

Iron (0) Mediated C-H Activation of 1-hexyne: A Mechanistic Study Using Time-Resolved Infrared Spectroscopy.

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SUPPORTING INFORMATION

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Experimental

Methods and Materials

Unless specifically stated, all syntheses and manipulations were performed using standard Schlenk-line and syringe/rubber septa techniques under N₂ or in an Ar atmosphere glovebox. All reagents and solvents were of > 99% purity and anhydrous grade to include tetrahydrofuran, pyridine, 1-hexene, 1-hexyne, and heptane. The [2,5-(SiMe₃)₂-3,4-(CH₂)₄(η⁴-C₄C=O)]Fe(CO)₃ (**1-CO**) complex was synthesized according to previously published procedure.¹

Physical Measurements

All infrared spectra in the kinetic study were recorded using a Bruker Vertex 80 FTIR spectrometer equipped with both step-scan and rapid-scan capabilities. A temperature controlled 0.5 mm path length IR transmission cell (Harrick Scientific) with CaF₂ windows was used to acquire the spectra. The cell temperature was controlled with the use of a circulating water bath (± 0.1 °C). Photolysis of the solution was achieved using a Quantel Brilliant B Nd:YAG laser operating at 355 nm (70 mJ/pulse).

a) Kinetic Studies

In all studies including those focused on the activation of 1-hexyne and kinetics of 1-hexene exchange by pyridine all reagents were purged with N₂ prior to use. In a typical kinetic study involving the displacement of 1-hexene by pyridine, an appropriate amount of complex **1-CO** was degassed under N₂ and dissolved in degassed heptane solvent to yield a ~0.5 mM solution. The appropriate amount of pyridine and 1-hexene were added to this solution using a gas tight syringe. For each experiment, the concentration of 1-hexene was kept constant at 1.74 M and the amount of pyridine was varied between 0.24M and 1.49 M. The resulting solution was transferred to the IR cell using a syringe. After injection into the cell, the sample was allowed to thermally equilibrate for a few minutes before the experiment was initiated by photolysis.

All experiments were conducted under pseudo first-order conditions with the concentration of the pyridine ligand at least 10 times greater than that of the reactant metal complex. Observed rate constants (*k*_{obs}) were obtained from single exponential fits to the temporal profile of either reactant or product complexes.

To study the photochemistry of **1-CO** in the presence of THF, ~11 mg of **1-CO** was purged and dissolved in 4.9 mL heptane and THF was added to this solution using a gas tight syringe. The solution was then transferred to the IR cell for kinetic studies.

b) Computational studies

All computations were carried out using the development version of the Gaussian¹ suite of programs. Geometries were optimized using the ωB97XD² functional and the Def2-SVP^{3,4} basis set in the gas phase. Vibrational analysis was performed to confirm that the optimized geometries corresponded to minima or transition states based on the number of imaginary frequencies. Single point energy calculations were performed on the optimized geometries using

the larger basis set Def2-TZVPP^{3,4}. Thermal corrections computed using Def2-SVP were added to the electronic energy computed using Def2-TZVPP to get the enthalpy value H. The bond dissociation enthalpies were then calculated for the removal of a ligand (L) from the metal complex that binds it ([M]-L) as given below:

$$BDE = \Delta H_{[M]} + \Delta H_L - \Delta H_{[M]-L}.$$

References

- [1] Gaussian 09, Revision **E.01**, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.
- [2] J.-D. Chai and M. Head-Gordon, "Long-range corrected hybrid density functionals with damped atom-atom dispersion corrections," *Phys. Chem. Chem. Phys.*, **10** (2008) 6615-20.
- [3] F. Weigend and R. Ahlrichs, "Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy," *Phys. Chem. Chem. Phys.*, **7** (2005) 3297-305.
- [4] Weigend, "Accurate Coulomb-fitting basis sets for H to Rn," *Phys. Chem. Chem. Phys.*, **8** (2006) 1057-65.

FIGURES

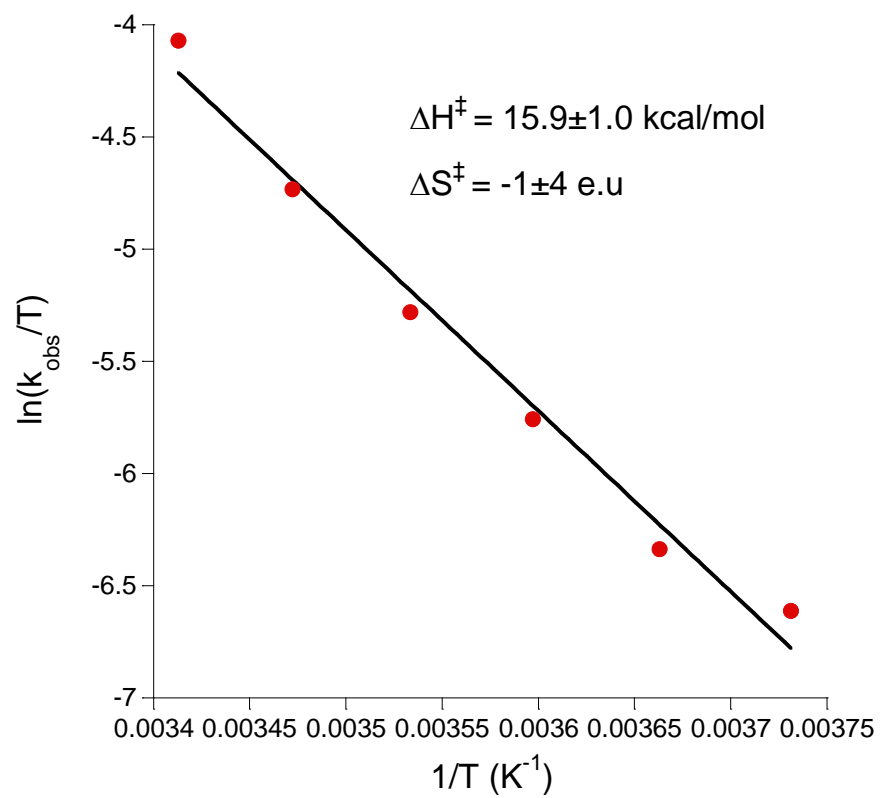


Figure S1. Eyring plot for the isomerization of **1-THF_a** to **1-THF_b**.

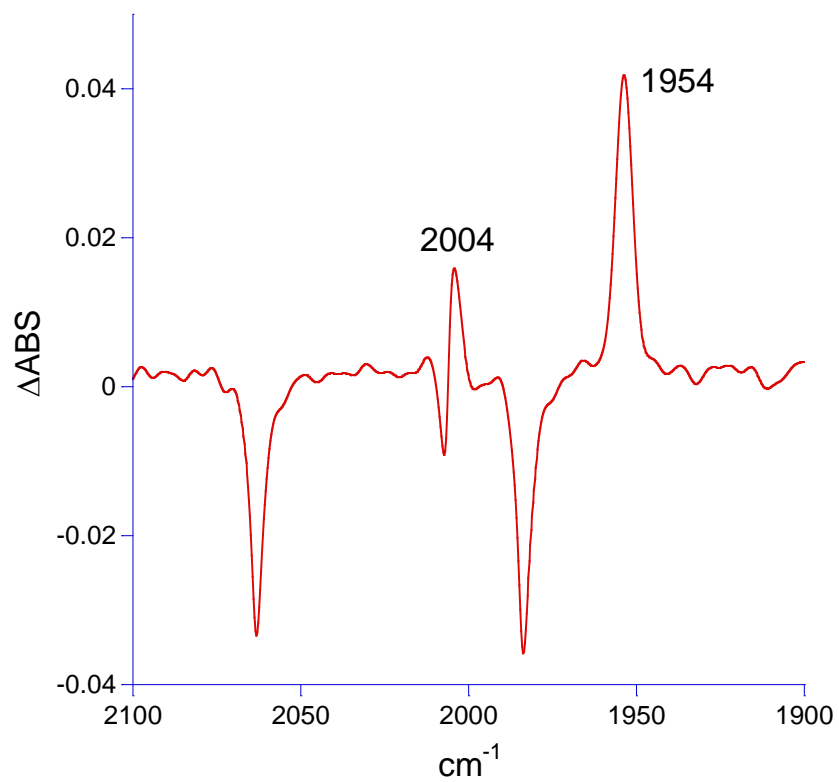


Figure S2. Difference FTIR spectrum resulting from the photolysis of a heptane solution of **1-CO** (5.21 mM) in the presence of 1-hexene (0.73 M) 293 K.

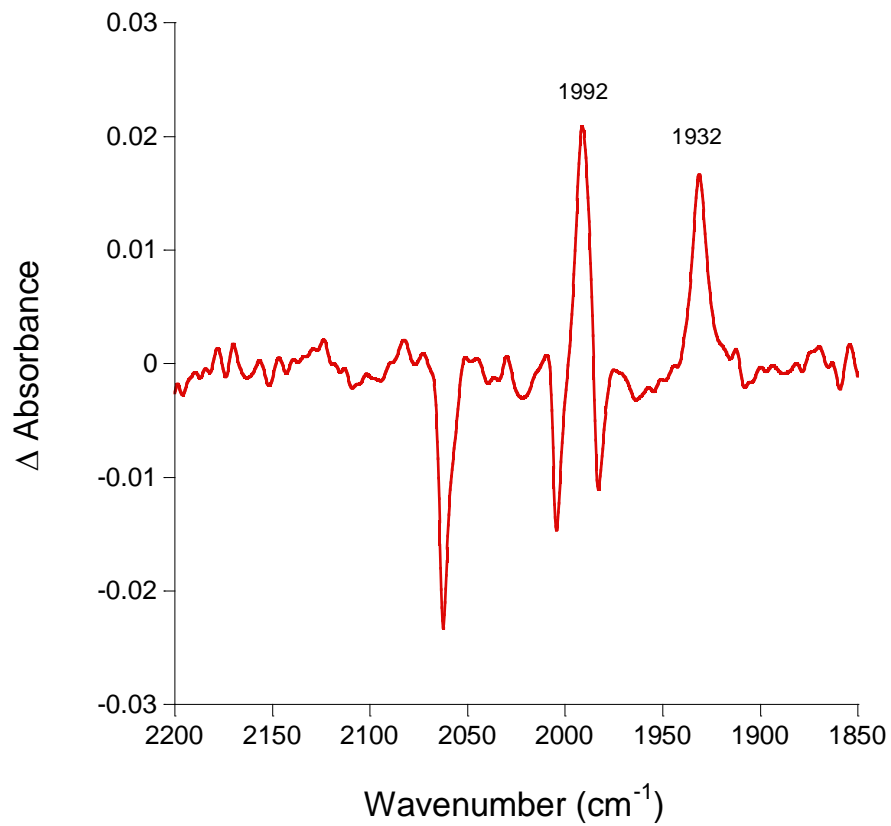


Figure S3. Difference FTIR spectrum resulting from the photolysis of a heptane solution of **1-CO** (4.49 mM) in the presence of pyridine (0.5 M) at 293 K.

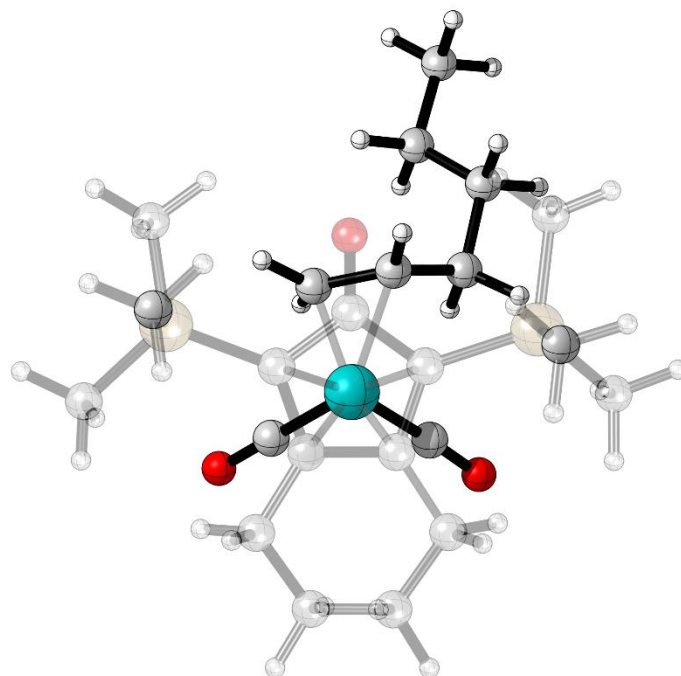


Figure S4: DFT calculated structure of **1**-(η^2 -1-hexene).

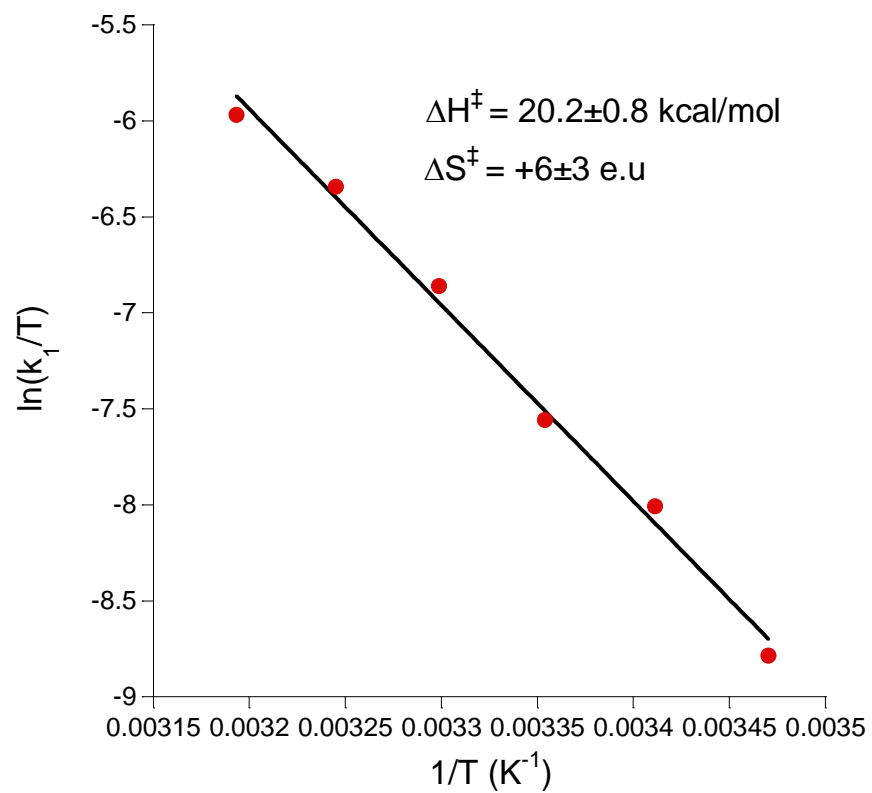


Figure S5: Eyring plot obtained from the limiting rate constant, k_1 , for the displacement of 1-hexene from $\mathbf{1}$ -(η^2 -1-hexene) by pyridine.

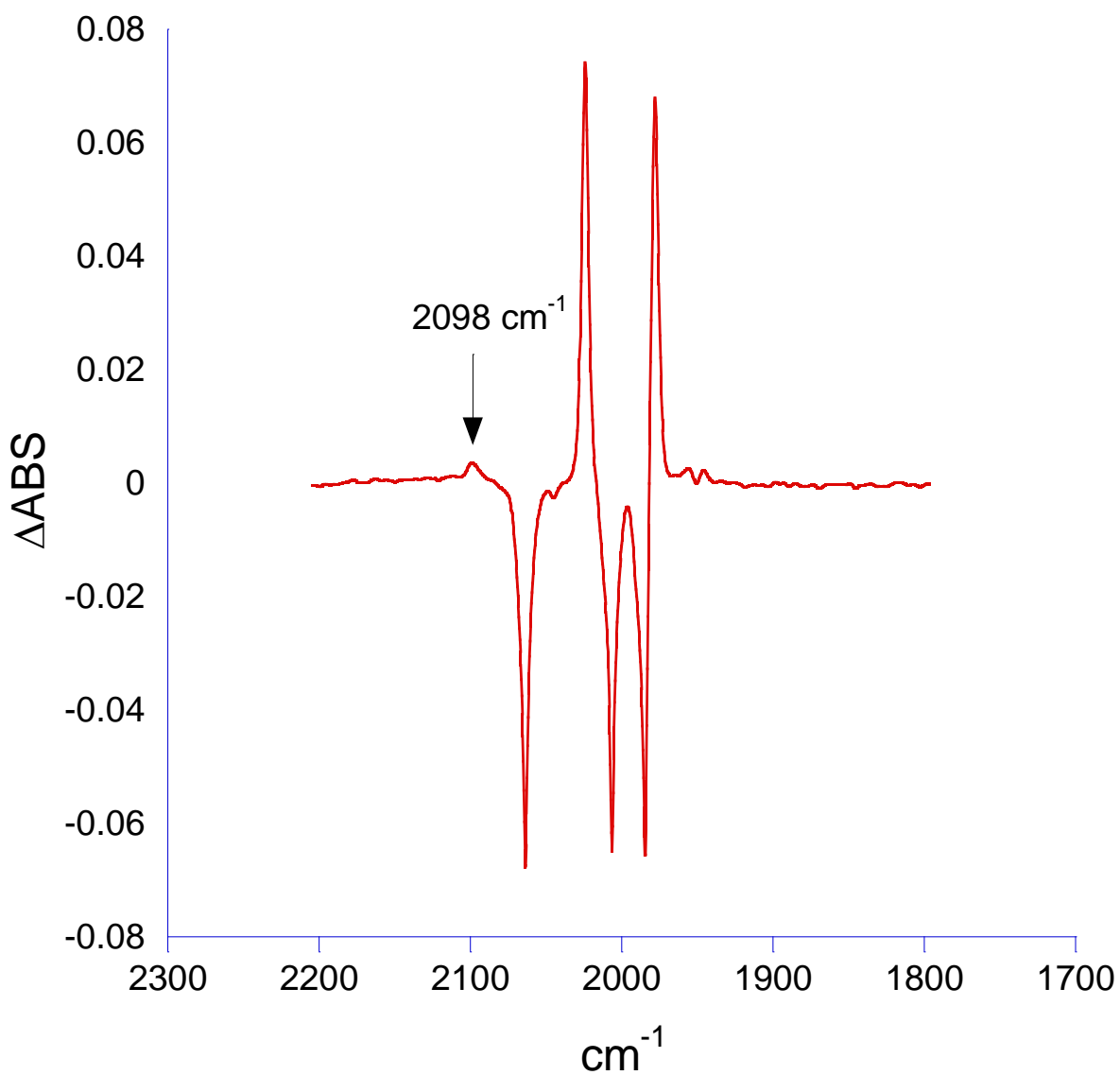


Figure S6: Difference FTIR obtained upon multiple shot photolysis of a heptane solution of 1-CO in the presence of 1-hexyne. The positive peaks are due to complex **2** and the negative peaks due to the destruction of **1** upon photolysis. The C≡C alkynyl stretching band in complex **2** is clearly observed at 2098 cm⁻¹.

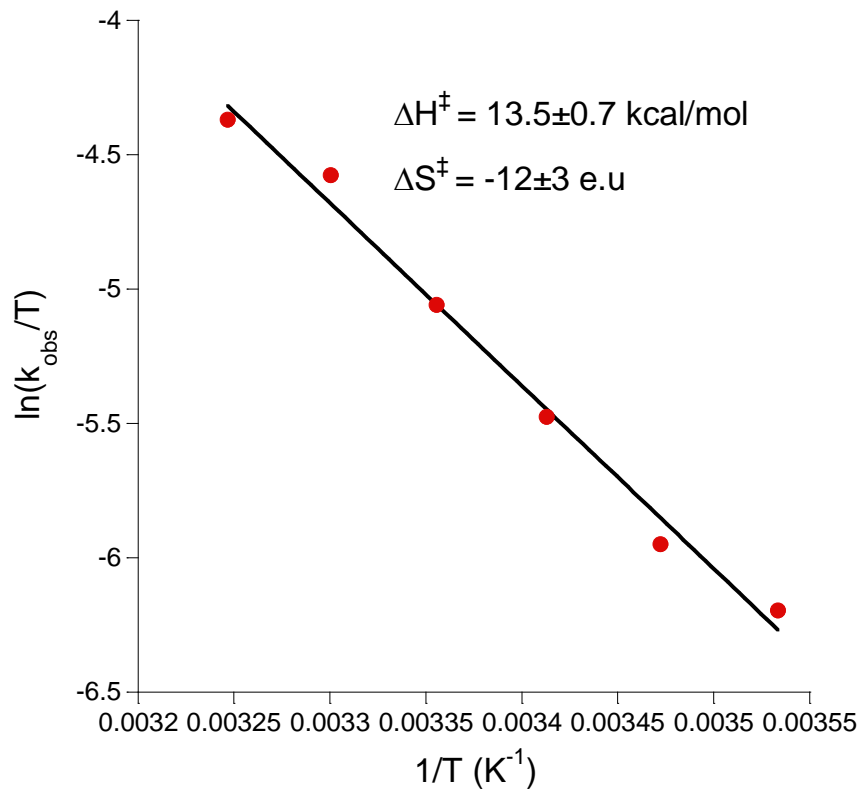


Figure S6: Eyring plot obtained for the conversion of **1**-(η^2 -1-hexyne) to **2**.

TABLES

Table S1: Experimental and calculated ν_{CO} 's, and calculated **1**-ligand bond dissociation enthalpies (BDE) for some of the complexes investigated.

Complex	ν_{CO} (cm^{-1} , experimental)	ν_{CO} (cm^{-1} , calculated, unscaled)	BDE (kcal/mol)
1 -CO	1984, 2006, 2063	-	-
1 -THF _a	1930, 1990	2128, 2180	26.7
1 -THF _b	1937, 1996	2123, 2167	28.5
1 -(η^2 - 1 -hexene)	1954, 2004	2132, 2166	30.8
1 -pyridine	1932, 1992	-	-
1 -(η^2 - 1 -hexyne)	1951, 2003	2120, 2171	28.2
2	1977, 2024	2154, 2188	-

Table S2. Relevant rate constants associated with reactions involving **1**-THF (isomerization), **1**-(η^2 -**1**-hexyne) (activation), and **1**-(η^2 -**1**-hexene) (displacement).

T (K)	1 -THF (isomerization) ^a (s^{-1})	1 -hexyne (activation) ^b (s^{-1})	1 -hexene (displacement) ^c	
			k_1 (s^{-1})	k_2/k_{-1}
313			0.80±0.06	4.9±1.2
308		3.90±0.3	0.54±0.05	3.5±1.0
303		3.12±0.2	0.32±0.05	2.7±1.0
298		1.90±0.1	0.16±0.01	3.5±0.5
293	5.01±0.90	1.23±0.05	0.098±0.007	2.0±0.3
288	2.53±0.10	0.75±0.02	0.044±0.008	2.7±1.1
283	1.44±0.10	0.58±0.02		
278	0.88±0.04			
273	0.48±0.02			
268	0.36±0.02			

Conditions: ^a**1**-CO (4.9 mM), THF (0.246 M), ^b**1**-CO (4.9 mM), **1**-hexyne (0.174 M), ^c**1**-CO (\approx 5 mM), **1**-hexene (1.6 M), Py (0.25-1.49 M) in heptane,