Supporting Information

Catalytic Reactivity of a Zirconium(IV) Redox-Active Ligand Complex with 1,2-Diphenylhydrazine

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Experimental Procedures

General Experimental Considerations. The complexes described below are extremely air- and moisture sensitive. All manipulations were carried out under an atmosphere of argon or nitrogen gas using standard Schlenk, vacuum-line, and glovebox techniques. High-purity solvents were first sparged with argon and then purified dried by passage through activated alumina and Q5 columns to remove water and oxygen, respectively. The metal salt $ZrCl_4$ was purchased from Alfa-Aesar and used as received. $Zr(NMePh)_4$ was prepared according to literature procedures[1]. All complexes were characterized by ^1H and ^{13}C NMR spectroscopy, IR spectroscopy, and elemental analysis. NMR spectra were collected on Bruker Avance 500 or 600 MHz spectrometers in either benzene-d_6 or THF-d_8 solvents that were degassed by several freeze-pump-thaw cycles, dried over sodium benzophenone ketyl radical, and vacuum-distilled before use. ^1H and ^{13}C NMR spectra were referenced to TMS using the residual ^1H and natural abundance ^{13}C impurities, respectively, of the solvent. All chemical shifts are reported using the standard δ notation in parts-per-million. Infrared spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer as KBr pellets. Elemental analyses were provided by Desert Analytics and Schwarzkopf Microanalytical Laboratory, Inc.

***N*,*N*'-bis(3,5-di-*tert*-butyl-2-hydroxyphenyl)-1,2-phenylenediamine $H_4[N_2O_2^{red}]$.** The same procedure as previously reported was used with an additional purification step[2]. After collection of the yellow product the solid is dissolved in ether (30 mL) and run through a silica plug (150 mL medium frit 2/3 full) of 100% ether. A blue solution is collected in about 250 mL of ether which is concentrated to dryness. The blue solid is stirred in pentane for 1 hour or until a fine white powder is observed in a blue solution. The white solid is collected, washed with pentane and dried under vacuum. Overall yield 40-44%.

$[N_2O_2^{red}]Zr(THF)_3$ (1). In a 20 ml scintillation vial, a 10 ml ether solution containing 1.93 mmol of $[N_2O_2^{red}]Li_4$ (1 equiv, prepared in situ from 1.00 g of $H_4[N_2O_2^{red}]$ and 2.86 ml of 2.71 M *n*-butyllithium) was frozen in a liquid-nitrogen cold well. Immediately upon thawing, the $apLi_2$ mixture was added to a stirring suspension of 0.46 g of $ZrCl_4THF_2$ (1.93 mmol, 1 equiv) in cold pentane/THF (3 ml) The reaction mixture was allowed to warm to 26 ºC and was stirred overnight affording an orange solution with a white precipitate. Filtration and solvent removal gave an orange residue that was triturated with pentane (3 x 10 mL), and then cooled to –35 °C. Collection of the yellow crystals gave 0.26 mg of **1** (55% yield). X-ray quality crystals of **5** were obtained by chilling saturated ether solutions of the complex to –35 °C. Anal. Calcd. for $C_{46}H_{68}N_2O_5Zr$: C, 67.36; H, 8.36; N, 3.42. Found: C, 67.42: H, 8.39; N, 3.20. ^{1}H NMR (600 MHz, C_6D_6) δ/ppm: 0.87 (*s*, 12H, THF), 1.50 (*s*, 18H, C(CH_3)$_3$), 1.67(*s*, 18H, C(CH_3)$_3$), 3.81 (*s*, 12H, THF), 6.98 (*q*, 2H, aryl-*H*, $^3J_{HH}$ = 4.2 Hz), 7.08 (*d*, 2H, aryl-*H*, $^3J_{HH}$ = 2.4 Hz) , 7.83 (*q*, 2H, aryl-*H*, $^3J_{HH}$ = 2.4 Hz), 7.93 (*d*, 2H, aryl-*H*, $^3J_{HH}$ = 4.2 Hz). ^{13}C NMR (125.8 MHz, C_6D_6) δ/ppm: 30.4 (C(*C*H$_3$)$_3$), 32.5 (C(*C*H$_3$)$_3$), 34.9 (C(*C*H$_3$)$_3$), 109.4 (aryl-*C*), 109.7 (aryl-*C*), 113.3 (aryl-*C*), 118.8 (aryl-*C*), 132.2 (aryl-*C*), 139.2 (aryl-*C*), 145.5 (aryl-*C*), 147.2 (aryl-*C*), 156.3 (aryl-*C*).

$[N_2O_2^{ox}]ZrCl_2(THF)$ (2). Complex **1** (0.40 g, 0.49 mmol) was dissolved in 8 mL of ether and the solution was frozen in a coldwell. Upon melting, freshly prepared $PhICl_2$ (0.134 g, 0.49 mmol) was added as a solid. The solution was shaken until all the $PhICl_2$ dissolved (2-3 min). The solution changed from yellow to dark green. A dark green precipitate began forming and the solution was placed at -35 °C overnight. The solution was filtered and a dark green microcrystalline solid was collected (153 mg, 42% yield). Anal. Calcd. for $C_{38}H_{52}N_2O_3Cl_2Zr$: C, 61.10; H, 7.02; N, 3.75. Found: C, 60.87; H, 7.56; N, 3.68. ^{1}H NMR (600 MHz, C_6D_6) δ/ppm:

1.32 (*s*, 18H, C(CH_3)$_3$), 1.70 (*s*, 18H, C(CH_3)$_3$), 6.35 (*q*, 2H, aryl-*H*, $^3J_{HH}$ = 3.6 Hz), 7.52 (*q*, 2H, aryl-*H*, $^3J_{HH}$ = 3.6 Hz) , 7.63 (*s*, 2H, aryl-*H*), 7.68 (*s*, 2H, aryl-*H*). ^{13}C NMR (125.8 MHz, d8-THF) δ/ppm: 27.3 (C(*C*H$_3$)$_3$), 31.0 (C(*C*H$_3$)$_3$), 32.5 (C(*C*H$_3$)$_3$), 117.7 (aryl-*C*), 124.9 (aryl-*C*), 129.5 (aryl-*C*), 129.9 (aryl-*C*), 134.5 (aryl-*C*), 141.0 (aryl-*C*), 143.1 (aryl-*C*), 145.9 (aryl-*C*), 153.8 (aryl-*C*). UV-Vis λ_{max}= 945 nm

Disproportionation Reactions of 1 with 1,2-diphenylhydrzine. In a typical experiment, complex **1** (20 mg, 1 eqiv) and 1,2-diphenylhydrazine (45 mg, 10 eqiv.) were weighed into a NMR tube and C_6D_6 was added. Both reagents dissolved and the solution turned green within a minute (UV-Vis λ_{max}= 739 nm). The reaction was monitored by NMR for conversion to azobenzene. Once the reaction was complete, GC/MS confirmed the formation of both aniline and azobenzene in a two to one molar ratio.

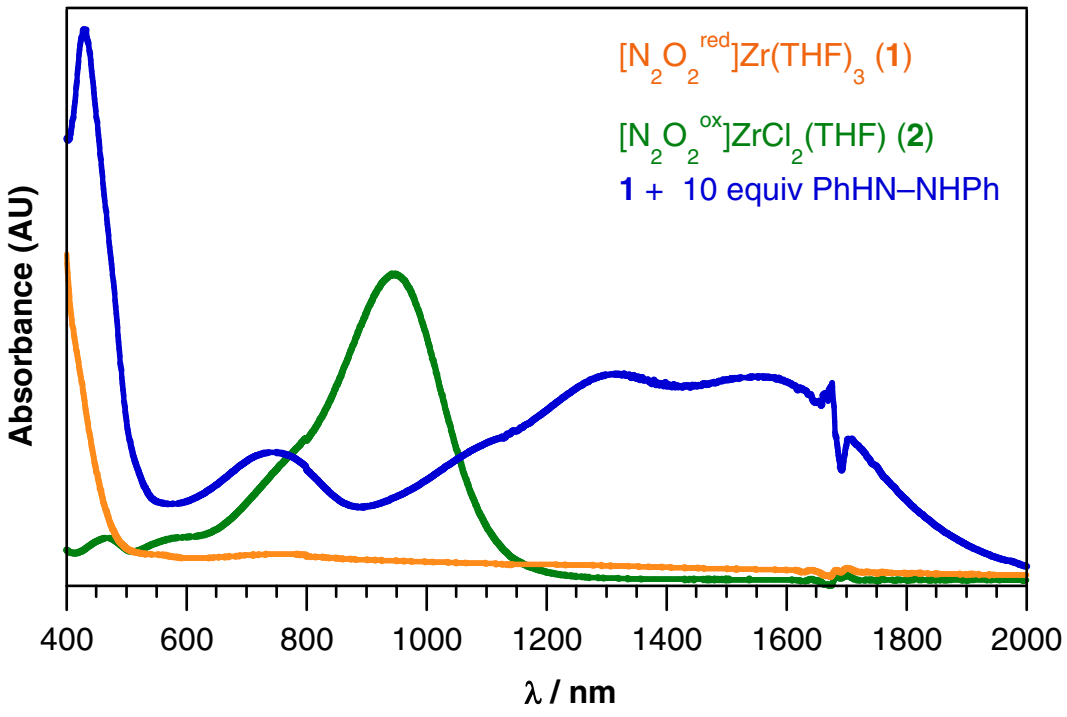


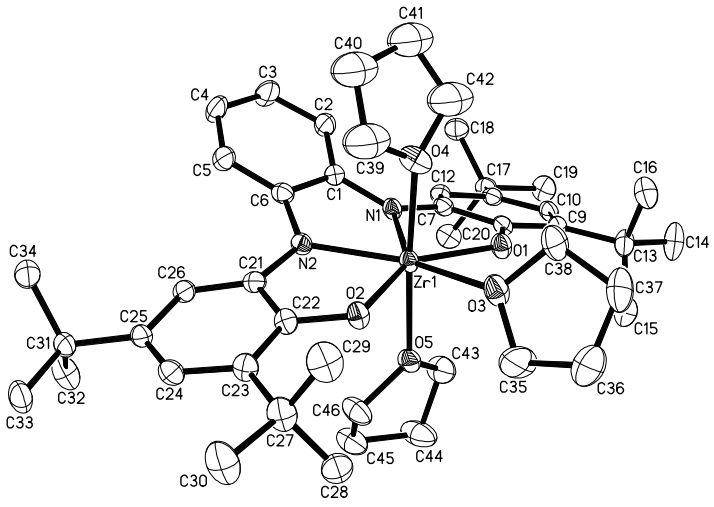
Figure S1. Representative UV-vis spectra of **1**, **2** and an *in situ* reaction between **1** and 1,2-diphenylhydrazine.

X-ray Crystallographic Details

$[N_2O_2^{red}]Zr(THF)_3$ (1). A yellow crystal of approximate dimensions 0.06 x 0.27 x 0.40 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[3] program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[4] and SADABS[5] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[6] program. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/c$ that was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[7] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

Least-squares analysis yielded wR2 = 0.2313 and Goof = 1.095 for 482 variables refined against 7929 data (0.85Å), R1 = 0.0713 for those 6431 data with $I > 2.0\sigma(I)$. There were several large residual peaks observed in the final difference-Fourier map. These peaks were probably due to solvent, which could not be identified.



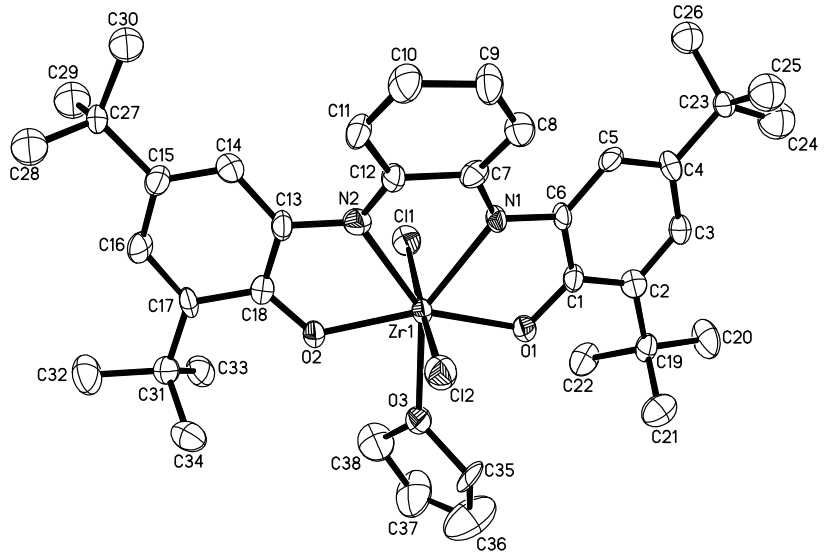
$[N_2O_2^{ox}]ZrCl_2(THF)$ (2). A blue crystal of approximate dimensions 0.07 x 0.15 x 0.31 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART[3] program package was used to determine the unit-cell parameters and for data collection (45 sec/frame scan time for a hemisphere of diffraction data). The raw frame data was processed using SAINT[4] and SADABS[5] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[6] program. The diffraction symmetry was *mmm* and the systematic absences were consistent with the orthorhombic space groups $Pna2_1$ and *Pnma*. It was later determined that space group $Pna2_1$ was the best choice for the final least-squares refinement.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[7] for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model. Carbon atoms C(24), C(25), C(26), C(28), C(29) and C(30) were disordered and included using multiple components, partial site-occupancy-factors and isotropic thermal parameters.

Least-squares analysis yielded wR2 = 0.1623 and Goof = 1.039 for 450 variables refined against 6247 data (0.85Å), R1 = 0.0564 for those 4382 data with $I > 2.0\sigma(I)$. The structure was refined as a racemic twin (BASF = 0.44(8)).

The structure could also be solved in the centrosymmetric space group *Pnma*, however, this solution proved less satisfactory. The molecule is located on a mirror plane resulting in disorder of the THF ligand and the THF solvent molecule. In general, thermal parameters on several carbon atoms were higher than expected and became non-positive-definite when refined anisotropically. R1 and wR2 are also significantly higher ($wR2 \approx 40\%$) in space group *Pnma*.

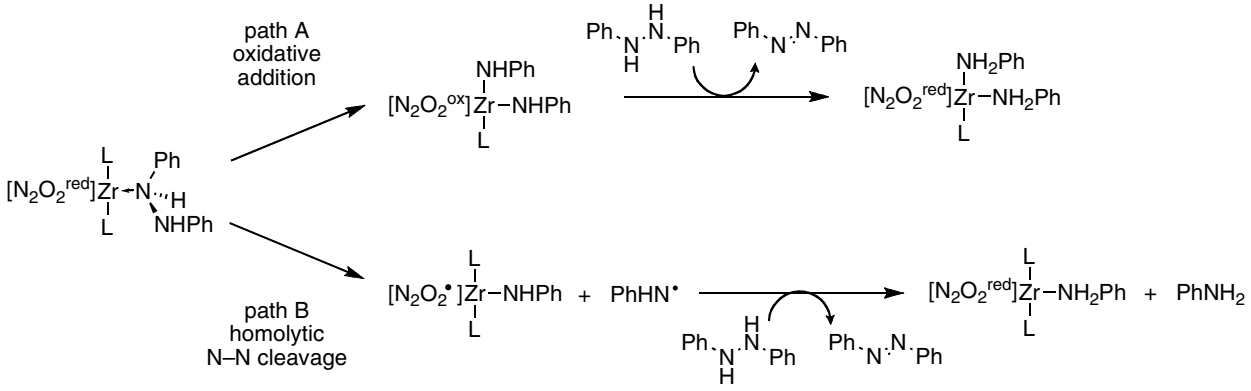
While space group *Pnma* should be considered as an alternative, it was decided that the structure was better described using the non-centrosymmetric space group $Pna2_1$.



Further Discussion

Alternative Zirconium Oxidants. We have also considered the possibility of homolytic N–N bond cleavage pathways that might lead to the observed disproportionation of 1,2-diphenylhydrazine to aniline and azobenzene. Two related mechanisms are shown in Scheme S1. In path A, N–N oxidative addition to **1a** would afford a putative bis(amide) complex, $[N_2O_2^{ox}]Zr(NHPh)_2L$. This species could be the active oxidant with each amide ligand abstracting a hydrogen atom from another molecule of 1,2-diphenylhydrazine. In path B, homolytic cleavage of the N–N bond of 1,2-diphenylhydrazine would release a PhHN• radical and a putative monoamide radical complex, $[N_2O_2•]Zr(NHPh)L_2$ ($[N_2O_2•]^{3-}$ is the one-electron oxidized form of the redox active ligand). These two species could independently abstract hydrogen atoms from 1,2-diphenylhydrazine.

Scheme S1



We discount both mechanisms shown in Scheme S1 based on the lack of reaction observed for mixtures of **1a** with tetramethylhydrazine and 1-dimethylaminopyridine. According to path A of Scheme S1, tetramethylhydrazine could oxidatively add to **1a** to form $[N_2O_2^{ox}]Zr(NMe_2)_2L$. Alternatively, if tetramethyhydrazine reacted according to path B, it would generate $Me_2N•$ and $[N_2O_2•]Zr(NMe_2)L_2$. When 1a is mixed with tetramethylhydrazine, no reactivity is observed, even after 24 hours, and both 1a and tetramethylhydrazine can be recovered from the reaction.

The same result was obtained for 1-dimethylaminopyridine. These results suggest that homolytic N–N cleavage (with or without oxidative addition) is not the operating pathway in the catalytic decomposition of 1,2-diphenylhydrazine by **1a**.

References

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