Organometallics **1996,** *15,* 1223−1229

Unexpected Reactions of 2,5-Dimethylthiophene ($2,5\text{-}Me_2T$) in $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$, $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$, and $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ with Cobaltocene

Jiabi Chen,[†] Lee M. Daniels,[‡] and Robert J. Angelici*

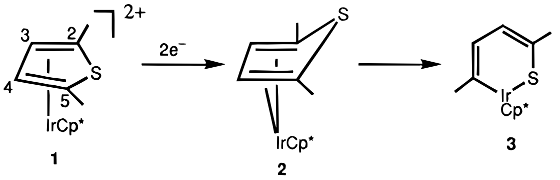
Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011

Received July 21, 1995[⊗]

The reaction of $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$ (**1**) ($Cp^* = \eta^5\text{-}C_5Me_5$) with the reducing agent Cp_2Co yields $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (**2**) and $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ (**3**), as well as the unexpected $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T{\cdot}C_5H_4)$ (**4**), which can also be prepared by reacting **1** with Cp^-. An X-ray diffraction study of **4** shows the $\eta^4\text{-}2,5\text{-}Me_2T{\cdot}C_5H_4$ ligand to be a ring-opened $2,5\text{-}Me_2T$ allyl thiolate conjugated to a cyclopentadienylidene unit. The reduced products **2** and **3** react with Cp_2Co to give a ferrole-type product $Cp^*[\overline{IrC(Me){=}CHCH{=}C}(Me)]CoCp$ in which the planar iridacyclopentadiene ring is π-bonded to the cobalt, as established by a structural investigation. The Cp*Co analog of **5** is prepared by the reaction of **2** or **3** with $Cp^*Co(CH_2{=}CH_2)_2$. These studies demonstrate that cobaltocene and $Cp^*Co(CH_2{=}CH_2)_2$ readily desulfurize the 2,5-dimethylthiophene ligand in **2** and **3**, which supports a previously proposed mechanism for thiophene hydrodesulfurization.

Introduction

In previous studies of thiophene binding and reactivity in transition metal complexes, as part of a broader investigation of the catalytic hydrodesulfurization of thiophenes,[1,2] we observed that the reduction of $Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)^{2+}$ (**1**), where $Cp^* = \eta^5\text{-}C_5Me_5$ and $2,5\text{-}Me_2T$ = 2,5-dimethylthiophene, by Cp_2Co or $Na[H_2Al(OCH_2CH_2OMe)_2]$ ("Red-Al") gave $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (**2**) and $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ (**3**) (eq 1).[3,4] Isomer **3** is more stable than **2** since bases (Et_3N and basic Al_2O_3)[3,4] and ultraviolet light[5] catalyze the isomerization of **2** to **3**. When Cp_2Co was used as the reducing agent, we observed upon closer inspection that a minor product **4** was also formed. Characterization of **4** and reactions designed to elucidate its mode of formation led to the studies described in this paper.



(1)

Experimental Section

General Procedures. All manipulations were carried out under an N_2 atmosphere in reagent grade solvents. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from Na/benzophenone; hexanes and CH_2Cl_2 were distilled from CaH_2. The solvents were stored over 4 Å molecular sieves under N_2. The neutral alumina (Brockmann, activity I) used in the chromatography columns ($1.5 \times 10{-}20$ cm) was deoxygenated at room temperature in high vacuum for 16 h, deactivated with 5% w/w N_2-saturated water, and stored under N_2. Dicyclopentadiene, $(Cp_2Co)PF_6$, and $CH_2{=}CHCH_2MgBr$ (1.0 M solution in Et_2O) were purchased from Aldrich. $[Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)](BF_4)_2$ (**1**), **2**, and **3** were prepared as described previously.[3,4] $Cp^*Co(CH_2{=}CH_2)_2$,[6a] $(H_2C{=}CH_2)Pt(PPh_3)_2$,[6b] and sodium/potassium alloy $NaK_{2.8}$[7] were prepared by literature methods.

Elemental analyses were performed by Galbraith Laboratories, Inc. The ^1H NMR spectra were obtained on a Nicolet NT-300 spectrometer using deuteriated solvents as internal locks and referenced to TMS; these spectra of compounds **2**−**7** are given in Table 1. Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 spectrometer. The melting points were determined in sealed nitrogen-filled capillaries and were not corrected.

Reaction of $[Cp^*Ir(\eta^5\text{-}2,5\text{-}Me_2T)](BF_4)_2$ (1) with Cp_2Co: Preparation of $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (2), $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ (3), and $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T{\cdot}C_5H_4)$ (4). (a) Reaction of 1 with 2 equiv of Cp_2Co. Compound **1** (0.300 g, 0.489 mmol) was dissolved in 30 mL of THF at room temperature. To this solution was added fresh Cp_2Co[8] prepared by reaction of $(Cp_2Co)PF_6$ (0.324 g, 0.970 mmol) with $NaK_{2.8}$ (0.035 g, 1.00 mmol) in THF solution. The pink-purple reaction solution was stirred for 8 h at room temperature. The solvent was evaporated under vacuum, and the purple-red residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. After removal of the purple band (Cp_2Co) from the column, a yellow and then a red band were eluted with hexanes/CH_2Cl_2 (10:1). Thereafter, a small bright-red band was eluted with hexanes/CH_2Cl_2/Et_2O (10:1:1). After removal

---

[†] Permanent address: Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, PRC.

[‡] Iowa State Molecular Structure Laboratory. Current address: Texas A&M University, College Station, TX 77843.

[⊗] Abstract published in *Advance ACS Abstracts,* January 1, 1996.

(1) Angelici, R. J. in *Encylopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley & Sons: New York, 1994; Vol. 3, pp 1433−1443.

(2) Angelici, R. J. *Bull. Soc. Chim. Belg.* 1995, *104*, 265−282.

(3) Chen, J.; Angelici, R. J. *Organometallics* **1989**, *8*, 2277.

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

(5) Chen, J.; Angelici, R. J. *Appl. Organomet. Chem.* **1992**, *6*, 479.

(6) (a) Frith, S. A.; Spencer, J. L. *Inorg. Synth.* **1985**, *23*, 19. (b) Blake, D. M.; Roundhill, D. M. *Inorg. Synth.* **1978**, *18*, 121.

(7) Ellis, J. E.; Flom, E. A. *J. Organomet. Chem.* **1975**, *99*, 263.

(8) The Cp_2Co was prepared by reduction of $(Cp_2Co)PF_6$ with $NaK_{2.8}$ alloy in THF (20−30 min at room temperature). The THF solution was filtered and the filtrate evaporated in vacuo to give a pink-purple residue of Cp_2Co.

0276-7333/96/2315-1223$12.00/0

Table 1. ^{1}H NMR Data (ppm) for Complexes 2−7 in $CDCl_3$

compd	δ(2,5-Me_2T)	δ(C_5Me_5)	δ(olefin)	δ (other)
2	4.53 (s, 2H), 1.11 (s, 6H)	1.92 (s, 15H)		
3	7.47 (d, 1H), 7.34 (d, 1H), 3.10 (s, 3H), 2.79 (s, 3H)	1.93 (s, 15H)		
4	5.47 (d, 1H), 3.80 (d, 1H), 2.35 (s, 3H), 2.01 (s, 3H)	1.73 (s, 15H)		6.53 (m, 1H), 6.48 (m, 1H), 6.41 (m, 2H), (C_5H_4)
5		2.08 (s, 15H)	4.71 (s, 2H), 2.07 (s, 6H)	4.54 (s, 5H) (Cp)
6		1.97 (s, 15H) 1.78 (s, 15H)	4.03 (s, 2H) 1.97 (s, 6H)	
7		1.85 (s, 15H)	3.99 (m, 1H), 3.28 (tt, 2H), 2.78 (tt, 2H)	

of solvents from the three eluates under vacuum, the residue from the first band was recrystallized from hexanes at −80 °C, and the second and third bands were recrystallized from hexanes/CH_2Cl_2 solution at −80 °C. From the first fraction separated 0.086 g (33%, based on **1**) of **2** as yellow crystals; mp 117−118 °C (dec). MS: *m/e* 440 (M^+). Anal. Calcd for $C_{16}H_{23}SIr$: C, 43.71; H, 5.27. Found: C, 43.68; H, 5.40. From the second fraction precipitated 0.017 g (7.9%) of dark-red crystals of **3**; mp 146−147 °C (dec). MS: *m/e* 440 (M^+). Anal. Calcd for $C_{16}H_{23}SIr$: C, 43.71; H, 5.27. Found: C, 43.80; H, 5.18. From the third fraction was obtained 0.009 g (4%) of **4** as deep-red crystals; mp 132−134 °C (dec). MS: *m/e* 504 (M^+). Anal. Calcd for $C_{21}H_{27}SIr$: C, 50.07; H, 5.40. Found: C, 50.21; H, 5.59.

(b) Reaction of 1 with 4 equiv of Cp_2Co. To a solution of **1** (0.250 g, 0.408 mmol) dissolved in 30 mL of THF at room temperature was added fresh Cp_2Co prepared by reaction of $(Cp_2Co)PF_6$ (0.540 g, 1.62 mmol) with $NaK_{2.8}$ (0.058 g, 1.63 mmol) in THF solution. The pink-purple reaction solution was stirred at room temperature for 8 h. Further treatment of the resulting mixture as described above for the reaction of **1** with 2 equiv of Cp_2Co gave 0.029 g (16%, based on **1**) of yellow crystalline **2**, 0.015 g (8.5%) of dark-red crystalline **3**, and 0.078 g (38%) of **4** as deep-red crystals, which were identified by their melting point and ^{1}H NMR and mass spectra.

Reaction of 2 with Cp_2Co: Preparation of Cp*[IrC(Me)=CHCH=C(Me)]CoCp (5). A solution was prepared by dissolving 0.030 g (0.068 mmol) of **2** in 15 mL of THF at room temperature. To this solution was added fresh Cp_2Co prepared by reduction of $(Cp_2Co)PF_6$ (0.044 g, 0.132 mmol) with $NaK_{2.8}$ (0.007 g, 0.200 mmol) in THF. The solution was stirred for 13 h at room temperature. After evaporation of the solution under vacuum, the dark-purple residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. After removal of unreacted Cp_2Co from the column, a red band eluted with hexanes/CH_2Cl_2 (10:1) first; then a dark-purple band was eluted with hexanes/CH_2Cl_2/Et_2O (10:1:1). 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 (16%, based on **2**) of **3** as dark-red crystals was obtained; mp 146−147 °C (dec). MS: *m/e* 440 (M^+). From the second fraction, 0.013 g (36%) of **5** as dark-purple crystals was isolated; mp 189−190 °C (dec). MS: *m/e* 532 (M^+), 408 (M^+ − CoCp). Anal. Calcd for $C_{21}H_{28}IrCo$: C, 47.45; H, 5.31. Found: C, 47.39; H, 5.29.

Reaction of 3 with Cp_2Co: Preparation of 5. To a solution of **3** (0.020 g, 0.045 mmol) in 15 mL of THF was added fresh Cp_2Co prepared by reduction of $(Cp_2Co)PF_6$ (0.030 g, 0.090 mmol) with $NaK_{2.8}$ (0.005 g, 0.14 mmol). After being stirred for 8 h at room temperature, the solution was evaporated in vacuo, and the residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. After removal of unreacted Cp_2Co from the column, a dark-purple band was eluted with hexanes/CH_2Cl_2/Et_2O (10:1:1). The solvent was removed from the eluate under vacuum, and the residue was recrystallized from hexanes at −80 °C to give 0.010 g (42%, based on **3**) of **5** as dark-purple crystals, which were identified by their melting point and ^{1}H NMR and mass spectra.

Reaction of 2 with Cp*Co(CH_2=CH_2)$_2$: Preparation of Cp*[IrC(CH_3)=CHCH=C(CH_3)]CoCp* (6). A solution containing 0.023 g (0.052 mmol) of **2** and 0.016 g (0.064 mmol) of Cp*Co(CH_2=CH_2)$_2$ in 20 mL of THF was refluxed under N_2 for 2 h. The resulting mixture was allowed to cool to room temperature, and the solvent was removed in vacuo. The residue was chromatographed on Al_2O_3 (neutral) with hexanes first and then hexanes/CH_2Cl_2 (10:1) as the eluant. A purple band was eluted and evaporated to dryness under vacuum; the crude product was recrystallized from hexanes at −80 °C to afford 0.011 g (35%, based on **2**) of dark-purple crystals of **6**; mp 185−186 °C (dec). MS: *m/e* 602 (M^+), 467 (M^+ − CoCp*). Anal. Calcd for $C_{26}H_{38}IrCo$: C, 51.90; H, 6.37. Found: C, 51.90; H, 6.33.

Reaction of 3 with Cp*Co(CH_2=CH_2)$_2$: Preparation of 6. A solution containing **3** (0.017 g, 0.039 mmol) and Cp*Co(CH_2=CH_2)$_2$ (0.015 g, 0.060 mmol) in 20 mL of THF was refluxed under N_2 for 2 h. After cooling of the solution to room temperature, further treatment of the resulting mixture as described above for the reaction of **2** gave 0.009 g (39%, based on **3**) of **6** as dark-purple crystals, which were identified by their melting point and, ^{1}H NMR and mass spectra.

Reaction of 2 with (CH_2=CH_2)Pt(PPh_3)$_2$ To Give 3. To a solution of **2** (0.020 g, 0.045 mmol) in 30 mL of THF was added 0.034 g (0.045 mmol) of (CH_2=CH_2)Pt(PPh_3)$_2$. The solution was stirred at room temperature for 70 h. The light yellow solution gradually turned orange. After vacuum removal of the solvent, the red residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (10:1) as the eluant. A red band was eluted, and the eluate was evaporated in vacuo; the residue was recrystallized from hexanes at −80 °C to give 0.014 g (70%, based on **2**) of dark-red crystals of **3**, which were identified by their melting point and ^{1}H NMR spectrum.

Reaction of 1 with K^+Cp^-: Preparation of 4. To a suspension of potassium (0.060 g, 1.53 mmol) cut into pieces in THF was added dropwise 0.110 g (1.67 mmol) of fresh cyclopentadiene[9] obtained by refluxing dicyclopentadiene for 10 min and then distilling. The light yellow solution was refluxed for 3 h, during which time the potassium metal dissolved; the resulting solution of KCp was allowed to cool to room temperature. To this solution was added 0.400 g (0.652 mmol) of **1**. The mixture was stirred for 8 h at room temperature. After vacuum removal of the solvent, the dark-red residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (10:1) as the eluant. The red eluate was evaporated in vacuo to dryness. Recrystallization of the crude product from hexanes/CH_2Cl_2 solution gave 0.150 g (45%, based on **1**) of **4** as deep-red crystals; mp 132−134 °C (dec). MS: *m/e* 504 (M^+). Anal. Calcd for $C_{21}H_{27}SIr$: C, 50.07; H, 5.40. Found: C, 49.77; H, 5.46.

Reaction of 1 with CH_2=$CHCH_2MgBr$: Preparation of Cp*Ir(η^3-C_3H_5)Br (7). To a solution of 0.300 g (0.489 mmol) of **1** dissolved in 50 mL of THF at room temperature was added 1.20 mL (1.17 mmol) of CH_2=$CHCH_2MgBr$ solution (1.0 M in Et_2O) with stirring. The reaction solution was stirred for 18

---

(9) Wilkinson, G. *Org. Synth.* **1956**, *36*, 33.

(10) Birmingham, J. M. *J. Organomet. Chem.* **1964**, *2*, 265.

Table 2. Crystal Data and Details of the Structure Determination for Complexes 4 and 5

	4	5
formula	$IrSC_{21}H_{29}$	$IrCoC_{21}H_{28}$
fw	503.71	531.59
space group	$P2_1/m$	$P2_1/m$
a, Å	7.648(1)	7.217(1)
b, Å	13.258(1)	14.314(1)
c, Å	9.534(1)	9.344(1)
β, deg	92.03(2)	103.167(7)
V, Å^3	966.1(6)	939.8(2)
Z	2	2
d_{calc}, g/cm^3	1.728	1.878
cryst size, mm	0.17 × 0.07 × 0.14	0.48 × 0.15 × 0.15
μ(Mo Kα), cm^{-1}	69.85	79.255
data collcn instrument	Enraf-Nonius CAD4	Enraf-Nonius CAD4
radiation (monochromated in incident beam)	Mo Kα(λ = 0.710 73 Å)	Mo Kα (λ = 0.710 73 Å)
orientation reflcns: no.; range (2θ), deg	25; 18.6−35.1	25; 21.2−32.3
temp, °C	22 ± 1	−80 ± 1
scan method	$\theta-2\theta$	$\theta-2\theta$
data collcn range, 2θ, deg	4−45	4−50
no. of unique data: tot.; with $F_o^2 > 3\sigma(F_o^2)$:	1332; 1178	1719; 1400
no. of params refined	152	109
transm factors (ψ-scans): max; min	1.00; 0.716	0.9987; 0.6570
R^a	0.0370	0.0470
$R_w{}^b$	0.0524	0.0609
quality-of-fit indicator^c	1.56	2.27
largest shift/esd, final cycle	0.01	0.01
largest peak, e/Å^3	1.3(2), 1.1 Å from Ir	5.0(2), 0.8 Å from Ir

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit = $[\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{params})]^{1/2}$.

h at room temperature, during which time the solution turned from light yellow to orange-yellow. After vacuum evaporation of the solvent, the residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluant. A yellow band was eluted, and the eluate was evaporated to dryness in vacuum; the yellow residue was recrystallized from hexanes at −80 °C to give 0.068 g (31%, based on **1**) of **7** as yellow crystals; mp 155−156 °C (dec). MS: *m/e* 448 (M$^+$), 407 (M$^+$ − C_3H_5). Anal. Calcd for $C_{13}H_{20}BrIr$: C, 34.82; H, 4.50. Found: C, 35.12; H, 4.63.

X-ray Structure Determinations of Cp*Ir(η^4-2,5-Me$_2$T·C$_5$H$_4$) (4) and Cp*[IrC(Me)=CHCH=C(Me)]CoCp (5). Deep-red crystals of **4** and dark-purple crystals of **5** suitable for X-ray diffraction study were obtained by recrystallization from hexanes/CH_2Cl_2 solution at −80 °C. Complexes **4** and **5** crystallize in the monoclinic crystal system. The cell constants of both complexes were determined from a list of reflections found by an automated search routine. Lorentz and polarization corrections were applied, and an absorption correction was also made on the basis of a series of ψ-scans for both complexes.

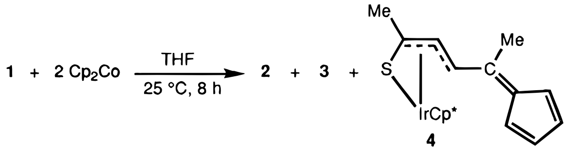
For **4**, since the absences indicated either of the space groups $P2_1$ or $P2_1/m$, solutions were tried in both space groups. $P2_1/m$ was used initially. The position of the Ir atom was taken from a Patterson map. A subsequent difference Fourier map clearly revealed the Cp* ligand, perpendicular to and bisected by the mirror plane, and a set of peaks corresponding to the sulfur ligand disordered about the mirror plane. A solution was then tried in the alternate space group, $P2_1$, but the disorder and the mirror symmetry persisted, so the switch back to $P2_1/m$ was made. Atoms C(1) and C(2) lie on the mirror plane and are therefore shared by both orientations of the disordered ligand. The other atoms (S, C(3)−C(6), and C(14)−C(18)) lie on general positions and were refined with occupancies fixed at 0.5. In the final model, all but atom C(3) were refined with anisotropic thermal parameters. Atom C(3) could not be refined anisotropically, possibly because of a high degree of correlation with the S atom due to the proximity of the two atoms in the disordered model (0.566 Å apart). Hydrogen atoms were not included in the model.

For **5**, the space group $P2_1/m$ was assigned on the basis of the systematic absences. The choice of the centric space group was suggested by intensity statistics and confirmed by the successful refinement of the structure. The position of the Ir and Co atoms were taken from a Patterson map, and the remainder of the atoms were located from a difference Fourier synthesis. The molecule has crystallographic mirror symmetry, so that the metal atoms, one carbon of the Cp ring, and two carbon atoms of the Cp* ring lie on a mirror plane. In the final steps of refinement, all atoms but one were given anisotropic temperature factors. The atom labeled C(11) could not be refined anisotropically and so was left with an isotropic temperature factor. Hydrogen atoms were not included in the model.

Pertinent data collection and structure solution information for **4** and **5** are given in Table 2. The final positional and thermal parameters are listed in Table 3. Bond lengths and major bond angles are presented in Tables 4 and 5, and ORTEP drawings of **4** and **5** are given in Figures 1 and 2, respectively. The data reduction and structure refinement were carried out with the SDP crystallographic programs.[11]

Results and Discussion

Reactions of Cp*Ir(η^5-2,5-Me$_2$T)$^{2+}$ (1) with Cp$_2$Co and KCp. As described in the Introduction, the reaction of **1** with 2 mol of Cp$_2$Co gives (eq 1) primarily complexes **2** and **3**, but we now find that a small amount (4%) of deep red Cp*Ir(η^4-2,5-Me$_2$T·C$_5$H$_4$) (**4**) (eq 2) is also produced. Elemental analyses and the mass spectrum confirm the composition of **4**, and an X-ray diffraction study establishes its structure as that shown in eq 2. The structure (Figure 1) is related to those of Cp*Ir(η^4-SC$_3$H$_2$MeC(=O)Me) (**A**)[12] and Cp*Rh(η^4-SC$_3$-



(2)

---

[11] Enraf-Nonius Structure Determination Package, Enraf-Nonius, Delft, The Netherlands.

[12] Chen, J.; Angelici, R. J. *Inorg. Chim. Acta*, in press.

Table 3. Positional Parameters and *B* Values (Å^2) and Their Estimated Standard Deviations for 4 and 5

	4				**5**			
atom	*x*	*y*	*z*	B^b	*x*	*y*	*z*	B^b
Ir	0.18432(7)	0.250	0.18553(5)	3.00(1)	0.23299(6)	0.250	0.21496(4)	1.48(1)
Co					0.1411(3)	0.250	-0.0689(2)	1.78(3)
S	0.3636(8)	0.3770(5)	0.0805(7)	4.4(1)				
C(1)	0.258(3)	0.250	-0.150(2)	6.4(5)	0.298(2)	0.4429(7)	0.086(1)	3.6(2)
C(2)	0.329(2)	0.250	-0.005(2)	4.3(4)	0.325(2)	0.3384(7)	0.0789(9)	2.8(2)
C(3)	0.374(2)	0.165(1)	0.071(2)	2.3(3)^a	0.409(1)	0.3012(7)	-0.0281(8)	2.6(2)
C(4)	0.444(2)	0.186(2)	0.217(2)	3.3(4)				
C(5)	0.464(3)	0.103(2)	0.319(3)	4.1(5)				
C(6)	0.421(5)	-0.007(2)	0.271(3)	7.6(8)				
C(11)	-0.102(2)	0.250	0.143(2)	4.7(4)	0.319(2)	0.250	0.446(1)	1.8(2)^a
C(12)	-0.053(1)	0.163(1)	0.224(1)	4.8(2)	0.200(2)	0.3313(6)	0.4108(9)	2.7(2)
C(13)	0.018(1)	0.1988(8)	0.350(1)	3.4(2)	0.018(1)	0.3008(6)	0.3372(9)	2.3(2)
C(14)	0.540(3)	0.119(2)	0.448(2)	4.4(5)				
C(15)	0.556(3)	0.047(2)	0.569(3)	6.7(6)				
C(16)	0.623(4)	0.102(2)	0.676(3)	6.5(7)				
C(17)	0.646(3)	0.209(2)	0.636(3)	5.2(6)				
C(18)	0.598(2)	0.217(1)	0.505(2)	3.8(5)				
C(21)	-0.182(3)	0.250	-0.004(2)	8.9(7)	0.513(3)	0.250	0.548(2)	6.1(6)
C(22)	-0.091(2)	0.052(1)	0.183(2)	7.9(4)	0.262(2)	0.4294(8)	0.450(1)	5.5(3)
C(23)	0.074(2)	0.131(1)	0.481(1)	6.1(3)	-0.151(2)	0.3638(8)	0.283(1)	4.2(2)
C(31)					-0.004(3)	0.250	-0.286(2)	8.1(8)
C(32)					-0.049(2)	0.3278(9)	-0.214(2)	6.9(3)
C(33)					-0.122(2)	0.299(1)	-0.115(1)	9.5(4)

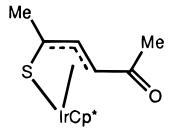
^{a} Atom refined isotropically. ^{b} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Table 4. Bond Distances (Å)^a for 4 and 5

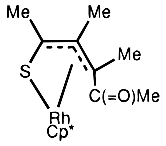
	4	**5**		**4**	**5**
Ir−S	2.411(6)		C(3)−C(4)	1.50(3)	
Ir−Co		2.584(1)	C(3)−C(3′)		1.46(1)
Ir−C(2)	2.16(1)	2.011(7)	C(4)−C(5)	1.48(3)	
Ir−C(3)	2.17(2)		C(5)−C(6)	1.56(3)	
Ir−C(4)	2.16(2)		C(5)−C(14)	1.37(3)	
Co−C(2)		2.107(6)	C(14)−C(15)	1.50(3)	
Co−C(3)		2.019(7)	C(14)−C(18)	1.46(3)	
S−C(2)	1.885(9)		C(15)−C(16)	1.34(4)	
C(1)−C(2)	1.47(2)	1.51(1)	C(16)−C(17)	1.49(4)	
C(2)−C(3)	1.38(2)	1.39(1)	C(17)−C(18)	1.30(3)	

^{a} Numbers in parentheses are estimated standard deviations in the least significant digits.

$Me_3C(=O)Me)$ (**B**).[13,14] Although there is disorder in the



A



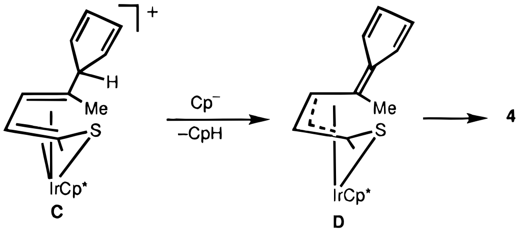
B

η^4-2,5-$Me_2T{\cdot}C_5H_4$ ligand, the C−C bond distances suggest that double bonds are located at C(5)−C(14) (1.37(3) Å), C(15)−C(16) (1.34(4)), and C(17)−C(18) (1.30(3)), and single bonds are at C(4)−C(5) (1.48(3) Å), C(14)−C(15) (1.50(3)), C(16)−C(17) (1.49(4)), and C(14)−C(18) (1.46(3)).[15] The conjugated triene system is conjugated with the allyl portion of the ligand. The C(2)−C(3) distance (1.38(2) Å) appears to be shorter than that of C(3)−C(4) (1.50(3)), although they may be the same within experimental error. In the rhodium analog (**B**), the C(2)−C(3) distance (1.39(2) Å) also appears, as in **4**, to be shorter than C(3)−C(4) (1.45(2) Å). The errors in all of these bond lengths are sufficiently large that it is not possible to state unequivocally the relative lengths of these bonds. The C(2)−S distance (1.885(9) Å) appears to be unusually long as compared with normal C(sp^2)−S (1.75 Å) and C(sp^3)−S (1.81 Å) single-bond distances.[15] However, the C(2)−S and C(2)−C(3) distances in **4** are less reliable than indicated by the esd's due to high correlation between these disordered atoms.

When the molar ratio of Cp_2Co to **1** in reaction 2 is increased from 2 to 4, the yield of the ring-opened product **4** increases from 4% to 38%, while the yield of **2** decreases from 33% to 16%. This result suggests that **4** may form from **2** or possibly from **3**. However, this is not the case since **2** and **3** react with Cp_2Co to give a totally different product (**5**); this reaction is discussed in the next section. Although the mechanism for the formation of **4** from **1** in reaction 2 is not obvious, it presumably results from the transfer of Cp^- from Cp_2Co to **1**. Indeed, compound **4** can also be prepared in relatively high yield (45%) from the reaction of **1** with 2 mol of KCp (eq 3). This reaction presumably occurs

$$\mathbf{1} + 2\,Cp^- \xrightarrow[\substack{25° \\ 8\text{ h}}]{\text{THF}} \mathbf{4} + C_5H_6 \qquad (3)$$

by nucleophilic addition of Cp^- on C(2) of **1** to give **C** (eq 4), in which the C(2)−S bond is cleaved, as shown



(4)

in eq 4 and observed in the addition of nucleophiles at C(2) in CpRu(η^5-thiophene)$^+$,[16] or the C(2)−S bond may

---

(13) Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *J. Am. Chem. Soc.* **1992**, *114*, 8521.

(14) Skaugset, A. E.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1990**, *9*, 2875.

(15) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

(16) (a) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897. (b) Hachgenei, J. W.; Angelici, R. J. *Organomet. Chem.* **1988**, *355*, 359.

Table 5. Selected Bond Angles (deg)[a] for 4 and 5

	4	5		4	5
S−C(2)−C(1)	116.7(4)		C(4)−C(5)−C(6)	120(2)	
S−C(2)−C(3)	118(1)		C(4)−C(5)−C(14)	121(2)	
C(2)−Ir−C(2′)		78.0(4)	C(6)−C(5)−C(14)	119(2)	
Ir−C(2)−Co		77.7(2)	C(5)−C(14)−C(15)	128(2)	
Ir−C(2)−C(1)		122.1(6)	C(5)−C(14)−C(18)	126(2)	
Ir−C(2)−C(3)		118.4(5)	C(15)−C(14)−C(18)	105(2)	
C(1)−C(2)−C(3)	124.9(9)	119.5(7)	C(14)−C(15)−C(16)	105(2)	
C(2)−C(3)−(4)	114(2)		C(15)−C(16)−C(17)	112(2)	
C(2)−C(3)−C(3′)		112.6(4)	C(16)−C(17)−C(18)	106(2)	
C(3)−C(4)−C(5)	119(2)		C(14)−C(18)−C(17)	111(2)	

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

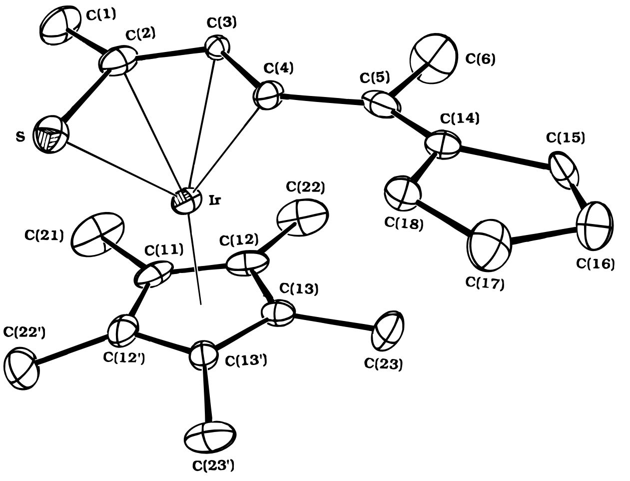
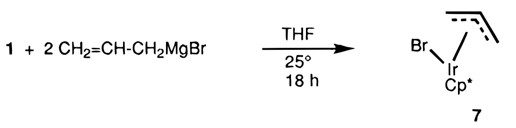


Figure 1. ORTEP drawing of $Cp^*(\eta^4\text{-}2,5\text{-}Me_2T{\cdot}C_5H_4)$ (**4**).

still be intact as observed in products obtained from nucleophilic attack on C(2) of $(CO)_3Mn(\eta^5\text{-thiophene})^+$,[17,18] or the C(2)−S bond may be relatively long and weak as established for the product $Cp^*Rh(\eta^4\text{-}Me_4T\text{-}2\text{-}OH)^+$ resulting from OH^- addition at C(2) of $Cp^*Rh(\eta^5\text{-}Me_4T)^{2+}$, where Me_4T is tetramethylthiophene.[13] Deprotonation of the relatively acidic cyclopentadiene hydrogen in **C** by another Cp^- gives intermediate **D**, which isomerizes to the final product **4**. The reaction of $Cp^*Rh(\eta^5\text{-}Me_4T)^{2+}$ with OH^- to give **B** has been proposed to follow a similar mechanism.[13]

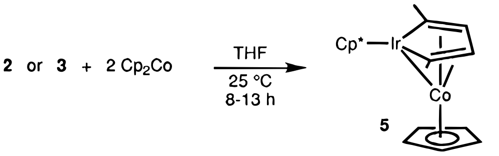
The formation of **4** by the reaction (eq 3) of **1** with Cp^- raises the possibility that in reaction 2 Cp^- is produced in the formation of Cp_2Co from $Cp_2Co^+PF_6^-$ (0.970 mmol) and $NaK_{2.8}$ (1.00 mmol) and that this Cp^- reacts (eq 3) with **1** to give **4**. This seems unlikely, however, since Cp_2Co that is purified by extraction into hexanes/THF (~5:1) away from other products of the reaction gives products **2**−**4** in essentially the same yields as are obtained in reactions using unextracted Cp_2Co. Also, there is no evidence[18] for the formation of Cp^- in the electrochemical reduction of Cp_2Co^+ in THF to Cp_2Co (−0.90 V) and even to Cp_2Co^- (−2.04 V); both of these reductions are reversible.

Unlike KCp (eq 4), the allyl Grignard reagent $CH_2{=}CHCH_2MgBr$ does not add at C(2) of **1** to give an intermediate which undergoes deprotonation to give a 1,3-diene product analogous to **4**. Instead (eq 5) the entire η^5-2,5-Me_2T ligand is displaced by the allyl group to give yellow $Cp^*Ir(\eta^3\text{-}C_3H_5)Br$, analogs of which have been prepared by other methods previously.[19−21] Complex **7** is readily soluble in both polar and nonpolar organic solvents, and the solid is air-stable for several days. Elemental analyses and the mass spectrum are consistent with the $Cp^*Ir(\eta^3\text{-}C_3H_5)Br$ composition. Its ^1H NMR spectrum (Table 1) shows resonances for the three types of protons characteristic of allyl groups.[19−21]



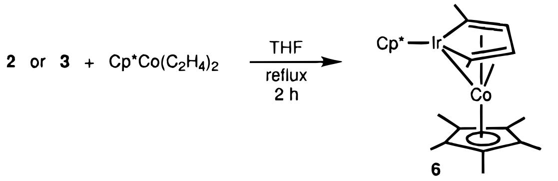
7 (5)

Reactions of $Cp^*Ir(\eta^4\text{-}2,5\text{-}Me_2T)$ (2) and $Cp^*Ir(C,S\text{-}2,5\text{-}Me_2T)$ (3) with Cp_2Co and $Cp^*Co(C_2H_4)_2$. Both **2** and **3** react at room temperature with 2 mol of Cp_2Co to give (eq 6) dark red $Cp^*[\overline{IrC(Me){=}CHCH{=}C}(Me)]CoCp$ (**5**). The reaction of **3** occurs somewhat more rapidly (8 h) than that of **2** (13 h) and gives a slightly higher yield (42% vs 36%). Also, in the reaction of **2** with Cp_2Co, a small amount of **3** was produced. These results suggest that the reaction of **2** with Cp_2Co occurs by initial isomerization to the more stable **3**, which reacts with Cp_2Co to give **5**. Other reactions of **2** and **3**, e.g., with Lewis acids,[4,22,23] bases,[24] and oxidizing agents,[12] also give the same products. Complex **5** is soluble in both polar and nonpolar organic solvents. Although its solutions are air-sensitive, the solid is stable for short periods in air.



5 (6)

The η^5-C_5Me_5 analog of **5** is prepared in reactions of **2** and **3** with $Cp^*Co(CH_2{=}CH_2)_2$ (eq 7). Dark-purple **6** was obtained in approximately the same yield (35−39%) from either **2** or **3**. Attempts to prepare the diiridium



6 (7)

---

(17) (a) Lesch, D. A.; Richardson, J. W., Jr.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901. (b) Huckett, S. C.; Sauer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 591.

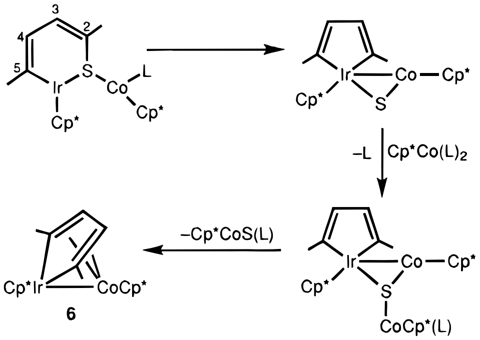
(18) Bard, A. J.; Garcia, E.; Kukharenko, S.; Strelets, V. V. *Inorg. Chem.* **1993**, *32*, 3528.

(19) Nesmeyanov, A. N.; Rubezhov, A. Z. *J. Organomet. Chem.* **1979**, *164*, 259.

(20) Rubezhov, A. Z.; Ivanov, A. S.; Gubin, S. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1974**, 2651.

(21) Leigh, G. J.; Richards, R. L. in *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: London, 1982; Vol. 5, p 609.

Scheme 1



analog of **6** by reacting **2** and **3** with $Cp^*Ir(CH_2{=}CH_2)_2$ under the conditions in eq 7 were unsuccessful; the $Cp^*Ir(CH_2{=}CH_2)_2$ did not react. Likewise, $Pt(PPh_3)_2(CH_2{=}CH_2)$ did not react with **2** or **3**.

Mechanisms for reactions 6 and 7 must account for the removal of sulfur from **2** and **3**; however, a specific sulfur-containing product was not identified in either reaction. Reaction 7 may occur by a pathway (Scheme 1; L = C_2H_4) similar to one proposed for the reaction of **3** with $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$.[25] As applied to reaction 7, this mechanism begins with coordination of the Cp*Co(L) fragment to the sulfur in **3** which promotes the migration of C(2) from sulfur to Ir giving an intermediate with a metallacyclopentadiene ring and a bridging sulfur. As shown in Scheme 1, this sulfur then coordinates to another Cp*Co(L) fragment to form an intermediate that has a structure similar to that of $\overline{\mathrm{Cp^*[IrC(Me){=}CHCH{=}C}}\mathrm{(Me)](\mu\text{-}SFe(CO)_4)Fe(CO)_2}$ (**8** in ref 25), whose structure was established by X-ray diffraction studies. Product **6** is then produced from this intermediate by loss of $Cp^*Co({=}S)(C_2H_4)$. This latter complex is a cobalt analog of $Cp^*Ir({=}S)(PMe_3)$ which is a proposed intermediate in the formation of sulfide-bridged iridium dimers.[26] While speculative, the mechanism in Scheme 1 provides a basis for understanding reaction 7. Reactions 6 and 7 demonstrate that cobalt complexes, like iron carbonyls,[25,27] can promote the desulfurization of the thiophene in **2** and **3**. This general type of desulfurization reactivity of **2** and **3** is consistent with the involvement of η^4 or ring-opened thiophenes in HDS, as proposed previously.[25]

Although $Cp^*Co(C_2H_4)_2$ reacts (eq 7) with 2,5-dimethylthiophene in **2** and **3** to give the desulfurized product **6**, $Cp^*Co(C_2H_4)_2$ reacts with thiophene itself to give $[Cp^*Co]_2(\mu\text{-}\eta^2,\eta^3\text{-}C_4H_4S)$ in which a C−S bond of the thiophene is cleaved.[27] The ring-opened thiophene bridges the two Co atoms which are bonded to each other. The rhodium analog $Cp^*Rh(C_2H_4)_2$ reacts with thiophene to give a product $[Cp^*Rh]_2(\mu\text{-}1,2,3,4\text{-}\eta^4{:}5,6,7,10\text{-}\eta^4\text{-}S(CH)_8S)$, in which two ring-opened thiophenes bridge two Rh atoms that are not bonded to each other.[29] Clearly, $Cp^*Co(C_2H_4)_2$ and $Cp^*Rh(C_2H_4)_2$ are highly reactive toward thiophene to give unusual products.

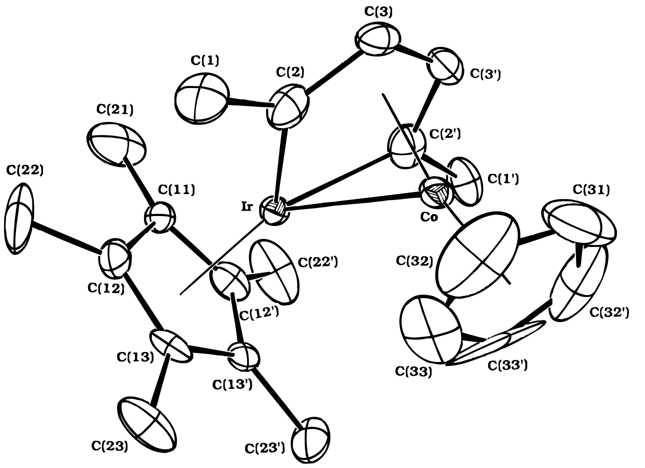


Figure 2. ORTEP drawing of $\overline{\mathrm{Cp^*[IrC(Me){=}CHCH{=}C}}\mathrm{(Me)]CoCp}$ (**5**).

The structure of **5** consists of a planar (±0.02 Å) iridacyclopentadiene (IrC_4) unit π-bonded to the cobalt. The dihedral angle between the IrC_4 and Cp planes is only 0.8(2)°, demonstrating that these planes are essentially parallel. The dihedral angle between the IrC_4 and Cp* (C(11), C(12), C(13), C(12′), (C(13′)) planes is 78.8(2)°. Within the iridacyclopentadiene ring, the Ir−C(2) distance (2.011(7) Å) is somewhat shorter than that of an Ir−C(sp^2) single bond (2.054(4) Å), as occurs in the vinyl complex $Cp^*(H)(PMe_3)IrCH{=}CH_2$,[30] but is significantly longer than the Ir=C double bonds (1.868(9) and 1.872(7) Å) in $[N(SiMe_2CH_2PPh_2)_2]Ir{=}CH_2$[31] and $(PPh_3)_2Cl_3Ir{=}CCl_2$.[32] This suggests that there is some π-bonding between Ir and C(2) but not as much as there is in **3** for which the Ir−C distance is 1.986(6) Å. The C(2)−C(3) distance (1.39(1) Å) in **5** is shorter than C(3)−C(3′) (1.46(1) Å), which indicates that the IrC_4 ligand has primarily diene character.

The dicobalt analog, $\overline{\mathrm{Cp[CoCH{=}CHCH{=}C}}\mathrm{H]CoCp}$, of **5** and **6** is known[33] and presumably has the same structure as **5**. At high temperatures (>90 °C), the Cp resonances of the dicobalt complex broaden and then coalesce (142 °C), which indicates that the two CpCo units exchange positions in and out of the cobaltacyclopentadiene ring. In **5**, it is the iridium rather than the cobalt that is incorporated into the metallacyclopentadiene unit, and there is no evidence for exchange of the Cp*Ir and CpCo groups.

Complex **6** presumably has the same structure as **5** on the basis of their ^1H NMR spectra (Table 1), which are similar except that the Cp*Ir and diene resonances are at higher field in **6** due to the greater electron density provided by the Cp* ligand on the cobalt. There

---

(22) Chen, J.; Angelici, R. J. *Organometallics* **1990**, *9*, 879.

(23) Chen, J.; Angelici, R. J. *Organometallics* **1990**, *9*, 849.

(24) Chen, J.; Daniels, L. M.; Angelici, R. J. *Polyhedron* **1990**, *9*, 1883.

(25) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 2544.

(26) Dobbs, D. A.; Bergman, R. G. *Inorg. Chem.* **1994**, *33*, 5329.

(27) (a) Luo, S.; Ogilvy, A. E.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1991**, *10*, 1002. (b) Ogilvy, A. E.; Skaugset, A. E.; Rauchfuss, T. B. *Organometallics* **1989**, *8*, 2739.

(28) (a) Jones, W. D.; Chin, R. M. *Organometallics* **1992**, *11*, 2698. (b) Jones, W. D.; Chin, R. M. *J. Organomet. Chem.* **1994**, *472*, 311.

(29) Chin, R. M.; Jones, W. D. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 357.

(30) (a) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1985**, *107*, 4580. (b) Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732.

(31) Fryzuk, M. D.; MacNeil, P. A.; Rettig, S. J. *J. Am. Chem. Soc.* **1985**, *107*, 6708.

(32) Clark, G. R.; Roper, W. R.; Wright, A. H. *J. Organomet. Chem.* **1982**, *236*, C7.

(33) Rosenblum, M.; North, B.; Wells, D.; Giering, W. P. *J. Am. Chem. Soc.* **1972**, *94*, 1239.

are numerous other metallacyclopentadiene complexes, prepared by a variety of routes.[34−36] A few are formed by the desulfurization of thiophenes.[25,27,37]

Conclusion

The reduction of Cp*Ir(η^5-2,5-Me$_2$T)(BF$_4$)$_2$ (**1**) with 2 mol of Cp$_2$Co gives (eq 2) Cp*Ir(η^4-2,5-Me$_2$T) (**2**) (33% yield) as the major product with smaller yields of Cp*Ir(*C*,*S*-2,5-Me$_2$T) (**3**) (7.9%) and Cp*Ir(η^4-2,5-Me$_2$T·C$_5$H$_4$) (**4**) (4%). However, the reduction of **1** with 4 mol of Cp$_2$Co yields **4** (38%) as the major product together with smaller amounts of **1** (16%) and **2** (8.5%). The formation of **4** apparently occurs by transfer of Cp$^-$ from Cp$_2$Co to C(2) of **1**. Compound **4** does not result from the reaction of **2** or **3** with the excess Cp$_2$Co, because these reactions lead (eq 6) to a quite different product Cp*[IrC(Me)═CHCH═C(Me)]CoCp (**5**), which is formed by the desulfurization of the 2,5-Me$_2$T ligand in **2** and **3**. The formation of **5** is related to reactions of **2** and **3**[25] and Cp*Rh(η^4-Me$_4$T)[27] with iron carbonyls which also give metallacyclopentadiene compounds, Cp*[IrC(Me)═CHCH═C(Me)](*μ*-CO)Fe(CO)$_2$ and Cp*Rh[FeC(Me)═C(Me)C(Me)═C(Me)](CO)$_3$. These reactions demonstrate that η^4- and *C*,*S*-thiophene ligands are readily desulfurized to give metallacyclopentadiene complexes.

Acknowledgment. This research was supported by the Office of Basic Energy Sciences, Chemical Sciences Division, of the U.S. Department of Energy under contract W-7045-Eng-82 to Iowa State University. We appreciate the loan of IrCl$_3$ by Johnson Matthey, Inc.

Supporting Information Available: Tables of bond distances, bond angles, displacement parameters, and least-squares planes for **4** and **5** (10 pages). Ordering information is given on any current masthead page.

OM9505625

---

(34) Fehlhammer, W. P.; Stolzenberg, H. in *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: London, 1982; Vol. 4, p 550.

(35) (a) Yamazaki, H.; Yasufuku, K.; Wakatsuki, Y. *Organometallics* **1983**, *2*, 726. (b) King, M.; Holt, E. M.; Radnia, P.; McKennis, J. S. *Organometallics* **1982**, *1*, 1718. (c) Astier, A.; Daran, J.-C.; Jeannin, Y.; Rigault, C. *J. Organomet. Chem.* **1983**, *241*, 53. (d) Müller, J.; Qiao, K.; Schubert, R. Tschampel, M. *Z. Naturforsch., B: Chem. Sci.* **1993**, *48*, 1558.

(36) (a) Bruce, M. I.; Low, P. J.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1994**, *464*, 191. (b) Kraatz, H. B.; Went, M. J.; Jeffrey, J. C. *J. Organomet. Chem.* **1990**, *394*, 167. (c) Müller, J.; Akhnoukh, T.; Pickardt, J.; Siewing, M.; Westphal, B. *J. Organomet. Chem.* **1993**, *459*, 325.

(37) (a) Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1988**, *7*, 1171. (b) Hübener, P.; Weiss, E. *J. Organomet. Chem.* **1977**, *129*, 105.