Filling the Void: Controlled Donor-Acceptor Interaction Facilitates the Formation of an M-M Single Bond in the Zero Oxidation State of M (M = Zn, Cd, Hg)

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Supporting Information

Computational Details

Geometry optimization followed by the frequency calculation were carried out at the B3LYP-D3(BJ)/def2-TZVPPD and BP86-D3(BJ)/def2-TZVPPD levels of theory, respectively.[1,2] For the Cd and Hg atoms, quasi-relativistic effective core potentials (ECPs) were used for 28 and 46 core electrons. Note that in this study B3LYP functional has been chosen as in a recent benchmark study this combination was found to be superior to the other levels to reproduce experimental IR spectra and other properties for Hg systems–the systems for which relativistic effect would be the most important among Group 12 elements.[3] Moreover, the computed geometrical parameters for $M_2(Ph^{Me})_2$ are in good agreement with the same for the experimentally reported $M_2(Ph^{Dipp})_2$ complexes,[4] considering different side substituents and crystal effects. All of the above computations were performed using the GAUSSIAN 16 program package.[5] All these computations were done by using an ultrafine grid, a grid with 99 radial shells per atom, and 590 angular points per shell. The natural population analysis has been carried out to compute the charges on each atom and Wiberg bond indices (WBI) have been computed for atomic pairs using the NBO scheme at BP86-D3(BJ)/def2-TZVPPD level.

Energy decomposition analysis (EDA)[6] was performed at the BP86-D3(BJ)/TZ2P-ZORA and B3LYP-D3(BJ)/TZ2P-ZORA level using the ADF2017 software.[7] In the EDA scheme, the interaction energy (ΔE_{int}) has been decomposed into four terms as,

$$\Delta E_{int} = \Delta E_{Pauli} + \Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp} \quad (1)$$

where the ΔE_{elstat} term corresponds to the classical electrostatic energy between those fragments and it is generally attractive in nature. The next attractive term is orbital interaction energy, ΔE_{orb},

which arises from the charge transfer and mixing of the occupied and unoccupied orbitals on the fragments and polarization effects. The ΔE_{disp} represents the dispersion energy correction towards the total attraction energy. The only repulsive contribution is the Pauli interaction energy (ΔE_{Pauli}) and it is originated from the repulsion between the occupied orbitals of the interacting fragments.

The EDA-NOCV calculation combines the energy and charge decomposition schemes and divides the deformation density, $\Delta\rho(r)$, associated with the bond formation into different components (σ, π, δ) of a chemical bond. From the mathematical point of view, each NOCV, ψ_i is defined as an eigenvector of the deformation density matrix on the basis of fragment orbitals.

$$\Delta P\psi_i = \nu_i\psi_i \tag{2}$$

In EDA-NOCV, ΔE_{orb} is given by the following equation,

$$\Delta E_{orb} = \sum_k \Delta E_k^{orb} = \sum_{k=1}^{N/2} \nu_k [-F_{-k}^{TS} + F_k^{TS}] \tag{3}$$

where, $-F_{-k}^{TS}$ and F_k^{TS} are diagonal Kohn-Sham matrix elements corresponding to NOCVs with the eigenvalues $-\nu_k$ and ν_k, respectively. The ΔE_k^{orb} terms are assigned to a particular type of bond by visual inspection of the shape of the deformation density, $\Delta\rho_k$. The EDA-NOCV scheme thus provides both qualitative ($\Delta\rho_{\text{orb}}$) and quantitative (ΔE_{orb}) information about the strength of orbital interactions in chemical bonds.

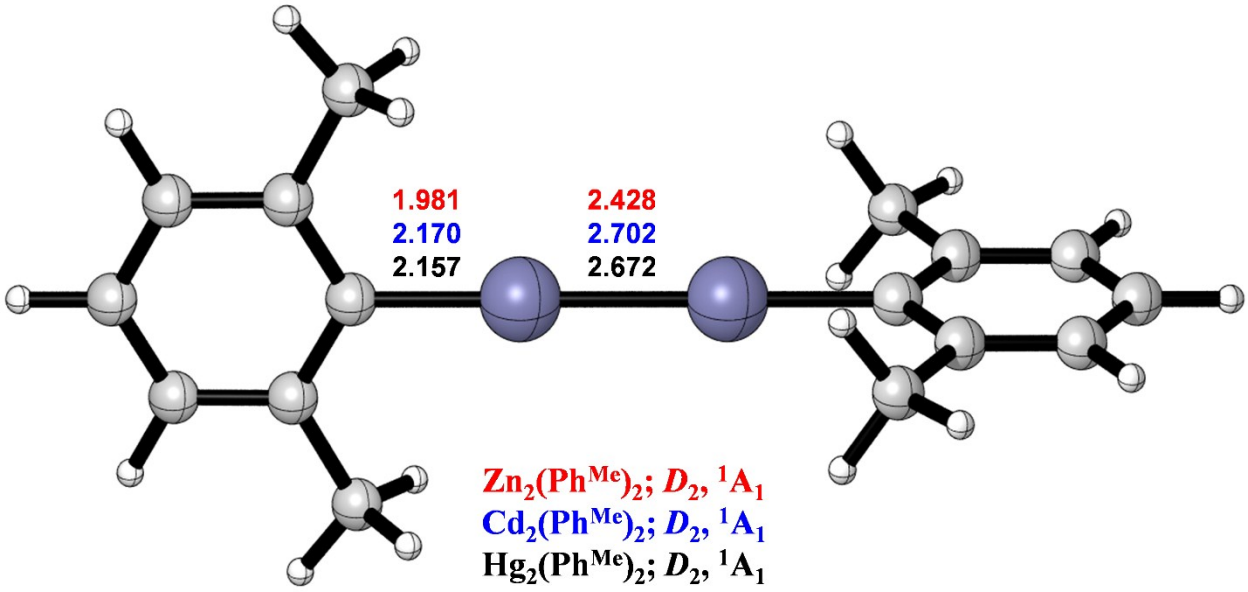

Figure S1. The B3LYP-D3(BJ)/def2-TZVPPD geometry of $M_2(Ph^{Me})_2$ complexes. The values in the red, blue, and black present the structural parameters and relative energies for Zn, Cd and Hg analogues, respectively. The experimental parameters (in Å) for $M_2(Ph^{Dipp})_2$ complexes: Zn-Zn (2.359), Zn-C (1.966, 1.975), Cd-Cd (2.626), Cd-C (2.138), Hg-Hg (2.574), Hg-C (2.098).[4]

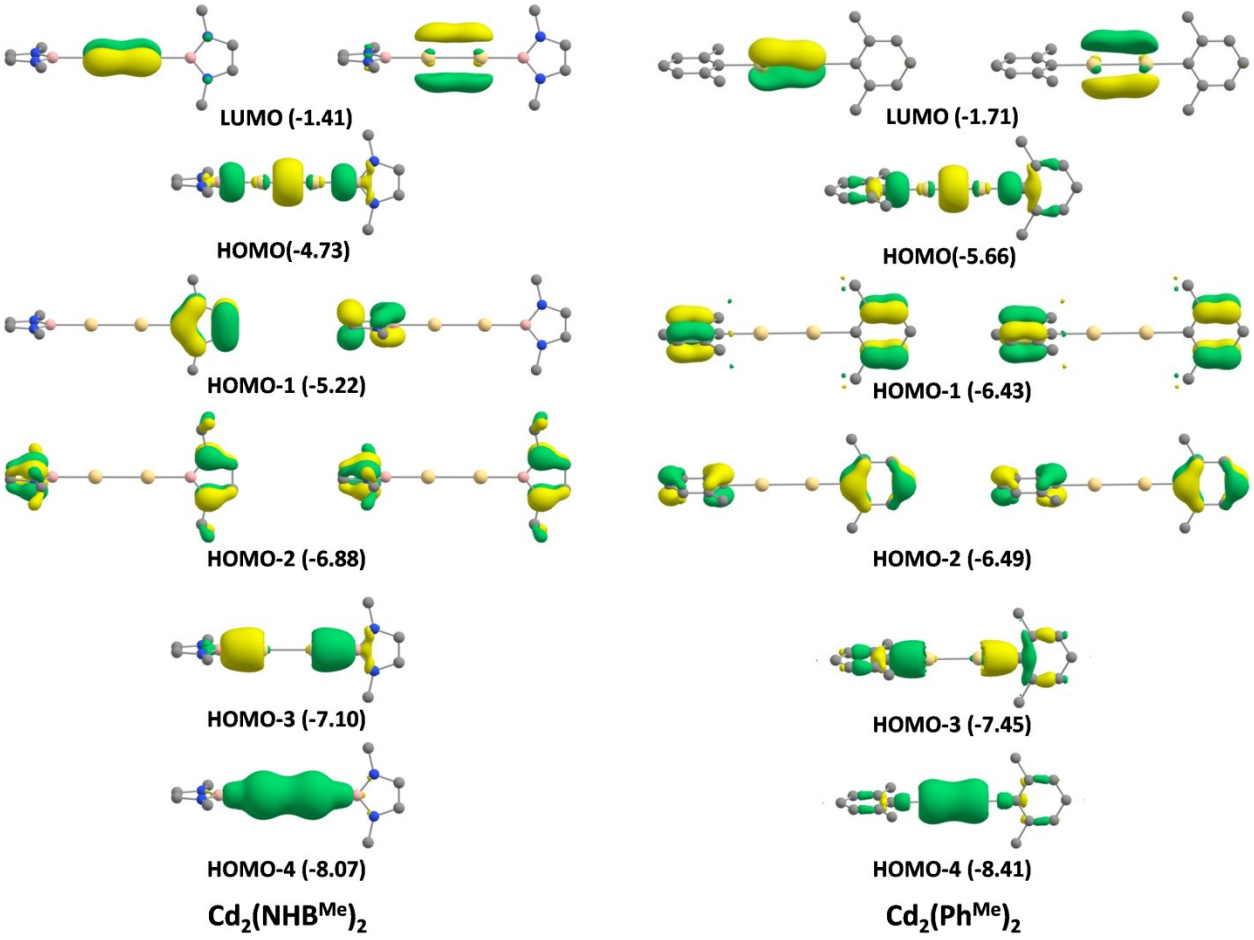

Figure S2. The shape of the MOs in $Cd_2(NHB^{Me})_2$ and $Cd_2(Ph^{Me})_2$ complexes. The MO energy eigen values are in eV.

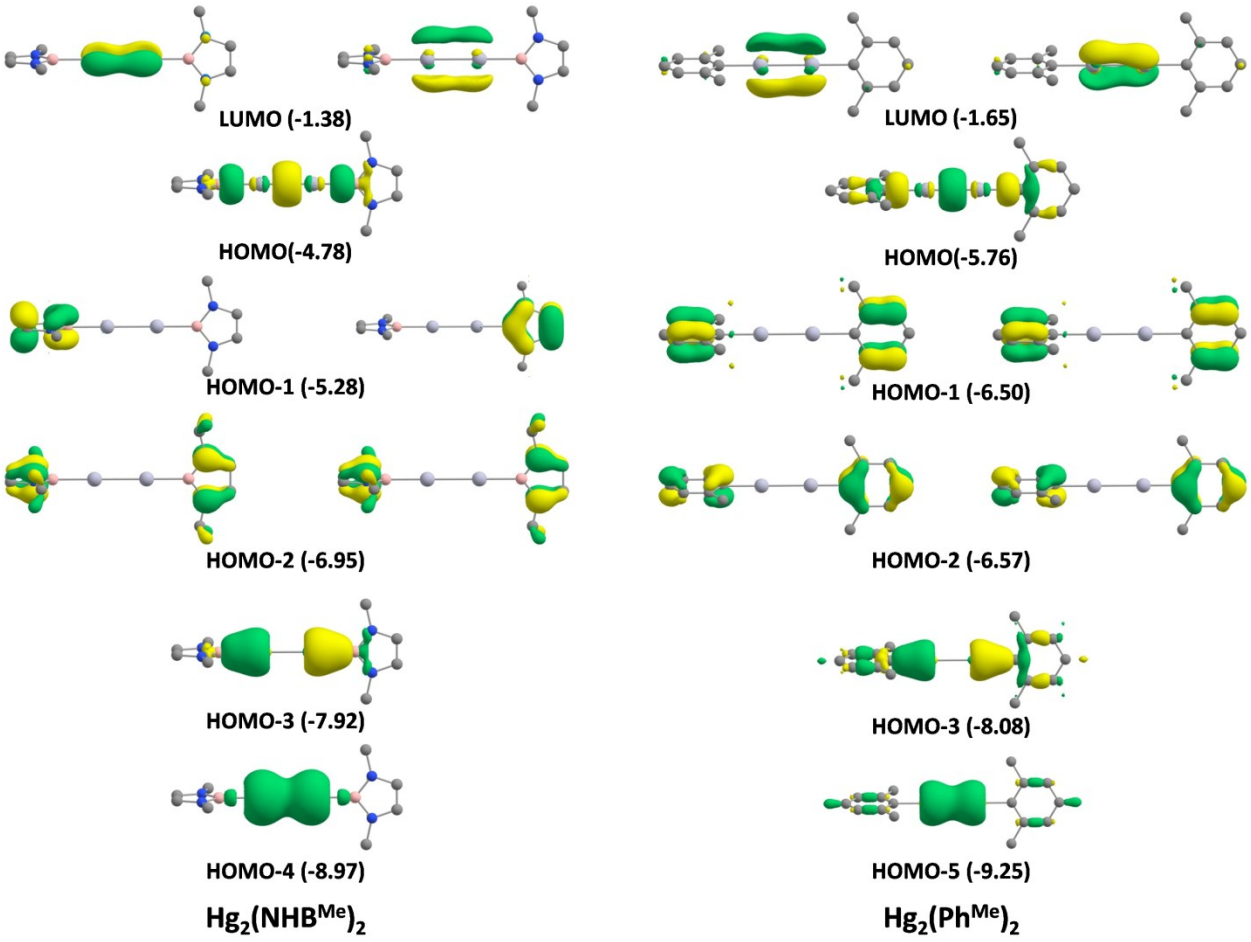

Figure S3. The shape of the MOs in $Hg_2(NHB^{Me})_2$ and $Hg_2(Ph^{Me})_2$ complexes. The MO energy eigen values are in eV.

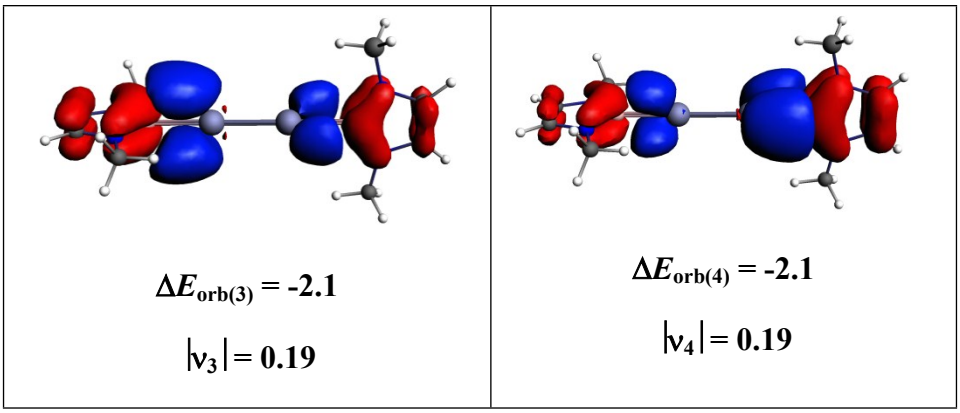

Figure S4. The shape of the deformation densities $\Delta\rho_{(3)}$ and $\Delta\rho_{(4)}$ that are associated with $\Delta E_{orb(3)}$ and $\Delta E_{orb(4)}$ in **1a**. Isosurface value is 0.0001.

Table S1. Dissociation energies (D_0, kcal/mol), and free energy changes at 298 K (ΔG, kcal/mol) for different dissociation and transformation paths of $M_2(Ph^{Me})_2$ at the at the B3LYP-D3(BJ)/def2-TZVPPD level.

Complex	P1		P2		P3		P4		P5	
	D_0	ΔG	D_0	ΔG	D_0	ΔG	D_0	ΔG	D_0	ΔG
$Zn_2(Ph^{Me})_2$	57.4	46.6	97.7	74.7	548.8	528.6	0.2	-4.4	-14.6	-20.7
$Cd_2(Ph^{Me})_2$	49.1	37.2	76.0	51.4	510.6	488.6	-3.4	-7.7	-36.2	-44.1
$Hg_2(Ph^{Me})_2$	48.2	35.6	61.0	35.6	555.8	533.4	-12.0	-16.0	-51.2	-59.9

Table S2. EDA-NOCV results for $M_2(NHB^{Me})_2$ complexes at the BP86-D3(BJ)/TZ2P-ZORA//BP86-D3(BJ)/def2-TZVPPD level. Energies are in kcal/mol.

Fragments	**1a** Zn_2 [T, $(7\sigma_g^+)^2(7\sigma_u^+)^1(8\sigma_g^+)^1$] + 2($NHB^{Me}$) [T]	**2a** Cd_2 [T, $(10\sigma_g^+)^2(10\sigma_u^+)^1(11\sigma_g^+)^1$] + 2($NHB^{Me}$) [T]	**3a** Hg_2 [T, $(14\sigma_g^+)^2(14\sigma_u^+)^1(15\sigma_g^+)^1$] + 2($NHB^{Me}$) [T]
ΔE_{int}	-178.1	-163.6	-186.2
ΔE_{Pauli}	218.3	231.8	301.0
ΔE_{disp}[a]	-7.0 (1.8%)	-8.5 (2.2%)	-10.2 (2.1%)
ΔE_{elstat}[a]	-237.8 (60.0%)	-246.3 (62.3%)	-315.7 (64.8%)
ΔE_{orb}[a]	-151.5 (38.2%)	-140.5 (35.5%)	-161.4 (33.1%)
$\Delta E_{orb(1)}$[b] (+,+) NHB^{Me}–M_2–NHB^{Me} σ-bond	-80.3 (53.0%)	-73.0 (52.0%)	-75.5 (46.8%)
$\Delta E_{orb(2)}$[b] (+,–) NHB^{Me}–M_2–NHB^{Me} σ-bond	-59.5 (39.3%)	-56.7 (40.4%)	-69.7 (43.2%)
$\Delta E_{orb(3)}$[b] $NHB^{Me}\rightarrow M_2\leftarrow NHB^{Me}$ π-donation	-2.1 (1.4%)	-1.7 (1.2%)	-1.9 (1.2%)
$\Delta E_{orb(4)}$[b] $NHB^{Me}\rightarrow M_2\leftarrow NHB^{Me}$ π-donation	-2.1 (1.4%)	-1.7 (1.2%)	-1.9 (1.2%)
$\Delta E_{orb(rest)}$[b]	-7.5 (5.0%)	-7.4 (5.3%)	-12.4 (7.7%)

[a]The values in parentheses are the percentage contributions to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$).

[b]The values in parentheses are the percentage contributions to ΔE_{orb}.

Table S3. EDA-NOCV results for $M_2(NHB^{Me})_2$ complexes at the BP86-D3(BJ)/TZ2P-ZORA//BP86-D3(BJ)/def2-TZVPPD level. Energies are in kcal/mol

Fragments	**1a** Zn_2^{2+} [S, $(7\sigma_g^+)^2(7\sigma_u^+)^0$] + $2(NHB^{Me})^-$ [S]	**2a** Cd_2^{2+} [S, $(10\sigma_g^+)^2(10\sigma_u^+)^0$] + $2(NHB^{Me})^-$ [S]	**3a** Hg_2^{2+} [S, $(14\sigma_g^+)^2(14\sigma_u^+)^0$] + $2(NHB^{Me})^-$ [S]
ΔE_{int}	-659.2	-610.5	-667.4
ΔE_{Pauli}	306.6	357.6	488.8
ΔE_{disp}[a]	-7.0 (0.7%)	-8.6 (0.9%)	-10.2 (0.9%)
ΔE_{elstat}[a]	-705.4 (73.0%)	-738.4 (76.3%)	-863.0 (74.6%)
ΔE_{orb}[a]	-253.5 (26.2%)	-221.0 (22.8%)	-283.1 (24.5%)
$\Delta E_{orb(1)}$[b]	-95.7 (37.8%)	-77.7 (35.2%)	-90.4 (31.9%)
(+,+) $(NHB^{Me})^- \rightarrow M_2^{2+} \leftarrow (NHB^{Me})^-$ σ-donation			
$\Delta E_{orb(2)}$[b]	-102.3 (40.4%)	-91.1 (41.2%)	-130.3 (46.0%)
(+,–) $(NHB^{Me})^- \rightarrow M_2^{2+} \leftarrow (NHB^{Me})^-$ σ-donation			
$\Delta E_{orb(3)}$[b]	-11.9 (4.7%)	-9.8 (4.4%)	-10.9 (3.9%)
$(NHB^{Me})^- \rightarrow M_2^{2+} \leftarrow (NHB^{Me})^-$ π-donation			
$\Delta E_{orb(4)}$[b]	-11.9 (4.7%)	-9.8 (4.4%)	-10.9 (3.9%)
$(NHB^{Me})^- \rightarrow M_2^{2+} \leftarrow (NHB^{Me})^-$ π-donation			
$\Delta E_{orb(rest)}$[b]	-31.7 (12.5%)	-32.6 (14.8%)	-40.6 (14.3%)

[a]The values in parentheses are the percentage contributions to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$).

[b]The values in parentheses are the percentage contributions to ΔE_{orb}.

Table S4. EDA-NOCV results for $M_2(NHB^{Me})_2$ complexes at the B3LYP-D3(BJ)/TZ2P-ZORA//B3LYP-D3(BJ)/def2-TZVPPD level. Energies are in kcal/mol.

Fragments	**1a** Zn_2 [S, $(7\sigma_g^+)^2(7\sigma_u^+)^2$] + 2($NHB^{Me}$) [S]	**2a** Cd_2 [S, $(10\sigma_g^+)^2(10\sigma_u^+)^2$] + 2($NHB^{Me}$) [S]	**3a** Hg_2 [S, $(14\sigma_g^+)^2(14\sigma_u^+)^2$] + 2($NHB^{Me}$) [S]
ΔE_{int}	-141.6	-129.6	-120.2
ΔE_{Pauli}	230.2	241.8	326.0
ΔE_{disp}[a]	-6.2 (1.7%)	-7.6 (2.0%)	-9.1 (2.0%)
ΔE_{elstat}[a]	-215.7 (58.0%)	-226.5 (61.0%)	-293.8 (65.8%)
ΔE_{orb}[a]	-149.8 (40.3%)	-137.4 (37.0%)	-143.3 (32.1%)
$\Delta E_{orb(1)}$[b] (+,–) $NHB^{Me}\leftarrow M_2\rightarrow NHB^{Me}$ σ-back donation	-94.7 (63.2%)	-90.0 (65.5%)	-82.6 (57.6%)
$\Delta E_{orb(2)}$[b] (+,+) $NHB^{Me}\rightarrow M_2\leftarrow NHB^{Me}$ σ-donation	-45.0 (30.0%)	-38.0 (27.7%)	-46.2 (32.2%)
$\Delta E_{orb(3)}$[b] $NHB^{Me}\rightarrow M_2\leftarrow NHB^{Me}$ π-donation	-1.6 (1.1%)	-1.2 (0.9%)	-1.5 (1.0%)
$\Delta E_{orb(4)}$[b] $NHB^{Me}\rightarrow M_2\leftarrow NHB^{Me}$ π-donation	-1.6 (1.1%)	-1.2 (0.9%)	-1.5 (1.0%)
$\Delta E_{orb(rest)}$[b]	-6.9 (4.6%)	-7.0 (5.1%)	-11.5 (8.0%)

[a]The values in parentheses are the percentage contributions to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$).

[b]The values in parentheses are the percentage contributions to ΔE_{orb}.

Table S5. EDA-NOCV results for $M_2(NHB^{Me})_2$ complexes at the B3LYP-D3(BJ)/TZ2P-ZORA//B3LYP-D3(BJ)/def2-TZVPPD level. Energies are in kcal/mol.

Fragments	**1a** Zn_2 [T, $(7\sigma_g^+)^2(7\sigma_u^+)^1(8\sigma_g^+)^1$] + 2($NHB^{Me}$) [T]	**2a** Cd_2 [T, $(10\sigma_g^+)^2(10\sigma_u^+)^1(11\sigma_g^+)^1$] + 2($NHB^{Me}$) [T]	**3a** Hg_2 [T, $(14\sigma_g^+)^2(14\sigma_u^+)^1(15\sigma_g^+)^1$] + 2($NHB^{Me}$) [T]
ΔE_{int}	-174.7	-160.1	-181.2
ΔE_{Pauli}	233.5	239.2	313.2
ΔE_{disp}[a]	-6.2 (1.6%)	-7.6 (1.9%)	-9.1 (1.8%)
ΔE_{elstat}[a]	-240.1 (60.3%)	-251.4 (62.9%)	-324.9 (65.7%)
ΔE_{orb}[a]	-151.9 (38.1%)	-140.4 (35.2%)	-160.4 (32.4%)
$\Delta E_{orb(1)}$[b] (+,+) NHB^{Me}–M_2–NHB^{Me} σ-bond	-82.9 (54.6%)	-75.0 (53.4%)	-78.0 (48.6%)
$\Delta E_{orb(2)}$[b] (+,–) NHB^{Me}–M_2–NHB^{Me} σ-bond	-58.9 (38.8%)	-55.9 (39.8%)	-67.9 (42.3%)
$\Delta E_{orb(3)}$[b] $NHB^{Me}\rightarrow M_2\leftarrow NHB^{Me}$ π-donation	-1.5 (1.0%)	-1.2 (0.9%)	-1.4 (0.9%)
$\Delta E_{orb(4)}$[b] $NHB^{Me}\rightarrow M_2\leftarrow NHB^{Me}$ π-donation	-1.5 (1.0%)	-1.2 (0.9%)	-1.4 (0.9%)
$\Delta E_{orb(rest)}$[b]	-7.1 (4.7%)	-7.1 (5.1%)	-11.7 (7.3%)

[a]The values in parentheses are the percentage contributions to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$).

[b]The values in parentheses are the percentage contributions to ΔE_{orb}.

Table S6. EDA-NOCV results for $M_2(NHB^{Me})_2$ complexes at the B3LYP-D3(BJ)/TZ2P-ZORA//B3LYP-D3(BJ)/def2-TZVPPD level. Energies are in kcal/mol

Fragments	**1a** Zn_2^{2+} [S, $(7\sigma_g^+)^2(7\sigma_u^+)^0$] + $2(NHB^{Me})^-$ [S]	**2a** Cd_2^{2+} [S, $(10\sigma_g^+)^2(10\sigma_u^+)^0$] + $2(NHB^{Me})^-$ [S]	**3a** Hg_2^{2+} [S, $(14\sigma_g^+)^2(14\sigma_u^+)^0$] + $2(NHB^{Me})^-$ [S]
ΔE_{int}	-650.2	-602.7	-657.5
ΔE_{Pauli}	304.2	351.9	485.8
ΔE_{disp}[a]	-6.2 (0.6%)	-7.6 (0.8%)	-9.1 (0.8%)
ΔE_{elstat}[a]	-712.7 (74.7%)	-743.5 (77.9%)	-871.7 (76.2%)
ΔE_{orb}[a]	-235.4 (24.7%)	-203.4 (21.3%)	-262.5 (23.0%)
$\Delta E_{orb(1)}$[b] (+,+) $(NHB^{Me})^- \rightarrow M_2^{2+} \leftarrow (NHB^{Me})^-$ σ-donation	-92.4 (39.3%)	-72.9 (35.8%)	-85.2 (32.5%)
$\Delta E_{orb(2)}$[b] (+,–) $(NHB^{Me})^- \rightarrow M_2^{2+} \leftarrow (NHB^{Me})^-$ σ-donation	-92.7 (39.4%)	-82.4 (40.5%)	-119.5 (45.5%)
$\Delta E_{orb(3)}$[b] $(NHB^{Me})^- \rightarrow M_2^{2+} \leftarrow (NHB^{Me})^-$ π-donation	-10.3 (4.4%)	-8.6 (4.2%)	-9.6 (3.7%)
$\Delta E_{orb(4)}$[b] $(NHB^{Me})^- \rightarrow M_2^{2+} \leftarrow (NHB^{Me})^-$ π-donation	-10.3 (4.4%)	-8.6 (4.2%)	-9.6 (3.7%)
$\Delta E_{orb(rest)}$[b]	-29.7 (12.6%)	-30.9 (15.2%)	-38.6 (14.7%)

[a]The values in parentheses are the percentage contributions to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$).

[b]The values in parentheses are the percentage contributions to ΔE_{orb}.

Table S7. EDA-NOCV results for $M_2(Ph^{Me})_2$ complexes at the B3LYP-D3(BJ)/TZ2P-ZORA//B3LYP-D3(BJ)/def2-TZVPPD level. Energies in kcal/mol.

Fragments	$Zn_2(Ph^{Me})_2$ Zn_2 [S, $(7\sigma_g^+)^2(7\sigma_u^+)^2$] + 2($Ph^{Me}$) [S]	$Cd_2(Ph^{Me})_2$ Cd_2 [S, $(10\sigma_g^+)^2(10\sigma_u^+)^2$] + 2($Ph^{Me}$) [S]	$Hg_2(Ph^{Me})_2$ Hg_2 [S, $(14\sigma_g^+)^2(14\sigma_u^+)^2$] + 2($Ph^{Me}$) [S]
ΔE_{int}	-161.1	-143.2	-126.3
ΔE_{Pauli}	289.2	267.2	315.8
ΔE_{disp}[a]	-10.3 (2.3%)	-12.0 (2.9%)	-13.2 (3.0%)
ΔE_{elstat}[a]	-224.1 (49.8%)	-208.3 (50.8%)	-243.7 (55.1%)
ΔE_{orb}[a]	-216.0 (48.0%)	-190.1 (46.3%)	-185.2 (41.9%)
$\Delta E_{orb(1)}$[b] (+,–) $Ph^{Me}\leftarrow M_2\rightarrow Ph^{Me}$ σ-backdonation	-164.4 (109.7%)	-148.0 (107.7%)	-134.2 (93.6%)
$\Delta E_{orb(2)}$[b] (+,+) $Ph^{Me}\rightarrow M_2\leftarrow Ph^{Me}$ σ-donation	-36.1 (24.1%)	-29.9 (21.8%)	-34.9 (24.4%)
$\Delta E_{orb(3)}$[b] $Ph^{Me}\rightarrow M_2\leftarrow Ph^{Me}$ π-donation	-2.2 (1.5%)	-1.5 (1.1%)	-1.8 (1.3%)
$\Delta E_{orb(4)}$[b] $Ph^{Me}\rightarrow M_2\leftarrow Ph^{Me}$ π-donation	-2.2 (1.5%)	-1.5 (1.1%)	-1.8 (1.3%)
$\Delta E_{orb(rest)}$[b]	-11.1 (7.4%)	-9.2 (6.7%)	-12.5 (8.7%

[a]The values in parentheses are the percentage contributions to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$).

[b]The values in parentheses are the percentage contributions to ΔE_{orb}.

Table S8. EDA-NOCV results for $M_2(Ph^{Me})_2$ complexes at the B3LYP-D3(BJ)/TZ2P-ZORA//B3LYP-D3(BJ)/def2-TZVPPD level. Energies are in kcal/mol

Fragments	**1a** Zn_2 [T, $(7\sigma_g^+)^2(7\sigma_u^+)^1(8\sigma_g^+)^1]$ + 2(Ph^{Me}) [T]	**2a** Cd_2 [T, $(10\sigma_g^+)^2(10\sigma_u^+)^1(11\sigma_g^+)^1]$ + 2(Ph^{Me}) [T]	**3a** Hg_2 [T, $(14\sigma_g^+)^2(14\sigma_u^+)^1(15\sigma_g^+)^1]$ + 2(Ph^{Me}) [T]
ΔE_{int}	-191.2	-170.6	-183.5
ΔE_{Pauli}	313.5	293.8	341.4
ΔE_{disp}[a]	-10.3 (2.0%)	-12.0 (2.6%)	-13.2 (2.5%)
ΔE_{elstat}[a]	-260.4 (51.6%)	-243.8 (52.5%)	-287.1 (54.7%)
ΔE_{orb}[a]	-234.0 (46.4%)	-208.6 (44.9%)	-224.6 (42.8%)
$\Delta E_{orb(1)}$[b] (+,+) Ph^{Me}–M_2–Ph^{Me} σ-bond	-132.8 (56.8%)	-119.6 (57.3%)	-123.6 (55.0%)
$\Delta E_{orb(2)}$[b] (+,–) Ph^{Me}–M_2–Ph^{Me} σ-bond	-84.9 (36.3%)	-76.0 (36.4%)	-84.0 (37.4%)
$\Delta E_{orb(3)}$[b] $Ph^{Me}\rightarrow M_2\leftarrow Ph^{Me}$ π-donation	-2.3 (1.0%)	-1.5 (0.7%)	-1.8 (0.8%)
$\Delta E_{orb(4)}$[b] $Ph^{Me}\rightarrow M_2\leftarrow Ph^{Me}$ π-donation	-2.3 (1.0%)	-1.5 (0.7%)	-1.8 (0.8%)
$\Delta E_{orb(rest)}$[b]	-11.7 (5.0%)	-10.0 (4.8%)	-13.4 (6.0%)

[a]The values in parentheses are the percentage contributions to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$).

[b]The values in parentheses are the percentage contributions to ΔE_{orb}.

Table S9. EDA-NOCV results for $M_2(Ph^{Me})_2$ complexes at the B3LYP-D3(BJ)/TZ2P-ZORA//B3LYP-D3(BJ)/def2-TZVPPD level. Energies in kcal/mol

Fragments	**1a** Zn_2^{2+} [S, $(7\sigma_g^+)^2(7\sigma_u^+)^0$] + $2(Ph^{Me})^-$ [S]	**2a** Cd_2^{2+} [S, $(10\sigma_g^+)^2(10\sigma_u^+)^0$] + $2(Ph^{Me})^-$ [S]	**3a** Hg_2^{2+} [S, $(14\sigma_g^+)^2(14\sigma_u^+)^0$] + $2(Ph^{Me})^-$ [S]
ΔE_{int}	-616.5	-563.2	-609.7
ΔE_{Pauli}	283.9	301.0	396.3
ΔE_{disp}[a]	-10.3 (1.1%)	-12.0 (1.4%)	-13.2 (1.3%)
ΔE_{elstat}[a]	-679.2 (75.4%)	-669.6 (77.5%)	-758.5 (75.4%)
ΔE_{orb}[a]	-210.9 (23.4%)	-182.7 (21.1%)	-234.3 (23.3%)
$\Delta E_{orb(1)}$[b] (+,+) $(Ph^{Me})^- \rightarrow M_2^{2+} \leftarrow (Ph^{Me})^-$ σ-donation	-64.1 (30.4%)	-49.9 (27.3%)	-58.0 (24.8%)
$\Delta E_{orb(2)}$[b] (+,–) $(Ph^{Me})^- \rightarrow M_2^{2+} \leftarrow (Ph^{Me})^-$ σ-donation	-66.1 (31.3%)	-63.2 (34.6%)	-98.8 (42.2%)
$\Delta E_{orb(3)}$[b] $(Ph^{Me})^- \rightarrow M_2^{2+} \leftarrow (Ph^{Me})^-$ π-donation	-17.2 (8.2%)	-13.6 (7.4%)	-14.7 (6.3%)
$\Delta E_{orb(4)}$[b] $(Ph^{Me})^- \rightarrow M_2^{2+} \leftarrow (Ph^{Me})^-$ π-donation	-17.2 (8.2%)	-13.6 (7.4%)	-14.7 (6.3%)
$\Delta E_{orb(rest)}$[b]	-46.3 (22.0%)	-42.4 (23.2%)	-48.1 (20.5%)

[a]The values in parentheses are the percentage contributions to the total attractive interactions ($\Delta E_{elstat} + \Delta E_{orb} + \Delta E_{disp}$).

[b]The values in parentheses are the percentage contributions to ΔE_{orb}.

Table S10. The results of the NBO analysis of $M_2(NHB^{Me})_2$ complexes.

Complex	q_M	$q_{C/B}$	q_L	Bond	WBI	Occ.	% orbital contribution
$Zn_2(NHB^{Me})_2$	0.39	0.16	-0.39	Zn-Zn	0.700	1.70	Zn(50): 4s(42.4)4p(57.0)3d(0.6) Zn(50): 4s(42.4)4p(57.0)3d(0.6)
				Zn-B	0.655	1.89	Zn(29.7): 4s(56.6)4p(42.1)3d(1.2) B(70.3): 2s(40.6)2p(59.2)
$Cd_2(NHB^{Me})_2$	0.36	0.21	-0.36	Cd-Cd	0.639	1.66	Cd(50): 5s(41.1)5p(57.7)4d(1.2) Cd(50): 5s(41.1)5p(57.7)4d(1.2)
				Cd-B	0.639	1.87	Cd(31.2): 5s(56.3)5p(41.3)4d(2.4) B(68.8): 2s(38.8)2p(64.1)
$Hg_2(NHB^{Me})_2$	0.29	0.27	-0.29	Hg-Hg	0.552	1.61	Hg(50): 6s(38.3)6p(58.2)5d(3.4) Hg(50): 6s(38.3)6p(58.2)5d(3.4)
				Hg-B	0.646	1.84	Hg(35.2): 6s(53.5)6p(40.4)5d(6.0) B(64.8): 2s(37.7)2p(62.1)

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Coordinates

At B3LYP-D3(BJ)/def2-TZVPPD
$Zn_2(NHB^{Me})_2$ isomers

1a

Sum of electronic and zero-point Energies= -4142.224709
Sum of electronic and thermal Energies= -4142.204671
Sum of electronic and thermal Enthalpies= -4142.203727
Sum of electronic and thermal Free Energies= -4142.279079

30	-1.239588000	-0.000471000	-0.000482000
6	5.540683000	0.479498000	0.480196000
6	5.541621000	-0.478592000	-0.477095000
6	-5.541292000	-0.478441000	0.479045000
6	-5.541014000	0.479737000	-0.478160000
1	-6.383547000	0.954902000	-0.952350000
1	-6.384095000	-0.952880000	0.953481000
1	6.382888000	0.954514000	0.955119000
5	3.331568000	0.000106000	-0.000307000
1	6.384751000	-0.953095000	-0.950884000
7	-4.229260000	0.799056000	-0.798057000
7	-4.229721000	-0.799045000	0.798421000
7	4.230272000	-0.798707000	-0.797873000
7	4.228707000	0.799260000	0.798738000
6	3.920541000	1.798207000	1.796559000
30	1.239590000	-0.000170000	-0.000840000
1	4.325529000	2.775533000	1.521906000
1	2.840536000	1.892093000	1.889031000
1	4.324015000	1.523838000	2.774589000
6	3.924040000	-1.797723000	-1.796226000
1	4.330106000	-1.523754000	-2.773293000
1	4.327807000	-2.775220000	-1.520385000
1	2.844216000	-1.890977000	-1.891388000
5	-3.331569000	-0.000449000	0.000011000
6	-3.922800000	-1.798314000	1.796308000
1	-4.327870000	-2.775446000	1.521087000
1	-2.842911000	-1.892554000	1.889741000
1	-4.327079000	-1.524005000	2.774022000
6	-3.921783000	1.797905000	-1.796189000
1	-4.325513000	2.775541000	-1.520785000
1	-2.841842000	1.890857000	-1.890339000
1	-4.327002000	1.524008000	-2.773629000

1b

Sum of electronic and zero-point Energies= -4142.238630
Sum of electronic and thermal Energies= -4142.218381
Sum of electronic and thermal Enthalpies= -4142.217437
Sum of electronic and thermal Free Energies= -4142.293458

30	-1.974342000	2.024068000	0.002669000
6	4.453826000	1.069225000	0.001443000
6	4.788738000	-0.243354000	0.000838000
6	-3.772177000	-1.030176000	0.677805000
6	-3.772542000	-1.027454000	-0.679027000
1	-4.614987000	-1.065312000	-1.349065000
1	-4.614261000	-1.070693000	1.348142000
1	5.104401000	1.927771000	0.002358000
5	2.482297000	-0.132445000	-0.000675000
1	5.770943000	-0.685631000	0.001181000
7	-2.464547000	-0.993999000	-1.131092000
7	-2.463949000	-0.998308000	1.129313000
7	3.629938000	-1.005817000	-0.000343000
7	3.071752000	1.184264000	0.000439000
6	2.425666000	2.478096000	0.000554000
30	0.474987000	-0.609422000	-0.001571000
1	2.696871000	3.058779000	-0.884565000
1	1.345811000	2.343742000	-0.000176000
1	2.695743000	3.058045000	0.886497000
6	3.680737000	-2.450178000	-0.001308000
1	4.196190000	-2.830867000	-0.886682000
1	4.195159000	-2.832107000	0.884130000
1	2.666926000	-2.845027000	-0.002195000
5	-1.564202000	-0.946153000	-0.001006000
6	-2.156434000	-0.911896000	2.538722000
1	-2.592992000	-1.746097000	3.091929000
1	-1.077406000	-0.941736000	2.672792000
1	-2.529897000	0.020805000	2.970495000
6	-2.157776000	-0.902181000	-2.540314000
1	-2.531410000	0.032206000	-2.968289000
1	-1.078819000	-0.931556000	-2.675088000
1	-2.594673000	-1.734214000	-3.096507000

1c

Sum of electronic and zero-point Energies= -4142.275461
Sum of electronic and thermal Energies= -4142.255581
Sum of electronic and thermal Enthalpies= -4142.254637
Sum of electronic and thermal Free Energies= -4142.326997

5	0.233764000	-0.804315000	-1.110204000
7	1.479659000	-1.380286000	-0.659599000
7	-0.517265000	-1.949871000	-1.560635000
6	1.428342000	-2.757404000	-0.819786000

6	0.233764000	-3.097248000	-1.360152000
1	-0.130183000	-4.076135000	-1.622074000
1	2.244556000	-3.399491000	-0.536105000
5	-0.233764000	0.804315000	-1.110204000
7	0.517265000	1.949871000	-1.560635000
7	-1.479659000	1.380286000	-0.659599000
6	-0.233764000	3.097248000	-1.360152000
6	-1.428342000	2.757404000	-0.819786000
1	-2.244556000	3.399491000	-0.536105000
1	0.130183000	4.076135000	-1.622074000
6	1.836764000	2.003416000	-2.149586000
6	-2.616183000	0.745902000	-0.030358000
6	-1.836764000	-2.003416000	-2.149586000
6	2.616183000	-0.745902000	-0.030358000
1	-3.524912000	0.876653000	-0.622735000
1	-2.422609000	-0.317168000	0.079257000
1	-2.791849000	1.158149000	0.966252000
1	2.178714000	0.992951000	-2.357935000
1	1.822484000	2.559328000	-3.089115000
1	2.555921000	2.482587000	-1.479811000
1	-2.178714000	-0.992951000	-2.357935000
1	-1.822484000	-2.559328000	-3.089115000
1	-2.555921000	-2.482587000	-1.479811000
1	2.422609000	0.317168000	0.079257000
1	2.791849000	-1.158149000	0.966252000
1	3.524912000	-0.876653000	-0.622735000
30	0.422638000	1.659220000	1.863807000
30	-0.422638000	-1.659220000	1.863807000

1d

Sum of electronic and zero-point Energies= -4142.157755
Sum of electronic and thermal Energies= -4142.137287
Sum of electronic and thermal Enthalpies= -4142.136343
Sum of electronic and thermal Free Energies= -4142.217623

30	0.297841000	1.280454000	0.000000000
6	1.813915000	-5.085837000	0.000000000
6	2.891630000	-4.265550000	0.000000000
6	-2.891630000	4.265551000	0.000000000
6	-1.813914000	5.085837000	0.000000000
1	-1.788386000	6.162520000	0.000000000
1	-3.935772000	4.529456000	0.000000000
1	1.788387000	-6.162520000	0.000000000
5	1.030656000	-2.933380000	0.000000000

1	3.935773000	-4.529455000	0.000000000
7	-0.656546000	4.317794000	0.000000000
7	-2.463834000	2.944260000	0.000000000
7	2.463834000	-2.944260000	0.000000000
7	0.656546000	-4.317794000	0.000000000
6	-0.656546000	-4.924375000	0.000000000
30	-0.297842000	-1.280455000	0.000000000
1	-0.804984000	-5.545895000	0.885926000
1	-1.412109000	-4.141698000	0.000000000
1	-0.804984000	-5.545895000	-0.885926000
6	3.405958000	-1.845052000	0.000000000
1	4.044015000	-1.874848000	0.886101000
1	4.044015000	-1.874848000	-0.886101000
1	2.857976000	-0.904807000	0.000000000
5	-1.030656000	2.933380000	0.000000000
6	-3.405958000	1.845053000	0.000000000
1	-4.044015000	1.874849000	-0.886101000
1	-2.857976000	0.904807000	0.000000000
1	-4.044015000	1.874849000	0.886101000
6	0.656547000	4.924374000	0.000000000
1	0.804985000	5.545895000	0.885926000
1	1.412110000	4.141697000	0.000000000
1	0.804985000	5.545895000	-0.885926000

1ab‡

Sum of electronic and zero-point Energies= -4142.173642
Sum of electronic and thermal Energies= -4142.154190
Sum of electronic and thermal Enthalpies= -4142.153246
Sum of electronic and thermal Free Energies= -4142.226131

30	1.642798000	-2.139994000	0.000476000
6	-4.246543000	0.905013000	-0.000292000
6	-3.426077000	1.983490000	-0.000559000
6	2.653510000	2.227732000	0.679715000
6	2.654476000	2.227401000	-0.678963000
1	2.943479000	3.021576000	-1.347573000
1	2.941536000	3.022244000	1.348347000
1	-5.323190000	0.879357000	-0.000174000
5	-2.092665000	0.121254000	-0.000423000
1	-3.689554000	3.027764000	-0.000687000
7	2.216970000	0.995537000	-1.127222000
7	2.215396000	0.996083000	1.127956000
7	-2.106533000	1.555370000	-0.000662000
7	-3.478898000	-0.250718000	-0.000213000

6	-4.085084000	-1.564421000	0.000065000
30	-0.481459000	-1.152964000	-0.000321000
1	-4.706532000	-1.712555000	-0.885884000
1	-3.301968000	-2.319119000	0.000414000
1	-4.706818000	-1.712029000	0.885898000
6	-1.004730000	2.495492000	-0.000981000
1	-1.034733000	3.135137000	-0.885709000
1	-1.033459000	3.134339000	0.884372000
1	-0.066746000	1.950669000	-0.001893000
5	1.912430000	0.138789000	0.000365000
6	2.059423000	0.713917000	2.537584000
1	1.315155000	1.370610000	2.994974000
1	1.726238000	-0.314210000	2.661345000
1	3.002089000	0.835972000	3.075903000
6	2.063340000	0.712572000	-2.536949000
1	3.007027000	0.833751000	-3.073679000
1	1.729794000	-0.315445000	-2.660649000
1	1.320261000	1.369400000	-2.996070000

1ac‡

Sum of electronic and zero-point Energies= -4142.177127
Sum of electronic and thermal Energies= -4142.157863
Sum of electronic and thermal Enthalpies= -4142.156918
Sum of electronic and thermal Free Energies= -4142.226213

5	0.209023000	-1.193421000	-0.501301000
7	0.634817000	-2.114592000	0.523778000
7	1.336237000	-1.122122000	-1.389543000
6	1.935553000	-2.521842000	0.249755000
6	2.355876000	-1.920284000	-0.887257000
1	3.310080000	-2.007766000	-1.378941000
1	2.467007000	-3.215206000	0.879892000
5	0.208624000	1.193496000	0.501347000
7	1.335891000	1.122617000	1.389556000
7	0.634084000	2.114752000	-0.523798000
6	2.355264000	1.921060000	0.887175000
6	1.934704000	2.522422000	-0.249853000
1	2.465909000	3.215929000	-0.880043000
1	3.309461000	2.008868000	1.378815000
6	1.507191000	0.333725000	2.585858000
6	-0.113865000	2.643483000	-1.638667000
6	1.507195000	-0.333188000	-2.585865000
6	-0.112884000	-2.643529000	1.638716000
1	0.454205000	2.570381000	-2.568388000

1	-1.034136000	2.074452000	-1.762747000
1	-0.383965000	3.692132000	-1.485958000
1	2.163471000	-0.520888000	2.410738000
1	1.926047000	0.938006000	3.393412000
1	0.538526000	-0.040268000	2.908967000
1	2.163245000	0.521618000	-2.410815000
1	1.926143000	-0.937352000	-3.393460000
1	0.538391000	0.040526000	-2.908878000
1	0.455226000	-2.570217000	2.568396000
1	-1.033326000	-2.074786000	1.762841000
1	-0.382662000	-3.692269000	1.486059000
30	-1.946380000	0.916790000	0.807488000
30	-1.946062000	-0.917430000	-0.807463000

$Cd_2(NHB^{Me})_2$ isomers

2a

Sum of electronic and zero-point Energies= -918.989734
Sum of electronic and thermal Energies= -918.969288
Sum of electronic and thermal Enthalpies= -918.968344
Sum of electronic and thermal Free Energies= -919.045921

48	-1.379574000	-0.000302000	-0.000161000
6	5.835827000	0.479351000	0.479111000
6	5.836383000	-0.479091000	-0.476901000
6	-5.836186000	-0.478187000	0.478931000
6	-5.836015000	0.479261000	-0.478075000
1	-6.678295000	0.954412000	-0.952621000
1	-6.678630000	-0.952818000	0.953707000
1	6.677915000	0.954798000	0.953698000
5	3.629899000	0.000218000	-0.000271000
1	6.679015000	-0.954406000	-0.950658000
7	-4.523207000	0.799327000	-0.798796000
7	-4.523490000	-0.799264000	0.799094000
7	4.523817000	-0.799963000	-0.797795000
7	4.522890000	0.800309000	0.798416000
6	4.216281000	1.800095000	1.795548000
1	4.621913000	2.776755000	1.519609000
48	1.379568000	0.000048000	-0.000464000
1	3.136444000	1.894613000	1.888391000
1	4.620257000	1.525870000	2.773377000
6	4.218332000	-1.799785000	-1.795231000
1	4.624561000	-1.526188000	-2.772301000
1	4.622493000	-2.776750000	-1.518206000

1	3.138599000	-1.893272000	-1.890263000
6	-4.217608000	-1.798283000	1.797214000
1	-4.622868000	-2.775208000	1.521664000
1	-3.137838000	-1.892548000	1.891048000
1	-4.622462000	-1.523370000	2.774485000
6	-4.216988000	1.797944000	-1.797216000
5	-3.629895000	-0.000251000	0.000036000
1	-4.621134000	2.775293000	-1.521529000
1	-3.137186000	1.891161000	-1.891757000
1	-4.622719000	1.523307000	-2.774200000

2b

Sum of electronic and zero-point Energies= -919.009627
Sum of electronic and thermal Energies= -918.989116
Sum of electronic and thermal Enthalpies= -918.988172
Sum of electronic and thermal Free Energies= -919.066211

6	-4.654501000	1.333170000	0.000031000
6	-5.104521000	0.056186000	0.000110000
6	3.653177000	-1.504153000	-0.678069000
6	3.653159000	-1.504477000	0.677631000
1	4.489972000	-1.603836000	1.348397000
1	4.490007000	-1.603189000	-1.348861000
1	-5.225825000	2.246323000	0.000027000
5	-2.799836000	-0.038180000	-0.000045000
1	-6.121999000	-0.297368000	0.000192000
7	2.349380000	-1.375850000	1.130208000
7	2.349407000	-1.375325000	-1.130617000
7	-4.017469000	-0.807501000	0.000107000
7	-3.266372000	1.325160000	-0.000113000
6	-2.509144000	2.556898000	-0.000231000
1	-2.727471000	3.158772000	0.885344000
1	-1.445414000	2.327905000	-0.000333000
1	-2.727658000	3.158721000	-0.885794000
6	-4.197873000	-2.241230000	0.000211000
1	-4.744886000	-2.574464000	0.885757000
1	-4.745001000	-2.574576000	-0.885221000
1	-3.223489000	-2.725036000	0.000178000
5	1.458272000	-1.266776000	-0.000188000
6	2.050790000	-1.271086000	-2.540471000
1	2.419911000	-2.139734000	-3.089923000
1	0.972873000	-1.215827000	-2.675166000
1	2.497197000	-0.372968000	-2.976117000
6	2.050719000	-1.272284000	2.540102000

1	2.497086000	-0.374359000	2.976187000
1	0.972796000	-1.217122000	2.674790000
1	2.419850000	-2.141181000	3.089154000
48	-0.695877000	-0.731182000	-0.000130000
48	2.057427000	1.839290000	0.000329000

2c

Sum of electronic and zero-point Energies= -4142.237873
Sum of electronic and thermal Energies= -4142.218451
Sum of electronic and thermal Enthalpies= -4142.217507
Sum of electronic and thermal Free Energies= -4142.290242

30	-0.001414000	-0.623301000	0.005773000
6	4.247269000	-0.143028000	-0.635887000
6	4.290345000	-0.747299000	0.575620000
6	-4.293407000	-0.755049000	-0.560660000
6	-4.249394000	-0.124732000	0.637466000
1	-5.068607000	0.236097000	1.236624000
1	-5.156454000	-1.019085000	-1.148663000
1	5.066976000	0.204061000	-1.242440000
5	2.064932000	-0.581344000	-0.018167000
1	5.152982000	-0.999363000	1.169451000
7	-2.925894000	0.002277000	1.032939000
7	-2.999338000	-1.048298000	-0.966185000
7	2.995882000	-1.030369000	0.987078000
7	2.923994000	-0.023305000	-1.034368000
6	2.566703000	0.611085000	-2.281567000
30	0.005976000	2.349801000	-0.021877000
1	3.022137000	0.101602000	-3.134168000
1	1.486080000	0.578563000	-2.405145000
1	2.877980000	1.659047000	-2.301167000
6	2.732194000	-1.673884000	2.253758000
1	3.216124000	-2.651947000	2.312616000
1	3.084632000	-1.067098000	3.091848000
1	1.659694000	-1.819302000	2.365216000
5	-2.067663000	-0.578370000	0.028764000
6	-2.736595000	-1.719264000	-2.218743000
1	-3.087434000	-1.129794000	-3.069770000
1	-1.664374000	-1.869340000	-2.326631000
1	-3.222609000	-2.697318000	-2.256861000
6	-2.567788000	0.662420000	2.266470000
1	-3.021945000	0.170251000	3.129867000
1	-1.487010000	0.633260000	2.389525000
1	-2.879853000	1.710314000	2.264841000

2d

Sum of electronic and zero-point Energies= -918.928135
Sum of electronic and thermal Energies= -918.907241
Sum of electronic and thermal Enthalpies= -918.906296
Sum of electronic and thermal Free Energies= -918.988226

48	0.053605000	1.501208000	0.000000000
6	3.209652000	-4.643537000	0.000000000
6	4.003000000	-3.546760000	0.000000000
6	-3.209652000	4.643537000	0.000000000
6	-4.003000000	3.546760000	0.000000000
1	-5.078779000	3.496151000	0.000000000
1	-3.496891000	5.681530000	0.000000000
1	3.496891000	-5.681530000	0.000000000
5	1.837829000	-2.812514000	0.000000000
1	5.078779000	-3.496151000	0.000000000
7	-3.209652000	2.404727000	0.000000000
7	-1.877553000	4.243802000	0.000000000
7	3.209652000	-2.404727000	0.000000000
7	1.877553000	-4.243802000	0.000000000
6	0.797793000	-5.206700000	0.000000000
1	0.835994000	-5.843758000	0.886559000
48	-0.053605000	-1.501208000	0.000000000
1	-0.153148000	-4.677794000	0.000000000
1	0.835994000	-5.843758000	-0.886559000
6	3.791836000	-1.079767000	0.000000000
1	4.411458000	-0.923019000	0.886104000
1	4.411458000	-0.923019000	-0.886104000
1	2.996807000	-0.337124000	0.000000000
6	-0.797793000	5.206700000	0.000000000
1	-0.835994000	5.843758000	0.886559000
1	0.153148000	4.677794000	0.000000000
1	-0.835994000	5.843758000	-0.886559000
6	-3.791836000	1.079767000	0.000000000
5	-1.837829000	2.812514000	0.000000000
1	-4.411458000	0.923019000	-0.886104000
1	-2.996807000	0.337124000	0.000000000
1	-4.411458000	0.923019000	0.886104000

2ab‡

Sum of electronic and zero-point Energies= -918.937302
Sum of electronic and thermal Energies= -918.917459
Sum of electronic and thermal Enthalpies= -918.916515

Sum of electronic and thermal Free Energies= -918.991625

6	-4.643211000	0.528518000	-0.000102000
6	-3.976051000	1.707226000	-0.000072000
6	1.927618000	3.069139000	0.678872000
6	1.927795000	3.069156000	-0.678739000
1	1.998820000	3.911289000	-1.347497000
1	1.998464000	3.911254000	1.347672000
1	-5.706302000	0.357005000	-0.000133000
5	-2.409904000	0.045965000	-0.000051000
1	-4.377503000	2.706493000	-0.000078000
7	1.825988000	1.763968000	-1.127094000
7	1.825700000	1.763938000	1.127166000
7	-2.609075000	1.462115000	-0.000038000
7	-3.726372000	-0.515599000	-0.000092000
6	-4.150830000	-1.898658000	-0.000079000
1	-4.746867000	-2.127971000	-0.885992000
1	-3.273711000	-2.541547000	-0.000229000
1	-4.746616000	-2.128042000	0.885984000
6	-1.642115000	2.541567000	-0.000007000
1	-1.756894000	3.170253000	-0.885185000
1	-1.756936000	3.170236000	0.885179000
1	-0.638774000	2.128467000	0.000016000
5	1.758092000	0.855691000	0.000014000
6	1.757451000	1.453083000	2.536857000
1	0.872466000	1.895997000	3.001477000
1	1.702180000	0.373712000	2.660449000
1	2.640478000	1.814064000	3.069679000
6	1.758161000	1.453148000	-2.536814000
1	2.641396000	1.814047000	-3.069347000
1	1.702817000	0.373784000	-2.660441000
1	0.873371000	1.896162000	-3.001708000
48	-0.491521000	-1.039116000	-0.000020000
48	2.092897000	-1.629499000	0.000046000

2ac‡

Sum of electronic and zero-point Energies= -918.943568
Sum of electronic and thermal Energies= -918.924002
Sum of electronic and thermal Enthalpies= -918.923058
Sum of electronic and thermal Free Energies= -918.994584

5	-0.621968000	1.388835000	-0.253368000
7	-1.091057000	2.030250000	0.944529000
7	-1.759276000	1.389367000	-1.124397000

6	-2.433661000	2.358052000	0.776252000
6	-2.832035000	1.967979000	-0.456397000
1	-3.805238000	2.061918000	-0.907977000
1	-3.006831000	2.849759000	1.544315000
5	-0.622097000	-1.388809000	0.253365000
7	-1.759409000	-1.389208000	1.124389000
7	-1.091252000	-2.030177000	-0.944531000
6	-2.832224000	-1.967723000	0.456395000
6	-2.433889000	-2.357846000	-0.776250000
1	-3.007112000	-2.849487000	-1.544315000
1	-3.805436000	-2.061559000	0.907975000
6	-1.890708000	-0.859502000	2.460581000
6	-0.371355000	-2.367216000	-2.149035000
6	-1.890648000	0.859612000	-2.460563000
6	-0.371130000	2.367198000	2.149041000
1	-0.877048000	-1.980419000	-3.036510000
1	0.623997000	-1.927942000	-2.111785000
1	-0.260626000	-3.448758000	-2.264098000
1	-2.556365000	0.005111000	2.480119000
1	-2.277307000	-1.616301000	3.147198000
1	-0.911930000	-0.545404000	2.814723000
1	-2.556220000	-0.005068000	-2.480019000
1	-2.277389000	1.616357000	-3.147158000
1	-0.911872000	0.545605000	-2.814793000
1	-0.876864000	1.980438000	3.036509000
1	0.624178000	1.927824000	2.111786000
1	-0.260291000	3.448727000	2.264121000
48	1.693727000	-1.220538000	0.648106000
48	1.693846000	1.220415000	-0.648109000

$Hg_2(NHB^{Me})_2$ isomers

3a

Sum of electronic and zero-point Energies= -890.442192
Sum of electronic and thermal Energies= -890.421760
Sum of electronic and thermal Enthalpies= -890.420816
Sum of electronic and thermal Free Energies= -890.498793

80	-1.367207000	0.000000000	-0.000105000
5	3.575750000	0.000079000	0.000014000
6	5.775938000	-0.479099000	0.478888000
6	5.776284000	0.478323000	-0.478175000
6	-5.776210000	-0.478748000	-0.478148000
6	-5.776020000	0.478876000	0.478716000

1	-6.617951000	0.954059000	0.953588000
1	-6.618324000	-0.953818000	-0.952807000
1	6.617796000	-0.954251000	0.953921000
80	1.367210000	0.000119000	-0.000068000
1	6.618475000	0.953233000	-0.952858000
7	-4.463240000	0.800256000	0.799711000
7	-4.463555000	-0.800241000	-0.799548000
7	4.463679000	0.799998000	-0.799606000
7	4.463106000	-0.800222000	0.799931000
6	4.153058000	-1.798734000	1.797946000
1	4.557332000	-1.523758000	2.775218000
1	3.073155000	-1.890548000	1.889818000
1	4.557214000	-2.775899000	1.522417000
5	-3.575751000	-0.000036000	-0.000064000
6	4.154311000	1.798412000	-1.797932000
1	4.559345000	2.775325000	-1.522805000
1	4.558189000	1.522758000	-2.775179000
1	3.074470000	1.891102000	-1.889632000
6	-4.154031000	-1.798908000	-1.797573000
1	-4.558249000	-1.523771000	-2.774824000
1	-3.074175000	-1.891206000	-1.889506000
1	-4.558614000	-2.775881000	-1.521994000
6	-4.153350000	1.798837000	1.797705000
1	-4.557255000	1.523649000	2.775071000
1	-3.073461000	1.891098000	1.889293000
1	-4.557984000	2.775845000	1.522326000

3b

Sum of electronic and zero-point Energies= -890.471249
Sum of electronic and thermal Energies= -890.450740
Sum of electronic and thermal Enthalpies= -890.449796
Sum of electronic and thermal Free Energies= -890.529251

6	-0.495130000	4.936895000	0.000000000
6	0.832228000	5.204453000	0.000000000
6	1.248087000	-3.617094000	0.677660000
6	1.248087000	-3.617094000	-0.677660000
1	1.259639000	-4.459360000	-1.348771000
1	1.259639000	-4.459360000	1.348771000
1	-1.319752000	5.629794000	0.000000000
5	0.604057000	2.912109000	0.000000000
1	1.324307000	6.162551000	0.000000000
7	1.248087000	-2.306586000	-1.130879000
7	1.248087000	-2.306586000	1.130879000

7	1.536601000	4.007852000	0.000000000
7	-0.681130000	3.561150000	0.000000000
6	-2.004848000	2.979138000	0.000000000
1	-2.570933000	3.277999000	-0.885569000
1	-1.922456000	1.894415000	0.000000000
1	-2.570933000	3.277999000	0.885569000
6	2.981729000	3.983208000	0.000000000
1	3.388569000	4.477767000	-0.885511000
1	3.388569000	4.477767000	0.885511000
1	3.322316000	2.950201000	0.000000000
5	1.233338000	-1.413451000	0.000000000
6	1.187582000	-1.996306000	2.541046000
1	2.030044000	-2.434529000	3.080749000
1	1.222787000	-0.917244000	2.672106000
1	0.261833000	-2.365989000	2.989665000
6	1.187582000	-1.996306000	-2.541046000
1	0.261833000	-2.365989000	-2.989665000
1	1.222787000	-0.917244000	-2.672106000
1	2.030044000	-2.434529000	-3.080749000
80	0.987829000	0.761090000	0.000000000
80	-2.017188000	-1.701587000	0.000000000

3c

Sum of electronic and zero-point Energies= -890.526057
Sum of electronic and thermal Energies= -890.506023
Sum of electronic and thermal Enthalpies= -890.505078
Sum of electronic and thermal Free Energies= -890.580930

5	-0.440529000	-0.712577000	1.933742000
7	-1.788157000	-0.936393000	1.468374000
7	-0.026653000	-2.014497000	2.393732000
6	-2.111201000	-2.275633000	1.636368000
6	-1.057379000	-2.920145000	2.191304000
1	-0.972329000	-3.958685000	2.462623000
1	-3.067196000	-2.676818000	1.345936000
5	0.440529000	0.712577000	1.933742000
7	0.026653000	2.014497000	2.393732000
7	1.788157000	0.936393000	1.468374000
6	1.057379000	2.920145000	2.191304000
6	2.111201000	2.275633000	1.636368000
1	3.067196000	2.676818000	1.345936000
1	0.972329000	3.958685000	2.462623000
6	-1.223406000	2.413660000	3.000716000
6	2.703810000	0.021556000	0.824819000

6	1.223406000	-2.413660000	3.000716000
6	-2.703810000	-0.021556000	0.824819000
1	3.625768000	-0.092237000	1.400407000
1	2.233029000	-0.952521000	0.728982000
1	2.965050000	0.367741000	-0.178065000
1	-1.829566000	1.530837000	3.187201000
1	-1.052850000	2.918029000	3.954160000
1	-1.786608000	3.090505000	2.352475000
1	1.829566000	-1.530837000	3.187201000
1	1.052850000	-2.918029000	3.954160000
1	1.786608000	-3.090505000	2.352475000
1	-2.233029000	0.952521000	0.728982000
1	-2.965050000	-0.367741000	-0.178065000
1	-3.625768000	0.092237000	1.400407000
80	-0.026653000	1.893137000	-1.223455000
80	0.026653000	-1.893137000	-1.223455000

3d

Sum of electronic and zero-point Energies= -890.376863
Sum of electronic and thermal Energies= -890.355751
Sum of electronic and thermal Enthalpies= -890.354806
Sum of electronic and thermal Free Energies= -890.440010

80	0.082735000	1.522400000	0.000000000
5	1.779314000	-2.835443000	0.000000000
6	3.146005000	-4.662131000	0.000000000
6	3.939040000	-3.565159000	0.000000000
6	-3.939040000	3.565159000	0.000000000
6	-3.146005000	4.662131000	0.000000000
1	-3.433170000	5.700041000	0.000000000
1	-5.014723000	3.514098000	0.000000000
1	3.433170000	-5.700041000	0.000000000
80	-0.082735000	-1.522400000	0.000000000
1	5.014723000	-3.514098000	0.000000000
7	-1.812644000	4.263468000	0.000000000
7	-3.146005000	2.421903000	0.000000000
7	3.146005000	-2.421903000	0.000000000
7	1.812644000	-4.263468000	0.000000000
6	0.729164000	-5.221790000	0.000000000
1	0.766316000	-5.859351000	0.886007000
1	-0.219166000	-4.689647000	0.000000000
1	0.766316000	-5.859351000	-0.886007000
5	-1.779314000	2.835443000	0.000000000
6	3.724639000	-1.094417000	0.000000000

1	4.343121000	-0.936847000	0.886199000
1	4.343121000	-0.936847000	-0.886199000
1	2.927944000	-0.353497000	0.000000000
6	-3.724639000	1.094417000	0.000000000
1	-4.343121000	0.936847000	-0.886199000
1	-2.927944000	0.353497000	0.000000000
1	-4.343121000	0.936847000	0.886199000
6	-0.729164000	5.221790000	0.000000000
1	-0.766316000	5.859351000	0.886007000
1	0.219166000	4.689647000	0.000000000
1	-0.766316000	5.859351000	-0.886007000

3ab‡

Sum of electronic and zero-point Energies= -890.374731
Sum of electronic and thermal Energies= -890.354791
Sum of electronic and thermal Enthalpies= -890.353847
Sum of electronic and thermal Free Energies= -890.429924

6	-4.857594000	0.273469000	-0.002515000
6	-4.329100000	1.520535000	-0.000118000
6	1.396749000	3.607301000	0.677123000
6	1.394410000	3.607306000	-0.679960000
1	1.394355000	4.452329000	-1.348944000
1	1.398968000	4.452304000	1.346127000
1	-5.893612000	-0.019066000	-0.004572000
5	-2.598108000	0.055222000	0.000945000
1	-4.841047000	2.467617000	0.000207000
7	1.407859000	2.296633000	-1.128751000
7	1.411750000	2.296601000	1.125831000
7	-2.941946000	1.437191000	0.002126000
7	-3.829319000	-0.662366000	-0.001960000
6	-4.089831000	-2.086832000	-0.003673000
1	-4.653788000	-2.379721000	-0.891119000
1	-3.143749000	-2.622356000	-0.002753000
1	-4.656430000	-2.381360000	0.881546000
6	-2.103277000	2.621565000	0.004461000
1	-2.290460000	3.230622000	-0.881174000
1	-2.294028000	3.229581000	0.890058000
1	-1.059315000	2.325777000	0.006304000
5	1.418365000	1.388714000	-0.001504000
6	1.377901000	1.978785000	2.534603000
1	0.455254000	2.332287000	3.003496000
1	1.429701000	0.899068000	2.655168000
1	2.222811000	2.423983000	3.065743000

6	1.369131000	1.978824000	-2.537394000
1	2.213770000	2.421555000	-3.071044000
1	1.417492000	0.898952000	-2.657961000
1	0.446132000	2.334899000	-3.003614000
80	-0.633057000	-0.785625000	0.002242000
80	2.013856000	-1.087728000	-0.001249000

3ac‡

Sum of electronic and zero-point Energies= -890.387981
Sum of electronic and thermal Energies= -890.368263
Sum of electronic and thermal Enthalpies= -890.367318
Sum of electronic and thermal Free Energies= -890.439999

5	1.434033000	0.464177000	1.009068000
7	2.250135000	-0.581661000	1.548208000
7	1.197314000	1.350515000	2.103124000
6	2.455227000	-0.319753000	2.901286000
6	1.822064000	0.829369000	3.230958000
1	1.767832000	1.314650000	4.190739000
1	3.042061000	-0.968928000	3.529048000
5	-1.434033000	-0.464177000	1.009068000
7	-1.197314000	-1.350515000	2.103124000
7	-2.250135000	0.581661000	1.548208000
6	-1.822064000	-0.829369000	3.230958000
6	-2.455227000	0.319753000	2.901286000
1	-3.042061000	0.968928000	3.529048000
1	-1.767832000	-1.314650000	4.190739000
6	-0.420037000	-2.566530000	2.152398000
6	-2.849074000	1.721823000	0.894146000
6	0.420037000	2.566530000	2.152398000
6	2.849074000	-1.721823000	0.894146000
1	-2.575063000	2.654156000	1.392533000
1	-2.499708000	1.773547000	-0.134836000
1	-3.939166000	1.648204000	0.880986000
1	0.430937000	-2.459928000	2.826700000
1	-1.028977000	-3.410552000	2.484115000
1	-0.042377000	-2.786039000	1.157046000
1	-0.430937000	2.459928000	2.826700000
1	1.028977000	3.410552000	2.484115000
1	0.042377000	2.786039000	1.157046000
1	2.575063000	-2.654156000	1.392533000
1	2.499708000	-1.773547000	-0.134836000
1	3.939166000	-1.648204000	0.880986000
80	1.197314000	0.721374000	-1.275047000

80 -1.197314000 -0.721374000 -1.275047000

$Zn_2(Ph^{Me})_2$

Sum of electronic and zero-point Energies= -4179.470533
Sum of electronic and thermal Energies= -4179.449026
Sum of electronic and thermal Enthalpies= -4179.448082
Sum of electronic and thermal Free Energies= -4179.528729

30	0.000000000	0.000000000	1.211322000
1	-1.511545000	-1.512009000	5.844110000
1	0.000000000	0.000000000	7.078042000
6	0.855484000	0.855814000	3.905934000
6	0.849236000	0.849506000	5.300351000
1	1.511545000	1.512009000	5.844110000
30	0.000000000	0.000000000	-1.211322000
6	0.855484000	-0.855814000	-3.905934000
6	0.849236000	-0.849506000	-5.300351000
6	0.000000000	0.000000000	-3.192082000
6	-0.855484000	-0.855814000	3.905934000
1	1.511545000	-1.512009000	-5.844110000
1	0.000000000	0.000000000	-7.078042000
6	-0.855484000	0.855814000	-3.905934000
6	0.000000000	0.000000000	3.192082000
6	-0.849236000	0.849506000	-5.300351000
1	-1.511545000	1.512009000	-5.844110000
6	1.788851000	-1.790111000	-3.173159000
1	2.480451000	-1.238706000	-2.531411000
1	1.236281000	-2.485315000	-2.536305000
6	0.000000000	0.000000000	-5.995879000
6	0.000000000	0.000000000	5.995879000
1	2.386999000	-2.384402000	-3.863112000
6	-1.788851000	1.790111000	-3.173159000
1	-2.480451000	1.238706000	-2.531411000
1	-1.236281000	2.485315000	-2.536305000
6	-0.849236000	-0.849506000	5.300351000
1	-2.386999000	2.384402000	-3.863112000
6	-1.788851000	-1.790111000	3.173159000
1	-2.480451000	-1.238706000	2.531411000
1	-1.236281000	-2.485315000	2.536305000
1	-2.386999000	-2.384402000	3.863112000
6	1.788851000	1.790111000	3.173159000
1	2.480451000	1.238706000	2.531411000
1	1.236281000	2.485315000	2.536305000
1	2.386999000	2.384402000	3.863112000

$Cd_2(Ph^{Me})_2$

Sum of electronic and zero-point Energies= -956.224448
Sum of electronic and thermal Energies= -956.202885
Sum of electronic and thermal Enthalpies= -956.201941
Sum of electronic and thermal Free Energies= -956.281582

48	0.000428000	1.351020000	0.000148000
6	-0.000072000	3.520593000	-0.000068000
1	-1.512287000	6.167175000	-1.511967000
1	-0.001416000	7.402049000	-0.000169000
6	0.855539000	4.229011000	0.856072000
6	0.848121000	5.624433000	0.849094000
1	1.510295000	6.168305000	1.511717000
48	-0.000428000	-1.351020000	0.000148000
6	0.001033000	-6.319931000	-0.000146000
6	-0.001033000	6.319931000	-0.000146000
6	-0.848121000	-5.624433000	0.849094000
6	0.000072000	-3.520593000	-0.000068000
1	-1.510295000	-6.168305000	1.511717000
1	0.001416000	-7.402049000	-0.000169000
6	0.849709000	-5.623796000	-0.849345000
1	1.512287000	-6.167175000	-1.511967000
6	-1.790003000	-3.498828000	1.790338000
1	-1.238315000	-2.858199000	2.482792000
1	-2.484886000	-2.861203000	1.238212000
1	-2.384068000	-4.190269000	2.387025000
6	-0.855539000	-4.229011000	0.856072000
6	1.790003000	-3.497518000	-1.790638000
6	-0.849709000	5.623796000	-0.849345000
1	1.237655000	-2.858500000	-2.484059000
1	2.483484000	-2.858179000	-1.238734000
6	0.856174000	-4.228368000	-0.856249000
1	2.385585000	-4.188552000	-2.386273000
6	-1.790003000	3.497518000	-1.790638000
1	-1.237655000	2.858500000	-2.484059000
6	-0.856174000	4.228368000	-0.856249000
1	-2.483484000	2.858179000	-1.238734000
1	-2.385585000	4.188552000	-2.386273000
6	1.790003000	3.498828000	1.790338000
1	1.238315000	2.858199000	2.482792000
1	2.484886000	2.861203000	1.238212000
1	2.384068000	4.190269000	2.387025000

$Hg_2(Ph^{Me})_2$

Sum of electronic and zero-point Energies= -927.664642
Sum of electronic and thermal Energies= -927.643242
Sum of electronic and thermal Enthalpies= -927.642297
Sum of electronic and thermal Free Energies= -927.722373

80	-1.336037000	-0.068758000	0.000053000
6	-4.192643000	0.827730000	-0.825014000
6	-5.588024000	0.824050000	-0.813027000
6	-3.493179000	-0.059679000	0.004664000
1	-6.129670000	1.509143000	-1.453535000
1	-7.367418000	-0.043399000	0.013183000
6	-4.196421000	-0.941204000	0.837420000
6	-5.591763000	-0.925785000	0.831574000
1	-6.136327000	-1.606307000	1.474477000
6	6.285024000	-0.101399000	-0.011460000
6	4.189315000	-0.921763000	-0.894683000
6	-6.285403000	-0.047947000	0.010802000
6	5.584730000	-0.918850000	-0.887118000
6	3.492802000	-0.089437000	-0.007434000
1	6.124103000	-1.561424000	-1.572070000
1	7.367039000	-0.106032000	-0.013025000
6	4.198994000	0.736876000	0.877788000
6	5.594300000	0.722006000	0.866208000
1	6.141137000	1.359924000	1.549593000
6	3.455342000	-1.821357000	-1.858465000
1	2.817557000	-1.245038000	-2.532389000
80	1.335659000	-0.080132000	-0.004293000
1	4.147570000	-2.396959000	-2.471754000
1	2.814047000	-2.530301000	-1.330038000
6	3.475561000	1.642708000	1.843674000
1	2.838781000	2.357072000	1.317104000
1	2.834881000	1.071859000	2.519494000
1	4.174473000	2.212404000	2.454890000
6	-3.461871000	1.787650000	-1.731310000
1	-2.825948000	1.256061000	-2.442719000
1	-4.156130000	2.401073000	-2.304318000
1	-2.819202000	2.461560000	-1.160416000
6	-3.469777000	-1.907222000	1.740553000
1	-2.835317000	-2.586534000	1.166891000
1	-2.826287000	-1.380993000	2.449131000
1	-4.166647000	-2.514767000	2.316644000