

Supplementary Information for

Catalytic hydrazine disproportionation mediated by a
thiolate-bridged VFe complex

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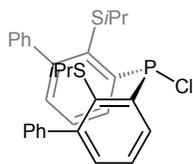
Experimental methods.....	2
Synthesis and characterization of compounds 3-11	2-5
NMR spectra.....	5-7
IR spectra.....	7-8
UV-Visible spectra.....	8-9
X-ray data.....	9-12
Catalytic runs.....	12-15
References.....	15

General considerations. All syntheses and measurements, unless otherwise stated, were carried out under an inert atmosphere (N₂) in a glovebox or using standard Schlenk techniques, and solvents were dried and degassed by thoroughly sparging with N₂ and then passing through an activated alumina column in a solvent purification system supplied by SG Water, LLC. 2-phenylbenzenethiol,¹ VMes₃(py),² VMes₃(THF),³ PhPS₃H₃,⁴ **2**,⁵ **4**,⁶ and **9**⁷ were prepared according to literature procedures. All other reagents were purchased from commercial vendors and used without further purification unless otherwise stated.

Physical methods. NMR spectra (¹H, ³¹P) were collected on Varian 300 or 400 MHz spectrometers (25 °C unless otherwise specified). ¹H chemical shifts are reported in ppm, relative to tetramethylsilane using residual proton and ³¹P chemical shifts are reported in ppm relative to 85% aqueous H₃PO₄. Thin film IR spectra were obtained using a Bruker Alpha Platinum ATR spectrometer with OPUS software in a glovebox under an N₂ atmosphere. Optical spectroscopy measurements were taken on a Cary 50 UV–Vis spectrophotometer using a 1 cm quartz cell, unless otherwise noted. Combustion analysis was carried out by either Midwest Microlabs (Indianapolis) or the Beckman Institute Crystallography Facility (Caltech). H₂ was analyzed on an Agilent 7890A gas chromatograph (HP-PLOT U, 30 m, 0.32 mm ID; 30 °C isothermal; nitrogen carrier gas) using a thermal conductivity detector. Mass spectroscopy data for **5** and **6** were obtained using a Thermo LCQ ion trap mass spectrometer. High-resolution mass spectroscopy data for **7** was collected by direct infusion electrospray ionization in the positive ion mode using an LCT Premier XE time-of-flight mass spectrometer (Waters).

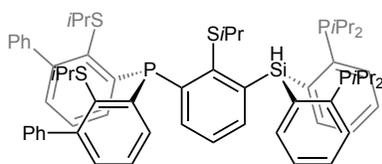
X-ray crystallography. X-ray diffraction (XRD) measurements were carried out in the Beckman Institute Crystallography Facility. XRD measurements were collected using a dual source Bruker D8 Venture, four-circle diffractometer with a PHOTON CMOS detector. Structures were solved using SHELXT and refined against *F*² on all data by full-matrix least squares with SHELXL. The crystals were mounted on a glass fiber under Paratone N oil.

Synthesis and characterization of 3-11.



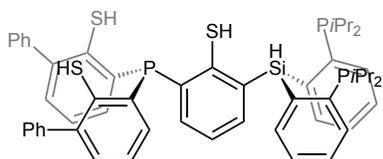
Chlorobis(2-(isopropylthio)-[1,1'-biphenyl]-3-yl)phosphine (3).

Neat P(NEt₂)Cl₂ (1.3 g, 7.1 mmol) was added dropwise to a stirring suspension of **2** (5.0 g, 14.3 mmol) in Et₂O (100 mL) at -78 °C. The reaction was stirred overnight with slow warming to 25 °C. The volatiles were subsequently removed under reduced pressure, and the resulting solids were extracted with pentane (3 x 25 mL), then dried and redissolved in Et₂O (100 mL). HCl (2 M in Et₂O, 28.5 mL) was added dropwise to the stirring reaction mixture at 0 °C, and the reaction was allowed to stir at 25 °C for 1 h. The reaction volatiles were subsequently removed under reduced pressure, and the crude product was extracted from the mixture with pentane (3 x 50 mL). The pentane solution was concentrated to 15 mL and chilled to -78 °C to precipitate the product. The title compound was isolated by filtration as a white solid. The filtrate was collected, concentrated, and cooled to -78 °C to yield additional material (1.94 g, 26%). ¹H NMR (C₆D₆, 400 MHz, 298 K, δ): 7.81 (d, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.2 Hz 2H), 7.12-7.03 (m, 16H), 2.84 (hept, *J* = 7.0 Hz, 1H), 1.00 (d, *J* = 6.7 Hz, 6H), 0.84 (d, *J* = 6.8 Hz, 6H). ³¹P NMR (C₆D₆, 300 MHz, 298 K, δ): 49.81 (s).



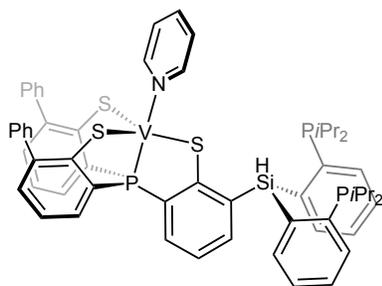
(((3-(bis(2-(isopropylthio)-[1,1'-biphenyl]-3-yl) phosphino)-2-(isopropylthio)phenyl)silanediy)bis(2,1-phenylene))bis(diisopropylphosphine) (5).

N-BuLi (1.6 M in hexane, 0.9 mL, 1.4 mmol) was added dropwise to a stirring solution of **4** (0.82 g, 1.3 mmol) in Et₂O (20 mL) at -78 °C. The reaction was allowed to stir at -78 °C for 1 h and subsequently allowed to stir at 25 °C for 1 h. The volatiles were removed under reduced pressure, and the resulting off-white solid was redissolved in toluene (20 mL). A cold solution of **3** (0.66 g, 1.3 mmol) in toluene (20 mL) was added dropwise to the stirring reaction, and the reaction mixture was stirred overnight with slow warming to 25 °C. The volatiles were subsequently removed *in vacuo*. The resulting residue was redissolved in Et₂O (20 mL) and filtered through Celite. The filtrate was concentrated to yield the title compound as an off-white solid (1.10 g, 82%). The title compound can be recrystallized from a concentrated pentane solution at 25 °C. ¹H NMR (C₆D₆, 400 MHz, 298 K, δ): 7.52 (dd, *J* = 17.5, 7.4 Hz, 4H), 7.41 (t, *J* = 8.6 Hz, 2H), 7.36 – 7.02 (m, 20H), 6.96 (t, *J* = 7.4 Hz, 1H), 4.59 (bs, 1H), 3.31 (hept, 1H), 3.10 (hept, 1H), 2.20 – 1.89 (m, 4H), 1.52 (d, *J* = 6.8 Hz, 6H), 1.36 – 1.25 (m, 3H), 1.25 – 0.94 (m, 21H), 0.90 – 0.79 (m, 12H). ³¹P NMR (C₆D₆, 300 MHz, 298 K, δ): 2.12 (s), 1.84 (s), -17.00 (s). ESI-MS (positive ion, amu): Calcd. 1089.4 ([M-Na]⁺); Found. 1089.2.



3,3''-((3-(bis(2-(diisopropylphosphino)phenyl)silyl)-2-mercaptophenyl)phosphinediy)bis([1,1'-biphenyl]-2-thiol) (6).

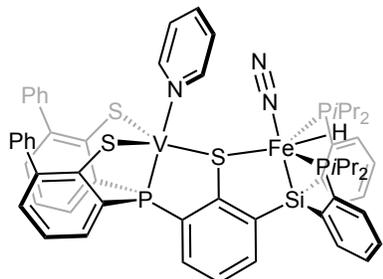
A suspension of KC₈ (0.470 g, 3.5 mmol) in THF (15 mL) was added dropwise to a stirring solution of **5** (1.108 g, 1.05 mmol) in THF (50 mL) at -78 °C. The reaction was stirred at 25 °C for 1 h to yield a deep red solution. The reaction mixture was filtered to remove graphite, and solid pyridinium chloride (0.670 g, 5.8 mmol) was added at 25 °C to the stirring solution. The color of the reaction mixture changed from deep red to pale yellow during the addition of acid. The reaction was stirred at 25 °C for 1 h, and the volatiles were subsequently removed *in vacuo*. The product was extracted from the remaining white solid with pentane (3 x 25 mL), and the volatiles were removed under reduced pressure to afford the title compound as an off-white solid and used as is (0.803 g, 82%). ¹H NMR (C₆D₆, 300 MHz, 298 K, δ): 7.43-7.01 (m, 19 H), 6.91 (t, *J* = 7.6 Hz, 5H), 6.83 (t, *J* = 7.4 Hz, 3H), 4.72 (d, *J* = 3.7 Hz, 2H), 4.65 (bs, 1H), 2.06-1.88 (m, 4H), 1.09 (ddd, *J* = 14.4, 9.4, 6.9 Hz, 12H), 0.93 (dd, *J* = 12.0, 7.1 Hz, 6H), 0.86 (dd, *J* = 11.7, 7.2 Hz, 6H). ³¹P NMR (C₆D₆, 162 MHz, 298 K, δ): 0.95 (s), -24.15 (s). ESI-MS (positive ion, amu): Calcd. 925.3 ([M-H]⁺); Found. 925.0.



V-(SAr) (7)

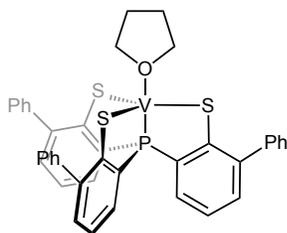
A solution of VMes₃(py) (0.218 g, 0.45 mmol) and pyridine (0.1 mL) in THF (10 mL) was added dropwise to a stirring solution of **6** (0.376 g, 0.41 mmol) in THF at 25 °C. The reaction mixture was stirred for 5 h at 25 °C, and the volatiles were subsequently removed *in vacuo* to yield a dark yellow-brown residue. The resulting solids were washed with THF (3 x 5 mL) to yield the title compound as a yellow-orange solid. The filtrate was concentrated and pentane was allowed to slowly diffuse onto the solution to precipitate additional material (0.125 g, 29%). Yellow-orange crystals suitable for XRD were grown from slow diffusion of pentane into a concentrated THF solution at 25 °C. ¹H and ³¹P NMR

in C₆D₆ at 25 °C were silent. μ_{eff} (THF, Evans method, 298 K): 3.3 μ_{B} . Anal. Calcd. for C₅₉H₆₁NP₃S₃SiV: C, 67.34; H, 5.84; N, 1.33. Found: C, 66.52, H, 6.00; N, 1.23. UV-vis (THF, 298 K, nm {cm⁻¹ M⁻¹}): 462 {3600}. ESI-MS (positive ion, amu): Calc (M⁺): 1051.2388, Found: 1051.2361.



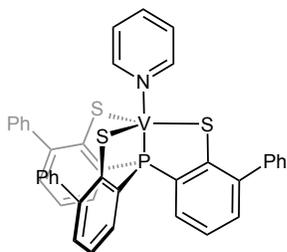
V-(μ -SAr)-Fe(N₂)(H) (**8**)

A solution of **7** (44.9 mg, 0.043 mmol) in THF (10 mL) was added to solid FeBr₂ (10.1 mg, 0.047 mmol) and stirred at 25 °C for 1 h to yield an orange solution. The volatiles were subsequently removed under reduced pressure, and the remaining orange solid was suspended in Et₂O (5 mL) and allowed to stir for 10 min at 23 °C. The volatiles were removed *in vacuo*, and the resulting dark orange solid was dissolved in 10 mL of benzene and added to Na(Hg) amalgam (2.1 mg of Na, 0.091 mmol). The reaction was allowed to vigorously stir at 25 °C for 2 h, which yielded a dark orange-brown solution. The solution was filtered through Celite and lyophilized. The resulting material was washed with pentane (3 x 5 mL) and extracted with diethyl ether (10 mL) to afford the title complex as a dark orange-brown solid (26.7 mg, 55% yield). Dark orange-brown crystals were grown from slow concentration of a solution of **8** (3 mL Et₂O with *ca.* 100 μ L pyridine) at -35 °C. ¹H and ³¹P NMR in C₆D₆ at 25 °C were silent. μ_{eff} (C₆D₆, Evans method, 298 K): 3.1 μ_{B} . μ_{eff} (toluene-*d*₈, Evans method, 223K): 3.3 μ_{B} . Anal. Calcd. for C₅₉H₆₁FeN₃P₃S₃SiV: C, 62.37; H, 5.41; N, 3.70. Found: C, 62.58; H, 5.45; N, 1.73 (Note: low nitrogen content may be due to lability of the coordinated N₂). UV-vis (THF, 298 K, nm {cm⁻¹ M⁻¹}): 446 {5100}, 613 {2700}, 726 {2600}. IR (solid, cm⁻¹): 2054 (N₂), 1898 (Fe-H).



PhPS₃V(THF).

A solution of VMes₃(THF) (30.1 mg, 0.063 mmol) in THF (5 mL) was added dropwise to a stirring solution of PhPS₃H₃ (36.8 mg, 0.063 mmol) in THF (5 mL) at 25 °C. The reaction was stirred for 2 h, and the volatiles were subsequently removed *in vacuo*. The resulting yellow-brown solid was washed with pentane (3 x 5 mL) and Et₂O (5 mL). The solids were dissolved in THF and filtered through Celite. The solution was concentrated to yield the product as a yellow-orange solid (35.0 mg, 79.0% yield). The product was recrystallized in a THF/pentane vapor diffusion cell at 25 °C, which yielded yellow-orange crystals suitable for XRD. ¹H and ³¹P NMR in C₆D₆ at 25 °C were silent. μ_{eff} (C₆D₆, Evans method, 298 K): 2.6 μ_{B} . Anal. Calcd. for C₄₀H₃₂OPS₃V: C, 67.97; H, 4.56; N, 0.00. Found: C, 68.04; H, 4.88; N, -0.08. UV-vis (THF, 298 K, nm {cm⁻¹ M⁻¹}): 462 {3800}.



PhPS₃V(py) (**11**).

Pyridine (*ca.* 100 μ L) was added to a solution of PhPS₃V(THF) (0.040 g, 0.056 mmol) in benzene (10 mL) and stirred at 25 °C overnight. The reaction mixture was lyophilized to yield the title compound as a yellow-orange solid. The product was recrystallized in a C₆H₆/pentane vapor diffusion cell at 25 °C, which yielded yellow-orange crystals suitable for XRD. ¹H and ³¹P NMR in C₆D₆ at 25 °C were silent. μ_{eff} (C₆D₆, Evans method, 298 K): 2.4 μ_{B} . Anal. Calcd. for C₄₁H₂₉NPS₃V: C, 68.99; H, 4.10; N, 1.96. Found: C, 68.89; H, 4.26; N, 1.94. UV-vis (THF, 298 K, nm {cm⁻¹ M⁻¹}): 464 {4800}.

Quantification of H₂ from the protonation of compound 8

A solution of [H(OEt₂)] [BAr^F] in Et₂O (2.4 mM, 1.0 mL) was added dropwise to a stirring solution of **8** in Et₂O (1.2 mM, 2.0 mL) in a septum-sealed round bottom, yielding a dark red solution. The solution was stirred at 25 °C for 10 min, then an aliquot of the headspace was sampled and analyzed for H₂ by GC. Yield of H₂: 91%

NMR spectra

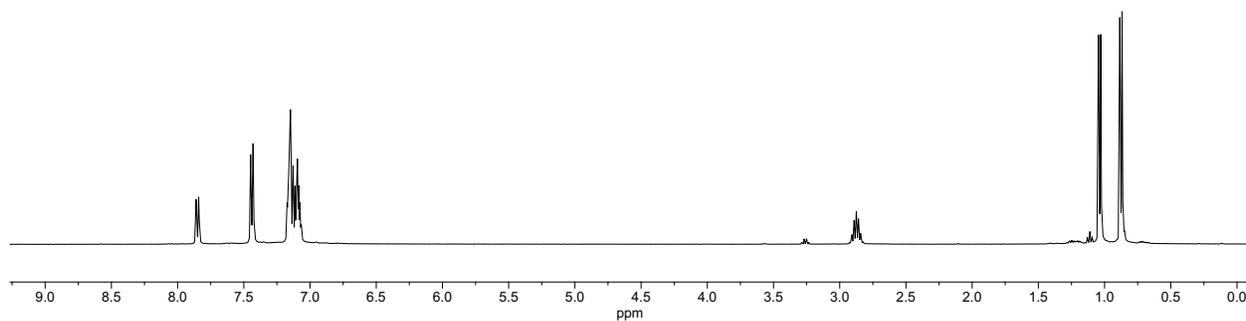


Figure S1. ¹H NMR spectrum of **3** in C₆D₆ (400 MHz)

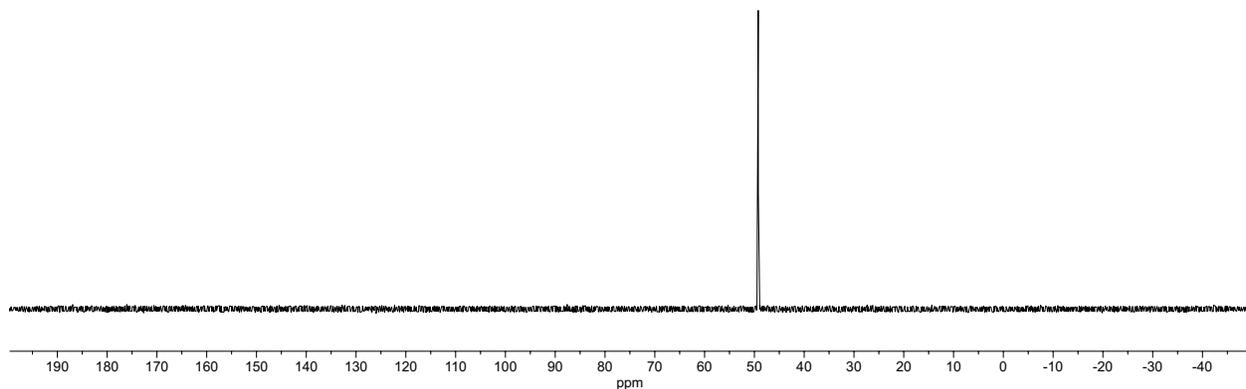


Figure S2. ³¹P NMR spectrum of **3** in C₆D₆ (162 MHz)

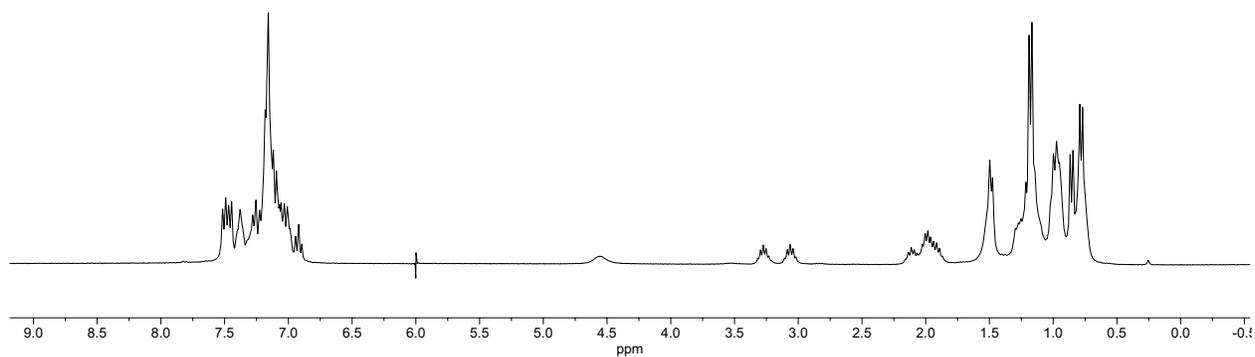


Figure S3. ^1H NMR spectrum of **4** in C_6D_6 (300 MHz)

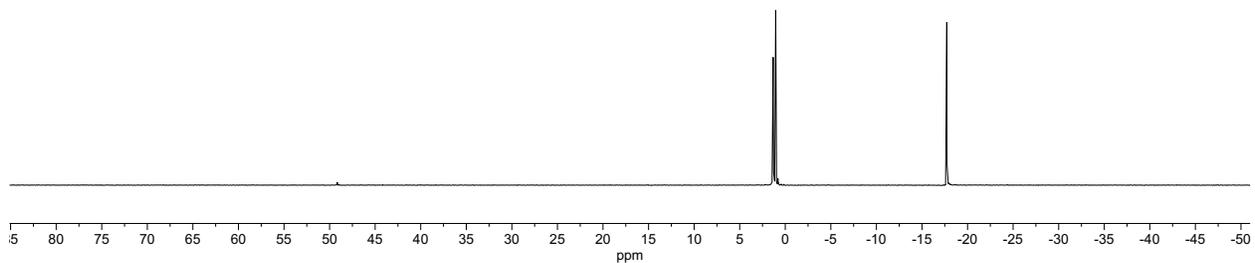


Figure S4. ^{31}P NMR spectrum of **4** in C_6D_6 (162 MHz)

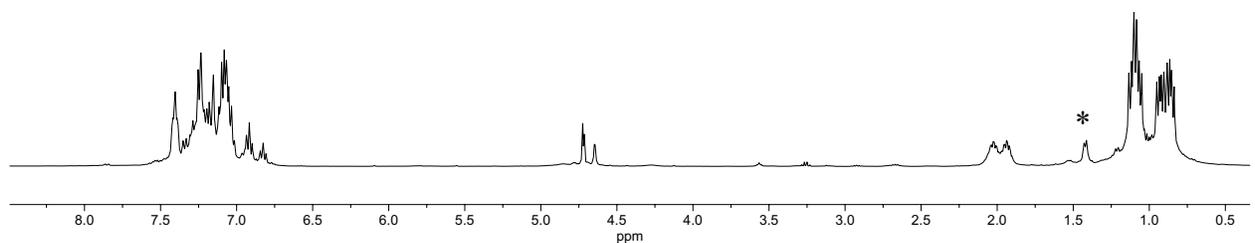


Figure S5 ^1H NMR spectrum of **6** in C_6D_6 (400 MHz). *impurity

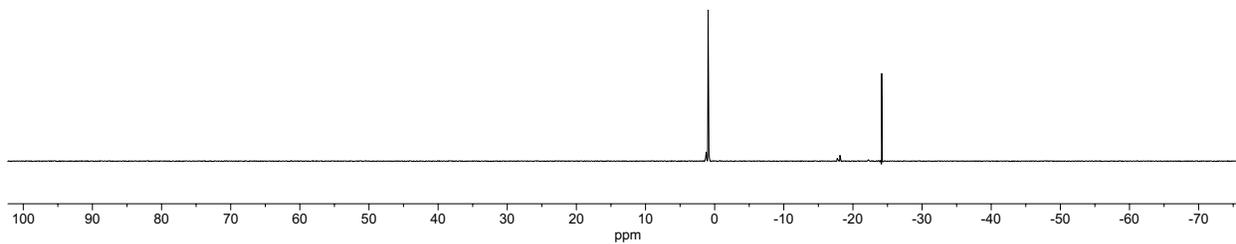


Figure S6. ^{31}P NMR spectrum of **6** in C_6D_6 (162 MHz)

IR spectra

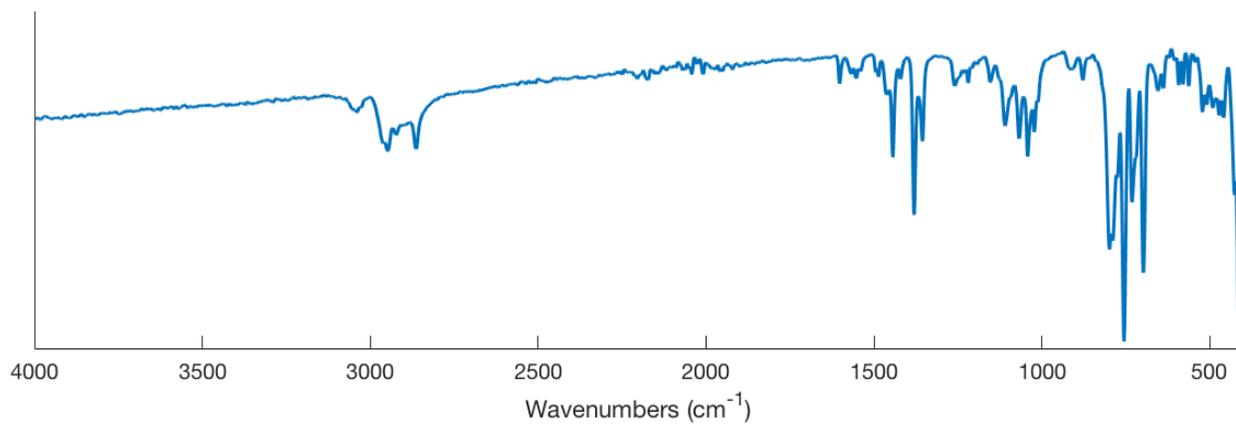


Figure S7. IR spectrum of **7** (solid sample)

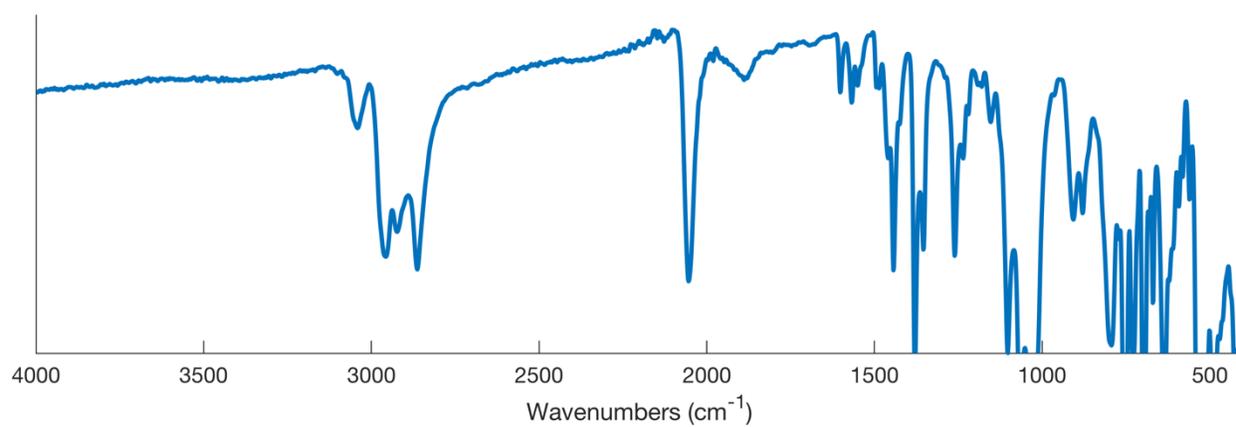


Figure S8. IR spectrum of **8** (solid sample)

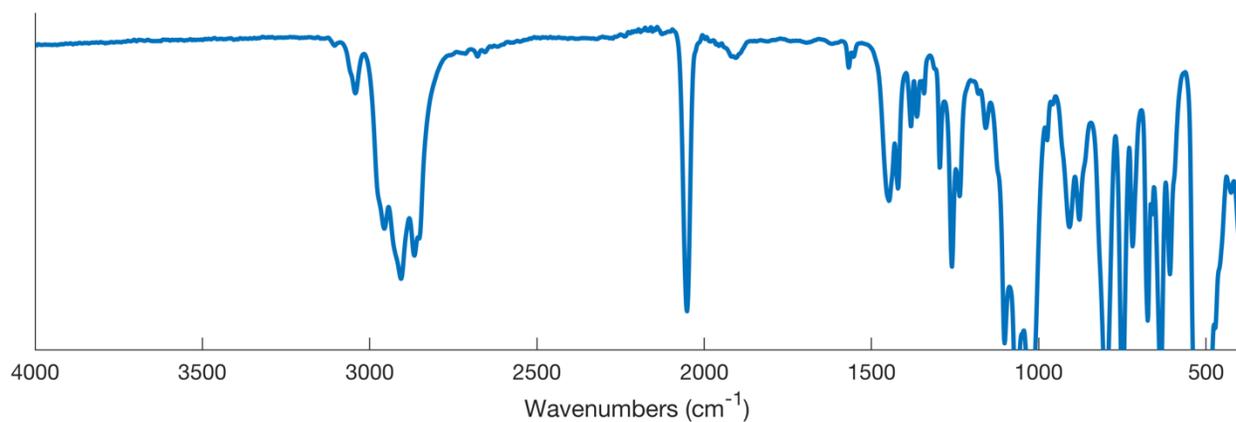


Figure S9. IR spectrum of **9** (solid sample)

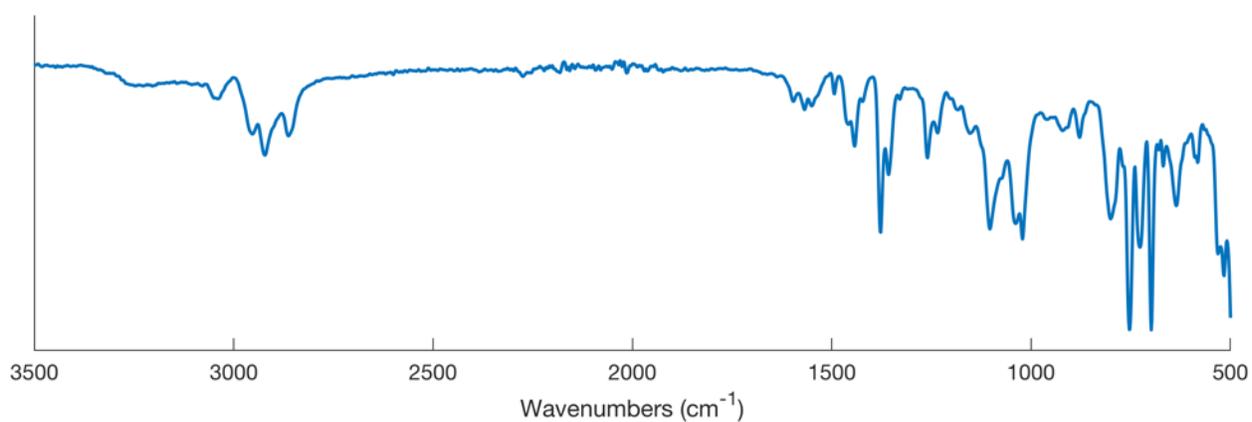


Figure S10. Representative IR spectrum of solids remaining after vacuum transfer of volatiles in a N₂H₄ disproportionation catalytic run with **8** (solid sample)

UV-Visible spectra

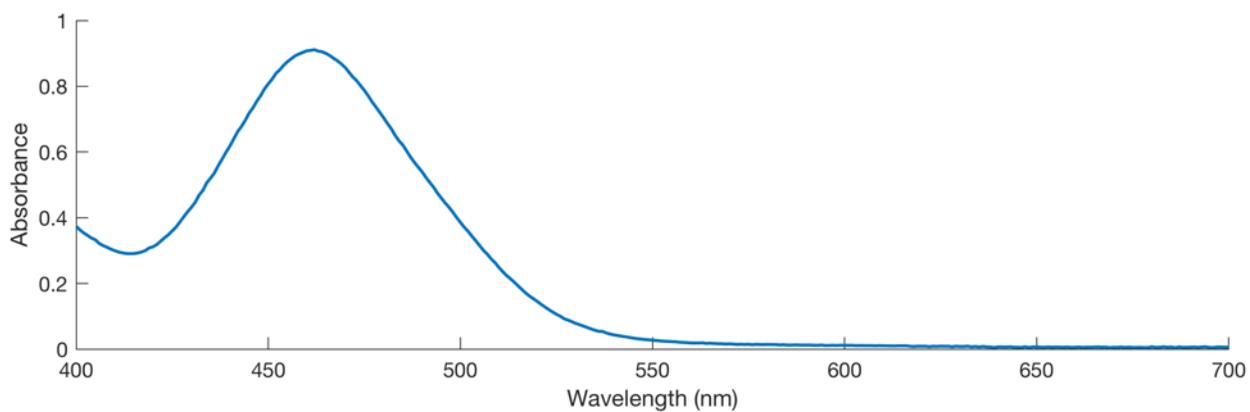


Figure S11. UV-Vis spectrum of **7** in THF

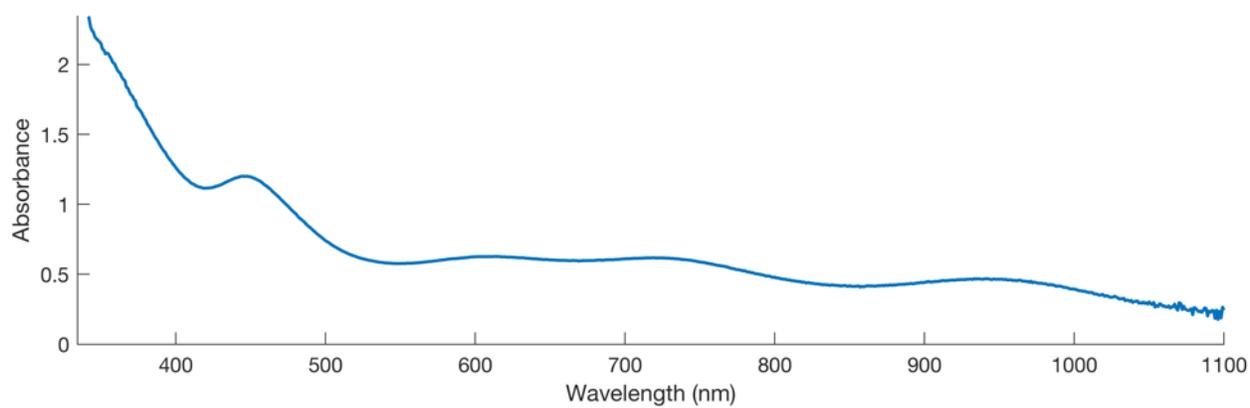


Figure S12. UV-Vis spectrum of **8** in THF

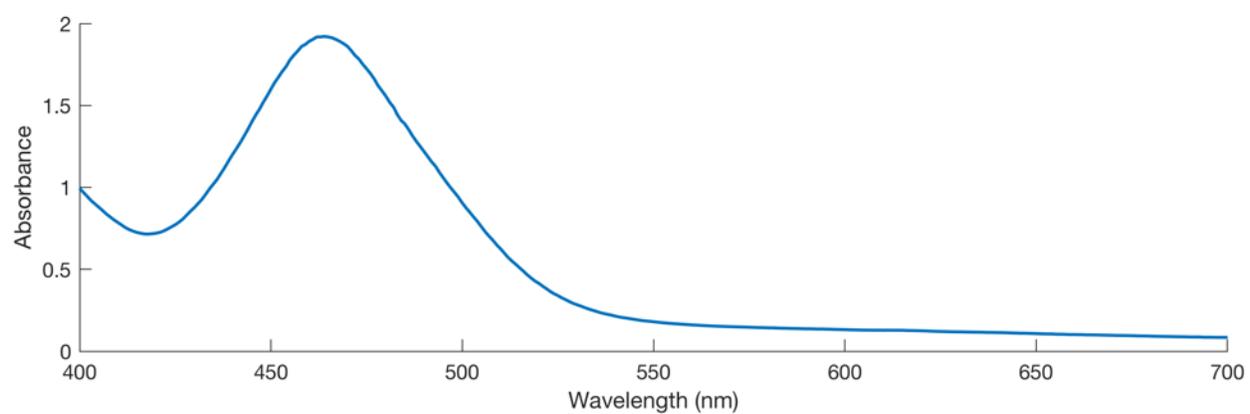


Figure S13. UV-Vis spectrum of **11** in THF

X-ray diffraction data

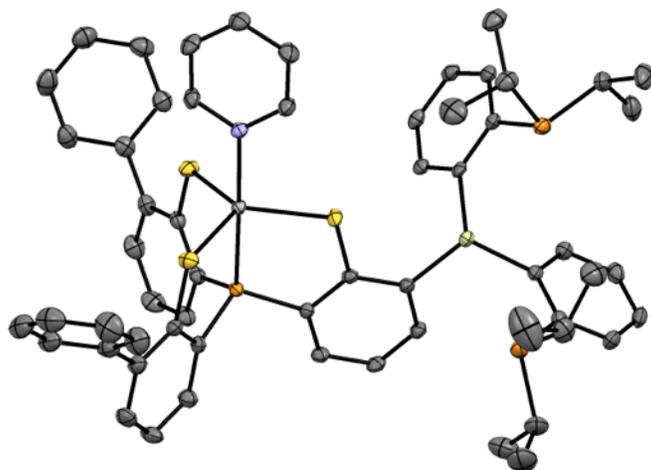


Figure S14. Structure of **7** with omission of hydrogen atoms and solvent molecules. Thermal ellipsoids at 50% probability.

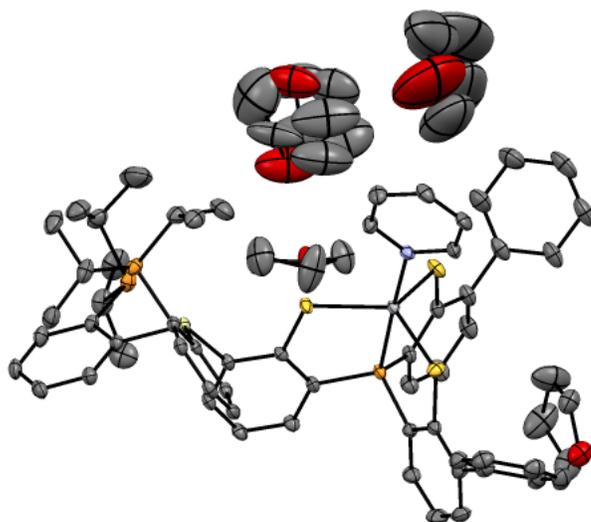


Figure S15. Full asymmetric unit of **7** including solvent and disordered components. Hydrogen atoms omitted; thermal ellipsoids at 50% probability.

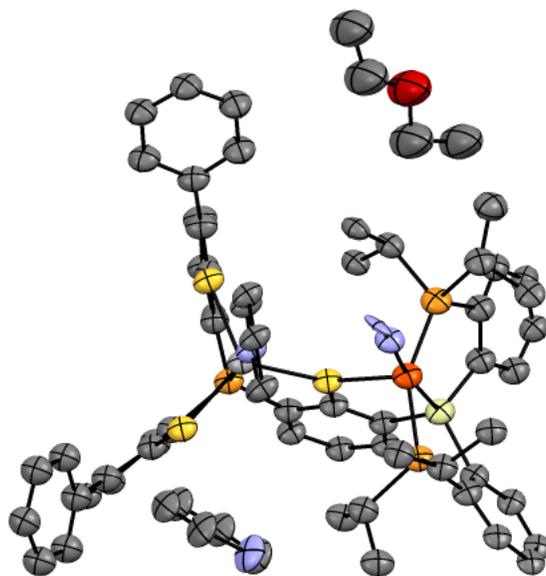


Figure S16. Full asymmetric unit of **8** including solvent. Hydrogen atoms omitted; thermal ellipsoids at 50% probability.

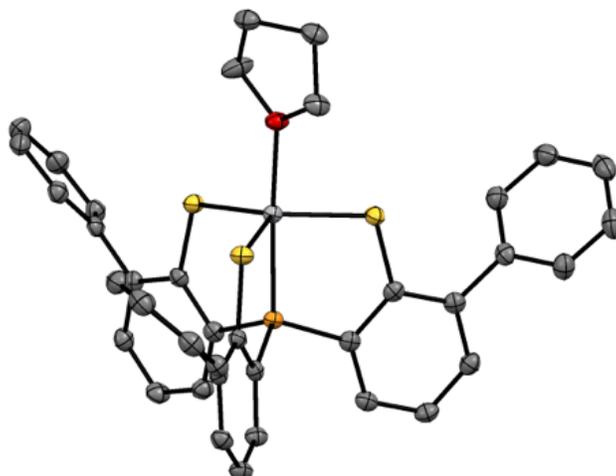


Figure S17. Structure of PhPS₃V(THF) with omission of hydrogen atoms and solvent molecules. Thermal ellipsoids at 50% probability.

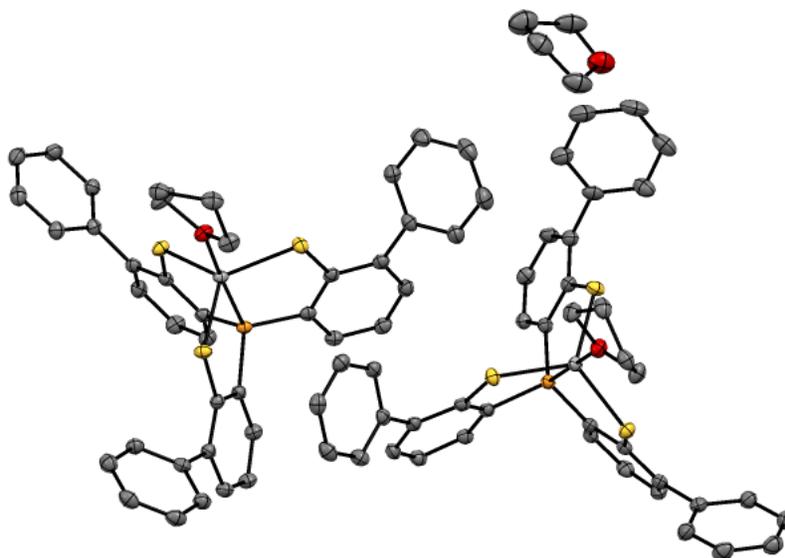


Figure S18. Full asymmetric unit of PhPS₃V(THF) including solvent. Hydrogen atoms omitted; thermal ellipsoids at 50% probability.

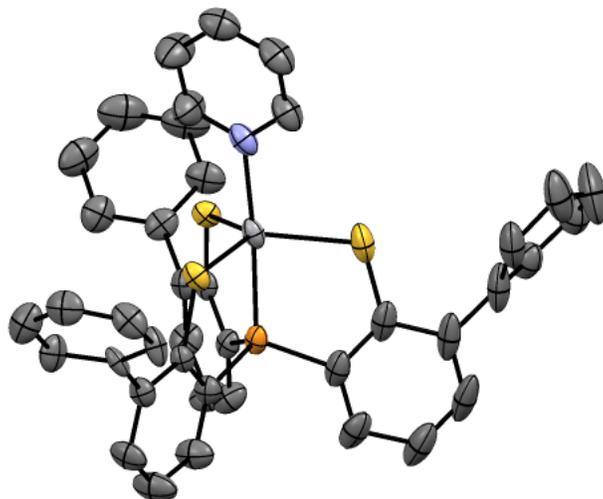


Figure S19. Structure of **11** with omission of disordered components and hydrogen atoms. Thermal ellipsoids at 50% probability.

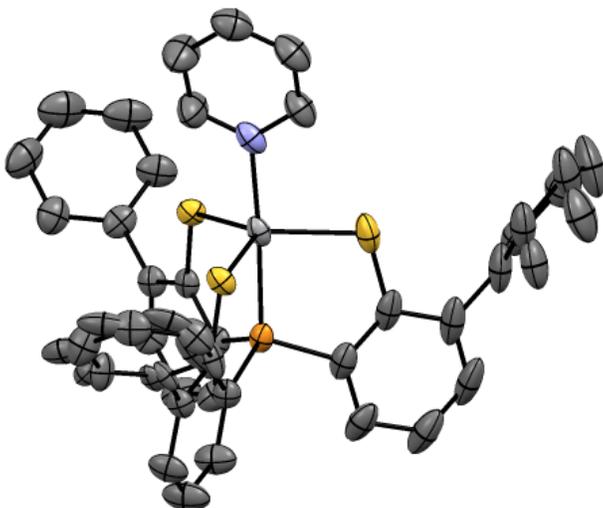


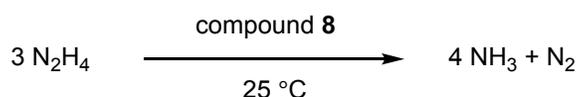
Figure S20. Full asymmetric unit of **11** including solvent and disordered components. Hydrogen atoms omitted; thermal ellipsoids at 50% probability.

General procedure for catalytic hydrazine disproportionation

Caution: All catalytic runs were performed on small scales to avoid a significant buildup of pressure from gas generated during catalysis

A solution of catalyst (1 mM catalyst, 2.5 mL solvent, unless otherwise noted) is transferred into a Schlenk tube and frozen. Neat N₂H₄ is added in one portion to the vessel, which is then immediately sealed and allowed to stir at 25 °C. After the appropriate amount of time elapsed, the volatiles are vacuum transferred into a Schlenk tube containing HCl (2M in Et₂O, 5 mL), which is analyzed for ammonia content (in the form of [NH₄][Cl]) by the indophenol method.⁸ (Note: Upon thawing of the evacuated frozen vessels, care is taken to allow the vacuum transfer to proceed at 25 °C. Hydrazine is a thermally-sensitive compound, and heating a vessel containing solely N₂H₄ in THF during the work-up results in positive ammonia detection)

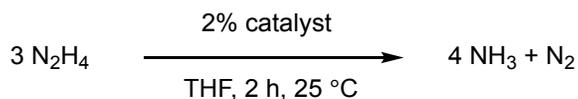
Single runs from Table 1



Entry	Solvent	Time	N ₂ H ₄ (equiv./ 8)	NH ₃ (equiv./ 8)
<i>a</i>	THF	2 h	50	4.0, 5.5
<i>b</i>	Et ₂ O	2 h	50	9.7, 11
<i>c</i>	Et ₂ O	12 h	50	41, 50
<i>d</i>	Et ₂ O	24 h	50	57, 62
<i>e</i>	Et ₂ O	24 h	100	80, 98
<i>f</i>	Et ₂ O	48 h	100	102, 124
<i>g</i> ¹	Et ₂ O	17 d	1440	1014, 1132
<i>S1</i> [*]	Et ₂ O	12 h	50	46
<i>S2</i> [‡]	Et ₂ O	12 h	50	42
<i>S3</i> [#]	Et ₂ O	12 h	50	39

Runs performed at catalyst concentrations of 1 mM in 2.5 mL solvent. ¹Run performed with at 0.1 mM catalyst concentration in 2.5 mL solvent. ^{*}Performed in the presence of elemental Hg. [‡]Performed in the presence of 0.3 equivalents of PPh₃ per equivalent of **8** (1 mM in 2 mL Et₂O). [#] Performed in the presence of 10 equivalents of pyridine per equivalent of **8** (1 mM in 2 mL Et₂O).

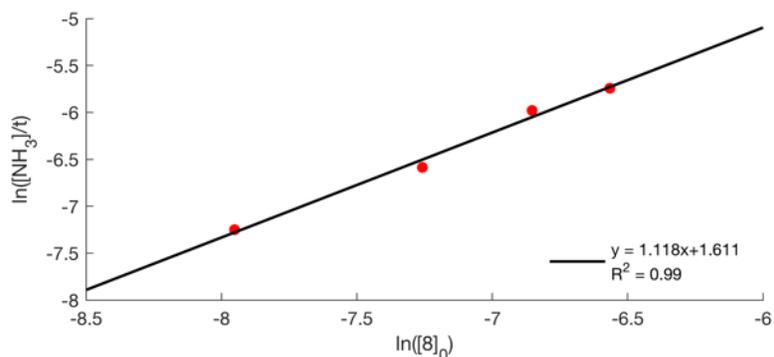
Single runs from Table 2



Entry	Catalyst	NH ₃ (equiv./catalyst)
<i>h</i>	9	0.26, 0.51
<i>i</i>	11	0.27, 0.13
<i>j</i> [*]	9 + 11	0.88, 1.19

Runs performed at catalyst concentrations of 1 mM in 2.5 mL solvent. ^{*} [**9**] = [**11**] = 1 mM

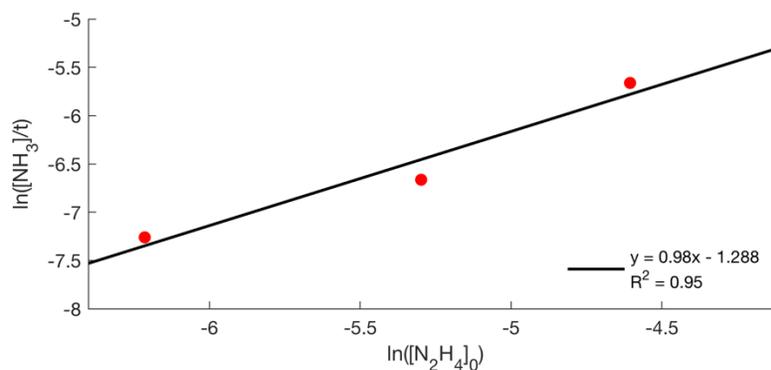
Reaction order of compound **8** – method of initial rates



8 (mg)	NH ₃ (μmol)	ln([8] ₀) ¹	ln([NH ₃]/t) ¹
1	3.5, 3.6	-8.0	-7.3
2	5.7, 8.1	-7.3	-6.6
3	12.2, 13.1	-6.9	-6.0
4	16.0, 16.1	-6.6	-5.7

Runs performed with 0.13 mmol N₂H₄ in 2.5 mL THF. Yield of NH₃ determined after 2 h of reaction time. ¹concentrations in M, time in h

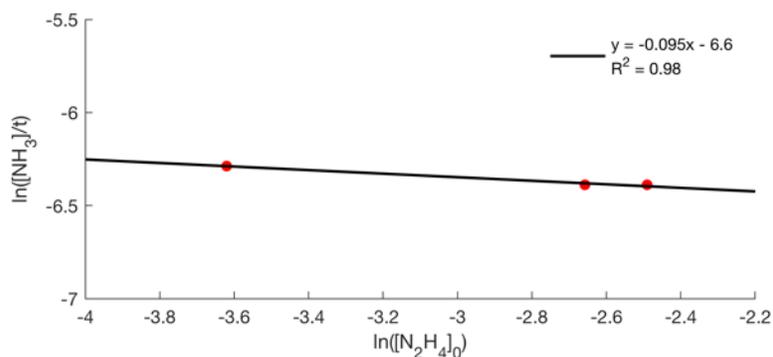
Reaction order of substrate – method of initial rates



[N ₂ H ₄]	NH ₃ (μmol)	ln([N ₂ H ₄] ₀) ¹	ln([NH ₃]/t) ¹
0.002	0.23, 0.24	-6.2	-7.3
0.005	0.39, 0.46	-5.3	-6.7
0.010	0.97, 1.4	-4.6	-5.7

Runs performed in 2 mL THF with 1 mM catalyst (a THF solution of substrate is added at 25 °C to a Schlenk tube containing a stirring THF solution of catalyst and immediately sealed). Yield of NH₃ determined after 10 min of reaction time. ¹concentrations in M, time in h

Reaction order of substrate – method of initial rates (saturation kinetics)



$[N_2H_4]$	NH_3 (μmol)	$\ln([N_2H_4]_0)^1$	$\ln([NH_3]/t)^1$
0.025	9.0, 9.6	-3.6	-6.3
0.070	7.9, 8.8	-2.7	-6.4
0.083	8.3, 8.5	-2.5	-6.4

Runs performed in 2.5 mL THF with 1 mM catalyst. Yield of NH_3 determined after 2 h of reaction time.

¹concentrations in M, time in h

Toepler pump quantification of gaseous products

Neat N_2H_4 (0.1 mmol) was added in one portion at 25 °C to a stirring Et_2O solution of **8** (2.4 mg, 0.002 mmol) in a 100 mL Kontes Schlenk tube equipped with a ground-glass side arm. The tube was degassed via three freeze-pump-thaw cycles and sealed. The reaction mixture stirred at 25 °C under static vacuum. The volatiles in the tube were passed through a cold trap (77 K), and the non-condensed gaseous products were quantified with a Toepler pump. The frozen volatiles condensed in the traps were vacuum transferred into a Schlenk tube containing an ethereal solution of HCl (5 mL, 2 M) and concentrated to dryness. The resulting material was quantified for ammonia (in the form of $[NH_4][Cl]$) via the indophenol method.⁸ Omitting the equivalent of N_2 that is introduced from **8**, 4.0 molecules of NH_3 per gas molecule was generated.

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