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

Electronic Supplementary Information

Weak-field Ligands Enable Inert Early Transition Metal Oxides to Convert Methane to Methanol: The Case of ZrO

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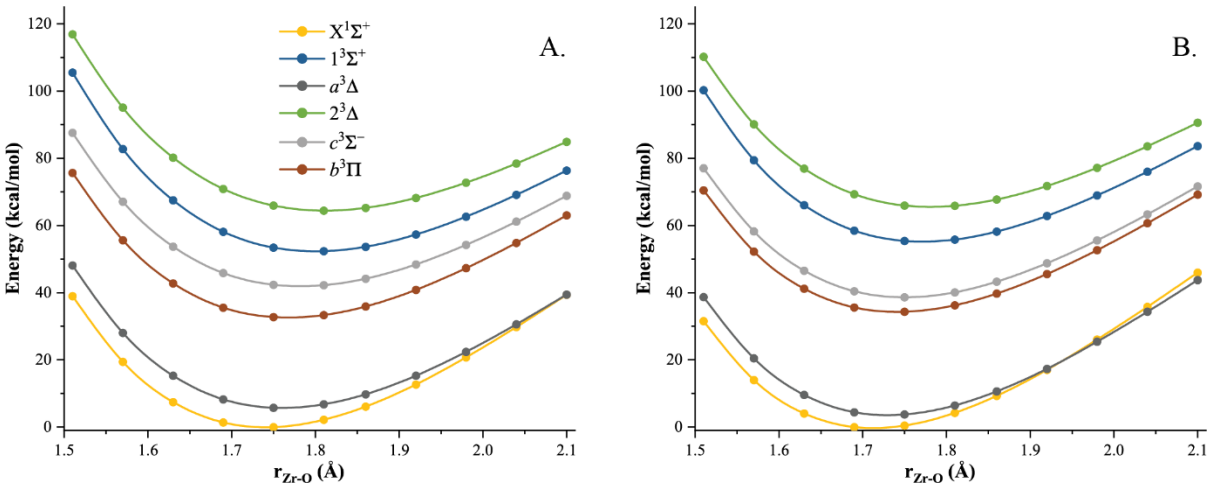

Figure S1. CCSD(T)/5Z PECs of ZrO with respect to Zr-O distance without and including the correlation energy of the zirconium sub-valence $4s^24p^6$ electrons. Shown in 5A is CCSD(T) and in 5B is C-CCSD(T). The zero of each scale is set equal to the equilibrium energy of the ground state $X^1\Sigma^+$ at the corresponding CCSD(T)/5Z level or C-CCSD(T)/5Z level.

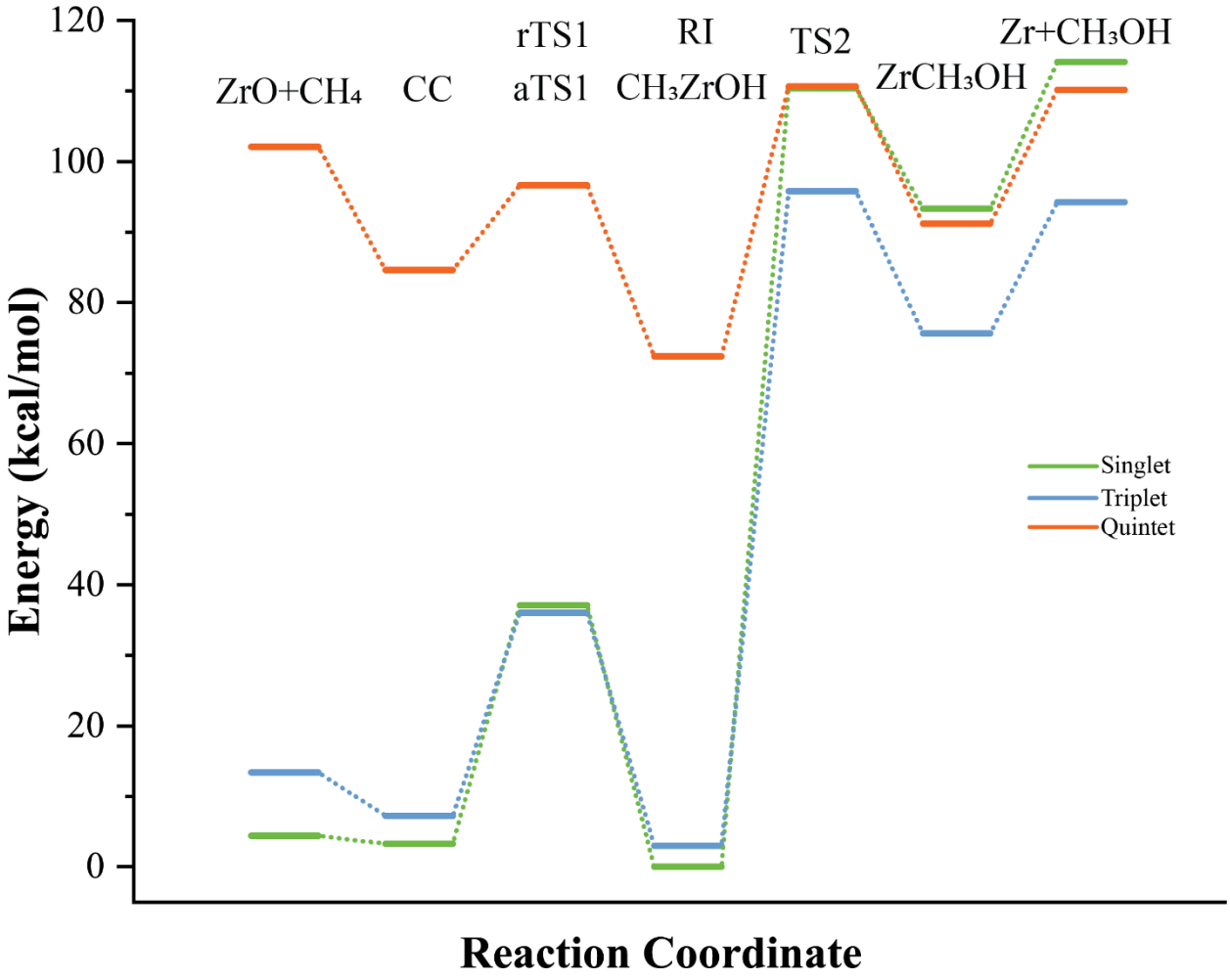

Figure S2. MN15/TZ. Full reaction pathway. The zero for all spins is relative to the lowest energy state along the overall reaction pathway.

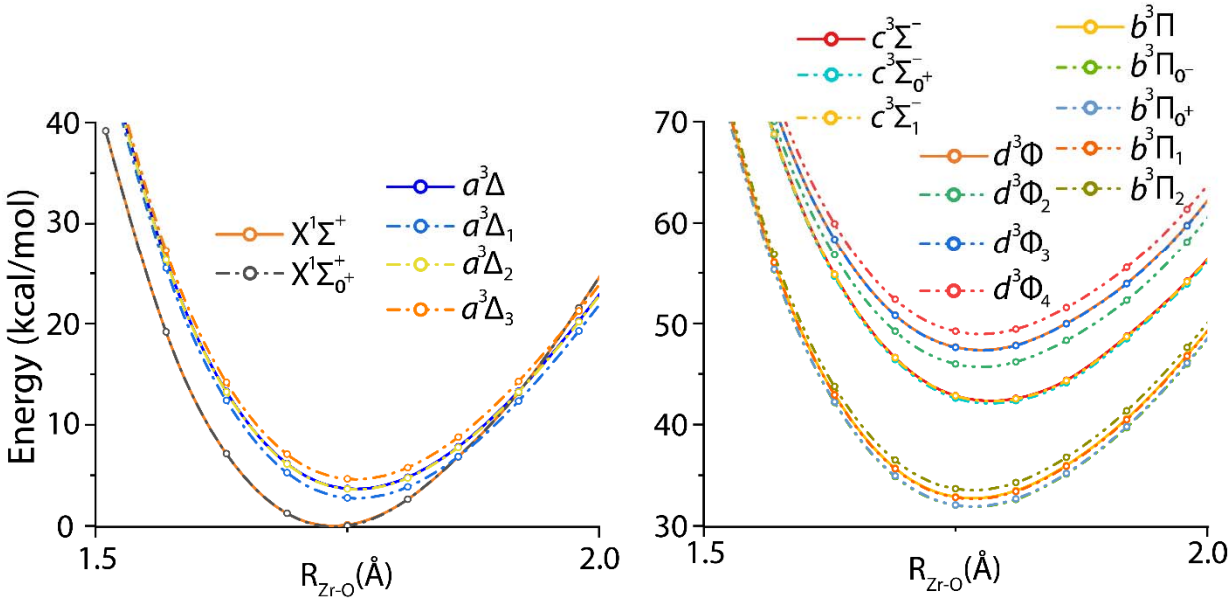

Figure S3. MRCI/TZ. Comparison of spin-orbit effects on plotted potential energy curves. Shown in solid lines are MRCI energies. Dashed/dotted lines show spin-orbit splitting for the low lying states of ZrO.

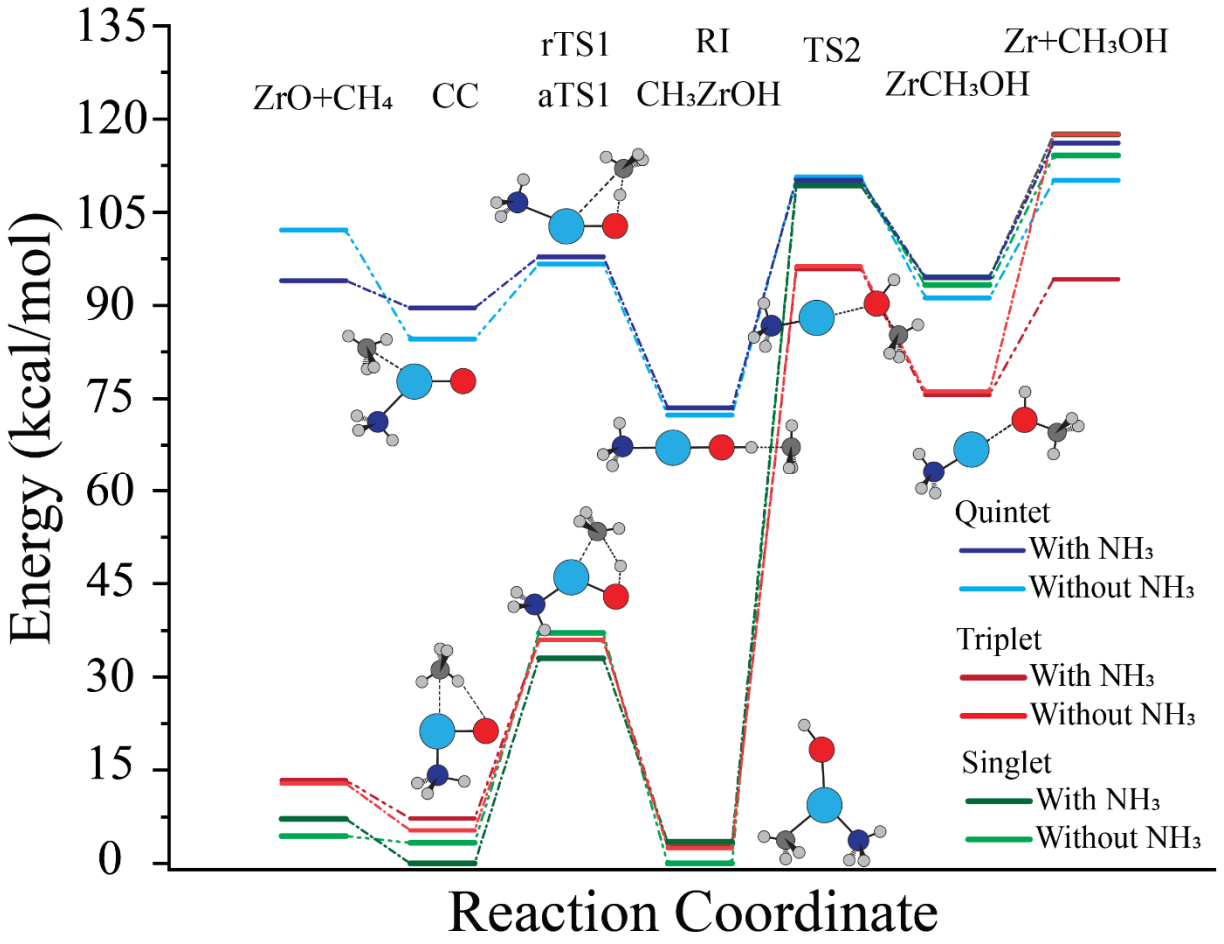

Figure S4. MN15/TZ. Reaction pathway for the conversion of methane to methanol catalyzed by ZrO with and without the addition of an NH_3 ligand for various ZrO spin multiplicities. Structures are shown for the triplet [2+2] reaction mechanism and the radical quintet.

Table S1. Spectroscopic constants for the low-lying triplet electronic states with and without Spin-Orbit. Equilibrium energy E_e (a.u.), bond length r_e (Å), harmonic vibrational frequency ω_e (cm^{-1}), anharmonicity $\omega_e x_e$ (cm^{-1}) and $\Delta G_{½} = E_{\upsilon=1} - E_{\upsilon=0}$ (cm^{-1}) for the $^3\Delta$ and $^3\Pi$ states for $^{90}Zr^{16}O$. Energies calculated at the MRCI/TZ level.

State	$-E_e$	r_e	ω_e	$\omega_e x_e$	$\Delta G_{½}$
$a^3\Delta$	121.60171	1.759	910	3.40	902
$a^3\Delta_1$	121.60320	1.759	909	3.38	901
$a^3\Delta_2$	121.60182	1.759	910	3.44	902
$a^3\Delta_3$	121.60022	1.759	910	3.41	902
$b^3\Pi$	121.55540	1.768	866	3.21	864
$b^3\Pi_{0^-}$	121.55678	1.768	867	3.18	865
$b^3\Pi_{0^+}$	121.55666	1.768	869	3.44	868
$b^3\Pi_1$	121.55550	1.768	866	3.19	864
$b^3\Pi_2$	121.55418	1.768	866	3.24	863

Table S2. MRCI/5Z Spin-Orbit splitting for the lowest electronic states at r(Zr-O) 1.75 Å and excitation energy T_e (cm^{-1}). Only the states labeled in [a] and [b] showed considerable second order coupling effects.

State	Ω	T_e	State	Ω	T_e	State	Ω	T_e
$X^1\Sigma^+$	0^-	0	$B^1\Pi$	1	15,579	$D^1\Gamma$	4	19,094
$a^3\Delta$	1	966	$d^3\Phi$	2	16,087	$f^3\Delta$	1	22,368
	2	1,269		3	16,653		2	22,667
	3	1,622		4	17,214		3	22,942
$A^1\Delta$	2	5,781	$C^1\Sigma^+$	0^+	18,579	$E^1\Phi$	3	23,871
$b^3\Pi$	0^-	11,204	$e^3\Pi$	0^-	19,024[a]	$F^1\Delta$	2	25,465
	0^+	11,219		0^+	19,086	$2^1\Pi$	1	27,390
	1	11,473		1	19,226[b]	$3^1\Sigma^+$	0^+	28,472
	2	11,776		2	19,244			
$C^3\Sigma^-$	0^+	14,904	$1^3\Sigma^+$	1	19,072[b]			
	1	14,983		0^-	19,167[a]			

Table S3. Cartesian coordinates of the MN15/TZ optimal structures without symmetry restrictions.

	Singlet			Triplet			Quintet		
	ZrO			ZrO			ZrO		
Zr	0.000000	0.000000	0.283611	0.000000	0.000000	0.286889	0.000000	0.000000	0.317828
O	0.000000	0.000000	-1.418053	0.000000	0.000000	-1.434444	0.000000	0.000000	-1.589141
	CC			CC			CC		
C	3.606386	-0.009322	-0.000111	-2.358773	0.193754	0.000076	-2.35523	0.000688	-0.001714
H	3.246892	0.123959	1.018641	-2.959541	0.333756	0.894627	-2.002205	-0.78249	-0.697649
H	3.249405	0.8083	-0.623756	-1.998064	-0.842776	-0.000219	-2.002325	0.996	-0.328947
H	3.242582	-0.956124	-0.395135	-1.564895	0.952926	-0.000046	-2.004057	-0.212996	1.024605
H	4.693793	-0.013457	-0.000205	-2.960013	0.334038	-0.894117	-3.439613	0.00069	-0.002752
Zr	-0.467703	0.007908	0.000095	0.409741	-0.316738	-0.000021	0.155844	-0.000303	0.00085
O	-2.170357	-0.027885	-0.000335	0.905688	1.341133	0.000019	2.168225	0.00085	-0.00237
	aTS1			aTS1			rTS1		
C	-1.846373	-0.139583	0.000001	-1.917699	-0.190402	0.000007	2.780425	-0.388258	-0.000003
H	-1.941222	-0.775364	0.893874	-2.498366	0.062252	0.888513	1.861056	0.393235	0.000009
H	-1.941033	-0.776	-0.893434	-1.840657	-1.290662	-0.000306	3.334366	-0.171631	-0.907015
H	-0.945884	1.02234	-0.000029	-0.981318	0.966239	-0.000015	3.334314	-0.171704	0.907056
H	-2.671985	0.568638	-0.000381	-2.498565	0.062701	-0.888241	2.344034	-1.382986	-0.000033
Zr	0.420334	-0.281331	-0.000001	0.456422	-0.269844	0	-0.831258	-0.12192	0
O	0.220626	1.506388	0.000001	0.133526	1.516957	0.000001	0.711752	1.06743	0.000002
	[2+2] Intermediate			[2+2] Intermediate			Radical Intermediate (RI)		
C	1.879427	0.579393	-0.000027	-1.955006	0.602277	-0.000008	-1.749166	0.003035	-0.003831
H	2.076573	-0.06875	-0.898189	-2.515013	0.2672	0.885658	-4.029399	-0.001109	0.001162
H	2.076569	-0.068715	0.898162	-2.515161	0.267184	-0.885568	-4.062315	1.032164	-0.296746
H	-2.38222	1.252378	0.000204	2.297486	1.435058	-0.000001	-4.053186	-0.77621	-0.74461
H	2.562547	1.418426	-0.000039	-1.964973	1.695094	-0.000009	-4.046193	-0.259837	1.045343
Zr	-0.035224	-0.252419	-0.000017	0.070576	-0.31932	-0.000001	1.109376	-0.000265	0.000289
O	-1.775135	0.510884	0.000087	1.700582	0.686823	0	-0.785974	0.002263	-0.002337
	TS2			TS2			TS2		
C	-2.053548	-0.568439	0.016392	2.077059	-0.590028	-0.013407	1.724548	-0.713785	-0.009664
H	-1.915616	-1.090651	0.955084	1.765062	-1.290881	-0.775173	0.969527	-1.513164	-0.2043
H	-1.8499	-1.172059	-0.859134	2.069731	-0.968534	0.997045	2.191948	-0.835143	0.956787
H	-2.974456	-0.006017	-0.052217	2.941595	0.001885	-0.274688	2.42372	-0.651921	-0.834306
H	-1.276191	1.44504	0.644416	1.251215	1.502894	-0.632744	1.541512	1.49105	-0.60551
Zr	0.71947	-0.069974	0.003936	-0.717246	-0.076742	-0.004108	-0.680419	-0.038342	-0.003275
O	-1.05517	0.879162	-0.117994	1.024987	0.920562	0.116289	1.217847	0.915698	0.109541
	Zr---OHCH3			Zr---OHCH3			Zr---OHCH3		
C	-2.481019	-0.329331	0.000118	2.466078	-0.328316	0.000066	-2.427353	-0.364842	-0.000015
H	-3.068429	-0.136727	0.896272	3.049697	-0.127894	-0.895479	-3.030221	-0.221014	0.894957

H	-2.141039	-1.36099	-0.002274	2.131357	-1.36121	-0.000351	-2.001423	-1.366095	-0.000289
H	-3.070894	-0.133344	-0.893682	3.04885	-0.128387	0.896269	-3.030479	-0.220639	-0.894752
H	-1.520251	1.421885	0.000798	1.478954	1.430533	0.000886	-1.584512	1.457458	-0.00016
Zr	0.876593	-0.041971	-0.000048	-0.868068	-0.042772	0.000012	0.867345	-0.043041	0.000005
O	-1.297126	0.483003	0.000012	1.277175	0.483466	-0.000273	-1.310381	0.532621	0.000016

Table S4. Harmonic vibrational frequencies (cm^{-1}) of the optimal structures for the coordination complex (CC), first transition state of the [2+2] mechanism(aTS1) and radical mechanism (rTS1), intermediate (I), second transition state (TS2), and the Zr---$OHCH_3$ intermediate (I2), $ZrO + CH_4 \rightarrow Zr + CH_3OH$ reaction for the lowest singlet, triplet, and quartet states at the MN15/TZ.

Singlet					Triplet					Quintet				
CC	aTS1	I	TS2	I2	CC	aTS1	I	TS2	I2	CC	rTS1	I	TS2	I2
-51	-1614	116	-741	92	70	-1590	96	-967	88	59	-1051	13	-956	94
40	184	175	136	186	128	116	144	95	167	72	46	16	140	124
41	264	352	186	327	143	300	300	205	323	228	71	95	290	310
62	310	418	362	382	177	480	309	387	325	465	321	96	390	313
119	526	453	550	1033	456	517	339	545	1029	468	358	97	446	1040
1033	710	494	665	1047	963	687	345	679	1052	600	647	426	735	1052
1320	930	658	769	1158	1220	904	491	710	1160	1302	773	426	879	1164
1321	1143	717	921	1304	1347	1057	697	860	1307	1304	1145	604	929	1308
1328	1194	1121	1197	1447	1390	1226	1136	1128	1450	1368	1227	720	1236	1448
1544	1405	1385	1420	1482	1495	1421	1402	1409	1485	1536	1263	1393	1359	1477
1545	1408	1417	1423	1485	1581	1450	1402	1423	1486	1537	1424	1393	1414	1489
3056	1979	2741	3116	3078	2977	1987	2974	3141	3090	2871	1432	3159	2754	3074
3162	2967	2802	3247	3163	3077	2966	3033	3271	3179	2983	3090	3336	3165	3162
3179	3031	3227	3250	3184	3142	3082	3102	3297	3195	2983	3211	3337	3255	3168
3183	3164	3966	3698	3822	3194	3131	3985	3676	3772	3205	3228	3846	3663	3836
ZrO					ZrO					ZrO				
1035					983					660				

Table S5. Harmonic vibrational frequencies (cm^{-1}) of the optimal structures for the coordination complex (CC), first transition state of the radical mechanism (rTS1), radical intermediate (I), second transition state (TS2), and the $(F_3/H_3)Zr$---$OHCH_3$ intermediate (I2), for the $(F_3/H_3)ZrO + CH_4 \rightarrow (F_3/H_3)Zr + CH_3OH$ reaction for the lowest doublet state at the MN15/TZ.

$H_3ZrO + CH_4$					$F_3ZrO + CH_4$						
CC	rTS1	I	TS2	I2	CC	rTS1	I	TS2	I2		
91	-1039	-14	-979	90	90	-1235	-1	-856	45		
106	5	39	182	102	99	44	22	31	85	H_3ZrO	H_3Zr
117	92	40	215	136	109	64	29	94	110	77	164
159	137	112	249	149	119	84	105	121	117	329	649
184	327	129	305	280	149	145	114	138	127	505	649
319	356	130	334	341	153	154	119	149	167	532	1655
393	367	397	472	477	163	158	154	170	201	577	1655
420	433	398	501	577	166	168	156	179	241	604	1694
512	504	492	530	597	176	175	175	243	331	1672	
535	569	492	590	600	181	363	181	317	443	1688	
563	597	518	606	1032	196	417	182	486	593	1746	
609	698	587	725	1077	640	647	464	608	620		
1253	790	588	821	1171	659	661	465	649	647	F_3ZrO	F_3Zr
1331	1107	639	967	1287	668	671	635	661	1065	48	75
1365	1260	789	1235	1462	680	681	657	749	1095	146	150
1512	1288	1393	1373	1483	1319	741	664	755	1176	158	152
1546	1415	1393	1432	1494	1326	1133	666	862	1326	161	640
1612	1421	1668	1607	1529	1329	1253	757	1070	1466	167	675
1685	1664	1669	1620	1585	1545	1295	1393	1419	1495	649	677
1729	1672	1725	1666	1630	1549	1419	1393	1433	1496	660	
2989	1723	3156	2985	3087	3037	1430	3157	3150	3090	671	
3079	3090	3334	3184	3176	3139	3092	3334	3302	3168	683	
3156	3210	3335	3269	3185	3160	3212	3335	3317	3211		
3213	3240	3762	3697	3811	3177	3241	3792	3898	3852		

Table S6. Electronic energies (a.u.) of the MN15/TZ optimal structures without symmetry restrictions for the $(F_3/H_3)ZrO + CH_4 \rightarrow Zr(F_3/H_3) + CH_3OH$ and $ZrO + CH_4 \rightarrow Zr + CH_3OH$ reactions.

Structure	Singlet	Triplet	Structure	Quintet
CC	-162.45735	-162.44272	CC	-162.32768
aTS1	-162.40341	-162.40508	rTS1	-162.30846
CH_3ZrOH	-162.46253	-162.45778	RI	-162.34720
TS2	-162.28664	-162.30981	TS2	-162.28612
$Zr{-}{-}{-}OHCH_3$	-162.31385	-162.34203	Zr---OHCH3	-162.31722
Zr	-46.64228	-46.67398	Zr	-46.64859
ZrO	-121.98693	-121.97264	ZrO	-121.84463
Structure	H_3	Structure	F_3	
H_3Zr CC	-164.17695	F_3Zr CC	-462.13092	
H_3Zr rTS1	-164.16770	F_3Zr rTS1	-462.12149	
H_3Zr RI	-164.20678	F_3Zr RI	-462.16048	
H_3Zr TS2	-164.14534	F_3Zr TS2	-462.10434	
$H_3Zr{-}{-}{-}OHCH_3$	-164.18308	$F_3Zr{-}{-}{-}OHCH_3$	-462.14193	
H_3Zr	-48.50013	F_3Zr	-346.46793	
H_3ZrO	-123.69967	F_3ZrO	-421.65405	

Table S7. Cartesian coordinates of the MN15/TZ optimal structures without symmetry restrictions for the $(F_3/H_3)ZrO + CH_4 \rightarrow (F_3/H_3)Zr + CH_3OH$ reaction.

H_3Zr				**F_3Zr**			
Zr	-0.000001	0	-0.015643	Zr	0.000635	-0.000026	0.000533
H	1.756298	-0.549921	0.208565	F	-1.137552	-1.527991	-0.000789
H	-0.401871	1.795917	0.208569	F	-0.75826	1.746671	-0.000789
H	-1.354382	-1.245995	0.208571	F	1.89299	-0.218563	-0.000791
H_3ZrO				**F_3ZrO**			
Zr	0.267192	0.000772	-0.005163	Zr	-0.005143	0.003836	0.001648
O	-1.675783	0.006823	-0.023239	O	-0.572959	0.669041	1.79229
H	0.657292	-0.114519	1.786608	F	-1.565462	-0.150427	-1.063411
H	1.072623	1.545396	-0.623177	F	0.845912	-1.682599	0.196283
H	0.988661	-1.516325	-0.770998	F	1.251703	1.221273	-0.73334
H_3Zr CC				**F_3Zr CC**			
Zr	0.574683	-0.189126	-0.000578	Zr	-0.317865	0.006206	-0.000212
O	-0.18389	1.593134	-0.036917	O	0.3549	-1.870512	0.131421
H	2.381644	-0.028169	-0.37383	F	-2.194913	-0.231601	0.018414
H	-0.043466	-1.571555	-1.082664	F	0.141874	0.8539	-1.64449
H	0.455937	-0.697086	1.769315	F	0.144249	1.081427	1.504702
C	-2.429777	-0.285659	0.002579	C	2.696948	-0.060961	0.004864
H	-2.883447	0.611678	0.410174	H	2.338371	-0.506358	0.934283

H	-1.854724	-0.022456	-0.894182	H	2.340986	-0.613231	-0.866308
H	-3.182478	-1.006771	-0.303408	H	3.782336	-0.12082	0.010076
H	-1.811002	-0.75171	0.777573	H	2.411111	0.988493	-0.057749
	H_3Zr rTS1				**F_3Zr rTS1**		
C	-2.589261	-0.384838	-0.000139	C	2.856062	-0.045875	0.031774
H	-2.053126	-1.330604	0.018062	H	2.458591	0.965595	-0.002831
H	-3.142992	-0.23655	-0.920402	H	3.077944	-0.450536	-0.948647
H	-1.780902	0.522727	-0.000632	H	1.996221	-0.786658	0.497807
H	-3.163898	-0.214019	0.903339	H	3.66329	-0.145393	0.749538
Zr	0.694678	-0.117832	-0.000012	Zr	-0.383739	-0.005318	0.001837
O	-0.653527	1.251775	-0.000012	O	0.826307	-1.298988	0.826678
H	2.401606	0.606294	-0.005473	F	-2.17938	-0.602734	0.219453
H	0.361388	-1.166283	1.493806	F	-0.102547	1.697501	0.81932
H	0.354584	-1.173442	-1.48728	F	0.104893	0.160443	-1.835818
	H_3Zr RI				**F_3Zr RI**		
Zr	-1.012547	0.00026	-0.000208	Zr	0.548883	0.000151	0.001287
H	1.829772	-0.006006	0.001576	H	-2.315308	0.015309	0.0498
C	4.031362	0.00125	-0.000805	C	-4.5329	0.001276	-0.002805
H	4.080142	-0.274744	1.038229	H	-4.600648	0.82223	0.68973
H	4.077885	-0.76005	-0.7601	H	-4.548928	0.191066	-1.06204
H	4.06199	1.039815	-0.281232	H	-4.57526	-1.010651	0.360699
O	0.86193	-0.002342	0.002155	O	-1.349545	0.012122	0.047219
H	-1.540924	1.738174	-0.383084	F	1.190074	-1.671947	0.663731
H	-1.546354	-0.536969	1.694195	F	1.226872	1.419764	1.082158
H	-1.544256	-1.199392	-1.31368	F	1.14734	0.237891	-1.795953
	H_3Zr TS2				**F_3Zr TS2**		
Zr	-0.624066	0.042357	0.004361	Zr	-0.468824	-0.00005	-0.011147
O	1.191153	-0.966415	-0.127862	O	1.397938	-0.000942	-0.884457
C	1.85926	0.674167	-0.03741	C	3.061184	-0.000134	-0.093695
H	1.283466	1.343873	0.616867	H	3.489888	-0.917901	-0.464876
H	1.989473	1.047837	-1.042857	H	2.764841	0.002836	0.9426
H	2.77386	0.350184	0.44173	H	3.491207	0.915028	-0.469762
H	1.495839	-1.56273	0.578158	H	1.570935	-0.002476	-1.831613
H	-1.809562	-0.963459	-1.034205	F	-1.477633	-1.602752	-0.278928
H	-0.803149	1.870285	-0.349379	F	-1.478489	1.601467	-0.28272
H	-0.652086	-0.09396	1.862611	F	0.498953	0.002712	1.662467
	H_3Zr---$OHCH_3$				**F_3Zr---$OHCH_3$**		
Zr	-0.817344	0.034919	0.000004	Zr	-0.524238	-0.027585	0.039483
O	1.342807	-0.433711	-0.00024	O	1.693461	0.52858	-0.113174
C	2.550513	0.332695	0.000072	C	2.894313	-0.218213	-0.321119
H	3.131332	0.117848	0.894342	H	3.267861	-0.060959	-1.331221
H	2.250123	1.377134	0.000214	H	2.634223	-1.26165	-0.178682

H	3.131607	0.118109	-0.89408	H	3.645814	0.074866	0.408819
H	1.473372	-1.392341	0.000425	H	1.820197	1.485573	-0.135179
H	-1.342016	0.847937	-1.616192	F	-2.303945	-0.427839	-0.537867
H	-0.653453	-1.843407	0.002424	F	-0.409653	1.897381	0.319521
H	-1.342747	0.851461	1.614181	F	0.345582	-1.69774	0.494909

Table S8. Harmonic vibrational frequencies (cm^{-1}) of the optimal structures for the coordination complex (CC), first transition state of the [2+2] mechanism(TS1a) and radical mechanism (TS1r), intermediate (I), second transition state (TS2), and the $ZrNH_3$---$OHCH_3$ intermediate (I2), $NH_3ZrO + CH_4 \rightarrow NH_3Zr + CH_3OH$ reaction for the lowest singlet, triplet, and quintet states at MN15/TZ

Singlet						Triplet						Quintet					
NH_3ZrO	**CC**	**aTS1**	**I**	**TS2**	**I2**	**NH_3ZrO**	**CC**	**aTS1**	**I**	**TS2**	**I2**	**NH_3ZrO**	**CC**	**rTS1**	**I**	**TS2**	**I2**
90	77	-1530	55	-748	35	129	57	-1516	55	-1133	34	33	37	-1202	-18	-839	29
127	96	34	68	49	46	139	80	57	68	61	64	72	54	35	4	38	51
357	96	62	92	72	68	325	125	82	92	71	80	300	84	37	6	73	80
425	123	82	101	84	103	471	127	124	101	79	107	358	127	45	20	105	96
546	170	183	118	178	124	488	160	140	118	110	154	383	159	72	26	146	151
989	228	248	251	206	279	940	168	274	251	200	294	584	171	92	84	283	262
1166	301	269	252	252	328	1151	194	313	252	282	308	1134	230	298	100	310	296
1583	370	331	281	351	353	1614	332	439	281	340	323	1595	294	336	115	357	315
1588	433	418	312	361	374	1614	468	449	312	373	365	1596	353	343	295	362	336
3399	517	461	363	434	390	3459	473	505	363	406	423	3438	435	364	338	412	405
3516	537	529	412	545	1038	3577	484	507	412	524	1045	3565	464	380	339	485	1028
3573	957	654	477	675	1062	3591	924	647	477	681	1054	3569	584	578	472	746	1059
	1138	903	519	791	1100		1140	880	519	714	1107		1137	747	474	906	1094
NH_3Zr	1293	1123	708	922	1164	**NH_3Zr**	1219	1063	708	855	1163	**NH_3Zr**	1253	1123	585	928	1165
312	1326	1143	1116	1114	1292	359	1352	1163	1116	1113	1299	287	1342	1156	675	1114	1296
424	1360	1187	1135	1188	1454	386	1387	1214	1135	1115	1454	300	1352	1214	1113	1244	1448
516	1543	1404	1386	1418	1483	441	1489	1420	1386	1407	1484	391	1495	1237	1392	1353	1479
1167	1549	1420	1398	1422	1488	1160	1587	1451	1398	1422	1487	1126	1559	1427	1393	1417	1489
1508	1575	1571	1547	1547	1536	1587	1611	1604	1547	1569	1557	1610	1599	1435	1592	1589	1575
1611	1594	1600	1594	1585	1569	1593	1612	1617	1594	1581	1576	1615	1603	1591	1592	1603	1600
3340	2851	1953	2978	3107	3094	3387	2976	1968	2978	3133	3085	3461	2928	1594	3160	2703	3067
3480	2961	2907	3044	3233	3178	3504	3076	2943	3044	3259	3168	3580	3022	3090	3337	3163	3149
3507	3063	3047	3114	3237	3206	3529	3141	3069	3114	3288	3196	3581	3118	3211	3339	3252	3166
	3200	3157	3330	3366	3361		3187	3116	3330	3384	3343		3191	3224	3433	3452	3429
	3399	3380	3441	3492	3487		3457	3452	3441	3517	3489		3444	3435	3566	3575	3552
	3508	3508	3562	3520	3507		3577	3570	3562	3536	3539		3559	3564	3566	3585	3580
	3608	3572	3993	3802	3598		3593	3576	3993	3748	3759		3587	3567	3896	3611	3842

Table S9. Cartesian coordinates of the MN15/TZ optimal structures without symmetry restrictions for the $NH_3ZrO + CH_4 \rightarrow NH_3Zr + CH_3OH$ reaction.

	Singlet			Triplet			Quintet		
	NH_3ZrO			**NH_3ZrO**			**NH_3ZrO**		
Zr	0.33500	-0.32475	-0.00003	0.35776	-0.32643	0.00002	0.16023	-0.15478	-0.00001
N	-1.90472	0.20007	-0.00016	-1.97856	0.16340	0.00013	-2.21648	0.24728	-0.00006
H	-2.05569	0.77572	0.83216	-2.52968	-0.06970	0.82179	-2.69768	-0.10790	0.82510
H	-2.05651	0.78327	-0.82691	-1.82151	1.17187	0.00220	-2.29008	1.26402	0.00267
H	-2.57679	-0.56458	-0.00322	-2.52490	-0.06682	-0.82556	-2.69789	-0.10359	-0.82692
O	0.82774	1.32438	0.00002	0.80198	1.35973	-0.00003	2.09897	0.42597	0.00001
	CC			**CC**			**CC**		
C	-2.49819	-0.30699	-0.00008	-2.77188	-0.28937	-0.00067	-2.17555	-1.36139	0.03691
H	-3.58119	-0.24417	0.00065	-3.39386	-0.30246	0.89041	-1.52761	-1.16755	0.90680
H	-2.13675	0.19642	0.91828	-2.16617	-1.20560	0.00227	-1.68908	-1.08956	-0.91018
H	-2.13746	0.19991	-0.91660	-2.18383	0.63733	0.00163	-3.10225	-0.79914	0.14776
H	-2.22435	-1.36865	-0.00183	-3.38744	-0.30300	-0.89615	-2.38318	-2.42662	0.00643
Zr	0.00207	-0.14362	-0.00001	0.04044	-0.15529	0.00035	0.41075	-0.03942	-0.03951
O	0.13668	1.58692	0.00003	0.12095	1.59514	-0.00016	2.41760	-0.26768	0.10309
N	2.28645	-0.40050	-0.00001	2.41243	-0.38640	-0.00064	-1.33889	1.64747	0.03906
H	2.71586	-1.32013	0.00039	2.85993	-0.77780	0.82376	-0.90160	2.40343	0.56090
H	2.58587	0.11551	-0.83155	2.85951	-0.77870	-0.82485	-1.49604	1.98180	-0.91112
H	2.58560	0.11608	0.83128	2.57103	0.62188	-0.00125	-2.24535	1.45182	0.45998
	aTS1			**aTS1**			**rTS1**		
C	2.21861	-0.54656	-0.11341	2.29274	-0.62278	0.00040	2.99762	1.10135	0.00003
H	3.19350	-0.07062	-0.19589	2.92436	-0.53246	-0.88590	2.34564	0.07883	-0.00006
H	2.17132	-1.34635	-0.86247	1.93879	-1.66977	-0.00025	3.59320	1.06224	-0.90581
H	1.57919	0.82569	-0.18480	1.64559	0.74645	0.00027	2.28894	1.92395	0.00036
H	2.17425	-1.02635	0.88591	2.92325	-0.53312	0.88756	3.59360	1.06183	0.90558
Zr	-0.05501	-0.15141	0.05704	-0.06963	-0.12192	-0.00024	-0.44669	-0.39624	0.00003
O	0.60125	1.54411	-0.02329	0.71375	1.53714	0.00015	1.47213	-0.89509	-0.00011
N	-2.39815	-0.14785	-0.10242	-2.50134	-0.18704	0.00038	-2.30016	1.14744	-0.00005
H	-2.67681	0.51962	-0.82421	-2.93698	-0.59605	0.82410	-2.89331	1.09574	0.82670
H	-2.81772	-1.04862	-0.32208	-2.72901	0.80726	0.00022	-2.89322	1.09574	-0.82687
H	-2.75806	0.16455	0.80563	-2.93770	-0.59656	-0.82270	-1.82890	2.05188	-0.00002
	[2+2] Intermediate			**[2+2] Intermediate**			**Radical Intermediate**		
C	-1.98077	-1.05825	-0.00041	0.77533	-1.98090	0.00003	-4.63876	0.07948	0.00225
H	-2.00856	-2.14944	-0.00011	1.42214	-2.08284	0.88578	-2.29879	-0.12715	-0.00326
H	-2.51909	-0.70151	-0.89073	1.42287	-2.08403	-0.88499	-4.67583	-0.10172	1.06192
H	-0.56887	2.76517	-0.00105	-3.04904	0.53584	0.00264	-4.84182	-0.71991	-0.68797
H	-2.51701	-0.70125	0.89118	0.09500	-2.83669	0.00035	-4.43145	1.06874	-0.36649
Zr	-0.03799	-0.02396	0.00018	-0.19712	0.05583	-0.00007	0.59045	-0.01414	-0.00044
O	-0.22370	1.87282	-0.00011	-2.09825	0.44166	-0.00024	-1.33916	-0.08861	-0.00216
N	2.17776	-0.67064	-0.00025	1.91574	1.20741	0.00024	3.01110	0.06452	0.00164

H	2.59724	-0.26210	0.84361	1.80156	2.21785	-0.00230	3.34672	0.69012	0.73309
H	2.36904	-1.67028	-0.00117	2.45830	0.96051	0.82606	3.39467	-0.86495	0.16899
H	2.59682	-0.26072	-0.84366	2.45797	0.95659	-0.82466	3.35683	0.40091	-0.89634
	TS2			**TS2**			**TS2**		
Zr	0.26475	0.04716	0.03739	0.26214	0.02028	0.01516	0.21923	-0.10723	0.05024
O	-1.56936	-0.86791	0.08068	-1.57560	-0.87848	0.09531	-1.83182	-0.75388	0.01996
C	-2.49309	0.61914	-0.06972	-2.51462	0.68816	-0.03484	-2.07302	0.91697	-0.04058
H	-2.27467	1.16997	-0.97750	-2.11494	1.38496	-0.76025	-1.17799	1.59209	-0.07437
H	-2.33082	1.18784	0.83814	-2.53033	1.04371	0.98414	-2.63262	1.06952	0.87117
H	-3.44438	0.10511	-0.08554	-3.41249	0.18084	-0.35489	-2.65744	1.03897	-0.94417
H	-1.83574	-1.44202	-0.65267	-1.85077	-1.44507	-0.64368	-2.15732	-1.22144	-0.77149
N	2.57840	0.04513	-0.07725	2.60720	0.10334	-0.03455	2.59093	0.21323	-0.09092
H	3.04007	0.94772	-0.19380	3.03914	0.63688	0.72018	2.93240	0.73057	0.71609
H	2.92676	-0.39872	0.77702	2.86666	-0.88131	0.06709	3.10353	-0.66236	-0.16845
H	2.79350	-0.54353	-0.88753	2.95911	0.44421	-0.93066	2.77629	0.77840	-0.91800
	NH_3Zr---$OHCH_3$			**NH_3Zr---$OHCH_3$**			**NH_3Zr---$OHCH_3$**		
Zr	0.39657	0.02418	-0.07848	0.40355	0.05759	-0.01738	0.39251	-0.08241	-0.00343
O	-1.78277	0.43177	0.00871	-1.81310	0.39801	0.02284	-1.87064	-0.42868	-0.00227
C	-2.95692	-0.39696	0.08309	-2.97618	-0.44142	0.01108	-2.94456	0.51417	0.00180
H	-3.22794	-0.56425	1.12281	-3.53486	-0.31303	0.93592	-3.57046	0.38594	-0.88071
H	-2.70829	-1.34243	-0.38663	-2.62228	-1.46493	-0.05987	-2.47743	1.49624	-0.01818
H	-3.76941	0.08262	-0.45790	-3.59774	-0.20523	-0.85059	-3.54168	0.41078	0.90703
H	-1.87583	1.25190	0.53155	-2.03474	1.33855	0.09006	-2.18234	-1.34059	0.02586
N	2.67217	-0.14606	0.15974	2.69920	-0.20572	0.04997	2.76642	0.25510	-0.01025
H	3.06472	0.75517	-0.12816	3.21330	0.59809	0.41092	3.30770	-0.50588	-0.41255
H	2.84748	-0.30577	1.15581	3.01116	-1.05298	0.52547	3.08682	1.13732	-0.40115
H	3.10499	-0.89448	-0.38475	2.89069	-0.29957	-0.95572	2.94427	0.27150	0.99597
	$ZrNH_3$			**$ZrNH_3$**			**$ZrNH_3$**		
Zr	0.48071	0.00000	-0.00295	0.48365	0.00001	-0.00067	0.50919	0.00019	0.00017
N	-1.81780	0.00001	-0.01976	-1.82660	0.00003	-0.00545	-1.92559	0.00134	0.00121
H	-2.29908	0.82642	-0.37611	-2.21695	0.82982	-0.45477	-2.28963	-0.80214	0.50754
H	-2.29806	-0.82813	-0.37346	-2.21618	-0.83060	-0.45391	-2.31860	0.83662	0.42812
H	-1.90656	0.00154	1.00581	-2.12649	0.00037	0.97381	-2.28007	-0.05147	-0.95068