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# Facile Activation of $H_2$ on 1,1- and 1,2-Dithio Complexes of Rhodium(III). An Experimental Study

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The reactions of dihydrogen with a series of 1,1-dithio transition-metal complexes with the tripodal phosphine $CH_3C(CH_2PPh_2)_3$, triphos, have been investigated. The compounds were stirred in $CH_2Cl_2$ solutions under 1 atm of $H_2$ at room temperature. Ligand-assisted activations of $H_2$ formally corresponding to heterolytic splittings have been observed for those complexes that contain $Rh^{III}SCS$ cycles with some $\pi$-electron delocalization. Also, the interactions of dihydrogen with some members of the [(triphos)Rh($\mu$-$C_2S_4$)Rh(triphos)]$^n$ family have been studied ($n$ = 4+, 2+, +, 0, 2-). For $n$ = 4+, $H_2$ is quantitatively oxidized to two $H^+$ ions whereas for $n$ = 0, two $H^+$ ions are reduced to $H_2$.

## Introduction

Oxidative addition (eq 1), homolysis (eq 2), and heterolysis (eq 3) are three well-recognized modes of activation of dihydrogen by transition-metal complexes.[1] As is often the case in chemistry,

$$M + H_2 \rightleftharpoons MH_2 \quad (1)$$

$$2M + H_2 \rightleftharpoons 2MH \quad (2)$$

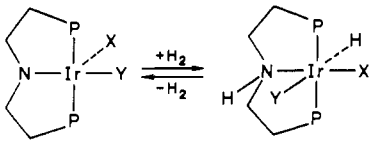
$$M + H_2 \rightleftharpoons MH^- + H^+ \quad (3)$$

a clear-cut border between the limiting mechanisms can hardly be established. However, the heterolytic $H_2$ cleavage is better substantiated for those systems involving metals in higher oxidation states eventually assisted by basic centers that stabilize the released proton.[2] Depending on the source of the basic center, i.e. an externally added base or a ligand that may remain coordinated to the metal also in the protonated form, the process may be described either as in (4) or as in (5).

$$M + H_2 + B \rightleftharpoons MH^- + BH^+ \quad (4)$$

$$MB + H_2 \rightleftharpoons MH(BH) \quad (5)$$

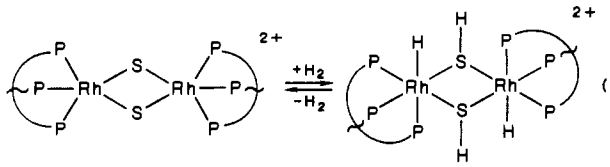
Some examples of $H_2$ activations formally corresponding to base-assisted heterolytic splittings of the type shown in (5) have recently appeared in the literature. Fryzuk et al. have described a family of iridium(III) amides that may add one molecular of dihydrogen to give iridium(III) amine hydrides.[3] Whether the process depicted in (6) occurs in a concerted fashion or involves



(6)

the preliminary oxidative addition of $H_2$ to give an Ir(V) intermediate, followed by reductive elimination, is still a subject of speculation. For X = Me and Y = I, structural arguments seem to favor the oxidative-addition/reductive-transfer pathway.[3a]

More recently, we reported on a dinuclear rhodium(III) species with a central RhSRhS ring that may alternatively add or release molecular hydrogen as shown in (7).[4]



(7)

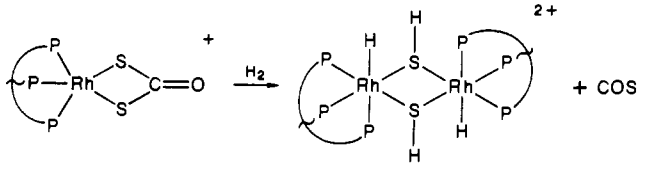
Qualitative MO arguments conform to the viewpoint that the capability of the $\mu$-S complex to add dihydrogen may be attributable to the polarized nature of each Rh-S linkage, which promotes "heterolytic" activation of $H_2$. On the other hand, by assuming some $\pi$ delocalization over the whole $Rh_2S_2$ cycle, concerted mechanisms of addition of $H_2$ to Rh=S bonds may also be considered.[5]

Understanding the nature of hydrogen-activating systems such as Fryzuk's Ir(III) amides and our Rh(III) $\mu$-sulfido dimer represents an intriguing and highly desirable goal, particularly as related to catalytic hydrogenations. In this respect, it is worth noticing that the active site of many hydrogenases is constituted by an iron-sulfur [4Fe-4S] cluster on which $H_2$ is heterolytically cleaved.[6] In addition, bridging sulfido ligands have been proposed to be the sites that react with $H_2$ in several hydrogenations of unsaturated substrates assisted by dimeric molibdenum complexes.[7]

Following our studies on the reactivity of the $\mu$-S complex [(triphos)Rh($\mu$-S)$_2$Rh(triphos)]$^{2+}$ [triphos = $CH_3C(CH_2PPh_2)_3$], we describe in this paper the reactions of dihydrogen with a series of rhodium(III) complexes containing RhSCS or RhSCCS rings. Purposefully, no mechanistic interpretation of the quite spectacular reactions herein presented is attempted. In our opinion, further multiform studies are necessary to draw out meaningful mechanistic conclusions.

## Results and Discussion

**1,1-Dithio Complexes.** When the dithiocarbonate [(triphos)Rh($S_2CO$)]$BPh_4$[8] (**1**) in $CH_2Cl_2$ is allowed to stir under 1 atm of $H_2$ for 2 h, carbonyl sulfide, COS, is quantitatively produced while the red brown solution decolorizes to pale pink. Adding ethanol to such solutions precipitates the $\mu$-SH hydride [(triphos)HRh($\mu$-SH)$_2$RhH(triphos)]$(BPh_4)_2$ (**2**) (eq 8).[4] This compound, synthesized by an alternative route, was also authenticated by an X-ray analysis.



(8)

Under 1 atm of $H_2$ at room temperature in $CH_2Cl_2$, deep violet solutions of the dithiocarbimate complex [(triphos)Rh-

(1) Brothers, J. P. *Prog. Inorg. Chem.* **1981**, *28*, 1. (b) Halpern, J. *J. Organomet. Chem.* **1980**, *200*, 133. (c) James, B. R. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, England, 1982, Vol. 8, p 285.

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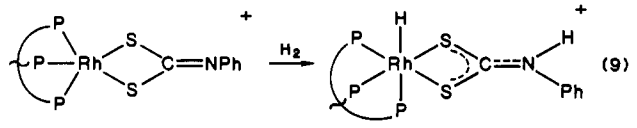
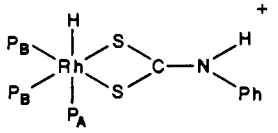
$(S_2CNPh)]BPh_4$[9] (**3**) completely decolorize within 3 h. Colorless crystals of the (hydrido)dithiocarbamato complex [(triphos)-$RhH(S_2CNHPh)]BPh_4$ (**4**) are obtained by addition of ethanol, followed by slow evaporation of the solvent (eq 9).



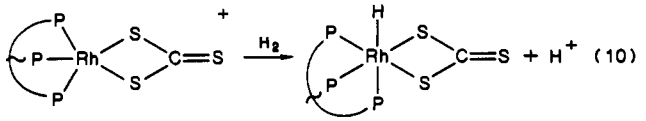
(9)

Compound **4** is stable in the solid state and in deoxygenated solutions. It is soluble in common organic solvents in which it behaves as a 1:1 electrolyte (molar conductance value in $10^{-3}$ M nitroethane solution, 43 $\Omega^{-1}$ cm$^2$ mol$^{-1}$). The $^{31}P\{^1H\}$NMR spectrum of this compound ($CD_3COCD_3$, 298K) with a doublet of doublets and a doublet of triplets is consistent with an $AB_2X$ spin system. This is typical of octahedral rhodium(III) complexes with triphos [$\delta(P_B)$ 26.25, $J(P_AP_B)$ = 21.13 Hz, $J(P_BRh)$ = 109.1 Hz; $\delta(P_A)$ −15.58, $J(P_ARh)$ = 70.7 Hz].[8,10] The IR spectrum exhibits a strong, broad band at 1520 cm$^{-1}$, which we assign to $\nu$(CN) of a dithiocarbamato group.[11] Reasonably, in these ligands the C=N stretch vibrates at lower wavenumbers than it does in the corresponding dithiocarbimato derivatives.[12] As a matter of fact, in the starting compound **3**, $\nu$(CN) is observed at 1570 cm$^{-1}$. Medium-intensity absorptions at 2000 and 1590 cm$^{-1}$ are attributed to $\nu$(Rh–H) and to an additional phenyl vibration, respectively. A weak, broad band at 3250 cm$^{-1}$, which is absent in the spectrum of **3**, is assigned to $\nu$(N–H) of a phenyldithiocarbamato group.[12b,13] Further evidence for the formation of the latter ligand is provided by $^1H$ NMR spectroscopy ($CD_3COCD_3$, 298 K), which shows a singlet at 3.81 ppm (1 H) attributable to NH. A doublet of multiplets centered at −7.13 ppm are due to the Rh–H proton [$J(HP_A)$ = 195 Hz, $J(HP_B)$ = 5 Hz, $J$(HRh) = 7.5 Hz]. The magnitude of the H–$P_A$ coupling constant is consistent with a trans orientation of these atoms (see I).[14]



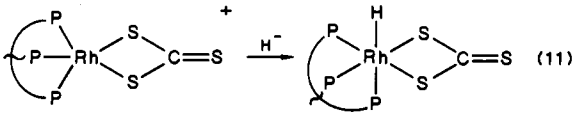
I

When dihydrogen is reacted with the trithiocarbonate complex $[(triphos)Rh(S_2CS)]BPh_4$[9] (**5**) under the conditions employed for the dithiocarbonate and dithiocarbimate derivatives, the (hydrido)trithiocarbonato complex $(triphos)RhH(S_2CS)$ (**6**) is obtained (eq 10).



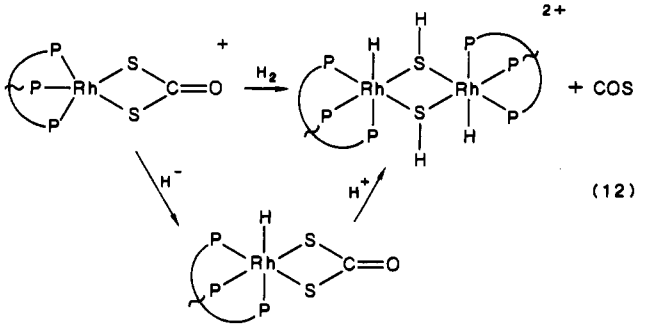
(10)

During the reaction a proton is released as evidenced by the formation of $[HNEt_3]^+$ upon addition of $NEt_3$ to the final reaction mixture. The spectrum of **6** exhibits $\nu$(Rh–H) at 2000 cm$^{-1}$ and $\nu$(C=S) of the $CS_3^{2-}$ ligand at 1030 cm$^{-1}$.[11] The typical absorptions of the $BPh_4^-$ are absent. The low solubility of the compound renders the recording of $^1H$ and $^{31}P$ NMR spectra meaningless. However, **6** is obtainable also by the alternative route reported in (11), a fact that indirectly supports the structural formulation given in (10).



(11)

Formally, reactions 8–10 correspond to heterolytic splittings of dihydrogen. Indeed, the presence at a certain stage of the reactions of metal-bound hydride and $H^+$ moieties is purported by several additional experiments. The hydride $(triphos)RhH(S_2CO)$ (**7**) obtained by $H^-$ addition to **1**, quickly reacts in $CH_2Cl_2$ with $H^+$ from $HOSO_2CF_3$ to give COS and, following the addition of $NaBPh_4$ in ethanol, the $\mu$-SH hydride **2** (eq 12). The formation

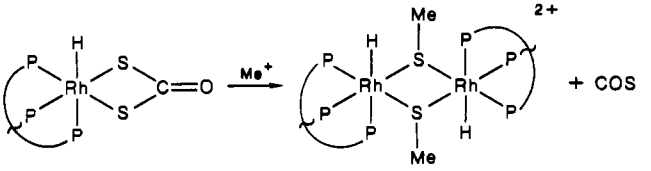


(12)

of carbonyl sulfide, which may appear quite spectacular, is unexceptional when the rhodium dithiocarbonate **1** is involved. The chelotropic elimination of COS from the RhSC(O)S ring can be easily produced also by UV irradiation of $CH_2Cl_2$ solutions of **1**.[15] More recently, we have found that a variety of electrophilic reagents such as strong acids and alkylating agents are capable of promoting the decomposition of **1** to COS and $[(triphos)Rh(\mu\text{-}S)_2Rh(triphos)]^{2+}$.[16]

The hydride **6**, like the parent trithiocarbonate **5**, does not react with $H^+$ (see ref 11), reflecting the well-known incapacity of both the endocyclic and exocyclic sulfur atoms of the $\eta^2$-$CS_3$ ligand to form stable adducts with the proton.[11,17] As for reaction 9, if it is taken for granted that the activation of $H_2$ takes place in proximity of the rhodium atom (vide infra), it is reasonable to think that the proton therein generated shifts over the complex surface to find a basic site where it can be stabilized.[18] Unfortunately, we did not succeed in synthesizing the neutral (dithiocarbimato)hydrido complex $(triphos)RhH(S_2CNPh)$ so that we could not try to reproduce reaction 9 by stepwise addition of a hydride and a proton to **3**. Noticeably, **3** is stable to strong acids. This leads us to think that, in reaction 9, however the $H^+$ and $H^-$ moieties are generated, their contemporaneous presence is necessary to obtain the dithiocarbamate product.

The (dithiocarbonato)hydrido complex **7** in $CH_2Cl_2$ reacts with $Me^+$ from $MeOSO_2CF_3$ to give, following the addition of $NaBPh_4$ in ethanol, dark brown crystals of $[(triphos)HRh(\mu\text{-}SMe)_2RhH(triphos)](BPh_4)_2$ (**8**) and COS (eq 13).



(13)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(15) Bianchini, C.; Meli, A. *Inorg. Chem.* **1987**, *26*, 1345.
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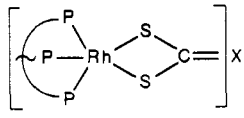
(18) A similar intramolecular migration path for a proton to a nitrogen atom has been reported in: Cecconi, F.; Ghilardi, C. A.; Innocenti, P.; Mealli, C.; Midollini, S.; Orlandini, A. *Inorg. Chem.* **1984**, *23*, 922.

Compound **8** is quite air stable in the solid state. It is moderately soluble in $CH_2Cl_2$, DMF, and nitroethane. In the latter solvent it behaves as a 1:2 electrolyte (molar conductance value in $10^{-3}$ M nitroethane solution, 102 $\Omega^{-1}$ cm$^2$ mol$^{-1}$). The IR spectrum contains $\nu$(Rh–H) at 2010 cm$^{-1}$. The NMR resonance of the hydride ligand appears as a doublet of unresolved multiplets centered at $\delta$ –6.70 with J(H–$P_{trans}$) = 100 Hz ($CD_2Cl_2$, 298 K). The resonances of the S-bonded and triphos methyl groups overlap to give a unique, broad signal at $\delta$ 1.52 (6 H). Meaningful $^{31}$P NMR spectra could not be recorded because the compound is neither sufficiently soluble nor very stable in solution. However, although of poor quality, the spectrum in DMF is qualitatively similar to that of the $\mu$-SH hydride **2**, which is fluxional.[4] In view of all of these data the compound is assigned the structure of **2**, previously established by X-ray methods.[4] Accordingly, each rhodium atom is coordinated by three terminal phosphine ligands, one hydride and two shared SMe groups (see eq 13).

Reaction 13 is unexceptional when compared to (12) but certainly thought provoking. The H and $CH_3$ moieties that have been separately added to **1** may be imagined as coming from $CH_4$. We have stirred **1** in $CH_2Cl_2$ under 1 atm of $CH_4$: no reaction was observed. However, we still believe in the potential application of bifunctional systems to the cleavage of saturated hydrocarbons. Indeed, homo- and heterodinuclear systems can efficiently activate rather unreactive substrates such as the $CO_2$ molecule.[19]

Provided that the 1,1-dithiolate rhodium(III) complexes **1**, **3**, and **5** are capable of activating dihydrogen under very mild conditions, it would be very interesting to know how and why the process occurs. Since the three compounds share a large part of their overall complex framework, it is reasonable to assume that the activation site(s) for $H_2$ must be sought just in the common portion of the molecules, bracketed in II. By contrast, the X

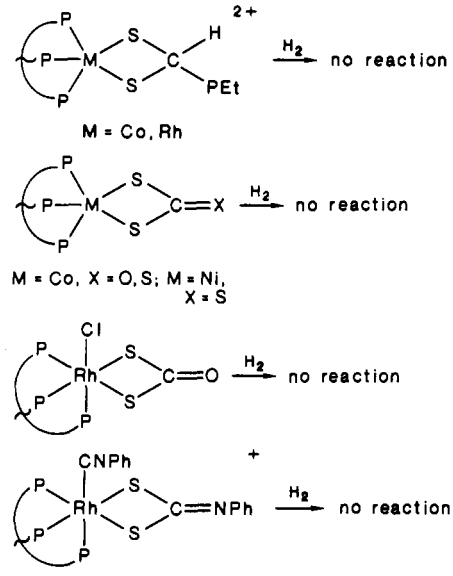


II

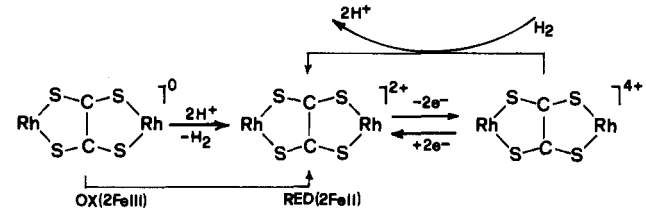
group, although extremely important for determining the nature of the final products, does not seem directly involved in the $H_2$ activation process. Accordingly, we focused our attention on the [(triphos)$RhS_2C$] fragment. The most evident features of the latter are (i) the presence of electron-deficient, coordinatively unsaturated rhodium(III), (ii) some $\pi$-electron delocalization over the RhSCS cycle, and (iii) rhodium and sulfur atoms in close proximity. As for the triphos ligand, we think that its role is just to confer stability to the products.

In order to shed some light on the present hydrogenations, we have investigated the reactions with dihydrogen of a number of (triphos)metal complexes with chelating 1,1-dithio ligands. The nature of the reactants was changed as systematically as possible both by varying the coordination number and oxidation state of the metals and by altering the type of the dithio ligand. In particular, five-coordinate d$^6$ metals are present in the phosphonium–betaine complexes [(triphos)M($S_2CH(PEt_3)$)]$^{2+}$ (M = Co,[20] Rh[21]), which display single-bond M–S distances; in the dithiocarbonate (triphos)RhCl($S_2CO$)[8] and in the dithiocarbimate [(triphos)Rh(CNPh)($S_2CNPh$)]$^+$,[22] the rhodium atoms are six-coordinate and therefore electronically and coordinatively saturated. Finally, d$^7$ and d$^8$ metals are contained in the dithiocarbonate (triphos)Co($S_2CO$)[23] and in the trithiocarbonates

**Chart I**



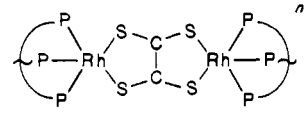

**Scheme I**




(triphos)M($S_2CS$) (M = Co,[23] Ni[17]) (Chart I). All of the compounds were stirred in $CH_2Cl_2$ solutions under 1 atm of $H_2$ at room temperature. In no case a reaction was observed.

We therefore conclude that the ability of **1**, **3**, and **5** to activate $H_2$ is evidently connected with the presence of five-coordinate rhodium(III) in 1,1-dithio complexes in which the Rh–S bonds have a partial double bond character. Whether the hydrogenations reported in reactions 8–10 have the features of a concerted addition to Rh–S bonds or of the acid/base interaction (heterolytic splitting) is a question that is impossible to address at this stage. Theoretical, structural, and kinetic measurements are presently under way, which hopefully will contribute to a better understanding of the processes.

**1,2-Dithio Complexes.** All of the rhodium(III) complexes that have been by far examined as $H_2$ activators contain 1,1-dithio ligands. These form four-membered RhSCS rings. Five-membered RhSCCS cycles with some $\pi$-electron delocalization characterize the members of the [(triphos)Rh($\mu$-$C_2S_4$)Rh(triphos)]$^n$ family ($n$ = 4+, 2+, 1+, 0, 2–).[24] Three of these, namely the 4+, 2+, and neutral members can be both chemically and electrochemically synthesized (III). An X-ray analysis was



$n$ = 4+, 2+, 1+, 0, 2–

III

carried out on the dicationic derivative, showing that the $C_2S_4$ bridge can be formally formulated as ethenetetrathiolate, $C_2S_4^{4-}$. The same structure can be assigned to the neutral dimer, which is paramagnetic with a magnetic moment corresponding to two unpaired spins. By contrast, on the basis of spectroscopic and

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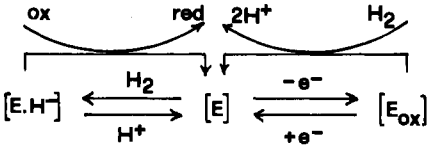
(21) Bianchini, C.; Dapporto, P.; Meli, A.; Tofanari, A.; Zanello, P. *Inorg. Chem.*, in press.
(22) This compound was obtained by *head-to-tail* dimerization of SCNPh promoted by the (triphos)Rh$^I$ fragment. Detailed synthetic and chemical–physical data will be provided elsewhere.
(23) Bianchini, C.; Meli, A.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4166.
(24) (a) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1984**, *23*, 4125. (b) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M.; Zanello, P. *J. Am. Chem. Soc.* **1987**, *109*, 185.

**Scheme II**




chemical evidence, the $C_2S_4$ ligand in the 4+ derivative assumes more tetrathiooxalate, $C_2S_4^{2-}$, character.

All of these $\mu$-$C_2S_4$ complexes display noticeable electron-transfer properties: the neutral derivative transfers electrons to 7,7,8,8-tetracyanoquinodimethane, TCNQ (eq 14) whereas the 4+ complex is able to extract electrons from tetrathiafulvalene, TTF (eq 15). We now report that this family of $\mu$-$C_2S_4$ dimers

$$(\text{triphos})\text{Rh}(\mu\text{-}C_2S_4)\text{Rh}(\text{triphos}) + 2\text{TCNQ} \rightarrow [(\text{triphos})\text{Rh}(\mu\text{-}C_2S_4)\text{Rh}(\text{triphos})]^{2+}(\text{TCNQ}^-)_2 \quad (14)$$

$$[(\text{triphos})\text{Rh}(\mu\text{-}C_2S_4)\text{Rh}(\text{triphos})]^{4+} + 3\text{TTF} \rightarrow [(\text{triphos})\text{Rh}(\mu\text{-}C_2S_4)\text{Rh}(\text{triphos})]^{2+} + (\text{TTF})_3^{2+} \quad (15)$$

is quite active also toward the $H_2/H^+$ system (Scheme I). In particular, the red $[\mu\text{-}C_2S_4]^{4+}$ member in $CH_2Cl_2$ quantitatively oxidizes $H_2$ to two $H^+$ while it is reduced to the green 2+ derivative. The latter species and $H_2$ are generated when the brown, neutral complex is reacted in $CH_2Cl_2$ with $H^+$. By contrast, neither $H_2$ nor $H^+$ react with the 2+ dimer in $CH_2Cl_2$ solution. Were the latter complex able to heterolytically activate hydrogen [as the $\mu$-S rhodium(III) dimer does, see eq 7], the $\mu$-$C_2S_4$ system would efficiently model the mode of activation of $H_2$ by some hydrogenases (Scheme II).[25] In this respect, very few inorganic systems capable of successfully modeling these enzymes have been so far discovered.[1b] Interestingly, the active sites of these systems are supposed to be metal–sulfur center(s) (metal = iron), a structural theme that characterizes many of our complexes.

## Experimental Section

**General Information.** All reactions and manipulations were performed under nitrogen. Reagent grade chemicals were used in the preparations of the complexes. THF and $CH_2Cl_2$ were purified by distillation from $LiAlH_4$ and $CaH_2$ under nitrogen, respectively. Literature methods were used for the preparation of $[(\text{triphos})\text{Rh}(S_2\text{CO})]\text{BPh}_4$,[8] $[(\text{triphos})\text{Rh}(S_2\text{CS})]\text{BPh}_4$,[9] $[(\text{triphos})\text{Rh}(S_2\text{CNPh})]\text{BPh}_4$,[9] $[(\text{triphos})\text{Rh}(C_2S_4)\text{Rh}(\text{triphos})](BF_4)_4$, and $(\text{triphos})\text{Rh}(C_2S_4)\text{Rh}(\text{triphos})$.[24] The solid complexes were collected on a sintered-glass frit and washed with approrpiate solvents before being dried in a stream of nitrogen. The formation of carbonyl sulfide was detected either by GC (Teflon column filled with Chromosil 310 purchased from Supelco) or by the methods reported in ref 26. Dihydrogen was detected by GC on a Carbosieve S-II column purchased from Supelco. Infrared spectra were recorded with a Perkin-Elmer 475 grating spectrophotometer on samples mulled in Nujol between KBr plates. $^1H$ and $^{31}P\{^1H\}$ NMR spectra were taken with a Varian CFT 20 spectrometer. Peak positions are relative to tetramethylsilane and phosphoric acid, respectively, with downfield values reported as positive. Conductance measurements were made with a WTW Model LBR/B conductivity bridge.

**Reaction of $[(\text{triphos})\text{Rh}(S_2\text{CO})]\text{BPh}_4$ (1) with $H_2$.** A solution of **1** (0.57 g, 0.5 mmol) in $CH_2Cl_2$ (20 mL) was stirred in a 100-mL vessel under 1 atm of dihydrogen at room temperature for 2 h. There was a gradual color change from red brown to pale pink and a contemporaneous COS evolution. Addition of ethanol (40 mL) gave pink crystals of $[(\text{triphos})\text{HRh}(\text{SH})_2\text{RhH}(\text{triphos})](BPh_4)_2$ (**2**), which were collected by filtration and washed with ethanol and petroleum ether; yield 65%.

**Reaction of $[(\text{triphos})\text{Rh}(S_2\text{CNPh})]\text{BPh}_4$ (3) with $H_2$.** A solution of **3** (0.61 g, 0.5 mmol) in $CH_2Cl_2$ (15 mL) was stirred in a 100-mL vessel under 1 atm of dihydrogen at room temperature for 3 h. During this time the color of the solution changed from deep red to pale yellow. Adding ethanol (35 mL) precipitated colorless crystals of $[(\text{triphos})\text{RhH}(S_2\text{CNHPh})]\text{BPh}_4$ (**4**). They were filtered off and washed with ethanol and petroluem ether; yield 80%. Anal. Calcd for $C_{72}H_{66}BNP_3RhS_2$: C, 71.11; H, 5.47; N, 1.15; Rh, 8.46; S, 5.27. Found: C, 70.76; H, 5.38; N, 1.07; Rh, 8.37; S, 5.14.

**Reaction of $[(\text{triphos})\text{Rh}(S_2\text{CS})]\text{BPh}_4$ (5) with $H_2$.** A solution of **5** (0.58 g, 0.5 mmol) in $CH_2Cl_2$ (20 mL) was stirred in a 100-mL vessel under 1 atm of dihydrogen at room temperature for 3 h. The initially orange solution turned pink. Addition of ethanol and slow concentration led to the precipitation of pink crystals of $(\text{triphos})\text{RhH}(S_2\text{CS})$ (**6**), which were filtered off and washed with ethanol and petroleum ether; yield 55%. The mother liquor was then concentrated to ca. 15 mL and equimolecular amounts of $NaBPh_4$ and $NEt_3$ were added; white crystals of $[HNEt_3]\text{BPh}_4$ began to precipitate in a few minutes. No reaction occurred between a pure sample of **6** in THF and $NEt_3$. Anal. Calcd for $C_{42}H_{40}P_3RhS_3$: C, 60.28; H, 4.82; Rh, 12.30; S, 11.49. Found: C, 60.21; H, 4.86; Rh, 12.17; S, 11.26. Compound **6** was obtained also in 85% yield by treating a THF (40 mL) suspension of **5** (0.5 mmol) with an equivalent amount of $NaBH_4$ in ethanol (20 mL).

**Preparation of $(\text{triphos})\text{RhH}(S_2\text{CO})$ (7).** A solution of $NaBH_4$ (0.04 g, 1 mmol) in ethanol (40 mL) was added dropwise to a stirred solution of **1** (1.13 g, 1 mmol) in THF (60 mL). The initially red-brown solution quickly turned pale yellow. Sandy crystals of **7** precipitated on standing in 85% yield. Anal. Calcd for $C_{42}H_{40}OP_3RhS_2$: C, 61.46; H, 4.91; Rh, 12.54; S, 7.81. Found: C, 61.31; H, 5.06; Rh, 12.21; S, 7.69.

**Reaction of 7 with $HSO_3CF_3$.** Addition of neat $HSO_3CF_3$ (40 $\mu$L, 0.45 mmol) to a suspension of **7** (0.32 g, 0.4 mmol) in $CH_2Cl_2$ (20 mL) caused the suspended solid to dissolve while COS was evolved. From the pale red solution, pink crystals of **2** precipitated on addition of $NaBPh_4$ (0.34 g, 1 mmol) in ethanol (40 mL).

**Reaction of 7 with $MeSO_3CF_3$.** Into a suspension of **7** (0.32 g, 0.4 mmol) in $CH_2Cl_2$ (25 mL) was pipetted neat $MeSO_3CF_3$ (50 $\mu$L, 0.45 mmol) which caused the suspended solid to dissolve giving a dark brown solution and COS. $NaBPh_4$ (0.34 g, 1 mmol) in ethanol (20 mL) was then added. Dark brown crystals of $[(\text{triphos})\text{HRh}(\text{SMe})_2\text{RhH}(\text{triphos})](BPh_4)_2$ (**8**) precipitated on standing overnight. They were collected by filtration and washed with ethanol and petroleum ether; yield 65%. Anal. Calcd for $C_{132}H_{126}B_2P_6Rh_2S_2$: C, 72.99; H, 5.68; Rh, 9.20; S, 2.87. Found: C, 72.79; H, 5.62; Rh, 9.09; S, 2.81.

**Reaction of $[(\text{triphos})\text{Rh}(C_2S_4)\text{Rh}(\text{triphos})](BF_4)_4$ with $H_2$.** A solution of $[(\text{triphos})\text{Rh}(C_2S_4)\text{Rh}(\text{triphos})](BF_4)_4$ (0.39 g, 0.2 mmol) in $CH_2Cl_2$ (40 mL) was stirred under 1 atm of dihydrogen for 30 min. The color changed from deep red to green. The $CH_2Cl_2$ solution was extracted four times with 25 mL of distilled water. Addition of *n*-heptane (40 mL) to the $CH_2Cl_2$ portion gave green crystals of $[(\text{triphos})\text{Rh}(C_2S_4)\text{Rh}(\text{triphos})](BF_4)_2$, which were separated by filtration; yield 95%. Potentiometric titrations of the aqueous portion from several experiments gave an average pH value of 2.7.

**Reaction of $(\text{triphos})\text{Rh}(C_2S_4)\text{Rh}(\text{triphos})$ with $HBF_4$.** $HBF_4$ (50% in diethyl ether) (1 mL, 0.5 mmol) was pipetted into a solution of $(\text{triphos})\text{Rh}(C_2S_4)\text{Rh}(\text{triphos})$ (0.4 g, 0.25 mmol) in $CH_2Cl_2$ (30 mL). Immediately a color change from dark brown to green occurred while $H_2$ was evolved, as determined by GC. On addition of *n*-heptane (30 mL) to the green solution, crystals of $[(\text{triphos})\text{Rh}(C_2S_4)\text{Rh}(\text{triphos})](BF_4)_2$ precipitated; yield 90%.

**Registry No.** **1**, 99955-64-3; **2**, 105162-40-1; **3**, 109637-05-0; **4**, 110637-34-8; **5**, 109637-03-8; **6**, 110637-35-9; **7**, 110637-36-0; **8**, 110637-38-2; $[(\text{triphos})\text{Rh}(C_2S_4)\text{Rh}(\text{triphos})](BF_4)_4$, 92669-53-9; $[(\text{triphos})\text{Rh}(C_2S_4)\text{Rh}(\text{triphos})](BF_4)_2$, 92760-74-2; $(\text{triphos})\text{Rh}(C_2S_4)\text{Rh}(\text{triphos})$, 92669-54-0; $HSO_3CF_3$, 1493-13-6; $MeSO_3CF_3$, 333-27-7; $H_2S_2CNPh$, 40231-24-1; $H_2S_2CO$, 4741-30-4; $HBF_4$, 16872-11-0; $H_2CS_3$, 594-08-1; $NaBH_4$, 16940-66-2; $H_2$, 1333-74-0.

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