Nature-Inspired Ligand Design for Pd-Catalyzed Cross-Couplings in Water

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Supporting Information 2. Computational Studies

Theoretical Methods. Complete geometry optimizations were carried out using density functional theory (DFT) methods at the B3LYP/6-31G(d) and B3LYPGD3BJ/6-31+G(d,p) levels with Grimme's D3 empirical dispersion corrections and Becke-Johnson damping, and M06/6-31+G(d,p) levels[1-3], and using SDD[4,5] effective core potentials for Pd and Br. All were done with the default Gaussian 'int=ultrafine' option. Frequency calculations were carried out in order to verify that the stationary points thus obtained were true minima or transition states and to determine thermodynamic parameters for the determination of reaction energetics. All were done with the default Gaussian 'int=ultrafine' option.

Single-point energies were also computed at various theoretical levels using B3LYPGD3BJ/6-31+G(d,p) geometries. Calculations of PAs for the small model ligands were done at the B3LYPGD3BJ/6-31+G(d,p), G4 and W1U levels and were were in close agreement with one another. Thermochemical data were calculated with zero-point energy corrections from scaled frequencies using a scaling factor of 0.993 for zero-point energies.[6] A scaling factor of 1.00 for frequencies for the thermal and entropy terms was used.[6ab] The quasiharmonic approximation was used for low frequencies to calculate entropies to avoid the large distortions found when many low-frequency vibrations are present in organometallic compounds.[6cd] Thus, frequencies below 100 cm^{-1} were treated as free rotors rather than by the harmonic approximation in calculating entropies. We have found that this treatment of the entropy term can make a very large difference for large floppy molecules.[7] We have chosen a polarized continuum model in chloroform and toluene (to mimic the interior of micelles) solvent for our calculations using the SMD method of Truhlar and Cramer.[8] In prior work we found that toluene solvent best mimics the micellar environment of our palladium complexes.[9] Energies for molecules not containing Pd or Br were computed with the 5d option when compared with energies computed with the ECP SDD basis in Gaussian. All calculations were performed using the Gaussian 16 program suite.[10] Thermochemical data and Cartesian coordinates are found in **Table S5** at the end of this document, and geometries are shown in **Figure S1**.

Theoretical Results. The reasons for the efficacy of the P3N ligands are not immediately obvious. The nature of these ligands has been explored with quantum calculations. The electronic properties of the P-N bond and the lone pair on phosphorus are unique and are revealed, for example, in calculated gas-phase electronic proton affinities (PAs) of the very simple model ligand, $P(NH_2)_3$ shown at in **Table S1a** for protonation on phosphorus along with related molecules for comparison. The structures at the top of **Figure S1** used for **Table S1a** are for the most stable optimized conformation, all C_s geometry, except for $N(NH_2)_3$, which is slightly more stable as C_3, by 0.15 kcal mol^{-1} at G4 level.

To compensate for well-known polarization effects of substituents in the gas phase,[11] the PAs of the model ligands $P(NH_2)_3$ and $N(NH_2)_3$ are compared with those of PMe_3 and NMe_3, respectively, where the methyl substituents are of comparable polarizability to the amino substituents. Thus, the relative electronic PAs in **Table SI1a** will reflect the remaining effects on the basicities, such as inductive and other effects, after the polarization effects from charge-induced dipole stabilization of the phosphonium and ammonium ions are subtracted out. In the case of $N(NH_2)_3$, the interpretation seems simple: the 17 kcal mol^{-1} difference in electronic PA relative to that of trimethylamine in **Table S1a** is almost surely due to a quite strong short-range inductive effect of the three amino substituents.

Table SIa. Computed electronic proton affinities energies, $\Delta E^o_{e,rel}$, for protonation at the central phosphorus (or nitrogen) at the G4 level of theory. All structures have C_3 geometry for comparison purposes, even though the more stable conformer is C_s, except for $N(NH_2)_3$, which is more stable as C_3 (see Figure S1 top). All energies in kcal mol^{-1}.

	Electronic Proton Affinity $\Delta E^o_{e,rel}$ G4	**Rel. Electronic Proton Affinity $\Delta\Delta E^o_{e,rel}$ vs. Me_3P or Me_3N**
$P(NH_2)_3$	237.83	4.33
PMe_3	233.51	0.00
$N(NH_2)_3$	218.46	-17.03
NMe_3	235.49	0.00

The structures used for energies in **Table S1b** are all C_3 geometry, as shown at the bottom of **Figure S1**, to make all of the geometries as similar as possible for comparisons of electronic behavior, noting, however, that the $PH^+(NH_2)_3$, structure has two imaginary frequencies and is not as stable as the C_s conformer, by 3.52 kcal mol^{-1} at the G4 level. For the other ions and molcules in **Figure S1**, both the C_s and C_3 geometries are

minima with the C_s form more stable by 3.41 and 2.13 kcal mol^{-1} at the G4 level for $P(NH_2)_3$ and $NH^+(NH_2)_3$, respectively. In the comparisons between the C_3 geometries in **Table S1b**, the results are quite similar to those for the most stable conformers, with the inductive effect in the triaminoamine raised to 19 kcal mol^{-1} and the sum of other effects for the triaminophosphene, vide infra, now 23 kcal mol^{-1}, instead of 21 kcal mol^{-1}.

Table S1b. Computed electronic proton affinities energies, $\Delta E^o_{e,rel}$, for protonation at the central phosphorus (or nitrogen) at the G4 level of theory. All structures have C_3 geometry(see Figure S1 bottom). For comparison, the C_3 structure was used for $PH^+(NH_2)_3$, though it has two imaginary frequencies and is not as stable as C_s. Energies in kcal mol^{-1}.

	Electronic Proton Affinity $\Delta E^o_{e,rel}$ G4	**Rel. Electronic Proton Affinity $\Delta\Delta E^o_{e,rel}$ vs. Me_3P or Me_3N**
$P(NH_2)_3$	237.73	4.22
PMe_3	233.51	0.00
$N(NH_2)_3$	216.33	-19.15
NMe_3	235.49	0.00

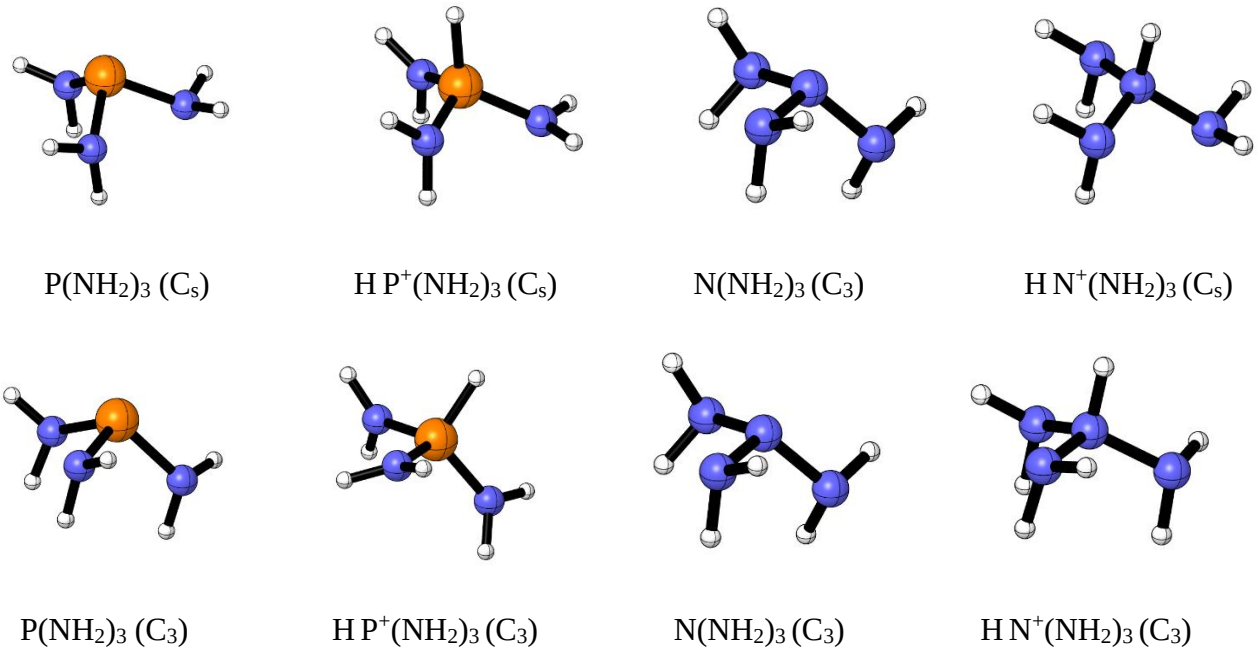


Figure S1. Structures simple model ligands at the B3LYPD3BJ/6-31+G(d,p) geometries. Color Key: Orange: phosphorus, Blue: nitrogen.

For $P(NH_2)_3$, interpreting the PA data is more complicated. Its electronic PA is remarkably much higher, by almost 20 kcal mol^{-1}, than that for $N(NH_2)_3$, in spite of the fact that protonation on N is slightly favored over P in trimethylamine versus trimethylphosphine. Why? The 4.33 kcal/mol higher basicity relative to PMe_3, must result from more than one effect. The strong 17 kcal mol^{-1} inductive effect in $N(NH_2)_3$, should be felt in $P(NH_2)_3$ in near equal force. So there must be another, even stronger, base strengthening effect(s) of 21 kcal mol^{-1} operating! Looking at the calculated structures in Figure 1 gives a hint of what this might be. The computed PNH bond angles in $P(NH_2)_3$ at the amino nitrogens lie well above 109.5°, up to 116.3° and 119.1 °, and the computed natural bond orbital analysis shows $sp^{1.98}$ and $sp^{2.84}$ hybridizations at N for the localized orbitals. The structure for $N(NH_2)_3$ shows no such behavior. It has near-tetrahedral geometry at the amino nitrogens and computed hybridizations near sp^3. This seems to point directly to d-orbital involvement in the phosphorus-containing model ligand, though, interestingly, little documentation of such a large d-orbital effect seems to appear in the aminophosphine literature. [12] Although one might expect the three amino substituents would exert a strong inductive electron withdrawal from the phosphorus, as in $N(NH_2)_3$, it would appear that considerable electron density may be donated back from the nitrogen lone pair to appropriately-oriented empty d-orbital(s) on P via a P-N pi bond, a type of "back bonding". This would explain the shift toward sp^2 hybridization on the amino N's to provide a nearly p lone-pair orbital on N. Looking at the computed charge on phosphorus and P-31 chemical shifts of aminophosphnes, however, it does not appear that the inductive effect of the amino groups has fully been mitigated by p-d back bonding in $P(NH_2)_3$. Looking at the computed structure of the protonated aminophosphine, $HP^+(NH_2)_3$, shows another, more remarkable, bond-angle change. There the amino nitrogens have assumed nearly trigonal geometry and a nearly 0.1 Å shorter P-N bond length than in $P(NH_2)_3$.. [12a] Thus, the large effect of d-orbitals is not just in the neutral $P(NH_2)_3$, but appears to exert a much stronger effect on the stabilization of the protonated species $HP^+(NH_2)_3$. This is not unexpected since P now has a full formal plus charge that can be very strongly stabilized by electron donation from three N lone-pair p orbitals. One would expect this to also affect the Pd-P bonding as electrons are donated from P to Pd in catalysts derived from P3N ligands. We are actively exploring this question.

The structure of the tris-(di-n-butylamino)phosphine ligand was optimized at the B3LYPD3BJ/6-31+G(d,p) level of theory with an unsymmetrical C_1 conformation **A** and an all-anti arrangement of the n-butyl groups chosen to have the groups arranged to have a minimum steric energy and keep the n-butyl groups away from the face of the phosphine to allow binding to palladium and it's oxidative addition substrate. A second reasonable conformation **B** like this was C_3 symmetry, but a bit less hindered sterically on the face of the phosphine, had about a 1.7 kcal/mol higher free energy at 298K in the gas phase and in toluene solvent, which mimics the solvation environment in the micelles (see SI-2 of ref. 9). The n-butyl groups could adopt numerous other comformations, but conformations **A** and **B** both appear to be reasonably low energy and representative.

Other conformations were not explored. Reaction energies for various reactions of **A** and **B** are shown in **Tables S2** and **S3**, with structures shown in **Figure S2**.

Table S2. Calculated electronic energies, enthalpies, and free energies in kcal/mol at 298 K for reactions of ligand conformers **A** and **B** with Pd and oxidative additions to bromobenzene at B3LYP/6-31G(d) and B3LYPD3BJ/6-31+G(d,p) levels of theory, with a SDD basis for Pd and Br, in the gas phase and in toluene solvent using solvation free energies from the SMD method.

Conformer:	B3LYP	B3LYPD3BJ			
	ΔE^o_e	ΔE^o_e	ΔH^o_{298K}	ΔG^o_{298K}	$\Delta G^o_{298K,tol}$
A to **B**	-0.57	0.88	0.95	1.42	1.68
PdA to **PdB**	-0.23	2.96	3.14	3.04	3.25
PdPhBrA to **PdPhBrB**	-1.86	-0.94	-0.68	-0.85	-1.04
Pd + **B** to **PdB**	-41.92	-50.74	-52.52	-43.36	-43.55
PdB + **B** to **PdB_2**	-34.90	-52.03	-53.47	-37.08	-34.39
PdB + **PhBr** to **PdPhBrB**	-38.55	-53.91	-52.17	-37.83	-31.19
PdB_2 + **PhBr** to **$PdPhBrB_2$**	-11.00	-33.52	-28.80	-11.52	-6.30
PdPhBrB + **B** to **$PdPhBrB_2$**	-7.35	-31.63	-30.10	-10.77	2.05

Attachment of Pd to conformers **A** and **B** led to formation of **PdA** and **PdB**, which were optimized at the B3LYP/6-31G(d)/SDD(Pd,Br) and B3LYPD3BJ/6-31+G(d,p)/SDD(Pd,Br) levels of theory, in this case, with the **PdA** conformer more stable by 3.3 kcal mol^{-1} in toluene. The ligand addition reaction was exoergonic by about -44 kcal mol^{-1}. A second ligand could be added on the **PdB** to give **PdB_2**, with a free energy of -35 kcal mol^{-1}. Oxidative addition of bromobenzene to **PdB** gave the intermediate **PdPhBrB** that is strongly downhill by -39 kcal mol^{-1}. In spite of a good deal of steric hindrance, we find that **PdB2** might also undergo oxidative addition with bromobenzene with a somewhat negative free energy of -12 kcal mol^{-1} in the gas phase and -6 kcal mol^{-1} in toluene. That product **$PdPhBrB_2$**, however, is predicted to be vulnerable to lose one ligand in toluene, though more stable in the gas phase. Thus, it appears that both the diligated and monoligated palladium molecules are candidates as catalytic activity with substrates that are not too sterically demanding, in which case the monoligated catalyst should be preferred.

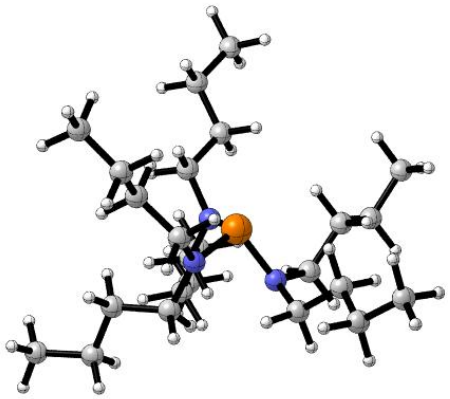
Table S3. Calculated electronic energies, enthalpies, and free energies in kcal/mol at 298 K for reactions of ligand conformers **A** and **B** with Pd and oxidative additions to bromobenzene with various theoretical methods and a 6-31+G(d,p) or 6-31+G(d,p)-SDD(Pd,Br) basis sets in the gas phase. All values in kcal/mol.

Conformer:	B3LYP[a]	B3LYPD3BJ[b]	M06-2X[a]	M06-2XD3[a]	M06[a]	M06D3[a]
	ΔE^o_e	ΔE^o_e	ΔE^o_e	ΔE^o_e	ΔE^o_e	ΔE^o_e
A to **B**	2.40	0.88	0.69	0.54	-0.97	-1.68
PdA to **PdB**	1.27	2.96	3.08	2.87	0.29	-0.50
PdPhBrA to **PdPhBrB**	-0.70	-0.94	-1.36	-1.55	-2.74	-3.89
Pd + **B** to **PdB**	-40.25	-50.74	-31.04	-31.48	-42.49	-43.80
PdB + **B** to **PdB_2**	-28.87	-52.03	-36.41	-41.18	-44.41	-51.97
PdB + **PhBr** to **PdPhBrB**	-33.36	-53.91	-42.28	-44.38	-41.54	-46.20
PdB_2 + **PhBr** to **$PdPhBrB_2$**	13.51	-33.52	-28.13	-33.17	-23.81	-35.41
PdPhBrB + **B** to **$PdPhBrB_2$**	18.00	-31.63	-22.26	-29.97	-26.68	-41.18

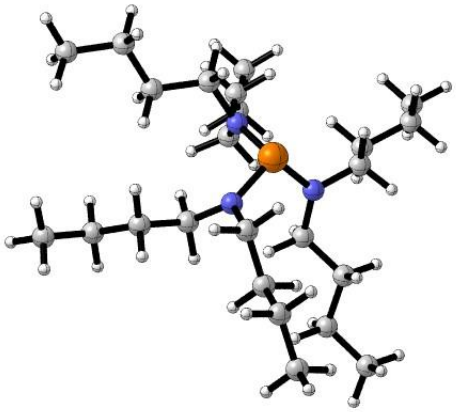
a) B3LYPD3BJ/6-31+G(d,p)-SDD(Pd,Br) geometry or B3LYPD3BJ/6-31+G(d,p) geometry without Pd.
b) optimized geometry, B3LYPD3BJ/6-31+G(d,p)-SDD(Pd,Br) or B3LYPD3BJ/6-31+G(d,p) without Pd.

The data in **Table S3** show comparisons between different methods using B3LYPD3BJ geometries in all cases. The effects of the inclusion of the empirical dispersion energies can bee seen, for example by compareing energies in the first two columns using the same same basis set and geometry for the B3LYP method. There dispersion correction changes the energies by 1-2 kcal/mol in the first two rows, with ligand conformation changes, up to almost 50 kcal/mol when two ligands are bound to Pd. Empirical dispersion effects for the Truhlar Minnesota methods M06-2X and M06, are considerably smaller, up to about 15 kcal/mol, less for the M06-2X method. This might be expected from the fact that some dispersion effects are accounted for within those methods before application of empirical dispersion methods. This serves as a warning that dispersion energy corrections can play a very large role in the chemistry of ligands with large floppy alkyl groups such as **A** and **B**, particularly in stabilizing complexes with additional ligation that causes them to become more sterically encumbered.

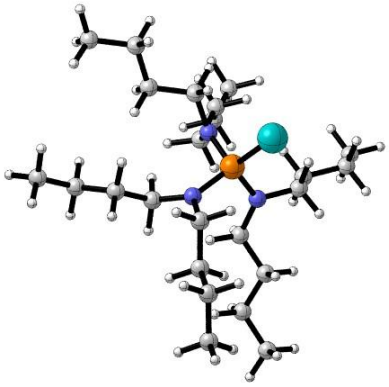
Also, one can look at compararisons between the theoretical methods. Here we see roughly similar energies, withi a few kcal/mol, for ligand conformation changes, but differences up to 10-20 kcal/mol for some ligand binding and oxidative addition reactions, including up to about 10 kcal/mol differences between the Minnesota methods, with or without dispersion corrections..



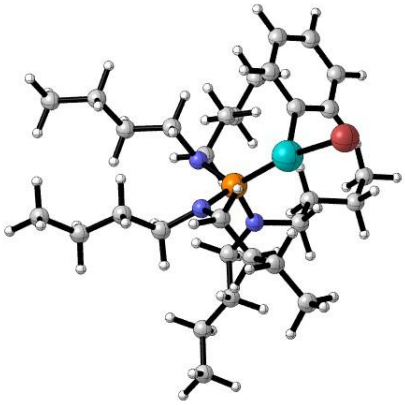
A Ligand conformer, C_3, all anti



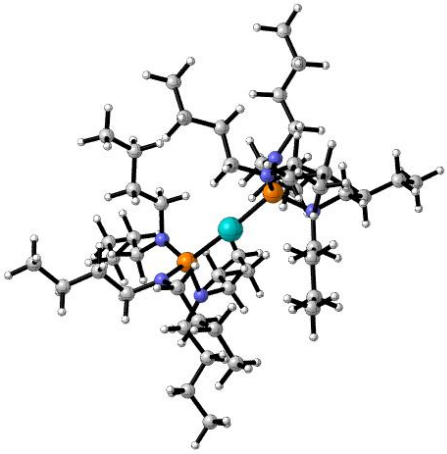
B Ligand conformer



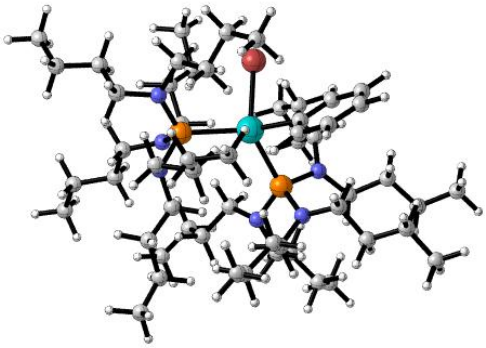
Pd**B,** Ligand + Pd



PdBPhBr, Oxidative addition product with PhBr



PdB$_2$, Two ligands on Pd



PdB$_2$PhBr, Oxidative addition product with PhBr

Figure S2. Structures of tris-(di-n-butylamino)phosphine ligand and Pd complexes at the B3LYPD3BJ/6-31+G(d,p) and B3LYPD3BJ/6-31+G(d,p)/SDD(Pd,Br) levels of theory. Color Key: Teal: palladium, Orange: phosphorus, Brown: bromine, Blue: nitrogen.

Conclusions. Ab initio calculated structures and proton affinities of the model ligands $P(NH_2)_3$ and $N(NH_2)_3$ give strong evidence of a previously unknown phenomenon in aminophosphines. The aminophosphine has p-d pi bonding and donation of lone-pair electrons into empty d orbitals on phosphorus that especially stabilizes the phosphonium ion after protonation. This effect should make the aminophosphine particularly effective as a donor ligand on palladium. DFT calculations on the P3N ligand $(n\text{-}Bu_2N)_3P$ gives a set of structures and relative energies for the ligand, its palladium binding complexes, and oxidative-addition products. These results reveal intermediate structures in the catalytic pathways of this P3N ligand, including sterically crowded, but stable structures with two $(n\text{-}Bu_2N)_3P$ structures on Pd.

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scaling factor close to 1.00 might be best for the dominant low frequencies (we get 1.005 for 111 frequencies below 150 cm^{-1})(see also ref. 6a). For zero point energies determined from experimental values and CCSD(T)-F12/cc-aug-pVDZ values, the scale factors 0.995 (B3LYP/6-311G(d,p)), 0.984 (M06-2X/6-311+G(d,p)), 0.991 (M06/6-31G(d)), 0.996 (M06/6-31+G(d,p)) give the best fit for large variety of organic molecules.

[7] We have seen differences of over 8 kcal/mol between the quasiharmonic and harmonic approxiamtions and emphasizes how important it is for workers in the field of computational chemistry to pay attention to this problem of low frequency distortions on entropy effects.[6c,d] Grimme has found examples of supermolecular complexes where differences in free energies of 3-4 kcal/mole can occur. Clearly, we see that organometallic complexes with many low-frequency vibrational modes can show much larger discrepancies.

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Table S3. Thermodynamic parameters and Cartesian coordinates optimized structures at the B3LYPD3BJ/6-31+G(d,p) and B3LYPD3BJ/6-31+G(d,p)/SDD(Pd,Br) levels of theory.

$P(NH_2)_3$:
Processing: pnh23-cs6pbed3j.log
PG=CS

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31+G(d,p)	0

HF Energy
-509.2849653

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
50.53563	54.335	74.225	74.225	54.335	39.016	25.003

10

P	-0.375789	0.398000	0.000000
N	-0.375789	-0.566986	1.423160
N	-0.375789	-0.566986	-1.423160
N	1.364935	0.579669	0.000000
H	0.254162	-1.363050	1.480242
H	-1.278481	-0.746149	1.844256
H	0.254162	-1.363050	-1.480242
H	-1.278481	-0.746149	-1.844256
H	1.695987	1.064261	0.829084
H	1.695987	1.064261	-0.829084

$PH^+(NH_2)_3$:
Processing: pnh23h-cs6pbed3j.log
PG=CS

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31+G(d,p)	0

HF Energy
-509.6558219

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
57.89952	61.661	73.912	73.912	61.661	39.054	25.004

11
H -1.510243 0.795542 -0.000000
P -0.273686 0.139803 -0.000000
N -0.273686 -0.622507 1.452838
N -0.273686 -0.622507 -1.452838
N 1.114325 1.004379 0.000000
H 0.533736 -1.147857 1.771363
H -1.149976 -0.893983 1.884846
H 0.533736 -1.147857 -1.771363
H -1.149976 -0.893983 -1.884846
H 1.439676 1.437765 0.856344
H 1.439676 1.437765 -0.856344

$N(NH_2)_3$:
Processing: nnh236pbed3j.log
PG=C03

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31+G(d,p)	0

HF Energy
-222.5516810

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
54.18556	57.556	68.767	68.767	57.556	38.296	21.857

10
N 0.000000 0.000000 0.396252
N 0.000000 1.353638 -0.059649
N 1.172285 -0.676819 -0.059649
N -1.172285 -0.676819 -0.059649
H -0.350792 1.397211 -1.024937
H -0.677031 1.846906 0.517893
H 1.385416 -0.394811 -1.024937
H 1.937983 -0.337127 0.517893
H -1.034624 -1.002400 -1.024937
H -1.260952 -1.509779 0.517893

$NH^+(NH_2)_3$:
Processing: nnh23h-cs6pbed3j.log
PG=CS

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31+G(d,p)	0

HF Energy
-222.8995025

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
64.11235	67.193	68.816	68.816	67.193	38.344	24.145

auelinux2:/aue/chem126/aue/ark/pj/pn> gtg nnh23h-cs6pbed3j.log
Processing: nnh23h-cs6pbed3j.log
11
H -1.146403 0.743941 -0.000000
N -0.285867 0.175420 -0.000000
N -0.285867 -0.527623 1.253660
N -0.285867 -0.527623 -1.253660
N 0.913926 0.964680 -0.000000
H 0.574559 -1.076019 1.295972
H -1.106734 -1.131102 1.298453
H 0.574559 -1.076019 -1.295972
H -1.106734 -1.131102 -1.298453
H 0.908241 1.538159 0.843538
H 0.908241 1.538159 -0.843538

Structure **A**:
Processing: bu2n3p-a6pbed3j.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31+G(d,p)	0

HF Energy
-1452.9693878

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
477.90579	502.378	247.743	217.493	502.522	43.963	36.797

82
P 0.265538 0.579821 0.374182
N -0.632199 -0.882404 0.188019
N -0.346520 1.396501 -1.056511
N 1.890560 0.336010 -0.128273
C -0.751120 -1.625375 -1.064717
C -0.773588 -1.674963 1.414201
C 0.410119 2.569970 -1.501990
C -1.805548 1.508831 -1.191641
C 2.302941 -0.186629 -1.425785
C 2.940301 0.612321 0.852020
C -2.122313 -2.276006 -1.280627
H -0.555344 -0.927059 -1.882452
H 0.019832 -2.412860 -1.122103
C -2.128331 -1.498615 2.107859
H -0.611127 -2.734447 1.171515
H 0.019795 -1.404967 2.123885
C 2.840888 -1.624428 -1.418192
H 1.439721 -0.123012 -2.093891
H 3.072787 0.476831 -1.853780
C 3.222329 -0.517914 1.852181

H	3.859621	0.855018	0.300368
H	2.669957	1.513022	1.418246
C	0.290618	3.845407	-0.651746
H	1.465574	2.289587	-1.551629
H	0.096725	2.792140	-2.531787
C	-2.592794	2.019256	0.025941
H	-1.998520	2.166525	-2.049041
H	-2.209978	0.527896	-1.459382
C	-2.237670	-2.929757	-2.660944
H	-2.304727	-3.033856	-0.507864
H	-2.906056	-1.517352	-1.161796
C	-3.589916	-3.611650	-2.887743
H	-2.076021	-2.167180	-3.435042
H	-1.430771	-3.665256	-2.783571
H	-3.648907	-4.066785	-3.882087
H	-3.761197	-4.401819	-2.147366
H	-4.412421	-2.892284	-2.799633
C	-2.275583	-2.370233	3.357652
H	-2.241320	-0.440882	2.378174
H	-2.933405	-1.723737	1.398185
C	-3.619708	-2.175182	4.065499
H	-2.157586	-3.427020	3.079707
H	-1.457516	-2.145362	4.055863
H	-3.702525	-2.808651	4.955093
H	-3.748343	-1.133830	4.382834
H	-4.454326	-2.422856	3.399170
C	2.992986	-2.194654	-2.831003
H	3.811452	-1.656713	-0.906671
H	2.160635	-2.256129	-0.834459
C	3.563796	-3.615539	-2.844408
H	2.012084	-2.187653	-3.325879
H	3.639276	-1.533340	-3.424617
H	3.653718	-4.003858	-3.864505
H	4.559359	-3.644406	-2.386306
H	2.920923	-4.301601	-2.280492
C	4.349554	-0.172548	2.829060
H	2.299500	-0.721548	2.411203
H	3.467679	-1.439957	1.312844
C	4.615321	-1.281776	3.851241
H	5.269539	0.033094	2.264100
H	4.100257	0.758994	3.355693
H	5.425133	-1.011571	4.537334
H	3.721045	-1.484037	4.452113
H	4.896799	-2.216777	3.352788
C	1.250000	4.942825	-1.120991
H	-0.737992	4.225098	-0.686400
H	0.496204	3.597057	0.397825
C	1.133579	6.232019	-0.302581
H	2.280827	4.566186	-1.068103
H	1.060131	5.163128	-2.180942
H	1.833318	6.997500	-0.654936

H	0.121629	6.648794	-0.366851
H	1.346848	6.045034	0.756334
C	-4.102694	2.010515	-0.226457
H	-2.370375	1.379534	0.887196
H	-2.265956	3.029537	0.296165
C	-4.912829	2.474941	0.987357
H	-4.334539	2.649454	-1.090299
H	-4.413759	0.994281	-0.505876
H	-5.989100	2.456860	0.784732
H	-4.723685	1.829875	1.853205
H	-4.642847	3.498406	1.272699

Structure **B**:
Processing: bu2n3p-b6pbed3j.log
PG=C03

Method	BasisSet	Imaginary Freqs
RB3LYP	6-31+G(d,p)	0

HF Energy
-1452.9679871

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
477.95387	502.450	243.997	215.930	502.586	43.963	34.607

82

P	0.000000	0.000000	1.359735
N	-0.875598	1.306507	0.635610
N	1.569267	0.105036	0.635610
N	-0.693669	-1.411543	0.635610
C	-0.584112	1.925899	-0.651373
C	-2.104530	1.712864	1.313803
C	1.959933	-0.457094	-0.651373
C	2.535649	0.966144	1.313803
C	-1.375821	-1.468805	-0.651373
C	-0.431119	-2.679009	1.313803
C	-0.570881	3.459287	-0.614827
H	0.401112	1.576983	-0.962217
H	-1.290583	1.602911	-1.436039
C	-3.399459	1.333742	0.584842
H	-2.101045	1.244815	2.305899
H	-2.093559	2.799104	1.485852
C	-2.710390	-2.224041	-0.614827
H	-1.566264	-0.441118	-0.962217
H	-0.742870	-1.919133	-1.436039
C	0.544675	-3.610888	0.584842
H	-0.027519	-2.441965	2.305899
H	-1.377316	-3.212628	1.485852
C	3.281271	-1.235246	-0.614827
H	1.165152	-1.135865	-0.962217

H	2.033453	0.316222	-1.436039
H	3.470875	0.413524	1.485852
C	2.854784	2.277146	0.584842
H	2.128563	1.197151	2.305899
C	0.038849	4.057890	-1.885802
H	-1.589229	3.848075	-0.486442
H	0.000000	3.789438	0.262505
C	0.046410	5.588950	-1.881124
H	1.066545	3.686919	-1.998710
H	-0.515822	3.695091	-2.762020
H	0.491624	5.991502	-2.797132
H	-0.971174	5.988550	-1.799683
H	0.622318	5.975030	-1.031897
C	-4.655585	1.786189	1.333898
H	-3.402758	1.775396	-0.421103
H	-3.426727	0.247771	0.449411
C	-5.948625	1.396277	0.611418
H	-4.652340	1.348916	2.341772
H	-4.625977	2.875588	1.473278
H	-6.834969	1.722982	1.165541
H	-5.992845	1.847616	-0.386810
H	-6.014755	0.309262	0.484845
C	-3.533660	-1.995301	-1.885802
H	-2.537916	-3.300350	-0.486442
H	-3.281750	-1.894719	0.262505
C	0.780907	-4.924950	1.333898
H	0.163841	-3.834573	-0.421103
H	1.498787	-3.091518	0.449411
C	1.765101	-5.849799	0.611418
H	1.157974	-4.703503	2.341772
H	-0.177343	-5.444008	1.473278
H	1.925338	-6.780748	1.165541
H	1.396340	-6.113764	-0.386810
H	2.739549	-5.363562	0.484845
C	-4.863378	-2.754283	-1.881124
H	-3.726238	-0.919805	-1.998710
H	-2.942131	-2.294261	-2.762020
H	-5.434605	-2.569992	-2.797132
H	-4.700650	-3.835336	-1.799683
H	-5.485687	-2.448572	-1.031897
C	3.494811	-2.062589	-1.885802
H	4.127145	-0.547725	-0.486442
H	3.281750	-1.894719	0.262505
C	4.816968	-2.834667	-1.881124
H	2.659694	-2.767114	-1.998710
H	3.457954	-1.400830	-2.762020
H	4.942981	-3.421510	-2.797132
H	5.671823	-2.153214	-1.799683
H	4.863369	-3.526458	-1.031897
C	3.874678	3.138760	1.333898
H	3.238917	2.059177	-0.421103

H	1.927940	2.843747	0.449411
C	4.183524	4.453522	0.611418
H	3.494366	3.354586	2.341772
H	4.803320	2.568420	1.473278
H	4.909631	5.057766	1.165541
H	4.596505	4.266148	-0.386810
H	3.275206	5.054299	0.484845

Structure **PdA**:
Processing: pdbu2n3p-a6psdbed3j.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-1580.9181149

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
478.95335	504.583	256.342	226.288	504.732	44.640	37.065

83

Pd	0.835823	-1.214069	-1.737885
P	0.258976	-0.132159	0.107093
N	1.481497	0.882379	0.726153
N	-1.198780	0.752595	-0.049921
N	-0.138985	-1.051984	1.514778
C	1.255524	1.761444	1.868935
C	2.741527	1.029538	-0.004070
C	-1.962197	1.295569	1.073053
C	-1.446252	1.369917	-1.358900
C	0.953164	-1.523623	2.375566
C	-1.302041	-1.941848	1.409737
C	0.977826	3.232181	1.525746
H	0.411906	1.362674	2.438849
H	2.130166	1.705602	2.535947
C	2.704756	1.983883	-1.204570
H	3.502721	1.357677	0.717172
H	3.049190	0.041620	-0.367415
C	2.054174	-2.374823	1.723917
H	1.429695	-0.655875	2.843170
H	0.484153	-2.094288	3.187917
C	-1.070135	-3.307585	0.746463
H	-1.706174	-2.086460	2.422600
H	-2.066358	-1.410913	0.838118
C	-3.479937	1.125317	0.937433
H	-1.629687	0.783669	1.978788
H	-1.743141	2.368440	1.205054
C	-2.317595	0.513443	-2.281282
H	-1.910054	2.351917	-1.194710

H	-0.490424	1.561780	-1.861584
C	0.493786	4.029266	2.740410
H	1.885285	3.698518	1.123229
H	0.227130	3.273407	0.727359
C	0.229586	5.503532	2.419900
H	-0.424270	3.567640	3.129525
H	1.237497	3.955338	3.546044
H	-0.121738	6.050559	3.301344
H	1.139524	5.997671	2.059704
H	-0.532109	5.603891	1.637639
C	4.044086	2.038082	-1.944005
H	1.924050	1.628163	-1.889405
H	2.415061	2.990872	-0.883133
C	4.011065	2.959997	-3.166928
H	4.832440	2.370996	-1.253987
H	4.320355	1.022111	-2.258092
H	4.976854	2.979830	-3.683476
H	3.252813	2.628069	-3.885747
H	3.764658	3.988706	-2.878149
C	3.161437	-2.730103	2.719767
H	1.628565	-3.289954	1.300041
H	2.483119	-1.822828	0.880487
C	4.285571	-3.556625	2.087368
H	3.579590	-1.805078	3.140952
H	2.730642	-3.283328	3.566588
H	5.068876	-3.795686	2.814869
H	3.900759	-4.501586	1.686238
H	4.752120	-3.012334	1.257946
C	-2.387683	-4.030096	0.453340
H	-0.515565	-3.150059	-0.189001
H	-0.444005	-3.940098	1.388050
C	-2.181934	-5.406914	-0.185568
H	-2.963513	-4.139113	1.383723
H	-2.997332	-3.404168	-0.212688
H	-3.136799	-5.900411	-0.396950
H	-1.632293	-5.320375	-1.130158
H	-1.603828	-6.064817	0.474155
C	-4.222962	1.617755	2.183484
H	-3.844379	1.675237	0.060582
H	-3.712199	0.067994	0.760059
C	-5.743813	1.479621	2.064603
H	-3.870001	1.056123	3.059325
H	-3.963617	2.669124	2.369867
H	-6.251374	1.834567	2.967909
H	-6.126385	2.059052	1.216112
H	-6.032352	0.433701	1.907402
C	-2.507503	1.140469	-3.664129
H	-1.826535	-0.464728	-2.379815
H	-3.292090	0.334366	-1.810685
C	-3.357716	0.273516	-4.598015
H	-2.971724	2.131587	-3.559303

H -1.521546 1.310435 -4.118347
H -3.475683 0.737084 -5.583507
H -2.897787 -0.711047 -4.743007
H -4.359245 0.111892 -4.181884

Structure **PdB**:
Processing: pdbu2n3p-b6psdbed3j.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-1580.9134052

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
479.07917	504.764	259.007	226.616	504.909	44.640	37.257

83
Pd -0.001762 -0.000323 2.931427
P -0.000152 0.000223 0.716125
N 1.087218 -1.123732 0.016153
N -1.516810 -0.378322 0.014622
N 0.430935 1.503464 0.016175
C 0.847212 -1.842374 -1.229956
C 2.358933 -1.364839 0.696557
C -2.016486 0.188106 -1.232908
C -2.363509 -1.357686 0.694673
C 1.172491 1.653985 -1.230568
C 0.004865 2.725660 0.696616
C 1.008369 -3.363479 -1.115690
H -0.173669 -1.623016 -1.544444
H 1.507644 -1.477148 -2.035049
C 3.593414 -0.883550 -0.072185
H 2.306931 -0.857459 1.667880
H 2.461289 -2.436856 0.917115
C 2.410393 2.552634 -1.117451
H 1.491409 0.659636 -1.544953
H 0.525803 2.043868 -2.035264
C -1.031409 3.553179 -0.070204
H -0.406345 2.427091 1.668890
H 0.882216 3.350815 0.915169
C -3.414762 0.808844 -1.122391
H -1.315362 0.962440 -1.546025
H -2.028415 -0.566801 -2.037722
H -3.343172 -0.909351 0.912891
C -2.563528 -2.668376 -0.072560
H -1.900022 -1.565367 1.667104
C 0.475570 -4.089454 -2.354833
H 2.063496 -3.627432 -0.970223

H	0.476108	-3.710415	-0.220781
C	0.626062	-5.610872	-2.265286
H	-0.583798	-3.834266	-2.493293
H	0.998793	-3.719053	-3.247166
H	0.236193	-6.106668	-3.160649
H	1.678329	-5.897949	-2.154493
H	0.082229	-6.007496	-1.399794
C	4.897060	-1.148427	0.686340
H	3.642224	-1.375250	-1.053797
H	3.498246	0.189627	-0.265377
C	6.132831	-0.650144	-0.069634
H	4.846312	-0.661691	1.669779
H	4.994075	-2.225060	0.882598
H	7.053728	-0.842264	0.491276
H	6.224835	-1.145266	-1.043724
H	6.071611	0.429198	-0.253034
C	3.304040	2.453910	-2.357647
H	2.112689	3.598631	-0.971286
H	2.977767	2.264231	-0.223326
C	-1.453714	4.813943	0.689429
H	-0.632142	3.841972	-1.052485
H	-1.912792	2.933076	-0.261926
C	-2.505410	5.634243	-0.064216
H	-1.847636	4.525963	1.673572
H	-0.570074	5.437112	0.884140
H	-2.799112	6.527449	0.497485
H	-2.124911	5.962008	-1.039026
H	-3.409391	5.040797	-0.245878
C	4.547470	3.343470	-2.268754
H	3.611349	1.408610	-2.497177
H	2.721000	2.723138	-3.249163
H	5.170769	3.253660	-3.164812
H	4.271249	4.398529	-2.156939
H	5.163425	3.069511	-1.404068
C	-3.773501	1.634048	-2.362070
H	-4.171161	0.026764	-0.979874
H	-3.452094	1.442637	-0.227172
C	-5.166751	2.264002	-2.276260
H	-3.022572	2.424161	-2.497647
H	-3.711480	0.996386	-3.254685
H	-5.398646	2.850164	-3.171875
H	-5.941652	1.495985	-2.168382
H	-5.241073	2.932602	-1.410472
C	-3.447376	-3.662879	0.685568
H	-3.011413	-2.465819	-1.055450
H	-1.586538	-3.123754	-0.262909
C	-3.633199	-4.983359	-0.068574
H	-3.002972	-3.861015	1.670401
H	-4.428313	-3.207348	0.878748
H	-4.262323	-5.683124	0.491888
H	-4.105177	-4.816627	-1.044225

H -2.667921 -5.471436 -0.248521

Structure **PdPhBrA**:
Processing: pdphbrbu2n3p-a6psdbed3j.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-1826.0549236

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
536.97686	567.156	288.401	255.862	567.324	45.420	38.056

auelinux2:/aue/chem126/aue/ark/pj/pn> gtg pdphbrbu2n3p-a6psdbed3j.log
Processing: pdphbrbu2n3p-a6psdbed3j.log
95
Pd -1.312550 -0.663645 -0.459103
P 0.638056 0.251331 0.286265
N 0.817649 0.638704 1.915564
N 1.800506 -0.926493 -0.129012
N 1.169457 1.620850 -0.561263
C 2.162567 0.737974 2.493918
C -0.308324 0.587942 2.865348
C 3.216342 -0.654705 -0.367776
C 1.401836 -2.324682 0.082011
C 1.639166 2.860802 0.056333
C 1.277808 1.497682 -2.024681
C 2.657514 -0.524021 3.208317
H 2.868171 0.997799 1.700675
H 2.172061 1.584572 3.195394
C -0.843826 -0.815035 3.167137
H 0.049395 1.055655 3.790513
H -1.123186 1.212626 2.494307
C 1.002652 4.140544 -0.493847
H 1.425184 2.800026 1.124121
H 2.735410 2.936979 -0.055260
C -0.015226 1.777419 -2.798232
H 2.079143 2.169363 -2.358742
H 1.605770 0.482248 -2.267639
C 3.775974 -1.334729 -1.621675
H 3.335638 0.427634 -0.467551
H 3.817068 -0.963790 0.503634
C 0.661795 -2.928973 -1.113326
H 2.303819 -2.909161 0.297036
H 0.769811 -2.403300 0.976395
C 4.110823 -0.392371 3.673816
H 2.015822 -0.735585 4.071804
H 2.558863 -1.378765 2.529253
C 4.620096 -1.646441 4.390578

H	4.750378	-0.180170	2.805663
H	4.203761	0.476016	4.340360
H	5.661244	-1.531517	4.709426
H	4.018870	-1.862120	5.281297
H	4.565202	-2.523208	3.734685
C	-1.950001	-0.796218	4.225075
H	-1.236848	-1.243289	2.236560
H	-0.024738	-1.467445	3.492627
C	-2.593240	-2.171504	4.425468
H	-1.539191	-0.435208	5.178623
H	-2.717589	-0.072820	3.924595
H	-3.377157	-2.140972	5.189557
H	-3.046372	-2.528481	3.493509
H	-1.850078	-2.914980	4.737770
C	1.530357	5.387285	0.224051
H	1.201145	4.233914	-1.568536
H	-0.084999	4.084244	-0.376515
C	0.913749	6.683148	-0.311151
H	1.324065	5.299353	1.299516
H	2.623552	5.431690	0.123754
H	1.301233	7.559564	0.218626
H	1.132727	6.812601	-1.377462
H	-0.176223	6.676859	-0.195559
C	0.135657	1.498781	-4.295772
H	-0.809120	1.137148	-2.393455
H	-0.334561	2.814235	-2.642459
C	-1.170453	1.720280	-5.064775
H	0.928273	2.135785	-4.714243
H	0.468367	0.460815	-4.434911
H	-1.047619	1.508430	-6.132129
H	-1.962392	1.069015	-4.679388
H	-1.514041	2.756714	-4.965888
C	5.239446	-0.958757	-1.874709
H	3.695641	-2.424762	-1.523432
H	3.164219	-1.055094	-2.487887
C	5.822931	-1.643655	-3.114150
H	5.317911	0.131539	-1.985839
H	5.840429	-1.220593	-0.993029
H	6.867040	-1.356360	-3.275792
H	5.787599	-2.734687	-3.014284
H	5.258304	-1.375177	-4.014447
C	0.093377	-4.321175	-0.840930
H	-0.174577	-2.265046	-1.413493
H	1.322871	-2.941369	-1.988633
C	-0.611790	-4.915375	-2.063484
H	0.907129	-4.984349	-0.513856
H	-0.615596	-4.256595	-0.005666
H	-1.009166	-5.911872	-1.844725
H	-1.446979	-4.277838	-2.369431
H	0.079684	-5.007916	-2.909808
C	-2.426447	0.764616	0.363039

C	-2.185011	2.118340	0.127614
C	-2.986071	3.090266	0.739297
C	-4.030546	2.711456	1.585170
C	-4.279618	1.352899	1.802201
C	-3.486355	0.376346	1.190710
H	-1.370553	2.422450	-0.515592
H	-2.786560	4.142391	0.551614
H	-4.650832	3.464527	2.062029
H	-5.101111	1.044340	2.443304
H	-3.702436	-0.673054	1.351075
Br	-3.211765	-1.868444	-1.541079

Structure **PdPhBrB**:
Processing: pdphbrbu2n3p-b6psdbed3j.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-1826.0564152

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
537.20157	567.414	290.160	256.425	567.578	45.420	38.150

95

Pd	-1.091383	-1.192106	-1.039425
P	0.441863	0.005574	0.171363
N	0.258819	-0.301380	1.821537
N	1.920474	-0.591285	-0.419269
N	0.731986	1.683272	0.110183
C	1.304408	0.004772	2.801208
C	-0.988713	-0.859682	2.355791
C	3.233491	-0.091211	-0.005985
C	1.884618	-1.918577	-1.054608
C	0.145336	2.604243	1.092741
C	1.043371	2.263112	-1.204208
C	2.123618	-1.216773	3.228984
H	1.970393	0.765866	2.384976
H	0.838775	0.463591	3.684495
C	-1.946187	0.200042	2.906241
H	-1.484096	-1.420328	1.555173
H	-0.736242	-1.588128	3.136713
C	-1.197342	3.233463	0.711061
H	0.019988	2.059461	2.027550
H	0.880014	3.395593	1.291587
C	2.167998	3.301032	-1.154135
H	1.339272	1.445153	-1.866217
H	0.144815	2.713597	-1.644473
C	4.152713	0.262513	-1.181121

H	3.071308	0.811916	0.586086
H	3.736706	-0.819723	0.647817
H	2.801708	-2.040354	-1.639146
C	1.713602	-3.106151	-0.099666
H	1.071333	-1.927072	-1.797927
C	3.230712	-0.858352	4.224220
H	1.459080	-1.969826	3.671376
H	2.559915	-1.679295	2.338270
C	4.062801	-2.072411	4.648270
H	3.888728	-0.101761	3.774181
H	2.787101	-0.387685	5.112359
H	4.850187	-1.792114	5.355667
H	3.434892	-2.831328	5.129155
H	4.542761	-2.541802	3.781559
C	-3.223729	-0.399830	3.498812
H	-1.438905	0.803149	3.671518
H	-2.210093	0.882800	2.092216
C	-4.229913	0.674743	3.921934
H	-3.689156	-1.065800	2.759725
H	-2.969859	-1.033445	4.359394
H	-5.140397	0.232126	4.338957
H	-3.801460	1.338954	4.681830
H	-4.517821	1.295239	3.065565
C	-1.764687	4.081102	1.853988
H	-1.091328	3.856945	-0.184750
H	-1.906216	2.443449	0.450589
C	2.604784	3.746739	-2.553341
H	1.846142	4.180248	-0.582059
H	3.024771	2.877850	-0.616506
C	3.752455	4.760086	-2.521084
H	2.910468	2.866019	-3.134578
H	1.745275	4.177772	-3.083982
H	4.049110	5.062162	-3.530840
H	3.465349	5.664359	-1.971951
H	4.634437	4.337627	-2.025498
C	-3.115288	4.714399	1.507090
H	-1.877176	3.450498	2.746653
H	-1.045303	4.867416	2.123092
H	-3.505274	5.308530	2.340461
H	-3.028288	5.373466	0.635379
H	-3.853022	3.943551	1.261564
C	5.444263	0.944393	-0.718083
H	4.407716	-0.636992	-1.754520
H	3.611909	0.923052	-1.867477
C	6.350444	1.349755	-1.884240
H	5.190384	1.834773	-0.126238
H	5.990493	0.273842	-0.040831
H	7.265405	1.836343	-1.530693
H	6.643608	0.476468	-2.478235
H	5.836778	2.048701	-2.554416
C	1.563912	-4.431317	-0.852285

H	2.567536	-3.156749	0.588567
H	0.825120	-2.941057	0.524214
C	1.363955	-5.623175	0.087914
H	0.707898	-4.357775	-1.535272
H	2.451688	-4.597738	-1.478310
H	1.258683	-6.558201	-0.471627
H	2.211935	-5.735348	0.774512
H	0.458480	-5.493975	0.691761
C	-2.399918	0.282226	-1.088460
C	-2.282231	1.265581	-2.074187
C	-3.253921	2.268116	-2.168827
C	-4.335070	2.291578	-1.284505
C	-4.453451	1.293005	-0.314686
C	-3.491013	0.281261	-0.217380
H	-1.452922	1.249390	-2.772088
H	-3.160606	3.030307	-2.937778
H	-5.083460	3.074807	-1.356710
H	-5.301350	1.288045	0.365029
H	-3.609610	-0.506039	0.517230
Br	-2.376199	-2.906274	-2.274168

Structure **PdB_2**:
Processing: pddibu2n3p-b6psdbed3j.log
PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-3033.9424805

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
957.61072	1008.973	459.221	389.114	1009.273	46.387	40.395

165

Pd	0.000044	-0.232318	-0.000502
P	-2.293062	-0.139196	0.071433
N	-2.994100	-1.133017	1.270154
N	-2.837966	1.465747	0.343606
N	-3.042332	-0.624804	-1.396064
C	-4.336874	-1.024754	1.837661
C	-2.237595	-2.334034	1.639105
C	-4.232807	1.880663	0.231040
C	-1.907461	2.370836	1.021386
C	-4.346394	-1.261021	-1.529518
C	-2.391704	-0.152139	-2.618789
C	-4.358455	-0.468121	3.265346
H	-4.958283	-0.388104	1.205477
H	-4.816036	-2.016546	1.826380
C	-2.439510	-3.517939	0.687840
H	-1.171184	-2.072457	1.659752

H	-2.520765	-2.618370	2.660889
C	-4.345855	-2.513793	-2.417467
H	-4.668914	-1.563808	-0.533830
H	-5.107884	-0.556655	-1.909411
C	-2.874880	1.210131	-3.128633
H	-1.313837	-0.092869	-2.411286
H	-2.517149	-0.908800	-3.402662
C	-4.432862	3.283974	-0.354222
H	-4.731131	1.164652	-0.428879
H	-4.753972	1.835069	1.202726
H	-2.012367	3.374918	0.591761
C	-2.035104	2.443484	2.545119
H	-0.895328	2.023810	0.774520
C	-5.767664	-0.437592	3.863698
H	-3.697464	-1.068668	3.903829
H	-3.939069	0.542700	3.251134
C	-5.801088	0.153092	5.276733
H	-6.426552	0.148046	3.206902
H	-6.181198	-1.455595	3.880151
H	-6.818065	0.168708	5.683268
H	-5.175398	-0.431172	5.961665
H	-5.422151	1.181787	5.280740
C	-1.657620	-4.761759	1.115441
H	-3.509869	-3.757632	0.613852
H	-2.117080	-3.207395	-0.312885
C	-1.859601	-5.946626	0.166362
H	-0.590183	-4.509797	1.168154
H	-1.954780	-5.052063	2.133030
H	-1.282912	-6.821324	0.484566
H	-2.915719	-6.237932	0.121268
H	-1.543493	-5.691417	-0.851685
C	-5.646829	-3.310910	-2.279408
H	-4.203767	-2.242521	-3.470838
H	-3.493717	-3.143075	-2.135060
C	-2.229980	1.593963	-4.462663
H	-3.968993	1.207584	-3.234434
H	-2.634218	1.962534	-2.370218
C	-2.607589	3.004282	-4.924323
H	-1.138770	1.521292	-4.366455
H	-2.517049	0.863950	-5.232238
H	-2.141524	3.253670	-5.883481
H	-3.693345	3.102561	-5.042638
H	-2.285301	3.753658	-4.191828
C	-5.683347	-4.552587	-3.175346
H	-5.772839	-3.612467	-1.230262
H	-6.501460	-2.661726	-2.515797
H	-6.618010	-5.110290	-3.052165
H	-5.594374	-4.277967	-4.233062
H	-4.854756	-5.230398	-2.938902
C	-5.898484	3.541735	-0.719200
H	-4.104170	4.046285	0.363049

H	-3.805640	3.397362	-1.245968
C	-6.137514	4.953775	-1.261995
H	-6.217779	2.802266	-1.466392
H	-6.529707	3.376102	0.164962
H	-7.189315	5.110917	-1.523995
H	-5.860144	5.712711	-0.520962
H	-5.537406	5.134802	-2.161432
C	-1.013078	3.405003	3.158696
H	-3.050053	2.755396	2.830150
H	-1.885320	1.437136	2.954674
C	-1.121375	3.501942	4.683027
H	-0.003403	3.074988	2.879614
H	-1.140334	4.403749	2.717919
H	-0.370224	4.181848	5.098118
H	-2.110073	3.868017	4.984099
H	-0.976718	2.520778	5.149990
P	2.293142	-0.139655	-0.071872
N	3.042226	-0.626033	1.395456
N	2.994367	-1.132866	-1.270992
N	2.838458	1.465328	-0.342893
C	4.345262	-1.264326	1.528722
C	2.391538	-0.153962	2.618335
C	4.233323	1.879848	-0.229352
C	1.908292	2.371153	-1.020115
C	4.337368	-1.024387	-1.837928
C	2.237610	-2.333241	-1.641414
C	4.342885	-2.517377	2.416266
H	4.667320	-1.567246	0.532928
H	5.107827	-0.561229	1.908833
C	4.359641	-0.465755	-3.264813
H	4.958901	-0.388967	-1.204610
H	4.816023	-2.016432	-1.827903
C	4.433414	3.282959	0.356375
H	4.731002	1.163493	0.430704
H	4.755094	1.834372	-1.200716
H	2.515271	-0.911764	3.401388
C	2.876447	1.206947	3.130153
H	1.313887	-0.092808	2.410225
H	2.013300	3.374876	-0.589677
C	2.036238	2.444981	-2.543767
H	0.896030	2.024140	-0.773735
H	2.521121	-2.616704	-2.663352
C	2.438698	-3.518135	-0.691202
H	1.171293	-2.071297	-1.662265
C	5.642523	-3.316572	2.277620
H	4.201512	-2.246217	3.469764
H	3.489661	-3.145201	2.133886
C	5.677258	-4.558572	3.173179
H	5.767751	-3.618024	1.228352
H	6.498272	-2.668848	2.513969
H	6.610990	-5.117746	3.049601

H	5.588990	-4.284127	4.231000
H	4.847519	-5.234978	2.936735
C	5.769010	-0.435160	-3.862779
H	3.698454	-1.065041	-3.904281
H	3.940818	0.545276	-3.249303
C	5.803119	0.157619	-5.274922
H	6.428082	0.149114	-3.204952
H	6.181956	-1.453377	-3.880652
H	6.820201	0.173243	-5.681193
H	5.177246	-0.425250	-5.960875
H	5.424789	1.186541	-5.277478
C	5.898809	3.540081	0.722690
H	4.105625	4.045542	-0.361025
H	3.805465	3.396431	1.247602
C	6.137919	4.951942	1.265914
H	6.217137	2.800369	1.470052
H	6.530750	3.374328	-0.160938
H	7.189554	5.108635	1.528845
H	5.861482	5.711104	0.524763
H	5.537108	5.133057	2.164863
C	1.014572	3.407244	-3.156772
H	3.051324	2.756860	-2.828351
H	1.886276	1.438993	-2.954142
C	1.123070	3.505253	-4.681017
H	0.004769	3.077326	-2.878045
H	1.142077	4.405632	-2.715255
H	0.372218	4.185742	-5.095693
H	2.111937	3.871178	-4.981720
H	0.978097	2.524482	-5.148707
C	1.656650	-4.761310	-1.120415
H	3.508942	-3.758223	-0.616895
H	2.115827	-3.208478	0.309656
C	1.858000	-5.947243	-0.172534
H	0.589297	-4.509028	-1.173254
H	1.954123	-5.050594	-2.138202
H	1.281160	-6.821437	-0.491850
H	2.914021	-6.238899	-0.127424
H	1.541651	-5.693035	0.845688
C	2.231283	1.590061	4.464263
H	3.970489	1.202654	3.236612
H	2.637333	1.960629	2.372520
C	2.610034	2.999528	4.927580
H	1.140053	1.518568	4.367443
H	2.517239	0.858958	5.233216
H	2.143839	3.248316	5.886831
H	3.695835	3.096685	5.046409
H	2.288709	3.749986	4.195767

Structure **PdPhBrB$_2$**:
Processing: pdphbrdibu2n3p-b6psdbed3j.log

PG=C01

Method	BasisSet	Imaginary Freqs
RB3LYP	GenECP	0

HF Energy
-3279.0529884

ZPE	E298	S298	Squasihar	Equasihar	Strans	Srot
1020.14486	1074.636	461.205	409.050	1074.915	46.846	40.575

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Pd	0.014408	-0.967799	-0.695582
P	-1.698651	0.501165	0.065063
N	-1.266517	2.010497	0.798606
N	-2.650045	0.778550	-1.329907
N	-2.865678	0.007290	1.214218
C	-2.355065	2.915879	1.225136
C	-0.089940	2.710548	0.266943
C	-3.958050	1.439477	-1.306432
C	-2.000459	0.765806	-2.647657
C	-2.585495	0.160604	2.647510
C	-3.972113	-0.894559	0.880257
C	-2.665185	4.087040	0.281674
H	-3.254805	2.315947	1.354134
H	-2.113683	3.309099	2.221900
C	0.485359	3.788303	1.200362
H	0.678015	1.968131	0.055666
H	-0.335296	3.194017	-0.687990
C	-2.454127	-1.140391	3.444050
H	-1.663005	0.733136	2.747461
H	-3.376082	0.774227	3.105705
C	-5.328888	-0.413886	1.406329
H	-4.002952	-1.008216	-0.201293
H	-3.777918	-1.896444	1.273335
C	-5.043292	0.702123	-2.103484
H	-4.280727	1.527454	-0.270641
H	-3.880956	2.463564	-1.695998
H	-2.733761	0.415953	-3.381443
C	-1.403268	2.095021	-3.117540
H	-1.199900	0.027354	-2.636093
C	-4.030180	4.711049	0.585767
H	-1.892784	4.860774	0.359120
H	-2.644578	3.741864	-0.755893
C	-4.349737	5.906551	-0.316289
H	-4.809009	3.945414	0.469067
H	-4.063432	5.023222	1.638867
H	-5.333440	6.330539	-0.088784
H	-3.605421	6.702208	-0.195158
H	-4.348360	5.611081	-1.372141
C	1.181111	4.905639	0.416225

H	-0.301090	4.236777	1.814223
H	1.188570	3.341038	1.907687
C	1.778267	5.982050	1.325018
H	1.965536	4.476847	-0.217749
H	0.455528	5.363998	-0.268966
H	2.279030	6.765474	0.746670
H	0.999140	6.458496	1.932015
H	2.516029	5.553989	2.012075
C	-1.958702	-0.857341	4.866993
H	-3.417072	-1.663267	3.494900
H	-1.762101	-1.813270	2.929963
C	-6.469409	-1.319285	0.929321
H	-5.322719	-0.393134	2.504037
H	-5.516800	0.616855	1.083301
C	-7.843239	-0.859361	1.424269
H	-6.467549	-1.354157	-0.167371
H	-6.278875	-2.347453	1.264140
H	-8.639422	-1.523464	1.071704
H	-7.883122	-0.840750	2.519816
H	-8.070849	0.152210	1.067645
C	-1.861434	-2.110057	5.741718
H	-0.975680	-0.371395	4.814837
H	-2.629968	-0.129428	5.343312
H	-1.534867	-1.862020	6.757256
H	-2.830963	-2.616189	5.816086
H	-1.145059	-2.826796	5.327499
C	-6.427354	1.322068	-1.883261
H	-4.810277	0.726787	-3.174321
H	-5.056005	-0.355120	-1.818459
C	-7.532165	0.596254	-2.656179
H	-6.665513	1.309503	-0.811718
H	-6.404635	2.380130	-2.178496
H	-8.511139	1.055673	-2.483401
H	-7.337513	0.616261	-3.734699
H	-7.597048	-0.454641	-2.351353
C	-0.861812	1.989242	-4.547106
H	-2.142141	2.906156	-3.059572
H	-0.580606	2.369563	-2.448688
C	-0.149426	3.264677	-5.005361
H	-0.172696	1.137352	-4.599847
H	-1.688165	1.759564	-5.233864
H	0.231661	3.165769	-6.027374
H	-0.825147	4.128485	-4.980919
H	0.703093	3.490058	-4.354479
P	2.259627	-0.537096	0.254403
N	2.929131	0.997263	-0.102705
N	2.350209	-0.485390	1.994221
N	3.380071	-1.783096	-0.043461
C	4.160631	1.470727	0.540181
C	2.666472	1.486913	-1.465708
C	4.741237	-1.740640	0.500386

C	3.100561	-2.954493	-0.896491
C	2.358421	-1.772938	2.705225
C	1.497032	0.543653	2.601874
C	4.214292	2.979040	0.785267
H	4.229424	0.967522	1.506909
H	5.045971	1.180860	-0.042673
C	1.008001	-2.488226	2.781588
H	3.068929	-2.429842	2.206187
H	2.752395	-1.599538	3.713340
C	5.825917	-1.445022	-0.541778
H	4.782232	-0.997578	1.298413
H	4.959062	-2.709618	0.976781
H	2.635185	2.582959	-1.441845
C	3.642840	1.013288	-2.544329
H	1.664133	1.149426	-1.747673
H	4.024284	-3.541859	-0.924241
C	1.970207	-3.851878	-0.398646
H	2.888445	-2.643048	-1.919966
H	0.430177	0.317461	2.457394
C	1.761106	0.779638	4.088769
H	1.684878	1.468613	2.059733
C	5.519024	3.378142	1.484393
H	4.135231	3.529589	-0.159718
H	3.357055	3.277358	1.397913
C	5.623547	4.881637	1.755472
H	5.605115	2.827600	2.431400
H	6.369508	3.057796	0.867435
H	6.578201	5.137009	2.227358
H	5.544851	5.456425	0.825330
H	4.821585	5.220647	2.420479
C	1.106664	-3.886502	3.400114
H	0.293078	-1.884611	3.348591
H	0.610466	-2.566969	1.765754
C	-0.149472	-4.732507	3.162273
H	1.972674	-4.409410	2.972276
H	1.305367	-3.800286	4.477161
H	-0.074540	-5.707947	3.654422
H	-1.046832	-4.234325	3.545307
H	-0.299768	-4.907477	2.092045
C	7.209838	-1.280546	0.092467
H	5.854307	-2.251089	-1.285780
H	5.558936	-0.536870	-1.090593
C	8.305420	-0.992024	-0.938430
H	7.173287	-0.463724	0.827087
H	7.465399	-2.187717	0.657470
H	9.284219	-0.870049	-0.462284
H	8.385592	-1.807930	-1.666046
H	8.086747	-0.073848	-1.496204
C	1.718069	-5.029095	-1.343025
H	2.196072	-4.213047	0.613268
H	1.047372	-3.262658	-0.327948

C	0.576070	-5.933692	-0.871690
H	1.484148	-4.630134	-2.337033
H	2.641822	-5.616898	-1.445776
H	0.429667	-6.778483	-1.553517
H	0.778647	-6.341866	0.126762
H	-0.364310	-5.376613	-0.822127
C	0.986350	1.994273	4.614695
H	1.468748	-0.101926	4.672752
H	2.837387	0.921774	4.253736
C	1.070136	2.137906	6.136442
H	1.367127	2.905146	4.136593
H	-0.065859	1.912212	4.311061
H	0.525932	3.021343	6.486861
H	0.642754	1.261106	6.637164
H	2.111049	2.232955	6.467304
C	3.233485	1.518724	-3.929812
H	4.663609	1.348999	-2.315515
H	3.650291	-0.081777	-2.550265
C	4.155743	1.010454	-5.040683
H	2.208657	1.185562	-4.130271
H	3.218509	2.618162	-3.932322
H	3.845957	1.386445	-6.021808
H	5.193117	1.325537	-4.872911
H	4.139366	-0.084350	-5.081454
C	-1.581728	-2.195900	-1.011546
C	-2.301057	-2.434238	-2.185596
C	-3.233675	-3.474637	-2.243412
C	-3.444788	-4.307905	-1.139597
C	-2.714405	-4.087851	0.028327
C	-1.802411	-3.027892	0.092372
H	-2.121189	-1.839212	-3.070870
H	-3.783445	-3.644869	-3.165677
H	-4.162798	-5.120997	-1.194488
H	-2.856115	-4.725636	0.897206
H	-1.278501	-2.849006	1.023947
Br	0.906051	-1.570108	-3.111668