

Synthesis, structure, and first-principles calculations of [TcBr₂(PMe₃)₄] and [Tc₂Br₄(PMe₃)₄] complexes†‡

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The new technetium(II) complexes, [TcBr₂(PMe₃)₄] **1** and [Tc₂Br₄(PMe₃)₄] **2**, were synthesized from TcBr₃ and characterized by single-crystal X-ray diffraction (XRD), first-principles calculations and UV-vis spectroscopy. Complex **1** is the first of the *trans*-dihalo-tetrakis-trialkylphosphine metallate(II) class reported for group VII, while **2** is the first Tc(II) dimer with bromide ligands. Compounds **1** and **2** are isostructural with their molybdenum analogs. XRD analysis indicates that **1** crystallizes in the tetragonal space group $I\bar{4}2m$, with D_{2d} molecular point-group symmetry, and with Tc–Br = 2.5925(7) Å and Tc–P = 2.4213(11) Å. Compound **2** crystallizes in the monoclinic space group $C2/c$ with Tc–Br = 2.520(1) Å, Tc–P = 2.441(1) Å and Tc–Tc = 2.1316(5) Å. Density functional theory (DFT) calculations for **1** and **2**, as well as for the molybdenum homologues, are in good overall agreement with the XRD structural data.

Introduction

Recently, we synthesized and characterized technetium tribromide and technetium tetrabromide, the first simple halides of technetium to be reported in the past 40 years.¹ Binary halides of transition metals are often used as precursors in the synthesis of low valent coordination compounds. Complexes with general formula [MX₂(PR₃)₄] (M = metal of group V, VI and VIII, X = halide, R = alkyl) have been extensively studied.² For group V and VI, the general route to [MX₂(PMe₃)₄] involves the sodium or sodium amalgam reduction of binary halides (NbCl₅, TaCl₅, WCl₄) or binary halide/THF adducts (VCl₃·3THF, MoCl₃·3THF) with excess trimethylphosphine (PMe₃). Concerning group VII, no complexes with general formula [MX₂(PR₃)₄] (X = halide, R = alkyl) have been reported to date. Technetium and rhenium compounds with the formula [MX₂L₂]^{+/+} (X = halide, L = chelating diphosphine) have been studied due to their potential medical applications for myocardial scintigraphy.³ Those complexes are formed by reaction between a hexachlorotechnetate(IV) or a perrhenate salt with excess of diphosphine, but reactions with binary halides have not been reported.

Herein, we report the synthesis of two new technetium(II) compounds derived from TcBr₃, which were characterized by XRD, UV-vis spectroscopy and first-principles calculations.

Experimental

Synthesis

Caution! Technetium-99 is a weak beta emitter ($E_{\max} = 292$ keV). All manipulations were performed in a radiochemistry laboratory designed for chemical synthesis using efficient HEPA-filtered fume hoods, Schlenk and glove box techniques, and following locally approved radioisotope handling and monitoring procedures. Technetium tribromide was synthesized by reaction between Tc metal and Br₂ in a sealed, evacuated tube at 400 °C for 6 h.¹ Technetium tribromide (32.6 mg, 0.096 mmol) was suspended in 2 mL of dry THF in a 10 mL Schlenk flask under an argon atmosphere. Trimethylphosphine (250 μL, 2.825 mmol) was added to the suspension and an orange color was observed. After 5 min, Na[Et₃BH] in THF (130 μL, 0.130 mmol) was added dropwise and the suspension was stirred overnight at room temperature. After 14 h, the suspension was removed with a glass pipette, placed in a 15 mL centrifuge tube and centrifuged. The yellow-brown supernatant was removed and pumped to dryness; a yellow oil was obtained. The oil was extracted with 2 mL of hexane and placed in a glass vial and stored in a freezer at –25 °C. After 4 d, crystals were observed at the bottom of the vial, the supernatant was removed. The vial was examined with a microscope, which revealed the presence of both red-orange **1** and green crystals **2** whose structures, [TcBr₂(PMe₃)₄] and [Tc₂Br₄(PMe₃)₄], respectively, were determined by single-crystal XRD. Assessing yields at this scale of reaction is problematic because mechanical losses are significant. We estimate that the combined isolated yield of **1** and **2** was on the order of 10%.

Computational details

All-electron scalar relativistic calculations for the [MBr₂(PMe₃)₄] and [M₂Br₄(PMe₃)₄] (M = Tc, Mo) complexes were performed using the spin-polarized density functional theory (DFT) implemented in the DMol3 software packages.⁴ The exchange

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correlation energy was calculated using the generalized gradient approximation (GGA) with the parametrization of Perdew and Wang (PW91).⁵ Double numerical basis sets including polarization functions on all atoms (DNP) were used in the geometry optimization calculation. The DNP basis set corresponds to a double- ζ quality basis set with d-type polarization functions added to atoms heavier than hydrogen. The DNP basis set is comparable to 6-31G** Gaussian basis sets⁶ with a better accuracy for a similar basis set size.⁴ In the generation of the numerical basis sets, a global orbital cutoff of 4.8 Å was used. The energy tolerance in the self-consistent field calculations was set to 10^{-6} Hartree. Optimized geometries were obtained using the direct inversion in a subspace method (DIIS) with an energy convergence tolerance of 10^{-5} Hartree and a gradient convergence of 2×10^{-3} Hartree Å⁻¹. This computational approach has shown previously to yield accurate structural results for Tc halide compounds.⁷

Other techniques

UV-vis spectra were recorded at room temperature in quartz cells (1 cm) on a Cary 6000i double beam spectrometer. Dichloromethane or benzene was used as the reference. Prior to analysis, solvents were flushed with argon and dried over 4 Å molecular sieves. ⁹⁹Tc concentrations were determined by liquid scintillation counting using a Packard 2500 scintillation analyzer. The scintillation cocktail was ULTIMA GOLD ABTM (Packard).

Results and discussion

Synthesis

[TcBr₂(PMe₃)₄] **1** is the first divalent complex with the formula [MX₂(PR₃)₄] (R = alkyl) reported for metals of group VII, while **2** is the first Tc(II) dimer with bromide ligands. For technetium, dimers with the formula [Tc₂Cl₄(PR₃)₄] were previously obtained by zinc metal reduction of the [TcCl₄(PR₃)₂] monomers, but the mechanism of formation is not well understood.⁸ Concerning the monomers, the tetravalent [TcCl₄(PMe₃)₂] is obtained by reduction of TcO₄⁻ with a stoichiometric amount of PMe₃ in aqueous HCl/methanol and the trivalent compounds, [*trans*-TcCl₂(PMe₃)₄][PF₆] and [*mer*-TcCl₃(PMe₃)₃] were obtained by reduction of Tc(VII) or Tc(V) precursors in the presence of excess PMe₃, respectively.⁹ No Tc(II) monomers were obtained using PMe₃ as a reducing agent. In our work, the use of the strong reducing agent Na[Et₃BH] combined with PMe₃ leads to Tc(II) formation.

For molybdenum and tungsten, monomer and dimer can be obtained in high yield using the same precursors and reactants: WCl₄, PMe₃ and sodium amalgam for tungsten and [MoCl₃(THF)₃], zinc powder and PMe₃ for molybdenum.^{2d,10} The specific formation of dimers or monomers arise from the contact time between WCl₄ or [MoCl₃(THF)₃] with PMe₃ prior to the addition of the reductant. If the precursors and PMe₃ are reacted until the complete formation of mononuclear [MCl_{4/3}(PMe₃)₃] and then the reducing agent is added, only monomers are obtained; for a congruent addition of PMe₃ and reducing agent, dimer formation is observed. For tungsten, the monomer can also be converted to the dimer by refluxing in dibutylether, it was proposed that the formation of [W₂Cl₄(PMe₃)₄] involves the dimerization of

Table 1 Crystallographic parameters for [TcBr₂(PMe₃)₄] **1** and [Tc₂Br₄(PMe₃)₄] **2**

Compound	1	2
Formula	TcBr ₂ P ₄ C ₁₂ H ₃₆	Tc ₂ Br ₄ P ₄ C ₁₂ H ₃₆
<i>M</i> , /g mol ⁻¹	562.11	819.92
Crystal system	Tetragonal	Monoclinic
Space group	<i>I</i> 4̄2 <i>m</i>	<i>C</i> 2/ <i>c</i>
<i>a</i> /Å	9.4771(10)	18.0903(19)
<i>b</i> /Å	9.4771(10)	9.3365(10)
<i>c</i> /Å	12.123(3)	17.232(3)
α /°	90	90
β /°	90	115.104(1)
γ /°	90	90
<i>V</i> /Å ³	1088.8(3)	2635.5(6)
<i>Z</i>	4	4
ρ /g cm ⁻³	1.715	2.066
<i>T</i> /K	149(2)	150(2)
Radiation	MoK α	MoK α
Wavelength	0.71073	0.71073
Reflections collected	2631	18 170
Independent reflections	889	3335
Parameters	33	101
<i>R</i> _{int}	0.0272	0.0261
<i>R</i> (<i>F</i> _o)/(<i>F</i> _o ² > 2 σ (<i>F</i> _o ²))	0.0236	0.0228
<i>R</i> (<i>F</i> _o ²) (all data)	0.0311	0.0272
<i>R</i> _w (<i>F</i> _o ²)	0.0538	0.0638
Goodness-of-fit	0.963	1.087

[WCl₂(PMe₃)₃] fragments.^{10a} For technetium, the monomer is likely formed by the reduction of [TcBr₃(PMe₃)₃] to [TcBr₂(PMe₃)₃] followed by complexation with PMe₃ while the reduction of polymeric TcBr₃ in the presence of PMe₃ leads to the production of **2**. In these preliminary studies, no attempt was made to optimize the formation of monomer over dimer or *vice versa*.

Crystallographic structures†

X-Ray diffraction analysis was performed on a single crystal of **1** grown at -25 °C from hexane solution. Compound **1** crystallizes in the tetragonal space group *I*4̄2*m* with the molecules having rigorous *D*_{2d} symmetry. (Table 1). The X-ray crystal structure of **1** (Fig. 1) can be described as a distorted octahedron with one pair of *trans*-phosphorous ligands lying above and the other below the equatorial plane.

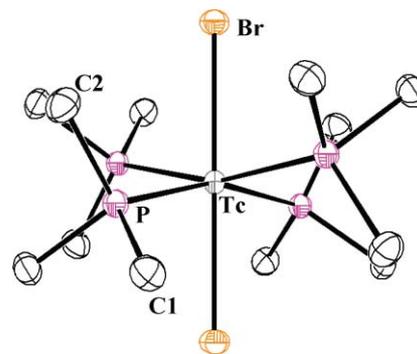


Fig. 1 ORTEP representation of [TcBr₂(PMe₃)₄] **1**.

Divalent and trivalent technetium complexes exhibiting a similar geometry have been reported (*i.e.*, [TcCl₂(PR₃)₄][PF₆] (PR₃ = PMe₃, PMe₂Ph), [TcBr₂(DPPE)₂][BF₄], [TcCl₂(DPPE)₂], [TcCl₂(DPPE)₂][NO₃·HNO₃]) but **1** is the first [TcX₂(PR₃)₄]

Table 2 Bond distances (Å) and angles (°) for [TcBr₂(PMe₃)₄] **1**

Tc–P	2.4213(11)	C(2)–P–C(1)	101.11(14)
Tc–Br	2.5925(7)	C(1)#4–P–C(1)	97.6(2)
P–C(2)	1.821(5)	C(2)–P–Tc	119.98(16)
P–C(1)	1.833(3)	C(1)–P–Tc	116.69(10)
P–Tc–P#1	162.38(4)	P–Tc–Br	81.19(2)
P–Tc–P#2	91.344(6)	P#2–Tc–Br	98.81(2)
		Br–Tc–Br#2	180.0(0)

Symmetry transformations used to generate equivalent atoms: #1: $-x + 2, -y + 2, z$; #2: $y, -x + 2, -z + 2$; #3: $-y + 2, x, -z + 2$; #4: y, x, z .

Table 3 Average bond lengths (Å) and angles (°) for [MBr₂(PMe₃)₄] (M = Tc, Mo) found by XRD and DFT (in bold)

	Distances/Å		Angles/°		
	M–Br	M–P	Br–M–P	P–M–P1	P–M–P2
M = Tc	2.5925(7)	2.4213(11)	81.19(2)	162.38(4)	91.344(6)
	2.612	2.446	82.26	164.51	91.04
M = Mo	2.614(1)	2.515(1)	81.2(1)	162.3(1)	91.4(1)
	2.623	2.523	81.91	163.81	91.13

complex to be characterized.^{3a–3b,10b} The average Tc–P distance in **1** (2.4213(11) Å) is comparable to the Tc–P distance in [TcCl₂(DPPE)₂] where DPPE = Ph₂PCH₂CH₂PPh₂ (*i.e.*, 2.428(6) Å). The Tc–Br distance in **1** (*i.e.*, 2.5925(7) Å) is longer than found in the Tc(III) complex [TcBr₂(DPPE)₂]⁺ (*i.e.*, 2.440(1) Å). Changes of a similar magnitude have been observed for chloro-compounds [TcCl₂(DPPE)₂]⁺ (Tc–Cl = 2.319(1) Å) and [TcCl₂(DPPE)₂] (Tc–Cl = 2.424(2) Å).

Complex **1** is isostructural with [MoBr₂(PMe₃)₄].¹¹ The Tc–Br and Tc–P distances are slightly shorter than those in [MoBr₂(PMe₃)₄] while the angles are essentially identical. The decrease of M–P distance when moving from Mo to Tc may indicate that the π -back bonding is slightly greater in the d⁵ technetium complex than in the d⁴ molybdenum analog. The distances and angles found in **1** and [MoBr₂(PMe₃)₄] by XRD are in good agreement with the ones found by DFT calculations for the isolated D_{2d} conformers (see Table 2 and Table 3).

Compound **2** crystallizes in the monoclinic space group C2/c with all the Tc–Tc units ordered in the same direction (Table 1). Similar to [M₂X₄(PMe₃)₄] compounds (M = Re, Mo, W; X = Cl, Br), **2** has the eclipsed conformation with overall D_{2d} symmetry, with the [TcBr₂(PMe₃)₂] units non-planar due to repulsion forces between individual ligands across the metal–metal bond (Fig. 2). The metal–metal distance (2.1316(5) Å) is in accordance with the presence of the electron rich $\sigma^2\pi^4\delta^2\delta^{*2}$ metal–metal triple bond and is comparable to the Tc–Tc distances found in the [Tc₂Cl₄(PR₃)₄] homologues.⁸ Apparently, the nature of the halogen and phosphine ligands does not have a strong influence on the metal–metal distance. Compound **2** is isostructural with [Mo₂Br₄(PMe₃)₄]. The M–M distance is only slightly shorter (~ 0.01 Å) in the molybdenum compound (a d⁴–d⁴ quadruple bond) indicating that the contribution of the δ bonding and antibonding orbitals to the overall metal–metal bonding in these [M₂X₄(PMe₃)₄] complexes is small. The metal–ligand distances, especially the M–P bond lengths, are longer in the molybdenum compound than in its Tc analogue, which may also be a reflection of greater π -back bonding

Table 4 Bond distances (Å) and angles (°) for [Tc₂Br₄(PMe₃)₄] **2**

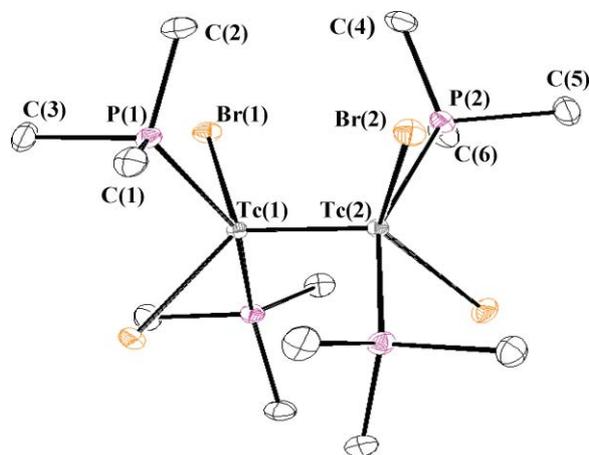
Tc(1)–Tc(2)	2.1316(5)	P(1)–C(2)	1.816(4)
Tc(1)–Br(1)	2.5218(4)	P(1)–C(3)	1.822(4)
Tc(1)–P(1)	2.4454(8)	P(2)–C(4)	1.819(3)
Tc(2)–Br(2)	2.5196(4)	P(2)–C(5)	1.819(3)
Tc(2)–P(2)	2.4415(8)	P(2)–C(6)	1.827(4)
P(1)–C(1)	1.832(4)		
Tc(2)–Tc(1)–Br(1)	114.393(11)	C(1)–P(1)–C(2)	102.08(18)
Tc(2)–Tc(1)–P(1)	102.20(2)	C(1)–P(1)–C(3)	102.12(18)
Br(1)–Tc(1)–P(1)	85.01(2)	C(2)–P(1)–C(3)	102.5(2)
Br(1)*1–Tc(1)–P(1)	84.98(2)	C(1)–P(1)–Tc(1)	107.49(13)
P(1)–Tc(1)–P(1)*	155.60(4)	C(2)–P(1)–Tc(1)	120.12(13)
Tc(1)–Tc(2)–Br(2)	114.305(11)	C(3)–P(1)–Tc(1)	119.79(13)
Br(2)*–Tc(2)–Br(2)	131.39(2)	C(4)–P(2)–C(6)	102.19(18)
Tc(1)–Tc(2)–P(2)*	102.46(2)	C(4)–P(2)–C(5)	102.54(17)
Br(2)–Tc(2)–P(2)*	85.12(2)	C(6)–P(2)–C(5)	102.29(18)
Tc(1)–Tc(2)–P(2)	102.46(2)	C(4)–P(2)–Tc(2)	118.86(12)
Br(2)–Tc(2)–P(2)	84.68(2)	C(6)–P(2)–Tc(2)	107.42(13)
P(2)*–Tc(2)–P(2)	155.07(4)	C(5)–P(2)–Tc(2)	120.88(12)

Symmetry transformations used to generate equivalent atoms: * $-x, y, -z + 1/2$.

Table 5 Average bond lengths (Å) and angles (°) for [M₂Br₄(PMe₃)₄] (M = Tc, Mo) complexes found by XRD and DFT (in bold)

	Distances/Å			Angles/°	
	M–M	M–Br	M–P	M–M–Br	M–M–P
M = Tc	2.1316(5)	2.520(1)	2.441(1)	114.35(1)	102.33(2)
	2.222	2.566	2.463	113.50	103.17
M = Mo	2.125(1)	2.549(1)	2.547(2)	113.5(1)	102.8(1)
	2.202	2.587	2.559	112.71	103.48

to phosphorous in the case of M = Tc (Table 4 and Table 5).¹² Both compounds exhibit similar MMBr and MMP angles.

**Fig. 2** ORTEP representation of [Tc₂Br₄(PMe₃)₄] **2**.

The metal–ligand distances in the technetium(II) dimer are distinct from the ones in the monomer. The average Tc–Br distance is 0.07 Å longer in **1** than in **2**, while the Tc–P distance is 0.02 Å longer in **2** than in **1**. A similar trend is observed for the analogous molybdenum complexes. The elongation of the M–Br distances in the monomers is likely due to the presence of four equatorial PMe₃ ligands on the Br–Tc–Br (*trans*) group.

Table 6 Energies (cm^{-1}) and absorption coefficients ($\text{M}^{-1} \text{cm}^{-1}$) of the low energy electronic transitions determined for **2** and $[\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4]$ in benzene

$[\text{Tc}_2\text{X}_4(\text{PR}_3)_4]$		Electronic data
X = Br	$\text{R}_3 = \text{Me}_3$	13 072(21), 15 949(24), 18 281(25), 21 436(28)
X = Cl^8	$\text{R}_3 = \text{Et}_3$	12 987(30), 15 432(30), 18 939 (sh), 20 161(56)
	$\text{R}_3 = n\text{-Pr}_3$	13 368(15), 17 006(22), 18 726 (sh), 20 491(54)
	$\text{R}_3 = \text{Me}_2\text{Ph}$	13 297(25), 16 077(30), 18 939(64), 20 491(75)
	$\text{R}_3 = \text{MePh}_2$	12 987(33), 15 151(47), 17 667 (sh), 19 607 (114)

UV-vis spectroscopy

Crystals of $[\text{TcBr}_2(\text{PMe}_3)_4]$ (**1**) and $[\text{Tc}_2\text{Br}_4(\text{PMe}_3)_4]$ (**2**) from the sample used for XRD measurements were separated manually and dissolved and UV-vis spectra recorded in dichloromethane (**1**) and benzene (**2**). The spectrum of **1** (Fig. 3) exhibits two intense bands at $23\,923 \text{ cm}^{-1}$ ($\epsilon = 2805 \text{ M}^{-1} \text{ cm}^{-1}$) and $21\,276 \text{ cm}^{-1}$ ($\epsilon = 592 \text{ M}^{-1} \text{ cm}^{-1}$). UV-vis studies on halogeno-diphosphine Tc(II) complexes have already been performed.^{3a} It was shown that the highest energy bands, located between $22\,026 \text{ cm}^{-1}$ and $22\,831 \text{ cm}^{-1}$ for the bromo complexes arise from bromine to technetium charge transfer transitions. Assignment of electronic transitions in the optical spectrum of **1** was then made by analogy with the diphosphine complexes and the band at $23\,923 \text{ cm}^{-1}$ is logically attributed to a bromine to technetium charge transfer.

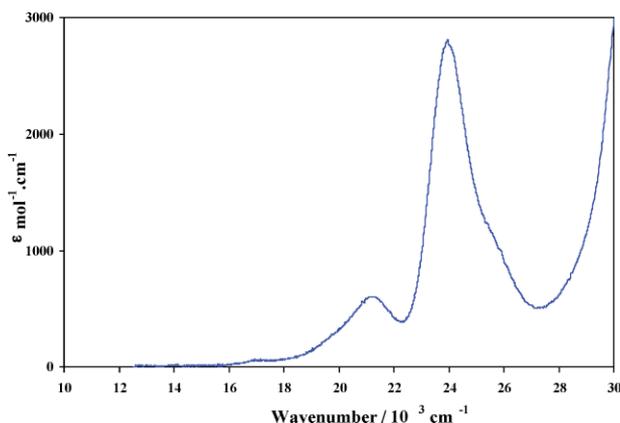


Fig. 3 Absorption spectrum of **1** in dichloromethane.

The UV-vis spectrum of **2** (Fig. 4) exhibits a series of weak absorption bands between $13\,072 \text{ cm}^{-1}$ and $21\,436 \text{ cm}^{-1}$. The position and intensity of the transitions in **2** were compared with the chlorine homologues $[\text{Tc}_2\text{Cl}_4(\text{PR}_3)_4]$ (Table 6).⁸ It was suggested that the lowest energy absorption band in the $[\text{M}_2\text{Cl}_4(\text{PR}_3)_4]$ ($\text{M} = \text{Tc}, \text{Re}$) complexes is likely the $\delta^* \rightarrow \sigma^*$ transition. The similarity between Tc(II) chlorine and bromine spectra allows us to assign the low energy band at $13\,072 \text{ cm}^{-1}$ in **2** to the $\delta^* \rightarrow \sigma^*$ transition.

Conclusion

Technetium tribromide was used for the preparation of two new divalent compounds, $[\text{TcBr}_2(\text{PMe}_3)_4]$ **1** and $[\text{Tc}_2\text{Br}_4(\text{PMe}_3)_4]$

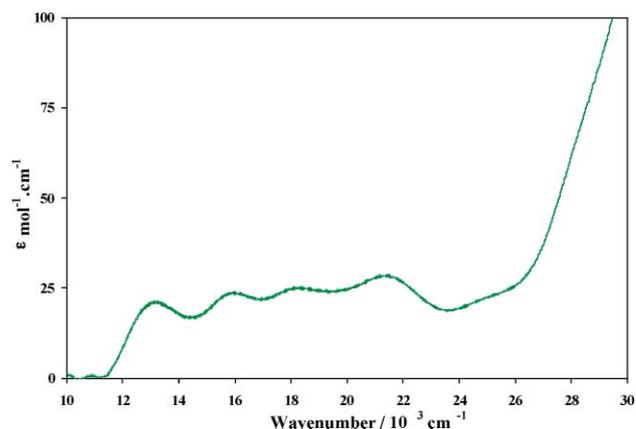


Fig. 4 Absorption spectrum of **2** in benzene.

2. Single-crystal X-ray diffraction shows that **1** and **2** are isostructural to their molybdenum analogues. Analysis of the structural parameters (found by XRD and DFT) in **1** and **2**, as well as in their molybdenum counterparts, reveals that the metal–ligand distances in the monomer are longer than those in the dimer. The variation of distances was explained by the presence of steric effects induced by the phosphine ligands. UV-vis spectroscopic measurements of **1** reveal an intense band that can be attributed to a ligand-to-metal charge transfer, while for **2** we observe several weak bands in the visible spectrum; the lowest energy band could be attributed to the $\delta^* \rightarrow \sigma^*$ transition. Electronic structure calculations are in progress that will facilitate more complete assignments of the electronic spectra of **1** and **2**. Interestingly, $[\text{TcCl}_2(\text{PMe}_3)_4]$ is still unknown, but preliminary DFT calculations suggest that this complex, perhaps not too surprisingly, is stable as well. It will be interesting to transpose to TcCl_4 the procedure that was used for $[\text{TcBr}_2(\text{PMe}_3)_4]$ and $[\text{Tc}_2\text{Br}_4(\text{PMe}_3)_4]$ to produce $[\text{TcCl}_2(\text{PMe}_3)_4]$ and $[\text{Tc}_2\text{Cl}_4(\text{PMe}_3)_4]$. It is expected that $[\text{TcX}_2(\text{PMe}_3)_4]$ complexes, produced in good yield, can be used as precursors in the synthesis of other new low-valent technetium complexes. Currently, optimization of $[\text{TcBr}_2(\text{PMe}_3)_4]$ preparation, as well as the synthesis of $[\text{TcCl}_2(\text{PMe}_3)_4]$ are in progress and the results will be reported in due course.

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