Electronic Supplementary Information for Dalton Transactions

6-Coordinate Tungsten(VI) Tris-*N*-isopropylanilide Complexes: Products of Terminal Oxo and Nitrido Transformations Effected by Main Group Electrophiles

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Supporting Information

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S1 General

X-ray data were collected on a Siemens Platform three-circle diffractometer equipped with a Bruker-AXS Apex CCD detector and an Oxford Cryosystems CryoStream 700 low-temperature device. Graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) was used in all cases. All software for diffraction data processing and crystal-structure solution and refinement are contained in the SHELXTL (v6.14) program suite (G. Sheldrick, Bruker XRD, Madison. WI).

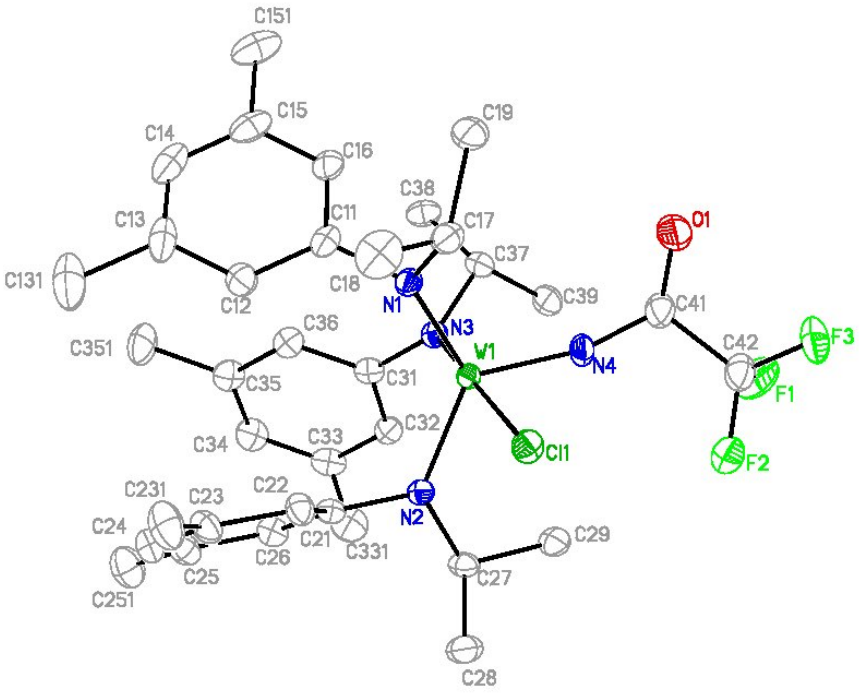

Figure S2.1 ORTEP diagram of **1**-(NC(O)CF_3)Cl with thermal ellipsoids at the 50% probability level.

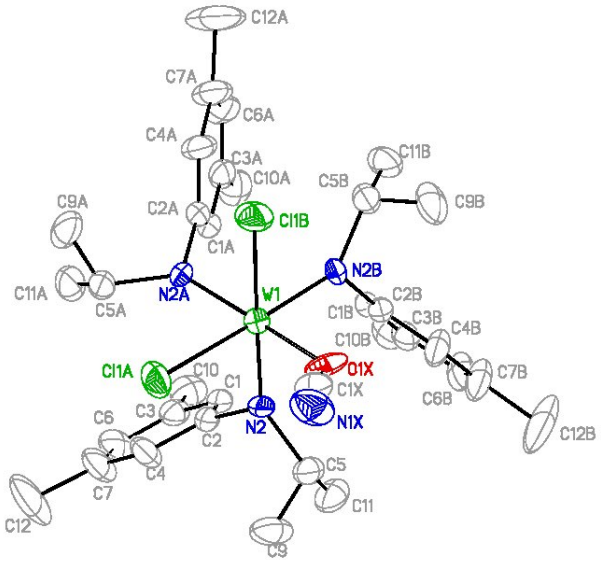

Figure S2.2 ORTEP diagram of **1**-(OCN)$(Cl)_2$ with thermal ellipsoids at the 35% probability level.

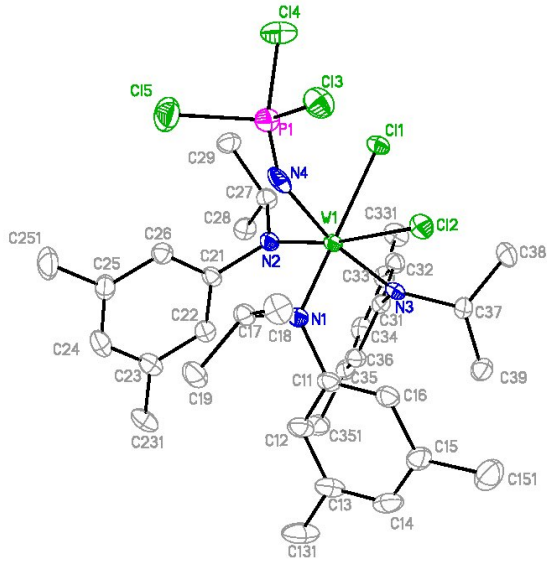

Figure S2.3 ORTEP diagram of **1**-(N=PCl_3)$(Cl)_2$ with thermal ellipsoids at the 50% probability level.

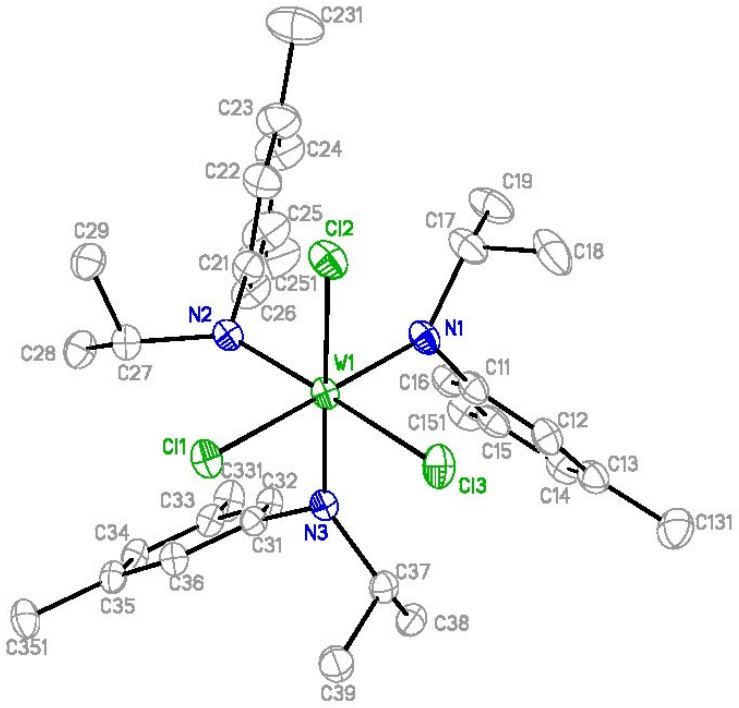

Figure S2.4 ORTEP diagram of **1**-$(Cl)_3$ with thermal ellipsoids at the 50% probability level.

S3 X-ray crystal structure of (Ar[*i*-Pr]N)$_3$W(NC(O)CF$_3$)(O$_2$CCF$_3$) (1-(NC(O)CF$_3$)Cl). Inside the glove box, crystals of **1**-(NC(O)CF$_3$)Cl, obtained from a saturated chlorotrimethylsilane solution stored at -35°C, were coated with Paratone N oil (an Exxon product) on a microscope slide. A dark red plate of approximate dimensions 0.14 × 0.08 × 0.02 mm^3 was selected and mounted on a glass fiber. A total of 73315 reflections ($-24 \le h \le 23$, $0 \le k \le 13$, $0 \le l \le 25$) were collected at 100(2) K using φ- and ω-scans in the θ range of 1.83 to 28.28°, of which 8376 were unique (R_{int} = 0.0907). The structure was solved by Patterson methods using SHELXS[1] and refined against F^2 on all data by full-matrix least squares with SHELXTL[1]. The systematic absences in the diffraction data are uniquely consistent with the assigned space group of $P2_1/n$. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. A semi-empirical absorption correction (SADABS) was applied to the diffraction data resulting in maximum and minimum transmissions equal to 0.9352 and 0.6477, respectively. The residual peak and hole electron density were 1.302 and -1.122 e·Å^{-3}, respectively. The least squares refinement converged normally with residual values of R_1 = 0.0359 for $I > 2\sigma(I)$, wR_2 = 0.0791 for all data, and GOF = 1.075 (based on F^2).

Crystal data: formula $C_{35}H_{48}F_3N_4OClW$, space group $P2_1/n$, a = 18.1298(6) Å, b = 10.4918(3) Å, c = 19.4084(5) Å, β = 107.0410(10)°, V = 3529.67 (18) Å^3, Z = 4, μ = 3.397 mm^{-1}, D_{calc} = 1.538 g·cm^{-3}, $F(000)$ = 1648.

[1]G. M. Sheldrick, *Acta Cryst. Sect. A*, 2008, **64**, 112-122.

Table S3.1 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^{2}x 10^3) for **1**-(NC(O)CF_3)Cl. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W(1)	928(1)	8431(1)	8278(1)	14(1)
Cl(1)	2224(1)	7323(1)	8622(1)	22(1)
F(1)	2266(2)	12110(3)	9410(2)	42(1)
N(1)	546(2)	7047(3)	8741(2)	17(1)
O(1)	1605(3)	9985(5)	10110(2)	77(2)
N(2)	996(2)	8405(3)	7294(2)	16(1)
F(2)	2865(1)	10530(3)	9120(1)	34(1)
F(3)	2996(2)	10920(3)	10236(1)	42(1)
N(3)	-35(2)	9418(3)	7987(2)	17(1)
N(4)	1412(2)	9609(3)	8919(2)	21(1)
C(11)	-236(2)	6580(4)	8504(2)	20(1)
C(12)	-439(3)	5644(4)	7971(2)	23(1)
C(13)	-1187(3)	5170(4)	7748(2)	32(1)
C(14)	-1728(3)	5635(4)	8061(2)	32(1)
C(15)	-1544(3)	6566(4)	8586(2)	30(1)
C(16)	-792(2)	7049(4)	8803(2)	23(1)
C(17)	1030(2)	6379(4)	9409(2)	25(1)
C(18)	1129(3)	4971(4)	9253(3)	35(1)
C(19)	715(3)	6564(5)	10051(2)	34(1)
C(21)	664(2)	7337(4)	6847(2)	18(1)
C(22)	925(2)	6102(4)	7056(2)	21(1)
C(23)	596(3)	5055(4)	6633(2)	23(1)
C(24)	5(2)	5266(4)	5998(2)	26(1)
C(25)	-251(2)	6497(4)	5772(2)	25(1)
C(26)	87(2)	7520(4)	6206(2)	21(1)
C(27)	1352(2)	9366(4)	6923(2)	21(1)
C(28)	1981(3)	8733(4)	6667(2)	28(1)
C(29)	1680(3)	10504(4)	7404(2)	24(1)
C(31)	-562(2)	9456(4)	7258(2)	18(1)
C(32)	-490(2)	10389(4)	6774(2)	21(1)
C(33)	-999(3)	10410(4)	6072(2)	26(1)
C(34)	-1572(2)	9498(4)	5879(2)	27(1)
C(35)	-1657(2)	8559(4)	6360(2)	25(1)
C(36)	-1141(2)	8548(4)	7055(2)	23(1)
C(37)	-274(2)	10275(4)	8510(2)	21(1)
C(38)	-1147(2)	10322(4)	8379(2)	25(1)
C(39)	36(3)	11620(4)	8473(2)	26(1)
C(41)	1782(3)	10079(4)	9564(2)	29(1)
C(42)	2485(3)	10908(4)	9576(2)	29(1)
C(131)	-1408(3)	4156(5)	7169(3)	50(2)
C(151)	-2136(3)	7069(5)	8931(3)	41(1)
C(231)	883(3)	3727(4)	6859(2)	32(1)
C(251)	-894(3)	6717(5)	5090(2)	36(1)
C(331)	-893(3)	11389(5)	5540(2)	37(1)
C(351)	-2281(3)	7564(5)	6153(3)	37(1)

Table S3.2 Bond lengths [Å] and angles [°] for **1**-($NC(O)CF_3$)Cl.

W(1)-N(4)	1.790(3)	N(2)-W(1)-N(3)	91.78(13)
W(1)-N(1)	1.940(3)	N(4)-W(1)-Cl(1)	84.60(11)
W(1)-N(2)	1.949(3)	N(1)-W(1)-Cl(1)	87.92(10)
W(1)-N(3)	1.965(3)	N(2)-W(1)-Cl(1)	86.10(9)
W(1)-Cl(1)	2.5298(10)	N(3)-W(1)-Cl(1)	175.12(10)
F(1)-C(42)	1.333(5)	C(11)-N(1)-C(17)	112.8(3)
N(1)-C(11)	1.442(5)	C(11)-N(1)-W(1)	123.9(2)
N(1)-C(17)	1.508(5)	C(17)-N(1)-W(1)	123.3(3)
O(1)-C(41)	1.199(5)	C(21)-N(2)-C(27)	113.5(3)
N(2)-C(21)	1.437(5)	C(21)-N(2)-W(1)	117.9(2)
N(2)-C(27)	1.491(5)	C(27)-N(2)-W(1)	128.6(2)
F(2)-C(42)	1.331(5)	C(31)-N(3)-C(37)	113.6(3)
F(3)-C(42)	1.342(5)	C(31)-N(3)-W(1)	124.6(2)
N(3)-C(31)	1.457(5)	C(37)-N(3)-W(1)	121.7(2)
N(3)-C(37)	1.512(5)	C(41)-N(4)-W(1)	156.8(3)
N(4)-C(41)	1.330(5)	C(16)-C(11)-C(12)	119.5(4)
C(11)-C(16)	1.393(6)	C(16)-C(11)-N(1)	120.7(4)
C(11)-C(12)	1.394(6)	C(12)-C(11)-N(1)	119.8(4)
C(12)-C(13)	1.388(6)	C(13)-C(12)-C(11)	120.3(4)
C(13)-C(14)	1.385(7)	C(14)-C(13)-C(12)	119.3(4)
C(13)-C(131)	1.514(6)	C(14)-C(13)-C(131)	120.4(4)
C(14)-C(15)	1.380(7)	C(12)-C(13)-C(131)	120.3(5)
C(15)-C(16)	1.398(6)	C(15)-C(14)-C(13)	121.6(4)
C(15)-C(151)	1.516(7)	C(14)-C(15)-C(16)	118.9(4)
C(17)-C(19)	1.527(6)	C(14)-C(15)-C(151)	121.5(4)
C(17)-C(18)	1.529(6)	C(16)-C(15)-C(151)	119.6(5)
C(21)-C(26)	1.385(5)	C(11)-C(16)-C(15)	120.4(4)
C(21)-C(22)	1.399(5)	N(1)-C(17)-C(19)	112.3(4)
C(22)-C(23)	1.396(5)	N(1)-C(17)-C(18)	110.6(3)
C(23)-C(24)	1.394(6)	C(19)-C(17)-C(18)	112.2(4)
C(23)-C(231)	1.507(6)	C(26)-C(21)-C(22)	119.5(4)
C(24)-C(25)	1.399(6)	C(26)-C(21)-N(2)	120.4(4)
C(25)-C(26)	1.392(6)	C(22)-C(21)-N(2)	120.1(3)
C(25)-C(251)	1.503(6)	C(23)-C(22)-C(21)	120.6(4)
C(27)-C(29)	1.524(5)	C(24)-C(23)-C(22)	118.7(4)
C(27)-C(28)	1.525(6)	C(24)-C(23)-C(231)	121.0(4)
C(31)-C(36)	1.388(6)	C(22)-C(23)-C(231)	120.3(4)
C(31)-C(32)	1.388(5)	C(23)-C(24)-C(25)	121.5(4)
C(32)-C(33)	1.405(6)	C(26)-C(25)-C(24)	118.4(4)
C(33)-C(34)	1.381(6)	C(26)-C(25)-C(251)	120.4(4)
C(33)-C(331)	1.508(6)	C(24)-C(25)-C(251)	121.2(4)
C(34)-C(35)	1.397(6)	C(21)-C(26)-C(25)	121.3(4)
C(35)-C(36)	1.397(6)	N(2)-C(27)-C(29)	112.4(3)
C(35)-C(351)	1.504(6)	N(2)-C(27)-C(28)	109.5(3)
C(37)-C(39)	1.528(6)	C(29)-C(27)-C(28)	110.2(4)
C(37)-C(38)	1.529(6)	C(36)-C(31)-C(32)	120.4(4)
C(41)-C(42)	1.537(6)	C(36)-C(31)-N(3)	118.9(3)
		C(32)-C(31)-N(3)	120.7(4)
N(4)-W(1)-N(1)	111.36(14)	C(31)-C(32)-C(33)	120.1(4)
N(4)-W(1)-N(2)	122.09(14)	C(34)-C(33)-C(32)	118.7(4)
N(1)-W(1)-N(2)	125.25(13)	C(34)-C(33)-C(331)	121.6(4)
N(4)-W(1)-N(3)	92.83(14)	C(32)-C(33)-C(331)	119.7(4)
N(1)-W(1)-N(3)	96.88(14)	C(33)-C(34)-C(35)	122.0(4)

C(34)-C(35)-C(36)	118.5(4)
C(34)-C(35)-C(351)	122.2(4)
C(36)-C(35)-C(351)	119.4(4)
C(31)-C(36)-C(35)	120.4(4)
N(3)-C(37)-C(39)	109.7(3)
N(3)-C(37)-C(38)	113.2(3)
C(39)-C(37)-C(38)	109.8(3)
O(1)-C(41)-N(4)	127.6(4)
O(1)-C(41)-C(42)	118.0(4)
N(4)-C(41)-C(42)	114.3(4)
F(2)-C(42)-F(1)	107.3(4)
F(2)-C(42)-F(3)	106.8(4)
F(1)-C(42)-F(3)	107.2(4)
F(2)-C(42)-C(41)	114.1(4)
F(1)-C(42)-C(41)	110.2(4)
F(3)-C(42)-C(41)	110.9(4)

Table S3.3 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1**-$(NC(O)CF_3)Cl$. 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}
W(1)	15(1)	13(1)	15(1)	0(1)	5(1)	-1(1)
Cl(1)	17(1)	24(1)	23(1)	-1(1)	4(1)	3(1)
F(1)	43(2)	24(1)	63(2)	8(1)	24(2)	-7(1)
N(1)	17(2)	19(2)	15(2)	2(1)	4(1)	-3(1)
O(1)	99(4)	109(4)	26(2)	-13(2)	25(2)	-79(3)
N(2)	17(2)	13(2)	17(2)	1(1)	7(1)	1(1)
F(2)	26(1)	41(2)	33(1)	-2(1)	7(1)	-7(1)
F(3)	33(2)	54(2)	31(2)	-12(1)	-3(1)	-10(1)
N(3)	20(2)	13(2)	20(2)	0(1)	7(1)	0(1)
N(4)	20(2)	19(2)	22(2)	-5(1)	4(1)	-4(1)
C(11)	17(2)	19(2)	19(2)	10(2)	-1(2)	-1(2)
C(12)	29(2)	16(2)	23(2)	1(2)	8(2)	-1(2)
C(13)	35(3)	23(2)	30(2)	4(2)	-5(2)	-11(2)
C(14)	21(2)	33(3)	38(3)	15(2)	0(2)	-6(2)
C(15)	26(2)	31(2)	34(2)	19(2)	10(2)	3(2)
C(16)	27(2)	19(2)	22(2)	5(2)	7(2)	-2(2)
C(17)	19(2)	34(3)	18(2)	6(2)	2(2)	-5(2)
C(18)	32(3)	28(3)	42(3)	13(2)	5(2)	10(2)
C(19)	31(3)	52(3)	17(2)	6(2)	4(2)	-11(2)
C(21)	18(2)	19(2)	17(2)	0(2)	8(2)	2(2)
C(22)	24(2)	20(2)	17(2)	0(2)	3(2)	-2(2)
C(23)	30(2)	18(2)	21(2)	-3(2)	9(2)	2(2)
C(24)	28(2)	26(2)	23(2)	-8(2)	7(2)	-5(2)
C(25)	24(2)	28(2)	22(2)	-3(2)	5(2)	6(2)
C(26)	23(2)	19(2)	20(2)	3(2)	6(2)	4(2)
C(27)	26(2)	19(2)	20(2)	1(2)	12(2)	-1(2)
C(28)	29(3)	30(3)	31(2)	-1(2)	17(2)	-2(2)
C(29)	30(2)	18(2)	25(2)	2(2)	12(2)	-4(2)
C(31)	19(2)	14(2)	22(2)	2(2)	8(2)	7(2)
C(32)	21(2)	17(2)	27(2)	-1(2)	9(2)	2(2)
C(33)	29(2)	26(2)	24(2)	6(2)	10(2)	9(2)
C(34)	19(2)	33(3)	25(2)	4(2)	1(2)	7(2)
C(35)	18(2)	29(2)	27(2)	3(2)	5(2)	5(2)
C(36)	23(2)	19(2)	26(2)	3(2)	7(2)	3(2)
C(37)	24(2)	21(2)	18(2)	-1(2)	8(2)	1(2)
C(38)	24(2)	27(2)	30(2)	3(2)	15(2)	5(2)
C(39)	29(2)	23(2)	30(2)	-8(2)	12(2)	1(2)
C(41)	33(3)	29(3)	23(2)	2(2)	5(2)	-11(2)
C(42)	30(3)	27(3)	28(2)	2(2)	4(2)	-8(2)
C(131)	53(4)	38(3)	43(3)	-5(3)	-7(3)	-14(3)
C(151)	28(3)	49(3)	50(3)	23(3)	19(2)	9(2)
C(231)	45(3)	17(2)	29(2)	-1(2)	3(2)	2(2)
C(251)	35(3)	36(3)	30(2)	-5(2)	1(2)	3(2)
C(331)	42(3)	37(3)	29(2)	10(2)	6(2)	6(2)
C(351)	26(3)	40(3)	35(3)	0(2)	-4(2)	-9(2)

S4 X-ray crystal structure of (Ar[*i*-Pr]N)$_3$W(OCN)(Cl)$_2$ (1-(OCN)(Cl)$_2$). Inside the glove box crystals of **1**-(OCN)(Cl)$_2$, obtained from a saturated tetrahydrofuran solution layered with pentane and stored at -35°C, were coated with Paratone N oil (an Exxon product) on a microscope slide. A yellow plate of approximate dimensions 0.27 x 0.23 x 0.04 mm^3 was selected and mounted on a glass fiber. A total of 10803 reflections ($-15 \leq h \leq 7$, $0 \leq k \leq 15$, $0 \leq l \leq 47$) were collected at 100(2) K using φ- and ω-scans in the θ range of 1.54 to 25.14°, of which 2442 were unique (R_{int} = 0.0634). The structure was solved by direct methods using SHELXS[1] and refined against F^2 on all data by full-matrix least squares with SHELXTL.[1] The systematic absences in the diffraction data are consistent with the assigned space group of $R\bar{3}$. Two heavily disordered molecules of tetrahydrofuran are present in the asymmetric unit. The disorders were refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The ratios were refined freely, while constraining the total occupancy of both components to unity. All hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. A semi-empirical absorption correction (SADABS) was applied to the diffraction data resulting in maximum and minimum transmissions equal to 0.8891 and 0.4972, respectively. The residual peak and hole electron density were 2.017 and -1.728 e·Å^{-3}, respectively. The least squares refinement converged normally with residuals of R_1 = 0.0450 for $I > 2\sigma(I)$, wR_2 = 0.1394 for all data, and GOF = 1.152 (based on F^2).

Crystal data: formula $C_{34}H_{48}Cl_2N_4OW$ (with two equiv of C_4H_8O), space group $R\bar{3}$, a = 13.3600(12) Å, c = 39.556(8) Å, V = 6114.5(14) Å^3, Z = 6, μ = 3.206 mm^{-1}, D_{calc} = 1.512 g·cm^{-3}, $F(000)$ = 2856.

Table S4.1 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**-$(OCN)(Cl)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W(1)	3333	6667	3666(1)	42(1)
Cl(1)	2155(4)	5037(4)	3264(1)	62(1)
O(1X)	2390(20)	5450(17)	3320(6)	55(5)
C(1X)	2610(20)	5405(18)	2990(6)	53(4)
N(1X)	2656(18)	5261(19)	2715(5)	68(5)
N(2)	3669(4)	5603(4)	3907(2)	43(1)
C(1)	4491(6)	6093(5)	4476(2)	47(2)
C(2)	4668(5)	6051(5)	4138(2)	46(2)
C(3)	5402(7)	6487(6)	4703(2)	55(2)
C(4)	5752(6)	6383(7)	4013(2)	62(2)
C(5)	3168(7)	4322(6)	3845(2)	66(2)
C(6)	6492(7)	6801(8)	4579(2)	74(3)
C(7)	6691(7)	6771(9)	4240(3)	80(3)
C(9)	3934(8)	4119(8)	3595(3)	86(3)
C(10)	5211(9)	6571(9)	5077(2)	81(3)
C(11)	2959(8)	3656(7)	4170(3)	81(3)
C(12)	7892(8)	7166(13)	4105(4)	146(6)
O(1S)	3260(40)	6550(40)	5671(4)	53(5)
C(1S)	4170(30)	7520(30)	5871(8)	59(7)
C(2S)	4110(30)	7170(30)	6266(7)	56(7)
C(3S)	3150(40)	5950(40)	6137(9)	65(7)
C(4S)	2580(30)	5800(40)	5807(9)	69(7)
O(1T)	2470(50)	6590(60)	5688(15)	69(7)
C(1T)	3240(70)	7170(50)	5984(17)	65(7)
C(2T)	3310(100)	6220(80)	6218(14)	63(8)
C(3T)	2910(80)	5490(50)	5882(16)	66(7)
C(4T)	2480(60)	5830(70)	5586(13)	68(8)
O(2S)	3370(40)	5940(50)	1534(11)	202(14)
C(5S)	3940(50)	5810(50)	1840(15)	217(15)
C(6S)	4790(40)	7070(60)	2006(13)	231(16)
C(7S)	4710(40)	7480(50)	1639(14)	205(15)
C(8S)	3710(40)	6790(70)	1417(12)	200(16)

Table S4.2 Bond lengths [Å] and angles [°] for **1**-(OCN)$(Cl)_2$.

W(1)-N(2A)	1.943(5)	O(1X)-W(1)-O(1XB)	79.0(10)
W(1)-N(2)	1.943(5)	N(2A)-W(1)-Cl(1A)	87.2(2)
W(1)-N(2B)	1.943(5)	N(2)-W(1)-Cl(1A)	170.1(2)
W(1)-O(1XA)	2.01(2)	N(2B)-W(1)-Cl(1A)	89.9(2)
W(1)-O(1X)	2.01(2)	O(1XA)-W(1)-Cl(1A)	4.3(7)
W(1)-O(1XB)	2.01(2)	O(1X)-W(1)-Cl(1A)	80.0(7)
W(1)-Cl(1A)	2.513(4)	O(1XB)-W(1)-Cl(1A)	83.2(8)
W(1)-Cl(1)	2.513(4)	N(2A)-W(1)-Cl(1)	89.9(2)
W(1)-Cl(1B)	2.513(4)	N(2)-W(1)-Cl(1)	87.2(2)
O(1X)-C(1X)	1.35(4)	N(2B)-W(1)-Cl(1)	170.1(2)
C(1X)-N(1X)	1.11(3)	O(1XA)-W(1)-Cl(1)	83.2(8)
N(2)-C(2)	1.475(8)	O(1X)-W(1)-Cl(1)	4.3(8)
N(2)-C(5)	1.514(8)	O(1XB)-W(1)-Cl(1)	80.0(7)
C(1)-C(2)	1.362(10)	Cl(1A)-W(1)-Cl(1)	84.26(19)
C(1)-C(3)	1.386(10)	N(2A)-W(1)-Cl(1B)	170.1(2)
C(2)-C(4)	1.378(10)	N(2)-W(1)-Cl(1B)	89.9(2)
C(3)-C(6)	1.388(11)	N(2B)-W(1)-Cl(1B)	87.2(2)
C(3)-C(10)	1.516(12)	O(1XA)-W(1)-Cl(1B)	80.0(7)
C(4)-C(7)	1.413(10)	O(1X)-W(1)-Cl(1B)	83.2(8)
C(5)-C(11)	1.507(12)	O(1XB)-W(1)-Cl(1B)	4.3(7)
C(5)-C(9)	1.541(12)	Cl(1A)-W(1)-Cl(1B)	84.26(19)
C(6)-C(7)	1.371(14)	Cl(1)-W(1)-Cl(1B)	84.26(19)
C(7)-C(12)	1.513(13)	C(1X)-O(1X)-W(1)	129.3(19)
O(1S)-C(4S)	1.10(5)	N(1X)-C(1X)-O(1X)	172(3)
O(1S)-C(1S)	1.49(4)	C(2)-N(2)-C(5)	111.1(5)
C(1S)-C(2S)	1.62(3)	C(2)-N(2)-W(1)	120.1(4)
C(2S)-C(3S)	1.57(5)	C(5)-N(2)-W(1)	127.8(4)
C(3S)-C(4S)	1.48(4)	C(2)-C(1)-C(3)	120.8(7)
O(1T)-C(4T)	1.10(5)	C(1)-C(2)-C(4)	121.1(6)
O(1T)-C(1T)	1.49(4)	C(1)-C(2)-N(2)	118.9(6)
C(1T)-C(2T)	1.62(3)	C(4)-C(2)-N(2)	120.0(7)
C(2T)-C(3T)	1.57(5)	C(1)-C(3)-C(6)	118.4(7)
C(3T)-C(4T)	1.48(4)	C(1)-C(3)-C(10)	120.8(7)
O(2S)-C(8S)	1.09(5)	C(6)-C(3)-C(10)	120.8(7)
O(2S)-C(5S)	1.49(4)	C(2)-C(4)-C(7)	119.1(8)
C(5S)-C(6S)	1.63(3)	C(11)-C(5)-N(2)	112.0(7)
C(6S)-C(7S)	1.57(5)	C(11)-C(5)-C(9)	112.7(7)
C(7S)-C(8S)	1.48(4)	N(2)-C(5)-C(9)	110.3(7)
		C(7)-C(6)-C(3)	121.7(7)
N(2A)-W(1)-N(2)	97.8(2)	C(6)-C(7)-C(4)	118.8(8)
N(2A)-W(1)-N(2B)	97.8(2)	C(6)-C(7)-C(12)	121.4(9)
N(2)-W(1)-N(2B)	97.8(2)	C(4)-C(7)-C(12)	119.8(9)
N(2A)-W(1)-O(1XA)	91.4(7)	C(4S)-O(1S)-C(1S)	118(2)
N(2)-W(1)-O(1XA)	166.7(7)	O(1S)-C(1S)-C(2S)	111(2)
N(2B)-W(1)-O(1XA)	90.3(8)	C(3S)-C(2S)-C(1S)	83.0(19)
N(2A)-W(1)-O(1X)	90.3(8)	C(4S)-C(3S)-C(2S)	122(3)
N(2)-W(1)-O(1X)	91.4(7)	O(1S)-C(4S)-C(3S)	100(3)
N(2B)-W(1)-O(1X)	166.7(7)	C(4T)-O(1T)-C(1T)	117(3)
O(1XA)-W(1)-O(1X)	79.0(10)	O(1T)-C(1T)-C(2T)	109(3)
N(2A)-W(1)-O(1XB)	166.7(7)	C(3T)-C(2T)-C(1T)	82(2)
N(2)-W(1)-O(1XB)	90.3(8)	C(4T)-C(3T)-C(2T)	123(3)
N(2B)-W(1)-O(1XB)	91.4(7)	O(1T)-C(4T)-C(3T)	100(3)
O(1XA)-W(1)-O(1XB)	79.0(10)	C(8S)-O(2S)-C(5S)	119(2)

O(2S)-C(5S)-C(6S)	110(2)	C(8S)-C(7S)-C(6S)	122(3)
C(7S)-C(6S)-C(5S)	82(2)	O(2S)-C(8S)-C(7S)	100(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+y,-x+1,z #2 -y+1,x-y+1,z

Table S4.3 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1**-$(OCN)(Cl)_2$. The anisotropicdisplacement 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}
W(1)	34(1)	34(1)	58(1)	0	0	17(1)
Cl(1)	60(2)	40(2)	74(3)	-16(2)	-23(2)	17(2)
O(1X)	94(14)	33(11)	52(8)	6(9)	-11(10)	43(10)
C(1X)	66(11)	44(10)	57(8)	5(9)	2(10)	34(9)
N(1X)	72(12)	84(13)	66(9)	-24(11)	-5(10)	51(11)
N(2)	36(3)	32(3)	69(4)	-5(2)	-9(3)	23(2)
C(1)	39(4)	35(3)	70(5)	-2(3)	-7(3)	21(3)
C(2)	33(3)	32(3)	71(5)	-10(3)	-11(3)	16(3)
C(3)	57(5)	48(4)	66(5)	-6(3)	-18(4)	30(4)
C(4)	40(4)	77(5)	79(5)	-28(4)	-8(4)	36(4)
C(5)	50(4)	45(4)	108(7)	-27(4)	-38(4)	28(4)
C(6)	57(5)	85(6)	95(7)	-34(5)	-39(5)	47(5)
C(7)	45(5)	101(7)	106(8)	-43(6)	-23(5)	45(5)
C(9)	85(6)	76(6)	120(8)	-57(6)	-51(6)	59(5)
C(10)	92(7)	80(6)	81(6)	-5(5)	-25(5)	52(6)
C(11)	72(6)	47(5)	124(8)	4(5)	-37(6)	29(4)
C(12)	46(6)	205(15)	191(14)	-86(12)	-24(7)	66(8)
O(1S)	41(10)	89(14)	32(6)	28(9)	-12(9)	34(10)
C(1S)	52(12)	87(14)	27(9)	21(9)	1(9)	28(10)
C(2S)	48(11)	92(14)	29(8)	24(10)	-7(8)	36(10)
C(3S)	50(12)	97(13)	33(9)	32(9)	-6(9)	26(11)
C(4S)	49(11)	101(14)	36(9)	27(10)	-8(9)	22(10)
O(1T)	51(12)	96(15)	42(10)	23(11)	-12(10)	24(12)
C(1T)	50(12)	96(13)	32(10)	28(10)	-6(10)	24(11)
C(2T)	49(13)	95(15)	34(10)	26(11)	-3(11)	28(12)
C(3T)	49(13)	97(14)	35(10)	25(11)	-7(11)	24(11)
C(4T)	52(13)	96(15)	39(10)	25(11)	-10(11)	25(12)
O(2S)	130(20)	270(30)	280(30)	-110(20)	-58(18)	150(20)
C(5S)	150(20)	280(30)	270(30)	-110(30)	-70(20)	140(20)
C(6S)	160(20)	280(30)	270(30)	-110(30)	-60(20)	130(20)
C(7S)	140(20)	270(30)	280(30)	-120(30)	-50(20)	150(20)
C(8S)	120(20)	270(30)	280(30)	-110(30)	-50(18)	150(20)

S5 X-ray crystal structure of (Ar[*i*-Pr]N)$_3$W(N=PCl$_3$)(Cl)$_2$ (1-(N=PCl$_3$)(Cl)$_2$). Inside the glove box crystals of **1**-(N=PCl$_3$)(Cl)$_2$, obtained from a saturated tetrahydrofuran solution layered with diethyl ether and stored at -35°C, were coated with Paratone N oil (an Exxon product) on a microscope slide. An orange shard of approximate dimensions 0.10 x 0.09 x 0.06 mm^3 was selected and mounted on a glass fiber. A total of 85345 reflections ($-20 \le h \le 20$, $-18 \le k \le 18$, $-24 \le l \le 24$) were collected at 100(2) K using φ- and ω-scans in the θ range of 1.84 to 27.88°, of which 9806 were unique (R_{int} = 0.0533). The structure was solved by Patterson methods using SHELXS[1] and refined against F^2 on all data by full-matrix least squares with SHELXTL.[1] The systematic absences in the diffraction data are uniquely consistent with the assigned space group of $P2_1/c$. A disordered molecule of tetrahydrofuran is present in the asymmetric unit. The disorder was refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The ratios were refined freely, while constraining the total occupancy of both components to unity. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. A semi-empirical absorption correction (SADABS) was applied to the diffraction data resulting in maximum and minimum transmissions equal to 0.8309 and 0.7399, respectively. The residual peak and hole electron density were 2.006 and -0.720 e·Å^{-3}, respectively. The least squares refinement converged normally with residuals of R_1 = 0.0332 for $I > 2\sigma(I)$, wR_2 = 0.0895 for all data, and GOF = 1.068 (based on F^2).

Crystal data: formula $C_{33}H_{48}Cl_5N_4PW$ (with one equiv of C_4H_8O), space group $P2_1/c$, a = 15.9389(6) Å, b = 16.7357(5) Å, c = 18.9527(6) Å, β = 97.4620(10)° V = 4114.2(3) Å^3, Z = 4, μ = 3.206 mm^{-1}, D_{calc} = 1.558 g·cm^{-3}, F(000) = 1952.

Table S5.1 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**-$(N{=}PCl_3)(Cl)_2$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W(1)	2727(1)	9620(1)	8403(1)	15(1)
Cl(1)	2529(1)	9545(1)	9676(1)	21(1)
P(1)	4505(1)	8424(1)	9153(1)	24(1)
N(1)	3074(2)	9721(2)	7455(2)	17(1)
Cl(2)	3697(1)	10944(1)	8824(1)	25(1)
N(2)	1976(2)	8495(2)	8216(2)	18(1)
Cl(3)	5502(1)	9308(1)	9357(1)	32(1)
N(3)	1819(2)	10614(2)	8263(2)	17(1)
Cl(4)	4347(1)	7940(1)	10126(1)	39(1)
N(4)	3755(2)	8750(3)	8700(2)	24(1)
Cl(5)	5026(1)	7250(1)	8730(1)	41(1)
C(11)	2748(3)	10481(3)	6960(2)	20(1)
C(12)	2125(3)	10256(3)	6395(2)	26(1)
C(13)	1794(3)	10985(4)	5925(2)	30(1)
C(14)	2094(3)	11931(4)	6027(2)	31(1)
C(15)	2712(3)	12163(3)	6587(2)	28(1)
C(16)	3044(3)	11426(3)	7047(2)	22(1)
C(17)	3816(2)	9189(3)	7205(2)	20(1)
C(18)	4616(3)	9810(3)	7342(2)	29(1)
C(19)	3648(3)	8867(3)	6424(2)	28(1)
C(21)	2009(3)	7915(3)	7574(2)	19(1)
C(22)	1379(3)	8017(3)	6993(2)	21(1)
C(23)	1410(3)	7460(3)	6378(2)	24(1)
C(24)	2084(3)	6815(3)	6356(2)	28(1)
C(25)	2713(3)	6701(3)	6936(2)	25(1)
C(26)	2664(3)	7255(3)	7549(2)	21(1)
C(27)	1469(2)	7990(3)	8733(2)	21(1)
C(28)	617(3)	7613(3)	8380(2)	25(1)
C(29)	2003(3)	7179(3)	9117(2)	26(1)
C(31)	932(2)	10313(3)	8145(2)	19(1)
C(32)	487(3)	10140(3)	8717(2)	22(1)
C(33)	-371(3)	9893(3)	8599(2)	23(1)
C(34)	-766(3)	9829(3)	7907(2)	24(1)
C(35)	-328(3)	9982(3)	7326(2)	23(1)
C(36)	522(3)	10232(3)	7455(2)	22(1)
C(37)	1887(3)	11706(3)	8376(2)	21(1)
C(38)	1809(3)	11963(3)	9151(2)	27(1)
C(39)	1256(3)	12273(3)	7862(2)	27(1)
C(131)	1119(4)	10741(5)	5317(3)	45(1)
C(151)	2985(3)	13206(4)	6717(3)	39(1)
C(231)	728(3)	7560(4)	5756(2)	32(1)
C(251)	3438(3)	6012(4)	6896(3)	37(1)
C(331)	-842(3)	9664(4)	9218(2)	30(1)
C(351)	-756(3)	9867(3)	6573(2)	31(1)
O(1S)	3256(4)	13995(4)	8634(3)	93(2)
C(1S)	3285(6)	14977(5)	8729(4)	45(2)
C(1SA)	2806(15)	14720(20)	8931(14)	64(8)
C(2S)	3362(6)	15144(5)	9515(4)	81(2)
C(3S)	3763(6)	14224(6)	9830(4)	88(3)
C(4S)	3823(5)	13603(5)	9217(5)	89(3)

Table S5.2 Bond lengths [Å] and angles [°] for **1**-$(N{=}PCl_3)(Cl)_2$.

W(1)-N(1)	1.953(3)	C(2S)-C(3S)	1.503(10)
W(1)-N(2)	1.959(3)	C(3S)-C(4S)	1.454(10)
W(1)-N(3)	1.982(3)		
W(1)-N(4)	2.047(4)	N(1)-W(1)-N(2)	97.45(13)
W(1)-Cl(2)	2.4525(10)	N(1)-W(1)-N(3)	96.74(13)
W(1)-Cl(1)	2.4764(9)	N(2)-W(1)-N(3)	95.80(14)
P(1)-N(4)	1.449(4)	N(1)-W(1)-N(4)	88.97(13)
P(1)-Cl(3)	1.9975(16)	N(2)-W(1)-N(4)	92.17(13)
P(1)-Cl(4)	2.0072(16)	N(3)-W(1)-N(4)	169.50(13)
P(1)-Cl(5)	2.0259(16)	N(1)-W(1)-Cl(2)	90.26(10)
N(1)-C(11)	1.453(5)	N(2)-W(1)-Cl(2)	171.34(9)
N(1)-C(17)	1.518(5)	N(3)-W(1)-Cl(2)	87.18(10)
N(2)-C(21)	1.461(5)	N(4)-W(1)-Cl(2)	83.98(10)
N(2)-C(27)	1.516(5)	N(1)-W(1)-Cl(1)	170.76(10)
N(3)-C(31)	1.462(5)	N(2)-W(1)-Cl(1)	89.48(9)
N(3)-C(37)	1.518(5)	N(3)-W(1)-Cl(1)	88.59(9)
C(11)-C(16)	1.384(6)	N(4)-W(1)-Cl(1)	84.65(9)
C(11)-C(12)	1.398(6)	Cl(2)-W(1)-Cl(1)	82.45(3)
C(12)-C(13)	1.397(6)	N(4)-P(1)-Cl(3)	120.05(15)
C(13)-C(14)	1.389(7)	N(4)-P(1)-Cl(4)	117.04(14)
C(13)-C(131)	1.507(6)	Cl(3)-P(1)-Cl(4)	102.41(7)
C(14)-C(15)	1.387(7)	N(4)-P(1)-Cl(5)	111.11(15)
C(15)-C(16)	1.395(6)	Cl(3)-P(1)-Cl(5)	101.78(7)
C(15)-C(151)	1.509(6)	Cl(4)-P(1)-Cl(5)	101.95(7)
C(17)-C(18)	1.527(6)	C(11)-N(1)-C(17)	111.9(3)
C(17)-C(19)	1.534(5)	C(11)-N(1)-W(1)	121.6(2)
C(21)-C(26)	1.389(6)	C(17)-N(1)-W(1)	125.3(2)
C(21)-C(22)	1.396(5)	C(21)-N(2)-C(27)	111.7(3)
C(22)-C(23)	1.400(5)	C(21)-N(2)-W(1)	119.5(2)
C(23)-C(24)	1.398(6)	C(27)-N(2)-W(1)	127.5(2)
C(23)-C(231)	1.504(6)	C(31)-N(3)-C(37)	110.5(3)
C(24)-C(25)	1.397(6)	C(31)-N(3)-W(1)	120.0(2)
C(25)-C(26)	1.399(5)	C(37)-N(3)-W(1)	128.7(3)
C(25)-C(251)	1.504(6)	P(1)-N(4)-W(1)	155.9(2)
C(27)-C(28)	1.524(6)	C(16)-C(11)-C(12)	119.7(4)
C(27)-C(29)	1.528(6)	C(16)-C(11)-N(1)	120.7(4)
C(31)-C(36)	1.388(5)	C(12)-C(11)-N(1)	119.7(4)
C(31)-C(32)	1.391(6)	C(13)-C(12)-C(11)	120.2(4)
C(32)-C(33)	1.399(6)	C(14)-C(13)-C(12)	119.0(4)
C(33)-C(34)	1.381(6)	C(14)-C(13)-C(131)	120.9(4)
C(33)-C(331)	1.507(6)	C(12)-C(13)-C(131)	120.1(4)
C(34)-C(35)	1.395(6)	C(15)-C(14)-C(13)	121.3(4)
C(35)-C(36)	1.388(6)	C(14)-C(15)-C(16)	119.0(4)
C(35)-C(351)	1.509(6)	C(14)-C(15)-C(151)	120.3(4)
C(37)-C(39)	1.521(6)	C(16)-C(15)-C(151)	120.6(4)
C(37)-C(38)	1.531(5)	C(11)-C(16)-C(15)	120.7(4)
O(1S)-C(1S)	1.360(9)	N(1)-C(17)-C(18)	110.2(3)
O(1S)-C(1SA)	1.393(15)	N(1)-C(17)-C(19)	113.2(3)
O(1S)-C(4S)	1.438(8)	C(18)-C(17)-C(19)	111.2(3)
C(1S)-C(2S)	1.497(9)	C(26)-C(21)-C(22)	120.3(4)
C(1SA)-C(2S)	1.444(15)	C(26)-C(21)-N(2)	119.5(3)

C(22)-C(21)-N(2)	120.2(3)	C(32)-C(33)-C(331)	120.1(4)
C(21)-C(22)-C(23)	120.1(4)	C(33)-C(34)-C(35)	121.8(4)
C(24)-C(23)-C(22)	118.8(4)	C(36)-C(35)-C(34)	118.4(4)
C(24)-C(23)-C(231)	121.0(4)	C(36)-C(35)-C(351)	120.2(4)
C(22)-C(23)-C(231)	120.2(4)	C(34)-C(35)-C(351)	121.3(4)
C(25)-C(24)-C(23)	121.5(4)	C(35)-C(36)-C(31)	121.0(4)
C(24)-C(25)-C(26)	118.8(4)	N(3)-C(37)-C(39)	112.8(3)
C(24)-C(25)-C(251)	120.5(4)	N(3)-C(37)-C(38)	110.5(3)
C(26)-C(25)-C(251)	120.7(4)	C(39)-C(37)-C(38)	111.5(3)
C(21)-C(26)-C(25)	120.4(4)	C(1S)-O(1S)-C(1SA)	40.9(14)
N(2)-C(27)-C(28)	113.0(3)	C(1S)-O(1S)-C(4S)	105.2(6)
N(2)-C(27)-C(29)	109.2(3)	C(1SA)-O(1S)-C(4S)	105.3(10)
C(28)-C(27)-C(29)	111.7(3)	O(1S)-C(1S)-C(2S)	106.2(6)
C(36)-C(31)-C(32)	119.7(4)	O(1S)-C(1SA)-C(2S)	107.4(11)
C(36)-C(31)-N(3)	119.7(3)	C(1SA)-C(2S)-C(1S)	38.1(14)
C(32)-C(31)-N(3)	120.6(3)	C(1SA)-C(2S)-C(3S)	99.0(11)
C(31)-C(32)-C(33)	120.3(4)	C(1S)-C(2S)-C(3S)	104.1(6)
C(34)-C(33)-C(32)	118.8(4)	C(4S)-C(3S)-C(2S)	104.1(5)
C(34)-C(33)-C(331)	121.0(4)	O(1S)-C(4S)-C(3S)	107.1(6)

Table S5.3 Anisotropic displacement parameters ($Å^2x\ 10^3$) for **1**-$(N{=}PCl_3)(Cl)_2$. 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}
W(1)	16(1)	17(1)	12(1)	0(1)	2(1)	0(1)
Cl(1)	24(1)	27(1)	14(1)	0(1)	4(1)	1(1)
P(1)	25(1)	25(1)	22(1)	0(1)	2(1)	2(1)
N(1)	21(2)	18(2)	14(1)	0(1)	4(1)	-1(1)
Cl(2)	27(1)	25(1)	23(1)	-2(1)	1(1)	-2(1)
N(2)	20(2)	18(2)	15(1)	0(1)	4(1)	-1(1)
Cl(3)	25(1)	38(1)	31(1)	-5(1)	2(1)	-2(1)
N(3)	20(2)	21(2)	11(1)	-1(1)	2(1)	0(1)
Cl(4)	39(1)	49(1)	28(1)	14(1)	-1(1)	-1(1)
N(4)	34(2)	26(2)	14(2)	-6(1)	12(1)	-14(2)
Cl(5)	39(1)	33(1)	49(1)	-9(1)	-2(1)	13(1)
C(11)	22(2)	26(2)	15(2)	2(2)	6(2)	2(2)
C(12)	31(2)	30(2)	17(2)	4(2)	5(2)	-5(2)
C(13)	34(2)	39(3)	17(2)	6(2)	3(2)	-3(2)
C(14)	36(3)	37(3)	23(2)	12(2)	9(2)	5(2)
C(15)	36(2)	25(2)	26(2)	5(2)	14(2)	1(2)
C(16)	26(2)	25(2)	16(2)	0(2)	5(2)	-2(2)
C(17)	21(2)	22(2)	18(2)	-1(2)	6(2)	2(2)
C(18)	21(2)	34(2)	33(2)	-2(2)	7(2)	-2(2)
C(19)	33(2)	32(2)	21(2)	-5(2)	10(2)	-2(2)
C(21)	24(2)	19(2)	15(2)	-2(1)	5(2)	-4(2)
C(22)	20(2)	21(2)	23(2)	0(2)	5(2)	-3(2)
C(23)	26(2)	27(2)	20(2)	-3(2)	5(2)	-11(2)
C(24)	33(2)	27(2)	25(2)	-7(2)	9(2)	-7(2)
C(25)	30(2)	19(2)	28(2)	-3(2)	8(2)	0(2)
C(26)	22(2)	22(2)	21(2)	0(2)	3(2)	0(2)
C(27)	22(2)	23(2)	20(2)	0(2)	7(2)	-2(2)

C(28)	26(2)	23(2)	26(2)	4(2)	9(2)	-4(2)
C(29)	31(2)	25(2)	22(2)	6(2)	5(2)	0(2)
C(31)	20(2)	16(2)	20(2)	0(1)	2(2)	3(2)
C(32)	21(2)	24(2)	21(2)	-2(2)	2(2)	3(2)
C(33)	20(2)	26(2)	26(2)	0(2)	6(2)	2(2)
C(34)	18(2)	23(2)	33(2)	-3(2)	2(2)	2(2)
C(35)	23(2)	21(2)	24(2)	-2(2)	-3(2)	5(2)
C(36)	25(2)	23(2)	18(2)	1(2)	1(2)	5(2)
C(37)	24(2)	18(2)	21(2)	-2(2)	1(2)	2(2)
C(38)	33(2)	26(2)	23(2)	-7(2)	7(2)	1(2)
C(39)	32(2)	24(2)	26(2)	2(2)	7(2)	6(2)
C(131)	46(3)	60(3)	26(2)	14(2)	-9(2)	-5(3)
C(151)	49(3)	28(2)	43(3)	7(2)	16(2)	1(2)
C(231)	32(2)	44(3)	19(2)	-7(2)	-1(2)	-7(2)
C(251)	39(3)	32(3)	42(3)	-11(2)	10(2)	10(2)
C(331)	23(2)	41(3)	28(2)	-1(2)	8(2)	-3(2)
C(351)	33(2)	31(2)	26(2)	2(2)	-9(2)	-1(2)
O(1S)	102(4)	86(4)	83(4)	-20(3)	-15(3)	14(3)
C(1S)	51(6)	45(4)	40(4)	13(3)	6(3)	8(4)
C(1SA)	44(13)	81(15)	63(13)	-12(10)	-13(9)	22(10)
C(2S)	121(7)	60(4)	55(4)	-5(3)	-17(4)	28(4)
C(3S)	122(7)	84(5)	57(4)	20(4)	7(4)	51(5)
C(4S)	84(6)	51(4)	122(7)	-5(4)	-26(5)	25(4)

S6 X-ray crystal structure of (Ar[*i*-Pr]N)$_3$W(Cl)$_3$ (1-(Cl)$_3$). Inside the glove box crystals of **1**-(Cl)$_3$, obtained from a saturated methylene chloride solution layered with diethyl ether stored at -35°C, were coated with Paratone N oil (an Exxon product) on a microscope slide. A yellow shard of approximate dimensions 0.13 x 0.10 x 0.09 mm^3 was selected and mounted on a glass fiber. A total of 38272 reflections ($-13 \le h \le 14$, $-17 \le k \le 17$, $0 \le l \le 17$) were collected at 100(2) K using φ- and ω-scans in the θ range of 1.53 to 28.28°, of which 9143 were unique (R_{int} = 0.0321). The structure was solved by Patterson methods using SHELXS[1] and refined against F^2 on all data by full-matrix least squares with SHELXTL.[1] One half of a heavily disordered molecule of methylene chloride is present in the asymmetric unit which results in a non-integer number of carbon atoms in the empirical formula. The fourfold disorder invloves a crystallographic inversion center and was refined with the help of similarity restraints on 1-2 and 1-3 distances and displacement parameters as well as rigid bond restraints for anisotropic displacement parameters. The ratios were refined freely, while constraining the total occupancy of all four components to unity. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically calculated positions and refined using a riding model. A semi-empirical absorption correction (SADABS) was applied to the diffraction data resulting in maximum and minimum transmissions equal to 0.7465 and 0.6626, respectively. The residual peak and hole electron density were 2.061 and -0.416 e·Å^{-3}, respectively. The least squares refinement converged normally with residuals of R_1 = 0.0293 for $I > 2\sigma(I)$, wR_2 = 0.0847 for all data, and GOF = 1.103 (based on F^2).

Crystal data: formula $C_{33}H_{48}Cl_3N_3W$ (with 0.5 equiv of CH_2Cl_2), space group $P\bar{1}$, a = 10.7751(3) Å, b = 13.3987(3) Å, c = 13.5032(4) Å, α = 88.8520(10)°, β = 71.9870(10)°, γ= 83.6570(10)°, V = 1842.39(9) Å^3, Z = 2, μ = 3.451 mm^{-1}, D_{calc} = 1.477 g·cm^{-3}, F(000) = 826.

Table S6.1 Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **1**-$(Cl)_3$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
W(1)	8698(1)	7569(1)	6679(1)	17(1)
Cl(1)	10366(1)	6490(1)	5390(1)	21(1)
N(1)	7641(3)	8506(2)	7783(3)	22(1)
Cl(2)	10086(1)	7026(1)	7766(1)	25(1)
N(2)	7701(3)	6421(2)	7127(2)	19(1)
Cl(3)	10287(1)	8781(1)	6061(1)	25(1)
N(3)	7883(3)	8039(2)	5623(2)	17(1)
C(11)	6753(4)	9329(3)	7577(3)	23(1)
C(12)	7209(4)	10238(3)	7224(3)	26(1)
C(13)	6323(4)	11046(3)	7098(3)	28(1)
C(14)	5014(4)	10909(3)	7315(3)	28(1)
C(15)	4545(4)	9992(3)	7660(3)	27(1)
C(16)	5427(4)	9198(3)	7799(3)	25(1)
C(17)	7768(4)	8616(3)	8862(3)	30(1)
C(18)	8706(5)	9383(4)	8866(4)	41(1)
C(19)	6442(5)	8870(4)	9684(3)	39(1)
C(21)	6656(4)	6446(3)	8112(3)	25(1)
C(22)	6945(4)	6264(3)	9033(3)	30(1)
C(23)	5932(5)	6265(4)	9978(4)	41(1)
C(24)	4637(5)	6447(4)	9970(4)	46(1)
C(25)	4326(5)	6629(4)	9047(4)	45(1)
C(26)	5354(4)	6630(3)	8118(4)	32(1)
C(27)	8006(4)	5369(3)	6651(3)	22(1)
C(28)	6801(4)	4916(3)	6603(3)	28(1)
C(29)	8773(4)	4687(3)	7230(3)	27(1)
C(31)	7030(3)	7424(3)	5310(3)	18(1)
C(32)	5677(3)	7641(3)	5722(3)	20(1)
C(33)	4838(4)	7095(3)	5404(3)	22(1)
C(34)	5381(4)	6341(3)	4656(3)	24(1)
C(35)	6734(4)	6120(3)	4222(3)	22(1)
C(36)	7568(3)	6668(3)	4562(3)	20(1)
C(37)	8169(4)	8934(3)	4926(3)	20(1)
C(38)	6932(4)	9515(3)	4792(3)	25(1)
C(39)	9155(4)	8597(3)	3873(3)	28(1)
C(131)	6826(5)	12044(3)	6741(4)	36(1)
C(151)	3105(4)	9847(4)	7910(4)	34(1)
C(231)	6238(6)	6078(5)	10996(4)	56(2)
C(251)	2930(5)	6816(6)	9027(6)	72(2)
C(331)	3373(4)	7333(3)	5878(4)	32(1)
C(351)	7309(4)	5302(3)	3411(3)	28(1)
C(1W)	354(3)	3488(2)	9571(2)	17(2)
Cl(1W)	40(3)	4589(2)	9586(2)	42(1)
Cl(2W)	384(3)	2594(2)	8571(2)	70(2)
C(1Z)	166(3)	1860(2)	9086(2)	35(3)
Cl(1Z)	-1267(3)	2225(2)	8587(2)	43(1)
Cl(2Z)	1521(3)	2408(2)	8609(2)	50(1)

Table S6.2 Bond lengths [Å] and angles [°] for **1**-$(Cl)_3$.

W(1)-N(1)	1.950(3)	N(1)-W(1)-Cl(1)	169.24(10)
W(1)-N(2)	1.953(3)	N(2)-W(1)-Cl(1)	89.29(9)
W(1)-N(3)	1.953(3)	N(3)-W(1)-Cl(1)	90.50(9)
W(1)-Cl(3)	2.4371(9)	Cl(3)-W(1)-Cl(1)	82.12(3)
W(1)-Cl(1)	2.4371(8)	N(1)-W(1)-Cl(2)	89.32(10)
W(1)-Cl(2)	2.4482(9)	N(2)-W(1)-Cl(2)	90.33(9)
N(1)-C(11)	1.459(5)	N(3)-W(1)-Cl(2)	169.83(9)
N(1)-C(17)	1.517(5)	Cl(3)-W(1)-Cl(2)	82.91(3)
N(2)-C(21)	1.452(5)	Cl(1)-W(1)-Cl(2)	82.33(3)
N(2)-C(27)	1.520(5)	C(11)-N(1)-C(17)	110.7(3)
N(3)-C(31)	1.458(4)	C(11)-N(1)-W(1)	121.1(2)
N(3)-C(37)	1.509(5)	C(17)-N(1)-W(1)	127.3(2)
C(11)-C(12)	1.384(6)	C(21)-N(2)-C(27)	110.5(3)
C(11)-C(16)	1.396(5)	C(21)-N(2)-W(1)	120.9(2)
C(12)-C(13)	1.406(5)	C(27)-N(2)-W(1)	127.8(2)
C(13)-C(14)	1.382(6)	C(31)-N(3)-C(37)	111.0(3)
C(13)-C(131)	1.513(6)	C(31)-N(3)-W(1)	120.5(2)
C(14)-C(15)	1.396(6)	C(37)-N(3)-W(1)	127.8(2)
C(15)-C(16)	1.397(5)	C(12)-C(11)-C(16)	121.0(4)
C(15)-C(151)	1.516(6)	C(12)-C(11)-N(1)	120.3(3)
C(17)-C(18)	1.520(7)	C(16)-C(11)-N(1)	118.6(4)
C(17)-C(19)	1.522(6)	C(11)-C(12)-C(13)	119.6(4)
C(21)-C(22)	1.384(6)	C(14)-C(13)-C(12)	119.0(4)
C(21)-C(26)	1.395(6)	C(14)-C(13)-C(131)	121.8(4)
C(22)-C(23)	1.399(6)	C(12)-C(13)-C(131)	119.2(4)
C(23)-C(24)	1.393(7)	C(13)-C(14)-C(15)	121.9(4)
C(23)-C(231)	1.520(7)	C(14)-C(15)-C(16)	118.8(4)
C(24)-C(25)	1.397(8)	C(14)-C(15)-C(151)	121.8(4)
C(25)-C(26)	1.393(6)	C(16)-C(15)-C(151)	119.4(4)
C(25)-C(251)	1.506(7)	C(11)-C(16)-C(15)	119.7(4)
C(27)-C(28)	1.512(5)	N(1)-C(17)-C(18)	110.8(4)
C(27)-C(29)	1.527(5)	N(1)-C(17)-C(19)	112.2(3)
C(31)-C(36)	1.390(5)	C(18)-C(17)-C(19)	111.4(4)
C(31)-C(32)	1.390(5)	C(22)-C(21)-C(26)	120.3(4)
C(32)-C(33)	1.391(5)	C(22)-C(21)-N(2)	120.4(3)
C(33)-C(34)	1.388(5)	C(26)-C(21)-N(2)	119.3(4)
C(33)-C(331)	1.508(5)	C(21)-C(22)-C(23)	120.1(4)
C(34)-C(35)	1.393(5)	C(24)-C(23)-C(22)	118.8(5)
C(35)-C(36)	1.404(5)	C(24)-C(23)-C(231)	120.6(4)
C(35)-C(351)	1.504(5)	C(22)-C(23)-C(231)	120.6(5)
C(37)-C(38)	1.525(5)	C(23)-C(24)-C(25)	121.8(4)
C(37)-C(39)	1.530(5)	C(26)-C(25)-C(24)	118.2(5)
C(1W)-Cl(1W)	1.4757	C(26)-C(25)-C(251)	119.5(5)
C(1W)-Cl(2W)	1.8145	C(24)-C(25)-C(251)	122.3(5)
C(1Z)-Cl(2Z)	1.6498	C(25)-C(26)-C(21)	120.7(4)
C(1Z)-Cl(1Z)	1.8817	C(28)-C(27)-N(2)	113.4(3)
		C(28)-C(27)-C(29)	111.1(3)
N(1)-W(1)-N(2)	97.55(13)	N(2)-C(27)-C(29)	110.2(3)
N(1)-W(1)-N(3)	96.88(13)	C(36)-C(31)-C(32)	120.6(3)
N(2)-W(1)-N(3)	96.81(12)	C(36)-C(31)-N(3)	120.1(3)
N(1)-W(1)-Cl(3)	90.17(10)	C(32)-C(31)-N(3)	119.2(3)
N(2)-W(1)-Cl(3)	169.69(9)	C(31)-C(32)-C(33)	120.6(3)
N(3)-W(1)-Cl(3)	89.00(9)	C(34)-C(33)-C(32)	118.6(3)

C(34)-C(33)-C(331)	121.9(3)	N(3)-C(37)-C(38)	112.9(3)
C(32)-C(33)-C(331)	119.5(3)	N(3)-C(37)-C(39)	109.8(3)
C(33)-C(34)-C(35)	121.8(3)	C(38)-C(37)-C(39)	111.3(3)
C(34)-C(35)-C(36)	118.9(3)	Cl(1W)-C(1W)-Cl(2W)	128.2
C(34)-C(35)-C(351)	121.2(3)	Cl(2Z)-C(1Z)-Cl(1Z)	119.3
C(36)-C(35)-C(351)	119.9(3)		
C(31)-C(36)-C(35)	119.5(3)		

Table S6.3 Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1**-$(Cl)_3$. 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}
W(1)	12(1)	19(1)	20(1)	-4(1)	-5(1)	-1(1)
Cl(1)	13(1)	23(1)	25(1)	-6(1)	-4(1)	-1(1)
N(1)	20(2)	25(2)	22(2)	-7(1)	-8(1)	2(1)
Cl(2)	19(1)	32(1)	27(1)	-6(1)	-12(1)	3(1)
N(2)	14(1)	22(1)	20(1)	-3(1)	-6(1)	0(1)
Cl(3)	16(1)	23(1)	36(1)	-4(1)	-9(1)	-4(1)
N(3)	13(1)	20(1)	19(1)	-3(1)	-3(1)	-3(1)
C(11)	22(2)	25(2)	22(2)	-7(1)	-8(1)	5(1)
C(12)	22(2)	26(2)	27(2)	-8(2)	-7(2)	1(1)
C(13)	31(2)	26(2)	24(2)	-6(2)	-9(2)	4(2)
C(14)	26(2)	31(2)	26(2)	-8(2)	-10(2)	9(2)
C(15)	21(2)	35(2)	22(2)	-9(2)	-6(2)	6(2)
C(16)	22(2)	29(2)	23(2)	-6(2)	-7(2)	2(2)
C(17)	30(2)	37(2)	24(2)	-10(2)	-12(2)	9(2)
C(18)	47(3)	43(3)	41(3)	-17(2)	-26(2)	1(2)
C(19)	38(3)	51(3)	23(2)	-13(2)	-10(2)	16(2)
C(21)	20(2)	24(2)	25(2)	-1(1)	-1(2)	0(1)
C(22)	24(2)	37(2)	25(2)	-2(2)	-3(2)	0(2)
C(23)	39(3)	48(3)	26(2)	2(2)	1(2)	0(2)
C(24)	26(2)	60(3)	36(3)	7(2)	10(2)	4(2)
C(25)	22(2)	53(3)	48(3)	13(2)	5(2)	1(2)
C(26)	19(2)	34(2)	38(2)	8(2)	-3(2)	-1(2)
C(27)	17(2)	21(2)	26(2)	-2(1)	-6(1)	-2(1)
C(28)	24(2)	24(2)	37(2)	2(2)	-11(2)	-8(2)
C(29)	26(2)	25(2)	30(2)	0(2)	-9(2)	4(2)
C(31)	17(2)	19(2)	21(2)	0(1)	-7(1)	-5(1)
C(32)	15(2)	19(2)	26(2)	-1(1)	-6(1)	-2(1)
C(33)	16(2)	20(2)	31(2)	2(1)	-10(1)	-3(1)
C(34)	22(2)	19(2)	36(2)	2(2)	-17(2)	-6(1)
C(35)	23(2)	18(2)	27(2)	-1(1)	-12(2)	-2(1)
C(36)	15(2)	20(2)	25(2)	-3(1)	-7(1)	0(1)
C(37)	18(2)	20(2)	23(2)	0(1)	-6(1)	-5(1)
C(38)	26(2)	22(2)	29(2)	3(1)	-12(2)	-4(1)
C(39)	26(2)	28(2)	26(2)	-2(2)	-3(2)	-7(2)
C(131)	39(2)	27(2)	43(3)	1(2)	-15(2)	2(2)
C(151)	22(2)	46(3)	32(2)	-7(2)	-8(2)	4(2)
C(231)	51(3)	85(4)	24(2)	3(3)	-1(2)	-3(3)
C(251)	16(2)	113(6)	72(4)	37(4)	5(2)	2(3)
C(331)	17(2)	28(2)	52(3)	-2(2)	-13(2)	-2(2)

C(351)	29(2)	24(2)	34(2)	-8(2)	-16(2)	-2(2)
C(1W)	2(4)	45(5)	6(4)	-2(4)	-2(4)	-3(4)
Cl(1W)	27(2)	57(3)	41(2)	6(2)	-9(2)	-1(2)
Cl(2W)	85(5)	84(4)	31(3)	-1(3)	-10(3)	4(4)
C(1Z)	58(6)	24(5)	18(5)	-1(4)	-13(5)	23(5)
Cl(1Z)	49(3)	43(2)	31(2)	-11(2)	-8(2)	15(2)
Cl(2Z)	66(3)	47(3)	43(3)	-12(2)	-32(3)	8(2)