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

Supplementary Information

Quantum Chemical Study on Gas Phase Decomposition Pathways of Triethylgallane (TEG, $Ga(C_2H_5)_3$) and Tertiarybutylphosphine (TBP, $PH_2(t\text{-}C_4H_9)$) under MOVPE Conditions

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Accuracy of structures investigated

For the title molecules, structural data from experiment were compared to PBE-D3/TZ and MP2/TZ results (see Figure SI-1). Solid TEG has four molecules in the unit cell, three triskel-shaped moieties and one exhibiting a rotated ethyl group. The triskel-shaped structure (more stable by ΔE(MP2/TZ) = 3.1 kJ mol^{-1}) will be prominently represented in the gas phase. Crystal packing effects cause the rotation of an ethyl group on one of the four units, as well as reduced mean bond lengths and disturbed molecular planarity as exhibited by the mean C_α-Ga-C_α-C_β torsion angle (12.4°) on the three triskel-shaped molecules with respect to calculated values.[1] For TBP only data derived from vibrational spectroscopy are available,[2] so mean values of the structure of tri-*tert*-butylphosphine, $P(t\text{-}C_4H_9)_3$, determined by electron diffraction were used as a reference.[3a] One value (indicated by an asterisk) was taken from an X-ray diffraction study.[3b] $P(t\text{-}C_4H_9)_3$ was measured at 90 - 95 °C with assumed C_3 overall symmetry and internal C_{3V} symmetry of the *tert*-butyl groups (with a possible deviation towards C_3 symmetry)[3], although “geometric constraints” might have a significant effect on the bond angles (C_β-C_α-C_β) of tri-*tert*-butyl groups, as was shown by a study on tri-*tert*-butylmethane.[4] Bulky *tert*-butyl groups presumably cause slightly extended mean bond distances, larger *ligand-P-ligand* angles (C_α-P-C_α as opposed to H-P-C_α) and increased twist angles in $P^t(C_4H_9)_3$ as opposed to TBP. In this exemplary comparison, PBE-D3/TZ as well as MP2/TZ give good agreement to available experimental structures.

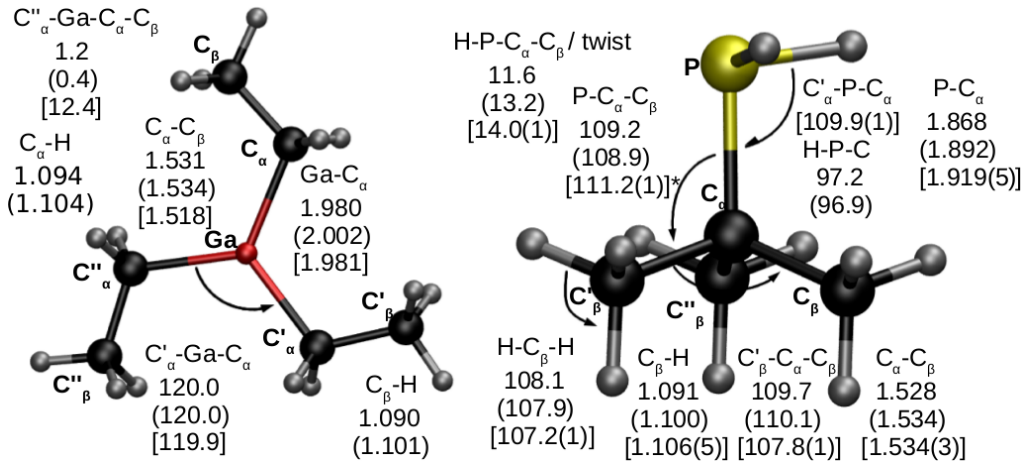

Figure S1: Optimized structures of TEG and TBP. Bond distances *A-B* (in Å), angles *A-B-C* (in °) and torsion angles *A-B-C-D* (in °) are given for MP2/TZ, PBE-D3/TZ (round brackets) and to averaged experimental values (in square brackets) of the three triskel-shaped molecules from X-ray diffraction results on TEG[1], electron diffraction data[3a] and X-ray analysis (designated by *)[3b] on P(*t*-Bu_3). Error of X-ray diffraction data approx. $3*10^{-4}$ Å and $2*10^{-2}$ °.

References

[1] N. W. Mitzel, C. Lustig, R. J. F. Berger, N. Runeberg, *Angew. Chem. Int. Ed. Engl.*, **2002**, *41*, 2519.

[2] J. R. Durig, *J. Mol. Struc.*, **1977**, *30*, 77.

[3] a) H. Oberhammer, R. Schmutzler, O. Stelzer, *Inorg. Chem.*, **1978**, *17*, 1254; b) J. Bruckmann, C. Krüger, *Acta Cryst. C*, **1995**, *51*, 1152.

[4] L. Bartell, H. Burgi, *J. Am. Chem. Soc.*, **1972**, *531*, 5239.

Table S1. Absolute values for electronic and Gibbs Energies of the species investigated in kJ mol^{-1}.

	PBE-D3/TZ			
	E	G (400 °C)	G (500 °C)	G (675 °C)
Ga(C2H5)3	-5676287.9	-5676141.8	-5676214.6	-5676352.7
(C2H5)2Ga(C2H4)·	-5674571.6	-5674463.4	-5674536.6	-5674674.9
(C2H5)2Ga(CH2)·	-5571443.0	-5571379.1	-5571445.4	-5571570.4
HGaEt2	-5470042.0	-5470000.5	-5470061.3	-5470175.5
Et2Ga'	-5468400.0	-5468366.8	-5468425.0	-5468534.1
EtGaC2H4	-5466774.6	-5466733.3	-5466789.1	-5466893.6
H2GaEt	-5263795.3	-5263833.0	-5263878.1	-5263961.8
HgaEt'	-5262150.2	-5262201.0	-5262244.1	-5262323.7
GaEt	-5260659.6	-5260720.8	-5260761.7	-5260837.2
GaC2H4'	-5258947.8	-5259040.0	-5259080.3	-5259154.1
H3Ga	-5057547.6	-5057673.0	-5057703.5	-5057759.0
H2Ga'	-5055898.0	-5056038.4	-5056067.1	-5056118.8
GaH	-5054406.0	-5054545.0	-5054570.3	-5054615.5
Ga(0)	-5052813.9	-5052945.4	-5052967.1	-5053005.8
H2PBu	-1312975.7	-1312879.4	-1312932.6	-1313033.2
HPBu'	-1311314.2	-1311240.9	-1311293.0	-1311391.3
Pbu	-1309673.5	-1309614.6	-1309664.8	-1309759.2
PH3	-900508.2	-900609.8	-900638.3	-900638.3
H2P'	-897191.4	-897317.0	-897340.9	-897383.6
HP	-897191.4	-897317.0	-897340.9	-897383.6
P(0)	-895565.8	-895690.4	-895711.2	-895748.1
isobutane	-415578.5	-415471.8	-415517.3	-415603.4
N-Butane	-415573.8	-415468.1	-415513.9	-415600.3
Bu'	-413856.8	-413797.2	-413844.1	-413931.9
isobutene	-412370.7	-412318.3	-412361.9	-412443.6
C2H6	-209347.8	-209339.3	-209372.8	-209434.8
Et'	-207595.6	-207630.7	-207665.0	-207728.1
C2H4	-206113.0	-206155.2	-206186.1	-206242.8
CH3'	-104468.6	-104544.1	-104571.0	-104619.7
H2	-3062.3	-3141.7	-3160.4	-3194.0
H'	-1311.7	-1407.7	-1424.1	-1453.6

	MP2/TZ			CCSD(T)/TZ//MP2/TZ
	E	G (400 °C)	G (500 °C)	G (675 °C)	E
Ga(C2H5)3	-5672574.9	-5672419.1	-5672493.0	-5672632.6	-5672899.1
(C2H5)2Ga(C2H4)·	-5670845.3	-5670707.3	-5670778.5	-5670913.0	-5671171.4
(C2H5)2Ga(CH2)·	-5567860.9	-5567773.2	-5567838.0	-5567960.1	-5568139.1
HGaEt2	-5466592.5	-5466527.7	-5466586.9	-5466697.9	-5466826.8
Et2Ga'	-5464936.7	-5464891.7	-5464949.9	-5465058.8	-5465161.7
EtGaC2H4	-5463292.6	-5463264.7	-5463320.4	-5463424.3	-5463501.5
H2GaEt	-5260611.4	-5260638.2	-5260682.8	-5260765.4	-5260755.6
HgaEt'	-5258954.2	-5258994.2	-5259036.7	-5259115.2	-5259088.9
GaEt	-5257460.4	-5257512.6	-5257553.1	-5257627.5	-5257592.3
GaC2H4'	-5255733.2	-5255811.7	-5255850.9	-5255922.8	-5255867.2
H3Ga	-5054631.5	-5054752.5	-5054782.8	-5054837.8	-5054685.2

H2Ga'	-5052972.4	-5053109.3	-5053137.9	-5053189.2	-5053016.3
GaH	-5051473.1	-5051610.8	-5051635.9	-5051681.0	-5051517.4
Ga(0)	-5049887.5	-895888.1	-5050040.7	-5050079.4	-5049917.2
H2PBu	-1311576.9	-1311461.8	-1311513.9	-1311612.6	-1311846.4
HPBu'	-1309912.4	-1309822.1	-1309873.3	-1309969.9	-1310176.7
Pbu	-1308282.3	-1308207.1	-1308256.4	-1308349.1	-1308537.5
PH3	-899638.8	-899736.0	-899764.3	-899815.7	-899730.8
H2P'	-897973.2	-898093.2	-898120.3	-898168.9	-898058.5
HP	-896341.8	-896466.4	-896490.2	-896532.8	-896417.2
P(0)	-894751.9	-894876.6	-894897.3	-894934.3	-894809.2
isobutane	-415036.0	-414913.8	-414958.7	-415043.5	-415244.7
N-Butane	-415028.2	-414907.0	-414952.3	-415037.4	-415238.3
Bu'	-413289.2	-413211.9	-413257.8	-413343.9	-413498.7
isobutene	-411826.4	-411762.2	-411805.3	-411886.1	-412019.3
C2H6	-209070.6	-209053.2	-209086.5	-209147.8	-209187.8
Et'	-207308.8	-207334.6	-207368.4	-207430.6	-207424.3
C2H4	-205840.7	-205877.6	-205908.4	-205964.8	-205944.5
CH3'	-104327.7	-104399.8	-104426.7	-104475.3	-104394.3
H2	-3057.8	-3135.7	-3154.4	-3188.0	-3077.9
H'	-1312.3	-1408.2	-1424.6	-1454.1	-1312.3

	Transition States	PBE-D3/TZ			
		E	G (400 °C)	G (500 °C)	G (675 °C)
AG11	Ga(C2H5)3 → Ga(C2H5)2H + C2H4	-5676156.3	-5675950.1	-5676019.4	-5676151.3
AG12	Ga(C2H5)2H → Ga(C2H5)H2 + C2H4	-5469913.9	-5469818.3	-5469874.0	-5469979.1
AG13	Ga(C2H5)H2 → GaH3 + C2H4	-5263671.5	-5263688.6	-5263731.1	-5263810.2
AG14	Ga(C2H5) → GaH + C2H4	-5260572.4	-5260624.3	-5260663.7	-5260736.4
AG15	Ga(C2H5)3 → Ga(C2H5) + nC4H10	-1312733.1	-1312625.9	-5675834.9	-5675967.2
AG17	Ga(C2H5)H2 → HGa + C2H6	-5263600.6	-5263616.2	-5263658.8	-5263738.0
AG19	Ga(C2H5)H2 → Ga(C2H5) + H2	-5263578.4	-5263602.6	-5263646.5	-5263728.1
AG20	GaH3 → HGa + H2	-5057336.1	-5057469.3	-5057499.9	-5057555.4
BG15	Ga(C2H5)3 + H2 → Ga(C2H5)2H + C2H6	-5679253.5	-5679020.2	-5679094.8	-5679236.8
BG16	Ga(C2H5)2H + H2 → Ga(C2H5)H2 + C2H6	-5473010.6	-5472888.7	-5472949.8	-5473065.1
BG17	Ga(C2H5)H2 + H2 → GaH3 + C2H6	-5266765.5	-5266750.3	-5266797.4	-5266885.3
BG18	Ga(C2H5) + H2 → GaH + C2H6	-5263654.6	-5263674.9	-5263719.0	-5263800.7
AP6	P tC4H9H2 → PH3 + tC4H8	-1312733.1	-1312625.9	-1312680.2	-1312782.8
BP8	PtC4H9H2 + H2 → PH3 + tC4H8 + H2	-1315773.4	-1315644.2	-1315703.8	-1315816.7

	Transition States	MP2/TZ//PBE-D3/TZ	CCSD(T)/TZ//PBE-D3/TZ
		E	E
AG11	Ga(C2H5)3 → Ga(C2H5)2H + C2H4	-5672422.3	-5672751.5
AG12	Ga(C2H5)2H → Ga(C2H5)H2 + C2H4	-5466441.8	-5466681.6
AG13	Ga(C2H5)H2 → GaH3 + C2H4	-5260461.9	-5260612.3
AG14	Ga(C2H5) → GaH + C2H4	-5257348.9	-5257482.5
AG15	Ga(C2H5)3 → Ga(C2H5) + nC4H10	-1311266.4	-1311553.3
AG17	Ga(C2H5)H2 → HGa + C2H6	-5260377.2	-5260518.7

AG19	Ga(C2H5)H2 → Ga(C2H5) + H2	-5260340.2	-5260499.9
AG20	GaH3 → HGa + H2	-5054362.4	-5054433.8
BG15	Ga(C2H5)3 + H2 → Ga(C2H5)2H + C2H6	-5675506.4	-5675852.3
BG16	Ga(C2H5)2H + H2 → Ga(C2H5)H2 + C2H6	-5469526.0	-5469782.0
BG17	Ga(C2H5)H2 + H2 → GaH3 + C2H6	-5263544.9	-5263710.9
BG18	Ga(C2H5) + H2 → GaH + C2H6	-5260412.7	-5260562.9
AP6	P tC4H9H2 → PH3 + tC4H8	-1311266.4	-1311553.3
BP8	PtC4H9H2 + H2 → PH3 + tC4H8 + H2	-1314268.9	-1314570.3

Table S2. Absolute values for entropies of the species investigated in kJ mol^{-1} K^{-1}.

	PBE-D3/TZ			MP2/TZ		
	S (400 °C)	S (500 °C)	S (675 °C)	S (400 °C)	S (500 °C)	S (675 °C)
Ga(C2H5)3	0.7053	0.7512	0.8251	0.7159	0.7609	0.8333
(C2H5)2Ga(C2H4)·	0.7097	0.7541	0.8253	0.6899	0.7333	0.8031
(C2H5)2Ga(CH2)·	0.6444	0.6827	0.7439	0.6292	0.6667	0.7267
HGaEt2	0.5915	0.6250	0.6789	0.5749	0.6077	0.6604
Et2Ga'	0.5667	0.5979	0.6479	0.5666	0.5971	0.6461
EtGaC2H4	0.5437	0.5731	0.6201	0.5416	0.5704	0.6165
H2GaEt	0.4400	0.4612	0.4949	0.4349	0.4555	0.4885
HgaEt'	0.4210	0.4399	0.4700	0.4153	0.4337	0.4631
GaEt	0.4014	0.4177	0.4437	0.3966	0.4125	0.4380
GaC2H4'	0.3951	0.4099	0.4332	0.3851	0.3993	0.4219
H3Ga	0.3013	0.3100	0.3237	0.2989	0.3074	0.3207
H2Ga'	0.2839	0.2904	0.3005	0.2822	0.2885	0.2983
GaH	0.2501	0.2547	0.2617	0.2493	0.2538	0.2607
Ga(0)	0.2036	0.2065	0.2107	0.2049	0.2065	0.2107
H2PBu	0.5148	0.5478	0.6010	0.5050	0.5372	0.5893
HPBu'	0.5054	0.5364	0.5864	0.4970	0.5273	0.5762
Pbu	0.4874	0.5161	0.5624	0.4785	0.5066	0.5519
PH3	0.2815	0.2892	0.3016	0.2799	0.2874	0.2995
H2P'	0.2685	0.2745	0.2837	0.2676	0.2734	0.2824
HP	0.2363	0.2406	0.2471	0.2359	0.2401	0.2466
P(0)	0.1935	0.1964	0.2006	0.1935	0.1964	0.2006
isobutane	0.4423	0.4692	0.5132	0.4362	0.4624	0.2006
N-Butane	0.4447	0.4715	0.5153	0.4390	0.4651	0.5079
Bu'	0.4553	0.4809	0.5225	0.4462	0.4711	0.5117
isobutene	0.4238	0.4474	0.4857	0.4197	0.4428	0.4803
C2H6	0.3281	0.3424	0.3659	0.3253	0.3392	0.3620
Et'	0.3363	0.3495	0.3709	0.3318	0.3447	0.3655
C2H4	0.3041	0.3151	0.3329	0.3026	0.3134	0.3309
CH3'	0.2653	0.2726	0.2839	0.2651	0.2722	0.2833
H2	0.1851	0.1891	0.1951	0.1848	0.1888	0.1948
H'	0.1508	0.1537	0.1579	0.1508	0.1537	0.1579

	Transition States			
	PBE-D3/TZ	S (400 °C)	S (500 °C)	S (675 °C)
AG11	Ga(C2H5)3 → Ga(C2H5)2H + C2H4	0.6705	0.7161	0.7893
AG12	Ga(C2H5)2H → Ga(C2H5)H2 + C2H4	0.5404	0.5736	0.6267
AG13	Ga(C2H5)H2 → GaH3 + C2H4	0.4146	0.4353	0.4684

AG14	Ga(C2H5) → GaH + C2H4	0.3861	0.4022	0.4279
AG15	Ga(C2H5)3 → Ga(C2H5) + nC4H10	0.5265	0.7191	0.7916
AG17	Ga(C2H5)H2 → HGa + C2H6	0.4157	0.4362	0.4689
AG19	Ga(C2H5)H2 → Ga(C2H5) + H2	0.4293	0.4497	0.4824
AG20	GaH3 → HGa + H2	0.3025	0.3106	0.3233
BG15	Ga(C2H5)3 + H2 → Ga(C2H5)2H + C2H6	0.7212	0.7707	0.8505
BG16	Ga(C2H5)2H + H2 → Ga(C2H5)H2 + C2H6	0.5916	0.6287	0.6884
BG17	Ga(C2H5)H2 + H2 → GaH3 + C2H6	0.4578	0.4825	0.5221
BG18	Ga(C2H5) + H2 → GaH + C2H6	0.4308	0.4508	0.4829
AP6	P tC4H9H2 → PH3 + tC4H8	0.5265	0.5593	0.6120
BP8	PtC4H9H2 + H2 → PH3 + tC4H8 + H2	0.5765	0.6143	0.6749

Table S3. Reaction entropies (changes) in kJ mol^{-1} K^{-1}.

Reaction Index	PBE-D3/TZ dS			MP2/TZ dS		
	673.15 K	773.15 K	948.15 K	673.15 K	773.15 K	948.15 K
AG1	0.1977	0.1962	0.1937	0.1825	0.1809	0.1783
AG2	0.1552	0.1566	0.1581	0.1247	0.1261	0.1277
AG3	0.2044	0.2041	0.2027	0.1783	0.1780	0.1768
AG4	0.1703	0.1685	0.1656	0.1825	0.1817	0.1789
AG5	0.1710	0.1693	0.1666	0.1617	0.1601	0.1575
AG6	0.1277	0.1288	0.1301	0.1257	0.1269	0.1283
AG7	0.1877	0.1863	0.1840	0.1753	0.1736	0.1709
AG8	0.1444	0.1458	0.1474	0.1393	0.1404	0.1417
AG9	0.1334	0.1341	0.1347	0.1340	0.1348	0.1355
AG10	0.1043	0.1055	0.1070	0.1051	0.1064	0.1080
AG11	0.1903	0.1889	0.1866	0.1615	0.1602	0.1580
AG12	0.1526	0.1512	0.1489	0.1626	0.1612	0.1590
AG13	0.1653	0.1639	0.1616	0.1667	0.1653	0.1630
AG14	0.1528	0.1521	0.1509	0.1553	0.1547	0.1535
AG15	0.1408	0.1379	0.1339	0.1197	0.1168	0.1126
AG16	0.1565	0.1544	0.1512	0.1437	0.1414	0.1378
AG17	0.1382	0.1360	0.1327	0.1397	0.1375	0.1342
AG18	0.1372	0.1372	0.1364	0.1515	0.1515	0.1509
AG19	0.1465	0.1456	0.1439	0.1465	0.1458	0.1443
AG20	0.1339	0.1338	0.1332	0.1351	0.1352	0.1348
BG1	0.0388	0.0354	0.0308	0.0252	0.0217	0.0169
BG2	-0.1260	-0.1265	-0.1270	-0.1425	-0.1431	-0.1436
BG3	0.0121	0.0086	0.0037	0.0045	0.0010	-0.0039
BG4	0.0069	0.0036	-0.0009	0.0149	0.0115	0.0068
BG5	-0.1318	-0.1324	-0.1330	-0.1312	-0.1319	-0.1325
BG6	0.0064	0.0036	-0.0003	0.0085	0.0056	0.0017
BG7	0.0212	0.0180	0.0135	0.0218	0.0185	0.0139

BG8	-0.0204	-0.0224	-0.0250	-0.0185	-0.0205	-0.0232
BG9	0.0169	0.0159	0.0140	0.0172	0.0162	0.0145
BG10	0.0005	-0.0003	-0.0016	0.0011	0.0005	-0.0007
BG11	-0.0122	-0.0128	-0.0137	-0.0117	-0.0122	-0.0130
BG12	-0.0302	-0.0314	-0.0328	-0.0421	-0.0434	-0.0448
BG13	-0.0312	-0.0319	-0.0328	-0.0315	-0.0322	-0.0331
BG14	-0.0145	-0.0150	-0.0155	-0.0180	-0.0188	-0.0196
BG15	0.0293	0.0271	0.0245	-0.0005	-0.0028	-0.0057
BG16	-0.0084	-0.0106	-0.0132	0.0005	-0.0018	-0.0046
BG17	0.0043	0.0021	-0.0005	0.0046	0.0023	-0.0006
BG18	-0.0082	-0.0097	-0.0113	-0.0068	-0.0083	-0.0101
BG19	-0.0153	-0.0137	-0.0111	-0.0168	-0.0153	-0.0128
	-0.0026	-0.0047	-0.0072	-0.0108	-0.0130	-0.0157
AP1	0.1414	0.1423	0.1433	0.1428	0.1438	0.1448
AP2	0.2091	0.2076	0.2052	0.2088	0.2073	0.2049
AP3	0.1862	0.1851	0.1832	0.1851	0.1840	0.1821
AP4	0.1379	0.1389	0.1400	0.1385	0.1397	0.1409
AP5	0.1080	0.1095	0.1115	0.1084	0.1099	0.1120
AP6	0.1905	0.1889	0.1864	0.1946	0.1930	0.1905
AP7	0.1727	0.1719	0.1704	0.1771	0.1764	0.1750
AP8	0.1638	0.1620	0.1593	0.1670	0.1654	0.0000
AP9	0.1304	0.1292	0.1274	0.1326	0.1315	-0.4464
AP10	0.1577	0.1575	0.1566	0.1583	0.1582	0.1575
AP11	0.1399	0.1404	0.1406	0.1408	0.1415	0.1419
AP12	0.1100	0.1111	0.1121	0.1107	0.1118	0.1130
BP1	0.0249	0.0241	0.0226	0.0260	0.0253	0.0238
BP2	0.0453	0.0422	0.0380	0.0480	0.0449	0.0406
BP3	-0.0024	-0.0042	-0.0065	0.0004	-0.0015	-0.0038
BP4	0.0214	0.0207	0.0193	0.0217	0.0211	0.0199
BP5	-0.0085	-0.0087	-0.0092	-0.0084	-0.0086	-0.0091
BP6	-0.0224	-0.0230	-0.0239	-0.0181	-0.0186	-0.0194
BP7	0.0239	0.0216	0.0187	0.0262	0.0238	0.0208
BP8	0.1905	0.1889	0.1864	0.1946	0.1930	0.1905
BP9	0.0203	0.0181	0.0154	0.0220	0.0197	0.0168
BP10	0.0061	0.0045	0.0027	0.0088	0.0071	0.0053

Table S4. Cartesian coordinates of structures investigated (PBE-TZ) in Å.

GaEt3			
	22		
	-2161.9838898290		
C	-0.004562	0.034882	-0.017162
C	0.025385	-0.022435	1.514050
Ga	1.778538	0.015846	-0.922255
C	3.452147	-0.081353	0.168002
C	4.763555	-0.088862	-0.625012
C	1.887067	0.093963	-2.917527
C	0.544795	0.156543	-3.654560
H	-0.080720	-0.720841	-3.434229
H	-0.038870	1.041254	-3.361020
H	0.669365	0.198966	-4.748295
H	5.648033	-0.144670	0.029297
H	4.816631	-0.944469	-1.314048
H	4.872217	0.817259	-1.238823
H	-0.984837	-0.009281	1.953126
H	0.523787	-0.933276	1.876723
H	0.574853	0.828933	1.941655
H	-0.587751	-0.806715	-0.428550
H	-0.536943	0.936856	-0.364396
H	3.374766	-0.979671	0.804100
H	3.428955	0.763454	0.877401
H	2.473937	-0.780337	-3.247107
H	2.515845	0.963188	-3.175669
Et2GaC2H4radical			
	21		
	-2161.3301860120		
C	0.019218	-0.000946	0.011380
Ga	-0.003840	0.022797	2.009401
C	1.708251	0.023455	2.958764
C	3.058047	0.009473	2.328537
C	-1.360641	-0.002800	-0.656537
C	-1.705770	0.046537	3.051568
C	-1.541585	0.046913	4.575234
H	3.647963	-0.867055	2.657687
H	3.025421	-0.002115	1.230521

H	3.657311	0.886513	2.638893
H	-2.510340	0.061495	5.099430
H	-0.997599	-0.842899	4.924529
H	-0.972775	0.922351	4.921304
H	-1.292720	-0.015984	-1.755908
H	-1.954775	-0.878989	-0.358410
H	-1.947148	0.885232	-0.379067
H	0.603540	-0.881881	-0.303445
H	0.611079	0.867276	-0.324060
H	-2.305780	-0.819033	2.724290
H	-2.281214	0.927840	2.721823
H	1.726267	0.034823	4.056046

Et2GaCH2radical

18

-2122.050591769

C	0.015971	-0.000636	0.011583
C	-1.361393	-0.002245	-0.660980
Ga	-0.006857	0.022293	2.005606
C	-1.705317	0.045473	3.051476
C	-1.540397	0.047846	4.574869
C	1.696508	0.022777	2.975645
H	2.674953	0.012461	2.484711
H	-2.509240	0.061721	5.098598
H	-0.995370	-0.840816	4.925169
H	-0.972876	0.924381	4.919961
H	-1.288528	-0.015313	-1.759867
H	-1.956622	-0.878574	-0.365612
H	-1.948735	0.885971	-0.386043
H	0.603116	-0.881117	-0.298920
H	0.610759	0.867384	-0.318875
H	-2.304209	-0.821044	2.724529
H	-2.281896	0.925357	2.719836
H	1.769221	0.033399	4.068060

GaEt2H

16

-2083.4289820670

C	-0.004039	-0.000016	-0.013916
C	0.049164	0.000064	1.517707

Ga	1.760323	-0.000004	-0.941468
C	3.461866	0.000778	0.097767
C	4.752095	-0.000401	-0.728051
H	1.811272	-0.000501	-2.530513
H	0.577978	-0.882356	1.906367
H	0.578031	0.882493	1.906274
H	-0.955660	0.000115	1.968457
H	5.651976	0.000296	-0.092904
H	4.814755	-0.883102	-1.380506
H	4.814938	0.880638	-1.382730
H	3.426313	0.874316	0.771168
H	3.426011	-0.871110	0.773270
H	-0.565356	0.872965	-0.388054
H	-0.565372	-0.873012	-0.387981

GaEt2radical

15

-2082.8035811270

Ga	0.007241	0.016538	0.004989
C	0.006724	0.000733	2.038318
C	1.818476	0.006282	-0.919108
C	1.829293	0.022641	-2.446030
C	-1.348928	0.004923	2.741167
H	1.306497	-0.849807	-2.863180
H	1.327040	0.915801	-2.844153
H	2.853451	0.015124	-2.851916
H	-1.245653	-0.004039	3.837971
H	-1.938686	0.893977	2.476142
H	-1.951028	-0.871727	2.462903
H	0.614372	0.876544	2.325552
H	0.602021	-0.887766	2.312094
H	2.351747	0.877915	-0.501099
H	2.331514	-0.886256	-0.520290

EtGaC2H4

14

-2082.1748186060

C	-0.016607	0.006097	-0.018060
C	0.034436	0.003649	1.512747
Ga	1.716880	-0.011321	-0.950654

C	2.946881	-0.087184	-2.285785
C	3.827466	1.024386	-2.797229
H	3.426147	2.023814	-2.577487
H	4.857077	0.993698	-2.400536
H	3.915942	0.955330	-3.895880
H	-0.978934	0.012397	1.942126
H	0.550072	-0.885216	1.900535
H	0.566045	0.882015	1.903055
H	-0.569410	-0.866447	-0.401979
H	-0.553731	0.889405	-0.399449
H	3.330474	-1.103815	-2.443761

GaEtH2

10

-2004.8737720130

Ga	0.010264	0.000562	-0.006681
H	-0.008002	-0.000860	1.575376
C	1.737259	-0.000606	-0.989230
C	1.639889	0.013316	-2.517961
H	-1.362985	0.001847	-0.794567
H	1.093043	-0.861524	-2.897580
H	1.106863	0.903007	-2.882425
H	2.632616	0.009726	-2.994235
H	2.313605	0.864972	-0.620618
H	2.301459	-0.880758	-0.636289

HGaEtradical

9

-2004.2471676880

Ga	0.017522	-0.001656	-0.008273
H	-0.015385	0.000655	1.610614
C	1.819876	0.000106	-0.925576
C	1.839009	-0.004782	-2.451584
H	1.333033	-0.890932	-2.859885
H	1.327889	0.875747	-2.865599
H	2.866702	-0.003086	-2.847552
H	2.334877	0.884687	-0.512176
H	2.339802	-0.878824	-0.506367

GaEt_sing

8

-2003.6794457200

Ga	-0.021750	-0.189563	0.024547
C	1.885437	-0.238396	-0.764321
C	2.111085	-1.473884	-1.651043
H	1.968572	-2.411688	-1.091156
H	1.409426	-1.502974	-2.499659
H	3.125239	-1.514161	-2.079616
H	2.054553	0.690280	-1.338601
H	2.613030	-0.216442	0.066947

GaC2H4radical

7

-2003.0274501650

C	0.048350	0.122602	-0.000942
C	0.029218	0.057658	1.491196
Ga	1.686265	0.363628	-1.178388
H	-0.406443	-0.893912	1.850216
H	1.025906	0.157330	1.948079
H	-0.614086	0.847495	1.923109
H	-0.955396	0.021574	-0.446614

GaH3

4

-1926.3181544450

Ga	0.000000	-0.000000	-0.000100
H	0.000000	0.000000	1.575510
H	1.364443	0.000000	-0.788117
H	-1.364443	0.000000	-0.788117

H2Garadical

3

-1925.6898734640

Ga	0.009033	0.000000	0.005191
H	-0.000957	0.000000	1.610990
H	1.401304	0.000000	-0.794968

GaH

2

-1925.1215912030

Ga	0.000000	0.000000	0.002711
H	0.000000	0.000000	1.701799

H2PBu

	16		
	-500.0860307843		
H	-0.010708	-0.008076	0.019461
C	-0.003819	-0.006996	1.118061
H	1.048040	-0.013736	1.450054
H	-0.459134	0.932911	1.459057
C	-0.745069	-1.222480	1.681672
C	-0.092705	-2.519283	1.180803
H	-0.095860	-2.573056	0.082646
H	0.955506	-2.565798	1.515602
H	-0.610968	-3.407921	1.567643
C	-0.727210	-1.188169	3.216824
H	0.311863	-1.215812	3.580883
H	-1.193171	-0.270695	3.604032
H	-1.258973	-2.048721	3.646517
P	-2.559999	-1.276764	1.151599
H	-2.340740	-1.000405	-0.237081
H	-2.863582	0.093517	1.440332

HPBuradical

	15		
	-499.4532169001		
H	-0.002141	-0.009787	0.014563
C	-0.002257	-0.006740	1.113763
H	1.045598	-0.013783	1.452346
H	-0.459677	0.934551	1.449924
C	-0.746653	-1.226115	1.678766
C	-0.086966	-2.521274	1.181592
H	-0.101910	-2.588179	0.084754
H	0.966776	-2.551738	1.506085
H	-0.591749	-3.409545	1.585729
C	-0.735092	-1.183783	3.214315
H	0.305512	-1.186646	3.579964
H	-1.222665	-0.276728	3.598088
H	-1.247531	-2.055695	3.643592
P	-2.525128	-1.148219	1.060737

H	-2.935401	-2.355693	1.726672

PBu_triplett

	14		
	-498.8282814328		
P	-0.000125	0.000000	-0.348455
C	-0.000018	0.000000	1.526729
C	1.455371	-0.000000	2.023630
C	-0.727675	1.260388	2.023623
C	-0.727675	-1.260388	2.023623
H	-0.736370	-1.275510	3.126339
H	-1.770113	-1.286948	1.677445
H	-0.229523	-2.176465	1.677356
H	-0.736370	1.275510	3.126339
H	-0.229523	2.176465	1.677356
H	-1.770113	1.286948	1.677445
H	1.472722	0.000000	3.126374
H	1.999706	-0.889481	1.677502
H	1.999706	0.889481	1.677502

H3P

	4		
	-342.9854494715		
P	0.002820	0.003049	0.002687
H	0.004650	0.004699	1.433405
H	1.432294	0.004539	-0.056848
H	-0.058935	1.431192	-0.056633

H2Pradical

	3		
	-342.3499143345		
P	0.003934	0.000000	0.003879
H	0.003324	0.000000	1.439219
H	1.439124	0.000000	-0.016758

HP

	2		
	-341.7221444147		
P	0.000000	0.000000	0.005751
H	0.000000	0.000000	1.445907

C4H10

14

-158.2854741665

C	-0.002774	0.005456	-0.001855
C	0.001095	-0.001798	1.529095
C	1.425354	-0.001889	-0.553528
C	-0.809293	-1.173139	-0.553447
H	1.431674	0.031841	-1.652430
H	2.003124	0.857760	-0.184725
H	0.554934	0.857528	1.933601
H	-1.020583	0.032514	1.933773
H	0.480471	-0.917268	1.910023
H	-1.844900	-1.159185	-0.184491
H	-0.357611	-2.128898	-0.244387
H	-0.840788	-1.159246	-1.652345
H	1.954478	-0.917104	-0.244534
H	-0.491251	0.937566	-0.336019

Nbutane

14

-158.2837031436

C	-0.017138	0.029674	-0.059161
C	-0.020896	0.036237	1.468848
H	1.010232	0.023368	-0.452584
H	-0.525615	-0.863094	-0.452529
H	0.465174	0.955110	1.837571
H	-1.059691	0.075255	1.837591
H	-0.526458	0.912074	-0.470489
C	0.680293	-1.179025	2.077256
C	0.676415	-1.172218	3.605259
H	0.193607	-2.097613	1.709034
H	1.719144	-1.217387	1.709001
H	1.185630	-2.054629	4.016962
H	1.185048	-0.279551	3.998814
H	-0.350938	-1.165896	3.998889

C4H9radical

13

-157.6297195014

C	0.000032	-0.000492	0.010780
C	-0.003048	-0.015540	1.500857
C	1.300233	0.000369	2.223208
C	-1.230405	0.424808	2.222131
H	-1.310093	1.532642	2.268336
H	-2.146321	0.071014	1.725253
H	0.172280	1.020446	-0.393989
H	0.798620	-0.634319	-0.403349
H	-0.961923	-0.337509	-0.403977
H	2.051840	-0.630900	1.725707
H	1.195157	-0.339086	3.264724
H	1.735622	1.022075	2.272026
H	-1.241473	0.071926	3.264394

C4H8

12

-157.0636885234

C	-0.000711	0.000212	0.000407
C	-0.001279	-0.000122	1.503235
C	1.134034	0.000161	-0.711947
C	-1.354365	0.000574	-0.652294
H	1.120828	0.000519	-1.802758
H	2.110701	-0.000268	-0.225987
H	-0.532407	0.882028	1.895819
H	-0.534323	-0.881231	1.895536
H	1.016285	-0.001255	1.913103
H	-1.939321	0.881750	-0.342891
H	-1.938889	-0.881483	-0.344563
H	-1.281065	0.001599	-1.746844

C2H6

8

-79.7363583008

C	-0.000016	-0.000019	0.003034
C	0.000012	-0.000023	1.530375
H	1.022713	-0.000167	-0.399358
H	-0.511521	-0.885666	-0.399311
H	0.511611	0.885568	1.932724
H	-1.022711	0.000226	1.932788
H	-0.511270	0.885775	-0.399305

H	0.511167	-0.885875	1.932719

C2H5radical

	7		
	-79.0689847665		
C	-0.000222	-0.000413	0.002743
C	-0.003255	-0.005852	1.485135
H	1.019979	-0.000649	-0.408530
H	-0.499813	-0.896991	-0.418215
H	-0.537259	0.867024	-0.408499
H	-0.848285	0.390277	2.045974
H	0.778658	-0.515308	2.046019

C2H4

	6		
	-78.5042915388		
C	0.000000	0.000000	0.005728
C	0.000000	-0.000000	1.338472
H	0.928304	-0.000000	-0.567736
H	-0.928304	-0.000000	-0.567736
H	-0.928293	0.000000	1.911926
H	0.928293	0.000000	1.911926

CH3radical

	4		
	-39.7900020184		
C	-0.000222	-0.000415	0.002744
H	-0.002444	-0.004398	1.088906
H	0.941537	-0.000037	-0.538421
H	-0.939759	0.003197	-0.542258

H2

	2		
	-1.1663651729		
H	0.000000	0.000000	0.008523
H	0.000000	0.000000	0.758969

Transition State Structures

AG11

	22		

		-2161.914820	
C	-1.847611	-1.062274	0.167494
C	-2.974086	-0.125181	-0.271940
Ga	-0.000015	-0.322456	-0.055618
C	0.000049	1.658417	0.891673
C	0.000021	1.963411	-0.485411
C	1.847587	-1.062276	0.167467
C	2.974057	-0.125149	-0.271910
H	2.885215	0.143531	-1.334608
H	2.974953	0.813982	0.302074
H	3.966448	-0.583082	-0.133069
H	-0.000031	0.573150	-1.497462
H	-0.917689	2.288130	-0.975661
H	0.917719	2.288093	-0.975706
H	-3.966473	-0.583120	-0.133091
H	-2.974999	0.813977	0.302000
H	-2.885232	0.143451	-1.334650
H	-1.968328	-1.345429	1.224222
H	-1.884152	-1.999605	-0.408568
H	-0.928001	1.734647	1.456488
H	0.928127	1.734606	1.456446
H	1.884148	-1.999580	-0.408637
H	1.968296	-1.345476	1.224184

AG12

	16		
	-2083.367770		
C	-0.121262	-0.396714	-0.018805
C	-0.075261	-0.119300	1.484769
Ga	1.561382	0.042191	-0.997798
C	3.218978	-0.905912	0.070870
C	3.368609	0.464437	0.373355
H	2.015334	0.033417	-2.495162
H	0.712017	-0.701847	1.986994
H	0.120618	0.942127	1.695118
H	-1.025756	-0.379341	1.977070
H	2.176758	1.470719	-0.343866
H	3.065384	0.845211	1.348595
H	4.129694	1.058291	-0.132215
H	2.777199	-1.570574	0.812089

H	3.857087	-1.361336	-0.683586
H	-0.923809	0.187569	-0.493375
H	-0.351098	-1.454900	-0.213684

AG13
10
-2004.826600

C	1.336054	-0.774959	0.000047
C	1.481974	0.629967	0.000115
Ga	-0.709697	-0.028486	-0.000110
H	-1.242230	-0.265267	1.443306
H	-1.242185	-0.265968	-1.443375
H	1.751948	1.151164	-0.918312
H	1.751465	1.151127	0.918681
H	0.003302	1.492297	-0.000478
H	1.472480	-1.325704	-0.928210
H	1.472089	-1.325769	0.928300

AG14
8
-2003.646230

C	0.002391	-0.000021	-0.010060
Ga	0.004261	0.001635	2.264158
C	1.385111	0.000123	0.167321
H	1.706147	0.000724	2.100656
H	1.963318	-0.921202	0.117751
H	1.963114	0.921558	0.116994
H	-0.525755	-0.921419	-0.258388
H	-0.525831	0.920951	-0.259772

AG15
22
-2161.864940

C	-0.143761	0.082583	0.520278
Ga	1.785981	-0.229919	1.580512
C	3.434328	0.961390	1.142892
C	4.661684	0.218541	0.628648
C	-1.109284	-1.054969	0.758110
C	1.688194	-0.596104	-0.862333
C	2.041122	0.418247	-1.897183

H	1.165241	1.041698	-2.144067
H	2.853240	1.083047	-1.574108
H	2.358411	-0.046759	-2.848729
H	4.477266	-0.271615	-0.339782
H	5.519917	0.893342	0.479278
H	4.984791	-0.564666	1.330786
H	-2.138694	-0.745126	0.507416
H	-0.878677	-1.922637	0.123476
H	-1.085621	-1.396353	1.800822
H	-0.255434	0.525993	-0.474215
H	-0.278794	0.905386	1.243725
H	3.111725	1.750974	0.446780
H	3.651276	1.439029	2.109833
H	0.888638	-1.288575	-1.133008
H	2.535360	-1.146316	-0.407455

AG17
10
-2004.799620

C	-0.607514	0.544548	1.042911
Ga	1.715203	-0.186195	0.808717
C	-0.656718	-0.888072	0.768584
H	1.033012	1.004818	0.020956
H	1.797305	-0.358888	2.380474
H	0.382623	-1.358331	0.315811
H	-0.827002	-1.518665	1.647095
H	-1.302249	-1.179549	-0.069881
H	-1.027511	1.229378	0.309930
H	-0.631140	0.887418	2.074488

AG19
10
-2004.791130

C	-0.219663	0.230132	0.639355
C	-1.004302	-1.062330	0.856024
Ga	1.759994	0.014218	0.858941
H	2.042388	1.823024	0.489344
H	3.070217	0.884276	0.783147
H	-0.705189	-1.846017	0.146508
H	-0.855729	-1.466222	1.866910

H	-2.084243	-0.891989	0.723980
H	-0.370934	0.643644	-0.368008
H	-0.520228	1.020768	1.341536

AG204

	-1926.237590		
Ga	-0.000808	0.000000	0.000027
H	-0.001268	-0.000000	1.562202
H	1.790514	0.000000	0.369952
H	1.165194	-0.000000	-1.045495

BG1524

	-2163.113440		
C	0.975617	1.002698	-2.024817
C	-0.288845	1.842659	-1.867779
Ga	1.716290	-0.069107	-0.186031
C	0.164102	-0.275157	1.037121
C	-0.231419	0.993054	1.800136
C	3.285502	-1.152181	-0.740661
C	4.247319	-0.416898	-1.677643
H	5.117341	-1.038169	-1.941407
H	4.630093	0.505898	-1.218553
H	3.756220	-0.129484	-2.617981
H	-1.105576	0.821306	2.447637
H	0.588061	1.351648	2.438139
H	-0.486695	1.815340	1.117836
H	-0.742786	2.100976	-2.836718
H	-1.052428	1.313856	-1.280239
H	-0.081394	2.789390	-1.345238
H	0.749450	0.036727	-2.506713
H	1.706473	1.485128	-2.692752
H	0.405132	-1.087313	1.739668
H	-0.680825	-0.640409	0.431938
H	3.807083	-1.485055	0.169102
H	2.901430	-2.066626	-1.220044
H	2.353282	1.604783	0.064190
H	1.832408	1.490631	-0.847300

BG16

18

	-2084.559640		
C	0.816086	0.774260	-2.174410
Ga	1.650437	0.567311	-0.105083
C	3.235057	-0.619113	-0.153912
C	4.181710	-0.332638	-1.322765
C	-0.452021	1.615482	-2.293852
H	0.431779	0.815660	0.834243
H	5.056473	-1.001012	-1.311117
H	4.557237	0.700203	-1.293520
H	3.682093	-0.467861	-2.292454
H	-0.950641	1.481253	-3.265614
H	-1.176149	1.357311	-1.509123
H	-0.234542	2.689452	-2.185930
H	0.585725	-0.302723	-2.215362
H	1.508125	0.947855	-3.013441
H	3.761157	-0.524565	0.807354
H	2.865924	-1.655714	-0.197726
H	2.226858	2.199385	-0.564681
H	1.695837	1.706415	-1.344821

BG17

12

	-2006.005060		
C	0.899693	0.921297	-2.209024
C	-0.496928	1.535418	-2.265439
Ga	1.859571	0.864128	-0.197559
H	3.264026	0.213283	-0.321555
H	0.695456	0.825924	0.829411
H	-1.005838	1.315103	-3.215610
H	-1.131173	1.156767	-1.452235
H	-0.462767	2.630908	-2.160964
H	0.853147	-0.177749	-2.254244
H	1.522382	1.214984	-3.068424
H	2.076763	2.571355	-0.620025
H	1.614113	1.997469	-1.399608

BG18

10

	-2004.820170		
C	0.075888	0.142156	2.167328
C	0.707281	-1.189363	2.574881
Ga	-0.424993	-0.345372	-0.087037
H	0.821997	0.558209	0.908988
H	1.251794	0.562430	-0.014461
H	-0.963134	0.231394	2.511126
H	0.616789	0.989691	2.620682
H	0.926824	-1.241622	3.652626
H	0.055037	-2.044371	2.339209
H	1.664345	-1.360227	2.051769

AP6

16

	-499.993642		
C	0.356405	-0.020454	1.346927
C	-0.536902	-1.180948	1.641025
C	-1.483984	-1.100385	2.700341
C	-0.211677	-2.491271	1.001722
P	-2.974843	-0.343103	0.444485
H	0.645658	0.019308	0.289293
H	1.290631	-0.114120	1.934820
H	-0.110956	0.932482	1.623850
H	0.033267	-2.382748	-0.062622
H	0.682494	-2.926286	1.489936
H	-1.027110	-3.216942	1.110141
H	-1.797635	-2.050996	3.144570
H	-1.307107	-0.308346	3.438073
H	-2.547062	-0.666391	2.193122
H	-4.127222	-0.250407	-0.434583
H	-3.091253	-1.767455	0.489517

BP8

18

	-501.151633		
C	1.501772	-0.259123	1.377282
C	1.274749	0.320059	0.015714
C	1.487383	1.790973	-0.139306
C	1.281623	-0.531469	-1.119505
P	-1.781072	0.817341	0.515731

H	1.050977	0.350521	2.173027
H	2.588781	-0.292930	1.583334
H	1.121462	-1.285379	1.459565
H	0.956793	2.371446	0.629377
H	2.564537	2.019072	-0.021375
H	1.178961	2.151406	-1.128460
H	1.626951	-0.077693	-2.055881
H	1.682055	-1.539657	-0.957547
H	0.106955	-0.806853	-1.410324
H	-0.723468	1.147727	1.412687
H	-1.493758	1.927098	-0.339868
H	-1.017822	-0.856106	-1.415996
H	-1.313078	-0.328286	-0.685321