Computational analysis of M-O covalency in $M(OC_6H_5)_4$ (M = Ti, Zr, Hf, Ce, Th, U)

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Supplementary Information

Table SI1: Benchmarking data, employing the Stuttgart-Bonn small-core relativistic effective core potential for U, to replace 60 core electrons with the associated segmented valence basis set, and cc-pVTZ basis sets on all other atoms.

$U(N'')_3$, $N'' = N(SiMe_3)_2$		Bond Distances, Å			Bond Angles			Out of plane displacement[a]	RMSD
Functional		**U-N**	**N-Si**	**U···C**	**N-U-N**	**Si-N-Si**	**U-N-Si**		
PBE	-	2.292	1.754	3.092	114.73	123.03	118.36	1.24	0.153
PBE	aug	2.291	1.754	3.093	114.69	122.89	118.43	1.24	0.156
PBE	D3	2.276	1.750	3.073	114.17	123.99	117.85	1.24	0.129
PBE	D3 + aug	2.276	1.749	3.074	114.15	123.88	117.92	1.24	0.132
PBE	D3BJ	2.273	1.746	3.039	113.15	123.86	117.86	1.25	0.128
PBE	D3BJ + aug	2.271	1.746	3.051	113.69	123.93	117.88	1.24	0.131
PBE0	-	2.303	1.733	3.069	115.73	124.15	117.82	1.22	0.111
PBE0	aug	2.303	1.732	3.072	115.74	124.03	117.89	1.22	0.113
PBE0	D3	2.287	1.728	3.055	115.42	125.17	117.31	1.22	0.097
PBE0	D3 + aug	2.287	1.728	3.057	115.41	125.04	117.38	1.22	0.098
PBE0	D3BJ	2.283	1.726	3.034	115.14	125.41	117.16	1.22	0.086
PBE0	D3BJ + aug	2.284	1.726	3.036	115.13	125.25	117.24	1.22	0.085
Experiment[†]		2.320(4)	1.713(1)	3.05	116.24(7)	125.8(2)	117(4.5)	1.23	-

[†]J. L. Stewart, R. A. Andersen, Polyhedron, 1998, 17, 953. [a]Plane formed by three N atoms.

$U(ODtbp)_3$, ODtbp = *O*-2,6-^{t}Bu$_2$C$_6$H$_3$		Bond Distances, Å			Bond Angles			Out of plane displacement[a]	RMSD
Functional		**U-O**	**O-C**	**U···C**	**O-U-O**	**U-O-C**	**U-O-Oi**		
PBE	-	2.139	1.359	3.672	115.35	170.16	32.32	1.14	0.256
PBE	aug	2.139	1.359	3.671	115.35	170.18	32.32	1.14	0.256
PBE	D3	2.128	1.355	3.598	113.39	169.07	33.31	1.17	0.263
PBE	D3 + aug	2.128	1.355	3.596	113.39	169.10	33.31	1.17	0.263
PBE	D3BJ	2.126	1.354	3.561	112.98	168.31	33.51	1.17	0.253
PBE	D3BJ + aug	2.126	1.354	3.559	112.98	168.34	33.51	1.17	0.253
PBE0	-	2.143	1.343	3.584	114.43	168.48	32.78	1.16	0.234
PBE0	aug	2.143	1.343	3.584	114.44	168.54	32.78	1.16	0.235
PBE0	D3	2.132	1.340	3.470	111.62	166.71	34.19	1.20	0.244
PBE0	D3 + aug	2.132	1.340	3.470	111.61	166.78	34.20	1.20	0.245
PBE0	D3BJ	2.131	1.339	3.431	111.33	165.71	34.34	1.20	0.227
PBE0	D3BJ + aug	2.131	1.339	3.433	111.35	165.83	34.33	1.20	0.228
Experiment[†]		2.164	1.353	3.227	106.80	158.36	36.60	1.29	-

[†]Unpublished. [a]Plane formed by three O atoms.

Table SI2: QTAIM metrics for the $M(OC_6H_5)_4$ systems at *r*(M-O) – 0.12 Å. Bond critical point metrics for the M-O bond, and integrated properties are presented.

System	*r*(M-O), Å	*q*(M)	*q*(O)	ρ_{BCP}	ε_{BCP}	$\nabla^2\rho_{BCP}$	H_{BCP}	δ(M,O)
$Ti(OC_6H_5)_4$	1.665	2.30	-1.21	0.198	0.01	1.067	-0.087	0.831
$Zr(OC_6H_5)_4$	1.817	2.68	-1.28	0.160	0.01	0.853	-0.063	0.749
$Hf(OC_6H_5)_4$	1.799	2.71	-1.29	0.177	0.01	1.041	-0.066	0.731
$Ce(OC_6H_5)_4$	1.966	2.50	-1.22	0.147	0.01	0.526	-0.066	0.904
$Th(OC_6H_5)_4$	2.027	2.84	-1.29	0.138	0.02	0.491	-0.061	0.824
$U(OC_6H_5)_4$	1.968	2.62	-1.25	0.165	0.10	0.598	-0.082	0.976

All QTAIM metrics are presented in atomic units (au).

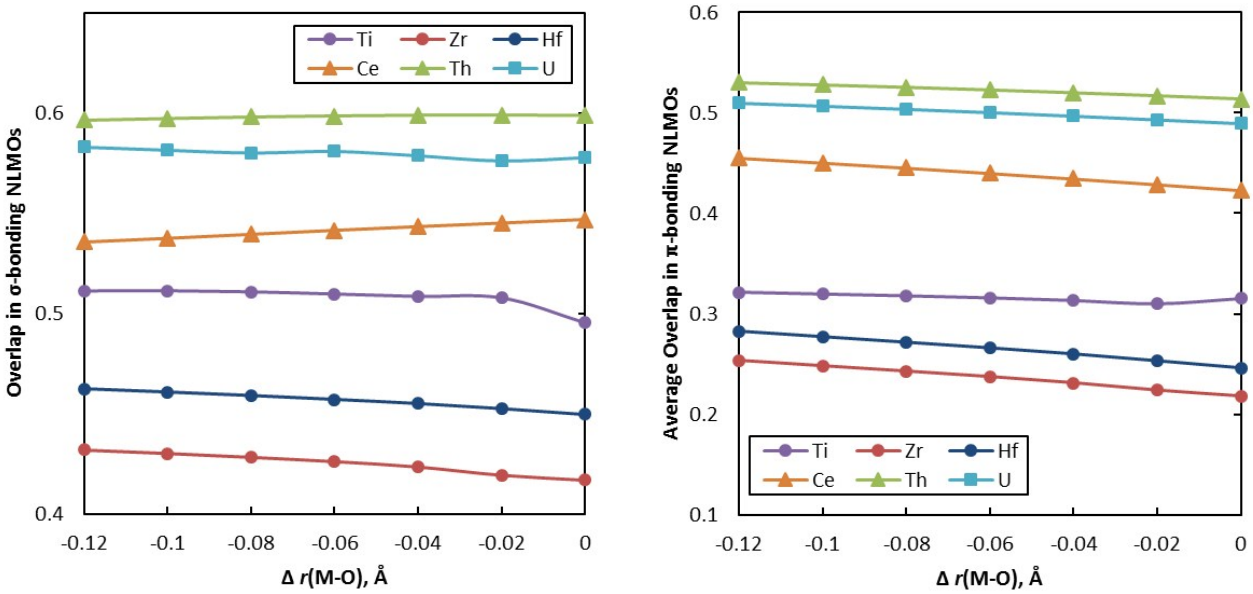
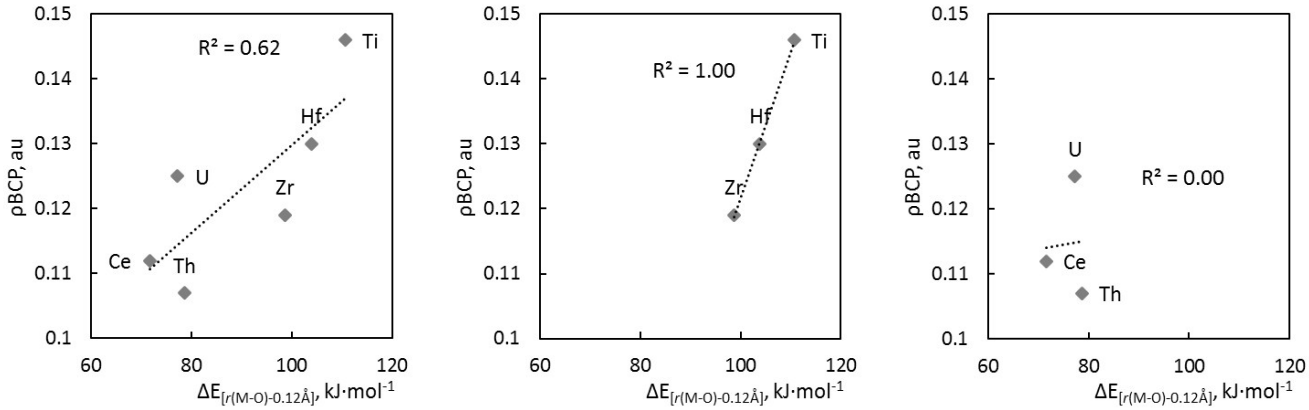


Figure SI1: Overlap integrals for the (a) σ and (b) average π M-O bonding NLMOs with changes in *r*(M-O) in $M(OC_6H_5)_4$.

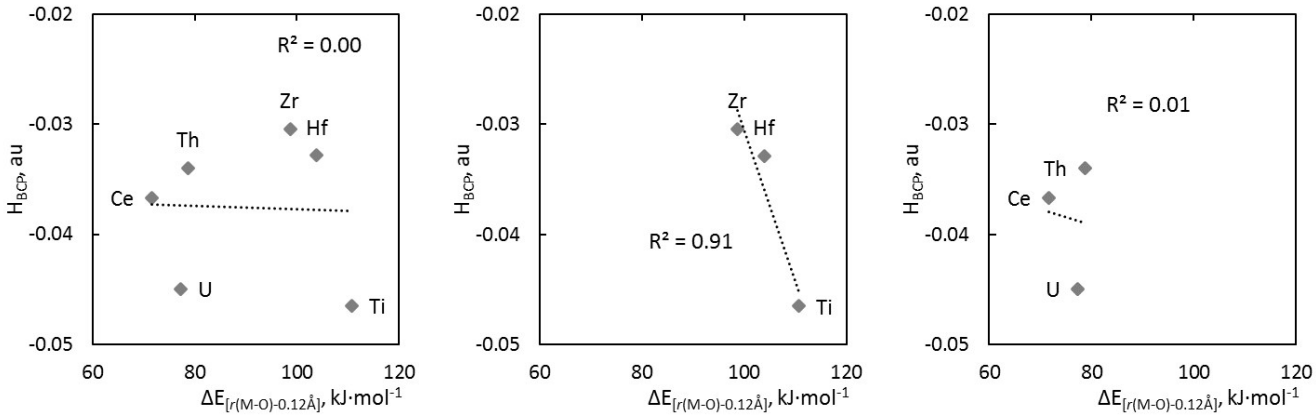
Table SI3: QTAIM and NBO atomic charges with changes in *r*(M-O) in $M(OC_6H_5)_4$.

		QTAIM atomic charge, au			NBO atomic charge, au		
		***q*(M)**	***q*(O)**	***q*(M) - *q*(O)**	***q*(M)**	***q*(O)**	***q*(M) - *q*(O)**
$Ti(OC_6H_5)_4$:	Optimized	2.327	-1.228	1.099	1.703	-0.675	1.027
	-0.02 Å	2.327	-1.226	1.101	1.681	-0.669	1.012
	-0.04 Å	2.324	-1.223	1.101	1.657	-0.662	0.995
	-0.06 Å	2.320	-1.220	1.100	1.634	-0.655	0.979
	-0.08 Å	2.314	-1.217	1.097	1.609	-0.648	0.961
	-0.10 Å	2.308	-1.213	1.095	1.583	-0.640	0.943
	-0.12 Å	2.299	-1.208	1.091	1.554	-0.631	0.923
$Zr(OC_6H_5)_4$:	Optimized	2.681	-1.293	1.388	2.657	-0.893	1.764
	-0.02 Å	2.683	-1.293	1.391	2.645	-0.890	1.755
	-0.04 Å	2.684	-1.292	1.393	2.631	-0.886	1.745
	-0.06 Å	2.685	-1.290	1.394	2.615	-0.881	1.734
	-0.08 Å	2.684	-1.288	1.396	2.596	-0.875	1.720
	-0.10 Å	2.683	-1.286	1.397	2.575	-0.869	1.706
	-0.12 Å	2.680	-1.283	1.397	2.552	-0.863	1.690
$Hf(OC_6H_5)_4$:	Optimized	2.742	-1.308	1.434	2.648	-0.891	1.758
	-0.02 Å	2.740	-1.307	1.433	2.631	-0.886	1.745
	-0.04 Å	2.737	-1.305	1.432	2.612	-0.881	1.731
	-0.06 Å	2.733	-1.303	1.430	2.590	-0.875	1.716
	-0.08 Å	2.728	-1.301	1.427	2.567	-0.868	1.699
	-0.10 Å	2.722	-1.297	1.424	2.541	-0.861	1.681
	-0.12 Å	2.715	-1.294	1.421	2.513	-0.853	1.661
$Ce(OC_6H_5)_4$:	Optimized	2.488	-1.240	1.248	2.212	-0.790	1.423
	-0.02 Å	2.490	-1.237	1.253	2.194	-0.784	1.410
	-0.04 Å	2.493	-1.235	1.258	2.174	-0.778	1.396
	-0.06 Å	2.495	-1.233	1.262	2.151	-0.771	1.380
	-0.08 Å	2.496	-1.230	1.266	2.127	-0.764	1.363
	-0.10 Å	2.497	-1.227	1.270	2.100	-0.756	1.344
	-0.12 Å	2.498	-1.224	1.273	2.071	-0.748	1.324
$Th(OC_6H_5)_4$:	Optimized	2.841	-1.305	1.537	2.692	-0.898	1.795
	-0.02 Å	2.841	-1.303	1.538	2.674	-0.893	1.781
	-0.04 Å	2.841	-1.301	1.539	2.653	-0.887	1.766
	-0.06 Å	2.840	-1.300	1.541	2.629	-0.880	1.749
	-0.08 Å	2.839	-1.298	1.542	2.603	-0.873	1.731
	-0.10 Å	2.839	-1.296	1.543	2.575	-0.865	1.710
	-0.12 Å	2.838	-1.293	1.545	2.543	-0.856	1.688
$U(OC_6H_5)_4$:	Optimized	2.635	-1.266	1.369	2.248	-0.800	1.449
	-0.02 Å	2.632	-1.264	1.368	2.219	-0.792	1.426
	-0.04 Å	2.630	-1.262	1.368	2.186	-0.784	1.402
	-0.06 Å	2.627	-1.260	1.368	2.150	-0.775	1.375
	-0.08 Å	2.624	-1.257	1.367	2.110	-0.765	1.346
	-0.10 Å	2.621	-1.255	1.367	2.068	-0.754	1.314
	-0.12 Å	2.618	-1.252	1.367	2.021	-0.742	1.280



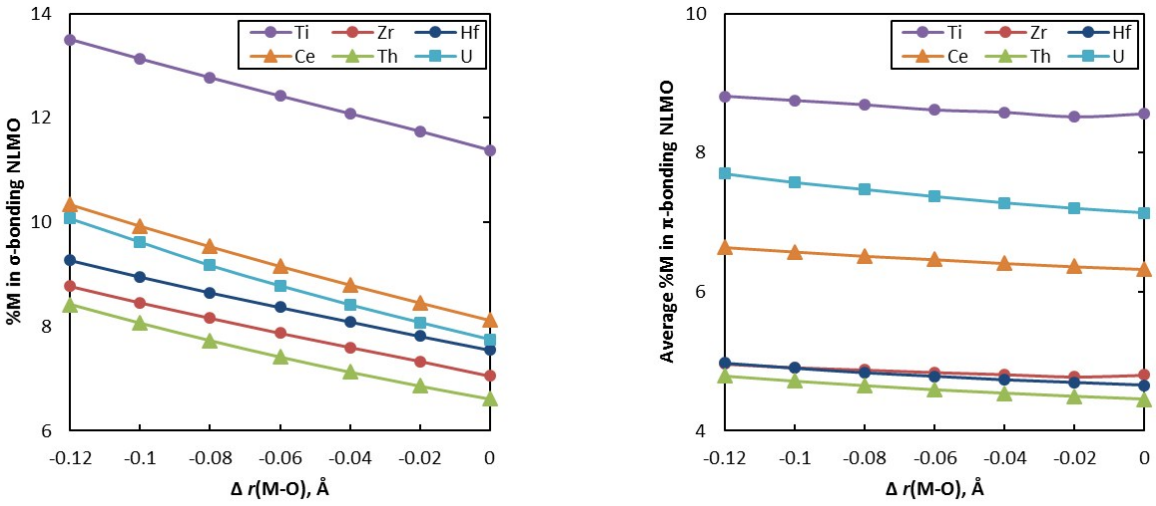
(a) (b) (c)

Figure SI2: Correlation between the deformation energy and ρ_{BCP} for (a) all $M(OC_6H_5)_4$ systems, (b) d-elements, and (c) f-elements.



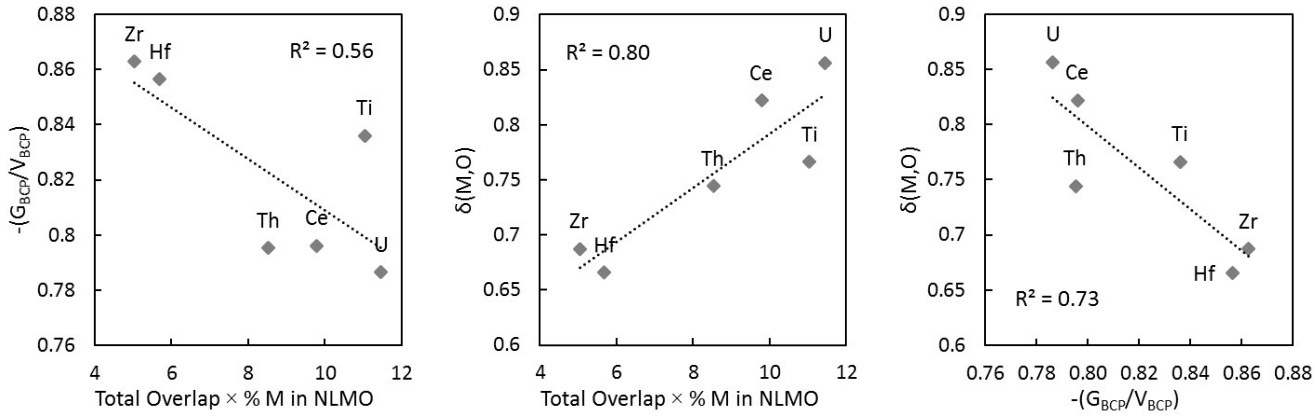
(a) (b) (c)

Figure SI3: Correlation between the deformation energy and H_{BCP} for (a) all $M(OC_6H_5)_4$ systems, (b) d-elements, and (c) f-elements.



(a) (b)

Figure SI4: The %M contribution to the (a) σ and (b) average π M-O bonding NLMOs with changes in *r*(M-O) in $M(OC_6H_5)_4$.



(a) (b) (c)

Figure SI5: Correlations are shown for the three measures of covalency for the optimized $M(OC_6H_5)_4$ systems investigated in this study. The product of the overlap integrals and %M contribution to the NLMOs with $-(G_{BCP}/V_{BCP})$ is shown in (a) and δ(M,O) in (b). The QTAIM metrics, $-(G_{BCP}/V_{BCP})$ and δ(M,O) are correlated in (c).