ogenous bridging ligand. Preceding examples have concerned only single types of bridging networks; thus, in the present system, this feature appears as an intrinsic property and not as the result of a combination of factors.

Registry No. **1**, 2242-96-8; **2**, 5862-32-8; **3**, 113177-61-0; **4**, 116179-36-3; **5**, 116102-25-1; H(L), 116102-15-9; *o*-phenylenediamine, 95-54-5; mercaptopropionic acid, 79-42-5; 2,6-bis(hydroxymethyl)-4-methylphenol, 91-04-3.

Supplementary Material Available: Listings of anisotropic thermal parameters (Tables S1-3), bond distances (Tables S4-6), and bond angles (Tables S7-9) (8 pages); listings of structure factors (Tables S10-12) (28 pages). Ordering information is given on any current masthead page.

Contribution from the Istituto per lo Studio della Stereochimica ed Energetica
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Stepwise Metal-Assisted Conversion of η^2-CSe$_2$ to η^1-Se$_2$CPEt$_3$, η^2-Se$_2$CO, and η^2-Se$_2$. Crystal Structures of the Complexes [(triphos)Rh(Se$_2$CO)]BPh$_4\cdot$0.5CH$_2$Cl$_2\cdot$0.5C$_4$H$_9$OH and [(triphos)Rh(μ-Se$_2$)$_2$Rh(triphos)](BPh$_4$)$_2\cdot$2DMF [triphos = MeC(CH$_2$PPh$_2$)$_3$]

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The reaction of (triphos)RhCl(η^2-CSe$_2$) (**1**) in CH$_2$Cl$_2$ with PEt$_3$ gives the phosphoniodiselenoformate complex (triphos)RhCl(Se$_2$CPEt$_3$) (**2**). Compound **2** reacts at room temperature in CH$_2$Cl$_2$ solution with dioxygen to yield OPEt$_3$ and (triphos)-RhCl(Se$_2$CO) (**3**). The chloride ligand can be removed from **3** in CH$_2$Cl$_2$ by NaBPh$_4$ in 1-butanol to give the 16-electron complex [(triphos)Rh(Se$_2$CO)]BPh$_4\cdot$0.5CH$_2$Cl$_2\cdot$0.5C$_4$H$_9$OH (**4**), which photochemically or thermally undergoes the chelotropic elimination of CO to form the bis(μ-diselenium) complex [(triphos)Rh(μ-Se$_2$)$_2$Rh(triphos)](BPh$_4$)$_2\cdot$2DMF (**5b**). The crystal structures of **4** and **5b** have been determined by X-ray crystallography. **4** crystallizes in the triclinic system, space group $P\bar{1}$, with a = 18.853 (6) Å, b = 16.744 (5) Å, c = 11.021 (3) Å, α = 69.45 (2)°, β = 81.23 (2)°, γ = 77.35 (2)°, and Z = 2. The structure was refined to an R factor of 0.071 (R_w = 0.072) for 4093 unique reflections. The structure consists of monomeric complex cations [triphos)Rh(Se$_2$CO)]$^+$, BPh$_4^-$ anions, and some amount of CH$_2$Cl$_2$ and 1-butanol molecules of crystallization. The metal atom is five-coordinated by the three phosphorus atoms of triphos and by the two selenium atoms of the diselenocarbonate ligand in a distorted-square-pyramidal environment. **5b** crystallizes in the triclinic system, space group $P\bar{1}$, with a = 16.950 (5) Å, b = 13.710 (4) Å, c = 13.379 (4) Å, α = 90.19 (1)°, β = 98.53 (2)°, γ = 104.03(2)°, and Z = 1. The structure was refined to a final R factor of 0.053 (R_w = 0.057) for 5458 unique reflections. The structure consists of binuclear [(triphos)Rh(μ-Se$_2$)$_2$Rh(triphos)]$^{2+}$ cations, BPh$_4^-$ anions, and DMF molecules of crystallization. The system consists of two (triphos)Rh(η^2-Se$_2$) fragments related by a crystallographic inversion center. Each rhodium atom is coordinated by the three phosphorus atoms of triphos, an η^2-diselenium molecule, and one selenium atom from the other (triphos)Rh(η^2-Se$_2$) moiety.

Introduction

Over the past decade there has been increasing interest in metal complexes containing selenium ligands because of their implication in catalysis and biology and their potential application in organic and organometallic synthesis.[1-4] A large number of preparative routes have been developed to introduce selenium into a complex framework,[5,6] including the reaction of CSe$_2$ with metal fragments.[7] This method is perhaps the most versatile and leads very frequently to η^2-CSe$_2$ derivatives. The latter complexes exhibit a rich ligand-centered reactivity, which is mainly due to the dual nature of the metal-η^2-CSe$_2$ moiety, i.e. electrophilic at the carbon atom and nucleophilic at the uncoordinated selenium atom.[7]

In this article we describe the stepwise metal-promoted transformation of the ligand CSe$_2$ within (triphos)RhCl(η^2-CSe$_2$) (**1**) into a variety of selenium-containing species such as η^1-Se$_2$CPEt$_3$, η^2-Se$_2$CO, and η^2-Se$_2$ [triphos = MeC(CH$_2$PPh$_2$)$_3$]. The structure of the first metal diselenocarbonate [(triphos)Rh(Se$_2$CO)]BPh$_4\cdot$0.5CH$_2$Cl$_2\cdot$0.5C$_4$H$_9$OH (**4**) and that of the diselenium complex [(triphos)Rh(μ-Se$_2$)$_2$Rh(triphos)](BPh$_4$)$_2\cdot$2DMF (**5b**) have been determined by X-ray methods. The latter complex is of particular interest because it exhibits a novel bonding mode of the diselenium unit.

A preliminary account of part of this work has already been published.[8]

Results and Discussion

Synthesis and Characterization of Se$_2$CPEt$_3$ and Se$_2$CO^{2-} Complexes. In previous MO studies on the bonding capabilities of heteroallene molecules,[9] we emphasized the percentage contribution of the heteroallene orbitals to the frontier orbitals as a very important tool to interpret the chemical reactivity. In

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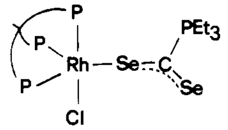
particular, the reactions of η^2-CX_2 complexes (X = S, Se) with nucleophiles occur at the carbon atom in nice agreement with the LUMO orbital centered on the CX_2 molecule and largely developed at its carbon atom. As a matter of fact, PEt_3 reacts with a CH_2Cl_2 solution of **1** to give the green phosphoniodiselenoformate complex (triphos)RhCl(Se_2CPEt_3) (**2**) (eq 1), which can be prepared also by adding the preformed zwitterion Et_3PCSe_2 to a solution of (triphos)RhCl(C_2H_4) (eq 2).

$$\text{(triphos)RhCl}(\eta^2\text{-CSe}_2) + \text{PEt}_3 \rightarrow \text{(triphos)RhCl(Se}_2\text{CPEt}_3) \quad (1)$$

$$\text{(triphos)RhCl(Cl}_2\text{H}_4) + \text{Et}_3\text{PCSe}_2 \rightarrow \text{(triphos)RhCl(Se}_2\text{CPEt}_3) + \text{C}_2\text{H}_4 \quad (2)$$

Compound **2** is air-sensitive both in the solid state and in solution, in which it is nonconducting. The IR spectrum closely resembles that of the sulfur analogue except for containing a $\nu(CSe_2)_{asym}$ stretching vibration at 970 cm^{-1} in the place of $\nu(CS_2)_{asym}$ observed at 1045 cm^{-1}.[10] Quite comparable is also the $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 293 K) containing a doublet of doublets at 30.45 ppm [J(P(triphos)–P(PEt_3)) = 17.2 Hz, J(P(triphos)–Rh) = 127.6 Hz] and a pseudoquintuplet at 23.9 ppm [J(P(PEt_3)–Rh) = 16.5 Hz] (relative intensities 3:1). In view of these data, it is reasonable to assign to **2** a structure in which



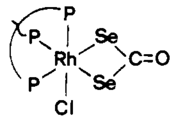
2

the rhodium atom is coordinated by the three phosphorus atoms of triphos, a chloride ligand, and only one selenium atom from Se_2CPEt_3. Note that a chelate coordination mode of the latter ligand can be dismissed by a simple electron counting, which would assign 20 electrons to the metal.

The reaction of **2** in CH_2Cl_2 solution with O_2 yields the yellow complex (triphos)RhCl(Se_2CO) (**3**) and $OPEt_3$ (eq 3). The

$$\text{(triphos)RhCl(Se}_2\text{CPEt}_3) + \text{O}_2 \rightarrow \text{(triphos)RhCl(Se}_2\text{CO)} + \text{OPEt}_3 \quad (3)$$

diselenocarbonate complex **3** is obtained also by exposure to air either of solid samples or of solutions of **2**. In this case, however, the phosphine oxide cannot be detected, as it is sensitive to moisture. Compound **3** is quite air-stable and soluble in chlorinated solvents, in which it is nonconducting. The IR spectrum contains a strong band at 1650 cm^{-1}, which is assigned to ν(C=O) of the diselenocarbonate ligand. The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 293 K) exhibits a typical AM_2X pattern with a doublet of doublets at 25.85 ppm [$J(P_A–P_B)$ = 27 Hz, $J(P_A–Rh)$ = 108.1 Hz] and a doublet of triplets at −6.24 ppm [$J(P_B–Rh)$ = 96.7 Hz] (relative intensities 1:2). On the basis of all of these data, compound **3** is assigned a structure in which the rhodium atom is

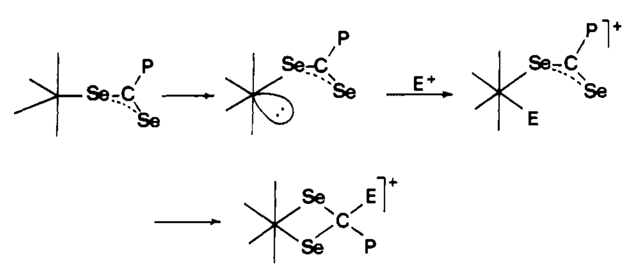


3

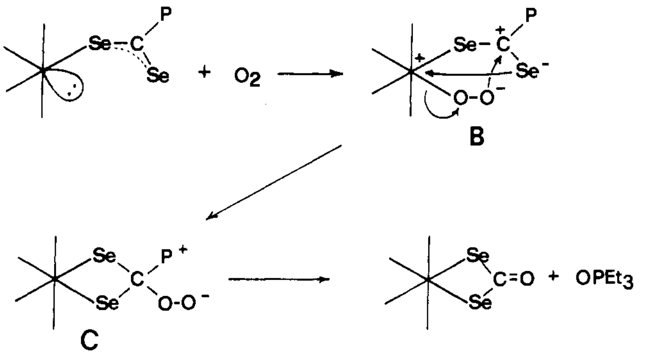
six-coordinated by the three phosphorus atoms of triphos, a chloride ligand, and the two selenium atoms of a diselenocarbonate group.

The present route to the diselenocarbonate complex **3**, occurring also in the solid state, is cleaner than the one that involves atmospheric decomposition of [(triphos)Rh(Se_2C(H)(PEt_3))](BPh_4)$_2$.[11] In fact, it is reasonable to assume that only one O_2 molecule is engaged in the present process of metal oxidation and formation of the reaction products. Although a detailed mechanistic study is beyond the purposes of the present work, we propose the following as a reasonable route for the oxidation reaction (3).

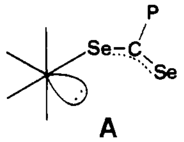
Scheme I



Scheme II

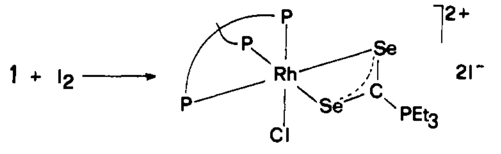


A slight displacement of the coordinated selenium atom in the equatorial plane of the trigonal bipyramid of **2** favors the localization of a metal lone pair at relatively high energy; see structure A. Substantially, the hybrid corresponds to the frontier σ orbital of a d^8-L_5M fragment,[12] and its populating electrons can easily be either removed by oxidants or attacked by electrophiles.

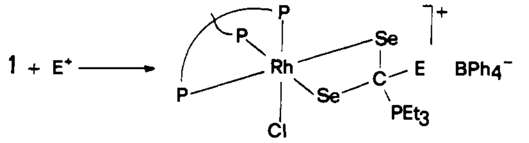


A

In particular, by using I_2 as an oxidant, we have been able to isolate the complex [(triphos)RhCl(Se_2CPEt_3)]I_2 (eq 4),[11] while the reaction with electrophiles E^+ (E = H, Me) yields the Rh(III) phosphonium–betaine-like derivatives [(triphos)RhCl(Se_2CE(PEt_3))]BPh_4 (eq 5).[11] The latter reaction has been suggested to proceed through a mechanism that involves attack by the electrophile at the metal, followed by migration of the E group to the carbon atom of the η^1-Se_2CPEt_3 group. Ultimately, the latter reaches the more stable chelate configuration (Scheme I).[11]



(4)



(5)

Accordingly, with the use of molecular oxygen, it is not unlikely that the series of intermediates B and C is formed, which after a complex rearrangement eventually gives the dithiocarbonate **4** and phosphine oxide as final products (Scheme II).

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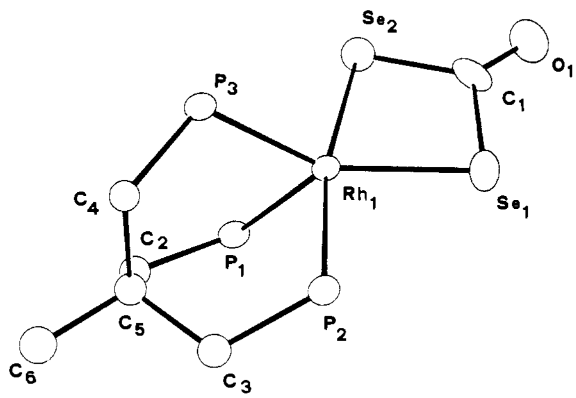
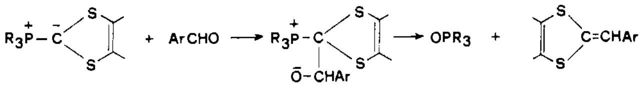


Figure 1. ORTEP drawing (30% probability ellipsoids) for the cation $[(\text{triphos})\text{Rh}(\text{Se}_2\text{CO})]^+$ in **4**.

Actually, we have no evidence for the formation of any intermediates A–C, but the mechanism has good precedent as shown by (6), which illustrates the Wittig reaction between dithio phosphorances and aromatic aldehydes[13] and the O_2 addition to phosphorances to give ketones and phosphine oxides.[14]



$$R_3P{=}CR'R'' + O_2 \longrightarrow R_3PO + R'R''C{=}O \qquad (6)$$

The chloride ligand in **3** is easily replaced by other monofunctional groups like N_3^- but can be also definitely removed from the complex by treatment of a CH_2Cl_2 solution of **3** with $NaBPh_4$ in 1-butanol. As a result, the 16-electron rhodium(III) complex $[(\text{triphos})\text{Rh}(\text{Se}_2\text{CO})]\text{BPh}_4{\cdot}0.5\text{CH}_2\text{Cl}_2{\cdot}0.5\text{C}_4\text{H}_9\text{OH}$ (**4**) is quantitatively obtained (eq 7).

$$(\text{triphos})\text{RhCl}(\text{Se}_2\text{CO}) + \text{NaBPh}_4 \rightarrow [(\text{triphos})\text{Rh}(\text{Se}_2\text{CO})]\text{BPh}_4 + \text{NaCl} \qquad (7)$$

Compound **4** is air-stable in the solid state and soluble in common organic solvents, in which it behaves as a 1:1 electrolyte (molar conductance value in 10^{-3} M 1,2-dichloroethane solution is 40 Ω^{-1} cm^2 mol^{-1}). The IR spectrum in the C=O stretching region has a strong band at 1680 cm^{-1}, which is assigned to ν(C=O) of the selenocarbonate ligand. The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 293 K) consists of a doublet at 34.15 ppm [J(P(triphos)–Rh) = 98.3 Hz]. Such a pattern is consistent with the rapid intramolecular exchange of the three phosphorus atoms, as commonly found for five-coordinate triphos complexes.[11,15] The structure of **4**, determined by X-ray methods, contains monomeric complex cations $[(\text{triphos})\text{Rh}(\text{Se}_2\text{CO})]^+$, BPh_4^- anions, and some amount of CH_2Cl_2 and 1-butanol solvent molecules. A perspective view of the complex cation is given in Figure 1. Selected bond distances and angles are reported in Table I. The metal atom is coordinated by the three phosphorus atoms of triphos and by the two selenium atoms of the diselenocarbonate ligand in a distorted-square-pyramidal environment. The distortion from the limit geometry is evidenced by the values of the Se2–Rh–P2 and Se1–Rh–P3 bond angles, 168.6 (1) and 144.2 (1)°, respectively, instead of the ideal 180°. The rhodium atom and the diselenocarbonate ligand are essentially coplanar, the maximum deviation from the least-squares plane being 0.03 Å. The Rh–P distances averaging 2.295 (4) Å fall in the usual range. A direct comparison with other diselenocarbonate complexes is precluded since **3** and **4** represent the first examples of such compounds; however, the bond distances within the Rh–η^2-Se_2CO moiety, Rh–Se(av) = 2.448 (2) Å and Se–C(av) = 1.923 (18) Å, may be compared with the corresponding values reported for the parent complex (triphos)RhCl(η^2-CSe_2), Rh–Se(endo) = 2.514 (4) Å Se(endo)–C = 1.90 (3) Å.[11f] The somewhat shorter Rh–Se distances may be likely due to a π-bonding interaction at work to partially relieve the electron deficiency of the 16-electron metal center. The C–O distance of 1.193 (23) Å well matches the values found for several dithiocarbonate complexes.[16]

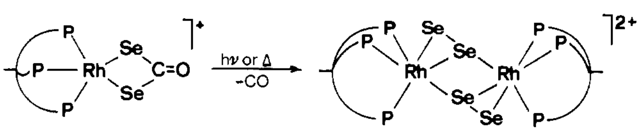
Table I. Selected Bond Lengths (Å) and Angles (deg) for **4**

Rh1–Se1	2.425 (1)	P2–C3	1.81 (2)
Rh1–Se2	2.471 (2)	P3–C4	1.82 (2)
Rh1–P1	2.251 (4)	O1–C1	1.19 (2)
Rh1–P2	2.347 (5)	C2–C5	1.55 (2)
Rh1–P3	2.289 (3)	C3–C5	1.55 (2)
Se1–C1	1.96 (2)	C4–C5	1.55 (2)
Se2–C1	1.89 (2)	C5–C6	1.56 (2)
P1–C2	1.81 (1)		
P2–Rh1–P3	89.0 (1)	Rh1–P1–C2	112.8 (5)
P1–Rh1–P3	85.8 (1)	Rh1–P2–C3	110.0 (5)
P1–Rh1–P2	91.4 (2)	Rh1–P3–C4	111.3 (5)
Se2–Rh1–P3	99.2 (1)	Se2–C1–O1	129 (1)
Se2–Rh1–P1	68.6 (1)	Se1–C1–O1	124 (1)
Se2–Rh1–P1	97.0 (1)	Se1–C1–Se2	107.0 (8)
Se1–Rh1–P3	144.2 (1)	P1–C2–C5	117.7 (9)
Se1–Rh1–P2	90.4 (1)	P2–C3–C5	116 (1)
Se1–Rh1–P1	130.0 (1)	P3–C4–C5	115.6 (9)
Se1–Rh1–Se2	78.30 (8)	C3–C5–C4	113 (1)
Se3–Rh1–Se2	88.93 (5)	C2–C5–C4	111 (1)
Se3–Rh1–P3	173.03 (8)	C2–C5–C3	109 (1)
Rh1–Se1–Rh'1	102.55 (5)	C4–C5–C6	107 (1)
Rh1–Se1–C1	87.3 (6)	C3–C5–C6	108 (1)
Rh1–Se2–C1	87.4 (6)	C2–C5–C6	107 (1)

Table II. Selected Bond Lengths (Å) and Angles (deg) for **5b**

Rh1–Se1	2.531 (1)	P2–C2	1.838 (8)
Rh1–Se2	2.494 (1)	P3–C3	1.83 (1)
Rh2–Se1	2.556 (1)	C1–C4	1.56 (1)
Rh1–P1	2.313 (2)	C2–C4	1.56 (1)
Rh1–P2	2.343 (3)	C3–C4	1.55 (1)
Rh1–P3	2.343 (3)	C4–C5	1.54 (1)
P1–C1	1.832 (9)		
P2–Rh1–P3	88.25 (9)	Rh1–P2–C2	110.0 (3)
P1–Rh1–P3	88.34 (8)	Rh1–P3–C3	110.5 (3)
P1–Rh1–P2	90.99 (9)	P1–C1–C4	117.9 (6)
Se2–Rh1–P3	87.76 (7)	P2–C2–C4	117.0 (6)
Se2–Rh1–P2	162.98 (7)	P3–C3–C4	116.6 (6)
Se2–Rh1–P1	105.42 (7)	C2–C4–C3	110.3 (7)
Se1–Rh1–P3	173.03 (8)	C1–C4–C3	111.5 (7)
Se1–Rh1–P2	93.16 (6)	C1–C4–C2	112.3 (7)
Se1–Rh1–P1	98.45 (6)	C3–C4–C5	107.3 (7)
Se1–Rh1–Se2	88.93 (4)	C2–C4–C5	107.9 (7)
Rh1–P1–C1	110.4 (3)	C1–C4–C5	107.2 (7)

Thermal and Photochemical Decomposition of 4. At variance with the six-coordinate diselenocarbonate **3**, which is quite thermally stable in solution, the five-coordinate derivative **4** readily decomposes even in the dark (see below) when refluxed in THF or DMF, forming CO and the binuclear μ-Se_2 complex $[(\text{triphos})\text{Rh}(\mu\text{-Se}_2)_2\text{Rh}(\text{triphos})](\text{BPh}_4)_2{\cdot}$solvent [solvent = THF (**5a**), 2DMF (**5b**)] (eq 8). Compounds **5a** and **5b** are air-stable both in the solid state and in solution. They are poorly soluble in common organic solvents except DMF. The $^{31}P\{^1H\}$ NMR spectrum of **5b** (DMF, 293 K, 32.12 MHz) (Figure 2) consists



(8)

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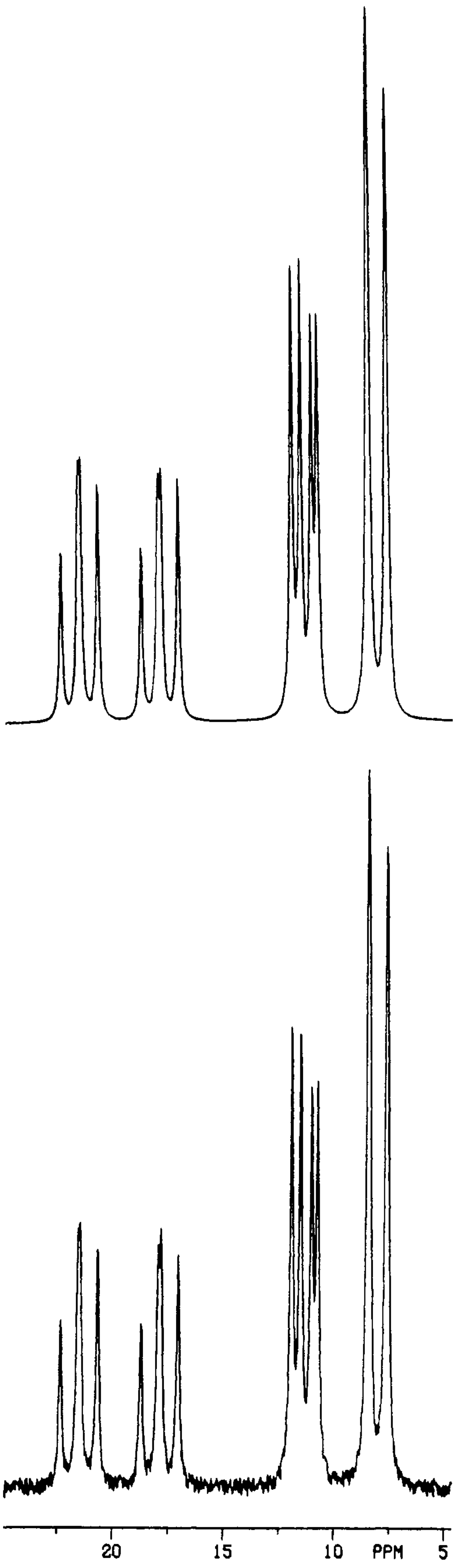


Figure 2. Experimental (DMF, 293 K, 32.12 MHz, H_3PO_4 reference) (bottom) and computed (top) $^{31}P\{^1H\}$ NMR spectra of **5b**.

of an ABCX spin system, constant in the temperature range 323–223 K, with $\delta(P_A)$ 19.66, $\delta(P_B)$ 9.59, and $\delta(P_C)$ 9.76 [$J(P_A-P_B) = 25.03$ Hz, $J(P_A-P_C) = 28.93$ Hz, $J(P_B-P_C) = 0.16$ Hz, $J(P_A-Rh) = 116.75$ Hz, $J(P_B-Rh) = 99.87$ Hz, $J(P_C-Rh) = 110.99$ Hz].

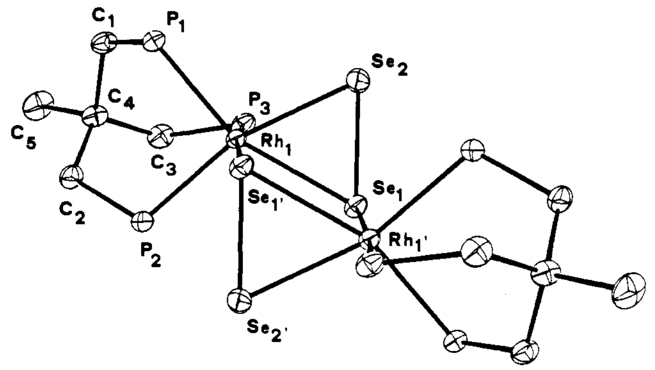
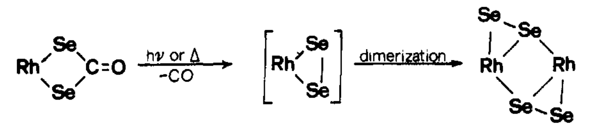


Figure 3. ORTEP drawing (30% probability ellipsoids) for the cation [(triphos)Rh(μ-Se$_2$)$_2$Rh(triphos)]$^{2+}$ in **5b**. Primed atoms are related by a center of symmetry.

Scheme III



The structure of **5b** consists of discrete [(triphos)Rh(μ-Se$_2$)$_2$Rh(triphos)]$^{2+}$ cations and BPh_4^- anions. The DMF solvent molecules are in no way coordinated to the metals. Figure 3 shows an ORTEP drawing of the complex cation. Selected bond distances and angles are summarized in Table II. The dimeric complex cation is located on a crystallographic inversion center. The two (triphos)Rh(η^2-Se$_2$) subunits are linked together by a selenium atom of each Se$_2$ moiety. In such a way, a four-membered RhSeRhSe ring is formed that exhibits nearly equal Rh–Se bond lengths [Rh1–Se(av) = 2.543 (1) Å]. The geometry of each rhodium atom can be described in terms of a distorted octahedron, as it occurs in the related cation [(triphos)Rh(μ-S$_2$)$_2$Rh(triphos)]$^{2+}$, which displays an identical bridging system.[17] Interestingly, the Rh–Se distances are very close to the distance of 2.514 (4) Å observed in the parent compound **2**, where one of the C–Se bond is η^2-coordinated to rhodium.[7f] Other authenticated examples of metal complexes containing bridging diselenium units are Fe$_2$(CO)$_6$(μ-Se$_2$)[18] and (η-C$_5$H$_5$)Cr$_2$(CO)$_4$(Se$_2$),[6f] in which the Se$_2$ unit was found to bridge two metals in the η^4-fashion. To the best of our knowledge, the present μ-η^2:η^1-bridging system has not been so far observed in solid-state structures although its existence was proposed on the basis of spectroscopic studies for some iridium compounds.[6c] The Se1–Se2 distances of 2.298(1) Å compares well with analogous distances in the monomeric complexes [Ir(η^2-Se$_2$)(dppe)$_2$]$^+$ [2.312 (3) Å][5c] and Os(η^2-Se$_2$)(CO)$_2$(PPh$_3$)$_2$ [2.321 (2) Å],[6a] in the previously mentioned binuclear systems [2.293 (2) and 2.277 Å for the Fe[18] and Cr[6f] derivatives, respectively], and in the complex [W$_2$(CO)$_{10}$Se$_4$]$^{2+}$, in which each η^2-coordinated Se$_2$ side of the bridging Se$_4$ unit has a length of 2.208 (1) Å.[6g] These data indicate that the η^2-Se$_2$ ligand does not change significantly while making additional bonds with other atoms.

Compound **4** is stable in CH$_2$Cl$_2$ solution even when refluxed for several hours under the condition that the reaction vessel is kept in the dark. By contrast, the exposure to the light of a standard tungsten lamp leads within 2 h to the quantitative conversion of **4** to [(triphos)Rh(μ-Se$_2$)$_2$Rh(triphos)](BPh$_4$)$_2$·CH$_2$Cl$_2$ (**5c**). Such a decomposition pathway is not influenced by the frequency of the radiation, **5c** being obtained as the only product also by UV irradiation of a CH$_2$Cl$_2$ solution of **4** (eq 8).

In view of the present results and of those found for the related sulfur derivative [(triphos)Rh(S$_2$CO)]BPh$_4$ (**6**),[19] a plausible

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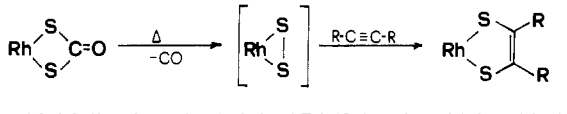
reaction pathway for the formation of **5a–c** is the one shown in Scheme III. This involves chelotropic elimination of CO from the RhSeC(O)Se ring, followed by dimerization of the coordinatively and electronically unsaturated (triphos)Rh(Se_2) moiety.

In effect, we have recently discovered that the thermal or photochemical decomposition of the sulfur derivative **6** gives the bis(μ-S_2) analogue of **5**[17] except in the presence of an activated alkyne such as dimethyl acetylenedicarboxylate, in which case the dithiolene complex [(triphos)Rh{$S_2C_2(CO_2Me)_2$}]BPh_4 is formed (eq 9).[20] Evidently, the chelotropic elimination of CO



(9)

from **4** initially gives the (triphos)Rh(S_2) unit, which oxidatively adds the alkyne. Unfortunately, all our attempts to trap the (triphos)Rh(Se_2) fragment with an alkyne were unsuccessful, likely because of a rate of dimerization faster than that for the sulfur analogue.

Another way by which **4** is converted to **5** is the reaction in CH_2Cl_2 with oxidizing agents such as O_2, H_2O_2, or *m*-chloroperbenzoic acid. Interestingly, we note that the formation of **5c** is accompanied by that of some CO_2. Such a result is hard to explain, especially when one considers the mild reaction conditions. Tentatively, we suggest that the chelotropically eliminated CO group may initially have a transient nature as it happens when CO is chemisorbed at metal surfaces. In this eventuality, the reaction with oxygen to give CO_2 is well documented.[21] In addition, we have recently reported that **6** can react with O_2 in CH_2Cl_2 to give the μ-SO complex [(triphos)Rh(μ-SO)$_2$Rh(triphos)](BPh_4)$_2$ and CO_2 or with H_2 to give the μ-SH hydride [(triphos)RhH(μ-SH)$_2$RhH(triphos)](BPh_4)$_2$ via heterolytic splitting of dihydrogen.[15b] On account of a much greater lability of the Se–O vs S–O bonds,[4,22] the cleavage of O_2 can be promoted by **4** without leading to any stable complex.

The reactivity of **5** toward alkylating agents, strong acids, and CO has been investigated. In no case was a reaction observed, and this is further evidence for the stability of the μ-η^2:η^1-dichalcogen bridge.

Experimental Section

All the reactions and manipulations were routinely performed under a nitrogen atmosphere unless otherwise stated. All materials and solvents were of reagent grade quality and were used without further purification. Et_3PCSe_2[10] and the complexes (triphos)RhCl(CSe_2)[7f] and (triphos)RhCl(C_2H_4)[23] were prepared by published procedures. The solid complexes were collected on a sintered-glass frit, appropriately washed, and finally dried in a stream of nitrogen. IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer as Nujol mulls between KBr plates. $^{31}P\{^1H\}$ NMR spectra were recorded with a Varian CFT 20 spectrometer. Downfield shifts are expressed with a positive sign, in ppm, relative to external 85% H_3PO_4. Conductance measurements were made with a WTW Model LBR/B conductivity bridge. CO and CO_2 were detected by using a Shimadzu GC-8A gas chromatograph on a Carbosieve S-II column purchased from Supelco, Inc. The $^{31}\{^1H\}$ NMR spectrum of **5b** was simulated by using an updated version of the LAOCN3 program.[24] The initial choices of shifts and coupling constants were refined by successive iterations, the assignment of the experimental lines being performed automatically. The final parameters gave a fit to the observed line positions better than 0.6 Hz.

(triphos)RhCl(Se_2CPEt_3) (2). Method A. Neat PEt_3 (0.1 mL, 0.7 mmol) was syringed into a suspension of (triphos)RhCl(η^2-CSe_2) (0.46 g, 0.5 mmol) in THF (40 mL); the mixture was then stirred for 3 h until the complete consumption of the starting rhodium compound. The resulting deep green solution, concentrated to ca. 5 mL, gave on addition of benzene (40 mL) green crystals. These were filtered off and washed with benzene and petroleum ether; yield 60%.

Table III. Crystallographic Data for **4** and **5b**

	5b	**4**
formula	$C_{136}H_{132}B_2P_6Rh_2Se_4N_2O_2$	$C_{68.5}H_{65}BClO_{1.5}P_3RHSe_2$
fw	2555.7	1312.19
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	16.950 (5)	18.853 (6)
b, Å	13.710 (4)	16.744 (5)
c, Å	13.379 (4)	11.021 (3)
α, deg	90.193 (1)	69.454 (2)
β, deg	98.533 (2)	81.231 (2)
γ, deg	104.031 (2)	77.351 (2)
V, Å^3	2980	3168
Z	1	2
T, °C	20	20
λ, Å	0.71069	0.71069
ρ_{calcd}, g cm^{-3}	1.423	1.290
μ, cm^{-1}	16.1	15.5
$R(F_o)$	0.053	0.071
$R_w(F_o)$	0.057	0.072
transmission coeff	0.82–0.87	0.80–0.92

Method B. Solid Et_3PCSe_2 (0.28 g, 1 mmol) was added to a stirred suspension of (triphos)RhCl(C_2H_4) (0.80 g, 1 mmol) in benzene (150 mL). After 30 min the stirring was stopped, and the resulting solution gave on standing green crystals, yield 80%. Anal. Calcd for $C_{48}H_{54}ClP_4RhSe_2$: C, 54.84; H, 5.17; Rh, 9.79; Se, 15.02. Found: C, 54.69; H, 5.17; Rh, 9.62; Se, 14.88.

(triphos)RhCl(Se_2CO) (3). Dioxygen was bubbled through a solution of **2** (0.42 g, 0.4 mmol) in CH_2Cl_2 (30 mL) for 5 min; during this time the color changed from deep green to brown yellow. After dioxygen was replaced with nitrogen, yellow crystals were formed following the addition of ethanol (40 mL) and the partial evaporation of the solvent. These were filtered off and washed with ethanol and petroleum ether; yield 80%. Instead of using oxygen, we also prepared this compound by stirring a solution of **2** in the air for 10 min and working up as above. Anal. Calcd for $C_{42}H_{39}ClOP_3RhSe_2$: C, 53.15; H, 4.14; Rh, 10.84; S, 16.64. Found: C, 53.09; H, 4.12; Rh, 10.69; Se, 16.51. A sample of **2** in CH_2Cl_2 was reacted with dioxygen in an NMR tube. The $^{31}P\{^1H\}$ NMR spectrum at 293 K showed, in addition to the AB_2X pattern of **3**, a singlet at 50.44 ppm, which is due to $OPEt_3$.

[(triphos)Rh(Se_2CO)]BPh_4·0.5CH_2Cl_2·0.5C_4H_9OH (4). A solution of **3** (0.38 g, 0.4 mmol) in CH_2Cl_2 (20 mL) was treated with $NaBPh_4$ (0.17 g, 0.5 mmol) in ethanol (20 mL). There was an immediate color change from yellow to brown. Brown crystals were obtained on partial evaporation of the solvent. These were filtered off and washed with ethanol and petroleum ether; yield 80%. Anal. Calcd for $C_{68.5}H_{65}BClO_{1.5}P_3RhSe_2$: C, 62.69; H, 4.99; Rh, 7.84. Found: C, 62.55; H, 4.91; Rh, 7.79.

Thermal Decomposition of 4. A solution of **4** (0.52 g, 0.4 mmol) in DMF (THF) (20 mL) was heated at 60 °C for 1 h. The resulting red-brown solution was allowed to reach room temperature, and then 1-butanol (30 mL) was added. The solution gave on standing crystals of **5b** (**5a**) in 87% yield, which were filtered off and washed with ethanol and petroleum ether. GC analyses of the gases evolved when the thermal decomposition of **4** was carried out in a sealed tube showed the formation of CO. Anal. Calcd for $C_{136}H_{132}B_2N_2O_2P_6Rh_2Se_4$: C, 63.91; H, 5.20; Rh, 8.05; Se, 12.35. Found: C, 63.85; H, 5.16; Rh, 8.01; S, 12.22.

Photochemical Decomposition of 4. A solution of **4** (0.52 g, 0.4 mmol) in CH_2Cl_2 (30 mL) was irradiated by a standard tungsten or UV lamp. On addition of ethanol (30 mL) and partial evaporation of the solvent, brown crystals of **5c** precipitated in 92% yield.

Reaction of 4 with Dioxygen. Method A. Dioxygen was slowly bubbled through a solution of **4** (0.52 g, 0.4 mmol) in CH_2Cl_2 (30 mL) for 1 h until the color turned to red-brown. On addition of 1-butanol (40 mL), the solution gave on standing brown crystals of **5c**, which were filtered off and washed with ethanol and petroleum ether; yield 70%. The formation of CO_2 during the course of the reaction was evidenced by the precipitation of $BaCO_3$ in an aqueous solution of $Ba(OH)_2$ that was kept in contact with the gas evolved from the reaction vessel.

Method B. A 250-mL Shlenk flask containing a stirring bar and a solution of **4** (0.52 g, 0.4 mmol) in CH_2Cl_2 (20 mL) was accurately evacuated and repressured with oxygen to 1 atm. The solution was stirred at room temperature for 3 h. The formation of CO_2 was evidenced by the GC analysis of gaseous phase. By treatment of the resulting solution as above, **5c** was obtained in 65% yield.

Reaction of 4 with H_2O_2. An excess of H_2O_2 (30% in water) was pipetted into a stirred solution of **4** (0.52 g, 0.4 mmol) in acetone (15 mL)

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Table IV. Atomic Positional Parameters ($\times 10^4$) for $[(triphos)Rh(Se_2CO)]BPh_4 \cdot 0.5CH_2Cl_2 \cdot 0.5C_4H_9OH$ (**4**)

atom	*x*	*y*	*z*
Rh1	945 (1)	69 (1)	1091 (1)
Se1	−528 (1)	−949 (1)	488 (1)
Se2	−312 (1)	280 (1)	1740 (1)
P1	2006 (1)	1364 (2)	1867 (2)
P2	1871 (1)	−603 (2)	339 (2)
P3	1181 (2)	−896 (2)	2496 (2)
C1	2795 (5)	859 (6)	2629 (7)
C2	2882 (5)	−309 (7)	1144 (7)
C3	2229 (5)	−1060 (7)	2656 (7)
C4	2893 (5)	−196 (6)	2304 (6)
C5	3738 (6)	−297 (8)	2842 (8)
B1	3775 (7)	6593 (8)	7157 (8)
C6	3936 (8)	5287 (10)	3941 (10)
C7	2966 (9)	4968 (11)	2310 (11)
C8	3459 (9)	6654 (11)	3140 (11)
N1	3421 (5)	5674 (7)	3156 (7)
O1	3070 (7)	7019 (9)	2438 (9)

Table V. Atomic Positional Parameters ($\times 10^4$) for $[(triphos)Rh(\mu\text{-}Se_2)_2Rh(triphos)](BPh_4)_2 \cdot 2DMF$ (**5b**)

atom	*x*	*y*	*z*
Rh1	2031 (1)	3370 (1)	1147 (1)
Se1	1280 (1)	4432 (1)	−502 (2)
Se2	2368 (1)	2795 (1)	−684 (2)
P1	3173 (2)	3329 (3)	1563 (4)
P2	1533 (2)	4113 (3)	2621 (4)
P3	2070 (2)	2089 (2)	2835 (4)
O1	1504 (7)	3888 (8)	−2687 (12)
C1	1684 (10)	3730 (12)	−1624 (16)
C2	3302 (7)	2902 (9)	3283 (12)
C3	2154 (8)	3866 (9)	3853 (13)
C4	2173 (7)	2229 (8)	4363 (12)
C5	2613 (7)	2937 (9)	4251 (13)
C6	2885 (8)	2732 (10)	5610 (14)
B	2274 (10)	9563 (12)	8390 (18)
Cl1	4564 (6)	7704 (7)	6745 (10)
Cl2	4310 (8)	7148 (10)	4711 (14)
C7	3907 (19)	7517 (22)	5986 (32)
C8	3990 (27)	4677 (32)	5187 (46)
C9	3013 (23)	5623 (26)	4473 (39)
C10	3538 (15)	5228 (18)	4198 (25)
C11	2664 (24)	5356 (28)	5636 (44)
C12	2840 (19)	5511 (22)	6573 (33)

and the resulting mixture stirred for 20 min. Addition of ethanol (30 mL) and DMF (5 mL) gave crystals of **5b**, yield 75%. The evolution of CO_2 was evidenced as above.

Reaction of 2 with Air. A mixture of **2** (1.05 g, 1 mmol) and $NaBPh_4$ (0.41 g, 1.2 mmol) in CH_2Cl_2 (80 mL) and ethanol (50 mL) was stirred in the air with 3 h. During this time the color changed from green to brown, and brown crystals precipitated. These were recrystallized from DMF/1-butanol to give **5b** in 70% yield.

X-ray Diffraction Studies. Crystal data for both compounds **4** and **5b** are summarized in Table III. A Philips PW 1100 diffractometer with Mo Kα graphite-monochromated radiation was used for experimental work. A set of 25 carefully centered reflections were used for the centering procedure of each crystal. As a general procedure, three standard reflections were collected every 2 h (no appreciable decay of intensities was observed in any case). The data were corrected for Lorentz and polarization effects. Numerical absorption corrections were applied with transmission factors 0.91–0.80 and 0.87–0.82 for **4** and **5b**, respectively. Atomic scattering factors were those tabulated by Cromer and Waber[25] with anomalous dispersion corrections taken from ref 26. The computational work was essentially performed by using the SHELX-76 system.[27] The final *R* factors are reported in Table III. The *R* factor of **4** is somewhat higher than usual. This is partly due to the persisting disorder of the solvent molecules even at the later stages of refinement.

$[(triphos)Rh(Se_2CO)]BPh_4 \cdot 0.5CH_2Cl_2 \cdot 0.5C_4H_9OH$ (4). The structure was solved by direct-method and Fourier techniques. Anisotropic thermal parameters were used only for Rh, Se, and P and the C and O atoms of the Se_2CO unit. All the phenyl rings were treated as rigid bodies with D_{6h} symmetry (C–C = 1.39 Å), and the hydrogen atoms were introduced at calculated positions (C–H = 1.0 Å). The non-hydrogen atoms of CH_2Cl_2 were assigned a population parameter of 0.5 and efined accordingly. Also, all the atoms of C_4H_9OH were treated as carbon atoms and assigned a population parameter of 0.5, which was not refined. Final coordinates of non-hydrogen atoms are reported in Table IV, excluding rigid-body atoms.

$[(triphos)Rh(\mu\text{-}Se_2)_2Rh(triphos)](BPh_4)_2 \cdot 2DMF$ (5b). The structure was solved by using direct-method routines in SHELX76 and Fourier techniques. During the least-squares refinement, Rh, Se, and P and the C atoms of the ligand chain were allotted anisotropic thermal parameters. As for the previous compound, the phenyl rings were treated as rigid bodies with D_{6h} symmetry and the hydrogen atoms were introduced at calculated positions. Final coordinates of all non-hydrogen atoms are reported in Table V, excluding rigid-body atoms.

Acknowledgment. We are grateful to Prof. A. Vacca and Dr. J. A. Ramirez for the simulation of the ^{31}P NMR spectrum of **5b**.

Supplementary Material Available: Table SI (complete crystal data), Tables SII and SIII (thermal parameters), Tables SIV and SV (atomic coordinates of rigid-body atoms), and Tables SVI and SVII (calculated coordinates of hydrogen atoms) for **4** and **5b** (13 pages); tables of observed and calculated structure factors for **4** and **5b** (55 pages). Ordering information is given on any current masthead page.

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