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Supporting Information

Weak Pnictogen Bond with Bismuth: Experimental Evidence Based on Bi—P Through-Space Coupling

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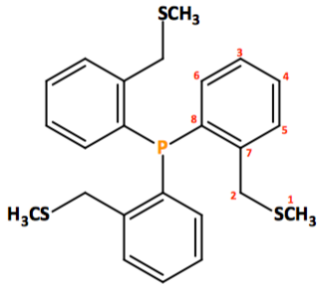
1. Materials and methods

All reactions were performed using standard Schlenk techniques under a dry nitrogen atmosphere. Sensitive chemicals were stored and weighed in a glove box under nitrogen atmosphere. All solvents were purified and dried by standard methods. All chemical reagents were used without further purification as received from commercial suppliers. The precise concentration of organolithium reagents was determined by titration prior to use. Solution NMR spectra were recorded on Bruker Avance 400 MHz or Varian VNMRS 600 MHz or VNMRS 700 MHz spectrometers. Deuterated solvents were further dried and purified prior to use following standard procedures. Chemical shifts are reported in ppm relative to $SiMe_4$ and 85% H_3PO_4 for ^{1}H, ^{13}C and ^{31}P, respectively; Coupling constants are given in Hz. Solid-state NMR spectra were recorded on a 400 MHz Bruker Avance III HD spectrometer. Elemental analyses were performed at the microanalysis laboratory of the Chemistry Department at Durham University and at the Science Centre at London Metropolitan University. X-ray diffraction experiments were carried out at T=120 K on a Bruker 3-circle D8 Venture diffractometer with a PHOTON 100 CMOS area detector, using Mo-K_α radiation (λ=0.71073 Å) from an Incoatec IμS microsource with focussing mirrors and a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat. The structures were solved by direct methods (SHELXS)[1] and refined by full-matrix least squares using SHELXL software[2] on OLEX2[3] platform.

2. Synthetic procedures

Tri(*o*-meththiomethylphenyl)phosphine ($P(C_6H_4$-*o*-$CH_2SCH_3)_3$ (PS_3, 1)



A) Synthesis of $(P(C_6H_4$-*o*-$CH_2M)_3$, M = Li/K

Tris (*o*-tolyl) phosphine (2.00 g, 6.58 mmol) and KO^{t}Bu (2.21 g, 19.7 mmol) were combined in hexane (40 mL) forming a cloudy suspension. *n*-BuLi (2.5 M in hexane, 11.2 mL, 26.3 mmol) was added dropwise at room temperature forming a deep red suspension, which was left to stir overnight at room temperature. The supernatant liquid was removed by cannula filtration and the obtained red solid was washed with toluene (3 × 50 mL) and dried *in vacuo*. This slightly pyrophoric material is insoluble in non-polar solvents (*e.g* hexane, toluene) and reacts with polar solvents (*e.g.* THF, dichloromethane, chloroform), thus analysis by NMR spectroscopy was not possible and the solid was directly employed as starting material for the next step.

B) Synthesis of $(P(C_6H_4$-*o*-$CH_2SCH_3)_3$ (**PS_3**)

Dimethyl disulfide (17.4 mL, 980 mmol) was added dropwise at −78 °C to a suspension of the metallated phosphane precursor (8.21 g, see part A) in toluene (50 mL). After stirring the reaction mixture for 2 h at −78 °C, the cooling bath was removed and the reaction mixture was stirred for 15 h at room temperature.

The reaction mixture was hydrolysed with water (20 mL) and the crude product was extracted with Et_2O (3 × 50 mL). The combined organic phases were washed with brine and dried over $MgSO_4$. The crude product (yellow oil) was purified by column chromatography (eluent: toluene) to yield the final product PS_3 as a colourless solid (3.10 g). Yield: 36% (calculated for step B assuming composition of precursor to be PK_3). Rf = 0.85: mono-substituted product, Rf = 0.68: bis-substituted product and Rf = 0.42: tri-substituted product (**1**, PS_3).

$^{31}P\{^{1}H\}$ NMR (243 MHz; $CDCl_3$, 298 K): δ (ppm) = −36.6 (s);

^{13}C NMR (151 MHz; $CDCl_3$, 298 K): δ (ppm) = 15.4 (d, $^{5}J_{PC}$ = 1.5 Hz, (1)), 36.9 (d, $^{3}J_{PC}$ = 24.5 Hz, (2)), 127.3 (s, (3)), 129.0 (s, (4)), 129.7 (d, $^{3}J_{PC}$ = 5.0 Hz, (5)), 134.4 (s, (6)), 135.2 (d, $^{2}J_{PC}$ = 12.0 Hz, (7)), 142.7 (d, $^{1}J_{PC}$ = 25.5 Hz, (8));

^{1}H NMR (600 MHz; $CDCl_3$, 298 K): δ (ppm) = 2.03 (9H, s, (1)), 3.95 (6H, s, (2)), 6.79-6.83 (3H, m, (6)), 7.11-7.16 (3H, m, (3)), 7.30-7.35 (3H, m, (4)), 7.45 (3H, m, (5));

$^{31}P\{^{1}H\}$ NMR (243 MHz; C_6D_6, 298 K): δ (ppm) = −36.9 (s);

^{13}C NMR (176 MHz; C_6D_6, 298 K): δ (ppm) = 15.4 (d, $^{5}J_{PC}$ = 1.6 Hz, (1)), 37.4 (d, $^{3}J_{PC}$ = 24.6 Hz, (2));

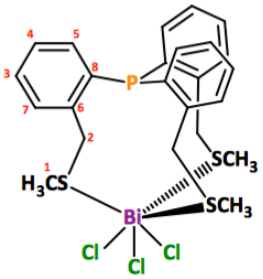
^{1}H NMR (700 MHz; C_6D_6, 298 K): δ (ppm) = 1.79 (9H, s, (1)), 3.93 (6H, s, (2));

Elemental analysis % (calc. %) $C_{24}H_{27}P_1S_3$: C 64.71 (65.12), 6.14 (6.15).

For a previously reported synthesis of **1** see[4]. Repetition of this procedure from PCl_3 and the organolithium derivative of *o*-bromo benzyl methyl sulfide delivered a mixture of products in the ^{31}P NMR spectrum.

Synthesis of $[PS_3BiCl_3]$ 2a

A solution of P(*o*-$CH_3SCH_2C_6H_4)_3$ (**1**) (0.50 g, 1.130 mmol) in toluene (5 mL) was added dropwise at room temperature to a suspension of $BiCl_3$ (0.32 g, 1.102 mmol) in toluene (5 mL). The reaction mixture was stirred for 30 minutes at room temperature forming a yellow suspension. After filtration, the isolated solid was washed with hexane (20 mL) and dried *in vacuo*, delivering the final product as a pale yellow solid (0.581 g, 76%). The synthesis can alternatively be performed in THF. Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of the yellow solid in MeCN.



$^{31}P\{^{1}H\}$ NMR (243 MHz; C_6D_6, 298 K): δ (ppm) = −37.0 (br s).

CP-MAS ^{31}P-NMR (162 MHz; 6 kHz spin-rate, 256 K): δ (ppm) = −37.0 (dectet, J_{TSC} = 2560 Hz);

For more details on the solid-state ^{31}P-NMR study see section below in this document.

^{1}H NMR (700 MHz; C_6D_6, 298 K): δ (ppm) = 1.95 (9H, s, (1)), 3.71 (6H, s, (2)), 6.79-6.82 (3H, m, (3)), 6.88-6.91 (3H, m, (7)), 6.94 - 6.97 (3H, m, (4)), 7.06 - 7.09 (3H, m, (5));

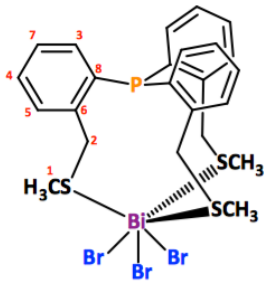
^{13}C NMR (176 MHz; C_6D_6, 298 K): δ (ppm) = 16.5 (s, (1)), 37.7 (d, $^3J_{PC}$ = 21 Hz, (2)), 127.5 (s, (3)), 129.4 (s, (4)), 130.5 (d, $^2J_{PC}$ = 5.5 Hz, (5)), 134.2 (d, $^2J_{PC}$ = 9.5 Hz, (6)), 134.3 (s, (7)), 142.5 (d, $^1J_{PC}$ = 25.5 Hz, (8));

Peak position of C3 (under solvent signal) can be identified from the HSQC NMR spectrum.

Elemental analysis % (calc. %) $BiCl_3C_{24}H_{27}P_1S_3$: C 39.21 (38.03), H 3.71 (3.59).

The low carbon value is presumably due to trace amounts of non-combustible solid residues.

Synthesis of [PS_3BiBr_3] 2b



A solution of P(*o*-$CH_3SCH_2C_6H_4)_3$ (**1**) (0.50 g, 1.130 mmol) in toluene (5 mL) was added dropwise at room temperature to a suspension of $BiBr_3$ (0.46 g, 1.020 mmol) in toluene (5 mL). The reaction mixture was subsequently stirred for 1 hour at room temperature to form a yellow suspension. Hexane was added to complete the precipitation of the product, which was filtered off, washed with hexane (20 mL) and dried *in vacuo*, delivering the final product as a pale yellow solid (0.485 g, 53%). The synthesis can alternatively be performed in THF. Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of the yellow solid in MeCN.

^{31}P{^{1}H} NMR (243 MHz; C_6D_6, 298 K): δ (ppm) = −38.7 (br s).

^{1}H NMR (600 MHz; C_6D_6, 298 K): δ (ppm) = 2.06 (9H, s, (1)), 3.74 (6H, s, (2)), 6.83-6.87 (3H, m, (3)), 6.92 - 6.95 (3H, m, (7)), 6.98-7.02 (3H, m, (4)), 7.08 - 7.11 (3H, m, (5));

^{13}C NMR (151 MHz; C_6D_6, 298 K): δ (ppm) = 17.5 (s, (1)), 38.4 (d, $^3J_{PC}$ = 20.0 Hz, (2)), 127.9 (s, (3)), 129.9 (s, (4)), 131.0 (d, $^3J_{PC}$ = 5.5 Hz, (5)), 134.2 (d, $^2J_{PC}$ = 9.0 Hz, (6)), 134.6 (s, (7)), 142.9 (d, $^1J_{PC}$ = 25.0 Hz, (8));

Peak position of C3 (under solvent signal) can be identified from the HSQC NMR spectrum.

Elemental analysis % (calc. %) $BiBr_3C_{24}H_{27}P_1S_3$: C 32.15 (32.34), H 3.03 (3.05).

Synthesis of [PS_3BiI_3] 2c

A solution of P(*o*-$CH_3SCH_2C_6H_4)_3$ (**1**) (0.13 g, 0.294 mmol) in THF (5 mL) was added dropwise at room temperature to a solution of BiI_3 (0.17 g, 0.294 mmol) in THF (5 mL). The reaction mixture was stirred for 15 hour at room temperature. Subsequently, the solvent was removed under reduced pressure

yielding a violet solid, which was dried in *in vacuo* (0.210 g, 70%). Single crystals suitable for X-ray diffraction analysis were obtained from a concentrated solution of the solid in MeCN.

$^{31}P\{^{1}H\}$ NMR (162 MHz; C_6D_6, 298 K): δ (ppm) = −39.2 (s);
^{1}H NMR (400 MHz; C_6D_6, 298 K): δ (ppm) = 1.87 (9H, s), 3.87 (6H, s), 6.9-6.85 (3 H_{arom}, m), 7.06 - 6.99 (6 H_{arom}, m), 7.29 - 7.24 (3 H_{arom}, m);
^{13}C NMR (100 MHz; C_6D_6, 298 K): δ (ppm) = 15.7 (s, 3 CH_3), 37.5 (d, $^{3}J_{PC}$ = 24.4 Hz, 3 CH_2), 127.6 (s, 1 $C_{arom.}$), 129.4 (s, 1 $C_{arom.}$), 130.3 (d, J_{PC} = 4.9 Hz, 1 $C_{arom.}$), 134.9 (s, 1 $C_{arom.}$), 135.3 (s, 1 $C_{arom.}$), 143.5 (d, J_{PC} = 25.2 Hz, 1 $C_{arom.}$).
Elemental analysis % (calc. %) $BiI_3C_{24}H_{27}P_1S_3$: C 28.04 (27.92), H 2.68 (2.64).

3. Supplementary solid-state NMR spectra

Comparing P-Bi atom distances with peak widths of resonances of solid-state ^{31}P NMR spectra

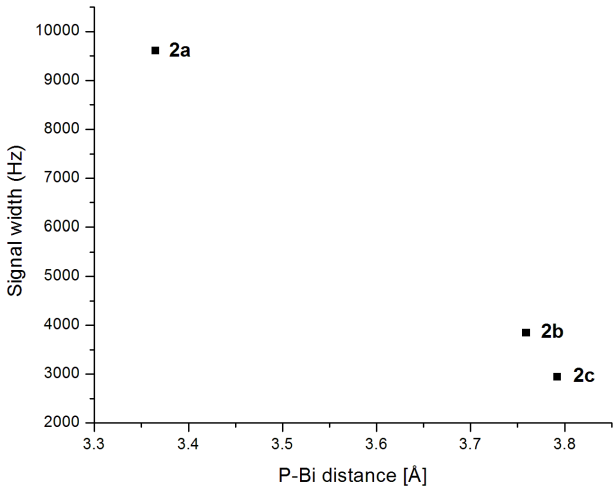


Figure S1: Almost linear correlation between the peak widths of solid-state ^{31}P NMR resonances of compounds **2** *vs.* the crystallographic P−Bi atom distances, illustrating their dependence on each other.

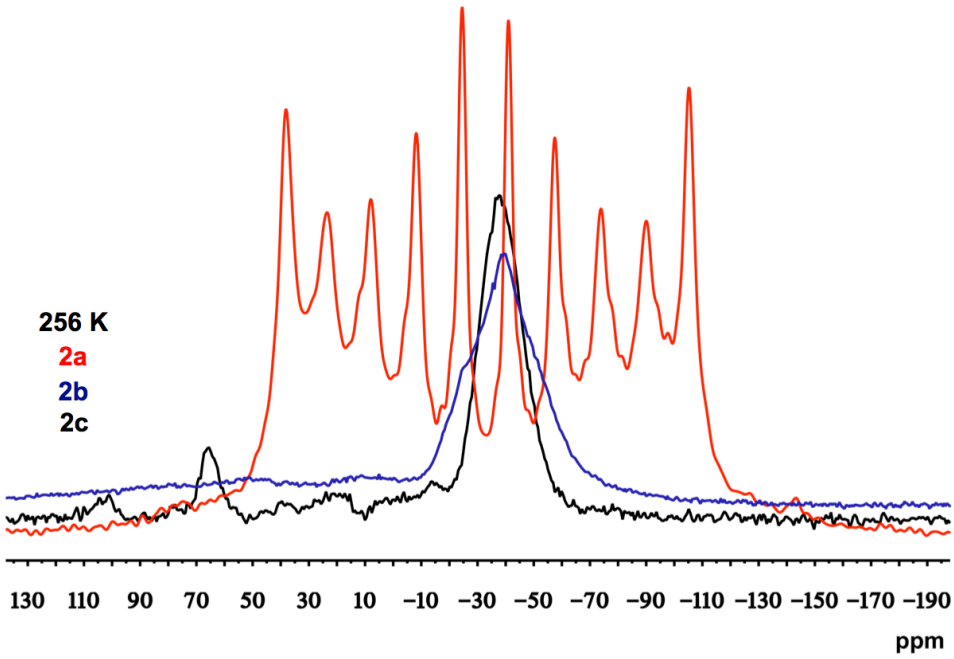


Figure S2: ^{31}P CP-MAS NMR spectra of solid samples of **2a** (red), **2b** (blue) and **2c** (black) measured at 256 K with spin rates of 6 kHz. **2c** contains and impurity at 65 ppm.

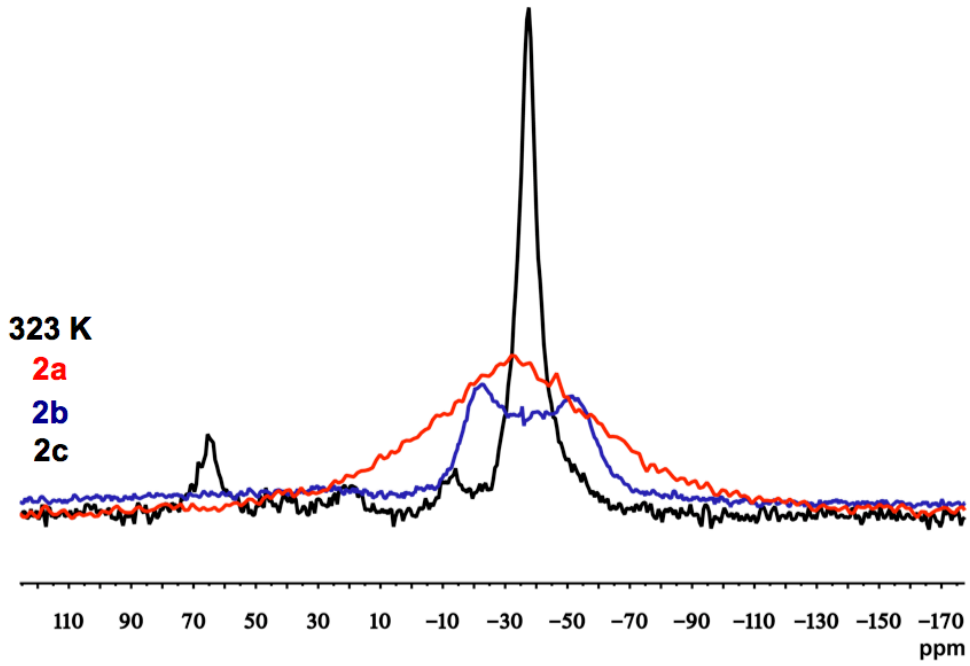


Figure S3: ^{31}P CP-MAS NMR spectra of solid samples of **2a** (red), **2b** (blue) and **2c** (black) measured at 323 K with spin rates of 6 kHz. **2c** contains and impurity at 65 ppm.

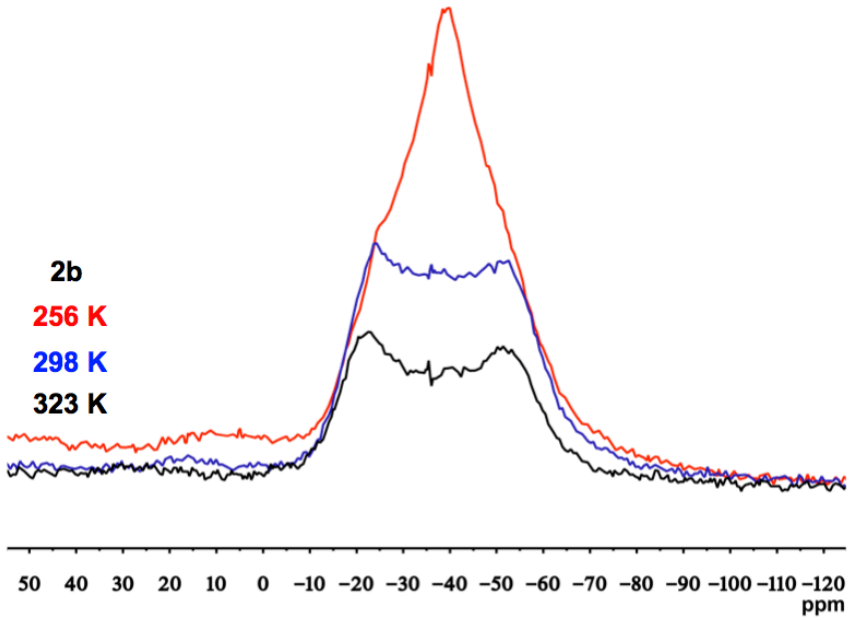


Figure S4: ^{31}P CP-MAS NMR spectrum of a solid sample of **2b** measured at 256 K (red), 298 K (blue) and 323 K (black) with spin rates of 6 kHz.

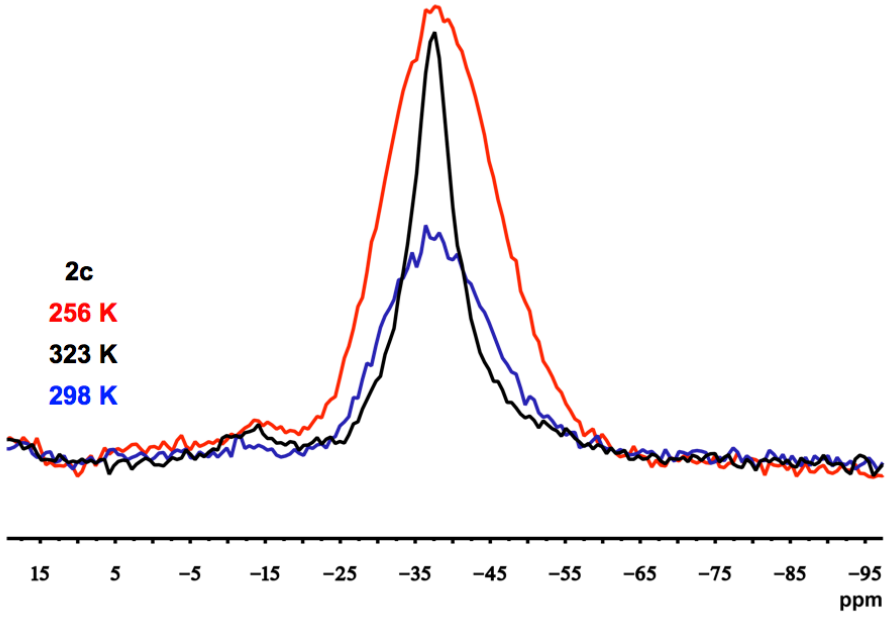


Figure S5: ^{31}P CP-MAS NMR spectrum of a solid sample of **2c** measured at 256 K, 298 K and 323 K with spin rates of 6 kHz.

4. Solution NMR spectra of 1 and 2a-c

4.1 Solution NMR spectra of 1 (PS_3)

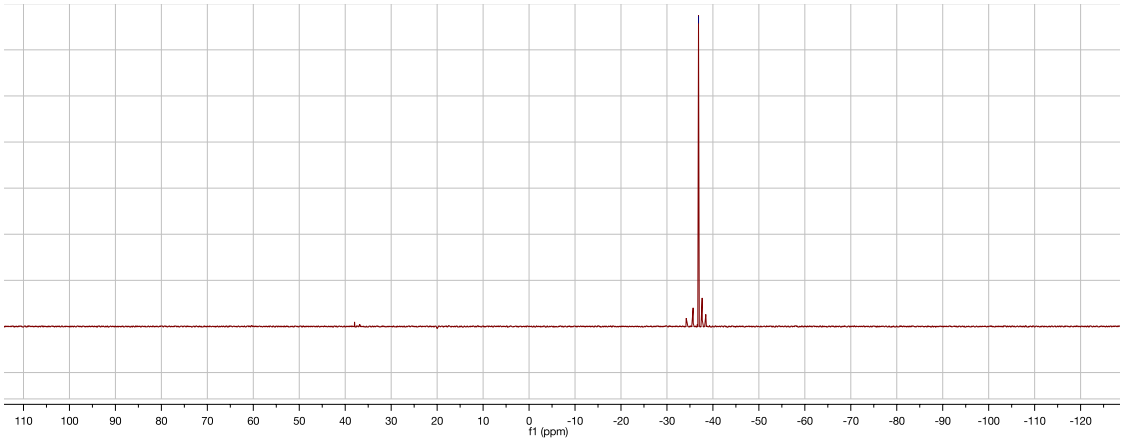


Figure S6: $^{31}P\{^{1}H\}$ NMR spectrum of **1** (243 MHz; C_6D_6, 298 K).

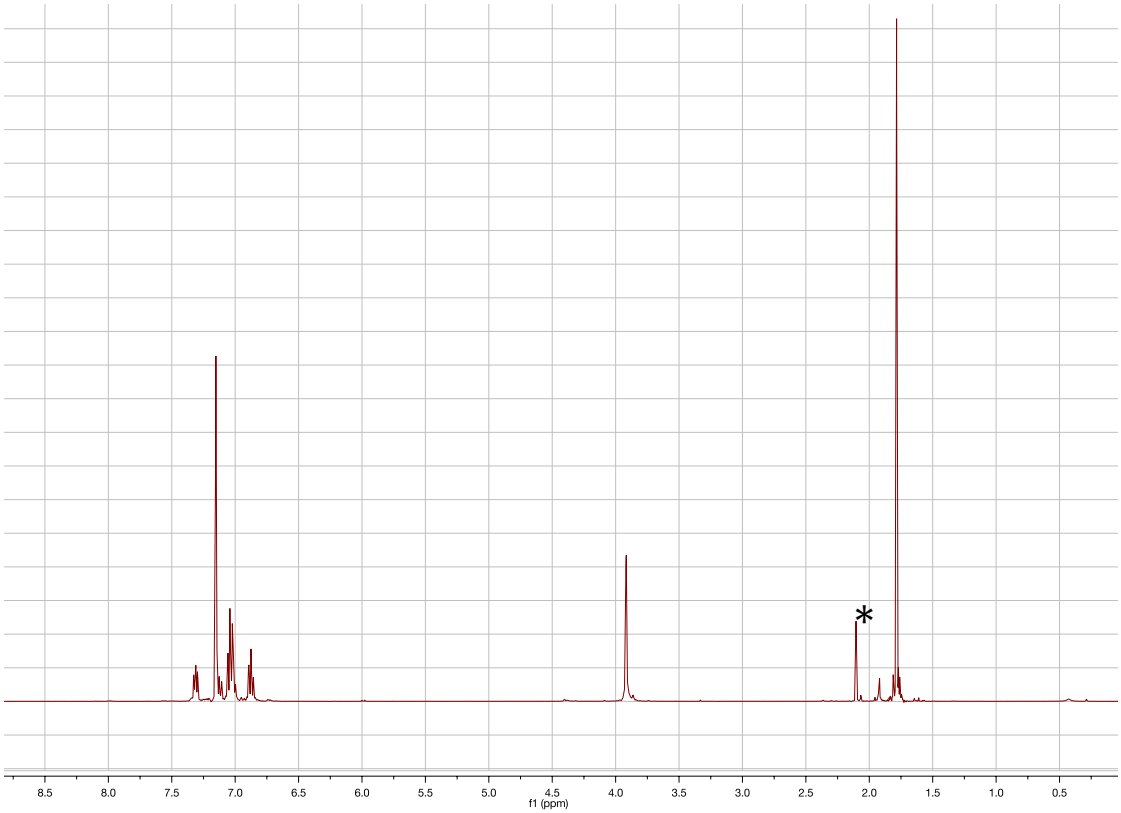


Figure S7: ^{1}H NMR spectrum of **1** (700 MHz; C_6D_6, 298 K). The sample contains traces of toluene, peaks marked with * and in the aromatic region.

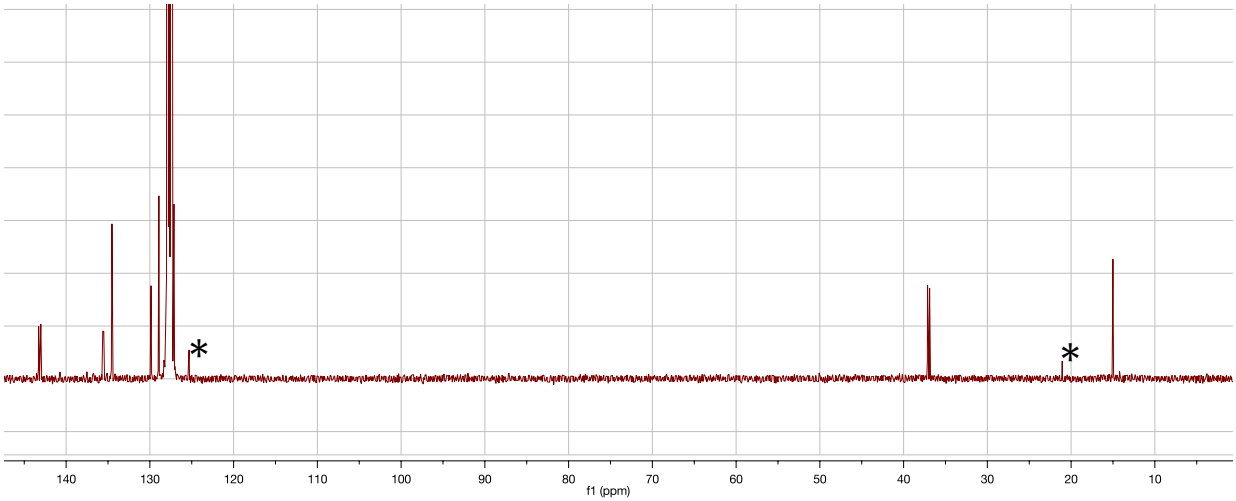


Figure S8: ^{13}C NMR spectrum of **1** (176 MHz; C_6D_6, 298 K). The sample contains traces of toluene, peaks marked with *. C_6D_6 signal cut off.

4.2 Solution NMR spectra of 2a

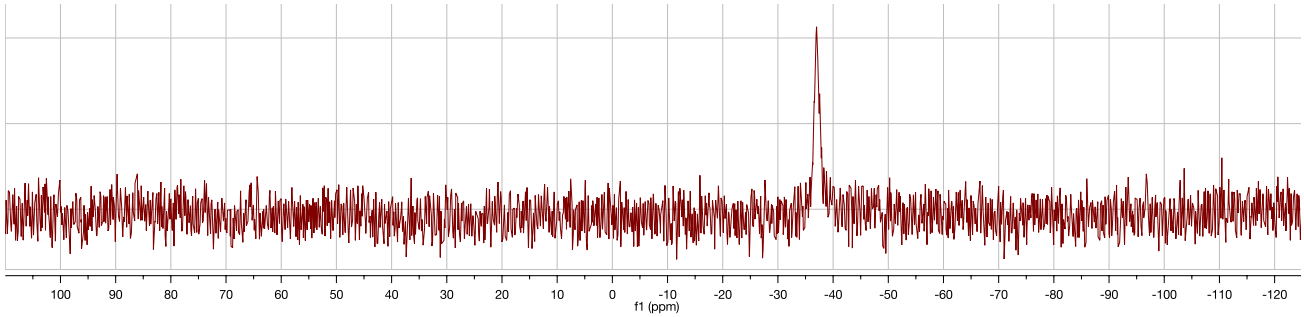


Figure S9: $^{31}P\{^1H\}$ NMR spectrum of **2a** (243 MHz; C_6D_6, 298 K).

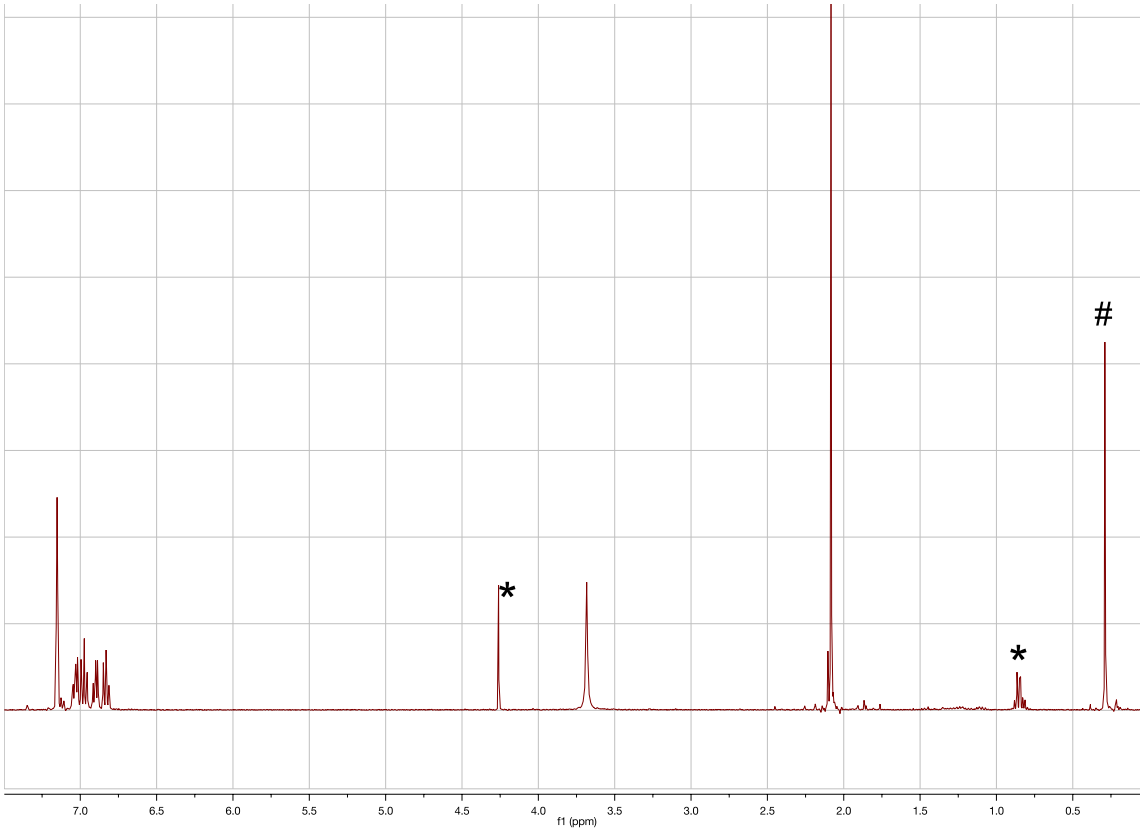


Figure S10: ^{1}H NMR spectrum of **2a** (700 MHz; C_6D_6, 298 K). Peaks corresponding to unknown impurity (likely from a plastic syringe) marked with *, grease impurity marked with #.

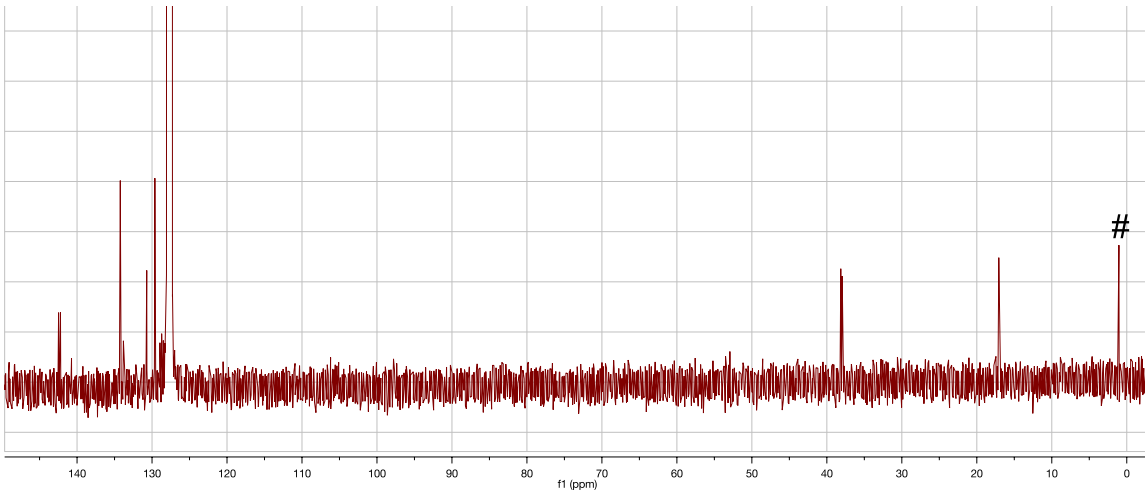


Figure S11: ^{13}C NMR spectrum of **2a** (176 MHz; C_6D_6, 298 K). Grease impurity marked with #. C_6D_6 signal cut off.

4.3 Solution NMR spectra of 2b

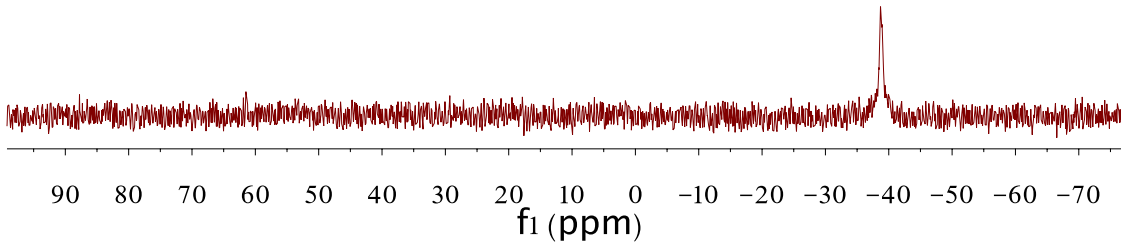


Figure S12: $^{31}P\{^{1}H\}$ NMR spectrum of **2b** (243 MHz; C_6D_6, 298 K).

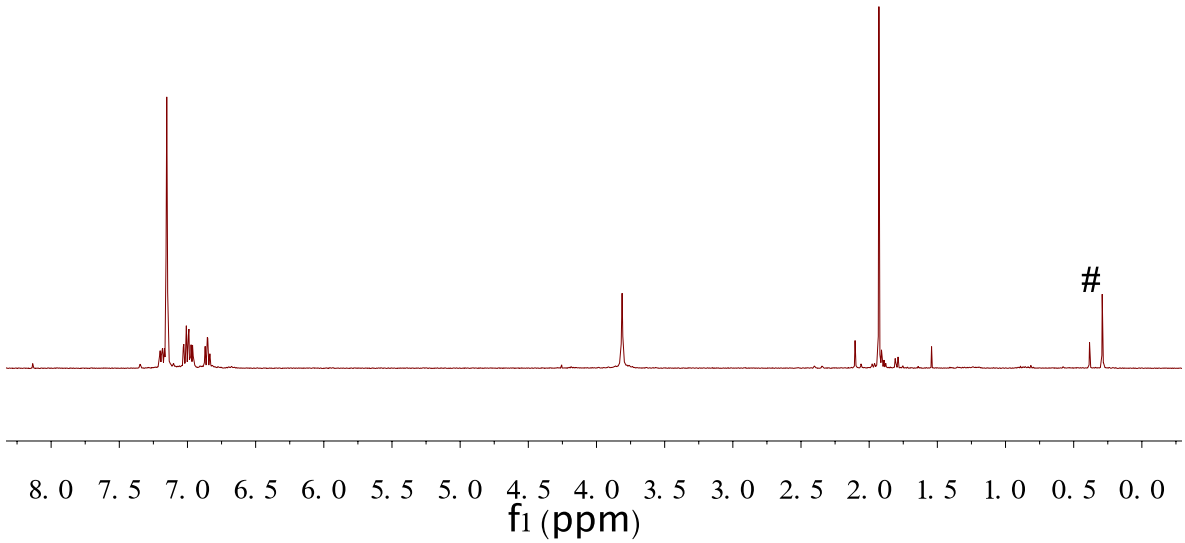


Figure S13: ^{1}H NMR spectrum of **2b** (600 MHz; C_6D_6, 298 K). Grease impurity marked with #.

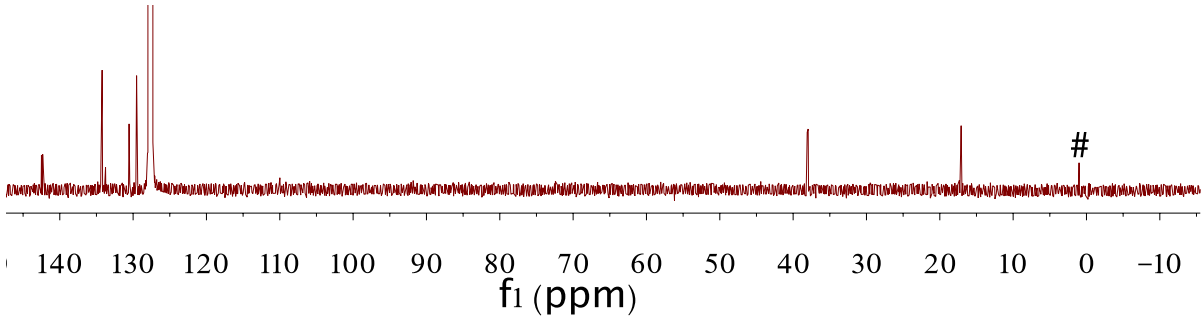


Figure S14: ^{13}C NMR spectrum of **2b** (151 MHz; C_6D_6, 298 K). Grease impurity marked with #. C_6D_6 signal cut off.

4.4 Solution NMR spectra of 2c

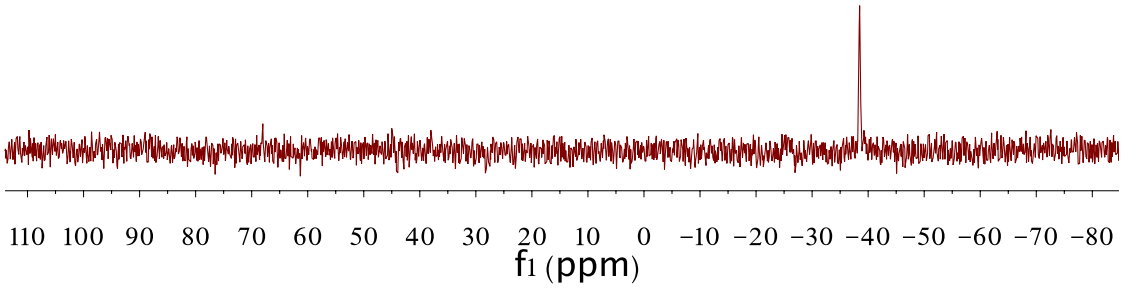


Figure S15: $^{31}P\{^{1}H\}$ NMR spectrum of **2c** (162 MHz; C_6D_6, 298 K).

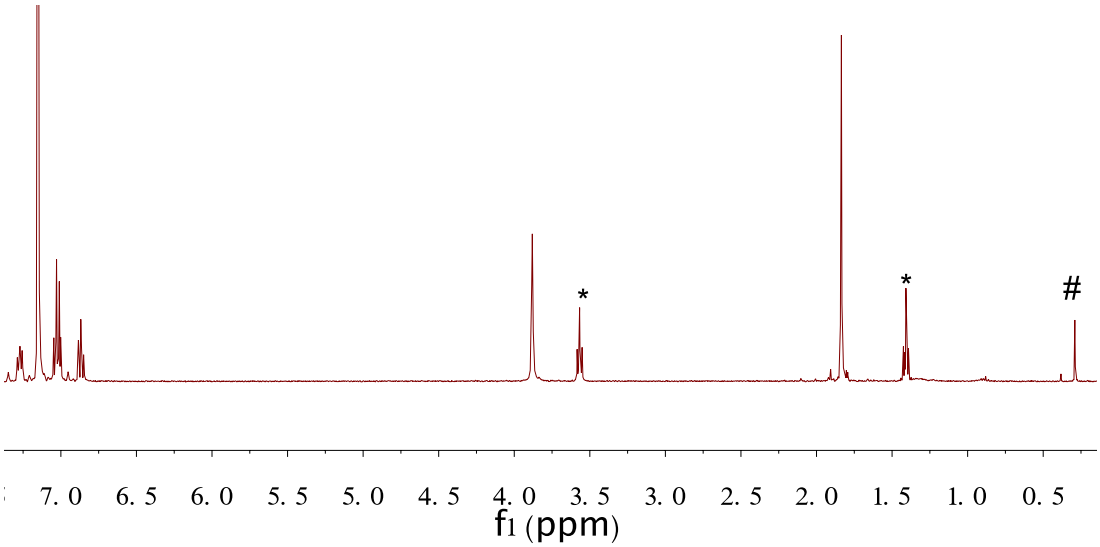


Figure S16: ^{1}H NMR spectrum of **2c** (400 MHz; C_6D_6, 298 K). The sample contains traces of THF (*) and grease (#). C_6D_6 signal cut off.

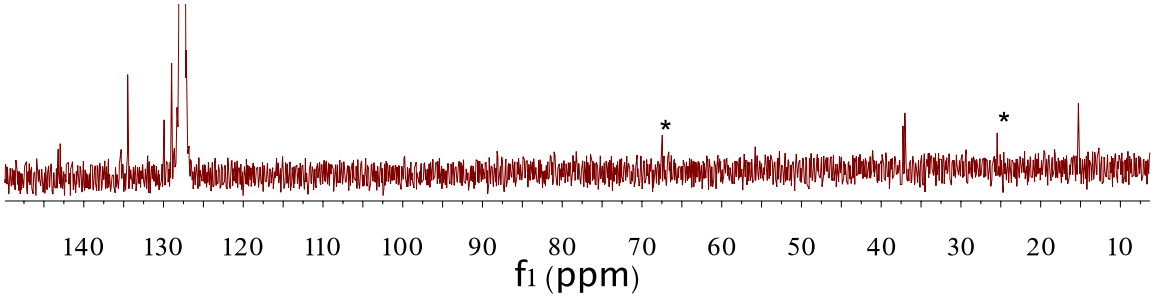


Figure S17: ^{13}C NMR spectrum of **2c** (100 MHz; C_6D_6, 298 K). The sample contains traces of THF (*). C_6D_6 signal cut off.

5. X-ray structure analyses

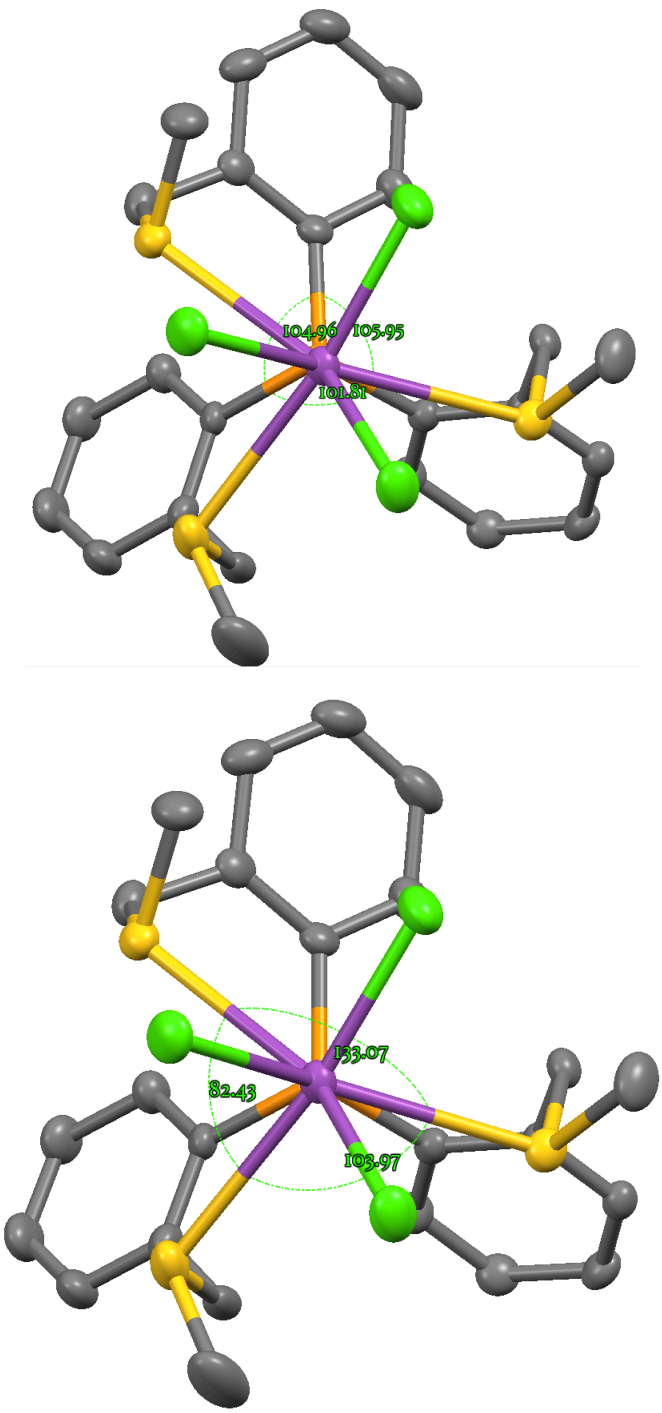


Figure S18: X-ray structure of **2a**, view along the Bi-P axis. Top: Angles around the P atom illustrating the symmetric geometry around the P centre. Bottom: Angles around the Bi atom illustrating the asymmetric geometry around the Bi centre.

Table S1 Crystal data and structure refinement for [PS_3BiCl_3] 2a	
Identification code	CCDC 1869085
Empirical formula	$C_{24}H_{27}BiCl_3PS_3$
Formula weight	757.93
Temperature/K	120
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	16.5636(8)
b/Å	12.1392(6)
c/Å	14.5910(7)
α/°	90
β/°	109.0940(16)
γ/°	90
Volume/$Å^3$	2772.4(2)
Z	4
$\rho_{calc}g/cm^3$	1.816
μ/mm^{-1}	6.945
F(000)	1472.0
Crystal size/mm^3	0.108 × 0.108 × 0.079
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.47 to 61.014
Index ranges	$-23 \leq h \leq 23$, $-17 \leq k \leq 17$, $-20 \leq l \leq 20$
Reflections collected	83475
Independent reflections	8458 [R_{int} = 0.0660, R_{sigma} = 0.0383]
Data/restraints/parameters	8458/0/295
Goodness-of-fit on F^2	1.114
Final R indexes [I>=2σ (I)]	R_1 = 0.0466, wR_2 = 0.1031
Final R indexes [all data]	R_1 = 0.0660, wR_2 = 0.1099
Largest diff. peak/hole / e $Å^{-3}$	3.92/-2.39

Table S2 Crystal data and structure refinement for $[PS_3BiBr_3]$ 2b	
Identification code	CCDC 1869086
Empirical formula	$C_{24}H_{27}BiBr_3PS_3$
Formula weight	891.31
Temperature/K	120.0
Crystal system	monoclinic
Space group	C2/c
a/Å	22.6375(10)
b/Å	13.2290(6)
c/Å	19.4080(8)
α/°	90
β/°	92.6399(18)
γ/°	90
Volume/Å^3	5806.0(4)
Z	8
ρ_{calc}g/cm^3	2.039
μ/mm^{-1}	10.486
F(000)	3376.0
Crystal size/mm^3	0.28 × 0.23 × 0.15
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.182 to 59.998
Index ranges	-31 ≤ h ≤ 31, -18 ≤ k ≤ 18, -27 ≤ l ≤ 27
Reflections collected	46844
Independent reflections	8465 [R_{int} = 0.0468, R_{sigma} = 0.0363]
Data/restraints/parameters	8465/0/292
Goodness-of-fit on F^2	1.014
Final R indexes [I>=2σ (I)]	R_1 = 0.0266, wR_2 = 0.0491
Final R indexes [all data]	R_1 = 0.0435, wR_2 = 0.0534
Largest diff. peak/hole / e Å^{-3}	0.80/-0.96

Table S3 Crystal data and structure refinement for $[PS_3BiI_3]$ 2c	
Identification code	CCDC 1869087
Empirical formula	$C_{24}H_{27}BiI_3PS_3$
Formula weight	1032.28
Temperature/K	120
Crystal system	monoclinic
Space group	C2/c
a/Å	23.1403(13)
b/Å	13.5350(7)
c/Å	19.9404(11)
α/°	90
β/°	94.303(2)
γ/°	90
Volume/Å^3	6227.8(6)
Z	8
ρ_{calc}g/cm^3	2.202
μ/mm^{-1}	8.901
F(000)	3808.0
Crystal size/mm^3	0.194 × 0.175 × 0.159
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.096 to 64.064
Index ranges	$-34 \leq h \leq 34$, $-20 \leq k \leq 20$, $-29 \leq l \leq 29$
Reflections collected	76044
Independent reflections	10821 [R_{int} = 0.0502, R_{sigma} = 0.0357]
Data/restraints/parameters	10821/0/296
Goodness-of-fit on F^2	1.039
Final R indexes [I>=2σ (I)]	R_1 = 0.0277, wR_2 = 0.0511
Final R indexes [all data]	R_1 = 0.0464, wR_2 = 0.0550
Largest diff. peak/hole / e Å^{-3}	1.40/-1.29

6. Computational details

The computations were performed with the Gaussian 09 program package[5a], the calculation of indirect spin-spin coupling constants was carried out with the ADF 2014 program. [5b] All structures were optimised using the ωB97XD and B3LYPD3 functionals, and second order Møller-Plessett perturbational method (MP2). The all valence cc-pVDZ basis set was applied for H, C, P, S, Cl and Br while for Bi and I the cc-pVDZ-PP basis sets were used, which include pseudopotentials for the modelling of relativistic effects. All the basis sets with pseudo potentials were obtained from the EMSL Basis Set Library.[6] At each of the optimised structures vibrational analysis was carried out to check that the stationary point located is a minimum of the potential energy hypersurface (no imaginary frequencies were obtained). The Wiberg Bond Indices and NPA charges were calculated with the NBO program version 3.1.[7] The AIM and NCI analyses were obtained with the Multiwfn code.[8] The molecular orbitals were plotted with Avogadro program.[9] The contributions of indirect spin-spin coupling constants have been determined at the PBE1/TZ2P level with scalar ZORA approximation on geometries optimized at ωB97XD/cc-pVDZ-PP.

The complex formation energies ($\Delta_f E$(**2**)) were calculated for the reactions **1**+BiX_3→**2** at different levels of theory. The values for a given complex obtained at the different levels are very similar (see Table S5). The basis set superposition error (BSSE) was estimated using counterpoise correction and the BSSE corrected values follow the same tendencies. The complex formation energies with a model ligand **1**' ($\Delta_f E$(**2**')) were also calculated: **1**' arises by the substitution of the P by a CH group. The energy corresponding to the S→Bi interaction was estimated from the complex formation energies with ligand **1**': ΔE_{int}(S→Bi)=1/3·$\Delta_f E$(**2**') from Table S5. The interaction energy for P→Bi donation was calculated as the following difference: ΔE_{int}(S→Bi)=$\Delta_f E$(**2**')–$\Delta_f E$(**2**). These interaction energies show no dependence on the method applied or the BSSE correction.

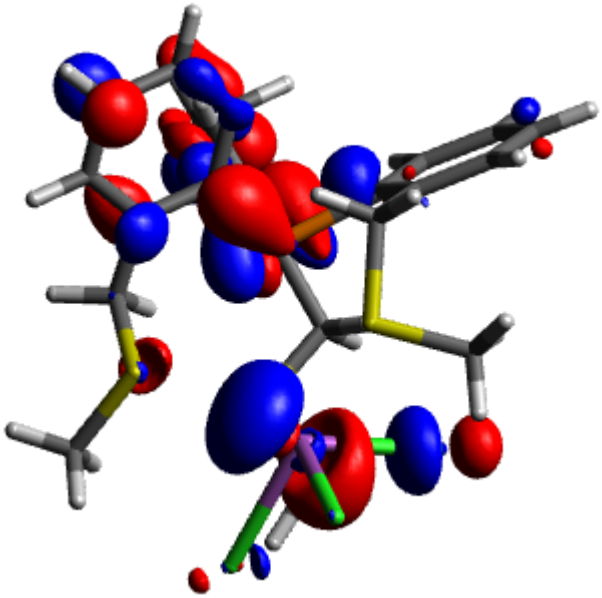


Figure S19: LUMO of **2a** at a contour value of 0.040 a.u. at the ωB97XD/cc-pVDZ(-PP) level of theory

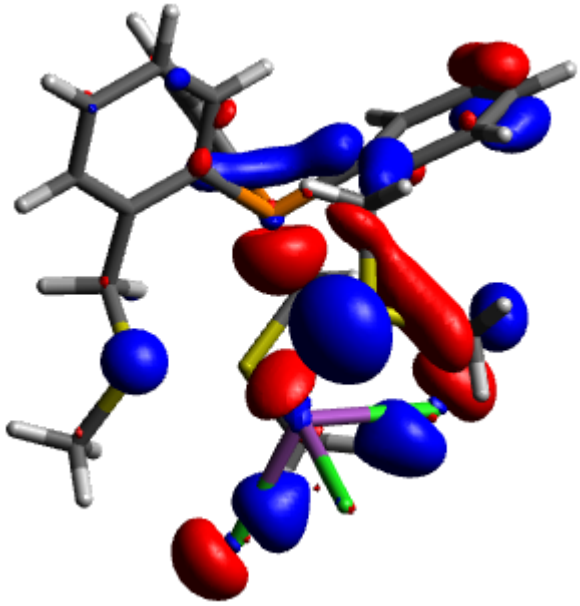


Figure S20: HOMO-16 of **2a** at a contour value of 0.040 a.u. at the ωB97XD/cc-pVDZ(-PP) level of theory.

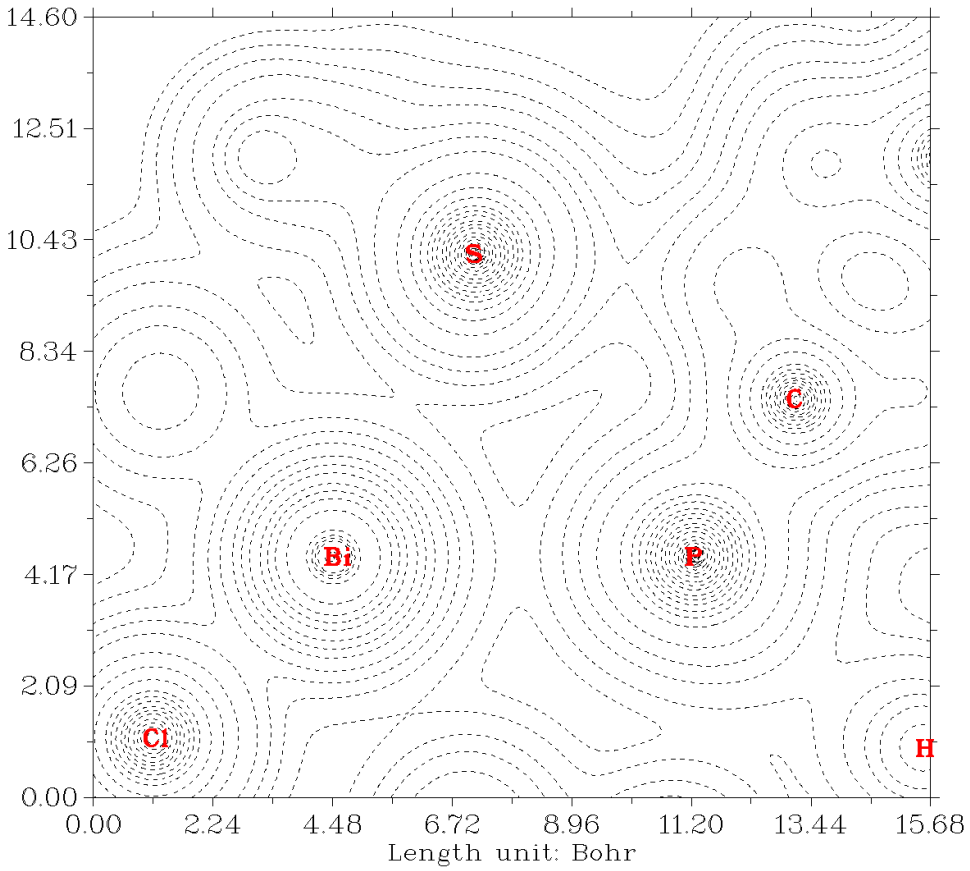


Figure S21: Counter Plot of the Virial field at the ωB97XD/cc-pVDZ(-PP) level of theory.

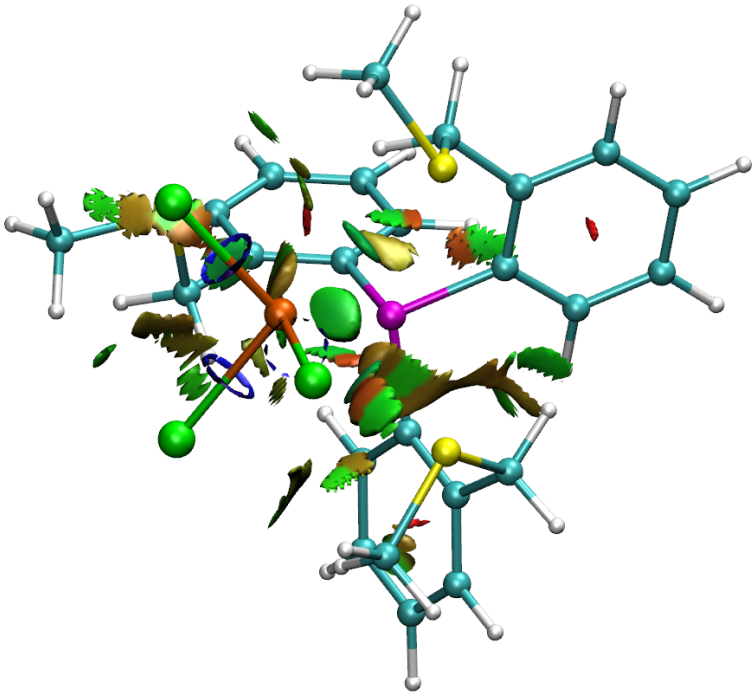


Figure S22: NCI (non-covalent interaction analysis) plot of **2a** at the ωB97XD/cc-pVDZ(-PP) level of theory at an RDG value of 0.35. Red and blue areas indicate repulsive and attractive interactions,

respectively. The green disc-shaped domain between the Bi (red) and the P (magenta) atoms indicates a weak interaction.

Table S4 Bond distances (d, Å) and electron densities at the bond critical points (ρ, a.u.), Lagrangian kinetic energy (G, a.u.), Hamiltonian kinetic energy at the bond critical point (K, a.u.), Laplacian of electron density at the bond critical point ($\nabla^2\rho$, a.u) and potential energy density at the bond critical point (V, a.u.) at Bi–P bond and at Bi–S bonds in complexes 2a-c at ωB97XD/cc-pvdz(-PP) level

Bi–P bond						
	d	ρ	G	K	$\nabla^2\rho$	V
2a	3.576	0.0131	0.00604	-0.000627	0.0267	-0.00542
2b	3.631	0.0121	0.00547	-0.000642	0.0244	-0.00482
2c	3.732	0.0103	0.00454	-0.000640	0.0207	-0.00390
Bi–S bonds						
	d	ρ	G	K	$\nabla^2\rho$	V
2a	3.272	0.0198	0.00996	-0.000274	0.0409	-0.00968
	3.232	0.0196	0.01051	-0.000442	0.0438	-0.01007
	3.313	0.0178	0.00913	-0.000419	0.0382	-0.00871
2b	3.250	0.0206	0.01037	-0.000209	0.0423	-0.01016
	3.250	0.0191	0.01016	-0.000484	0.0426	-0.00968
	3.332	0.0173	0.00884	-0.000451	0.0372	-0.00839
2c	3.278	0.0197	0.00984	-0.000294	0.0405	-0.00955
	3.375	0.0162	0.00819	-0.000525	0.0349	-0.00766
	3.315	0.0171	0.00895	-0.000619	0.0383	-0.00833

Table S5 Complex formation energies (Δ_fE, kcal/mol) for complexes 2a-c and 2'a-c and complex formation Gibbs free energies(Δ_fG, kcal/mol) for complexes 2a-c				
	Δ_fE(ωB97XD/cc-pvdz(-PP))	Δ_fE(B3LYPD3/cc-pvdz(-PP))	Δ_fE(MP2/cc-pvdz(-PP))	Δ_fG(ωB97XD/cc-pvdz(-PP))
2a	–32.9/–28.3*	–33.6	–32.5	-16.1
2'a	–23.3/–19.5*	–23.8	–21.7	-
2b	–31.9/–27.4*	–32.8	–33.2	-15.8
2'b	–23.0/–19.4*	–23.7	–22.6	-
2c	–29.4/–25.9*	–30.2	–31.7	-12.9
2'c	–21.6/–18.8*	–23.9	–22.3	-

*:Including correction for basis set superposition error (BSSE) using counterpoise correction

Table S6 Bond distances (*d*, Å) and Wiberg Bond Indices (WBI, –) for complexes 2a-c					
		ωB97XD/cc-pvdz(-PP)		B3LYPD3/cc-pvdz(-PP)	
		d	WBI	*d*	WBI
2a	Bi–Cl	2.537	0.651	2.567	0.657
	Bi–Cl	2.562	0.616	2.595	0.616
	Bi–Cl	2.566	0.615	2.598	0.616
	Bi–S	3.272	0.155	3.264	0.181
	Bi–S	3.313	0.142	3.309	0.162
	Bi–S	3.232	0.159	3.227	0.182
	Bi–P	3.576	0.085	3.571	0.097
2b	Bi–Cl	2.686	0.715	2.723	0.712
	Bi–Cl	2.710	0.680	2.747	0.674
	Bi–Cl	2.716	0.677	2.755	0.672
	Bi–S	3.250	0.161	3.217	0.193
	Bi–S	3.332	0.138	3.325	0.160
	Bi–S	3.250	0.155	3.249	0.176
	Bi–P	3.631	0.077	3.606	0.093
2c	Bi–Cl	2.930	0.762	2.971	0.745
	Bi–Cl	2.905	0.798	2.944	0.780
	Bi–Cl	2.918	0.765	2.955	0.747
	Bi–S	3.278	0.154	3.224	0.191
	Bi–S	3.315	0.138	3.310	0.160
	Bi–S	3.375	0.127	3.381	0.147
	Bi–P	3.732	0.062	3.701	0.076

Table S7 Bond distances (*d*, Å) for complexes 2a-c at MP2/cc-pvdz(-PP) level		
		d
2a	Bi–Cl	2.561
	Bi–Cl	2.564
	Bi–Cl	2.541
	Bi–S	3.189
	Bi–S	3.197
	Bi–S	3.232
	Bi–P	3.437
2b	Bi–Cl	2.719
	Bi–Cl	2.724
	Bi–Cl	2.700
	Bi–S	3.149
	Bi–S	3.201
	Bi–S	3.230
	Bi–P	3.445
2c	Bi–Cl	2.924
	Bi–Cl	2.937
	Bi–Cl	2.945
	Bi–S	3.145
	Bi–S	3.255
	Bi–S	3.231
	Bi–P	3.499

Table S8 Interaction energies ($E^{(2)}$, kcal/mol) from the second order perturbational theory on NBO basis for P→Bi and S→Bi donations at ωB97XD/cc-pvdz(-PP) level
These values were obtained as the sum of all donor-acceptor interactions above 0.05 kcal/mol from the lone pair at P or any lone pair at the S centres to any vacant orbital at the Bi centre.

		$E^{(2)}$
2a	P-Bi	19.8
	S1-Bi	43.8
	S2-Bi	42.7
	S3-Bi	48.9
2b	P-Bi	16.2
	S1-Bi	47.6
	S2-Bi	36.0
	S3-Bi	47.2
2c	P-Bi	12.3
	S1-Bi	36.1
	S2-Bi	32.9
	S3-Bi	29.6

Table S9 NPA partial charges (*q*, e) at ωB97XD/cc-pvdz(-PP) level
The net charge donation (Δ*q*, e) from the ligand towards the BiX_3 moiety is defined as the sum of partial charges in the ligand fragment.

		q
1	P	0.833
	S	0.164
	S	0.177
	S	0.173
$BiCl_3$	Bi	1.462
	Cl	-0.487
2a	Bi	1.360
	Cl	-0.544
	Cl	-0.571
	Cl	-0.571
	Δ*q*	0.326
	P	0.838
	S	0.209
	S	0.189
	S	0.217
$BiBr_3$	Bi	1.217
	Br	-0.406
2b	Bi	1.146
	Br	-0.471
	Br	-0.503
	Br	-0.504
	Δ*q*	0.332
	P	0.840
	S	0.216
	S	0.195
	S	0.220
BiI_3	Bi	0.850
	I	-0.284
2c	Bi	0.847
	I	-0.401
	I	-0.351
	I	-0.401
	Δ*q*	0.306
	P	0.839
	S	0.219
	S	0.218
	S	0.195

Total energies and Cartesian coordinates at the ωB97XD/cc-pVDZ(-PP) level

1

55

scf done: -2466.504433

C	-2.218550	2.084779	0.856857
C	-0.900920	1.792357	0.489272
C	0.028466	2.848069	0.369699
C	-0.385001	4.155285	0.637674
C	-1.699266	4.434418	1.005870
C	-2.619536	3.396099	1.110611
P	-0.315950	0.085658	0.074027
C	-1.889249	-0.894505	0.112883
C	-2.521218	-1.176688	-1.116277
C	-3.702313	-1.923517	-1.117373
C	-4.255221	-2.399918	0.069624
C	-3.625020	-2.132855	1.281382
C	-2.449895	-1.382713	1.297576
C	-1.926398	-0.734002	-2.430758
S	-0.602331	-1.901092	-2.947388
C	0.573958	-0.732193	-3.684674
C	1.446967	2.610176	-0.084893
S	1.529890	2.761170	-1.910637
C	3.145345	1.982239	-2.182518
C	0.469954	-0.445268	1.665381
C	1.237956	-1.630129	1.658607
C	1.835938	-2.054960	2.848663
C	1.712657	-1.319620	4.026622
C	0.975315	-0.140390	4.025711
C	0.355015	0.286673	2.851416
C	1.456849	-2.436302	0.402309
S	2.760709	-1.753356	-0.689068
C	4.219138	-2.000254	0.358455
H	3.134005	0.946948	-1.808990
H	3.949845	2.552924	-1.695223
H	3.321323	1.975824	-3.267078
H	0.830125	0.051462	-2.955349
H	0.168892	-0.282756	-4.602771
H	1.476100	-1.308726	-3.932008
H	5.081362	-1.614561	-0.202811
H	4.381490	-3.068312	0.568433
H	4.131347	-1.443725	1.302926
H	1.808053	1.606885	0.185100
H	2.124933	3.348469	0.368979
H	-1.468955	0.262704	-2.354781
H	-2.702432	-0.692517	-3.208055
H	0.566523	-2.476077	-0.242270
H	1.727852	-3.472981	0.652618
H	-2.946130	1.276646	0.946097
H	-3.653950	3.601239	1.392308
H	-2.002049	5.463859	1.205423
H	0.338721	4.968527	0.544130
H	-1.958407	-1.174838	2.250037
H	-4.045496	-2.506661	2.216749

H	-5.176979	-2.984200	0.044654
H	-4.191896	-2.141101	-2.069534
H	-0.234388	1.205633	2.861008
H	0.870955	0.446551	4.940032
H	2.193292	-1.671023	4.941408
H	2.412993	-2.983303	2.849339

1'

56

scf done: -2163.872189

C	-0.673374	-1.574210	1.881037
C	0.562362	-1.069477	1.430693
C	1.738639	-1.612116	1.959261
C	1.708421	-2.629653	2.909839
C	0.486840	-3.126413	3.353379
C	-0.690652	-2.597416	2.834688
C	0.611890	0.086494	0.429743
C	1.960470	0.163605	-0.286223
C	2.254799	-0.710248	-1.351625
C	3.513391	-0.651368	-1.957569
C	4.485233	0.246887	-1.525517
C	4.195808	1.110162	-0.473722
C	2.943343	1.063967	0.135003
C	1.230571	-1.667541	-1.905767
S	0.297121	-0.796280	-3.222541
C	-1.083474	-1.948714	-3.449318
C	-1.994651	-1.077299	1.350158
S	-2.618771	-2.276887	0.113723
C	-4.128265	-1.413074	-0.395236
C	0.236352	1.420957	1.073518
C	0.378898	1.620534	2.448711
C	0.094229	2.850662	3.040525
C	-0.339675	3.910818	2.252930
C	-0.489307	3.722862	0.880418
C	-0.213329	2.493248	0.274579
C	-0.426004	2.356199	-1.210791
S	-2.005522	1.542379	-1.663371
C	-3.186601	2.711157	-0.934180
H	-3.879049	-0.435890	-0.832037
H	-4.813812	-1.285562	0.455625
H	-4.618041	-2.036051	-1.156074
H	-1.611213	-2.098235	-2.496288
H	-0.732420	-2.911743	-3.848302
H	-1.765055	-1.485701	-4.175997
H	-4.190953	2.315724	-1.140900
H	-3.096026	3.705691	-1.396667
H	-3.051186	2.794837	0.153995
H	-1.922376	-0.091961	0.870968
H	-2.730217	-1.009200	2.166340
H	0.520540	-2.014479	-1.141817
H	1.723594	-2.551531	-2.336014
H	0.341194	1.734893	-1.692748
H	-0.401562	3.344442	-1.693093

H	2.701734	-1.229034	1.620141
H	2.643909	-3.031532	3.303336
H	0.448319	-3.922594	4.098645
H	-1.654704	-2.988153	3.169426
H	2.723377	1.745696	0.957916
H	4.942933	1.824275	-0.122815
H	5.461196	0.273622	-2.013008
H	3.728863	-1.325437	-2.790028
H	0.726085	0.795545	3.072555
H	0.219681	2.976528	4.117338
H	-0.559808	4.881557	2.700421
H	-0.827045	4.553687	0.255625
H	-0.148692	-0.116935	-0.338720

$BiCl_3$

4

scf done: -1595.433450

Bi	0.000000	0.000000	0.000000
Cl	0.000000	0.000000	2.458721
Cl	2.430697	0.000000	-0.373556
Cl	-0.433006	-2.394553	-0.363585

$BiBr_3$

4

scf done: -7937.400851

Bi	-0.009077	0.011160	-0.007129
Br	0.016363	-0.020550	2.600024
Br	2.558038	-0.020672	-0.466670
Br	-0.563139	-2.495177	-0.466893

BiI_3

4

scf done: -1102.196384

Bi	-0.015081	0.018697	-0.011393
I	0.021279	-0.024816	2.813398
I	2.755726	-0.027164	-0.556105
I	-0.683156	-2.673117	-0.550797

2a

59

scf done: -4061.990272

C	3.179501	-0.696597	-2.312863
C	2.405018	-1.164609	-1.236928
C	2.054649	-2.542356	-1.199670
C	2.497819	-3.377515	-2.237921
C	3.255261	-2.894464	-3.306425
C	3.599603	-1.544771	-3.340832
P	1.698735	0.057641	-0.013176
C	2.471469	-0.421399	1.617835
C	1.882747	0.027868	2.824768
C	2.446593	-0.377245	4.046093
C	3.570307	-1.200841	4.094755
C	4.157548	-1.636438	2.904268

C	3.609711	-1.246184	1.681077
C	0.671917	0.932970	2.869551
S	-0.896762	-0.053858	3.036464
C	-2.010424	1.218153	3.741009
C	1.271694	-3.186605	-0.080875
S	-0.567157	-2.968825	-0.062639
C	-1.051346	-3.651697	-1.685645
C	2.625799	1.635191	-0.413466
C	3.867573	1.926983	0.178238
C	4.538967	3.120572	-0.092061
C	3.972373	4.049963	-0.966595
C	2.739652	3.775051	-1.557438
C	2.049220	2.579766	-1.297367
C	0.709746	2.372015	-1.962190
S	-0.671585	2.856826	-0.817537
C	-1.912045	3.448818	-2.026251
Bi	-2.086850	-0.055799	-0.070986
Cl	-2.259178	-0.134113	-2.647707
Cl	-3.795948	1.773705	0.568892
Cl	-3.806591	-1.898173	0.375165
H	-2.144117	2.655310	-2.750045
H	-1.539045	4.354469	-2.526875
H	-2.812672	3.680599	-1.442464
H	-2.129795	2.070026	3.057736
H	-1.630350	1.543572	4.720817
H	-2.987748	0.731815	3.866278
H	-2.146550	-3.571672	-1.718098
H	-0.754294	-4.709124	-1.753186
H	-0.618545	-3.067509	-2.509172
H	0.542644	1.336599	-2.291740
H	0.626093	3.022299	-2.844149
H	0.594363	1.582851	1.987411
H	0.722802	1.575758	3.760961
H	1.575349	-2.813529	0.906666
H	1.453320	-4.271996	-0.084214
H	4.320038	1.210020	0.863762
H	5.503233	3.320506	0.380528
H	4.486523	4.987936	-1.187669
H	2.291705	4.504315	-2.237119
H	4.071002	-1.590077	0.753216
H	5.042003	-2.277172	2.924890
H	3.986928	-1.499304	5.059131
H	1.986034	-0.036603	4.976892
H	3.466105	0.354440	-2.350451
H	4.199999	-1.144646	-4.160809
H	3.577045	-3.572591	-4.099644
H	2.242591	-4.439714	-2.198162

2b

59

scf done: -10403.9561551

C	3.366670	-0.236660	-2.400621
C	2.673100	-0.907950	-1.385550

C	2.348562	-2.272727	-1.570721
C	2.725600	-2.897305	-2.764063
C	3.397301	-2.212784	-3.773300
C	3.722583	-0.875160	-3.586467
P	2.042599	0.051021	0.068220
C	2.830752	-0.761510	1.530918
C	2.272101	-0.564590	2.807949
C	2.852685	-1.208795	3.907332
C	3.970614	-2.021847	3.763509
C	4.535167	-2.201553	2.501733
C	3.967085	-1.573011	1.398862
C	1.065878	0.311550	3.052821
S	-0.475543	-0.689400	3.003676
C	-1.596882	0.405387	3.922412
C	1.642457	-3.116752	-0.539691
S	-0.164177	-2.890459	-0.382197
C	-0.706648	-3.312097	-2.058912
C	3.022301	1.625395	-0.025285
C	4.251604	1.767302	0.632058
C	4.967756	2.959161	0.572103
C	4.460352	4.034190	-0.152516
C	3.240632	3.905459	-0.807779
C	2.508955	2.714129	-0.758193
C	1.182069	2.655655	-1.469831
S	-0.174214	3.003014	-0.283066
C	-1.376125	3.785378	-1.396163
Bi	-1.587650	0.001961	0.028649
Br	-1.696026	0.258543	-2.666558
Br	-3.376704	1.823828	0.954430
Br	-3.444214	-1.923203	0.275108
H	-1.625331	3.108320	-2.224660
H	-0.970407	4.736258	-1.769261
H	-2.277412	3.968478	-0.797811
H	-1.643404	1.401646	3.462344
H	-1.281427	0.470184	4.973091
H	-2.593713	-0.051119	3.860262
H	-1.798782	-3.197261	-2.059596
H	-0.443416	-4.355388	-2.284859
H	-0.270835	-2.625784	-2.797629
H	0.994761	1.687936	-1.959685
H	1.140910	3.431728	-2.246260
H	0.991346	1.138144	2.331581
H	1.129043	0.751115	4.058745
H	2.023466	-2.941339	0.474570
H	1.809768	-4.181271	-0.760632
H	4.659963	0.934383	1.204575
H	5.923382	3.044456	1.091896
H	5.011077	4.974771	-0.206242
H	2.836333	4.750527	-1.369322
H	4.407901	-1.717748	0.409900
H	5.417976	-2.830287	2.375265
H	4.403517	-2.512110	4.636864
H	2.409472	-1.067952	4.895816

H	3.639634	0.810347	-2.266228
H	4.258458	-0.320936	-4.358680
H	3.667992	-2.727704	-4.696322
H	2.484276	-3.954005	-2.901444

2c

59

scf done: -3568.747709

C	2.936642	2.706962	-0.667960
C	3.436630	1.614355	0.068028
C	4.657788	1.751187	0.741087
C	5.378415	2.941081	0.692663
C	4.884547	4.019138	-0.036639
C	3.672814	3.895680	-0.707658
P	2.444141	0.045683	0.144938
C	3.226999	-0.782571	1.602305
C	2.655231	-0.608145	2.876288
C	3.234285	-1.258127	3.973217
C	4.363061	-2.055804	3.829206
C	4.939093	-2.215538	2.569734
C	4.372762	-1.580857	1.469685
C	1.434188	0.247687	3.118040
S	-0.093888	-0.771765	3.027044
C	-1.213694	0.240115	4.037591
C	1.617799	2.652090	-1.393944
S	0.243530	3.000484	-0.226577
C	-0.866668	3.932270	-1.318869
C	3.080788	-0.906832	-1.311447
C	3.779925	-0.233256	-2.321078
C	4.144030	-0.869496	-3.505752
C	3.823084	-2.207667	-3.696092
C	3.146204	-2.894642	-2.691915
C	2.759067	-2.271567	-1.501011
C	2.043275	-3.115374	-0.476704
S	0.231070	-2.907966	-0.361706
C	-0.266910	-3.389718	-2.035378
Bi	-1.286696	0.007193	0.074813
I	-3.267262	-2.091032	0.408819
I	-1.448031	0.284839	-2.825959
I	-3.192833	1.989997	1.085794
H	-1.147101	3.326131	-2.191561
H	-0.380407	4.867916	-1.628749
H	-1.765918	4.156851	-0.731701
H	-1.278271	1.266091	3.650379
H	-0.881813	0.235632	5.085339
H	-2.205788	-0.224975	3.960861
H	-1.359992	-3.289541	-2.069880
H	0.012121	-4.436814	-2.222016
H	0.180128	-2.724871	-2.786969
H	1.437219	1.685642	-1.887830
H	1.586220	3.428159	-2.170473
H	1.360881	1.085587	2.409886
H	1.475437	0.669374	4.132579

H	2.399189	-2.925891	0.543822
H	2.227350	-4.180013	-0.683716
H	5.056647	0.916580	1.317644
H	6.327506	3.022130	1.224978
H	5.439363	4.957777	-0.081733
H	3.278861	4.742774	-1.273609
H	4.822194	-1.710089	0.482470
H	5.829902	-2.832898	2.443261
H	4.795230	-2.550452	4.700473
H	2.781518	-1.134012	4.959621
H	4.051958	0.813551	-2.182999
H	4.683948	-0.313301	-4.273734
H	4.101530	-2.721182	-4.617594
H	2.908880	-3.952009	-2.831490

2'a

60

scf done: -3759.342830

C	-2.040346	-0.576292	2.494794
C	-2.726088	0.205039	1.547752
C	-3.739365	1.062898	1.992997
C	-4.070272	1.159638	3.340875
C	-3.384170	0.391638	4.278327
C	-2.377360	-0.463990	3.848775
C	-2.417615	0.084470	0.054904
C	-2.824750	1.345708	-0.710543
C	-2.082949	2.535968	-0.588641
C	-2.492772	3.672217	-1.296004
C	-3.625549	3.659207	-2.100944
C	-4.371819	2.488545	-2.206073
C	-3.970013	1.348909	-1.516133
C	-0.856021	2.659911	0.285145
S	0.670598	2.645088	-0.741900
C	1.781725	3.651124	0.288645
C	-0.921715	-1.520837	2.125334
S	0.693538	-0.723912	2.496510
C	1.705420	-2.163815	2.947261
C	-3.022931	-1.185102	-0.550363
C	-4.052980	-1.867550	0.102989
C	-4.639022	-3.006807	-0.446997
C	-4.200842	-3.484308	-1.676343
C	-3.180397	-2.809919	-2.341885
C	-2.582210	-1.667821	-1.800764
C	-1.486287	-1.005651	-2.592730
S	0.210710	-1.458270	-2.070661
C	0.162967	-3.265784	-2.010737
Bi	2.411212	-0.024065	-0.169291
Cl	3.816047	0.995525	-1.993636
Cl	3.355967	-2.392268	-0.220701
Cl	3.792722	0.882594	1.742946
H	1.750982	-2.892768	2.127641
H	1.308776	-2.620383	3.864569
H	2.716754	-1.776759	3.131537

H	1.905167	3.216382	1.290028
H	1.397546	4.678430	0.353756
H	2.755348	3.651208	-0.220259
H	1.155635	-3.568793	-1.650652
H	-0.007541	-3.680534	-3.013927
H	-0.609900	-3.618685	-1.314669
H	-0.949054	-1.837200	1.074163
H	-0.977820	-2.425959	2.747276
H	-0.796655	1.882952	1.057464
H	-0.872244	3.630970	0.801233
H	-1.511341	0.090106	-2.513929
H	-1.583346	-1.257939	-3.657981
H	-4.281355	1.669631	1.266585
H	-4.863859	1.838828	3.656650
H	-3.628064	0.461155	5.339508
H	-1.825475	-1.060250	4.579264
H	-4.557784	0.434710	-1.607774
H	-5.269070	2.458419	-2.826637
H	-3.924404	4.559623	-2.639747
H	-1.901961	4.587300	-1.210084
H	-4.412055	-1.498946	1.064395
H	-5.442437	-3.514474	0.089485
H	-4.650770	-4.373235	-2.121094
H	-2.836708	-3.175614	-3.312707
H	-1.324851	-0.011122	-0.050304

2'b

60

scf done: -10101.3097278

C	-2.587329	-0.619928	2.463376
C	-3.269241	0.177711	1.527466
C	-4.292616	1.019043	1.980848
C	-4.638516	1.082396	3.326967
C	-3.957250	0.297171	4.253751
C	-2.939644	-0.541360	3.815838
C	-2.944274	0.090622	0.036151
C	-3.348079	1.365248	-0.708235
C	-2.614630	2.556099	-0.548952
C	-3.021987	3.706417	-1.234280
C	-4.143639	3.705632	-2.054959
C	-4.880068	2.533049	-2.199630
C	-4.480918	1.379811	-1.530844
C	-1.395884	2.661812	0.338010
S	0.140993	2.641807	-0.674626
C	1.221194	3.704521	0.330983
C	-1.458466	-1.547516	2.082243
S	0.150702	-0.757705	2.495738
C	1.137088	-2.205572	2.976197
C	-3.539721	-1.167128	-0.601260
C	-4.591247	-1.850855	0.014789
C	-5.172680	-2.975594	-0.568961
C	-4.706895	-3.436773	-1.794445
C	-3.662683	-2.761805	-2.421904

C	-3.069203	-1.634211	-1.846404
C	-1.941275	-0.970391	-2.590582
S	-0.271860	-1.446775	-2.005472
C	-0.329055	-3.254793	-2.035339
Bi	1.962278	0.004742	-0.115845
Br	3.386231	1.173338	-2.046710
Br	3.035451	-2.466063	-0.221569
Br	3.368687	0.971293	1.941311
H	1.188122	-2.941346	2.162812
H	0.716865	-2.652477	3.887881
H	2.149759	-1.831631	3.179408
H	1.342552	3.304838	1.346973
H	0.814639	4.724936	0.357945
H	2.199336	3.708805	-0.169298
H	0.650742	-3.584242	-1.663074
H	-0.472272	-3.618102	-3.062544
H	-1.124254	-3.636234	-1.380675
H	-1.468659	-1.832378	1.021893
H	-1.518237	-2.470589	2.676677
H	-1.350636	1.877377	1.103547
H	-1.408067	3.628283	0.862338
H	-1.961116	0.124603	-2.498842
H	-1.998804	-1.208867	-3.661969
H	-4.830506	1.638512	1.262068
H	-5.440057	1.748825	3.649838
H	-4.213420	0.340056	5.313506
H	-2.391297	-1.150344	4.538484
H	-5.060845	0.464238	-1.652814
H	-5.767274	2.511927	-2.834853
H	-4.440809	4.616834	-2.576264
H	-2.438509	4.622913	-1.118641
H	-4.971129	-1.494581	0.972883
H	-5.994058	-3.484776	-0.061891
H	-5.153022	-4.314209	-2.265141
H	-3.295952	-3.115622	-3.388732
H	-1.850285	0.000950	-0.057756

2'c

60

scf done: -3266.103055

C	-3.079717	-1.238474	2.181230
C	-3.807052	-0.262335	1.475803
C	-4.903168	0.341444	2.102954
C	-5.291951	-0.015900	3.390555
C	-4.581199	-0.994516	4.080669
C	-3.481606	-1.590515	3.474576
C	-3.459486	0.081875	0.026726
C	-3.872943	1.510250	-0.331155
C	-3.098863	2.608793	0.088204
C	-3.533826	3.905080	-0.207201
C	-4.715638	4.133810	-0.902776
C	-5.479752	3.048431	-1.322449
C	-5.056301	1.753252	-1.037204

C	-1.784726	2.446519	0.811024
S	-0.380918	2.460427	-0.390254
C	0.667307	3.781693	0.284776
C	-1.831381	-1.876361	1.625377
S	-0.348059	-0.955137	2.225583
C	0.591486	-2.267928	3.055088
C	-4.028235	-0.948101	-0.951957
C	-5.117227	-1.749758	-0.600624
C	-5.675382	-2.657211	-1.500515
C	-5.146053	-2.776704	-2.779986
C	-4.057218	-1.986781	-3.141712
C	-3.486811	-1.075735	-2.248147
C	-2.284846	-0.291689	-2.702237
S	-0.700777	-0.990633	-2.097023
C	-0.765331	-2.705283	-2.669993
Bi	1.675218	0.005681	-0.080668
I	3.223190	1.409012	-2.089020
I	2.793836	-2.681721	-0.286033
I	3.024659	1.023641	2.263130
H	0.851007	-3.067047	2.347914
H	0.016007	-2.657377	3.905894
H	1.514929	-1.798257	3.420217
H	0.965192	3.554290	1.317371
H	0.140977	4.744068	0.226058
H	1.564004	3.811768	-0.349697
H	0.161046	-3.171821	-2.307054
H	-0.788438	-2.745448	-3.767929
H	-1.634426	-3.228294	-2.248500
H	-1.803204	-1.904408	0.528292
H	-1.728840	-2.908313	1.986895
H	-1.734260	1.532624	1.416484
H	-1.616704	3.290976	1.492481
H	-2.286027	0.745664	-2.337370
H	-2.237635	-0.252213	-3.799471
H	-5.467808	1.106288	1.567945
H	-6.152884	0.470608	3.851969
H	-4.875954	-1.287127	5.089714
H	-2.908842	-2.345237	4.019171
H	-5.661178	0.907943	-1.368815
H	-6.409839	3.206308	-1.870841
H	-5.035383	5.154651	-1.117440
H	-2.924762	4.753319	0.115006
H	-5.544959	-1.662504	0.398690
H	-6.526699	-3.267802	-1.194783
H	-5.572801	-3.481224	-3.495737
H	-3.633129	-2.078464	-4.144687
H	-2.366139	0.028437	-0.073437

Total energies and Cartesian coordinates at the B3LYPD3/cc-pVDZ(-PP) level

1

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scf done: -2466.919594

C	-0.526149	2.864213	0.165912
C	-1.248994	1.659836	0.355765
C	-2.611372	1.729469	0.687163
C	-3.257372	2.961482	0.831179
C	-2.542786	4.146945	0.651085
C	-1.186188	4.090430	0.321627
P	-0.350482	0.056155	0.061848
C	-1.718278	-1.207462	0.164578
C	-2.246311	-1.718180	-1.046256
C	-3.259538	-2.685655	-0.991631
C	-3.747396	-3.156573	0.230178
C	-3.221438	-2.658958	1.423852
C	-2.214521	-1.689517	1.385580
C	-1.710246	-1.288552	-2.391695
S	-0.156255	-2.229134	-2.795230
C	0.842760	-0.888311	-3.539956
C	0.926750	2.863066	-0.242605
S	1.053738	2.855918	-2.091564
C	2.807296	2.355361	-2.241076
C	0.513362	-0.212763	1.690782
C	0.275027	0.592083	2.815236
C	0.969359	0.388570	4.012652
C	1.908448	-0.639273	4.101284
C	2.152909	-1.447918	2.987203
C	1.479770	-1.246980	1.773082
C	1.829135	-2.119137	0.592004
S	3.023768	-1.330131	-0.584607
C	4.505586	-1.248994	0.481570
H	2.959190	1.369887	-1.773278
H	3.473571	3.102722	-1.781464
H	3.032612	2.288984	-3.315827
H	0.910201	-0.042141	-2.839567
H	0.418854	-0.559845	-4.501412
H	1.846924	-1.305259	-3.705155
H	5.301114	-0.779126	-0.115549
H	4.832908	-2.256746	0.785005
H	4.316382	-0.635549	1.375869
H	1.461648	1.976765	0.128506
H	1.440095	3.757010	0.145055
H	-1.450303	-0.220554	-2.408259
H	-2.454903	-1.471207	-3.180732
H	0.963419	-2.358351	-0.042097
H	2.270177	-3.070137	0.928930
H	-3.178321	0.809541	0.835957
H	-4.318797	2.989974	1.088791
H	-3.037633	5.114210	0.764171
H	-0.623463	5.015724	0.172128
H	-1.806769	-1.302348	2.321365
H	-3.591970	-3.021842	2.385445

H	-4.534442	-3.914072	0.246997
H	-3.665717	-3.081200	-1.926363
H	-0.468808	1.388799	2.756586
H	0.766053	1.028847	4.874296
H	2.450982	-0.815240	5.032989
H	2.885328	-2.256704	3.057243

1'

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scf done: -2164.278054

C	0.470923	1.878832	2.297997
C	0.285597	1.547478	0.947661
C	-0.185258	2.552458	0.064070
C	-0.428681	3.840844	0.567539
C	-0.236728	4.154890	1.914728
C	0.212367	3.163581	2.785667
C	0.637766	0.141124	0.431652
C	1.989598	0.117795	-0.305179
C	2.261992	-0.861347	-1.291833
C	3.517071	-0.871579	-1.920468
C	4.508076	0.053791	-1.591754
C	4.243825	1.016838	-0.617619
C	2.996904	1.042302	0.012715
C	1.237847	-1.878329	-1.733916
S	0.281095	-1.183916	-3.160850
C	-0.997896	-2.477998	-3.343448
C	-0.445034	2.301865	-1.401565
S	-2.107714	1.572101	-1.783591
C	-3.207876	2.939973	-1.274075
C	0.562352	-0.926157	1.539572
C	1.734163	-1.405446	2.148982
C	1.696918	-2.348102	3.178546
C	0.468623	-2.835957	3.626639
C	-0.704300	-2.370050	3.034278
C	-0.682400	-1.421148	1.998316
C	-2.007967	-0.985908	1.417856
S	-2.714544	-2.350113	0.379165
C	-4.253190	-1.530975	-0.170564
H	-4.020158	-0.619818	-0.741207
H	-4.896543	-1.286149	0.689266
H	-4.780880	-2.244448	-0.820040
H	-1.573736	-2.585590	-2.411902
H	-0.544890	-3.440953	-3.626827
H	-1.665759	-2.144645	-4.151061
H	-4.235448	2.598477	-1.468021
H	-3.016843	3.845589	-1.871621
H	-3.101960	3.169740	-0.203488
H	-1.931899	-0.087264	0.793275
H	-2.726833	-0.781153	2.227822
H	0.529132	-2.140716	-0.937046
H	1.735865	-2.802384	-2.065674
H	0.255071	1.581723	-1.844500
H	-0.359939	3.240244	-1.970560

H	2.700359	-1.033586	1.806488
H	2.629589	-2.697791	3.627305
H	0.421935	-3.573743	4.430800
H	-1.670984	-2.751731	3.372668
H	2.801112	1.801869	0.770669
H	5.004425	1.751956	-0.344460
H	5.476951	0.022348	-2.095174
H	3.712027	-1.624670	-2.688379
H	0.830928	1.113270	2.986547
H	0.370050	3.384159	3.843926
H	-0.434610	5.166707	2.275798
H	-0.769903	4.617803	-0.121794
H	-0.126596	-0.121041	-0.313176

$BiCl_3$

4

scf done: -1595.484978

Bi	0.000000	0.000000	0.000000
Cl	0.000000	0.000000	2.486855
Cl	2.452040	0.000000	-0.410771
Cl	-0.484006	-2.405170	-0.406507

$BiBr_3$

4

scf done: -7937.313268

Bi	0.000000	0.000000	0.000000
Br	0.000000	0.000000	2.639549
Br	2.593591	0.000000	-0.490017
Br	-0.591406	-2.525240	-0.490201

BiI_3

4

scf done: -1102.242473

Bi	-0.011521	0.013363	-0.008174
I	0.009220	-0.009166	2.847842
I	2.787943	-0.011044	-0.575077
I	-0.706874	-2.699554	-0.569488

2a

59

scf done: -4062.458114

C	2.933476	-0.860329	-2.319027
C	2.244688	-1.265570	-1.162141
C	1.924416	-2.640843	-1.005823
C	2.298837	-3.537910	-2.018339
C	2.966461	-3.118291	-3.169918
C	3.288931	-1.770280	-3.317013
P	1.593554	0.037900	-0.004266
C	2.355444	-0.358753	1.644870
C	1.807778	0.220036	2.812420
C	2.362469	-0.111805	4.058970
C	3.446569	-0.982418	4.164435

C	4.002964	-1.536321	3.007961
C	3.460132	-1.221596	1.761487
C	0.645541	1.184822	2.781426
S	-0.960688	0.285018	3.031163
C	-2.037869	1.705947	3.452499
C	1.216394	-3.213255	0.197231
S	-0.611525	-2.954540	0.290931
C	-1.138556	-3.676401	-1.303500
C	2.579986	1.550920	-0.484106
C	3.822719	1.832437	0.109727
C	4.546348	2.975424	-0.234062
C	4.033036	3.860856	-1.184353
C	2.801006	3.592400	-1.779978
C	2.061160	2.446275	-1.448894
C	0.726321	2.234469	-2.116239
S	-0.635136	2.821877	-1.001952
C	-1.900659	3.241917	-2.257332
Bi	-1.975986	-0.050809	-0.052504
Cl	-1.840169	-0.374208	-2.623567
Cl	-3.726840	1.824682	0.358445
Cl	-3.801853	-1.806471	0.366493
H	-2.103473	2.365949	-2.889346
H	-1.552702	4.095947	-2.857368
H	-2.807925	3.504961	-1.698884
H	-2.039117	2.450333	2.644417
H	-1.708754	2.149213	4.404294
H	-3.056455	1.307023	3.553064
H	-2.232750	-3.584430	-1.319968
H	-0.844611	-4.736082	-1.345067
H	-0.710562	-3.111485	-2.142913
H	0.529346	1.185512	-2.384233
H	0.663839	2.831970	-3.036877
H	0.591969	1.759601	1.845570
H	0.730031	1.901407	3.612392
H	1.586591	-2.798047	1.143183
H	1.376937	-4.301276	0.237641
H	4.235675	1.150461	0.853076
H	5.510412	3.170376	0.240867
H	4.588756	4.759545	-1.460893
H	2.393632	4.286841	-2.518947
H	3.895499	-1.655184	0.858761
H	4.859434	-2.210922	3.073933
H	3.859005	-1.223697	5.146356
H	1.928088	0.324687	4.961870
H	3.201108	0.188545	-2.447384
H	3.820004	-1.419158	-4.204344
H	3.234928	-3.843027	-3.941326
H	2.057349	-4.596539	-1.893486

2b

59

scf done: -10404.2851867

C	3.628254	-0.731337	-2.284227

C	2.857043	-1.180951	-1.198238
C	2.487084	-2.553001	-1.148432
C	2.908156	-3.401690	-2.184815
C	3.661841	-2.936627	-3.264003
C	4.025627	-1.592370	-3.310712
P	2.179298	0.055146	0.028131
C	2.973087	-0.425657	1.648530
C	2.399495	0.024411	2.862210
C	2.977126	-0.381774	4.076713
C	4.099681	-1.207704	4.111670
C	4.671524	-1.644861	2.914223
C	4.109891	-1.253304	1.697746
C	1.189397	0.929880	2.919767
S	-0.380210	-0.056715	3.082455
C	-1.466108	1.182512	3.881306
C	1.705368	-3.176072	-0.017001
S	-0.133468	-2.952135	0.003742
C	-0.619966	-3.678127	-1.599414
C	3.117046	1.620121	-0.395076
C	4.359609	1.917156	0.191927
C	5.034083	3.104998	-0.096390
C	4.470300	4.022469	-0.985109
C	3.236719	3.742027	-1.571898
C	2.543021	2.553236	-1.292582
C	1.202169	2.337347	-1.952127
S	-0.179637	2.846278	-0.816918
C	-1.379717	3.503006	-2.032465
Bi	-1.697907	-0.015409	0.019298
Br	-2.013834	-0.198080	-2.693399
Br	-3.437814	1.980406	0.712265
Br	-3.489236	-1.929239	0.711809
H	-1.647132	2.726349	-2.762692
H	-0.959103	4.391286	-2.526654
H	-2.271835	3.778240	-1.454541
H	-1.599888	2.067653	3.244278
H	-1.055906	1.457747	4.864382
H	-2.441647	0.693787	4.011487
H	-1.716353	-3.614731	-1.629162
H	-0.309249	-4.732981	-1.644674
H	-0.200769	-3.107671	-2.439502
H	1.034441	1.296397	-2.263096
H	1.119208	2.971504	-2.845689
H	1.109635	1.587913	2.043951
H	1.243577	1.563786	3.817132
H	2.014197	-2.789452	0.963541
H	1.881474	-4.262370	-0.004048
H	4.810306	1.209236	0.887950
H	5.998854	3.309519	0.373230
H	4.987216	4.955427	-1.220503
H	2.791086	4.461919	-2.263069
H	4.558369	-1.598845	0.764241
H	5.554406	-2.288032	2.924335
H	4.527221	-1.507214	5.070951

H	2.528617	-0.040596	5.013213
H	3.930662	0.314961	-2.330878
H	4.624215	-1.206681	-4.138925
H	3.966136	-3.624544	-4.055710
H	2.638652	-4.459926	-2.134957

2c

59

scf done: -3569.210126

C	2.979033	2.710485	-0.579961
C	3.446403	1.599412	0.161338
C	4.645773	1.719160	0.884358
C	5.376683	2.908728	0.881021
C	4.917055	4.003692	0.146463
C	3.727562	3.897416	-0.573970
P	2.431615	0.030850	0.189435
C	3.180081	-0.850683	1.646101
C	2.574963	-0.722055	2.916816
C	3.122002	-1.424737	4.003060
C	4.251369	-2.228424	3.855213
C	4.860827	-2.341286	2.601912
C	4.326921	-1.655048	1.511034
C	1.350587	0.129651	3.161190
S	-0.197315	-0.881496	2.956911
C	-1.350702	0.089189	3.997177
C	1.681987	2.679741	-1.347600
S	0.266878	3.023249	-0.197067
C	-0.847000	3.924419	-1.335561
C	3.062824	-0.899497	-1.295830
C	3.755685	-0.197717	-2.297738
C	4.093466	-0.797186	-3.513268
C	3.750005	-2.127420	-3.747373
C	3.082659	-2.844002	-2.752625
C	2.726287	-2.260372	-1.526880
C	2.023697	-3.136149	-0.519857
S	0.197058	-2.909192	-0.352956
C	-0.335506	-3.355407	-2.041632
Bi	-1.276330	0.025825	0.057641
I	-3.336055	-2.060865	0.321441
I	-1.269602	0.305478	-2.884026
I	-3.163146	2.050160	1.139079
H	-1.077887	3.303441	-2.212729
H	-0.376507	4.873014	-1.635352
H	-1.769268	4.120151	-0.772997
H	-1.396568	1.134468	3.660838
H	-1.043710	0.023345	5.051740
H	-2.342407	-0.365375	3.864025
H	-1.427653	-3.240742	-2.054901
H	-0.064732	-4.402014	-2.249453
H	0.111165	-2.678364	-2.782717
H	1.496369	1.723461	-1.859133
H	1.672312	3.470891	-2.110503
H	1.298462	1.002035	2.494346

H	1.346848	0.494100	4.199050
H	2.400590	-2.992331	0.500030
H	2.179034	-4.195643	-0.774639
H	5.018976	0.873870	1.462315
H	6.305565	2.975491	1.451760
H	5.480321	4.939375	0.135785
H	3.360188	4.755263	-1.142785
H	4.799953	-1.749109	0.531202
H	5.750211	-2.962009	2.472828
H	4.656146	-2.764071	4.716501
H	2.644062	-1.337869	4.982075
H	4.043670	0.839963	-2.129274
H	4.628268	-0.219535	-4.270294
H	4.004075	-2.610498	-4.693131
H	2.828422	-3.892950	-2.925016

2'a

60

scf done: -3759.800988

C	-2.077705	-0.742786	2.465845
C	-2.754270	0.093219	1.551889
C	-3.802950	0.897215	2.028130
C	-4.179610	0.887977	3.371775
C	-3.503934	0.064907	4.275708
C	-2.460369	-0.736311	3.817051
C	-2.411413	0.078549	0.055860
C	-2.814899	1.393964	-0.624657
C	-2.067984	2.576335	-0.426138
C	-2.485764	3.762954	-1.050963
C	-3.630213	3.807525	-1.844651
C	-4.380789	2.643583	-2.025283
C	-3.971406	1.455199	-1.419001
C	-0.820890	2.634666	0.426076
S	0.695730	2.605147	-0.654112
C	1.851486	3.634212	0.331631
C	-0.917640	-1.622519	2.066792
S	0.671121	-0.743807	2.471358
C	1.745385	-2.145196	2.962094
C	-2.997556	-1.154404	-0.650061
C	-4.015240	-1.907289	-0.047052
C	-4.581022	-3.018944	-0.678353
C	-4.135518	-3.398238	-1.943680
C	-3.129783	-2.652754	-2.561113
C	-2.552075	-1.535068	-1.939036
C	-1.475140	-0.797460	-2.688773
S	0.262665	-1.276189	-2.239313
C	0.190239	-3.097389	-2.138997
Bi	2.406068	-0.040569	-0.153864
Cl	3.820812	1.071854	-1.963102
Cl	3.317512	-2.458344	-0.238292
Cl	3.761319	0.862074	1.824496
H	1.840940	-2.874336	2.146078
H	1.344525	-2.610684	3.874474

H	2.731935	-1.704555	3.163043
H	2.011614	3.207842	1.331857
H	1.464137	4.661669	0.393926
H	2.803974	3.621789	-0.217157
H	1.187041	-3.403244	-1.790790
H	-0.011850	-3.528861	-3.130374
H	-0.575149	-3.423094	-1.420677
H	-0.923577	-1.900016	1.004749
H	-0.919589	-2.549946	2.657869
H	-0.760328	1.828173	1.167283
H	-0.783235	3.588788	0.972309
H	-1.503309	0.287665	-2.520736
H	-1.579604	-0.968551	-3.769803
H	-4.336915	1.542725	1.330372
H	-5.000452	1.524408	3.709476
H	-3.785154	0.048559	5.330768
H	-1.916230	-1.372232	4.520033
H	-4.560964	0.549570	-1.566073
H	-5.284673	2.657006	-2.638213
H	-3.934025	4.744287	-2.316383
H	-1.890177	4.668405	-0.909134
H	-4.377650	-1.618760	0.939343
H	-5.371814	-3.581489	-0.177325
H	-4.567180	-4.263374	-2.451286
H	-2.780531	-2.939507	-3.556440
H	-1.317217	-0.003995	-0.036702

2'b

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scf done: -10101.6291277

C	-2.605814	-1.225019	2.261683
C	-3.296894	-0.248447	1.511608
C	-4.405249	0.384511	2.097336
C	-4.832767	0.066692	3.387426
C	-4.149996	-0.902722	4.125217
C	-3.043298	-1.533015	3.559811
C	-2.907882	0.062939	0.058839
C	-3.344848	1.478036	-0.346521
C	-2.619910	2.612844	0.078998
C	-3.076692	3.891754	-0.278025
C	-4.236003	4.069004	-1.030697
C	-4.957970	2.947892	-1.446152
C	-4.510991	1.670547	-1.104426
C	-1.337179	2.516570	0.869036
S	0.120971	2.574968	-0.294334
C	1.282363	3.649111	0.633137
C	-1.364039	-1.913505	1.753355
S	0.131838	-0.964733	2.334376
C	1.228009	-2.316851	2.906875
C	-3.435347	-1.002894	-0.913877
C	-4.465005	-1.875712	-0.532965
C	-4.999643	-2.813355	-1.421300
C	-4.512410	-2.888631	-2.725618

C	-3.487498	-2.027001	-3.118699
C	-2.935034	-1.086785	-2.235073
C	-1.809195	-0.229293	-2.744625
S	-0.100502	-0.907311	-2.404936
C	-0.339030	-2.718403	-2.375102
Bi	1.952475	-0.007444	-0.099103
Br	3.341315	1.402408	-1.951975
Br	2.967259	-2.536079	-0.412009
Br	3.335572	0.834787	2.091722
H	1.452035	-3.011441	2.085623
H	0.758733	-2.832040	3.757669
H	2.158007	-1.825983	3.226387
H	1.509319	3.221366	1.619507
H	0.856004	4.659041	0.720444
H	2.203965	3.676055	0.034205
H	0.638728	-3.124099	-2.078561
H	-0.616144	-3.088970	-3.372036
H	-1.103628	-3.007860	-1.640978
H	-1.330421	-2.006110	0.660299
H	-1.276219	-2.922915	2.178816
H	-1.273095	1.615932	1.493056
H	-1.229685	3.386841	1.531788
H	-1.796350	0.777857	-2.307098
H	-1.882365	-0.116383	-3.835187
H	-4.948602	1.139912	1.529263
H	-5.699645	0.577244	3.812426
H	-4.472972	-1.163188	5.135331
H	-2.493207	-2.280289	4.137657
H	-5.079353	0.799887	-1.433474
H	-5.869407	3.064130	-2.036552
H	-4.571450	5.074727	-1.292222
H	-2.500295	4.764198	0.040504
H	-4.863639	-1.819633	0.479724
H	-5.801096	-3.477129	-1.089825
H	-4.924082	-3.610490	-3.434069
H	-3.098853	-2.081596	-4.138843
H	-1.809854	0.033315	-0.012275

2’c

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scf done: -3266.558607

C	5.006104	0.485632	-1.925669
C	3.849092	-0.158907	-1.461665
C	3.145322	-1.003809	-2.349727
C	3.627649	-1.182924	-3.655507
C	4.786650	-0.546962	-4.098534
C	5.476296	0.297981	-3.227208
C	3.401709	0.001066	-0.000673
C	3.849580	1.346151	0.591001
C	3.146350	2.537639	0.303416
C	3.628483	3.757904	0.801959
C	4.786857	3.823159	1.575164
C	5.476105	2.645807	1.871224

C	5.006145	1.425182	1.381953
C	1.845118	2.544480	-0.457835
S	0.428792	2.320277	0.742636
C	-0.621164	3.768964	0.351894
C	1.843697	-1.666424	-1.975626
S	0.426777	-0.515478	-2.381179
C	-0.621976	-1.578996	-3.440854
C	3.851988	-1.183615	0.867837
C	3.148509	-1.532282	2.042957
C	3.631129	-2.574826	2.849187
C	4.791075	-3.274649	2.519419
C	5.481430	-2.939296	1.353346
C	5.010400	-1.905340	0.541368
C	1.847683	-0.876479	2.431420
S	0.429669	-1.803417	1.639801
C	-0.617259	-2.193835	3.090694
Bi	-1.594748	-0.001190	-0.000161
I	-2.907078	-2.625197	-0.351076
I	-2.911282	1.617093	-2.093327
I	-2.907937	1.007820	2.446802
H	-0.953460	-2.468402	-2.886822
H	-0.065536	-1.850881	-4.349602
H	-1.497306	-0.967976	-3.703186
H	-0.954420	3.733137	-0.694705
H	-0.064884	4.692249	0.569750
H	-1.495536	3.690074	1.013454
H	-1.488423	-2.733040	2.692037
H	-0.956249	-1.271262	3.582458
H	-0.057334	-2.840448	3.781878
H	1.779620	-1.950391	-0.917721
H	1.679254	-2.575642	-2.569377
H	1.781353	1.769720	-1.232171
H	1.680445	3.513166	-0.948616
H	1.783977	0.181448	2.147674
H	1.684724	-0.935103	3.516003
H	5.552752	1.147051	-1.253001
H	6.381619	0.812799	-3.556070
H	5.143629	-0.705822	-5.118256
H	3.073357	-1.832204	-4.338329
H	5.552175	0.511707	1.619113
H	6.380755	2.672680	2.482518
H	5.143646	4.785502	1.948137
H	3.074223	4.673954	0.581242
H	5.557686	-1.651241	-0.366761
H	6.387707	-3.479754	1.071638
H	5.148413	-4.079255	3.165491
H	3.076348	-2.843725	3.751917
H	2.303635	-0.000413	0.000116

Total energies and Cartesian coordinates at the MP2/cc-pVDZ(-PP) level

1

55

scf done: -2461.6998414

C	0.275143	-0.834648	2.698641
C	-0.495623	-0.357028	1.617067
C	-1.909934	-0.270650	1.751874
C	-2.503134	-0.643719	2.974879
C	-1.729382	-1.119624	4.048115
C	-0.336485	-1.220764	3.905330
P	0.245000	0.146645	-0.007091
C	0.225419	1.988857	0.217507
C	0.254324	2.796833	-0.951385
C	0.243648	4.198878	-0.818013
C	0.203716	4.805761	0.449039
C	0.169702	4.006016	1.603670
C	0.184642	2.604888	1.486702
C	0.231166	2.171384	-2.325864
S	-1.489525	1.649544	-2.716496
C	-1.127385	0.119003	-3.628948
C	-2.785075	0.189990	0.613339
S	-3.061912	-1.118491	-0.644213
C	-3.993771	-2.288022	0.387360
C	2.034454	-0.215469	0.310226
C	2.980273	0.776329	0.648136
C	4.336237	0.446921	0.822011
C	4.762848	-0.882505	0.669421
C	3.828290	-1.875941	0.332192
C	2.468843	-1.560221	0.144389
C	1.507195	-2.644293	-0.277413
S	1.414492	-2.670497	-2.110248
C	-0.181976	-3.526334	-2.273318
H	-0.977697	-2.936089	-1.788416
H	-0.137390	-4.538498	-1.837911
H	-0.397125	-3.614167	-3.350466
H	-0.512654	-0.549610	-3.003316
H	-0.617346	0.331443	-4.582802
H	-2.096548	-0.362084	-3.836817
H	-4.243039	-3.151777	-0.249658
H	-4.931297	-1.835680	0.753610
H	-3.391250	-2.634546	1.242967
H	0.490261	-2.461703	0.113246
H	1.845036	-3.628034	0.094224
H	0.868600	1.270652	-2.371631
H	0.592587	2.888090	-3.083323
H	-2.339075	1.025537	0.046976
H	-3.767648	0.524060	0.993069
H	2.653629	1.813817	0.775050
H	5.056240	1.230602	1.082363
H	5.816991	-1.145404	0.808181
H	4.154847	-2.915269	0.205192
H	0.160387	1.981430	2.387812
H	0.135015	4.470147	2.595528

H	0.192892	5.897870	0.532628
H	0.262225	4.820561	-1.721259
H	1.364733	-0.894397	2.599067
H	0.278927	-1.587817	4.734182
H	-2.213043	-1.407236	4.987881
H	-3.590939	-0.554322	3.085563

1’

56

scf done: -2159.4532997

C	0.236522	0.961886	2.764185
C	0.156092	1.110184	1.364759
C	-0.248255	2.360667	0.824202
C	-0.561184	3.418599	1.702195
C	-0.479837	3.261733	3.096472
C	-0.081629	2.025184	3.627903
C	0.567737	-0.019732	0.427143
C	1.941422	0.236199	-0.181948
C	2.298751	-0.388957	-1.405067
C	3.593940	-0.199176	-1.926433
C	4.544683	0.577952	-1.244921
C	4.193838	1.190507	-0.030574
C	2.901934	1.015536	0.494924
C	1.292515	-1.178846	-2.204769
S	0.432596	0.019963	-3.296317
C	-0.971948	-1.001265	-3.833273
C	-0.372900	2.575836	-0.661537
S	-1.914631	1.862452	-1.362686
C	-3.120192	2.817693	-0.392385
C	0.517446	-1.374306	1.128794
C	1.698508	-2.025445	1.543467
C	1.649779	-3.238648	2.250984
C	0.409412	-3.818635	2.563607
C	-0.771334	-3.178343	2.156611
C	-0.734879	-1.958241	1.451447
C	-2.040059	-1.341765	1.011762
S	-2.597432	-2.244072	-0.483286
C	-4.099408	-1.283536	-0.837508
H	-3.840746	-0.227880	-1.014941
H	-4.820905	-1.363028	-0.007307
H	-4.554706	-1.705615	-1.747528
H	-1.542505	-1.349519	-2.958001
H	-0.631340	-1.860194	-4.434778
H	-1.612034	-0.357169	-4.457122
H	-4.121987	2.502897	-0.727186
H	-3.010725	3.899712	-0.578924
H	-3.019513	2.617876	0.687005
H	-1.942672	-0.271330	0.766576
H	-2.804059	-1.455308	1.802402
H	0.548307	-1.680666	-1.562782
H	1.799263	-1.946256	-2.815998
H	0.438115	2.085403	-1.224964
H	-0.349925	3.655156	-0.896040

H	2.667926	-1.576767	1.304175
H	2.581330	-3.725064	2.560068
H	0.360713	-4.763639	3.114985
H	-1.745754	-3.626165	2.386020
H	2.629515	1.493579	1.442044
H	4.923838	1.801571	0.511335
H	5.548327	0.709433	-1.663079
H	3.855157	-0.672663	-2.880450
H	0.554683	0.000307	3.180744
H	-0.010808	1.885803	4.712110
H	-0.725245	4.098718	3.758929
H	-0.863177	4.384913	1.279877
H	-0.165309	-0.038090	-0.400796

$BiCl_3$

4

scf done: -1592.6982221

Bi	0.000000	0.000000	0.000000
Cl	0.000000	0.000000	2.486855
Cl	2.452040	0.000000	-0.410771
Cl	-0.484006	-2.405170	-0.406507

$BiBr_3$

4

scf done: -7931.3428346

Bi	0.000000	0.000000	0.000000
Br	0.000000	0.000000	2.639549
Br	2.593591	0.000000	-0.490017
Br	-0.591406	-2.525240	-0.490201

BiI_3

4

scf done: -1098.1172152

Bi	-0.023472	0.028828	-0.017785
I	0.024638	-0.029062	2.813332
I	2.756978	-0.031293	-0.552870
I	-0.679376	-2.674874	-0.547574

2a

59

scf done: -4054.4498924

C	2.954136	0.112650	-2.386300
C	2.259161	-0.705825	-1.465971
C	2.022224	-2.072585	-1.797167
C	2.495170	-2.560853	-3.033659
C	3.174175	-1.737634	-3.945742
C	3.408791	-0.394788	-3.614439
P	1.505160	0.068985	0.035845
C	2.275006	-0.867805	1.430306
C	1.693874	-0.778273	2.722653
C	2.283194	-1.490835	3.788164
C	3.440454	-2.260724	3.598031

C	4.028922	-2.329345	2.322691
C	3.451354	-1.632201	1.249552
C	0.451497	0.035771	3.001150
S	-1.032451	-1.032926	2.795792
C	-2.254866	-0.024660	3.697578
C	1.319567	-3.041257	-0.880293
S	-0.487954	-2.795490	-0.704271
C	-0.967934	-2.957462	-2.449415
C	2.471007	1.649527	0.159373
C	3.679375	1.731383	0.887521
C	4.396508	2.936575	0.956673
C	3.918801	4.077418	0.290034
C	2.717657	4.004549	-0.431269
C	1.983148	2.803574	-0.510795
C	0.672823	2.796067	-1.255957
S	-0.689762	2.976239	-0.035919
C	-1.933481	3.785268	-1.091303
Bi	-1.928454	-0.008564	-0.088568
Cl	-1.918421	0.505475	-2.597480
Cl	-3.744452	1.555762	0.822652
Cl	-3.648028	-1.875352	-0.213297
H	-2.156535	3.153970	-1.964616
H	-1.562631	4.775822	-1.399705
H	-2.839177	3.891027	-0.477475
H	-2.320470	0.990529	3.278146
H	-1.997335	0.004886	4.768291
H	-3.229253	-0.518914	3.561271
H	-2.061866	-2.843581	-2.474902
H	-0.685798	-3.957090	-2.819219
H	-0.503177	-2.167474	-3.058628
H	0.510870	1.882296	-1.854928
H	0.623296	3.662388	-1.938019
H	0.373859	0.924429	2.349248
H	0.462640	0.382520	4.049624
H	1.708110	-2.995857	0.150035
H	1.472604	-4.072407	-1.246370
H	4.059867	0.849207	1.411560
H	5.330608	2.980281	1.527038
H	4.473631	5.020396	0.337023
H	2.333632	4.894501	-0.943813
H	3.908709	-1.682483	0.254123
H	4.938482	-2.918775	2.163814
H	3.881324	-2.803178	4.440907
H	1.823508	-1.433463	4.781987
H	3.156115	1.158462	-2.133584
H	3.944679	0.262848	-4.307134
H	3.521004	-2.145399	-4.900916
H	2.322201	-3.615355	-3.280324

2b

59

scf done: -10393.0956218

C	3.303198	0.410786	-2.331808

C	2.622017	-0.519243	-1.513041
C	2.359015	-1.825546	-2.020982
C	2.789625	-2.143725	-3.326391
C	3.452655	-1.208911	-4.137153
C	3.715603	0.072836	-3.631285
P	1.924323	0.041990	0.107530
C	2.724299	-1.098003	1.322722
C	2.164331	-1.229420	2.620736
C	2.785283	-2.092633	3.548042
C	3.951803	-2.798918	3.218562
C	4.516713	-2.652110	1.939103
C	3.908349	-1.802390	1.001784
C	0.905641	-0.505548	3.039441
S	-0.553141	-1.532762	2.585504
C	-1.796721	-0.836700	3.721907
C	1.672018	-2.903491	-1.222734
S	-0.132308	-2.681231	-0.986265
C	-0.642433	-2.669869	-2.729933
C	2.918699	1.577604	0.425406
C	4.123974	1.550511	1.162652
C	4.860679	2.726301	1.379067
C	4.406961	3.947065	0.852380
C	3.207940	3.982518	0.124658
C	2.452610	2.813340	-0.099216
C	1.141270	2.918747	-0.834388
S	-0.215355	2.950554	0.405774
C	-1.420860	3.975753	-0.493958
Bi	-1.519547	0.020867	0.022626
Br	-1.616808	0.878489	-2.555304
Br	-3.343055	1.555253	1.341497
Br	-3.384202	-1.919101	-0.202356
H	-1.678403	3.504054	-1.454467
H	-1.002362	4.983876	-0.644797
H	-2.317375	4.027808	0.140258
H	-1.874621	0.254389	3.602903
H	-1.546809	-1.107375	4.760116
H	-2.760158	-1.287479	3.436687
H	-1.735655	-2.545352	-2.727517
H	-0.376050	-3.632097	-3.198099
H	-0.179379	-1.828878	-3.268179
H	0.967750	2.094016	-1.548605
H	1.099608	3.867585	-1.396608
H	0.822156	0.497069	2.582585
H	0.893707	-0.383993	4.136815
H	2.078359	-2.989548	-0.202046
H	1.814924	-3.880168	-1.719313
H	4.487576	0.605924	1.578247
H	5.791759	2.684518	1.954468
H	4.977946	4.867486	1.013703
H	2.841299	4.934278	-0.277766
H	4.345946	-1.685193	0.003150
H	5.431675	-3.192319	1.672700
H	4.417065	-3.460981	3.956324

H	2.343231	-2.205929	4.545039
H	3.529609	1.408847	-1.943361
H	4.241501	0.814104	-4.242393
H	3.766408	-1.484380	-5.149376
H	2.596982	-3.153212	-3.709290

2c

59

scf done: -3559.8675777

C	2.875152	2.769945	0.055509
C	3.311063	1.516262	0.562928
C	4.500950	1.455332	1.322561
C	5.253085	2.614496	1.574173
C	4.831444	3.852044	1.060524
C	3.646621	3.921470	0.312093
P	2.294575	0.005600	0.192377
C	3.084729	-1.184883	1.366410
C	2.508781	-1.378611	2.649229
C	3.127718	-2.273723	3.547284
C	4.306324	-2.952608	3.203512
C	4.884835	-2.746830	1.938251
C	4.279486	-1.863848	1.030329
C	1.231145	-0.694048	3.074957
S	-0.202237	-1.697545	2.498754
C	-1.454397	-1.204287	3.727019
C	1.575883	2.908558	-0.694042
S	0.200150	2.917732	0.527554
C	-0.915869	4.100912	-0.289781
C	2.996979	-0.511739	-1.442117
C	3.694612	0.432264	-2.230170
C	4.117585	0.123052	-3.533592
C	3.851049	-1.144007	-4.073397
C	3.172828	-2.093447	-3.292592
C	2.730168	-1.803068	-1.984751
C	2.022845	-2.891731	-1.220540
S	0.211303	-2.671449	-1.039488
C	-0.240824	-2.669183	-2.798708
Bi	-1.201688	0.017677	0.059959
I	-3.237931	-2.067208	-0.183749
I	-1.357580	1.031850	-2.691520
I	-3.103590	1.640983	1.615446
H	-1.203955	3.730040	-1.285446
H	-0.418943	5.082031	-0.360422
H	-1.809650	4.177197	0.346173
H	-1.563247	-0.109914	3.761094
H	-1.185031	-1.608618	4.715910
H	-2.406090	-1.642490	3.387528
H	-1.333873	-2.547564	-2.837016
H	0.042273	-3.633670	-3.252713
H	0.239698	-1.831315	-3.326801
H	1.406710	2.106046	-1.434042
H	1.548960	3.872424	-1.230771
H	1.152399	0.337488	2.687136

H	1.179528	-0.652107	4.176946
H	2.396543	-2.989807	-0.188694
H	2.180556	-3.862813	-1.723811
H	4.841049	0.497988	1.728333
H	6.171614	2.546174	2.166941
H	5.415625	4.759066	1.248320
H	3.303923	4.886462	-0.079890
H	4.727426	-1.700820	0.042842
H	5.808116	-3.266833	1.660568
H	4.769728	-3.640259	3.918718
H	2.674495	-2.434826	4.532632
H	3.927000	1.417867	-1.814475
H	4.655784	0.874853	-4.120673
H	4.174122	-1.397147	-5.088523
H	2.978408	-3.092509	-3.701166

2'a

60

scf done: -3752.1860521

C	-2.014153	-0.555966	2.501837
C	-2.682606	0.242648	1.540363
C	-3.704004	1.117684	1.969656
C	-4.049398	1.220053	3.326779
C	-3.374999	0.439625	4.281363
C	-2.360801	-0.434031	3.863645
C	-2.371480	0.085200	0.055304
C	-2.802686	1.321652	-0.730429
C	-2.083051	2.537494	-0.602074
C	-2.515982	3.675070	-1.314918
C	-3.661800	3.637106	-2.122548
C	-4.391071	2.440791	-2.228258
C	-3.963002	1.297328	-1.534350
C	-0.855094	2.671559	0.268735
S	0.650353	2.622968	-0.789871
C	1.805041	3.565923	0.262680
C	-0.905234	-1.511472	2.130391
S	0.706556	-0.698813	2.493096
C	1.726236	-2.158128	2.883509
C	-2.994487	-1.190547	-0.508415
C	-4.024987	-1.860596	0.182139
C	-4.641088	-3.004003	-0.357115
C	-4.239178	-3.490790	-1.610254
C	-3.218501	-2.826043	-2.310390
C	-2.590786	-1.680183	-1.780553
C	-1.495491	-1.024124	-2.577243
S	0.181307	-1.471157	-1.982088
C	0.131709	-3.280731	-2.086658
Bi	2.404438	-0.016552	-0.165476
Cl	3.812813	1.022156	-1.976967
Cl	3.348078	-2.372454	-0.276590
Cl	3.821102	0.828837	1.742261
H	1.743082	-2.868569	2.044001
H	1.346126	-2.636177	3.800305

H	2.747746	-1.783911	3.052157
H	1.909302	3.108615	1.258756
H	1.459829	4.608397	0.349341
H	2.781707	3.538617	-0.245805
H	1.107470	-3.624153	-1.709157
H	0.007340	-3.600511	-3.133929
H	-0.679846	-3.688725	-1.464052
H	-0.944900	-1.829352	1.075246
H	-0.959217	-2.412979	2.766098
H	-0.803192	1.899360	1.053561
H	-0.861644	3.658014	0.765920
H	-1.533390	0.076943	-2.515074
H	-1.567994	-1.305612	-3.642343
H	-4.231261	1.726905	1.228288
H	-4.845213	1.906291	3.635498
H	-3.633455	0.513581	5.342835
H	-1.822064	-1.039229	4.602636
H	-4.532664	0.366195	-1.620059
H	-5.293368	2.395396	-2.847399
H	-3.982816	4.533675	-2.662907
H	-1.940130	4.604117	-1.226554
H	-4.351116	-1.480596	1.155445
H	-5.438469	-3.505588	0.201548
H	-4.714716	-4.377555	-2.042213
H	-2.905657	-3.192839	-3.295594
H	-1.273857	-0.012720	-0.057390

2'b

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scf done: -10090.8321715

C	-2.554858	-0.609082	2.478133
C	-3.225346	0.198588	1.525842
C	-4.274864	1.037869	1.958568
C	-4.648705	1.093855	3.310865
C	-3.974996	0.301998	4.256562
C	-2.931370	-0.534553	3.835388
C	-2.885513	0.085208	0.043350
C	-3.321615	1.335292	-0.717290
C	-2.612635	2.553019	-0.554734
C	-3.052112	3.704997	-1.239598
C	-4.193591	3.677944	-2.053890
C	-4.910442	2.477901	-2.196170
C	-4.475925	1.320436	-1.529860
C	-1.383597	2.667957	0.315828
S	0.124045	2.573372	-0.740761
C	1.250524	3.639928	0.219984
C	-1.410450	-1.519086	2.102096
S	0.172551	-0.659328	2.493971
C	1.192959	-2.078319	3.011097
C	-3.482788	-1.181163	-0.566162
C	-4.525615	-1.876045	0.079438
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C	-4.690799	-3.449726	-1.768068

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C	-1.924691	-0.952269	-2.582134
S	-0.271277	-1.429887	-1.943361
C	-0.328841	-3.233650	-2.123636
Bi	1.940350	0.006509	-0.107028
Br	3.370463	1.135421	-2.066467
Br	2.996342	-2.474358	-0.188148
Br	3.383548	0.994283	1.917437
H	1.257411	-2.832144	2.212615
H	0.776083	-2.511437	3.934353
H	2.200168	-1.679124	3.206512
H	1.372301	3.269486	1.249261
H	0.868304	4.673143	0.218567
H	2.224679	3.601717	-0.292250
H	0.634182	-3.600530	-1.735714
H	-0.427214	-3.507889	-3.186567
H	-1.159394	-3.660926	-1.540287
H	-1.426882	-1.820408	1.041501
H	-1.437487	-2.432152	2.722451
H	-1.349571	1.904090	1.109863
H	-1.365201	3.660184	0.800330
H	-1.960832	0.146528	-2.486326
H	-1.961423	-1.199774	-3.657477
H	-4.801703	1.655524	1.223883
H	-5.466125	1.752734	3.622717
H	-4.256309	0.339198	5.314148
H	-2.392658	-1.146993	4.568497
H	-5.036092	0.386570	-1.643754
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H	-2.485437	4.636833	-1.124548
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H	-5.931372	-3.526674	0.014081
H	-5.152962	-4.323680	-2.238931
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H	-1.785017	0.004728	-0.052089

2’c

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scf done: -3257.6061170

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C	-4.882153	0.147313	2.109704
C	-5.297471	-0.357989	3.353165
C	-4.588850	-1.413024	3.952164
C	-3.455797	-1.934756	3.309390
C	-3.390188	0.083313	0.041709
C	-3.844485	1.518933	-0.204564
C	-3.093771	2.602994	0.320041
C	-3.566538	3.919494	0.144799
C	-4.769706	4.176598	-0.530244
C	-5.511145	3.103934	-1.052970

C	-5.049361	1.787202	-0.887372
C	-1.769803	2.388117	1.008078
S	-0.413417	2.387958	-0.255160
C	0.658693	3.710796	0.395750
C	-1.749773	-1.961959	1.463132
S	-0.337797	-0.959485	2.118694
C	0.589991	-2.233434	3.029597
C	-3.952092	-0.870300	-1.010704
C	-5.035101	-1.723404	-0.717909
C	-5.605558	-2.542242	-1.709312
C	-5.101023	-2.512531	-3.018339
C	-4.016335	-1.671143	-3.318764
C	-3.434181	-0.847563	-2.334108
C	-2.238957	-0.010733	-2.699027
S	-0.677933	-0.782494	-2.107507
C	-0.738885	-2.393223	-2.940097
Bi	1.665276	0.006851	-0.076734
I	3.231955	1.484425	-2.032770
I	2.703743	-2.708318	-0.387714
I	3.036099	0.921496	2.304969
H	0.934341	-3.021746	2.342603
H	-0.040586	-2.645570	3.833285
H	1.462586	-1.723096	3.465506
H	1.014907	3.459650	1.406693
H	0.111673	4.666777	0.390985
H	1.520179	3.770061	-0.287940
H	0.166298	-2.930906	-2.615797
H	-0.715259	-2.260614	-4.033964
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H	-1.732143	1.451893	1.588757
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H	-4.909392	-1.820315	4.916771
H	-2.890305	-2.749033	3.778820
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H	-5.437897	-1.746867	0.299611
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H	-5.541338	-3.141490	-3.799140
H	-3.613670	-1.643371	-4.338628
H	-2.289402	0.058098	-0.057328

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