Title	The Synthetic and Structural Study of Platinum (II) Complexes Derived from 2-Substituted Benzothiazoline
Author(s)	長澤, 五十六
Citation	大阪大学, 1997, 博士論文
Version Type	VoR
URL	https://doi.org/10.11501/3128841
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The Synthetic and Structural Study of Platinum(II) Complexes Derived from 2-Substituted Benzothiazoline

Dissertation Presented by

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in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy (Science)

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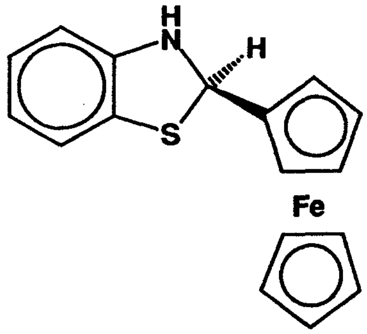
1997

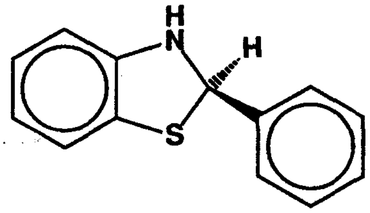
Contents

List of 2-Substituted Benzothiazoline with Their Abbreviations



2-(ferrocenyl)benzothiazoline

Hfabt



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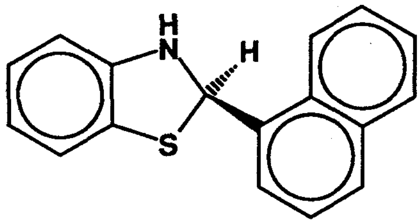
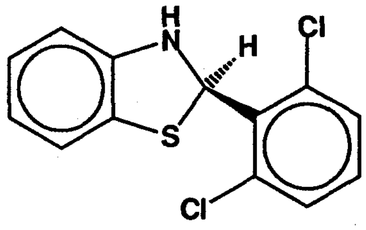
Hphbt



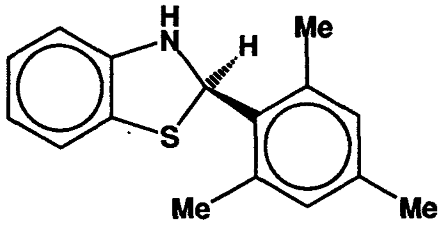
2-(1-naphtyl)benzothiazoline

H1-nabt



2-(2,6-dichlorophenyl)benzothiazoline

H2,6Cl-phbt



2-(2,4,6-trimethylphenyl)benzothiazoline

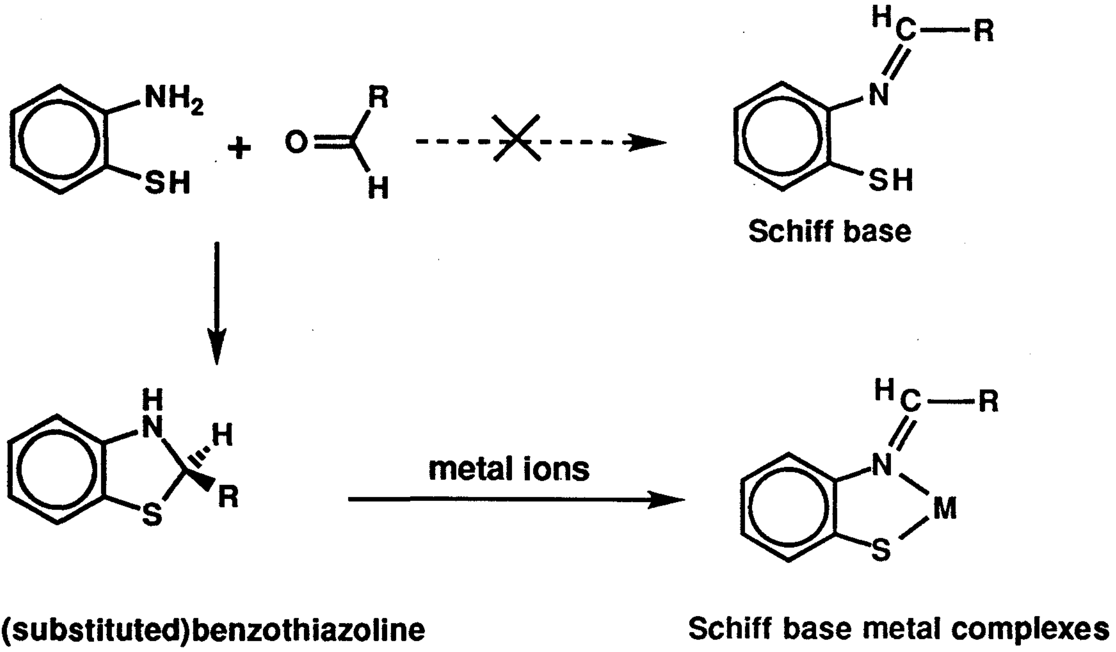
H2,4,6Me-phbt

Chapter 1.

General introduction.

1.1 General scope.

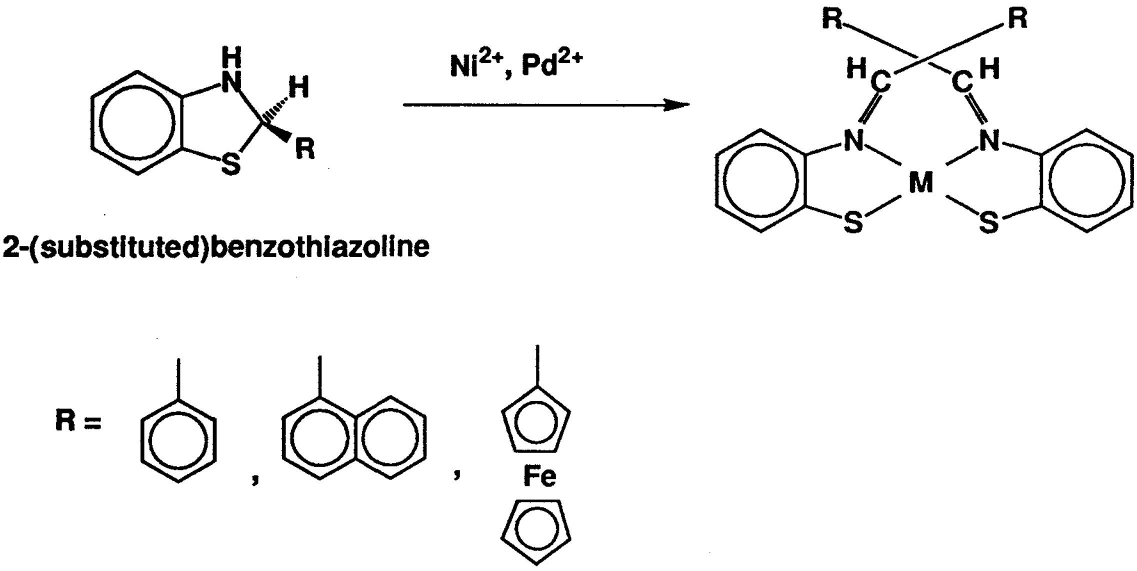
In the reaction shown in Scheme 1, it is expected that the reaction of 2-aminothiophenol with several typical aldehydes leads to the corresponding Schiff bases. The actual products are 2-substituted benzothiazolines. However, several metal ions induce rearrangement of these benzothiazolines to yield the corresponding Schiff base metal complexes. Many researchers have paid attention to such a reaction classified in " metal ions induced rearrangement ".



Scheme 1

In 1967, Lindoy and Livingstone had reported several metal complexes which were obtained by the reaction of metal ions with 2-(pyridyl)benzothiazoline.[1] They had seemed to be interested in the reaction of metal ions with sulfur containing ligands. They tried to determine whether the reaction shown in Scheme 1 leads to benzothiazoline derivatives or Schiff base ones, which had not been shown clear conclusion in those days. They could not determine the molecular structures of those complexes by X-ray diffraction method, since which technique had not been general method in those days. Moreover, they had not performed further investigation of the reaction of metal ions with the other 2-substituted benzothiazolines, though substituted groups of benzothiazoline derivatives can be easily changed by using various aldehydes. After these works, several studies in the reactions of metal ions with 2-substituted benzothiazolines had been reported, but these studies were not systematic ones.[2]

Recently, Kushi et al. have studied these reactions more systematically, and reported several metal complexes derived from benzothiazoline derivatives containing phenyl, 1-naphthyl, and ferrocenyl moieties as the pendant groups (Scheme 2).[3]



Scheme 2

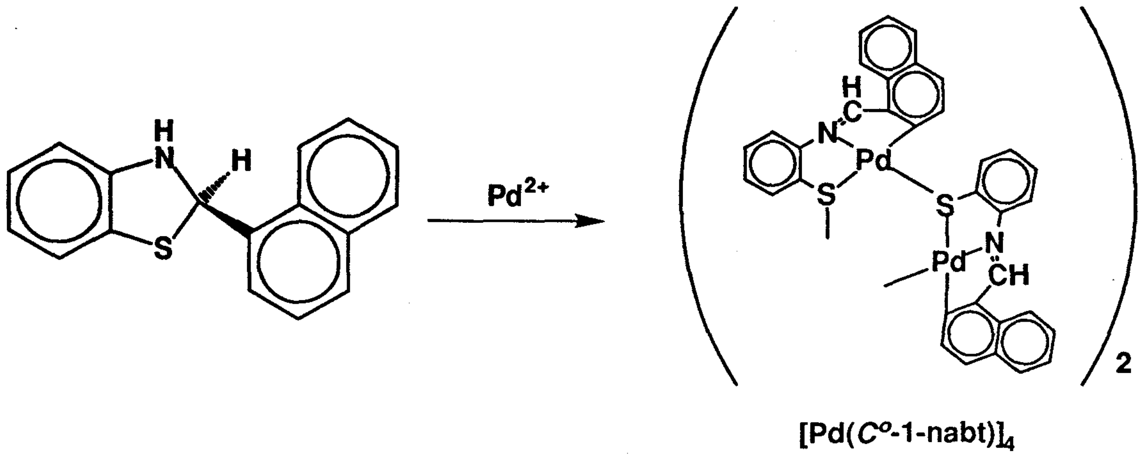
These Schiff bases derived from 2-substituted benzothiazolines act as a bidentate ligand and form a five membered *N*, *S*-bonded chelate ring. Comparing to the Schiff base complexes derived from salicylaldehyde and amines which form six-membered chelate ring having azomethine bond, in the present Schiff base complexes, the azomethine bond (C=N) is not included in the *N*, *S* five-membered chelate ring and protruded from the chelate ring (the exo-azomethine moiety). It means that the steric condition of the substituted group can be controlled more easily regarding its direction and bulkiness.

1.2 Reactions of nickel(II) and palladium(II) with 2-substituted benzothiazolines.

In the d^8 metal ions, nickel(II) exhibits a wide variety of stereochemistry; in the high spin state, octahedral and tetrahedral configuration are widely known. On the contrary, in the low spin state, square planar configuration is the typical coordination geometry.

It is known that the square planar nickel(II) complexes with *N*, *S* chelate Schiff base as a ligand exclusively prefer a *cis* N_2S_2 geometry to a *trans* one.[3] Indeed, the reactions of nickel(II) with 2-substituted benzothiazolines (Hphbt, H1-nabt, and Hfabt) afforded only mononuclear complexes having square planar configuration with *cis* geometry and no *trans*-planar complex has been reported.[4] Moreover, one of the important structural aspects of these complexes is that, with disposing *cis* geometry, these complexes showed a helical chirality with crossing its pendant substituted groups. Although many helical metal complexes have been reported in the double or the triple helical modes those containing several metal ions with a tetrahedral or an octahedral configuration,[5] the distinct examples of mononuclear and monohelical complexes with a square planar configuration are rare.[6]

The reactions of palladium(II) with 2-substituted benzothiazolines, for example H1-nabt, afforded not only mononuclear *cis*-planar complex corresponding to the nickel(II) one but also novel tetranuclear complex.[4d] The molecular structure of this tetranuclear palladium(II) complex formulated in $[Pd_4(C^o\text{-1-nabt})_4]$ has a Pd_4S_4 eight-membered skeletal ring bridged by the sulfur atoms (Scheme 3). Each palladium atom is coordinated by two sulfur atoms, one nitrogen atom and one *ortho*-carbon atom of the pendant side arm in a square planar configuration with the two sulfur atoms mutually *cis*. Thus this complex has a rare *C*°, *N*, *S*-tridentate ligand derived from orthometallation of the pendant side arm. It is interesting that palladium(II) afforded two different products having different coordination mode by the reaction with using the same starting material. The author expected that the expanded research around this field would give significant information for the formation of the polynuclear metal complexes with the sulfur bridging ligands.



Scheme 3

1.3 Reactions of platinum(II) with 2-substituted benzothiazolines.

In the course of the present study, the author has mainly investigated the reactions of platinum(II) with several 2-substituted benzothiazolines. It is well known that the platinum(II) complexes, as well as the palladium(II) ones, exhibit a square planar configuration exclusively, and give many examples of orthometallated reaction.[7] In the reactivity of the ligand exchange reaction, it is known that the platinum(II) complexes are more inert than the palladium(II) ones. Therefore, the selection of the starting materials for the platinum(II) source is very important. Then, as a starting material for syntheses of platinum(II) complexes, the author selected the following platinum(II) complex: bis(hexafluoroacetylacetonato)platinum(II), [Pt(hfacac)$_2$].[8] This complex is soluble in many organic solvents, and it is known that the ligand substitution reaction occurs easily by using the nitrogen or sulfur containing ligands. Thus the complex is expected to be the very useful starting material for the reaction with benzothiazoline derivative.

The present paper deals with the rection of this platinum(II) complex, [Pt(hfacac)$_2$], with several 2-substituted benzothiazolines.

In chapter 2, the reaction of [Pt(hfacac)$_2$] with Hfabt is described. Hfabt has a ferrocene as bulky substituted group. This steric condition gave two different novel platinum(II) complexes, comparing to the resulted complexes those derived from the same reactions using the nickel(II) or the palladium(II) with Hfabt.

In chapter 3, it is noted that the reactions of [Pt(hfacac)$_2$] with Hphbt or H1-nabt afforded novel tetranuclear complexes. Moreover, the reaction with the former benzothiazoline derivative, Hphbt, gave new non-innocent type mononuclear blue-platinum complex.

In chapter 4, it is shown that the reactions of [Pt(hfacac)$_2$] with 2-(2,6-disubstituted-phenyl)benzothiazolines afforded the novel *trans*-planar PtN$_2$S$_2$ complexes. It is revealed that the steric condition of the 2-substituted group of the benzothiazoline core directly influences the geometrical structure of the complexes.

The reactions of [Pt(hfacac)$_2$] with various 2-substituted benzothiazolines, thus, has been shown that the chemistry of the N, S chelate Schiff base metal complexes could be expanded more systematically.

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Chapter 2.

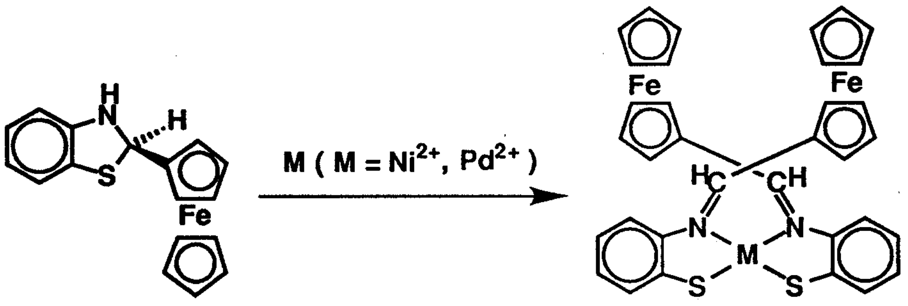
A trinuclear platinum(II) complex with C^o, N, S chelate and a pair of *trans* and *cis* isomers of platinum(II) complex with N, S chelate Schiff bases containing ferrocenyl pendant group.

Abstract.

The reaction of bis(hexafluoroacetylacetonato)platinum(II), [Pt(hfacac)$_2$], with 2-(ferrocenyl)benzothiazoline, Hfabt, affords trinuclear platinum(II) complex formulated in [Pt$_3$(C^o-fabt)$_3$] (**1**) (C^o-fabt = 2-*N*-(ferrocenylmethylideneamine)benzenethiolato-C^o, *N*, *S*) and *trans* and *cis* isomers of mononuclear complexes, *trans*-[Pt(fabt)$_2$] (**2**) (fabt = 2-*N*-(ferrocenylmethylideneamine)benzenethiolato) and *cis*-[Pt(fabt)$_2$] (**3**). The structures of **1**, **2**, and **3** have been determined by the single crystal X-ray diffraction method. Crystal data for complex **1** are monoclinic and space group $P2_1/n$ with $a = 21.439(7)$, $b = 11.990(7)$, $c = 20.919(4)$Å, $\beta = 90.79(2)°$, $V = 5376.7(37)$Å^3, $Z = 4$. Crystal data for complex **2** are triclinic and space group $P\bar{1}$ with $a = 15.283(15)$ Å, $b = 13.180(8)$ Å, $c = 9.847(12)$ Å; $\alpha = 72.91(6)°$, $\beta = 98.02(9)°$, $\gamma = 94.95(6)°$; $V = 1875.2(30)$ Å^3; $Z = 2$. Crystal data for complex **3** are orthorhombic and space group $P2_12_12_1$ with $a = 20.593(7)$ Å, $b = 12.300(5)$ Å, $c = 11.754(4)$ Å; $V = 2977.0(18)$ Å^3; $Z = 4$. The coordination geometry around each platinum atom in complex **1** is a square planar with C, N, S_2 donor atoms, and two sulfur atoms are located in *cis*-position. The platinum atoms are bridged by sulfur atoms, which form six-membered Pt$_3$S$_3$ ring. The complex **2** has a *trans*-planar N$_2$S$_2$ configuration and two fabt groups take an unique umbrella conformation. On the other hand, the complex **3** has a *cis*-planar N$_2$S$_2$ configuration and two fabt groups take a helical geometry with a stepped conformation. The space group $P2_12_12_1$, $Z = 4$ for **3** indicates that **3** is spontaneously resolved.

2.1 Introduction

As described in the previous chapter, it is well known that several metal ions induce rearrangement of the benzothiazoline derivatives to yield the corresponding Schiff base metal complexes with N, S or N, S, X (X = C, N) chelates.[1-4] To study about the stereochemistry related to the N, S chelate Schiff base complexes, recently, Kushi et al. reported on the mononuclear helical metal complexes which were obtained by the reaction of palladium(II) or nickel(II) with 2-(ferrocenyl)benzothiazoline (Hfabt) (Scheme 1).[3a] In these metal complexes, the possibility of the formation of the *cis*-planar N_2S_2 and the *trans*-planar N_2S_2 configurations is present. All resulted complexes had a *cis*-planar N_2S_2 configuration exclusively, and a molecular helicity was also generated by a crossing of two pendant ferrocenyl groups. No *trans*-planar complexes or polynuclear ones has been obtained in these systems. Then, the author planned to investigate the reaction of kinetically more inert platinum(II) with this Hfabt ligand to aim for obtaining the *trans*-planar PtN_2S_2 complex, and succeeded in syntheses of the novel trinuclear platinum(II) complex and a pair of *trans* and *cis* isomers of mononuclear PtN_2S_2 complexes. The detailed results is reported here.



2-(ferrocenyl)benzothiazoline *cis*-**[M(fabt)$_2$]**

Scheme 1: Reaction of palladium(II) and nickel(II) with 2-(ferrocenyl)benzothiazoline

2.2 Experimental section.

Materials. Bis(hexafluoroacetylacetonato)platinum(II), [Pt(hfacac)$_2$],[5] and 2-(ferrocenyl)benzothiazoline, Hfabt,[6] were prepared in the literature methods. The toluene and acetonitrile were dried over molecular sieve 3A. Dichloromethane was dried over $CaCl_2$. Unless otherwise stated, commercial grade chemicals were used without further purification.

Measurements. Electronic absorption spectra in dichloromethane solutions and Nujol mulls were recorded on a Hitachi U-3400 and a Shimadzu MPS-5000 spectrophotometer, respectively. Circular dichroism spectrum was recorded on a JASCO J-500A recording spectropolarimeter with a 1cm light-path cell. IR spectra were obtained on a Pirkin-Elmer 983G Infrared Spectrometer using Nujol mulls between CsI plates. NMR spectra in $CDCl_3$ solution were recorded on a JEOL JNM EX-270 instrument using tetramethylsilane as an internal standard ($\delta = 0$). Cyclic voltammetry was performed in a three - electrode cell with a grassy - carbon disk as working electrode, a platinum wire as counter electrode and a Ag - AgCl reference electrode, in dichloromethane containing 0.1 mol dm^{-3} tetra n-butylammonium tetrafluoroborate.

Reaction of [Pt(hfacac)$_2$] with Hfabt in 1:1 ratio.

Synthesis of Tris[2-*N*-(ferrocenylmethylideneamine)benzenethiolato-*C*°, *N*, *S*]triplatinum(II), [Pt$_3$(*C*°-fabt)$_3$] (1) To a solution of Hfabt (0.053 g, 0.16 mmol) in toluene (10 ml) was added an equimolar amount of [Pt(hfacac)$_2$] (0.100 g, 0.16 mmol) and the solution was stirred at reflux for 5 h. The solvent was removed from the reaction mixture by using a rotary evaporator. The remaining black solid was washed with ether. The solid was dissolved in a minimum amount of dichloromethane and then purified on a silica gel column with dichloromethane as the eluent. The eluted main green band was collected and evaporated to dryness. The resulting dark green powder of **1** was recrystallized from dichloromethane - acetonitrile solution: Yield 11.8%. NMR: ^{1}H (270MHz, $CDCl_3$) δ 4.09 (s, 5H), 4.11 (s, 5H), 4.21 (s, 5H), 4.35-4.50 (m, 9H), 7.10-7.90 (m, 12H), 8.63 (s, H), 8.67 (s,H), 8.74 (s, H). (Found: C, 39.47; H, 2.71; N, 2.64. Calc. for $C_{51}H_{39}Fe_3N_3Pt_3S_3$: C, 39.70; H, 2.55; N, 2.72 %).

Reaction of [Pt(hfacac)$_2$] with Hfabt in 1:2 ratio.

Synthesis of primary product. To a solution of Hfabt (0.110 g, 0.32 mmol) in toluene (20 ml) was added a 0.5 equiv. amount of [Pt(hfacac)$_2$] (0.100 g, 0.16 mmol) and the solution was heated under reflux for 3 h. The solvent was removed from the reaction mixture by using a rotary evaporator. The deep purple solid was obtained.

Separation by using a silica gel plate. The primary product was dissolved in a minimum amount of dichloromethane and then purified on a silica gel plate with dichloromethane as the eluent, which allowed clear separation of the three bands: Three colored bands, reddish purple, green, and red, were developed in this order. A considerable amount (about 50 %) of unidentified material as a dark red band did not move and remained on the original TLC plate.

***Trans*-bis[2-*N*-(ferrocenylmethylideneamine)benzenethiolato]platinum(II), *trans*-[Pt(fabt)$_2$] (2).** The first eluted reddish purple band was extracted with dichloromethane. The resulting fine red crystals were recrystallized from dichloromethane - pentane solution (yield 3.0 %). Infrared spectrum: 1576 cm^{-1} (C=N stretch). NMR: ^{1}H (270MHz, CDCl$_3$) δ 4.38 (s, 10H), 4.38-4.55 (m, 8H), 6.60 (t, 2H), 6.97(t, 2H), 7.11(d, 2H), 7.54(d, 2H), 8.72 (s, 2H): ^{13}C (68MHz, CDCl$_3$) δ 71.56, 72.31, 73.50, 77.97, 120.32, 123.29, 128.01, 129.38, 144.49, 151.27, 166.34. CV (v = 0.1 V s^{-1}) : Epa = 0.75, 1.13 V, Epc = 0.62, 0.93 V. (Found: C, 48.50; H, 3.38; N, 3.35. Calc. for $C_{34}H_{28}Fe_2N_2Pt_1S_2$: C, 48.88; H, 3.38; N, 3.35 %)

The second eluted green band was extracted with dichloromethane. The resulting green crystals corresponding to the previously mentioned complex **1** were recrystallized from dichloromethane - pentane solution (yield 1.4 %).

***Cis*-bis[2-*N*-(ferrocenylmethylideneamine)benzenethiolato]platinum(II), *cis*-[Pt(fabt)$_2$] (3).** The third red band was extracted with dichloromethane. The resulting deep red crystals were recrystallized from dichloromethane - pentane solution (yield 9.0 %). Infrared spectrum: 1592 cm^{-1} (C=N stretch). NMR: ^{1}H (270MHz, CDCl$_3$) δ 4.14 (s, 10H), 4.29 (m, 2H), 4.40 (m, 2H), 4.44 (m, 2H), 5.72 (m, 2H), 6.7-6.8 (m, 4H), 7.01 (t, 2H), 7.45 (d, 2H), 7.99 (s, 2H): ^{13}C (68MHz, CDCl$_3$) δ 69.21, 69.70, 69.90, 71.80, 72.34, 73.18, 73.75, 78.02, 78.46, 118.06, 121.83, 128.14, 129.26, 146.18, 152.89, 161.85. CV (v = 0.1 V s^{-1}) : Epa = 0.77, 1.04 V, Epc = 0.59, 0.85 V. (Found: C, 48.67; H, 3.49; N, 3.39. Calc. for $C_{34}H_{28}Fe_2N_2Pt_1S_2$: C, 48.88; H, 3.38; N, 3.35 %)

Crystal Structure Determination. The single crystals suitable for X-ray methods were obtained from chloroform-methanol solution for **1**, from 1,2-dichloroethane-pentane solution for **2**, from chloroform-methanol solution for **3**. All crystallographic measurements were made using a MAC science MXC3 diffractometer with Mo-Kα radiation (0.71073 Å). Empirical absorption corrections (ψ-scan) were applied.

Lattice parameters were determined by application of the automatic diffractometer indexing routine to the positions of 22 reflections. Data were measured in the range 3 $\leq 2\theta \leq 50°$ in the ω-2θ scan with three check reflections being measured every 100 data. Crystal data and relevant information for **1**, **2**, and **3** are summarized in Table 1, 2, and 3.

The structures were solved by direct methods (SIR) and refined by full-matrix least squares. Refinement for **1** was anisotropic only for the platinum, iron, chlorine, and sulfur atoms. All non-hydrogen atoms for **2** and **3** were refined with anisotropic temperature coefficients.[7] The correct choice of the P-helix absolute configuration for **3** was confirmed by the η factor[8] value of 0.87(11). Final atom coordinates for the non-hydrogen atoms of complexes **1**, **2**, and **3** are given in Tables 4, 5, and 6, respectively.

Anisotropic temperature factors for **1**, **2**, and **3** are given in Tables 3A-3C. The selected bond lengths and angles are shown in Tables 4A-4C and Table 5. Tables 3A-3C and 4A-4C are in the Appendix section (chapter 2).

Table 1A Crystallographic data for **1**

Formula	$C_{52}H_{40}Cl_3Fe_3N_3Pt_3S_3$
M	1662.25
Crystal system	Monoclinic
Space group	$P2_1/n$
a / Å	21.439(7)
b / Å	11.990(7)
c / Å	20.919(4)
β / °	90.79(2)
U / Å^3	5376.7(37)
Z	4
Dc	2.05
μ(Mo-Kα)/cm^{-1}	9.10
$2\theta_{max}$ / °	50
Crystal dimensions / mm	0.3 × 0.2 × 0.1
No. of measured reflections	10579
No. reflections used in refinement	2596 [$\|F_o\|>3.0\sigma(F_o)$]
No. of parameters	329
R^a	0.071
Rw^b	0.090

[a] $R = \Sigma\|\|Fo\| - \|Fc\|\| / \Sigma\|Fo\|$. [b] $Rw = [\Sigma w(\|Fo\| - \|Fc\|)^2 / \Sigma w(Fo)^2]^{1/2}$. Weighting scheme: $1/[\sigma^2(Fo)]$.

Table 1B Crystallographic data for **2**

Formula	$C_{35}H_{30}Cl_1Fe_2N_2Pt_1S_2$
M	885.00
Crystal system	Triclinic
Space group	$P\bar{1}$
a / Å	15.283(15)
b / Å	13.180(8)
c / Å	9.847(12)
α / °	72.91(6)
β / °	98.02(9)
γ / °	94.95(6)
U / Å^3	1875.2(30)
Z	2
Dc	1.78
μ(Mo-Kα)/cm^{-1}	4.80
$2\theta_{max}$ / °	50
Crystal dimensions / mm	0.2 × 0.1 × 0.05
No. of measured reflections	6052
No. reflections used in refinement	2500 [$\lvert F_o\rvert > 5.0\sigma(F_o)$]
No. of parameters	388
R[a]	0.069
Rw[b]	0.088

[a] $R = \Sigma\lvert\lvert Fo\rvert - \lvert Fc\rvert\rvert / \Sigma\lvert Fo\rvert$. [b] $Rw = [\Sigma w(\lvert Fo\rvert - \lvert Fc\rvert)^2 / \Sigma w(Fo)^2]^{1/2}$. Weighting scheme: $1/[\sigma^2(Fo)]$.

Table 1C Crystallographic data for **3**

Formula	$C_{34}H_{28}Fe_2N_2Pt_1S_2$
M	835.5
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a / Å	20.593(7)
b / Å	12.300(5)
c / Å	11.754(4)
U / Å^3	2977.0(18)
Z	4
Dc	1.86
μ(Mo-Kα)/cm^{-1}	5.86
$2\theta_{max}$ / °	50
Crystal dimensions / mm	0.3 × 0.2 × 0.1
No. of measured reflections	3074
No. reflections used in refinement	1689 [$\|F_o\|>3.2\sigma(F_o)$]
No. of parameters	371
R^a	0.053
Rw^b	0.059

[a] $R = \Sigma\|\|Fo\| - \|Fc\|\| / \Sigma\|Fo\|$. [b] $Rw = [\Sigma w(\|Fo\| - \|Fc\|)^2 / \Sigma w(Fo)^2]^{1/2}$. Weighting scheme: $1/[\sigma^2(Fo)]$.

Table 2A Atomic coordinates and isotropic thermal parameters for **1**

Atom	*x*	*y*	*z*	*U*
Pt1	0.1094(3)	0.2209(5)	0.0811(2)	0.032
Pt2	0.2677(3)	0.1406(5)	0.0926(3)	0.038
Pt3	0.2128(3)	0.2882(5)	-0.0528(3)	0.032
Fe1	-0.0132(10)	0.0817(17)	0.1742(10)	0.039
Fe2	0.2612(11)	-0.1089(20)	0.0071(13)	0.056
Fe3	0.1654(9)	0.3566(18)	-0.2169(10)	0.040
Cl1	0.417(4)	0.545(8)	0.021(3)	0.128
Cl2	0.451(5)	0.621(9)	-0.104(5)	0.152
Cl3	0.331(5)	0.543(11)	-0.081(8)	0.204
S1	0.1425(15)	0.3692(28)	0.0143(17)	0.036
S2	0.1931(17)	0.2404(32)	0.1488(17)	0.040
S3	0.2889(17)	0.2885(38)	0.0290(18)	0.044
N1	0.023(6)	0.221(13)	0.022(6)	0.05
N2	0.259(5)	0.008(10)	0.160(5)	0.04
N3	0.283(4)	0.235(9)	-0.106(5)	0.02
C1	0.071(5)	0.383(9)	-0.028(5)	0.02
C2	0.058(7)	0.483(12)	-0.067(7)	0.04
C3	0.009(6)	0.491(11)	-0.097(6)	0.03
C4	-0.045(6)	0.416(11)	-0.090(6)	0.03
C5	-0.038(5)	0.323(9)	-0.053(5)	0.02
C6	0.022(6)	0.307(11)	-0.021(6)	0.03
C7	-0.013(7)	0.140(13)	0.033(7)	0.05
C8	0.008(5)	0.058(9)	0.081(5)	0.02
C9	0.061(7)	0.085(13)	0.114(8)	0.05
C10	0.070(8)	-0.002(15)	0.163(8)	0.05
C11	0.016(6)	-0.080(11)	0.156(6)	0.03
C12	-0.026(10)	-0.036(19)	0.102(11)	0.08
C13	-0.071(8)	0.203(15)	0.187(8)	0.06
C14	-0.012(9)	0.226(19)	0.222(10)	0.07
C15	-0.015(6)	0.148(12)	0.264(6)	0.04
C16	-0.069(7)	0.076(13)	0.253(7)	0.05
C17	-0.101(8)	0.118(15)	0.200(8)	0.05
C18	0.190(8)	0.144(16)	0.219(8)	0.06
C19	0.153(8)	0.171(14)	0.270(8)	0.05
C20	0.159(8)	0.096(15)	0.325(9)	0.06
C21	0.183(8)	-0.003(16)	0.324(9)	0.06
C22	0.214(8)	-0.034(16)	0.273(9)	0.06
C23	0.218(8)	0.037(15)	0.219(8)	0.06
C24	0.278(8)	-0.085(15)	0.144(8)	0.06
C25	0.308(8)	-0.091(14)	0.086(8)	0.05
C26	0.313(12)	0.020(22)	0.046(12)	0.09
C27	0.343(8)	-0.016(15)	-0.007(8)	0.05
C28	0.356(8)	-0.136(16)	-0.012(8)	0.06
C29	0.332(7)	-0.181(13)	0.048(7)	0.05
C30	0.177(12)	-0.155(24)	0.033(13)	0.10
C31	0.178(14)	-0.049(26)	0.007(15)	0.11
C32	0.199(8)	-0.057(15)	-0.063(8)	0.06
C33	0.205(8)	-0.182(14)	-0.071(8)	0.06
C34	0.196(10)	-0.241(19)	-0.008(11)	0.08
C35	0.354(6)	0.247(10)	-0.022(6)	0.03

C36	0.415(9)	0.243(17)	0.006(10)	0.07
C37	0.465(9)	0.209(18)	-0.034(9)	0.07
C38	0.457(10)	0.208(20)	-0.102(10)	0.08
C39	0.394(6)	0.213(12)	-0.122(6)	0.03
C40	0.348(8)	0.238(14)	-0.089(8)	0.05
C41	0.268(9)	0.219(20)	-0.164(9)	0.08
C42	0.202(8)	0.207(15)	-0.182(8)	0.05
C43	0.162(7)	0.259(13)	-0.132(8)	0.05
C44	0.104(6)	0.262(10)	-0.159(6)	0.03
C45	0.106(6)	0.229(14)	-0.224(7)	0.04
C46	0.164(9)	0.191(15)	-0.245(9)	0.06
C47	0.240(7)	0.468(13)	-0.232(7)	0.04
C48	0.193(11)	0.516(19)	-0.187(11)	0.08
C49	0.135(13)	0.519(24)	-0.216(13)	0.10
C50	0.153(7)	0.464(14)	-0.290(8)	0.05
C51	0.207(10)	0.432(20)	-0.288(11)	0.08
C52	0.408(7)	0.515(14)	-0.060(8)	0.05

$T = \exp[-2\pi^2 U]$; $U = U_{iso}$ or $(U_{11} + U_{22} + U_{33}) / 3$

Table 2 B Atomic coordinates and isotropic thermal parameters for 2

Atom	*x*	*y*	*z*	*U*
Pt1	0.22397(17)	0.10126(22)	0.60964(26)	0.0345(9)
Fe1	0.1575(5)	0.0318(7)	0.1712(8)	0.048(5)
Fe2	0.4739(6)	0.3039(8)	0.3675(10)	0.062(5)
Cl1	0.4867(14)	0.1674(20)	0.9599(25)	0.10(1)
S1	0.3317(10)	-0.0218(13)	0.7042(17)	0.056(9)
S2	0.1072(11)	0.2133(13)	0.5648(17)	0.054(8)
N1	0.154(3)	-0.027(3)	0.580(5)	0.04(2)
N2	0.294(3)	0.227(4)	0.656(5)	0.05(3)
C1	0.256(4)	-0.127(4)	0.759(5)	0.04(3)
C2	0.282(5)	-0.219(6)	0.860(9)	0.09(5)
C3	0.218(6)	-0.308(6)	0.912(6)	0.08(5)
C4	0.130(6)	-0.293(5)	0.851(6)	0.07(4)
C5	0.101(5)	-0.204(5)	0.734(7)	0.07(4)
C6	0.170(4)	-0.123(5)	0.692(6)	0.05(3)
C7	0.104(3)	-0.037(5)	0.459(6)	0.06(4)
C8	0.092(3)	0.042(4)	0.325(5)	0.03(3)
C9	0.134(3)	0.140(5)	0.271(7)	0.06(3)
C10	0.102(4)	0.182(5)	0.119(7)	0.06(4)
C11	0.042(4)	0.099(5)	0.092(6)	0.06(3)
C12	0.030(4)	0.018(5)	0.215(5)	0.04(3)
C13	0.200(6)	-0.032(10)	0.025(11)	0.10(6)
C14	0.257(8)	0.045(9)	0.045(13)	0.12(8)
C15	0.289(5)	0.016(10)	0.195(12)	0.12(7)
C16	0.238(7)	-0.080(8)	0.249(11)	0.10(7)
C17	0.187(9)	-0.104(10)	0.143(17)	0.14(9)
C18	0.154(4)	0.289(4)	0.672(5)	0.05(3)
C19	0.104(5)	0.355(5)	0.718(9)	0.08(5)
C20	0.147(5)	0.414(4)	0.813(7)	0.06(3)
C21	0.238(4)	0.404(5)	0.858(6)	0.07(4)
C22	0.287(4)	0.348(5)	0.806(5)	0.05(3)
C23	0.249(3)	0.286(5)	0.715(7)	0.06(3)
C24	0.377(4)	0.262(4)	0.625(6)	0.05(3)
C25	0.433(4)	0.220(5)	0.552(5)	0.06(3)
C26	0.413(6)	0.163(7)	0.448(8)	0.09(5)
C27	0.492(5)	0.141(5)	0.400(7)	0.07(4)
C28	0.560(5)	0.189(6)	0.468(6)	0.08(4)
C29	0.526(4)	0.237(7)	0.565(8)	0.08(5)
C30	0.536(9)	0.416(9)	0.214(14)	0.13(9)
C31	0.521(9)	0.462(7)	0.322(11)	0.12(7)
C32	0.422(10)	0.454(9)	0.306(11)	0.13(8)
C33	0.393(8)	0.405(10)	0.208(13)	0.13(9)
C34	0.467(11)	0.369(8)	0.155(10)	0.13(8)
C35	0.527(4)	0.045(8)	0.948(9)	0.10(5)

$T = \exp[-2\pi^2 U]$; $U = (U_{11} + U_{22} + U_{33}) / 3$

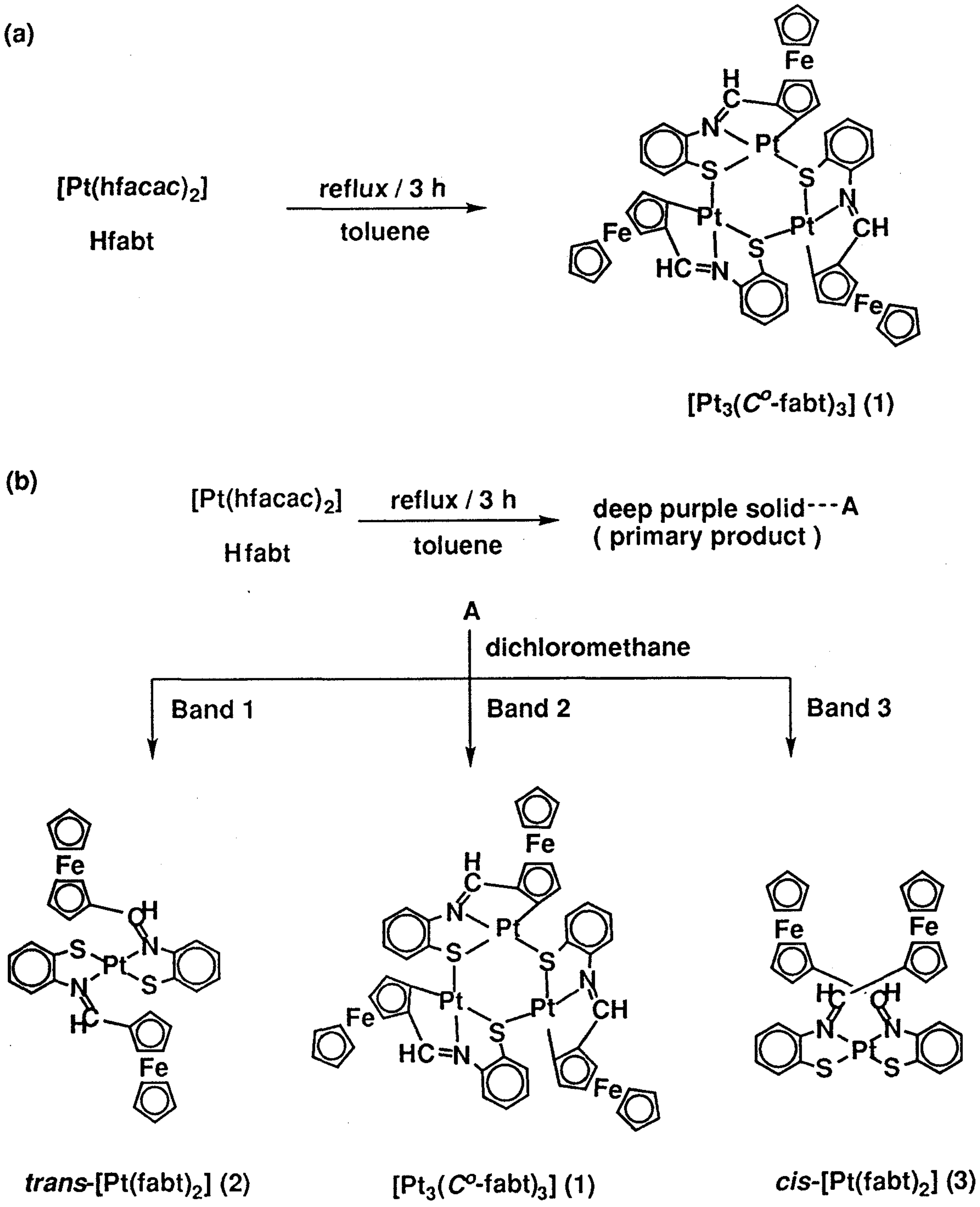
Table 2C Atomic coordinates and isotropic thermal parameters for **3**

Atom	*x*	*y*	*z*	*U*
Pt1	0.89753(8)	0.21699(12)	0.16372(16)	0.031(1)
Fe1	1.1253(3)	0.2508(5)	-0.0083(7)	0.047(3)
Fe2	0.8575(4)	0.5982(6)	0.0158(8)	0.053(4)
S1	0.8657(6)	0.1915(9)	0.3456(15)	0.054(8)
S2	0.8478(6)	0.0593(10)	0.1171(12)	0.047(6)
N1	0.9329(15)	0.3622(26)	0.2240(27)	0.02(2)
N2	0.9269(13)	0.2157(29)	-0.0007(36)	0.04(2)
C1	0.9180(19)	0.2846(52)	0.4090(42)	0.05(3)
C2	0.925(2)	0.270(5)	0.531(5)	0.07(3)
C3	0.972(3)	0.350(5)	0.575(5)	0.07(4)
C4	1.010(2)	0.421(4)	0.507(5)	0.05(3)
C5	0.997(2)	0.431(4)	0.393(5)	0.05(3)
C6	0.950(2)	0.358(4)	0.340(6)	0.05(3)
C7	0.9379(17)	0.4572(27)	0.1800(59)	0.04(2)
C8	0.9193(18)	0.4866(37)	0.0589(41)	0.04(2)
C9	0.870(3)	0.437(4)	-0.011(5)	0.05(3)
C10	0.871(3)	0.493(4)	-0.120(6)	0.07(3)
C11	0.916(3)	0.573(5)	-0.118(5)	0.07(3)
C12	0.953(2)	0.567(4)	-0.011(6)	0.06(3)
C13	0.825(3)	0.667(5)	0.158(10)	0.11(6)
C14	0.773(4)	0.621(6)	0.110(10)	0.12(6)
C15	0.771(5)	0.663(10)	-0.015(12)	0.2(1)
C16	0.811(4)	0.739(6)	-0.025(7)	0.09(5)
C17	0.845(4)	0.751(7)	0.083(7)	0.11(6)
C18	0.841(2)	0.086(4)	-0.029(6)	0.06(3)
C19	0.794(3)	0.027(5)	-0.104(8)	0.08(4)
C20	0.790(3)	0.057(6)	-0.218(7)	0.07(4)
C21	0.825(3)	0.135(5)	-0.264(7)	0.09(5)
C22	0.866(2)	0.191(3)	-0.189(3)	0.04(2)
C23	0.8770(18)	0.1652(33)	-0.0883(39)	0.03(2)
C24	0.978(2)	0.249(4)	-0.053(4)	0.05(2)
C25	1.0320(19)	0.3062(34)	0.0047(43)	0.04(2)
C26	1.0581(17)	0.2932(55)	0.1110(39)	0.05(3)
C27	1.115(3)	0.367(5)	0.115(5)	0.06(3)
C28	1.120(3)	0.416(5)	0.005(6)	0.08(4)
C29	1.072(3)	0.375(4)	-0.062(4)	0.06(3)
C30	1.136(4)	0.104(7)	-0.084(7)	0.09(5)
C31	1.157(3)	0.095(6)	0.023(9)	0.11(6)
C32	1.215(3)	0.170(6)	0.044(6)	0.08(4)
C33	1.213(2)	0.217(6)	-0.080(6)	0.08(4)
C34	1.168(3)	0.177(5)	-0.148(6)	0.08(4)

$T = \exp[-2\pi^2 U]$; $U = (U_{11} + U_{22} + U_{33}) / 3$

Results and Discussion

Syntheses of 1, 2, and 3. Treatment of Hfabt with equimolar amount of [Pt(hfacac)$_2$] in hot toluene afforded trinuclear complex formulated in [Pt$_3$(C^{o}-fabt)$_3$]. Treatment of Hfabt with 0.5 molar equiv. of [Pt(hfacac)$_2$] in hot toluene followed by separation using a silica gel plate gave the mononuclear complexes **2**, **3**, and trinuclear complex **1** (yield 3.0, 9.3, 1.4 %, respectively) (Scheme 2). The neutral complexes **2** and **3**, which were obtained from the first and the third bands respectively, had the same chemical composition of [Pt(fabt)$_2$]. The complexes **2** and **3** are *trans* and *cis* isomeric forms as described below. The second green band was the trinuclear complex **1**. At room temperature, this reaction did not afford *trans* complex **2**. The yields of *cis* complex **3** and trinuclear complex **1** decreased with increasing of the yield of the unidentified dark red compound. Moreover, when K$_2$[PtCl$_4$] or bis(acetylacetonato)-platinum(II), [Pt(acac)$_2$], were used as starting materials for this reaction, these complexes could not be obtained. This result indicates that [Pt(hfacac)$_2$] is suitable as a starting material for the reaction of platinum(II) with benzothiazoline delivatives.

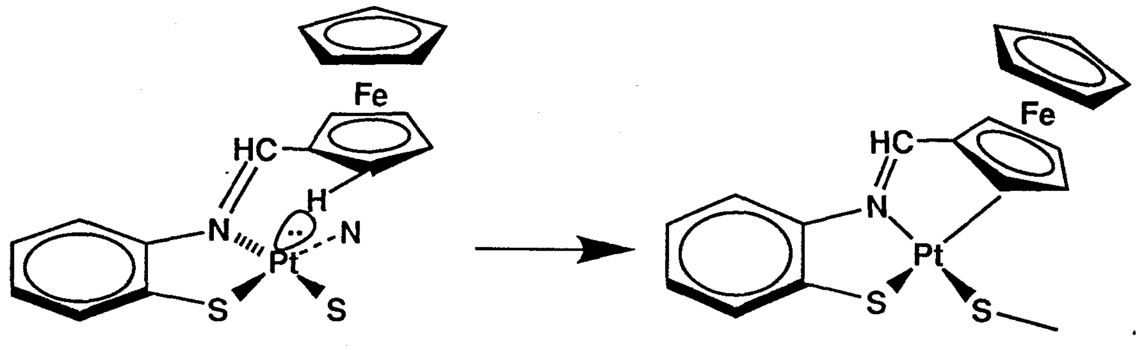


Scheme 2. The reaction of [Pt(hfacac)$_2$] with Hfabt (a) in 1:1 (b) in 1:2 stoichiometry ratio.

Molecular Structure of Complex 1. The molecular structure of **1** with a partial atoms labeling scheme is shown in Fig. 1.

The complex **1** is trinuclear platinum(II) complex. The coordination geometry around each platinum atom is square planar with C^o, N, S_2 donor atoms and two sulfur atoms are located in *cis*-position. The platinum atoms are bridged by sulfur atoms. The bond distances between platinum atoms and the coordinated ones are normal.[9,10] It is interesting to note that the Pt-terminal S distances (av. 2.35 Å) are longer than the Pt-bridging S ones (av. 2.28 Å). This result indicates the strong *trans* influence of the coordinated carbon atoms of the cyclometallated ligands.[10] The average Pt-S-Pt angle of 103.6(15)° is not close to ideal tetrahedral value of 109.5°, in contrast to those of tetranuclear platinum(II) complexes, $[Pt_4(C^o\text{-phbt})_4]$ and $[Pt_4(C^o\text{-1-nabt})_4]$ (110.8(8) and 110.4(3)°, respectively) (See chapter 3). Although the framework of the tetranuclear Pd(II) complex with 1-naphthyl groups consists of eight-membered Pd_4S_4 ring having $\bar{4}$ symmetry[4], that of complex **1** with ferrocenyl groups consists of six-membered Pt_3S_3 ring in chair form.[9] This difference arises from the difference of substituent groups in benzothiazoline derivative. Three ferrocene units in **1** occupy general positions and the molecule **1** has no threefold axis C_3. The Pt(2)···Fe(2) distance being 3.49(3)Å is shorter than the other two Pt···Fe distances (Pt(1)···Fe(1) 3.69(3)Å, Pt(3)···Fe(3) 3.66(3)Å).

It is worth of noting that the corresponding polynuclear palladium complex could not be obtained by the reaction of $[Pd(hfacac)_2]$ with Hfabt. The result suggests that the platinum(II) activates the *ortho*-hydrogen-carbon bond of substituted ferrocenyl group more strongly than palladium(II).



cis-$[Pt(fabt)_2]$ (3)

1

Scheme 3.

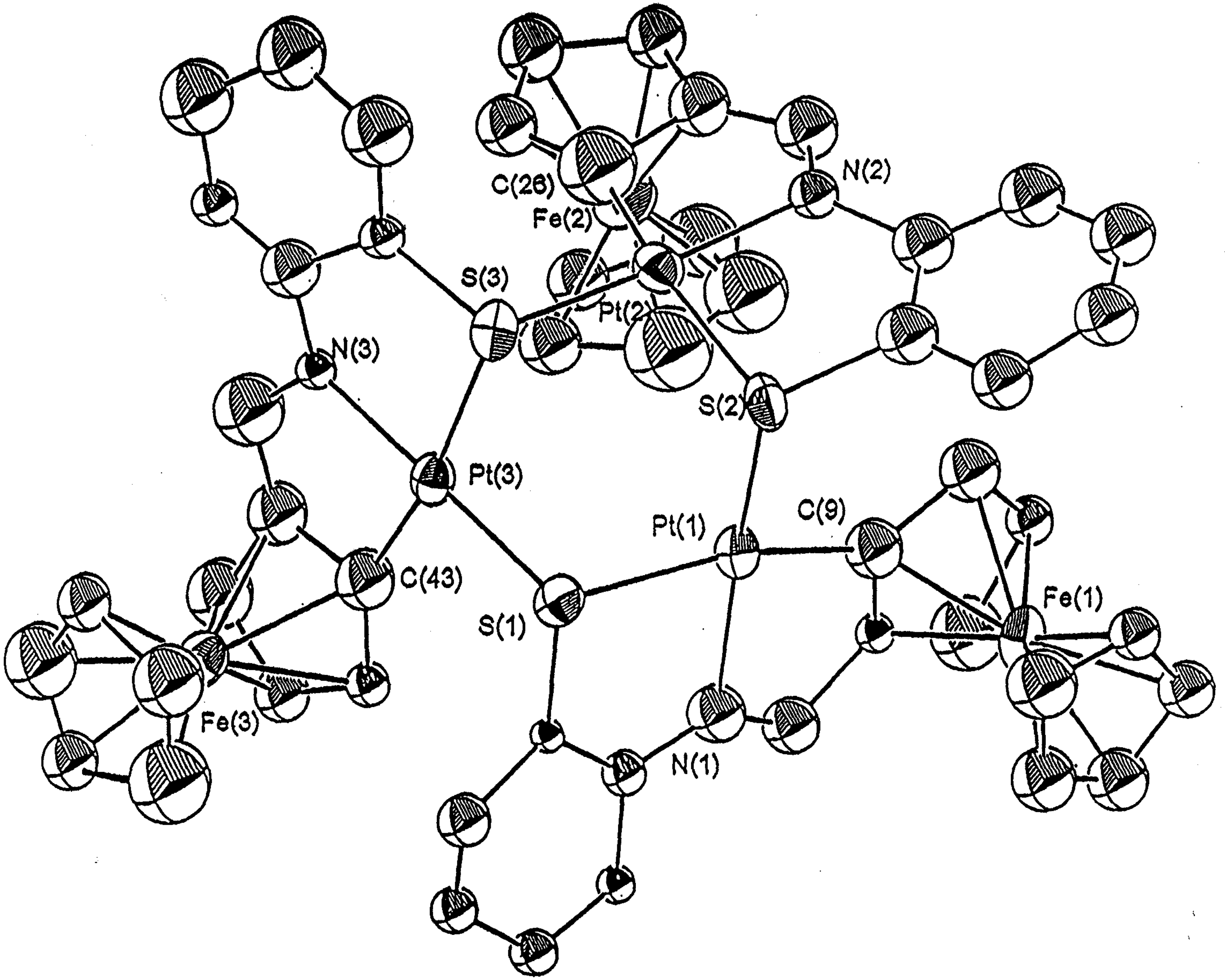


Fig. 1A. Molecular structure of 1 (top view).

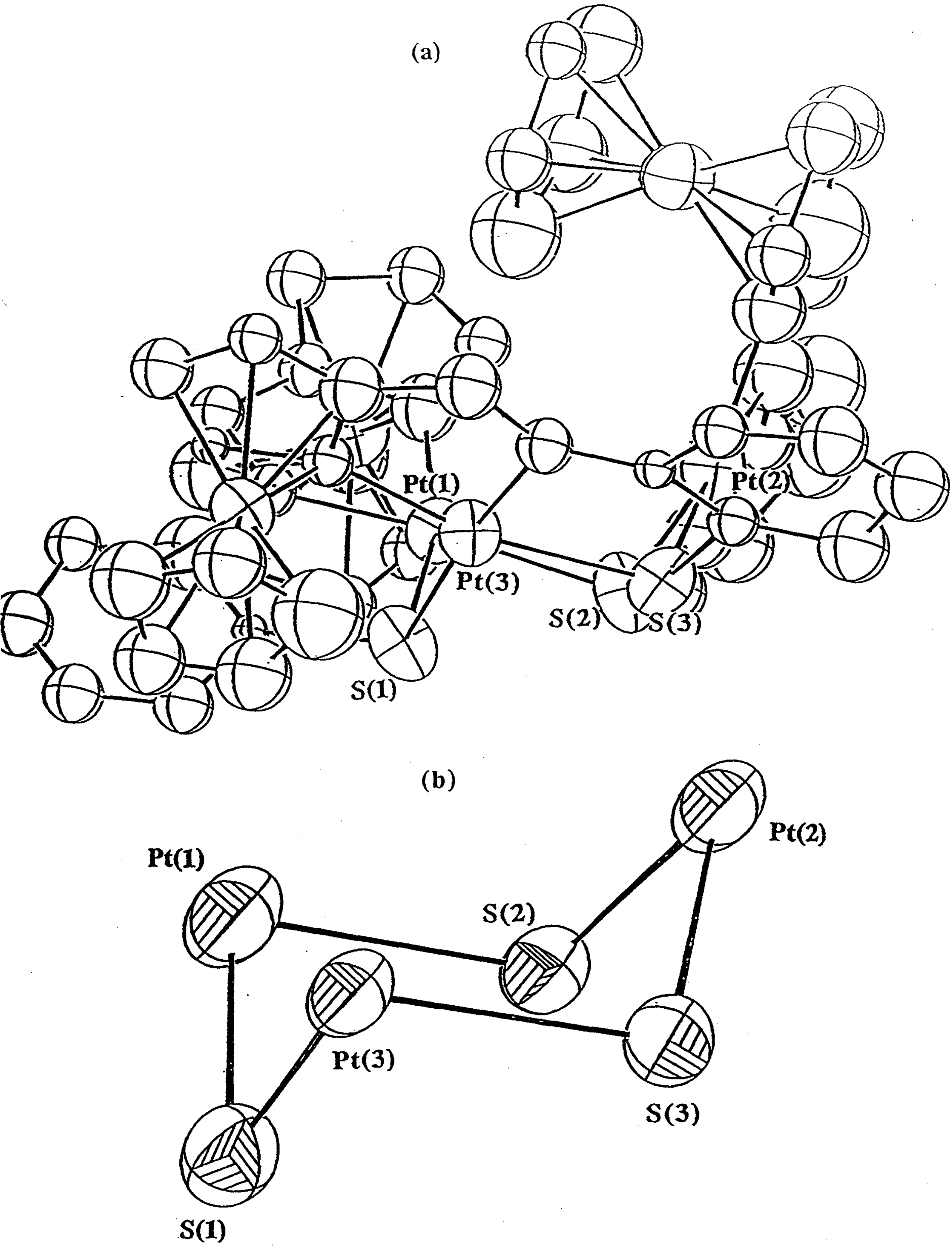
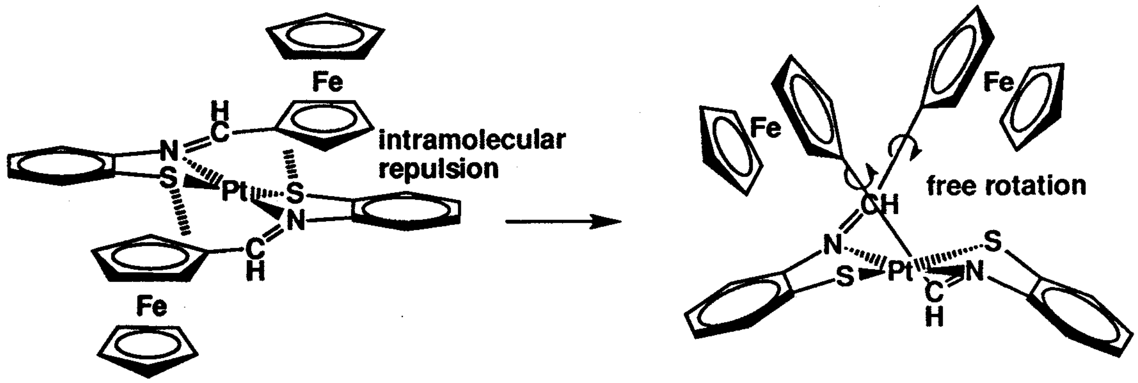


Fig. 1B. (a) Molecular structure of 1 (side view) and (b) framework of 1.

Molecular Structure of Complex 2. The complex **2** is a square planar N_2S_2 Schiff base complex with nitrogen and sulfur atoms *trans* to each other (Fig. 2). To our knowledge, this is the first example of *trans* platinum (II) Schiff base complex in an N_2S_2 environment. The dihedral angle between the two five membered N-Pt-S chelate planes is 13(9)°, which is regarded as noticeable distortion toward tetrahedral arrangement. Moreover, the complex **1** has an unique umbrella conformation and the ϕ value between two phenyl moieties is 104(3)°.[11] This umbrella conformation is comparable to the corresponding one found for *trans*-bis(1-isopropyl-3-methyl-4-cyclohexylaldimine-5-thiopyrazolate)palladium(II), which ϕ value was 100°.[12] In addition, the complex **2** is a C_2 chiral, and the space group $P1$ and $Z = 2$ indicates that the crystals are racemic.

The molecular model examination exhibits that if the complex **2** had a stepped conformation,[1] the ferrocenyl groups would be too close to sulfur atom on the opposite side.[13] Thus, the complex **2** prefers an umbrella conformation to relax the C···S intramolecular repulsion and to allow free rotation of pendant ferrocenyl groups (Scheme 4).



stepped conformation **umbrella comformation**

Scheme 4.

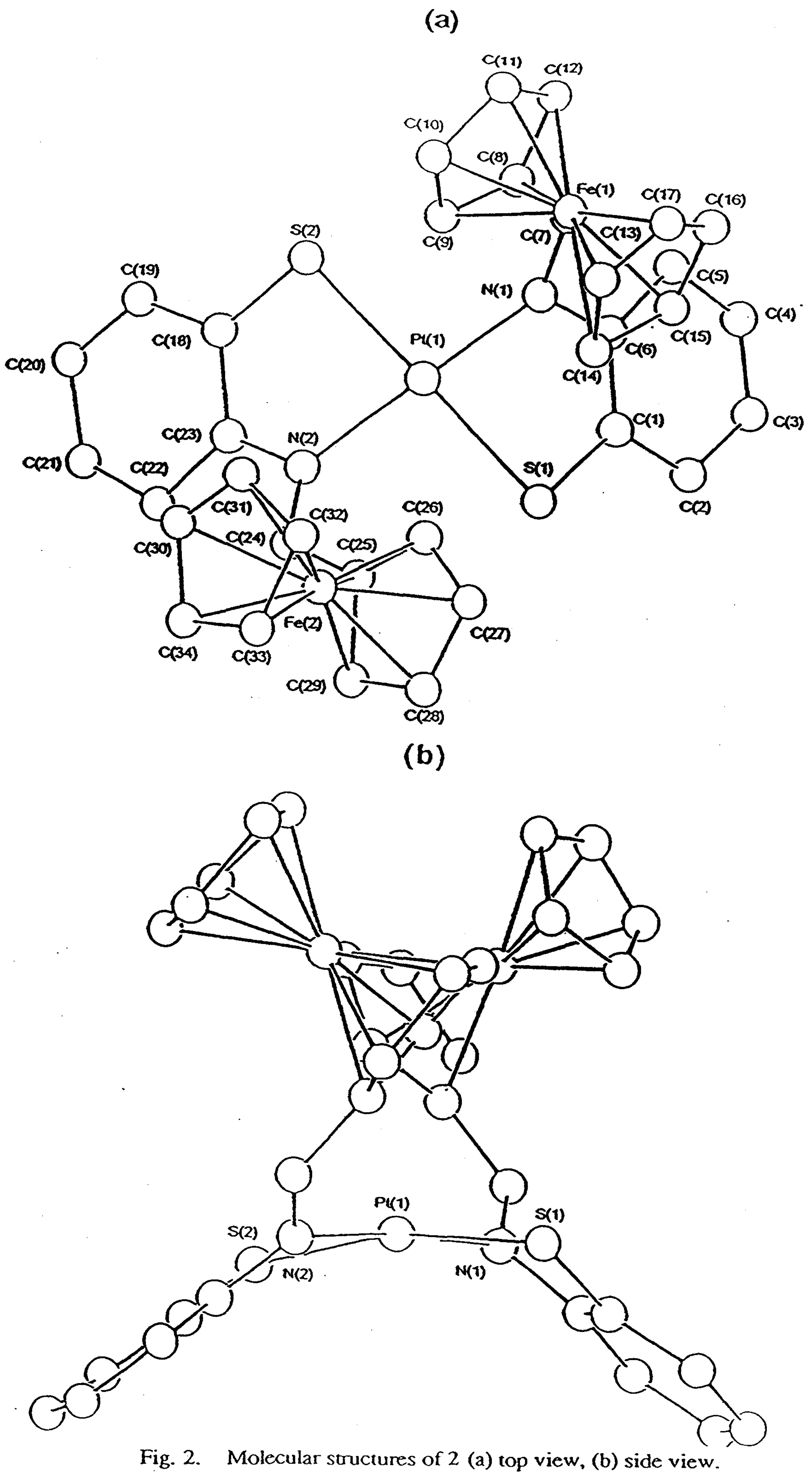


Fig. 2. Molecular structures of 2 (a) top view, (b) side view.

Molecular Structure of Complex 3. As shown in Fig. 3, the complex **3** is a square planar configuration and its coordination environment has a *cis* geometry with N_2S_2 donor atoms. In contrast to **2**, the complex **3** has a stepped conformation and its stepped angles θ between the phenyl moieties and the coordination plane are 155(3)° and 151(3)°. The dihedral angle between the two five-membered N-Pt-S chelate planes is 6(11)°. This complex **3** shows a molecular helicity with crossing of two pendant ferrocenyl groups which is quite similar to the mode of [Pd(fabt)$_2$] and [Ni(fabt)$_2$].[3a] Although many helical metal complexes had been reported in double helical mode containing several metal ions favoring the tetrahedral or the octahedral geometry,[14-22] this complex **3** is an example of the rare mononuclear monohelical complex.[3,23,24] In addition, in complex **3**, the space group $P2_12_12_1$ and $Z = 4$ indicates that the crystals are spontaneously resolved. This resolution behavior was reported previously in a few helical compounds.[3,24-26] Based on the X-ray abnormal dispersion effect, the absolute configuration for **3** is determined to be right handed P-helix configuration.[27]

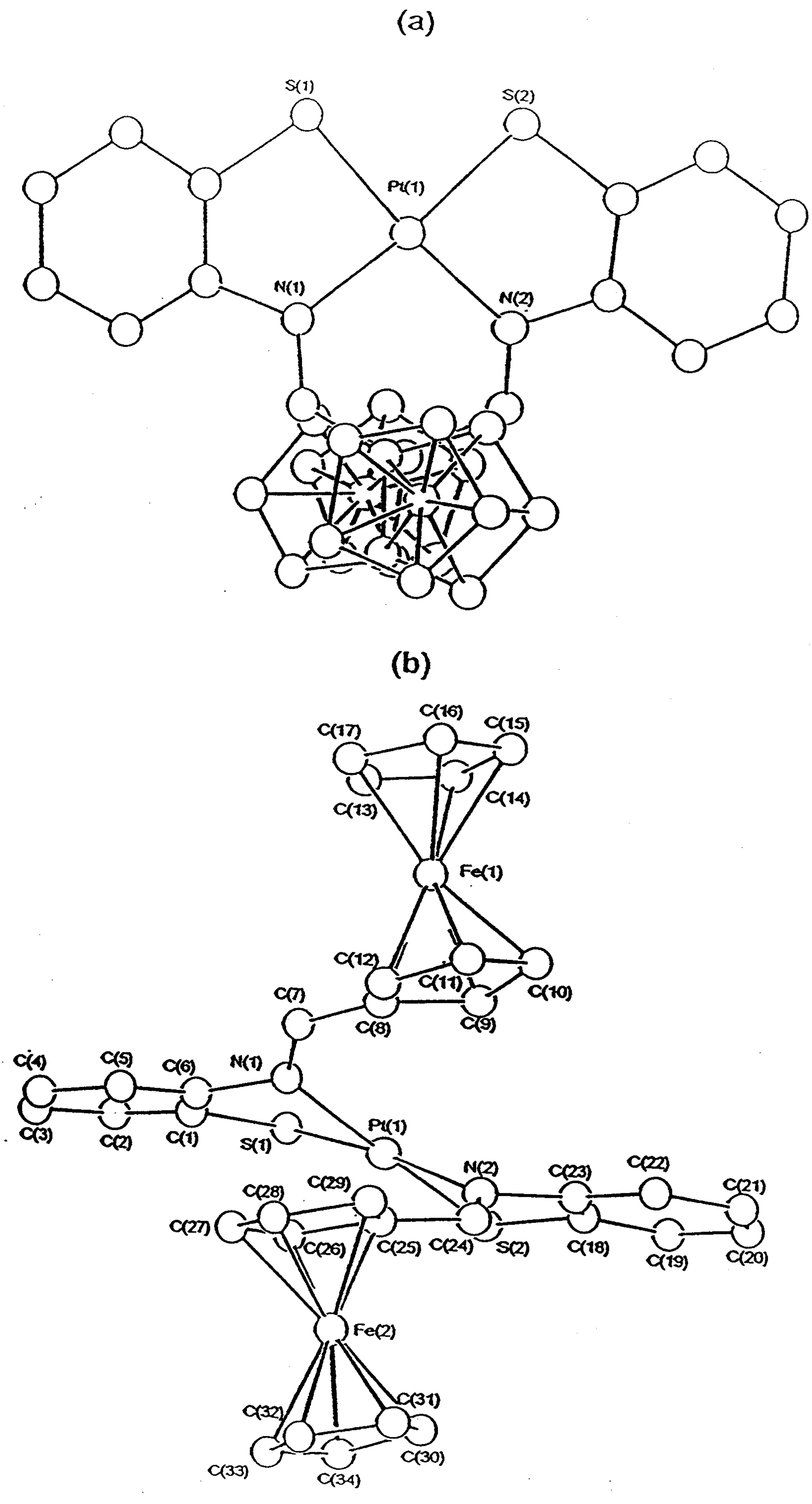


Fig. 3. Molecular structures of 3 (a) top view, (b) side view.

Comparison of mononuclear complexes 2 and 3. The notable differences between **2** and **3** are observed in bond distances of the platinum atom and the coordination atoms (see Table 5). The Pt-S bond distances of 2.31(2) and 2.33(2) Å for **2** are longer than those of 2.26(2) and 2.26(1) Å for **3**. On the other hand, the Pt-N bond distances, 2.00(5) and 2.02(6) Å, for **2** are slightly shorter than those of 2.05(4) and 2.02(5) Å for **3**. These results suggest the *trans* influence of the coordinated thiolate. The distances of C=N for **2** are 1.35(8) and 1.36(8) Å, which are longer than those found in **3** (1.28(6) and 1.28(6) Å). This result indicates that the double bond character of the azomethine groups in **2** is weaken than those of **3** (NMR and IR data for **2** and **3** support these observations, *vide infra*) and this is caused by the steric repulsion between two pendant ferrocenyl groups. This steric repulsion is also reflected in the torsion angles of C6-N1-C7-C8 and C23-N2-C24-C25 in **2** and **3**. In complex **2**, the torsion angles of C6-N1-C7-C8 and C23-N2-C24-C25 are 12(8)° and 6(9)°, respectively. These values are regarded as slightly large angle by comparing with the corresponding angles of **3** (3(7)° and 3(6)°, respectively).

Table 5 Selected bond lengths(Å) and angles(°)

	2	**3**
Bond lengths		
Pt-S1	2.314(16)	2.256(18)
Pt-S2	2.326(16)	2.259(13)
Pt-N1	2.00(5)	2.05(4)
Pt-N2	2.02(6)	2.02(5)
N1-C7	1.35(8)	1.28(6)
N2-C24	1.36(8)	1.28(6)
Bond angles		
S1-M-S2	167.5(6)	88.8(5)
S1-M-N1	81.5(13)	84.1(10)
S1-M-N2	97.3(15)	171.5(11)
S2-M-N1	97.8(13)	171.8(10)
S2-M-N2	82.4(15)	84.1(11)
N1-M-N2	175.6(18)	103.3(14)

Spectroscopic Characterization of the Complexes 1, 2, and 3.

NMR spectra. Proton NMR spectra of **1**, **2**, and **3** in $CDCl_3$ solution are shown in Figs. 4, 5, and 6A, respectively.

In trinuclear complex **1**, the spectrum gives three signals corresponding to the non-substituted cyclopentadienyl ring protons (δ 4.09, 4.11, and 4.21) and also three azomethine signals (δ 8.63, 8.67, and 8.74). This result indicates that the low symmetry of the complex **1** without C_3 axis is also maintained in solution.

In mononuclear complexes **2** and **3**, the appearance of only one azomethine signal for each compound as well as the presence of four sets for phenyl protons shows that both **2** and **3** complexes have C_2 symmetry. The C_2 axes in these complexes are perpendicular to the coordination plane for **2** and parallel to one for **3**. However, cyclopentadienyl protons were observed as different patterns in **2** and **3**. The spectrum of **2** gave three signals in ferrocenyl region, of which the high field sharp singlet (δ 4.38) was assigned to the non-substituted cyclopentadienyl rings and two proton resonances (δ 4.38 and 4.55) were assigned to mono-substituted cyclopentadienyl α and β protons. This result indicates that the rotation of two ferrocenyl groups is not hindered. On the other hand, the spectrum of **3** gave five signals in the ferrocenyl region; the high field sharp singlet (δ 4.14) was assigned to the non-substituted cyclopentadienyl rings and four proton resonances (δ 4.29, 4.40, 4.44 and 5.72) were assigned to mono-substituted cyclopentadienyl α and β protons. Since mono-substituted cyclopentadienyl ligands normally provide just two proton resonances, the observation of the four signals suggests the existence of a certain rotational barrier involving the ferrocenyl groups in *cis* complex **3**. Moreover, by comparison with *trans* complex **2**, significant downfield shift was clearly observed in one of α protons of *cis* complex **3** (δ 5.72). This deshielding indicates that the Pt···H-C interaction between α proton and platinum metal center has occurred. And this interaction can be considered to be the driving-force affording the related orthometallated trinuclear complex **1** (see Scheme 3). The signals of azomethine protons appear at δ 8.72 for **2** and 7.99 ppm for **3**. These results may indicate that the double bond character of azomethine groups of **2** is weaker than that of **3**. This view is supported by IR data, for which the complexes **2** and **3** revealed the ν(C=N) at 1576 cm^{-1} and 1592 cm^{-1}, respectively (X-ray results also supported these obserbations).

In addition, large splitting of proton NMR signals was observed upon addition of one enantiomer of Pirkle's reagent[28] (R)-(-)-[9-(1-hydroxy-2,2,2-trifluoroethyl)-anthracene] in a solution of **3** (Fig. 6B). This is a clear demonstration that this system is chiral in solution state.

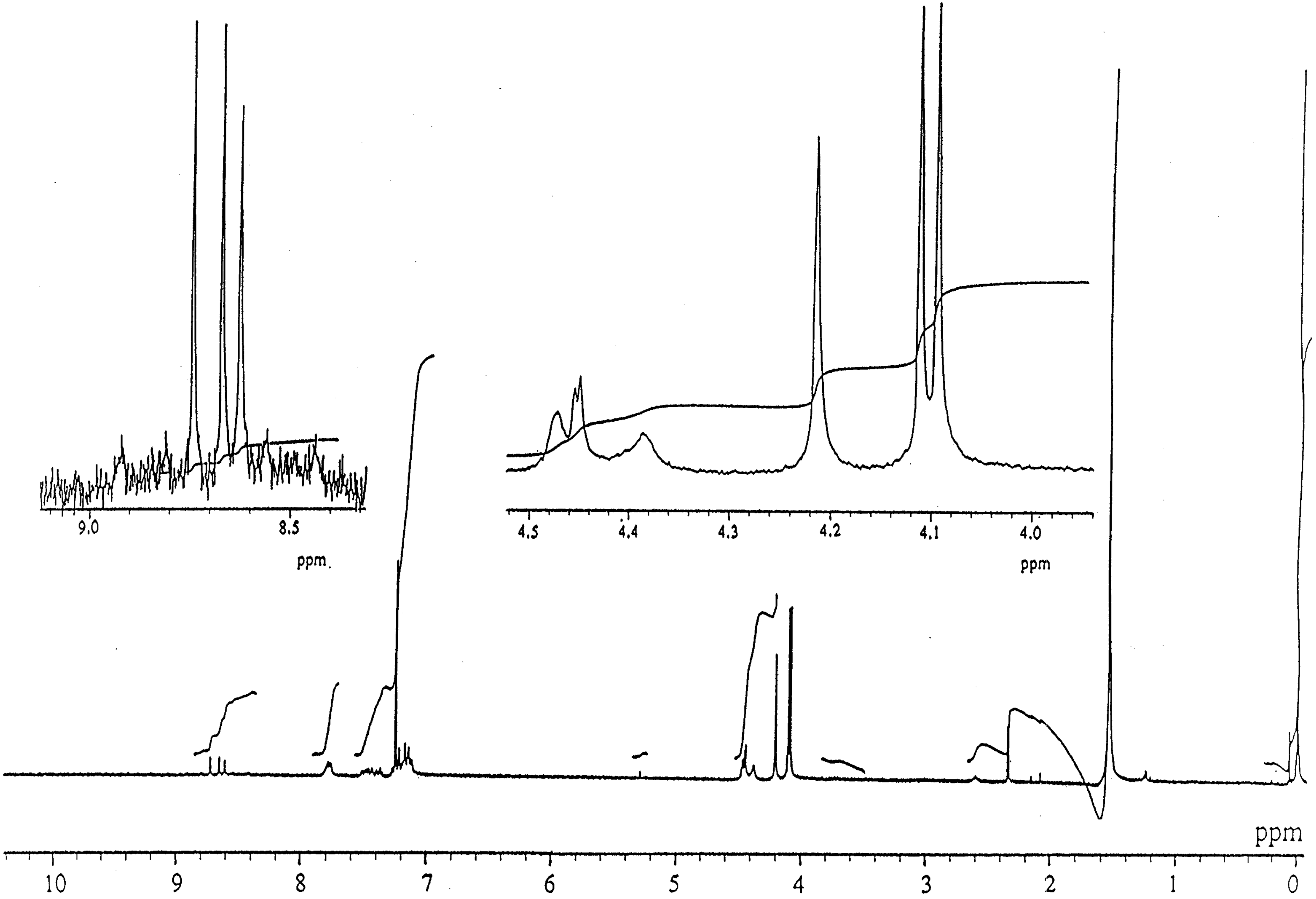


Fig. 4. ^1H NMR spectrum of 1 in $CDCl_3$ solution.

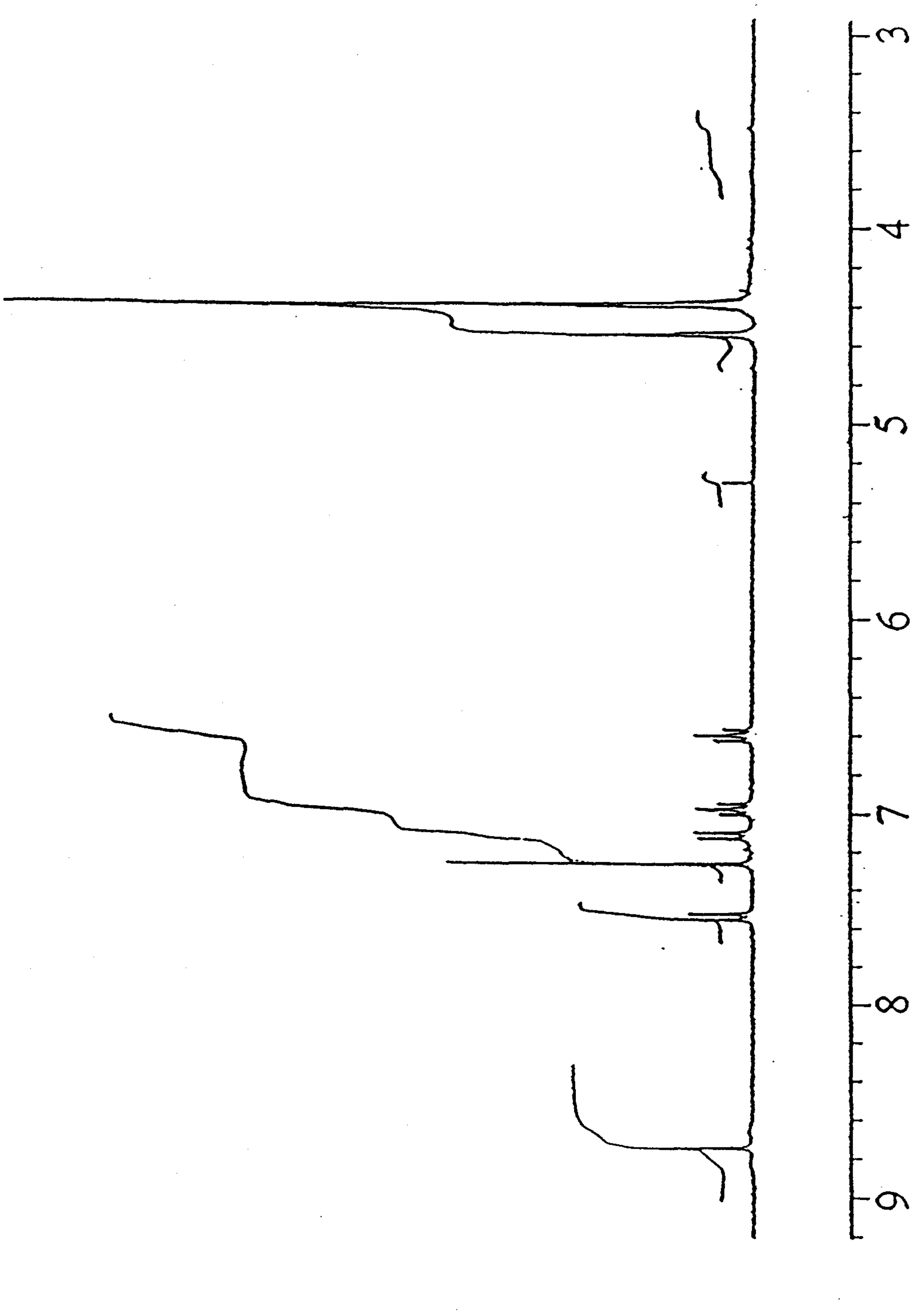


Fig. 5. ^1H NMR spectrum of 2 in $CDCl_3$ solution.

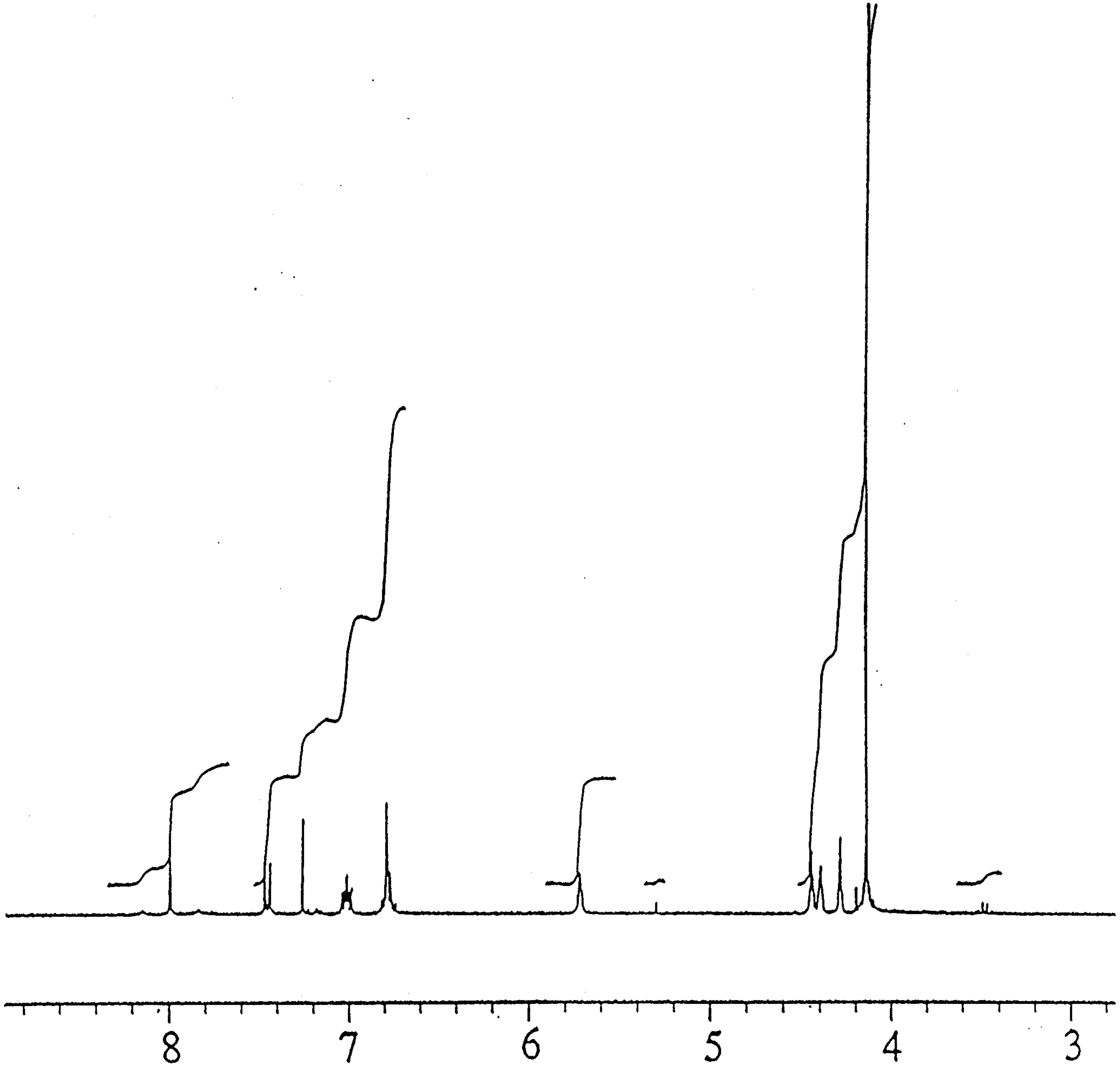


Fig. 6A. ^{1}H NMR spectrum of 3 in $CDCl_3$ solution.

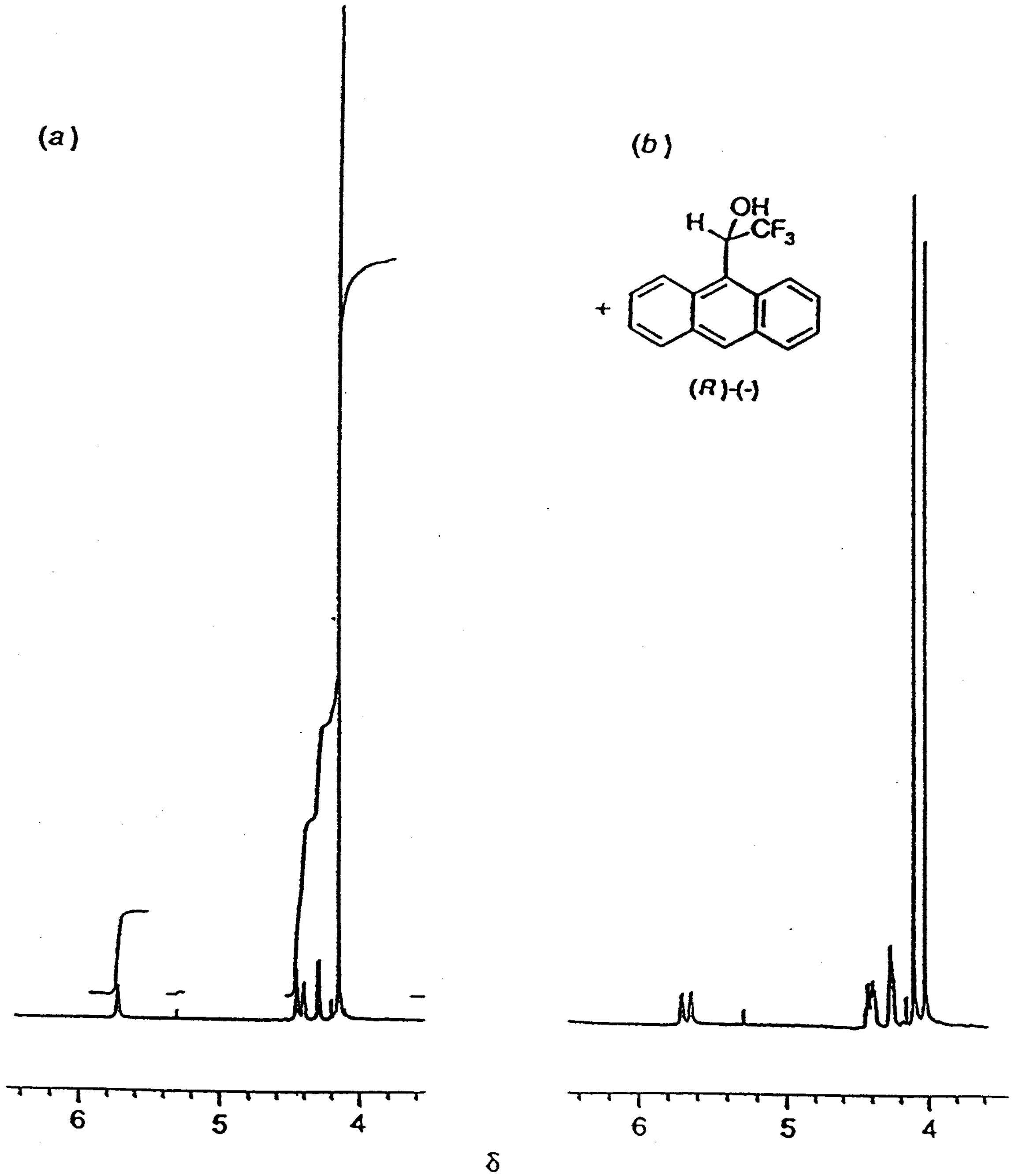


Fig. 6B. ^{1}H NMR spectra for cyclopentadienyl region of (a) 3 and (b) 3 in the presence of Pirkle's reagent.

Absorption spectra. The electronic absorption spectra of **1**, **2**, and **3** in dichloromethane solution are shown in Fig. 7. These complexes exhibit strong absorptions in the visible region, consistent with their intense colors, and their bands mask the d-d transitions.

First, it is worthy of note that the trinuclear complex **1** is green. The electronic absorption spectrum of **1** in dichloromethane solution has four bands at 13.6 (ε = 1600), 17.1 (4900), 21.3 (4000), and 25.2 × 10^3cm^{-1} (7200 dm^3 mol^{-1} cm^{-1}). In general, platinum(II) and palladium(II) complexes with the N, S chelate ligands, which have square planar configuration, are yellow - red and actually the analogous tetranuclear Pt(II) and Pd(II) complexes with *C, N*, S_2 donor atoms are dark red (see ref. 3 and chapter 3). By comparing this spectrum with those of the tetranuclear Pt(II) complex 12.5 (170), 15.7 (2290), 18.4 (6030), and 25.2 × 10^3cm^{-1} (21380 dm^3 mol^{-1} cm^{-1}), the intensity of the band around 13 × 10^3 cm^{-1} in complex **1** is about 10 times as strong as that in tetranuclear complex and this band causes the complex **1** to be colored green.

The electronic absorption spectrum of **2** showed four bands at 13.6 (ε = 1300), 19.3 (9100), 26.4 (sh, 13000), and 28.1 × 10^3 cm^{-1} (16400 dm^3 mol^{-1} cm^{-1}) and that of **3** showed four bands at 13.8 (sh, ε = 340), 16.9 (sh, 1700), 19.4 (6800), and 26.6 × 10^3cm^{-1} (8330 dm^3 mol^{-1} cm^{-1}). It is known that the spectra of the complexes with ferrocenyl groups show the band based on ferrocenyl groups around 20 × 10^3cm^{-1}.[29] Moreover, in the complex $[Pt(mnt)_2]^{2-}$ (mnt = maleonitriledithiolate) having thiolate coordinating to platinum(II), Gray et al. had reported that the bands at 18.5 × 10^3cm^{-1} (ε = 1220 dm^3 mol^{-1} cm^{-1}) and 21.1 × 10^3cm^{-1} (ε = 3470 dm^3 mol^{-1} cm^{-1}) were assigned to metal to ligand charge transfer.[30] Thus we can consider that the low - resolution bands in 16 × 10^3cm^{-1} $\rightarrow$ 20 × 10^3cm^{-1} region correspond to these bands.

The spectrum of *cis* complex **3** is similar to those of *cis*-[Pd(fabt)$_2$] and *cis*-[Ni(fabt)$_2$][3] but shows different curve from that of *trans* complex **2**. In comparison with the spectra of **2** and **3**, the noticeable difference is observed on the intensity of the bands at about 14.0 × 10^3cm^{-1}. We could not assign these bands, but it is interesting that such a difference appear in *trans* and *cis* isomers.[31]

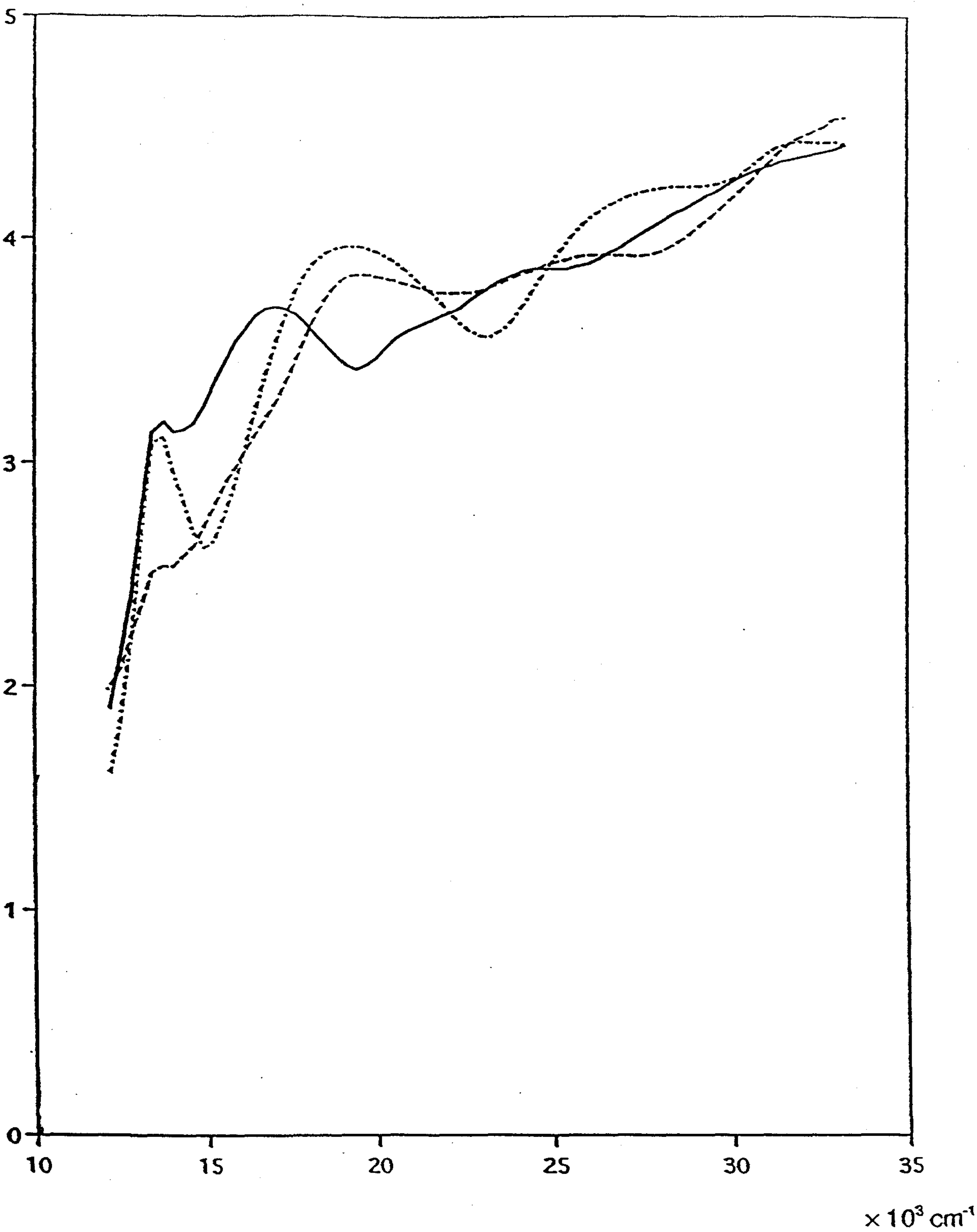


Fig. 7. Absorption spectra in dichloromethane solution of **1** (——), **2** (·-·-·-·), and **3** (-----)

Conclusion. Three novel complexes, a trinuclear complex formulated in $[Pt_3(C^{\circ}\text{-fabt})_3]$ and a pair of *trans* and *cis* isomers formulated in $[Pt(\text{fabt})_2]$ were isolated and their molecular structures were determined by the X-ray diffraction method. This pair of *trans* and *cis* isomers is the first example of Schiff base complexes bearing PtN_2S_2 configuration. The structure of $[Pt_3(C^{\circ}\text{-fabt})_3]$ has a rare C°, *N*, *S*-tridentate ligand and the framework consists of six membered Pt_3S_3 ring in chair form. The structure of *trans*-$[Pt(\text{fabt})_2]$ has an N_2S_2 coordination geometry with a rare umbrella conformation, which allowed to rotate the substituted ferrocenyl groups freely. The structure of *cis*-$[Pt(\text{fabt})_2]$ has an N_2S_2 coordination geometry with a stepped conformation, and the molecule shows molecular helicity by crossing substituted ferrocenyl groups. The absolute configuration determined by the X-ray diffraction method is P-helix.

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31. For cyclic voltammetry, each of **1** and **2** shows two oxidation potentials at 0.75 and 1.13 V for **1** and at 0.77 and 1.04 V for **2** (see experimental section). Though we cannot explain the cause of such a large difference of oxidation potential values between **1** and **2** (1.13 and 1.04 V, respectively), we consider that this difference reflect to the obserbed difference in the absorption spectra of **1** and **2**.

Chapter 3.

The tetranuclear platinum(II) and palladium(II) complexes with C^{o}, N, S-tridentate Schiff base ligands and the dithiolene-like non-innocent type platinum complex with N_2S_2- quadridentate ligand.

Abstract.

The reaction of bis(hexafluoroacethylacetonato)platinum(II), [Pt(hfacac)$_2$], with 2-(phenyl)benzothiazoline, Hphbt, leads to non-innocent type mononuclear platinum complex, [Pt(ddbt)](**1**) (ddbt = bis-2,2'-(1,2-diphenylethylenediimine)benzenethiolato), and orthometallated tetranuclear platinum(II) one, [Pt$_4$(C^{o}-phbt)$_4$](**2**) (C^{o}-phbt = 2-N-(phenylmethylideneamine)benzenethiolato-C^{o}, N, S). The reaction of Pd(CH$_3$COO)$_2$ with Hphbt leads to orthometallated tetranuclear palladium(II) complex, [Pd$_4$(C^{o}-phbt)$_4$](**3**). The reaction of [Pt(hfacac)$_2$] with 2-(1-naphthyl)benzothiazoline, H1-nabt, leads to orthometallated tetranuclear platinum(II) complex, [Pt$_4$(C^{o}-1-nabt)$_4$](**4**) (C^{o}-1-nabt = 2-N-(1-naphthylmethylideneamine)benzenethiolato-C^{o}, N, S). The molecular structures of **1**, **2**, **3**, and **4** have been determined by single-crystal X-ray diffraction method. Crystal data for the complex **1** are monoclinic and space group $P2_1/n$ with a = 14.208(3) Å, b = 18.227(4) Å, c = 14.398(8) Å; β = 94.55(3)°; V = 3717.0(23) Å^3; Z = 4. Crystal data for the complex **2** are monoclinic and space group $P2_1/n$ with a = 19.893(5) Å b = 17.950(7) Å, c = 14.844(4) Å; V = 5286.5(23) Å^3; Z = 4. Crystal data for the complex **3** are monoclinic and space group $P2_1/n$ with a = 20.018(8) Å, b = 18.16(2) Å, c = 14.454(6) Å; V = 5233.8(75) Å^3; Z = 4. Crystal data for the complex **4** are tetragonal and space group $I4_1/a$ with a = b = 15.496(2) Å, c = 24.348(3) Å; V = 5846.3(20) Å^3; Z = 16 for Pt(C^{o}-1-nabt) unit. The complex **1** is non-innocent type platinum complex having N$_2$S$_2$-quadridentate ddbt ligand derived from bond formation between two independent imino carbon atoms in coordinated phbt ligands. The molecular structures of **2** , **3**, and **4** confirm the formation of unusual tetranuclear complexes featuring a rare C^{o}, N, S-tridentate Schiff base ligand derived from orthometallation of the pendant side arm.

3.1 Introduction.

The reaction of nickel(II) or palladium(II) with 2-(phenyl)benzothiazoline (Hphbt) in the 1 : 2 stoichiometry ratio afforded only mononuclear complexes which have a square planar configuration with *cis* geometry[1] and this reaction did not afford tetranuclear palladium(II) complex corresponding to $[Pd_4(C^{\sigma}\text{-1-nabt})_4]$ (H1-nabt = 2-(1-naphthyl)benzothiazoline) [2] in which the activation of C-H bond in 1-naphthyl group should occure. There has been considerable interest in the activation of C-H bonds by transition metal complexes. In relation to this, many metal complexes showing the agostic three-center two-electron M···H-C interaction have been reported.[3] Moreover, recently a few examples of the three-center four-electron M···H-N interaction have been reported.[4] In addition, in many important transition-metal-catalyzed reactions, the particular attention has been focused on the M···H-C interaction between *ortho*-hydrogen atom and the central transition metal atom in the complex because of the selective activation of the *ortho*-hydrogen-carbon bonds.[5] Although many examples of the orthometallation reaction, in which σ bonds between the aryl carbon atom and the metal atom are formed by the replacement of the *ortho*-hydrogens to the metal atoms, have been known,[6] it is a rare example that both an intermediate metal complex containing an activated C-H bond interacting with metal atom and the corresponding orthometallated complex resulting from the dissociation of the C-H bond are isolated in crystals, respectively.[7]

In this chapter, the syntheses and structures of mononuclear non-innocent type platinum complex and orthometallated tetranuclear platinum(II) and palladium(II) complexes are presented.

3.2 Experimental Section

Materials. Bis(hexafluoroacetylacetonato)platinum(II), $[Pt(hfacac)_2]$,[8] and 2-(phenyl)benzothiazoline, Hphbt[9], were prepared in the literature methods. The toluene and acetonitrile were dried over molecular sieve 3A. Dichloromethane was dried over $CaCl_2$. Unless otherwise stated, commercial grade chemicals were used without further purification.

Measurements. Electronic absorption spectra in dichloromethane solutions and Nujol mulls were recorded on a Hitachi U-3400 and a Shimadzu MPS-5000 spectrophotometer, respectively. IR spectra were obtained on a Pirkin-Elmer 983G Infrared Spectrometer using Nujol mulls between CsI plates. NMR spectra in $CDCl_3$ solution were recorded on a JEOL JNM EX-270 instrument using tetramethylsilane as an internal standard (δ = 0).

added a 0.5 equiv. amount of [Pt(hfacac)$_2$] and then stirred at ca. 70 °C for 3 h. After the mixture was allowed to stand for a day, the solvent was removed from the mixture then the resulting dark red precipitate was dissolved in a minimum amount of dichloromethane and purified on a silica gel plate with dichloromethane as the eluent. The first eluted blue band, which corresponded to compound **1**, was collected. Crystals suitable for X-ray diffraction were obtained from the 1,2-dichloroethane - pentane solution. NMR ($CDCl_3$, 23 °C): ^{1}H (270 MHz), δ 8.84-7.79 (m, 2H), 7.72 (d, 2H), 7.44-6.76 (m, 14H), and 6.72 (d, 2H); ^{13}C(67.8 MHz), δ 142.64, 129.79, 128.61, 128.27, 127.19, 127.11, 126.94, 126.53, 126.70, 125.70, 125.55, 124.93, and 121.20.

Synthesis of Tetrakis[2-N-(phenylmethylideneamine)benzenethiolato-*C^o^*,*N*,*S*]tetraplatinum(II) [Pt$_4$(*C*^{o}-phbt)$_4$] (2). To a solution of 2-(phenyl)benzothiazoline (0.033 g, 0.32 mmol) in toluene (20mL) was added an equimolar amount of [Pt(hfacac)$_2$] (0.100 g, 0.32 mmol), and the mixture was refluxed over 1 h. The solvent was removed from the reaction mixture. Then the resulting dark red precipitate was dissolved in a minimum amount of dichloromethane and purified on a silica gel plate with dichloromethane as the eluent. The first band, which corresponded to compound **2**, was collected and recrystallized from acetone solution. The yield was 20 % based on the amount of the starting [Pt(hfacac)$_2$]. Single crystals of **2** suitable for X-ray analysis were obtained from 1,2-dichloroethane - pentane solution. It is intrest to note that the mononuclear platinum(II) complex corresponding to *cis*-[Pd(phbt)$_2$]^1 or *cis*-[Ni(phbt)$_2$]^{10} could not be obtained, even in 1 : 2 ratio of [Pt(hfacac)$_2$] and Hphbt. NMR ($CDCl_3$, 23 °C): ^{1}H (270 MHz), δ 7.59 (d, 4H), 7.43 (s, 4H), 7.17 (d, 4H), and 7.1-6.8 (m, 24H); ^{13}C (67.8 MHz), δ 167.04, 160.04, 149.67, 146.47, 141.36, 136.88, 132.29, 131.21, 130.71, 129.16, 125.51, 122.17, and 117.78. Anal. Calcd for $C_{52}H_{36}Pt_4N_4S_4\cdot(CH_3)_2CO$: C, 39.24; H, 2.51; N, 3.33. Found: C, 39.13; H, 2.62; N, 3.37 %.

Synthesis of Tetrakis[2-N-(phenylmethylideneamine)-benzenethiolato-*C^o^*,*N*,*S*]tetrapalladium(II) [Pd$_4$(*C*^{o}-phbt)$_4$] (3). To a solution of 2-(phenyl)benzothiazoline (0.090 g, 0.42 mmol) in toluene (20 mL) was added an equimolar amount of palladium acetate (0.100 g, 0.45 mmol) and refluxed for 3 h. The solvent was removed from the reaction mixture. Then the resulting red precipitate was dissolved in a minimum amount of dichloromethane and purified on a silica gel plate with dichloromethane as the eluent. A red complex **3** was obtained from dichloromethane - pentane solution. The yield was 16 % based on the amount of the starting palladium acetate. Single crystals of **3** suitable for X-ray analysis were obtained from dichloromethane - 1,2-dichloroethane - pentane solution. NMR ($CDCl_3$, 23 °C): ^1H (270 MHz), δ 7.65-7.60 (m, 4H), 7.35 (s, 4H), 7.12 (d, 4H), 7.03-6.98 (m, 16H), and 6.90-6.82 (m, 8H); ^{13}C (67.8 MHz), δ 169.79, 163.74, 151.01, 145.24, 143.65, 137.19, 133.44, 130.53, 129.76, 128.69, 124.91, 123.32, and 117.07. Anal. Calcd for $C_{52}H_{36}Pd_4N_4S_4 \cdot 2CH_2Cl_2$: C, 45.02; H, 2.80; N, 3.89. Found: C, 44.51; H, 2.99; N, 3.84 %.

Reflux a solution of *cis*-[Pd(phbt)$_2$] in toluene. A solution of *cis*-[Pd(phbt)$_2$][1] (0.050 g, 0.112 mmol) in toluene (20 mL) was refluxed for 10 h. The formation of the complex **3** was clearly identified on a silica gel plate.

Synthesis of Tetrakis[2-N-(1-naphthylmethylideneamine)benzenethiolato-*C^o,N,S*]tetraplatinum(II) [Pt$_4$(*C^o*-1-nabt)$_4$] (4). To a solution of 2-(1-naphthyl)benzothiazoline (0.088 g, 0.32 mmol) in toluene (20mL) was added an equimolar amount of [Pt(hfacac)$_2$] (0.200 g, 0.32 mmol), and the mixture was refluxed over 3 h. The solvent was removed from the reaction mixture by using a rotary evaporator. The resulting dark red precipitate was dissolved in a minimum amount of dichloromethane and purified on a silica gel (230 - 400 mesh) column with dichloromethane as the eluent. The first band, which corresponded to compound **3**, was collected and the yield was 35 % based on the amount of the starting [Pt(hfacac)$_2$]. Single crystals of **3** suitable for X-ray analysis were grown by the slow evaporation of a dichloromethane solution. It is interest to note that the mononuclear non-innocent type platinum complex corresponding to complex **1** and the mononuclear platinum(II) complex corresponding to *cis*-[Pd(1-nabt)$_2$][1] or *cis*-[Ni(1-nabt)$_2$] could not be obtained, even in 1 : 2 ratio of [Pt(hfacac)$_2$] and H1-nabt . Anal. Calcd for $C_{68}H_{44}N_4Pt_4S_4$: C, 44.73; H, 2.43; N, 3.07. Found: C, 44.19; H, 2.62; N, 3.11 %. We could not get sharp high resolution NMR spectra for **4** even at -50 °C. This fact may suggest that the height of the barrier for the exchange process in **4** is not suitable to be observed by NMR spectroscopy because of slow conformational changes for tetranuclear complex. This slow conformational equilibrium is consistent with the results of IR spectroscopy which exhibit four bands (1611, 1583, 1561, and 1553 cm^{-1}) for ν(N=C) and ν(aromatic C=C) of **4**.[11,12]

Crystal Structure Determination. All crystals were attached to the end of glass fiber and coated with epoxy. X-Ray measurements of [Pt(ddbt)] (**1**), [Pt(*C^o*-phbt)$_4$] (**2**), and [Pd$_4$(*C^o*-phbt)$_4$] (**3**) were made on a Mac Science MXC3 diffractometer with Mo-Kα radiation; X-ray measurement of [Pt$_4$(*C^o*-1-nabt)$_4$] (**4**) was made on a Rigaku AFC-5R diffractometer with Cu-Kα radiation; ω-2θ scans were used. Crystallographic data are summarized in Tables 1A-1D. Empirical absorption corrections were applied for all samples. The intensities of three standard reflections were monitored every 100 reflections and showed no greater fluctuations during the data collection than expected from Poisson statistics. The structures of **1**, **2**, and **3** were solved by the direct methods (SIR) and that of **4** was solved by direct methods (SHELXS-86).[13] The calculation for **4** was carried out using the program HBLS-V[14] on an ACOS&SX NEC computer at Computation Center Osaka University. All structures were refined by full-matrix least-squares with anisotropic thermal parameters for non-H atoms and isotropic one for H atoms. Atomic scattering factors and anomalous scattering coefficients were taken from ref. 14. Final atomic coordinates for the non-hydrogen atoms of **1**, **2**, **3**, and **4** are given in Table 2A-2D, respectively. Fractional positional parameters and equivalent isotropic temperature factors for the hydrogen atoms for **1** and **4** are given in Tables 3A and 3B. Anisotropic temperature factors for **1**, **2**, **3**, and **4** are given in Tables 4A-4D. The selected bond lengths and angles are shown in Tables 5A-5D. Tables 3A-3B, 4A-4D, and 5A-5D are in the Appendix section (chapter 3).

Table 1A Crystal data for **1**

Formula	$C_{26}H_{18}N_2S_2Pt_1$
M	617.00
Crystal system	Monoclinic
Space group	$P2_1/n$
a / Å	10.789(6)
b / Å	24.541(19)
c / Å	8.631(11)
β / °	102.71(7)
V / Å^3	2229.2 (36)
Z	4
Crystal size (mm)	0.35 × 0.30 × 0.20
T / °C	25
λ/	0.71073
Dc / g cm^{-1}	1.835
μ / cm^{-1}	6.546
$2\theta_{max}$ / °	50
No. of measured reflections	4444
No. reflections used in refinement	2087 (refl observed if $I>3.00\sigma(I)$)
R^a	0.057
$R_w{}^b$	0.065

[a] $R = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$. [b] $Rw = [\Sigma w(|Fo| - |Fc|)^2 / \Sigma w(Fo)^2]^{1/2}$. Weighting scheme: $1/[\sigma^2(Fo)]$.

Table 1B Crystal data for 2

Formula	$C_{56}H_{42}Cl_4N_4Pt_4S_4$
M	1823.39
Crystal system	Monoclinic
Space group	$P2_1/n$
a / Å	19.893(5)
b / Å	17.950(7)
c / Å	14.844(4)
β / °	93.68(2)
V / $Å^3$	5286.5(23)
Z	4
Crystal size (mm)	0.35 × 0.30 × 0.20
T / °C	25
λ/	0.71073
Dc / g cm^{-1}	2.292
μ(Mo-Kα)/mm^{-1}	13.161
$2\theta_{max}$ / °	50
No. of measured reflections	10232
No. reflections used in refinement	4388 (refl observed if $I>3.00\sigma(I)$)
R^a	0.066
$R_w{}^b$	0.083

[a] $R = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$. [b] $Rw = [\Sigma w(|Fo| - |Fc|)^2 / \Sigma w(Fo)^2]^{1/2}$. Weighting scheme: $1/[\sigma^2(Fo)]$.

Table 1C Crystal data for **3**

Formula	$C_{55} H_{42} Cl_4 N_4 Pd_4 S_4$
M	1454.72
Crystal system	Monoclinic
Space group	$P2_1/n$
a / Å	20.018(8)
b / Å	18.16(2)
c / Å	14.454(6)
β / °	95.14(3)
V / Å^3	5233.8(75)
Z	4
Crystal size (mm)	0.25 × 0.20 × 0.10
T / °C	25
λ/	0.71073
Dc / g cm^{-1}	1.847
μ(Mo-Kα)/mm^{-1}	1.7375
$2\theta_{max}$ / °	50
No. of measured reflections	7997
No. reflections used in refinement	2676 (refl observed if $I>3.00\sigma(I)$)
R[a]	0.067
R_w[b]	0.079

[a] $R = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$. [b] $Rw = [\Sigma w(|Fo| - |Fc|)^2 / \Sigma w(Fo)^2]^{1/2}$. Weighting scheme: $1/[\sigma^2(Fo)]$.

Table 1D Crystal data for **4**

Formula	$C_{17} H_{11} N_1 Pt_1 S_1$
M	456.44
Crystal system	Tetragonal
Space group	$I4_1/a$
a / Å	15.496(2)
b / Å	
c / Å	24.348(3)
V / Å^3	5846.3(20)
Z	16
Crystal size (mm)	0.15 × 0.15 × 0.15
T / °C	23
λ/	1.54184
Dc / g cm^{-1}	2.08
μ / cm^{-1}	193.6
$2\theta_{max}$ / °	110
No. of measured reflections	2558
No. reflections used in refinement	1275 (refl observed if $Fo>3.00\sigma(Fo)$)
R^a	0.083
$R_w{}^b$	0.085

[a] $R = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$. [b] $Rw = [\Sigma w(|Fo| - |Fc|)^2 / \Sigma w(Fo)^2]^{1/2}$. Weighting scheme: $1/[\sigma^2(Fo)]$.

Table 2A Atomic coordinates and isotropic thermal parameters for **1**

Atom	*X/a*	*Y/b*	*Z/c*	*U*
Pt1	-0.68924(5)	-0.08927(3)	-0.49663(6)	0.0404(3)
S1	-0.6255(3)	-0.0244(2)	-0.6441(4)	0.052(2)
S2	-0.5726(3)	-0.0752(2)	-0.2538(4)	0.063(2)
N1	-0.8170(9)	-0.1082(5)	-0.6878(10)	0.037(4)
N2	-0.7591(10)	-0.1523(6)	-0.4082(16)	0.046(6)
C1	-0.7351(13)	-0.0358(6)	-0.8145(13)	0.055(6)
C2	-0.7402(15)	-0.0005(10)	-0.9454(18)	0.059(9)
C3	-0.8321(18)	-0.0108(12)	-1.0878(29)	0.07(1)
C4	-0.9278(18)	-0.0578(7)	-1.0925(23)	0.079(8)
C5	-0.9252(14)	-0.0826(9)	-0.9592(12)	0.058(9)
C6	-0.8296(10)	-0.0781(5)	-0.8239(16)	0.049(5)
C7	-0.9101(11)	-0.1504(5)	-0.6683(15)	0.035(5)
C8	-1.0295(10)	-0.1249(6)	-0.6433(14)	0.044(5)
C9	-1.0453(16)	-0.0874(10)	-0.5510(17)	0.06(1)
C10	-1.1480(18)	-0.0598(11)	-0.5105(20)	0.063(9)
C11	-1.2634(14)	-0.0883(13)	-0.5980(23)	0.10(1)
C12	-1.2571(17)	-0.1293(12)	-0.6965(31)	0.08(1)
C13	-1.1416(18)	-0.1487(8)	-0.7121(25)	0.070(8)
C14	-0.6384(15)	-0.1279(7)	-0.1613(21)	0.065(7)
C15	-0.5945(14)	-0.1404(10)	0.0003(19)	0.051(8)
C16	-0.633(2)	-0.182(1)	0.074(3)	0.09(1)
C17	-0.707(2)	-0.220(1)	-0.014(3)	0.07(1)
C18	-0.7600(15)	-0.2102(9)	-0.1765(14)	0.066(8)
C19	-0.7196(10)	-0.1634(6)	-0.2472(14)	0.048(6)
C20	-0.8438(9)	-0.1864(5)	-0.5204(14)	0.037(4)
C21	-0.7757(12)	-0.2365(6)	-0.5756(14)	0.036(5)
C22	-0.8561(14)	-0.2765(7)	-0.6415(16)	0.061(7)
C23	-0.798(3)	-0.322(1)	-0.708(3)	0.08(1)
C24	-0.673(2)	-0.328(1)	-0.692(2)	0.08(1)
C25	-0.6003(16)	-0.2842(9)	-0.6083(21)	0.072(9)
C26	-0.6520(14)	-0.2416(7)	-0.5524(19)	0.060(7)

$T = \exp[-2\pi 2U]$; $U = U_{iso}$ or $(U_{11} + U_{22} + U_{33}) / 3$

Table 2B Atomic coordinates and isotropic thermal parameters for **2**

Atom	*X/a*	*Y/b*	*Z/c*	*U*
Pt1	0.46550(13)	0.29656(17)	0.25753(20)	0.043(1)
Pt2	0.63793(13)	0.21111(17)	0.21428(19)	0.041(1)
Pt3	0.51316(13)	0.15558(15)	0.07492(19)	0.039(1)
Pt4	0.54054(13)	0.36168(16)	0.08338(20)	0.041(1)
Cl1	0.726(3)	0.323(2)	0.672(3)	0.12(3)
Cl2	0.623(3)	0.193(2)	0.569(3)	0.13(3)
Cl3	0.437(3)	0.193(3)	0.668(3)	0.13(3)
Cl4	0.423(4)	0.350(3)	0.546(3)	0.15(3)
S1	0.5646(9)	0.2435(11)	0.3208(13)	0.049(9)
S2	0.6446(9)	0.3270(10)	0.1448(14)	0.047(8)
S3	0.4297(9)	0.1981(10)	0.1681(12)	0.044(8)
S4	0.5195(9)	0.2599(10)	-0.0127(12)	0.044(8)
N1	0.491(4)	0.387(3)	0.335(5)	0.05(3)
N2	0.700(3)	0.178(4)	0.118(5)	0.05(3)
N3	0.511(3)	0.060(4)	0.148(4)	0.05(3)
N4	0.448(3)	0.395(3)	0.035(5)	0.05(3)
C1	0.599(4)	0.328(5)	0.373(7)	0.07(5)
C2	0.665(4)	0.327(5)	0.416(8)	0.07(5)
C3	0.683(5)	0.388(8)	0.458(7)	0.09(7)
C4	0.642(5)	0.452(5)	0.468(7)	0.07(5)
C5	0.584(5)	0.453(6)	0.425(7)	0.07(5)
C6	0.559(4)	0.388(4)	0.382(6)	0.06(4)
C7	0.447(5)	0.435(5)	0.337(6)	0.07(5)
C8	0.389(7)	0.426(6)	0.276(9)	0.09(7)
C9	0.382(5)	0.360(6)	0.231(7)	0.08(5)
C10	0.325(4)	0.343(7)	0.171(6)	0.08(5)
C11	0.273(6)	0.401(7)	0.166(7)	0.08(6)
C12	0.277(4)	0.466(5)	0.215(8)	0.07(5)
C13	0.330(6)	0.479(8)	0.276(11)	0.11(8)
C14	0.690(3)	0.292(4)	0.051(6)	0.06(4)
C15	0.702(5)	0.349(6)	-0.016(7)	0.07(5)
C16	0.741(5)	0.321(7)	-0.091(7)	0.08(5)
C17	0.762(5)	0.243(4)	-0.096(5)	0.06(4)
C18	0.749(4)	0.199(5)	-0.026(6)	0.06(4)
C19	0.714(3)	0.222(5)	0.049(5)	0.05(4)
C20	0.723(4)	0.109(5)	0.134(6)	0.07(5)
C21	0.699(4)	0.067(5)	0.201(7)	0.06(5)
C22	0.655(3)	0.105(5)	0.261(4)	0.05(3)
C23	0.633(4)	0.065(5)	0.340(6)	0.06(4)
C24	0.653(4)	-0.002(5)	0.355(5)	0.06(4)
C25	0.700(4)	-0.036(5)	0.305(7)	0.07(5)
C26	0.719(4)	-0.006(4)	0.232(6)	0.06(3)
C27	0.436(3)	0.117(3)	0.243(5)	0.04(3)
C28	0.401(6)	0.124(7)	0.319(8)	0.08(6)
C29	0.393(5)	0.057(6)	0.379(7)	0.08(5)
C30	0.444(6)	-0.006(6)	0.360(9)	0.09(7)
C31	0.473(5)	-0.001(6)	0.283(7)	0.07(5)
C32	0.473(3)	0.059(4)	0.228(4)	0.04(3)
C33	0.551(3)	0.004(4)	0.121(5)	0.04(3)
C34	0.583(4)	0.023(4)	0.040(6)	0.05(4)

C35	0.576(4)	0.097(4)	0.004(5)	0.05(4)
C36	0.607(4)	0.103(5)	-0.068(5)	0.05(4)
C37	0.648(3)	0.060(3)	-0.117(5)	0.04(3)
C38	0.659(5)	-0.009(7)	-0.078(8)	0.08(6)
C39	0.625(5)	-0.035(4)	0.006(6)	0.06(4)
C40	0.438(3)	0.285(4)	-0.046(6)	0.05(3)
C41	0.400(4)	0.238(4)	-0.099(6)	0.05(4)
C42	0.329(5)	0.256(5)	-0.135(9)	0.08(6)
C43	0.301(4)	0.323(5)	-0.106(8)	0.07(5)
C44	0.343(4)	0.369(5)	-0.057(5)	0.06(4)
C45	0.409(3)	0.353(5)	-0.027(5)	0.06(4)
C46	0.430(4)	0.463(4)	0.062(6)	0.05(3)
C47	0.481(3)	0.499(4)	0.128(4)	0.04(3)
C48	0.543(4)	0.461(4)	0.147(4)	0.04(3)
C49	0.589(5)	0.494(4)	0.202(6)	0.06(4)
C50	0.579(5)	0.570(5)	0.238(8)	0.08(5)
C51	0.518(4)	0.601(4)	0.219(5)	0.05(3)
C52	0.472(4)	0.574(5)	0.158(8)	0.07(5)
C53	0.644(8)	0.303(9)	0.698(12)	0.1(1)
C54	0.625(7)	0.221(10)	0.682(14)	0.1(1)
C55	0.406(10)	0.199(7)	0.555(16)	0.2(1)
C56	0.441(9)	0.258(10)	0.512(10)	0.1(1)

$T = \exp[-2\pi 2U]$; $U = U_{iso}$ or $(U_{11} + U_{22} + U_{33}) / 3$

Table 2C Atomic coordinates and isotropic thermal parameters for 3

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	*U*
Pd1	0.98362(16)	0.15042(23)	0.92862(24)	0.064(2)
Pd2	1.03517(17)	0.29183(25)	0.74505(26)	0.073(3)
Pd3	0.95997(15)	0.35383(23)	0.92513(25)	0.066(2)
Pd4	0.86059(16)	0.21455(24)	0.78403(25)	0.069(2)
Cl1	1.0685(16)	0.3412(19)	0.4456(19)	0.23(3)
Cl2	1.090(2)	0.184(2)	0.397(3)	0.31(4)
Cl3	0.906(4)	0.192(3)	0.378(8)	0.6(1)
Cl4	0.807(5)	0.324(3)	0.326(4)	0.54(9)
S1	1.0684(6)	0.1899(7)	0.8343(10)	0.078(8)
S2	0.9321(7)	0.2458(9)	0.6743(9)	0.084(9)
S3	0.9764(6)	0.2516(8)	1.0238(8)	0.072(8)
S4	0.8529(5)	0.3297(7)	0.8582(10)	0.074(7)
N1	0.983(2)	0.058(2)	0.848(3)	0.06(2)
N2	1.010(2)	0.384(3)	0.668(3)	0.08(3)
N3	1.0567(17)	0.3794(23)	0.9786(31)	0.07(2)
N4	0.7966(16)	0.1755(25)	0.8800(25)	0.07(2)
C1	1.059(2)	0.116(3)	0.755(4)	0.09(3)
C2	1.095(3)	0.117(4)	0.684(5)	0.12(5)
C3	1.101(4)	0.069(8)	0.627(6)	0.21(9)
C4	1.056(3)	0.002(6)	0.625(4)	0.15(6)
C5	1.021(3)	-0.004(3)	0.706(4)	0.11(5)
C6	1.020(2)	0.058(3)	0.770(4)	0.08(3)
C7	0.950(3)	0.006(3)	0.879(3)	0.07(3)
C8	0.912(2)	0.018(3)	0.962(4)	0.06(3)
C9	0.9200(19)	0.0865(28)	1.0022(33)	0.07(3)
C10	0.891(2)	0.107(3)	1.079(3)	0.07(3)
C11	0.854(3)	0.055(3)	1.120(4)	0.09(4)
C12	0.841(2)	-0.012(4)	1.083(4)	0.11(4)
C13	0.875(3)	-0.034(3)	0.999(4)	0.09(4)
C14	0.902(3)	0.330(5)	0.628(4)	0.12(5)
C15	0.835(3)	0.335(5)	0.588(4)	0.13(5)
C16	0.815(4)	0.400(4)	0.540(5)	0.13(5)
C17	0.859(4)	0.457(4)	0.531(4)	0.13(6)
C18	0.926(3)	0.455(4)	0.574(4)	0.11(5)
C19	0.949(3)	0.392(4)	0.620(3)	0.10(4)
C20	1.056(3)	0.431(3)	0.677(4)	0.09(4)
C21	1.120(3)	0.415(3)	0.728(4)	0.10(4)
C22	1.122(2)	0.351(4)	0.775(3)	0.08(4)
C23	1.177(2)	0.332(3)	0.835(4)	0.09(3)
C24	1.232(3)	0.381(4)	0.852(5)	0.12(5)
C25	1.231(4)	0.444(6)	0.803(6)	0.14(7)
C26	1.173(4)	0.466(4)	0.741(5)	0.13(5)
C27	1.063(2)	0.267(2)	1.061(4)	0.07(3)
C28	1.096(2)	0.218(4)	1.127(4)	0.12(4)
C29	1.162(3)	0.236(3)	1.156(4)	0.10(4)
C30	1.193(3)	0.299(2)	1.133(4)	0.08(3)
C31	1.160(2)	0.348(3)	1.072(4)	0.09(4)
C32	1.090(2)	0.332(3)	1.040(3)	0.07(3)
C33	1.073(2)	0.443(3)	0.949(3)	0.07(3)
C34	1.026(3)	0.487(4)	0.887(4)	0.09(4)

C35	0.963(2)	0.452(3)	0.861(3)	0.08(3)
C36	0.914(3)	0.488(3)	0.807(4)	0.09(4)
C37	0.928(3)	0.560(3)	0.777(3)	0.08(3)
C38	0.993(3)	0.594(3)	0.798(4)	0.09(4)
C39	1.042(3)	0.561(4)	0.858(4)	0.10(4)
C40	0.8069(17)	0.2990(32)	0.9540(36)	0.08(3)
C41	0.794(2)	0.351(3)	1.024(4)	0.09(4)
C42	0.758(3)	0.324(4)	1.097(4)	0.10(4)
C43	0.734(3)	0.247(5)	1.097(5)	0.13(6)
C44	0.749(3)	0.199(3)	1.030(4)	0.09(4)
C45	0.785(2)	0.225(3)	0.954(3)	0.07(3)
C46	0.776(2)	0.110(3)	0.865(4)	0.08(3)
C47	0.7988(19)	0.0749(28)	0.7893(36)	0.07(3)
C48	0.8416(19)	0.1150(27)	0.7329(32)	0.07(3)
C49	0.864(3)	0.083(3)	0.656(4)	0.09(4)
C50	0.842(3)	0.013(5)	0.630(5)	0.12(5)
C51	0.797(4)	-0.027(4)	0.682(5)	0.13(5)
C52	0.776(2)	0.003(3)	0.765(4)	0.10(4)
C53	1.057(4)	0.253(6)	0.486(6)	0.19(8)
C54	0.890(8)	0.236(8)	0.290(7)	0.3(1)
C55	0.879(5)	0.328(9)	0.338(5)	0.2(1)

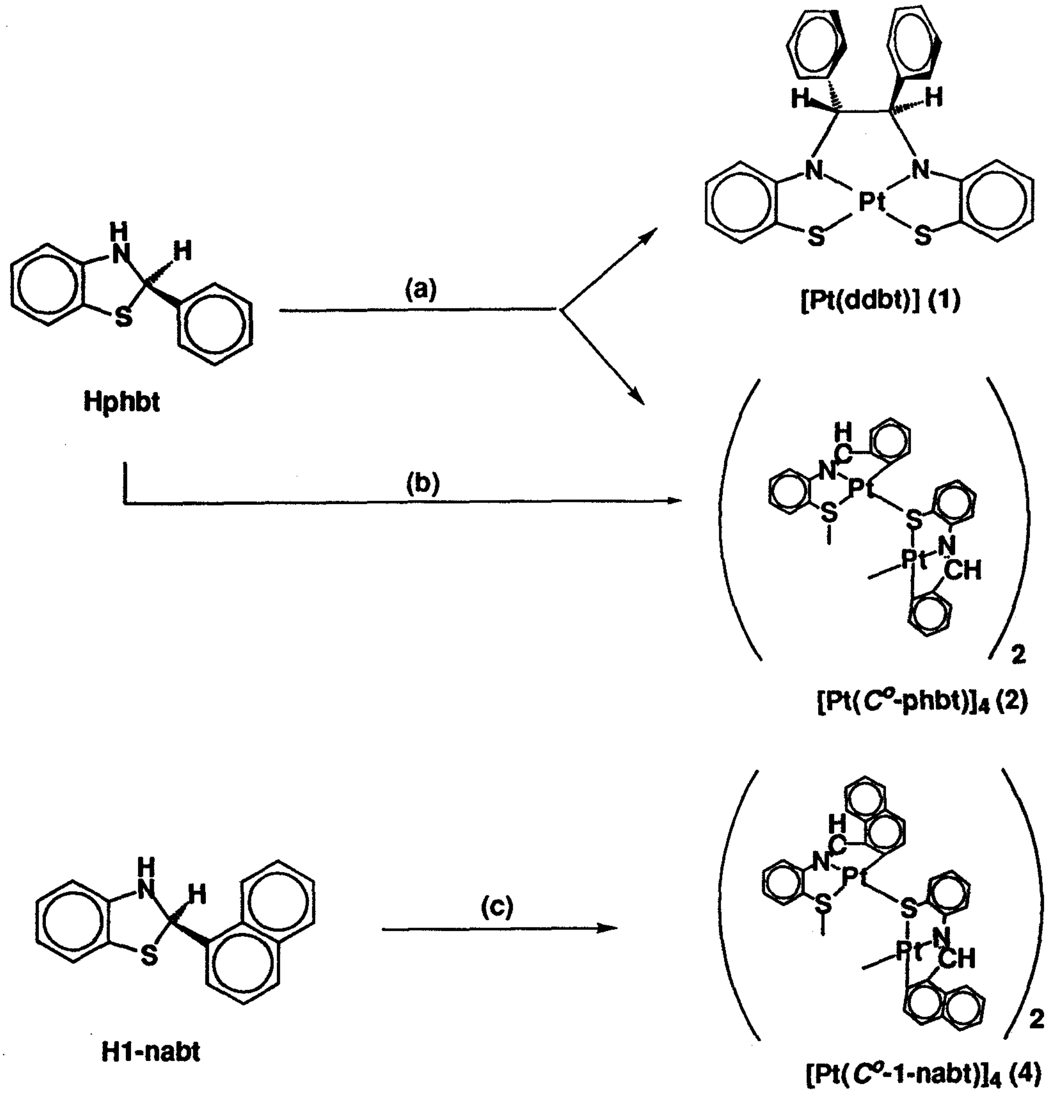
$T = \exp[-2\pi 2U]$; $U = U_{iso}$ or $(U_{11} + U_{22} + U_{33}) / 3$

Table 2D Fractional atomic coordinates for **4**

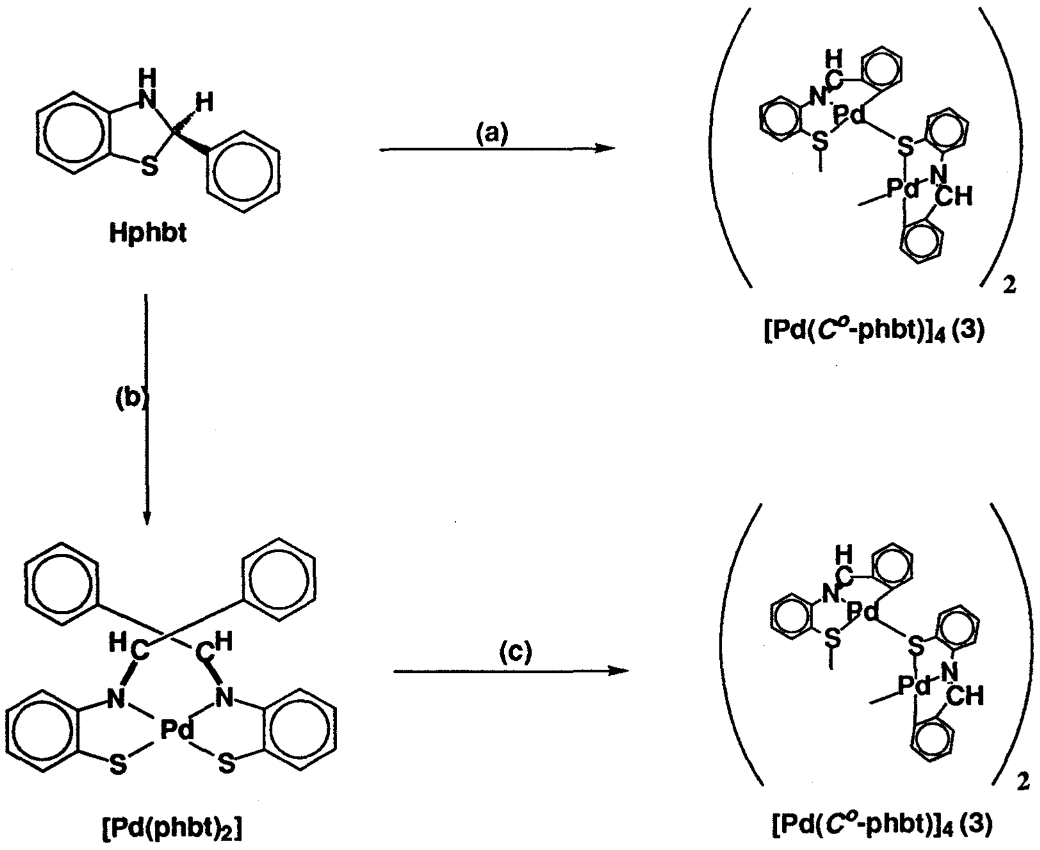
Atom	X/a	Y/b	Z/c	*Beq*
Pt1	0.0516(2)	0.3398(2)	0.0616(2)	3.064
S1	-0.0267(3)	0.4054(3)	0.1328(2)	3.219
N1	-0.0339(3)	0.3965(3)	0.0119(2)	2.849
C1	-0.1111(3)	0.4435(3)	0.0929(2)	2.745
C2	-0.1141(3)	0.4353(3)	0.0345(2)	2.991
C3	-0.1749(3)	0.4696(3)	0.0038(2)	4.776
C4	-0.2503(3)	0.5012(3)	0.0293(2)	3.301
C5	-0.2455(3)	0.5170(3)	0.0822(2)	7.203
C6	-0.1877(3)	0.4793(3)	0.1142(2)	5.519
C7	-0.198(3)	0.3916(3)	-0.0428(2)	3.271
C8	0.0614(4)	0.3355(4)	-0.0559(2)	4.513
C9	0.1029(3)	0.3090(3)	-0.0089(2)	3.933
C10	0.1824(4)	0.2584(4)	-0.0189(3)	4.565
C11	0.2078(3)	0.2346(3)	-0.0768(2)	6.166
C12	0.1593(3)	0.2734(3)	-0.1208(2)	4.411
C13	0.1895(3)	0.2497(4)	-0.1711(2)	8.619
C14	0.1389(3)	0.2838(4)	-0.2152(2)	8.014
C15	0.0646(4)	0.3437(4)	-0.2057(2)	7.563
C16	0.0311(4)	0.3595(4)	-0.1554(3)	3.981
C17	0.0901(4)	0.3221(4)	-0.1085(3)	5.492

3.3 Results and Discussion

Synthesis of 1, 2, 3, and 4. Treatment of Hphbt with 0.5 molar equivalent of platinum(II) in toluene gave a small amount of non-innocent type mononuclear complex **1** together with a large amount of the orthometallated tetranuclear complex **2**. In the case of the 1 : 1 stoichiometry for the reaction of Hphbt with platinum(II), only a tetranuclear complex **2** was obtained in high yield together with a small amount of unidentified red compound. Treatment of Hphbt with one molar equivalent of $Pd(CH_3COO)_2$ gave the orthometallated tetranuclear complex **3** together with an unidentified red compound. When the complex $[Pd(hfacac)_2]$ was used for the reaction as a starting material instead of $Pd(CH_3COO)_2$, the complex **3** could be obtained more rapidly. The result indicates that the $hfacac^-$ anion acts as a good proton acceptor in this system. This complex **3** was also obtained by refluxing the solution of mononuclear *cis*-$[Pd(phbt)_2]$[1] in toluene. This result is clear demonstration that *cis*-$[Pd(phbt)_2]$ is intermediate complex of tetranuclear complex **3**. In the case of the 1 : 1 stoichiometry for the reaction of H1-nabt with platinum(II), only a tetranuclear complex **4** was obtained together with a small amount of unidentified red compound.



Scheme 1. (a) Reaction with 0.5 equiv. of [Pt(hfacac)$_2$] in toluene; (b) Reaction with equimolar amount of [Pt(hfacac)$_2$] in toluene; (c) Reaction with 0.5 equiv. or equimolar amount of [Pt(hfacac)$_2$] in toluene.



Scheme 2. (a) Reaction with a equimolar amount of $Pd(CH_3COO)_2$ in toluene; (b) Reaction with 0.5 equiv. of $Pd(CH_3COO)_2$ in EtOH; (c) Reflux over 10 h in toluene.

Molecular Structure of [Pt(ddbt)] (1). The molecular structure of **1** together with the adopted numbering scheme is shown in Fig. 1. The complex **1** is a mononuclear platinum complex having square planar configuration. The quadridentate ddbt ligand is derived from bond formation between two independent imino carbon atoms in coordinated phbt ligands, similar to [Ni(ddbt)] and *cis*-[Ni(phbt)$_2$] system.[10] However, mononuclear platinum(II) complexes corresponding to *cis*-[Ni(phbt)$_2$] could not be obtained. It is considered that the *cis*-[Pt(phbt)$_2$] affords the related orthometallated tetranuclear complex **2** immediately (*vide infra*). The Pt-S (2.240(4) and 2.223(4) Å) and Pt-N (1.960(10) and 1.950(14) Å) bond distances are clearly shorter than the normal values of Pt-thiolato and Pt-imino bond distances.[15,16] The average C-S bond distances of 1.724(16) Å are typical of values found for the other non-innocent type structures (1.722(8) Å in [Pt{$S_2C_2(CN_2)$}][17], 1.704(5) Å in [Pt{N(CH_2Ph)NC(S)SMe}$_2$][18]; and 1.713 Å in [Pt{S(NH)C_6H_4}$_2$][19]) and the average C-N bond distances of 1.379(17) Å also show a characteristic pattern found for the other non-innocent type structures. The results indicate that [Pt(ddbt)] corresponds to the non-innocent type complex.[18-20] Moreover, the Pt-S bond distances are slightly shorter than those of other non-innocent type platinum complexes (2.271(2) Å in [Pt{$S_2C_2(CN_2)$}][17], 2.280(1) Å in [Pt{N(CH_2Ph)NC(S)SMe}$_2$][18] and 2.278(2) Å in [Pt{S(NH)C_6H_4}$_2$][19]). Judging from the structures of these complexes, this result suggests the strong *trans* influence of coordinated sulfur atoms.

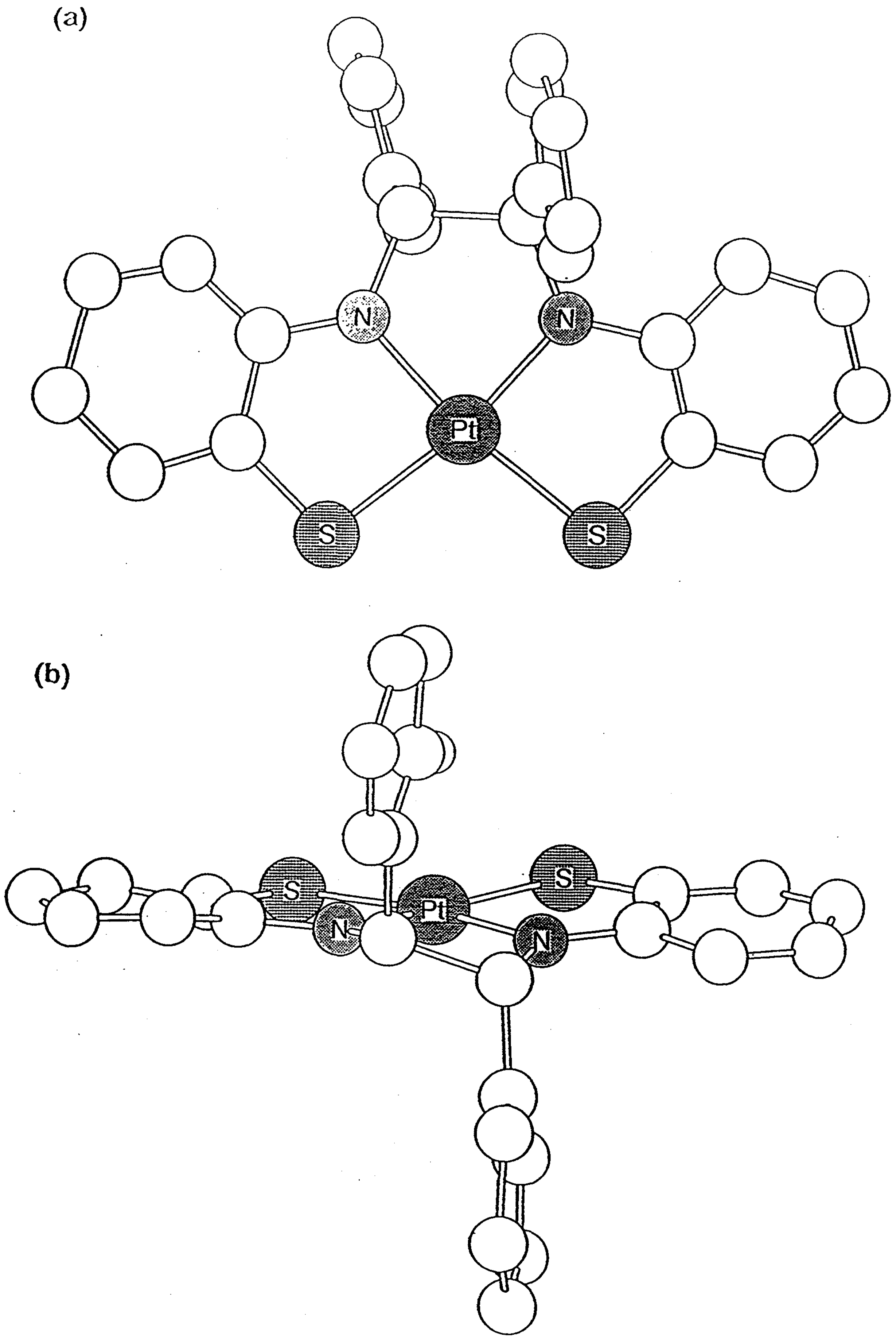


Fig. 1A. Molecular structures of **1** (a) top view, (b) side view.

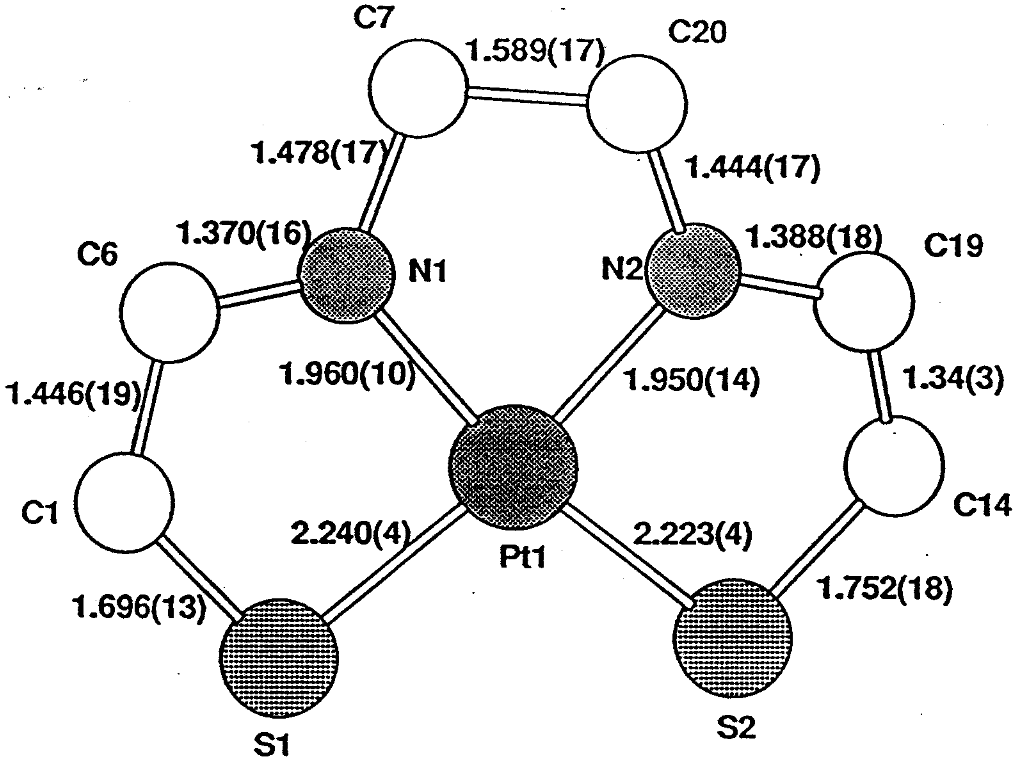
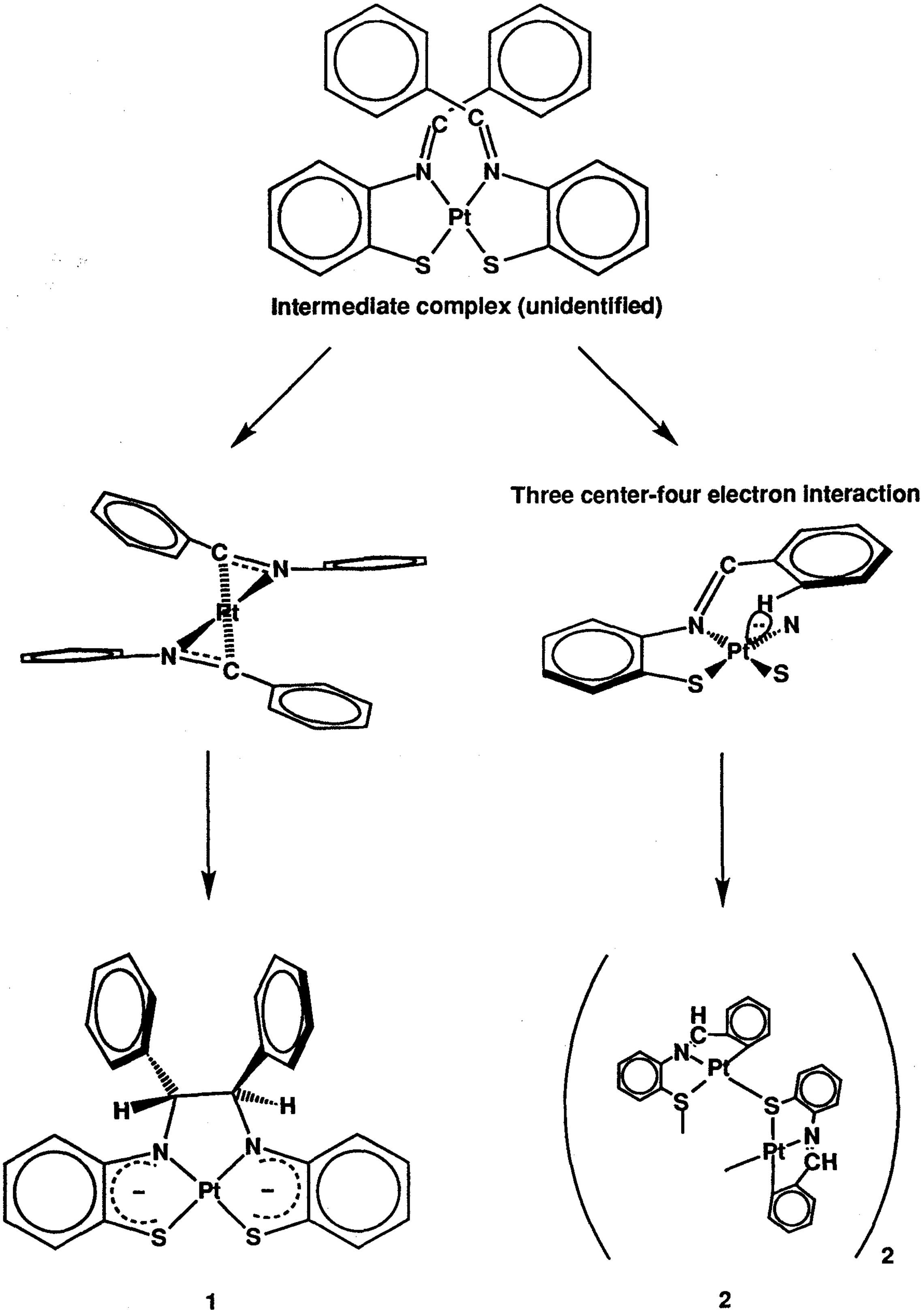


Fig. 1B. The coordination environment of complex 1 with bond lengths(Å).

Molecular Structure of [$Pt_4(C^o$-phbt$)_4$] (2). The molecular structure of complex **2** together with the adopted numbering scheme is shown in Fig. 2. This molecular structure does not have a crystallographically imposed symmetry $\bar{4}$ in contrast to **4** (*vide infra*) and the core of **2** consists of an eight-membered ring of alternating Pt and S atoms similar to the skeletal structure of braggite[21] (Fig. 2). Each platinum atom is coordinated by two sulfur atoms, one nitrogen atom and one *ortho* carbon atom of the phenyl group in square planar geometry with the two sulfur atoms mutually *cis*. Thus this complex is an unusual tetranuclear complex having a rare C^o, *N*, *S*-tridentate ligand derived from orthometallation of the pendant side arm. The mononuclear complex, *cis*-[Pt(phbt)$_2$], considered as the intermediate of **2**, could not be obtained. The result indicates that since the platinum(II) activates the *ortho*-hydrogen-carbon bond of substituted phenyl group strongly, the complex *cis*-[Pt(phbt)$_2$] could not retain its structure (Scheme 3). The average Pt-S-Pt angle (110.8°) is fairly close to the ideal tetrahedral value of 109.5°. The Pt-N and Pt-C bond lengths compare well with the reported structural data for the similar complexes.[22] The average Pt-bridging S distances (2.29(2) Å) are in the range of distances found in other platinum thiolato complexes.[23] The average Pt-terminal S distances (2.339(19) Å) are longer than bridging ones and also are relatively longer than reported Pt-S bond lengths. This disparity results from the considerable *trans* influence of Pt-C sp^2 bond. The closest Pt-Pt distance of 3.280(1) Å demonstrates that the direct Pt-Pt bond is not present.[24]



Scheme 3. Proposed reaction mechanism

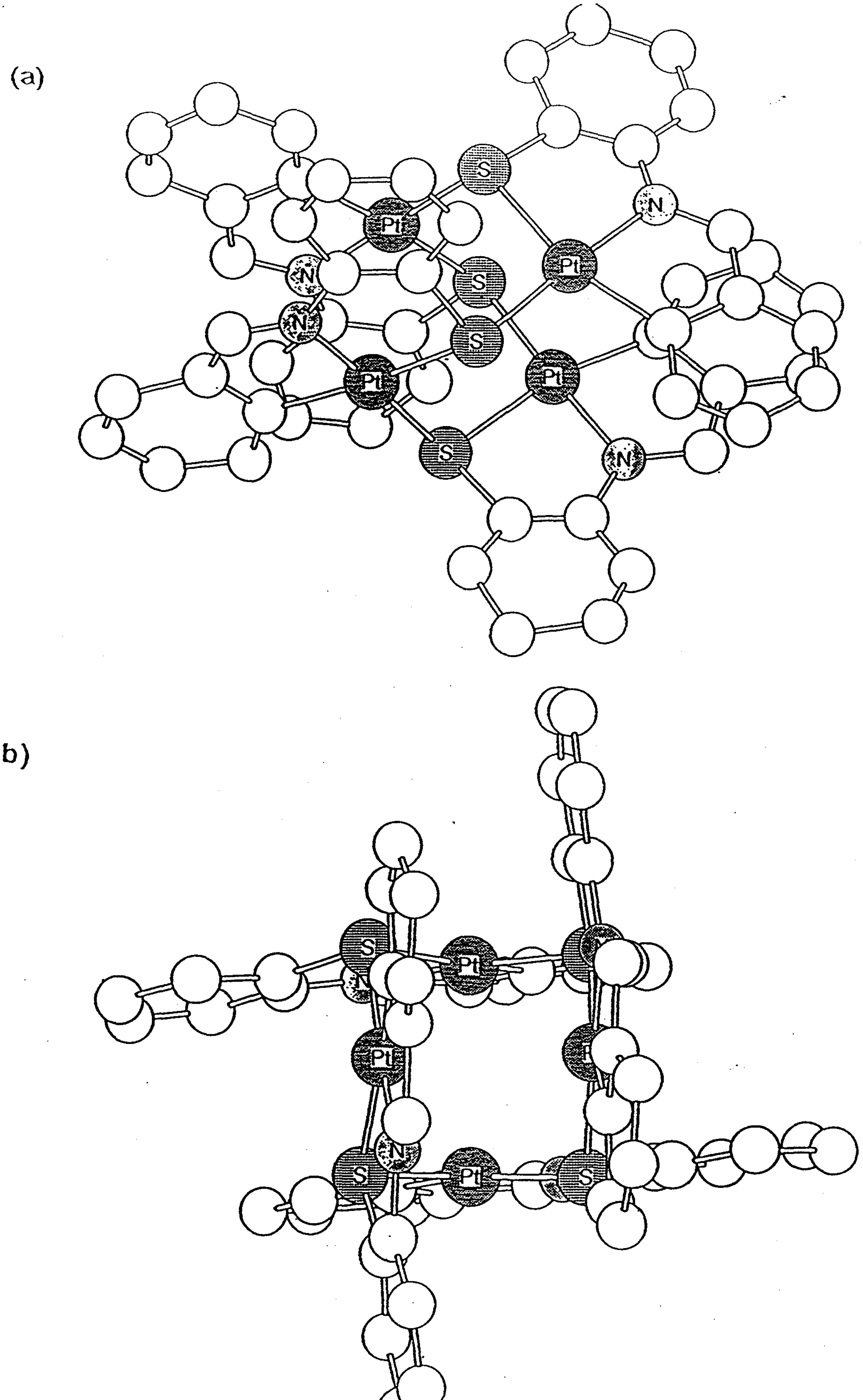


Fig. 2A. Molecular structures of 2 (a) top view, (b) side view.

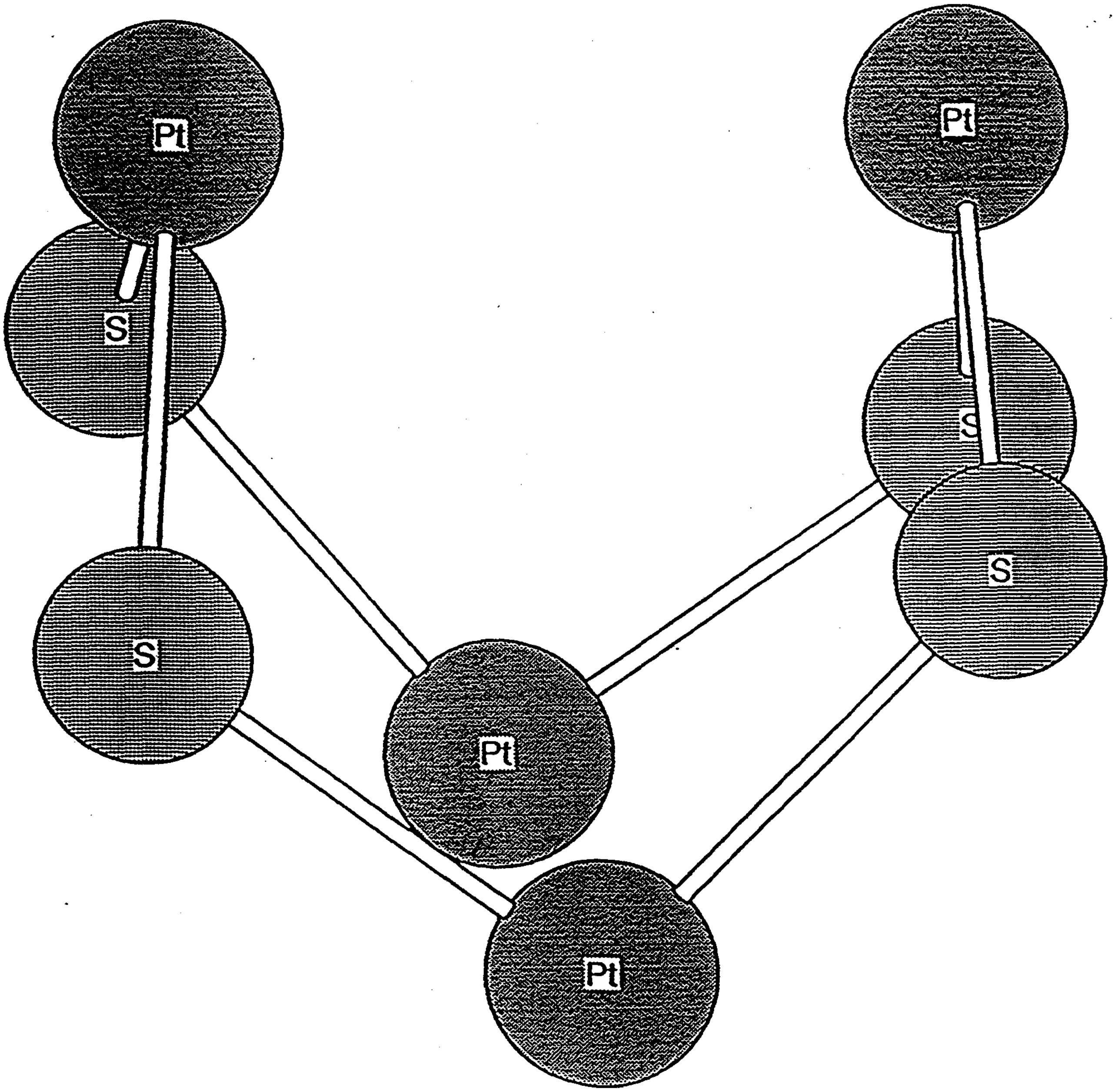
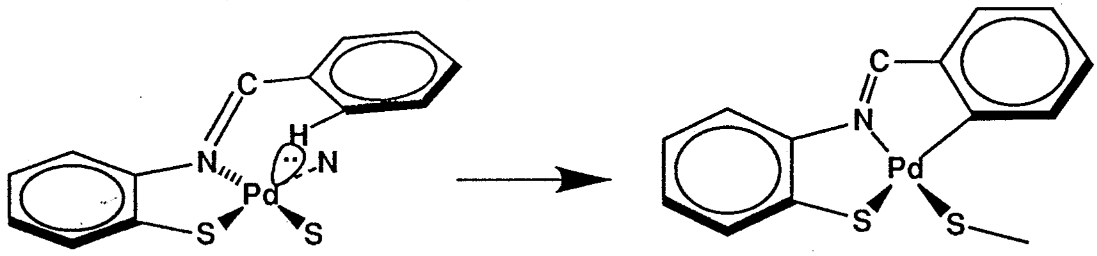


Fig. 2B. Framework of 2.

Molecular Structure of $[Pd_4(C^o\text{-phbt})_4]$ (3). This molecular structure does not have a crystallographically imposed symmetry $\bar{4}$ and consists of four square planes with a Pd_4S_4 eight-membered ring bridged by the sulfur atoms as well as complex 2. (Fig. 3). Each palladium atom is coordinated by two sulfur atoms, one nitrogen atom, and one *ortho* carbon atom of the phenyl group in square-planar geometry with the two sulfur atoms mutually *cis*. This palladium(II) complex with a heteroatomic C^o, *N*, *S*-tridentate ligand is a new type. The Pd-N and Pd-C bond lengths are normal.[25,26] The average Pd-terminal S and Pd-bridging S distances are 2.364(14) and 2.311(14) Å, respectively, and are relatively longer than other reported Pd-S bond lengths of 2.25 - 2.31 Å.[27,28] The average Pd-terminal S distances is longer than bridging ones. This disparity probably results from the considerable *trans* influence of Pd-C sp^2 bond as well as that in the platinum complex 2. Bond lengths involving Pd and Pt atoms are very similar as a consequence of the essential equality of the covalent radii of the two metals. The closest Pd-Pd distance of 3.296(5) Å is regarded as nonbonding.[29] For reference, the interatomic spacing in palladium metal is 2.75 Å.[30] Recently a similar tetranuclear complex has been described by Nicholas et al.[25] However, each of the four monomeric units of their palladium(II) complex consists of six-membered *N*, *O*-bonded chelate and five-membered *N*, *C*-bonded chelate rings and the C=N bond is not included in the *N*, *C*-bonded chelate ring. On the contrary, those of the complex 2 consists of five-membered *N*, *S*-bonded chelate and five-membered *N*, *C*-bonded chelate rings and the C=N bond is included in the *N*, *C*-bonded chelate ring.

Three center-four electron interaction



cis-$[Pd(phbt)_2]$ 3

Scheme 4.

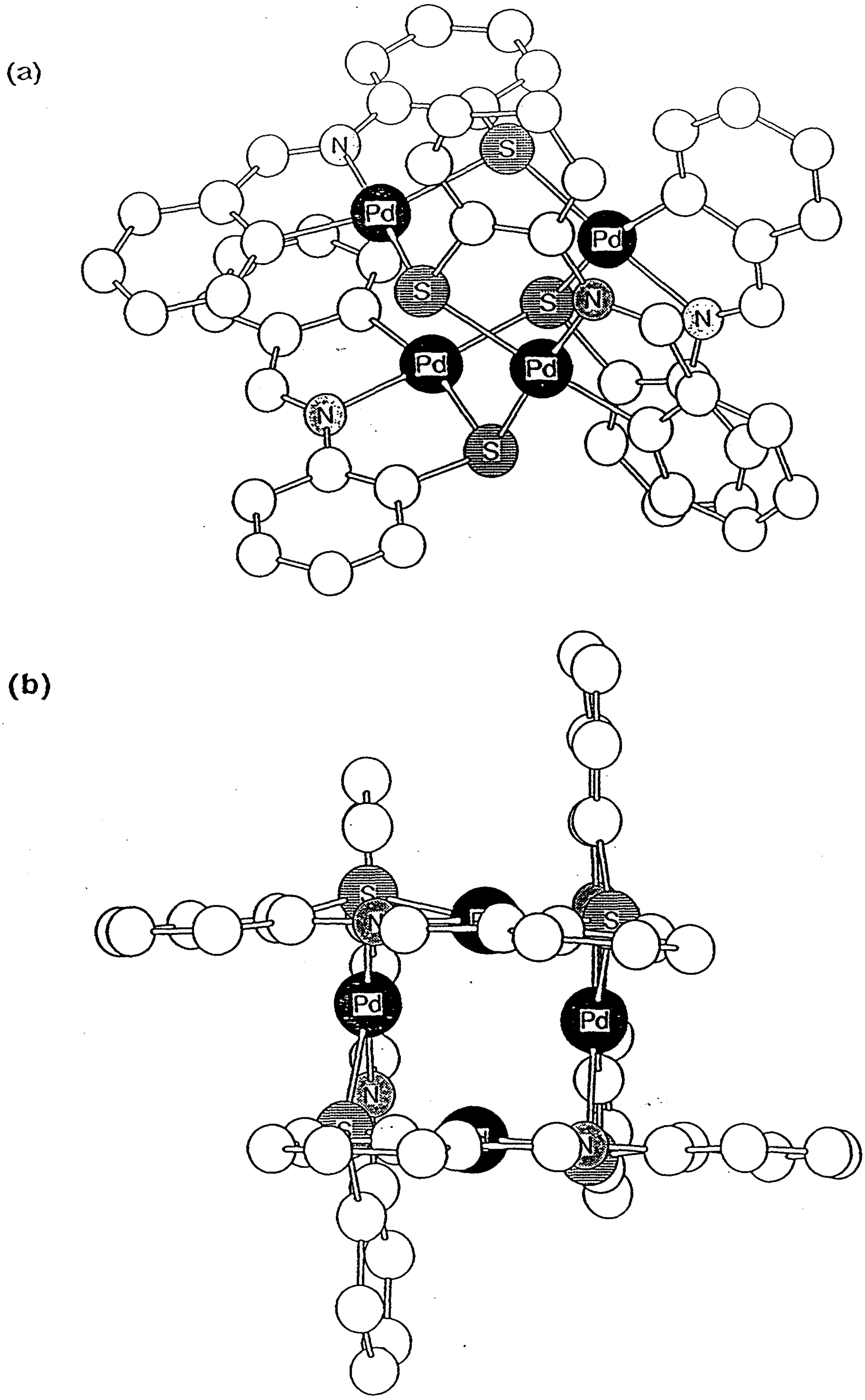


Fig. 3A. Molecular structures of 3 (a) top view, (b) side view.

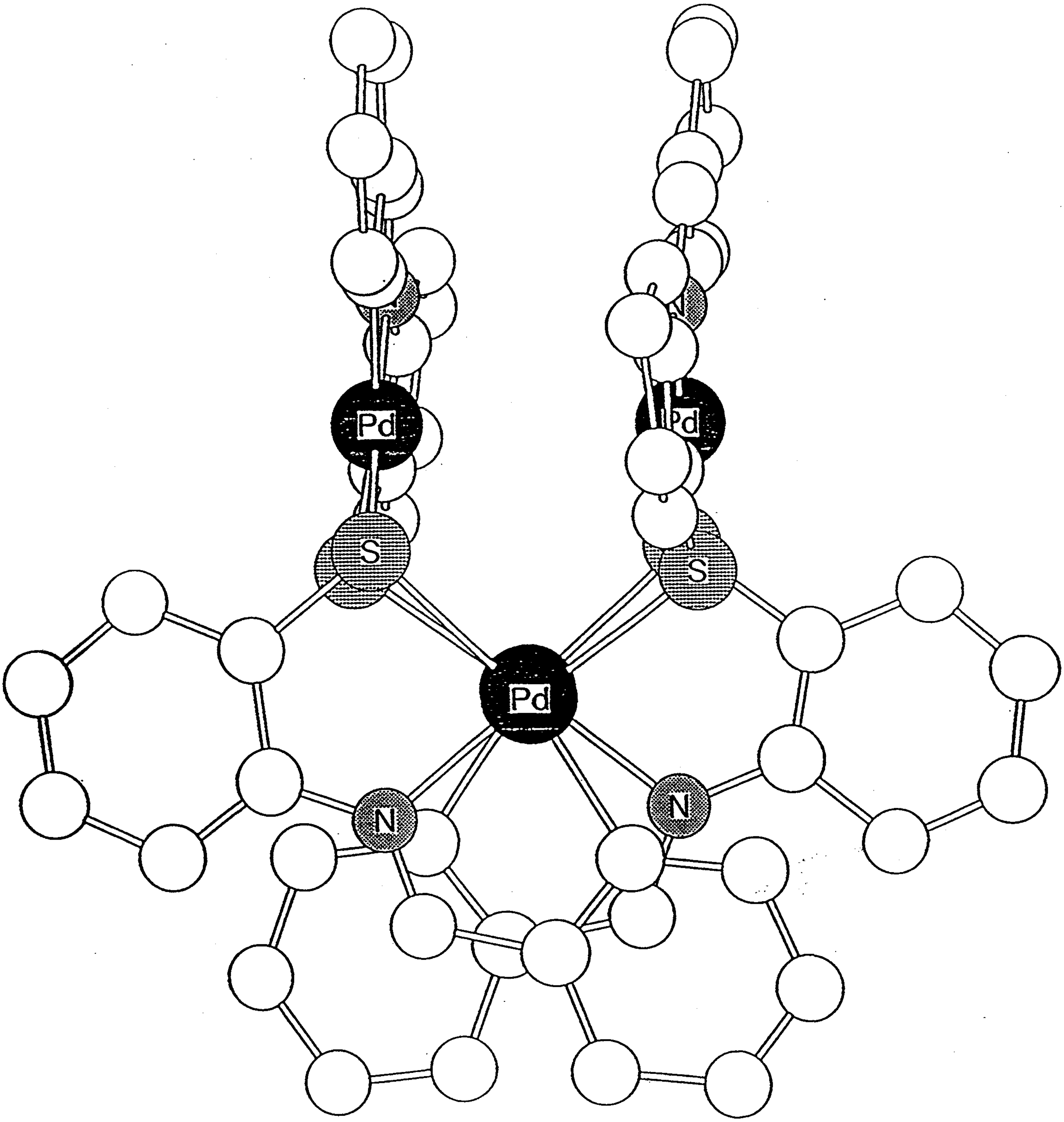


Fig. 3B. Stacking view of molecular structures of 3.

Molecular Structure of [Pt$_4$(C^o-1-nabt)$_4$] (4). Complex 4 is isostructural with [Pd$_4$(C^o-1-nabt)$_4$][2] ; these almost identical cell parameters reflect the equivalence in size of the Pd and Pt atoms. This platinum(II) complex with a heteroatomic C^o, *N*, *S*-tridentate ligand is a new type. The core of **4** consists of an eight-membered ring of alternating Pt and S atoms similar to the skeletal structure of braggite.[21] The Pt-N and Pt-C bond lengths compare well with the reported structural data for the similar complexes.[22] The Pt-bridging S distances (2.316(8) Å) are in range of distances found in other platinum thiolato complexes.[23] The Pt-terminal S distances (2.350(8) Å) are longer than bridging ones and also are relatively longer than reported Pt-S bond lengths. This disparity probably results from the considerable *trans* influence of Pt-C sp^2 bond as well as those in the tetranuclear complex **2** and **3**. Bond lengths involving Pd and Pt atoms are very similar as a consequence of the essential equality of the covalent radii of the two metals. The Pt-Pt distance of 3.210(3) Å is regarded as nonbonding.[24]

Table 6. Selected bond lengths(Å) and angles(°)

Bond Lengths			
Pt- S_{terminal}	2.350(8)	N-C7	1.31(4)
Pt-S_{bridging}	2.316(8)	C1-C2	1.45(4)
Pt-N1	2.01(2)	C7-C8	1.58(5)
Pt-C9	2.00(3)	C8-C9	1.37(5)
S_{terminal}-C1	1.75(3)	Pt···Pt	3.210(3)
N-C2	1.48(4)		

Bond Angles			
S_{terminal} -Pt- S_{bridging}	96.3(3)	Pt-N-C2	121(2)
S_{terminal} -Pt-N1	85.5(7)	Pt-N-C7	118(2)
S_{bridging} -Pt-C9	96(1)	Pt-C9-C8	115(3)
N-Pt-C9	82(1)	N-C7-C8	112(3)
Pt- S_{bridging} -Pt	110.4(3)	C7-C8-C9	114(3)
Pt- S_{terminal} -C1	97(1)		

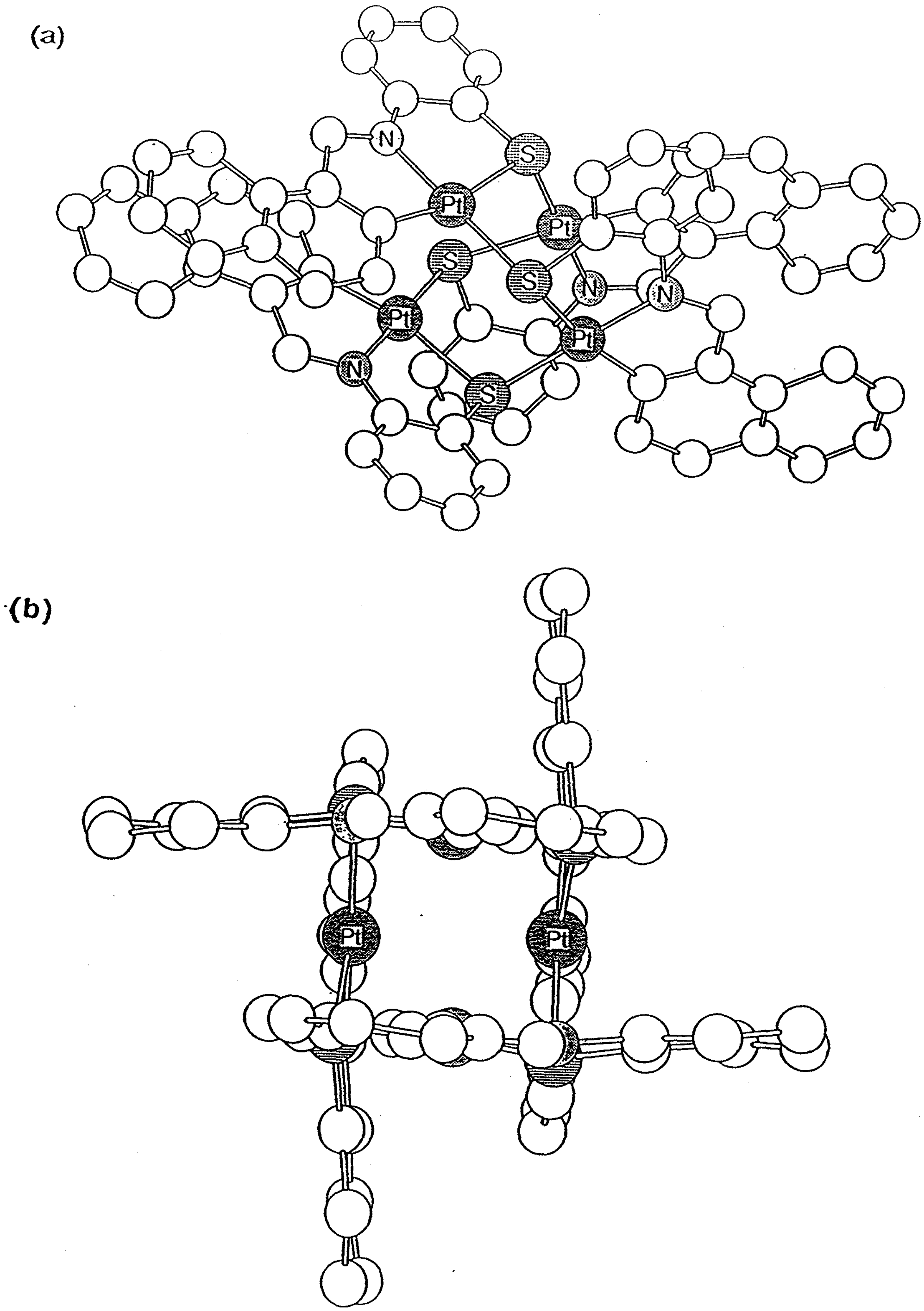


Fig. 4A. Molecular structures of 4 (a) top view, (b) side view.

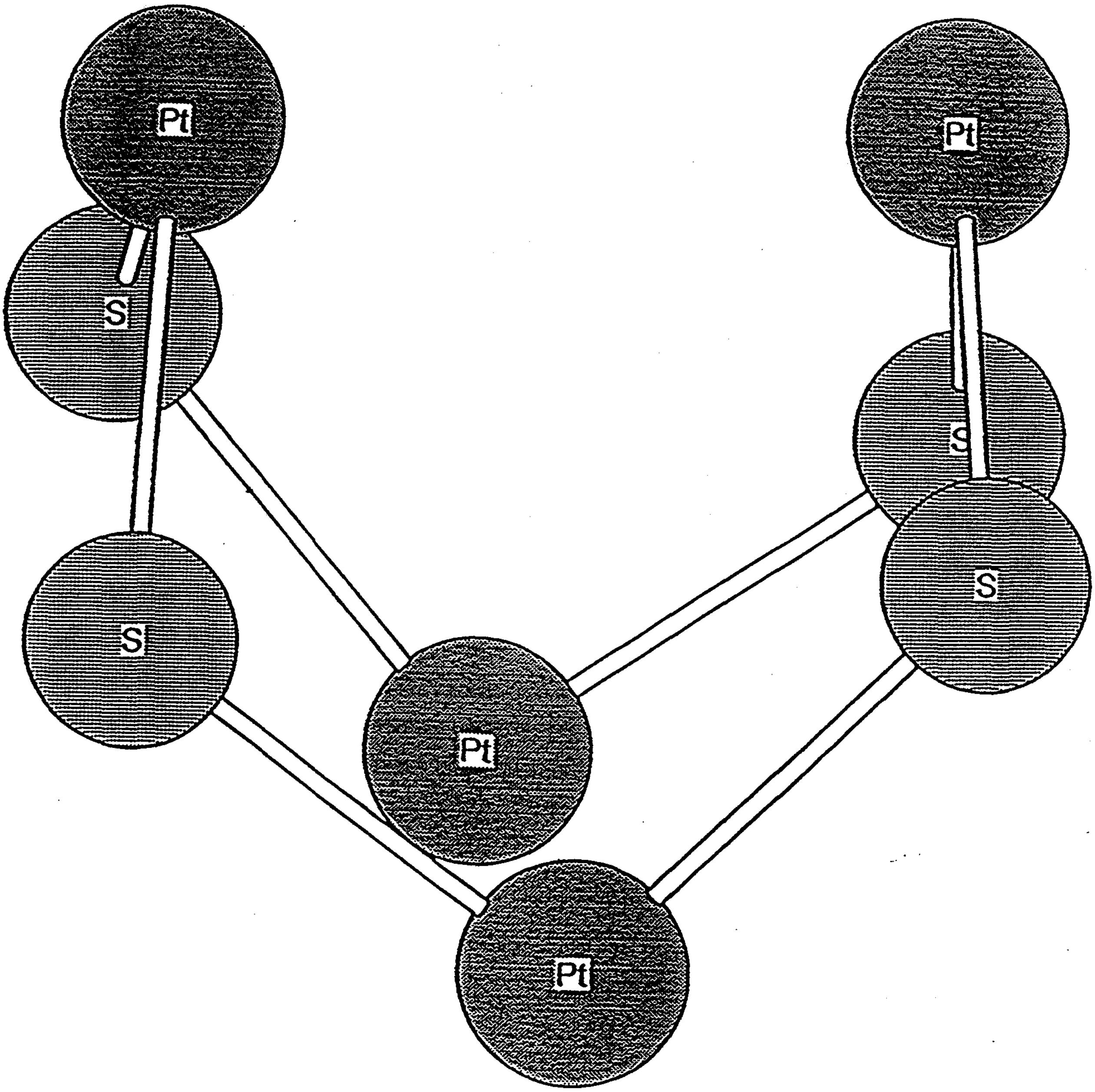


Fig. 4B. Framework of **4**.

Spectroscopic Characterization of the Complexes 1, 2, 3, and 4.

NMR spectra. The ^{13}C NMR spectrum of **1** gave the thirteen signals in phenyl region. This result indicates that the complex **1** has C_2 symmetrical structure in $CDCl_3$. In the proton NMR spectrum of **1**, one sharp singlet due to the protons on asymmetric carbon atoms, which are generated by the imino carbon-carbon bond formation, was observed at 6.72 ppm (Fig. 5). However, any other phenyl protons did not exhibit clear peak sets. This behavior may be corresponded to the delocalized ground state of **1**.

The proton NMR spectrum of **2** is shown in Fig 6 . First, the appearance of only one azomethine signal shows that the complex **2** has a imposed symmetry $\bar{4}$ in $CDCl_3$ solution, and this observation is supported by ^{13}C NMR of **2** giving thirteen signals. However, any other phenyl protons did not exhibit clear peak sets.

The proton NMR spectrum of **3** is shown in Fig 7 . First, the appearance of only one azomethine signal shows that the complex **3** has also a imposed symmetry $\bar{4}$ in $CDCl_3$ solution as well as complex **2**, and this observation is supported by ^{13}C NMR of **3** giving thirteen signals. The azomethine signal revealed at 7.35 ppm, which is shifted higher field than that of related mononuclear complex, *cis*-[Pd(phbt)$_2$] (7.80 ppm).[1] This may be caused by ring current effect from the stacked phenyl group of a neighbor side. The proton NMR spectrum of the related mononuclear palladium(II) complex, *cis*-[Pd(phbt)$_2$][1], shows the notable downfield shifts observed for the aromatic *ortho*-proton (7.95 ppm). Similar downfield shifts for hydrogen atoms involved in Pt···H-C interactions have been shown by Albinati et al.[28] and *cis*-[Pd(1-nabt)$_2$].[2] In addition, G. van Koten et al. have reported that proton NMR studies show downfield shifts for the resonance of the interacting proton (Pt···H-N).[4] Thus the present low-field resonance can be attributed to an intramolecular three-center four-electron Pd···H-C interaction in contrast to the known three-center two-electron agostic interaction showing high-field resonance.

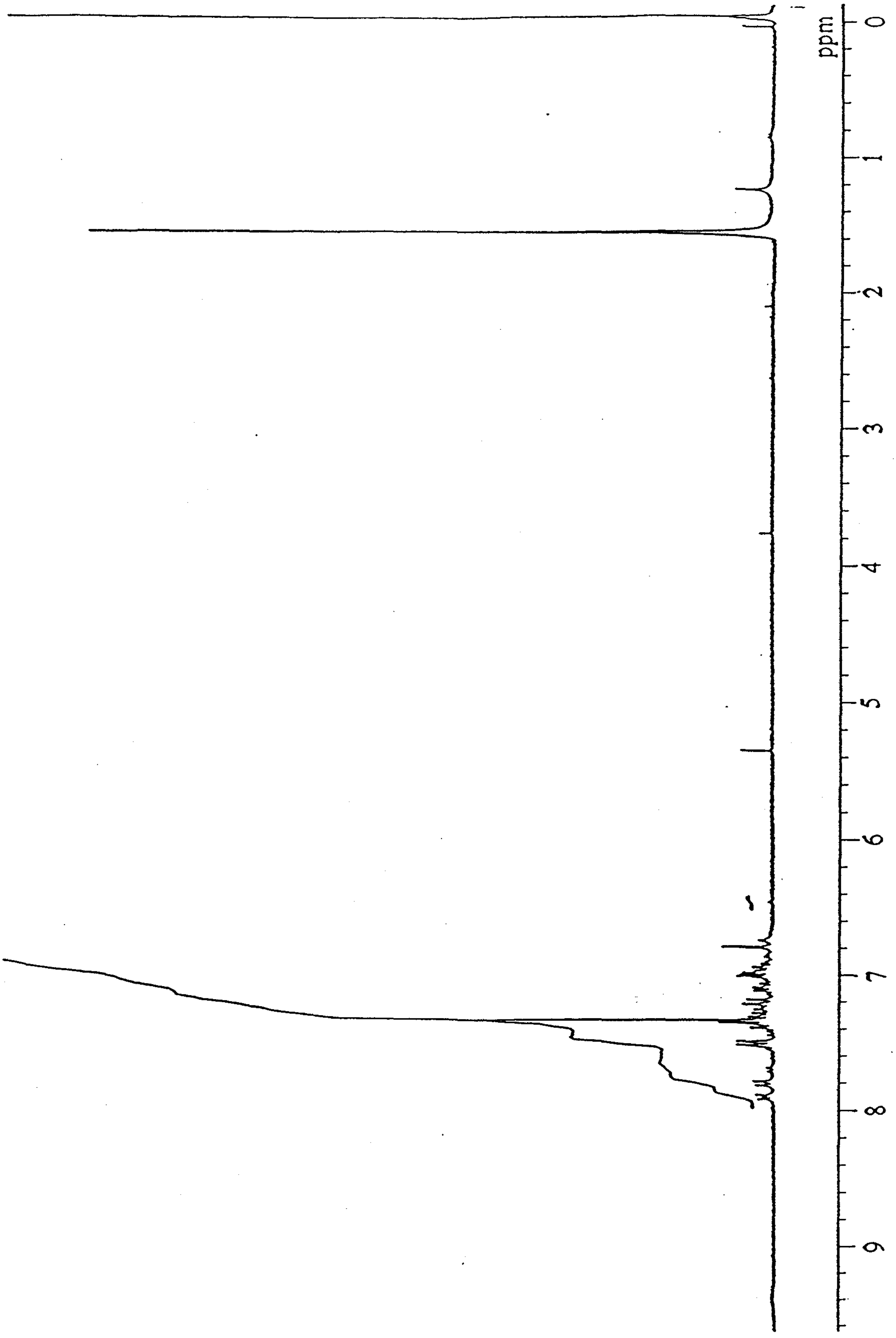


Fig. 5. ^{1}H NMR spectrum of 1 in $CDCl_3$ solution.

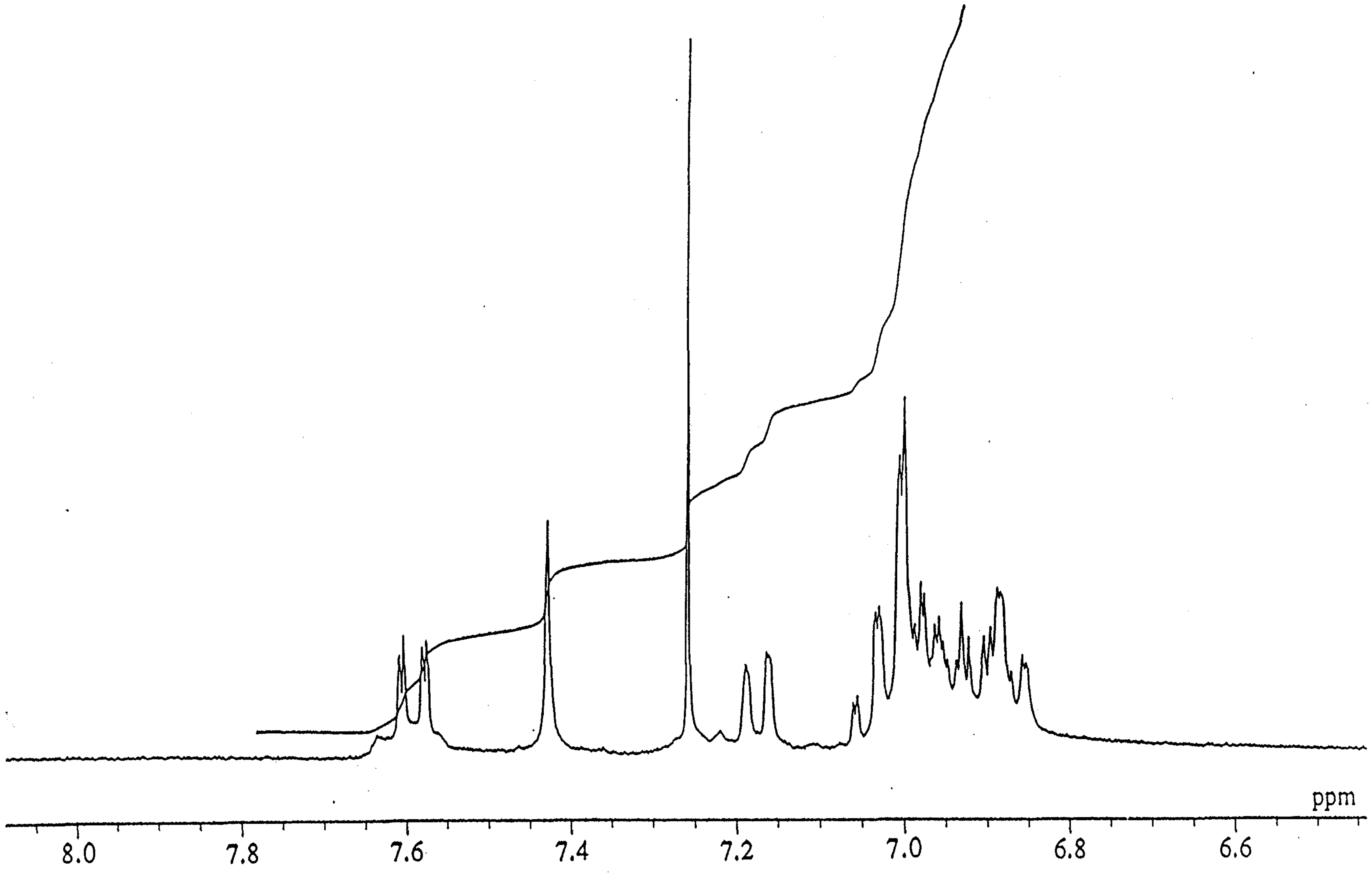


Fig. 6. ${}^1H$ NMR spectrum of 2 in $CDCl_3$ solution.

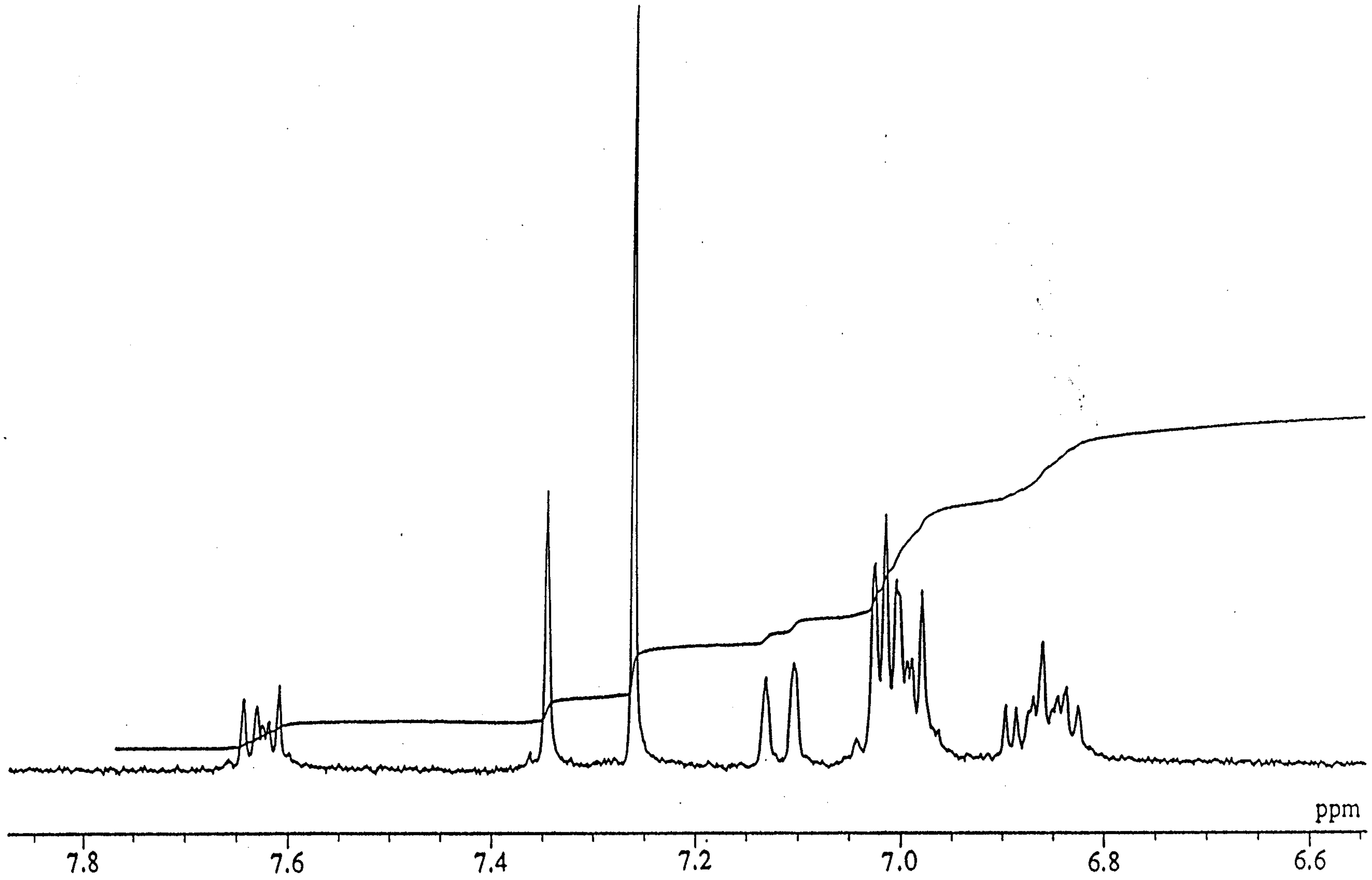


Fig. 7. ¹H NMR spectrum of 3 in $CDCl_3$ solution.

Absorption spectra. Electronic absorption spectra of **1**, **2**, **3**, and **4** in dichloromethane are adequately summarized by the following $\nu_{max}/10^3$ cm^{-1} (ε / cm^3 mol^{-1} cm^{-1}) data: 9.9(5030), 10.3(2180)sh, 11.3(3290), 13.3(32768)sh, 13.6(36560), 19.2(1000), 21.4(1000), 27.2(1780)sh, and 31.1(4260) for **1**, 19.8(8960) and 28.1(31990) for **2**, 20.4(6700)sh and 21.9(8400) for **3**, 15.7(2290)sh, 18.4(6030)br, and 25.2(21380) for **4**. These complexes exhibit strong absorptions in the visible region, consistent with intense colours, and their bands mask d-d transitions. The complex **1** shows very strong absorption bands at 13.3 and 13.6 × 10^3 cm^{-1}. These bands are features common to dithiolene-like complexes with electron-transfer properties.[17-19,31] By comparing tetranuclear platinum(II) complex **2** with palladium(II) one **3**, the platinum(II) complex **2** shows the bands at lower energy than palladium(II) one, and, moreover, the transitions in the tetranuclear complex **3** have higher intensities than those in mononuclear complex *cis*-[Pd(phbt)$_2$].[1]

3.4 Conclusions.

A new non-innocent type platinum complex and several new tetranuclear platinum(II) and palladium(II) complexes containing a rare *C*°, *N*, *S*-tridentate ligand derived from orthometallation of the pendant side arm have been synthesized and characterized. The tetranuclear palladium(II) complex could be obtained from a dissociation of the *ortho*-hydrogen-carbon bond in a mononuclear helical palladium(II) intermediate complex containing an unique Pd···H-C moiety. The presence of the Pd···H-C interaction caused by the ideally positioned *ortho* C-H bond can be deduced by the X-ray crystal structure and proton NMR spectroscopy. The Pd···H-C moiety can be described as a three-center four-electron interaction rather than a known agostic three-center two-electron interaction. The majority of examples of orthometallated complexes which have been reported are with d^8 or d^6 transition metals and, in particular, Pd(II) and Pt(II) compounds readily orthometallate a variety of organic ligands. This study suggests that the orthometallation reactions in Pd(II) and Pt(II) compounds involve the intermediacy of the species containing the three-center four-electron M···H-C interactions. Any mononuclear complex corresponds to *cis*-$[Pd(phbt)_2]$ or *cis*-$[Pd(1\text{-}nabt)_2]$ could not obtained. These results show that the platinum(II) activates *ortho*-hydrogen-carbon bond more strongly than the palladium(II) in this system.

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Chapter 4.

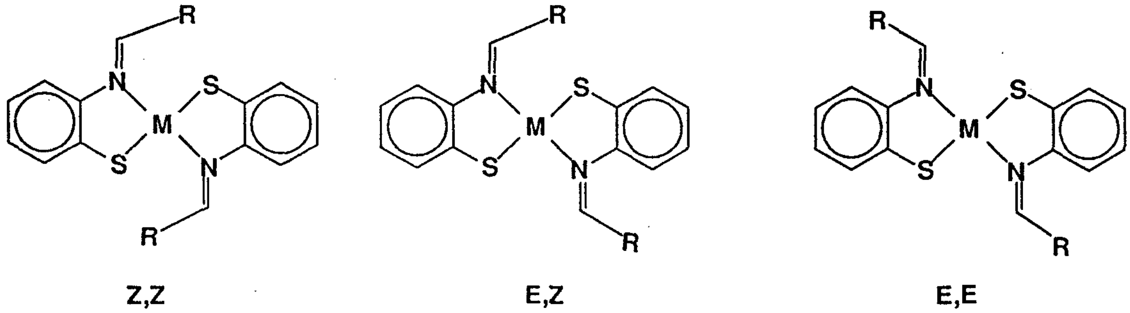
Structural study of *trans* N_2S_2 platinum(II) complexes with *N, S* chelate Schiff base ligands derived from 2-(2,6-disubstitutedphenyl)benzothiazolines.

Abstract.

The reactions of [Pt(hfacac)$_2$] with 2-(2,6-dichlorophenyl)benzothiazoline, H2,6-Clphbt, or 2-(2,4,6-trimethylphenyl)benzothiazoline, H2,4,6-Mephbt, afforded mononuclear *trans*-planar platinum(II) complexes formulated in *trans*-[Pt(2,6-Clphbt)$_2$](1) and *trans*-[Pt(2,4,6-Mephbt)$_2$](2), respectively. The structures of these complexes were determined by single crystal X-ray diffraction method. Crystal data for **1** are orthorhombic and space group *P*cnb with a = 17.544(11), b = 19.121(7), c = 7.688(3) Å, V = 2579.1(20) Å^3, Z = 4. Crystal data for **2** are monoclinic and space group $P2_1/a$ with a = 14.209(9), b = 15.227(15), c = 13.527(8) Å; β = 96.25(4)°, V = 2910.4(38) Å^3, Z = 4. Both of complexes **1** and **2** were the rare *trans*-planar PtN_2S_2 complexes having an unique umbrella conformation. In complex **1**, the azomethine groups of Schiff base had a Z,Z configuration. In complex **2**, those azomethine groups had an E,Z configuration in solid state. The reaction of palladium(II) with H2,4,6-Mephbt afforded mononuclear palladium(II) complex formulated in *trans*-[Pd(2,4,6-Mephbt)$_2$](3). The NMR study showed that the complex **3** has also a rare *trans*-planar PdN_2S_2 configuration as well as complex **2**.

4.1 Introduction.

It was well known that the N, S chelate Schiff base complexes with square planar configuration exclusively prefer a *cis* geometry to a *trans* one.[1] However, as shown in chapter 2, the author prepared a novel example of *trans*-planar PtN_2S_2 complex. Moreover, in chapter 3, the author showed that the reaction of $[Pt(hfacac)_2]$ with Hphbt afforded non-innocent type mononuclear platinum complex, [Pt(ddbt)], and novel tetranuclear one, $[Pt_4(C^o\text{-phbt})_4]$, but any mononuclear platinum(II) complexes corresponding to *cis*-$[M(phbt)_2]$ (M = Ni(II) and Pd(II))[2] were not obtained. The result means that the platinum(II) activates the *ortho*-carbon-hydrogen bond of phenyl pendant group more strongly than the corresponding palladium(II) in this system. To synthesize related mononuclear platinum(II) complex, probably, it is need to interrupt the cyclometallation more severely. Then, the benzothiazoline derivatives derived from the substitution of methyl- or chloro- group at the 2,6-position in pendant phenyl group, on which the carbon-hydrogen bonds are activated by the metal ions, were used. Moreover, it is interested that, in the present systems, the azomethine double bond (C=N) of the Schiff base is located on the exo-position of the five membered N, S chelate ring. As shown in Scheme 1, three possibility of the E or Z type geometrical isomerization is present. Thus, related to the pendant side arms, it is need to check more systematically on this isomerization based on the bulkiness of the substituted groups.



Scheme 1.

The Z,Z configuration has been known as a most abundant isomer. The only known example of the other configuration was the following one; 2-(2,4,6-trimethylphenyl)benzothiazoline, H2,4,6-Mephbt, is a typical example having a bulky pendant group, and the reaction of this with nickel(II) afforded a rare *trans*-planar complex in which the Schiff base derived from this benzothiazoline took an E,E configuration.[3] In this chapter, the present author shows the further study of the rare *trans*-planar mononuclear platinum(II) complexes which were obtained by the reactions of [Pt(hfacac)$_2$] with 2-(2,6-dichlorophenyl)benzothiazoline, H2,6-Clphbt, or H2,4,6-Mephbt.

4.2 Experimental Section.

Materials. Bis(hexafluoroacetylacetonato)platinum(II), [Pt(hfacac)$_2$],[4] was prepared in the literature methods. The toluene was dried over molecular sieve 3A. Dichloromethane was dried over CaCl$_2$. Unless otherwise stated, commercial grade chemicals were used without further purification.

Measurements. Electronic absorption spectra in dichloromethane solutions and reflectance spectra were recorded on a Hitachi U-3400 spectrophotometer. IR spectra were obtained on a Pirkin-Elmer 983G Infrared Spectrometer using Nujol mulls between CsI plates. NMR spectra in CDCl$_3$ solution were recorded on a JEOL JNM EX-270 instrument using tetramethylsilane as an internal standard ($\delta = 0$). Cyclic voltammetry was performed in a three - electrode cell with a grassy - carbon disk as working electrode, a platinum wire as counter electrode and a Ag - AgCl reference electrode, in dichloromethane containing 0.1 mol dm^{-3} tetra-n-butylammonium tetrafluoroborate. Elemental analyses were performed at Osaka University.

Synthesis of *Trans*[2-N-(2,6-dichlorophenylmethylideneamine)benzene-thiolato]platinum(II) *trans*-[Pt(2,6-Clphbt)$_2$] (1). To a solution of 2,6-dichlorobenzaldehyde (0.088 g, 1.0 mmol) in ethanol (20mL) was added an equimolar amount of 2-aminothiophenol (0.125 g, 1.0 mmol), and the mixture was refluxed over 1 h. After the solvent was removed from the reaction mixture, a 0.5 equiv. of [Pt(hfacac)$_2$] (0.300 g, 0.49 mmol) was added to the toluene solution (20mL) of the resulting yellow product, and the mixture was refluxed over 3 h. The solvent was removed from the reaction mixture by using a rotary evaporator. The resulting green precipitate was dissolved in a minimum amount of dichloromethane and purified on a silica gel plate with dichloromethane as the eluent. The second band,[5] which corresponded to compound 2, was collected. Single crystals suitable for X-ray analysis were grown from 1,2-dichloroethane - pentane solution.

Synthesis of *Trans*[2-N-(2,4,6-trimethylphenylmethylideneamine)benzene-thiolato]platinum(II) *trans*-[Pt(2,4,6-Mephbt)$_2$] (2). To a solution of mesitaldehyde (0.150 g, 1.0 mmol) in ethanol (20mL) was added an equimolar amount of 2-aminothiophenol (0.125 g, 1.0 mmol), and the mixture was refluxed over 1 h. After the solvent was removed from the reaction mixture, a 0.5 equiv. of [Pt(hfacac)$_2$] (0.300 g, 0.49 mmol) was added to the toluene solution (20mL) of the resulting yellow product, then the mixture was refluxed over 3 h. After the solvent was removed from the reaction mixture, the purple precipitate was suspended in 1,2-dichloroethane, then the purple product which afforded the purple crystals was filtered off the suspension. The purple crystals were recrystallized from hot 1,2-dichloroethane solution. The yield was 25 % based on the amount of the starting [Pt(hfacac)$_2$]. Single crystals suitable for X-ray analysis were obtained from the 1,2-dichloroethane - pentane solution. Infrared spectrum: ν(C=N) at 1604 and 1560 cm^{-1}. NMR (CDCl$_3$, 23 °C): ^{1}H (270 MHz), δ 9.24 (s, 2H), 7.45 (d, 2H), 7.0-6.8 (m, 2H), 6.80 (s, 4H), 6.35 (d, 2H), 2.26 (s, 3H), and 2.04 (s, 6H); ^{13}C (67.8 MHz), δ 170.82, 150.83, 145.42, 140.40, 135.31, 131.14, 129.65, 129.15, 129.04, 122.37, 121.04, 21.28, and 19.35. CV (ν = 0.1 V s^{-1}) : *Epa* = 0.94 V, *Epc* = 0.76 V. Anal. Calcd for $C_{32}H_{32}N_2Pt_1S_2$: C, 54.61; H, 4.58; N, 3.98. Found: C, 53.81; H, 4.61; N, 4.10 %.

Synthesis of *Trans*-[2-N-(2,4,6-trimethylphenylmethylideneamine)-benzenethiolato]palladium(II) *trans*-[Pd(2,4,6-Mephbt)$_2$] (3). To a solution of mesitlaldehyde (0.150 g, 1.0 mmol) in ethanol (20mL) was added an equimolar amount of 2-aminothiophenol (0.125 g, 1.0 mmol), and the mixture was refluxed over 0.5 h. After the solvent was removed from the reaction mixture, a 0.5 equiv. of Pd(CH$_3$COO)$_2$ (0.110 g, 0.50 mmol) was added to the toluene solution (20mL) of the resulting yellow product, then the mixture was refluxed over 3 h. After the solvent was removed from the reaction mixture, the brown precipitate was suspended in 1,2-dichloroethane, then the brownish product was filtered off. The yield was 65 % based on the amount of the starting palladium acetate. The brown crystals were recrystallized from hot 1,2-dichloroethane solution. Infrared spectrum: ν(C=N) at 1599 and 1569 cm^{-1}. NMR (CDCl$_3$, 23 °C): ^{1}H (270 MHz), δ 9.24 (s, 2H), 7.36 (d, 2H), 6.9-6.8 (m, 2H), 6.80 (s, 4H), 6.38 (t, 2H), 6.22 (d, 2H), 2.27 (s, 3H), and 2.18 (s, 6H); ^{13}C (67.8 MHz), δ 146.51, 136.50, 133.87, 130.03, 128.95, 126.65, 126.56, 125.93, 125.45, 123.72, 122.77, 121.94, 120.70, 110.15, and 66.76. Anal. Calcd for $C_{32}H_{32}N_2Pd_1S_2$: C, 62.48; H, 5.24; N, 4.55. Found: C, 61.99; H, 5.21; N, 5.27 %.

Crystal Structure Determination. All crystallographic measurements were made using a MAC science MXC3 diffractometer with Mo-Kα radiation (0.71073 Å). Empirical absorption corrections (ψ-scan) were applied. Lattice parameters were determined by application of the automatic diffractometer indexing routine to the positions of 22 reflections. Data were measured in the range $3 \leq 2\theta \leq 50°$ in the ω-2θ scan with three check reflections being measured every 100 data.

Crystal data and relevant information for **1** and **2** are summarized in Tables 1A and 1B. The structures were solved by direct methods (SIR) and refined by full-matrix least squares. All non-hydrogen atoms were refined with anisotropic temperature coefficients.[6] Final atom coordinates for the non-hydrogen atoms of complexes **1** and **2** are given in Tables 2A and 2B, respectively. Fractional positional parameters and equivalent isotropic temperature factors for the hydrogen atoms for **1** and **2** are given in Tables 3A and 3B. Anisotropic temperature factors for **1** and **2** are given in Tables 4A and 4B. The selected bond lengths and angles are shown in Tables 5A and 5B. Tables 3A-3B, 4A-4B, and 5A-5B are in the Appendix section (chapter 4).

Table 1A Crystal data for **1**

Formula	$C_{26}H_{16}N_2S_2Cl_4Pt_1$
M	757.45
Crystal system	Orthorhombic
Space group	*Pcnb*
a / Å	17.544(11)
b / Å	19.121(7)
c / Å	7.688(3)
V / Å^3	2579.1(20)
Z	4
Crystal size (mm)	0.35 × 0.30 × 0.20
T / °C	25
λ/	0.71073
Dc / g cm^{-1}	1.951
μ / cm^{-1}	11.335
$2\theta_{max}$ / °	53
No. of measured reflections	2526
No. reflections used in refinement	1764 (refl observed if $I>3.00\sigma(I)$)
R^a	0.041
$R_w{}^b$	0.044

[a] $R = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$. [b] $Rw = [\Sigma w(|Fo| - |Fc|)^2 / \Sigma w(Fo)^2]^{1/2}$. Weighting scheme: $1/[\sigma^2(Fo)]$.

Table 1B Crystal data for **2**

Formula	$C_{32} H_{32} N_2 Pt_1 S_2$
M	703.80
Crystal system	Monoclinic
Space group	$P2_1/a$
a / Å	14.211(6)
b / Å	15.227(15)
c / Å	13.531(6)
β / °	96.25(4)
V / Å^3	2910.4(37)
Z	4
Crystal size (mm)	0.35 × 0.30 × 0.20
T / °C	25
λ/	0.71073
Dc / g cm^{-1}	1.607
μ / cm^{-1}	5.0344
$2\theta_{max}$ / °	53
No. of measured reflections	7451
No. reflections used in refinement	3808 (refl observed if $I>3.00\sigma(I)$)
R^a	0.054
$R_w{}^b$	0.069

[a] $R = \Sigma||Fo| - |Fc|| / \Sigma|Fo|$. [b] $Rw = [\Sigma w(|Fo| - |Fc|)^2 / \Sigma w(Fo)^2]^{1/2}$. Weighting scheme: $1/[\sigma^2(Fo)]$.

Table 2A Atomic coordinates and isotropic thermal parameters for **1**

Atom	*X/a*	*Y/b*	*Z/c*	*U*
Pt1	0.50000	0.25000	0.32806(5)	0.0287(3)
Cl1	0.4384(2)	0.3295(2)	0.7592(4)	0.071(2)
Cl2	0.63531(17)	0.46539(16)	0.34869(49)	0.072(2)
S1	0.37150(11)	0.22481(12)	0.29455(31)	0.0418(9)
N1	0.4632(3)	0.3488(3)	0.3290(9)	0.032(3)
C1	0.3489(4)	0.3063(5)	0.1965(10)	0.039(4)
C2	0.2818(5)	0.3172(6)	0.1006(13)	0.050(5)
C3	0.2672(6)	0.3814(7)	0.0315(14)	0.063(6)
C4	0.3164(7)	0.4360(6)	0.0487(14)	0.060(6)
C5	0.3823(6)	0.4266(6)	0.1448(11)	0.046(5)
C6	0.3976(5)	0.3625(5)	0.2167(10)	0.036(4)
C7	0.4859(4)	0.3992(4)	0.4289(12)	0.039(4)
C8	0.5452(5)	0.3913(5)	0.5602(13)	0.043(4)
C9	0.5286(7)	0.3594(6)	0.7176(14)	0.060(6)
C10	0.5874(9)	0.3498(7)	0.8406(17)	0.077(8)
C11	0.6586(9)	0.3735(9)	0.8068(20)	0.09(1)
C12	0.6743(6)	0.4083(7)	0.6565(22)	0.076(8)
C13	0.6174(6)	0.4190(6)	0.5363(15)	0.053(5)

$T = \exp[-2\pi 2U]$; $U = U_{iso}$ or $(U_{11} + U_{22} + U_{33}) / 3$

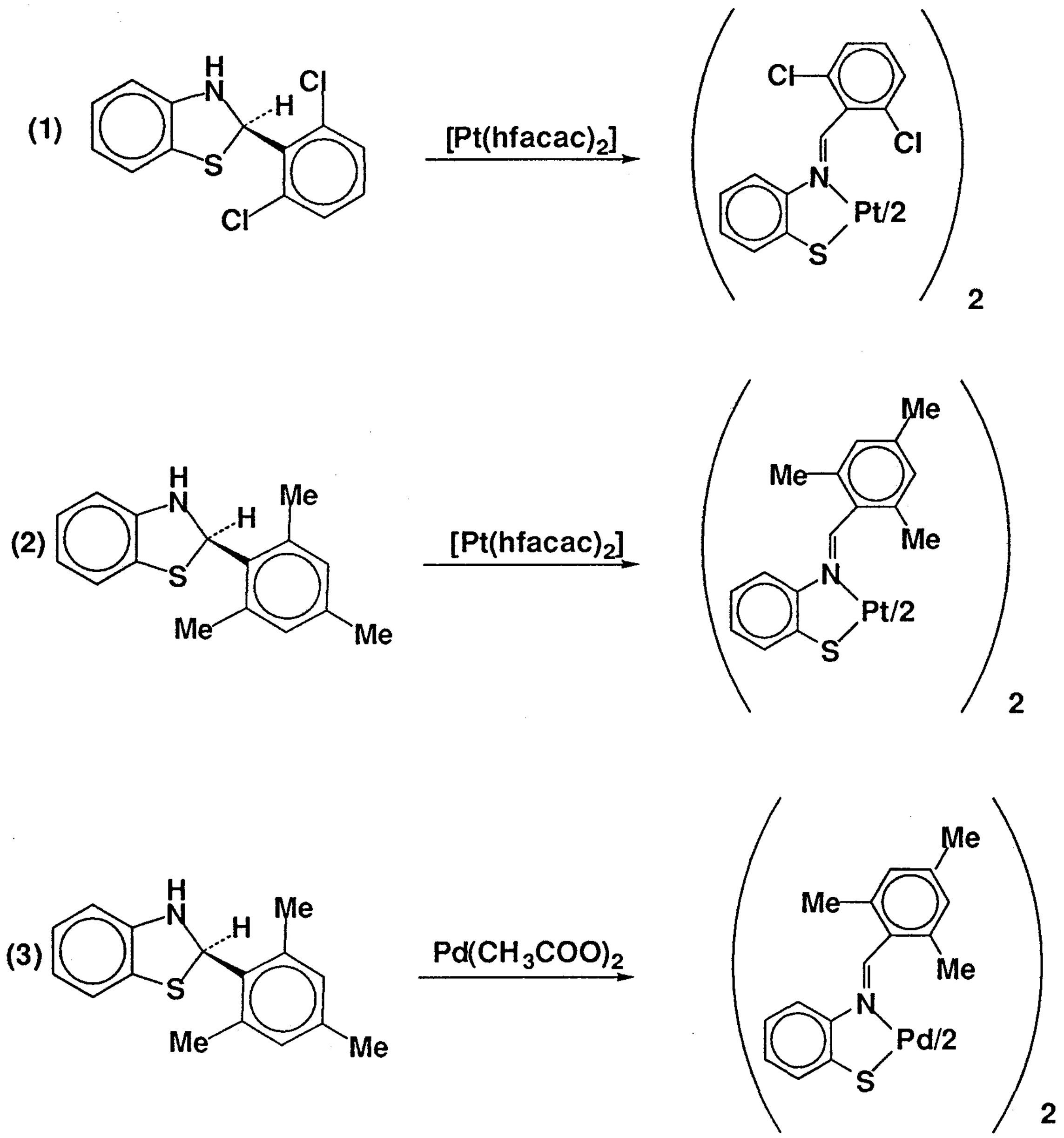
Table 2 B Atomic coordinates and isotropic thermal parameters for **2**

Atom	*X/a*	*Y/b*	*Z/c*	*U*
Pt1	0.82141(4)	0.37422(4)	0.58821(4)	0.0404(3)
S1	0.7401(3)	0.3443(3)	0.7235(3)	0.049(2)
S2	0.9088(3)	0.3829(4)	0.4541(3)	0.057(2)
N1	0.9345(7)	0.3763(8)	0.6894(9)	0.048(5)
N2	0.7105(9)	0.3782(8)	0.4840(8)	0.050(5)
C1	0.8386(12)	0.3052(9)	0.8006(10)	0.046(6)
C2	0.8298(16)	0.2515(13)	0.8819(13)	0.063(9)
C3	0.9063(19)	0.2188(15)	0.9390(16)	0.08(1)
C4	0.9956(18)	0.2365(14)	0.9148(17)	0.08(1)
C5	1.0091(13)	0.2884(12)	0.8325(15)	0.056(8)
C6	0.9294(11)	0.3239(8)	0.7801(11)	0.047(6)
C7	1.0007(10)	0.4364(10)	0.6850(12)	0.046(6)
C8	1.0687(10)	0.4659(10)	0.7677(12)	0.047(6)
C9	1.0372(12)	0.5151(11)	0.8453(12)	0.054(7)
C10	1.1045(15)	0.5410(12)	0.9200(14)	0.073(8)
C11	1.1995(13)	0.5216(12)	0.9221(13)	0.050(7)
C12	1.2307(12)	0.4766(13)	0.8428(14)	0.062(8)
C13	1.1670(12)	0.4468(10)	0.7628(13)	0.051(6)
C14	0.9358(16)	0.5411(14)	0.8417(17)	0.062(9)
C15	1.2744(19)	0.5480(23)	1.0091(20)	0.08(1)
C16	1.1998(15)	0.4007(14)	0.6740(18)	0.071(9)
C17	0.8199(15)	0.3446(10)	0.3644(11)	0.045(7)
C18	0.837(2)	0.312(1)	0.271(2)	0.07(1)
C19	0.765(3)	0.280(1)	0.206(1)	0.09(1)
C20	0.674(3)	0.277(2)	0.229(2)	0.09(1)
C21	0.6563(17)	0.3079(15)	0.3222(16)	0.06(1)
C22	0.7248(13)	0.3438(11)	0.3893(10)	0.057(7)
C23	0.6296(11)	0.4162(8)	0.4887(10)	0.041(6)
C24	0.5963(9)	0.4537(8)	0.5815(9)	0.039(5)
C25	0.5269(10)	0.4089(10)	0.6252(12)	0.045(6)
C26	0.4972(11)	0.4408(12)	0.7086(13)	0.057(7)
C27	0.5317(12)	0.5164(13)	0.7535(11)	0.054(7)
C28	0.6009(13)	0.5642(10)	0.7109(13)	0.056(7)
C29	0.6359(10)	0.5325(9)	0.6217(12)	0.051(6)
C30	0.4891(16)	0.3225(13)	0.5818(17)	0.07(1)
C31	0.4978(18)	0.5499(20)	0.8508(18)	0.07(1)
C32	0.7081(14)	0.5849(11)	0.5806(17)	0.067(8)

T = exp[-2π2U]; U = U_{iso} or (U_{11} + U_{22} + U_{33}) / 3

4.3 Results and Discussion.

Synthesis of 1, 2, and 3. Treatment of H2,6-Clphbt with 0.5 molar equivalent of platinum(II) in toluene gave a small amount of *trans*-planar mononuclear complex **1**. Treatment of H2,4,6-Mephbt with 0.5 molar equivalent of platinum(II) in toluene gave a *trans*-planar mononuclear complex **2**. Treatment of H2,4,6-Mephbt with 0.5 molar equivalent of palladium(II) in toluene gave a mononuclear complex **3** (Scheme 2).

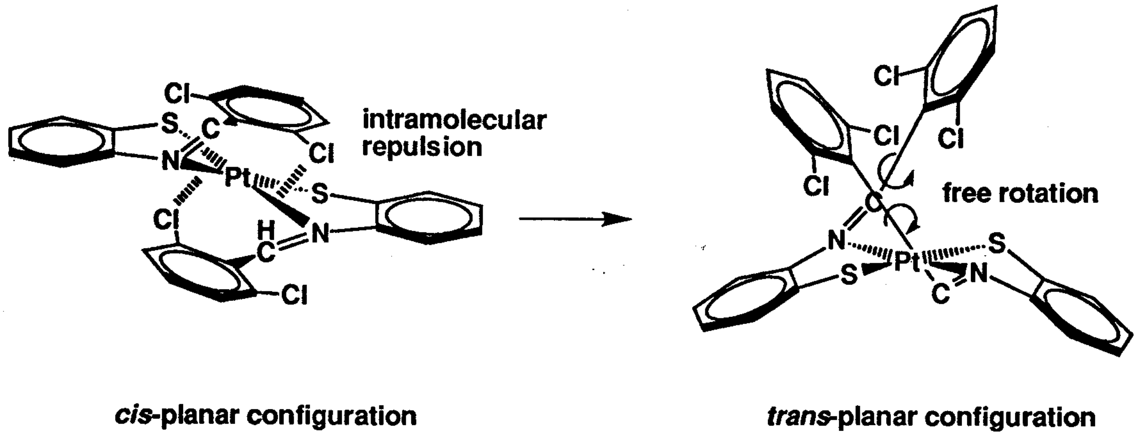


Scheme 2.

Molecular Structure of Complex 1. The molecular structure of **1**, which has been determined by X-ray analysis, is shown in Fig. 1.

The complex **1** has a crystallographical C_2 symmetry with C_2 axis perpendicular to the coordination plane and **1** is a mononuclear complex having a *trans*-planar PtN_2S_2 configuration. This is a rare example of *trans* Schiff base complex in an N_2S_2 environment. Moreover, the complex **1** has an unique umbrella conformation and the ϕ value between two phenyl moieties is 121(10)°.[7] This umbrella conformation is comparable to the corresponding one found for *trans*-bis(1-isopropyl-3-methyl-4-cyclohexylaldimine-5-thiopyrazolate)palladium(II), which ϕ value was 100°.[8] The Pt-S bond distance of 2.320(2) Å is a normal value of Pt-thiolato bond distances[9] and corresponds to that of *trans*-[Pt(fabt)$_2$] but slightly longer than that of *cis*-[Pt(fabt)$_2$] (see chapter 2). The Pt-N bond distance of 1.996(7) is normal value of Pt-imino bond distances[10] and corresponds to that of *trans*-[Pt(fabt)$_2$] but slightly shorter than that of *cis*-[Pt(fabt)$_2$]. The results suggest the existence of the *trans* influence of coordinated sulfur atoms.

The molecular model examination exhibited that any *cis* isomers could not be obtained, since if the complex had a *cis*-planar configuration, the pendant substituted phenyl groups would be suffered from the severe steric hindrance. Thus, the complex **1** prefer an *trans*-planar configuration to relax the intramolecular repulsion of two substituted bulky phenyl groups and to allow a free rotation of pendant substituted phenyl groups (Scheme 3).



Scheme 3.

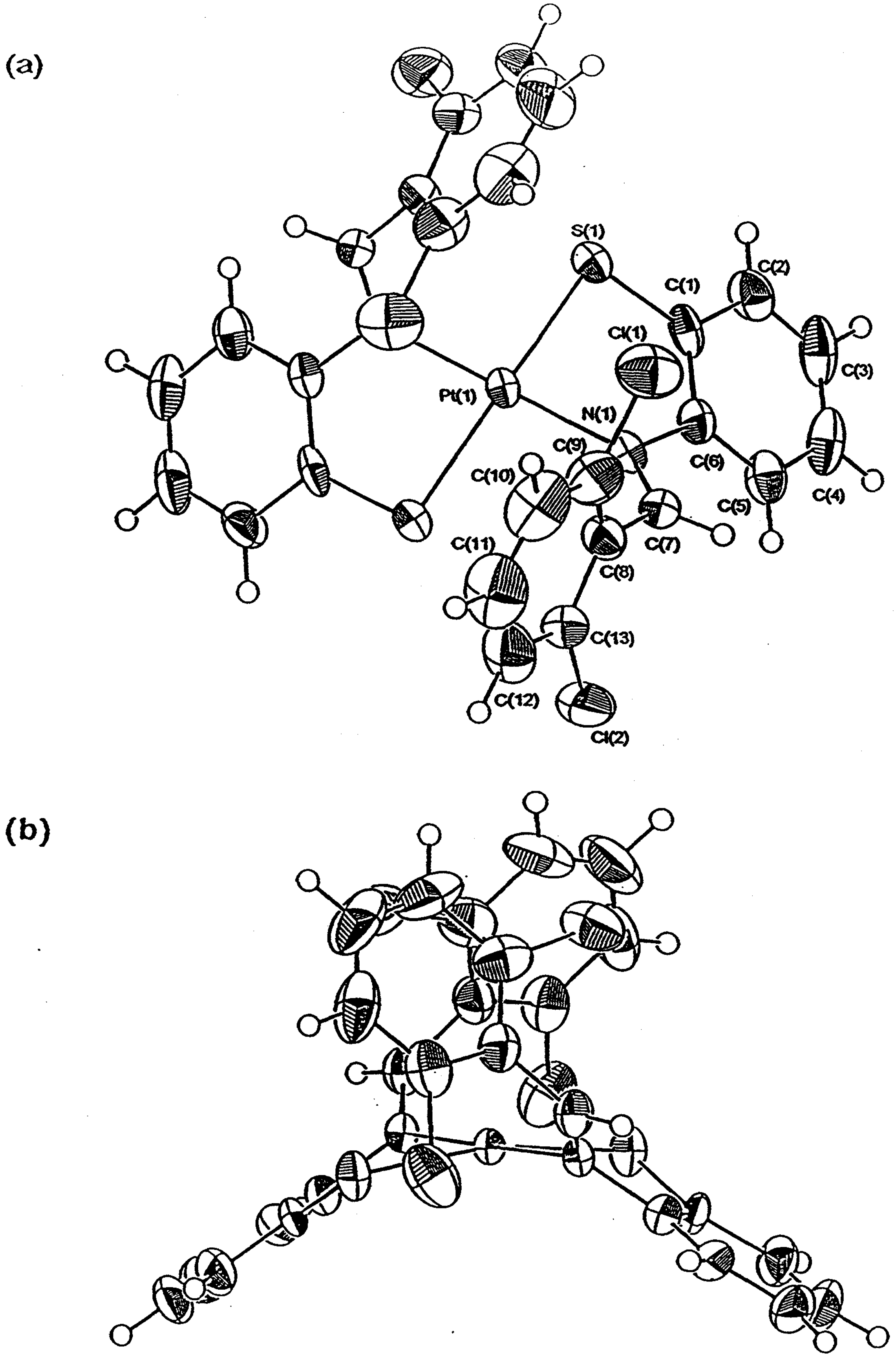


Fig. 1. Molecular structures of 1 (a) top view, (b) side view.

Molecular Structure of Complex 2. As shown in Fig. 2, the complex **2** is a mononuclear complex having a *trans*-planar configuration. This is also a rare example of *trans* Schiff base complex in an N_2S_2 environment as well as complex **1**. The dihedral angle between the two five membered N-Pt-S chelate planes is 9(11)°. Moreover, the complex **2** has an unique umbrella conformation and the ϕ value between two phenyl moieties is 120(4)°.[7] This umbrella conformation is also comparable to the corresponding one found for *trans*-bis(1-isopropyl-3-methyl-4-cyclohexylaldimine-5-thiopyrazolate)palladium(II), which ϕ value was 100°.[8] The Pt-S bond distances of 2.314(4) and 2.311(5) Å are normal value of Pt-thiolato bond distances[9] and corresponds to that of *trans*-[Pt(fabt)$_2$] but slightly longer than that of *cis*-[Pt(fabt)$_2$]. The Pt-N bond distances of 1.995(11) and 1.998(12) Å are normal value of Pt-imino bond distances[10] and corresponds to that of *trans*-[Pt(fabt)$_2$] but slightly shorter than that of *cis*-[Pt(fabt)$_2$]. These results suggest that the *trans* influence of coordinated sulfur atoms is present.

It is interested that, though the Schiff base derived from benzothiazoline normally takes a Z,Z configuration (like **1**) in this system exclusively,[2,11] the Schiff base of **2** exhibits the E,Z configuration in solid state (Scheme 4). This result may be caused by the intramolecular steric repulsion between coordinated sulfur atoms and methyl groups of pendant phenyl moieties. This suggestion is partly supported by the result observed in the related nickel(II) complex in which the Schiff base pendant groups exhibited an E,E configuration.[3] In nickel(II) complex, such steric hindrance is severer than that in platinum one, since the covalent radii of nickel(II) is shorter than that of platinum(II). The azomethine bond distances (C=N) are 1.317(19) Å and 1.29(2) Å for N1-C7 and N2-C23, respectively. The torsion angles of C6-N1-C7-C8 and C22-N2-C23-C24 are 7.1(14) and 3.1(20)°, respectively. These values indicate that the double bond character of azomethine group for the E configuration is weaken than that of the Z configuration. The *cis* isomers could not obtained since if the complex had *cis*-planar configuration, the pendant substituted phenyl groups would be suffered the severe steric hindrance. Thus, the complex **2** prefer a *trans*-planar configuration in which the unique umbrella conformation relaxes the intramolecular repulsion between two substituted phenyl groups and allows free rotation of pendant substituted phenyl groups as well as complex **1**.

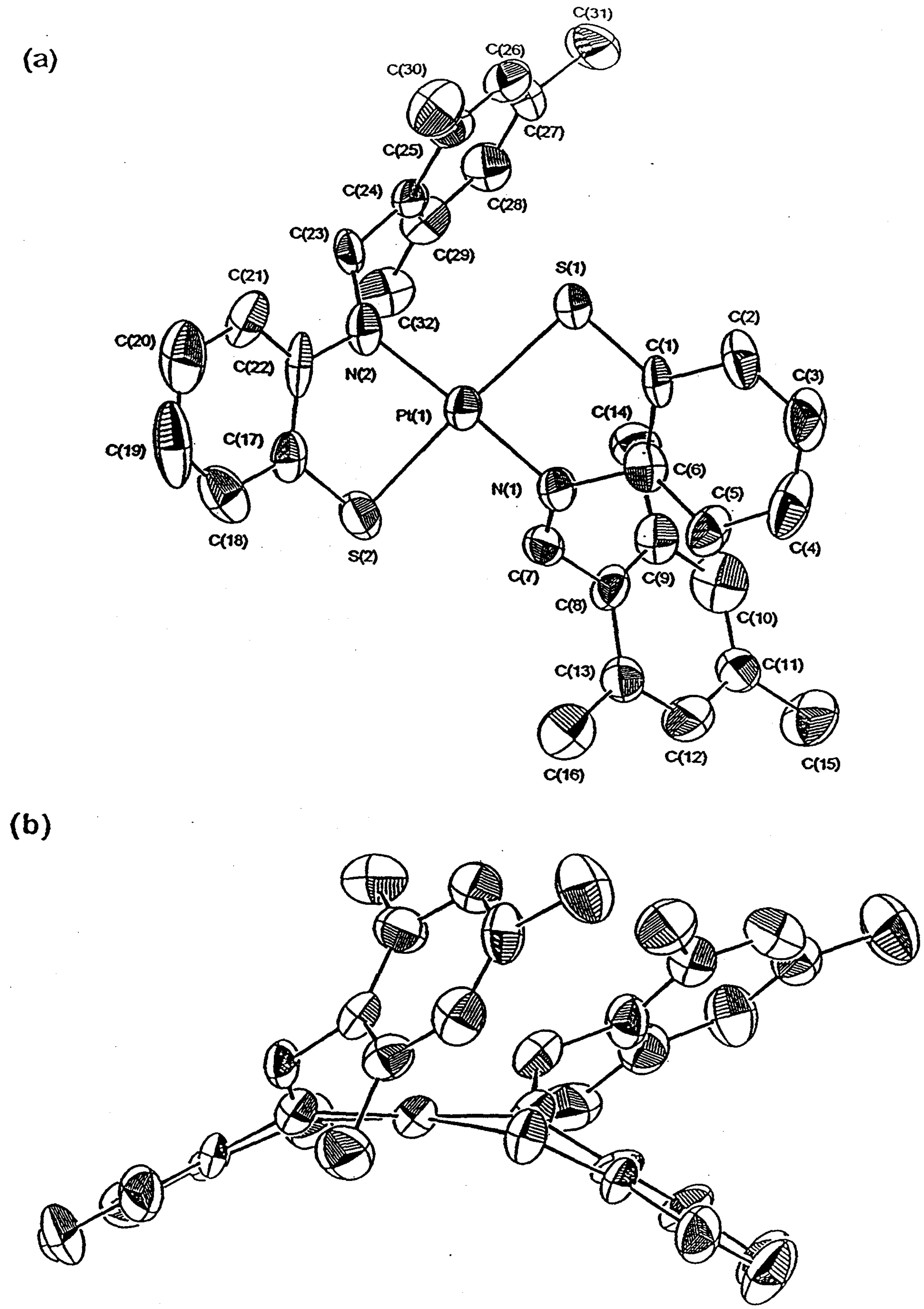
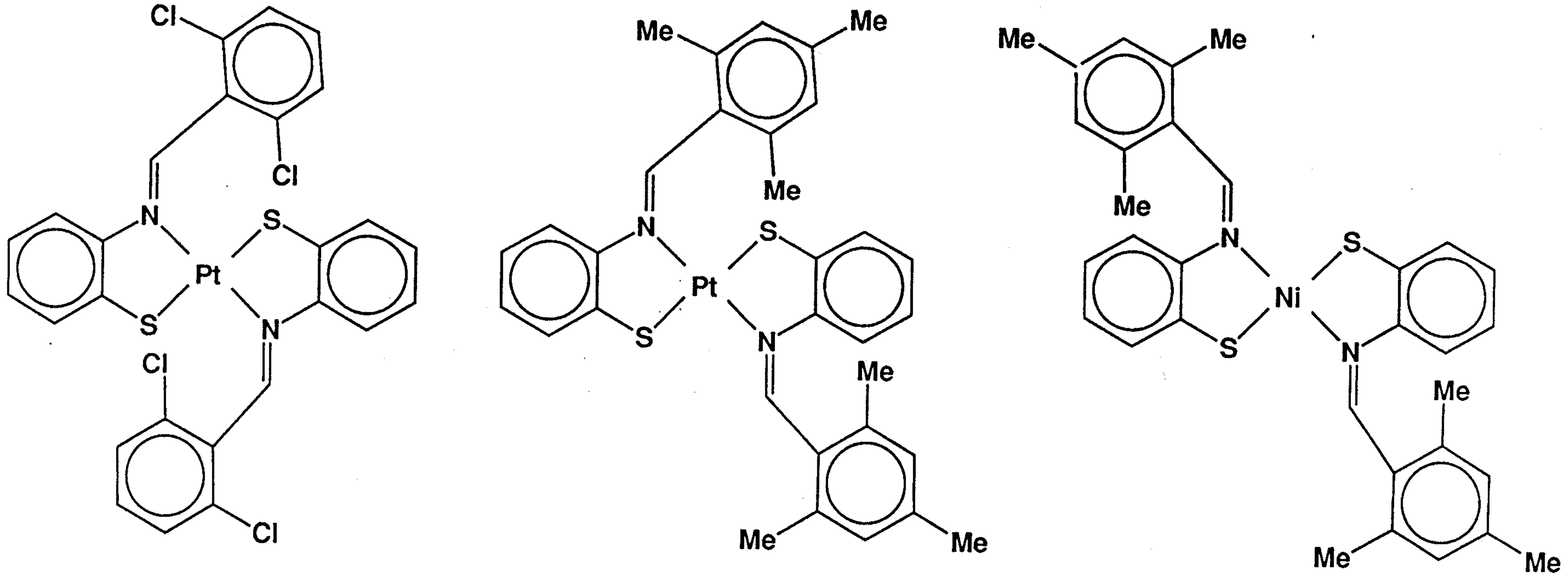


Fig. 2. Molecular structures of 2 (a) top view, (b) side view.



Z,Z

(1)

E,Z

(2)

E,E

ref. 3

Scheme 4.

Spectroscopic Characterization of the Complexes 1, 2 and 3.

IR and NMR spectra. In complex **2**, Infrared spectrum gave the two ν(C=N) bands at 1604 and 1560 cm^{-1}. This result indicates that the two azomethine groups are quite different character in complex **2** as revealed by X-ray analysis (Fig. 2).

Proton NMR spectra of **2** in $CDCl_3$ solution is reported in Fig. 3 and experimental section. First, the appearance of only one azomethine signal shows that complex **2** has C_2 symmetry in solution different from solid state. The C_2 axis in this complex is perpendicular to the coordination plane. The spectrum of **2** gave two signals of 1 : 2 intensity in methyl region and ^{13}C NMR spectrum also gave two signals in the methyl region. This result indicates that the rotation of two substituted phenyl groups is not hindered. In proton NMR spectrum, the signal of azomethine protons appears at δ 9.24 ppm, which value is considered as significant down field shift. This result may indicate that double bond character of azomethine groups of **2** is weaken.

In complex **3**, Infrared spectrum gave the two ν(C=N) bands at 1599 and 1564 cm^{-1}. This result suggests that the two azomethine groups are quite different character in complex **3** as well as complex **2**.

Proton NMR spectra of **3** in $CDCl_3$ solution is reported in Fig. 4 and experimental section. The appearance of only one azomethine signal shows that complex **3** has C_2 symmetry in solution. The C_2 axis in this complex is perpendicular to the coordination plane. The spectrum of **3** gave two signals of 1 : 2 intensity in methyl region and ^{13}C NMR spectrum also gave two signals in methyl region. This result indicates that the rotation of two substituted phenyl groups is not hindered. In proton NMR spectrum, the signal of azomethine protons appears at δ 9.24 ppm, which value is considered as significant down field shift as seen in complex **2**. This result may indicate that double bond character of azomethine groups of **3** is weaken as well as complex **2**. The molecular structure of **3** can be considered almost the same as the structure of complex **2**, judging from IR and NMR spectra and essential equality of the covalent radii of platinum(II) and palladium(II) systems.

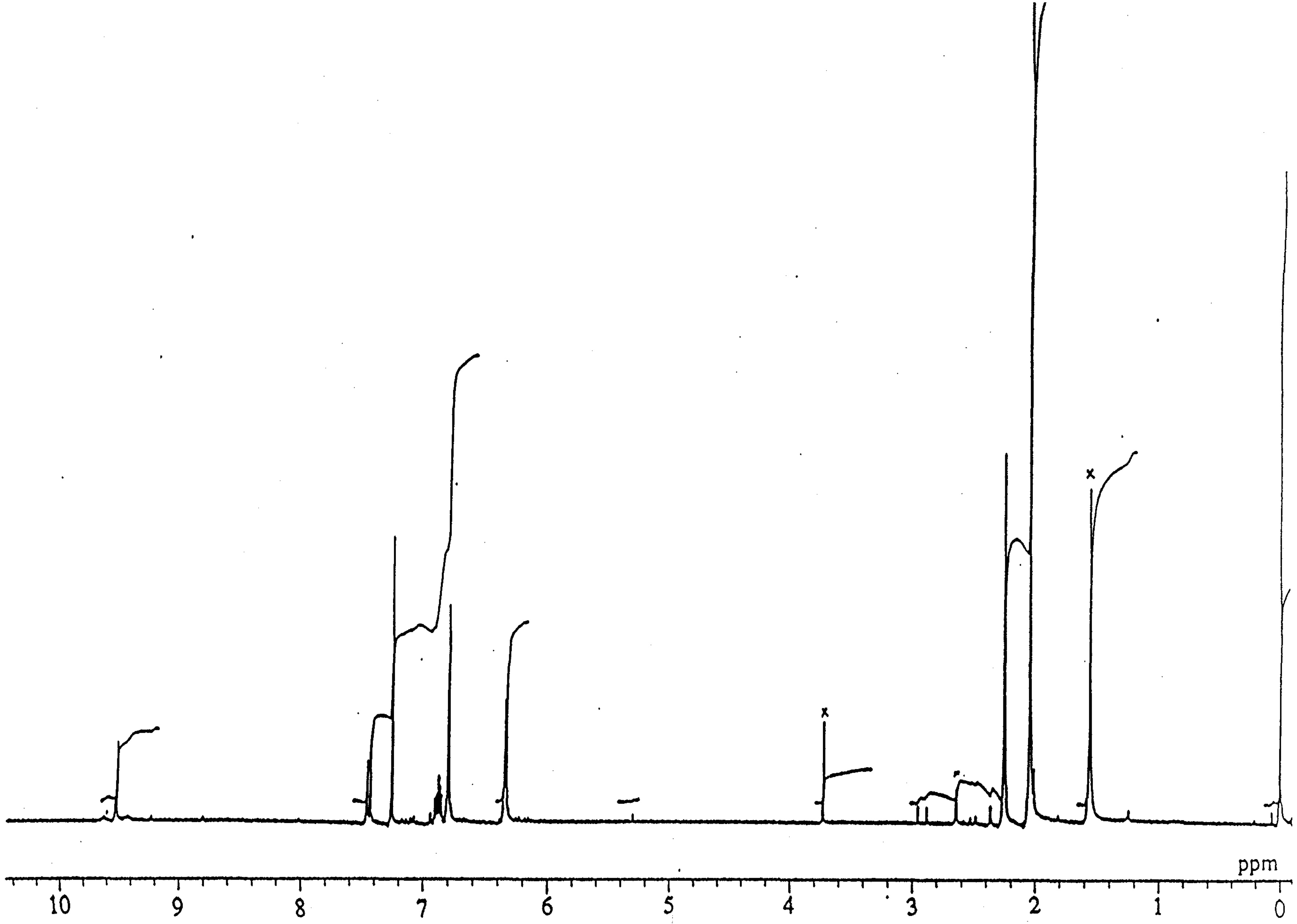


Fig. 3. ^{1}H NMR spectrum of 2 in $CDCl_3$ solution.

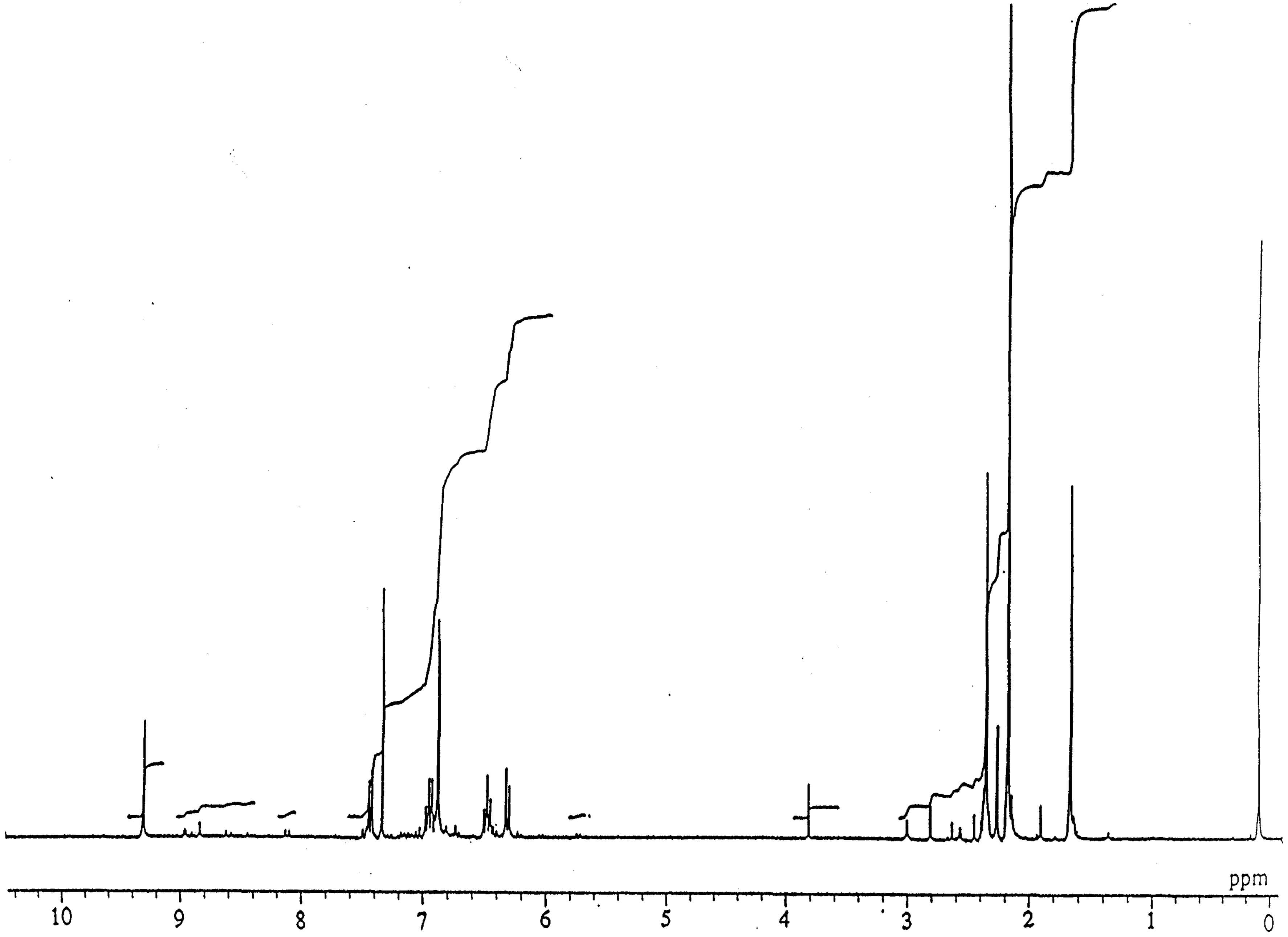


Fig. 4. ^{1}H NMR spectrum of 3 in $CDCl_3$ solution.

Absorption spectra. The electronic absorption spectra of **1**, **2** and **3** in dichloromethane solution are shown in Fig. 5. These complexes exhibit strong absorptions in the visible region, consistent with their intense colours, and their bands mask the d-d transitions. The electronic absorption spectrum of **1** showed four bands at 13.7 ($\varepsilon = 140$), 18.0 (6431), 25.1 (sh, 11912), and 27.3×10^3 cm^{-1} (16698 dm^3 mol^{-1} cm^{-1}) and that of **2** showed three bands at 19.0 (sh, $\varepsilon = 3620$), 28.6 (sh, 13450), and $32.1 \times 10^3 cm^{-1}$ (32140 dm^3 mol^{-1} cm^{-1}) and that of **3** showed four bands at 14.9 (sh, $\varepsilon = 210$), 18.3 (760), 21.7 (2480), and $24.0 \times 10^3 cm^{-1}$ (3610 dm^3 mol^{-1} cm^{-1}). In the spectrum of the complex $[Pt(mnt)_2]^{2-}$ (mnt = maleonitriledithiolate) having thiolato coordinating to platinum(II), Gray et al. had reported that the bands revealed at $18.5 \times 10^3 cm^{-1}$ ($\varepsilon = 1220$ dm^3 mol^{-1} cm^{-1}) and $21.1 \times 10^3 cm^{-1}$ ($\varepsilon = 3470$ dm^3 mol^{-1} cm^{-1}) were assigned to be metal to ligand charge transfer bands.[12] Thus we can estimate that the low - resolution bands in $16 \times 10^3 cm^{-1} \rightarrow 20 \times 10^3 cm^{-1}$ region correspond to these bands.

The spectra of *trans*-planar platinum(II) complexes **1** and **2** are similar to each other but show much different curve from that of palladium(II) complex **3**. The reflectance spectrum of **2** in solid state gave the bands similar to those in solution state but low intensity band appeared at $13.1 \times 10^3 cm^{-1}$. It is considered that this band is corresponded to the observed one in $13.7 \times 10^3 cm^{-1}$ of complex **1**.

Conclusion. By the reaction of platinum(II) with benzothiazoline derivatives with substituted groups at 2,6-positions of pendant phenyl group, the author succeeded in syntheses of mononuclear platinum(II) complexes. These complexes have a rare *trans*-planar configuration bearing MN_2S_2 coordination geometry with N, S chelate Schiff base. Moreover, these complexes have an unique umbrella conformation caused by serious steric hindrance between two pendant 2,6-substituted phenyl groups. The Schiff base in the complex *trans*-[Pt(2,6-Clphbt)$_2$] have an usual Z,Z configuration, but, in the complex *trans*-[Pt(2,4,6-Mephbt)$_2$], those azomethine groups have an E,Z conformation. This result is caused by the steric repulsion between the substituted methyl groups and coordinated sulfur atoms. Judging from spectral data, related palladium(II) complex, *trans*-[Pd(2,4,6-Mephbt)$_2$], has a *trans*-planar configuration as well as *trans*-[Pt(2,4,6-Mephbt)$_2$].

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Chapter 5.

General Discussions

5.1. The reaction of d^8 metal ions with 2-(substituted)benzothiazolines in 1:1 stoichiometry.

The complexes obtained from the reaction of d^8 metal ions with 2-substituted benzothiazolines (Hfabt, Hphbt, and H1-nabt) in 1:1 stoichiometry are summarized in Fig. 1.

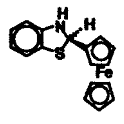
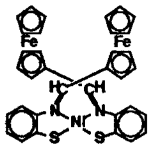
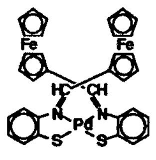
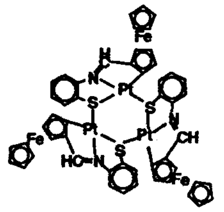
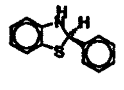
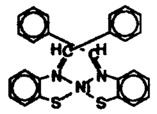
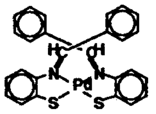
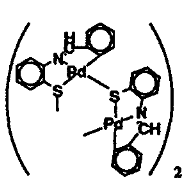
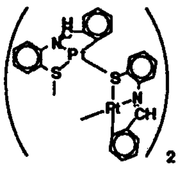
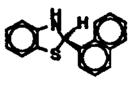
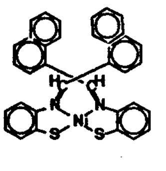
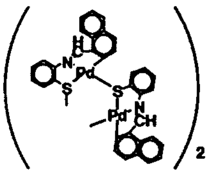
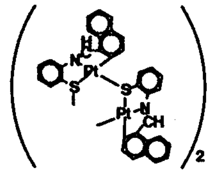
	Benzothiazolines	Ni(II)	Pd(II)	Pt(II)
Chapter 2.	 Hfabt	 *cis*-[Ni(fabt)$_2$]	 *cis*-[Pd(fabt)$_2$]	 [Pt$_3$(C^o-fabt)$_3$]
Chapter 3.	 Hphbt	 *cis*-[Ni(phbt)$_2$]	 *cis*-[Pd(phbt)$_2$]  [Pd$_4$(C^o-phbt)$_4$]	 [Pt$_4$(C^o-phbt)$_4$]
	 H1-nabt	 *cis*-[Ni(1-nabt)$_2$]	 [Pd$_4$(C^o-1-nabt)$_4$]	 [Pt$_4$(C^o-1-nabt)$_4$]

Fig. 1.

In the reaction of Hfabt with d^8 metal ions, the polynuclear complex was only obtained by the reaction with platinum(II) ion. In the reaction of Hphbt with d^8 metal ions, any mononuclear platinum(II) complex could not be obtained, though the related mononuclear nickel(II) and palladium(II) complexes could be obtained. In the reaction of H1-nabt with d^8 metal ions, only the tetranuclear platinum(II) and palladium(II) complexes were obtained, and corresponding tetranuclear nickel(II) complexes could not be obtained. These results indicate that the platinum(II) ion activates the *ortho*-hydrogen-carbon bond more strongly than palladium(II) and nickel(II).

5.2. The reactions of d^8 metal ions with 2-(substituted)benzothiazolines in 1:2 stoichiometry.

The complexes obtained from the reactions of d^8 metal ions with 2-substituted benzothiazolines (Hfabt, Hphbt, and H1-nabt) in 1:2 stoichiometry are sammarized in Fig. 2.

Although any mononuclear platinum(II) complexes could not be obtained by the reaction of platinum(II) ion with Hfabt in 1:1 stoichiometry, the same reaction in 1:2 stoichiometry afforded the mononuclear *trans*- and *cis*-planar platinum(II) complexes together with small amount of the trinuclear complex. In the reaction of Hphbt or H1-nabt with d^8 metal ions in 1:2 stoichiometry, any mononuclear platinum(II) complex could not be obtained (except the [Pt(ddbt)]), though the related mononuclear nickel(II) and palladium(II) complexes could be obtained. These results may indicate that the platinum(II) ion activates the *ortho*-hydrogen-carbon bond more strongly than palladium(II) and nickel(II) and that the *ortho*-hydrogen-carbon bond of Hfabt is more difficult to be activated by the metal ions than those of Hphbt and H1-nabt.

A notable reaction is that, by refluxing the solution of mononuclear *cis*-$[Pd(phbt)_2]$ in toluene, related tetranuclear complex, $[Pd_4(C^o\text{-phbt})_4]$ was obtained. This can be the clear demonstration that the mononuclear *cis*-$[Pd(phbt)_2]$ is probably one of the main intermediate of the tetranuclear complex, $[Pd_4(C^o\text{-phbt})_4]$.

The proton NMR spectrum of the *cis*-$[Pd(phbt)_2]$, shows the notable downfield shifts observed for the aromatic *ortho*-proton at 7.95 ppm. Similar downfield shifts for hydrogen atoms involved in Pt···H-C interactions have been shown by Albinati et al.[1] In addition, G. van Koten et al. have reported that proton NMR studies show downfield shifts for the resonance of the interacting proton (Pt···H-N).[2] The present low-field resonance can be also attributed to an intramolecular Pd···H-C interaction between *ortho*-proton and palladium metal center.

The mononuclear complex, *cis*-$[Pt(fabt)_2]$ can be considered as the intermediate of the trinuclear complex, $[Pt_3(C^o\text{-fabt})_3]$. In the proton NMR spectrum for *cis*-$[Pt(fabt)_2]$, significant downfield shift was clearly observed in one of α protons of monosubstituted cyclopentadienyl at 5.72 ppm. Thus the present low-field resonance can be attributed to an intramolecular Pt···H-C interaction between α proton and platinum metal center. And this interaction can be considered one of the main driving-force affording the related orthometallated trinuclear complex [$Pt_3(C^o\text{-fabt})_3$].

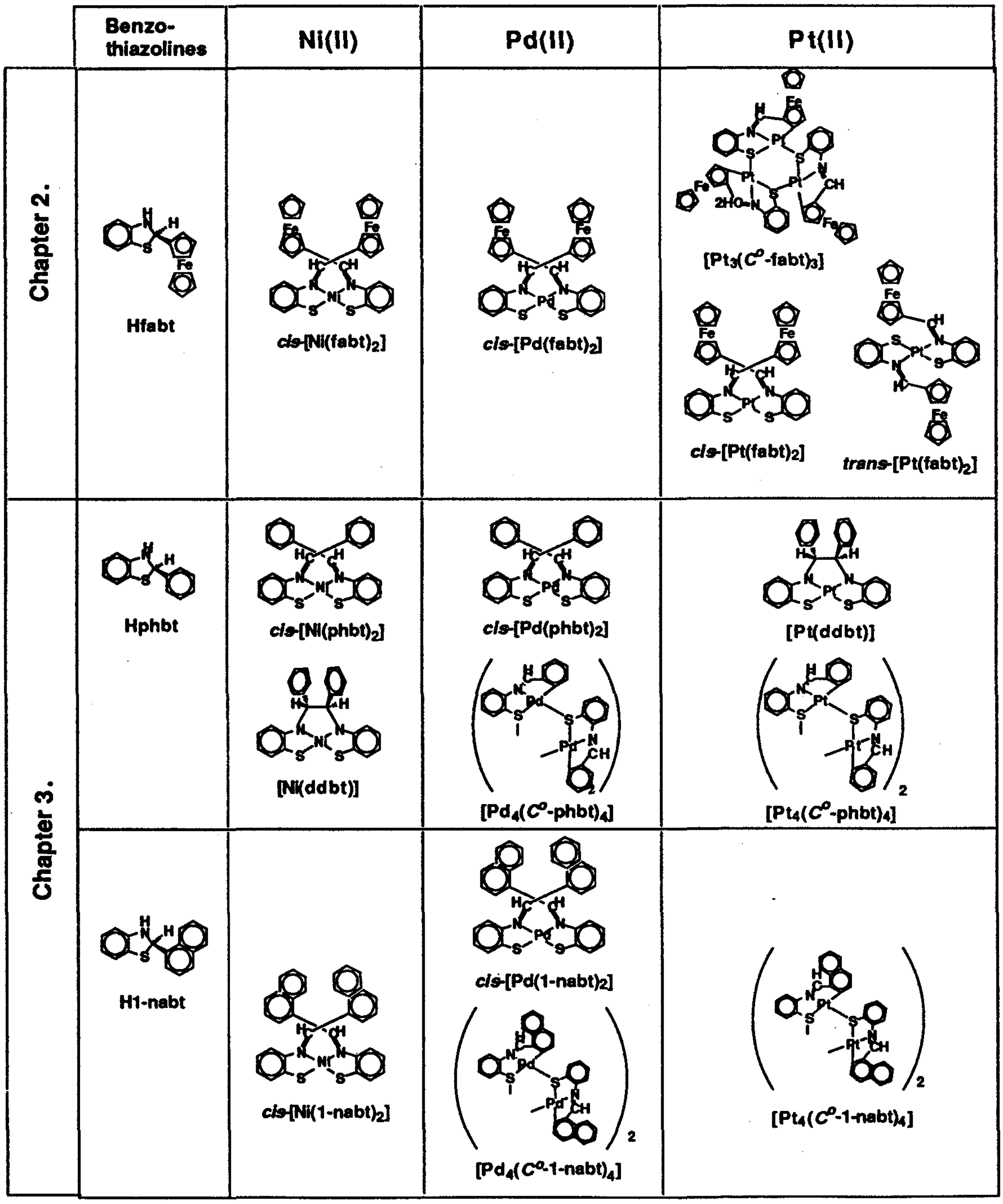


Fig. 2.

To obtain the clear demonstration for this consideration, the author performed the refluxing of a toluene solution of *cis*-[Pt(fabt)$_2$]. Though the related trinuclear complex could not be obtained from this solution, but by addition of [Pt(hfacac)$_2$] to this solution, [Pt$_3$(C^{o}-fabt)$_3$] could be obtained. The result indicates that the addition of platinum(II) ion and suitable proton acceptor for the orthometallate reaction in this system is an unavoidable condition.

From these results, it is considered that the activation of the *ortho*-hydrogen-carbon bond of the substituted phenyl group can be easily occured comparing to that of the substituted cyclopentadienyl group.

By comparing of these X-ray structures, the bond distances between palladium atom and *ortho*-carbon atoms of phenyl groups in *cis*-[Pd(phbt)$_2$] were 3.25(13) and 3.29(3) Å which are shorter than those between platinum atom and α proton of cyclopentadienyl groups in *cis*-[Pt(fabt)$_2$] (3.45(6) and 3.49(4) Å). The result is caused from the difference of six-membered phenyl ring and five-membered cyclopentadienyl ring. It is considered that this structural difference between phenyl ring and cyclopentadienyl ring influence on the activetion of the *ortho*-hydrogen-carbon bond in the substituted groups.

5.3. Comparison of mononuclear platinum(II) complexes.

It was well known that the N, S chelate Schiff base complexes with square planar configuration exclusively prefer a *cis* geometry to a *trans* one.[3]

The reactions of nickel(II) and palladium(II) with Hfabt afforded only the *cis*-planar complexes, though the Hfabt has a bulky pendant ferrocenyl group. The molecular structures of these complexes showed that the two ferrocenyl groups were crossing or stacking each other. This leads the complexes to be *cis*-planar configuration which has an advantage over the *trans*-planar one. However, the reaction of [Pt(hfacac)$_2$] with Hfabt in 1:2 stoichiometry afforded *trans* and *cis* isomeric pair of mononuclear square planar platinum(II) complexes. The reason why the *trans*-[Pt(fabt)$_2$] could be obtained can be considered that the platinum(II) complex is more inert than the corresponding *trans* palladium(II) and nickel(II) ones.

On the contrary, the reactions of [Pt(hfacac)$_2$] with 2-(2,6-disubstituted)-benzothiazolines afforded only *trans*-planar complexes, [Pt(2,6-Clphbt)$_2$] and [Pt(2,4,6-Mephbt)$_2$]. The results is caused by the steric condition of pendant substituted phenyl groups. If the complexes had *cis*-planar configuration, distinct from ferrocenyl group, the pendant substituted phenyl groups would be suffered the severe steric hindrance. Thus the complexes have a *trans*-planar configuration which is generally considered to be a disadvantage compared to the *cis*-planar one.

References and Notes

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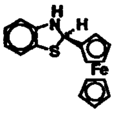
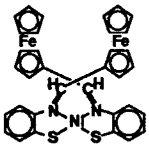
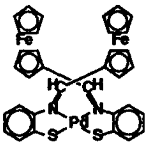
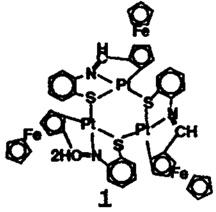
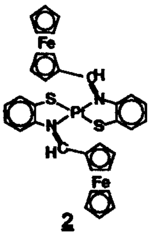
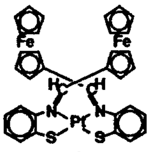
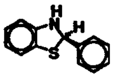
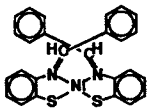
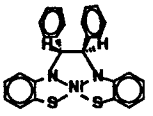
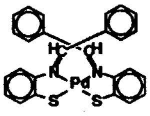
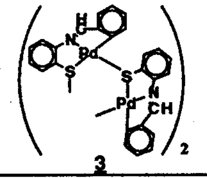
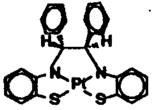
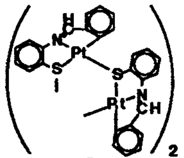
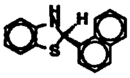
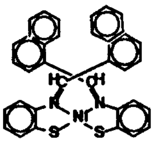
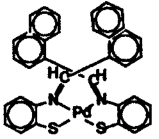
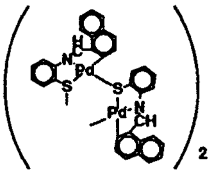
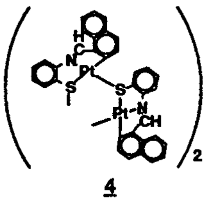
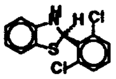
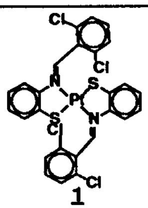
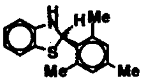
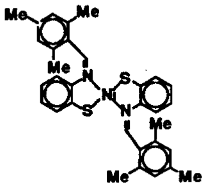
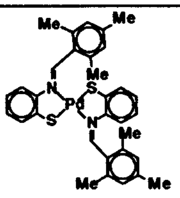
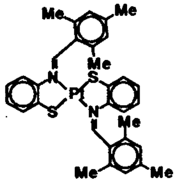
Chapter 6.

General Conclusions

In the present paper, the author reports the syntheses of eight new platinum(II) complexes by the reactions of [Pt(hfacac)$_2$] with various 2-substituted benzothiazolines, and their structures were determined by single crystal X-ray diffraction method and / or spectrochemical study.

In chapters 2 and 3, it is found that the benzothiazoline derivative coordinate in various modes with changing the metal ions. Especially, 2-(ferrocenyl)benzothiazoline could coordinate to platinum(II) as a C^{o}, *N*, *S*-tridentate ligand, in contrast to coordinating to nickel(II) and palladium(II) only as a *N*, *S*-bidentated ligand. The result shows that the platinum(II) activates *ortho*-hydrogen-carbon bond more strongly. This interaction can be considered as mainly originated from the three-center four-electron interaction. Moreover, the author found that with changing substituted group in benzothiazoline, trinuclear or tetranuclear platinum(II) complexes were obtained.

In chapters 2 and 4, the author established that the rare *trans*-planar platinum(II) complexes with *N*, *S*-bidentate Schiff base could be obtained by controlling the steric condition of 2-substituted group of benzothiazoline derivatives. Especially, the reaction of platinum(II) with 2-(ferrocenyl)benzothiazoline afforded a pair of *trans* and *cis*-planar complex. This result gives the first example of the geometrical isomeric pairs of the Schiff base complex bearing PtN_2S_2 configuration.

	Benzo-thiazolines	Ni(II)	Pd(II)	Pt(II)
Chapter 2.	 **Hfabt**			 1  2  3
Chapter 3.	 **Hphbt**	 	  3	 1  2
	 **H1-nabt**		 	 4
Chapter 4.	 **H2,6-Clphbt**			 1
	 **H2,4,6-Mephbt**		 3	 2

List of the d^8 metal complexes

Acknowledgments

The author would like to express his grateful acknowledgment to Professor Yoshihiko Kushi (Graduate School of Science, Osaka University) for his constant encouragement and guidance throughout this study. He also wishes to express his sincere gratitude to Professor Sumio Kaizaki (Graduate School of Science, Osaka University) and Professor Shinnichiro Suzuki (Graduate School of Science, Osaka University) for their encouragement and helpful advice.

He would like to acknowledge Dr. Tatsuya Kawamoto (Graduate School of Science, Osaka University) for his guidance, instructive discussions, and encouragement. He is deeply indebted to Dr. Hiro Kuma (Graduate School of Science, Osaka University) for his kindly instructive discussions. Grateful acknowledgments are made to Dr. Akira Takeuchi, Dr. Seiko Komorita, and Dr. Kazuaki Yamanari for their numerous helpful discussions. Acknowledgment is also made to Dr. Hiroshi Shimomura for his warm encouragement and helpful discussion.

It is a great pleasure to thank Professor Seichi Okeya (Wakayama University), Professor Ichiro Takagi (Wakayama University), and Professor Wakako Kanda (Wakayama University) for their encouragement and helpful discussion.

Acknowledgments are also made to Mr. Shouzou Koshino, Mr. Hiroshi Nakao, Mr. Takashiro Akitsu, Mr. Jun Hamabata, Mr. Shigehiro Asai, Mr. Naoki Okoshi, and Miss Ito Fukuda for their encouragement and friendship.

Finally, he would like to thank to Mrs. Toyo Nagasawa for her warm moral support and encouragement.

February, 1997

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Appendix

Table 3A. Anisotropic Temperature Factors of $[Pt_3(C^{o}\text{-fabt})_3]$(**1**) with esd's in parentheses.

ATOM	*U*(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)
Pt1	0.035(3)	0.029(3)	0.031(3)	-0.003(3)	0.001(2)	-0.001(3)
Pt2	0.039(3)	0.039(3)	0.037(3)	-0.004(3)	-0.006(2)	0.004(3)
Pt3	0.036(3)	0.027(3)	0.034(3)	-0.004(3)	0.005(2)	0.001(3)
Fe1	0.05(1)	0.03(1)	0.04(1)	-0.01(1)	0.01(1)	-0.01(1)
Fe2	0.05(1)	0.05(1)	0.07(2)	-0.01(1)	0.01(1)	0.00(1)
Fe3	0.04(1)	0.04(1)	0.05(1)	0.00(1)	0.00(1)	0.00(1)
Cl1	0.16(7)	0.14(6)	0.08(4)	0.04(6)	-0.01(4)	-0.03(4)
Cl2	0.18(9)	0.15(8)	0.13(6)	-0.05(7)	0.02(6)	-0.02(6)
Cl3	0.13(8)	0.18(11)	0.31(17)	-0.01(8)	-0.04(9)	0.08(11)
S1	0.03(2)	0.03(2)	0.05(2)	0.00(2)	0.00(1)	0.00(2)
S2	0.04(2)	0.05(2)	0.03(2)	-0.01(2)	0.00(1)	0.01(2)
S3	0.05(2)	0.05(2)	0.04(2)	-0.01(2)	0.01(2)	0.00(2)

Table 3B. Anisotropic Temperature Factors for Non-Hydrogen Atoms of *trans*-$[Pt(fabt)_2]$(**2**) with esd's in parentheses.

ATOM	*U*(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)
Pt1	0.035(1)	0.038(1)	0.029(1)	-0.001(1)	0.006(1)	-0.016(1)
Fe1	0.051(5)	0.054(6)	0.035(4)	0.005(4)	0.004(4)	-0.014(4)
Fe2	0.058(5)	0.067(7)	0.055(5)	-0.007(4)	0.018(4)	-0.022(5)
Cl1	0.08(1)	0.12(2)	0.10(1)	0.02(1)	0.00(1)	-0.05(1)
S1	0.042(8)	0.060(10)	0.062(9)	0.000(7)	0.006(7)	-0.027(8)
S2	0.052(9)	0.051(10)	0.054(9)	0.003(7)	0.009(7)	-0.022(8)
N1	0.05(3)	0.03(3)	0.04(2)	-0.01(2)	0.03(2)	-0.02(2)
N2	0.05(3)	0.08(4)	0.03(2)	0.01(3)	-0.01(2)	-0.01(2)
C1	0.07(4)	0.01(3)	0.04(3)	0.00(2)	0.03(3)	0.00(2)
C2	0.09(5)	0.07(5)	0.11(6)	0.01(4)	0.02(4)	-0.07(5)
C3	0.12(6)	0.09(5)	0.04(3)	0.03(5)	-0.01(4)	-0.04(4)
C4	0.13(7)	0.04(4)	0.03(3)	-0.02(4)	0.02(4)	0.03(3)
C5	0.11(5)	0.04(4)	0.06(4)	-0.01(4)	0.06(4)	-0.03(3)
C6	0.05(3)	0.05(4)	0.04(3)	0.03(3)	-0.01(2)	-0.01(3)
C7	0.04(3)	0.09(5)	0.07(4)	-0.02(3)	0.02(3)	-0.06(4)
C8	0.05(3)	0.02(3)	0.03(2)	0.00(2)	-0.03(2)	0.00(2)
C9	0.04(3)	0.05(4)	0.08(4)	-0.01(3)	0.04(3)	-0.02(3)
C10	0.06(4)	0.06(4)	0.07(4)	0.02(3)	-0.03(3)	-0.04(3)
C11	0.06(4)	0.07(4)	0.03(3)	0.02(3)	-0.01(3)	-0.02(3)
C12	0.04(3)	0.06(4)	0.02(2)	0.01(2)	0.01(2)	0.01(3)
C13	0.09(6)	0.11(8)	0.10(7)	0.02(5)	0.01(5)	-0.03(6)
C14	0.13(8)	0.09(7)	0.12(9)	0.04(7)	0.04(7)	0.02(6)
C15	0.06(5)	0.16(10)	0.14(8)	0.03(6)	-0.01(5)	-0.11(8)
C16	0.12(7)	0.09(7)	0.10(6)	0.02(6)	0.03(6)	-0.04(6)
C17	0.2(1)	0.1(1)	0.2(1)	0.0(1)	0.1(1)	-0.1(1)
C18	0.05(3)	0.05(3)	0.04(3)	0.00(2)	0.00(2)	-0.01(2)
C19	0.10(5)	0.03(4)	0.12(6)	-0.01(3)	0.04(5)	-0.03(4)
C20	0.10(5)	0.01(3)	0.06(4)	0.01(3)	0.04(4)	0.01(3)

C21	0.06(3)	0.09(5)	0.05(3)	0.00(3)	0.01(3)	-0.06(3)
C22	0.07(4)	0.06(4)	0.02(2)	-0.02(3)	-0.01(2)	-0.01(2)
C23	0.04(3)	0.05(3)	0.08(4)	0.01(2)	0.02(3)	-0.03(3)
C24	0.06(4)	0.04(3)	0.05(3)	-0.02(3)	0.01(3)	-0.02(3)
C25	0.09(5)	0.05(3)	0.02(2)	0.02(3)	-0.01(3)	0.00(2)
C26	0.10(6)	0.12(7)	0.06(4)	-0.04(5)	0.04(4)	-0.05(4)
C27	0.10(5)	0.05(4)	0.06(4)	-0.02(3)	0.04(4)	-0.01(3)
C28	0.08(5)	0.11(6)	0.04(3)	0.06(4)	-0.02(3)	-0.03(4)
C29	0.04(4)	0.11(6)	0.08(5)	-0.02(4)	0.02(3)	-0.06(5)
C30	0.2(1)	0.1(1)	0.1(1)	0.0(1)	0.0(1)	0.0(1)
C31	0.2(1)	0.1(1)	0.1(1)	0.0(1)	0.0(1)	0.0(1)
C32	0.2(1)	0.1(1)	0.1(1)	0.0(1)	0.0(1)	0.0(1)
C33	0.2(1)	0.1(1)	0.1(1)	0.0(1)	0.1(1)	0.0(1)
C34	0.2(1)	0.1(1)	0.1(1)	0.0(1)	0.0(1)	0.0(0)
C35	0.05(4)	0.15(8)	0.11(6)	-0.01(4)	0.01(3)	-0.12(6)

Table 3C. Anisotropic Temperature Factors for Non-Hydrogen Atoms of *cis*-[Pt(fabt)$_2$](**3**) with esd's in parentheses.

ATOM	*U*(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)
Pt1	0.0265(5)	0.0267(6)	0.0390(7)	-0.0016(9)	0.0065(9)	0.0058(10)
Fe1	0.035(3)	0.048(4)	0.057(5)	-0.015(3)	0.010(3)	-0.009(3)
Fe2	0.064(5)	0.032(3)	0.065(6)	0.000(3)	-0.016(4)	0.008(4)
S1	0.061(7)	0.047(7)	0.054(8)	-0.024(6)	0.019(8)	-0.003(8)
S2	0.041(6)	0.038(6)	0.063(8)	-0.011(5)	0.005(6)	0.006(6)
N1	0.03(2)	0.02(2)	0.01(2)	0.00(1)	0.01(1)	0.00(1)
N2	0.01(1)	0.02(1)	0.09(3)	0.01(1)	0.00(2)	0.00(2)
C1	0.03(2)	0.05(2)	0.07(3)	-0.02(3)	0.00(2)	-0.01(3)
C2	0.06(3)	0.08(4)	0.06(3)	0.05(3)	-0.02(3)	-0.05(3)
C3	0.08(4)	0.08(4)	0.04(3)	0.02(3)	-0.01(3)	-0.02(3)
C4	0.03(2)	0.07(3)	0.05(3)	-0.01(2)	0.02(2)	-0.03(3)
C5	0.05(3)	0.04(2)	0.06(3)	0.02(2)	-0.03(2)	-0.02(2)
C6	0.05(2)	0.05(2)	0.05(3)	0.01(2)	-0.01(3)	0.00(3)
C7	0.02(2)	0.01(1)	0.10(4)	0.00(1)	-0.01(2)	0.01(3)
C8	0.02(2)	0.05(2)	0.04(3)	0.00(2)	0.00(2)	0.02(2)
C9	0.06(3)	0.03(2)	0.07(4)	0.02(2)	-0.01(3)	-0.02(3)
C10	0.07(3)	0.02(2)	0.11(6)	-0.01(2)	-0.03(3)	-0.01(3)
C11	0.09(5)	0.07(4)	0.04(3)	0.02(3)	-0.01(3)	-0.01(3)
C12	0.05(3)	0.05(3)	0.07(4)	0.01(2)	0.01(3)	0.02(3)
C13	0.06(4)	0.07(4)	0.20(9)	0.01(3)	0.02(6)	0.08(6)
C14	0.09(5)	0.06(4)	0.22(12)	-0.03(4)	0.10(7)	-0.01(5)
C15	0.09(7)	0.16(10)	0.22(13)	0.06(7)	-0.05(8)	-0.01(11)
C16	0.14(7)	0.08(5)	0.07(5)	0.06(5)	0.01(5)	0.04(5)
C17	0.11(6)	0.10(8)	0.13(6)	-0.01(5)	0.01(5)	-0.08(6)
C18	0.03(3)	0.05(3)	0.10(5)	0.02(2)	0.00(3)	-0.06(3)
C19	0.09(5)	0.04(3)	0.12(7)	0.02(3)	0.08(5)	0.00(4)
C20	0.06(4)	0.08(5)	0.08(5)	-0.03(3)	0.00(3)	0.00(4)
C21	0.09(5)	0.06(4)	0.14(7)	0.02(4)	-0.05(5)	-0.01(5)
C22	0.07(3)	0.03(2)	0.02(3)	0.01(2)	0.04(2)	0.00(2)
C23	0.01(2)	0.04(2)	0.04(3)	0.00(2)	-0.01(2)	0.00(2)
C24	0.05(3)	0.04(3)	0.05(3)	-0.01(2)	0.01(2)	-0.01(2)
C25	0.03(2)	0.04(3)	0.05(3)	0.02(2)	0.01(2)	0.00(2)

C26	0.01(2)	0.09(4)	0.05(2)	-0.02(3)	0.01(2)	-0.01(3)
C27	0.07(4)	0.07(3)	0.05(4)	0.00(3)	0.00(3)	-0.01(3)
C28	0.09(5)	0.05(3)	0.09(5)	0.01(3)	0.03(4)	-0.02(4)
C29	0.09(4)	0.06(3)	0.03(3)	-0.06(3)	0.01(3)	0.01(3)
C30	0.07(5)	0.10(5)	0.11(6)	-0.02(4)	0.04(5)	0.01(5)
C31	0.07(4)	0.10(5)	0.15(8)	0.07(4)	0.06(5)	0.02(6)
C32	0.06(4)	0.09(5)	0.08(5)	0.04(4)	-0.05(4)	-0.01(4)
C33	0.05(3)	0.07(4)	0.13(6)	-0.01(3)	0.04(3)	-0.08(5)
C34	0.07(3)	0.11(5)	0.07(4)	-0.02(3)	0.05(3)	-0.02(4)

Table 4A. Selected Bond Lengths(Å) and Angles(°) for [Pt$_3$(C^{o}-fabt)$_3$](**1**).

Bond Lengths

Pt1-S1	2.37(4)	Fe3-C49	2.05(29)	C13-C16	2.06(24)
Pt1-S2	2.28(4)	Fe3-C50	2.01(17)	C13-C17	1.24(26)
Pt1-N1	2.22(13)	Fe3-C51	1.98(24)	C14-C15	1.29(26)
Pt1-C9	2.06(17)	Cl1-C52	1.75(19)	C14-C16	2.27(27)
Pt2-S2	2.33(4)	Cl2-C52	1.81(20)	C14-C17	2.36(27)
Pt2-S3	2.27(5)	Cl3-C52	1.73(21)	C15-C16	1.47(21)
Pt2-N2	2.14(12)	S1-C1	1.76(11)	C15-C17	2.31(22)
Pt2-C26	2.00(27)	S2-C18	1.87(19)	C16-C17	1.39(24)
Pt3-S1	2.29(4)	S3-C35	1.84(13)	C18-C19	1.37(25)
Pt3-S3	2.35(4)	N1-C5	2.36(18)	C18-C20	2.38(26)
Pt3-N3	2.00(10)	N1-C6	1.36(19)	C18-C23	1.42(26)
Pt3-C43	1.99(16)	N1-C7	1.27(22)	C19-C20	1.46(25)
Fe1-C8	2.03(12)	N1-C8	2.34(19)	C19-C23	2.38(25)
Fe1-C9	2.03(17)	N2-C23	1.56(21)	C20-C21	1.28(27)
Fe1-C10	2.07(18)	N2-C24	1.25(21)	C20-C22	2.24(26)
Fe1-C11	2.08(14)	N2-C25	2.23(21)	C21-C22	1.34(26)
Fe1-C12	2.08(23)	N3-C35	2.30(16)	C22-C23	1.41(26)
Fe1-C13	1.93(18)	N3-C40	1.42(20)	C24-C25	1.37(24)
Fe1-C14	2.01(22)	N3-C41	1.27(23)	C25-C26	1.56(32)
Fe1-C15	2.05(14)	N3-C42	2.38(19)	C25-C27	2.27(24)
Fe1-C16	2.05(16)	C1-C2	1.47(19)	C25-C28	2.37(25)
Fe1-C17	2.02(18)	C1-C3	2.34(17)	C25-C29	1.44(24)
Fe2-C25	1.92(17)	C1-C6	1.41(17)	C26-C27	1.37(31)
Fe2-C26	2.06(27)	C2-C3	1.22(20)	C27-C28	1.46(26)
Fe2-C27	2.10(17)	C3-C4	1.47(19)	C27-C29	2.30(24)
Fe2-C28	2.10(18)	C4-C5	1.36(18)	C28-C29	1.48(24)
Fe2-C29	1.95(16)	C5-C6	1.45(17)	C30-C31	1.38(43)
Fe2-C30	1.97(28)	C7-C8	1.48(19)	C30-C33	2.29(33)
Fe2-C31	1.92(31)	C8-C9	1.35(20)	C30-C34	1.41(37)
Fe2-C32	2.07(18)	C8-C10	2.27(21)	C31-C32	1.55(36)
Fe2-C33	2.19(18)	C8-C11	2.28(18)	C31-C33	2.36(36)
Fe2-C34	2.13(23)	C8-C12	1.42(26)	C31-C34	2.36(39)
Fe3-C42	2.08(18)	C9-C10	1.47(24)	C32-C33	1.51(25)
Fe3-C43	2.14(16)	C9-C11	2.36(21)	C33-C34	1.52(29)
Fe3-C44	2.12(13)	C9-C12	2.37(28)	C35-C36	1.44(24)
Fe3-C45	2.00(16)	C10-C11	1.49(22)	C35-C39	2.30(18)
Fe3-C46	2.07(19)	C11-C12	1.54(26)	C35-C40	1.40(22)
Fe3-C47	2.12(16)	C13-C14	1.49(27)	C36-C37	1.43(28)
Fe3-C48	2.09(23)	C13-C15	2.12(22)	C37-C38	1.45(30)

C37-C39	2.38(23)	C42-C45	2.24(22)	C47-C49	2.36(32)
C38-C39	1.40(25)	C42-C46	1.55(26)	C47-C50	2.23(22)
C38-C40	2.38(27)	C43-C44	1.37(20)	C47-C51	1.44(28)
C39-C40	1.26(21)	C43-C45	2.30(22)	C48-C49	1.36(36)
C40-C41	2.32(26)	C44-C45	1.42(19)	C48-C51	2.37(33)
C41-C42	1.47(26)	C44-C46	2.38(23)	C49-C50	1.73(33)
C42-C43	1.51(23)	C45-C46	1.40(24)	C50-C51	1.23(28)
C42-C44	2.25(21)	C47-C48	1.51(28)		

Bond Angles

S1-Pt1-S2	92.8(13)	C11-Fe1-C13	158.0(64)
S1-Pt1-N1	85.6(38)	C11-Fe1-C14	153.5(69)
S1-Pt1-C9	161.2(46)	C11-Fe1-C15	122.5(55)
S2-Pt1-N	172.5(39)	C11-Fe1-C16	107.5(58)
S2-Pt1-C9	105.6(46)	C11-Fe1-C17	122.7(63)
N1-Pt1-C9	76.5(58)	C12-Fe1-C13	121.8(81)
S2-Pt2-S3	92.2(14)	C12-Fe1-C14	162.0(86)
S2-Pt2-N2	88.9(32)	C12-Fe1-C15	158.0(75)
S2-Pt2-C26	163.0(76)	C12-Fe1-C16	119.0(77)
S3-Pt2-N2	172.1(32)	C12-Fe1-C17	102.8(80)
S3-Pt2-C26	100.4(77)	C13-Fe1-C14	44.4(77)
N2-Pt2-C26	80.2(82)	C13-Fe1-C15	64.3(65)
S1-Pt3-S3	90.5(13)	C13-Fe1-C16	62.0(69)
S1-Pt3-N3	171.2(30)	C13-Fe1-C17	36.6(73)
S1-Pt3-C43	103.0(47)	C14-Fe1-C15	37.0(72)
S3-Pt3-N3	83.3(29)	C14-Fe1-C16	68.1(74)
S3-Pt3-C43	165.6(46)	C14-Fe1-C17	71.7(76)
N3-Pt3-C43	83.7(53)	C15-Fe1-C16	42.0(58)
C8-Fe1-C9	38.8(56)	C15-Fe1-C17	69.2(62)
C8-Fe1-C10	67.3(57)	C16-Fe1-C17	39.8(66)
C8-Fe1-C11	67.7(48)	C25-Fe2-C26	46.1(90)
C8-Fe1-C12	40.4(70)	C25-Fe2-C27	68.7(68)
C8-Fe1-C13	113.0(62)	C25-Fe2-C28	72.1(69)
C8-Fe1-C14	127.2(68)	C25-Fe2-C29	43.8(69)
C8-Fe1-C15	161.1(52)	C25-Fe2-C30	105.0(96)
C8-Fe1-C16	155.4(55)	C25-Fe2-C31	115.3(106)
C8-Fe1-C17	120.8(60)	C25-Fe2-C32	153.7(73)
C9-Fe1-C10	42.0(66)	C25-Fe2-C33	162.4(70)
C9-Fe1-C11	70.2(59)	C25-Fe2-C34	122.6(81)
C9-Fe1-C12	70.4(77)	C26-Fe2-C27	38.4(86)
C9-Fe1-C13	125.2(70)	C26-Fe2-C28	71.3(89)
C9-Fe1-C14	106.8(74)	C26-Fe2-C29	75.3(88)
C9-Fe1-C15	125.7(60)	C26-Fe2-C30	125.8(111)
C9-Fe1-C16	164.7(64)	C26-Fe2-C31	102.1(119)
C9-Fe1-C17	154.1(69)	C26-Fe2-C32	113.3(90)
C10-Fe1-C11	42.2(61)	C26-Fe2-C33	151.4(87)
C10-Fe1-C12	72.5(78)	C26-Fe2-C34	163.8(97)
C10-Fe1-C13	159.7(72)	C27-Fe2-C28	40.8(71)
C10-Fe1-C14	118.0(75)	C27-Fe2-C29	69.3(66)
C10-Fe1-C15	108.4(61)	C27-Fe2-C30	162.9(98)
C10-Fe1-C16	126.4(65)	C27-Fe2-C31	125.2(106)
C10-Fe1-C17	161.7(71)	C27-Fe2-C32	105.9(68)
C11-Fe1-C12	43.6(72)	C27-Fe2-C33	123.6(65)

C27-Fe2-C34	156.8(78)
C28-Fe2-C29	42.6(67)
C28-Fe2-C30	154.4(100)
C28-Fe2-C31	162.8(107)
C28-Fe2-C32	121.6(69)
C28-Fe2-C33	108.2(67)
C28-Fe2-C34	119.3(80)
C29-Fe2-C30	117.9(96)
C29-Fe2-C31	152.7(104)
C29-Fe2-C32	160.6(69)
C29-Fe2-C33	124.7(66)
C29-Fe2-C34	103.8(78)
C30-Fe2-C31	41.6(126)
C30-Fe2-C32	72.3(95)
C30-Fe2-C33	66.7(93)
C30-Fe2-C34	40.0(104)
C31-Fe2-C32	45.4(104)
C31-Fe2-C33	69.7(103)
C31-Fe2-C34	71.1(112)
C32-Fe2-C33	41.3(67)
C32-Fe2-C34	72.9(79)
C33-Fe2-C34	41.2(77)
C42-Fe3-C43	41.8(62)
C42-Fe3-C44	64.9(56)
C42-Fe3-C45	66.7(64)
C42-Fe3-C46	43.7(71)
C42-Fe3-C47	108.2(61)
C42-Fe3-C48	125.8(78)
C42-Fe3-C49	158.7(91)
C42-Fe3-C50	149.2(67)
C42-Fe3-C51	118.8(82)
C43-Fe3-C44	37.4(54)
C43-Fe3-C45	67.5(59)
C43-Fe3-C46	73.3(69)
C43-Fe3-C47	120.0(59)
C43-Fe3-C48	105.5(76)
C43-Fe3-C49	120.0(89)
C43-Fe3-C50	168.3(63)
C43-Fe3-C51	154.5(79)
C44-Fe3-C45	40.1(52)
C44-Fe3-C46	69.0(62)
C44-Fe3-C47	153.7(52)
C44-Fe3-C48	119.5(72)
C44-Fe3-C49	107.8(85)
C44-Fe3-C50	134.1(57)
C44-Fe3-C51	165.1(75)
C45-Fe3-C46	40.2(68)
C45-Fe3-C47	163.5(59)
C45-Fe3-C48	154.0(76)
C45-Fe3-C49	121.8(91)
C45-Fe3-C50	110.5(63)
C45-Fe3-C51	126.0(79)
C46-Fe3-C47	125.1(67)
C46-Fe3-C48	164.7(82)
C46-Fe3-C49	155.3(95)
C46-Fe3-C50	113.2(73)
C46-Fe3-C51	103.1(88)
C47-Fe3-C48	41.9(75)
C47-Fe3-C49	68.9(89)
C47-Fe3-C50	65.2(61)
C47-Fe3-C51	41.1(77)
C48-Fe3-C49	38.3(100)
C48-Fe3-C50	71.0(80)
C48-Fe3-C51	71.3(94)
C49-Fe3-C50	50.3(91)
C49-Fe3-C51	73.8(104)
C50-Fe3-C51	36.0(80)
Pt1-S1-Pt3	104.3(14)
Pt1-S1-C1	95.9(37)
Pt3-S1-C1	107.5(38)
Pt1-S2-Pt2	100.1(14)
Pt1-S2-C18	112.7(56)
Pt2-S2-C18	96.4(56)
Pt2-S3-Pt3	106.5(17)
Pt2-S3-C35	106.7(44)
Pt3-S3-C35	95.7(43)
Pt1-N1-C5	145.2(75)
Pt1-N1-C6	112.0(93)
Pt1-N1-C7	113.5(107)
Pt1-N1-C8	79.4(52)
C5-N1-C6	33.9(67)
C5-N1-C7	101.1(102)
C5-N1-C8	135.2(71)
C6-N1-C7	134.5(134)
C6-N1-C8	168.1(105)
C7-N1-C8	34.1(83)
Pt2-N2-C23	114.2(89)
Pt2-N2-C24	116.5(106)
Pt2-N2-C25	83.4(60)
C23-N2-C24	128.3(133)
C23-N2-C25	160.9(106)
C24-N2-C25	33.2(96)
Pt3-N3-C35	92.7(49)
Pt3-N3-C40	125.9(90)
Pt3-N3-C41	113.1(108)
Pt3-N3-C42	82.1(52)
C35-N3-C40	34.9(78)
C35-N3-C41	154.1(115)
C35-N3-C42	171.5(70)
C40-N3-C41	119.4(132)
C40-N3-C42	151.7(99)
C41-N3-C42	32.4(101)
S1-C1-C2	120.8(86)
S1-C1-C3	147.5(66)
S1-C1-C6	122.3(85)
C2-C1-C3	26.7(69)
C2-C1-C6	116.3(102)
C3-C1-C6	89.9(77)

C1-C2-C3	120.5(132)
C1-C3-C2	32.8(84)
C1-C3-C4	92.5(84)
C2-C3-C4	124.8(133)
C3-C4-C5	118.3(114)
N1-C5-C4	148.6(96)
N1-C5-C6	31.5(65)
C4-C5-C6	117.7(107)
N1-C6-C1	123.6(112)
N1-C6-C5	114.6(110)
C1-C6-C5	121.5(107)
N1-C7-C8	117.1(130)
Fe1-C8-N1	115.1(60)
Fe1-C8-C7	118.9(88)
Fe1-C8-C9	70.9(83)
Fe1-C8-C10	57.1(52)
Fe1-C8-C11	57.2(44)
Fe1-C8-C12	71.8(102)
N1-C8-C7	28.8(71)
N1-C8-C9	87.6(93)
N1-C8-C10	125.8(73)
N1-C8-C11	163.8(71)
N1-C8-C12	153.9(118)
C7-C8-C9	116.1(119)
C7-C8-C10	154.0(102)
C7-C8-C11	166.0(97)
C7-C8-C12	125.1(133)
C9-C8-C10	38.2(87)
C9-C8-C11	76.4(90)
C9-C8-C12	117.9(138)
C10-C8-C11	38.2(58)
C10-C8-C12	79.8(111)
C11-C8-C12	41.6(101)
Pt1-C9-Fe1	128.5(82)
Pt1-C9-C8	116.0(108)
Pt1-C9-C10	136.6(120)
Pt1-C9-C11	173.2(89)
Pt1-C9-C12	147.9(97)
Fe1-C9-C8	70.3(83)
Fe1-C9-C10	70.2(92)
Fe1-C9-C11	55.7(51)
Fe1-C9-C12	55.7(68)
C8-C9-C10	107.1(134)
C8-C9-C11	69.9(87)
C8-C9-C12	31.9(83)
C10-C9-C11	37.3(84)
C10-C9-C12	75.3(108)
C11-C9-C12	38.1(68)
Fe1-C10-C8	55.5(51)
Fe1-C10-C9	67.9(91)
Fe1-C10-C11	69.3(83)
C8-C10-C9	34.6(79)
C8-C10-C11	71.5(87)
C9-C10-C11	106.1(132)
Fe1-C11-C8	55.1(44)
Fe1-C11-C9	54.0(51)
Fe1-C11-C10	68.5(84)
Fe1-C11-C12	68.3(98)
C8-C11-C9	33.7(52)
C8-C11-C10	70.3(88)
C8-C11-C12	37.6(93)
C9-C11-C10	36.6(83)
C9-C11-C12	71.2(104)
C10-C11-C12	107.8(133)
Fe1-C12-C8	67.8(100)
Fe1-C12-C9	53.9(66)
Fe1-C12-C11	68.1(97)
C8-C12-C9	30.2(79)
C8-C12-C11	100.9(149)
C9-C12-C11	70.7(104)
Fe1-C13-C14	70.4(109)
Fe1-C13-C15	60.5(64)
Fe1-C13-C16	61.8(70)
Fe1-C13-C17	75.3(120)
C14-C13-C15	36.8(100)
C14-C13-C16	77.9(120)
C14-C13-C17	118.8(174)
C15-C13-C16	41.2(67)
C15-C13-C17	82.2(126)
C16-C13-C17	41.1(107)
Fe1-C14-C13	65.2(106)
Fe1-C14-C15	73.2(120)
Fe1-C14-C16	56.9(70)
Fe1-C14-C17	54.3(68)
C13-C14-C15	99.3(162)
C13-C14-C16	62.2(109)
C13-C14-C17	27.5(93)
C15-C14-C16	37.1(94)
C15-C14-C17	71.9(118)
C16-C14-C17	34.8(66)
Fe1-C15-C13	55.3(60)
Fe1-C15-C14	69.8(112)
Fe1-C15-C16	69.1(82)
Fe1-C15-C17	54.7(55)
C13-C15-C14	43.9(110)
C13-C15-C16	67.1(93)
C13-C15-C17	32.2(68)
C14-C15-C16	110.9(142)
C14-C15-C17	76.0(117)
C16-C15-C17	34.9(82)
Fe1-C16-C13	56.2(64)
Fe1-C16-C14	55.0(65)
Fe1-C16-C15	68.9(81)
Fe1-C16-C17	68.7(96)
C13-C16-C14	39.9(76)
C13-C16-C15	71.7(97)
C13-C16-C17	36.1(96)
C14-C16-C15	31.9(82)

C14-C16-C17	75.9(112)	C26-C25-C28	72.8(124)
C15-C16-C17	107.8(137)	C26-C25-C29	108.8(155)
Fe1-C17-C13	68.1(112)	C27-C25-C28	36.7(69)
Fe1-C17-C14	54.0(67)	C27-C25-C29	72.8(103)
Fe1-C17-C15	56.1(56)	C28-C25-C29	36.1(88)
Fe1-C17-C16	71.5(98)	Pt2-C26-Fe2	118.6(127)
C13-C17-C14	33.6(108)	Pt2-C26-C25	108.8(152)
C13-C17-C15	65.5(115)	Pt2-C26-C27	149.5(195)
C13-C17-C16	102.8(158)	Fe2-C26-C25	62.4(110)
C14-C17-C15	32.0(67)	Fe2-C26-C27	72.4(134)
C14-C17-C16	69.3(108)	C25-C26-C27	101.4(189)
C15-C17-C16	37.3(87)	Fe2-C27-C25	52.0(58)
S2-C18-C19	119.5(136)	Fe2-C27-C26	69.2(130)
S2-C18-C20	152.9(106)	Fe2-C27-C28	69.7(96)
S2-C18-C23	122.3(129)	Fe2-C27-C29	52.2(56)
C19-C18-C20	33.8(96)	C25-C27-C26	42.4(129)
C19-C18-C23	117.8(162)	C25-C27-C28	75.4(106)
C20-C18-C23	84.7(115)	C25-C27-C29	36.7(65)
C18-C19-C20	114.9(157)	C26-C27-C28	117.8(176)
C18-C19-C23	31.7(98)	C26-C27-C29	79.1(140)
C20-C19-C23	83.8(112)	C28-C27-C29	38.7(89)
C18-C20-C19	31.3(90)	Fe2-C28-C25	50.5(56)
C18-C20-C21	96.1(134)	Fe2-C28-C27	69.4(95)
C18-C20-C22	64.2(81)	Fe2-C28-C29	63.0(86)
C19-C20-C21	126.4(173)	C25-C28-C27	67.9(101)
C19-C20-C22	95.0(121)	C25-C28-C29	35.1(86)
C21-C20-C22	32.0(107)	C27-C28-C29	103.0(140)
C20-C21-C22	117.5(182)	Fe2-C29-C25	67.3(91)
C20-C22-C21	30.5(106)	Fe2-C29-C27	58.4(60)
C20-C22-C23	90.4(124)	Fe2-C29-C28	74.4(95)
C21-C22-C23	120.9(174)	C25-C29-C27	70.5(101)
N2-C23-C18	116.8(140)	C25-C29-C28	108.7(143)
N2-C23-C19	147.3(118)	C27-C29-C28	38.3(93)
N2-C23-C22	122.2(146)	Fe2-C30-C31	67.2(168)
C18-C23-C19	30.5(91)	Fe2-C30-C33	61.2(88)
C18-C23-C22	120.6(159)	Fe2-C30-C34	76.0(150)
C19-C23-C22	90.4(118)	C31-C30-C33	75.2(179)
N2-C24-C25	116.9(158)	C31-C30-C34	115.2(249)
Fe2-C25-N2	114.5(84)	C33-C30-C34	40.1(126)
Fe2-C25-C24	121.4(127)	Fe2-C31-C30	71.2(172)
Fe2-C25-C26	71.4(117)	Fe2-C31-C32	72.5(138)
Fe2-C25-C27	59.3(63)	Fe2-C31-C33	60.5(96)
Fe2-C25-C28	57.4(61)	Fe2-C31-C34	58.6(101)
Fe2-C25-C29	68.9(92)	C30-C31-C32	109.0(240)
N2-C25-C24	29.8(89)	C30-C31-C33	70.2(176)
N2-C25-C26	87.4(126)	C30-C31-C34	32.7(150)
N2-C25-C27	123.6(94)	C32-C31-C33	38.8(108)
N2-C25-C28	160.0(100)	C32-C31-C34	76.3(150)
N2-C25-C29	163.2(130)	C33-C31-C34	37.6(85)
C24-C25-C26	117.3(167)	Fe2-C32-C31	62.1(128)
C24-C25-C27	153.4(141)	Fe2-C32-C33	73.5(97)
C24-C25-C28	169.6(143)	C31-C32-C33	101.1(169)
C24-C25-C29	133.7(161)	Fe2-C33-C30	52.1(79)
C26-C25-C27	36.1(112)	Fe2-C33-C31	49.8(83)

Fe2-C33-C32	65.2(91)	Fe3-C42-C45	55.0(60)
Fe2-C33-C34	67.3(106)	Fe3-C42-C46	67.9(93)
C30-C33-C31	34.6(108)	N3-C42-C41	27.6(88)
C30-C33-C32	74.7(120)	N3-C42-C43	83.4(96)
C30-C33-C34	36.8(119)	N3-C42-C44	119.5(82)
C31-C33-C32	40.1(109)	N3-C42-C45	155.5(94)
C31-C33-C34	71.3(131)	N3-C42-C46	164.1(124)
C32-C33-C34	111.2(152)	C41-C42-C43	109.3(146)
Fe2-C34-C30	64.0(140)	C41-C42-C44	144.3(137)
Fe2-C34-C31	50.3(89)	C41-C42-C45	165.5(147)
Fe2-C34-C33	71.6(108)	C41-C42-C46	136.6(156)
C30-C34-C31	32.1(148)	C43-C42-C44	36.1(78)
C30-C34-C33	103.1(191)	C43-C42-C45	72.7(96)
C31-C34-C33	71.2(130)	C43-C42-C46	110.8(137)
S3-C35-N3	88.2(55)	C44-C42-C45	36.8(55)
S3-C35-C36	117.5(113)	C44-C42-C46	74.8(100)
S3-C35-C39	150.7(75)	C45-C42-C46	38.1(88)
S3-C35-C40	122.6(104)	Pt3-C43-Fe3	124.8(76)
N3-C35-C36	154.2(116)	Pt3-C43-C42	110.5(108)
N3-C35-C39	63.1(51)	Pt3-C43-C44	146.0(119)
N3-C35-C40	35.5(79)	Pt3-C43-C45	178.2(92)
C36-C35-C39	91.0(105)	Fe3-C43-C42	67.1(88)
C36-C35-C40	118.9(136)	Fe3-C43-C44	70.8(83)
C39-C35-C40	28.2(80)	Fe3-C43-C45	53.4(55)
C35-C36-C37	117.1(167)	C42-C43-C44	103.4(128)
C36-C37-C38	119.8(176)	C42-C43-C45	68.6(93)
C36-C37-C39	88.2(123)	C44-C43-C45	35.0(75)
C38-C37-C39	32.6(99)	Fe3-C44-C42	56.7(54)
C37-C38-C39	113.6(170)	Fe3-C44-C43	71.8(83)
C37-C38-C40	89.6(130)	Fe3-C44-C45	65.3(78)
C39-C38-C40	24.6(81)	Fe3-C44-C46	54.5(54)
C35-C39-C37	63.0(64)	C42-C44-C43	40.5(86)
C35-C39-C38	96.6(113)	C42-C44-C45	71.2(86)
C35-C39-C40	31.8(89)	C42-C44-C46	38.9(66)
C37-C39-C38	33.9(105)	C43-C44-C45	111.5(120)
C37-C39-C40	94.7(111)	C43-C44-C46	79.3(97)
C38-C39-C40	127.9(153)	C45-C44-C46	32.3(79)
N3-C40-C35	109.6(127)	Fe3-C45-C42	58.4(59)
N3-C40-C38	155.8(125)	Fe3-C45-C43	59.0(55)
N3-C40-C39	128.5(147)	Fe3-C45-C44	74.5(83)
N3-C40-C41	28.4(73)	Fe3-C45-C46	72.7(99)
C35-C40-C38	92.9(109)	C42-C45-C43	38.7(63)
C35-C40-C39	120.1(146)	C42-C45-C44	72.0(86)
C35-C40-C41	137.8(124)	C42-C45-C46	42.9(99)
C38-C40-C39	27.6(89)	C43-C45-C44	33.5(71)
C38-C40-C41	128.0(103)	C43-C45-C46	81.5(109)
C39-C40-C41	100.4(120)	C44-C45-C46	114.9(133)
N3-C41-C40	32.1(81)	Fe3-C46-C42	68.4(96)
N3-C41-C42	120.1(164)	Fe3-C46-C44	56.5(55)
C40-C41-C42	152.0(145)	Fe3-C46-C45	67.1(100)
Fe3-C42-N3	112.4(79)	C42-C46-C44	66.3(96)
Fe3-C42-C41	111.4(132)	C42-C46-C45	99.1(143)
Fe3-C42-C43	71.1(90)	C44-C46-C45	32.8(80)
Fe3-C42-C44	58.5(53)	Fe3-C47-C48	68.2(102)

Fe3-C47-C49	54.1(79)	Fe3-C49-C50	63.9(109)
Fe3-C47-C50	55.1(57)	C47-C49-C48	36.7(128)
Fe3-C47-C51	64.1(107)	C47-C49-C50	64.0(109)
C48-C47-C49	32.7(115)	C48-C49-C50	100.7(198)
C48-C47-C50	76.8(114)	Fe3-C50-C47	59.7(58)
C48-C47-C51	107.2(155)	Fe3-C50-C49	65.8(110)
C49-C47-C50	44.1(84)	Fe3-C50-C51	70.3(132)
C49-C47-C51	74.6(128)	C47-C50-C49	71.9(115)
C50-C47-C51	30.8(105)	C47-C50-C51	36.9(124)
Fe3-C48-C47	69.9(105)	C49-C50-C51	108.2(175)
Fe3-C48-C49	68.9(153)	Fe3-C51-C47	74.8(114)
Fe3-C48-C51	52.0(78)	Fe3-C51-C48	56.7(80)
C47-C48-C49	110.6(201)	Fe3-C51-C50	73.7(132)
C47-C48-C51	35.6(94)	C47-C51-C48	37.3(99)
C49-C48-C51	75.1(163)	C47-C51-C50	112.3(191)
Fe3-C49-C47	57.0(81)	C48-C51-C50	75.6(142)
Fe3-C49-C48	72.8(156)		

Table 4B. Selected Bond Lengths(Å) and Angles(°) for *trans*-[Pt(fabt)$_2$](**2**).

Bond Lengths

Pt1-S1	2.314(16)	N2-C23	1.38(8)	C16-C17	1.32(19)
Pt1-S2	2.326(16)	N2-C24	1.36(8)	C18-C19	1.42(9)
Pt1-N1	2.00(5)	C1-C2	1.36(10)	C18-C23	1.44(8)
Pt1-N2	2.02(6)	C1-C6	1.39(8)	C19-C20	1.44(10)
Fe1-C8	1.96(5)	C2-C3	1.48(12)	C20-C21	1.41(10)
Fe1-C11	2.00(7)	C3-C4	1.40(12)	C21-C22	1.35(9)
Fe1-C15	2.01(9)	C4-C5	1.44(9)	C22-C23	1.42(8)
Fe1-C16	1.92(11)	C5-C6	1.44(9)	C24-C25	1.43(8)
Fe1-C17	1.99(13)	C7-C8	1.42(8)	C25-C26	1.42(10)
Fe2-C25	1.98(6)	C8-C9	1.39(8)	C25-C29	1.41(10)
Fe2-C26	1.99(9)	C8-C12	1.42(8)	C26-C27	1.44(11)
Fe2-C29	1.96(8)	C9-C10	1.47(9)	C27-C28	1.36(11)
Fe2-C34	2.01(10)	C10-C11	1.43(10)	C28-C29	1.46(11)
Cl1-C35	1.82(10)	C11-C12	1.38(9)	C30-C31	1.43(16)
S1-C1	1.73(6)	C13-C14	1.32(17)	C30-C34	1.32(20)
S2-C18	1.70(6)	C13-C17	1.30(19)	C31-C32	1.50(20)
N1-C6	1.42(7)	C14-C15	1.44(17)	C32-C33	1.32(17)
N1-C7	1.35(8)	C15-C16	1.43(16)	C33-C34	1.48(19)

Bond Angles

S1-Pt1-S2	167.5(6)	C11-Fe1-C15	157.8(39)
S1-Pt1-N1	81.5(13)	C11-Fe1-C16	157.6(38)
S1-Pt1-N2	97.3(15)	C11-Fe1-C17	122.7(45)
S2-Pt1-N1	97.8(13)	C15-Fe1-C16	42.5(48)
S2-Pt1-N2	82.4(15)	C15-Fe1-C17	68.2(53)
N1-Pt1-N2	175.6(18)	C16-Fe1-C17	39.5(53)
C8-Fe1-C11	68.6(22)	C25-Fe2-C26	41.8(28)
C8-Fe1-C15	123.7(37)	C25-Fe2-C29	41.9(27)
C8-Fe1-C16	108.2(34)	C25-Fe2-C34	157.1(47)
C8-Fe1-C17	124.2(46)	C26-Fe2-C29	69.1(32)

C26-Fe2-C34	120.4(41)	Fe1-C16-C15	72.1(58)
C29-Fe2-C34	159.1(50)	Fe1-C16-C17	73.2(74)
Pt1-S1-C1	93.9(18)	C15-C16-C17	109.4(103)
Pt1-S2-C18	95.9(20)	Fe1-C17-C13	74.2(78)
Pt1-N1-C6	115.1(34)	Fe1-C17-C16	67.3(72)
Pt1-N1-C7	127.7(39)	C13-C17-C16	108.3(113)
C6-N1-C7	116.5(47)	S2-C18-C19	121.6(47)
Pt1-N2-C23	115.4(37)	S2-C18-C23	118.9(42)
Pt1-N2-C24	126.9(41)	C19-C18-C23	119.5(54)
C23-N2-C24	117.5(51)	C18-C19-C20	119.2(66)
S1-C1-C2	121.1(49)	C19-C20-C21	118.9(59)
S1-C1-C6	120.2(39)	C20-C21-C22	122.0(57)
C2-C1-C6	118.4(54)	C21-C22-C23	121.4(54)
C1-C2-C3	122.2(67)	N2-C23-C18	115.6(50)
C2-C3-C4	115.8(63)	N2-C23-C22	125.7(49)
C3-C4-C5	124.1(67)	C18-C23-C22	118.7(50)
C4-C5-C6	114.3(62)	N2-C24-C25	127.5(53)
N1-C6-C1	113.0(46)	Fe2-C25-C24	122.4(41)
N1-C6-C5	122.6(49)	Fe2-C25-C26	69.4(39)
C1-C6-C5	124.3(51)	Fe2-C25-C29	68.3(40)
N1-C7-C8	127.2(55)	C24-C25-C26	131.6(62)
Fe1-C8-C7	118.6(39)	C24-C25-C29	123.2(56)
Fe1-C8-C9	72.8(32)	C26-C25-C29	105.0(61)
Fe1-C8-C12	72.1(29)	Fe2-C26-C25	68.8(43)
C7-C8-C9	132.4(51)	Fe2-C26-C27	74.0(44)
C7-C8-C12	117.9(48)	C25-C26-C27	111.5(67)
C9-C8-C12	109.6(46)	C26-C27-C28	105.7(61)
C8-C9-C10	108.8(49)	C27-C28-C29	109.7(62)
C9-C10-C11	102.8(50)	Fe2-C29-C25	69.9(36)
Fe1-C11-C10	74.1(36)	Fe2-C29-C28	70.8(41)
Fe1-C11-C12	71.5(34)	C25-C29-C28	108.0(63)
C10-C11-C12	112.6(52)	C31-C30-C34	117.4(126)
C8-C12-C11	105.8(50)	C30-C31-C32	99.3(96)
C14-C13-C17	113.1(111)	C31-C32-C33	109.1(110)
C13-C14-C15	106.5(102)	C32-C33-C34	111.6(117)
Fe1-C15-C14	71.2(62)	Fe2-C34-C30	72.7(72)
Fe1-C15-C16	65.4(54)	Fe2-C34-C33	71.0(65)
C14-C15-C16	102.5(92)	C30-C34-C33	101.3(99)

Table 4C. Selected Bond Lengths(Å) and Angles(°) for *cis*-[Pt(fabt)$_2$](**3**).

Bond Lengths

Pt1-S1	2.256(18)	S1-C1	1.74(6)	C4-C5	1.37(8)
Pt1-S2	2.259(13)	S2-C18	1.76(7)	C5-C6	1.46(8)
Pt1-N1	2.05(4)	N1-C6	1.42(8)	C7-C8	1.52(9)
Pt1-N2	2.02(5)	N1-C7	1.28(6)	C8-C9	1.44(7)
Fe1-C29	1.99(6)	N2-C23	1.58(6)	C8-C12	1.46(8)
Fe2-C8	1.94(5)	N2-C24	1.28(6)	C9-C10	1.46(9)
Fe2-C9	2.02(5)	C1-C2	1.45(8)	C10-C11	1.35(9)
Fe2-C11	2.01(6)	C1-C6	1.38(8)	C11-C12	1.47(9)
Fe2-C13	1.98(11)	C2-C3	1.47(9)	C13-C14	1.34(12)
Fe2-C15	1.99(11)	C3-C4	1.41(8)	C13-C17	1.42(13)

C14-C15	1.56(19)	C21-C22	1.40(9)	C28-C29	1.35(9)
C15-C16	1.27(14)	C22-C23	1.25(7)	C30-C31	1.34(14)
C16-C17	1.45(12)	C24-C25	1.48(7)	C30-C34	1.35(11)
C18-C19	1.49(10)	C25-C26	1.37(7)	C31-C32	1.52(10)
C18-C23	1.41(7)	C25-C29	1.42(8)	C32-C33	1.57(11)
C19-C20	1.39(12)	C26-C27	1.48(8)	C33-C34	1.32(9)
C20-C21	1.31(11)	C27-C28	1.43(10)		

Bond Angles

S1-Pt1-S2	88.8(5)	Fe2-C9-C10	71.0(27)
S1-Pt1-N1	84.1(10)	C8-C9-C10	107.0(43)
S1-Pt1-N2	171.5(11)	C9-C10-C11	109.5(53)
S2-Pt1-N1	171.8(10)	Fe2-C11-C10	73.4(38)
S2-Pt1-N2	84.1(11)	Fe2-C11-C12	69.3(31)
N1-Pt1-N2	103.3(14)	C10-C11-C12	109.7(52)
C8-Fe2-C9	42.5(21)	C8-C12-C11	105.7(44)
C8-Fe2-C11	72.4(23)	Fe2-C13-C14	74.4(64)
C8-Fe2-C13	107.4(28)	Fe2-C13-C17	72.1(57)
C8-Fe2-C15	157.0(36)	C14-C13-C17	105.8(87)
C9-Fe2-C11	69.5(25)	C13-C14-C15	106.6(81)
C9-Fe2-C13	126.1(29)	Fe2-C15-C14	70.2(55)
C9-Fe2-C15	118.7(38)	Fe2-C15-C16	73.7(59)
C11-Fe2-C13	157.8(27)	C14-C15-C16	108.1(98)
C11-Fe2-C15	117.4(45)	C15-C16-C17	108.1(91)
C13-Fe2-C15	71.6(47)	C13-C17-C16	109.6(73)
Pt1-S1-C1	97.8(18)	S2-C18-C19	122.5(47)
Pt1-S2-C18	96.5(18)	S2-C18-C23	124.6(41)
Pt1-N1-C6	112.9(26)	C19-C18-C23	112.9(58)
Pt1-N1-C7	132.9(35)	C18-C19-C20	118.4(60)
C6-N1-C7	113.9(41)	C19-C20-C21	124.2(71)
Pt1-N2-C23	115.6(23)	C20-C21-C22	115.0(72)
Pt1-N2-C24	134.1(34)	C21-C22-C23	125.7(50)
C23-N2-C24	110.3(40)	N2-C23-C18	107.0(41)
S1-C1-C2	113.9(42)	N2-C23-C22	129.8(39)
S1-C1-C6	118.4(42)	C18-C23-C22	122.9(45)
C2-C1-C6	127.6(51)	N2-C24-C25	123.5(46)
C1-C2-C3	109.3(50)	C24-C25-C26	131.0(45)
C2-C3-C4	125.2(52)	C24-C25-C29	118.0(45)
C3-C4-C5	119.7(47)	C26-C25-C29	110.2(41)
C4-C5-C6	119.3(48)	C25-C26-C27	105.3(46)
N1-C6-C1	118.1(43)	C26-C27-C28	106.9(50)
N1-C6-C5	123.7(46)	C27-C28-C29	108.5(54)
C1-C6-C5	118.0(57)	Fe1-C29-C25	71.5(28)
N1-C7-C8	125.2(43)	Fe1-C29-C28	72.5(35)
Fe2-C8-C7	125.6(32)	C25-C29-C28	108.8(49)
Fe2-C8-C9	71.6(26)	C31-C30-C34	114.8(72)
Fe2-C8-C12	71.4(28)	C30-C31-C32	110.8(73)
C7-C8-C9	127.8(41)	C31-C32-C33	93.4(57)
C7-C8-C12	124.6(39)	C32-C33-C34	115.7(58)
C9-C8-C12	107.4(45)	C30-C34-C33	105.2(67)
Fe2-C9-C8	65.9(26)		

Table 3A. Isotropic Temperature Factors (Å^2) for the hydrogen atoms of [Pt(ddbt)](**1**) with esd's in parentheses.

ATOM	*X*	*Y*	*Z*	*U*
H2	-0.68010	0.02852	-0.94273	0.04(9)
H3	-0.83587	0.01167	-1.17967	0.075
H4	-0.98851	-0.06475	-1.18965	0.070
H5	-0.99065	-0.10920	-0.96113	0.1(1)
H7	-0.92833	-0.17258	-0.76210	0.040
H9	-0.96648	-0.07157	-0.49604	0.060
H10	-1.14710	-0.02957	-0.43981	0.10(7)
H11	-1.34319	-0.07545	-0.58051	0.070
H12	-1.33536	-0.14522	-0.75257	0.1(2)
H13	-1.14026	-0.17946	-0.78026	0.1(1)
H15	-0.53626	-0.11547	0.06454	0.1(1)
H16	-0.60477	-0.18773	0.18645	0.080
H17	-0.72819	-0.25271	0.03617	0.097
H18	-0.82135	-0.23472	-0.23719	0.02(2)
H20	-0.90860	-0.20170	-0.47296	0.07(4)
H22	-0.94639	-0.27467	-0.65133	0.055
H23	-0.85130	-0.35035	-0.76561	0.09(8)
H24	-0.63471	-0.35861	-0.73036	0.075
H25	-0.50974	-0.28674	-0.59465	0.070
H26	-0.59840	-0.21354	-0.49671	0.1(2)

Table 3B. Isotropic Temperature Factors (Å^2) for the hydrogen atoms of [Pt$_4$(C^{o}-1-nabt)$_4$](**4**) with esd's in parentheses.

ATOM	*X*	*Y*	*Z*	*B*
H(3)	-0.1672(4)	0.4728(4)	-0.0405(2)	2.9973(2)
H(4)	-0.3099(4)	0.5120(5)	0.0071(3)	2.9973(2)
H(5)	-0.2858(4)	0.5643(5)	0.1000(3)	2.9973(2)
H(6)	-0.2004(4)	0.4757(4)	0.1580(3)	2.9973(2)
H(7)	-0.0601(4)	0.4227(5)	-0.0735(3)	2.9973(2)
H(9)	0.0799(4)	0.3242(4)	0.0321(3)	2.9973(3)
H(10)	0.2222(4)	0.2385(5)	0.0157(3)	2.9973(2)
H(11)	0.2605(4)	0.1902(5)	-0.0850(3)	2.9973(2)
H(13)	0.2470(4)	0.2094(5)	-0.1769(3)	2.9973(3)
H(14)	0.1551(4)	0.2649(5)	-0.2572(3)	2.9973(3)
H(15)	0.0359(4)	0.3749(5)	-0.2414(3)	2.9973(3)
H(16)	-0.0285(4)	0.3944(4)	-0.1483(3)	2.9973(2)

Table 4A. Anisotropic Temperature Factors for Non-Hydrogen Atoms of [Pt(ddbt)](**1**) with esd's in parentheses.

ATOM	*U*(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)
Pt1	0.0342(2)	0.0515(2)	0.0327(2)	-0.0040(3)	0.0033(1)	0.0066(3)

S1	0.046(2)	0.062(2)	0.046(2)	-0.008(1)	0.004(1)	0.001(1)
S2	0.048(1)	0.105(4)	0.032(1)	-0.014(2)	-0.004(1)	0.004(2)
N1	0.023(4)	0.066(6)	0.019(4)	-0.002(4)	0.001(3)	0.013(4)
N2	0.021(4)	0.060(7)	0.054(6)	-0.006(5)	0.006(4)	0.003(6)
C1	0.075(7)	0.057(8)	0.026(5)	0.001(6)	0.000(5)	0.020(5)
C2	0.058(8)	0.079(15)	0.045(6)	-0.020(9)	0.041(6)	-0.007(8)
C3	0.033(8)	0.083(18)	0.082(12)	-0.004(10)	0.017(8)	0.020(12)
C4	0.041(9)	0.091(10)	0.099(10)	0.013(7)	-0.003(7)	-0.028(8)
C5	0.074(7)	0.050(7)	0.043(4)	0.023(9)	-0.002(5)	0.012(7)
C6	0.026(4)	0.081(8)	0.038(6)	0.004(4)	0.003(4)	0.008(5)
C7	0.045(5)	0.028(6)	0.030(6)	-0.005(4)	0.005(5)	0.019(5)
C8	0.026(4)	0.045(7)	0.057(5)	0.013(4)	-0.003(4)	0.001(5)
C9	0.050(8)	0.080(8)	0.045(6)	-0.005(10)	0.008(6)	-0.020(9)
C10	0.043(9)	0.106(14)	0.039(8)	0.006(9)	0.005(7)	-0.017(8)
C11	0.050(6)	0.141(14)	0.105(10)	0.050(11)	0.036(6)	0.043(14)
C12	0.045(8)	0.070(19)	0.118(15)	0.005(9)	0.029(8)	-0.046(13)
C13	0.064(9)	0.073(8)	0.061(10)	0.008(7)	-0.018(7)	-0.016(7)
C14	0.069(7)	0.085(8)	0.044(8)	-0.036(6)	0.045(6)	-0.037(6)
C15	0.046(6)	0.069(15)	0.032(7)	-0.002(8)	-0.011(5)	0.019(8)
C16	0.07(1)	0.11(2)	0.08(1)	0.01(1)	0.05(1)	0.02(1)
C17	0.05(1)	0.09(1)	0.07(1)	0.02(1)	-0.02(1)	0.04(1)
C18	0.068(7)	0.122(14)	0.004(5)	-0.033(8)	0.006(5)	0.007(6)
C19	0.039(6)	0.068(7)	0.030(5)	0.043(5)	-0.009(4)	-0.003(5)
C20	0.020(5)	0.026(5)	0.067(6)	0.003(3)	0.021(4)	0.013(5)
C21	0.035(5)	0.031(7)	0.042(6)	-0.007(5)	0.021(4)	0.017(5)
C22	0.068(7)	0.056(8)	0.058(7)	0.008(6)	0.019(5)	0.003(6)
C23	0.13(2)	0.04(1)	0.07(1)	0.01(1)	0.03(1)	-0.01(1)
C24	0.10(1)	0.06(1)	0.07(1)	0.03(1)	0.03(1)	0.01(1)
C25	0.067(8)	0.083(12)	0.067(8)	0.013(8)	0.031(7)	0.024(8)
C26	0.037(6)	0.069(9)	0.072(8)	0.042(6)	0.018(6)	0.016(7)

Table 4B. Anisotropic Temperature Factors for Non-Hydrogen Atoms of [Pt_4(C^o-phbt)$_4$](2) with esd's in parentheses.

ATOM	*U*(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)
Pt1	0.049(1)	0.044(1)	0.037(1)	0.002(1)	0.013(1)	0.002(1)
Pt2	0.040(1)	0.047(1)	0.037(1)	0.003(1)	0.002(1)	0.002(1)
Pt3	0.044(1)	0.038(1)	0.033(1)	0.001(1)	0.003(1)	0.000(1)
Pt4	0.044(1)	0.040(1)	0.040(1)	0.003(1)	0.008(1)	0.010(1)
Cl1	0.16(3)	0.10(2)	0.11(3)	0.00(2)	0.01(2)	0.02(2)
Cl2	0.18(4)	0.08(2)	0.12(3)	-0.01(2)	0.01(3)	0.01(2)
Cl3	0.18(4)	0.11(3)	0.11(3)	-0.05(3)	0.00(3)	0.02(2)
Cl4	0.26(6)	0.10(3)	0.08(2)	-0.02(3)	0.04(3)	0.00(2)
S1	0.050(9)	0.051(10)	0.045(10)	-0.005(7)	0.014(8)	-0.006(8)
S2	0.056(9)	0.038(8)	0.046(10)	0.000(7)	0.009(8)	0.011(8)
S3	0.055(8)	0.041(9)	0.036(9)	-0.005(7)	0.008(7)	-0.002(7)
S4	0.046(8)	0.043(8)	0.042(9)	0.004(6)	0.008(7)	0.002(7)
N1	0.08(4)	0.04(3)	0.05(4)	0.00(3)	0.01(3)	0.00(3)
N2	0.04(3)	0.06(4)	0.05(4)	-0.03(3)	0.00(3)	-0.04(3)
N3	0.07(4)	0.06(4)	0.03(3)	-0.02(3)	-0.01(3)	0.02(3)
N4	0.03(2)	0.02(2)	0.10(5)	0.00(2)	-0.02(3)	0.02(3)
C1	0.05(4)	0.06(5)	0.09(6)	-0.02(4)	0.05(4)	-0.04(5)

C2	0.03(3)	0.08(5)	0.11(7)	-0.03(3)	0.00(4)	-0.06(5)
C3	0.09(5)	0.14(10)	0.04(6)	-0.03(6)	0.00(4)	0.03(6)
C4	0.11(6)	0.05(5)	0.05(5)	0.00(5)	0.00(5)	0.02(4)
C5	0.07(5)	0.09(7)	0.06(6)	0.00(5)	0.03(5)	0.01(5)
C6	0.07(4)	0.04(4)	0.07(5)	-0.04(3)	0.01(4)	0.00(4)
C7	0.09(6)	0.06(5)	0.05(5)	0.02(4)	0.04(4)	0.02(4)
C8	0.1(1)	0.0(1)	0.1(1)	0.0(1)	0.0(1)	0.0(0)
C9	0.08(5)	0.08(6)	0.07(6)	-0.01(4)	0.06(5)	0.00(5)
C10	0.06(4)	0.15(9)	0.03(4)	-0.03(5)	0.02(3)	0.03(5)
C11	0.10(7)	0.09(7)	0.05(6)	0.02(5)	0.01(5)	0.04(5)
C12	0.05(4)	0.07(5)	0.11(7)	0.01(4)	0.03(4)	0.06(5)
C13	0.09(8)	0.10(8)	0.15(12)	0.08(7)	0.04(8)	0.02(8)
C14	0.02(2)	0.04(3)	0.10(6)	0.01(3)	0.04(3)	-0.01(4)
C15	0.07(5)	0.10(7)	0.05(4)	0.00(5)	0.01(4)	0.03(5)
C16	0.05(4)	0.12(8)	0.06(6)	-0.03(4)	-0.02(4)	0.01(5)
C17	0.10(5)	0.04(4)	0.04(4)	-0.01(4)	-0.01(4)	-0.02(3)
C18	0.07(4)	0.06(5)	0.04(5)	0.00(4)	0.01(4)	0.02(4)
C19	0.05(3)	0.09(5)	0.02(3)	0.00(3)	0.02(3)	0.01(3)
C20	0.08(5)	0.08(5)	0.05(5)	0.04(4)	-0.01(4)	-0.01(4)
C21	0.05(4)	0.07(5)	0.07(6)	0.00(4)	-0.04(4)	0.01(5)
C22	0.04(3)	0.09(5)	0.02(3)	-0.01(3)	0.00(2)	-0.01(3)
C23	0.06(4)	0.06(5)	0.06(5)	0.03(4)	0.01(3)	0.01(4)
C24	0.07(4)	0.06(4)	0.04(4)	-0.01(4)	0.02(3)	0.04(4)
C25	0.07(5)	0.06(5)	0.07(6)	-0.01(4)	0.00(4)	0.04(4)
C26	0.07(4)	0.02(3)	0.09(5)	-0.01(3)	-0.02(3)	-0.02(3)
C27	0.05(3)	0.02(3)	0.06(4)	-0.01(2)	0.01(3)	-0.01(3)
C28	0.10(7)	0.09(7)	0.06(7)	0.00(5)	0.03(6)	0.03(6)
C29	0.09(5)	0.09(6)	0.06(5)	-0.03(5)	-0.02(4)	0.06(5)
C30	0.12(8)	0.06(6)	0.09(8)	-0.03(5)	0.01(6)	0.03(6)
C31	0.09(6)	0.07(5)	0.05(5)	-0.01(5)	0.00(4)	0.02(4)
C32	0.02(2)	0.07(4)	0.03(3)	0.00(3)	-0.01(2)	-0.01(3)
C33	0.05(3)	0.05(4)	0.03(3)	-0.01(3)	0.01(3)	-0.03(3)
C34	0.06(4)	0.04(4)	0.05(4)	0.01(3)	0.00(3)	0.00(3)
C35	0.08(4)	0.03(3)	0.04(4)	-0.02(3)	-0.01(3)	0.01(3)
C36	0.07(5)	0.06(5)	0.03(4)	0.02(4)	0.00(3)	0.00(3)
C37	0.06(3)	0.02(3)	0.06(4)	-0.01(2)	0.01(3)	-0.02(3)
C38	0.08(6)	0.10(8)	0.06(6)	-0.04(6)	0.01(5)	-0.03(6)
C39	0.10(5)	0.04(4)	0.05(5)	-0.01(4)	0.04(4)	0.00(4)
C40	0.05(3)	0.02(3)	0.08(5)	-0.01(3)	0.01(3)	0.02(3)
C41	0.06(4)	0.02(3)	0.07(5)	0.01(3)	-0.01(4)	0.03(3)
C42	0.08(6)	0.06(6)	0.10(8)	-0.02(4)	0.02(6)	0.03(5)
C43	0.06(4)	0.05(4)	0.10(7)	0.01(3)	-0.03(5)	0.04(5)
C44	0.06(4)	0.08(5)	0.03(4)	-0.01(4)	0.01(3)	0.01(4)
C45	0.03(3)	0.08(5)	0.05(4)	0.01(3)	-0.01(3)	0.03(4)
C46	0.07(4)	0.03(3)	0.06(5)	0.00(3)	0.04(3)	0.02(3)
C47	0.06(3)	0.05(4)	0.02(3)	-0.02(3)	0.01(2)	0.00(3)
C48	0.06(4)	0.04(4)	0.02(3)	-0.01(3)	0.00(3)	-0.01(3)
C49	0.10(5)	0.03(3)	0.06(5	)0.00(3)	0.05(5)	0.00(3)
C50	0.06(5)	0.07(5)	0.09(7)	0.02(4)	-0.02(4)	-0.01(5)
C51	0.07(4)	0.03(3)	0.04(4)	-0.02(3)	0.03(3)	-0.01(3)
C52	0.03(3)	0.05(5)	0.13(9)	0.01(3)	0.05(5)	0.03(5)
C53	0.10(9)	0.12(11)	0.13(13)	-0.02(8)	-0.03(8)	-0.05(9)
C54	0.10(8)	0.16(13)	0.12(14)	0.01(8)	0.03(9)	0.07(11)
C55	0.3(2)	0.0(1)	0.2(2)	0.0(1)	-0.1(1)	0.0(1)

C56	0.1(1)	0.1(1)	0.1(1)	0.0(1)	0.0(1)	0.0(1)

Table 4C. Anisotropic Temperature Factors for Non-Hydrogen Atoms of [Pd$_4$(C^{o}-phbt)$_4$](**3**) with esd's in parentheses.

ATOM	*U*(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)
Pd1	0.060(2)	0.069(3)	0.061(2)	-0.001(2)	-0.002(2)	-0.001(2)
Pd2	0.067(2)	0.081(3)	0.072(3)	-0.001(2)	0.018(2)	-0.004(2)
Pd3	0.055(2)	0.068(3)	0.074(3)	-0.004(2)	0.004(2)	-0.015(2)
Pd4	0.053(2)	0.085(3)	0.066(2)	-0.004(2)	-0.001(2)	0.003(2)
Cl1	0.29(3)	0.23(3)	0.16(2)	0.07(3)	0.03(2)	0.05(2)
Cl2	0.29(4)	0.31(5)	0.32(5)	0.02(4)	0.07(4)	-0.01(4)
Cl3	0.47(9)	0.24(6)	1.13(23)	-0.03(5)	-0.39(13)	0.09(9)
Cl4	1.0(2)	0.3(1)	0.3(1)	-0.2(1)	-0.3(1)	0.0(0)
S1	0.070(7)	0.073(10)	0.091(9)	-0.008(6)	0.010(6)	0.007(7)
S2	0.079(8)	0.109(11)	0.066(7)	0.002(8)	0.016(6)	0.002(9)
S3	0.069(7)	0.066(7)	0.080(8)	0.005(6)	0.010(6)	-0.019(8)
S4	0.053(6)	0.068(9)	0.099(10)	0.002(6)	-0.010(6)	-0.005(7)
N1	0.10(3)	0.04(2)	0.06(2)	0.02(2)	0.01(2)	-0.01(2)
N2	0.06(2)	0.09(3)	0.10(3)	-0.01(2)	0.03(2)	-0.02(3)
N3	0.06(2)	0.04(2)	0.11(3)	0.01(2)	0.02(2)	-0.02(2)
N4	0.05(2)	0.11(4)	0.06(2)	0.02(2)	-0.02(2)	-0.01(2)
C1	0.05(2)	0.10(5)	0.11(4)	-0.01(3)	0.02(3)	-0.03(3)
C2	0.10(4)	0.13(6)	0.14(6)	0.04(4)	0.09(4)	-0.02(4)
C3	0.14(7)	0.36(15)	0.13(6)	0.15(8)	0.12(6)	0.11(8)
C4	0.10(4)	0.31(12)	0.05(4)	-0.01(6)	0.03(3)	-0.01(5)
C5	0.14(5)	0.09(5)	0.10(5)	0.06(4)	-0.04(4)	-0.01(4)
C6	0.05(2)	0.11(5)	0.08(3)	0.01(3)	0.01(2)	-0.01(3)
C7	0.10(4)	0.05(3)	0.07(3)	0.00(3)	-0.02(3)	-0.03(3)
C8	0.07(3)	0.03(3)	0.09(4)	0.00(2)	-0.01(3)	0.00(3)
C9	0.04(2)	0.08(4)	0.07(3)	-0.01(2)	0.00(2)	0.02(3)
C10	0.05(2)	0.08(4)	0.08(3)	-0.02(2)	0.02(2)	0.02(3)
C11	0.08(3)	0.08(4)	0.10(4)	-0.01(3)	-0.01(3)	-0.01(4)
C12	0.05(3)	0.18(7)	0.11(5)	-0.05(4)	-0.03(3)	0.07(5)
C13	0.07(3)	0.09(4)	0.11(5)	-0.03(3)	0.00(3)	0.04(4)
C14	0.10(4)	0.22(9)	0.06(3)	0.01(5)	0.02(3)	0.02(4)
C15	0.12(5)	0.21(9)	0.07(4)	0.05(5)	0.02(3)	0.04(5)
C16	0.16(6)	0.11(6)	0.13(6)	0.01(5)	0.05(5)	0.07(5)
C17	0.20(8)	0.14(7)	0.07(4)	0.07(6)	0.05(4)	0.05(4)
C18	0.15(5)	0.13(6)	0.06(3)	0.08(4)	0.03(3)	0.02(3)
C19	0.10(4)	0.13(6)	0.06(3)	0.04(4)	0.04(3)	0.01(3)
C20	0.13(5)	0.08(4)	0.06(4)	0.01(4)	0.06(4)	-0.01(3)
C21	0.12(5)	0.06(4)	0.11(5)	0.02(3)	0.05(4)	0.01(4)
C22	0.07(3)	0.10(4)	0.06(3)	-0.01(3)	0.04(2)	-0.04(3)
C23	0.07(3)	0.12(5)	0.09(4)	-0.02(3)	0.02(3)	-0.05(3)
C24	0.10(4)	0.12(6)	0.15(7)	-0.03(4)	0.04(4)	-0.01(5)
C25	0.10(5)	0.19(10)	0.14(7)	-0.06(6)	0.06(5)	-0.06(6)
C26	0.14(5)	0.09(5)	0.16(7)	-0.05(5)	0.08(5)	-0.03(4)
C27	0.08(3)	0.02(3)	0.11(4)	0.01(2)	-0.02(3)	-0.03(2)
C28	0.06(3)	0.16(6)	0.11(4)	0.04(4)	-0.05(3)	-0.05(4)
C29	0.11(4)	0.07(5)	0.11(4)	0.01(3)	-0.05(3)	-0.02(3)
C30	0.11(4)	0.02(3)	0.11(4)	0.00(3)	-0.02(3)	0.00(3)

C31	0.07(3)	0.07(3)	0.12(4)	-0.01(3)	0.03(3)	-0.05(4)
C32	0.07(3)	0.05(4)	0.08(3)	0.01(2)	0.00(2)	-0.03(3)
C33	0.06(3)	0.07(4)	0.07(3)	0.02(3)	0.01(2)	-0.04(3)
C34	0.10(4)	0.11(5)	0.08(4)	0.01(4)	0.03(3)	-0.03(4)
C35	0.06(3)	0.10(4)	0.07(3)	0.01(3)	0.02(2)	-0.02(3)
C36	0.13(5)	0.07(4)	0.07(4)	0.05(4)	0.02(3)	-0.01(3)
C37	0.14(5)	0.04(3)	0.07(3)	0.04(3)	0.01(3)	-0.02(3)
C38	0.14(5)	0.05(3)	0.08(4)	-0.03(3)	0.03(4)	-0.05(3)
C39	0.12(5)	0.12(6)	0.06(4)	-0.01(4)	0.03(3)	0.01(4)
C40	0.02(2)	0.10(4)	0.12(4)	0.01(2)	0.00(2)	0.00(4)
C41	0.07(3)	0.11(5)	0.09(4)	0.02(3)	0.01(3)	-0.04(4)
C42	0.07(3)	0.16(6)	0.08(4)	0.02(3)	0.03(3)	-0.05(4)
C43	0.10(5)	0.15(7)	0.15(6)	0.03(5)	0.01(4)	-0.02(6)
C44	0.12(4)	0.09(5)	0.07(3)	0.02(4)	0.04(3)	0.00(3)
C45	0.09(3)	0.05(3)	0.07(3)	0.02(3)	-0.03(3)	0.01(2)
C46	0.06(3)	0.09(4)	0.10(4)	-0.02(3)	-0.04(3)	-0.02(3)
C47	0.05(2)	0.08(4)	0.08(3)	-0.03(2)	-0.01(2)	0.00(3)
C48	0.04(2)	0.09(4)	0.08(3)	0.03(2)	-0.01(2)	0.02(3)
C49	0.09(4)	0.06(4)	0.12(5)	-0.01(3)	-0.01(3)	-0.04(3)
C50	0.09(4)	0.16(8)	0.12(5)	0.01(4)	0.02(4)	-0.01(5)
C51	0.14(6)	0.15(7)	0.08(5)	0.00(5)	0.00(4)	-0.05(5)
C52	0.07(3)	0.13(5)	0.10(4)	-0.04(3)	-0.03(3)	0.01(4)
C53	0.22(9)	0.20(9)	0.14(6)	0.07(7)	0.10(6)	0.09(7)
C54	0.4(2)	0.2(2)	0.1(1)	0.0(1)	0.0(1)	-0.1(1)
C55	0.18(8)	0.43(23)	0.08(5)	-0.04(10)	0.00(5)	-0.11(8)

Table 4D. Anisotropic Temperature Factors for Non-Hydrogen Atoms of [Pt_4(C^o-1-nabt)$_4$](**4**) with esd's in parentheses.

ATOM	*B*(11)	*B*(22)	*B*(33)	*B*(12)	*B*(13)	*B*(23)
Pt	0.0030(2)	0.0029(2)	0.0015(3)	-0.0004(2)	0.0002(3)	0.0001(3)
S	0.0043(2)	0.0024(2)	0.0014(3)	0.0007(3)	0.0002(4)	0.0001(4)
N	0.0010(2)	0.0033(2)	0.0019(3)	-0.0021(3)	-0.0019(4)	0.0030(4)
C(1)	0.0037(2)	0.0015(2)	0.0014(4)	0.0011(3)	-0.0001(4)	0.0001(4)
C(2)	0.0045(2)	0.0033(2)	0.0006(3)	-0.0006(3)	0.0026(4)	-0.0019(4)
C(3)	0.0036(2)	0.0082(2)	0.0013(4)	-0.0015(3)	-0.0017(4)	0.0030(5)
C(4)	0.0005(2)	0.0033(2)	0.0027(4)	-0.0017(3)	-0.0010(4)	0.0011(5)
C(5)	0.0124(2)	0.0042(2)	0.0024(4)	0.0020(3)	0.0012(4)	0.0007(5)
C(6)	0.0101(2)	0.0052(2)	0.0008(4)	-0.0002(3)	-0.0027(4)	0.0003(5)
C(7)	0.0032(2)	0.0032(2)	0.0015(4)	-0.0051(3)	-0.0011(4)	-0.0010(5)
C(8)	0.0047(2)	0.0036(3)	0.0023(4)	-0.0016(4)	-0.0004(5)	-0.0006(5)
C(9)	0.0069(2)	0.0023(2)	0.0013(4)	0.0030(3)	-0.0025(4)	0.0004(4)
C(10)	0.0034(2)	0.0040(3)	0.0028(5)	0.0041(4)	0.0004(5)	-0.0010(6)
C(11)	0.0114(2)	0.0033(2)	0.0018(4)	-0.0016(3)	0.0009(4)	-0.0008(5)
C(12)	0.0015(2)	0.0085(2)	0.0015(4)	-0.0002(3)	0.0010(4)	-0.0041(4)
C(13)	0.0148(2)	0.0056(3)	0.0026(5)	-0.0068(4)	0.0036(5)	0.0002(6)
C(14)	0.0100(2)	0.0125(3)	0.0010(4)	0.0088(4)	0.0037(5)	0.0045(6)
C(15)	0.0028(2)	0.0077(3)	0.0053(5)	0.0000(4)	0.0030(5)	0.0103(5)
C(16)	0.0040(3)	0.0036(3)	0.0020(6)	-0.0022(4)	-0.0005(6)	0.0032(6)
C(17)	0.0035(3)	0.0080(3)	0.0023(6)	-0.0066(4)	-0.0018(6)	-0.0014(6)

Table 5A. Selected Bond Lengths(Å) and Angles(°) for [Pt(ddbt)](**1**).

Bond Lengths

Pt1-S1	2.240(4)	C3-C4	1.54(4)	C15-C16	1.32(4)
Pt1-S2	2.223(4)	C4-C5	1.30(3)	C16-C17	1.35(4)
Pt1-N1	1.960(10)	C5-C6	1.383(18)	C17-C18	1.42(3)
Pt1-N2	1.950(14)	C7-C8	1.490(17)	C18-C19	1.42(3)
S1-C1	1.696(13)	C7-C20	1.589(17)	C20-C21	1.560(18)
S2-C14	1.752(18)	C8-C9	1.25(3)	C21-C22	1.35(3)
N1-C6	1.370(16)	C8-C13	1.36(3)	C21-C26	1.312(19)
N1-C7	1.478(17)	C9-C10	1.41(3)	C22-C23	1.47(3)
N2-C19	1.388(18)	C10-C11	1.48(3)	C23-C24	1.33(4)
N2-C20	1.444(17)	C11-C12	1.33(4)	C24-C25	1.42(4)
C1-C2	1.42(3)	C12-C13	1.37(3)	C25-C26	1.33(3)
C1-C6	1.446(19)	C14-C15	1.41(3)		
C2-C3	1.42(3)	C14-C19	1.34(3)		

Bond Angles

S1-Pt1-S2	104.2(2)	C7-C8-C13	118.1(13)
S1-Pt1-N1	86.4(4)	C9-C8-C13	111.3(14)
S1-Pt1-N2	168.8(5)	C8-C9-C10	137.4(18)
S2-Pt1-N1	168.3(3)	C9-C10-C11	105.3(19)
S2-Pt1-N2	86.6(4)	C10-C11-C12	121.9(17)
N1-Pt1-N2	83.1(5)	C11-C12-C13	120.1(20)
Pt1-S1-C1	97.7(6)	C8-C13-C12	123.4(19)
Pt1-S2-C14	96.5(6)	S2-C14-C15	122.1(14)
Pt1-N1-C6	120.9(9)	S2-C14-C19	120.6(13)
Pt1-N1-C7	116.1(8)	C15-C14-C19	116.5(17)
C6-N1-C7	122.3(10)	C14-C15-C16	125.0(19)
Pt1-N2-C19	119.2(10)	C15-C16-C17	118.3(21)
Pt1-N2-C20	116.1(10)	C16-C17-C18	120.1(23)
C19-N2-C20	124.6(13)	C17-C18-C19	118.1(17)
S1-C1-C2	119.3(13)	N2-C19-C14	116.6(14)
S1-C1-C6	121.1(10)	N2-C19-C18	122.3(12)
C2-C1-C6	119.5(13)	C14-C19-C18	121.0(13)
C1-C2-C3	118.6(20)	N2-C20-C7	108.9(10)
C2-C3-C4	119.5(21)	N2-C20-C21	113.0(10)
C3-C4-C5	116.4(18)	C7-C20-C21	110.6(10)
C4-C5-C6	125.3(17)	C20-C21-C22	113.6(12)
N1-C6-C1	113.9(11)	C20-C21-C26	124.1(13)
N1-C6-C5	126.6(13)	C22-C21-C26	122.1(15)
C1-C6-C5	119.4(13)	C21-C22-C23	115.8(16)
N1-C7-C8	110.7(11)	C22-C23-C24	122.9(20)
N1-C7-C20	106.5(9)	C23-C24-C25	114.5(20)
C8-C7-C20	111.6(10)	C24-C25-C26	123.1(17)
C7-C8-C9	130.0(13)	C21-C26-C25	121.1(16)

Table 5B. Selected Bond Lengths(Å) and Angles(°) for [Pt$_4$(C^o-phbt)$_4$](**2**).

Bond Lengths

Pt1-S1	2.333(19)	N3-C33	1.36(10)	C27-C28	1.36(15)
Pt1-S3	2.296(18)	N4-C45	1.38(11)	C27-C32	1.29(10)
Pt1-N1	2.04(7)	N4-C46	1.34(9)	C28-C29	1.51(17)
Pt1-C9	2.03(10)	C1-C2	1.43(12)	C29-C30	1.56(16)
Pt2-S1	2.29(2)	C1-C6	1.35(12)	C30-C31	1.32(17)
Pt2-S2	2.329(19)	C2-C3	1.31(17)	C31-C32	1.35(13)
Pt2-N2	2.04(7)	C3-C4	1.42(17)	C33-C34	1.44(11)
Pt2-C22	2.05(9)	C4-C5	1.28(15)	C34-C35	1.45(11)
Pt3-S3	2.355(18)	C5-C6	1.41(14)	C34-C39	1.43(12)
Pt3-S4	2.288(19)	C7-C8	1.42(18)	C35-C36	1.27(12)
Pt3-N3	2.03(7)	C8-C9	1.37(16)	C36-C37	1.35(11)
Pt3-C35	1.98(8)	C8-C13	1.52(19)	C37-C38	1.39(15)
Pt4-S2	2.293(19)	C9-C10	1.44(14)	C38-C39	1.53(15)
Pt4-S4	2.339(19)	C10-C11	1.46(16)	C40-C41	1.36(11)
Pt4-N4	2.02(6)	C11-C12	1.39(16)	C40-C45	1.37(11)
Pt4-C48	2.01(7)	C12-C13	1.35(18)	C41-C42	1.51(14)
Cl1-C53	1.75(17)	C14-C15	1.46(14)	C42-C43	1.41(14)
Cl2-C54	1.76(22)	C14-C19	1.33(11)	C43-C44	1.35(13)
Cl3-C55	1.75(24)	C15-C16	1.49(15)	C44-C45	1.39(11)
Cl4-C56	1.78(19)	C16-C17	1.46(15)	C46-C47	1.51(10)
S1-C1	1.82(10)	C17-C18	1.34(13)	C47-C48	1.42(10)
S2-C14	1.82(9)	C18-C19	1.42(12)	C47-C52	1.44(12)
S3-C27	1.84(7)	C20-C21	1.36(14)	C48-C49	1.33(12)
S4-C40	1.73(8)	C21-C22	1.44(12)	C49-C50	1.48(13)
N1-C6	1.47(11)	C21-C26	1.44(12)	C50-C51	1.35(12)
N1-C7	1.23(12)	C22-C23	1.46(12)	C51-C52	1.33(13)
N2-C19	1.34(11)	C23-C24	1.28(13)	C53-C54	1.53(25)
N2-C20	1.33(12)	C24-C25	1.38(13)	C55-C56	1.44(25)
N3-C32	1.46(9)	C25-C26	1.28(13)		

Bond Angles

S1-Pt1-S3	98.1(7)	S4-Pt4-N4	83.6(19)
S1-Pt1-N1	85.7(20)	S4-Pt4-C48	166.8(20)
S1-Pt1-C9	165.2(31)	N4-Pt4-C48	84.2(27)
S3-Pt1-N1	176.1(20)	Pt1-S1-Pt2	112.6(9)
S3-Pt1-C9	95.8(30)	Pt1-S1-C1	96.4(29)
N1-Pt1-C9	80.3(36)	Pt2-S1-C1	105.9(30)
S1-Pt2-S2	97.8(7)	Pt2-S2-Pt4	110.1(8)
S1-Pt2-N2	177.1(19)	Pt2-S2-C14	94.1(25)
S1-Pt2-C22	95.9(19)	Pt4-S2-C14	105.7(25)
S2-Pt2-N2	84.1(20)	Pt1-S3-Pt3	112.6(8)
S2-Pt2-C22	165.3(19)	Pt1-S3-C27	104.7(24)
N2-Pt2-C22	82.4(27)	Pt3-S3-C27	94.3(23)
S3-Pt3-S4	97.8(7)	Pt3-S4-Pt4	107.9(8)
S3-Pt3-N3	85.7(19)	Pt3-S4-C40	106.9(25)
S3-Pt3-C35	167.1(22)	Pt4-S4-C40	95.4(26)
S4-Pt3-N3	176.5(19)	Pt1-N1-C6	117.3(49)
S4-Pt3-C35	94.0(22)	Pt1-N1-C7	114.8(63)
N3-Pt3-C35	82.6(28)	C6-N1-C7	127.9(73)
S2-Pt4-S4	98.8(7)	Pt2-N2-C19	121.6(53)
S2-Pt4-N4	177.3(22)	Pt2-N2-C20	111.0(57)
S2-Pt4-C48	93.6(21)	C19-N2-C20	127.4(72)

Pt3-N3-C32	118.1(50)	C21-C26-C25	124.0(79)
Pt3-N3-C33	116.3(49)	S3-C27-C28	114.0(62)
C32-N3-C33	125.4(64)	S3-C27-C32	123.4(58)
Pt4-N4-C45	122.2(48)	C28-C27-C32	122.5(78)
Pt4-N4-C46	114.6(51)	C27-C28-C29	120.1(94)
C45-N4-C46	123.0(64)	C28-C29-C30	111.2(89)
S1-C1-C2	118.6(67)	C29-C30-C31	116.1(103)
S1-C1-C6	120.1(65)	C30-C31-C32	126.1(97)
C2-C1-C6	120.7(86)	N3-C32-C27	117.7(67)
C1-C2-C3	114.3(89)	N3-C32-C31	121.2(71)
C2-C3-C4	125.8(97)	C27-C32-C31	121.0(70)
C3-C4-C5	118.4(99)	N3-C33-C34	111.6(65)
C4-C5-C6	119.7(98)	C33-C34-C35	119.1(68)
N1-C6-C1	118.4(74)	C33-C34-C39	115.1(69)
N1-C6-C5	120.9(72)	C35-C34-C39	125.6(74)
C1-C6-C5	120.3(81)	Pt3-C35-C34	110.1(54)
N1-C7-C8	116.8(88)	Pt3-C35-C36	139.7(63)
C7-C8-C9	117.7(104)	C34-C35-C36	109.8(72)
C7-C8-C13	121.8(104)	C35-C36-C37	138.2(82)
C9-C8-C13	119.0(119)	C36-C37-C38	112.0(78)
Pt1-C9-C8	109.6(83)	C37-C38-C39	122.2(92)
Pt1-C9-C10	127.4(79)	C34-C39-C38	111.8(78)
C8-C9-C10	123.0(104)	S4-C40-C41	117.9(53)
C9-C10-C11	114.0(97)	S4-C40-C45	124.5(58)
C10-C11-C12	124.1(95)	C41-C40-C45	117.4(67)
C11-C12-C13	120.6(98)	C40-C41-C42	122.2(70)
C8-C13-C12	118.1(120)	C41-C42-C43	117.1(91)
S2-C14-C15	112.5(58)	C42-C43-C44	115.8(85)
S2-C14-C19	122.4(65)	C43-C44-C45	126.3(86)
C15-C14-C19	124.9(78)	N4-C45-C40	113.4(64)
C14-C15-C16	112.6(92)	N4-C45-C44	125.2(76)
C15-C16-C17	121.5(94)	C40-C45-C44	120.6(77)
C16-C17-C18	117.3(83)	N4-C46-C47	114.1(63)
C17-C18-C19	124.2(85)	C46-C47-C48	116.6(59)
N2-C19-C14	116.7(70)	C46-C47-C52	121.1(63)
N2-C19-C18	124.0(79)	C48-C47-C52	121.4(62)
C14-C19-C18	119.2(78)	Pt4-C48-C47	110.3(47)
N2-C20-C21	121.2(81)	Pt4-C48-C49	132.5(58)
C20-C21-C22	116.0(82)	C47-C48-C49	117.2(66)
C20-C21-C26	129.4(81)	C48-C49-C50	121.8(80)
C22-C21-C26	113.6(80)	C49-C50-C51	116.6(84)
Pt2-C22-C21	108.9(55)	C50-C51-C52	124.8(78)
Pt2-C22-C23	132.0(56)	C47-C52-C51	116.6(70)
C21-C22-C23	119.2(77)	Cl1-C53-C54	112.8(112)
C22-C23-C24	119.1(77)	Cl2-C54-C53	114.6(136)
C23-C24-C25	122.8(81)	Cl3-C55-C56	108.7(132)
C24-C25-C26	120.7(82)	Cl4-C56-C55	116.4(126)

Table 5C. Selected Bond Lengths(Å) and Angles(°) for [Pd$_4$(C^{o}-phbt)$_4$](**3**).

Bond Lengths					
Pd1-S1	2.380(14)	Pd1-S3	2.308(14)	Pd1-N1	2.03(4)

Pd1-C9	2.08(5)	N4-C45	1.43(7)	C25-C26	1.46(12)
Pd2-S1	2.320(14)	N4-C46	1.28(8)	C27-C28	1.43(8)
Pd2-S2	2.370(14)	C1-C2	1.31(9)	C27-C32	1.34(7)
Pd2-N2	2.06(5)	C1-C6	1.35(8)	C28-C29	1.37(8)
Pd2-C22	2.06(5)	C2-C3	1.22(14)	C29-C30	1.35(8)
Pd3-S3	2.347(14)	C3-C4	1.52(16)	C30-C31	1.39(8)
Pd3-S4	2.313(12)	C4-C5	1.42(9)	C31-C32	1.47(7)
Pd3-N3	2.07(4)	C5-C6	1.45(9)	C33-C34	1.48(8)
Pd3-C35	2.01(6)	C7-C8	1.47(7)	C34-C35	1.43(8)
Pd4-S2	2.301(14)	C8-C9	1.38(7)	C34-C39	1.46(10)
Pd4-S4	2.362(14)	C8-C13	1.36(8)	C35-C36	1.36(8)
Pd4-N4	2.09(4)	C9-C10	1.34(7)	C36-C37	1.41(8)
Pd4-C48	1.98(5)	C10-C11	1.38(8)	C37-C38	1.44(9)
Cl1-C53	1.72(11)	C11-C12	1.35(10)	C38-C39	1.40(9)
Cl2-C53	1.95(11)	C12-C13	1.49(9)	C40-C41	1.43(8)
Cl3-C54	1.51(16)	C14-C15	1.42(9)	C40-C45	1.42(8)
Cl4-C55	1.44(14)	C14-C19	1.47(11)	C41-C42	1.40(8)
S1-C1	1.76(6)	C15-C16	1.41(11)	C42-C43	1.47(12)
S2-C14	1.75(9)	C16-C17	1.36(12)	C43-C44	1.37(11)
S3-C27	1.80(5)	C17-C18	1.44(11)	C44-C45	1.45(8)
S4-C40	1.82(5)	C18-C19	1.38(10)	C46-C47	1.38(8)
N1-C6	1.40(7)	C20-C21	1.45(10)	C47-C48	1.43(7)
N1-C7	1.27(7)	C21-C22	1.33(9)	C47-C52	1.41(8)
N2-C19	1.35(8)	C21-C26	1.41(10)	C48-C49	1.37(8)
N2-C20	1.24(8)	C22-C23	1.38(7)	C49-C50	1.39(11)
N3-C32	1.36(7)	C23-C24	1.43(9)	C50-C51	1.42(11)
N3-C33	1.28(7)	C24-C25	1.35(13)	C51-C52	1.42(9)

Bond Angles

S1-Pd1-S3	100.8(5)	Pd1-S1-Pd2	112.1(6)
S1-Pd1-N1	83.4(12)	Pd1-S1-C1	95.9(17)
S1-Pd1-C9	163.7(14)	Pd2-S1-C1	103.7(20)
S3-Pd1-N1	175.7(12)	Pd2-S2-Pd4	111.2(6)
S3-Pd1-C9	93.7(15)	Pd2-S2-C14	96.4(23)
N1-Pd1-C9	82.2(18)	Pd4-S2-C14	105.6(21)
S1-Pd2-S2	98.8(6)	Pd1-S3-Pd3	106.3(5)
S1-Pd2-N2	177.4(13)	Pd1-S3-C27	101.1(15)
S1-Pd2-C22	96.2(17)	Pd3-S3-C27	97.9(16)
S2-Pd2-N2	83.7(13)	Pd3-S4-Pd4	105.2(5)
S2-Pd2-C22	163.8(15)	Pd3-S4-C40	104.6(15)
N2-Pd2-C22	81.2(20)	Pd4-S4-C40	97.6(19)
S3-Pd3-S4	100.3(5)	Pd1-N1-C6	119.7(33)
S3-Pd3-N3	82.8(13)	Pd1-N1-C7	112.6(33)
S3-Pd3-C35	166.6(14)	C6-N1-C7	127.6(44)
S4-Pd3-N3	176.7(13)	Pd2-N2-C19	121.6(40)
S4-Pd3-C35	92.2(14)	Pd2-N2-C20	110.6(38)
N3-Pd3-C35	84.8(18)	C19-N2-C20	127.7(54)
S2-Pd4-S4	99.4(6)	Pd3-N3-C32	119.0(31)
S2-Pd4-N4	174.5(14)	Pd3-N3-C33	109.8(32)
S2-Pd4-C48	94.5(14)	C32-N3-C33	131.1(40)
S4-Pd4-N4	86.0(13)	Pd4-N4-C45	115.7(32)
S4-Pd4-C48	164.0(12)	Pd4-N4-C46	114.3(34)
N4-Pd4-C48	80.2(18)	C45-N4-C46	129.9(43)

S1-C1-C2	118.0(46)	S3-C27-C32	117.3(35)
S1-C1-C6	122.0(42)	C28-C27-C32	122.6(45)
C2-C1-C6	119.9(56)	C27-C28-C29	114.7(53)
C1-C2-C3	128.3(76)	C28-C29-C30	125.5(55)
C2-C3-C4	119.9(75)	C29-C30-C31	119.4(50)
C3-C4-C5	112.2(70)	C30-C31-C32	117.5(46)
C4-C5-C6	120.5(64)	N3-C32-C27	121.9(43)
N1-C6-C1	117.9(50)	N3-C32-C31	118.2(42)
N1-C6-C5	124.1(49)	C27-C32-C31	119.3(44)
C1-C6-C5	117.8(48)	N3-C33-C34	120.7(44)
N1-C7-C8	119.9(45)	C33-C34-C35	115.5(53)
C7-C8-C9	115.6(41)	C33-C34-C39	121.3(50)
C7-C8-C13	124.1(47)	C35-C34-C39	123.2(52)
C9-C8-C13	120.2(48)	Pd3-C35-C34	109.1(37)
Pd1-C9-C8	109.5(33)	Pd3-C35-C36	129.4(39)
Pd1-C9-C10	126.1(39)	C34-C35-C36	121.3(52)
C8-C9-C10	124.4(45)	C35-C36-C37	116.8(51)
C9-C10-C11	116.9(49)	C36-C37-C38	123.1(49)
C10-C11-C12	123.0(53)	C37-C38-C39	120.7(51)
C11-C12-C13	118.4(56)-	C34-C39-C38	114.5(54)
C8-C13-C12	116.8(54)	S4-C40-C41	118.3(41)
S2-C14-C15	119.3(61)	S4-C40-C45	118.0(38)
S2-C14-C19	119.8(46)	C41-C40-C45	123.7(45)
C15-C14-C19	120.4(67)	C40-C41-C42	115.6(56)
C14-C15-C16	117.8(70)	C41-C42-C43	121.4(60)
C15-C16-C17	122.1(69)	C42-C43-C44	121.5(62)
C16-C17-C18	121.5(68)	C43-C44-C45	118.5(59)
C17-C18-C19	118.9(62)	N4-C45-C40	121.6(43)
N2-C19-C14	116.0(55)	N4-C45-C44	119.2(45)
N2-C19-C18	124.5(60)	C40-C45-C44	119.2(46)
C14-C19-C18	119.1(57)	N4-C46-C47	116.2(48)
N2-C20-C21	121.8(54)	C46-C47-C48	118.4(47)
C20-C21-C22	115.2(54)	C46-C47-C52	119.9(46)
C20-C21-C26	123.7(58)	C48-C47-C52	121.6(46)
C22-C21-C26	120.5(59)	Pd4-C48-C47	111.0(34)
Pd2-C22-C21	110.7(38)	Pd4-C48-C49	128.8(37)
Pd2-C22-C23	127.0(45)	C47-C48-C49	120.2(46)
C21-C22-C23	122.3(53)	C48-C49-C50	119.2(53)
C22-C23-C24	120.1(57)	C49-C50-C51	122.2(64)
C23-C24-C25	118.3(65)	C50-C51-C52	119.4(66)
C24-C25-C26	121.4(73)	C47-C52-C51	117.2(53)
C21-C26-C25	117.2(65)	Cl1-C53-Cl2	108.6(46)
S3-C27-C28	118.8(35)		

Table 5D. Selected Bond Lengths(Å) and Angles(°) for [Pt$_4$(C^{σ}-1-nabt)$_4$](**4**).

Bond Lengths					
Pt-S1	2.348(8)	N-C7	1.31 (4)	C4-C5	1.43 (6)
Pt-N1	2.02(2)	C1-C2	1.45(4)	C5-C6	1.42(6)
Pt-C9	2.00(3)	C1-C6	1.41(5)	C7-C8	1.57(5)
S-C1	1.76(3)	C2-C3	1.35(5)	C8-C9	1.38(5)
N-C2	1.46 (4)	C3-C4	1.33(5)	C8-C17	1.43(6)

C9-C10	1.449(49)	C12-C13	1.43(7)	C14-C15	1.46(7)
C10-C11	1.53(7)	C12-C17	1.31(6)	C15-C16	1.39(6)
C11-C12	1.51(7)	C13-C14	1.38(7)	C16-C17	1.52(6)

Bond Angles

S-Pt-N	85.5(7)	C1-C6-C5	119.3(34)
S-Pt-C9	166.0(10)	N-C7-C8	111.9(28)
Pt-S-C1	96.6(10)	C7-C8-C9	113.7(30)
Pt-N-C2	120.9(18)	C7-C8-C17	121.6(33)
C2-N-C7	120.7(24)	Pt-C9-C8	114.8(26)
S-C1-C2	123.8(22)	Pt-C9-C10	126.4(25)
S-C1-C6	121.5(25)	C9-C10-C11	117.6(35)
N-C2-C1	111.4(24)	C10-C11-C12	116.3(42)
N-C2-C3	125.7(28)	C11-C12-C13	112.9(40)
C1-C2-C3	121.7(29)	C12-C13-C14	115.1(45)
C2-C3-C4	122.1(33)	C13-C14-C15	122.3(46)
C3-C4-C5	118.2(35)	C14-C15-C16	123.7(44)
C4-C5-C6	119.4(36)	C15-C16-C17	109.9(37)

Chapter 4.

Table 3A. Isotropic Temperature Factors (Å^2) for the hydrogen atoms of *trans*-[Pt(2,6-Clphbt)$_2$](**1**) with esd's in parentheses.

ATOM	*X*	*Y*	*Z*	*U*
H10	0.57610	0.32678	0.94857	0.06(3)
H11	0.69883	0.36515	0.88898	0.06(3)
H12	0.72483	0.42546	0.63447	0.10(8)
H7	0.46304	0.44436	0.41532	0.04(2)
H5	0.41742	0.46473	0.16018	0.06(3)
H4	0.30488	0.48026	-0.00395	0.04(3)
H3	0.22077	0.38850	-0.03237	0.04(3)
H2	0.24674	0.27926	0.08417	0.03(2)

Table 3B. Isotropic Temperature Factors (Å^2) for the hydrogen atoms of *trans*-[Pt(2,4,6-Mephbt)](**2**) with esd's in parentheses.

ATOM	*X*	*Y*	*Z*	*U*
H15A	1.34008	0.53292	1.00996	0.2(2)
H15B	1.25338	0.52302	1.06806	0.2(2)
H15C	1.27168	0.61092	1.01356	0.0(2)
H16A	1.26580	0.38870	0.67108	0.1(1)
H16B	1.17920	0.43560	0.61658	0.1(1)
H16C	1.16790	0.34500	0.66848	0.00(9)
H14A	0.91455	0.57587	0.89419	0.06(7)
H14B	0.89955	0.48777	0.83859	0.07(9)
H14C	0.92055	0.57337	0.78109	0.16(8)
H32A	0.73422	0.63856	0.60900	0.2(1)
H32B	0.68232	0.59936	0.51410	0.1(1)

H32C	0.76092	0.54596	0.57780	0.08(8)
H30A	0.44052	0.29014	0.60995	0.3(2)
H30B	0.54282	0.28404	0.58335	0.06(8)
H30C	0.46562	0.33414	0.51385	0.14(9)
H31A	0.52382	0.60294	0.88098	0.3(2)
H31B	0.50942	0.50394	0.89908	0.6(4)
H31C	0.43072	0.55874	0.83708	0.12(9)
H28	0.62460	0.61845	0.74031	0.04(5)
H26	0.44869	0.40983	0.73852	0.03(5)
H3	0.89922	0.18275	0.99596	0.1(1)
H4	1.04950	0.21205	0.95419	0.12(9)
H2	0.76769	0.23735	0.89883	0.02(5)
H5	1.07110	0.30166	0.81466	0.14(7)
H10	1.08406	0.57491	0.97360	0.16(7)
H12	1.29638	0.46199	0.84271	0.07(4)
H18	0.90112	0.31414	0.25383	0.10(6)
H19	0.77783	0.26026	0.14106	0.1(1)
H20	0.62507	0.25189	0.18285	0.03(7)
H21	0.59301	0.30555	0.34063	0.15(9)
H23	0.58690	0.42022	0.42881	0.050

Table 4A. Anisotropic Temperature Factors for Non-Hydrogen Atoms of *trans*-[Pt(2,6-Clphbt)$_2$](**1**) with esd's in parentheses.

ATOM	*U*(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)
Pt1	0.0242(1)	0.0326(2)	0.0294(1)	0.0071(3)	0.0000	0.0000
Cl1	0.076(2)	0.082(2)	0.055(2)	-0.011(2)	0.017(1)	0.001(2)
Cl2	0.059(1)	0.064(2)	0.093(2)	-0.014(1)	0.024(2)	-0.001(2)
S1	0.0271(8)	0.0417(9)	0.0566(13)	0.0023(7)	-0.0020(9)	-0.0014(9)
N1	0.023(3)	0.040(3)	0.034(3)	0.005(2)	0.002(3)	-0.001(3)
C1	0.027(3)	0.057(5)	0.034(4)	0.019(3)	-0.010(3)	-0.006(4)
C2	0.037(4)	0.062(6)	0.053(5)	0.002(4)	-0.014(4)	-0.012(5)
C3	0.058(6)	0.076(8)	0.056(6)	0.037(6)	-0.023(5)	-0.018(5)
C4	0.071(7)	0.059(7)	0.050(5)	0.034(6)	-0.008(5)	0.003(5)
C5	0.046(5)	0.055(5)	0.037(5)	0.013(4)	-0.003(4)	0.006(4)
C6	0.032(4)	0.041(4)	0.035(4)	0.008(3)	-0.002(3)	0.003(3)
C7	0.033(7)	0.032(4)	0.051(4)	0.001(3)	-0.001(3)	-0.001(3)
C8	0.033(4)	0.044(5)	0.052(5)	0.000(4)	-0.003(4)	-0.005(4)
C9	0.073(7)	0.056(6)	0.052(6)	-0.001(5)	-0.003(5)	0.006(5)
C10	0.11(1)	0.07(1)	0.05(1)	0.01(1)	-0.03(1)	0.00(1)
C11	0.082(9)	0.098(11)	0.085(10)	0.012(8)	-0.051(9)	-0.019(9)
C12	0.047(6)	0.074(8)	0.106(10)	0.005(5)	-0.030(7)	-0.033(8)
C13	0.043(5)	0.043(5)	0.073(7)	-0.006(4)	0.003(5)	-0.004(5)

Table 4B. Anisotropic Temperature Factors for Non-Hydrogen Atoms of *trans*-[Pt(2,4,6-Mephbt)](**2**) with esd's in parentheses.

ATOM	*U*(11)	*U*(22)	*U*(33)	*U*(12)	*U*(13)	*U*(23)
Pt1	0.0485(3)	0.0365(3)	0.0352(3)	0.0043(3)	0.0013(1)	0.0060(2)
S1	0.052(2)	0.059(2)	0.036(2)	0.000(1)	0.004(1)	0.010(1)

S2	0.066(2)	0.061(2)	0.045(2)	0.005(2)	0.016(1)	0.010(2)
N1	0.050(4)	0.050(4)	0.044(5)	0.000(5)	0.005(4)	0.018(5)
N2	0.071(6)	0.042(4)	0.035(5)	0.007(5)	0.004(4)	0.009(4)
C1	0.069(8)	0.042(6)	0.025(6)	0.004(5)	0.004(5)	0.013(5)
C2	0.09(1)	0.06(1)	0.04(1)	-0.02(1)	0.00(1)	0.01(1)
C3	0.09(1)	0.08(1)	0.07(1)	-0.02(1)	-0.01(1)	0.05(1)
C4	0.10(1)	0.07(1)	0.07(1)	0.00(1)	-0.03(1)	0.03(1)
C5	0.061(8)	0.045(8)	0.061(9)	0.009(7)	-0.006(7)	0.021(7)
C6	0.064(7)	0.021(5)	0.055(7)	-0.006(5)	0.008(6)	0.014(5)
C7	0.046(6)	0.046(6)	0.048(7)	0.010(5)	0.013(5)	0.015(5)
C8	0.042(6)	0.058(7)	0.039(7)	-0.010(5)	-0.010(5)	0.004(5)
C9	0.065(8)	0.052(7)	0.044(7)	0.005(6)	0.004(6)	0.003(5)
C10	0.09(1)	0.05(1)	0.07(1)	0.00(1)	0.00(1)	-0.02(1)
C11	0.05(1)	0.05(1)	0.05(1)	0.00(1)	0.01(1)	0.00(1)
C12	0.047(7)	0.079(10)	0.058(9)	-0.006(6)	-0.004(7)	-0.005(7)
C13	0.053(7)	0.052(6)	0.047(8)	0.005(5)	0.007(6)	0.003(6)
C14	0.06(1)	0.06(1)	0.07(1)	0.00(1)	0.01(1)	0.01(1)
C15	0.07(1)	0.10(2)	0.07(1)	-0.01(1)	-0.01(1)	-0.03(1)
C16	0.08(1)	0.05(1)	0.09(1)	0.02(1)	0.01(1)	0.00(1)
C17	0.07(1)	0.03(0)	0.04(1)	0.02(1)	0.00(1)	0.01(0)
C18	0.10(2)	0.05(1)	0.07(1)	0.02(1)	0.04(1)	0.01(1)
C19	0.20(3)	0.05(1)	0.03(1)	0.03(1)	0.01(1)	0.00(1)
C20	0.13(2)	0.08(1)	0.04(1)	0.01(1)	-0.01(1)	-0.02(1)
C21	0.07(1)	0.07(1)	0.05(1)	0.03(1)	-0.02(1)	0.00(1)
C22	0.10(1)	0.04(1)	0.02(1)	0.01(1)	-0.01(1)	0.01(0)
C23	0.056(7)	0.049(5)	0.020(5)	0.009(5)	0.007(5)	0.002(4)
C24	0.036(6)	0.043(5)	0.039(5)	0.002(4)	0.002(4)	0.015(4)
C25	0.036(6)	0.043(5)	0.054(7)	0.002(5)	0.000(5)	0.007(5)
C26	0.040(7)	0.068(7)	0.062(8)	-0.002(6)	-0.003(6)	0.005(6)
C27	0.053(8)	0.076(9)	0.032(7)	0.002(7)	0.011(6)	0.004(6)
C28	0.059(9)	0.052(6)	0.056(8)	0.004(6)	0.008(7)	-0.002(6)
C29	0.052(6)	0.044(6)	0.057(7)	0.002(5)	-0.002(5)	-0.007(5)
C30	0.07(1)	0.06(1)	0.08(1)	-0.01(1)	-0.01(1)	-0.01(1)
C31	0.07(1)	0.10(2)	0.06(1)	0.01(1)	0.02(1)	-0.02(1)
C32	0.058(9)	0.049(7)	0.092(12)	0.000(6)	0.007(8)	-0.001(7)

Table 5A. Selected Bond Lengths(Å) and Angles(°) for *trans*-[Pt(2,6-Clphbt)$_2$](**1**).

Bond Lengths

Pt1 - S1	2.320(2)	C3 - C4	1.361(18)	C2 - H2	0.959(11)
Pt1 - N1	1.996(7)	C4 - C5	1.384(16)	C3 - H3	0.960(11)
Cl1 - C9	1.712(14)	C5 - C6	1.372(14)	C4 - H4	0.960(12)
Cl2 - C13	1.722(13)	C7 - C8	1.456(13)	C5 - H5	0.961(11)
S1 - C1	1.776(10)	C8 - C9	1.386(15)	C7 - H7	0.959(8)
N1 - C6	1.462(11)	C8 - C13	1.386(14)	C10 - H10	0.960(14)
N1 - C7	1.295(11)	C9 - C10	1.412(19)	C11 - H11	0.960(16)
C1 - C2	1.403(13)	C10 - C11	1.35(3)	C12 - H12	0.960(12)
C1 - C6	1.382(13)	C11 - C12	1.36(3)		
C2 - C3	1.363(17)	C12 - C13	1.376(18)		

Bond angles

S1-Pt1-S1	167.2(1)	C3-C4-C5	118.9(11)
S1-Pt1-N1	83.3(2)	C4-C5-C6	119.6(10)
S1-Pt1-N1	96.8(2)	N1-C6-C1	114.5(8)
S1-Pt1-N1	96.8(2)	N1-C6-C5	123.5(8)
S1-Pt1-N1	83.3(2)	C1-C6-C5	121.9(8)
N1-Pt1-N1	179.6(3)	N1-C7-C8	123.6(8)
Pt1-S1-C1	94.7(3)	C7-C8-C9	120.0(9)
Pt1-S1-C1	94.7(3)	C7-C8-C13	121.4(9)
Pt1-N1-C6	115.0(6)	C9-C8-C13	118.4(10)
Pt1-N1-C7	127.3(6)	Cl1-C9-C8	120.3(9)
Pt1-N1-C6	115.0(6)	Cl1-C9-C10	120.4(10)
Pt1-N1-C7	127.3(6)	C8-C9-C10	119.2(12)
C6-N1-C7	117.3(7)	C9-C10-C11	120.2(13)
S1-C1-C2	122.7(8)	C10-C11-C12	120.9(14)
S1-C1-C6	119.7(6)	C11-C12-C13	119.7(12)
C2-C1-C6	117.5(9)	Cl2-C13-C8	118.3(9)
C1-C2-C3	119.8(10)	Cl2-C13-C12	120.5(9)
C2-C3-C4	122.3(11)	C8-C13-C12	121.2(11)

Table 5B. Selected Bond Lengths(Å) and Angles(°) for *trans*-[Pt(2,4,6-Mephbt)](**2**).

Bond Lengths

Bond lengths (Å)		C4-C5	1.40(3)	C19-C20	1.36(6)
Pt1-S1	2.314(4)	C5-C6	1.38(3)	C20-C21	1.39(4)
Pt1-S2	2.311(5)	C7-C8	1.47(3)	C21-C22	1.37(3)
Pt1-N1	1.995(11)	C8-C9	1.40(3)	C23-C24	1.502(19)
Pt1-N2	1.998(12)	C8-C13	1.44(3)	C24-C25	1.38(2)
S1-C1	1.757(16)	C9-C10	1.37(3)	C24-C29	1.408(19)
S2-C17	1.754(19)	C9-C14	1.49(3)	C25-C26	1.34(3)
N1-C6	1.472(19)	C10-C11	1.38(3)	C25-C30	1.51(3)
N1-C7	1.317(19)	C11-C12	1.39(3)	C26-C27	1.37(3)
N2-C22	1.418(18)	C11-C15	1.55(4)	C27-C28	1.40(3)
N2-C23	1.29(2)	C12-C13	1.41(3)	C27-C31	1.54(3)
C1-C2	1.39(3)	C13-C16	1.51(3)	C28-C29	1.44(3)
C1-C6	1.38(3)	C17-C18	1.40(3)	C29-C32	1.46(3)
C2-C3	1.36(4)	C17-C22	1.43(3)		
C3-C4	1.37(4)	C18-C19	1.38(4)		

Bond Angles

S1-Pt1-S2	171.7(2)	C6-N1-C7	121.0(12)
S1-Pt1-N1	84.0(4)	Pt1-N2-C22	116.5(11)
S1-Pt1-N2	98.1(4)	Pt1-N2-C23	128.0(10)
S2-Pt1-N1	94.4(4)	C22-N2-C23	115.1(13)
S2-Pt1-N2	83.9(4)	S1-C1-C2	122.4(15)
N1-Pt1-N2	176.9(5)	S1-C1-C6	120.9(11)
Pt1-S1-C1	95.8(6)	C2-C1-C6	116.7(16)
Pt1-S2-C17	96.7(7)	C1-C2-C3	122.0(21)
Pt1-N1-C6	117.0(9)	C2-C3-C4	119.8(21)
Pt1-N1-C7	120.4(11)	C3-C4-C5	120.8(22)

C4-C5-C6	117.1(19)	C17-C18-C19	120.7(26)
N1-C6-C1	114.4(13)	C18-C19-C20	121.7(22)
N1-C6-C5	121.9(15)	C19-C20-C21	117.8(26)
C1-C6-C5	123.4(15)	C20-C21-C22	123.4(24)
N1-C7-C8	126.3(14)	N2-C22-C17	116.3(14)
C7-C8-C9	119.8(14)	N2-C22-C21	125.7(18)
C7-C8-C13	117.8(14)	C17-C22-C21	117.9(16)
C9-C8-C13	122.3(15)	N2-C23-C24	124.9(12)
C8-C9-C10	116.8(16)	C23-C24-C25	118.3(12)
C8-C9-C14	120.3(16)	C23-C24-C29	119.8(12)
C10-C9-C14	122.9(17)	C25-C24-C29	121.9(13)
C9-C10-C11	123.8(18)	C24-C25-C26	119.0(14)
C10-C11-C12	119.0(17)	C24-C25-C30	120.1(15)
C10-C11-C15	123.3(18)	C26-C25-C30	120.8(16)
C12-C11-C15	117.6(18)	C25-C26-C27	123.4(16)
C11-C12-C13	121.4(16)	C26-C27-C28	119.3(15)
C8-C13-C12	116.5(15)	C26-C27-C31	122.0(18)
C8-C13-C16	121.1(16)	C28-C27-C31	118.7(18)
C12-C13-C16	122.3(16)	C27-C28-C29	119.6(15)
S2-C17-C18	123.7(19)	C24-C29-C28	116.8(14)
S2-C17-C22	117.9(12)	C24-C29-C32	125.9(15)
C18-C17-C22	118.4(19)	C28-C29-C32	117.3(15)