Elaborate Network of Hydrolysis and Methanolysis Reactions Involving the 2,5-Dimethylthiophene Ligand in Cp*Ir(η^5-2,5-Me_2T)$^{2+}$

M. Angeles Paz-Sandoval,*,† Marisol Cervantes-Vasquez,† Victor G. Young, Jr.,‡ Ilia A. Guzei,§ and Robert J. Angelici§

Centro de Investigación y de Estudios Avanzados, Department of Chemistry, Ap. Postal 14-740, México, D.F. 07000, Mexico, Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, and Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011

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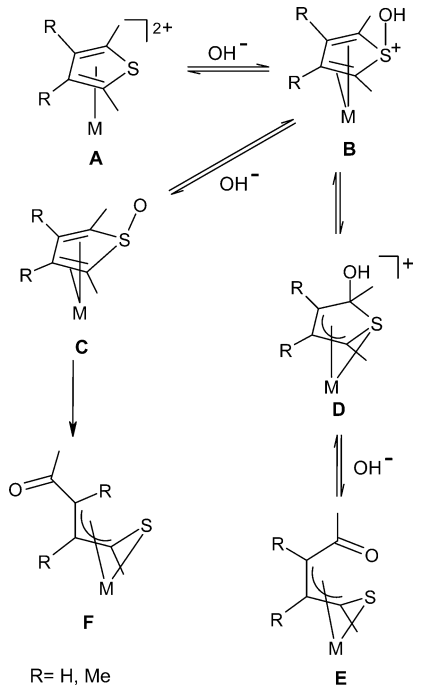
Reactions of aqueous base with the dicationic iridium and rhodium thiophene complexes [Cp*Ir(η^5-2,5-Me_2T)]$(X)_2$ (X = BF_4, **1(BF$_4$)**; X = OSO_2CF_3, **1(OTf)**) and [Cp*Rh(η^5-2,5-Me_2T)]-$(BF_4)_2$ (**8(BF$_4$)**) and the acid/base reactivity of these products are discussed. The reaction of **1(BF$_4$)** with 1 equiv of aqueous KOH (0.01 M) affords the following mixture of mono-, di-, and tetranuclear compounds: [Cp*Ir(η^4-SC(Me)CHCHC(O)Me)] (**3**), (Cp*Ir)[Cp*Ir(η^4-SC-(Me)CHCHC(O)Me)]$_3(BF_4)_2$ (**4(BF$_4$)**), [(Cp*Ir)$_2$(μ_2,η^4-SC(Me)CHCC(O)Me)](BF_4) (**5(BF$_4$)**), and [Cp*Ir(μ_2,η^3-SC(Me)CHCH_2C(O)Me)]$_2(BF_4)_2$ (**6(BF$_4$)**). The ^{1}H and ^{13}C NMR data are consistent with the single-crystal X-ray diffraction structures of the cationic complexes **4-(BF$_4$)**, **5(OTf)**, and **6(BF$_4$)**. These products are formed by a complex series of reactions that begin with the displacement of the 2,5-dimethylthiophene (2,5-Me_2T) ligand from **1** and reaction of the resulting "[Cp*Ir]$^{2+}$" fragment with **3**. In the synthesis of **8(BF$_4$)**, the new complex [(Cp*Rh)$_2$(μ_2,η^4-SC(Me)CHCC(O)Me)](BF_4) (**9(BF$_4$)**), analogous to **5(BF$_4$)**, is produced. Studies of the reactions of [Cp*Rh(η^5-2,5-Me_2T)]$(BF_4)_2$ (**8(BF$_4$)**) with OH^- and MeO^- show a type of reactivity quite different from that observed for **1(BF$_4$)** and **1(OTf)**. The solvolysis of **8(BF$_4$)** in acetone affords the mononuclear complex [Cp*Rh$(OCMe_2)_2$(OH)](BF_4) (**10(BF$_4$)**), whose crystal structure is described. Detailed NMR studies establish the pathways by which [Cp*Ir(η^5-2,5-Me_2T)]$^{2+}$ (**1**) and [Cp*Rh(η^5-2,5-Me_2T)]$^{2+}$ (**8**) react with H_2O/OH^- and $MeOH/MeO^-$ to give the variety of observed products.

Introduction

Of the many known reactions of coordinated thiophenes,[1] those involving nucleophilic attack on η^5-thiophene ligands can lead to products in which the thiophene is oxidized, reduced, or cleaved at a C−S bond. One of the more interesting reactions of this type is the attack of OH^- on the η^5-thiophene ligands in Cp*Rh(η^5-Me_4T)$^{2+}$ [2−4] (Cp* = η^5-C_5Me_5 and Me_4T = tetramethylthiophene) and (ring)Ru(η^5-T*)$^{2+}$, where ring = η^6-cymene, η^6-C_6Me_6, η^5-Me_4T and T* = T, 2,5-Me_2T, Me_4T.[2,5] The OH^- reactions of both of these systems are summarized in Scheme 1. Reaction of the η^5-thiophene dicationic complex **A** with 1 equiv of aqueous KOH gives the *S*-hydroxythiophene complex **B**,

Scheme 1



which was characterized by NMR spectroscopy in the (ring)Ru(η^5-Me_4T)$^{2+}$ system;[5] there is other very good

* To whom correspondence should be addressed: E-mail: mpaz@mail.cinvestav.mx.
† Centro de Investigación y de Estudios Avanzados.
‡ University of Minnesota.
§ Iowa State University.

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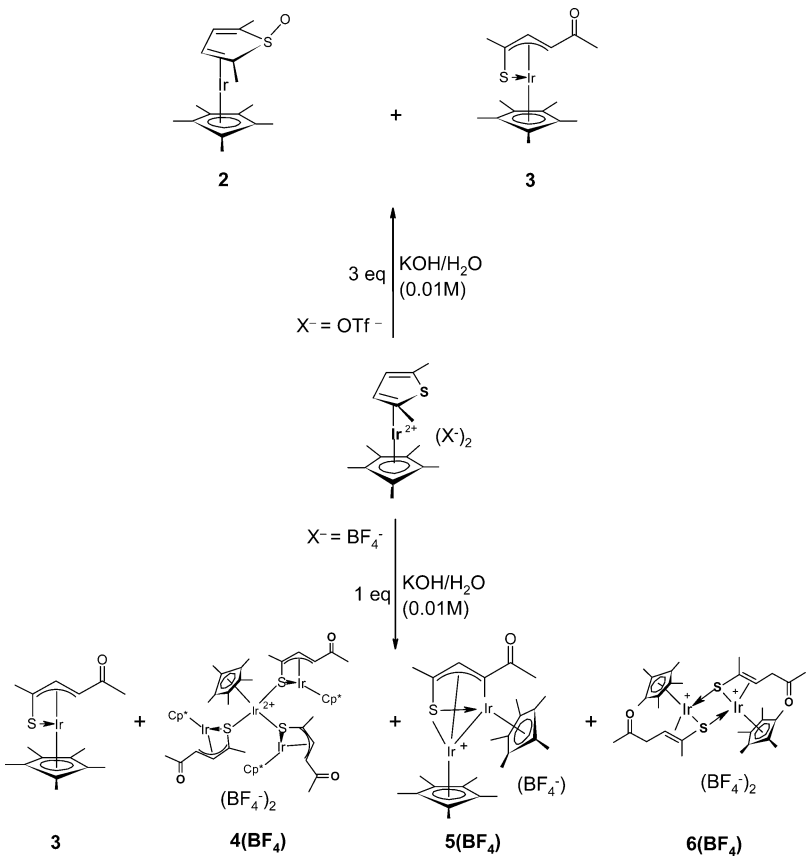
Scheme 2



evidence for nucleophilic attack on the sulfur in η^5-thiophene ligands.[6] Upon standing in solution, **B** rearranges to **D**, which was characterized crystallographically in the Cp*Rh(η^5-Me_4T)$^{2+}$ system.[4] Then **D** reacts with another OH^- to give the ring-opened anti acyl thiolate **E**, which rearranges to the syn isomer **F** for the Ru complexes but remains as isomer **E** for the Rh complex. Isomer **E** reacts rapidly with CF_3SO_3H to give back **A**. Thus, the acid reverses all steps (through intermediates **D** and **B**) to eliminate H_2O. The syn isomer **F** does not react with acid to give **A**.

When an excess of KOH is used initially, **A** is converted to **C** because deprotonation of the *S*-hydroxy group in **B** is faster than migration of the OH^- from the sulfur to carbon 2. Although **C** is formed initially, it rearranges over a period of hours at room temperature in solution to give the acyl thiolate isomer, **E** or **F**, presumably via the protonated intermediate **B**. In fact, the *S*-oxide **C** reacts rapidly with CF_3SO_3H to give **A**. Depending on the ring and η^5-T* ligands in the (ring)-Ru(η^5-T*)$^{2+}$ complexes, equilibrium constants and rates of each step in Scheme 1 vary, but the patterns of reactivity are the same for both the Rh[4] and Ru[5] series of complexes.

Analogous OH^- reactions of (η^6-cymene)Os(η^5-T*)$^{2+}$, where T* = 2,5-Me_2T,[7] Me_4T,[7,8a] and Cp*Ir(η^5-T*)$^{2+}$, where T* = Me_4T,[8a] 2,5-Me_2T,[8b] have been investigated, but in much less detail. In this paper are described much more thorough studies of the reactions of Cp*Ir(η^5-2,5-Me_2T)$^{2+}$ (**1**) with OH^- and MeO^-. While some aspects of this chemistry are the same as those of Cp*Rh(η^5-Me_4T)$^{2+}$ as represented in Scheme 1, four additional species that were not observed in the reaction of Cp*Rh(η^5-Me_4T)$^{2+}$ participate in a more elaborate network of reactions that occurs when **1** reacts with OH^- and MeO^-. Three of these new species have been characterized by X-ray diffraction studies. Also, studies of the reactions of [Cp*Rh(η^5-2,5-Me_2T)](BF_4)$_2$ (**8(BF$_4$)**) with OH^- show a type of reactivity quite different from that observed for Cp*Ir(η^5-2,5-Me_2T)$^{2+}$ (**1**).

Results

Overall Reactions of [Cp*Ir(η^5-2,5-Me_2T)](X)$_2$ (X = OTf, 1(OTf); X = BF_4, 1(BF_4)) with OH^-. The Cp*Ir(η^5-2,5-Me_2T)$^{2+}$ salts **1(OTf)** and **1(BF_4)** react with different concentrations of KOH/H_2O to give different products.

(a) The addition of 3 equiv of aqueous KOH (0.01 M) to a salt of Cp*Ir(η^5-2,5-Me_2T)$^{2+}$ (**1(OTf)**) gives a mixture of the sulfoxide Cp*Ir[η^4-2,5-Me_2T(O)] (**2**) and acyl thiolate [Cp*Ir(η^4-SC(Me)CHCHC(O)Me)] (**3**) (Scheme 2).

The formation of the mixture of **2** and **3** from the reaction of **1(BF_4)**[8b] with 2 equiv of (*n*-Bu)$_4N^+OH^-$ has been previously published. In our hands, the reaction of **1(BF_4)** with (*n*-Bu)$_4N^+OH^-$ in CH_3CN, under conditions virtually identical with those reported previously,[8b] shows exclusive formation of compound **3**, without

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evidence of **2**. These different results are attributed to the different chromatographic procedures used in the purification of both reaction mixtures (see the Experimental Section). There is clear evidence that compound **2** is transformed to compound **3** in solution[9] and under chromatographic treatment. The acyl thiolate **3** can also be isolated in 77% yield,[8b] from the reaction of O_2 with Cp*Ir(η^4-2,5-Me_2T). The rhodium sulfoxide Cp*Rh[η^4-Me_4T(O)], an analogue of **2**, has been obtained quantitatively from the corresponding reaction of O_2 with Cp*Rh[η^4-Me_4T][4] and also from the reaction of [Cp*Rh(η^5-Me_4T)]$(OTf)_2$[4] with 3 equiv of KOH/H_2O (0.085 M).

(b) The dicationic salt **1(OTf)** reacts with 3 equiv of KOH/H_2O (0.03 M), giving a trace precipitate of the orange-red acyl thiolate **3** and a solution that yields as the major product the white to slightly beige solid **2**, which is identical with the sulfoxide **2** previously reported;[8b] in addition, red crystals of [$(Cp^*Ir)_2(\mu_2,\eta^4$-SC(Me)CHCC(O)Me)](OTf) (**5(OTf)**) were obtained by recrystallization from methylene chloride/diethyl ether. These results are in contrast with those obtained from the rhodium analogue [Cp*Rh(η^5-Me_4T)][$OTf]_2$,[4] which under virtually identical conditions gave only Cp*Rh-[η^4-SC_3Me_3C(O)Me], the acyl thiolate analogue of **3**.

Using the same concentrations of KOH/H_2O (0.03 and 0.01 M) as described above, but now with only 1 equiv of OH^-, **1(OTf)** and **1(BF_4)** react to give a different set of new dinuclear and tetranuclear iridium species (vide infra).

(c) Complex **1(OTf)** reacts with 1 equiv of KOH/H_2O (0.03 M) to give the compounds **3**, (Cp*Ir)[Cp*Ir(η^4-SC(Me)CHCHC(O)Me)]$_3(OTf)_2$ (**4(OTf)**), and [$(Cp^*Ir)_2(\mu_2,\eta^4$-SC(Me)CHCC(O)Me)](BF_4) (**5(OTf)**), as well as free 2,5-dimethylthiophene.

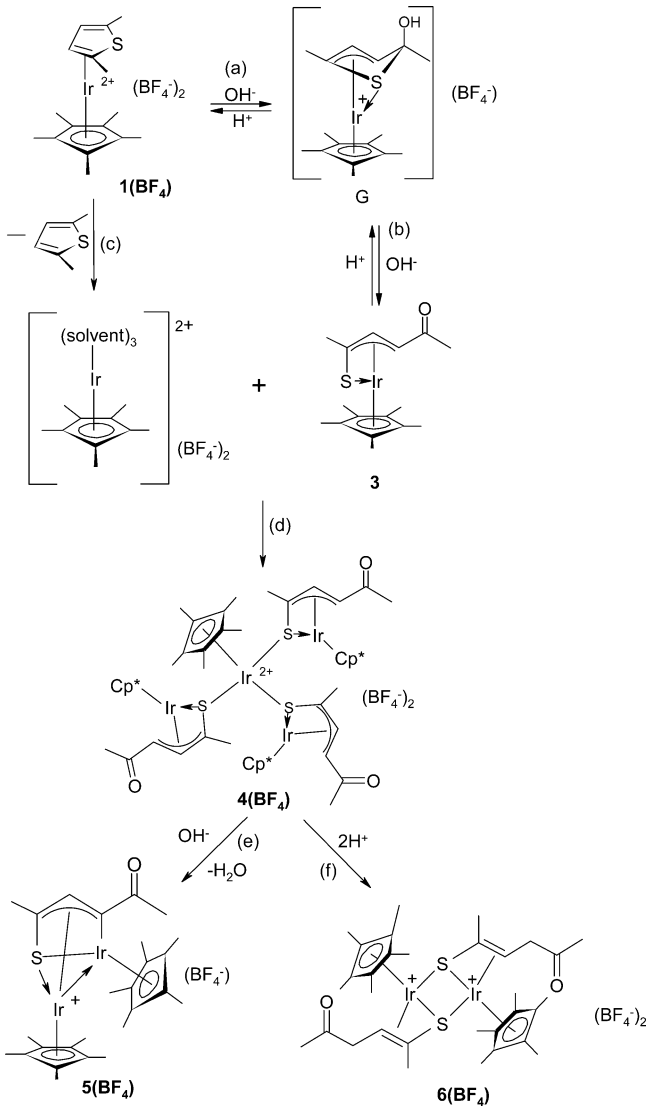
(d) The reaction of **1(BF_4)** with 1 equiv of a mixture having a lower concentration of KOH in H_2O (0.01 M) affords the corresponding mixture of compounds **3**, **4(BF_4)**, **5(BF_4)** and free 2,5-dimethylthiophene, as above, but also the new dimeric compound [$Cp^*Ir(\mu_2,\eta^3$-SC(Me)$CHCH_2$C(O)Me)]$_2(BF_4)_2$ (**6(BF_4)**) (vide infra) (Schemes 2 and 3).

Compounds **2**[9] and **3** were identified by their spectra, which are the same as those previously reported by one of us.[8b]

The new compounds **4**−**6** were characterized by their ^{1}H, ^{19}F, and ^{13}C NMR spectra (Experimental Section), which are consistent with their molecular structures in the solid state determined by X-ray diffraction studies. Crystal data for compounds **4(BF_4)**, **5(OTf)**, and **6(BF_4)** are presented in Table 1, while selected bond lengths and angles for the compounds are given in Tables 2−4, respectively.

An ORTEP drawing of the tetrameric compound **4(BF_4),** which is shown in Figure 1, contains three Ir atoms in similar coordination environments (Ir(2), Ir(3), and Ir(4)), while Ir(1) is unique. Atom Ir(1) is coordinated in a piano-stool fashion to an η^5-Cp* ligand and three sulfur atoms of three MeC(O)CH=CHC(S)Me ligands that are part of three acyl thiolate complexes **3**. The average Ir(1)−S bond length (2.406(5) Å) is statistically indistinguishable from the other Ir−S bond

Scheme 3



distances in **4(BF_4)** (average 2.396(11) Å). All Ir−S bond lengths are longer than those in compound **6(BF_4)** but fall in the usual range for Ir−S bonds.[10]

The structure of the dinuclear monocationic complex **5(OTf)** is presented in Figure 2. The structure has a C_3S bridge between the iridium atoms. The S atom is unsymmetrically placed with respect to the Ir1 and Ir2 atoms (2.270(2) and 2.429(2) Å, respectively), which suggests more σ character in the Ir1−S bond; these distances can be compared with Ir−S distances in **3** (2.390(5) Å)[8b] and **4(BF_4)** (average 2.4008 Å). The Ir1−C24 (2.019(9) Å) and Ir2−C24 (2.247(9) Å) distances are quite different. The Ir2−Cp* (average 2.197 Å) lengths are slightly shorter than those for the cationic fragment Ir1−Cp* (average 2.2186 Å). The acyl thiolate derivative **3** has an average Ir−Cp* bond length of 2.174 Å.[8b]

A molecular drawing of the compound **6(BF_4)** is presented in Figure 3. The complex occupies a crystallographic inversion center which is located in the middle of the Ir−S−Ir−S rhombus, and only half of the complex is symmetry independent. Each Ir atom is coordinated to a η^5-Cp* ligand, a η^3-MeC(O)CH_2CH=C(Me)S ligand

(9) Compound **2** in $CDCl_3$ and C_6D_6 at room temperature converts to **3**. We presume that traces of acid present in the deuterated solvents cause this transformation.

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Table 1. Crystal Data for the Iridium Compounds 4(BF$_4$), 5(OTf), 6(BF$_4$), and 10(BF$_4$)

	4(BF$_4$)	5(OTf)	6(BF$_4$)	10(BF$_4$)
formula	$C_{62}H_{96}B_2F_8Ir_4N_4O_{11}S_3$	$C_{27}H_{37}F_3Ir_2O_4S_2$	$C_{34}H_{54}B_2F_8Ir_2N_2O_6S_2$	$C_{19}H_{34}BF_4O_4Rh$
mol wt	2112.03	931.09	1208.93	516.18
space group	*C*2/*c*	*P*2$_1$	*P*1	*P*2$_1$/*c*
a (Å)	28.1666(13)	8.4086(1)	10.212(3)	10.154(2)
b (Å)	15.5261(7)	13.5617(2)	11.148(4)	13.941(3)
c (Å)	33.6260(16)	13.1486(2)	11.480(4)	16.209(4)
α (deg)	90	90	101.58(3)	90
β (deg)	98.537(1)	92.860(1)	114.66(2)	99.629(11)
γ (deg)	90	90	106.31(3)	90
V (Å^3)	14542.3(12)	1497.53(4)	1061.5(6)	2262.2(9)
Z	8	2	1	4
cryst size (mm)	0.32 × 0.28 × 0.22	0.38 × 0.16 × 0.05	0.3 × 0.3 × 0.3	0.75 × 0.2 × 0.1
D_{calcd} (g cm^{-3})	1.929	2.065		1.516
θ limit (deg)	1.46−28.90	1.55−24.97	2.10−23.09	7.04−54.96
h, *k*, *l* ranges	$-35 \le h \le 36$	$-9 \le h \le 9$	$-10 \le h \le 9$	$-13 \le h \le 13$
	$-19 \le k \le 20$	$-15 \le k \le 16$	$-11 \le k \le 11$	$-18 \le k \le 17$
	$-44 \le l \le 43$	$0 \le l \le 15$	$0 \le l \le 11$	$-21 \le l \le 17$
total no. of data	60 472	11 067	3440	22 199
total no. of unique data	17 155 (*R*(int) = 0.0314)	4940 (*R*(int) = 0.0406)	2684 (*R*(int) = 0.0235)	5149 (*R*(int) = 0.0622)
final R1	0.0256	0.0288	0.0238	0.0650
final wR2	0.0599	0.0695	0.0558	0.1913
GOF	1.014	1.056	1.118	1.035

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) of 4(BF$_4$)

Ir1−S1	2.4098(9)	Ir3−C214	2.198(4)
Ir1−S3	2.4060(9)	Ir4−C311	2.159(4)
Ir2−C111	2.168(4)	Ir4−C314	2.181(4)
Ir2−C113	2.150(4)	S1−C111	1.777(4)
Ir2−C114	2.176(4)	C111−C112	1.516(6)
Ir2−S1	2.4045(9)	C113−C114	1.435(6)
Ir3−S2	2.3835(9)	C114−C115	1.482(6)
Ir4−S3	2.4002(9)	C115−C116	1.519(8)
Ir3−C213	2.158(4)	O1−C115	1.218(6)
S2−Ir1−S3	87.63(3)	C111−Ir2−S1	45.37(10)
S3−Ir1−S1	90.89(3)	C114−Ir2−S1	81.79(10)
Ir2−S1−Ir1	130.39(4)	C111−S1−Ir2	60.27(13)
Ir3−S2−Ir1	128.90(4)	C111−S1−Ir1	121.30(13)
C113−Ir2−C111	37.72(15)	C111−C113−C114	121.6(4)
C113−Ir2−C114	38.75(17)	O1−C115−C116	121.7(4)
C113−Ir2−S1	73.31(11)		

Table 3. Selected Bond Lengths (Å) and Angles (deg) of 5(OTf)

Ir1−Ir2	2.8436(4)	Ir2−C23	2.195(10)
Ir1−S1	2.270(2)	Ir2−C24	2.247(9)
Ir2−S1	2.429(2)	C25−O1	1.183(12)
Ir1−C24	2.019(9)	C25−C26	1.550(14)
Ir2−C21	2.208(9)		
C24−Ir1−C1	170.5(4)	C24−Ir1−Ir2	51.7(3)
C24−Ir1−C2	133.6(3)	S1−Ir1−Ir2	55.36(6)
C24−Ir1−C3	108.1(3)	S1−Ir2−Ir1	50.25(6)
C24−Ir1−C4	113.1(4)	C21−C23−C24	117.8(9)
C24−Ir1−C5	144.5(4)	C23−C21− S1	114.0(7)
C24−Ir1−S1	82.3(3)	Ir1−C24−Ir2	83.4(3)

(L) through atoms C(21), C(23) and S(1), and the symmetry-related atom S(1a). Interestingly, the Ir−S(1) distance to the L ligand (2.382(2) Å) is slightly longer than the Ir−S(1a) distance (2.342(2) Å). This difference is statistically significant and may reflect a higher *σ* character in the Ir−S(1a) bond. However, both Ir−S bond distances are within the typical range for Ir bonds to bridging sulfur atoms.[10] The Ir−S−Ir−S rhombus is planar and is defined by Ir(1a)−S(1)−Ir(1) (97.64(6)°) and S(1)−Ir(1)−S(1a) (82.36(6)°) angles. The Ir−C(21) distance (2.183(5) Å) is significantly shorter than the other Ir−C(23) bond length (2.259(5) Å) to the same vinyl group.

Reactions of [Cp*Ir(η^5-2,5-Me$_2$T)](X)$_2$ (X = OTf, 1(OTf); X = BF$_4$, 1(BF$_4$)) with MeOH. Although **1-(BF$_4$)** is not completely soluble in methanol, it reacts with continuous stirring to give three products, [(Cp*Ir)$_2$-(μ_2,η^4-SC(Me)CHCC(O)Me)](BF$_4$) (**5(BF$_4$)**), [Cp*Ir((μ_2,η^3-SC(Me)CHCH$_2$C(O)Me)]$_2$(BF$_4$)$_2$ (**6(BF$_4$)**), and [Cp*Ir(η^4-SC(Me)CHCHC(OMe)Me)](BF$_4$) (**7(BF$_4$)**) (Scheme 4).

Table 4. Selected Bond Lengths (Å) and Bond Angles (deg) of 6(BF$_4$)

Ir1−S1	2.382(2)	C21−C23	1.392(9)
Ir1−S1A	2.3421(16)	C21−C22	1.492(8)
S1−C21	1.745(6)	C23−C24	1.495(9)
Ir1−C21	2.184(6)	C24−C25	1.473(10)
Ir1−C23	2.259(6)	C25−C26	1.481(10)
O1−C25	1.197(9)	C25−O1	1.197(9)
S1−Ir1−S1A	82.36(6)	C23−C21−C22	124.5(6)
Ir1A−S1−Ir1	97.64(6)	C21−C23−C24	122.9(5)
C21−Ir1−C23	36.5(2)	C24−C25−C26	116.4(7)
C21−Ir1−S1A	99.24(16)	O1−C25−C26	121.2(8)
C23−Ir1−S1A	79.79(16)	S1−C21−Ir1	73.7(2)
C23−C21−Ir1	74.7(3)	C21−S1−Ir1A	112.5(2)
C21−C23−Ir1	68.8(3)		

Immediately after the addition of **1(BF$_4$)** to CH_3OH at room temperature, there is ^{1}H NMR evidence for the compound **7(BF$_4$)**. To isolate this species, it is necessary to stop the reaction after 10 min. The formation of **7(BF$_4$)** is related to that of the analogous [(C$_5$R$_5$)Rh(η^4-C$_4$Me$_4$S-2-OH)]$^+$,[4] which is a precursor to the compounds Cp*Rh[η^4-Me$_4$T(O)] and Cp*Rh[η^4-SC$_3$Me$_3$C(O)-Me] (Scheme 1). The NMR studies show that the formation of **7(BF$_4$)** can be reversed, giving **1(BF$_4$)** in the presence of H^+, which presumably comes from the MeOH solvent. Addition of HOTf to **7(BF$_4$)** in CD_3NO_2 immediately gives total transformation to **1**. We also attempted to synthesize the 2-hydroxy analogue (Scheme 3, intermediate G) of **7(BF$_4$)** by reacting **3** (150 mg, 0.33 mmol) with NH_4PF_6 (60 mg, 0.37 mmol) in CH_2Cl_2 (40 mL) as reported for [(Cp*)Rh(η^4-C$_4$Me$_4$S-2-OH)][PF$_6$],[4] but only compound **3** (105 mg, 0.23 mmol, 70%) was recovered, even after 24 h at room temperature and 3 h under reflux.

When **1(BF$_4$)** reacts in methanol at room temperature overnight, bright lemon yellow **6(BF$_4$)** precipitates and is isolated in 23% yield after recrystallization from nitromethane/diethyl ether. The remaining methanol solution afforded a red oil that after recrystallization

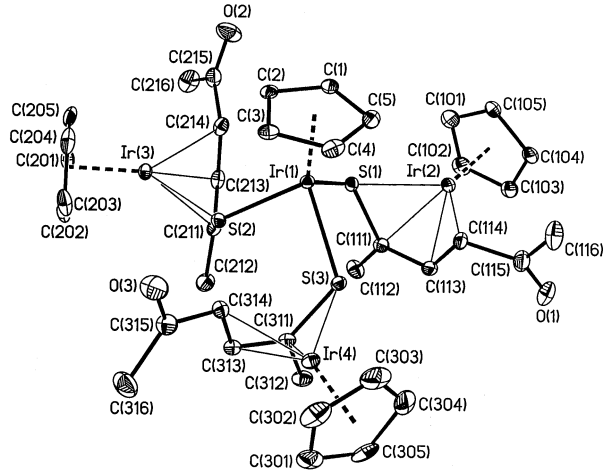


Figure 1. ORTEP drawing of the cationic portion of **4-(BF$_4$)**. Methyl groups of Cp* ligands have been omitted for clarity.

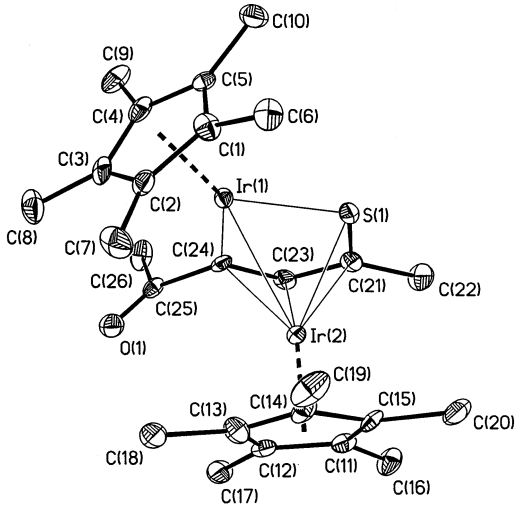


Figure 2. ORTEP drawing of the cationic portion of **5-(OTf)**.

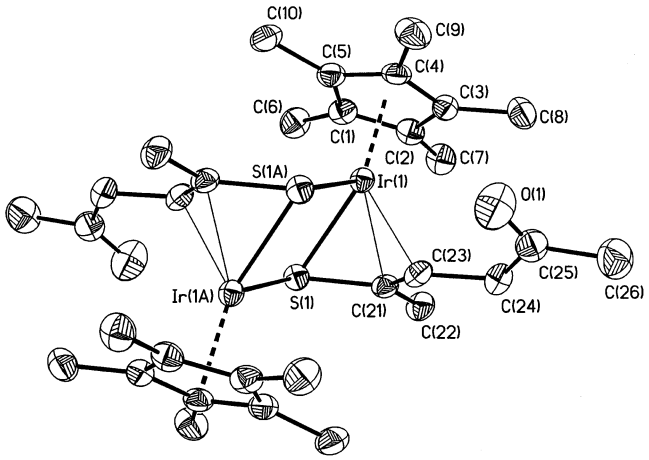
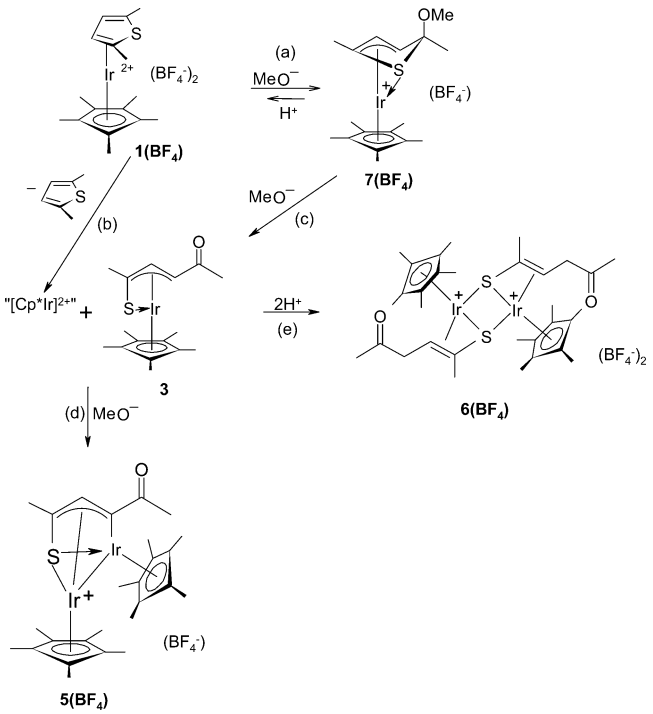


Figure 3. ORTEP drawing of the cationic portion of **6-(BF$_4$)**.

from methylene chloride/diethyl ether gave red crystals (9.2%) of **5(BF$_4$)**. In contrast to **1(BF$_4$)**, **1(OTf)** is completely soluble in methanol and affords, after 12 h at room temperature, almost exclusively **5(OTf)** (31.6%) and a small amount (1.2%) of **6(OTf)**. This result suggests that the solubility of **1(BF$_4$)** or **1(OTf)** determines whether **5** or **6** is the major product of the reaction. It also indicates that **5** and **6** do not interconvert under the conditions of these reactions. Compounds **6(BF$_4$)** and **6(OTf)** are quite stable and soluble in CD_3NO_2 and D_2O.

Scheme 4



A vinyl thiolate dimer analogous to **6(BF$_4$)**, (η^6-cymene)Ru[μ_2,η^3-SC(Me)CHCH$_2$COMe]$_2^{2+}$, was previously obtained as a bright yellow precipitate by Rauchfuss et al.[5] It formed upon addition of HOTf to a CH_2Cl_2 solution of the thermodynamic syn isomer (η^6-cymene)-Ru[η^4-SC(Me)CHCHCOMe], which is the analogue of the acyl thiolate derivative **3**. Protonation of **3** with HBF_4 and HOTf afford the corresponding salts **1(BF$_4$)** and **1(OTf)**. In contrast, only the kinetic isomer (anti) of (η^6-cymene)Ru[η^4-SC(Me)CHCHCOMe] reacts with acid to give (η^6-cymene)Ru(2,5-Me$_2$T)$^{2+}$.[5]

The formation of **7(OTf)** is observed only in NMR tube experiments as described below, but the analogous **7-(BF$_4$)** has been isolated and characterized by elemental analysis and its NMR spectrum (vide infra).

Discussion

Base Hydrolysis Interconversions among Reactants and Products. The reaction of **1(BF$_4$)** with H_2O gives directly the dinuclear monocationic compound **5-(BF$_4$)** in 46% yield, while **1(BF$_4$)** with 1 equiv of KOH/H_2O (0.01 M) allows the isolation of **3**, **4(BF$_4$)**, **5(BF$_4$)**, and traces of **6(BF$_4$)**, as described in Scheme 2. The reaction of **1(OTf)** with H_2O gives **5(OTf)**, even in the presence of a drop of $HOSO_2CF_3$, which might have been expected to give the protonated complex **6(OTf)**. Scheme 3 rationalizes the formation of all of the products, which are formed upon reaction with neutral or basic water solutions.

NMR studies of **1(BF$_4$)** and **1(OTf)** in CD_3NO_2 show that, when a drop of KOH/D_2O (0.01 M) is added, there is evidence for some of the intermediate species de-

scribed in Scheme 3. The reaction occurs faster for **1-(OTf)** than for **1(BF_4)**. However, both dicationic salts gave evidence of compounds **5(X)** (X = BF_4, OTf) as the final product, along with free 2,5-dimethylthiophene.

As **1(BF_4)** reacts more slowly than **1(OTf)**, the reaction of the former salt was monitored by ^{1}H NMR in CD_3NO_2. According to Scheme 3, OH^- first adds to **1(BF_4)** (step a) to give intermediate G, which was not observed, but a similar compound, **7(BF_4)**, was isolated from the corresponding methanolysis reaction (vide supra, Scheme 4). A second molecule of OH^- (step b) deprotonates G to give the acyl thiolate **3**, which is observed in traces, along with **4(BF_4)** (step d), which shows only one set of signals for the acyl thiolate fragment, suggesting that all three fragments are equivalent, as shown by X-ray diffraction studies (Figure 1); two methyl singlets in a 45:15 ratio are observed for the two different Cp* ligands. Evidence of free 2,5-dimethylthiophene, as described in step c, suggests the formation of [Cp*Ir(solvent)$_3$]$^{2+}$, which reacts immediately with three molecules of compound **3** to give **4(BF_4)**, which is converted to **5(BF_4)** by deprotonation with OH^- (step e) or to **6(BF_4)** by protonation ($2H^+$) in step f. The ^{1}H NMR spectrum of **5(BF_4)**, which shows one singlet at 5.90 ppm, two methyl singlets at 2.53 and 2.29 ppm, and two singlets for the different Cp* ligands at 2.10 and 2.11 ppm, is consistent with the X-ray diffraction structure of **5(OTf)** (Figure 2). For **6(BF_4)**, there is a triplet at 4.39 ppm and a doublet of doublets at 3.50 ppm for CH and CH_2, respectively, along with two methyl singlets at 2.55 and 2.35 ppm and the Cp* ligand at 1.95 ppm, which is consistent with the X-ray structure of **6(BF_4)** (Figure 3).

NMR studies of solutions of **1(BF_4)** and **3** or compounds **3**, **4(BF_4)**, **1(BF_4)**, and **1(OTf)** under different conditions (vide infra) confirm the formation of the different species described in Scheme 3. The studies were carried out in different deuterated solvents: CD_3NO_2, $CDCl_3$, CD_2Cl_2, CD_3COCD_3, CD_3OD, and D_2O for **4**, CD_3NO_2, $CDCl_3$, CD_3COCD_3, and CD_3OD for **3**, and CD_3NO_2, CD_3COCD_3, CD_3OD, and D_2O for **1(BF_4)** or **1(OTf)**. The reactions are quite dependent on the solvent and on the concentrations of the reactants. In general, CD_3NO_2 is the best solvent, because reactions in $CDCl_3$ and CD_2Cl_2 generated even more products that were not characterized. While the reactions in CD_3COCD_3 and CD_3OD were fastest, it was not possible to identify some of the new species. Of particular interest is the observation that at the end of all the reactions only **5(BF_4)** or **5(OTf)** and 2,5-dimethylthiophene were present. Therefore, compound **5** is the most stable species in this system because it does not convert to any other compounds.

Other experiments also support the interconversions in Scheme 3. These experiments are as follows. (i) Although **1(BF_4)** and **3** are stable in separate CD_3NO_2 solutions for at least 1 month, they react immediately when mixed to give **4(BF_4)** and **5(BF_4)** (Scheme 3, steps a−e). (ii) The reaction of **3** in CD_3NO_2 with a drop of $HOSO_2CF_3$ gives **6(OTf)** (Scheme 3, steps d and f), as well as **1(OTf)** (Scheme 3, steps b and a), without evidence of **4(OTf)** or **5(OTf)**, suggesting that **6(OTf)** is preferentially formed in acidic media. (iii) **3** in CD_3COCD_3 is stable for at least 8 days; however, **3** reacts with the dicationic labile complex [Cp*Ir(CD_3COCD_3)$_3$]-(BF_4)$_2$ within 45 min, giving complete transformation into **4(BF_4)** and **5(BF_4)** (Scheme 3, steps d and e). (iv) **4(BF_4)** is the most reactive species in all of the solvents because it converts within 15 min to **5(BF_4)**. (v) A solution of **1(BF_4)** in CD_3COCD_3 shows no evidence of other products for 10 h, but after 12 h there is evidence of traces of **5(BF_4)**, and after 2 and 3 days the mixture of **1(BF_4)** and **5(BF_4)** is present in ratios of 1:0.18 and 1:0.5, along with free 2,5-dimethylthiophene (Scheme 3, steps c−e). The source of oxygen for the acyl group in **5(BF_4)** is not obvious, and the only source of oxygen in this reaction is the deuterated solvent or adventitious water.

There was no reaction between **5(BF_4)** and LiCl (in CD_3OD), NaF (in CD_3OD), (NMe_4)Br (in $CDCl_3$), PMe_3 (in $CDCl_3$), (PPN)Cl (in $CDCl_3$), or MeOTf (in $CDCl_3$), even with heating at ∼55 °C.

Interconversions among Reactants and Products in Methanol. According to the summary of reactions of **1(BF_4)** in MeOH in Scheme 4, **1(BF_4)** is attacked by MeO^-, affording **7(BF_4)** (step a), which can partially revert to **1(BF_4)** with H^+ (step a) or suffer a second nucleophilic attack to give **3** (step c). Compound **3** can then react with "[Cp*Ir]$^{2+}$" resulting from the decoordination of 2,5-dimethylthiophene from **1(BF_4)** (step b). The reaction of **3** with MeO^- gives **5(BF_4)**, (step d) or with two H^+ to give **6(BF_4)** (step e). NMR studies on the methanolysis were preferentially made with **1-(BF_4)** because of its slower reactivity, due to low solubility, compared with that for **1(OTf)**.

Some complementary NMR studies of compounds **1-(BF_4)**, **3**, and **7(BF_4)** under methanolysis conditions support the chemistry described in Scheme 4.

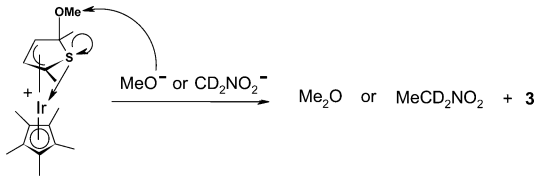
(i) **1(BF_4)** in CD_3OD immediately gives evidence of **7(BF_4)**. After 45 min compound **5(BF_4)** and free 2,5-dimethylthiophene are observed. Compound **6(BF_4)** precipitates from solution, and after 5 days there is a 1:1:13 ratio of **7(BF_4)**, **1(BF_4)**, and **5(BF_4)**, respectively. There is no evidence for compound **4(BF_4)**; however, it may be an intermediate (as in Scheme 3) that is rapidly converted in methanol to **5(BF_4)**; this is supported by the observation that pure **4(BF_4)** when dissolved in CD_3OD immediately gives **5(BF_4)**.

(ii) **1(BF_4)** or **1(OTf)** in CD_3NO_2 requires an excess of MeOH in order to give **5**, traces of **7**, and free 2,5-dimethylthiophene, the amounts depending on the concentration of MeOH. A solution of **1(BF_4)** in CD_3NO_2 with NaOMe gives evidence of **7(BF_4)**, but after some minutes, only **5(BF_4)** is observed in solution. There is no evidence of the soluble complex **6(BF_4)**, as expected because of the absence of H^+, which would be formed from MeOH.

(iii) The addition of a drop of HBF_4/Et_2O to a CD_3OD solution of **3** gives **1(BF_4)** along with traces of **5(BF_4)**; this is in contrast to the reaction of **3** in CD_3NO_2 with one drop of HOTf, which gives **6(OTf)** and **1(OTf)**.

(iv) **7(BF_4)** transforms in CD_3NO_2 to give spectroscopic evidence of methanol and **1(BF_4)**, which suggests that the methoxide group of **7(BF_4)** is protonated (Scheme 4, step a). As noted above, the source of H^+ has not been identified but presumably comes from the

Scheme 5



CD_3NO_2 solvent.[11] Once compound **1(BF$_4$)** forms and there is a 1:1 ratio of **1(BF$_4$)** to **7(BF$_4$)**, traces of free 2,5-dimethylthiophene are observed; after that, compound **5(BF$_4$)** appears. When the **5(BF$_4$)** to **1(BF$_4$)** ratio reaches 1:1, there is no further change. As methanol is liberated from **7(BF$_4$)** in order to give **1(BF$_4$)**, we propose tentatively the attack of MeO^- (or $^-CD_2NO_2$ from deprotonated solvent) on **7(BF$_4$)** as the pathway to the formation of compound **3** (vide infra), according to Scheme 5. However, we were not able to detect the volatile ether MeOMe or the other possible product $MeCD_2NO_2$.

To determine the source of oxygen in the conversion of **7(BF$_4$)** to **3**, we explored the possibility that it comes from air, water, or the solvent. When O_2 is bubbled through the solution of **7(BF$_4$)** in CD_3NO_2, the conversion to **1(BF$_4$)** is only slightly faster than without O_2; this suggests that oxygen from air is not the main source of the oxygen in **3**. When NaOMe and $NaOCD_3$ are added to the reaction mixture, it actually proceeds more slowly and intermediates such as **3** can be observed in solution. Thus, we propose that the oxygen is either coming from traces of water in the solvent or by nucleophilic attack of $^-CD_2NO_2$ on the methoxy methyl group of **7(BF$_4$)**, (Scheme 5).

Synthesis and Reactivity of [Cp*Rh(η^5-2,5-Me$_2$T)](BF$_4$)$_2$ (8(BF$_4$)). [Cp*Rh(η^5-2,5-Me$_2$T)](BF$_4$)$_2$ (**8(BF$_4$)**) was prepared in two steps from $(Cp^*RhCl_2)_2$ in a manner analogous to the synthesis of **1(BF$_4$)**. However, while the iridium complex **1(BF$_4$)** was the only product, the synthesis of **8(BF$_4$)** also produces the new complex [(Cp*Rh)$_2$(μ_2,η^4-SC(Me)CHCC(O)Me)](BF$_4$) (**9(BF$_4$)**), analogous to **5(BF$_4$)**. **9(BF$_4$)** was characterized by its elemental composition and the similarity of its ^{1}H and ^{13}C NMR spectra to those of **5(BF$_4$)**. Base hydrolysis of **8(BF$_4$)** under conditions identical with those for **1**, using KOH/H_2O (0.01 and 0.03 M) gave only free 2,5-dimethylthiophene and unidentified "Cp*Rh" complexes that did not contain 2,5-Me$_2$T or its derivatives, as determined by ^{1}H and ^{13}C NMR spectroscopy. This result contrasts with that previously observed for Cp*Rh(η^5-Me$_4$T)](OTf)$_2$, which after base hydrolysis afforded the acyl thiolate derivative [Cp*Rh(η^4-SC$_3$Me$_3$C(O)Me)],[3,4] the analogue of complex **3**. Even though there is no spectroscopic evidence of the corresponding acyl thiolate in the base hydrolysis of **8(BF$_4$)**, traces of **9(BF$_4$)** are formed, which implies the formation of such an acyl thiolate complex. Also, the reaction between **8(BF$_4$)** and (*n*-Bu)$_4$NOH in CH_3CN at 0 °C gave no evidence for the formation of the acyl thiolate complex ([(*n*-Bu)$_4$N](BF$_4$)[12] was isolated in 66% yield); under the same conditions, **1(BF$_4$)** was converted to **3**.

(11) Since CH_3NO_2 (pK_a = 10) is more acidic than MeOH (pK_a = 15), **7** is more likely to be protonated by the CD_3NO_2. **7** + CD_3NO_2 → **1**$^+$ + MeOH + $^-CD_2NO_2$. $^-CD_2NO_2$ would attack **7** to give **3**.

(12) Pouchert, C. J.; Behnke, J. *The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra*, 1st ed.; Aldrich: Milwaukee, WI, 1993; Vol. I, 610 B.

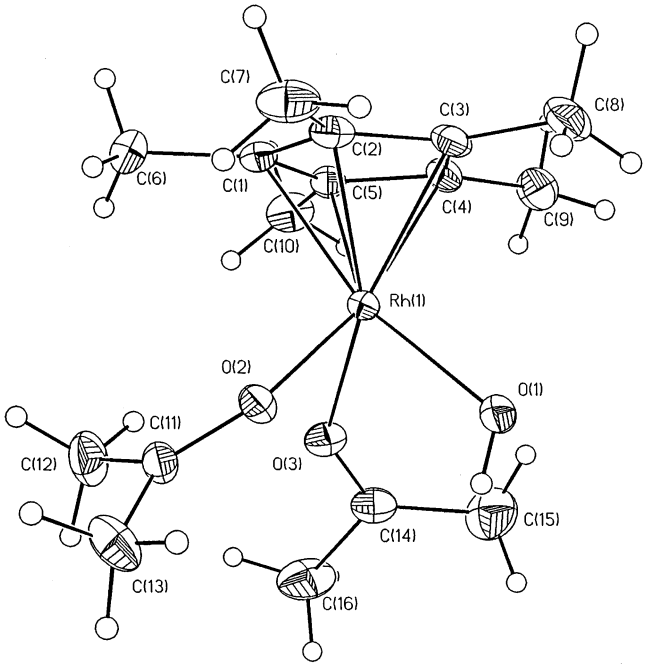
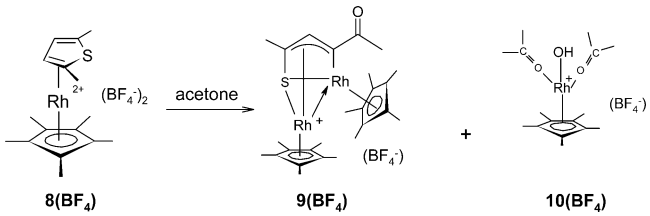


Figure 4. ORTEP drawing of the cationic portion of **10(BF$_4$)**.

Scheme 6



As in the reactions of **1(BF$_4$)**, **8(BF$_4$)** reacts with D_2O in CD_3NO_2 and MeOH to afford the monocationic binuclear species **9(BF$_4$)**, analogous to **5**, in ~7% yield as determined by ^{1}H NMR spectroscopy. Once again, there was no evidence for a rhodium analogue of the iridium acyl thiolate **3**. If the reaction is carried out in acetone, at room temperature, the solvolysis of **8(BF$_4$)** affords after 18 h or after 5 days **9(BF$_4$)** in 6.1 and 13% yields, respectively (see Experimental Section), along with the mononuclear complex [Cp*Rh(OCMe$_2$)$_2$(OH)](BF$_4$) (**10(BF$_4$)**) in 54 and 41% yields, respectively.Formation of **10(BF$_4$)** occurs by losing the thiophene ligand and coordinating two solvent molecules and a hydroxide ligand. The source of the hydroxide ligand is presumably adventitious water, but dried acetone was used in the experiment. Recently, the molecular structure of the tris(solvent)rhodium complex [Cp*Rh(OCMe$_2$)$_2$(H_2O)](BF$_4$)$_2$ was reported.[13] The crystal structure of compound **10(BF$_4$)** is shown in Figure 4, and crystal data and selected bond lengths and angles are given in Tables 1 and 5. Compound **10(BF$_4$)** crystallized with one molecule of acetone in the unit cell. The related mononuclear complex Cp*Rh(H_2O)$_2$(OH)$^+$ was proposed as a precursor to the putative dimer complex [Cp*Rh(μ-OH)(H_2O)]$_2$(OTf)$_2$.[14]

(13) Amouri, H.; Guyard-Duhayon, C.; Vaissermann, J. *Inorg. Chem.* **2002**, *41*, 1397.

(14) Eisen, M. S.; Haskel, A.; Chen, H.; Olmstead, M. M.; Smith, D. P.; Maestre, M. F.; Fish, R. H. *Organometallics* **1995**, *14*, 2806.

Table 5. Selected Bond Lengths (Å) and Bond Angles (deg) of 10(BF$_4$)

O1−Rh1	2.180(4)	C11−C12	1.479(10)
O2−Rh1	2.157(4)	C11−C13	1.468(10)
O3−Rh1	2.134(4)	C14−C15	1.455(13)
C11−O2	1.251(7)	C14−C16	1.494(11)
C14−O3	1.237(8)	C17−C18	1.302(14)
O2−Rh1−O1	76.31(17)	O3−C14−C15	122.7(7)
O3−Rh1−O1	89.78(17)	O3−C14−C16	117.1(7)
O3−Rh1−O2	84.25(17)	C13−C12−C11	118.4(6)
O2−C11−C13	119.0(6)	C15−C14−C16	120.1(8)
O2−C11−C12	122.6(6)		

Conclusions

The 2,5-dimethylthiophene ligand in Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ (**1**) reacts with 0.03 M KOH/H$_2$O to give a mixture of the sulfoxide complex Cp*Ir[η^4-2,5-Me$_2$T(O)] (**2**) and the acyl thiolate Cp*Ir(η^4-SC(Me)CHCHC(O)Me) (**3**); however, in a less basic solution (0.01 M KOH/H$_2$O) or in pure water, tetra- and dinuclear complexes **4**−**6** are formed. These products are formed by a complex series of reactions (Scheme 3) that begin with the displacement of the 2,5-Me$_2$T ligand from Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ (**1**) and reaction of the resulting "[Cp*Ir]$^{2+}$" fragment with **3**. The amount of each of the products depends on the basicity/acidity of the solution and the solvent. The reaction of Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ (**1**) with MeOH leads to many of the same products, but the reaction pathways (Scheme 4) involve different intermediates.

The rhodium analogue of **1**, Cp*Rh(η^5-2,5-Me$_2$T)$^{2+}$ (**8(BF$_4$)**), reacts with D$_2$O, MeOH, and acetone to give the dinuclear complex **9(BF$_4$)**, the analogue of **5(BF$_4$)**, but there is no evidence for the other products observed in the reactions of **1** with these solvents. The reaction of **8(BF$_4$)** in acetone also afforded the solvolysis product [Cp*Rh(OCMe$_2$)$_2$(OH)][BF$_4$] (**10(BF$_4$)**). Although all of these reactions are complicated, they lead to a series of products that illustrate new ways that derivatives of 2,5-Me$_2$T can coordinate to two and four metal centers.

Experimental Section

General Procedures. All reactions were performed under an N$_2$ atmosphere in reagent grade solvents. Diethyl ether was distilled from Na/benzophenone, CH$_2$Cl$_2$ and hexane from CaH$_2$, acetone from K$_2$CO$_3$, acetonitrile from CaCl$_2$, and methanol from Mg/I$_2$. [Cp*IrCl$_2$]$_2$[15] and Cp*Ir(η^5-2,5-Me$_2$T)-[BF$_4$]$_2$[16] were prepared by literature methods. 2,5-Dimethylthiophene was used without further purification. Elemental analyses were performed by ISU services. Infrared spectra were collected on Perkin-Elmer 6FPC-FT and Nicolet 560 spectrophotometers. The ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded on JEOL GSX-270, JEOL Eclipse-400, Bruker 300, Bruker DRX 400, and Varian 300 MHz spectrometers using deuterated solvents as internal locks and references with respect to TMS. Electron ionization mass spectra (EIMS, ESI, and HRMS) were run on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB) spectra were run on a Kratos MS-50 mass spectrometer using a 3-NBA/CH$_3$NO$_2$ or 3-NBA/CH$_2$-Cl$_2$ matrix. The melting points were determined in sealed N$_2$-filled capillaries and were not corrected. NMR tube reactions were performed under a nitrogen atmosphere in septum-capped NMR tubes. All reactions were performed at room temperature, except when otherwise described.

[Cp*Ir(η^5-2,5-Me$_2$T)](X)$_2$ (X = BF$_4$, 1(BF$_4$); X = OSO$_2$CF$_3$, 1(OTf)). The following procedure was adapted from the procedure of Angelici and co-workers.[16] The synthesis of **1(BF$_4$)** was modified, using a stoichiometric amount of 2,5-dimethylthiophene, instead of a great excess. A 1.00 g portion (1.26 mmol) of [Cp*IrCl$_2$]$_2$ in acetone (30 mL) was reacted with AgBF$_4$ (0.98 g, 4.94 mmol) to give [Cp*Ir(acetone)$_3$][BF$_4$]$_2$. The silver chloride was filtered from the solution, and 2,5-dimethylthiophene (0.29 mL, 2.52 mmol) was added drop by drop to give a gray precipitate. The solution was refluxed for 15 min. After it was cooled to room temperature, the solution was evaporated and the solid product was purified by recrystallization from CH$_3$NO$_2$ and diethyl ether. After three filtrations through small-pore filter paper, 1.1 g (1.79 mmol) of the white product **1(BF$_4$)** was obtained in 72% yield. ^{1}H NMR (CD$_3$NO$_2$): δ 2.74 (s, 6H; 2,5-Me), 7.23 (s, 2H; H3, H4), 2.43 (s, 15H; Cp*). ^{1}H NMR ((CD$_3$)$_2$CO)): δ 2.83 (s, 6H; 2,5-Me), 7.54 (s, 2H; H3, H4), 2.47 (s, 15H; Cp*). ^{1}H NMR (CD$_3$OD): δ 2.66 (s, 6H; 2,5-Me), 7.38 (s, 2H; H3, H4), 2.35 (s, 15H; Cp*). ^{1}H NMR (D$_2$O): δ 2.48 (s, 6H; 2,5-Me), 7.17 (s, 2H; H3, H4), 2.18 (s, 15H; Cp*). ^{13}C{^{1}H} NMR (CD$_3$NO$_2$): δ 111.80 (C2, C5), 105.00 (C3, C4), 12.40 (2,5-Me), 8.70 (Me, Cp*), 99.10 (C, Cp*). ^{11}B NMR (CD$_3$NO$_2$): δ −2.23.

The white dicationic salt **1(OTf)** was synthesized in a manner analogous to that described for the similar BF$_4$ salt,[16] in 83% yield. Mp: 262 °C dec. Anal. Calcd (found) for C$_{18}$H$_{23}$F$_6$-IrO$_6$S$_3$: C, 29.31 (29.46); H, 3.14 (3.16). ^{1}H NMR (CD$_3$NO$_2$): δ 2.74 (s, 6H; 2,5-Me), 7.29 (s, 2H; H3, H4), 2.42 (s, 15H; Cp*). ^{13}C{^{1}H} NMR (CD$_3$NO$_2$): δ 113.32 (C2, C5), 106.35 (C3, C4), 13.75 (2,5-Me), 10.04 (Me, Cp*), 100.47 (C, Cp*).

Cp*Ir[η^4-2,5-Me$_2$T(O)] (2) and [(Cp*Ir)$_2$(μ_2,η^4-SC(Me)-CHCC(O)Me)](OTf) (5(OTf)). To 500 mg of **1(OTf)** (0.68 mmol) was added 67.7 mL of 0.03 M aqueous KOH (2.04 mmol). The initial pale yellow solution immediately became darker, and after a couple of hours a small amount of an orange-red precipitate was observed. The solution was stirred overnight, and a very small amount of red solid was removed by filtration. The solvent was slowly removed under vacuum using a warm water bath. The resulting brown-white solid residue was dissolved in CH$_2$Cl$_2$ to give an orange solution, which was filtered. After the volume was reduced under vacuum and Et$_2$O was added, the solution was allowed to stand at 5 °C for several days, which gave crystals of **5(OTf)**. The material that was insoluble in CH$_2$Cl$_2$ was dissolved in a minimum amount of CH$_3$NO$_2$; the addition of Et$_2$O afforded 144 mg of a white to slightly beige precipitate, which was twice recrystallized from CH$_3$NO$_2$/Et$_2$O. Yield: 46.5%. This compound is identical with **2**, which was previously reported. Mp 156-157 °C (lit.[8b] mp 133-135 °C). Anal. Calcd (found) for C$_{16}$H$_{24}$IrOS: C, 42.18 (42.17); H, 5.08 (4.98). ^{1}H NMR (CDCl$_3$): δ 1.69 (s, 6H; 2,5-Me), 4.50 (s, 2H; H3, H4), 1.98 (s, 15H; Cp*). ^{1}H NMR (C$_6$D$_6$): δ 0.30 (s, 6H; 2,5-Me), 4.10 (s, 2H; H3, H4), 1.55 (s, 15H; Cp*). ^{13}C{^{1}H} NMR (CDCl$_3$): δ 65.02 (C2, C5), 69.28 (C3, C4), 2.83 (2,5-Me), 10.07 (Me, Cp*), 90.34 (C, Cp*). EIMS: m/z 455 (M$^+$), 440 (M − O)$^+$, 410, 360. IR (CHCl$_3$): ν_{SO} 1005 cm^{-1}.

[Cp*Ir(η^4-SC(Me)CHCHC(O)Me)] (3). The following procedure is similar to that previously reported,[8b] which gave a mixture of products **2** and **3** in 23 and 37% yields, respectively, using H$_2$O-treated alumina. In this work, we obtained **3** as the exclusive product in 56.3% yield by reacting 300 mg (0.49 mmol) of **1(BF$_4$)** in MeCN (30 mL) at 0 °C, with n-Bu$_4$N$^+$OH$^-$ (1.02 mL, 1 M solution in CH$_3$OH, 1.02 mmol), which was added dropwise. After each drop, the solution changed from white to orange-yellow and then to wine red. After 1 h the solution was brown-red. This solution was stirred for 7 h at room temperature. The solvent was evaporated under vacuum, and the remaining solid was dissolved in CH$_2$Cl$_2$. The resulting solution was chromatographed on neutral alumina (Brock-

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mann I, 58 Å, ~150 mesh) with diethyl ether as the eluting solvent. The product was collected in a small amount. However, after 2 h, more compound **3** was eluted from the chromatographic column with diethyl ether. Evaporation of the solvent gave 126 mg (0.28 mmol) of orange-yellow compound **3** in 56.3% yield. Mp: 131−132 °C. ^{1}H NMR (CD_3NO_2): δ 2.28 (s, 3H; 2-Me), 5.62 (d, 1H, J = 6.2 Hz; H3), 2.52 (d, 1H, J = 6.2 Hz; H4), 1.98 (s, 3H; 5-Me), 1.88 (s, 15H; Cp*). ^{1}H NMR ($CDCl_3$): δ 2.29 (s, 3H; 2-Me), 5.69 (d, 1H; H3), 2.65 (d, 1H; H4), 2.04 (s, 3H; 5-Me), 1.87 (s, 15H; Cp*). ^{1}H NMR (CD_2Cl_2): δ 2.26 (s, 3H; 2-Me), 5.62 (d, 1H; J = 6.2 Hz; H3), 2.57 (d, 1H; J = 6.2 Hz; H4), 1.99 (s, 3H; 5-Me), 1.85 (s, 15H; Cp*). ^{1}H NMR (CD_3OD): δ 2.27 (s, 3H; 2-Me), 5.68 (d, 1H; J = 6.2 Hz; H3), 2.65 (d, 1H; J = 6.2 Hz; H4), 2.01 (s, 3H; 5-Me), 1.87 (s, 15H; Cp*). ^{1}H NMR ($(CD_3)_2CO$): δ 2.27 (s, 3H; 2-Me), 5.61 (d, 1H; J = 6.2 Hz; H3), 2.54 (d, 1H; J = 6.22 Hz; H4), 1.96 (s, 3H; 5-Me), 1.87 (s, 15H; Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 92.28 (C2), 78.47 (C3), 55.21 (C4), 203.19 (C5), 24.71 (2-Me), 30.73 (5-Me), 9.19 (Me, Cp*), 90.75 (C, Cp*).

Mixture of Compounds 2 and 3. To 200 mg of **1(OTf)** (0.27 mmol) was added 80 mL of 0.01 M aqueous KOH (0.81 mmol). The initial pale yellow solution was stirred at room temperature for 1 day, after which it became darker. The deep yellow solution was filtered, and the solvent was removed slowly under vacuum using a warm water bath. The resulting brown-white solid residue was dissolved in CH_2Cl_2 to give a yellow solution, which was filtered. The solvent was evaporated under vacuum and the remaining solid showed to be a mixture of compounds **2** and **3** in a 3:7 ratio (^{1}H NMR, $CDCl_3$). This solid was chromatographed on neutral alumina using diethyl ether as the eluting solvent. The product was collected in three different fractions, during a period of 24 h, giving exclusively compound **3** in 61% yield (75 mg, 0.17 mmol).

(Cp*Ir)[Cp*Ir(η^4-SC(Me)CHCHC(O)Me)]$_3$(BF$_4$)$_2$ (4(BF$_4$)). To 400 mg of **1(BF$_4$)** (0.65 mmol) was added 65 mL of 0.01 M KOH/H_2O (0.65 mmol); an immediate color change to yellow and finally to orange-yellow was observed. After 10 min a yellow-brown solid was observed. After a further 10 min, the solution was filtered to give a small amount of compound **3**. The solution was stirred for 5 h, giving a brown-orange color. As no more precipitate was observed, the solvent was removed under vacuum. The solid residue was dissolved in THF containing a small amount of $CHCl_3$. Precipitation was induced by adding Et_2O to give 7 mg of **5(BF$_4$)**. The material, which was insoluble in THF/$CHCl_3$, was dissolved in a minimum amount of CH_3NO_2; the addition of Et_2O gave 110 mg of a yellow-brown solid, which was a mixture of compounds **4(BF$_4$)**, **5(BF$_4$)**, and **6(BF$_4$)** in the ratio 2:1:trace. Recrystallization with CH_3NO_2/Et_2O using a diffusion technique afforded orange-yellow single crystals of **4(BF$_4$)**, which cocrystallized with four molecules of nitromethane. When the crystals lose contact with Et_2O, they become opaque. **4(BF$_4$)**. Mp: 165−168 °C dec. Anal. Calcd (found) for $C_{58}H_{84}B_2F_8Ir_4O_3S_3$: C, 35.73 (35.64); H, 4.31 (4.07). ^{1}H NMR (CD_3NO_2): δ 2.51 (s, 3H; 2-Me), 6.48 (d, 1H, J = 6.7 Hz; H3), 2.50 (d, 1H, J = 6.7 Hz; H4), 2.29 (s, 3H; 5-Me), 1.87 (s, 45H; Cp*), 1.47 (s, 15H; Cp*). ^{1}H NMR ($CDCl_3$): δ 2.41 (s, 3H; 2-Me), 6.66 (d, 1H, J = 6.8 Hz; H3), 2.29 (d, 1H J = 6.9 Hz; H4), 2.04 (s, 3H; 5-Me), 1.82 (s, 45H; Cp*), 1.48 (s, 15H; Cp*). ^{13}C{^{1}H} NMR (CD_3NO_2): δ 95.96 (C2), 89.77 (C3), 57.97 (C4), 75.20 (C5), 24.75 (2-Me), 30.82 (5-Me), 9.21 (Me, Cp*), 95.54 (C, Cp*). ESMS: m/z [847] (M^+), IR ($CHCl_3$): ν_{CO} 1652 cm^{-1}.

[(Cp*Ir)$_2$(μ_2,η^4-SC(Me)CHCC(O)Me)](BF$_4$) (5(BF$_4$)). (a) The dissolution of 300 mg of **1(BF$_4$)** (0.49 mmol) in 10 mL of H_2O gave a yellow solution from which an orange solid precipitated within 5 min. The reaction mixture was stirred overnight at room temperature, giving a bright yellow solution and an orange precipitate, which after filtration was recrystallized in a minimum amount of CH_2Cl_2 and Et_2O, giving 195 mg (0.22 mmol) of the red-orange powder **5(BF$_4$)**. Yield: 46.0%. Mp: 260−262 °C dec. Anal. Calcd (found) for $C_{26}H_{37}BF_4Ir_2OS$: C, 35.9 (35.1); H, 4.26 (3.94) S, 4.45 (4.64). ^{1}H NMR (CD_3NO_2): δ 2.53 (s, 3H; 2-Me), 5.90 (s, 1H, H3), 2.29 (s, 3H, 5-Me), 2.10 (s, 15H; Cp*), 2.11 (s, 15H; Cp*). ^{1}H NMR ($CDCl_3$): δ 2.54 (s, 3H; 2-Me), 6.22 (s, 1H, H3), 2.35 (s, 3H; 5-Me), 2.05 (s, 15H; Cp*), 2.08 (s, 15H; Cp*). ^{1}H NMR (CD_2Cl_2): δ 2.50 (s, 3H; 2-Me), 5.70 (s, 1H; H3), 2.28 (s, 3H; 5-Me), 2.05 (s, 30H; Cp*). ^{1}H NMR (CD_3OD): δ 2.51 (s, 3H; 2-Me), 6.08 (s, 1H; H3), 2.37 (s, 3H; 5-Me), 2.09 (s, 30H; Cp*). ^{1}H NMR ($(CD_3)_2CO$): δ 2.57 (s, 3H; 2-Me), 6.26 (s, 1H; H3), 2.31(s, 3H; 5-Me), 2.12 (s, 15H; Cp*), 2.15 (s, 15H; Cp*). ^{13}C{^{1}H} NMR (CD_3NO_2): δ 102.19 (C2), 99.42 (C3), 146.42 (C4), 207.62 (C5), 16.58 (2-Me), 29.96 (5-Me), 10.16, 10.23 (Me, Cp*), 94.91, 97.55 (C, Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 101.80 (C2), 98.78 (C3), 145.01 (C4), 206.80 (C5), 16.22 (2-Me), 29.75 (5-Me), 9.71, 9.75 (Me, Cp*), 93.13, 95.92 (C, Cp*). HRMS: calcd, 780.172 53; found, 780.170 81. IR (CH_2Cl_2): ν_{CO} 1650 cm^{-1}.

(b) The same reaction as described above was carried out, but the mixture was stirred for only 2 h at room temperature. The yield of **5(BF$_4$)** in this case was 39% (165 mg, 0.19 mmol). After filtration, the solution was stirred overnight; evaporation of the H_2O solvent gave only about 5 mg more of **5(BF$_4$)**.

Mixture of Compounds 4(OTf) and 5(OTf). To 600 mg of **1(OTf)** (0.82 mmol) was added 27.2 mL of 0.03 M aqueous KOH (0.82 mmol). The initial pale yellow solution changed immediately to a strongly mustard yellow cloudy solution. A black-red sticky product formed in the bottom of the two-neck round-bottom flask. After 1 h, the solution turned more orange, and a precipitate was observed. After it was stirred overnight, the dark mustard yellow solution was filtered and then evaporated under vacuum. The resulting solid was dissolved in a minimum amount of CH_2Cl_2. Addition of hexane (15 mL) to this solution gave a sticky oil; the orange solution was decanted and the volume reduced to ~8 mL, affording an orange precipitate which after filtration gave 28 mg of **5(OTf)**. The yellow solution that remained after this filtration gave after evaporation of the hexane a small amount of the acyl thiolate compound **3**. The sticky oil was treated with CH_2Cl_2 and Et_2O, affording 42 mg of the orange compound **4(OTf)**. Mp: 151−153 °C dec. ^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3H; 2-Me), 6.66 (d, 1H, J = 6.8 Hz; H3), 2.28 (d, 1H, J = 7 Hz; H4), 2.06 (s, 3H; 5-Me), 1.81 (s, 45H, Cp*), 1.47 (s, 15H; Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 96.04 (C2), 88.60 (C3), 57.52 (C4), 73.85 (C5), 23.98 (2-Me), 29.61 (5-Me), 9.85, 8.96 (Me, Cp*), 93.83 (C, Cp*). Attempts to recrystallize **4(OTf)** in CH_2Cl_2 transformed it into the more stable **5(OTf)**.

[(Cp*Ir)$_2$(μ_2,η^4-SC(Me)CHCC(O)Me)](OTf) (5(OTf)). To 250 mg of **1(OTf)** (0.34 mmol) was added 15 mL of freshly distilled MeOH. The mixture was stirred at room temperature for 2.45 h and then was allowed to sit without stirring overnight. The resulting orange solution was evaporated to dryness under vacuum. The remaining brown-orange oil was dissolved in CH_2Cl_2. The solution was filtered and concentrated under vacuum; the addition of Et_2O gave 100 mg (0.11 mmol) of the deep red solid **5(OTf)**. Yield: 31.6%. Mp: >270 °C. Anal. Calcd (found) for $C_{27}H_{37}F_3Ir_2O_4S_2$: C, 34.80 (34.89); H, 3.98 (3.87); S, 6.88 (6.48). ^{1}H NMR (CD_3NO_2): δ 2.53 (s, 3H; 2-Me), 5.91(s, 1H, H3), 2.28 (s, 3H, 5-Me), 2.10 (s, 15H; Cp*), 2.11 (s, 15H; Cp*). ^{1}H NMR ($CDCl_3$): δ 2.56 (s, 3H; 2-Me), 6.32 (s, 1H; H3), 2.37 (s, 3H; 5-Me), 2.06 (s, 15H, Cp*), 2.09 (s, 15H; Cp*). ^{13}C{^{1}H} NMR (CD_3NO_2): δ 100.81 (C2), 98.09 (C3), 145.04 (C4), 206.0 (C5), 15.14 (2-Me), 28.52 (5-Me), 8.75, 8.80 (Me, Cp*), 93.54, 96.16 (C, Cp*). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 98.80 (C3), 145.13 (C4), 202.20 (C5), 16.35 (2-Me), 29.87 (5-Me), 9.85, 10.01 (Me, Cp*), 93.11, 96.04 (C, Cp*) (C2 not observed). FAB MS (3-NBA CH_2Cl_2): m/z 778.6 (M^+). IR ($CHCl_3$): ν_{CO} 1650 cm^{-1}. The insoluble fraction in CH_2Cl_2 was evaporated under vacuum to give an oil and yellow solid mixture which was treated with Et_2O, giving a yellow solid, which after filtration and drying afforded only 5 mg (0.004 mmol) of **6(OTf)**. Yield:

1.2%. ^{1}H NMR (CD_3CN): δ 2.55 (s, 6H; 2-Me), 4.35 (t, 1H, J = 6.8 Hz; H3), 3.49 (dd, 2H, H4), 2.37 (s, 6H; 5-Me), 2.0(s, 30H; Cp*).

[Cp*Ir(μ_2,η^3-SC(Me)CHCH$_2$C(O)Me)]$_2$(BF$_4$)$_2$ (6(BF$_4$)). To 308 mg of **1(BF$_4$)** (0.50 mmol) was added 15 mL of freshly distilled MeOH; the mixture was stirred at room temperature for 3 h and then kept overnight without stirring. A yellow to slightly brown microcrystalline product precipitated and was filtered, giving 34 mg (0.028 mmol) of **6(BF$_4$)**. The remaining solution was reduced to 7 mL, under vacuum; the addition of Et_2O induced precipitation of 92 mg more of the bright lime yellow product **6(BF$_4$)**. Yield: 23.1% (126 mg, 0.12 mmol). Mp: 240−242 °C dec. Anal. Calcd (found) for $C_{32}H_{50}B_2F_8Ir_2O_2S_2$: C, 35.36 (35.06); H, 4.45 (4.64). ^{1}H NMR (CD_3NO_2): δ 2.55 (s, 6H; 2-Me), 4.39 (t, 1H, J = 6.6 Hz; H3), 3.50 (dd, 2H, J = 6.8; H4), 2.35 (s, 6H, 5-Me), 1.95 (s, 30H; Cp*). ^{1}H NMR (D_2O): δ 2.38 (s, 6H; 2-Me), 4.12 (t, 1H, J = 7.5 Hz; H3), 3.43 (dd, br, 2H; H4), 2.26 (s, 6H, 5-Me), 1.72 (s, 15H; Cp*). ^{13}C{^{1}H} NMR (CD_3NO_2): δ 104.60 (C2), 78.75 (C3), 43.86 (C4), 206.10 (C5), 18.16 (2-Me), 29.98 (5-Me), 9.35 (Me, Cp*), 102.72 (C, Cp*). EIMS: m/z 914 (M^{2+}), 457 $(M/2)^+$. IR (KBr): ν_{CO} 1652 cm^{-1}. The red oil obtained after complete evaporation of MeOH and Et_2O was recrystallized from CH_2Cl_2 and Et_2O to give red crystals of **5(BF$_4$)** (4 mg, 0.005 mmol) in 9.2% yield.

[Cp*Ir(η^4-SC(Me)CHCHC(OMe)Me)](BF$_4$) (7(BF$_4$)). To 217 mg of **1(BF$_4$)** (0.35 mmol) was added 30 mL of freshly distilled MeOH; the mixture was stirred at room temperature for only 10 min. The solution was evaporated under vacuum, and the residue was extracted three times with CH_2Cl_2 (1 mL). The extraction solution was concentrated to approximately 1.5 mL, and 80 mL of diethyl ether was added in order to precipitate pale yellow **7(BF$_4$)** in 13.3% yield (25.5 mg, 0.047 mmol). Mp: 110−114 °C dec. Anal. Calcd (found) for $C_{16}H_{24}BF_4IrOS$: C, 36.61, (36.71); H, 4.70 (4.52). ^{1}H NMR (CD_3NO_2): δ 2.50 (s, 3H; 2-Me), 5.88 (d, 1H, J = 3.4 Hz; H3), 4.30 (d, 1H, J = 3.4 Hz; H4), 2.01 (s, 3H, 5-Me), 2.14 (s, 15H; Cp*), 3.20 (OMe). ^{1}H NMR (CD_3OD): δ 2.48 (s, 6H; 2-Me), 5.99 (d, 1H, J = 3.5 Hz; H3), 4.31 (d, 1H; J = 3.5 Hz; H4), 1.99 (s, 3H, 5-Me), 2.12 (s, 15H; Cp*), 3.29 (OMe). ^{13}C NMR (CD_3NO_2): δ 95.75 (s, C2), 80.52 (d, J = 184 Hz, C3), 56.36 (d, J = 172 Hz, C4), 121.2 (s, C5), 23.27 (q, J = 131 Hz, 2-Me), 13.68 (q, J = 132 Hz, 5-Me), 9.02 (q, J = 129 Hz, Me, Cp*), 81.86 (s, C, Cp*), 53.61 (q, J = 144 Hz, OMe).

[Cp*Rh(η^5-2,5-Me$_2$T)](BF$_4$)$_2$ (8(BF$_4$)). A 1.00 g portion (1.41 mmol) of $[Cp^*RhCl_2]_2$ in acetone (25 mL) reacted with $AgBF_4$ (1.10 g, 5.65 mmol) to give $[Cp^*Rh(acetone)_3][BF_4]_2$. The silver chloride was filtered from solution, and 2,5-dimethylthiophene (0.32 mL, 2.8 mmol) was added drop by drop, which resulted in the formation of a yellow precipitate. The solution was refluxed for 30 min. After the mixture was cooled to room temperature, the precipitate was separated by filtration and washed with $CHCl_3$ (3 × 10 mL), affording 910 mg (1.74 mmol) of the yellow product **8(BF$_4$)** in 62% yield. It does not melt up to 230 °C. Anal. Calcd (found) for $C_{16}H_{23}B_2F_8Rh$: C, 36.68 (36.82); H, 4.42 (4.34). ^{1}H NMR (CD_3NO_2): δ 2.65 (s, 6H; 2,5-Me), 7.15(s, 2H; H3, H4), 2.28 (s, 15H; Cp*). ^{1}H NMR ((CD_3)$_2$CO)): 2.76 (s, 6H; 2,5-Me), 7.40(s, 2H; H3, H4), 2.38 (s, 15H; Cp*). ^{13}C{^{1}H} NMR ((CD_3)$_2$CO)): δ 123.80 (C2, C5), 111.50 (C3, C4), 107.29 (C, Cp*), 12.83 (2,5-Me), 9.25 (Me, Cp*).

[(Cp*Rh)$_2$(μ_2,η^4-SC(Me)CHCC(O)Me)](BF$_4$) (9(BF$_4$)) and [Cp*Rh(OCMe$_2$)$_2$(OH)](BF$_4$) (10(BF$_4$)). (a) To 200 mg of **8(BF$_4$)** (0.38 mmol) was added 30 mL of freshly distilled acetone, and the yellow mixture was stirred at room temperature for 18 h. The resulting red solution was evaporated under vacuum, and the residue was extracted three times with CH_2Cl_2 or $CHCl_3$ (5 mL), giving a yellow-orange solid and a red solution. The solution was concentrated to approximately 1.5 mL; the addition of 10 mL of diethyl ether gave a red precipitate, which was chromatographed on neutral alumina with acetone as eluant. Recrystallization with $CHCl_3$/diethyl ether afforded red crystals of **9(BF$_4$)** in 6.1% yield (16 mg, 0.023 mmol). It does not melt up to 230 °C. Anal. Calcd (found) for $C_{26}H_{37}BF_4ORh_2S$: C, 45.24 (45.48); H, 5.40 (5.19). ^{1}H NMR ($CDCl_3$): δ 2.43 (s, 3H; 2-Me), 5.99 (d, 1H, J = 6.8 Hz; H3), 2.30 (s, 3H; 5-Me), 1.96 (s, 15H, Cp*), 1.86 (s, 15H; Cp*). ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 114.00 (C2), 103.19 (C3), 166.20 (C4), 206.10 (C5), 18.88 (2-Me), 30.15 (5-Me), 10.17, 10.29 (Me, Cp*), 99.43, 102.29 (C, Cp*). EIMS: 603.1 [M − BF_4]$^+$. IR (KBr): ν_{CO} 1658 cm^{-1}.

The yellow-orange solid was recrystallized three times with acetone/diethyl ether, affording orange crystals of **10(BF$_4$)** in 54% yield (95 mg, 0.21 mmol). Mp: 165−168 °C dec. ^{1}H NMR (CD_3NO_2): δ 4.69 (s, OH), 2.31 (s, 6H; Me), 1.74 (s, 15H; Cp*). ^{13}C NMR ((CD_3)$_2$CO)): δ 30.48 (Me), 96.43 (d, J_{RhC} = 10 Hz; C, Cp*), 7.97 (Me, Cp*) (C=O was not observed). ^{11}B NMR ((CD_3)$_2$CO)): δ −1.84. ^{19}F NMR ((CD_3)$_2$CO)): δ −151.61.

(b) The same reaction as described above, using 300 mg (0.57 mmol) of **8(BF$_4$)**, was carried out, but the mixture was stirred for 5 days at room temperature. The yield of **9(BF$_4$)** in this case was 13% (50 mg, 0.07 mmol), and the yield of **10(BF$_4$)** was 41% (109 mg, 0.24 mmol).

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Supporting Information Available: Complete tables of bond distances, bond angles, anisotropic thermal parameters, fractional atomic coordinates and some torsion angles for **4(BF$_4$)**, **5(OTf)**, **6(BF$_4$)**, and **10(BF$_4$)**. This material is available free of charge via the Internet at http://pubs.acs.org.

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