Contribution from the Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Via J. Nardi 39, 50132 Florence, Italy, and Dipartimento di Chimica dell'Università di Siena, 53100 Siena, Italy

Novel Reactions of the $[BPh_4]^-$ Salt of the Bifunctional Complex $[(triphos)Rh(S_2CO)]^+$ (triphos = $MeC(CH_2PPh_2)_3$): One-Electron Reduction, Cleavage of B-H and B-C Bonds, and Metathesis of CS_2-like Heteroallene Molecules

Claudio Bianchini,*[†] Andrea Meli,[†] Franco Laschi,[‡] Francesco Vizza,[†] and Piero Zanello[‡]

Received May 3, 1988

The redox properties of the Rh(III) dithiocarbonate complex $[(triphos)Rh(S_2CO)][BPh_4]$ ($[1][BPh_4]$) have been studied in detail. One-electron reduction of $[1][BPh_4]$ gives the stable, paramagnetic Rh(II) derivative $(triphos)Rh(S_2CO)$ (**4**), which maintains the square-pyramidal (SQ) structure of the Rh(III) precursor as determined by ESR spectroscopy. The complex $[1][BPh_4]$ is able straightforwardly to cleave a B-H bond from BH_3 to yield the hydride $(triphos)RhH(S_2CO)$ (**5**). In the presence of $[Cu(PPh_3)_3][ClO_4]$ B-C bond cleavage occurs to give the σ-phenyl complex $(triphos)RhPh(S_2CO)$ (**9**). Compound $[1][BPh_4]$ reacts with CS_2 or SCNR with evolution of COS and formation of trithiocarbonate $[(triphos)Rh(S_2CS)][BPh_4]$ (**10**) or dithiocarbonimidates $[(triphos)Rh(S_2CNR)][BPh_4]$ (R = Ph (**11**), Et (**12**)), respectively. Trithiocarbonate **10** and dithiocarbonimidates **11** and **12** are readily converted into each other with evolution of CS_2 or SCNR by reaction with SCNR or CS_2, respectively. The nature of the functionality that connects the two sulfur atoms of the 1,1-dithio ligands (i.e. >C=O, >C=S, or >C=NR) is of crucial importance in determining the electronic structure of the four-membered RhS_2C metalla ring and, consequently, many physical and chemical properties of the complexes. The fluxional behavior in solution of a family of five-coordinate 1,1-dithio metal complexes of triphos is discussed on the basis of ESR and NMR techniques.

Introduction

A great number of stoichiometric and catalytic reactions involve as intermediates coordinatively and electronically unsaturated metal species which very often have an exclusively transient nature. In some cases, however, these intermediates can be stabilized either intramolecularly (ortho metalation, agostic interactions, etc.) or intermolecularly (externally added ligands, solvent molecules, polymerization, etc.). A clear example of intramolecular stabilization of a formally 16-electron complex is provided by $[(triphos)Rh(S_2CO)][BPh_4]$ ($[1][BPh_4]$; triphos = $MeC(CH_2PPh_2)_3$).[1] Compound $[1][BPh_4]$ is obtained by chloride elimination from the octahedral (OCT) 18-electron complex $(triphos)RhCl(S_2CO)$ (**2**) and can be stored for an indefinite time in the solid state and for several days in ambient-temperature solutions even under aerobic conditions.

The exceptional stability of $[1]^+$ has been attributed to a π-bonding interaction between the sulfur atoms of the dithiocarbonate ligand and the metal center.[2] As a matter of fact, an X-ray analysis of the isoelectronic and isomorphous congener $[(triphos)Rh(Se_2CO)][BPh_4]$[3] (**3**) has shown that the Rh-Se bond distances are shorter than that of a typical Rh-Se single bond. However, the electron deficiency at the Rh(III) center is only partially relieved in $[1]^+$ as the metal exhibits a marked electrophilic character and the sulfur atoms still possess nucleophilic properties.[1,2,4] Given the presence of electrophilic and nucleophilic sites in close proximity, $[1]^+$ appears appropriately designed to interact with bifunctional substrates and, in principle, with all of those molecules that can be polarized and eventually cleaved in a heterolytic fashion. For example the reaction of $[1][BPh_4]$ with dihydrogen to give the μ-SH dimer $[(triphos)RhH(\mu\text{-}SH)_2HRh(triphos)][BPh_4]_2$ has been interpreted in terms of heterolytic splitting.[2]

In actuality, $[1]^+$ represents a excellent opportunity to gain further insight into many chemical transformations such as the enzymatic activations of H_2 or O_2, which require the use of bifunctional metal-ligand systems, especially of those containing metal-sulfur linkages.[5]

Herein we report some novel reactions that ultimately endorse the bifunctional nature of $[1]^+$. In addition, we discuss in detail the solution structure and the redox properties of $[1]^+$ and of a family of related 1,1-dithiolate rhodium and cobalt complexes.

A preliminary account of part of this work has already been given.[6]

Results

The transformations observed in this study together with the identifying compound numbers are summarized in Schemes I and II. Results of ESR and electrochemical studies are presented in Figures 1-5, introduced as appropriate in the Discussion.

Discussion

Solution Structure of the Cation $[1]^+$. Complex $[1]^+$ is stereochemically nonrigid in solution; the intramolecular exchange of the three phosphorus atoms of triphos is rapid on the NMR time scale to -100 °C so that the phosphorus atoms appear magnetically equivalent to one another. As a matter of fact, the $^{31}P\{^1H\}$ NMR spectrum of $[1]^+$ consists of a doublet independent of the temperature and solvent. As is natural, the solvent affects the chemical shift of the A_3 portion of the A_3X spin system (in $(CD_3)_2CO$ 37.00 ppm, in CD_2Cl_2 35.22 ppm, $J(P\text{-}Rh) = 98.7$ Hz). A surprisingly high field shift of the resonance of triphos is observed in DMF (10.62 ppm), which is accompanied by a higher value of $J(P\text{-}Rh)$ (102.8 Hz). This may be due to some interaction of the electrophilic metal center with the solvent. The fluxional behavior of five-coordinate triphos complexes of transition metals is well-known.[7] The exchange of the phosphorus atoms occurs through an intramolecular non-bond-breaking isomerization between SQ and trigonal-bipyramidal (TBP) conformations,[7c,8] and in effect, both limiting structures have been authenticated by X-ray analysis[7c,8,9] or spectroscopic (ESR, NMR) techniques.[7b,c]

Compound $[1]^+$ is assigned a SQ structure in the solid state. This can be postulated on the basis of an X-ray analysis of the isomorphous SQ congener **3**, which exhibits an identical fluxionality in solution.[3] Indirect evidence for the SQ structure of $[1]^+$ is provided also by the spectroscopic characterization of the

---

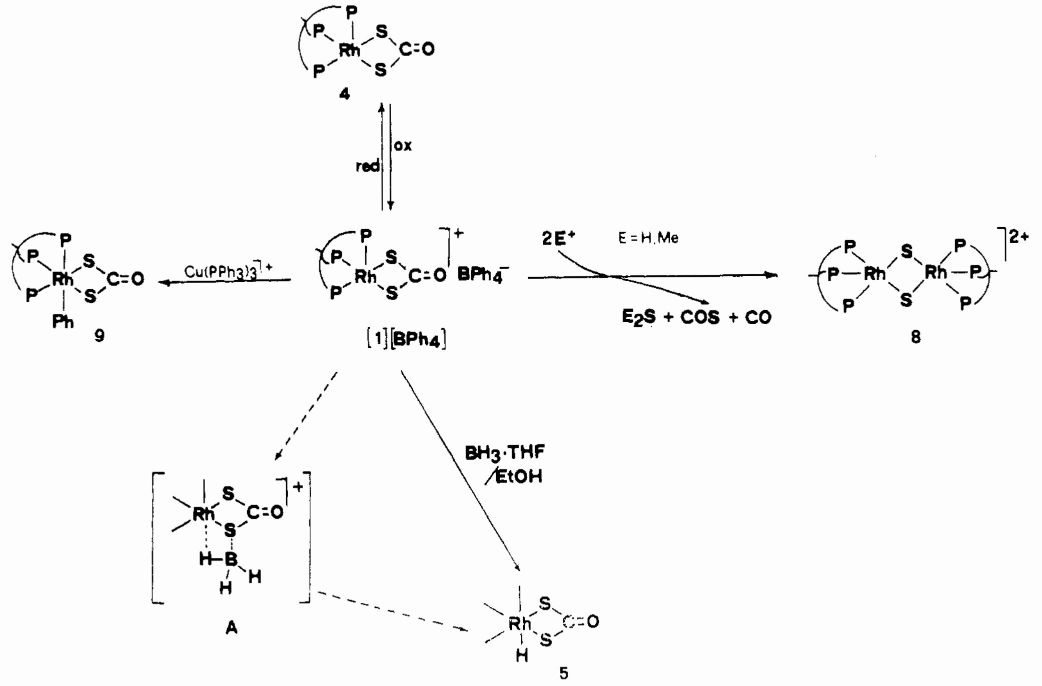
[†] ISSECC, CNR.

[‡] Università di Siena.

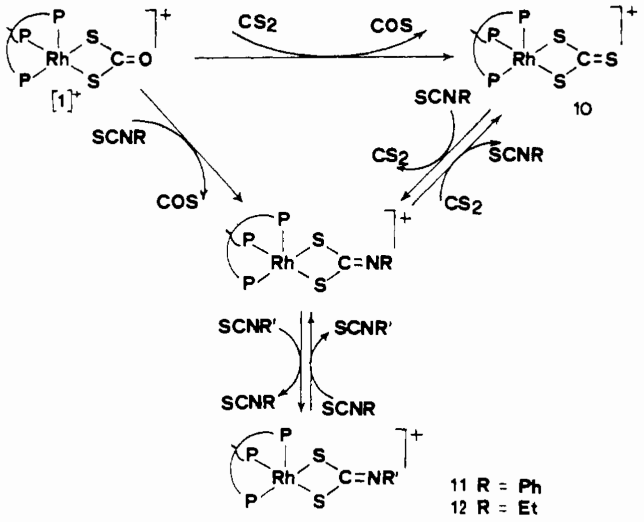
(1) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *J. Chem. Soc., Chem. Commun.* **1985**, 1024.
(2) Bianchini, C.; Meli, A. *Inorg. Chem.* **1987**, *26*, 4268.
(3) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M.; Vizza, F. *Inorg. Chem.* **1988**, *27*, 3716.
(4) Bianchini, C.; Laschi, F.; Meli, A.; Vacca, A.; Zanello, P. *J. Am. Chem. Soc.* **1988**, *110*, 3913.
(5) Spiro, T. G. *Iron-Sulfur Proteins*; Wiley: New York, 1982.
(6) Bianchini, C.; Meli, A.; Vizza, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 767.
(7) (a) DuBois, D. L.; Meek, D. W. *Inorg. Chem.* **1976**, *15*, 3076. (b) Dahlenburg, L.; Mirzaei, F. *Inorg. Chim. Acta* **1985**, *97*, L1. (c) Bianchini, C.; Masi, D.; Mealli, C.; Meli, A.; Martini, G.; Laschi, F.; Zanello, P. *Inorg. Chem.* **1987**, *26*, 3683.
(8) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.
(9) Janser, P.; Venanzi, L. M.; Bachechi, F. *J. Organomet. Chem.* **1985**, *296*, 229.

0020-1669/89/1328-0227$01.50/0

Scheme I



Scheme II



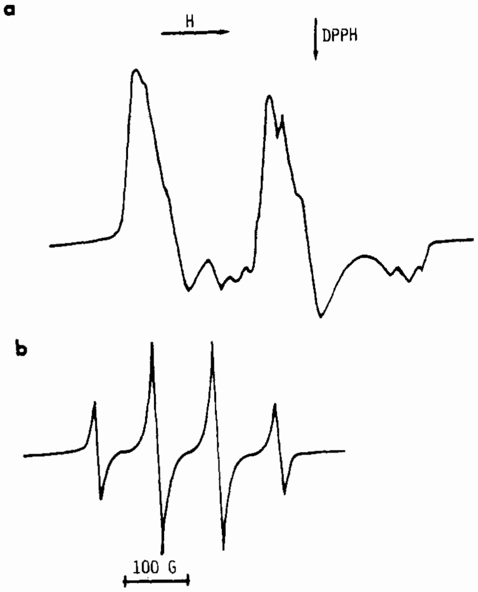


Figure 1. X-Band ESR spectra of (triphos)Rh(S_2CO) in CH_2Cl_2 at 100 K (a) and 300 K (b).

Rh(II) derivative (triphos)Rh(S_2CO) (**4**) as well as a family of Rh(II) and Rh(III) 1,1-dithiolate complexes derived from [**1**]$^+$.

Reversible One-Electron Reduction of [1][BPh$_4$]. Compound **4** is synthesized as green crystals by treatment of [**1**]$^+$ in THF with a variety of reducing agents, including $NaBH_4$, $LiHBEt_3$, $(C_5H_5)_2Co$, LiMe, LiPh, $NaC_{10}H_8$, and $(NP_3)Ni$[10] (NP_3 = $N(CH_2CH_2PPh_2)_3$) (Scheme I). The exposure of solutions of **4** to air readily regenerates [**1**][BPh_4]. When hydride-containing reagents are used, the formation of **4** is accompanied by that of the OCT Rh(III) hydride (triphos)RhH(S_2CO)^2 (**5**) in yields varying from 20 to 30% over 12 preparations. Owing to the poor solubility of **5** in common organic solvents, the two compounds can be easily separated from each other by recrystallization. Compound **4** is stable under a nitrogen or argon atmosphere both in the solid state and in solution, in which it is a nonconductor. It is paramagnetic with a magnetic moment corresponding to one unpaired spin (μ_{eff} = 1.90 μB). The IR spectrum contains two bands at 1685 (m) and 1590 (vs) cm^{-1} whose position and relative intensities are typical of a dithiocarbonate ligand η^2-S,S-coordinated to a transition metal.[11] In particular, the absorption at the high frequency is assigned to the Fermi resonance between the carbon–oxygen stretching mode and the first overtone band of the carbon–sulfur stretching mode.[12] No band attributable to the $[BPh_4]^-$ anion is present.

ESR Spectrum of 4. While the powder X-band ESR spectrum (298 K) consists of a single broad resonance at $\langle g \rangle$ = 2.062 ($\langle \Delta H \rangle$ = 120.0 G) which is indicative of strong exchange interactions between nearest neighbors, the spectrum in a CH_2Cl_2 glass at 100 K is well resolved (Figure 1a). This can be interpreted by using a $S = {}^1/_2$ spin Hamiltonian with $g_\parallel$ = 1.990 ($A_\parallel$ = 249.0 G) and $g_\perp$ = 2.092 ($A_\perp$ = 213.3 G). A three-line resolution is present in each perpendicular (A_P = 21.8 G) and parallel (A_P = 23.0 G)

---

(10) Mealli, C.; Sacconi, L. *J. Chem. Soc., Chem. Commun.* **1973**, 886.

(11) (a) Lin, J. B.; Chen, H. W.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 394. (b) Gould, R. O.; Gunn, A. M.; Van der Hark, T. E. M. *J. Chem. Soc., Dalton Trans.* **1976**, 1713. (c) Bianchini, C.; Meli, A.; Orlandini, A. *Inorg. Chem.* **1982**, *21*, 4166. (d) Bianchini, C.; Meli, A.; Dapporto, P.; Tofanari, A.; Zanello, P. *Ibid.* **1987**, *26*, 3677.

(12) Burke, J. M.; Fackler, J. P. Jr. *Inorg. Chem.* **1972**, *11*, 2744.

Table I. Formal Electrode Potentials (in V, vs SCE) for the Redox Changes Exhibited by the Complexes [**1**][BPh_4], **3**, **11**, and **7** in CH_2Cl_2

	$E°(1+/0)$	$E_p(0/1-)^a$	$E°'(0/1+)$
[(triphos)Rh(S_2CO)][BPh_4]	−0.21	−1.21	
[(triphos)Rh(Se_2CO)][BPh_4]	−0.24	−1.13	
[(triphos)Rh(S_2CNPh)][BPh_4]	−0.34	−1.22	
(triphos)Co(S_2CO)			+0.27

^{a}Recorded at 0.2 V s^{-1}.

absorption. As has been recently reported for the low-spin mononuclear Rh(II) complex [(NP_3)Rh(σ-C≡CPh)][BPh_4], the present set of ESR parameters is strongly diagnostic for a SQ symmetry with the unpaired electron in the d_{z^2} orbital.[13] In particular, the large $A_\parallel$ and $A_\perp$ values are due to a strong interaction with the apical phosphorus, which looks at the d_{z^2} SOMO. The splitting observed in the perpendicular and parallel absorptions is attributed to interaction of the electron with the two basal phosphorus atoms. The room-temperature X-band ESR spectrum consists of a quartet centered at $\langle g\rangle = 2.059$ ($\langle A_P\rangle = 95.6$ G) ($\langle g_{calcd}\rangle = {}^1/_3(g_\parallel + 2g_\perp) = 2.058$). The spectrum (Figure 1b) has an intensity ratio closer to 1:2:2:1 than the theoretical 1:3:3:1, almost certainly because the central lines are somewhat broader as expected if the three phosphorus atoms of triphos are instantaneously nonequivalent.[14] The line shape of the spectrum does not show any additional hyperfine structure, most likely because the coupling constants to rhodium ($I = {}^1/_2$) are generally small.[15] The parent Rh(III) derivative [**1**]$^+$ interconverts rapidly between SQ and TBP geometries in ambient-temperature solutions. As there is no reason to believe that an extra electron would induce a high-energy barrier for such an interconversion, a fluxionality of the same type can be ascribed to **4**.

The selenium complex (triphos)Rh(Se_2CO) (**6**) obtained by electrochemical reduction of the SQ Rh(III) derivative **3** (see Table I) exhibits frozen and room-temperature ESR spectra in CH_2Cl_2 quite similar to those of **4** (see the supplementary material), thus providing further support for our structural assignment. The ESR parameters in CH_2Cl_2 solutions are as follows: 100 K, $g_\parallel = 1.998$, $A_\parallel$(P apical) = 260.0 G, $A_\parallel$(P basal) = 21.8 G, $g_\perp = 2.086$, $A_\perp$(P apical) = 210.7 G, $A_\perp$(P basal) = 22.7 G; 300 K, quartet, $\langle g\rangle = 2.065$, $\langle g_{calcd}\rangle = {}^1/_3(g_\parallel + g_\perp) = 2.057$, $\langle A_P\rangle = 93.3$ G.

The cobalt(II) complex (triphos)Co(S_2CO) (**7**), which is isoelectronic with **4**, has been authenticated by an X-ray analysis.[11c] The cobalt center is coordinated by the three phosphorus atoms of triphos and by the two sulfur atoms of the dithiocarbonate ligand in a distorted SQ environment. The bond distances within the CoS_2CO moiety are consistent with an overall π-electron delocalization over the four-membered metalla ring. The ESR spectrum of this paramagnetic compound ($\mu_{eff} = 1.97\ \mu_B$) has now been recorded in order to verify whether replacement of rhodium by cobalt affects the solution behavior of the (triphos)M(S_2CO) unit. The spectrum in CH_2Cl_2 at 298 K consists of 14 lines (Figure 2) and can be interpreted by considering either two isomeric species with $\langle g\rangle = 2.130$ and $\langle g\rangle = 2.115$ or one species with $\langle g\rangle = 2.122$. In the former case, the hyperfine structure ($\langle A\rangle = 42.2$ and 40.2 G, respectively) is attributed to coupling of the unpaired electron to the ^{59}Co nucleus ($I = {}^7/_2$),[7c] while the couplings to the ^{31}P nuclei appear negligible. The stronger coupling of the electron to cobalt rather than to phosphorus is not new; in particular, it has recently been observed for a family of Co(II) catecholate complexes of general formula (triphos)Co(cat) (cat = 3,5-di-*tert*-butylcatecholate, tetrachlorocatecholate).[7c] According to this interpretation, **7** is assigned a much lower fluxionality as compared to that of the rhodium analogue, the two limiting SQ and TBP geometries now being observable on the NMR time scale. Alternatively, the spectrum shown in Figure 2 can reasonably be interpreted by considering the presence of one fluxional species with $\langle g\rangle = 2.122$ and $\langle A_P\rangle \cong {}^1/_2\langle A_{Co}\rangle = 42$ G. In this respect, as observed for **4**, the central lines of the expected 1:3:3:1 quartets are significantly broader than the outer lines because of the instantaneous nonequivalence of the three phosphorus atoms of triphos.[14]

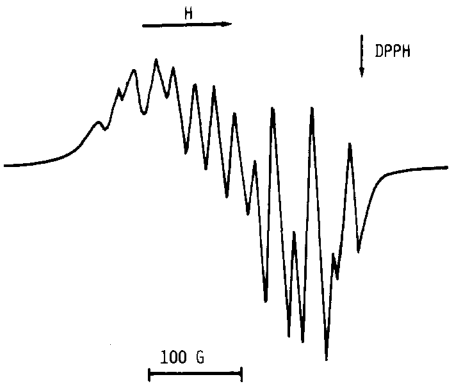


Figure 2. X-Band ESR spectrum of (triphos)Co(S_2CO) in CH_2Cl_2 at 298 K.

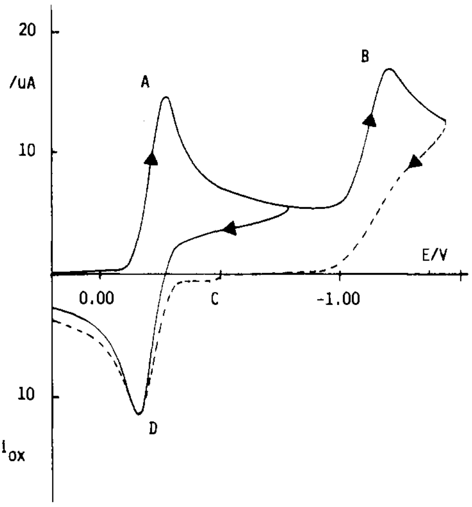


Figure 3. Cyclic voltammogram recorded at a platinum electrode of a CH_2Cl_2 solution of [(triphos)Rh(S_2CO)][BPh_4] (1.02×10^{-3} mol dm^{-3}) and [NBu_4][ClO_4] (0.1 mol dm^{-3}) (scan rate 0.2 V s^{-1}).

Reduction of [**1**]$^+$ to **4** is accomplished regardless of the stoichiometry and nature of the reagent employed except for NaC_8H_{10}, $NaBH_4$, and $LiHBEt_3$. The alternative pathway that the last two may follow has already been discussed (i.e. hydride addition to give **5**). When sodium naphthalenide, which is the strongest reducing agent within the series, is used to reduce [**1**]$^+$, a rigorous 1:1 molar ratio is required to have a good yield of **4**. In fact, a 2-fold excess of NaC_8H_{10} gives an ill-defined product that contains sulfur but not the dithiocarbonate ligand as evidenced by analytical and spectroscopic methods. In order to shed some light on the redox properties of [**1**]$^+$, a detailed electrochemical study has been carried out. In fact, it might be expected that the Rh(III) complex [**1**]$^+$ would add as many as two electrons to give a Rh(I) derivative (recall that five-coordinate Rh(I) complexes of triphos are generally stable).[2,3]

Figure 3 shows the cyclic voltammetric response exhibited by [**1**][BPh_4] in deareated CH_2Cl_2 solution. Two successive cathodic processes take place in correspondence to peaks A and B, respectively. The first reduction process displays a directly associated response in the reverse scan (peak D); in contrast, the second reduction step exhibits the minor peak C in the reverse scan, which is very far from the reoxidation of the species directly electrogenerated at peak B.

---

(13) Bianchini, C.; Laschi, F.; Ottaviani, F.; Peruzzini, M.; Zanello, P. *Organometallics* **1988**, *7*, 1660.

(14) Casagrande, L. V.; Chen, T.; Rieger, P. H.; Robinson, B. H.; Simpson, J.; Visco, S. J. *Inorg. Chem.* **1984**, *23*, 2019. DeGray, J. A.; Meng, Q.; Rieger, P. H. *J. Chem. Soc., Faraday Trans. 1* **1987**, *83*, 3565.

(15) (a) Pilloni, G.; Zotti, G.; Zecchin, S. *J. Organomet. Chem.* **1986**, *317*, 357. (b) Zotti, G.; Zecchin, S.; Pilloni, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *175*, 241.

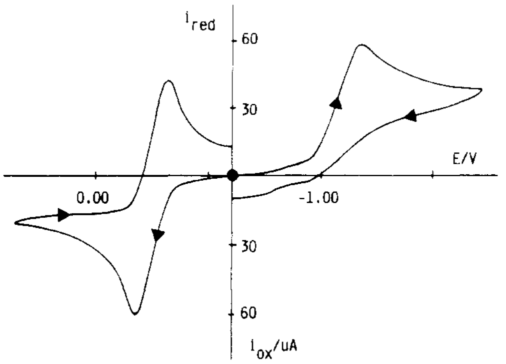


Figure 4. Cyclic voltammogram recorded at a platinum electrode on a CH_2Cl_2 solution of $[(triphos)Rh(S_2CO)][BPh_4]$ (4.8×10^{-3} mol dm^{-3}) exhaustively one-electron reduced at -0.4 V ($[NBu_4][ClO_4]$ supporting electrolyte, scan rate 0.2 V s^{-1}).

Analysis of the cyclic voltammograms relevant to the peak system A/D with scan rates ranging from 0.02 to 50 V s^{-1} shows features that are diagnostic for a quasi-reversible one-electron charge transfer:[16] the $i_p(D)/i_p(A)$ ratio is constantly equal to 1; the $E_p(D) - E_p(A)$ difference gradually increases from 78 to 510 mV; the current function $i_p(A)^{-1/2}$ decreases less than 10%. The full chemical reversibility of the $[(triphos)Rh(S_2CO)]^{+/0}$ redox change is indicated also by the cyclic voltammogram recorded on the exhaustively one-electron-reduced CH_2Cl_2 solution of $[(triphos)Rh(S_2CO)]^+$. As shown in Figure 4, the voltammogram is quite complementary to that reported in Figure 3 and identical with that exhibited by a pure sample of **4**. Controlled-potential coulometric tests performed in correspondence to the first cathodic process ($E_w = -0.4$ V) led to the consumption of 1 mol of electrons/mol of $[\mathbf{1}]^+$. Solution samples systematically withdrawn at different stages of the electrolysis were revealed to be ESR-active with spectra exhibiting the typical quartet of **4**.

The same behavior is exhibited by $[\mathbf{1}][BPh_4]$ in THF solution ($E^{\circ\prime}(1+/0) = -0.24$ V; $E_p(0/1-) = -1.20$ V). As far as the species electrogenerated in correspondence to the second cathodic step is concerned (reasonably the monoanion $[(triphos)Rh(S_2CO)]^-$, its extreme instability is evidenced by the fact that, even at the highest scan rate of 50 V s^{-1}, no directly associated reoxidation response could be detected. Accordingly, we conclude that the monoanion decomposes as soon as it forms. As a matter of fact, GC analysis of the gaseous phase evolved during the macroelectrolysis of $[\mathbf{1}][BPh_4]$ at -1.7 V (or during the reaction of $[\mathbf{1}][BPh_4]$ with excess NaC_8H_{10}) showed an abundant presence of COS. Indeed, the dithiocarbonate ligand, which in the free form is very unstable to disproportionation, can be stabilized by transition-metal species but these are required to contain high-valent metals. Evidently, the ligand needs to delocalize as many electrons as possible onto the metal to reduce and eventually impede its natural tendency to decomposition. This may explain both the extraordinary stability of $[\mathbf{1}]^+$, even higher than that of the electronically and coordinatively saturated parent complex **2**, and its reluctance to reversibly add more than one electron.

Table I summarizes the redox potentials for the 1+/0 and 0/1− steps in CH_2Cl_2 of $[\mathbf{1}][BPh_4]$ as well as a family of related 1,1-dithiolate rhodium complexes (see below). Also, it reports the $E^{\circ\prime}$ value of the $(triphos)Co(S_2CO)/(triphos)Co(S_2CO)^+$ redox change. Since the compounds share so many elements of their complex framework, it is natural that they also show similar redox properties. As an example, Figure 5 illustrates the cyclic voltammetric behavior of **7** in CH_2Cl_2 solution. A single anodic process is displayed, which, in controlled-potential coulometry, leads to a consumption of one electron per molecule. Diagnostic analysis of the cyclic voltammetric parameters indicates it involves a quasi-reversible, uncomplicated, one-electron charge transfer. A solution sample withdrawn at the end of the electrolysis was revealed to be ESR silent, in good agreement with the formation of the Co(III) species $[(triphos)Co(S_2CO)]^+$. An irreversible multielectron reduction process is also present at $E_p = -1.85$ V, the peak height of which, ca. 10 times greater than the preceding anodic one, strongly indicates its ligand-centered nature.

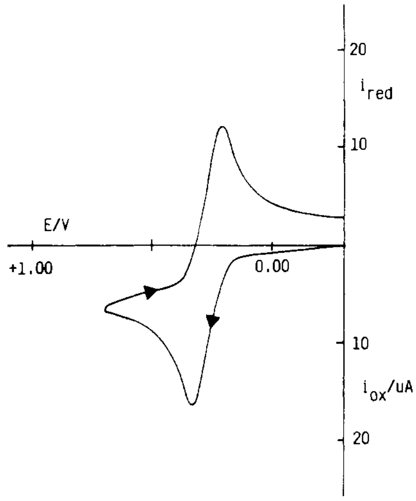


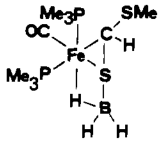
Figure 5. Cyclic voltammogram recorded at a platinum electrode of a CH_2Cl_2 solution of $(triphos)Co(S_2CO)$ (1.10×10^{-3} mol dm^{-3}) and $[NBu_4][ClO_4]$ (0.1 mol dm^{-3}) (scan rate 0.2 V s^{-1}).

Cleavage of B–H and B–C Bonds in $[BH_4]^-$ and $[BPh_4]^-$. Other reactions that clearly show the presence of both nucleophilic and electrophilic sites on $[\mathbf{1}]^+$ are the following (Scheme I).

Treatment of **1** in THF with $HOSO_2CF_3$ or $MeOSO_2CF_3$, followed by $NaBPh_4$ addition, yields the $(\mu\text{-}S)_2$ complex $[(triphos)Rh(\mu\text{-}S)_2Rh(triphos)][BPh_4]_2$[4,17] (**8**) together with a variety of mainly gaseous products, including hydrogen sulfide, dimethyl sulfide, CO, and COS.

As reported for the reactions of $(PMePh_2)_2Pt(S_2CO)$ with alkyl halides, such byproducts form upon electrophilic attack at the sulfur atoms of the η^2-S,S-coordinated dithiocarbonate ligand.[18]

In the preceding section, we have shown that $[\mathbf{1}][BPh_4]$ reacts with $NaBH_4$ or $LiHBEt_3$ to give mixtures of the Rh(II) and Rh(III) dithiocarbonates **4** and **5**. Such a result stems from the use of reagents that may alternatively function as reducing agents or hydride ligand releasers. A reaction that exclusively yields the Rh(III) hydride **5** is the one between $[\mathbf{1}][BPh_4]$ and $BH_3\cdot THF$. The most straightforward interpretation of this reaction is to think of the electrophilic attack by BH_3 at a sulfur atom of the dithiocarbonate ligand (intermediate A). In this way, the flow of electron density from sulfur to rhodium is presumably diminished and, consequently, the electrophilic character of the metal increased to such a point that a B–H bond is cleaved. Actually, we have no evidence for the formation of intermediate A, which, however, has good precedent in the complex $Fe(CO)(PMe_3)_2[\eta^3\text{-}HC(SMe)SBH_3]$ (I).[19]



I

Much more intriguing is the copper-assisted cleavage of a B–C bond from $[BPh_4]^-$ promoted by $[\mathbf{1}]^+$. As previously stressed, the complex cation $[(triphos)Rh(S_2CO)]^+$ forms, with the $[BPh_4]^-$ anion, the quite stable salt $[\mathbf{1}][BPh_4]$. However, under certain circumstances, the cation is able to cleave one of the B–C bonds

---

[16] Brown, E. R.; Sandifer, J. R. In *Physical Methods of Chemistry. Electrochemical Methods*; Rossiter, B. W., Hamilton, J. F., Eds.; Wiley: New York, 1986; Vol. 2, Chapter 4.

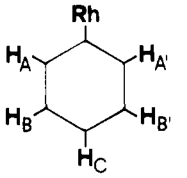
[17] Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. *Inorg. Chem.* **1986**, *25*, 4618.

[18] Fackler, J. P., Jr.; Seidel, W. C. *Inorg. Chem.* **1969**, *8*, 1631.

[19] Khasnis, D. V.; Toupet, L.; Dixneuf, P. H. *J. Chem. Soc., Chem. Commun.* **1987**, 23.

from the counteranion, affording the novel complex (triphos)RhPh(S_2CO) (**9**).

Compound **9** is obtained as pale yellow crystals by reaction of [**1**][BPh_4] in THF with coordinatively unsaturated copper(I) tris(triphenylphosphine) fragments from $(PPh_3)_3CuClO_4$.[20b] The copper complexes remain unaltered after the reaction, as evidenced by the ^{31}P NMR spectrum of either the reaction mixture or the crude crystalline products precipitated from the mixture by addition of ethanol. Compound **9** is stable both in the solid and in deoxygenated solutions, in which it behaves as a nonelectrolyte. The IR spectrum exhibits a reinforced phenyl vibration at 1580 cm^{-1} and two absorptions at 1730 (m) and 1600 (vs) cm^{-1} whose positions and relative intensities are attributed to an η^2-dithiocarbonate-*S*,*S'* ligand. The $^{31}P\{^1H\}$ NMR spectrum (CD_2Cl_2, 298 K) shows an AM_2X spin system with a doublet of doublets at 5.28 ppm ($J(P_M-P_A)$ = 25.4 Hz; $J(P_M-Rh)$ = 110.0 Hz) and a doublet of triplets at −28.38 ppm ($J(P_A-Rh)$ = 54.4 Hz). Such a pattern is typical of OCT rhodium complexes of triphos;[2] however, the P_A resonance is unusually high field. This is most likely due to the much larger differential shielding of the P_A phosphorus by the trans phenyl ring. A perusal of the aromatic proton region in the ^1H NMR spectrum of **9** in CD_2Cl_2 (see the supplementary material) reveals the presence of at least two additional groups of bands as compared to the same region in the spectrum of the OCT congener (triphos)RhCl(S_2CO) (**2**), which differs from **9** only in having chloride in the place of σ-phenyl. Such additional resonances have been simulated[21] as the BB′CX part of an AA′BB′CX spin system (II) by using the following parameters:



II

$\delta(H_B) = \delta(H_{B'})$ = 6.46 ppm; $\delta(H_C)$ = 6.62 ppm; $J(H_A-H_B) = J(H_A-H_{B'})$ = 7.51 Hz; $J(H_B-H_{B'})$ = 0.56 Hz; $J(H_C-H_A) = J(H_C-H_{A'})$ = 0.98 Hz; $J(H_C-H_B) = J(H_C-H_{B'})$ = 7.49 Hz; $J(Rh-H_B) = J(Rh-H_{B'})$ = 2.60 Hz; $J(Rh-H_C)$ = 1.02 Hz. Unfortunately, the AA′X part of the spectrum is masked by the resonances of the aromatic C–H protons of the phenyl substituents of triphos. Accordingly, neither $\delta(H_A)$ nor $J(Rh-H_A)$ could be detected.

Conclusive evidence for the presence of a phenyl group σ-bonded to rhodium in **9** is provided by the results of the acidolysis (eq 1) and hydrogenolysis (eq 4) reactions, which show the formation

$$\mathbf{9} + 2H^+ \rightarrow \mathbf{8} + COS + C_6H_6 \qquad (1)$$

$$\mathbf{9} + H_2 \rightarrow \mathbf{5} + C_6H_6 \qquad (2)$$

of benzene. In addition, thermal decomposition of **9** in THF directly accomplished in a gas chromatograph at 250 °C gives benzene.

While there is no doubt about the origin of the phenyl ligand, i.e. the [BPh_4]$^-$ anion as demonstrated by the crossover experiments 3–5, the overall reaction mechanism and, in particular, the

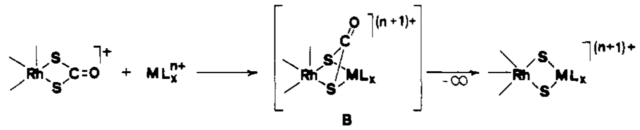
$$[\mathbf{1}][BPh_4] + [(PPh_3)_3Cu][ClO_4] \rightarrow \mathbf{9} \qquad (3)$$

$$[\mathbf{1}][PF_6] + [(PPh_3)_3Cu][ClO_4] \rightarrow \text{no reaction} \qquad (4)$$

$$[\mathbf{1}][PF_6] + [(PPh_3)_3Cu][BPh_4]^{20a} \rightarrow \mathbf{9} \qquad (5)$$

role played by the copper complex are not completely elucidated.

We have recently reported that [**1**][BPh_4] is able to react with coordinatively unsaturated metal fragments, yielding homo- and heterodinuclear (μ-S)$_2$ complexes and CO.[4] As shown in (6), the two metal systems interact through the sulfur atoms of the dithiocarbonate ligand. In other cases, the reactions between dithiocarbonate complexes and metal fragments conclude with the stabilization of μ-S_2CO dimers of type B.[22]



(6)

If it is taken for granted that [(triphos)Rh(S_2CO)]$^+$ and [$(PPh_3)_3Cu$]$^+$ may interact as shown in (6), then it remains to explain why their interconversion does not lead to the formation of any stable adduct between the two but results in a net increase of electrophilic character of rhodium, which ultimately becomes able to cleave in heterolytic fashion a B–C bond from [BPh_4]$^-$. Tentatively, we suggest that, whatever the interaction between the two metal complexes, this is sufficiently strong to disengage totally or partially electrons of the sulfur atoms from π-bonding to rhodium. Accordingly, the (triphos)Rh(S_2CO) fragment may acquire a pure "electronically unsaturated" character with all of its chemical prerogatives such as the extraction and stabilization via complex formation of a phenyl group from the tetraphenylborate anion.[23]

The mobility of the sulfur π-electrons over the RhS_2CO moiety is indirectly shown up also by the stretching frequencies of the C=O double bond in the dithiocarbonates [**1**]$^+$, **2**, **4**, **5**, and **9**. In effect, ν(C=O) decreases by ca. 80 cm^{-1} on going from the 16-electron complex to the 17- and 18-electron compounds. A similar trend has been observed for the analogous diselenocarbonate derivatives. The only way by which ν(C=O) may decrease is given by the population of the CO π^* orbital by electrons from the sulfur atoms. Such an electron density is much less available in [**1**]$^+$ since it is engaged in π bonding to rhodium but certainly may become available when the metal is saturated by externally added electrons, as occurs in **2**, **4**, **5**, and **9**. In good agreement with this interpretation, the C=O bond distance is longer in the 17-electron complex **7** (1.27 (3) Å)[11c] than in the 16-electron species **3** (1.19 (2) Å).[3]

Metathesis of CS_2-like Heteroallene Molecules. The heterocumulenes of formula X=C=Y, where X and Y may be O, S, Se, and NR, constitute a well-distinguished class of bifunctional substrates. A variety of reactions of these molecules have been found that show the carbon to function as an active electrophile and the heteroatoms as active nucleophiles.[24] In view of the results and considerations reported in the preceding sections, [**1**]$^+$ and the heteroallenes CS_2, SCNPh, and SCNEt appear to be appropriately designed to react with each other, and indeed they do.

The dithiocarbonate complex [**1**]$^+$ readily reacts in CH_2Cl_2 at room temperature with an equimolar amount of either CS_2 or SCNR to quantitatively give COS and [(triphos)Rh(S_2CS)][BPh_4] (**10**) or [(triphos)Rh(S_2CNR)][BPh_4] (R = Ph (**11**), Et (**12**)), respectively (Scheme II). In turn, trithiocarbonate **10** is converted into dithiocarbonimidate **11** or **12** by treatment with a 2-fold excess of SCNR. These reactions are reversible; i.e., the addition of a 2-fold excess of CS_2 to **11** or **12** in CH_2Cl_2 leads to quantitative formation of **10** and liberates SCNPh or SCNEt, respectively. Both of the last two heteroallenes are metathesized by the rhodium system, the only condition being an excess of the appropriate organoisothiocyanate. Compounds **10**–**12** are not converted into [**1**]$^+$ even when treated with a large excess of COS. Monitoring the reactions by ^{31}P NMR spectroscopy (see later) reveals that the replacement of COS in [**1**]$^+$ by CS_2 or SCNR

---

[20] (a) Reichle, W. T. *Inorg. Chim. Acta* **1971**, *5*, 325. (b) Cariati, F.; Naldini, F. *Gazz. Chim. Ital.* **1965**, *95*, 3.

[21] The spectrum was simulated by using an updated version of the LAOCNN3 program: Castellano, S.; Bothner-By, A. A. *J. Chem. Phys.* **1964**, *41*, 3863.

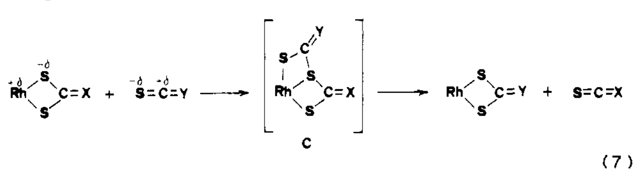
[22] Fornies, J.; Uson, M. A.; Gil, J. I.; Jones, P. *J. Organomet. Chem.* **1986**, *311*, 243.

[23] (a) Sacconi, L.; Dapporto, P.; Stoppioni, P. *Inorg. Chem.* **1976**, *15*, 325. (b) Albano, P.; Aresta, M.; Manassero, M. *Ibid.* **1980**, *19*, 1069.

[24] (a) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M. In *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1986; and references therein. (b) Bianchini, C.; Masi, D.; Mealli, C.; Meli, A. *Inorg. Chem.* **1984**, *23*, 2838.

is the most favored reaction pathway, as it is achieved by equimolar amounts of the coreactants. In contrast, **10**–**12** seem to have comparable thermodynamic stabilities as their quantitative interconversion requires the use of a 2-fold excess of the appropriate heterocumulene. Stoichiometric reactions of SCNR or CS_2 with **10** and **11** (or **12**) give equimolar mixtures of **11** (or **12**) and **10**, respectively.

The most palatable mechanistic interpretation for the unprecedented metathesis reactions shown in Scheme II is the one that implies the formation of intermediary metallacycles of type C (eq 7). The extrusion of one of the two heteroallene moieties,



(7)

which may be envisaged in C as connected head to head by a sulfur atom, completes the reactions. The driving forces to the selective cleavage of one of the two S–C bonds in C appear to be the nature of the bound heteroallene (COS is more easily eliminated) and the concentration of the free heteroallene in the reaction mixture.

In support for intermediate C, recall that metallacycles built up by Rh(III) fragments and two heteroallene molecules coupled head to head are well-known.[24a,25] In some cases, the complexes can be isolated; in others, they spontaneously decompose to more stable products via rupture of a C–S linkage.[25b]

Compounds **10**–**12** have been isolated as crystals and have been fully characterized by spectroscopic methods. They all are fairly stable in the solid state and in deoxygenated solutions, in which they behave as 1:1 electrolytes. The IR spectra are very similar to each other except for the absorptions due to the functionality that, case by case, connects the sulfur atoms of the 1,1-dithio ligands, i.e. >C=O, >C=S, or >CNR. In particular, strong bands at 995 and 1570 cm^{-1} in the IR spectra of **10** and **11** (or **12**) are easily assigned to ν(C=S) and ν(C=N), respectively. The IR spectra of the dithiocarbonimidate complexes **11** and **12** differ from each other only in a reinforced phenyl vibration (NPh) at 1590 cm^{-1}, which is absent in the spectrum of **12**. On the other hand, the ^{1}H NMR spectrum of the latter compound (CD_2Cl_2, 298 K) exhibits a quartet at δ 4.40 and a triplet at δ 1.35 (J(H–H) = 6.9 Hz), which are due to the ethyl substituent on the carbonimidate nitrogen.

Although sharing large part of the overall complex framework, [**1**]$^+$, **10**, and **11** display a number of different chemical and physical properties. Indeed, the substituent on the carbon atom appears to be of critical importance in determining the electronic structure of the RhS_2C metalla ring and therefore the chemistry of the present 1,1-dithio complexes. Certainly, on account of the different electronegativities of the carbon substituents (S < NPh < O), the composition of the frontier orbitals of the η^2-bonded 1,1-dithio ligands may significantly change as recently demonstrated for the heteroallene ligands CS_2, SCNR, and COS.[24b] In good agreement with the electronegativity criterion, the complex that exhibits the most pronounced differences in the chemical–physical behavior is trithiocarbonate **10**. Unlike [**1**]$^+$ and **11** (or **12**), which are fluxional in the temperature range 300–173 K (^{31}P{^{1}H} NMR of **11** and **12** in CD_2Cl_2: A_3X spin system, 34.21 ppm (d, J(P–Rh) = 98.4 Hz) and 33.70 ppm (d, J(P–Rh) = 98.0 Hz), respectively), compound **10** is rigid in CH_2Cl_2 solution at room temperature. In fact, it shows a well-resolved first-order ^{31}P{^{1}H} NMR AM_2X splitting pattern with $\delta(P_A)$ 11.65 ppm (dt, $J(P_A–P_M)$ = 30.0 Hz, $J(P_A–Rh)$ = 95.2 Hz) and $\delta(P_M)$ −4.20 ppm (dd, $J(P_M–Rh)$ = 96.7). In good agreement with our previous conclusions on the geometry of the present 1,1-dithio complexes, the $J(P_A–P_M)$ value is diagnostic for an SQ structure of the complex.[7a] Interestingly, trithiocarbonate **10** is fluxional in DMF. At −70 °C the spectrum consists of an AM_2X pattern ($\delta(P_A)$ 26.68 ppm (dt, $J(P_A–P_M)$ = 30.4, $J(P_A–Rh)$ = 114.2 Hz), $\delta(P_M)$ 3.20 ppm (dd, $J(P_M–Rh)$ = 96.3 Hz)), which begins to broaden at −24 °C and collapses at 30 °C into a sharp doublet centered at 9.80 ppm. The J(P–Rh) value in the high-temperature limit, 103.5 Hz, is equal to the weighted average of the low-temperature-limit coupling constants.

Although difficult to interpret in detail, the different solution behavior of trithiocarbonate **10** as compared to that dithiocarbonate [**1**]$^+$ and dithiocarbonimidate **11** certainly originates in electronic factors. In fact, **10** is not able to reversibly add one electron to give the corresponding Rh(II) derivative as the congeners [**1**]$^+$ and **11** do; in cyclic voltammetry, the compound gives rise to ill-defined reduction processes, indicating that the monocation is the only stable member of its potential redox family. In contrast, **11** exhibits redox properties qualitatively similar to those of [**1**]$^+$ (see Table I) and can be reduced to the Rh(II) derivative (triphos)Rh(S_2CNPh) (**13**). Like **4**, compound **13** is fluxional on the ESR time scale in room-temperature CH_2Cl_2 solution and displays a well-resolved quartet at $\langle g\rangle = 2.062$ ($\langle A_P\rangle$ = 95.0 G). Given the minor negativity of sulfur vs that of O or NPh, the inability of trithiocarbonate **10** to accept electrons may be due to a major π-electron interaction between the rhodium and sulfur atoms. In other words, the metal in **10** is sufficiently saturated by intramolecular interaction with the sulfur atoms. In a similar way, the π interaction in **10** between rhodium and sulfur may be strong enough to make the molecule more rigid and therefore less fluxional on the NMR time scale. In this respect, if it is taken for granted that the fluxionality goes through a turnstile rotation mechanism, a strong π-bonding interaction between S and Rh does increase the barrier to rotation.[26]

Experimental Section

General Information. All reactions and manipulations were carried out under a nitrogen atmosphere. Reagent grade chemicals were used in the preparations of the complexes. The solid complexes were collected on sintered-glass frits and washed with appropriate solvents before being dried under a stream of nitrogen.

Physical Measurements. Infrared spectra were recorded with a Perkin-Elmer 475 grating spectrophotometer using samples mulled in Nujol between KBr plates. ^{1}H and ^{31}P{^{1}H} NMR spectra were taken with Varian CFT 20 and VXR 300 spectrometers. 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. Magnetic susceptibility of solid samples were measured on a Faraday balance. The materials and the apparatus used for the electrochemical experiments have been described elsewhere.[27] The potential values are relative to an aqueous calomel electrode (SCE). The temperature was controlled at 20 ± 0.1 °C. Under the present experimental conditions the ferrocenium/ferrocene couple was located at +0.38 V. X-Band EPR spectra were recorded with an ER 200-SRCB Bruker spectrometer operating at ν^0 = 9.78 GHz. The control of the external magnetic field was obtained with a microwave bridge ER 041 MR Bruker wave meter. The temperature was varied and controlled with a Bruker ER 4111 VT device with an accuracy of ±1 K. In order to estimate accurate g_{iso} and g_{aniso} values over the temperature range of interest, the diphenylpicrylhydrazyl (DPPH) free radical was used as field maker (g_{iso}(DPPH) = 2.0036). To avoid Co dipole–dipole interaction low concentrations were used (less than 10^{-3} M). In order to assure quantitative reproducibility, the samples were placed into calibrated quartz capillary tubes permanently positioned in the resonance cavity.

GC analyses were performed on a Shimadzu GC-8A gas chromatograph fitted with a thermal conductivity detector and an appropriate column: 6 ft 0.1% SP-1000 on Carbopack C $^1/_8$ in. stainless-steel column (benzene); 6 ft Chromosil 330 $^1/_8$ in. OD Teflon (FEP) column (COS, CS_2, H_2S, Me_2S); 10 ft 100/120 Carbosieve S-II $^1/_8$ in. stainless-steel column (CO). All the columns were purchased from Supelco Inc.

Synthesis. (triphos)Rh(S_2CO) (4). Addition of an equimolar amount of LiMe (1 M THF), LiPh (1 M THF), or $NaC_{10}H_8$ (THF) to a solution of **1** (0.34 g, 0.3 mmol) in THF (20 mL) made the color to turn from red to deep green. Elution with ethanol (30 mL) gave green crystals on standing. They were collected by filtration and washed with ethanol and

---

(25) (a) Cowie, M.; Dwight, S. K. *J. Organomet. Chem.* **1981**, *214*, 233. (b) Thewissen, D. H. M. W. *Ibid.* **1980**, *188*, 211.

(26) Howell, J. A. In *Advances in Dynamic Stereochemistry*; Gielen, M. F., Ed.; Freund Publishing House: London, 1985.

(27) Bianchini, C.; Mealli, C.; Meli, A.; Sabat, M.; Zanello, P. *J. Am. Chem. Soc.* **1987**, *109*, 185.

petroleum ether; yield 87%. When $NaBH_4$ (ethanol) or $LiHBEt_3$ (1 M THF) were employed as reducing agents, the isolated crude product contained **4** together with some amount (20-30%) of (triphos)RhH(S_2CO) (**5**). Compound **4** was separated from **5** by recrystallization from CH_2Cl_2/ethanol. When the reduction of **1** to **4** was achieved by using $(C_5H_5)_2Co$ (CNMe) or $(NP_3)Ni$ (THF), the compounds $[(C_5H_5)_2Co][BPh_4]$ and $[(NP_3)Ni][BPh_4]$ were also isolated from the reaction mixture, respectively. Anal. Calcd for $C_{42}H_{39}OP_3RhS_2$: C, 61.54; H, 4.79; Rh, 12.55. Found: C, 61.46; H, 4.78; Rh, 12.31.

(triphos)RhH(S_2CO) (5). Addition of BH_3·THF (1 M THF) (0.5 mL, 0.5 mmol) to a solution of **1** (0.34 g, 0.3 mmol) in THF (20 mL) caused an immediate color change from red to yellow. On addition of ethanol (5 mL) white crystals of **5** precipitated within a few minutes, which were filtered off and washed with ethanol and petroleum ether; yield 92%. Anal. Calcd for $C_{42}H_{40}OP_3RhS_2$: C, 61.46; H, 4.91; Rh, 12.53. Found: C, 61.29; H, 4.82; Rh, 12.38.

Reaction of 1 with HSO_3CF_3 (or $MeSO_3CF_3$). Neat HSO_3CF_3 (or $MeSO_3CF_3$) (0.3 mmol) was syringed into a magnetically stirred THF (20 mL) solution of **1** (0.34 g, 0.3 mmol) in a Schlenk flask equipped with a rubber septum. After 30 min the gaseous phase was analyzed by using a gas chromatograph, which revealed the presence of H_2S, Me_2S, CO, and COS. The resulting red-brown solution, treated with $NaBPh_4$ (0.17 g, 0.5 mmol) in ethanol (20 mL), gave brown crystals of [(triphos)Rh(μ-S)$_2$Rh(triphos)]$[BPh_4]_2$ (**8**); yield 78%.

(triphos)RhPh(S_2CO) (9). A mixture of **1** (0.34 g, 0.3 mmol) and $(PPh_3)_3CuClO_4$ (0.28 g, 0.3 mmol) in THF (20 mL) was stirred at room temperature for 1 h. The solution color changed from red to yellow-orange, and pale yellow crystals of **9** precipitated. They were separated by filtration (yield 55%) from the mother liquor, which gave on addition of ethanol (20 mL) a precipitate containing further **9** and the starting copper complex. Anal. Calcd for $C_{48}H_{44}OP_3RhS_2$: C, 64.28; H, 4.94; Rh, 11.47. Found: C, 63.99; H, 4.88; Rh, 11.32.

Reaction of 9 with HSO_3CF_3. Neat HSO_3CF_3 (0.3 mmol) was syringed into a magnetically stirred solution of **9** (0.27 g, 0.3 mmol) in CH_2Cl_2 (20 mL) in a Schlenk flask equipped with a rubber septum. After 10 min the GC analysis of the gaseous and the liquid phase showed the presence of COS and benzene, respectively. The resulting red-brown solution, treated with $NaBPh_4$ (0.17 g, 0.5 mmol) in ethanol (20 mL), gave brown crystals of **8**; yield 85%.

Reaction of 9 with H_2. Hydrogen was bubbled for 1 h through a suspension of **9** (0.27 g, 0.3 mmol) in THF (20 mL), during which the starting solid dissolved and new crystals of **5** precipitated in 91% yield. The GC analysis of the reaction mixture showed the formation of benzene.

[(triphos)Rh(S_2CS)][BPh_4] (10). Neat CS_2 (0.06 mL, 1 mmol) was syringed into a solution of [**1**][BPh_4] (1.14 g, 1 mmol) in 30 mL of CH_2Cl_2 in a Schlenk flask equipped with a rubber septum. There was an immediate color change from red-brown to brilliant red and, simultaneously, COS evolution as determined by the GC analysis of the gaseous phase. Addition of ethanol (40 mL) gave red crystals of **10**, which were collected by filtration and washed with ethanol and petroleum ether; yield 95%. Anal. Calcd for $C_{66}H_{59}BP_3RhS_3$: C, 68.63; H, 5.14; Rh, 8.91; S, 8.32. Found: C, 68.45; H, 5.07; Rh, 8.73; S, 8.21.

[(triphos)Rh(S_2CNR)][BPh_4] (R = Ph (11), Et (12)). Dark violet crystals of **11** and **12** were obtained in 95% yield by following the same procedure as above but replacing CS_2 with SCNR (R = Ph, Et). Alternatively, **10** was treated in CH_2Cl_2 with a 2-fold excess of SCNR and worked up as above. The interconversion between **11** and **12** was simply achieved by adding an excess of SCNEt or SCNPh to a CH_2Cl_2 solution of **11** or **12**, respectively. The formation of COS, CS_2, and SCNR in the course of the reactions was determined by GC. Anal. Calcd for $C_{72}H_{64}BNP_3RhS_2$ (**11**): C, 71.23; H, 5.31; N, 1.15; Rh, 8.47. Found: C, 71.04; H, 5.19; N, 1.01; Rh, 8.33. Anal. Calcd for $C_{72}H_{64}BNP_3RhS_2$ (**12**): C, 70.04; H, 5.53; N, 1.20; Rh, 8.82. Found: C, 69.87; H, 5.34; N, 1.12; Rh, 8.73.

Acknowledgment. Thanks are due to Aldo Traversi for technical assistance.

Registry No. [**1**][BPh_4], 99955-64-3; **4**, 117896-52-3; **5**, 110637-36-0; **6**, 117896-54-5; **7**, 82590-72-5; **8**, 105139-43-3; **9**, 117896-53-4; **10**, 109637-03-8; **11**, 109637-05-0; **12**, 109637-07-2; **13**, 117896-57-8; LiMe, 917-54-4; LiPh, 591-51-5; $NaC_{10}H_8$, 3481-12-7; BH_3·THF, 14044-65-6; S_2CO^{2-}, 30981-29-4; HSO_3CF_3, 1493-13-6; $MeSO_3CF_3$, 333-27-7; $(PPh_3)_3CuClO_4$, 34010-81-6; BPh_4^-, 4358-26-3; CS_2, 75-15-0; SCNPh, 103-72-0; SCNEt, 542-85-8; [(triphos)Rh(S_2CO)][BPh_4], 97689-99-1; [(triphos)Rh(S_2CO)]$^-$, 117896-55-6; [(triphos)Co(S_2CO)]$^+$, 117896-56-7; CS_3^{2-}, 15644-49-2; $PhNCS_2^{2-}$, 117861-48-0; $EtNCS_2^{2-}$, 117861-49-1.

Supplementary Material Available: Figure 1S (X-band ESR spectra of (triphos)Rh(Se_2CO) in CH_2Cl_2 at 100 K (a) and 300 K (b)) and Figure 2S (experimental (a) (CD_2Cl_2, 298 K, 300 MHz, $MeSi_4$ reference) and computed (b) ^1H NMR spectra of (triphos)RhPh(S_2CO) in the interval between 6.7 and 6.4 ppm) (2 pages). Ordering information is given on any current masthead page.

Contribution from the Laboratoire de Chimie Moléculaire,
Unité Associée au CNRS No. 426, Université de Nice, 06034 Nice, France

The Iron-Nitrato/Iron-Nitrosyl Couple in the Presence of Hexamethylphosphoric Triamide and Its Relevance to Oxygen Activation and Transfer. X-ray Structure of $Fe(NO_3)(Cl)_2(HMPA)_2$

Henri Li Kam Wah, Michèle Postel,* and Félix Tomi

Received April 14, 1988

The nitrosyl dimer $[Fe(NO)_2(Cl)]_2$ (**1**) in the presence of hexamethylphosphoric triamide (HMPA) yields the unstable compound $Fe(NO)_2(Cl)(HMPA)$ (**2**), which gives through NO dissociation $Fe(NO)(Cl)_2(HMPA)\cdot{}^1/_2HMPA$ (**3**). Oxidation by oxygen (1 atm) of the Fe-NO moiety in **2**, **3**, or **1** in the presence of HMPA results in the formation of the nitrato—and not nitro—complexes $Fe(NO_3)(Cl)_2(HMPA)\cdot{}^1/_2HMPA$ (**4**), $Fe(NO_3)_2(Cl)(HMPA)\cdot{}^1/_2HMPA$ (**6**), $Fe(NO_3)_2(Cl)(HMPA)_2$ (**7**) and $Fe(NO_3)(Cl)_2(HMPA)_2$ (**8**). The molecular structure of **8** has been determined by X-ray diffraction. Crystal data (at −100 °C): monoclinic, space group $P2_1/c$, $a = 15.994$ (5) Å, $b = 10.172$ (3) Å, $c = 16.571$ (5) Å, $\beta = 104.7$ (1)°, $V = 2608$ Å^3, $Z = 4$, $R_w = 0.051$ for 3029 reflections with $I > 3.0\sigma(I)$. The nitrates **7** and **8** are capable of oxygen transfer to phosphines, thus regenerating the Fe-NO moiety. The nitrato complexes were found to be catalysts in the autoxidation of cyclohexene.

Introduction

There is a need for developing nonradical systems for oxidation and, in particular, for the epoxidation of olefins by molecular oxygen. A possible route consists of splitting the oxygen molecule on a ligand of a transition metal to form a complex with the ligand in the oxidized form; the oxygen of the oxidized ligand would then transfer to an organic substrate. This chemistry was first demonstrated for the nitro/nitrosyl redox couple.[1,2]

We have found[3] that the iron-nitrato-iron-nitrosyl couple could constitute a new alternative for the activation and transfer of molecular oxygen; the nitrosyl ligands in the dinitrosyliron dimers

---

(1) Solar, J. P.; Mares, F.; Diamond, S. E. *Catal. Rev.—Sci. Eng.* **1985**, *27*, 1 and references therein.

(2) Andrews, M. A.; Chang, T. C. T.; Cheng, C. W. F. *Organometallics* **1985**, *4*, 268 and references therein.

(3) Tomi, F.; Li Kam Wah, H.; Postel, M. *New J. Chem.* **1988**, *12*, 289.

0020-1669/89/1328-0233$01.50/0