

Ferrocene End-Capped Palladium(II) and Platinum(II) Complexes with Thiophene Spacers

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A series of heterobimetallics containing ferrocene and Pd(II) or Pt(II) have been synthesized by oxidative addition of ferrocene-substituted halothiophenes with zerovalent palladium or platinum precursors. The stable solids were thoroughly characterized by elemental analysis, NMR, UV–vis spectroscopy, and cyclic voltammetry. The rich redox chemistry of the complexes depends on the conjugation length that separates the two metal sites. The crystal structure of a platinum σ -thienyl complex, $(C_5H_5)Fe(C_5H_4CH=CH-th-Pt(PPh_3)_2(Br))$ (th = 2,5-disubstituted thiophene) has been determined.

Introduction

Organo-palladium complexes are versatile reagents in organic chemistry, as exemplified by known palladium-catalyzed molecular rearrangements, oxidations, substitutions, eliminations, and C–C and C–X (X = N, S, O) cross-coupling processes.^{1–5} The C–C and C–heteroatom coupling reactions involve oxidative addition to afford $Pd\{P(aryl)_3\}_2(R)X$ complexes in the initial stage. It is known in some cases that initially the cis isomer is formed which subsequently transforms into the thermodynamically stable trans isomer. The stability of these complexes was found to be crucial for the subsequent transmetalation and reductive-elimination steps in the catalytic cycle.

An array of σ -aryl complexes has been isolated from aryl halides and zerovalent Pd or Pt precursors.^{6,7} Also, it is known that binuclear complexes obtained from the double oxidative addition of dihalo aromatics and $M(PPh_3)_4$ (M = Pd, Pt) are useful building blocks in the design and self-assembly of novel cationic organometallic macrocycles.⁸ Despite extensive studies of C–C and related coupling reactions involving heteroaromatics^{9,10} such as thiophene, only a few oxidative-addition

products of heteroaromatics have been isolated and characterized.¹⁰ Trapping of the catalytic intermediates would provide useful information regarding the reactivity differences of thienyl halides in such cross-coupling reactions.

In this paper, we wish to present the synthesis and characterization of a series of heterobimetallics obtained by the oxidative addition of Pd(0) and Pt(0) precursors such as $M(PPh_3)_4$ (M = Pd, Pt) with ferrocenyl-substituted bromothiophenes. These bromothiophenes can be considered as relatively electron rich, as they are linked by conjugation with ferrocene, an electron-donating organometallic group. Thienylvinyl and thienyl moieties were used as spacers in these heterobimetallics, since oligo(thienylvinylene) and oligo(thiophene), which find use in electronic materials,¹² have stability surpassing that of polyene and conduct electrons with better efficiency than their phenyl analogues. Furthermore, the trinuclear congeners reported herein are potential building blocks for organometallic supramolecules.

Experimental Section

The general procedures pertaining to the synthesis of the compounds reported in this paper and their physical measurements are identical with those previously published.¹³ Column chromatography for **3** was performed with use of silica gel (230–400 mesh, Macherey-Nagel GmbH & Co.) as the stationary phase in a column 30 cm in length and 2.0 cm in diameter. All other chromatography separations were performed using a column 30 cm in length and 4.0 cm in diameter. (Ferrocenylmethyl)triphenylphosphonium bromide,¹⁴ (5-bromo-2-thie-

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- (1) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508.
- (2) (a) Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*, 852. (b) Shaughnessy, K. H.; Hammann, B. C.; Hartwig, J. F. *J. Org. Chem.* **1998**, *63*, 6546.
- (3) Wolfe, J. P.; Wagaw, S.; Jean-Francois, M.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*, 805.
- (4) Louie, J.; Hartwig, J. F. *J. Am. Chem. Soc.* **1996**, *118*, 7217. (b) Louie, J.; Hartwig, J. F. *Tetrahedron Lett.* **1995**, *36*, 3609.
- (5) (a) Wolfe, J. P.; Wagaw, S.; Buchwald, S. L. *J. Am. Chem. Soc.* **1996**, *118*, 7215. (b) Guram, A. S.; Rennels, R. A.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1348.
- (6) (a) Chin, C. C. H.; Yeo, J. S. L.; Loh, Z. H.; Vittal, J. J.; Henderson, W.; Hor, T. S. A. *J. Chem. Soc., Dalton Trans.* **1998**, 3777. (b) Casado, A. L.; Espinet, P. *Organometallics* **1998**, *17*, 954. (c) Paul, F.; Patt, J.; Hartwig, J. F. *Organometallics* **1995**, *14*, 3030. (d) Portnoy, M.; Milstein, D. *Organometallics* **1993**, *12*, 1665.
- (7) (a) Cavell, K. J.; Jin, H.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1992**, 2923. (b) Tam, W.; Calabrese, J. C. *Chem. Phys. Lett.* **1986**, *25*, 508.
- (8) Hicke, A.; Cava, M. P. *J. Org. Chem.* **1998**, *63*, 7413. (b) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.
- (9) Abbotto, A.; Bradamante, S.; Fachetti, A.; Pagani, G. A. *J. Org. Chem.* **1997**, *62*, 5755.

(10) Xie, Y.; Wu, B.; Xue, F.; Ng, S.-C.; Mak, T. C. W.; Hor, T. S. A. *Organometallics* **1998**, *17*, 3988.

(11) (a) Müllen, K.; Wegner, G., Eds. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: New York, 1998. (b) Brisset, H.; Moustarder, S. L.; Blanchard, P.; Illien, B.; Riou, A.; Orduna, J.; Garin, J.; Roncali, J. *J. Mater. Chem.* **1997**, *7*, 2027. (c) Elandaloussi, E. H.; Frère, P.; Roncali, J.; Richomme, P.; Jubault, M.; Gorgues, A. *Adv. Mater.* **1995**, *7*, 390. (d) Petty, M. C.; Bryce, M. R.; Bloor, D., Eds. *An Introduction to Molecular Electronics*; Oxford University Press: New York, 1995.

(12) Manna, J.; Kuehl, C. J.; Whiteford, J. A.; Stang, P. J. *Organometallics* **1997**, *16*, 1897.

(13) Justin Thomas, K. R.; Lin, J. T.; Wen, Y. S. *J. Organomet. Chem.* **1999**, *575*, 301.

nylmethyl)triphenylphosphonium bromide,¹⁴ and ferrocene-carboxaldehyde¹⁵ were prepared according to the literature procedures. (4-Iodobenzyl)phosphonic acid diethyl ester was prepared from 1-iodo-4-(bromomethyl)benzene and phosphorus triethyl ester by a procedure similar to that described for (4-bromobenzyl)phosphonic acid diethyl ester.¹⁶ Cyclic voltammetry experiments were performed with a BAS-100 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgNO₃ reference electrode (0.01 M AgNO₃, 0.1 M TBAP/CH₃CN). The solvent in all experiments was CH₂Cl₂, and the supporting electrolyte was 0.1 M tetrabutylammonium perchlorate. The $E_{1/2}$ values were determined as $1/2(E_p^a + E_p^c)$, where E_p^a and E_p^c are the anodic and cathodic peak potentials, respectively. All potentials reported are not corrected for the junction potential. Ferrocene was used as an external reference both for potential calibration and for reversibility criteria. Under similar conditions the ferrocene has $E_{1/2} = 217$ mV relative to Ag/Ag⁺ and the anodic peak–cathodic peak separation is 90 mV.

2-Bromo-5-[(E)-2-ferrocenyl-1-ethenyl]thiophene (1a). Sodium methoxide was generated in situ by treating sodium (0.23 g, 10 mmol) with MeOH (50 mL). To this vigorously stirred solution was added (5-bromothiophenyl)methyltriphenylphosphonium bromide (5.18 g, 10 mmol). After the mixture was stirred at room temperature for 30 min, ferrocenecarboxaldehyde (2.14 g, 10 mmol) was added. The reddish mixture was slowly heated to 60 °C and allowed to reflux for 6 h. The cooled solution was then poured into ice water and extracted with Et₂O (2 × 50 mL). The combined ether extracts were dried using MgSO₄ and evaporated to leave the crude product. It was chromatographed on silica gel using hexane/CH₂Cl₂ (4:1) mixture as eluant. A 200 mL portion of the eluant was required to collect the desired product. Removal of the solvent and recrystallization of the crude product from hot hexane gave an analytically pure sample in 64% yield. MS (EI): *m/e* 372 (M⁺). ¹H NMR (CDCl₃, TMS): δ 6.88 (d, $J_{H-H} = 3.72$ Hz, 1 H, SCCH), 6.65 (m, 2 H, SCCH and =CH), 6.55 (d, $J_{H-H} = 15.9$ Hz, 1 H, =CH), 4.39 (m, 2 H, C₅H₄), 4.27 (m, 2 H, C₅H₄), 4.12 (s, 5 H, Cp). Anal. Calcd for C₁₆H₁₄BrSFe: C, 51.51; H, 3.51. Found: C, 51.70; H, 3.38.

5'-Bromo-5-(2-ferrocenylvinyl)-2,2'-bithiophene (1b). To a suspension of (ferrocenylmethyl)triphenylphosphonium bromide (2.70 g, 5.00 mmol) and THF (50 mL) was added potassium *tert*-butoxide (0.63 g, 5.66 mmol) through a sidearm with vigorous stirring. After 30 min, 1.36 g (5.00 mmol) of 5'-bromobithiophene-5-carbaldehyde was added at once. The resulting red mixture was refluxed for 6 h; after cooling it was poured into crushed ice and extracted with CH₂Cl₂. The CH₂Cl₂ extracts were washed with brine solutions, dried over MgSO₄, and evaporated to dryness. The crude product, containing mixture of *cis* and *trans* isomers (1.5 g, 66%), was separated from triphenylphosphine oxide by column chromatography on silica using hexane/CH₂Cl₂ (2:3) mixture as eluant. A 200 mL portion of the eluant was required to collect the desired product. Subsequent removal of the solvent and recrystallization of the residue from hot hexane gave pure *trans* isomer (1.3 g, 57%). MS (EI): *m/e* 456 (M⁺). ¹H NMR (acetone-*d*₆, TMS): δ 7.10 (m, 3 H, SCCH), 6.96 (d, $J_{H-H} = 3.87$ Hz, 1 H, SCCH), 6.92 (d, $J_{H-H} = 16.0$ Hz, 1 H, =CH), 6.76 (d, $J_{H-H} = 16.0$ Hz, 1 H, =CH), 4.54 (m, 2 H, C₅H₄), 4.31 (m, 2 H, C₅H₄), 4.15 (s, 5 H, Cp). Anal. Calcd for C₂₀H₁₅BrS₂Fe: C, 52.77; H, 3.32. Found: C, 52.95; H, 3.18.

2-[(E)-2-(5-Bromo-2-thienyl)-1-ethenyl]-5-[(E)-2-ferrocenyl-1-ethenyl]thiophene (1c). Compound **1c** was synthe-

sized by the same procedure as employed for **1b**, except that 2-[(E)-2-(5-bromo-2-thienyl)-1-ethenyl]-2-thiophenecarbaldehyde was utilized instead of 5'-bromobithiophene-5-carbaldehyde. Compound **1c** was isolated in 62% yield. MS (EI): *m/e* 482 (M⁺). ¹H NMR (acetone-*d*₆, TMS): δ 7.09 (d, $J_{H-H} = 3.73$ Hz, 1 H, SCCH), 7.04 (m, 3 H, SCCH and =CH), 6.99 (d, $J_{H-H} = 3.75$ Hz, 1 H, SCCH), 6.92 (d, $J_{H-H} = 3.75$ Hz, 1 H, SCCH), 6.92 (d, $J_{H-H} = 15.8$ Hz, 1 H, =CH), 6.74 (d, $J_{H-H} = 15.8$ Hz, 1 H, =CH), 4.54 (m, 2 H, C₅H₄), 4.32 (m, 2 H, C₅H₄), 4.14 (s, 5 H, Cp). Anal. Calcd for C₂₂H₁₇BrS₂Fe: C, 54.91; H, 3.56. Found: C, 54.71; H, 3.56.

2-[(E)-2-Ferrocenyl-1-ethenyl]-5-iodothiophene (1d). Compound **1d** was synthesized by the same procedure as employed for **1b**, except that 5'-iodothiophene-2-carbaldehyde was utilized instead of 5'-bromobithiophene-5-carbaldehyde. Compound **1d** was isolated in 62% yield. MS (EI): *m/e* 420 (M⁺). ¹H NMR (acetone-*d*₆, TMS): δ 7.08 (d, $J_{H-H} = 3.6$ Hz, 1 H, SCCH), 6.71 (d, $J_{H-H} = 15.9$ Hz, 1 H, =CH), 6.57 (d, $J_{H-H} = 3.6$ Hz, 1 H, SCCH), 6.57 (d, $J_{H-H} = 15.9$ Hz, 1 H, =CH), 4.42 (s, br, 2 H, C₅H₄), 4.29 (s, br, 2 H, C₅H₄), 4.13 (s, 5 H, Cp). Anal. Calcd for C₁₆H₁₂ISFe: C, 45.75; H, 3.12. Found: C, 45.82; H, 2.97.

1-[(E)-2-ferrocenyl-1-ethenyl]-4-iodobenzene (1e). To a stirred mixture of (4-iodobenzyl)phosphonic acid diethyl ester (3.54 g, 10.0 mmol) in THF (100 mL) was added a slight excess of potassium *tert*-butoxide (1.20 g). After 30 min, ferrocenecarboxaldehyde (2.14 g, 10.0 mmol) was added through a sidearm. The mixture was slowly heated to 65 °C and maintained at that temperature for 6 h. The cooled solution was poured into ice water, extracted with diethyl ether, washed with brine solutions, and finally dried over MgSO₄. Evaporation of the ethereal extract left behind a red residue, which was chromatographed on silica gel using hexane/CH₂Cl₂ (4:1) mixture as eluant. A 200 mL portion of the eluant was required to collect the desired product. Removal of the solvent gave the title compound in 59% (2.46 g) yield. MS (FAB): *m/e* 414 (M⁺). ¹H NMR (CDCl₃, TMS): δ 7.61 (d, $J_{H-H} = 8.2$ Hz, 2 H, C₆H₄), 7.13 (d, $J_{H-H} = 8.2$ Hz, 2 H, C₆H₄), 6.85 (d, $J_{H-H} = 16.1$ Hz, 1 H, =CH), 6.564 (d, $J_{H-H} = 16.1$ Hz, 1 H, =CH), 4.47 (m, 2 H, C₅H₄), 4.31 (m, 2 H, C₅H₄), 4.14 (s, 5 H, Cp). Anal. Calcd for C₁₈H₁₅IFe: C, 52.21; H, 3.65. Found: C, 52.34; H, 3.48.

General Procedure for the Synthesis of Palladium-(II) Complexes 2 and Platinum(II) Complexes 3 Derived from 1a–d. A mixture of M(PPh₃)₄ (M = Pd, Pt; 1.00 mmol) and **1a–d** (1.01 mmol) was stirred in deoxygenated benzene (50 mL) for 6 h at room temperature. The color of the solution darkened during the progress of the reaction. The solvent was removed under vacuum and the residue redissolved in 5 mL of CH₂Cl₂. To the reddish CH₂Cl₂ solution was added dry Et₂O (20 mL), and the mixture was cooled to 0 °C to give the desired compounds in excellent yield. The precipitate was filtered, washed thoroughly with Et₂O (3 × 5 mL) and hexane (2 × 10 mL), and dried in vacuo. The platinum(II) complexes **3** are further purified by column chromatography on silica gel using hexane/CH₂Cl₂ (1:1) mixture as eluant. A 50 mL portion of the eluant was required to collect the desired product.

2a: yield 71%. ¹H NMR (CDCl₃, TMS): δ 7.59–7.24 (m, 30 H, C₆H₅), 6.40 (d, $J_{H-H} = 15.7$ Hz, 1 H, =CH), 6.15 (d, $J_{H-H} = 3.4$ Hz, 1 H, SCCH), 5.91 (d, $J_{H-H} = 15.7$ Hz, 1 H, =CH), 5.79 (d, $J_{H-H} = 3.4$ Hz, 1 H, SCCH), 4.26 (m, 2 H, C₅H₄), 4.16 (m, 2 H, C₅H₄), 4.05 (s, 5 H, Cp). ³¹P NMR (CDCl₃, TMS): δ 23.1. Anal. Calcd for C₅₂H₄₃BrP₂S₂FePd: C, 62.20; H, 4.32. Found: C, 62.34; H, 4.48.

2b: yield 92%. ¹H NMR (CDCl₃, TMS): δ 7.56–7.26 (m, 30 H, C₆H₅), 6.75–6.53 (m, 5 H, SCCH and =CH), 6.27 (d, $J_{H-H} = 15.6$ Hz, 1 H, =CH), 6.20 (d, $J_{H-H} = 3.5$ Hz, 1 H, SCCH), 5.76 (d, $J_{H-H} = 3.5$ Hz, 1 H, SCCH), 4.39 (m, 2 H, C₅H₄), 4.26 (m, 2 H, C₅H₄), 4.12 (s, 5 H, Cp). ³¹P NMR (CDCl₃, TMS): δ 23.3. Anal. Calcd for C₅₈H₄₇BrP₂S₂FePd: C, 62.63; H, 4.26. Found: C, 62.88; H, 4.36.

(14) Zhang, J.-X.; Dubois, P.; Jerome, R. *Synth. Commun.* **1996**, *26*, 3091.

(15) Rosenblum, M.; Banerjee, A. K.; Danieli, N.; Fish, R. W.; Schlatter, V. *J. Am. Chem. Soc.* **1963**, *85*, 316.

(16) Kennedy, G.; Perboni, A. D. *Tetrahedron Lett.* **1996**, *42*, 7611.

2c: yield 90%. ^1H NMR (CDCl_3 , TMS): δ 7.66–7.33 (m, 30 H, C_6H_5), 6.83 (d, $J_{\text{H-H}} = 16.0$ Hz, 1 H, =CH), 5.75 (d, $J_{\text{H-H}} = 3.7$ Hz, 1 H, SCCH), 6.57 (d, $J_{\text{H-H}} = 16.0$ Hz, 1 H, =CH), 6.48 (d, $J_{\text{H-H}} = 3.7$ Hz, 1 H, SCCH), 6.42 (d, $J_{\text{H-H}} = 3.7$ Hz, 1 H, SCCH), 5.87 (d, $J_{\text{H-H}} = 3.7$ Hz, 1 H, SCCH), 4.49 (m, 2 H, C_5H_4), 4.27 (m, 2 H, C_5H_4), 4.13 (s, 5 H, Cp). ^{31}P NMR (CDCl_3 , TMS): δ 23.3. Anal. Calcd for $\text{C}_{56}\text{H}_{45}\text{BrP}_2\text{S}_2\text{FePd}$: C 61.92; H, 4.18. Found: C, 62.04; H, 3.91.

2d: yield 93%. ^1H NMR (CDCl_3 , TMS): δ 7.57 (m, 12 H, $\sigma\text{-C}_6\text{H}_5$), 7.31 (m, 18 H, m - and $p\text{-C}_6\text{H}_5$), 6.38 (d, $J_{\text{H-H}} = 15.7$ Hz, 1 H, =CH), 6.14 (d, $J_{\text{H-H}} = 3.5$ Hz, 1 H, SCCH), 5.90 (d, $J_{\text{H-H}} = 15.7$ Hz, 1 H, =CH), 5.77 (d, $J_{\text{H-H}} = 3.5$ Hz, 1 H, SCCH), 4.26 (m, 2 H, C_5H_4), 4.16 (m, 2 H, C_5H_4), 4.05 (s, 5 H, Cp). ^{31}P NMR (CDCl_3 , TMS): δ 23.3. Anal. Calcd for $\text{C}_{52}\text{H}_{43}\text{IP}_2\text{S}_2\text{FePd}$: C, 59.42; H, 4.12. Found: C, 59.08; H, 4.01.

2e: yield 90%. ^1H NMR (CDCl_3 , TMS): δ 7.54–7.19 (m, 30 H, C_6H_5), 6.50–6.29 (m 6 H, C_6H_4 and =CH), 4.35 (m, 2 H, C_5H_4), 4.20 (m, 2 H, C_5H_4), 4.08 (s, 5 H, Cp). ^{31}P NMR (CDCl_3 , TMS): δ 23.0. Anal. Calcd for $\text{C}_{54}\text{H}_{45}\text{IP}_2\text{FePd}$: C, 62.06; H, 4.34. Found: C, 61.88; H, 4.10.

3a: yield 42%. ^1H NMR (CDCl_3 , TMS): δ 7.65–7.30 (m, 30 H, C_6H_5), 6.41 (d, $J = 15.9$ Hz, 1 H, =CH), 6.06 (d, $J = 3.4$ Hz, 1 H, SCCH), 5.93 (d, $J_{\text{H-H}} = 15.9$ Hz, 1 H, =CH), 5.75 (d, $J_{\text{H-H}} = 3.7$ Hz, $J_{\text{H-Pt}} = 46$ Hz, 1 H, SCCH), 4.27 (m, 2 H, C_5H_4), 4.16 (m, 2 H, C_5H_4), 4.06 (s, 5 H, Cp). ^{31}P NMR (CDCl_3 , TMS): δ 23.8 ($J_{\text{H-Pt}} = 2874$ Hz). Anal. Calcd for $\text{C}_{52}\text{H}_{43}\text{BrP}_2\text{S}_2\text{FePt}$: C, 57.16; H, 3.97. Found: C, 56.78; H, 3.79.

3b: yield 48%. ^1H NMR (CDCl_3 , TMS): δ 7.64–7.29 (m, 30 H, C_6H_5), 6.78–6.56 (m, 5 H, SCCH and =CH), 6.26 (d, $J_{\text{H-H}} = 15.9$ Hz, 1 H, =CH), 6.15 (d, $J_{\text{H-H}} = 3.5$ Hz, 1 H, SCCH), 5.75 (d, $J_{\text{H-H}} = 3.4$ Hz, $J_{\text{H-Pt}} = 45$ Hz, 1 H, SCCH), 4.43 (m, 2 H, C_5H_4), 4.28 (m, 2 H, C_5H_4), 4.13 (s, 5 H, Cp). ^{31}P NMR (CDCl_3 , TMS): δ 23.9 ($J_{\text{H-Pt}} = 2858$ Hz). Anal. Calcd for $\text{C}_{58}\text{H}_{47}\text{BrP}_2\text{S}_2\text{FePt}$: C, 58.01; H, 3.94. Found: C, 57.79; H, 3.76.

3c: yield 52%. ^1H NMR (CDCl_3 , TMS): δ 7.69–7.34 (m, 30 H, C_6H_5), 6.83 (d, $J_{\text{H-H}} = 15.9$ Hz, 1 H, =CH), 6.73 (d, $J_{\text{H-H}} = 3.8$ Hz, 1 H, SCCH), 6.56 (d, $J_{\text{H-H}} = 15.9$ Hz, 1 H, =CH), 6.46 (d, $J_{\text{H-H}} = 3.6$ Hz, 1 H, SCCH), 6.32 (d, $J_{\text{H-H}} = 3.6$ Hz, 1 H, SCCH), 5.78 (d, $J_{\text{H-H}} = 3.6$ Hz, $J_{\text{H-Pt}} = 46$ Hz, 1 H, SCCH), 4.40 (m, 2 H, C_5H_4), 4.27 (m, 2 H, C_5H_4), 4.12 (s, 5 H, Cp). ^{31}P NMR (CDCl_3 , TMS): δ 23.8 ($J_{\text{H-Pt}} = 2842$ Hz). Anal. Calcd for $\text{C}_{56}\text{H}_{45}\text{BrP}_2\text{S}_2\text{FePt}$: C, 57.25; H, 3.86. Found: C, 57.33; H, 3.79.

1,1'-Bis(*p*-iodophenylvinyl)ferrocene (4). Compound **4** was prepared in 59% yield by following a procedure similar to that described for **1d** using 1,1'-ferrocenedicarboxaldehyde and diethyl (4-iodobenzyl)phosphonate. MS (FAB): m/e 642 (M^+). ^1H NMR (CDCl_3 , TMS): δ 7.48 (d, $J = 8.3$ Hz, 4 H, C_6H_4), 6.90 (d, $J = 8.3$ Hz, 4 H, C_6H_4), 6.63 (d, $J = 16.1$ Hz, 2H, =CH), 6.41 (d, $J = 16.1$ Hz, 2 H, =CH), 4.41 (m, 4 H, C_5H_4), 4.26 (m, 4 H, C_5H_4). Anal. Calcd for $\text{C}_{26}\text{H}_{20}\text{I}_2\text{Fe}$: C, 48.64; H, 3.14. Found: C, 48.36; H, 3.03.

Synthesis of Trinuclear FePd₂ Complex 5 from 4. Compound **5** was synthesized in 75% yield by the same procedure as employed for **2**, except that **4** was used instead of **1**. ^1H NMR (CD_2Cl_2 , TMS): δ 7.68–7.31 (m, 60 H, C_6H_5), 7.31–7.19 (m, 8 H, C_6H_4 and =CH), 4.46 (m, 2 H, C_5H_4), 4.28 (m, 2 H, C_5H_4), 4.08 (s, 5 H, Cp). ^{31}P NMR (CDCl_3 , TMS): δ 22.9. Anal. Calcd for $\text{C}_{98}\text{H}_{80}\text{I}_2\text{P}_4\text{FePd}_2$: C, 61.82; H, 4.23. Found: C, 61.79; H, 3.91.

1,1'-Bis[2-(5-bromo-2-thienyl)ethenyl]ferrocene (6). Sodium metal (0.12 g, 5.2 mmol) was dissolved in methanol (50 mL) under nitrogen. (5-Bromo-2-thienylmethyl)triphenylphosphonium bromide (2.7 g, 5.0 mmol) was added with vigorous stirring followed by 1,1'-ferrocenedicarboxaldehyde (0.48 g, 2.0 mmol). The red mixture was refluxed overnight, cooled, and poured into ice water. The resulting reddish residue was extracted with CH_2Cl_2 and the extract dried over anhydrous MgSO_4 . Evaporation of the organic extract left a red syrup. It was purified by column chromatography on silica gel using CH_2Cl_2 /hexane (1:4) as eluant. A 100 mL portion of the eluant

was collected. Removal of the solvent gave a red oil which contained three inseparable isomers (eg., cis,cis, cis,trans, and trans,trans). It was dissolved in toluene and heated at reflux for 2 h. A small amount of iodine was used as catalyst. This effectively converted the products into the all-trans isomer. Crystallization from hot hexane gave reddish brown powdery **6** (0.76 g, 66%). MS (FAB): m/e 558 (M^+). ^1H NMR (CD_2Cl_2 , TMS): δ 6.85 (d, $J = 3.75$ Hz, 2 H, SCCH), 6.59 (d, $J = 16.1$ Hz, 2 H, =CH), 6.53 (d, $J = 3.75$ Hz, 2H, SCCH), 6.35 (d, $J = 16.1$ Hz, 2 H, =CH), 4.41 (t, $J = 1.7$ Hz, 4 H, C_5H_4), 4.27 (t, $J = 1.7$ Hz, 4 H, C_5H_4). Anal. Calcd for $\text{C}_{22}\text{H}_{16}\text{Br}_2\text{S}_2\text{Fe}$: C, 47.17; H, 2.88. Found: C, 47.06; H, 3.02.

Synthesis of Trinuclear FePd₂ Complex 7 from 6. Compound **7** was synthesized in 71% yield by the same procedure as employed for **5**, except that **6** was used instead of **4**. ^1H NMR (CD_2Cl_2 , TMS): δ 7.68–7.23 (m, 60 H, C_6H_5), 6.35 (d, 8 H, $J = 15.9$ Hz, 2 H, =CH), 6.16 (d, $J = 3.36$ Hz, 2H, SCCH), 5.95 (d, 2 H, $J = 15.9$ Hz, 2 H, =CH), 5.92 (d, $J = 3.36$ Hz, 2H, SCCH), 4.13 (br, s, 4 H, C_5H_4), 4.04 (br, s, 4 H, C_5H_4). ^{31}P NMR (CD_2Cl_2 , TMS): δ 25.3. Anal. Calcd for $\text{C}_{96}\text{H}_{76}\text{Br}_2\text{P}_4\text{S}_2\text{FePd}_2$: C, 61.96; H, 4.20. Found: C, 62.12; H, 4.32.

Structure Determination of 3a. Crystals of **3a** were grown by slow diffusion of hexane into a concentrated solution of **3a** in CH_2Cl_2 . Diffraction data were collected with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated $\text{Mo K}\alpha$ ($\lambda = 0.7107$ Å) radiation with the θ - 2θ scan mode at room temperature. Absorption corrections according to ψ scans of three reflections were made. All the data processing was performed using the Shelxl¹⁷ package. The Fe and Pt atoms were located by Patterson techniques; all other atoms were located by subsequent Fourier maps and cycles of least-squares refinement. All non-hydrogen atoms were refined anisotropically, and all non-hydrogen atoms were placed in idealized positions with $d_{\text{C-H}} = 0.95$ Å. At the end of refinement there existed four peaks near platinum. Modeling them for a diffused solvent, either CH_2Cl_2 or hexane, did not lead to any significant improvement. The results provided here are for a CH_2Cl_2 solvate. Relevant experimental details are listed in Table 1. All other crystal data for **3a** are given in the Supporting Information.

Results and Discussion

Synthesis of Ferrocenyl Derivatives. The ferrocenyl derivatives required for the present study were easily available from conventional Wittig or Wittig-Horner reactions (Scheme 1). The Wittig reaction generally leads to a mixture of *E* and *Z* isomers. Careful recrystallization from hot hexane by exploiting the higher solubility of the *Z* isomers led to the separation of analytically pure *E* isomers in good yields. Only the *E* isomer was subjected to the oxidative-addition reactions. The *E* isomers are characterized by their AB quartet with a coupling constant of ca. 16.0 Hz. In the proton NMR spectra recorded in CDCl_3 /acetone- d_6 all the three ligands **1a–c** exhibited three upfield signals corresponding to the ferrocene group. Two unresolved multiplets were observed for the substituted Cp ring, while the unsubstituted Cp ring resonated at a upfield position as a sharp singlet. Thiophene protons appear as two doublets in **1a**, and four doublets are seen for **1b** and **1c**.

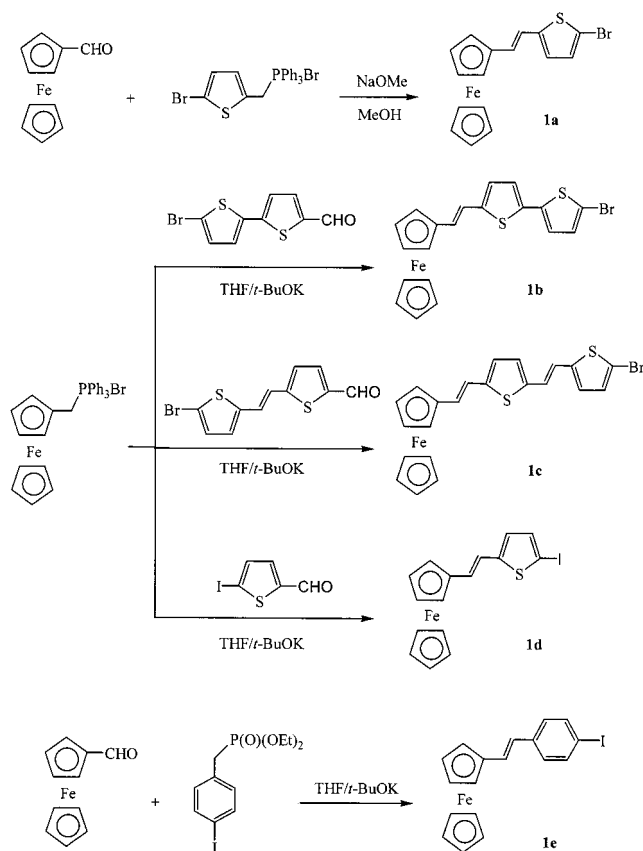
Synthesis of M(PPh₃)₂(th)Br Derivatives. The utility of zerovalent $\text{M}(\text{PPh}_3)_4$ in the preparation of *trans*- $\text{M}(\text{PPh}_3)_2(\text{R})\text{X}$ complexes ($\text{X} = \text{halide}$ and $\text{R} =$

(17) Sheldrick, G. M. SHELXL-Structure Determination Package; University of Göttingen, Göttingen, Germany.

Table 1. Crystal Data for Compound 2d

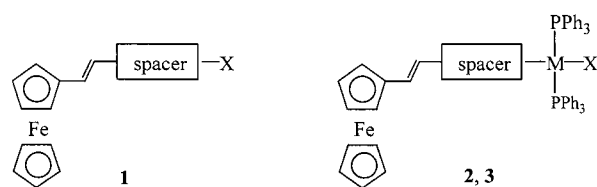
chem formula	C ₅₃ H ₄₅ BrCl ₂ P ₂ SFePt
fw	1177.64
space group	P $\bar{1}$
a, Å	12.190(2)
b, Å	13.078(3)
c, Å	17.502(4)
α , deg	79.64(1)
β , deg	71.63(1)
γ , deg	65.22(2)
V, Å ³	2400.6(9)
Z	2
T, °C	+20
F(000)	1164
λ (Mo K α), Å	0.7107
ρ_{calcd} , g cm ⁻³	1.629
μ , cm ⁻¹	43.02
transmissn coeff	0.41–0.17
2 θ_{max} , deg	50
hkl range	-12 to +14, 0–15, -20 to +20
no. of rflns collected	8883
no. of indep rflns	8446
refinement method	full-matrix least squares on F ²
GOF on F ² b	0.993
final R indices (I > 2 σ (I)) ^a	R1 = 0.0815, wR2 = 0.2187
R indices (all data)	R1 = 0.1073, wR2 = 0.2391
largest diff peak and hole (e Å ⁻³)	4.075 and -4.938

^a R1 = $\sum(|F_o| - |F_c|)/\sum|F_o|$; wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_c^2)^2]^{1/2}$.
^b GOF = $[\sum w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$, where n = no. of observed reflections and p = number of variables. w = $[o^2(F_o^2 - F_c^2) + (g_1P) + g_2P]^{-1}$; P = $[\max(F_o^2, 0) + 2F_c^2]/3$.

Scheme 1

alkyl, aryl, alkenyl, acyl) is well-documented.^{12,18} In fact, it has been demonstrated that the relative reactivity

(18) (a) Sen, A.; Chen, J.-T.; Vetter, W. M.; Whittle, R. R. *J. Am. Chem. Soc.* **1987**, *109*, 148. (b) Stille, J. K. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S. Eds.; Wiley: Chichester, England, 1985; Vol. 2, Chapter 9.

Scheme 2

2a: spacer = thiophene, M = Pd, X = Br
2b: spacer = bithiophene, M = Pd, X = Br
2c: spacer = dithienylethylene, M = Pd, X = Br
2d: spacer = thiophene, M = Pd, X = I
2e: spacer = *p*-C₆H₄, M = Pd, X = I

3a: spacer = thiophene, M = Pt, X = Br
3b: spacer = bithiophene, M = Pt, X = Br
3c: spacer = dithienylethylene, M = Pt, X = Br

order for group 10 M(PPh₃)₄ complexes with the C(aryl)–halide bond is Ni(0) > Pd(0) > Pt(0) and C–I > C–Br > C–Cl.¹⁹ It is also established that electron-withdrawing groups (e.g., CN, CF₃, NO₃) *para* to the C–X bond of the phenyl derivatives activate the aryl–X bond for Pd(PPh₃)₄. Conversely, electron-donating groups suppress the reactivity of aryl halides. Enhanced reactivity of triethylphosphine complexes was reported by Parshall¹⁹ and is attributed to the increase in nucleophilicity of the reactive species “M(PEt₃)₂” resulting from the increase in basicity of phosphine (P(alkyl)₃ vs PPh₃). Similar generalizations are not yet known for the halothiophenes.

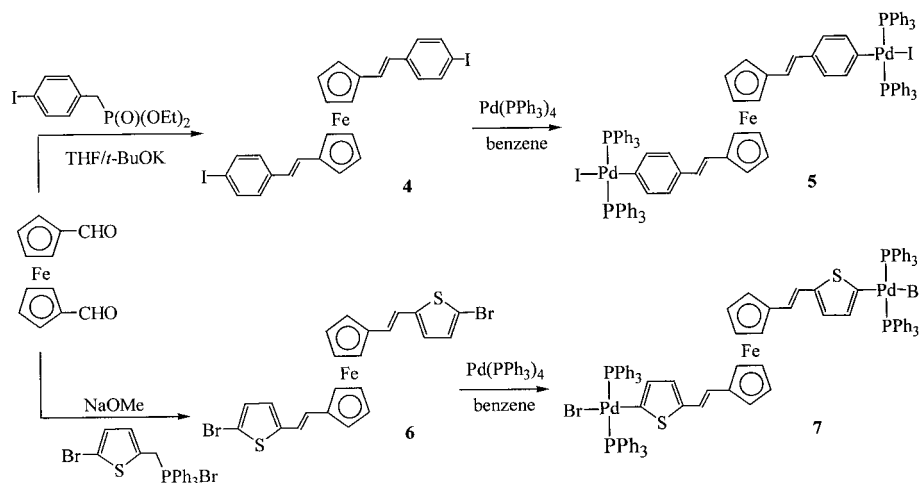
Reaction of 1 equiv of Pd(PPh₃)₄ with the respective bromothiophenes (Scheme 2) in benzene at room temperature generates the reddish orange *trans*-Pd(PPh₃)₂-(th)Br (th = 2,5-disubstituted thiophene) complexes in excellent yields. However, Pt(PPh₃)₄ required harsh conditions (refluxing for 24 h). The decreased reactivity of the Pt(0) complex is in accordance with previous findings for aryl halides.¹² To the best of our knowledge, oxidative-addition products of Pt(PPh₃)₄ and bromothiophenes have not yet been reported. Owing to the electron-donating nature of ferrocene, it was expected that compounds **1a–c** would exhibit reduced reactivity in comparison to the unsubstituted bromothiophenes. It was found, however, that the reactivity is very similar to that observed for bromothiophenes.¹¹ The heterobimetallic complexes are orange or red air- and moisture-stable solids. However, in solution the Pd(PPh₃)₂(th)Br complexes decompose if exposed to air for 1 week.

The ¹H NMR spectra of the palladium and platinum complexes **2** and **3** display a downfield resonance at ca. 7.7–7.3 ppm attributed to the PPh₃ hydrogens. The ferrocene hydrogens appear as a singlet and two unresolved multiplets. The β -proton in the thiophene moiety adjacent to the metal site exhibits significant upfield resonances when compared to the free ligands, **1**. A similar behavior was also reported recently by Hor and co-workers for σ -thienyl complexes of palladium(II).²⁰ This shielding is a consequence of the η^1 -M–C bond and is more pronounced for thienyl derivatives (**2a–d**) than

(19) (a) Mantovani, A. *J. Organomet. Chem.* **1983**, *255*, 385. (b) Parshall, G. W. *J. Am. Chem. Soc.* **1974**, *96*, 2360. (c) Gerlack, D. H.; Kane, A. R.; Parshall, G. W.; Jesson, J. P.; Mutttert, E. L. *J. Am. Chem. Soc.* **1971**, *93*, 3543.

(20) Xie, Y.; Ng, S. C.; Wu, B.-M.; Xue, F.; Mak, T. C. W.; Hor, T. S. *A. J. Organomet. Chem.* **1997**, *531*, 175.

Scheme 3

Table 2. Optical Absorption Spectral Data for the Complexes^a

compd	λ_{\max} (nm)	ϵ_{\max} ($\times 10^{-3}$ M ⁻¹ cm ⁻¹)	compd	λ_{\max} (nm)	ϵ_{\max} ($\times 10^{-3}$ M ⁻¹ cm ⁻¹)
1a	463	1.32	2d	449	2.57
	<i>333</i>	<i>20.58</i>		<i>353</i>	<i>28.08</i>
1b	460 (sh)	25.92	2e	452	1.46
	<i>378</i>			<i>327</i>	<i>26.77</i>
1c	480 (sh)			270 (sh)	
	<i>411</i>	32.41	3a	<i>356</i>	23.22
	<i>314</i>	6.82	3b	<i>403</i>	25.09
1d	463	1.87	3c	<i>433</i>	39.23
	<i>337</i>	23.6		<i>324</i>	7.27
1e	460	1.30	4	470	2.08
	370 (sh)			<i>302</i>	40.00
	<i>315</i>	23.26	5	470	2.48
	<i>275</i>	13.60		<i>340</i>	52.40
2a	441	2.24	6	468	2.52
	<i>353</i>	23.60		<i>354</i> (sh)	
	<i>308</i> (sh)			<i>325</i>	38.52
2b	398	28.04	7	454	4.73 (sh)
	<i>306</i>			<i>375</i>	
2c	429	40.00		<i>346</i>	41.98 (sh)
	<i>320</i> (sh)	15.56		<i>318</i>	

^a Measured in CH₂Cl₂. λ_{\max} values for the π - π^* transition are given in italics.

for the aryl derivative **2e**. For the platinum complexes **3**, the β -proton resonance is accompanied by a pair of doublets centered about the major peak due to coupling to platinum (ca. 45 Hz). The ³¹P{¹H} NMR spectra of the palladium complexes display a downfield shift at ca. 23 ppm referenced to 85% phosphoric acid (δ 0 ppm). For the corresponding platinum species, the ³¹P{¹H} signal is observed as a sharp singlet accompanied by platinum satellites. The J_{P-Pt} coupling ranges from 2842 to 2874 Hz, as expected for *trans*-PtP₂ systems.²¹

When both Cp rings are derivatized with aryl halides, a similar synthetic strategy can be applied for the synthesis of trinuclear complexes (Scheme 3).

Electronic Spectroscopy. The UV-vis spectra (Table 2) of the heterobimetallic complexes show two prominent bands. The high-energy intense band is ascribed to the π - π^* transition of the organic ligand. The low-energy weak absorption may arise from a forbidden d-d transition.²² In the platinum and the palladium complexes the π - π^* transition is shifted to

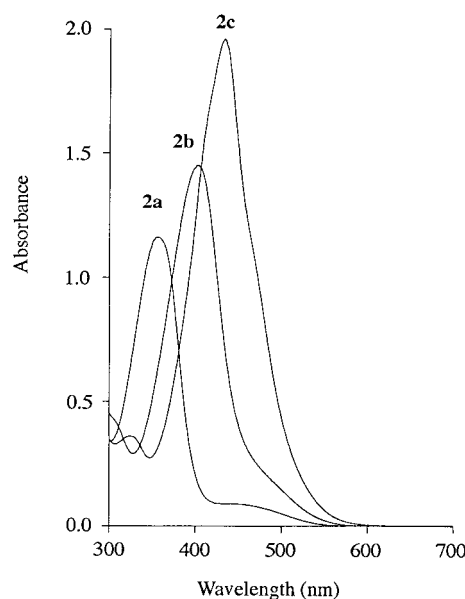


Figure 1. Electronic spectra (5.0×10^{-5} M in CH₂Cl₂) of **2a-c**.

lower energy and the intensity is increased (Figure 1), suggesting additional charge-transfer character from the platinum or palladium centers.²³ As expected, within a series the π - π^* transition progressively shifts to longer wavelengths with increasing chain length.

Cyclic Voltammetric Studies. Pertinent cyclic voltammetric data for the complexes were presented in Table 3. All the ligands **1** exhibit a reversible oxidation of the ferrocene moiety slightly positive of the standard ferrocene. It is noteworthy that the conjugated polyenes and polynes can be considered as electron-accepting groups. When the conjugation length is increased, the oxidation of ferrocene becomes easier; i.e., $E_{1/2}$ shifts to more negative potential. This is in analogy with what is observed for phenylene derivatives, where oxidation is favored by the delocalization of the charge along the conjugation system.²⁴

All the heterobimetallic complexes exhibit two reversible redox processes (for example, see Figure 2). The

(21) (a) Crociani, B.; DiBianci, F.; Giovenco, A.; Berton, A.; Bertini, R. *J. Organomet. Chem.* **1989**, *361*, 255. (b) Anderson, G. K.; Clark, H. C.; Davies, J. A. *Organometallics* **1982**, *1*, 64.

(22) Sohn, Y. S.; Hendrickson, D. A.; Gray, H. B. *J. Am. Chem. Soc.* **1971**, *93*, 3603.

(23) (a) Lopez, C.; Granell, J. *J. Organomet. Chem.* **1998**, *555*, 211. (b) Burdeniuk, J.; Milstein, D. *J. Organomet. Chem.* **1993**, *451*, 213.

Table 3. Electrochemical Data for the Complexes^a

compd	E_1	E_2	ΔE
1a	0.023 (102)		
1b	0.009 (101)		
1c	-0.002 (93)		
1d	0.088 (101)		
1e	0.006 (120)		
2a	-0.076 (87)	0.335 (84)	411
2b	-0.030 (90)	0.258 (87)	288
2c	-0.018 (86)	0.199 (79)	217
2d	-0.003 (89)	0.511 (132)	514
2e	-0.026 (80)		
3a	-0.094 (88)	0.255 (87)	349
3b	-0.025 (89)	0.125 (89)	150
3c	-0.032 (90)	0.200 (87)	232
4	-0.003 (96)		
5	-0.039 (107)		
6	-0.015 (96)	0.810 (i)	
7	-0.119 (90)	0.291 (100)	410

^a All the potential values are in V for a scan rate of 100 mV/s. The ΔE_p values are given in parentheses in mV. All potentials in V vs ferrocene (0.00 V with $\Delta E_p = 90$ mV under similar conditions).

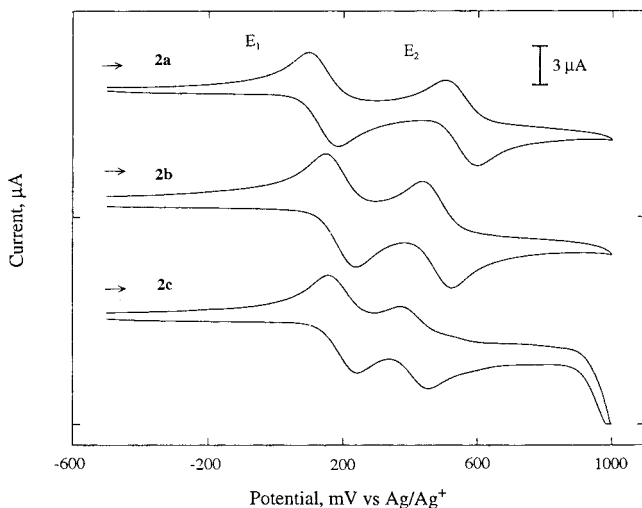
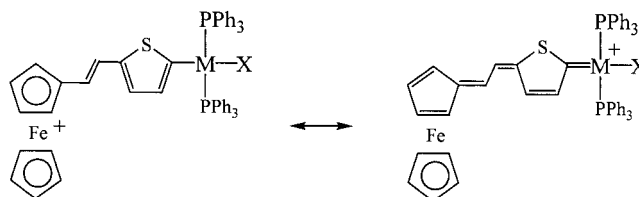


Figure 2. Cyclic voltammetric responses of **2a–c** (scan rate 100 mV/s).

peak separation and virtually equal currents indicate two reversible one-electron oxidations. The less positive oxidation wave is ascribed to the Fe(III)/Fe(II) couple. The more positive redox process (E_2) is proposed to arise from the linker (thienyl moiety) between the Fe and Pd/Pt metal centers. The reasons for this assumption are as follows: (1) E_2 is unlikely to be due to Pd(II) or Pt(II), since it differs only slightly between **2** and **3**; (2) no such oxidation wave is observed in complexes with phenyl linkers, such as **2e** and **5**. The Fe(III)/Fe(II) reduction potentials of **2** and **3** are considerably lower than those of **1**, implying the presence of delocalization of Pd/Pt electron density into the spacer chain through a $d\pi \rightarrow p\pi$ interaction (Scheme 4). The reversibility of CV waves for oligothiophenyl ligands was reported to be enhanced as the length of the oligothiophene increased in ruthenium oligo(thienylacetylde) complexes.²⁵ The reversibilities of the redox waves for the thienyl linker in complexes **2** and **3** are remarkable in view of the relatively short chain length of the linker. No reversible

(24) Matas, J.; Uriel, S.; Peris, U.; Llusar, R.; Houbrechts, S.; Persoons, A. *J. Organomet. Chem.* **1998**, *562*, 197.

(25) Zhu, Y.; Millet, D. B.; Wolf, M. O.; Rettig, S. J. *Organometallics* **1999**, *18*, 1930.

Scheme 4

redox wave was observed for the thiophene segment of **1**, indicating a significant contribution from ferrocene and $M(PPh_3)_2X$ ($M = Pd, Pt$) to the stability of the thiophene cations resulting from **2** and **3**. It has been reported previously that electron donor substituents greatly stabilized the radical cations and dications of short-chain oligo(thiophenes).²⁶

Within a series of heterobimetallic complexes the Fe(III)/Fe(II) couple is shifted cathodically on increasing the conjugation length. Thus, for instance, in compound **2a** the Fe(III)/Fe(II) couple is located at 0.141 V, which is 58 mV negative of that of **2c**. It is interesting to note that a reverse effect is observed for the monometallic ferrocene derivatives **1**. In **2a** and **3a** the smaller conjugation length favors electron transfer from Pd/Pt to ferrocene and, thus, the oxidation. The sensitivity of the ferrocenyl fragment to the presence of remote substituents attached via a conjugated linker is frequently observed in complexes where ferrocenyl groups have been used as redox spectators.^{27–29} The lower oxidation potential of **2a** (0.141 V) compared to that of **2e** (0.191 V) and of **7** (0.098 V) compared to that of **5** (0.178 V) can be attributed to a more effective conjugation by the thiophene moiety compared to the benzenoid moiety.³⁰ The presence of two Pd moieties has a greater influence on the oxidation potential of ferrocene: e.g., **5** (0.178 V) vs **2e** (0.191) and **7** (0.098 V) vs **2a** (0.141 V). It is well-documented that oligo(thiophenes) and oligo(thienylene–vinylene) have lower oxidation potentials as the conjugation length increases.^{31,32} Recently Wolf and co-workers have also reported a similar trend in some ruthenium oligo(thienylacetylde) complexes.²⁵ We found that the oxidation of the thiophene linker is indeed easier as the conjugation length increases. Consequently, the separation between the two redox processes (ΔE), $E_{Fc} - E_{linker}$, diminishes as the conjugation length increases.

On scanning to more positive potentials, we observed polymer deposition on the working electrode, with concomitant deterioration in current response.

X-ray Crystal Structure of 3a. A ORTEP drawing of **3a** is shown in Figure 3. Selected bond distances and angles are listed in Table 4. The structure is the first

(26) Garcia, P.; Pernaut, M.; Hapiot, P.; Wintgens, V.; Valat, P.; Garnier, F.; Delabouglise, D. *J. Phys. Chem.* **1993**, *97*, 513.

(27) Bhadhade, M. M.; Das, A.; Jeffery, J. C.; McCleverty, J. A.; Bodiola, J. A. N.; Ward, M. D. *J. Chem. Soc., Dalton Trans.* **1995**, 2769.

(28) Constable, E. C. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 407.

(29) Lee, S.-M.; Marcaccio, M.; McCleverty, J. A.; Ward, M. D. *Chem. Mater.* **1998**, *10*, 3272.

(30) Ito, S.; Kobayashi, H.; Kikuchi, S.; Morita, N.; Asao, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 3225.

(31) (a) Nakanishi, H.; Sumi, N.; Aso, Y.; Otsubo, T. *J. Org. Chem.* **1998**, *63*, 8632. (b) Noma, N.; Kawaguchi, K.; Imae, I.; Nakano, H.; Shirota, Y. *J. Mater. Chem.* **1996**, *6*, 117. (c) Martinez, F.; Voelkel, R.; Naegele, D.; Naarmann, H. *Mol. Cryst. Liq. Cryst.* **1989**, *167*, 227.

(32) Jestin, I.; Frère, P.; Mercier, N.; Levillain, E.; Stievenard, D.; Roncali, J. *J. Am. Chem. Soc.* **1998**, *120*, 8150.

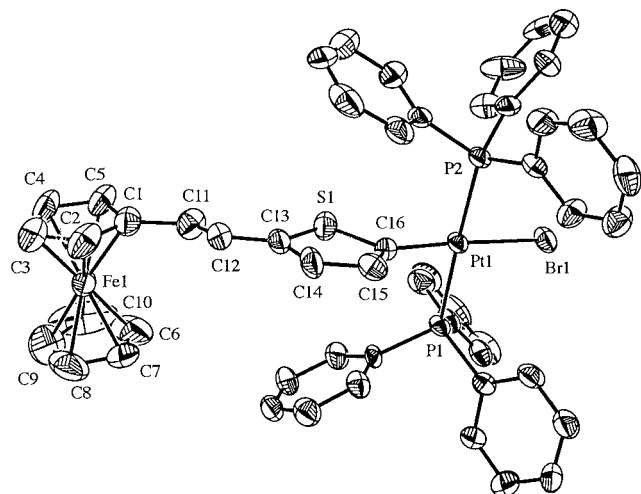


Figure 3. ORTEP drawing of **3a**. Thermal ellipsoids are drawn with 50% probability boundaries.

platinum σ -thienyl complex. The platinum assumes a square-pyramidal geometry with two trans-disposed triphenylphosphine ligands. The Pt–C distance (1.98(1) Å) is in accordance with that of a related phenyl analogue.¹² The thienyl plane is nearly perpendicular to the coordination plane derived from P(1), Br(1), C(16), and P(2). All other distances and angles are similar to those observed for related derivatives.^{10,12}

Conclusions

The heterobimetallic complexes incorporating ferrocene and Pd or Pt separated by a varying conjugation

Table 4. Selected Bond Distances (Å) and Angles (deg) for **3a**

Distances			
Pt1–C16	1.98(1)	C13–C14	1.35(2)
Pt1–P1	2.309(3)	C14–C15	1.41(2)
Pt1–P2	2.312(3)	C15–C16	1.38(2)
Pt1–Br1	2.512(1)	S1–C13	1.73(2)
		S1–C16	1.73(1)
Angles			
C16–Pt1–P1	89.0(4)	C16–Pt1–Br1	177.4(3)
C16–Pt1–P2	91.2(4)	P1–Pt1–Br1	88.70(8)
P1–Pt1–P2	177.0(1)	P2–Pt1–Br1	91.02(9)

length constructed from vinylthiophene subunits have been successfully obtained in good to excellent yields. They show reversible redox behavior that may be useful for the study of intervalence electron transfer and near-IR spectra. Efforts in this direction and in extending this protocol to synthesize heterobimetallics incorporating other transition metals are underway.

Acknowledgment. We thank Academia Sinica and the National Science Council (Grant NSC-88-2113-M-001-045) for financial support.

Supporting Information Available: Tables of atomic coordinates and thermal parameters, all bond distances and angles, and experimental data for X-ray diffraction studies of **3a**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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