ligand.[4b,11,16] The observation of a new strong IR absorption (Nujol mull) at 1536 cm^{-1} is also consistent with the formulation of **6**-$(PF_6)_2$ as having a coordinated NO^- ligand, thus affirming the conclusion that the nitrosonium cation has been reduced by the dicopper(I) center in **3**.[4b,11,16-18]

As was found for the reactions of the $\{Cu_2-O_2\}^{n+}$ complexes with various reagents such as H^+ and CO_2, the present investigation indicates that the ligands in **1**-**3** are exerting pronounced differential effects upon the reactivity of these species. While vacant coordination sites potentially exist in all of these complexes,[19] only **3** reacts with NO^+ to give a coordinated nitrosyl ligand. Of course, copper-nitrosyl intermediates cannot as yet be ruled out in the cases where simple oxidation of Cu(I) by NO^+ occurs in **1** and **2**.

There are a number of reasons that compound **6** is of interest. The nitrosyl moiety is a very common ligand in inorganic chemistry, and it readily forms complexes with most transition metals. Yet, there are only a few examples of systems where evidence for a copper-nitrosyl moiety exists,[20,21] and until this study there were no structurally characterized synthetic examples. There is a biological relevance as well, since nitric oxide (NO) adducts of a number of copper proteins apparently do exist.[20,22,23] Most importantly, Averill and co-workers[20] have recently proposed that a copper-nitrosyl intermediate (Cu^+-NO^+ or equivalent) is present in the copper-containing nitrite reductase of *Achromobacter cycloclastes* (catalysis of $NO_2^- \rightarrow N_2O$). Since NO^+ ion is an oxidation-state equivalent of NO_2^-,[24] our reaction of nitrosonium ion with the dicopper(I) complex may represent a model for an early step in copper ion mediated nitrite reduction. Interconversions of nitrogen oxide species such as NO_2^-, NO, and N_2O have previously been shown to be effected by polynuclear copper centers in enzymes such as hemocyanin, tyrosinase, and laccase.[22,23] A nitrous oxide reductase ($N_2O \rightarrow N_2$), possibly containing a dinuclear copper site, has also been recently characterized.[25] Further investigations in our laboratories will be directed toward the development of the redox and atom-transfer chemistry of nitrogen oxides with copper complexes.

Acknowledgment. We thank the National Institutes of Health (Grant GM 28962) for support of this research.

Supplementary Material Available: Listing of crystallographic data, atomic coordinates and temperature factors, bond lengths, bond angles, anisotropic temperature factors, and hydrogen coordinates and temperature factors for complex $[Cu_2(XYL\text{-}O^-)(NO)](PF_6)_2\cdot 2CH_2Cl_2$ (6 pages); observed and calculated structure factors for complex $[Cu_2(XYL\text{-}O^-)(NO)](PF_6)_2\cdot 2CH_2Cl_2$ (12 pages). Ordering information is given on any current masthead page.

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(17) (a) Assignment of the ν(NO) IR band was made by the observation of the strong absorption observed for **6**, but not seen either in the precursor **3** nor in $[Cu_2(XYL\text{-}O^-)(OH)](PF_6)_2$. (b) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th ed.; Wiley-Interscience: New York, 1986; p 309.

(18) The formulation of **6** as a $Cu(I)-NO^+-Cu(I)$ complex is unlikely due to (a) the low energy of the ν(NO) IR stretch, (b) the presence of a d-d absorption (>600 nm) indicative of Cu(II) and not the d^{10} Cu(I) ion, and (c) the pentacoordination found in **6**, which is untypical of Cu(I).

(19) Copper(I) complexes with TMPA always are isolated as adducts, $[Cu(TMPA)(L)]^+$ (L = RCN, CO, or PPh_3),[1b] and compound **2** readily reacts with the same ligands L to give $[Cu_2(N4)(L)_2]^{2+}$.[1c]

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Oxidation of Coordinated Thiophene: The Preparation of Cp*Rh(tetramethylthiophene *S*-oxide)

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Received November 9, 1989

The coordination chemistry of thiophene is an active area of research[1] that is relevant to a molecular-level understanding of metal-catalyzed fossil fuel desulfurization.[2-5] Previous research in this area has emphasized the role of the metal in promoting the reduction of the heterocycle. We have discovered a pathway whereby metals facilitate the *oxidation* of coordinated thiophene.

η^4-Thiophene complexes have been described very recently.[6,7] Our studies[7] have focused on Cp*Rh(η^4-TMT), $[\mathbf{1}]^0$ (TMT is 2,3,4,5-tetramethylthiophene), prepared by the cobaltocene reduction of $[Cp^*Rh(\eta^5\text{-TMT})]^{2+}$, $[\mathbf{1}]^{2+}$. The present communication is based on the following experiment: when a toluene solution of $[\mathbf{1}]^0$ is stirred under a dry oxygen atmosphere for 24 h, we observe a clean conversion to the corresponding thiophene S-oxide complex Cp*Rh(TMTO), **2**[8] (Figure 1). Thiophenes are completely unreactive toward oxygen under normal laboratory conditions. 2,5-Di-*tert*-butylthiophene *S*-oxide and 2,5-di-*tert*-octylthiophene *S*-oxide, the only known examples of thiophenic sulfoxides, are prepared by peroxy acid oxidations of the corresponding bulky thiophenes.[9]

The oxygenation reaction of $[\mathbf{1}]^0$ is accompanied by a color change from red to orange and reproducibly affords >90% isolated yields after removal of solvent. The ^{1}H NMR spectrum of **2** consists of three singlets in the ratio 6:15:6. The formulation has been confirmed by the observation of a parent ion in its field desorption mass spectrum (FDMS). The ^{13}C NMR spectrum of **2** shows three resonances in the range for ring carbon atoms, each of which shows coupling to ^{103}Rh. Compared with the data for $[\mathbf{1}]^0$, ^{13}C NMR resonances[10] for the carbon centers adjacent to

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(8) Anal. Calcd for $C_{13}H_{27}ORhS$: C, 54.82; H, 6.90. Found: C, 54.80; H, 6.86. ^{1}H NMR: benzene-d_6 solution, 1.55 (s, 6 H), 1.41 (s, 15 H), 1.39 (s, 6 H); acetone-d_6 solution, 1.81 (s, 6 H), 1.77 (s, 15 H), 1.57 (s, 6 H). ^{13}C NMR: acetone-d_6 solution, 95.4 (s), 88.71 (d, J = 88.7 Hz), 75.46 (d, J = 13.3 Hz). IR (KBr): $\nu_{SO} = 1011$, $\nu_{S^{18}O} = 976$ cm^{-1}.

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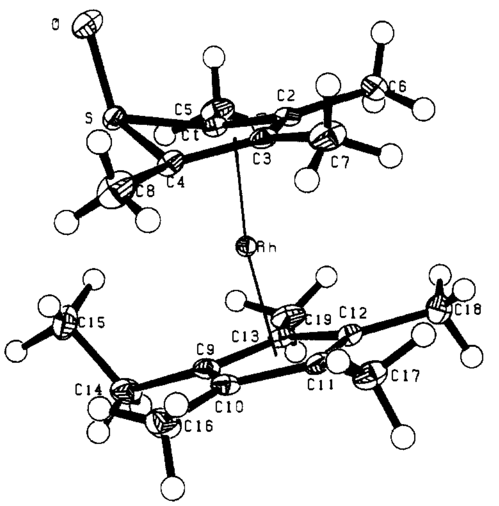


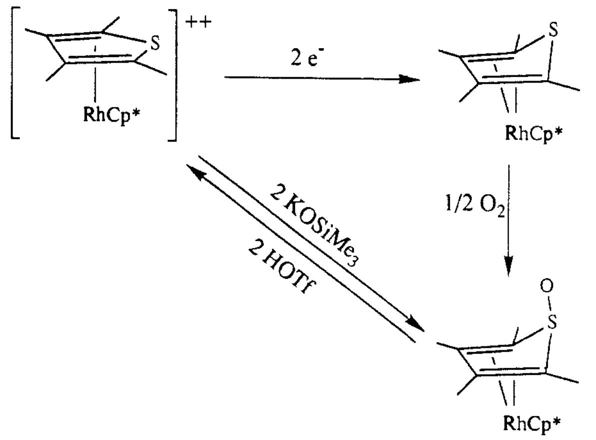
Figure 1. The structure of $(C_5Me_4Et)Rh(C_4Me_4SO)$. Selected bond distances for Rh–C1 through Rh–C4 range from 2.106 (4) to 2.146 (4) Å, and for Rh–C9 through Rh–C13, the range is 2.197 (4)–2.219 (4) Å. Within the thiophene *S*-oxide ring, the distances (in angstroms) are as follows: S-C1, 1.778 (4); C1–C2, 1.430 (4); C2–C3, 1.422 (6); C3–C4, 1.434 (5); C4–S, 1.778 (4).

sulfur are shifted 33 ppm downfield. The IR spectrum of **2** is dominated by a strong band at 1010 cm^{-1} which shifts to 976 cm^{-1} when the compound is prepared under $^{18}O_2$. These absorptions are assigned to ν_{SO} and are about 30 cm^{-1} lower in energy than for conventional sulfoxides.[11]

The structure of $(EtMe_4C_5)Rh(TMTO)$ was confirmed by a high quality single-crystal X-ray diffraction study.[12] The central rhodium atom is coordinated to nine carbon atoms, and the oxygen is bound to sulfur. The TMTO ligand is nonplanar, with the sulfur atom puckered up from the plane of the four ring carbon atoms with a dihedral angle of 30.6 (4)° and a Rh-S distance of 2.846 (2) Å. The oxygen is axial, with an S–O distance of 1.505 (3) Å, slightly longer than those previously observed for sulfoxides. This indicates a more polar S–O bond.[11]

Oxygenation of the TMT ligand strongly modifies the redox properties of the complex. Whereas $[\mathbf{1}]^0$ can be reversibly oxidized at −394 mV vs the Ag/AgCl couple, a cyclic voltammetry experiment shows that **2** resists oxidation until far more positive potentials (≈900 mV). Compound **2** features a reduced metal center (Rh(I)) and an oxidized ligand (S(IV)) whereas $[\mathbf{1}]^{2+}$ features an oxidized metal center (Rh(III)) and a reduced ligand (S(II)). We have explored methods for "redistributing" the sites of oxidation. Thus, protonation of **2** (acetone solution, 2 equiv of HOTf, 0 °C) gives $[\mathbf{1}]^{2+}$,[13] whereas treatment of an Et_2O suspension of $[\mathbf{1}]^{2+}$ with 2 equiv of $KOSiMe_3$ (Aldrich), an anhydrous source of O^{2-}, gave **2** (see Scheme I). Previous work on cationic π-thiophene complexes has shown that nucleophiles attack at carbon;[3] ours is the first example of nucleophilic addition to the sulfur atom.

Scheme I



The direct oxygenation of a thioether is unprecedented, although metal ions are well-known to catalyze this process.[14,15] An oxygen uptake experiment (toluene, 30 min, 25 °C) showed that $[\mathbf{1}]^0$ consumes 0.54 equiv of O_2. The material isolated after 1 h analyzed well for **2**, and the FDMS shows only Cp*Rh(TMTO). The ^1H NMR spectrum, however, shows a mixture of two compounds in a 1:3 ratio, the more abundant of which is Cp*Rh(TMTO), **2**. The minor component has the same ^1H NMR spectral pattern with slightly different shifts. Since the two compounds have the same formula (FDMS) and have very similar ^1H NMR spectra, they could be isomeric forms of Cp*Rh(TMTO).[16] When we monitored the UV-vis spectra for the conversion of $[\mathbf{1}]^0$ into **2**, we observed initial isosbestic behavior corresponding to first-order decay of $[\mathbf{1}]^0$, followed by a slower process. The rate of oxygenation of $[\mathbf{1}]^0$ was first order in $[\mathbf{1}]^0$ and was shown to qualitatively depend on P_{O_2}.

A double labeling experiment[17] confirmed that the thiophene is not released in the course of the oxidation. The stoichiometry and the rate information indicate that the reaction involves the activation of O_2 by $[\mathbf{1}]^0$ followed by a rapid transfer of an oxygen atom to give **2**. The rhodium center in $[\mathbf{1}]^0$ is coordinatively saturated (18e), requiring that the mechanism of dioxygen activation be unconventional. Recent work[6,7] has demonstrated that the sulfur atom in $[\mathbf{1}]^0$ is highly basic.

In summary, we have developed two methods for the oxidation of thiophene giving the first examples of transition-metal thiophene *S*-oxide complexes. Our method involves the activation of molecular oxygen, and the other entails nucleophilic addition to thiophenic sulfur. Both are unprecedented and merit further work with respect to their generality and mechanism.

Acknowledgment. This research was supported by the National Science Foundation. Rhodium trichloride was obtained on loan from Johnson Matthey. We thank Drs. E. A. Ganja for the TMT-d_2 and Ann Ogilvy for useful comments.

Supplementary Material Available: Tables of atomic coordinates and thermal parameters for $C_{19}H_{29}ORhS$ (4 pages); table of observed and calculated structure factors for $C_{14}H_{24}ORhS$ (9 pages). Ordering information is given on any current masthead page.

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(10) The methyl shifts were assigned by using long-range ^1H–^{13}C chemical shift correlation spectroscopy and by comparisons to the spectra for Cp*Rh(TMT-β,β'-d_2) and its oxide.

(11) *The Chemistry of Sulfones and Sulfoxides*; Patai, S., Rappoport, Z.; Stirling, C., Eds.; Wiley: Chichester, 1988.

(12) X-ray crystallography of $C_{19}H_{29}ORhS$: orange, prismatic crystal, 0.2 × 0.3 × 0.5 mm, orthorhombic, $P2_12_12_1$ (D^4_2, No. 19); a = 11.178 (3) Å, b = 11.316 (3) Å, c = 14.366 (3) Å, V = 1817 (1) Å^3, Z = 4, ρ_{calcd} = 1.493 g/cm^3. Diffraction data: mounted in oil (Paratone-N, Exxon) at −100 °C, Enraf-Nonius CAD4 automated κ-axis diffractometer, Mo radiation ($\lambda(K\alpha)$ = 0.71073 Å), graphite monochromator, $2\theta < 14.0°$ ($\pm h,\pm k,\pm l$) and $2\theta < 48.0°$ ($-h,+k,-l$), 2010 intensities, 1663 unique (R_i = 0.018), 1597 observed ($I > 2.58\sigma(I)$); corrected for anomalous dispersion, absorption, extinction, Lorentz, and polarization effects. Solution: direct methods (SHELXS-86); Rh position deduced from E map; remaining atoms located by difference Fourier syntheses. Refinement: least squares (SHELX-76), 316 variables against 1597 data converged with R = 0.018 and R_w = 0.022.

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(16) Isosbestic points at 316, 334, and 388 nm. ^1H NMR shifts for proposed second isomer (C_6D_6): 1.54 (s, 6 H), 1.48 (s, 6 H), 1.43 (s, 15 H).

(17) This experiment was conducted as follows: (1) We prepared $(C_5Me_4Et)Rh(SC_4\text{-}2,5\text{-}Me_2\text{-}3,4\text{-}(CH_2D)_2)$, $[\mathbf{1}'\text{-}d_2]^0$. (2) We showed that solutions of $[\mathbf{1}]^0$ and $[\mathbf{1}'\text{-}d_2]^0$ do not redistribute their ligands in toluene solution for 12 h, followed by evaporation and then collection of the FDMS. (3) We subjected a 1:1 toluene solution of $[\mathbf{1}]^0$ and $[\mathbf{1}'\text{-}d_2]^0$ to standard oxidation conditions (12 h, 1 atm of O_2) followed by analysis by FDMS, which showed only **2** and **2**′-d_2. $SC_4\text{-}2,5\text{-}Me_2\text{-}3,4\text{-}(CH_2D)_2$ was prepared by reaction of $SC_4\text{-}2,5\text{-}Me_2\text{-}3,4\text{-}(CH_2Cl)_2$ with $LiAlD_4$.