Volume 26
Number 9
May 6, 1987

# Inorganic Chemistry

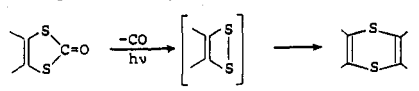


# Communications

## Photochemistry of Metal Dithio- and Diselenocarbonates. A New Route to Sulfido, Disulfur, and Diselenium Complexes

*Sir:*

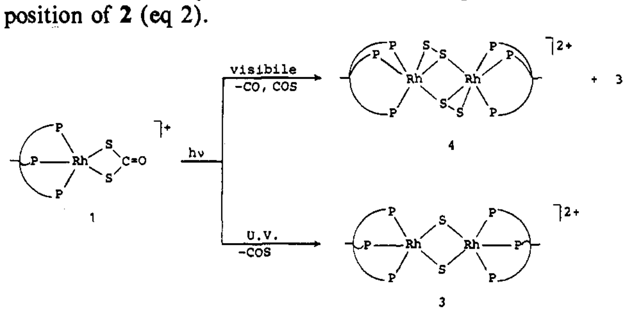
UV irradiation of organic dithiocarbonates is known to induce the chelotropic elimination of CO to give tetrasubstituted dithiins via dithiete intermediates[1] (eq 1). Eventually, low-valent transition-metal fragments may oxidatively add the dithiete.




(1)

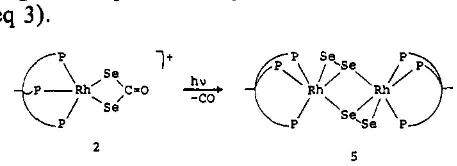
We have now found that reaction 1 can be extended also to metal dithio- and diselenocarbonates, thus providing a new, clean method to introduce sulfido, disulfur, or diselenium ligands into complex frameworks.

The dichalcogenocarbonates [(triphos)Rh($S_2$CO)]$BPh_4$ (**1**)[2] and [(triphos)Rh($Se_2$CO)]$BPh_4$ (**2**)[3] [triphos = MeC($CH_2PPh_2$)$_3$] are stable in $CH_2Cl_2$ solution even when refluxed for several hours on condition that the reaction vessel is kept in the darkness. By contrast, the exposure of **1** or of **2** in $CH_2Cl_2$ to the light of a standard tungsten lamp leads within 2 h to their complete decomposition to [(triphos)Rh($\mu$-S)$_2$Rh(triphos)]($BPh_4$)$_2$·$CH_2Cl_2$ (**3**) (yield 10%), [(triphos)Rh($\mu$-$S_2$)$_2$Rh(triphos)]($BPh_4$)$_2$·1.75 $CH_2Cl_2$ (**4**) (yield 70%), and [(triphos)Rh($\mu$-$Se_2$)$_2$Rh(triphos)]($BPh_4$)$_2$·$CH_2Cl_2$ (**5**) (yield 85%), respectively. Two gaseous products evolve during the formation of **3** and **4**, namely CO and COS,[4] whereas only carbon monoxide accompanies the decomposition of **2** (eq 2).




(2)

Under UV irradiation[5] in the temperature range −10 to +35 °C, the chelotropic elimination of COS from **1** in $CH_2Cl_2$ is favored over CO elimination. As a result only **3** (yield 75%) and COS are obtained. Interestingly, the frequency of the radiation that interacts with the RhSeC(O)Se ring apparently does not influence its decomposition pattern, the $\mu$-$Se_2$ compound **5** and CO being almost quantitatively formed also after UV irradiation of **2** (eq 3).




(3)

All of the compounds precipitate from the reaction mixture by addition of ethanol. The red $\mu$-disulfur complex **4** is easily separated from the brown $\mu$-sulfido complex **3** because of its lower solubility in $CH_2Cl_2$/ethanol. While compound **4** is a novel disulfur metal complex, **3** and **5** have been previously synthesized by different synthetic routes.[3,6] Their structures as given in eq 2 and 3 have been established by spectroscopic and X-ray methods. The crystal structure[7] of **4** consists of dimeric complex cations [(triphos)Rh($\mu$-$S_2$)$_2$Rh(triphos)]$^{2+}$ and $BPh_4^-$ anions. The $CH_2Cl_2$ molecules are in no way coordinated to the rhodium atoms. The system consists of two (triphos)Rh($\eta^2$-$S_2$) subunits related by a crystallographic inversion center (Figure 1). Binding of one of the sulfur atoms from a side-on coordinated $S_2$ group to the other

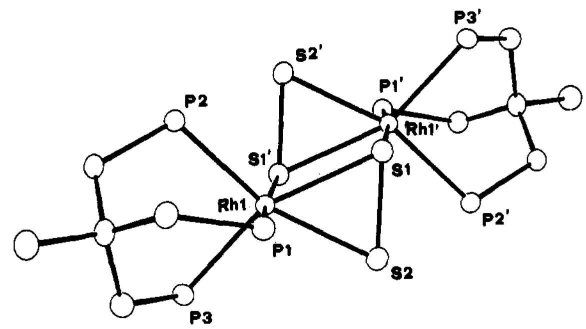



**Figure 1.** ORTEP drawing (30% probability ellipsoids) for the cation [(triphos)Ru($\mu$-$S_2$)$_2$Rh(triphos)]$^{2+}$. Selected distances (Å) and angles (deg) are as follows: Rh1–S1, 2.441 (2); Rh1–S2, 2.357 (3); Rh1–S1′, 2.411 (2); S1–S2, 2.022 (2); S1–Rh1–S2, 49.81 (6); S1′–Rh1–S2, 89.24 (6); Rh1–S1–Rh1′, 102.43 (2); S1′–Rh1–S1, 77.57 (7).

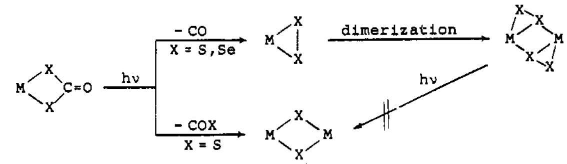
(1) Kusters, W.; de Majo, P. *J. Am. Chem. Soc.* **1974**, *96*, 3502.
(2) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1024.
(3) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Am. Chem. Soc.* **1985**, *107*, 5317.
(4) Carbon monoxide and carbonyl sulfide were determined both by GC and according to the methods reported in: Treadwell, F. P.; Hall, W. T. *Analytical Chemistry*, 7th ed.; Wiley: New York, 1930; Vol. 2.
(5) The photolysis experiments were done by externally irradiating $CH_2Cl_2$ solutions of the compounds in quartz Schlenk tubes. The irradiation source was a quartz-jacketed water-cooled high-pressure mercury lamp GN 400 W.
(6) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1986**, *25*, 4617.
(7) Crystal data: $C_{131.75}H_{121.5}B_2P_6Rh_2S_4Cl_{3.5}$; $M_r$ = 2370.18; triclinic, space group $P\bar{1}$; $a$ = 17.911 (5) Å, $b$ = 14.436 (4) Å, $c$ = 13.262 (3) Å, $\alpha$ = 91.47 (1)°, $\beta$ = 102.01 (3)°, $\gamma$ = 113.49 (3)°; $Z$ = 1; $D_{calcd}$ = 1.30 g cm$^{-3}$; $\mu$(Mo K$\alpha$) = 5.90 cm$^{-1}$. The structure was solved by Patterson and Fourier techniques and refined to a conventional $R$ = 0.057 ($R_w$ = 0.062) using 6432 absorption-corrected reflections with $I > 3\sigma(I)$ measured on a Philips PW 1100 diffractometer (Mo K$\alpha$ radiation, $\lambda$ = 0.71069 Å, 5 < $\theta$ < 50°). Phenyl rings were treated as rigid bodies.

0020-1669/87/1326-1345$01.50/0 

rhodium atom results in the formation of a four-membered RhSRhS ring with all Rh–S bond lengths nearly equal. The value of the S–S bond distance is 2.022 (3) Å. The same type of $\mu,\eta^2$–$\eta^1$ bonding mode of the $S_2$ ligand occurs also in the disulfur complexes $[Mo_4(NO)_4S_{13}]^{4-}$,[8] $[Mo_2Fe_6S_{12}(S\text{-}p\text{-}(C_6H_4Br))]^{4-}$,[9] and $(\eta\text{-}C_5Me_5)_2Co_2S_4$,[10] which have close S–S distances [2.048 (7), 1.99 (5) and 2.062 (6) Å, respectively].

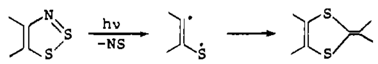
From a comparison between reaction paths 1 and 4, it is apparent that the elimination of CO is followed in both cases by the formation of new heterocyclic rings containing S–S or Se–Se bonds. While the dithiete decomposes to the dithiin, the Rh-$\eta^2$-$X_2$ (X = S, Se) rings, which belong to coordinatively and electronically unsaturated metal fragments, are stabilized by dimerization of the latter.

At variance with the reactions of organic dithiocarbonates, the inorganic analogues tend to lose also COS, a reaction pattern that, to a certain extent, resembles the photochemical decomposition




(4)

of 4,5-diphenyl-1,2,3-dithiazole (eq 5).[11]




(5)

(8) Muller, A.; Eltzner, W.; Mohan, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *8*, 168.
(9) Kovacs, J. A.; Bashkin, J. K.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 1784.
(10) Brunner, H.; Janietz, N.; Meier, W.; Sergerson, G.; Wachter, J.; Zahn, T.; Ziegler, M. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1060.

**Supplementary Material Available:** Fractional atomic coordinates and thermal parameters for compound **4** (4 pages). Ordering information is given on any current masthead page.

(11) Kirmse, W.; Horner, L. *Justus Liebigs Ann. Chem.* **1958**, *4*, 614.

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

**Claudio Bianchini*** 
**Andrea Meli**

*Received November 13, 1986*

# Articles

Contribution from the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

## Characterization of Large Cationic Transition-Metal–Gold Clusters by Fast Atom Bombardment Mass Spectroscopy (FABMS). New Re–Au and Pt–Au Clusters: $[Au_4Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_4]^+$, $[Au_2Re_2(H)_6(PPh_3)_6]^+$, and $[Au_6Pt(PPh_3)_7]^{2+}$.

Paul D. Boyle, Brian J. Johnson, Bruce D. Alexander, Joseph A. Casalnuovo, Patrick R. Gannon, Steven M. Johnson, Edmund A. Larka, Ann M. Mueting, and Louis H. Pignolet*

*Received October 7, 1986*

Fast atom bombardment mass spectroscopy has been used to examine a large number of cationic phosphine-containing transition-metal–gold clusters including polyhydrides, which ranged in mass from 1000 to 4000. Many of these clusters have been previously characterized and were examined in order to test the usefulness of the FABMS technique. Results showed that FABMS is excellent in giving the correct molecular formula including the number of hydride ligands, and when combined with NMR, conductance and analytical data gave complete and reliable characterization. Four new complexes have been synthesized and completely characterized by the above techniques. These are $[Au_2Pt(PPh_3)_4NO_3]NO_3$, $[Au_6Pt(PPh_3)_7](BPh_4)_2$, $[Au_2Re_2(H)_6(PPh_3)_6]PF_6$, and $[Au_4Re(H)_4[P(p\text{-tol})_3]_2(PPh_3)_4]PF_6$. The FABMS of these and other similar cationic and dicationic clusters with use of *m*-nitrobenzyl alcohol (MNBA) as the matrix always gave well-resolved peaks for either the parent molecular ion $(M)^+$ or the ion pair $(M + X)^+$ where X = the counterion. Comparison of observed and calculated isotopic ion distributions for these peaks reliably gave the correct molecular formulas. Cluster fragments were also observed that in general resulted from loss of one or more of the following species: $PPh_3$, H, CO, Ph, $AuPPh_3$. Small peaks that resulted from the addition of matrix fragments to unsaturated cluster ions were also observed. It is important to emphasize the necessity to compare the observed with the calculated isotopic ion distribution in order to accurately determine the formula of all cluster ions.

### Introduction

Cationic transition-metal–gold clusters with predominantly phosphine ligands are a class of compounds of great current interest.[1-8] These compounds are important because of their novel structural features, because of their potential use as catalyst materials, and in understanding gold and gold alloy surface catalysis.[9,10] The characterization of such compounds has been a major problem in this area and generally has required the use of single-crystal X-ray crystallography. Since many of these clusters also contain hydride ligands, even crystallography has not always lead to a definitive answer, and of course it is often impossible

(1) Alexander, B. D.; Johnson, B. J.; Johnson, S. M.; Casalnuovo, A. L.; Pignolet, L. H. *J. Am. Chem. Soc.* **1986**, *108*, 4409 and references cited therein.
(2) Boyle, P. D.; Johnson, B. J.; Buehler, A.; Pignolet, L. H. *Inorg. Chem.* **1986**, *25*, 5.
(3) Gilmour, D. I.; Mingos, M. P. *J. Organomet. Chem.* **1986**, *302*, 127 and references cited therein.
(4) Briant, C. E.; Gilmour, D. I.; Mingos, D. M. P. *J. Chem. Soc., Dalton Trans.* **1986**, 835.
(5) Lehner, H.; Matt, D.; Pregosin, P. S.; Venanzi, L. M.; Albinati, A. *J. Am. Chem. Soc.* **1982**, *104*, 6825.
(6) Braunstein, P.; Lehner, H.; Tiripicchio, D. M. A.; Tiripicchio-Camellini, M. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 304.
(7) Teo, B. K.; Keating, K. *J. Am. Chem. Soc.* **1984**, *106*, 2224.
(8) Melnik, M.; Parish, R. V. *Coord. Chem. Rev.* **1986**, *70*, 157.
(9) Schwank, J. *Gold Bull.* **1983**, *16*, 103.
(10) Sinfelt, J. H. *Bimetallic Catalysis*; Wiley: New York, 1983; Chapter 2. Wachs, I. E. *Gold Bull.* **1983**, *16*, 98.

0020-1669/87/1326-1346$01.50/0 