Table S1: Structure parameters in terms of the crystal (rhombohedral) axes before and after geometry relaxation.

			start			relaxed		
compound	site	Wyckoff position	$\bar{x}$	$\bar{y}$	$\bar{z}$	$\bar{x}$	$\bar{y}$	$\bar{z}$
α-rB_{12}	B(1)	18h	0.51019	0.15362	0.51019	0.50997	0.15436	0.50997
	B(2)	18h	0.72118	0.13061	0.72118	0.72055	0.13131	0.72055
$B_{12}P_2$	B(1)	18h	0.17292	0.48695	0.48695	0.17340	0.48716	0.48716
	B(2)	18h	0.31542	0.78325	0.31542	0.31602	0.78262	0.31602
	P	6c	0.09462	0.09462	0.09462	0.09487	0.09487	0.09487
$B_{12}As_2$	B(1)	18h	0.01600	0.32470	0.01600	0.01527	0.32485	0.01527
	B(2)	18h	0.17930	0.72680	0.17930	0.17783	0.72804	0.17783
	As	6c	0.39981	0.39981	0.39981	0.39903	0.39903	0.39903
$B_{12}O_2$	B(1)	18h	0.99790	0.65320	0.99790	0.99756	0.66686	0.99756
	B(2)	18h	0.80040	0.32340	0.80040	0.79951	0.32233	0.79951
	O	6c	0.37570	0.37570	0.37570	0.37907	0.37907	0.37907

Table S2: Chemical shift parameters δ_{iso}, δ_{csa} in ppm and η_{cs} without macroscopic correction of magnetic susceptibility[a] together with corresponding susceptibilies χ.[1] All values according to PAW PPs.

		without correction[a]			$-\chi$	
compound	site	δ_{iso}	δ_{csa}	η_{cs}	$[(8\pi/3)\,\text{ppm}]$	$[10^{-6}\,\text{cm}^3/\text{mol}]$
α-rB_{12}	B(1)	16.8	−9.8	0.58	12.3	77.6
	B(2)	19.7	18.3	0.98		
$B_{12}P_2$	B(1)	15.6	−7.1	0.55	16.4	143.4
	B(2)	7.5	18.9	0.36		
$B_{12}As_2$	B(1)	16.3	5.2	0.54	14.8	138.3
	B(2)	9.7	14.2	0.91		
$B_{12}O_2$	B(1)	0.5	−12.1	0.11	14.2	105.4
	B(2)	17.7	13.9	0.93		

[a] correction term given by $\sigma(\mathbf{G}=\mathbf{0}) = -(8\pi/3)\chi$.[2]

Table S3: Parameters used for spectrum simulation (beside PAW calculated values) with relative intensity I, gaussian/lorentzian width w, approximated relative area A and occupied site multiplicity. Overall distribution of gaussian to lorentzian line type was assumed to be 50 %; See additional report files for more details.

compound	site	I [%]	w [ppm]	A [%]	occ. [%]
α-rB_{12}	B(1)	48	22	48	50
	B(2)	52	22	52	50
$B_{12}P_2$	B(1)	25	15	36	50
	B(2)	75	9	64	50

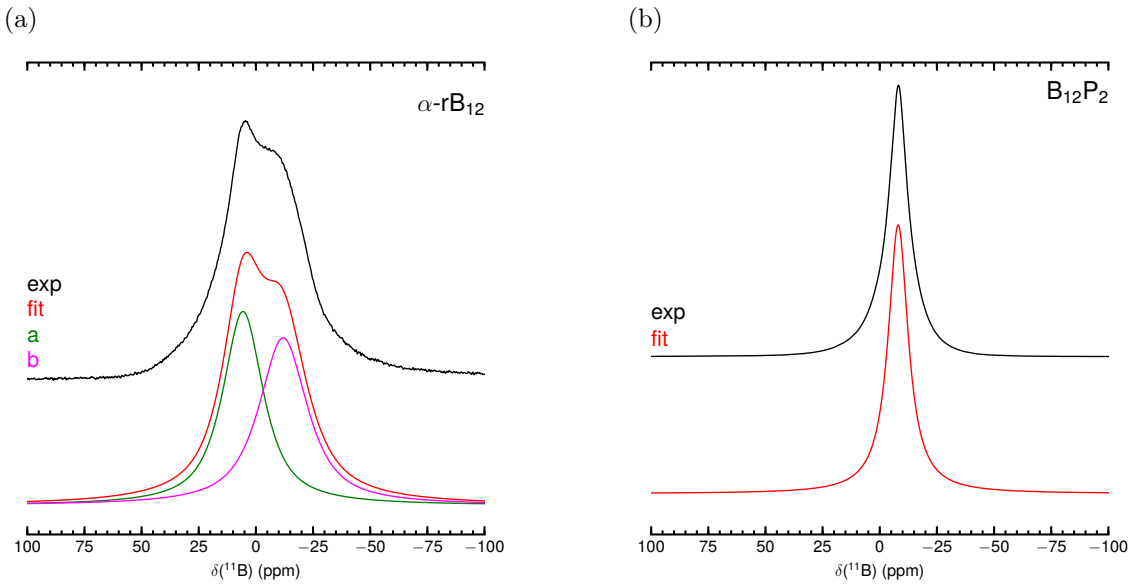

Figure S1: Central transition fits applying the "Gaus/Lor" model in the DMfit program[3] to the recorded spectra of (a) α-rB_{12} and (b) $B_{12}P_2$: For α-rB_{12} we obtain $I_a/I_b = 53.65\,\%/46.35\,\%$, the positions $\delta^a_{ctf} = 5.6$ ppm, $\delta^b_{ctf} = -11.9$ ppm, the widths $w_a = 21.1$ ppm, $w_b = 25.3$ ppm with the distributions of gaussian to lorentzian line type $x_a = 14\,\%$ and $x_b = 16\,\%$; For $B_{12}P_2$ the fit yields $\delta_{ctf} = -8.1$ ppm, the width $w = 10.6$ ppm with full lorentzian line type (see also report files).

Table S4: Euler angles α, β and γ in $^\circ$ correspond to the calculated magnetic shielding principal axis system relative to the principal axis system of the electric field gradient tensor obtained by MagresView.[4] Values follow the ZYZ convention according to the book of M. E. Rose, Elementary Theory of Angular Momentum, Wiley, New York, 1957.

		NC			PAW		
compound	site	α	β	γ	α	β	γ
α-rB_{12}	B(1)	−90	22	−4	−90	24	180
	B(2)	0	157	0	0	156	0
$B_{12}P_2$	B(1)	−90	90	−161	−90	90	19
	B(2)	180	126	−180	1	177	−179
$B_{12}As_2$	B(1)	−180	131	90	−180	131	90
	B(2)	90	94	0	154	90	−90
$B_{12}O_2$	B(1)	0	21	−90	0	23	−90
	B(2)	180	90	−156	180	90	−158

Table S5: Additional information of geometry related angles (Table 6 of the manuscript) in $^\circ$ with root-mean-square deviation (rmsd) θ_{rmsd} of θ_{av} and θ'_{rmsd} of θ'_{av}, respectively. φ is the kink angle between the exohedral bond and radial direction defined by the icosahedral center of mass. All values correspond to optimized geometry.

compound	site	φ	θ_{rmsd}	θ'_{rmsd}
α-rB_{12}	B(1)	7.19	0.48	0.38
	B(2)	8.64[a]	0.26	0.05
$B_{12}P_2$	B(1)	9.88	1.23	1.15
	B(2)	3.76	1.86	0.80
$B_{12}As_2$	B(1)	11.74	1.80	1.59
	B(2)	1.22	2.39	1.05
$B_{12}O_2$	B(1)	1.83	1.38	1.19
	B(2)	2.03	0.94	0.66
$(B_{12}H_{12})^{2-}$		0.00	0.00	0.00

[a] related to the center of intericosahedral 2e3c bond.

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