

Supporting Information

Gas-Phase Reactions of bis(η^5 -Cyclopentadienyl)methylzirconium Cations with Ketones
and Aldehydes

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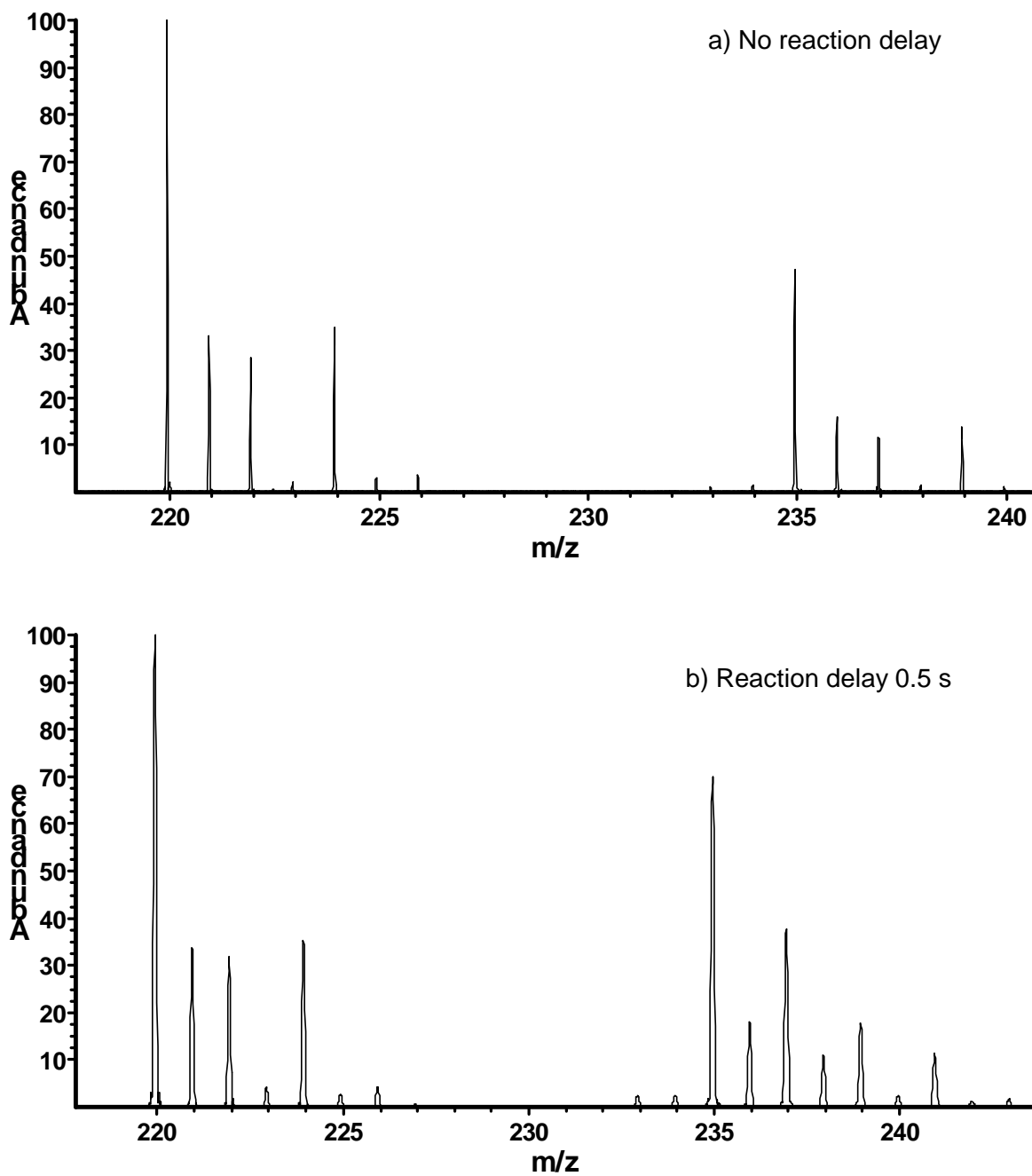


Figure S1. EI mass spectrum of Cp₂Zr(CH₃)₂: Cp₂ZrCH₃⁺ (m/z 235-242), Cp₂Zr⁺ (m/z 220-227) and Cp₂ZrOH⁺ (m/z 237-244).

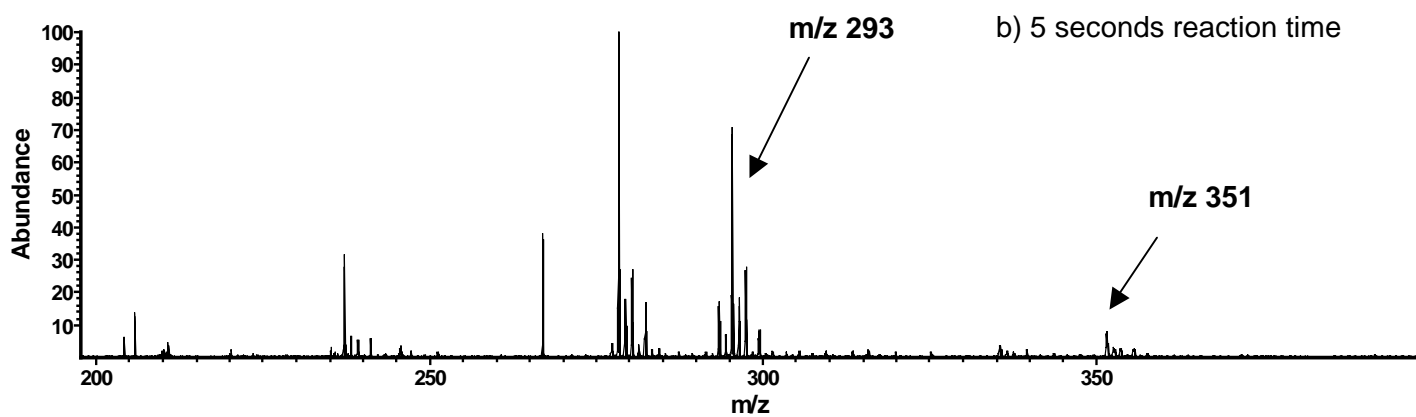
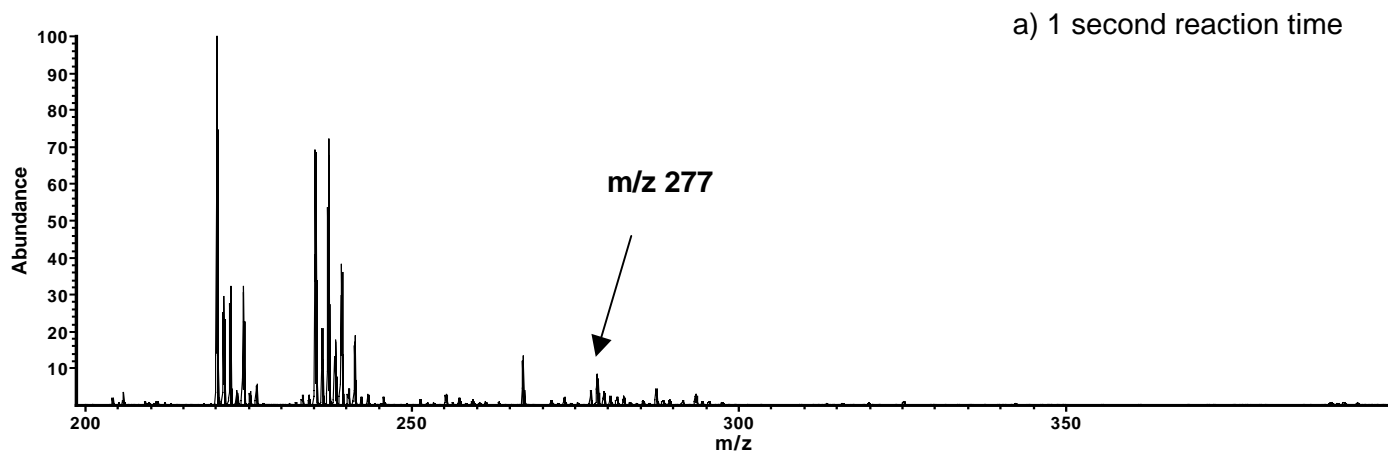


Figure S2. Mass spectra of ions formed in the reaction of Cp_2ZrMe^+ with acetone.

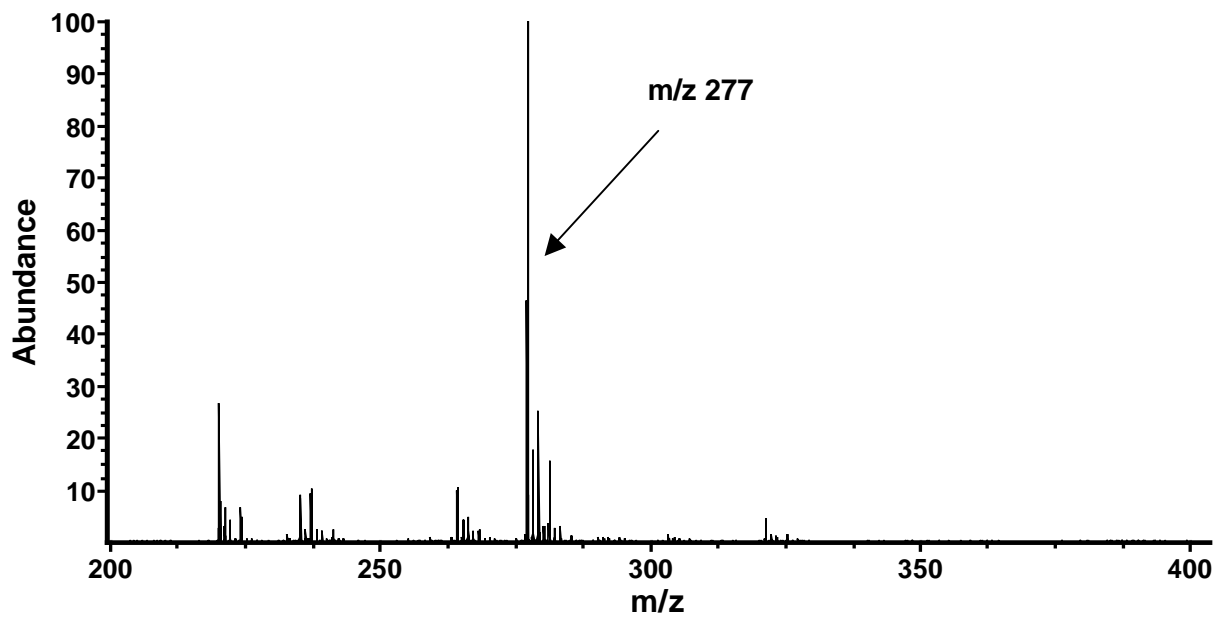


Figure S3. Mass spectrum of ions formed in the reaction of Cp_2ZrMe^+ with acetaldehyde, 1 second reaction delay.

Reaction	Observed Reaction Products		Neutral eliminated
	m/z	Suggested Empirical Formula	
1 (m/z 235) + 2-butanone (nominal molecular weight 72 amu)	307	$[\text{Cp}_2\text{ZrCH}_3 \cdot \text{O}=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5]^+$	
	379	$[\text{Cp}_2\text{ZrCH}_3 \cdot 2\text{O}=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5]^+$	
	277	$\text{Cp}_2\text{ZrC}_3\text{H}_5\text{O}^+$	C_2H_6
	291	$\text{Cp}_2\text{ZrC}_4\text{H}_7\text{O}^+$	CH_4
2 (m/z 238) + 2-butanone (nominal molecular weight 72 amu)	310	$[\text{Cp}_2\text{ZrCD}_3 \cdot \text{O}=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5]^+$	
	382	$[\text{Cp}_2\text{ZrCD}_3 \cdot 2\text{O}=\text{C}(\text{CH}_3)\text{C}_2\text{H}_5]^+$	
	279	$\text{Cp}_2\text{ZrC}_3\text{H}_3\text{D}_2\text{O}^+$	$\text{C}_2\text{H}_5\text{D}$
	280	$\text{Cp}_2\text{ZrC}_3\text{H}_2\text{D}_3\text{O}^+$	C_2H_6
	291	$\text{Cp}_2\text{ZrC}_4\text{H}_7\text{O}^+$	CHD_3
	293	$\text{Cp}_2\text{ZrC}_4\text{H}_5\text{D}_2\text{O}^+$	CH_3D
	294	$\text{Cp}_2\text{ZrC}_4\text{H}_4\text{D}_3\text{O}^+$	CH_4
1 (m/z 235) + methyl isobutyl ketone (nominal molecular weight 100 amu)	335	$[\text{Cp}_2\text{ZrCH}_3 \cdot \text{O}=\text{C}(\text{CH}_3)\text{i-C}_4\text{H}_9]^+$	
	435	$[\text{Cp}_2\text{ZrCH}_3 \cdot 2\text{O}=\text{C}(\text{CH}_3)\text{i-C}_4\text{H}_9]^+$	
	277	$\text{Cp}_2\text{ZrC}_3\text{H}_5\text{O}^+$	C_4H_{10}
	319	$\text{Cp}_2\text{ZrC}_6\text{H}_{11}\text{O}^+$	CH_4
	377	$[\text{Cp}_2\text{ZrC}_3\text{H}_5\text{O}^+ \cdot \text{O}=\text{C}(\text{CH}_3)\text{i-C}_4\text{H}_9]^+$	
2 (m/z 238) + methyl isobutyl ketone (nominal molecular weight 100 amu)	338	$[\text{Cp}_2\text{ZrCD}_3 \cdot \text{O}=\text{C}(\text{CH}_3)\text{i-C}_4\text{H}_9]^+$	
	438	$[\text{Cp}_2\text{ZrCD}_3 \cdot 2\text{O}=\text{C}(\text{CH}_3)\text{i-C}_4\text{H}_9]^+$	
	279	$\text{Cp}_2\text{ZrC}_3\text{H}_3\text{D}_2\text{O}^+$	$\text{C}_4\text{H}_9\text{D}$
	280	$\text{Cp}_2\text{ZrC}_3\text{H}_2\text{D}_3\text{O}^+$	C_4H_{10}
	319	$\text{Cp}_2\text{ZrC}_6\text{H}_{11}\text{O}^+$	CHD_3

	321	$\text{Cp}_2\text{ZrC}_6\text{H}_9\text{D}_2\text{O}^+$	CH_3D
	322	$\text{Cp}_2\text{ZrC}_6\text{H}_8\text{D}_3\text{O}^+$	CH_4
1 (m/z 235) + cyclohexanone (nominal molecular weight 98 amu)	333	$[\text{Cp}_2\text{ZrCH}_3 \cdot \text{O}=\text{C}(\text{CH}_2)_5]^+$	
	431	$[\text{Cp}_2\text{ZrCH}_3 \cdot 2\text{O}=\text{C}(\text{CH}_2)_5]^+$	
	317	$\text{Cp}_2\text{ZrC}_6\text{H}_9\text{O}^+$	CH_4
2 (m/z 235) + cyclohexanone (nominal molecular weight 98 amu)	336	$[\text{Cp}_2\text{ZrCD}_3 \cdot \text{O}=\text{C}(\text{CH}_2)_5]^+$	
	434	$[\text{Cp}_2\text{ZrCD}_3 \cdot 2\text{O}=\text{C}(\text{CH}_2)_5]^+$	
	317	$\text{Cp}_2\text{ZrC}_6\text{H}_9\text{O}^+$	CHD_3

Table S1. Major reaction products observed in the reactions of **1** and **2** with 2-butanone, methyl isobutyl ketone, and cyclohexanone at various reaction times (1 to 5 seconds).

Reaction	Observed Reaction Products	
	m/z	Suggested Empirical Formula
1 (m/z 235) + acetaldehyde (nominal molecular weight 44 amu)	277	$[\text{Cp}_2\text{ZrC}_3\text{H}_5\text{O}^+]$
	321	$[\text{Cp}_2\text{ZrC}_3\text{H}_5\text{O}^+ \cdot \text{CH}_3\text{CHO}]^+$
2 (m/z 238) + acetaldehyde (nominal molecular weight 44 amu)	279/280 (ion abundance ratio ~1/3)	$[\text{Cp}_2\text{ZrC}_3\text{H}_3\text{D}_2\text{O}]^+ / [\text{Cp}_2\text{ZrC}_3\text{H}_2\text{D}_3\text{O}]^+$
	323/324 (ion abundance ratio ~1/3)	$[\text{Cp}_2\text{ZrC}_3\text{H}_3\text{D}_2\text{O} \cdot \text{CH}_3\text{CHO}]^+ / [\text{Cp}_2\text{ZrC}_3\text{H}_2\text{D}_3\text{O} \cdot \text{CH}_3\text{CHO}]^+$
1 (m/z 235) + benzaldehyde (nominal molecular weight 106 amu)	339	$[\text{Cp}_2\text{ZrC}_2\text{H}_2(\text{C}_6\text{H}_5)\text{O}]^+$
2 (m/z 238) + benzaldehyde (nominal molecular weight 106 amu)	341	$[\text{Cp}_2\text{ZrC}_2\text{D}_2(\text{C}_6\text{H}_5)\text{O}]^+$
1 (m/z 235) + propanal (nominal molecular weight 70 amu)	291	$[\text{Cp}_2\text{ZrC}_4\text{H}_7\text{O}]^+$

(nominal molecular weight 58 amu)	293	$[\text{Cp}_2\text{ZrCH}_3 \cdot \text{C}_2\text{H}_5\text{CHO}]^+$
	349	$[\text{Cp}_2\text{ZrC}_4\text{H}_7\text{O} \cdot \text{C}_2\text{H}_5\text{CHO}]^+$
2 (m/z 238) + propanal (nominal molecular weight 58 amu)	293/294 (ion abundance ratio ~1/1)	$[\text{Cp}_2\text{ZrC}_4\text{H}_5\text{D}_2\text{O}]^+ / [\text{Cp}_2\text{ZrC}_4\text{H}_4\text{D}_3\text{O}]^+$
	295	$[\text{Cp}_2\text{ZrCD}_3 \cdot \text{C}_2\text{H}_5\text{CHO}]^+$
	351/352 (ion abundance ratio ~1/1)	$[\text{Cp}_2\text{ZrC}_4\text{H}_5\text{D}_2\text{O} \cdot \text{C}_2\text{H}_5\text{CHO}]^+ /$ $[\text{Cp}_2\text{ZrC}_4\text{H}_4\text{D}_3\text{O} \cdot \text{C}_2\text{H}_5\text{CHO}]^+$
1 (m/z 235) + n-hexanal (nominal molecular weight 100 amu)	333	$[\text{Cp}_2\text{ZrC}_7\text{H}_{13}\text{O}]^+$
	335	$[\text{Cp}_2\text{ZrCH}_3 \cdot \text{C}_5\text{H}_{11}\text{CHO}]^+$
	433	$[\text{Cp}_2\text{ZrC}_7\text{H}_{13}\text{O} \cdot \text{C}_5\text{H}_{11}\text{CHO}]^+$
2 (m/z 238) + n-hexanal (nominal molecular weight 100 amu)	335/336 (ion abundance ratio ~3/2)	$[\text{Cp}_2\text{ZrC}_7\text{H}_{11}\text{D}_2\text{O}]^+ /$ $[\text{Cp}_2\text{ZrC}_7\text{H}_{10}\text{D}_3\text{O}]^+$
	338	$[\text{Cp}_2\text{ZrCD}_3 \cdot \text{C}_5\text{H}_{11}\text{CHO}]^+$
	435/436 (ion abundance ratio ~3/2)	$[\text{Cp}_2\text{ZrC}_7\text{H}_{11}\text{D}_2\text{O} \cdot \text{C}_5\text{H}_{11}\text{CHO}]^+ /$ $[\text{Cp}_2\text{ZrC}_7\text{H}_{10}\text{D}_3\text{O} \cdot \text{C}_5\text{H}_{11}\text{CHO}]^+$

Table S2. Major reaction products observed in the reactions of **1** and **2** with acetaldehyde, benzaldehyde, propanal and *n*-hexanal at various reaction times (1 to 5 seconds).

Method	Basis Set	E_A	ΔE_B	ΔE_C	ΔE_D	ΔE_E	ΔE_F
<i>MPW1PW91</i>	<i>sdd(97),</i>	-393191	9.6	18.4	24.4	26.1	27.7
	<i>6-311+G(d,p)</i> <i>cep-121g,</i>	-393117		18.4			
	<i>6-311+G(d,p)</i> <i>crenbl,</i>	-393107					
	<i>6-311+G(d,p)</i> <i>lanl2dz</i>	-392738					33.5
<i>B3LYP</i>	<i>sdd(97),</i>	-393269	9.9	20.6		30.1	31.0
	<i>6-311+G(d,p)</i> <i>cep-121g,</i>	-393193	10.0	20.6	26.7	30.0	30.9
	<i>6-311+G(d,p)</i> <i>crenbl,</i>	-393183		20.6		30.1	31.0
	<i>6-311+G(d,p)</i> <i>lanl2dz,</i>	-392866	8.6	25.6	32.0	34.9	34.0
	<i>6-31G(d)</i> <i>lanl2dz</i>	-392810	11.8	23.2	21.7		34.3
<i>RHF</i>	<i>lanl2dz</i>	-390081	11.4	22.0	13.4	32.4	35.2

Table S3. The absolute electronic energy (kcal/mol) of the most stable m/z 277 structure and the relative energy differences (in kcal/mol) between the most stable and other calculated structures. Lettering corresponds to the structures pictured in Figure 5, A through F.