Supplementary Material (ESI) for Dalton Transactions

Phosphorus Stabilized Carbene Complexes: Bisphosphonate Dianion Synthesis, Reactivity and DFT Studies of O~C~O Zirconium(IV) Complexes

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Electronic supplementary information

X-Ray crystal structure analysis:

General: Data were collected at 150.0-(1) K on a Nonius Kappa CCD diffractometer using a Mo Kα (λ = 0.71070 Å) X-ray source and a graphite monochromator. All data were measured using phi and omega scans. Experimental details are described in Tables S1-1 – S3-1. The crystal structures were solved using SIR 97[1] and Shelxl-97.[2] ORTEP drawings were made using ORTEP III for Windows.[3] CCDC XXX- XXX contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at **www.ccdc.cam.ac.uk/conts/** retrieving.html or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk

Crystallographic data for 5:

Figure S1: Molecular structure of 5

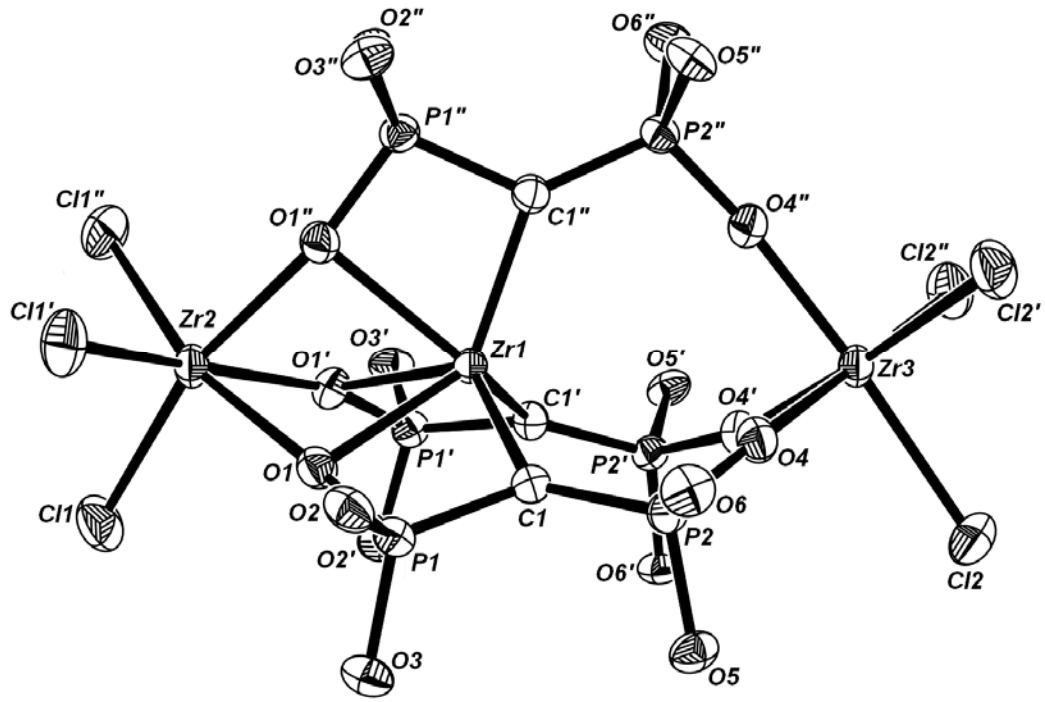


Table S1-1. Crystal data for 5

Compound	5
Molecular formula	$C_{39}H_{84}Cl_6O_{18}P_6Zr_3$
Molecular weight	1513.24
Crystal habit	colorless block
Crystal dimensions(mm)	0.50x0.20x0.16
Crystal system	hexagonal
Space group	R3c
a(Å)	14.063(1)
b(Å)	14.063(1)
c(Å)	57.883(1)
α(°)	90.00
β(°)	90.00
γ(°)	120.00
V(Å^3)	9913.7(1)
Z	6
d(g-cm^{-3})	1.521
F(000)	4644
μ(cm^{-1})	0.909
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069
Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	30.03

HKL ranges	-15 15 ; -19 12 ; -50 81
Reflections measured	12120
Unique data	5068
Rint	0.0227
Reflections used	4079
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	226
Reflections / parameter	18
wR2	0.0921
R1	0.0336
Flack's parameter	0.25(4)
Weights a, b	0.0533 ; 0.0000
GoF	1.023
difference peak / hole (e $Å^{-3}$)	2.001(0.083) / -0.730(0.083)

Table S1-2: Atomic Coordinates and equivalent isotropic displacement parameters for 5

atom	x	y	z	U(eq)
Zr(1)	3333	6667	330(1)	23(1)
Zr(2)	3333	6667	1114(1)	19(1)
Zr(3)	3333	6667	1681(1)	25(1)
Cl(1)	3693(1)	8257(1)	95(1)	40(1)
Cl(2)	4945(1)	7041(1)	1887(1)	44(1)
P(1)	3190(1)	4656(1)	731(1)	20(1)
P(2)	3460(1)	4760(1)	1253(1)	21(1)
O(1)	3103(2)	5388(2)	549(1)	26(1)
O(2)	2192(2)	3464(2)	706(1)	27(1)
O(3)	4181(2)	4468(2)	680(1)	26(1)
O(4)	3539(2)	5695(2)	1413(1)	23(1)
O(5)	2459(2)	3633(2)	1326(1)	26(1)
O(6)	4457(2)	4579(3)	1307(1)	28(1)
C(1)	3351(4)	5220(3)	991(1)	21(1)
C(2)	1060(4)	3185(4)	750(1)	52(2)
C(3)	523(5)	3160(6)	527(2)	115(4)
C(4)	483(5)	2109(8)	861(1)	150(5)
C(5)	4163(3)	3737(3)	499(1)	25(1)
C(6)	5300(4)	4338(4)	387(1)	44(1)
C(7)	3920(4)	2660(3)	609(1)	36(1)
C(8)	2471(3)	2847(3)	1495(1)	29(1)
C(9)	1374(4)	2312(4)	1608(1)	37(1)
C(10)	2722(4)	2068(4)	1374(1)	42(1)
C(11)	5578(4)	5333(5)	1235(1)	49(2)
C(12)	6163(4)	6056(5)	1436(2)	94(3)
C(13)	6060(4)	4636(4)	1163(1)	51(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table S1-3: Bond lengths (Å) and angles (°) for 5

Zr(1)-C(1)	2.168(3)	Zr(1)-C(1)#3	2.168(3)
Zr(1)-C(1)#2	2.168(3)	Zr(1)-O(1)#3	2.310(3)
Zr(1)-O(1)#2	2.310(3)	Zr(1)-O(1)	2.311(3)
Zr(1)-P(1)	2.889(1)	Zr(1)-P(1)#2	2.889(1)
Zr(1)-P(1)#3	2.889(1)	Zr(1)-Zr(2)	3.2785(8)
Zr(2)-O(1)	2.178(3)	Zr(2)-O(1)#3	2.178(3)
Zr(2)-O(1)#2	2.178(3)	Zr(2)-Cl(1)#3	2.376(1)
Zr(2)-Cl(1)	2.376(1)	Zr(2)-Cl(1)#2	2.376(1)
Zr(3)-O(4)#3	2.089(3)	Zr(3)-O(4)	2.089(3)
Zr(3)-O(4)#2	2.089(3)	Zr(3)-Cl(2)#2	2.444(1)
Zr(3)-Cl(2)#3	2.444(1)	Zr(3)-Cl(2)	2.444(1)
P(1)-O(3)	1.562(3)	P(1)-O(1)	1.566(3)
P(1)-O(2)	1.575(3)	P(1)-C(1)	1.687(5)
P(2)-O(4)	1.519(3)	P(2)-O(6)	1.564(3)
P(2)-O(5)	1.570(3)	P(2)-C(1)	1.665(5)
O(2)-C(11)	1.453(6)	O(3)-C(8)	1.484(5)
O(5)-C(5)	1.461(4)	O(6)-C(2)	1.459(5)
C(2)-C(4)	1.46(1)	C(2)-C(3)	1.48(1)
C(5)-C(7)	1.516(5)	C(5)-C(6)	1.528(6)
C(8)-C(10)	1.485(6)	C(8)-C(9)	1.486(6)
C(11)-C(12)	1.49(1)	C(11)-C(13)	1.503(7)

C(1)-Zr(1)-C(1)#3	109.7(1)	C(1)-Zr(1)-C(1)#2	109.7(1)
C(1)#3-Zr(1)-C(1)#2	109.7(1)	C(1)-Zr(1)-O(1)#3	118.2(1)
C(1)#3-Zr(1)-O(1)#3	68.2(1)	C(1)#2-Zr(1)-O(1)#3	129.7(1)
C(1)-Zr(1)-O(1)#2	129.7(1)	C(1)#3-Zr(1)-O(1)#2	118.2(1)
C(1)#2-Zr(1)-O(1)#2	68.2(1)	O(1)#3-Zr(1)-O(1)#2	70.1(1)

C(1)-Zr(1)-O(1)	68.2(1)	C(1)#3-Zr(1)-O(1)	129.7(1)
C(1)#2-Zr(1)-O(1)	118.2(1)	O(1)#3-Zr(1)-O(1)	70.1(1)
O(1)#2-Zr(1)-O(1)	70.1(1)	C(1)-Zr(1)-P(1)	35.5(1)
C(1)#3-Zr(1)-P(1)	125.5(1)	C(1)#2-Zr(1)-P(1)	120.6(1)
O(1)#3-Zr(1)-P(1)	92.77(7)	O(1)#2-Zr(1)-P(1)	99.66(7)
O(1)-Zr(1)-P(1)	32.71(7)	C(1)-Zr(1)-P(1)#2	125.5(1)
C(1)#3-Zr(1)-P(1)#2	120.6(1)	C(1)#2-Zr(1)-P(1)#2	35.5(1)
O(1)#3-Zr(1)-P(1)#2	99.65(7)	O(1)#2-Zr(1)-P(1)#2	32.71(7)
O(1)-Zr(1)-P(1)#2	92.76(7)	P(1)-Zr(1)-P(1)#2	112.56(2)
C(1)-Zr(1)-P(1)#3	120.6(1)	C(1)#3-Zr(1)-P(1)#3	35.5(1)
C(1)#2-Zr(1)-P(1)#3	125.5(1)	O(1)#3-Zr(1)-P(1)#3	32.71(7)
O(1)#2-Zr(1)-P(1)#3	92.77(7)	O(1)-Zr(1)-P(1)#3	99.65(7)
P(1)-Zr(1)-P(1)#3	112.56(2)	P(1)#2-Zr(1)-P(1)#3	112.56(2)
C(1)-Zr(1)-Zr(2)	109.2(1)	C(1)#3-Zr(1)-Zr(2)	109.2(1)
C(1)#2-Zr(1)-Zr(2)	109.2(1)	O(1)#3-Zr(1)-Zr(2)	41.52(6)
O(1)#2-Zr(1)-Zr(2)	41.52(7)	O(1)-Zr(1)-Zr(2)	41.52(6)
P(1)-Zr(1)-Zr(2)	73.83(2)	P(1)#2-Zr(1)-Zr(2)	73.83(2)
P(1)#3-Zr(1)-Zr(2)	73.83(2)	O(1)-Zr(2)-O(1)#3	75.0(1)
O(1)-Zr(2)-O(1)#2	75.0(1)	O(1)#3-Zr(2)-O(1)#2	75.0(1)
O(1)-Zr(2)-Cl(1)#3	91.26(8)	O(1)#3-Zr(2)-Cl(1)#3	94.84(8)
O(1)#2-Zr(2)-Cl(1)#3	164.57(7)	O(1)-Zr(2)-Cl(1)	94.84(8)
O(1)#3-Zr(2)-Cl(1)	164.57(7)	O(1)#2-Zr(2)-Cl(1)	91.26(8)
Cl(1)#3-Zr(2)-Cl(1)	97.02(4)	O(1)-Zr(2)-Cl(1)#2	164.57(7)
O(1)#3-Zr(2)-Cl(1)#2	91.26(8)	O(1)#2-Zr(2)-Cl(1)#2	94.84(8)
Cl(1)#3-Zr(2)-Cl(1)#2	97.02(4)	Cl(1)-Zr(2)-Cl(1)#2	97.02(4)
O(1)-Zr(2)-Zr(1)	44.69(7)	O(1)#3-Zr(2)-Zr(1)	44.68(7)
O(1)#2-Zr(2)-Zr(1)	44.68(7)	Cl(1)#3-Zr(2)-Zr(1)	120.12(3)
Cl(1)-Zr(2)-Zr(1)	120.12(3)	Cl(1)#2-Zr(2)-Zr(1)	120.12(3)
O(4)#3-Zr(3)-O(4)	87.0(1)	O(4)#3-Zr(3)-O(4)#2	87.0(1)
O(4)-Zr(3)-O(4)#2	87.0(1)	O(4)#3-Zr(3)-Cl(2)#2	88.88(8)
O(4)-Zr(3)-Cl(2)#2	91.98(8)	O(4)#2-Zr(3)-Cl(2)#2	175.76(7)
O(4)#3-Zr(3)-Cl(2)#3	175.75(8)	O(4)-Zr(3)-Cl(2)#3	88.87(8)
O(4)#2-Zr(3)-Cl(2)#3	91.98(8)	Cl(2)#2-Zr(3)-Cl(2)#3	92.11(4)
O(4)#3-Zr(3)-Cl(2)	91.99(8)	O(4)-Zr(3)-Cl(2)	175.76(8)
O(4)#2-Zr(3)-Cl(2)	88.88(8)	Cl(2)#2-Zr(3)-Cl(2)	92.11(4)
Cl(2)#3-Zr(3)-Cl(2)	92.10(4)	O(3)-P(1)-O(1)	110.0(2)
O(3)-P(1)-O(2)	102.0(2)	O(1)-P(1)-O(2)	108.9(2)
O(3)-P(1)-C(1)	115.0(2)	O(1)-P(1)-C(1)	101.1(2)
O(2)-P(1)-C(1)	119.8(2)	O(3)-P(1)-Zr(1)	125.0(1)
O(1)-P(1)-Zr(1)	52.9(1)	O(2)-P(1)-Zr(1)	132.6(1)
C(1)-P(1)-Zr(1)	48.2(1)	O(4)-P(2)-O(6)	109.3(2)
O(4)-P(2)-O(5)	111.3(2)	O(6)-P(2)-O(5)	101.5(2)
O(4)-P(2)-C(1)	109.9(2)	O(6)-P(2)-C(1)	115.3(2)
O(5)-P(2)-C(1)	109.2(2)	P(1)-O(1)-Zr(2)	166.2(2)
P(1)-O(1)-Zr(1)	94.4(1)	Zr(2)-O(1)-Zr(1)	93.8(1)
C(11)-O(2)-P(1)	123.7(3)	C(8)-O(3)-P(1)	126.4(2)
P(2)-O(4)-Zr(3)	166.8(2)	C(5)-O(5)-P(2)	123.2(2)
C(2)-O(6)-P(2)	123.1(3)	P(2)-C(1)-P(1)	130.4(2)
P(2)-C(1)-Zr(1)	133.1(2)	P(1)-C(1)-Zr(1)	96.3(2)
O(6)-C(2)-C(4)	108.6(6)	O(6)-C(2)-C(3)	109.3(6)
C(4)-C(2)-C(3)	110.2(5)	O(5)-C(5)-C(7)	108.4(3)
O(5)-C(5)-C(6)	105.6(3)	C(7)-C(5)-C(6)	112.5(4)
O(3)-C(8)-C(10)	109.4(4)	O(3)-C(8)-C(9)	105.7(3)
C(10)-C(8)-C(9)	113.8(4)	O(2)-C(11)-C(12)	107.6(5)
O(2)-C(11)-C(13)	106.4(4)	C(12)-C(11)-C(13)	112.7(4)

Estimated standard deviations are given in the parenthesis.

Symmetry operators ::

1: x, y, z 2: -y, x-y, z 3: -x+y, -x, z
4: -y, -x, z+1/2 5: x, x-y, z+1/2 6: -x+y, y, z+1/2
7: x+2/3, y+1/3, z+1/3 8: -y+2/3, x-y+1/3, z+1 9: -x+y+2/3, -x+1/3, z+
10: -y+2/3, -x+1/3, z+5/11: x+2/3, x-y+1/3, z+5/12: -x+y+2/3, y+1/3, z+5
13: x+1/3, y+2/3, z+2/3 14: -y+1/3, x-y+2/3, z+215: -x+y+1/3, -x+2/3, z+
16: -y+1/3, -x+2/3, z+7/17: x+1/3, x-y+2/3, z+7/18: -x+y+1/3, y+2/3, z+7

Table S1-4: Anisotropic displacement parameters for 5

atom	U11	U22	U33	U23	U13	U12
Zr(1)	19(1)	19(1)	18(1)	0	0	10(1)
Zr(2)	29(1)	29(1)	17(1)	0	0	14(1)
Zr(3)	27(1)	27(1)	17(1)	0	0	13(1)
Cl(1)	40(1)	57(1)	30(1)	-2(1)	-12(1)	22(1)
Cl(2)	50(1)	39(1)	30(1)	11(1)	2(1)	22(1)
P(1)	21(1)	21(1)	22(1)	1(1)	-2(1)	11(1)
P(2)	21(1)	19(1)	21(1)	-2(1)	-2(1)	9(1)
O(1)	26(1)	25(1)	21(1)	-2(1)	-2(1)	14(1)
O(2)	20(1)	26(2)	36(2)	3(1)	-3(1)	11(1)
O(3)	23(1)	25(1)	30(2)	6(1)	-3(1)	11(1)
O(4)	30(1)	29(1)	20(1)	0(1)	-2(1)	15(1)
O(5)	24(1)	25(1)	31(2)	-10(1)	-3(1)	13(1)
O(6)	22(1)	19(1)	32(2)	-4(1)	-1(1)	5(1)
C(1)	23(1)	24(2)	19(1)	-2(2)	0(1)	14(2)
C(2)	19(2)	49(3)	74(4)	-36(3)	5(2)	5(2)
C(3)	31(3)	70(4)	210(10)	82(5)	-28(4)	3(3)
C(4)	32(3)	200(10)	95(6)	93(6)	-21(3)	-33(4)
C(5)	32(2)	24(2)	22(2)	-4(2)	-1(2)	17(2)
C(6)	51(3)	45(3)	42(3)	-2(2)	17(2)	29(3)
C(7)	43(3)	27(2)	40(3)	1(2)	3(2)	20(2)
C(8)	31(2)	26(2)	30(2)	7(2)	1(2)	14(2)
C(9)	34(2)	34(2)	48(3)	9(2)	7(2)	22(2)
C(10)	46(3)	28(2)	55(3)	6(2)	10(2)	21(2)
C(11)	22(2)	46(3)	76(4)	27(3)	0(2)	14(2)
C(12)	31(3)	72(4)	183(8)	-76(5)	-31(4)	28(3)
C(13)	33(2)	56(3)	62(4)	-15(3)	3(2)	23(2)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table S1-5: Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 5

atom	x	y	z	U(eq)
H(2)	1051	3748	854	63
H(3A)	915	3886	455	172
H(3B)	-241	2964	556	172
H(3C)	540	2615	425	172
H(4A)	321	1536	746	225
H(4B)	-205	1997	928	225
H(4C)	946	2072	983	225
H(5)	3586	3605	381	30
H(6A)	5405	5008	312	66
H(6B)	5359	3861	271	66
H(6C)	5863	4530	506	66
H(7A)	4527	2786	710	54
H(7B)	3837	2136	488	54
H(7C)	3240	2363	699	54
H(8)	3050	3260	1614	35
H(9A)	1251	2873	1679	55
H(9B)	1342	1801	1726	55
H(9C)	805	1909	1491	55
H(10A)	2230	1750	1241	63
H(10B)	2618	1481	1480	63
H(10C)	3485	2460	1320	63
H(11)	5581	5786	1101	59
H(12A)	5809	6481	1478	141
H(12B)	6931	6558	1394	141
H(12C)	6132	5603	1567	141
H(13A)	6111	4242	1298	76
H(13B)	6794	5105	1098	76
H(13C)	5588	4105	1046	76

Crystallographic data for 6:

Figure S2: Molecular structure of 6

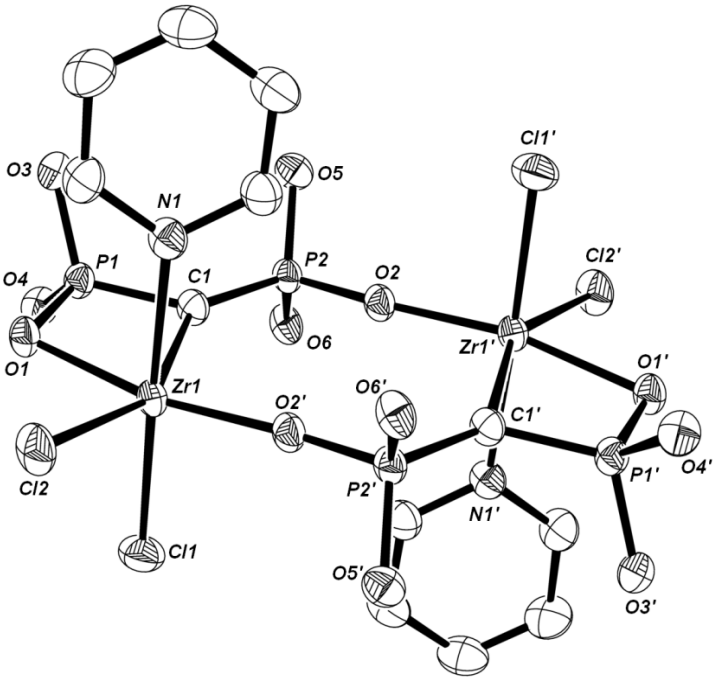


Table S2-1. Crystal data for 6

Compound	6
Molecular formula	$C_{36}H_{66}Cl_4N_2O_{12}P_4Zr_2$,2($CH_2Cl_2$)
Molecular weight	1336.88
Crystal habit	Colorless Block
Crystal dimensions(mm)	0.22x0.18x0.18
Crystal system	triclinic
Space group	P-1
a(Å)	13.038(1)
b(Å)	13.797(1)
c(Å)	17.773(1)
α(°)	103.393(1)
β(°)	91.348(1)
γ(°)	104.745(1)
V(Å^3)	2996.1(4)
Z	2
d(g-cm^{-3})	1.482
F(000)	1368
μ(cm^{-1})	0.862
Absorption corrections	multi-scan ; 0.8330 min, 0.8603 max
Diffractometer	KappaCCD
X-ray source	MoKα
λ(Å)	0.71069

Monochromator	graphite
T (K)	150.0(1)
Scan mode	phi and omega scans
Maximum θ	27.48
HKL ranges	-14 16 ; -17 16 ; -22 23
Reflections measured	29970
Unique data	13554
Rint	0.0332
Reflections used	10551
Criterion	I > 2σI)
Refinement type	Fsqd
Hydrogen atoms	constr
Parameters refined	611
Reflections / parameter	17
wR2	0.1059
R1	0.0383
Weights a, b	0.0453 ; 3.1145
GoF	1.017
difference peak / hole (e Å^{-3})	1.379(0.078) / -1.085(0.078)

Table S2-2: Atomic Coordinates and equivalent isotropic displacement parameters for 6

atom	x	y	z	U(eq)
Zr(1)	5620(1)	1933(1)	4986(1)	23(1)
Cl(1)	5904(1)	2626(1)	6387(1)	38(1)
Cl(2)	4852(1)	3302(1)	4704(1)	36(1)
P(1)	7733(1)	1988(1)	4684(1)	24(1)
P(2)	3139(1)	168(1)	5093(1)	22(1)
O(1)	7125(1)	2826(1)	4751(1)	26(1)
O(2)	4255(1)	873(1)	5055(1)	25(1)
O(3)	8161(2)	1754(1)	3860(1)	28(1)
O(4)	8810(2)	2420(1)	5220(1)	31(1)
O(5)	2587(2)	760(1)	5757(1)	30(1)
O(6)	2412(2)	103(1)	4356(1)	29(1)
N(1)	5269(2)	1226(2)	3615(1)	28(1)
C(1)	6787(2)	1004(2)	4859(1)	24(1)
C(2)	9082(2)	2444(2)	3619(2)	37(1)
C(3)	8796(4)	3375(3)	3484(3)	89(2)
C(4)	9400(3)	1811(3)	2912(2)	65(1)
C(5)	8816(3)	2699(2)	6066(2)	40(1)
C(6)	9650(3)	2279(3)	6370(2)	66(1)
C(7)	9052(4)	3848(3)	6337(2)	70(1)
C(8)	3089(2)	1295(2)	6548(2)	33(1)
C(9)	3018(3)	2389(3)	6683(2)	56(1)
C(10)	2509(3)	716(3)	7100(2)	58(1)
C(11)	2125(2)	1026(2)	4226(2)	37(1)
C(12)	2254(3)	1010(3)	3382(2)	53(1)
C(13)	1009(3)	974(3)	4448(2)	56(1)
C(14)	5685(2)	1775(2)	3108(2)	34(1)
C(15)	5656(3)	1341(3)	2322(2)	43(1)
C(16)	5171(3)	301(3)	2037(2)	44(1)
C(17)	4731(3)	-273(2)	2549(2)	40(1)
C(18)	4799(2)	208(2)	3324(2)	33(1)
Zr(2)	4410(1)	3051(1)	-32(1)	22(1)
Cl(3)	5091(1)	1671(1)	318(1)	34(1)
Cl(4)	4638(1)	2485(1)	-1400(1)	38(1)
P(3)	2203(1)	2822(1)	-147(1)	24(1)
P(4)	6899(1)	4931(1)	124(1)	22(1)

O(7)	2851(1)	2074(1)	0(1)	26(1)
O(8)	5789(1)	4200(1)	133(1)	25(1)
O(9)	1458(1)	2352(1)	-922(1)	28(1)
O(10)	1340(1)	2906(1)	457(1)	29(1)
O(11)	7433(1)	4503(1)	-620(1)	26(1)
O(12)	7656(1)	4821(1)	786(1)	27(1)
N(2)	4456(2)	3701(2)	1343(1)	26(1)
C(19)	3188(2)	3873(2)	-152(1)	23(1)
C(20)	447(2)	1536(2)	-1002(2)	33(1)
C(21)	658(3)	539(2)	-930(2)	54(1)
C(22)	-88(3)	1462(3)	-1781(2)	45(1)
C(23)	1624(2)	3263(2)	1293(2)	32(1)
C(24)	1571(3)	2326(2)	1611(2)	42(1)
C(25)	835(3)	3853(2)	1617(2)	45(1)
C(26)	7686(2)	3494(2)	-781(2)	35(1)
C(27)	7508(3)	3074(3)	-1646(2)	48(1)
C(28)	8822(3)	3657(3)	-469(2)	52(1)
C(29)	7442(2)	5035(2)	1604(1)	32(1)
C(30)	8420(3)	5797(3)	2057(2)	47(1)
C(31)	7178(3)	4016(3)	1834(2)	48(1)
C(32)	4618(2)	4728(2)	1615(2)	30(1)
C(33)	4638(3)	5199(2)	2390(2)	40(1)
C(34)	4473(3)	4590(3)	2919(2)	47(1)
C(35)	4291(3)	3536(3)	2648(2)	44(1)
C(36)	4283(2)	3114(2)	1863(2)	34(1)
Cl(5)	2302(2)	4305(2)	5712(1)	186(1)
Cl(6)	2022(1)	3895(1)	4026(1)	108(1)
C(37)	2778(3)	4661(3)	4901(2)	54(1)
Cl(7)	8106(1)	1466(1)	676(1)	82(1)
Cl(8)	7428(1)	282(1)	-911(1)	79(1)
C(38)	7177(3)	396(2)	65(2)	48(1)

U(eq) is defined as 1/3 the trace of the Uij tensor.

Table S2-3: Bond lengths (Å) and angles (°) for 6

Zr(1)-O(2)	2.022(2)	Zr(1)-O(1)	2.142(2)
Zr(1)-C(1)	2.210(3)	Zr(1)-N(1)	2.391(2)
Zr(1)-Cl(1)	2.4334(7	Zr(1)-Cl(2)	2.4894(7)
Zr(1)-P(1)	2.8039(7	P(1)-O(1)	1.545(2)
P(1)-O(3)	1.572(2)	P(1)-O(4)	1.575(2)
P(1)-C(1)	1.679(3)	P(2)-O(2)	1.544(2)
P(2)-O(6)	1.571(2)	P(2)-O(5)	1.572(2)
P(2)-C(1)#2	1.665(2)	O(3)-C(2)	1.471(3)
O(4)-C(5)	1.463(3)	O(5)-C(8)	1.476(3)
O(6)-C(11)	1.479(3)	N(1)-C(14)	1.345(3)
N(1)-C(18)	1.351(3)	C(1)-P(2)#2	1.665(2)
C(2)-C(4)	1.488(5)	C(2)-C(3)	1.492(5)
C(2)-H(2)	1.0000	C(3)-H(3A)	0.9800
C(3)-H(3B)	0.9800	C(3)-H(3C)	0.9800
C(4)-H(4A)	0.9800	C(4)-H(4B)	0.9800
C(4)-H(4C)	0.9800	C(5)-C(7)	1.494(5)
C(5)-C(6)	1.500(5)	C(5)-H(5)	1.0000
C(6)-H(6A)	0.9800	C(6)-H(6B)	0.9800
C(6)-H(6C)	0.9800	C(7)-H(7A)	0.9800
C(7)-H(7B)	0.9800	C(7)-H(7C)	0.9800
C(8)-C(9)	1.500(4)	C(8)-C(10)	1.505(4)
C(8)-H(8)	1.0000	C(9)-H(9A)	0.9800
C(9)-H(9B)	0.9800	C(9)-H(9C)	0.9800
C(10)-H(10A)	0.9800	C(10)-H(10B)	0.9800
C(10)-H(10C)	0.9800	C(11)-C(13)	1.505(5)
C(11)-C(12)	1.509(4)	C(11)-H(11)	1.0000
C(12)-H(12A)	0.9800	C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800	C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800	C(13)-H(13C)	0.9800
C(14)-C(15)	1.383(4)	C(14)-H(14)	0.9500
C(15)-C(16)	1.378(5)	C(15)-H(15)	0.9500
C(16)-C(17)	1.384(4)	C(16)-H(16)	0.9500

C(17)-C(18)	1.373(4)	C(17)-H(17)	0.9500
C(18)-H(18)	0.9500	Zr(2)-O(8)	2.034(2)
Zr(2)-O(7)	2.144(2)	Zr(2)-C(19)	2.211(2)
Zr(2)-N(2)	2.392(2)	Zr(2)-Cl(4)	2.4267(7)
Zr(2)-Cl(3)	2.4864(7	Zr(2)-P(3)	2.8118(8)
P(3)-O(7)	1.551(2)	P(3)-O(9)	1.570(2)
P(3)-O(10)	1.579(2)	P(3)-C(19)	1.677(2)
P(4)-O(8)	1.542(2)	P(4)-O(11)	1.572(2)
P(4)-O(12)	1.577(2)	P(4)-C(19)#2	1.672(2)
O(9)-C(20)	1.479(3)	O(10)-C(23)	1.459(3)
O(11)-C(26)	1.477(3)	O(12)-C(29)	1.464(3)
N(2)-C(32)	1.347(3)	N(2)-C(36)	1.351(3)
C(19)-P(4)#2	1.672(2)	C(20)-C(21)	1.502(4)
C(20)-C(22)	1.506(4)	C(20)-H(20)	1.0000
C(21)-H(21A)	0.9800	C(21)-H(21B)	0.9800
C(21)-H(21C)	0.9800	C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800	C(22)-H(22C)	0.9800
C(23)-C(25)	1.513(4)	C(23)-C(24)	1.513(4)
C(23)-H(23)	1.0000	C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800	C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800	C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800	C(26)-C(27)	1.503(4)
C(26)-C(28)	1.512(4)	C(26)-H(26)	1.0000
C(27)-H(27A)	0.9800	C(27)-H(27B)	0.9800
C(27)-H(27C)	0.9800	C(28)-H(28A)	0.9800
C(28)-H(28B)	0.9800	C(28)-H(28C)	0.9800
C(29)-C(30)	1.503(4)	C(29)-C(31)	1.512(4)
C(29)-H(29)	1.0000	C(30)-H(30A)	0.9800
C(30)-H(30B)	0.9800	C(30)-H(30C)	0.9800
C(31)-H(31A)	0.9800	C(31)-H(31B)	0.9800
C(31)-H(31C)	0.9800	C(32)-C(33)	1.377(4)
C(32)-H(32)	0.9500	C(33)-C(34)	1.386(4)
C(33)-H(33)	0.9500	C(34)-C(35)	1.377(5)
C(34)-H(34)	0.9500	C(35)-C(36)	1.381(4)
C(35)-H(35)	0.9500	C(36)-H(36)	0.9500
Cl(5)-C(37)	1.707(4)	Cl(6)-C(37)	1.773(4)
C(37)-H(37A)	0.9900	C(37)-H(37B)	0.9900
Cl(7)-C(38)	1.765(3)	Cl(8)-C(38)	1.751(4)
C(38)-H(38A)	0.9900	C(38)-H(38B)	0.9900

O(2)-Zr(1)-O(1)	169.23(7)	O(2)-Zr(1)-C(1)	101.98(8)
O(1)-Zr(1)-C(1)	69.87(8)	O(2)-Zr(1)-N(1)	84.85(7)
O(1)-Zr(1)-N(1)	87.12(7)	C(1)-Zr(1)-N(1)	83.02(8)
O(2)-Zr(1)-Cl(1)	93.06(5)	O(1)-Zr(1)-Cl(1)	95.06(5)
C(1)-Zr(1)-Cl(1)	98.22(7)	N(1)-Zr(1)-Cl(1)	177.76(6)
O(2)-Zr(1)-Cl(2)	99.15(5)	O(1)-Zr(1)-Cl(2)	86.99(5)
C(1)-Zr(1)-Cl(2)	153.60(6)	N(1)-Zr(1)-Cl(2)	83.31(6)
Cl(1)-Zr(1)-Cl(2)	96.26(3)	O(2)-Zr(1)-P(1)	138.26(5)
O(1)-Zr(1)-P(1)	33.09(5)	C(1)-Zr(1)-P(1)	36.78(6)
N(1)-Zr(1)-P(1)	83.67(6)	Cl(1)-Zr(1)-P(1)	98.44(2)
Cl(2)-Zr(1)-P(1)	119.06(2)	O(1)-P(1)-O(3)	110.4(1)
O(1)-P(1)-O(4)	110.7(1)	O(3)-P(1)-O(4)	100.8(1)
O(1)-P(1)-C(1)	101.2(1)	O(3)-P(1)-C(1)	114.6(1)
O(4)-P(1)-C(1)	119.4(1)	O(1)-P(1)-Zr(1)	49.21(7)
O(3)-P(1)-Zr(1)	126.18(8)	O(4)-P(1)-Zr(1)	132.27(7)
C(1)-P(1)-Zr(1)	52.0(1)	O(2)-P(2)-O(6)	108.6(1)
O(2)-P(2)-O(5)	108.0(1)	O(6)-P(2)-O(5)	101.2(1)
O(2)-P(2)-C(1)#2	110.8(1)	O(6)-P(2)-C(1)#2	110.8(1)
O(5)-P(2)-C(1)#2	116.8(1)	P(1)-O(1)-Zr(1)	97.69(8)
P(2)-O(2)-Zr(1)	172.6(1)	C(2)-O(3)-P(1)	124.0(2)
C(5)-O(4)-P(1)	121.1(2)	C(8)-O(5)-P(2)	124.9(2)
C(11)-O(6)-P(2)	121.3(2)	C(14)-N(1)-C(18)	117.1(2)
C(14)-N(1)-Zr(1)	121.4(2)	C(18)-N(1)-Zr(1)	120.6(2)
P(2)#2-C(1)-P(1)	129.3(2)	P(2)#2-C(1)-Zr(1)	139.4(1)
P(1)-C(1)-Zr(1)	91.2(1)	O(3)-C(2)-C(4)	105.9(3)
O(3)-C(2)-C(3)	110.3(3)	C(4)-C(2)-C(3)	113.3(3)
O(3)-C(2)-H(2)	109.1	C(4)-C(2)-H(2)	109.1
C(3)-C(2)-H(2)	109.1	C(2)-C(3)-H(3A)	109.5
C(2)-C(3)-H(3B)	109.5	H(3A)-C(3)-H(3B)	109.5

C(2)-C(3)-H(3C)	109.5	H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5	C(2)-C(4)-H(4A)	109.5
C(2)-C(4)-H(4B)	109.5	H(4A)-C(4)-H(4B)	109.5
C(2)-C(4)-H(4C)	109.5	H(4A)-C(4)-H(4C)	109.5
H(4B)-C(4)-H(4C)	109.5	O(4)-C(5)-C(7)	108.6(3)
O(4)-C(5)-C(6)	106.1(3)	C(7)-C(5)-C(6)	112.8(3)
O(4)-C(5)-H(5)	109.8	C(7)-C(5)-H(5)	109.8
C(6)-C(5)-H(5)	109.8	C(5)-C(6)-H(6A)	109.5
C(5)-C(6)-H(6B)	109.5	H(6A)-C(6)-H(6B)	109.5
C(5)-C(6)-H(6C)	109.5	H(6A)-C(6)-H(6C)	109.5
H(6B)-C(6)-H(6C)	109.5	C(5)-C(7)-H(7A)	109.5
C(5)-C(7)-H(7B)	109.5	H(7A)-C(7)-H(7B)	109.5
C(5)-C(7)-H(7C)	109.5	H(7A)-C(7)-H(7C)	109.5
H(7B)-C(7)-H(7C)	109.5	O(5)-C(8)-C(9)	106.4(2)
O(5)-C(8)-C(10)	107.6(2)	C(9)-C(8)-C(10)	114.0(3)
O(5)-C(8)-H(8)	109.6	C(9)-C(8)-H(8)	109.6
C(10)-C(8)-H(8)	109.6	C(8)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5	H(9A)-C(9)-H(9B)	109.5
C(8)-C(9)-H(9C)	109.5	H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5	C(8)-C(10)-H(10A)	109.5
C(8)-C(10)-H(10B)	109.5	H(10A)-C(10)-H(10B)	109.5
C(8)-C(10)-H(10C)	109.5	H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5	O(6)-C(11)-C(13)	108.4(2)
O(6)-C(11)-C(12)	106.3(2)	C(13)-C(11)-C(12)	113.8(3)
O(6)-C(11)-H(11)	109.4	C(13)-C(11)-H(11)	109.4
C(12)-C(11)-H(11)	109.4	C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5	H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5	H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5	C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5	H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5	H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5	N(1)-C(14)-C(15)	123.0(3)
N(1)-C(14)-H(14)	118.5	C(15)-C(14)-H(14)	118.5
C(16)-C(15)-C(14)	119.0(3)	C(16)-C(15)-H(15)	120.5
C(14)-C(15)-H(15)	120.5	C(15)-C(16)-C(17)	118.8(3)
C(15)-C(16)-H(16)	120.6	C(17)-C(16)-H(16)	120.6
C(18)-C(17)-C(16)	119.0(3)	C(18)-C(17)-H(17)	120.5
C(16)-C(17)-H(17)	120.5	N(1)-C(18)-C(17)	123.2(3)
N(1)-C(18)-H(18)	118.4	C(17)-C(18)-H(18)	118.4
O(8)-Zr(2)-O(7)	167.24(7)	O(8)-Zr(2)-C(19)	102.63(8)
O(7)-Zr(2)-C(19)	69.64(8)	O(8)-Zr(2)-N(2)	81.18(7)
O(7)-Zr(2)-N(2)	88.21(7)	C(19)-Zr(2)-N(2)	87.41(8)
O(8)-Zr(2)-Cl(4)	91.53(5)	O(7)-Zr(2)-Cl(4)	99.46(5)
C(19)-Zr(2)-Cl(4)	97.80(6)	N(2)-Zr(2)-Cl(4)	171.85(6)
O(8)-Zr(2)-Cl(3)	99.79(5)	O(7)-Zr(2)-Cl(3)	86.09(5)
C(19)-Zr(2)-Cl(3)	154.60(6)	N(2)-Zr(2)-Cl(3)	84.36(5)
Cl(4)-Zr(2)-Cl(3)	93.36(3)	O(8)-Zr(2)-P(3)	138.80(5)
O(7)-Zr(2)-P(3)	33.12(5)	C(19)-Zr(2)-P(3)	36.60(6)
N(2)-Zr(2)-P(3)	89.19(6)	Cl(4)-Zr(2)-P(3)	98.73(2)
Cl(3)-Zr(2)-P(3)	119.11(2)	O(7)-P(3)-O(9)	111.3(1)
O(7)-P(3)-O(10)	111.0(1)	O(9)-P(3)-O(10)	100.0(1)
O(7)-P(3)-C(19)	100.7(1)	O(9)-P(3)-C(19)	114.7(1)
O(10)-P(3)-C(19)	119.5(1)	O(7)-P(3)-Zr(2)	49.07(7)
O(9)-P(3)-Zr(2)	124.49(8)	O(10)-P(3)-Zr(2)	134.77(7)
C(19)-P(3)-Zr(2)	51.8(1)	O(8)-P(4)-O(11)	109.9(1)
O(8)-P(4)-O(12)	107.8(1)	O(11)-P(4)-O(12)	101.1(1)
O(8)-P(4)-C(19)#2	110.8(1)	O(11)-P(4)-C(19)#2	110.5(1)
O(12)-P(4)-C(19)#2	116.3(1)	P(3)-O(7)-Zr(2)	97.81(8)
P(4)-O(8)-Zr(2)	168.9(1)	C(20)-O(9)-P(3)	123.5(2)
C(23)-O(10)-P(3)	122.3(2)	C(26)-O(11)-P(4)	123.3(2)
C(29)-O(12)-P(4)	122.8(2)	C(32)-N(2)-C(36)	117.4(2)
C(32)-N(2)-Zr(2)	117.4(2)	C(36)-N(2)-Zr(2)	125.2(2)
P(4)#2-C(19)-P(3)	128.2(2)	P(4)#2-C(19)-Zr(2)	139.5(1)
P(3)-C(19)-Zr(2)	91.6(1)	O(9)-C(20)-C(21)	110.6(2)
O(9)-C(20)-C(22)	105.3(2)	C(21)-C(20)-C(22)	113.2(3)
O(9)-C(20)-H(20)	109.2	C(21)-C(20)-H(20)	109.2
C(22)-C(20)-H(20)	109.2	C(20)-C(21)-H(21A)	109.5
C(20)-C(21)-H(21B)	109.5	H(21A)-C(21)-H(21B)	109.5
C(20)-C(21)-H(21C)	109.5	H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5	C(20)-C(22)-H(22A)	109.5

C(20)-C(22)-H(22B)	109.5	H(22A)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	109.5	H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5	O(10)-C(23)-C(25)	106.1(2)
O(10)-C(23)-C(24)	108.1(2)	C(25)-C(23)-C(24)	113.1(2)
O(10)-C(23)-H(23)	109.8	C(25)-C(23)-H(23)	109.8
C(24)-C(23)-H(23)	109.8	C(23)-C(24)-H(24A)	109.5
C(23)-C(24)-H(24B)	109.5	H(24A)-C(24)-H(24B)	109.5
C(23)-C(24)-H(24C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5	C(23)-C(25)-H(25A)	109.5
C(23)-C(25)-H(25B)	109.5	H(25A)-C(25)-H(25B)	109.5
C(23)-C(25)-H(25C)	109.5	H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5	O(11)-C(26)-C(27)	106.0(2)
O(11)-C(26)-C(28)	108.9(2)	C(27)-C(26)-C(28)	112.9(3)
O(11)-C(26)-H(26)	109.6	C(27)-C(26)-H(26)	109.6
C(28)-C(26)-H(26)	109.6	C(26)-C(27)-H(27A)	109.5
C(26)-C(27)-H(27B)	109.5	H(27A)-C(27)-H(27B)	109.5
C(26)-C(27)-H(27C)	109.5	H(27A)-C(27)-H(27C)	109.5
H(27B)-C(27)-H(27C)	109.5	C(26)-C(28)-H(28A)	109.5
C(26)-C(28)-H(28B)	109.5	H(28A)-C(28)-H(28B)	109.5
C(26)-C(28)-H(28C)	109.5	H(28A)-C(28)-H(28C)	109.5
H(28B)-C(28)-H(28C)	109.5	O(12)-C(29)-C(30)	107.3(2)
O(12)-C(29)-C(31)	107.3(2)	C(30)-C(29)-C(31)	112.9(2)
O(12)-C(29)-H(29)	109.7	C(30)-C(29)-H(29)	109.7
C(31)-C(29)-H(29)	109.7	C(29)-C(30)-H(30A)	109.5
C(29)-C(30)-H(30B)	109.5	H(30A)-C(30)-H(30B)	109.5
C(29)-C(30)-H(30C)	109.5	H(30A)-C(30)-H(30C)	109.5
H(30B)-C(30)-H(30C)	109.5	C(29)-C(31)-H(31A)	109.5
C(29)-C(31)-H(31B)	109.5	H(31A)-C(31)-H(31B)	109.5
C(29)-C(31)-H(31C)	109.5	H(31A)-C(31)-H(31C)	109.5
H(31B)-C(31)-H(31C)	109.5	N(2)-C(32)-C(33)	123.2(3)
N(2)-C(32)-H(32)	118.4	C(33)-C(32)-H(32)	118.4
C(32)-C(33)-C(34)	118.7(3)	C(32)-C(33)-H(33)	120.6
C(34)-C(33)-H(33)	120.6	C(35)-C(34)-C(33)	118.7(3)
C(35)-C(34)-H(34)	120.6	C(33)-C(34)-H(34)	120.6
C(34)-C(35)-C(36)	119.5(3)	C(34)-C(35)-H(35)	120.2
C(36)-C(35)-H(35)	120.2	N(2)-C(36)-C(35)	122.3(3)
N(2)-C(36)-H(36)	118.8	C(35)-C(36)-H(36)	118.8
Cl(5)-C(37)-Cl(6)	113.6(2)	Cl(5)-C(37)-H(37A)	108.8
Cl(6)-C(37)-H(37A)	108.8	Cl(5)-C(37)-H(37B)	108.8
Cl(6)-C(37)-H(37B)	108.8	H(37A)-C(37)-H(37B)	107.7
Cl(8)-C(38)-Cl(7)	111.3(2)	Cl(8)-C(38)-H(38A)	109.4
Cl(7)-C(38)-H(38A)	109.4	Cl(8)-C(38)-H(38B)	109.4
Cl(7)-C(38)-H(38B)	109.4	H(38A)-C(38)-H(38B)	108.0

Estimated standard deviations are given in the parenthesis.
Symmetry operators ::
1: x, y, z 2: -x, -y, -z

Table S2-4: Anisotropic displacement parameters for 6

atom	U11	U22	U33	U23	U13	U12
Zr(1)	27(1)	17(1)	26(1)	7(1)	3(1)	7(1)
Cl(1)	43(1)	38(1)	28(1)	-2(1)	4(1)	10(1)
Cl(2)	40(1)	25(1)	51(1)	16(1)	5(1)	16(1)
P(1)	27(1)	21(1)	25(1)	10(1)	2(1)	7(1)
P(2)	26(1)	18(1)	26(1)	8(1)	2(1)	8(1)
O(1)	29(1)	19(1)	33(1)	10(1)	3(1)	6(1)
O(2)	28(1)	19(1)	30(1)	8(1)	3(1)	7(1)
O(3)	31(1)	27(1)	28(1)	11(1)	5(1)	6(1)
O(4)	30(1)	33(1)	29(1)	10(1)	-1(1)	7(1)
O(5)	30(1)	29(1)	32(1)	5(1)	3(1)	12(1)
O(6)	35(1)	22(1)	32(1)	10(1)	-4(1)	10(1)
N(1)	33(1)	25(1)	28(1)	9(1)	0(1)	11(1)
C(1)	27(1)	21(1)	27(1)	8(1)	2(1)	9(1)
C(2)	35(2)	39(2)	42(2)	21(1)	11(1)	7(1)

C(3)	93(3)	66(3)	147(4)	78(3)	73(3)	39(3)
C(4)	70(3)	68(3)	57(2)	20(2)	36(2)	12(2)
C(5)	42(2)	45(2)	29(1)	7(1)	-3(1)	5(1)
C(6)	85(3)	49(2)	58(2)	19(2)	-33(2)	7(2)
C(7)	95(3)	51(2)	59(2)	-9(2)	-22(2)	33(2)
C(8)	35(2)	28(1)	32(1)	0(1)	4(1)	9(1)
C(9)	61(2)	33(2)	68(2)	-10(2)	-13(2)	22(2)
C(10)	67(2)	58(2)	32(2)	1(2)	12(2)	-9(2)
C(11)	43(2)	25(1)	47(2)	17(1)	-6(1)	14(1)
C(12)	63(2)	56(2)	51(2)	31(2)	-5(2)	19(2)
C(13)	52(2)	60(2)	73(2)	32(2)	6(2)	33(2)
C(14)	43(2)	32(2)	33(1)	15(1)	1(1)	13(1)
C(15)	57(2)	49(2)	32(2)	19(1)	4(1)	20(2)
C(16)	55(2)	51(2)	27(1)	5(1)	-1(1)	22(2)
C(17)	49(2)	34(2)	35(2)	1(1)	-1(1)	13(1)
C(18)	39(2)	28(1)	34(1)	9(1)	3(1)	11(1)
Zr(2)	27(1)	16(1)	24(1)	6(1)	2(1)	7(1)
Cl(3)	39(1)	23(1)	45(1)	14(1)	2(1)	14(1)
Cl(4)	48(1)	36(1)	27(1)	1(1)	5(1)	13(1)
P(3)	28(1)	19(1)	27(1)	8(1)	3(1)	7(1)
P(4)	26(1)	17(1)	24(1)	7(1)	1(1)	7(1)
O(7)	30(1)	18(1)	33(1)	11(1)	3(1)	7(1)
O(8)	28(1)	18(1)	29(1)	8(1)	2(1)	6(1)
O(9)	31(1)	22(1)	29(1)	7(1)	1(1)	4(1)
O(10)	30(1)	30(1)	28(1)	8(1)	5(1)	8(1)
O(11)	33(1)	23(1)	28(1)	8(1)	6(1)	12(1)
O(12)	31(1)	28(1)	26(1)	9(1)	-1(1)	12(1)
N(2)	32(1)	24(1)	24(1)	8(1)	1(1)	8(1)
C(19)	25(1)	17(1)	28(1)	8(1)	2(1)	6(1)
C(20)	30(2)	24(1)	39(2)	6(1)	0(1)	0(1)
C(21)	50(2)	26(2)	82(3)	14(2)	-10(2)	2(2)
C(22)	36(2)	50(2)	40(2)	6(1)	-5(1)	1(2)
C(23)	37(2)	30(1)	28(1)	7(1)	8(1)	6(1)
C(24)	49(2)	45(2)	39(2)	22(1)	12(1)	15(2)
C(25)	60(2)	38(2)	42(2)	10(1)	19(2)	19(2)
C(26)	43(2)	22(1)	42(2)	7(1)	11(1)	15(1)
C(27)	51(2)	41(2)	46(2)	-5(1)	9(2)	15(2)
C(28)	57(2)	53(2)	55(2)	9(2)	6(2)	36(2)
C(29)	39(2)	35(2)	24(1)	11(1)	2(1)	13(1)
C(30)	57(2)	41(2)	34(2)	8(1)	-8(1)	2(2)
C(31)	57(2)	45(2)	44(2)	25(2)	-4(2)	4(2)
C(32)	33(2)	29(1)	31(1)	9(1)	1(1)	11(1)
C(33)	44(2)	35(2)	35(2)	-2(1)	4(1)	9(1)
C(34)	52(2)	62(2)	27(1)	6(1)	7(1)	18(2)
C(35)	50(2)	59(2)	34(2)	24(2)	9(1)	22(2)
C(36)	39(2)	34(2)	37(2)	18(1)	7(1)	14(1)
Cl(5)	322(3)	174(2)	176(2)	132(2)	172(2)	174(2)
Cl(6)	89(1)	58(1)	157(1)	-5(1)	-34(1)	17(1)
C(37)	54(2)	34(2)	79(3)	21(2)	13(2)	16(2)
Cl(7)	85(1)	37(1)	114(1)	9(1)	-25(1)	9(1)
Cl(8)	74(1)	81(1)	85(1)	33(1)	17(1)	16(1)
C(38)	40(2)	33(2)	74(2)	17(2)	4(2)	11(1)

The anisotropic displacement factor exponent takes the form
2 pi^2 [h^2a*^2U(11) +...+ 2hka*b*U(12)]

Table S2-5: Hydrogen Coordinates (A x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for 6

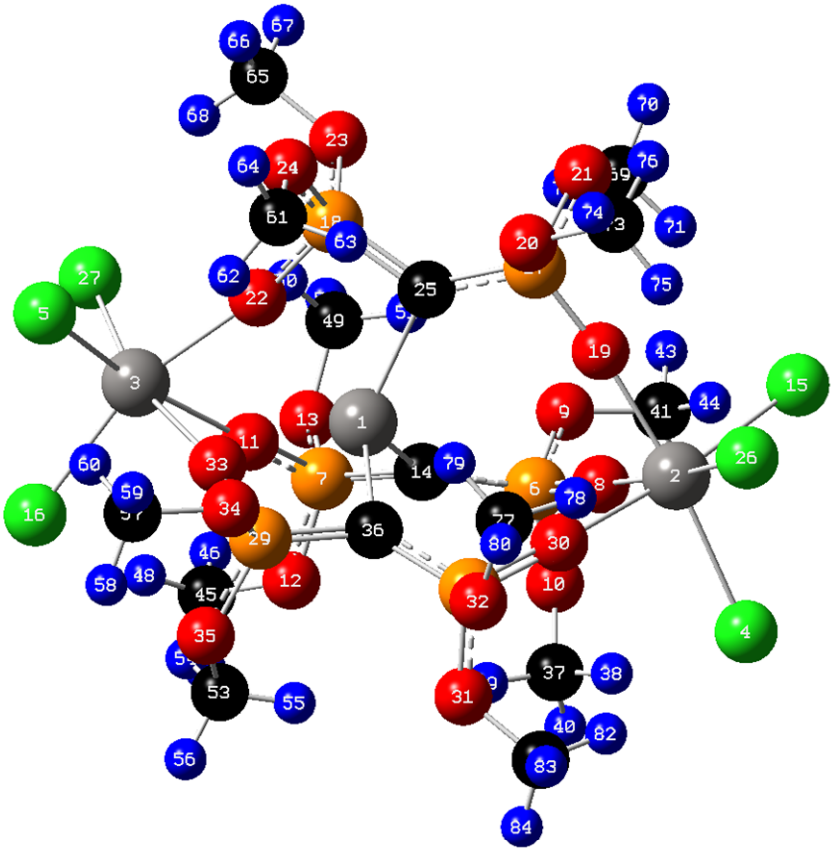
atom	x	y	z	U(eq)
H(2)	9679	2669	4038	45
H(3A)	8621	3773	3973	133
H(3B)	8180	3157	3100	133
H(3C)	9401	3806	3292	133
H(4A)	8842	1635	2486	98

H(4B)	9500	1175	3021	98
H(4C)	10068	2206	2764	98
H(5)	8105	2370	6223	48
H(6A)	10340	2579	6195	99
H(6B)	9459	1525	6174	99
H(6C)	9697	2456	6937	99
H(7A)	8466	4078	6147	105
H(7B)	9714	4169	6136	105
H(7C)	9133	4051	6906	105
H(8)	3854	1287	6577	39
H(9A)	2269	2394	6637	84
H(9B)	3398	2711	6296	84
H(9C)	3341	2778	7205	84
H(10A)	2602	15	6984	88
H(10B)	1750	678	7043	88
H(10C)	2799	1077	7634	88
H(11)	2627	1664	4559	44
H(12A)	1787	370	3055	79
H(12B)	2996	1046	3278	79
H(12C)	2062	1605	3265	79
H(13A)	513	362	4109	83
H(13B)	818	1597	4390	83
H(13C)	968	928	4989	83
H(14)	6013	2493	3299	41
H(15)	5966	1753	1983	52
H(16)	5140	-15	1499	52
H(17)	4386	-989	2368	48
H(18)	4502	-194	3671	40
H(20)	-7.0000	1758	-585	39
H(21A)	981	628	-407	81
H(21B)	1144	344	-1313	81
H(21C)	-15	-6.0000	-1023.0001	81
H(22A)	365	1263	-2190	67
H(22B)	-201	2133	-1794	67
H(22C)	-776	939	-1867	67
H(23)	2362	3734	1399	39
H(24A)	2057	1946	1351	63
H(24B)	842	1876	1517	63
H(24C)	1780	2550	2170	63
H(25A)	115	3383	1526	68
H(25B)	862	4413	1359	68
H(25C)	1015	4144	2176	68
H(26)	7192	3017	-522	41
H(27A)	7995	3542	-1899	72
H(27B)	6771	3016	-1820	72
H(27C)	7641	2390	-1785	72
H(28A)	8905	3973	89	77
H(28B)	9306	4113	-732	77
H(28C)	8993	2989	-564	77
H(29)	6822	5341	1672	38
H(30A)	8554	6441	1885	70
H(30B)	9033	5508	1969	70
H(30C)	8313	5940	2611	70
H(31A)	7802	3740	1797	72
H(31B)	6584	3525	1483	72
H(31C)	6978	4124	2369	72
H(32)	4724	5149	1254	36
H(33)	4762	5928	2559	48
H(34)	4486	4893	3457	57
H(35)	4171	3102	3000	53
H(36)	4152	2386	1682	41
H(37A)	3522	4612	4873	65
H(37B)	2787	5392	4949	65
H(38A)	7213	-243	214	58
H(38B)	6449	478	132	58

Theoretical Calculations

Computational details: Calculations were performed with the GAUSSIAN 03 series of programs.[4] The B3PW91 functional[5,6] was used in combination with the 3-21G* basis set for all non-metal-bound atoms (C, H), the 6-31G* for all metal-bound-atoms (C, H, P, O) and the LANL2DZ basis[7] for zirconium. The stationary points were characterized as minima by full vibration frequencies calculations (no imaginary frequency).

Cartesian coordinates, three lower frequencies and thermochemistry of 5t



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	40	0	-0.620964	0.001524	-0.001258
2	40	0	3.964682	0.003476	-0.007810
3	40	0	-3.956716	0.001558	-0.016658
4	17	0	5.245605	-1.912830	0.906622
5	17	0	-5.119915	1.914646	0.924149
6	15	0	1.590183	-2.223977	-1.626059
7	15	0	-1.462100	-2.467316	-1.339716
8	8	0	2.665215	-1.329494	-0.990283
9	8	0	1.655528	-2.136460	-3.223277
10	8	0	1.964096	-3.767107	-1.386813
11	8	0	-2.395683	-1.363459	-0.661004
12	8	0	-1.722652	-3.870468	-0.634245
13	8	0	-2.000456	-2.755013	-2.817709
14	6	0	0.041275	-1.779712	-1.094719
15	17	0	5.265168	0.185766	-2.107996
16	17	0	-5.119645	-1.780947	1.153136
17	15	0	1.588452	2.529369	-1.095924
18	15	0	-1.466014	2.409024	-1.444162
19	8	0	2.663694	1.508722	-0.694813
20	8	0	1.666460	3.835733	-0.173814
21	8	0	1.950133	3.145306	-2.534222
22	8	0	-2.394121	1.247772	-0.859615
23	8	0	-1.736586	2.545296	-3.006614
24	8	0	-2.011148	3.812936	-0.906028
25	6	0	0.039265	1.846893	-0.987571
26	17	0	5.243809	1.736033	1.221368
27	17	0	-5.109912	-0.130297	-2.151236
28	15	0	1.575339	-0.309720	2.721503
29	15	0	-1.489577	0.054236	2.802815
30	8	0	2.627481	-0.158381	1.611104
31	8	0	1.667523	-1.752359	3.407940
32	8	0	1.956666	0.642492	3.956649
33	8	0	-2.413486	0.121671	1.502461
34	8	0	-1.756949	1.355145	3.681887
35	8	0	-2.038924	-1.093903	3.770692
36	6	0	0.017747	-0.072034	2.095228
37	6	0	2.280357	-4.211180	-0.037494
38	1	0	3.186075	-3.712046	0.317859
39	1	0	1.439160	-4.010343	0.634501
40	1	0	2.445028	-5.287527	-0.114271
41	6	0	2.929005	-2.427561	-3.882346
42	1	0	3.206871	-3.470487	-3.709094
43	1	0	2.752623	-2.254782	-4.945515
44	1	0	3.707481	-1.753958	-3.511795
45	6	0	-2.987128	-4.583322	-0.812378
46	1	0	-3.169604	-4.765159	-1.873721
47	1	0	-2.861249	-5.527724	-0.280622
48	1	0	-3.805750	-4.008381	-0.370496
49	6	0	-1.876128	-1.722235	-3.837752
50	1	0	-2.537639	-0.884991	-3.600771
51	1	0	-0.835671	-1.394723	-3.913013
52	1	0	-2.192920	-2.194793	-4.769003
53	6	0	-1.887981	-2.492089	3.391052
54	1	0	-2.560126	-2.726158	2.561540
55	1	0	-0.847227	-2.697968	3.126158
56	1	0	-2.173697	-3.065077	4.274851
57	6	0	-3.045445	1.556258	4.344562
58	1	0	-3.254633	0.723444	5.019613
59	1	0	-2.937366	2.484600	4.907541
60	1	0	-3.837315	1.658486	3.596990
61	6	0	-1.850099	4.140661	0.504710

62	1	0	-2.404526	3.429573	1.122807
63	1	0	-0.788567	4.140752	0.765772
64	1	0	-2.273108	5.139919	0.620311
65	6	0	-3.020812	3.037573	-3.504954
66	1	0	-3.226174	4.030179	-3.098117
67	1	0	-2.908716	3.085746	-4.589140
68	1	0	-3.816787	2.336480	-3.238748
69	6	0	2.264591	2.235934	-3.626033
70	1	0	2.468354	2.873107	-4.488571
71	1	0	3.147529	1.640465	-3.377218
72	1	0	1.407043	1.587830	-3.836470
73	6	0	2.935979	4.559974	-0.097456
74	1	0	2.764712	5.373344	0.609953
75	1	0	3.725295	3.897187	0.269304
76	1	0	3.193950	4.961418	-1.080864
77	6	0	2.243340	2.045571	3.698676
78	1	0	3.143008	2.136049	3.083844
79	1	0	1.388829	2.522933	3.207178
80	1	0	2.406528	2.496515	4.679247
81	6	0	2.942145	-2.164857	3.997344
82	1	0	3.727489	-2.160110	3.235783
83	1	0	3.201703	-1.498552	4.823980
84	1	0	2.777171	-3.178814	4.366054

	1	2	3
	A	A	A
Frequencies --	13.4237	20.5265	25.1465
Red. masses --	6.5391	5.3237	5.7574
Frc consts --	0.0007	0.0013	0.0021
IR Inten --	0.0542	0.4873	1.1087

Sum of electronic and zero-point Energies= -4221.897330
Sum of electronic and thermal Energies= -4221.827840
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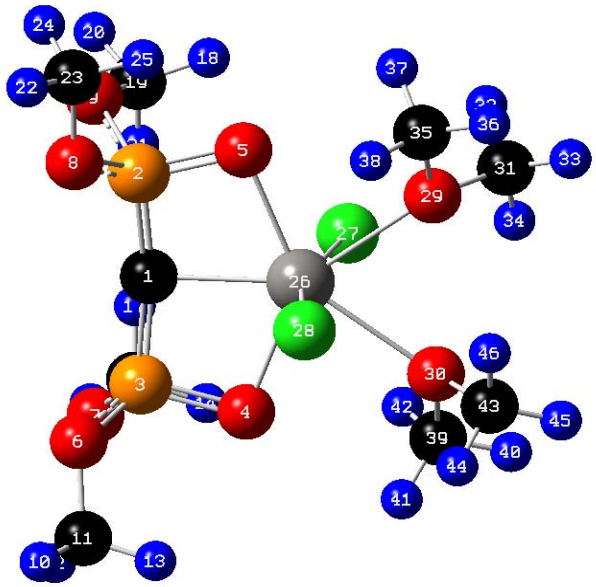
Sum of electronic and thermal Free Energies= -4222.009240

HF=-4222.482639

Cartesian coordinates, three lower frequencies and thermochemistry of compound 8t



Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.520936	0.042946	0.034109
2	15	0	-1.681986	-1.597805	-0.049430
3	15	0	-1.589106	1.679814	-0.167586
4	8	0	-0.065918	2.038683	-0.140344
5	8	0	-0.180759	-2.038429	-0.021328
6	8	0	-2.308163	2.179793	-1.504406
7	8	0	-2.369231	2.572980	0.927898
8	8	0	-2.458352	-2.147832	-1.334334
9	8	0	-2.483679	-2.367437	1.120676
10	1	0	-2.669176	3.647666	-2.871206
11	6	0	-2.172341	3.568278	-1.902498
12	1	0	-2.660243	4.223035	-1.174082
13	1	0	-1.114611	3.829945	-2.005075
14	1	0	-0.954312	2.803522	2.460418
15	6	0	-1.975375	2.439451	2.314480
16	1	0	-2.679918	3.045984	2.887980
17	1	0	-2.033511	1.393248	2.630767
18	1	0	-1.018719	-2.579234	2.609824
19	6	0	-2.029243	-2.180378	2.483543
20	1	0	-2.736446	-2.723936	3.114017
21	1	0	-2.030379	-1.117339	2.742969
22	1	0	-3.007291	-3.695495	-2.541088
23	6	0	-2.469651	-3.574034	-1.598811
24	1	0	-2.988614	-4.106888	-0.796673
25	1	0	-1.446171	-3.947721	-1.705023
26	40	0	0.674783	-0.020090	-0.031053
27	17	0	1.040699	0.027914	2.487056
28	17	0	1.044565	-0.090118	-2.518977
29	8	0	2.566102	-1.493032	-0.086492
30	8	0	2.636960	1.355858	0.069367
31	6	0	3.482712	-1.621429	1.018476
32	1	0	3.102012	-2.348262	1.744890
33	1	0	4.459185	-1.944291	0.633773
34	1	0	3.561479	-0.642713	1.489403

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  35          6             0        2.486145   -2.728613   -0.828027
  36          1             0        3.497716   -3.015635   -1.143058
  37          1             0        2.039349   -3.512038   -0.207705
  38          1             0        1.861799   -2.534743   -1.699883
  39          6             0        2.592399    2.603802    0.791765
  40          1             0        3.612357    2.870079    1.097751
  41          1             0        2.160297    3.388748    0.163494
  42          1             0        1.969618    2.437526    1.670448
  43          6             0        3.552436    1.445967   -1.041476
  44          1             0        3.189445    2.175366   -1.774014
  45          1             0        4.539564    1.743082   -0.663355
  46          1             0        3.599588    0.460405   -1.502223
---------------------------------------------------------------------


                     1                      2                      3
                     A                      A                      A
Frequencies --    37.7541                42.7721                49.6818
Red. masses --     4.0868                 4.1781                 3.4029
Frc consts  --     0.0034                 0.0045                 0.0049
IR Inten    --     0.6414                 2.9457                 3.6222

Sum of electronic and zero-point Energies=          -1716.191390
Sum of electronic and thermal Energies=             -1716.158732
Sum of electronic and thermal Enthalpies=           -1716.157788
Sum of electronic and thermal Free Energies=        -1716.255773

HF=-1716.552328
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Table S2. Comparison between the computed structure of complex **5** (DFT) and the experimental X-ray data.

Atoms	X-ray values	Calculated values	|Δ(X-ray-calc.)|
Zr(3)-Zr(2)	3.279 Å	3.336 Å	0.057 Å
Zr(1)-Zr(2)	4.540 Å	4.585 Å	0.045 Å
Zr(2)-C(1)	2.168 Å	2.194 Å	0.026 Å
Zr(1)-O(1)	2.089 Å	2.106 Å	0.017 Å
C(1)-P(2)	1.687 Å	1.670 Å	0.017 Å
C(1)-P(1)	1.665 Å	1.695 Å	0.03 Å
P(1)-O(1)	1.519 Å	1.536 Å	0.014 Å
P(2)-O(4)	1.566 Å	1.597 Å	0.031 Å
Zr(3)-Zr(2)-Zr(1)	180.0°	179.7°	0.3°
P(1)-C(1)-P(2)	130.4°	133.1°	2.7°
C(1)-Zr(2)-C(1”)	109.7°	111.7°	2.0°
Zr(3)-O(4)-P(2)	166.2°	168.5°	2.3°

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