shorter Cu-Cl distances of 2.254 (1) Å and two angles at 97.6 (1)°, two at 100.0 (1)°, and two at 133.9 (1)°. This distortion is typical of $CuCl_4^{2-}$ ions in the presence of non-hydrogen-bonding cations, as is the observed bond distance.[15] Thus it is clear structurally that the Cu(I) and Cu(II) ions are localized at sites Cu(1) and Cu(2), respectively. Since the geometries of the two sites are so similar, this material would be best described as a type IIb mixed-valence system in the Robin and Day classification.[16]

The intense blue color of this salt, in contrast to the normal yellow to red color of copper(II) chloride salts, deserves comment. Although sufficient sample is not available to obtain a spectrum, the blue would imply a strong absorption in the low-energy end of the visible region. The band is strongly polarized along the crystal *c* axis, that is, along the chain direction. The logical origin of this band would likely be an intervalence charge-transfer transition. Further work will be carried out as soon as a repeatable synthetic scheme is worked out.

Acknowledgment. This research was supported in part by NSF Grant DMR-8219430. The X-ray diffraction facility was established through funds provided by NSF Grant CHE-8408407 and The Boeing Co.

Supplementary Material Available: Tables of data collection parameters, positional and isotropic thermal parameters of non-hydrogen atoms, bond lengths and angles, anisotropic thermal parameters for non-hydrogen atoms, and hydrogen atom positional and thermal parameters and a stereographic view of the unit cell contents (8 pages); a listing of observed and calculated structure factors (6 pages). Ordering information is given on any current masthead page.

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Synthesis, Structure, and Reactivity of [Fe(dbt)(CO)$_2$(Cp)][BF$_4$] and Related S-Bonded Thiophene Complexes

Sir:

Hydrodesulfurization and hydroliquefaction are two essential steps in the effective utilization of abundant, high-sulfur coal.[1,2] These reactions are catalyzed by a variety of metal compounds, usually heterogeneously. Organometallic compounds, including $[Fe(CO)_5]$, $[Fe_2(CO)_4(Cp)_2]$ ($Cp = \eta\text{-}C_5H_5$), and $[Mo(CO)_6]$, are effective coal hydroliquefaction catalysts, alone or in the presence of added sulfur.[2,3] These carbonyls have also demonstrated hydrodesulfurization activity with coal[4] and coal model compounds.[4,5] The thiophenes, especially dibenzothiophene (dbt), are the best model compounds for organically bound sulfur in coal,[6] yet the transition-metal coordination chemistry of thiophene ligands is not well investigated.

Chromium,[7] manganese,[8] iron,[9] ruthenium,[10] rhodium, and iridium[11] form η^5-complexes with certain thiophenes, especially tetramethylthiophene, and η^6-complexes with the arene rings of benzothiophenes have been reported.[12] Thiophenes are weak S-donor ligands. A few S-bonded complexes of thiophene and 2,5-dimethylthiophene are known for iron[13] and ruthenium,[14] but these are not fully characterized because they are so labile. Incorporating thiophenes into chelating ligands leads to some increase in stability. $[RuCl_2\{P(4\text{-}MeC_6H_4)_2(SC_{12}H_7)\}_2]$ with a chelating phosphine-dibenzothiophene ligand has been prepared and structurally characterized.[15] Copper and silver form structurally characterized complexes with chelating imide-thiophene ligands in which the thiophenes interact only weakly with the metals.[16] Thus, there are few good models for the attachment of thiophenes to metallic catalysts via sulfur, a bonding mode believed to be the first step in catalytic desulfurization of coal.[17] We report here the preparation and structure of an iron-dibenzothiophene complex in which the thiophene is not part of a chelating ligand system.

Displacement of isobutene from $[Fe(\eta^2\text{-}H_2C{=}CMe_2)(CO)_2(Cp)][BF_4]$[18] by dibenzothiophene (dbt), thiophene (th), benzo-

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0020-1669/87/1326-3424$01.50/0

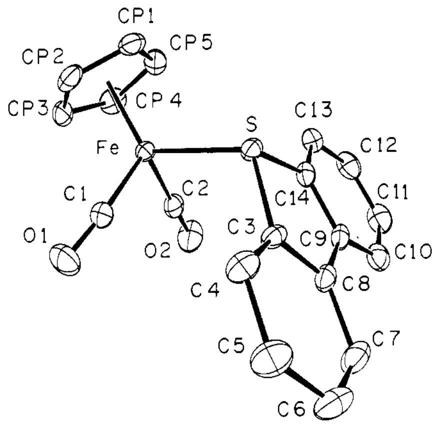
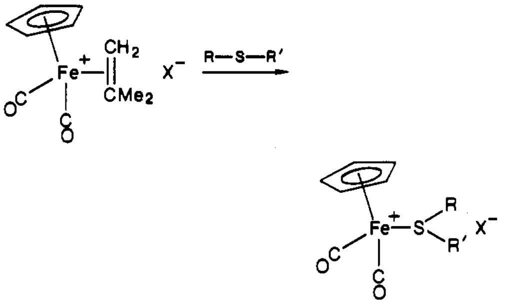


Figure 1. ORTEP[29] plot of the structure **1** showing 50% probability ellipsoids. Selected bond distances (Å): Fe–S, 2.289 (1); Fe–Cl, 1.780 (6); Fe–C2, 1.779 (7); Fe–Cp0, 1.725 (5); S–C3, 1.723 (5); SiC14, 1.773 (5); C3–C8, 1.390 (7); C8–C9, 1.451 (7); C9–C14, 1.392 (7). Selected bond angles (deg): S–Fe–C1, 96.9 (2); S–Fe–C2, 91.7 (2); S–Fe–Cp0, 121.2 (2); C1–Fe–C2, 94.8 (3); Fe–S–C3, 111.1 (2); Fe–S–C14, 108.2 (2); Fe–S–Tp, 119.4 (2); C3–S–C14, 90.5 (2); S–C3–C8, 112.0 (4); C3–C8–C9, 112.6 (4); C10–C9–C14, 118.3 (5); S–C14–C9, 112.1 (4). Cp0 is the centroid of the cyclopentadienyl ligand; Tp is the midpoint of the C8–C9 bond.

[*b*]thiophene (bt), and phenyl methyl sulfide in refluxing dichloromethane produced complexes **1–4**, respectively, in good to excellent yields (eq 1).[19] In our hands, the displacement of



(1)

	RSR′	X	yield, %
1	dibenzothiophene	BF4	94
2	thiophene	PF6	48
3	benzo[*b*]thiophene	BF4	91
4	PhSMe	PF6	82

tetrahydrofuran from $[Fe(thf)(CO)_2(Cp)][BF_4]$ by thiophene gave intractable mixtures, contrary to the reported preparation of $[Fe(th)(CO)_2(Cp)][BF_4]$ by this method.[13a] Similarly, the use of "$[Fe(BF_4)(CO)_2(Cp)]$"[20] in dichloromethane did not give satifactory yields of thiophene complexes. Complex **4** had been previously prepared in 74% yield by oxidizing $[Fe_2(CO)_4(Cp)_2]$ with $AgPF_6$ in acetone in the presence of PhSMe.[21] Reactions of $[Fe(\eta^2\text{-}H_2C{=}CMe_2)(CO)_2(Cp)]^+$ salts with dibenzofuran and tetraphenylthiophene produced no tractable products.

Spectroscopic evidence[22] suggested that the thiophene ligands in **1–4** are bonded to iron via sulfur only, and this was confirmed by single-crystal X-ray diffraction of **1**.[23] A plot of the cation is shown in Figure 1, along with significant bond distances and angles. The Fe–S bond length is 2.289 (1) Å, slightly shorter than the sum of the covalent radii (2.38 Å).[24] Fe–S distances in other Fp–S (Fp = $[Fe(CO)_2(Cp)]$) compounds[25] range from 2.109 (2) Å in $[Fe(SO_2)(CO)_2(Cp)]^+$ [25a] to 2.35 (1) Å in $[(Cp)(CO)\text{-}FeSC(Fp)SCS(Fp)][SO_3CF_3]$;[25b] in general, the higher the oxidation state of sulfur, the shorter the Fp–S bond. The Fe–S distance in **1** is close to those in $[Fe(SC_2H_5)(CO)_2(Cp)]$ (2.296 (2) Å) and $[(Fp)_2(\mu\text{-}SC_2H_5)][BF_4]$ (2.297 (2), 2.304 (2) Å).[25c] The dimensions of the $[Fe(CO)_2(Cp)]$ group in **1** are similar to those in related compounds.[24,25] The dbt ligand in **1** is oriented anti to the cyclopentadienyl group, presumably minimizing intramolecular steric contacts, with a Cp(centroid)–Fe–S–Tp torsional angle of −156.8° (Tp is the midpoint of the C8–C9 bond). The dbt ligand is tipped away from iron with pyramidal geometry at sulfur and an Fe–S–Tp angle of 119.4°, more acute than the 132.0° and 130.1° Ru–S–Tp angles observed in $[RuCl_2\{P(4\text{-}MeC_6H_4)_2(SC_{12}H_7)\}_2]$.[15] The dimensions of the dbt ligand are similar to those in free dbt.[26] The mean C–S bond length in **1** (1.748 Å) is about the same as that of free dbt (1.740 Å), and the C–S–C angle has decreased slightly from 91.5° in dbt to 90.5 (2)° in **1**. The dbt ligand is nearly planar, with a slight "bowing" of the benzo rings relative to the thiophene ring, with dihedral angles of 1.55° (ring C3–C8) and 0.96° (ring C9–C14). This bowing is slightly greater than that in free dbt (1.2° and 0.4°) but less than that in $[RuCl_2\{P(4\text{-}MeC_6H_4)_2(SC_{12}H_7)\}_2]$ (9° and 3.5°). Perhaps the distortions in the ruthenium compound are attributable to strain in the chelate ring.

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(19) Experimental Procedure for 1: A solution of $[Fe(\eta^2\text{-}H_2C{=}CMe_2)(CO)_2(Cp)][BF_4]$[18] (0.270 g, 0.844 mmol) and dibenzothiophene (0.188 g, 1.02 mmol) in 20 mL of dichloromethane was refluxed under nitrogen for 4 h. An orange precipitate formed during the reaction. The mixture was evaporated to dryness in vacuo, and the residue was rinsed with three 5-mL portions of ethyl ether and dried in vacuo. The resulting orange, microcrystalline solid (0.355 g, 94% yield) was pure $[Fe(dbt)(CO)_2(Cp)][BF_4]$ (**1**) by ^1H NMR. Crystals for X-ray diffraction were grown by diffusion of ethyl ether saturated N_2 into a CH_2Cl_2 solution of **1**. $[Fe(th)(CO)_2(Cp)][PF_6]$ (**2**, 48%), $[Fe(bt)(CO)_2(Cp)][BF_4]$ (**3**, 91%), and $[Fe(PhSMe)(CO)_2(Cp)][PF_6]$ (**4**, 82%) were prepared similarly.

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(22) Spectroscopic and physical data are as follows. For **1**: ^1H NMR (CD_3NO_2, 90 MHz) δ 8.4–7.6 (3 m, 8 H, dbt), 5.55 (s, 5 H, Cp): IR (ν(CO), Nujol) 2061, 2024 cm^{-1}; ^{13}C NMR (CD_3NO_2, 50.29 MHz) δ_C 209.0 (CO), 140.9, 138.8, 131.3, 130.8, 127.0, and 124.9 (dbt), and 88.9 (Cp); mp 176.5–178.5 °C. For **2**: ^1H NMR[13a,27] (CD_2Cl_2, 200 MHz) δ 7.5–7.2 (2 m, 4 H, thiophene), 5.42 (s, 5 H, Cp): IR (ν(CO), Nujol) 2064, 2016 cm^{-1}; ^{13}C NMR (CD_2Cl_2, 50.29 MHz) δ_C 207.0 (CO), 138.4 and 134.4 (th), and 87.1 (Cp); mp 70 °C dec. For **3**, ^1H NMR (CD_3NO_2, 90 MHz) δ 8.2–7.3 (3 m, 6 H, bt), 5.54 (s, 5 H, Cp); IR (ν(CO), Nujol) 2061, 2011 cm^{-1}; ^{13}C NMR (CD_2Cl_2, 50.29 MHz, 300 K) δ_C 207.4 (CO), 143.1, 140.7, 132.9, 132.7, 129.8, 128.3, 127.2, and 125.2 (bt), and 87.5 (Cp); ^{13}C NMR (CD_2Cl_2, 50.29 MHz, 170 K) δ_C 207.8, 207.0 (CO); mp 99–102 °C; Anal. Calcd for $C_{15}H_{11}BF_4FeO_2S$: C, 45.27; H. 2.78; S, 8.06. Found: C, 45.57; H, 2.76; S, 7.73. For **4**: ^1H NMR ($(CD_3)_2CO$, 90 MHz) δ 7.8–7.5 (m, 5 H, Ph), 5.70 (s, 5H, Cp), 3.01 (s, 3 H, CH_3); ^{13}C NMR ($(CD_3)_2CO$, 50.29 MHz, 300 K) δ_C 208.9 (CO), 134.6, 131.5, 131.3, and 129.4 (Ph), 88.8 (Cp), and 27.2 (CH_3); ^{13}C NMR ($(CD_3)_2CO$, 50.29 MHz, 185 K) δ_C 209.4, 208.4 (CO).

(23) X-ray diffraction data for **1**: irregular red-orange prism, 0.2 mm × 0.3 mm × 0.4 mm, triclinic, space group $P\bar{1}$ (No. 2), $Z = 2$, $a = 10.359$ (2) Å, $b = 10.931$ (3) Å, $c = 9.320$ (2) Å, $\alpha = 112.75$ (2)°, $\beta = 93.36$ (2)°, $\gamma = 102.85$ (2)°, $V = 936.45$ Å^3, $\rho_{calcd} = 1.59$ g cm^{-3}. Data were collected at 23 °C on an Enraf-Nonius CAD4 diffractometer using graphite-monochromatized Mo Kα radiation. A total of 4304 reflections were measured ($+h,\pm k,\pm l$; $0 < \theta < 27.5°$; ω-2θ scans) and of these 2354 with $(F_o)^2 \geq 3\sigma(F_o)^2$ were used. Agreement between equivalent reflections was satisfactory. The iron atom was located by using Patterson methods, and remaining non-hydrogen atoms were located by using DIRDIF[29] or difference Fourier methods. Hydrogen atoms were placed in calculated positions with d(C–H) = 0.95 Å. All non-hydrogen atoms were refined with anisotropic thermal parameters, and hydrogens with $B = B$(attached C) + 1.0 Å^2 were included as a fixed contribution. Corrections for extinction and absorption ($\mu = 9.59$ cm^{-1}) were not necessary. Full-matrix least-squares refinement led to $R = 4.8\%$ and $R_w = 5.7\%$.

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The thiophene ligands of complexes **1**–**3** are labile. The dbt ligand of **1** is displaced by ca. 2 equiv of CH_3CN in CD_3NO_2 solution at room temperature in about 1 week to give $[Fe(CH_3CN)(CO)_2(Cp)][BF_4]$ and free dbt. In contrast, the thiophene ligand of **2** is quantitatively displaced by CD_3NO_2 in ca. 3 h at room temperature.[27] The benzothiophene ligand of **3** is also displaced by CH_3CN or CD_3NO_2. Decomposition of **3** to $[Fe(CO)_3(Cp)][BF_4]$ occurs during attempted slow recrystallization from dichloromethane/ethyl ether.

The ^{13}C NMR spectrum of benzothiophene complex **3** shows a singlet at room temperature for the two diasterotopic carbonyl ligands but two separate signals at 170 K ($\Delta G^* = 39$ kJ/mol at 190 K, the coalescence temperature in CD_2Cl_2) due to slowing of the stereochemical inversion at sulfur.[22,28] Free benzothiophene signals remained sharp and distinct from those of complex **3** at room temperature, ruling out an intermolecular mechanism for coalescence in **3**. To our knowledge, this is the first reported sulfur inversion barrier for a thiophene complex. For comparison, the ^{13}C NMR signals of the carbonyl ligands of $[Fe(PhSMe)(CO)_2(Cp)][PF_6]$ coalesce at 249 K with $\Delta G^* = 52$ kJ/mol.[22] In general, inversion barriers for π-conjugated sulfide ligands are about 10 kJ/mol lower than for saturated sulfide ligands, whereas cyclic sulfide ligands have inversion barriers slightly higher than acyclic ones.[28b]

Recent work by Angelici[8a,10a–c] suggests that π-bonded thiophene species are responsible for C–S bond cleavage and hydrogen/deuterium exchange on hydrodesulfurization catalysts. The isolation and characterization of **1** provides a structural model for the interaction of organic sulfur in coal with a metallic catalyst via sulfur only, which is a viable initial step in hydrodesulfurization.[17]

Acknowledgment. We thank the Consortium for Fossil Fuel Liquefaction Science, funded by the Pittsburgh Energy Technology Center, United States Department of Energy, for financial support, and Robert Angelici for helpful discussions and a preprint of ref 10c.

Supplementary Material Available: For the structure of **1**, tables of crystal data and details of the intensity collection and refinement, positional and thermal parameters, bond distances, bond angles, and least-squares planes (9 pages); a table of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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[27] In our hands, the ^1H NMR spectrum of **2** in $(CD_3)_2CO$[13a] shows free thiophene and $[Fe\{(CD_3)_2CO\}(CO)_2(Cp)]^+$.

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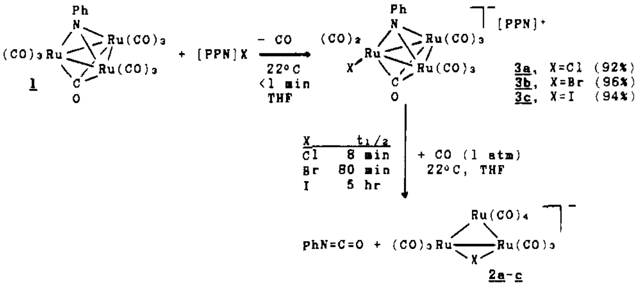
Received May 19, 1987

Halide-Promoted Formation and Carbonylation of μ_3-Nitrene Ligands on Ru_3 Clusters

Sir:

Bridging carbene ligands in polynuclear compounds often undergo facile carbonylation to form ketene ligands, μ-CR_2 + CO → μ-CR_2=C=O.[1] However, the related carbonylation of bridging nitrene ligands to form isocyanates, μ-NR + CO → μ-RN=C=O, has proven difficult to achieve,[2–5] even though such a reaction has been invoked as an important step in catalytic nitroaromatic carbonylation.[6] We earlier demonstrated that halides accelerate the methylene to ketene conversion,[1b] and herein we show that they also dramatically promote nitrene carbonylation to form isocyanates. Furthermore, halides have also been found to accelerate the *formation* of nitrene ligands from nitrosobenzene.

Scheme I



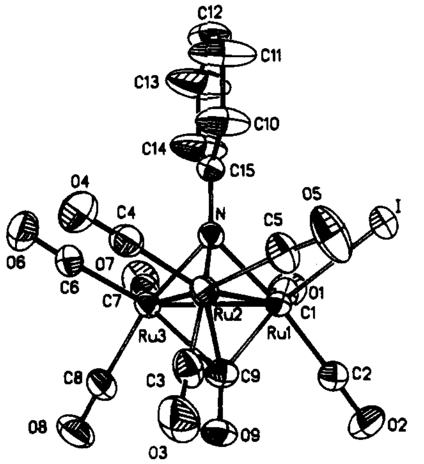


Figure 1. ORTEP drawing of the cluster anion in [Na(18-crown-6)][$Ru_3(\mu_3$-NPh)$(CO)_9$(I)] (**3c**): Ru(1)–Ru(2), 2.770 (1) Å; Ru(1)–Ru(3), 2.740 (1) Å; Ru(2)–Ru(3), 2.711 (1) Å; Ru(1)–I, 2.762 (1) Å; Ru(1)–N, 2.056 (5) Å; Ru(2)–N, 2.077 (5) Å; Ru(3)–N, 2.052 (6) Å; Ru(1)–C(9), 2.053 (7) Å; Ru(2)–C(9), 2.168 (6) Å; Ru(3)–C(9), 2.329 (7) Å; Na···I, 3.680 (5) Å; Na···O(6), 2.871 (7) Å; Ru(1)–Ru(2)–Ru(3), 60.0 (0)°; Ru(2)–Ru(3)–Ru(1), 61.1 (0)°; Ru(3)–Ru(1)–Ru(2), 58.9 (0)°; Ru(1)–C(9)–O(9), 139.1 (5)°; Ru(2)–C(9)–O(9), 132.8 (5)°; Ru(3)–C(9)–O(9), 126.8 (6)°.

The resistance of nitrene clusters to carbonylation is particularly well illustrated by the high yield recovery of $M_3(\mu_3$-NPh$)_2(CO)_9$ (M = Fe, Ru) following attempted carbonylation at 120 atm, 150

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