SUPPORTING INFORMATION

For the manuscript

Benzonitrile Extrusion from Molybdenum(IV) Ketimide Complexes Obtained via Radical C-E (E = O, S, Se) Bond Formation: Toward a New Nitrogen Atom Transfer Reaction

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Table S1. Kinetics of β-elimination (PhCN extrusion) from **3b**.

T (K)	k_{400} (s^{-1})	k_{475} (s^{-1})	k_{580} (s^{-1})
298	2.91×10^{-5}	3.00×10^{-5}	2.85×10^{-5}
308	9.14×10^{-5}	1.07×10^{-4}	1.04×10^{-4}
318	3.38×10^{-4}	3.22×10^{-4}	3.31×10^{-3}
328	9.49×10^{-4}	9.47×10^{-4}	1.01×10^{-3}
338	2.71×10^{-3}	2.77×10^{-3}	2.85×10^{-3}

Table S2. Kinetics of β-elimination (PhCN extrusion) from **3c**.

T (K)	k_{400} (s^{-1})	k_{475} (s^{-1})	k_{580} (s^{-1})
288	7.36×10^{-4}	7.04×10^{-4}	7.56×10^{-4}
298	2.04×10^{-3}	1.88×10^{-3}	2.15×10^{-3}
308	5.33×10^{-3}	5.42×10^{-3}	5.56×10^{-3}
318	1.21×10^{-2}	1.24×10^{-2}	1.23×10^{-2}
328	2.50×10^{-1}	2.80×10^{-2}	2.90×10^{-2}

Table S3. Rate constants of formation of **3d** from complex **1** (0.3 mM), PhCN (3 mM), and benzoyl peroxide (0.3 mM) measured by stopped-flow spectrophotometry.

T, K	k, $M^{-1}s^{-1}$
193	3670
203	5330
213	6530
223	8270
233	10670

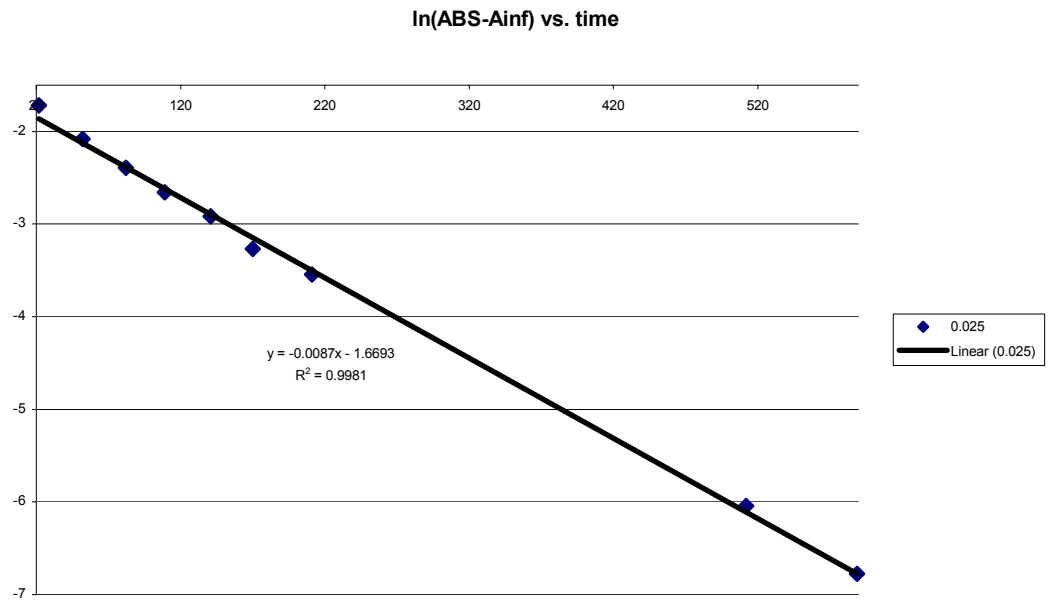

Figure S1. Plot of ln (A-A∞) for nitrile elimination from **3d** at 1.3 °C showing first order character of the reaction through over three half lives.

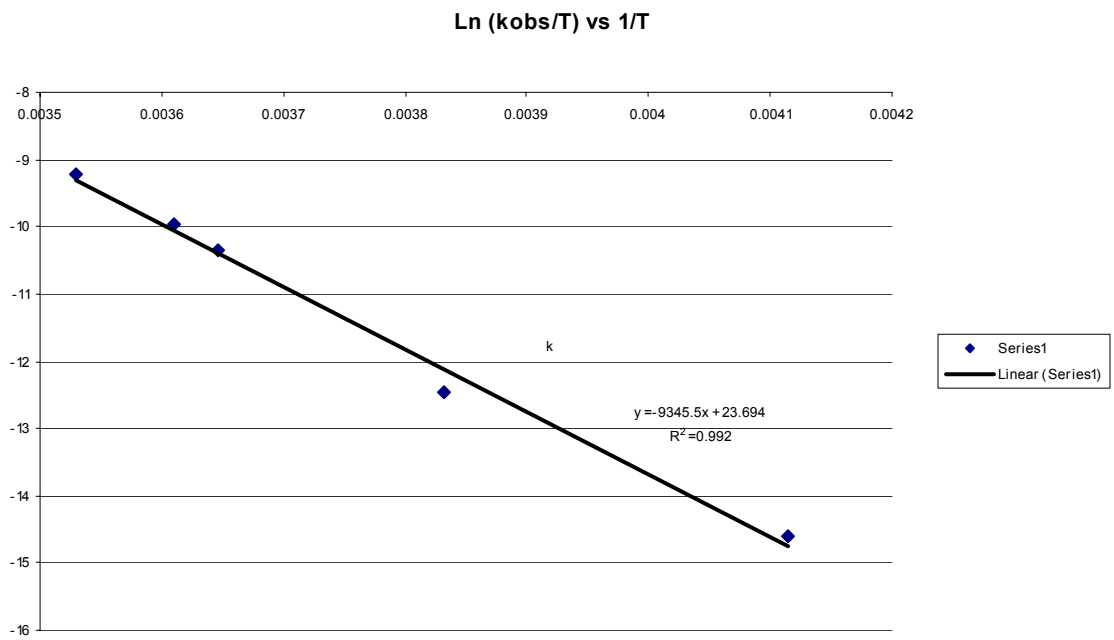

Figure S2. Eyring plot of data for nitrile elimination from **3-**(NC(-OC(=O)(Ph))Ph (**3d**), yielding activation parameters $\Delta H^{\ddagger}$ =18.6 kcal mol^{-1} and $\Delta S^{\ddagger}$ = - 0.1 cal mol^{-1} K^{-1} .

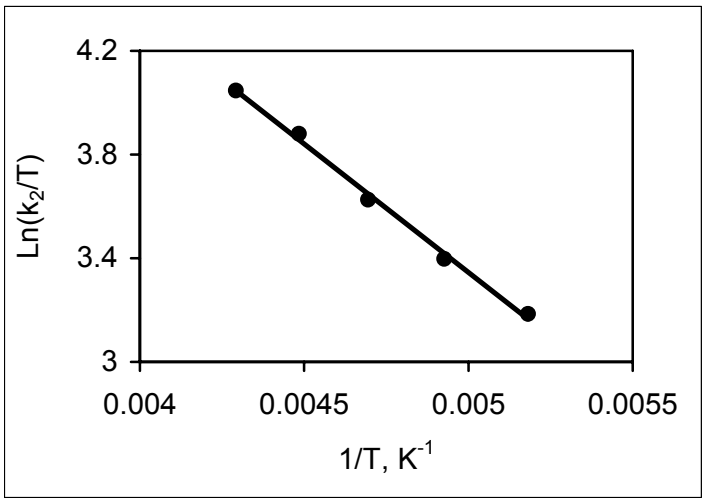

Figure S3. Plot of the temperature dependence of the second-order rate constant for the reaction of (PhCN)Mo(N[*t*-Bu]Ar)$_3$, **5**, with $(PhCO)_2O_2$ in toluene. The fit is to the linear form of the Eyring equation, giving activation parameters of $\Delta H^{\ddagger} = 2.0$ kcal·mol^{-1}, $\Delta S^{\ddagger} = -31$ eu.

($R^2 = 0.996$)

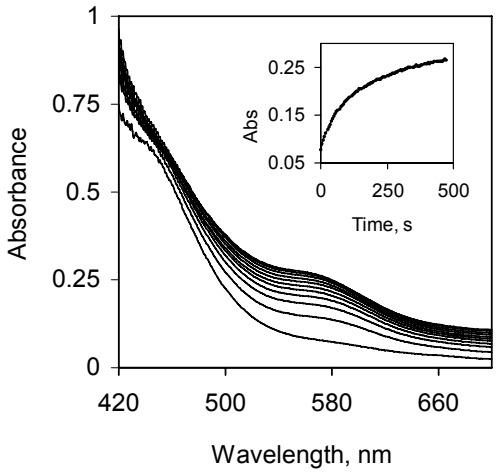

Figure S4. Time-resolved (45 s intervals) spectral changes and a kinetic trace (at 570 nm) overlaid with a second-order fit obtained upon mixing of toluene solutions of $Mo[N(t\text{-}Bu)Ar]_3$ (0.45mM before mixing) and $(PhCOO)_2$ (0.225mM) in the stopped-flow apparatus at -60°C.

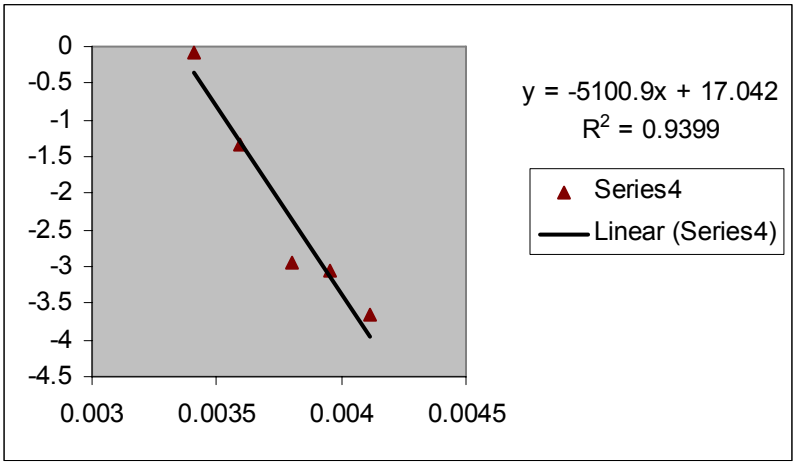

Figure S5. Eyring plot for the reaction between **1** and $(PhCO)_2O_2$ in toluene. The fit is to the linear form of the Eyring equation, giving activation enthalpy $\Delta H^{\ddagger} = 10 \pm 2$ kcal·mol^{-1}.

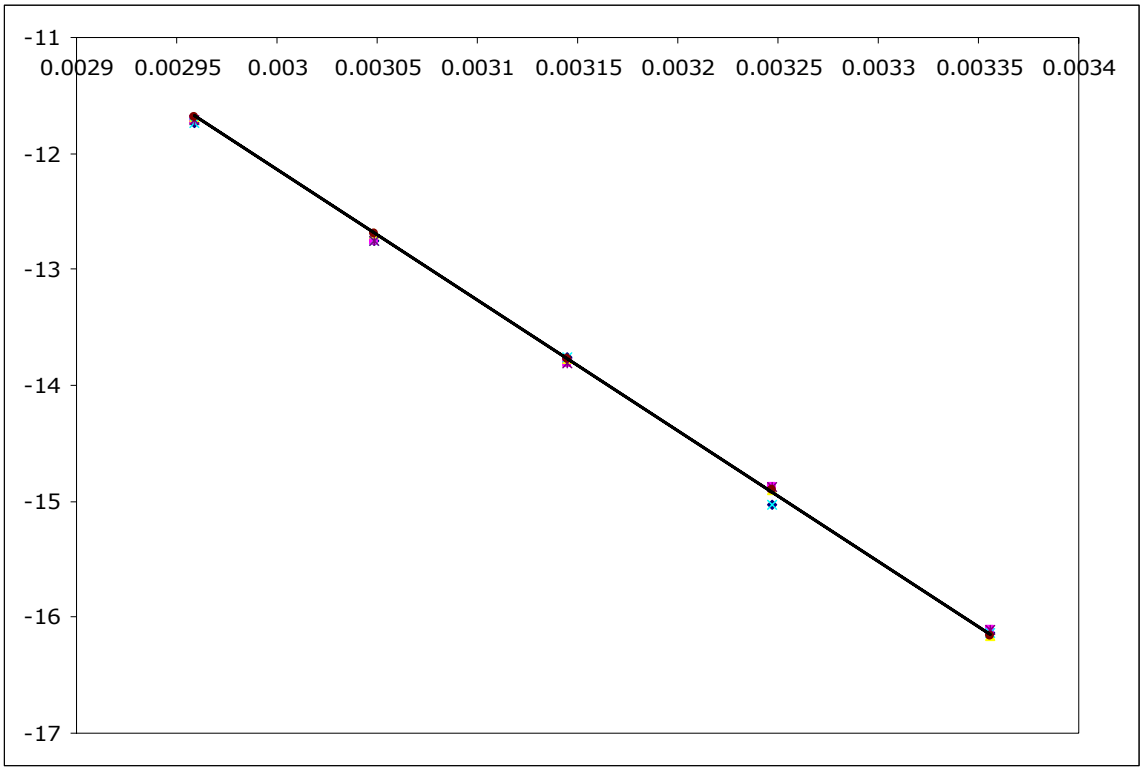

Figure S6. Eyring plot for β-elimination from **3b**.

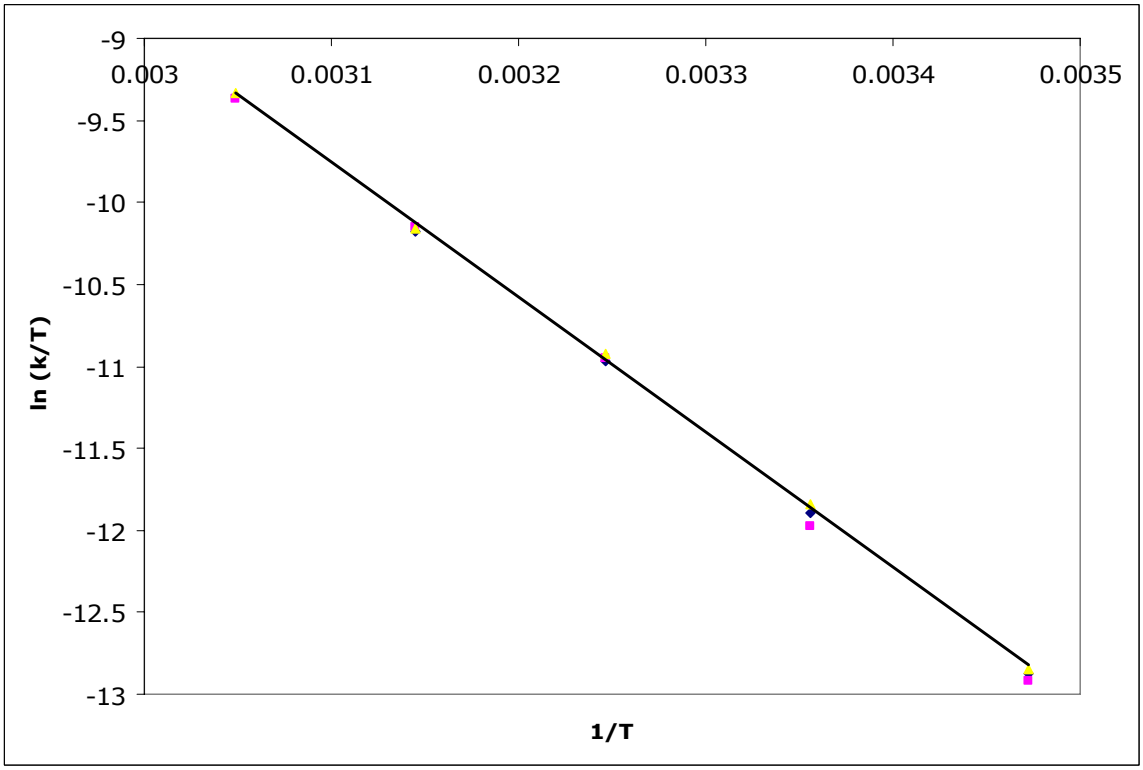

Figure S7. Eyring plot for β-elimination from **3c.**

Computational Details. All DFT calculations were carried out utilizing the Amsterdam Density Functional (ADF) program suite,[1, 2] version 2004.01.[3] The all-electron, Slater-type orbital (STO) basis sets employed were of triple-ζ quality augmented with two polarization functions and incorporated relativistic effects using the zero-order regular approximation[4, 5] (ADF basis ZORA/TZ2P). The local exchange-correlation potential of Vosko et al.[6] (VWN) was augmented self-consistently with gradient-corrected functionals for electron exchange according to Becke,[7] and electron correlation according to Perdew.[8, 9] This nonlocal density functional is termed BP86 in the literature and has been shown to give excellent results for the geometries and energetics of transition metal systems.[10] Crystallographically determined atomic coordinates were used as input where appropriate. Due to the large size of each model investigated, harmonic frequencies calculations to validate characterization as local minima on the potential energy surface (zero imaginary frequencies) were not performed.

References

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