Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

The Reaction of $HV(CO)_4dppe$ with MoO_3: a Well-Defined Model of Hydrogen Spillover

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Supporting Information

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General Experimental

All experiments were carried out under inert atmosphere using standard Schlenk and glovebox techniques. Pentane, toluene, dichloromethane, and acetonitrile were purified by filtration through activated alumina columns and degassed by argon sparging. Deuterated benzene was purified by freeze-pump-thaw degassing and dried using 4Å molecular sieves. a-MoO_3 (6 m^2 g^{-1}), VCl_3, tert-BuBr, 1,2-bisdiphenylphosphinoethane (dppe), 2-methylnaphthalene, NEt_4Br, and $Pt(NH_3)_4Cl_2$ were purchased and used as received. $HV(CO)_4$dppe[1] and Pt/MoO_3 (0.01 wt%)[2] were prepared according to known literature procedures.

IR spectra were measured on a Nicolet 6700 IR spectrometer in transmission mode using a 0.01 cm pathlength solution cell with KBr windows. EPR spectroscopy was carried out at 4-15 K on an X-band cw Bruker EMX spectrometer. EPR simulation was performed using the EasySpin toolbox for MATLAB.[3] UV-Vis spectroscopy was measured in diffuse reflectance mode using a J&M TIDAS UV/Vis-NIR spectrometer (Essingen, Germany) using barium sulfate as a standard and displayed in Kubelka-Munk units. Raman spectroscopy was measured by excitation using a 785 nm laser (power) coupled with an ocean optics 785 Raman spectrometer.

Synthesis of **2**

Complex **1** (10 mg, 0.018 mmol) was dissolved in acetonitrile (5 mL) and mixed with 1 equiv (3 mg, 0.019) of 2,2,6,6-tetramethylpiperidineoxyl (TEMPO). This reaction was stirred for 15 min after which time the IR spectrum was measured (shown below as Figure S1). The IR spectrum obtained for **2** matched previous literature reports. The molar absorbtivities of **2** were obtained from these experiments by assuming quantitative conversion of **1** to **2**.

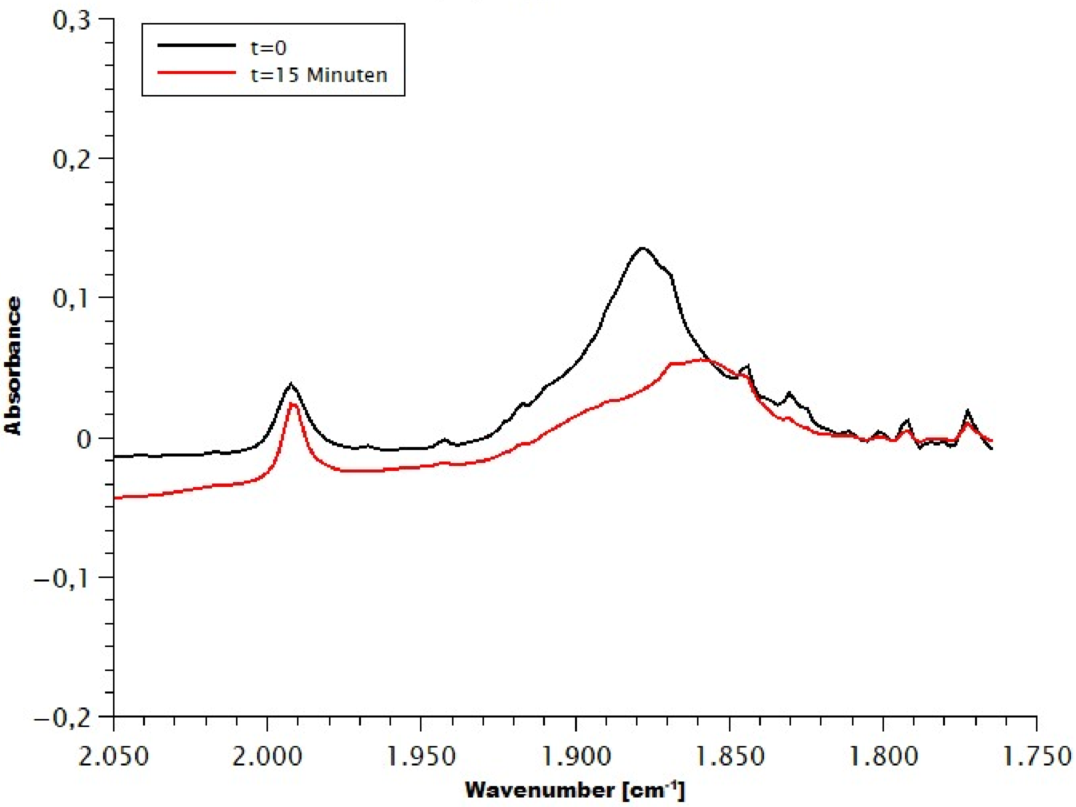

Figure S1. IR spectrum of complex **1** (black) and complex **2** (red) in CH_3CN.

Reaction of 1 with MoO_3

Five mL of a 0.005 M solution of **1** in the desired solvent was added under Ar to 200 mg of MoO_3 and stirred vigorously for 3h. During this time the white MoO_3 powder turned deep blue. Samples (ca. 0.2 mL) were taken at 5, 30, 60, and 180 min and the concentration of **1** and **2** determined by solution IR spectroscopy. After the reaction, the powder was filtered and washed with three aliquots of solvent, dried under vacuum, and stored under Ar. Concentrations were determined using our determined molar absorbtivity coefficients at 1857 and 1878 cm^{-1} ($\varepsilon_{\mathbf{1},1878} = 5150\ M^{-1}cm^{-1}$, $\varepsilon_{\mathbf{1},1857} = 2341\ M^{-1}cm^{-1}$, $\varepsilon_{\mathbf{2},1878} = 1657\ M^{-1}cm^{-1}$, $\varepsilon_{\mathbf{2},1857} = 2341\ M^{-1}cm^{-1}$). Reaction in DCM was measured for 6h, due to low conversion.

EPR Spectra

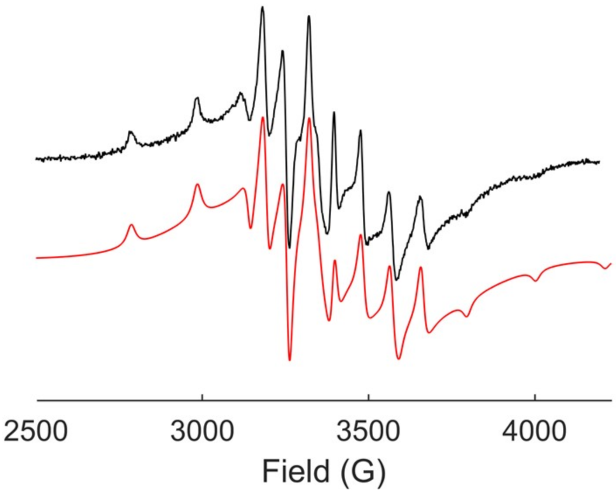

Figure S2. X-band EPR spectrum of **2** at 4 K (black) and simulation (red) with $g_{\perp} = 1.980, g_{\parallel} = 1.930, A_{\perp} = 205\ MHz, A_{\parallel} = 550\ MHz$ with a very broad underlying signal, attributed to dipolar broadening of aggregated species.

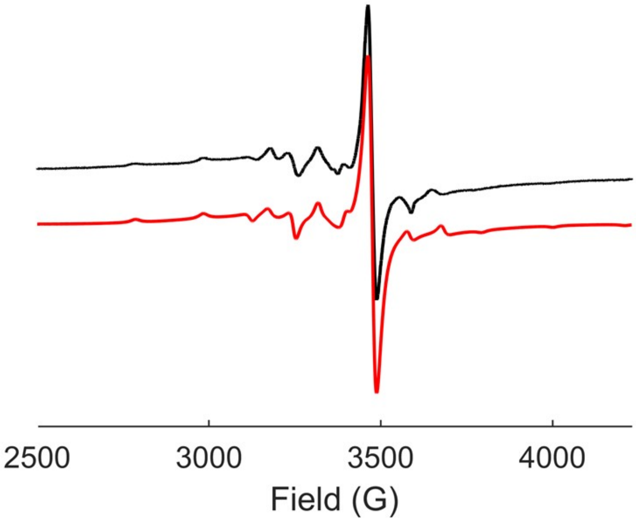

Figure S3. X-band EPR spectrum of $MoO_{3\text{-red}}$ at 4 K (black) and simulation (red) with $g_{\perp} = 1.980, g_{\parallel} = 1.930, A_{\perp} = 220\ MHz, A_{\parallel} = 550\ MHz$ for Vanadium and $g_{iso} = 1.945$ for Molybdenum.

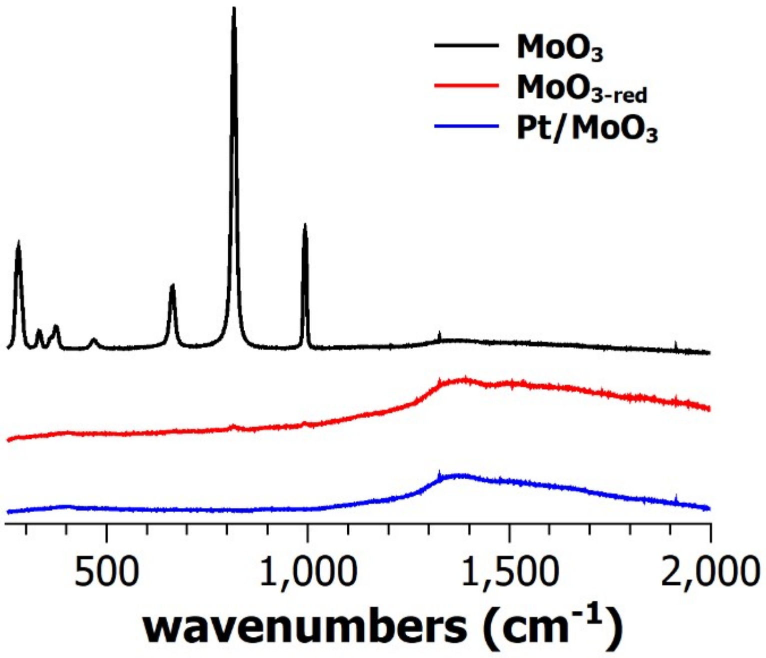

Figure S4. Raman Spectra of MoO_3 (black), $MoO_{3\text{-red}}$ (red), and Pt/MoO_3 (blue).

IR Spectra and Kinetic Traces of Reactions of 1 with MoO_3

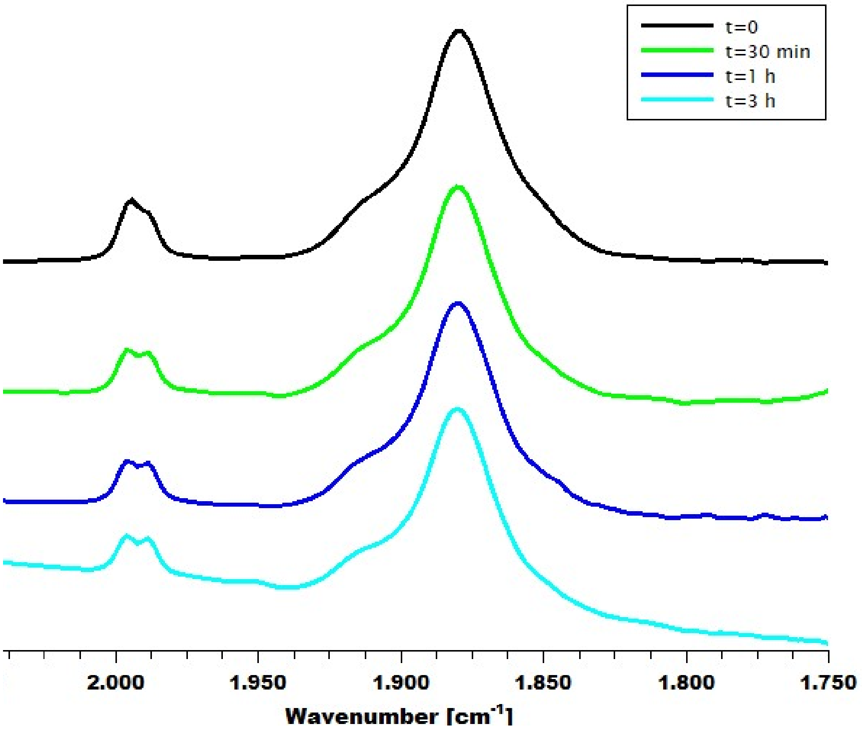

Figure S5. IR spectra of reaction of **1** with MoO_3 in toluene

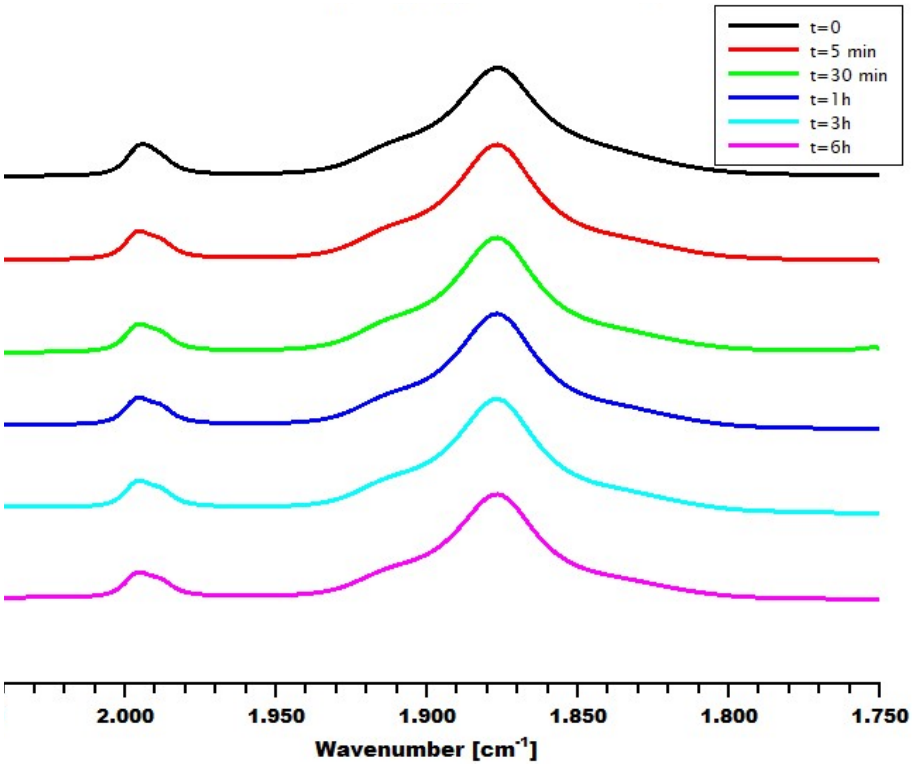

Figure S6. IR spectra of reaction of **1** with MoO_3 in dichloromethane.

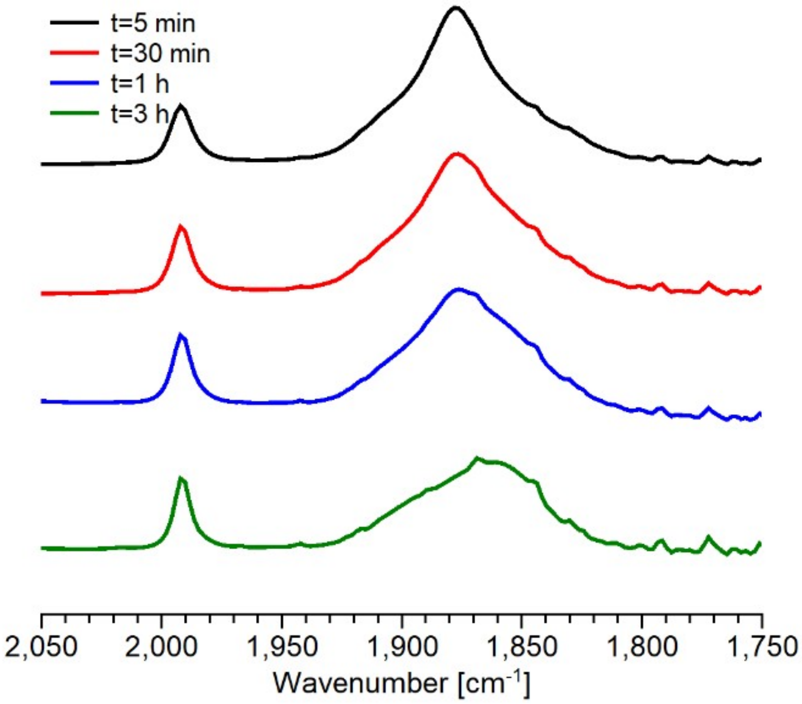

Figure S7. IR spectra of reaction of **1** with MoO_3 in acetonitrile.

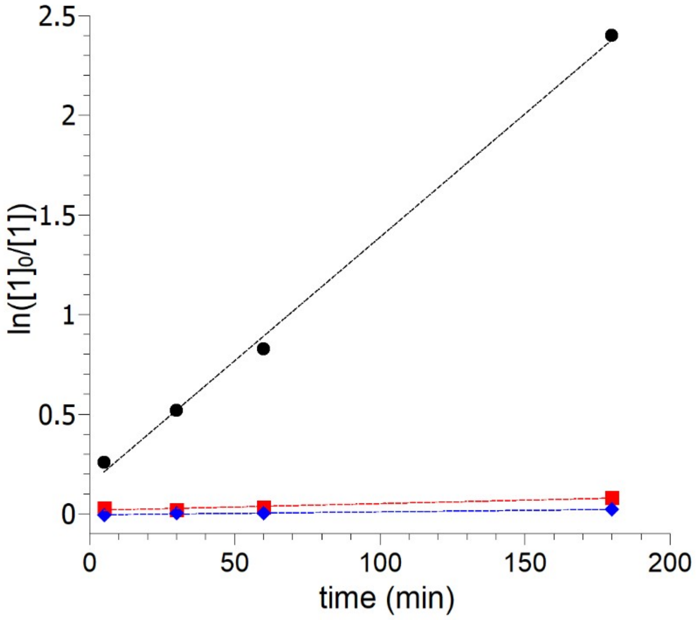

Figure S8. 1st order kinetic traces of the reaction of **1** with MoO_3 in acetonitrile (black), toluene (red), and dichloromethane (blue).

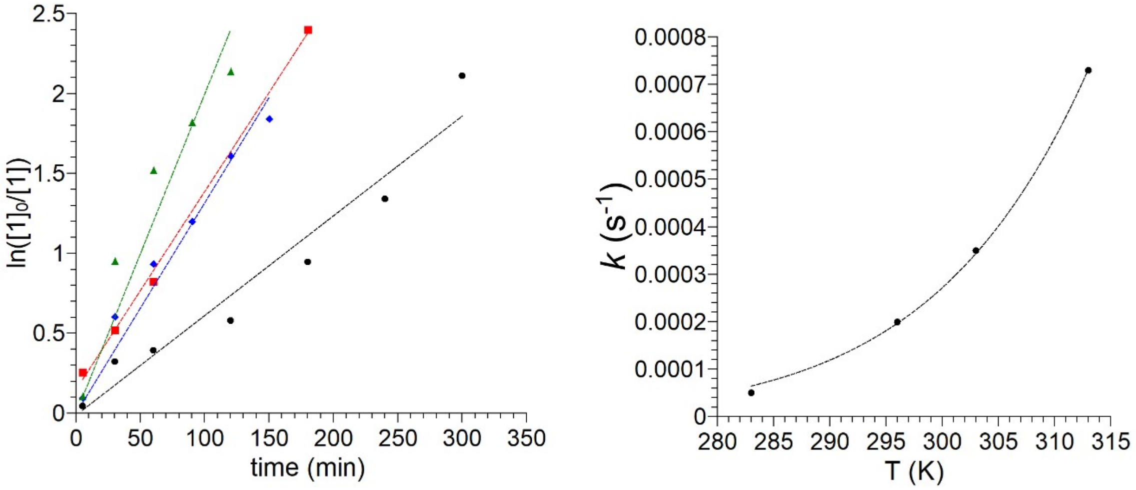

Figure S9. 1st order kinetic traces of the reaction of **1** with MoO_3 in acetonitrile at 40, 30, 23, and 10 °C (left) and Arrhenius Plot (T vs k) (right).

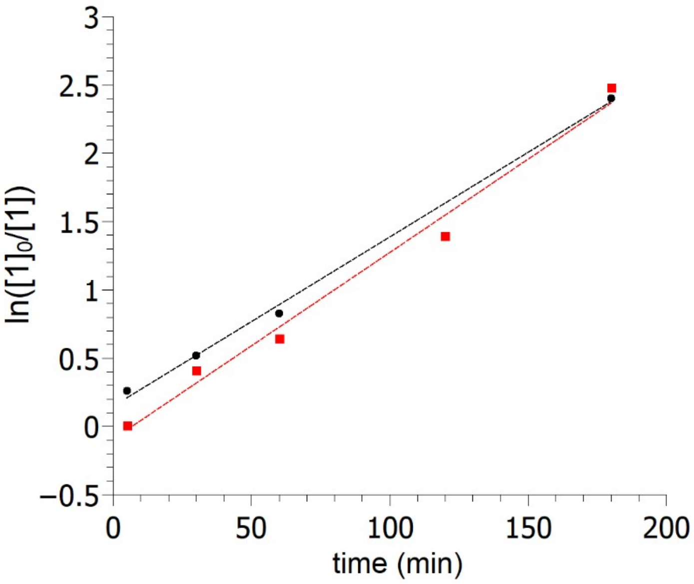

Figure S10. 1st order kinetic traces of the reaction of **1** and **1**-*d*$_1$ with MoO_3 in acetonitrile at 23 °C.

Table S1. Rate constants of reaction of **1** with MoO_3 under various conditions.

Reactant	solvent	temperature (K)	*k* (s^{-1})
1	CH_3CN	313	$7.3(7)\times10^{-4}$
1	CH_3CN	303	$3.5(7)\times10^{-4}$
1	CH_3CN	296	$2.0(5)\times10^{-4}$
1	CH_3CN	283	$5(3)\times10^{-5}$
1	CH_2Cl_2	296	$2.5(4)\times10^{-6}$
1	toluene	296	$5(1)\times10^{-6}$
1-*d*$_1$	CH_3CN	296	$3.3(1.0)\times10^{-4}$

References

[1]. Choi, J.; Pulling, M. E.; Smith, D. M.; Norton, J. R., *J. Am. Chem. Soc.* **2008,** *130*, 4250.
[2]. Dyballa, M.; Rieg, C.; Dittmann, D.; Li, Z.; Buchmeiser, M.; Plietker, B.; Hunger, M., *Microporous and Mesoporous Materials* **2020,** *293*, 109778.
[3]. Stoll, S.; Schweiger, A., *J. Mag. Res.* **2006,** *178*, 42.