Electronic Supplementary Material (ESI) for Dalton Transactions

New chemistry of 1,2-*closo*-$P_2B_{10}H_{10}$ and 1,2-*closo*-$As_2B_{10}H_{10}$; *in silico* and gas electron diffraction structures, and new metalladiphospha- and metalladiarsaboranes

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Supplementary Information

Table S1 Selected refined and calculated geometric parameters for **1** (distances in Å, angles in °) from the GED study. Figures in parentheses are estimated standard deviations of the last digits. See supporting data for parameter definitions.

No.	Parameter	GED (r_{h1})	MP2/6-31G** (r_e)	Restraint
Independent parameters				
p_1	rP–P	2.310(2)	2.321	
p_2	rP–B_{av}	2.055(1)	2.055	2.055(5)
p_3	rP–B_{dif}	0.075(2)	0.080	0.080(6)
p_4	rB–B_{avg}	1.796(1)	1.788	
p_5	rB–B_{dif1}	0.037(3)	0.048	0.048(5)
p_6	rB–B_{dif2}	0.020(1)	0.019	0.019(5)
p_7	rB–B_{dif3}	0.011(4)	0.012	0.012(5)
p_8	rB–B_{dif4}	0.001(4)	0.002	0.002(5)
p_9	rB–H_{avg}	1.201(2)	1.184	
p_{10}	ϕB(4)–P(1)–B(3)–P(2)	-137.2(1)	-137.2	
p_{11}	ϕB(3)–P(2)–P(1)–B(6)	-120.9(fixed)	-120.9	
p_{12}	dropH(13)	3.1(4)	2.7	2.7(5)
Dependent parameters				
dp_1	rP(1)–B(4)	2.018(2)		
dp_2	rB(4)–B(9)	1.785(2)		
dp_3	rB(3)–B(8)	1.770(2)		
dp_4	rB(9)–B(12)	1.785(4)		

Table S2 Selected refined and calculated geometric parameters for **2** (distances in Å, angles in °) from the GED study. Figures in parentheses are estimated standard deviations of the last digits. See supporting data for parameter definitions.

No.	Parameter	GED (r_{h1})	BP86 (r_e)	Restraint
Independent parameters				
p_1	*r*As–As	2.496(1)	2.527	
p_2	*r*As–B_{av}	2.198(2)	2.201	
p_3	*r*As–B_{dif}	0.121(8)	0.122	0.122(10)
p_4	*r*B–B_{avg}	1.817(2)	1.801	
p_5	*r*B–B_{dif1}	0.076(16)	0.068	
p_6	*r*B–B_{dif2}	0.027(5)	0.027	0.027(5)
p_7	*r*B–B_{dif3}	0.014(5)	0.015	0.015(5)
p_8	*r*B–B_{dif4}	0.006(1)	0.006	0.006(1)
p_9	*r*B–H_{avg}	1.210(4)	1.197	1.197(5)
p_{10}	ϕB(4)–As(1)–B(3)–As(2)	-135.4(3)	-136.9	-136.9(15)
p_{11}	ϕB(3)–As(2)–As(1)–B(6)	-118.3(5)	-115.5	-115.5(20)
p_{12}	dropH(13)	1.6(5)	1.8	1.8(5)
Dependent parameters				
dp_1	*r*As(1)–B(3)	2.259(5)		
dp_2	rAs(1)–B(4)	2.138(4)		
dp_3	*r*B(3)–B(4)	1.873(12)		
dp_4	*r*B(4)–B(9)	1.794(5)		
dp_5	*r*B(9)–B(12)	1.800(5)		
dp_6	*r*B(8)–B(9)	1.809(5)		
dp_7	*r*B(3)–B(8)	1.775(9)		

Table S3 Refined and calculated (HF/6-31G*) amplitudes of vibration (u), associated r_a distances and corresponding correction values (k) for the r_{h1} refinement of $P_2B_{10}H_{10}$.[a]

	Atom pair	r_a	u_{GED}	k	$u_{calc.}$
u_{50}	B(8)–H(18)	119.8(2)	9.06(22)	0.43	8.61
u_{20}	B(3)–H(13)	119.8(2)	9.05(Tied to u_{50})	0.43	8.60
u_{58}	B(9)–H(19)	119.8(2)	8.93(Tied to u_{50})	0.43	8.49
u_{35}	B(4)–H(14)	119.9(2)	8.81(Tied to u_{50})	0.43	8.37
u_{17}	B(3)–B(8)	171.8(18)	8.01(8)	-4.87	7.53
u_{53}	B(9)–B(12)	177.9(4)	7.50(Tied to u_{17})	-0.36	7.05
u_{30}	B(4)–B(9)	179.4(2)	7.27(Tied to u_{17})	1.24	6.83
u_{44}	B(8)–B(9)	180.2(3)	6.95(Tied to u_{17})	0.87	6.53
u_{29}	B(4)–B(8)	180.5(12)	7.55(Tied to u_{17})	3.25	7.10
u_{27}	B(4)–B(5)	183.2(6)	8.25(Tied to u_{17})	0.07	7.75
u_{14}	B(3)–B(4)	185.0(3)	8.54(Tied to u_{17})	3.07	8.03
u_3	P(1)–B(4)	199.7(2)	6.16(21)	-1.88	7.36
u_2	P(1)–B(3)	212.9(2)	8.18(37)	3.92	8.24
u_1	P(1)–P(2)	229.2(3)	9.10(25)	-1.48	7.79
u_{24}	B(3)...H(18)	250.4(25)	13.05(fixed)	-5.79	13.05
u_{46}	B(8)...H(13)	252.9(13)	12.86(fixed)	-5.29	12.86
u_{40}	B(4)...H(19)	255.1(3)	13.20(fixed)	-4.9	13.20
u_{39}	B(4)...H(18)	261.9(19)	13.06(fixed)	2.79	13.06
u_{57}	B(9)...H(18)	262.7(7)	12.56(fixed)	-0.92	12.56
u_{47}	B(8)...H(14)	263.1(6)	12.86(fixed)	1.48	12.86
u_{21}	B(3)...H(14)	264.0(3)	13.49(fixed)	0.75	13.49
u_{59}	B(9)...H(22)	264.3(4)	13.34(fixed)	2.17	13.34
u_{36}	B(4)...H(15)	264.4(7)	13.07(fixed)	-2.38	13.07
u_{51}	B(8)...H(19)	265.2(6)	12.54(fixed)	2.13	12.54
u_{55}	B(9)...H(14)	266.5(2)	12.49(fixed)	3.42	12.49
u_{34}	B(4)...H(13)	267.4(4)	13.51(fixed)	2.34	13.51
u_9	P(1)...H(14)	270.7(2)	13.43(fixed)	1.1	13.43
u_{45}	B(8)...B(10)	280.0(21)	12.77(14)	-9.92	10.53
u_{63}	H(13)...H(18)	286.0(25)	20.54(fixed)	-6.78	20.54
u_8	P(1)...H(13)	286.2(5)	13.68(fixed)	2.63	13.68
u_{18}	B(3)...B(9)	289.1(3)	8.60(Tied to u_{45})	-3.02	7.09
u_{28}	B(4)...B(7)	290.0(4)	9.72(Tied to u_{45})	-1.61	8.01
u_{31}	B(4)...B(10)	294.8(13)	10.17(Tied to u_{45})	3.87	8.38
u_{16}	B(3)...B(6)	294.9(3)	13.21(Tied to u_{45})	-8.28	10.89
u_{66}	H(14)...H(15)	294.9(10)	22.96(fixed)	-14.59	22.96
u_{33}	B(4)...B(12)	297.9(2)	11.39(Tied to u_{45})	8.5	9.39
u_{69}	H(14)...H(19)	299.3(3)	20.54(fixed)	-3.75	20.54
u_{75}	H(19)...H(22)	300.5(6)	20.57(fixed)	-4.29	20.57
u_{15}	B(3)...B(5)	301.4(2)	9.97(Tied to u_{45})	3.51	8.22
u_{68}	H(14)...H(18)	308.4(15)	21.30(fixed)	7.39	21.30
u_{73}	H(18)...H(19)	308.5(4)	20.37(fixed)	2.13	20.37
u_{60}	H(13)...H(14)	311.3(5)	21.71(fixed)	7.04	21.71
u_6	P(1)...B(9)	313.8(3)	8.09(16)	-6.37	9.02
u_5	P(1)...B(8)	319.9(20)	5.76(Tied to u_6)	-1.78	6.42
u_{19}	B(3)...B(10)	334.3(19)	11.00(fixed)	-11.15	11.00
u_4	P(1)...B(7)	337.8(2)	9.10(Tied to u_6)	9.14	10.15
u_{32}	B(4)...B(11)	354.6(3)	10.83(fixed)	10.11	10.83
u_7	P(1)...B(12)	383.3(3)	12.28(41)	4.36	8.02
u_{52}	B(8)...H(20)	387.4(18)	13.58(fixed)	-10.67	13.58
u_{54}	B(9)...H(13)	392.3(4)	11.49(fixed)	-5.3	11.49
u_{25}	B(3)...H(19)	394.9(4)	11.39(fixed)	-3.23	11.39

u_{38}	B(4)...H(17)	395.4(5)	12.11(fixed)	-2.97	12.11
u_{41}	B(4)...H(20)	399.2(14)	12.78(fixed)	1.24	12.78
u_{48}	B(8)...H(15)	400.7(11)	11.33(fixed)	2.04	11.33
u_{56}	B(9)...H(17)	404.2(3)	13.05(fixed)	7.17	13.05
u_{23}	B(3)...H(16)	404.4(5)	14.17(fixed)	-8.8	14.17
u_{43}	B(4)...H(22)	405.1(3)	13.64(fixed)	8.85	13.64
u_{37}	B(4)...H(16)	406.8(3)	13.57(fixed)	0.71	13.57
u_{22}	B(3)...H(15)	408.6(3)	12.32(fixed)	3.79	12.32
u_{12}	P(1)...H(19)	411.9(4)	14.14(fixed)	-10.31	14.14
u_{11}	P(1)...H(18)	419.9(23)	11.06(fixed)	-4.19	11.06
u_{10}	P(1)...H(17)	440.5(2)	13.46(fixed)	7.97	13.46
u_{26}	B(3)...H(20)	453.1(19)	13.49(fixed)	-12.38	13.49
u_{49}	B(8)...H(16)	453.3(19)	14.14(fixed)	-12.04	14.14
u_{42}	B(4)...H(21)	473.4(4)	13.38(fixed)	8.85	13.38
u_{74}	H(18)...H(20)	485.4(14)	17.59(fixed)	-11.27	17.59
u_{64}	H(13)...H(19)	486.7(6)	15.80(fixed)	-5.71	15.80
u_{67}	H(14)...H(17)	488.8(6)	16.76(fixed)	-5.95	16.76
u_{70}	H(14)...H(20)	497.4(12)	16.85(fixed)	1.7	16.85
u_{72}	H(14)...H(22)	502.2(4)	17.56(fixed)	8.51	17.56
u_{13}	P(1)...H(22)	502.3(4)	11.33(fixed)	3.16	11.33
u_{61}	H(13)...H(15)	505.0(4)	16.24(fixed)	1.41	16.24
u_{62}	H(13)...H(16)	506.1(9)	17.50(fixed)	-9.27	17.50
u_{65}	H(13)...H(20)	571.6(19)	15.68(fixed)	-13.77	15.68
u_{71}	H(14)...H(21)	592.0(5)	15.52(fixed)	7.47	15.52

[a] Distances in pm. Values in parentheses are the standard deviations in terms of the last digits. See Figure 1 in the main text for atom numbering.

Table S4 Refined and calculated (HF/6-31G*) amplitudes of vibration (u), associated r_a distances and corresponding correction values (k) for the r_{h1} refinement of $As_2B_{10}H_{10}$.[a]

	Atom pair	r_a	u_{GED}	k	$u_{calc.}$
u_{50}	B(8)–H(18)	120.4(4)	10.91(Tied to u_{20})	0.43	8.39
u_{58}	B(9)–H(19)	120.4(4)	10.90(Tied to u_{20})	0.43	8.38
u_{35}	B(4)–H(14)	120.4(4)	10.90(Tied to u_{20})	0.44	8.38
u_{20}	B(3)–H(13)	120.4(4)	10.83(50)	0.43	8.33
u_{29}	B(4)–B(8)	176.4(7)	6.97(Tied to u_{17})	0.34	6.99
u_{17}	B(3)–B(8)	178.0(9)	7.05(17)	0.85	7.07
u_{53}	B(9)–B(12)	179.6(5)	7.23(Tied to u_{17})	-0.14	7.25
u_{30}	B(4)–B(9)	180.5(5)	7.01(Tied to u_{17})	1.32	7.03
u_{44}	B(8)–B(9)	181.2(5)	7.22(Tied to u_{17})	0.60	7.24
u_{14}	B(3)–B(4)	187.8(12)	8.03(Tied to u_{17})	0.84	8.06
u_{27}	B(4)–B(5)	188.0(17)	8.25(Tied to u_{17})	0.30	8.28
u_3	As(1)–B(4)	213.7(4)	8.83(Tied to u_2)	0.33	7.50
u_2	As(1)–B(3)	226.6(5)	10.43(39)	1.21	8.86
u_1	As(1)–As(2)	248.9(1)	8.13(12)	-0.50	7.51
u_{24}	B(3)...H(18)	251.9(8)	12.96(fixed)	-0.06	12.96
u_{39}	B(4)...H(18)	256.9(8)	12.58(fixed)	-0.07	12.58
u_{47}	B(8)...H(14)	261.2(10)	12.95(fixed)	-0.85	12.95
u_{40}	B(4)...H(19)	261.3(8)	12.77(fixed)	0.44	12.77
u_{59}	B(9)...H(22)	264.0(5)	12.74(fixed)	-0.68	12.74
u_{46}	B(8)...H(13)	264.5(13)	12.73(fixed)	0.41	12.73
u_{21}	B(3)...H(14)	265.0(12)	13.42(fixed)	-0.58	13.42
u_{57}	B(9)...H(18)	265.2(6)	13.05(fixed)	-0.41	13.05
u_{51}	B(8)...H(19)	266.3(6)	12.82(fixed)	0.20	12.82
u_{55}	B(9)...H(14)	266.4(4)	12.90(fixed)	1.05	12.90
u_{36}	B(4)...H(15)	271.9(19)	13.64(fixed)	-0.36	13.64
u_{34}	B(4)...H(13)	273.5(15)	13.24(fixed)	0.35	13.24
u_9	As(1)...H(14)	277.3(5)	13.83(fixed)	0.28	13.83
u_{45}	B(8)...B(10)	289.9(8)	8.07(fixed)	-0.53	8.07
u_{33}	B(4)...B(12)	292.2(3)	7.60(fixed)	0.54	7.60
u_{63}	H(13)...H(18)	292.7(15)	20.73(fixed)	-0.73	20.73
u_{28}	B(4)...B(7)	293.7(14)	8.12(fixed)	-0.26	8.12
u_{31}	B(4)...B(10)	294.2(5)	8.06(fixed)	1.57	8.06
u_8	As(1)...H(13)	297.5(9)	14.54(fixed)	0.33	14.54
u_{68}	H(14)...H(18)	299.1(13)	20.63(fixed)	-0.46	20.63
u_{18}	B(3)...B(9)	301.2(6)	7.74(fixed)	1.57	7.74
u_{69}	H(14)...H(19)	305.8(7)	20.49(fixed)	1.09	20.49
u_{75}	H(19)...H(22)	307.0(6)	20.63(fixed)	-1.39	20.63
u_{60}	H(13)...H(14)	310.0(18)	20.79(fixed)	-0.05	20.79
u_{73}	H(18)...H(19)	310.3(8)	20.63(fixed)	0.10	20.63
u_{15}	B(3)...B(5)	310.6(6)	8.92(fixed)	1.24	8.92
u_{66}	H(14)...H(15)	315.8(28)	21.02(fixed)	-1.26	21.02
u_{16}	B(3)...B(6)	323.1(12)	9.91(fixed)	0.20	9.91
u_6	As(1)...B(9)	333.1(3)	8.78(Tied to u_4)	-0.96	7.82
u_5	As(1)...B(8)	334.0(2)	8.56(Tied to u_4)	0.52	7.62
u_4	As(1)...B(7)	345.4(5)	9.53(38)	0.53	8.48
u_{32}	B(4)...B(11)	349.9(8)	8.26(fixed)	0.91	8.26
u_{19}	B(3)...B(10)	354.8(7)	8.57(fixed)	0.79	8.57
u_7	As(1)...B(12)	394.7(4)	10.91(60)	-0.82	7.95
u_{52}	B(8)...H(20)	398.3(10)	11.95(fixed)	-1.72	11.95
u_{43}	B(4)...H(22)	398.5(5)	11.67(fixed)	-0.51	11.67
u_{38}	B(4)...H(17)	399.6(17)	12.24(fixed)	-1.46	12.24

u_{56}	B(9)...H(17)	400.2(5)	11.91(fixed)	0.10	11.91
u_{41}	B(4)...H(20)	400.9(7)	12.11(fixed)	0.52	12.11
u_{48}	B(8)...H(15)	401.3(7)	12.20(fixed)	-0.32	12.20
u_{25}	B(3)...H(19)	405.7(6)	11.99(fixed)	0.57	11.99
u_{54}	B(9)...H(13)	407.9(8)	11.95(fixed)	0.62	11.95
u_{22}	B(3)...H(15)	416.9(7)	12.90(fixed)	0.36	12.90
u_{37}	B(4)...H(16)	419.3(7)	12.80(fixed)	0.53	12.80
u_{23}	B(3)...H(16)	431.8(14)	13.64(fixed)	-1.03	13.64
u_{12}	As(1)...H(19)	433.1(5)	14.41(Tied to u_{10})	-1.96	12.47
u_{11}	As(1)...H(18)	434.2(4)	13.86(Tied to u_{10})	-0.27	12.00
u_{10}	As(1)...H(17)	447.9(7)	14.51(101)	-0.43	12.56
u_{42}	B(4)...H(21)	469.6(9)	11.38(fixed)	-0.34	11.38
u_{26}	B(3)...H(20)	474.4(8)	11.62(fixed)	-0.43	11.62
u_{49}	B(8)...H(16)	474.9(8)	11.48(fixed)	0.01	11.48
u_{67}	H(14)...H(17)	494.4(23)	16.64(fixed)	-3.14	16.64
u_{72}	H(14)...H(22)	496.1(7)	16.22(fixed)	-1.32	16.22
u_{74}	H(18)...H(20)	497.6(13)	16.54(fixed)	-2.98	16.54
u_{70}	H(14)...H(20)	499.6(10)	16.45(fixed)	-0.03	16.45
u_{64}	H(13)...H(19)	501.9(10)	16.34(fixed)	-0.11	16.34
u_{13}	As(1)...H(22)	514.5(5)	11.23(fixed)	-2.04	11.23
u_{61}	H(13)...H(15)	515.7(9)	16.70(fixed)	-0.93	16.70
u_{62}	H(13)...H(16)	532.5(18)	17.14(fixed)	-2.52	17.14
u_{71}	H(14)...H(21)	589.1(11)	13.84(fixed)	-1.71	13.84
u_{65}	H(13)...H(20)	593.9(11)	14.03(fixed)	-1.85	14.03

[a] Distances in pm. Values in parentheses are the standard deviations in terms of the last digits. See Figure 1 in the main text for atom numbering.

Table S5 Least-squares correlation matrix (×100) for the GED refinement of $P_2B_{10}H_{10}$.[a]

	p_3	p_6	p_{10}	u_1	u_5	u_{12}	u_{13}	u_{28}	k_2
p_1	66				-63	-51			
p_2				61					
p_3					-74	-85			
p_4		62	71						
p_6							57		
p_{10}		65							
u_1					79				
u_5						84			
u_{12}								58	
u_{28}									64

[a] Only absolute values ≥±50 are shown. k_2 is a scale factor.

Table S6 Least-squares correlation matrix (×100) for the GED refinement of $As_2B_{10}H_{10}$.[a]

	p_2	p_5	p_7	p_{11}	u_6	u_{13}	u_{48}	k_2
p_1	57							
p_3					-92		51	
p_4			60					
p_5						-60		
p_{10}		74		-87			57	51
p_{11}		-70						-66
u_4								79
u_6							-50	
u_{48}								71

[a] Only absolute values ≥±50 are shown. k_2 is a scale factor.

Table S7 GED-determined coordinates / Å for the refinement of $P_2B_{10}H_{10}$.

	x	*y*	*z*
P(1)	1.7712	1.1551	0.0000
P(2)	1.7712	-1.1551	0.0000
B(3)	0.9111	0.0000	1.5187
B(4)	0.0000	1.4598	0.9173
B(5)	0.0000	1.4598	-0.9173
B(6)	0.9111	0.0000	-1.5187
B(7)	0.0000	-1.4598	0.9173
B(8)	-0.8577	0.0000	1.4524
B(9)	-1.4223	0.8926	0.0000
B(10)	-0.8577	0.0000	-1.4524
B(11)	0.0000	-1.4598	-0.9173
B(12)	-1.4223	-0.8926	0.0000
H(13)	1.4724	0.0000	2.5801
H(14)	0.0000	2.4765	1.5561
H(15)	0.0000	2.4765	-1.5561
H(16)	1.4724	0.0000	-2.5801
H(17)	0.0000	-2.4765	1.5561
H(18)	-1.4682	0.0000	2.4863
H(19)	-2.4393	1.5309	0.0000
H(20)	-1.4682	0.0000	-2.4863
H(21)	0.0000	-2.4765	-1.5561
H(22)	-2.4393	-1.5309	0.0000

Table S8 GED-determined coordinates / Å for the refinement of $As_2B_{10}H_{10}$.

	x	*y*	*z*
As(1)	1.9069	1.2481	0.0000
As(2)	1.9069	-1.2481	0.0000
B(3)	0.9420	0.0000	1.6161
B(4)	0.0000	1.4711	0.9404
B(5)	0.0000	1.4711	-0.9404
B(6)	0.9420	0.0000	-1.6161
B(7)	0.0000	-1.4711	0.9404
B(8)	-0.8251	0.0000	1.4535
B(9)	-1.4174	0.9001	0.0000
B(10)	-0.8251	0.0000	-1.4535
B(11)	0.0000	-1.4711	-0.9404
B(12)	-1.4174	-0.9001	0.0000
H(13)	1.5221	0.0000	2.6776
H(14)	0.0000	2.4903	1.5920
H(15)	0.0000	2.4903	-1.5920
H(16)	1.5221	0.0000	-2.6776
H(17)	0.0000	-2.4903	1.5920
H(18)	-1.4222	0.0000	2.5055
H(19)	-2.4385	1.5486	0.0000
H(20)	-1.4222	0.0000	-2.5055
H(21)	0.0000	-2.4903	-1.5920
H(22)	-2.4385	-1.5486	0.0000

Table S9A Computed coordinates (BP86/SDD(ζ=0.387)/6-31G**) / Å for $P_2B_{10}H_{10}$.

	x	*y*	*z*
P(1)	0.0000	1.1791	-1.3986
P(2)	0.0000	-1.1791	-1.3986
B(3)	1.5472	0.0000	-0.5124
B(4)	0.9274	1.4719	0.3998
B(5)	-0.9274	1.4719	0.3998
B(6)	-1.5472	0.0000	-0.5124
B(7)	0.9274	-1.4719	0.3998
B(8)	1.4565	0.0000	1.2526
B(9)	0.0000	0.8924	1.8078
B(10)	-1.4565	0.0000	1.2526
B(11)	-0.9274	-1.4719	0.3998
B(12)	0.0000	-0.8924	1.8078
H(13)	2.5452	0.0000	-1.1692
H(14)	1.5629	2.4855	0.3676
H(15)	-1.5629	2.4855	0.3676
H(16)	-2.5452	0.0000	-1.1692
H(17)	1.5629	-2.4855	0.3676
H(18)	2.4877	0.0000	1.8586
H(19)	0.0000	1.5354	2.8163
H(20)	-2.4877	0.0000	1.8586
H(21)	-1.5629	-2.4855	0.3676
H(22)	0.0000	-1.5354	2.8163

BP86 Energy = -267.837589

Table S9B Root-mean-square deviations (Å) between experimental (GED) and computational (BP86/SDD(ζ=0.387)/6-31G**) models for individual P and B atoms, together with the overall rms misfit, for $P_2B_{10}H_{10}$.

Atoms	
P1,2	0.031
B3,6	0.029
B4,7,11,5	0.017
B8,10	0.006
B9,12	0.006
overall	0.0204

Table S10A Computed coordinates (BP86/6-31G**) / Å for $P_2B_{10}H_{10}$.

	x	*y*	*z*
P(1)	-1.1689	0.0000	-1.3888
P(2)	1.1689	0.0000	-1.3888
B(3)	0.0000	1.5401	-0.5176
B(4)	-1.4713	0.9256	0.3947
B(5)	-1.4713	-0.9256	0.3947
B(6)	0.0000	-1.5401	-0.5176
B(7)	1.4713	0.9256	0.3947
B(8)	0.0000	1.4561	1.2486
B(9)	-0.8926	0.0000	1.8050
B(10)	0.0000	-1.4561	1.2486
B(11)	1.4713	-0.9256	0.3947
B(12)	0.8926	0.0000	1.8050
H(13)	0.0000	2.5351	-1.1786
H(14)	-2.4836	1.5628	0.3589
H(15)	-2.4836	-1.5628	0.3589
H(16)	0.0000	-2.5351	-1.1786
H(17)	2.4836	1.5628	0.3589
H(18)	0.0000	2.4883	1.8527
H(19)	-1.5364	0.0000	2.8128
H(20)	0.0000	-2.4883	1.8527
H(21)	2.4836	-1.5628	0.3589
H(22)	1.5364	0.0000	2.8128

BP86 Energy = -937.428161

Table S10B Root-mean-square deviations (Å) between experimental (GED) and computational (BP86/6-31G**) models for individual P and B atoms, together with the overall rms misfit, for $P_2B_{10}H_{10}$.

Atoms	
P1,2	0.016
B3,6	0.022
B4,7,11,5	0.015
B8,10	0.004
B9,12	0.007
overall	0.0144

Table S11A Computed coordinates (B3LYP/6-31G**) / Å for $P_2B_{10}H_{10}$.

	x	*y*	*z*
P(1)	-1.1634	0.0000	-1.3841
P(2)	1.1634	0.0000	-1.3841
B(3)	0.0000	1.5389	-0.5148
B(4)	-1.4675	0.9233	0.3937
B(5)	-1.4675	-0.9233	0.3937
B(6)	0.0000	-1.5389	-0.5148
B(7)	1.4675	0.9233	0.3937
B(8)	0.0000	1.4508	1.2429
B(9)	-0.8888	0.0000	1.7966
B(10)	0.0000	-1.4508	1.2429
B(11)	1.4675	-0.9233	0.3937
B(12)	0.8888	0.0000	1.7966
H(13)	0.0000	2.5263	-1.1675
H(14)	-2.4711	1.5542	0.3634
H(15)	-2.4711	-1.5542	0.3634
H(16)	0.0000	-2.5263	-1.1675
H(17)	2.4711	1.5542	0.3634
H(18)	0.0000	2.4723	1.8448
H(19)	-1.5251	0.0000	2.7970
H(20)	0.0000	-2.4723	1.8448
H(21)	2.4711	-1.5542	0.3634
H(22)	1.5251	0.0000	2.7970

MP2 Energy = -937.418714

Table S11B Root-mean-square deviations (Å) between experimental (GED) and computational (B3LYP/6-31G**) models for individual P and B atoms, together with the overall rms misfit, for $P_2B_{10}H_{10}$.

Atoms	
P1,2	0.008
B3,6	0.022
B4,7,11,5	0.011
B8,10	0.004
B9,12	0.014
overall	0.0128

Table S12A Computed coordinates (MP2/6-31G**) / Å for $P_2B_{10}H_{10}$.

	x	*y*	*z*
P(1)	-1.1604	0.0000	-1.3778
P(2)	1.1604	0.0000	-1.3778
B(3)	0.0000	1.5176	-0.5183
B(4)	-1.4611	0.9171	0.3908
B(5)	-1.4611	-0.9171	0.3908
B(6)	0.0000	-1.5176	-0.5183
B(7)	1.4611	0.9171	0.3908
B(8)	0.0000	1.4451	1.2404
B(9)	-0.8877	0.0000	1.7956
B(10)	0.0000	-1.4451	1.2404
B(11)	1.4611	-0.9171	0.3908
B(12)	0.8877	0.0000	1.7956
H(13)	0.0000	2.5054	-1.1684
H(14)	-2.4603	1.5518	0.3557
H(15)	-2.4603	-1.5518	0.3557
H(16)	0.0000	-2.5054	-1.1684
H(17)	2.4603	1.5518	0.3557
H(18)	0.0000	2.4685	1.8348
H(19)	-1.5257	0.0000	2.7929
H(20)	0.0000	-2.4685	1.8348
H(21)	2.4603	-1.5518	0.3557
H(22)	1.5257	0.0000	2.7929

MP2 Energy = -934.177738

Table S12B Root-mean-square deviations (Å) between experimental (GED) and computational (MP2/6-31G**) models for individual P and B atoms, together with the overall rms misfit, for $P_2B_{10}H_{10}$.

Atoms	
P1,2	0.008
B3,6	0.006
B4,7,11,5	0.004
B8,10	0.009
B9,12	0.014
overall	0.0082

Table S13A Computed coordinates (BP86/SDD(ζ=0.303)/6-31G**) / Å for $As_2B_{10}H_{10}$.

	x	*y*	*z*
As(1)	-1.0531	1.2636	0.0000
As(2)	-1.0532	-1.2636	0.0000
B(3)	-0.0516	0.0000	-1.5858
B(4)	0.8583	1.4761	-0.9383
B(5)	0.8583	1.4761	0.9383
B(6)	-0.0516	0.0000	1.5858
B(7)	0.8583	-1.4761	-0.9383
B(8)	1.7048	0.0000	-1.4580
B(9)	2.2545	0.8930	0.0000
B(10)	1.7048	0.0000	1.4580
B(11)	0.8583	-1.4761	0.9383
B(12)	2.2545	-0.8931	0.0000
H(13)	-0.6785	0.0000	-2.6038
H(14)	0.8618	2.4922	-1.5722
H(15)	0.8618	2.4922	1.5722
H(16)	-0.6785	0.0000	2.6038
H(17)	0.8618	-2.4922	-1.5722
H(18)	2.3216	0.0000	-2.4836
H(19)	3.2662	1.5316	0.0000
H(20)	2.3216	0.0000	2.4836
H(21)	0.8618	-2.4922	1.5722
H(22)	3.2662	-1.5316	0.0000

BP86 Energy = -267.197180

Table S13B Root-mean-square deviations (Å) between experimental (GED) and computational (BP86/SDD(ζ=0.303)/6-31G**) models for individual As and B atoms, together with the overall rms misfit, for $As_2B_{10}H_{10}$.

Atoms	
As1,2	0.018
B3,6	0.041
B4,7,11,5	0.007
B8,10	0.018
B9,12	0.027
overall	0.0228

Table S14A Computed coordinates (BP86/6-31G**) / Å for $As_2B_{10}H_{10}$.

	x	*y*	*z*
As(1)	0.0000	1.2642	-1.0453
As(2)	0.0000	-1.2642	-1.0453
B(3)	1.5845	0.0000	-0.0626
B(4)	0.9381	1.4779	0.8510
B(5)	-0.9381	1.4779	0.8510
B(6)	-1.5845	0.0000	-0.0626
B(7)	0.9381	-1.4779	0.8510
B(8)	1.4546	0.0000	1.6917
B(9)	0.0000	0.8918	2.2443
B(10)	-1.4546	0.0000	1.6917
B(11)	-0.9381	-1.4779	0.8510
B(12)	0.0000	-0.8918	2.2443
H(13)	2.6066	0.0000	-0.6808
H(14)	1.5779	2.4893	0.8642
H(15)	-1.5779	2.4893	0.8642
H(16)	-2.6066	0.0000	-0.6808
H(17)	1.5779	-2.4893	0.8642
H(18)	2.4770	0.0000	2.3128
H(19)	0.0000	1.5254	3.2587
H(20)	-2.4770	0.0000	2.3128
H(21)	-1.5779	-2.4893	0.8642
H(22)	0.0000	-1.5254	3.2587

BP86 Energy = -4722.009624

Table S14B Root-mean-square deviations (Å) between experimental (GED) and computational (BP86/6-31G**) models for individual As and B atoms, together with the overall rms misfit, for $As_2B_{10}H_{10}$.

Atoms	
As1,2	0.017
B3,6	0.039
B4,7,11,5	0.009
B8,10	0.011
B9,12	0.031
overall	0.0226

Table S15A Computed coordinates (B3LYP/6-31G**) / Å for $As_2B_{10}H_{10}$.

	x	*y*	*z*
As(1)	-1.2597	0.0000	-1.0430
As(2)	1.2597	0.0000	-1.0430
B(3)	0.0000	1.5848	-0.0595
B(4)	-1.4745	0.9364	0.8498
B(5)	-1.4745	-0.9364	0.8498
B(6)	0.0000	-1.5848	-0.0595
B(7)	1.4745	0.9364	0.8498
B(8)	0.0000	1.4496	1.6859
B(9)	-0.8881	0.0000	2.2351
B(10)	0.0000	-1.4496	1.6859
B(11)	1.4745	-0.9364	0.8498
B(12)	0.8881	0.0000	2.2351
H(13)	0.0000	2.5987	-0.6699
H(14)	-2.4769	1.5698	0.8686
H(15)	-2.4769	-1.5698	0.8686
H(16)	0.0000	-2.5987	-0.6699
H(17)	2.4769	1.5698	0.8686
H(18)	0.0000	2.4611	2.3052
H(19)	-1.5142	0.0000	3.2422
H(20)	0.0000	-2.4611	2.3052
H(21)	2.4769	-1.5698	0.8686
H(22)	1.5142	0.0000	3.2422

B3LYP Energy = -4721.561722

Table S15B Root-mean-square deviations (Å) between experimental (GED) and computational (B3LYP/6-31G**) models for individual As and B atoms, together with the overall rms misfit, for $As_2B_{10}H_{10}$.

Atoms	
As1,2	0.015
B3,6	0.042
B4,7,11,5	0.007
B8,10	0.008
B9,12	0.038
overall	0.0245

Table S16A Computed coordinates (MP2/6-31G**) / Å for $As_2B_{10}H_{10}$.

	x	*y*	*z*
As(1)	0.0000	1.2542	-1.0394
As(2)	0.0000	-1.2542	-1.0394
B(3)	1.5661	0.0000	-0.0660
B(4)	0.9304	1.4692	0.8464
B(5)	-0.9304	1.4692	0.8464
B(6)	-1.5661	0.0000	-0.0660
B(7)	0.9304	-1.4692	0.8464
B(8)	1.4439	0.0000	1.6825
B(9)	0.0000	0.8867	2.2334
B(10)	-1.4439	0.0000	1.6825
B(11)	-0.9304	-1.4692	0.8464
B(12)	0.0000	-0.8867	2.2334
H(13)	2.5838	0.0000	-0.6689
H(14)	1.5680	2.4676	0.8621
H(15)	-1.5680	2.4676	0.8621
H(16)	-2.5838	0.0000	-0.6689
H(17)	1.5680	-2.4676	0.8621
H(18)	2.4577	0.0000	2.2936
H(19)	0.0000	1.5148	3.2371
H(20)	-2.4577	0.0000	2.2936
H(21)	-1.5680	-2.4676	0.8621
H(22)	0.0000	-1.5148	3.2371

MP2 Energy = -4716.050072

Table S16B Root-mean-square deviations (Å) between experimental (GED) and computational (MP2/6-31G**) models for individual As and B atoms, together with the overall rms misfit, for $As_2B_{10}H_{10}$.

Atoms	
As1,2	0.017
B3,6	0.056
B4,7,11,5	0.012
B8,10	0.011
B9,12	0.038
overall	0.0297

Model description for $P_2B_{10}H_{10}$ and $As_2B_{10}H_{10}$

The geometric structures of $P_2B_{10}H_{10}$ and $As_2B_{10}H_{10}$ were described by a set of parameters which were then refined to obtain the best fit to the experimental data. Twelve parameters were required to define both molecules in C_{2v} symmetry, as indicated by the *ab initio* calculations and the same model was used for each molecule.

Parameter p_1 defines the X–X distance (X = P or As), and p_2 and p_3 define the average and difference of the X–B distances. There are five parameters defining the B–B distances, an average (p_4) with four difference parameters (p_5-p_8) defined as follows. p_5 is *r*B(3)–B(4) minus the average of [4 × *r*B(4)–B(9) + *r*B(9)–B(12) + 4 × *r*B(8)–B(9) + 2 × *r*B(3)–B(8)]. p_6 is defined as the average of [4 × *r*B(4)–B(9) + *r*B(9)–B(12) + 4 x *r*B(8)–B(9)] minus *r*B(3)–B(8). p_7 is defined as *r*B(8)–B(9) minus the average of [4 × *r*B(4)–B(9) + *r*B(9)–B(12)]. p_8 is defined as *r*B(9)–B(12) minus *r*B(4)–B(9). One parameter defines the average B–H distance (p_9).

Three torsion angles are then used to define the various planes of the molecules, p_{10} is ϕB(4)–X(1)–B(3)–X(2) and p_{11} is ϕB(3)–X(2)–X(1)–B(6). Most of the B-H distances are on a direct axis from the centre of gravity of the molecule, but H(13) and its symmetry equivalent are defined by a drop angle due to their proximity to the X atoms (p_{12}).

Figure S1 Experimental and weighted difference (experimental – theoretical) molecular scattering intensities for $P_2B_{10}H_{10}$.

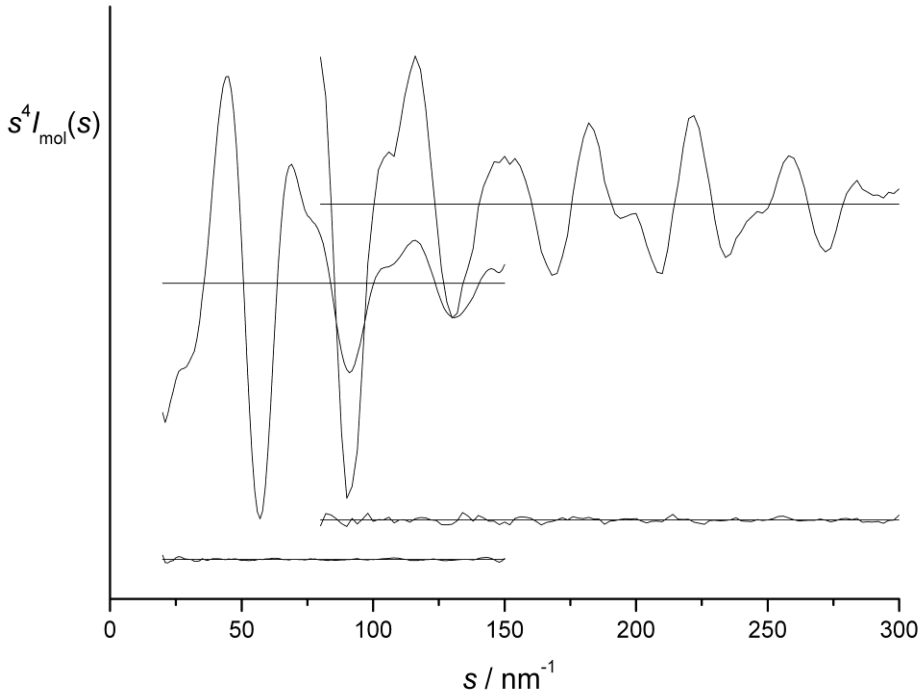

Figure S2 Experimental and weighted difference (experimental – theoretical) molecular scattering intensities for $As_2B_{10}H_{10}$.