Redox-Induced Conversion Pathways in Rhodium and Iridium Complexes Containing C-S Bond Cleaved Benzo[b]thiophene

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The thermally generated 16-electron fragments [(triphos)MH] (M = Rh, Ir) react with benzo[b]thiophene by C-S bond scission to yield the 2-vinylthiophenolate derivatives $(triphos)M[\eta^3-S(C_6H_4)CH=CH_2]$ (M = Rh, 1; Ir, 2) which display a rich redox-induced reactivity [triphos = $MeC(CH_2PPh_2)_3$]. Removal of one electron from 1 or 2 leads to the corresponding paramagnetic cations 1^+ and 2^+ , respectively; these compounds undergo a radical reaction with H[•] in solution to form the diamagnetic 2-ethylidenecyclohexadienethione complexes anti-[(triphos)M{ η^4 -S(C₆H₄)CH(CH₃)}]⁺ (M = Rh, **anti-3**⁺; Ir, **anti-6**⁺) which isomerize to $syn-3^+$ and $syn-6^+$, respectively. Addition of one electron to $syn-3^+$ and $syn-6^+$ gives the neutral paramagnetic derivatives $syn-[(triphos)M\{\eta^4-S(C_6H_4)CH(CH_3)\}]$ (M = Rh, syn-3; Ir, syn-6) which convert back to the starting complexes 1 and 2 by homolytic C-Hbond cleavage liberating H[•], and thus completing a full electrochemical cycle by addition/ elimination of one electron and one H atom. The related 2-(3,3,3-triphenylpropylidene)cyclohexadienethione complex [(triphos)Rh{ η^4 -S(C₆H₄)CH(CH₂CPh₃)}]PF₆ (**4PF**₆) undergoes similar reactions including loss of a trityl radical by a C-C bond cleavage reaction in the neutral derivative (triphos)Rh{ η^4 -S(C₆H₄)CH(CH₂CPh₃)} (4). Removal of a second electron from 1^+ or 2^+ leads to the dicationic species 1^{2+} and 2^{2+} , which spontaneously lose a proton and produce the cationic metallabenzothiabenzene complexes $[(triphos)M(\eta^2-C,S-C_8H_6S)]^+$ $(M = Rh, 5^+; Ir, 7^+)$. Finally, addition of one elecytron to 5^+ or 7^+ produces the corresponding neutral paramagnetic metallabenzothiabenzene complexes [(triphos) $M(\eta^2 - C_s - C_8 H_6 S)$] (M = Rh, 5; Ir, 7). All the long-lived paramagnetic compounds have been characterized by X-band ESR spectroscopy.

Introduction

Given the complexity of the processes occurring in the hydrodesulfurization (HDS) process of fossil fuels as well as the relative scarcity of analytical and spectroscopic tools to investigate *in situ* heterogeneous reactions, the study of the coordination and reactivity of various sulfur-contaminants in crude oil with soluble metal complexes has emerged as a valid modeling approach for the elucidation of the HDS mechanism.²

Various bonding modes of model substrates such as thiophene (T), benzo[b]thiophene (BT), or dibenzothiophene (DBT),³ and reactions leading to C-S bond cleavage, $^{4-11}$ hydrogenation, $^{4b,d,8a,12-15}$ and desulfurization $^{4d,8a,10,16-19}$ have been described in detail. In contrast, few studies have been reported on the electrontransfer chemistry of metal complexes containing intact

or cleaved thiophenic molecules^{8a,20} although electrontransfer processes on the catalyst surface have been suggested to play an important role in the HDS with molybdenum studies supported on alumina.²¹⁻²⁴

In MoS_2/Al_2O_3 catalysts promoted by cobalt or nickel, there are metal sites in different oxidation states and environment. A number of model surface studies agree

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to consider edge Mo(II) as the active sites for the chemisorption of $T.^{21,23}$ The reduction Mo(IV) \rightarrow Mo-(II) has been proposed to be brought about by either bulk Mo valence band electrons or electron-transfer from neighboring molybdenum or promoter (Co, Ni) atoms connected by sulfur bridges.^{21,24a}

Based on the observation that a pretreatment of the catalyst surface with H_2 is mandatory to make the catalyst susceptible for **T** chemisorption, it has also been suggested that H_2 participates in the reduction of Mo-(IV).²³ Actually, electrons may be provided by H_2 when this reagent, adsorbed molecularly, dissociates heterolytically on the catalyst surface. As a matter of fact, the occurrence of heterolytic splitting reactions in hydrotreating catalysis has widely been demonstrated.²⁴ Thus, in addition to various bases (O²⁻, OH⁻, S²⁻), a catalyst surface may host electrons, H⁺ and H⁻ species, the latter two probably in the form of sulfhydryl (SH) and hydryl (MH) moieties.^{24a}

To the best of our knowledge, the only works in which electrochemistry has been used as a method to study how electron transfers may influence the chemistry of thiophene ligands are those reported by Angelici and Rauchfuss (Chart 1).^{5c,20d-f} In all cases, the addition of electrons to the starting complex results in a change of the bonding mode of the thiophene ligand from η^5 to η^4 and thus in increased chemical reactivity.^{5c,8b,c} Elec-

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trochemical studies of complexes in which the metal center has inserted into a C–S bond of a thiophenic molecule are much rarer and of limited scope. In particular, Dessy and Pohl^{20a} and later Rauchfuss^{8a} have reported the electrochemical behavior of the benzothiaferroles $Fe_2(C_8H_6S)(CO)_6$ and $Fe_2(2,2'-C_4H_3SC_4-H_3S)(CO)_6$ which undergo two one-electron reversible reductions.

In this paper, we report a study of the electrontransfer chemistry of various rhodium and iridium complexes obtained by metal-insertion into a C-S bond of **BT**, which is one of the most representative compounds of the least reactive sulfur-containing constituents of crude oil.²⁵

Experimental Section

General Information. All reactions and manipulations were routinely performed under a nitrogen atmosphere by using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from LiAlH₄, stored over molecular sieves, and purged with nitrogen prior to use. Cobaltocene, LiHBEt₃ (1 M solution in THF), and AgPF₆ were purchased from Aldrich. All other chemicals were commercial products and were used as received without further purification. Literature methods were employed for the synthesis of (triphos)Rh[η^3 -S(C₆H₄)-CH=CH₂](1),^{4c} [(triphos)Rh{ η^4 -S(C₆H₄)CH(CH₃)}]PF₆ (**3PF**₆),^{4c} [(triphos)Rh{ η^4 -S(C₆H₄)CH(CH₂CPh₃)}]PF₆ (**4PF**₆),^{4c} syn-[(triphos)Rh{ η^4 -SCHCHCH(CH₃)}]BPh₄,^{4c} anti-[(triphos)Rh{ η^4 -SC-HCHCH(CH₃)}]BPh₄,^{4c} (triphos)Ir[η^3 -S(C₆H₄)CH=CH₂] (**2**),^{4b} [(triphos)Ir{ η^4 -S(C₆H₄)CH(CH₃)}]PF₆ (**6PF**₆),^{4b} and [(triphos)-Ir(η^2 -C,S-C₈H₆S)]PF₆ (**7PF**₆).^{4b}

Deuterated solvents for NMR measurements were dried over molecular sieves. ¹H NMR and ¹H, ¹H 2D-COSY NMR spectra were obtained on either a Bruker ACP 200 (200.13 MHz) or a Bruker AVANCE DRX 500 (500.13 MHz) spectrometer. ¹H NMR shifts are recorded relative to tetramethylsilane (TMS) with the residual ¹H resonance in the deuterated solvent as secondary reference. ¹³C{¹H} NMR spectra were recorded on the Bruker ACP 200 instrument operating at 50.32 MHz. The ¹³C{¹H} NMR shifts are given relative to TMS with solvent as secondary reference. ³¹P{¹H} NMR spectra were recorded on a Bruker ACP 200 spectrometer operating at 81.01

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M = Rh (1), Ir (2)

MHz. Chemical shifts are relative to external 85% H₃PO₄ with downfield values reported as positive. Broad band and selective ¹H{³¹P} NMR experiments were carried out on the Bruker ACP 200 instrument equipped with a 5-mm inverse probe and a BFX-5 amplifier device. ¹³C-DEPT and ¹H, ¹³C 2D-HETCOR experiments were conducted on the Bruker ACP 200 spectrometer. Conductivities were measured with an Orion Model 990101 conductance cell connected to a Model 101 conductivity meter. The conductivity data were obtained at sample concentrations of ca. 10^{-3} M in nitroethane solutions at room temperature. The materials and the apparatus used for the electrochemical experiments have been described elsewhere.²⁶ Direct current voltammograms at a platinum electrode with periodical renewal of the diffusion layer (DCV) have been obtained as previously described.²⁶ Deaeration of solutions was performed by bubbling nitrogen for 15 min. Unless otherwise stated, the potential values are referred to an aqueous calomel electrode (SCE). Low-temperature macroelectrolysis tests were performed by using the Ag/AgCl reference electrode, the potential of which was -0.04 V vs SCE. Under the present experimental conditions, the ferrocenium/ ferrocene couple was located at +0.44 V in dichloromethane solutions. X-Band ESR spectra were recorded with an ER 200 D-SRC Bruker spectrometer operating at $\omega_0 = 9.78$ GHz. The operational microwave frequency (Bruker Microwave Bridge ER 041 MR) was tested with an XL 3120 microwave frequency counter. The control of the external magnetic field was obtained with a microwave bridge ER 041 MR Bruker wavemeter. The temperature was varied and controlled with an ER 4111 VT Bruker device with an accuracy of ± 1 °C. In order to estimate accurate g_{iso} and g_{aniso} values over the temperature range of interest, the diphenylpicrylhydrazyl free radical (DPPH) was used as the H_0 external magnetic field marker $(g_{iso}(DPPH) = 2.0036)$. In order to ensure quantitative reproducibility, the samples were placed into calibrated quartz capillary tubes permanently positioned in the resonance cavity.

Reactions of [(triphos)Rh{ η^4 -S(C₆H₄)CH(CH₃)}]PF₆ (3PF₆) and [(triphos)Rh{ η^4 -S(C₆H₄)CH(CH₂CPh₃)}]PF₆ (4PF₆) with CoCp₂. To a CH₂Cl₂ (20 mL) solution of either 3PF₆ or 4PF₆ (0.30 mmol) at room temperature was added 1 equiv of CoCp₂ (0.06 g, 0.30 mmol) in CH₂Cl₂ (20 mL). The resulting solution was stirred for ca. 3 h and then concentrated to dryness under vacuum. The ¹H and ³¹P{¹H} NMR spectra of the residue, dissolved in CH₂Cl₂, showed the complete transformation of **3PF₆** or **4PF₆** to **1**. The reduction of **4PF₆** to **1** gave CPh₃H (¹H NMR singlet at 5.51 ppm).

Preparation of [(triphos)Rh(η^2 -C,S-C₈H₆S)]**PF**₆ (5**PF**₆). To a stirred solution of (triphos)Rh[η^3 -S(C₆H₄)CH=CH₂] (1) (0.20 g, 0.23 mmol) in THF (30 mL) at room temperature was added to a 2-fold excess of AgPF₆ (0.12 g, 0.46 mmol). There was an immediate color change from yellow to red. After 15 min, the reaction mixture was concentrated to ca. 10 mL under vacuum. The portionwise addition of *n*-heptane (20 mL) led to the precipitation of **5PF**₆ as red microcrystals. They were collected by filtration on sintered-glass frits, washed with *n*-pentane, and dried in a stream of nitrogen; yield 86%. Anal. Calcd (found) for $C_{49}H_{45}F_6P_4RhS$: C, 58.46 (58.11); H, 4.50 (4.41); Rh, 10.22 (10.00); S, 3.18 (3.01). ³¹P{¹H} NMR (CD₂-Cl₂): 20 °C, A₃X spin systems, δ 27 (br); -70 °C, AM₂X spin system, δ -4.9 (dt, $J(P_AP_M)$ 23.3Hz, $J(P_ARh)$ 69.8 Hz, P_A), 42.5 (dd, $J(P_MRh)$ 104.6 Hz, P_M). ¹H NMR (THF- d_8 , 20 °C): δ 8.39 (d, $J(H_4H_5)$ 7.8 Hz, H₄), 8.13 (m, $J(H_3H_2)$ 10.1 Hz, H₃), 8.04 (m, $J(H_2Rh)$ 2.4 Hz, H₂), 7.91 (d, $J(H_7H_6)$ 7.7 Hz, H₇), 7.68 (t, H₆), 7.62 (t, $J(H_5H_6)$ 7.6 Hz, H₅). ¹³C{¹H} NMR (THF- d_8 , 20 °C): δ 173.4 (quintet, $J(C_2P) \cong J(C_2Rh) \cong$ 24.6 Hz, C_2); the resonances of the other **BT** carbons are masked by those of the phenyl carbons of the triphos ligand. Λ_M : 78 Ω^{-1} cm² mol⁻¹. When NEt₃ was added to the red solution, [NHEt₃]PF₆ precipitated by addition of *n*-heptane.

Reaction of [(triphos)Rh(\eta^2-C,S-C₈H₆S)]PF₆ (5PF₆) with LiHBEt₃. A solution of the rhodabenzothiabenzene complex 5PF₆ (0.03 g, 0.03 mmol) in THF-d₈ (1 mL) was placed into a Teflon capped resealable NMR tube under nitrogen. The solution was cooled to -70 °C and a 2-fold excess of LiHBEt₃ (1 M solution in THF, 60 \muL, 0.06 mmol) was syringed into the tube. The ¹H and ³¹P{¹H} NMR spectra, recorded at -70 °C, showed the immediate conversion of 5PF₆ to 1 with no detection of intermediate species.

Results and Discussion

The 16-electron fragments [(triphos)RhH] and [(triphos)IrH], generated *in situ* by thermolysis in THF of (triphos)RhH₃ and (triphos)Ir(H)₂(C₂H₅), respectively, have previously been shown to be active toward the oxidation addition of a C-S bond from **BT** [triphos = MeC(CH₂PPh₂)₃].^{4c,e} The C-S insertion products are actually 2-vinylthiophenolate complexes of the formula (triphos)M{ η^3 -S(C₆H₄)CH=CH₂} (M = Rh, 1; Ir, 2) formed by reductive coupling of a terminal hydride with the vinyl moiety of a metallabenzothiabenzene intermediate (Scheme 1).^{4b,c,e}

Formally, complexes 1 and 2 may be seen as the first reduction product of **BT** once the latter reagent has been cleaved by a metal center. In fact, the addition of H^+ to 1 or 2 results in the hydrogenation of the olefinic end of the 2-vinylthiophenolate ligand,^{4b,c} while further reaction of the resulting 2-ethylidenecyclohexadienethione iridium complex with H₂ gives complete hydrogenation to 2-ethylthiophenolate (Scheme 2).^{4b} On the other hand, the rhodium derivative 1 has recently been found to be an efficient catalyst precursor for the opening and hydrogenation of **BT** to 2-ethylthiophenol in homogeneous phase.¹² In light of these results as well as the importance of electron-transfer processes in the heterogeneous HDS, it seemed interesting to us to study the redox chemistry of 1 and 2.

Electrochemistry of the 2-Vinylthiophenolate Rhodium Complex [(triphos) $Rh(\eta^3-S(C_6H_4)CH=$ CH₂)] (1) and Characterization of its Redox Products. Figure 1a shows an overall picture of the redox

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(BF₄)₂

Scheme 2



Figure 1. Cyclic voltammetric responses recorded at a platinum electrode on a CH_2Cl_2 solution containing 1 (0.7 \times 10⁻³ mol dm⁻³) and [NBu₄]ClO₄ (0.2 mol dm⁻³). Scan rate: (a) 0.2 V s⁻¹; (b) 10.24 V s⁻¹.

behavior of the neutral complex 1 in dichloromethane solution at 20 $^{\circ}\mathrm{C}.$

Complex 1 displays two main sequential oxidation processes with some features of chemical reversibility at the peak-systems A/E and B/D, respectively, together with a few minor redox steps (namely, peaks C, F, and G), which, based on the response at high scan rates illustrated in Figure 1b, are clearly attributable to chemical complications following the two primary electron removals.

Controlled potential coulometric experiments directly performed in correspondence to the second anodic step $(E_{\rm w}=+0.5 \text{ V})$ consume about 1.1 electrons/molecule. Cyclic voltammetry (CV) and direct current voltammetry with periodical renewal of the diffusion layer on the solutions resulting from step-by-step macroelectrolysis, rationalize the underlying electrode mechanism.

After consumption of about 0.8 electrons/molecule at the first anodic step ($E_w = +0.15$ V), the electrolysis current almost drops out, and the original yellow solution turns green. The voltammetric profiles show the two peak-systems A/E and B/D (in a complementary fashion according to the formation of the monocation 1⁺, see below) in a peak-height ratio reduced of about one-half as compared to the starting CV. Furthermore, in addition to the products responsible for the processes C and F, a new catho-anodic peak system is now visible at potentials slightly more negative than the peak system G/H (for comparative purposes with the electrochemistry of the iridium complex 2, this new cathoanodic system will be hereafter as I/L). The further consumption of about 0.3 electron/molecule at the second anodic process puts an end to the electrolysis current, the solution becomes red and the voltammetric tests show only the presence of the almost overlapping catho-anodic peak-systems G/H and I/L.

On standing, the green solution obtained after exhaustive macroelectrolysis of 1 at the first anodic step slowly turns red-violet. CV measurements carried out in the course of this color change show that the intensity of the peak-system *I/L* increases with time at the expense of peak F which completely disappears after 1 h at room temperature, while peak C remains unaltered.

These experimental observables indicate that the neutral complex 1 undergoes two subsequent oneelectron oxidations to the congeners 1^+ and 1^{2+} , respectively, both processes being complicated by chemical reactions.

Analysis²⁷ of the cyclic voltammograms relevant to the first anodic step with scan rates (varying from $0.02\,$ V s⁻¹ to 10.24 V s⁻¹) show the following: the i_{pc}/i_{pa} current ratio progressively increases from 0.65 to 1; the peak-to-peak separation progressively increases from 71 mV to 260 mV; the current function $i_{\rm pc}/v^{-1/2}$ remains substantially constant. Taking into account that, under the same experimental conditions, the one-electron oxidation of ferrocene ($E^{\bullet} = +0.44 \text{ V}$) exhibits a rather similar trend in the peak-to-peak separation, these data suggest that the one-electron redox change $1/1^+$ involves an electrochemically reversible oxidation complicated by subsequent chemical reactions. Similar diagnostic parameters are observed for the second anodic process which converts 1^+ to 1^{2+} . Accordingly, both the transient monocation 1^+ and the dication 1^{2+} are expected to substantially maintain the geometry of the neutral precursor and thus can be formulated as [(triphos)Rh- $(\eta^3-S(C_6H_4)CH=CH_2)]^+$ and $[(triphos)Rh(\eta^3-S(C_6H_4) CH=CH_2)$]²⁺, respectively.²⁸

On the basis of an X-ray structure analysis and

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M = Rh, syn-3*; ir, syn-6*

solution NMR data, the bonding interaction between rhodium and the double bond of the 2-vinylthiophenolate ligand in 1 was assigned a metallacyclopropane structure.^{4c} Since removal of electrons from 1 is expected to reduce considerably the extent of $d\pi$ (metal) $\rightarrow \pi^*$ (olefin) back-bonding, 1⁺ and 1²⁺ are represented as π -olefin complexes in Scheme 3 which summarizes all the redox-induced transformations described in this work.

As shown above, the monocation 1^+ is fairly unstable in solution at room temperature $(t_{1/2} \approx 0.5 \text{ s})$, which is confirmed by the fact that the value of the ratio $i_p(1/1^+)/i_p(1^+/1^{2+})$ is about 2 at low scan rates (below 0.5 V s⁻¹) and is 1 only at high scan rates (10.24 V s⁻¹). However, the complex is sufficiently stable in solution even at room temperature to allow its characterization by ESR spectroscopy. A detailed discussion of the ESR spectrum of 1^+ as well as all the other ESR-active compounds described in this work will be made in a forthcoming section to let the reader concentrate here on the type and nature of the chemical reactions which follow up the electron-transfer processes.

After macroelectrolysis of 1 in CH_2Cl_2 at -18 °C (E_w = +0.15 V), a sample of the solution was withdrawn and transferred under nitrogen into an ESR tube immersed in liquid nitrogen. The tube was positioned into an ESR spectrometer precooled at 100 K and variable-temperature spectra in X-band were acquired.

After the first ESR spectrum of 1^+ at 20 °C was acquired, subsequent spectra showed a significant decay of the paramagnetism with time. The green solution, however, became ESR-silent much before assuming a stable red-violet color. This evidence coupled with the electrochemical results indicate that the green paramagnetic cation 1^+ transforms into three diamagnetic compounds. Two of these are evidently related to each other: the complex responsible for peak F appears kinetically unstable as it spontaneously converts to a more stable species (responsible for the peak system I/L), which definitely imparts the red-violet color to the solution. The third minor species (responsible for peak C) apparently remains unaltered with time.

The stable red-violet complex has successfully been identified by means of the following procedure. A 100-mg sample of 1 was exhaustively electrolyzed at the potential of the first anodic step ($E_w = +0.15$ V) at room temperature. After *ca*. 1 h, the resulting solution was transferred under nitrogen into a Schlenk-type flask and the solvent was removed in vacuo. The dry residue was dissolved in CD₂Cl₂ and analyzed by ³¹P{¹H} NMR spectroscopy which showed the formation of the known 2-ethylidenecyclohexadienethione complex [(triphos)Rh-{ η^4 -S(C₆H₄)CH(CH₃)]⁺ (**3**⁺) in 90% yield.

Unequivocal experimental evidence in favor of the transformation of electrogenerated 1^+ into the thermodynamically stable product 3^+ was provided by a study of the electron-transfer properties of pure $3PF_6$ independently prepared by protonation of 1 (Scheme 2).^{4c} In fact, the redox fingerprint of $3PF_6$ shown in Figure 2a, is identical with that of the red-violet product of degradation of 1^+ in CH_2Cl_2 solution (peak system I/L).

The reduction process of **3PF**₆ consumes one electron/ molecule in controlled potential coulometry ($E_w = -1.1$ V) and the CV parameters show that this redox step consists of an electrochemically reversible reduction complicated by slow chemical rearrangement of the electrogenerated product (the i_{pa}/i_{pc} ratio is 0.8 at 0.2 V s⁻¹ and reaches the value of 1 at 2.0 V s⁻¹). Indeed, in accord with the backward profile shown in Figure 2a, exhaustive reduction of red-violet solutions of 3⁺ obtained from either isolated **3PF**₆ or exhaustive oneelectron oxidation of 1, ultimately restore the precursor 1 via the intermediacy of the neutral 2-ethylidenecyclohexadienethione complex (triphos)Rh{ η^4 -S(C₆H₄)CH-(CH₃)} (**3**) (see below) (Scheme 3).

On the basis of these results, one may conclude that





Figure 2. Cyclic voltammetric responses recorded at a platinum electrode on a CH_2Cl_2 solution containing [NBu₄]-ClO₄ (0.2 mol dm⁻³) and (a) **3PF**₆ (0.5 × 10⁻³ mol dm⁻³), scan rate 0.2 V s⁻¹; (b) **4PF**₆ (0.7 × 10⁻³ mol dm⁻³), scan rate 0.02 V s⁻¹; (c) **5PF**₆ (0.5 × 10⁻³ mol dm⁻³), scan rate 0.2 V s⁻¹.

the radical complex 1^+ converts in solution to the diamagnetic 2-ethylidenecyclohexadienethione complex 3^+ . This transformation formally requires that a hydrogen atom is added to 1^+ . The uptake of H[•] species by paramagnetic complexes is not unusual; in most instances, hydrogen atoms are provided by the solvent or adventitious water.²⁹ In other cases, intermolecular hydrogen transfer between two radicals may occur.³⁰ In the second mechanistic hypothesis, two diamagnetic species would form which, however, is not observed in the case at hand. Accordingly, we are inclined to think that the formation of 3^+ proceeds by a radical mechanism in which a hydrogen atom is abstracted from the solvent by the paramagnetic complex 1^+ (although disfavored by bond energies, it is also possible that adventitious water can provide a hydrogen atom through an alternative pathway).

All our efforts to isolate or characterize in solution the product responsible for the cathodic peak F in Figure 1a were unsuccessful due to its spontaneous conversion to 3^+ . This evidence coupled with the fact that the thermodynamically unstable species responsible for peak F regenerates the starting 2-vinylthiophenolate complex 1 by exhaustive reduction at $E_w = -0.45$ V suggest that the two products responsible for peaks F and I may be stereoisomers differing from each other

Scheme 4



in the orientation of the methyl group with respect to the ethylidene double bond. Indeed, it has recently been reported that treatment of the butadienethiolate complex (triphos)Rh(η^3 -SCH=CH-CH=CH₂) (similarly prepared by reaction of the trihydride (triphos)RhH₃ with T) with a protic acid gives the thiocrotonaldehyde complex *anti*-[(triphos)Rh{ η^4 -SCHCHCH(CH₃)}]⁺ as kinetic product which isomerizes in solution to syn-[(triphos)Rh{ η^4 -SCHCHCH(CH₃)}]⁺ (Scheme 4).^{4c} Most importantly, the two thiocrotonaldehyde isomeric complexes exhibit irreversible reduction processes at quite different potentials (-1.3 and -1.0 V, respectively) as is observed for the 2-ethylidenecyclohexadienethione complexes presently discussed (-0.88 and -0.40 V, respectively).

In view of the overall experimental results and considerations, we suggest that the compound which spontaneously converts to 3^+ is actually *anti*-[(triphos)-Rh{ η^4 -S(C₆H₄)CH(CH₃)}]⁺ (*anti*-3⁺). Thus the stable, red-violet isomer can be quoted as *syn*-3⁺ (Scheme 3).

In light of these results, a reaction between 1 and HBF₄·OEt₂ was carried out at -80 °C in an NMR tube (THF- d_8 as solvent) with the aim of intercepting the kinetic isomer **anti-3**⁺. Even at this low temperature, **syn-3**⁺ immediately formed, which suggests that, in contrast to the protonation of 1,^{4c} the radical reaction between 1⁺ and H[•] is still regioselective but not stereo-selective.

All our attempts to identify the third product of degradation of 1^+ (the one responsible for peak C) were unsuccessful due to its low concentration.

The transformation of $syn\cdot3^+$ into 1 upon exhaustive one-electron reduction at $E_w = -1.1$ V has been studied at low temperature. As anticipated by the CV studies, one-electron reduction of $syn\cdot3^+$ gives the neutral derivative $syn\cdot(triphos)Rh\{\eta^4-S(C_6H_4)CH(CH_3)\}$ ($syn\cdot3$). Compound $syn\cdot3$, which is sufficiently stable to allow its characterization by ESR spectroscopy, slowly converts ($t_{1/2} \approx 20$ s) at room temperature to 1 (Scheme 5a). The overall transformation of $syn\cdot3^+$ into 1 has also been performed by chemical reduction of isolated $3PF_6$ in CH_2Cl_2 with 1 equiv of cobaltocene (Scheme 5a).

From a chemical viewpoint, the spontaneous conversion of the paramagnetic complex syn-3, to the diamagnetic product 1 necessarily requires that a C-H bond in the former complex is homolytically cleaved. Examples of redox-promoted homolytic C-H bond cleavages in organometallic compounds have already been reported,^{30,31} but certainly the occurrence of such a reaction path in a **BT** C-S insertion product assumes a particular relevance.

In an attempt to confirm the radical nature of the C–H bond cleavage undergone by the neutral 2-ethylidenecyclohexadienethione complex **syn-3**, the redox chemistry of the known 2-(3,3,3-triphenylpropylidene)cyclohexadienethione congener [(triphos)Rh{ η^4 -S(C₆-H₄)CH(CH₂CPh₃)}]PF₆ (**4PF₆**) has been studied (Scheme 5b).^{4c}

⁽²⁹⁾ Gotzig, J.; Otto, H.; Werner, H. J. Organomet. Chem. 1985, 287, 247.

⁽³⁰⁾ Mandon, D.; Astruc, D. Organometallics 1989, 8, 2372.

^{(31) (}a) Connelly, N. G. Chem. Soc. Rev. **1989**, 18, 153. (b) Hayes, J. C.; Cooper, N. J. J. Am. Chem. Soc. **1982**, 104, 5570.

Scheme 5



(a) CoCp₂ or macroelectrolysis in CH₂Cl₂ (E_w = -1.1 V)



(a) CoCp₂ or macroelectrolysis in CH₂Cl₂ (E_w = -1.0 V)

Figure 2b shows the cyclic voltammetric response exhibited by **4PF**₆ in CH₂Cl₂. Controlled-potential coulometry ($E_w = -1.0$ V) shows that the reduction process involves one electron/molecule. The CV diagnostic criteria indicate that the redox change is complicated by slow degradation of the reduced species, while the large peak-to-peak separation (at 0.02 V s⁻¹ ΔE_p is equal to 109 mV) suggests that a significative structural reorganization accompanies the one-electron addition. Consistently, the electrogenerated blue complex (triphos)Rh{ η^4 -S(C₆H₄)CH(CH₂CPh₃)} (**4**) is sufficiently stable ($t_{1/2} \approx 10$ s) to be characterized by ESR spectroscopy, but quantitatively converts in solution to the yellow starting complex **1** by homolytic C-C bond cleavage.

The driving force which makes C-C bond cleavage in 4 prevail over C-H bond cleavage is most likely due to the greater stability of the trityl radical as compared to H[•]. Although rarer than redox-promoted C-H bond cleavage reactions, examples of homolytic C-C bond scissions have also been reported.³²

In conclusion, with the exception of the product responsible for peak C in Figure 1a (so far unidentified), all the redox-induced chemical transformations which follow the first oxidation step of 1 have been rationalized. It remains now to discuss the fate of the two-electron oxidized product 1^{2+} .

As previously shown, the dication 1^{2+} is fairly stable in solution even at room temperature. However, on long standing $(t_{1/2} \approx 15 \text{ s})$, it decomposes to give a red solution containing the product responsible for the peak system G/H of Figure 1a. Since this product is fully stable in solution, its preparation by chemical oxidation of 1 in THF with 2 equiv of AgPF₆ has been successful (Scheme 6). From this reaction, in fact, a diamagnetic red crystalline compound is obtained in quantitative yield which displays a reduction process in CH₂Cl₂ exactly in correspondence to the peak system G/H of Figure 1a with identical CV features (Figure 2c).

The diamagnetism of the compound obtained by twoelectron oxidation of 1 has allowed its unambiguous Scheme 6 P P $2 Ag^{+} 2 Ag^{0}$ P P + $20 \circ C$ $5^{+} 2 G^{-7}$ + H^{+} LiHBEt₃ $-70 \circ C$

characterization by multinuclear NMR spectroscopy as the rhodabenzothiabenzene complex [(triphos)Rh(η^2 -C,S-C₈H₆S)]PF₆ (**5PF**₆).

Compound $5PF_6$ exhibits NMR parameters which are fully comparable with those of the iridium derivative $[(triphos)Ir(\eta^2 - C, S - C_8H_6S)]BPh_4$ recently authenticated by an X-ray diffraction analysis.^{4b} In particular, like the Ir analog, the rhodium complex is stereochemically nonrigid on the NMR timescale. At room temperature, the ³¹P{¹H} NMR spectrum consists of a broad resonance centered at 27 ppm (A_3X spin system), while the slow exchange AM_2X regime is attained already at -50 $C[J(PP) = 23.3, J(P_ARh) = 69.8, and J(P_MRh) = 104.6$ Hz]. As previously suggested on the basis of a computer simulation of the dynamic spectra of the iridium congener, the magnetic equivalence of the three phosphorus atoms of 5^+ can be interpreted in terms of a non-bondbreaking interconversion between trigonal-bipyramidal and square-pyramidal structures. The spectrum in the slow exchange regime is consistent with a trigonalbipyramidal geometry which, in fact, is the preferred one by the iridium analog in the solid state.^{4b} The positions of C₂ (δ 173.4) in the ¹³C{¹H} NMR spectrum and of the methyne hydrogens H_2 and H_3 (δ 8.04 and 8.13, respectively) in the ¹H NMR spectrum are in the proper range for delocalized six-membered metallathia rings4a,5c and match very close those found for the related iridium complex [δ 162.1 (C₂), 8.33 (H₂), 8.26 (H_3)].^{4b} Conclusive experimental evidence in favor of the proposed structure of 5^+ is provided by the reaction of isolated $[5]PF_6$ in THF with LiHBEt₃ which quantitatively gives the 2-vinylthiophenolate precursor 1. By analogy with the same reaction of the iridabenzothiabenzene derivative,^{4b,e} the formation of 1 most likely proceeds via a rhodium hydride intermediate, (triphos)-

⁽³²⁾ Connelly, N. G. in *Paramagnetic Organometallic Species in Activation Selectivity, Catalysis;* Chanon, M., Julliard, M., Poite, J. C., Eds.; Kluwer Academic Publishers: Holland, 1989.

Table 1. Formal Electrode Potentials (V, vs SCE)and Peak-to-Peak Separations (mV) for the RedoxChanges Exhibited by the Present Complexes in
CH2Cl2 Solution

rhod	ium		iridium				
redox change	E°'	$\Delta E \mathbf{p}^a$	redox change	E°'	$\Delta E \mathbf{p}^a$		
1/1+	+0.04	84	2/2+	+0.09	66		
$1^{+}/1^{2+}$	+0.39	70	$2/2^{2+}$	+0.32	87		
anti-3 ⁺ /anti-3	-0.40^{b}		anti-6 ⁺ /anti-6	-0.50^{b}			
syn-3 ⁺ /syn-3	-0.88	72	syn-6 ⁺ /syn-6	-0.89	72		
4 ⁺ / 4	-0.79	111	• •				
5 ⁺ / 5	-0.78	66	7+/7	-1.04	74		

 a Measured at 0.2 V s $^{-1}$ b Peak potential value for irreversible process.

RhH(η^2 -C,S-C₈H₆S), characterized by a localized electronic structure in the metallathiacycle (a double bond between C₂ and C₃).^{4b} Like the Ir analog, the Rh hydrido complex rearranges to the 2-vinylthiophenolate complex by reductive coupling between the terminal hydride and the vinyl C₂ carbon atom. The energy barrier to this process is apparently much lower for rhodium than for iridium as no intermediate species was seen on the NMR timescale even when the reaction between **5PF**₆ and LiHBEt₃ was carried out at -70 °C, whereas the hydride complex (triphos)IrH(η^2 -C,S-C₈H₆S) can be isolated at low temperature.^{4b,e}

The transformation of 1^{2+} into the rhodabenzothiabenzene complex 5^+ necessarily involves the loss of a proton from the dication, which, in fact, has experimentally been observed when the reaction between 1 and 2 equiv of Ag⁺ was carried out in the presence of a proton scavenger such triethylamine.

Redox-induced heterolytic C-H bond cleavages resulting in H⁺ elimination are well known in the literature. As an example, treatment of Ru₂(μ -CO)(μ -CH₂)(μ -dppm)Cp₂ with 2 equiv of [FeCp₂]⁺ as oxidant gives Ru₂(μ -CO)(μ -CH)(μ -dppm)Cp₂ and H⁺.³³

As is evident from the electrochemical studies, 5^+ (either isolated or electrogenerated) displays a reduction process in correspondence to the peak-system G/H. The cyclic voltammetric features and the results of a controlled potential coulometry experiment are all consistent with a chemically and electrochemically reversible one-electron addition. As a matter of fact, the complex (triphos)Rh(η^2 -C,S-C₈H₆S) (5) can be electrogenerated in CH₂Cl₂ at $E_w = -1.0$ V, and this neutral species is rather long-lived under inert atmosphere ($t_{1/2} \approx 15$ s) to be characterized by ESR spectroscopy.

The formal electrode potentials for the redox changes exhibited by the rhodium complexes isolated or electrogenerated are summarized in Table 1.

Electrochemistry of the 2-Vinylthiophenolate Iridium complex [(triphos)Ir(η^3 -S(C₆H₄)CH=CH₂)] (2) and Characterization of Its Redox Products. Figure 3a shows that the neutral complex 2^{4b} gives rise to a cyclic voltammetric picture rather similar to that shown by the rhodium analog 1, the only significant difference being the presence of the peak-system (I/L) already in the reverse scan (Figure 1a). Peak F, which, as above discussed, is due to the chemical rearrangement of the one-electron oxidized product, is signifi-





Figure 3. Cyclic voltammetric responses recorded at a platinum electrode on a CH_2Cl_2 solution containing [NBu₄]-ClO₄ (0.2 mol dm⁻³) and (a) 2 (0.8 × 10⁻³ mol dm⁻³); (b) 6PF₆ (0.4 × 10⁻³ mol dm⁻³); (c) 7PF₆ (0.6 × 10⁻³ mol dm⁻³). Scan rate 0.1 V s⁻¹.

cantly more intense than in Figure 1a (correspondingly, the height of peak B is much lower than that of peak A, while an $i_p(A)/i_p(B)$ ratio of ca. 2.5 is observed at a scan rate of 0.2 V s⁻¹). Also, unlike the rhodium congener, comparable peak heights for the two one-electron steps $2/2^+$ and $2^+/2^{2+}$ are not observed even at high scan rates (the $i_p(A)/i_p(B)$ ratio is 1.5 at 10.24 V s⁻¹). These data are thus consistent with a faster chemical rearrangement of the electrogenerated mono-cation [(triphos)Ir(η^3 -S(C₆H₄)CH=CH₂)]⁺ (2⁺) as compared to the rhodium analog 1⁺.

Apart from the different stabilities of some electrogenerated products (see below), the overall scheme of the redox-induced transformations of 2 is analogous to that of the rhodium congener 1 (Scheme 3). The monocation 2^+ converts to the 2-ethylidenecyclohexadienethione complex anti-[(triphos)Ir{ η^4 -S(C₆H₄)CH-(CH₃)}]⁺ (anti- 6^+) (peak F) by abstraction of a hydrogen atom from the environment. The anti-complex rearranges in solution to the thermodynamically stable isomer syn-[(triphos)Ir{ η^4 -S(C₆H₄)CH(CH₃)}]⁺ (syn- 6^+), which can reversibly be reduced to the neutral paramagnetic derivative syn-(triphos)Ir{ η^4 -S(C₆H₄)CH(CH₃)} (syn-6). In turn, the dication 2^{2+} loses a proton convert-

^{(33) (}a) Connelly, N. G.; Forrow, N. J.; Gracey, B. P.; Knox, S. A. R.; Orpen, A. G. J. Chem. Soc., Chem. Commun. **1985**, 14. (b) Connelly, N. G.; Forrow, N. J.; Knox, S. A. R.; Macpherson, K. A.; Orpen, A. G. J. Chem. Soc., Chem. Commun. **1985**, 16.

Table 2.	X-Band ES	R Parameters	for the l	Present (Complexes	in CH ₂ Cl ₂
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	100 K				100 K					
complex	$g_{l^{a,b}}$	$g_{m}{}^{a,b}$	$g_{h^{a,b}}$	$\langle g \rangle^{a,c}$	$300 \mathrm{K}g_{\mathrm{iso}^a}$	$\overline{a_1}^{b,d}$	$a_{\mathrm{m}}{}^{b,d}$	$a_{h}^{b,d}$	$\langle a angle^{c,d}$	$300~{ m K}~a_{ m iso}{}^d$
syn-3	2.091	2.008	1.997	2.032	2.033	< 30	<30	<30	<30	<30
5	2.088	2.009	1.998	2.032	2.033	<25	<20	<20	<22	$<\!25$
1+	2.0	080	2.018 ^e	2.056	2.058	1	.45	175^{f}	155	$\begin{array}{c} 155\\ 15\end{array}$
4	2.094	2.008	2.003	2.035	2.032	<	30	<30	<30	<25
svn-6	2.151	2.0	003	2.052	2.047	<	30	$<\!25$	<30	<35
ŤĂ	2.1	116	1.928	2.053	2.050	1	.97	231	208	228
							31	22	<28	<25
							26	18	<23	<25
7 B	2.1	121	1.908	2.050	2.043	1	.99	229	209	232
							31	22	<28	<25
							26	18	<23	<25

 $a \pm 0.005, \ b \ g_1 = g_m = g_\perp, \ g_h = g_{\parallel}, \ a_1 = a_m = a_\perp \text{ and } a_h = a_{\parallel} \text{ for } \mathbf{1}^+, \ \mathbf{4}, \ \mathbf{7A}, \text{ and } \mathbf{7B}. \ c \ \langle g \rangle = 1/3(g_1 + g_m + g_h), = 1/3(g_{\parallel} + 2g_{\perp}); \ \langle a \rangle = 1/3(a_{\parallel} + 2g_{\parallel}), = 1/3(a_{\parallel} + 2g_{\parallel}),$ $+a_{\rm m} + a_{\rm h}$, $= 1/3(a_{\parallel} + 2a_{\perp})$; 1 = 10w, m = medium, h = high. $d \pm 3$ G. e Evaluated from $g_{\rm iso}$ and g_{\perp} calculations. F Evaluated from $a_{\rm iso}$ and a_{\perp} calculations.

ing to the iridabenzothiabenzene [(triphos)Ir(η^2 -C,S- C_8H_6S]⁺ (7⁺), which is reversibly reduced to the neutral derivative (triphos) $Ir(\eta^2 - C, S - C_8 H_6 S)$ (7).

When possible, all the redox products of **2** have been identified with the use of isolated compounds in independent electrochemical and/or chemical reactions. In particular, the complexes syn-[(triphos)Ir{ η^4 -S(C₆H₄)- $CH(CH_3)$]PF₆ (**6PF**₆) and [(triphos)Ir(η^2 -C,S-C₈H₆S)]- PF_6 (**7PF**₆) have been prepared according to published procedures^{4b} and their redox properties compared with those of analogous products obtained by one- or twoelectron oxidation of 2 (Figure 3). The paramagnetic complexes syn-6 and 7 were characterized by ESR spectroscopy, whereas the inherent instability of 2^+ precluded its characterization.

The formal electrode potentials for the redox changes exhibited by the iridium complexes isolated or electrogenerated are summarized in Table 1. An inspection of the redox data shows that both oxidation steps of the starting Ir complex 2 occur at about the same potential values of the rhodium analog 1, whereas a significant difference (ca. 0.3 V) is found only for the reduction of the metallabenzothiabenzene complexes 5^+ and 7^+ .

Electron Spin Resonance of the Paramagnetic Rhodium and Iridium Complexes. Upon one- or two-electron oxidation of the 2-vinylthiophenolate complexes 1 or 2 in CH_2Cl_2 , as many as three paramagnetic products each are directly or indirectly generated (Scheme 3). Five of these are sufficiently long-lived in solution to be characterized by X-band ESR spectroscopy: the Rh complexes 1^+ , syn-3 and 5, and the Ir complexes syn-6 and 7 (Table 2).

Rhodium Complexes. The room-temperature spectrum of 1^+ in CH₂Cl₂ solution is shown in Figure 4 (a, first derivative; b, second derivative).

The spectrum can confidently be interpreted in terms of a S = 1/2 spin Hamiltonian. The ESR parameters are consistent with the presence of one unpaired electron localized on the metal center $(g_{iso} > g_e)$ and strongly interacting with one phosphorus nucleus of triphos. The second derivative spectrum clearly shows two very different superhyperfine (shpf) ³¹P couplings (155 and 15 G), which indicates that, like the diamagnetic precursor, 1^+ is not fluxional in solution even on the ESR timescale^{34,35} (hyperfine (hpf) couplings to the ¹⁰³-Rh nucleus (I = 1/2) are generally small or not visible in Rh(II) complexes with triphos).³⁴

The spectrum at liquid nitrogen temperature yields



Figure 4. X-band ESR spectrum of 1⁺ at 300 K (a), second derivative (b).

little additional information as it consists of a broad and partially resolved axial lineshape $(g_{\parallel} < g_{\perp})$. The large ³¹P shpf coupling, still observed in the spectrum at 100 K, indicates that no major structural changes occur in going from fluid to glassy solution.

The neutral precursor 1 has previously been assigned an octahedral structure in which the Rh center is coordinated by a fac triphos ligand, a strongly bound double bond and a thiolate sulfur atom.^{4c} Since the electrochemical properties relative to the $1/1^+$ redox step indicate an electrochemically reversible process, the monocation 1^+ is expected to maintain the primary geometry of the neutral precursor. Indeed, the large coupling constants observed in both the fluid and frozen solution spectra are consistent with a strong interaction of the unpaired electron with a phosphorus donor which faces the SOMO, as occurs for a low-spin d^7 metal ion in octahedral geometry $(d_z 2 \text{ SOMO})$.³⁶ A significant distortion from the idealized geometry, imposed by the Jahn-Teller effect, is confirmed by the coupling of the unpaired electron to one basal phosphorus only (15 G). Mononuclear Rh(II) complexes are quite rare because

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Zanello, P. Inorg. Chem. 1990, 29, 3402.
(36) Dunbar, K. R.; Haefner, S. C.; Pence, L. E. J. Am. Chem. Soc.

^{1989, 111, 5504} and references therein.

of their propensity for dimerization.³⁷ For this reason, most of the known mononuclear Rh(II) complexes are stabilized by bulky ligands among which tripodal polyphosphines with phenyl substituents play a predominant role.^{34,36} A few Rh(II) compounds have been authenticated by X-ray analyses: the square-planar complexes [Rh(MNT)₂]²⁻ [MNT = maleonitriledithiolate]³⁸ and [Rh(C₆Cl₅)₂{P(OPh)₃}₂],³⁹ and the distorted octahedral cation [Rh(TMPP)₂]²⁺ [TMPP = tris(2,4,6trimethoxyphenyl)phosphine].³⁶ Interestingly, the ESR spectrum of the latter complex exhibits axial symmetry with a d_z2 ground state.

The ESR spectra of the rhodium complexes **syn-3** and **5** are similar to each other and, like that of 1^+ , can be interpreted in terms of a $S = \frac{1}{2}$ spin Hamiltonian with the unpaired electron localized on the metal center. In actuality, the method of formation of the two compounds is consistent with a different formal oxidation state of the metal: +2 in **5** and 0 in **syn-3**.

The spectral lineshapes of both compounds as a glass display three groups of anisotropic signals with $g_1 > g_m$ > g_h . Analogous rhombic structure and spectral parameters characterize the ESR spectrum of the Rh(0) complex 4, which differs from **syn-3** only for the trityl substituent on the ylidene moiety. All glassy spectra are characterized by the absence of detectable couplings to either P or Rh nuclei (only upper limits for the magnetic couplings may be calculated from the linewidth of the signals).

As the temperature of the paramagnetic samples is increased, the intensities of the signals significantly decrease for **syn-3**, **4**, and **5**. The process is reversible with the temperature. At the glassy-fluid transition, the spectra consist of weak and relatively broard isotropic signals ($g_{av} = 2.033$) which reflect a large geometrical distortion of the coordination polyhedra.

As already mentioned, tripodal polyphosphine ligands such as triphos or $P(CH_2CH_2PPh_2)_3$ (PP₃) are capable of stabilizing a large number of mononuclear and dinuclear Rh(II) compounds,^{34,40,41} while only one Rh-(0) complex, namely the dimer (triphos)Rh(μ -CO)₂Rh-(triphos), has been described.⁴² All known mononuclear Rh(II) complexes with triphos or PP₃ are five-coordinate and generally exhibit distorted square-pyramidal structure,³⁴ although some examples of trigonal-bipyramidal compounds have also been reported.⁴⁰ The frozensolution ESR spectra of the square-pyramidal complexes invariably show axial structure with a d₂2 ground state and are characterized by a strong magnetic interaction of the unpaired electron with one phosphorus nucleus of the polyphosphine ligand ($a_{\perp} \simeq 210-213$ G; $a_{\parallel} \simeq 249-$

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Figure 5. X-band ESR spectra of syn-6 at 100 K (a), second derivative (b), and at 300 K (c).

262 G).³⁴ The rhombic structure and the absence of such a large coupling constant in the frozen solution spectra of **5** is thus suggestive of a trigonal-bipyramidal structure⁴⁰ which, in fact, is the structure adopted by the diamagnetic precursor **5**⁺ in solution at low temperature.

By analogy with the ESR parameters (Table 2), a trigonal-bipyramidal structure may be assigned also to the Rh(0) complexes **syn-3** and **4** at low temperature. In actuality, based on low-temperature ³¹P NMR studies, the diamagnetic precursors **syn-3⁺** and **4⁺** have been assigned distorted square-pyramidal structures.^{4c} Both compounds, however, are fluxional in solution where a low energy process allows a fast exchange between square-pyramidal and trigonal-bipyramidal structures.⁴³ The addition of one electron apparently stabilizes the trigonal-bipyramidal geometry.

Iridium Complexes. Figure 5 shows the X-band ESR spectra of the electrogenerated Ir(0) complex syn-6 recorded at 100 K (a, first derivative; b, second derivative) and at room temperature (c) in CH₂Cl₂ solution.

Like the Rh analog **syn-3**, the remarkable orbital contribution of the Ir unpaired spin system causes extensive broadening of the anisotropic signals and the corresponding g_{aniso} values significantly differ from that of the free electron ($g_{iso} = 2.0023$).

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Figure 6. X-band ESR spectra of 7 at 100 K [experimental (a), computed (b)] and at 300 K [experimental (c), computed (d)].

The lineshape analysis of the glassy absorption pattern can be carried out in terms of a $S = \frac{1}{2}$ spin Hamiltonian, consistent with a low-spin d⁷ metal ion. The second derivative spectrum and a computer simulation procedure⁴⁴ allow one to interpret the liquid nitrogen spectrum in terms of a well resolved axial symmetry $(g_{\parallel} > g_{\perp})$ with one unpaired electron localized on the metal center. A significant line-broadening effect largely biases the spectral anisotropic features and reflects the asymmetry of the overall coordination polyhedron. Neither hpf coupling of the electron to the ¹⁹¹Ir and ¹⁹³Ir nuclei ($I = \frac{3}{2}$) nor shpf coupling to the ³¹P nuclei is observed. Accordingly, only an upper limit for such magnetic interactions, if any, can be estimated from the corresponding anisotropic linewidths.

At the glassy-fluid transition phase, the axial spectrum evolves to the relevant unresolved isotropic one, with g_{iso} (190 K) = 2.038 ± 0.008 and ΔH_{iso} (190 K) = 55 ± 5 G. Raising the temperature, the signal sharpens (c) $[\Delta H_{iso}$ (300 K) = 35 ± 5 G], likely due to fast molecular dynamics which mediate the original anisotropies. Correspondingly, the g_{iso} value raises to 2.047 ± 0.005 at 300 K. This value well matches the calculated $\langle g \rangle$ value at 100 K [$^{1}/_{3}(g_{ii} + 2g_{\perp})$] and confirms that the complex maintains the same structure in the temperature range investigated.

From these data we can conclude that **syn-6** has a structure similar to that of the Rh analog **syn-3**, namely distorted trigonal-bipyramidal.

Figure 6 shows the X-band ESR spectra of the iridabenzothiabenzene complex 7 in CH_2Cl_2 at different temperatures. The glassy spectrum (Figure 6a) displays a complex lineshape, particularly broadened in the high-field regions. On the basis of computer simulation procedures,⁴² the glassy spectrum can be interpreted in terms of a S = 1/2 spin Hamiltonian with a well resolved metal-in-character axial structure ($g_{\parallel} < g_{\perp}$). Both the g_{\perp} and g_{\parallel} regions show shpf resolution with one large anisotropic splitting attributable to the strong magnetic coupling of the electron with one P nucleus and a less

intense coupling to two slightly different P nuclei. Interestingly, the high-field parallel region exhibits a broad pseudo-quintuplet, resulting from the partial overlapping of two nearly equivalent 1:2:1 triplets. This spectral behavior can be interpreted assuming the presence of two geometric isomers, **7A** and **7B** (see below), with a slight prevalence of species A, characterized by similar g_{aniso} values (Table 2).

At the glassy-fluid transition, the axial structure collapses in a broad isotropic doublet with g_{iso} (190 K) $= 2.056 \pm 0.005$ and $a_{iso}(P) = 220 \pm 5$ G. The isotropic spectrum remains unaltered in the temperature range from 180 to 330 K where the magnetic parameters are in good agreement with the averaged anisotropic ones (Figure 6c). At higher temperature, the fluid solution doublet broadens [ΔH (330 K) = 30 ± 5 G] losing both spectral intensity and shpf resolution, while the g_{iso} value slightly decreases. Like syn-6, compound 7 displays ESR reversibility in the overall temperature range investigated. The observation of a broad doublet in fluid solution, which can properly be simulated only by assuming the presence of two isomers (Figure 6d), suggests that species 7A and 7B still exist at room temperature.

As previously mentioned, the diamagnetic precursor of 7 adopts a trigonal-bipyramidal structure in the solid state.^{4b} In solution 7^+ is fluxional on the NMR timescale. The magnetic equivalence of the three phosphorus atoms of triphos in the fast exchange regime (³¹P NMR A_3 spin system) is due to a fast interconversion between trigonal-bipyramidal and square-pyramidal structures which are separated by a very low energy barrier.⁴³ The glassy ESR spectra of 7A and 7B are unequivocally consistent with a distorted square-pyramidal structure such as that of the related Ir(II) complex (triphos)Ir-(DBTC) (DBTC = 3,5-di-tert-butylcatecholate), which shows fully comparable ESR parameters.⁴¹ It is therefore reasonable to conclude that, unlike the Rh analog 5, the addition of one electron to 7^+ tips the balance in favor of the square-pyramidal structure.

ESR evidence for the existence of geometric isomers is not surprising for five-coordinate low-spin d^7 metal

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complexes with tripodal polyphosphine ligands, particularly when they adopt a distorted square-pyramidal structure and contain two different donor atoms in the basal plane.^{34,40,45} Consistently, although it is only speculation, the difference between **7A** and **7B** may be caused by slightly different Jahn–Teller distortions related to the asymmetry of the cleaved **BT** ligand, which has a sulfur and a carbon atom bound to the metal.

Mononuclear Ir(II) complexes are a rarity,⁴⁶ although in the last few years some work has been done on the subject.^{41,47,48} Single crystal X-ray structure determinations have been reported for the square-planar complexes [Ir(mes)₂(SEt₂)₂]⁴⁷ (mes = mesityl) and [Ir(C₆-Cl₅)₄]^{2-.48}

Conclusions

We have previously shown that the thermally generated 16-electron fragments [(triphos)MH] (M = Rh, Ir) readily react with **BT** by a ring-opening C-S bond scission reaction to ultimately yield 2-vinylthiophenolate derivatives (triphos)M{ η^3 -S(C₆H₄) CH=CH₂} (M = Rh,^{4c} 1; Ir,^{4b,e} 2). These complexes display a rich redoxinduced reactivity; by using a combination of chemical reactions, electrochemical studies, and EPR and NMR spectroscopic methods it has been possible to understand in depth a series of transformations that take place once the redox processes are initiated. The redoxinduced transformations of the cleaved and partially reduced **BT** molecule include both homolytic and heterolytic C-H bond cleavage and formation.

In particular, removal of one electron from 1 or 2 leads to the corresponding paramagnetic cations 1⁺ and 2⁺; these complexes are rather unstable and undergo a radical reaction with H[•] in solution to form, as the kinetic products, the diamagnetic 2-ethylidenecyclohexadienethione compounds *anti*-[(triphos)M{ η^4 -S(C₆H₄)-CH(CH₃)}]⁺ (M = Rh, *anti*-3⁺; Ir, *anti*-6⁺) which isomerize to the thermodynamically stable *syn*-3⁺ (Rh) and *syn*-6⁺ (Ir). Addition of one electron to *syn*-3⁺ and $syn-6^+$ gives the neutral paramagnetic derivatives syn-[(triphos)M{ η^4 -S(C₆H₄)CH(CH₃)}] (M = Rh, syn-3; Ir, syn-6) which spontaneously convert back to the starting complexes 1 and 2 by a homolytic C-H bond cleavage liberating H[•]. In this way a full electrochemical cycle is completed by addition/elimination of one electron and one H atom. The radical nature of the C-H bond cleavage undergone by syn-3 was confirmed by the redox chemistry of the related complex [(triphos)Rh{ η^4 -S(C₆H₄)CH(CH₂CPh₃)]PF₆ (**4PF₆**), which induces loss of a trityl radical by a C-C bond cleavage reaction in the paramagnetic neutral derivative **4**.

On the other hand, removal of a second electron from 1^+ or 2^+ leads to the corresponding dicationic species 1^{2+} and 2^{2+} , which undergo a heterolytic C-H bond splitting to lose a proton and produce the cationic metallabenzothiabenzene complexes [(triphos)M(η^2 -C,S-C₈H₆S)]⁺ (M = Rh, 5⁺; Ir, 7⁺). Although the Ir derivative 7⁺ has previously been prepared by chemical methods,^{4b} the Rh analogue seems to be available only by the electrochemical route herein described. Finally, additon of one electron to the monocationic complexes 5⁺ and 7⁺ produces the corresponding paramagnetic metallabenzothiabenzene complexes [(triphos)M(η^2 -C,S-C₈H₆S)] (M = Rh, 5; Ir, 7).

In conclusion, the homogeneous modeling study reported in this paper provides new information which may contribute a better understanding of the mechanisms of HDS reactions on the surfaces of solid catalysts. One- and two-electron transfer processes have often been invoked to account for the activity of some Mo sites of HDS catalysts, as well as for the promoting effects of Co or Ni sites. Furthermore, the presence or possible formation of surface H[•], H⁺, and H⁻ species, associated with either the metal or the sulfur sites of the catalysts has long been recognized in the HDS literature. Thus the redox-induced reactions of ring-opened **BT** ligands identified in this paper are of particular interest since analogous transformations and species are to be expected also on HDS-active surfaces.

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