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SYNTHESIS AND REACTIVITY OF TECHNETIUM(VII) IMIDO COMPLEXES

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Abstract—The synthesis, characterization and electrochemistry of a series of new technetium complexes, $Tc(NAr)_3X$ and $Tc(NAr')_3X$ ($X = OSiMe_3$, alkyl, I)†, is reported. These complexes are shown to be resistant to reduction and moderately air-sensitive. The siloxy complex $Tc(NAr)_3(OSiMe_3)$ (**1a**) reacts with fluoride ion to give the tris(imido)oxo anion $[TcO(NAr)_3]^-$. Less sterically hindered $M(NAr')_3(OSiMe_3)$ complexes react with Ar′NCO in a net [2+2] fashion to give the urylene complexes $\overline{M(NAr')_2(NAr'C(O)N}Ar')(OSiMe_3)$ (**2a**, M = Tc; **2b**, M = Re). The X-ray crystal structures of **1a**, **2b** and $Tc(NAr)_3I$ (**4a**) suggest that the imido ligands moderate their level of electron donation to reflect the electronic requirements of the metal and the ancillary ligands.

The coordination of multiple π-donors to a metal centre (π-loading) can result in increased stabilization of high-valent metal centres and/or in increased nucleophilicity of relatively inert ligands such as oxo (O^{2-}) or imido (RN^{2-}).[1,2] Technetium(VII) complexes are relatively rare, usually requiring stabilization by highly electronegative oxo, fluoride or chloride ligands, and are typically very sensitive to moist air and unstable towards reduction.[3] We set out to prepare new, stable technetium(VII) complexes using imido ligands. Rhenium complexes containing the imido (NR^{2-}) ligand are known for a variety of oxidation states and coordination numbers,[1,4–6] while technetium imido complexes have only recently been reported.[7] This paper describes the preparation of a series of new technetium(VII) imido complexes that are only slightly air-sensitive and remarkably stable towards reduction. Some of these complexes have been previously communicated.[8]

RESULTS

Synthesis

When a hexamethyldisiloxane solution of $TcO_3(OSiMe_3)$[9] is treated with 3 equivalents of 2,6-diisopropylphenylisocyanate at 100°C for 18 h deep green $Tc(NAr)_3(OSiMe_3)$ (**1a**, Ar = 2,6-diisopropylphenyl) is formed (Scheme 1). Similar reactivity is observed for 2,6-dimethylphenylisocyanate and $TcO_3(OSiMe_3)$, forming $Tc(NAr')_3(OSiMe_3)$ (**1b**, Ar′ = 2,6-dimethylphenyl),[10] although the reaction temperature must be lowered to 60°C and the reaction time shortened to 6 h. This prevents formation and subsequent thermal decomposition of the urylene complex $\overline{Tc(NAr')_2(NAr'C(O)N}Ar')(OSiMe_3)$ (**2a**, described below). Complex reactivity, involving the loss of $SiMe_3$, is observed when the less sterically hindered *p*-tolylisocyanate reacts with $TcO_3(OSiMe_3)$ under similar conditions. The latter result suggests that steric bulk about nitrogen is critical to the success of this reaction.

Preparations of **1b** can be complicated by the formation of the urylene complex $\overline{Tc(NAr')_2(NAr'C(O)N}Ar')(OSiMe_3)$ (**2a**). This complex most likely arises from the net [2+2] addition of the C═N bond of Ar′NCO with a Tc═N bond of **1b**. Similar [2+2] additions between imido ligands

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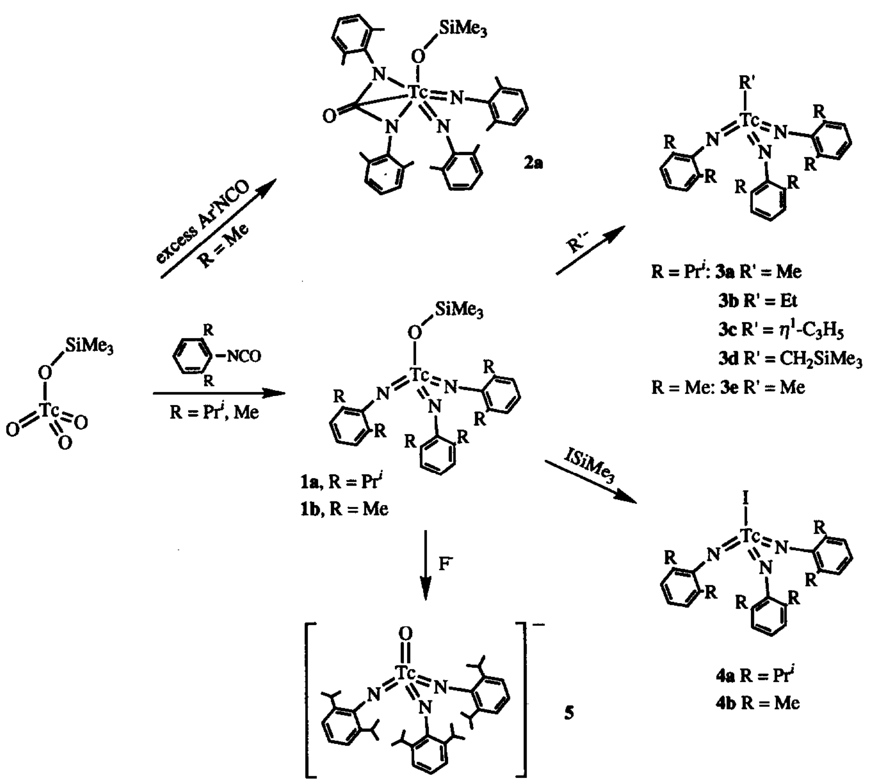
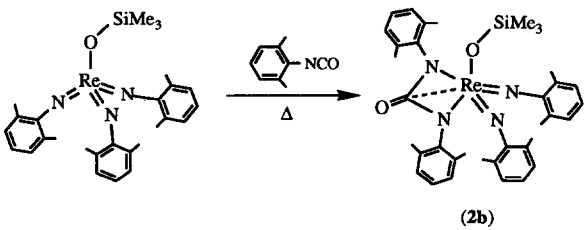
† Abbreviations: Ar = 2,6-diisopropylphenyl; Ar′ = 2,6-dimethylphenyl; PPN^+ = bis(triphenylphosphine) iminium.



Scheme 1.

and isocyanates have recently been reported.[6,11] Formation of the urylene complex **2a** can be minimized by careful control of the relative amounts of reactants, temperature and time of reaction. Complex **2a** can be prepared in reasonable yield by heating an excess of Ar′NCO with $TcO_3(OSiMe_3)$ to 80°C in hexamethyldisiloxane solvent overnight. The rhenium analogue of **2a**, $Re(NAr')_2(NAr'C(O)NAr')(OSiMe_3)$ (**2b**), can be prepared by heating $Re(NAr')_3(OSiMe_3)$[5] and an excess of Ar′NCO in hexamethyldisiloxane solvent to 120°C for 15 h [eq. (1)].



(2b)

(1)

The bulkier tris(2,6-diisopropylphenylimido) complexes **1a** and $Re(NAr)_3(OSiMe_3)$[5] are not observed to react with excess ArNCO to form urylene complexes analogous to **2a** and **2b**.

The trimethylsiloxy ($^-OSiMe_3$) ligand in **1a**, **b** is readily substituted (Scheme 1). THF solutions of $Tc(NAr)_3(OSiMe_3)$ (**1a**) react quickly at room temperature with Grignard reagents to form deep blue–green $Tc(NAr)_3R$ (**3a–c**, R = Me, Et, η^1-allyl) and with $LiCH_2SiMe_3$ to form $Tc(NAr)_3(CH_2SiMe_3)$ (**3d**). Similarly, $Tc(NAr')_3(OSiMe_3)$ (**1b**) reacts with methyl Grignard in THF to form $Tc(NAr')_3Me$ (**3e**). Complexes **1a** and **1b** also react with trimethylsilyliodide in toluene forming $Tc(NAr)_3I$ (**4a**)[8c] and $Tc(NAr')_3I$ (**4b**), respectively. When this reaction is performed in a sealed NMR tube 1 equivalent of hexamethyldisiloxane is the only other observed product.

The trimethylsilyl group can be selectively removed from the trimethylsiloxy ligand in **1a** by fluoride ions (Scheme 1). A methylene chloride solution of **1a** reacts with [PPN]F [$PPN^+ = (Ph_3P)_2N^+$] to form the tris(imido)oxo anion $[TcO(NAr)_3]^-$ (**5**).[12] Complex **5** is a tris(imido) analogue of pertechnetate and is also formed, albeit in lower yields, when **1a** is treated with $^-OSiMe_3$.

Characterization

Complexes **1–5** have been characterized by NMR and combustion analysis. Additionally, complexes **1**, **2b** and **3a–c** have been characterized by UV–vis and complexes **1b**, **2** and **5** by IR. Generally, NMR spectra show a single set of resonances for the terminal imido ligands at room temperature, indi-

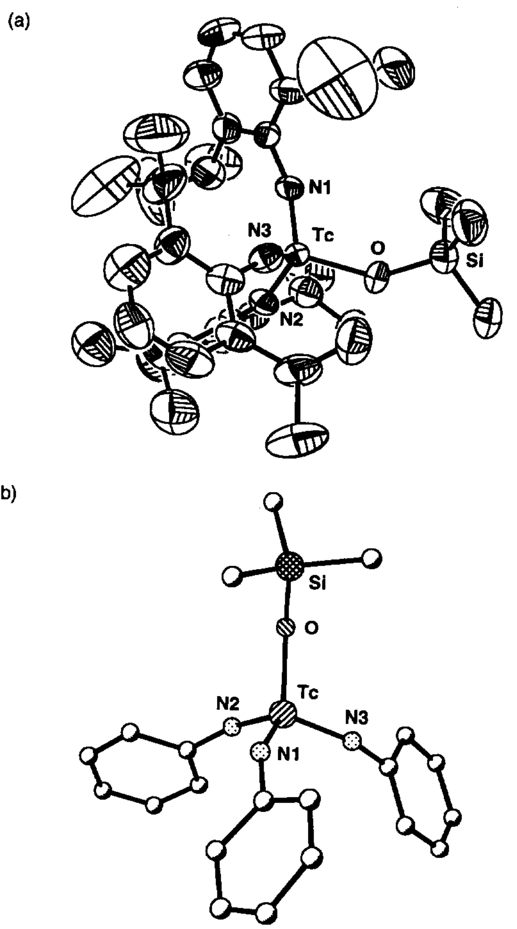


Fig. 1. Representations of Tc(N-2,6-$Pr^i_2C_6H_3)_3(OSiMe_3)$ (**1a**). (a) 40% thermal ellipsoids with hydrogen atoms omitted. (b) Ball and stick diagram with hydrogen atoms and isopropyl groups omitted. Selected bond angles (°) not already presented in Table 1. O—Tc—N(1) 111.3(3), O—Tc—N(2) 105.2(3), O—Tc—N(3) 109.9(3), N(1)—Tc—N(2) 111.3(3), N(1)—Tc—N(3) 109.9(3), N(2)—Tc—N(3) 109.1(3).

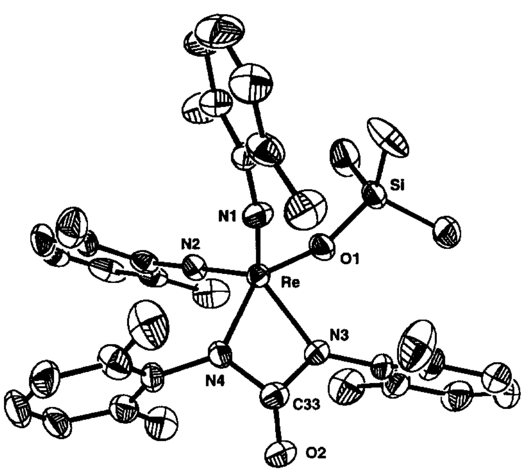


Fig. 2. ORTEP representation of $\overline{Re(NAr')_2(NAr'C}$ $\underline{(O)N}Ar')(OSiMe_3)$ (**2b**, Ar′ = 2,6-dimethylphenyl) with hydrogen atoms omitted. Selected bond distances (Å) and angles (°) not already presented in Table 1: Re—N(3) 2.035(7), Re—N(4) 2.052(7), Re···C(33), 2.627(9), O(1)—Re—N(1) 100.8(3), O(1)—Re—N(2) 100.2(3), O(1)—Re—N(3) 84.0(3), O(1)—Re—N(4) 146.0(3), N(1)—Re—N(2) 110.3(3), N(1)—Re—N(3) 119.6(3), N(1)—Re—N(4) 102.4(3), N(2)—Re—N(3) 128.1(3), N(2)—Re—N(4) 94.6(3), N(3)—Re—N(4) 63.0(3).

cating free rotation about the N—C bonds. The urylene complexes **2** exhibit three resonances in a 2:2:4 ratio attributable to CH_3 on the 2,6-dimethylphenyl groups. The largest of these three resonances can be assigned to the terminal imido ligands and the smaller two to the methyls on each of the Ar′ groups of the urylene ligand. This assumes free rotation about all N—C bonds, symmetry-related terminal imido groups and inequivalent environments for the 2,6-dimethylphenyl groups on the urylene ligand. This is consistent with the solid state structure (described below, see Fig. 2) determined for **2b**, where a mirror plane relates the two imido ligands and one urylene Ar′ is *cis* to the siloxy ligand and the other *trans*. The urylene carbonyl functionality is observed in the IR at 1676 and 1696 cm^{-1} and in the $^{13}C\{^1H\}$ NMR at δ 165.8 and 161.6 ppm for **2a** and **2b**, respectively. These values are comparable to known urylene complexes.[6,11] NMR spectra of $Tc(NAr)_3(C_3H_5)$ (**3c**) indicate that the allyl ligand is σ-bound to technetium in an η^1 fashion, as observed for a related rhenium complex, $Re(NBu^t)_3(C_3H_5)$,[6] and for the cyclopentadienyl ligand in $CpTc(NAr)_3$.[8b]

Complexes **1a**, **2b** and **4a** have been characterized by X-ray crystallography. The structures are shown in Figs 1–3, as are selected bond distances and angles specific to an individual structure. Additional bond distances and angles are presented in Table 1. The coordination geometry about the metal is approximately tetrahedral in all three complexes, assuming the urylene ligand in **2b** occupies one coordination site. Alternatively, the urylene complex **2b** could be described as a distorted square-based pyramid, where N(1) occupies the apex. All three structures exhibit short M—N bond lengths and large M—N—C angles for the terminal imido ligands, indicating considerable multiple bond character.[1] Similarly the M—O bond lengths and the M—O—Si angles in **1a** and **2b** suggest that there may be multiple bond character to the trimethylsiloxy ligand. In general, the bond distances and angles in **1a** and **4a** are similar to those observed for related $M(NR)_3X$ (X = monoanionic ligand) complexes.[2a,8b,13]

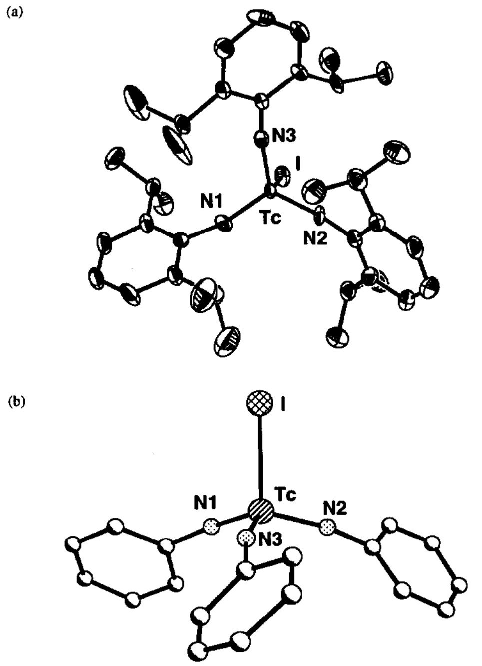


Fig. 3. Representations of Tc(N-2,6-$\text{Pr}^i_2\text{C}_6\text{H}_3$)$_3$I (**4a**). (a) 40% thermal ellipsoids with hydrogen atoms omitted. (b) Ball and stick diagram with hydrogen atoms and isopropyl groups omitted. Selected bond distance (Å) and angles (°) not already presented in Table 1 : Tc—I 2.654(1), I—Tc—N(1) 107.5(2), I—Tc—N(2) 105.7(2), I—Tc—N(3) 105.0(2), N(1)—Tc—N(2) 114.3(3), N(1)—Tc—N(3) 111.4(3), N(2)—Tc—N(3) 112.2(3).

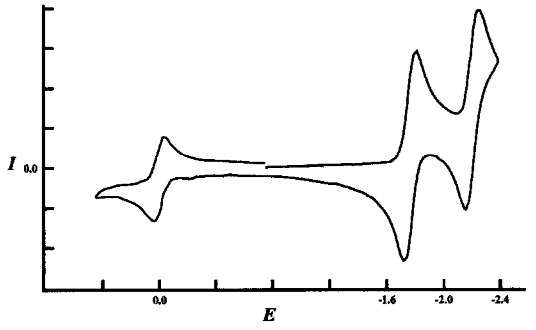


Fig. 4. Cyclic voltammogram showing reversible reductions of Tc(NAr)$_3$(OSiMe$_3$) (**1a**, −1.77 V) and Re(NAr)$_3$(OSiMe$_3$) (−2.21 V) and the $\text{Cp}_2\text{Fe}/\text{Cp}_2\text{Fe}^+$ couple as a reference (0.0 V).

The UV–vis spectra of these complexes exhibit very intense absorptions. Since these are d^0 complexes it is assumed that ligand-to-metal charge transfer is responsible for the observed transitions. The lowest energy absorption in the spectrum (200–800 nm) for Tc(NAr)$_3$(OSiMe$_3$) (**1a**) is red shifted by 120 cm^{-1} relative to the same feature observed in the spectrum for Re(NAr)$_3$(OSiMe$_3$). Such a shift is expected since the empty technetium-based 4*d* orbitals should be lower in energy, and therefore closer in energy to the filled ligand-based orbitals, than the analogous rhenium-based 5*d* orbitals.

Electrochemistry

Reductions of the d^0 complexes **1**, **3a**, **4a** and **5** were explored by cyclic voltammetry. Results are presented in Table 2. The tris(imido) complexes **1** and **3a** exhibit only a single reversible reduction up to −2.5 V. When scanned beyond this value additional features (irreversible reductions and oxidations) are observed in the voltammogram and the reversibility of the original reduction becomes questionable. As expected,[3a] the rhenium complex Re(NAr)$_3$(OSiMe$_3$) is more difficult (440 mV) to reduce than its technetium analogue **1a** (Fig. 4). The tris(imido)iodide complex **4a** exhibits an irreversible reduction wave at −1.62 V when scanned at 0.20 V s^{-1}, which becomes reversible at higher scan rates (see Table 3). The chemical reduction of **4a** has been previously communicated.[8c] Additional details of

Table 1. Selected bond lengths (Å) and angles (°) in Tc(NAr)$_3$(OSiMe$_3$) (**1a**), Re(NAr′)$_2$(NAr′C(O)NAr′)(OSiMe$_3$) (**2b**) and Tc(NAr)$_3$I (**4a**)

	Tc(NAr)$_3$(OSiMe$_3$)	Re(NAr′)$_2$(NAr′C(O)NAr′)(OSiMe$_3$)	Tc(NAr)$_3$I
M═N(1)	1.759(6)	1.746(7)	1.740(7)
M═N(2)	1.753(6)	1.749(7)	1.759(7)
M═N(3)	1.749(7)		1.763(6)
M—O	1.909(6)	1.889(6)	
Si—O	1.615(7)	1.654(7)	
M—N(1)—C	154.3(6)	165.8(6)	164.8(6)
M—N(2)—C	158.5(5)	175.5(6)	169.4(6)
M—N(3)—C	154.7(6)		165.6(6)
M—O—Si	145.7(4)	148.0(4)	

Table 2. Electrochemically measured *reduction* potentials for **1a**, **1b**, Re(NAr)$_3$(OSiMe$_3$), **3a**, **4a** and **5**

Complex	No.	Ep_{red} (V)[a]	Ep_{ox} (V)[a]	ΔEp (V)
Tc(NAr)$_3$(OSiMe$_3$)	**1a**	−1.82	−1.72	0.10
Tc(NAr')$_3$(OSiMe$_3$)	**1b**	−1.76	−1.55	0.21
Re(NAr)$_3$(OSiMe$_3$)		−2.16	−2.26	0.10
Tc(NAr)$_3$Me	**3a**	−2.02	−1.80	0.22
Tc(NAr)$_3$I[b]	**4a**	−1.62	−1.39	0.23
[PPN][Tc(NAr)$_3$O][c]	**5**	−2.51		

[a] Peak potentials relative to ferrocene/ferrocenium internal standard.
[b] Scan rate 0.5 V s^{-1}.
[c] CH$_3$CN was used as the solvent.

the chemical and electrochemical reductions of **4a** will be the subject of a future publication. The tris (imido)oxo anion **5** is the most difficult to reduce of all the complexes reported here, exhibiting an irreversible reduction wave at −2.51 V. Since complexes **1a**, **3a**, **4a** and **5** all contain the [Tc(NAr)$_3$]$^+$ fragment and differ only in the identity of the final ligand, an arrangement of these complexes by ease of reduction should reflect the relative donor ability of the unique ligand:

$$I^-, \mathbf{4a} > {}^-OSiMe_3, \mathbf{1a} > Me^-, \mathbf{3a} > O^{2-}, \mathbf{5}$$

$\longleftarrow$ ease of reduction

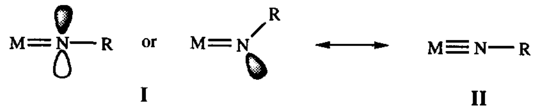
Finally, it is more difficult to reduce **1a** than **1b**, which may indicate that 2,6-diisopropylphenylimido is a better donor than 2,6-dimethylphenylimido.

DISCUSSION

The complexes reported here contain several strong π-donor ligands, as such they are heavily "π-loaded". As a result of the competition between the strong π-donor ligands the imido ligands in these complexes are best represented by resonance structure **I**:

Table 3. Crystallographic data for Tc(NAr)$_3$(OSiMe$_3$) (**1a**), Re(NAr')$_2$(NAr'C(O)NAr')(OSiMe$_3$) (**2b**) and Tc(NAr)$_3$I (**4a**)

Complex	Tc(NAr)$_3$(OSiMe$_3$)	Re(NAr')$_2$(NAr'C(O)NAr')(OSiMe$_3$)	Tc(NAr)$_3$I·(THF)$_{0.5}$
Formula	$C_{39}H_{60}N_3OSiTc$	$C_{36}H_{45}N_4O_2SiRe$	$C_{38}H_{55}IN_3O_{0.5}Tc$
f_w	713.9	781.0	787.7
Crystal dimensions (mm)	0.20 × 0.24 × 0.40	0.49 × 0.40 × 0.08	0.39 × 0.36 × 0.37
Space group	*Cc*	$P2_1/n$	*Fdd*2
a (Å)	12.077(2)	10.541(4)	36.867(6)
b (Å)	19.477(4)	19.581(12)	39.261(10)
c (Å)	17.914(4)	17.388(4)	10.485(2)
β (°)	95.90(3)	94.71(2)	
V (Å^3)	4191.3(14)	3577(3)	15,177(5)
Z	4	4	16
ρ_{calc} (g cm^{-3})	1.13	1.45	1.38
μ (cm^{-1})	3.91	35.1	12.2
Temperature (K)	298	298	203
θ limits (°)	1–25	1–25	2–27.5
Transmission factors	0.888–0.829	0.514–0.812	0.223–0.324
Total number of reflections	8136 $\pm h, k, \pm l$	6734 $\pm h, k, l$	9528 $h, k, \pm l$
Observed reflections	5341 $F > 6\sigma_F$	4554 $F > 2.5\sigma_F$	6552 $F > 3\sigma_F$
Final number of variables	404	398	381
R	0.044	0.048	0.060
R_w	0.066	0.048	0.072



where the metal–nitrogen bond order is lowered, bending at nitrogen *may* be observed and electron density is displaced from the metal–nitrogen bond to the nitrogen atom making the imido ligand more nucleophilic at nitrogen.[1,2]

The effects of π-loading can be observed in the structures of **1a** and **4a**. Terminal imido ligands can generally be expected to be linear at nitrogen when they are able to donate both pairs of p-π electrons. All the Tc—N—C angles in complexes **1a** ($\angle$Tc—N—C_{av} = 155.8°) and **4a** ($\angle$Tc—N—C_{av} = 166.6°) are bent significantly from 180°, falling within the range often observed for complexes with multiple π-donors.[1,2a,8b,13] The iodo complex (**4a**) is closer to being linear at nitrogen than the siloxy complex (**1a**), and while **1a** is very close to tetrahedral about technetium **4a** is distorted towards a trigonal-based pyramid where the iodide occupies the apex. These differences are probably due to the greater electronic dominance of the imido ligands in **4a**, where there is less competition from the more weakly donating I^-. Similar comparison of the structures for **1a** and **2b** ($\angle$Tc—N—C_{av} = 170.6°) suggests that replacement of an imido with a urylene ligand allows the remaining imido ligands to donate more strongly. These three structures suggest that the imido ligands moderate their donor ability depending on donor strength of the other ligands.

π-loading can also be used to rationalize some of the reactivity reported here. Extra electron density at the imido nitrogen is observed in the formation of the urylene complexes **2**, if the reaction is viewed as nucleophilic attack by an imido nitrogen on the isocyanate carbon.[11a,14] Subsequent reaction of the remaining imido ligands in **2** with isocyanate, forming additional urylene ligands, is probably inhibited because the imido ligands in **2** have less competition for π-electron density, are able to donate to technetium more strongly and are, therefore, less nucleophilic at nitrogen.[11a] Since the trimethylsiloxy ligand in complexes **1** is a good π-donor on a π-loaded complex, it may also exhibit nucleophilic character at oxygen. This is observed in the reactions of Me_3SiI with complexes **1**, which can be thought of as electrophilic attack of Me_3Si^+ at the siloxy oxygen.

The tris(imido) fragment "$[Tc(NAr)_3]^+$" imparts a high degree of stability to the normally oxidizing Tc^{VII} centre. For instance, electrochemical studies on the tris(imido) complexes demonstrate that they are difficult to reduce. Additionally, the tris(imido)siloxy (**1**) and tris(imido)alkyl (**3**) complexes are stable to air as solids for extended periods. Complex **1a** decomposes in solutions exposed to air over 2–3 days. $Tc(NAr)_3(CH_2SiMe_3)$ (**3d**) is stable to 1 equivalent of water in Et_2O solution at room temperature for 18 h! The tris(imido)technetium fragment is even capable of stabilizing iodide, a ligand that is quite susceptible to oxidation.[15] In fact, complexes **4** are the first examples of technetium(VII) iodide complexes.[16] $Tc(NAr)_3I$ (**4a**) is also stable to moist air in solution for short periods. All of this contrasts strongly with known oxotechnetium(VII) complexes, which are generally more sensitive to moist air and unstable towards reduction.[3]

EXPERIMENTAL

General considerations

CAUTION! ^{99}Tc is a weak β^--emitter ($E = 0.3$ MeV, $t_{1/2} = 2.12 \times 10^5$ years). All experiments are performed in designated laboratories approved for low-level radioactive materials following procedures and techniques described below and elsewhere.[17] All manipulations were performed in a helium atmosphere dry-box equipped with a freezer (−40°C) or in a well-ventilated fume hood with the appropriate secondary containment. Personnel are trained in the safe handling of radioactive materials, use beta–gamma counters to detect areas of contamination and wear protective lab. coats, approved safety glasses and disposable gloves at all times. Every reasonable effort was made to recover ^{99}Tc from reaction residues. Radioactive wastes were disposed of in appropriate containers.

Toluene, hexane, THF, diethyl ether, hexamethyldisiloxane and dimethoxyethane were distilled under nitrogen from sodium or sodium/potassium alloy and methylene chloride from phosphorous pentoxide. Ammonium pertechnetate was obtained from Oak Ridge National Laboratory and was purified as described previously.[18] $[(Ph_3P)_2N]F$,[19] $Tc(O)_3(OSiMe_3)$,[9] $Re(NAr')_3(OSiMe_3)$[5] and **4a**[8c] were prepared following published procedures. Arylisocyanates and $ISiMe_3$ (Aldrich) were distilled and stored in a dry-box prior to use. Alkylating reagents were used as supplied from Aldrich.

NMR spectra were recorded in C_6D_6 on an IBM AF-250 or a Bruker WM-300 spectrometer, referenced to solvent unless otherwise noted and reported below as chemical shift in δ (multiplicity, integral, coupling constant in Hz, assignment). IR spectra were obtained as Nujol mulls using a Perkin–Elmer 1500 or a Bio–Rad FTS-40 spectrometer and are reported in cm^{-1}. Elemental analyses were obtained on a Perkin–Elmer 2400 analyser. UV–vis spectra were recorded on a Hewlett–Packard 8450A spectrophotometer and are reported as λ_{max} (ε) unless otherwise noted. Cyclic voltammograms were measured with a Princeton Applied Research Model 273 electrochemistry system using a platinum disk working electrode (BAS Model MF2013), a platinum wire counter electrode and a silver wire quasi-reference electrode separated from the bulk solution via a fine porosity glass frit. Test solutions were approximately 2 mM of the measured compound with approximately 0.1 M of $[Bu^n_4N]BF_4$ (anhydrous and recrystallized) as the supporting electrolyte in THF. The scan rate was 0.2 V s^{-1} unless otherwise noted. Potentials are quoted relative to the ferrocene/ferrocenium redox couple used as an internal reference standard.

$Tc(NAr)_3(OSiMe_3)$ (**1a**)

A solution of $TcO_3(OSiMe_3)$ (0.50 g, 2.1 mmol) and ArNCO (1.28 g, 6.3 mmol) in hexamethyldisiloxane (12 cm^3) was stirred at 110°C under argon for 21 h. The reaction mixture was concentrated to 5 cm^3 and cooled to -40°C. The resulting solids were filtered, washed with cold hexamethyldisiloxane (3 × 2 cm^3) and dried *in vacuo*, yielding 0.88 g (60%) of deep green **1a**. ^{1}H NMR: 7.00 (m, 9, Ar), 3.50 (sept, 6, $J = 6.8$, $CHMe_2$), 1.10 (d, 36, $J = 6.8$, $CHCH_3$), 0.45 (s, 9, $SiCH_3$). $^{13}C\{^1H\}$ NMR: 139.5 (Ar), 126.9 (Ar), 122.7 (Ar), 29.1 ($CHMe_2$), 23.7 ($CHCH_3$), 2.6 ($SiCH_3$). Found: C, 65.8; H, 8.3; N, 5.9. Calc. for $C_{39}H_{60}N_3OSiTc$: C, 65.6; H, 8.4; N, 5.9%. UV–vis (nm): 277 (30,000), 319 (35,000), 588 (4500).

$Tc(NAr')_3(OSiMe_3)$ (**1b**)

A solution of $TcO_3(OSiMe_3)$ (0.24 g, 1.0 mmol) and Ar′NCO (0.45 g, 3.1 mmol) in hexamethyldisiloxane (15 cm^3) was stirred at 62°C under argon for 5 h. The reaction mixture was cooled to -40°C. The resulting solids were filtered, washed with hexamethyldisiloxane (2 × 5 cm^3) and dried *in vacuo*, yielding 0.33 g (61%) of **1b**. Preparations of **1b** often contain **2a**, which can be selectively crystallized from hexane or hexamethyldisiloxane. ^{1}H NMR: 6.75 (m, 9, Ar), 2.24 (s, 18, $ArCH_3$), 0.37 (s, 9, $SiCH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 130.2 (Ar), 127.9 (Ar), 126.5 (Ar), 18.9 ($ArCH_3$), 2.1 ($SiCH_3$). IR: 1274 vs, 1246 s, 1158 m, 1094 m, 951 vs br, 834 s, 772 vs, 762 m, 744 m, 726 m. Found: C, 59.5; H, 6.2; N, 8.1. Calc. for $C_{27}H_{36}N_3OSiTc$: C, 59.4; H, 6.6; N, 7.7%. UV–vis (nm): 237 (40,000), 310 (30,000), 584 (4500).

$Tc(NAr')_2(NAr'C(O)NAr')(OSiMe_3)$ (**2a**)

A solution of $TcO_3(OSiMe_3)$ (0.22 g, 0.92 mmol) and Ar′NCO (1.02 g, 6.9 mmol) in hexamethyldisiloxane (40 cm^3) was stirred at 80°C under argon for 11 h. The reaction mixture was cooled to -40°C. The resulting solids were filtered, washed with cold hexamethyldisiloxane (3 × 4 cm^3) and dried *in vacuo*, yielding 0.32 g (50%) of red–brown **2a**. ^{1}H NMR: 6.69 (m br, 5, Ar), 6.57 (m, 7, Ar), 2.80 (s, 6, $ArCH_3$), 2.33 (s, 6, $ArCH_3$), 2.23 (s, 12, $ArCH_3$), -0.15 (s, 9, $SiCH_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 165.8 (CO), 137.3 (Ar), 136.9 (Ar), 131.6 (Ar), 128.7 (Ar), 128.5 (Ar), 128.0 (Ar), 126.7 (Ar), 126.4 (Ar), 19.3 ($ArCH_3$), 18.8 ($ArCH_3$), 1.6 ($SiCH_3$). IR: 1676 vs [ν(CO)], 1312 w sh, 1284 m, 1247 m, 899 s, 890 m sh, 840 m, 774 m, 764 m. Found: C, 62.7; H, 6.5; N, 8.3. Calc. for $C_{36}H_{45}N_4O_2SiTc$: C, 62.5; H, 6.6; N, 8.1%.

$Re(NAr')_2(NAr'C(O)NAr')(OSiMe_3)$ (**2b**)

A solution of $Re(NAr')_3(OSiMe_3)$ (0.10 g, 0.2 mmol) and Ar′NCO (0.26 g, 1.8 mmol) in hexamethyldisiloxane (5 cm^3) was stirred at 120°C for 15 h. Volatiles were pumped away and hexane (3 cm^3) was added. The suspension was cooled to -40°C and the resulting solids were filtered, washed with hexane (3 × 2 cm^3) and dried *in vacuo*, yielding 0.84 g (68%) of red **2b**. ^{1}H NMR: 7.02 (m, 2, Ar), 6.73 (m, 8, Ar), 6.56 (m, 2, Ar), 2.78 (s, 6, $ArCH_3$), 2.39 (s, 6, $ArCH_3$), 2.29 (s, 12, $ArCH_3$), -0.22 (s, 9, $SiCH_3$). $^{13}C\{^1H\}$ NMR (THF-d_8): 161.6 (CO), 153.6 (Ar), 147.5 (Ar), 145.7 (Ar), 141.0 (Ar), 140.6 (Ar), 139.8 (Ar), 133.3 (Ar), 131.7 (Ar), 131.2 (Ar), 130.1 (Ar), 129.7 (Ar), 19.9 ($ArCH_3$), 19.2 ($ArCH_3$), 18.4 ($ArCH_3$), 1.4 ($SiCH_3$). IR: 1696 vs [ν(CO)], 1315 w sh, 1294 s, 1249 m, 907 vs, 841 m, 772 m, 763 m. Found: C, 55.6; H, 5.7; N, 7.0. Calc. for $C_{36}H_{45}N_4O_2ReSi$: C, 55.4; H, 5.8; N, 7.2%. UV–vis (all λ_{sh}) (nm): 236 (40,000), 275 (25,000), 396 (9000), 486 (4500).

$Tc(NAr)_3Me$ (**3a**)

A solution (3 M) of MeMgCl (0.04 cm^3, 0.1 mmol) in THF was added dropwise to a THF (20 cm^3) solution of $Tc(NAr)_3(OSiMe_3)$ (0.082 g, 0.1 mmol). The reaction mixture was stirred for 90 min. Volatiles were pumped away and hexane (3 cm^3) was then added. The resulting suspension was filtered through Celite®, which was then washed with hexane (2 × 5 cm^3). The filtrates were pumped to dryness, yielding 0.055 g (75%) of deep blue–green **3a**. ^{1}H NMR: 7.01 (m, 9, Ar), 3.72 (sept, 6, $J = 7.0$, $\mathrm{C}H\mathrm{Me_2}$), 2.61 (s, 3, $\mathrm{TcC}H_3$), 1.13 (d, 36, $J = 7.0$, $\mathrm{CHC}H_3$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): 140.2 (Ar), 132.2 (Ar), 126.4 (Ar), 122.6 (Ar), 30.1 ($\mathrm{Tc}C\mathrm{H_3}$), 29.0 ($C\mathrm{HMe_2}$), 23.2 ($\mathrm{CH}C\mathrm{H_3}$). Found: C, 69.5; H, 8.1; N, 6.1. Calc. for $\mathrm{C_{37}H_{54}N_3Tc}$: C, 69.6; H, 8.5; N, 6.6%. UV–vis (nm): 257 (30,000), 336 (30,000), 598 (5500).

$\mathrm{Tc(NAr)_3Et}$ (**3b**)

This was prepared from EtMgCl in 86% yield as a deep blue–green solid following the procedure for **3a**. ^{1}H NMR: 7.02 (m, 9, Ar), 3.75 (sept, 6, $J = 6.8$, $\mathrm{C}H\mathrm{Me_2}$), 3.74 (q, 2, $J = 7.3$, $\mathrm{C}H_2\mathrm{CH_3}$), 2.21 (t, 3, $J = 7.3$, $\mathrm{CH_2C}H_3$), 1.14 (d, 36, $J = 6.8$, $\mathrm{CHC}H_3$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): 155.4 (Ar), 140.5 (Ar), 126.3 (Ar), 122.6 (Ar), 34.7 ($C\mathrm{H_2CH_3}$), 28.8 (CH), 23.4 ($\mathrm{CH}C\mathrm{H_3}$), 22.0 ($\mathrm{CH_2}C\mathrm{H_3}$). Found: C, 69.9; H, 8.6; N, 6.4. Calc. for $\mathrm{C_{38}H_{56}N_3Tc}$: C, 69.8; H, 8.6; N, 6.4%. UV–vis (nm): 258 (35,000), 339 (30,000), 604 (6000).

$\mathrm{Tc(NAr)_3(C_3H_5)}$ (**3c**)

This was prepared from $\mathrm{(C_3H_5)MgCl}$ in 70% yield as a deep blue–green solid following the procedure for **3a**. ^{1}H NMR: 7.01 (m, 9, Ar), 6.66 (m, 1, $\mathrm{C}H\mathrm{{=}CH_2}$), 5.25 (d, 1, $J = 17$, *trans*-$\mathrm{CH{=}C}H\mathrm{H'}$), 4.99 (d, 1, $J = 10$, *cis*-$\mathrm{CH{=}CH}H'$), 4.33 (d, 2, $J = 8$, $\mathrm{TcC}H_2$), 3.71 (sept, 6, $J = 6.8$, $\mathrm{C}H\mathrm{Me_2}$), 1.12 (d, 36, $J = 6.8$, $\mathrm{CHC}H_3$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): 143.3 (Ar), 140.9 (Ar), 126.7 (Ar), 122.7 (Ar), 113.4 ($C\mathrm{H{=}CH_2}$), 66.2 ($\mathrm{CH{=}}C\mathrm{H_2}$), 34.8 ($\mathrm{Tc}C\mathrm{H_2}$), 28.8 ($C\mathrm{HMe_2}$), 23.5 ($\mathrm{CH}C\mathrm{H_3}$). Found: C, 70.8; H, 9.1; N, 5.9. Calc. for $\mathrm{C_{39}H_{56}N_3Tc}$: C, 70.3; H, 8.5; N, 6.3%. UV–vis (nm): 255 (45,000), 339 (30,000), 606 (6500).

$\mathrm{Tc(NAr)_3(CH_2SiMe_3)}$ (**3d**)

This was prepared from $\mathrm{Li(CH_2SiMe_3)}$ in 70% yield as a deep blue–green solid following the procedure for **3a**. ^{1}H NMR: 7.00 (m, 9, Ar), 3.84 (sept, 6, $J = 6.9$, $\mathrm{C}H\mathrm{Me_2}$), 2.69 (s, 2, $\mathrm{TcC}H_2$), 1.18 (d, 36, $J = 6.9$, $\mathrm{CHC}H_3$), 0.25 (s, 9, $\mathrm{SiC}H_3$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR ($\mathrm{CD_2Cl_2}$): 155.3 (Ar), 141.7 (Ar), 126.9 (Ar), 122.9 (Ar), 34.3 ($C\mathrm{H_2Si}$), 28.6 ($C\mathrm{HMe_2}$), 23.7 ($\mathrm{CH}C\mathrm{H_3}$), 1.4 ($\mathrm{Si}C\mathrm{H_3}$). Found: C, 67.3; H, 8.9; N, 6.0. Calc. for $\mathrm{C_{40}H_{62}N_3SiTc}$: C, 67.6; H, 8.8; N, 5.9%.

$\mathrm{Tc(NAr')_3Me}$ (**3e**)

This was prepared from $\mathrm{Tc(NAr')_3(OSiMe_3)}$ in 74% yield [together with < 10% yield of red $\mathrm{Tc_2(NAr')_4(\mu\text{-}NAr')_2}$[20]] as a deep green oil following the procedure for **3a**. ^{1}H NMR: 6.75 (m, 9, Ar), 2.48 (s, 3, $\mathrm{TcC}H_3$), 2.27 (s, 18, $\mathrm{ArC}H_3$). Found: C, 64.0; H, 6.6; N, 9.1. Calc. for $\mathrm{C_{25}H_{30}N_3Tc}$: C, 63.8; H, 6.4; N, 8.9%.

$\mathrm{Tc(NAr')_3I}$ (**4b**)

A solution of $\mathrm{Tc(NAr')_3(OSiMe_3)}$ (0.10 g, 0.19 mmol) and $\mathrm{Me_3SiI}$ (0.027 cm^3, 0.19 mmol) in toluene (10 cm^3) was stirred at room temperature for 40 min. Volatiles were pumped away yielding 0.085 g (76%) of **4b** as a deep green solid. ^{1}H NMR: 6.70 (m, 9, Ar), 2.21 (s, 3, $\mathrm{ArC}H_3$). Found: C, 49.5; H, 4.8; N, 7.0. Calc. for $\mathrm{C_{24}H_{27}N_3ITc}$: C, 49.5; H, 4.7; N, 7.2%.

$\mathrm{[(Ph_3P)_2N][TcO(NAr)_3]}$ (**5**)

A solution of $\mathrm{Tc(NAr)_3(OSiMe_3)}$ (0.10 g, 0.14 mmol) and $\mathrm{[(Ph_3P)_2N]F}$ (0.10 g, 0.16 mmol) in $\mathrm{CH_2Cl_2}$ (10 cm^3) was stirred at room temperature for 5 min. Volatiles were pumped away and dimethoxyethane/$\mathrm{Et_2O}$ (5:1, 12 cm^3) was then added. The resulting suspension was cooled to −40°C and filtered through Celite®, which was then washed with $\mathrm{Et_2O}$ (2×3 cm^3). The filtrates were pumped to dryness, yielding 0.12 g (73%) of red **5**. ^{1}H NMR: 7.45 (m, 30, $\mathrm{P}Ph_3$), 6.97 (m, 9, Ar), 4.06 (sept, 6, $J = 6.8$, $\mathrm{C}H\mathrm{Me_2}$), 1.29 [d, 36, $J = 6.8$, $\mathrm{CH(C}H_3\mathrm{)_2}$]. IR: 1411 s, 1324 vs, 1264 vs br, 1183 w, 1111 s, 997 w, 960 m, br, 932 w sh, 834 m, 808 m, 744 s, 720 vs, 691 s, 545 s, 533 vs, 497 m. Found: C, 72.8; H, 6.5; N, 4.7. Calc. for $\mathrm{C_{72}H_{81}N_4OP_2Tc}$: C, 73.3; H, 6.9; N, 4.7%.

X-ray structure determinations for $\mathrm{Tc(NAr)_3(OSiMe_3)}$ (**1a**), $\overline{\mathrm{Re(NAr')_2(NAr'C(O)N}}\mathrm{Ar')(OSiMe_3)}$ (**2b**) *and* $\mathrm{Tc(NAr)_3I}$ (**4a**)

Data were collected on crystals mounted on glass fibres. Preliminary photographic examination and data collection were performed on a Siemans R3m/V diffractometer with graphite monochromated Mo-K_α radiation. Cell constants and an orientation matrix were obtained by least-squares refinement, using the setting angles of at least 25 reflections. Good crystal quality was also suggested by measuring omega scans of several intense reflections and by examining axial photographs. Intensity data were obtained using θ–2θ (**1a** and **2b**) or ω scans (**4a**). The data were scaled for linear decay and a semi-empirical absorption correction based on the average relative intensity curve of azimuthal scan data was applied. The structures were solved using standard heavy atom methods and refined with full-matrix least-squares. All non-hydrogen atoms were refined anisotropically, hydrogen atom positions were calculated (C—H = 0.96 Å) and were added to the structure-factor calculations without refinement. All calculations were performed using SHELXTL PLUS programs provided by Siemans Analytical. Crystallographic data are given in Table 3. Positional and thermal parameters and complete tabulations of bond lengths and angles are available as supplementary material from the Cambridge Crystallographic Data Center.

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