Electronic Supplementary Information for

Reactions of [Cu(X)(BPEP-Ph)] (X = SbF_6, PF_6) with silyl compounds. Cooperative bond activation involving non-coordinating anions

Y. Nakajima,*[a] T. Tsuchimoto,[b] Y.-H. Chang,[b] K. Takeuchi[b] and F. Ozawa*[b]

[a] *Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology, Higasi, Tsukuba, Ibaraki 305-8565, Japan*

[b] *International Research Center for Elements Science (IRCELS), Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan*

E-mail: yumiko-nakajima@aist.go.jp

Contents

Table S1 Crystallographic data for **1c**, **2b** and **3b**.

Compound	**1c**	**2b**	**3b**
Empirical formula	$C_{87}H_{83}BCuF_{24}NP_2$	$C_{56}H_{71}CuF_5N_2P_2Sb$	$C_{59}H_{80}CuF_6N_2P_2SbSi \cdot Et_2O$
Fw	1734.83	1114.38	11280.69
Crystal system	Monoclinic	Monoclinic	Monoclinic
space group	$P2_1/a$	$P2_1/c$	$P2_1/c$
a (Å)	22.251(2)	16.0869(4)	17.454(8)
b (Å)	17.9388(13)	18.6680(5)	21.139(8)
c (Å)	23.884(3)	18.6526(5)	19.014(8)
α (deg)	90.00	90.00	90.00
β (deg)	116.157(4)	95.9373(12)	98.995(11)
γ (deg)	90.00	90.00	90.00
V (Å^3)	8557.4(14)	5571.5(3)	6929(5)
Z	4	4	4
μ(Mo $K\alpha$) (mm^{-1})	1.347	0.977	1.228
temp (K)	173(2)	173(2)	173(2)
reflections collected	85475	68671	54096
unique reflections	19505 (R_{int} = 0.0997)	6951 (R_{int} = 0.0946)	15699 (R_{int} = 0.1632)
GOF	1.259	1.178	1.301
final R indices ($I > 2\sigma(I)$)	$R1$ = 0.0985, $wR2$ = 0.2337	$R1$ = 0.0717, $wR2$ = 0.1763	$R1$ = 0.1713, $wR2$ = 0.3056
R indices (all data)	$R1$ = 0.1419, $wR2$ = 0.2592	$R1$ = 0.0778, $wR2$ = 0.1808	$R1$ = 0.2854, $wR2$ = 0.3644

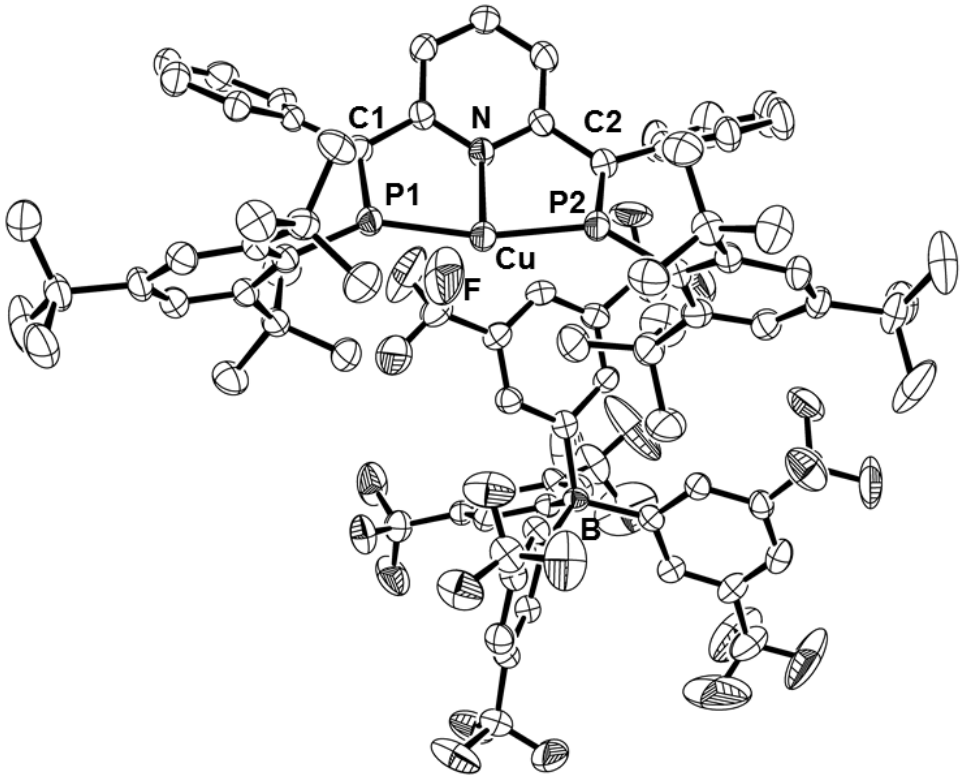


Fig. S1 ORTEP drawing of **1c** with 50% probability ellipsoids. Hydrogen atoms were omitted for clarity.

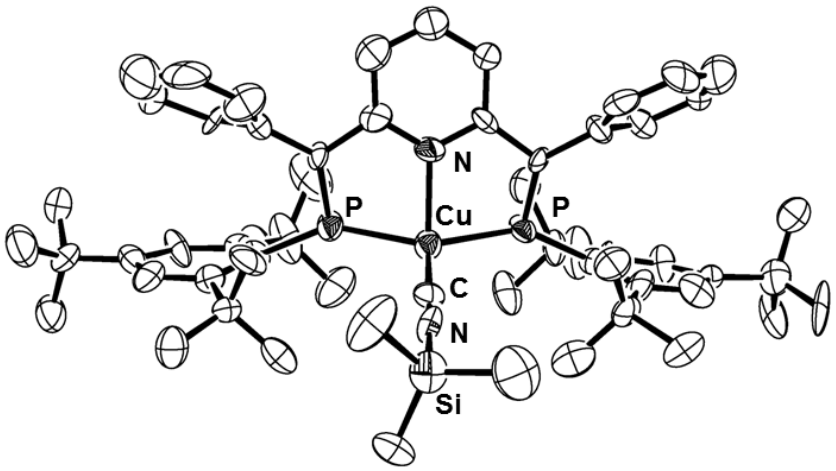
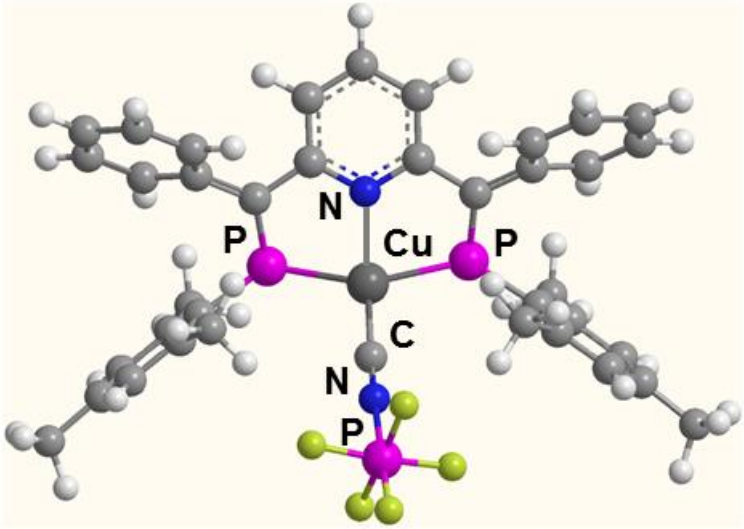
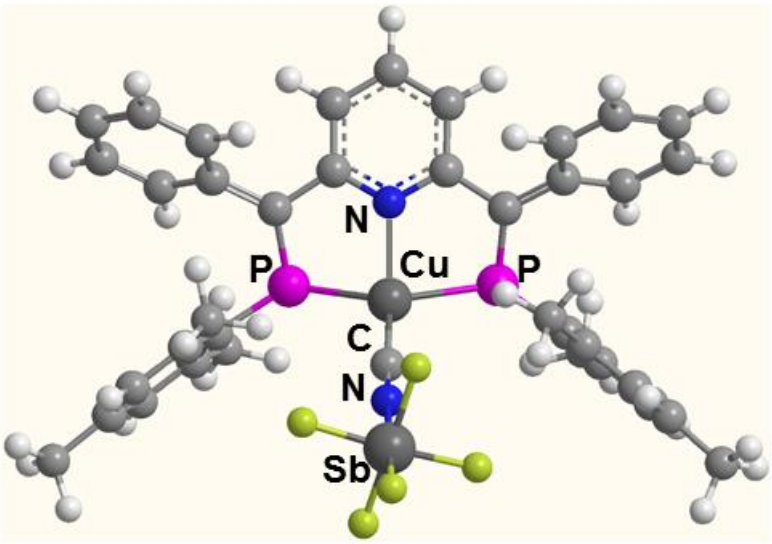


Fig. S2 ORTEP drawing of **3b** with 50% probability ellipsoids. Hydrogen atoms, the SbF_6^- anion and the Et_2O molecule were omitted for clarity.



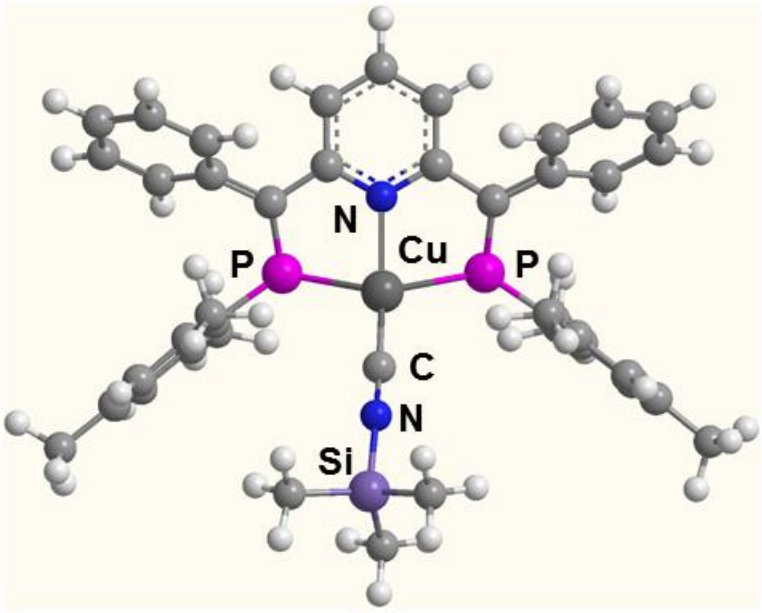
(Energy –3298.77867882 a.u.)

Fig. S3 Optimized structure of [Cu(CN–PF_5)(BPEP-Ph')]. Selected bond distances (Å) and angles (deg): Cu–P = 2.34, 2.35, Cu–N = 2.06, Cu–C = 1.90, C–N = 1.16, N–P = 1.87, N–Cu–C = 138.9, Cu–C–N = 173.8, C–N–P = 172.6.



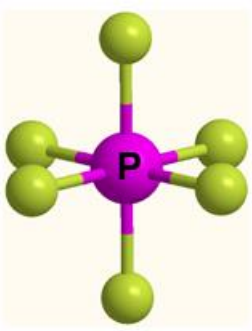
(Energy –2962.86124162 a.u.)

Fig. S4 Optimized structure of [Cu(CN–SbF_5)(BPEP-Ph')]. Selected bond distances (Å) and angles (deg): Cu–P = 2.32 (×2), Cu–N = 2.04, Cu–C = 1.89, C–N = 1.16, N–Sb = 2.13, N–Cu–C = 136.4, Cu–C–N = 175.0, C–N–Sb = 166.6.



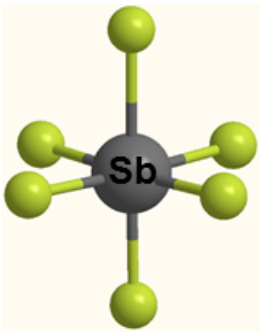
(Energy –2867.20958577 a.u.)

Fig. S5 Optimized structure of a cationic part of [Cu($CNSiMe_3$)(BPEP-Ph')]$^+$. Selected bond distances (Å) and angles (deg): Cu–P = 2.36 (×2), Cu–N = 2.07, Cu–C = 1.90, C–N = 1.17, N–Si = 1.81, N–Cu–C = 145.0, Cu–C–N = 174.8, C–N–P = 178.4.



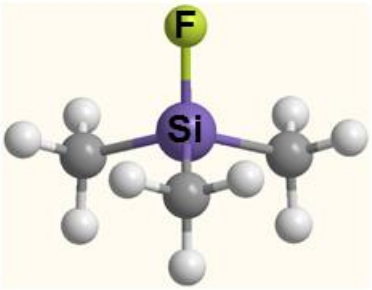
(Energy –940.673693678 a.u.)

Fig. S6 Optimized structure of $\mathbf{PF_6^-}$. Selected bond distance (Å) and angle (deg): P–F = 1.64 (av.), F–P–F = 90.0 (av.).



(Energy –604.749000582 a.u.)

Fig. S7 Optimized structure of $\mathbf{SbF_6^-}$. Selected bond distance (Å) and angle (deg): Sb–F = 1.88 (av.), F–Sb–F = 90.0 (av.).



(Energy –509.111961763 a.u.)

Fig. S8 Optimized structure of $\mathbf{Me_3SiF}$. Selected bond distances (Å): Si–F = 1.63, Si–C = 1.88 (×3).

Table S2. Cartesian coordination of all species

Compund [Cu(CN–PF_5)(BPEP-Ph')]				Compund [Cu(CN–SbF_5)(BPEP-Ph')]			
Atomic Coordinates (Angstroms)				Atomic Coordinates (Angstroms)			
Number	X	Y	Z	Number	X	Y	Z
29	-0.102813	0.831933	-0.851408	29	-0.097310	0.832589	-0.804263
15	2.030191	1.231844	-1.742526	15	1.989802	1.244837	-1.736998
15	-2.351266	1.433988	-1.099141	15	-2.320636	1.424775	-1.060995
7	0.070539	2.808330	-0.293519	7	0.073090	2.786326	-0.237829
6	-0.029904	-0.893274	-0.054285	6	0.042306	-0.850846	0.036763
7	0.071893	-1.890770	0.529579	7	0.174524	-1.836578	0.629708
15	0.326583	-3.366486	1.651721	51	0.566303	-3.348440	2.085289
9	1.742787	-3.588173	0.884580	9	2.209048	-3.650939	1.166566
9	-0.424010	-4.254891	0.530678	9	-0.313500	-4.568458	0.928210
9	1.060564	-2.327667	2.663664	9	1.414050	-1.954873	3.075312
9	0.553044	-4.612436	2.629946	9	0.923275	-4.655903	3.402451
9	-1.109044	-2.985282	2.314031	9	-1.107148	-2.855910	2.850929
6	4.997112	-1.029111	-3.429858	6	4.797301	-1.093905	-3.523442
6	5.567783	-1.738237	-2.361662	6	5.441222	-1.757056	-2.472891
6	3.955467	-0.117210	-3.234193	6	3.780624	-0.169194	-3.294076
6	5.071521	-1.506842	-1.075421	6	5.044960	-1.463930	-1.168872
6	3.471800	0.117499	-1.914328	6	3.407966	0.132937	-1.957112
6	4.029409	-0.599596	-0.821113	6	4.041132	-0.532815	-0.878891
6	-5.870320	-0.531694	-1.828709	6	-5.788932	-0.513897	-1.962546
6	-4.735120	0.275906	-1.957878	6	-4.645197	0.281832	-2.041469
6	4.879205	3.045709	-1.295239	6	4.839987	3.026068	-1.313373
6	6.159026	3.424703	-0.885296	6	6.124027	3.400143	-0.927787
6	-6.181299	-1.180114	-0.624814	6	-6.169523	-1.140864	-0.773148
6	-3.880731	0.463474	-0.834369	6	-3.863069	0.481441	-0.876793
6	2.443217	2.611123	-0.797383	6	2.425402	2.590006	-0.769075
6	3.802558	3.032345	-0.384053	6	3.788174	3.000905	-0.381537
6	6.394523	3.794140	0.444713	6	6.386516	3.752518	0.397063
6	-5.323473	-0.996639	0.465151	6	-5.372154	-0.949669	0.357462
6	-4.171805	-0.196946	0.391170	6	-4.222211	-0.155767	0.337471
6	1.288243	3.432231	-0.403903	6	1.281965	3.404451	-0.346134
6	-2.355959	2.847225	-0.114363	6	-2.341665	2.818574	-0.066205
6	1.402509	4.819666	-0.189809	6	1.401702	4.784656	-0.116214
6	-4.784833	3.510477	0.068741	6	-4.762048	3.487369	0.066350
6	-1.063915	3.549398	-0.073675	6	-1.052337	3.517985	-0.006757
6	4.054477	3.414069	0.953498	6	4.066556	3.362411	0.950977
6	5.337590	3.786078	1.362506	6	5.353548	3.730921	1.335049
6	0.261995	5.570983	0.088325	6	0.267199	5.530888	0.175282
6	-0.979478	4.939010	0.139356	6	-0.970816	4.900584	0.220323
6	-5.858651	4.017383	0.803404	6	-5.844995	3.995325	0.778714
6	-3.501820	3.401043	0.644718	6	-3.496104	3.373963	0.665745
6	-5.677967	4.422754	2.131475	6	-5.689190	4.396892	2.106060
6	-3.334003	3.819948	1.984590	6	-3.352547	3.787480	2.005336
6	-4.411654	4.320775	2.719363	6	-4.439087	4.289711	2.717051
1	5.369222	-1.193915	-4.437635	1	5.086642	-1.311789	-4.545424
1	-6.524283	-0.660109	-2.687172	1	-6.390616	-0.655055	-2.853415
1	5.492975	-2.055062	-0.237093	1	5.512691	-1.986381	-0.342215

1	4.705019	2.767956	-2.328263	1	4.641657	2.760730	-2.342788
1	6.971825	3.433576	-1.604235	1	6.919338	3.417925	-1.661735
1	-4.933591	3.207404	-0.961087	1	-4.889561	3.186020	-0.964116
1	7.390663	4.084746	0.762123	1	7.386384	4.039874	0.695652
1	2.374631	5.289021	-0.262087	1	2.372525	5.250686	-0.191656
1	-5.544294	-1.497965	1.403652	1	-5.641168	-1.442841	1.284356
1	-6.835673	4.098539	0.338183	1	-6.810217	4.078990	0.296201
1	0.336656	6.642187	0.240280	1	0.342441	6.597689	0.338458
1	-1.883719	5.503310	0.324711	1	-1.874324	5.460483	0.408532
1	3.244425	3.394174	1.675464	1	3.274530	3.325722	1.688254
1	5.512174	4.063230	2.397173	1	5.550638	3.993013	2.366673
1	-6.514497	4.813623	2.701471	1	-6.533225	4.788284	2.659023
1	-2.359242	3.730332	2.453232	1	-2.390293	3.689268	2.492002
1	-4.263209	4.625420	3.750369	1	-4.310785	4.590083	3.749069
6	6.663692	-2.751406	-2.601304	6	6.500284	-2.791793	-2.743347
1	6.241266	-3.743705	-2.809738	1	6.068814	-3.797536	-2.739449
1	7.286324	-2.475426	-3.459169	1	6.970407	-2.639503	-3.716177
1	7.313110	-2.852733	-1.725764	1	7.281443	-2.771687	-1.981438
6	3.538560	-0.489165	0.607211	6	3.687103	-0.319481	0.568949
1	2.914290	0.388549	0.777399	1	4.479468	0.232371	1.082002
1	2.951825	-1.373143	0.882999	1	2.762382	0.237033	0.703611
1	4.386825	-0.434869	1.298627	1	3.563321	-1.276726	1.076044
6	-3.281056	-0.134161	1.614425	6	-3.408840	-0.022846	1.597012
1	-2.567707	-0.968021	1.624442	1	-2.347980	-0.208979	1.423869
1	-2.708649	0.792653	1.676691	1	-3.504517	0.976045	2.029524
1	-3.881839	-0.218326	2.525744	1	-3.736688	-0.743855	2.344786
6	-7.391403	-2.079740	-0.517894	6	-7.381161	-2.032466	-0.719645
1	-8.179847	-1.776902	-1.214906	1	-8.094475	-1.786249	-1.507634
1	-7.128644	-3.120129	-0.752592	1	-7.097271	-3.081530	-0.848717
1	-7.808514	-2.071619	0.494561	1	-7.894428	-1.951444	0.240214
6	-4.460532	0.940096	-3.294093	6	-4.281298	0.919673	-3.360825
1	-4.499462	2.035356	-3.230016	1	-4.340329	2.011497	-3.321832
1	-3.469509	0.678132	-3.685683	1	-3.263024	0.664662	-3.668664
1	-5.201398	0.628228	-4.036257	1	-4.955643	0.583431	-4.148964
6	3.382830	0.606700	-4.438343	6	3.111272	0.495711	-4.473356
1	2.303139	0.439750	-4.541577	1	2.028922	0.336351	-4.469037
1	3.534192	1.692623	-4.381880	1	3.276315	1.577072	-4.487446
1	3.859994	0.256013	-5.358343	1	3.497583	0.092903	-5.410177

Compund $[Cu(CNSiMe_3)(BPEP\text{-}Ph')]^+$				Compund $\mathbf{SbF_6^-}$			
Atomic Coordinates (Angstroms)				Atomic Coordinates (Angstroms)			
Number	X	Y	Z	Number	X	Y	Z
29	-0.017606	0.905111	-0.586994	51	0.369370	-2.983481	3.639041
15	2.104735	1.298965	-1.534877	9	1.620934	-4.083465	2.738209
15	-2.275738	1.457834	-1.004315	9	-1.041231	-4.091414	3.029971
7	0.097472	2.938492	-0.214835	9	1.780131	-1.875513	4.247818
6	-0.028348	-0.827700	0.202908	9	0.543449	-4.056865	5.190191
7	-0.077678	-1.928260	0.598618	9	-0.882537	-1.884417	4.540654
6	5.034732	-1.102270	-3.085405	9	0.195883	-1.909844	2.088116

6	5.714179	-1.615575	-1.970362
6	3.968843	-0.205307	-2.952942
6	5.295224	-1.209413	-0.697168
6	3.571678	0.215440	-1.650972
6	4.237752	-0.306621	-0.508061
6	-5.594490	-0.817443	-1.749423
6	-4.493531	0.034870	-1.894508
6	4.874783	3.244776	-1.353427
6	6.141277	3.742255	-1.040280
6	-6.010125	-1.283881	-0.493844
6	-3.779463	0.453712	-0.734928
6	2.478376	2.771024	-0.724129
6	3.823175	3.305646	-0.414334
6	6.388518	4.305201	0.218064
6	-5.279102	-0.885919	0.633403
6	-4.173730	-0.026100	0.545569
6	1.293439	3.585641	-0.400242
6	-2.340962	2.938184	-0.125812
6	1.363170	4.991889	-0.358196
6	-4.787451	3.548689	-0.131285
6	-1.060495	3.667741	-0.109402
6	4.085696	3.885767	0.849506
6	5.356714	4.373830	1.162224
6	0.199589	5.736588	-0.176170
6	-1.021574	5.075304	-0.064674
6	-5.902404	4.119925	0.484837
6	-3.528288	3.553880	0.506408
6	-5.787931	4.703791	1.752842
6	-3.426653	4.154898	1.783787
6	-4.546479	4.718123	2.400385
1	5.342182	-1.407091	-4.081935
1	-6.139698	-1.124933	-2.637379
1	5.805521	-1.603428	0.177383
1	4.690273	2.824463	-2.335157
1	6.933218	3.697158	-1.780223
1	-4.883295	3.111636	-1.118298
1	7.373622	4.690318	0.458621
1	2.318515	5.480417	-0.494154
1	-5.577782	-1.250705	1.612462
1	-6.858743	4.116457	-0.027141
1	0.240056	6.819717	-0.155729
1	-1.945818	5.628989	0.030066
1	3.293938	3.934923	1.590364
1	5.541143	4.806478	2.139920
1	-6.655989	5.146807	2.229101
1	-2.470824	4.160342	2.297935
1	-4.450471	5.166338	3.383735
6	6.848841	-2.598570	-2.142794
1	6.472614	-3.593450	-2.415767
1	7.531877	-2.284190	-2.939685
1	7.429652	-2.706429	-1.222075
6	3.856151	0.066727	0.908523
1	2.772893	0.030687	1.069009

Compund **PF_6^-**

Atomic Coordinates (Angstroms)

Number	X	Y	Z
15	0.369435	-2.983523	3.639149
9	1.451814	-3.933228	2.859450
9	-0.850453	-3.940438	3.111909
9	1.589276	-2.026648	4.166262
9	0.519307	-3.912661	4.979313
9	-0.713025	-2.033902	4.418793
9	0.219645	-2.054601	2.299123

Compund **Me_3SiF**

Atomic Coordinates (Angstroms)

Number	X	Y	Z
9	-0.002998	-1.961202	0.891449
14	-0.014210	-3.476163	1.497884
6	-1.794641	-3.908908	1.902438
1	-2.213432	-3.215817	2.642142
1	-2.426278	-3.864841	1.006899
1	-1.868739	-4.923637	2.314807
6	1.057531	-3.475139	3.037972
1	0.671131	-2.776509	3.789964
1	1.091745	-4.473036	3.494271
1	2.087286	-3.179050	2.803562
6	0.682854	-4.616090	0.180564
1	0.078990	-4.580360	-0.734342
1	1.709395	-4.335249	-0.084467
1	0.699873	-5.656635	0.530103

1	4.324164	-0.617194	1.622562
1	4.187179	1.081035	1.159804
6	-3.452260	0.344459	1.823774
1	-3.747791	-0.325986	2.636119
1	-2.363414	0.287278	1.719054
1	-3.693427	1.366455	2.137687
6	-7.220711	-2.178327	-0.361652
1	-8.144045	-1.584963	-0.321118
1	-7.312005	-2.859298	-1.214252
1	-7.179819	-2.778705	0.552479
6	-4.105383	0.496388	-3.286270
1	-4.206794	1.582706	-3.403563
1	-3.065553	0.243953	-3.529936
1	-4.743628	0.025102	-4.038874
6	3.282204	0.305931	-4.205082
1	2.204581	0.098148	-4.198147
1	3.398403	1.390359	-4.326532
1	3.703038	-0.169815	-5.095281
14	-0.202716	-3.634771	1.194437
6	-1.821739	-3.691230	2.131597
1	-1.805195	-3.017778	2.996160
1	-2.664451	-3.404709	1.491943
1	-2.011998	-4.706089	2.503128
6	1.301305	-3.875371	2.281168
1	1.302519	-3.174129	3.123401
1	1.314009	-4.891944	2.694203
1	2.229830	-3.733180	1.716627
6	-0.190694	-4.688797	-0.350271
1	-1.038781	-4.453687	-1.003345
1	0.731694	-4.548401	-0.925213
1	-0.259268	-5.751168	-0.083826