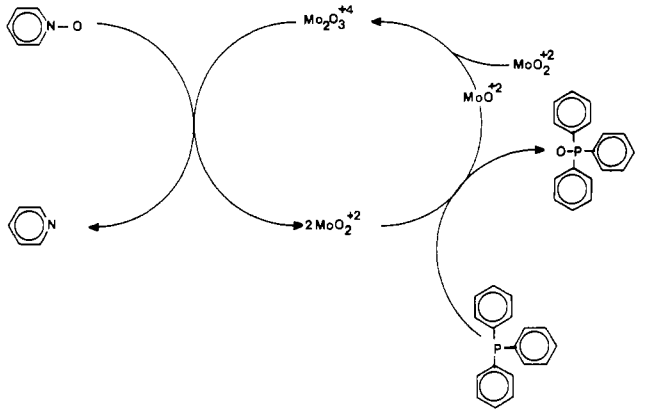
Scheme I



The above oxidation and reduction reactions can be coupled to produce catalytic oxygen atom transfer processes. For example, oxygen atom transfer from pyridine *N*-oxide to TPP to produce pyridine, py, and TPPO can be catalyzed if small quantities of I are added to the reaction mixture.

With high-performance liquid chromatography, HPLC, used to monitor the progress of this reaction system,[9] it was verified that there was little or no reaction between py-O and TPP in the absence of I. A solution was made that contained 4.12×10^{-4} mol of py-O and 2.13×10^{-4} mol of TPP in 100 mL of dry, degassed THF that had been freshly distilled from Na/benzophenone under argon. After 24 h, HPLC analysis of the mixture indicated that no TPPO or py had formed. On the other hand, if 1.73×10^{-5} mol of I was added to a freshly prepared mixture of 4.12×10^{-4} mol of py-O and 2.13×10^{-4} mol of TPP in 100 mL of dry, degassed THF, the HPLC analysis showed that 100% of the starting TPP had been converted to TPPO in an 18-h period. An equivalent amount of pyridine was also formed in the same period of time. This corresponds to 12.3 turnovers and clearly demonstrates the catalytic nature of this process.

To verify the catalytic role of I, it was reacted with a large excess of dimethyl sulfoxide, DMSO, in the presence of a 35-fold excess of TPP (based on the quantity of I). Under these conditions, the TPP was quantitatively coverted to TPPO and an equivalent amount of DMSO was converted to dimethyl sulfide, DMS. The production of DMS was followed by the method outlined by Holm and Berg.[10] In the absence of I, no DMSO was converted to DMS in a 24-h period.

Thus, for the first time, catalysis of oxygen atom transfer has been accomplished by using an oxo-bridged Mo(V) complex as an active participant in the catalytic cycle. This is apparently due to the presence of an empty or at least accessible coordination site on the molybdenum atoms where an oxygen-donating substrate may approach the Mo(V) atom. The entire process can be summarized in Scheme I. This shows that significant catalytic chemistry may be built around oxo-bridged Mo(V) complexes. It also suggests that the role of oxo-bridged Mo(V) complexes in oxygen atom transfer reactions of systems designed to model enzyme behavior cannot necessarily be ignored. This is particularly true in those cases where significant quantities of oxo-bridged Mo(V) species are present due to reaction 1.

Note Added in Proof. During the course of manuscript preparation Craig and co-workers reported the oxygen atom transfer reactions of a series of Schiff base complexes, $Mo_2O_3L_2(solv)_2$ and their Mo(VI) analogues.[11]

Acknowledgment. D.M.B. wishes to acknowledge financial support from the Research Corp. J.E.H. acknowledges support from the Florida Atlantic University Division of Sponsored Research.

(9) Haky, J. E.; Falzone, S.; Baird, D. M. *Anal. Lett.*, in press.
(10) Berg, J. M.; Holm, R. H. *J. Am. Chem. Soc.* **1985**, *107*, 925.
(11) Craig, J. A.; Harlan, E. W.; Snyder, B. S.; Whitener, M. A.; Holm, R. H. *Inorg. Chem.* **1989**, *28*, 2082.

Registry No. $Mo_2O_3(dtc)_2I_2(THF)_2$, 103817-70-5; pyridine *N*-oxide, 694-59-7; nicotinamide *N*-oxide, 1986-81-8; dimethyl sulfoxide, 67-68-5; diphenyl sulfoxide, 945-51-7; biotin *S*-oxide, 7553-42-6; triphenylphosphine, 603-35-0.

Department of Chemistry
Florida Atlantic University
Boca Raton, Florida 33431

D. M. Baird*
S. Falzone
J. E. Haky

Received May 15, 1989

Conversion of Long-Chain Terminal Alcohols and Secondary Amines into Tertiary Amines Using Dichlorotris(triphenylphosphine)ruthenium(II) as Catalyst

The catalyzed synthesis of amines having long-chain alkyl groups is of potential commercial value because of the use of these compounds in the production of detergents. A plausible preparative route involves the condensation reaction between long-chain terminal alcohols and secondary amines (eq 1). The reaction

$$CH_3(CH_2)_nOH + R_2NH \rightarrow CH_3(CH_2)_nNR_2 + H_2O \quad (1)$$

between alcohols and amines has been previously catalyzed by metal oxides and by ruthenium phosphine complexes.[1] Furthermore, it has been recently reported that ethylene glycol can be converted into both monoamines and diamines by using solutions of ruthenium phosphine complexes as catalysts.[2] We now report that ruthenium triphenylphosphine complexes are also homogeneous catalysts for the conversion of long-chain terminal alcohols and secondary amines to tertiary amines.

The complex chosen for this study is $RuCl_2(PPh_3)_3$.[3] We find that this complex acts as a homogeneous catalyst for the conversion of terminal alcohols $CH_3(CH_2)_nOH$ (n = 9, 13, 15, 17) and secondary amines R_2NH (R = Me, Et, 1-Pr, Ph) into tertiary amines $CH_3(CH_2)_nNR_2$. The tertiary amine formed has been identified by GC-MS, and the yield of $CH_3(CH_2)_nNR_2$ after a 2.5-h reaction time at 120 °C is measured by comparison with an internal reference. The data obtained for four alcohols ROH (R = 1-$C_{10}H_{21}$, 1-$C_{14}H_{29}$, 1-$C_{16}H_{33}$, 1-$C_{18}H_{37}$) and amines $R'NH_2$ (R' = Me, Et, 1-Pr, Ph) are collected in Table I. The catalyst to reagent mole ratio is 1:200:200 for $RuCl_2(PPh_3)_3$-alcohol-secondary amine at the beginning of the reaction. A typical loading of the reaction vessel is given in Table I. The data in Table I show that yields in the 14-82% range are obtained. For diphenylamine the yield is relatively constant in the 47-52% range, but for diethylamine and dipropylamine the yields are lower (14-28%). The highest yield is observed for dimethylamine, with an 82% yield of $C_{18}H_{37}NMe_2$ being formed from $C_{18}H_{37}OH$. Longer reaction times do not give any significant increases in yield. Adding triphenylphosphine to the reaction mixture increases the yield of tertiary amine; the addition of 1, 2, and 4 mol of triphenylphosphine to $RuCl_2(PPh_3)_3$ causes the yield of $C_{16}H_{33}NEt_2$ to increase from 21%, in the absence of excess triphenylphosphine, to 30, 35, and 42%, respectively, with the added moles. Triphenylphosphine itself is not a catalyst for the reaction. Carrying out the reaction under 1300 psig of hydrogen rather than under

(1) Fong, P. Y.; Smith, K. R.; Sauer, J. D. Eur. Pat. Appl. EP 281,417; *Chem. Abstr.* **1989**, *110*, 40803k. Twigg, M. V. Eur. Pat. Appl. EP 211,552; *Chem. Abstr.* **1987**, *107*, 25122g. Renken, T. L.; Knifton, J. F. U.S. Pat. 4,618,717; *Chem. Abstr.* **1987**, *106*, 20303m. Dudzinski, Z. W. U.S. Pat. 4,594,455; *Chem. Abstr.* **1986**, *105*, 62724j. Larkin, J. M. U.S. Pat. 4,415,755; *Chem. Abstr.* **1984**, *100*, 85279d. Swift, H. E.; Innes, R. A.; Onopchenko, A. U.S. Pat. 4,409,399; *Chem. Abstr.* **1984**, *100*, 5833s. Fenton, D. M. U.S. Pat. 3,708,539; *Chem. Abstr.* **1973**, *78*, 124001f. Baiker, A.; Kijenski, J. *Catal. Rev.-Sci. Eng.* **1985**, *27*, 653-697. Baiker, A.; Richarz, W. *Tetrahedron Lett.* **1977**, 1937-1938. Tsuji, Y.; Huh, K.-T.; Ohsugi, Y.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1365-1370. Watanabe, Y.; Tsuji, Y.; Ige, H.; Ohsugi, Y.; Ohta, T. *J. Org. Chem.* **1984**, *49*, 3359-3363. Murahashi, S.-I.; Kondo, L.; Hakata, T. *Tetrahedron Lett.* **1982**, *23*, 229-232.
(2) Marsella, J. A. *J. Org. Chem.* **1987**, *52*, 467-468.
(3) Schroder, M.; Stephenson, T. A. *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England 1987.

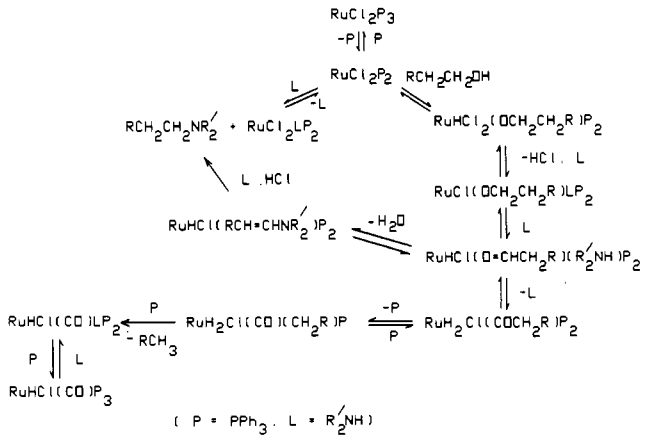
0020-1669/89/1328-4562$01.50/0

Table I. Catalyzed Conversion of Terminal Alcohols and Secondary Amines into Tertiary Amines in the Presence of $RuCl_2(PPh_3)_3$

alcohol[a]	amine[a]	product	yield, %[b]	turnovers[c]
$C_{10}H_{21}OH$	$NHMe_2$	$C_{10}H_{21}NMe_2$	52	104
	$NHEt_2$	$C_{10}H_{21}NEt_2$	24	48
	$NHPr_2$	$C_{10}H_{21}NPr_2$	18	36
	$NHPh_2$	$C_{10}H_{21}NPh_2$	52	104
$C_{14}H_{29}OH$	$NHMe_2$	$C_{14}H_{29}NMe_2$	75	150
	$NHEt_2$	$C_{14}H_{29}NEt_2$	28	56
	$NHPr_2$	$C_{14}H_{29}NPr_2$	23	46
	$NHPh_2$	$C_{14}H_{29}NPh_2$	50	100
$C_{16}H_{33}OH$	$NHMe_2$	$C_{16}H_{33}NMe_2$	45	90
	$NHEt_2$	$C_{16}H_{33}NEt_2$	21	42
	$NHPr_2$	$C_{16}H_{33}NPr_2$	24	48
	$NHPh_2$	$C_{16}H_{33}NPh_2$	49	98
$C_{18}H_{37}OH$	$NHMe_2$	$C_{18}H_{37}NMe_2$	82	164
	$NHEt_2$	$C_{18}H_{37}NEt_2$	14	28
	$NHPr_2$	$C_{18}H_{37}NPr_2$	21	42
	$NHPh_2$	$C_{18}H_{37}NPh_2$	47	94

[a] A typical reaction contains $C_{16}H_{33}OH$ (2.42 g, 10 mmol), $NHEt_2$ (1.04 mL, 10 mmol) and $RuCl_2(PPh_3)_3$ (48 mg, 50 μmol) in a Parr pressure vessel. After being heated for 2.5 h at 120 °C, the product mixture was analyzed by GC–MS. The moles of $C_{16}H_{33}NEt_2$ formed were measured by comparison with those of added dodecane (0.75 g, 4.4 mmol) as an internal standard. [b] The selectivity to formation of the product is greater than 90%. [c] These values are the moles of product formed per mole of $RuCl_2(PPh_3)_3$ catalyst over the 2.5-h reaction time.

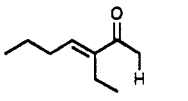
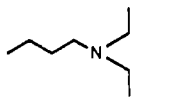
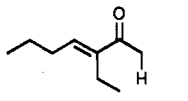
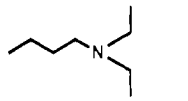
Scheme I



an ambient pressure of nitrogen reduces the yield of $C_{16}H_{33}NEt_2$ from 21 to 17%.

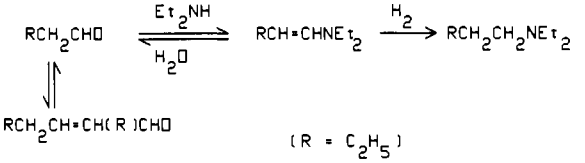
At the end of the reaction the $RuCl_2(PPh_3)_3$ has been converted into $RuHCl(CO)L(PPh_3)_2$ (L = amine). Removal of the amine from the solution containing $RuHCl(CO)L(PPh_3)_2$ and triphenylphosphine gives $RuHCl(CO)(PPh_3)_3$.[4] This carbonyl complex shows no catalytic activity for the conversion of alcohols and secondary amines into tertiary amines. A side product in all these reactions is the alkane C_nH_{2n+2} (n = 9, 13, 15, 17), which is the byproduct from the decarbonylation of the alcohol. Trace amounts of side products are also observed, which result from alkyl-scrambling reactions of the product amine.[5] We propose

Table II. Reaction Products from Butyraldehyde and Diethylamine

conditions[a]	product ratio	yield, %
no catalyst	 44 : 1	77
no catalyst (1300 psi H_2)	 1.9 : 1	66
$RuCl_2(PPh_3)_3$	 8.9 : 1	77
$RuCl_2(PPh_3)_3$ (1300 psi H_2)		32

[a] Conditions are 120 °C for 2.5 h.

Scheme II



that the reaction pathway follows that depicted in Scheme I. This pathway corresponds to those proposed by others for the catalyzed reaction between alcohols and secondary or primary amines to give tertiary amines.[6] The path involves a ruthenium alkoxide intermediate that undergoes reductive elimination of hydrogen chloride. Subsequent β-hydrogen transfer gives a π-bonded aldehyde complex. Schiff base formation between aldehyde and secondary amine, followed by the addition of two hydrogens to the intermediate imine, results in the formation of the tertiary amine product. Alternately, the aldehyde complex can undergo oxidative addition of the aldehydic carbon–hydrogen bond to give an acyl intermediate. Decarbonylation of this acyl complex followed by reductive elimination of a carbon–hydrogen bond explains the formation of alkane.

As a probe of the potential intermediacy of aldehydes in the catalytic reaction, we have compared the products obtained in the uncatalyzed and catalyzed reactions of both 1-butanol and butyraldehyde with diethylamine. Under catalytic conditions with 1-butanol, we obtain 1-butyldiethylamine and 1-butylethylamine as major and minor products, respectively. Four reactions with butyraldehyde are summarized in Table II. The eneal $CH_3(CH_2)_2CH{=}C(C_2H_5)CHO$, which is formed as the major product in the absence of catalyst, is the aldol condensation product. We observe no 1-butyldiethylamine in the absence of catalyst, but a small quantity of eneamine $CH_3CHCH{=}CHN(C_2H_5)_2$ is formed. In the presence of $RuCl_2(PPh_3)_3$ we observe small amounts of 1-butyldiethylamine, but the aldol product is still formed as the major product. Under catalytic conditions in the presence of hydrogen the aldol reaction is suppressed, and 1-butyldiethylamine is the sole product. These data confirm that eneamines can be hydrogenated by $RuCl_2(PPh_3)_3$ and that this complex does not suppress Schiff base formation. The selective formation of 1-butyldiethylamine with $RuCl_2(PPh_3)_3$ under hydrogen pressure can be explained on the basis of Scheme II, where the hydrogenation of eneamine to tertiary amine is an irreversible step.

(4) The complex $RuHCl(CO)(PPh_3)_3$ has been characterized by the following methods: ^1H NMR δ −7.2 ($^2J(PH_{cis})$ = 23.7 Hz, $^2J(PH_{trans})$ = 104.9 Hz); $^{31}P\{^1H\}$ NMR δ 13.5 s, 39.6 s ($^2J(PP) \approx 0$ Hz); IR ν(CO) 2020, 1922, 1903 cm^{-1} (see: Ahmad, N.; Levison, J. J.; Robinson, S. D.; Uttley, M. F. *Inorg. Synth.* **1974**, *15*, 45–64). The complex $RuHCl(CO)(HNEt_2)(PPh_3)_2$ has been characterized by the following methods: ^1H NMR δ −14.5 t ($^2J(PH)$ = 19.6 Hz); $^{31}P\{^1H\}$ NMR δ 47.6 s. $RuHCl(CO)(HNEt_2)(PPh_3)_2$ can also be prepared by the addition of excess diethylamine to $RuHCl(CO)(PPh_3)_3$.

(5) Amine redistribution reactions are well-known. Examples have been reported with $RuCl_2(PPh_3)_3$ (Arcelli, A.; Khai, B. T.; Porzi, G. *J. Organomet. Chem.* **1982**, *231*, C31–C32. Jung, C. W.; Fellmann, J. D.; Garrou, P. E. *Organometallics* **1983**, *2*, 1042–1044) and with $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ (Shvo, L.; Laine, R. M. *J. Chem. Soc., Chem. Commun.* **1980**, 753–754. Adams, R. D.; Babin, J. E. *Organometallics* **1988**, *7*, 963–969).

(6) Vultier, R.; Baiker, A.; Wokaun, A. *Appl. Catal.* **1987**, *30*, 167–176. Watanabe, Y.; Tsuji, Y.; Ohsugi, Y. *Tetrahedron Lett.* **1981**, *22*, 2667–2670.

The overall pathway in Scheme I can explain the inhibition by hydrogen and the acceleration by triphenylphosphine.[7] Possible explanations are that the oxidative addition of an alcohol to $RuCl_2(PPh_3)_3$ 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).[8]

Acknowledgment. We thank the Louisiana Board of Regents for support of this research through the Louisiana Educational Quality Support Fund.

(7) No increase in conductivity of solutions of $RuCl_2(PPh_3)_3$ is observed in the presence of excess triphenylphosphine, thereby eliminating the possibility that chloride ion substitution occurs.
(8) Crabtree, R. H.; Pearman, A. J. *J. Organomet. Chem.* **1978**, *157*, 335-344.

Department of Chemistry
Tulane University
New Orleans, Louisiana 70118

Sanjoy Ganguly
Frederick L. Joslin
D. Max Roundhill*

Received June 16, 1989

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

The isoelectronic $[Tc{=}O]^{3+}$, *trans*-$[O{=}Tc{=}O]^{+}$, and $[Tc{\equiv}N]^{2+}$ 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.[1]

It has been shown that the formation of a terminal TcX multiple bond may have a key importance in the preparation of ^{99m}Tc radiopharmaceuticals through the so-called "substitution route".[2] 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 $[Tc{=}S]^{3+}$ group, which constitutes the sulfido analogue of the $[Tc{=}O]^{3+}$ group.

Many terminal transition-metal-sulfido bonds have been reported.[3] In particular, the $[Re{=}S]^{3+}$ group has been prepared by reaction of $[ReCl_6]^{2-}$ with 1,2-ethanedithiol, in the presence of NEt_3, to give the square-pyramidal complex $[ReS(SCH_2CH_2S)_2]^{-}$.[3e] Since the chemical similarity between technetium and rhenium is well-known, we carried out the same reaction on the complex $[TcCl_6]^{2-}$, but without obtaining the formation of a Tc=S bond.[4] We tried, therefore, to follow a different synthetic method, which was successfully applied to the preparation of other terminal metal-sulfido groups.[3a,g,h] This approach involves the use of B_2S_3 as a source of 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 $[MoOCl_2\{HB(Me_2pz)_3\}]$ [$HB(Me_2pz)_3$ = anionic hydrotris(3,5-dimethyl-1-pyrazolyl)borate] with B_2S_3 in anhydrous CH_2Cl_2, to produce the corresponding sulfido complex $[MoSCl_2\{HB(Me_2pz)_3\}]$. In such reaction, the sterically encumbering ligand $[HB(Me_2pz)_3]^{-}$ 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, $[TcOCl_2(HB(pz)_3)]$ [$HB(pz)_3$ = anionic hydrotris(1-pyrazolyl)borate], has been reported,[5] we used this compound for the preparation of the first complex containing a terminal $[Tc{=}S]^{3+}$ group, namely $[TcSCl_2(HB(pz)_3)]$ (**1**), through the same route described for the synthesis of the above-mentioned Mo(V)-sulfido complex.[3d] 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 $[ReOCl_2(HB(pz)_3)]$[6] to give the corresponding terminal-sulfido complex $[ReSCl_2(HB(pz)_3)]$ (**2**).

The reaction of $[MOCl_2(HB(pz)_3)]$ (M = Tc, Re) with B_2S_3 in dry deoxygenated dichloromethane produces (deep dark green for Tc and deep dark blue for Re) $[MSCl_2(HB(pz)_3)]$ in satisfactory yield.[7] The sulfido complexes **1** and **2** were recrystallized following the removal of excess B_2S_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 $[MSCl_2(HB(pz)_3)]$ (M = Tc, Re) are almost entirely generated by the absorptions due to the $[HB(pz)_3]^{-}$ ligand; these bands are slightly influenced by the change of the central metal ion, so that the spectra of the Tc and Re complexes

(1) (a) Deutsch, E.; Libson, K.; Jurisson, S.; Lindoy, L. F. *Prog. Inorg. Chem.* **1983**, *30*, 75-139. (b) Duatti, A.; Marchi, A.; Magon, L.; Deutsch, E.; Bertolasi, V. *Inorg. Chem.* **1987**, *26*, 2182-2186. (c) Melnik, M.; Van Lier, J. E. *Coord. Chem. Rev.* **1987**, *77*, 275-324.
(2) Nicolini, M., Bandoli, G., Mazzi, U., Eds. *Technetium in Chemistry and in Nuclear Medicine*; Cortina International: Verona, Italy, 1986.
(3) (a) Callahan, P. K.; Durand, P. J. *Inorg. Chem.* **1980**, *19*, 3211-3217. (b) Nicholson, J. R.; Huffman, J. C.; Douglas, M. H.; Christou, G. *Inorg. Chem.* **1987**, *26*, 3030-3034. (c) Martin, M. J.; Qiang, G.-H.; Schleich, D. M. *Inorg. Chem.* **1988**, *27*, 2804-2808. (d) Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Zubieta, J. A. *Inorg. Chim. Acta* **1982**, *65*, L225-L226. (e) Blower, P. J.; Dilworth, J. R.; Hutchinson, J. P.; Nicholson, T.; Zubieta, J. *J. Chem. Soc., Dalton Trans.* **1986**, 1339-1345. (f) Cotton, F. A.; Kibala, P. A.; Matusz, M. *Polyhedron* **1988**, *7*, 83-86. (g) Young, C. G.; Roberts, S. A.; Ortega, R. B.; Enemark, J. H. *J. Am. Chem. Soc.* **1987**, *109*, 2938-2946. (h) Young, C. G.; Enemark, J. H.; Collison, D.; Mabbs, F. E. *Inorg. Chem.* **1987**, *26*, 2925-2927. (i) Roberts, S. A.; Young, C. G.; Cleland, W. E., Jr.; Yamanouchi, K.; Ortega, R. B.; Enemark, J. H. *Inorg. Chem.* **1988**, *27*, 2647-2652.
(4) Tisato, F.; Refosco, F.; Duatti, A.; Mazzi, U.; Bandoli, G.; Nicolini, M. Manuscript in preparation.
(5) (a) Thomas, R. W.; Estes, G. W.; Elder, R. C.; Deutsch, E. *J. Am. Chem. Soc.* **1979**, *101*, 4581-4585. (b) Thomas, R. W.; Davison, A.; Trop, H. S.; Deutsch, E. *Inorg. Chem.* **1980**, *19*, 2840-2845.
(6) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125-128.
(7) ^{99}Tc emits a low-energy (0.292 MeV) β-particle with a half-life of 2.12×10^5 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 β-particle emission, but normal radiation safety procedures must be used at all times to prevent contamination. Preparation of $[MSCl_2(HB(pz)_3)]$ [M = Tc (**1**), Re (**2**)] is as follows. A suspension of $[MOCl_2(HB(pz)_3)]$[5,6] (2.0 mmol) and B_2S_3 (0.3 g, 2.5 mmol) in dry, deoxygenated CH_2Cl_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 CH_2Cl_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 $C_9H_{10}BCl_2TcN_6S$: 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 (cm^{-1}): 2510 (B-H); 350, 300 (Tc-Cl). Anal. Calcd for $C_9H_{10}BCl_2ReN_6S$: 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 (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 $[TcSCl_2(HB(pz)_3)]$ (*m/e* 414) and $[ReSCl_2(HB(pz)_3)]$ (*m/e* 502) with their characteristic isotope distribution pattern consistent with a species containing the grouping of atoms $TcCl_2$ and $ReCl_2$, 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).

0020-1669/89/1328-4564$01.50/0