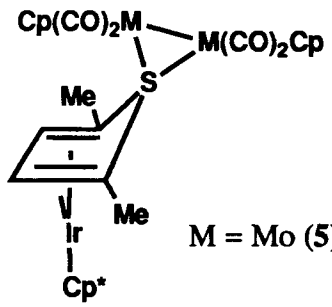
APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 6, 479–487 (1992)

2,5-Dimethylthiophene coordination to three metal centers in the complexes (η^4, S-μ_3-2,5-Me_2T)(IrCp*) $[M(CO)_2Cp]_2$ where M = Mo or W

Jiabi Chen and Robert J Angelici*
Department of Chemistry and Ames Laboratory, USDOE, Iowa State University, Ames, IA 50011, USA

The 2,5-dimethylthiophene (2,5-Me_2T) ligand in the isomers Cp*Ir(η^4-2,5-Me_2T) (1) and Cp*Ir(*C*,*S*-2,5-Me_2T) (2) is activated to react with the dimers $Cp(CO)_2M{\equiv}M(CO)_2Cp$[M = Mo (3), W (4)] to give complexes (5, 6) in which the thiophene is coordinated to three metals. Oxidation of 5 with Cp_2Fe^+ removes



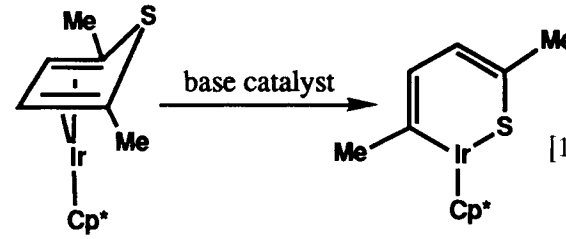
M = Mo (5), W (6)

the Mo dimer to give Cp*Ir($\eta^5-2,5$-Me_2T)$^{2+}$. Reaction of 5 with CO displaces the Mo as $[CpMo(CO)_3]_2$ to give Cp*Ir(CO)(*C*,*S*-2,5-Me_2T) (7). Ultraviolet photolysis of 1 provides a convenient route to the ring-opened isomer 2. Despite the remarkable nature of the thiophene coordination in 5 and 6, its reactivity does not suggest new pathways that would lead to the hydrodesulfurization of thiophenes.

Keywords: Thiophene, hydrodesulfurization, iridium, molybdenum, tungsten

INTRODUCTION

One aspect of understanding how thiophene undergoes hydrodesulfurization (HDS) on transition-metal-based heterogeneous catalysts[1] is knowing how it is adsorbed to the catalyst surface. In its metal complexes, thiophene has been reported to coordinate in six different ways.[2] The *S*- and η^5-modes have been known for several years,[1] whilst the η^4-, η^4,*S*-μ_2-, η^4,*S*-μ_3- and η^2-forms were reported only recently.[3–8] In the present study, we begin with an η^4-thiophene complex. A two-electron reduction of Cp*Ir(η^5-2,5-Me_2T)$^{2+}$, where 2,5-Me_2T is 2,5-dimethylthiophene and Cp* is η^5-C_5Me_5, gives[3,4] the η^4-thiophene complex Cp*Ir(η^4-2,5-Me_2T) (1), which in the presence of base catalysts rearranges (Eqn [1]) to the more stable ring-opened *C*,*S*-isomer Cp*Ir(*C*,*S*-2,5-Me_2T) (2). Both 1 and 2 are unusually reactive, combining with Lewis acids such as BH_3[3,9] and metal complexes[6,10] (Eqn



[1]

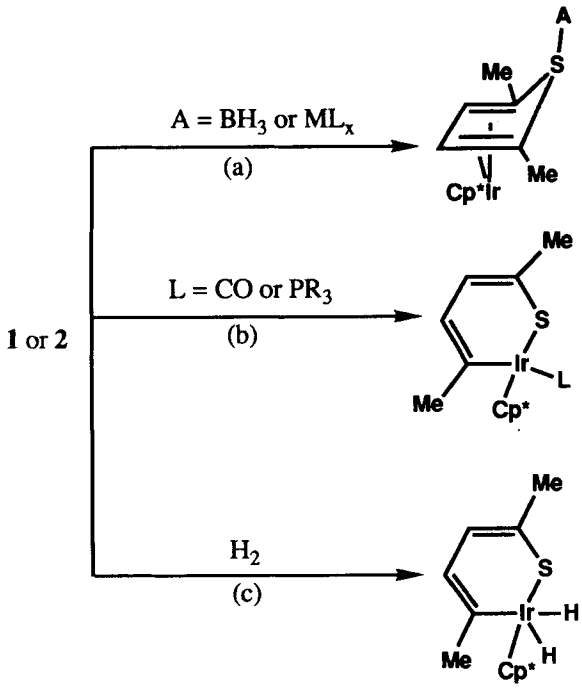
1 2

[2a]), with Lewis bases such as phosphines and CO (Eqn [2b]),[11] and with oxidative-addition agents such as hydrogen (Eqn [2c]).[11] In this paper, we describe the reactions of 1 and 2 with the metal–metal triple-bonded dimers $Cp(CO)_2M{\equiv}M(CO)_2Cp$ (M = Cr, Mo, W). Given the varied reactivities of 1 and 2, it seemed possible that the dimers would react at either the iridium or the sulfur atom of these complexes. The observed result is that the two metal atoms of the dimer add to the sulfur to give a new type of thiophene coordination and the first examples in which thiophene is coordinated to three metal atoms. A preliminary communication[7] of some of these results has already appeared.

* Author to whom correspondence should be addressed.

0268–2605/92/050479–09 $09.50

Accepted 10 December 1991



[2]

EXPERIMENTAL

General procedures

All manipulations were carried out under a dry, oxygen-free nitrogen atmosphere, using standard Schlenk techniques. All solvents employed were reagent grade and dried by refluxing over appropriate drying agents and stored over 4A molecular sieves under a nitrogen atmosphere until used. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from potassium benzophenone ketyl or sodium benzophenone ketyl, whilst hexane and CH_2Cl_2 were distilled from CaH_2. The neutral Al_2O_3 (80–100 mesh, Brockmann, activity I) used for chromatography was deoxygenated under high vacuum at room temperature for 16 h, deactivated with 5% (w/w) nitrogen-saturated water, and stored under nitrogen. In all of the chromatographic separations, the column diameter was 1.5 cm and the height was 5–8 cm. The gases carbon monoxide (CO) and hydrogen were used as purchased. $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (**1**) and $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ (**2**) were prepared as previously reported.[3,4] $Cp(CO)_2Cr{\equiv}Cr(CO)_2Cp$,[12,13] $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ (**3**),[13,14] $Cp(CO)_2W{\equiv}W(CO)_2Cp$ (**4**),[13] and $Cp_2Fe(PF_6)$[15] were prepared by literature methods.

Elemental analyses were performed by Galbraith Laboratory, Inc. IR spectra were recorded in CH_2Cl_2 or hexane solution by using a Perkin–Elmer 681 spectrophotometer. All ^1H NMR spectra were recorded at ambient temperature in $CDCl_3$ solution with $CHCl_3$ as an internal reference, using a Nicolet NT-300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. Fast atom bombardment (FAB) spectra were run on a Kratos MS-50 mass spectrometer using a 2-nitrophenyl octyl ether/CH_2Cl_2 matrix.

Reaction of $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (1) with $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ (3) to give $(\eta^4, S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)(IrCp^*)[Mo(CO)_2Cp]_2$ (5)

To a solution of 0.025 g (0.057 mmol) of **1** dissolved in 30 cm^3 of THF at room temperature was added 0.030 g (0.069 mmol) of **3**. The resulting purple solution gradually turned green as it was stirred at room temperature. After being stirred for 24 h, the solvent was evaporated under vacuum, and the dark-green residue was chromatographed on Al_2O_3 with hexanes as the eluant. After small amounts of unreacted **3** had been removed from the column, the green product band was eluted with hexanes/CH_2Cl_2/Et_2O (10:2:1) and collected. After vacuum removal of the solvent, the green powdery product was recrystallized from hexane/CH_2Cl_2 at −80 °C to give 0.019 g (38%, based on **5**) of deep-green crystals of **5** (m.p. > 230 °C, decomp). IR(CH_2Cl_2), ν(CO): 1910s, 1870vs, 1828s, 1805m cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.29 (s, 5H, Cp), 5.16 (s, 5H, Cp), 4.73 (s, 1H), 4.62 (s, 1H), 1.98 (s, 15H, Cp*), 0.947 (s, 3H, CH_3), 0.873 (s, 3H, CH_3). EIMS: m/z 878 (M^+, based on ^{98}Mo). Analysis: calcd for $C_{30}H_{33}O_4SIrMo_2$: C, 41.24; H, 3.81. Found: C, 41.46; H, 3.86%.

Reaction of $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ (2) with 3 to give 5

A solution of **2** (0.025 g, 0.057 mmol) in THF (30 cm^3) was cooled to 0 °C. Compound **3** (0.030 g, 0.069 mmol) was then added and the mixture was stirred at 0–15 °C. The solution gradually changed from red or red–purple to deep green. After being stirred for 8 h, the solvent was removed under vacuum; the residue was treated in the same manner as described directly above to give 0.022 g (44 %, based on **2**) of **5** as deep-green crystals (m.p. > 230 °C, decomp). Compound **5** was identified by its IR and ^1H NMR spectra.

Reaction of 1 with $Cp(CO)_2W{\equiv}W(CO)_2Cp$ (4) to give $(\eta^4,S\text{-}\mu_3\text{-}2,5\text{-}Me_2T)(IrCp^*)[W(CO)_2Cp]_2$ (6)

Using the same procedure above, a solution of **1** (0.025 g, 0.057 mmol) in 30 cm^3 of THF was treated with **4** (0.038 g, 0.070 mmol). The mixture was stirred at room temperature for 24 h during which time the solution turned purple–red gradually. After evaporating the solution under vacuum to dryness, further treatment of the resulting red–purple residue as described in the preparation of **5** gave 0.024 g (40 %, based on **1**) of red–purple crystalline **6** (m.p. > 240 °C, decomp). IR (CH_2Cl_2), ν(CO): 1905s, 1862vs, 1818s, 1792m cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.40 (s, 5H, Cp), 5.25 (s, 5H, Cp), 4.62 (s, 1H), 4.59 (s, 1H), 1.98 (s, 15H, Cp*), 0.908 (s, 3H, CH_3), 0.802 (s, 3H, CH_3). EIMS: *m/z* 966 ($M^+ - 3CO$), 938 ($M^+ - 4CO$), 440 ($M^+ - [Cp(CO)_2W]_2$). Analysis: calcd for $C_{30}H_{33}O_4SIrW_2$: C, 34.33; H, 3.17. Found: C, 33.56; H, 3.15%.

Reaction of 2 with 4 to give 6

To a solution of **2** (0.050 g, 0.114 mmol) in THF (30 cm^3) was added **4** (0.073 g, 0.120 mmol) at 0 °C. The mixture was stirred at 0–15 °C for 8 h, during which time the red solution gradually turned red–purple. The solvent was removed under vacuum, and then the resulting residue was treated in a manner similar to that described for **5** to yield 0.056 g (47 %, based on **2**) of red–purple crystalline **6** (m.p. > 240 °C, decomp). Compound **6** was identified by its IR and ^1H NMR spectra.

Reaction of 1 with $Cp(CO)_2Cr{\equiv}Cr(CO)_2Cp$ to give $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)(CO)$ (7)

Compound **1** (0.030 g, 0.068 mmol) was dissolved in 30 cm^3 of THF at room temperature. To this solution was added $Cp(CO)_2Cr{\equiv}Cr(CO)_2Cp$ (0.027 g, 0.078 mmol). While being stirred at room temperature, the solution gradually turned from blue–green to dark-green. After 24 h, the solvent was evaporated under vacuum, and the dark-green residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. After removing unreacted $Cp(CO)_2Cr{\equiv}Cr(CO)_2Cp$ from the column, the yellow product band was eluted with hexanes/Et_2O (15:1) and collected. The solvent was removed *in vacuo*, and the crude orange–yellow product was recrystallized from hexanes at −80 °C to yield 0.010 g (31 %, based on **1**) of orange–yellow needles of $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)(CO)$ (**7**)[11] (m.p. 121–122 °C, decomp). IR (hexanes), ν(CO): 2020 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.74 (d, 1H), 5.40 (d, 1H), 2.26 (s, 3H), 1.94 (s, 3H), 1.86 (s, 15H). EIMS: *m/z* 468 (M^+), 440 ($M^+ - CO$), 356 ($M^+ - Me_2T$). Analysis: calcd for $C_{17}H_{23}OSIr$: C, 43.66; H, 4.96. Found: C, 43.09; H, 4.86%.

Reaction of 2 with $Cp(CO)_2Cr{\equiv}Cr(CO)_2Cp$ to give 7

A solution of **2** (0.044 g, 0.100 mmol) in THF (30 cm^3) was cooled to −10 °C. To this solution was added $Cp(CO)_2Cr{\equiv}Cr(CO)_2Cp$ (0.038 g, 0.110 mmol). The mixture was stirred at 0–15 °C for 8 h, during which time the green solution turned dark-green. After evaporating the solution *in vacuo* to dryness, further treatment of the resulting dark-green residue as described above for the reaction of **1** with $Cp(CO)_2Cr{\equiv}Cr(CO)_2Cp$ gave 0.018 g (38%, based on **2**) of **7** as orange–yellow needles (m.p. 121 °C, decomp). IR (hexanes), ν(CO): 2020 cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.74 (d, 1H), 5.40 (d, 1H), 2.26 (s, 3H), 1.94 (s, 3H), 1.86 (s, 15H).

Reaction of 5 with $Cp_2Fe(PF_6)$ to give $[Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)](PF_6)_2$ (8) and $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ (3)

To a solution of **5** (0.020 g, 0.023 mmol) in CH_2Cl_2 (15 cm^3) was added $Cp_2Fe(PF_6)$ (0.016 g, 0.048 mmol) at −10 °C. The color of the solution changed quickly from essentially green to orange–purple. After being stirred for 0.5–1 h at −10–0 °C, the solution was reduced under vacuum to about 5 cm^3, to which was added 1 cm^3 of hexanes. White solid, $[Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)](PF_6)_2$ (**8**)[4] precipitated from the resulting solution. After decanting the solution, **8** was dried *in vacuo*: yield 0.007 g (44 %, based on **5**). ^1H NMR (CD_3NO_2): δ 7.22 (s, 2H), 2.74 (s, 6H), 2.42 (s, 15H). FAB MS: *m/z* 440 (M^+). The decanted solution was evaporated under vacuum to dryness, and the residue was recrystallized from hexanes/CH_2Cl_2 at −80 °C to give 0.004 g (40%, based on **5**) of **3** as deep red–purple crystals. IR (CH_2Cl_2) ν(CO): 1888vs, 1855vs cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.22 (s).

Reaction of 6 with $Cp_2Fe(PF_6)$ to give 8 and $Cp(CO)_2W{\equiv}W(CO)_2Cp$ (4)

To a solution of 0.018 g (0.017 mmol) of **6** in 15 cm^3 of CH_2Cl_2 at −10 °C was added 0.012 g (0.036 mmol) of $Cp_2Fe(PF_6)$. The color of the solution turned from dark-green to dark-purple quickly. After 0.5–1 h of stirring at −10–0 °C, the volume of the solution was reduced under vacuum to about 5 cm^3. Further treatment of the resulting mixture as described above for the reaction of **5** with $Cp_2Fe(PF_6)$ gave 0.005 g (42%, based on **6**) of white solid **8** {^{1}H NMR (CD_3NO_2): δ 7.22 (s, 2H), 2.74 (s, 6H), 2.42 (s, 15H)} and 0.004 g (45%, based on **6**) of **4** as deep red–purple crystals [IR (CH_2Cl_2), ν(CO): 1886s, br, 1826s, br cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.32].

Reaction of 5 with CO to give $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)(CO)$ (7) and $Cp(CO)_3Mo\text{-}Mo(CO)_3Cp$

Method A

Into a solution of 0.035 g (0.040 mmol) of **5** dissolved in 30 cm^3 of CH_2Cl_2 at room temperature was bubbled CO gas over a period of 12 h, during which time the green solution gradually turned red–purple. After evaporating the solution, the residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. The red–purple band which eluted first was collected; then the yellow band was eluted with hexanes/CH_2Cl_2 (20:1). After vacuum removal of the solvent from the above two eluates, the residues were recrystallized from hexanes at −80 °C. From the red–purple fraction, 0.006 g (30%) of deep red–purple crystals of $[Cp(CO)_3Mo]_2$[13] were obtained. IR(CH_2Cl_2), ν(CO): 1956vs, 1910vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.27 (s). From the yellow fraction, 0.004 g (21%) of **7** as orange–yellow needles (m.p. 121 °C, decomp.) were obtained. IR (hexanes), ν(CO): 2020 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.73 (d, 1H), 5.40 (d, 1H), 2.25 (s, 3H), 1.93 (s, 3H), 1.86 (s, 15H). EIMS: *m/z* 468 (M^+), 440 ($M^+ - CO$), 356 ($M^+ - Me_2T$).

Method B

In a quartz photolysis tube equipped with a CO bubbler was placed a solution of **5** (0.035 g, 0.040 mmol) dissolved in THF (30 cm^3) at room temperature. Then CO gas was bubbled through the solution. The reaction solution was photolyzed with a Canrad–Hanovia medium-pressure, 450-W mercury vapor lamp (254 nm) for 15 min, during which time the green solution turned red–purple quickly. After evaporation of the solvent under vacuum, further treatment of the resulting residue in a similar manner as described above in method A gave 0.007 g (35%) of deep red–purple crystalline $[Cp(CO)_3Mo]_2$. {IR(CH_2Cl_2), ν(CO): 1956vs, 1910vs cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.27 (s)} and 0.006 g (31%) of orange–yellow needles of **7** (m.p. 122 °C, decomp.); IR (hexanes), ν(CO): 2020 cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.73 (d, 1H), 5.40 (d, 1H), 2.25 (s, 3H), 1.93 (s, 3H), 1.86 (s, 15H).

Reaction of 6 with CO to give 7 and $Cp(CO)_3W\text{-}W(CO)_3Cp$

Into 0.025 g (0.024 mmol) of **6** dissolved in 20 cm^3 of CH_2Cl_2 at 0 °C was bubbled CO gas at 0–15 °C for 3 h. During this time the red–purple solution turned yellow. After vacuum evaporation of the solvent, the residue was treated in a simlar manner as described above for the reaction of **5** with CO to yield 0.007 g (44 %) of deep red–purple crystalline $[Cp(CO)_3W]_2$[14] and 0.004 g (36 %) of orange–yellow crystalline **7**, which was identified by its m.p. and IR and ^{1}H NMR spectra. $[Cp(CO)_3W]_2$: IR(CH_2Cl_2), ν(CO): 1956vs, 1905vs cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.37 (s).

Photolytic Reaction of 5 with hydrogen to give 2

A solution of 0.025 g (0.029 mmol) of **5** in 30 cm^3 of THF was put in a quartz photolysis tube equipped with a gas bubbler; hydrogen gas was bubbled through the solution, which was also photolyzed with a 450-W, 254-nm lamp for 1–2 h. During this time the green solution gradually turned orange–red. After removal of the solvent *in vacuo*, the residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. The red band was collected, and the solvent was evaporated under vacuum to give a red residue which was recrystallized from hexanes at −80 °C to give 0.009 g (69%) of dark-red crystalline **2** (mp 147 °C, decomp.). ^{1}H NMR ($CDCl_3$): δ 7.47 (d, 1H), 7.34 (d, 1H), 3.10 (s, 3H), 2.79 (s, 3H), 1.93 (s, 15H).

Conversion of $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (1) into $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ (2)

A solution of 0.015 g (0.034 mmol) of **1** dissolved in 30 cm^3 of THF in a quartz photolysis tube was photolyzed with a 450-W, 254-nm lamp for 1–2 h,

during which time the light yellow solution gradually turned red. The solvent was removed under vacuum. Further treatment of the resulting residue as described in the reaction of **5** with hydrogen gave 0.014 g (93%) of dark-red crystals of **2**, which was identified by its melting point and ^{1}H NMR spectrum.

Thermolysis of 5 to give $Cp(CO)_2Mo[\mu$-(*C,S*-2,5-Me_2T)$IrCp^*]$-$Mo(CO)_2Cp$ (9) and 3

A solution of **5** (0.020 g, 0.023 mmol) in THF (20 cm^3) was refluxed for 24 h, during which time the green solution gradually turned purple. After evaporation of the solvent *in vacuo*, the residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. A red–purple band eluted first. This was followed by a blue–purple band which eluted with hexanes/Et_2O (20:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexanes at −80 °C. From the first fraction, 0.005 g (50%, based on **5**) of deep red–purple crystals of **3** were obtained. From the second fraction, 0.003 g (15%, based on **5**) of blue–green crystals of **9** (m.p. > 240 °C, decomp.) were obtained. IR(CH_2Cl_2), ν(CO): 1908s, 1865vs, 1825s, 1800m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.67 (d, 1H), 7.52 (d, 1H), 5.28 (s, 10H), 1.98 (s, 15H), 1.30 (s, 3H), 1.23 (s, 3H). EIMS: *m/z* 878 (M^+, based on ^{98}Mo). Analysis: calcd for $C_{30}H_{33}O_4SIrMo_2$: C, 41.24; H, 3.81. Found: C, 41.34; H, 3.73 %.

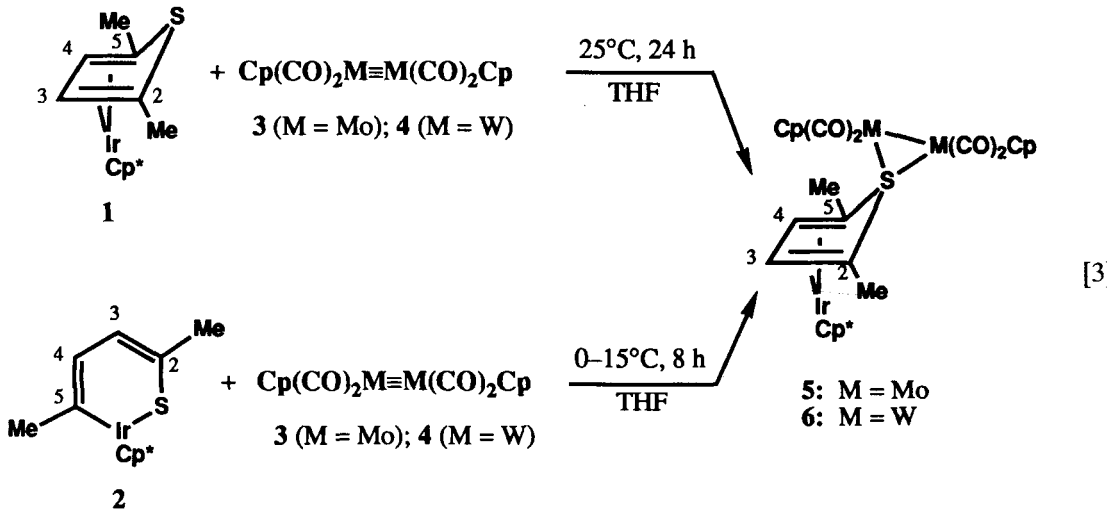
RESULTS AND DISCUSSION

Reactions of $Cp^*Ir(\eta^4$-2,5-$Me_2T)$ (1) and Cp^*Ir(*C,S*-2,5-Me_2T) (2) with $Cp(CO)_2M{\equiv}M(CO)_2Cp$ [M = Mo (3), W (4)]

As noted in the Introduction (Eqn [2a]), the sulfur in $Cp^*Ir(\eta^4$-2,5-$Me_2T)$ (**1**) is a stronger donor than thiophene itself or Me_2S toward Lewis acids such as BH_3[3,9] and $Fe(CO)_4$.[10] Similarly the sulfur in **1** donates to two metal centers in its reactions with **3** and **4** (Eqn [3]) to give complexes **5** and **6** in 38–40 % yield.

The reaction appears to be related to the known reaction[16] of $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ (**3**) with tetrahydrothiophene [$S(CH_2)_4$] to give the sulfur-bridged analog (S-μ_2-$S(CH_2)_4$)-$[Mo(CO)_2Cp]_2$ of **5**; however, this reaction appears to require more strenuous conditions (refluxing toluene for 'several hours')[16] than that of **1** with **3**. The milder conditions for the latter reaction may reflect the stronger donor ability of the sulfur in **1** or possibly that **1** reacts by a different mechanism than $S(CH_2)_4$, perhaps involving initial isomerization of **1** to **2**, which then rapidly reacts with **3** or **4** (see below).

Whilst the triple-bonded dimers **3** and **4** are known[17,18] to react with donor ligands and their reactions with **1** fit this pattern, it is interesting that the ring-opened complex **2** also reacts with **3** and **4** to form (Eqn [3]) the same products **5** and **6** (44–47 % yield). Moreover, the reactions of **3** and **4** occur under milder conditions with **2** than with **1**. This faster reaction with **2** and the observation (Eqn [1]) that **2** is more stable than **1** indicates that **2** does not first convert to **1** which



[3]

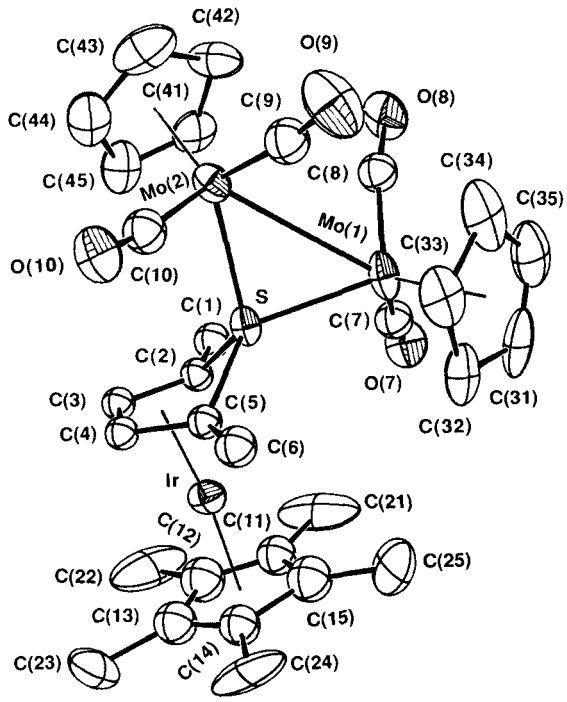


Figure 1 ORTEP drawing of (η^4, S-μ_3-2,5-Me_2T)-(IrCp*)[$Mo(CO)_2Cp]_2$ (**5**). Selected bond distances (Å) and angles (deg): C(2)–S = 1.81(2), C(5)–S = 1.83(1), C(2)–C(3) = 1.44(2), C(3)–C(4) = 1.48(2), C(4)–C(5) = 1.40(2), C(1)–C(2) = 1.55(2), C(5)–C(6) = 1.52(2), Mo(1)–S = 2.342(3), Mo(2)–S = 2.343(5), Mo(1)–Mo(2) = 3.144(2), Mo(1)–C(7) = 1.92(2), Mo(1)–C(8) = 1.95(2), Mo(2)–C(9) = 1.90(2), Mo(2)–C(10) = 1.97(1), Ir–C(2) = 2.12(2), Ir–C(3) = 2.14(2), Ir–C(4) = 2.13(2), Ir–C(5) = 2.14(2); C(2)–S–C(5) = 81.7(6), C(1)–C(2)–C(3) = 122(1), C(4)–C(5)–C(6) = 124(1), C(7)–Mo(1)–C(8) = 81.8(8), C(9)–Mo(2)–C(10) = 80.3(6), Mo(1)–S–Mo(2) = 84.3(1), S–Mo(1)–Mo(2) = 47.9(1), S–Mo(2)–Mo(1) = 47.9(1).

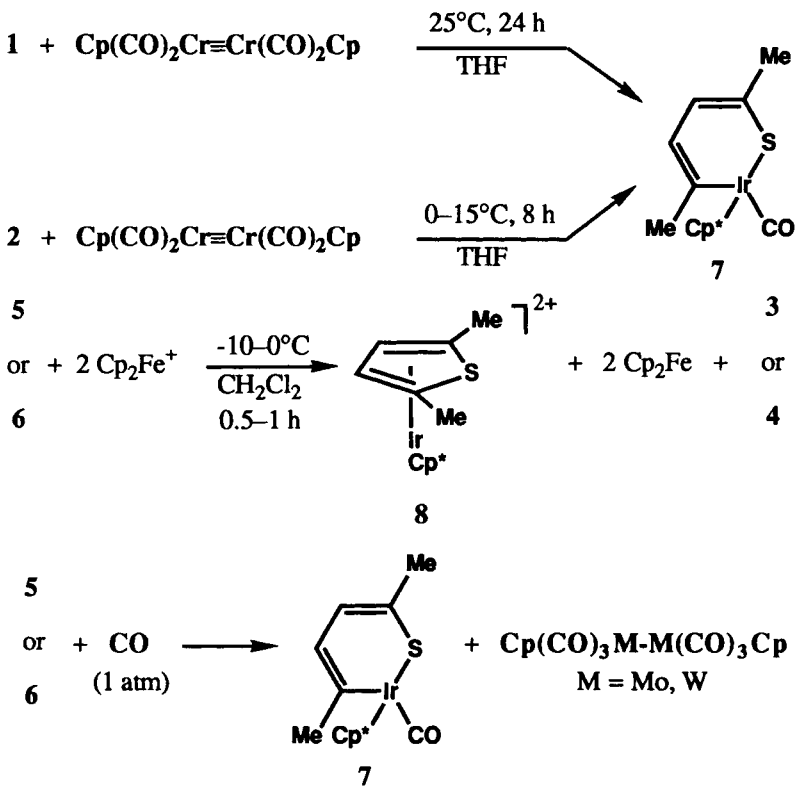
then reacts with **3** or **4** to give the product **5** or **6**. Perhaps the M≡M dimers initially add to the sulfur or the diene portion of **2** and this intermediate then rearranges with closure of the thiophene to give the final product. The reactions of **2** with **3** and **4** to give **5** and **6** are similar to that of **2** with the other Lewis acids BH_3[3,9] and $Fe(CO)_4$[10] which also give closed-ring products (Eqn [2a]).

Complexes **5** and **6** are diamagnetic and have deep-green and red–purple colors, respectively. They are soluble in polar organic solvents but are only slightly soluble in non-polar organic solvents. Both are moderately air-sensitive in the solid state but are very air-sensitive in solution.

An X-ray study of **5**, which was communicated previously,[7] establishes (Fig. 1) the structure shown in Eqn [3]. The structural features of the Cp*Ir(η^4-2,5-Me_2T) part of **5** are very similar to those in free Cp*(η^4-2,5-Me_2T) (**1**), except the C–S bond distances (1.81(2) and 1.83(1) Å) are slightly longer than the corresponding distances (1.76(2), 1.79(2) Å)[3] in **1**. The thiophene ring is folded with an angle of 43.6(8)° between the C(2)–C(3)–C(4)–C(5) and C(2)–S–C(5) planes; this compares with 42° for the same angle in **1**.[3] The methyl carbons, C(1) and C(6), lie in the C(2)–C(3)–C(4)–C(5) plane within experimental error, while the sulfur is 0.95 Å out of this plane. The S–Mo(1)–Mo(2) plane is essentially perpendicular to both the C(2)–C(3)–C(4)–C(5) [92.4(5)°] and C(2)–S–C(5) [91.2(5)°] planes. The Mo(1)–Mo(2) distance [3.144(2) Å] is much longer than that (2.448(1) Å)[14,17,18] in the reacting dimer **3**, $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$, but is slightly shorter than the Mo–Mo distance (3.235(1) Å)[19] in $Cp(CO)_3Mo$-$Mo(CO)_3Cp$ and the W–W distance [3.288(1) Å][20] in $Cp^*(CO)_3W$-$W(CO)_3Cp^*$. The structure of the $Cp(CO)_2Mo(\mu-S)Mo(CO)_2Cp$ part of **5** is very similar to that[16] in (S-μ_2-$S(CH_2)_6$)[$Mo(CO)_2Cp]_2$, which has a Mo–Mo distance of 3.211(2) Å, and to that[21] in (S-μ_2-1,4-dithiane)[$Mo(CO)_2Cp]_2$ with a 3.149 Å Mo–Mo distance. Dinuclear complexes with bridging R_2S ligands have been observed in other systems.[22–27]

The ^{1}H NMR spectrum of **5** shows inequivalent protons at δ 4.62 and 4.73 ppm for H3 and H4 (see Eqn [3] for numbering system) and inequivalent methyls at 0.95 and 0.87 ppm, as expected from the structure of the molecule. These chemical shifts are not appreciably different than those (δ 4.53 and 1.11 ppm)[4] of free Cp*Ir(η^4-2,5-Me_2T) (**1**). The ^{1}H NMR and IR spectra of **6** are very similar to those of **5**, indicating that **6** has the same structure as **5**.

Not all triple-bonded dimers react in the same manner as **3** and **4**, since $Cp^*(CO)_2M{\equiv}M(CO)_2Cp^*$ ($Cp^* = \eta^5$-C_5Me_5 and M = Mo, W) do not react with **1** or **2** under the same conditions. The chromium analog of **3** and **4** does not form an adduct with **1** or **2** but simply transfers (Eqn [4]) a CO ligand to give Cp*Ir(CO)(*C*,*S*-2,5-Me_2T) (**7**) (31–38% yield), a complex that was previously prepared[11] by reacting **1** or **2** with CO. It is noteworthy that neither thiophene nor 2,5-Me_2T reacts with $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ under the conditions for the reactions of **1** or **2** (Eqn [3]). Thus, the thiophene in **1** and **2** is activated to react as compared with the non-reactivity of the free thiophene.



Reactions of (η^4,*S*-μ_3-2,5-Me_2T)[$M(CO)_2Cp]_2$, 5 and 6

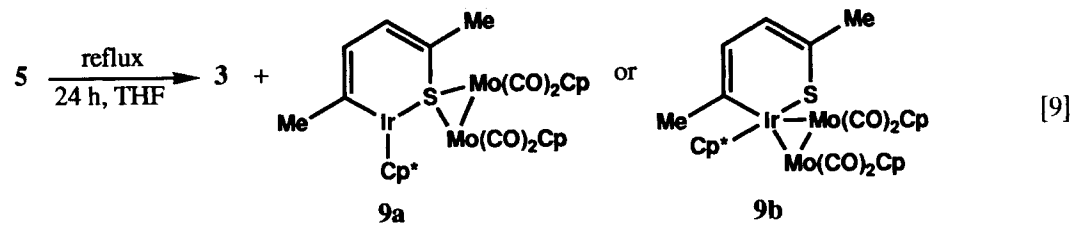
The trimetal complexes, **5** and **6**, are oxidized rapidly by two equivalents of Cp_2Fe^+ to release (Eqn [5]) the dimers $[CpM(CO)_2]_2$ (**3** and **4**) and form the known[4] di-cation $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$. It seems likely that oxidation occurs at the more electron-rich iridium, which then forces the dissociation of $Cp(CO)_2M{\equiv}M(CO)_2Cp$ to give the 18-electron η^5-2,5-Me_2T complex **8**. A related reaction is that of **1** with Cp_2Fe^+, which also rapidly gives **8**.[4]

Another way in which the molybdenum and tungsten dimers are displaced from the sulfur in **5** and **6** is by reaction with carbon monoxide (Eqn [6]). The reaction of **6** occurs readily in CH_2Cl_2 (0–15 °C, 3 h) to give the known[11] orange–yellow adduct $Cp^*Ir(CO)(C,S\text{-}2,5\text{-}Me_2T)$ (**7**) and red–purple $Cp(CO)_3W\text{-}W(CO)_3Cp$ in 36% and 44% yields, respectively. Complex **5** also reacts with CO to give **7** and $Cp(CO)_3Mo\text{-}Mo(CO)_3Cp$, but more vigorous conditions (25 °C, 12 h) are required and the yields are somewhat lower (21 % and 30 %, respectively). When the reaction solution of **5** with CO was photolyzed with ultraviolet light, the products, **7** and $Cp(CO)_3Mo\text{-}Mo(CO)_3Cp$, were formed in only 15 min in 31% and 35% yields, respectively.

Seeking reactions of the η^4,S-μ_3-2,5-Me_2T ligand in **5** that might model reactions of adsorbed thiophene on HDS catalysts, we reacted **5** with H_2 (1 atm) at room temperature in CH_2Cl_2 and THF solvents; however, there was no reaction. When the reaction solution was photolyzed with ultraviolet light (Eqn [7]), complex **2** in 69 % yield was the only product isolated. It was expected that $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ would be the other product; however it was not detected. It is known that **2** reacts with hydrogen in hexanes at room temperature, but this is a slow reaction requiring 24 h, which is presumably the reason why the dihydride complex $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)(H)_2$ (Eqn [2]) is not observed in reaction [7]. Reaction [7] may be similar to the photolytic reaction (Eqn [6]) of **5** under a CO atmosphere, except that the CO subsequently reacts with **2** to give **7**.

$$\mathbf{5} \xrightarrow[\text{THF, } H_2]{h\nu,\ 1\text{–}2\text{ h}} \mathbf{2} \qquad [7]$$

One could imagine that reaction [7] proceeds by initial photodissociation of



9a **9b** [9]

$Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (**1**) from the molybdenum dimer. However, since the conversion of **1** to **2** is slow except in the presence of bases,[4] the formation of **2** would occur only if the isomerization of **1** to **2** were catalyzed by the photolysis. Indeed, when **1** is photolyzed in THF solution for 1–2 h, the isomer **2** is produced (Eqn [8]) in nearly quantitative (93 %) isolated yield. Thus, this photolysis is a convenient method for converting the η^4-thiophene complex **1** to the *C,S*-isomer **2**.

$$\mathbf{1} \xrightarrow[\text{THF}]{h\nu,\ 1\text{-}2\ \text{h}} \mathbf{2} \qquad [8]$$

Whilst the photolysis of **5** (Eqn [7]) in THF results in loss of the molybdenum-containing part of the molecule, refluxing **5** in THF for 24 h yields (Eqn [9]) $Cp(CO)_2Mo{\equiv}Mo(CO)_2Cp$ (**3**) in 50% yield and a low yield (15%) of a new compound **9**, which has the same elemental analysis and molecular ion peak in the mass spectrum as **5**, but a distinctly different ^1H NMR spectrum. Especially notable are the low field doublets at δ 7.67 and 7.52 ppm for H(3) and H(4), which are characteristic of the ring-opened structure in **2**. The ν(CO) bands of **9** are nearly the same as in **5**, which suggests that the $Cp(CO)_2Mo\text{-}Mo(CO)_2Cp$ unit remains intact and perhaps is coordinated to the sulfur as in structure **9a** of Eqn [9]. However, the triangular cluster **9b** cannot be excluded as a possible structure. We have been unable to grow crystals suitable for an X-ray diffraction study.

CONCLUSION

These studies demonstrate that the 2,5-dimethylthiophene ligand in both the η^4- and *C,S*-isomers (**1** and **2**) react (Eqn [3]) with the unsaturated metal dimers $Cp(CO)_2M{\equiv}M(CO)_2Cp$ (M = Mo, W) to give complexes **5** and **6** in which the thiophene ring is coordinated to three metal atoms. Reactions of **5** with the oxidizing agent Cp_2Fe^+, CO and hydrogen did not provide evidence that this new type of coordination activates the thiophene in new ways that lead to desulfurization. HDS mechanisms[1,10,28] based on other organometallic model compounds appear to account best for the HDS of thiophenes.

Acknowledgements This work was supported by the US Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under contract W-7405-Eng-82. We thank Johnson Matthey, Inc for a loan of $IrCl_3$.

REFERENCES

1. Angelici, R J *Acc. Chem. Res.*, 1988, 21: 387
2. Angelici, R J *Coord. Chem. Rev.*, 1990, 105: 61
3. Chen, J and Angelici, R J *Organometallics*, 1989, 8: 2277
4. Chen, J and Angelici, R J *J. Am. Chem. Soc.*, 1990, 112: 199
5. Ogilvy, A E, Skaugset, A E and Rauchfuss, T B *Organometallics*, 1989, 8: 2739
6. Luo, S, Ogilvy, A E, Rauchfuss, T B, Rheingold, A L and Wilson, S R *Organometallics*, 1991, 10: 1002
7. Chen, J and Angelici, R J *Organometallics*, 1990, 9: 879
8. Cordone, R, Harman, W D and Taube, H *J. Am. Chem. Soc.*, 1989, 111: 5969
9. Chen, J and Angelici, R J *Organometallics*, 1990, 9: 849
10. Chen, J, Daniels, L M and Angelici, R J *J. Am. Chem. Soc.*, 1991, 113: 2544
11. Chen, J and Angelici, R J *Polyhedron*, 1990, 9: 1883
12. Hackett, P, O'Neill, P S and Manning, A R *J. Chem. Soc., Dalton Trans.*, 1974, 1625
13. Ginley, D S, Bock, C R and Wrighton, M S *Inorg. Chim. Acta*, 1977, 23: 85
14. Klingler, R J, Butler, W and Curtis, M D *J. Am. Chem. Soc.*, 1975, 97: 3535
15. Smart, J C and Pinsky, B L *J. Am. Chem. Soc.*, 1980, 102: 1009
16. Blechschmitt, K, Guggolz, E and Ziegler, M L *Z. Naturforsch.*, 1985, 40b: 85
17. Curtis, M D *Polyhedron*, 1987, 6: 759
18. Winter, M J *Adv. Organomet. Chem.*, 1989, 29: 101
19. Adams, R D, Collins, D M and Cotton, F A *Inorg. Chem.*, 1974, 13: 1086

20. Rheingold, A L and Harper, J R *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.,* 1991, C47: 184
21. Bock, H, Nuber, B, Korswagen, R P and Ziegler, M L *Bol. Soc. Quim. Peru,* 1988, 54: 211
22. Adams, R D and Pompeo, M P *J. Am. Chem. Soc.,* 1991, 113: 1619 and references therein
23. Kuhn, N, Zauder, E, Boese, R and Blaeser, D *J. Chem. Soc., Dalton Trans.,* 1988, 2171
24. Uson, R, Fornies, J, Tomas, M and Ara, I *J. Chem. Soc., Dalton Trans.,* 1989, 1011
25. Moynihan, K J, Gao, X, Boorman, P M, Fait, J F, Freeman, G K W, Thornton, P and Ironmonger, D J *Inorg. Chem.,* 1990, 29: 1648
26. Guggolz, E, Layer, K, Oberdorfer, F and Ziegler, M *Z. Naturforsch.,* 1985, 40b: 77
27. Cotton, F A, Diebold, M P and Roth, W J *J. Am. Chem. Soc.,* 1987, 109: 5506
28. Sauer, N N, Markel, E J, Schrader, G L and Angelici, R J *J. Catal.,* 1989, 117: 295
29. Markel, E J, Schrader, G L, Sauer, N N and Angelici, R J *J. Catal.,* 1989, 116: 111