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Synthesis and properties of 2- or 2,5-substituted thiophene and 2- or 2,5'-substituted dithiophene derivatives of platinum

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Abstract

The reaction of $[\text{PtCl}_2(\text{COD})]$ (COD = cycloocta-1,5-diene) with 2,5-bis(trimethylstannyl)thiophene or with 2,5'-bis(trimethylstannyl)-5-(2'-thienyl)thiophene gives diplatinum complexes bridged with 2,5-thienylene or 2,5'-di(5,2'-thienylene), $[\text{Cl}(\text{COD})\text{Pt}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{Pt}(\text{COD})\text{Cl}]$ (1) and $[\text{Cl}(\text{COD})\text{Pt}(\mu\text{-}2,5'\text{-C}_4\text{H}_2\text{S}\text{-C}_4\text{H}_2\text{S})\text{Pt}(\text{COD})\text{Cl}]$ (4). On treatment with tri-*n*-butylphosphine these give the corresponding tributylphosphine derivatives, *trans,trans*- $[\text{Cl}(\text{PBU}_3)_2\text{Pt}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{Pt}(\text{PBU}_3)_2\text{Cl}]$ (2) and *trans,trans*- $[\text{Cl}(\text{PBU}_3)_2\text{Pt}(\mu\text{-}2,5'\text{-C}_4\text{H}_2\text{S}\text{-C}_4\text{H}_2\text{S})\text{Pt}(\text{PBU}_3)_2\text{Cl}]$ (5), respectively. Treatment of 2 with 2-thienyllithium in THF gives *trans,trans*- $[(2\text{-C}_4\text{H}_3\text{S})(\text{PBU}_3)_2\text{Pt}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{Pt}(\text{PBU}_3)_2(2\text{-C}_4\text{H}_3\text{S})]$ (3). The di-2-thienyl and bis-2-dithienyl complexes, $[\text{M}(2\text{-C}_4\text{H}_3\text{S})_2(\text{PBU}_3)_2]$ (6) and $[\text{M}\{5\text{-(}2'\text{-C}_4\text{H}_3\text{S)}\text{-}2\text{-C}_4\text{H}_2\text{S}\}_2(\text{PBU}_3)_2]$ (M = Pt (7a), Pd (7b), Ni (7c)), have also been prepared by treatment of $[\text{M}(\text{PBU}_3)_2\text{X}_2]$ (X = Cl or Br) with 2-thienyllithium and 5-(2'-thienyl)-2-thienyllithium in THF. The electronic spectra of the above complexes contain metal to ligand charge transfer bands, suggesting that $d_\pi\text{-}p_\pi$ interaction between two platinum atoms through thienylene groups appears to play an important role.

Introduction

Thiophene derivatives are receiving much attention as possible intermediates for the production of pharmaceuticals [1,2], agrochemicals [3,4], and conductive polymers [5]. Dinuclear transition metal complexes bridged with π -conjugated groups can also help to elucidate the $d_\pi\text{-}p_\pi$ interactions between transition metals and π -conjugated groups such as ethynediyl[6,7], butadiynediyl[8,9], and 1,4-phenylene [10]. These facts prompt us to investigate synthesis of 2- σ -thienyl and 2,5-thienylene-bridged transition metal complexes.

Although the syntheses of mono- and di-2- σ -thienyl platinum complexes by reaction with 2-trimethylstannylthiophene [11], mono-2- σ -thienyl palladium complex with thienylmercury chloride [12], and mono-2- σ -thienyl nickel derivative with

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thienyllithium [13] are already known, there is no report on the systematic synthesis of σ -thienyl complexes containing the Group 10 metals nickel, palladium and platinum.

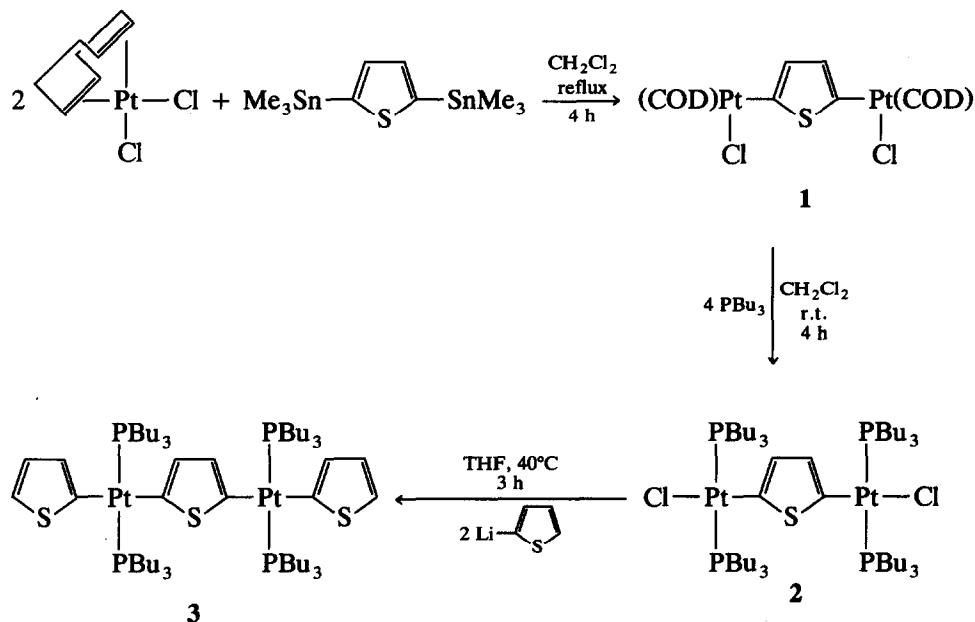
In this paper, we report on the synthesis and characterization of di-2-thienyl and di-5-(2'-thienyl)-2-thienyl derivatives with Group 10 metals and diplatinum complexes with 2,5-thienylene- or 2,5'-dithienylene-bridge.

Results and discussion

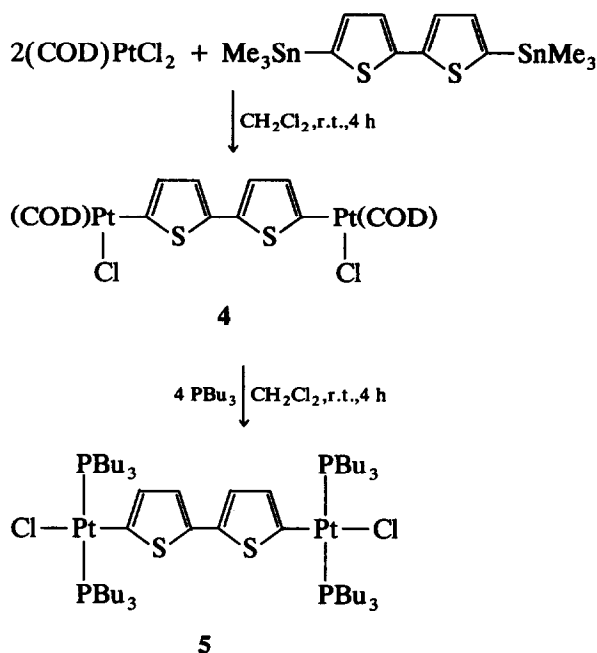
Synthesis of thiophene and dithiophene derivatives of transition metals

The diplatinum complex with 2,5-thienylene bridge, $[\text{Cl}(\text{COD})\text{Pt}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{Pt}(\text{COD})\text{Cl}]$ (**1**) (COD = cycloocta-1,5-diene), was synthesized by the reaction of 2,5-bis(trimethylstannyl)thiophene with $[\text{PtCl}_2(\text{COD})]$ under reflux of dichloromethane for 4 h, using the method [8] by which the 1,4-phenylene bridge analogue was prepared (Scheme 1). Attempts to prepare *trans,trans*- $[\text{Cl}(\text{PBu}_3)_2\text{Pt}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{Pt}(\text{PBu}_3)_2\text{Cl}]$ (**2**) by the reaction of molar ratio 2:1 of *trans*- $[\text{PtCl}_2(\text{PBu}_3)_2]$ and 2,5-thienyldilithium in tetrahydrofuran (THF) at 40°C were unsuccessful. The tributylphosphine derivative **2** was produced by ligand exchange of diplatinum complex **1** with tri-*n*-butylphosphine in dichloromethane at room temperature for 2 h. The di-2-thienyl derivative, *trans,trans*- $[(2\text{-C}_4\text{H}_3\text{S})(\text{PBu}_3)_2\text{Pt}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{Pt}(\text{PBu}_3)_2(2\text{-C}_4\text{H}_3\text{S})]$ (**3**), was synthesized by the reaction of **2** with an excess of 2-thienyllithium in THF at 40°C. The synthesis of the complexes **1**–**3** are summarized in Scheme 1.

Diplatinum complexes with 2,5'-dithienylene bridge, $[\text{Cl}(\text{COD})\text{Pt}(\mu\text{-}2,5'\text{-C}_4\text{H}_2\text{S-C}_4\text{H}_2\text{S})\text{Pt}(\text{COD})\text{Cl}]$ (**4**) and *trans,trans*- $[\text{Cl}(\text{PBu}_3)_2\text{Pt}(\mu\text{-}2,5'\text{-C}_4\text{H}_2\text{S-C}_4\text{H}_2\text{S})\text{Pt}(\text{PBu}_3)_2\text{Cl}]$ (**5**), were synthesized by procedures similar to those for 2,5-thienylene derivatives (Scheme 2).



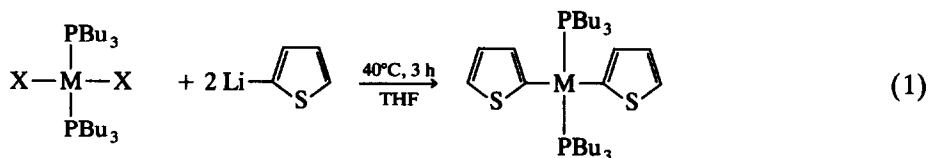
Scheme 1.



Scheme 2.

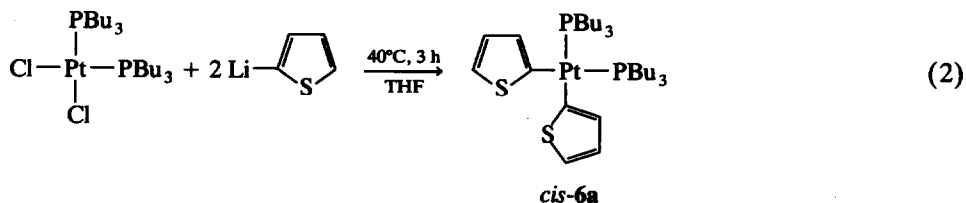
The 1 : 2 reaction of $[\text{PtCl}_2(\text{COD})]$ and 2-trimethylstannylthiophene in dichloromethane at room temperature afforded $[\text{Pt}(2\text{-C}_4\text{H}_3\text{S}_2)(\text{COD})]$, although a similar reaction of $[\text{PdCl}_2(\text{COD})]$ with 2-trimethylstannylthiophene gave only palladium metal. Therefore, we examined the reactions of $[\text{MCl}_2(\text{PBu}_3)_2]$ ($\text{M} = \text{Pt}, \text{Pd}$, or Ni) with an excess of 2-thienyllithium.

The di-2-thienyl complex, *trans*- $[\text{Pt}(2\text{-C}_4\text{H}_3\text{S}_2)_2(\text{PBu}_3)_2]$ (**6a**), was prepared by the metathetical exchange reaction of *trans*- $[\text{PtCl}_2(\text{PBu}_3)_2]$ with $2\text{-C}_4\text{H}_3\text{SLi}$ in THF at 40°C as shown in eq. 1. The *cis*-isomer, *cis*- $[\text{Pt}(2\text{-C}_4\text{H}_3\text{S}_2)_2(\text{PBu}_3)_2]$

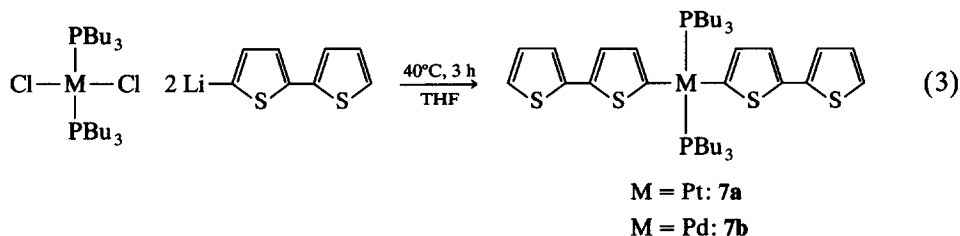


$\text{M} = \text{Pt}, \text{Pd}, \text{X} = \text{Cl}$
 $\text{M} = \text{Ni}, \text{X} = \text{Br}$

$\text{M} = \text{Pt}$: *trans*-**6a**
 $\text{M} = \text{Pd}$: *trans*-**6b**
 $\text{M} = \text{Ni}$: *trans*-**6c**



cis-(**6a**), was also prepared by the reaction of *cis*-[PtCl₂(PBu₃)₂] with 2-C₄H₃SLi (eq. 2). Similar reactions of *trans*-[MX₂(PBu₃)₂] (M = Pd, X = Cl; M = Ni, X = Br) with 2-C₄H₃SLi afford *trans*-**6b** and **6c**, respectively (eq. 1). The bis-2-dithienyl complexes, *trans*-[M(5-(2'-C₄H₃S)-2-C₄H₂S)₂(PBu₃)₂] (M = Pt (**7a**), Pd (**7b**)), were prepared by the metathetical exchange reaction of *trans*-[MCl₂(PBu₃)₂] with an excess of 5-(2'-thienyl)-2-thienyllithium (eq. 3). The bis-2-dithienyl nickel derivative was too unstable to be isolated. The complexes **1**–**5**, **6a**–**c** and **7a**, **7b**, were characterized by ¹H- and ¹³C-NMR, electronic spectra and elemental analysis.



Characterization of thiophene and dithiophene derivatives of transition metals

The ¹H- and ¹³C-NMR spectral data of the complexes **2**, **3**, **5**, *trans*-**6a**, *cis*-**6a**, **6b**, **6c**, **7a** and **7b**, are summarized in Table 1. The *trans,trans*-structure for **2**, **3** and **5**, *trans*-structure for *trans*-**6a**, **6b**, **7a** and **7b**, and *cis*-structure for *cis*-**6a** were spectrometrically identified by using ²J(P–C) nuclear spin–spin coupling pattern for the α-carbon of thienyl group (triplet for *trans* isomer and double doublet for *cis*-isomer): α-carbon for **2**, triplet (123.52 ppm, ²J(P–C) 11.0 Hz); **3**, triplets (154.04 ppm, ²J(P–C) 11.8 Hz and 147.27 ppm, ²J(P–C) 11.8 Hz); **5**, triplet (139.85 ppm, ²J(P–C) 11.0 Hz); *trans*-**6a**, triplet (151.09 ppm, ²J(P–C) 12.5 Hz); **6b**, triplet (156.25 ppm, ²J(P–C) 11.8 Hz); **7a**, triplet (153.32 ppm, ²J(P–C) 11.87 Hz); **7b**, triplet (158.64 ppm, ²J(P–C) 14.0 Hz); *cis*-**6a**, doublet of doublets (156.73 ppm, ²J(P–C) 127.7 and 16.2 Hz).

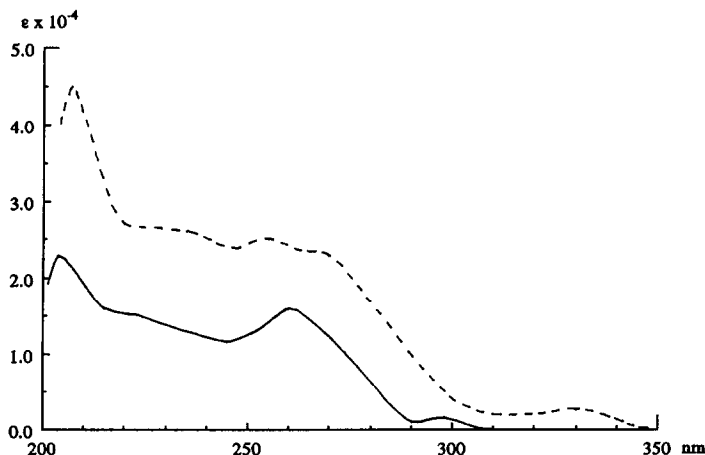


Fig. 1. Electronic spectra of di-2-thienyl-mono and -di-platinum complexes: — *trans*-**6a**; ---- **3**.

The electronic spectral data of **2**, **3**, **5**, **6**, and **7** are summarized in Table 2. There seem to be few systematic studies of the σ -aryl complexes of transition metals because of the difficulty in obtaining useful information. For the thienyl

Table 1

^1H - and ^{13}C -NMR data of thienyl complexes **2**, **3**, **5**, **6**, and **7**

Complex	^1H -NMR ppm ^a		^{13}C -NMR ppm ^b	
	P- <i>Bu</i>	thiophene (Hz)	P- <i>Bu</i>	thiophene (Hz)
2	0.93	6.39	13.64	123.52 ($^2J(\text{P}-\text{C})$ 11.0; triplet)
	1.42		19.99	128.74 ($^2J(\text{Pt}-\text{C})$ 48.4)
	1.52		24.01	
	1.62		25.75	
3	0.90	6.65	13.97	125.33
	1.35	7.70	20.89	127.29
	1.44	7.49	24.37	129.82
			26.21	131.34
				147.27 ($^2J(\text{P}-\text{C})$ 11.8; triplet)
				154.04 ($^2J(\text{P}-\text{C})$ 11.8; triplet)
5	0.90	6.84 ($^3J(\text{H}-\text{H})$ 3.67)	13.78	122.28
	1.38	6.37 (d)	20.86	126.12
	1.49		24.30	128.26
	1.69		25.99	139.85 ($^2J(\text{P}-\text{C})$ 11.0; triplet)
<i>trans</i> - 6a	0.90	7.05 ($^3J(\text{Pt}-\text{H})$ 27.34)	13.50	125.69 ($^3J(\text{Pt}-\text{C})$ 36.7)
	1.32	7.39 ($^3J(\text{H}-\text{H})$ 3.18, 4.64)	20.75	127.42 ($^2J(\text{Pt}-\text{C})$ 39.9; triplet)
	1.44	7.73 ($^3J(\text{H}-\text{H})$ 4.89)	24.03	129.91 ($^3J(\text{Pt}-\text{C})$ 33.8)
			25.77	151.09 ($^2J(\text{P}-\text{C})$ 12.5; triplet. $^1J(\text{Pt}-\text{C})$ 696.9)
<i>cis</i> - 6a	0.90	7.03 ($^3J(\text{Pt}-\text{H})$ 36.86)	13.50	124.38 ($^3J(\text{Pt}-\text{C})$ 46.9)
	1.33	7.19 ($^3J(\text{H}-\text{H})$ 3.30, 4.76)	23.13	126.27 ($^2J(\text{Pt}-\text{C})$ 64.6)
	1.56	7.49 ($^3J(\text{H}-\text{H})$ 4.88)	24.14	126.76 ($^3J(\text{Pt}-\text{C})$ 49.8)
			25.77	156.73 ($^2J(\text{P}-\text{C})$ 16.2; 127.7: double doublets)
<i>trans</i> - 6b	0.97	7.07 ($^3J(\text{H}-\text{H})$ 2.98)	13.38	126.84
	1.34	7.37 ($^3J(\text{H}-\text{H})$ 3.17, 4.64)	21.96	130.48
	1.52	7.68 ($^3J(\text{H}-\text{H})$ 4.89)	24.46	156.25 ($^2J(\text{P}-\text{C})$ 11.8; triplet)
<i>trans</i> - 6c	0.93	7.03		
	1.24	7.31		
	1.37	7.65		
	1.65			
7a	0.89	6.55 ($^3J(\text{H}-\text{H})$ 1.83,	13.81	120.76
	1.33	$^3J(\text{Pt}-\text{H})$ 26.86)	21.21	121.39
		6.96 (dd)		
	1.46	7.03 (d)	24.33	125.21 ($^2J(\text{Pt}-\text{C})$ 46.9)
		7.04 (d)	26.13	127.46
		7.18 ($^3J(\text{H}-\text{H})$ 3.06)		131.14 (triplet)
				138.22 ($^3J(\text{Pt}-\text{C})$ 38.1)
				140.76
				153.32 ($^2J(\text{P}-\text{C})$ 11.8; triplet. $^1J(\text{Pt}-\text{C})$ 695.3)

Table 1 (continued)

Complex	¹ H-NMR ppm ^a		¹³ C-NMR ppm ^b	
	P-Bu	thiophene (Hz)	P-Bu	thiophene (Hz)
7b	0.89	6.56 (³ J(H-H) 3.35)	13.79	120.92
	1.35	6.96 (dd)	22.21	121.52
	1.44	7.03 (d)	24.45	124.70
		7.04 (d)	26.47	127.46
		7.18 (³ J(H-H) 3.05)		131.69
				139.38
				140.33
				158.64 (² J(P-C) 14.0; triplet)

^a In C₆D₆, chemical shifts are referred to tetramethylsilane as an internal standard. ^b In CDCl₃, chemical shifts are referred to tetramethylsilane as an internal standard.

Table 2

Electronic spectra data of thienyl complexes 2, 3, 5, 6, and 7

complex	UV nm (ε) ^a				
2	204 (34000)	224 (20000)	241 (18000)	262 (13000)	291 (6900)
3	207 (45000)	235 (26000)	255 (25000)	270 (23000)	330 (2600)
5	205 (39000)	221 (26000)	238 (21000)	352 (19000)	432 (3400)
trans-6a	204 (23000)	224 (15000)	260 (16000)	298 (1600)	
cis-6a	203 (20000)	259 (16000)	298 (2600)		
trans-6b	213 (25000)	238 (23000)	255 (25000)		
trans-6c	211 (30000)	244 (19000)	271 (16000)	288 (11000)	313 (4700)
7a	208 (15000)	237 (12000)	252 (11000)	344 (34000)	415 (210)
7b	215 (28000)	235 (21000)	340 (36000)	414 (88)	

^a In cyclohexane.

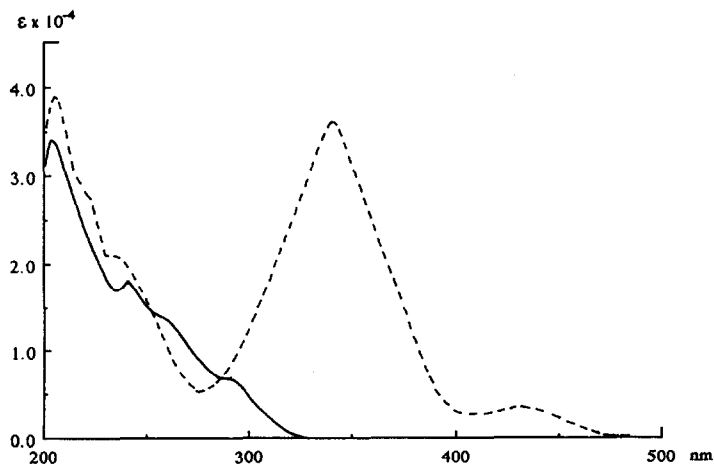


Fig. 2. Electronic spectra of 2,5-thienylen- and 2,5'-dithienylene-bridged diplatinum complexes: — 2; ---- 5.

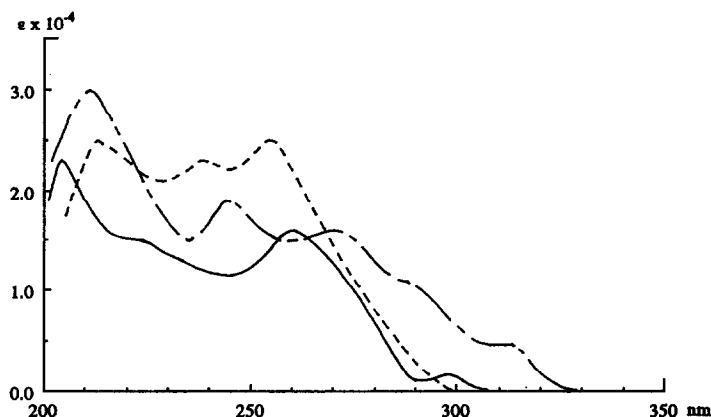


Fig. 3. Electronic spectra of di-2-thienyl complexes of nickel triad: — *trans*-6a; ---- *trans*-6b; - · - *trans*-6c.

complexes, however, significant information concerning interactions between the metals and thienyl groups was obtained in this work. The electronic spectra of **3** and *trans*-6a are shown in Fig. 1, where the spectral pattern among the complexes are considerably similar. The absorption bands due to both the lowest and the second energy transitions of **3** show a red shift relative to those of *trans*-6a. This may be a result of longer conjugation in **3** than *trans*-6a, since the lowest band is due to the metal to thienyl ligand charge transfer transition (MLCT transition) and the second one is due to the π - π^* transitions of the thienyl groups. Electronic spectra of thienylene and dithienylene bridged diplatinum complexes, **2** and **5**, show the same trend as above (Fig. 2). The electronic spectra for the di-2-thienyl complexes of Group 10 metals, **6a**–**c**, are shown in Fig. 3. The spectrum of **6b** is difficult to interpret because of poor resolution which is also observed in the acetylide complexes [14]. The lowest energy band of **6b** may be overlapped by that

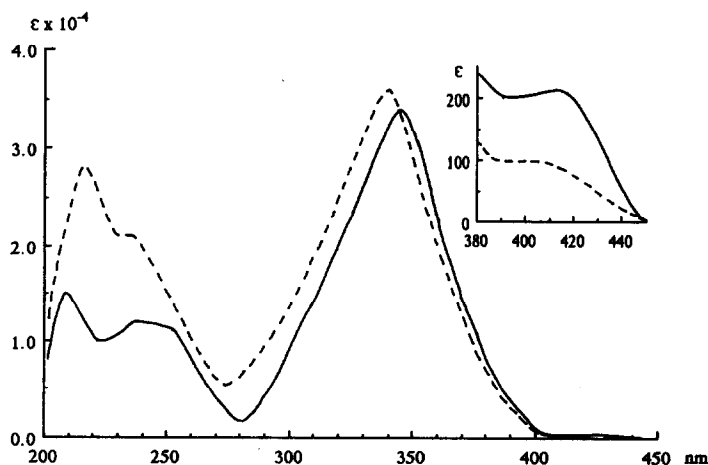


Fig. 4. Electronic spectra of 2-dithienyl platinum and palladium complexes: — **7a**; ---- **7b**.

of the second one. Therefore, we may speculate that the lowest energy band moves to lower energy in the series $\text{Pd} < \text{Pt} < \text{Ni}$ which is the same order as found in ethynyl derivatives [15]. The maximum values of the lowest energy band for *cis*- and *trans*-isomers of **6a** are explained by PR_3 having the same strength as 2-thienyl in *trans* influence (Table 2). The spectral pattern of **7a**, **7b** are remarkably similar to each other, where the MLCT transitions from metal to dithienyl ligand in the palladium and platinum complexes are in the same order (Fig. 4). Similarity of absorption pattern for palladium and platinum complexes have also been observed in the polyyne-polymer complexes of palladium and platinum [15].

Experimental

Materials and methods

THF was distilled from sodium/benzophenone ketyl. Dichloromethane, tri-*n*-butylphosphine, and thiophene were purchased from Wako Pure Chemical Co. and used without further purification. The following compounds were prepared according to literature methods: *trans*- $[\text{PtCl}_2(\text{PBU}_3)_2]$ [16], *cis*- $[\text{PtCl}_2(\text{PBU}_3)_2]$ [16], *trans*- $[\text{PdCl}_2(\text{PBU}_3)_2]$ [17], *trans*- $[\text{NiBr}_2(\text{PBU}_3)_2]$ [18], $[\text{PtCl}_2(\text{COD})]$ [19], 2,5-bis(trimethylstannyl)thiophene [20], 2,2'-dithiophene [21].

Electronic spectra were recorded in cyclohexane solution with a Hitachi 200-10 spectrometer. ^1H - and ^{13}C -NMR spectra were run on a JEOL GX 400 spectrometer in CDCl_3 referred to tetramethylsilane as an internal standard.

$[\text{Cl}(\text{COD})\text{Pt}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{Pt}(\text{COD})\text{Cl}]$ (**1**)

2,5-Bis(trimethylstannyl)thiophene (587 mg, 1.43 mmol) was added to a suspension of dichloro(η^4 -cycloocta-1,5-diene)platinum (1.076 g, 2.88 mmol) in dichloromethane (30 mL). The reaction mixture was heated under reflux for 4 h. The resulting pale yellow precipitate was filtered off and washed with hexane (30 mL) and vacuum dried. Pale yellow solids **1**, dec. 197–203°C, were obtained in 80% yield. Anal. Found: C, 31.80; H, 3.44; S, 4.20; Cl, 9.38. $\text{C}_{20}\text{H}_{26}\text{SCl}_2\text{Pt}_2$ calc.: C, 31.62; H, 3.45; S, 4.22; Cl, 9.34%.

trans-trans- $[\text{Cl}(\text{PBU}_3)_2\text{Pt}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{Pt}(\text{PBU}_3)_2\text{Cl}]$ (**2**)

Tri-*n*-butylphosphine (552 mg, 2.73 mmol) was added to a suspension of **1** (514 mg, 0.68 mmol) in dichloromethane (30 mL). The reaction mixture was stirred at room temperature for 2 h and then evaporated to dryness under reduced pressure. The residue was dissolved in benzene and the solution was filtered through a column of alumina (30 × 60 mm). The filtrate was evaporated to give white solids. Recrystallization from ethanol gave white needle crystals of **2**, m.p. 104°C, in yield 85%. Anal. Found: C, 46.06; H, 8.09; P, 9.01. $\text{C}_{52}\text{H}_{110}\text{SP}_4\text{Cl}_2\text{Pt}_2$ calc.: C, 46.18; H, 8.20; P, 9.16%.

trans,trans- $[(2\text{-C}_4\text{H}_3\text{S})(\text{PBU}_3)_2\text{Pt}(\mu\text{-}2,5\text{-C}_4\text{H}_2\text{S})\text{Pt}(\text{PBU}_3)_2(2\text{-C}_4\text{H}_3\text{S})]$ (**3**)

n-Butyllithium/hexane (1.2 mL, 2.0 mmol) was added dropwise to a solution of thiophene (155 mg, 1.84 mmol) in THF (10 mL) under an argon atmosphere at 0°C. The reaction mixture was heated at 40°C for 3 h, cooled to room temperature and a solution of **2** (220 mg, 0.16 mmol) in THF (10 mL) was added dropwise. The reaction mixture was heated at 40°C for 3 h and then evaporated to dryness under

reduced pressure. The residue was dissolved in hexane and the solution was washed twice with aqueous saturated ammonium chloride. The organic layer was separated, and filtered through alumina (30 × 50 mm). The solvent was evaporated under reduced pressure to give white solids. Recrystallization from methanol gave **3** as yellow needle crystals in 47% yield, m.p. 91–92°C. Anal. Found: C, 49.58; H, 8.04; P, 8.67. $C_{60}H_{116}S_3P_4Pt_2$ calc.: C, 49.78; H, 8.08; P, 8.56%.

2,5'-Bis(trimethylstannyl)-5-(2'-thienyl)thiophene

n-Butyllithium/hexane (74.0 mL, 121 mmol) was added dropwise to a solution of 2,2'-dithiophene (7.51 g, 45.2 mmol) in THF (50 mL) under an atmosphere of argon at 0°C. The reaction mixture was heated at 40°C for 3 h, cooled to room temperature and a solution of trimethyltin chloride (25.0 g, 126 mmol) in THF (50 mL) was added dropwise. The reaction mixture was stirred at room temperature for 24 h and then the solvent was evaporated. The residue was dissolved in benzene and the solution was washed twice with aqueous saturated ammonium chloride. The organic layer was evaporated to dryness *in vacuo*. Recrystallization from hexane/ethanol gave 18.9 g (85%) of 2,5'-bis(trimethylstannyl)-5-(2'-thienyl)thiophene as white crystals, m.p. 95.5–96.5°C. Anal. Found: C, 34.46; H, 4.28; S, 12.93. $C_{14}H_{22}S_2Sn_2$ calc.: C, 34.19; H, 4.51; S, 13.01%.

[Cl(COD)Pt(μ-2,5'-C₄H₂S-C₄H₂S)Pt(COD)Cl] (4)

2,5'-Bis(trimethylstannyl)-5-(2'-thienyl)thiophene (267 mg, 0.543 mmol) was added to a suspension of [PtCl₂(COD)] (408 mg, 1.09 mmol) in CH₂Cl₂ (30 mL). The reaction mixture was stirred at room temperature for 4 h. The resulting pale yellow precipitate was filtered, washed with CH₂Cl₂ (30 mL) and dried to give a pale yellow solid **4**, dec. 210–215°C, 86% yield. Anal. Found: C, 35.23; H, 3.06. $C_{24}H_{28}S_2PtCl_2$ calc.: C, 34.25; H, 3.35%.

trans,trans-[Cl(PBu₃)₂Pt(μ-2,5'-C₄H₂S)Pt(PBu₃)₂Cl] (5)

Tri-n-butylphosphine (109 mg, 0.540 mmol) was added to a suspension of **4** (103 mg, 0.122 mmol) in CH₂Cl₂ (30 mL). The reaction mixture was stirred at room temperature for 4 h and then evaporated to dryness under reduced pressure. The residue was dissolved in benzene and the solution was filtered through alumina (30 × 100 mm). The solvent was removed under reduced pressure to give red solids of **5**, m.p. 80–81°C, in 50% yield. Anal. Found: C, 47.19; H, 7.57; S, 4.21; Cl, 5.05; P, 8.56. $C_{56}H_{112}S_2P_4Cl_2Pt_2$ calc.: C, 46.89; H, 7.87; S, 4.47; Cl, 4.94; P, 8.54%.

trans-[Pt(2-C₄H₃S)₂(PBu₃)₂], trans-6a

n-Butyllithium/hexane (6.0 mL, 9.7 mmol) was added dropwise to a solution of thiophene (846 mg, 10.1 mmol) in THF (10 mL) under an atmosphere of argon at 0°C. The reaction mixture was heated at 40°C for 3 h, cooled to room temperature and a solution of *trans*-[PtCl₂(PBu₃)₂] (670 mg, 1.0 mmol) in THF (10 mL) was added dropwise. The reaction mixture was heated at 40°C for 3 h and then evaporated to dryness under reduced pressure. The residue was dissolved in hexane and the solution was washed twice with aqueous saturated ammonium chloride. The organic layer was separated, and filtered through alumina (30 × 50 mm). The solvent of filtrate was removed under reduced pressure to give white solids. Recrystallization from ethanol gave 685 mg (90%) of *trans*-**6a** as white

needle crystals, m.p. 118–119°C. Anal. Found: C, 50.30; H, 7.92; P, 8.36. $C_{32}H_{60}P_2S_2Pt$ calc.: C, 50.18; H, 7.90; P, 8.01%.

cis-[Pt(2- C_4H_3S)₂(PBu_3)₂], *cis*-6a

The di-2-thienyl complex *cis*-6a was synthesized as above, starting with *cis*-[PtCl₂(PBu_3)₂] (250 mg, 3.23 mmol) and 2-thienyllithium, prepared from thiophene (638 mg, 7.55 mmol) and n-butyllithium/hexane (5.0 mL, 7.7 mmol). White needle crystals, m.p. 103–104°C, 60% yield. Anal. Found: C, 49.72; H, 8.00; P, 8.00. $C_{32}H_{60}P_2S_2Pt$ calc.: C, 50.18; H, 7.90; P, 8.01%.

trans-[Pd(2- C_4H_3S)₂(PBu_3)₂], *trans*-6b

Synthesized as above, starting *trans*-[PdCl₂(PBu_3)₂] (607 mg, 1.04 mmol) and 2-thienyllithium, prepared from thiophene (845 mg, 10.0 mmol) and n-butyllithium/hexane (6.0 mL, 9.7 mmol). White needle crystals, m.p. 110–110.5°C, 75% yield. Anal. Found: C, 56.82; H, 8.99; P, 9.22. $C_{32}H_{60}P_2S_2Pd$ calc.: C, 56.75; H, 8.93; P, 9.15%.

trans-[Ni(2- C_4H_3S)₂(PBu_3)₂], *trans*-6c

Synthesized as above, starting *trans*-[NiBr₂(PBu_3)₂] (1.37 g, 2.21 mmol) and 2-thienyllithium, prepared from thiophene (1.69 g, 20.12 mmol) and n-butyllithium/hexane (12.0 mL, 18.6 mmol). Pale yellow needles, m.p. 100–102°C, 20% yield. Anal. Found: C, 61.17; H, 9.54; P, 9.75. $C_{32}H_{60}P_2S_2Ni$ calc.: C, 61.05; H, 9.61; P, 9.84%.

trans-[Pt{5-(2'- C_4H_3S)-2- C_4H_2S }₂(PBu_3)₂] (7a)

Synthesized as above, starting *trans*-[PtCl₂(PBu_3)₂] (498 mg, 0.743 mmol) and 5-(2'-thienyl)-2-thienyllithium, prepared from 2,2'-dithiophene (507 mg, 3.05 mmol) and n-butyllithium/hexane (1.5 mL, 2.4 mmol). Yellow crystals, m.p. 137–138°C, 80% yield. Anal. Found: C, 51.79; H, 6.66; P, 6.63; S, 13.82. $C_{40}H_{64}P_2S_4Pt$ calc.: C, 51.65; H, 6.93; P, 6.66; S, 13.79%.

trans-Pd{5-(2'- C_4H_3S)-2- C_4H_2S }₂(PBu_3)₂] (7b)

Synthesized as above, starting *trans*-[PdCl₂(PBu_3)₂] (524 mg, 0.901 mmol) and 5-(2'-thienyl)-2-thienyllithium, prepared from 2,2'-dithiophene (1.855 g, 11.16 mmol) and n-butyllithium/hexane (6.0 mL, 9.8 mmol). Red crystals, m.p. 130–131°C, 80% yield. Anal. Found: C, 57.30; H, 7.45; P, 7.20; S, 15.14. $C_{40}H_{64}P_2S_4Pd$ calc.: C, 57.09; H, 7.67; P, 7.36; S, 15.24%.

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