with respect to As–N bond cleavage to give *cis*-$Pt(PPh_3)_2(NSO)_2$, which was isolated in ca. 70% yield. The identity of the final product is based on elemental analyses, characteristic infrared frequencies at 1243 and 1228 (ν_{as} NSO) and 1098 and 1062 (ν_sNSO) cm^{-1}, the observation of a single 1:4:1 triplet in the $^{31}P\{^1H\}$ NMR spectrum at δ +8.8 with $^1J_{^{195}Pt-^{31}P}$ = 3191 Hz, and the isolation of an identical product from the reaction of $Pt(C_2H_4)(Ph_3P)_2$ with 2 mol of Me_3SiNSO.[39,40] The appearance of two IR bands for both ν_{as}(NSO) and ν_s(NSO) indicates inequivalent NSO groups in *cis*-$Pt(PPh_3)_2(NSO)_2$.[41]

Conversion of $R_{3-n}As(NSO)_n$ into $R_{3-n}As(NSN)_2AsR_{3-n}$ and Preparation of *cis*-$Cr(CO)_4(R_2As_2S_2N_4)$ (R = *t*-Bu (5a), (5b)). The treatment of metal complexes of I (E = P) with potassium *tert*-butoxide produces the corresponding sulfur diimides in high yields.[5b] By contrast, the reactions of **1**, **2a**, or **2b** with potassium *tert*-butoxide were accompanied by extensive cleavage of As–N bonds,[42] and only low yields of sulfur diimides could be obtained. The self-condensation reaction of (thionylimino)arsines can, however, be promoted by heating.

$$2PhAs(NSO)_2 \xrightarrow{100\ ^\circ C} Ph_2As_2S_2N_4 + SO_2 \qquad (3)$$

Attempts to convert **4a** or **4b** to complexes of $R_2As_2S_2N_4$ by thermolysis were unsuccessful, but such complexes were obtained by direct reaction of the ligands with labile metal carbonyl derivatives.[43]

$$\begin{array}{l} Cr(CO)_4C_7H_8 + R_2As_2S_2N_4 \xrightarrow{-C_7H_8} cis\text{-}Cr(CO)_4(R_2As_2S_2N_4) \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{5a},\ R = t\text{-Bu} \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \mathbf{5b},\ R = Ph \end{array} \qquad (4)$$

Conclusion. A preliminary investigation of the coordination chemistry of the novel ligands Ph_2AsNSO and $RAs(NSO)_2$ (R = Ph, *t*-Bu) has revealed the expected pattern of coordination through arsenic with the 16-electron fragment $Cr(CO)_5$. Side-on N=S coordination followed by As–N bond cleavage occurs with the 14-electron fragment $(Ph_3P)_2Pt$. The latter tendency may prove to be a limiting factor in studies of complex formation by these new ligands.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for financial support in the form of an operating grant (T.C.) and an infrastructure grant for the X-ray structural service. A generous gift of $(Me_3N)_3S^+$-$Me_3SiF_2^-$ from Dr. F. Edelmann (Universität Göttingen) is gratefully acknowledged.

Registry No. **1**, 113585-02-7; **2a**, 113585-03-8; **2b**, 113585-04-9; **3**, 113585-05-0; **4a**, 113585-07-2; **4b**, 113585-06-1; **5a**, 113585-09-4; **5b**, 113585-08-3; TAS^+NSO^-, 111718-75-3; $(TAS)^+Me_3SiF_2^-$, 59218-87-0; Me_3SiNSO, 7522-26-1; Ph_2AsCl, 712-48-1; KNSO, 73400-02-9; *t*-$BuAsCl_2$, 4262-41-3; $PhAsCl_2$, 696-28-6; $Me_3SiNSNSiMe_3$, 18156-25-7; $Ph_2As_2S_2N_4$, 70369-32-3; $Pt(C_2H_4)(PPh_3)_2$, 12120-15-9; $Cr(CO)_5(THF)$, 15038-41-2; *cis*-$Pt(PPh_3)_2(NSO)_2$, 108450-77-7; $Cr(CO)_4(C_7H_8)$, 12146-36-0.

Supplementary Material Available: Tables SI–SIII, giving anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, and all bond lengths and bond angles for non-hydrogen atoms (3 pages); Table SIV, giving observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, and Department of Radiology, Harvard Medical School and Brigham and Women's Hospital, Boston, Massachusetts 02115

Complexes of Technetium(III) with Sterically Hindered Arenethiolates and Their Interactions with Small π-Accepting Molecules

Nadine de Vries,[1a] John C. Dewan,[1a] Alun G. Jones,[1b] and Alan Davison*[1a]

Received November 6, 1987

A series of neutral Tc(III) compounds with sterically hindered arenethiolate ligands is reported. They contain a $Tc(SAr)_3$ core (SAr = 2,3,5,6-tetramethylbenzenethiolate (tmbt) or 2,4,6-triisopropylbenzenethiolate (tibt)) capped by two π-accepting ligands (MeCN, *i*-PrNC, py, or CO) to form a trigonal bipyramid and are air stable, diamagnetic, 14-electron compounds. Although the acetonitrile ligands in the parent compound $Tc(SAr)_3(MeCN)_2$ do not self-exchange with solvent MeCN-d_3, they are readily displaced by CO or *i*-PrNC to yield $Tc(SAr)_3(CO)_2$ or $Tc(SAr)_3(i\text{-}PrNC)_2$, respectively. One of the carbonyl ligands in $Tc(SAr)_3(CO)_2$ is labile, and this property has been exploited to prepare the monocarbonyl complexes $Tc(SAr)_3(CO)(MeCN)$ and $Tc(SAr)_3(CO)(py)$. Single-crystal X-ray structure determinations were carried out on $Tc(SC_{10}H_{13})_3(CH_3CN)_2$ (crystal data: monoclinic, a = 11.227 (1) Å, b = 15.784 (1) Å, c = 20.411 (1) Å, β = 105.36 (1)°, space group $P2_1/n$, Z = 4, final R = 0.066, R_w = 0.073), $Tc(SC_{10}H_{13})_3(CO)(CH_3CN)$ (monoclinic, a = 13.072 (2) Å, b = 15.153(2) Å, c = 17.149 (2) Å, β = 98.46 (1)°, space group $P2_1/n$, Z = 4, final R = 0.046, R_w = 0.059), and $Tc(SC_{10}H_{13})_3(CO)(C_5H_5N)$ (triclinic, a = 10.773 (1) Å, b = 18.018 (1) Å, c = 9.034 (1) Å, α = 93.67 (1)°, β = 96.05 (1)°, γ = 87.08 (1)°, space group $P\bar{1}$, Z = 2, final R = 0.044, R_w = 0.063). The coordination sphere is similar for all three structures, in which the sulfur atoms sit in the equatorial plane of a trigonal bipyramid and the π-accepting ligands occupy the axial positions. Two of the aryl rings are consistently on the same side of the plane defined by the sulfur atoms, while the other is on the opposite side. Spectroscopic data suggest that every compound in the series shares this conformation.

Due to its role in a number of enzymatic systems, the chemistry of transition-metal thiolate complexes has received much attention.[2] However, the analogous technetium chemistry remains essentially unexplored. The affinity of Tc(V) oxo complexes for

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thiolate ligands has been established,[3-6] but with the exception of $Tc_2(SC_6H_4S)_4$,[7] a dimeric Tc(IV) compound with bidentate ligands, no complexes in lower oxidation states have been reported. tris(2-aminobenzenethiolato)technetium has been claimed to be a Tc(III) complex,[8] but there is no evidence that it is not in fact the fully deprotonated, well-characterized Tc(VI) complex.[9-11]

Through the use of sterically hindered arenethiolate ligands, we have been able to stabilize a number of monomeric complexes of Tc(III) with two sites that can accommodate small π-accepting molecules. We have already reported that the reduction of $[TcO(tmbt)_4]^-$ (tmbt = 2,3,5,6-tetramethylbenzenethiolate) by PEt_3 yields $Tc(tmbt)_3(PEt_3)_2$, a Tc(III) compound.[12] This complex, $Tc(tmbt)_3(PEt_3)_2$, is an undesirable intermediate for the synthesis of the species described here. Therefore, we undertook the preparation of the more synthetically useful compounds $Tc(tmbt)_3(MeCN)_2$ and $Tc(tibt)_3(MeCN)_2$ (tibt = 2,4,6-triisopropylbenzenethiolate) directly from $(NH_4)_2[TcCl_6]$. The reactivity of these compounds toward CO and CNR (R = alkyl group) and the chemistry and properties of the resulting complexes are described herein.

Experimental Section

Syntheses. *Caution*! Technetium-99 is a weak β^--emitter (E = 0.292 MeV, $t_{1/2} = 2.12 \times 10^5$ years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[4]

Ammonium pertechnetate was supplied as a gift by Du Pont/Biomedical Products. Reagents and solvents were used as received unless otherwise indicated. Column chromatography was performed by using Keiselgel TLC grade silica gel. The ligands, 2,3,5,6-tetramethylbenzenethiol (Htmbt) and 2,4,6-triisopropylbenzenethiol (Htibt), were supplied by Michelle Millar.[13] ^{1}H and ^{13}C NMR spectra were recorded on Bruker WM 250 and WM 270 and Varian XL-300 and VXR-500 FTNMR spectrometers. Routine infrared spectra were obtained on an IBM System 9000 FTIR, high-resolution infrared spectra on a Nicolet 7000 FTIR, and UV-visible spectra on an HP 8451A diode array spectrophotometer. Fast atom bombardment mass spectra of samples dissolved in a 3-nitrobenzyl alcohol matrix were recorded with a MAT 731 mass spectrometer equipped with an Ion Tech B11N FAB gun and operating at an accelerating voltage of 8 kV. The FAB gun produced a beam of 6–8-keV xenon neutrals. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA.

$Tc(tmbt)_3(MeCN)_2$ (1). The following reaction was performed under an atmosphere of dinitrogen. Sodium methoxide (180 mg, 3.3 mmol) and Htmbt (330 mg, 2.0 mmol) were dissolved in 15 mL of freshly distilled MeOH, and the solution was added via cannula to a suspension of $(NH_4)_2[TcCl_6]$[14] (225 mg, 0.65 mmol) and Zn dust (75 mg) in 15 mL of distilled MeCN. The resulting mixture was stirred at room temperature for 30 min, opened to the air, and filtered to separate a blue precipitate, which was then dissolved in CH_2Cl_2. The solvent was removed from the filtrate under reduced pressure, and the residual solid was extracted with 3:1 hexanes/CH_2Cl_2. The extract was combined with the CH_2Cl_2 solution, and the solvent was removed from the combined mixture under reduced pressure. Recrystallization of the blue solid from hot 1:1 MeCN/MeOH produced X-ray quality crystals; yield 303 mg (70%).

Anal. Calcd for $C_{34}H_{45}N_2S_3Tc$: C, 60.34; H, 6.70; N, 4.14; S, 14.21. Found: C, 60.25; H, 6.85; N, 4.11; S, 14.24. IR (KBr): ν(NC) = 2255 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} = 328 nm (ϵ = 40 500 L cm^{-1} mol^{-1}), 648 (1100). ^{1}H NMR ($CDCl_3$): δ 1.12 (s, 3 H, CH_3CN), 1.85 (s, 3 H, CH_3CN), 2.09 (s, 6 H, ArCH_3), 2.15 (s, 6 H, ArCH_3), 2.19 (s, 12 H, ArCH_3), 2.25 (s, 6 H, ArCH_3), 2.28 (s, 6 H, ArCH_3), 6.81 (s, 2 H, Ar H), 6.94 (s, 1 H, Ar H). FABMS(+): m/z = 676 (M)$^+$, 652 (M – MeCN)$^+$, 594 (M – 2MeCN)$^+$, 428 (Tc(tmbt)$_2$ – H)$^+$, 330 ((tmbt)$_2$)$^+$.

$Tc(tibt)_3(MeCN)_2$ (2). This compound was prepared similarly to **1**; yield 74% as dark blue crystals.

Anal. Calcd for $C_{49}H_{75}N_2S_3Tc$: C, 66.33; H, 8.52; N, 3.16; S, 10.84. Found: C, 66.10; H, 8.61; N, 3.16; S, 10.89. IR (KBr): ν(NC) = 2256 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} = 328 nm (ϵ = 43 000 L mol^{-1} cm^{-1}), 590 sh, 650 (1000). ^{1}H NMR ($CDCl_3$): δ 1.0–1.3 (m, 57 H, ArCH(CH_3)$_2$ and CH_3CN), 1.79 (s, 3 H, CH_3CN), 2.81 (m, 3 H, ArCHMe$_2$), 3.26 (m, 2 H, ArCHMe$_2$), 3.65 (m, 2 H, ArCHMe$_2$), 3.87 (m, 2 H, ArCHMe_2), 6.83 (s, 2 H, Ar H), 6.88 (s, 2 H, Ar H), 7.01 (s, 2 H, Ar H). FABMS(+): m/z = 886 (M)$^+$, 844 (M – MeCN – H)$^+$, 803 (M – 2MeCN – H)$^+$, 788 (M – 2MeCN – Me)$^+$, 567 (M – tibt – 2MeCN – 2H)$^+$.

$Tc(tmbt)_3(i\text{-}PrNC)_2$ (3). Isopropyl isocyanide (1.0 mL, excess) was added to a solution of **1** (49 mg, 0.073 mmol) in 15 mL of CH_2Cl_2. Within 1 min the color of the solution changed from blue to purple-pink. The solvent was removed under reduced pressure, leaving a deposit of analytically pure purple crystals that were suspended in distilled H_2O, collected, and dried in vacuo; yield 50 mg (94%).

Anal. Calcd for $C_{38}H_{53}N_2S_3Tc$: C, 62.27; H, 7.29; N, 3.82; S, 13.12. Found: C, 62.16; H, 7.42; N, 3.85; S, 13.11. IR (KBr): ν(CN) = 2108 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} = 334 nm (ϵ = 68 000 L mol^{-1} cm^{-1}), 560 nm (2400). ^{1}H NMR ($CDCl_3$): δ 0.40 (d, 6 H, CNCH(CH_3)$_2$), 1.00 (d, 6 H, CNCH(CH_3)$_2$), 2.15 (s, 6 H, ArCH_3), 2.16 (s, 6 H, ArCH_3), 2.20 (s, 12 H, ArCH_3), 2.25 (s, 6 H, ArCH_3), 2.28 (s, 6 H, ArCH_3), 2.89 (m, 1 H, CNCHMe$_2$), 3.65 (m, 1 H, CNCHMe$_2$), 6.81 (s, 2 H, Ar H), 6.93 (s, 1 H, Ar H). FABMS(+): m/z = 732 (M)$^+$, 663 (M – *i*-PrNC)$^+$, 567 (M – tmbt)$^+$, 330 ((tmbt)$_2$)$^+$.

$Tc(tibt)_3(i\text{-}PrNC)_2$ (4). This compound was prepared similarly to **3**; yield 93% as purple crystals.

Anal. Calcd for $C_{53}H_{83}N_2S_3Tc$: C, 67.48; H, 8.87; N, 2.97; S, 10.20. Found: C, 67.29; H, 8.91; N, 2.96; S, 10.21. IR (KBr): ν(CN) = 2106 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} 336 nm (ϵ = 51 000 L mol^{-1} cm^{-1}), 526 (1200), 564 (1400). ^{1}H NMR ($CDCl_3$): δ 1.09 (d, 6 H, CNCH(CH_3)$_2$), 1.00–1.35 (m, 60 H, ArCH_3 and CNCH(CH_3)$_2$), 2.85 (m, 4 H, –CHMe$_2$), 3.26 (m, 2 H, –CHMe$_2$), 3.59 (m, 3 H, –CHMe$_2$), 3.82 (m, 2 H, –CHMe$_2$), 6.81 (d, 2 H, Ar H), 6.92 (d, 2 H, Ar H), 7.00 (s, 2 H, Ar H). FABMS(+): m/z 942 (M)$^+$, 873 (M – *i*-PrNC)$^+$, 707 (M – tibt)$^+$, 567 (M – tibt – 2*i*-PrNC – 2 H)$^+$, 470 ((tibt)$_2$)$^+$.

$Tc(tmbt)_3(CO)_2$ (5). Compound **1** (52 mg, 0.077 mmol) was dissolved in 100 mL of CH_2Cl_2, and CO was bubbled through the solution overnight, evaporating all of the solvent. The product was chromatographed on a silica gel column eluted with $CHCl_3$ under pressure (2 psi) of CO. An equal volume of methanol was added to the major fraction and the $CHCl_3$ removed with a stream of CO to produce a crystalline, orange product that was collected, washed with methanol, and dried in vacuo; yield 32 mg (64%).

Anal. Calcd for $C_{32}H_{39}O_2S_3Tc$: C, 59.06; H, 6.04; S, 14.78; N, 0. Found: C, 58.54; H, 6.19; S, 14.77; N, 0.0. IR (methylcyclohexane): ν(CO) = 1997 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} = 276 nm (ϵ = 16 000 L mol^{-1} cm^{-1}), 276 (16 000), 358 (60 000). ^{1}H NMR (CD_2Cl_2): δ 2.10–2.3 (m, 36 H, ArCH_3), 6.93 (s, 2 H, Ar H), 7.07 (s, 1 H, Ar H). ^{13}C NMR ($CDCl_3$): δ 197 (br, 350 Hz) (*C*O). FABMS(+): m/z = 651 (MH)$^+$, 622 (M – CO)$^+$, 593 (M – 2CO – H)$^+$, 428 (Tc(tmbt)$_2$ – H)$^+$.

$Tc(tibt)_3(CO)_2$ (6). This compound was prepared similarly to **5**; yield 62% as orange crystalline material.

Anal. Calcd for $C_{47}H_{69}O_2S_3Tc$: C, 65.55; H, 8.08; S, 11.21. Found: C, 65.25; H, 8.12; S, 11.17. IR (methylcyclohexane): ν(CO) = 1997 cm^{-1}. UV–vis (CH_2Cl_2): λ_{max} = 362 nm (ϵ = 58 000 L mol^{-1} cm^{-1}). ^{1}H NMR ($CDCl_3$): δ 1.0–1.4 (m, 54 H, ArCH(CH_3)$_2$), 2.83 (m, 2 H,

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$\mathrm{ArC}H\mathrm{Me}_2$), 2.94 (m, 1 H, $\mathrm{ArC}H\mathrm{Me}_2$), 3.30 (m, 2 H, $\mathrm{ArC}H\mathrm{Me}_2$), 3.41 (m, 2 H, $\mathrm{ArC}H\mathrm{Me}_2$), 3.63 (m, 2 H, $\mathrm{ArC}H\mathrm{Me}_2$), 6.87 (s, 2 H, Ar H), 6.97 (m, 2 H, Ar H), 7.05 (m, 2 H, Ar H). ^{13}C NMR ($\mathrm{CDCl_3}$): δ 197 (br, 350 Hz) (*C*O). FABMS(+): m/z = 860 $(\mathrm{M})^+$, 832 $(\mathrm{M} - \mathrm{CO})^+$, 804 $(\mathrm{M} - 2\mathrm{CO})^+$.

$\mathbf{Tc(tmbt)_3(CO)(MeCN)}$ (7). A solution of compound **5** (10.34 mg, 0.015 mmol) in MeCN (20 mL) was allowed to reflux for 3 days. The solvent was removed under reduced pressure, and the product was chromatographed on a silica gel column eluted with $\mathrm{CHCl_3}$. Recrystallization from hot MeCN yielded 7.27 mg (62%) of orange crystals.

Anal. Calcd for $\mathrm{C_{33}H_{42}NOS_3Tc}$: C, 59.71; H, 6.38; N, 2.11; S, 14.49. Found: C, 59.95; H, 6.64; N, 1.87; S, 14.65. IR (methylcyclohexane): ν(CO) = 1960 cm^{-1}. UV–vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ = 344 nm (ϵ = 53 000 L mol^{-1} cm^{-1}), 460 sh. ^{1}H NMR ($\mathrm{CDCl_3}$):[15] δ 1.06 (s, 30% of 3 H, $\mathrm{C}H_3\mathrm{CN}$), 1.82 (s, 70% of 3 H, $\mathrm{C}H_3\mathrm{CN}$), 2.1–2.4 (m, 36 H, $\mathrm{ArC}H_3$), 6.83 (s, 24% of 3 H, Ar H), 6.87 (s, 46% of 3 H, Ar H), 6.97 (s, 20% of 3 H, Ar H); 7.00 (s, 10% of 3 H, Ar H). FABMS(+): m/z = 1244 $(\mathrm{M_2} - 2\mathrm{MeCN})^+$, 1215 $(\mathrm{M_2} - 2\mathrm{MeCN} - \mathrm{CO})^+$, 1079 $(\mathrm{M_2} - \mathrm{tmbt} - 2\mathrm{MeCN})^+$, 1051 $(\mathrm{M_2} - \mathrm{tmbt} - 2\mathrm{MeCN} - \mathrm{CO})^+$, 622 $(\mathrm{M} - \mathrm{MeCN})^+$, 593 $(\mathrm{M} - 2\mathrm{MeCN} - \mathrm{H})^+$, 428 $(\mathrm{M} - \mathrm{tmbt} - 2\mathrm{MeCN} - \mathrm{H})^+$.

$\mathbf{Tc(tibt)_3(CO)(MeCN)}$ (8). This compound was prepared analogously to **7**; yield 68% of orange crystals.

Anal. Calcd for $\mathrm{C_{48}H_{72}NOS_3Tc}$: C, 65.95; H, 8.30; N, 1.60; S, 11.00. Found: C, 66.23; H, 8.39; N, 1.38; S, 11.21. IR (methylcyclohexane): ν(CO) = 1962 cm^{-1}. UV–vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ = 346 nm (ϵ = 33 000 L mol^{-1} cm^{-1}). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.8–1.4 (m, 54 H + 60% of 3 H, $\mathrm{ArCH(C}H_3)_2$ and $\mathrm{C}H_3\mathrm{CN}$), 1.78 (s, 40% of 3 H, $\mathrm{CH_3CN}$), 2.6–3.9 (m, 9 H, $\mathrm{ArC}H\mathrm{(CH_3)_2}$), 6.6–7.1 (m, 6 H, Ar H). FABMS(+): m/z = 832 $(\mathrm{M} - \mathrm{MeCN})^+$, 817 $(\mathrm{M} - \mathrm{MeCN} - \mathrm{Me})^+$, 567 $(\mathrm{M} - \mathrm{tibt} - \mathrm{MeCN})^+$.

$\mathbf{Tc(tmbt)_3(CO)(py)}$ (9). Compound **5** (79 mg, 0.11 mmol) was dissolved in pyridine (25 mL), and the solution was set to reflux for 3 h. The resulting red solution was cooled, the volume reduced to an oil, and the product purified on a silica gel column eluted with $\mathrm{CHCl_3}$. Methanol (5 mL) was added to the major orange band, and the $\mathrm{CHCl_3}$ was allowed to evaporate, producing a crop of crystals that was collected, washed with MeOH, and dried in vacuo; yield 76 mg (90%).

Anal. Calcd for $\mathrm{C_{36}H_{44}NOS_3Tc}$: C, 61.60; H, 6.22; S, 13.70; N, 1.99. Found: C, 61.58; H, 6.49; S, 13.62; N, 2.08. IR (methylcyclohexane): ν(CO) = 1955 cm^{-1}. UV–vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ = 284 nm (ϵ = 36 000 L mol^{-1} cm^{-1}), 344 (100 000), 482 (4000). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 2.0–2.4 (m, 36 H, $\mathrm{ArC}H_3$), 6.61 (s, 1 H, Ar H), 6.72 (s, 2 H, Ar H), 7.03 (t, 2 H, py β-H), 7.54 (t, 1 H, py γ-H), 8.89 (d, 2 H, py α-H). FABMS(+): m/z = 1402 $(\mathrm{M_2})^+$, 1322 $(\mathrm{M_2} - \mathrm{py} - \mathrm{H})^+$, 1243 $(\mathrm{M_2} - 2\mathrm{py} - \mathrm{H})^+$, 1237 $(\mathrm{M_2} - \mathrm{tmbt})^+$, 1158 $(\mathrm{M_2} - \mathrm{tmbt} - \mathrm{py})^+$, 701 $(\mathrm{M})^+$, 673 $(\mathrm{M} - \mathrm{CO})^+$, 622 $(\mathrm{M} - \mathrm{py})^+$, 593 $(\mathrm{M} - \mathrm{CO} - \mathrm{py})^+$, 536 $(\mathrm{M} - \mathrm{tmbt})^+$, 428 $(\mathrm{M} - \mathrm{tmbt} - \mathrm{CO} - \mathrm{py} - \mathrm{H})^+$, 389 $(\mathrm{Tc_2(CO)(tmbt)})^+$.

$\mathbf{Tc(tibt)_3(CO)(py)}$ (10). This compound was prepared analogously to **9**; yield 77% as orange crystals.

Anal. Calcd for $\mathrm{C_{49}H_{72}NOS_3Tc}$: C, 67.14; H, 8.17; S, 10.54; N, 1.54. Found: C, 66.47; H, 8.20; S, 10.42; N, 1.51. IR (methylcyclohexane): ν(CO) = 1963 cm^{-1}. UV–vis ($\mathrm{CH_2Cl_2}$): $\lambda_{\max}$ = 348 nm (ϵ = 100 000 L mol^{-1} cm^{-1}). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 0.8–1.4 (m, 54 H, $\mathrm{ArCH(C}H_3)_2$), 2.5–3.0 (m, 4 H, $\mathrm{ArC}H\mathrm{(CH_3)_2}$), 3.1–3.4 (m, 3 H, $\mathrm{ArC}H\mathrm{(CH_3)_2}$), 3.4–3.6 (m, 2 H, $\mathrm{ArC}H\mathrm{(CH_3)_2}$), 3.7–3.9 (m, 2 H, $\mathrm{ArC}H\mathrm{(CH_3)_2}$), 2.29 (s, 2 H, Ar H), 6.70 (s, 2 H, Ar H), 7.02 (t, 2 H, py β-H), 7.09 (s, 2 H, Ar H), 7.49 (t, 1 H, py γ-H), 8.88 (d, 2 H, py α-H). FABMS(+): m/z = 911 $(\mathrm{M})^+$, 832 $(\mathrm{M} - \mathrm{py})^+$, 804 $(\mathrm{M} - \mathrm{CO} - \mathrm{Py})^+$, 676 $(\mathrm{M} - \mathrm{tibt})^+$, 554 $(\mathrm{M} - \mathrm{CO} - \mathrm{py} - \mathrm{tibt} - \mathrm{Me})^+$.

Rhenium Complexes $\mathbf{Re(SAr)_3L_2}$. Rhenium compounds were made either by modification of the method of Dilworth et al.[16] (L = MeCN, CO) or by the methods described above for the analogous technetium complexes (L = *i*-PrNC). Compounds were characterized by IR, ^{1}H NMR, and UV–visible spectroscopies and by FABMS(+). The chemical properties and spectral characteristics of $\mathrm{Re(tmbt)_3(MeCN)_2}$ and $\mathrm{Re(tmbt)_3(CO)_2}$ were consistent with those previously reported.[16] The spectra and chemical properties of $\mathrm{Re(tmbt)_3(\mathit{i}\text{-}PrNC)_2}$ indicated that it was the direct analogue of the fully characterized technetium compound.

X-ray Crystal Structures. Crystal data are presented in Table I.

$\mathbf{Tc(tmbt)_3(MeCN)_2}$. X-ray-quality crystals (prisms) were grown from hot 1:1 acetonitrile/methanol. Data collection, reduction, and refinement procedures have been described in detail elsewhere.[17] Solution and refinement of the structure were carried out by using SHELX-76. The structure was solved by using Patterson methods, and an absorption correction was applied. Hydrogen atoms were ignored, and all other atoms were refined anisotropically.

$\mathbf{Tc(tmbt)_3(CO)(MeCN)}$. Thick needles were grown by slow evaporation of methylene chloride from a methylene chloride/methanol solution of **7**. The data set was collected at room temperature on a Rigaku AFC6R diffractometer with graphite Mo Kα radiation and a 12KW rotating anode generator. Solution and refinement were carried out by using the TEXSAN programs of the Molecular Structure Corp. The structure was solved by using Patterson methods, and an absorption correction was applied. At least one hydrogen atom per methyl group was located on a difference map, with the positions of the others being calculated on the basis of that position. All non-hydrogen atoms were refined anisotropically.

$\mathbf{Tc(tmbt)_3(CO)(py)}$. Thick needles were grown by slow evaporation of methylene chloride from a methylene chloride/methanol solution of **9**. Data collection and refinement conditions were the same as for **7**, above. The structure was solved by using direct methods. At least one hydrogen atom per methyl group was located on a difference map, and the others were refined as above. All non-hydrogen atoms were refined anisotropically.

NMR Studies. High-temperature ^{1}H NMR studies were carried out on samples of **3** in DMSO-d_6 on a Bruker 270-MHz FTNMR spectrometer. Spectra were recorded at 10° intervals from 293 to 383 K. Low-temperature ^{13}C NMR studies were carried out on **5** by using a Varian XL-300 FTNMR spectrometer. Samples were dissolved in 60:27:13 $\mathrm{CD_2Cl_2/CHCl_3/CCl_4}$ and spectra recorded at 22, −30, and −60 °C. Magnetization transfer experiments were conducted by using two methods. In the first method, conducted on a Varian XL-300 FTNMR spectrometer, one of the MeCN signals of **7** was continuously irradiated by using a homonuclear decoupler and the change in the intensity of the other MeCN resonance was recorded. The second experiment was carried out on a Varian VXR-500 FTNMR spectrometer using a pulse sequence consisting of a selective 180° pulse, a variable time delay of 0.03–1.4 s, and a 90° observation pulse.[18]

Results and Discussion

Syntheses and Reactivities. The complexes $\mathrm{Tc(tmbt)_3(MeCN)_2}$ (**1**) and $\mathrm{Tc(tibt)_3(MeCN)_2}$ (**2**) are prepared under an inert atmosphere by adding an alkaline methanolic solution of HSAr to a suspension of $\mathrm{(NH_4)_2[TcCl_6]}$ and zinc dust in acetonitrile. Unlike in the synthesis of the analogous rhenium compounds, which requires elevated temperatures for the reduction from Re(IV) to Re(III),[16] Tc(IV) is reduced rapidly to Tc(III) at room temperature. Thiolate alone is sufficient as the reductant, but zinc has been shown to be an effective reductant in basic methanolic solutions[19] and improves the yield. If the reaction is performed in air, oxidation takes place and Tc(V) oxo species are isolated as the major products.[12] The bright blue compounds **1** and **2** unlike their rhenium analogues, are air stable indefinitely as solids. They decompose slowly in solution over a period of days whereas the rhenium complexes undergo marked decomposition in a matter of minutes.

The alkyl isocyanide analogues, $\mathrm{Tc(tmbt)_3(\mathit{i}\text{-}PrNC)_2}$ (**3**) and $\mathrm{Tc(tibt)_3(\mathit{i}\text{-}PrNC)_2}$ (**4**), are easily and quantitatively prepared by ligand substitution from **1** and **2** and are extremely robust compounds. Addition of an excess of an alkyl isocyanide (R = *i*-Pr, *t*-Bu, Cy) to a solution of **1** or **2** is immediately followed by a color change from blue to pink-purple. At room temperature the reaction stops with the substitution of CNR for MeCN in the Tc(III) complexes, but at elevated temperatures the excess isocyanide reacts further to produce the Tc(I) complexes $[\mathrm{Tc(CNR)_6}]^+$.[20]

The displacement of the acetonitrile ligands on **1** and **2** by carbon monoxide is not as rapid as their replacement by alkyl isocyanides. When compound **1** or **2** is placed in $\mathrm{CH_2Cl_2}$ and CO is bubbled through the solution, there is a color change within minutes, but the reaction goes to completion slowly, and total conversion to the dicarbonyl takes approximately 12 h. The reaction appears to proceed stepwise through a $\mathrm{Tc(SAr)_3(CO)(MeCN)}$ intermediate that, like the final product, is orange. Separating the small amount of monocarbonyl formed in these

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(15) Integral intensities of peaks due to different conformations are given as the percent of the total integral for the compound.

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Table I. X-ray Data for Structure Determinations of **1**, **7**, and **9**

compd	1	7	9
empirical formula	$C_{34}H_{45}N_2S_3Tc$	$C_{33}H_{42}NOS_3Tc$	$C_{36}H_{44}NOS_3Tc$
fw	676.93	661.88	701.93
cryst color, habit	blue prism	orange needle	orange needle
cryst dimens, mm	0.3 × 0.5 × 0.4	0.2 × 0.2 × 0.5	0.2 × 0.4 × 0.5
cryst system	monoclinic	monoclinic	triclinic
a, Å	11.227 (1)	13.072 (2)	10.773 (1)
b, Å	15.784 (1)	15.153 (2)	18.018 (1)
c, Å	20.411 (1)	17.149 (2)	9.034 (1)
α, deg			93.67 (1)
β, deg	105.36 (1)	98.46 (1)	96.05 (1)
γ, deg			87.08 (1)
space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$
Z	4	4	2
D(calcd), g/cm^3	1.29	1.31	1.34
D(exptl), g/cm^3	1.27	1.30	1.31
μ, cm^{-1}	49.9	6.18	6.02
diffractometer	Enraf-Nonius CAD4F-11	Rigaku AFC-6R	Rigaku AFC-6R
radiation (λ, Å) (graphite monochromated)	Cu Kα (1.5418)	Mo Kα (0.71069)	Mo Kα (0.71069)
temp, °C	23	23	23
no. of reflcns used in cell detmn (2θ range, deg)	25 (>30)	25 (28.9–29.9)	25 (29.6–30.0)
scan mode	ω–2θ	ω–2θ	ω–2θ
scan width, deg	$0.8 + 0.14 \tan\theta$	$1.05 + 0.35 \tan\theta$	$1.15 + 0.35 \tan\theta$
scan rate, deg/min	4.0 (in ω)	8.0 (in ω)	32 (in ω)
max 2θ, deg	120	55	55
no. of reflcns measd			
total	5171	8398	8456
unique	3470	8056	8028
octant collcd	$\pm h,+k,+l$	$+h,+k,\pm l$	$+h,\pm k,\pm l$
R_{int}	0.005	0.005	0.006
cor (Lorentz–polarization)	empirical	empirical abs using DIFABS[a]	empirical abs using DIFABS[a]
T_{max}, T_{min}	1.33, 0.85	1.00, 0.97	1.23, 0.66
structure soln	Patterson method	Patterson method	direct methods
refinement	full-matrix LS		
function minimized	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\sum w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
least-squares, wt	$0.71/(\sigma^2(F_o) + 0.0004F_o^2)$	$4F_o^2/\sigma^2(F_o^2)$	$4F_o^2/\sigma^2(F_o^2)$
atomic scatt factors[b]	neutral-atom scatt factors used throughout		
anomalous dispersion[c]	all non-H atoms		
extinction effects	not obsd		
criterion, no. of obsvns	$I > 2\sigma(I)$, 3470	$I > 3\sigma(I)$, 4606	$I > 3\sigma(I)$, 6432
no. of variables	361	352	379
R, R_w	0.066, 0.073	0.046, 0.059	0.044, 0.063
max shift/error in final cycle	0.001	0.02	0.071
max peak in final diff map, e Å^{-3}	0.55	0.61	0.82

[a] TEXSAN software of the Molecular Structure Corp. [b] *International Tables for X-Ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV. [c] Anomalous dispersion effects were included in F_c: Ibers, J. A.; Hamilton, W. C. *Acta Crystallogr.* **1964**, *17*, 781.

reactions from the dicarbonyl that is always present is difficult because of their similar solubilities. However, comparison of the infrared CO stretching mode with that of isolated $Tc(SAr)_3(CO)(MeCN)$, synthesized via a different route, confirms its identity. Longer reaction times cause the disappearance of the monocarbonyl species and lead solely to the air-stable dicarbonyl compounds **5** and **6**. One of the carbonyl ligands in **5** and **6** is labile, and in order to avoid any decomposition, the subsequent workup must be carried out under an atmosphere of CO. Lability of mutually trans carbonyl ligands is well documented. For example, the complexes $[Ru(porphyrin)(CO)_2]$[21] and $[Mo(tibt)_3(CO)_2]^-$[22] can easily lose one CO and coordinate a variety of trans ligands. The second CO, however, is tightly bound, does not dissociate, and is not readily displaced.

Monocarbonyl compounds are conveniently made by exploiting the trans-labilizing effect of the CO ligands in **5** and **6**. The complexes $Tc(SAr)_3(CO)(MeCN)$ and $Tc(SAr)_3(CO)(py)$ are prepared by refluxing $Tc(SAr)_3(CO)_2$ in acetonitrile or pyridine, respectively. Both reactions can be easily reversed by bubbling CO through a solution of the monocarbonyl in a noncoordinating solvent. Alternatively, $Tc(SAr)_3(CO)(MeCN)$ can be prepared by bubbling CO though a solution of the bis(acetonitrile) complexes, **1** and **2**, in acetonitrile. Competition of CO and MeCN for the site trans to the first CO can then be controlled to favor the retention of MeCN because of its much greater concentration. However, even under these conditions, formation of small quantities of the dicarbonyl compound cannot be suppressed.

The most likely mechanism for axial ligand substitution is an associative process. Solutions of **1** in MeCN-d_3 show no incorporation of the label after 3 days at room temperature whereas displacement by CO and CNR occurs in minutes. This suggests that the reaction is initiated by attack of a strong π-accepting ligand rather than loss of MeCN. Loss of a ligand would require a 12-electron, four-coordinate species, while an associative mechanism would produce a more favorable intermediate, a 16-electron, six-coordinate species. In support of this, the isoelectronic complex $[Mo(tibt)_3(CO)_2]^-$ is reported to bind CO reversibly,[22] yielding a species that is analogous to the proposed intermediates.

Ligands such as CO and CNR are stronger π-accepting ligands than MeCN, and once one is bound, the remaining trans MeCN ligand, in a five-coordinate complex, is easily displaced. The reaction of **1** with only 1 equiv of CNR does not lead to $Tc(tmbt)_3(MeCN)(CNR)$, or to a statistical mixture of products, but to 0.5 equiv each of the bis(isocyanide) complex and $Tc(tmbt)_3(MeCN)_2$.

Crystal Structures. Single-crystal X-ray structure determinations were carried out on a representative sample of compounds: **1**, **7**, and **9**. Atomic positional parameters are listed in Tables II–IV, the ORTEP-drawn diagrams are shown in Figure 1, and some relevant bond distances and angles are summarized in Tables V–VII.

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[21] Eaton, S. S.; Eaton, G. R.; Holm, R. H. *J. Organomet. Chem.* **1971**, *32*, C52.

[22] Blower, P. J.; Dilworth, J. R.; Hutchinson, J.; Nicholson, T.; Zubieta, J. A. *J. Chem. Soc., Dalton Trans.* **1985**, 2639.

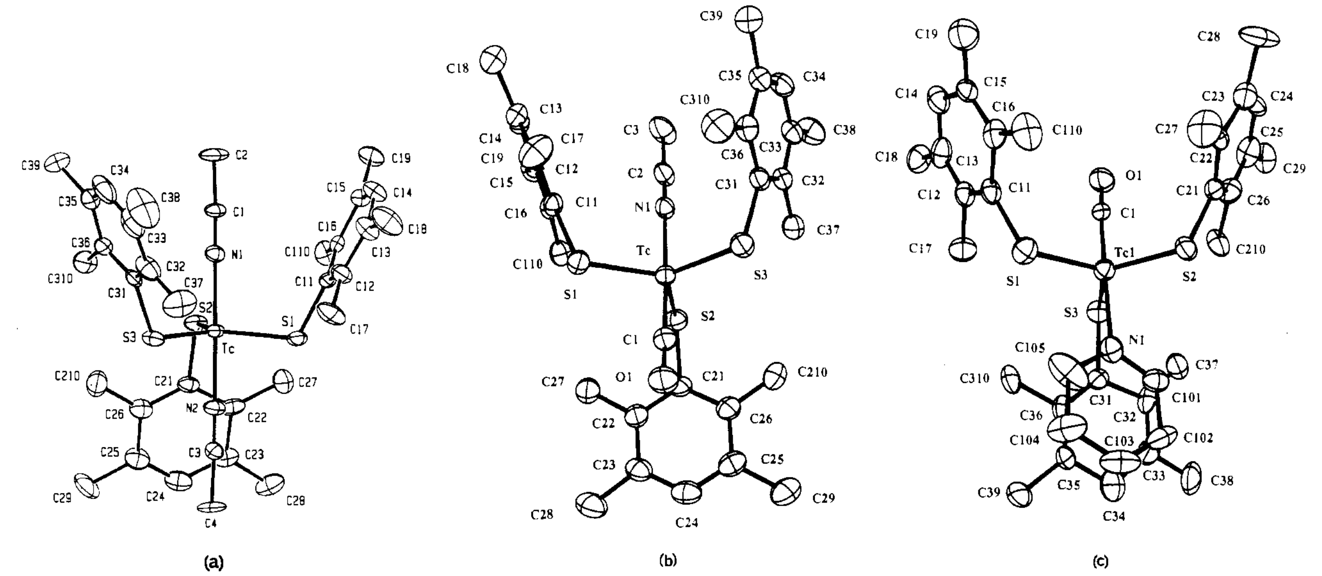

Figure 1. ORTEP representations of the structures of (a) Tc(tmbt)$_3$(MeCN)$_2$ (**1**), (b) Tc(tmbt)$_3$(CO)(MeCN) (**7**), and (c) Tc(tmbt)$_3$(CO)(py) (**9**) showing the atom-labeling schemes and 30% probability ellipsoids. The hydrogen atoms on **7** and **9** have been omitted for clarity.

Table II. Atomic Positional Parameters for **1**

atom	*x*	*y*	*z*
Tc	0.10188 (7)	0.13274 (5)	0.26041 (4)
S1	0.1259 (3)	0.10360 (15)	0.15650 (14)
S2	−0.0855 (3)	0.17205 (15)	0.26922 (15)
S3	0.2554 (3)	0.11134 (15)	0.35483 (15)
N1	0.1380 (7)	0.2591 (5)	0.2565 (4)
N2	0.0635 (8)	0.0068 (5)	0.2657 (4)
C1	0.1500 (9)	0.3311 (6)	0.2534 (6)
C2	0.1609 (12)	0.4242 (7)	0.2507 (7)
C3	0.0427 (10)	−0.0639 (7)	0.2687 (5)
C4	0.0202 (14)	−0.1562 (6)	0.2753 (7)
C11	0.1762 (10)	0.1914 (6)	0.1152 (5)
C12	0.2964 (11)	0.1853 (7)	0.1061 (6)
C13	0.3383 (11)	0.2525 (8)	0.0716 (6)
C14	0.2632 (13)	0.3235 (8)	0.0520 (6)
C15	0.1449 (12)	0.3292 (7)	0.0616 (6)
C16	0.0989 (10)	0.2604 (6)	0.0925 (5)
C17	0.3810 (11)	0.1091 (7)	0.1308 (7)
C18	0.4641 (13)	0.2467 (10)	0.0553 (8)
C19	0.0652 (13)	0.4080 (7)	0.0367 (7)
C110	−0.0335 (10)	0.2631 (7)	0.0980 (6)
C21	−0.1730 (10)	0.0792 (6)	0.2776 (6)
C22	−0.2484 (10)	0.0428 (6)	0.2164 (7)
C23	−0.3141 (9)	−0.0335 (7)	0.2242 (7)
C24	−0.2988 (10)	−0.0679 (7)	0.2891 (7)
C25	−0.2249 (10)	−0.0320 (8)	0.3478 (7)
C26	−0.1596 (10)	0.0440 (7)	0.3431 (6)
C27	−0.2557 (12)	0.0794 (8)	0.1470 (6)
C28	−0.3964 (11)	−0.0775 (8)	0.1621 (7)
C29	−0.2130 (14)	−0.0718 (9)	0.4175 (7)
C210	−0.0743 (13)	0.0838 (9)	0.4059 (6)
C31	0.3483 (10)	0.2056 (6)	0.3825 (5)
C32	0.4692 (11)	0.2056 (9)	0.3727 (7)
C33	0.5423 (14)	0.2760 (12)	0.3952 (8)
C34	0.4959 (18)	0.3428 (12)	0.4256 (8)
C35	0.3766 (15)	0.3430 (8)	0.4351 (6)
C36	0.3001 (11)	0.2705 (7)	0.4154 (5)
C37	0.5170 (12)	0.1341 (10)	0.3390 (8)
C38	0.6758 (14)	0.2830 (14)	0.3916 (9)
C39	0.3324 (16)	0.4164 (8)	0.4718 (7)
C310	0.1743 (11)	0.2621 (8)	0.4303 (6)

The unit cell of **1** is monoclinic with the space group $P2_1/n$. The ligating atoms form a trigonal bipyramid with the sulfur atoms in the equatorial plane and the acetonitrile ligands occupying the axial positions. The bulky aryl groups are arranged such that two are above and one is below the plane containing the sulfur atoms. Bond lengths and angles are within normal ranges. The N1–Tc–N2 angle is nearly linear (178.8 (3)°), and the S–Tc–S angles are all close to 120° (118.7 (1), 121.4 (1), and 119.7 (1)°).

Table III. Non-Hydrogen Atomic Positional Parameters for **7**

atom	*x*	*y*	*z*
Tc1	−0.15237 (3)	−0.12171 (2)	0.14066 (2)
S1	−0.3261 (1)	−0.13310 (7)	0.12675 (8)
S2	−0.0833 (1)	−0.10151 (9)	0.03022 (8)
S3	−0.0431 (1)	−0.13471 (8)	0.25473 (8)
O1	−0.1550 (3)	−0.3207 (2)	0.1321 (3)
N1	−0.1567 (3)	0.0205 (2)	0.1527 (2)
C1	−0.1518 (4)	−0.2455 (3)	0.1340 (3)
C2	−0.1613 (4)	0.0927 (3)	0.1628 (3)
C3	−0.1707 (6)	0.1867 (4)	0.1811 (5)
C11	−0.3873 (3)	−0.0282 (3)	0.1309 (3)
C12	−0.4386 (4)	−0.0105 (3)	0.1946 (3)
C13	−0.4868 (4)	0.0700 (4)	0.1989 (3)
C14	−0.4782 (4)	0.1326 (3)	0.1415 (4)
C15	−0.4301 (4)	0.1157 (3)	0.0775 (3)
C16	−0.3864 (3)	0.0335 (3)	0.0690 (3)
C17	−0.4443 (5)	−0.0781 (5)	0.2581 (4)
C18	−0.5482 (5)	0.0927 (5)	0.2646 (4)
C19	−0.4276 (5)	0.1868 (4)	0.0154 (4)
C21	−0.0612 (4)	−0.2079 (4)	−0.0097 (3)
C22	−0.1404 (4)	−0.2499 (4)	−0.0593 (3)
C23	−0.1252 (5)	−0.3353 (4)	−0.0833 (3)
C24	−0.0319 (6)	−0.3753 (4)	−0.0583 (4)
C25	0.0478 (5)	−0.3354 (4)	−0.0116 (4)
C26	0.0343 (4)	−0.2477 (4)	0.0138 (3)
C27	−0.2422 (5)	−0.2043 (4)	−0.0835 (4)
C28	−0.2074 (6)	−0.3854 (5)	−0.1358 (4)
C29	0.1488 (6)	−0.3834 (5)	0.0152 (5)
C31	−0.0195 (4)	−0.0295 (3)	0.3014 (3)
C32	0.0526 (4)	0.0279 (3)	0.2759 (3)
C33	0.0670 (4)	0.1106 (4)	0.3113 (3)
C34	0.0122 (5)	0.1323 (4)	0.3714 (3)
C35	−0.0574 (4)	0.0756 (4)	0.3980 (3)
C36	−0.0743 (4)	−0.0066 (4)	0.3624 (3)
C37	0.1113 (4)	0.0033 (4)	0.2102 (4)
C38	0.1392 (6)	0.1789 (4)	0.2840 (4)
C39	−0.1128 (5)	0.1027 (5)	0.4648 (4)
C110	−0.3417 (4)	0.0121 (4)	−0.0043 (3)
C310	−0.1505 (5)	−0.0696 (5)	0.3896 (4)
C210	0.1189 (5)	−0.2019 (5)	0.0676 (5)

Crystals of **7** are also monoclinic with the space group $P2_1/n$, and the compound has essentially the same structure as **1**. The acetonitrile ligand, including the hydrogen atoms, was found on the more sterically hindered side of the molecule. The bond lengths and temperature factors of the atoms in the two mutually trans ligands were found to be normal. There is no apparent disorder of the axial ligands despite the fact that NMR evidence indicates that there are two isomers present in solution. The two isomers result from having the acetonitrile syn or anti to the unique thiolate

Table IV. Non-Hydrogen Atomic Positional Parameters for **9**

atom	*x*	*y*	*z*
Tc1	0.07457 (2)	−0.24251 (1)	−0.26062 (3)
S1	0.07091 (8)	−0.15060 (5)	−0.0834 (1)
S2	0.07353 (8)	−0.36324 (5)	−0.2092 (1)
S3	0.09213 (8)	−0.20648 (5)	−0.4913 (1)
O1	−0.2035 (2)	−0.2309 (2)	−0.3389 (4)
N1	0.2827 (2)	−0.2586 (2)	−0.2039 (3)
C1	−0.0967 (3)	−0.2347 (2)	−0.3093 (4)
C11	−0.0787 (3)	−0.1063 (2)	−0.0595 (4)
C12	−0.1208 (3)	−0.0470 (2)	−0.1483 (4)
C13	−0.2323 (3)	−0.0091 (2)	−0.1191 (4)
C14	−0.2944 (3)	−0.0307 (2)	−0.0037 (4)
C15	−0.2534 (4)	−0.0878 (2)	0.0828 (4)
C16	−0.1440 (4)	−0.1279 (2)	0.0545 (4)
C17	−0.0489 (4)	−0.0240 (2)	−0.2686 (5)
C18	−0.2862 (4)	0.0536 (2)	−0.2117 (5)
C19	−0.3231 (5)	−0.1050 (3)	0.2126 (5)
C21	−0.0749 (3)	−0.4039 (2)	−0.2405 (4)
C22	−0.1338 (3)	−0.4214 (2)	−0.1164 (4)
C23	−0.2454 (4)	−0.4569 (2)	−0.1399 (5)
C24	−0.2964 (3)	−0.4732 (2)	−0.2861 (6)
C25	−0.2398 (4)	−0.4569 (2)	−0.4056 (5)
C26	−0.1270 (3)	−0.4218 (2)	−0.3863 (4)
C27	−0.0762 (5)	−0.4051 (3)	0.0411 (5)
C28	−0.3139 (5)	−0.4789 (3)	−0.0130 (7)
C29	−0.3007 (5)	−0.4786 (3)	−0.5626 (6)
C31	0.2515 (3)	−0.2079 (2)	−0.5296 (4)
C32	0.2939 (4)	−0.2645 (2)	−0.6280 (4)
C33	0.4207 (4)	−0.2689 (2)	−0.6513 (5)
C34	0.4992 (4)	−0.2174 (2)	−0.5758 (5)
C35	0.4565 (4)	−0.1583 (2)	−0.4834 (4)
C36	0.3297 (3)	−0.1524 (2)	−0.4628 (4)
C37	0.2074 (5)	−0.3196 (3)	−0.7070 (5)
C38	0.4732 (5)	−0.3292 (3)	−0.7537 (7)
C39	0.5465 (4)	−0.1052 (3)	−0.4112 (6)
C101	0.3514 (4)	−0.2149 (3)	−0.1083 (5)
C102	0.4802 (4)	−0.2225 (4)	−0.0879 (6)
C103	0.5408 (4)	−0.2781 (4)	−0.1654 (7)
C104	0.4718 (4)	−0.3234 (3)	−0.2627 (6)
C105	0.3450 (3)	−0.3120 (2)	−0.2800 (5)
C110	−0.0990 (5)	−0.1914 (3)	0.1465 (5)
C210	−0.0627 (4)	0.4028 (2)	0.5205 (5)
C310	0.2801 (4)	−0.0867 (2)	−0.3738 (5)

Table V. Selected Bond Lengths and Angles for **1**

	Bond Lengths (Å)		
Tc–S1	2.255 (3)	Tc–N2	2.043 (8)
Tc–S2	2.246 (3)	N1–C1	1.148 (11)
Tc–S3	2.245 (3)	N2–C3	1.145 (12)
Tc–N1	2.042 (8)		
	Bond Angles (deg)		
N1–Tc–N2	178.8 (3)	N2–Tc–S3	86.2 (3)
N1–Tc–S1	95.0 (2)	S1–Tc–S2	118.7 (1)
N1–Tc–S2	86.2 (2)	S1–Tc–S3	121.4 (1)
N1–Tc–S3	93.7 (2)	S2–Tc–S3	119.7 (1)
N2–Tc–S1	86.0 (2)	Tc–N1–C6	175.4 (8)
N2–Tc–S2	92.8 (2)	Tc–N2–C3	179.6 (7)

Table VI. Selected Bond Lengths and Angles for **7**

	Bond Lengths (Å)		
Tc–S1	2.255 (1)	Tc–C1	1.879 (5)
Tc–S2	2.236 (1)	N1–C2	1.112 (6)
Tc–S3	2.255 (1)	C1–O1	1.141 (6)
Tc–N1	2.166 (4)		
	Bond Angles (deg)		
N1–Tc–C1	177.5 (2)	C1–Tc–S3	87.9 (2)
N1–Tc–S1	92.6 (1)	S1–Tc–S2	116.54 (5)
N1–Tc–S2	87.9 (1)	S1–Tc–S3	125.78 (5)
N1–Tc–S3	91.5 (1)	S2–Tc–S3	117.63 (6)
C1–Tc–S1	86.0 (2)	Tc–N1–C2	175.9 (5)
C1–Tc–S2	94.5 (2)	Tc–C1–O1	176.8 (5)

Table VII. Selected Bond Lengths and Angles for **9**

	Bond Lengths (Å)		
Tc–S1	2.234 (6)	Tc–N1	2.25 (2)
Tc–S2	2.248 (6)	Tc–C1	1.87 (2)
Tc–S3	2.258 (6)	C1–O1	1.15 (2)
	Bond Angles (deg)		
N1–Tc–C1	175.0 (7)	C1–Tc–S3	87.3 (6)
N1–Tc–S1	89.9 (4)	S1–Tc–S2	122.0 (2)
N1–Tc–S2	82.2 (4)	S1–Tc–S3	114.5 (2)
N1–Tc–S3	95.0 (4)	S2–Tc–S3	123.4 (2)
C1–Tc–S1	93.2 (6)	Tc–C1–O1	175 (2)
C1–Tc–S2	92.8 (5)		

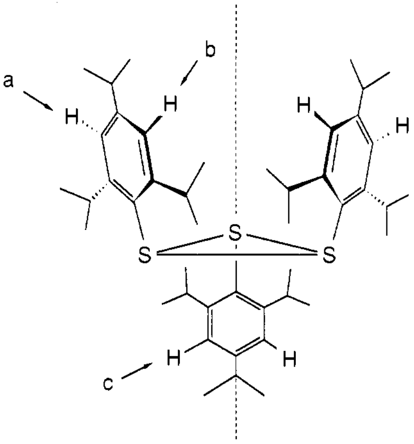

Figure 2. Schematic representation of the disposition of the thiolate rings in the tibt compounds. The central atom and the axial ligands have been omitted for clarity.

ring. It is not clear why the compound crystallized with the acetonitrile on the more sterically hindered side of the molecule despite its larger size when compared to CO. It is interesting to note that the Tc–N distance of **7** is 0.12 Å longer than that found in **1**. This is consistent with the coordination of the acetonitrile ligand trans to a stronger π-accepting ligand in **7** than in **1**.

Replacing MeCN with pyridine results in a change in packing, and crystals of **9** are triclinic with the space group $P\bar{1}$. Again, the compound has a slightly distorted trigonal-bipyramidal geometry and shares the same disposition of the thiolate rings as the above two compounds. Unlike the conformation found in compound **7**, in this case pyridine sits on the side of the unique aryl ring where it is easily accommodated and CO is found on the more sterically hindered side of the molecule. Bond lengths and angles do not deviate significantly from normal values.

Trigonal-bipyramidal coordination and the 2:1 disposition of the thiolate rings is a recurring theme in the crystal structures of compounds in this class. Equivalent structures have been observed for the rhenium analogues[16] as well as the isoelectronic molybdenum complexes.[22]

Spectroscopic Properties. Trigonal-bipyramidal compounds have a 3-fold rotation axis that causes the d orbitals to split as a, e′, and e″, with the e″ the lowest lying set of orbitals.[23] Therefore, these d^4, (e″)^4 systems are diamagnetic and exhibit NMR spectra with narrow line widths and normal chemical shifts.

The disposition of the thiolate rings observed in the crystal structures of **1**, **7**, and **9** persists in solution for all the compounds reported herein. In the ^{1}H NMR spectra of the tmbt compounds **1**, **3**, and **5**, there is a characteristic 2:1 integral ratio for the aromatic para proton signals that is suggestive of the "two-up–one-down" conformation of the thiolate rings. The methyl group pattern is too complex for an unambiguous assignment but is consistent with the observed symmetry. The ^{1}H NMR spectra of the tibt compounds **2**, **4**, and **6** indicate that they, too, contain a 2:1 thiolate conformation. Each compound shows three aromatic peaks of equal intensity, which is consistent with the compounds having a mirror plane. The equivalent sets of aromatic protons are shown as a, b, and c in Figure 2. In **4**, there is overlap of the methine signals in the tibt ligands and *i*-PrNC, but the spectra

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(23) Rossi, A. R.; Hoffmann, R. *Inorg. Chem.* **1975**, *14*, 365.

Table VIII. IR Stretching Frequencies (cm^{-1})

axial ligand (L)	$Tc(tmbt)_3L_2$	$Re(tmbt)_3L_2$	Δ
MeCN	2255	2235	20
CO	1997	1973	24
i-PrNC	2108	2086	22

of **2** and **6** show five distinct methine septets arising from the tibt ligands (2:2:2:2:1 ratio). Again, the methyl group pattern is complex.

The ring conformation causes the axial ligands in compounds **1**–**6** to be both chemically and magnetically inequivalent. Two distinct proton NMR signals are observed for MeCN in **1**[24] and **2** and *i*-PrNC in **3** and **4**. Because of its stability and easily interpretable ^1H NMR spectrum, **3** was used for high-temperature studies. No fluxional behavior was observed at 110 °C, indicating that the aryl rings are tightly locked into position within the time scale of the experiment (20 ms). For the mono(acetonitrile) compounds, **7** and **8**, two MeCN[24] signals of unequal integration are present in the ^1H NMR spectra, suggesting that two conformations may exist in solution and that on a longer time scale the rings may be fluxional. To confirm that the signals are due to two interconverting conformers and not two distinct species, magnetization-transfer experiments were performed on **7**. When the larger of the two MeCN signals was saturated, the other signal decreased in intensity, indicating that the two species are interconverting. The rate of interconversion was established by using a time-delay pulse sequence. A 180° selective pulse was applied to one resonance, and after a variable-time delay the 90° observation pulse was applied. Analysis of the data according to Dahlquist et al.[18] showed that the interconversion was occurring on the order of seconds ($k_1 + k_2 = 0.22\ s^{-1}$). This is consistent with the observation that both species are present in solution in equilibrium regardless of how the compound is prepared.

For **5** and **6**, a single broad (350-Hz) resonance was observed in the room-temperature ^{13}C NMR spectrum due to CO, but at −60 °C two individual peaks can be resolved, while the signals arising from the thiolate rings are not affected by temperature. The technetium isotope ^{99}Tc has a quadrupolar nucleus with $I = {}^9/_2$, and coupling with two ^{13}C nuclei should produce two 10-line multiplets. However, relaxation of ^{99}Tc at room temperature is relatively fast and the spectrum is partially decoupled. Increasing the viscosity of the sample by lowering the sample temperature further decreases T_1 and leads to the fully decoupled spectrum in which two singlets are resolved. This phenomenon has previously been observed in the ^1H NMR spectra of systems containing other quadrupolar metal nuclei.[25]

If the ring conformation is ignored, compounds **1**–**6** have local D_{3h} symmetry, and the axial ligands should exhibit a single asymmetric stretch in the IR spectra. Analogous tmbt and tibt compounds show identical CNR, MeCN, and CO bands. There is no significant change in the IR stretching frequency between free and bound acetonitrile (2253 and 2255 cm^{-1}, respectively), but the IR stretching frequency of the bound alkyl isocyanide (2108 cm^{-1}) is lowered 32 cm^{-1} from that of the free ligand by π-back-bonding. Compounds **5** and **6** each exhibit a sharp band at 1997 cm^{-1}. In contrast, the CO stretches in the monocarbonyl compounds not only vary with the trans ligand but also depend on the thiolate ligand and are significantly broader. The high-resolution (0.03-cm^{-1}) infrared spectrum of **7** confirms that there is only one carbonyl absorption. The modes from the two conformers of **7** found in the ^1H NMR experiments must be accidentally degenerate.

Comparison of the IR spectra of compounds **1**–**6** and their rhenium analogues (taken in the same medium) indicates that π-back-bonding is stronger in the rhenium compounds (Table VIII). The stretching frequencies of the π-accepting moieties of the Re compounds are consistently lower than those of their Tc analogues. This suggests that there is greater orbital overlap of 5d orbitals (Re) than 4d orbitals (Tc), allowing Re to donate more electron density into the π* orbitals of the axial ligands. Rhenium oxo complexes also exhibit stronger oxo-to-Re π-bonding than their technetium counterparts.[4]

The fast atom bombardment mass spectra of these compounds have some interesting features. Ions that have lost at least one ligand often exhibit peaks at 1 (all compounds) or 15 (tibt compounds only) mass units lower than the expected value. These losses are assigned to fragments in which back-biting of the metal on the thiolate ligand has caused elimination of either a proton or a methyl group from the ortho benzylic position. Dimerization of the tmbt monocarbonyl compounds upon oxidation in the *m*-nitrobenzyl alcohol matrix also occurs. Peaks corresponding to the dimeric species and their fragments are strong and numerous for **7** and **9** but entirely nonexistent for the more sterically hindered tibt analogues, **8** and **10**. The molecular ions of neither **7** nor **8** are observed, suggesting that the MeCN ligand trans to CO is extremely labile. The facile loss of one CO from the dicarbonyl compounds, **5** and **6**, to give $Tc(SAr)_3(CO)$ as the dominant species in the FABMS(+) also demonstrates the lability of one CO ligand.

Acknowledgment. We wish to thank Catherine E. Costello and Chen-Hui Zeng of the NIH Northeast Regional Mass Spectrometry Laboratory for the FAB mass spectra, Terrence Nicholson and Andy H. Liu for assistance with X-ray crystallography, Jeanne Owens for help with the magnetization transfer NMR experiments, and Kent Young for taking the high-resolution IR spectrum. N.d.V. is grateful to the National Science Foundation for a Graduate Fellowship. We also wish to thank Michelle Millar for supplying the Htmbt and Htibt.

Registry No. **1**, 113584-53-5; **2**, 113584-54-6; **3**, 113584-55-7; **4**, 113584-56-8; **5**, 113584-57-9; **6**, 113584-58-0; **7**, 113584-59-1; **8**, 113584-60-4; **9**, 113584-61-5; **10**, 113584-62-6; $(NH_4)_2[TcCl_6]$, 73045-21-3; $Re(tmbt)_3(MeCN)_2$, 113584-63-7; $Re(tmbt)_3(CO)_2$, 113584-64-8; $Re(tmbt)_3(i\text{-}PrNC)_2$, 113584-65-9.

Supplementary Material Available: Tables SI–SIII (**1**), SV–SVIII (**7**), and SX–SXIII (**9**), listing respectively hydrogen atom positional parameters (**7** and **9** only), intramolecular bond distances, intramolecular bond angles, and anisotropic thermal parameters (22 pages); Tables SIV (**1**), SIX (**7**), and SXIV (**9**), listing calculated and observed structure factors (90 pages). Ordering information is given on any current masthead page.

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[24] Assignment of the CH_3CN resonances in the ^1H NMR spectra confirmed by preparing the compounds with CD_3CN.

[25] Whitesides, G. M.; Mitchell, H. L. *J. Am. Chem. Soc.* **1969**, *91*, 2245.