

The overall pathway in Scheme I can explain the inhibition by hydrogen and the acceleration by triphenylphosphine.<sup>7</sup> Possible explanations are that the oxidative addition of an alcohol to  $\text{RuCl}_2(\text{PPh}_3)_3$  is competitively inhibited by hydrogen or that the formation of aldehyde is reversible. The increased conversion in the presence of triphenylphosphine may result from an extended catalyst life due to inhibition of the deactivating decarbonylation step (Scheme I).<sup>8</sup>

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- (7) No increase in conductivity of solutions of  $\text{RuCl}_2(\text{PPh}_3)_3$  is observed in the presence of excess triphenylphosphine, thereby eliminating the possibility that chloride ion substitution occurs.  
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Department of Chemistry  
 Tulane University  
 New Orleans, Louisiana 70118

Sanjoy Ganguly  
 Frederick L. Joslin  
 D. Max Roundhill\*

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### Dichloro[hydrotris(1-pyrazolyl)borato]sulfidotechnetium(V): The First Technetium Complex Containing a Tc=S Bond

The isoelectronic  $[\text{Tc}=\text{O}]^{3+}$ ,  $\text{trans}-[\text{O}=\text{Tc}=\text{O}]^+$ , and  $[\text{Tc}=\text{N}]^{2+}$  groups are characteristic functional moieties for technetium in the +5 oxidation state: all the known Tc(V) compounds belong, almost invariably, to one of the three categories of terminal oxo, *trans*-dioxo, or nitrido complexes.<sup>1</sup>

It has been shown that the formation of a terminal TcX multiple bond may have a key importance in the preparation of <sup>99m</sup>Tc radiopharmaceuticals through the so-called "substitution route".<sup>2</sup> We considered the possibility to extend the range of possible types of Tc(V) compounds by preparing complexes containing new terminal TcX multiple bonds. The most obvious candidate for this purpose was the  $[\text{Tc}=\text{S}]^{3+}$  group, which constitutes the sulfido analogue of the  $[\text{Tc}=\text{O}]^{3+}$  group.

Many terminal transition-metal-sulfido bonds have been reported.<sup>3</sup> In particular, the  $[\text{Re}=\text{S}]^{3+}$  group has been prepared by reaction of  $[\text{ReCl}_6]^{2-}$  with 1,2-ethanedithiol, in the presence of  $\text{NEt}_3$ , to give the square-pyramidal complex  $[\text{ReS}(\text{SCH}_2\text{C}_6\text{H}_5)_2]^{3-}$ .<sup>3c</sup> Since the chemical similarity between technetium and rhenium is well-known, we carried out the same reaction on the complex  $[\text{TcCl}_6]^{2-}$ , but without obtaining the formation of a Tc=S bond.<sup>4</sup> We tried, therefore, to follow a different synthetic method,

which was successfully applied to the preparation of other terminal metal-sulfido groups.<sup>3a,b</sup> This approach involves the use of  $\text{B}_2\text{S}_3$  as a source of  $\text{S}^{2-}$  ligands, in strictly anhydrous conditions. One reaction looked particularly suitable for its application to technetium chemistry: the first mononuclear Mo(V) complex possessing a terminal Mo=S bond was prepared by reacting the molybdenum(V)-oxo complex  $[\text{MoOCl}_2\{\text{HB}(\text{Me}_2\text{pz})_3\}]$  [ $\text{HB}(\text{Me}_2\text{pz})_3$  = anionic hydrotris(3,5-dimethyl-1-pyrazolyl)borate] with  $\text{B}_2\text{S}_3$  in anhydrous  $\text{CH}_2\text{Cl}_2$ , to produce the corresponding sulfido complex  $[\text{MoSCl}_2\{\text{HB}(\text{Me}_2\text{pz})_3\}]$ . In such reaction, the sterically encumbering ligand  $[\text{HB}(\text{Me}_2\text{pz})_3]^-$  stabilizes the overall structure of both the initial and final complexes, so allowing the oxo ligand to be substituted by the sulfido ligand.

Since an analogous Tc(V)-oxo complex,  $[\text{TcOCl}_2\{\text{HB}(\text{pz})_3\}]$  [ $\text{HB}(\text{pz})_3$  = anionic hydrotris(1-pyrazolyl)borate], has been reported,<sup>5</sup> we used this compound for the preparation of the first complex containing a terminal  $[\text{Tc}=\text{S}]^{3+}$  group, namely  $[\text{TcSCl}_2\{\text{HB}(\text{pz})_3\}]$  (1), through the same route described for the synthesis of the above-mentioned Mo(V)-sulfido complex.<sup>3d</sup> We report here the first results of this attempt and the characterization of the resulting technetium(V)-sulfido complex. Furthermore, in order to have a comparison with rhenium chemistry, we describe the same synthesis carried out on the rhenium(V)-oxo complex  $[\text{ReOCl}_2\{\text{HB}(\text{pz})_3\}]$ <sup>6</sup> to give the corresponding terminal-sulfido complex  $[\text{ReSCl}_2\{\text{HB}(\text{pz})_3\}]$  (2).

The reaction of  $[\text{MOCl}_2\{\text{HB}(\text{pz})_3\}]$  (M = Tc, Re) with  $\text{B}_2\text{S}_3$  in dry deoxygenated dichloromethane produces (deep dark green for Tc and deep dark blue for Re)  $[\text{MSCl}_2\{\text{HB}(\text{pz})_3\}]$  in satisfactory yield.<sup>7</sup> The sulfido complexes 1 and 2 were recrystallized following the removal of excess  $\text{B}_2\text{S}_3$  from the reaction mixture. Although relatively air stable in the solid state, these complexes are air sensitive in solution. Thus, their synthesis, isolation, and characterization must be performed under anhydrous and anaerobic conditions.

The complexes 1 and 2, which have been characterized by elemental analysis, infrared and mass spectra, and magnetic susceptibility measurements, show largely parallel properties.

The infrared spectra of  $[\text{MSCl}_2\{\text{HB}(\text{pz})_3\}]$  (M = Tc, Re) are almost entirely generated by the absorptions due to the  $[\text{HB}(\text{pz})_3]^-$  ligand; these bands are slightly influenced by the change of the central metal ion, so that the spectra of the Tc and Re complexes

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- (7) <sup>99</sup>Tc emits a low-energy (0.292 MeV)  $\beta$ -particle with a half-life of  $2.12 \times 10^5$  years. All manipulations were carried out in a laboratory approved for low-level radioactivity with monitored hoods and gloveboxes. Bremsstrahlung radiation is not a significant problem due to the low energy of the  $\beta$ -particle emission, but normal radiation safety procedures must be used at all times to prevent contamination. Preparation of  $[\text{MSCl}_2\{\text{HB}(\text{pz})_3\}]$  [M = Tc (1), Re (2)] is as follows. A suspension of  $[\text{MOCl}_2\{\text{HB}(\text{pz})_3\}]$ <sup>3,6</sup> (2.0 mmol) and  $\text{B}_2\text{S}_3$  (0.3 g, 2.5 mmol) in dry, deoxygenated  $\text{CH}_2\text{Cl}_2$  (50 mL) was stirred, at room temperature for 20 h when M = Tc, or at reflux temperature for 3 h when M = Re, under an argon stream. The reaction mixture was filtered anaerobically and the filtrate evaporated to dryness by passing an argon flow through the solution. The resulting residue was dissolved in dry, deoxygenated  $\text{CH}_2\text{Cl}_2$  (30 mL), and hexane was slowly added to the solution until a precipitate began to form. This solid was filtered out and discarded, and an additional argon stream was passed through the filtrate. A powder (dark green for M = Tc, blue ink for M = Re) was obtained, filtered out, washed with hexane, and stored in a sealed vial filled with argon. (Yield: 26% for Tc, 45% for Re.) Anal. Calcd for  $\text{C}_9\text{H}_{10}\text{BCl}_2\text{TcN}_6\text{S}$ : C, 26.05; H, 2.43; N, 20.29; S, 7.72; Tc, 23.86. Found: C, 25.96; H, 2.35; N, 20.01; S, 8.00; Tc, 23.46. IR ( $\text{cm}^{-1}$ ): 2510 (B-H); 350, 300 (Tc-Cl). Anal. Calcd for  $\text{C}_9\text{H}_{10}\text{BCl}_2\text{ReN}_6\text{S}$ : C, 21.52; H, 2.01; N, 16.73; S, 6.38. Found: C, 21.47; H, 1.96; N, 16.24; S, 5.84. IR ( $\text{cm}^{-1}$ ): 2460 (B-H); 330, 300 (Re-Cl). Mass spectra for 1 and 2, obtained by using a VG 7070E mass spectrometer with ionization effected by electron impact, showed the respective parent ions for  $[\text{TcSCl}_2\{\text{HB}(\text{pz})_3\}]$  ( $m/e$  414) and  $[\text{ReSCl}_2\{\text{HB}(\text{pz})_3\}]$  ( $m/e$  502) with their characteristic isotope distribution pattern consistent with a species containing the grouping of atoms  $\text{TcCl}_2$  and  $\text{ReCl}_2$ , respectively, and an identical fragmentation behavior: M = Tc,  $m/e$  379, 381 (M-Cl),  $m/e$  344 (M-2Cl),  $m/e$  312 (M-2Cl-S); M = Re,  $m/e$  465, 467, 469 (M-Cl),  $m/e$  430, 432 (M-2Cl),  $m/e$  398, 400 (M-2Cl-S).

appear almost identical, they differing mainly in the values of the metal-halogen stretching frequencies.<sup>7</sup> Moreover, the ligand stretchings appear unaffected by the change in the terminal MX groups (X = O, S), considering that the spectra of the sulfido complexes resemble those of the corresponding oxo analogues except for the lack of the characteristic strong M=O absorptions (in the ranges 890–1020 cm<sup>-1</sup> for Tc<sup>5+</sup> and 910–1000 cm<sup>-1</sup> for Re<sup>6+</sup>). No attempts were made to identify the M=S stretchings, which seem hidden by the ligand bands.<sup>3e,f</sup>

Complexes **1** and **2** are particularly well suited for analysis by mass spectrometry.<sup>7</sup> The mass spectrum of [TcSCl<sub>2</sub>(HB(pz)<sub>3</sub>)] shows a cluster of peaks at *m/e* 414 resulting from the molecular ion M<sup>+</sup> and exhibits an isotope distribution pattern that is consistent with a species containing two chlorine atoms. Additionally, the spectrum exhibits other peaks that may be assigned as fragments of the complex resulting from the loss of a monodentate ligand. That is, the doublet at *m/e* 379 and 381 represents the molecular ion minus a chlorine, the singlet at *m/e* 344 represents loss of two chlorines, and the singlet at *m/e* 312 represents loss of two chlorines and the sulfur from the molecular ion.

The parent ion M<sup>+</sup>, with an isotope distribution pattern characteristic for a rhenium complex containing two chlorine atoms<sup>8</sup> and the same fragmentation behavior found for complex **1**, is observed in the mass spectrum of [ReSCl<sub>2</sub>(HB(pz)<sub>3</sub>)].<sup>7</sup>

Faraday measurements showed that the complexes [MSCl<sub>2</sub>(HB(pz)<sub>3</sub>)] are diamagnetic in the solid state consistent with a +5 oxidation state for Tc and Re and with the existence of a terminal metal-sulfido multiple bond analogous to the isoelectronic metal-oxo multiple bond.<sup>1b,9</sup>

The present results show the possibility to prepare technetium(V) complexes containing a terminal Tc=S multiple bond; however, the formation and stability of such a group appear strongly dependent upon the nature of the other ancillary ligands coordinated to the metal ion, a factor that must be carefully taken into account for the development of possible technetium(V)-sulfido radiopharmaceuticals.

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Dipartimento di Chimica Fisica ed Inorganica **Adriano Duatti\***  
 Università di Bologna  
 40136 Bologna, Italy

Istituto di Chimica e Tecnologia dei **Francesco Tisato**  
 Radioelementi **Fiorenzo Refosco**  
 Area di Ricerca CNR  
 35020 Padova, Italy

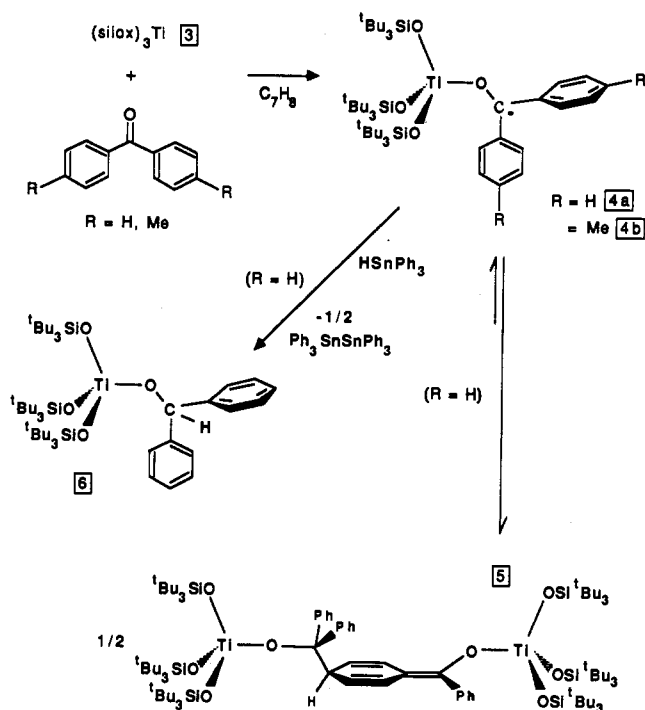
Dipartimento di Scienze Farmaceutiche **Ulderico Mazzi**  
 Università di Padova **Marino Nicolini**  
 35131 Padova, Italy

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### Reversible Dimerization of a Titanium Ketyl: (silox)<sub>3</sub>TiOCPh<sub>2</sub>\* (silox = <sup>t</sup>Bu<sub>3</sub>SiO<sup>-</sup>)

Inherently reactive organic fragments are often trapped and stabilized by transition metal centers. It has been shown that d<sup>1</sup> complexes, typically those containing Ti(III), promote alkyl cyclizations<sup>1,2</sup> and pinacol-type couplings<sup>3–13</sup> characteristic of car-

Scheme I



bon-centered radicals. In each instance, it is convenient to view the odd electron as transposed from the metal to a reducible adduct. For example, treatment of CpTiCl<sub>2</sub> with acetone<sup>7</sup> leads to [CpCl<sub>2</sub>Ti]<sub>2</sub>O<sub>2</sub>C<sub>2</sub>(Me)<sub>4</sub>, the acetone-coupled dimer structurally characterized by Caulton et al.<sup>10</sup> While unhindered dialkyl ketones clearly lead to coupled products, evidence for the reversible coupling of benzophenone,<sup>7</sup> although often cited,<sup>11,12</sup> is far less compelling.<sup>8,9</sup> By employment of the sterically demanding silox (<sup>t</sup>Bu<sub>3</sub>SiO<sup>-</sup>) ligand,<sup>14–16</sup> a reactive fragment may be shielded within

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