

Coordination of *cyclo*-Octasulfur and *cyclo*-Heptaselenium to Dinuclear Rhenium(I) Systems

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By substitution reactions of the coordinated THF ligands of $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{THF})_2$ by elemental chalcogens (S_8 and red selenium), the complexes $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{S}_8)$ ($\text{X} = \text{Br}$, **1**; I , **2**), and $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{Se}_7)$, ($\text{X} = \text{I}$, **3**; Br , **4**) have been prepared. Binuclear compound **3** was crystallographically established to be a coordination compound of *cyclo*-heptaselenium, two adjacent selenium atoms of the Se_7 ligand [$\text{Se}\text{--}\text{Se}$ distance, 2.558(3) Å] being bonded to rhenium(I), at an average $\text{Re}\text{--}\text{Se}$ distance of 2.586(3) Å, and the nonbonding $\text{Re}\cdots\text{Re}$ distance being 4.077(3) Å. Spectroscopic evidence of the existence of these chalcogen complexes in solution is reported. The $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{S}_8)$ complexes undergo S_8 displacement by THF, while the coordinated Se_7 moiety is less readily displaced from **3**.

Introduction

Reaction of an element in its polyatomic form (as the homonuclear species H_2 , N_2 , O_2 , P_4 , and I_2) with a transition metal complex can produce (a) coordination to the metal center, (b) interaction with one of the ligands, or (c) oxidation of the metal center. The electron-transfer process of type c is well-known, whereas reactions of types a and b are less common and require some considerations. In particular, suitable steric and electronic properties of the metal-containing reagent are required to avoid irreversible oxidation of the metal center. Nonclassical dihydrogen complexes were first recognized by Kubas et al., the dihydrogen complex $\text{W}(\text{CO})_3(\text{P}^i\text{Pr}_3)_2(\eta^2\text{-H}_2)^1$ being present in solution in a tautomeric equilibrium with the classical dihydrido species. Coordination complexes of C_{60} were reported in the 1990s, namely $(\text{PPh}_3)_2\text{Pt}(\eta^2\text{-C}_{60})$, $[\text{Ir}_2\text{Cl}_2(1,5\text{-COD})]_2(\text{C}_{60})$, and $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\eta^2\text{-C}_{60})$.² The discovery of the first coordination

complexes of dinitrogen and dioxygen in the 1960s, $[\text{Ru}(\text{NH}_3)_5(\text{N}_2)]^{2+3}$ and $\text{IrCl}(\text{CO})(\text{PPh}_3)_2(\text{O}_2)$,⁴ opened a new field of investigation in relation to nitrogen fixation, reduction to ammonia,⁵ dioxygen transport, and selective oxidation of organic substrates.⁶ Complexes containing P_n or As_n moieties are known,⁷ and the I_2 ligand has been found in the platinum-(II) complex $\text{PtI}(\eta^1\text{-I}_2)[(\text{C}_6\text{H}_3(\text{CH}_2\text{NMe}_2)_2\text{-}o,o']$.^{8a-c} Relevant

- (3) Allen, A. D.; Senoff, C. V. *Chem. Commun.* **1965**, 621.
 (4) Vaska, L. *Science* **1963**, *140*, 809.
 (5) Chatt, J.; Dilworth, J. R.; Richards, R. L. *Chem. Rev.* **1978**, *78*, 589.
 (6) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, *84*, 137.
 (7) (a) Di Vaira, M.; Sacconi, L. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 330. (b) Ginsberg, A. P.; Lindsell, W. E.; McCullough, K. J.; Sprinkle, C. R.; Welch, A. J. *J. Am. Chem. Soc.* **1986**, *108*, 403. (c) Scheer, M.; Herrmann, E.; Sieler, J.; Oehme, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 969. (d) Goh, L. Y.; Chu, C. K.; Wong, R. C. S.; Hambly, T. W. *J. Chem. Soc., Dalton Trans.* **1989**, 1951. (e) Goh, L. Y.; Wong, R. C. S.; Sinn, E. *Organometallics* **1993**, *12*, 888. (f) Huttner, G.; Weber, U.; Sigwarth, B.; Scheidsteiger, O. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 215. (g) Scherer, O. *J. Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1104.
 (8) (a) van Beek, J. A. M.; van Koten, G.; Smeets, W. J. J.; Spek, A. L. *J. Am. Chem. Soc.* **1986**, *108*, 5010. (b) van Beek, J. A. M.; van Koten, G.; Dekker, G. P. C. M.; Wissing, E.; Zoutberg, M. C.; Stam, C. H. *J. Organomet. Chem.* **1990**, *394*, 659. (c) Gossage, R. A.; Ryabov, A. D.; Spek, A. L.; Stufkens, D. J.; van Beek, J. A. M.; van Eldik, R.; van Koten, G. *J. Am. Chem. Soc.* **1999**, *121*, 2488. (d) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *Angew. Chem., Int. Ed.* **2000**, *39*, 2362. (e) Cotton, F. A. *Inorg. Chem.* **2002**, *41*, 643. (f) Brookhart, M.; Green, M. L. H.; Wong, L.-L. *Prog. Inorg. Chem.* **1988**, *36*, 1. (g) Baratta, W.; Herdtweck, E.; Rigo, P. *Angew. Chem., Int. Ed.* **1999**, *38*, 1629.

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- (1) Kubas, G. J.; Ryan, R. R.; Swanson, B. I.; Vergamini, P. J.; Wasserman, H. J. *J. Am. Chem. Soc.* **1984**, *106*, 451.
 (2) (a) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160. (b) Rasinkangas, M.; Pakkanen, T. T.; Pakkanen, T. A.; Ahlgrén, M.; Rouvinen, J. *J. Am. Chem. Soc.* **1993**, *115*, 4901. (c) Balch, A. L.; Catalano, V. J.; Lee, J. W. *Inorg. Chem.* **1991**, *30*, 3980.

to this Introduction section is also the recent finding^{8d} that $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ gives the di-iodine complex of formula $\{[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4 \cdot \text{I}_2] \cdot \text{I}_2\}$. Finally, nonconventional low-energy agostic interactions have been recognized in compounds of transition metals, particularly those of nd^6 electronic configuration.^{8e-g} Within pathways of type b, di-iodine was found to interact with the Re–I moiety of $\text{ReI}(\text{CO})_3\text{L}_2$ ($\text{L} = \text{P}^n\text{Bu}_3$) giving $\text{ReI}_3(\text{CO})_3\text{L}_2$ which contains a linear tri-iodide ligand,⁹ with intraligand I–I distances of 3.162(1) and 2.757–(2) Å. The thermodynamic parameters of this reaction were found to be $\Delta H^\circ = -6.4 \pm 0.4 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = -11.0 \pm 0.6 \text{ eu}$.

The study of the donor properties of elemental sulfur and selenium in their polyatomic forms toward transition metal cations of electronic configuration d^n ($0 < n < 10$) has initiated only recently. Chalcogens E_n in their reaction with metal-containing complexes usually yield polychalcogenides, because of (a) the oxidizing power of E_n , (b) the relatively easy cleavage of the E–E bond, and (c) the potentially high hapticity of the resulting chalcogenide ligand. On the other hand, weak sulfur–halide or sulfur–sulfur interactions are responsible for the formation of the following crystallographically established adducts: $\text{CH}_3 \cdot 3\text{S}_8$,¹⁰ $\text{SnL}_4 \cdot 2\text{S}_8$,¹¹ $\text{Al}_3 \cdot 3\text{S}_8$ ($\text{A} = \text{Sb, As}$),¹² $\text{SbCl}_3 \cdot \text{S}_8$,¹³ $\text{Ti}_4\text{O}(\text{S}_2)_4\text{Cl}_6 \cdot 2\text{S}_8$,¹⁴ $\text{WCl}_6 \cdot \text{S}_8$,¹⁵ $\text{WCl}_4\text{S}(\text{THF}) \cdot \text{S}_8$,^{16a} $\text{WCl}_4\text{S} \cdot \text{S}_8$,^{16b} $\text{S}_4(\text{NH})_4 \cdot 3\text{S}_8$,¹⁷ $\text{Co}_6(\mu_3\text{-S})_8(\text{CO})_6 \cdot 3\text{S}_8$,¹⁸ $(\text{PPh}_4)_4(\text{Ag}_2\text{S}_{20}) \cdot \text{S}_8$,¹⁹ and $[(\text{PPh}_3)_2\text{N}][\text{Ag}(\text{S}_9)] \cdot \text{S}_8$.²⁰ In these compounds, S_8 displays weak interactions with some peripheral atoms of the coordination sphere rather than with the central metal atom. On the other hand, the results of X-ray diffraction studies show that the d^{10} systems of $[\text{Ag}(\text{S}_8)_2][\text{AsF}_6]$,²¹ $[\text{CuXS}_8]_n$ ($\text{X} = \text{Br, I}$),²² and $[\text{CuClSe}_8]_n$ ²³ are to be classified as genuine coordination adducts of chalcogens.

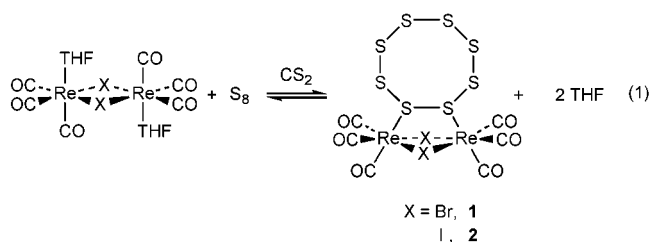
We describe here the synthesis and properties of the coordination complexes of chalcogens, $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{S}_8)$ ($\text{X} = \text{Br, I, 2}$) and $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_7)$, **3**. Preliminary

data concerning these complexes have been reported in earlier communications.²⁴ An important recent contribution to this field came from the solid-state isolation by Cotton and co-workers of two adducts of S_8 with $\text{Rh}_2(\text{O}_2\text{CCF}_3)_4$ (electronic configuration d^7), namely $[\text{Rh}_2(\text{O}_2\text{CCF}_3)_4]_n(\text{S}_8)_m$ ($n/m = 1, 1.5$). These complexes have been explicitly stated to be “decomposed by coordinating solvents and slowly decompose even by noncoordinating dichloromethane to release elemental sulfur”.²⁵ Our report^{24b} on the coordination compound of Se_7 with rhenium(I) deals with the unique example of an adduct of an elemental form of selenium with a transition metal cation. Experimental evidence is reported in this paper about the existence in solution of complexes of rhenium(I) with both S_8 and Se_7 , together with important details about their preparation and properties.

Result and Discussion

The rhenium(I) derivatives $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{THF})_2$ ($\text{X} = \text{Br, I}$) promptly react²⁶ with organic dichalcogenides E_2R_2 ($\text{E} = \text{S, Se, Te}$) forming the dinuclear rhenium(I) derivatives $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{E}_2\text{R}_2)$, containing an “intact” E–E bond and the E–Re coordinative ligation (vide infra for references about specific crystallographic details concerning these products). The earlier results suggested that the $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{THF})_2$ derivatives could be good precursors for the coordination of elemental chalcogens.

1. Coordination of cyclo-Octasulfur. Although CS_2 reacts with a large number of complexes in a low oxidation state,²⁷ $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{THF})_2$ is stable in CS_2 for several hours, as inferred from IR spectroscopy. Taking advantage of this property, $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{THF})_2$ was treated with an equimolar amount of cyclo-octasulfur in CS_2 , which resulted in an equilibrium, the $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{S}_8)$ complex, **1**, being formed by displacement of THF, see eq 1.



The infrared spectrum of the reddish solution, 10 min after the addition of the reagent, shows four carbonyl stretching vibrations at 2056 m, 2041 s, 1968 s, and 1940 cm^{-1} , along with the bands at 2031 m and 1922 cm^{-1} of the starting

- (9) Ambrosetti, R.; Baratta, W.; Belli Dell'Amico, D.; Calderazzo, F.; Marchetti, F. *Gazz. Chim. Ital.* **1990**, *120*, 511.
 (10) Bjorvatten, T. *Acta Chem. Scand.* **1962**, *16*, 749.
 (11) Laitinen, R.; Steidel, J.; Steudel, R. *Acta Chem. Scand., Ser. A* **1980**, *34*, 687.
 (12) (a) Bjorvatten, T.; Hassel, O.; Lindheim, H. *Acta Chem. Scand.* **1963**, *17*, 689. (b) Fernando, W. S. *J. Inorg. Nucl. Chem.* **1981**, *43*, 1141.
 (13) Müller, U.; Mohammed, A. T. *Z. Anorg. Allg. Chem.* **1983**, *506*, 110.
 (14) Cotton, F. A.; Feng, X.; Kibala, P. A.; Sandor, R. B. W. *J. Am. Chem. Soc.* **1989**, *111*, 2148.
 (15) Cotton, F. A.; Kibala, P. A.; Sandor, R. B. W. *Acta Crystallogr.* **1989**, *C45*, 1287.
 (16) (a) Baratta, W.; Calderazzo, F.; Daniels, L. M. *Inorg. Chem.* **1994**, *33*, 3842. (b) Hughes, D. L.; Lane, J. D.; Richards, R. L. *J. Chem. Soc., Dalton Trans.* **1991**, 1627.
 (17) Gasperin, M.; Freymann, R.; Garcia-Fernandez, H. *Acta Crystallogr.* **1982**, *B38*, 1728.
 (18) Diana, E.; Gervasio, G.; Rossetti, R.; Valdemarin, F.; Bor, G.; Stanghellini, P. L. *Inorg. Chem.* **1991**, *30*, 294.
 (19) Müller, A.; Römer, M.; Bögge, H.; Krickemeyer, E.; Baumann, F.-W.; Schmitz, K. *Inorg. Chim. Acta* **1984**, *89*, L7.
 (20) Müller, A.; Römer, M.; Bögge, H.; Krickemeyer, E.; Zimmermann, M. Z. *Anorg. Allg. Chem.* **1986**, *534*, 69.
 (21) Roesky, H. W.; Thomas, M.; Schimkowiak, J.; Jones, P. J.; Pinkert, W.; Sheldrick, G. M. *J. Chem. Soc., Chem. Commun.* **1982**, 895.
 (22) (a) Haendler, H. M.; Carkner, P. M. *J. Solid. State Chem.* **1979**, *29*, 35. (b) Milius, W.; Rabenau, A. *Mater. Res. Bull.* **1987**, *22*, 1493.
 (23) Milius, W.; Rabenau, A. *Z. Naturforsch., B: Chem. Sci.* **1988**, *43*, 243.

- (24) (a) Baratta, W.; Calderazzo, F. *Organometallics* **1993**, *12*, 1489. (b) Bacchi, A.; Baratta, W.; Calderazzo, F.; Marchetti, F.; Pelizzi, G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 193.
 (25) Cotton, F. A.; Dikarev, E. V.; Petrukhina, M. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 1521.
 (26) (a) Calderazzo, F.; Vitali, D. *Coord. Chem. Rev.* **1975**, *16*, 13. (b) Boag, N. M.; Kaesz, H. D. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York, 1982; Vol. 4, p 161.
 (27) (a) Mason, R.; Rae, A. I. M. *J. Chem. Soc. A* **1970**, 1767. (b) Baird, M. C.; Hartwell, G.; Wilkinson, G. *J. Chem. Soc. A* **1967**, 2037. (c) Ibers, J. A. *Chem. Soc. Rev.* **1982**, *11*, 57. (d) Werner, H. *Coord. Chem. Rev.* **1982**, *43*, 165. (e) Pandey, K. K. *Coord. Chem. Rev.* **1995**, *140*, 37.

Table 1. IR Carbonyl Stretching Vibrations of $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{S}_8)$, $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{Se}_7)$ and $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{E}_2\text{Ph}_2)$ (X = Br, I; E = S, Se, Te)

complex	ν_{CO} (cm^{-1})				ref
$\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{S}_8)$, 1 ^a	2056m	2041s	1968s	1940s	24a
$\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{S}_8)$, 2 ^a	2052m	2037s	1967s	1942s	24a
$\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_7)$, 3 ^a	2045m	2030s	1960s	1934s	24b
$\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{Se}_7)$, 4 ^a	2050m	2035s	1962s	1933s	this work
$\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{S}_2\text{Ph}_2)$ ^b	2059m	2043s	1964s	1937s	d
Idem ^c	2057m	2043s	1966s	1940s	e
$\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{S}_2\text{Me}_2)$ ^c	2060m	2043s	1966s	1935s	e
$\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{S}_2\text{Ph}_2)$ ^b	2053m	2038s	1963s	1938s	d
$\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_2\text{Ph}_2)$ ^b	2051m	2035s	1961s	1936s	d
$\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Te}_2\text{Ph}_2)$ ^b	2049m	2034s	1960s	1933s	d

^a In CS_2 . ^b In CCl_4 . ^c In heptane. ^d Atwood, J. L.; Bernal, I.; Calderazzo, F.; Canada L. G.; Poli, R.; Rogers, R. D.; Veracini, C. A.; Vitali, D. *Inorg. Chem.* **1983**, *22*, 1797. ^e Bernal, I.; Atwood, J. L.; Calderazzo, F.; Vitali, D. *Isr. J. Chem.* **1976–77**, *15*, 153.

product, the relative intensity indicating the equilibrium to be shifted toward the reagents. The frequency values and the relative intensity of the four main absorption bands leave no doubt that the new complex possesses a $\text{Re}_2(\text{CO})_6$ core of idealized C_{2v} symmetry similar to that of the related crystallographically established dinuclear rhenium(I) complexes containing organic dichalcogenides as ligands, see Table 1.

To isolate complex **1**, we have found that addition of an oxophilic Lewis acid, such as ZrCl_4 , to the CS_2 solution containing the rhenium(I) precursor and S_8 leads quantitatively to **1**, equilibrium 1 being displaced to the right and THF being subtracted by complexation. Thus, treatment of $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{THF})_2$ with *cyclo*-octasulfur in CS_2 in the presence of a large excess of ZrCl_4 at -5°C afforded a dark red product, which satisfactorily analyzed as **1**, the excess of the added halide and its THF adduct being easily eliminated by filtration.

The diamagnetic red product, which can be stored under an inert atmosphere over a long period of time at room temperature, is poorly soluble in hydrocarbons but well soluble in CS_2 . In the latter solvent, $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{S}_8)$ decomposes at 25°C to give unidentified rhenium sulfides and *cyclo*-octasulfur. The process follows approximate first-order kinetics, with $\tau_{1/2}$ of 2.8 h. According to eq 1, treatment of **1** with 2 molar equiv of THF in CS_2 promptly leads to $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{THF})_2$ as the major product, whereas dissolution of **1** in neat THF gives $\text{ReBr}(\text{CO})_3(\text{THF})_2$ and a yellow precipitate of the little soluble *cyclo*- S_8 . This suggests that S_8 is weakly bonded to the $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6$ moiety, the THF ligand²⁸ possessing a coordinating power comparable to S_8 . In this connection, it is useful to recall that the BDE for manganese(I) in $\text{Mn}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}$ was calculated to be $16.1 \pm 1.4 \text{ kcal mol}^{-1}$ and $28.7 \pm 2.2 \text{ kcal mol}^{-1}$ for $\text{L} = \text{THF}$ and Bu_2S , respectively. Despite the different nature of the central metal atom [$\text{Mn}(\text{I})$ vs $\text{Re}(\text{I})$], our data suggest that S_8 is presumably a weaker ligand than Bu_2S for rhenium.

Similar to the bromide derivative, equimolar amounts of $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{THF})_2$ and *cyclo*-octasulfur in CS_2 gave $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{S}_8)$, **2**, in equilibrium with the rhenium(I) reagent,

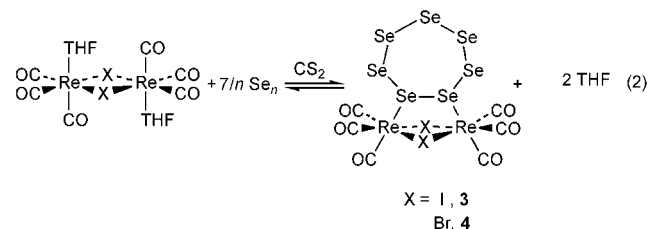
(28) Klassen, J. K.; Selke, M.; Sorensen, A. A.; Yang, G. K. *J. Am. Chem. Soc.* **1990**, *112*, 1267.

see eq 1. Formation of **2** was observed in solution as evidenced by four carbonyl stretching bands at 2052 m, 2037 s, 1967 s, and 1942 s cm^{-1} , whereas the THF adduct of rhenium(I) exhibits two bands at 2027 m and 1922 s cm^{-1} .

Comparison of the IR spectra shows that, under similar conditions, equilibrium 1, pertaining to the displacement of coordinated THF by S_8 in $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{THF})_2$ (X = Br, I) to give the *cyclo*-octasulfur derivatives, is shifted toward the product in the sequence $\text{I} > \text{Br}$. Thus, isolation of dark red **2** does not require treatment with Lewis acids: stirring a suspension of an equimolar mixture of $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{THF})_2$ and *cyclo*-octasulfur in heptane, in which **2** is sparingly soluble, is sufficient, the process being driven to completion by removal of THF from the system in vacuo and addition of fresh heptane.

Similar to **1**, complex **2** is stable in the solid state but, in CS_2 , decomposes to S_8 and to a dark-blue precipitate of unknown composition,²⁹ approximately following first-order kinetics with a $\tau_{1/2}$ of 1.7 h.

2. Coordination of *cyclo*-Heptaselenium. Reaction of $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{THF})_2$ with red selenium, obtained by sublimation of commercial selenium,³⁰ in CS_2 leads to an equilibrium involving the coordination complex of *cyclo*-heptaselenium $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_7)$, **3**, see eq 2.



The brown product, **3**, was isolated by treatment of the rhenium–THF adduct with a slight excess of red selenium in CS_2 for 1 day and by repeated evaporation of the volatiles under reduced pressure in order to eliminate THF. Complex **3**, which gave an elemental analysis consistent with a coordination of a seven-membered selenium ring, shows four carbonyl stretching vibrations at 2045 m, 2030 s, 1960 s, and 1934 s cm^{-1} , at lower wavenumbers as compared to the analogous *cyclo*-octasulfur complex **2**, in agreement with the previous studies on the effect of the nature of the chalcogen on ν_{CO} 's for the dichalcogenide complexes $\text{Re}_2(\mu\text{-X})_2(\text{CO})_6(\text{E}_2\text{Ph}_2)$ (E = S, Se), see Table 1.²⁶

The ^{77}Se NMR spectrum of **3** in CS_2 shows four peaks at δ 1150, 1011, 973, and 927 in a 2:2:2:1 ratio close to the peak of the fluxional Se_7 at δ 996, and relatively far from the peaks of the other selenium rings Se_6 and Se_8 at δ 684 and 614, respectively.³¹ The downfield peak at δ 1150 is clearly due to two coordinated selenium atoms, on the basis

(29) The dark-blue precipitate from **2** was washed with CS_2 and toluene and dried under reduced pressure. Elemental analysis showed a low sulfur content as compared to **2** (Anal. Found: C, 8.7; S, 4.5). IR (Nujol): 2035, 2017, 1971, 1935 cm^{-1} .

(30) (a) *Gmelin Handbuch der Anorganischen Chemie*; Selen, Springer-Verlag: New York: 1979; Ergänzungsband A1. (b) *Gmelin Handbuch der Anorganischen Chemie*; Selen, Springer-Verlag: New York, 1980; Ergänzungsband A2.

(31) Stuedel, R.; Papavassiliou, M.; Krampe, W. *Polyhedron* **1988**, *7*, 581.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_7)$, **3**

Re(1)–I(1)	2.826(2)	Re(2)–I(1)	2.820(2)
Re(1)–I(2)	2.823(2)	Re(2)–I(2)	2.821(2)
Re(1)–Se(1)	2.585(3)	Re(2)–Se(2)	2.587(3)
Re(1)–C(1)	1.89(2)	Re(2)–C(4)	1.92(1)
Re(1)–C(2)	1.90(2)	Re(2)–C(5)	1.90(2)
Re(1)–C(3)	1.97(2)	Re(2)–C(6)	1.91(2)
Se(1)–Se(2)	2.558(3)	Se(4)–Se(5)	2.318(3)
Se(2)–Se(3)	2.309(3)	Se(5)–Se(6)	2.321(3)
Se(3)–Se(4)	2.338(3)	Se(6)–Se(7)	2.346(4)
Se(1)–Se(7)	2.311(3)		
I(2)–Re(1)–I(1)	84.12(6)	I(1)–Re(2)–I(2)	84.27(6)
Re(2)–I(1)–Re(1)	92.44(6)	Re(2)–I(2)–Re(1)	92.49(6)
Se(1)–Re(1)–I(1)	86.81(8)	Se(2)–Re(2)–I(1)	84.01(7)
Se(1)–Re(1)–I(2)	87.97(8)	Se(2)–Re(2)–I(2)	89.70(8)
Se(2)–Se(1)–Re(1)	106.45(8)	Se(1)–Se(2)–Re(2)	107.53(8)
Se(7)–Se(1)–Re(1)	101.7(1)	Se(3)–Se(2)–Re(2)	99.7(1)
Se(3)–Se(2)–Se(1)	104.28(9)	Se(7)–Se(1)–Se(2)	103.40(9)
Se(2)–Se(3)–Se(4)	102.2(1)	Se(1)–Se(7)–Se(6)	100.7(1)
Se(5)–Se(4)–Se(3)	99.3(1)	Se(5)–Se(6)–Se(7)	100.3(1)
Se(4)–Se(5)–Se(6)	102.6(1)		

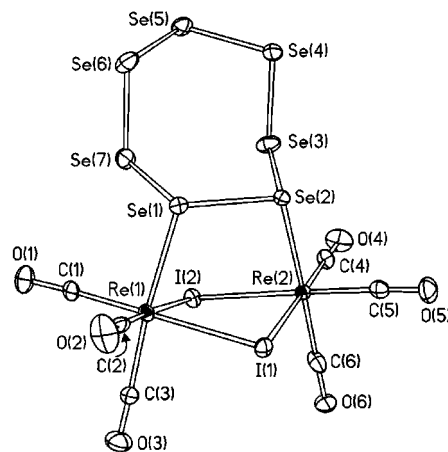
of the shorter relaxation time and in agreement with the ^{77}Se NMR resonance of the related complex $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6[\text{Se}_2(\text{CH}_2\text{Ph})_2]$ showing a signal at δ 562,³² in comparison with the single resonance of the free ligand at δ 397. The ^{13}C NMR spectrum of **3** shows three signals for the carbonyl ligands at δ 187.1, 184.5, and 182.6 in a 1:1:1 ratio. These data are consistent with the presence of a mirror plane that contains the bridging iodides and bisects the *cyclo*-heptaselenium ligand.

The reaction of $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{THF})_2$ with red selenium in CS_2 leads to $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{Se}_7)$, **4**, see eq 2. Although we did not isolate the corresponding complex, the four carbonyl stretching vibrations at 2050m, 2035s, 1962s, and 1933 s cm^{-1} and the four ^{77}Se NMR signals at δ 1137, 1002, 984, and 929 in the 2:2:2:1 ratio leave no doubt that a rhenium(I) complex with a seven-membered selenium cycle analogous to **3** was formed.

3. Crystal Structure of $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_7)$. An X-ray diffraction experiment was carried out in order to completely characterize what the spectroscopic data appeared to indicate as the first example of a transition metal complex containing a coordinated selenium ring. Solid-state metrical data were essential to exclude the formation of a dinuclear rhenium(II) complex containing a heptaselenide ligand. Selected bond distances and angles are given in Table 2.

Figure 1 shows an ORTEP plot of the crystal structure of $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_7)$, **3**. Each rhenium atom has octahedral geometry, being coordinated to two bridging iodides, to three terminal carbonyl groups, and to one selenium atom of the *cyclo*-heptaselenium ligand, which adopts a chairlike conformation. The selenium ligand is 1,2-coordinated to rhenium.

The molecular symmetry is close to C_s , the mirror plane containing the Se(5), I(1), and I(2) atoms. The $\text{Re}\cdots\text{Re}$ nonbonding distance is 4.077(3) Å, a result which excludes the formation of a diamagnetic rhenium(II) complex of d^7 electronic configuration, requiring the rupture of the Se–Se

**Figure 1.** ORTEP representation of $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_7)$, **3**. Thermal ellipsoids are at 30% probability.

bond and the formation of the Re–Re bond. The bridging iodides, which share the two coordination polyhedra, show similar Re–I distances with a mean value of 2.823(2) Å. The Re(1)–Se(1) and Re(2)–Se(2) distances are similar with a mean value of 2.586(3) Å, which is close to that observed in $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{Se}_2\text{Ph}_2)$ [2.604(4) Å],³³ in which the diphenyldiselenide ligand acts as a neutral four-electron donor. In the chairlike puckered *cyclo*-heptaselenium ring of compound **3**, the atoms lie on three different planes {plane 1, Se(1)–Se(2)–Se(3)–Se(7), max deviation 0.039 Å; plane 2, Se(3)–Se(4)–Se(6)–Se(7), max deviation 0.015 Å; plane 3, Se(4)–Se(5)–Se(6)}. Plane 2 forms dihedral angles of 78.0° and 74.9° with planes 1 and 3, respectively. Moreover, plane 2 is almost parallel to the Re(1)–Re(2)–Se(1)–Se(2) plane (max deviation 0.07 Å), the dihedral angle being 5.9° only.

Finally, the Se(1)–Se(2) bond distance, that is, the distance pertaining to the atoms coordinated to rhenium(I), is 2.558(3) Å, whereas the other Se–Se distances in the heptaselenium ring range from 2.309(3) to 2.346(4) Å. It would be interesting to compare the metrical data of the Se_7 ligand of **3** with those of the free molecule. However, although the allotropic modification of elemental selenium *cyclo*- Se_7 has been obtained by Steudel and co-workers by reacting $\text{Cp}_2\text{-TiSe}_5$ with Se_2Cl_2 ,³⁴ no crystallographic data for it have been reported. Therefore, the interatomic distances of the *cyclo*- Se_7 ligand in **3** can be compared with those observed in *cyclo*- Se_6 and *cyclo*- Se_8 (Se–Se bond distances are 2.36 and 2.34 Å, respectively).³⁵ The conformation of the *cyclo*- Se_7 ligand is to be compared, see Figure 2, with the Se_7 component of $(\text{NET}_4^+)_2[\text{Se}_5^{2-}\cdot\frac{1}{2}\text{Se}_6\cdot\text{Se}_7]$ ^{36a} and $[\text{Na}(12\text{-crown-4})_2^+][\text{Se}_8^{2-}\cdot\text{Se}_6\cdot\text{Se}_7]$.^{36b} A similar chairlike conformation was also found in *cyclo*- S_7 .³⁷

(32) Baratta, W.; Bernal, I.; Calderazzo, F.; Korp, J. D.; Magill, L. S.; Marchetti, F.; Vitali, D. *Gazz. Chim. Ital.* **1996**, *126*, 469.

(33) Korp, J.; Bernal, I.; Atwood, J. L.; Calderazzo, F.; Vitali, D. *J. Chem. Soc., Dalton Trans.* **1979**, 1492.

(34) Steudel, R.; Papavassiliou, M.; Strauss, E.-M.; Laitinen, R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 99.

(35) (a) Miyamoto, Y. *Jpn. J. Appl. Phys.* **1980**, *19*, 1813. (b) Burbank, R. D. *Acta Crystallogr.* **1951**, *4*, 140.

(36) (a) Dietz, J.; Müller, U.; Müller, V.; Dehnicke, K. *Z. Naturforsch., B: Chem. Sci.* **1991**, *46*, 1293. (b) Staffel, R.; Müller, U.; Ahle, A.; Dehnicke, K. *Z. Naturforsch., B: Chem. Sci.* **1991**, *46*, 1287.

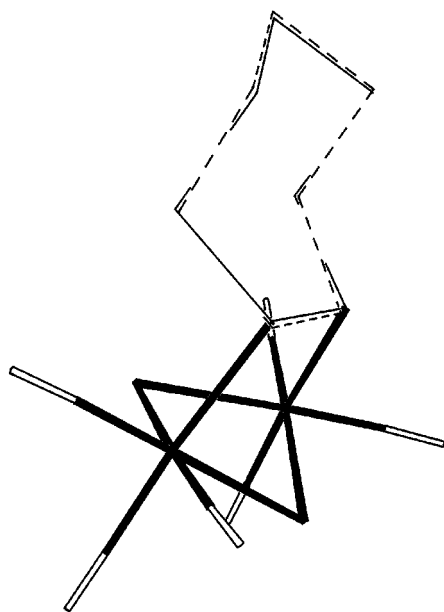


Figure 2. Conformation of *cyclo-Se*₇^{36a} (— — —) in comparison with that of the Se₇ ligand in Re₂(μ-I)₂(CO)₆(Se₇), **3**.

As it is quite clear from the superposed seven-membered rings of Figure 2, the coordination of *cyclo-Se*₇ to rhenium(I) does not correspond to any serious conformational rearrangement. The Se—Se bond bisected by the symmetry plane of Se₇ was found to be 2.409 Å long in (NEt₄⁺)₂[Se₅²⁻·1/2Se₆·Se₇],^{36a} to be compared with the value of 2.342 Å for the average of the other Se—Se distances within the ring. This is in good agreement with a theoretical study which has predicted a relatively long distance of 2.48 Å for the unique Se—Se distance bisected by the symmetry plane of *cyclo-Se*₇.³⁸ If we consider the available metrical parameters in the solid state, we can conclude that the coordination of *cyclo-Se*₇ to rhenium(I) causes a lengthening of the Se—Se bond by about 0.15 Å. In conclusion, the formation of the rhenium(I) complex containing the seven-membered selenium cycle may be ascribed to the favorable structural parameters of *cyclo-Se*₇ which exhibits one long Se—Se bond, with respect to *cyclo-Se*₆ or *cyclo-Se*₈.

Figure 3 shows the crystal packing of Re₂(μ-I)₂(CO)₆(Se₇), where the molecules face in pairs by showing each other the Se₇ ring. The shortest Se···Se contacts are 3.68 Å, similar to 3.53 Å observed in monoclinic *cyclo-Se*₈.³⁹ The shortest intra- and intermolecular Se···I contacts are 3.62 and 3.68 Å, respectively, to be compared with the distance of 3.50 Å observed in I₂.⁴⁰

4. Properties of Se_n and Re₂(μ-X)₂(CO)₆(Se₇). Red selenium is generally prepared by reduction of SeO₂ or H₂-SeO₃ with hydrazine at 20 °C or at lower temperature.^{30a} When red selenium is dissolved in CS₂ at 25 °C, an equilibrium takes place within a few minutes leading to Se₆,

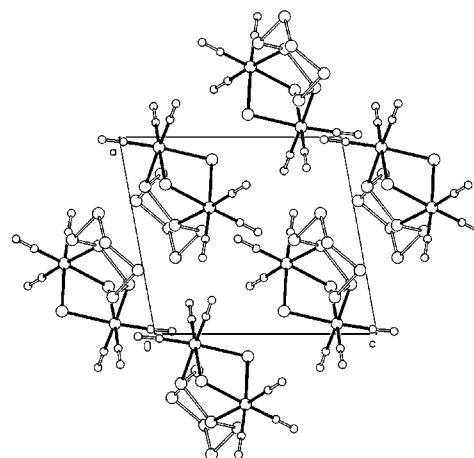


Figure 3. Crystal packing of Re₂(μ-I)₂(CO)₆(Se₇), **3**, in the β direction. The disordered heptane molecule placed at 0 1/2 1/2 has been omitted.

Se₇, and Se₈ in a molar ratio of about 1:2:10, as established by Steudel and Strauss.⁴¹ Red selenium used for the synthesis of complexes **3** and **4** was obtained by sublimation of commercial gray selenium. Thus, selenium was pyrolyzed at about 240 °C in vacuo (10⁻² Torr), and the vapor was condensed at -196 °C, thus within a temperature gradient of about 440 °C. This form of selenium is sparingly soluble in CS₂, and the resulting solution separates α-Se₈ by slow evaporation of the solvent, as confirmed by comparing the cell constants of the solid, see the Experimental Section, with the literature data.⁴² Red selenium prepared by sublimation can be kept for months at -30 °C, whereas it turns gray if exposed to light or heated slightly above room temperature, giving a little soluble form of selenium. In connection with the composition of sublimed selenium, it is interesting to note that, in the synthesis of **3** from Re₂(μ-I)₂(CO)₆(THF)₂ and red selenium, the infrared spectra of the CS₂ solution after a few minutes exhibit four carbonyl stretching vibrations at 2045, 2034, 1968, and 1940 cm⁻¹, that is, at slightly higher wavenumbers as compared to **3**. These data can be attributed to the formation of an intermediate compound of formula Re₂(μ-I)₂(CO)₆(Se_n), which rapidly converts into **3**. The low stability of this intermediate did not allow the nuclearity of the Se_n ligand in this compound to be established by ⁷⁷Se NMR spectroscopy. These observations suggest that other rhenium(I) complexes of *cyclo-Se*_n may be formed which then convert to the more stable compound containing the seven-membered ring. Finally, it is noteworthy that commercial gray selenium, which may contain small amounts of cyclic selenium, shows low or no reactivity with Re₂(μ-I)₂(CO)₆(THF)₂.

Similar to the reactivity of complex **1**, addition of an excess of THF to a CS₂ solution of **3** gave Re₂(μ-I)₂(CO)₆(THF)₂ by slow displacement of selenium, the latter being characterized as the red α-Se₈ through an X-ray powder diagram. Treatment of complex **3** with PPh₃ (PPh₃/3 molar ratio = 6) in CS₂ leads promptly to ReI(CO)₃(PPh₃)₂, red

(37) Steudel, R.; Steidel, J.; Pickardt, J.; Schuster, F. *Z. Naturforsch., B: Chem. Sci.* **1980**, *35*, 1378.

(38) Hohl, D.; Jones, R. O.; Car, R.; Parrinello, M. *Chem. Phys. Lett.* **1987**, *139*, 540.

(39) Cherin, P.; Unger, P. *Acta Crystallogr., Sect. B* **1972**, *28*, 313.

(40) van Bolhuis, F.; Koster, P. B.; Migchelsen, T. *Acta Crystallogr.* **1967**, *23*, 90.

(41) Steudel, R.; Strauss, E.-M. *Z. Naturforsch., B: Chem. Sci.* **1981**, *36*, 1085.

(42) α-Se₈: *a* = 9.054 Å, *b* = 9.083 Å, *c* = 11.601 Å, β = 90.81°. See ref 39.

selenium, and (Se)PPh₃. The formation of these products is in agreement with both the stronger donor properties of PPh₃, as compared to *cyclo*-Se₇, and the known reactivity of PPh₃ with red selenium.⁴³

Treatment of **2** with red selenium suspended in CS₂ leads to complete substitution of S₈ and formation of **3** within a few hours. This is in agreement with the previous studies on the donor properties of the organic dichalcogenides E₂-Ph₂ (E = S, Se, Te) within the Re₂(μ-Br)₂(CO)₆ fragment. The equilibrium constants for the formation of the dichalcogenide complexes decrease in the order Te > Se > S (see footnote d of Table 1), whereas the ν_{CO} values decrease in the sequence S > Se > Te (Table 1), suggesting that the strength of the rhenium–ligand bond is mainly related to the σ-donor ability in the order Te > Se > S. On the other hand, the complex Re₂(μ-I)₂(CO)₆[Se₂(CH₂Ph)₂] does not show displacement of the diselenide ligand by red selenium after 1 day in CS₂, suggesting that *cyclo*-heptaselenium is a weaker ligand than Se₂(CH₂Ph)₂. By combining the results contained in this paper, the following sequences of preferential ligation for rhenium(I) can be suggested: Se₇ > Se₈; Se₇ > S₈; SBU₂ > S₈; Se₂(CH₂Ph)₂ > Se₇.

5. Conclusions. The complexes Re₂(μ-X)₂(CO)₆(S₈) (X = Br, **1**; I, **2**) and Re₂(μ-X)₂(CO)₆(Se₇) (X = I, **3**; Br, **4**) are the only derivatives of elemental sulfur and selenium, respectively, observed both in solution and in the solid state, in the case of a transition metal cation. From the spectroscopic results, the Se₇ ring seems to be a stronger ligand as compared to S₈. Complexes **1–4** may be regarded as the primary step of the reactions leading to polychalcogenides through cleavage of the chalcogen–chalcogen bond. Thanks to the new findings in the literature since our preliminary data,²⁴ it is possible to better define the nature of our system. The rhenium(I) complexes described in this paper well complement the literature data, as far as metal-coordinated chalcogens are concerned. As a matter of fact, the Re(I)–Se average bond distance of 2.586(3) Å in Re₂(μ-I)₂(CO)₆(Se₇), which, as noted above, compares well with the Re(I)–Se distance of 2.604(4) Å in the diphenyldiselenide complex Re₂(μ-Br)₂(CO)₆(Se₂Ph₂),^{33,44a} should be compared with the Rh(II)–S distances of 2.519–2.547 Å observed for the supramolecular structures of [Rh₂(O₂CCF₃)₄]_n(S₈)_m (n/m = 1, 1.5), in which the sulfur ligand is 1,3-coordinated (for n/m = 1) to the central metal atom.²⁵ As the size of selenium is about 0.13 Å larger than that of sulfur,^{44b} the conclusion can be reached that the Re(I)–Se₇ bond should be somewhat stronger than that of *cyclo*-octasulfur with rhodium(II).

The chalcogen complexes of Group 11 cations copper(I) and silver(I) mentioned in the Introduction can now be compared with the rhenium(I) complexes of the present paper. In the [Ag(S₈)₂]⁺ cation, the two sulfur ligands are

1,3-coordinated at Ag–S bond distances of 2.744 and 2.803 Å.²¹ In [CuXSe₃]_n (X = Br, I),²² the selenium ligand is intercalated in the crystal lattice as a linear noncyclic entity. Finally, in [CuClSe₂]_n,²³ Se₆ rings are present which are 1,2 coordinated to different copper(I) ions, the Se–Se distance between the Se atoms interacting with copper being 2.390 Å.

The information contained in this paper is believed to be important for planning the synthesis of new transition metal complexes of chalcogens and chalcogen-containing ligands.

Experimental Section

General Methods. All operations were carried out with dry oxygen-free solvents and under dinitrogen following conventional Schlenk techniques. *cyclo*-Octasulfur was recrystallized from CS₂. Infrared spectra were recorded in the appropriate solvent on Perkin-Elmer Model 883 and FT-IR Perkin Elmer Model 1725 X instruments. The NMR spectra were measured on Bruker AC-250 (5.87 T) and Varian Gemini-200 BB (4.7 T) instruments. ¹³C, ³¹P, and ⁷⁷Se NMR chemical shifts were referenced to SiMe₄, H₃PO₄, and SeMe₂, respectively. Re₂(μ-Br)₂(CO)₆(THF)₂^{44a} and Re₂(μ-I)₂(CO)₆(THF)₂⁴⁵ were prepared as reported in the literature.

Sublimed Selenium. Commercial gray selenium (20 g) was pyrolyzed under reduced pressure (10^{−2} Torr) at about 240 °C in a 1-L flask equipped with a coldfinger (cooled with liquid nitrogen). The red sublimed Se_n was scraped from the coldfinger and kept at about −30 °C until it was used for the subsequent reaction with the rhenium(I) complexes. From a CS₂ saturated solution of the sublimed Se_n (about 0.05% w/v), monoclinic α-Se₈ separated out slowly at room temperature. The cell constants of the precipitate (a = 9.068 Å, b = 9.080 Å, c = 11.572 Å, β = 90.75°) compare well with the values for α-Se₈ reported in the literature.⁴²

Synthesis of Re₂(μ-Br)₂(CO)₆(S₈), **1.** The THF adduct Re₂(μ-Br)₂(CO)₆(THF)₂ (0.575 g, 0.68 mmol) was dissolved in 35 mL of CS₂ together with *cyclo*-S₈ (0.178 g, 0.69 mmol). The yellow solution was cooled to about −10 °C, and anhydrous ZrCl₄ (2.33 g, 10.0 mmol) was added. The suspension was stirred at about −5 °C for 4 h and then filtered. The dark red solution was concentrated under reduced pressure (0 °C) to about 5 mL, and heptane (10 mL) was added. The red precipitate was filtered off and dried under reduced pressure (0.32 g, 49% yield). Anal. Calcd for C₆Br₂O₆-Re₂S₈: C, 7.5; Br, 16.7; Re, 38.9; S, 26.8. Found: C, 7.4; Br, 17.2; Re, 38.5; S, 26.7.

Synthesis of Re₂(μ-I)₂(CO)₆(S₈), **2.** The THF adduct Re₂(μ-I)₂(CO)₆(THF)₂ (1.09 g, 1.16 mmol) and *cyclo*-S₈ (0.40 g, 1.56 mmol) were added to 50 mL of heptane. The resulting colorless suspension was stirred in the dark at 23–25 °C for 1 day, and the solvent was evaporated under reduced pressure in order to remove THF. The operation was repeated until no more starting material was observed (IR). The final suspension was filtered and washed with heptane. The brick red product was dried under reduced pressure (0.75 g, 62% yield). Anal. Calcd for C₆I₂O₆Re₂S₈: C, 6.9; I, 24.1; Re, 35.4; S, 24.4. Found: C, 6.9; I, 22.8; Re, 35.8; S, 23.4.

Decomposition of Re₂(μ-X)₂(CO)₆(S₈) (X = Br, **1; X = I, **2**) in CS₂.** Complex **1** was dissolved in CS₂ (10^{−3} M), and the infrared spectra were recorded at 25 °C within 4 h. From the values of the absorbance at ν = 1968 cm^{−1}, the decomposition was found to follow approximate first-order kinetics with a τ_{1/2} = 2.8 h. Similarly,

(43) (a) Brown, D. H.; Cross, R. J.; Keat, R. *J. Chem. Soc., Dalton Trans.* **1980**, 871. (b) Kroshefsky, R. D.; Weiss, R.; Verkade, J. G. *Inorg. Chem.* **1979**, *18*, 469. (c) McFarlane, H. C. E.; McFarlane, W. *NMR of Newly Accessible Nuclei*; Laszlo, P., Ed.; Academic Press: New York, 1983; Vol. 2, p 275.

(44) (a) Vitali, D.; Calderazzo, F. *Gazz. Chim. Ital.* **1972**, *102*, 587. (b) Wells, A. F. *Structural Inorganic Chemistry*, 5th ed.; Clarendon Press: Oxford, 1986; pp 700–702.

(45) Calderazzo, F.; Vitali, D.; Poli, R.; Atwood, J. L.; Rogers, R. D.; Cummings, J. M.; Bernal, I. *J. Chem. Soc., Dalton Trans.* **1981**, 1004.

Table 3. Crystallographic Data for $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_7)$, **3**

empirical formula	$\text{C}_6\text{I}_2\text{O}_6\text{Re}_2\text{Se}_7^{1/2}\text{C}_7\text{H}_{16}$
fw	1397.1
T , K	293(2)
cryst syst	triclinic
space group	$P\bar{1}$ (No.2)
a , Å	10.468(6)
b , Å	10.823(10)
c , Å	11.699(7)
α , deg	105.66(6)
β , deg	95.85(6)
γ , deg	104.15(4)
V , Å ³	1217(2)
Z	2
ρ_{calcd} , g/cm ³	3.812
μ , mm ⁻¹	22.959
obsd reflns [$I > 2\sigma(I)$]	4422
data/restraints/params	7104/0/224
$R(F_o)$ [$I > 2\sigma(I)$]	0.0573
$R_w(F_o^2)$	0.1795

$$^a R(F_o) = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; R_w(F_o^2) = \left[\frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right]^{1/2}$$

$$w = 1/[\sigma^2(F_o^2) + (0.1281P)^2].$$

2 decomposed at 25 °C with a $\tau_{1/2} = 1.7$ h, leading to a uncharacterized dark blue precipitate containing both rhenium and sulfur.²⁹

Synthesis of $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_7)$, **3.** The precursor $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{THF})_2$ (0.476 g, 0.507 mmol) was treated with sublimed Se_n (0.345 g, 4.37 mmol for $n = 1$) in CS_2 (15 mL). The suspension was stirred in the dark for 21 h at room temperature; throughout this time, the volatiles were removed under reduced pressure. The dry residue was dissolved in fresh CS_2 , and this operation was repeated three times until the IR spectrum of the supernatant solution in the carbonyl stretching region showed that the starting carbonyl derivative had disappeared. The final suspension was filtered, and CS_2 was evaporated. The resulting brown product was washed with heptane and dried under reduced pressure (300 mg, 44% yield). Anal. Calcd for $\text{C}_6\text{I}_2\text{O}_6\text{Re}_2\text{Se}_7$: C, 5.4; Se, 41.0. Found: C, 5.5; Se, 40.8. ¹³C NMR (CS_2 , 20 °C): $\delta = 187.1, 184.5, 182.6$ (CO). ⁷⁷Se NMR (CS_2 , 20 °C): $\delta = 1150, 1011, 973, 927$ (2 Se, 2 Se, 2 Se, 1 Se). The *cyclo*-heptaselenium rhenium(I) complex is readily soluble in CS_2 (about 4% w/v) and stable in air under dry conditions.

Spectroscopic Evidence of $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{Se}_7)$, **4.** $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{THF})_2$ (0.311 g, 0.368 mmol) was treated with sublimed Se_n (0.280 g, 3.55 mmol for $n = 1$) in 10 mL of CS_2 . After 1 d at room temperature, the red solution showed the presence of $\text{Re}_2(\mu\text{-Br})_2(\text{CO})_6(\text{Se}_7)$, **4**. ⁷⁷Se NMR (CS_2 , 20 °C): $\delta = 1137, 1002, 984, 929$ (2 Se, 2 Se, 2 Se, 1 Se).

X-ray Diffraction Study. A red prismatic crystal of $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_7)$, **3** ($0.38 \times 0.29 \times 0.24$ mm³), obtained by slow evaporation of a CS_2 /heptane solution, was sealed in a glass capillary and was mounted on a Philips PW1100 diffractometer, equipped with a graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The lattice showed the parameters listed in Table 3. The collection of data with $3.1^\circ < \theta < 30^\circ$, $\theta/2\theta$ scan mode, gave 7104 intensities with 4422 $I > 2\sigma(I)$. The intensities were corrected for Lorentz and polarization effects and for absorption by the ψ -scan technique⁴⁶ (transmission factor 0.1–1.0). The structure solution was obtained by means of the automatic Patterson method and

completed by the standard difference Fourier maps (SHELXS-86).⁴⁷ Residual absorption effects were accounted for empirically by using DIFABS program (transmission factor 0.6–1.0).⁴⁸ A heptane molecule disordered around the special position at $0^{1/2}1/2$ was also found, 3.5 carbon atoms, located by the difference Fourier map, being introduced in the calculations and refined without constraints, while the hydrogen atoms were omitted. The refinement, based on full-matrix least-squares on F^2 , was done by means of the SHELX92 program,⁴⁹ giving the reliability factors listed in Table 3. The final goodness of fit on F^2 was 0.954. Residual electron density peaks of intensity among 3.978 and $-3.782 \text{ e} \cdot \text{Å}^{-3}$ were present in the final difference Fourier map in the vicinity of the rhenium atoms probably because of a defective description of their thermal motion and absorption effects.

Reaction of $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_7)$, **3, with THF.** Compound **3** (100 mg) was dissolved in CS_2 (15 mL), and THF (4 mL) was added. Insoluble red selenium precipitated out slowly from the orange solution at +4 °C. After a few hours, the solid was washed with pentane, dried under reduced pressure, and characterized as $\alpha\text{-Se}_8$ as established by an X-ray powder diagram measurement ($a = 9.072$ Å, $b = 9.079$ Å, $c = 11.625$ Å, $\beta = 90.99^\circ$).⁴²

Reaction of $\text{Re}_2(\mu\text{-I})_2(\text{CO})_6(\text{Se}_7)$, **3, with PPh₃.** Compound **3** (15 mg, 0.011 mmol) was dissolved in CS_2 (0.5 mL), and PPh₃ (6 mg, 0.023 mmol) was added. Red insoluble selenium precipitated out readily from the solution, with disappearance of **3** in solution, as confirmed by IR spectroscopy. By addition of the phosphine with a PPh₃/Re molar ratio > 3 , the compounds $\text{ReI}(\text{CO})_3(\text{PPh}_3)_2$ [IR (CS_2): $\nu_{\text{CO}} = 2034, 1945, 1909 \text{ cm}^{-1}$] and SePPh_3 [³¹P NMR (CS_2 , C_6D_6 lock): $\delta = 35.1, ^1J(\text{Se}, \text{P}) = 760 \text{ Hz}$] were formed in solution after 10 min.⁴³

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Note Added after ASAP: An error introduced during production was identified in the version of this paper posted ASAP on June 21, 2002, and corrected in the version posted ASAP on June 25, 2002. The first sentence in the last paragraph of the Experimental Section should read as follows: Compound **3** (15 mg, 0.011 mmol) was dissolved in CS_2 (0.5 mL), and PPh₃ (6 mg, 0.023 mmol) was added.

Supporting Information Available: X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(46) North, C. T.; Phillips, C.; Mathews, F. S. *Acta Crystallogr.* **1968**, A24, 351.

(47) Sheldrick, G. M. *Crystallographic Computing 3*; Sheldrick, G. M., Krüger, C., Goddard, R., Eds.; Oxford University Press: New York, 1985; pp 175–189.

(48) Walker, N.; Stuart, D. DIFABS. *Acta Crystallogr.* **1983**, A39, 158.

(49) Sheldrick, G. M. *SHELX-92, Program for Crystal Structure Refinement*; Institut für Anorganische Chemie der Universität: Göttingen, Germany, 1992.