Supplemental information

Crystal Structure Determination. Crystals of **1** and **2** were selected directly from the residual mother liquor and quickly moved by needle into a drop of paratone oil. The paratone-covered crystal was then mounted on a glass fiber and immediately cooled in a nitrogen cold stream to 150 K. A full hemisphere of data was then collected on a Bruker APEX II diffractometer. The structure was solved by direct methods and refined against F^2 using SHELX-97.[1] Hydrogen atoms were added geometrically and refined using the riding model. No other constraints/restraints were needed to obtain a reasonable structure for non-hydrogen atoms. The structure refined down to an R_1 value of 2.38 % for **1** and 2.28 % for **2**. In the case of [**1**], the Flack parameter refined to approx. 7% towards the end of the refinement, suggesting a small degree of racemic twinning. Refinements using an inversion twin law indicated 7.208% racemic twinning for this crystal and improved the R_1 value to 2.36%.

[1] G. M. Sheldrick, *Acta Cryst. A*, 2008, **64**, 112.

Tables presenting complete crystallographic parameters, bond distances/angles and atomic coordinates of $TcBr_2(PMe_3)_4$ and $Tc_2Br_4(PMe_3)_4$ are presented below:

Table 1. Crystal data and structure refinement for $TcBr_2(PMe_3)_4$

Empirical formula	C12 H36 Br2 P4 Tc	
Formula weight	562.11	
Temperature	149(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I-42m	
Unit cell dimensions	a = 9.4771(10) Å	α= 90°.
	b = 9.4771(10) Å	β= 90°.
	c = 12.123(3) Å	γ = 90°.
Volume	1088.8(3) $Å^3$	
Z	2	
Density (calculated)	1.715 Mg/m^3	
Absorption coefficient	4.614 mm^{-1}	
F(000)	562	
Crystal size	50 x 50 x 50 mm^3	
Theta range for data collection	2.73 to 30.49°.	
Index ranges	-11<=h<=9, -13<=k<=13, -6<=l<=17	
Reflections collected	2631	

Independent reflections	889 [R(int) = 0.0272]
Completeness to theta = 30.49°	99.4 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	889 / 0 / 34
Goodness-of-fit on F^2	0.963
Final R indices [I>2sigma(I)]	R1 = 0.0236, wR2 = 0.0516
R indices (all data)	R1 = 0.0311, wR2 = 0.0538
Absolute structure parameter	0.000(15)
Largest diff. peak and hole	0.773 and -0.324 e.$Å^{-3}$

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for TcBr3PMe3_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Tc(1)	10000	10000	10000	15(1)
Br(1)	10000	10000	7862(1)	24(1)
P(1)	8215(1)	8215(1)	9694(1)	18(1)
C(1)	6679(3)	8738(3)	8870(2)	26(1)
C(2)	7364(4)	7364(4)	10865(4)	30(1)

Table 3. Bond lengths [Å] and angles [°] for TcBr3PMe3_0m.

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

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y+2,z #2 -y+2,x,-z+2 #3 y,-x+2,-z+2 #4 y,x,z

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for TcBr3PMe3_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Tc(1)	14(1)	14(1)	15(1)	0	0	0
Br(1)	28(1)	28(1)	16(1)	0	0	-4(1)
P(1)	18(1)	18(1)	18(1)	0(1)	0(1)	-2(1)
C(1)	22(2)	30(2)	27(1)	-3(1)	-4(1)	2(1)
C(2)	31(2)	31(2)	27(3)	4(1)	4(1)	-4(2)

Table 5. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^{\ 3}$) for TcBr3PMe3_0m.

	x	y	z	U(eq)
H(1A)	6997	9224	8202	39
H(1B)	6080	9372	9304	39
H(1C)	6139	7896	8665	39
H(1C2)	6890(40)	7930(40)	11270(30)	44
H(2C2)	6640(40)	6640(40)	10660(40)	44

Table 6. Crystal data and structure refinement for $Tc_2Br_4(PMe_3)_4$

Empirical formula	C6 H18 Br2 P2 Tc	
Formula weight	409.96	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 18.0903(19) Å	α= 90°.
	b = 9.3365(10) Å	β= 115.1040(10)°.
	c = 17.232(3) Å	γ = 90°.
Volume	2635.5(6) $Å^3$	
Z	4	
Density (calculated)	2.066 Mg/m^3	
Absorption coefficient	7.352 mm^{-1}	
F(000)	1576	
Theta range for data collection	2.49 to 28.52°.	
Index ranges	-24<=h<=24, -12<=k<=12, -23<=l<=23	
Reflections collected	18170	
Independent reflections	3335 [R(int) = 0.0261]	
Completeness to theta = 28.52°	99.7 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3335 / 0 / 101	
Goodness-of-fit on F^2	1.087	
Final R indices [I>2sigma(I)]	R1 = 0.0228, wR2 = 0.0620	
R indices (all data)	R1 = 0.0272, wR2 = 0.0638	
Largest diff. peak and hole	0.786 and -0.404 $e.Å^{-3}$	

Table 7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for $Tc_2Br_4(PMe_3)_4$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Tc(1)	5000	3258(1)	2500	16(1)
Tc(2)	5000	975(1)	2500	16(1)
Br(1)	3877(1)	4374(1)	1202(1)	29(1)
Br(2)	5828(1)	-135(1)	1793(1)	26(1)
P(1)	5874(1)	3812(1)	1778(1)	24(1)
P(2)	3829(1)	411(1)	1157(1)	22(1)
C(1)	5947(3)	5765(4)	1741(3)	37(1)
C(2)	6940(2)	3280(4)	2257(3)	39(1)
C(3)	5547(3)	3319(4)	658(2)	36(1)
C(4)	2816(2)	947(4)	1024(2)	32(1)
C(5)	3821(2)	897(4)	131(2)	34(1)
C(6)	3739(2)	-1538(4)	1079(2)	36(1)

Table 8. Bond lengths [Å] and angles [°] for $Tc_2Br_4(PMe_3)_4$.

Tc(1)-Tc(2)	2.1316(5)
Tc(1)-P(1)#1	2.4454(8)
Tc(1)-P(1)	2.4454(8)
Tc(1)-Br(1)#1	2.5218(4)
Tc(1)-Br(1)	2.5218(4)
Tc(2)-P(2)	2.4415(8)
Tc(2)-P(2)#1	2.4415(8)
Tc(2)-Br(2)#1	2.5196(4)
Tc(2)-Br(2)	2.5196(4)
P(1)-C(2)	1.816(4)
P(1)-C(3)	1.822(4)
P(1)-C(1)	1.832(4)
P(2)-C(4)	1.819(3)
P(2)-C(5)	1.819(3)

P(2)-C(6)	1.827(4)
Tc(2)-Tc(1)-P(1)#1	102.20(2)
Tc(2)-Tc(1)-P(1)	102.20(2)
P(1)#1-Tc(1)-P(1)	155.60(4)
Tc(2)-Tc(1)-Br(1)#1	114.394(11)
P(1)#1-Tc(1)-Br(1)#1	85.01(2)
P(1)-Tc(1)-Br(1)#1	84.98(2)
Tc(2)-Tc(1)-Br(1)	114.393(11)
P(1)#1-Tc(1)-Br(1)	84.98(2)
P(1)-Tc(1)-Br(1)	85.01(2)
Br(1)#1-Tc(1)-Br(1)	131.21(2)
Tc(1)-Tc(2)-P(2)	102.46(2)
Tc(1)-Tc(2)-P(2)#1	102.46(2)
P(2)-Tc(2)-P(2)#1	155.07(4)
Tc(1)-Tc(2)-Br(2)#1	114.305(11)
P(2)-Tc(2)-Br(2)#1	85.12(2)
P(2)#1-Tc(2)-Br(2)#1	84.68(2)
Tc(1)-Tc(2)-Br(2)	114.305(11)
P(2)-Tc(2)-Br(2)	84.68(2)
P(2)#1-Tc(2)-Br(2)	85.12(2)
Br(2)#1-Tc(2)-Br(2)	131.39(2)
C(2)-P(1)-C(3)	102.5(2)
C(2)-P(1)-C(1)	102.08(18)
C(3)-P(1)-C(1)	102.12(18)
C(2)-P(1)-Tc(1)	120.12(13)
C(3)-P(1)-Tc(1)	119.79(13)
C(1)-P(1)-Tc(1)	107.49(13)
C(4)-P(2)-C(5)	102.54(17)
C(4)-P(2)-C(6)	102.19(18)
C(5)-P(2)-C(6)	102.29(18)
C(4)-P(2)-Tc(2)	118.86(12)
C(5)-P(2)-Tc(2)	120.88(12)
C(6)-P(2)-Tc(2)	107.42(13)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,y,-z+1/2

Table 9. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $Tc_2Br_4(PMe_3)_4$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Tc(1)	16(1)	17(1)	15(1)	0	6(1)	0
Tc(2)	16(1)	17(1)	14(1)	0	6(1)	0
Br(1)	26(1)	29(1)	24(1)	6(1)	4(1)	5(1)
Br(2)	29(1)	29(1)	26(1)	-1(1)	15(1)	6(1)
P(1)	25(1)	24(1)	28(1)	4(1)	14(1)	-1(1)
P(2)	22(1)	24(1)	17(1)	-2(1)	5(1)	-2(1)
C(1)	44(2)	26(2)	45(2)	2(2)	24(2)	-4(2)
C(2)	27(2)	42(2)	52(2)	9(2)	22(2)	-1(2)
C(3)	51(2)	36(2)	30(2)	6(2)	25(2)	2(2)
C(4)	18(2)	41(2)	29(2)	-2(1)	2(1)	-4(1)
C(5)	36(2)	43(2)	18(2)	-2(1)	9(1)	0(2)
C(6)	43(2)	24(2)	35(2)	-9(1)	10(2)	-7(2)

Table 10. Hydrogen coordinates ($x\ 10^4$) and isotropic displacement parameters ($Å^2 x\ 10^3$) for $Tc_2Br_4(PMe_3)_4$.

	x	y	z	U(eq)
H(1A)	5409	6171	1490	55
H(1B)	6232	6019	1401	55
H(1C)	6239	6129	2312	55
H(2A)	7176	3497	2859	58
H(2B)	7228	3792	1987	58
H(2C)	6980	2269	2179	58
H(3A)	4982	3562	340	54
H(3B)	5618	2307	617	54
H(3C)	5870	3829	427	54
H(4A)	2755	738	1539	48
H(4B)	2412	429	554	48
H(4C)	2746	1956	909	48

H(5A)	4337	654	131	51
H(5B)	3729	1908	40	51
H(5C)	3393	384	-320	51
H(6A)	3736	-1917	1595	54
H(6B)	4194	-1928	1000	54
H(6C)	3240	-1794	599	54