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Supplementary Material to the paper

$\{Tc(NO)(Cp)(PPh_3)\}^+$ - A Novel Technetium(I) Core

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1. Procedures and Analytical Data

Materials: All chemicals were reagent grade and used without further purification. Solvents were dried and used freshly distilled unless otherwise stated. The synthesis of $[Tc(NO)Cl_2(PPh_3)_2(MeCN)]$ was prepared by the procedure of Blanchard et al. (*Inorg. Chim. Acta* **1996**, *244*, 121) and $(NBu_4)[Tc(NO)Br_4(MeOH)]$ was prepared by the standard procedure of Orvig et al. (*J. Labelled Compd. Radiopharm*. **1981**, *18*, 148). The synthesis of KCp was performed by the procedure of Roesky et al. (*Organometallics* **2003**, *22*, 877).

Physical Measurements: Infrared spectra were measured as KBr pellets on a Shimadzu FTIR-spectrometer between 400 and 4000 cm^{-1}. NMR spectra were recorded on a JEOL-400MHz spectrometer. Tc values were determined by liquid scintillation counting. EPR spectra have been measured on a Miniscope MS400 spectrometer (Magnetech).

1.1 $[Tc(NO)Br_2(PPh_3)_2(MeCN)]$

$(NBu_4)[Tc(NO)Br_4(MeOH)]$ (231 mg, 0.3 mmol) and PPh_3 (393 mg, 1.50 mmol) were dissolved in 20 mL MeCN. The red solution was heated under reflux for 5 h. The sparingly soluble red precipitate formed was filtered off, washed with diethylether and dried under vacuum. Yield 83 % (235 mg).

Elemental analysis: Calcd. for $C_{37}H_{33}N_2OP_2Br_2Tc$: Tc, 11.6 %. Found: Tc, 10.8 %. IR (KBr, cm^{-1}): 3424 (w), 3055 (m), 2916 (w), 1721 (vs), 1572 (w), 1481 (m), 1435 (s), 1366 (w), 1315 (w), 1188 (m), 1161 (w), 1119 (w), 1092 (m), 1074 (w), 1028 (m), 997 (m), 847 (w), 746 (s), 696 (s), 619 (w), 598 (w), 519 (s), 498 (m), 543 (m).

1.2. $[Tc(NO)(Cp)(PPh_3)Cl]$:

$[Tc(NO)Cl_2(PPh_3)_2(MeCN)]$ (618 mg, 0.81 mmol) was suspended in 5 mL toluene. KCp (208 mg, 2.00 mmol) was dissolved in 5 mL toluene and added to the yellow-orange suspension. The reaction mixture was heated under reflux for 2 h. The solvent was removed under vacuum and the red residue was suspended in CH_2Cl_2 (2 mL) and filtered over a 2 cm layer of silica gel. Hexane (2 mL) was added and the solvents were slowly evaporated, which resulted in the formation of a red solid of crude $[Tc(NO)(Cp)(PPh_3)Cl]$, which was isolated by filtration, washed with hexane and recrystallized from CH_2Cl_2/hexane. Yield 73 % (291 mg).

Elemental analysis: Calcd. for $C_{23}H_{20}NOPClTc$: Tc, 20.1 %. Found: Tc, 19.5 %. IR (KBr, cm^{-1}): 3075 (w), 3053 (w), 2961 (w), 2922 (w), 1682 (vs), 1478 (m), 1433 (s), 1310 (w), 1183 (m), 1157 (w), 1094 (s), 1070 (w), 1026 (w), 999 (m), 833 (w), 810 (m), 748 (m), 694 (s), 583 (m), 527 (s), 503 (m), 434 (w) .

^{1}H-NMR ($CDCl_3$, ppm): 7.48 - 7.52 (m, 9H), 7.40 - 7.42 (m, 6H), 5.12 (s, 5H). $^{31}P\{^{1}H\}$-NMR ($CDCl_3$, ppm): 29.5. ^{99}Tc-NMR ($CDCl_3$, ppm): -231, Δpp = 7170 Hz.

1.3. [Tc(NO)(Cp)(PPh_3)Br]

Method a). [Tc(NO)Br_2(PPh_3)$_2$(MeCN)] (256 mg, 0.3 mmol) was suspended in 5 mL toluene. KCp (62.4 mg, 0.6 mmol) was dissolved in 5 mL toluene and added to the red suspension. The reaction mixture was heated under reflux for 2 h. The solvent was removed under vacuum and the red residue was suspended in CH_2Cl_2 (2 mL) and filtered over a 2 cm layer of silica gel. Hexane (2 mL) was added and the solvents were slowly evaporated, which resulted in the formation of a red precipitate of crude [Tc(NO)(Cp)(PPh_3)Cl], which was isolated by filtration and washed with hexane. A pure product and single crystals for X-ray diffraction were obtained from CH_2Cl_2/*n*-hexane (1:5, v/v). Yield 60 % (97 mg).

Method b). [Tc(NO)(Cp)(PPh_3)Cl] (49 mg, 0.1 mmol) was dissolved in 2 mL CH_2Cl_2 and cooled to 0°C. HBr (0.1 mL, 48%) was added and the red reaction mixture was stirred at room temperature for 2 h. The solvent was concentrated to 1 mL and filtered over a 2 cm layer of silica gel. The resulting solution was overlayered with diethylether. Red crystals were obtained after slow diffusion of the solvents. Yield: 38 % (21 mg).

Method c). [Tc(NO)(Cp)(PPh_3)Cl] (25 mg, 0.05 mmol) was dissolved in 1 mL CH_2Cl_2 and Me_3SiBr (1 mL) was added. The mixture was stirred for 2 h at room temperature. The reaction mixture was filtered over 2 cm silica gel. The red solution was concentrated and covered with a layer of diethylether (2 mL). Red crystals were obtained upon diffusion of the solvents. Yield: 24 % (7 mg).

Elemental analysis: Calcd. for $C_{23}H_{20}NOPBrTc$: Tc, 18.5 %. Found Tc, 18.2 %. IR (KBr, cm^{-1}): 3073(w), 3053 (w), 2918 (w), 2851 (w), 1684 (vs), 1479 (m), 1435 (s), 1310 (w), 1261 (m), 1182 (w), 1159 (w), 1119 (w), 1094 (s), 1028 (w), 999 (m), 897 (w), 835 (w), 810 (m), 745 (m), 694 (s), 581 (m), 527 (s), 498 (m), 446 (w), 434 (w). ^{1}H-NMR ($CDCl_3$, ppm): 7.64 - 7.69 (m, 9H), 7.40 - 7.55 (m, 6H), 5.11 (s, 5H). $^{31}P\{^{1}H\}$-NMR ($CDCl_3$, ppm): 29.7. ^{99}Tc-NMR ($CDCl_3$, ppm): -350, Δpp = 6500 Hz.

1.4. [Tc(NO)(Cp)(PPh_3)(CO)]BF_4

[Tc(NO)(Cp)(PPh_3)Cl] (25 mg, 0.05 mmol) was dissolved in 2 mL CH_2Cl_2 and treated with a solution of $AgBF_4$ (19 mg, 0.1 mmol) in 2 mL CH_2Cl_2/MeOH (2/1, v/v). CO gas was bubbled through the red solution for 1 h. The solution was filtered and the solvent was removed under vacuum. The red-brown residue was dissolved in CH_2Cl_2 (1 mL) and covered with *n*-hexane (4 mL). Red crystals were obtained by slow diffusion of the solvents. Yield 36 % (11 mg).

Elemental analysis: Calcd. for $C_{24}H_{20}NO_2PBF_4Tc$: Tc, 17.3 %. Found Tc, 17.1 %. IR (KBr, cm^{-1}): 3112 (w), 2920 (w), 2851 (w), 2037 (vs), 1776 (vs), 1477 (m), 1473 (m), 1096 (s), 1065 (s), 1047 (s), 997 (m), 845 (w), 754 (m), 694 (s), 615 (w), 583 (m), 522 (s), 453 (w), 420 (w). ^{1}H-NMR ($CDCl_3$, ppm): 7.53 – 7.61 (m, 9H), 7.25 - 7.33 (m, 6H), 5.81 (s, 5H). $^{31}P\{^1H\}$-NMR ($CDCl_3$, ppm): 63.8 (very broad). ^{99}Tc-NMR ($CDCl_3$, ppm): -1753, Δpp = 3900 Hz.

1.5. [Tc(NO)(Cp)(PPh_3)(Ph)]

[CuBr(SMe_2)] (0.7 mL, 0.66 mmol, 1.0 M in diethylether) was suspended 2 mL THF and cooled to 0 °C. Phenylmagnesiumbromide (123 mg, 0.68 mmol) was slowly added to the suspension and stirred for 30 min at room temperature. [Tc(NO)(Cp)(PPh_3)Cl] (49 mg, 0.1 mmol) in 2 mL CH_2Cl_2 was added to the yellow suspension and the reaction mixture was stirred at 0 °C for 2 h. The mixture was filtered and the solvent was removed under vacuum. The orange-red residue was dissolved in 0.5 mL CH_2Cl_2 and filtered over a 2 cm layer of silica gel. The solution was concentrated to 1 mL and covered with 3 mL *n*-hexane. An orange-red solid was obtained after slow diffusion of the solvents. Single crystals for X-ray diffraction were obtained from CH_2Cl_2/ *n*-hexane (1:5, v/v). Yield 44 % (25 mg).

Elemental analysis: Calcd. for $C_{29}H_{25}NOPTc$: Tc, 18.5 %, found: Tc, 18.5 %. IR (KBr, cm^{-1}): 3262 (w), 3046 (w), 2959 (w), 2920 (w), 2851 (w), 1651 (vs), 1639 (vs), 1560 (m), 1545 (m), 1477 (m), 1462 (m), 1435 (m), 1308 (m), 1260 (m), 1242 (m), 1180 (w), 1092 (m), 1013 (m), 997 (w), 834 (w), 820 (m), 804 (m), 736 (m), 698 (s), 637 (m), 584 (m), 557 (m), 526 (s), 500 (m), 447 (w), 424 (w). ^{1}H-NMR ($CDCl_3$, ppm): δ = 7.25 - 7.33 (m, 15H), 7.07 (d, *J* = 6.8 Hz, 2H), 6.7 (m, 3H), 5.10 (s, 5H). ^{13}C-NMR ($CDCl_3$, ppm): δ = 142.0 (s, 1C, q-C-Ph), 135.3 (s, 2C, o-C-Ph), 134.8 (s, 1C, q-C-PPh_3), 133.6 (d, *J* = 10.8 Hz, 6C, m-C-PPh_3), 129.9 (s, 3C, p-C-PPh_3), 128.1 (d, J = 10 Hz, 6C, o-C-PPh_3), 125.9 (s, 2C, m-C-Ph), 120.7 (s, 1C, p-C-Ph), 94.1 (s, 5C, Cp). $^{31}P\{^1H\}$-NMR ($CDCl_3$, ppm): 58.0 (broad). ^{99}Tc-NMR ($CDCl_3$, ppm): -1201, Δpp = 8820 Hz.

1.6. [Tc(NO)Br_3($OPPh_3$)$_2$]

[Tc(NO)(Cp)Br(PPh_3)] (27 mg, 0.05 mmol) was dissolved in 1 mL benzene. The red solution was treated with Br_2 (0.025 mmol) in 0.5 mL benzene. A purple solid precipitated from the dark solution. It was isolated by filtration and recrystallized from CH_2Cl_2/MeOH. Red crystals. Yield 40 % (18 mg).

Elemental analysis: Calcd. for $C_{36}H_{30}NO_3P_2Br_3Tc$: Tc, 10.7 %, found: Tc, 10.3 %. IR (KBr, cm^{-1}): 3059 (w), 2963 (w), 2918 (w), 2851 (w), 1769 (vs), 1481 (w), 1435 (m), 1317 (w), 1188 (w), 1092 (m), 1020 (m), 951 (m), 826 (w), 740 (m), 702 (m), 691(m), 621 (w), 594 (w), 520 (m), 496 (m), 449 (w).

EPR (CH_2Cl_2, 298 K): $g_0 = 2.056 \pm 0.001$, $a_0^{Tc} = 147.93 \pm 1.0 \cdot 10^{-4}$ cm^{-1}.

EPR (CH_2Cl_2, 77 K): $g_{\parallel}$ = 2.042 $\pm$ 0.001, $A_{\parallel}^{Tc}$ = 237.26 $\pm$ 1.0 · 10^{-4} cm^{-1}, $g_{\perp}$ = 2.059 $\pm$ 0.001, $A_{\parallel}^{Tc}$ = 104.21 $\pm$ 1.0 · 10^{-4} cm^{-1}

2. Crystal Structure Determinations

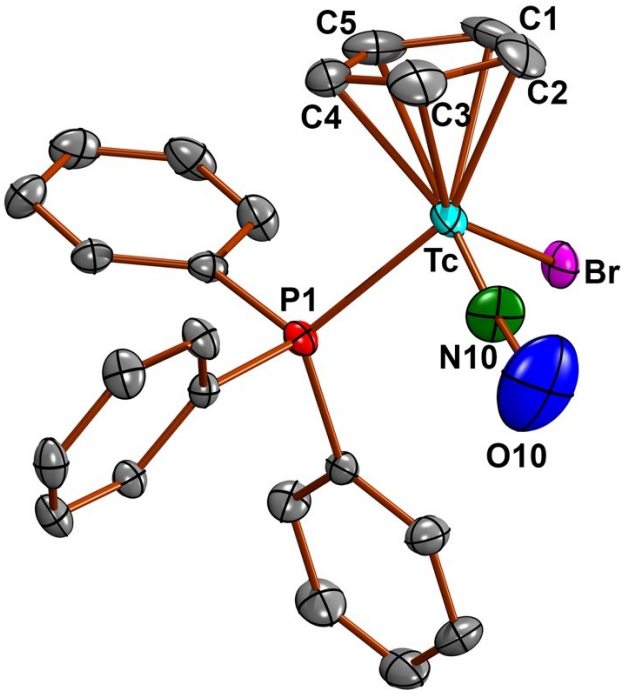
The intensities for the X-ray determinations of $[Tc(NO)Cl(Cp)(PPh_3)]$, $[Tc(NO)Br(Cp)(PPh_3)]$ and $[Tc(NO)(CO)(PPh_3)]BF_4$ were collected on a D8 Venture Bruker instrument at 100 K with Mo Kα radiation (λ = 0.71073 Å) using a TRIUMPH monochromator. The data for $[Tc(NO)Br_3(OPPh_3)_2]$ were measured on a STOE IPDS at T = 200 K. Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS14 and SHELXL14. Hydrogen atom positions were calculated for idealized positions and treated with the 'riding model' option of SHELXL. Additional information on the structure determinations has been deposited with the Cambridge Crystallographic Data Centre.

2.1. $[Tc(NO)Br(Cp)(PPh_3)]$

2.1.1. Table S1: Structure Determination and Refinement Parameters

	$[Tc(NO)Br(Cp)(PPh_3)]$
Formula	$C_{23}H_{20}BrNOPTc$
Mw	535.28
Crystal system	monoclinic
a/ Å	22.001(1)
b/ Å	13.607(1)
c/ Å	17.541(1)
β/°	126.91(1)°
V/ Å^3	4198.8(6)
Space group	C2/c
Crystal size/mm^3	0.45 x 0.18 x 0.05
Z	8
D_{cal}/ g cm^{-3}	1.694
μ/mm^{-1}	2.679
No. of reflections	61770
No. of independent, R_{int}	5012, 0.0542
No. parameters	262
R1/wR2	0.0481/0.0945
GOF	1.299
CCDC	1491441

2.1.2. Fig. S1: Ellipsoid plot of [Tc(NO)Br(Cp)(PPh_3)]



2.1.3. Table S2: Selected bond lengths and angles in [Tc(NO)Br(Cp)(PPh_3)]

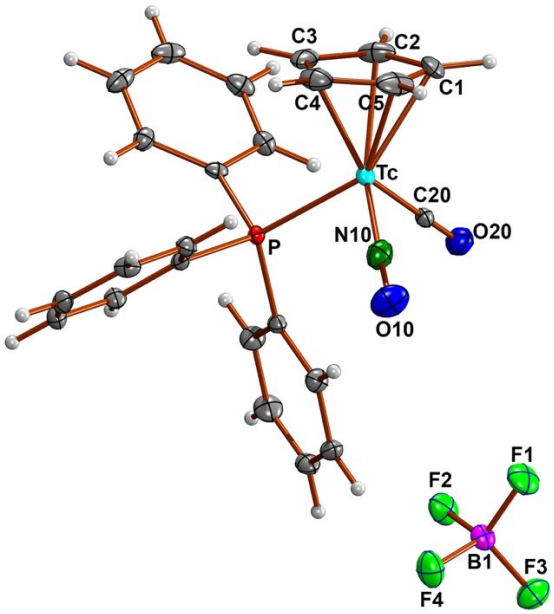
Bond lengths (Å)			
Tc-C1	2.268(4)	Tc-Cp (centroids)	1.937(2)
Tc-C2	2.287(4)	Tc-Br	2.471(9)
Tc-C3	2.282(4)	Tc-N10	1.869(9)
Tc-C4	2.283(4)	Tc-P	2.369(8)
Tc-C5	2.276 (4)	N10-O10	1.03(1)
Angles (°)			
Tc-N10-O10	171.9(9)		

2.2. $[Tc(NO)(CO)(Cp)(PPh_3)]BF_4$

2.2.1. Table S3: Structure Determination and Refinement Parameters

	$[Tc(NO)(CO)(Cp)(PPh_3)]BF_4$
Formula	$C_{24}H_{20}NO_2PBF_4Tc$
Mw	570.19
Crystal system	monoclinic
a/ Å	9.270(1)
b/ Å	17.374(1)
c/ Å	14.270(1)
β/°	100.29(1)°
V/ Å^3	2261.3(3)
Space group	$P2_1/c$
Crystal size/mm^3	0.40 x 0.07 x 0.01
Z	4
D_{cal}/ g cm^{-3}	1.675
μ/mm^{-1}	0.763
No. of reflections	47238
No. of independent, R_{int}	4651, 0.0554
No. parameters	307
R1/wR2	0.0268/0.0622
GOF	1.044
CCDC	1491442

2.2.2. Fig. 2: Ellipsoid plot of $[Tc(NO)(CO)(Cp)(PPh_3)]BF_4$



2.2.3. Table S4: Selected bond lengths and angles in $[Tc(NO)(CO)(Cp)(PPh_3)]BF_4$

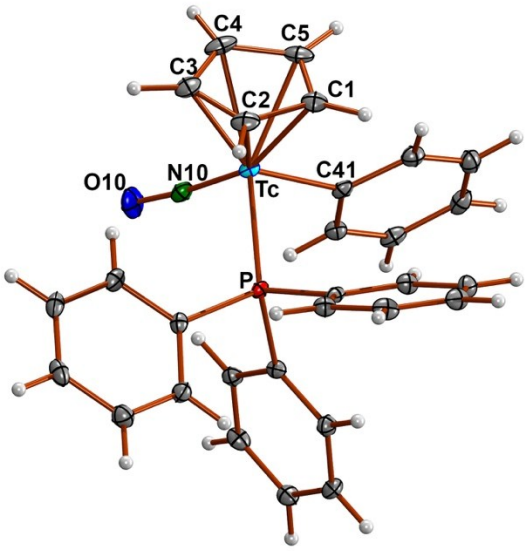
Bond lengths (Å)			
Tc-C1	2.261(3)	Tc-N10	1.832(2)
Tc-C2	2.276(3)	Tc-C20	1.903(2)
Tc-C3	2.311(3)	Tc-P	2.401(6)
Tc-C4	2.271(3)	N10-O10	1.155(3)
Tc-C5	2.298(3)	C20-O20	1.133(3)
Tc-Cp (centroid)	1.944(1)		
Angles (°)			
Tc-N10-O10	170.7(8)	N10-Tc-C20	96.5(1)
Tc-C20-O20	178.9(2)		

2.3. [Tc(NO)(Cp)(Ph)(PPh_3)]

2.3.1. Table S5: Structure Determination and Refinement Parameters

	[Tc(NO)(Cp)(Ph)(PPh_3)]
Formula	$C_{29}H_{25}NOPTc$
Mw	532.47
Crystal system	monoclinic
a/ Å	9.179(1)
b/ Å	13.937(1)
c/ Å	10.048(7)
α/°	90 °
β/°	112.89(2)°
γ/°	90°
V/ $Å^3$	1184(2)
Space group	$P2_1$
Crystal size/mm^3	0.25 x 0.16 x 0.12
Z	2
D_{cal}/ g cm^{-3}	1.493
μ/mm^{-1}	0.698
No. of reflections	46079
No. of independent, R_{int}	5631, 0.0220
No. parameters	298
R1/wR2	0.0141/0.0358
GOF	0.714
Flack	-0.006(4)
CCDC	1491443

2.3.2. Fig. S3: Ellipsoid plot of [Tc(NO)(Cp)(Ph)(PPh_3)]



2.3.3. Table S6: Selected bond lengths and angles in [Tc(NO)(Cp)(Ph)(PPh_3)]

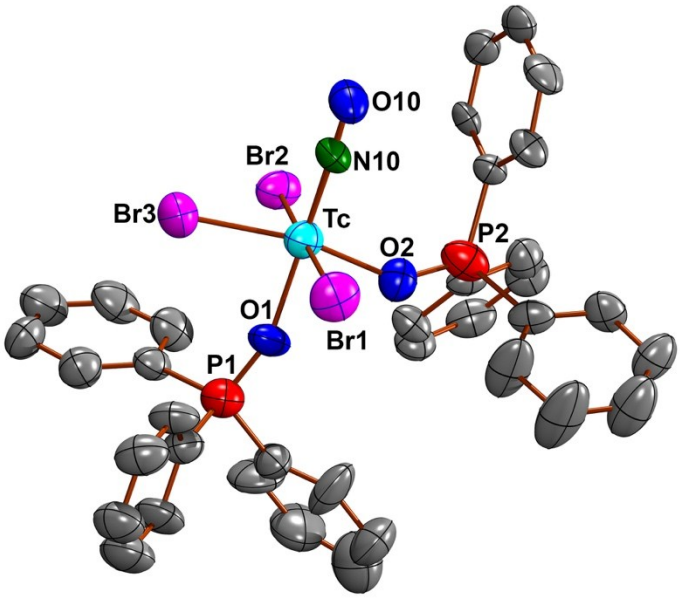
Bond lengths (Å)			
Tc-C1	2.296(3)	Tc-Cp (centroid)	1.972(2)
Tc-C2	2.326(3)	Tc-N10	1.758(2)
Tc-C3	2.343(3)	Tc-C41	2.149(2)
Tc-C4	2.316(2)	Tc-P	2.357(1)
Tc-C5	2.294(2)	N10-O10	1.198(2)
Angles (°)			
Tc-N10-O10	174.2(2)	N10-Tc-C41	95.5(1)

2.4. $[Tc(NO)Br_3(OPPh_3)_2]$

2.4.1. Table S7: Structure Determination and Refinement Parameters

	$[Tc(NO)Br_3(OPPh_3)_2]$ x 0.5 CH_2Cl_2
Formula	$C_{36.50}H_{31}Br_3ClNO_3P_2Tc$
Mw	966.74
Crystal system	Monoclinic
a/ Å	12.551(1)
b/ Å	14.394(1)
c/ Å	44.488(4)
α/°	90 °
β/°	97.55(1)°
γ/°	90°
V/ $Å^3$	7967.5(11)
Space group	$P2_1/c$
Crystal size/mm^3	0.1 x 0.08 x 0.06
Z	8
D_{cal}/ g cm^{-3}	1.612
μ/mm^{-1}	1.612
No. of reflections	47263
No. of independent, R_{int}	13834, 0.1777
No. parameters	881
R1/wR2	0.0673/0.1388
GOF	0.867
CCDC	1491444

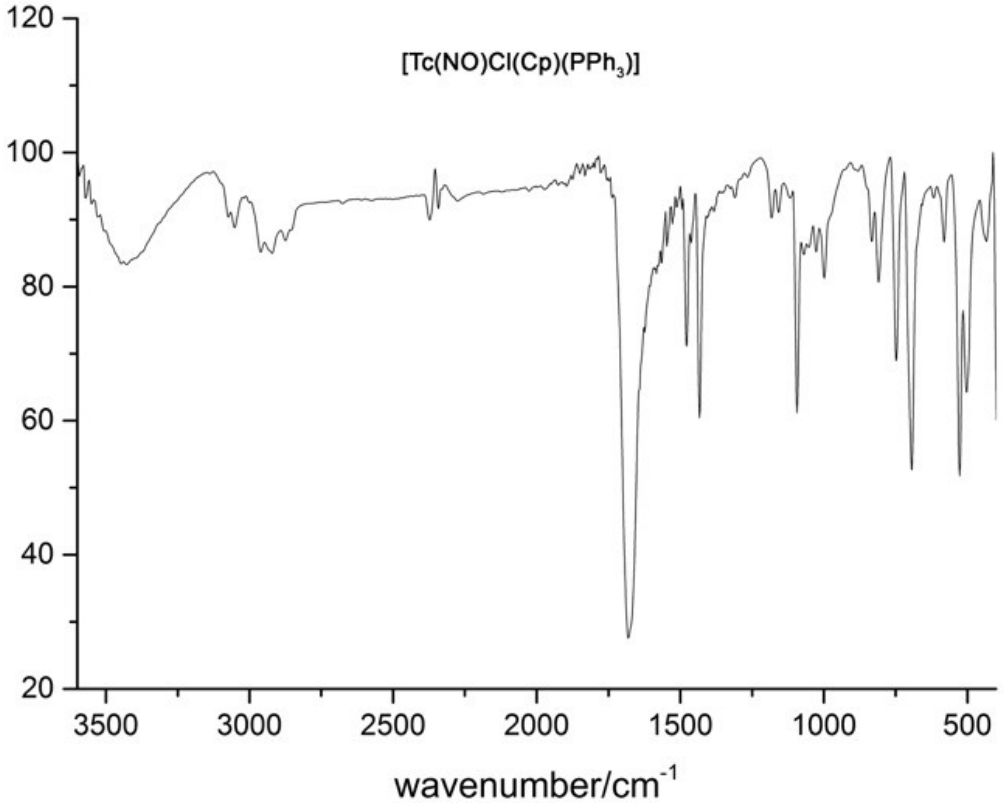
2.3.2. Fig. S4: Ellipsoid plot of $[Tc(NO)Br_3(OPPh_3)_2]$

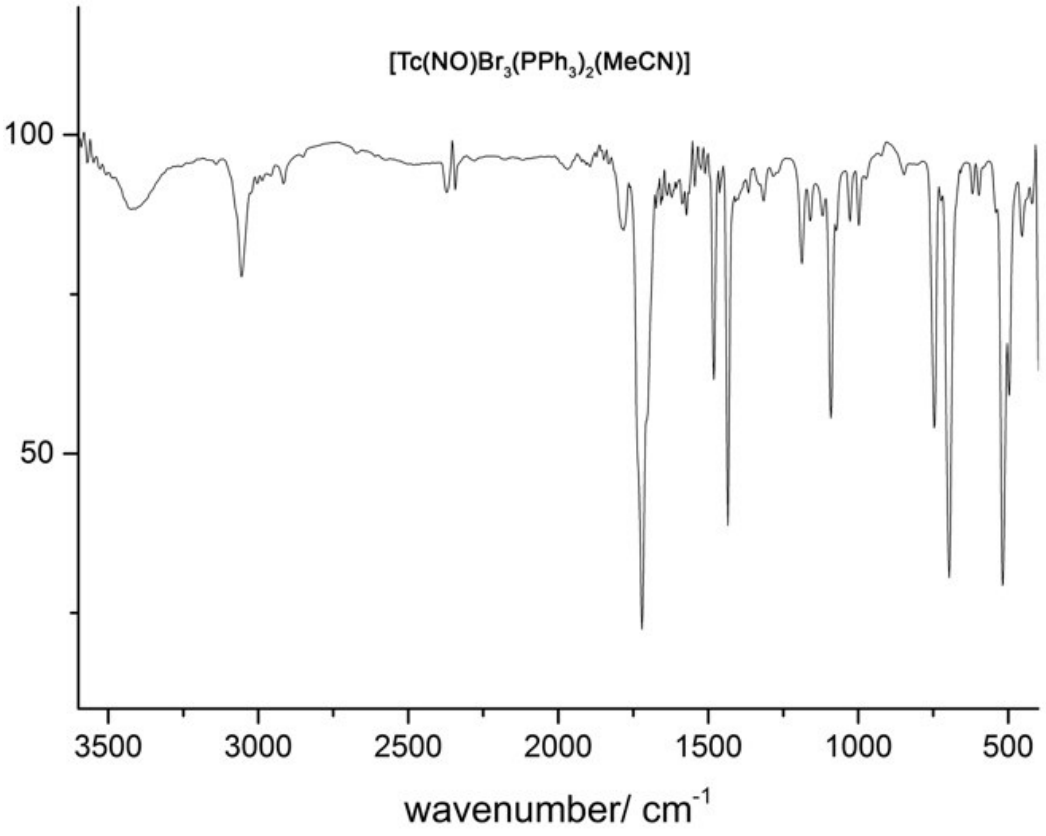


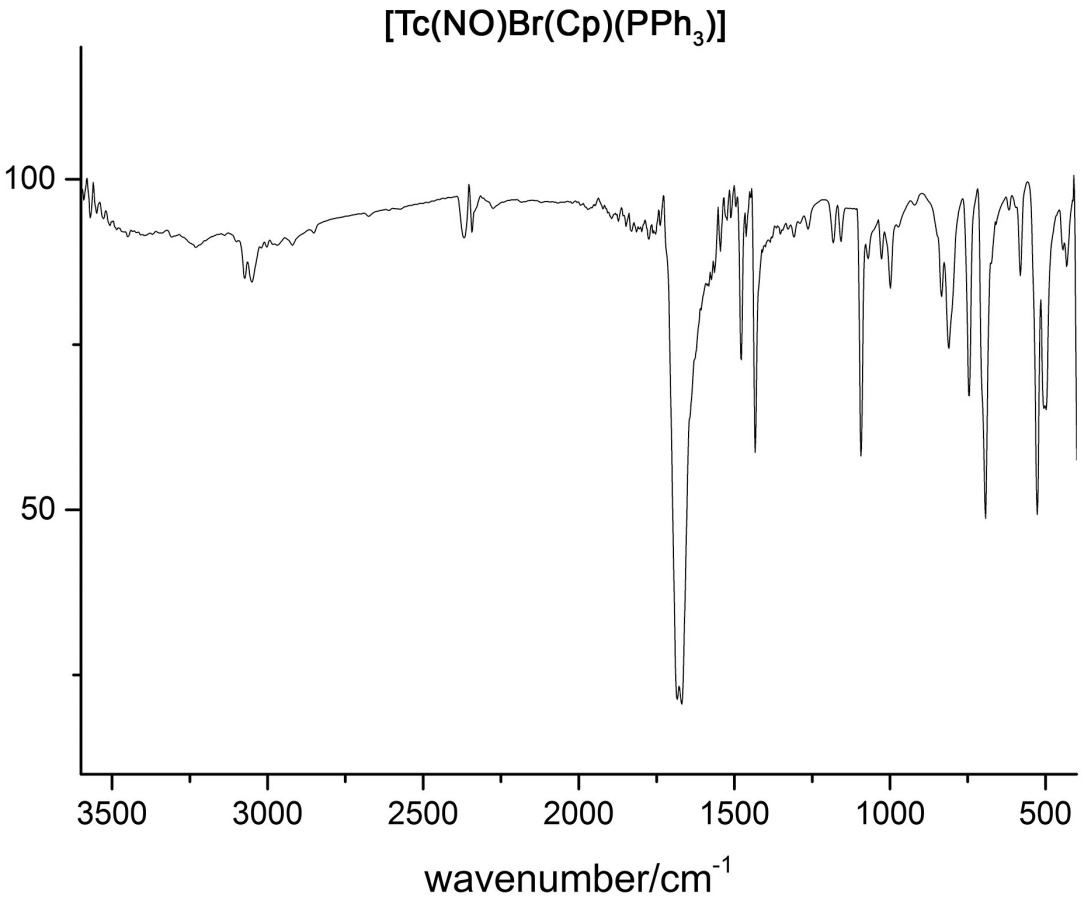
2.3.3. Table S8: Selected bond lengths and angles in $[Tc(NO)Br_3(OPPh_3)_2]$

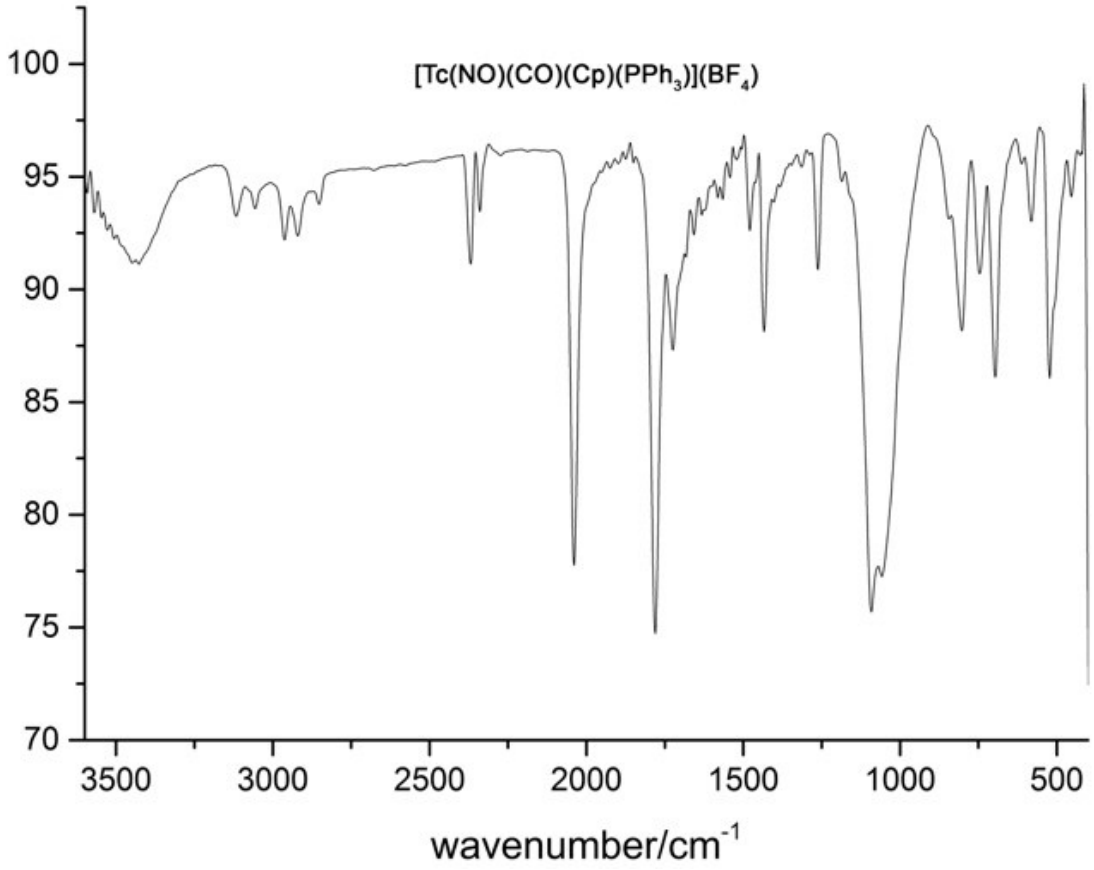
Bond lengths (Å)			
Tc-N10	1.77(1)	Tc-O1	2.076(8)
Tc-Br1	2.500(2)	Tc-O2	2.016(9)
Tc-Br2	2.505(2)	N10-O10	1.07(1)
Tc-Br3	2.484(2)		
Angles (°)			
N10-Tc-Br1	91.4(3)	N10-Tc-O2	99.3(4)
N10-Tc-Br2	91.3(3)	Tc-N10-O10	175(1)
N10-Tc-Br3	92.1(3)		

3. IR spectra


[Tc(NO)Cl(Cp)(PPh3)]
120
100
80
60
40
20
3500
3000
2500
2000
1500
1000
500
wavenumber/cm-1


[Tc(NO)Br3(PPh3)2(MeCN)]
100
50
3500
3000
2500
2000
1500
1000
500
wavenumber/ cm-1


[Tc(NO)Br(Cp)(PPh3)]
100
50
3500
3000
2500
2000
1500
1000
500
wavenumber/cm-1


[Tc(NO)(CO)(Cp)(PPh3)](BF4)
100
95
90
85
80
75
70
3500
3000
2500
2000
1500
1000
500
wavenumber/cm-1

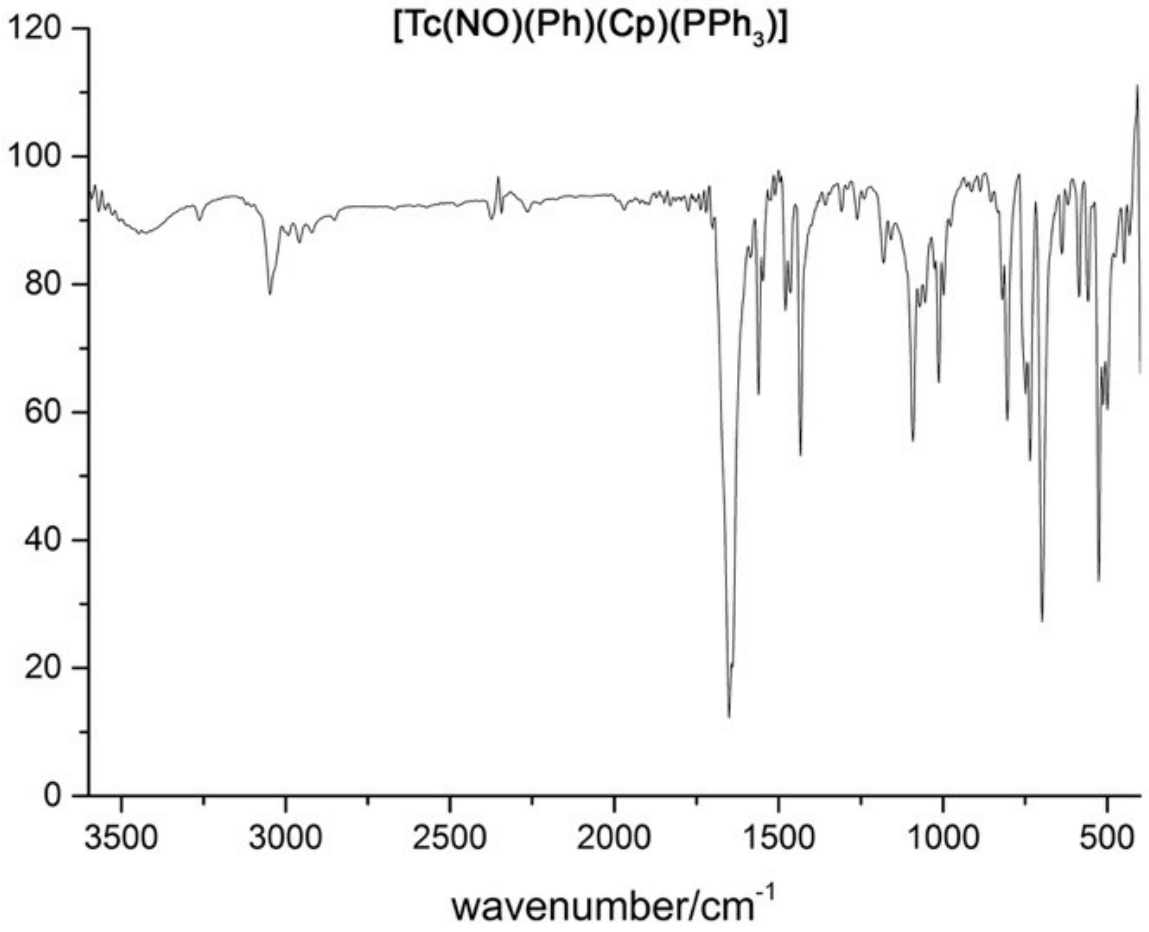

[Tc(NO)(Ph)(Cp)(PPh3)]
120
100
80
60
40
20
0
3500
3000
2500
2000
1500
1000
500
wavenumber/cm-1

Table S9: Comparison of the ν(NO) bands in [Tc(NO)X(Cp)(PPh_3)] and [Tc(NO)X(Cp)(PPh_3)] complexes

	[M(NO)Cl(Cp)(PPh_3)]	[M(NO)Br(Cp)(PPh_3)]	[M(NO)Ph(Cp)(PPh_3)]	[M(NO)(CO)(Cp)(PPh_3)]
Tc	1682	1684	1651	1776
Re	1674[a)]	1673[a)]	1633[b)]	1760[c)]

[a)] J.H. Merrifield, J.M. Fernandez, W.E. Buhro, J.A. Gladysz, Inorg. Chem. **1984**, 23, 4022. [b)] W. Tam, G.-Y. Lin, W.-K. Wong, W.A. Kiel, V.K. Wong, J.A. Gladysz, J. Am. Chem. Soc. **1982**, 104, 141. [c)] S.K. Agbossou, G.S. Bodner, A.T.Patton, J.A. Gladysz, Organometallics **1990**, 9, 1184,