Tweaking the charge transfer: Bonding analysis of bismuth(III) complexes with a flexidentate phosphane ligand

Supporting Information

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1. Materials and methods

All the reactions reported here 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 the solvents employed were purified and dried by standard methods.
Tri(*o*-meththiomethylphenyl)phosphine $P(C_6H_4\text{-}o\text{-}CH_2SCH_3)_3$ (**PS_3**) was prepared according to a previously published protocol.[1] The water content of commercially available bismuth triflate was determined by thermogravimetric analysis and the compound has a composition of $Bi[OTf]_3(H_2O)_n$ ($n \approx 14$). Bismuth triflate used for the synthesis of [**PS_3**Bi]$_2$[**BOT**] was previously dried for 10 days at 160°C in a dynamic vacuum to obtain $[Bi(OTf)_3(H_2O)_{2.8}]$ (water content determined by elemental analysis). This agrees with previous reports highlighting the (to date) sheer impossibility to synthesize strictly anhydrous $Bi(OTf)_3$.[2]
Solution NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts are reported in ppm relative to $SiMe_4$ (^{1}H, ^{13}C), $CFCl_3$ (^{19}F) and 85% H_3PO_4 (^{31}P). 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 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)[3] and refined by full-matrix least squares using SHELXL software[4] on OLEX2 platform.[5]

2. Synthetic procedures

Reaction of PS_3 with $Bi[OTf]_3(H_2O)_n$ (n ≈ 14)

A suspension of **PS_3** (40 mg, 0.0914 mmol) in ACN-d3 (D_3CCN) (0.3 mL) was added at room temperature to a suspension of commercially available bismuth trifluoromethanesulfonate ($Bi[OTf]_3(H_2O)_{14}$) (83 mg, 0.0914 mmol) in ACN-d3 (0.4 mL). The reaction solution containing the phosphonium salt $[HP(C_6H_4\text{-}o\text{-}CH_2SCH_3)_3]^+[OTf]^-$ was analysed by multinuclear NMR spectroscopy. Colourless needle-shaped crystals of this compound suitable for a single crystal X-ray diffraction study were grown by slow evaporation of the solvent (see Figure S7).

^{31}P-NMR (162 MHz; ACN-d3, 298 K): δ (ppm) = −21.0 (d, $^1J_{PH}$ = 536 Hz);
^{1}H NMR (400 MHz; ACN-d3, 298 K): δ (ppm) = 1.81 (9H, s, CH_3), 3.90 (6H, CH_2), 7.90-7.30 (12H, m, $H_{arom.}$), 10.12 (1H, d, $^1J_{PH}$ = 536 Hz, PH) ;
^{13}C NMR (101 MHz; ACN-d3, 298 K): δ (ppm) = 14.9 (s, CH_3), 37.3 (d, $^3J_{PC}$ = 6 Hz, CH_2), 119.6 (s, $C_{arom.}$), 122.8 (s, $C_{arom.}$), 129.8 (d, J_{PC} = 12.4 Hz, $C_{arom.}$), 133.8 (d, J_{PC} = 8.5 $C_{arom.}$), 136.1 (s, $C_{arom.}$), 143.5 (d, J_{PC} = 7.6 Hz, $C_{arom.}$).

Preparation of $[PS_3Bi]_2\{Bi_6O_4(OH)_4[OTf]_{12}\}(H_2O)(CH_3CN)_6$, $[PS_3Bi]_2$[BOT]

A solution of **PS_3** (40 mg, 0.0914 mmol) in toluene (5 mL) was added dropwise to a suspension of ($[Bi(OTf)_3\times(H_2O)_{2.8}]$ (65 mg, 0.0914 mmol) in toluene (5 mL) at room temperature. The resulting yellow suspension was stirred for 20 minutes at room temperature, filtered and the obtained yellow solid (mixture of $[H\mathbf{PS_3}]^+[OTf]^-$ and $[\mathbf{PS_3}Bi]_2[\mathbf{BOT}]$) was dried *in vacuo*. $[\mathbf{PS_3}Bi]_2[\mathbf{BOT}]$ was isolated in low yield (ca. 20 mg, 15%) by crystallisation from a saturated solution of this yellow solid in acetonitrile and its purity was tested by elemental analysis. Single crystals of $[\mathbf{PS_3}Bi]_2[\mathbf{BOT}]$ suitable for a single crystal X-ray

diffraction analysis were also obtained from acetonitrile. Since [**PS$_3$**Bi]$_2$[**BOT**] decomposes in solution to form [H**PS$_3$**]$^+$[OTf]$^-$ (see Figures S2 for solution NMR spectrum of isolated crystals), the NMR spectroscopic characterisation was only possible in the solid state by solid CP-MAS ^{31}P-NMR spectroscopy.

Elemental analysis % (calc. %) [$C_{60}H_{58}Bi_8F_{36}O_{44}P_2S_{18}(H_2O)(C_2H_3N)_6$]: C 18.97 (18.24), H 1.82 (1.66).

CP-MAS ^{31}P-NMR (162 MHz; 8 kHz spin-rate): δ (ppm) = +56.0 (s, $h_{1/2}$ = 1600 Hz);
^{31}P-NMR (162 MHz; ACN, C_6D_6 lock tube, 298 K): δ (ppm) = +67.6 (s);
CP-MAS ^{1}H-NMR (400 MHz; 20 kHz spin-rate): δ (ppm) = +10.0 to +5.5 (broad band, aromatic protons), +5.5 to 0 (broad band, CH_2, CH_3, acetonitrile);
CP-MAS ^{19}F-NMR (377 MHz; 20 kHz spin-rate): δ (ppm) = − 78.33 (s), −79.71 (s);
CP-MAS ^{13}C-NMR (101 MHz; 11 kHz spin-rate): δ (ppm) = 23.1−11.7 (CH_3), 41.7−32.2 (CH_2), 124.4−110.8 (broad band, C*arom.,* acetonitrile), 141.0−126.8 (broad band, C*arom.*).

3. NMR spectroscopic investigations

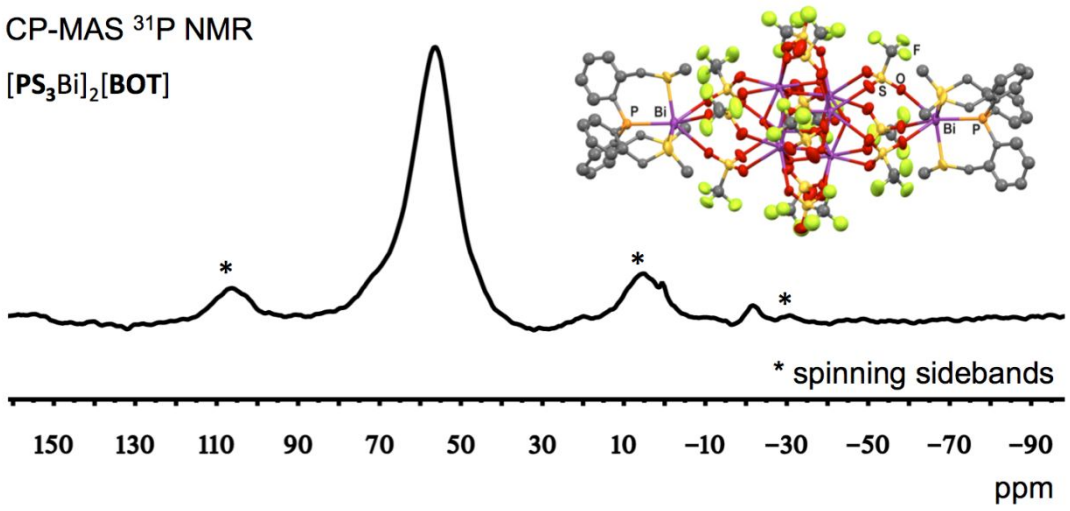

Figure S1: CP-MAS solid-state ^{31}P NMR spectrum of crystals of [**PS$_3$**Bi]$_2$[**BOT**].

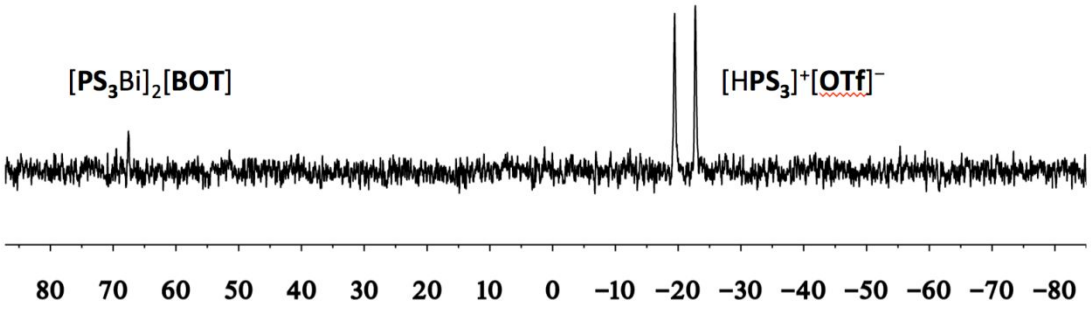

Figure S2: ^{31}P solution NMR spectrum of an acetonitrile solution containing crystals of [**PS$_3$**Bi]$_2$[**BOT**] showing the decomposition to the phosphonium salt [H**PS$_3$**]$^+$[OTf]$^-$.

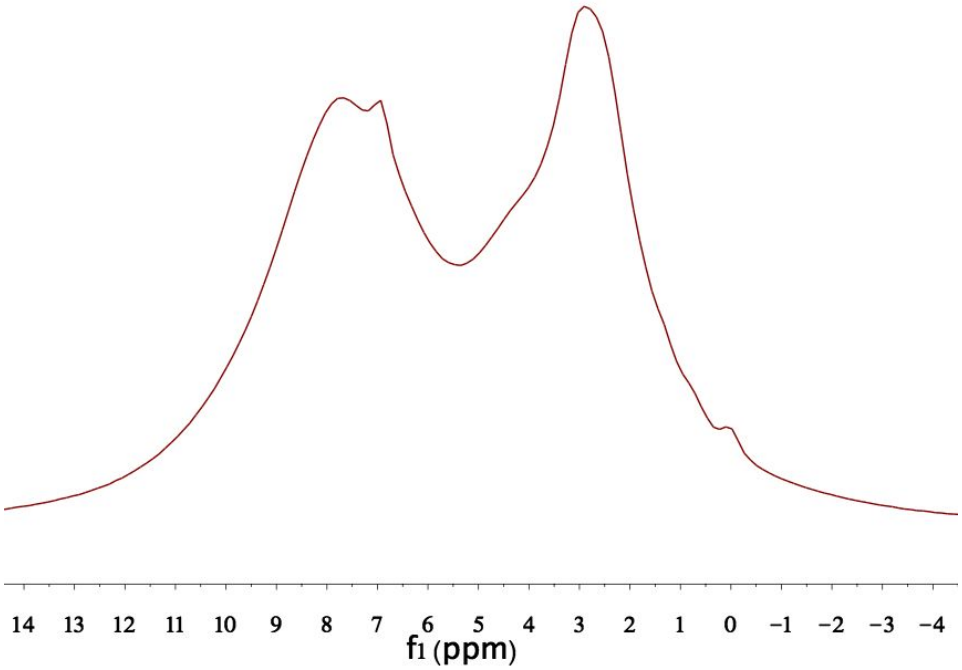

Figure S3: Solid-state CP-MAS ^{1}H NMR spectra of crystals of [$\mathbf{PS_3}$Bi]$_2$[**BOT**] (20 kHz).

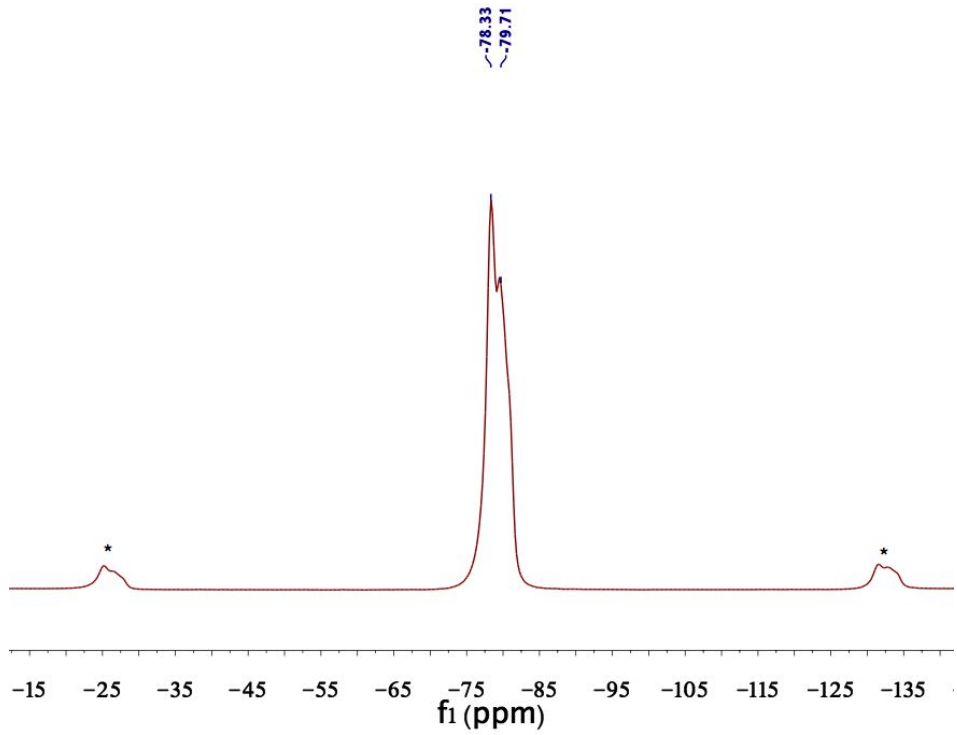

Figure S4: Solid-state CP-MAS ^{19}F NMR spectra of crystals of [$\mathbf{PS_3}$Bi]$_2$[**BOT**] (20 kHz);
* spinning sidebands.

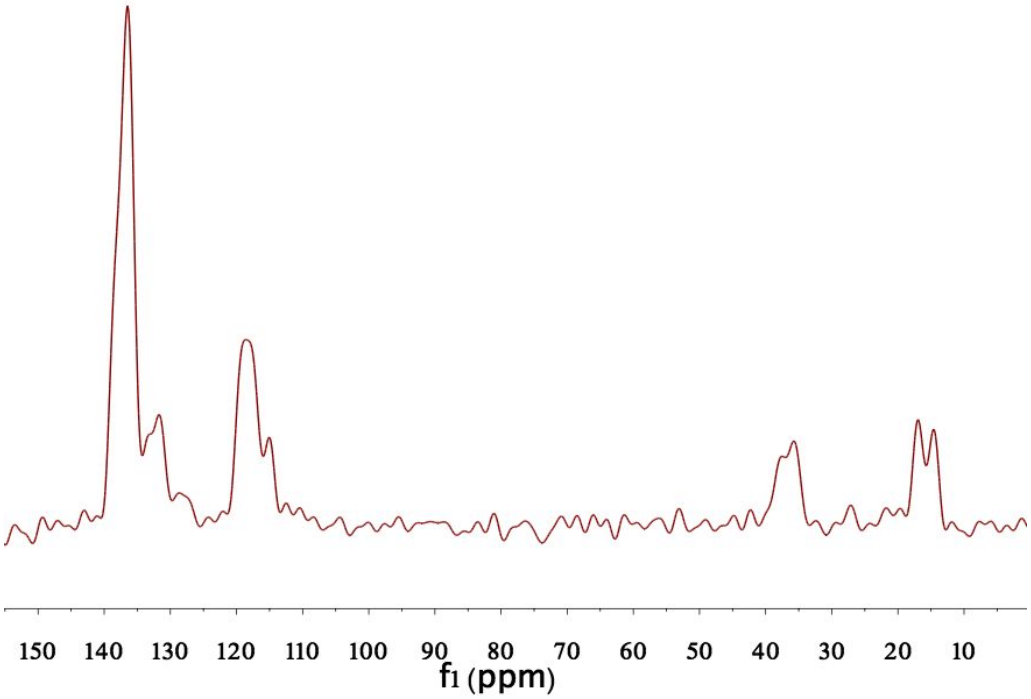

Figure S5: Solid-state CP-MAS ^{13}C NMR spectra of crystals of [**PS$_3$**Bi]$_2$[**BOT**] (11 kHz).

4. X-ray structure analyses

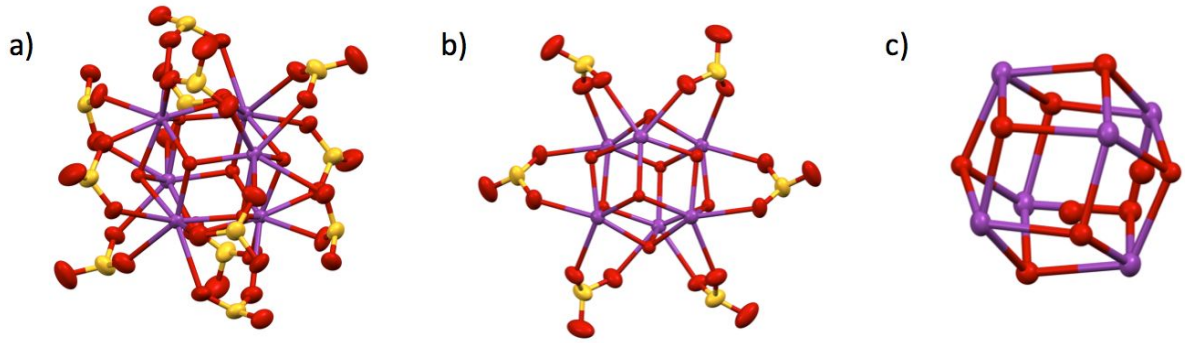

Figure S6: Details of the solid-state structure of compound [**PS$_3$**Bi]$_2$[**BOT**]: a) plot of the central $\{Bi_6O_4(OH)_4[OTf]_{12}\}^{6-}$ unit (CF_3 groups have been omitted for clarity); b) side view of the formally neutral $\{Bi_6O_4(OH)_4[OTf]_6\}$ fragment (hydrogen atoms and CF_3 groups have been omitted for clarity); e) plot of central $[Bi_6O_4(OH)_4]^{6+}$ cluster (triflate anions have been omitted for clarity).

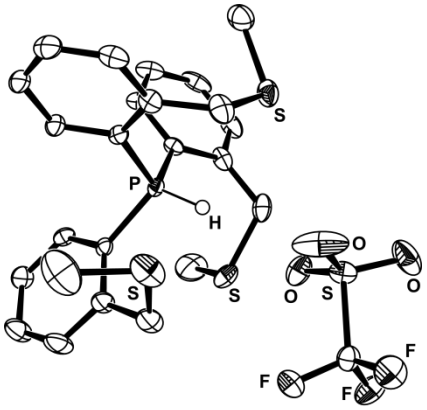

Figure S7: ORTEP representation of phosphonium triflate salt $[H\mathbf{PS_3}]^+[OTf]^-$ (thermal ellipsoids are drawn at 50% probability). Carbon-bonded hydrogen atoms have been omitted for clarity.

Table S1 Crystal data and structure refinement for [$PS_3Bi]_2$[BOT]	
Identification code	1941695
Empirical formula	$C_{60}H_{54}Bi_8F_{36}N_6O_{44}P_2S_{18}$ x $6CH_3CN$ x H_2O
Formula weight	4736.21
Temperature/K	120.0
Crystal system	cubic
Space group	Pa-3
a/Å	24.6874(12)
b/Å	24.6874(12)
c/Å	24.6874(12)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	15046(2)
Z	4
$\rho_{calc}g/cm^3$	2.091
μ/mm^{-1}	9.706
F(000)	8848.0
Crystal size/mm^3	0.16 × 0.12 × 0.09
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.666 to 52.916
Index ranges	$-30 \leq h \leq 30$, $-30 \leq k \leq 30$, $-30 \leq l \leq 30$
Reflections collected	192695
Independent reflections	5186 [R_{int} = 0.1420, R_{sigma} = 0.0390]
Data/restraints/parameters	5186/64/286
Goodness-of-fit on F^2	1.157
Final R indexes [I>=2σ (I)]	R_1 = 0.0545, wR_2 = 0.1156
Final R indexes [all data]	R_1 = 0.1096, wR_2 = 0.1494
Largest diff. peak/hole / e $Å^{-3}$	1.60/-1.01

On the refinement of $[PS_3Bi]_2[BOT]$

The asymmetric unit contains two MeCN molecules in general positions (i.e. not having crystallographic symmetry). Of these, molecule N(1)CMe is incompatible with one of the two alternative conformations of the disordered CH2-S-Me chain, as this would result in an impossibly short contact S(1A)…N(1). However, the actual degree of the disorder is not rigorously imposed by crystal symmetry and may vary. The molecule N(2)CMe can, in principle, have a stoichiometric (100%) occupancy, but the actual electron density is lower than this. The 50% occupancies of both acetonitrile molecules, as well as S(1A), give the best fit to the observed X-ray data. This corresponds to six MeCN molecules per formula unit. The water molecule is disordered between three positions (with optimised occupancy of 1/6) slightly offset from a 3-fold rotation axis and related by this axis. Because of this disorder, it was impossible to locate the hydrogen atoms reliably, so the latter were not included into the refined model – however, they were included in the formula and taken into account in all formula-related parameters (f.w., F000, density). The use of restraints was necessitated by extensive disorder of the structure. The bond distances in the two alternative positions of each disordered moiety were restrained to similarity (SADI). The atomic displacement parameters in the disordered arene ring and part-occupied MeCN molecules were restrained using rigid-bond model (RIGU).[6]

Regarding the B-alerts in the Cif-file:

1) Much of the molecule is disordered and some of the disordered F, O and C atoms were refined in isotropic approximation, anisotropic refinement proving unstable due to small distances between alternative positions of these atoms.

2) The structure contains voids with the nominal volume of 158 A3, however, the awkward shape of these voids (as thin fragments of spherical shells) make them unsuitable to accommodate solvent molecules. No substantial residual electron density was detected in these voids.

Table S2 Crystal data and structure refinement for $[HPS_3]^+[OTf]^-$	
Identification code	1941566
Empirical formula	$C_{25}H_{28}F_3O_3PS_4$
Formula weight	592.68
Temperature/K	120
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	17.1492(15)
b/Å	10.6339(10)
c/Å	17.2896(14)
α/°	90
β/°	119.091(3)
γ/°	90
Volume/Å^3	2755.2(4)
Z	4
ρ_{calc}g/cm^3	1.429
μ/mm^{-1}	0.449
F(000)	1232.0
Crystal size/mm^3	0.122 × 0.085 × 0.061
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.668 to 52.032
Index ranges	$-21 \leq h \leq 21$, $-13 \leq k \leq 13$, $-21 \leq l \leq 21$
Reflections collected	41749
Independent reflections	5412 [R_{int} = 0.0775, R_{sigma} = 0.0505]
Data/restraints/parameters	5412/0/335
Goodness-of-fit on F^2	1.084
Final R indexes [I>=2σ (I)]	R_1 = 0.0581, wR_2 = 0.1304
Final R indexes [all data]	R_1 = 0.0868, wR_2 = 0.1429
Largest diff. peak/hole / e Å^{-3}	0.67/-0.60

5. Computational details

The computations were carried out with the Gaussian 09 suite of programs.[7] All structures were optimised using the ωB97XD and B3LYPD3 functionals. We employed the all valence cc-pVDZ basis set for H, C, P, S, Cl, O, and F while for Bi the cc-pVDZ-PP basis set including pseudopotentials for the modelling of relativistic effects was used. The basis set with pseudo potentials was obtained from the EMSL Basis Set Library (https://www.basissetexchange.org/).[8-9] At each of the optimised structures vibrational analysis was performed to check whether the stationary point located is a minimum or a saddle point of the potential energy hypersurface. For Wiberg Bond Indices and NPA charges the NBO program version 3.1 was used.[10] The AIM analysis was obtained with the Multiwfn code.[11] The calculation of indirect spin-spin coupling constants was carried out with the ADF 2014 program[12-14] at the PBE1/TZ2P level with scalar ZORA approximation on geometries optimized at ωB97XD/cc-pVDZ-PP.

Table S3: Bond distances (d, Å) and Lagrangian kinetic energy (G, a.u.), potential energy density at the bond critical point (V, a.u.), total electronic energy density H, $|V/G|$, Laplacian of electron density at the bond critical point ($\nabla^2\rho$, a.u), eta index and electron densities at the bond critical points (ρ, a.u.), at Bi–P bond and at Bi–S bonds at ωB97XD/cc-pvdz(-PP) level. Wiberg Bond Indices (WBI, –) and NPA partial charges (q, e) at ωB97XD/cc-pvdz(-PP) level. SP[$\mathbf{PS_3}$Bi]$^{3+}$ indicates the second order saddle point on the potential energy surface of [$\mathbf{PS_3}$Bi]$^{3+}$, while [$\mathbf{PS_3}$Bi]$^{3+}$ shows the bonding parameters belonging to the energy minimum.

		d	G	V	H	|V/G|	$\nabla^2\rho$	eta index	ρ	WBI	q
	Bi-P	2.715	0.02395	-0.04409	-0.02015	1.84	0.0152	0.44100	0.0671	0.766	-
	Bi-S	2.819	0.02407	-0.03046	-0.00639	1.27	0.0707	0.26685	0.0463	0.521	-
	Bi-S	2.817	0.02425	-0.03074	-0.00648	1.27	0.0711	0.26708	0.0465	0.522	-
	Bi-S	2.816	0.02422	-0.03068	-0.00646	1.27	0.0711	0.26688	0.0464	0.522	-
SP [$\mathbf{PS_3}$Bi]$^{3+}$	Bi	-	-	-	-	-	-	-	-	-	1.147
	P	-	-	-	-	-	-	-	-	-	1.058
	S	-	-	-	-	-	-	-	-	-	0.289
	S	-	-	-	-	-	-	-	-	-	0.289
	S	-	-	-	-	-	-	-	-	-	0.289
	Bi-P	2.697	0.02477	-0.04611	-0.02134	1.86	0.0138	0.45019	0.0689	0.788	-
	Bi-S	2.829	0.02252	-0.02755	-0.00504	1.22	0.0699	0.24599	0.0422	0.463	-
	Bi-S	2.662	0.03340	-0.04612	-0.01272	1.38	0.0828	0.28466	0.0612	0.711	-
	Bi-S	2.869	0.02410	-0.03037	-0.00627	1.26	0.0713	0.25577	0.0457	0.395	-
[$\mathbf{PS_3}$Bi]$^{3+}$	Bi	-	-	-	-	-	-	-	-	-	1.113
	P	-	-	-	-	-	-	-	-	-	1.038
	S	-	-	-	-	-	-	-	-	-	0.278
	S	-	-	-	-	-	-	-	-	-	0.347
	S	-	-	-	-	-	-	-	-	-	0.236
	Bi-P	2.909	0.02090	-0.02868	-0.00778	1.37	0.0525	0.28972	0.0449	0.417	-
	Bi-S	2.840	0.02340	-0.02904	-0.00565	1.24	0.0710	0.25732	0.0442	0.430	-
	Bi-S	2.884	0.02173	-0.02613	-0.00440	1.20	0.0693	0.24683	0.0405	0.358	-
	Bi-S	2.742	0.02750	-0.03618	-0.00869	1.32	0.0753	0.27294	0.0524	0.560	-
[$\mathbf{PS_3}$BiCl$_2$]$^{+}$	Bi	-	-	-	-	-	-	-	-	-	1.197
	P	-	-	-	-	-	-	-	-	-	0.885
	S	-	-	-	-	-	-	-	-	-	0.283
	S	-	-	-	-	-	-	-	-	-	0.236
	S	-	-	-	-	-	-	-	-	-	0.320
	Bi-P	3.058	0.01551	-0.01884	-0.00332	1.21	0.0488	0.25570	0.0335	0.302	-
	Bi-S	3.105	0.01408	-0.01483	-0.00075	1.05	0.0533	0.21780	0.0269	0.233	-
	Bi-S	3.062	0.01510	-0.01638	-0.00128	1.08	0.0553	0.22805	0.0294	0.274	-
	Bi-S	2.864	0.02206	-0.02661	-0.00455	1.21	0.0700	0.24791	0.0413	0.382	-
[$\mathbf{PS_3}$BiCl]$^{2+}$	Bi	-	-	-	-	-	-	-	-	-	1.284
	P	-	-	-	-	-	-	-	-	-	0.867
	S	-	-	-	-	-	-	-	-	-	0.221
	S	-	-	-	-	-	-	-	-	-	0.232
	S	-	-	-	-	-	-	-	-	-	0.237

Table S4: Bond distances (d, Å) and Lagrangian kinetic energy (G, a.u.), potential energy density at the bond critical point (V, a.u.), total electronic energy density H, $|V/G|$, Laplacian of electron density at the bond critical point ($\nabla^2\rho$, a.u), eta index and electron densities at the bond critical points (ρ, a.u.), at Bi–P bond and at Bi–S bonds at B3LYPd3/cc-pvdz(-PP) level. Wiberg Bond Indices (WBI, –) and NPA partial charges (q, e) at B3LYPd3/cc-pvdz(-PP) level. SP[$\mathbf{PS_3}$Bi]$^{3+}$ indiacates the second order saddle point on the potential energy surface of [$\mathbf{PS_3}$Bi]$^{3+}$, while [$\mathbf{PS_3}$Bi]$^{3+}$ shows the bonding parameters belonging to the energy minimum.

		d	G	V	H	|V/G|	$\nabla^2\rho$	eta index	ρ	WBI	q
	Bi-P	2.763	0.02105	-0.03744	-0.01639	1.78	0.0187	0.42251	0.0613	0.748	-
	Bi-S	2.856	0.02142	-0.02673	-0.00530	1.25	0.0645	0.26868	0.0437	0.542	-
	Bi-S	2.854	0.02151	-0.02685	-0.00534	1.25	0.0647	0.26857	0.0438	0.542	-
	Bi-S	2.855	0.02145	-0.02676	-0.00531	1.25	0.0646	0.26865	0.0437	0.541	-
SP [$\mathbf{PS_3}$Bi]$^{3+}$	Bi	-	-	-	-	-	-	-	-	-	1.010
	P	-	-	-	-	-	-	-	-	-	1.061
	S	-	-	-	-	-	-	-	-	-	0.308
	S	-	-	-	-	-	-	-	-	-	0.307
	S	-	-	-	-	-	-	-	-	-	0.307
	Bi-P	2.746	0.02160	-0.03900	-0.01740	1.81	0.0168	0.43219	0.0629	0.767	-
	Bi-S	2.877	0.02031	-0.02470	-0.00440	1.22	0.0636	0.25073	0.0406	0.469	-
	Bi-S	2.699	0.02953	-0.04021	-0.01068	1.36	0.0754	0.28558	0.0572	0.727	-
	Bi-S	2.900	0.02088	-0.02589	-0.00501	1.24	0.0635	0.25966	0.0425	0.415	-
[$\mathbf{PS_3}$Bi]$^{3+}$	Bi	-	-	-	-	-	-	-	-	-	1.000
	P	-	-	-	-	-	-	-	-	-	1.080
	S	-	-	-	-	-	-	-	-	-	0.290
	S	-	-	-	-	-	-	-	-	-	0.353
	S	-	-	-	-	-	-	-	-	-	0.245
	Bi-P	3.056	0.01502	-0.01831	-0.00329	1.22	0.0469	0.26101	0.0338	0.326	-
	Bi-S	3.100	0.01390	-0.01477	-0.00088	1.06	0.0521	0.22395	0.0277	0.263	-
	Bi-S	3.074	0.02002	-0.02396	-0.00393	1.20	0.0644	0.25032	0.0395	0.296	-
	Bi-S	2.895	0.01436	-0.01555	-0.00118	1.08	0.0528	0.23146	0.0292	0.391	-
[$\mathbf{PS_3}$BiCl$_2$]$^{+}$	Bi	-	-	-	-	-	-	-	-	-	1.148
	P	-	-	-	-	-	-	-	-	-	0.881
	S	-	-	-	-	-	-	-	-	-	0.233
	S	-	-	-	-	-	-	-	-	-	0.245
	S	-	-	-	-	-	-	-	-	-	0.249
[$\mathbf{PS_3}$BiCl]$^{2+}$	Bi-P	2.942	0.01887	-0.02550	-0.00663	1.35	0.0490	0.28883	0.0425	0.422	-
	Bi-S	2.886	0.02410	-0.03129	-0.00719	1.30	0.0677	0.27518	0.0489	0.433	-
	Bi-S	2.900	0.02037	-0.02037	-0.04074	1.00	0.0651	0.25118	0.0399	0.379	-
	Bi-S	2.784	0.02051	-0.02503	-0.00452	1.22	0.0640	0.25826	0.0412	0.572	-
	Bi	-	-	-	-	-	-	-	-	-	1.078
	P	-	-	-	-	-	-	-	-	-	0.892
	S	-	-	-	-	-	-	-	-	-	0.289
	S	-	-	-	-	-	-	-	-	-	0.243
	S	-	-	-	-	-	-	-	-	-	0.331

Table S5: NPA charges (q, electron) in $[\mathbf{PS_3}BiCl_n]^{3-n}$ (n = 0, 1, 2, 3) and $[\mathbf{PS_3}Bi(ACN)_3]^{3+}$and net charge donation from the ligand to the $[BiCl_n]^{3-n}$ moiety (Δq calculated as the sum of partial NPA charges in the ligand fragment). All data obtained at the ωB97XD/cc-pVDZ(-PP) level of theory. The values obtained with the solvent model PCM are shown in italics.

	$\mathbf{PS_3}BiCl_3$	$[\mathbf{PS_3}BiCl_2]^+$	$[\mathbf{PS_3}BiCl]^{2+}$	$[\mathbf{PS_3}Bi]^{3+}$	$[\mathbf{PS_3}Bi(ACN)_3]^{3+}$
q(P)	0.838 *0.841*	0.867 *0.884*	0.885 *0.891*	1.038 *1.008*	0.957 *0.942*
q(Bi)	1.360 *1.346*	1.284 *1.310*	1.197 *1.321*	1.113 *1.361*	1.292 *1.374*
Δq	0.326 *0.516*	0.816 *0.912*	1.301 *1.266*	1.887 *1.639*	1.400 *1.289*

Table S6: Bond distances (d, Å) and bond valances (*s*, valence units) of Bi–P, Bi–S and Bi–Cl or Bi–N bonds at ωB97XD/cc-pvdz(-PP) level.

d	$\mathbf{PS_3}BiCl_3$	$[\mathbf{PS_3}BiCl_2]^+$	$[\mathbf{PS_3}BiCl]^{2+}$	$[\mathbf{PS_3}Bi]^{3+}$	$[\mathbf{PS_3}Bi(ACN)_3]^{3+}$
Bi-P	3.576	3.058	2.909	2.697	2.817
Bi-S1	3.272	3.105	2.840	2.869	2.892
Bi-S2	3.232	3.062	2.884	2.662	2.768
Bi-S3	3.313	2.864	2.742	2.829	2.890
Bi-Cl1	2.562	2.564	2.530	-	-
Bi-Cl2	2.566	2.558	-	-	-
Bi-Cl3	2.537	-	-	-	-
Bi-N1	-	-	-	-	2.697
Bi-N2	-	-	-	-	2.857
Bi-N3	-	-	-	-	2.883
s	$\mathbf{PS_3}BiCl_3$	$[\mathbf{PS_3}BiCl_2]^+$	$[\mathbf{PS_3}BiCl]^{2+}$	$[\mathbf{PS_3}Bi]^{3+}$	$[\mathbf{PS_3}Bi(ACN)_3]^{3+}$
Bi-P	0.077	0.315	0.470	0.835	0.603
Bi-S1	0.142	0.223	0.457	0.422	0.397
Bi-S2	0.158	0.251	0.406	0.739	0.554
Bi-S3	0.127	0.428	0.594	0.471	0.399
Bi-Cl1	0.801	0.798	0.873	-	-
Bi-Cl2	0.792	0.809	-	-	-
Bi-Cl3	0.857	-	-	-	-
Bi-N1	-	-	-	-	0.291
Bi-N2	-	-	-	-	0.189
Bi-N3	-	-	-	-	0.176
Σ*s*	2.955	2.824	2.800	2.467	2.609

Table S7: Bond distances (d, Å) and bond valances (*s*, valence units) of Bi–P, Bi–S and Bi–Cl or Bi–N bonds at ωB97XD/cc-pvdz(-PP) level employing the PCM model with acetonitrile as a solvent.

d	$\mathbf{PS_3}BiCl_3$	$[\mathbf{PS_3}BiCl_2]^+$	$[\mathbf{PS_3}BiCl]^{2+}$	$[\mathbf{PS_3}Bi]^{3+}$	$[\mathbf{PS_3}Bi(ACN)_3]^{3+}$
Bi-P	3.422	3.001	2.923	2.743	2.849
Bi-S1	3.112	3.044	2.935	2.873	2.909
Bi-S2	3.123	3.048	2.730	2.692	2.795
Bi-S3	3.146	2.848	2.858	2.862	2.901
Bi-Cl1	2.632	2.644	2.602	-	-
Bi-Cl2	2.623	2.601	-	-	-
Bi-Cl3	2.611	-	-	-	-
Bi-N1	-	-	-	-	2.625
Bi-N2	-	-	-	-	2.762
Bi-N3	-	-	-	-	2.767
s	$\mathbf{PS_3}BiCl_3$	$[\mathbf{PS_3}BiCl_2]^+$	$[\mathbf{PS_3}BiCl]^{2+}$	$[\mathbf{PS_3}Bi]^{3+}$	$[\mathbf{PS_3}Bi(ACN)_3]^{3+}$
Bi-P	0.118	0.367	0.452	0.737	0.554
Bi-S1	0.219	0.263	0.353	0.418	0.379
Bi-S2	0.213	0.260	0.615	0.682	0.516
Bi-S3	0.200	0.447	0.435	0.430	0.387
Bi-Cl1	0.663	0.642	0.720	-	-
Bi-Cl2	0.679	0.721	-	-	-
Bi-Cl3	0.702	-	-	-	-
Bi-N1	-	-	-	-	0.354
Bi-N2	-	-	-	-	0.244
Bi-N3	-	-	-	-	0.241
Σs	2.793	2.700	2.575	2.267	2.674

Table S8: Bond distances (d, Å) and bond valances (*s*, valence units) of Bi–P, Bi–S and Bi–Cl, Bi–Br, Bi–I or Bi–O bonds obtained from solid-state structures (the bond distances for **PS$_3$**BiX$_3$ are taken from reference 1).

d	**PS$_3$**BiCl$_3$ X = Cl	**PS$_3$**BiBr$_3$ X = Br	**PS$_3$**BiI$_3$ X = I	[**PS$_3$**Bi]$_2$[**BOT**] X = O
Bi-P	3.365	3.759	3.792	2.800
Bi-S1	3.106	3.047	3.074	2.749
Bi-S2	3.075	3.088	3.136	2.749
Bi-S3	3.076	3.079	3.130	2.749
Bi-X1	2.572	2.700	2.911	2.760
Bi-X2	2.547	2.712	2.923	2.760
Bi-X3	2.574	2.680	2.893	2.760
s	**PS$_3$**BiCl$_3$ X = Cl	**PS$_3$**BiBr$_3$ X = Br	**PS$_3$**BiI$_3$ X = I	[**PS$_3$**Bi]$_2$[**BOT**] X = O
Bi-P	0.137	0.047	0.043	0.632
Bi-S1	0.223	0.261	0.243	0.584
Bi-S2	0.242	0.234	0.205	0.584
Bi-S3	0.241	0.239	0.209	0.584
Bi-X1	0.780	0.806	0.825	0.164
Bi-X2	0.834	0.780	0.799	0.164
Bi-X3	0.776	0.850	0.867	0.164
Σ*s*	3.233	3.217	3.191	2.874

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

[**PS$_3$**Bi]$^{3+}$

Total energy: -2680.290033

C	2.042299	2.001415	1.918934
C	0.899796	1.208425	1.738843
C	0.228629	0.659474	2.856097
C	0.759707	0.887930	4.127383
C	1.905444	1.664759	4.302033
C	2.540229	2.232146	3.199914
P	0.273725	1.017371	0.046211
C	-1.123012	2.163602	-0.167328
C	-1.061054	3.322338	0.625978
C	-2.023356	4.320030	0.491573
C	-3.057109	4.164119	-0.425833
C	-3.132533	3.007296	-1.202690
C	-2.176336	1.997143	-1.098134
C	-2.351362	0.767544	-1.946908
S	-2.989831	-0.615270	-0.895403
C	-3.632299	-1.787683	-2.139811
C	-1.050245	-0.123068	2.741166
S	-0.725552	-1.875324	2.202509
C	-2.372511	-2.646681	2.374382
C	1.569206	1.278119	-1.197649
C	1.279487	2.191962	-2.222571
C	2.186982	2.404250	-3.258782
C	3.384051	1.697986	-3.278965
C	3.680034	0.791565	-2.257594
C	2.797529	0.558541	-1.201244
C	3.254577	-0.368527	-0.102546
S	2.430316	-2.011787	0.030519
C	2.918183	-2.806281	-1.536893
Bi	-0.328443	-1.571138	-0.412220
H	-2.875939	-2.036533	-2.895676
H	-4.507525	-1.319781	-2.610666
H	-3.954931	-2.687797	-1.600342
H	-3.149268	-2.033713	1.900196
H	-2.548220	-2.736350	3.456065
H	-2.314465	-3.652200	1.937150
H	2.403513	-3.774803	-1.593079
H	4.000757	-2.985798	-1.481945
H	2.674248	-2.174417	-2.401476
H	-1.430720	0.457844	-2.471046
H	-3.114980	0.934588	-2.718796
H	-1.789816	0.316747	2.055162
H	-1.524836	-0.241854	3.725933
H	3.143751	0.057700	0.902045
H	4.318796	-0.613353	-0.227147
H	-0.258306	3.461770	1.350621

H	-1.957812	5.219027	1.105405
H	-3.815034	4.940817	-0.538049
H	-3.955400	2.894463	-1.911194
H	2.542756	2.454347	1.059718
H	3.422582	2.859414	3.332983
H	2.294981	1.834430	5.306822
H	0.262691	0.467626	5.004085
H	0.348492	2.761302	-2.206816
H	1.957270	3.129463	-4.040028
H	4.104978	1.858813	-4.081942
H	4.640369	0.271847	-2.275036

SP [$\mathbf{PS_3}$Bi]$^{3+}$

Total energy: -2680.284062

Bi	0.000810	0.012792	-1.745054
P	-0.000450	-0.007763	0.969881
S	-2.663369	0.918060	-1.568186
S	2.115780	1.863497	-1.563836
S	0.547167	-2.746419	-1.594003
C	2.298728	-3.000632	-2.033229
C	2.501040	1.992066	0.231897
C	1.400612	2.480318	1.135134
C	0.299156	1.689601	1.555526
C	-0.603976	2.192548	2.505657
C	-0.450374	3.478526	3.019475
C	0.605440	4.272486	2.585403
C	1.521023	3.768932	1.659562
C	1.460465	3.512542	-1.984683
C	-1.623692	-0.602774	1.539926
C	-2.857494	-0.040455	1.118964
C	-4.036199	-0.586958	1.631837
C	-4.019160	-1.641332	2.546812
C	-2.805453	-2.163253	2.980692
C	-1.612990	-1.646632	2.478822
C	1.323281	-1.121334	1.537274
C	1.456988	-2.466583	1.103991
C	2.515209	-3.218930	1.618765
C	3.412877	-2.685269	2.545647
C	3.254773	-1.377440	2.990437
C	2.214665	-0.598448	2.487773
C	-2.981010	1.166242	0.228132
C	-3.763163	-0.467292	-2.011767
C	0.481650	-3.167462	0.196959
H	2.629401	-4.260680	1.311032
H	4.223378	-3.304914	2.932290
H	3.931466	-0.960047	3.736892
H	2.093318	0.420060	2.860027
H	0.638562	-4.255179	0.227608
H	-0.569765	-2.992643	0.468122

H	-3.602562	-1.333438	-1.357792
H	-4.792350	-0.092462	-1.921933
H	-3.565389	-0.713571	-3.063525
H	-4.996625	-0.161096	1.333219
H	-4.959060	-2.037862	2.933650
H	-2.778999	-2.965399	3.719186
H	-0.668585	-2.054282	2.842999
H	-4.000163	1.576285	0.272472
H	-2.299343	1.984102	0.503619
H	2.485604	-4.081824	-1.970412
H	2.421293	-2.679089	-3.075949
H	2.965047	-2.447234	-1.359967
H	2.368605	4.390144	1.361662
H	0.735288	5.281026	2.980906
H	-1.152907	3.849797	3.766429
H	-1.425585	1.574418	2.871514
H	3.367167	2.667571	0.279048
H	2.869185	0.988882	0.492304
H	1.140929	3.474671	-3.034819
H	0.634698	3.797555	-1.321269
H	2.299258	4.216913	-1.893661

$[\mathbf{PS_3}BiCl_2]^+$

Total energy: -3601.545502

C	-1.300813	-1.821460	-2.356269
C	-2.050050	-1.272906	-1.294510
C	-3.362712	-1.714322	-1.079958
C	-3.936081	-2.683239	-1.897816
C	-3.195402	-3.232437	-2.939890
C	-1.890589	-2.801976	-3.160383
P	-1.329869	-0.027103	-0.139468
C	-2.279695	-0.320699	1.407138
C	-1.921704	-1.393152	2.249936
C	-2.640082	-1.584340	3.433909
C	-3.700854	-0.752372	3.779356
C	-4.070130	0.287727	2.930355
C	-3.363121	0.498822	1.749693
C	-0.806425	-2.356301	1.924301
S	0.808469	-1.715991	2.524911
C	1.873248	-3.157267	2.219435
C	0.101981	-1.385019	-2.688492
S	1.339661	-2.081898	-1.511306
C	2.858156	-1.990350	-2.507978
C	-1.811199	1.622296	-0.784636
C	-2.346176	1.699158	-2.076046
C	-2.588642	2.928318	-2.683667
C	-2.306825	4.102891	-1.996875
C	-1.789997	4.036401	-0.705737
C	-1.520494	2.815316	-0.079274

C	-0.983401	2.868019	1.330932
S	0.841855	2.788084	1.554821
C	1.429070	4.107172	0.457979
Bi	1.700154	0.168051	0.223458
Cl	1.914941	1.529073	-1.932186
Cl	4.121024	-0.607540	0.554203
H	2.968649	-0.980433	-2.924974
H	2.797773	-2.749956	-3.297692
H	3.692562	-2.206793	-1.828852
H	1.728507	-3.537873	1.198896
H	1.650539	-3.940176	2.956075
H	2.909579	-2.814127	2.337596
H	2.523026	4.120558	0.550862
H	1.024092	5.067262	0.805275
H	1.151633	3.906185	-0.584810
H	0.227568	-0.291738	-2.710535
H	0.392358	-1.772618	-3.673806
H	-0.732236	-2.569606	0.847270
H	-0.978108	-3.312044	2.438666
H	-1.355422	2.054220	1.966436
H	-1.295969	3.807962	1.807170
H	-3.948611	-1.297865	-0.259931
H	-4.961523	-3.007251	-1.716680
H	-3.631155	-3.996111	-3.585282
H	-1.315022	-3.233389	-3.981814
H	-3.658076	1.312413	1.083617
H	-4.910409	0.935683	3.183077
H	-4.243192	-0.922616	4.710140
H	-2.361822	-2.405998	4.097073
H	-2.582898	0.783913	-2.620243
H	-3.006122	2.961592	-3.690542
H	-2.495621	5.072911	-2.458078
H	-1.594437	4.963313	-0.161989

[**PS$_3$**BiCl]$^{2+}$

Total energy: -3140.968811

C	1.714271	2.508105	-1.239435
C	2.256928	1.461100	-0.461362
C	3.552704	1.585141	0.058552
C	4.313018	2.725184	-0.187594
C	3.780197	3.758905	-0.951181
C	2.492004	3.646102	-1.468712
P	1.303116	-0.050095	-0.048097
C	1.941510	-0.615702	1.563958
C	1.383978	-0.083579	2.743330
C	1.859132	-0.537407	3.975881
C	2.873186	-1.491260	4.044656
C	3.430564	-2.004030	2.875646
C	2.964848	-1.567592	1.637051

C	0.317710	0.981498	2.713828
S	-1.360722	0.284489	2.378227
C	-2.411612	1.706672	2.805414
C	0.335774	2.467676	-1.849384
S	-0.972424	2.835954	-0.593622
C	-2.367308	3.362869	-1.643788
C	1.639317	-1.334280	-1.307283
C	2.340529	-0.965929	-2.462330
C	2.503663	-1.862790	-3.517163
C	1.963679	-3.140297	-3.425448
C	1.272024	-3.519244	-2.275458
C	1.088268	-2.638908	-1.204825
C	0.384596	-3.170631	0.020820
S	-1.393506	-2.737815	0.259641
C	-2.171858	-3.431776	-1.230194
Bi	-1.589782	0.030406	-0.342795
Cl	-4.064293	0.148228	0.172959
H	-2.548852	2.644838	-2.454870
H	-2.139603	4.355966	-2.051722
H	-3.250276	3.420736	-0.993905
H	-2.026951	2.621990	2.337452
H	-2.402756	1.790254	3.900254
H	-3.424821	1.473176	2.455066
H	-3.229617	-3.135968	-1.202076
H	-2.101965	-4.526008	-1.170345
H	-1.685643	-3.064310	-2.144157
H	0.117629	1.504230	-2.342995
H	0.237484	3.246801	-2.617099
H	0.516102	1.780405	1.983433
H	0.215762	1.450972	3.702324
H	0.851483	-2.850924	0.961295
H	0.396726	-4.269592	0.018312
H	3.977946	0.786595	0.667425
H	5.320635	2.802833	0.221912
H	4.365130	4.658197	-1.147290
H	2.083459	4.462391	-2.067602
H	3.398300	-1.975469	0.720829
H	4.229895	-2.744214	2.925227
H	3.231513	-1.830699	5.017205
H	1.436992	-0.134844	4.898906
H	2.780101	0.030372	-2.537451
H	3.062203	-1.560888	-4.403804
H	2.090624	-3.853758	-4.240443
H	0.880375	-4.536204	-2.200576

[**PS$_3$**Bi(ACN)$_3$]$^{3+}$

Total energy:-3078.586199

C	3.203165	1.946086	-0.127996
C	2.336492	1.141644	-0.877545

C	1.961742	1.534832	-2.187490
C	2.464183	2.743130	-2.678643
C	3.316245	3.547695	-1.920337
C	3.694371	3.144131	-0.644827
P	1.628040	-0.320386	-0.034920
Bi	-1.135146	0.218669	0.072440
S	-0.620157	0.401631	-2.765839
C	-1.325427	2.036632	-3.133836
C	1.152100	0.684314	-3.135238
C	2.505064	-0.590730	1.554533
C	2.197870	0.109352	2.741690
C	2.923912	-0.180380	3.898763
C	3.946746	-1.126552	3.895789
C	4.258098	-1.803220	2.721197
C	3.539095	-1.540214	1.558233
C	1.129175	1.162560	2.819369
S	-0.543650	0.394571	2.897543
C	-1.530282	1.826260	3.437846
C	1.977428	-1.823585	-1.009120
C	2.999447	-1.789811	-1.966982
C	3.336364	-2.938185	-2.679947
C	2.655857	-4.127902	-2.434808
C	1.661222	-4.173946	-1.459290
C	1.317198	-3.037426	-0.723556
C	0.312347	-3.172849	0.390072
S	-1.345159	-2.535869	-0.108097
C	-2.355819	-3.046592	1.318455
N	-0.329728	2.791111	0.149883
C	-0.045459	3.911059	0.053645
C	0.306071	5.315936	-0.069332
N	-3.408919	-0.358421	-1.557457
C	-4.282392	-0.667309	-2.254313
C	-5.376781	-1.054142	-3.132727
N	-3.577399	-0.018685	1.585002
C	-4.654162	0.033486	2.012644
C	-6.001120	0.097882	2.561371
H	-1.422467	2.663645	2.736723
H	-1.185892	2.109919	4.441152
H	-2.573805	1.497617	3.487001
H	-1.941601	-2.659411	2.257807
H	-2.377355	-4.144546	1.320291
H	-3.363974	-2.653053	1.148131
H	-2.379161	2.013766	-2.827014
H	-1.267088	2.194705	-4.218913
H	-0.782957	2.824192	-2.596381
H	1.154832	1.870171	1.977982
H	1.232742	1.738157	3.748862
H	0.623648	-2.667730	1.316776
H	0.144341	-4.232995	0.624573
H	1.559236	-0.329463	-3.235020
H	1.161205	1.124892	-4.141771
H	3.798067	-2.083391	0.649758
H	5.062701	-2.538767	2.702483
H	4.500444	-1.329365	4.813282
H	2.690054	0.350926	4.823378

H	3.552662	-0.865491	-2.147715
H	4.137409	-2.902563	-3.419045
H	2.911867	-5.031690	-2.989122
H	1.158258	-5.120822	-1.253260
H	3.523056	1.629454	0.865934
H	4.386589	3.745502	-0.054148
H	3.707498	4.473488	-2.345688
H	2.212470	3.048538	-3.696709
H	-6.018398	-1.787042	-2.624855
H	-5.973193	-0.168408	-3.392437
H	-4.970631	-1.501964	-4.050129
H	-6.640295	-0.644194	2.063782
H	-5.971403	-0.115926	3.638962
H	-6.418480	1.101573	2.400751
H	1.057897	5.433516	-0.861709
H	-0.591535	5.898773	-0.320486
H	0.719029	5.677889	0.882637

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

[**PS$_3$**Bi]$^{3+}$

Total energy: -2680.743872

C	1.803897	1.111736	-2.587779
C	1.820301	0.373169	-1.398982
C	2.747430	-0.684669	-1.223423
C	3.623649	-0.962479	-2.274054
C	3.594728	-0.233675	-3.462742
C	2.688206	0.807659	-3.619219
P	0.568584	0.793291	-0.146633
Bi	-0.963104	-1.469222	0.096182
S	1.583069	-2.749965	0.356938
C	1.630342	-3.739517	-1.167869
C	2.886307	-1.498534	0.037107
C	-0.351686	2.289696	-0.651099
C	-1.380677	2.292789	-1.617762
C	-1.987959	3.507754	-1.937740
C	-1.589297	4.698287	-1.335243
C	-0.570845	4.690128	-0.388804
C	0.044559	3.490938	-0.044656
C	-1.877400	1.051753	-2.304396
S	-2.988886	0.134318	-1.159816
C	-3.717927	-1.102810	-2.277346
C	1.399181	1.209931	1.421284
C	2.755279	1.554725	1.366069
C	3.434025	1.909741	2.527707
C	2.762788	1.916074	3.746477
C	1.408972	1.592281	3.800963
C	0.702445	1.250300	2.646661
C	-0.775219	1.000792	2.758948

S	-1.175143	-0.801085	2.695237
C	-2.962617	-0.784287	3.040061
H	-2.942002	-1.653279	-2.822115
H	-4.377957	-0.570578	-2.973150
H	-4.307042	-1.781913	-1.649289
H	-3.482145	-0.064240	2.398528
H	-3.054234	-0.510594	4.098312
H	-3.330804	-1.804272	2.882752
H	0.820829	-4.475833	-1.094479
H	2.599223	-4.253555	-1.193488
H	1.503228	-3.108097	-2.055572
H	-1.072052	0.394515	-2.663379
H	-2.491422	1.316192	-3.174507
H	-1.372186	1.531768	2.005260
H	-1.139375	1.306007	3.748607
H	2.899367	-0.893886	0.952273
H	3.823433	-2.069648	0.017031
H	0.840409	3.504181	0.698496
H	-0.246235	5.614747	0.087930
H	-2.079874	5.632775	-1.608592
H	-2.788493	3.518247	-2.678470
H	3.287648	1.557091	0.413913
H	4.488147	2.180593	2.471958
H	3.289738	2.184635	4.662217
H	0.885009	1.619512	4.757411
H	1.107829	1.941276	-2.713178
H	2.664966	1.392515	-4.538450
H	4.293006	-0.481190	-4.262511
H	4.354367	-1.763857	-2.153880

[**PS$_3$**BiCl]$^{2+}$

Total energy: -3141.176548

C	1.259747	-2.384372	-1.519449
C	1.734440	-1.052196	-1.422875
C	2.452126	-0.490213	-2.484117
C	2.700975	-1.220765	-3.644166
C	2.234362	-2.525809	-3.749096
C	1.531212	-3.098355	-2.690308
P	1.289096	0.023342	-0.009129
Bi	-1.622666	0.039683	-0.270045
Cl	-4.154076	-0.121113	0.308636
C	0.532617	-3.110862	-0.414631
S	-1.272784	-2.796430	-0.233606
C	-1.904577	-3.233110	-1.879731
C	2.173226	1.620003	-0.192377
C	1.631655	2.692777	-0.932778
C	2.340759	3.896012	-0.982899
C	3.560783	4.045188	-0.329373
C	4.094886	2.982321	0.392817

C	3.401570	1.777734	0.463127
C	0.328550	2.613473	-1.686092
S	-1.102324	2.913717	-0.558498
C	-2.408970	3.335163	-1.750279
C	1.959586	-0.760671	1.500376
C	1.362264	-0.507728	2.750564
C	1.840032	-1.187963	3.873145
C	2.897496	-2.088878	3.768946
C	3.501429	-2.315773	2.535045
C	3.031241	-1.655473	1.402946
C	0.276380	0.518578	2.936140
S	-1.401236	-0.081475	2.448283
C	-2.423667	1.301888	3.041596
H	-2.493186	2.575035	-2.536467
H	-2.171709	4.313390	-2.186060
H	-3.343885	3.394142	-1.179551
H	-1.996294	2.257478	2.715547
H	-2.444369	1.226122	4.135584
H	-3.427220	1.151212	2.627045
H	-2.976047	-2.997453	-1.876833
H	-1.763405	-4.312545	-2.015746
H	-1.386084	-2.672503	-2.668389
H	0.201718	1.658418	-2.220262
H	0.281907	3.406780	-2.443190
H	0.485254	1.459838	2.412351
H	0.155870	0.753206	4.001853
H	0.934057	-2.900686	0.584018
H	0.606524	-4.195713	-0.566881
H	3.825824	0.954560	1.037982
H	5.052156	3.084831	0.904437
H	4.093130	4.995103	-0.388410
H	1.926855	4.731593	-1.549880
H	3.496430	-1.847021	0.434275
H	4.336247	-3.011542	2.447684
H	3.253647	-2.608685	4.658823
H	1.380624	-1.003049	4.845577
H	2.831727	0.529473	-2.405742
H	3.263138	-0.764579	-4.459347
H	2.423377	-3.108602	-4.651124
H	1.190587	-4.132496	-2.771523

[**PS$_3$**BiCl$_2$]$^+$

Total energy: -3601.610207

C	-1.250510	-1.831642	-2.360687
C	-2.001552	-1.301359	-1.292066
C	-3.305923	-1.763851	-1.069601
C	-3.867727	-2.738397	-1.888638
C	-3.124054	-3.271079	-2.937756
C	-1.827679	-2.819075	-3.165343

P	-1.310425	-0.040043	-0.137295
C	-2.242116	-0.363813	1.412432
C	-1.868701	-1.442546	2.239954
C	-2.586238	-1.660926	3.419718
C	-3.659930	-0.848430	3.773766
C	-4.044180	0.196741	2.937580
C	-3.339140	0.433841	1.760654
C	-0.747757	-2.391389	1.898148
S	0.874161	-1.732017	2.458820
C	1.940087	-3.170753	2.146548
C	0.142636	-1.373593	-2.697122
S	1.379914	-2.039952	-1.505042
C	2.900611	-1.946594	-2.493100
C	-1.825492	1.599151	-0.782626
C	-2.339179	1.657112	-2.083942
C	-2.610683	2.878223	-2.696066
C	-2.377327	4.061405	-2.004762
C	-1.880708	4.012748	-0.704394
C	-1.586134	2.800364	-0.071708
C	-1.072018	2.870394	1.345472
S	0.747787	2.775395	1.580925
C	1.341478	4.118209	0.518587
Bi	1.657784	0.195696	0.237214
Cl	1.874285	1.593457	-1.945804
Cl	4.193169	-0.489681	0.542260
H	3.012192	-0.937493	-2.909896
H	2.835412	-2.703000	-3.284681
H	3.728883	-2.171488	-1.810634
H	1.786974	-3.552396	1.128457
H	1.716668	-3.949374	2.886615
H	2.975104	-2.824540	2.260724
H	2.435215	4.120794	0.609033
H	0.937245	5.069449	0.889013
H	1.057178	3.944355	-0.526827
H	0.247278	-0.279189	-2.731722
H	0.444640	-1.769305	-3.674966
H	-0.691344	-2.613082	0.822405
H	-0.891745	-3.344950	2.423017
H	-1.456687	2.068170	1.986593
H	-1.381105	3.819811	1.802895
H	-3.895225	-1.360778	-0.245918
H	-4.886320	-3.079757	-1.701568
H	-3.550766	-4.039672	-3.583268
H	-1.247605	-3.236677	-3.990000
H	-3.649983	1.248699	1.104343
H	-4.894756	0.828730	3.195303
H	-4.201901	-1.040006	4.700633
H	-2.298987	-2.490477	4.068606
H	-2.535543	0.735993	-2.633500
H	-3.010728	2.896437	-3.710361

H	-2.586863	5.025311	-2.469903
H	-1.719990	4.944848	-0.159059

[**PS$_3$**Bi(ACN)$_3$]$^{3+}$

Total energy: -3078.976372

C	3.204742	1.933074	-0.099603
C	2.343787	1.135052	-0.859867
C	1.936537	1.561510	-2.147820
C	2.393921	2.799820	-2.604960
C	3.226819	3.605116	-1.828831
C	3.645293	3.165038	-0.578716
P	1.632715	-0.344628	-0.051382
Bi	-1.159210	0.202205	0.092377
S	-0.687609	0.577164	-2.745727
C	-1.270002	2.271612	-3.034886
C	1.102566	0.734869	-3.094000
C	2.519866	-0.642623	1.531468
C	2.229008	0.055829	2.722180
C	2.941035	-0.267203	3.879741
C	3.928744	-1.247883	3.873537
C	4.222273	-1.925164	2.694854
C	3.520263	-1.625317	1.531479
C	1.190476	1.138131	2.812333
S	-0.491010	0.405920	2.916609
C	-1.448001	1.864427	3.429953
C	2.022125	-1.813504	-1.067665
C	3.054583	-1.730129	-2.009186
C	3.389731	-2.835748	-2.785219
C	2.695785	-4.031145	-2.620043
C	1.685832	-4.125292	-1.665602
C	1.341413	-3.030931	-0.868753
C	0.298993	-3.218453	0.201727
S	-1.334129	-2.555383	-0.326860
C	-2.414456	-3.190228	0.989447
N	-0.257842	2.664574	0.203976
C	0.079699	3.771628	0.173186
C	0.508626	5.155479	0.131901
N	-3.428112	-0.255673	-1.423173
C	-4.443660	-0.423907	-1.951621
C	-5.720061	-0.636638	-2.611592
N	-3.410677	-0.198877	1.641379
C	-4.523407	-0.164706	1.959086
C	-5.920521	-0.125434	2.352417
H	-1.287443	2.699536	2.737660
H	-1.128906	2.132244	4.444976
H	-2.502574	1.566525	3.434697
H	-2.062515	-2.869678	1.976445
H	-2.413961	-4.283772	0.901226
H	-3.416757	-2.797257	0.786629

H	-2.329435	2.299028	-2.751567
H	-1.165913	2.480269	-4.107019
H	-0.694429	2.991199	-2.441338
H	1.224491	1.839620	1.968476
H	1.327087	1.718255	3.733611
H	0.580403	-2.765935	1.161485
H	0.125170	-4.287727	0.376799
H	1.444979	-0.304286	-3.162852
H	1.157940	1.154351	-4.106915
H	3.762795	-2.168294	0.619146
H	4.997835	-2.690701	2.671725
H	4.468826	-1.478390	4.792390
H	2.715530	0.266797	4.804209
H	3.605751	-0.796887	-2.136883
H	4.194711	-2.758319	-3.516121
H	2.948298	-4.901317	-3.226799
H	1.161673	-5.071857	-1.524416
H	3.544549	1.594888	0.879761
H	4.313787	3.773107	0.030992
H	3.558653	4.569567	-2.214770
H	2.099936	3.137752	-3.600240
H	-6.353049	-1.272158	-1.978915
H	-6.211850	0.331725	-2.769878
H	-5.553312	-1.127856	-3.578740
H	-6.528626	-0.594884	1.568390
H	-6.049937	-0.668939	3.296971
H	-6.229424	0.919615	2.483105
H	0.622389	5.462939	-0.915774
H	-0.245461	5.782089	0.625331
H	1.470800	5.248133	0.652353

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

[**PS$_3$**Bi]$^{3+}$

Total energy: -2680.708042

C	2.220113	1.968611	1.826858
C	1.021023	1.240159	1.708235
C	0.360429	0.765571	2.876100
C	0.953530	1.014149	4.122778
C	2.146926	1.734958	4.233162
C	2.775292	2.221861	3.085125
P	0.337958	1.021944	0.022530
C	-1.027988	2.228147	-0.204789
C	-0.941911	3.385530	0.598279
C	-1.880567	4.411892	0.470118
C	-2.922727	4.288196	-0.449037
C	-3.023789	3.136330	-1.236178
C	-2.090513	2.095294	-1.142172

C	-2.295614	0.889403	-2.018928
S	-3.060057	-0.500230	-1.018171
C	-3.681131	-1.641531	-2.324714
C	-0.961467	0.049967	2.855036
S	-0.764745	-1.770091	2.383998
C	-2.452588	-2.450348	2.679196
C	1.624984	1.189332	-1.267835
C	1.373342	2.133155	-2.284174
C	2.271267	2.303637	-3.341103
C	3.425850	1.523956	-3.397317
C	3.685616	0.586524	-2.389570
C	2.811679	0.391515	-1.310538
C	3.247305	-0.571153	-0.233380
S	2.355118	-2.204628	-0.076978
C	2.751754	-3.048822	-1.662063
Bi	-0.457509	-1.602628	-0.304194
H	-2.890889	-1.924998	-3.033080
H	-4.500138	-1.123077	-2.844202
H	-4.082300	-2.525028	-1.808945
H	-3.222093	-1.844794	2.183381
H	-2.585431	-2.443844	3.771949
H	-2.449824	-3.489462	2.321561
H	2.192600	-3.994953	-1.671259
H	3.828709	-3.271974	-1.641249
H	2.498187	-2.425957	-2.530196
H	-1.375712	0.528273	-2.505792
H	-3.023762	1.105687	-2.812935
H	-1.710423	0.488441	2.180884
H	-1.392152	-0.003511	3.865586
H	3.168406	-0.157779	0.780497
H	4.297149	-0.862583	-0.381158
H	-0.133238	3.502887	1.319382
H	-1.788867	5.306107	1.089382
H	-3.661964	5.084505	-0.556342
H	-3.848101	3.048432	-1.947573
H	2.718061	2.361469	0.938155
H	3.695309	2.804681	3.162429
H	2.577240	1.922608	5.218889
H	0.463163	0.654274	5.030434
H	0.481963	2.760048	-2.242986
H	2.068170	3.052303	-4.108967
H	4.137809	1.649519	-4.215603
H	4.612081	0.008869	-2.432170

SP [**PS$_3$**Bi]$^{3+}$

Total energy: -2680.705206

C	2.267848	0.356160	2.525892
C	1.644865	-0.495296	1.591650
C	2.297971	-1.693500	1.177551

C	3.573636	-1.959759	1.694651
C	4.194848	-1.098326	2.606457
C	3.534501	0.054442	3.033071
P	-0.009640	0.012580	0.995118
C	-1.293502	-1.157971	1.571137
C	-2.647601	-1.122168	1.125952
C	-3.533565	-2.081206	1.636687
C	-3.124531	-3.040205	2.570723
C	-1.805359	-3.048274	3.025387
C	-0.893804	-2.114244	2.526022
C	-3.211410	-0.076638	0.203011
S	-2.825282	-0.252025	-1.616520
C	-3.289783	-1.994155	-1.980834
C	1.679170	-2.733581	0.284152
S	1.633826	-2.366512	-1.547895
C	3.375158	-1.914596	-1.931789
Bi	0.017088	-0.024648	-1.767298
S	1.237262	2.552943	-1.613899
C	-0.031729	3.818038	-2.030238
C	-0.396880	1.715603	1.544466
C	0.318064	2.867208	1.101868
C	-0.086477	4.118867	1.586981
C	-1.144546	4.251885	2.493881
C	-1.817293	3.116657	2.947522
C	-1.447454	1.855487	2.473034
C	1.529646	2.824504	0.211020
H	4.086010	-2.878741	1.399991
H	5.185848	-1.342586	2.994253
H	3.994639	0.717807	3.767745
H	1.758480	1.252581	2.881865
H	2.231102	-3.682865	0.347337
H	0.628941	-2.953733	0.522248
H	-2.825052	-2.685042	-1.265332
H	-4.387491	-2.042607	-1.920256
H	-2.974690	-2.203512	-3.012777
H	-4.578776	-2.062979	1.318641
H	-3.844777	-3.766351	2.952933
H	-1.481649	-3.771446	3.776222
H	0.129121	-2.123143	2.904888
H	-4.310664	-0.074301	0.238923
H	-2.877329	0.945027	0.432618
H	3.962548	-2.841165	-1.844633
H	3.396826	-1.568824	-2.974868
H	3.746207	-1.146587	-1.240779
H	0.456275	5.012937	1.270792
H	-1.426293	5.242454	2.856499
H	-2.623312	3.204279	3.678411
H	-1.971539	0.976615	2.850805
H	2.077889	3.777262	0.249594
H	2.242759	2.029536	0.471220

H	-0.338760	3.638023	-3.070123
H	-0.883431	3.765088	-1.339518
H	0.469935	4.795256	-1.964215

[**PS$_3$**BiCl]$^{2+}$

Total energy: -3141.404649

C	1.657604	2.542684	-1.302140
C	2.227586	1.516091	-0.505756
C	3.528100	1.677741	0.004829
C	4.264706	2.833397	-0.262297
C	3.703296	3.849322	-1.037287
C	2.411844	3.699571	-1.547245
P	1.309995	-0.020116	-0.049653
C	1.954280	-0.507154	1.599088
C	1.378353	0.055638	2.762606
C	1.861741	-0.344615	4.015830
C	2.903883	-1.269733	4.123919
C	3.480153	-1.810738	2.971902
C	3.005157	-1.432109	1.712987
C	0.281077	1.086050	2.697931
S	-1.396689	0.311014	2.399235
C	-2.494025	1.737753	2.757928
C	0.282697	2.463058	-1.916040
S	-1.062666	2.799748	-0.653897
C	-2.473504	3.291563	-1.729180
C	1.711810	-1.341369	-1.264259
C	2.408752	-0.978087	-2.429796
C	2.618968	-1.899424	-3.459695
C	2.129408	-3.199383	-3.335571
C	1.441724	-3.573644	-2.177028
C	1.213746	-2.670422	-1.127381
C	0.516560	-3.195205	0.104291
S	-1.304430	-2.821642	0.312975
C	-2.024924	-3.587109	-1.190429
Bi	-1.615914	-0.031504	-0.354563
Cl	-4.117946	0.089924	0.131927
H	-2.582232	2.597457	-2.574520
H	-2.291983	4.314413	-2.087084
H	-3.375684	3.262371	-1.102446
H	-2.129069	2.637328	2.243801
H	-2.486081	1.874809	3.848749
H	-3.499344	1.460471	2.415200
H	-3.087569	-3.306051	-1.212787
H	-1.936778	-4.678143	-1.088135
H	-1.505464	-3.241247	-2.095394
H	0.083912	1.490825	-2.398767
H	0.155461	3.238491	-2.683633
H	0.440515	1.855085	1.927430

H	0.161709	1.595166	3.665042
H	0.949953	-2.827847	1.042706
H	0.560733	-4.293448	0.133139
H	3.975711	0.896709	0.619942
H	5.275106	2.935768	0.137334
H	4.267930	4.759133	-1.248497
H	1.981221	4.498062	-2.155671
H	3.453111	-1.862263	0.814417
H	4.300859	-2.526144	3.049742
H	3.267341	-1.563346	5.110206
H	1.423583	0.079442	4.922286
H	2.805217	0.033608	-2.531230
H	3.173161	-1.599082	-4.350657
H	2.291453	-3.929604	-4.130340
H	1.089851	-4.603221	-2.076282

$[\mathbf{PS_3}BiCl_2]^+$

Total energy: -3601.999666

C	-1.238754	-1.840544	-2.388149
C	-2.005380	-1.316260	-1.318568
C	-3.306476	-1.804257	-1.101116
C	-3.850025	-2.796858	-1.917829
C	-3.091210	-3.325217	-2.963423
C	-1.799769	-2.847462	-3.188870
P	-1.327076	-0.045668	-0.145440
C	-2.274998	-0.386303	1.405744
C	-1.899372	-1.468235	2.238928
C	-2.620239	-1.686024	3.422220
C	-3.700199	-0.875719	3.776824
C	-4.086168	0.171642	2.937517
C	-3.377308	0.411033	1.758397
C	-0.767216	-2.408416	1.903123
S	0.858520	-1.738070	2.503948
C	1.957622	-3.156614	2.125950
C	0.148617	-1.361719	-2.726978
S	1.425905	-2.043039	-1.550382
C	2.951411	-1.824566	-2.546548
C	-1.859100	1.602080	-0.780755
C	-2.383978	1.671212	-2.082069
C	-2.656192	2.899283	-2.688172
C	-2.414494	4.082348	-1.991396
C	-1.907957	4.024207	-0.691766
C	-1.612284	2.804533	-0.063090
C	-1.088822	2.866691	1.351285
S	0.758175	2.812888	1.591548
C	1.324086	4.135784	0.462836
Bi	1.693008	0.212001	0.245999
Cl	1.859576	1.616461	-1.922537

Cl	4.132928	-0.584472	0.601445
H	2.988772	-0.798096	-2.936828
H	2.941174	-2.567721	-3.355746
H	3.794951	-1.997704	-1.865175
H	1.777193	-3.517011	1.102970
H	1.780636	-3.958683	2.856157
H	2.987954	-2.782929	2.204788
H	2.421204	4.144566	0.522336
H	0.926251	5.097780	0.816497
H	1.012760	3.923871	-0.568343
H	0.251239	-0.266474	-2.730798
H	0.450380	-1.731137	-3.716423
H	-0.685618	-2.608768	0.824392
H	-0.909468	-3.372285	2.412497
H	-1.446969	2.046798	1.985854
H	-1.408472	3.805771	1.825605
H	-3.905848	-1.407160	-0.281528
H	-4.864278	-3.155364	-1.732618
H	-3.501720	-4.107253	-3.604852
H	-1.210016	-3.260930	-4.010242
H	-3.686101	1.226411	1.101535
H	-4.940523	0.800837	3.194326
H	-4.243995	-1.069054	4.703266
H	-2.329578	-2.512733	4.074634
H	-2.587247	0.752583	-2.633704
H	-3.062715	2.924730	-3.700812
H	-2.626097	5.049538	-2.450724
H	-1.742299	4.953318	-0.141181

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