SUPPORTING INFORMATION

for

Kinetics of Reductive Elimination from Pt(IV) as a Probe for Non-thermal Effects in Microwave-Heated Reactions

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Plot of $\ln([1]_{t}/[1]_{o})$ vs time for the stirred thermolyses of 1 in THF- d_8 under both microwave (\circ , \cdots) and oil bath (\blacksquare , -) heating conditions. Data correspond to entry 2 in Table 1: 2.5 mL of 0.017 M 1 were heated in a 2-cm-wide vessel.



Plot of $\ln([1]_{t}/[1]_{o})$ vs time for the stirred thermolyses of 1 in THF- d_8 under both microwave (\circ , \cdots) and oil bath (\blacksquare , -) heating conditions. Data correspond to entry 3 in Table 1: 1.5 mL of 0.031 M 1 were heated in a 2-cm-wide vessel.



Plot of $\ln([1]/[1]_{\circ})$ vs time for the stirred thermolyses of 1 in THF- d_8 under both microwave (\circ , \cdots) and oil bath (\blacksquare , -) heating conditions. Data correspond to entry 4 in Table 1: 2.5 mL of 0.019 M 1 were heated in a 3-cm-wide vessel.



Plot of $\ln([1]_{t}/[1]_{0})$ vs time for the stirred thermolyses of 1 in THF- d_{8} under both microwave (\circ , \cdots) and oil bath (\blacksquare , -) heating conditions. Data correspond to entry 5 in Table 1: 7.5 mL of 0.011 M 1 were heated in a 3-cm-wide vessel.



 $\begin{array}{c} -3.0 \\ -4.0 \\ -5.0 \\ -5.0 \\ -6.0 \\ -7.0 \\ -7.0 \\ -8.0 \\ 0.0026 \end{array}$

Plot of $\ln([1]_t/[1]_o)$ vs time for the *unstirred* thermolyses of 1 in THF- d_8 under both microwave (\circ , \cdots) and oil bath (\blacksquare , -) heating conditions. 2.0 mL of 0.010 M 1 were heated in a 2-cm-wide vessel.

Eyring plot for thermolysis of **1** based on observed rate constants in THF- d_8 . These data indicate activation parameters of $\Delta S^{\ddagger} = 24$ cal/mol·K and $\Delta H^{\ddagger} = 31$ kcal/mol, both of which are consistent with the dissociative mechanism previously described in the literature.



Plot of temperatures profiles, upon microwave heating at a 1600 W constant power, of 3.0 mL of mineral oil (×), 3.0 mL of anhydrous THF (\blacksquare) and 3.0 mL of 0.020 M 1 in anhydrous THF (\circ). All three data sets comprise two experiments conducted in 85 mL GreenChem vessels yielding nearly identical results. These data demonstrate that although some heating via glassware occurred, THF was the primary microwave absorber in the system and complex 1 also absorbed a significant fraction of microwave radiation. For a discussion of microwave absorption by pyrex reaction vessels vs. reaction mixtures themselves, see: Loones, K. T. J.; Maes, B. U. W.; Rombouts, G.; Hostyn, S.; Diels, G. *Tetrahedron* 2005, 61, 10338-10348.



Representatvie ¹H NMR Spectrum (300 MHz) for Kinetics in THF-d₈

Quantification of 2 and 3 in THF- d_8 by ¹H and ¹H{³¹P} 300 MHz NMR Spectroscopy: Calculation of total integration values of 2 and 3 (i_2 and i_3) from overlapping or partial resonances.

