

Figure S1. a

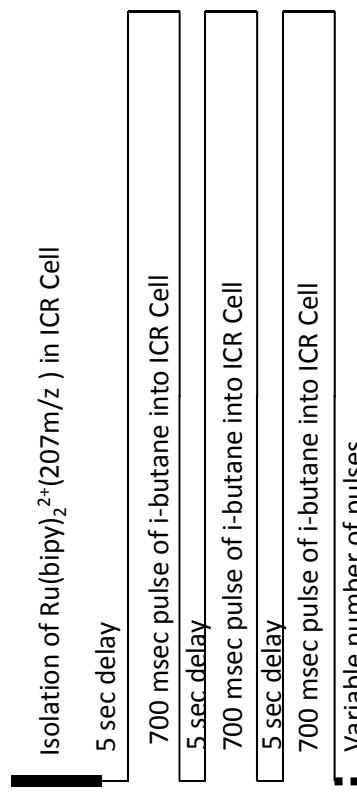


Figure S1. b

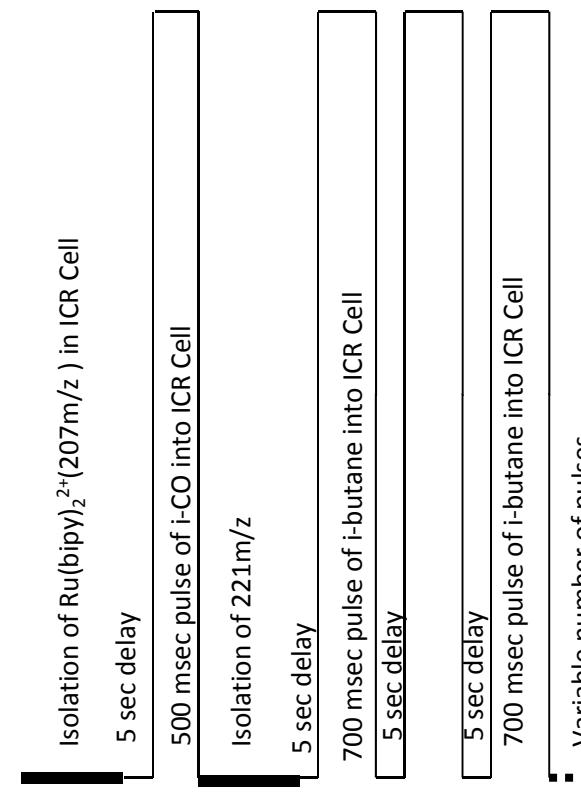


Figure S1. Pulse sequences for experiments conducted on the reaction of a) $[\text{Ru}(\text{bipy})_2]^{2+}$ and b) $[\text{Ru}(\text{bipy})_2\text{CO}]^{2+}$.

221 $[\text{Ru}(\text{bipy})_2\text{CO}]^{2+}$

Figure S2. Mass spectra following the isolation of a) $^{102}\text{Ru}(\text{bipy})_2\text{CO}]^{2+}$ and b) its reaction with 2-methylpropane on a day where water impurities were low.

a

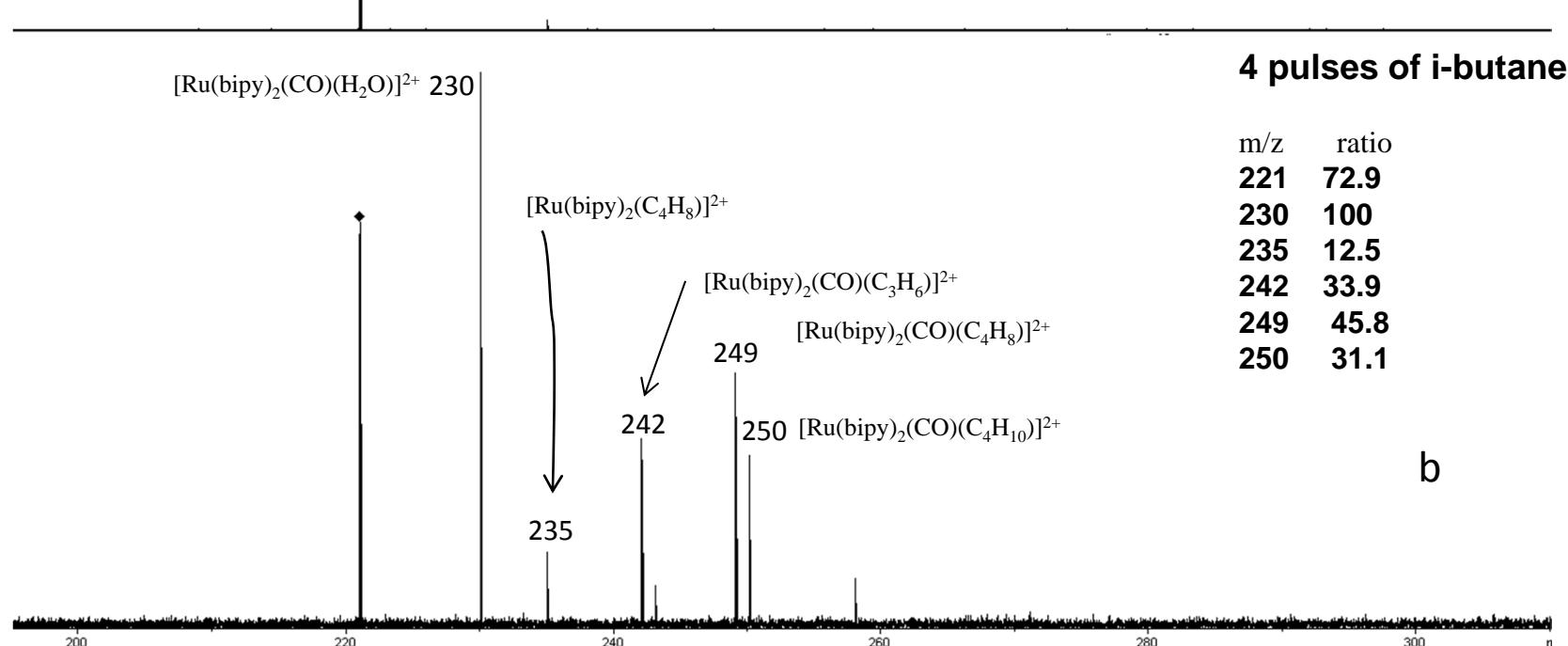
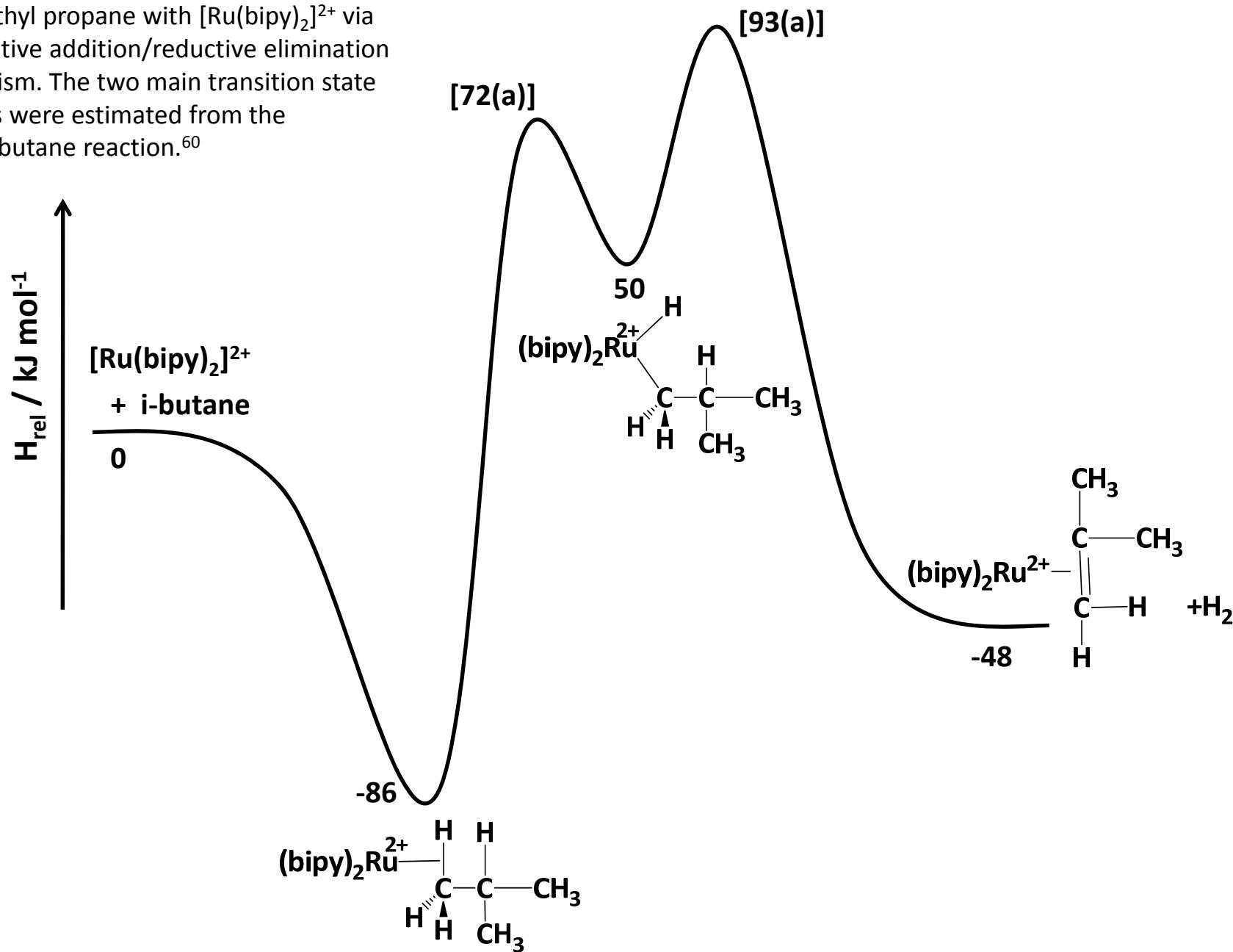


Figure S3. Calculated potential energy diagram for the dehydrogenation reaction of 2-methyl propane with $[\text{Ru}(\text{bipy})_2]^{2+}$ via an oxidative addition/reductive elimination mechanism. The two main transition state energies were estimated from the $\text{Co}^{2+}/\text{iobutane}$ reaction.⁶⁰



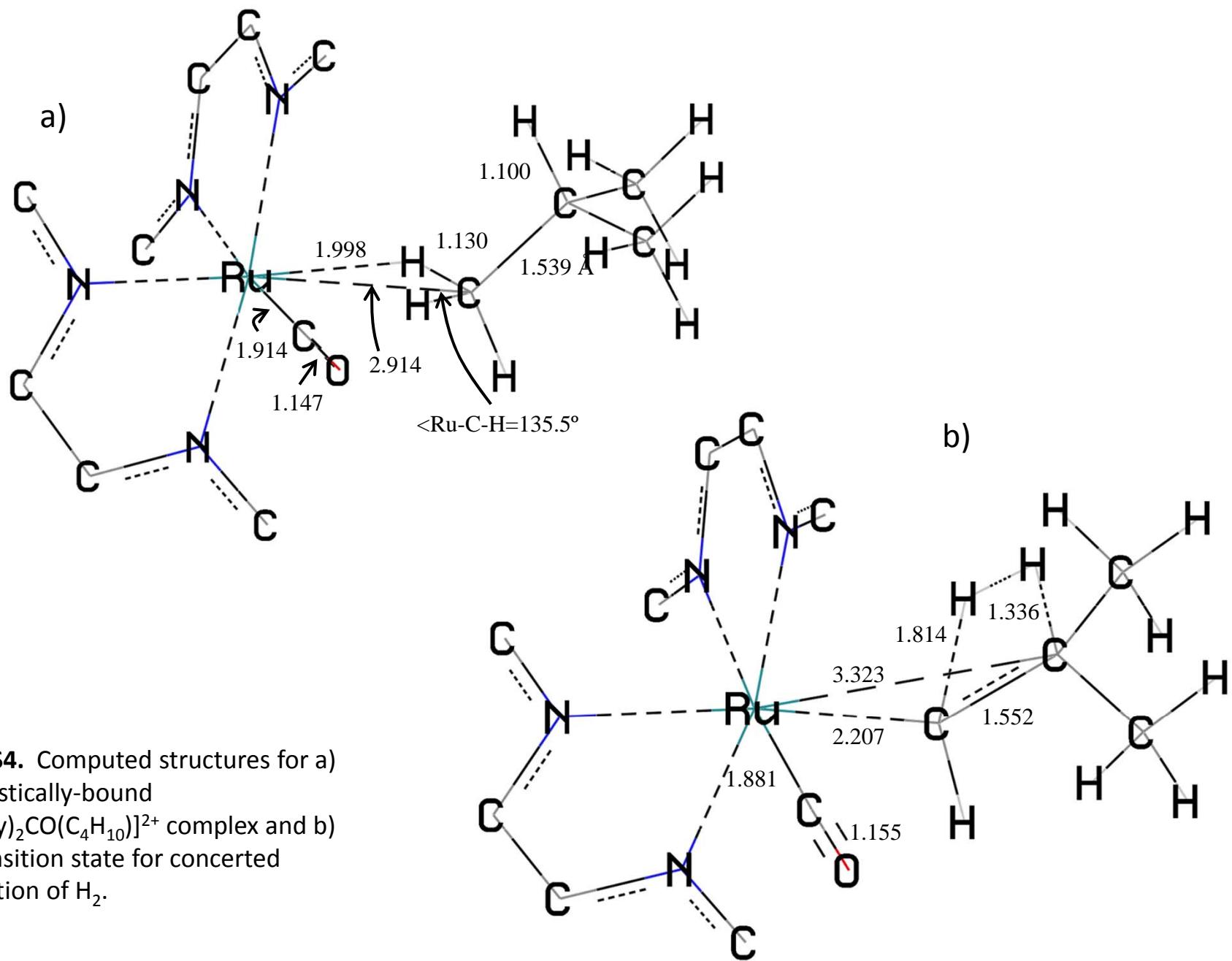


Figure S4. Computed structures for a) the agostically-bound $[\text{Ru}(\text{bipy})_2\text{CO}(\text{C}_4\text{H}_{10})]^{2+}$ complex and b) the transition state for concerted elimination of H_2 .

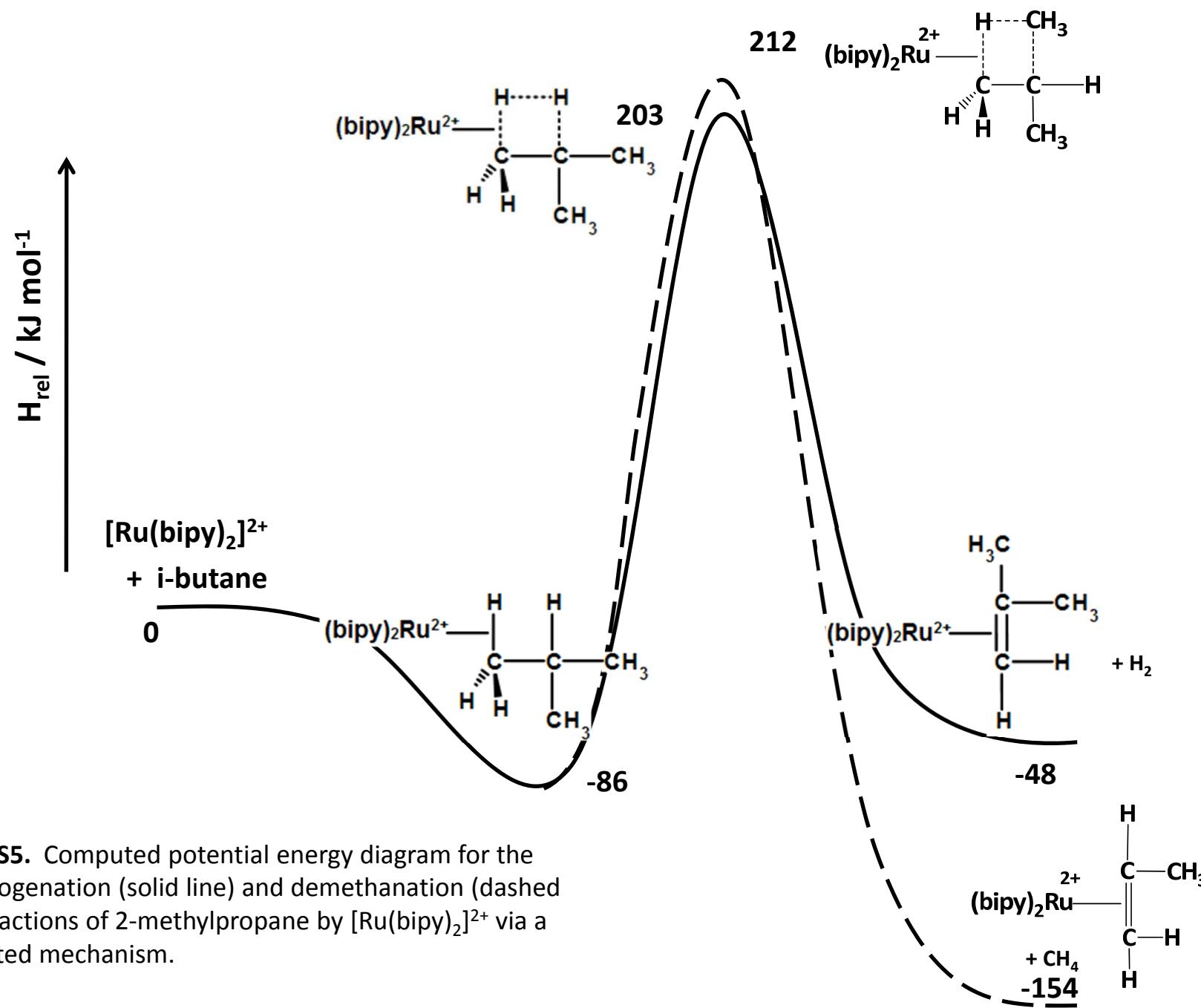


Figure S5. Computed potential energy diagram for the dehydrogenation (solid line) and demethanation (dashed line) reactions of 2-methylpropane by $[\text{Ru}(\text{bipy})_2]^{2+}$ via a concerted mechanism.

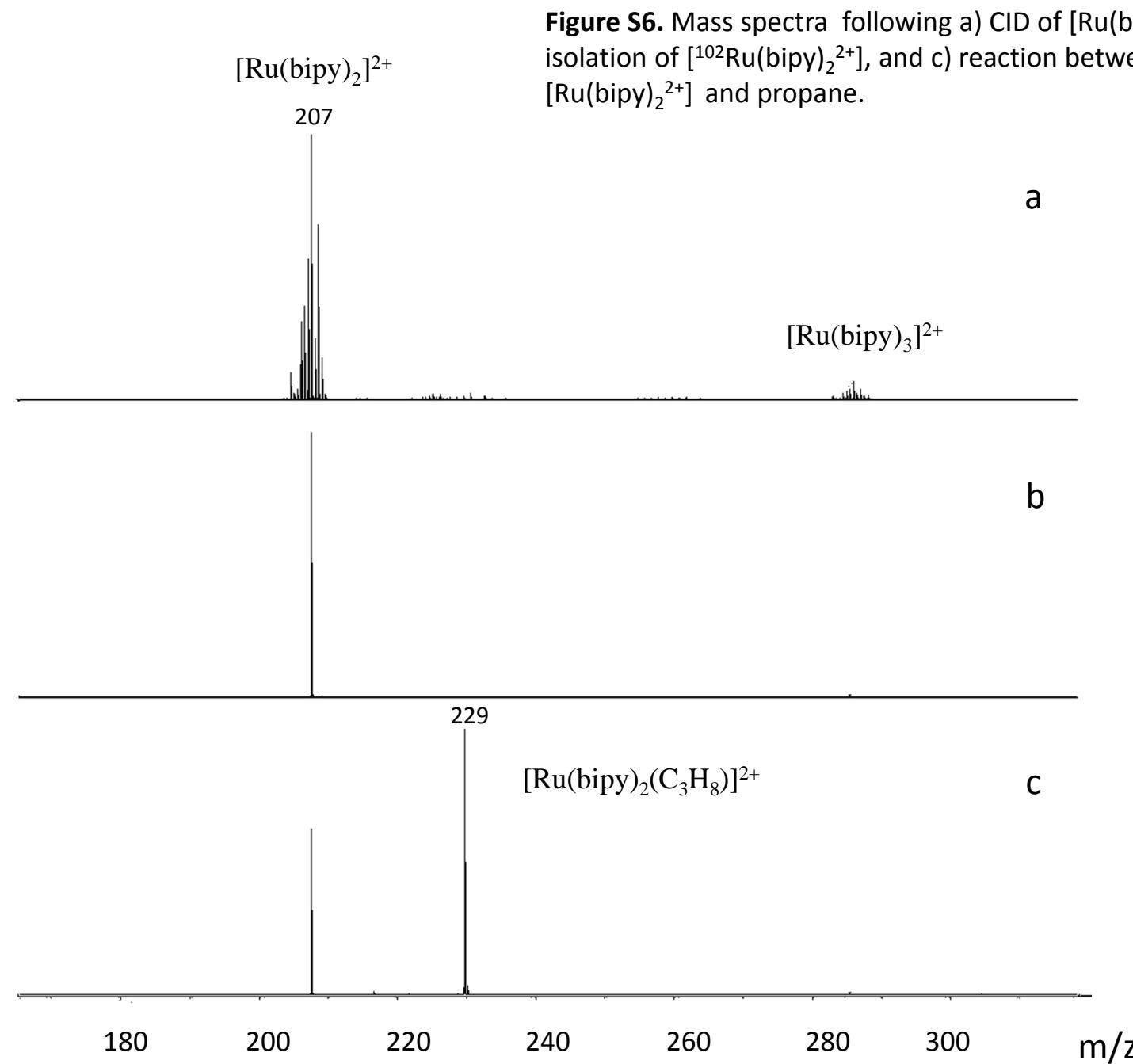
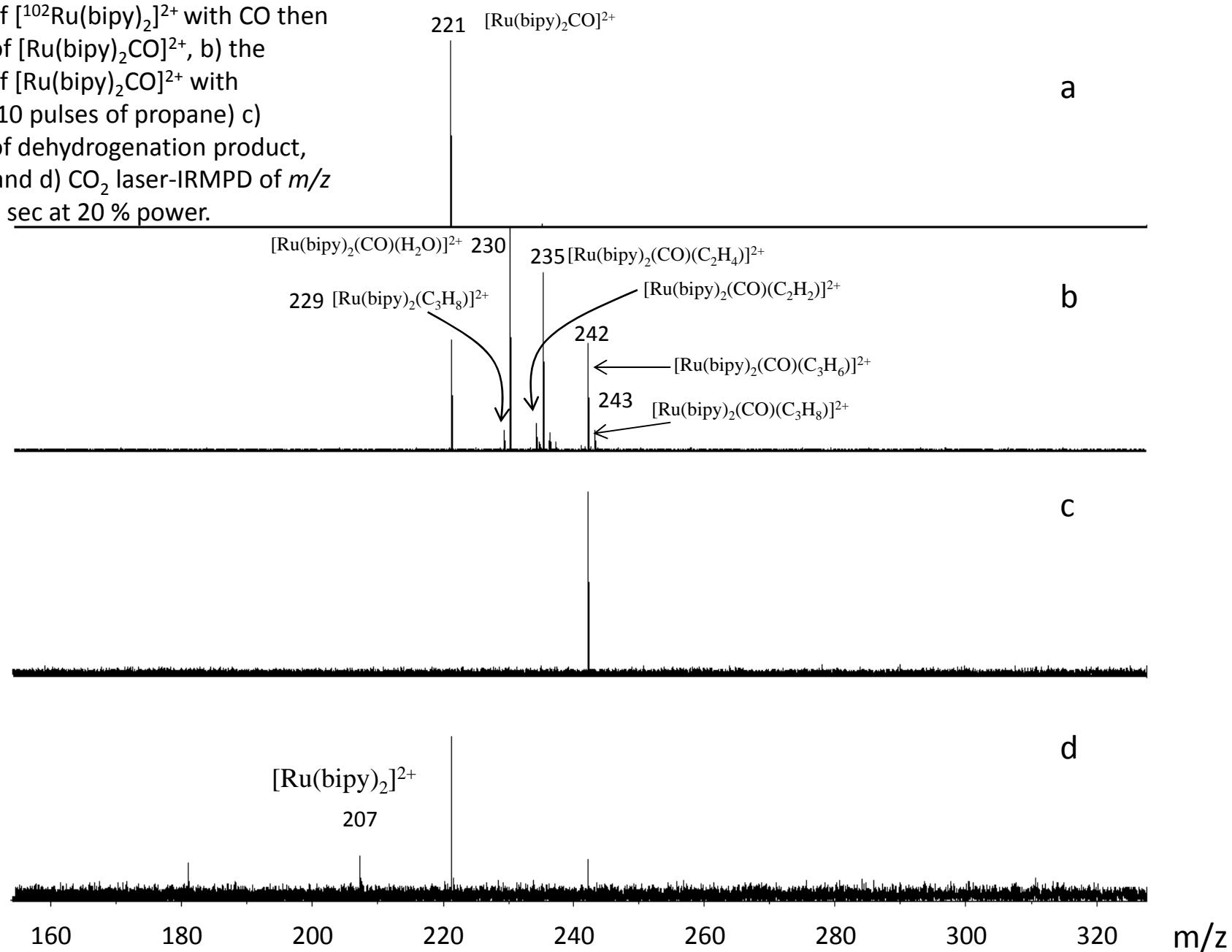


Figure S6. Mass spectra following a) CID of $[\text{Ru}(\text{bipy})_3]^{2+}$ b) isolation of $^{102}\text{Ru}(\text{bipy})_2^{2+}$, and c) reaction between $[\text{Ru}(\text{bipy})_2]^{2+}$ and propane.

Figure S7. Mass spectra following a) reaction of $[^{102}\text{Ru}(\text{bipy})_2]^{2+}$ with CO then isolation of $[\text{Ru}(\text{bipy})_2\text{CO}]^{2+}$, b) the reaction of $[\text{Ru}(\text{bipy})_2\text{CO}]^{2+}$ with propane (10 pulses of propane) c) isolation of dehydrogenation product, m/z 242, and d) CO_2 laser-IRMPD of m/z 242 for 10 sec at 20 % power.



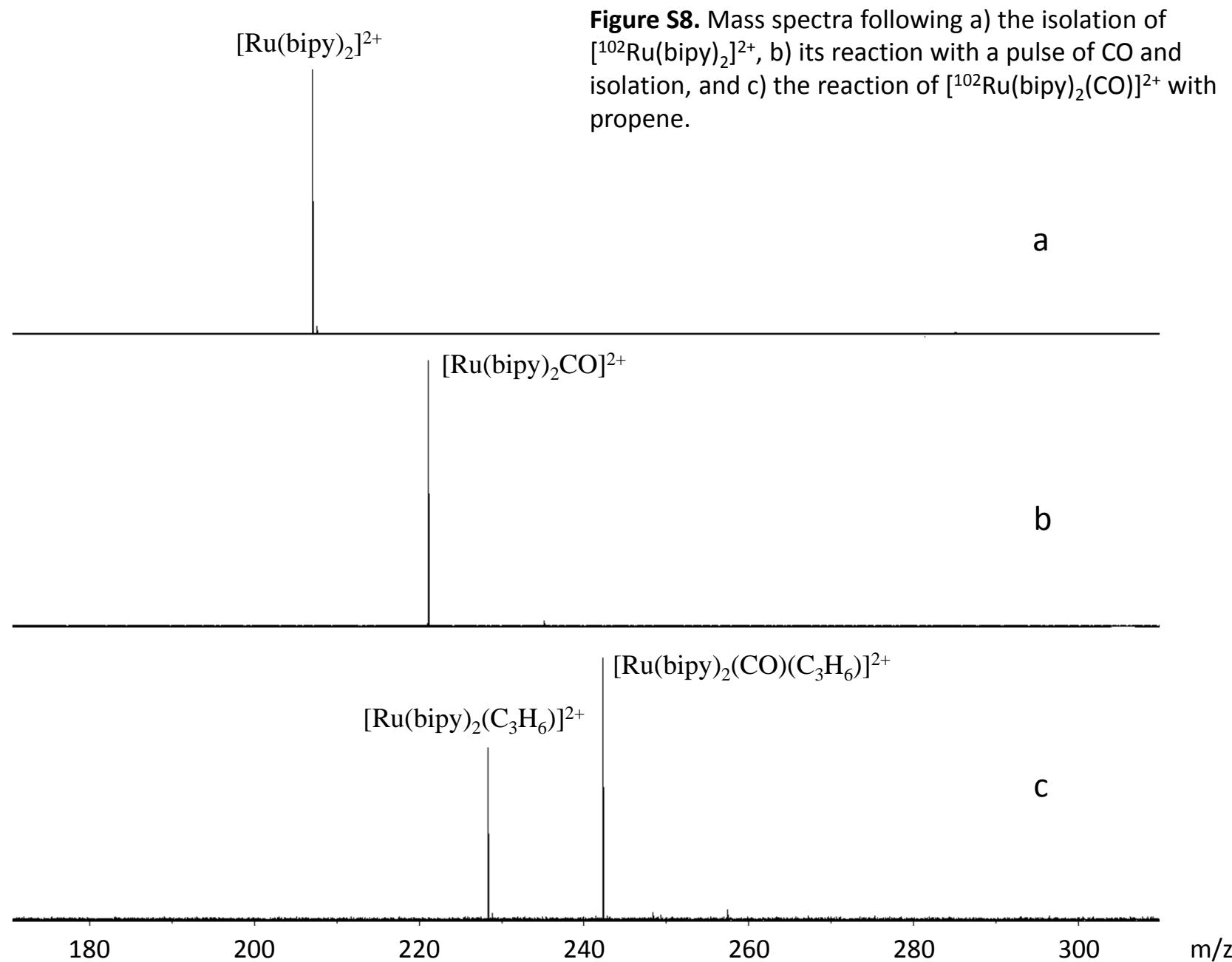


Figure S8. Mass spectra following a) the isolation of [¹⁰²Ru(bipy)₂]²⁺, b) its reaction with a pulse of CO and isolation, and c) the reaction of [¹⁰²Ru(bipy)₂(CO)]²⁺ with propene.

Figure S9. Computed potential energy diagram for the concerted dehydrogenation of 2-methylpropane.

