Thiophene Complexes of the Platinum Group Metals. 2. Preparation and Characterization of Cationic Thiophene Complexes of [(cyclooctadiene)Ir][BF$_4$] and [(norbornadiene)Rh][BF$_4$] and X-ray Crystal Structure of [(η^5-2,5-dimethylthiophene)(cyclooctadiene)Rh][BF$_4$]

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Cleavage of chloro-bridged rhodium and iridium dimers, [(NBD)RhCl]$_2$ and [(COD)IrCl]$_2$, in methanol leads to the formation of cationic (COD)$_2$Ir$^+$ and (NBD)Rh$^+$ monomers, respectively. Reaction of these cationic species with 2-methylthiophene and 2,5-dimethylthiophene results in the formation of complexes in which the thiophene coordinates in an η^5 manner. With benzothiophene and dibenzothiophene, complexes bearing a 1:1 metal:ligand stoichiometry are obtained with the ligand coordinating in an η^6 fashion using the six carbon atoms of the arene ring. Good yields of these Rh and Ir products are obtained with the exception of those of reactions involving thiophene, where only small amounts of product were obtained. A crystal structure determination of the cationic (cyclooctadiene)rhodium 2,5-dimethylthiophene complex shows that the thiophene ligand binds to the transition metal center in an η^5 manner. The S atom is displaced 0.1888 Å from the least-squares plane defined by the four carbon ring atoms and displays C–S bond lengths similar to those found in free thiophene. The structure crystallizes in the monoclinic space group $P2_1/n$ with lattice parameters a = 8.731(7) Å, b = 21.57(2) Å, c = 8.833(7) Å, β = 104.43(6)°, and V = 1611(2) Å^3. Convergence to conventional R values of R = 0.0418 and R_w = 0.0652 was obtained for 190 variable parameters and 2113 reflections with $F > 0\sigma(F)$.

Introduction

A number of key features associated with the commercially important process of catalytic hydrodesulfurization currently remain poorly understood. Many aspects of the process, such as how thiophenes bind to the catalyst surface, are not yet well-established. In addition, correlations between particular binding modes and the various patterns of reactivity that are observed remain to be more fully developed.

Much of what has been deduced concerning the possible binding modes of thiophenes rests on information gained from investigations involving the interaction of thiophenes with small, well-characterized transition metal complexes.[1] Periodic trends in HDS activity suggest that the most active catalysts are to be found among the platinum group metals;[2] hence a considerable body of work has centered on the reactions of thiophenes with cyclopentadienyl complexes of Rh, Ir, and Ru.[3–8] Examples of thiophene

coordination in these and related second- and third-row transition metal systems include complexes containing S-bound thiophenes,[3] η^2 binding involving the π-electrons of the ring,[3g,4] and η^4 binding,[3f,5] as well as η^5 binding modes in which all four carbon atoms and the sulfur of the

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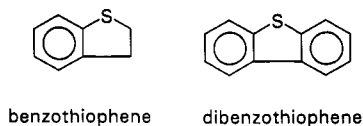
benzothiophene   dibenzothiophene

Figure 1.

thiophene ring are involved.[6] For benzothiophene and dibenzothiophene, crystallographic investigations have established the preferred mode of π-bonding is one that involves the six carbon atoms of the fused ring and not the five-membered ring containing the heteroatom.[7] In some instances, ring-opening reactions have also been observed.[8]

Recently we described the preparation of several cationic Rh(COD)⁺ complexes containing a variety of thiophene ligands.[9] From these investigations it was established that thiophene and methyl-substituted thiophenes formed complexes in which the thiophene coordinated to the transition metal in an η^5 manner. For reactions involving benzothiophene (BT) and dibenzothiophene (DBT), products in which the rhodium center coordinated to the six carbon atoms of the arene ring in an η^6 manner were obtained. In no instances were more complicated forms of behavior such as ring openings observed, and the information derived was based largely on a detailed examination of the chemical shifts observed in the ¹H and ¹³C spectra of these complexes.

To learn more about the binding of thiophenes in these systems, we extended our investigations to include both (NBD)Rh⁺ and (COD)Ir⁺. Compared with the case of cyclooctadiene complexes of rhodium, much less is known concerning the chemistry of (NBD)Rh⁺, and it was also of interest to compare the reactivity of rhodium with that of iridium. In this paper we report the results of these investigations and describe the X-ray crystal structure of a (COD)Rh⁺ complex containing a covalently bound 2,5-dimethylthiophene ligand.

Experimental Section

General Considerations. All manipulations were carried out using standard Schlenk techniques under oxygen-free nitrogen or an inert atmosphere glovebox. Solvents were freshly distilled prior to use using Mg metal for methanol and P_2O_5 for all halogenated solvents. Thiophene, 2-methylthiophene, 2,5-dimethylthiophene, benzothiophene, and dibenzothiophene were purchased from Aldrich Chemical Co., Inc., and used as received. Rhodium chloride hydrate was obtained from the Engelhard Corp. Iridium chloride hydrate was obtained from the Johnson Matthey Co. NMR spectra were recorded on a Bruker AM-250 spectrometer using $CDCl_3$ dried over molecular sieves and referenced to TMS. Elemental analyses were performed by Texas Analytical Laboratories, Inc.

Preparation of (NBD)Rh⁺. The chloro-bridged dimer [(NBD)RhCl]₂ was prepared according to the literature procedure.[10] The Rh(NBD)(MeOH)₂⁺ cation was prepared by adding a slight excess of AgBF₄ (88 mg, 0.45 mmol) to 100 mg (0.20 mmol) of the chloro-bridged norbornadiene Rh dimer in 10.0 mL of freshly distilled methanol. The reaction appeared to be instantaneous, as evidenced by the immediate formation of a precipitate of AgCl, but was allowed to continue to stir at room temperature for 30 min. The AgCl precipitate was removed by filtration and the resulting yellow product dried under vacuum at 56 °C for 4 h.

Preparation of Ir(COD)⁺. [IrCl(COD)]₂ was prepared as described previously.[11] In all reactions 100 mg (0.51 mmol) of AgBF₄ was dissolved in 10.0 mL of methanol followed by the addition of 75 mg (0.11 mmol) of [IrCl(COD)]₂. The reaction mixture was stirred a room temperature for 2 h, after which time the AgCl precipitate was separated from the solution by transferring the supernatant to a new Schlenk flask via a cannula, one end of which was covered with filter paper. The methanol solvent was removed under reduced pressure, yielding the product as a clean yellow powder.

Preparation of [(η⁵-thiophene)(norbornadiene)Rh][BF₄] (1). To a solution of 150 mg (0.43 mmol) of [Rh(NBD)(methanol)₂][BF₄] in 10.0 mL of CHCl₃ was added 1.0 mL (1.05 g, 125 mmol) of thiophene. The mixture was refluxed for 6 h, during which time a change in solution color from yellow to brown was observed, along with the formation of a small amount of an insoluble oily materials adhering to sides of the flask. The solution fraction was separated from the mixture and transferred to a second Schlenk flask in which the solvent was removed under reduced pressure. This resulted in a highly air-sensitive brown oil; however, spectroscopic analysis of the product indicated that it consisted largely of (NBD)₂Rh⁺ and a small amount of (η⁵-thiophene)(NBD)Rh⁺, as well some residual free thiophene. ¹H NMR (CDCl₃), δ: 5.60 (b, 1 H) 5.03 (b, 1 H) (T); 4.09 (b, 4 H), 3.92 (s, 2 H), 1.17 (s, 2 H) (NBD). ¹³C NMR (CDCl₃), δ: 106.4, 92.9 (T); 60.4, 50.7, 47.8 (NBD).

Preparation of [(η⁵-2-methylthiophene)(norbornadiene)-Rh][BF₄] (2). A 0.5-mL portion (510 mg, 51 mmol) of 2-methylthiophene was added to 150 mg (0.43 mmol) of freshly prepared [Rh(NBD)(methanol)₂][BF₄] and the mixture refluxed for 6 h in 10.0 mL of CHCl₃. The solvent fraction was separated from the mixture and transferred to a new Schlenk flask where the CHCl₃ was removed under reduced pressure. The product was isolated in 77% yield as an air-sensitive brown oil. Anal. Calcd for $C_{12}H_{18}BF_4SRh$: C, 38.09; H, 3.70. Found: C, 37.91; H, 3.65. ¹H NMR (CDCl₃), δ: 6.94 (t, J = 3.66 Hz, 1 H), 6.77 (d, J = 3.78 Hz, 1 H), 6.15 (d, J = 3.81 Hz, 1 H), 2.10 (s, 3 H) (2-MT); 4.30 (b, 4 H), 3.50 (s, 2 H), 1.23 (s, 2 H) (NBD). ¹³C NMR (CDCl₃), δ: 111.3, 106.1, 91.4, 91.0, 13.6 (2-MT); 60.2 (d, J_{Rh-C} = 6.78 Hz), 51.0 (b), 47.8 (NBD).

Preparation of [(η⁵-2,5-dimethylthiophene)(norbornadiene)Rh][BF₄] (3). This reaction was carried out as described above although, in this case, the reaction appeared to be complete in less than 1 h, as evidenced by the change in solution color. A 0.5-mL portion (490 mg, 43 mmol) of 2,5-dimethylthiophene was added to 150 mg (0.43 mmol) of freshly prepared [Rh(NBD)-(methanol)₂][BF₄] dissolved in 10.0 mL of CHCl₃, and the mixture was refluxed under N₂ for 6 h. The solvent fraction was separated from the mixture and transferred to a second Schlenk flask where the solvent was removed under reduced pressure, yielding a brown oil in 89% yield. Anal. Calcd for $C_{13}H_{20}BF_4SRh$: C, 39.79; H, 4.08. Found: C, 39.71; H, 4.02. ¹H NMR (CDCl₃), δ: 6.80 (b, 2 H), 2.01 (s, 6 H) (2,5-DMT); 4.24 (b, 4 H), 3.64 (s, 2 H) 1.25 (s, 2H) (NBD). ¹³C NMR (CDCl₃), δ: 109.0, 105.0, 13.6 (2,5-DMT); 60.1 (d, J_{Rh-C} = 7.45 Hz), 51.9 (b), 47.8 (NBD).

Preparation of [(η⁶-benzothiophene)(norbornadiene)Rh]-[BF₄] (4). A stoichiometric amount of benzothiophene (58 mg, 0.43 mmol) was weighed out and transferred to a solution containing 150 mg (0.43 mmol) of [Rh(NBD)(methanol)₂][BF₄] in 10.0 mL of freshly distilled CHCl₃. The solution was refluxed under N₂ for 6 h, during which time the solution color changed from yellow to dark brown. The solvent fraction was transferred to a second Schlenk flask and the solvent removed under reduced pressure. The resulting brown oil was then washed with 5.0 mL of pentane in order to remove any unreacted benzothiophene, and the product was isolated as an air-sensitive brown powder in 65% yield, based on the amount of [(NBD)IrCl]₂ dimer used. Anal. Calcd for $C_{15}H_{18}BF_4SRh$: C, 43.26; H, 3.84. Found: C, 43.31; H, 3.89. ¹H NMR (CDCl₃), δ: 7.91 (m, J = 5.53 Hz, 1 H), 7.70 (m, J = 5.98 Hz, 1 H), 7.47 (m, J = 5.53 Hz, 1 H), 7.30 (m,

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J = 5.92 Hz, 1 H), 6.96 (t, J = 6.63 Hz, 1 H), 6.82 (t, J = 6.38 Hz, 1 H) (BT); 3.81 (b, 4 H), 3.24 (s, 2 H), 0.96 (s, 2 H) (NBD). ^{13}C NMR (CDCl$_3$), δ: 135.2, 126.0, 123.9, 123.6, 123.3, 122.0, 100.4, 96.9 (BT); 57.6 (d, J_{Rh-C} = 7.34 Hz), 46.0 (b), 45.4 (NBD).

Preparation of [(η^6-dibenzothiophene)(norbornadiene)-Rh][BF$_4$] (5). A 79-mg sample (0.43 mmol) of dibenzothiophene was refluxed under N$_2$ in 10.00 mL of CHCl$_3$ containing a stoichiometric amount (150 mg, 0.43 mmol) of freshly prepared Rh(NBD)(methanol)$_2^+$. After 6 h, the reaction was stopped and the solvent fraction transferred to a second Schlenk flask where the solvent was removed under reduced pressure. The resulting product was then washed with 5.0 mL of pentane in order to remove any unreacted dibenzothiophene. The product, in the from of a brown oil, was isolated in 71% yield. This reaction was repeated with a 2-fold molar excess of the [Rh(NBD)(methanol)$_2$]-[BF$_4$] complex. Identical ^{1}H and ^{13}C spectra were obtained, indicating that the same product bearing a 1:1 metal:ligand stoichiometry was obtained. Anal. Calcd for C$_{19}$H$_{20}$BF$_4$SRh: C, 48.71; H, 4.27. Found: C, 48.59; H, 4.32. ^{1}H NMR (CDCl$_3$), δ: 8.20 (d, J = 6.05 Hz, 1 H), 8.00 (d, J = 5.92 Hz, 1 H), 7.71 (m, J = 5.82 Hz, 1 H), 7.54 (m, J = 5.96 Hz, 1 H), 7.34 (m, J = 6.12 Hz, 1 H), 7.20 (m, J = 5.92 Hz, 1 H), 6.94 (t, J = 6.03 Hz, 1 H), 6.81 (t, J = 5.85 Hz, 1 H) (DBT); 3.71 (b, 4 H), 3.15 (b, 2 H), 0.85 (s, 2 H) (NBD). ^{13}C NMR (CDCl$_3$), δ: 138.8, 135.3, 130.3, 126.5, 126.3, 123.3, 121.4, 115.9, 101.7, 100.4, 97.9, 96.0 (DBT); 57.5 (d, J_{Rh-C} = 7.24 Hz), 46.6 (b), 45.5 (NBD).

Preparation of [(η^5-2,5-dimethylthiophene)(cyclooctadiene)Rh][BF$_4$] (6). This complex was prepared from the chloro-bridged (cyclooctadiene)rhodium dimer as described previously and isolated as a slightly air-sensitive yellow-brown powder.[9] The ^{1}H and ^{13}C NMR spectra of the complex were identical to those reported for this complex.

Preparation of [(η^5-thiophene)(cyclooctadiene)Ir][BF$_4$] (7). The (COD)Ir$^+$ cation was prepared from 75 mg (0.11 mmol) of [IrCl(COD)]$_2$. After isolation, the product was immediately redissolved in 10.0 mL of CH$_2$Cl$_2$, followed by the addition of 0.20 mL (0.18 mmol) of 2,5-DMT. The reaction appeared to be instantaneous, as evidenced by a change in color from orange to brown, and the mixture was allowed to stir at room temperature for 20 min. The dichloromethane solvent was removed under reduced pressure, and the crude product remaining was extracted into CDCl$_3$. Evidence for a small amount of coordinated thiophene could be seen in the ^{13}C spectrum of the reaction mixture; however, we were unable to purify a quantity of this air-sensitive product sufficient for an elemental analysis to be carried out. ^{1}H NMR (CDCl$_3$), δ: 6.48 (m, J = 7.42 Hz, 2 H), 4.98 (m, J = 7.24 Hz, 2 H) (T); 4.57 (b, 4 H), 2.52 (s, 8 H) (COD). ^{13}C NMR (CDCl$_3$), δ: 108.0, 93.6 (T); 67.2, 31.2 (COD).

Preparation of [(η^5-2-methylthiophene)(cyclooctadiene)-Ir][BF$_4$] (8). To the (COD)Ir$^+$ cation prepared using 75 mg (0.11 mmol) of [IrCl(COD)]$_2$ in 10.0 mL of CH$_2$Cl$_2$ was added 0.20 mL (202 mg, 2.1 mmol) of 2-DMT. The reaction appeared to be instantaneous, as evidenced by a change in color from orange to a lighter shade of orange, but the mixture was allowed to continue to stir at room temperature for 20 min. The solvent volume was then reduced to approximately 1 mL, and the solution was then triturated with 10.0 mL of anhydrous diethyl ether. This resulted in the immediate formation of 80 mg (0.17 mmol) of an air-sensitive light brown powder in 74% yield, based on the amount of [IrCl(COD)]$_2$ starting material used. Anal. Calcd for C$_{13}$H$_{18}$BF$_4$SIr: C, 32.15; H, 3.70. Found: C, 31.93; H, 3.78. ^{1}H NMR (CD$_3$NO$_3$), δ: 6.90 (t, J = 3.20 Hz, 1 H), 6.80 (d, J = 2.50 Hz, 1 H), 6.28 (d, J = 2.69 Hz, 2 H), 2.15 (s, 3 H) (2-MT); 4.89 (m, J = 3.98 Hz, 2 H), 4.67 (m, J = 3.62 Hz, 2H), 2.32 (m, J = 3.81 Hz, 8 H) (COD). ^{13}C NMR (CD$_3$NO$_2$), δ: 103.78, 102.56, 101.28, 81.98, 12.57 (2-MT); 67.83, 66.30, 33.77, 32.08 (COD).

Preparation of [(η^5-2,5-dimethylthiophene)(cyclooctadiene)Ir][BF$_4$] (9). This reaction was carried out using the (COD)-Ir$^+$ cation prepared from 75 mg (0.100 mmol) of starting material dissolved in CH$_2$Cl$_2$ to which was added 0.10 mL (98.5 mg, 0.88 mmol) of 2,5-DMT. The reaction mixture was stirred at room

temperature for 20 min, after which time the solvent volume was reduced to approximately 1 mL under reduced pressure, followed by the addition of 10.0 mL of anhydrous diethyl ether. The brown precipitate was separated from the solvent fraction and isolated as an air-sensitive solid in 75% yield, based on the amount of [IrCl(COD)]$_2$ starting material used. Anal. Calcd for C$_{14}$H$_{20}$BF$_4$SIr: C, 33.65; H, 4.01. Found: C, 33.47; H, 4.18. ^{1}H NMR (CD$_3$NO$_3$), δ: 6.76 (s, 2 H), 2.15 (s, 6 H) (2,5-DMT); 4.61 (b, 4 H), 2.38 (s, 8 H) (COD). ^{13}C NMR (CD$_3$NO$_2$), δ: 103.09, 100.23, 12.40 (2,5-DMT); 67.56, 32.84 (COD).

Preparation of [(η^6-benzothiophene)(cyclooctadiene)Ir]-[BF$_4$] (10). A 40-mg sample (0.29 mmol) of benzothiophene was added to a CH$_2$Cl$_2$ solution of the freshly prepared (COD)Rh$^+$ cation obtained from 75 mg (0.10 mmol) of the [IrCl(COD)]$_2$ dimer by halide abstraction in methanol. The solution was refluxed for 1 h, after which the solvent was removed under reduced pressure. The resulting brown oil was washed with 5.0 mL of pentane to remove any excess benzothiophene, followed by the addition 10.0 mL of ether, which resulted in the formation of 80 mg of an air-sensitive brown powder in 70% yield. Anal. Calcd for C$_{16}$H$_{18}$BF$_4$SIr: C, 36.82; H, 3.45. Found: C, 36.75; H, 3.41. ^{1}H NMR (CD$_3$NO$_3$), δ: 8.07 (d, J = 5.64 Hz, 1 H), 7.34 (d, J = 5.81 Hz, 1 H), 7.23 (d, J = 6.24 Hz, 1 H), 6.92 (d, J = 6.18 Hz, 1 H), 6.88 (m, J = 5.98 Hz, 1 H), 6.79 (m, J = 5.84 Hz, 1 H) (BT); 4.20 (m, J = 4.29 Hz, 2 H), 4.14 (m, J = 4.39 Hz, 2 H), 1.86 (m, J = 4.66 Hz, 8 H) (COD). ^{13}C NMR (CD$_3$NO$_2$), δ: 139.45, 122.91, 121.32, 120.48, 98.50, 98.18, 89.34, 89.30 (BT); 67.71, 66.53, 33.22, 33.06 (COD).

Preparation of [(η^6-dibenzothiophene)(cyclooctadiene)-Ir][BF$_4$] (11). A slight excess (50 mg, 0.27 mmol) of dibenzothiophene was weighed out and transferred to a Schlenk tube containing a 10.0 mL of CH$_2$Cl$_2$ and the (COD)Ir$^+$ cation prepared using 75 mg (0.11 mmol) of the [IrCl(COD)]$_2$ dimer starting material. The reaction mixture was refluxed for 1 h under an atmosphere of N$_2$, after which time the solvent was removed under reduced pressure. The resulting brown oil was washed with 5.0 mL of pentane to remove any unreacted dibenzothiophene, followed by the addition of 10 mL of anhydrous diethyl ether, which resulted in the formation of 86 mg (68%) yield) of an air-sensitive brown powder. This reaction was repeated using a 2-fold excess of benzothiophene; however, attempts to isolate a complex bearing a 2:1 metal:ligand stoichiometry were unsuccessful. Anal. Calcd for C$_{20}$H$_{20}$BF$_4$SIr: C, 41.99; H, 3.49. Found: C, 40.36; H, 3.72. ^{1}H NMR (CD$_3$NO$_2$), δ: 8.23 (d, J = 8.02 Hz, 1 H), 8.00 (d, J = 7.79 Hz, 1 H), 7.75 (m, J = 6.67 Hz, 1 H), 7.69 (m, J = 6.47 Hz, 1 H), 7.57 (d, J = 6.20 Hz, 1 H), 7.44 (d, J = 5.94 Hz, 1 H), 7.00 (m, J = 5.16 Hz, 1 H), 6.94 (m, J = 5.12 Hz, 1 H) (DBT); 4.21 (b, 4 H), 1.91 (m, J = 11.22 Hz, 8 H) (COD). ^{13}C NMR (CD$_3$NO$_3$), δ: 142.30, 132.37, 130.18, 130.13, 128.08, 125.13, 122.51, 113.58, 98.43, 96.20, 90.58, 88.31 (DBT); 68.50, 68.30, 33.32, 33.26 (COD).

Structure Determination of [(η^5-2,5-dimethylthiophene)-(1,5-cyclooctadiene)Rh][BF$_4$] (6). A yellow plate with dimensions 0.10 × 0.60 × 0.12 mm was selected and mounted on the end of a glass fiber in a random orientation. Refined cell parameters were determined from the setting angles of 50 reflections with 15° < 2θ < 30°. Data collection was carried out at ambient temperature using the ω-scanning technique in bisecting geometry on a Siemens R3m/V diffractometer equipped with graphite-monochromated Mo Kα radiation: scan rate variable, 3–20° min^{-1}; scan range, 1.2° in ω. Three standards measured every 97 data displayed only minor variations in intensity (<1.0%) over the period of data collection. A total of 2270 reflections (+h,+k,+l; h_{max} = 9, k_{max} = 23, l_{max} = 9) with 3.5° < 2θ < 45° were obtained and corrected for Lorentz and polarization effects. Absorption corrections were applied numerically following careful measurement of crystal dimensions and assignment of indices to the crystal faces (minimum and maximum transmission: 0.858 and 0.892, respectively). This led to 2113 unique reflections (R_{int} = 1.84%) with I > 0σ(I). Structure solution and refinement were carried out using the

SHELXTL-PC collection of crystallographic software.[12] The position of the Rh atom was located from a sharpened Patterson map and used as an initial phasing model. All remaining non-hydrogen atoms were located using standard difference-Fourier techniques. All non-hydrogen atoms were refined anisotropically using scattering factors that included terms for anomalous dispersion taken from ref 13. Hydrogen atoms were included in idealized positions with fixed isotropic $U = 0.08 \text{ Å}^2$. Refinement was based on F using weights of the form $w^{-1} = [\sigma^2(F) + 0.0058(F^2)]$. For the final cycle, the maximum shift/σ was 0.001 with minimum and maximum residual electron densities of +0.46 and −0.76 e Å^{-3} located in the vicinity of the BF_4^- counterion. Convergence to conventional R values of $R = 0.0418$ and $R_w = 0.0652$ with a goodness-of-fit of 0.77 was obtained for 190 variable parameters and 2113 reflections with $F > 0\sigma(F)$.

Results and Discussion

Cleavage of the chloro-bridged Rh and Ir dimers in methanol leads to the formation of monomeric species containing weakly coordinating molecules of solvent. Both complexes can be isolated as reasonably air-stable yellow solids. While integrated ^{1}H NMR data for the (NBD)-Rh$^+$ complex suggest that two coordinated molecules of methanol are present, the number of solvent molecules is most likely variable.[14] For this reason, calculated yields are based on a knowledge of the amount of dimeric starting material used.

With the exception of those of reactions involving thiophene, good product yields were obtained following reaction with the (NBD)Rh$^+$ and (COD)Ir$^+$ cations. Chloroform proved to be the best solvent for carrying out reactions involving Rh. The (COD)Ir$^+$ complex, on the other hand, displayed poor solubility in this solvent but fair solubility in dichloromethane. No products were formed when coordinating solvents such as methanol or THF were used, and reaction times for the two transition metal complexes differed. Longer reaction times were required for the (NBD)Rh$^+$ complex. Reactions involving the (COD)Ir$^+$ complex, in contrast, were complete in a less than 1 h, and longer reaction times resulted in a complex mixture of products which proved to be difficult to separate and identify. Interestingly, isomerization of the double bonds in the COD ligand appeared to be taking place when the iridium complex was reacted with 2-methylthiophene, benzothiophene, and dibenzothiophene but not thiophene or 2,5-dimethylthiophene. On the basis of the ^{13}C NMR data, it appears as though the thermodynamically more stable 1,3-cyclooctadiene isomer was being formed, although a more detailed investigation would be needed in order to firmly establish this point.

Thiophenes are capable of acting as both σ-donor and π-donor ligands. In the systems investigated, elucidation of the thiophene binding modes derives from a combination of crystallographic data and interpretation of the ^{1}H and ^{13}C NMR spectra. Previous studies have established that substantial upfield shifts are observed in the ^{13}C spectra of thiophene ligands coordinated in an η^5 or η^6 manner. Conversely, coordination involving the S atom leads invariably to a decrease in the shielding of the atoms comprising the thiophene ring. As a result, complexes
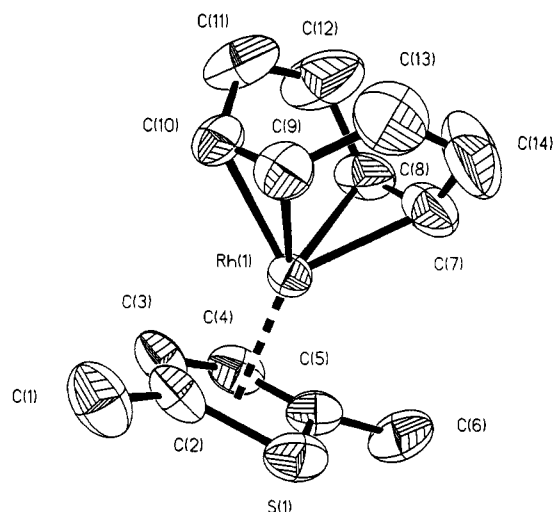
Figure 2. View of the cation in [η^5-2,5-dimethylthiophene)-cyclooctadiene)Rh][BF$_4$]. Hydrogen atoms have been omitted for clarity. Not shown is the BF$_4^-$ counterion.

displaying S-bound thiophenes display chemical shifts for the ring C and H atoms that are shifted downfield relative to the free thiophene.

For the complexes prepared in this investigation, upfield shifts, typically 10–20 ppm, are observed in the ^{13}C spectra of the coordinated thiophene ligands. Coupling between the rhodium and coordinated carbon atoms of the NBD ligands was observed but was absent for the thiophene ligands. With the exception of reactions involving thiophene, for which only small amounts of an air-sensitive product were obtained, the elemental analyses also indicate that complexes bearing a 1:1 metal:ligand stoichiometry are being obtained. For thiophene, 2-methylthiophene, and 2,5-dimethylthiophene, this suggests that the thiophene ligands are coordinating in a η^5 manner using all five atoms of the ring. A π-bonding mode is also indicated for benzothiophene and dibenzothiophene. However, with these latter thiophenes, the presence of two or more available ring sites affords the opportunity for the transition metal to coordinate at either the five-membered ring containing the S atom or the arene ring containing the six C atoms. While attempts to grow crystals suitable for an X-ray crystal structure determination for any of these complexes were unsuccessful, the pattern of upfield chemical shifts associated with the benzothiophene and dibenzothiophene complexes of (NBD)Rh$^+$ and (COD)-Ir$^+$ are in agreement with the NMR data for other platinum group metal complexes for which crystallographic data have documented coordination involving the six-membered arene ring.[7] In fact, coordination to the five-membered ring in an η^5 manner has yet to be observed for either benzothiophene or dibenzothiophene.

Interpretation of the chemical shift data in these systems is aided by the X-ray crystal structure determination of a related Rh complex obtained following the reaction of (COD)Rh$^+$ with 2,5-dimethylthiophene. The crystal structure of this complex confirms the stoichiometry of the complex and mode of thiophene binding proposed earlier on the basis of elemental analyses and ^{1}H and ^{13}C NMR data.[9]

The complex possesses approximate C_s point group symmetry with the rhodium atom sandwiched between the COD ligand and a molecule of 2,5-dimethylthiophene which coordinates in an η^5 manner. Bonds to the C atoms

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Table I. Crystal Data and Data Collection Summary for [(C₈H₁₂)Rh(C₆H₈S)][BF₄]

empirical formula	$C_{14}H_{20}BF_4RhS$
color and habit	regularly shaped yellow plate
crystal size	$0.10 \times 0.6 \times 0.12$ mm
space group	$P2_1/n$
unit cell dimens	$a = 8.731(7)$ Å
	$b = 21.57(2)$ Å
	$c = 8.833(7)$ Å
	$\beta = 104.43(6)°$
vol	$1611(2)$ Å²
Z	4
fw	410.1
density (calcd)	1.691 Mg/m³
abs coeff	1.196 mm⁻¹
F(000)	824
temp	295 K
monochromator	highly oriented graphite crystal
2θ range	$3.5–45.0°$
scan type	ω
scan speed	variable; $3.00–20.00°$/min in ω
scan range (ω)	$1.20°$
std reflns	3 measd every 97 reflns
index ranges	$0 \leq h \leq 9, 0 \leq k \leq 23, -9 \leq l \leq 9$
no. of reflns collected	2270
no. of indep reflns	2113 ($R_{int} = 1.84\%$)
no. of obsd reflns	2113 ($I > 0.0\sigma(I)$)
abs cor	face-indexed numerical
min/max transm	0.8575/0.8920
weighting scheme	$w^{-1} = \sigma^2(F) + 0.0058F^2$
no. of params refined	190
final R indices (all data)	$R = 4.08\%, R_w = 6.48\%$
goodness-of-fit	0.77
largest and mean Δ/σ	0.001, 0.000
data-to-parameter ratio	11.1:1
largest diff peak	0.45 e Å⁻³
largest diff hole	−0.76 e Å⁻³

Table II. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10³) for [(C₈H₁₂)Rh(C₆H₈S)][BF₄]

	x	y	z	U(eq)ᵃ
Rh(1)	2257(1)	1250(1)	2118(1)	37(1)
S(1)	1369(2)	1523(1)	4475(2)	60(1)
F(4)	1587(12)	8687(3)	3645(12)	191(5)
F(3)	1837(10)	9281(2)	1768(8)	187(4)
F(2)	3905(8)	8880(3)	3359(9)	174(4)
F(1)	2264(6)	8283(2)	1609(6)	113(2)
B(1)	2426(11)	8775(2)	2604(11)	65(3)
C(1)	−591(6)	2282(2)	2153(8)	74(2)
C(2)	85(6)	1656(3)	2619(7)	57(2)
C(3)	−361(6)	1087(3)	1855(8)	59(2)
C(4)	442(7)	585(2)	2636(7)	57(2)
C(5)	1510(7)	740(2)	4034(7)	52(2)
C(6)	2540(8)	302(3)	5199(6)	75(2)
C(7)	4693(7)	994(3)	2595(8)	69(3)
C(8)	3819(8)	618(3)	1380(8)	66(2)
C(9)	3807(11)	711(4)	−301(8)	120(4)
C(10)	2838(10)	1212(2)	−1092(8)	79(3)
C(11)	2207(6)	1650(2)	−115(5)	51(2)
C(12)	3134(6)	2019(2)	1059(6)	56(2)
C(13)	4906(8)	2047(3)	1445(8)	88(3)
C(14)	5707(8)	1538(4)	2449(11)	112(4)

ᵃ Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

of the COD ligand display only minor variations in length and are well within the range observed in other Rh(I) complexes possessing these ligands (Rh–C(av) = 2.139 Å).[15,16] Bonds to the C atoms of the thiophene ligand similarly display only minor variations in length, with the rhodium center separated from the centroid defined by the five ring atoms of the 2,5-DMT ligand by a distance of 1.892 Å and a Rh–S distance of 2.467(3) Å.

Table III. Selected Bond Lengths (Å) and Angles (deg) for [(C₈H₁₂)Rh(C₆H₈S)][BF₄]

Rh(1)–S(1)	2.467(3)	Rh(1)–C(2)	2.232(6)
Rh(1)–C(3)	2.267(6)	Rh(1)–C(4)	2.267(6)
Rh(1)–C(5)	2.247(6)	Rh(1)–C(7)	2.135(6)
Rh(1)–C(8)	2.141(7)	Rh(1)–C(11)	2.143(5)
Rh(1)–C(12)	2.137(6)	S(1)–C(2)	1.764(6)
S(1)–C(5)	1.743(6)	F(4)–B(1)	1.324(16)
F(3)–B(1)	1.346(9)	F(2)–B(1)	1.317(10)
F(1)–B(1)	1.362(9)	C(1)–C(2)	1.488(8)
C(2)–C(3)	1.409(8)	C(3)–C(4)	1.377(8)
C(4)–C(5)	1.390(7)	C(5)–C(6)	1.517(8)
C(7)–C(8)	1.408(9)	C(7)–C(14)	1.495(11)
C(8)–C(9)	1.496(10)	C(9)–C(10)	1.440(10)
C(10)–C(11)	1.476(9)	C(11)–C(12)	1.395(7)
C(12)–C(13)	1.500(9)	C(13)–C(14)	1.474(11)

C(2)–S(1)–C(5)	90.8(3)	F(4)–B(1)–F(3)	107.1(8)
F(4)–B(1)–F(2)	108.4(8)	F(3)–B(1)–F(2)	109.2(7)
F(4)–B(1)–F(1)	110.5(6)	F(3)–B(1)–F(1)	108.3(7)
F(2)–B(1)–F(1)	113.1(7)	S(1)–C(2)–C(1)	121.4(4)
S(1)–C(2)–C(3)	109.8(4)	C(1)–C(2)–C(3)	127.9(5)
C(2)–C(3)–C(4)	113.5(5)	C(3)–C(4)–C(5)	113.6(5)
S(1)–C(5)–C(4)	111.2(4)	S(1)–C(5)–C(6)	121.0(4)
C(4)–C(5)–C(6)	127.3(5)	C(8)–C(7)–C(14)	127.3(7)
C(7)–C(8)–C(9)	123.2(6)	C(8)–C(9)–C(10)	116.1(7)
C(9)–C(10)–C(11)	117.2(6)	C(10)–C(11)–C(12)	124.6(5)
C(11)–C(12)–C(13)	124.5(5)	C(12)–C(13)–C(14)	114.5(6)
C(7)–C(14)–C(13)	115.7(6)		

Many of the structural features associated with the coordinated thiophene ligand are similar to those observed in other transition metal complexes containing thiophene and thiophene derivatives. Related systems based on the platinum group metals whose crystal structures have been reported include [(η⁵-thiophene)(PPh₃)₂Rh](PF₆),[6b] [(η⁵-tetramethylthiophene)(H₂O)₃Ru](OTf)₂,[6h] the symmetrical sandwich complex [(η⁵-tetramethylthiophene)₂Ru]-(BF₄),[6f] and the unusual cubane-like complex [((η⁵-tetramethylthiophene)Ru)₃S](BF₄).[6f] In the structure described here, the four carbon atoms of the thiophene ring are essentially coplanar with an average deviation from the least-squares plane defined by these atoms of only 0.004 Å. The lengths of the three C–C bonds of the ring are all similar within experimental error and are in good agreement with those reported for the structure of a cationic triphenylphosphine complex of Rh containing an η⁵-thiophene ligand.[6b] S(1) is displaced from the least-squares plane defined by the C(2)–C(3)–C(4)–C(5) atoms by 0.1888 Å away from Rh(1), and the C–S–C angle measures 90.8(3)°. The two C–S bonds in this structure measure 1.764(6) and 1.743(6) Å for S(1)–C(2) and S(1)–C(5), respectively. Both are longer than those observed in free thiophenes (C–S = 1.718(4) Å)[17] but shorter than those typically observed in complexes possessing η⁴-bound thiophenes.[3f,5a]

The use of the (NBD)Rh⁺ and (COD)Ir⁺ as starting materials in these reactions affords a convenient route for the preparation of new complexes containing π-bound thiophene ligands. Complexes containing weakly coordinated molecules of acetone or THF can also be prepared using this technique; however, in reactions involving thiophenes, the methanol adduct proved to be the most useful. With the exception of those involving thiophene reactions, good product yields were obtained following reaction with 2-methylthiophene (2-MT), 2,5-dimethylthiophene (2,5-DMT), benzothiophene (BT), and dibenzothiophene (DBT).

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It is interesting to note that attempts to prepare a dibenzothiophene complex containing two coordinated metal ions were unsuccessful, even when a 2-fold excess of the (NBD)Rh$^+$ or (COD)Ir$^+$ starting material was used. Interestingly, the same result was observed using [Rh-(COD)(methanol)$_2$][BF$_4$] and the underlying reasons remain uncertain at this juncture.[9] It may be that binding of the metal to the dibenzothiophene ligand occurs in a stepwise fashion and that coordination to one of the benzene rings deactivates the other arene ring with respect to coordination of a second transition metal center. Alternately, it may be that complexes possessing a 2:1 metal:ligand stoichiometry are obtained only with a very large excess of the transition metal or perhaps under more forcing reaction conditions than those used in the syntheses described here. Nor is it clear, at this juncture, why good product yields were obtained when thiophene was reacted with (COD)Rh$^+$, while poor product yields (<10%) were repeatedly obtained when (NBD)Rh$^+$ was used. It may be that formation of the norbornadiene dimer is a competing side reaction in all cases and that, once formed,

it is stable with respect to subsequent ligand displacement by thiophene, but not thiophenes whose Lewis basicity is enhanced by the presence of one or more methyl groups.

Supplementary Material Available: Lists of atomic positional parameters for hydrogen atom coordinates and anisotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

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