Journal of Molecular Structure 1079 (2015) 281–290

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: www.elsevier.com/locate/molstruc

Easy oxidative addition of the carbon–halogen bond by dimethylplatinum(II) complexes containing a related series of diimine ligands: Synthesis, spectral characterization and crystal structure

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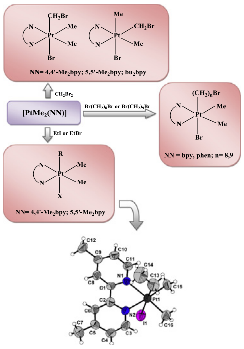
HIGHLIGHTS

- New alkyl and haloalkyl organoplatinum(IV) complexes were prepared.
- The organoplatinum(IV) products were fully characterized by NMR spectroscopy.
- There is a characteristic sequence in the polymethylene chain region in NMR spectra.
- The crystal structure of *trans*-[$PtMe_2EtI(4,4'-Me_2bpy)$] is reported.

GRAPHICAL ABSTRACT

The oxidative addition of primary ethyl bromide and iodide to organoplatinum(II) complexes [$PtMe_2(NN)$] {NN = 4,4′-Me_2bpy (4,4′-dimethyl-2,2′-bipyridine); 5,5′-Me_2bpy (5,5′-dimethyl-2,2′-bipyridine)} has been investigated. On the other hand, the reaction of [$PtMe_2(NN)$] {NN = bu_2bpy (4,4′-di-*tert*-butyl-2,2′-bipyridine); 4,4′-Me_2bpy; 5,5′-Me_2bpy} with CH_2Br_2 gave a mixture of *cis* and *trans*-[$PtMe_2(CH_2Br)Br(NN)$] formed by the oxidative addition of one of the C–Br bonds. The reaction of organoplatinum(II) complexes [$PtMe_2(NN)$] (NN = bpy, phen) with 1,8-dibromooctane or 1,9-dibromononae resulted in the formation of the complexes $PtMe_2\{(CH_2)_nBr\}Br(NN)$] ($n$ = 8–9). The crystal structure of *trans*-[$PtMe_2EtI(4,4'-Me_2bpy)$] is reported.



ARTICLE INFO

Article history:
Received 10 August 2014
Received in revised form 16 September 2014
Accepted 16 September 2014
Available online 8 October 2014

Keywords:
Platinum
Imine
Oxidative addition

ABSTRACT

Dimethylplatinum(II) complexes [$PtMe_2(NN)$] {NN = 4,4′-Me_2bpy (4,4′-dimethyl-2,2′-bipyridine); 5,5′-Me_2bpy (5,5′-dimethyl-2,2′-bipyridine)} were reacted with alkyl halides (RX = EtI, EtBr) to yield the organoplatinum(IV) complexes [$PtMe_2RX(NN)$]. On the basis of NMR data, the platinum(IV) product of each reaction contains almost exclusively the *trans* isomer but small traces of the *cis* isomers are also observed. On the other hand, the reaction of [$PtMe_2(NN)$] {NN = bu_2bpy (4,4′-di-*tert*-butyl-2,2′-bipyridine); 4,4′-Me_2bpy; 5,5′-Me_2bpy} with CH_2Br_2 gave a mixture of *cis* and *trans*-[$PtMe_2(CH_2Br)Br(NN)$] formed by the oxidative addition of one of the C–Br bonds. The formation of the *cis* isomer increases in the order of 5,5′-Me_2bpy > bu_2bpy > 4,4′-Me_2bpy. The reaction of [$PtMe_2(NN)$] {NN = bpy (2,2′-bipyridine), phen (1,10-phenanthroline)} with 1,8-dibromooctane or 1,9-dibromononane afforded the mononuclear complexes [$PtMe_2\{(CH_2)_nBr\}Br(NN)$] ($n$ = 8–9). The products were fully characterized by

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http://dx.doi.org/10.1016/j.molstruc.2014.09.049

NMR
Crystal structure

elemental analysis, ^{1}H, ^{13}C, HH COSY, HMQC, DEPT and DEPTQ-135 NMR spectroscopy. The crystal structure of [PtMe$_2$EtI(4,4′-Me$_2$bpy)] reveals that Pt(IV) atom is six-coordinated in a slightly distorted octahedral geometry with the ethyl group *trans* to iodide.

Introduction

There has been a great interest to study the oxidative addition of organoplatinum(II) complexes [1–6]. Oxidative addition of a variety of polar and nonpolar reagents including alkyl halide, aryl halide, peroxide, Sn–X, aryl-S and Bi–X to organoplatinum(II) compounds have been reported [7–12]. The organoplatinum polymers and dendrimers can be prepared by oxidative addition using substituted diimine ligands containing bromoalkyl [13,14]. Haloalkyl complexes of transition metals can be considered as functional alkyl compounds of transition metals. These complexes are of particular interest since they can be used as precursors for the preparation of methylene-bridged compounds [15]. On the other hand, the chemistry of haloalkyl complexes of transition metals have been attracted due to their applications in many catalytic processes such as Fischer–Tropsch synthesis which involves the polymerization of methylene group on a metal surface [16].

The chemistry of platinum complexes bridged by organic donors of (CH$_2$)$_n$ is less developed due to the bulky nature of the platinum atom. A common synthetic method involves the reaction between platinum(II) complex and α,ω-dihaloalkanes. For example, several binuclear organoplatinum(II) complexes containing Pt(CH$_2$)$_n$Pt units have been reported [10,17]. It has been known that the reactivity of dibromoalkanes toward platina(II)cycloalkane depends upon the chain length of dibromoalkanes [10]. On the other hand, oxidative addition of alkyl halides to electron-rich organoplatinum(II) complexes have been extensively studied and is considered as a key step in many catalytically important chemical processes [18–21]. It has been shown that the electronic and steric effects are influenced on the reactivity of the organoplatinum(II) complexes toward oxidative addition reactions [22].

The reaction of chlorinated solvents such as dichloromethane and chloroform and carbon tetrachloride with the dimethylplatinum(II) compounds yields the corresponding chloromethyl, dichloromethyl and trichloromethyl derivatives of dimethylplatinum(IV) compounds as a mixture of the *cis* and *trans* isomers by the oxidative addition of C–Cl bond [23–25].

Interestingly, the activation of C–H bond by platinum(II) complexes is of great current interest [26–29]. The activation occurs by oxidative addition or by metathesis. For example, the carbon–hydrogen bond cleavage of anisole was carried out by the reaction of dimethylplatinum(II) complex [PtMe$_2$(NN)] {NN = (2-C$_6$H$_4$N)$_2$CO} by B(C$_6$H$_5$)$_3$ [30]. In addition, C–H activation of 6-substituted-2,2′-bipyridine has been reported by electron rich Pt(II) species to yield cyclometalated platinum compound [31].

Although, there are a variety of oxidative addition reactions of organoplatinum(II) complexes in literature, but there are still unusual reactions which can be useful to prepare a wide range of functionalized organoplatinum complexes [12].

We have previously examined the oxidative addition of a wide range of organic halides to organoplatinum(II) complexes [32]. In continuation of our interest in the investigation of oxidative addition of halo and dihaloalkanes to organoplatinum complexes, we have used several substituted derivatives of 2,2′- bipyridine containing alkyl groups to increase the solubility of the Pt(II) complexes.

Experimental

General remarks

The preparation of dimethylplatinum(II) compounds were performed under an atmosphere of argon. Diethyl ether was distilled over sodium/benzophenone ketyl. All other reagents were used without further purification. Elemental analyses were performed by Perkin–Elmer 2400 II and Thermo Finnigan Flash Ea 1112 elemental analyzers. The ^{1}H, ^{13}C{^{1}H}, HHCOSY, HMQC, DEPT and DEPTQ-135 NMR spectra were recorded using Bruker DPX 300, Biospin GmbH 400 and 500 MHz spectrometers. All the chemical shifts and coupling constants are reported in ppm and Hz, respectively. Chemical shifts were referenced to residual solvent peaks. UV–visible measurements were performed using a Philips PU 8675 spectrophotometer at room temperature. The starting complexes [PtMe$_2$(NN)] {NN = 4,4′-Me$_2$bpy (**1**); 5,5′-Me$_2$bpy (**2**); bu$_2$bpy (**3**); bpy (**4**); phen (**5**)} were prepared according to known procedure [33–35].

Synthesis of [PtMe$_2$EtI(4,4′-Me$_2$bpy)], **6**

To a solution of [PtMe$_2$(4,4′-Me$_2$bpy)] (80 mg, 0.19 mmol) in acetone (30 mL) was added a large excess of ethyl iodide (0.3 mL, 12.0 M). The reaction mixture was stirred for 1 h after which a pale yellow solution had developed. The solvent was removed at reduced pressure and the residue was solidified using CH$_2$Cl$_2$/n-hexane to give a pale yellow solid. Yield: 70%; m.p. 230–232 °C (dec.). Anal. Calc. for C$_{16}$H$_{23}$IN$_2$Pt: C, 33.99; H, 4.10; N, 4.96. Found: C, 34.11; H, 3.80; N, 5.70%. NMR data in CDCl$_3$: δ(^{1}H) (*trans* isomer) 2.54 (s, 6H, CH$_3$ of Me$_2$bpy), 1.47 [s, 6H, ^{2}J(PtH) = 70.8 Hz, Pt–Me], 0.03 [t, 3H, ^{3}J(PtH) = 69.1 Hz, ^{3}J(HH) = 8.0 Hz, CH$_3$ group of Et], 1.42 [q, 2H, ^{2}J(PtH) not resolved, ^{3}J(HH) = 8.0 Hz, PtCH$_2$]; 4,4′-Me$_2$bpy protons: 7.42 (dd, 2H, ^{3}J(HH) = 5.4 Hz, ^{4}J(HH) = 1.1 Hz, H^{5}), 8.07 (s, 2H, H^{3}), 8.78 (d, 2H, ^{3}J(PtH) = 22.8 Hz, ^{3}J(HH) = 5.8 Hz, H^{6}); Resolved ^{1}H NMR data for *cis* isomer: 2.19 (s, 3H, CH$_3$ of Me$_2$bpy), 1.53 (m, 3H, CH$_3$ group of Et), 0.60 [s, 3H, ^{2}J(PtH) = 74.0 Hz, Pt–Me], 0.63 [s, 3H, ^{2}J(PtH) = 73.8 Hz, Pt–Me]; δ(^{13}C) (*trans* isomer) 21.6 (s, CH$_3$ of 4,4′-Me$_2$bpy), −4.9 [s, ^{1}J(PtC) = 697 Hz, Pt–Me], 20.1 [s, ^{1}J(PtC) = 669 Hz, PtCH$_2$], 14.9 [s, ^{2}J(PtC) = 37 Hz, CH$_3$ group of Et]; 4,4′-Me$_2$bpy carbons: 154.8 (C$_2$), 124.1 (C$_3$, ^{3}J(PtC) = 9 Hz), 150.6 (C$_4$), 127.5 (C$_5$, ^{3}J(PtC) = 14 Hz), 146.7 (C$_6$, ^{2}J(PtC) = 15 Hz); Resolved ^{13}C NMR data for *cis* isomer: 21.5 (s, CH$_3$ of 4,4′-Me$_2$bpy), −6.5 [s, ^{1}J(PtC) = 667 Hz, Pt–Me], 7.8 [s, ^{1}J(PtC) = 682 Hz, Pt–Me], 6.1 [s, ^{1}J(PtC) = 667 Hz, PtCH$_2$]. Crystals suitable for X-ray analysis were grown from the CH$_2$Cl$_2$/n-hexane solution.

Synthesis of [PtMe$_2$EtBr(4,4′-Me$_2$bpy)], **7**

Following the same procedure as the preparation of **6**, the reaction of [PtMe$_2$(4,4′-Me$_2$bpy)] (100 mg, 0.24 mmol) and a large excess of ethyl bromide (0.4 mL, 13.3 M) in acetone (30 mL) gave a pale yellow solid after 1 day. Yield: 47%; m.p. 265–267 °C (dec.). Anal. Calc. for C$_{16}$H$_{23}$BrN$_2$Pt: C, 37.07; H, 4.47; N, 5.40. Found: C, 37.44; H, 4.39; N, 5.78%. NMR data in CDCl$_3$: δ(^{1}H) (*trans* isomer) 2.54 (s, 6H, CH$_3$ of Me$_2$bpy), 1.35 [s, 6H, ^{2}J(PtH) = 70.4 Hz, Pt–Me], 0.13 [t, 3H, ^{3}J(PtH) = 65.0 Hz, ^{3}J(HH) = 7.5 Hz, CH$_3$ group of Et], 1.41 [m, 2H, ^{2}J(PtH) not resolved, PtCH$_2$]; 4,4′-Me$_2$bpy protons: