type $[L_yM\{CH_2)_nX\}]$ (L_y = ligands, M = transiton metal, X = halogen) [1,2]. The complexes in which $n > 1$ have been shown to be precursors for homo- and heteronuclear complexes [3–5] and also for building up large dendritic macromolecules by extention from the ω functionality [6].

Coordinatively unsaturated 16-electron organoplatinum(II) complexes have proved highly amenable for the study of the oxidative addition process. The related complexes with nitrogen-donor ligands, especially diimines, have been particularly interesting, as the ‘hard’ nature of nitrogen enhances the nucleophilicity of the platinum(II) center, an important feature in S_N2-type reactions where electron-rich metal centers are required to activate the substrate; for an excellent review see Ref. [7]. The oxidative addition of $[PtMe_2(NN)]$ complexes, in which NN are various diimine ligands such as bpy (2,2′-bipyridyl) and phen (1,10-phenanthroline), with a great variety of substrates has been extensively studied [7]. In particular, the reaction with α,ω-dihaloalkyls, $I(CH_2)_nI$ gave ω-monoiodoalkyl platinum(IV) complexes $[PtIMe_2\{(CH_2)_nI\}(phen)]$ that for $n = 3$–5 further reacted with $[PtMe_2(phen)]$ to produce binuclear complexes $[Pt_2I_2Me_4\{\mu\text{-}(CH_2)_n\}(phen)_2]$. However, the platina(II)cyclopentane analogues, $[Pt(CH_2CH_2CH_2CH_2)(NN)]$, **1**, have not been studied much, despite the fact that the metallacycles are of great interest because of their possible role in catalysis [8,9]. The oxidative addition of CH_2Cl_2 to $[Pt(CH_2CH_2CH_2CH_2)(bpy)]$, **1a**, to give $[PtCl(CH_2CH_2CH_2CH_2)(CH_2Cl)(bpy)]$ has been briefly examined by Young and Whitesides in 1978 [10]. A recent study has shown that the chelating $(CH_2)_4$ ligand has a stronger donor ability compared to the CH_3 ligand [11–13]. Thus, EtI reacted more than two times faster with the platina(II) cyclopentane complex **1a** than with the dimethyl ana-

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logue [$PtMe_2(bpy)$] [13]. It was therefore concluded that the platinacycle complex **1a** is more electron-rich than [$PtMe_2(bpy)$] towards oxidative addition reactions. The latter is among the most active of noble-metal complex in oxidative addition reactions [3,14].

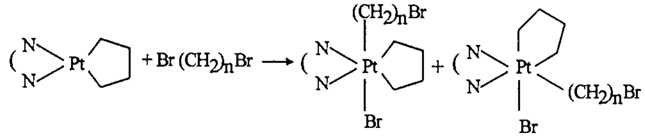
We now report on the kinetics of reactions of complex **1a** and [$Pt(CH_2CH_2CH_2CH_2)(phen)$], **1b**, with α,ω-dibromoalkanes. The platina(IV)cyclopentane products are fully characterized by NMR spectroscopy. Assignments made for the platina(IV)cyclopentane protons may be used as a finger-print in the characterization of other alkyl halide adducts of diimine platina(IV) cyclopentane complexes.

2. Results and discussion

The bright red complex [$Pt(CH_2CH_2CH_2CH_2)(bpy)$], **1a**, was prepared by the reaction of [$\{Pt(CH_2CH_2CH_2CH_2)(\mu\text{-}SEt_2)\}_2$] with bpy and characterized by ^{1}H-NMR spectroscopy [13]. A similar procedure was used to prepare the red complex [$Pt(CH_2CH_2CH_2CH_2)(phen)$], **1b**. The ^{1}H-NMR spectrum of **1b** contained (see Section 3) two signals at $\delta = 2.3$ [$J(PtH) = 95$ Hz] and $\delta = 3.6$ [$J(PtH) = 100$ Hz] which were assigned to α-CH_2 and β-CH_2 protons of the metallacycle. The color of these complexes is due to the presence of a metal to ligand charge transfer band in the visible region of the spectrum. The complexes are electron rich and are particularly reactive to oxidative addition [1,15].

2.1. Synthesis and characterization of the platina(IV)cyclopentane complexes

The bright red complexes **1** reacted cleanly with excess $Br(CH_2)_nBr$ ($n = 3$–6) in benzene to form pale yellow solutions, from which solid products having the general formula [$PtBr(CH_2CH_2CH_2CH_2)\{(CH_2)_nBr\}(NN)$] were obtained. Generally, slightly lower yields were obtained when the reactions were carried out in acetone solutions. The reactions are shown in Eq. (1). The product of each reaction is predominately that for *trans* addition of the α,ω-dibromides, but very small traces of the *cis* isomers were observed.



(1)

1a NN=bpy
1b NN=phen

	NN	n
2a	bpy	3
2b	phen	3
3a	bpy	4
3b	phen	4
4a	bpy	5
4b	phen	5
5a	bpy	6
5b	phen	6

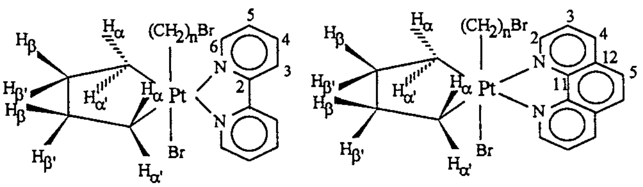
The reaction of complexes **1** with $Br(CH_2)_2Br$ in benzene produced an insoluble product. Due to the insolubility of these products, no NMR spectral data could be obtained. However, the elemental analyses (Table 1) of the complexes are consistent with dimeric complexes of the general formula [$Pt_2Br_2(CH_2CH_2CH_2CH_2)\{\mu\text{-}(CH_2)_2\}(NN)_2$], **6a** (NN = bpy) and **6b** (NN = phen). The reaction between [$PtMe_2(phen)$] and $Br(CH_2)_2Br$ yielded a similar insoluble compound which is believed to be [$Pt_2Br_2Me_4\{\mu\text{-}(CH_2)_2\}(phen)_2$] [15].

Table 1
Characterization data for [$PtBr(CH_2CH_2CH_2CH_2)\{(CH_2)_nBr\}(NN)$], **2–5** and [$Pt_2Br_2(CH_2CH_2CH_2CH_2)_2\{(\mu\text{-}(CH_2)_2\}(NN)_2$], **6**

Complex	n	Yield (%)	m.p. (°C)[b]	Elemental analysis (%)[a]		
				C	H	N
2a	3	85	125–130	33.8 (33.4)	3.6 (3.6)	4.9 (4.6)
2b	3	70	235	35.6 (35.0)	3.5 (3.4)	4.4 (4.3)
3a	4	90	157–160	34.1 (34.5)	3.1 (3.8)	4.6 (4.5)
3b	4	84	207–210	36.2 (36.0)	3.5 (3.6)	4.3 (4.2)
4a	5	88	130–135	35.2 (35.7)	3.9 (4.1)	4.3 (4.4)
4b	5	66	248	37.3 (37.3)	3.9 (3.8)	4.2 (4.1)
5a	6	60	145	36.2 (36.7)	4.1 (4.3)	4.5 (4.3)
5b	6	62	120–125	38.6 (38.1)	4.5 (4.1)	4.1 (4.0)
6a	2	85	273–5	35.0 (35.8)	3.5 (3.6)	5.5 (5.6)
6b	2	77	285	37.3 (37.6)	3.6 (3.3)	4.8 (5.2)

[a] Found (Calc.).
[b] Decomposed.

The complexes **2**–**5** were fully characterized by microanalysis (Table 1), ^{1}H- (Table 2) and ^{13}C- (Table 3) NMR spectroscopy. H/C HETCOR experiments were performed for all complexes **2**–**5** to ascertain the assignments. The NMR labelling is as follows:



In the ^{1}H-NMR spectra of all complexes **2**–**5** (Table 2), two multiplets at δ ca. 2 and 3.2 with ^{195}Pt satellites with ^{2}J(PtH) ca. 40–50 Hz and ^{2}J(PtH) ca. 100–110 Hz, respectively, are assigned to the two different α-CH$_2$ protons (Hα and Hα') of the platinacycle ring. This pattern may be used as a finger-print in the characterization of other alkyl halide adducts of diimineplatina(IV)cyclopentane complexes of general formula [PtRX(CH$_2$CH$_2$CH$_2$CH$_2$)(NN)] in which the ligands R and X are *trans* to each other (more symmetrical isomer). A similar pattern was reported previously for [PtRX(CH$_2$CH$_2$CH$_2$CH$_2$)(bpy)] complexes [13] at $\delta = 3.9$ [^{2}J(PtH) = 92 Hz) and $\delta = 2.03$ [^{2}J(PtH) = 58 Hz] for R = Et and at $\delta = 3.42$ [^{2}J(PtH) = 106 Hz] and $\delta = 2.15$ [^{2}J(PtH) = 60 Hz] for R = Me, which were assigned tentatively to the α-CH$_2$ protons of the platina(IV)cycle rings. The β-CH$_2$ (Hβ and Hβ') appeared at δ ca. 1.3 and 1.5 which were overlapped with some of the polymethylene protons and were assigned using HETCOR experiments. The characteristic triplet in the region of δ ca. 3 (^{3}J(HH) ca. 7 Hz) was assigned to the protons of the ω-methylene unit (bonded to bromine atom) while the PtCH$_2$ protons of the polymethylene chain resonated further upfield at δ ca. 1.5. The data for other methylene protons are collected in Table 2. A triplet at δ ca. 3.5 (^{3}J(HH) ca. 7 Hz) in the spectra of all the complexes (Table 2) was assigned tentatively to a CH$_2$Br resonance of traces of the *cis* isomer.

In the ^{13}C-NMR spectra of the complexes **2**–**5** (Table 3), a peak at δ ca. 26 with satellites due to coupling to ^{195}Pt with ^{1}J(PtC) ca. 682–702 Hz is assigned to the carbons of the two α-CH$_2$Pt groups of the platina(IV)cycle ring. The presence of only one such signal clearly indicates the symmetrical stereochemistry of the complexes. The carbons of β-CH$_2$ groups of ring appeared at δ ca. 33.8 with ^{2}J(PtC) ca. 18 Hz. For carbon atoms of the polymethylene chain, the ω-carbon atom which is adjacent to the bromo group resonates at the highest chemical shift value of δ ca. 34. A peak at δ ca. 15.5–19.8 has ^{195}Pt satellites, with coupling to carbon of ca. 750–772 Hz. This indicates direct bonding to platinum, and the resonance is assigned to the carbon atom of PtCH$_2$ group of polymethylene chain (C$_1$). Note that the ^{1}J(PtC$_1$) value decreases as the chain length increases. This should mean that the Pt–C$_1$ bond strength increases as the chain length decreases, which may be related to the kinetics of reactions of complexes **1** with Br(CH$_2$)$_n$Br (Section 2.2). The remaining assignments, for the alkyl chain, are made using H/C HETCOR experiments and also on the basis of the magnitude of ^{195}Pt–C coupling constants, assuming the coupling decreases the further the carbon atom is from the platinum.

2.2. The kinetic study

The kinetics of oxidative addition of Br(CH$_2$)$_n$Br ($n = 3$–6) to [Pt(CH$_2$CH$_2$CH$_2$CH$_2$)(bpy)], **1a,** in acetone was studied by using UV–vis spectroscopy. In each case, excess dibromide was used and the disappearance of the MLCT band at 480 nm was used to monitor the reaction. The changes in the spectrum during a typical run are shown in Fig. 1. The reactions with Br(CH$_2$)$_n$Br ($n = 3$–6) followed good first-order kinetics (Fig. 2). Graphs of these first-order rate constants against the concentration of dibromides gave good straight line plots passing through the origin, showing a first-order dependence of the rate on the concentration of dibro-

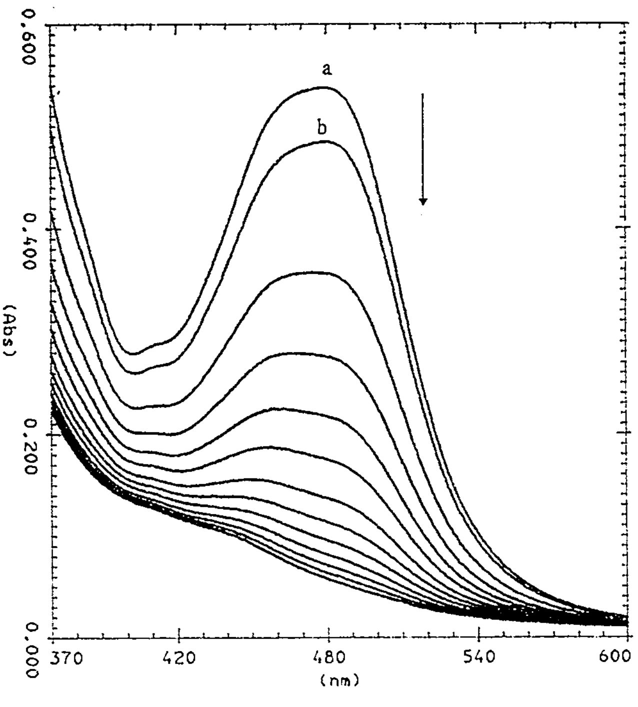


Fig. 1. Changes in the UV–vis spectrum during the reaction of complex **1a** (4.88×10^{-4} M) and Br(CH$_2$)$_6$Br (0.11 M) in acetone at 25°C; (a) initial spectrum; (b) $t = 0$; intervals 135 s.

Table 2
^{1}H-NMR data[a] for [$PtBr(CH_2CH_2CH_2CH_2)\{(CH_2)_nBr\}(NN)$], complexes **2**–**5**

Complex	n	$\overline{\text{Pt}\ (CH_2CH_2CH_2CH_2)}$		Polymethylene chain					CH_2Br of traces *cis* isomer ($^3J(HH)$)[b]	NN	
		α-CH_2 ($^2J(PtH)$)	β-CH_2	$PtCH_2$	$PtCH_2CH_2$	Other	CH_2CH_2Br	CH_2Br ($^3J(HH)$)		δ	J
										NN = bpy	
2a	3	2.08(m,2H) (49.5) 3.14(m,2H) (101.8)	1.38 1.57	1.54	1.26(m,2H)	—	—	3.09(t,2H) (7.25)	—	8.25(H3) 8.05(H4) 7.62(H5) 8.83(H6)	8.25(J3,4) 1.15(J4,6) 7.25(J4,5) 1.00(J5,3) 6.52(J5,6)
3a	4	2.07(m,2H) (47.5) 3.11(m,2H) (106.1)	1.37 1.52	1.58	0.65(m,2H)	—	1.28	3.14(t,2H) (6.75)	3.60(t) (7.00)	8.24(H3) 8.00(H4) 7.56(H5) 8.84(H6)	8.25(J3,4) 0.75(J4,6) 7.75(J4,5) 1.00(J5,3) 6.50(J5,6)
4a	5	2.05(m,2H) (39.0) 3.13(m,2H) (103.3)	1.28 1.60	1.55	0.53(m,2H)	1.13	1.41	3.16(t,2H) (7.00)	3.51(t) (7.00)	8.24(H3) 8.00(H4) 7.58(H5) 8.16(H6)	8.25(J3,4) 1.50(J4,6) 7.50(J4,5) 5.75(J5,6)
5a	6	2.06(m,2H) (43.5) 3.15(m,2H) (109.0)	1.39 1.59	1.54	0.54(m,2H)	1.10(4H)	1.60	3.26(t,2H) (7.00)	3.48(t) (6.75)	8.23(H3) 8.01(H4) 7.59(H5) 8.84(H6)	8.25(J3,4) 7.25(J4,6) 6.38(J5,6)
										NN = phen	
2b	3	2.04(m,2H) (51.4) 3.10(m,2H) (107.5)	1.24 1.38	1.41	1.05(m,2H)	—	—	2.77(t,2H) (7.24)	3.53(t)	8.93(H2) 7.66(H3) 8.29(H4) 7.75(H5)	4.94(J2,3) 8.20(J3,4)
3b	4	2.18(m,2H) (42.2) 3.28(m,2H) (104.06)	1.34 1.50	1.50	0.50(m,2H)	—	1.27	3.01(t,2H) (6.75)	3.55(t) (6.50)	9.14(H2) 7.87(H3) 8.48(H4) 7.95(H5)	5.00(J2,3) 8.13(J3,4)
4b	5	2.19(m,2H) (41.44) 3.21(m,2H) (108.6)	1.18 1.54	1.50	0.37(m,2H)	0.98	1.35	3.00(t,2H) (6.75)	3.45(t) (6.75)	9.07(H2) 7.83(H3) 8.43(H4) 7.91(H5)	5.00(J2,3) 8.25(J3,4)
5b	6	2.14(m,2H) (49.8) 3.21(m,2H) (110.1)	1.39 1.60	1.54	0.37(m,2H)	0.90(4H)	1.42	3.10(t,2H) (6.75)	3.41(t) (6.50)	9.07(H2) 7.81(H3) 8.43(H4) 7.90(H5)	5.00(J2,3) 8.13(J3,4)

[a] Solvent $CDCl_3$; chemical shift relative to TMS; J values in Hz.

[b] Assignments are tentative (see text).

Table 3
^{13}C-NMR data for complexes [PtBr(CH$_2$CH$_2$CH$_2$CH$_2$){(CH$_2$)$_n$Br}(NN)]^a, **2–5** in CDCl$_3$

Complex	n	$\overline{\text{Pt}\ (\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)}$		Polymethylene chain						NN
		C_α (^1J (Pt–C))	C_β (^2J (Pt–C))	PtC$_1$ (^1J (Pt–C))	C$_2$ (^2J (Pt–C))	C$_3$ (^3J (Pt–C))	C$_4$ (^4J (Pt–C))	C$_5$	C$_6$	
										NN = bpy
2a	3	26.48 (682.6)	33.72 ^{b}	15.72 (771.7)	33.62 (139.0)	33.86 ^{b}				155.00(C$_2$) 123.82(C$_3$) 139.16(C$_4$) 127.30(C$_5$) 149.20(C$_6$)
3a	4	26.71 (704.7)	34.08 ^{b}	18.12 (759.5)	29.17 (33.0)	34.25 ^{b}	34.36			155.23(C$_2$) 124.12(C$_3$) 139.36(C$_4$) 127.54(C$_5$) 149.56(C$_6$)
4a	5	26.37 (695.5)	33.77 (17.6)	19.38 (752.2)	30.01 (94.1)	29.91 (33.4)	32.74 (6.5)	34.19		154.85(C$_2$) 123.79(C$_3$) 139.03(C$_4$) 127.24(C$_5$) 149.24(C$_6$)
5a	6	26.35 (697.9)	33.77 (18.0)	19.80 (751.0)	30.51 (92.1)	30.50 (33.2)	28.00 (7.2)	32.96	34.22	154.90(C$_2$) 123.79(C$_3$) 138.99(C$_4$) 127.15(C$_5$) 149.20(C$_6$)
										NN = phen
2b	3	26.02 (688.0)	33.74 ^{b}	15.53 (771.6)	33.60 (138.6)	33.99 ^{b}				149.21(C$_2$) 126.04(C$_3$) 138.16(C$_4$) 128.12(C$_5$) 147.53(C$_{11}$) 131.43(C$_{12}$)
3b	4	25.98 (695.6)	33.81 (19.0)	17.51 (756.8)	28.68 (32.6)	33.96 ^{b}	34.04			149.31(C$_2$) 125.84(C$_3$) 137.92(C$_4$) 128.04(C$_5$) 146.64(C$_{11}$) 131.39(C$_{12}$)
4b	5	25.92 (700.3)	33.81 (18.8)	19.12 (750.9)	29.99 (93.99)	29.75 (33.1)	32.63 (8.5)	34.17		149.11(C$_2$) 125.94(C$_3$) 137.94(C$_4$) 128.03(C$_5$) 146.61(C$_{11}$) 131.33(C$_{12}$)
5b	6	25.94 (702.4)	33.83 (19.0)	19.56 (749.6)	30.55 (92.7)	30.39 (38.3)	27.92 (7.2)	32.91	34.28	149.12(C$_2$) 125.91(C$_3$) 138.09(C$_4$) 128.02(C$_5$) 146.67(C$_{11}$) 131.33(C$_{12}$)

[a] $n = 3$–6.
[b] Not measured.

mides (Fig. 3). 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 4. These reactions followed good second-order kinetics with remarkable reproducibility and the rates were not af-

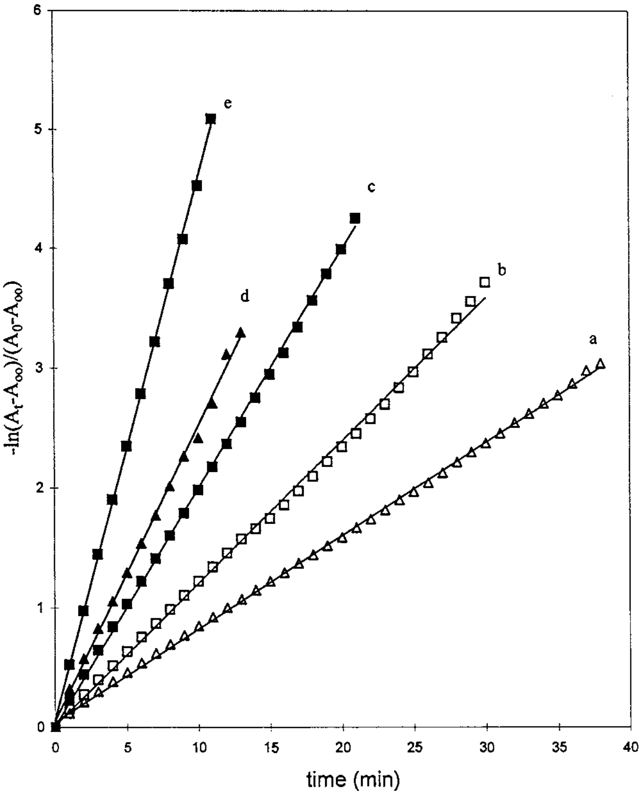
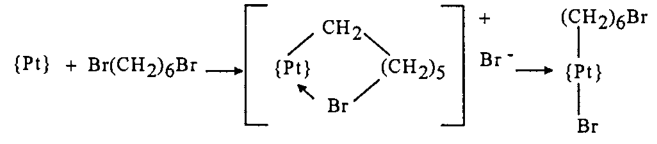


Fig. 2. First-order plots for the reaction of complex **1a** with dibromoalkanes at different temperatures: (a) $Br(CH_2)_3Br$, 0.32 M, $T=10°C$: (b) $Br(CH_2)_4Br$, 0.22 M, $T=30°C$: (c) $Br(CH_2)_6Br$, 0.11 M, $T=40°C$: (d) $Br(CH_2)_5Br$, 0.24 M, $T=40°C$: (e) $Br(CH_2)_6Br$, 0.21 M, $T=40°C$.

fected by radical scavengers. The rates of reactions in benzene were too slow to be measured and therefore they were measured in the more polar acetone solvent. Thus, these observations strongly suggest an S_N2 mechanism of oxidative addition of dibromides to the platina(II)cycles [3]. Also, the large negative values of $\Delta S^{\neq}$ are typical of oxidative addition by a common S_N2 mechanism which involves a polar transition state.

In the reaction of $[PtMe_2(phen)]$ with $I(CH_2)_nI$ ($n=3$–5) to give $[PtIMe_2\{(CH_2)_nI\}(phen)]$, it has been shown that the distant halogeno substituent has a small activating effect on the rate of reaction when $n=3$, and this effect falls off as the length of the alkyl chain increases and is absent when $n=5$ [3]. The complex **1a** reacted with $Br(CH_2)_nBr$ ($n=3$–5) in a similar trend. Thus, on average k_2 is ~80% greater when $n=3$ than when $n=4$ or 5 (with nearly the same k_2 values). However, when $n=6$ a considerable rate increase (by a factor of more than 2 compared to when $n=4$ or 5) is observed. We believe that in this case the chain length is probably large enough to somehow span across the coordination sites in the polar transition state, as depicted in Eq. (2), and to stabilize the resulting 6-coordinate transition state.



(2)

Complex **1a** reacts rapidly with $Br(CH_2)_2Br$ in acetone to give **6a** which is believed to involve the intermediacy of $[PtBr(CH_2CH_2CH_2CH_2)\{(CH_2)_2Br\}(bpy)]$, and the platinum atom presumably activates the C–Br bond of this intermediate to such a great extent that this complex further reacts with **1a** very rapidly to form **6a**. The reaction, using an excess of 1,2-dibromoethane followed a good first-order kinetics for ~80% of the reaction. From plots at different concentrations of $Br(CH_2)_2Br$ a second-order rate constant was obtained. Also the activation parameters were determined from measurement at different temperatures, and the data are given in Table 4. The $\Delta S^{\neq}$ is a large negative value and tests for free-radical mechanisms were negative. We thus believe that at least for the first 80% of the reaction, probably an S_N2 mechanism is operative. As expected, complex **1a** at different temperatures reacted 20–50 times faster with $Br(CH_2)_2Br$ than with $Br(CH_2)_3Br$. Overall, rate of reaction of complex **1a** with $Br(CH_2)_nBr$ follows the sequence $n=2 \gg 6 > 3 > 4 \cong 5$. For the products of these reactions, i.e. complexes **2a**–**5a**, using the $^1J(PtC)$ values of Pt–C_1 bond of polymethylene chain (see Section 2.1), we observed

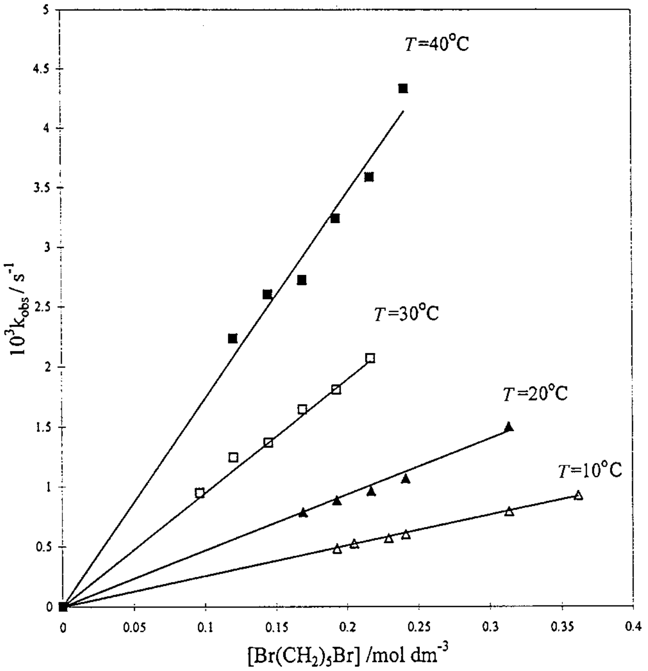


Fig. 3. Plots of first-order rate constants (k_{obs}/s^{-1}) for the reaction of complex **1a** with $Br(CH_2)_5Br$ in acetone at different temperatures versus concentration of $Br(CH_2)_5Br$.

Table 4
Second-order rate constants and activation parameters for reaction of [Pt($CH_2CH_2CH_2CH_2$)(NN)], **1**, with Br(CH_2)$_n$Br ($n = 2$–6) in acetone

n	10^3 k_2 (10°C) l mol^{-1} s^{-1}	10^3 k_2 (20°C) l mol^{-1} s^{-1}	10^3 k_2 (30°C) l mol^{-1} s^{-1}	10^3 k_2 (40°C) l mol^{-1} s^{-1}	E_a kJ mol^{-1}	$\Delta S^{\neq}$ (20°C)[a] J K^{-1} mol^{-1}
[Pt($CH_2CH_2CH_2CH_2$)(bpy)]						
2[b]	182.36 ± 4.19	244.76 ± 0.73	384.35 ± 33.83	485.51 ± 87.48	24.97 ± 1.97	-180 ± 6
3	3.73 ± 0.19	7.69 ± 0.34	16.08 ± 0.29	24.25 ± 2.69	46.88 ± 3.20	-134 ± 11
4	2.02 ± 0.14	4.54 ± 0.20	9.22 ± 1.32	17.01 ± 1.59	52.35 ± 1.18	-120 ± 4
5	2.61 ± 0.13	4.78 ± 0.55	8.69 ± 0.58	16.01 ± 3.48	44.40 ± 0.44	-146 ± 3
6	5.65 ± 0.91	9.09 ± 1.64	16.72 ± 0.72	30.19 ± 5.85	41.45 ± 2.37	-150 ± 8
[Pt($CH_2CH_2CH_2CH_2$)(phen)]						
2[b]	219.82 ± 28.29	314.66 ± 66.58	463.24 ± 45.10	657.54 ± 136.3	27.04 ± 0.59	-170 ± 2
4	5.18 ± 0.82	10.02 ± 1.69	17.19 ± 1.34	31.12 ± 4.30	43.59 ± 0.90	-143 ± 3
6	10.31 ± 1.31	17.31 ± 0.92	26.06 ± 1.14	33.04 ± 2.22	28.68 ± 2.69	-189 ± 9

[a] Obtained from the Arrhenius equation.

[b] Data are for the first 80% of the reaction (see text).

that Pt–C_1 bond strength increases as the chain length decreases. This may be related to the above rate sequence. Thus, when $n = 3$, the Pt–C_1 bond is stronger and the rate of reaction is greater than when $n = 4$ or 5. For $n = 6$, although the ^1J(Pt–C_1) value is smallest in the series, the greater rate, as mentioned above, is attributed to the stabilization of the intermediate as depicted in Eq. 2.The kinetics of reaction of complex **1b** with Br(CH_2)$_n$Br in acetone was studied similarly using the disappearance of the MLCT band at 475 nm to monitor the reaction. When $n = 3$, a precipitate was formed during the study and good measurements could not be performed. For the cases studied, i.e. when $n = 2$,4 and 6, the data are collected in Table 4. Overall, the trend of rates of reactions was similar to that obtained above for the bpy analogue complex **1a**, i.e. $n = 2 \gg 6 > 4$. The reactions were faster at different temperatures when compared to the corresponding reactions of the bpy analogue by a factor of 1.1–2.6, which further confirms the operation of the S_N2 mechanism in all cases.

3. Experimental

The ^1H- and ^{13}C-NMR spectra were recorded as $CDCl_3$ solutions on a Bruker Avance DPX 250 MHz spectrometer and TMS (0.00 ppm) was used as external reference. All the chemical shifts and coupling constants are in ppm and Hz, respectively. UV–vis spectra were recorded using a Philips PU 8750 spectrometer. Kinetic studies were carried out by using a Philips PU 8675 Vis spectrometer, with temperature control using a poly-science 900 constant temperature bath. Microanalyses were performed by the N.I.O.C. Research Institute of Petroleum Industry, Iran. Melting points were recorded on a Buchi 530 apparatus and are uncorrected. The complexes [{Pt($CH_2CH_2CH_2CH_2$)(μ-SEt_2)}$_2$] and [Pt($CH_2CH_2CH_2CH_2$)-(bpy)] were prepared as described previously [13].

3.1. Synthesis of [Pt($CH_2CH_2CH_2CH_2$)(phen)], **1b**

A solution of 1,10-phenanthroline (074 g, 0.013 mmol) in benzene (10 ml) was added to a solution of [{Pt($CH_2CH_2CH_2CH_2$)(μ-SEt_2)}$_2$] (0.366 g, 0.539 mmol) in benzene (30 ml). The mixture was stirred for 30 min in the absence of light, during which the solution 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 hexane and thoroughly dried in vacue. The yield was 80%, m.p. > 200°C (decomp.). Found: C, 43.9; H, 3.8; N, 6.2. Calc. for $C_{16}H_{16}N_2Pt$: C, 44.5; H, 3.7; N, 6.5%}. ^1H-NMR in C_6D_6: $\delta = 2.3$ [m, J(PtH) = 95 Hz, 4H of ring]; 3.6 [m, J(PtH) = 100 Hz, 4H of ring]; 9.1 [d, $^3J(H^2H^3) = 4.3$ Hz, ^3J(PtH) = 20 Hz, $2H^2$ of phen]; 6.9–7.3 [other phen protons].

3.2. Synthesis of [Pt_2Br_2($CH_2CH_2CH_2CH_2$)$_2$\{μ-(CH_2)$_2$\}(bpy)$_2$], **6a**

To a solution of [Pt($CH_2CH_2CH_2CH_2$)(bpy)] (0.167 g) in benzene (50 ml) a large excess of 1,2-dibromoethane (2.6 ml) was added. The reaction mixture was stirred in the absence of light for 1 h after which time an orange solution had developed. This was filtered to remove a small amount of precipitate. The solvent was removed under vacuum and the brown solid was washed with ether and dried in vacuo.

[Pt_2Br_2($CH_2CH_2CH_2CH_2$)$_2$\{μ-(CH_2)$_2$\}(phen)$_2$], **6b**, was prepared similarly using [Pt($CH_2CH_2CH_2CH_2$)-(phen)], except that the final brown residue was recrystallized from CH_2Cl_2/ether and dried in vacuo.

3.3. *[PtBr($CH_2CH_2CH_2CH_2$){(CH_2)$_3$Br}(bpy)]*, ***2a***

To a solution of [Pt($CH_2CH_2CH_2CH_2$)(bpy)] (0.25 g) in benzene (50 ml) a large excess of 1,3-dibromopropane (1 ml) was added. The reaction mixture was stirred in the absence of light for 8 h after which time a pale yellow solution had developed along with a small amount of precipitate. The solution was filtered and the solvent removed under vacuum. The solid residue was redissolved in a little CH_2Cl_2 (3 ml) and recovered by precipitation using ether (20 ml). The reaction in acetone, instead of benzene, gave a similar product, checked by ^{1}H-NMR. In a similar way were prepared other ω-monobromoalkyl platina(IV)-cyclopentane complexes [PtBr($CH_2CH_2CH_2CH_2$){(CH_2)$_n$Br}(NN)], **2**–**5**.

3.4. *Kinetic studies of the reaction of [Pt($CH_2CH_2CH_2CH_2$)(NN)],* ***1****, with Br(CH_2)$_n$Br, $n = 3$–6*

A solution of [Pt($CH_2CH_2CH_2CH_2$)(bpy)], **1a**, in acetone (3 ml, 4.88×10^{-4} M) in a cuvette was thermostated at 20°C and a known excess of Br(CH_2)$_5$Br was added using a microsyringe. After rapid stirring, the absorbance at $\lambda = 480$ nm was collected with time and a graph of $-\ln(A_t - A_\infty/A_0 - A_\infty)$ versus time gave a good straight line (Fig. 2) from which the observed first-order rate constants and standard deviations were obtained. A plot of k_{obs} versus [Br(CH_2)$_5$Br] was linear (Fig. 3), and the slope gave the second-order rate constant. The same method was used at other temperatures, and activation parameters were obtained from the Arrhenius equation. In a similar way the rate constants and activation parameters were determined for the reaction of [Br(CH_2)$_3$Br] and [Br(CH_2)$_4$Br] and [Br(CH_2)$_6$Br] with complex **1a** and the results are collected in Table 4. The reactions of [Br(CH_2)$_4$Br] and [Br(CH_2)$_6$Br] with complex [Pt($CH_2CH_2CH_2CH_2$)(phen)], **1b**, were monitored in a similar way but with $\lambda = 475$ nm.

3.5. *Kinetic studies of the reaction of Br(CH_2)$_2$Br with complex* ***1***

The reaction between [Pt($CH_2CH_2CH_2CH_2$)(bpy)], **1a**, (3 ml, 4.88×10^{-4} M) and Br(CH_2)$_2$Br (7.58×10^{-2} M) in acetone at 20°C was followed by monitoring the decay with time of the band due to complex **1a** at $\lambda = 480$ nm in the UV–vis spectrum, in a similar way as described in Section 3.4. A plot of $-\ln(A_t - A_\infty/A_0 - A_\infty)$ versus time was linear for $\sim 80\%$ completion of the reaction. The procedure was repeated for the same concentration of **1a** but varying the concentration of Br(CH_2)$_2$Br. Using the linear portion of these plots an overall second-order rate constant was determined for the reaction. The same method was used at other temperatures, and activation parameters were obtained from the Arrhenius equation. The reaction of Br(CH_2)$_2$Br with [Pt($CH_2CH_2CH_2CH_2$)(phen)], **1b**, was monitored similarly but with $\lambda = 475$ nm. The data are collected in Table 4.

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