Article

Mechanism of Deoxygenation and Cracking of Fatty Acids by Gas-Phase Cationic Complexes of Ni, Pd, and Pt

Kevin Parker [1], Victoria Pho [1], Richard A.J. O'Hair [2] and Victor Ryzhov [1,*]

CID of [(phen)Pd($O_2CC_{17}H_{35}$)]$^+$ is shown in previous work [13]

A

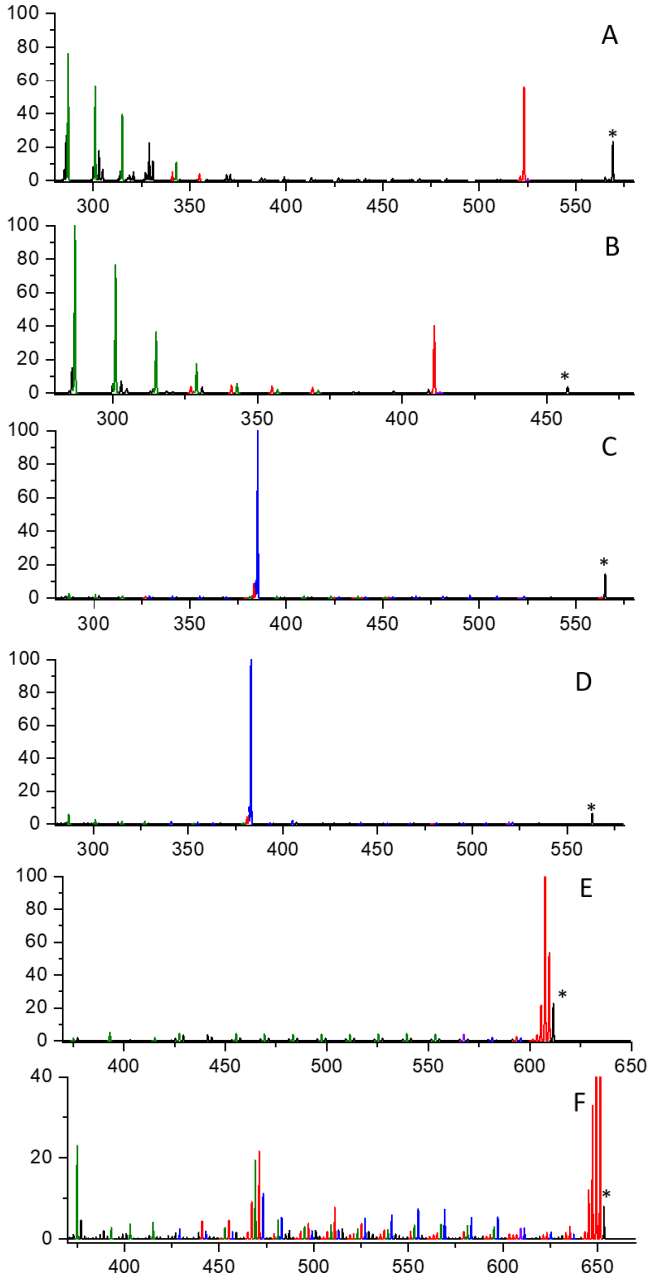


Figure S1. (A) CID of [(phen)Pd($O_2CC_{17}H_{35}$)]$^+$ (stearic acid) is shown elsewhere [13] (B) CID of [(phen)Pd($O_2CC_{10}H_{21}$)]$^+$ (undecanoic acid) (C) CID of [(phen)Pd($O_2CC_{17}H_{31}$)]$^+$ (linoleic acid) (D) CID of [(phen)Pd($O_2CC_{17}H_{29}$)]$^+$ (linolenic acid)

(E) CID of [(phen)Pt($O_2CC_{17}H_{35}$)]$^+$ (stearic acid) (F) CID of [(phen)Pt($O_2CC_{17}H_{31}$)]$^+$ (linoleic acid) *Experiment done on Thermo LTQ at 15 NCE.*

Oleic acid hi-res MS CID

experimental neutral loss	m/z	theoretical neutral loss	ppm error	assigned neutral loss
	567.2224			
16.033	551.1894	16.0313	106.0426	CH4
28.0361	539.1863	28.0313	171.2372	C2H4
42.047	525.1754	42.047	6.76E-10	C3H6
56.0654	511.157	56.0626	49.94417	C4H8
70.0781	497.1443	70.0783	-2.85395	C5H10
84.0945	483.1279	84.0939	7.134881	C6H12
98.1103	469.1121	98.11	3.057792	C7H14
112.1234	455.099	112.1252	-16.0535	C8H16
126.1427	441.0797	126.1409	14.26976	C9H18
140.1584	427.064	140.1565	13.55627	C10H20
154.1721	413.0503	154.1722	-0.64863	C11H22
168.1895	399.0329	168.1878	10.10775	C12H24
182.2054	385.017	182.2035	10.4279	C13H26
196.2209	371.0015	196.2191	9.173419	C14H28
210.2377	356.9847	210.2348	13.7941	C15H30

Table S1. Mass list for high resolution experiment of [(phen)Pd(Oleate)]$^+$. The highlighted yellow lines show that the neutral losses of CH_4 and C_2H_4 do not agree as their ppm error is much higher than allowed. *Experiment done on Bruker Maxis.*

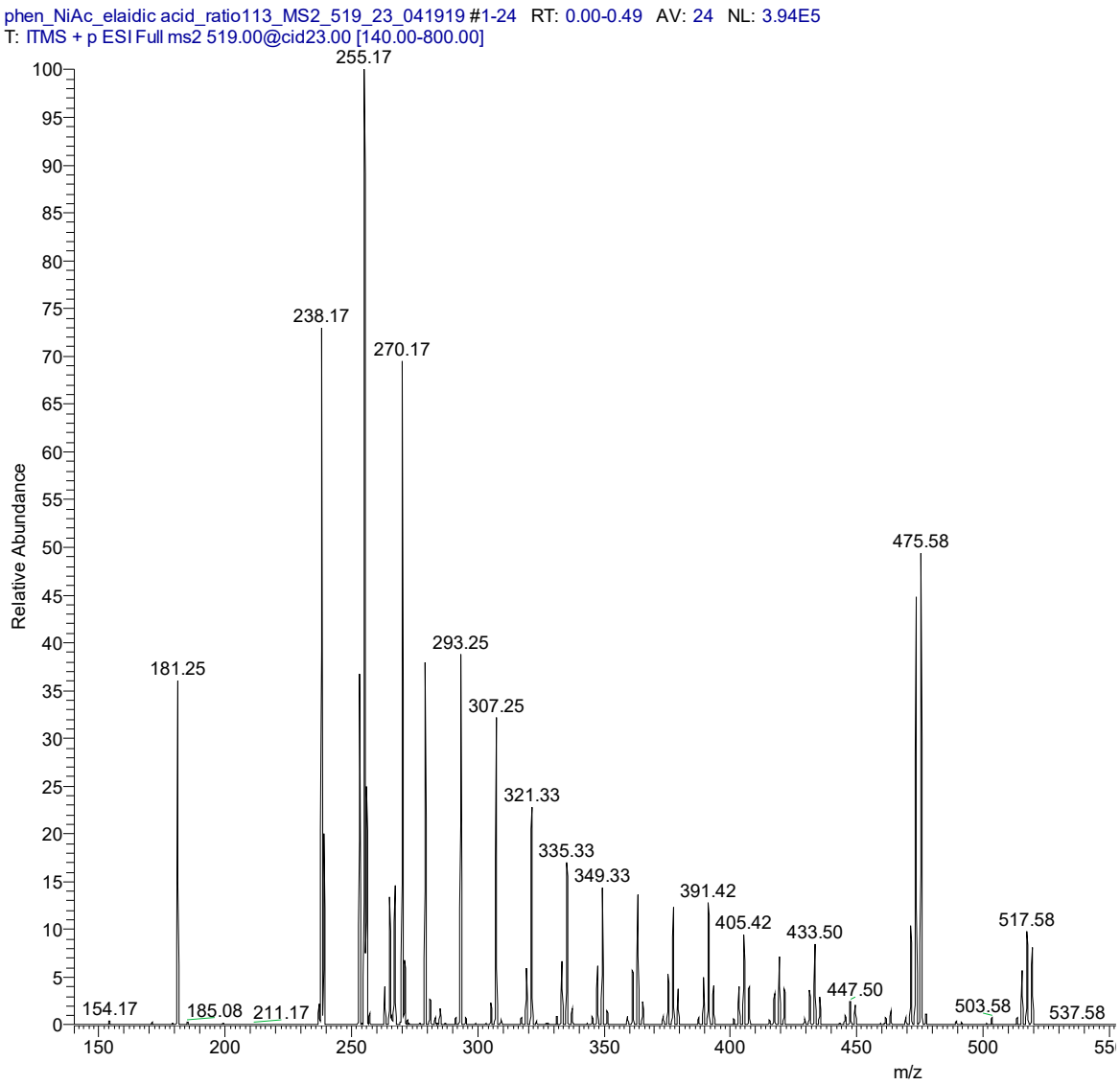


Figure S2. CID (23 NCE) spectrum of $[(phen)Ni(O_2CC_{17}H_{33})]^+$ (elaidic acid). *Experiment done on Thermo LTQ*

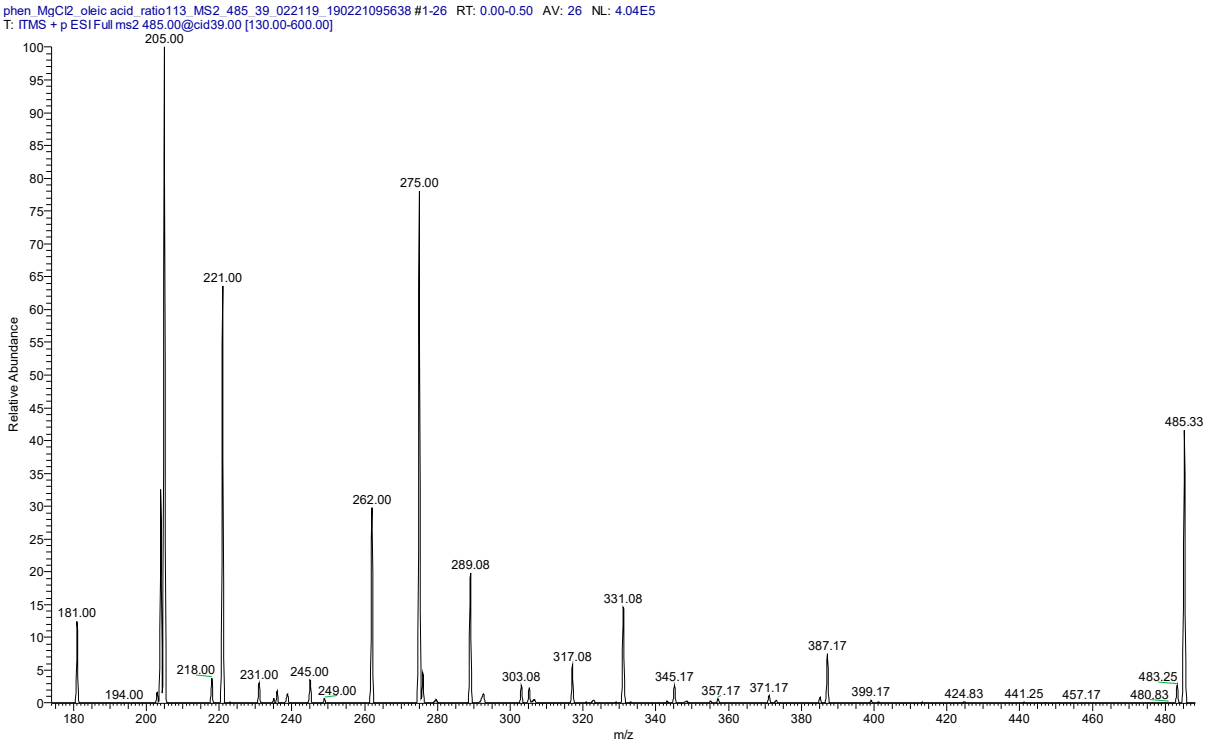


Figure S3. CID of $[(phen)Mg(O_2CC_{17}H_{33})]^+$ for identification of double bond position. *Experiment done on Thermo LTQ at 32 NCE*

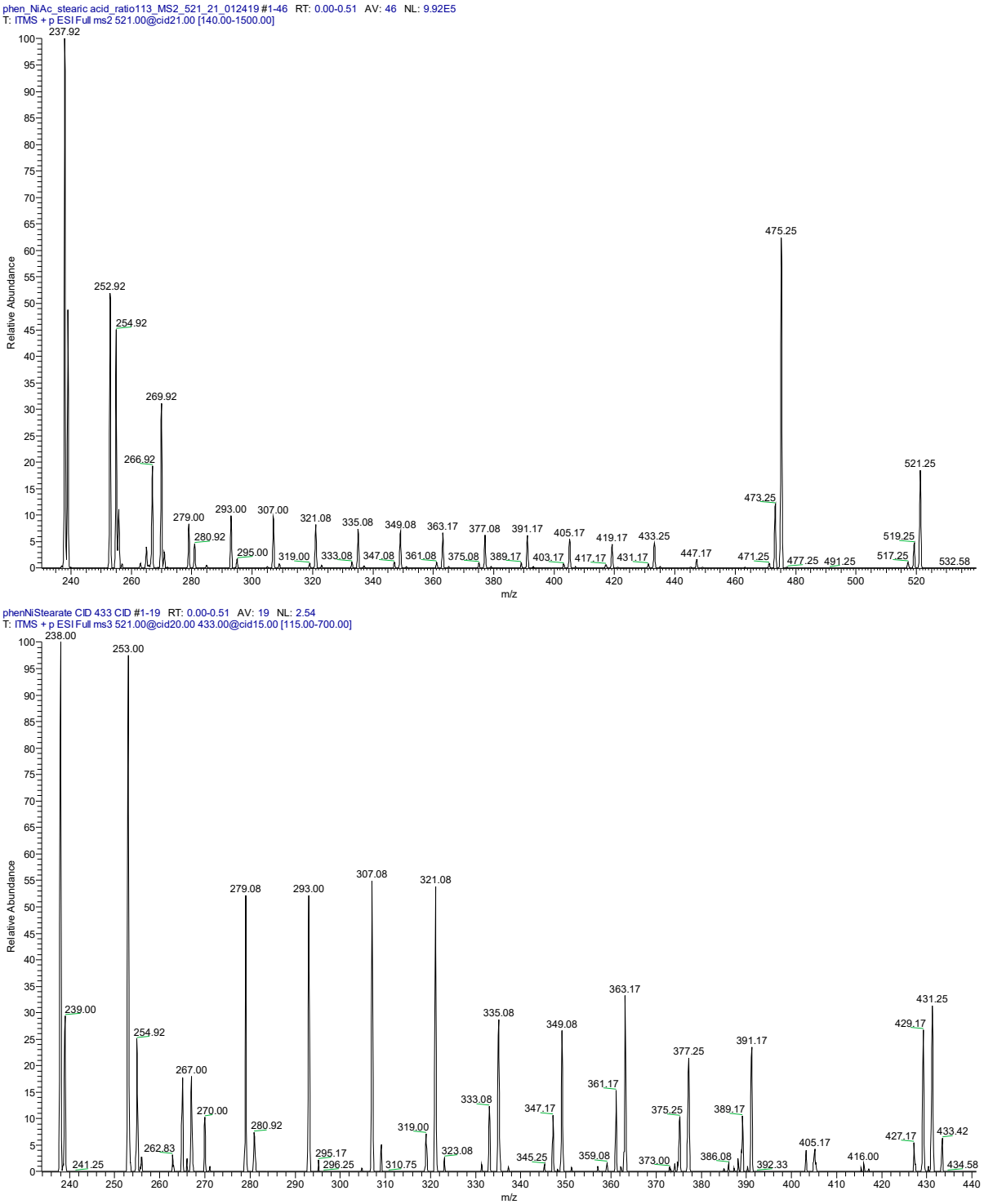


Figure S4. (A) CID of $[(phen)Ni(O_2CC_{17}H_{35})]^+$ with neutral loss of CO_2, H_2, and C_3H_6 at m/z 433. (B) CID of m/z 433, $[(phen)Ni(C_{14}H_{29})]^+$ *Experiment done on Thermo LTQ at 21 and 15 NCE respectively*

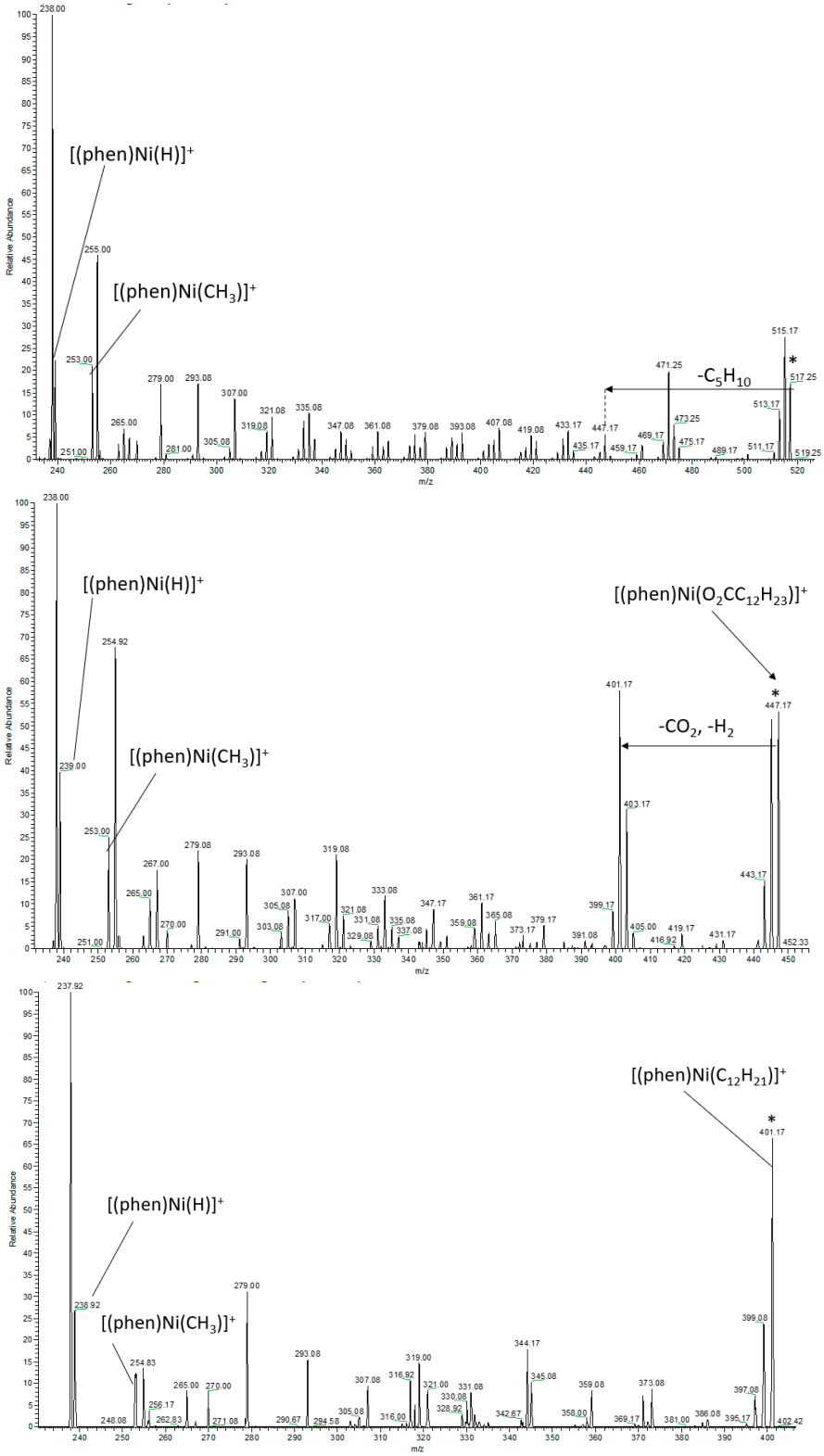


Figure S5. MS^n experiments of unsaturated fatty acid complexes leading to formation of metal hydride, methyl, and vinyl species. (A) CID of $[(phen)Ni(O_2CC_{17}H_{31})]^+$ (B) CID of $[(phen)Ni(O_2CC_{12}H_{21})]^+$ (C) CID of $[(phen)Ni(C_{12}H_{21})]^+$ *Experiment done on Thermo LTQ*

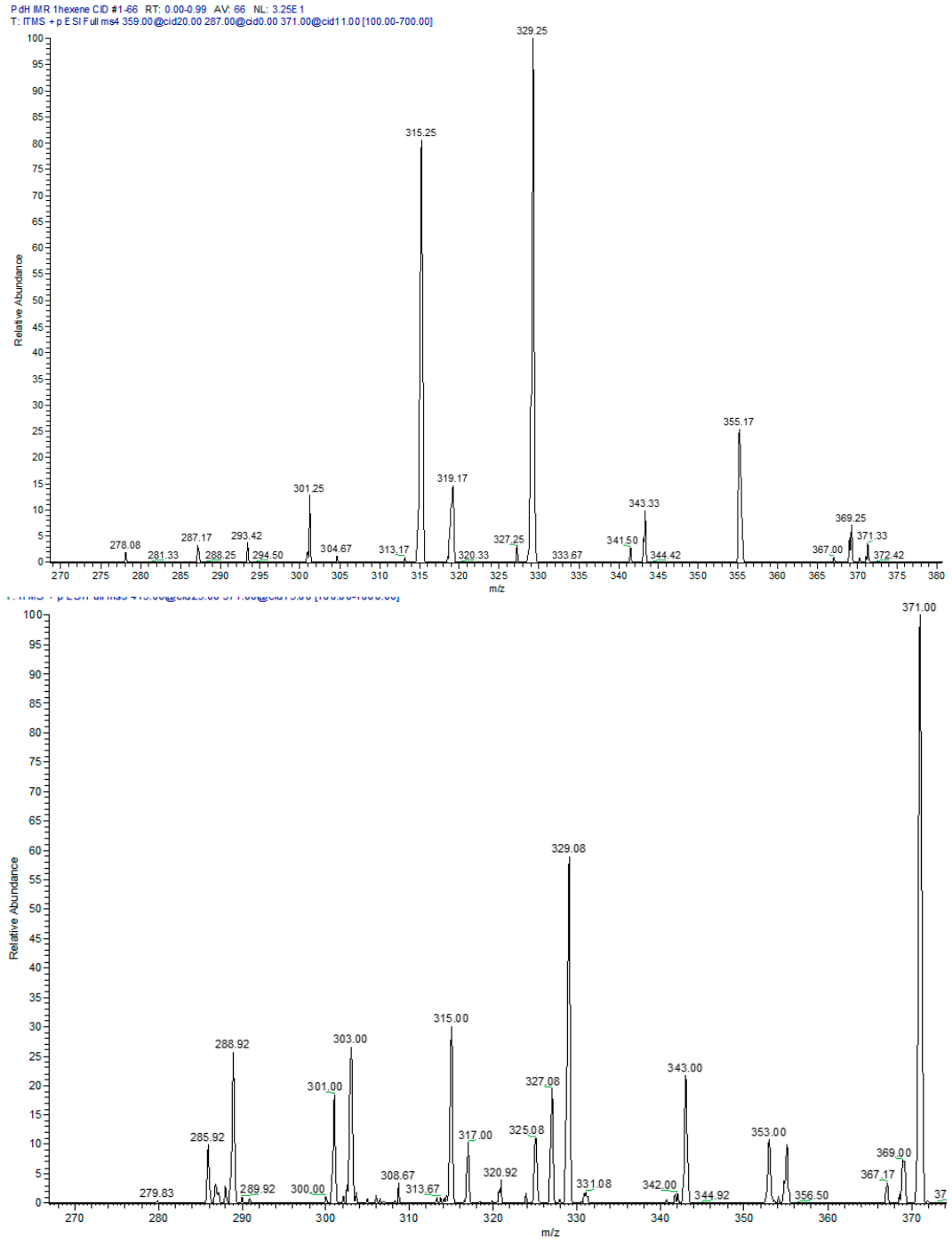


Figure S6. CID of $[(phen)Pd(C_6H_{11})]^+$ formed via IMR between metal hydride and 1-hexene (A) and the decarboxylation of heptanoic acid (B) *Experiment done on Thermo LTQ at 15 and 11 NCE respectively*

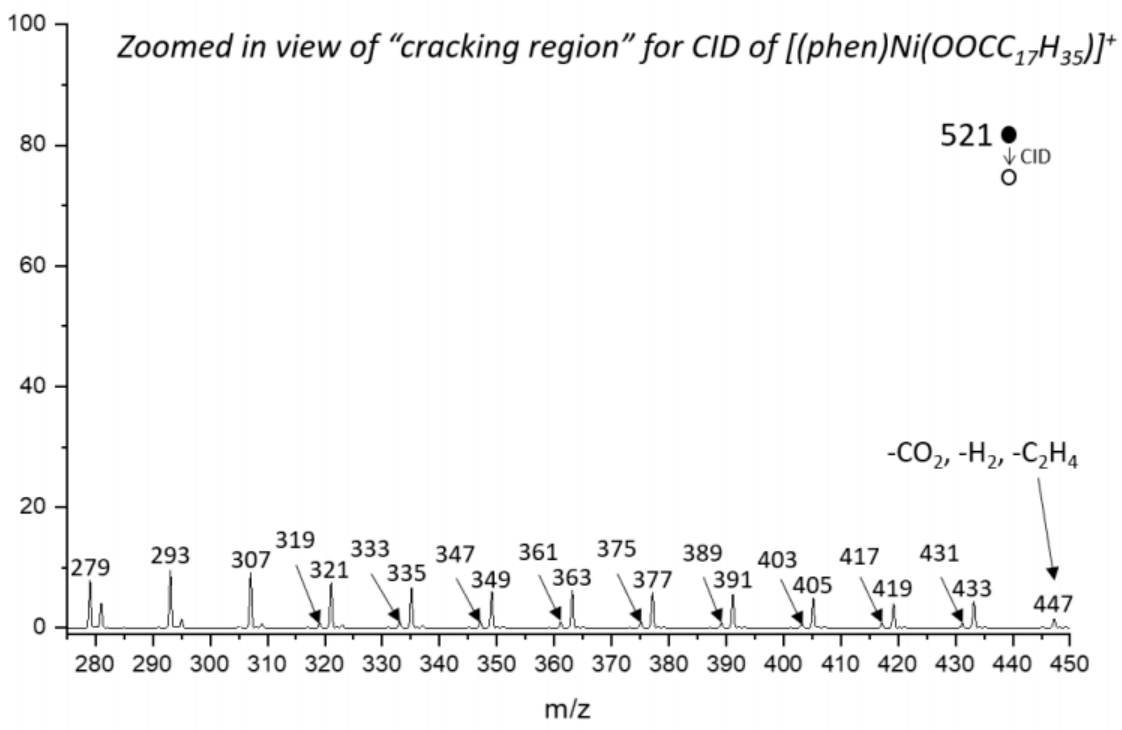


Figure S7. Zoomed in region of deoxygenation for CID of $[(phen)Ni(O_2CC_{17}H_{35})]^+$ *Experiment done on Bruker Maxis*

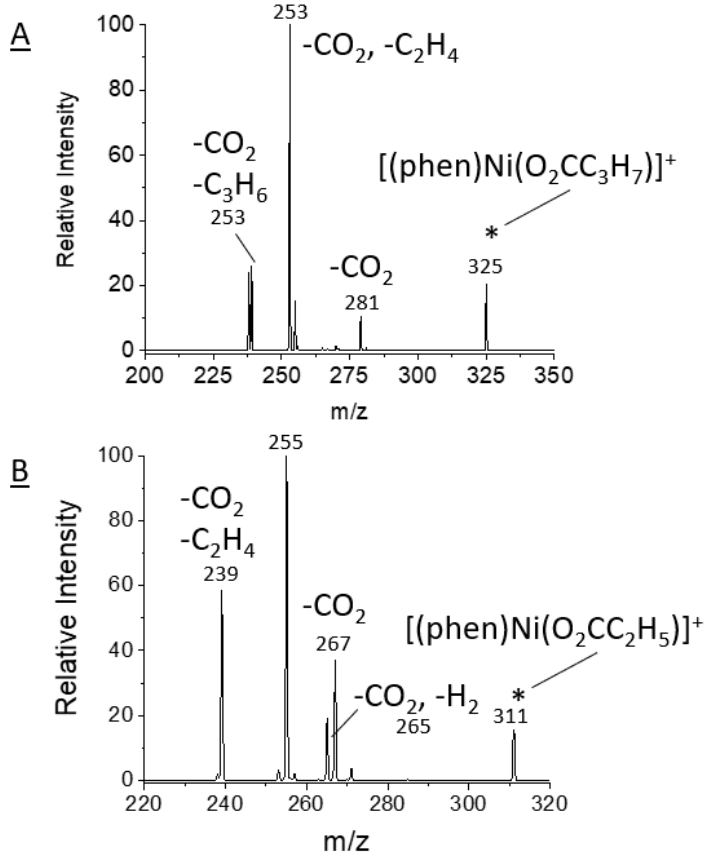
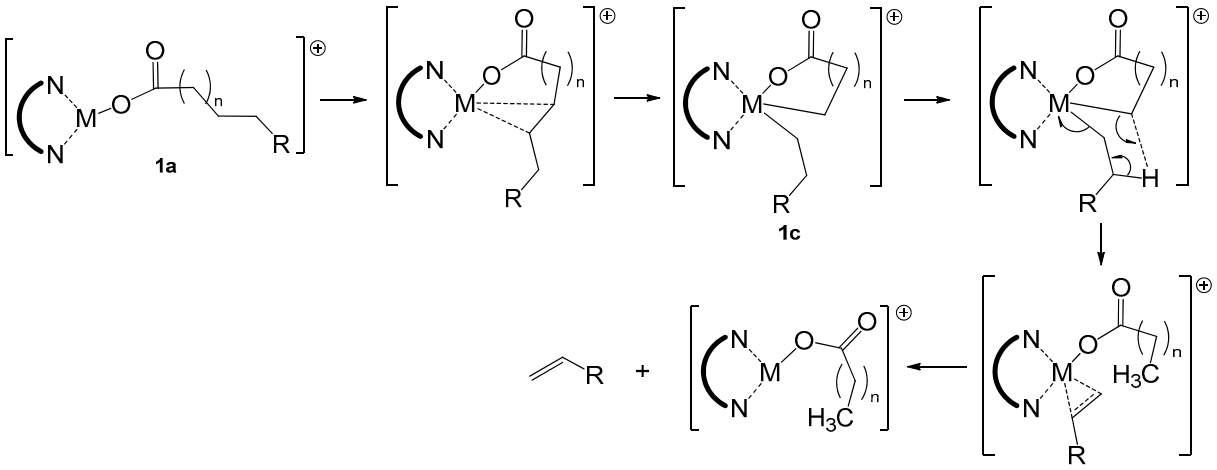


Figure S8. (A) CID of $[(phen)Ni(O_2CC_3H_7)]^+$ (B) CID of $[(phen)Ni(O_2CC_2H_5)]^+$ *Experiment done on Thermo LTQ at 15 NCE.* (Data previously published Parker, Kevin, et al. "Gas-Phase Models for the Nickel-and Palladium-Catalyzed Deoxygenation of Fatty Acids." *ChemCatChem* 12.21 (2020): 5476-5485.)



Scheme S1. Lactone carbon bound to the metal can abstract hydrogen from the free R-containing chain, forming a saturated carboxylate complex and extruding R-CH=CH_2