metal sulfide catalysts where reactivity at sulfur is apparently critical to their function. Efforts to isolate 2 without the SO_2 groups and to determine the reactivity of the μ_2-S ligands are underway.

Acknowledgment. This work was performed under the auspices of the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences.

Registry No. 1, 92468-48-9; 1·SO_2, 94024-80-3; 2, 94024-81-4; $CpMo(CO)_3(SO_2H)$, 94024-82-5; $[CpW(CO)_3]_2$, 12091-65-5; $[CpMo(CO)_3]_2S$, 94024-83-6; $Cp^*_2W_2(CO)_2S_3$, 94024-84-7; $CpW(CO)_3H$, 12128-26-6; $CpMo(CO)_3H$, 12176-06-6; $Cp^*W(CO)_3H$, 32839-62-6; SO_2, 7446-09-5.

Supplementary Material Available: Lists of structure factor amplitudes, positional and thermal parameters, and distances and angles (16 pages). Ordering information is given on any current masthead page.

Synthesis and Structure of a Rhodacyclobutene Complex Formed by Addition of Two $F_3CC{\equiv}CCF_3$ Molecules to a Rh–η^2-CS_2 Moiety

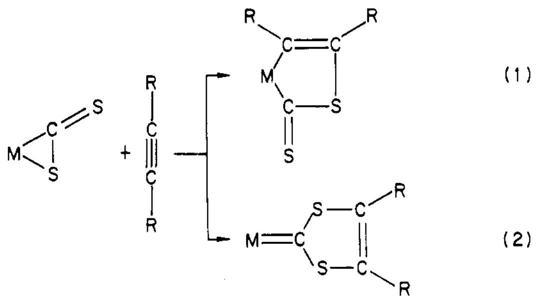
Claudio Bianchini,* Carlo Mealli,* Andrea Meli,* and Michal Sabat*

*Istituto per lo Studio della Stereochimica ed
Energetica dei Composti di Coordinazione
CNR, 50132 Firenze, Italy*

Received September 20, 1984

Summary: The complex (triphos)RhCl(η^2-CS_2) [triphos = 1,1,1-tris((diphenylphosphino)methyl)ethane] reacts with two molecules of $F_3CC{\equiv}CCF_3$, to give the rhodacyclobutene complex (triphos)ClRhC(CF_3)=C(CF_3)CSC(CF_3)=C(CF_3)S whose structure has been established by X-ray methods.

Acetylenes with electron-withdrawing substituents are known to react with η^2-CS_2 metal complexes. Generally, one molecule of activated acetylene adds to the metal–η^2-CS_2 moiety. The nature of the metal fragment and of the coligands determine whether heterocyclic five-membered metalla ring complexes (eq 1)[1,2] or 1,3-dithiol-2-ylidene derivatives (eq 2)[2,3] are formed.



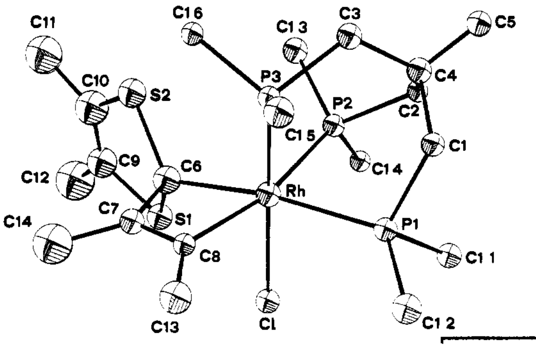
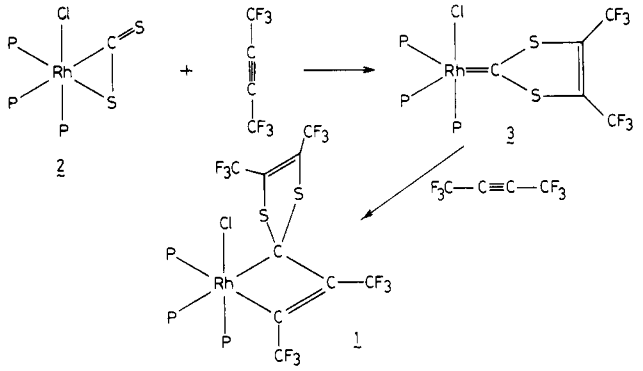


Figure 1. ORTEP drawing of the (triphos)ClRhC(CF_3)=C(CF_3)CSC(CF_3)=C(CF_3)S molecule. For the sake of clarity the phenyl rings (except for the connecting C atoms) and the F atoms of the trifluoromethyl groups are not shown. Some relevant bond lengths (Å) and angles (deg) are as follows: Rh–Cl = 2.427 (9); Rh–P1 = 2.446 (8); Rh–P2 = 2.454 (10); Rh–P3 = 2.305 (9); Rh–C6 = 2.15 (3); Rh–C8 = 2.09 (3); S1–C6 = 1.83 (3); S2–C6 = 1.85 (3); C6–C7 = 1.50 (4); C7–C8 = 1.30 (4); C9–C10 = 1.36 (5). C6–Rh–C8 = 64 (1); S1–C6–C2 = 105 (2).

Scheme I



Herein we report the synthesis and the crystal structure of the rhodacyclobutene complex (triphos)ClRhC(CF_3)=C(CF_3)CSC(CF_3)=C(CF_3)S (1) [triphos = 1,1,1-tris(diphenylphosphino)methyl)ethane], which is obtained by the unprecedented addition of two molecules of $F_3CC{\equiv}CCF_3$ to the Rh–η^2-CS_2 moiety of (triphos)RhCl(η^2-CS_2)[4] (2). Yellow crystals of 1[5] are formed in 90% yield by reacting at room temperature a twofold excess of hexafluorobut-2-yne with a methylene chloride solution of 2.[6] The crystal structure of 1[7] consists of mononuclear units where the rhodium atom has a pseudooctahedral coordination given by the three phosphorus atoms of triphos, one chlorine atom, and two carbon atoms from the chelating ligand SC(CF_3)C(CF_3)SCC(CF_3)C(CF_3), which is formed in situ (Figure 1). The latter ligand contains the five-membered

---

(1) Wakatsuki, Y.; Yamazaki, H.; Iwasaki, H. *J. Am. Chem. Soc.* **1973**, *95*, 5781.

(2) Le Bozec, H.; Gorgues, A.; Dixneuf, P. H. *Inorg. Chem.* **1981**, *20*, 2486.

(3) (a) Le Marouille, J. Y.; Lelay, C.; Benoit, A.; Grandjean, D.; Touchard, D.; Le Bozec, H.; Dixneuf, P. *J. Organomet. Chem.* **1980**, *191*, 133. (b) Frazier, C. C.; Magnussen, N. D.; Osuji, L. H.; Parker, K. O. *Organometallics* **1982**, *1*, 903. (c) Schenk, W. A.; Schwietzke, T.; Müller, H. *J. Organomet. Chem.* **1982**, *232*, C41. (d) Bianchini, C.; Meli, A. *J. Chem. Soc., Chem. Commun.* **1983**, 1309. (e) Bianchini, C.; Meli, A.; Scapacci, G. *Organometallics*, in press.

(4) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.*, in press.

(5) IR (Nujol mulls): ν(C=C) 1625, 1605 cm^{-1}, ν(CF) 1270, 1240, 1170, 1130 cm^{-1}. Anal. Calcd: C, 51.62; H, 3.37; Rh, 8.84; S, 5.51. Found: C, 51.43; H, 3.48; Rh, 8.79; S, 5.46.

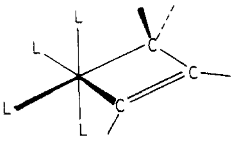
(6) When equimolecular amounts of hexafluorobut-2-yne and 2 are reacted, yellow crystals of 1 are obtained in ca. 40% yield. Unreacted 2 can be recovered in almost the same yield from the reaction mixture.

(7) Crystallographic data for 1: hexagonal, a = 23.425 (6) Å, c = 18.982 (5) Å, space group $P6_1$, Z = 6, d_{calcd} = 1.28 g/cm^3, μ(Mo Kα) = 5.33 cm^{-1}. Intensity data were collected by standard methods in this institute. The structure was solved by Patterson and Fourier techniques using the SHELX76 program package.[8] Refinement converged at R = 0.064 and R_w = 0.061 for 1339 absorption corrected reflections with $I > 3\sigma(I)$ measured on a Philips PW 1100 diffractometer with Mo Kα radiation (2.5 < θ < 25°). The fluorine atoms of one of the hexafluorobut-2-yne molecules were found disordered. The phenyl rings were treated as rigid groups of the D_{6h} symmetry.

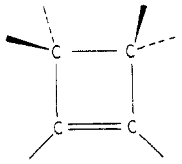
(8) Sheldrick, G. M., SHELX76, Program for Crystal Structure Determinations, University of Cambridge, Cambridge, England, 1976.

0276-7333/85/2304-0421$01.50/0

$\overline{\mathrm{CSC(CF_3)C(CF_3)S}}$ heterocycle. To achieve a simple but useful description of the complicated structure of 1, the concept of isolobal analogy[9] is used. The fragment (triphos)ClRh(I) may be taken as a d^8 L_4M fragment with C_{2v} symmetry, which in turn is isolobal with CH_2. Thus the skeleton 3 of the complex may be related to a cyclobutene derivative, 4. This description is supported by the value of the C(7)–C(8) double bond distance of 1.30 (4) Å and by the almost tetrahedral geometry about C(6). The latter atom is displaced ca. 0.39 Å from the plane of the CS_2C_2 ring, and such a deformation from planarity is another evidence of the strong tendency of C(6) toward sp^3 hybridization. Accordingly, we may consider this compound as a new unusual example of a spirane-like organometallic structure where C(6) is shared by two cyclic groups.

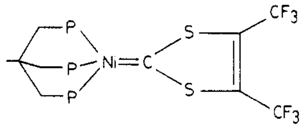


3

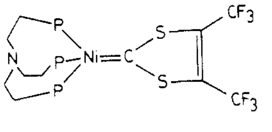


4

In the absence of kinetic measurements as well as of detectable intermediates, it should be hazardous to propose a detailed mechanism for the formation of 1. Tentatively, a reasonable reaction pathway is the one shown in Scheme I, in which the intermediacy of a dithiocarbene complex of type 3 is hypothesized. As mentioned above, in fact, the formation of 1,3-dithiol-2-ylidene complexes by reaction of η^2-CS_2 compounds with activated alkynes is quite common. In particular, the compounds (triphos)Ni[$CS_2C_2(CF_3)_2$][3d] (5) and (np$_3$)Ni[$CS_2C_2(CF_3)_2$][3e] (6) have been obtained by reacting $F_3CC{\equiv}CCF_3$ with (triphos)Ni(η^2-CS_2) and (np$_3$)Ni(η^2-CS_2), respectively. Unfortunately, all our attempts to isolate the 1,3-dithiol-2-ylidene derivative were unsuccessful.



4



This communication reports a new reaction of η^2-CS_2 metal complexes and might provide useful information on alkene and alkyne metathesis reactions. Key intermediates of these reactions are believed to be, in fact, metallacyclobutane or metallacyclobutadiene complexes which may be formed by metal-assisted coupling of alkenes or alkynes with carbene or carbyne ligands.[10]

Registry No. 1, 94070-31-2; 2, 92669-51-7; hexafluorobut-2-yne, 692-50-2.

Supplementary Material Available: Listings of atomic parameters for (triphos)Cl$\overline{\mathrm{RhC(CF_3)}{=}\mathrm{C(CF_3)C}}$$\underline{\mathrm{SC(CF_3)}{=}\mathrm{C(CF_3)S}}$ (Tables I and II) and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

---

(9) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711.

(10) (a) Grubbs, R. H. *Prog. Inorg. Chem.* **1978**, *24*, 1. (b) Calderon, N.; Lawrence, J. P.; Ofstead, E. *Adv. Organomet. Chem.* **1979**, *17*, 449. (c) Wengrovious, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932. (d) Churchill, M. R.; Wasserman, N. J. *J. Organomet. Chem.* **1984**, *270*, 201.

Vinyloxomolybdenum(VI) Complexes Produced by Protonation of Coordinated Acetylenes[†]

Grace. J.-J. Chen, John W. McDonald,* and W. E. Newton*[‡]

Battelle-C.F. Kettering Research Laboratory
Yellow Springs, Ohio 45387

Received September 6, 1984

Summary: Vinyloxomolybdenum(VI) complexes have been prepared from substituted acetylene adducts of $OMo(S_2CNMe_2)_2$ by stereospecific protonation with trifluoroacetic acid and characterized by elemental analysis and IR and NMR spectroscopy. The isolation of these compounds suggests routes for the catalyzed reduction of acetylene by both nitrogenase and certain model systems for this enzyme.

Because C_2H_2 is a substrate of nitrogenase,[1] studies of the binding and subsequent reduction of acetylenes in model systems may be relevant to the understanding of the mechanism of action of this enzyme. Of particular interest is the chemistry of molybdenum–acetylene complexes because it is commonly believed[2–5] that this metal binds the nitrogenase substrates. It is certainly a constituent of FeMo-co,[6–8] the substrate-reducing prosthetic group of nitrogenase.[9] Previously,[3,10–12] we reported the preparation of $OMo(S_2CNMe_2)_2(CH_3O_2CC{\equiv}CCO_2CH_3)$ (1) from $OMo(S_2CNMe_2)_2$ and dimethyl acetylenedicarboxylate and the analogous adducts of ditoluoylacetylene ($CH_3C_6H_4COC{\equiv}CCOC_6H_4CH_3$) (2), methyl propiolate ($HC{\equiv}CCO_2CH_3$) (3), and of C_2H_2 itself. Their varying reactivities and the X-ray structural characterization of 2 have been reported also.[10–12] Herein, we report the protonation of 1, 2, and 3 with trifluoroacetic acid to form vinyloxomolybdenum(VI) complexes. Closely related reactions have been reported[13] for $Mo(C_2R_2)_2(S_2CNR'_2)_2$. These new compounds extend a very short list of vinylmolybdenum compounds with extreme examples[14,15] being

---

[†] Contribution No. 854.

[‡] Present address: Western Regional Research Center, USDA, ARS, Albany, CA 94710.

(1) Schollhorn, R.; Burris, R. H. *Proc. Natl. Acad. Sci. U.S.A.* **1967**, *58*, 213. Dilworth, M. J. *Biochim. Biophys. Acta* **1966**, *127*, 285.

(2) Stiefel, E. I. *Prog. Inorg. Chem.* **1976**, *22*, 1. Stiefel, E. I.; Newton, W. E.; Watt, G. D.; Hadfield, K. L.; Bulen, W. A. *Adv. Chem. Ser.* **1977**, *No. 162*, 353. Newton, W. E. *Adv. Chem. Ser.* **1980**, *No. 191*, 351.

(3) Schneider, P. W.; Bravard, D. C.; McDonald, J. W.; Newton, W. E. *J. Am. Chem. Soc.* **1972**, *94*, 8640.

(4) Chatt, J.; Pearman, A. J.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1977**, 1852. Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.

(5) Schrauzer, G. N. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 514.

(6) Shah, V. K.; Brill, W. J. *Proc. Natl. Acad. Sci. U.S.A.* **1977**, *76*, 4986.

(7) Yang, S.-S.; Pan, W.-H.; Friesen, G. D.; Burgess, B. K.; Corbin, J. L.; Stiefel, E. I.; Newton, W. E. *J. Biol. Chem.* **1982**, *257*, 8042.

(8) Hoffman, B. M.; Roberts, J. E.; Orme-Johnson, W. H. *J. Am. Chem. Soc.* **1982**, *104*, 860.

(9) Hawkes, T. R.; McLean, P. A.; Smith, B. E. *Biochem. J.* **1984**, *217*, 317.

(10) Newton, W. E.; McDonald, J. W.; Corbin, J. L.; Ricard, L.; Weiss, R. *Inorg. Chem.* **1980**, *19*, 1977.

(11) Maatta, E. A.; Wentworth, R. A. D.; Newton, W. E.; McDonald, J. W.; Watt, G. D. *J. Am. Chem. Soc.* **1978**, *100*, 1320. Templeton, J. L.; Ward, B. C.; Chen, G. J.-J.; McDonald, J. W.; Newton, W. E. *Inorg. Chem.* **1981**, *20*, 1248.

(12) McDonald, J. W.; Corbin, J. L.; Newton, W. E. *J. Am. Chem. Soc.* **1975**, *97*, 1970. McDonald, J. W.; Newton, W. E.; Creedy, C. T. C.; Corbin, J. L. *J. Organomet. Chem.* **1975**, *92*, C25. Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318.

(13) Morrow, J. R.; Templeton, J. L. Presented at 188th National Meeting of the American Chemical Society, Philadelphia, PA, Aug 1984; American Chemical Society: Washington, DC, 1984; Abstract INOR 73.

0276-7333/85/2304-0422$01.50/0