Organometallics **1999,** *18,* 5721−5724

Reactions of $Co_4(CO)_{12}$ and $Cr(CO)_6$ with Dibenzothiophene and Benzothiophene[†]

Jiabi Chen[‡] and Robert J. Angelici*

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

Received August 23, 1999

*Summary: Reaction of $Co_4(CO)_{12}$ with dibenzothiophene (DBT) gives (η^6-DBT)$Co_4(CO)_9$ (**1**), in which one arene ring of DBT is η^6-coordinated to a Co. This cluster **1** reacts with $Cr(CO)_6$ to give (η^6-DBT)$Cr(CO)_3$ and $[(CO)_3Cr]_2$(μ-DBT) but reacts with $Cr(CO)_3(NCMe)_3$ to give the desulfurized (η^6-benzene)$Co_4(CO)_9$ (**4**). Benzothiophene yields the same desulfurized product **4** upon reaction with $Co_4(CO)_{12}$.*

Introduction

Despite the importance of cobalt to the activity of commercial Co−Mo/Al_2O_3 catalysts for the hydrodesulfurization (HDS) of petroleum feedstocks,[1] very few studies of reactions of thiophenes with cobalt complexes have been reported.[2] The earliest[3] describes the reaction of thiophene with $Co_2(CO)_8$ and $Fe(CO)_5$ at 200 °C in an atmosphere of CO and H_2. Desulfurization of the thiophene occurs to give a triangular cluster, $Co_2Fe(CO)_9(\mu_3\text{-}S)$, capped by sulfur; the organic product was not identified. More recently, Jones and Chin[4,5] reported reactions of (η^5-C_5Me_5)Co($H_2C{=}CH_2$)$_2$ with thiophene, benzothiophene, and dibenzothiophene to give dinuclear complexes in which the two (η^5-C_5Me_5)Co units are bridged by a thiophene ligand in which one C−S bond is cleaved. In the present Note, we report reactions of dibenzothiophene (DBT) and benzothiophene (BT) with $Co_4(CO)_{12}$, as well as reactions of chromium carbonyl complexes with DBT.

Experimental Section

General Procedures. All reactions were performed under an argon atmosphere following standard Schlenk techniques. Solvents were reagent grade and dried by refluxing over appropriate drying agents and stored over 4 Å molecular sieves under an argon atmosphere prior to 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 vacuum at room temperature for 16 h, deactivated with 5% (w/w) N_2-saturated water, and stored under argon; neutral SiO_2 (Scientific Adsorbents Incorporated, 40 μm flash) was deoxygenated under vacuum at room temperature for 12 h. Chromatography columns were 1.5 × (5−10) cm. Dibenzothiophene (DBT) and benzo[*b*]thiophene (BT) were purchased from Aldrich Chemical Co. $Co_2(CO)_8$ and $Co_4(CO)_{12}$ were purchased from Strem Chemical Co. $Cr(CO)_6$ was purchased from Pressure Chemical Company. The complexes $Cr(CO)_3(CH_3CN)_3$[6,7] and (DBT)$Cr(CO)_3$[8] were prepared by literature methods. All elemental analyses were performed by Iowa State University or the Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, PRC. The IR spectra were measured on a Nicolet Magna-IR 560 spectrophotometer using a solution cell with NaCl plates. All ^{1}H NMR spectra were recorded at ambient temperature in $CDCl_3$ solution with $CHCl_3$ as the internal reference using a Varian VXR 300 MHz spectrometer. The ^{13}C NMR spectra were recorded at ambient temperature in acetone-d_6 or $CDCl_3$ solution using a Bruker AC 200 spectrometer. Electron ionization mass spectra (EIMS) were run on a Finnigan 4000 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 Dibenzothiophene with $Co_4(CO)_{12}$ To Give (η^6-DBT)$Co_4(CO)_9$ (1). A mixture of dibenzothiophene (DBT) (1.50 g, 8.14 mmol) and $Co_4(CO)_{12}$ (0.50 g, 0.87 mmol) in 80 mL of hexanes was refluxed with stirring for 48 h, during which time the dark purple solution turned dark brown. After cooling, the mixture was directly chromatographed on SiO_2 with hexanes as the eluent. After the brown band containing unreacted $Co_4(CO)_{12}$ and dibenzothiophene was eluted from the column, a dark green band was eluted with hexanes/CH_2Cl_2/Et_2O (10:3:1) and collected. The solvent was removed in vacuo, and the residue was recrystallized from hexanes/CH_2Cl_2 at −80 °C to give 0.26 g (44%, based on $Co_4(CO)_{12}$) of dark green crystals of **1**; mp 185−186 °C (dec). IR (CH_2Cl_2): ν(CO) 2073 (s), 2030 (vs), 2013 (w), 1821 (s, br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.31 (d, 1H), 7.93 (d, 1H), 7.68 (t, 2H), 7.20 (d, 1H), 7.04 (d, 1H), 6.32 (t, 1H), 6.18 (t, 1H). MS(FAB): *m*/*e* 672 (M^+), 671 ($M^+ - 1$), 644 ($M^+ -$ CO), 616 ($M^+ -$ 2CO), 184 (DBT). Anal. Calcd for $C_{21}H_8O_9SCo_4$: C, 37.53; H, 1.20. Found: C, 37.77; H, 1.14.

Reaction of Dibenzothiophene with $Co_2(CO)_8$ To Give 1. A mixture of DBT (0.81 g, 4.40 mmol) and $Co_2(CO)_8$ (0.50 g, 1.46 mmol) in 80 mL of hexanes was refluxed with stirring for 50 h, during which time the dark orange solution turned dark blue. Further treatment of the resulting mixture as described above for the reaction of DBT with $Co_4(CO)_{12}$ gave 0.12 g (24%, based on $Co_2(CO)_8$) of dark green crystals of **1**, which was identified by its mp and IR and ^{1}H NMR spectra.

Reaction of 1 with $Cr(CO)_6$ To Give (DBT)$Cr(CO)_3$ (2) and $[(CO)_3Cr]_2$(μ-DBT) (3). A mixture of **1** (0.080 g, 0.12 mmol) and 0.038 g (0.17 mmol) of $Cr(CO)_6$ in 40 mL of *n*-butyl ether was refluxed for 10 h, during which time the dark

---

[†] Dedicated to Professor Fausto Calderazzo on the occasion of his 70th birthday.

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

(1) Topsøe, H.; Clausen, B. S.; Massoth, F. E. Hydrotreating Catalysis. In *Catalysis: Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer-Verlag: Berlin, Heidelberg, 1996; Vol. 11.

(2) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259.

(3) Khattab, S. A.; Markó, L.; Bor, G.; Markó, B. *J. Organomet. Chem* **1964**, *1*, 373.

(4) Jones, W. D.; Chin, R. M. *Organometallics* **1992**, *11*, 2698.

(5) Jones, W. D.; Chin, R. M. *J. Organomet. Chem.* **1994** *472*, 311.

(6) Tate, D. P.; Knipple, W. R.; Augl, J. M. *Inorg. Chem.* **1962**, *1*, 433.

(7) King, R. B.; Fronzaglia, A. *Inorg. Chem.* **1966**, *5*, 1837.

(8) Fischer, E. O.; Goodwin, H. A.; Kreiter, C. G.; Simmons, H. D.; Sonogashira, K., Jr.; Wild, S. B. *J. Organomet. Chem.* **1968**, *14*, 359.

10.1021/om990675e CCC: $18.00
Publication on Web 11/17/1999

solution turned light yellow with the formation of a black precipitate on the flask wall. After removal of the solvent under vacuum, the residue was chromatographed on SiO_2 with hexanes/CH_2Cl_2 (5:1) as the eluent. A yellow band was eluted and collected. Then, an orange band was eluted with hexanes/CH_2Cl_2/Et_2O (10:3:2). 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, 0.021 g (55%, based on **1**) of orange-yellow crystals of **2** was obtained; mp164−166 °C (dec) (lit. 165−166 °C).[8] IR (CH_2Cl_2): ν(CO) 1966 (vs), 1892 (vs, br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 7.97 (m, 1H), 7.76 (m, 1H), 7.53 (m, 2H), 6.40 (d, 1H), 6.16 (d, 1H), 5.56 (t, 1H), 5.31 (t, 1H). MS(EI): *m/e* 320 (M^+). From the second fraction was obtained 0.015 g (28% based on **1**) of orange crystalline **3**; mp 195−198 °C (dec). IR (CH_2Cl_2): ν(CO) 1965 (vs), 1904 (vs, br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.17 (d, 2H), 5.96 (d, 2H), 5.56 (t, 2H), 5.29 (t, 2H). ^{13}C NMR (acetone-d_6): δ 232-(CO), 94 (DBT), 91 (DBT), 88 (DBT). MS(EI): *m/e* 456 (M^+), 400 ($M^+ - 2CO$), 372 ($M^+ - 3CO$), 344 ($M^+ - 4CO$), 316 ($M^+ - 5CO$), 288 ($M^+ - 6CO$), 236 ($M^+ - 6CO - Cr$), 184 (DBT). Anal. Calcd for $C_{18}O_6SCr_2$: C, 47.38; H, 1.77. Found: C, 47.47; H, 1.71.

Reaction of (DBT)Cr(CO)$_3$ (2) with Cr(CO)$_6$ To Give 3. A mixture of **2** (0.110 g, 0.34 mmol) and $Cr(CO)_6$ (0.150 g, 0.68 mmol) in 40 mL of *n*-butyl ether was refluxed for 12 h, during which time the orange-yellow solution turned orange. After evaporation of the solvent, the residue was chromatographed on Al_2O_3 (neutral) with hexanes as the eluent. After elution of the light yellow band containing unreacted $Cr(CO)_6$, an orange band was eluted with hexanes/CH_2Cl_2/Et_2O (2:1:1). The solvent was removed under vacuum, and the crude product was recrystallized from hexanes/CH_2Cl_2 at −80 °C to give 0.11 g (69%, based on **2**) of **3** as orange crystals, which were identified by their mp and IR and ^1H NMR spectra.

Reaction of 1 with Cr(CO)$_3$(CH$_3$CN)$_3$ To Give (η^6-C$_6$H$_6$)-Co$_4$(CO)$_9$ (4). To a solution of **1** (0.060 g, 0.09 mmol) in 40 mL of THF at −50 °C was added 0.036 g (0.14 mmol) of $Cr(CO)_3(CH_3CN)_3$. The dark green-yellow solution was stirred for 18 h while warming from −50 to 10 °C; during this time the solution gradually turned dark orange. After vacuum removal of the solvent, the residue was chromatographed on SiO_2 with hexanes as the eluent. A brown band eluted first; a yellow band was then eluted with hexanes/CH_2Cl_2 (5:1). The third band, which was dark green, eluted with hexanes/CH_2Cl_2/Et_2O (10:3:1). After evaporation of the solvents from the above three fractions, the residues were recrystallized from hexanes/CH_2Cl_2 at −80 °C. From the first fraction, 0.005 g (31%, based on **1**) of white needle crystals of dibenzothiophene (DBT) was obtained; the DBT was identified by its mp and ^1H NMR spectrum compared with that of an authentic sample. From the second fraction, 0.008 g of yellow crystals of unreacted $Cr(CO)_3(CH_3CN)_3$ was obtained; it was identified by its ^1H NMR spectrum compared with that of the starting material $Cr(CO)_3(CH_3CN)_3$. From the third fraction, 0.024 g (47%, based on **1**) of black crystalline **4** was obtained; mp 185 °C (dec). IR (CH_2Cl_2): ν(CO) 2074 (s), 2030 (vs), 2012 (w) 1821 (s, br) cm^{-1}. ^1H NMR ($CDCl_3$): δ 6.19 (s). MS(FAB): *m/e* 566 (M^+), 538 ($M^+ - CO$), 510 ($M^+ - 2CO$), 482 ($M^+ - 3CO$), 454 ($M^+ - 4CO$), 426 ($M^+ - 5CO$). Anal. Calcd for $C_{15}H_6O_9Co_4$: C, 31.83; H, 1.07. Found: C, 32.23; H, 1.37.

Reaction of Benzo[*b*]thiophene (BT) with Co$_4$(CO)$_{12}$ To Give (η^6-benzene)Co$_4$(CO)$_9$ (4). A mixture of benzo[*b*]thiophene (BT) (0.80 g, 5.96 mmol) and $Co_4(CO)_{12}$ (0.50 g, 0.87 mmol) in 80 mL of hexanes was refluxed for 60 h, during which time the dark purple solution turned dark brown. After cooling, the solution was chromatographed directly on SiO_2 with hexanes as the eluent. After eluting a brown band that contained unreacted $Co_4(CO)_{12}$ and BT, a dark green band was eluted with hexanes/CH_2Cl_2/Et_2O (10:3:2) and collected. The solvent was removed under vacuum, and the residue was recrystallized from hexanes at −80 °C to afford 0.20 g (41%, based on $Co_4(CO)_{12}$) of **4**[9,10] as black crystals, mp 184−185 °C (dec).

Table 1. Crystal Data and Experimental Details for (η^6-DBT)Co$_4$(CO)$_9$ (1)

formula	$C_{21}O_9H_8SCo_4$
fw	672.08
space group	*P*21/*c* (No. 14)
a (Å)	11.076(6)
b (Å)	14.453(9)
c (Å)	14.188(6)
β (deg)	91.41(4)
V (Å^3)	2270(2)
Z	4
D_{calcd} (g/cm^3)	1.966
cryst size (mm)	0.20 × 0.20 × 0.30
μ (Mo Kα) (cm^{-1})	30.16
radiation (monochromated in incident beam)	Mo Kα (λ= 0.71069 Å)
diffractometer	Rigaku AFC7R
temp (°C)	20
orientation reflns: no.; range (2θ) (deg)	10; 13.5−16.2
scan method	$\omega-2\theta$
data coll range, 2θ (deg)	5−45
no. of unique data, total	2966
with $I > 3.00\sigma(I)$	1813
no. of params refined	316
correction factors, max, min	0.5319−1.0000
R^a	0.042
$R_w{}^b$	0.049
quality-of-fit indicator[c]	1.65
largest shift/esd. final cycle	0.03
largest peak, e$^-$/Å^3	0.68
minimum peak, e$^-$/Å^3	−0.56

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

X-ray Crystal Structure Determination of (η^6-DBT)-Co$_4$(CO)$_9$ (1). Single crystals of **1** suitable for X-ray diffraction study were obtained by recrystallization from petroleum ether/CH_2Cl_2 solution at −80 °C. A single crystal was mounted on a glass fiber and sealed with epoxy glue. The X-ray diffraction intensity data for 2966 independent reflections, of which 1813 with $I > 3.00\sigma(I)$ were observable, were collected with a Rigaku AFC7R diffractometer at 20 °C using Mo Kα radiation and an $\omega-2\theta$ scan mode within the range 5° ≤ 2θ ≤ 45°.

The structure of **1** was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included but not refined. The final cycle of the full-matrix least-squares refinement was based on the 1813 observed reflections ($I > 3.00\sigma(I)$) and 316 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.042$ and $R_w = 0.049$. All calculations were performed using the TEXSAN crystallographic software package of Molecular Structure Corporation. Crystallographic data and experimental details for data collection and reduction for **1** are given in Table 1. Selected bond lengths and angles are listed in Table 2. The molecular structure of **1** is presented in Figure 1.

Results and Discussion

Synthesis of (η^6-DBT)Co$_4$(CO)$_9$ (1). The reaction of $Co_4(CO)_{12}$ with 9 equiv of DBT in refluxing hexanes gives **1** in 44% yield (eq 1). The same product is isolated in somewhat lower yield (24%) from the reaction of $Co_2(CO)_8$ with 3 equiv of DBT under the same conditions. Attempts to prepare a complex in which $Co_4(CO)_9$ units were coordinated to both arene rings by refluxing 2

---

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

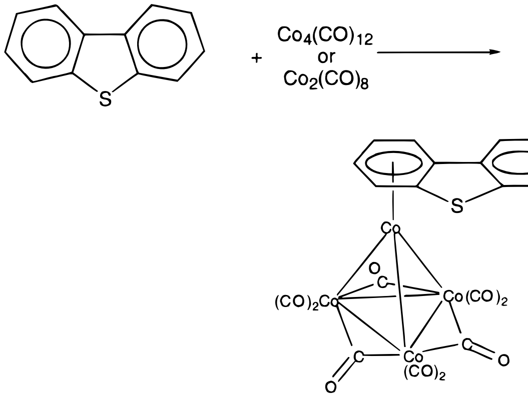
(10) Bird, P. H.; Fraser, A. R. *J. Organomet. Chem.* **1974**, *73*, 103.

Table 2. Selected Bond Lengths (Å)[a] and Angles (deg)[a] for (η^6-DBT)$Co_4(CO)_9$ (1)

Co(1)−Co(2)	2.461(2)	Co(2)−Co(3)	2.468(2)
Co(1)−Co(4)	2.477(2)	Co(1)−Co(3)	2.443(2)
Co(2)−Co(4)	2.481(2)	Co(3)−Co(4)	2.473(2)
Co(4)−C(10)	2.188(10)	C(10)−C(11)	1.39(1)
Co(4)−C(11)	2.15(1)	C(11)−C(12)	1.37(1)
Co(4)−C(12)	2.12(1)	C(12)−C(13)	1.40(1)
Co(4)−C(13)	2.11(1)	C(13)−C(14)	1.41(1)
Co(4)−C(14)	2.147(10)	C(14)−C(15)	1.41(1)
Co(4)−C(15)	2.178(10)	C(16)−C(17)	1.38(1)
S(1)−C(10)	1.77(1)	C(17)−C(18)	1.38(2)
S(1)−C(21)	1.77(1)	C(18)−C(19)	1.36(2)
C(10)−C(15)	1.42(1)	C(19)−C(20)	1.36(2)
C(15)−C(16)	1.47(1)	C(20)−C(21)	1.38(2)
C(16)−C(21)	1.39(1)		
Co(2)−Co(1)−Co(3)	60.43(6)	Co(2)−Co(1)−Co(4)	60.32(6)
Co(2)−Co(4)−Co(3)	59.76(6)	Co(1)−Co(2)−Co(3)	59.42(6)
Co(1)−C(3)−Co(2)	79.1(5)	Co(2)−C(6)−Co(3)	78.6(5)
Co(1)−C(9)−Co(3)	79.7(4)	C(10)−S(1)−C(21)	93.3(6)

[a] Estimated standard deviations in the least significant figure are given in parentheses.

equiv of $Co_4(CO)_{12}$ with DBT gave only **1** in 27% yield. The conditions for the syntheses of **1** are similar to those used previously for the preparations of a variety of (η^6-arene)$Co_4(CO)_9$ complexes.[9,11−13]



(1)

1

The infrared spectrum in the ν(CO) region for (η^6-DBT)$Co_4(CO)_9$ exhibits absorptions at 2073 (s), 2030 (vs), 2013 (w), 1821 (s, br) cm^{-1}, which are very similar to those (2074 (s), 2030 (vs), 2012 (w), 1821 (s, br)) of (η^6-benzene)$Co_4(CO)_9$ (**4**) in CH_2Cl_2 solution. The structure of **1** (Figure 1) determined by X-ray diffraction studies shows that the $Co_4(CO)_9$ unit is very similar to that in $Co_4(CO)_{12}$,[14] except three CO groups on one Co have been replaced by the η^6-bonded DBT. Complex **1** is related to (η^6-arene)$Co_4(CO)_9$ compounds, where the arene is benzene or xylene; their structures have been established by X-ray diffraction studies.[10] The Co−Co distances in the tetrahedral core of **1** are all essentially the same (2.472 ± 0.01 Å) except for Co(1)−Co(3), which has a somewhat shorter distance (2.443(2) Å), perhaps as a result of the asymmetric bonding of the η^6-DBT ligand (discussed below). The average Co−C distance to the bidging CO groups in the basal plane is longer (1.93 Å) than that to the terminal CO groups (1.78 Å). The angle between the Co(1)−Co(2)−Co(3) plane and the plane of the DBT ligand is 9.16°, which suggests that the Co(4)−C distances to the coordinated η^6-DBT ligand may not all be the same. Indeed, the Co(4)−C distances are shortest for C(12) and C(13) (2.11, 2.12 Å), longer for C(11) and C(14) (2.15, 2.15 Å), and longest for C(10) and C(15) (2.19, 2.18 Å). Thus, the bonding appears to be weakest to the carbons that are part of the thiophene ring of the DBT ligand. Such an asymmetric bonding has been observed[15] previously in CpRu(η^6-BT)$^+$, where the average Ru−C bond distance to carbons corresponding to C(12) and C(13) in **1** is 0.07 Å shorter than the distance to the thiophene carbons (C(10) and C(15)). In **1**, this difference is also 0.07 Å. The bond distances within the DBT ligand are the same within experimental error as those in free DBT.[16]

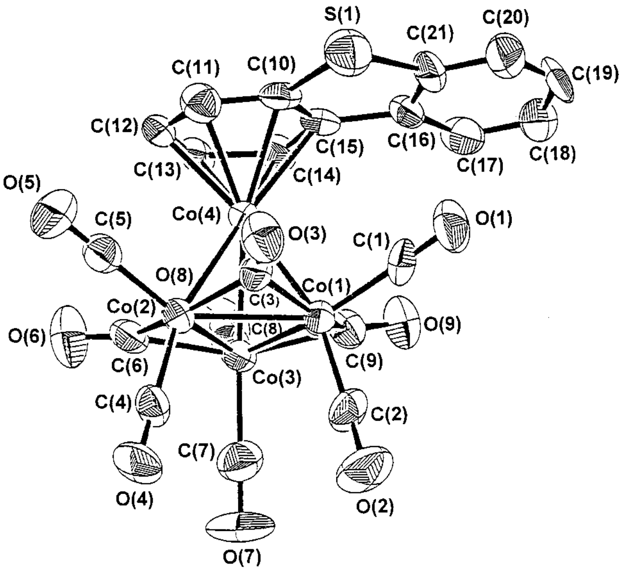
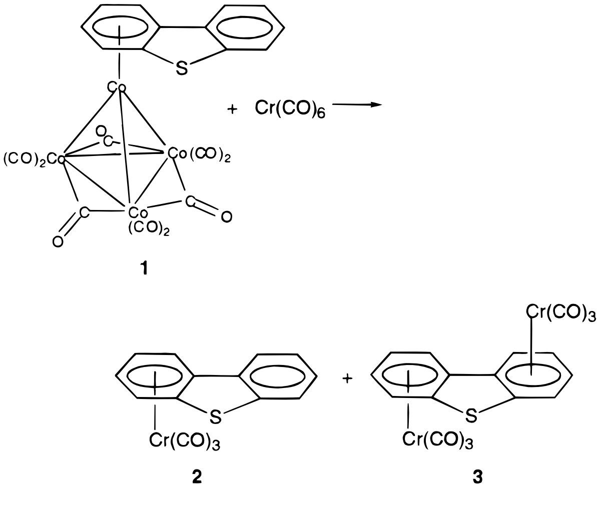


Figure 1. Thermal ellipsoid drawing of (η^6-DBT)$Co_4(CO)_9$ (**1**).

Reactions of DBT with Chromium Carbonyl Complexes. Since DBT reacts with $Cr(CO)_6$ to form (η^6-DBT)$Cr(CO)_3$,[8] we sought to bind $Cr(CO)_3$ to the uncoordinated arene ring of (η^6-DBT)$Co_4(CO)_9$ (**1**) by reacting **1** with $Cr(CO)_6$. However, this reaction in refluxing n-butyl ether gave (eq 2) only the chromium complexes **2** (55%) and **3** (28%). Although crystals of the new



(2)

2 3

---

[11] Bor, G.; Sbrignadello, G.; Marcati, F. *J. Organomet. Chem.* **1972**, *46*, 337.

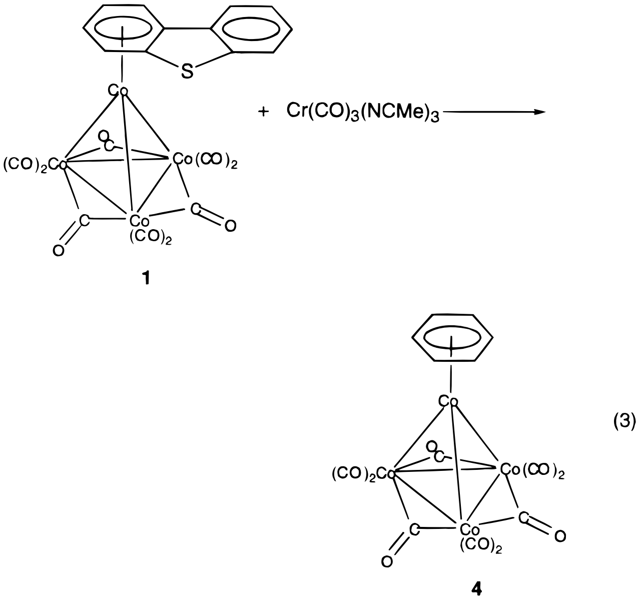
[12] Kaganovich, V. S.; Rybinskaya, M. I. *J. Organomet. Chem.* **1988**, *344*, 383.

[13] Braga, D.; Dyson, P. J.; Grepioni, F.; Johnson, B. F. G. *Chem. Rev.* **1994**, 1585.

[14] Wei, C. H. *Inorg. Chem.* **1969**, *8*, 2384.

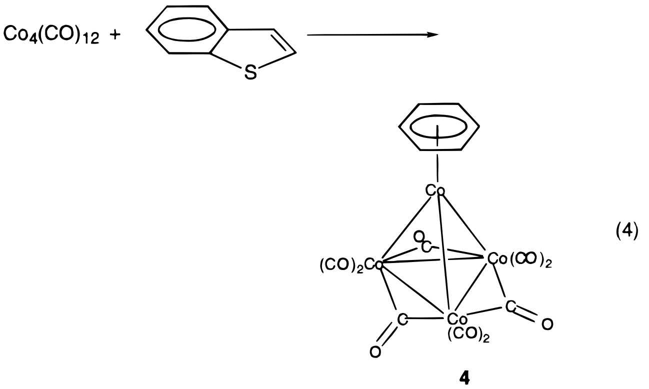
complex **3** suitable for X-ray diffraction analysis could not be obtained, the compound presumably has an anti structure in which the two $Cr(CO)_3$ units are on opposite sides of the DBT ligand. Structural studies of $(CpRu)_2$-(μ-DBT) demonstrated this arrangement.[17] The related $(CpRu)_2(\mu\text{-DBT})^{2+}$ [17] and $(CpFe)_2((\mu\text{-DBT})^{2+}$ [18] presumably have the anti structure also. The complex $[(CO)_3Cr]_2$-(μ-DBT) (**3**) was prepared in higher yield (69%) by reacting (η^6-DBT)$Cr(CO)_3$ with excess $Cr(CO)_6$ in refluxing *n*-butyl ether.

In a further attempt to bind a $Cr(CO)_3$ unit to the uncoordinated arene ring of DBT in **1**, this complex was reacted (eq 3) with $Cr(CO)_3(NCMe)_3$. Because of the highly reactive nature of $Cr(CO)_3(NCMe)_3$, the reactants were combined at −50 °C and allowed to warm to 10 °C over an 18 h period. Neither the target product nor **2** or **3** observed in reaction 2 was obtained. Instead, a 47% yield of (η^6-benzene)$Co_4(CO)_9$ (**4**)[11,13] was isolated along with 31% free DBT. The IR and NMR spectra of **4** were identical to those obtained from an authentic sample of the complex. Also, an X-ray diffraction study[19] of **4** gave the same structure as that previously reported for this compound.[10]



The formation of **4** in reaction 3 strongly suggests that the DBT ligand in **1** has undergone C−C and C−S bond cleavages. Furthermore, two hydrogen atoms have been added in order to form the η^6-benzene ligand. The other organic products of this reaction were not identified. To our knowledge, no other reactions of free or coordinated DBT with metal complexes result in such a dramatic transformation of this molecule.

Reaction of BT with $Co_4(CO)_{12}$. Benzothiophene (BT) reacts with $Co_4(CO)_{12}$ under the same conditions (refluxing hexanes) that were used for the reaction (eq 1) of $Co_4(CO)_{12}$ with DBT. Expecting to obtain (η^6-BT)-$Co_4(CO)_9$, the analogue of (η^6-DBT)$Co_4(CO)_9$ (**1**), we were surprised to find (η^6-benzene)$Co_4(CO)_9$ (**4**) as the only isolated metal complex in 41% yield (eq 4). The other products resulting from the C−C and C−S bond cleavages were not identified. Unlike reaction 3, $Cr(CO)_3$-$(NCMe)_3$ is not required for the fracturing of BT in reaction 4; the $Co_4(CO)_{12}$ is sufficient. These unexpected results indicate that although there are few reports of reactions of cobalt complexes with thiophenes, there is perhaps much to be learned from such reactions with this HDS-active metal.



Acknowledgment. We appreciate the support of this research by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82 with Iowa State University. We also thank Mr. Jie Sun, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, PRC, for the crystal structure determination of compound **1**.

Supporting Information Available: X-ray crystallographic data for **1**, including tables of atomic coordinates, anisotropic displacement parameters, bond lengths and angles, least-squares planes and dihedral angles, and torsion angles.

OM990675E

---

(15) Huckett, S. C.; Miller, L. L.; Jacobson, R. A.; Angelici, R. J. *Organometallics* **1988**, *7*, 686.

(16) Bechtel, F.; Chasseau, D.; Gaultier, J.; Hauw, C. *Cryst. Struct. Commun.* **1977**, *6*, 699.

(17) Wang, C.-M.; Angelici, R. J. *Organometallics* **1990**, *9*, 1770.

(18) Lee, C. L.; Steele, B. R.; Sutherland, R. G. *J. Organomet. Chem.* **1980**, *186*, 265.

(19) Guzei, I. A. Unpublished results.