Supporting Information for

Reactive Metallocene Cations as Sensitive Indicators of Gas-Phase Oxygen and Water

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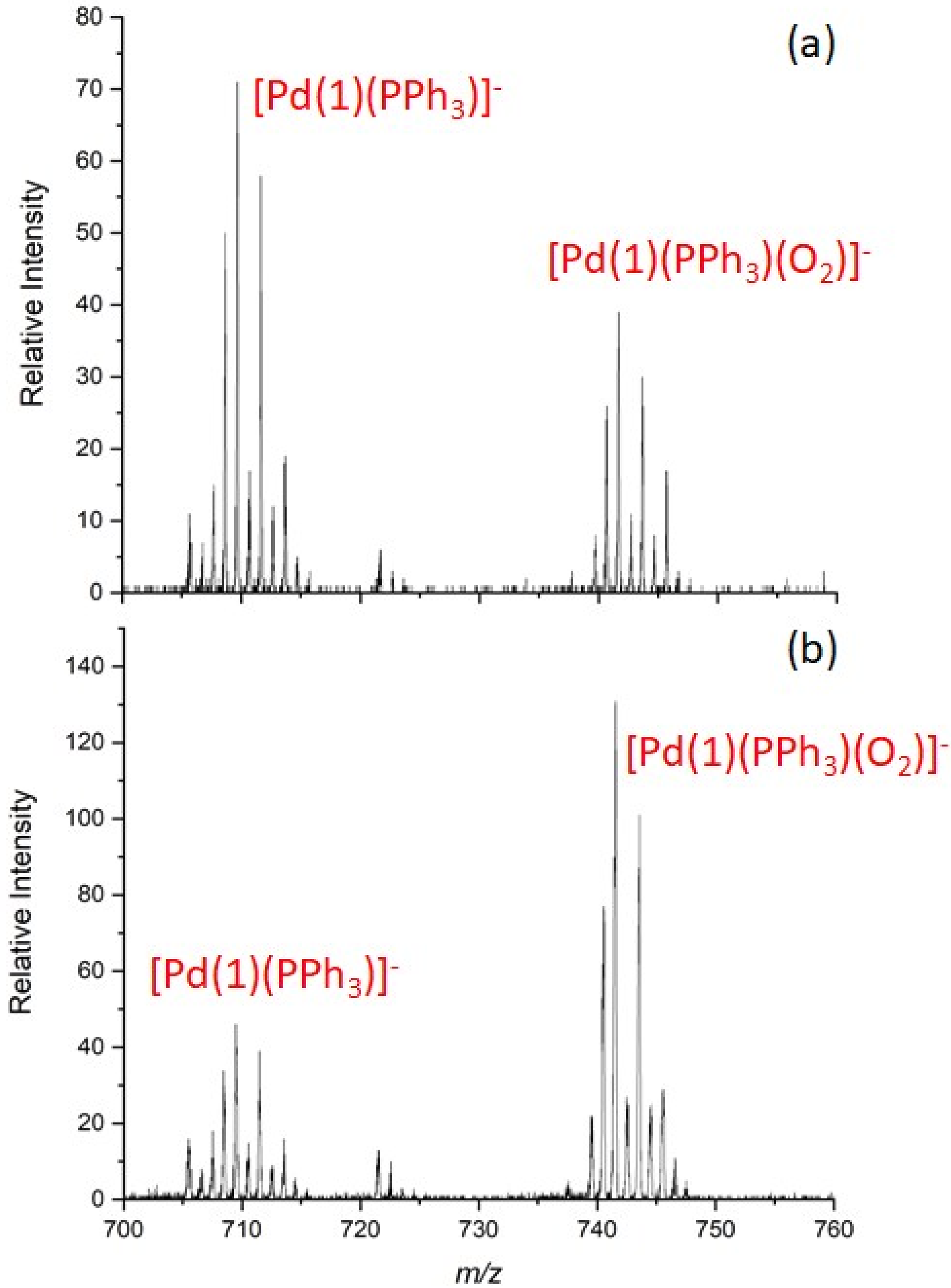


Fig S1: ESI MS of $[Pd(0)(\mathbf{1})(PPh_3)]^-$ complexes in MeOH solution [Pd] = 0.4 mM with desolvation gas supply from (a) 4.0 N_2 cylinder or (b) N_2 generator.

1 = sulfonated triphenylphosphine, $[PPh_2(m\text{-}C_6H_4SO_3)]^-$.

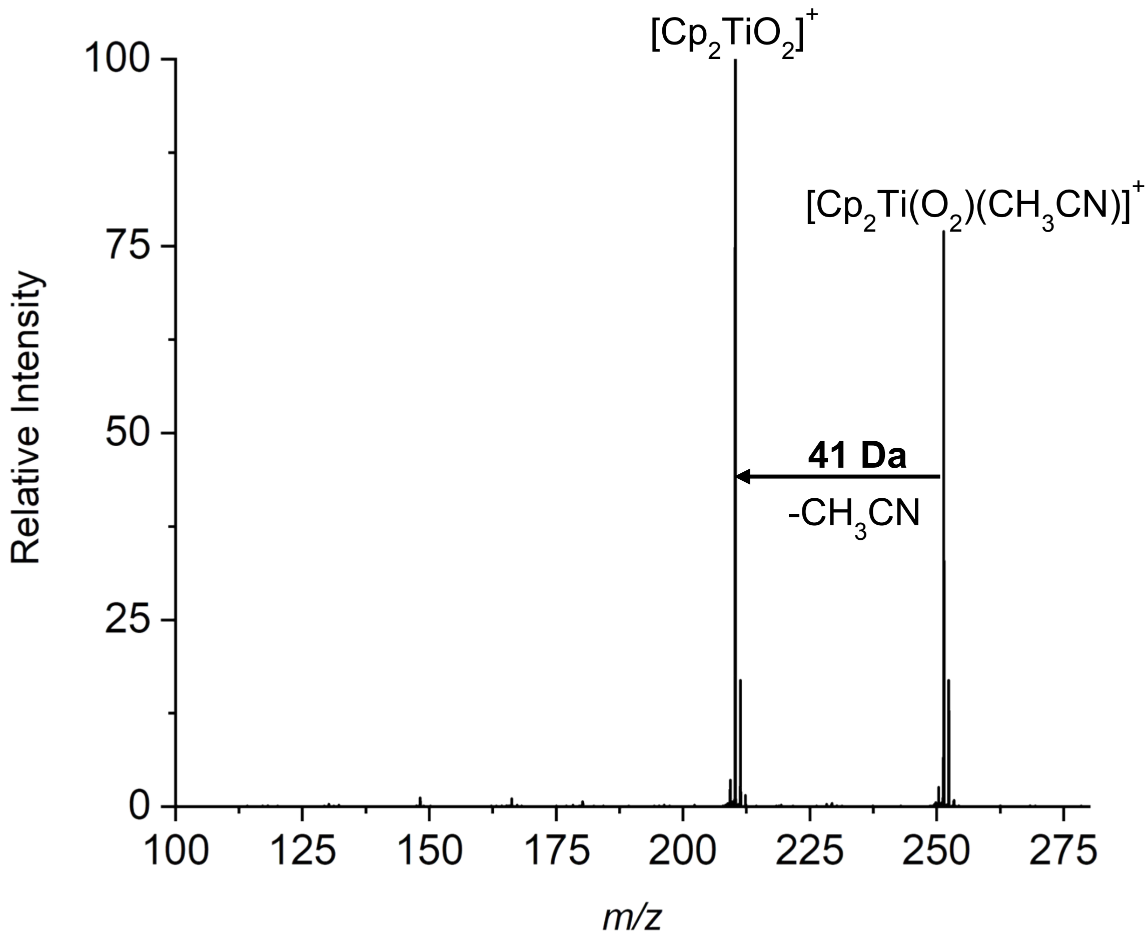


Fig S2: MS-MS of m/z 251 species showing loss of Acetonitrile ligand.

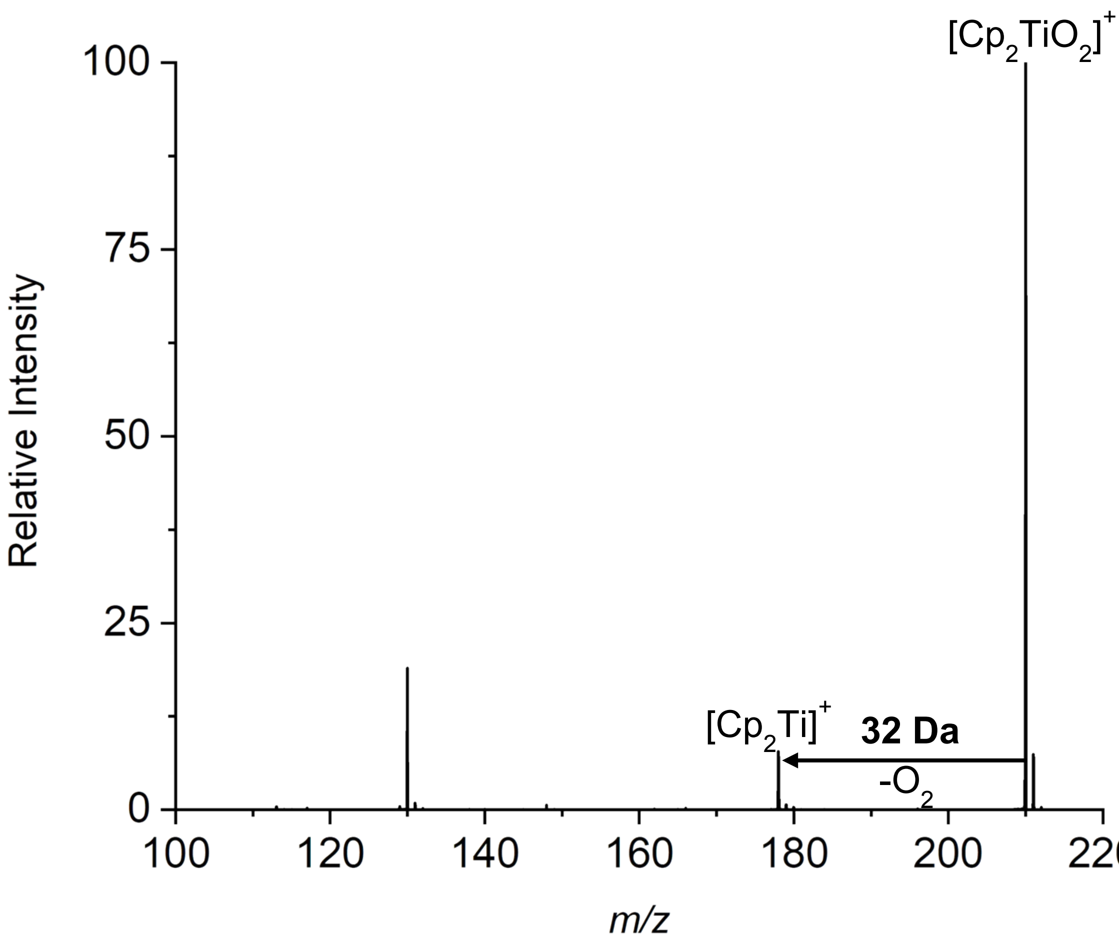


Fig S3: MS-MS of $[Cp_2TiO_2]^+$ (*m/z* 210) species showing loss of oxygen. A prominent fragment ion with *m/z* 130 could correspond to loss of cyclopentadienone from the parent ion (*vide infra*).

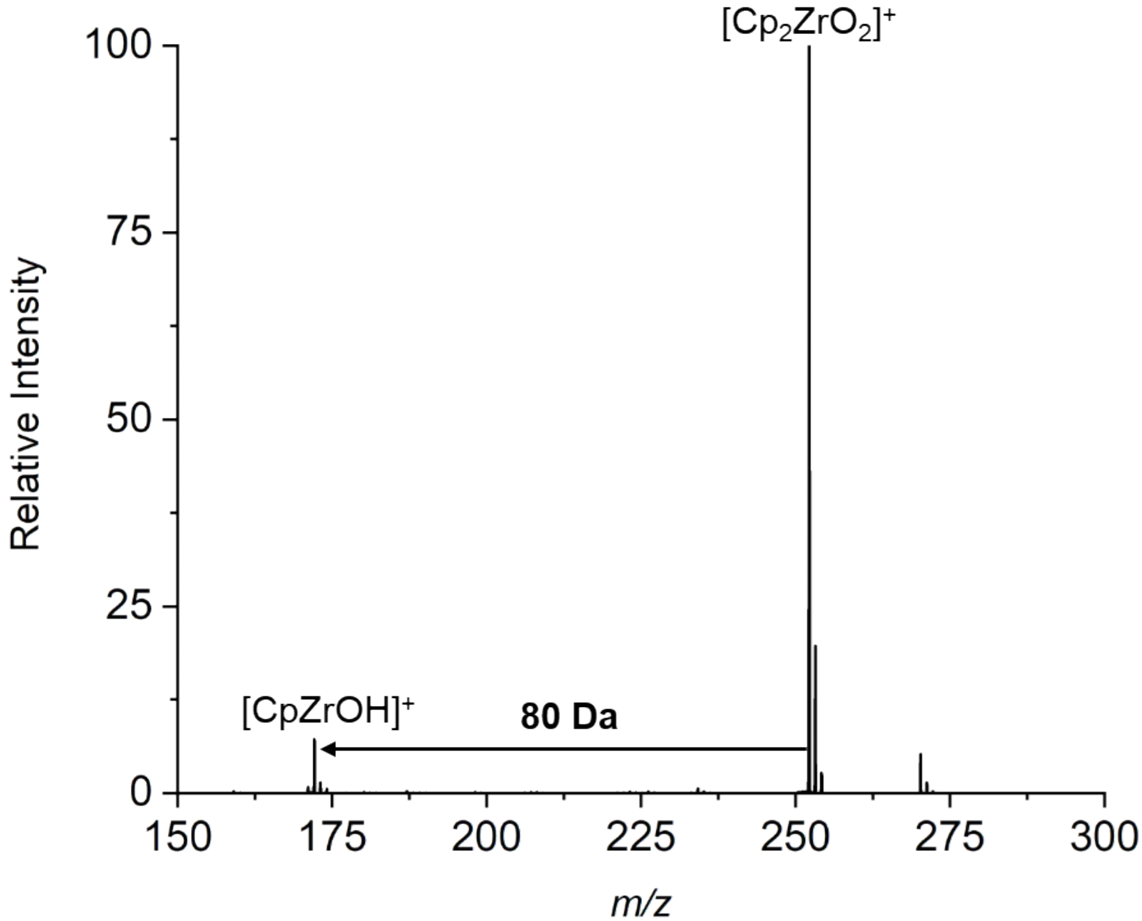
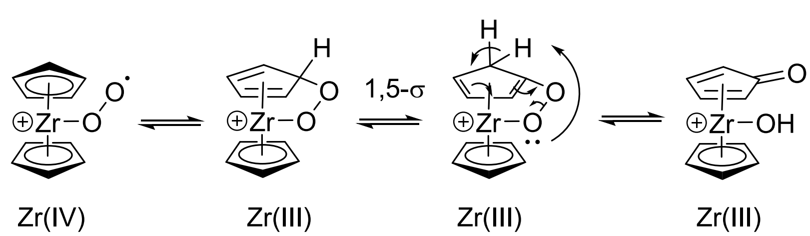


Fig S4: MS-MS of *m/z* 252 species showing that there is no direct loss of O_2 but instead a rearrangement (shown below) to lose the fragment with *m/z* 80.

At low collision pressures, the lowest energy fragmentation of *m/z* 252 involves loss of 80 Da. Neutral losses with this MW involving only C, H and O could correspond to either C_5H_4O or C_6H_8. A logical fragment for the former is cyclopentadienone, while e.g. methylcyclopentadiene does not make as much sense. We are not sure of the most stable structure for *m/z* 252 but if it adopts a metal-peroxo radical cation structure, as postulated by Schwartz and co-workers, one might explain loss of 80 Da as shown in the Scheme where rearrangement proceeds the loss. Note that *m/z* 252 could also have the structure shown on the right which makes some sense for its strong tendency to bind water to form *m/z* 270.



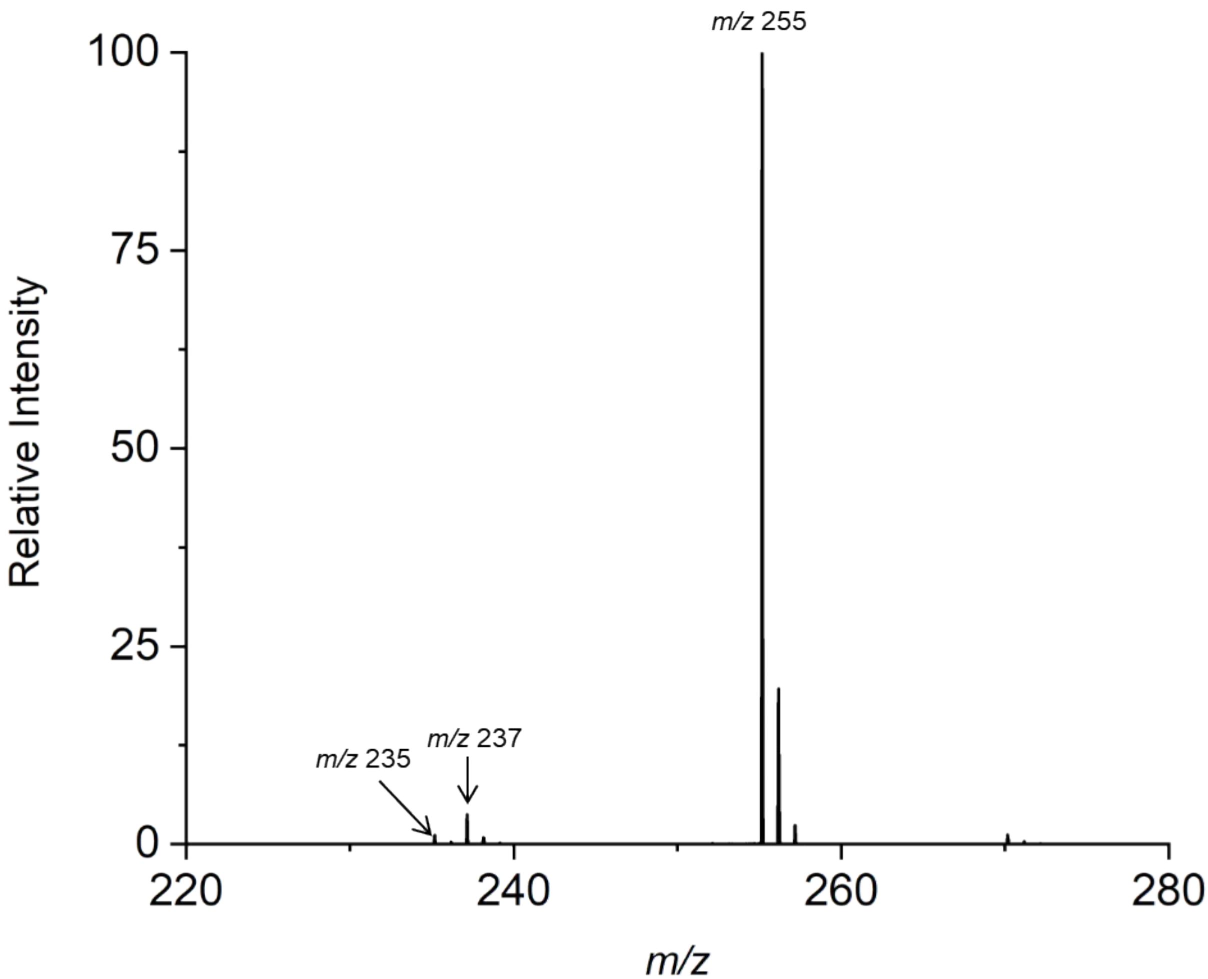


Fig S5: MS-MS of m/z 235 species showing hydrolysis at reduced collision energy. Due to water in the collision cell we see *m/z* 237 [*m/z* 235 + 18 – 16 (CH_4) Da] and *m/z* 255 which is 18 Da higher in mass.

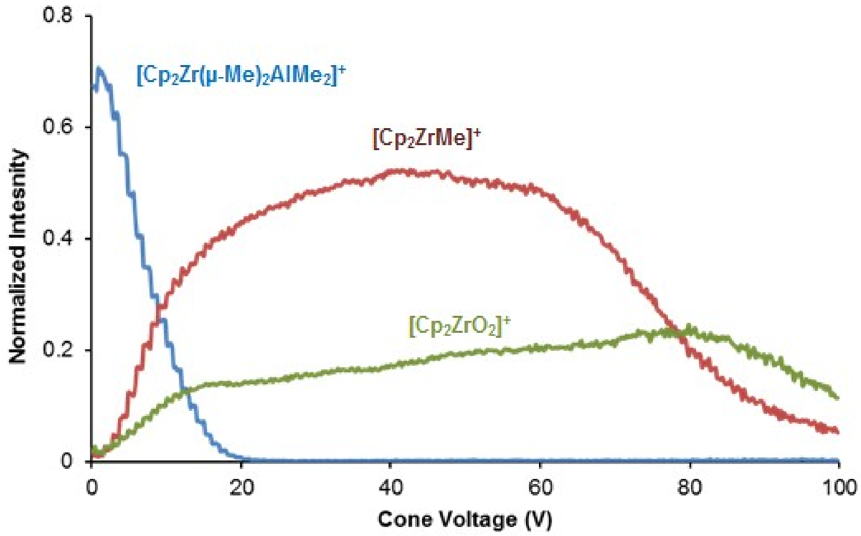


Figure S6: Normalized ion intensities for $[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$ (blue), $[Cp_2ZrMe]^+$ (red) and $[Cp_2ZrO_2]^+$ (green) using generator N_2 vs. cone voltage. The latter was systematically ramped from 0-100V using an AutoHotKey script (https://www.autohotkey.com/).

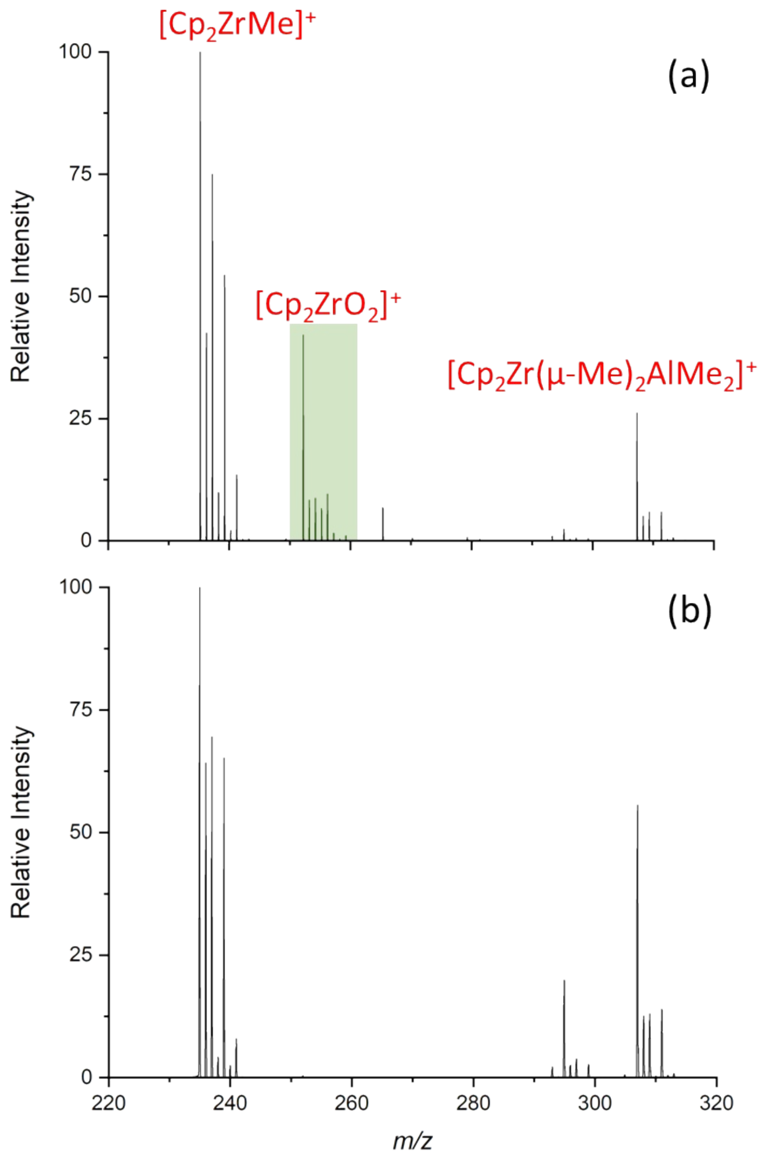


Fig S7: ESI-MS in positive mode of the ($[Cp_2Zr(\mu\text{-}Me)_2AlMe_2]^+$) system at a cone voltage of 24V with an N_2 supply from (a) factory refurbished N_2 generator and (b) brand new N_2 generator. The ion with m/z 252 i..e ($[Cp_2ZrO_2]^+$) was much less prominent when using the new generator.

ΔE (kJ/mol)		DFT Method					
		(SIESTA) UPBE-D2	UPBE0/TZVP //UPBE-D2	UPBE0-D2/TZVP //UPBE-D2	UPBE0-D3/TZVP //UPBE-D2	RI-UB2PLYP-D3/TZVP //UPBE-D2	RI-UB2PLYP-D3/TZVP Opt
Reaction Step	**1 2**	137	102	207	150	122	129
	2 3	−86	−97	−155	−140	−94	−104
	3 4 (κ^1)	159	112	145	128	167	143
	3 4 (η^2)	77	52	79	67	55	75

Table S1: The single point energies calculated in SIESTA were benchmarked against a range of basis sets in Orca.

Geometry Optimized Structures:

$[Cp_2Ti(NCMe)_2]^+$

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   35

H      15.699381   11.940825    8.900696
H      17.158701   15.597901    9.662232
C      15.971458   11.772505    9.958287
H      18.180865   12.208351    9.972588
H      18.835439   14.086210   11.195484
C      17.056267   15.403903   10.745198
C      17.268267   11.927543   10.525500
H      13.983365   11.242752   10.913235
C      17.932832   14.613381   11.547763
C      15.069332   11.414414   11.016781
N      14.072263   13.574444   12.761008
C      16.014671   15.898177   11.605680
H      15.173122   16.544200   11.300567
C      17.180105   11.646135   11.933045
C      15.827675   11.322876   12.235570
C      17.428828   14.599563   12.893040
H      18.013997   11.686891   12.655046
C      16.258619   15.413332   12.926340
Ti     15.838430   13.555297   11.490316
H      17.872839   14.064420   13.751062
H      15.426560   11.074246   13.234352
H      15.628697   15.603947   13.813085
C      13.056447   13.539522   13.347854
C      11.775961   13.510945   14.057145
H      11.003391   13.038035   13.402426
H      11.460617   14.553676   14.304750
H      11.872162   12.919482   14.999697
N      14.370212   14.191711   10.013369
C      13.557774   14.613277    9.277902
C      12.578478   15.180110    8.345935
H      13.082060   15.950876    7.711903
H      11.743564   15.656153    8.915736
H      12.166823   14.375707    7.688087
O       5.481443   12.812440   12.793840
O       6.237235   12.812549   11.737561
```

[$Cp_2TiNCMe$]$^+$

35

H	15.760173	11.710952	8.870337
H	17.072888	15.890806	9.734740
C	15.979386	11.650631	9.951621
H	18.216822	11.952938	10.023867
H	18.860716	14.350633	11.107018
C	16.977896	15.562741	10.785453
C	17.262363	11.788293	10.555428
H	13.923181	11.343355	10.862782
C	17.914843	14.762199	11.503958
C	15.012099	11.475393	11.002762
N	3.760176	19.270411	12.161644
C	15.880886	15.852757	11.671538
H	14.989331	16.455492	11.423785
C	17.098636	11.667955	11.978648
C	15.709824	11.476532	12.259667
C	17.410321	14.562242	12.835912
H	17.907128	11.718885	12.728668
C	16.156924	15.234681	12.937675
Ti	15.895217	13.574857	11.309417
H	17.900203	13.981155	13.637135
H	15.260887	11.344354	13.262068
H	15.512644	15.263562	13.837151
C	2.743189	19.286933	12.754394
C	1.479206	19.300523	13.513480
H	0.660300	18.856778	12.898605
H	1.207910	20.349651	13.780480
H	1.593809	18.704282	14.450006
N	14.376994	14.201184	9.885860
C	13.506098	14.591535	9.200201
C	12.418055	15.073175	8.344717
H	12.808453	15.854437	7.646917
H	11.605801	15.514312	8.973965
H	12.004653	14.220536	7.751165
O	5.481590	12.812692	12.793928
O	6.237453	12.812489	11.737112

[$Cp_2TiNCMeO_2$]$^+$

35

H	16.100855	11.836821	8.762227
O	14.840923	14.062956	8.751076
H	17.450335	15.219889	9.392865
H	18.578410	12.386886	9.739760
C	16.451533	11.638878	9.791198
O	14.692104	13.749833	9.999040
C	17.736963	11.958750	10.312737
C	17.299729	15.178867	10.487270
H	14.610486	10.780454	10.793555
C	15.666871	11.095796	10.861628
H	15.316954	16.236261	10.743013
H	3.078894	18.036634	10.796992
H	4.034750	19.577116	10.945557
C	16.177099	15.710440	11.195754
Ti	16.167416	13.331500	11.409180
H	19.144487	14.090691	11.225035
C	17.757041	11.607729	11.709606
C	18.177444	14.574085	11.445365
C	3.692186	18.663276	11.488434
C	16.486727	11.049698	12.035969
C	4.860525	17.894384	11.960370
H	18.616868	11.720191	12.394710
N	5.791605	17.284059	12.343475

H	3.064933	18.968977	12.360335
C	16.337984	15.395323	12.578399
C	17.565408	14.663986	12.733975
H	16.175460	10.691933	13.033812
N	14.830446	13.117838	13.059557
H	15.634120	15.660642	13.386893
H	17.977187	14.268817	13.680241
C	14.103155	13.035168	13.976537
H	12.213700	12.523331	14.770319
C	13.202020	12.910216	15.120526
H	13.056773	13.904984	15.610214
H	13.646126	12.194876	15.855494

κ^1 $[Cp_2TiO_2]^+$

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H	16.015455	11.668026	8.903584
H	17.300864	15.475622	9.635873
C	16.297294	11.546060	9.967029
H	18.477996	12.161146	9.986738
O	13.109015	13.752204	10.462721
C	17.584084	11.816001	10.537942
C	17.138830	15.288245	10.714530
H	3.086618	18.060917	10.780067
H	14.359825	10.854848	10.921139
O	14.235249	13.592174	10.943828
C	15.430648	11.109975	11.026244
H	4.051907	19.590599	10.968666
H	15.112725	16.230973	11.082692
Ti	16.081677	13.326018	11.472654
H	19.024304	14.188889	11.328647
C	15.994979	15.691807	11.475050
C	18.039538	14.608986	11.600251
C	3.697603	18.668736	11.489891
C	17.514490	11.546446	11.949679
C	4.858901	17.888376	11.958939
C	16.179996	11.121845	12.248920
N	5.788670	17.274336	12.341355
H	3.064852	18.962495	12.361466
H	18.343225	11.656159	12.671463
C	16.164453	15.227286	12.821403
C	17.430395	14.555302	12.899725
H	15.787459	10.861403	13.251062
H	15.442854	15.367166	13.648539
H	17.873614	14.097339	13.802959
N	7.361087	14.546180	17.143847
C	6.347376	14.589534	17.742183
H	4.261089	14.184333	17.882965
C	5.080943	14.626314	18.499049
H	4.818948	15.682578	18.750101
H	5.183347	14.040155	19.443963

η^1 $[Cp_2TiO_2]^+$

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O	14.225246	13.597430	11.081251
O	14.838112	13.902784	9.855732
H	16.176893	11.470911	8.875727
H	17.591380	15.723725	9.820204
C	16.427558	11.445631	9.953218
H	18.643314	11.953634	9.984329
H	19.180862	14.162198	11.412464
C	17.367421	15.406920	10.856856
C	17.715463	11.717187	10.537560

H	14.436239	10.958349	10.906778
C	18.191886	14.573639	11.682381
C	15.517471	11.161785	11.015207
N	7.355433	14.555637	17.142903
C	16.180878	15.725902	11.592137
H	15.321377	16.307326	11.210967
C	17.591979	11.585511	11.957949
C	16.228686	11.270726	12.257383
C	17.500830	14.364625	12.923483
H	18.403687	11.725102	12.692509
C	16.255246	15.078658	12.861262
Ti	16.244721	13.378584	11.240024
H	17.867946	13.782077	13.788120
H	15.794419	11.149181	13.268951
H	15.473669	15.102994	13.644109
C	6.342069	14.592300	17.743457
C	5.080940	14.623967	18.505561
H	4.258858	14.179840	17.892825
H	4.819455	15.679114	18.759823
H	5.195670	14.038792	19.450261
N	5.779968	17.222585	12.158075
C	4.848458	17.872054	11.843791
C	3.672568	18.678503	11.472476
H	3.998316	19.618749	10.966052
H	3.090727	18.938035	12.389159
H	3.019227	18.098267	10.776133

$[Cp_2ZrMe]^+$

27

O	6.250016	23.424340	6.556650
O	6.249988	24.544352	7.037008
H	15.954091	11.267915	8.851216
H	17.215168	15.840108	9.613822
C	16.162370	11.308021	9.939794
H	18.355065	11.894125	10.020502
H	18.883258	14.368184	11.198361
C	17.026765	15.553366	10.668343
C	17.416097	11.645964	10.549757
H	13.573036	13.530261	10.822736
H	14.164625	10.719319	10.841882
C	17.897090	14.775408	11.490243
C	15.222558	11.010327	10.984994
H	13.242504	12.634147	12.362684
C	13.794682	13.509224	11.953275
C	15.859768	15.891449	11.439662
H	14.999558	16.494254	11.089152
C	17.241791	11.567750	11.975065
C	15.885889	11.169387	12.241172
H	13.397588	14.454727	12.384509
C	17.264901	14.625986	12.776028
H	18.028745	11.734739	12.732662
C	16.021218	15.346611	12.751955
Zr	15.861252	13.427175	11.173144
H	17.696250	14.109833	13.654172
H	15.432698	11.008860	13.237436
H	15.315965	15.457492	13.595947

$\kappa^1[Cp_2ZrO_2]^+$

27

O	14.378918	13.593785	7.972825
Zr	16.534727	13.541538	10.459395
O	15.309160	13.750020	8.902243
H	17.826001	16.225301	9.294224

H	15.825747	10.741085	9.170237
C	17.422314	15.854898	10.257033
H	18.258638	10.833136	10.429057
C	16.023053	11.138018	10.183694
H	15.237801	16.434482	10.128519
H	19.263337	14.987463	11.286070
C	16.071615	15.995746	10.708318
C	17.295428	11.192722	10.842976
C	18.177756	15.205774	11.306063
H	13.961750	11.794417	10.855948
C	15.040196	11.684481	11.076229
C	15.976653	15.396732	12.007640
C	17.111804	11.790506	12.130032
C	17.285108	14.941128	12.392137
C	15.713869	12.099675	12.272594
H	17.898284	11.960667	12.887985
H	15.063183	15.335794	12.629613
H	17.548055	14.461842	13.352953
H	15.241477	12.547174	13.166762
C	3.039004	13.046174	15.232457
H	4.099237	12.726239	15.175007
H	2.478665	12.946933	16.184316
H	2.533943	13.459986	14.335986

$\eta^1[Cp_2ZrO_2]^+$

27

O	13.435697	13.437404	11.256899
Zr	15.570838	13.413954	11.314328
O	13.908544	13.593666	9.993590
H	17.157261	15.395154	9.328951
H	15.674725	10.597881	9.839068
C	16.812847	15.388569	10.381774
H	18.084687	11.616107	10.689696
C	15.893001	11.000915	10.847343
H	14.740772	16.293685	10.230931
H	18.578609	14.476219	11.476946
C	15.550273	15.876246	10.857943
C	17.158387	11.539150	11.291209
C	17.559964	14.906380	11.506032
H	13.930286	10.725825	11.935100
C	14.988209	11.047964	11.948470
C	15.511547	15.694910	12.274311
C	17.026284	11.905168	12.669340
C	16.753206	15.085611	12.680082
C	15.679437	11.627524	13.069534
H	17.817388	12.344346	13.304058
H	14.666637	15.961628	12.938757
H	17.049857	14.835574	13.715114
H	15.252302	11.795032	14.077282
C	3.055848	13.047920	15.234353
H	4.114803	12.725059	15.153072
H	2.519487	12.957329	16.200563
H	2.534699	13.461161	14.346934