we propose initial formation of azaoxametallacycle **8**, followed by subsequent insertion of a second nitrile into the Zr—N bond of this molecule. Investigations designed to resolve these mechanistic questions are continuing and will be reported in a full paper.

Acknowledgment. We thank the National Institutes of Health (Grant No. GM-25457) for financial support of this work. M.J.C. gratefully acknowledges a postdoctoral (NRSA) fellowship from the NIH. We also thank Prof. Gregory Hillhouse and his colleagues for their generous gift of $Cp^*_2Zr(OCPh{=}CPh)$ and Drs. J. O'Connor, K. H. Theopold, and D. M. Roddick for helpful mechanistic suggestions.

Supplementary Material Available: Spectroscopic and analytical data for complexes **2–5** and details of the structure determinations for **2**, **4**, and **5** including experimental descriptions, ORTEP drawings showing full atomic numbering, crystal and data collection parameters, general temperature factor expressions (*B*'s), positional parameters and their estimated standard deviations, and intramolecular distances and angles (51 pages); tables of structure factors for **2**, **4**, and **5** (63 pages). Ordering information is given on any current masthead page.

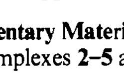
Reaction of the Sulfur-Coordinated Thiophene in $Cp^*(CO)_2Re(SC_4H_4)$ To Give the Thiophene-Bridged $Cp^*(CO)_2Re(\mu\text{-}SC_4H_4)Fe(CO)_3$

Moon-Gun Choi and Robert J. Angelici*

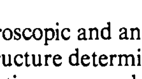
Department of Chemistry and Ames Laboratory[1]
Iowa State University, Ames, Iowa 50011

Received July 27, 1989

In a mechanism proposed in these laboratories[2,3] for the catalytic hydrodesulfurization (HDS) of thiophenes, the thiophene adsorbs via the entire π ring in the η^5 mode.[4] Thiophenes coordinated



η^5- bound



S - bound

in this manner in Mn and Ru complexes[5] are susceptible to attack by hydride sources, and this reactivity is the basis for the proposed HDS mechanism.[2,3] Another mechanism[6] assumes initial coordination of the thiophene through only the sulfur atom, and this coordination is presumed to activate the thiophene so as to give the H_2S and C_4 hydrocarbon products. However, in model complexes with S-bound thiophene (T) ligands such as $CpFe(CO)_2(T)^+$,[7] or even $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2{}^+$,[8] where the thiophene is part of a cyclopentadienyl chelate ligand, the thiophene is so weakly coordinated to the metal that all attempted reactions of the ligand have simply led to thiophene dissociation from the metal. Thus, there is no evidence that S-coordinated thiophene is activated to react. In this communication, we describe the synthesis of an unusually stable S-bound thiophene complex $Cp^*Re(CO)_2(T)$ ($Cp^* = \eta^5\text{-}C_5Me_5$) and its subsequent reaction with "$Fe(CO)_3$" to give a dinuclear complex $Cp^*(CO)_2Re(\mu\text{-}T)Fe(CO)_3$ in which the thiophene is S-bound to the Re and η^4-bound through the four carbons to the $Fe(CO)_3$.

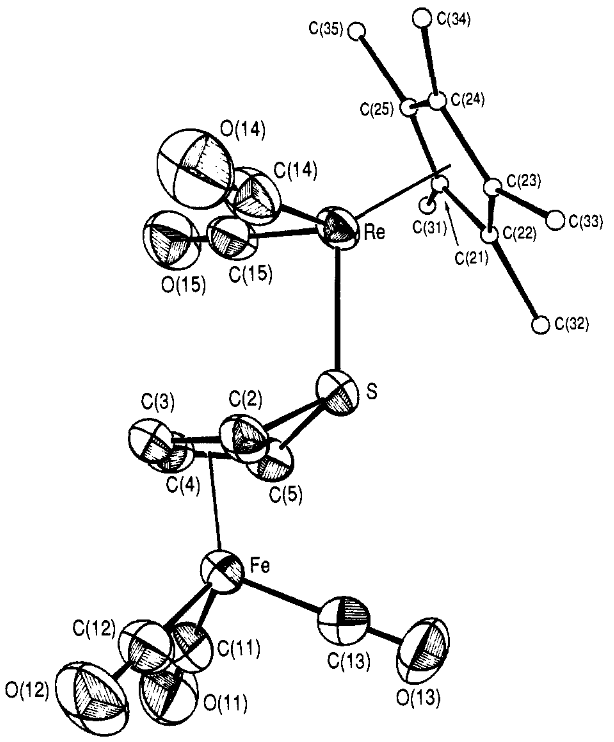


Figure 1. ORTEP drawing of $Cp^*Re(CO)_2(\mu\text{-}T)Fe(CO)_3$ (**2**). Selected bond distances (Å) and angles (deg) are Re–S = 2.330 (1), Re–C(14) = 1.884 (7), Re–C(15) = 1.883 (6), Fe–C(2) = 2.086 (6), Fe–C(3) = 2.044 (6), Fe–C(4) = 2.048 (6), Fe–C(5) = 2.099 (6), Fe–C(11) = 1.769 (8), Fe–C(12) = 1.789 (7), Fe–C(13) = 1.798 (6), S–C(2) = 1.807 (6), S–C(5) = 1.802 (5), C(2)–C(3) = 1.458 (8), C(3)–C(4) = 1.379 (9), C(4)–C(5) = 1.427 (8), C(2)–S–C(5) = 82.3 (3), C(11)–Fe–C(12) = 91.4 (3), C(11)–Fe–C(13) = 100.9 (3), C(12)–Fe–C(13) = 99.0 (3), S–Re–C(14) = 93.4 (2), S–Re–C(15) = 93.0 (2), C(14)–Re–C(15) = 87.5 (3), C(2)–C(3)–C(4) = 110.1 (5), and C(3)–C(4)–C(5) = 110.4 (5).

A solution of $Cp^*(CO)_2Re(THF)$, prepared by UV irradiation[9] of a THF solution (120 mL) of $Cp^*Re(CO)_3$ (0.74 mmol), is stirred with thiophene (5.0 mL, 62 mmol) at room temperature for 6–8 h. After removal of the solvent in vacuo, the residue is chromatographed in CH_2Cl_2/hexanes (1:4) on neutral alumina. Slow evaporation of the solvent from the yellow band gives light yellow, air-stable crystals of $Cp^*(CO)_2Re(T)$ (**1**) (38% yield), which is characterized by its elemental analyses and IR, ^1H NMR, ^{13}C NMR, and mass spectra;[10] these data support its formulation as a complex with an S-coordinated thiophene. Although there are no crystal structures of simple thiophene complexes, the sulfur in **1** is presumed to be pyramidal, as found in the chelated thiophene complex[8] $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2{}^+$ and in several thiaporphyrin complexes,[11] and the thiophene may be folded slightly (12–15°)[11] along a line from C(2) to C(5).

When a solution of $Cp^*(CO)_2Re(T)$ (**1**) (0.076 mmol) in THF (15 mL) is treated with $Fe_2(CO)_9$ (0.274 mmol) at −40 °C and then slowly warmed to room temperature and stirred for 20 h,

---

[1] Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research is supported by the Office of Basic Energy Sciences, Chemical Sciences Division.

[2] Angelici, R. J. *Acc. Chem. Res.* **1988**, *21*, 387.

[3] (a) Sauer, N. N.; Markel, E. J.; Schrader, G. L.; Angelici, R. J. *J. Catal.* **1989**, *117*, 295. (b) Markel, E. J.; Schrader, G. L.; Sauer, N. N.; Angelici, R. J. *J. Catal.* **1989**, *116*, 11.

[4] Hachgenei, J. W.; Angelici, R. J. *Organometallics* **1989**, *8*, 14.

[5] (a) Lesch, D. A.; Richardson, J. W.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901. (b) Spies, G. H.; Angelici, R. J. *Organometallics* **1987**, *6*, 1897. (c) Hachgenei, J. W.; Angelici, R. J. *J. Organomet. Chem.* **1988**, *355*, 359.

[6] Lipsch, J. M. J. G.; Schuit, G. C. A. *J. Catal.* **1969**, *15*, 179.

[7] (a) Goodrich, J. D.; Nickias, P. N.; Selegue, J. P. *Inorg. Chem.* **1987**, *26*, 3424. (b) Kuhn, N.; Schumann, H. *J. Organomet. Chem.* **1984**, *276*, 55.

[8] Draganjac, M.; Ruffing, C. J.; Rauchfuss, T. B. *Organometallics* **1985**, *4*, 1909.

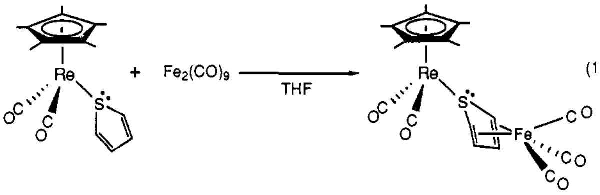
[9] Einstein, F. W. B.; Klahn-Oliva, A. H.; Sutton, D.; Tyers, K. G. *Organometallics* **1986**, *5*, 53.

[10] **1**: IR (hexanes) ν(CO) 1934, 1874 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.19 (br, s, 2 H, T), 7.11 (br s, 2 H, T), 1.95 (s, 15 H, Cp*); ^{13}C NMR ($CDCl_3$) δ 205.2 (CO), 138.9 and 129.9 (T), 96.0 (C of Cp*), 10.5 (Me of Cp*); EIMS (70 eV) *m/e* 462 (M^+), 404 ($M^+ - C_2H_2S$), 376 ($M^+ - (C_2H_2S + CO)$), 348 ($M^+ - (C_2H_2S + 2CO)$), 84 (T^+), 58 ($C_2H_2S^+$). Anal. Calcd for $C_{16}H_{19}O_2ReS$: C, 41.63; H, 4.15. Found: C, 41.70; H, 4.14.

[11] (a) Latos-Grażyński, L.; Lisowski, J.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1989**, *28*, 1183. (b) Latos-Grażyński, L.; Lisowski, J.; Olmstead, M. M.; Balch, A. L. *Inorg. Chem.* **1989**, *28*, 3328.

0002-7863/89/1511-8753$01.50/0

the solution color changes from orange-yellow to dark purple. Evaporation of the solution under vacuum and chromatography of the residue on neutral alumina in CH_2Cl_2/hexanes (1:4) give $Cp^*(CO)_2Re(\mu\text{-}T)Fe(CO)_3$ (**2**) in the yellow band, which upon slow evaporation yields (59%) **2** as air-stable, yellow crystals, which were fully characterized.[12] Thus, the reaction proceeds as in eq 1.



1

2

An X-ray diffraction study[13] shows that **2** contains a bridging thiophene ligand that is coordinated to the Re atom via the sulfur and to the Fe through the four carbons of the diene system. The sulfur is pyramidal as indicated by the angle (125°) between the Re–S vector and the vector from S to the midpoint of the line from C(2) to C(5). The longer distances for C(2)–C(3) (1.458 (8) Å) and C(4)–C(5) (1.427 (8) Å) as compared to that for C(3)–C(4) (1.379 (9) Å) are often found in η^4-1,3-diene complexes;[14] this pattern of C–C bond distances is similar to that found in the S-coordinated thiophene in thiaporphyrin complexes[11] but is just the opposite of that in free thiophene, where C(2)–C(3) and C(4)–C(5) are shorter (1.37 Å) than C(3)–C(4) (1.42 Å),[15] and that in $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2^+$.[8] The C(2)–S and C(5)–S distances (1.807 (6), 1.802 (5) Å) are substantially longer than the corresponding distances (1.715 Å)[15] in free thiophene, and the C(2)–S–C(5) angle (82.3°) is much smaller than in thiophene (92°). The thiophene ring is folded with an angle of 36.9 ± 0.4° between the C(2)–C(3)–C(4)–C(5) and C(2)–S–C(5) planes. In general, the geometry (the fold at the C(2)–C(5) line, the long C–S bonds, and the small C(2)–S–C(5) angle of the thiophene) in **2** is different from that of free thiophene[15] and the S-coordinated thiophene in $(C_5H_4CH_2C_4H_3S)Ru(PPh_3)_2^+$ [8] but very similar to that of the η^4-thiophene ligand in $Cp^*Ir(\eta^4\text{-}T)$[16] and $Cp^*Ir(\eta^4\text{-}T{\cdot}BH_3)$ (in which the BH_3 is coordinated to the sulfur).[17]

It is interesting that the ν(CO) values for the $Cp^*(CO)_2Re$ group in **2** (1922, 1862 cm^{-1}) are lower than those in **1** (1934, 1874 cm^{-1}), which means that the thiophene sulfur is a better donor to Re when the thiophene is η^4-coordinated to $Fe(CO)_3$. This is consistent with the previous observation[16] that the thiophene sulfur in $Cp^*Ir(\eta^4\text{-}T)$ is a stronger Lewis base toward BH_3 than free thiophene or even Me_2S. Presumably the η^4 coordination of thiophene to a metal separates the diene and sulfur segments of the thiophene and drastically reduces the delocalization of electron density from the sulfur to the diene system, which makes the sulfur much more basic.

In conclusion, we report herein the first example of an S-coordinated thiophene undergoing reaction. In fact, it appears that the thiophene in **1** is activated to react with "$Fe(CO)_3$" since thiophene itself does not react[18] with $Fe_2(CO)_9$ under conditions very similar to those in eq 1. (Under more vigorous conditions, $Fe_3(CO)_{12}$ reacts with thiophene to give thiaferroles and ferroles.[19]) Thus, it is possible that on an HDS catalyst initial S adsorption of thiophene to a single metal site would activate the diene system to coordinate to a second metal. Perhaps in this bridging position with weakened C–S bonds, the thiophene undergoes C–S bond cleavage and hydrogenation. Investigations of such reactivity are in progress.

Acknowledgment. We thank Dr. L. M. Daniels for help in solving the X-ray crystal structure. The diffractometer was funded in part by the National Science Foundation (Grant No. CHE-8520787).

Supplementary Material Available: ORTEP drawing of **2** and tables of crystal data, positional and thermal parameters, complete bond distances and angles, and least-squares planes for **2** (11 pages); calculated and observed structure factors for **2** (15 pages). Ordering information is given on any current masthead page.

---

(12) **2**: IR (hexanes) ν(CO) 2064, 2002, 1988, 1922, 1862 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 5.95 (m, 2 H, T), 3.56 (m, 2 H, T), 1.98 (s, 15 H, Cp*); ^{13}C NMR ($CDCl_3$) δ 208.5 and 207.0 (CO), 95.5 (C of Cp*), 83.9 and 57.1 (T), 10.5 (C of Cp*); CIMS (methane) *m/e* 603 (M^+ + H), 574 (M^+ – CO), 546 (M^+ – 2CO), 519 (M^+ + H – 3CO), 491 (M^+ + H – 4CO), 462 (M^+ – 5CO). Anal. Calcd for $C_{19}H_{19}O_5FeReS$: C, 37.94; H, 3.18. Found: C, 38.08; H, 3.16.

(13) Crystallographic data for **2**: mol wt 601.47; monoclinic, space group $P2_1/c$ (No. 14); $a = 11.395$ (2) Å, $b = 13.310$ (1) Å, $c = 14.636$ (3) Å, $\beta = 109.151$ (8)°, $V = 2096.8$ (6) Å^3, $\rho_{calcd} = 1.905$ g/cm^3 for $Z = 4$ at 22 ± 1 °C, $\mu = 66.59$ cm^{-1} (Mo Kα). Diffraction data were collected at 22 ± 1 °C using an Enraf-Nonius CAD4 automated diffractometer. A total of 7716 reflections were collected. Of the 3684 unique data, 2850 data were considered observed, having $F_o^2 > 3\sigma(F_o^2)$. An empirical absorption correction was applied to the data based on a series of φ-scans. The positions of the metal atoms were given by direct methods. (SHELXS-86, G. M. Sheldrick, Institut für Anorganische Chemie der Universität, Göttingen, F.R.G.). The remainder of the non-hydrogen atoms were located in difference Fourier maps following least-squares refinement of the known atoms. $R = 0.0263$ and $R_w = 0.0372$.

(14) (a) Pearson, A. J. *Metallo-organic Chemistry*; Wiley-Interscience: New York, 1985; p 11. (b) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley-Interscience: New York, 1986; p 64.

(15) (a) Bak, B.; Christensen, D.; Hansen-Nygaard, L.; Rastrup-Andersen, J. *J. Mol. Spectrosc.* **1961**, *7*, 58. (b) Bonham, R. A.; Momany, F. A. *J. Phys. Chem.* **1963**, *67*, 2474. (c) Harshbarger, W. R.; Bauer, S. H. *Acta Crystallogr.* **1970**, *B26*, 1010.

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

(17) Chen, J.; Daniels, L. M.; Angelici, R. J. *J. Am. Chem. Soc.*, accepted for publication.

(18) Determined by studying the ^{1}H NMR spectrum of a THF-d_8 solution of $Fe_2(CO)_9$ (10 mg, 0.028 mmol) with thiophene (3.0 μL, 0.037 mmol) at room temperature for 24 h.

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

Determination of $\delta(^{187}Os)$, $J(Os,X)$, and $T_1(^{187}Os)$ in Osmium Complexes via Indirect 2D NMR Spectroscopy

Reinhard Benn,* Eckhard Joussen, Herbert Lehmkuhl,
Fernando López Ortiz, and Anna Rufińska

Max-Planck-Institut für Kohlenforschung
Kaiser-Wilhelm-Platz 1
D-4330 Mülheim a.d. Ruhr, West Germany

Received June 26, 1989

Osmium-187 is the most insensitive nucleus in NMR spectroscopy,[1] and also for this reason until now no $\delta(^{187}Os)$ data have been published except for the standard OsO_4[2] and a μ-bridged binuclear complex.[3] Using the indirect two- and one-dimensional (X,Os) NMR spectroscopy (X = ^{1}H or ^{31}P)[4,5] we have determined to the best of our knowledge for the first time the ^{187}Os chemical shift range, the magnitude and sign of J(Os,X), and $T_1(^{187}Os)$ in quasitetrahedral $[(\eta^5\text{-cyclopentadienyl})(phosphine)_2(R)]Os$ complexes.[6]

---

(1) Mason, J., Ed. *Multinuclear NMR*; Plenum Press: New York, 1987. Benn, R. In *Metal NMR Spectroscopy*; Elsevier: New York, 1990; in press.

(2) Schwenk, A. *Z. Phys.* **1968**, *213*, 482. Schwenk, A. *Progr. NMR Spectrosc.* **1985**, *17*, 69.

(3) Cabeza, J. A.; Mann, B. E.; Brevard, C.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1985**, 65.

(4) Müller, L. *J. Am. Chem. Soc.* **1979**, *101*, 4481. Bodenhausen, G.; Ruben, D. J. *Chem. Phys. Lett.* **1980**, *69*, 185. Bax, A.; Griffey, R. H.; Hawkins, B. L. *J. Magn. Reson.* **1983**, *55*, 301.

(5) Benn, R.; Brenneke, H.; Frings, A.; Lehmkuhl, H.; Mehler, G.; Rufińska, A.; Wildt, T. *J. Am. Chem. Soc.* **1988**, *110*, 5661. Benn, R.; Rufińska, A. *Magn. Reson. Chem.* **1988**, *26*, 895.

(6) **1a**: Bruce, M. I.; Williams, M. L.; Patrick, J. M.; White, A. H. *Aust. J. Chem.* **1983**, *36*, 1353. **2a**: Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601. **2b**, **4a**, **4c**, **7c**: Joussen, E.; Lehmkuhl, H. Unpublished. **2c**: Bruce, M. I.; Tomkins, J. B.; Wong, F. S.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1982**, 687. **3a**: Wilczewski, T. *J. Organomet. Chem.* **1982**, *224*, C1. **5a**: Bruce, M. I.; Humphrey, M. G.; Swincer, A. G.; Wallis, R. C. *Aust. J. Chem.* **1984**, *37*, 1747. **6**: Liles, D. C.; Shaver, A.; Singleton, E.; Wiege, M. B. *J. Organomet. Chem.* **1985**, *288*, C33.

0002-7863/89/1511-8754$01.50/0