2026 *Inorg. Chem.* **2010**, *49*, 2026–2028
DOI: 10.1021/ic902289h

Inorganic Chemistry
Communication

Platinum Complexes of η^2-Thiophenes

Runyu Tan and Datong Song*

Davenport Chemical Research Laboratories, Department of Chemistry, University of Toronto,
80 St. George Street, Toronto, Ontario, Canada M5S 3H6

Received November 18, 2009

Two novel ligands, 3,4-bis(quinolin-8-yl)thiophene and 3,4-bis-[6-(trifluoromethoxyl)quinolin-8-yl]thiophene, and their corresponding diplatinum complexes have been synthesized and fully characterized. These two complexes feature the inverse sandwich structures and the η^2-C,C thiophenes on platinum centers.

With the increasing demands for sulfur removal from natural gas and petroleum products, a lot of research efforts have been expended to develop new hydrodesulfurization (HDS) catalysts.[1] Homogeneous models of heterogeneous HDS processes have regained a lot of interest recently because it is difficult to understand the mechanisms of heterogeneous processes.[2] Information obtained from the homogeneous model systems not only shines light on the heterogeneous processes but also leads to the discovery of efficient homogeneous catalytic systems. Several model studies have focused on the reactions between transition-metal complexes and thiophenes. Accordingly, a variety of transition-metal complexes of thiophenes with various coordination modes have been observed, including the sulfur-bound η^1 mode with groups 6 and 8 metals,[3] the η^4 mode (π-bound via four carbon atoms) with group 9 metals,[4] the η^5 mode with groups 6, 8, and 9 metals.[5] Some of these have been proposed as relevant intermediates in the HDS processes.

Mas-Ballesté et al. have proposed that a platinum(II) complex of η^2-thiophene is an important intermediate prior to hydride transfer in their thiophene activation process.[2c] Jones has proposed that a platinum(0) complex of η^2-C,C (π-bound via two carbon atoms at the 2 and 3 positions) thiophene is an important intermediate prior to the η^2-C,S (π-bound via sulfur and carbon) mode and the C−S bond activation step.[2b,6] Despite the importance of the η^2-bound thiophene, to the best of our knowledge, no η^2-thiophene complex or any π-bound thiophene complex of group 10 metals has been isolated and structurally characterized to date. In fact, the η^2-thiophene complexes, in general, are scarce,[7] implying the labile nature of such a coordination mode. We envisioned that an adjacent auxiliary ligand may help to anchor a metal center onto the thiophene ring and stabilize the η^2-C,C mode through the chelate effect, allowing the isolation of η^2-thiophene complexes. In addition, such an auxiliary ligand must also block the reaction pathways toward the η^2-C,S mode and cyclometalation. In our latest ligand design, quinoline moieties, as auxiliary ligands, have been installed onto a thiophene ring. This strategy allows us to isolate the unprecedented platinum complexes with η^2-C,C-thiophenes. Herein, we report the synthesis and full characterization of these novel ligands and the corresponding inverse sandwich diplatinum complexes.

---

*To whom correspondence should be addressed. E-mail: dsong@chem.utoronto.ca.

(1) (a) Afanasiev, P.; Bezverkhyy, I. *Appl. Catal., A* **2007**, *322*, 129. (b) Bianchini, C.; Meli, A.; Vizza, F. *J. Organomet. Chem.* **2004**, *689*, 4277. (c) Diaz, B.; Sawhill, S. J.; Bale, D. H.; Main, R.; Phillips, D. C.; Korlann, S.; Self, R.; Bussell, M. E. *Catal. Today* **2003**, *86*, 191.

(2) (a) Torres-Nieto, J.; Brennessel, W. W.; Jones, W. D.; Garcia, J. J. *J. Am. Chem. Soc.* **2009**, *131*, 4120. (b) Atesin, T. A.; Jones, W. D. *Inorg. Chem.* **2008**, *47*, 10889. (c) Nova, A.; Novio, F.; González-Duarte, P.; Lledós, A.; Mas-Ballesté, R. *Eur. J. Inorg. Chem.* **2007**, 5707. (d) Li, H.; Carpenter, G. B.; Sweigart, D. A. *Organometallics* **2000**, *19*, 1823. (e) Myers, A. W.; Jones, W. D. *Organometallics* **1996**, *15*, 2905. (f) Dullaghan, C. A.; Sun, S.; Carpenter, G. B.; Weldon, B.; Sweigart, D. A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 212. (g) Bianchini, C.; Frediani, P.; Herrera, V.; Jiménez, M. V.; Meli, A.; Rincón, L.; Sánchez-Delgado, R.; Vizza, F. *J. Am. Chem. Soc.* **1995**, *117*, 4333. (h) Dong, L.; Duckett, S. B.; Ohman, K. F.; Jones, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 151.

(3) (a) Choi, M. G.; Angelici, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 8753. (b) Wasserman, H. J.; Kubas, G. J.; Ryan, R. R. *J. Am. Chem. Soc.* **1986**, *108*, 2294.

(4) (a) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2544. (b) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1990**, *112*, 199.

(5) (a) Howard, K. E.; Lockemeyer, J. R.; Massa, M. A.; Rauchfuss, T. B.; Wilson, S. R.; Yang, X. *Inorg. Chem.* **1990**, *29*, 4385. (b) Lockemeyer, J. R.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *J. Am. Chem. Soc.* **1989**, *111*, 8828. (c) Skaugset, A. E.; Rauchfuss, T. B.; Stern, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 2432. (d) Luo, S.; Ogilvy, A. E.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1991**, *10*, 1002. (e) Waldbach, T. A.; van Eldik, R.; van Rooyen, P. H.; Lotz, S. *Organometallics* **1997**, *16*, 4056. (f) Du Toit, A.; Landman, M.; Lotz, S. *J. Chem. Soc., Dalton Trans.* **1997**, 2955. (g) Landman, M.; Waldbach, T.; Gorls, H.; Lotz, S. *J. Organomet. Chem.* **2003**, *678*, 5.

(6) (a) Atesin, T. A.; Jones, W. D. *Organometallics* **2008**, *27*, 53. (b) Atesin, T. A.; Atesin, A. C.; Skugrud, K.; Jones, W. D. *Inorg. Chem.* **2008**, *47*, 4596.

(7) (a) Doshi, A.; Venkatasubbaiah, K.; Rheingold, A. L.; Jäkle, F. *Chem. Commun.* **2008**, 4264. (b) Zhao, L.; Mak, T. C. W. *Organometallics* **2007**, *26*, 4439. (c) Baier, M.; Gleiter, R.; Rominger, F. *Eur. J. Org. Chem.* **2006**, 5264. (d) Delafuente, D. A.; Myers, W. H.; Sabat, M.; Harman, W. D. *Organometallics* **2005**, *24*, 1876. (e) Meiere, S. H.; Brooks, B. C.; Gunnoe, T. B.; Carrig, E. H.; Sabat, M.; Harman, W. D. *Organometallics* **2001**, *20*, 3661. (f) Wang, D.; Hwang, W.; Liang, L.; Wang, L.; Lee, L.; Chiang, M. Y. *Organometallics* **1997**, *16*, 3109. (g) Deeming, A. J.; Jayasuriya, S. N.; Arce, A. J.; De Sanctis, Y. *Organometallics* **1996**, *15*, 786. (h) Choi, M.-G.; Angelici, R. J. *Organometallics* **1992**, *11*, 3328. (i) Deeming, A. J.; Arce, A. J.; De Sanctis, Y.; Day, M. W.; Hardcastle, K. I. *Organometallics* **1989**, *8*, 1408.

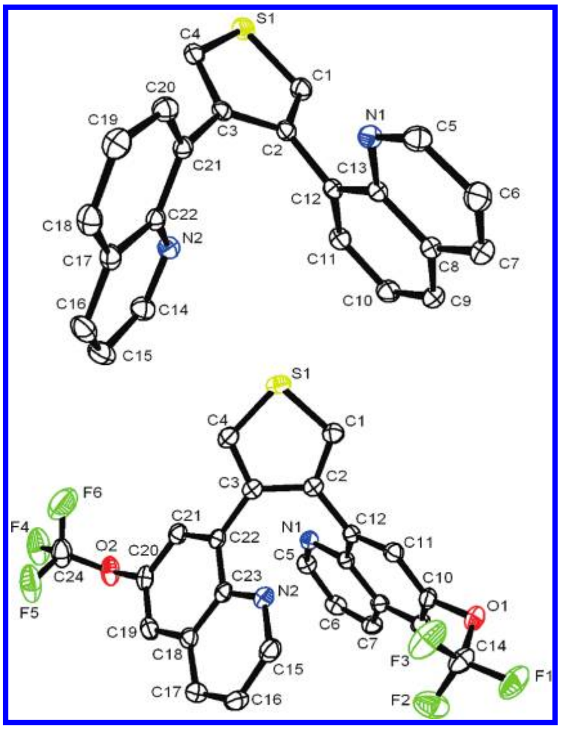
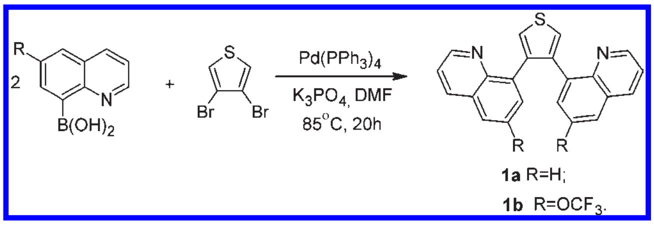


Figure 1. Molecular structures of **1a** (top) and **1b** (bottom) with thermal ellipsoids plotted at 50% probabilities. Hydrogen atoms are omitted for clarity.

Scheme 1. Syntheses of Ligands **1a** and **1b**



The ligands **1a** and **1b** can be synthesized via Suzuki coupling reactions[8] from the appropriate boronic acids[9] and 3,4-dibromothiophene catalyzed by Pd(PPh$_3$)$_4$ in *N*,*N*-dimethylformamide/H$_2$O mixed solvents in the presence of K$_3$PO$_4$ (Scheme 1). X-ray crystallography confirms the solid-state structures of **1a** and **1b** (Figure 1). The ^{1}H and ^{13}C NMR spectra of **1a** and **1b** show only one set of quinolinyl signals and one singlet from the thiophene linker, suggesting fast rotation of the quinolinyl groups in solution. The thiophene protons resonate as singlets in the typical aromatic region at 7.66 and 7.70 ppm for **1a** and **1b**, respectively.

The air- and moisture-stable complexes **2** can be prepared in nearly quantitative yield by reacting the corresponding ligands **1** with 1 equiv of Pt$_2$(CH$_3$)$_4$(SMe$_2$)$_2$ (Scheme 2). The molecular structures of complexes **2** have been unambiguously confirmed by X-ray crystallography and are shown in Figure 2. The two platinum centers in each molecule of **2** are located on opposite sides of the central thiophene ring, forming an inverse sandwich. Each square-planar Pt^{II} center, displaying typical bond lengths and angles in its coordination sphere,[10] is coordinated with two mutually cis methyl ligands, a nitrogen donor atom from a quinolinyl group, and a C=C double bond from the thiophene ring. The solution ^{1}H and ^{13}C NMR spectra of compounds **2** indicate symmetric structures,

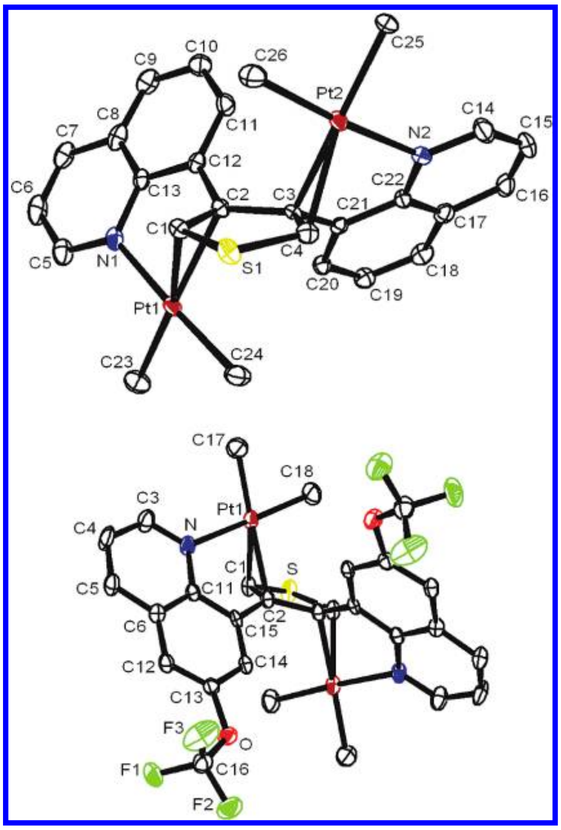
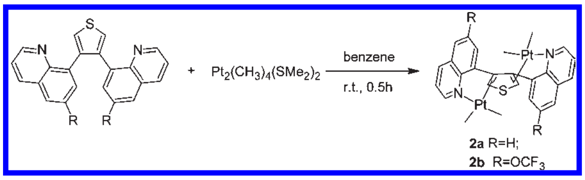


Figure 2. Molecular structures of **2a** (top) and **2b** (bottom) with thermal ellipsoids plotted at the 50% probability. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): for **2a**, Pt(1)−C(24) 2.046(4), Pt(1)−C(23) 2.047(4), Pt(1)−N(1) 2.130(3), Pt(1)−C(1) 2.218(3), Pt(1)−C(2) 2.256(3), Pt(2)−C(26) 2.041(4), Pt(2)−C(25) 2.047(4), Pt(2)−N(2) 2.130(3), Pt(2)−C(4) 2.218(4), Pt(2)−C(3) 2.245(3), C(24)−Pt(1)−C(23) 86.2(2), C(24)−Pt(1)−N(1) 173.8(1), C(23)−Pt(1)−N(1) 92.2(2), C(24)−Pt(1)−C(1) 96.1(1), C(23)−Pt(1)−C(1) 158.4(2), N(1)−Pt(1)−C(1) 87.6(1), C(24)−Pt(1)−C(2) 100.9(1), C(23)−Pt(1)−C(2) 163.2(2), N(1)−Pt(1)−C(2) 79.1(1), C(1)−Pt(1)−C(2) 36.8(1), C(26)−Pt(2)−C(25) 85.4(2), C(26)−Pt(2)−N(2) 174.2(1), C(25)−Pt(2)−N(2) 91.2(1), C(26)−Pt(2)−C(4) 95.8(1), C(25)−Pt(2)−C(4) 159.7(2), N(2)−Pt(2)−C(4) 89.1(1), C(26)−Pt(2)−C(3) 103.0(1), C(25)−Pt(2)−C(3) 161.8(2), N(2)−Pt(2)−C(3) 79.1(1), C(4)−Pt(2)−C(3) 36.9(1);for **2b**, Pt(1)−C(18) 2.041(4), Pt(1)−C(17) 2.048(4), Pt(1)-N 2.134(3), Pt(1)−C(1) 2.197(4), Pt(1)−C(2) 2.251(4), C(18)−Pt(1)−C(17) 84.4(2), C(18)−Pt(1)−N 174.0(2), C(17)−Pt(1)−N 93.1(2), C(18)−Pt(1)−C(1) 97.6(2), C(17)−Pt(1)−C(1) 158.9(2), N−Pt(1)-C(1) 86.8(1), C(18)−Pt(1)−C(2) 101.9(2), C(17)−Pt(1)−C(2) 162.9(2), N−Pt(1)-C(2) 79.1(1), C(1)−Pt(1)−C(2) 36.9(1).

Scheme 2. Syntheses of **2a** and **2b**



---

(8) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147.

(9) Tan, R.; Jia, P.; Rao, Y.; Jia, W.; Hadzovic, A.; Yu, Q.; Li, X.; Song, D. *Organometallics* **2008**, *27*, 6614–6622.

(10) (a) Wei, F.; Bönnemann, H. *Appl. Organometal. Chem.* **2005**, *19*, 94. (b) Bennett, M. A.; Chee, H.; Jeffery, J. C.; Robertson, G. B. *Inorg. Chem.* **1979**, *18*, 1071.

consistent with the solid-state structure established by X-ray crystallography. The two protons of the thiophene ring resonate as a singlet at 5.82 and 5.86 ppm for **2a** and **2b**, respectively, significantly upfield-shifted compared to those of the free ligands. These large upfield shifts presumably originate from the back-donation from the electron-rich platinum centers to the thiophene rings and the consequent decrease in the aromaticity of the thiophene ring. The well-resolved platinum satellites around the thiophene−proton signal also suggest that the bonds between platinum and the thiophene ring are retained in solution. The Pt−H coupling constant ($^2J_{\mathrm{Pt-H}}$ = 50 Hz) is slightly larger than that of [(COD)Pt(CH$_3$)$_2$] ($^2J_{\mathrm{Pt-H}}$ = 40 Hz).[10b] The two types of methyl groups give rise to two singlets in the ^{1}H NMR spectra at 1.16 and −0.19 ppm for **2a** and at 1.23 and −0.06 ppm for **2b**. Platinum satellites are observed for all of these methyl signals. We tentatively assign the relatively downfield methyl signals to the methyl groups trans to the C═C double bond because of the deshielding effect of the π-accepting ligand. The crystal structures of complexes **2** show that the methyl groups trans to the quinoline nitrogen are located in the shielding regions of the thiophene rings, consistent with the relatively upfield chemical shifts.

It is worth pointing out that a few important structural features of the ligands allow the isolation of complexes **2**. The nitrogen donors from quinoline moieties along with the C═C double bonds create a chelating situation and, therefore, provide sufficient thermodynamic stability to the complexes. Moreover, the existence of the two adjacent quinoline moieties helps to prevent cyclometalation, which would cause the two quinolinyl groups to be in close contact and thus generate repulsions. In addition, the positions of the quinolinyl groups prevent the metal centers from reaching the C−S bonds without breaking the Pt−N bonds first and thus block another reaction pathway.

In summary, we have synthesized two novel multidentate quinoline-functionalized thiophene ligands, which have allowed the isolation of the first group 10 complexes with η^2-C,C thiophenes. The possibility of using a related ligand design (i.e., blocking cyclometalation but allowing the metal center to reach the CS bond) to probe the relevance of the η^2-C,C thiophene intermediate in the CS activation process is being investigated in our laboratory.

Acknowledgment. This research is supported by grants to D.S. from the Natural Science and Engineering Research Council (NSERC) of Canada, the Canadian Foundation for Innovation, the Ontario Research Fund, and the ERA program of Ontario. R.T. is grateful for a postgraduate scholarship from the OGS program of Ontario.

Supporting Information Available: Experimental procedures, characterization data, and crystallographic data in CIF format for **1a**, **1b**, **2a**, and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.