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Preparation and Structure of $[Cr(\eta^6\text{-}C_8H_6S)(CO)_3]$: The First Transition Metal Complex of Benzo[3,4-*c*]thiophene

John P. Selegue* and Karsten A. Swarat†

Department of Chemistry
University of Kentucky
Lexington, Kentucky 40506-0055

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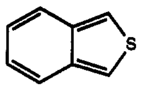
The organometallic chemistry of the thiophenes has been developed extensively during the past few years.[1-3] Much of the study has been motivated by the desire to model essential steps of the metal-catalyzed hydrodesulfurization of fossil fuels. Because much of the "organic sulfur" in fossil fuels is contained in benzo[2,3-*b*]thiophene and dibenzothiophene groupings, the coordination chemistry of these thiophenes has received considerable attention.[1,3] In contrast, the coordination chemistry of the nonclassical thiophenes (for which all singlet, uncharged resonance forms invoke C–S double bonding)[4] and benzo[3,4-*c*]thiophene (**1**, "isothianaphthene")[5-7] is completely undeveloped, due at least in part to the fact that many of these compounds decompose at room temperature.



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Benzo[*c*]thiophene (**1**) is prepared by the dehydration of dihydrobenzo[*c*]thiophene oxide on alumina.[8] It degrades rapidly at room temperature, requiring storage below about −40 °C. Traces of Lewis acids promote its rapid polymerization to "poly(dihydroisothianaphthene)" with a saturated backbone, which can be readily dehydrogenated to "poly(isothianaphthene)" (PITN).[9] Oxidatively doped PITN is an optically transparent, electrochromic polymer of considerable technological interest, having an amazingly small energy gap (~ 1 eV) and an electrical conductivity up to $\sim 50\ \Omega^{-1}\ cm^{-1}$.[10] These properties piqued our interest in the synthesis and behavior of transition metal complexes with benzo[3,4-*c*]thiophene and nonclassical thiophenes as ligands.

The reaction of benzo[3,4-*c*]thiophene with photolytically generated $[Cr(thf)(CO)_5]$ at room temperature leads to $[Cr(C_8H_6S)(CO)_3]$ (**2**) in up to 62% yield (eq 1).[11] Infrared monitoring shows only $[Cr(thf)(CO)_5]$ in solution until most of the THF has been removed *in vacuo*. At that point, a distinct color change from orange to deep red occurs as the infrared spectrum of **2** appears. Complex **2** is less labile than free benzo[*c*]thiophene. Whereas **1** deteriorates under inert gas in the solid state at room temperature within minutes, **2** is stable for several days under these conditions. NMR spectra indicate that the benzo[*c*]thiophene ligand is rapidly displaced from **2** at room temperature by d_6-acetone but not by d_6-benzene.

$$[Cr(thf)(CO)_5] + \mathbf{1} \rightarrow \underset{\mathbf{2}}{[Cr(C_8H_6S)(CO)_3]} + 2CO + THF \qquad (1)$$

To distinguish between possible η^6-coordination of the benzo ring and η^5-coordination of the thiophene ring, an X-ray crystallographic study of **2** was carried out.[12] The crystallographic results are summarized in Figure 1. The benzo ring is asymmetrically η^6-coordinated to chromium with slightly longer Cr–C bonds to the carbon atoms shared by the thiophene and benzo rings (C5 and C10) than to the other four benzo carbon atoms (C6–C9), resembling the structures of $[Cr(\eta^6\text{-}naphthalene)(CO)_3]$[13,14] and $[Cr(\eta^6\text{-}benzo[2,3\text{-}b]thiophene)(CO)_3]$.[15] The coordinated benzo[*c*]thiophene ligand in **2** is practically planar, with a dihedral angle of 2.20° between thiophene (S–C4–C5–C10–C11) and benzene (C5–C6–C7–C8–C9–C10) planes. The $[Cr(CO)_3]$ group is staggered with respect to the arene carbons, with carbonyls directly below the C5–C6, C7–C8, and C9–C10 bonds. The magnitude of the C–S–C angle (93.9(2)°) falls between those of classical thiophene (91.9(3)°)[16-21] and nonclassical tetraphenylthieno[3,4-*c*]thiophene (**3**) (96.1(2)°).[22] The average C_α–S bond distance in **2** (1.670(7) Å) is significantly shorter than the comparable bonds in thiophene (1.717(4) Å) and **3** (1.706(5) Å), consistent with C–S multiple bond character. The carbon–carbon bond lengths in **2** indicate a major contribution of resonance structure **2a**, with the average thiophenic C_α–C_β bond length (1.382(6) Å) falling between the values for thiophene (1.368(4) Å) and **3** (1.407(6) Å). Overall, the structure is best described as the resonance hybrid of **2a**, **2b**, and **2c**. Compound **2** is a stabilized $[Cr(o\text{-}quinodimethane)(CO)_3]$ complex, similar to the reactive intermediates generated and trapped by Kündig[23] and Butenschön.[24]

The bonding of a transition metal to the benzo ring, rather than to the thiophene ring, of benzo[*c*]thiophene is consistent

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† Feodor Lynen Fellow of the Alexander von Humboldt Stiftung, 1991–1993.

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(11) Experimental and spectroscopic data for **2**: $[Cr(CO)_6]$ (4.00 g, 18.2 mmol) was photolyzed in THF (650 mL) to give $[Cr(thf)(CO)_5]$. Freshly sublimed benzo[*c*]thiophene (0.96 g, 7.16 mmol) was added, and the solution was immediately evaporated. The dark red residue was extracted with toluene, and the extract was filtered, layered with hexane, and cooled to −20 °C to give red crystals of **2** (1.2 g, 62%). Anal. Calcd for $C_{11}H_6CrOS$: C, 48.89; H, 2.24. Found: C, 48.82; H, 2.25. IR (toluene): 1965 s, 1900 s, 1874 s cm⁻¹. MS: *m*/*e* 270 (M^+), 242, 214, 186, 134. ^1H NMR (200 MHz, C_6D_6): δ 4.82 and 5.57 (each 2 H, benzo AA′BB′), 6.50 (2 H, thiophene, s). ^{13}C NMR (50 MHz, C_6D_6): δ_C 85.4 (benzo *C*H), 92.2 (benzo *C*H), 113.0 (fused *C*), 120.4 (thiophene *C*H), 233.5 (*C*O). This reaction is not highly reproducible, sometimes resulting in a mass of poly(dihydroisothianaphthene) from which no **2** can be extracted.

(12) X-ray diffraction data for **2**: deep red prismatic crystal, Enraf-Nonius CAD4 diffractometer, Mo Kα radiation, 1949 reflections $0° < \theta < 25°$, 1508 with $I \geq 3\sigma(I)$, $P2_1/n$ (No. 14), $Z = 4$, $a = 8.4643(8)$ Å, $b = 11.7415(8)$ Å, $c = 10.5810(9)$ Å, $\beta = 92.157(8)°$, $V = 1050.8(2)$ Å^3, $\rho_{calcd} = 1.703$ g·cm^{-1}, $\mu = 12.337$ cm^{-1}, empirical absorption correction (DIFABS).[34] Cr, S, C, and O atoms refined with anisotropic thermal parameters; H atoms located and refined with isotropic thermal parameters. Full-matrix least-squares refinement, 169 variables, $R = 3.0\%$, $R_w = 3.9\%$.

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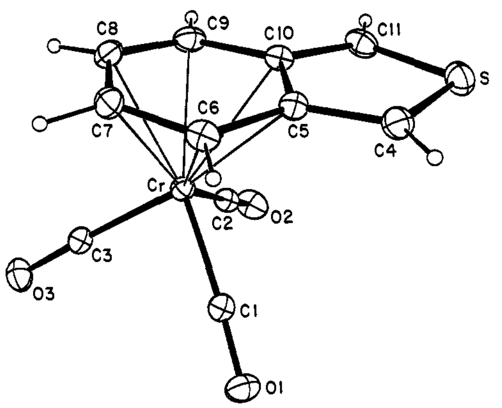
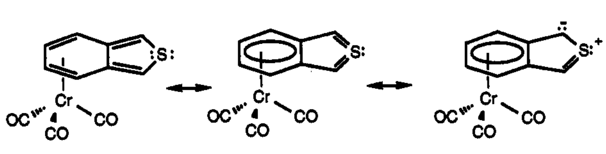
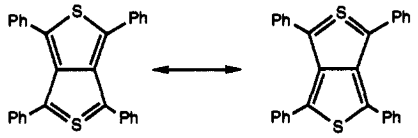


Figure 1. Perspective drawing of the molecular structure of $[Cr(\eta^6\text{-}C_8H_6S)(CO)_3]$ (**2**) showing ellipsoids corresponding to 50% probability contours of atomic displacement on non-hydrogen atoms. Selected bond distances: Cr–C8 2.207(3), Cr–C7 2.214(3), Cr–C9 2.221(3), Cr–C6 2.226(3), Cr–C10 2.341(3), Cr–C5 2.355(3), Cr–Ph centroid 1.770, S–C11 1.665(4), S–C4 1.675(3), C4–C5 1.378(4), C5–C6 1.423(4), C5–C10 1.443(4), C6–C7 1.371(5), C7–C8 1.416(5), C8–C9 1.381(5), C9–C10 1.421(5), C10–C11 1.386(5). Selected bond angles (deg): C11–S–C4 93.9(2); C5–C4–S 111.8(3); C4–C5–C6 130.0(3); C4–C5–C10 111.2(3); C6–C5–C10 118.7(3); C7–C6–C5 120.4(3); C6–C7–C8 120.4(3); C9–C8–C7 120.9(3); C8–C9–C10 119.7(3); C11–C10–C9 129.8(3); C11–C10–C5 111.1(3); C9–C10–C5 119.1(3); C10–C11–S 111.9(3).



2a **2b** **2c**



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with the behavior of Cr,[15,25,26] Fe,[27] Ru,[28,29] and Ir[28] centers toward benzo[*b*]thiophene or dibenzothiophene. Phenylthiophenes similarly react with $[Cr(CO)_3]$ sources to give products in which chromium is complexed to the arene, not the thiophene, portion of the ligand.[30]

Thiophenes and benzothiophenes are very weak S-donors, resulting from delocalization of the sulfur nonbonding electrons into the π-system of the hydrocarbon and development of a partial positive charge on sulfur.[3] Benzo[*c*]thiophene is at least as poor a nucleophile as the other thiophenes, so the failure to detect an S-bonded intermediate such as $[Cr(\eta^1\text{-}C_8H_6S\text{-}S)(CO)_5]$ is not unexpected. However, the facility of carbonyl loss from the chromium pentacarbonyl fragment under these unusually mild reaction conditions is surprising. There is some precedent for CO loss from a complex with a η^1,S-bonded sulfur-containing ligand, *i.e.*, $[Cr(\eta^1\text{-}PhSPh\text{-}S)(CO)_5]$ converts to $[Cr(\eta^6\text{-}PhSPh)(CO)_3]$, but this process requires elevated temperatures.[31,32] Thermal reactions of **1** with $[Cr(EtCN)_3(CO)_3]$, $[Cr(NH_3)_3(CO)_3]$, and $[Cr(\eta^6\text{-}naphthalene)(CO)_3]$, which are suitable η^6-arene precursors, failed to produce any isolable amount of $[Cr(C_8H_6S)(CO)_3]$.[33] Together, these observations suggest that initial coordination of **1** to $[Cr(CO)_5]$ *via* sulfur, rather than direct coordination of the benzo ring of **1** to a $[Cr(CO)_3]$ precursor, may be an essential step in the formation of **2**.

We have yet not been able to characterize any other π-complexes of benzo[*c*]thiophene. The low thermal stability of **1** and its ready polymerization in the presence of even mild oxidants such as Ag^+ severely limit the range of metallic reagents which can be employed. We are continuing to search for other suitable metal fragments.

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Supplementary Material Available: Experimental details of the preparation and crystal structure of **2**, including atomic positions and equivalent *B* values, anisotropic displacement parameters, bond distances, bond angles, least squares planes, and torsion angles (9 pages); observed and calculated structure factors for **2** (10 pages). Ordering information is given on any current masthead page.

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