Supporting Information

Mechanistic Studies of $[AlCp^*]_4$ Combustion

Xin Tang[1+], Jeffery B. DeLisio[2+], Sufian Alnemrat[3+], Zachary Hicks[1], Lauren Stevens[2], Chad A. Stoltz[4], Joseph P. Hooper[3*], Bryan W. Eichhorn[2*], Michael R. Zachariah[2*] Kit H. Bowen[1*], and Dennis H. Mayo[2,4*]

[1] *Department of Chemistry, Johns Hopkins University, Baltimore MD 21218 United States*

[2] *Department of Chemistry and Biochemistry, University of Maryland–College Park, College Park Maryland 20742 United States*

[3] *Department of Physics, Naval Postgraduate School, Monterey California 93943 United States*

[4] *Research Department, Naval Surface Warfare Center Indian Head EOD Tech Division, Indian Head Maryland 20640 United States*

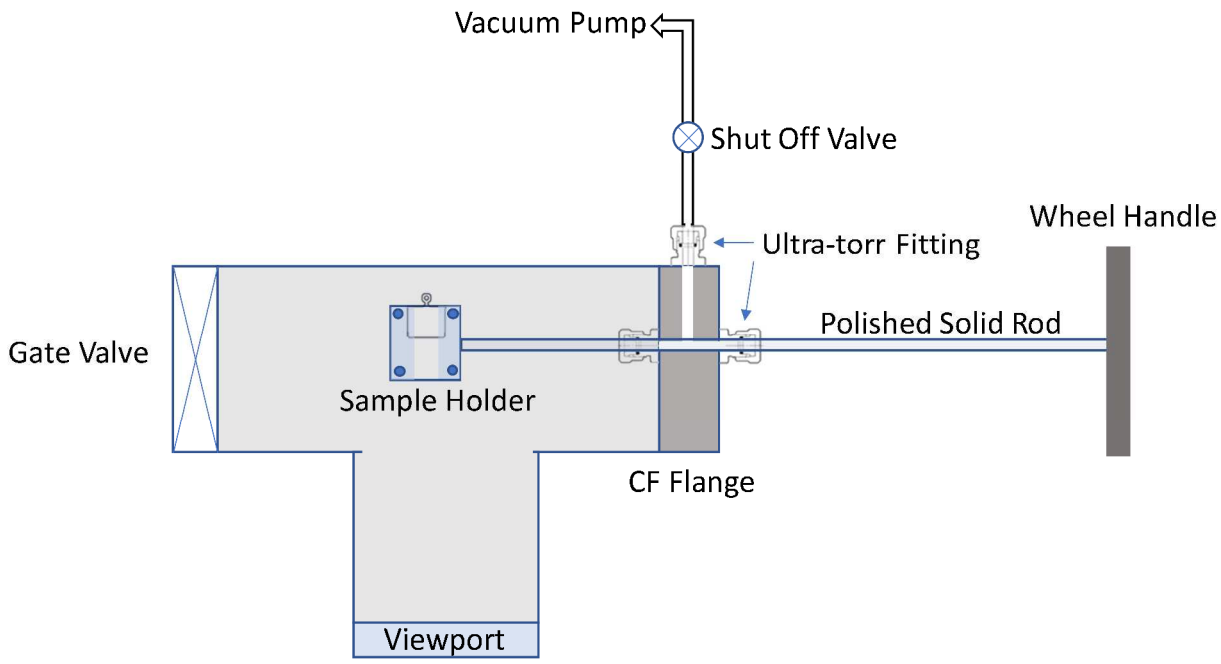

Figure S1. Schematic of the Home-built Vacuum Suitcase for the TPR experiments. The suitcase is pumped via the port connected to the gate valve using a turbomolecular pump and the area between the three Ultra-torr fittings is pumped by a scroll pump. Once the suitcase is evacuated, both the gate valve and the shut off valve are closed and the suitcase is transferred into a glove box. Inside the glove box, the $[AlCp^*]_4$ sample is loaded onto the sample plate located at the sample holder. A fresh cut sodium is put into the suitcase as oxygen/water getter. With both valves shut, the suitcase is removed from the glove box and connected to the load-lock chamber of the analytic instrument. After the load-lock chamber is pumped down via a turbomolecular pump, the turbomolecular pump is shut down and the gate valve is slowly opened to let the suitcase to be evacuated. With the area between the three Ultra-torr fitting also being pumped down, the sample can be freely moved into the load-lock chamber, where a transfer arm can fetch the sample and transfer it into the analytic chamber.

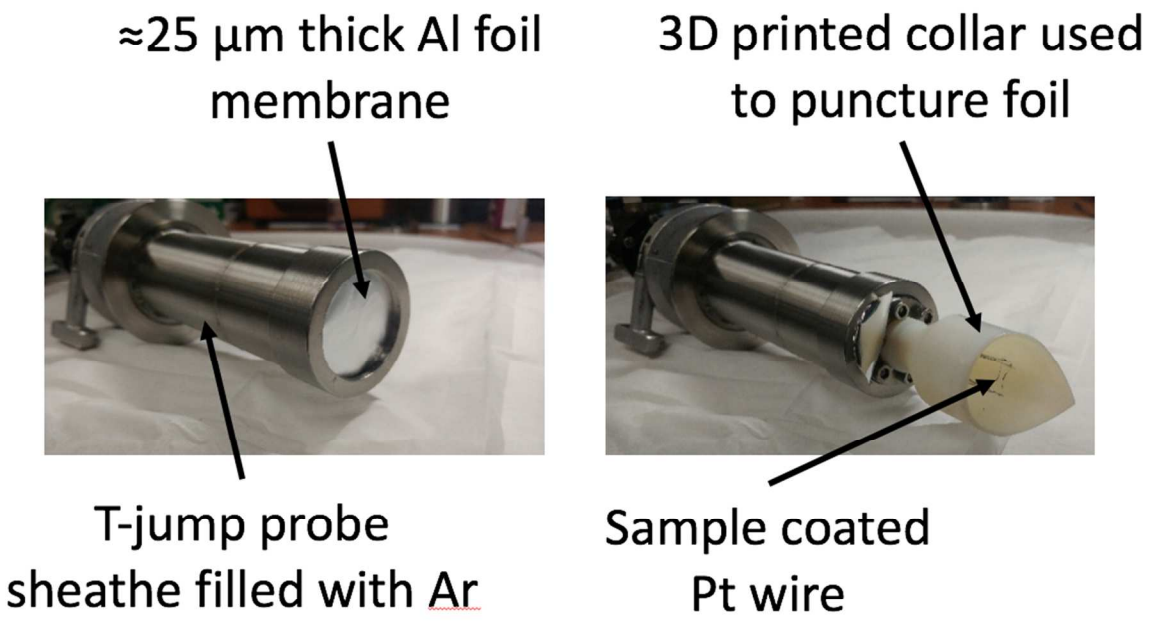

Figure S2. Picture of Home-built Vacuum Suitcase used for T-jump experiments. The air-sensitive sample is coated on the wire in the glove box and sealed with an Al foil membrane. The suitcase is then transferred to the T-jump chamber, the chamber purged with N_2 and then the foil is punctured with the collar prior to T-jump analysis.

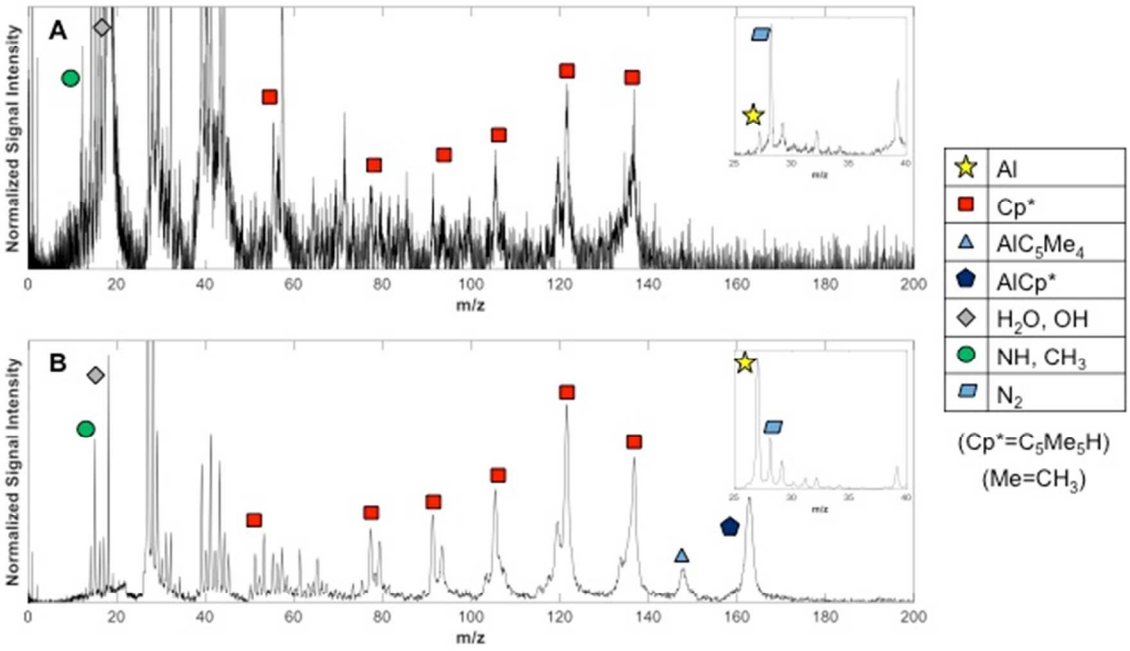

Figure S3. TOF-MS spectra of A) KCp* and B) $[AlCp^*]_4$. Insets show spectra for m/z = 26-40, highlighting differences in m/z = 27 (i.e. Al ions).

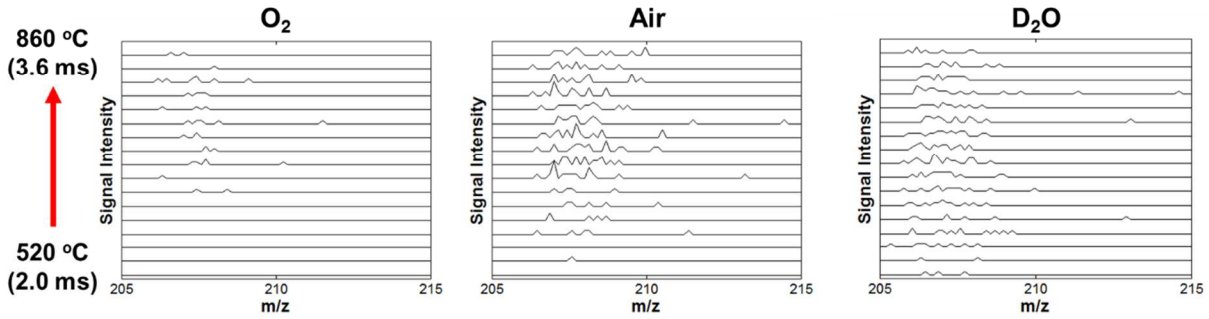

Figure S4. MS of $[AlCp^*]_4$ oxidized in pure oxygen, air, and oxygen with a partial pressure of D_2O from 520 to 860 ^oC in the m/z = 205-215 range.

Table 3
Ignition temperature of various n-Al based nanothermites listed in terms of the oxidizer. The oxygen release temperature from the nanothermite reactions and the bare oxidizer as detected by TOFMS is also tabulated. Heating rate ~5×10^5 K/s.

Nanothermite (Al + oxidizer)	Ignition temperature (K) (±50 K)	O_2 release temperature in thermite (K) (±50 K)	O_2 release from bare oxidizer (K) (±50 K)
$AgIO_3$	890	880	890
$KClO_4$	905	905	875
CuO	1040	1050	975
Fe_2O_3	1410	1400	1340
Co_3O_4	1370	1020	1030
Bi_2O_3	850	930	1620
Sb_2O_3	950	–	–
MoO_3	850	–	–
WO_3	1030	–	–
SnO_2	1050	MS shutdown	1680

Figure S5. Table 3 from ref. 22 showing the O_2 release temperatures of oxidizers. Bi_2O_3 is 1620 K.