1414 Organometallics 1996, 15, 1414−1421

Reactions of the Iridathiabenzene Complex Cp*Ir(2,5-dimethylthiophene) with $Co_2(CO)_8$, $Co_4(CO)_{12}$, and $(\eta^6\text{-}C_6H_3Me_3)Co_4(CO)_9$[†]

Jiabi Chen,[‡] Victor G. Young, Jr.,[§] and Robert J. Angelici*

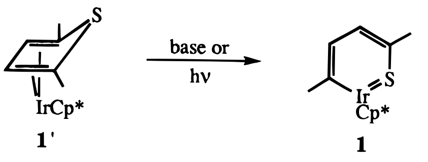
Department of Chemistry and Ames Laboratory, Iowa State University, Ames, Iowa 50011

Received September 5, 1995[⊗]

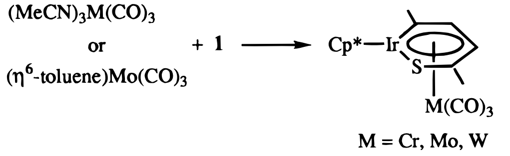
With the goal of preparing an η^6-iridathiabenzene complex of $Co_4(CO)_{12}$, the ring-opened iridathiabenzene complex Cp*Ir(*C*,*S*-2,5-Me_2T) (**1**), where 2,5-Me_2T is 2,5-dimethylthiophene, was reacted with $Co_4(CO)_{12}$, $Co_2(CO)_8$, and $(\eta^6\text{-}C_6H_3Me_3)Co_4(CO)_9$. Only in the reaction of $(\eta^6\text{-}C_6H_3Me_3)Co_4(CO)_9$ under mild conditions (35−40 °C) was the η^6-iridathiabenzene cluster [η^6-Cp*Ir(*C*,*S*-2,5-Me_2T)]$Co_4(CO)_9$ (**7**) obtained. At higher temperatures, the reaction yielded Cp*Ir(η^4-2,5-Me_2T·$Co_4(CO)_{11}$) (**6**), in which the 2,5-Me_2T ligand is coordinated through its diene to the Ir and through its sulfur to a Co of the cluster. Reactions of $Co_4(CO)_{12}$ and $Co_2(CO)_8$ with **1** yielded Cp*Ir(η^4-2,5-Me_2T·$Co_4(CO)_{11}$) (**2**), an isomer of **6**, which converts to the desulfurized linear tetranuclear cluster [Cp*Ir(C(Me)═CHCH═C(Me))(μ-CO)$_2$Co]$_2$ (**3**); this species contains bridging iridacyclopentadiene units. Cluster **3** has a structure with a $Co_2(\mu\text{-}CO)_2$ core and Cp*Ir(C(Me)═CHCH═C(Me))(CO) (**4**) end groups. In fact, **3** can be prepared from $Co_2(CO)_8$ and **4**. Molecular structures of **2**−**4** are reported, together with a discussion of pathways that lead to their formation.

Introduction

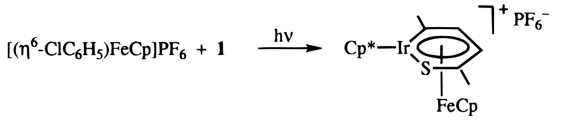
In conjunction with our studies of the catalytic hydrodesulfurization (HDS) of organosulfur compounds in petroleum feedstocks,[1] we have examined a variety of coordination modes[2] and reactions of thiophenes in their metal complexes. One of the most versatile systems is that of Cp*Ir(2,5-Me_2T), where Cp* = η^5-C_5Me_5 and 2,5-Me_2T is 2,5-dimethylthiophene.[3] The red Cp*Ir(*C*,*S*-Me_2T) (**1**) is formed from the yellow isomer Cp*Ir(η^4-2,5-Me_2T) (**1′**) by ultraviolet photolysis or base catalysis (eq 1).[4,5] The isomers, **1** and **1′**, usually both react to give the same products; this has been observed in their reactions with Lewis acids,[4,6] bases,[7] and oxidizing agents.[8] Structural and NMR studies[4,7] of **1** demonstrated that its six-membered iridathiabenzene ring can be considered to have a delocalized π-system. And recently,[9] we reported the synthesis of η^6-iridathiabenzene complexes by displacement (eq 2) of either three MeCN ligands or η^6-toluene from Cr, Mo, and W precursors. Chlorobenzene is similarly substituted[9] by **1** under UV-photolysis of the Fe complex in eq 3.



(1)



(2)



(3)

Several cluster complexes are known to contain η^6-arene ligands.[10] In some cases, the arene is η^6-coordinated to one metal atom, as in $Co_4(CO)_9(\eta^6\text{-arene})$; in others, the arene is bonded as a μ_3-η^2:η^2:η^2 ligand to three metal atoms on a triangular face of the cluster, as in $Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)$. In the present study, we examined the coordinating ability of the iridathiabenzene ligand **1** in the $Co_4(CO)_{12}$ cluster system. As described in detail in this paper, **1** reacts with $Co_4(CO)_{12}$, $Co_2(CO)_8$, and $(\eta^6\text{-}C_6H_3Me_3)Co_4(CO)_9$ to give products ranging from those in which **1** and **1′** are coordinated to the Co_4 cluster to those in which the iridathiabenzene ring has been desulfurized.

Experimental Section

General Procedures. All reactions were performed under an argon atmosphere following standard Schlenk techniques.

[†] Dedicated to Professor Dr. Max Herberhold, Universität Bayreuth, on the occasion of his 60th birthday.

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

[§] Iowa State University Molecular Structure Laboratory. Current address: University of Minnesota, Minneapolis, MN 55455.

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

(1) Angelici, R. J. In *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; Wiley: New York, 1994; Vol. 3, pp 1433−1443.

(2) (a) Angelici, R. J. *Bull. Soc. Chim. Belg.* **1995**, *104*, 265−282. (b) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61.

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

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

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

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

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

(8) Chen, J.; Angelici, R. J. *Inorg. Chim. Acta* **1995**, *235*, 61.

(9) Chen, J.; Young, V. G., Jr.; Angelici, R. J. *J. Am. Chem. Soc.* **1995**, *117*, 6362.

(10) Braga, D.; Dyson, P. J.; Grepioni, F.; Johnson, B. F. G. *Chem. Rev.* **1994**, *94*, 1585.

Solvents were reagent grade and dried by refluxing over appropriate drying agents and stored over 4-Å molecular sieves under an argon atmosphere until use. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were distilled from sodium benzophenone ketyl, while hexanes and CH_2Cl_2 were distilled from CaH_2. The neutral Al_2O_3 (Brockman, Activity I, 80−100 mesh) used for chromatography was deoxygenated under high vacuum at room temperature for 16 h, deactivated with 5% (w/w) N_2-saturated water, and stored under argon; neutral SiO_2 (s x 0143U-1, 60−200 mesh) was deoxygenated under high vacuum at room temperature for 12 h. Columns were 1.5 × (5−15) cm. $Co_2(CO)_8$ and $Co_4(CO)_{12}$ were purchased from Strem Chemical Co. The complex Cp*Ir(*C,S*-2,5-Me_2T) (**1**) was prepared as previously described.[4] (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$, where $C_6H_3Me_3$ is mesitylene, was prepared by a literature method.[11] All elemental analyses were performed by Galbraith Laboratories, Inc., or National Chemical Consulting, Inc. The IR spectra were measured on a Nicolet 710 FT-IR spectrophotometer using a solution cell with NaCl salt plates. All ^{1}H NMR spectra were recorded at ambient temperature in $CDCl_3$ solution with $CHCl_3$ as the internal reference using a Nicolet NT-300 spectrometer. Electron ionization mass spectra (EIMS) were run on a Finnigan 4500 spectrometer at 70 eV, and fast atom bombardment (FAB) spectra were run on a Kratos MS-50 mass spectrometer with samples in a 3-nitrobenzyl alcohol/CH_3NO_2 matrix. Melting points were recorded on compounds in sealed argon-filled capillaries and are uncorrected.

Reaction of 1 with $Co_4(CO)_{12}$ at 35−40 °C To Give Cp*Ir(η^4-2,5-Me_2T·$Co_4(CO)_{11}$) (2) and [Cp*Ir(C(Me)=CHCH=C(Me))(μ-CO)$_2$Co]$_2$ (3). A mixture of **1** (0.040 g, 0.091 mmol) and $Co_4(CO)_{12}$ (0.056 g, 0.098 mmol) in hexanes (40 mL) in a 100 mL Schlenk flask connected to a mineral oil bubbler was heated at 35−40 °C for 12 h, during which time the red solution turned gradually dark brown-red. The resulting solution was cooled to room temperature and then evaporated under vacuum to dryness. The residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (10:1) as the eluant. A green band which eluted first was collected; then a red band was eluted with hexanes/CH_2Cl_2/Et_2O (5:1:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexanes/CH_2Cl_2 at −80 °C. From the first fraction, 0.031 g (35%, based on **1**) of black crystals of **2** were obtained (mp 115−116 °C dec). IR (hexanes) ν(CO): 2079 s, 2031 s, 2019 vs, 1999 m, 1953 vs, 1843 w, 1826 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.74 (s, 2 H), 1.33 (s, 6 H), 1.88 (s, 15 H). MS (FAB): *m/e* 676 (M^+ − 11CO), 440 (M^+ − $Co_4(CO)_{11}$). Anal. Calcd for $C_{27}H_{23}O_{11}SIrCo_4$: C, 32.97; H, 2.36. Found: C, 33.31; H, 2.43. From the second fraction was obtained 0.003 g (6%, based on **1**) of **3** as brown-red crystals; mp 245−246 °C dec. IR (CH_2Cl_2) ν(CO): 1858 vs, br, 1782 vs, br cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.56 (s, 2 H), 2.24 (s, 6 H), 1.87 (s, 15 H). MS (FAB): *m/e* 1046 (M^+). Anal. Calcd for $C_{36}H_{46}O_4Ir_2Co_2$: C, 41.37; H, 4.44. Found: C, 41.50; H, 4.49.

Reaction of 1 with $Co_4(CO)_{12}$ at Reflux for 1 h To Give 2 and 3. A mixture of **1** (0.040 g, 0.091 mmol) and $Co_4(CO)_{12}$ (0.055 g, 0.096 mmol) in 40 mL of hexanes was refluxed for 1 h. Further treatment of the resulting mixture as described above for the reaction at 35−40 °C gave 0.014 g (16%, based on **1**) of **2** as black crystals and 0.015 g (31%, based on **1**) of **3** as brown-red crystals. Compounds **2** and **3** were identified by their mp and IR and ^{1}H NMR spectra.

Reaction of 1 with $Co_4(CO)_{12}$ at Reflux for 10 h To Give 3. A mixture of **1** (0.040 g, 0.091 mmol) and $Co_4(CO)_{12}$ (0.055 g, 0.096 mmol) in hexanes (40 mL) was refluxed for 10 h. Further treatment of the resulting mixture as described above for the reaction of **1** with $Co_4(CO)_{12}$ in hexanes at 35−40 °C yielded 0.027 g (56%, based on **1**) of **3**, which was identified by its mp and IR and ^{1}H NMR spectra.

Conversion of 2 into 3. A solution of 0.015 g (0.015 mmol) of black crystalline **2** dissolved in hexanes (20 mL) was refluxed for 10 h. After vacuum removal of the solvent, the residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (10:1) as the eluant. A red band was collected. The solvent was removed, and the residue was recrystallized from hexanes/CH_2Cl_2 at −80 °C to give 0.006 g (75%) of **3**, which was identified by its mp and IR and ^{1}H NMR spectra.

Reaction of 1 with $Co_2(CO)_8$ at Reflux for 1 h To Give 2 and 3. As described for the reaction of **1** with $Co_4(CO)_{12}$, 0.040 g (0.091 mmol) of **1** in hexanes (40 mL) was reacted with $Co_2(CO)_8$ (0.062 g, 0.181 mmol) under reflux for 1 h. Further treatment of the resulting mixture as described above for the reaction of **1** with $Co_4(CO)_{12}$ at 35−40 °C gave 0.014 g (16%, based on **1**) of **2** and 0.015 g (31%, based on **1**) of **3**. Compounds **2** and **3** were identified by their mp and IR and ^{1}H NMR spectra.

Reaction of 1 with $Co_2(CO)_8$ at Reflux for 10 h To Give 3 and Cp*Ir(C(Me)=CHCH=C(Me))(CO) (4). As described for the reaction of **1** with $Co_4(CO)_{12}$, a mixture of **1** (0.030 g, 0.068 mmol) and $Co_2(CO)_8$ (0.047 g, 0.137 mmol) in hexanes (40 mL) was refluxed for 10 h. After evaporation of the reaction solution to dryness under vacuum, the residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (15:1) as the eluant. An orange-yellow band eluted first; then a red band was eluted with hexanes/CH_2Cl_2/Et_2O (10:1:1). After removal of the solvents from the above two eluates, the residues were recrystallized from hexanes/CH_2Cl_2 at −80 °C. From the first fraction, 0.006 g (20%, based on **1**) of **4** as orange-yellow crystals was obtained (mp 90−91 °C dec). IR (hexanes) ν(CO): 2019 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 6.21 (s, 2 H), 2.37 (s, 6 H), 1.97 (s, 15 H). MS: *m/e* 436 (M^+), 435 (M^+ − H), 408 (M^+ − CO). Anal. Calcd for $C_{17}H_{23}OIr$: C, 46.88; H, 5.32. Found: C, 46.33; H, 5.30. From the second fraction was obtained 0.015 g (42%, based on **1**) of **3**, which was identified by its mp and IR and ^{1}H NMR spectra.

Reaction of 1 with $Co_2(CO)_8$ at Reflux for 24 h To Give 3. A mixture of **1** (0.030 g, 0.068 mmol) and $Co_2(CO)_8$ (0.047 g, 0.137 mmol) in 40 mL of hexanes was refluxed for 24 h. The reaction mixture, which was then worked up as described above for the reaction with $Co_2(CO)_8$ at reflux for 10 h, afforded 0.020 g (56%, based on **1**) of **3** as brown-red crystals, which were identified by their mp and IR and NMR spectra.

Reaction of 4 with $Co_2(CO)_8$ To Give 3. A mixture of **4** (0.010 g, 0.023 mmol) and $Co_2(CO)_8$ (0.007 g, 0.021 mmol) in hexanes (30 mL) was refluxed with stirring for 12 h, during which time the solution turned gradually from orange-yellow to dark brown. After removal of the solvent under vacuum, the residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (10:1) as the eluant. A red band was collected. The solvent was removed from it in vacuo, and the crude product was recrystallized from hexanes/CH_2Cl_2 at −80 °C to give 0.007 g (58%, based on **4**) of **3**, which was identified by its mp and IR and ^{1}H NMR spectra.

Reaction of 3 with CO To Give 4. Into a solution of 0.010 g (0.010 mmol) of **3** dissolved in THF (30 mL) was bubbled CO gas at room temperature for 26 h, during which time the brown-red solution gradually turned orange. After vacuum evaporation of the solvent, the residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (10:1) as the eluant. An orange band eluted first; then a brown-red 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/CH_2Cl_2 at −80 °C. From the first fraction, 0.002 g (25%) of **4** was obtained, which was identified by its mp and ^{1}H NMR spectrum. From the second fraction, 0.004 g of unreacted starting material (**3**) was isolated.

Reaction of 1 with (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ at 60−70 °C for 12 h To Give Cp*Ir(*C,S*-2,5-Me_2T)(CO) (5) and Cp*Ir(η^4-2,5-Me_2T·$Co_4(CO)_{11}$) (6). A mixture of **1** (0.030 g, 0.068 mmol) and (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ (0.042 g, 0.069 mmol) in hexanes (50 mL) was heated at 60−70 °C for 12 h, during which time the solution turned from black-green to dark

---

[11] Kayannovych, V. S.; Rybinskaya, M. I. *J. Organomet. Chem.* **1988**, *344*, 383.

yellow. After the solvent was evaporated in vacuo, the residue was chromatographed on SiO_2 (neutral) with hexanes/CH_2Cl_2 (15:1) as the eluant. After unreacted (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ was eluted from the column, a dark orange band was eluted with hexanes/CH_2Cl_2/Et_2O (15:1:1); then a dark purple band eluted with CH_2Cl_2/Et_2O (10:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from hexanes/CH_2Cl_2 at −80 °C. From the first fraction, 0.005 g (16%, based on **1**) of orange crystals (**5**)[7,12] was obtained (mp 121−122 °C dec). IR (hexanes) ν(CO): 2020 s cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.79 (d, 1 H), 5.45 (d, 1 H), 2.29 (s, 3 H), 1.97 (s, 3 H), 1.88 (s, 15 H). MS: *m/e* 468 (M^+). From the second fraction, 0.021 g (31%, based on **1**) of dark purple crystals (**6**) were obtained (mp >250 °C dec). IR (CH_2Cl_2) ν(CO): 2079 vs, 2032 vs,br, 2019 w, 2011 s, 1941 w, 1828 w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 4.64 (s, 2 H), 1.88 (s, 15 H), 1.33 (s, 6 H). MS (FAB): *m/e* 544 ($Co_4(CO)_{11}^+$), 440 (M^+ − $Co_4(CO)_{11}$). Anal. Calcd for $C_{27}H_{23}O_{11}SIrCo_4 \cdot C_6H_{14}$ (hexane): C, 37.05; H, 3.49. Found: C, 36.74; H, 3.53.

Reaction of 1 with (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ at Reflux for 10 h To Give 3 and 6. A mixture of **1** (0.030 g, 0.068 mmol) and (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ (0.041 g, 0.067 mmol) in hexanes (30 mL) was refluxed for 10 h. After vacuum removal of the solvent, the residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (10:1). After unreacted (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ (green band) was eluted from the column, a brown-red band was eluted with hexanes/CH_2Cl_2 (5:1); then a dark purple band was eluted with hexanes/CH_2Cl_2/Et_2O (1:1:1). After evaporation of the solvents from the above two eluates, the residues were recrystallized from hexanes/CH_2Cl_2 at −80 °C. From the brown-red fraction, 0.011 g (31%, based on **1**) of **3** was obtained. From the dark purple fraction, 0.021 g (31%, based on **1**) of **6** were obtained. Compounds **3** and **6** was identified by their mp and IR and ^{1}H NMR spectra.

Reaction of 1 with (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ in THF at Reflux for 12 h To Give 3 and 6. A mixture of **1** (0.040 g, 0.091 mmol) and (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ (0.055 g, 0.090 mmol) in THF (30 mL) was refluxed for 12 h. Further treatment of the resulting mixture as described above for the reaction in hexanes by reflux for 10 h gave 0.016 g (33% based on **1**) of **3** and 0.007 g (8%, based on **1**) of **6**. Compounds **3** and **6** were identified by their mp and IR and ^{1}H NMR spectra.

Reaction of 1 with (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ at Room Temperature for 22 h To Give 6 and [η^6-Cp*Ir(*C*,*S*-2,5-Me_2T)]$Co_4(CO)_9$ (7). A mixture of **1** (0.040 g, 0.091 mmol) and (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ (0.055 g, 0.090 mmol) in 50 mL of hexanes was stirred at room temperature for 22 h, during which time the solution turned from black-green to dark yellow. After vacuum removal of the solvent, the residue was chromatographed on SiO_2 (neutral) with hexanes/CH_2Cl_2 (15:1). After unreacted (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ (green band) and **1** (red band) were eluted from the column, a dark orange band was eluted with hexanes/benzene (5:1); then a dark purple band was eluted with hexanes/CH_2Cl_2/Et_2O (1:1:1). The solvents were removed from the above two eluates, and the residues were recrystallized from hexanes/CH_2Cl_2 at −80 °C. From the first fraction, 0.004 g (5%, based on **1**) of **7** as dark yellow crystals was obtained (mp 134−135 °C dec). IR (hexanes) ν(CO): 2039 w, 2011 vs, br, 1985 w, 1794 m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.78 (d, 1 H), 5.44 (d, 1 H), 2.29 (s, 3 H), 1.97 (s, 3 H), 1.89 (s, 15 H). MS (FAB): *m/e* 488 ($Co_4(CO)_9^+$), 440 (M^+ − $Co_4(CO)_9$). Anal. Calcd for $C_{25}H_{23}O_9SIrCo_4$: C, 32.38; H, 2.50. Found: C, 32.86; H, 2.32. From the second fraction was isolated 0.019 g (21%, based on **1**) of dark purple crystals of **6**, which was identified by its mp and IR and ^{1}H NMR spectra.

Reaction of 1 with (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ at 35−40 °C To Give 6 and 7. A mixture of **1** (0.040 g, 0.091 mmol) and (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ (0.055 g, 0.090 mmol) in hexanes (40 mL) was stirred at 35−40 °C for 2−24 h. Isolation of the products according to the procedure above after different reaction times gave the following yields of **6** and **7**: after 2−6 h (**6**, 20%; **7**, 5−8%); after 12 h (**6**, 25%; **7**, 20%); after 24 h (**6**, 30%; **7**, 10%).

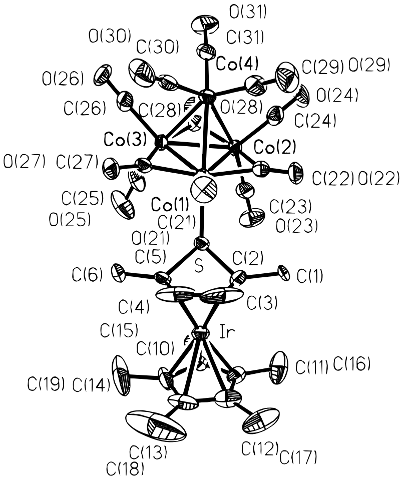


Figure 1. Thermal ellipsoid drawing of Cp*Ir(η^4-2,5-Me_2-T$\cdot Co_4(CO)_{11}$) (**2**).

Reaction of 1 with (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ at 35−40 °C for 48 h To Give 2 and 6. A mixture of **1** (0.040 g, 0.091 mmol) and (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ in hexanes (40 mL) was stirred at 35−40 °C for 48 h. After evaporation of the solution to dryness under vacuum, the residue was chromatographed on Al_2O_3 (neutral) with hexanes/CH_2Cl_2 (10:1) as the eluant. A green band eluted first; then a dark purple band was eluted with hexanes/CH_2Cl_2/Et_2O (1:1:1). After vacuum removal of the solvents from the above two eluates, the residues were recrystallized from the hexanes/CH_2Cl_2 solution at −80 °C. From the first fraction was obtained 0.009 g (10%, based on **1**) of black crystals (**2**); 0.031 g (35%, based on **1**) of **6** as dark purple crystals was obtained from the second fraction. Compounds **2** and **6** were identified by their mp and IR and ^{1}H NMR spectra.

X-ray Structure Determinations of 2−4. Crystals of **2**−**4** were mounted on either an Enraf-Nonius CAD4 or a Siemens P4RA single-crystal diffractometer, and data were collected under the conditions indicated in Table 1. Cell constants for the data collections were determined either from a list of reflections found in a random search routine (CAD4) or from a 360° rotation photograph (P4RA). High-angle cell constants were determined from a subset of intense reflections in the range of 35.0−50.0° 2θ (Cu Kα) for **3**. Lorentz and polarization corrections were applied, as well as a correction for radiation damage based on three standard reflections for all three structure determinations. **2** and **3** were corrected for absorption effects by use of the semiempirical method based on a series of azimuthal scans. **4** was corrected for absorption effects in like manner based on redundant data instead. All calculations were performed on a Digital Equipment Vax Station 3100 computer using SHELXTL-PLUS[13] and SHELXL-93[14] for **4** only. All structure determinations were solved using direct methods.[13,15] All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were treated as riding atoms with C−H distances fixed at 0.96 Å with refined isotropic displacement parameters.

Thermal ellipsoid drawings for **2**−**4** are provided at 50% probability in Figures 1−3, respectively. Selected bond distances and angles are presented in Tables 2−7.

---

[12] Chen, J.; Daniels, L. M.; Angelici, R. J. *Acta Crystallogr.* **1992**, *C48*, 2120.

[13] SHELXTL-PLUS, Siemens Analytical X-ray, Inc., Madison, WI.

[14] SHELXL-93: Sheldrick, G. M. *J. Appl. Crystallogr.*, manuscript in preparation.

[15] All X-ray scattering factors and anomalous dispersion terms were obtained from: *International Tables for Crystallography*; Wilson, A. J. C., Ed.; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C, pp 4.2.6.8 and 6.1.1.4.

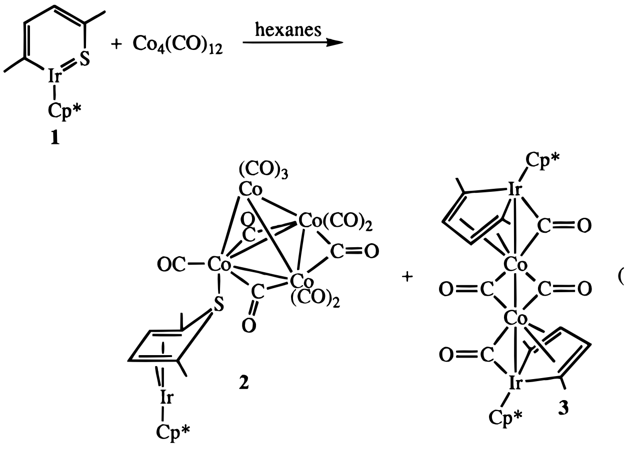
Table 1. Summary of Crystallographic Data for 2−4

	2	3	4
formula	$C_{26}H_{23}Co_4IrO_{12}S$	$C_{43}H_{54}Co_2Ir_2O_4$	$C_{17}H_{23}IrO$
fw	987.4	1137.1	435.55
space group	$P2_1/c$	$P2_1/c$	$P2_1/n$
a, Å	13.901(1)	16.699(2)	7.622(1)
b, Å	14.463(2)	14.202(1)	14.256(3)
c, Å	16.057(3)	17.107(3)	14.696(3)
β, deg	98.34(1)	96.45(1)	100.93(2)
V, Å^3	3195.6(8)	4031.4(8)	1567.9(5)
Z	4	4	4
d_{calc}, g cm^{-3}	2.047	1.874	1.845
cryst size, mm	0.55 × 0.30 × 0.15	0.07 × 0.08 × 0.55	0.35 × 0.33 × 0.26
μ, mm^{-1}	6.29	19.12	8.51
data collecn instrument	Enraf-Nonius CAD4	Siemens P4RA	Enraf-Nonius CAD4
radiation	Mo Kα (λ = 0.710 73 Å)	Cu Kα (λ = 1.541 78 Å)	Mo Kα (λ = 0.710 73Å)
temp, °C	−80	−80	25
scan method	$\omega-2\theta$	$\theta-2\theta$	$\omega-2\theta$
2θ range, deg	2.0−50.0	4.0−115.0	4.0−50.0
no. of rflns collected	7196	11252	5472
no. of indep rflns	5620 (R_{int} = 0.032)	5410 (R_{int} = 0.032)	2741 (R_{int} = 0.039)
no. of obsd rflns	4549 ($F \geq 4.0\sigma(F)$)	3869 ($F \geq 4.0\sigma(F)$)	2481 ($F \geq 4.0\sigma(F)$)
no. of params refined	400	481	189
transmissn: min, max	0.602, 1.000	0.656, 0.845	0.90, 0.27
refinement package	SHELXTL-PLUS (VMS)	SHELXTL-PLUS (VMS)	SHELXL-93 (VMS)
R^a	0.044	0.034	0.033
$R_w{}^b$ or wR2^c	0.058^b	0.034^b	0.087^c
goodness of fit^{d,e}	1.03^d	0.97^d	1.18^e
largest shift/esd	0.003	0.009	0.04
residual peak/hole, e Å^{-3}	+2.06/−2.41	+0.72/−1.71	+2.77/−1.35

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] $wR2 = [\sum\{w(F_o{}^2 - F_c{}^2)^2\}/\sum\{w(F_o{}^2)^2\}]^{1/2}$; $w = 9/\{\sigma^2(F_o{}^2) + (a^*p)^2 + (b^*p) + d + (e^* \sin\theta)\}$.[14] [d] $S = \{\sum w(|F_o| - |F_c|)^2/(N_{obs} - N_{parameters})\}^{1/2}$. [e] $S = [\sum\{w(F_o{}^2 - F_c{}^2)^2/(N_{obs} - N_{parameters})\}^{1/2}$.[14]

Results and Discussion

Reactions of Cp*Ir(*C,S*-2,5-Me$_2$T) (1) with Co$_4$(CO)$_{12}$. The η^6-mesitylene complex (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$ is prepared by heating mesitylene with $Co_4(CO)_{12}$ at 60−70 °C for 6 h.[10,16] With the goal of preparing the analogous η^6-iridathiabenzene cluster, **1** and $Co_4(CO)_{12}$ were reacted in hexanes at different temperatures and reaction times. Under no conditions was the desired (η^6-iridathiabenzene)$Co_4(CO)_9$ complex obtained. Instead, two other clusters, **2** and **3**, were obtained (eq 4)



(4)

in varying amounts depending on the reaction temperature and time. Under the mildest conditions (35−40 °C, 2 h), **2** was the major isolated product (35%) and **3** was formed in only a small amount (6%). At higher temperature, refluxing hexanes (bp 68−69 °C) for 1 h, **2** was the minor product (16%) and **3** became the major product (31%). Under the most vigorous conditions, refluxing hexanes for 10 h, **2** was not detected and **3** was isolated in 56% yield. Thus, as the reaction conditions become more rigorous, the amount of **2** decreases and **3** increases. This suggests that **3** is formed from **2**. Indeed, **2** is converted to **3** (eq 5) in 75%

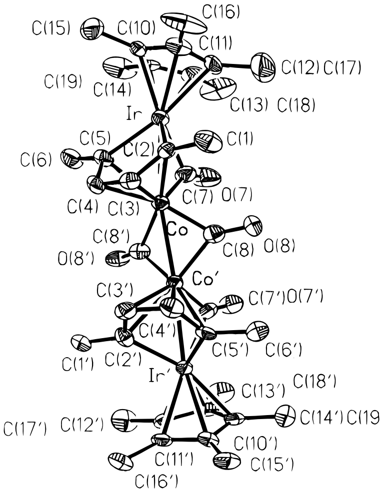


Figure 2. Thermal ellipsoid drawing of [Cp*Ir(C(Me)=C-HCH=C(Me))(μ-CO)$_2$Co]$_2$ (**3**).

$$\mathbf{2} \xrightarrow[\text{reflux, 10 h}]{\text{hexanes}} \mathbf{3} + Co_xS_y\ (?) + CO\ (?) \qquad (5)$$

isolated yield in refluxing hexanes for 10 h. The other products in this reaction were not identified; however, the sulfur that is removed from **2** presumably combines with the excess Co in **2** to give a cobalt sulfide. The mechanism of the conversion of **2** to **3** is not known, but it could be related to those proposed[17−19] for the desul-

---

(16) Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E. *J. Chem. Soc., Perkin Trans. 1* **1973**, 975.

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

(18) Luo, S.; Ogilvy, A. E.; Rauchfuss, T. B.; Rheingold, A. L.; Wilson, S. R. *Organometallics* **1991**, *10*, 1002.

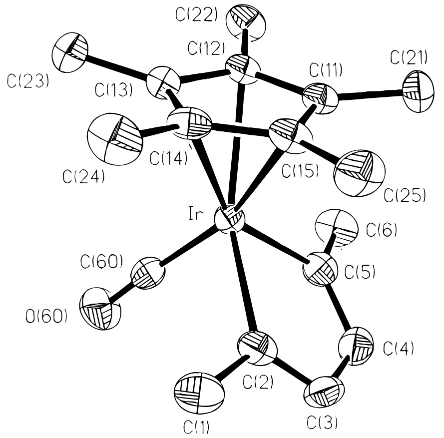


Figure 3. Thermal ellipsoid drawing of Cp*Ir(C(Me)═C-HCH═C(Me))(CO) (**4**).

Table 2. Selected Bond Distances (Å) for Cp*Ir(η^4-2,5-Me_2T·$Co_4(CO)_{11}$) (2)[a]

Ir−S	2.869(2)	Ir−C(2)	2.12(1)
Ir−C(3)	2.11(1)	Ir−C(4)	2.10(1)
Ir−C(5)	2.112(8)	Ir−C(10)	2.183(8)
Ir−C(11)	2.186(9)	Ir−C(12)	2.230(9)
Ir−C(13)	2.223(9)	Ir−C(14)	2.16(1)
S−C(2)	1.773(10)	S−C(5)	1.783(8)
S−Co(1)	2.230(2)	C(1)−C(2)	1.50(2)
C(2)−C(3)	1.45(2)	C(3)−C(4)	1.39(2)
C(4)−C(5)	1.44(2)	C(5)−C(6)	1.48(2)
C(10)−C(11)	1.42(1)	C(10)−C(14)	1.45(1)
C(10)−C(15)	1.51(1)	C(11)−C(12)	1.39(1)
C(11)−C(16)	1.52(1)	C(12)−C(13)	1.42(2)
C(12)−C(17)	1.52(1)	C(13)−C(14)	1.44(2)
C(13)−C(18)	1.53(2)	C(14)−C(19)	1.51(2)
Co(1)−Co(2)	2.448(1)	Co(1)−Co(3)	2.455(1)
Co(1)−Co(4)	2.544(1)	Co(1)−C(21)	1.763(7)
Co(1)−C(22)	1.896(8)	Co(1)−C(27)	1.902(8)
Co(2)−Co(3)	2.442(1)	Co(2)−Co(4)	2.519(2)
Co(2)−C(22)	1.945(7)	Co(2)−C(23)	1.777(9)
Co(2)−C(24)	1.780(9)	Co(2)−C(28)	1.936(8)
Co(3)−Co(4)	2.518(2)	Co(3)−C(25)	1.76(1)
Co(3)−C(26)	1.794(8)	Co(3)−C(27)	1.949(7)
Co(3)−C(28)	1.946(8)	Co(4)−C(29)	1.797(9)
Co(4)−C(30)	1.794(9)	Co(4)−C(31)	1.799(8)

[a] Estimated standard deviations are given in parentheses.

Table 3. Selected Bond Angles (deg) for Cp*Ir(η^4-2,5-Me_2T·$Co_4(CO)_{11}$) (2)

Ir−S−Co(1)	152.8(1)	C(2)−S−C(5)	83.6(4)
C(5)−S−Co(1)	118.9(3)	C(2)−S−Co(1)	116.0(4)
C(1)−C(2)−C(3)	124.8(13)	S−C(2)−C(1)	118.0(9)
C(3)−C(4)−C(5)	111.8(11)	S−C(2)−C(3)	111.4(9)
C(4)−C(5)−C(6)	125.9(10)	C(2)−C(3)−C(4)	108.0(10)
S−Co(1)−Co(3)	104.3(1)	S−C(5)−C(4)	109.1(8)
S−Co(1)−Co(4)	159.1(1)	S−C(5)−C(6)	118.7(7)
Co(3)−Co(1)−Co(4)	60.5(1)	S−Co(1)−Co(2)	100.0(1)
Co(2)−Co(1)−C(21)	148.3(3)	Co(2)−Co(1)−Co(3)	59.7(1)
Co(4)−Co(1)−C(21)	104.4(3)	Co(2)−Co(1)−Co(4)	60.6(1)
Co(2)−Co(1)−C(22)	51.3(2)	S−Co(1)−C(21)	96.3(3)
Co(4)−Co(1)−C(22)	79.0(2)	Co(3)−Co(1)−C(21)	140.6(3)
Co(1)−Co(2)−Co(3)	60.3(1)	S−Co(1)−C(22)	95.0(2)
Co(3)−Co(2)−Co(4)	61.0(1)	Co(3)−Co(1)−C(22)	110.5(2)
Co(1)−Co(3)−Co(4)	61.5(1)	C(21)−Co(1)−C(22)	100.5(3)
Co(1)−Co(4)−Co(2)	57.8(1)	Co(1)−Co(2)−Co(4)	61.6(1)
Co(2)−Co(4)−Co(3)	58.0(1)	Co(1)−Co(2)−C(22)	49.5(2)
Co(1)−C(22)−Co(2)	79.2(3)	Co(1)−Co(3)−Co(2)	60.0(1)
Co(2)−C(22)−O(22)	137.5(6)	Co(2)−Co(3)−Co(4)	61.0(1)
Co(1)−C(21)−O(21)	176.7(7)	Co(1)−Co(4)−Co(3)	58.0(1)
Co(1)−C(22)−O(22)	143.2(6)		

Table 4. Selected Bond Distances (Å) for [Cp*Ir(C(Me)═CHCH═C(Me))(μ-CO)$_2$Co]$_2$ (3)

Ir−C(2)	2.05(1)	Ir−C(5)	2.05(1)
Ir−Co	2.524(2)	Ir−C(7)	2.14(1)
C(2)−C(3)	1.38(1)	C(1)−C(2)	1.51(1)
C(3)−C(4)	1.41(2)	C(2)−Co	2.14(1)
C(4)−C(5)	1.38(1)	C(3)−Co	2.11(9)
C(5)−C(6)	1.51(2)	C(4)−Co	2.11(1)
Co−C(7)	1.81(1)	C(5)−Co	2.15(1)
Co−Co′	2.413(2)	Co−C(8)	1.89(1)
C(7)−O(7)	1.17(1)	Co−C(8′)	1.87(1)
C(8)−Co′	1.87(1)	C(8)−O(8)	1.19(1)
Ir′−C(5′)	2.045(9)	Ir′−C(2′)	2.05(1)
Ir′−C(7′)	2.09(1)	Ir′−Co′	2.518(2)
C(1′)−C(2′)	1.49(1)	C(2′)−C(3′)	1.37(1)
C(2′)−Co′	2.158(9)	C(3′)−C(4′)	1.43(2)
C(3′)−Co′	2.15(1)	C(4′)−C(5′)	1.38(2)
C(4′)−Co′	2.16(1)	C(5′)−C(6′)	1.50(1)
C(5′)−Co′	2.17(1)	Co′−C(7′)	1.85(1)
Co′−C(8′)	1.89(1)	C(7′)−O(7′)	1.17(1)
C(8′)−O(8′)	1.18(1)		

furization of thiophene in other complexes that lead to metallacyclopentadiene products.

The formation of **2** from **1** and $Co_4(CO)_{12}$ represents an example of reactions of **1** and **1′** with transition-metal complexes to give products in which the sulfur is coordinated to another metal. Thus, **1** and **1′** react with $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$ to give Cp*Ir(η^4-2,5-Me_2T·Fe-$(CO)_4$)[17] and with $Cp(CO)_2M{\equiv}M(CO)_2Cp$ (M = Mo, W) to form (η^4,*S*-μ_3-2,5-Me_2T)(IrCp*)[M$(CO)_2$Cp]$_2$, in which sulfur of the η^4-2,5-Me_2T ligand bridges the two M atoms.[5,20] All of these reactions demonstrate that **1** is easily converted to a ligand having the structure of **1′**, which is an excellent sulfur donor ligand to a variety of metal centers. Related examples of reactions that lead to complexes with S-donor η^4-tetramethylthiophene ligands are those of Cp*Rh(η^4-Me_4T) and (η^5-Me_4T)Ru(η^4-Me_4T) with $Fe(CO)_5$ and Me_3NO to give the S-coordinated adducts Cp*Rh(η^4-Me_4T·Fe$(CO)_4$)[18] and (η^5-Me_4T)-Ru(η^4-Me_4T·Fe$(CO)_4$).[21]

The molecular structure of Cp*Ir(η^4-2,5-Me_2T·Co_4-$(CO)_{11}$) (**2**), established by an X-ray diffraction study, is shown in Figure 1. The Cp*Ir(SC_6H_8) fragment displays a high degree of torsional motion arising from libration about the Co(1)−S bond. Atoms displaced farthest from this vector have the highest librational effects. These are C(1), C(3), C(4), C(6), C(17), C(18), and C(19). These all have positive definite thermal ellipsoids as presented. An attempt was made to model the 2,5-dimethylthiophene fragment as two partially occupied parts which were idealized with proper restraints and constraints. This model did not improve the residuals but instead caused several partial atoms to become nonpositive definite. The $Co_4(CO)_{11}$ fragment, on the other hand, displays no thermal problems. The structure of the Cp*Ir(η^4-2,5-Me_2T) portion of the molecule (Tables 2 and 3) is very similar to that of **1′** itself,[3] except that the Ir−S distance (2.869(2) Å) in **2** is shorter than it is in **1′** (2.969(4) Å), and the dihedral angle between the C(2)−C(3)−C(4)−C(5) and C(2)−S−C(5) planes is smaller in **2** (35.2°) than in **1** (42°). This shortening of the Ir−S distance in **2** suggests that coordination of the sulfur reduces the antibonding interaction between Ir and S that occurs in **1′**.[22] The C(2)−S and C(5)−S distances (1.773(10), 1.783(8) Å) are

---

(19) Ogilvy, A. E.; Draganjac, M.; Rauchfuss, T. B; Wilson, S. R. *Organometallics* **1988**, *7*, 1171.

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

(21) Luo, S.; Rauchfuss, T. B.; Wilson, S. R. *Organometallics* **1992**, *11*, 3497.

(22) Harris, S. *Organometallics* **1994**, *13*, 2628.

Table 5. Selected Bond Angles (deg) for [Cp*Ir(C(Me)═CHCH═C(Me))(μ-CO)$_2$Co]$_2$ (3)

C(2)−Ir−C(5)	77.6(4)	C(2)−Ir−Co	54.6(3)
C(5)−Ir−Co	55.0(3)	C(2)−Ir−C(7)	92.5(4)
C(5)−Ir−C(7)	81.4(4)	Co−Ir−C(7)	44.6(3)
Ir−C(2)−C(1)	122.8(7)	Ir−C(2)−C(3)	116.3(7)
C(1)−C(2)−C(3)	120.8(9)	C(3)−C(4)−C(5)	114.7(9)
C(2)−C(3)−C(4)	115.0(9)	Ir−C(5)−C(6)	123.1(7)
Ir−C(5)−C(4)	116.3(8)	C(2)−Co−C(5)	73.5(4)
C(4)−C(5)−C(6)	120.5(9)	C(2)−Co−C(7)	99.9(4)
Ir−Co−C(7)	56.4(4)	Ir−Co−C(8)	120.0(3)
C(5)−Co−C(7)	87.0(5)	Ir−Co−Co′	169.7(1)
C(7)−Co−C(8)	94.7(5)	C(8)−Co−Co′	49.7(3)
C(7)−Co−Co′	120.2(4)	C(7)−Co−C(8′)	97.2(4)
Ir−Co−C(8′)	137.2(3)	Co′−Co−C(8′)	50.4(3)
C(8)−Co−C(8′)	92.6(5)	Ir−C(7)−O(7)	133.5(9)
Ir−C(7)−Co	79.0(4)	Co−C(8)−O(8)	139.6(9)
Co−C(7)−O(7)	147.5(10)	O(8)−C(8)−Co′	140.4(9)
Co−C(8)−Co′	79.9(4)	C(2′)−Ir′−Co′	55.2(3)
C(2′)−Ir′−C(5′)	78.0(4)	C(2′)−Ir′−C(7′)	94.8(4)
C(5′)−Ir′−Co′	55.6(3)	Co′−Ir′−C(7′)	46.2(3)
C(5′)−Ir′−C(7′)	82.8(4)	Ir′−C(2′)−C(3′)	116.2(7)
Ir′−C(2′)−C(1′)	122.8(7)	Ir′−C(2′)−Co′	73.5(3)
C(1′)−C(2′)−C(3′)	120.9(10)	C(3′)−C(4′)−C(5′)	113.8(9)
C(2′)−C(3′)−C(4′)	115.5(10)	Ir′−C(5′)−C(6′)	123.4(7)
Ir′−C(5′)−C(4′)	116.5(7)	Co−Co′−Ir′	169.4(1)
C(4′)−C(5′)−C(6′)	120.0(8)	Co−Co′−C(5′)	139.5(2)
Co−Co′−C(8)	50.4(3)	Co−Co′−C(7′)	119.3(4)
C(8)−Co′−Ir′	134.8(4)	Ir′−Co′−C(7′)	54.5(3)
C(8)−Co′−C(2′)	162.7(4)	C(8)−Co′−C(8′)	92.7(4)
C(2′)−Co′−C(5′)	73.1(4)	C(7′)−Co′−C(8′)	94.7(5)
C(8)−Co′−C(7′)	95.9(5)	Ir′−C(7′)−O(7′)	136.6(9)
Co−Co′−C(8′)	49.7(3)	Co−C(8′)−Co′	79.9(4)
Ir′−Co′−C(8′)	120.1(3)	Co′−C(8′)−O(8′)	139.5(8)
Ir′−C(7′)−Co′	79.3(4)	Co−C(8′)−O(8′)	140.6(9)
Co′−C(7′)−O(7′)	143.9(9)		

Table 6. Selected Bond Distances (Å) for Cp*Ir(C(Me)═CHCH═C(Me))(CO) (4)

Ir−C(60)	1.823(6)	C(5)−C(6)	1.472(8)
Ir−C(2)	2.080(5)	C(11)−C(12)	1.416(8)
Ir−C(5)	2.081(6)	C(11)−C(15)	1.442(8)
Ir−C(15)	2.242(5)	C(11)−C(21)	1.508(8)
Ir−C(11)	2.260(5)	C(12)−C(13)	1.421(8)
Ir−C(14)	2.270(5)	C(12)−C(22)	1.501(8)
Ir−C(12)	2.269(5)	C(13)−C(14)	1.425(8)
Ir−C(13)	2.270(5)	C(13)−C(23)	1.494(8)
C(1)−C(2)	1.505(9)	C(14)−C(15)	1.408(9)
C(2)−C(3)	1.326(8)	C(14)−C(24)	1.516(8)
C(3)−C(4)	1.445(9)	C(15)−C(25)	1.493(8)
C(4)−C(5)	1.345(9)	C(60)−O(60)	1.165(7)

Table 7. Selected Bond Angles (deg) for Cp*Ir(C(Me)═CHCH═C(Me))(CO) (4)

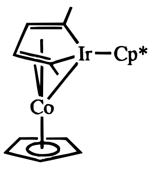
C(60)−Ir−C(2)	87.8(2)	C(5)−C(4)−C(3)	116.6(5)
C(60)−Ir−C(5)	87.3(3)	C(4)−C(5)−C(6)	123.9(6)
C(2)−Ir−C(5)	78.5(2)	C(4)−C(5)−Ir	113.6(4)
C(3)−C(2)−C(1)	123.5(5)	C(6)−C(5)−Ir	122.4(4)
C(3)−C(2)−Ir	114.6(5)	C(25)−C(15)−Ir	126.5(4)
C(1)−C(2)−Ir	121.8(4)	O(60)−C(60)−Ir	177.5(5)
C(2)−C(3)−C(4)	116.2(5)		

approximately the same as those in **1′** (1.76(2), 1.79(2) Å), although the standard deviations in **1′** are quite large. In the Fe(CO)$_4$ adduct of **1′**, Cp*Ir(η^4-2,5-Me$_2$T·Fe(CO)$_4$),[17] the dihedral angle between the C(2)−C(3)−C(4)−C(5) and C(2)−S−C(5) planes is 37.9°, and the C−S distances are 1.811(6) and 1.808(5) Å. In **2**, the C(2)−C(3), C(3)−C(4), and C(4)−C(5) distances follow a long−short−long pattern (1.45(2), 1.39(2), 1.44(2) Å), while a similar but less pronounced pattern (1.464(8), 1.421(8), 1.452(7) Å) is observed in the Fe(CO)$_4$ adduct. The dihedral angle (6.5°) between the C(2)-through-C(5) and C(10)-through-C(14) planes indicates that the two π-ligands are nearly coplanar.

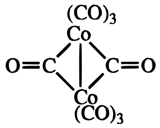
The Co$_4$(CO)$_{11}$ portion of **2** has a structure which is generally the same as that in (Me$_3$P)Co$_4$(CO)$_{11}$.[23] In both, the apical Co has three terminal CO ligands while the three basal Co atoms are bridged by CO groups, and the ligand, Cp*Ir(η^4-2,5-Me$_2$T) in **2** and Me$_3$P in (Me$_3$P)Co$_4$(CO)$_{11}$, is in an "apical" position. As in (Me$_3$P)Co$_4$(CO)$_{11}$, the Co−Co distances (2.544(1), 2.519(2), 2.518(2) Å) to the apical Co(4) are longer than those (2.448(1), 2.455(1), 2.442(1) Å) between the three CO-bridged cobalt atoms. The Co−C distances (average 1.93 Å) to the bridging carbonyl groups are longer than those (average 1.78 Å) to the terminal CO ligands. Also, the Co(1)−C(bridging) distances (average 1.90 Å) are slightly shorter than Co(2)− and Co(3)−C(bridging) bond lengths (average 1.94 Å), presumably due to better π-back-donation from the sulfur-substituted Co(1) to its bridging CO ligands.

The ^{1}H NMR spectrum of **2** exhibits signals for H(3) and H(4) at δ 4.74 and for the methyl groups at C(2) and C(5) at δ 1.33. These values are very similar to those (δ 4.54 and 1.35) for the analogous protons in the η^4-2,5-Me$_2$T ligand in Cp*Ir(η^4-2,5-Me$_2$T·Fe(CO)$_4$).[17]

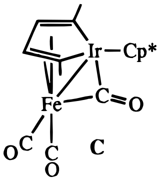
The structure of **3** (Figure 2) may be viewed as resulting from the displacement of three CO ligands from each Co in Co$_2$(CO)$_8$ by the iridacyclopentadiene unit Cp*Ir(C(Me)═CHCH═C(Me))(CO) (**4**); indeed, **4** reacts with Co$_2$(CO)$_8$ to give **3** (see next section). The structure of **3** is conveniently compared with those of the related molecules Cp*Ir(C(Me)═CHCH═C(Me))-CoCp (**A**)[24] and Co$_2$(CO)$_8$ (**B**).[25] In the Cp*Ir(C(Me)═CHCH═C(Me))portion of **3**, the iridacyclopentadiene (IrC$_4$) group is essentially planar (±0.04 Å) and is oriented at an angle of 59.4° with respect to the Cp* plane defined by C(10)-through-C(14). In **A**, the dihedral angle between these planes is 78.8°. Within the IrC$_4$ ring, the Ir−C(2) and Ir−C(5) and the corresponding Ir−C(2′) and Ir−C(5′) distances range from 2.045(9) to 2.052(10) Å, which is slightly longer than that (2.011(7) Å) in **A** but is very similar to the nominal single Ir−C(sp^2) bond distance (2.054(4) Å) in the vinyl complex Cp*(H)(PMe$_3$)Ir−CH═CH$_2$.[26] The C(2)−C(3), C(3)−C(4), and C(4)−C(5) bonds in the IrC$_4$ ring appear to exhibit a short−long−short pattern, as in **A**, but the errors in these distances do not establish this pattern unequivocally. The Ir−Co distances (2.524(2) and 2.518(2) Å) in **3** are shorter than that (2.584(1) Å) in **A**.



A



B



C

The central Co$_2$(μ-CO)$_2$ core of **3** resembles the same unit in Co$_2$(CO)$_8$. In both, this core is folded so that C(8) and C(8′) lie on the same side of the Co−Co′ bond.

---

[23] Bartl, K.; Boese, R.; Schmid, G. *J. Organomet. Chem.* **1981**, *206*, 331.

[24] Chen, J.; Daniels, L. M.; Angelici, R. J. *Organometallics*, in press.

[25] Summer, G. G.; Klug, H. P.; Alexander, L. E. *Acta Crystallogr.* **1964**, *17*, 732.

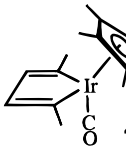
[26] Stoutland, P. O.; Bergman, R. G. *J. Am. Chem. Soc.* **1988**, *110*, 5732.

The Co–C(8)–Co′ (79.9(4)°) and Co–C(8′)–Co′ (79.9(4)°) angles in **3** are slightly smaller than those in $Co_2(CO)_8$ (82 and 84°), while the C(8)–Co–C(8′) (92.6(5)°) and C(8)–Co′–C(8′) (92.7(4)°) angles are somewhat larger than those in $Co_2(CO)_8$ (85.0(5)°). The Co–C(bridging) bond distances in **3** range from 1.87(1) to 1.89(1) Å, which are similar to those (1.91(1) and 1.93(1) Å) in $Co_2(CO)_8$. The Co–Co′ bond is significantly shorter in **3** (2.413(2) Å) than in $Co_2(CO)_8$ (2.524(2) Å). It is interesting that the Co–C(bridging) distances are shorter to the CO groups that bridge the Co–Ir (1.81(1)) and Co′–Ir (1.85(1) Å) bonds than to those that bridge the Co–Co′ bond (1.89(1), 1.87(1) Å).

The ^1H NMR chemical shift of the H(3) and H(4) protons in **3** is δ 5.56 s, while the methyl protons are observed at δ 2.24 s. The corresponding protons in **A** (δ 4.71, 2.07)[24] and **C** (δ 5.77, 2.22)[17] have chemical shifts in the same range.

Reactions of Cp*Ir(*C,S*-2,5-Me$_2$T) (1) with $Co_2(CO)_8$. Like the reaction of **1** with $Co_4(CO)_{12}$ (eq 4), **1** combines with $Co_2(CO)_8$ to give **2** and **3** (eq 6). In refluxing hexanes for 1 h, the isolated yields of **2** (16%) and **3** (31%) are the same as those obtained from reaction 4 under the same conditions. When the reaction is run for 24 h in refluxing hexanes, only **3** (56%) is obtained; undoubtedly, the absence of product **2** reflects its conversion into **3**, as demonstrated in reaction 5. When reaction 6 is conducted in refluxing hexanes for an intermediate reaction time (10 h), **3** is the major product (42%); **2** is not obtained, presumably because of its conversion to **3** (eq 5). However, the new orange-yellow product Cp*Ir(C(Me)=CHCH=C(Me))(CO)(**4**) is also isolated in 20% yield. The absence of product **4** in the reactions conducted at shorter (1 h) and longer (24 h) reaction times is somewhat puzzling. The formation of **4** may occur by the reaction of **3** with CO that is liberated during the formation of **2** and **3**. That this is possible was demonstrated by the reaction (eq 7) of **3** with CO (1 atm) at room temperature over a period of 20 h in THF solvent, which gives **4** (25% yield) and $Co_2(CO)_8$ (identified by its mp and IR spectrum); some unreacted **3** was also recovered. The formation of **4** in reaction 6 is presumably observed at intermediate times (10 h) because there is sufficient CO in solution for reaction 7; at shorter times (1 h), however, insufficient CO is liberated. The absence of **4** as a product at long times (24 h) probably results from its conversion to **3** upon prolonged reflux. That this could occur was shown by the reaction (eq 8, which is the reverse of eq 7) of **4** with $Co_2(CO)_8$ in refluxing hexanes for 12 h, which gives **3** in 58% isolated yield. The above studies of reaction 6 suggest that the products are formed by the sequence of reactions summarized in eq 9. The first step in eq 9 probably proceeds by initial formation of $Co_4(CO)_{12}$ from $Co_2(CO)_8$, since this reaction is known[27] to occur readily under conditions (61 °C, toluene solvent) similar to those of reaction 6. Thus, the formation of **2** probably occurs, in much the same way as it forms in the reaction (eq 4) of **1** with $Co_4(CO)_{12}$; this is supported by the fact that the yields of **2** and **3** from reactions 4 and 6 are essentially the same. With time, **2** converts to the final product **3**, as described by eq 5. The side product **4** is formed (third step in eq 9) by reaction of **3** with CO present in solution (eq 7).

$$\mathbf{1} + 2\,Co_2(CO)_8 \longrightarrow \mathbf{2} + \mathbf{3} + \quad (6)$$



4

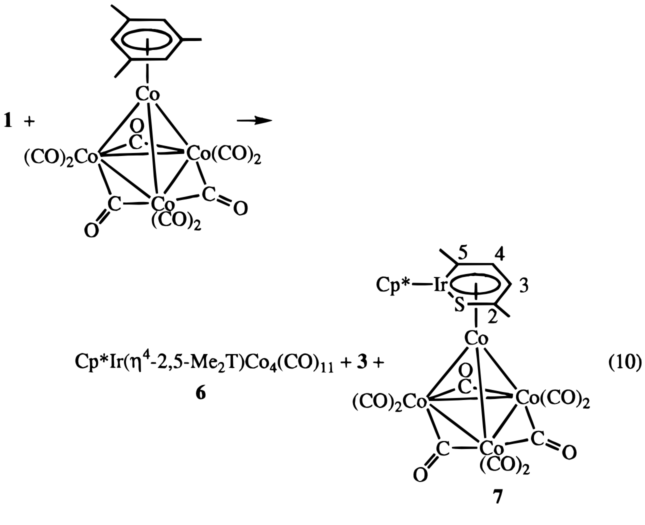
$$\mathbf{3} + 6CO \rightarrow 2\,\mathbf{4} + Co_2(CO)_8 \qquad (7)$$

$$2\,\mathbf{4} + Co_2(CO)_8 \rightarrow \mathbf{3} + 6CO \qquad (8)$$

$$\mathbf{1} + Co_2(CO)_8 \xrightarrow{-CO} \mathbf{2} \xrightarrow[-CO]{-Co_xS_y} \mathbf{3} \underset{-CO}{\overset{CO}{\rightleftharpoons}} \mathbf{4} + Co_2(CO)_8 \qquad (9)$$

As was noted in the discussion of its structure (Figure 2), **3** may be viewed as consisting of the Cp*Ir(C(Me)=CHCH=C(Me))(CO) (**4**) and $Co_2(\mu\text{-}CO)_2$ fragments. Indeed, **3** can be prepared by reacting **4** with $Co_2(CO)_8$ (eq 8); formally, **4** acts as a six-electron-donor ligand by displacing three CO groups from each Co to give **3**. The molecular structure of **4** contains an iridacyclopentadiene unit in which the Ir is 0.16 Å out of the plane defined by C(2)-through-C(5); the deviation from planarity of the IrC_4 ring in **4** contrasts with the planarity of the IrC_4 rings in **3** and **A**. Within the IrC_4 ring of **4**, the C(2)–C(3), C(3)–C(4), and C(4)–C(5) distances clearly exhibit a short–long–short pattern (1.326(8), 1.445(9), 1.345(9) Å), which is the same but less well-defined pattern that is observed in **3** and **A**. The Ir–C bonds to C(2) (2.080(5) Å) and C(5) (2.081(6) Å) are somewhat longer than the analogous iridacyclopentadiene bonds in **3** (2.05 Å) and **A** (2.01 Å). They are even longer than the nominal Ir–C(sp^2) single-bond distance (2.054(4) Å) in the vinyl complex Cp*(H)(PMe$_3$)Ir–CH=CH$_2$.[26] The geometry around the Ir atom may be described as approximately octahedral, with the Cp* ligand occupying one face and the other three Ir–C bonds being compressed from 90 to 87.8(2)° for C(60)–Ir–C(2), 87.3(3)° for C(60)–Ir–C(5), and 78.5(2)° for C(2)–Ir–C(5).

Reactions of Cp*Ir(*C,S*-2,5-Me$_2$T) (1) with (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$. Since we had previously demonstrated (eqs 2 and 3) that arene rings in (η^6-toluene)Mo(CO)$_3$ and [(η^6-ClC$_6$H$_5$)FeCp]$^+$ are displaced by **1** to give η^6-iridathiabenzene complexes, **1** was reacted with (η^6-$C_6H_3Me_3$)$Co_4(CO)_9$. When this reaction (eq 10) was



---

(27) Ungváry, F.; Marko, L. *Inorg. Chim. Acta* **1970**, *4*, 324.

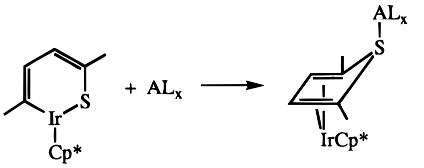
run at room temperature for 22 h, products **6** and **7** were isolated in 21% and 5% yields, respectively; compound **3** was not among the products under these mild conditions. We were not able to obtain crystals of either of these new products that were suitable for X-ray diffraction studies. The structure of **7** shown in eq 10 is based on its ^{1}H NMR and IR spectra. The ^{1}H NMR spectrum exhibits inequivalent H(3)−H(4) protons at δ 5.78 and 5.44, while the inequivalent methyl groups on C(2) and C(5) occur at δ 2.29 and 1.97. These chemical shifts are similar to those in [η^6-Cp*Ir(*C*,*S*-2,5-Me$_2$T)]Cr(CO)$_3$, which occur at δ 5.86, 5.46 for H(3), H(4) and at δ 2.72, 2.52 for the methyl groups at C(2), C(5).[9] In the IR spectrum of **7**, there are ν(CO) bands at 2039 w, 2011 vs, br, 1985 w, and 1794 m cm^{-1}. The number and relative intensities of the bands are very similar to those in (η^6-C$_6$Me$_6$)Co$_4$(CO)$_9$ (2070 m, 2025 s, 2010 m, 1997 w, and 1817 m cm^{-1}), as well as in a variety of (η^6-arene)Co$_4$(CO)$_9$ analogs.[11] The major difference is that the ν(CO) bands for **7** occur at wavenumbers somewhat lower than those for the η^6-arene derivatives. This is expected, since the ν(CO) values for [η^6-Cp*Ir-(*C*,*S*-2,5-Me$_2$T)]M(CO)$_3$ (M = Cr, Mo, W) are lower than those for (η^6-arene)M(CO)$_3$, which indicates the relatively strong donor nature of the iridathiabenzene ring **1** as compared with that of arenes. The low-wavenumber band at 1794 m in **7** indicates the presence of bridging CO groups. Thus, the IR and ^{1}H NMR spectra of **7** suggest that it has a structure (eq 10) analogous to that of the (η^6-arene)Co$_4$(CO)$_9$ clusters.

The other product **6** of reaction 10 at room temperature appears to be an isomer of **2** in which the Cp*Ir-(η^4-2,5-Me$_2$T) ligand is sulfur-coordinated at another site in the Co$_4$(CO)$_{11}$ cluster, perhaps at an equatorial position on a basal cobalt or at the apical cobalt. The ^{1}H NMR resonances of the η^4-2,5-Me$_2$T ligand in **6** occur at δ 4.64 for H(3), H(4) and at δ 1.33 for the methyl groups at C(2), C(5). These are very similar to those in **2** (δ 4.74 for H(3), H(4) and δ 1.33 for the CH$_3$ groups). The IR spectrum of **6** exhibits a ν(CO) band at 1828 w cm^{-1} that indicates the presence of bridging CO groups. In general the IR spectra of **6** and **2** are similar yet are distinctly different. The mass spectrum of **6**, like that of **2**, does not show a parent ion; however, +1 ions for the Cp*Ir(2,5-Me$_2$T) and Co$_4$(CO)$_{11}$ fragments are observed. Overall, the spectroscopic evidence suggests that **6** is an isomer of **2** with the sulfur of the Cp*Ir-(η^4-2,5-Me$_2$T) ligand coordinated at a different site in the Co$_4$(CO)$_{11}$ cluster than it is in **2**.

Yields of the desired η^6-iridathiabenzene product **7** in reaction 10 are low (5%) when the reaction is run at room temperature. If the reaction is run at 35−40 °C in hexanes, the isolated yield is in the range 5−8% during the first 2−6 h and increases to 20% after 12 h. If the reaction is allowed to continue for 24 h, the yield of **7** decreases to 10%; after 48 h, no **7** is obtained. Thus, the maximum yield of **7** is obtained after 12 h; at longer times, **7** is converted to other products. While the yield of **7** goes through a maximum with time, the isolated yield of **6** during the same time period (at 35−40 °C in hexanes) increases from 20% (2−6 h) to 35% (48 h). After 48 h, a small amount (10%) of **2** (Figure 1), the isomer of **6**, is also isolated. At higher temperature (60−70 °C) in hexanes for 12 h, **6** is the major product (31%) together with a smaller amount (16%) of Cp*Ir(*C*,*S*-2,5-Me$_2$T)(CO) (**5**); this latter product is known[7,12] to form in the reaction of **1** with CO. The source of the CO required to generate the major product Cp*Ir(η^4-2,5-Me$_2$T)Co$_4$(CO)$_{11}$ (**6**) and **5** must come from the decomposition of (η^6-C$_6$H$_3$Me$_3$)Co$_4$(CO)$_9$. When reaction 10 is carried out in refluxing hexanes for 10 h, not only is **6** (31%) formed but also **3** (31%), which was not observed under milder conditions. Possibly **3** forms from **6**; this conversion would be analogous to the formation (eq 5) of **3** from **2** in refluxing hexanes for 10 h. Thus, as for the reactions of **1** with Co$_4$(CO)$_{12}$ (eq 4) and Co$_2$(CO)$_8$ (eq 6), the major product formed when (η^6-C$_6$H$_3$Me$_6$)-Co$_4$(CO)$_9$ reacts (eq 10) with **1** under the most vigorous conditions (refluxing hexanes for 10−24 h) is **3**.

Conclusions

The goal of synthesizing the η^6-iridathiabenzene cluster complex [η^6-Cp*Ir(*C*,*S*-2,5-Me$_2$T)]Co$_4$(CO)$_9$ (**7**) is achieved (eq 10) by replacing the η^6-mesitylene ligand in (η^6-C$_6$H$_3$Me$_3$)Co$_4$(CO)$_9$ with Cp*Ir(*C*,*S*-2,5-Me$_2$T) (**1**) under mild conditions (35−40 °C, 12 h). At longer reaction times and/or higher temperatures, the yield of **7** is low or negligible. Under these more strenuous conditions, the major product is Cp*Ir(η^4-2,5-Me$_2$T)Co$_4$-(CO)$_{11}$ (**6**), in which the Cp*Ir(η^4-2,5-Me$_2$T) ligand is coordinated through the sulfur to a Co of the cluster. Another isomer of the same composition Cp*Ir(η^4-2,5-Me$_2$T·Co$_4$(CO)$_{11}$) (**2**; Figure 1) is formed when **1** reacts with Co$_4$(CO)$_{12}$ (eq 4) or Co$_2$(CO)$_8$ (eq 6). These reactions are similar to those (eq 11) of **1** with Lewis acids and metal complexes, where AL$_x$ = BH$_3$,[4,6] Fe(CO)$_4$,[17] Fe$_2$(CO)$_7$,[17] [M(CO)$_2$Cp]$_2$ (M = Mo, W),[5] which give η^4-2,5-Me$_2$T complexes coordinated through the diene to Ir and to the Lewis acid through sulfur. Under more forcing conditions (refluxing hexanes for 10−24 h) **2**, and probably **6**, are converted to the desulfurized tetranuclear cluster [Cp*$\overline{\text{Ir(C(Me)=CHCH=C}}$(Me))($\mu$-CO)$_2$Co]$_2$ (**3**), which contains bridging iridacyclopentadiene ligands (Figure 2). The sulfur-containing product of this reaction is presumably a cobalt sulfide. Other cobalt complexes, Cp*Co(C$_2$H$_4$)$_2$[24,28,29] and Cp$_2$Co,[24] also are known to promote C−S cleavage and/or desulfurization of thiophene and its complexes. It is of interest to note that cobalt is also an excellent promoter of the catalytic hydrodesulfurization of thiophenes and benzothiophenes.[30]



(11)

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-7405-Eng-82 to Iowa State University. The loan of IrCl$_3$ by Johnson Matthey, Inc., is greatly appreciated.

Supporting Information Available: Tables of atomic coordinates, bond angles, least-squares planes for **2**−**4** (38 pages). Ordering information is given on any current masthead page.

OM950702A

---

[28] Jones, W. D.; Chin, R. M. *Organometallics* **1992**, *11*, 2698.
[29] Jones, W. D.; Chin, R. M. *J. Organomet. Chem.* **1994**, *472*, 311.
[30] Chianelli, R. R.; Daage, M.; Ledoux, M. J. *Adv. Catal.* **1994**, *40*, 177.