Supporting Information for

A Calorimetric Study of the Activation of Hydrogen by tris(pentafluorophenyl)borane and trimesitylphosphine.

Adrian Y. Houghton, Tom Autrey

Institute for Integrated Catalysis, Pacific Northwest National Laboratory. 902 Battelle Boulevard P.O. Box 999, Richland, WA. 99352 USA.

General Considerations

All manipulations were carried out under an inert nitrogen (N_2) atmosphere using standard Schlenk or glovebox techniques unless otherwise stated. Dichloromethane was passed through a neutral alumina column under argon prior to use. *tris*(pentafluorophenyl)borane was obtained from Boulder Scientific and purified by sublimation under reduced pressure at 90 °C. All NMR spectra were recorded on 500 MHz Varian INOVA spectrometers. ^{19}F NMR spectra were referenced to fluorobenzene as an external standard ($\delta = -113.15$ ppm). Calorimetric measurements were performed on a Setaram C80 Calvet calorimeter, and instrument was operated in isothermal mode. Measurements were conducted in modified Hastealloy® reversal mixing cells (6.7 mL). The commercial mixing vessels were modified to include an inlet with 0.030" ID PEEK tubing that allowed gases to be introduced.

Time Constant Determination

The two compartments of a C80 cell were charged with CH_2Cl_2 solutions of $B(C_6F_5)_3$ (51.2 mg, 0.100 mmol, 1.0 mL) and pyrazine (80.1 mg, 1.00 mmol, 1.0 mL), and a reference cell was charged with CH_2Cl_2 (2.0 mL). The cells were pressurized with N_2 (100 psig) and placed in the calorimeter. Once heatflow had stabilized near zero, the reaction was initiated by reversal mixing. This experiment was carried out at 29.1˚C and 88.5˚C, and the heat curves were fit to the following formula:

$$\frac{\partial Q(t)}{\partial t} = A\frac{e^{-(t-t_o)/\tau_1} - e^{-(t-t_o)/\tau_2}}{1/\tau_2 - 1/\tau_1}$$

Where $\partial Q(t)/\partial t$ is the heatflow at time t, τ_1 is the mixing time, τ_2 is the instrument time constant, and A is a fitting parameter. $\tau_1 = 15.1$ s; $\tau_2 = 310$ s (29.1˚C), 278 s (88.5 ˚C). ΔH = XX kJ/mol. It was assumed that τ_2 varied linearly over the experimental temperature range.

C80 Experiments

In a typical experiment, the two compartments of a C80 cell were charged with CH_2Cl_2 solutions of $B(C_6F_5)_3$ (1.0 mL) and $P(mes)_3$ (1.0 mL), and a reference cell was charged with CH_2Cl_2 (2.0 mL). The cells were pressurized with H_2 (100 - 400 psig) and placed in the calorimeter at the desired reaction temperature (30 – 90˚C). Once heatflow had stabilized near zero, the reaction

was initiated by reversal mixing, and data points were collected every 1.2 s until heatflow returned to the baseline. The degree of reaction was confirmed by ^{19}F and ^{31}P NMR spectroscopy.

Berkeley Madonna Model

Method RK4

{1: H2gas <--> H2soln}
RXN1 = K1f*H2gas - K1r*H2soln
K1f = 1000
K1r=K1f/Kh
Kh=1/(X*exp(Y*(1-298.15/T)))*Rg*T*rho/mwt {H2soln/H2gas} {J. Chem. Eng. Data, 2008, 53, 1867}
rho=-0.0016942*T+1.8204 {ref}
INIT(H2soln)=Kh*INIT(H2gas)
INIT(H2gas) = (PH2*T/294)*1000/T/Rg {mol/L}
d/dt(H2soln)=RXN1-RXN3
d/dt(H2gas)=-V/Vg*RXN1

{2a: A --> LA}
RXN2a=1/taumix*A
taumix=2.92
INIT(A) = Ao
INIT(LA)=0
d/dt(A)= -RXN2a

{2b: B --> LB}
RXN2b=1/taumix*B
INIT(B) = Bo
d/dt(B)=-RXN2b
INIT(LB)=0
d/dt(LA)=RXN2a-RXN3-RXN5
d/dt(LB)=RXN2b-RXN3-RXN5

{2c: C—> W}
RXN2c=1/taumix*C
INIT(C)=Co
d/dt(C)=-RXN2c
INIT(W)=0
d/dt(W)=RXN2c-RXN5

{3: LA + LB + H2soln —> IP}
RXN3=k3*LA*LB*H2soln
INIT(IP)=0
d/dt(IP)= RXN3

{4: Q --> R} {C80 heat flow processes}
RXN4=Q/tc
INIT(Q) =0
INIT(R) =0
tc = 357.55
d/dt(Q)=(RXN1*DH1*(V+Vg)+RXN3*V*DH3+RXN5*V*DH5)*1e+6-RXN4
d/dt(R) = RXN4

{5: 2LA + LB + W—> HP}
RXN5=k5*LA*LA*LB*W
INIT(HP)=0
d/dt(HP)=RXN5
k5=72955

METHOD STIFF
DT=0.01
STARTTIME = 0
STOPTIME= 7040

OUTPUT= -RXN4+Pf+Po+m1*(time-starttime)+m2*(time-starttime)^2+m3*(time-starttime)^3

{parameters}
Pf=0
Po=-0.03
m1=0
m2=0
m3=0
mwt=84.93
X=537
Y=-3.57
k3=100
Rk=1.9872041
Rg=8.3144598 {mL MPa K-1 mol-1}
PH2=(117-14.4)*0.00689475728 {conversion from psi to MPa}
T=302.8
DH1=10.376 {DCM}
DH3=-92.7
DH5=-176
Ao=0.04995
Bo=0.04965
Co=0
V=0.002*1.32/rho-0.0000083 {adjusted for density changes and loss of vapour, using the Clausius-Clapeyron equation}

Vg=0.0067-V

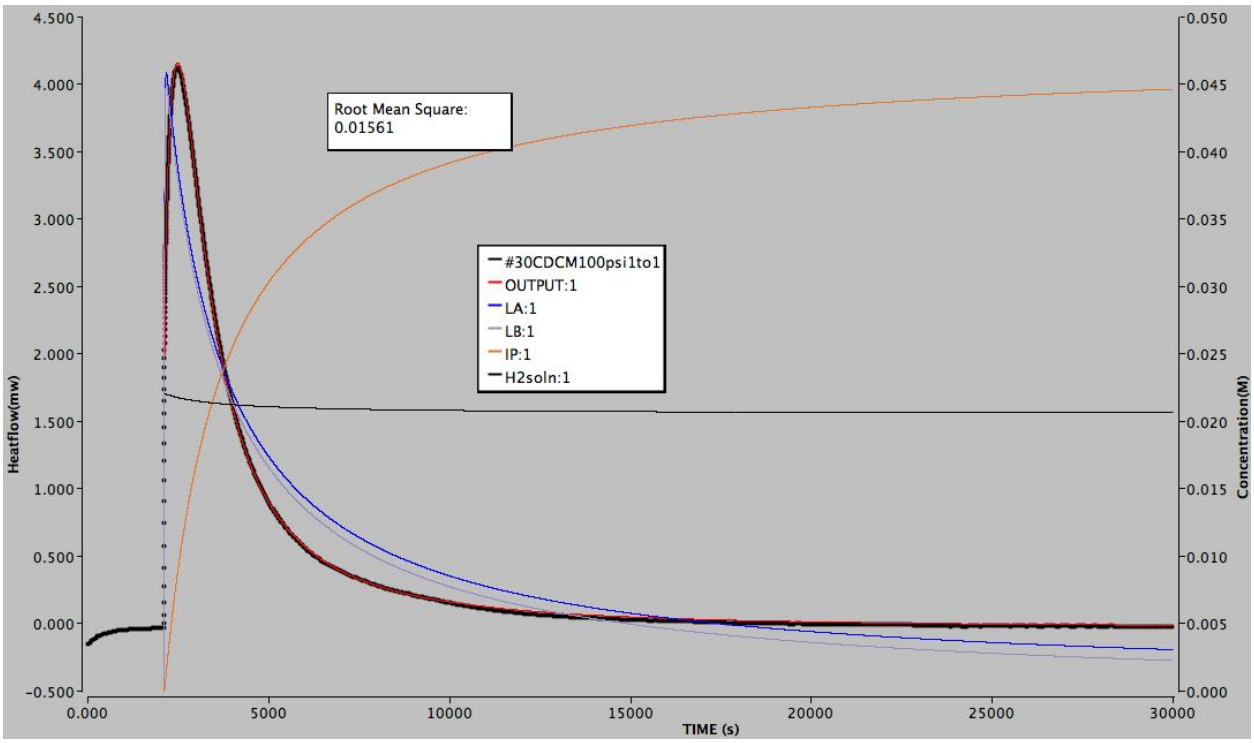

Figure SX: Heat trace and fitted data for the reaction of $P(mes)_3$ (0.0497 M), $B(C_6F_5)_3$ (0.0500 M), and H_2 (6.98 atm, 4.7 mL) in CH_2Cl_2 (2.0 mL) at 302.8 K

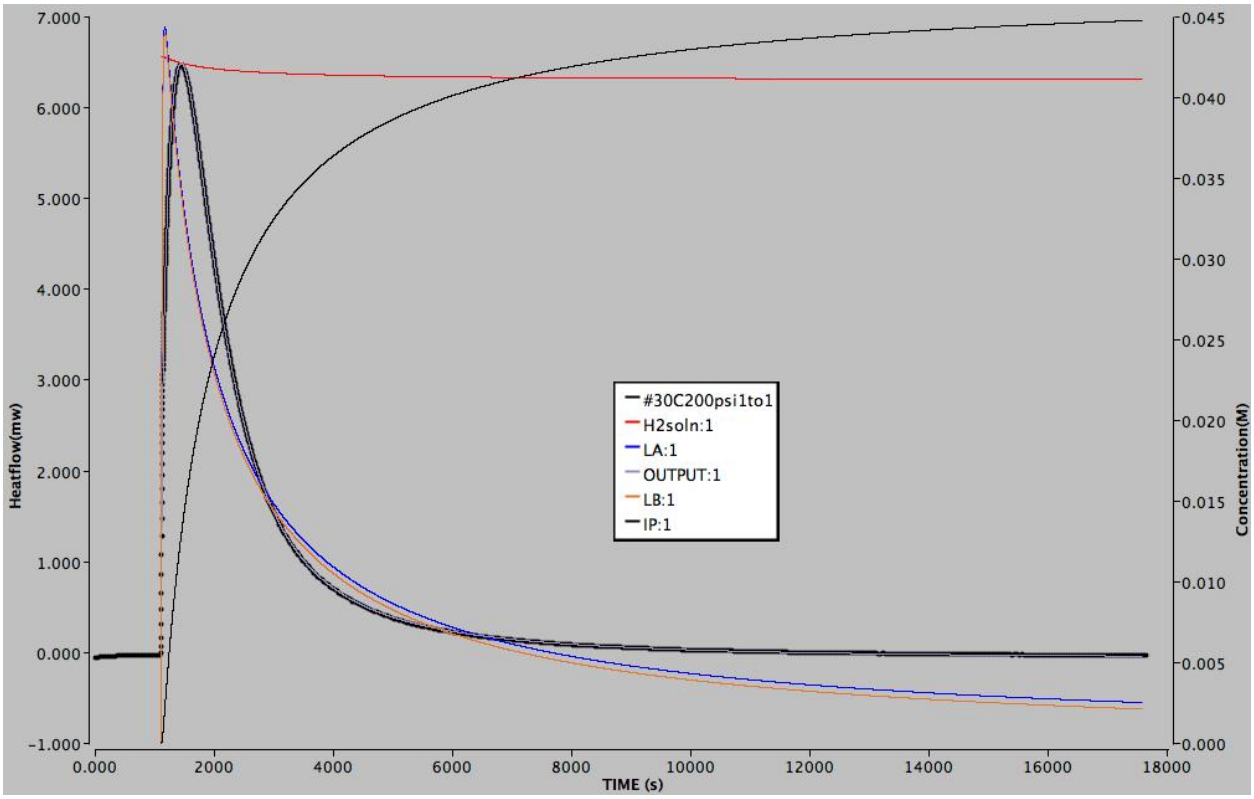

Figure SX: Heat trace and fitted data for the reaction of $P(mes)_3$ (0.0496 M), $B(C_6F_5)_3$ (0.0500 M), and H_2 (13.5 atm, 4.7 mL) in CH_2Cl_2 (2.0 mL) at 302.4 K

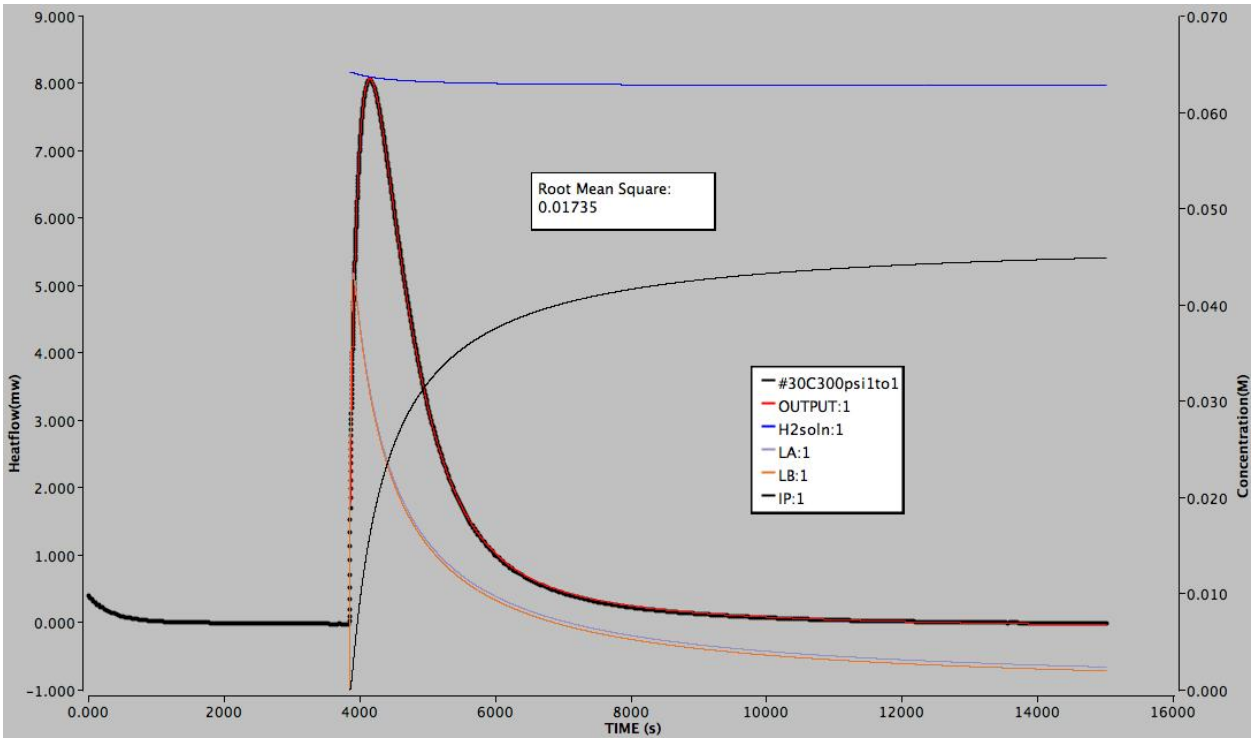

Figure SX: Heat trace and fitted data for the reaction of $P(mes)_3$ (0.0496 M), $B(C_6F_5)_3$ (0.0500 M), and H_2 (20.4 atm, 4.7 mL) in CH_2Cl_2 (2.0 mL) at 302.4 K

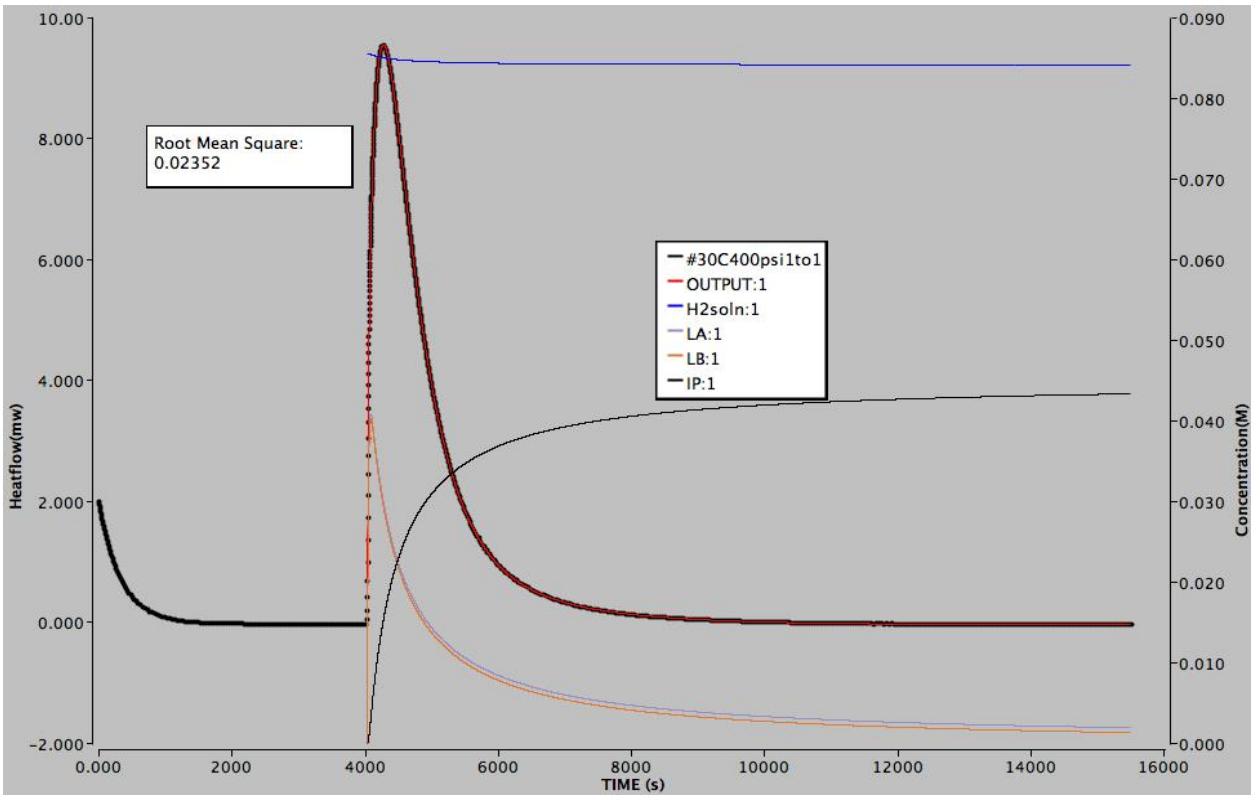

Figure SX: Heat trace and fitted data for the reaction of $P(mes)_3$ (0.0493 M), $B(C_6F_5)_3$ (0.0499 M), and H_2 (27.2 atm, 4.7 mL) in CH_2Cl_2 (2.0 mL) at 302.4 K

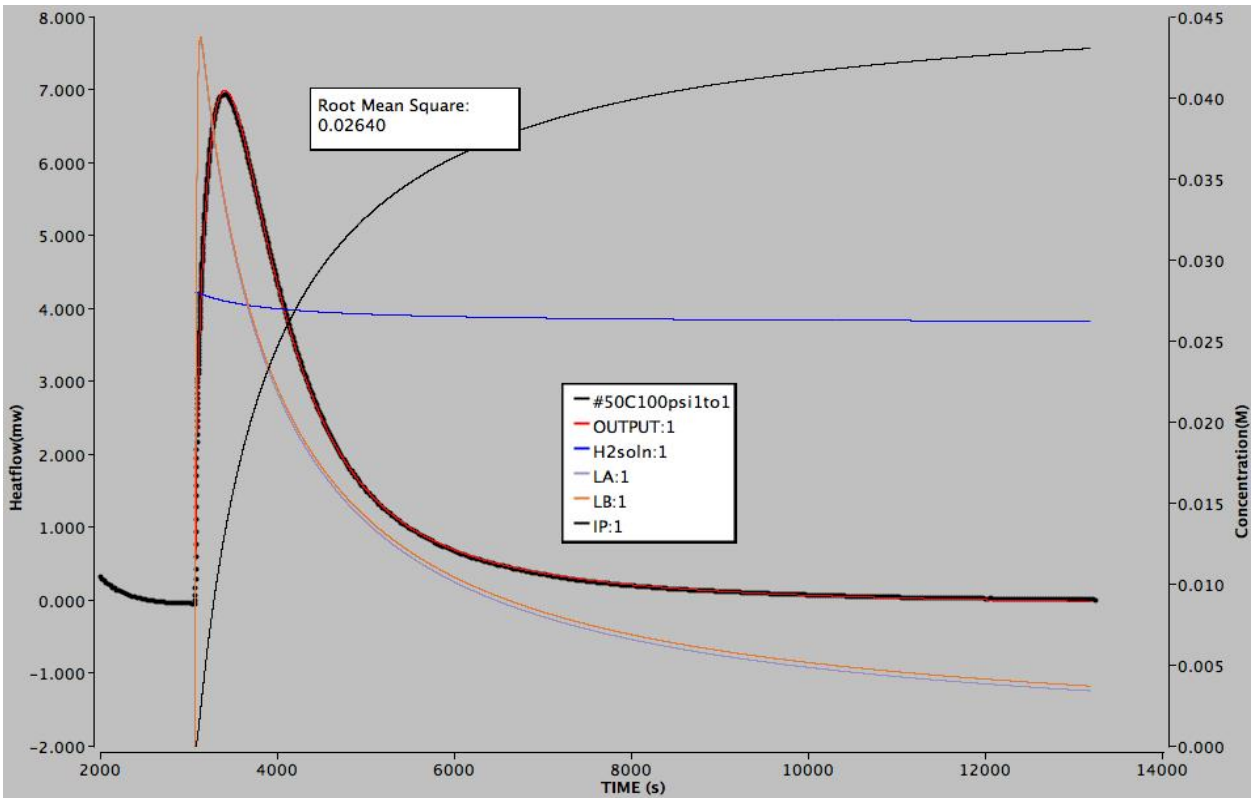

Figure SX: Heat trace and fitted data for the reaction of $P(mes)_3$ (0.0494 M), $B(C_6F_5)_3$ (0.0489 M), and H_2 (6.91 atm, 4.7 mL) in CH_2Cl_2 (2.0 mL) at 322.3 K

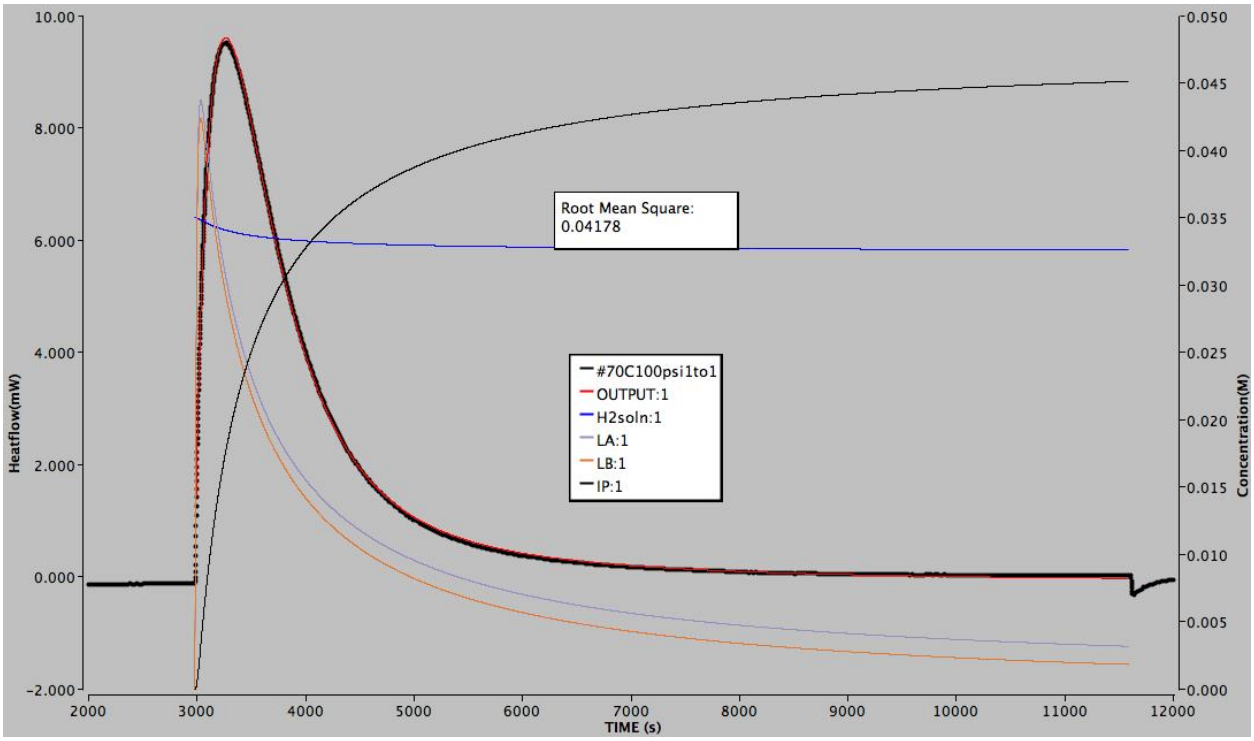

Figure SX: Heat trace and fitted data for the reaction of $P(mes)_3$ (0.0505 M), $B(C_6F_5)_3$ (0.0500 M), and H_2 (6.91 atm, 4.7 mL) in CH_2Cl_2 (2.0 mL) at 341.9 K

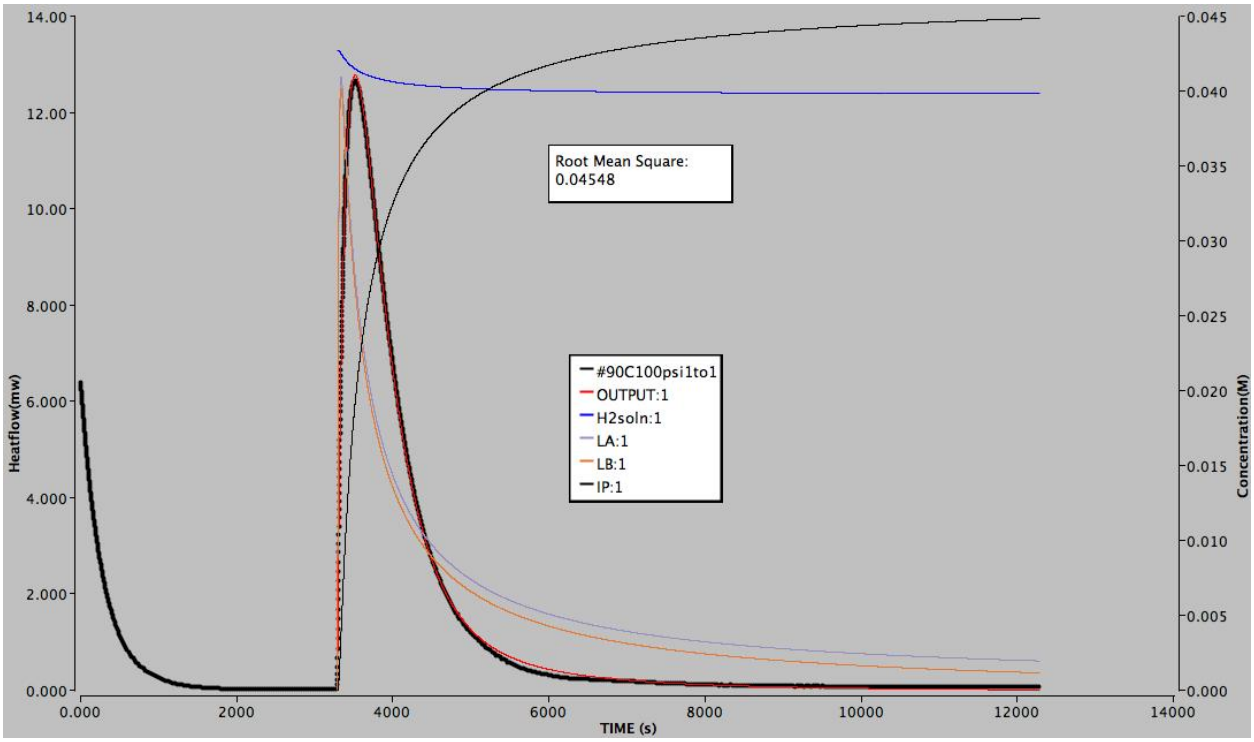

Figure SX: Heat trace and fitted data for the reaction of $P(mes)_3$ (0.0505 M), $B(C_6F_5)_3$ (0.0500 M), and H_2 (6.91 atm, 4.7 mL) in CH_2Cl_2 (2.0 mL) at 361.7K

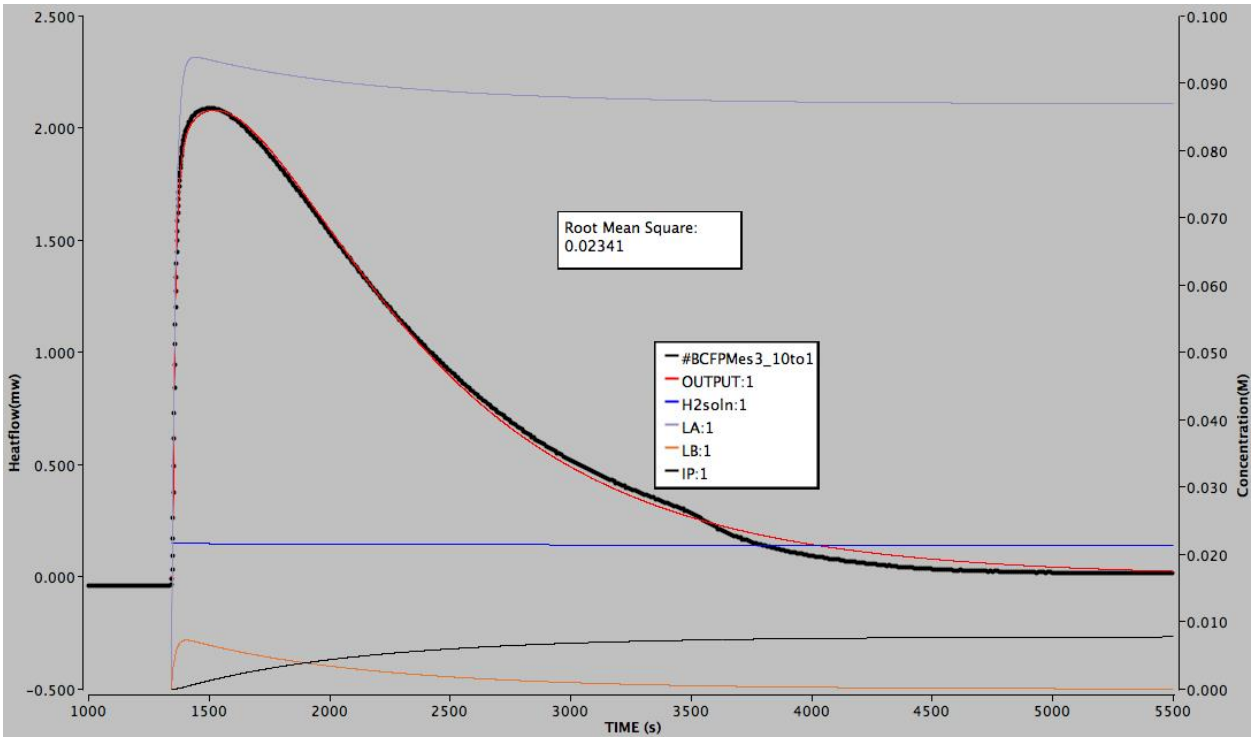

Figure SX: Heat trace and fitted data for the reaction of $P(mes)_3$ (0.00955 M), $B(C_6F_5)_3$ (0.0965 M), and H_2 (6.89 atm, 4.7 mL) in CH_2Cl_2 (2.0 mL) at 302.8 K

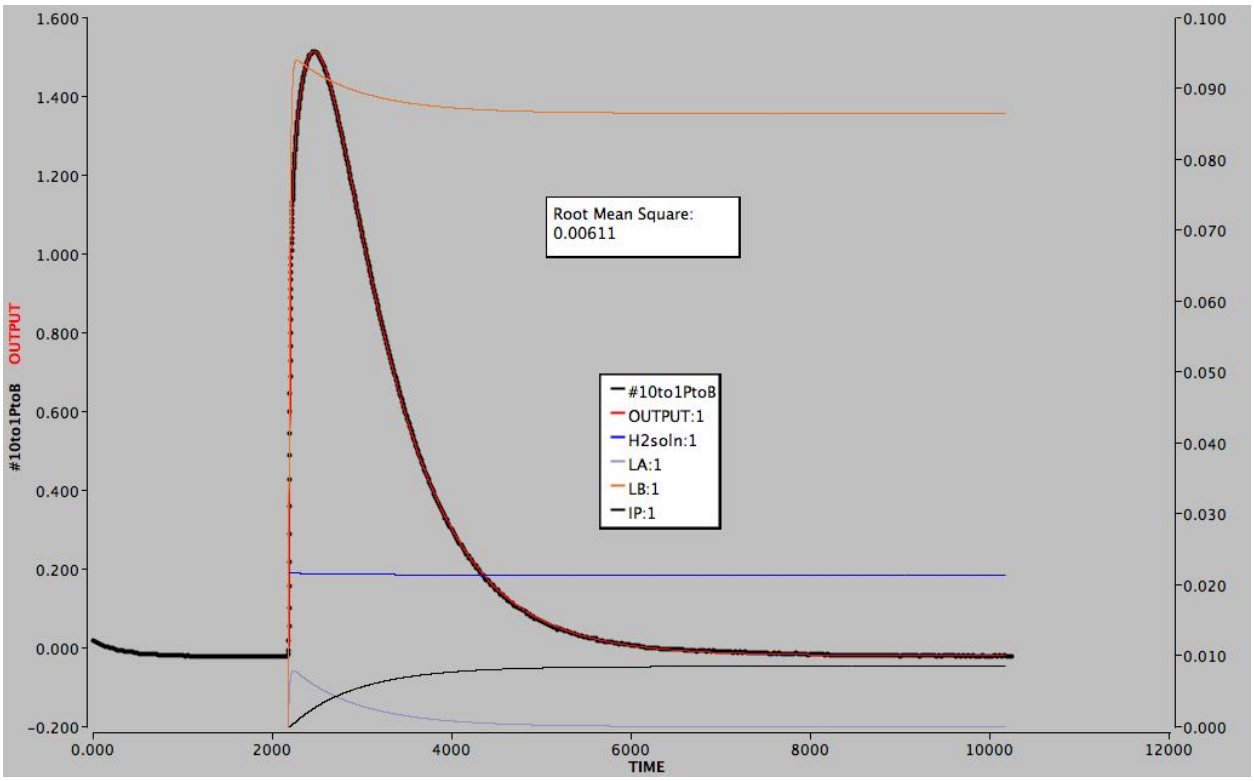

Figure SX: Heat trace and fitted data for the reaction of $P(mes)_3$ (0.096 M), $B(C_6F_5)_3$ (0.0095 M), and H_2 (6.89 atm, 4.7 mL) in CH_2Cl_2 (2.0 mL) at 302.4 K

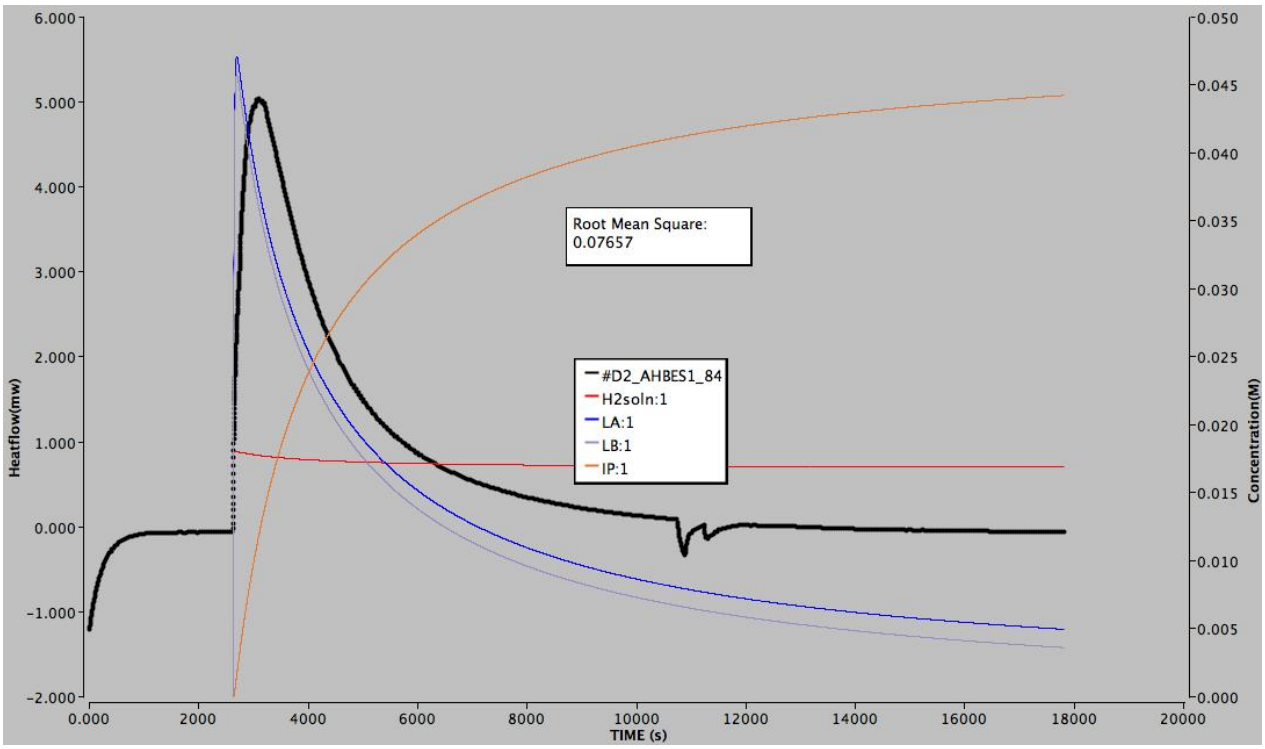

Figure SX: Heat trace and fitted data for the reaction of $P(mes)_3$ (0.0505 M), $B(C_6F_5)_3$ (0.0505 M), and D_2 (6.80 atm, 4.7 mL) in CH_2Cl_2 (2.0 mL) at 302.8 K (trial 1)

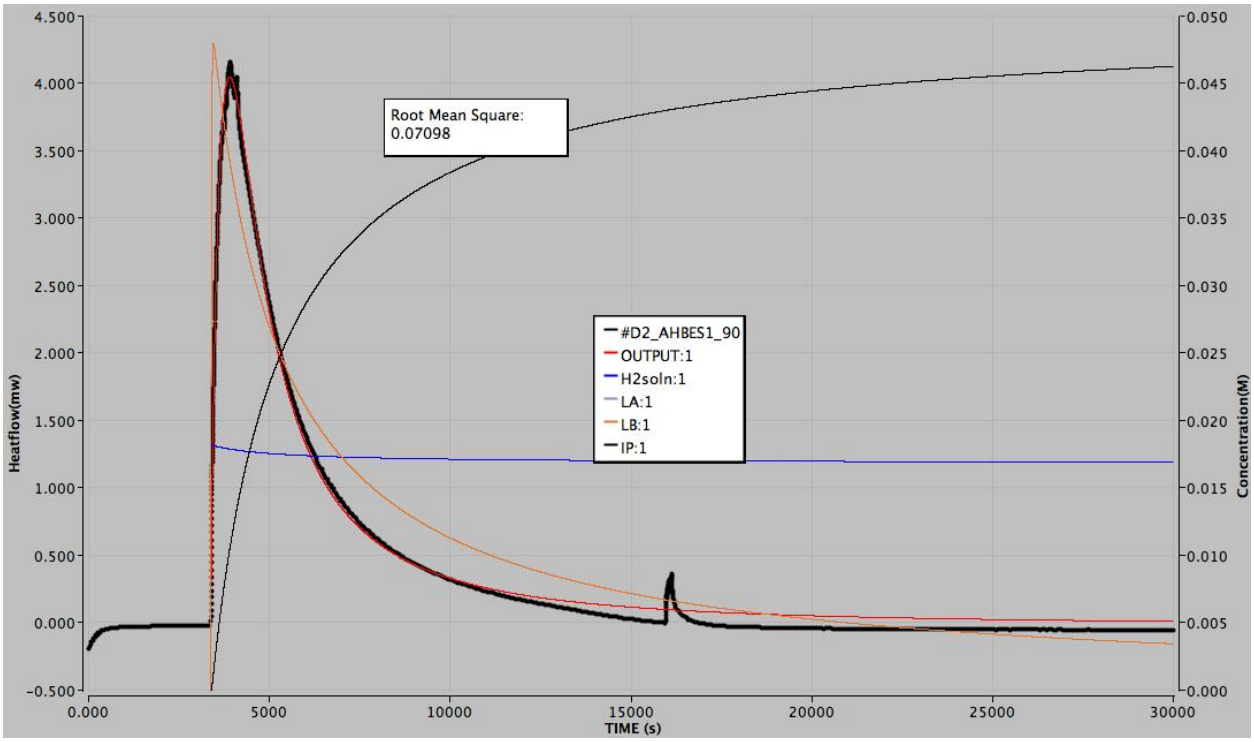

Figure SX: Heat trace and fitted data for the reaction of $P(mes)_3$ (0.0505 M), $B(C_6F_5)_3$ (0.0505 M), and D_2 (6.80 atm, 4.7 mL) in CH_2Cl_2 (2.0 mL) at 302.8 K (trial 2)