3790 *Organometallics* **1993,** *12,* 3790–3791

Facile Transformation of a Metal Carbonyl to a Metal Carbonyl Sulfide by Reaction with Elemental Sulfur

Peng-Fei Fu, Masood A. Khan, and Kenneth M. Nicholas*

Department of Chemistry and Biochemistry, University of Oklahoma,
Norman, Oklahoma 73019

Received July 8, 1993®

Summary: Elemental sulfur (S_8) enters into a remarkably facile and unprecedented addition reaction with $(MeCp)_2Nb(CO)CH_2Si(CH_3)_3$ (1) at room temperature, converting it to the carbonyl sulfide complex $(MeCp)_2Nb(\eta^2\text{-}COS)CH_2Si(CH_3)_3$ (2). The following key spectroscopic features of 2 indicate the presence of coordinated COS: (1) mass spectral peaks at m/e 398 (M^+), 370 ($M^+ - CO$), and 338 ($M^+ - COS$) (2) a ^{13}C NMR resonance at 249.1 ppm assigned to coordinated COS, and (3) an isotopically shifted $\nu(C{=}O)$ IR band of 2 at 1639 cm^{-1} (THF) when prepared from $(MeCp)_2Nb(^{13}CO)CH_2Si(CH_3)_3$ and S_8, consistent with an $\eta^2(C,S)$ mode. The presence of the C,S-coordinated COS molecule has been established by an X-ray diffraction study. Complex 2 is also produced (25% yield) by Na/Hg reduction of $(MeCp)_2Nb(Cl)CH_2Si(CH_3)_3$ (THF/20 °C/1 h) under an atmosphere of COS.*

The sulfurization of carbon monoxide to carbonyl sulfide (COS) over heterogeneous transition-metal-based catalysts is an important process for both the manufacture of the latter[1] and the production of synthesis gas from sulfur-rich coal.[2] Homogeneous transition-metal models for this reaction, however, are lacking. Scattered examples of reactions of sulfur with metal carbonyls document the formation of metal sulfides[3] and dithiocarbonates.[4] Furthermore, the coordination chemistry of COS is surprisingly limited,[5] with only a small number of adducts having been isolated[6] (none apparently crystallographically characterized) and a marked tendency of COS to undergo C–S cleavage reactions, resulting in S-transfer and carbonylation.[5,7] In seeking to define the reactivity of metal carbonyl compounds with group 16 elements,[8] we have now discovered that elemental sulfur enters into a remarkably facile and unprecedented insertion reaction with $(MeCp)_2Nb(CO)CH_2Si(CH_3)_3$ (1), converting it to the carbonyl sulfide complex $(MeCp)_2Nb(\eta^2\text{-}COS)CH_2Si(CH_3)_3$ (2).

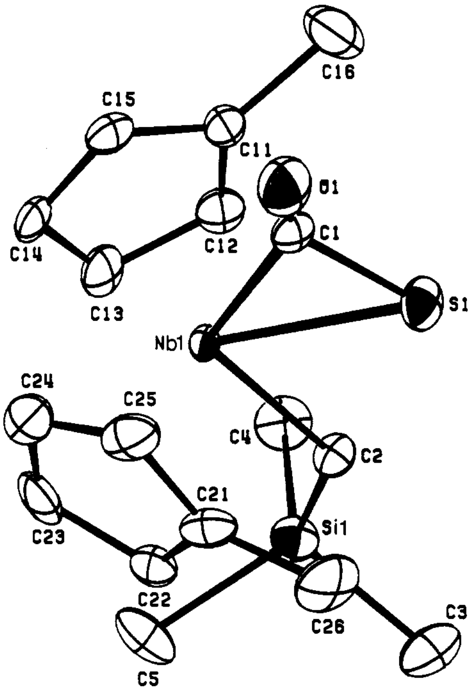
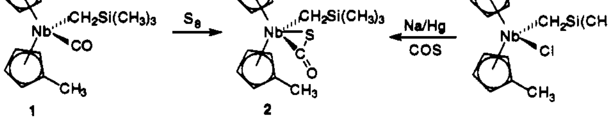


Figure 1. ORTEP drawing of $(\eta^5\text{-}MeCp)_2Nb(\eta^2\text{-}COS)CH_2Si(CH_3)_3$ (2).

Treatment of dark green 1[8,9] (1.0 mmol) with S_8 (1.0 mmol) in THF at 20 °C causes a gradual color change to a yellow solution over 1 h, accompanied by disappearance of the M–CO IR absorption of 1 (1884 cm^{-1}) and the appearance of a prominent new band at 1679 cm^{-1} (eq 1).



(1)

After solvent evaporation golden yellow crystals of 2 (54% yield) of composition $(MeCp)_2Nb(COS)CH_2Si(CH_3)_3$[10] were isolated upon recrystallization of the residue from hexane. The following key spectroscopic features[10] of 2 indicate the presence of coordinated COS: (1) mass

---

® Abstract published in *Advance ACS Abstracts,* September 1, 1993.

[1] Review: *Kirk-Othmer Concise Encyclopedia of Chemical Technology*; Wiley: New York, 1985; p 1131. Imanari, M.; Hoya, T.; Mogi, H. Jpn. Kokai JP60,251,111; *Chem. Abstr.* **1986,** *104,* 13247y. Luo, D. *Huanjing Kexue* **1989,** *10,* 42; *Chem. Abstr.* **1989,** *111,* 236038e.

[2] Reviews: Weissermel, K.; Arpe, H.-J. In *Industrial Organic Chemistry*; Verlag Chemie: Weinheim, Germany, 1978; p 20.

[3] Lincoln, S.; Soong, S.-L.; Koch, S. A.; Sato, M.; Enemark, J. H. *Inorg. Chem.* **1985,** *24,* 1355. Johnson, B. F. G.; Lewis, J.; Lodge, P. G.; Raithby, P. R. *J. Chem. Soc., Chem. Commun.* **1979,** 719.

[4] Namethkin, N. S.; Kolobkov, B. I.; Tyurin, V. D.; Muratov, A. N.; Nekhaev, A. I.; Aleksandrov, G. G.; Lebedev, A. V.; Tashev, M. T.; Dustov, H. B. *J. Organomet. Chem.* **1984,** *276,* 393.

[5] Ibers, J. A. *Chem. Soc. Rev.* **1982,** *11,* 57.

[6] (a) Baird, M. C.; Wilkinson, G. *J. Chem. Soc. A* **1967,** 865. (b) van Gaal, H. L. M.; Verlaan, L. P. J. *J. Organomet. Chem.* **1977,** *133,* 93. (c) Uhlig, E.; Poppitz, W. *Z. Chem.* **1979,** *19,* 191. (d) Gaffney, T. R.; Ibers, J. A. *Inorg. Chem.* **1982,** *21,* 2851, 2854, 2860.

[7] (a) Bryan, J. C.; Geib, S. J.; Reingold, A. L.; Mayer, J. M. *J. Am. Chem. Soc.* **1987,** *109,* 2826. (b) Nemetkin, N. S.; Kolobkov, B. J.; Tyurin, V. D.; Muratov, A. N.; Nekhaev, A. I.; Mavlonov, M.; Sideridu, A. Y.; Aleksandrov, G. G.; Lebedev, A. V.; Tashkev, M. T.; Dustov, H. B. *J. Organomet. Chem.* **1984,** *276,* 393. (c) Glidewell, C. *J. Organomet. Chem.* **1985,** *295,* 73.

[8] Fu, P.; Khan, M. A.; Nicholas, K. M. *J. Am. Chem. Soc.* **1992,** *114,* 6579.

[9] Fu, P. Ph.D. Dissertation, University of Oklahoma, 1993.

[10] 2: yellow crystals; IR (KBr, cm^{-1}) 3102 (w), 2969 (m), 2923 (m), 2856 (w), 1656 (vs), 1259 (s), 1094 (vs), 1026 (vs), 845 (s), 812 (vs), 674 (s); MS (FAB) *m/e* (%) 398.0 (4), 370.0 (70), 338.0 (99.5), 282.9 (100); ^1H NMR (300 MHz, C_6D_6, δ) 5.24 (m, 1H, Cp), 5.10 (m, 2H, Cp), 4.62 (m, 2H, Cp), 4.53 (m, 2H, Cp), 1.72 (s, 2H, CH_2), 1.53 (s, 6H, Cp–CH_3), 0.04 (s, 9H, $Si(CH_3)_3$); ^{13}C NMR (100 MHz, C_6D_6, δ) 249.1, 120.1, 112.3, 105.8, 96.9, 95.6, 17.5, 14.2, 4.0. Anal. Calcd for $C_{17}H_{25}NbOSiS$: C, 51.26; H, 6.28; S, 8.04. Found: C, 51.05; H, 6.20; S, 8.37.

0276-7333/93/2312-3790$04.00/0

spectral peaks at *m/e* 398 (M^+), 370 ($M^+ - CO$), and 338 ($M^+ - COS$), (2) a ^{13}C NMR resonance at 249.1 ppm assigned to coordinated *C*OS,[11,12] and, most importantly, (3) an isotopically shifted $\nu_{C=O}$ IR band of 2 from 1679 to 1639 cm^{-1} (THF) when derived from the reaction of $(MeCp)_2Nb(^{13}CO)CH_2Si(CH_3)_3$ with S_8, consistent with an η^2(C,S) mode.[14] Furthermore, we find that 2 is also produced (25% yield) by Na/Hg reduction of $(MeCp)_2Nb(Cl)CH_2Si(CH_3)_3$ (THF/20 °C/1 h) under an atmosphere of COS (eq 1).

Formulation of 2 as an η^2(*C*,*S*)-COS complex has been confirmed by single-crystal X-ray diffraction (Figure 1).[15] Despite an apparent disorder problem in the C–O unit of 2 which causes unrealistic Nb–C(1) and C(1)–O(1) bond lengths, the presence of the C,S-coordinated COS molecule is unambiguous. The structure of 2 consists essentially of a bent niobocene unit (Cp′-Nb-Cp′ = 131.5°) bisected by the Nb(COS) plane (Cp′NbCp′/COS = 92.9°). All other bond lengths and angles[16] are comparable to those in related, crystallographically characterized $(MeCp)_2Nb(\eta^2\text{-}CO_2)R$[17] and $Cp_2Nb(\eta^2\text{-}CS_2)R$[18] complexes. Compound 2 thus simultaneously provides the first X-ray crystallographically verified COS complex and the first early-transition-metal COS complex, and it also completes the first trio of $CO_2/COS/CS_2$ adducts of the same organometallic fragment, paving the way for comparative reactivity studies. The preferential η^2(C,S) coordination in 2 is especially noteworthy in light of the oxophilic nature of the Cp_2NbR fragment.[20] Whether this represents the kinetically or thermodynamically favored bonding mode is not yet clear, but the energetic dividend of Nb–O bond formation of the alternative η^2(C,O) mode would come at the expense of the strong C=O bond.

The addition process exemplified by eq 1 represents a new reaction type for elemental sulfur and may serve as a model for the key step in the catalytic conversion of CO and sulfur to COS over metal oxide/sulfide catalysts.[1] Its apparent similarity to the recently discovered conversion of carbonyl complex 1 to $Cp'_2Nb(\eta^2\text{-}CO_2)R$ by dioxygen[8] is striking, considering the usually divergent reactions of these group 16 elements.[21] Their extraordinary facility and unknown mechanisms are intriguing, especially given the coordinative saturation of carbonyl complex 1. We hope to address these issues in studies which are underway.

Acknowledgment. We are grateful for financial support provided by the U.S. Department of Energy, Chemistry Program, Office of Basic Energy Sciences (Grant No. 89ER 13997).

Supplementary Material Available: X-ray data for 2, including tables of atomic positional and thermal parameters, bond lengths, and angles (7 pages). Ordering information is given on any current masthead page.

OM930461B

---

[11] Compare with the ^{13}C NMR chemical shifts (δ) for *C*XY of $(RCp)_2Nb(\eta^2\text{-}CXY)CH_2R'$: $(CH_3Cp)_2Nb(\eta^2\text{-}CO_2)CH_2Si(CH_3)_3$, 201;[12] $(Cp)_2Nb(\eta^2\text{-}CS_2)CH_3$, 317 ppm.[13]

[12] Bristow, G. S.; Hitchcock, P. B.; Lappert, M. F. *J. Chem. Soc., Chem. Commun.* **1981**, 1145.

[13] Amaudrut, J.; Sala-Pala, J.; Guerchais, J. E.; Mercier, R.; Douglade, J. *J. Organomet. Chem.* **1982**, *235*, 301.

[14] IR ν(C=O) bands for previously claimed η^2(*C*,*S*)-COS complexes are between 1700 and 1740 cm^{-1}.[6]

[15] Crystals of 2 were obtained from ether/hexane; X-ray data on crystals from two different preparations were collected at 295 and 160 K on a CAD-4 diffractometer using monochromated Mo Kα radiation. Crystal data at 160 K: $C_{17}H_{25}NbOSSi$, $M_r = 398.44$, space group *Pbca*, $a = 13.474(3)$ Å, $b = 17.534(4)$ Å, $c = 15.101(4)$ Å, $V = 3567.7$ Å^3, $Z = 8$, $D_c = 1.484$ g cm^{-3}, $F(000) = 1648$, $\lambda = 0.710\,69$ Å (Mo Kα), $\mu = 7.9$ cm^{-1}, 3139 total reflections measured, 2045 reflections observed ($I > 2\sigma(I)$), $R = 0.043$, $R_w = 0.056$, $S = 1.9$, (Δ/σ) in the final cycle 0.01, $(\Delta\epsilon)_{max}$ in the final difference map 0.60 e Å^{-3}. The structure was solved by the heavy-atom method and refined by the full-matrix least-squares method (SHELX-76). Difficulties were encountered during the refinement because of a disorder in the C(1)–O(1) unit manifested by a peak of 5 e Å^{-3} between C(1) and O(1) present in the data sets at both temperatures. Various models using minor isomorphous contaminants or a constrained COS group did not lead to satisfactory refinement, so finally the O(1) and C(1) atoms were refined anisotropically without any restraints, giving final atomic positions with an unrealistically short C–O length (0.950(8) Å).

[16] $(CH_3Cp)_2Nb(\eta^2\text{-}COS)CH_2Si(CH_3)_3$: Nb–*C* = 2.312(8) Å, Nb–S = 2.503(2) Å, C–S = 1.833(7) Å, C=O = 0.950(8) Å (see comments in ref 15).

---

[17] $(CH_3Cp)_2Nb(\eta^2\text{-}CO_2)CH_2Ph$:[8] Nb–*C* = 2.15 Å, Nb–O = 2.17 Å, C–O = 1.29 Å, C=O = 1.21 Å. $(CH_3Cp)_2Nb(\eta^2\text{-}CO_2)CH_2Si(CH_3)_3$:[12] Nb–*C* = 2.14 Å, Nb–O = 2.17 Å, C–O = 1.28 Å, C=O = 1.22 Å.

[18] $Cp_2Nb(\eta^2\text{-}CS_2)CH_3$:[19a] Nb–*C* = 2.21 Å, Nb–S = 2.50 Å, C–S = 1.67 Å, C=S = 1.60 Å. $Cp_2Nb(\eta^2\text{-}CS_2)CH_2CH{=}CH_2$:[19b] Nb–*C* = 2.24 Å, Nb–S = 2.51 Å, C–S = 1.72 Å, C=S = 1.57 Å.

[19] (a) Mercier, R.; Douglade, J.; Amaudrut, J.; Sala-Pala, J.; Guerchais, J. *Acta Crystallogr.* **1980**, *B36*, 2986. (b) Drew, M. G. B.; Pu, L. S. *Acta Crystallogr.* **1977**, *B33*, 1207.

[20] Fu, P.-F.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1991**, *10*, 382. Fu, P.-F.; Khan, M. A.; Nicholas, K. M. *Organometallics* **1992**, *11*, 2607. Savaranamuthu, A.; Bruce, A. E.; Bruce, M. R. M.; Fermin, M. C.; Hneihen, A. S.; Bruno, J. W. *Organometallics* **1992**, *11*, 2190.

[21] Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed., Wiley: New York, 1980; pp 503–505.