Supporting Information

E−H (E = N and P) Bond Activation of $PhEH_2$ by a Trinuclear Yttrium Methylidene Complex: Theoretical Insights into Mechanism and Multimetal Cooperation Behavior

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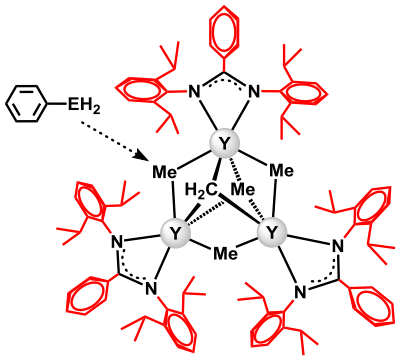

Figure S1. The Division of the ONIOM Layers. The part shown in black represents the inner layer and the one in red was included in outer layer.

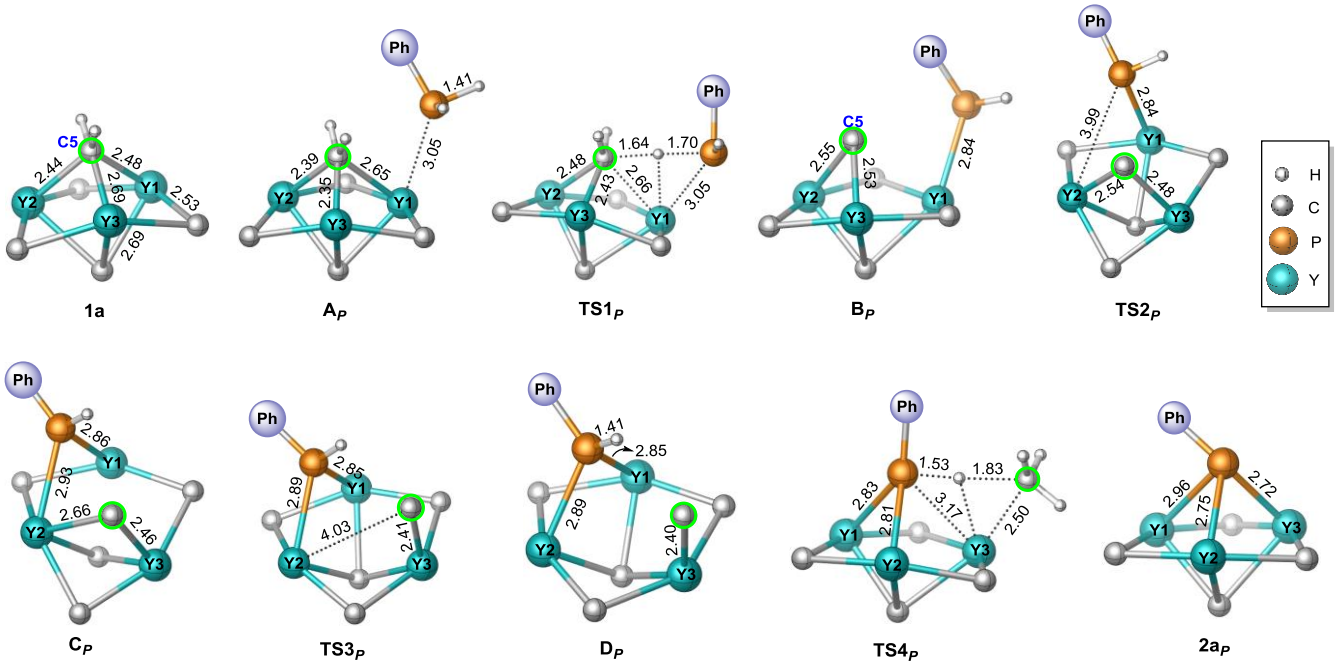

Figure S2. Structures (distances in Å) of optimized stationary points involved the reaction of **1a** with $PhPH_2$. The $PhC[NC_6H_4(^{i}Pr\text{-}2,6)_2]_2$ ligands and part of the H atoms are omitted for clarity.

Table S1. Selected Wiberg Bond Indexes (WBIs) for the Stationary Points Involved in the Reaction of 1a with $PhNH_2$[a]

bond[b]	**1a**	$\mathbf{A}_N$	$\mathbf{TS1}_N$	$\mathbf{B}_N$	$\mathbf{TS2}_N$	$\mathbf{C}_N$	$\mathbf{TS3}_N$	$\mathbf{D}_N$	$\mathbf{TS4}_N$	$\mathbf{2a}_N$
Y1−Y2	0.19	0.19	0.19	0.16	0.19	0.23	0.22	0.22	0.21	0.21
Y1−Y3	0.24	0.23	0.20	0.17	0.17	0.13	0.14	0.15	0.20	0.21
Y2−Y3	0.24	0.24	0.24	0.23	0.30	0.29	0.21	0.16	0.18	0.21
Y1−C1	0.27	0.26	0.25	0.20	0.24	0.24	0.29	0.28	0.29	0.30
Y2−C1	0.26	0.28	0.30	0.33	0.29	0.30	0.26	0.27	0.23	0.26
Y3−C1	0.28	0.27	0.26	0.28	0.29	0.29	0.26	0.24	0.27	0.22
Y1−C2	0.39	0.36	0.36	0.32	0.36	0.36	0.36	0.35	0.39	0.40
Y2−C2	0.35	0.37	0.38	0.42	0.34	0.34	0.32	0.33	0.31	0.33
Y1−C3	0.36	0.36	0.34	0.32	0.31	0.30	0.37	0.38	0.34	0.37
Y3−C3	0.39	0.37	0.39	0.42	0.39	0.40	0.33	0.34	0.40	0.33
Y2−C4	0.38	0.38	0.38	0.38	0.36	0.35	0.36	0.37	0.34	0.37
Y3−C4	0.36	0.36	0.36	0.35	0.37	0.38	0.34	0.34	0.38	0.31
Y1−C5	0.43	0.34	0.19	0.10	-	-	-	-	-	-
Y2−C5	0.45	0.47	0.43	0.36	0.37	0.35	0.13	-	-	-
Y3−C5	0.63	0.64	0.50	0.35	0.35	0.38	0.45	0.47	0.37	-
N−H1	0.82[c]	0.73	0.41	-	-	-	-	-	-	-
N−H2	0.82[c]	0.79	0.79	0.80	0.79	0.77	0.74	0.71	0.45	-
Y1−N	-	0.21	0.24	0.46	0.40	0.36	0.34	0.31	0.27	0.34
Y2−N	-	-	-	-	0.13	0.22	0.22	0.24	0.31	0.37
Y3−N	-	-	-	-	0.13	0.05	0.06	0.08	0.20	0.38
Y1−H1	-	-	0.04	-	-	-	-	-	-	-
Y3−H2	-	-	-	-	-	-	-	-	0.06	-
C5−H1	-	-	0.33	0.83	0.87	0.88	0.91	0.92	0.90	0.94[d]
C5−H2	-	-	-	-	-	-	-	-	0.29	0.94[d]

[a]The values less than 0.03 were ignored. [b]Atom labeling is defined in Figure 1. [c]The value is obtained from the isolated $PhNH_2$. [d]Data for the released methane molecule.

Table S2. Selected Wiberg Bond Indexes (WBIs) for the Stationary Points Involved in the Reaction of 1a with $PhPH_2$[a]

bond[b]	**1a**	**A_P**	**$TS1_P$**	**B_P**	**$TS2_P$**	**C_P**	**$TS3_P$**	**D_P**	**$TS4_P$**	**$2a_P$**
Y1−Y2	0.19	0.20	0.19	0.17	0.19	0.24	0.21	0.20	0.19	0.23
Y1−Y3	0.24	0.22	0.21	0.17	0.15	0.16	0.16	0.16	0.18	0.24
Y2−Y3	0.24	0.25	0.23	0.22	0.24	0.23	0.16	0.15	0.18	0.20
Y1−C1	0.27	0.28	0.27	0.25	0.24	0.28	0.30	0.30	0.30	0.29
Y2−C1	0.26	0.28	0.29	0.30	0.28	0.26	0.25	0.26	0.26	0.28
Y3−C1	0.28	0.25	0.27	0.26	0.29	0.30	0.26	0.23	0.26	0.23
Y1−C3	0.36	0.37	0.37	0.39	0.36	0.38	0.39	0.40	0.40	0.34
Y3−C3	0.39	0.37	0.38	0.35	0.35	0.35	0.32	0.31	0.34	0.39
Y1−C2	0.39	0.40	0.36	0.34	0.33	0.34	0.31	0.31	0.37	0.34
Y2−C2	0.35	0.34	0.38	0.42	0.37	0.37	0.34	0.34	0.33	0.41
Y2−C4	0.38	0.38	0.39	0.39	0.32	0.37	0.38	0.39	0.38	0.39
Y3−C4	0.36	0.35	0.36	0.33	0.37	0.36	0.32	0.31	0.35	0.34
Y1−C5	0.43	0.34	0.30	0.14	0.05	0.07	0.05	-	-	-
Y2−C5	0.45	0.53	0.42	0.35	0.35	0.34	0.07	-	-	-
Y3−C5	0.63	0.59	0.45	0.32	0.36	0.37	0.45	0.46	0.44	-
P−H1	0.98[c]	0.96	0.59	-	-	-	-	-	-	-
P−H2	0.98[c]	0.93	0.94	0.95	0.95	0.94	0.94	0.94	0.69	-
Y1−P	-	0.48	0.44	0.84	0.75	0.60	0.59	0.59	0.56	0.48
Y2−P	-	-	-	-	0.16	0.56	0.53	0.52	0.54	0.73
Y3−P	-	-	-	-	-	-	0.06	0.08	0.29	0.72
Y1−H1	-	-	0.11	-	-	-	-	-	-	-
Y3−H2	-	-	-	-	-	-	-	-	0.09	-
C5−H1	-	-	0.26	0.83	0.86	0.88	0.91	0.91	0.91	0.94[d]
C5−H2	-	-	-	-	-	-	-	-	0.16	0.94[d]

[a]The values less than 0.03 were ignored. [b]Atom labeling is defined in Figure 3. [c]The value is obtained from the isolated $PhPH_2$. [d]Data for the released methane molecule.

Table S3. Gas-phase thermal correction to enthalpy ($\Delta\Delta H_{gas}$, a.u.) and to Gibbs free energy ($\Delta\Delta G_{gas}$, a.u.), single-point energy in solution (E_{sp}, a.u.), relative enthalpy in solution (ΔH_{sol}, kcal/mol), relative free energy in solution (ΔG_{sol}, kcal/mol)

	$\Delta\Delta H$	$\Delta\Delta G$	E_{SP}	ΔH_{sol}	ΔG_{sol}
CH_4	0.048819	0.027681	-40.51079	/	/
$PhNH_2$	0.122511	0.086478	-287.5776	/	/
1a	2.487101	2.20821	-4256.923	0.0	0.0
A_N	2.613175	2.32395	-4544.532	-16.9	-0.8
$TS1_N$	2.607781	2.319106	-4544.514	-9.3	7.2
B_N	2.612521	2.321152	-4544.554	-31.2	-16.4
$TS2_N$	2.613532	2.329675	-4544.555	-31.5	-12.0
C_N	2.614686	2.328677	-4544.561	-34.3	-16.1
$TS3_N$	2.612915	2.328657	-4544.558	-33.8	-14.6
D_N	2.613986	2.328294	-4544.564	-36.7	-18.3
$TS4_N$	2.609765	2.323626	-4544.555	-33.4	-15.3
$2a_N$	2.563752	2.280291	-4504.092	-62.1	-55.7
NH_3	0.037873	0.014978	-56.55117	/	/
1a	2.487101	2.20821	-4256.923	0.0	0.0
A'_N	2.528803	2.249165	-4313.511	-20.4	-6.5
$TS1'_N$	2.522095	2.243215	-4313.48	-5.1	9.3
B'_N	2.527429	2.245379	-4313.513	-22.8	-10.4
D'_N	2.527305	2.245704	-4313.525	-30.4	-17.7
$TS4'_N$	2.52328	2.243935	-4313.511	-23.7	-9.6
$2a'_N$	2.477279	2.200461	-4273.046	-51.0	-48.6
$PhPH_2$	0.114678	0.075685	-574.1449	/	/
1a	2.487101	2.20821	-4256.923	0.0	0.0
A_P	2.606054	2.314242	-4831.094	-13.5	2.8
$TS1_P$	2.602396	2.315705	-4831.075	-4.0	15.6
B_P	2.607815	2.317517	-4831.118	-27.1	-9.8
$TS2_P$	2.607303	2.317456	-4831.11	-22.5	-4.9
C_P	2.609401	2.321679	-4831.124	-30.1	-11.1
$TS3_P$	2.607778	2.31912	-4831.112	-23.6	-5.3
D_P	2.608351	2.316587	-4831.112	-23.2	-6.8
$TS4_P$	2.60636	2.3159	-4831.099	-16.3	0.9
$2a_P$	2.562371	2.278121	-4790.649	-51.3	-43.5

PH_3	0.028111	0.003226	-343.1205	/	/
1a	2.487101	2.20821	-4256.923	0.0	0.0
A′$_P$	2.51934	2.238397	-4600.06	-7.4	7.0
TS1′$_P$	2.515218	2.23866	-4600.042	1.4	18.5
B′$_P$	2.520841	2.238436	-4600.077	-17.3	-3.9
D′$_P$	2.521256	2.239377	-4600.078	-17.7	-4.0
TS4′$_P$	2.519024	2.240142	-4600.069	-13.1	2.6
2a′$_P$	2.474356	2.192104	-4559.594	-33.1	-32.9