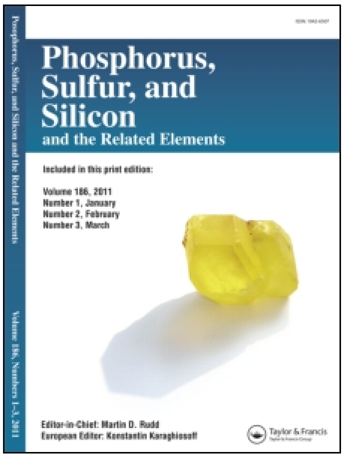

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Synthesis and Characterization of Dirhodium Complexes Containing μ-SO, μ-SH, and μ-S_2 Groups Stabilized by the Tripodal Ligand $CH_3C(CH_2PPh_2)_3$

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SYNTHESIS AND CHARACTERIZATION OF DIRHODIUM COMPLEXES CONTAINING μ-SO, μ-SH, AND μ-S_2 GROUPS STABILIZED BY THE TRIPODAL LIGAND $CH_3C(CH_2PPh_2)_3$

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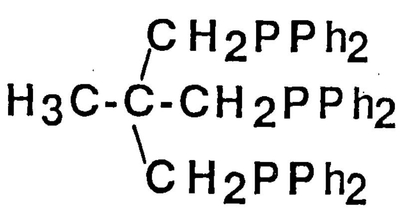
Abstract A family of dirhodium complexes containing bridging chalcogen compounds has been synthesized and fully characterized by X-ray methods and NMR spectroscopy. The reactivity of the disulphido complex $[(triphos)Rh(\mu\text{-}S)_2Rh(triphos)][BPh_4]_2$ has been studied in detail.

Polyphosphine ligands are eliciting considerable attention in some topical areas of inorganic and organometallic chemistry,[1] including: (a) synthesis of metal complexes with unusual coordination geometries, (b) formation of stable complexes of low-valent metals, (c) stabilization of highly reactive molecules (such as P_4, As_3, Te_2, η^2-H_2 *etc.*) trough complexation, (d) selective and efficient homogeneous catalytic reactions.

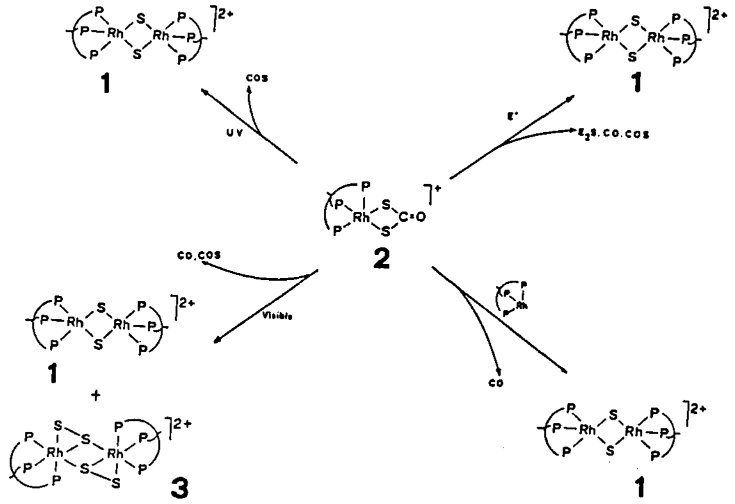
In this respect, an effective role is certainly played by the tripodal phosphine 1,1,1-tris(diphenylphosphinomethyl)ethane, hereafter **triphos**, which is particularly suitable for the coordination of rhodium(I) and rhodium(III) ions.[2]



$$H_3C\text{-}C(CH_2PPh_2)\text{-}CH_2PPh_2\ (CH_2PPh_2)$$

A great variety of mono- and binuclear rhodium complexes with triphos have been obtained in which the ligand invariably occupies three contiguous *fac* positions of the coordination polyhedron around rhodium. In this way, a facile metal-assisted breaking and making of chemical bonds is allowed on the rest of the polyhedron.

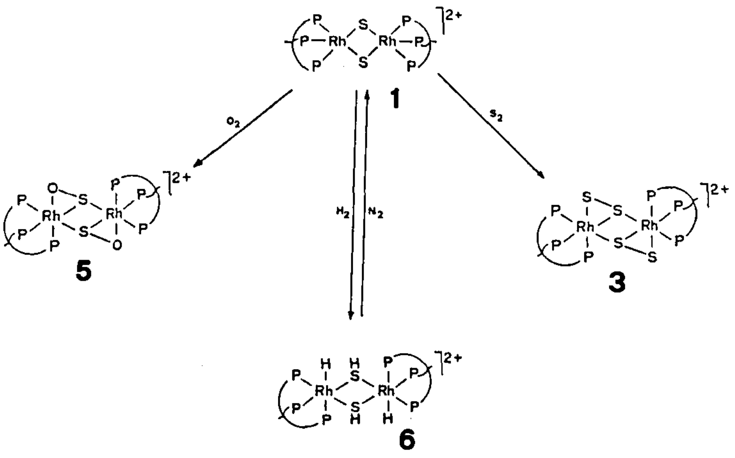
Herein, we report on the rich chemistry of the coordinatively and electronically unsaturated complex $[(triphos)Rh(\mu\text{-}S)_2Rh(triphos)][BPh_4]_2$ (**1**). Scheme 1 illustrates the different synthetic strategies to the synthesis of **1** using as starting reagent the S,S-dithiocarbonate complex $[(triphos)Rh(S_2CO)][BPh_4]$ (**2**).



The photochemical decomposition of **2** gives COS and **1** in excellent yield only when the irradiation is accomplished in CH_2Cl_2 with UV light. An alternative decomposition pathway becomes competitive when the photolysis is performed with visible light. In this case, the concomitant formation of the bis(μ-S) complex **3** and CO evolution is observed.[3] Treatment of **2** with alkylating agents ($MeOSO_2CF_3$) or strong protic acids ($HOSO_2CF_3$ or $HOEt_2BF_4$) affords **1** together with a variety of gaseous products including dialkylsulphides, H_2S, COS and CO. Finally, the μ-sulphide complex **1** can be prepared in high yield by reaction of **2** with the coordinatively unsaturated (triphos)Rh fragment generated *in situ* by chloride ion rlimination with silver salts from $[(triphos)RhCl(C_2H_4)]$ (**4**). The reaction proceeds trough chelotropic elimination of CO from the RhSC(O)S four-membered cycle promoted by interaction of the additional metal fragment with the two sulphur atoms of the S_2CO ligand.[3]

Although the two bridging sulphur atoms contribute *via* π interaction to stabilize **1**, the complex still results coordinatively and electronically unsaturated. Indeed, in addition to the two nucleophilic S atoms, the complex contains two electrophilic sites, namely the two Rh metal centers. In other words, complex **1** exhibits a *dual nature*, which results in the facile activation of several small molecules.

Scheme 2 summarizes the reactions of **1** with O_2, H_2, and S_2^{2-}.



Reaction of **1** with dioxygen affords the dimeric μ-SO dark red complex **5**. Compound **5**, which represents the first example of a dimeric η^2,η^1-SO complex, can be also obtained by thermal or photochemical decomposition of **2** in the presence of O_2. Noticeably, both the chemical oxidation of **1** with peroxoacids such as *m*-CPBA, and reaction of **4** with a transient SO molecule, generated by thermal decomposition of a thiirane-S-oxide, give a yellow isomer of **5**.

Reversible, heterolytic activation of molecular hydrogen takes place by reacting **1** with H_2 (1 atm) at room temperature. In this way, the dimeric μ-SH hydride **6** is obtained. Compound **6**, which under nitrogen converts to **1** evolving H_2, is also accessible by the direct oxidative addition of H_2S to **4**. An X-ray analysis of **6** has shown that each Rh atom is coordinated by the three phosphorus donors of triphos, a hydride ligand, and two shared SH groups in a distorted octahedral environment.

Compound **1** proves an active catalyst for the homogeneous hydrogenation of alkynes and alkenes at room temperature and 1 atm H_2. The catalyzed alkyne hydrogenation yields largely the olephin. In the catalytic cycle the dinuclear framework of complex **1** appears to be maintained.

Reaction of **1** with Li_2S_2 in THF yields the μ-S_2 dimeric derivative **3** whose crystal structure has been determined by X-ray methods. The structure consists of dimeric cations $[(triphos)Rh(\mu\text{-}S_2)_2Rh(triphos)]^{2+}$ and BPh_4^- anions. The cation contains two $[(triphos)Rh(\eta^2\text{-}S_2)]$ subunits related by a crystallographic inversion center (Figure 1). One of the sulphur atoms of the S_2 ligands bridges the other Rh, thus forming a nearly planar Rh_2S_2 ring. A closely related structure has been found for the μ-SO congener **5**. In this case, the sulphur atoms of the η^2-SO ligands, rather than the oxygens, connect the two metal-subunits.

Compounds **3**, **5**, and **6** have been studied by ^{31}P NMR spectroscopy and their spectroscopic properties compared with those of structurally related complexes containing μ-Se_2 and μ-SO_2 ligands.[4] All of the compounds are fluxional and exhibit an interconversion from AB_2X to ABCX spin systems (X = Rh) with a scrambling process involving only two P atoms of the tripodal triphosphine, namely those lying in the plane which contains the Rh·····Rh vector. Computational methods have been developed to gain insight into the dynamic behaviour of the complexes.

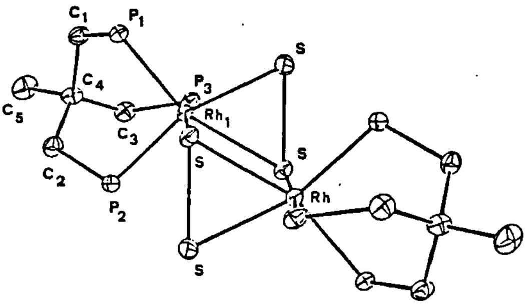


Figure 1. ORTEP drawing of the complex cation $[(triphos)Rh(\mu\text{-}S_2)_2Rh(triphos)]^{2+}$.

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