Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supporting Information (ESI)

of

Viability of Aromatic All-Pnictogen Anions

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Content

1. Comparison between energies of optimized singlet and triplet electronic states

Table S1. Zero point energy (ZPE) corrected relative electronic energy (ΔE_{ZPE}), relative free energy (ΔG_{298}), relative Enthalpy (ΔH) in kcal/mol for the $X_2Y_3^-$ and $X_3Y_2^-$ molecules in their singlet and triplet electronic states.

Molecule	ΔE_{ZPE} (kcal/mol)	ΔG_{298} (kcal/mol)	ΔH (kcal/mol)
$P_2N_3^-$	65.89	64.79	66.39
$As_2P_3^-$	43.94	42.41	44.35
$Sb_2As_3^-$	24.76	22.91	25.06
$Bi_2Sb_3^-$	7.06	5.11	7.29
$P_3N_2^-$	52.18	51.17	52.59
$As_3P_2^-$	41.85	40.20	42.28
$Sb_3As_2^-$	22.91	21.16	23.18
$Bi_3Sb_2^-$	2.08	-0.57	2.40

The relative energy values are calculated by taking the difference between the triplet state (T) energy and the corresponding singlet state (S) energy ($\Delta E_{\text{T-S}}$). Triplet states are always found to be higher in energy than the corresponding singlet states.

2. Molecular orbitals and reactivity descriptors

The frontier molecular orbitals are generated for the singlet state geometries at the same level of theory, that is, M06-2X/def2-TZVPPD. Conceptual density functional theory (CDFT) based reactivity descriptors are employed to analyze the stability and reactivity of these molecules. Several electronic properties like total electronic energy (E), ionisation potential (IP), electron affinity (EA), hardness (η),[1] electronegativity (χ)[2] and electrophilicity ($\omega = \chi^2/2\eta$)[3] have been calculated for these systems using the Koopmans theorem.[4] In the following expressions E_{HOMO} and E_{LUMO} are the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), respectively.

$$\text{IP} = -E_{\text{HOMO}} \quad (1)$$
$$\text{EA} = -E_{\text{LUMO}} \quad (2)$$
$$\eta = (\text{IP} - \text{EA}) \quad (3)$$
$$\chi = (\text{IP} + \text{EA})/2 \quad (4)$$
$$\omega = \chi^2/2\eta \quad (5)$$

Table S2. The energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), the energy gap between LUMO and HOMO ($E_{L–H}$), ionisation potential (IP), electron affinity (EA), hardness (η), electronegativity (χ) and electrophilicity (ω) for $X_2Y_3^-$ and $X_3Y_2^-$ molecules in singlet electronic state.

Molecule	E_{HOMO} (eh)	E_{LUMO} (eh)	$E_{L–H}$ (eV)	IP (eV)	EA (eV)	η (eV)	χ (eV)	ω (eV)
$P_2N_3^-$	-0.118	0.147	7.208	3.208	-4.000	7.208	1.604	0.178
$As_2P_3^-$	-0.116	0.091	5.652	3.165	-2.487	5.652	1.583	0.222
$Sb_2As_3^-$	-0.107	0.069	4.795	2.906	-1.889	4.795	1.453	0.220
$Bi_2Sb_3^-$	-0.094	0.066	4.352	2.565	-1.787	4.352	1.282	0.189
$P_3N_2^-$	-0.112	0.130	6.570	3.037	-3.533	6.570	1.519	0.175
$As_3P_2^-$	-0.114	0.088	5.490	3.107	-2.383	5.490	1.554	0.220
$Sb_3As_2^-$	-0.105	0.065	4.628	2.855	-1.773	4.628	1.427	0.220
$Bi_3Sb_2^-$	-0.091	0.068	4.303	2.465	-1.838	4.303	1.233	0.177

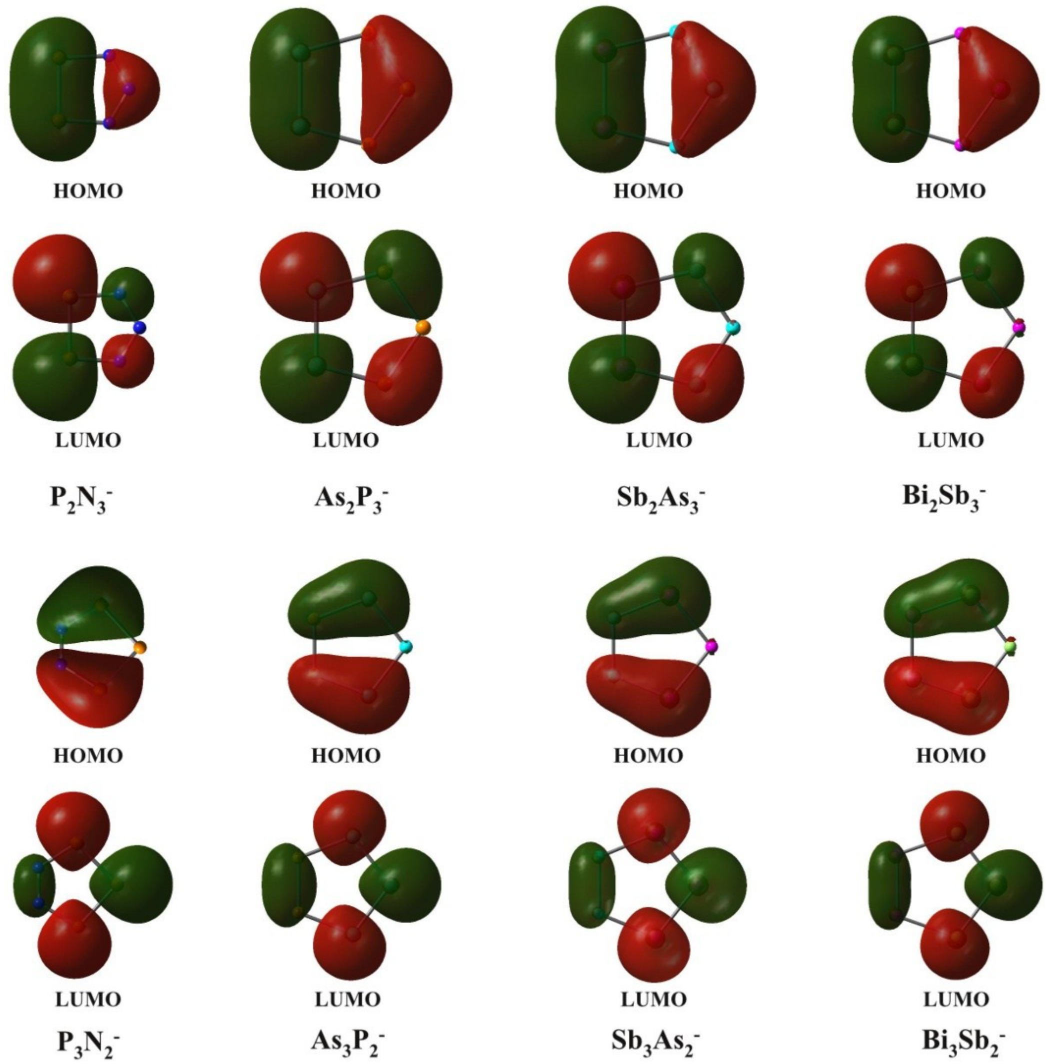


Figure S2. HOMO and LUMO of singlet $X_2Y_3^-$ and $X_3Y_2^-$molecules.

3. Quantum theory of atoms in molecules (QTAIM) analysis

QTAIM analysis is performed with Multiwfn software[5] using the wave functions (.wfn) generated at M06-2X/def2-TZVPPD level of theory in Gaussian 09. According to the Quantum Theory of Atoms In Molecules (QTAIM) principle,[6] the validation of bonding is through the existence of a bond path between two atoms and a bond-critical point (BCP) associated with the path. BCPs are point in space where the electron density ($\rho(r_c)$) is maximum. (3, -1) critical points are situated between two neighbouring atoms defining a bond between them. These points are therefore also called a bond critical point. The topological parameters obtained at the bond critical points (located at r_c) for the various X–X, X–Y and Y–Y bonds are provided in **Table S3a** and **S3b**.

Table S3a. Electron density descriptors (in a.u.) of the molecules having $X_2Y_3^-$ framework at the bond critical points (BCP) obtained from the wave function generated at M06-2X/WTBS//M06-2X/def2-TZVPPD level.

Molecules	BCP	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	$H(r_c)$	$-G(r_c)/V(r_c)$	ELF
	N-N	0.333	-0.384	0.223	-0.541	-0.319	0.411	0.809
$P_2N_3^-$	N-P	0.130	0.526	0.200	-0.269	-0.069	0.744	0.185
	P-P	0.104	-0.074	0.039	-0.096	-0.057	0.403	0.746
	P-P	0.099	-0.062	0.036	-0.088	-0.052	0.412	0.739
$As_2P_3^-$	P-As	0.088	-0.006	0.037	-0.076	-0.039	0.491	0.643
	As-As	0.079	0.007	0.033	-0.064	-0.031	0.514	0.621
	As-As	0.078	0.009	0.033	-0.063	-0.030	0.518	0.614
$Sb_2As_3^-$	As-Sb	0.065	0.035	0.030	-0.051	-0.021	0.585	0.504
	Sb-Sb	0.056	0.020	0.022	-0.040	-0.017	0.564	0.531
	Sb-Sb	0.056	0.021	0.022	-0.039	-0.017	0.568	0.527
$Bi_2Sb_3^-$	Sb-Bi	0.053	0.030	0.023	-0.038	-0.015	0.598	0.477
	Bi-Bi	0.052	0.036	0.023	-0.037	-0.014	0.621	0.438

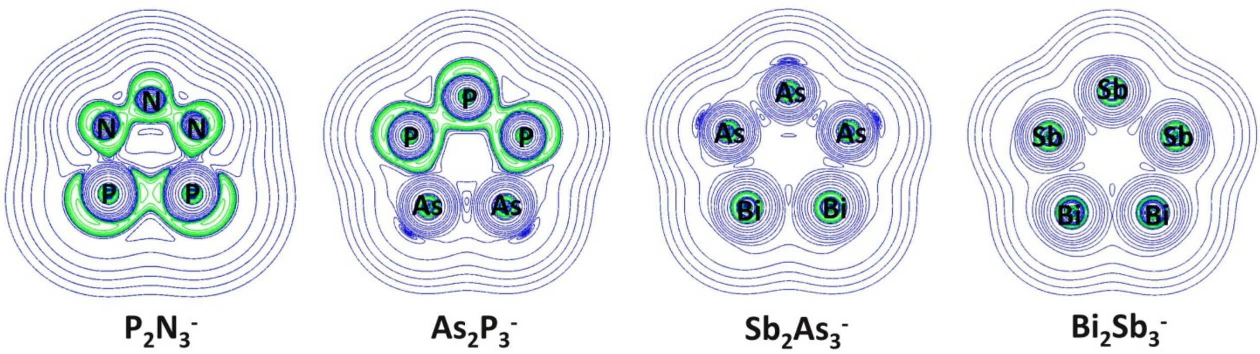


Figure S3a. Contour plot of the Laplacian of electron density of $X_2Y_3^-$ molecules in the molecular plane.

Table S3b. Electron density descriptors (in a.u.) of the molecules having $X_3Y_2^-$ framework at the bond critical points (BCP) obtained from the wave function generated at M06-2X/WTBS//M06-2X/def2-TZVPPD level.

Molecules	BCP	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	$H(r_c)$	$-G(r_c)/V(r_c)$	ELF
$P_3N_2^-$	N-N	0.337	-0.416	0.226	-0.556	-0.330	0.406	0.811
	N-P	0.131	0.544	0.205	-0.273	-0.069	0.749	0.183
	P-P	0.100	-0.059	0.038	-0.090	-0.052	0.418	0.730
$As_3P_2^-$	P-P	0.100	-0.064	0.037	-0.090	-0.053	0.410	0.739
	As-P	0.087	-0.005	0.037	-0.075	-0.038	0.492	0.642
	As-As	0.079	0.008	0.033	-0.064	-0.031	0.515	0.619
$Sb_3As_2^-$	As-As	0.078	0.009	0.033	-0.063	-0.030	0.518	0.613
	As-Sb	0.065	0.036	0.030	-0.051	-0.021	0.587	0.502
	Sb-Sb	0.056	0.020	0.022	-0.039	-0.017	0.566	0.530
$Bi_3Sb_2^-$	Sb-Sb	0.055	0.021	0.022	-0.038	-0.017	0.567	0.530
	Sb-Bi	0.054	0.030	0.023	-0.038	-0.015	0.599	0.476
	Bi-Bi	0.051	0.036	0.023	-0.037	-0.014	0.621	0.439

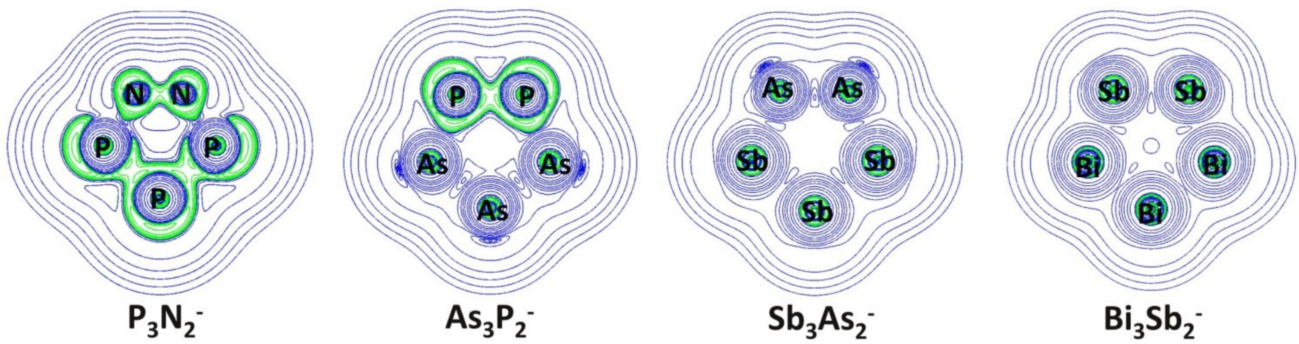


Figure S3b. Contour plot of the Laplacian of electron density of $X_3Y_2^-$ molecules in the molecular plane.

4. Natural bond orbital (NBO) analysis

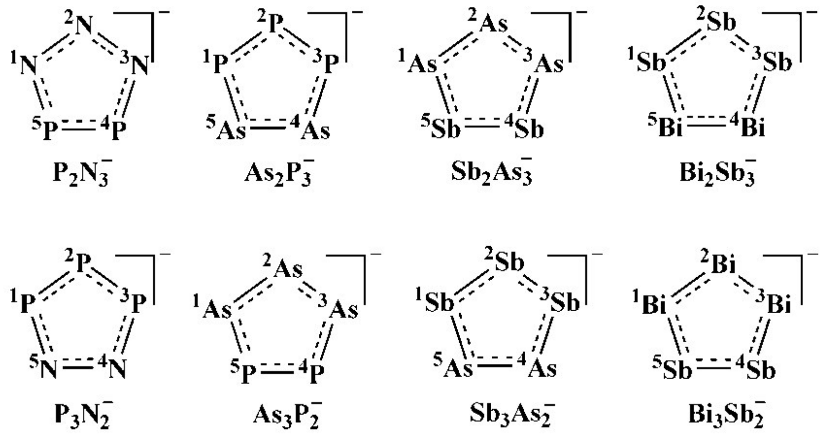


Figure S4. Visualization of atom indexes in molecules those are used in **Table T4a** and **T4b**.

Table S4a. Natural Charges (Q_K) on atoms (as shown in **Figure S4**) of $X_2Y_3^-$ and $X_3Y_2^-$ molecules (Q_K^n is the natural charges on n-th atom).

System	Q_K1	Q_K2	Q_K3	Q_K4	Q_K5
$P_2N_3^-$	-0.646	-0.076	-0.646	+0.184	+0.184
$As_2P_3^-$	-0.251	-0.188	-0.251	-0.155	-0.155
$Sb_2As_3^-$	-0.337	-0.154	-0.337	-0.086	-0.086
$Bi_2Sb_3^-$	-0.252	-0.198	-0.252	-0.149	-0.149
$P_3N_2^-$	+0.290	-0.398	+0.290	-0.591	-0.591
$As_3P_2^-$	-0.151	-0.214	-0.151	-0.242	-0.242
$Sb_3As_2^-$	-0.062	-0.246	-0.062	-0.315	-0.315
$Bi_3Sb_2^-$	-0.140	-0.212	-0.140	-0.254	-0.254

Table S4b. Wiberg bond index (WBI) values of $X_2Y_3^-$ and $X_3Y_2^-$ molecules.

System	WBI_{1-2}	WBI_{2-3}	WBI_{3-4}	WBI_{4-5}	WBI_{5-1}
$P_2N_3^-$	1.466	1.466	1.192	1.495	1.192
$As_2P_3^-$	1.422	1.422	1.404	1.386	1.405
$Sb_2As_3^-$	1.412	1.412	1.364	1.417	1.364
$Bi_2Sb_3^-$	1.391	1.391	1.382	1.410	1.382
$P_3N_2^-$	1.404	1.404	1.223	1.493	1.223
$As_3P_2^-$	1.402	1.402	1.382	1.459	1.459
$Sb_3As_2^-$	1.395	1.395	1.378	1.412	1.378
$Bi_3Sb_2^-$	1.390	1.390	1.404	1.366	1.404

5. Resonance structures (through NRT analysis)

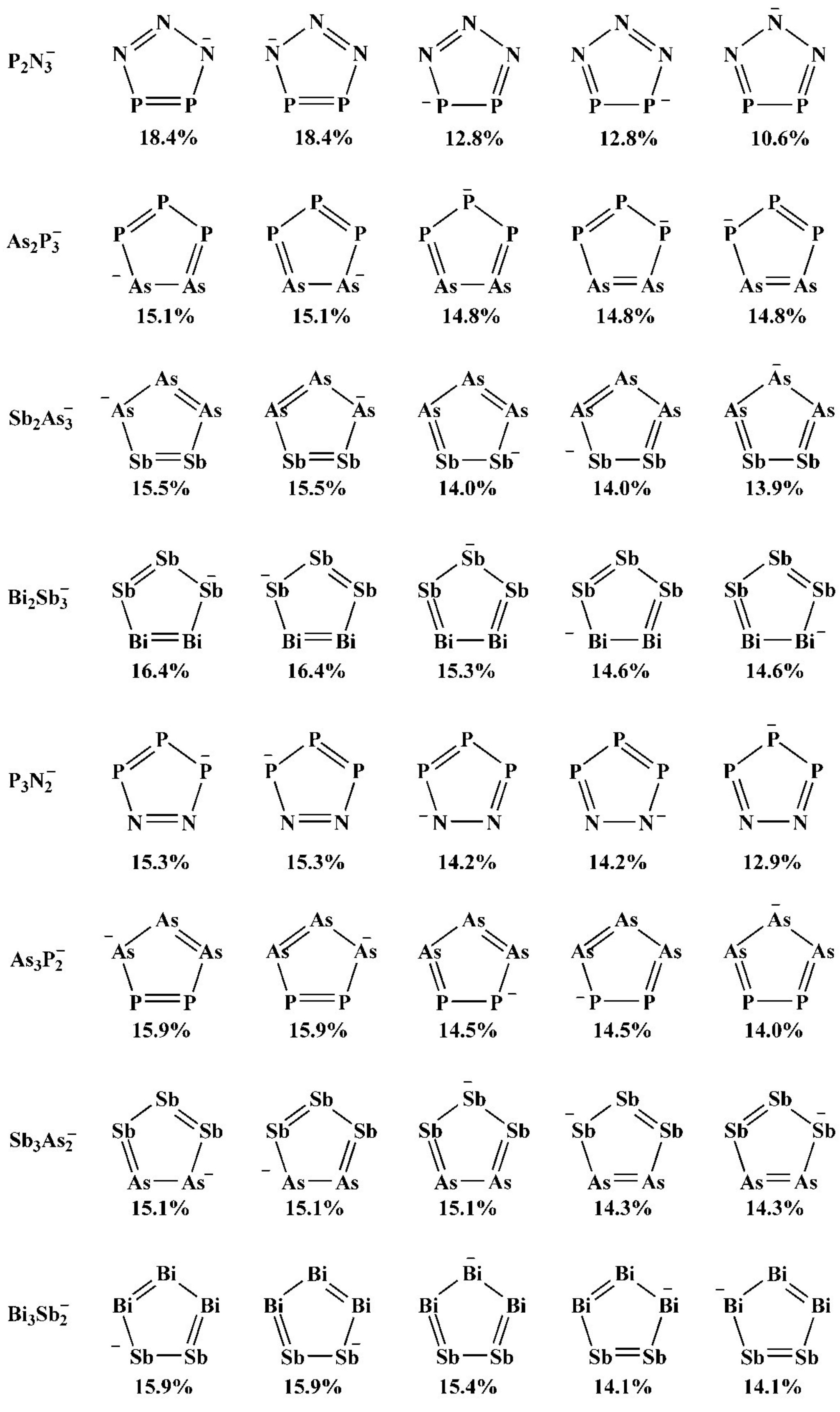


Figure S5. Contribution (in %) of different resonance structures of the $X_2Y_3^-$ and $X_3Y_2^-$ molecules.

6. Nucleus-independent chemical shift (NICS)

NICS

Nucleus independent chemical shift (NICS)[7] is used as the aromaticity index to measure the aromaticity of the systems. The NICS values were calculated at M06-2X/def2-TZVPPD level of theory in Gaussian 09 through the gauge-independent atomic orbital method (GIAO). As in the Schleyer proposal, NICS is the negative of the isotropic shielding constant (σ_{iso}) and equivalent to the induced magnetic field where the magnetic field is induced by the electrons of the molecule itself.[7] Negative and positive NICS values of planar rings suggest the aromaticity and the antiaromaticity respectively, whereas the zero values are associated with nonaromatic species. There are several NICS indices in common use and since the NICS is a tensor, different components of the tensor are considered as appropriate indices of aromaticity. NICS calculated at the ring centre [$NICS_{total}(0)$] and 1 Å above the ring center [$NICS_{total}(1)$] are among the most used NICS indices. We have calculated $NICS_{total}(0)$ by doping the dummy atom at the centre of the ring and $NICS_{total}(1)$ at 1 Å above the ring.

$NICS_{zz}$

NICS could be decomposed into three components along the three coordinates as NICS = $-1/3(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$, where σ_{xx}, σ_{yy}, σ_{zz} are the isotropic shielding constants along x, y and z directions respectively. The separation between the in-plane and out-of-plane components of the isotropic NICS is necessary for assigning the diamagnetic and paramagnetic properties for a system. The “perpendicular to the ring plane” component of NICS [$NICS_{zz}$] is known to give precise result towards predicting aromatic nature. The NICS “perpendicular to the ring plane” components are evaluated at the ring center [$NICS_{zz}(0)$] and 1 Ǻ above the ring plane [$NICS_{zz}(1)$]. $NICS_{zz}$–scan[8] was also performed at same level of theory from the ring centre to 5Å above of the ring center. In this approach the nonchemical probe (dummy atom, Bq) atom is placed in the centre of the ring and the distance of the probe from the centre is increased.

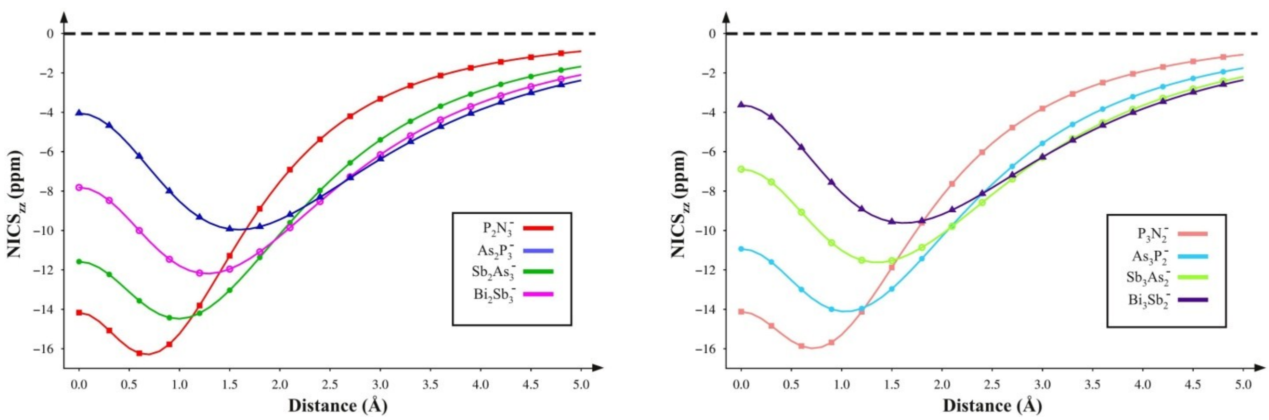


Figure S6a. $NICS_{zz}$ versus r (distance from the ring centre) plots for $X_2Y_3^-$ and $X_3Y_2^-$ molecules.

FiPC−NICS

To substantiate the results of $NICS_{zz}$ scan, we have performed the FiPC−NICS scan at M06-2X/def2-TZVPP level of theory. Tiznado *et al.*[9] have calculated "Free of in-plane component NICS" (FiPC−NICS) by plotting the $NICS_{in\text{-}plane}$ vs $NICS_{out\text{-}of\text{-}plane}$ components. If the molecule is aligned in xy plane and the z axis is perpendicular to the molecular plane then the previous components are described as, $NICS_{in\text{-}plane} = -1/3(\sigma_{xx} + \sigma_{yy})$ and $NICS_{out\text{-}of\text{-}plane} = -1/3(\sigma_{zz})$. Aromatic rings should have negative $NICS_{out\text{-}of\text{-}plane}$ values and antiaromatic rings should have positive $NICS_{out\text{-}of\text{-}plane}$ values. For the nonaromatic molecules the FiPC-NICS curve has a linear shape.

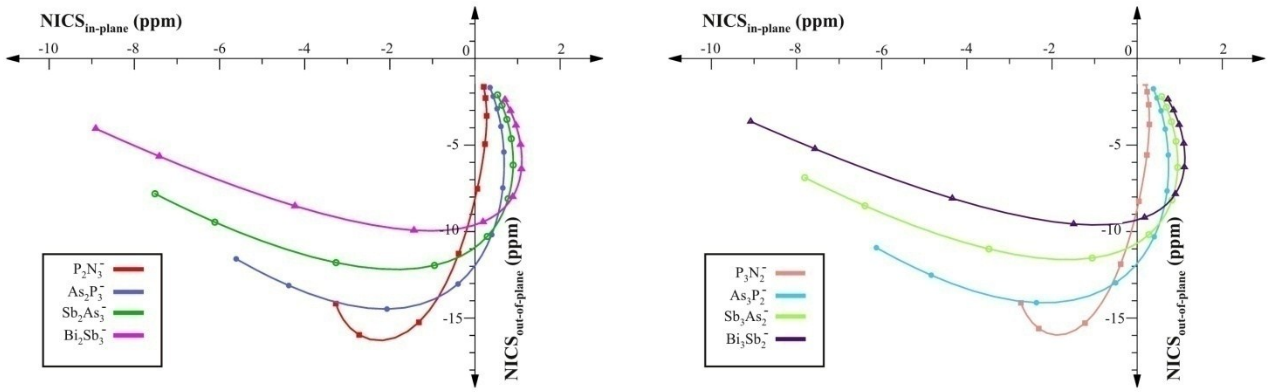


Figure S6b. $NICS_{in\text{-}plane}$ versus $NICS_{out\text{-}of\text{-}plane}$ plot for $X_2Y_3^-$ and $X_3Y_2^-$ molecules.

NICS−rate

Previously Dardab *et al.*[10] have introduced the NICS-rate as an aromaticity index where the maximum/minimum in the NICS−rate curve (ΔNICS/Δr versus r) of a molecule indicates aromaticity/antiaromaticity of the system. NICS−rate is calculated by taking the difference between two successive $NICS_{out\text{-}of\text{-}plane}$ component values.

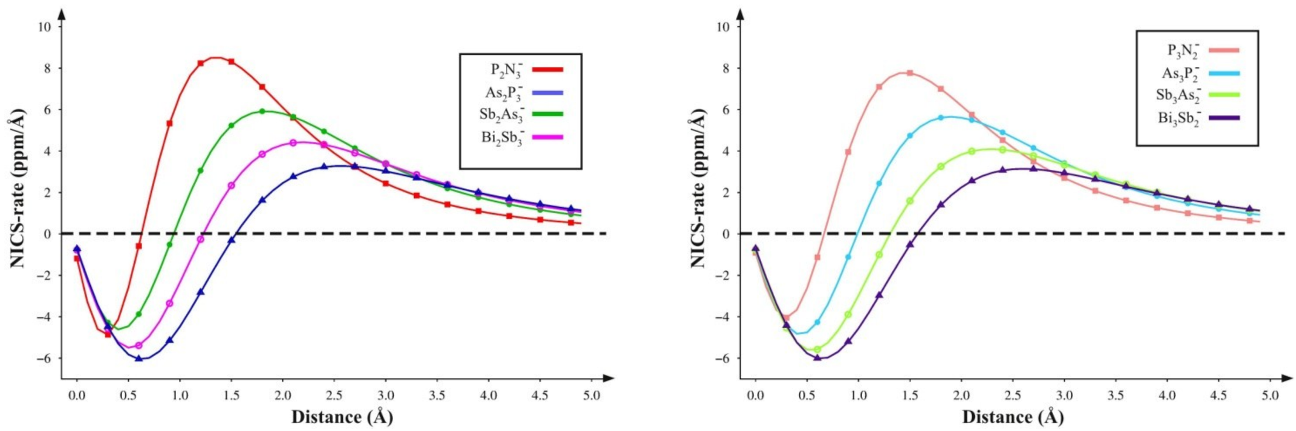
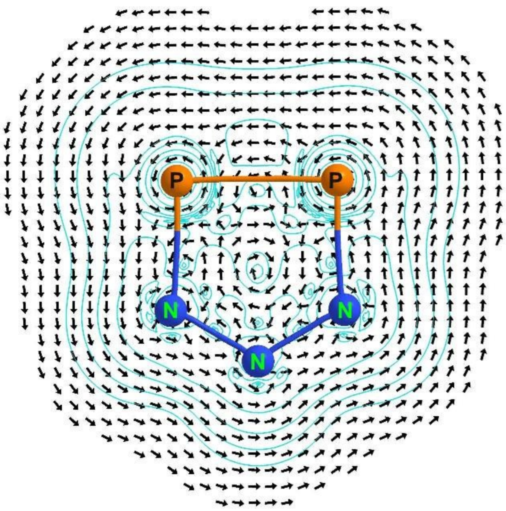
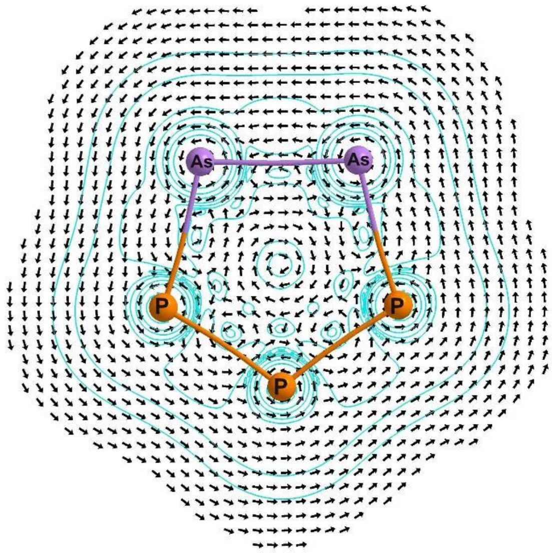


Figure S6c. NICS−rate versus r (distance from the ring centre) plot for $X_2Y_3^-$ and $X_3Y_2^-$ molecules.

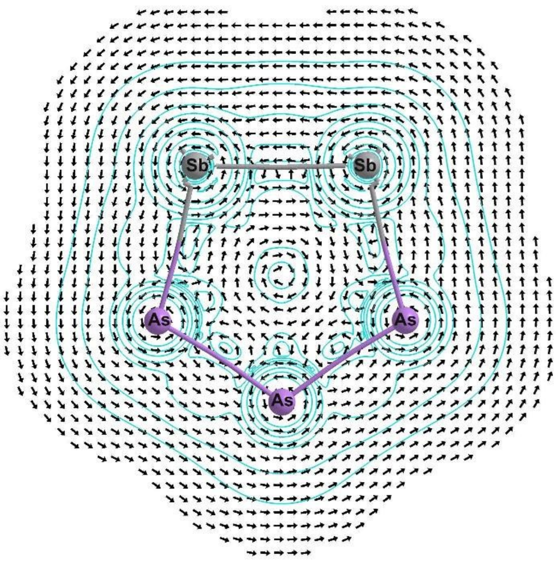
7. Ring current density plots



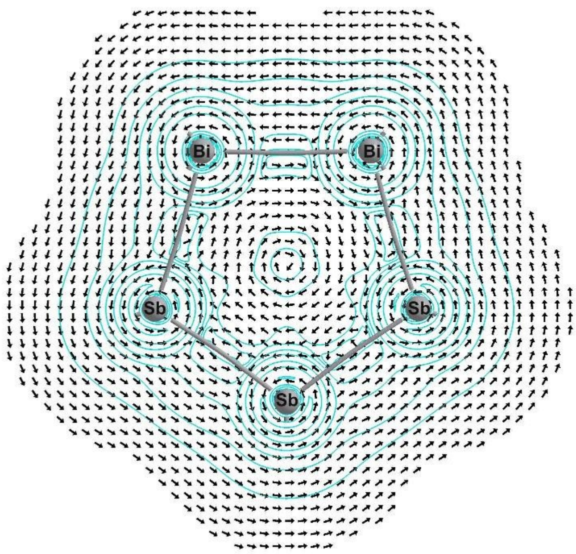
$P_2N_3^-$



$As_2P_3^-$



$Sb_2As_3^-$



$Bi_2Sb_3^-$

Figure S7a. Ring current density plots for $X_2Y_3^-$ molecules.

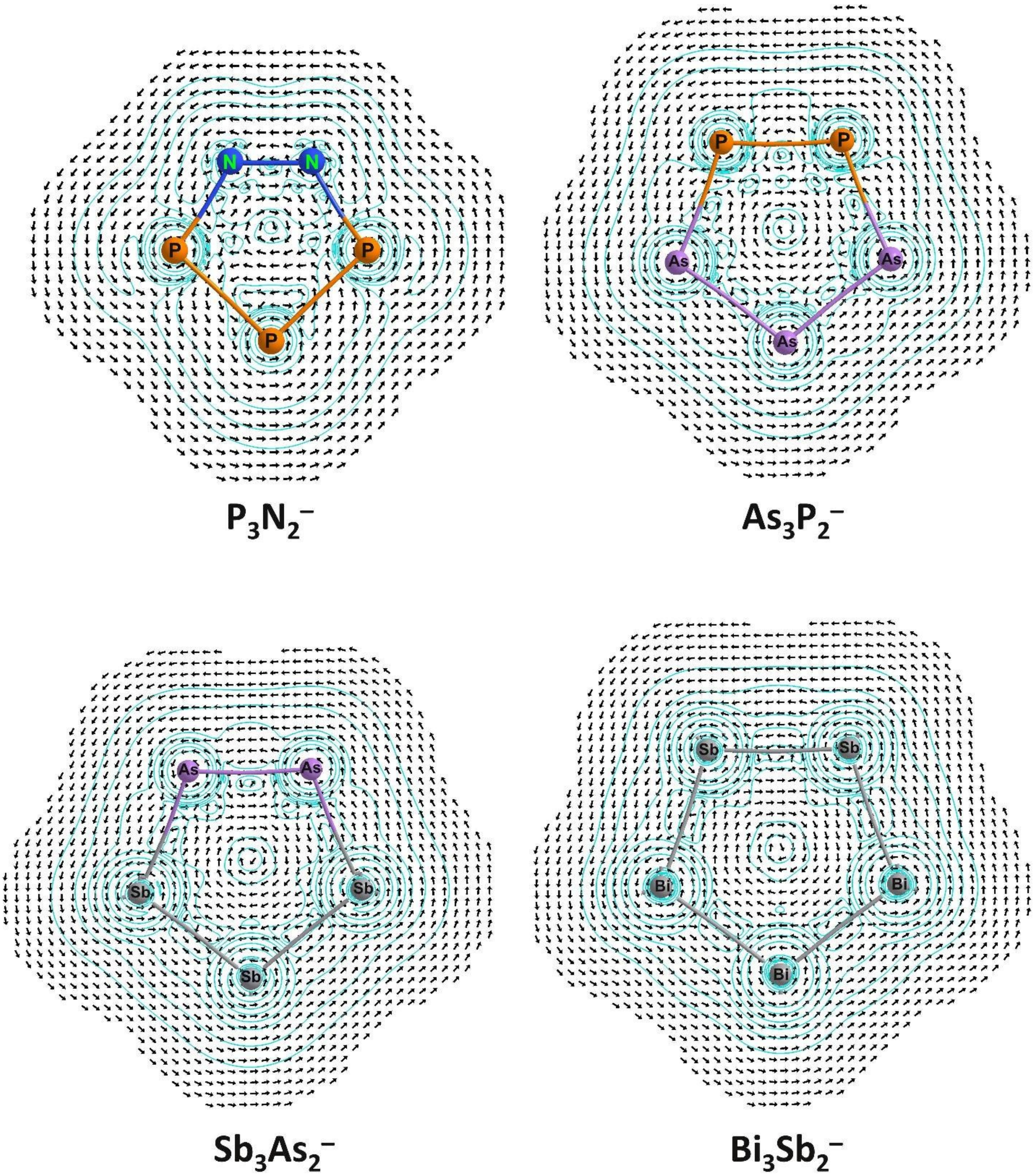


Figure S7b. Ring current density plots for $X_3Y_2^-$ molecules.

8. Atom-centered density matrix propagation (ADMP) simulation results

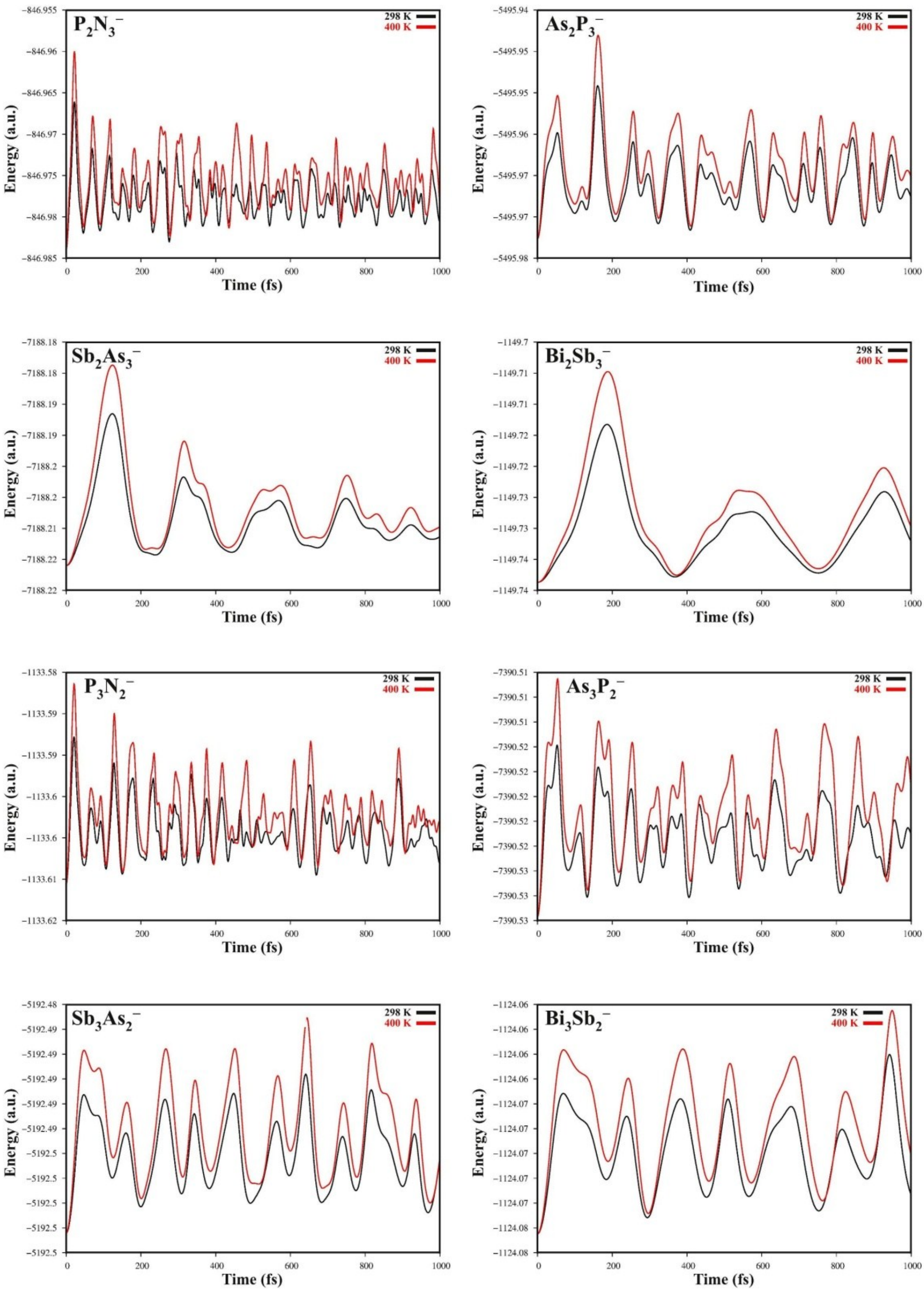


Figure S8. Evolution of energy (a.u.) with time (fs) for $X_2Y_3^-$ and $X_3Y_2^-$ molecules.

9. Reaction mechanism study

Table S9. Relative energies (in kcal/mol) for the reaction between P_3^- and N_2. Energy of linear singlet ($^1D_{\infty h}$) geometry of P_3^- is taken as the reference (0.0).

Type of Energy	Minima of P_3^-	P_3^-	$P_3^- + N_2$	TS($P_3^- + N_2$)	$P_3N_2^-$	ΔE_{act}	$\Delta E_{reaction}$
E_{ZPE}	$^1D_{\infty h}$	**0.00**	**-1.49**	**25.34**	**-8.85**	**26.83**	**-7.36**
	$^1C_{2v}$	3.30	-0.34	--	-8.85	--	-8.51
	$^3C_{2v}$	24.71	23.10	--	43.33	--	20.23
	$^3D_{3h}$	-7.04	-9.50	--	43.33	--	52.83
H	$^1D_{\infty h}$	**0.00**	**-1.23**	**24.24**	**-10.45**	**25.47**	**-9.22**
	$^1C_{2v}$	3.20	-0.32	--	-10.45	--	-10.13
	$^3C_{2v}$	24.81	23.53	--	42.14	--	18.61
	$^3D_{3h}$	-7.23	-9.35	--	42.14	--	51.49
G	$^1D_{\infty h}$	**0.00**	**2.86**	**33.21**	**0.24**	**30.35**	**-2.61**
	$^1C_{2v}$	1.88	5.55	--	0.24	--	-5.31
	$^3C_{2v}$	21.92	27.14	--	51.01	--	23.87
	$^3D_{3h}$	-9.03	-4.98	--	51.01	--	55.99
E	$^1D_{\infty h}$	**0.00**	**-1.83**	**24.58**	**-10.84**	**26.41**	**-9.01**
	$^1C_{2v}$	3.79	-0.65	--	-10.84	--	-10.19
	$^3C_{2v}$	25.63	23.40	--	42.16	--	18.77
	$^3D_{3h}$	-6.71	-9.75	--	42.16	--	51.92

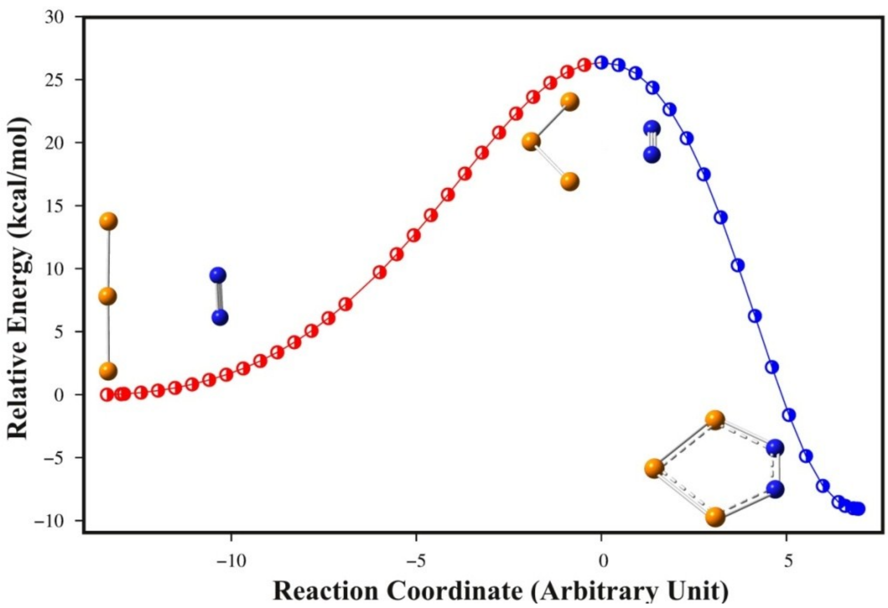


Figure S9. IRC plot from the transition state structure.

10. Cartesian coordinates, energy (in eh) and first three vibrational frequencies (in cm^{-1}) of optimized geometries

Optimized geometries in singlet state

$P_2N_3^-$ (Singlet, C_{2v})

Electronic Energy = -846.988219
Sum of electronic and zero-point Energies = -846.972511
Sum of electronic and thermal Enthalpies = -846.967593
Sum of electronic and thermal Free Energies = -846.999765
Frequencies = 390.9498, 488.8842, 537.5306

N	0.00000000	1.12419700	0.89537900
N	0.00000000	0.00000000	1.55642700
N	0.00000000	-1.12419700	0.89537900
P	0.00000000	-1.03714800	-0.78101000
P	0.00000000	1.03714800	-0.78101000

$As_2P_3^-$ (Singlet, C_{2v})

Electronic Energy = -5495.977367
Sum of electronic and zero-point Energies= -5495.970610
Sum of electronic and thermal Enthalpies= -5495.963144
Sum of electronic and thermal Free Energies= -5496.003171
Frequencies = 141.1965, 197.8219, 198.3045

P	0.00000000	1.72199600	1.10755900
P	0.00000000	0.00000000	2.28372700
P	0.00000000	-1.72199600	1.10755900
As	0.00000000	-1.15756300	-1.02246500
As	0.00000000	1.15756300	-1.02246500

$Sb_2As_3^-$ (Singlet, C_{2v})

Electronic Energy= -7188.220375
Sum of electronic and zero-point Energies= -7188.216379
Sum of electronic and thermal Enthalpies= -7188.207389
Sum of electronic and thermal Free Energies= -7188.253597
Frequencies = 82.3444, 107.5545, 115.6789

As	0.00000000	1.93114900	1.02510300
As	0.00000000	0.00000000	2.29764400
As	0.00000000	-1.93114900	1.02510300
Sb	0.00000000	-1.33931000	-1.40665700
Sb	0.00000000	1.33931000	-1.40665700

$Bi_2Sb_3^-$ (Singlet, C_{2v})

Electronic Energy= -1149.745710
Sum of electronic and zero-point Energies= -1149.743103
Sum of electronic and thermal Enthalpies= -1149.733123
Sum of electronic and thermal Free Energies= -1149.784646
Frequencies = 51.6341, 59.8740, 73.9220

Sb	0.00000000	2.18865500	1.12126000
Sb	0.00000000	0.00000000	2.67049700
Sb	0.00000000	-2.18865500	1.12126000
Bi	0.00000000	-1.40220700	-1.50942100
Bi	0.00000000	1.40220700	-1.50942100

$P_3N_2^-$ (Singlet, C_{2v})

Electronic Energy= -1133.614803
Sum of electronic and zero-point Energies= -1133.601970
Sum of electronic and thermal Enthalpies= -1133.596447
Sum of electronic and thermal Free Energies= -1133.630274
Frequencies = 286.3379, 381.5464, 464.5645

N	0.00000000	0.64642500	-1.44851100
N	0.00000000	-0.64642500	-1.44851100
P	0.00000000	-1.52444100	-0.02952200
P	0.00000000	0.00000000	1.41098700
P	0.00000000	1.52444100	-0.02952200

$As_3P_2^-$ (Singlet, C_{2v})

Electronic Energy= -7390.534795
Sum of electronic and zero-point Energies= -7390.528685
Sum of electronic and thermal Enthalpies= -7390.520903
Sum of electronic and thermal Free Energies= -7390.562195
Frequencies = 125.7891, 177.3181, 179.4590

As	0.00000000	1.83649100	0.11937400
As	0.00000000	0.00000000	1.52549500
As	0.00000000	-1.83649100	0.11937400
P	0.00000000	-1.03815400	-1.94066800
P	0.00000000	1.03815400	-1.94066800

$Sb_3As_2^-$ (Singlet, C_{2v})

Electronic Energy= -5192.505971
Sum of electronic and zero-point Energies= -5192.502369
Sum of electronic and thermal Enthalpies= -5192.493112
Sum of electronic and thermal Free Energies= -5192.540533
Frequencies = 73.1871, 92.5940, 103.7116

Sb	0.00000000	2.09595500	0.30839200
Sb	0.00000000	0.00000000	1.98248700
Sb	0.00000000	-2.09595500	0.30839200
As	0.00000000	-1.15441100	-2.00852800
As	0.00000000	1.15441100	-2.00852800

$Bi_3Sb_2^-$ (Singlet, C_{2v})

Electronic Energy= -1124.078454
Sum of electronic and zero-point Energies= -1124.075983
Sum of electronic and thermal Enthalpies= -1124.065897
Sum of electronic and thermal Free Energies= -1124.118204
Frequencies = 47.6512, 60.1252, 68.3083

Bi	0.00000000	2.24827000	0.35454300
Bi	0.00000000	0.00000000	2.03627100
Bi	0.00000000	-2.24827000	0.35454300
Sb	0.00000000	-1.34373500	-2.23396800
Sb	0.00000000	1.34373500	-2.23396800

Optimized geometries in triplet state

$P_2N_3^-$ (Triplet)

Electronic Energy= -846.880741
Sum of electronic and zero-point Energies= -846.867511
Sum of electronic and thermal Enthalpies= -846.861792
Sum of electronic and thermal Free Energies= -846.897166
Frequencies = 186.5401, 331.1851, 401.4836

N	1.43069400	0.40911100	0.21946500
N	0.67954200	1.38940600	0.07833500
N	-0.58452200	1.18036600	-0.34788800
P	-1.35238900	-0.25013200	0.14112600
P	0.64038900	-1.14001300	-0.11775200

$As_2P_3^-$ (Triplet)

Electronic Energy= -5495.906296
Sum of electronic and zero-point Energies= -5495.900585
Sum of electronic and thermal Enthalpies= -5495.892472
Sum of electronic and thermal Free Energies= -5495.936236
Frequencies = 83.9564, 90.7242, 139.6266

P	2.09604900	-0.26635100	-0.48696100
P	1.49821700	1.62675600	0.10056600
P	-0.59330700	1.86384700	0.31433100
As	-1.63272700	-0.02225600	-0.24794400
As	0.26865500	-1.44331400	0.28070000

$Sb_2As_3^-$ (Triplet)

Electronic Energy= -7188.180300
Sum of electronic and zero-point Energies= -7188.176924
Sum of electronic and thermal Enthalpies= -7188.167461
Sum of electronic and thermal Free Energies= -7188.217748
Frequencies = 35.6045, 47.8198, 87.7056

As	2.06300700	0.80689200	-0.35904400
As	0.26627400	2.20589100	0.00891300
As	-1.81437000	1.26489500	0.34452300
Sb	-1.53443900	-1.22557400	-0.32089100
Sb	1.20126200	-1.54233600	0.32451900

$Bi_2Sb_3^-$ (Triplet)

Electronic Energy= -1149.734009
Sum of electronic and zero-point Energies= -1149.731855
Sum of electronic and thermal Enthalpies= -1149.721503
Sum of electronic and thermal Free Energies= -1149.777160
Frequencies = 20.1206, 38.2610, 52.1188

Sb	-1.49838000	-2.01191900	-0.13236600
Sb	1.25731400	-2.21852700	-0.36376000
Sb	2.39017300	0.03347900	0.76618900
Bi	0.66885400	1.85942000	-0.48762900
Bi	-1.98939000	0.71944000	0.32168600

$P_3N_2^-$ (Triplet)

Electronic Energy= -1133.530337
Sum of electronic and zero-point Energies= -1133.518817
Sum of electronic and thermal Enthalpies= -1133.512644
Sum of electronic and thermal Free Energies= -1133.549380
Frequencies = 200.8082, 284.0230, 410.2125

N	-0.61375500	-1.52904100	0.28232500
N	0.61302700	-1.52892400	0.28309700
P	1.44713600	-0.01284300	-0.26825800
P	-0.00063800	1.45300300	0.27286800
P	-1.44615900	-0.01311000	-0.26847300

$As_3P_2^-$ (Triplet)

Electronic Energy= -7390.467158
Sum of electronic and zero-point Energies= -7390.461982
Sum of electronic and thermal Enthalpies= -7390.453523
Sum of electronic and thermal Free Energies= -7390.498781
Frequencies = 58.9425, 92.4625, 135.6989

As	-1.68557200	-0.12422700	0.35244900
As	0.00342800	-1.58600900	-0.41705100
As	1.68674100	-0.11665000	0.35155800
P	1.00211600	2.01180000	-0.31448200
P	-1.01222800	2.00734700	-0.31681900

$Sb_3As_2^-$ (Triplet)

Electronic Energy= -5192.468891
Sum of electronic and zero-point Energies= -5192.465867
Sum of electronic and thermal Enthalpies= -5192.456166
Sum of electronic and thermal Free Energies= -5192.507467
Frequencies = 33.1123, 60.4301, 73.1965

Sb	1.49349200	-1.32636900	0.46741800
Sb	-1.21763700	-1.65503900	-0.35834600
Sb	-1.87960600	0.95227400	0.18154400
As	0.33363600	2.21562300	0.14492500
As	2.14488900	0.92031100	-0.59405800

$Bi_3Sb_2^-$ (Triplet)

Electronic Energy= -1124.074518
Sum of electronic and zero-point Energies= -1124.072672
Sum of electronic and thermal Enthalpies= -1124.062066
Sum of electronic and thermal Free Energies= -1124.119768
Frequencies = 10.4604, 36.9548, 49.5802

Bi	-1.95100900	-1.09669100	-0.22563000
Bi	0.87270400	-1.98438000	-0.00479000
Bi	2.20417600	0.60143100	0.23929200
Sb	0.13791100	2.43321900	-0.75728300
Sb	-1.97021200	1.60227300	0.74284500

Optimized geometries as found in reaction mechanism study

P_3^- (Singlet, $D_{\infty h}$)

Electronic Energy = -1024.061170
Sum of electronic and zero-point Energies= -1024.057251
Sum of electronic and thermal Enthalpies= -1024.052486
Sum of electronic and thermal Free Energies= -1024.081627
Frequencies = 181.6794, 181.6794, 515.0547

P	0.00000000	0.00000000	-1.93226900
P	0.00000000	0.00000000	0.00000000
P	0.00000000	0.00000000	1.93226900

P_3^- (Singlet, C_{2v})

Electronic Energy = -1024.055133
Sum of electronic and zero-point Energies= -1024.051994
Sum of electronic and thermal Enthalpies= -1024.047384
Sum of electronic and thermal Free Energies= -1024.078633
Frequencies = 325.3216, 396.4272, 655.8939

P	0.00000000	0.00000000	1.10408900
P	0.00000000	1.20227600	-0.55204400
P	0.00000000	-1.20227600	-0.55204400

P_3^{-} (Triplet, D_{3h})

Electronic Energy = -1024.071865
Sum of electronic and zero-point Energies= -1024.068473
Sum of electronic and thermal Enthalpies= -1024.064000
Sum of electronic and thermal Free Energies= -1024.096017
Frequencies = 444.2355, 447.2635, 597.6611

P	0.00000000	-1.07382400	-0.61997100
P	0.00000000	0.00000000	1.23994200
P	0.00000000	1.07382400	-0.61997100

P_3^{-} (Triplet, C_{2v})

Electronic Energy = -1024.020329
Sum of electronic and zero-point Energies= -1024.017866
Sum of electronic and thermal Enthalpies= -1024.012946
Sum of electronic and thermal Free Energies= -1024.046698
Frequencies = 203.1517, 309.1365, 568.7611

P	1.47776200	-0.48375800	0.00000000
P	0.00000000	0.96798400	0.00000000
P	-1.47776200	-0.48422600	0.00000000

N_2

Electronic Energy = -109.536359
Sum of electronic and zero-point Energies= -109.530619
Sum of electronic and thermal Enthalpies= -109.527315
Sum of electronic and thermal Free Energies= -109.549036
Frequencies = 2519.1343

N	0.00000000	0.00000000	0.54298100
N	0.00000000	0.00000000	-0.54298100

[P_3^{-} ($D_{\infty h}$) + N_2] (Singlet)

Electronic Energy = -1133.600446
Sum of electronic and zero-point Energies= -1133.590238
Sum of electronic and thermal Enthalpies= -1133.581757
Sum of electronic and thermal Free Energies= -1133.626107
Frequencies = 24.1053, 40.9073, 89.6083

N	2.80805600	-0.54244200	-0.04291900
N	2.80674600	0.54118600	0.04293800
P	-0.86418600	1.93218700	-0.00561800
P	-0.89058100	0.00019900	-0.00000900
P	-0.86547400	-1.93180000	0.00561800

[P_3^- (C_{2v}) + N_2] (Singlet)

Electronic Energy = -1133.598564
Sum of electronic and zero-point Energies= -1133.588414
Sum of electronic and thermal Enthalpies= -1133.580306
Sum of electronic and thermal Free Energies= -1133.621815
Frequencies = 73.1742, 86.8629, 96.5426

N	-2.55334900	0.54569700	0.23508100
N	-2.55335900	-0.54570000	0.23510500
P	0.54785600	-1.19209300	-0.56976200
P	1.28742100	-0.00000400	0.92009100
P	0.54785300	1.19209900	-0.56975000

[P_3^- (D_{3h}) + N_2] (Triplet)

Electronic Energy = -1133.613069
Sum of electronic and zero-point Energies= -1133.603004
Sum of electronic and thermal Enthalpies= -1133.594697
Sum of electronic and thermal Free Energies= -1133.638600
Frequencies = 52.4390, 59.0810, 66.0809

N	2.73983200	0.50731300	-0.00000800
N	2.61617000	-0.57289700	0.00002300
P	-0.85364700	-0.60833100	1.07269200
P	-0.85375700	-0.60899900	-1.07230800
P	-0.79206400	1.24793600	-0.00039000

[P_3^- (C_{2v}) + N_2] (Triplet)

Electronic Energy = -1133.560242
Sum of electronic and zero-point Energies= -1133.551052
Sum of electronic and thermal Enthalpies= -1133.542305
Sum of electronic and thermal Free Energies= -1133.587415
Frequencies = 46.6929, 47.6531, 85.0539

N	2.74581500	-0.53798600	0.18782700
N	2.74876100	0.54713400	0.12595400
P	-0.66351400	1.47360300	-0.48501100
P	-1.25069600	-0.00794600	0.83915500
P	-0.64992600	-1.46992600	-0.50057500

Transition State of [P_3^- ($D_{\infty h}$) + N_2] (Singlet)

Electronic Energy = -1133.558356
Sum of electronic and zero-point Energies= -1133.547486
Sum of electronic and thermal Enthalpies= -1133.541168
Sum of electronic and thermal Free Energies= -1133.577740
Frequencies = -287.7030, 127.9598, 199.5900

N	0.56446400	1.80904100	0.00000000
N	-0.56588700	1.80850900	0.00000000
P	-1.73753800	-0.24126000	0.00000000
P	0.00041700	-1.20660400	0.00000000
P	1.73778500	-0.24032600	0.00000000

Optimized geometries of metallocenes (M = Fe, Ru, Os) and $P_3N_2^-$ substituted metallocenes.

$Fe(\eta^5\text{–}C_5H_5)_2$

Electronic Energy = -510.062773
Sum of electronic and zero-point Energies= -509.893610
Sum of electronic and thermal Enthalpies= -509.884216
Sum of electronic and thermal Free Energies= -509.927112
Frequencies = 62.2447, 158.7515, 162.5174

C	-1.60931200	0.06244200	1.20866400
H	-1.57837600	0.11822700	2.28532000
C	-1.60959800	1.16890100	0.31399300
H	-1.57927300	2.21024400	0.59362000
C	-1.60924900	0.65972700	-1.01446000
H	-1.57904800	1.24733600	-1.91848300
C	-1.60870200	-1.13069200	0.43311800
H	-1.57812300	-2.13734200	0.81906900
C	-1.60923200	-0.76140900	-0.94101500
H	-1.57826100	-1.43932300	-1.77933500
C	1.60925700	0.06573700	1.20851100
H	1.57825200	0.12442300	2.28501400
C	1.60957600	1.16976600	0.31086000
H	1.57923400	2.21187800	0.58762900
C	1.60926500	0.65696800	-1.01620900
H	1.57905300	1.24211700	-1.92182400
C	1.60870600	-1.12950400	0.43618700
H	1.57811500	-2.13510900	0.82485500
C	1.60926500	-0.76395800	-0.93894100
H	1.57831100	-1.44413600	-1.77541900
Fe	0.00001000	0.00053100	-0.00018100

$Fe(\eta^5\text{–}C_5H_5)(\eta^5\text{–}P_3N_2)$

Electronic Energy = -1450.123804
Sum of electronic and zero-point Energies= -1450.023836
Sum of electronic and thermal Enthalpies= -1450.013162
Sum of electronic and thermal Free Energies= -1450.059758
Frequencies = 35.2546, 153.3062, 155.0521

C	2.10948200	-0.71140700	-0.74618100
H	2.17931900	-1.34447300	-1.61604000
C	2.11011400	0.70596700	-0.75004900
H	2.18043200	1.33425200	-1.62332900
C	1.88712900	1.15081700	0.57844000
H	1.79169700	2.17569800	0.89781300
C	1.88603800	-1.14879000	0.58478300
H	1.78948500	-2.17180700	0.90974400
C	1.73886800	0.00335900	1.40306200
H	1.50600800	0.00632900	2.45541500
N	-0.86666300	-0.65899700	-1.52114400
N	-0.86659200	0.65895000	-1.52116500
P	-1.31393100	1.57371600	-0.11746300
P	-1.31400300	-1.57368100	-0.11742900
P	-1.64608400	0.00005000	1.26743600
Fe	0.32332000	-0.00002500	-0.06292100

$Fe(\eta^5\text{–}C_5Me_5)(\eta^5\text{–}P_3N_2)$

Electronic Energy = -1646.774975
Sum of electronic and zero-point Energies= -1646.534088
Sum of electronic and thermal Enthalpies= -1646.515296
Sum of electronic and thermal Free Energies= -1646.578128
Frequencies = 28.1825, 113.2132, 117.9485

C	1.77092400	-0.00367400	-0.82197900
C	2.13159300	-0.01072600	-2.26000500
C	1.53859200	1.15598000	-0.02379700
C	1.66417500	2.55951900	-0.48759400
C	1.14714400	0.72161000	1.27872500
C	0.80999300	1.59104800	2.43322000
C	1.53990700	-1.15527400	-0.01188500
C	1.66876000	-2.56340700	-0.46060000
C	1.14771900	-0.70782800	1.28602200
C	0.81140400	-1.56609100	2.44922700
N	-1.12829500	-0.66033000	-1.73178500
N	-1.12978500	0.66042300	-1.73011000
P	-1.76249200	1.57073800	-0.39293700
P	-1.75857500	-1.57552400	-0.39688600
P	-2.27507000	-0.00466300	0.93280900
Fe	-0.14999600	-0.00063000	-0.12349600

H	1.73626900	-0.89073500	-2.76425400
H	1.73575000	0.86409500	-2.77275300
H	3.21591500	-0.01109000	-2.39307200
H	1.31922800	2.67336500	-1.51495600
H	1.08334100	3.24154900	0.13004800
H	2.70521000	2.88921400	-0.45460700
H	0.43042800	2.55987900	2.11327300
H	0.05064000	1.13565200	3.06741100
H	1.68971900	1.77245200	3.05549800
H	1.32676500	-2.68879600	-1.48752600
H	2.71033000	-2.89083800	-0.42168600
H	1.08778800	-3.24000600	0.16278800
H	0.42905400	-2.53707800	2.13913700
H	1.69226900	-1.74372800	3.07099000
H	0.05453500	-1.10340300	3.08108600

Fe(η^5–P_3N_2)$_2$

Electronic Energy = -2390.158452
Sum of electronic and zero-point Energies= -2390.129230
Sum of electronic and thermal Enthalpies= -2390.117069
Sum of electronic and thermal Free Energies= -2390.167507
Frequencies = 27.0409, 113.4972, 132.7149

N	-1.51469100	-0.65387700	1.41945500
N	-1.51455000	0.65333100	1.41973600
P	-1.65875400	1.57593400	-0.03627300
P	-1.65896600	-1.57592200	-0.03672500
P	-1.66552900	0.00019000	-1.46177400
N	1.51479400	-0.65361300	1.41943500
N	1.51454600	0.65387300	1.41929500
P	1.65861800	1.57604200	-0.03636400
P	1.65923400	-1.57582500	-0.03628100
P	1.66545200	0.00004600	-1.46202000
Fe	-0.00005900	-0.00019200	0.24215800

Ru(η^5–C_5H_5)$_2$

Electronic Energy = -480.695823
Sum of electronic and zero-point Energies= -480.527764
Sum of electronic and thermal Enthalpies= -480.517911
Sum of electronic and thermal Free Energies= -480.562510
Frequencies = 43.1949, 132.4234, 135.8397

C	-1.81256900	1.09196200	-0.52414000
H	-1.81472100	2.06396800	-0.99074800
C	-1.81334900	-0.16154400	-1.20019300
H	-1.81600800	-0.30552700	-2.26865200
C	-1.81181900	-1.19189700	-0.21706400

H	-1.81304800	-2.25251600	-0.41044900
C	-1.81041700	0.83612500	0.87690200
H	-1.81169000	1.58028300	1.65719600
C	-1.80953500	-0.57523300	1.06654800
H	-1.80954400	-1.08719900	2.01552800
C	1.81264700	1.09046900	-0.52715300
H	1.81486000	2.06117100	-0.99646600
C	1.81333600	-0.16489000	-1.19973400
H	1.81599700	-0.31180900	-2.26779100
C	1.81172400	-1.19252900	-0.21377200
H	1.81292300	-2.25366900	-0.40427300
C	1.81047600	0.83850900	0.87459100
H	1.81177500	1.58484100	1.65281000
C	1.80949600	-0.57233200	1.06814000
H	1.80945400	-1.08167500	2.01853400
Ru	0.00000100	0.00023400	-0.00069200

Ru(η^5–C_5H_5)(η^5–P_3N_2)

Electronic Energy = -1420.763197
Sum of electronic and zero-point Energies= -1420.664358
Sum of electronic and thermal Enthalpies= -1420.653228
Sum of electronic and thermal Free Energies= -1420.701138
Frequencies = 42.7880, 117.4739, 118.3622

C	2.27201500	-0.71381300	-0.78201000
H	2.37727600	-1.34852400	-1.64730200
C	2.27246400	0.70955700	-0.78508900
H	2.37807100	1.34046200	-1.65312200
C	2.07487000	1.15283900	0.54900000
H	2.01234600	2.17811300	0.87565100
C	2.07412300	-1.15121400	0.55400300
H	2.01093500	-2.17501800	0.88511900
C	1.93500500	0.00266100	1.37660200
H	1.75559900	0.00503900	2.43947000
N	-1.16913500	-0.65693500	-1.51592500
N	-1.16906900	0.65690700	-1.51592700
P	-1.49722800	1.57554500	-0.06790900
P	-1.49728400	-1.57551200	-0.06788300
P	-1.74879100	0.00003800	1.34225700
Ru	0.30027000	-0.00002500	-0.07383800

Ru(η^5–C_5Me_5)(η^5–P_3N_2)

Electronic Energy = -1617.411838
Sum of electronic and zero-point Energies= -1617.173260
Sum of electronic and thermal Enthalpies= -1617.153456
Sum of electronic and thermal Free Energies= -1617.219975
Frequencies = 13.3564, 79.1015, 82.0877

C	1.85610900	0.00392100	-0.97577000
C	2.12718400	0.00191000	-2.43379400
C	1.70155500	1.16137400	-0.14901700
C	1.82697100	2.57089800	-0.59577000
C	1.42677800	0.71801200	1.18408600
C	1.25002300	1.58347000	2.37651500
C	1.70288500	-1.15682600	-0.15298500
C	1.83026900	-2.56314000	-0.60884300
C	1.42856600	-0.71918800	1.18184200
C	1.25388100	-1.58888700	2.37143300
N	-1.56659300	-0.67202800	-1.63794100
N	-1.56714300	0.64184400	-1.65073200
P	-1.97814300	1.57202900	-0.23258500
P	-1.97798500	-1.57456300	-0.20225300
P	-2.31665500	0.01205500	1.17668200
Ru	-0.16961000	-0.00020700	-0.10553400
H	1.65623300	-0.84909000	-2.92323500
H	1.75024700	0.90485200	-2.91062900
H	3.19978100	-0.05469300	-2.63548500
H	1.45823000	2.70422800	-1.61185900
H	1.26763900	3.24748300	0.04761300
H	2.87115500	2.89307800	-0.58277800
H	0.81305900	2.54490500	2.11267100
H	0.59811700	1.11877800	3.11401400
H	2.20892700	1.77972700	2.86306200
H	1.44737500	-2.69225900	-1.62029100
H	2.87655000	-2.87873900	-0.61374600
H	1.28489200	-3.24703100	0.03874600
H	0.82709200	-2.55360700	2.10310800
H	2.21209700	-1.77721800	2.86241700
H	0.59403000	-1.13206400	3.10678100

Ru(η^5–P_3N_2)$_2$

Electronic Energy = -2360.805689
Sum of electronic and zero-point Energies= -2360.777278
Sum of electronic and thermal Enthalpies= -2360.764756
Sum of electronic and thermal Free Energies= -2360.816455
Frequencies = 25.1246, 99.5033, 108.6722

N	-1.73456700	0.70136100	-1.38767500
N	-1.74921100	-0.60505400	-1.42163900
P	-1.84502200	-1.56428500	0.02409500
P	-1.80843600	1.58450400	0.10882300
P	-1.80178200	-0.02957200	1.50200000
N	1.74979400	0.60482500	-1.42150400
N	1.73545200	-0.70162100	-1.38733200
P	1.80895700	-1.58438000	0.10930100

P	1.84493700	1.56431900	0.02382700
P	1.80122000	0.03010400	1.50248100
Ru	-0.00019000	-0.00015800	-0.22115600

$Os(\eta^5\text{–}C_5H_5)_2$

Electronic Energy = -478.022177
Sum of electronic and zero-point Energies= -477.853456
Sum of electronic and thermal Enthalpies= -477.843959
Sum of electronic and thermal Free Energies= -477.888119
Frequencies = 50.3493, 153.5192, 153.7381

C	-1.77004800	-1.21617100	0.02700800
H	-1.80369400	-2.29386500	0.05102800
C	-1.76885700	-0.35008800	1.16510300
H	-1.80303000	-0.66029700	2.19735300
C	-1.76744000	1.00036200	0.69341600
H	-1.79887800	1.88630000	1.30778800
C	-1.76940600	-0.40098600	-1.14831400
H	-1.80271000	-0.75683700	-2.16587900
C	-1.76828200	0.96886700	-0.73643700
H	-1.80120800	1.82664300	-1.38925500
C	1.77001600	-1.21612300	0.03017400
H	1.80363700	-2.29374400	0.05699700
C	1.76882700	-0.34705500	1.16600300
H	1.80301600	-0.65456800	2.19905300
C	1.76747200	1.00217400	0.69081200
H	1.79893100	1.88971500	1.30286000
C	1.76940400	-0.40400900	-1.14725200
H	1.80269900	-0.76249500	-2.16388200
C	1.76831300	0.96692000	-0.73895000
H	1.80121800	1.82297400	-1.39401700
Os	0.00000000	-0.00035700	-0.00015000

$Os(\eta^5\text{–}C_5H_5)(\eta^5\text{–}P_3N_2)$

Electronic Energy = -1418.086882
Sum of electronic and zero-point Energies= -1417.987707
Sum of electronic and thermal Enthalpies= -1417.976851
Sum of electronic and thermal Free Energies= -1418.024320
Frequencies = 55.9605, 130.2689, 131.3463

C	2.15235200	-0.71557000	-0.77232300
H	2.27903600	-1.35145900	-1.63454800
C	2.15271600	0.71143500	-0.77536900
H	2.27973300	1.34358900	-1.64029100
C	1.97520700	1.15436500	0.56851000
H	1.94031300	2.17986800	0.90006000
C	1.97458400	-1.15272800	0.57345100

H	1.93915900	-2.17679800	0.90937700
C	1.84881700	0.00263200	1.40209900
H	1.72093900	0.00497900	2.47259700
N	-1.13476000	-0.66743000	-1.50718400
N	-1.13467000	0.66739400	-1.50720500
P	-1.53235500	1.58280900	-0.07457900
P	-1.53247200	-1.58273800	-0.07451200
P	-1.81423300	0.00008100	1.32049100
Os	0.24066700	-0.00004000	-0.04547000

Os(η^5–C_5Me_5)(η^5–P_3N_2)

Electronic Energy = -1614.735534
Sum of electronic and zero-point Energies= -1614.496366
Sum of electronic and thermal Enthalpies= -1614.476938
Sum of electronic and thermal Free Energies= -1614.541863
Frequencies = 27.4988, 87.3783, 91.9753

C	1.81642400	-0.09209100	-0.98572400
C	2.07015200	-0.21919700	-2.44268200
C	1.69113000	1.13591600	-0.25461100
C	1.81052700	2.50049900	-0.82781200
C	1.45240500	0.81004000	1.12417500
C	1.33015800	1.77321100	2.24790100
C	1.67670600	-1.17665400	-0.05868000
C	1.81099500	-2.61906900	-0.38513100
C	1.43960200	-0.62292900	1.24418000
C	1.30113000	-1.39088700	2.50739400
N	-1.46222000	-0.66285300	-1.61275400
N	-1.47036100	0.67259100	-1.60093800
P	-1.93607000	1.57022300	-0.17711100
P	-1.91616100	-1.59252900	-0.20552200
P	-2.27456400	-0.02548100	1.19058600
Os	-0.14678500	-0.00087500	-0.07842700
H	1.61565500	-1.12295000	-2.84513900
H	1.65405400	0.62366800	-2.99197500
H	3.14023300	-0.26081800	-2.65795900
H	1.38696000	2.54862400	-1.83012500
H	1.28853700	3.23621100	-0.21874600
H	2.85629600	2.80846500	-0.89531100
H	0.91491200	2.72381500	1.91817200
H	0.67914200	1.38841700	3.03107000
H	2.30458400	1.97576400	2.69840900
H	1.45524100	-2.83694700	-1.39116100
H	2.85593300	-2.93298400	-0.33114300
H	1.24363700	-3.24174700	0.30426000
H	0.82077700	-2.35274400	2.33587800
H	2.27620600	-1.58301300	2.96100200
H	0.69807500	-0.85162800	3.23568900

$Os(\eta^5-P_3N_2)_2$

Electronic Energy = -2358.125951
Sum of electronic and zero-point Energies= -2358.097284
Sum of electronic and thermal Enthalpies= -2358.084910
Sum of electronic and thermal Free Energies= -2358.136465
Frequencies = 28.4831, 103.8436, 117.6136

N	-1.63153200	0.66469400	-1.38071700
N	-1.63103700	-0.66202600	-1.38161800
P	-1.80331700	-1.57974100	0.08488800
P	-1.80448000	1.57921400	0.08849900
P	-1.82716300	-0.00172900	1.51623800
N	1.63146200	0.66277700	-1.38130600
N	1.63017800	-0.66397100	-1.38129100
P	1.80249100	-1.58029200	0.08707000
P	1.80503000	1.57896300	0.08663000
P	1.82692300	-0.00065100	1.51600700
Os	0.00018800	0.00070000	-0.15809800

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