Supplementary Material to the paper

Technetium Complexes with Arylselenolato and Aryltellurolato Ligands

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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 $(NBu_4)[TcOCl_4]$ was prepared by the standard procedure of Davison et al. (*Inorg. Synth.* **1982**, *21*, 160) and $[Tc(PPh_3)_2(MeCN)Cl_3]$ was prepared by the procedure of Davison et al. (*Inorg. Chem.* **1989**, *28*, 3332). The preparation of $(ArE)_2$ (Ar = -Ph, -Me_2Ph and -Mesityl; E= Se, Te) derivatives, were performed by the general procedure of Irgolic et al. (*J. Organomet. Chem.* **1972**, *38*, 1972).

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.

1.1 $(TBA)[TcO(SePh)_4] \cdot CH_2Cl_2$

To a stirred solution of $(PhSe)_2$ (78 mg, 0.25 mmol) in 3 mL of a mixture of $CHCl_3$/MeOH (1:2, v/v), was added dropwise a 2 M solution of $LiBH_4$ in THF (0.25 mL, 0.5 mmol) in an atmosphere of dry argon. The reduction was completed when the yellow color of diphenyl diselenide disappeared, yielding a colorless solution of Li(SePh). Solid $(NBu_4)[TcOCl_4]$ (50 mg, 0.1 mmol) was added to the solution. After 5 minutes, a dark green precipitate was formed. It was filtered off, washed with 1 mL of MeOH, 5mL of Et_2O and dried under vacuum. Recrystallization from MeOH/CH_2Cl_2 (1 mL: 1 mL) by slow evaporation at -10°C gave dark green single crystals. Yield: 60% (59 mg).

Elemental Analysis: Calcd. for $C_{41}H_{58}NOSe_4TcCl_2$: Tc, 9.2%. Found: Tc, 9.5%. ^{1}H NMR (CD_2Cl_2, ppm) δ = 7.53 – 7.78 (m, 8H), 7.10 – 7.28 (m, 12H), 2.70 – 2.86 (m, 8H), 1.25 – 1.42 (m, 16H), 0.96 (t, *J*= 7.2 Hz, 12H).^{13}C NMR (CD_2Cl_2, ppm) δ = 137.7, 131.4, 127.4, 125.8, 58.7, 23.7, 19.6, 13.4. ^{77}Se NMR ($CDCl_3$, ppm) δ = 346.7.

Experimental IR (KBr, cm^{-1}): 3053 (w), 2958 (m), 2871(w), 1579 (m), 1476 (s), 1437 (w), 1383 (w), 1301 (w), 1066 (w), 1024 (m), 1000 (w), 940(s), 897 (m), 736 (vs), 691 (s), 663 (w), 472 (m).

Calculated Vibrational Frequencies (DFT): The values reported correspond to the peaks of a Lorentzian fit, with 12 cm^{-1} band width at the ½ height. IR (cm^{-1}): 3242, 3230, 3215, 1666, 1522, 1480, 1376, 1344, 1227, 1110, 1055, 1034, 974, 896, 788, 731, 685, 640, 502.

1.2. (TBA)[TcO(TePh)$_4$] · CH_2Cl_2

To a stirred solution of $(PhTe)_2$ (102 mg, 0.25 mmol) in 3 mL of a $CHCl_3$/MeOH (1:2, v/v), was added dropwise a 2 M solution of $LiBH_4$ in THF (0.25 mL, 0.5 mmol) in an atmosphere of dry argon. The reduction was completed when the red color of diphenyl ditelluride disappeared, yielding a colorless solution of Li(TePh). Solid $(NBu_4)[TcOCl_4]$ (50 mg, 0.1 mmol) was added to the solution and after 5 minutes, a dark brown precipitate was formed. It was filtered off, washed with 1mL of MeOH, 5mL of Et_2O and dried under vacuum. Recrystallization from MeOH/CH_2Cl_2 (1 mL: 1 mL) by slow evaporation at -10°C gave dark brown crystals. Yield: 57% (67 mg).

Elemental Analysis: Calcd. for $C_{41}H_{58}NOTcTe_4Cl_2$: Tc, 8.4%. Found: Tc, 8.9%. ^{1}H NMR (CD_2Cl_2, ppm) δ = 7.73 – 7.90 (m, 8H), 7.04 – 7.25 (m, 12H), 3.00 (t, *J*= 8.9 Hz, 8H), 1.47 – 1.54(m, 8H), 1.38 (h, *J* = 7.3 Hz, 8H), 0.98 (t, *J*= 7.3 Hz, 12H). ^{13}C NMR (CD_2Cl_2, ppm) δ = 137.5, 129.2, 128.0, 127.6, 58.8, 23.8, 19.7, 13.0. ^{125}Te NMR ($CDCl_3$, ppm) δ = 593.0.

Experimental IR (KBr, cm^{-1}): 3045 (m), 2956 (w), 2872(w), 1570 (s), 1469 (s), 1431 (s), 1379 (w), 1323 (w), 1176 (w), 1062 (w), 1014 (m), 997 (m), 894 (s), 726 (vs), 688 (s), 650 (w), 451 (m).

Calculated Vibrational Frequencies (DFT): The values reported correspond to the peaks of a Lorentzian fit, with 12 cm^{-1} band width at the ½ height. IR (cm^{-1}): 3247, 3238, 3229, 1664, 1520, 1474, 1372, 1339, 1231, 1108, 1051, 1036, 976, 901, 783, 732, 675, 639, 492.

1.3. [Tc(2,6-Me_2PhSe)$_3$(AN)(PPh_3)]

To a stirred solution of (2,6-Me_2PhSe)$_2$ (73 mg, 0.2 mmol) in 3 mL of a mixture of $CHCl_3$/MeOH (1:2, v/v), was added dropwise a 2 M solution of $LiBH_4$ in THF (0.2 mL, 0.4 mmol). The reduction of the diselenide was completed when the yellow color of the solution disappeared, yielding a colorless solution of Li(Me_2-PhSe). Solid [Tc(PPh_3)$_2$(MeCN)Cl_3] (77 mg, 0.1 mmol) was added to the solution, which slowly dissolved. After 10 min, from the resulting clear solution, a dark green solid precipitated. It was filtered off, washed with 1 mL of MeOH, 2 mL of Et_2O and dried under vacuum. Recrystallization from MeCN/CH_2Cl_2 (1 mL: 1 mL) by slow evaporation at -10°C yielded dark green crystals. Yield: 68% (65 mg).

Elemental Analysis: Calcd. for $C_{47}H_{51}NPSe_3Tc$: Tc, 10.36%. Found: Tc, 10.30%. ^{1}H NMR ($CDCl_3$, ppm) δ = 7.78 – 7.88 (m, 6H), 7.38 – 7.46 (m, 9H), 6.69 (t, *J*= 7.4 Hz, 3H), 6.83 (d, *J*= 7.4 Hz, 6H), 1.99 (s, 18H), 0.93 (s, 3H. ^{13}C NMR ($CDCl_3$, ppm) δ = 142.5, 142.0, 137.0, 136.6, 134.9, 129.4, 127.7, 126.6, 126.3, 24.1, 1.6. ^{31}P NMR ($CDCl_3$; *δ*, ppm): 29.2.

IR (KBr, cm^{-1}): 3430 (w), 3365 (w), 3047 (w), 2977 (m), 2278 (w), 1913 (w), 1585 (w), 1500 (s), 1488 (s), 1461 (s), 1439 (s), 1405 (s), 1370 (m), 1179 (s), 1095 (s), 1009 (s), 899 (w), 795 (m), 776 (m), 695 (s), 625 (w), 524 (s).

Calculated Vibrational Frequencies (DFT): The values reported correspond to the peaks of a Lorentzian fit, with 15 cm^{-1} band width at the ½ height. IR (cm^{-1}): 3260, 3244, 3220, 3168, 3072, 2393, 1664, 1528, 1486, 1454, 1348, 1242, 1214, 1136, 1108, 1066, 1033, 829, 804, 739, 703, 575, 549.

1.4. [Tc(MesitylSe)$_3$(AN)(PPh$_3$)]

(MesitylSe)$_2$ (80 mg, 0.2 mmol) was dissolved in 3 mL of a mixture of $CHCl_3$/MeOH (1:2, v/v), and a 2 M solution of $LiBH_4$ in THF (0.2 mL, 0.4 mmol) was added dropwise under an atmosphere of dry argon. The reduction of the diselenide was completed when the yellow colour of the solution disappeared, giving colorless solution of Li(MesitylSe). Solid [Tc(PPh$_3$)$_2$(MeCN)Cl$_3$] (77 mg, 0.1 mmol) was added to the solution. It dissolved within a period of 10 min, and after further 10 min, a dark green precipitate was formed. It was filtered off, washed with 1 mL of MeOH, 2 mL of Et_2O and dried under vacuum. Recrystallization from MeCN/CH_2Cl_2 (1 mL: 1 mL) by slow evaporation at -10°C gave dark green crystals. Yield: 73% (73 mg).

Elemental Analysis: Calcd. for $C_{47}H_{51}NPTcSe_3$: Tc, 9.9%. Found: Tc, 10.1%. IR (KBr, cm^{-1}): 3062 (w), 2920 (m), 2850 (m), 2380 (w), 1589 (m), 1483 (m), 1454 (m), 1437 (s), 1409 (s), 1363 (m), 1313 (w), 1172 (m), 1155 (s), 1120 (s), 1083 (m), 1072 (m), 1026 (m), 997 (m), 899 (w), 819 (m), 746 (m), 725 (s), 694 (s), 675 (m), 540 (s), 503 (m), 486(w) 449 (w). ^{1}H NMR ($CDCl_3$, ppm) δ = 7.71 – 7.37 (m, 15H), 7.26 (s, 6H), 2.43 (s, 9H), 2.21 (s, 18H), 1.25 (s, 3H). ^{31}P NMR ($CDCl_3$; *δ*, ppm): 30.0. ^{77}Se NMR ($CDCl_3$, ppm) δ = 215.7.

1.5. [Tc(MesitylTe)$_3$(AN)(PPh$_3$)]

(MesitylTe)$_2$ (99 mg, 0.2 mmol) was dissolved in 3 mL of a mixture of $CHCl_3$/MeOH (1:2, v/v), and a 2 M solution of $LiBH_4$ in THF (0.2 mL, 0.4 mmol) was added dropwise under an atmosphere of dry argon. The reduction of the ditelluride was completed when the red color of the solution disappeared, giving colorless solution of Li(MesitylTe). Solid [Tc(PPh$_3$)$_2$(MeCN)Cl$_3$] (77 mg, 0.1 mmol) was added to the solution. It dissolved within a period of 10 min, and after further 10 min, a dark red precipitate was formed. It was filtered off, washed with 1 mL of MeOH, 2 mL of Et_2O and dried under vacuum. Recrystallization from MeCN/CH_2Cl_2 (1 mL: 1 mL) by slow evaporation at -10°C gave dark green crystals. Yield: 62% (71 mg).

Elemental Analysis: Calcd. for $C_{47}H_{51}NPTcTe_3$: Tc, 8.7%. Found: Tc, 8.7%. ^{1}H NMR ($CDCl_3$, ppm) δ = 7.79 – 7.91 (m, 6H), 7.22 – 7.45 (m, 9H), 6.72 (s, 6H), 2.19 (s, 9H), 2.02 (s, 18H), 0.77 (s, 3H). ^{13}C NMR ($CDCl_3$, ppm) δ = 143.7, 141.7, 138.8, 138.5, 136.4, 135.5, 129.2, 126.7, 126.7, 28.2, 20.1, 2.0. ^{31}P NMR ($CDCl_3$; *δ*, ppm): 29.2. ^{125}Te NMR (CD_2Cl_2, ppm) δ = 504.6.

Experimental IR (KBr, cm^{-1}): 3049 (w), 2959 (m), 2914 (m) 2274 (w), 1579 (w), 1486 (w), 1459 (m), 1439 (s), 1379 (w), 1297 (w), 1192 (w), 1090 (m), 1033 (w), 899 (w), 849 (s), 750 (s), 724 (w), 697 (s), 546 (m), 523 (s), 447(w).

Calculated Vibrational Frequencies (DFT): The values reported correspond to the peaks of a Lorentzian fit, with 15 cm^{-1} band width at the ½ height. IR (cm^{-1}): 3205, 3166, 3066, 2390, 1687, 1651, 1530, 1485, 1460, 1454, 1384, 1364, 1243, 1110, 1059, 990, 923, 805, 738, 701, 548, 534, 443.

2. Crystal Structure Determinations

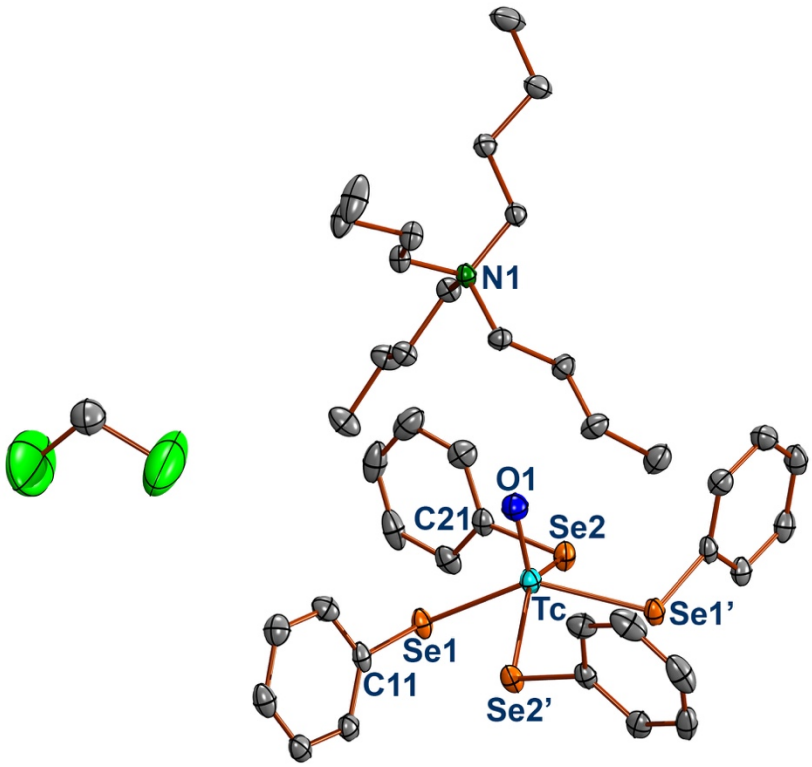
The intensities for the X-ray determinations of $(NBu_4)[TcO(SePh)_4$, $[Tc(Se\text{-}Me_2Ph)_3(AN)(PPh_3)]$ and $[Tc(MesitylTe)_3(AN)(PPh_3)]$ were collected on a D8 Venture Bruker instrument at 100K with Mo Kα radiation (λ = 0.71073 Å) using a TRIUMPH monochromator. The data for $(NBu_4)[TcO(TePh)_4]$ were measured on a STOE IPDS at T = 200K. Standard procedures were applied for data reduction and absorption correction. Structure solution and refinement were performed with SHELXS-2014 and SHELXL-2014. 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. $(NBu_4)[TcO(SePh)_4] \cdot CH_2Cl_2$

2.1.1. Table S1: Structure Determination and Refinement Parameters

	$(NBu_4)[TcO(SePh)_4] \cdot CH_2Cl_2$
Formula	$C_{41}H_{58}Cl_2NOSe_4Tc$
Mw	1065.62
Crystal system	monoclinic
a/ Å	15.4526(8)
b/ Å	18.320(1)
c/ Å	15.7324(8)
α/°	90
β/°	90.029(2)
γ/°	90
V/ $Å^3$	4453.6(4)
Space group	C2/c
Crystal size/mm^3	0.60 x 0.30 x 0.20
Z	4
D_{cal}/ g cm^{-3}	1.589
μ/mm^{-1}	3.743
No. of reflections	29773
No. of independent, R_{int}	4392, 0.0421
No. parameters	265
Final R indices [I>2sigma(I)]	R1 = 0.0349, wR2 = 0.0867
R indices (all data)	R1 = 0.0409, wR2 = 0.0907
GOF	1.025
CCDC	1536444

2.1.2. Fig. S1: Ellipsoid plot of $(NBu_4)[TcO(SePh)_4] \cdot CH_2Cl_2$



Ellipsoids drawn at 50% probability. Hydrogen atoms were removed for clarity.

2.1.3. Table S2: Selected bond lengths and angles in $(NBu_4)[TcO(SePh)_4] \cdot CH_2Cl_2$

Bond lengths (Å)			
Tc-Se1	2.4727(4)	Tc-O1	1.655(4)
Tc-Se2	2.4765(4)	Se1-C11	1.934(3)
Se2-C21	1.929(3)		
Angles (°)			
Se1-Tc-Se2	83.68(1)	O1-Tc-Se1	109.44(1)
Se1-Tc-Se1'	141.12(3)	O1-Tc-Se2	109.32(1)

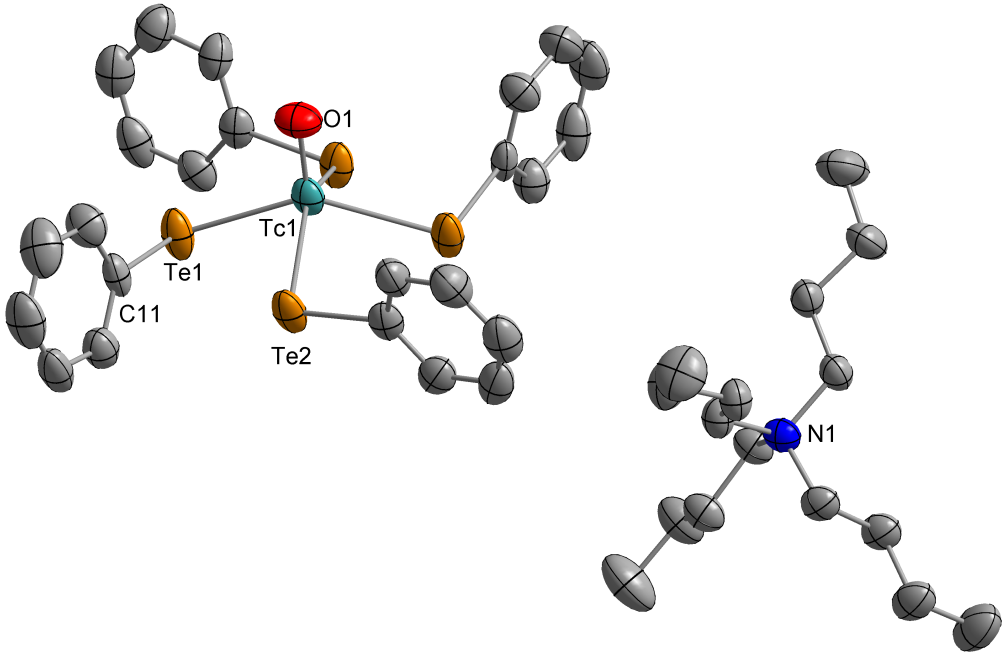
Symmetry operation: (') 1-x, y, 1.5-z

2.2. $(NBu_4)[TcO(TePh)_4] \cdot CH_2Cl_2$

2.2.1. Table S3: Structure Determination and Refinement Parameters

	$(NBu_4)[TcO(TePh)_4] \cdot CH_2Cl_2$
Formula	$C_{41}H_{58}Cl_2NOTcTe_4$
Mw	1260.16
Crystal system	monoclinic
a/ Å	15.907(2)
b/ Å	18.392(2)
c/ Å	16.246(2)
α/°	90
β/°	90.35(1)
γ/°	90
V/ $Å^3$	4753(1)
Space group	C2/c
Crystal size/mm^3	0.24 x 0.10 x 0.08
Z	4
D_{cal}/ g cm^{-3}	1.761
μ/mm^{-1}	2.851
No. of reflections	22751
No. of independent, R_{int}	5191, 0.0904
No. parameters	233
Final R indices [I>2sigma(I)]	R1 = 0.0464, wR2 = 0.1127
R indices (all data)	R1 = 0.0861, wR2 = 0.1320
GOF	0.930
CCDC	1536445

2.2.2. Fig. 2: Ellipsoid plot of $(NBu_4)[TcO(TePh)_4] \cdot CH_2Cl_2$



Ellipsoids drawn at 50% probability. Disordered CH_2Cl_2 solvate and hydrogen atoms were removed for clarity.

2.2.3. Table S4: Selected bond lengths and angles in $(NBu_4)[TcO(TePh)_4] \cdot CH_2Cl_2$

Bond lengths (Å)			
Tc1-Te1	2.6622(6)	Tc1-O1	1.662(6)
Tc1-Te2	2.6567(6)	Te1-C11	2.146(6)
Te2-C21	2.151(7)		
Angles (°)			
Te1-Tc1-Te2	83.57(2)	O1-Tc1-Te1	108.19(2)
Te1-Tc1-Te1’	143.62(4)	O1-Tc1-Te2	110.04(2)

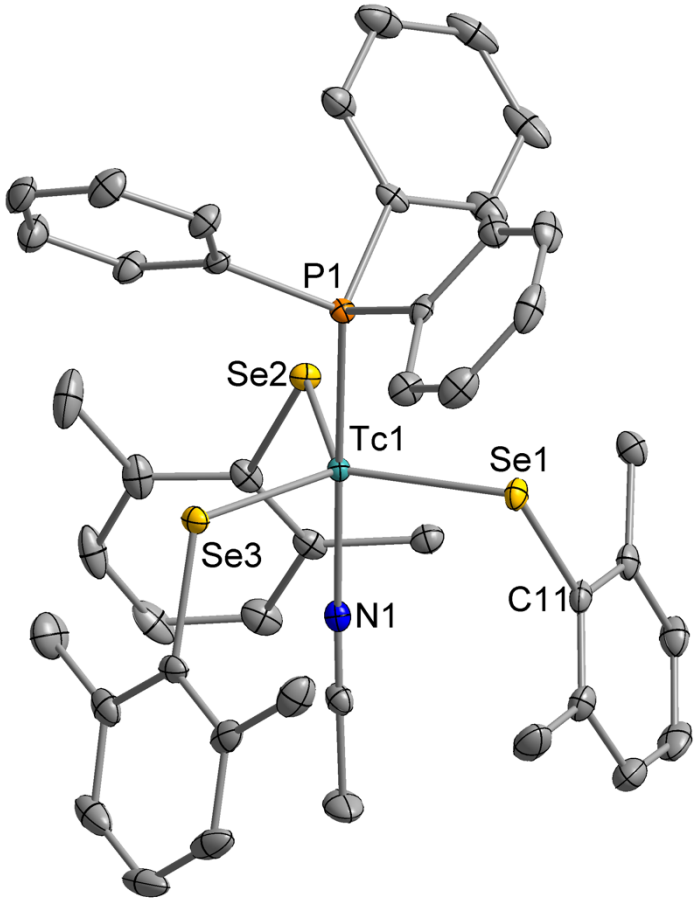
Symmetry operation: (‘) x, -y, 1.5-z

2.3. [Tc(2,6-Me_2PhSe)$_3$(AN)(PPh_3)].

2.3.1. Table S5: Structure Determination and Refinement Parameters.

	[Tc(2,6-Me_2PhSe)$_3$(AN)(PPh_3)]
Formula	$C_{44}H_{45}NPSe_3Tc$
Mw	953.66
Crystal system	triclinic
a/ Å	10.7142(6)
b/ Å	11.2883(7)
c/ Å	10.301(1)
α/°	86.201(2)
β/°	79.812(2)
γ/°	68.285(2)
V/ Å^3	2024.0(2)
Space group	$P\bar{1}$
Crystal size/mm^3	0.2 x 0.18 x 0.1
Z	2
D_{cal}/ g cm^{-3}	1.565
μ/mm^{-1}	3.124
No. of reflections	52493
No. of independent, R_{int}	9680, 0.0525
No. parameters	452
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0679
R indices (all data)	R1 = 0.0456, wR2 = 0.0728
GOF	1.043
CCDC	1536446

2.3.2. Fig. S3: Ellipsoid plot of [Tc(2,6-Me_2PhSe)$_3$(AN)(PPh_3)].



Ellipsoids drawn at 50% probability. Hydrogen atoms were removed for clarity.

2.3.3. Table S6: Selected bond lengths and angles in [Tc(2,6-Me_2PhSe)$_3$(AN)(PPh_3)].

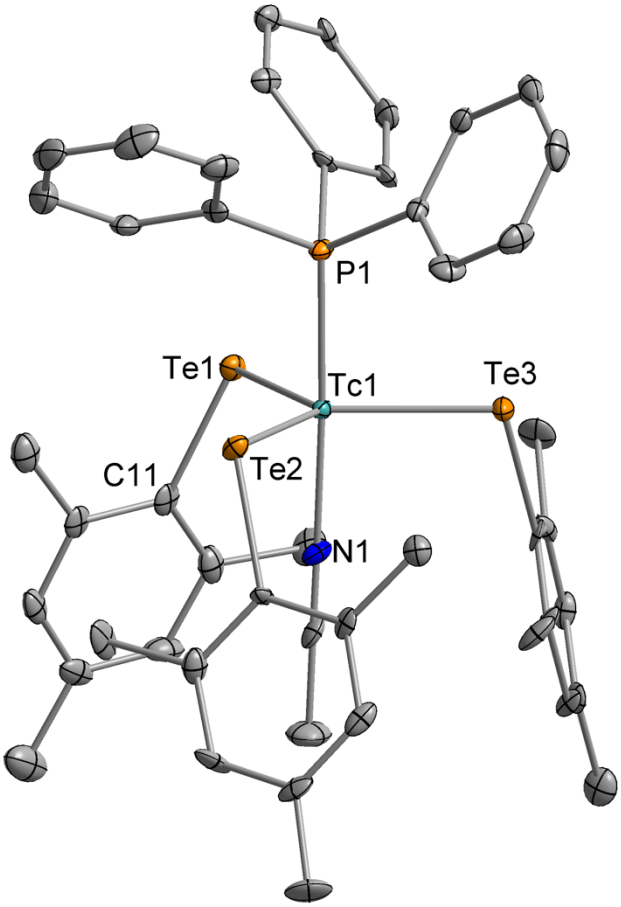
Bond lengths (Å)			
Tc1-Se1	2.3884(4)	Tc1-P1	2.3372(8)
Tc1-Se2	2.3726(4)	Tc1-N1	2.099(2)
Tc1-Se3	2.3760(4)		
Angles (°)			
Se1-Tc1-Se2	118.18(1)	P1-Tc1-Se11	87.72(2)
Se1-Tc1-Se3	122.85(1)	P1-Tc1-Se2	89.52(2)
Se2-Tc1-Se3	118.76(1)	P1-Tc1-Se3	88.21(2)
P1-Tc-N1	176.73(7)	N1-Tc1-Se1	90.59(7)
N1-Tc1-Se2	93.75(6)	N1-Tc1-Se3	90.37(6)

2.4. [Tc(MesitylTe)$_3$(AN)(PPh$_3$)].

2.4.1. Table S7: Structure Determination and Refinement Parameters.

	[Tc(MesitylTe)$_3$(AN)(PPh$_3$)]
Formula	$C_{47}H_{51}NPTcTe_3$
Mw	1141.66
Crystal system	triclinic
a/ Å	11.3440(6)
b/ Å	18.514(1)
c/ Å	21.827(1)
α/°	87.249(2)
β/°	83.169(2)
γ/°	89.829(2)
V/ Å^3	4546.3(4)
Space group	$P\bar{1}$
Crystal size/mm^3	0.2 x 0.15 x 0.1
Z	4
D_{cal}/ g cm^{-3}	1.668
μ/mm^{-1}	2.270
No. of reflections	135937
No. of independent, R_{int}	18689, 0.0975
No. parameters	933
Final R indices [I>2sigma(I)]	R1 = 0.0621, wR2 = 0.1051
R indices (all data)	R1 = 0.0851, wR2 = 0.1118
GOF	1.110
CCDC	1536447

2.3.2. Fig. S4: Ellipsoid plot of [Tc(MesitylTe)$_3$(AN)(PPh$_3$)].



Ellipsoids drawn at 50% probability. Hydrogen atoms were removed for clarity.

2.3.3. Table S8: Selected bond lengths and angles in [Tc(MesitylTe)$_3$(AN)(PPh$_3$)].

Bond lengths (Å)			
Tc1-Te1	2.5561(8) / 2.5553(8)	Tc1-P1	2.330(2) / 2.321(2)
Tc1-Te2	2.5695(8) / 2.5590(7)	Tc1-N1	2.082(6) / 2.082(6)
Tc1-Te3	2.5550(8) / 2.5705(7)		
Angles (°)			
Te1-Tc1-Te2	122.20(3) / 117.63(3)	P1-Tc1-Te1	90.44(5) / 89.69(5)
Te1-Tc1-Te3	115.57(3) / 119.15(3)	P1-Tc1-Te2	88.08(5) / 89.42(5)
Te2-Tc1-Te3	122.23(3) / 123.22(3)	P1-Tc1-Te3	91.32(5) / 91.19(5)
P1-Tc-N1	177.1(2) / 177.5(2)	N1-Tc1-Te1	90.0(2) / 92.6(2)
N1-Tc1-Te2	89.3(2) /88.7(2)	N1-Tc1-Te3	91.0(2) / 88.5 (2)