Csp3-Cl bond Activation Promoted by a Methylplatinum(II) Complex: Synthesis, Structural Characterization, and Density Functional Approach to Oxidative Addition Reaction with Dichloromethane

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Dimethylplatinum(II) complex [PtMe$_2$(pbt)], 1, with pbt = 2-(2-pyridyl)benzothiazole ligand, can react with dichloromethane solvent to give the corresponding organoplatinum(IV) complex [Pt(Cl)(CH$_2$Cl)Me$_2$(pbt)]. The reaction gives exclusively *trans* addition product in which Cl and CH$_2$Cl are located trans to each other. The suggested mechanism for this oxidative addition reaction was computationally investigated and related species during this process are proposed. DFT calculations show that the reaction proceeds through a transition state with the energy barrier of 97.5 kJ mol^{-1}. Attempts to grow crystals of the Pt(II) complex 1 in CH$_2$Cl$_2$/*n*-hexane mixture of solvents forms the dichloro Pt(IV) complex [PtCl$_2$Me$_2$(bpt)], which its structure is determined by X-ray crystallography.

INTRODUCTION

Oxidative addition of small organic molecules to d^8 square planar complexes such as Pd(II) and Pt(II) complexes is of great interest because this kind of reaction is an elementary reaction, usually first step, in many catalytic processes [1-3]. Among small organic compounds, the reactions of alkyl halides such as MeI and EtI containing C-I bond, with Pd(II) and Pt(II) complexes are widely studied [4-11]. In comparison to C-I bond, limited studies on the activation of C-Cl bond have been previously reported [12-14]. This is very important because most of common organic solvents such as chloroform and dichloromethane include the C-Cl bond. For example, Puddephatt *et al.* reported [13] the oxidative addition reaction of dichloromethane and chloroform to electron rich dimethylplatinum(II) complexes [PtMe$_2$(N^N)], where N^N is diimine ligands such as 2,2′-bipyridine and 1,10-phenanthroline. The activation of C-Cl bonds

in CCl$_4$, CHCl$_3$, CH$_2$Cl$_2$, and CH$_3$Cl by [(κ^2-*P,N*)-Ph$_2$PCH$_2$CH$_2$NMe$_2$]PtMe$_2$ were also investigated by Schubert *et al.* [14].

This paper describes the reaction of CH$_2$Cl$_2$ solvent with [PtMe$_2$(pbt)] including an unsymmetrical supporting ligand pbt (= 2-(2-pyridyl)benzothiazole)), leading to organoplatinum(IV) products, and the structure determination on a dichloroplatinum(IV) complex. Computational study is also used to investigate the suggested mechanism.

EXPERIMENTAL

General Remarks

^{1}H NMR spectrum in CDCl$_3$ was recorded using Bruker Avance DPX 250 spectrometer (with TMS as reference). The chemical shifts and coupling constants are in ppm and Hz, respectively. The microanalyses were performed using a ThermoFinigan Flash EA-1112 CHNSO rapid elemental analyzer and melting points were recorded on a Buchi 530 apparatus. Kinetic studies were carried out by using a

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Perkin-Elmer Lambda 25 spectrophotometer with temperature control using an EYELA NCB-3100 constant-temperature bath. 2-(2-Pyridyl)benzothiazole (abbreviated as pbt) was purchased from commercial sources and the precursor complex [PtMe₂(pbt)], 1 [15] was prepared according to literature review.

Synthesis of [PtCl(CH₂Cl)Me₂(pbt)], 2

[PtMe₂(pbt)], 1, (0.03 g, 0.069 mmol) was added to 20 mL CH_2Cl_2. The reaction mixture was stirred at room temperature for 24 h under dark condition. The solvent was evaporated and the residue was washed with cold diethyl ether and dried under vacuum to give final product 2. Yield: 63%. Anal. Calcd. for $C_{15}H_{16}Cl_2N_2PtS$: C 34.5, H 3.1, N 5.4, S 6.1. Found: C, 34.4; H, 3.0; N, 5.2; S, 5.9. m. p.: 241 °C. ¹H NMR data in CDCl₃: δ 1.60 (s, $^2J_{PtH}$ = 72.5 Hz, 3H, Me *trans* to N of pyridyl ring), 1.80 (s, $^3J_{PtH}$ = 75.0 Hz, Me *trans* to N of benzothiazole ring), 3.62 (d, $^2J_{HH}$ = 7.5 Hz, $^2J_{PtH}$ = 45.0 Hz, , 1H of CH₂Cl group), 3.83 (d, $^2J_{HH}$ = 7.5 Hz, $^2J_{PtH}$ = 60.0 Hz, , 1H of CH₂Cl group) aromatic protons 7.58-7.75 (m, 3H, H⁶ , H⁷ and H⁸) : 8.02 (d, $^3J_{HH}$ = 8.1, 1H, H⁵),8.16 (m, 2H, H² and H³), 8.52 (d, $^3J_{HH}$ = 8.0 Hz, 1H, H⁴), 8.92 (d, $^3J_{PtH}$ = 11.4 Hz, $^3J_{HH}$ = 5.0, 1H, CH group adjacent to coordinated pyridyl N atom).

Crystallographic Data

Single crystal X-ray diffraction data for complex 3 were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromator with a Mo Kα X-ray source (λ = 0.71073 Å). The crystals were mounted on a cryoloop under Paratone-N oil and kept under nitrogen. Absorption correction of the data was carried out using the multiscan method SADABS [16]. Subsequent calculations were carried out using SHELXTL [17]. Structure determination was done using intrinsic methods. Structure solution, refinement, and creation of publication data was performed using SHELXTL. Crystallographic information is reported in Table 1. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Center, No. CCDC 2013003. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, Email: deposit@ccdc.cam.ac.uk, or www.ccdc.cam.ac.uk.
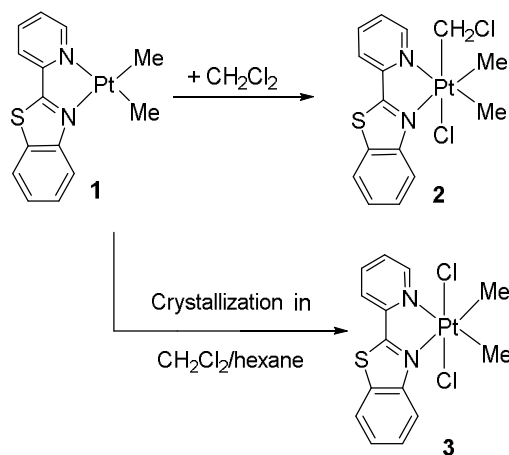
Computational Details

Gaussian 09 was used[18] to fully optimize the compounds using B3LYP level of DFT. The starting structures were created by the GaussView program and optimized using the CPCM solvation method [19] as implemented in the Gaussian program. The effective core potential of Hay and Wadt with a double-ξ valence basis set (LANL2DZ) was chosen to describe Pt. [20] The 6-31G(d) basis set was used for all other atoms [21]. Frequency calculations were carried out at the same level of theory to identify whether the calculated stationary point is a minimum (zero imaginary frequency) or a transition-state structure (one imaginary frequency). All data were calculated at standard temperature and pressure (298.15 K and 1.0 atm.). We have also checked that imaginary frequencies exhibit the expected motion.

RESULTS AND DISCUSSION

Compounds reported in this work (2-3) are synthesized as outlined in Scheme 1. As reported, Puddephatt and co-workers [13] have investigated the oxidative addition reactions of some platinum(II) complexes with CH_2Cl_2 and CHCl₃. For example, Pt(II) complexes such as [PtMe₂(N^N)] (N^N = 2,2′-bipyridine or 1,10-phenanthroline) were reacted with CH_2Cl_2 and CHCl₃, to give the Pt(IV) products, [Pt(Cl)(CH₂Cl)Me₂(N^N)] and [Pt(Cl)(CHCl₂)Me₂(N^N)], respectively. In the present work, the oxidative addition of CH_2Cl_2, as both reagent and solvent, to the Pt(II) complex [PtMe₂(pbt)], 1, cleanly gave pale yellow solutions at room temperature under dark condition from which the trans addition platinum(IV) product [PtCl(CH₂Cl)Me₂(pbt)], 2, was obtained in 63% yield. Complex 2 is a yellowish solid that is characterized by elemental analysis and NMR spectroscopy. In the ¹H NMR spectrum of the complex 2 (Fig. 1), the two singlet resonances at δ = 1.60 and 1.80 ppm were assigned to the two different methyl ligands being *trans* to the two different N ligating atoms of the pbt chelating ligand with $^2J_{PtH}$ = 72.5 and 75.0 Hz, respectively. These $^2J_{PtH}$ values are smaller than corresponding values reported for the methyl

Table 1. Crystal and Structure Refinement for Complex 3

Empirical formula	$C_{14}H_{14}Cl_2N_2PtS$	Volume (Å^3)	3250.8(11)
Formula weight	508.32	Z	8
Temperature (K)	298(2) K	Density (calculated) (mg m^{-3})	2.077
Wavelength (Å)	0.71073	Absorption coefficient (mm^{-1})	9.080
Crystal system	Orthorhombic	F(000)	1920
Space group	Pbca	Theta range for data collection	1.54 to 29.26°
Unit cell dimensions		Reflections collected	14909
a (Å)	9.4654(19)	Independent reflections, [R(int.)]	4372 [0.0447]
b (Å)	12.968(3)	Data/restraints/parameters	4372 / 0 / 183
c (Å)	26.483(5)	Goodness-of-fit on F^2	1.036
α (°)	90	R1/wR2 [I > 2sigma(I)]	0.0868/0.2031
β (°)	90		
γ (°)	90		

Scheme 1. Reactions studied in the present work

groups of complex 1 ($^2J_{PtH}$ = 88.8 and 89.6, respectively) [15], confirming the oxidation of Pt(II) center to Pt(IV) by dichloromethane. Due to the different chemical environments, the methylene protons of the CH_2Cl group are diastereotopic and appeared as two doublets at δ = 3.62 ($^2J_{HH}$ = 7.5 Hz, $^2J_{PtH}$ = 45.0 Hz) and δ = 3.83 ($^2J_{HH}$ = 7.5 Hz, $^2J_{PtH}$ = 60.0 Hz). The doublet signal at 8.92 ppm showing a $^3J_{PtH}$ coupling of 11.4 (with $^3J_{HH}$ = 5.0) is attributed to the proton of CH group adjacent to nitrogen ligating atom of the pyridyl group of the pbt ligand.
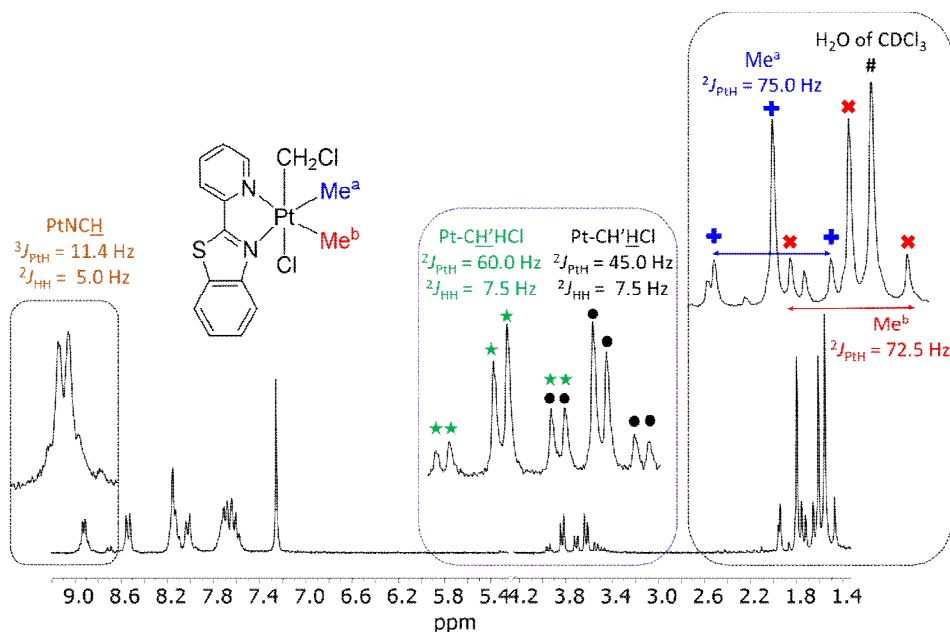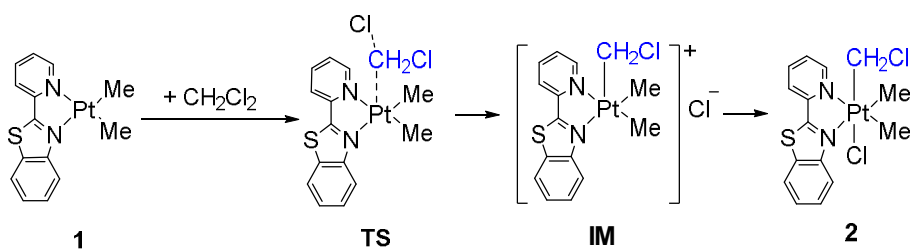
Fig. 1. (A) ^{1}H NMR spectrum of complex 2 in CDCl$_3$. Peak assignments and platinum satellites are shown for the complex.

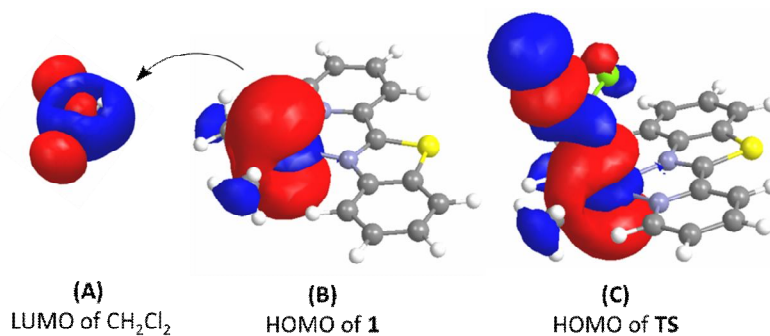*Scheme 2.* Proposed mechanism for oxidative addition of complex 1 with CH$_2$Cl$_2$

(A)
LUMO of CH$_2$Cl$_2$

(B)
HOMO of **1**

(C)
HOMO of **TS**

Fig. 2. S$_N$2 oxidative addition reaction between complex 1 and dichloromethane by interaction of LUMO of CH$_2$Cl$_2$ (A) and HOMO of 1 (B) to form TS (C).

It is experimentally and computationally accepted that organic halides oxidative addition to square planar Pt(II) compounds normally occurs in S_N2 fashion [22-23] including nucleophilic substitution of halide by Pt center to form a Pt-C bond, followed by subsequent coordination of halide to form an octahedral Pt(IV) product. To get more insight to the oxidation of 1 to 2, we have computationally investigated this reaction using DFT calculations. The possible structures of the reactants, transition states, intermediates and products for the reaction of complex 1 with CH_2Cl_2 are shown in Scheme 2.

As shown in Scheme 2 and Fig. 2, the computational study proposed the formation of transition state TS including Pt-CH_2Cl-Cl fragment. First, the Pt center of 1 attacks on carbon atom of CH_2Cl_2 to simultaneously remove the chloride ion and form Pt-CH_2Cl bond. TS includes the Pt-CH_2Cl-Cl moiety with bond angle of 154.6°, showing a deviation from the linear arrangement. The Cl and H atoms of CH_2Cl group are located in the equatorial plane of the 5-coordinated carbon atom to give almost a trigonal bipyramidal geometry around the carbon of CH_2Cl group. Formation of TS accompanied by the significant changes for Cl-CH_2Cl and Pt-CH_2Cl bonds. As shown in Fig. 3, Cl···CH_2Cl distance changes from 1.795 Å in CH_2Cl_2 to 2.373 Å in TS. In contrast, the Pt···CH_2Cl distance changes from far, at the beginning of the reaction, to 2.615 Å in TS. The formation of TS followed by the formation of the ionic 5-coordinate [Pt(CH_2Cl)Me$_2$(pbt)]$^+$ intermediate, IM. DFT calculation suggests a square pyramidal geometry for IM with the CH_2Cl group in the apical position and with the chloride ion situated on the outer sphere of Pt complex. The Pt-CH_2Cl bond length in IM is about 2.041 Å, shorter than that in TS (2.615 Å), showing the completeness of bond formation between Pt center and incoming CH_2Cl group. The last step includes the coordination of the free chloride ion to the Pt center of IM to form the final Pt(IV) complex 2 in which the geometry of the ligands around the Pt center is octahedral (see Fig. 3). It is clear that the bond distances of Pt(II) center with ligands in complex 1 (with dsp^2 hybridization) should be shorter than those of the corresponding Pt(IV) product 2. For example, the two Pt(II)-Me bond distances in complex 1 is 2.054 and 2.046 Å, while those for corresponding Pt(IV)-Me ligands are 2.068 and 2.065 Å, in complex 2.

In an attempt to grow crystals of the new starting Pt(II) complex 1 in CH_2Cl_2/n-hexane mixture of solvents, the appropriate single crystals of the new Pt(IV) complex [PtCl$_2$Me$_2$(bpt)], 3, was obtained and determined by X-ray crystallography. The compound 3 should be resulted from chlorine atom abstraction as shown in Scheme 3. A reaction with solvent should be occurred to give 3. A similar mechanism is suggested for this process [14,24-26]. Formation of a dichloro platinum(IV) complex has also been proposed during the reaction of the Pt(II) complexes [Pt(Cl)$_2$(bpy)] (bpy = 2,2′-bipyridine) and [PtMe$_2$(dpm)] (dpm = di-2-pyridylmethane) with CHCl$_3$ [13]. The structure of complex 3 (see Fig. 4) confirms that the pbt chelating ligand is coordinated to the Pt center *via* the two N atoms while the S atom of benzothiazole moiety is stayed uncoordinated. The N2-Pt1-N1 angle, 75.9(4)°, is considerably less than the ideal value of 90°. The two chlorine ligands are located mutually *trans* to each other, with the angle C1(2)-Pt1-Cl(1) = 162.5(3)° being significantly less than the ideal angle of 180° and leaning towards the bpt chelate with for example the C1(2)-Pt1-N2 angle being 76.6(3)°. The Pt1-C(13) distance of 2.039(17) Å seems to be slightly shorter than that of the Pt1-C(14) of 2.06(2) Å and we tentatively assign this to be due to the *trans* influence of N ligating atom of pyridyl group being marginally greater than that of the benzothiazole moiety. This may help us in assigning the NMR data for complex 2 in which the $^2J_{PtH}$ values in the ^{1}H NMR spectrum of the complex 2 for the two methyl ligands are 72.5 Hz and 75.0 Hz, complying with the former being for the signal of the Me ligand being *trans* to the N ligating atom of pyridyl group.

CONCLUSIONS

The reaction of dimethyplatinum(II) complex [PtMe$_2$(pbt)], 1, with dichloromethane, as both solvent and reagent, formed a platinum(IV) complex in which the carbon-chloride bond in CH_2Cl_2 was oxidatively added to Pt center. The Pt(IV) complex 2 included two new bonds, Pt-Cl and Pt-CH_2Cl, which are trans to each other. The computational study suggests an S_N2 mechanism which is usually accepted for oxidative addition of small organic molecules to square planar platinum complexes [22-23]. In
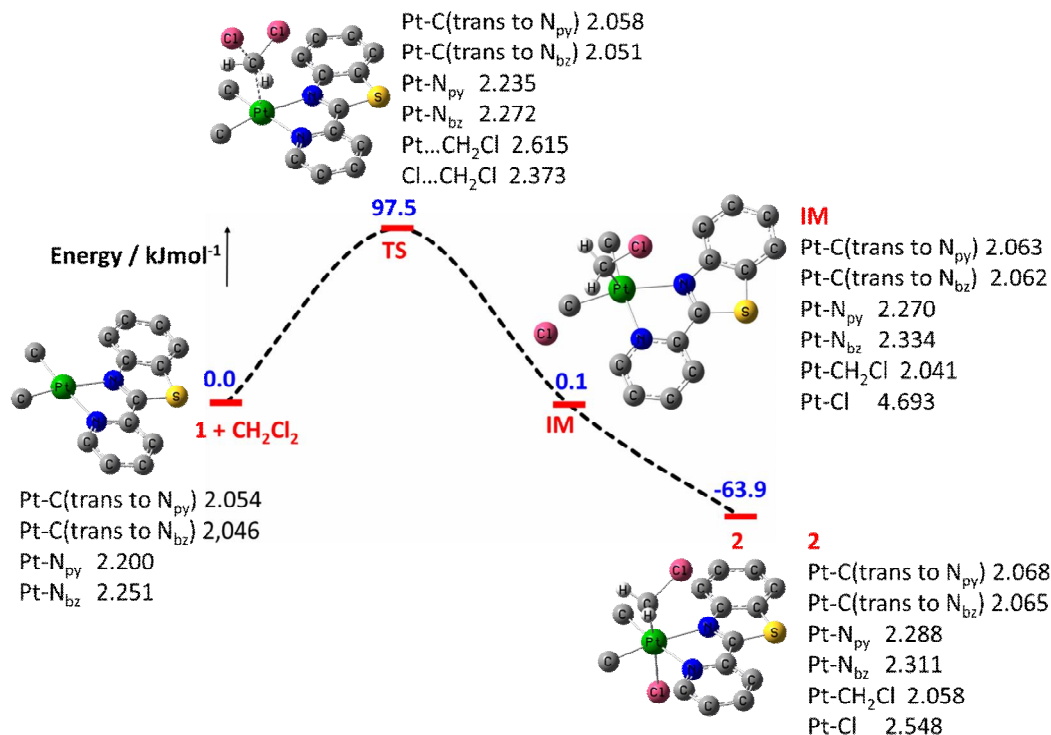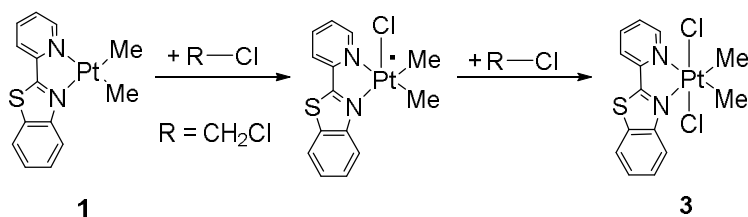
Pt-C(trans to N_{py}) 2.058
Pt-C(trans to N_{bz}) 2.051
Pt-N_{py} 2.235
Pt-N_{bz} 2.272
Pt...CH_2Cl 2.615
Cl...CH_2Cl 2.373

97.5
TS

IM
Pt-C(trans to N_{py}) 2.063
Pt-C(trans to N_{bz}) 2.062
Pt-N_{py} 2.270
Pt-N_{bz} 2.334
Pt-CH_2Cl 2.041
Pt-Cl   4.693

Energy / kJmol^{-1}

0.0

1 + CH_2Cl_2

0.1
IM

Pt-C(trans to N_{py}) 2.054
Pt-C(trans to N_{bz}) 2,046
Pt-N_{py} 2.200
Pt-N_{bz} 2.251

-63.9

2   2
Pt-C(trans to N_{py}) 2.068
Pt-C(trans to N_{bz}) 2.065
Pt-N_{py} 2.288
Pt-N_{bz} 2.311
Pt-CH_2Cl 2.058
Pt-Cl   2.548

Fig. 3. Energy profile for oxidative addition of 1 with CH_2Cl_2. The optimized structures of the species involved in the reactions are shown. Selected bond distances (Å) are also shown. The summation of the energies of the 1 and CH_2Cl_2 was considered to be zero, and the other energy levels vary relative to this.

Scheme 3. Suggested route for formation of complex 3 from 1 in CH_2Cl_2 solvent

this mechanism, the Pt center of complex 1 as a nucleophile donates electrons to the σ*-orbital of the Cl_2HC-Cl bond by attacking the carbon atom of CH_2Cl_2 to eliminate the Cl atom of Cl_2HC-Cl. The polar transition states obtained for these reactions contain Pt-CH_2Cl-Cl arrangements. The cationic five-coordinate intermediate [Pt(CH_2Cl)Me_2(pbt)]$^+$, has the square pyramidal geometries. Recoordination of free

chloride to the empty site of the cationic intermediate forms the product [PtCl(CH_2Cl)Me_2(pbt)], 2. The energy barrier for the rate determining step, i.e. formation of transition state, was calculated to be 97.5 kJ mol^{-1}. Attempts to get a suitable crystal for Pt(II) complex 1 in the mixture of CH_2Cl_2/n-hexane, was ended up to a new dichloro platinum(IV) complex [PtCl$_2$Me$_2$(bpt)], 3.
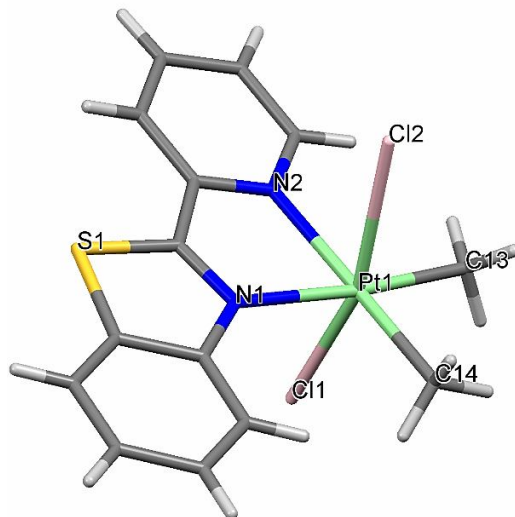
Fig. 4. (A) Crystal structure of the new Pt(IV) complex [PtCl₂Me₂(bpt)], 3. Selected geometrical parameters (Å and °): Pt1-N1 2.198(11), Pt1-N2 2.204(12), Pt1-C(13) 2.039(17), Pt1-C(14) 2.06 (2), Pt1-Cl(2) 2.824(7), Pt1-Cl(1) 2.647(9), N2-Pt1-N1 75.9(4), N2-Pt1-Cl(1) 86.0(4), N2-Pt1-C(14) 176.4(10), N2-Pt1-C(13) 97.5(7), Cl(1)-Pt1-C(13) 91.5(8), Cl(1)-Pt1-C(14) 96.3(11), C(14)-Pt1-C(13) 85.2 (8), Cl(2)-Pt1-C(13) 93.2(7), Cl(2)-Pt1-C(14) 100.9(11), C1(2)-Pt1-Cl(1) 162.5(3), C1(2)-Pt1-N1 85.3(3), C1(2)-Pt1-N2 76.6(3), N1-Pt1-Cl(1) 88.1(4), N1-Pt1-C(14) 101.4(7), N1-Pt1-C(13) 173.4(7).

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