Supporting Information

Identification of Second Shell Coordination in Transition Metal Species using Theoretical XANES: Example of Ti-O-(C,Si,Ge) Complexes

*Charles S. Spanjers,[1] Pascal Guillo,[3] T. Don Tilley,[3] Michael J. Janik,[1] and Robert M. Rioux[1,2,]**

[1]Department of Chemical Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA
[2]Department of Chemistry, Pennsylvania State University, University Park, Pennsylvania 16802, USA
[3]Department of Chemistry, University of California, Berkeley, California 94720, USA

*Author to which correspondence should be addressed: rioux@engr.psu.edu

Structural Data for Geometry Optimized Structures

Table S1. XYZ coordinates for DFT-optimized Ti[O^{i}Pr]$_4$.

	x (Å)	*y (Å)*	*z (Å)*	*Distance from Ti (Å)*
Ti	0.000	0.000	0.000	0.000
O	-0.077	1.718	0.561	1.809
O	0.019	-1.090	1.456	1.819
O	1.506	-0.302	-0.991	1.829
O	-1.457	-0.414	-1.025	1.829
C	2.902	-0.012	-1.000	3.070
C	-2.869	-0.222	-1.075	3.071
C	0.148	-2.390	2.015	3.129
H	2.813	1.264	0.758	3.175
C	-0.210	2.878	1.365	3.192
H	-3.125	0.036	1.068	3.303
C	3.388	0.406	0.387	3.435
H	-2.783	1.920	-0.759	3.465
H	3.273	-0.422	1.101	3.479
H	1.448	-3.149	0.455	3.496
C	-3.518	-0.595	0.257	3.577
H	-1.169	-3.340	0.579	3.586
H	3.052	0.835	-1.696	3.590
C	1.446	-3.043	1.550	3.708
C	-3.190	1.210	-1.493	3.724
H	-3.315	-1.643	0.509	3.735
H	-1.659	1.999	2.714	3.757
H	0.957	2.077	3.005	3.776
C	-1.074	-3.236	1.670	3.797
H	-0.160	3.748	0.683	3.813
H	2.314	-2.435	1.839	3.830
H	-3.247	-0.911	-1.853	3.848
H	0.190	-2.258	3.112	3.850
C	-1.569	2.878	2.060	3.871
C	0.946	2.966	2.358	3.905
H	-2.383	2.850	1.325	3.944
H	-2.749	1.437	-2.472	3.967
H	-1.990	-2.771	2.055	3.983
H	1.908	3.026	1.833	4.020
C	3.670	-1.221	-1.528	4.159
H	3.541	-2.080	-0.855	4.195
H	3.315	-1.503	-2.527	4.431
H	4.450	0.691	0.358	4.517
H	-4.607	-0.455	0.209	4.634
H	-4.278	1.360	-1.556	4.751
H	1.559	-4.040	1.998	4.769
H	-0.985	-4.240	2.109	4.837
H	-1.689	3.783	2.672	4.930
H	0.845	3.859	2.990	4.954
H	4.744	-0.991	-1.591	5.101

Table S2. XYZ coordinates for DFT-optimized $Ti[OGeMe_3]_4$.

	x (Å)	*y (Å)*	*z (Å)*	*Distance from Ti (Å)*
Ti	0.000	0.000	0.000	0.000
O	0.078	-1.083	1.459	1.818
O	1.484	-0.214	-1.034	1.822
O	-1.464	-0.370	-1.020	1.822
O	-0.093	1.735	0.561	1.826
Ge	-0.199	3.424	-0.067	3.430
Ge	-2.099	-0.725	-2.669	3.472
Ge	0.137	-1.268	3.251	3.492
Ge	3.232	-0.575	-1.285	3.525
H	0.170	-0.208	-3.699	3.709
H	-2.142	2.646	-1.507	3.723
H	1.310	2.884	-2.054	3.775
H	3.614	-0.538	1.229	3.855
H	1.640	0.773	3.507	3.948
H	-1.682	0.480	3.599	4.002
C	-0.857	0.081	-3.959	4.051
C	1.303	3.683	-1.302	4.118
C	3.961	-1.200	0.426	4.161
C	-1.925	3.588	-0.989	4.191
H	-0.934	1.175	-3.929	4.206
C	1.696	-0.256	3.882	4.244
H	-1.162	-3.098	-2.698	4.270
C	-1.537	-0.543	3.968	4.290
H	3.625	-2.222	0.640	4.300
H	2.254	3.657	-0.755	4.362
H	2.623	-0.720	3.521	4.449
C	-2.167	-2.678	-2.833	4.461
H	-2.385	-1.160	3.645	4.507
H	4.045	1.841	-1.058	4.568
C	4.098	1.091	-1.856	4.629
H	2.799	-2.853	-2.355	4.639
H	-2.829	-3.093	-2.063	4.672
H	-2.730	3.786	-0.270	4.675
C	3.320	-1.945	-2.684	4.691
C	-3.883	0.084	-2.765	4.767
H	3.605	1.492	-2.751	4.774
H	-3.815	1.171	-2.629	4.779
C	0.318	-3.190	3.593	4.815
C	-0.064	4.596	1.498	4.834
H	2.847	-1.576	-3.603	4.855
H	1.235	-3.570	3.125	4.903
H	0.862	4.382	2.045	4.912
H	-0.541	-3.728	3.174	4.926
H	-4.527	-0.330	-1.980	4.952
H	-0.918	4.432	2.167	5.018
H	-1.894	4.404	-1.724	5.094
H	-1.082	-0.262	-4.977	5.100
H	1.215	4.652	-1.811	5.138
H	5.059	-1.180	0.401	5.210
H	1.719	-0.234	4.980	5.274
H	-1.507	-0.527	5.066	5.311
H	-2.545	-2.970	-3.822	5.469
H	5.154	0.900	-2.090	5.634

H	4.367	-2.196	-2.903	5.685
H	-4.339	-0.120	-3.743	5.731
H	-0.056	5.649	1.185	5.772
H	0.366	-3.383	4.673	5.781

Table S3. XYZ coordinates for DFT-optimized $Ti[OSiMe_3]_4$.

	x (Å)	*y (Å)*	*z (Å)*	*Distance from Ti (Å)*
Ti	0.000	0.000	0.000	0.000
O	1.184	-0.149	-1.369	1.816
O	0.324	1.466	1.028	1.819
O	0.082	-1.502	1.023	1.820
O	-1.702	0.102	-0.644	1.823
Si	-3.280	0.306	-0.136	3.297
Si	-0.054	-3.160	1.115	3.351
Si	0.353	2.490	2.338	3.434
Si	1.942	-0.455	-2.816	3.451
H	-2.660	0.354	2.290	3.527
H	-1.619	-3.292	-0.828	3.761
C	-3.393	-0.190	1.677	3.790
H	-3.194	-1.264	1.805	3.880
H	-0.018	0.571	3.875	3.917
H	1.607	-3.516	-0.700	3.929
C	-1.604	-3.698	0.194	4.035
H	-3.004	2.769	0.112	4.087
H	0.027	-1.775	-3.720	4.122
C	0.638	1.454	3.878	4.190
C	1.464	-3.920	0.313	4.196
H	-2.515	-3.354	0.705	4.251
C	1.111	-1.934	-3.628	4.259
H	0.722	1.350	-4.023	4.305
H	-2.139	2.712	2.575	4.308
C	-3.745	2.109	-0.361	4.313
H	1.269	-2.853	-3.045	4.361
C	-1.288	3.400	2.468	4.394
H	1.676	1.096	3.930	4.411
C	1.778	1.069	-3.899	4.416
H	2.373	-3.703	0.891	4.488
H	-1.470	4.027	1.583	4.570
C	3.752	-0.828	-2.485	4.576
H	2.304	1.926	-3.453	4.576
H	3.867	-1.701	-1.827	4.603
C	1.726	3.742	2.085	4.619
C	-4.401	-0.787	-1.167	4.621
H	-4.107	-1.844	-1.099	4.634
H	2.704	3.253	1.976	4.669
C	-0.168	-3.641	2.925	4.673
H	4.253	0.025	-2.005	4.701
H	-3.800	2.373	-1.427	4.702
H	1.544	4.341	1.181	4.756
H	-1.051	-3.193	3.401	4.782
H	0.721	-3.308	3.479	4.855
H	-4.392	0.017	2.088	4.863
H	-4.379	-0.496	-2.227	4.938
H	-1.657	-4.794	0.122	5.074

H	1.367	-5.012	0.228	5.200
H	0.431	2.027	4.793	5.222
H	-4.724	2.325	0.092	5.266
H	1.513	-2.109	-4.637	5.314
H	-1.286	4.062	3.347	5.418
H	2.202	0.896	-4.899	5.445
H	-5.442	-0.706	-0.818	5.548
H	4.284	-1.044	-3.424	5.582
H	1.786	4.435	2.938	5.612
H	-0.244	-4.733	3.035	5.628

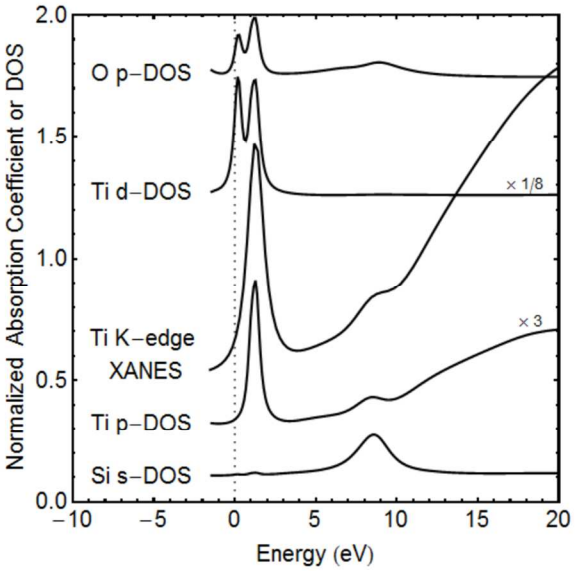

Figure S1. Theoretical Ti K-edge XANES for $Ti[OSiMe_3]_4$ and corresponding partial density of states for O p-DOS, Ti d-DOS, Ti p-DOS, and Ge s-DOS. The energy is relative to the Fermi level (-7.725 eV) calculated with FEFF9. The spectra are shifted vertically for clarity.

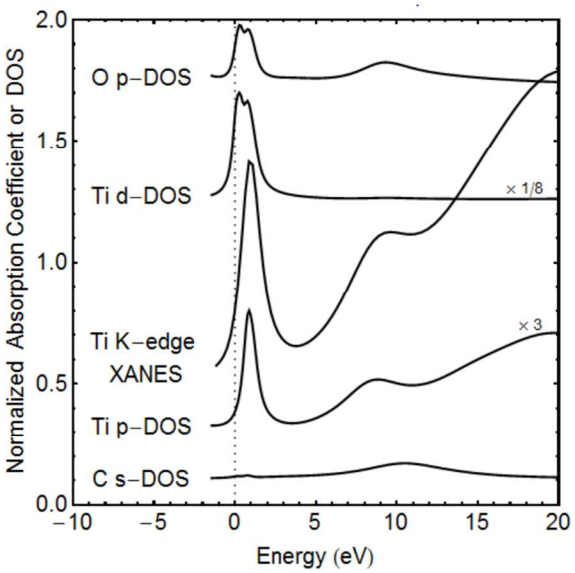

Figure S2. Theoretical Ti K-edge XANES for Ti[O^{i}Pr]$_4$ and corresponding partial density of states for O p-DOS, Ti d-DOS, Ti p-DOS, and Ge s-DOS. The energy is relative to the Fermi level (-7.725 eV) calculated with FEFF9. The spectra are shifted vertically for clarity.