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Articles

Synthesis and Characterization of Nitrido Tc(V) and Re(V) Complexes with Ferrocenedithiocarboxylate $\{FcCS_2 = [Fe(C_5H_4CS_2)(C_5H_5)]^-\}$

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The first mixed technetium−iron complexes $[^{99g}Tc(N)(FcCS_2)_2]$ $\{FcCS_2 = [Fe^{II}(C_5H_5)(C_5H_4CS_2)]^-\}$ (**1**) and $[^{99g}Tc(N)(FcCS_2)(FcCS_2^\star)]^+$ $\{FcCS_2 = [Fe^{II}(C_5H_5)(C_5H_4CS_2)]^-;\ FcCS_2^\star = Fe^{III}(C_5H_5)(C_5H_4CS_2)\}$ (**2**) have been prepared and characterized. Complex **1** was obtained by reaction of the precursor complex $[^{99g}Tc(N)Cl_2(PPh_3)_2]$ with the piperidinium salt of the ligand $FcCS_2$. The resulting biferrocene complex is formed by two $FcCS_2$ ligands bound to the Tc atom through the four sulfur atoms of the two CS_2^- groups and bridged by a Tc≡N multiple bond. The mixed-valence $Fe^{2+}-Fe^{3+}$, monocationic complex **2** was isolated as secondary product of the reaction of the precursor complex $[^{99g}Tc(N)Cl_4]^-$ with the ligand $FcCS_2$. It has the same composition as **1** except for the fact that the Fe(II) center of one $FcCS_2$ ligand has been oxidized to Fe(III). The electrochemical properties of **1** and **2** are consistent with their formulations. Cyclic voltammetric studies and controlled potential electrolyses showed that complex **1** undergoes a quasi-reversible, *two*-electron exchange at 0.320 V (*vs* ferrocene/ferrocenium couple) attributed to the oxidation of the two Fe(II) ions, while complex **2** undergoes a quasi-reversible, *one*-electron exchange at nearly the same potential (0.344 V) assigned to the oxidation of the residual Fe(II) ion. These results indicate that in complex **1** the two Fe(II) atoms behave as independent redox centers. The synthesis, characterization, and electrochemical behavior of the analogous, six-coordinated rhenium(V) complex $[Re(N)(FcCS_2)_2(PPh_3)]$ are also reported.

Introduction

Recently, the introduction in diagnostic nuclear medicine of an efficient procedure for producing ^{99m}Tc radiopharmaceuticals containing the $[Tc{\equiv}N]^{2+}$ core, in sterile and pyrogen-free conditions,[2] has opened the possibility to further explore the chemistry and biological properties of technetium(V) complexes characterized by the presence of the terminal Tc≡N multiple bond.[3] As a part of our studies on the synthesis of nitrido Tc(V) complexes with dithiocarbamate and dithiocarboxylate ligands,[3,4] we describe here the reactions of the complexes $[^{99g}Tc(N)Cl_4]^-$, $[^{99g}Tc(N)Cl_2(PPh_3)_2]$, and $[Re(N)Cl_2(PPh_3)_2]$ with the ligand ferrocenedithiocarboxylate $\{FcCS_2 = [Fe^{II}(C_5H_4CS_2)(C_5H_5)]^-\}$ (Figure 1). The resulting complexes constitute the first examples of Tc−Fe and Re−Fe mixed-metal complexes incorporating a ferrocene moiety. Previous works on the preparation of ionic compounds containing a ferrocenium cation and anionic technetium and rhenium complexes have been reported.[5]

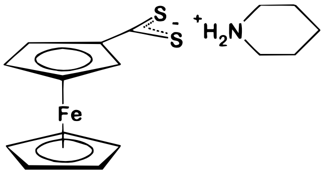

Figure 1. The ligand piperidinium ferrocenedithiocarboxylate.

The new class of mixed-metal complexes might be of interest in two respects. First, they should easily undergo redox processes as a consequence of the incorporation of the ferrocene unit into their structure. It is in fact well-established that ferrocene exhibits a reversible one-electron exchange to give the iron(III) ferrocenium cation.[6] Thus, coordination of one or

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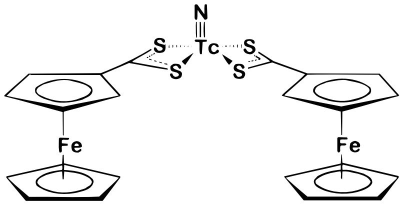

Figure 2. Proposed structure of complex **1**.

more $FcCS_2$ ligands to Tc and Re centers would produce species showing single or multiple electron exchange at suitable potentials. Second, the resulting redox behavior might be conveniently utilized for the application to nuclear medicine of these complexes as diagnostic or therapeutic[7] agents. In fact, it has been previously shown by Deutsch[8] that redox-active complexes of technetium and rhenium may exhibit specific *in vivo* biodistributions as a consequence of their participation in some biological process involving the transfer of one or more electrons. Incorporation of a ferrocene moiety in various technetium and rhenium complexes might therefore yield species exhibiting electron transfer within a window of potentials which is partly superimposed on that of some relevant biological redox process. Obviously, nuclear medicine applications of complexes of this type as radiopharmaceuticals are limited to compounds that have some stability in the presence of water. Studies carried out with the γ-emitting isomer ^{99m}Tc on the preparation of the mixed technetium−ferrocene complexes described in the present work have shown that these compounds could be obtained, in high yield, in water solution and under conditions suitable for *in vivo* applications. These results will be reported elsewhere.[9]

In the following, the synthesis, characterization, and electrochemical properties of square-pyramidal and octahedral nitrido complexes of Tc(V) and Re(V) with the ligand $FcCS_2$ will be discussed. The synthesis of the monocationic, Fe(II)−Fe(III) mixed-valence complex $[Fe^{II}(C_5H_4CS_2)(C_5H_5)Tc(N)Fe^{III}(C_5H_4CS_2)(C_5H_5)]Cl$ containing one ferrocene group connected to one oxidized ferrocenium moiety by a $-CS_2-Tc(N)-S_2C-$ bridge will be also reported.

Results and Discussion

Synthesis and Characterization. The reaction of the complex $[^{99g}Tc(N)Cl_2(PPh_3)_2]$ with the ligand $FcCS_2$, in chloroform or dichloromethane and at room temperature, yields the deep violet complex $[^{99g}Tc(N)(FcCS_2)_2]$ (**1**). The characterization of this compound showed that it comprises a terminal $Tc{\equiv}N$ multiple bond and two $FcCS_2$ ligands coordinated to the metal center through the two sulfur atoms of the dithiocarboxylic functional group. Previous studies on the structures of nitrido Tc(V) complexes with dithiocarbamate and dithiocarboxylate ligands[3,4,10] suggest that the most probable geometry of **1** is square-pyramidal with an apical $Tc{\equiv}N$ group and two $FcCS_2$ ligands spanning the four positions on the basal plane (Figure 2). The ^1H NMR spectrum of **1** is consistent with this formulation. It shows a singlet at $\delta = 4.23$ attributed to the equivalent, five-proton sets on the unsubstituted cyclopentadienyl rings of the two $FcCS_2$ ligands, and two triplets, at $\delta = 5.19$ and $\delta = 4.91$, assigned to the α and β protons of the two substituted cyclopentadienyl rings of the $FcCS_2$ ligands.[11] **1** is nonconducting in CH_3CN/CH_2Cl_2 solutions. The R_f value of **1** on silica gel plates using a mixture of CH_2Cl_2/*n*-hexane/glacial acetic acid (2:1.5:0.02) as mobile phase was 0.6.

When the reaction of the ligand $FcCS_2$ was carried out with the precursor complex $[^{99g}Tc(N)Cl_4]^-$, in ethanol and at room temperature, the sudden precipitation of a deep blue solid was observed. The chromatographic analysis on silica gel TLC plates of this solid showed that it was composed of three different products. The main component in the mixture was a violet compound showing a R_f value (0.6) identical to that of complex **1**. A second, ink-blue product in the mixture was found to possess a slightly different R_f value (0.5) on silica gel plates. In the same chromatographic system, a third, green product was observed to remain at the origin. The three products were separated by chromatography on a silica gel column using a CH_2Cl_2/*n*-hexane/glacial acetic acid (2:1.5:0.02) mixture as mobile phase. Solid samples of the violet and blue compounds were obtained by collecting the corresponding chromatographic bands. The green component of the mixture remained fixed at the top of the column. Any attempt to extract this compound from the solid phase gave rise to extensive decomposition, so that it was not further characterized. The FT IR and ^1H NMR spectra of the violet product were superimposable on those of complex **1**, indicating that the two compounds were identical. The peaks in the ^1H NMR spectrum of the ink-blue product were difficult to assign because of characteristic broadening and shifting that are commonly associated with the presence of unpaired electrons. Conductivity measurements were carried out in solutions prepared by dissolving **2** in a 70:30 mixture of CH_2Cl_2 and CH_3CN. Although the recorded conductivity values were lower than that expected for a monocationic complex, and not completely reproducible due to partial decomposition of the compound in solution, they definitely showed a significant increase of the conductivity relative to that observed for **1**. We interpreted these features by assuming that the ink-blue compound corresponds to the mixed-valence, monocationic complex $[^{99g}Tc(N)(FcCS_2)(FcCS_2^{\star})]^+$ (**2**) $\{FcCS_2^{\star} = [Fe^{III}(C_5H_5)(C_5H_4CS_2)]\}$, in which one $FcCS_2$ ligand contains the iron atom in the +3 oxidation state and the other $FcCS_2$ ligand contains the same atom in the +2 oxidation state. A strong support for the characterization of **2** as a mixed-valence compound was obtained through electrochemical measurements (see below). Complex **2** is sufficiently stable only in CH_2Cl_2 or $CHCl_3$ solutions, but it decomposes in the presence of acetone, CH_3CN, tetrahydrofuran, methanol, and ethanol.

A tentative explanation for the formation of the mixed-valence complex **2** starting from $[^{99g}Tc(N)Cl_4]^-$ may be based on the finding that no formation of **2** was observed starting from $[^{99g}Tc(N)Cl_2(PPh_3)_2]$. In addition, the ligand $FcCS_2$ was found to be stable in solution for several hours also in the presence of air oxygen. Thus, by considering that in the precursor complex the technetium atom has a +6 oxidation state, but in **2** it is in the reduced +5 oxidation state, the occurrence of a redox process between one $FcCS_2$ ligand and the complex $[^{99g}Tc(N)Cl_4]^-$, resulting in the oxidation of the Fe(II) atom to Fe(III) and the concomitant reduction of the Tc(VI) center to Tc(V), might be envisaged. It is interesting to note that we did not observe any redox reaction when unsubstituted ferrocene was added to a solution of $[^{99g}Tc(N)Cl_4]^-$. This result suggests that the presence of the CS_2 group on the ligand $FcCS_2$ favors the oxidation of the Fe(II) atom by the precursor technetium complex, a fact that is probably related to the existence of the resonance forms depicted in Figure 3. Specifically, in form II,

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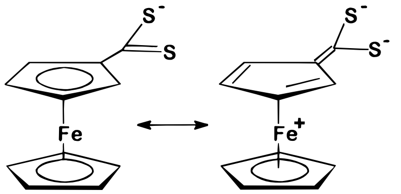

Figure 3. Resonance forms for the monoanionic ligand $FeCS_2$.

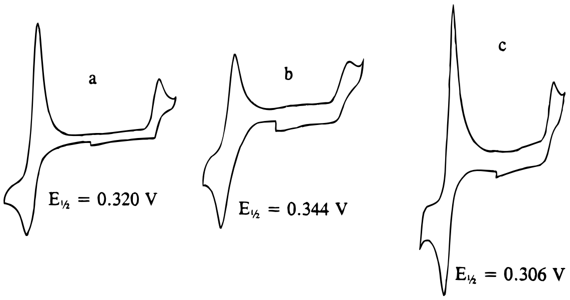

Figure 4. Cyclic voltammograms of (a) **1**; (b) **2**; (c) **3**. Potentials are relative to the Fc/Fc^+ couple used as internal standard.

the electronic density is driven toward the CS_2 group and the Fe atom becomes more positive.[12]

However, reduction of the Tc^{6+} ion by the Fe^{2+} center is not the only redox process which could be active in solution. Indeed, previous studies have shown that dithiocarbamate and dithiocarboxylate ligands are capable of efficient reduction of Tc(VI) to Tc(V) in the reaction with the complex $[^{99g}Tc(N)Cl_4]^-$.[3,4,10] This suggests that, in the presence of different redox processes, a mixture of complexes containing all three possible combinations of $FcCS_2$ and $FcCS_2^{\star}$ ligands should be expected. Experimentally, we isolated the symmetrical complex **1** and the mixed-valence complex **2**. The complex $[^{99g}Tc(N)(FcCS_2^{\star})_2]^{2+}$, containing two symmetrically oxidized $FcCS_2^{\star}$ ligands, was not isolated due to its intrinsic instability in solution (see electrochemical results below).

When the nitrido rhenium(V) complex $[Re(N)Cl_2(PPh_3)_2]$ was reacted with $FcCS_2$, in CH_2Cl_2 and at room temperature, the compound $[Re(N)(FcCS_2)_2(PPh_3)]$ (**3**) was obtained as a blue precipitate. Complex **3** is six-coordinated comprising a terminal Re≡N multiple bond and two $FcCS_2$ ligands bound to the metal center through the four sulfur atoms of the two CS_2 groups. The octahedron is completed by the coordination of a PPh_3 ligand. The formation of an octahedral nitrido rhenium(V) species is not surprising due to the stronger tendency of this metal to achieve six-coordination with respect to technetium. The ^1H NMR spectrum of **3** shows the presence of two singlets at $\delta = 4.27$ and $\delta = 4.12$ each assigned to one of the two five-proton sets on the two unsubstituted cyclopentadienyl rings, and of a series of not-well-resolved multiplets in the interval $\delta = 5.02-4.53$ attributed to the protons of the two substituted cyclopentadienyl rings. The phenyl protons of the phosphine group appear as a multiplet at $\delta = 7.50$. These findings indicate that presumably the two $FcCS_2$ ligands are not symmetrically positioned inside the octahedron and are therefore not equivalent. The presence of PPh_3 in the complex has been confirmed also by ^{31}P NMR ($\delta = 41.5$).

Electrochemistry. Cyclic voltammetry of complex **1** in CH_2Cl_2 solutions, at a stationary platinum-disk electrode, is reported in Figure 4a. The voltammogram shows a quasi-reversible oxidation wave at $E_{1/2} = 0.320$ V quoted relative to the ferrocene/ferrocenium couple (Fc/Fc^+) taken as internal standard at 0.0 V. An irreversible cathodic wave was observed at −1.670 V. Due to the proximity of the oxidation potential of **1** to that of the free ligand $FcCS_2$ ($E° = 0.337$, *vs* Fc/Fc^+), the cathodic wave was attributed to the oxidation of the Fe(II) atom to Fe(III) in the coordinated ligand $FcCS_2$. Controlled potential electrolysis in CH_2Cl_2 at $E = 0.960$ V (relative to an Ag/Ag^+ pseudo reference electrode) showed that the oxidation process occurs through a two-electron exchange involving both Fe(II) centers of the two coordinated $FcCS_2$ ligands. Isolation of the dioxidized, dicationic complex $[^{99g}Tc(N)(FcCS_2^{\star})_2]^{2+}$ containing two Fe(III) atoms was not possible because of decomposition of this product in solution. This result accounts also for the failure to isolate the dioxidized complex in the reaction of the precursor complex $[^{99g}Tc(N)Cl_4]^-$ with $FcCS_2$. The nature of the irreversible anodic process observed in the cyclic voltammogram of **1** was not investigated.

Figure 4b reports the cyclic voltammogram of complex **2** in CH_2Cl_2 solutions. It looks very similar to that of **1**. Indeed, a quasi-reversible oxidation wave is found at $E_{1/2} = 0.344$ V along with an irreversible cathodic wave at −1.681 V (*vs* Fc/Fc^+). The oxidation process of **2** was established to be monoelectronic by controlled potential electrolysis in CH_2Cl_2 solutions at 0.960 V (*vs* Ag/Ag^+ pseudo reference electrode). As specified before, this one-electron transfer was attributed to the oxidation of the residual Fe(II) atom in the mixed-valence complex **2** to yield the dicationic complex $[^{99g}Tc(N)(FcCS_2^{\star})_2]^{2+}$.

The fact that complexes **1** and **2** are both oxidized at nearly the same potential indicates that there is not electronic communication between the two iron centers transmitted through the Tc-containing bridge.[13] The small difference between the two oxidation potentials of **1** and **2** can be attributed to the increased electrostatic interaction between the two iron atoms in **2**.[13,14] Thus, formation of the mixed-valence complex **2** cannot be obtained through the electrochemical oxidation of one iron center in **1**, but only through the reaction occurring between the precursor complex $[^{99g}Tc(N)Cl_4]^-$ and the ligand $FcCS_2$, which caused the formation of the oxidized species $FcCS_2^{\star}$.

A further support to the interpretation of electrochemical data for complexes **1** and **2** was obtained by studying the electrochemical behavior of the rhenium complex **3**. Cyclic voltammetry of a CH_2Cl_2 solution of **3** is shown in Figure 4c. A quasi-reversible oxidation process occurring at 0.306 V relative to the Fc/Fc^+ couple was established to involve a two-electron transfer by controlled electrolysis at 0.960 V (*vs* Ag/Ag^+ pseudo reference electrode). This electron transfer was assigned to the oxidation of the two Fe(II) atoms of the ligand $FcCS_2$. It is apparent that no substantial differences exist between the electrochemical behavior of **1** and that of **3**, supporting the conclusion that the observed redox processes do not involve the M≡N (M = Re, Tc) group, but they take place on the ligand $FcCS_2$. Once more, electronic communication can be ruled out on the basis of the results of controlled electrolysis.

Experimental Section

Caution! ^{99g}Tc is a weak β-emitter ($E_\beta = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All manipulations were carried out in a laboratory approved for low-level radioactivity using monitored hoods and gloveboxes. When handled in milligram amounts, ^{99g}Tc does not present a serious health hazard since common laboratory glassware provides adequate shielding. Bremsstrahlung is not a significant problem due to the low energy of the β-particles. However, normal radiation safety procedures must be used at all times, especially with solid samples, to prevent contamination and inhalation.

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Starting Materials. Technetium in the form $[NH_4][^{99g}TcO_4]$ was obtained from Oak Ridge National Laboratory. Samples were dissolved in water and treated with excess aqueous ammonia and H_2O_2 (30%) at 80 °C prior to use to eliminate residual TcO_2. Solid samples of purified ammonium pertechnetate were obtained by slow evaporation of the solvent with heating at 40 °C. General literature methods were used to prepare the precursor complexes $[As(C_6H_5)_4][^{99g}Tc(N)Cl_4]$,[15] $[^{99g}Tc(N)Cl_2(PPh_3)_2]$,[10b,16] and $[Re(N)Cl_2(PPh_3)_2]$.[17] Common solvents were used as purchased. The piperidinium salt of the ligand ferrocenedithiocarboxylate ($FcCS_2$) was prepared using a procedure described previously.[11]

Physical Measurements. Elemental analyses (C, H, N, S) were performed on a Carlo Erba model 1106 elemental analyzer. Analysis of radioactive technetium was performed by dissolving weighted samples of the complexes in a HNO_3/H_2O_2 mixture and by counting the activity of the resulting solutions in a Packard TRICARB 300 scintillation counter using Instagel as scintillator. Analysis of the Re:P ratio in rhenium complexes was determined by integral counting of the back-scattered X-ray fluorescence radiation from a Philips XL 40 model scanning electron microscope equipped with an EDAX model data station, using a procedure described elsewhere.[18] FT IR spectra were recorded on a Nicolet 510P Fourier-transform spectrometer (4000−200 cm^{-1}) in KBr mixtures, using a Spectra-Tech diffuse-reflectance collector accessory. Proton and ^{31}P NMR spectra were run on a Bruker AC-200 instrument using $Si(CH_3)_4$ as internal reference (^1H spectra) and 85% aqueous H_3PO_4 (^{31}P spectra) as external reference. Conductivity measurements were performed in CH_3CN/CH_2Cl_2 (30:70) solutions (2.0×10^{-4} mol dm^{-3}), at $T = 293$ K, using a Metrohm Herison E518 conductometer. Fast-atom-bombardment mass spectra in the positive mode (FAB^+) were recorded in a 3-nitrobenzyl alcohol matrix on a VG ZAB-2F spectrometer. Xenon was used as the primary beam gas, and the ion gun was operated at 8 keV. Data were collected over the mass range 100−1000 at 0.7 s/scan. The chromatographic behavior of radioactive samples on thin-layer (TLC) 60 F254 silica gel plates (Merck) developed with a CH_2Cl_2/*n*-hexane/glacial acetic acid mixture (2:1.5:0.02) was determined by placing each air-dried plate into close contact with an X-ray film (Kodak Industrex AX) for 18 h, in a dark box. After development of the negative, the location of the radioactive complexes appeared as single, dark spots on the film.[2,3] Radioactivity profiles were quantitated using a Chromatoscan Berthold LR 2382 radiochromatograph.

Syntheses. $[^{99g}Tc(N)(FcCS_2)_2]$ $\{FcCS_2 = [Fe^{II}(C_5H_5)(C_5H_4CS_2)]^-\}$ (1). $[^{99g}Tc(N)Cl_2(PPh_3)_2]$ (0.153 g; 0.220 mmol) was suspended in 25 mL of CH_2Cl_2, and 0.191 g (0.550 mmol) of the piperidinium salt of the ligand $FeCS_2$ was successively added. The initial deep-orange color of the mixture turned rapidly to deep violet, and the reaction mixture was kept at room temperature for 30 min. The solvent was removed by passing an argon stream through the resulting solution, causing the precipitation of a deep-violet, microcrystalline powder, which was filtered, washed repeatedly with methanol to eliminate excess PPh_3, and dried under vacuum. The isolated product was insoluble in water, slightly soluble in ethanol, methanol, diethyl ether, and *n*-hexane, and soluble in CH_2Cl_2, $CHCl_3$, and CH_3CN. Yield: 76% (based on ^{99g}Tc). $R_f = 0.6$. Nonconducting in solution. FT IR (cm^{-1}): 1040 [ν(Tc≡N)]. FAB MS: *m/z*, 636 [MH^+]. ^1H NMR ($CDCl_3$, ppm): 4.23 (s, 10H, C_5H_5); 4.91, 5.19 (t, t, 8H, $C_5H_4CS_2$). Anal. Calcd for $C_{22}H_{18}NS_4Fe_2Tc$: C, 41.59; H, 2.86; N, 2.20; S, 20.18; Tc, 15.58. Found: C, 41.69; H, 2.92; N, 2.23; S, 19.98; Tc, 15.17.

$[^{99g}Tc(N)(FcCS_2)(FcCS_2^{\star})]Cl$ $\{FcCS_2 = [Fe^{II}(C_5H_5)(C_5H_4CS_2)]^-$; $FcCS_2^{\star} = [Fe^{III}(C_5H_5)(C_5H_4CS_2)]\}$ (2). $[As(C_6H_5)_4][^{99g}Tc(N)Cl_4]$ (0.150 g; 0.227 mmol) was dissolved in 20 mL of methanol, and 0.200 (0.576 mmol) of the piperidinium salt of the ligand $FcCS_2^-$ was successively added. The initial deep-orange color of the solution suddenly changed to deep-blue, and after 15 min of stirring at room temperature, the precipitation of a blue solid was observed. The resulting blue solid was collected by filtration, washed with methanol and diethyl ether, and dried under a stream of argon. TLC chromatography showed that the blue product was composed of a mixture of three different species: a green compound remaining at the origin ($R_f = 0$), an ink-blue compound ($R_f = 0.5$), and a deep-violet compound ($R_f = 0.6$). The three products were separated by column chromatography (SiO_2, Aldrich, 35 cm × 2 cm) using CH_2Cl_2/*n*-hexane/glacial acetic acid (2:1.5:0.02) as mobile phase. A deep-violet band was collected first, followed by a deep-blue band. A green component remaining at the origin of the column was not collected. The blue and violet solutions recovered from the column were taken to dryness in a rotary evaporator and then the residues extracted with CH_2Cl_2. The resulting solutions were evaporated under an argon stream, causing the precipitation of a deep-violet solid (yield 50% based on ^{99g}Tc) and of an ink-blue compound (yield 28% based on Tc), which were dried under vacuum. Characterization of the deep-violet compound showed that it corresponds to the above reported complex $[^{99g}Tc(N)(FcCS_2)_2]$. The ink-blue compound was found to be insoluble in water and diethyl ether, slightly soluble in ethanol, methanol, and CH_3CN, and soluble in CH_2Cl_2 and $CHCl_3$. It is stable in halogenated solvents, but partially decomposes in other solvents and, in particular, in the presence of methanol and ethanol. Analytical data for the ink-blue product were as follows. The product was found to be conducting in solution, although it was not possible to obtain a reproducible value of its molar conductivity due to the instability of the compound in the presence of CH_3CN (observed range at 25 °C, $\Lambda_M = 47{-}73$ ohm^{-1} cm^2 mol^{-1}). FT IR (cm^{-1}): 1057 [ν(Tc≡N)]. FAB MS: *m/z*, 635 [M^+]. Anal. Calcd for $C_{22}H_{18}NS_4ClFe_2Tc$: C, 39.39; H, 2.70; N, 2.09; S, 19.12; Tc, 14.76. Found: C, 40.01; H, 2.83; N, 2.12; S, 18.97; Tc, 14.58.

The corresponding tetraphenylborate salt was obtained by adding to a concentrated solution of **2** in $CHCl_3$ a stoichiometric amount of $Na[B(C_6H_5)_4]$. The chloroform solution was filtered to eliminate a black precipitate and then evaporated under a stream of argon. Anal. Calcd for $C_{46}H_{38}NS_4BFe_2Tc$: C, 57.88; H, 4.01; N, 1.47; S, 13.43; Tc, 10.37. Found: C, 57.90; H, 4.06; N, 1.43; S, 12.97; Tc, 10.12.

$[Re(N)(FcCS_2)_2(PPh_3)]$ $\{FcCS_2 = [Fe^{II}(C_5H_5)(C_5H_4CS_2)]^-\}$ (3). $[Re(N)Cl_2(PPh_3)_2]$ (0.300 g; 0.384 mmol) and 0.350 g (1.00 mmol) of the piperidinium salt of the ligand $FcCS_2$ were mixed in 30 mL of CH_3CN. The resulting red-orange suspension was kept at room temperature, with stirring for 12 h. The precipitation of a deep-blue solid was observed, which was collected by filtration, washed with CH_3CN and methanol, and dried under vacuum. The blue compound was insoluble in water, ethanol, methanol, CH_3CN, and diethyl ether and slightly soluble in CH_2Cl_2 and $CHCl_3$ (yield = 78% based on Re; $R_f = 0.8$). FT IR (cm^{-1}): 1041 [ν(Re≡N)]. FAB MS: *m/z*, 984, 986 [MH^+]. ^1H NMR ($CDCl_3$, ppm): 4.27, 4.12 (s, s, 10H, C_5H_5); 5.02−4.53 (m, 8H, $C_5H_4CS_2$); 7.61−7.42 (m, 15H, PPh_3). ^{31}P NMR ($CDCl_3$, ppm): 41.5 [s, $P(C_6H_5)_3$]. Anal. Calcd for $C_{40}H_{33}NPS_4Fe_2Re$: C, 48.78; H, 3.38; N, 1.42; S, 13.02. Found: C, 48.92; H, 3.42; N, 1.46; S, 12.96. SEM microanalysis, 1:1 (Re:P).

Electrochemical Measurements. Cyclic voltammetry of complexes **1**−**3** has been carried out in CH_2Cl_2 solutions (3.5×10^{-3} mol dm^{-3}), with [*n*-Bu_4N][ClO_4] (0.1 mol dm^{-3}) as supporting electrolyte, at a stationary platinum-disk electrode (area *ca.* 1.28 mm^2), which was cleaned after each run, with scan rate 0.2 V s^{-1}, at $T = 293$ K. Potentials were measured relative to an Ag-wire pseudo reference electrode using the Fc/Fc^+ couple as internal reference. Controlled potential coulometries of CH_2Cl_2 solutions of **1**−**3** were performed using an Amel model 721 integrator, in an H-shaped cell containing, in arm 1, a platinum-gauze working electrode and an Ag/Ag^+ reference isolated inside a salt bridge by a medium, glass frit, and, in arm 2, an auxiliary, platinum-foil electrode.

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