Supplementary Information

Single-Site N–N Bond Cleavage by Mo(IV) to Produce a Terminal Nitrido

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Table of Contents:

A. General Considerations for the Experiments 2
B. Determination of Second-Order Rate Constants for Table 1 3
C. Initial Rates Experiments on 1,1-Dimethylhydrazine Concentration 5
D. Initial Rates Experiments on **1** Concentration 8
E. Thermal Conversion of *syn*-**2** into *anti*-**2** 10
F. UV-Vis trace of *anti*-**2** formation using H_2NNMe_2 and **1** (60 s intervals) 11
G. Powder diffraction on samples of **1** 12
H. Eyring Plot for H_2NNMe_2 reaction with **1** 13
I. Kinetics on the reaction of $Zr(NMe_2)_2(dpma^{mes})$ (**3**) with H_2NNMe_2 15
J. ^1H NMR Assignment of (**2**-*syn*) via HOMO Decoupling 19

A. General Considerations for the Experiments

Reactions and manipulations of air sensitive materials were carried out in an MBraun glovebox under a nitrogen atmosphere and/or using standard Schlenk techniques. Ethereal solvents, pentane, hexane, and toluene were purchased from Aldrich Chemical Co. and purified through alumina columns to remove water after sparging with dinitrogen to remove oxygen. Other compounds, such as formalin and methylamine hydrochloride, were purchased from commercial sources and used as received.

All NMR solvents were purchased from Cambridge Isotopes Laboratories, Inc. Deuterated toluene and benzene were distilled from sodium benzophenone ketyl. Deuterated chloroform was distilled from CaH_2 under dry a dinitrogen atmosphere. The NMR solvents were stored in the glovebox in glass containers with a stopcock. Spectra were taken on Varian instruments located in the Max T. Rogers Instrumentation Facility at Michigan State University.

B. Determination of Second-Order Rate Constants for Table 1

The reactions of **1** with various hydrazines were followed over ~3 half-lives. All kinetic data were obtained on an Evolution 600 model Thermo UV-Vis spectrometer. Temperature control was possible through a Peltier sample holder which maintained ± 0.2 °C throughout the run. Hydrazine was injected through a septum directly into an airtight UV-Vis absorption cell. Reactions were performed in toluene (3.5 mL) with constant stirring throughout the run. Single wavelength absorbance measurements were taken at 651 nm. This point was chosen due to the large difference in the absorbance of **1** (starting material) and **2-*anti*** (product) at this wavelength (ε_{651} = 621.46 for **1** vs ε_{651} = 24.23 for **2**). Absorbance data were fit to the Second-order Equation below using OriginPro 7.5 software, where Abs = absorbance, y_∞ and y_0 are floating parameters corresponding to the ending and starting absorptions respectively.[1] (The expression is only applicable when $rate = k[A]^2$ or when $rate = k[A][B]$ for [A] = [B].)[1] A minimum of 3 runs was used to obtain the rate constants in Table 1 of the manuscript, and the errors are at the 99% confidence level.

$$Abs = y_\infty + \frac{(y_0 + y_\infty)}{(1 + [\mathbf{1}]k_{obs}t)}$$

Shown below is one of the fits to absorption data for one of the kinetics runs where the hydrazine derivative was 1-aminopyrrole as a representative example. The black line is for the data, and the red line is the fit to the 2nd order equation above.

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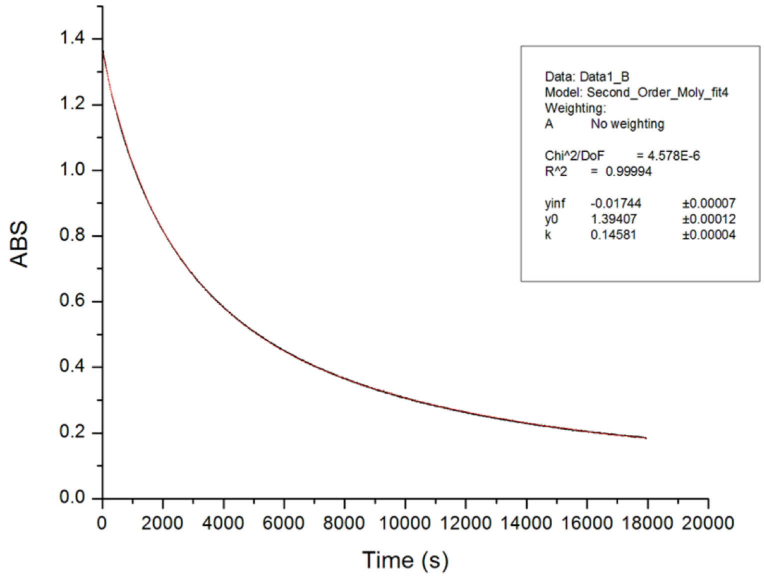
[1] Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd Ed., McGraw-Hill: New York, 2002, p24.



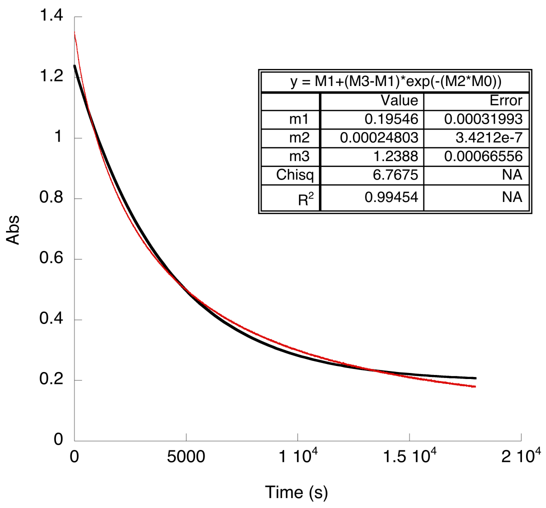
Data: Data1_B
Model: Second_Order_Moly_fit4
Weighting:
A No weighting

Chi^2/DoF = 4.578E-6
R^2 = 0.99994

yinf	-0.01744	±0.00007
y0	1.39407	±0.00012
k	0.14581	±0.00004

It is also useful to consider how well the 1st order expression fits the same curve. The first order equation used is shown below where the parameters have the same meaning as above.[2] The fit (red line in the plot) is much worse in comparison with the fit to the 2nd order expression.

$$Abs = y_\infty + (y_0 - y_\infty)\exp(-k_{obs}t)$$



y = M1+(M3-M1)*exp(-(M2*M0))		
	Value	Error
m1	0.19546	0.00031993
m2	0.00024803	3.4212e-7
m3	1.2388	0.00066556
Chisq	6.7675	NA
R^2	0.99454	NA

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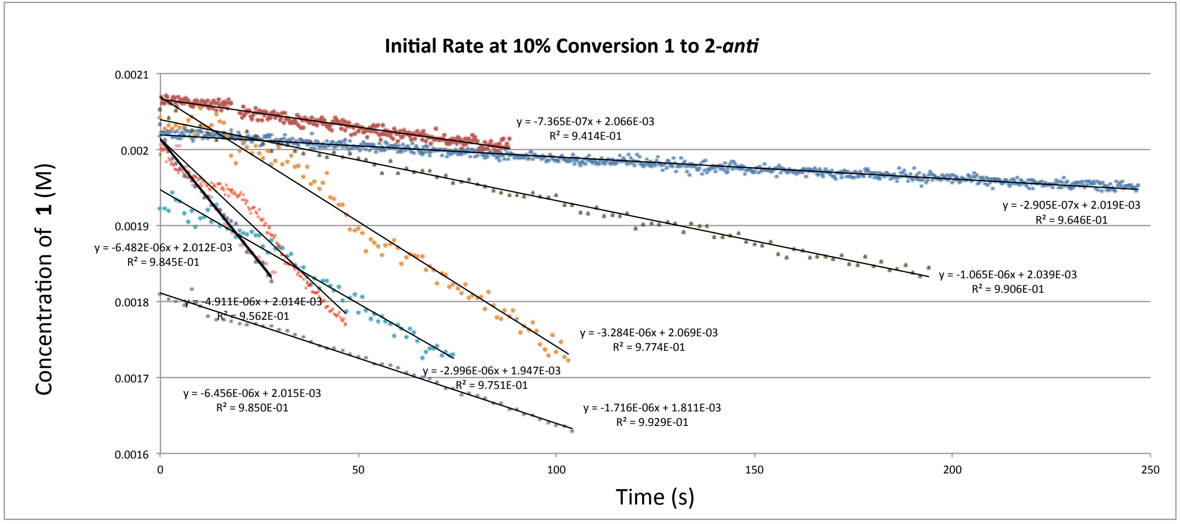
[2] Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd Ed., McGraw-Hill: New York, 2002, p23.

C. Initial Rates Experiments on 1,1-Dimethylhydrazine Concentration

To determine the order in hydrazine, considering pseudo-first order conditions were not possible with the system, we used initial rates. All kinetic data were obtained on an Evolution 600 model Thermo UV-Vis spectrometer. Temperature control was possible through a Peltier sample holder which maintained ± 0.2 °C throughout the run. 1,1-Dimethylhydrazine was injected through a septum directly into an airtight UV-Vis absorption cell. Reactions were performed in toluene (3.5 mL) with constant stirring throughout the run. Single wavelength absorbance measurements were taken at 651 nm. This point was chosen due to the large difference in the absorbance of **1** (starting material) and **2-*anti*** (product) at this wavelength (ε_{651} = 621.46 vs ε_{651} = 24.23 respectively). The data were truncated around 10% conversion of **1** as judged by the decrease from the absorbance at *t* = 0. The initial rate is determined from the slope of the linear fit to the line.[3] The initial absorbances, intercept of the lines, were allowed to fit and did vary slightly from run to run for this extremely reactive and air-sensitive compound even though reactions were run from stock solutions. The [**1**] vs time plot is shown below with the linear fits.



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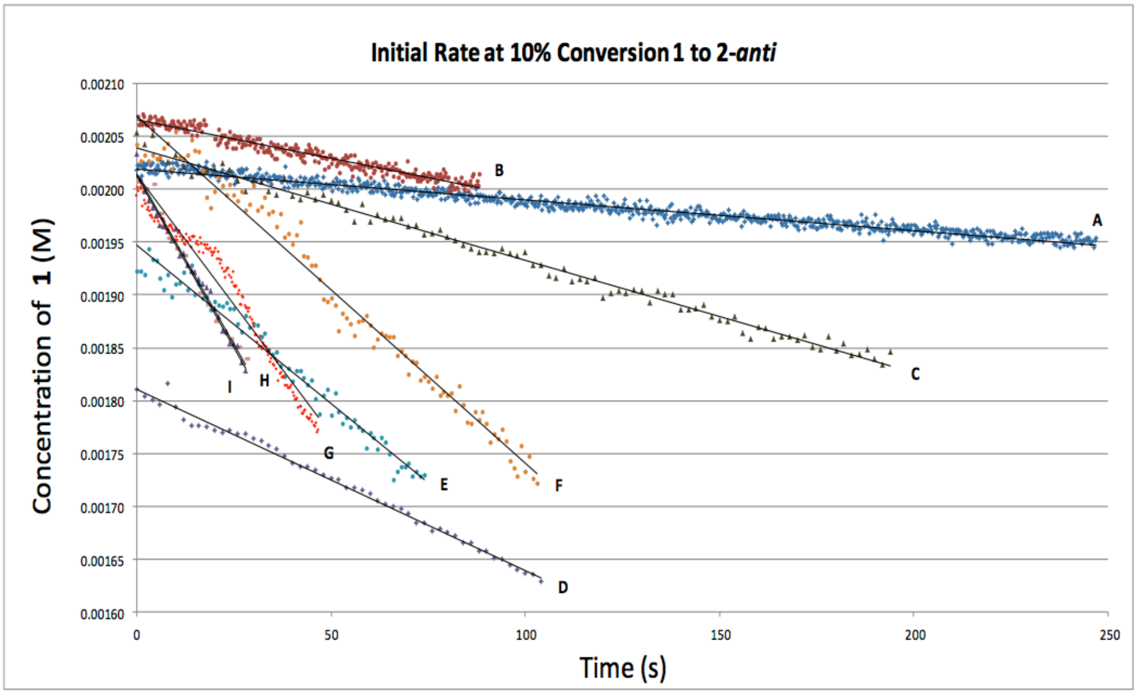
[3] Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*, 2nd Ed., McGraw-Hill: New York, 2002, p 8.

The tabulated hydrazine concentrations and rates are shown in the figure and table below.



	Hydrazine Concentration (M)	Rate Conversion of 1 (M/s*10^{-6})
A	0.00012441	-0.2905
B	0.00031147	-0.7365
C	0.00093175	-1.065
D	0.00203940	-1.716
E	0.00307520	-2.996
F	0.00458054	-3.284
G	0.00487908	-4.911
H	0.00606497	-6.482
I	0.00897284	-6.456

Since the reaction is cleanest when the [**1**] to [hydrazine] are 1:1 and the reaction produces unidentified by-products when the [hydrazine] goes either higher or lower than [**1**], we chose to use Run D, which has these two concentrations closest, as the most accurate run for the analysis below.

For any two reactions in the set, the following equation should apply where $rate_D$ is the rate of reaction D determined from the slopes above, $[\mathbf{1}]_D^a$ is the concentration of **1** in Run D to the power of *a*, and $[hydrazine]_D^b$ is the concentration of the hydrazine in Run D to the power of *b*.

$$\frac{rate_D}{rate_X} = \frac{k_{obs}[\mathbf{1}]_D^a[hydrazine]_D^b}{k_{obs}[\mathbf{1}]_X^a[hydrazine]_X^b}$$

If we assume that $k_{obs}[\mathbf{1}]_D^a \sim k_{obs}[\mathbf{1}]_X^a$, those terms can be eliminated. Rearrangement and using *ln* to isolate the order gives the equation below where the order in hydrazine, *b*, is related to the rates and concentrations of any two runs.

$$b = \frac{\ln\left(\frac{rate_D}{rate_X}\right)}{\ln\left(\frac{[hydrazine]_D}{[hydrazine]_X}\right)}$$

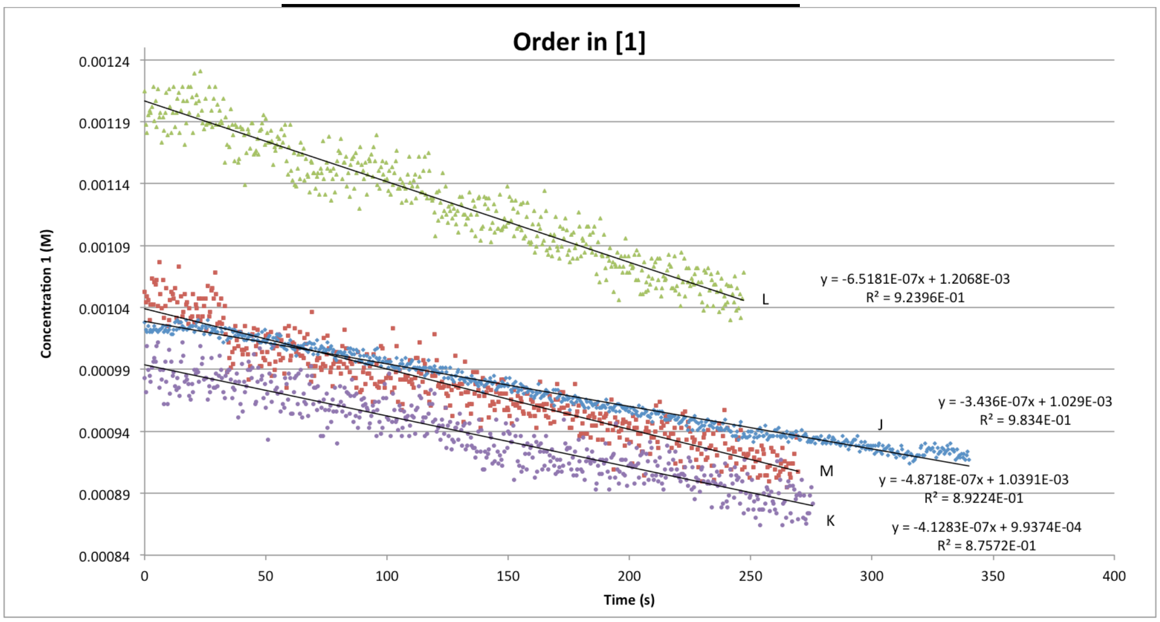
To find the orders in hydrazine relative to Run D (where the reagents are ~1:1) we applied the above expression. The run with the lowest order was Run B displaying an apparent order of 0.45; this run also had the worst R^2 factor for the fit. The highest order obtained was 1.35 for Run E. The average order for all of the runs was *b* = 0.90, and the reaction was assigned as first order in hydrazine.

D. Initial Rates Experiments on **1** Concentration

As a final check on the rate law, we did briefly examine the dependence of the reaction on the concentration of **1**. The conditions and procedure were very similar to the procedure above for the initial rates experiments on hydrazine concentration. The exception being that raising the concentration of **1** much over that used in the hydrazine initial rates experiments leads to solutions that are too concentrated for accurate absorption measurement. Consequently, the concentrations of the hydrazine and **1** were lowered somewhat relative to those above.

The raw data are tabulated below with the initial concentration of **1** and the rate of the disappearance of the **1**. The plots and linear fits are given.

	[1] (M)	**[hydrazine] (M)**	**Rate (10^{-7})**
J	0.00122	0.000607	–3.44
K	0.00122	0.000866	–4.13
L	0.00142	0.0011	–6.52
M	0.00132	0.0011	–4.87



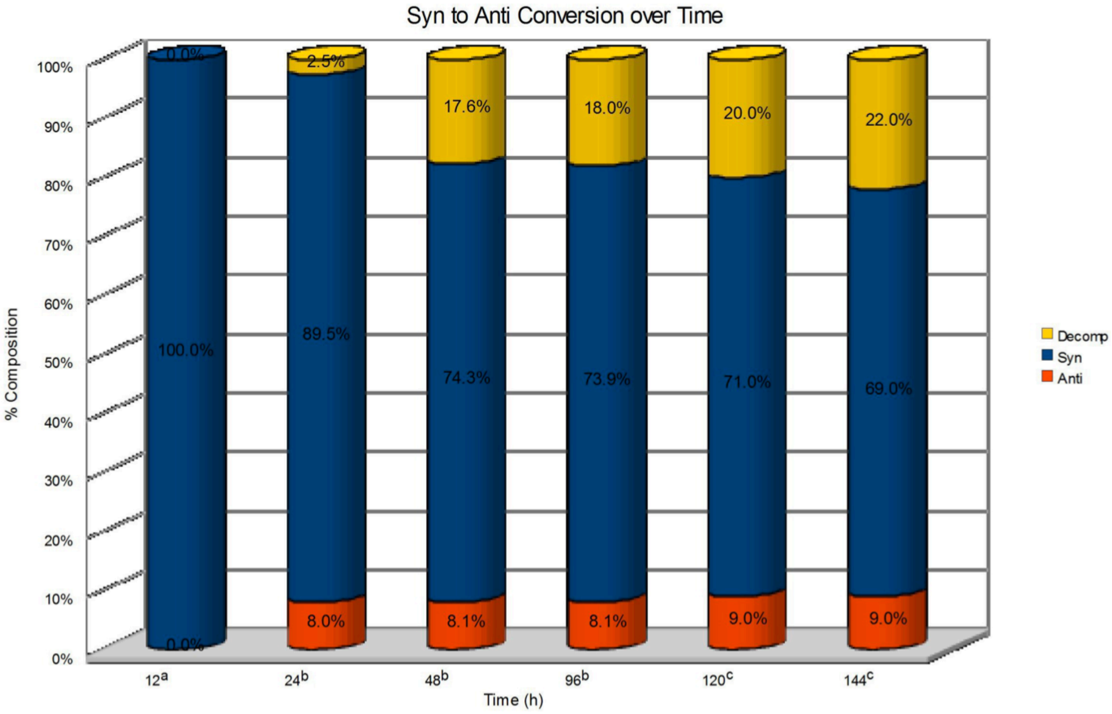
As before, the analysis was done using Run D, where the concentrations of **1** and hydrazine are equal, as the reference Run. We then assumed that the order in hydrazine, exponential *b*, was unity as found in the experiments described previous. This gives the expression below for the order in **1**, *a*.

$$\frac{rate_D}{rate_X} = \frac{k_{obs}[\mathbf{1}]_D^a[hydrazine]_D^b}{k_{obs}[\mathbf{1}]_X^a[hydrazine]_X^b}$$

$$a = \frac{\ln\left(\dfrac{rate_D}{rate_X}\right)}{\ln\left(\dfrac{[\mathbf{1}]_D}{[\mathbf{1}]_X}\right)}$$

Again, the metal complex is extremely reactive and there is some variation in the data. However, for the four Runs the orders in [**1**], *a* in the expression above, were found to be 0.77, 1.11, 0.97, and 1.48 for Runs J–M respectively. This gives an average order of 1.08. Based on this data, the reaction being 2nd order overall, and 1st order in hydrazine, the reaction was assigned as 1st order in metal.

E. Thermal Conversion of *syn*-**2** into *anti*-**2**

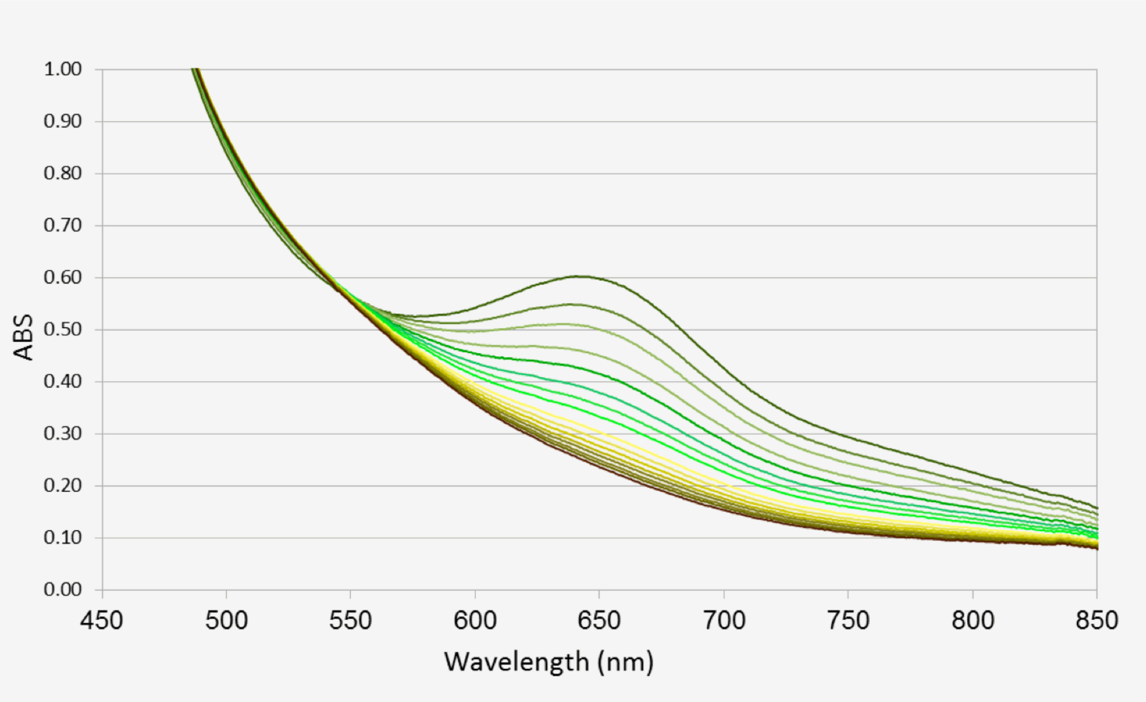


[a] 75 °C

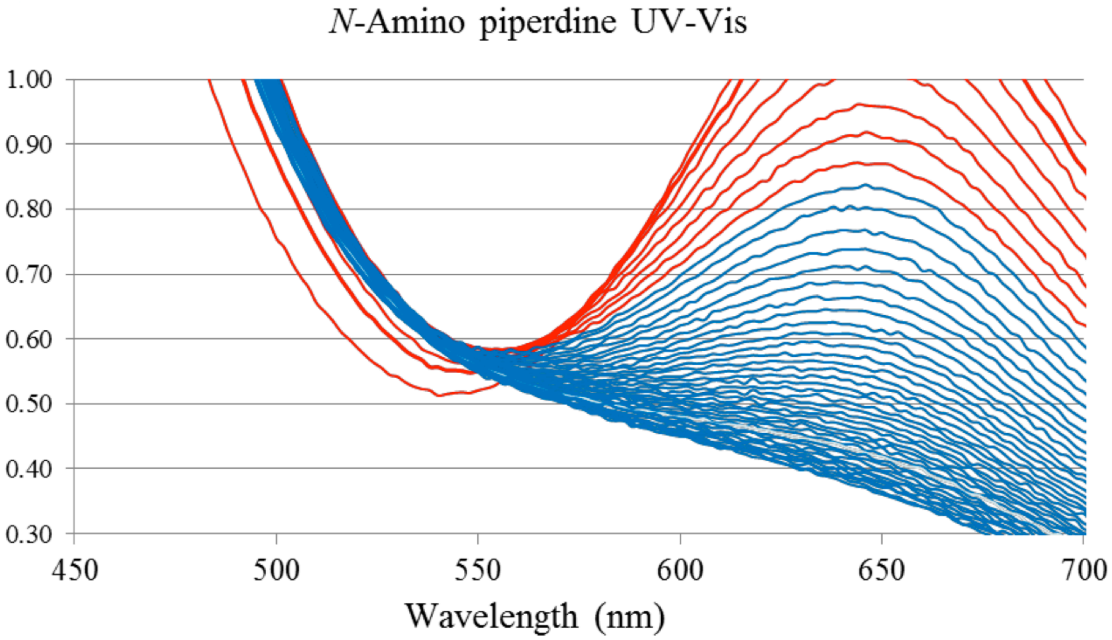
[b] 100 °C

[c] 120 °C

F. UV-Vis trace of *anti*-**2** formation using H_2NNMe_2 and **1** (60 s intervals)

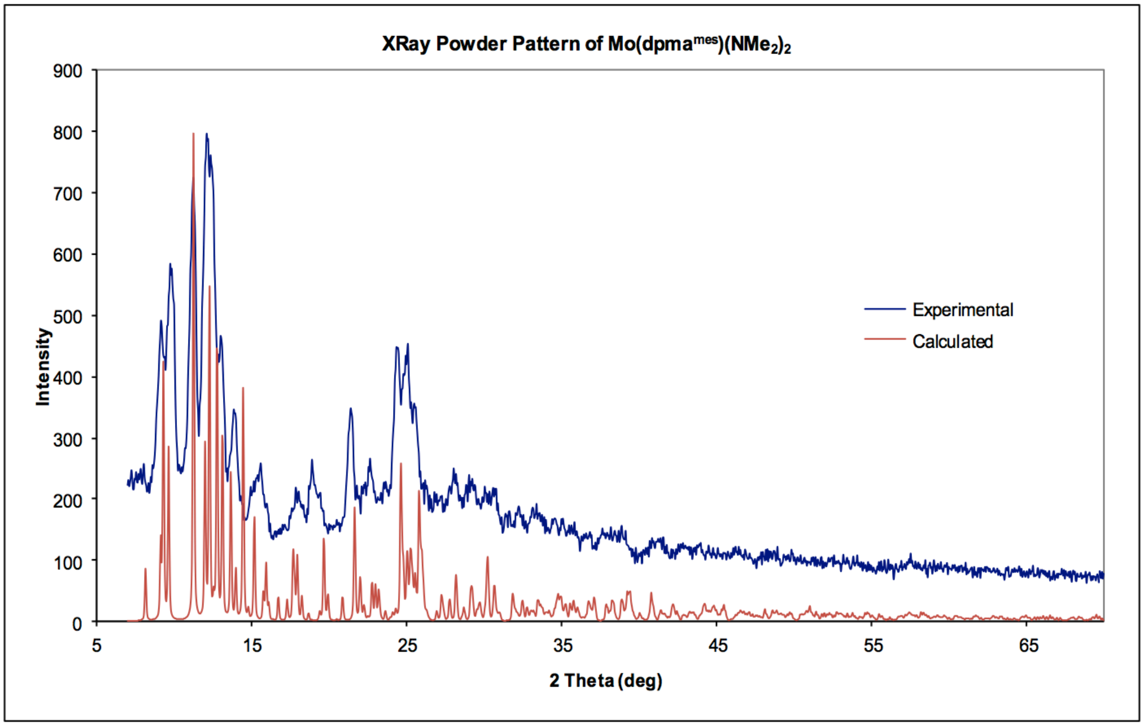


The trace shows an isobestic point, as do all of the substrates with **1** with the exception of *N*-aminopiperidine. It was shown independently that the piperidine by-product reacts rapidly with **1** on the time scale of the experiment, which leads to its anomalous behavior.



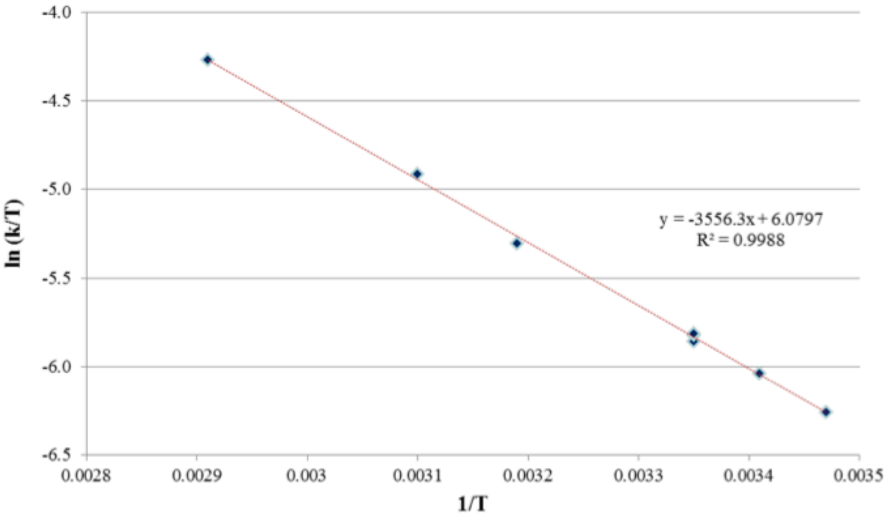
G. Powder diffraction on samples of **1**

Presumably due to the high reactivity of **1** and it's tendency to retain toluene in the lattice, we had difficulty getting an adequate elemental analysis on the paramagnetic compound. One method used to examine the purity of new samples of the compound was to calculate the powder structure of the complex from the single crystal X-ray diffraction experiment and to examine the new sample by power diffraction. One such comparison is shown below.



H. Eyring Plot for H_2NNMe_2 reaction with **1**

The reaction of 1,1-dimethylhydrazine with **1** was carried out over as large a temperature range accessible. The Eyring plot or ln(k/T) vs 1/T is shown below with the linear fit.



$$\ln\left(\frac{k}{T}\right)=\frac{\Delta S^{\ddagger}}{R}+\ln\left(\frac{k_B}{h}\right)-\frac{\Delta H^{\ddagger}}{RT} \quad (1)$$

$$\Delta H^{\ddagger}=-m\times R \qquad (2)$$

$$\Delta S^{\ddagger}=R\left[b-\ln\left(\frac{k_B}{h}\right)\right] \qquad (3)$$

Equation 1 above is the Eyring Equation itself, with R = gas constant, h = Planck's constant, k_B = Boltzmann constant, T = Temperature in Kelvin, and k = observed rate constant. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are found from the slope (m) and intercept (b) of the plot using Equations 2 and 3. Using R = 1.986 cal/K•mol, k_B = 1.381 × 10^{-23} J/K, and h = 6.626 × 10^{-24} J•s, the equations set up as below.

$$\Delta H^{\ddagger}=-(-3556.3\times 1.986)$$
$$\Delta H^{\ddagger}=+7.1\ \text{kcal/mol}$$

$$\Delta S^{\ddagger} = 1.986\left[6.08 - \ln\left(\frac{1.381\times10^{-23}}{6.626\times10^{-34}}\right)\right]$$

$$\Delta S^{\ddagger} = 1.986\left[6.08 - 23.76\right]$$

$$\Delta S^{\ddagger} = -35.1\ \text{cal/mol•K}$$

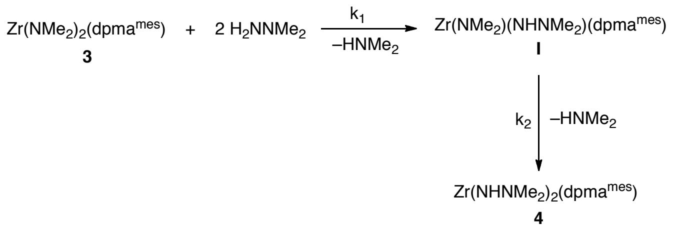
I. Kinetics on the reaction of $Zr(NMe_2)_2(dpma^{mes})$ (**3**) with H_2NNMe_2

Kinetic data for the reaction of **3** with hydrazine was obtained on a Varian 600 MHz NMR instrument. A stock solution of *N,N*-dimethylhydrazine (2 equiv.) in C_6D_6 was injected through a septum into an 5 mm NMR tube containing **3** (1 equiv.) in C_6D_6 (1.2 mL). The reaction was monitored by the ^{1}H NMR integration of the methylene resonances of **3** and **4**. There was an observed intermediate with steady-state behavior with NMR resonances suggestive of $Zr(NMe_2)(NHNMe_2)(dpma^{mes})$.

Data was fit using the OriginPro 7.5 software package to a 2nd-order equation, where Y_t is the methylene integral value for **3**, Y_∞ is the integral value at "infinite" time, and Y_0 is the initial integral value. The factor Δ_0 is the difference in concentration between dimethylhydrazine and **3** at the start of the reaction. The initial dimethylhydrazine concentration, $[\text{hydrazine}]_0$, and zirconium concentration, $[\mathbf{3}]_0$, were 0.0633 M and 0.0317 M respectively, giving $\Delta_0 = 0.0317$.

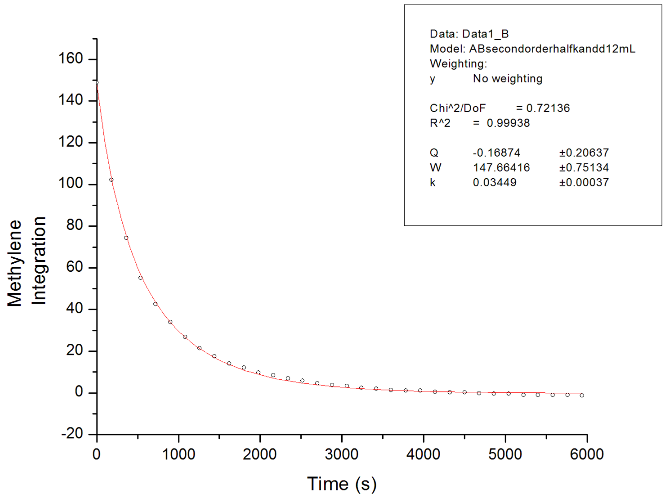
$$\mathrm{Y}_t = \frac{Y_\infty + \left\{Y_0\left(1 - \frac{[\mathbf{3}]_0}{[hydrazine]_0}\right) - Y_\infty\right\} e^{-\Delta_0 k_{obs} t}}{1 - \frac{[\mathbf{3}]_0}{[hydrazine]_0} e^{-\Delta_0 k_{obs} t}}$$

The proposed reaction pathway involves reaction of **3** with hydrazine in a stepwise fashion. An intermediate assigned as mono(dimethylamido) (**I**) is observable at low concentrations (~steady state) throughout the reaction.

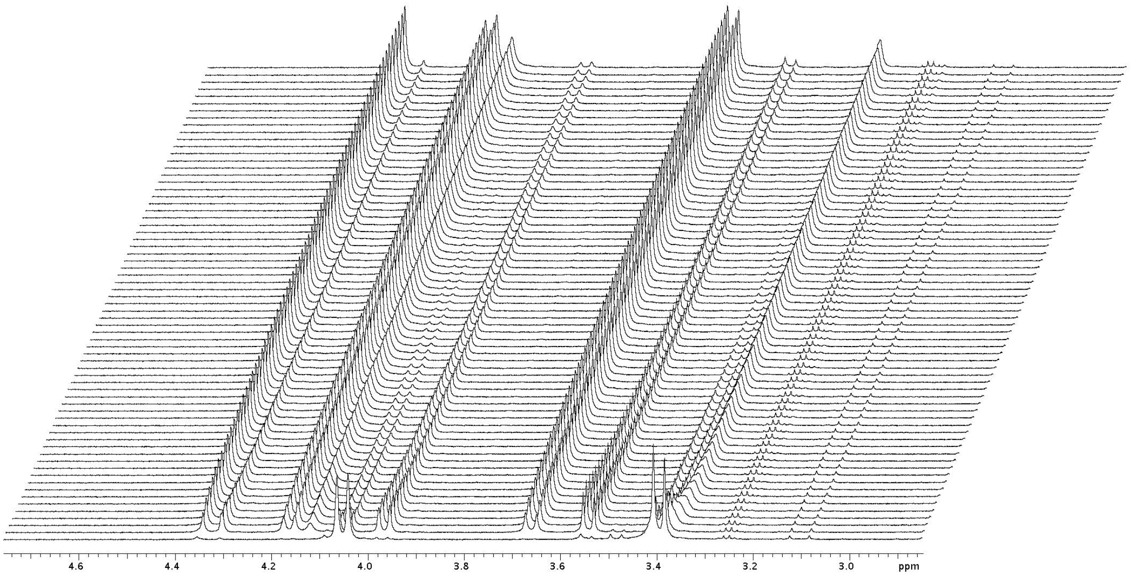


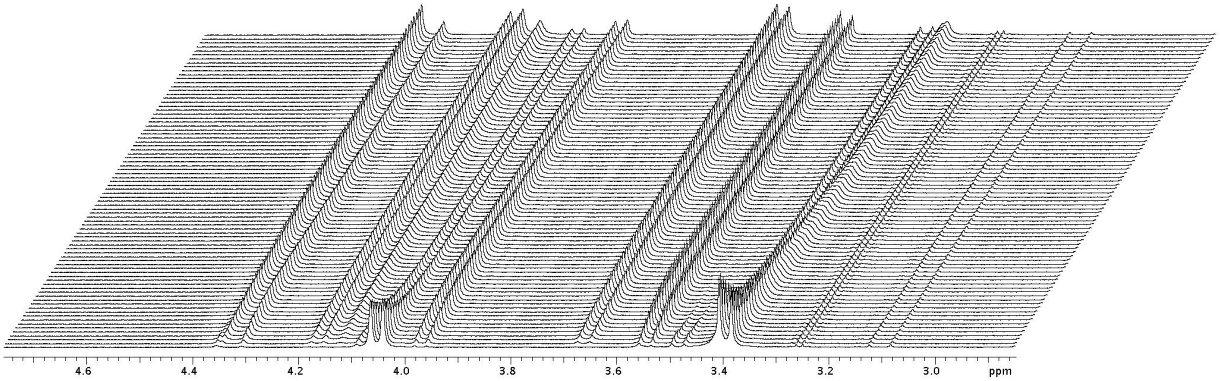
If a second order rate law is applied to the formation of **4** and the steady-state approximation is used to eliminate the concentration of the intermediate **I**, it is simply found that the rate law should be $d[\mathbf{4}]/dt = k_{obs}[\mathbf{3}][\text{hydrazine}]$ consistent with experiment.

One of the 2nd-order fits is shown below as an example.



Below is a stacked ^{1}H NMR of the methylene region in the 25 °C kinetics run. The run lasted around 20 h with traces every 20 min. The second stacked ^{1}H NMR is the same run showing the first 160 min of the reaction with traces every 2 min.

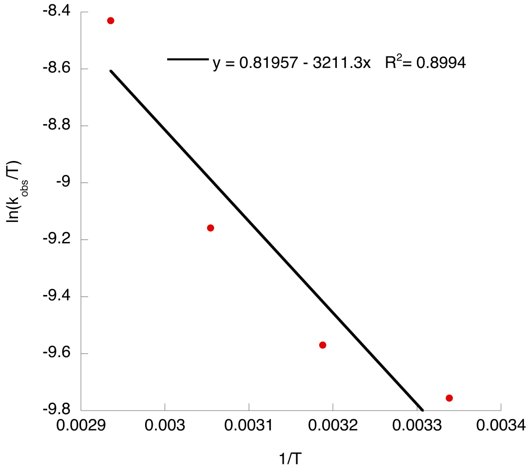




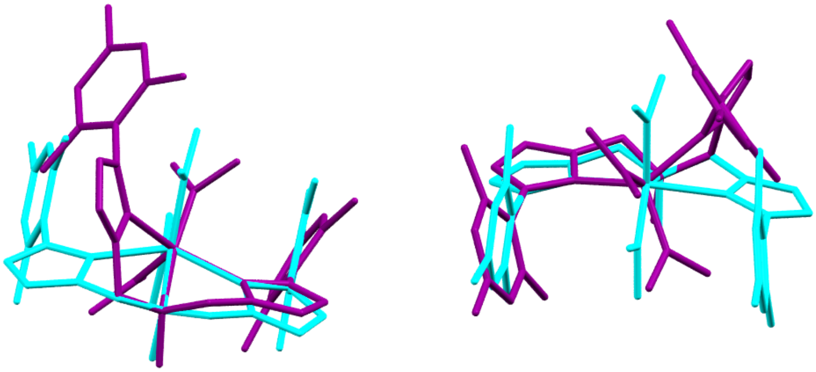
The reaction rate was examined versus temperature as well. The results are tabulated below along with a ln(k/T) vs 1/T (Eyring) plot.

Temp(°C)	k_{obs} ($\times10^{-2}$)	Error in k_{obs} ($\times10^{2}$)
26.54	1.736	0.017
40.71	2.191	0.061
54.41	3.449	0.037
67.68	7.434	0.137

The calculated activation parameters from the Eyring plot are ΔH‡ = +6 kcal/mol and ΔS‡ = –45 cal/mol•K. These are similar to the activation parameters for the molybdenum analog of ΔH‡ = +7 kcal/mol and ΔS‡ = –35 cal/mol•K.



The reactions with the zirconium analog are somewhat slower and there are some differences in the structures for the two compounds, most of which are discussed in the text. An overlay of the two structures is provided below.

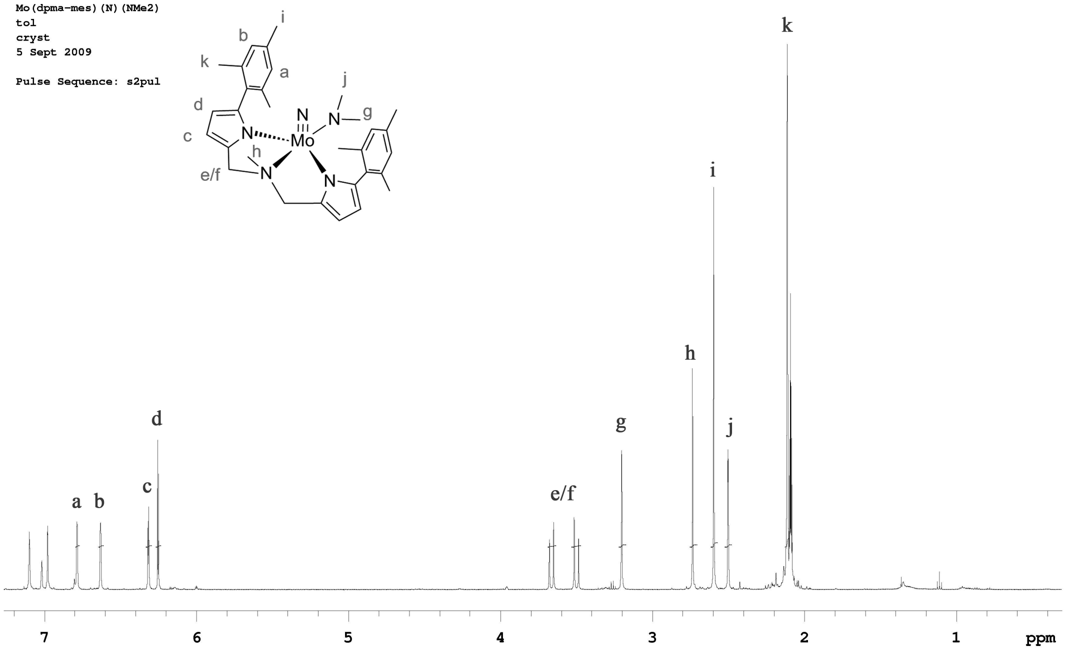


Mo(dpma^{mes})(NMe$_2$)$_2$ (**1**) in purple
Zr(dpma^{mes})(NMe$_2$)$_2$ (**3**) in blue

J. ^{1}H NMR Assignment of (**2**-*syn*) via HOMO Decoupling

Compound (**2**-*syn*) shows interesting couplings in its room temperature ^{1}H NMR spectrum. To investigate these small couplings a series of homo decoupled ^{1}H NMR spectra were taken. In each spectrum a single resonance was saturated resulting in a change in multiplicity of any other resonance coupled to it. This allowed the assignment of two distinguishable dimethylamido proton environments (3.20 and 2.50 ppm) with a 1 Hz coupling. These methyl protons are likely too far from the *N*-methyl protons of the dpma^{mes} ligand (5.45 Å *syn* and 5.55 Å *anti* in the solid state) to be coupling to those, and no 2D NOESY cross-peak was identified.

Furthermore, the methylene resonances from the backbone in the dpma^{mes} ligand displayed a small coupling (J_{HH} = 0.5 Hz) in addition to the geminal coupling caused by hindered rotation upon chelation (J_{HH} = 14.0 Hz). Saturation of each of the β-pyrrolyl resonances showed the origin of this coupling and allowed for the assignment pyrrolyl resonances.


Mo(dpma-mes)(N)(NMe2)
tol
cryst
5 Sept 2009
Pulse Sequence: s2pul
a
b
c
d
e/f
g
h
i
j
k
N
Mo
7
6
5
4
3
2
1
ppm