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

Supplementary information for

Quantum Chemical Topology and Natural Bond Orbital Analysis of M-O Covalency in $M(OC_6H_5)_4$ (M = Ti, Zr, Hf, Ce, Th, Pa, U, Np)

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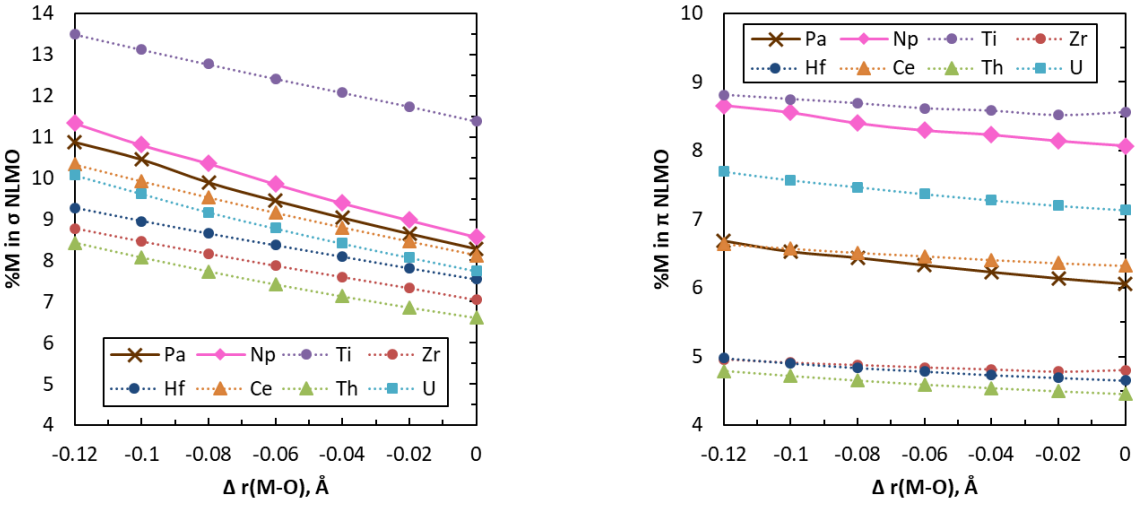
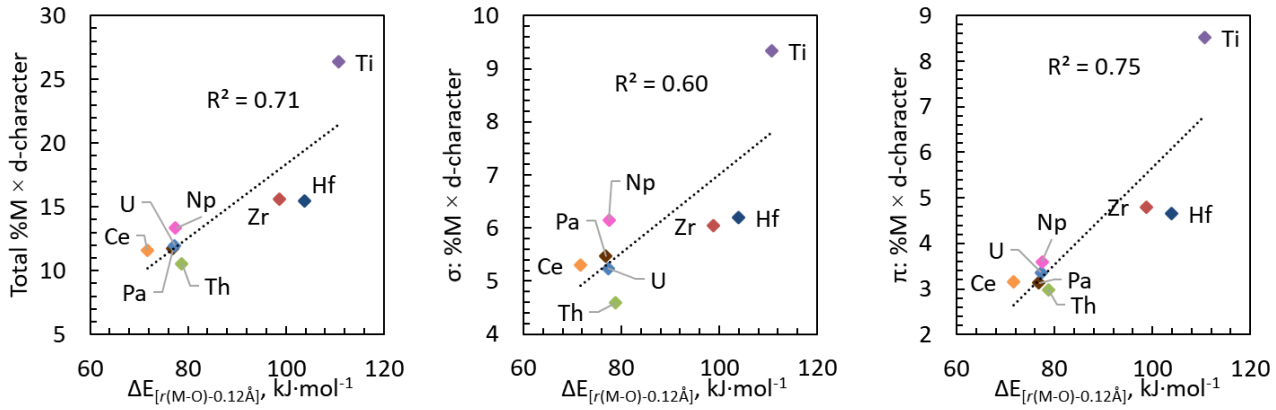


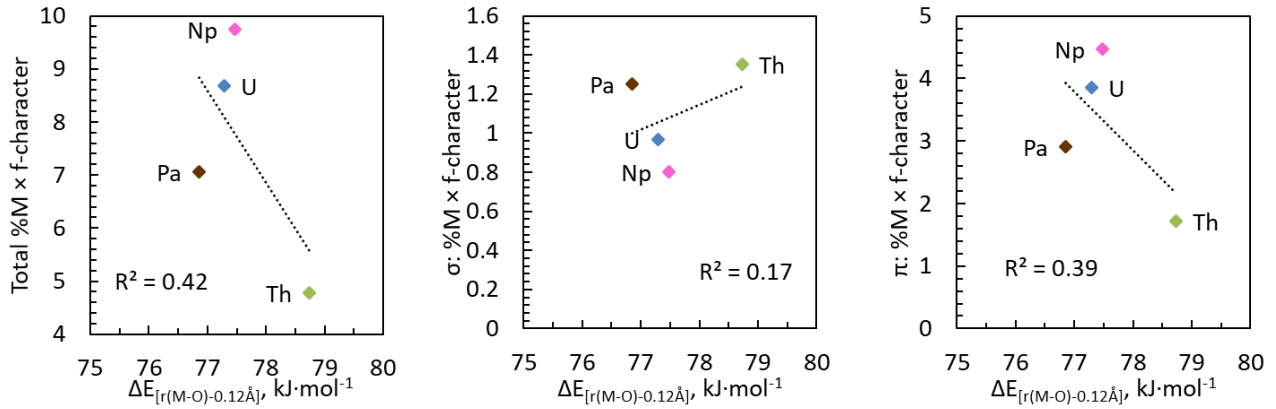
(a) (b)

Figure S1. The metal contribution (%M) to the σ-type (a) and π-type (b) M-O bonding NLMOs as a function of *r*(M-O) in $M(OC_6H_5)_4$.



(a) (b) (c)

Figure S2. Correlation between the deformation energy and %M contribution from d-character orbitals in (a), decomposed into σ-type NLMOs in (b) and π-type NLMOs in (c).



(a) (b) (c)

Figure S3. Correlation for the actinides between the deformation energy and %M contribution from f-character orbitals in (a), decomposed into σ-type NLMOs in (b) and π-type NLMOs in (c).

Table S1: QTAIM and NBO atomic charges with shortening of *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
$Pa(OC_6H_5)_4$:	Optimized	2.725	-1.286	1.439	2.311	-0.821	1.490
	-0.02 Å	2.725	-1.285	1.440	2.274	-0.813	1.462
	-0.04 Å	2.725	-1.283	1.441	2.234	-0.803	1.431
	-0.06 Å	2.725	-1.282	1.443	2.191	-0.793	1.398
	-0.08 Å	2.726	-1.281	1.445	2.143	-0.781	1.362
	-0.10 Å	2.727	-1.279	1.448	2.091	-0.769	1.322
	-0.12 Å	2.729	-1.278	1.452	2.035	-0.755	1.280
$U(OC_6H_5)_4$:	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
$Np(OC_6H_5)_4$:	Optimized	2.561	-1.251	1.309	2.046	-0.757	1.289
	-0.02 Å	2.559	-1.249	1.310	2.003	-0.746	1.257
	-0.04 Å	2.557	-1.247	1.310	1.959	-0.735	1.223
	-0.06 Å	2.554	-1.244	1.310	1.910	-0.723	1.187
	-0.08 Å	2.551	-1.241	1.309	1.858	-0.711	1.147
	-0.10 Å	2.547	-1.238	1.308	1.804	-0.697	1.106
	-0.12 Å	2.542	-1.235	1.307	1.746	-0.683	1.063

Table S2. QTAIM and IQA metrics (in au) for the $M(OC_6H_5)_4$ systems at -0.12 Å.

Compound	r(M-O), Å	ρ_{BCP}	$\nabla^2\rho_{BCP}$	$-(G_{BCP}/V_{BCP})$	H_{BCP}	δ(M,O)	V_{XC}(M,O)	$\%V_{XC}$
$Ti(OC_6H_5)_4$	1.665	0.198	1.067	0.802	-0.087	0.831	-0.210	21.5
$Zr(OC_6H_5)_4$	1.817	0.160	0.853	0.814	-0.063	0.749	-0.179	16.4
$Hf(OC_6H_5)_4$	1.799	0.177	1.041	0.811	-0.066	0.731	-0.178	16.5
$Ce(OC_6H_5)_4$	1.966	0.147	0.526	0.749	-0.066	0.904	-0.206	21.2
$Th(OC_6H_5)_4$	2.027	0.138	0.491	0.750	-0.061	0.824	-0.190	17.2
$Pa(OC_6H_5)_4$	1.981	0.163	0.545	0.724	-0.084	0.979	-0.223	20.2
$U(OC_6H_5)_4$	1.968	0.165	0.598	0.738	-0.082	0.976	-0.224	21.3
$Np(OC_6H_5)_4$	1.960	0.164	0.644	0.749	-0.081	0.972	-0.222	21.9

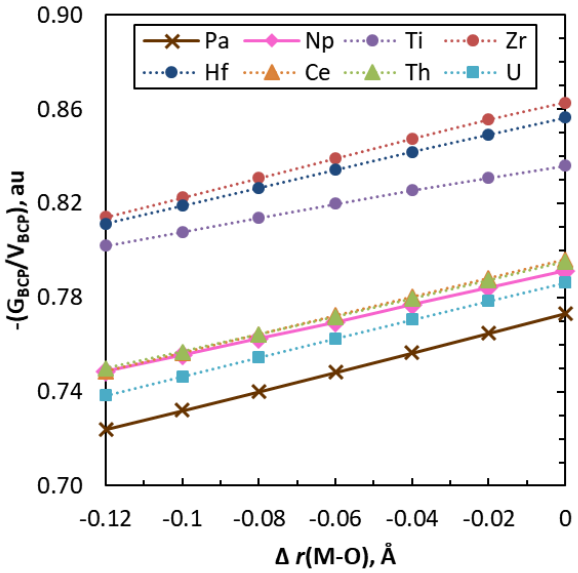


Figure S4. The $-(G_{BCP}/V_{BCP})$ for the M-O bond as a function of r(M-O) in $M(OC_6H_5)_4$.

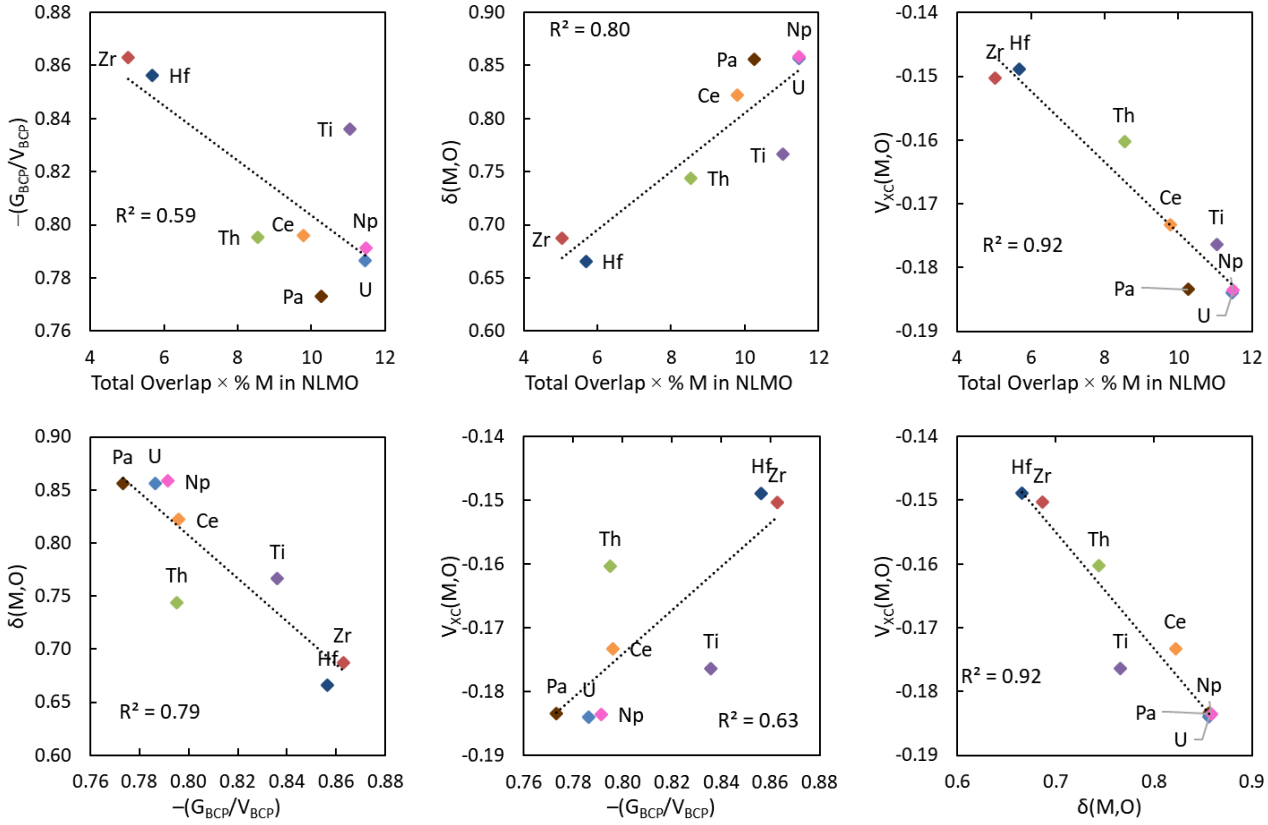


Figure S5. Correlations for the covalency metrics summarized in Table 4.

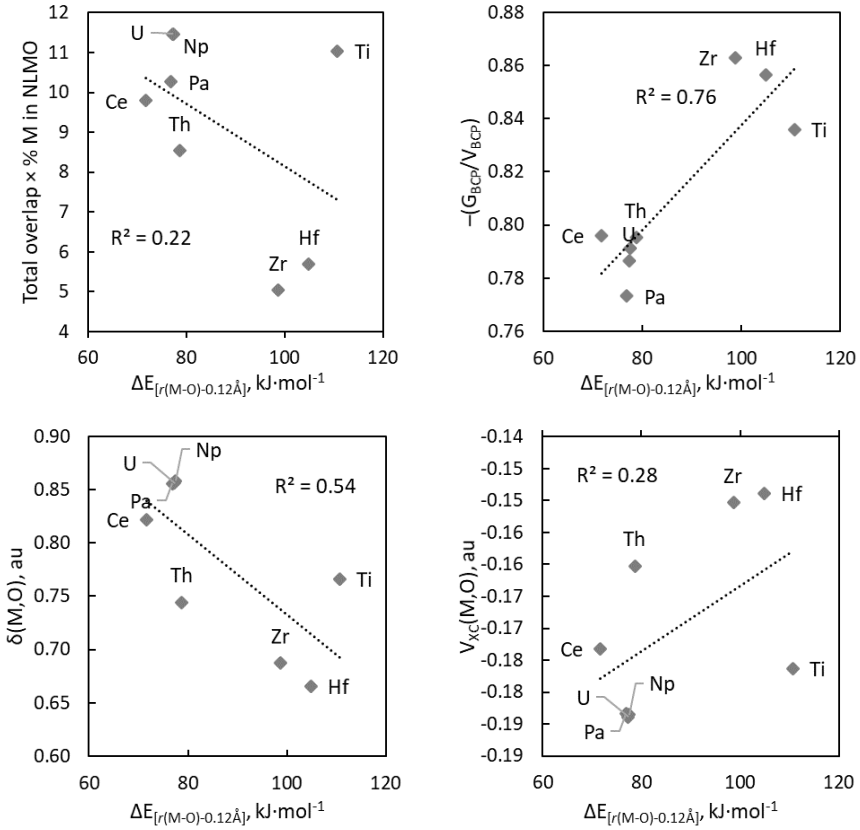


Figure S6. Correlation between covalency metrics and deformation energy.