S1. Crystal data and structure refinement for 1.

Identification code	hill1c
Empirical formula	$H_{162}Fe_2Na_{16}O_{192}P_4W_{30}$
Formula weight	9354.22
Temperature	193(2) K
Wavelength	0.71073 Å
Crystal size, color	0.30 x 0.26 x 0.36 mm, yellow block
Crystal system	Triclinic
Space group	P-1 (No. 2)
Unit cell dimensions	*a* = 12.8027(3) Å alpha = 79.30°
	b = 13.9668(3) Å beta = 78.4880(10)°
	c = 23.5073(5) Å gamma = 80.3650(10)°
Volume, Z	4009.9(2) $Å^3$, 1
Density (calculated)	3.874 Mg/m^3
Absorption coefficient	21.816 mm^{-1}
F(000)	4206
θ range for data collection	0.90 to 22.50°
Limiting indices	$-14 \leq h \leq 12$, $-15 \leq k \leq 15$, $-25 \leq l \leq 26$
Reflections collected	16592
Independent reflections	10449 (R_{int} = 0.0902)
Absorption corrections	Psi scan
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9657 / 0 / 620
Goodness-of-fit on F^2	1.036
Final R indices [$I>2\sigma(I)$]	R1 = 0.0798, wR2 = 0.2033
R indices (all data)	R1 = 0.1048, wR2 = 0.2468
Extinction coefficient	0.00000(3)
Largest diff. peak and hole	4.493 and -3.598 $eÅ^{-3}$

S2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for 1. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
W(1)	881(1)	2909(1)	5669(1)	32(1)
W(2)	3269(1)	1477(1)	5786(1)	32(1)
W(3)	2814(1)	3774(1)	6159(1)	32(1)
W(4)	-545(1)	917(1)	6611(1)	32(1)
W(5)	1801(1)	-472(1)	6752(1)	31(1)
W(6)	3891(1)	471(1)	7283(1)	31(1)
W(7)	3402(1)	2719(1)	7649(1)	30(1)
W(8)	825(1)	4262(1)	7489(1)	31(1)
W(9)	-1060(1)	3404(1)	7008(1)	32(1)
W(10)	-1742(1)	-128(1)	8195(1)	36(1)
W(11)	611(1)	-1512(1)	8330(1)	31(1)
W(12)	2659(1)	-548(1)	8836(1)	30(1)
W(13)	2188(1)	1717(1)	9200(1)	30(1)
W(14)	-368(1)	3209(1)	9042(1)	31(1)
W(15)	-2266(1)	2324(1)	8575(1)	34(1)
Fe(1)	231(3)	-1094(3)	9829(2)	32(1)
Na(1)	2458(14)	-170(10)	10205(6)	61(4)
P(1)	1432(6)	1929(5)	7064(3)	27(2)
P(2)	139(6)	792(5)	8787(3)	26(2)
O(1)	348(17)	3424(15)	5029(9)	39(5)
O(2)	2148(16)	2114(14)	5342(9)	35(5)
O(3)	4246(17)	1012(14)	5245(9)	37(5)
O(4)	3676(16)	2805(13)	5731(8)	31(4)
O(5)	3476(17)	4737(14)	5822(9)	38(5)
O(6)	1824(18)	3883(16)	5631(10)	43(5)
O(7)	244(17)	1775(14)	5927(9)	37(5)
O(8)	2473(16)	449(14)	6083(9)	34(5)
O(9)	3951(17)	1110(15)	6446(9)	39(5)
O(10)	3531(16)	3232(14)	6783(8)	32(4)
O(11)	1672(17)	4322(15)	6707(9)	39(5)
O(12)	-96(16)	3534(14)	6222(9)	35(5)
O(13)	1939(16)	2367(13)	6396(8)	32(4)
O(14)	-1488(17)	730(15)	6253(9)	37(5)
O(15)	545(15)	-134(13)	6396(8)	30(4)
O(16)	2361(16)	-1511(14)	6450(9)	35(5)
O(17)	2895(17)	-268(15)	7106(9)	39(5)
O(18)	5054(18)	-266(15)	7173(9)	42(5)
O(19)	4428(16)	1612(14)	7420(9)	35(5)
O(20)	4268(17)	3433(15)	7776(9)	39(5)
O(21)	2142(16)	3583(14)	7725(9)	33(5)
O(22)	900(17)	5426(14)	7575(9)	36(5)
O(23)	-372(16)	4481(14)	7136(9)	36(5)
O(24)	-2193(18)	4061(16)	6786(10)	44(5)
O(25)	-1081(16)	2134(13)	6825(8)	32(4)

O(26)	963(16)	997(14)	7029(9)	35(5)
O(27)	2390(16)	1670(14)	7392(9)	35(5)
O(28)	572(16)	2758(14)	7298(8)	31(4)
O(29)	-963(16)	265(14)	7314(9)	34(5)
O(30)	1079(17)	-997(15)	7458(9)	40(5)
O(31)	3441(18)	95(15)	8072(9)	42(5)
O(32)	3028(16)	2093(14)	8385(9)	34(5)
O(33)	151(17)	3829(14)	8190(9)	37(5)
O(34)	-1570(18)	3060(16)	7757(10)	44(5)
O(35)	-2785(18)	-407(15)	7934(9)	42(5)
O(36)	-716(15)	-1348(13)	8104(8)	31(4)
O(37)	1038(16)	-2733(14)	8257(9)	36(5)
O(38)	1939(15)	-1120(13)	8380(8)	30(4)
O(39)	3687(19)	-1449(16)	8935(10)	47(5)
O(40)	3067(16)	451(13)	9166(8)	32(4)
O(41)	2944(17)	2271(15)	9540(9)	38(5)
O(42)	1157(15)	2758(13)	8964(8)	29(4)
O(43)	-462(17)	4273(15)	9315(9)	38(5)
O(44)	-1732(17)	3351(14)	8844(9)	37(5)
O(45)	-3546(17)	2945(15)	8444(9)	41(5)
O(46)	-2074(16)	1283(14)	8157(8)	32(4)
O(47)	-109(14)	120(12)	8394(8)	23(4)
O(48)	1347(13)	813(12)	8699(7)	19(4)
O(49)	-493(17)	1857(15)	8652(9)	37(5)
O(50)	-2147(19)	-418(16)	8946(10)	48(6)
O(51)	187(17)	-1615(15)	9113(9)	38(5)
O(52)	1726(17)	-878(14)	9493(9)	36(5)
O(53)	1278(16)	1224(14)	9830(9)	34(5)
O(54)	-672(16)	2414(13)	9723(8)	32(4)
O(55)	-2569(18)	1631(16)	9282(10)	45(5)
O(56)	-256(16)	351(13)	9459(8)	31(4)
O(57)	4301(44)	-579(37)	10355(24)	148(17)
Na(2)	8944(12)	-2482(9)	6454(6)	53(3)
Na(3)	-9640(11)	5702(8)	8648(5)	41(3)
Na(4)	6215(11)	-1479(10)	6581(6)	51(3)
Na(5)	-6184(12)	4893(11)	8325(6)	58(4)
Na(6)	-6243(13)	3289(11)	10030(6)	59(4)
Na(7)	-3840(12)	3695(10)	7450(5)	52(3)
Na(8)	-2673(11)	989(10)	5506(6)	51(3)
O(1S)	7051(30)	-4295(25)	16073(16)	95(10)
O(2S)	-10192(20)	6349(17)	9535(11)	53(6)
O(3S)	-1615(20)	-202(17)	5004(11)	54(6)
O(4S)	-6065(20)	6242(18)	8788(11)	55(6)
O(5S)	-3661(22)	1675(19)	4714(11)	61(7)
O(6S)	-6357(21)	7649(18)	7764(11)	57(6)
O(7S)	-11339(23)	6369(20)	8386(12)	65(7)
O(8S)	10006(24)	-3997(20)	6104(13)	71(8)
O(9S)	9835(19)	-1288(16)	5707(10)	47(6)
O(10S)	-4630(24)	4286(21)	6590(13)	72(8)
O(11S)	-1476(21)	2183(19)	5079(11)	60(7)
O(12S)	6262(21)	-6165(18)	15402(11)	60(7)
O(13S)	7063(22)	-4836(19)	8637(12)	63(7)
O(14S)	5797(22)	-1824(19)	8285(12)	64(7)
O(15S)	7748(19)	-1084(17)	6823(10)	50(6)
O(16S)	-3885(23)	2020(20)	6125(12)	66(7)

O(17S)	4607(21)	-2053(18)	6557(11)	60(7)
O(18S)	-3526(17)	2048(14)	7271(9)	38(5)
O(19S)	-8013(21)	4624(18)	8795(11)	56(6)
O(20S)	7541(19)	-2382(16)	5935(10)	48(6)
O(21S)	6349(16)	-6522(14)	14319(9)	35(5)
O(22S)	-4003(21)	-170(18)	5806(11)	57(6)
O(23S)	4891(37)	-4829(28)	15006(21)	76(9)
O(24S)	7362(26)	3456(22)	10150(14)	82(9)
O(25S)	-7044(26)	5955(22)	7605(14)	80(9)
O(26S)	8320(26)	-3660(22)	7270(14)	80(8)
O(27S)	-5495(26)	4360(22)	10482(14)	81(9)
O(28S)	-7764(21)	4507(18)	9956(11)	58(6)
O(29S)	10354(23)	-2588(20)	6987(12)	67(7)
O(30S)	6181(24)	-2911(21)	7375(13)	73(8)
O(31S)	-5509(27)	3670(23)	9001(15)	86(9)
O(32S)	-7155(22)	2390(19)	10866(12)	61(7)
O(33S)	8216(25)	-5449(22)	15251(14)	76(8)
O(34S)	8069(20)	-6741(17)	14003(11)	52(6)
O(35S)	-4327(21)	5149(18)	7843(11)	56(6)
O(36S)	4638(27)	-780(24)	11429(15)	85(9)
O(37S)	5513(23)	-3710(20)	15349(12)	67(7)
O(38S)	-5680(33)	6107(28)	6560(17)	106(11)
O(39S)	-4530(33)	2327(28)	10052(18)	107(12)

S3. Bond lengths [Å] and angles [°] for 1.

W(1)-O(1)	1.76(2)	W(1)-O(7)	1.85(2)
W(1)-O(12)	1.85(2)	W(1)-O(2)	1.92(2)
W(1)-O(6)	1.94(2)	W(1)-O(13)	2.33(2)
W(2)-O(3)	1.73(2)	W(2)-O(8)	1.85(2)
W(2)-O(9)	1.88(2)	W(2)-O(2)	1.94(2)
W(2)-O(4)	1.98(2)	W(2)-O(13)	2.34(2)
W(3)-O(5)	1.69(2)	W(3)-O(10)	1.86(2)
W(3)-O(11)	1.90(2)	W(3)-O(4)	1.90(2)
W(3)-O(6)	1.92(2)	W(3)-O(13)	2.35(2)
W(4)-O(14)	1.68(2)	W(4)-O(29)	1.76(2)
W(4)-O(25)	1.84(2)	W(4)-O(15)	1.92(2)
W(4)-O(7)	2.02(2)	W(4)-O(26)	2.36(2)
W(5)-O(16)	1.72(2)	W(5)-O(30)	1.82(2)
W(5)-O(17)	1.85(2)	W(5)-O(15)	1.91(2)
W(5)-O(8)	1.99(2)	W(5)-O(26)	2.29(2)
W(6)-O(18)	1.67(2)	W(6)-O(31)	1.83(2)
W(6)-O(17)	1.92(2)	W(6)-O(19)	1.94(2)
W(6)-O(9)	1.99(2)	W(6)-O(27)	2.33(2)
W(7)-O(20)	1.71(2)	W(7)-O(32)	1.80(2)
W(7)-O(21)	1.85(2)	W(7)-O(19)	1.94(2)
W(7)-O(10)	2.01(2)	W(7)-O(27)	2.34(2)
W(8)-O(22)	1.70(2)	W(8)-O(33)	1.75(2)
W(8)-O(23)	1.84(2)	W(8)-O(21)	1.92(2)
W(8)-O(11)	1.93(2)	W(8)-O(28)	2.31(2)
W(9)-O(24)	1.70(2)	W(9)-O(34)	1.76(2)
W(9)-O(25)	1.91(2)	W(9)-O(23)	1.96(2)
W(9)-O(12)	2.00(2)	W(9)-O(28)	2.31(2)
W(10)-O(35)	1.70(2)	W(10)-O(50)	1.73(2)
W(10)-O(46)	1.93(2)	W(10)-O(36)	1.99(2)
W(10)-O(29)	2.13(2)	W(10)-O(47)	2.33(2)
W(11)-O(37)	1.73(2)	W(11)-O(51)	1.80(2)
W(11)-O(36)	1.85(2)	W(11)-O(38)	1.90(2)
W(11)-O(30)	2.05(2)	W(11)-O(47)	2.33(2)
W(12)-O(39)	1.68(2)	W(12)-O(52)	1.79(2)
W(12)-O(38)	1.90(2)	W(12)-O(40)	1.90(2)
W(12)-O(31)	2.00(2)	W(12)-O(48)	2.34(2)
W(13)-O(41)	1.72(2)	W(13)-O(53)	1.80(2)
W(13)-O(42)	1.87(2)	W(13)-O(40)	1.94(2)
W(13)-O(32)	2.02(2)	W(13)-O(48)	2.38(2)
W(14)-O(43)	1.70(2)	W(14)-O(54)	1.78(2)
W(14)-O(44)	1.87(2)	W(14)-O(42)	1.93(2)
W(14)-O(33)	2.05(2)	W(14)-O(49)	2.29(2)
W(15)-O(55)	1.77(2)	W(15)-O(45)	1.78(2)
W(15)-O(46)	1.86(2)	W(15)-O(44)	1.94(2)
W(15)-O(34)	2.11(2)	W(15)-O(49)	2.29(2)
Fe(1)-O(53)#2	1.96(2)	Fe(1)-O(51)	1.97(2)
Fe(1)-O(52)	1.97(2)	Fe(1)-O(54)#2	2.00(2)
Fe(1)-O(56)	2.09(2)	Fe(1)-O(56)#2	2.14(2)
Na(1)-O(55)#2	2.17(3)	Na(1)-O(50)#2	2.23(3)
Na(1)-O(53)	2.40(2)	Na(1)-O(57)	2.41(6)
Na(1)-O(40)	2.45(2)	Na(1)-O(52)	2.49(2)

Na(1)-O(56)#2	2.81(3)	P(1)-O(27)	1.54(2)
P(1)-O(26)	1.54(2)	P(1)-O(28)	1.56(2)
P(1)-O(13)	1.62(2)	P(2)-O(48)	1.52(2)
P(2)-O(47)	1.54(2)	P(2)-O(49)	1.58(2)
P(2)-O(56)	1.60(2)	O(14)-Na(8)	2.48(2)
O(18)-Na(4)	2.50(3)	O(20)-Na(7)#1	2.46(3)
O(20)-Na(5)#1	2.54(2)	O(22)-Na(3)#1	2.56(2)
O(24)-Na(7)	2.43(3)	O(37)-Na(3)#3	2.44(2)
O(41)-Na(6)#1	2.45(2)	O(43)-Na(3)#1	2.54(2)
O(45)-Na(7)	2.45(2)	O(50)-Na(1)#2	2.23(3)
O(53)-Fe(1)#2	1.96(2)	O(54)-Fe(1)#2	2.00(2)
O(55)-Na(1)#2	2.17(3)	O(56)-Fe(1)#2	2.14(2)
O(56)-Na(1)#2	2.81(3)	Na(2)-O(20S)	2.34(3)
Na(2)-O(29S)	2.36(3)	Na(2)-O(26S)	2.38(3)
Na(2)-O(9S)	2.43(3)	Na(2)-O(15S)	2.45(3)
Na(2)-O(8S)	2.50(3)	Na(3)-O(2S)	2.36(3)
Na(3)-O(7S)	2.37(3)	Na(3)-O(19S)	2.40(3)
Na(3)-O(37)#4	2.44(2)	Na(3)-O(43)#5	2.54(2)
Na(3)-O(22)#5	2.56(2)	Na(4)-O(15S)	2.33(3)
Na(4)-O(17S)	2.34(3)	Na(4)-O(22S)#1	2.35(3)
Na(4)-O(20S)	2.40(3)	Na(4)-O(30S)	2.47(3)
Na(5)-O(31S)	2.29(4)	Na(5)-O(25S)	2.35(3)
Na(5)-O(4S)	2.38(3)	Na(5)-O(19S)	2.44(3)
Na(5)-O(35S)	2.47(3)	Na(5)-O(20)#5	2.54(2)
Na(6)-O(32S)	2.34(3)	Na(6)-O(28S)	2.37(3)
Na(6)-O(39S)	2.38(4)	Na(6)-O(27S)	2.40(3)
Na(6)-O(31S)	2.41(4)	Na(6)-O(41)#5	2.45(2)
Na(7)-O(35S)	2.33(3)	Na(7)-O(18S)	2.37(2)
Na(7)-O(10S)	2.39(3)	Na(7)-O(20)#5	2.46(3)
Na(8)-O(3S)	2.31(3)	Na(8)-O(16S)	2.39(3)
Na(8)-O(11S)	2.40(3)	Na(8)-O(5S)	2.42(3)
Na(8)-O(22S)	2.46(3)	O(22S)-Na(4)#5	2.35(3)
O(23S)-O(23S)#6	0.51(7)		

O(1)-W(1)-O(7)	103.0(9)	O(1)-W(1)-O(12)	100.6(9)
O(7)-W(1)-O(12)	90.1(9)	O(1)-W(1)-O(2)	100.3(9)
O(7)-W(1)-O(2)	88.1(9)	O(12)-W(1)-O(2)	158.9(8)
O(1)-W(1)-O(6)	97.8(9)	O(7)-W(1)-O(6)	159.1(9)
O(12)-W(1)-O(6)	88.4(9)	O(2)-W(1)-O(6)	85.8(9)
O(1)-W(1)-O(13)	167.0(9)	O(7)-W(1)-O(13)	87.6(8)
O(12)-W(1)-O(13)	86.8(8)	O(2)-W(1)-O(13)	72.2(7)
O(6)-W(1)-O(13)	71.5(8)	O(3)-W(2)-O(8)	103.2(9)
O(3)-W(2)-O(9)	101.5(9)	O(8)-W(2)-O(9)	87.8(9)
O(3)-W(2)-O(2)	101.7(9)	O(8)-W(2)-O(2)	89.1(8)
O(9)-W(2)-O(2)	156.7(9)	O(3)-W(2)-O(4)	100.8(9)
O(8)-W(2)-O(4)	156.0(8)	O(9)-W(2)-O(4)	86.7(8)
O(2)-W(2)-O(4)	86.8(8)	O(3)-W(2)-O(13)	169.7(8)
O(8)-W(2)-O(13)	84.7(8)	O(9)-W(2)-O(13)	85.1(8)
O(2)-W(2)-O(13)	71.6(7)	O(4)-W(2)-O(13)	71.6(7)
O(5)-W(3)-O(10)	103.3(9)	O(5)-W(3)-O(11)	104.3(9)
O(10)-W(3)-O(11)	88.3(9)	O(5)-W(3)-O(4)	97.6(9)
O(10)-W(3)-O(4)	88.0(8)	O(11)-W(3)-O(4)	158.1(9)
O(5)-W(3)-O(6)	98.7(9)	O(10)-W(3)-O(6)	157.8(9)
O(11)-W(3)-O(6)	88.9(9)	O(4)-W(3)-O(6)	86.4(9)
O(5)-W(3)-O(13)	166.3(8)	O(10)-W(3)-O(13)	86.4(8)

O(11)-W(3)-O(13)	85.5(8)	O(4)-W(3)-O(13)	72.7(7)
O(6)-W(3)-O(13)	71.5(8)	O(14)-W(4)-O(29)	100.6(10)
O(14)-W(4)-O(25)	102.1(9)	O(29)-W(4)-O(25)	94.3(9)
O(14)-W(4)-O(15)	98.8(9)	O(29)-W(4)-O(15)	93.1(8)
O(25)-W(4)-O(15)	156.1(8)	O(14)-W(4)-O(7)	96.0(9)
O(29)-W(4)-O(7)	163.3(8)	O(25)-W(4)-O(7)	80.6(8)
O(15)-W(4)-O(7)	85.9(8)	O(14)-W(4)-O(26)	170.8(8)
O(29)-W(4)-O(26)	82.0(8)	O(25)-W(4)-O(26)	86.4(8)
O(15)-W(4)-O(26)	72.2(7)	O(7)-W(4)-O(26)	81.8(8)
O(16)-W(5)-O(30)	101.5(9)	O(16)-W(5)-O(17)	101.8(9)
O(30)-W(5)-O(17)	90.9(9)	O(16)-W(5)-O(15)	99.2(8)
O(30)-W(5)-O(15)	94.1(9)	O(17)-W(5)-O(15)	157.0(8)
O(16)-W(5)-O(8)	94.7(9)	O(30)-W(5)-O(8)	163.6(8)
O(17)-W(5)-O(8)	83.4(9)	O(15)-W(5)-O(8)	85.7(8)
O(16)-W(5)-O(26)	171.6(8)	O(30)-W(5)-O(26)	83.8(8)
O(17)-W(5)-O(26)	84.4(8)	O(15)-W(5)-O(26)	73.8(7)
O(8)-W(5)-O(26)	80.4(7)	O(18)-W(6)-O(31)	100.9(10)
O(18)-W(6)-O(17)	102.6(9)	O(31)-W(6)-O(17)	90.3(9)
O(18)-W(6)-O(19)	98.9(9)	O(31)-W(6)-O(19)	91.8(9)
O(17)-W(6)-O(19)	157.6(8)	O(18)-W(6)-O(9)	95.9(9)
O(31)-W(6)-O(9)	163.1(9)	O(17)-W(6)-O(9)	84.0(9)
O(19)-W(6)-O(9)	87.5(8)	O(18)-W(6)-O(27)	172.6(9)
O(31)-W(6)-O(27)	82.9(8)	O(17)-W(6)-O(27)	83.5(8)
O(19)-W(6)-O(27)	74.6(8)	O(9)-W(6)-O(27)	80.6(8)
O(20)-W(7)-O(32)	99.4(9)	O(20)-W(7)-O(21)	99.8(9)
O(32)-W(7)-O(21)	90.9(9)	O(20)-W(7)-O(19)	99.4(9)
O(32)-W(7)-O(19)	93.0(9)	O(21)-W(7)-O(19)	159.6(8)
O(20)-W(7)-O(10)	95.4(9)	O(32)-W(7)-O(10)	165.1(8)
O(21)-W(7)-O(10)	85.3(8)	O(19)-W(7)-O(10)	85.9(8)
O(20)-W(7)-O(27)	173.1(8)	O(32)-W(7)-O(27)	84.5(8)
O(21)-W(7)-O(27)	85.8(8)	O(19)-W(7)-O(27)	74.6(8)
O(10)-W(7)-O(27)	80.9(7)	O(22)-W(8)-O(33)	99.7(9)
O(22)-W(8)-O(23)	100.1(9)	O(33)-W(8)-O(23)	95.2(9)
O(22)-W(8)-O(21)	100.9(9)	O(33)-W(8)-O(21)	88.2(9)
O(23)-W(8)-O(21)	157.9(8)	O(22)-W(8)-O(11)	96.7(9)
O(33)-W(8)-O(11)	162.8(9)	O(23)-W(8)-O(11)	87.0(9)
O(21)-W(8)-O(11)	83.6(9)	O(22)-W(8)-O(28)	173.0(8)
O(33)-W(8)-O(28)	82.6(8)	O(23)-W(8)-O(28)	73.1(8)
O(21)-W(8)-O(28)	85.7(7)	O(11)-W(8)-O(28)	81.8(8)
O(24)-W(9)-O(34)	99.5(10)	O(24)-W(9)-O(25)	102.6(9)
O(34)-W(9)-O(25)	93.2(9)	O(24)-W(9)-O(23)	99.6(9)
O(34)-W(9)-O(23)	94.4(9)	O(25)-W(9)-O(23)	154.9(8)
O(24)-W(9)-O(12)	97.4(9)	O(34)-W(9)-O(12)	163.1(9)
O(25)-W(9)-O(12)	81.4(8)	O(23)-W(9)-O(12)	84.4(8)
O(24)-W(9)-O(28)	170.6(9)	O(34)-W(9)-O(28)	83.1(9)
O(25)-W(9)-O(28)	86.1(7)	O(23)-W(9)-O(28)	71.1(7)
O(12)-W(9)-O(28)	80.5(7)	O(35)-W(10)-O(50)	101.7(11)
O(35)-W(10)-O(46)	102.3(9)	O(50)-W(10)-O(46)	96.2(9)
O(35)-W(10)-O(36)	99.5(9)	O(50)-W(10)-O(36)	96.1(9)
O(46)-W(10)-O(36)	152.1(8)	O(35)-W(10)-O(29)	89.1(9)
O(50)-W(10)-O(29)	169.1(10)	O(46)-W(10)-O(29)	82.7(8)
O(36)-W(10)-O(29)	80.5(7)	O(35)-W(10)-O(47)	168.6(8)
O(50)-W(10)-O(47)	87.1(9)	O(46)-W(10)-O(47)	83.5(7)
O(36)-W(10)-O(47)	72.2(7)	O(29)-W(10)-O(47)	81.9(7)
O(37)-W(11)-O(51)	100.9(9)	O(37)-W(11)-O(36)	100.1(9)

O(51)-W(11)-O(36)	99.4(9)	O(37)-W(11)-O(38)	99.8(9)
O(51)-W(11)-O(38)	91.4(9)	O(36)-W(11)-O(38)	155.1(8)
O(37)-W(11)-O(30)	94.3(9)	O(51)-W(11)-O(30)	164.2(8)
O(36)-W(11)-O(30)	82.0(8)	O(38)-W(11)-O(30)	81.8(8)
O(37)-W(11)-O(47)	174.6(8)	O(51)-W(11)-O(47)	80.6(8)
O(36)-W(11)-O(47)	74.4(7)	O(38)-W(11)-O(47)	85.4(7)
O(30)-W(11)-O(47)	84.7(7)	O(39)-W(12)-O(52)	99.8(10)
O(39)-W(12)-O(38)	99.9(9)	O(52)-W(12)-O(38)	92.0(9)
O(39)-W(12)-O(40)	100.4(9)	O(52)-W(12)-O(40)	91.3(8)
O(38)-W(12)-O(40)	158.5(8)	O(39)-W(12)-O(31)	93.6(10)
O(52)-W(12)-O(31)	166.5(9)	O(38)-W(12)-O(31)	86.8(8)
O(40)-W(12)-O(31)	85.1(8)	O(39)-W(12)-O(48)	174.3(9)
O(52)-W(12)-O(48)	82.9(7)	O(38)-W(12)-O(48)	84.9(7)
O(40)-W(12)-O(48)	74.4(7)	O(31)-W(12)-O(48)	83.6(7)
O(41)-W(13)-O(53)	99.7(9)	O(41)-W(13)-O(42)	102.8(9)
O(53)-W(13)-O(42)	93.5(8)	O(41)-W(13)-O(40)	100.2(9)
O(53)-W(13)-O(40)	92.0(8)	O(42)-W(13)-O(40)	155.1(8)
O(41)-W(13)-O(32)	94.3(9)	O(53)-W(13)-O(32)	166.0(8)
O(42)-W(13)-O(32)	84.5(8)	O(40)-W(13)-O(32)	84.3(8)
O(41)-W(13)-O(48)	172.7(8)	O(53)-W(13)-O(48)	83.2(7)
O(42)-W(13)-O(48)	83.6(7)	O(40)-W(13)-O(48)	72.9(7)
O(32)-W(13)-O(48)	82.8(7)	O(43)-W(14)-O(54)	98.2(9)
O(43)-W(14)-O(44)	100.0(9)	O(54)-W(14)-O(44)	95.8(9)
O(43)-W(14)-O(42)	101.7(9)	O(54)-W(14)-O(42)	93.1(8)
O(44)-W(14)-O(42)	155.1(8)	O(43)-W(14)-O(33)	94.0(9)
O(54)-W(14)-O(33)	166.8(8)	O(44)-W(14)-O(33)	87.0(9)
O(42)-W(14)-O(33)	79.4(8)	O(43)-W(14)-O(49)	171.6(9)
O(54)-W(14)-O(49)	83.0(8)	O(44)-W(14)-O(49)	71.6(8)
O(42)-W(14)-O(49)	86.6(7)	O(33)-W(14)-O(49)	85.6(7)
O(55)-W(15)-O(45)	102.9(10)	O(55)-W(15)-O(46)	96.6(9)
O(45)-W(15)-O(46)	102.2(9)	O(55)-W(15)-O(44)	95.1(9)
O(45)-W(15)-O(44)	99.9(9)	O(46)-W(15)-O(44)	151.9(9)
O(55)-W(15)-O(34)	168.1(10)	O(45)-W(15)-O(34)	88.8(9)
O(46)-W(15)-O(34)	82.6(8)	O(44)-W(15)-O(34)	80.7(8)
O(55)-W(15)-O(49)	86.7(9)	O(45)-W(15)-O(49)	167.2(9)
O(46)-W(15)-O(49)	84.8(8)	O(44)-W(15)-O(49)	70.5(8)
O(34)-W(15)-O(49)	81.3(8)	O(53)#2-Fe(1)-O(51)	94.2(8)
O(53)#2-Fe(1)-O(52)	176.4(8)	O(51)-Fe(1)-O(52)	87.9(9)
O(53)#2-Fe(1)-O(54)#2	89.4(8)	O(51)-Fe(1)-O(54)#2	94.2(8)
O(52)-Fe(1)-O(54)#2	93.3(8)	O(53)#2-Fe(1)-O(56)	89.0(8)
O(51)-Fe(1)-O(56)	92.9(8)	O(52)-Fe(1)-O(56)	88.1(8)
O(54)#2-Fe(1)-O(56)	172.9(8)	O(53)#2-Fe(1)-O(56)#2	87.1(8)
O(51)-Fe(1)-O(56)#2	172.8(8)	O(52)-Fe(1)-O(56)#2	90.5(8)
O(54)#2-Fe(1)-O(56)#2	92.9(7)	O(56)-Fe(1)-O(56)#2	80.1(8)
O(55)#2-Na(1)-O(50)#2	87.4(9)	O(55)#2-Na(1)-O(53)	145.9(11)
O(50)#2-Na(1)-O(53)	88.3(9)	O(55)#2-Na(1)-O(57)	74(2)
O(50)#2-Na(1)-O(57)	85.6(14)	O(53)-Na(1)-O(57)	139(2)
O(55)#2-Na(1)-O(40)	132.9(9)	O(50)#2-Na(1)-O(40)	136.4(10)
O(53)-Na(1)-O(40)	67.3(7)	O(57)-Na(1)-O(40)	90(2)
O(55)#2-Na(1)-O(52)	86.8(9)	O(50)#2-Na(1)-O(52)	147.6(11)
O(53)-Na(1)-O(52)	79.0(8)	O(57)-Na(1)-O(52)	123.1(14)
O(40)-Na(1)-O(52)	64.7(7)	O(55)#2-Na(1)-O(56)#2	80.5(9)
O(50)#2-Na(1)-O(56)#2	81.2(8)	O(53)-Na(1)-O(56)#2	65.5(7)
O(57)-Na(1)-O(56)#2	152(2)	O(40)-Na(1)-O(56)#2	116.2(8)
O(52)-Na(1)-O(56)#2	66.4(7)	O(27)-P(1)-O(26)	111.1(11)

O(27)-P(1)-O(28)	113.4(11)	O(26)-P(1)-O(28)	113.7(11)
O(27)-P(1)-O(13)	104.9(11)	O(26)-P(1)-O(13)	106.4(10)
O(28)-P(1)-O(13)	106.5(10)	O(48)-P(2)-O(47)	110.2(10)
O(48)-P(2)-O(49)	111.6(11)	O(47)-P(2)-O(49)	109.9(10)
O(48)-P(2)-O(56)	108.0(10)	O(47)-P(2)-O(56)	108.5(10)
O(49)-P(2)-O(56)	108.5(11)	W(1)-O(2)-W(2)	123.1(10)
W(3)-O(4)-W(2)	122.5(10)	W(3)-O(6)-W(1)	123.7(11)
W(1)-O(7)-W(4)	147.1(11)	W(2)-O(8)-W(5)	151.2(11)
W(2)-O(9)-W(6)	148.4(12)	W(3)-O(10)-W(7)	146.8(11)
W(3)-O(11)-W(8)	150.3(12)	W(1)-O(12)-W(9)	147.4(11)
P(1)-O(13)-W(1)	122.0(11)	P(1)-O(13)-W(2)	123.9(10)
W(1)-O(13)-W(2)	93.1(7)	P(1)-O(13)-W(3)	122.9(10)
W(1)-O(13)-W(3)	93.3(7)	W(2)-O(13)-W(3)	93.3(7)
W(4)-O(14)-Na(8)	159.7(12)	W(5)-O(15)-W(4)	121.2(9)
W(5)-O(17)-W(6)	156.0(12)	W(6)-O(18)-Na(4)	147.2(12)
W(6)-O(19)-W(7)	118.7(10)	W(7)-O(20)-Na(7)#1	138.5(11)
W(7)-O(20)-Na(5)#1	127.8(11)	Na(7)#1-O(20)-Na(5)#1	93.2(8)
W(7)-O(21)-W(8)	154.3(11)	W(8)-O(22)-Na(3)#1	112.8(10)
W(8)-O(23)-W(9)	122.3(10)	W(9)-O(24)-Na(7)	113.6(11)
W(4)-O(25)-W(9)	158.0(12)	P(1)-O(26)-W(5)	130.6(12)
P(1)-O(26)-W(4)	127.3(11)	W(5)-O(26)-W(4)	91.4(7)
P(1)-O(27)-W(6)	130.2(11)	P(1)-O(27)-W(7)	129.1(11)
W(6)-O(27)-W(7)	91.1(7)	P(1)-O(28)-W(9)	129.0(10)
P(1)-O(28)-W(8)	128.5(11)	W(9)-O(28)-W(8)	92.1(7)
W(4)-O(29)-W(10)	163.5(11)	W(5)-O(30)-W(11)	164.8(12)
W(6)-O(31)-W(12)	161.8(12)	W(7)-O(32)-W(13)	161.6(11)
W(8)-O(33)-W(14)	169.6(12)	W(9)-O(34)-W(15)	164.9(12)
W(11)-O(36)-W(10)	120.9(9)	W(11)-O(37)-Na(3)#3	136.3(11)
W(12)-O(38)-W(11)	145.0(11)	W(12)-O(40)-W(13)	121.7(10)
W(12)-O(40)-Na(1)	98.2(9)	W(13)-O(40)-Na(1)	93.7(8)
W(13)-O(41)-Na(6)#1	170.1(12)	W(13)-O(42)-W(14)	144.0(11)
W(14)-O(43)-Na(3)#1	118.1(10)	W(14)-O(44)-W(15)	123.3(10)
W(15)-O(45)-Na(7)	121.1(11)	W(15)-O(46)-W(10)	145.3(11)
P(2)-O(47)-W(10)	130.5(10)	P(2)-O(47)-W(11)	128.2(10)
W(10)-O(47)-W(11)	91.5(6)	P(2)-O(48)-W(12)	126.1(9)
P(2)-O(48)-W(13)	124.8(9)	W(12)-O(48)-W(13)	90.8(6)
P(2)-O(49)-W(15)	129.5(12)	P(2)-O(49)-W(14)	126.6(11)
W(15)-O(49)-W(14)	94.1(7)	W(10)-O(50)-Na(1)#2	143.9(13)
W(11)-O(51)-Fe(1)	146.1(12)	W(12)-O(52)-Fe(1)	145.8(12)
W(12)-O(52)-Na(1)	100.0(9)	Fe(1)-O(52)-Na(1)	108.7(9)
W(13)-O(53)-Fe(1)#2	145.6(11)	W(13)-O(53)-Na(1)	99.2(9)
Fe(1)#2-O(53)-Na(1)	111.1(10)	W(14)-O(54)-Fe(1)#2	143.4(11)
W(15)-O(55)-Na(1)#2	145.2(12)	P(2)-O(56)-Fe(1)	123.2(11)
P(2)-O(56)-Fe(1)#2	122.8(11)	Fe(1)-O(56)-Fe(1)#2	99.9(8)
P(2)-O(56)-Na(1)#2	116.5(10)	Fe(1)-O(56)-Na(1)#2	93.6(8)
Fe(1)#2-O(56)-Na(1)#2	93.7(7)	O(20S)-Na(2)-O(29S)	179.5(11)
O(20S)-Na(2)-O(26S)	97.5(11)	O(29S)-Na(2)-O(26S)	82.0(11)
O(20S)-Na(2)-O(9S)	92.2(9)	O(29S)-Na(2)-O(9S)	88.3(10)
O(26S)-Na(2)-O(9S)	170.3(11)	O(20S)-Na(2)-O(15S)	80.1(9)
O(29S)-Na(2)-O(15S)	99.8(10)	O(26S)-Na(2)-O(15S)	94.5(10)
O(9S)-Na(2)-O(15S)	87.2(9)	O(20S)-Na(2)-O(8S)	96.3(10)
O(29S)-Na(2)-O(8S)	83.8(10)	O(26S)-Na(2)-O(8S)	81.5(11)
O(9S)-Na(2)-O(8S)	97.4(10)	O(15S)-Na(2)-O(8S)	174.3(11)
O(2S)-Na(3)-O(7S)	89.0(10)	O(2S)-Na(3)-O(19S)	103.5(9)
O(7S)-Na(3)-O(19S)	163.1(10)	O(2S)-Na(3)-O(37)#4	85.0(8)

O(7S)-Na(3)-O(37)#4	90.6(9)	O(19S)-Na(3)-O(37)#4	101.6(9)
O(2S)-Na(3)-O(43)#5	79.2(8)	O(7S)-Na(3)-O(43)#5	90.2(9)
O(19S)-Na(3)-O(43)#5	81.1(9)	O(37)#4-Na(3)-O(43)#5	164.2(8)
O(2S)-Na(3)-O(22)#5	166.5(9)	O(7S)-Na(3)-O(22)#5	84.8(9)
O(19S)-Na(3)-O(22)#5	85.2(8)	O(37)#4-Na(3)-O(22)#5	83.1(7)
O(43)#5-Na(3)-O(22)#5	112.7(8)	O(15S)-Na(4)-O(17S)	167.1(11)
O(15S)-Na(4)-O(22S)#1	97.8(10)	O(17S)-Na(4)-O(22S)#1	93.9(10)
O(15S)-Na(4)-O(20S)	81.5(9)	O(17S)-Na(4)-O(20S)	103.9(10)
O(22S)#1-Na(4)-O(20S)	90.6(9)	O(15S)-Na(4)-O(30S)	90.8(10)
O(17S)-Na(4)-O(30S)	77.5(10)	O(22S)#1-Na(4)-O(30S)	171.4(11)
O(20S)-Na(4)-O(30S)	91.7(10)	O(15S)-Na(4)-O(18)	90.7(9)
O(17S)-Na(4)-O(18)	85.5(9)	O(22S)#1-Na(4)-O(18)	82.1(9)
O(20S)-Na(4)-O(18)	168.5(10)	O(30S)-Na(4)-O(18)	96.8(10)
O(31S)-Na(5)-O(25S)	170.5(13)	O(31S)-Na(5)-O(4S)	97.2(11)
O(25S)-Na(5)-O(4S)	91.1(11)	O(31S)-Na(5)-O(19S)	90.2(12)
O(25S)-Na(5)-O(19S)	83.9(11)	O(4S)-Na(5)-O(19S)	97.6(10)
O(31S)-Na(5)-O(35S)	89.6(12)	O(25S)-Na(5)-O(35S)	96.1(11)
O(4S)-Na(5)-O(35S)	83.0(10)	O(19S)-Na(5)-O(35S)	179.4(10)
O(31S)-Na(5)-O(20)#5	77.7(10)	O(25S)-Na(5)-O(20)#5	95.6(10)
O(4S)-Na(5)-O(20)#5	163.6(10)	O(19S)-Na(5)-O(20)#5	97.9(9)
O(35S)-Na(5)-O(20)#5	81.5(8)	O(32S)-Na(6)-O(28S)	91.9(11)
O(32S)-Na(6)-O(39S)	96.5(13)	O(28S)-Na(6)-O(39S)	169.1(14)
O(32S)-Na(6)-O(27S)	100.0(11)	O(28S)-Na(6)-O(27S)	88.8(10)
O(39S)-Na(6)-O(27S)	82.9(13)	O(32S)-Na(6)-O(31S)	155.8(12)
O(28S)-Na(6)-O(31S)	92.8(11)	O(39S)-Na(6)-O(31S)	82.3(13)
O(27S)-Na(6)-O(31S)	103.8(12)	O(32S)-Na(6)-O(41)#5	81.5(9)
O(28S)-Na(6)-O(41)#5	88.6(9)	O(39S)-Na(6)-O(41)#5	99.5(12)
O(27S)-Na(6)-O(41)#5	177.0(11)	O(31S)-Na(6)-O(41)#5	74.9(10)
O(35S)-Na(7)-O(18S)	166.7(10)	O(35S)-Na(7)-O(10S)	95.6(10)
O(18S)-Na(7)-O(10S)	92.9(9)	O(35S)-Na(7)-O(24)	99.9(10)
O(18S)-Na(7)-O(24)	91.2(9)	O(10S)-Na(7)-O(24)	83.2(10)
O(35S)-Na(7)-O(45)	84.8(9)	O(18S)-Na(7)-O(45)	84.1(8)
O(10S)-Na(7)-O(45)	163.4(11)	O(24)-Na(7)-O(45)	113.1(9)
O(35S)-Na(7)-O(20)#5	86.3(9)	O(18S)-Na(7)-O(20)#5	85.9(8)
O(10S)-Na(7)-O(20)#5	76.2(10)	O(24)-Na(7)-O(20)#5	159.0(9)
O(45)-Na(7)-O(20)#5	87.3(8)	O(3S)-Na(8)-O(16S)	171.3(12)
O(3S)-Na(8)-O(11S)	92.6(10)	O(16S)-Na(8)-O(11S)	95.6(10)
O(3S)-Na(8)-O(5S)	93.9(10)	O(16S)-Na(8)-O(5S)	89.5(10)
O(11S)-Na(8)-O(5S)	86.5(10)	O(3S)-Na(8)-O(22S)	86.0(9)
O(16S)-Na(8)-O(22S)	86.3(10)	O(11S)-Na(8)-O(22S)	171.4(10)
O(5S)-Na(8)-O(22S)	85.1(10)	O(3S)-Na(8)-O(14)	92.7(9)
O(16S)-Na(8)-O(14)	86.1(9)	O(11S)-Na(8)-O(14)	79.1(9)
O(5S)-Na(8)-O(14)	164.4(10)	O(22S)-Na(8)-O(14)	109.4(9)
Na(4)-O(15S)-Na(2)	94.8(9)	Na(3)-O(19S)-Na(5)	126.7(12)
Na(2)-O(20S)-Na(4)	95.9(9)	Na(4)#5-O(22S)-Na(8)	119.5(11)
Na(5)-O(31S)-Na(6)	127(2)	Na(7)-O(35S)-Na(5)	98.2(10)

Symmetry transformations used to generate equivalent atoms:

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

#5 x-1,y,z #6 -x+1,-y-1,-z+3

S4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for 1.

The anisotropic displacement factor exponent takes the form:
$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^*b^*U_{12}]$

	U11	U22	U33	U23	U13	U12
W(1)	40(1)	35(1)	21(1)	1(1)	-11(1)	-7(1)
W(2)	40(1)	36(1)	21(1)	-1(1)	-10(1)	-7(1)
W(3)	40(1)	35(1)	22(1)	0(1)	-9(1)	-7(1)
W(4)	39(1)	35(1)	23(1)	-1(1)	-11(1)	-7(1)
W(5)	40(1)	33(1)	23(1)	-1(1)	-11(1)	-6(1)
W(6)	39(1)	33(1)	22(1)	-1(1)	-10(1)	-4(1)
W(7)	38(1)	33(1)	21(1)	0(1)	-10(1)	-7(1)
W(8)	40(1)	31(1)	23(1)	-1(1)	-11(1)	-5(1)
W(9)	39(1)	33(1)	25(1)	0(1)	-12(1)	-5(1)
W(10)	44(1)	37(1)	27(1)	-1(1)	-12(1)	-7(1)
W(11)	41(1)	31(1)	22(1)	-1(1)	-10(1)	-6(1)
W(12)	38(1)	32(1)	22(1)	-1(1)	-10(1)	-4(1)
W(13)	38(1)	32(1)	21(1)	-1(1)	-10(1)	-6(1)
W(14)	39(1)	31(1)	23(1)	-1(1)	-10(1)	-4(1)
W(15)	40(1)	35(1)	26(1)	-1(1)	-11(1)	-5(1)
Fe(1)	42(3)	33(2)	19(2)	1(2)	-11(2)	-2(2)
Na(1)	87(11)	59(9)	31(7)	-4(6)	-5(7)	-4(8)
P(1)	39(5)	22(4)	21(4)	-6(3)	-3(3)	-5(3)
P(2)	32(4)	27(4)	19(4)	-2(3)	-7(3)	-4(3)
Na(2)	57(9)	46(8)	57(8)	-2(6)	-7(7)	-20(7)
Na(3)	55(8)	37(7)	32(6)	-7(5)	-10(6)	-7(6)
Na(4)	45(8)	63(8)	48(8)	-5(7)	-7(6)	-18(6)
Na(5)	60(9)	67(9)	48(8)	-9(7)	-11(7)	-12(7)
Na(6)	72(10)	63(9)	52(9)	-18(7)	-22(7)	-13(8)
Na(7)	70(10)	53(8)	32(7)	-1(6)	-9(6)	-14(7)
Na(8)	55(9)	58(8)	44(8)	0(6)	-28(6)	-2(7)

Synthesis of Two Representative $TM_3Fe^{III}_2$ Sandwich POMs

Na**1** (0.0750 g, 0.00825 mmol) was dissolved in a minimal amount of 0.5M NaCl by gentle heating. $Co(NO_3)_2{\bullet}6H_2O$ (0.0250 g, 0.0825 mmol) was slowly added to the solution and gently heated for approximately 10 min. A slight color change in the solution (from dark red to reddish-brown) was observed upon heating. After approximately seven days, a reddish-brown precipitate formed. The solution was filtered, and the precipitate was redissolved in 0.5M NaCl. Elemental analysis gave a Fe/Co/P/W ratio of 2/3/4/28 indicating that an average of two W atoms per molecule is missing or substituted. ^{31}P analysis (Figure SI1 below) confirms the formation of at least one new compound by the formation of new peaks shifted upfield from the parent compound. The Ni complex was made analogously by using $NiCl_2{\bullet}6H_2O$ (0.0320 g, 0.0825 mmol) in place of $Co(NO_3)_2{\bullet}6H_2O$.

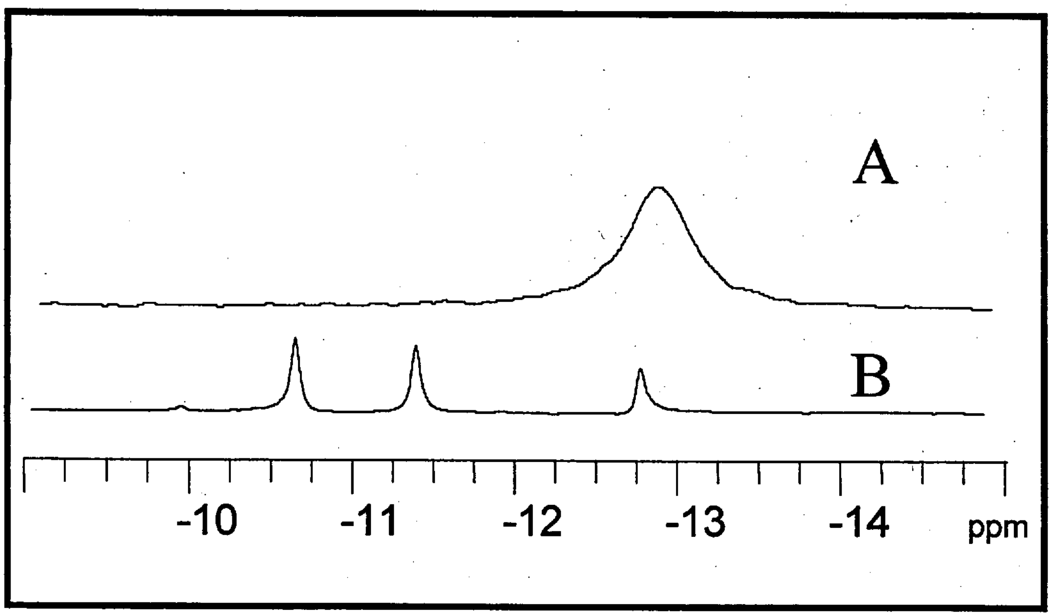

Figure SI1. ^{31}P NMR spectra of **1** before (A) and after (B) 10 equivalents of first-row transition metals were added.