

Ligand Substitution Reactions of Tetrachlorobis(triphenylphosphine)technetium(IV)

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Abstract

The synthesis and characterization of tetrachlorobis(dimethyl sulfoxide)technetium(IV), tetrachlorobis(pyridine)technetium(IV), trichlorotris(pyridine)technetium(III), trichlorotris(4-methylpyridine)technetium(III), and trichlorotris(3,5-dimethylpyridine)technetium(III) are described, as well as the reaction of tetrachlorobis(triphenylphosphine)technetium(IV) with acetonitrile. Fast atom bombardment mass spectrometry, proton nuclear magnetic resonance, and cyclic voltammetry studies of the new complexes are reported. The Tc(IV) and Tc(III) species are paramagnetic, but the latter give well-resolved contact-shifted ^1H NMR spectra.

Introduction

The impetus for elucidation of the chemistry of technetium originates in the widespread use of the metastable isomer $^{99\text{m}}\text{Tc}$ in diagnostic nuclear medicine and is fueled by the desire to design new radiopharmaceuticals [1]. Interest in the basic inorganic chemistry of technetium has intensified recently as knowledge of this second-row transition metal and its wide range of accessible oxidation states has expanded. However, only a limited number of useful synthetic starting materials are known, particularly for lower oxidation state technetium complexes. Novel Tc(IV) and Tc(III) complexes derived from reaction of $\text{TcCl}_4(\text{PPh}_3)_2$ with coordinating solvents such as dimethyl sulfoxide, pyridine and acetonitrile are reported here. Easily synthesized, these species promise to be reactive starting materials.

Experimental

Caution: Technetium-99 is a weak β^- -emitter ($E = 0.292$ MeV, $t_{1/2} = 2.12 \times 10^5$ y). All manipulations

involving radioactive materials were performed in laboratories approved for low-level radioactivity following precautions detailed elsewhere [2].

Technetium as $\text{NH}_4[^{99}\text{TcO}_4]$ was obtained as a gift from Du Pont/Biomedical Products. Solvents and reagents were used as received. Triphenylphosphine (PPh_3), 4-methylpyridine (4-picoline, 99%, abbreviated as pic) and 3,5-dimethylpyridine (3,5-lutidine, 98+%, abbreviated as lut) were obtained from Aldrich Chemical Company.

Elemental analyses were performed by Atlantic Microlab Inc., Norcross, GA. Fourier transform IR spectra were measured from 4000 to 400 cm^{-1} on either an IBM System 9000 spectrometer or a Mattson Cygnus 100 spectrometer using a 2 cm^{-1} bandwidth. Electronic absorption spectra were recorded using a Hewlett Packard 8451A photodiode array spectrophotometer. Fast atom bombardment mass spectra (FAB⁺) were obtained with a MAT 731 mass spectrometer operating at an accelerating voltage of 8 kV and equipped with an Ion Tech B11N FAB gun, which produced a beam of 6–8 keV xenon neutrals. The samples were dissolved in a 3-nitrobenzyl alcohol (NBA) matrix. Proton NMR spectra were recorded at 300 MHz on a Varian XL-300 spectrometer and were referenced to the resonance of the residual protons in the deuterated solvent. For each compound, spectra were obtained for several spectral widths to check for and eliminate any spectral folding; generally, a spectral window of 30030 Hz was employed. Cyclic voltammetry was performed on N_2 -purged acetonitrile solutions of the metal complexes with 0.1 M tetrabutylammonium perchlorate (TBAP, GFS Chemicals) as supporting electrolyte. The acetonitrile was of spectrophotometric grade and was kept over 3 Å molecular sieves to remove water. Experiments were conducted using a one-compartment cell with a Pt disk as the working electrode, a Pt wire as the auxiliary electrode, and an SCE (KCl saturated calomel electrode, Fisher) as the reference electrode. $E_{1/2}$ values were calculated from the average of the anodic and cathodic peak

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potentials, $E_{1/2} = (E_{p,a} + E_{p,c})/2$. $E_{1/2}$ values were measured relative to SCE and are uncorrected for junction potentials. The potentiostat employed was a PAR model 174 polarographic analyzer and the data were plotted with a Hewlett Packard 7044A XY recorder.

Preparation of Tetrachlorobis(dimethyl sulfoxide)-technetium(IV)

Green $\text{TcCl}_4(\text{PPh}_3)_2$ [3] (95.84 mg, 0.125 mmol) was suspended in acetonitrile (8 ml) and dimethyl sulfoxide (1 ml) was added. The reaction mixture was brought just to reflux, then allowed to cool to room temperature. The golden solution was concentrated under reduced pressure until the total volume was 2–3 ml and was then flooded with diethyl ether to obtain a pale yellow precipitate. This was filtered onto a small fritted glass funnel, washed well with diethyl ether, and dried. Yield of $\text{TcCl}_4(\text{DMSO})_2$, 36.70 mg (74%). *Anal.* Calc. for $\text{C}_4\text{H}_{12}\text{Cl}_4\text{O}_2\text{S}_2\text{Tc}$: C, 12.10; H, 3.02; S, 16.15; Cl, 35.72. Found: C, 12.83; H, 3.11; S, 15.48; Cl, 34.43%. IR (KBr): 3003(m), 2917(m), 1421(m), 1409(m), 1394(m), 1320(w), 1298(w), 1031(m), 982(m), 949(w), 894(vs), 723(w), 686(w), 500(m), 488(m) cm^{-1} . ^1H NMR (d_6 -acetone): δ 14.0 (br s). FAB⁺: m/z 548 ($M + \text{NBA matrix}$)⁺; 513 ($M - \text{Cl} - \text{NBA matrix}$)⁺; 361 ($M - \text{Cl} + \text{H}$)⁺; 326 ($M - 2\text{Cl} + \text{H}$)⁺.

Preparation of Tetrachlorobis(pyridine)technetium(IV)

To $\text{TcCl}_4(\text{PPh}_3)_2$ (106 mg, 0.14 mmol) was added pyridine (5 ml) and the reaction mixture slowly heated to 52 °C over 25 min. The green starting material reacted quickly to give a red solution with yellow precipitate. The reaction mixture was allowed to cool to room temperature, filtered onto a small fritted glass funnel, and the bright yellow product was washed copiously with pyridine, methylene chloride, and diethyl ether, then dried *in vacuo*. Yield of $\text{TcCl}_4(\text{py})_2$, 35 mg (63%). The product is insoluble in water, dimethyl sulfoxide, methanol, methylene chloride, chloroform, acetone, THF, diethyl ether and benzene. *Anal.* Calc. for $\text{C}_{10}\text{H}_{10}\text{Cl}_4\text{N}_2\text{Tc}$: C, 30.10; H, 2.51; N, 7.02; Cl, 35.54. Found: C, 30.17; H, 2.54; N, 7.01; Cl, 35.50%. IR (KBr): 3114(w), 3092(w), 3074(w), 1607(s), 1480(m), 1449(vs), 1351(w), 1239(w), 1209(m), 1158(w), 1090(w), 1064(vs), 1045(m), 1016(m), 942(w), 756(s), 682(vs), 649(m), 646(m), 446(m) cm^{-1} .

Preparation of Trichlorotris(pyridine)technetium(III)

To a solution of $\text{TcCl}_4(\text{PPh}_3)_2$ (310 mg, 0.405 mmol) in pyridine (25 ml) was added PPh_3 (100 mg, 0.38 mmol). The reaction mixture was allowed to reflux (6 h) under an atmosphere of dinitrogen until a clear red–orange solution was obtained. The pyridine was removed under reduced pressure and the

orange–brown residue dissolved in a minimum volume of methylene chloride. Hexane (250 ml) was added and the solution chilled overnight at 0 °C to precipitate the crude product. This was taken up in a minimum volume of methylene chloride and diluted with methanol (50 ml). Slow solvent reduction (by rotary-evaporator) gave the product as red–orange flakes. Yield of $\text{TcCl}_3(\text{py})_3$, 154 mg (86%). The product is slightly soluble in methanol and moderately soluble in acetone, diethyl ether, methylene chloride, and chloroform. After several days in chlorinated solvents, solutions of $\text{TcCl}_3(\text{py})_3$ turn green. *Anal.* Calc. for $\text{C}_{15}\text{H}_{15}\text{Cl}_3\text{N}_3\text{Tc}$: C, 40.71; H, 3.39; N, 9.49; Cl, 24.03. Found: C, 40.76; H, 3.44; N, 9.48; Cl, 23.95%. IR (KBr): 3125(w), 3078(w), 3045(m), 1602(m), 1481(s), 1445(vs), 1342(w), 1233(w), 1212(w), 1156(w), 1071(w), 1063(m), 1047(w), 1010(w), 779(s), 763(s), 755(s), 704(s), 697(s), 692(s), 466(m), 457(w), 450(m) cm^{-1} . UV–Vis (MeOH): λ_{max} (nm) (ϵ (l mol⁻¹ cm⁻¹)) 208 (24 000), 240sh, 256 (8400), 288 (8300), 326sh, 404 (3800). FAB⁺: m/z 441 (M)⁺; 406 ($M - \text{Cl}$)⁺; 362 ($M - \text{py}$)⁺; 327 ($M - \text{Cl} - \text{py}$)⁺. $E_{1/2}$ (MeCN): +0.67 V (rev), –0.92 V (rev).

Preparation of Trichlorotris(4-methylpyridine)-technetium(III)

4-Methylpyridine (10 ml) was added to $\text{TcCl}_4(\text{PPh}_3)_2$ (96.7 mg, 0.13 mmol) and the reaction mixture was refluxed under dinitrogen for 3 h. As the reaction progressed, the green starting material reacted to give a deep red solution, which then turned orange; no solid was apparent during reflux. After cooling to room temperature the solution was filtered, flooded with hexane (200 ml), and chilled to obtain the crude product as a yellow–tan precipitate. Crystalline yellow–orange $\text{TcCl}_3(\text{pic})_3$ was obtained by slow concentration of a methanol solution or by recrystallization from acetone/hexane. Yield of $\text{TcCl}_3(\text{pic})_3$, 29.6 mg (48%). The compound is soluble in methanol, ethanol, acetone, methylene chloride and chloroform. *Anal.* Calc. for $\text{C}_{18}\text{H}_{21}\text{Cl}_3\text{N}_3\text{Tc}$: C, 44.59; H, 4.38; N, 8.67; Cl, 21.94. Found: C, 44.67; H, 4.37; N, 8.65; Cl, 21.85%. IR (KBr): 3130(w), 3075(w), 3039(w), 2961(w), 2918(w), 2852(w), 1685(w), 1653(w), 1619(vs), 1501(s), 1447(m), 1425(m), 1400(w), 1395(w), 1383(w), 1334(w), 1210(m), 1107(w), 1069(w), 1065(w), 1040(w), 1026(m), 1003(w), 816(s), 721(m), 503(s), 498(s) cm^{-1} . UV–Vis (MeOH): λ_{max} (nm) (ϵ (l mol⁻¹ cm⁻¹)) 208 (29 000), 252 (10 000), 282 (12 000), 312sh, 398 (5100). FAB⁺: m/z 483 (M)⁺; 448 ($M - \text{Cl}$)⁺; 390 ($M - \text{pic}$)⁺; 355 ($M - \text{Cl} - \text{pic}$)⁺. $E_{1/2}$ (MeCN): +0.59 V (rev), –1.02 V (rev).

Preparation of Trichlorotris(3,5-dimethylpyridine)-technetium(III)

This compound was prepared analogously to $\text{TcCl}_3(\text{pic})_3$, using 93.47 mg $\text{TcCl}_4(\text{PPh}_3)_2$ (0.12

mmol) in 10 ml 3,5-lutidine with a 2 h reflux. The product was recrystallized from methanol as a dark orange microcrystalline solid. Yield of $\text{TcCl}_3(\text{lut})_3$, 28.34 mg (44%). *Anal. Calc.* for $\text{C}_{21}\text{H}_{27}\text{Cl}_3\text{N}_3\text{TcH}_2\text{O}$: C, 46.29; H, 5.38; N, 7.71; Cl, 19.52. *Found*: C, 46.31; H, 5.00; N, 7.67; Cl, 19.51%. IR (KBr): 3084(m), 3081(m), 3017(m), 2920(s), 2865(m), 2742(w), 1628(m), 1598(s), 1448(s), 1443(s), 1383(m), 1328(w), 1245(m), 1193(w), 1160(s), 1150(s), 1045(m), 1039(m), 1018(w), 865(s), 768(w), 699(vs), 539(w), 459(m), 443(m), 429(w) cm^{-1} . UV-Vis (MeOH): λ_{max} (nm) (ϵ ($\text{l mol}^{-1} \text{cm}^{-1}$)) 208 (33 000), 250 (15 000), 300 sh, 406 (10 000), 506 (1800). FAB⁺: m/z 633 ($M + \text{lut} + \text{H}$)⁺; 597 ($M - \text{Cl} + \text{lut}$)⁺; 525 (M)⁺; 490 ($M - \text{Cl}$)⁺; 418 ($M - \text{lut}$)⁺; 383 ($M - \text{Cl} - \text{lut}$)⁺; 276 ($M - \text{Cl} - 2 \text{lut}$)⁺. $E_{1/2}$ (MeCN): +0.60 V (rev), -0.98 V (rev).

Reaction of Tetrachlorobis(triphenylphosphine)-technetium(IV) with Acetonitrile

Solid $\text{TcCl}_4(\text{PPh}_3)_2$ (25.0 mg, 0.033 mmol) was suspended in 15 ml of acetonitrile and set to reflux under dinitrogen for 1.5 h, giving a clear orange solution. After cooling to room temperature, the solvent was removed under reduced pressure and the resulting orange oil was dried *in vacuo* to give a glassy solid. When dissolved in methylene chloride and allowed to sit at room temperature overnight, green $\text{TcCl}_4(\text{PPh}_3)_2$ is regenerated. In other solvents, the orange material rapidly decomposes. IR (KBr): 3094(w), 2930(w), 2318(w), 2289(w), 1629(w), 1587(w), 1482(m), 1436(vs), 1314(w), 1121(m), 1089(m), 1027(m), 998(w), 881(w), 746(m), 724(m), 693(vs), 542(m), 521(m), 495(m) cm^{-1} . FAB⁺: m/z 775 [$\text{TcCl}_2(\text{PPh}_3)_2(\text{MeCN})_2$]⁺; 693 [$\text{TcCl}_2(\text{PPh}_3)_2$]⁺; 658 [$\text{TcCl}(\text{PPh}_3)_2$]⁺; 513 [$\text{TcCl}_2(\text{PPh}_3)(\text{MeCN})_2$]⁺; 472 [$\text{TcCl}_2(\text{PPh}_3)(\text{MeCN})$]⁺; 431 [$\text{TcCl}_2(\text{PPh}_3)$]⁺.

Results and Discussion

The neutral complex $\text{TcCl}_4(\text{PPh}_3)_2$ reacts with coordinating solvents such as dimethyl sulfoxide, acetonitrile and pyridine (Fig. 1). In the reaction of $\text{TcCl}_4(\text{PPh}_3)_2$ with dimethyl sulfoxide, the phosphine ligands are displaced by the DMSO to give the neutral yellow product $\text{TcCl}_4(\text{DMSO})_2$. This Tc(IV) species contains oxygen-bound dimethyl sulfoxide as determined from the IR spectrum [4], which displays a very strong $\nu(\text{S}=\text{O})$ stretch at 894 cm^{-1} . The ^1H NMR spectrum, which shows a single broad resonance at 14 ppm, is consistent with the paramagnetism expected for an octahedrally-coordinated Tc(IV) complex. The highest mass peak in the FAB⁺ spectrum, at m/z 548, has the correct isotope pattern for four chloride ligands and corresponds to the molecular ion $\text{TcCl}_4(\text{DMSO})_2(\text{NBA matrix})^+$. The fragmentation pattern

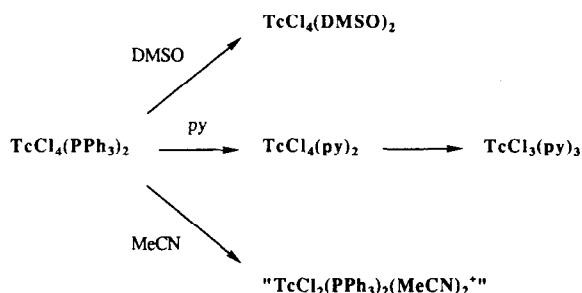


Fig. 1. Reaction scheme for $\text{TcCl}_4(\text{PPh}_3)_2$ with dimethyl sulfoxide, pyridine and acetonitrile.

indicates preferential loss of chloride ligand over DMSO. Interestingly, under the same FAB⁺ conditions the parent complex $\text{TcCl}_4(\text{PPh}_3)_2$ does not appear to ionize.

When green $\text{TcCl}_4(\text{PPh}_3)_2$ is set to reflux in acetonitrile, a clear orange solution results. Numerous attempts to isolate and fully characterize the orange species have been unsuccessful. The parent ion in the FAB⁺ spectrum of the acetonitrile solution corresponds to $[\text{TcCl}_2(\text{PPh}_3)_2(\text{MeCN})_2]^+$, but it is not clear whether the material contains a Tc(IV) or a Tc(III) center. The bis(acetonitrile) compound results from substitution of two acetonitrile ligands for ionic chlorides, whereas in the reactions of $\text{TcCl}_4(\text{PPh}_3)_2$ with dimethyl sulfoxide or pyridine the incoming ligand substitutes for the neutral phosphines. A closely related complex has recently been reported [5]; $\text{TcCl}_3(\text{PPh}_3)_2(\text{MeCN})$ is obtained from the reaction of TcOCl_4^- with PPh_3 in acetonitrile.

The reaction of $\text{TcCl}_4(\text{PPh}_3)_2$ with pyridine gives both Tc(IV) and Tc(III) complexes; prolonged reflux produces $\text{TcCl}_3(\text{py})_3$ in good yield. Substitution of the phosphine ligands apparently occurs prior to the reduction from Tc(IV) to Tc(III), as evidenced by the isolation and identification of the yellow insoluble $\text{TcCl}_4(\text{py})_2$ intermediate. The IR spectrum of this Tc(IV) complex is identical to that reported for the material obtained by decomposition of $(\text{pyH})_2[\text{TcCl}_6]$ in a stream of dry nitrogen at 300 °C [6]. Excess PPh_3 present during the reaction of $\text{TcCl}_4(\text{PPh}_3)_2$ with pyridine increases the rate of formation of the final product $\text{TcCl}_3(\text{py})_3$, suggesting that the free phosphine is the reducing agent. Reaction of $\text{TcCl}_4(\text{PPh}_3)_2$ with 4-methylpyridine or 3,5-dimethylpyridine proceeds analogously, although more rapidly due to the increased basicity of the methyl-substituted ligands. However, lower isolated yields of $\text{TcCl}_3(\text{pic})_3$ and $\text{TcCl}_3(\text{lut})_3$ are achieved due to the work-up procedure necessitated by the elevated boiling points of the substituted pyridines. While numerous examples of $\text{MCl}_3(\text{py})_3$ complexes are known [7], there are no reports of such species being obtained by substitution of pyridine for phosphine ligands.

The octahedral Tc(III) complex possesses a d^4 electronic configuration, and the two resultant unpaired electrons are responsible for the dramatic changes in chemical shift and linewidth that are seen in the ^1H NMR spectra of $\text{TcCl}_3(\text{py})_3$ and its picoline and lutidine analogues [8]. Successful observation of the proton spectrum is due to the extremely short electronic spin relaxation time (T_{1e}) of the Tc(III) center, which must be no longer than 10^{-11} s [9]. Several paramagnetic Tc(III) species, such as $\text{TcCl}_3(\text{PMe}_2\text{Ph})_3$ [3] and $\text{Tc}(\text{F}_3\text{acac})_3$ (where F_3acac is trifluoroacetylacetonato) [10], have been previously characterized by ^1H NMR spectroscopy.

The meridional geometry of the $\text{TcCl}_3(\text{py})_3$ molecule is revealed by its ^1H NMR spectrum (Fig. 2), which consists of six proton resonances and thus indicates two types of pyridine ligands, the two which are mutually *trans* and the unique pyridine. The facial isomer would give only three resonances. The signals can be assigned from relative integrations, relative linewidths, and spin–spin splittings. The two farthest upfield signals are slightly-broadened singlets and arise from the α -protons on the pyridine ligands. Being closest to the paramagnetic technetium center, these protons experience the dipolar interaction to the greatest extent, as seen from their linewidths (35 Hz compared to 5 Hz for the other protons). As a result, the fast-relaxing α -protons do not noticeably affect the spin–spin splitting of their immediate neighbors. The β -protons give the two farthest downfield resonances, doublets which are split by the γ -protons. In turn, the γ -proton resonances are distinct triplets. For each ring position, the resonance due to the unique pyridine ligand appears at higher field compared to the signal arising from the mutually *trans* pyridines. This reflects the fact that the unique pyridine ligand receives greater unpaired electron spin density from the technetium through backbonding than do each of the mutually *trans* pyridines, which are competing against each other.

It is really apparent from the ^1H NMR spectrum of $\text{TcCl}_3(\text{py})_3$ that the contact shift is occurring predominantly via spin delocalization through the π -system of the aromatic ligands [11]. This is evidenced by the alternating sign pattern of the ring position chemical shifts (the α - and γ -protons are shifted upfield while the β -protons are shifted down-

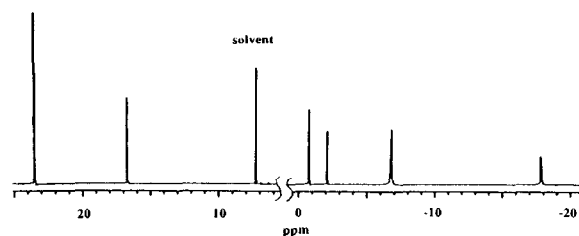


Fig. 2. ^1H NMR spectrum of *mer*- $\text{TcCl}_3(\text{py})_3$ taken in CDCl_3 .

field relative to the expected diamagnetic values) and by the lack of attenuation of the isotropic shifts with increasing distance from the technetium center. To substantiate this observation, the methyl-substituted pyridine analogues $\text{TcCl}_3(\text{pic})_3$ and $\text{TcCl}_3(\text{lut})_3$ were synthesized for ^1H NMR studies. In substituting a methyl group for a proton, the chemical shift of the methyl protons will be opposite in sign to that of the original proton if π -spin delocalization is occurring [12]. This effect is believed to arise from hyperconjugation between the methyl group and the aromatic ring [13].

Comparison of the chemical shifts of $\text{TcCl}_3(\text{pic})_3$ and $\text{TcCl}_3(\text{lut})_3$ with those of $\text{TcCl}_3(\text{py})_3$ shows the expected results for π -spin delocalization of the technetium unpaired electrons via the contact shift mechanism (Table 1). The methyl resonances of the picoline and lutidine complexes are easily identified by relative integrations, and no spin–spin splitting is observed due to the fast-relaxing α -protons and the methyl substituents. For $\text{TcCl}_3(\text{pic})_3$, where the methyl group is in the γ -position, the methyl resonances (30.01, 21.52 ppm) are shifted significantly downfield of the γ -protons in $\text{TcCl}_3(\text{py})_3$, -0.81 , -2.20 ppm). Likewise $\text{TcCl}_3(\text{lut})_3$, with methyl groups in the β ring positions, displays methyl signals (0.28, -2.17 ppm) which are upfield of the β -protons in $\text{TcCl}_3(\text{py})_3$ (23.44, 16.68 ppm). As observed in the case of $\text{TcCl}_3(\text{py})_3$, for the picoline and lutidine complexes each ring position substituent resonates at higher field for the unique nitrogen-donor ligand than for the mutually *trans* ligands.

All of these meridional complexes are orange in the solid state, and yellow–orange in solution. The electronic absorption spectra of these complexes are accordingly very similar, with the major difference being a band in the visible region ($\lambda_{\text{max}} = 506$ nm) which is unique to $\text{TcCl}_3(\text{lut})_3$. The FAB^+ mass spectra of the pyridine, picoline and lutidine compounds are also similar. All three complexes give fragments which correspond to the molecular ion, loss of one chloride ligand, loss of one pyridine

TABLE 1. Chemical shifts of meridional Tc(III) complexes in CDCl_3

Compound	Ligand	δ of ring position (ppm)		
		α	β	γ
$\text{TcCl}_3(\text{py})_3$	<i>trans</i>	-6.77	23.44	-0.81
	unique	-17.88	16.68	-2.20
$\text{TcCl}_3(\text{pic})_3$	<i>trans</i>	-6.07	23.95	30.01
	unique	-20.88	16.87	21.52
$\text{TcCl}_3(\text{lut})_3$	<i>trans</i>	-6.78	0.28	-1.38
	unique	-19.16	-2.17	-3.53

ligand, and loss of both one chloride and one nitrogen-donor ligand.

Cyclic voltammetry was performed on acetonitrile solutions of $\text{TcCl}_3(\text{py})_3$, $\text{TcCl}_3(\text{pic})_3$ and $\text{TcCl}_3(\text{lut})_3$. The complexes exhibit well-defined electrochemistry and display a reversible oxidation and a reversible reduction, both presumably metal-based. Due to the electron-donating methyl substituents on picoline and lutidine, $\text{TcCl}_3(\text{pic})_3$ and $\text{TcCl}_3(\text{lut})_3$ are relatively more electron-rich than is $\text{TcCl}_3(\text{py})_3$ and thus slightly easier to oxidize than the pyridine compound. Likewise, the picoline and lutidine complexes are slightly more difficult to reduce, but they do remain intact after electron-transfer. From electrochemical measurements, there appears to be little difference between picoline and lutidine as ligands in these complexes. The related species $\text{mer-TcCl}_3(\text{PMe}_2\text{Ph})_3$ is reported to undergo a reversible oxidation [14] and an irreversible reduction [15]; both of these processes occur at much more positive potentials for $\text{TcCl}_3(\text{PMe}_2\text{Ph})_3$ (+0.86, -0.75 V) than for $\text{TcCl}_3(\text{py})_3$ (+0.67, -0.92 V). The $E_{1/2}$ values reflect the better π -accepting capability of dimethylphenylphosphine relative to pyridine.

The neutral complexes $\text{TcCl}_4(\text{DMSO})_2$, $\text{TcCl}_4(\text{py})_2$, $\text{TcCl}_3(\text{py})_3$, $\text{TcCl}_3(\text{pic})_3$ and $\text{TcCl}_3(\text{lut})_3$ have been synthesized from $\text{TcCl}_4(\text{PPh}_3)_2$. The Tc(III) species exhibit contact-shifted ^1H NMR spectra which give useful structural information. These novel species are proving useful as starting materials in the synthesis of lower oxidation state complexes of technetium.

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