1. General Procedures and Instrumentation

All experiments were carried out in a dry nitrogen atmosphere using an MBraun glovebox and/or standard Schlenk techniques. 4A molecular sieves were activated in vacuo at 180 °C for 24 h. Dry benzene was purchased from Aldrich and was stored over activated 4A molecular sieves. Pentane was first washed with conc. HNO₃ / H₂SO₄ to remove olefins, stored over CaCl₂ and then distilled before use from sodium/benzophenone. Dichloromethane were purchased anhydrous and stored over 4 A molecular sieves. All solvents were tested before use with a drop of sodium benzophenone ketyl in THF solution. All deuterated solvents were sparged with nitrogen, dried over activated 4 A molecular sieves and stored under nitrogen. Celite was dried overnight at 200 °C under vacuum.

¹H and ¹³C{¹H} spectra were recorded on a Varian 400 MHz Spectrometer (400 or 100.54 MHz). All NMR spectra were recorded at room temperature unless otherwise noted and were indirectly referenced to residual solvent signals. EPR spectra were collected on a JEOL FA-200 spectrometer. ESI-MS analyses was done using Varian 500 Ion Trap LC/MS using positive mode.

All reagents were obtained commercially unless otherwise noted. iPr₂TpZn(NO₂) and iPr₂TpZn(NO₃) were synthesized according to a literature procedure.¹

2. Synthesis and Characterization of $^{i}$Pr$_2$TpZn-SAr (2)

To solution of $^{i}$Pr$_2$TpZn(NO$_2$) (0.200 g, 0.35 mmol) in dichloromethane (4 mL), was added as solution of $p$-toluenethiol (0.0876 g, 0.71 mmol) in dichloromethane (2 mL). The resulting solution was stirred for 1 h and then all volatiles were removed in vacuo. The white solid was washed with methanol (2 × 2 mL) and recrystallized from pentane to provide 0.160 g of the product (70% yield). $^1$H NMR (400 MHz, 298 K, CDCl$_3$): $\delta$ 7.36 (d, 2H, Zn-SAr), 6.88 (d, 2H, Zn-SAr), 5.81 (s, 3H, pz), 3.44 (sept, 3, CHMe$_2$), 3.07 (sept, 3, CHMe$_2$), 2.23 (s, 3, $p$-Me), 1.25 (d, 18, CHMe$_2$), 1.09 (d, 18, CHMe$_2$); $^{13}$C{$^1$H} (100 MHz, 298 K, CDCl$_3$): $\delta$ 160.4, 156.1, 137.0, 132.5, 132.0, 128.9, 97.1, 27.1, 26.1, 23.5, 23.4, 20.7. ESI-MS Calculated: 653.344 (M$^+$ + 1) Found: 653.430 (M$^+$ + 1).

![Figure S1. $^1$H NMR spectrum (400 MHz, 298 K, CDCl$_3$) of $^{i}$Pr$_2$TpZn-SAr (2).](image)

![Figure S2. $^{13}$C{$^1$H} NMR spectrum (100 MHz, 298 K, CDCl$_3$) of $^{i}$Pr$_2$TpZn-SAr (2).](image)
3. Reaction of $^{iPr}_2$TpZn(NO$_2$) with H-SAr

To a solution of $^{iPr}_2$TpZn(NO$_2$) (50.0 mg, 0.09 mmol) in CDCl$_3$ (1.0 mL), was added 2.2 equiv. p-toluenethiol (H-SAr; 25 mg, 0.20 mmol). A CDCl$_3$ solution (1.0 mL) containing 1,2,4,5-tetrachlorobenzene (9.4 mg, 0.044 mmol) was added as standard. A green color immediately formed.

After 10 min, analysis by $^1$H NMR spectroscopy showed signals for $^{iPr}_2$TpZn-SAr (0.79 eq, 79% yield, $\delta$ 2.23 ppm for $p$-Me group), ArSNO (0.45 eq, 45% yield, $\delta$ 2.47 ppm), ArS-SAr (0.18 eq, 36% yield, $\delta$ 2.31 ppm for $p$-Me group) and unreacted thiol (0.83 eq, $\delta$ 2.29 ppm for $p$-Me group).

After 24 h, analysis by $^1$H NMR spectroscopy showed signals for $^{iPr}_2$TpZn-SAr (0.88 eq, 88% yield, $\delta$ 2.23 ppm for $p$-Me group), ArS-SAr (0.43 eq, 86% yield, $\delta$ 2.31 ppm for $p$-Me group) and unreacted thiol (0.45 eq, $\delta$ 2.29 ppm for $p$-Me group). The amount of disulfide (ArS-SAr) corresponds to a total conversion of 86% H-SAr to ArSNO which is rather thermally sensitive, decomposing to the disulfide ArS-SAr.

Using an identical procedure, no reaction of H-SAr with $^{iPr}_2$TpZn(NO$_3$) was observed.

**Figure S3.** $^1$H NMR spectrum (400 MHz, 298 K, CDCl$_3$) of the reaction of $^{iPr}_2$TpZn(NO$_2$) (1) with H-SAr after 24 h at RT. The inset shows the $p$-Me resonances for ArSNO, ArS-SAr, ArS-H, and $^{iPr}_2$TpZn-SAr 10 min after the addition of H-SAr to 1.
4. Reaction of \(^{iPr_2}TpZn(NO_2)\) with H-SCH\(_2\)Ph

To a solution of \(^{iPr_2}TpZn(NO_2)\) (50.0 mg, 0.09 mmol,) in CDCl\(_3\) (1.0 mL) was added H-SCH\(_2\)Ph (27 mg, 0.22 mmol, 2.38 eq wrt to \(^{iPr_2}TpZn(NO_2)\)). A CDCl\(_3\) (1.0 mL) solution containing 1,2,4,5-tetrachlorobenzene (9.4 mg, 0.044 mmol) was also added as standard. A pink color appeared after 1 h indicating formation of the 1° alkyl S-nitrosothiol PhCH\(_2\)SNO. After 24 h, analysis by \(^1\)H NMR spectroscopy showed peaks for \(^{iPr_2}TpZn-SCH\(_2\)Ph\) (0.86 eq, 86% yield, \(\delta\) 4.03 ppm), PhCH\(_2\)SNO (0.50 eq, 50 % yield, \(\delta\) 4.68 ppm), PhCH\(_2\)SSCH\(_2\)Ph (0.12 eq, 24 % yield, \(\delta\) 3.60 ppm), unreacted thiol (0.72 eq, \(\delta\) 3.74 ppm) and water (0.64 eq. 64 % yield, \(\delta\) 1.56 ppm).

Using an identical procedure, no reaction of the bulky H-SCPh\(_3\) with \(^{iPr_2}TpZn(NO_2)\) was observed.

Using an identical procedure, no reaction of H-SCH\(_2\)Ph with \(^{iPr_2}TpZn(NO_3)\) was observed.

**Figure S4.** \(^1\)H NMR spectrum (400 MHz, 298 K, CDCl\(_3\)) of the reaction of \(^{iPr_2}TpZn(NO_2)\) (I) with H-SCH\(_2\)Ph after 24 h at RT.
5. Synthesis and Characterization of $^{\text{1Pr}}_{2}$TbZn(OAc)(4)

In the absence of air-free conditions, solid Zn(OAc)$_2$·H$_2$O (0.100 g, 0.455 mmol) was added to a solution of $^{\text{1Pr}}_{2}$TpK (0.100 g, 0.20 mmol) in methanol (10 mL). The resulting solution was stirred for 24 h and the solvent was removed in vacuo. The white solid was washed with methanol (2 × 20 mL) and redissolved in dichloromethane, filtered, and recrystallized by slow evaporation to provide 0.087 g of the product (73% yield). $^1$H NMR (400 MHz, 298 K, CDCl$_3$) $\delta$ 5.81 (s, 3H, pz), 3.43 (sept, 3, CHMe$_2$), 3.21 (sept, 3, CHMe$_2$), 2.19 (s, 3, CH$_2$COO), 1.24 (d, 18, CHMe$_2$), 1.21 (d, 18, CHMe$_2$); $^{13}$C $^1$H (100 MHz, 298 K, CDCl$_3$): $\delta$ 155.9, 155.8, 97.3, 132.0, 26.6, 26.1, 23.2, 23.1, 23.0. ESI-MS Calculated: 589.330 (M$^+$ + 1) Found: 589.488 (M$^+$ + 1)

Figure S5. $^1$H NMR spectrum (400 MHz, 298 K, CDCl$_3$) of $^{\text{1Pr}}_{2}$TpZn(OAc) (4).

Figure S6. $^{13}$C NMR spectrum (100 MHz, 298 K, CDCl$_3$) of $^{\text{1Pr}}_{2}$TpZn(OAc) (4).
6. Reaction of $^{1}$Pr$_2$TpZn(OAc) with H-SAr.

To a solution of $^{1}$Pr$_2$TpZn(OAc) (34 mM, 29 μmol) in CDCl$_3$ (0.86 mL), was added a CDCl$_3$ solution of p-toluenethiol (H-SAr; 1.72 mL of a 17.4 mM soln, 30 μmol). A 1,2,4,5-tetrachlorobenzene standard was also added (1/2 eq). The solution was stirred and then monitored by NMR. After 3h, $^1$H NMR indicated the following yields: $^{1}$Pr$_2$TpZn-SAr (B: 63%) and acetic acid (C: 77%) in addition to thiol (A: 35%) and trace of free 3,5-diisopropylpyrazole due to degradation of the $^{1}$Pr$_2$Tp ligand.

Figure S7. $^1$H NMR spectrum (400 MHz, 298 K, CDCl$_3$) of the reaction of $^{1}$Pr$_2$TpZn(OAc) (4) with H-SAr at room temperature after 3 h at RT.
7. Reaction of $^{iPr_2}TpZn(OAc)$ with H-SCH$_2$Ph

To a solution of $^{iPr_2}TpZn(OAc)$ (34 mM, 29 μmol) in CDCl$_3$ (0.86 mL) was added a CDCl$_3$ solution of H-SCH$_2$Ph (1.72 mL of 17.4 mM soln, 30 μmol). 1,2,4,5-tetrachlorobenzene was added as a standard (1/2 eq). The solution was stirred and then monitored by NMR. After 3 h, $^1$H NMR indicated the following yields: $^{iPr_2}TpZn$-SCH$_2$Ph (A: 41%) and acetic acid (D: 8%) in addition to unreacted thiol (B: 54%) and unreacted $^{iPr_2}TpZn$($OAc$) (C: 46%). A small amount of free 3,5-diisopropylpyrazole was observed due to degradation of the $^{iPr_2}Tp$ ligand.

Figure S8. $^1$H NMR spectrum (400 MHz, 298 K, CDCl$_3$) of the reaction of $^{iPr_2}TpZn$($OAc$) reaction with H-SCH$_2$Ph at room temperature after 3 h at RT.
8. Qualitative determination of NO gas produced with the decomposition of MeArSNO generated from iPr2TpZn(NO2) and MeArSH.

Bis(N,N-diethylthiocarbamato)iron(II) (Fe(Et2(dtc))2) was synthesized using a reported procedure.1

iPr2TpZn(NO2) (0.100 g 0.18 mmol) was dissolved in dichloromethane (3 mL). The resulting solution was stirred in a sealed vial with rubber septum. Using a syringe, p-toluenethiol (50.0 mg, 0.40 mmol) in dichloromethane (2 mL) was added to the vial. The resulting solution was stirred for 15 min until the green color that formed immediately almost completely disappeared. Using a 3 mL syringe, the headspace gas was sampled and bubbled through an air-free solution of Fe(Et2(dtc))2 (60 mg, 0.17 mmol) in dichloromethane (5 mL). The headspace was sampled in this manner a total of five times. The spin trap solution was collected and subjected to EPR spectroscopy. The EPR spectrum showed a triplet signal with $g_{iso} = 2.04$ and $A^{(14N)} = 12.9$ G characteristic of Fe(NO)(Et2(dtc))2.2

![Figure S9](image.png)

**Figure S9.** X-band EPR spectrum of Fe(NO)(Et2(dtc))2 spin trap solution at room temperature. (Frequency = 8.915923000 GHz, Power = 0.50 mW, Mod.Width = 0.01 mT, Time Constant = 0.1s, Scans = 10).

Crystallographic Details

Single crystals of compounds \textsuperscript{1}Pr\textsuperscript{2}TpZn-SAr (2) and \textsuperscript{1}Pr\textsuperscript{2}TpZn(OAc) (4) were mounted under mineral oil or perfluoroalkyl ether oil on glass fibers in a cold nitrogen stream at 100(2) K on a Bruker SMART CCD system at Georgetown. Either full spheres (triclinic) or hemispheres (monoclinic or higher) of data were collected (0.3° or 0.5° ω-scans; 2θ_{max} ≥ 50°; monochromatic Mo Ka radiation, λ = 0.7107 Å) depending on the crystal system and integrated with the Bruker SAINT program. Structure solutions were performed using the SHELXTL/PC suite\textsuperscript{a} and XSEED.\textsuperscript{b} Intensities were corrected for Lorentz and polarization effects and an empirical absorption correction was applied using Blessing’s method as incorporated into the program SADABS.\textsuperscript{c} Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions.

References for X-ray structure refinement details

(a) SHELXTL-PC, Vers. 5.10; 1998, Bruker-Analytical X-ray Services, Madison, WI; G. M. Sheldrick, SHELX-97, Universität Göttingen, Göttingen, Germany.
(b) L. Barbour, XSEED, 1999.
**Figure S10.** Fully labeled thermal ellipsoid diagram of \( \text{ipn}^2 \text{-TpZn-SAr} (2) \) (all H atoms omitted). Selected bond distances (Å) and angles (deg): Zn-S 2.2310(6), Zn-N1 2.0332(19), Zn-N2 2.0475(18), Zn-N3 2.0486(19), N1-Zn-S 127.55(5), N2-Zn-S 116.95(5), N3-Zn-S 126.08(5).
Figure S11. Fully labeled thermal ellipsoid diagram of $^{19}$Pr$_2$TpZn(OAc) (4) (all H atoms omitted).
Selected bond distances (Å) and angles (deg): Zn-O1 1.9385(17), Zn-O2 2.578(2), Zn-N1 2.042(2), Zn-N2 2.038(2), Zn-N3 2.009(2), N1-Zn-O1 107.98(8), N2-Zn-O2 124.77(8), N3-Zn-O1 133.85(8).