

Polyhedron 20 (2001) 1939-1945



Syntheses and characterization of heterobimetallic complexes (dppf)Pt(dithiolate) (dppf: bis(diphenylphosphino)ferrocene); X-ray crystal structures of (dppf)PtL where L = dmit, phdt and *i*-mnt

Dong-Youn Noh^{a,*}, Eun-Me Seo^a, Ha-Jin Lee^a, Hong-Young Jang^b, Moon-Gun Choi^b, Young Hwan Kim^c, Jongki Hong^c

^a Department of Chemistry, Seoul Women's University, Seoul 139-774, South Korea ^b Department of Chemistry, Yonsei University, Seoul 120-749, South Korea ^c Mass Spectrometry Analysis Group, Korea Basic Science Institute, Taejon 305-333, South Korea

Received 18 December 2000; accepted 9 March 2001

Abstract

Heterobimetallic complexes of the type (dppf)PtL (dppf = 1,1'-bis(diphenylphosphino)ferrocene; L = dmit (1,3-dithiole-2-thione-4,5-dithiolate), dddt (5,6-dihydro-1,4-dithiin-2,3-dithiolate), phdt (6-hydro-5-phenyl-1,4-dithiin-2,3-dithiolate), dphdt (5,6-diphenyl-1,4-dithiin-2,3-dithiolate), mtdt (1,2-bis(methylthio)ethylene-1,2-dithiolate), *i*-mnt (2,2-dicyano-1,1-ethylenedithiolate)) have been synthesized and studied by a high-resolution FAB-MS, cyclic voltammetry and ³¹P NMR. (Dppf)Pt(*i*-mnt) exhibits one reversible redox peak at $E_{1/2} = 1.225$ V and a strong Pt–P coupling constant ($J_{Pt-P} = 3237$ Hz) due to the electron-accepting property of *i*-mnt ligand. On the contrary, (dppf)Pt(mtdt) shows three reversible redox peaks corresponding to [dppf]^{0/+} ($E_{1/2}^1 = 0.470$ V), [Pt(mtdt)]^{0/+} ($E_{1/2}^2 = 1.050$ V) and [Pt(mtdt)]^{+/2+} ($E_{1/2}^3 = 1.405$ V) processes and a weak Pt–P coupling constant ($J_{Pt-P} = 2962$ Hz) due to relatively strong electron-donor property of mtdt ligand. X-ray structural analyses were performed for the three complexes: (dppf)PtL where L = dmit, phdt and *i*-mnt. The P₂PtS₂ core shows a distorted square planar geometry for the three complexes with P(1)–Pt–P(2) bite angle being larger than 96°. The S(1)–Pt–S(2) bite angle of the *i*-mnt complex is the smallest (74.42°) because of the formation of the four-membered ring. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Pt(II); Dithiolate; Dppf; X-ray crystal structures; Cyclic voltammetry; ³¹P NMR

1. Introduction

Since the discovery of ferrocene (di(η^5 -cyclopentadienyl)iron: Fe(C₅H₅)₂: Fc) [1], the cylindrical molecule with electron-rich aromatic systems has been widely used in the development of catalyst, conducting/optical material, molecular magnet, liquid crystal and polymer because it shows the reversible redox behaviour [2]. One of the representative ligand containing ferrocene is 1,1'bis(diphenylphosphino)ferrocene (dppf) [2–4] which is frequently utilized as a bidentate ligand in the design of catalyst such as (dppf)MX₂ heterobimetallic complex where M = Ni, Pd, Pt, Co, Zn, Cd, Hg and X = Cl, Br, I [2,5–7]. Some variations of these complexes have been reported, among which chloride ions are replaced by the dithiolate ligand to obtain (phosphine)₂M-(dithiolate) complexes [8–10]. They were studied in the light of charge-transfer property, coordination chemistry and the development of water-soluble phosphine complex.

Here, we report the syntheses of new heterobimetallic (dppf)Pt(dithiolate) complexes where dithiolate ligands are 1,3-dithiole-2-thione-4,5-dithiolate (dmit), 5,6-dihy-dro-1,4-dithiin-2,3-dithiolate (dddt), 6-hydro-5-phenyl-1,4-dithiin-2,3-dithiolate (phdt), 5,6-diphenyl-1,4-dithiin-2,3-dithiolate (dphdt), 1,2-bis(methylthio)-1,2-ethylenedithiolate (mtdt) and 2,2-dicyano-1,1-ethylene-dithiolate (*i*-mnt), along with a facile synthetic way of (dppf)PtCl₂ in the three-components solvent system. Chemical properties of [(dppf)Pt] unit are sensitive to

^{*} Corresponding author. Tel.: + 82-2-9705656; fax: + 82-2-9705660.

E-mail address: dynoh@swu.ac.kr (D.-Y. Noh).



Scheme 1. Dithiolate ligand precursors.

the dithiolate ligand, which is studied by means of ${}^{31}P$ NMR and cyclic voltammetry. The crystal structures of (dppf)PtL (L = dmit, phdt, *i*-mnt) are elucidated and compared each other.

2. Experimental

2.1. Instrumentation

Melting points were determined using an electrothermal digital melting point apparatus IA9100 without calibration. The normal FAB mass spectra were taken with the first of the two mass spectrometers of a JMS-HX110/110A tandem mass spectrometer (JEOL, Tokyo, Japan) with mass resolution of 1000 (10% valley) using a JMS-DA 9000 data system. ³¹P NMR spectra were obtained on Varian Unity plus 300 spectrometer using H₃PO₄ as an external reference, infrared spectra by KBr pellet method on MIDAC FT-IR spectrometer, UV-Vis spectra in acetonitrile on HP 8452A diode array spectrometer. Cyclic voltammetry measurements were carried out at room temperature with an EG&G VersaStat model potentiostat/galvanostat in 10 ml CH₂Cl₂ solution containing 0.1 M n-Bu₄N·BF₄ as electrolyte, Ag/Ag⁺ as a reference electrode, Pt-button working electrode, platinum wire as a counter electrode and a 0.05 V s⁻¹ scan rate ($E_{1/2} = 0.705$ V for Fc/Fc⁺ couple).

2.2. X-ray data collection and structure determination

Single crystals suitable for X-ray diffraction study were mounted on a glass capillary, transferred to a

Bruker AXS SMART diffractometer equipped with CCD area detector and Mo K α ($\lambda = 0.71073$ Å) radiation, and centered in the beam at 293(2) K. The structures were solved and refined with the SHELX-97 [11] using direct method and expanded using Fourier techniques. All non-hydrogen atoms were refined anisotropically and hydrogens isotropically.

2.3. Synthesis

Nitrogen bubbling with heating was performed prior to use degassed solvent water. Dithiolate ligand precursors (4,5-dimethylthio-1,3-dithiole-2-one (DMT–DTO) [12], 4,5-ethylenedithio-1,3-dithiole-2-one (EDT– DTO) [13], 4,5-phenylethylenedithio-1,3-dithiole-2-one (PhEDT–DTO) [14], 4,5-diphenyl-ethylenedithio-1,3dithiole-2-one (dPhEDT–DTO) [14] (Scheme 1), Na₂(dmit) [13] and K₂(*i*-mnt) [15] (Scheme 2) were prepared under a dry nitrogen condition according to the literature procedures. All reactions and recrystallizations involving platinum complex were carried out under the protection from light and air.

2.3.1. (dppf) $PtCl_2$

To a 12 ml ethanol suspension of K_2PtCl_4 (0.5 mmol, 21 mg) was added minimum amount of water until the suspension becomes clear. A 12 ml benzene solution of dppf (0.5 mmol, 28 mg) was slowly dropped to this solution with continuous stirring for 12 h. The yellow product was filtered and washed with distilled water and MeOH, and recrystallized from $CH_2Cl_2 + MeOH$. Yield 93%; M.p. 305°C (dec.); HR-FABMS Calc. for $C_{34}H_{28}P_2Cl_2PtFe$ 820.0035. Found 820.0062 (M^+); FT-IR (KBr, cm⁻¹) 3077, 3054 (Ar C–H), 1620, 1481, 1435 (Ar, C=C), 1387, 1308, 1264, 1171, 1096, 1038, 999, 824, 747, 694 (Ar, C–H), 640, 563, 519, 496, 471, 448 (ring-tilt and Fe–Cp in Fc); UV (CH₃CN, nm) 218(st), 268(sh), 432(w).

2.3.2. (dppf)Pt(dmit)

To a 5 ml ethanol solution of Na_2 dmit (0.11 mmol, 27 mg) was slowly added a 5 ml CHCl₃ solution of (dppf)PtCl₂ (0.1 mmol, 82 mg). The yellow product



Scheme 2. Synthesis of platinum complexes.

obtained after 1 h stirring was filtered and washed with distilled water and MeOH, and recrystallized from CHCl₃ + MeOH. Yield 91%; M.p. 218 ~ 220°C (dec.); FABMS (m/z) 945.65 (M^+); FT-IR(KBr, cm⁻¹) 3052 (Ar, C–H), 1636, 1462, 1435 (Ar, C=C), 1387, 1306, 1262, 1167, 1096, 1053, 1032 (C=S), 997, 911, 845, 814, 745, 693 (Ar, C–H), 637, 554, 517, 492, 471, 438, 417 (ring-tilt and Fe–Cp in Fc); UV (CH₃CN, nm) 212(st), 268(sh), 312(w), 466(w).

2.3.3. (dppf)PtL (L = dddt, phdt, dphdt and mtdt)

Dddt complex was prepared as follows: to a 5 ml ethanol suspension of EDT-DTO (0.11 mmol, 23 mg) was added KOH (0.22 mmol, 12 mg) with stirring until it dissolved completely by forming K_2 (dddt), and then a 5 ml CHCl₃ solution of (dppf)PtCl₂ (0.1 mmol, 82 mg). This solution turned to orange colour immediately and yellow precipitate was formed after stirring for 3 h. The yellow product was filtered and washed with distilled water and MeOH, and recrystallized from CH₂Cl₂ + MeOH. Phdt, dphdt and mtdt complexes were also prepared by using an equimolar amount of PhEDT–DTO, dPhEDT–DTO and DMT–DTO, respectively, instead of EDT–DTO.

(dppf)Pt(dddt): yield 86%; m.p. 221 ~ 223°C (dec.); HR-FABMS Calc. for $C_{38}H_{32}P_2PtFeS_4$ 929.9866. Found 929.9865 (M^+); FT-IR (KBr, cm⁻¹) 3050 (Ar, C-H), 2913 (-CH₂), 1636, 1480, 1435 (Ar, C=C), 1385, 1306, 1165, 1096, 1028, 999, 920, 884, 849, 820, 745, 694 (Ar, C-H), 637, 554, 515, 494, 469, 440 (ring-tilt and Fe-Cp in Fc); UV (CH₃CN, nm) 220(st), 246(sh), 316(w), 448(w).

(dppf)Pt(phdt): yield 84%; m.p. $185 \sim 187^{\circ}$ C (dec.); HR-FABMS Calc. for C₄₄H₃₆P₂PtFeS₄ 1006.0181. Found 1006.0173 (*M*⁺); FT-IR (KBr, cm⁻¹) 3052 (Ar, C-H), 2907 (-CH₂), 1638, 1480, 1435 (Ar, C=C), 1385, 1306, 1167, 1096, 1026, 999, 858, 820, 745, 694 (Ar, C-H), 639, 588, 556, 515, 494, 471, 442 (ring-tilt and Fe-Cp in Fc); UV (CH₃CN, nm) 220(st), 246(sh), 316(w), 444(w).

(dppf)Pt(dphdt): yield 93%; m.p. 173 ~ 174°C (dec.); FABMS (m/z) 1081.77 (M^+); FT-IR (KBr, cm⁻¹) 3055, 3034 (Ar, C–H), 1636, 1481, 1435 (Ar, C=C), 1387, 1304, 1265, 1167, 1098, 1028, 999, 889, 849, 818, 745, 694 (Ar, C–H), 637, 588, 554, 517, 492, 469, 442 (ring-tilt and Fe–Cp in Fc); UV (CH₃CN, nm) 222(st), 248(sh), 304(w), 450(w).

(dppf)Pt(mtdt): yield 93%; m.p. $250 \sim 252^{\circ}$ C (dec.); HR-FABMS Calc. for C₃₈H₃₄P₂PtFeS₄ 932.0023. Found 932.0037 (*M*⁺); FT-IR (KBr, cm⁻¹) 3052 (Ar, C–H), 2976, 2913 (–CH₃), 1638, 1480, 1435 (Ar, C=C), 1385, 1304, 1165, 1096, 1028, 999, 965, 870, 849, 826, 747, 696 (Ar, C–H), 637, 554, 517, 496, 471, 438 (ring-tilt and Fe–Cp in Fc); UV (CH₃CN, nm) 214(st), 314(w), 438(w).

2.3.4. (dppf)Pt(i-mnt)

This was prepared following the procedure for (dppf)Pt(dddt) by using excess $K_2(i\text{-mnt})$ (0.2 mmol, 44 mg) instead of K_2 (dddt). Yield 90%; m.p. 217 ~ 220°C (dec.); HR-FABMS Calc. for $C_{38}H_{29}P_2N_2PtFeS_2$ 890.0249. Found 890.0245 (M^+); FT-IR (KBr, cm⁻¹) 3057 (Ar, C–H), 2209 (C=N), 1630, 1481, 1439 (Ar, C=C), 1385, 1308, 1169, 1098, 1026, 997, 926, 889, 824, 748, 696 (Ar, C–H), 637, 559, 515, 494, 473, 440 (ring-tilt and Fe–Cp in Fc); UV (CH₃CN, nm) 214(st), 274(sh), 340(m), 432(w).

3. Results and discussion

3.1. Synthesis and IR/UV-Vis/FABMS analysis

(dppf)PtCl₂ was synthesized in three-solvent system (ethanol:water:benzene = 1:1:1, v/v) by stirring the reaction mixture for 12 h at room temperature without exposure to air and light (Scheme 2). This is a much more facile way of preparing (dppf)PtCl₂ compared to the previous method [6,7] in which a benzene solution of dppf suspended with PtCl₂ was refluxed for 20 h. The yield is 93% for the two cases. (dppf)PtL complexes were easily prepared by mixing (dppf)PtCl₂ prepared thereby and the corresponding dithiolates (Scheme 2) in chloroform via a salt elimination process. The elemental compositions of these complexes were identified by the high-resolution FAB mass measurements except dmit and dphdt complexes that showed relatively low abundance of the molecular ion peaks in the normal FAB mass spectra. In all of the FAB mass spectra measured in this study, the peak at m/z 749 corresponding to [(dppf)Pt]⁺ ion was detected as one of the major peaks.

Infrared spectra of the platinum complexes exhibit v(ring-tilt and Fe–Cp in Fc) at 555 ~ 440 cm⁻¹ in common. The characteristic vibrational peaks originated from the dithiolate ligands are also observed for each complexes: v(C=S) at 1053 and 1032 cm⁻¹ for (dppf)Pt(dmit); v(–CH₂) at 2913 and 2907 cm⁻¹ for (dppf)Pt(ddt) and (dppf)Pt(phdt), respectively; v(–CH₃) at 2976 cm⁻¹ for (dppf)Pt(mtdt); v(C=N) at 2208 cm⁻¹ for (dppf)Pt(*i*-mnt). UV–Vis spectra of (dppf)PtL show a weak band at 432 ~ 450 nm which is attributed to an $e_{2g} \rightarrow e_{1g}$ transition of the ferrocenyl moiety [7]. As for (dppf)Pt(dmit) complex, however, a medium intensity band observed at 466 nm (an $n \rightarrow \pi^*$ transition of C=S moiety) is overlapped with the weak band from the ferrocenyl moiety.

3.2. X-ray molecular structure

Molecular structures of (dppf)PtL (L = dmit, phdt and *i*-mnt) with the selected atom numbering scheme



Fig. 1. ORTEP plot of $(dppf)Pt(dmit) \cdot 1.5(CHCl_3)$ structure (30% ellipsoids). Solvent molecules are omitted for clarity.



Fig. 2. ORTEP plot of (dppf)Pt(phdt) structure (30% ellipsoids).



Fig. 3. ORTEP plot of $(dppf)Pt(i-mnt) \cdot (CH_2Cl_2)$ structure (30% ellipsoids). Solvent molecules are omitted for clarity.

are shown in Figs. 1–3. The crystal data and the selected bond lengths and angles are collected in Tables 1–4. Dithiolate and dppf coordinate to Pt(II) as bidentate ligands, and that the P₂PtS₂ core has a distorted square planar geometry with P(1)–Pt–P(2) bite angle being larger than 96°. This bite angle is also larger than that observed in (dppe)Pt(dmit) (85.2(1)°; dppe = 1,2-bis(diphenylphosphino)ethane) [9] due to the ferrocenyl group in dppf ligand. As for the (dppf)Pt(*i*-mnt) complex, in addition, the S(1)–Pt–S(2) angle is as small as 74.42(11)° due to the four-membered ring formation of 1,1-dithiolate ligand (*i*-mnt) with Pt(II). The strained structure of Pt(*i*-mnt) moiety can cause the less effective overlap between p(S) and d(Pt) orbitals and thereby the longer Pt–S distance (2.352(3) Å). This fact is distinctly

compared to the complexes which contain the less strained five-membered rings such as (dppf)Pt(dmit) (2.327(2) Å), (dppe)Pt(dmit) (2.312(3) Å) [9] and(dppf)Pt(phdt) (2.311(1) Å). And it also affects the electrochemical properties of the complexes as will be discussed below. Two types of (dppf)Pt(dmit) molecules (denoted by A and B as shown in Fig. 1) are in a unit cell, which are crystallographically independent. [Pt(dmit)] units are almost planar but the torsion angle of P(1)-P(2)-S(2)-S(1) for molecule A (6.0°) is larger than the corresponding angle for molecule B (2.9°) . The triclinic unit cell contains, together with six CHCl₃ molecules, two A molecules and two B molecules which form centrosymmetric pairs of A-A and B-B with a head-to-tail mode. Crystal structures of (dppf)Pt(*i*-mnt) and (dppf)Pt(phdt) show a similar pairing arrangement. Molecular planarity of (dppf)Pt(phdt) is the worst out of the three complexes: the ethylene moiety at the periphery of phdt ligand is folded up with 55° of folding angle and P₂PtS₂ core deviates from the planarity with 10.0° of torsion angle for P(2)-S(2)-S(1)-P(1)plane.

3.3. ³¹P NMR and cyclic voltammetry

The ³¹P NMR parameters for the platinum complexes are collected in Table 5 along with the data obtained by cyclic voltammetry measurements. The ³¹P NMR spectra give a typical 1:4:1 triplet [16] centered at 12.760-14.631 ppm depending upon the dithiolate ligands. The magnitude for the Pt-P coupling (J_{Pt-P}) falls in the range of 2962–3237 Hz suggesting a cis coordination of the phosphine ligand [5]. The variation of the NMR parameters can be attributed to the difference of an electron-donation ability of the dithiolate ligand: The better donor property of the dithiolate ligand like phdt the complex contains, the weaker the electron donation of $P \rightarrow Pt$ becomes. Therefore, ³¹P NMR resonance peak at the higher field (14.518-14.631 ppm) and the weaker Pt-P coupling $(J_{Pt-P} = 2989 - 3000 \text{ Hz})$ was observed for (dppf)PtL complexes (L = dddt, phdt anddphdt). On the other hand, the complex with a poor electron-donor (or a good electron-acceptor) such as *i*-mnt ligand, the $P \rightarrow Pt$ donation becomes promoted due to the electron-withdrawing effect of *i*-mnt ligand resulting in the low-field resonance (12.760 ppm) and a strong Pt–P coupling ($J_{Pt-P} = 3237$ Hz). This behaviour can be observed more obviously in (dppf)PtCl₂ complex $(\delta = 11.152 \text{ ppm and } J_{\text{Pt}-P} = 3764 \text{ Hz}).$

The platinum complexes show different redox behaviour in CH₂Cl₂ depending upon the donor ability of a dithiolate ligand. (Dppf)Pt(*i*-mnt) exhibits only one reversible redox peak at $E_{1/2} = 1.225$ V, which is very close to that of (dppf)PtCl₂ ($E_{1/2} = 1.275$ V). It means that the *i*-mnt ligand undergoes the strong electron-withdrawing effect as the chloride ligand in (dppf)PtCl₂

Crystal data and structure refinement for (dppf)Pt(dmit)·1.5(CHCl ₃), (dppf)Pt(phdt) and (dppf)Pt(<i>i</i> -mnt)·(CH ₂ Cl ₂)					
	(dppf)Pt(dmit)·1.5(CHCl ₃)	(dppf)Pt(phdt)	(dppf)Pt(<i>i</i> -mnt)·(CH ₂ Cl ₂)		
Empirical formula	C77H59Cl9Fe2P4Pt2S10	C44H36FeP2PtS4	$C_{39}H_{30}Cl_2FeN_2P_2PtS_2$		
Formula weight	2249.65	1005.85	974.55		
Crystal system	triclinic	monoclinic	monoclinic		
Space group	$P\overline{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)		
Unit cell dimensions					
a (Å)	15.3323(8)	11.8051(2)	13.0408(2)		
b (Å)	17.3610(10)	11.8712(2)	17.35960(10)		
<i>c</i> (Å)	19.1005(11)	28.9891(4)	16.6756(2)		
α (°)	69.3370(10)	90.0	90.0		
β (°)	69.0170(10)	97.6270(10)	96.8030(10)		
γ (°)	66.3340(10)	90.0	90.0		
$V(Å^3)$	4215.9(4)	4026.61(11)	3748.49(8)		
Z	2	4	4		
$D_{\rm calc}$ (Mg m ⁻³)	1.772	1.659	1.727		
Absorption coeff. (mm^{-1})	4.296	4.149	4.486		
F(000)	2204	1992	1912		
Crystal size (mm ³)	$0.95 \times 0.53 \times 0.23$	$0.71 \times 0.42 \times 0.34$	$0.21 \times 0.22 \times 0.71$		
Colour	yellow	red brown	red brown		
2θ range for data collection (°)	1.18 to 24.69	1.42 to 24.71	1.70 to 24.85		
Index ranges	$-18 \le h \le 16, -20 \le k \le 20,$ $-22 \le l \le 13$	$-13 \le h \le 13, -13 \le k \le 9,$ $-33 \le l \le 34$	$-11 \le h \le 15, -20 \le k \le 5,$ $-11 \le l \le 19$		
Reflections collected/unique	$19675/13680 [R_{\odot} = 0.0735]$	$18712/6812 [R_{\odot} = 0.0408]$	$6133/5265 [R_{\odot} = 0.0623]$		
Data/restraints/parameters	13680/0/937	6812/0/469	5265/0/442		
Goodness-of-fit on F^2	1 1 3 9	1 213	1 279		
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0502$ $wR_2 = 0.1329$	$R_{\rm r} = 0.0343$ $wR_{\rm r} = 0.0683$	$R_1 = 0.0658$ $wR_2 = 0.1424$		
R indices (all data)	$R_1 = 0.0569, wR_2 = 0.1525$ $R_2 = 0.0569, wR_2 = 0.1442$	$R_1 = 0.0392$ $wR_2 = 0.0704$	$R_1 = 0.0712$ $wR_2 = 0.1460$		
Largest difference peak and hole (e, \mathring{A}^{-3})	1.510 and 1.938	0.755 and 1.202	1.213 and 1.363		

does: (dppf)PtCl₂ has been known to show more anodic half-wave potential than that of uncoordinated dppf due to the electron-withdrawing property of the chloride ligand as well as the Lewis-acid character of Pt(II)

Table 1

Table 2 Selected bond lengths (Å) and bond angles (°) for (dppf)Pt(dmit)·1.5(CHCl₃)

Bond lengths			
Pt-P(1)	2.284(2)	Pt-P(2)	2.3053(19)
Pt-S(1)	2.3302(19)	Pt-S(2)	2.323(2)
S(1)-C51)	1.748(8)	S(2)–C(52)	1.736(8)
S(3)–C(53)	1.728(9)	S(3)–C(51)	1.752(8)
S(4)–C(53)	1.715(9)	S(4)–C(52)	1.750(8)
S(5)–C(53)	1.661(8)	C(51)–C(52)	1.333(11)
Pt'-P(1')	2.281(2)	Pt'-P(2')	2.3131(19)
Pt'-S(1')	2.322(2)	Pt'-S(2')	2.3306(19)
S(1')–C(51')	1.732(8)	S(2')-C(52')	1.740(8)
S(3')-C(53')	1.728(9)	S(3')–C51')	1.745(9)
S(4')-C(53')	1.718(9)	S(4')-C(52')	1.744(8)
S(5')-C(53')	1.662(9)	C(51')-C(52')	1.350(11)
Bond angles			
P(1)–Pt–P(2)	95.96(7)	P(1)-Pt-S(2)	173.85(7)
P(2)–Pt–S(2)	86.54(7)	P(1)-Pt-S(1)	88.20(7)
P(2)–Pt–S(1)	174.97(7)	S(2)-Pt- $S(1)$	89.59(7)
P(1')–Pt'–P(2')	96.37(7)	P(1')-Pt'-S(1')	174.87(8)
P(2')-Pt'-S(1')	87.03(7)	P(1')-Pt'-S(2')	87.30(7)
P(2')-Pt'-S(2')	176.33(7)	S(1')-Pt'-S(2')	89.33(7)

ion [2,7]. The platinum complexes containing 1,2-dithiolate ligands such as mtdt, dmit, dddt, phdt, dphdt give richer cyclic voltammograms than that of *i*-mnt complex: mtdt complex shows three reversible redox peaks and the others exhibit two reversible and one quasi-reversible peaks. The cyclic voltammograms of mtdt and phdt complexes are demonstrated in Fig. 4. As to the mtdt complex, for example, the electron density on the ferrocene moiety is no more significantly withdrawn by Pt(II) ion and diphenylphosphine moiety because the mtdt ligand is a good electron-donor compared to the *i*-mnt ligand. This can be further supported by the ${}^{31}P$

Table 3								
Selected	bond	lengths	(Å) ai	nd boi	nd angles	(°) f	or	(dppf)Pt(phdt)

Bond lengths			
Pt-P(1)	2.2921(13)	Pt-P(2)	2.2767(13)
Pt-S(1)	2.3119(14)	Pt-S(2)	2.3097(13)
S(1)–C(51)	1.742(6)	S(2)-C(52)	1.756(5)
S(3)–C(51)	1.756(6)	S(3)–C(54)	1.770(8)
S(4)-C(52)	1.746(5)	S(4)–C(53)	1.764(9)
C(51)–C(52)	1.336(8)	C(53)-C(54)	1.331(11)
Bond angles			
P(1) - Pt - P(2)	98.25(5)	P(2) - Pt - S(2)	88.80(4)
P(1)-Pt-S(2)	169.84(5)	P(2) - Pt - S(1)	173.19(5)
P(1)-Pt-S(1)	85.81(5)	S(2)-Pt-S(1)	87.90(5)

Table 4

Selected bond lengths (Å) and bond angles (°) for (dppf)Pt(*i*-mnt)·(CH_2Cl_2)

Bond lengths			
Pt-P(1)	2.285(3)	Pt-P(2)	2.271(3)
Pt-S(2)	2.338(3)	Pt-S(1)	2.365(3)
S(1)–C(51)	1.739(13)	S(2)–C(51)	1.728(12)
N(1)–C(53)	1.137(19)	N(2)-C(54)	1.121(18)
C(51)–C(52)	1.372(17)	C(52)–C(53)	1.42(2)
C(52)–C(54)	1.43(2)		
Bond angles			
P(1) - Pt - P(2)	8.80(11)	P(2) - Pt - S(2)	2.96(11)
P(1) - Pt - S(2)	168.22(11)	P(2)-Pt-S(1)	167.26(11)
P(1) - Pt - S(1)	93.80(11)	S(2)-Pt-S(1)	74.42(11)

Table 5

 $^{31}\mathrm{P}$ NMR and cyclic voltammetry parameters for (dppf)PtL complexes

L	³¹ P NMR	a	Cyclic voltammetry ^b (V)		
	δ (ppm)	$J_{\mathrm{Pt-P}}$ (Hz)	$E^{1}_{1/2}$	$E_{1/2}^{2}$	$E_{1/2}^{3}$
2C1	11.152	3764	1.275		
<i>i-</i> mnt	12.760	3237	1.225		
mtdt	13.213	2962	0.470	1.050	1.405
dmit	13.902	3024	0.915	1.325	1.69 °
dddt	14.593	2989	0.660	1.340	1.56 °
phdt	14.631	3000	0.625	1.295	1.51 °
dphdt	14.518	2989	0.615	1.245	1.47 °

^a δ (ppm) = -19.227 for dppf.

^b 0.01 M samples in CH₂Cl₂ at ca. 298 K, 0.1 M (*n*-Bu₄N)·BF₄ supporting electrolyte, 0.05 V s⁻¹ scan rate, Pt-button working electrode vs. Ag/Ag⁺, Pt wire counter electrode, $E_{1/2} = 0.705$ V for ferrocene.

 $^{\rm c}E_{\rm pa}$ of the quasi-reversible processes.



Fig. 4. Cyclic voltammograms of (dppf)Pt(mtdt) and (dppf)Pt(phdt) measured in CH_2Cl_2 with Pt-button working electrode vs. Ag/Ag⁺, Pt wire counter electrode and 0.05 V s⁻¹ scan rate.

NMR results: the Pt–P coupling of *i*–mnt complex $(J_{Pt-P} = 3237 \text{ Hz})$ is stronger than that of mtdt complex $(J_{Pt-P} = 2962 \text{ Hz})$ due to the increased π -bonding between phosphorus and Pt(II) by the electron-withdrawing effect of *i*-mnt ligand [5]. Considering these facts together, the first half-wave potential of mtdt complex can be attributed to the redox process of Fc/Fc⁺ in dppf and is observed at the most cathodic potential

 $(E_{1/2}^1 = 0.470 \text{ V})$ among those of the platinum complexes measured in this study. It also suggests that [dppf]⁺ formed during the first oxidation process is well stabilized by [Pt(mtdt)] moiety. Consequently, the second and the third half-wave potentials of mtdt complex $(E_{1/2}^2 = 1.050 \text{ V} \text{ and } E_{1/2}^3 = 1.405 \text{ V})$ correspond to the redox processes of $[Pt(mtdt)]^{o/+}$ and $[Pt(mtdt)]^{+/2+}$, respectively. Compared to the redox behaviour of mtdt complex, the platinum complex containing a cyclic 1,2-dithiolate ligand such as phdt, for example, gives two reversible redox peaks at 0.625 and 1.295 V, and one quasi-reversible peak at $E_{pa} = 1.51$ V. The $E_{1/2}^1$ is observed at a higher potential than that of mtdt complex, indicating that phdt is not a better donor than mtdt ligand. Judging from the J_{Pt-P} and $E_{1/2}^1$ values, the order of the donor ability of the dithiolate ligands can be estimated as follows:

mtdt > dddt \approx phdt \approx dphdt > dmit > *i*-mnt.

The dddt, phdt and dphdt ligands contain a 1,4-dithiin ring in common which are known to be an extended π -electron system [14]. The quasi-reversibility of the third redox peak could be attributed to the properties of these ligands as can be seen in the electrochemical studies of [Pt(dddt)₂]²⁻ complex [17]. This can be applied to the dmit complex, too.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 145445-145447 for compounds (dppf)Pt(dmit)·1.5(CHCl₃), (dppf)Pt(phdt) and (dppf)Pt(i-mnt)·(CH₂Cl₂), respectively. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336-033; e-mail: deposit@ccdc.cam. ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by Korea Research Foundation Grant (KRF-99-D00272).

References

- (a) P.L. Pauson, T.L. Kealy, Nature, 168 (1951) 1039. (b) G.
 Wilkinson, M. Rosenblum, M.C. Whiting, R.B. Woodward, J.
 Am. Chem. Soc. 74 (1952) 2125.
- [2] T. Hayashi, A. Togni (Eds.), Ferrocenes, VCH, Weinheim, 1995.
- [3] P. Zanello, G. Opromolla, G. Giorgi, G. Sasso, A. Togni, J.
- Organomet. Chem. 506 (1996) 61.
- [4] G. Pilloni, B. Longato, B. Corain, J. Organomet. Chem. 420 (1991) 57.

- [5] S.O. Grim, R.L. Keiter, W. McFarlane, Inorg. Chem. 6 (1967) 1133.
- [6] D.A. Clemente, G. Pilloni, B. Corain, B. Longato, M. Tiripicchio-Camellini, Inorg. Chim. Acta 115 (1986) L9.
- [7] B. Corain, B. Longato, G. Favero, D. Ajo, G. Pilloni, U. Russo, F.R. Kreissl, Inorg. Chim. Acta 157 (1989) 259.
- [8] C.E. Keefer, S.T. Purrington, R.D. Bereman, B.W. Knight, D.R. Bedgood, P.D. Boyle, Inorg. Chim. Acta 282 (1998) 200.
- [9] R. Vicente, J. Ribas, X. Solans, M. Font-Altaba, A. Mari, P. De Loth, P. Cassoux, Inorg. Chim. Acta 132 (1987) 229.
- [10] (a) C.E. Keefer, R.D. Bereman, S.T. Purrington, B.W. Knight, P.D. Boyle, Inorg. Chem. 38 (1999) 2294. (b) T.R. Jensen, J. McGinley, V. McKee, C.J. McKenzie, Acta Chem. Scand. 52 (1998) 622. (c) C.J. Smith, V.S. Reddy, S.R. Karra, K.V. Katti, L.J. Barbour, Inorg. Chem. 36 (1997) 1786. (d) W. Su, R. Cao,

M. Hong, Z. Zhou, F. Xie, H. Liu, T.C.W. Mak, Polyhedron 16 (1997) 2531.

- [11] G.M. Sheldrick, SHELX-97, Institut fur Anorganische chemie der Universitat, Göttingen, Germany, 1997.
- [12] N. Svenstrup, J. Becker, Synthesis (1995) 215.
- [13] K.S. Varma, A. Bury, N.J. Harris, A.E. Underhill, Synthesis (1987) 837.
- [14] (a) D.Y. Noh, H.J. Lee, J. Hong, A.E. Underhill, Tetrahedron Lett. 37 (1996) 7603. (b) H.J. Lee, D.Y. Noh, Bull. Korean Chem. Soc. 19 (1998) 340. (c) D.Y. Noh, H.J. Lee, A.E. Underhill, Synth. Met. 86 (1997) 1837. (d) H.J. Lee, D.Y. Noh, Polyhedron 19 (2000) 425.
- [15] K.A. Jensen, L. Henriksen, Acta Chem. Scand. 22 (1968) 1107.
- [16] M. Zhou, C.F. Lam, K.F. Mok, P.H. Leung, T.S.A. Hor, J. Organomet. Chem. 476 (1994) C32.
- [17] C. Faulmann, P. Cassoux, E.B. Yagubskii, L.V. Vetoshkina, New J. Chem. 17 (1993) 385.