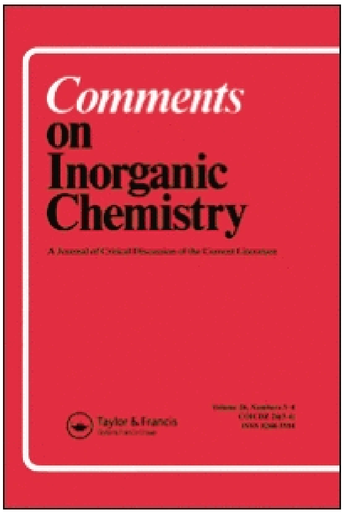

**Comments on Inorganic Chemistry**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455155

# Reactions of Coordinated Ligands Exemplified by the Formation and Transformation of the Dithiocarbonate Ligand in the Rhodium(III) Complex [(triphos)Rh($S_2$CO)]$BPh_4$

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**To cite this Article** Bianchini, Claudio(1988) 'Reactions of Coordinated Ligands Exemplified by the Formation and Transformation of the Dithiocarbonate Ligand in the Rhodium(III) Complex [(triphos)Rh($S_2$CO)]$BPh_4$', Comments on Inorganic Chemistry, 8: 1, 27 — 43

**To link to this Article: DOI:** 10.1080/02603598808048671

**URL:** http://dx.doi.org/10.1080/02603598808048671

# Reactions of Coordinated Ligands Exemplified by the Formation and Transformation of the Dithiocarbonate Ligand in the Rhodium(III) Complex [(triphos)Rh($S_2$CO)]$BPh_4$

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The genesis and chemistry of the S,S-chelate dithiocarbonate ligand in the Rh(III) complex [(triphos)Rh($S_2$CO)]$BPh_4$, (**1**), [triphos = MeC($CH_2PPh_2$)$_3$] have been investigated by means of a variety of chemical and physical techniques. Compound **1** in $CH_2Cl_2$ or THF solutions thermically or photochemically decomposes affording, depending on the reaction conditions, CO and the bis($\mu$-$S_2$) complex [(triphos)Rh ($\mu$-$S_2$)$_2$Rh(triphos)]($BPh_4$)$_2$ or COS and the bis($\mu$-S) complex [(triphos)Rh ($\mu$-S)$_2$Rh(triphos)]($BPh_4$)$_2$. The latter, which can be also obtained by treatment of **1** with $H^+$ or $Me^+$, reacts with $O_2$ yielding the bis($\mu$-SO) derivative [(triphos)Rh($\mu$-SO)$_2$Rh(triphos)]($BPh_4$)$_2$. Nucleophiles such as halides, pseudohalides and $H^-$, add to rhodium to form neutral, octahedral complexes of general formula (triphos)Rh($S_2$CO)(Nu). Heteroallene molecules of the S=C=X type (X = S, O, NR) are metathesized by **1** to give the trithiocarbonate or dithiocarbimate derivatives [(triphos)Rh($S_2$CS)]$BPh_4$ and [(triphos)Rh($S_2$CNR)]$BPh_4$ (R = Ph, Et), which, together with **1**, are able to heterolytically split dihydrogen under very mild conditions. As a result, the hydride (triphos)RhH($S_2$CS), the hydrido(dithiocarbamate) (triphos)RhH($S_2$CNHR) or the $\mu$-SH dimeric hydride [(triphos)RhH($\mu$-SH)$_2$RhH(triphos)]($BPh_4$)$_2$ are obtained, respectively. Finally, **1** is chemically or electrochemically reduced to the Rh(II) congener (triphos)Rh($S_2$CO) which represents one of the very few examples of mononuclear Rh(II) complexes stable both in the solid state and in solution.

**Key Words:** *reactivity of coordinated ligands, sulfur coordination chemistry, dithiocarbonate metal complexes*

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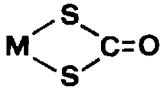
*Comments Inorg. Chem.*
1988, Vol. 8, Nos. 1 & 2, pp. 27–43
Reprints available directly from the publisher

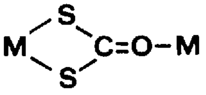
Printed in Great Britain

## I. INTRODUCTION

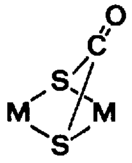
With very few exceptions,[1] dithiocarbonate metal complexes cannot be straightforwardly prepared by reacting metal fragments with the dianion $S_2CO^{2-}$ which is too unstable to disproportionation. Paradoxically, however, dithiocarbonates constitute a ubiquitous class of transition metal complexes. In fact, the indirect synthetic methodology to these compounds is extremely wide, including (a) addition of tertiary phosphines to metal xanthates[2]; (b) reaction of $\eta^2$-$CS_2$ complexes with $O_2$[3] or $SO_2$[4] and vice versa reaction of $O_2$[5] or $SO_2$[4] complexes with $CS_2$; (c) decomposition of 1,1-dithiolate metal compounds in the presence of $O_2$[6]; (d) reaction of $S_8$ with polynuclear metal carbonyls[7]; (e) metal-promoted reductive disproportionation of COS[8]; (f) reaction of $O_2$ with phosphoniodithioformate complexes.[9] The high nucleophilicity of the sulfur atoms and, to a lesser extent, of the ketonic oxygen confer to the dithiocarbonate ligand excellent ligating properties which vary from the quite common $\eta^2$-S,S chelating mode (**I**) in mononuclear complexes[2b,7c,8a,10] to the $\mu,\eta^3$-S,S,O (**II**)[8b] and $\mu,\eta^4$-S,S (**III**)[7] modes in polynuclear species.



(I)



(II)

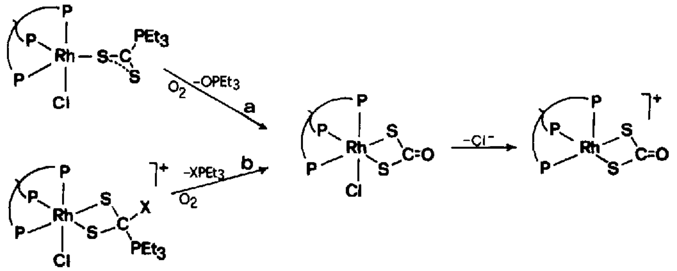


(III)

In spite of the large number of dithiocarbonate complexes, surprisingly little was known about the metal chemistry of this ligand prior to our studies on the rhodium(III) derivative $[(triphos)Rh(S_2CO)]BPh_4$ (**1**) [triphos = $MeC(CH_2PPh_2)_3$]. It is now apparent that the S,S-chelate dithiocarbonate group is a powerful synthon for the generation of a great variety of sulfur-containing ligands, including many very unstable species such as $S_2$ and SO. It is the purpose of this Comment to review the chemistry of **1** and, also, draw attention to the many tools that a current chemist has in hand to check out the reactivity of a coordinated ligand.

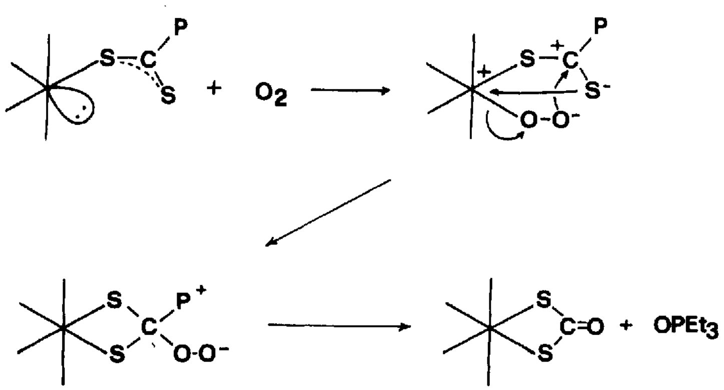
## II. SYNTHESIS AND PHYSICAL PROPERTIES OF 1

Compound **1** can be synthesized by the two procedures shown in (**IV**) (in the sketches of the complexes, the phosphorus atoms of triphos and their connectivity are often omitted).



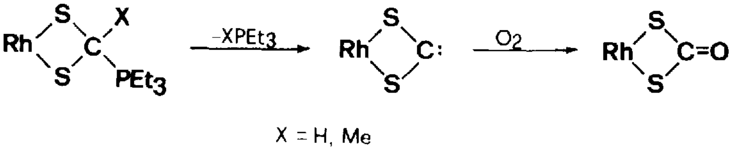
(**IV**)

Route **a** is perhaps the cleanest ever reported to prepare a dithiocarbonate metal complex.[9] It involves reaction of the phosphoniodithioformate [(triphos)RhCl($S_2CPEt_3$)] (**2**) with dioxygen and can occur both in the solid state and in solution. Dioxygen attacks the occupied frontier $\sigma$ orbital that **2** can generate upon slight displacement of the coordinated sulfur atom in the equatorial plane of the trigonal bipyramid (**V**).[6c]



(**V**)

In such a way, an intermediate peroxo complex forms. Successive steps are supposed to be nucleophilic attack by the peroxo group at the $Et_3PCS_2$ carbon atom, followed by a complex intramolecular rearrangement to [(triphos)RhCl($S_2CO$)], (**3**), and phosphine oxide. Although no direct evidence for the formation of any intermediate was provided, the overall mechanism has good precedent, i.e., the Wittig reaction between dithiophosphoranes and aromatic aldehydes[11] as well as the reactions of phosphoranes with $O_2$ to give ketones and phosphine oxides.[12] Once formed, the octahedral dithiocarbonate **3** is readily converted to the five-coordinate derivative **1** by chloride ion elimination with $NaBPh_4$. Alternatively, **1** is synthesized by decomposition in solution of some Rh(III) 1,1-dithiolate complexes of formula [(triphos)Rh($S_2CX(PEt_3)$)]$BPh_4$ (X = H, Me) in the presence of dioxygen (route **b**).[6c] The latter diatomic molecule is believed to attack the electron rich carbenoid carbon atom which forms upon reductive elimination of the $[XPEt_3]^+$ fragments from the starting 1,1-dithiolate complexes (**VI**).

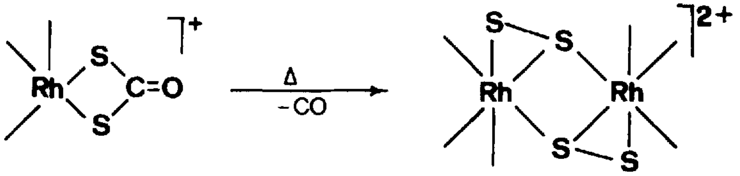


(**VI**)

Compound **1** is isolated as diamagnetic red brown crystals. It is quite air-stable in the solid state and soluble in common organic solvents in which it behaves as a 1:1 electrolyte. The IR spectrum exhibits two absorptions at 1685(vs) and 1600(m) $cm^{-1}$ which are assigned to $\nu(C{=}O)$ of a bidentate dithiocarbonate ligand. The $^{31}P\{^1H\}$ NMR spectrum ($CD_2Cl_2$, 303–213 K) consists of a doublet at 35.22 ppm ($J_{PRh}$ = 98.7 Hz), indicating equivalence of the three phosphorus atoms of triphos. Such a fluxional behavior of five-coordinate triphos complexes is well established and interpreted in terms of a non-bond-breaking isomerization between square planar and trigonal bipyramidal conformations. In the solid state, the complex is square planar as authenticated by an X-ray analysis.

## III. THERMAL AND PHOTOCHEMICAL DECOMPOSITION

Compound **1** is stable for hours in deareated boiling $CH_2Cl_2$ on condition that the reaction vessel is kept in the darkness. By contrast, it quantitatively and almost immediately decomposes when refluxed in THF producing CO and the bis(disulfur)-bridged complex $[(\text{triphos})\text{Rh}(\mu\text{-}S_2)_2\text{Rh}(\text{triphos})](\text{BPh}_4)_2$, (**4**), (**VII**).[13,14] The structure of **4** has been established by X-ray methods (Fig. 1).[13]



**(VII)**

The dimeric complex cation is located on a crystallographic inversion center. The two (triphos)Rh($S_2$) subunits are linked together by the sulfur atoms of the $S_2$ moieties, thus generating a four-membered RhSRhS ring in which all Rh–S bond lengths are nearly equal. A different decomposition pathway of **1** is observed

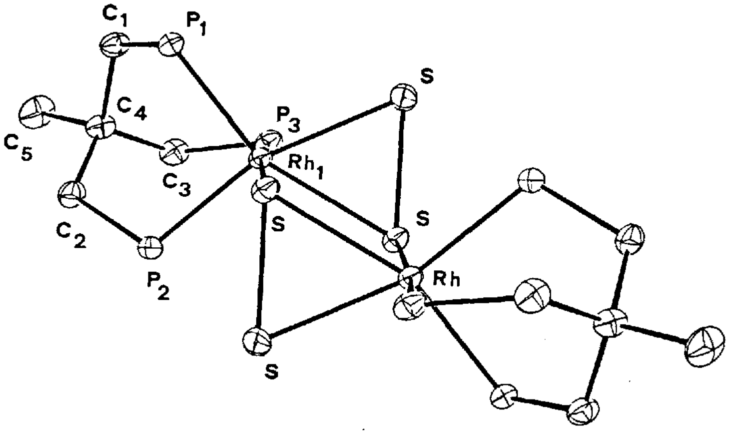
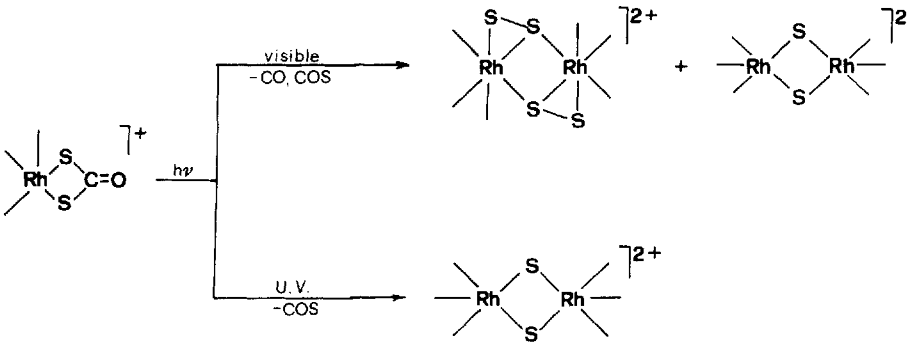


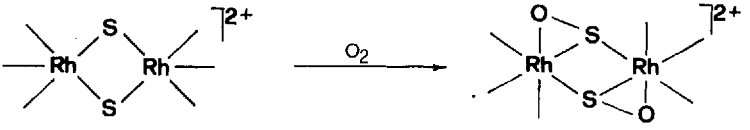
FIGURE 1 ORTEP drawing of the complex cation $[(\text{triphos})\text{Rh}(\mu\text{-}S_2)_2\text{Rh}(\text{triphos})]^{2+}$

when the compound is exposed to the light of a standard tungsten lamp.[13] Within 2 h, **1** transforms into a 6:1 mixture of **4** and the bis(sulfido)-bridged complex [(triphos)Rh($\mu$-S)$_2$Rh(triphos)](BPh$_4$)$_2$, (**5**), evolving COS and CO (**VIII**).



(VIII)

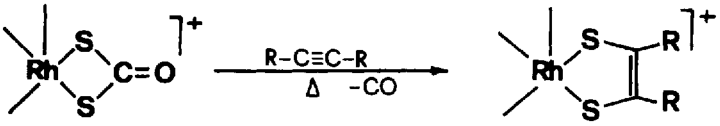
Under UV irradiation in the temperature range −10 to +35°C, the chelotropic elimination of COS prevails over CO elimination. As a result, the $\mu$-S complex **5** is quantitatively obtained. Interestingly, when the latter photochemical reaction is carried out in the presence of dioxygen, instead of **5**, the $\mu$-SO derivative [(triphos)Rh($\mu$-SO)$_2$Rh(triphos)](BPh$_4$)$_2$, (**6**), is formed.[9] Most likely, the first step of the reaction is the chelotropic elimination of COS from **1** to give **5**, which is successively oxydized at the sulfur bridges by O$_2$. Indeed, the $\eta^2$-S,O:$\eta^1$-S sulfur monoxide complex **6** is quantitatively obtained by reaction of **5** with O$_2$ (**IX**).[15]



(IX)

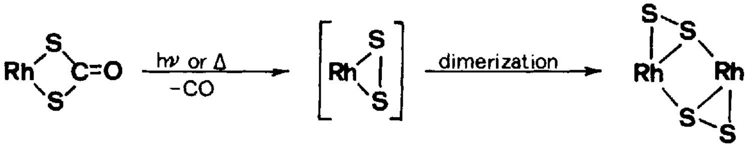
The structure of the $\mu$-SO complex cation, consisting of two (triphos)Rh($\eta^2$-SO) fragments related by a crystallographic inversion center, closely resembles that of the $\mu$-S$_2$ congener. Binding of the sulfur atom from a side-on coordinated SO ligand to the other rhodium results in the formation of a four-membered RhSRhS ring.

Analogously to the UV irradiation of organic dithiocarbonates which promotes the chelotropic elimination of CO to give dithiete intermediates,[16] the thermal or photochemical decomposition of the inorganic dithiocarbonate **1** proceeds through an Rh-$\eta^2$-$S_2$ monomeric species which can be trapped by oxidative addition of an activated alkyne. In such a way, dithiolene complexes are formed (X).[14]



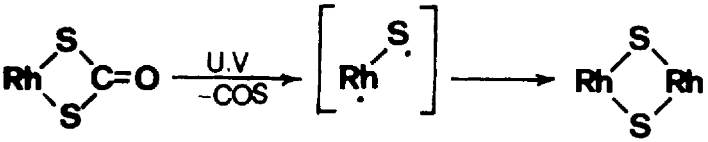
(X)

In the light of the latter results, the formation of the bis($\mu$-$S_2$) complex **4** can be reasonably interpreted in terms of coupling of two coordinatively and electronically unsaturated (triphos)Rh($\eta$-$S_2$) units (XI).



(XI)

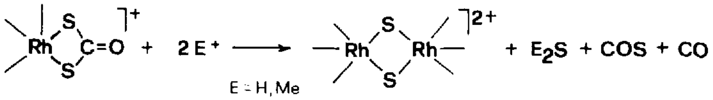
At variance with the photochemical reactions of organic dithiocarbonates, **1** may also lose COS, a reaction pathway that resembles the decomposition of disubstituted dithiazoles (XII).[17]



(XII)

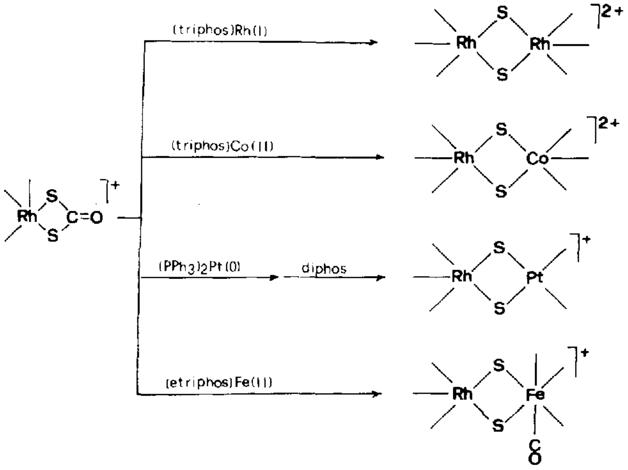
## IV. REACTIONS WITH ELECTROPHILES

The chemistry of **1** is highly influenced by the nucleophilic character of the sulfur atoms, each of which, although engaged in bonding with rhodium and carbon atoms, still possesses enough electron density to interact with electrophiles. As a matter of fact, treatment of **1** with alkylating agents or strong protic acids yields the bis-μ-sulfido complex **5** together with a variety of byproducts, including dialkyl sulfides, $H_2S$, COS and CO (**XIII**).[14]



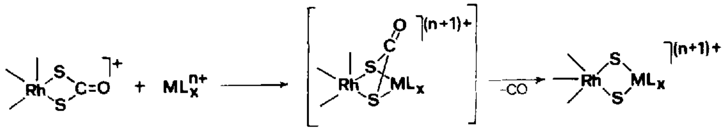
(XIII)

Of much more practical relevance are the reactions of **1** with coordinatively unsaturated metal fragments generally leading to homo- or heterobimetallic bis(μ-sulfido) compounds.[18] In a typical procedure, **1** in $CH_2Cl_2$ is added to a solution of the appropriate metal fragment. In most instances, the reactions complete within the time of mixing of the coreactants. An overview of the bis(μ-S) complexes which are obtainable by the so-called "metal-assisted three fragment demolition of the dithiocarbonate ligand" is shown in (**XIV**) [etriphos = $MeC(CH_2PEt_2)_3$; diphos = $Ph_2PCH_2CH_2PPh_2$].



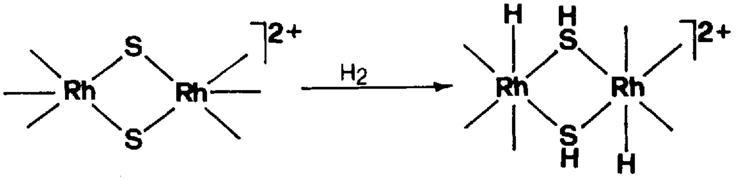
(XIV)

The reaction proceeds through chelotropic elimination of CO from the RhSCOS cycle, induced by interaction of the externally added metal fragment with the sulfur atoms of the dithiocarbonate group (XV).



(XV)

Since the formal oxidation state of the entering metals is generally raised by two, it has been suggested that electrons are transferred from the these into strongly antibonding C–S orbitals of the rhodium dithiocarbonate system. Bridging-sulfido metal complexes are receiving much interest, in large part because of their use as models for biological systems as well as the variety of their applications in stoichiometric and catalytic reactions. As a matter of fact, we have found that some of the bis($\mu$-S$)_2$ complexes shown in (XIV) exhibit effectiveness in activating molecular hydrogen. In particular, the derivative with the [Rh($\mu$-S$)_2$Rh] core, **5**, is able to heterolytically cleave $H_2$ according to (XVI).[15]



(XVI)

The process is reversible, i.e., the $\mu$-SH hydride [(triphos)RhH($\mu$-SH$)_2$RhH(triphos)](BPh$_4)_2$, (**7**), loses $H_2$ in solution under a stream of nitrogen or argon.

Preliminary results show that **5** is an excellent catalyst precursor for the selective hydrogenation of alkynes and alkenes.[14]

It is worth noticing that the mode of activation of dihydrogen by **5** closely resembles that of the hydrogenase enzymes constituted by [4Fe-4S] clusters and whose active sites are believed to be bridging sulfido groups.[19]

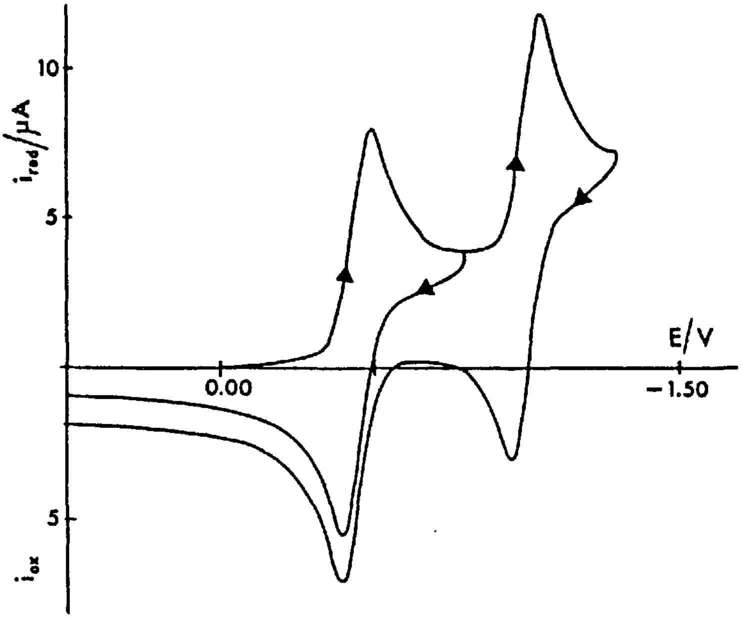
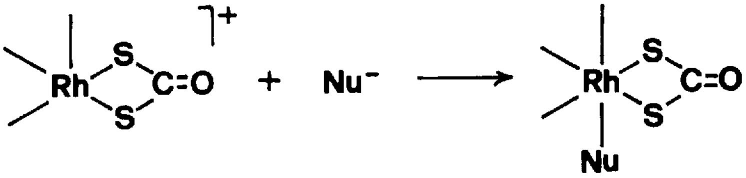


FIGURE 2 Cyclic voltammogram recorded at a platinum electrode on a $CH_2Cl_2$ solution containing $[NBu_4]ClO_4$ (0.1 mol $dm^{-3}$) and $[(triphos)Rh(\mu\text{-}S)_2Rh(triphos)](BPh_4)_2$ ($4.9 \times 10^{-4}$ mol $dm^{-3}$). Scan rate: 0.2 $Vs^{-1}$.

Chemical and electrochemical studies have pointed out that it is possible to add or remove valence electrons from the bis(μ-S) compounds containing the $[(triphos)M(\mu\text{-}S)_2M'(triphos)]$ moiety (M,M′ = Rh, Co) with no consequential change of the primary geometry.[18] In particular, the dimers with the $[Rh(\mu\text{-}S)_2Rh]$ and $[Rh(\mu\text{-}S)_2Co]$ cores undergo electron transfer reactions that encompass the 0, +1 and +2 charges. As an example, Fig. 2 shows the cyclic voltammetric responses exhibited by the complex cation $[(triphos)Rh(\mu\text{-}S)_2Rh(triphos)]^{2+}$.

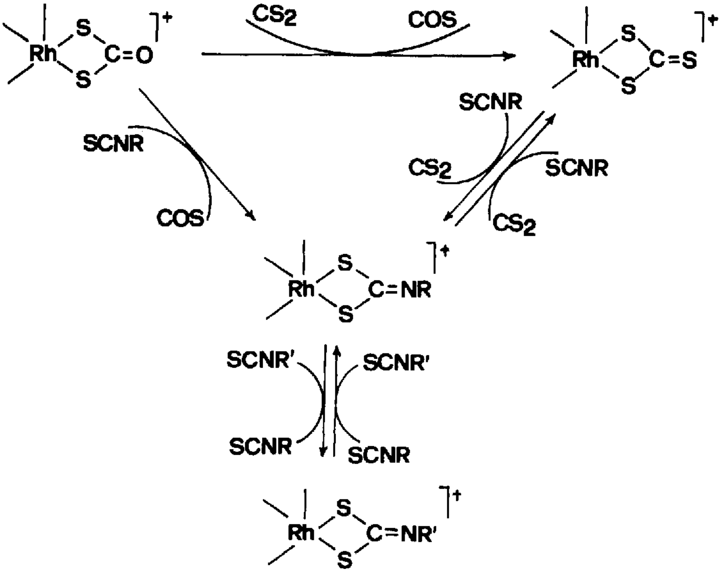
## V. REACTIONS WITH HETEROALLENE MOLECULES AND $H_2$

In addition to the two basic sulfur atoms, **1**, which is coordinatively and electronically unsaturated, contains an electrophilic metal center susceptible to attack by a great variety of nucleophiles, including halides, pseudohalides and H$^-$.[9,14] Invariably, neutral octahedral rhodium complexes of formula (triphos)Rh($S_2CO$)(Nu) are formed **(XVII)**.



(XVII)

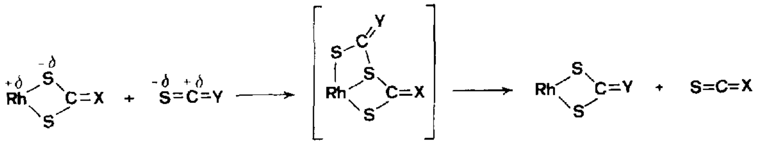
Apparently, the two sulfur atoms of the dithiocarbonate ligand, although capable of transferring electron density to rhodium via π interaction, do not adequately satisfy the electronic requirement of the metal which therefore still remains an electrophilic center. Indeed, the dual nature of 1 makes it capable of metathesizing polarizable molecules such as the heterocumulenes COS, $CS_2$ and SCNR (R = Ph, Et) to give hitherto not obtainable trithiocarbonate and dithiocarbimate derivatives of rhodium(III) **(XVIII)**.[20]



(XVIII)

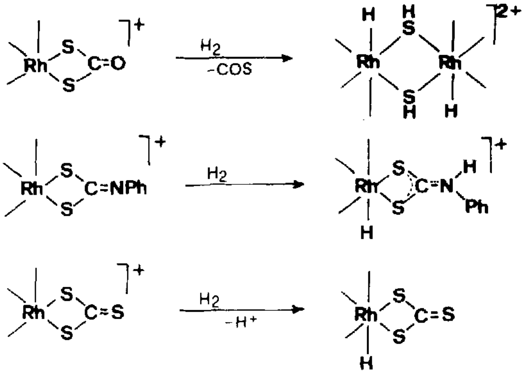
In a typical reaction, treatment of **1** in $CH_2Cl_2$ at room temperature with the appropriate heteroallene readily yields the corresponding 1,1-dithiolate derivative and COS. Similarly, the trithiocarbonate (triphos)Rh($S_2CS$), (**8**), and dithiocarbimates, (triphos)Rh($S_2CNR$) (R = Ph, **9**; Et, **10**), transform into each other by reaction with SCNR and $CS_2$, respectively. The dithiocarbamates **9** and **10** seem to have comparable thermodynamic stabilities since their interconversion is achieved only when large excess of the appropriate SCNR molecule are used.

The formation of bimetallacycle intermediates via [2 + 2] cycloaddition of the entering heteroallene to the 1,1-dithiolate complex is considered an important mechanistic step of these reactions (**XIX**).



(XIX)

Owing to the polarized nature of the Rh–S linkages, the present 1,1-dithiolate complexes of rhodium(III) are able to activate $H_2$ under very mild conditions.[21] Stirring of the compounds in $CH_2Cl_2$ under 1 atm of $H_2$ at room temperature results in the heterolytic splitting of the latter diatomic into $H^-$ and $H^+$.



(XX)

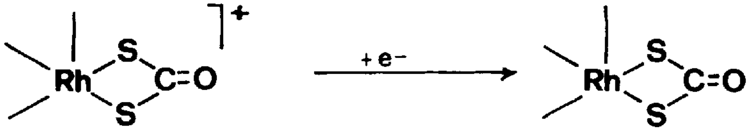
As shown in (**XX**), the hydridic hydrogen invariably remains coordinated at rhodium whereas the proton shifts over the complex surfaces to find a basic site where it can be stabilized. This may be the sulfur atom of the dithiocarbonate ligand, thus promoting the chelotropic elimination of COS (see **XIII**) or the nitrogen atom of the dithiocarbimate group which is consequently transformed into dithiocarbamate. As a result the derivatives [(triphos)RhH($\mu$-SH)$_2$RhH(triphos)](BPh$_4$)$_2$, (triphos)RhH(S$_2$CNHR) and (triphos)RhH(S$_2$CS) are obtained. Only in the case of **8** does the proton remain formally free; however its formation during the reaction was unequivocally determined by addition of NEt$_3$.[21]

## VI. ELECTROCHEMISTRY

Figure 3 shows the cyclic voltammetric behavior of **1** at a platinum electrode in deaerated CH$_2$Cl$_2$ solution.

The analysis of the cyclic voltammogram with scan rates indicates that the cathodic electron-transfer at $E^\circ = -0.21$ V (vs. S.C.E.) is quasireversible in character. Macroelectrolysis experiments performed at the potential of $-0.5$ V are consistent with the consumption of 1 mol of electrons/mol of **1**. During this process the red-brown starting solution turns green and, by addition of *n*-heptane, separates green crystals of formula (triphos)Rh(S$_2$CO), (**11**).

Compound **11** which is paramagnetic with a magnetic moment corresponding to one unpaired spin, can also be obtained by chemical reduction of **1** in THF with NaC$_{10}$H$_8$ (**XXI**).



(XXI)

The structure of **12**, which represents one of the very few examples of stable, monomeric Rh(II) complexes, has been established by ESR spectroscopy.[14] The complex is square pyramidal in the solid state and exhibits fluxional behavior in ambient tem-

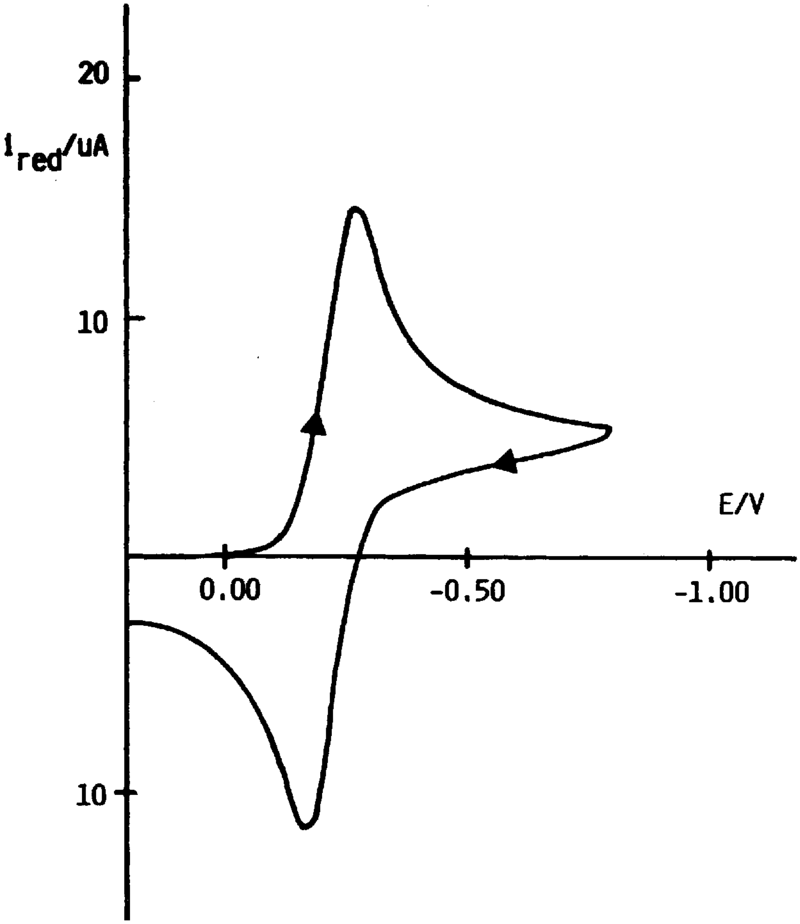
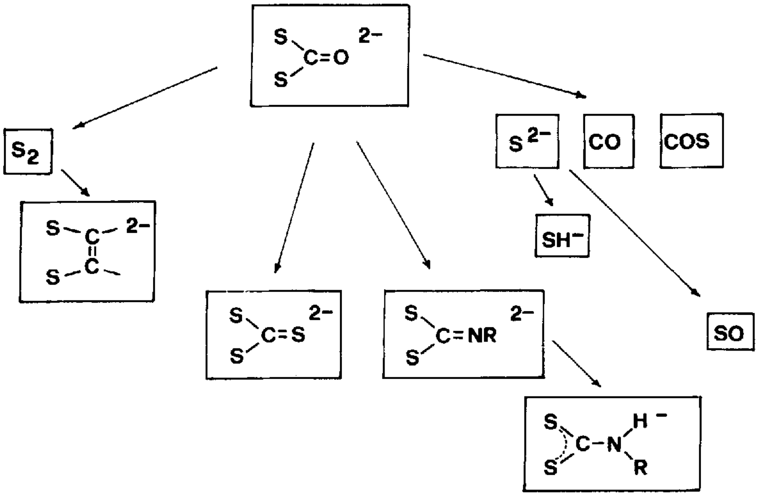


FIGURE 3 Cyclic voltammogram recorded at a platinum electrode on a $CH_2Cl_2$ solution of $[(triphos)Rh(S_2CO)]^+$. Scan rate 0.2 $Vs^{-1}$.

perature solutions. This is clearly shown by the ESR spectrum at 303 K (Fig. 4) which consists of a quartet at ⟨g⟩ = 2.059 (Ap = 91 G), thus indicating equivalence of the three phosphorus atoms of triphos. A fast interconversion between square pyramidal and trigonal bipyramidal geometries characterizes the solution behavior of the Rh(III) parent compound **1**. As there is no reason to believe that an extra electron in the system may raise a high energy barrier for such an interconversion, the same type of fluxionality can be ascribed to **11**.

## VII. CONCLUSIONS

It is well known that the reactivity of many chemical species may be greatly enhanced upon coordination to metal centers. In this respect, very few examples are as pertinent as the dithiocarbonate case presented in this Comment and conveniently summarized in **(XXII)**.



**(XXII)**

In the light of the present results, it is possible that in the next few years dithiocarbonate metal complexes will prove to be largely used starting compounds for the introduction of different types of sulfur ligands into complex frameworks.

**Acknowledgments**

I am deeply indebted to the co-workers, listed in the references, who have contributed efforts and ideas to the research which has inspired this manuscript and, especially, to Andrea Meli for his great help.

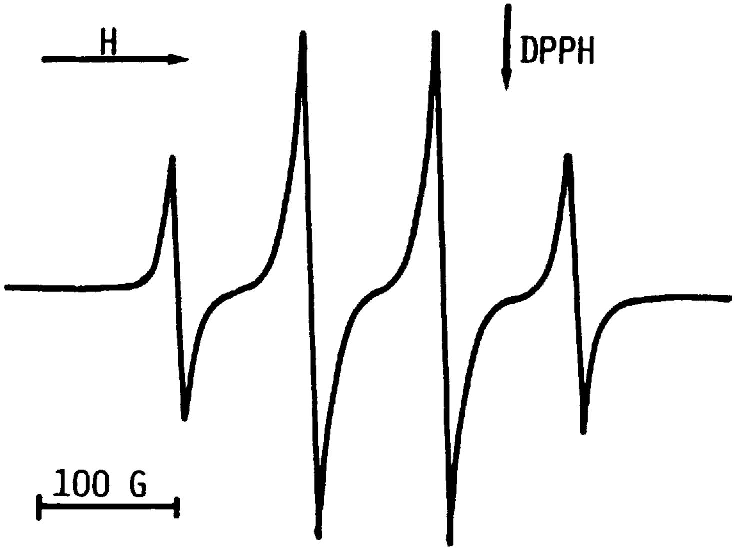


FIGURE 4 X-Band ESR spectrum of [(triphos)Rh($S_2$CO)]$BPh_4$ in $CH_2Cl_2$ solution at 303 K.

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