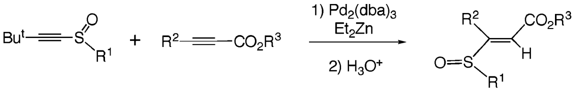
J|A|C|S
COMMUNICATIONS

Sulfoxide Carbon−Sulfur Bond Activation

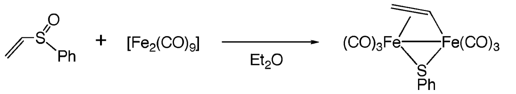
Joseph M. O'Connor,* Kevin D. Bunker, Arnold L. Rheingold,* and Lev Zakharov
Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093

Received January 10, 2005; E-mail: jmoconnor@ucsd.edu

Transition metal insertion into the carbon−sulfur bond of sulfides to give well-characterized oxidative addition products has been achieved for cases involving sp-, sp^2-, and sp^3-hybridized carbon atoms.[1] The widespread use of sulfoxides in synthesis makes carbon−sulfur insertion reactions particularly desirable for higher oxidation state sulfur. Despite the existence of numerous metal−sulfoxide complexes,[2] carbon−sulfur bond activation has not previously been directly observed for sulfoxides. However, indirect evidence for transition metal insertion into the carbon−sulfur bond of sulfoxides is found in the sulfinylzincation reactions of alkynoates (eq 1)[3] and the conversion of phenylsulfinyl ethene and $Fe_2(CO)_9$ to $[Fe_2(\mu\text{-CH=CH}_2)(\mu\text{-SPh})(CO)_6]$ (eq 2).[4]



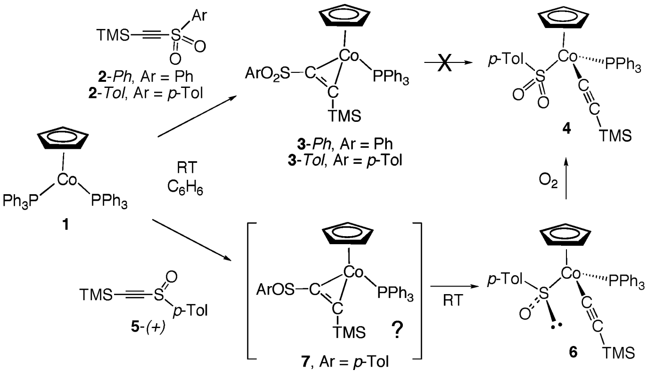
(eq 1)



(eq 2)

We previously reported that $(\eta^5\text{-C}_5H_5)Co(PPh_3)_2$ (**1**) undergoes reaction with alkynyl sulfone **2**-Ph at room temperature to give the η^2-alkyne complex **3**-Ph in 75−80% yield (Scheme 1).[5] There was no evidence for conversion of either **3**-Ph or **3**-Tol to a cobaltosulfone complex (e.g., **4**). We now report that reaction of **1** and an alkynylsulfoxide leads to the first direct observation of carbon−sulfur bond activation involving a sulfoxide.

Scheme 1



When the reaction of **1** (0.013 mmol) and alkynyl sulfoxide **5** (0.013 mmol) was monitored by ^{1}H NMR spectroscopy in benzene-d_6, the cobaltosulfoxide complex **6** was observed to form in 72% yield.[6] In a larger scale reaction, **5** (0.30 mmol) was added to a dry benzene solution (20 mL) of **1** (0.30 mmol), and the mixture was allowed to stir at room temperature under a nitrogen atmosphere for 18 h. Removal of the volatiles and recrystallization of the residue led to isolation of **6** as dark purple, slightly air-sensitive crystals (54% yield). In the IR spectrum (NaCl) of **6**, $\nu(C\equiv C)$ is observed at 2030 cm^{-1} and a strong band at 1064 cm^{-1} is assigned to $\nu(S=O)$.[7] The carbon−carbon triple bond stretch occurs 264 cm^{-1} wavenumbers lower than that for noncoordinated **5**, and this compares with a $\nu(C\equiv C)$ shift of 338 cm^{-1} upon going from **2**-Ph to **3**-Ph. In the $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of **6**, the alkynyl sp-carbons resonate at 90.2 (d, J_{CP} = 62.0 Hz) and 113.1 (d, J_{PC} = 40.4 Hz) ppm, shifted from 90.1 and 100.1 ppm in **5**. For comparison, the sp-carbons of the alkyne ligand in **3**-Ph are observed at 105.5 (d, J_{PC} = 3.5 Hz) and 118.1 (d, J_{PC} = 11.6 Hz) ppm. The observation of an sp-carbon resonance at 90 ppm and the large J_{PC} coupling constants indicated that the expected η^2-alkyne complex (**7**), if formed, had not been isolated. The spectroscopic data and the known insertion of metals into the silicon−carbon bond of trimethylsilyl acetylenes[8] raised the possibility of a $(Cp)Co(PPh_3)(TMS)(C\equiv CSOTol)$ structure for **6**. However, in the mass spectrum (FAB) of **6**, the base peak at 483 *m/z* $[M^+ - SOTol]$ and a fragment at 386 *m/z* [483 − CCTMS] suggested that cobalt had selectively inserted into the (sp)carbon−sulfur bond of **5**.

The metallosulfoxide structure of **6** was conclusively established by an X-ray crystallographic analysis (Figure 1, Table 1). Data collected on a needle of **6**, obtained as described above, refined in the centrosymmetric triclinic space group $P\bar{1}$, indicating that the sample

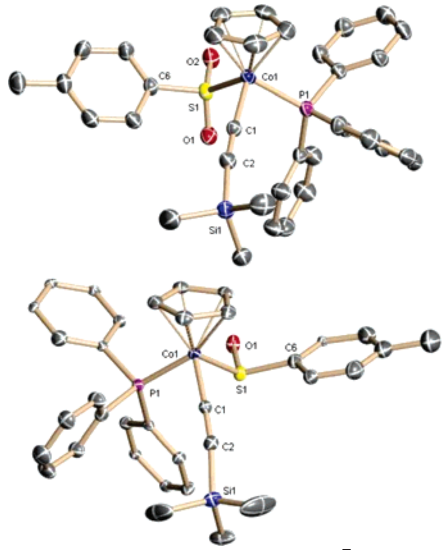


Figure 1. Solid-state molecular structures of **6**-$P\bar{1}$ (bottom) and **4** (top). Ellipsoids at the 30% probability level.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **4** and **6**

complex	**6**-$P\bar{2}(1)/n$	**6**-$P\bar{1}$	**4**-$P\bar{2}(1)/n$
Co(1)−S(1)	2.2196(7)	2.2438(9)	2.2014(8)
Co(1)−P(1)	2.2108(7)	2.2047(9)	2.2391(9)
S(1)−O(1)	1.508(2)	1.513(2)	1.4588(17)
S(1)−O(2)			1.4698(16)
C(1)−Co(1)−S(1)	88.30(8)	88.91(10)	93.54(7)
Co(1)−S(1)−O(1)	108.61(8)	109.54(9)	104.11(11)
Co(1)−S(1)−O(2)			105.29(10)
Co(1)−S(1)−C(6)	106.33(8)	103.92(10)	107.34(8)
O(1)−S(1)−C(6)	105.03(12)	104.43(13)	114.27(7)
O(2)−S(1)−C(6)			109.47(7)
S(1)−Co(1)−P(1)	91.97(3)	90.73(3)	95.40(3)
Co(1)−C(1)−C(2)	176.1(2)	176.1(3)	174.5(2)
C(1)−Co(1)−P(1)	87.30(8)	91.98(9)	89.84(7)

10.1021/ja050160g CCC: $30.25 © 2005 American Chemical Society

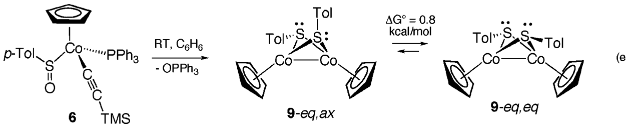
was a racemate.[9] Structural analysis of a second crystal, grown by slow evaporation of a benzene solution containing **6**, belonged to the centrosymmetric monoclinic space group $P2(1)/n$. Both polymorphs exhibited the same $S_{Co},R_S/R_{Co},S_S$ relative configurations. The sulfur atom in both structures of **6** exhibits a trigonal pyramidal geometry and is situated an average of 0.686 Å from the plane defined by Co(1), C(6), and O(1). This displacement is typical of other sulfenato ligands and organic sulfoxides (0.7−0.8 Å range). The average S(1)−O(1) [1.510(2) Å] and S(1)−C(6) [1.804(3) Å] distances in **6** are remarkably similar to those found in MeS(═O)-Tol [1.493(6) and 1.797(6) Å]. However, the Co(1)−S(1)−C(6) angle of 105.1° in **6** is 7.5° larger than the Me−S−Tol angle for MeS(═O)Tol,[10] which may be attributed to greater steric congestion in **6**.

There are four structurally characterized cobaltosulfoxide complexes, all of which involve chelating [η^2-(N,S)-$H_2N(CHR)(CH_2)_nS(O)$] sulfenate ligands.[11−13] The average Co−S and S−O distances in this set of structures is 2.232 and 1.540 Å, respectively. More specifically, $(NH_2CH_2CH_2NH_2)_2Co(NH_2CH_2CH_2SO)][SCN]_2$ (**8**) exhibits a 96.51° Co−S−C angle, a S−O distance of 1.552(3) Å, and ν(S═O) of 986 cm^{-1}.[11a] The sulfur−oxygen bond in **6** is significantly less polarized than that in **8**, based on the shorter S−O distance (1.510 Å) and higher frequency ν(S═O) stretch (1064 cm^{-1}) observed for **6**.

Metallosulfoxide **6** is capable of acting as both an oxygen atom acceptor and an oxygen atom donor. Exposure of a benzene solution of **6** to oxygen gas led to the formation of the metallosulfone **4**, which was isolated as bright-red crystals in 18% yield (Scheme 1).[14] Ground state O_2 is known to oxidize both thiolato and *cis*-disulfenato ligands;[12b,15] however, we are unaware of a precedent for conversion of a single sulfenato ligand to a sulfinato ligand upon reaction with O_2.[16] Although it would be attractive to assume direct O_2 oxidation of sulfur, the current data do not allow for such a conclusion to be made.[17]

A comparison of the solid-state structure of **4** (Figure 1) to that for **6** reveals slightly larger S(1)−Co(1)−P(1) and S(1)−Co(1)−C(1) angles in the more congested metallosulfone. The sulfur ligands adopt very similar conformations with Cp−Co(1)−S(1)−O(1) and C(7)−C(6)−S(1)−O(1) torsion angles of −59.6 and −20.5° for **6** versus Cp−Co(1)−S(1)−O(2) and C(7)−C(6)−S(1)−O(2) torsion angles of +51.2 and −12.4° in **4**.

In benzene-d_6, **6** is slowly (months) transformed into a 4:1 ratio of thiolato-bridged cobalt dimers, **9**-*eq*,*ax* and **9**-*eq*,*eq*, in 85% combined yield (eq 3).[18] In addition, $OPPh_3$ (77%) and TMSC≡CC≡CTMS (43%) are observed as byproducts. Chromatographic workup of a large-scale reaction led to the collection of two distinct fractions (orange and green), but with the orange fraction rapidly turning green over the course of 15 min. ^{1}H NMR spectroscopic analysis of the two fractions indicated the same 4:1 ratio of dimers. Dark-green crystals of **9**-*eq*,*eq* were grown by slow evaporation of solvent, and an X-ray crystallographic analysis provided the first structural characterization of an *eq*,*eq*-$[CpM(SR)]_2$ complex. In benzene-d_6 at 70 °C, the two isomers of **9** interconvert rapidly on the NMR time scale, and the E_{act} for conversion of **9**-*eq*,*ax* to **9**-*eq*,*eq* was determined to be 74.9 ± 0.5 kJ/mol. For comparison, both at low temperature and in the solid state, $[CpCo(SBu^t)]_2$ is observed only as an *eq*,*ax*-isomer, which is reported to rapidly interconvert with the *ax*,*eq*-isomer at higher temperature (E_{act} = 60 kJ/mol).[19]



(eq 3)

Acknowledgment. Support of the National Science Foundation (CHE-9975939) is gratefully acknowledged.

Supporting Information Available: Experimental procedures, characterization data for all new compounds, and crystallographic data for **4**, **6**, and **9**-*eq*,*eq*. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For leading references, see: (a) Matsunaga, P. T.; Hillhouse, G. L. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1748. (b) Vicic, D. A.; Jones, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 7606. (c) Chen, J.; Angelici, R. J. *Coord. Chem. Rev.* **2000**, *206−207*, 63. (d) Savarin, C.; Srogl, J.; Liebeskind, L. S. *Org. Lett.* **2001**, *3*, 91.

(2) Alessio, E. *Chem. Rev.* **2004**, *104*, 4203.

(3) Maezaki, N.; Yagi, S.; Ohsawa, S.; Ohishi, H.; Tanaka, T. *Tetrahedron* **2003**, *59*, 9895 and references therein.

(4) Ibbotson, A.; Reduto dos Reis, A. C.; Saberi, S. P.; Slawin, A. M. Z.; Thomas, S. E.; Tustin, G. J.; Williams, D. J. *J. Chem. Soc.*, *Perkin Trans. 1* **1992**, 1251.

(5) O'Connor, J. M.; Ji, H.-L.; Iranpour, M.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 1586.

(6) We are aware of only two organometallic sulfenato complexes: (a) George, T. A.; Watkins, D. D. *Inorg. Chem.* **1973**, *12*, 398. (b) Heinrich, L.; Mary-Verla, A.; Li, Y.; Vaissermann, J.; Chottard, J.-C. *Eur. J. Inorg. Chem.* **2001**, 2203.

(7) The SO stretch assignment is supported by the absence of the 1064 cm^{-1} band in the spectrum of metallosulfone **4** (vide infra).

(8) Müller, C.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **2002**, *21*, 1190 and references therein.

(9) For racemization of sulfenate ligands, see: Kita, M.; Yamanari, K.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2873.

(10) De la Camp, U.; Hope, H. *Acta Crystallogr.* **1970**, *B26*, 846.

(11) (a) Adzamli, I. K.; Libson, K.; Lydon, J. D.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1979**, *18*, 303. (b) Jackson, W. G.; Sargeson, A. M.; Whimp, P. O. *J. Chem. Soc.*, *Chem. Commun.* **1976**, 934. (c) Kita, M.; Yamanari, K.; Kitahama, K.; Shimura, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2995. (d) Okamoto, K.; Konno, T.; Einaga, H.; Hidaka, J. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 393.

(12) For metallosulfoxide structures of other metals, see: (a) Weigand, W.; Wünsch, R. *Chem. Ber.* **1996**, *129*, 1409. (b) Grapperhaus, C. A.; Darensbourg, M. Y. *Acc. Chem. Res.* **1998**, *31*, 451. (c) Kovacs, J. A. *Chem. Rev.* **2004**, *104*, 825.

(13) Reaction of **1** with **5** may involve precoordination at the alkyne, the sulfoxide oxygen, or the sulfoxide sulfur. The observation that **4** does not undergo carbon−sulfur bond activation suggests one of the latter two possibilities. For a structurally characterized cobalt η^2-sulfenate complex, see: Kung, I.; Schweitzer, D.; Shearer, J.; Taylor, W. D.; Jackson, H. L.; Lovell, S.; Kovacs, J. A. *J. Am. Chem. Soc.* **2000**, *122*, 8299.

(14) For organometallic metallosulfones, see: (a) Wojcicki, A. *Adv. Organomet. Chem.* **1974**, *12*, 31. (b) Lefort, L.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 1420 and references therein.

(15) Buonomo, R. M.; Font, I.; Maguire, M. J.; Reibenspies, J. H.; Tuntulani, T.; Darensbourg, M. Y. *J. Am. Chem. Soc.* **1995**, *117*, 963.

(16) Conversion of a bis(sulfenate) complex to a bis(sulfinate) upon reaction with triplet oxygen has been suggested to involve addition of a single O_2 across the two *cis*-sulfur atoms (see ref 15).

(17) Nickel sulfenates serve as O atom donors/acceptors: Farmer, P. J.; Verpeaux, J.-N.; Amatore, C.; Darensbourg, M. Y.; Musie, G. *J. Am. Chem. Soc.* **1994**, *116*, 9355.

(18) Complex **9** has been previously reported, but with no characterization data or comment on the existence of two isomers: Frisch, P. D.; Lloyd, M. K.; McCleverty, J. A.; Seddon, D. *J. Chem. Soc.*, *Dalton Trans.* **1973**, 2268.

(19) Shaver, A.; Morris, S.; Turrin, R.; Day, V. W. *Inorg. Chem.* **1990**, *29*, 3622.

JA050160G