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Journal of Organometallic Chemistry 490 (1995) 117–123

Journal of Organometallic Chemistry

Insertion reaction of isocyanide into the Pt–C bonds of 2,5-thienylene-bridged diplatinum complexes and 2-thienyl platinum complexes: molecular structure of $Cl(Et_3P)_2PtC(=NC_6H_4OMe\text{-}p)C_4H_2SC(=NC_6H_4OMe\text{-}p)Pt(PEt_3)_2Cl \cdot CH_2Cl_2$

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Received 20 July 1994; in revised form 7 September 1994

Abstract

Treatments of 2,5-thienylene-bridged diplatinum complexes $Cl(R_3P)_2PtC_4H_2SPt(PR_3)_2Cl$ (**1**) with two equivalents of isocyanide cause the insertion of isocyanide into each of the two Pt–C bonds to produce $Cl(R_3P)_2PtC(=NAr)C_4H_2SC(=NAr)Pt(PR_3)_2Cl$ (**2**). 2-Thienyl platinum complexes $C_4H_3SPt(PR_3)_2Cl$ (**4**) also react with isocyanide to give iminoacyl complexes $C_4H_3SC(=NAr)Pt(PR_3)_2Cl$ (**5**). Further insertion of isocyanide into Pt–C bonds of **2** and **5** was not observed even in the reaction with excess isocyanide. When **1a** was treated with an equimolar amount of *p*-tolyl isocyanide, a single-insertion product $Cl(Et_3P)_2PtC(=NC_6H_4Me\text{-}p)C_4H_2SPt(PEt_3)_2Cl$ (**3b**) was obtained altogether with the mixture of **1a** and **2a**. The molecular structure of $Cl(Et_3P)_2PtC(=NC_6H_4OMe\text{-}p)C_4H_2SC(=NC_6H_4OMe\text{-}p)Pt(PEt_3)_2Cl \cdot CH_2Cl_2$ (**2b**) was determined by an X-ray crystallographic analysis and the crystallographic data are as follows: space group, $P2_1/n$; $a = 11.044(2)$, $b = 28.086(3)$ and $c = 18.396(3)$ Å; $\beta = 93.96°$; $V = 5692(2)$ Å^3; $Z = 4$.

Keywords: Platinum; Isocyanide; Crystal structure

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1. Introduction

Our current research is focused on the chemistry of unsaturated hydrocarbon-bridged multinuclear complexes since they may provide useful information to elucidate active species on the surface of the heterogeneous catalyst [1]. Previously we prepared 2,5-thienylene- and 2,5′-dithienylene-bridged diplatinum complexes and found that they have the d_π–p_π interaction between two platinum atoms through the thienylene group [2]. It is of interest to study the reactivities of these complexes because they may have unique properties owing to the mutual interaction between the two metal atoms through the π-conjugated system. For example, μ-ethynediyl complexes of palladium and platinum, in which two metal atoms are linked by just one acetylene unit, have a unique reactivity towards isocyanide [3]. Therefore we have investigated the reaction of 2,5-thienylene-bridged diplatinum complexes as well as 2-thienyl platinum complexes with isocyanide. We wish to report here the results of the reaction and an X-ray crystallographic analysis of the insertion product.

2. Results and discussion

2.1. Reactions of 2,5-thienylene-bridged diplatinum complexes and 2-thienyl platinum complexes with isocyanide

Migratory insertion of isocyanide into the M–C bond was explained by the fact that the organic group make

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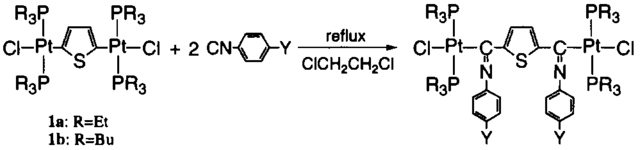
SSDI 0022-328X(94)05193-3

the nucleophilic attack to the carbon atom of isocyanide on transition metal [4], and it was reported that isocyanide smoothly inserts into the Pd–C bond of 2-thienyl palladium complex owing to the high nucleophilicity of the thienyl group [5]. Thus we examined the reaction of 2,5-thienylene-bridged diplatinum complex (**1a**) with *p*-tolyl isocyanide in dichloromethane at room temperature, although Pt–C bonds are significantly stronger than Pd–C bonds, but no insertion reaction occurred. When **1a** was treated with two equivalents of *p*-tolyl isocyanide in 1,2-dichloroethane under reflux for 18 h, the insertion of isocyanide proceeded and an orange complex (**2a**), which is stable to air even in solution, was isolated with a 41% yield. Complex **2a** was characterized by means of spectroscopic methods. The IR spectrum of **2a** showed an absorption at 1530 cm^{-1} due to ν(C=N), the value being in a reasonable region for an iminoacyl platinum complex [4]. In the ^{1}H NMR of **2a** the resonance attributed to the protons of thienylene are observed at $\delta = 7.85$ ppm as a singlet, and the ^{31}P NMR exhibited a singlet signal at $\delta = 15.09$ ppm altogether with the satellite signals ($J_{Pt-P} = 2809$ Hz). These data suggest that one molecule of isocyanide has inserted into each Pt–C bond of **1a**, which was also supported by the elemental analysis.

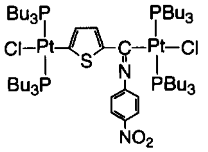


1a: R=Et
1b: R=Bu

2a: R=Et, Y=Me
2b: R=Et, Y=OMe
2c: R=Et, Y=NO$_2$
2d: R=Bu, Y=Me
2e: R=Bu, Y=OMe

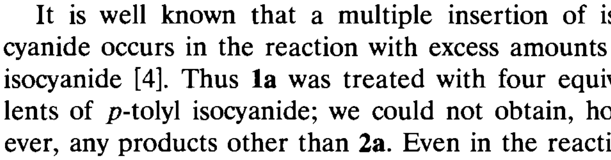
(1)

Similar reactions of **1a** with *p*-methoxyphenyl or *p*-nitrophenyl isocyanide gave insertion products **2b** and **2c** respectively. Although the insertion was accelerated by the electron-withdrawing group on isocyanide [6], such a phenomenon was not observed in this reaction. An analogous 2,5-thienylene-bridged complex (**1b**) containing a tributylphosphine ligand also reacted with *p*-tolyl or *p*-methoxyphenyl isocyanide to



3a

produce **2d** and **2e** respectively. On treatment of **1b** with two equivalents of *p*-nitrophenyl isocyanide, however, insertion hardly occurred and the mixture of **2f** and the single-insertion product **3a** was obtained with a low yield. In contrast, when **1b** was treated with four equivalents of *p*-nitrophenyl isocyanide, **2f** was isolated with a 35% yield. Isocyanides having a bulky substituent such as 2,6-xylyl or *tert*-butyl isocyanide did not afford the insertion products. These results indicate that insertion of isocyanide into the Pt–C bonds of 2,5-thienylene-bridged diplatinum complex is affected by the bulkiness of isocyanide and ligands on platinum.

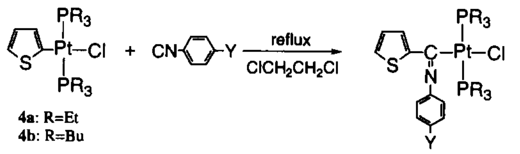


1b

2f

(2)

2-Thienyl platinum complex (**4a**) was treated with one equivalent of *p*-tolyl isocyanide in 1,2-dichloroethane under reflux to give an insertion product **5a** with a 77% yield. Similarly, the treatment of **4a** with *p*-methoxyphenyl or *p*-nitrophenyl isocyanides afforded **5b** and **5c** respectively. It should be noted that **4b** produced an iminoacyl complex with a moderate yield not only by the reaction with *p*-tolyl or *p*-methoxyphenyl isocyanide but also by treatment with *p*-nitrophenyl isocyanide, suggesting that the steric influence in the reaction of 2,5-thienylene-bridged diplatinum complex is greater than that of 2-thienyl platinum complex.



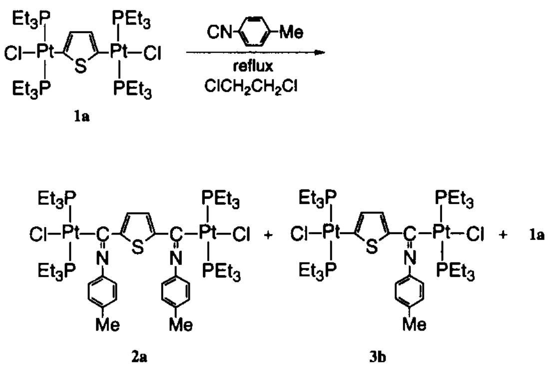
4a: R=Et
4b: R=Bu

5a: R=Et, Y=Me
5b: R=Et, Y=OMe
5c: R=Et, Y=NO$_2$
5d: R=Bu, Y=Me
5e: R=Bu, Y=OMe
5f: R=Bu, Y=NO$_2$

(3)

It is well known that a multiple insertion of isocyanide occurs in the reaction with excess amounts of isocyanide [4]. Thus **1a** was treated with four equivalents of *p*-tolyl isocyanide; we could not obtain, however, any products other than **2a**. Even in the reaction with 20 equivalents of *p*-nitrophenyl isocyanide a multiple-insertion product was not produced. Attempt to observe a multiple insertion into the Pt–C bond of 2-thienyl complex **4** was also unsuccessful.

When **1a** was treated with an equimolar amounts of *p*-tolyl isocyanide, a single-insertion product **3b** was isolated with a 47% yield altogether with the mixture of the starting complex **1a** and double-insertion product **2a**, the yields of which were determined by means of ^{1}H NMR as 5% and 11% respectively. In the reaction of butadiyne- or *p*-diethynylbenzene-bridged dipalladium complex, the insertion of isocyanide into either site of the two Pd–C bonds caused a marked decrease in reactivity of the other palladium site, which may depend on the lower nucleophilicity of acetylide group by the electron-withdrawing property of the iminoacyl group [3b]. A similar tendency was confirmed in the reaction of **1a**, but the difference between the reactivities of **1a** and **3b** is not so large. On the basis of this result it can be regarded that the 2,5-thienylene-bridged diplatinum complex reacts with isocyanide at the two reaction sites independently.



(4)

2.2. *Molecular structure of* $Cl(Et_3P)_2PtC(=NC_6H_4OMe\text{-}p)C_4H_2SC(=NC_6H_4OMe\text{-}p)\text{-}Pt(PEt_3)_2Cl \cdot CH_2Cl_2$ *(2b)*

The molecular structure of $Cl(Et_3P)_2PtC(=NC_6H_4OMe\text{-}p)C_4H_2SC(=NC_6H_4OMe\text{-}p)Pt(PEt_3)_2Cl \cdot CH_2Cl_2$ (**2b**) shown in Fig. 1 was determined by a single-crystal X-ray study. The crystallographic data and positional parameters with B_{eq} values for all non-hydrogen atoms are summarized in Tables 1 and 2, and selected bond distances and angles are listed in Table 3. The molecule consists of a geometry in which two platinum atoms are linked by the bis(iminoacyl)-2,5-thienylene group. The Pt–C bond lengths are 2.01(2) and 1.99(2) Å, which are comparable with that of 2.027(11) Å in *trans*-$Pt(CMe=NC_6H_4Cl)(PEt_3)_2I$ [7]. The imino N atoms are located at distances of 3.01(2) and 2.99(2) Å respectively from Pt atoms. These are clearly non-bonding distances. The dihedral angle between two coordination planes of Pt is 96.80°, in contrast with the result that the two coordination planes are parallel in $Cl(Et_3P)_2PdC(=NC_6H_5)\text{-}C{\equiv}CC(=NC_6H_5)Pd(PEt_3)_2Cl$ [3d]. The square planes of Pt atom are twisted away from the plane of iminoacyl group PtC(=N)C for 83.99 and 81.90° respectively, which are slightly larger than that of 78.05° in $Cl(Et_3P)_2PdC(=NC_6H_5)C{\equiv}CC\text{-}(=NC_6H_5)Pd(PEt_3)_2Cl$ [3d]. It is noteworthy that the bis(iminoacyl)-2,5-thienylene group has a nearly planar conformation and the dihedral angles between thienylene and iminoacyl groups are 8.13 and 16.04° respectively. However, this can probably be attributed to the crystal-packing force because the significant difference of bond distances and angles was not found in bis(iminoacyl)-2,5-thienylene owing to the conjugation.

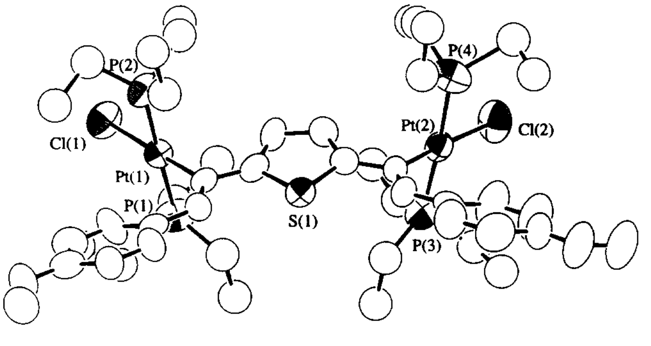


Fig. 1. Molecular structure of $Cl(Et_3)_2C(=NC_6H_4OMe\text{-}p)\text{-}C_4H_2SC(=NC_6H_4OMe\text{-}p)Pt(PEt_3)_2Cl$ (**2b**). Hydrogen atoms are omitted for clarity.

Table 1
Crystallographic data for $\mathbf{2b} \cdot CH_2Cl_2$

Empirical formula	$C_{45}H_{78}N_2O_2Cl_4P_4SPt_2$
Formula weight	1367.07
Crystal color; habit	Pale yellow, prismatic
Crystal dimensions	0.30×0.20×0.15 mm
Crystal system	Monoclinic
Lattice parameters	
a	11.044 (2) Å
b	28.086 (3) Å
c	18.396 (3) Å
β	93.96 (2)°
V	5692 (2) Å^3
Space grou	$P2_1/n$ (No. 14)
Z value	4
D_{calc}	1.595 g cm^{-3}
F_{000}	2712
μ(Mo Kα)	53.30 cm^{-1}
2θ range	$6° < 2\theta < 50.1°$
Number of reflections measured	10859
Number of observations	3225 ($I > 9.0\sigma(I)$)
Number of variables	403
Reflection to parameter ratio	8.00
Residuals R; R_w	0.039; 0.044
Goodness-of-fit indicator	3.04
Maximum peak in final difference map	1.02 electrons Å^{-3}
Minimum peak in final difference map	−0.61 electrons Å^{-3}

$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$; $w = 4F_o^2/\sigma^2(F_o)^2$. The goodness-of-fit indicator is the standard deviation of an observation of unit weight $[\Sigma w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$ where N_o is the number of observations and N_v the number of variables.

3. Experimental section

All reactions were carried out under a nitrogen atmosphere, but the work-up was performed in air. ^1H NMR (399.65 MHz), ^{13}C NMR (100.10 MHz) and ^{31}P NMR (161.70 MHz) were measured on a JEOL JMN-A400 spectrometer in $CDCl_3$. As an internal standard,

Table 2
Positional parameters and B_{eq} for complex **2b**$\cdot CH_2Cl_2$

Atom	x	y	z	B_{eq} (Å^2)
Pt(1)	0.21462(7)	0.22075(3)	0.02555(4)	4.89(4)
Pt(2)	0.24680(7)	−0.00654(3)	0.27494(5)	5.46(5)
Cl(1)	0.3805(5)	0.2682(2)	−0.0128(3)	7.5(3)
Cl(2)	0.4165(5)	−0.0533(2)	0.3205(3)	8.8(4)
S(1)	0.0162(4)	0.1020(2)	0.1412(3)	5.3(3)
P(1)	0.2598(6)	0.1632(2)	−0.0569(4)	8.1(4)
P(2)	0.1751(5)	0.2773(2)	0.1105(3)	6.5(3)
P(3)	0.2732(6)	−0.0376(2)	0.1619(3)	7.1(4)
P(4)	0.2392(7)	0.0289(3)	0.3873(4)	10.3(5)
O(1)	−0.293(1)	0.3020(5)	−0.1576(8)	7(1)
O(2)	−0.245(1)	−0.1292(7)	0.373(1)	10(0)
N(1)	−0.035(2)	0.1809(5)	0.0430(8)	5(1)
N(2)	−0.012(2)	0.0211(5)	0.2392(8)	5(1)
C(1)	0.078(2)	0.1811(7)	0.060(1)	4(1)
C(2)	0.114(2)	0.1445(7)	0.113(1)	5(1)
C(3)	0.229(2)	0.1380(7)	0.151(1)	6(1)
C(4)	0.235(2)	0.0986(8)	0.197(1)	6(1)
C(5)	0.128(2)	0.0746(7)	0.198(1)	5(1)
C(6)	0.102(2)	0.0304(7)	0.238(1)	5(1)
C(11)	−0.094(2)	0.2119(7)	−0.009(1)	4(1)
C(12)	−0.219(2)	0.2146(8)	−0.009(1)	6(1)
C(13)	−0.289(2)	0.2443(8)	−0.055(1)	6(1)
C(14)	−0.236(2)	0.2717(8)	−0.107(1)	6(1)
C(15)	−0.107(2)	0.2695(8)	−0.104(1)	7(1)
C(16)	−0.039(2)	0.2394(9)	−0.059(1)	7(1)
C(17)	−0.421(2)	0.3025(7)	−0.163(1)	8(1)
C(21)	−0.062(2)	−0.0183(9)	0.274(1)	5(1)
C(22)	−0.183(2)	−0.0163(8)	0.282(1)	8(2)
C(23)	−0.239(2)	−0.054(1)	0.316(1)	8(2)
C(24)	−0.178(3)	−0.095(1)	0.342(1)	7(2)
C(25)	−0.057(3)	−0.097(1)	0.330(2)	9(2)
C(26)	0.001(2)	−0.060(1)	0.298(1)	9(2)
C(27)	−0.186(2)	−0.171(1)	0.397(2)	11(2)
C(31)	0.181(2)	0.1082(9)	−0.053(1)	9.5(7)
C(32)	0.209(2)	0.068(1)	−0.108(2)	14(1)
C(33)	0.208(3)	0.182(1)	−0.163(2)	14(1)
C(34)	0.229(3)	0.226(2)	−0.178(2)	20(1)
C(35)	0.411(3)	0.157(1)	−0.073(2)	19(1)
C(36)	0.479(2)	0.1396(9)	0.004(2)	11.6(8)
C(41)	0.039(2)	0.2719(8)	0.155(1)	9.4(6)
C(42)	0.009(2)	0.3116(9)	0.211(1)	10.0(7)
C(43)	0.209(3)	0.336(1)	0.094(2)	15(1)
C(44)	0.105(3)	0.346(1)	0.028(2)	13.2(9)
C(45)	0.284(3)	0.271(1)	0.195(1)	12.8(9)
C(46)	0.400(3)	0.267(1)	0.187(1)	13.1(9)
C(51)	0.162(2)	−0.0239(9)	0.090(1)	10.9(8)
C(52)	0.175(3)	−0.046(1)	0.013(2)	15(1)
C(53)	0.289(2)	−0.103(1)	0.155(1)	11.0(8)
C(54)	0.173(3)	−0.128(1)	0.171(1)	14(1)
C(55)	0.410(5)	−0.023(2)	0.125(3)	24(2)
C(56)	0.472(4)	0.013(1)	0.138(2)	20(1)
C(61)	0.095(3)	0.068(1)	0.396(2)	14(1)
C(62)	0.099(3)	0.094(1)	0.467(2)	22(2)
C(63)	0.286(5)	−0.003(2)	0.483(3)	30(2)
C(64)	0.193(4)	−0.031(1)	0.473(2)	18(1)
C(65)	0.355(5)	0.078(2)	0.406(3)	27(2)
C(66)	0.463(4)	0.073(1)	0.376(2)	20(1)
C(101)	0.753(3)	0.159(2)	0.236(1)	35(2)
Cl(11)	0.624(2)	0.1318(8)	0.1926(9)	43(1)
Cl(12)	0.781(1)	0.1394(6)	0.3270(8)	29.1(6)

Table 3
Selected bond distances (Å) and angles (°) for **2b**

Bond distances			
Pt(1)–Cl(1)	2.410(5)	Pt(2)–Cl(2)	2.392(6)
Pt(1)–P(1)	2.295(7)	Pt(2)–P(3)	2.292(6)
Pt(1)–P(2)	2.291(6)	Pt(2)–P(4)	2.300(7)
Pt(1)–C(1)	2.01(2)	Pt(2)–C(6)	1.99(2)
C(1)–C(2)	1.46(3)	C(5)–C(6)	1.47(3)
C(1)–N(1)	1.26(3)	C(6)–N(2)	1.28(3)
C(2)–C(3)	1.42(3)	C(4)–C(5)	1.36(3)
C(2)–S(1)	1.71(2)	C(5)–S(1)	1.74(2)
C(3)–C(4)	1.39(3)		
Bond angles			
Cl(1)–Pt(1)–P(1)	89.5(2)	Cl(2)–Pt(2)–P(3)	87.9(2)
Cl(1)–Pt(1)–P(2)	90.1(2)	Cl(2)–Pt(2)–P(4)	89.9(2)
Cl(1)–Pt(1)–C(1)	178.8(3)	Cl(2)–Pt(2)–C(6)	178.1(6)
P(1)–Pt(1)–P(2)	178.0(2)	P(3)–Pt(2)–P(4)	174.0(3)
P(1)–Pt(1)–C(1)	91.1(2)	P(3)–Pt(2)–C(6)	91.9(6)
P(2)–Pt(1)–C(1)	89.3(3)	P(4)–Pt(2)–C(6)	90.4(6)
Pt(1)–C(1)–N(1)	133(1)	Pt(2)–C(6)–N(2)	130(1)
Pt(1)–C(1)–C(2)	115(1)	Pt(2)–C(6)–C(5)	116(1)

$SiMe_4$ was used for ^1H and ^{13}C NMR, and PPh_3 was used for ^{31}P NMR external standard. IR spectra were recorded on a JASCO A-202 IR spectrophotometer.

The 2,5-thienylene-bridged diplatinum complexes $Cl(COD)PtC_4H_2SPt(COD)Cl$ and $Cl(Bu_3P)_2PtC_4H_2SPt(PBu_3)_2Cl$ were synthesized as described previously [2], and the 2-thienyl platinum complex $C_4H_3SPt(COD)Cl$ was prepared by the literature method [8]. Aryl isocyanides were prepared by either the dehydration of formanilide analogues [9] or the carbylamine reaction in the presence of a phase transfer catalyst [10]. *tert*-Butyl isocyanide and triethylphosphine were purchased from Aldrich, and tributylphosphine from Wako Chemicals.

3.1. Preparation of $Cl(Et_3P)_2PtC_4H_2SPt(PEt_3)_2Cl$ (1a)

$Cl(COD)PtC_4H_2SPt(COD)Cl$ (1.3 g, 1.7 mmol) was dissolved in 70 ml of dichloromethane, and 1 M tetrahydrofuran (THF) solution of triethylphosphine (6.9 ml, 6.9 mmol) was added. After the reaction mixture had been stirred at room temperature for 15 h, the solvent was removed in vacuo. The residue was purified by alumina column chromatography with benzene followed by recrystallization from ethanol to give colorless crystals (1.75 g (53%)).

Melting point (m.p.), 171–174°C. ^1H NMR: δ 6.39 (s, $^3J_{Pt-H} = 45.9$ Hz, 2H, thienylene), 1.72 (m, 24H, CH_2), 1.11 (dt, $J = 15.6$, 7.8 Hz, 36H, CH_3). ^{13}C NMR: δ 128.77 ($^2J_{Pt-C} = 76.9$ Hz, $^3J_{Pt-C} = 59.6$ Hz, thienylene), 124.08 ($^1J_{Pt-C} = 1089$ Hz, $^2J_{P-C} = 11.2$ Hz, thienylene), 12.85 (t, $J = 17.0$ Hz, CH_2), 7.83(CH_3). ^{31}P NMR: δ 18.91 ($^1J_{Pt-P} = 2673$ Hz). Anal. Found: C, 33.16; H, 6.36; Cl, 6.70; P, 11.96; S, 3.22. $C_{28}H_{62}Cl_2P_4SPt_2$ Calc.: C, 33.11; H, 6.15; Cl, 6.98; P, 12.20; S, 3.16%.

3.2. Preparation of $C_4H_3SPt(PEt_3)_2Cl$ (*4a*)

$C_4H_3SPt(COD)Cl$ (2.0 g, 2.8 mmol) was treated with 1 M THF solution of triethylphosphine (9.6 ml, 9.6 mmol) in 140 ml of dichloromethane at room temperature for 24 h. The volatile was removed and the residue was purified by alumina column chromatography using benzene as an eluent. Recrystallization from ethanol gave colorless crystals (1.53 g (58%)).

M.p., 70–74°C. ^1H NMR: δ 7.36 (d, $J = 4.9$ Hz, 1H, thienyl), 6.93 (dd, $J = 4.9$, 3.4 Hz, 1H, thienyl), 6.58 (d, $J = 3.4$, $^3J_{Pt-H} = 47.3$ Hz, 1H, thienyl), 1.72–1.65 (m, 12H, CH_2), 1.10 (dt, $J = 16.6$, 7.8 Hz, 18H, CH_3). ^{31}P NMR: δ 18.90 ($^1J_{Pt-P} = 2674$ Hz). Anal. Found: C, 34.95; H, 6.28; Cl, 6.28; P, 11.22; S, 5.66. $C_{16}H_{33}ClP_2SPt$ Calc.: C, 34.94; H, 6.05; Cl, 6.45; P, 11.26; S, 5.83%.

3.3. Preparation of $C_4H_3SPt(PBu_3)_2Cl$ (*4b*)

A similar treatment of $C_4H_3SPt(COD)Cl$ (1.0 g, 1.2 mmol) with tributylphosphine (0.98 g, 4.8 mmol) as described above gave colorless crystals (0.92 g (73%)).

M.p., 34–37°C. ^1H NMR: δ 7.34 (d, $J = 4.9$ Hz, 1H, thienyl), 6.92 (dd, $J = 4.9$, 3.4 Hz, 1H, thienyl), 6.54 (d, $J = 3.4$ Hz, $^3J_{Pt-H} = 45.9$ Hz, 1H, thienyl), 1.66–1.33 (m, 36H, CH_2), 0.92 (t, $J = 7.1$ Hz, 18H, CH_3), ^{31}P NMR: δ 12.19($^1J_{Pt-P} = 2573$ Hz). Anal. Found: C, 46.65; H, 8.14; Cl, 4.78; P, 8.61; S, 4.47. $C_{28}H_{57}ClP_2SPt$ Calc.: C, 46.82; H, 8.00; Cl, 4.94; P, 8.62; S, 4.46%.

3.4. Preparation of $Cl(Et_3P)_2PtC(=NC_6H_4Me\text{-}p)\text{-}C_4H_2SC(=NC_6H_4Me\text{-}p)Pt(PEt_3)_2Cl$ (*2a*)

To a solution of **1a** (200 mg, 0.20 mmol) in 20 ml of 1,2-dichloroethane was added *p*-tolyl isocyanide (46 mg, 0.39 mmol). After being stirred for 18 h under reflux, the solvent was removed under reduced pressure and the residue purified by chromatography on alumina using dichloromethane as an eluent. Recrystallization from dichloromethane–hexane gave yellow crystals (102 mg (41%)).

M.p., 226–228°C. IR: ν(C=N) 1525 cm^{-1}. ^1H NMR: δ 8.01 (d, $J = 8.3$ Hz, 4H, C_6H_4), 7.84 (s, 2H, thienylene), 7.1 (d, $J = 8.3$ Hz, 4H, C_6H_4), 2.31 (s, 6H, $C_6H_4CH_3$), 1.75–1.69 (m, 24H, CH_2), 1.03 (dt, $J = 16.1$, 7.8 Hz, 36H, CH_2CH_3). ^{31}P NMR: δ 15.09 ($^1J_{Pt-P} = 2815$ Hz). Anal. Found: C, 42.09; H, 6.01; N, 1.98; Cl, 5.71; P, 9.93; S, 2.60. $C_{44}H_{76}N_2Cl_2P_4SPt_2$ Calc.: C, 42.27; H, 6.13; N, 2.24; Cl, 5.67; P, 9.91; S, 2.57%.

3.5. Preparation of $Cl(Et_3P)PtC(=NC_6H_4OMe\text{-}p)C_4H_2SC(=NC_6H_4OMe\text{-}p)Pt(PEt_3)_2Cl$(*2b*) and $Cl\text{-}(Et_3P)_2PtC(=NC_6H_4NO_{2-p})C_4H_2SC(=NC_6H_4NO_2\text{-}p)Pt(PEt_3)_2Cl$ (*2c*)

These reactions were carried out by a method similar to that of **2a** to give **2b** with a 44% yield and **2c** with a 47% yield respectively. The crystals of **2b** contained one equivalent of CH_2Cl_2, which is confirmed by ^1H NMR.

2b: m.p., 210–214°C. IR: ν(C=N) 1490 cm^{-1}. ^1H NMR: δ 8.17 (d, $J = 8.8$ Hz, 4H, C_6H_4), 7.84 (s, 2H, thienylene), 6.86 (d, $J = 8.8$ Hz, 4H, C_6H_4), 3.81 (s, 6H, OCH_3), 1.76–1.69 (m, 24H, CH_2), 1.03 (dt, $J = 15.6$, 7.8 Hz, 36H, CH_3). ^{31}P NMR: δ 15.09($^1J_{Pt-P} = 2809$ Hz). Anal. Found: C 39.50; H, 5.81; N, 2.03; Cl, 10.27; P, 8.80; S, 2.25. $C_{44}H_{76}N_2Cl_2O_2P_4SPt_2 \cdot CH_2Cl_2$ Calc.: C, 39.54; H, 5.75; N, 2.05; Cl, 10.37; P, 9.06; S, 2.34%.

2c: m.p., 254–264°C (decomposition). IR: ν(C=N) 1530 cm^{-1}. ^1H NMR: δ 8.21 (d, $J = 8.8$ Hz, 4H, C_6H_4), 8.08 (d, $J = 8.8$ Hz, 4H, C_6H_4), 7.96 (s, 2H, thienylene), 1.80–1.72 (m, 24H, CH_2), 1.03 (dt, $J = 16.1$, 8.1 Hz, 36H, CH_3). ^{31}P NMR: δ 15.74 ($^1J_{Pt-P} = 2720$ Hz). Anal. Found: C, 38.58; H, 5.35; N, 4.14; Cl, 5.68; P, 9.32; S, 2.46. $C_{42}H_{70}N_4Cl_2O_4P_4SPt_2$ Calc.: C, 38.45; H, 5.38; N, 4.27; Cl, 5.40; P, 9.44; S, 2.44%.

3.6. Preparation of $Cl(Bu_3P)_2PtC(=NC_6H_4Me\text{-}p)C_4H_2SC(=NC_6H_4Me\text{-}p)Pt(PBu_3)_2Cl$ (*2d*)

Complex **1b** (200 mg, 0.15 mmol) was treated with *p*-tolyl isocyanide (36 mg, 0.30 mmol) in 20 ml of 1,2-dichloroethane under reflux for 18 h. A pure sample of **2d** (218 mg (92%)) was obtained as yellow oil by alumina column chromatography with benzene.

IR: ν(C=N) 1540 cm^{-1}. ^1H NMR: δ 7.89 (d, $J = 8.3$ Hz, 4H, C_6H_4), 7.82 (s, 2H, thienylene), 7.08 (d, $J = 8.3$ Hz, 4H, C_6H_4), 2.31 (s, 6H, $C_6H_4CH_3$), 1.68–1.63 (m, 24H, PCH_2), 1.41–1.24 (m, 48H, CH_2), 0.86 (t, $J = 7.1$ Hz, 36H, CH_2CH_3). ^{31}P NMR: δ 8.82 ($^1J_{Pt-P} = 2809$ Hz). Anal. Found: C, 51.25; H, 8.07; N, 1.76; Cl, 4.68; P, 8.07; S, 2.28. $C_{68}H_{124}N_2Cl_2P_4SPt_2$ Calc.: C, 51.47; H, 7.88; N, 1.77; Cl, 4.46; P, 7.81; S, 2.02%.

3.7. Preparation of $Cl(Bu_3P)_2PtC(=NC_6H_4OMe\text{-}p)C_4H_2SC(=NC_6H_4OMe\text{-}p)Pt(PBu_3)_2Cl$ (*2e*)

A similar treatment of **1b** with two equivalents of *p*-methoxyphenyl isocyanide to that of **2d** gave **2e** as yellow oil with a 41% yield.

IR: ν(C=N) 1495 cm^{-1}. ^1H NMR: δ 8.07 (d, $J = 8.8$ Hz, 4H, C_6H_4), 7.81 (s, 2H, thienylene), 6.83 (d, $J = 8.8$ Hz, 4H, C_6H_4), 3.80 (s, 6H, OCH_3), 1.70–1.65 (m, 24H, PCH_2), 1.42–1.25 (m, 48H, CH_2), 0.86 (t, $J = 7.1$ Hz, 36H, CH_3). ^{31}P NMR: δ 8.86 ($^1J_{Pt-P} = 2803$ Hz).

Anal. Found: C, 50.46; H, 7.89; N, 1.54; Cl, 4.22; P, 7.66; S, 2.26. $C_{68}H_{124}N_2Cl_2O_2P_4SPt_2$ Calc.: C, 50.45; H, 7.72; N, 1.73; Cl, 4.38; P, 7.65; S, 1.98%.

3.8. Preparation of $Cl(Bu_3P)_2PtC(=NC_6H_4NO_2\text{-}p)C_4H_2SC(=NC_6H_4NO_2\text{-}p)Pt(PBu_3)_2Cl$ (2f)

Complex **1b** (200 mg, 0.15 mmol) was treated with *p*-nitrophenyl isocyanide (89 mg, 0.60 mmol) in 1,2-dichloroethane under reflux. After 20 h the solvent was evaporated under reduced pressure, and the product was isolated by alumina column chromatography. Elution with benzene followed by recrystallization from hexane gave **2f** (101 mg (35%)) as orange crystals.

M.p., 164–167°C. IR: ν(C=N) 1520 cm^{-1}, ^{1}H NMR: δ 8.20 (d, J = 8.8 Hz, 4H, C_6H_4), 7.98 (d, J = 8.8 Hz, 4H, C_6H_4), 7.92 (s, 2H, thienylene), 1.74–1.68 (m, 24H, PCH_2), 1.40–1.26 (m, 48H, CH_2), 0.86 (t, J = 7.1 Hz, 36H, CH_3). ^{31}P NMR: δ 7.36 ($^1J_{Pt-P}$ = 2779 Hz). Anal. Found: C, 48.08; H, 6.95; N, 3.33; Cl, 4.33; P, 7.31; S, 1.88. $C_{66}H_{118}N_4Cl_2O_4P_4SPt_2$ Calc.: C, 48.08; H, 7.21; N, 3.40; Cl, 4.30; P, 7.51; S, 1.94%.

3.9. Preparation of $C_4H_3SC(=NC_6H_4Me\text{-}p)Pt(PEt_3)_2Cl$ (5a)

A solution of **4a** (200 mg, 0.36 mmol) in 20 ml of 1,2-dichloroethane was treated with *p*-tolyl isocyanide (43 mg, 0.36 mmol). After the reaction mixture had been stirred for 17 h under reflux, the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on alumina with benzene followed by recrystallization from dichloromethane–hexane to give yellow crystals (187 mg (77%)).

M$_P$, 167–169°C; IR: ν(C=N) 1530 cm^{-1}. ^{1}H NMR: δ 7.96 (d, J = 8.3 Hz, 2H, C_6H_4), 7.92 (dd, J = 3.5, 1.0 Hz, 1H, thienyl), 7.35 (dd, J = 4.9, 1.0 Hz, 1H, thienyl), 7.11 (d, J = 8.3 Hz, 2H, C_6H_4), 7.03 (dd, J = 4.9, 3.5 Hz, 1H, thienyl), 2.31 (s, 3H, $C_6H_4CH_3$), 1.77–1.64 (m, 12H, CH_2), 1.02 (dt, J = 15.6, 7.8 Hz, 18H, CH_2CH_3). ^{31}P NMR: δ 15.09 ($^1J_{Pt-P}$ = 2815 Hz), Anal. Found: C, 43.19; H, 6.11; N, 2.10; Cl, 5.20; P, 9.10; S, 4.77. $C_{24}H_{40}NClP_2SPt$ Calc.: C, 43.21; H, 6.04; N, 2.10; Cl, 5.31; P, 9.29; S, 4.81%.

3.10. Preparation of $C_4H_3SC(=NC_6H_4OMe\text{-}p)Pt(PEt_3)_2Cl$(5b) and $C_4H_3SC(=NC_6H_4NO_2\text{-}p)Pt(PEt_3)_2Cl$(5c)

These reactions were performed by a method similar to that of **5a** to afford **5b** with a 57% yield and **5c** with a 41% yield.

5b: m.p., 162–163°C. IR: ν(C=N) 1530 cm^{-1}. ^{1}H NMR: δ 8.12 (d, J = 8.3 Hz, 2H, C_6H_4), 7.91 (d, J = 3.9 Hz, 1H, thienyl), 7.34 (d, J = 4.9 Hz, 1H, thienyl), 7.03 (dd, J = 4.9, 3.9 Hz, 1H, thienyl), 6.86 (d, J = 8.3 Hz, 2H, C_6H_4), 3.81 (s, 3H, OCH_3), 1.78–1.64 (m, 12H, CH_2), 1.03 (dt, J = 15.6, 7.8 Hz, 18H, CH_3). ^{31}P NMR: δ 15.16 ($^1J_{Pt-P}$ = 2797 Hz). Anal. Found: C, 42.41; H, 6.01; N, 2.11; Cl, 5.22; P, 9.05; S, 4.69. $C_{24}H_{40}NClOP_2SPt$ Calc.: C, 42.20; H, 5.90; N, 2.05; Cl, 5.19; P, 9.07; S, 4.69%.

5c: m.p., 168–170°C. IR: ν(C=N) 1510 cm^{-1}. ^{1}H NMR: δ 8.21 (d, J = 8.8 Hz, 2H, C_6H_4), 8.03 (d, J = 8.8 Hz, 2H, C_6H_4), 8.00 (d, J = 3.4 Hz, 1H, thienyl), 7.46 (d, J = 5.3 Hz, 1H, thienyl), 7.08 (dd, J = 5.3, 3.4 Hz, 1H, thienyl), 1.77–1.69 (m, 12H, CH_2), 1.02 (dt, J = 15.6, 7.8 Hz, 18H, CH_3). ^{31}P NMR: δ 15.82 ($^1J_{Pt-P}$ = 2720 Hz). Anal. Found: C, 39.37; H, 5.24; N, 3.82; Cl, 4.87; P, 8.65; S, 4.44. $C_{23}H_{37}N_2ClO_2P_2SPt$ calc.: C, 39.57; H, 5.34; N, 4.01; Cl, 5.08; P, 8.87; S, 4.59%.

3.11. Preparation of $C_4H_3SC(=NC_6H_4Me\text{-}p)Pt(PBu_3)_2Cl$(5d)

To a solution of **4b** (200 mg, 0.28 mmol) in 20 ml of 1,2-dichloroethane was added *p*-tolyl isocyanide (33 mg, 0.28 mmol). The reaction mixture was stirred for 16 h under reflux, and the solvent was removed in vacuo. The residue was purified by alumina column chromatography with benzene. Recrystallization from hexane to give yellow crystals (128 mg (55%)).

M.p., 83–85°C. IR: ν(C=N) 1525 cm^{-1}. ^{1}H NMR: δ 7.88 (d, J = 2.9 Hz, 1H, thienyl), 7.80 (d, J = 8.3 Hz, 2H, C_6H_4), 7.33 (d, J = 5.4 Hz, 1H, thienyl), 7.08 (d, J = 8.3 Hz, 2H, C_6H_4), 7.00 (dd, J = 5.4, 2.9 Hz, 1H, thienyl), 2.31 (s, 3H, $C_6H_4CH_3$), 1.67–1.60 (m, 12H, PCH_2), 1.39–1.23 (m, 24H, CH_2), 0.85 (t, J = 7.1 Hz, 18H, CH_2CH_3). ^{31}P NMR: δ 6.88 ($^1J_{Pt-P}$ = 2785 Hz). Anal. Found: C, 51.59; H, 7.63; N, 1.61; Cl, 4.19; P, 7.34; S, 4.04. $C_{36}H_{64}NClP_2SPt$ calc.: C, 51.76; H, 7.72; N, 1.68; Cl, 4.24; P, 7.41; S, 3.84%.

3.12. Preparation of $C_4H_3SC(=NC_6H_4OMe\text{-}p)Pt(PBu_3)_2Cl$(5e) and $C_4H_3SC(=NC_6H_4NO_2\text{-}p)$ + $Pt(PBu_3)_2Cl$(5f)

By a similar method to that mentioned above, **5e** and **5f** were produced with 74% and 66% yields respectively.

5e m.p., 111–113°C. IR: ν(C=N) 1530 cm^{-1}. ^{1}H NMR: δ 7.97 (d, J = 8.8 Hz, 2H, C_6H_4), 7.87 (d, J = 2.9 Hz, 1H, thienyl), 7.32 (d, J = 5.4 Hz, 1H, thienyl), 7.00 (dd, J = 5.4, 2.9 Hz, 1H, thienyl), 6.83 (d, J = 8.8 Hz, 2H, C_6H_4), 3.80 (s, 3H, OCH_3), 1.68–1.61 (m, 12H, PCH_2), 1.40–1.24 (m, 24H, CH_2), 0.85 (t, J = 7.1 Hz, 18H, CH_3). ^{31}P NMR: δ 8.75 ($^1J_{Pt-P}$ = 2785 Hz). Anal. Found: C, 50.97; H, 7.73; N, 1.73; Cl, 4.11; P, 7.19; S, 3.78. $C_{36}H_{64}NClOP_2SPt$ Calc.: C, 50.78; H, 7.58; N, 1.65; Cl, 4.16; P, 7.28; S, 3.77%.

5f: m.p., 151–153°C: IR: ν(C=N) 1510 cm^{-1}. ^{1}H NMR: δ 8.19 (d, J = 8.8 Hz, 2H, C_6H_4), 7.96 (d,

$J = 3.9$ Hz, 1H, thienyl), 7.91 (d, $J = 8.8$ Hz, 2H, C_6H_4), 7.44 (d, $J = 4.9$ Hz, 1H, thienyl), 7.05 (dd, $J = 4.9$, 3.9 Hz, 1H, thienyl), 1.71–1.62 (m, 12H, PCH_2), 1.38–1.25 (m, 24H, CH_2), 0.85 (t, $J = 7.1$ Hz, 18H, CH_3). ^{31}P NMR: δ 9.45 ($^1J_{Pt-P} = 2708$ Hz). Anal. Found: C, 48.28; H, 7.04; N, 3.25; Cl, 4.35; P, 7.11; S, 3.77. $C_{35}H_{61}N_2ClO_2P_2SPt$ Calc.: C, 48.52; H, 7.10; N, 3.23; Cl, 4.09; P, 7.15; S, 3.70%.

3.13. *Preparation of* $Cl(Et_3P)_2PtC(=NC_6H_4Me\text{-}p)C_4H_2SPt(PEt_3)_2Cl$ *(6)*

A solution of **1a** (172 mg, 0.17 mmol) in 20 ml of 1,2-dichloroethane was treated with *p*-tolyl isocyanide (20 mg, 0.17 mmol) under reflux for 46 h. The solvent was removed under reduced pressure, and the products were separated by silica gel column chromatography. Elution with dichloromethane gave the mixture (30 mg) of **1a** and **2a** in 2 : 1 molar ratio, and elution with ethyl acetate gave **6** (90 mg (47%)). An analytically pure sample of **6** was obtained as yellow crystals by recrystallization from dichloromethane–hexane.

M.p., 182–185°C (decomposition). IR: ν(C=N) 1520 cm^{-1}. ^1H NMR: δ 7.85 (d, $J = 7.8$ Hz, 2H, C_6H_4), 7.84 (d, $J = 3.4$ Hz, 1H, thienylene), 7.07 (d, $J = 7.8$ Hz, 2H, C_6H_4), 6.62 (d, $J = 3.4$ Hz, $^3J_{Pt-H} = 49.3$ Hz, 1H, thienylene), 2.29 (s, 3H, $C_6H_4CH_3$), 1.79–1.71 (m, 24H, CH_2), 1.10 (dt, $J = 16.6$, 7.8 Hz, 18H, CH_2CH_3), 1.01 (dt, $J = 15.6$, 7.8 Hz, 18H, CH_2CH_3). ^{31}P NMR: δ 19.73 ($^1J_{Pt-P} = 2613$ Hz), 14.90 ($^1J_{Pt-P} = 2872$ Hz). Anal. Found: C, 37.97; H, 5.96; N, 1.17; Cl, 6.27; P, 10.97; S, 2.81. $C_{36}H_{69}NCl_2P_4SPt_2$ Calc.: C, 38.16; H, 6.14; N, 1.24; Cl, 6.26; P, 10.94; S, 2.83%.

3.14. *X-ray crystallography of* $Cl(Et_3P)_2PtC(=NC_6H_4OMe\text{-}p)C_4H_2SC(=NC_6H_4OMe\text{-}p)Pt(PEt_3)_2Cl\text{-}CH_2Cl_2$*(2b)*

A single crystal (0.30 × 0.20 × 0.15 mm) suitable for an X-ray diffraction analysis was mounted on glass fibers with epoxy resin. Diffraction measurements were made on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å) using a ω–2θ scan technique with a scan rate of 8° min^{-1}. The unit cell was determined and refined by a least-squares method using 24 reflections in the range $25.0° < 2\theta < 27.6°$. The data of weak reflections ($I < 10\sigma(I)$) were rescanned two times and averaged. Three standard reflections were monitored at every 150 measurements and no damage was observed. Intensities were collected for Lorentz and polarization effects and an empirical absorption collection was applied using DIFABS [11]. The scattering factors were taken from the *International Tables for X-ray Crystallography* [12].

The structure was solved by the direct method. The non-hydrogen atoms except the carbon atoms of triethylphosphine were refined anisotropically, and isotropic thermal parameters were used for the carbon atoms of triethylphosphine. The large thermal parameters for the carbon atoms of triethylphosphine are related to the slight disorder as well as thermal motion, but a satisfactory disorder model could not be devised. All hydrogen atoms were included at the calculated positions. The final cycles of full-matrix least-squares refinement was converged; the largest parameter shift against its error was 0.54. The unweighted and weighted agreement factors are $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.039$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2]^{1/2} = 0.044$ respectively. All calculations were performed on VAX station 3100 using the TEXSAN crystallographic software package [13].

Acknowledgments

We are grateful for support of this work by the Grant-in-Aid for Scientific Research on Priority Area of Reactive Organometallics No. 05236106 from the Ministry of Education, Science and Culture, Japan.

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