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# Synthesis, electrochemical properties and reactivity of $[Fe(\eta^5-C_5H_4PPh_2)_2]Pt(benzenethiolate)_2$ complexes: X-ray crystal structure of $[Fe(\eta^5-C_5H_4PPh_2)_2]Pt(SC_6HF_4)_2$

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#### ABSTRACT

Three heteroleptic Pt(II) complexes with 1,1'-bis(diphenylphosphino)ferrocene (dppf) and benzenemonothiolate (BzT) ligands such as benzenethiolate (BT), 2,3,5,6-tetrafluorobenzenethiolate (TFBT) and 3,5-dimethylbenzenethiolate (DMBT), (dppf)Pt(BzT)<sub>2</sub>, were synthesized from (dppf)PtCl<sub>2</sub> and the corresponding benzene-monothiols. X-ray structural analysis of (dppf)Pt(TFBT)<sub>2</sub> showed that the two TFBT ligands are parallel and in an anti-conformation with respect to a slightly distorted P<sub>2</sub>PtS<sub>2</sub> plane. The redox properties of the three Pt(II) complexes are correlated with the electron-donating capability of the monothiolate ligands. The more-electronegative TFBT ligand induces a short Pt–P bond distance (2.273(2) Å), a large Pt–P coupling constant ( $J_{Pt-P}$  = 3171 Hz) and a high oxidation potential ( $E_{pa}^{3}$  = 1.355 V). A charge-transfer complex of (dppf)Pt(DMBT)<sub>2</sub> was prepared by the reaction with F4TCNQ and characterized.

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The heteroleptic Pt(II) complexes with P<sub>2</sub>PtS<sub>2</sub> core have been investigated so far, mainly focusing on structural properties [1-5], and in some cases on redox and luminescent properties [6-8]. These complexes, as other Pd(II) analogues tend to do, show catalytic activity in some organic reactions [9]. Recently, we have reported serial results of our investigation on the P<sub>2</sub>Pt(dithiolate) complexes, where P<sub>2</sub> is an electron-rich diphosphine chelate such as 1,1'-bis(diphenylphosphino)ferrocene (dppf), 1,2-bis(diphenylphosphino)acetylene (dppa) and 3,4-dimethyl-3',4'-bis(diphenylphosphino)tetrathiafulvalene (P2), and (dithiolate) is either 1, 2-ethylenedithiolate or benzene-1,2-dithiolate (bdt) [10-12]. For the (dppa)Pt(bdt) complex [11], we elucidated the redox properties of the P<sub>2</sub>PtS<sub>2</sub> core and luminescent properties varying with substituents such as H, CH<sub>3</sub>, and Cl on the benzene moiety. As for the (P2)Pt(1,2-ethylenedithiolate) system, however, it was found that the redox behavior of the complexes was determined by competition of redox capability between two heteroleptic ligands [12].

As a next step in ongoing investigation of these compounds, we expanded our interests to the monothiolate system  $(P_2)Pt(BzT)_2$  where BzT denotes a benzene-monothiolate such as benzenethiolate (BT), 3,5-dimethylbezenethiolate (DMBT) and 2,3,5,6-tetrafluorobenzenethiolate (TFBT), with a different number of functional groups (H, CH<sub>3</sub> and F) on the benzene moiety. Among them, we

present in this paper the synthesis, electrochemical properties, and reactivity of (dppf)Pt(BzT)<sub>2</sub> complexes.

The  $(dppf)Pt(BzT)_2$  complexes [13] were synthesized by the reaction of  $(dppf)PtCl_2$  with monothiols such as 2,3,5,6-tetrafluorobenzenethiol ((TFBT)H) and 3,5-dimethylbezenethiol ((DMBT)H), and with a lead derivative  $(Pb(BT)_2)$  [14], as shown in Scheme 1. The  $(dppf)Pt(BT)_2$  complex prepared using  $Pb(BT)_2$  is chemically and spectroscopically identical with that prepared by using benzenethiol [6]. The yields (56–72%) were comparatively lower than those of the dithiolate analogues such as  $(dppf)Pt(C_3S_5)$  (91%) and  $(dppf)Pt(S_4C_4H_4)$  (86%) [10], possibly due to the lack of a chelate effect in the monothiolate system. The low stability of the monothiolate system is demonstrated in its FAB-MS data, in which the most intense peak corresponds to that with a loss of one thiolate ligand  $([M-BzT]^+)$ , while the mother peak  $[M]^+$  is less than 11%.

The X-ray crystal structure of  $(dppf)Pt(TFBT)_2$  (Fig. 1) [15] shows that the two TFBT ligands are in an *anti*-conformation with respect to the P<sub>2</sub>PtS<sub>2</sub> plane, as in many metal complexes with a fluorinated benzenethiolate ligand [2–5]. Two TFBT ligands are parallel with the dihedral angle of 15.2(1)°, which is somewhat larger than that found in  $(dppf)Pt(SC_6F_5)_2$  (2.7(2)° and 9.8(3)°) [2] and (dppe)-Ni(SC<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (4.9°) [5]. Therefore, the centroid-centroid distance between the two TFBT rings (4.76(1)Å) is more than 3.6Å, the maximum inter-planar separation between two neighboring  $\pi$ -systems for an intramolecular  $\pi$ – $\pi$  interaction [17]. The  $\Box$ P1P2S2S1 plane in the P<sub>2</sub>PtS<sub>2</sub> core is almost planar, with a torsion angle of 9.52(3)°. The averaged Pt–S bond distance in the  $(dppf)Pt(TFBT)_2$ 

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Scheme 1. Synthesis of (dppf)Pt(BzT)<sub>2</sub> complexes.



**Fig. 1.** The molecular structure of (dppf)Pt(TFBT)<sub>2</sub> with a selected numbering scheme. Selected bond lengths (Å) and angles (°): Pt1–P1 2.273(2), Pt1–P2 2.273(2), Pt1–S1 2.347(2), Pt1–S2 2.358(2), P1–Pt1–P2 98.65(7), P1–Pt1–S1 83.58(7), P2–Pt1–S2 87.90(7), S1–Pt1–S2 90.66(7).

compound (2.353(2) Å) is very close to that found in other monothiolate systems such as  $(dppf)Pt(SC_6F_5)_2$  (2.369(1) Å) [2] and  $(dppf)Pt(SC_6H_5)_2$  (2.359(1) Å) [6], but longer than that in the corresponding dithiolate system such as  $(dppf)Pt(C_3S_5)$  (2.327(2) Å) [10] and  $(dppf)Pt(S_2C_6H_4)$  (2.309(1) Å) [18]. It coincides with the well-known fact that the dithiolate system contains a shorter Pt–S bond distance than that of the monothiolate one because of the delocalized five-membered metallacyclic system [19].

The results of cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of (dppf)Pt(BzT)<sub>2</sub> are shown in Figs. 2 and 3. Their parameters are compared with those of (dppf)PtCl<sub>2</sub> in Table 1. The DMBT and BT complexes exhibit two cycles, within the measured potential range (0.0-2.0 V). The first one, observed at around  $E_{1/2}^3 = 1.228$  V, is reversible, no doubt associated with the redox process of the coordinated dppf ligand ( $[dppf]^{+/0}$ ), as compared to that of (dppf)PtCl<sub>2</sub> ( $E_{1/2}^3 = 1.139$  V). The second one observed at a lower potential region is irreversible, as shown in Fig. 2; since it is not observed in the CV of (dppf)PtCl<sub>2</sub>, it must be responsible for the PtS<sub>2</sub> centered oxidation. Moreover, it is noteworthy that this peak is not observed in CV of TFBT complex (Fig. 3) even though it also has a P<sub>2</sub>PtS<sub>2</sub> core as do the DMBT and BT complexes. This can be explained by the electronegativity difference of the BzT ligands: Pauling's electronegativity (PEN) [20] of the F atom (3.98) is much larger than that of H atom (2.20) and the group electronegativity (GEN) of  $-CH_3$  (2.27–2.55) [21], but is relatively close to that of Cl atom (3.16), and the GEN of TFBT ligand (2.92) [9] is close to the PEN of Br atom (2.96). These facts together suggest that the reason that no redox peak in the Pt(TFBT)<sub>2</sub> moiety was observed in the measured potential region is because of the high electronwithdrawing capability of the TFBT ligand, as in the case of (dppf)PtCl<sub>2</sub>. On the contrary, the DMBT and BT complexes, with a weaker electron-withdrawing capability of the ligands, show such redox cycles at 0.613 V and 0.696 V, respectively. This rationale is also supported by the <sup>31</sup>P NMR results. The P-Pt coupling constant of the TFBT complex ( $J_{P-Pt}$  = 3171 Hz) is much larger than that of DMBT and BT complexes (3000 and 3001 Hz, respectively), which means that the more electron-withdrawing TFBT ligand induces the stronger P–Pt coupling and the larger  $J_{P-Pt}$  value than those of the DMBT and BT complexes (see Table S1 in Supplementary data).

Also noteworthy from the CV results of TFBT complex is that two more irreversible anodic peaks ( $E_{pa}^2 = 1.125$  V and 1.224 V) were detected in the lower potential region of the coordinated dppf cycle ( $E_{pa}^3 = 1.355$  V). The shape and potential of these two irreversible peaks are very sensitive to the scan rate and solvent (see Figs. S1 and S2 in Supplementary data). These two peaks are tentatively thought to represent a rearrangement of the electron-withdrawing TFBT ligand [3].

As a preliminary study on the reactivity of the complexes, the charge-transfer (CT) complex of  $(dppf)Pt(TFBT)_2$  was prepared by reacting it with F4TCNQ (2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-*p*-quinodimethane) in CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>CN, giving a species with composition [ $(dppf)Pt(TFBT)_2$ ]<sub>3</sub>(F4TCNQ)<sub>2</sub> as indicated by elemental analysis data [22]. The UV–Vis spectra of the CT complex in CH<sub>2</sub>Cl<sub>2</sub> show a red-shift of two intense absorption peaks of a neutral F4TCNQ appearing at 394 and 372 nm to 458 nm [23] (see Fig. S3 in Supplementary data). The IR peaks for the C=N vibration observed at 2215



Fig. 2. The cyclic voltammogram (A) and its differential pulse voltammogram (B) of (dppf)Pt(DMBT)<sub>2</sub> measured in CH<sub>2</sub>Cl<sub>2</sub>. The (dppf)Pt(BT)<sub>2</sub> shows the same CV and DPV cycles. Their potentials are compared in Table 1.



Fig. 3. The cyclic voltammogram (A) and its differential pulse voltammogram (B) of (dppf)Pt(TFBT)<sub>2</sub> measured in CH<sub>2</sub>Cl<sub>2</sub>. It was measured between 0.0 V and 2.0 V but only the observed redox cycle is represented (0.8–1.7 V).

#### Table 1

The cyclic voltammetry parameters of (dppf)Pt(BzT) and (dppf)PtCl<sub>2</sub> (in volt).<sup>a</sup>

Compounds	$E_{\rm pa}^1$	$E_{\rm pa}^2$	$E_{\rm pa}^3$	$E_{\rm pc}^3$	$E_{1/2}^{3}$
(dppf)Pt(TFBT) <sub>2</sub>	-	1.125/1.224	1.355	1.221	1.288
(dppf)Pt(DMBT) <sub>2</sub>	0.613	-	1.343	1.114	1.229
(dppf)Pt(BT) <sub>2</sub>	0.696	-	1.341	1.114	1.228
(dppf)PtCl <sub>2</sub>	-	-	1.191	1.087	1.139

<sup>&</sup>lt;sup>a</sup> Scan rate: 50 mV s<sup>-1</sup>; supporting electrolyte: 0.10 M *n*-Bu<sub>4</sub>N·PF<sub>6</sub>; working electrode: Pt-button; counter electrode: Pt-wire; ref. electrode: Ag/AgCl; 1.0 mM samples in CH<sub>2</sub>Cl<sub>2</sub>;  $E_{1/2}$  = 0.565 V for Fc/Fc<sup>+</sup> couple.

and 2227 cm<sup>-1</sup> also shifted to 2137 and 2197 cm<sup>-1</sup> upon formation of the CT complex. Furthermore, the IR peaks of the ferrocenyl group observed in the region of 456–553 cm<sup>-1</sup> were not greatly altered by the F4TCNQ complexation, implying that it may be the P<sub>2</sub>PtS<sub>2</sub> core, rather than the dppf moiety, that is oxidized.

In summary, we successfully synthesized a series of (dppf) Pt(BzT) complexes with BzT = benzenethiolate (BT), 3,5-dimethylbenzenethiolate (DMBT) and 2,3,5,6-tetrafluorobenzenethiolate (TFBT) for the purpose of investigating the dependency of their redox properties on the electronegativity of the functionalized benzenethiolate ligand. The more-electronegative TFBT ligand can induce a shorter Pt–P bond distance, a larger Pt–P coupling constant ( $J_{Pt-P}$ ), and a higher oxidation potential of dppf ligand ( $E_{pa}^{3}$ ) than those of the less electronegative DMBT and BT ligands. Further investigation on the CT complexes of (dppf)Pt(BzT)<sub>2</sub>, as well as (P2)Pt(BzT)<sub>2</sub>, are currently under investigation.

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#### Appendix A. Supplementary material

CCDC 748161 contains the supplementary crystallographic data for (dppf)Pt(TFBT)<sub>2</sub>. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/ j.inoche.2009.11.010.

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  [13] Synthesis of (dppf)Pt(BzT): A CH<sub>2</sub>Cl<sub>2</sub> solution (25 mL) of (dppf)PtCl<sub>2</sub>
- (0.2 mmol, 164 mg), triethylamine (0.8 mmol, 81 mg) and benzenethiols (0.4 mmol, 73 mg of 2,3,5,6-tetrafluorobenzenethiol, 55 mg of 3,5dimethylbenzenethiol) was stirred for 24 h at room temperature under argon atmosphere. The yellow solution was evaporated to obtain the solid residue. (dppf)Pt(TFBT)<sub>2</sub> was purified by column chromatography (SiO<sub>2</sub>, CHCl<sub>3</sub>) and recrystallized from CHCl<sub>3</sub>/MeOH. Yield 56% (124 mg). Mp. > 211 °C (decomp.), HR-FABMS Calc. for C<sub>46</sub>H<sub>30</sub>/<sub>8</sub>FeP<sub>2</sub>PtS<sub>2</sub> 1111.0135 Found 1111.0126 (*M*<sup>+</sup>). FAB-MS (*m*/*z*, %) 1111(*M*<sup>+</sup>, 7), 930([*M*-C<sub>6</sub>HF<sub>4</sub>S]<sup>+</sup>, 100). FT-IR (KBr, cm<sup>-1</sup>) 3054 (Ar C–H), 1624, 1588, 1481, 1436, 1425 (Ar C=C), 1216 (Ar C–F str), 1097 (P-Ph), 1041, 1025, 999 (Ar C-H ip def), 910 (C-F def), 884, 824, 742, 712, 692, SC<sub>6</sub>F<sub>4</sub>H), 4.39 (4H, s, Fc), 4.27 (4H, d, *J* = 1.60 Hz, Fc), <sup>31</sup>P NMR (202 MHz, CDCI<sub>3</sub>, ppm)  $\delta$  17.47 (*J*<sub>Pt-P</sub> = 3171 Hz). <sup>19</sup>F NMR (282 MHz, CDCI<sub>3</sub>, ppm) –134.6 (qn, o-F), -142.9 (qr, m-F). UV-Vis (CH<sub>2</sub>Cl<sub>2</sub>, nm) 238s, 268sh, 356w. (dppf)Pt (DMBT)<sub>2</sub> was purified by column chromatography (SiO<sub>2</sub>, CHCl<sub>3</sub>:MeOH = 30:1) and recrystallized from acetone/n-hexane. Yield 62% (127 mg). Mp. 224-225 °C. HR-FABMS Calc. for  $C_{50}H_{46}FeP_2PtS_2$  1023.1514 Found 1023.1518 ( $M^+$ ). FAB-MS (m/z, %) 1023(M<sup>+</sup>, 11), 866([M-C<sub>8</sub>H<sub>9</sub>S]<sup>+</sup>, 100). FT-IR (KBr, cm<sup>-1</sup>) 3021, 3053 (Ar C-H), 2913, 2855 (-CH<sub>3</sub>), 1592, 1573, 1480, 1436 (Ar C=C), 1095 (P-Ph), 1029, 999 (Ar C-H ip def), 833, 744, 690, 639 (Ar C-H oop def), 553, 515, 494, 471, 456 (Fe-ring vib). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.80 (8H, m, Ph), 7.36 (4H, t, Ph), 7.28 (8H, t, Ph), 6.78 (4H, s, CH in DMBT), 6.37 (2H, s, CH in DMBT), 4.28 (4H, s, Fc), 4.13 (4H, d, *J* = 1.05 Hz, Fc), 2.02 (12H, s, CH<sub>3</sub>). <sup>31</sup>P NMR (202 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  17.68 ( $J_{Pt-P}$  = 3000 Hz). UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>, nm) 232s, 262sh. Synthesis of (dppf)Pt(BT)<sub>2</sub> An acetone solution (20 mL) of Pb(BT)<sub>2</sub> (0.05 mmol, 21 mg) was added to a  $CH_2Cl_2$  solution (10 mL) of (dppf)PtCl\_2 (0.05 mmol, 41 mg) with stirring for 24 h at room temperature. The  $PbCl_2$ precipitate was separated by filtration with Celite, and the purified product recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/n-hexane. Yield 72% (36 mg) Mp. was 245 °C > (decomp.). HR-FABMS Calc. for  $C_{46}H_{38}FeP_{2}FtS_{2}$  967.0857 Found 967.0893 ( $M^{*}$ ). FAB-MS (m/z, %) 967.1 ( $M^{*}$ , 10), 858.1 ( $[M-C_{6}H_{5}S]^{*}$ , 100). FT-IR (KBr, cm<sup>-1</sup>) 3057 (Ar C–H), 1577, 1477, 1435 (Ar C=C), 1095 (P–Ph), 1024, 999 (Ar C-H ip def), 824, 735, 696, 639 (Ar C-H oop def), 552, 515, 494, 470 (Fe-ring vib). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.79 (8H, m, Ph), 7.37 (4H, m, Ph), 7.29 (8H, t, Ph), 7.17 (4H, m, CH in BT), 6.77 (6H, m, CH in BT), 4.29 (4H, s,

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Fc), 4.13 (4H, s, Fc).  $^{31}{\rm P}$  NMR (202 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  18.85 ( $J_{\rm Pt-P}$  = 3001 Hz). UV–Vis (CH<sub>2</sub>Cl<sub>2</sub>, nm) 232s, 262sh.

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