Electronic Supporting Information for:

Reversible RS-NO Bond Cleavage and Formation at Copper(I) Thiolates

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Contents

General Experimental Details

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 ºC for 24 h. Dry toluene and dichloromethane were purchased from Aldrich and were stored over activated 4A molecular sieves under nitrogen. Diethyl ether and tetrahydrofuran (THF) were first sparged with nitrogen and then dried by passage through activated alumina columns.[1] Pentane was first washed with conc. HNO_3/H_2SO_4 to remove olefins, stored over $CaCl_2$ and then distilled before use from sodium/benzophenone. All deuterated solvents were sparged with nitrogen, dried over activated 4A molecular sieves and stored under nitrogen. ^{1}H and ^{13}C NMR spectra were recorded on an Inova Varian 300 MHz, 400, or 500 MHz spectrometer (300, 400, or 500 and 75.4, 100.5, or 125.8 MHz, respectively). ^{19}F NMR spectra were recorded at 282.3 or 375.8 MHz using an internal or external reference of C_6F_6 set to δ = -164.9 ppm. ^{15}N NMR spectra were recorded at 50.6 MHz using an external reference of $Na^{15}NO_2$ (in D_2O) set to δ = 232 ppm[1] or ^{t}BuO^{15}NO (in toluene-d_8 or chloroform-d_1) set to δ = 196 ppm. All NMR spectra were recorded at room temperature unless otherwise noted and were indirectly referenced to TMS using residual solvent signals as internal standards. Elemental analyses were performed on a Perkin-Elmer PE2400 microanalyzer in our laboratories.

^{t}BuSH and BnSH were obtained from Acros, anhydrous CuCl and $NOBF_4$ from Strem, and TlOEt, KO^{t}Bu as well as (4-*tert*-butylphenyl)methanethiol from Aldrich; all were used as received. The thallium thiolates TlS^{t}Bu, TlSBn, and $TlSCH_2Ar^{tBu}$ (^{tBu}Ar = 4-*t*ert-butylphenyl) were synthesized following a modified literature procedure by the reaction of free thiol with TlOEt in ether followed by washing of the solids with pentane.[1] The *S*-nitrosothiols ^{t}BuSNO, BnSNO, and $^{tBu}ArCH_2SNO$ (^{tBu}Ar = *p*-$^{t}BuC_6H_4$) were synthesized *in situ* by the reaction of the corresponding thallium thiolates with 1 eq. $NOBF_4$ in $CDCl_3$ or C_6D_6. Use of an internal standard indicates > 95% purity of resulting RSNOs.[2] Caution! ^{t}BuSH is extremely volatile and possesses a pungent odor indistinguishable from ethanethiol contained in natural gas. Glyoxal-bis-(2,6-

diisopropylphenyl)imine,[3] 1,3-bis-(diisopropylphenyl)imidazolium chloride,[3] IPrCuCl,[4] and [IPrCu(NCMe)]BF_4[5] were synthesized according to published literature procedures.

Synthesis and reactivity of 1 - 5 with spectroscopic and analytical details included.

IPrCu-SBn (1). A yellow slurry of TlSBn (0.135 g, 0.411 mmol) in 3 mL of THF was added to a stirring solution of IPrCuCl (0.200 g, 0.411 mmol) in 5 mL of THF upon which TlCl immediately precipitates. The solution was allowed to stir for 1 h. The white precipitate was filtered out and the solution was concentrated down to 2 mL. Crystals suitable for X-ray analysis grew overnight at -30 ºC yielding 0.161 mg of product (68%). ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.486 (t, 2, *p*-Ar*H*- NHC), 7.300 (d, 4, *m*-Ar*H*-NHC), 7.112 (s, 2, C*H*-NHC), 7.067-6.900 (m, 5, CH_2*Ph*), 3.275 (s, 2, CH_2Ph), 2.600 (sept, 4, C*H*Me_2), 1.300 (d, 12, CH*Me*$_2$), 1.226 (d, 12, CH*Me*$_2$); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) δ 181.72, 145.63, 144.83, 134.55, 130.32, 127.93, 127.74, 124.76, 124.03, 122.75, 28.68, 25.26, 24.77, 23.80. Anal. Calcd. for $C_{34}H_{43}CuN_2S$: C, 70.98; H, 7.53; N, 4.87. Found C, 71.22; H, 7.56; N, 4.87.

IPrCu-S^{t}Bu (2). A yellow solution of TlS^{t}Bu (0.151 g, 0.514 mmol) in 3 mL of THF was added to a stirring solution of IPrCuCl (0.250 g, 0.514 mmol) in 5 mL of THF upon which TlCl immediately precipitates. The solution was allowed to stir for 1 h. The volatiles were removed *in vacuo* and the white residue was extracted with 3 × 5 mL of CH_2Cl_2 and filtered through Celite. The solvent was removed *in vacuo* and the residue washed with 5 mL of *n*-pentane. The remaining solid was dried *in vacuo* to afford 0.206 g (74%) of the product. ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.451 (t, 2, *p*-ArH- NHC), 7.277 (d, 4, *m*-ArH-NHC), 7.123 (s, 2, C*H*-NHC), 2.615 (sept, 4, C*H*Me_2), 1.328 (d, 12, CH*Me*$_2$), 1.221 (d, 12, CH*Me*$_2$), 1.040 (s, 9, ^{t}*Bu*); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) δ 182.73, 145.79, 134.88, 130.36, 124.20, 122.85, 39.27, 34.41, 28.88, 24.88, 24.22. Anal. Calcd. for $C_{31}H_{45}CuN_2S$: C, 68.78; H, 8.38; N, 5.18. Found C, 69.04; H, 8.37; N, 4.77.

IPrCu-SCH$_2$Ar^{tBu} (3). A yellow solution of TlSCH$_2$Ar^{tBu} (0.330 g, 0.860 mmol) in 3 mL of THF was added to a stirring solution of IPrCuCl (0.419 g, 0.860 mmol) in 8 mL of THF upon which TlCl immediately precipitates. The solution was allowed to stir for 1 h. The white precipitate was filtered out and the solution was concentrated down to 2 mL. Crystals suitable for X-ray analysis grew overnight at -30 ºC yielding 0.420 mg of product (77 % yield). ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.490 (t, 2, *p*-Ar*H*- NHC), 7.305 (d, 4, *m*-Ar*H*-NHC), 7.118 (s, 2, C*H*-NHC), 7.069 (d, 2, *o*-Ar*H*-CH$_2$Ar^{tBu}), 6.833 (d, 2, *m*-Ar*H*- CH$_2$Ar^{tBu}) 3.322 (s, 2, CH_2Ar^{tBu}), 2.615 (sept, 4, C*H*Me_2), 1.328 (d, 12, CH*Me*$_2$), 1.304 (s, 9, CH$_2$Ar^{tBu}), 1.221 (d, 12, CH*Me*$_2$), 1.040 (s, 9, ^{t}*Bu*); ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) δ 182.24, 145.95, 143.82, 134.86, 130.61, 127.83, 127.82, 125.01, 124.33, 122.98, 34.42, 31.65, 28.99, 25.83, 25.05, 24.10. Anal. Calcd. for $C_{38}H_{51}CuN_2S$: C, 72.28; H, 8.14; N, 4.44. Found C, 71.99; H, 7.80; N, 4.15.

^{1}H NMR Experiments for transnitrosation reactions of IPrCu-SR + R'SNO.

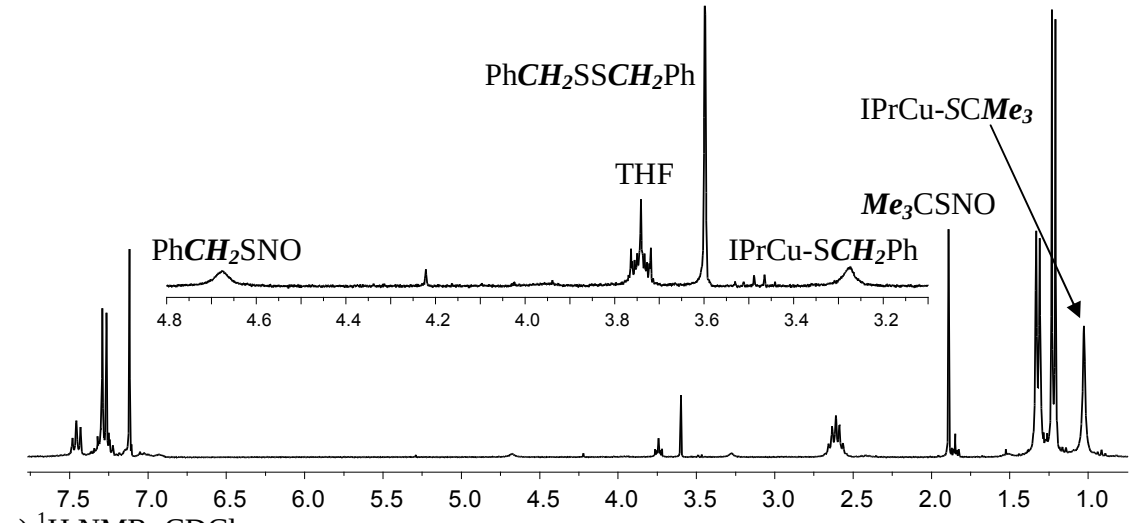
IPrCu-S^{t}Bu + BnSNO. BnSNO was generated from the addition of TlSBn (0.018 g, 0.055 mmol) in 0.500 mL $CDCl_3$ to stirring $NOBF_4$ (0.007 g, 0.055 mmol) crystals. The colorless solution immediately turned bright red and the solution was allowed to stir for 5 min. This solution is added to a light tan solution of IPrCu-S^{t}Bu (0.030 g, 0.055 mmol) in 0.500 mL $CDCl_3$. The color of the red solution dimished and a hint of green appeared. This sample was analyzed by ^{1}H NMR spectroscopy. IPrCu-SBn and ^{t}BuSNO were both seen as new products (δ 3.278 and 1.939 ppm) with IPrCu-S^{t}Bu (δ 1.065 ppm) and BnSNO (δ 4.670 ppm) reactants still present. We repeated this experiment three times and calculated the equilibrium constant of the reaction from the NMR integrals of all four species after letting the sample equilibrate for ca. 10 – 15 minutes (Figure S1a).

The experiment was similarly repeated in C_6D_6. The SC*H*$_2$Ph peaks from IPrCu-SCH$_2$Ph and BnSNO formed one new peak at δ 3.978 ppm, similar to what is seen in the degenerate reaction between IPrCu-SBn and BnSNO in C_6D_6. The two types of S^t*Bu* peaks from IPrCu-S^{t}Bu and ^{t}BuSNO overlap and equilibrium information cannot be taken from these spectra since the pure components appear at δ 1.480 and 1.506 ppm, respectively.

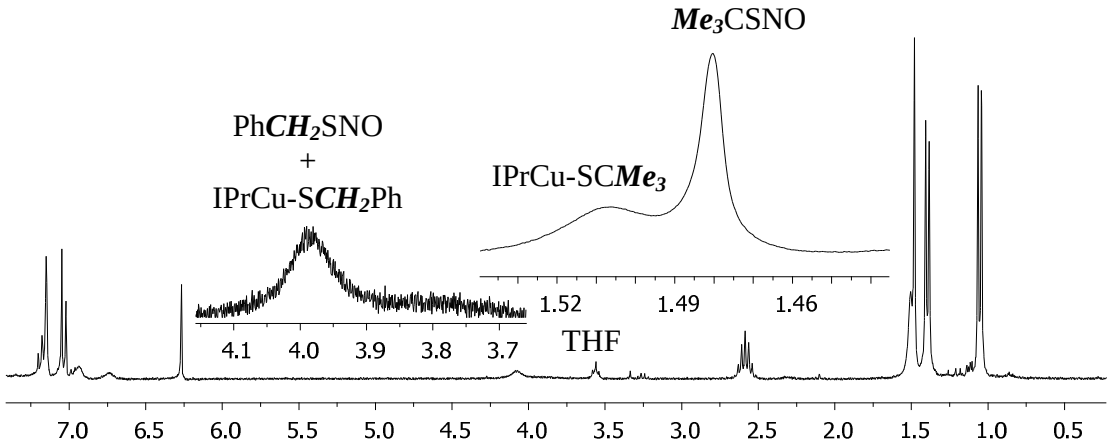
$$\text{IPrCu-S}^{t}\text{Bu} + \text{BnSNO} \rightleftharpoons \text{IPrCu-SBn} + {}^{t}\text{BuSNO}$$

2 $K_{eq} = 0.25(5)$ in $CDCl_3$ **1**

Scheme S1. Transnitrosation between IPrCu-S^{t}Bu (**2**) and BnSNO. The equilibrium favors the bulky, more strongly electron-donating S^{t}Bu group at copper.



a) ^{1}H NMR, $CDCl_3$

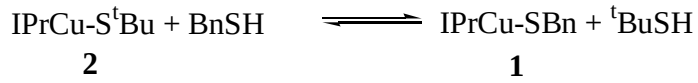


b) ^{1}H NMR, C_6D_6

Figure S1. ^{1}H NMR spectra (300 MHz, 25 °C) in (a) $CDCl_3$ or (b) C_6D_6 illustrating transnitrosation between IPrCu-S^{t}Bu (**2**) and BnSNO.

Transthiolation experiment between IPrCu-S^{t}Bu + BnSH.

IPrCu-S^{t}Bu + BnSH. BnSH (0.007 g, 0.055 mmol) in 0.100 mL $CDCl_3$ was added to a light tan solution of IPrCu-S^{t}Bu (0.030 g, 0.055 mmol) in 0.500 mL $CDCl_3$. No color change is observed. This sample is analyzed by ^{1}H NMR and IPrCu-SBn (δ 3.278 ppm) and ^{t}BuSH (δ 1.469 and 1.786 ppm for *^{t}Bu* and S*H* resonances, respectively) are both seen as new products with complete consumption of IPrCu-S^{t}Bu and BnSNO reactants. Thus the reaction favors the primary copper thiolate and the tertiary thiol.



2 **1**

Scheme S2. Transthiolation between IPrCu-S^{t}Bu (**2**) and BnSH. The reaction goes to completion, favoring the less bulky copper complex IPrCu-SR.

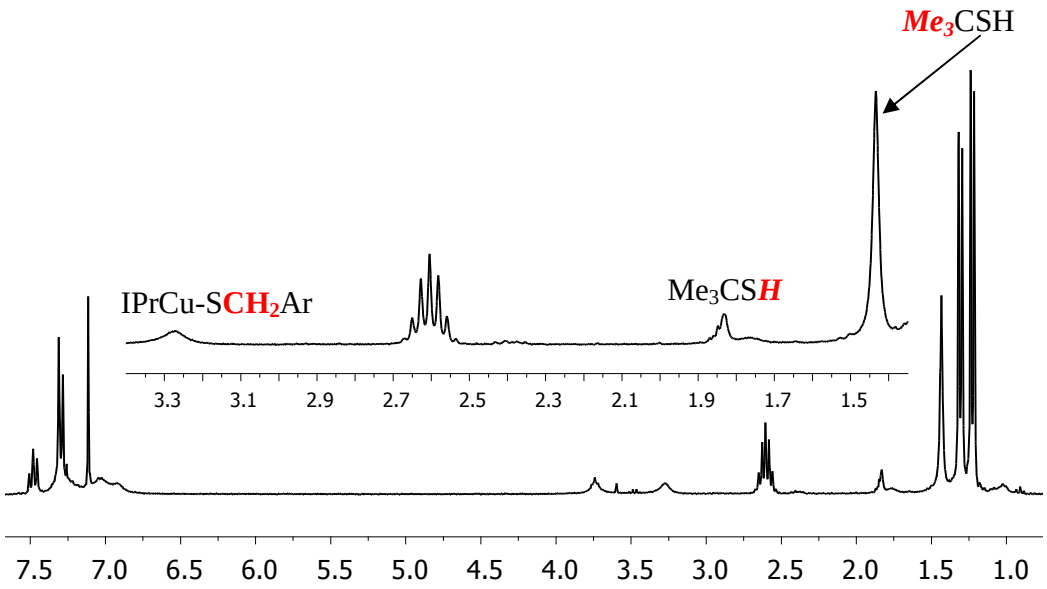


Figure S2. ^{1}H NMR spectrum (300 MHz, 25 °C, $CDCl_3$) illustrating transthiolation between IPrCu-S^{t}Bu (**2**) and BnSH.

Degenerate transnitrosation experiments

IPrCu-S^{t}Bu with ^{t}BuSNO. ^{t}BuSNO was generated from the addition of TlS^{t}Bu (0.016 g, 0.055 mmol) in 0.500 mL $CDCl_3$ to stirring $NOBF_4$ (0.007 g, 0.055 mmol) crystals. The colorless solution turned green and the solution was allowed to stir for 5 min. This solution was added to a light tan solution of IPrCu-S^{t}Bu (0.030 g, 0.055 mmol) in 0.500 mL $CDCl_3$. No major color change was observed. This sample was then analyzed by ^{1}H NMR spectroscopy. Resonances for IPrCu-S^{t}Bu (δ 1.065 ppm) and ^{t}BuSNO (δ 1.939 ppm) were both seen as sharp unshifted peaks. This suggests that the transnitrosation reaction is not fast on the ^{1}H NMR timescale. The experiment was repeated in C_6D_6 with identical results to the $CDCl_3$ experiment, IPrCu-S^{t}Bu (δ 1.517 ppm; *^{t}Bu*) and ^{t}BuSNO (δ 1.485 ppm) appear at different chemical shifts in C_6D_6.

IPrCu-S^{t}Bu + ^{t}BuSNO ⇌ IPrCu-S^{t}Bu + ^{t}BuSNO
2 **2**

Scheme S3. Degenerate transnitrosation of ^{t}BuSNO and IPrCu-S^{t}Bu (**2**).

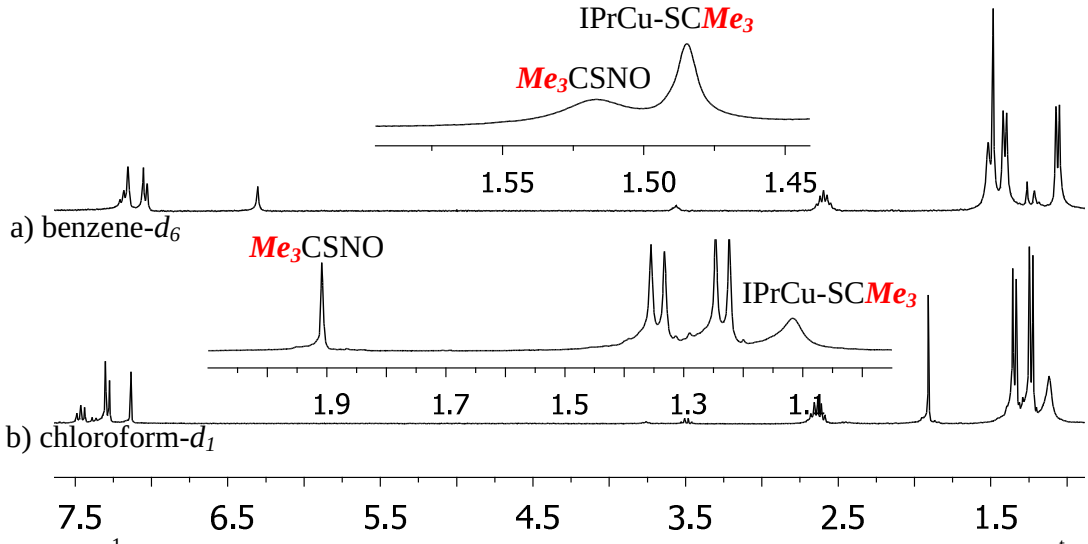
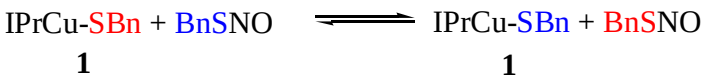


Figure S3. ^{1}H NMR spectra (300 MHz, 25 °C) of degenerate transnitrosation between ^{t}BuSNO and IPrCu-S^{t}Bu (**2**) in (a) benzene-d_6 and (b) chloroform-d_1.

IPrCu-SBn with BnSNO. BnSNO was generated from the addition of TlSBn (0.018 g, 0.055 mmol) in 0.500 mL $CDCl_3$ to stirring $NOBF_4$ (0.007 g, 0.055 mmol) crystals. The colorless solution immediately turned bright red and the solution wass allowed to stir for 5 min. This solution was added to a light tan solution of IPrCu-SBn (0.032 g, 0.055 mmol) in 0.500 mL $CDCl_3$. No major color changes was observed. This sample was analyzed by ^{1}H NMR. The SC*H*$_2$Ph resonances in IPrCu-SBn (δ 3.814 ppm) and BnSNO (δ 4.670 ppm) were both broad, but remain at the same chemical shift.



Scheme S4. Degenerate transnitrosation between BnSNO and IPrCu-SBn (**1**).

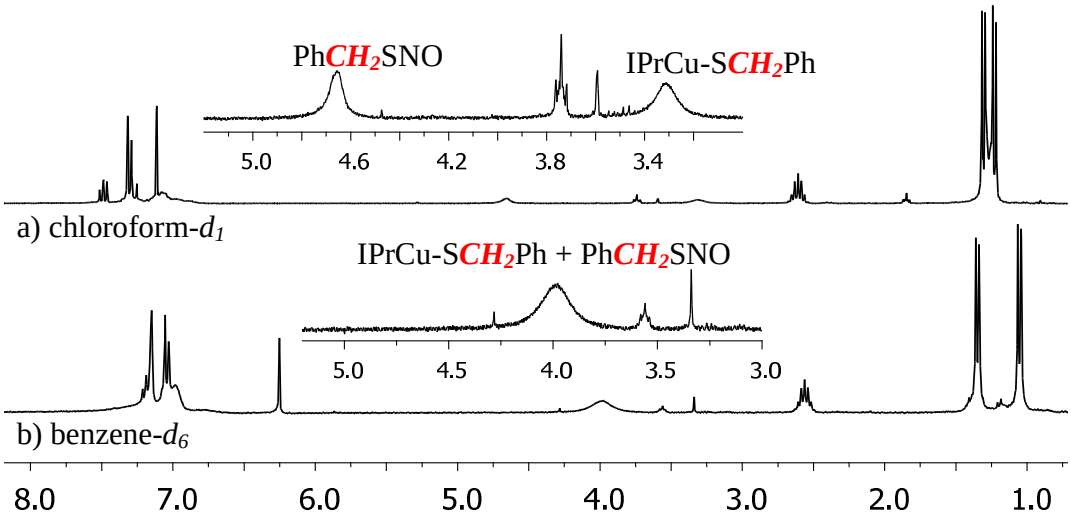


Figure S4. ^{1}H NMR spectra (300 MHz, 25 °C) in: (a) $CDCl_3$ of transnitrosation between IPrCu-SBn and BnSNO, two S*CH*$_2$Ph peaks present or (b) C_6D_6 of transnitrosation between IPrCu-SBn and BnSNO, one S*CH*$_2$Ph peak present.

When the reaction was performed analogously in benzene-d_6 one ^{1}H NMR peak at δ 3.988 ppm was observed for the S*CH*$_2$Ph protons. When different stoichiometric amounts (1/2, 1, and 2 eq.) of BnSNO are added to IPrCu-SBn, the chemical shift of the broad peak moved toward chemical shift for the pure compound that was in greater excess. A 200 mM stock solution of $PhCH_2SNO$ was generated from the addition of TlSBn (0.131 g, 0.400 mmol) in 0.200 mL $CDCl_3$ to stirring $NOBF_4$ (0.047 g, 0.400 mmol) crystals. A 100 mM stock solution of IPrCu-SBn was prepared by dissolving (0.115 g, 0.200 mmol) in 0.200 mL of $CDCl_3$. ^{1}H NMR spectra were taken in C_6D_6 varying the ratio $PhCH_2SNO$ to IPrCu-SBn: (1) 0:1, (2) 1:2, (3) 1:1, (4) 1:1/2, (5) 1:0. The final concentration of copper was kept constant throughout the reaction.

Table S1. Experimental set up for reaction of IPrCu-SBn (**1**) and BnSNO using varying equivalents of each reactant.

Spectrum	RSNO:CuSR Ratio	$PhCH_2SNO$ 200 mM	IPrCu-SCH_2Ph 100 mM	C_6D_6	δ (ppm)
1	0:1	0.200 mL	0 mL	0.800 mL	4.082
2	1:2	0.400 mL	0.400 mL	0.200 mL	4.021
3	1:1	0.200 mL	0.400 mL	0.400 mL	3.979
4	1:1/2	0.100 mL	0.400 mL	0.500 mL	3.867
5	0:1	0 mL	0.400 mL	0.600 mL	3.816

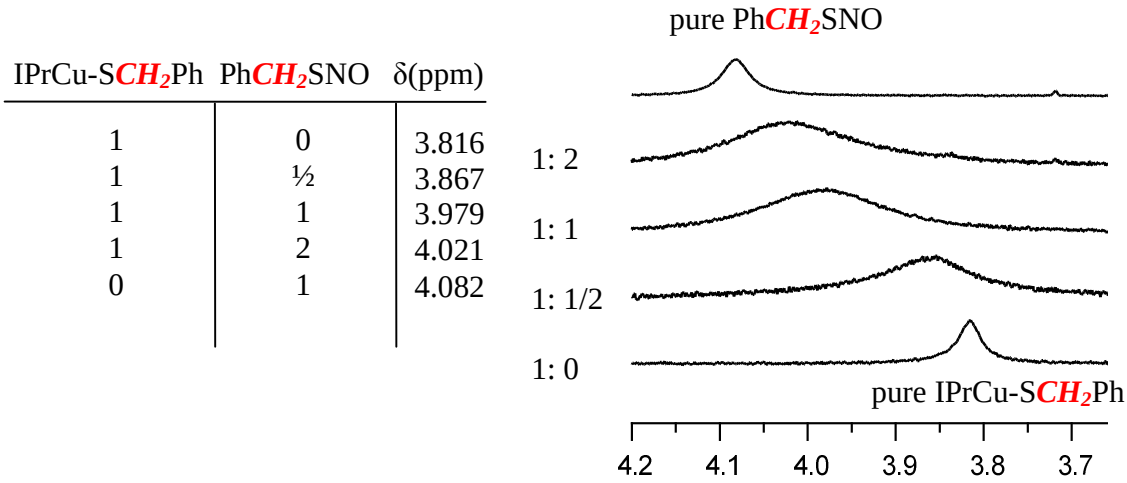


Figure S5. ^{1}H NMR spectra (300 MHz, 25 °C, C_6D_6) of mixtures containing different ratios of IPrCu-SBn and BnSNO. Only the SCH_2Ph region (δ 4.3 - 3.6 ppm) shown.

Table S1. Estimation of observed rate k for transnitrosation between IPrCu-SBn (**1**) and BnSNO when each is 40 mM in benzene-d_6.

Compound	δ (ppm)	FWHH (Hz)
IPrCuSBn	3.816	10.2
BnSNO	4.082	10.8
IPrCuSBn + BnSNO	3.978	48.9

$$k = \frac{\pi(\Delta\nu_0)^2}{2(h_e - h_0)} = \frac{\pi(79.8)^2}{2(48.9 - 10.5)}$$
$$= 260(10)\ s^{-1}$$

$$\Delta\nu_0 = 300MHz(4.082 - 3.816ppm)$$
$$= 79.8\ Hz$$

h_e and h_0 are the FWHH peakwidths during exchange and in the absence of exchange. h_e = 48.9 Hz and h_0 estimated at 10.5 Hz, the average of the peakwidths for the two pure compounds.

Synthesis of ^{15}N-labeled S-nitrosothiols; NMR spectroscopy of S-nitrosothiols

^{t}BuO^{15}NO. ^{t}BuO^{15}NO was synthesized according to the reported procedure from an acidic solution of sodium nitrite with slight modifications.[6] To an ice cold solution of 18 M H_2SO_4 (1.04 ml, 19.55 mmol) and H_2O (1.04 mL) was added ^{t}BuOH (1.447 g, 19.55 mmol) dropwise followed by the addition of a solution of $Na^{15}NO_2$ (1.500 g, 21.4 mmol) in 2 mL of H_2O. The reaction was kept at 0 °C during the addition. The reaction mixture was warmed to room temperature and allowed to stir for 2 hr. The aqueous layer was separated and the organic portion was washed with aq $NaHCO_3$ (0.500 g) and NaCl (0.200 g). The organic layer was dried over Na_2SO_4 and filtered through silica gel to remove any remaining alcohol to yield 1.580 g (78 % yield) of a yellow oil. ^{1}H NMR (toluene-d_8, 500 MHz, 25 °C): δ 1.263 (s, 9, Me_3CO^{15}NO). ^{15}N NMR (toluene-d_8, 500 MHz, 25 °C): δ 196 (s, 1, Me$_3$CO^{15}NO) (referenced using external $Na^{15}NO_2$ in D_2O set to δ 232 ppm).[7]

^{tBu}ArCH$_2$S^{15}NO and PhCH$_2$S^{15}NO. ^{tBu}ArCH$_2$S^{15}NO was generated from the addition of ^{tBu}ArCH$_2$SH (112 μL, 0.060 mmol) in 0.300 mL chloroform-d_1 or toluene-d_8 followed by ^{t}BuO^{15}NO (7 μL, 0.060 mmol) to give ^{tBu}ArCH$_2$S^{15}NO at a concentration of 100 mM. ^{1}H NMR (toluene-d_8, 500 MHz, 25 °C): δ 7.072 (d, 2, *o*-Ar*H*), 6.778 (d, 2, *m*-Ar*H*), 4.260 (s, 2, *CH*$_2$Ar^{tBu}), 1.128 (s, 9, *Me*$_3$CAr). ^{15}N NMR (toluene-d_8, 500 MHz, 25 °C): δ 196.430 (s, 1, ^{tBu}ArCH$_2$S^{15}*N*O). ^{15}N NMR (toluene-d_8, 500 MHz, -70 °C): δ 195.860 (s, *syn*, ^{tBu}ArCH$_2$S^{15}NO), 360.564 (s, *anti*, ^{tBu}ArCH$_2$S^{15}NO).

An analogous procedure was used to prepare PhCH$_2$S^{15}NO. ^{1}H and ^{13}C NMR data for PhCH$_2$S^{15}NO are identical to those previously reported for PhCH$_2$SNO.[8]

Table S2. ^{1}H NMR chemical shifts (500 MHz) for syn / anti rotamers of the methylene peak of ^{tBu}ArC*H*$_2$SNO.

Spectrum	^{tBu}Ar***CH*$_2$**SNO -60 °C, $CDCl_3$	^{tBu}Ar***CH*$_2$**SNO -70 °C, $C_6D_5CD_3$
Syn	4.402	3.695
Anti	6.207	5.488
Average (25 °C)	4.656	4.158

Table S3. ^{1}H and ^{15}N NMR data for syn and anti rotomers of PhCH$_2$SNO and ^{tBu}ArCH$_2$SNO in toluene-d_8 at -70 °C. All chemical shifts given in ppm. ^{15}N chemical referenced to external ^{t}BuO^{15}NO in toluene-d_8 set to 196 ppm.

S-nitrosothiol	^{1}H Shift Anti	^{1}H Shift Syn	Syn:Anti ^{1}H NMR	^{15}N Shift Anti	^{15}N Shift Syn	Syn:Anti ^{15}N NMR
PhCH$_2$SNO	5.973	3.560	14:1	209.3	137.9	13:1
^{tBu}ArCH$_2$SNO	6.027	4.402	14:1	360.6	195.9	13:1

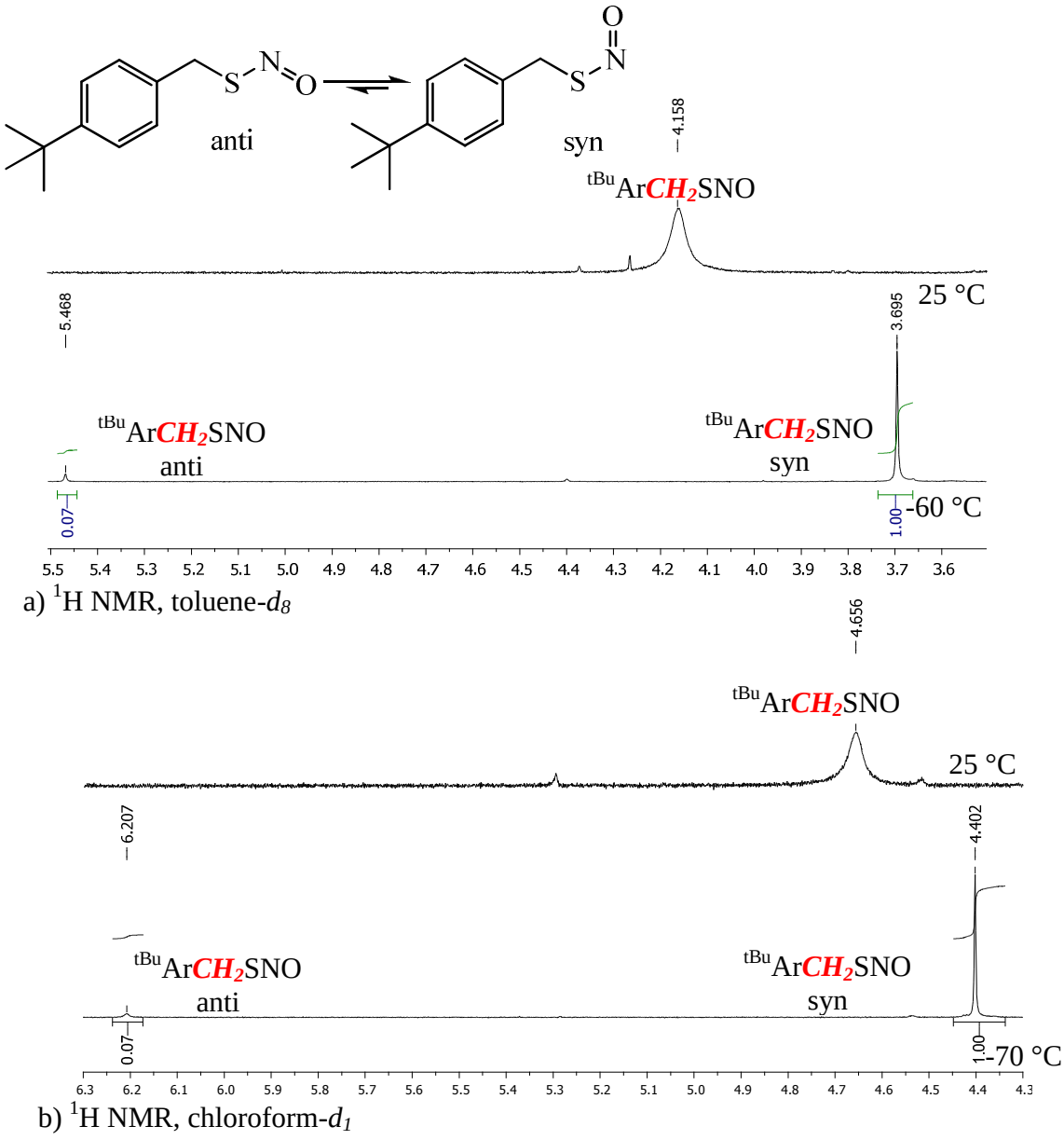


Figure S6. a) ^{1}H NMR spectra (300 MHz, toluene-d_8) of ^{tBu}ArCH$_2$SNO at 25 °C and -60 °C, CH_2 region shown only. b) ^{1}H NMR spectra (300 MHz, chloroform-d_1) of ^{tBu}ArCH$_2$SNO at 25 °C and -70 °C, CH_2 region shown only.

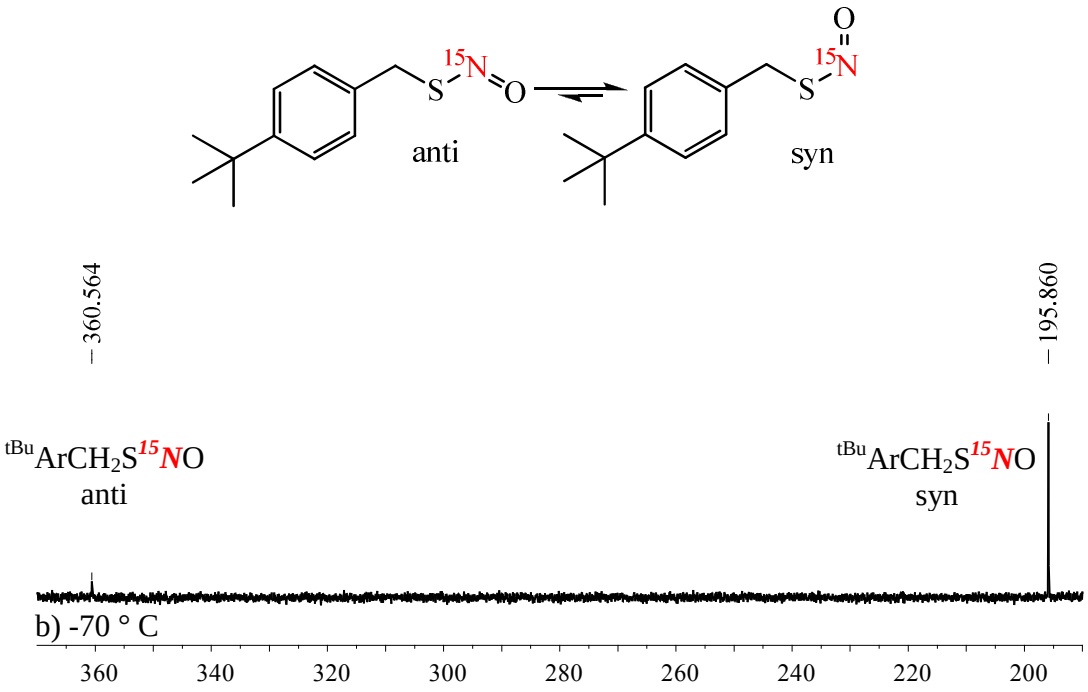
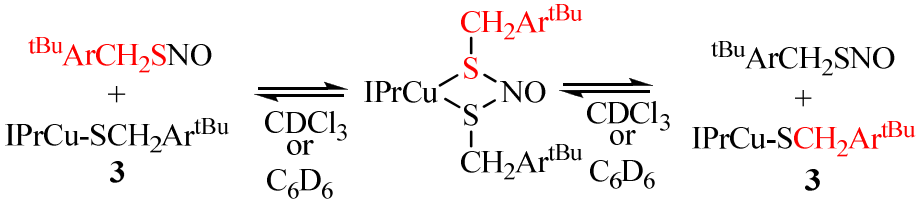


Figure S7. $^{15}N\{^{1}H\}$ NMR spectra (30.428 MHz, toluene-d_8) at -70 °C, anti/syn 0.08:1.

Transnitrostation between $^{tBu}ArCH_2S^{15}NO$ and IPrCu-$SCH_2Ar^{t}Bu$ observed by ^{15}N NMR. $^{tBu}ArCH_2S^{15}NO$ was generated from the addition of $^{tBu}ArCH_2SH$ (112 µL, 0.060 mmol) in 0.300 mL chloroform-d_1 or toluene-d_8 followed by $^{t}BuO^{15}NO$ (7 µL, 0.060 mmol) to give concentrations of 100 mM of $^{tBu}ArCH_2S^{15}NO$. This solution was added to a light tan solution of IPrCu-SCH_2Ar^{tBu} (0.038 g, 0.060 mmol) in 0.300 mL chloroform-d_1 or toluene-d_8. No major color changes were observed. Theses sample was analyzed by ^{15}N NMR at -50 and 25 °C (chloroform-d_1) or -70 °C to 25 °C (toluene-d_8). The only ^{15}N containing molecule in this reaction mixture is the *S*-nitrosothiol in both solvents. No new species was formed. This confirms that we do not observe the nitroxyl disulfide intermediate using our ligand system in these reaction conditions.



Scheme S5. Transnitrosation reaction between **3** and $^{tBu}ArCH_2SNO$.

NO_{gas} and NO^+ reactions with IPrCu-SR complexes

IPrCu-SR with NO_{gas}. When 1 equiv. NO_{gas} was added to IPrCu-SR (R = Bn (**1**) or ^{t}Bu (**2**), there was no reaction by ^{1}H NMR in $CDCl_3$ at 25 °C. Addition of 2, 5, or 10 equiv. NO_{gas} did not cause a change in the ^{1}H NMR spectra. Thus NO_{gas} does not react with IPrCu-SR species under anaerobic conditions.

IPrCu-SBn with $NOBF_4$. To a stirring solution of IPrCu-SBn (0.100 g, 0.174 mmol) in 1.5 mL $CDCl_3$ was added $NOBF_4$ (0.020 g, 0.174 mmol). The solution immediately turned from light tan to red. This color change suggests the formation of BnSNO. This formation was confirmed by ^{1}H NMR spectroscopy (δ 4.684 ppm, Ar*CH*$_2$SNO). The IPrCu-S*CH*$_2$Ar peak was broad and almost completely disappeared into the baseline. A broad peak is also detected from 6.8-6.3 ppm. This peak is attributed to the aromatic peaks on the benzyl ring. Crystallization of this reaction mixture from toluene layered with pentane reveals this peak to be from the formation of a dicopper thiolate cation, [{IPrCu}$_2$(μ-SBn)]BF_4 (**4**).

Independent synthesis of [{IPrCu}$_2$(μ-SBn)]BF_4 (4). **[**IPrCu(MeCN)]BF_4 (0.200 g, 0.352 mmol) in 5 mL THF was added to a stirring solution of IPrCu-SBn (0.202 g, 0.352 mmol) in 5 mL THF. The reaction was allowed to stir for 10 minutes. The volatiles were removed *in vacuo* and the white residue was extracted with 3 × 5 mL of CH_2Cl_2 and filtered through Celite. The solvent was removed *in vacuo* and the residue washed with 5 mL of *n*-pentane. The remaining solid was dried *in vacuo* to afford 0.346 g (89 % yield) Analysis of this solid ^{1}H NMR confirmed it to be [{IPrCu)$_2$(μ-SBn)]BF_4. ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.480 (t, 4, *p*-ArH- NHC), 7.268 (d, 8, *m*-ArH-NHC), (s, 4, 7.191, C*H*-NHC), 6.988 (br S, 3, *p*-Ar-Bn, *m*-Ar-Bn), 6.632 (br s, 2, *o*-Ar-Bn), 2.929 (br s, 2, *CH*$_2$-Bn), 2.512 (br sept, 8, C*H*Me$_2$), 1.208 (d, 24, CH*Me*$_2$), 1.137 (br s, 24, CH*Me*$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$, 25 °C) δ 180.26, 145.78, 134.51, 130.72, 128.28, 127.84, 124.35, 123.73, 29.24, 28.84, 25.05, 23.94, ^{19}F{^{1}H} NMR ($CDCl_3$, 25 °C) δ -161.81. Several peaks in the ^{1}H NMR spectrum are broad (all of the Bn peaks, C*H*-NHC CH*Me*$_2$ on the NHC ligand) and two carbon peaks were missing in the ^{13}C NMR spectra. We attribute this to exchange between IPrCuSBn and $IPrCu^+$ in $CDCl_3$. Anal Calcd. for $C_{61}H_{79}BCu_2F_4N_4S$: C, 65.75; H, 7.15; N, 5.03. Found C, 65.56; H, 7.42; N, 5.20.

IPrCu-S^{t}Bu with $NOBF_4$. To a stirring solution of IPrCu-S^{t}Bu (0.100 g, 0.185 mmol) in 1.5 mL $CDCl_3$ was added $NOBF_4$ (0.022 g, 0.185 mmol). The solution immediately turned from light tan to green. This color change suggests the formation of ^{t}BuSNO. This formation is confirmed by ^{1}H NMR spectroscopy (δ 1.895 ppm, *Me*$_3$CSNO). A new S*^{t}Bu* peak appeared at δ 0.582 ppm. Crystallization of this reaction mixture from THF reveals this peak to be from the formation of a dicopper thiolate cation, [{IPrCu}$_2$(μ-S^{t}Bu)]BF_4 (**5**).

Independent synthesis of [{IPrCu}$_2$(μ-S^{t}Bu)]BF_4 (5). **[**IPrCu(MeCN)]BF_4 (0.200 g, 0.352 mmol) in 5 mL THF was added to a stirring solution of IPrCu-S^{t}Bu (0.190 g, 0.352 mmol) in 5 mL THF. The reaction was allowed to stir for 10 minutes. The volatiles were removed *in vacuo* and the white residue was extracted with 3 × 5 mL of CH_2Cl_2 and filtered through Celite. The solvent was removed *in vacuo* and the residue washed with 5 mL of *n*-pentane. The remaining solid was dried *in vacuo* to afford 0.325 g (86 % yield) Analysis of this solid ^{1}H NMR confirms it to be [{IPrCu)$_2$(μ-S^{t}Bu)]BF_4 (**7**). ^{1}H NMR ($CDCl_3$, 25 °C) δ 7.486 (t, 4, *p*-ArH- NHC), 7.330

(d, 8, *m*-ArH-NHC), 7.241 (s, 4, C*H*-NHC), 2.514 (sept, 8, C*H*Me_2), 1.227 (d, 24, CH*Me*$_2$), 1.090 (d, 24, CH*Me*$_2$), 0.582 (s, 9, ^{t}*Bu*); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ 178.36, 145.52, 134.36, 130.70, 124.46, 124.14, 46.68, 38.58, 28.99, 24.99, 24.03, $^{19}F\{^1H\}$ NMR ($CDCl_3$, 25 °C) δ -165.03. $C_{58}H_{83}BCu_2F_4N_4S$: Anal. Calcd. for C, 64.37; H, 7.73; N, 5.18. Found C, 64.22; H, 7.64; N, 5.25.

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X-ray Structure Refinement Details

Single crystals of each compound (**3** from pentane; **4** from toluene / pentane; **5** from THF) were mounted under mineral oil on glass fibers and immediately placed in a cold nitrogen stream at -100(2) °C or -173(2) °C on a Bruker SMART CCD system or Bruker APEX II CCD system. Either full spheres (triclinic) or hemispheres (monoclinic or higher) of data were collected (0.3° ω-scans; $2\theta_{max}$ = 56°; 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[a] and XSEED.[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.[c] Non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were included in idealized positions.

Because disordered pentanes of solvation were found in the initial refinement of **3** and **4** that could not be satisfactorily modeled, the SQUEEZE subroutine of PLATON was used.[d] For **3**, 105 solvent electrons were identified in the unit cell corresponding to 2.5 molecules of pentane (ca. 1/3 molecule of pentane per IPrCu-SCH_2Ar^{tBu}). For **4**, 319 solvent electrons were identified corresponding to 1 molecule of pentane per $[\{IPrCu\}_2(\mu\text{-SBn})]BF_4$. The reflection data were refined excluding the solvent to give the results reported below.

In the structure of **5 • 2 THF**, disorder was observed in the positions of the bridging S^tBu group, the BF_4^- anion, and each THF. The SBu^t moiety was modeled over two sets of positions in which S1A, C55A, C56A, C57A, C58A and S1B, C55B, C56B, C57B, C58B were assigned occupancies of 0.530 and 0.470. Both positions were refined aniosotropically. Disorder in the BF_4^- anion was modeled by refining the fluorine atoms of BF_4 group over two sets of positions constrained by DFIX to be regular tetrahedra. F1A, F2A, F3A, F4A and F1B, F2B, F3B, F4B were assigned occupancies of 0.640 and 0.360 and were anisotropically refined. One THF (C59-C62;O63) was modeled with the O atom over two sets of positions (O63A and O63B) with equal occupancies. The other THF was modeled as two separate THF rings (C63-C66;O67) and (O68;C69-C72) with occupancies of 0.74 and 0.26, each sharing a common O atom (O67) at full occupancy. The major occupancy was refined aniostropically while the minor occupancy was refined isotropically.

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.
(c) SADABS; G. M. Sheldrick, 1996, based on the method described in R. H. Blessing, *Acta Crystallogr., Sect. A*, 1995, **51**, 33.
(d) PLATON; Spek, A. L. Acta Crystallogr. 1990, A46, C-34.

Table S4. Crystallographic parameters for **3**, **4**, and **5**.

Cmpd.	**3**	**4**	**5**
Formula	$C_{38}H_{51}CuN_2S$	$C_{61}H_{79}BCu_2F_4N_4S$	$C_{58}H_{81}BCu_2F_4N_4S$ • 2 C_4H_8O
Mol. Wt.	631.39	1114.23	1224.43
Temp.(K)	100(2)	100(2)	100(2)
Crystal description	Block	Plate	Block
Crystal color	Colorless	Colorless	Colorless
Crystal size (mm^3)	0.60×0.58×0.58	0.20×0.10×0.08	0.20×0.18×0.18
System	Monoclinic	Monoclinic	Triclinic
Space group	C2/c	C2/c	P-1
a (Å)	29.689(3)	32.857(3)	12.348(3)
b (Å)	15.6315(13)	12.3716(12)	17.138(4)
c (Å)	17.0794(14)	31.680(3)	17.187(4)
α (deg)	90	90	75.961(3)
β (deg)	94.8040(10)	95.4190(10)	75.033(3)
γ (deg)	90	90	72.937(3)
Volume ($Å^3$)	7898.4(11)	12820(2)	3303.9(14)
Z	8	8	2
θ range (deg)	1.86-27.00	1.25-25.00	1.25-25.00
Measd reflns	32710	46584	32174
Unique reflns	8618	11276	11602
GOF of F^2	1.078	0.898	1.059
R_1 ($I > 2\sigma(I)$)	0.0405	0.0684	0.0503
wR2 (all data)	0.1078	0.1697	0.1377
Largest diff. peak and hole ($e^-.Å^{-3}$)	0.366 and -0.298	0.866 and -0.443	1.564 and -0.666

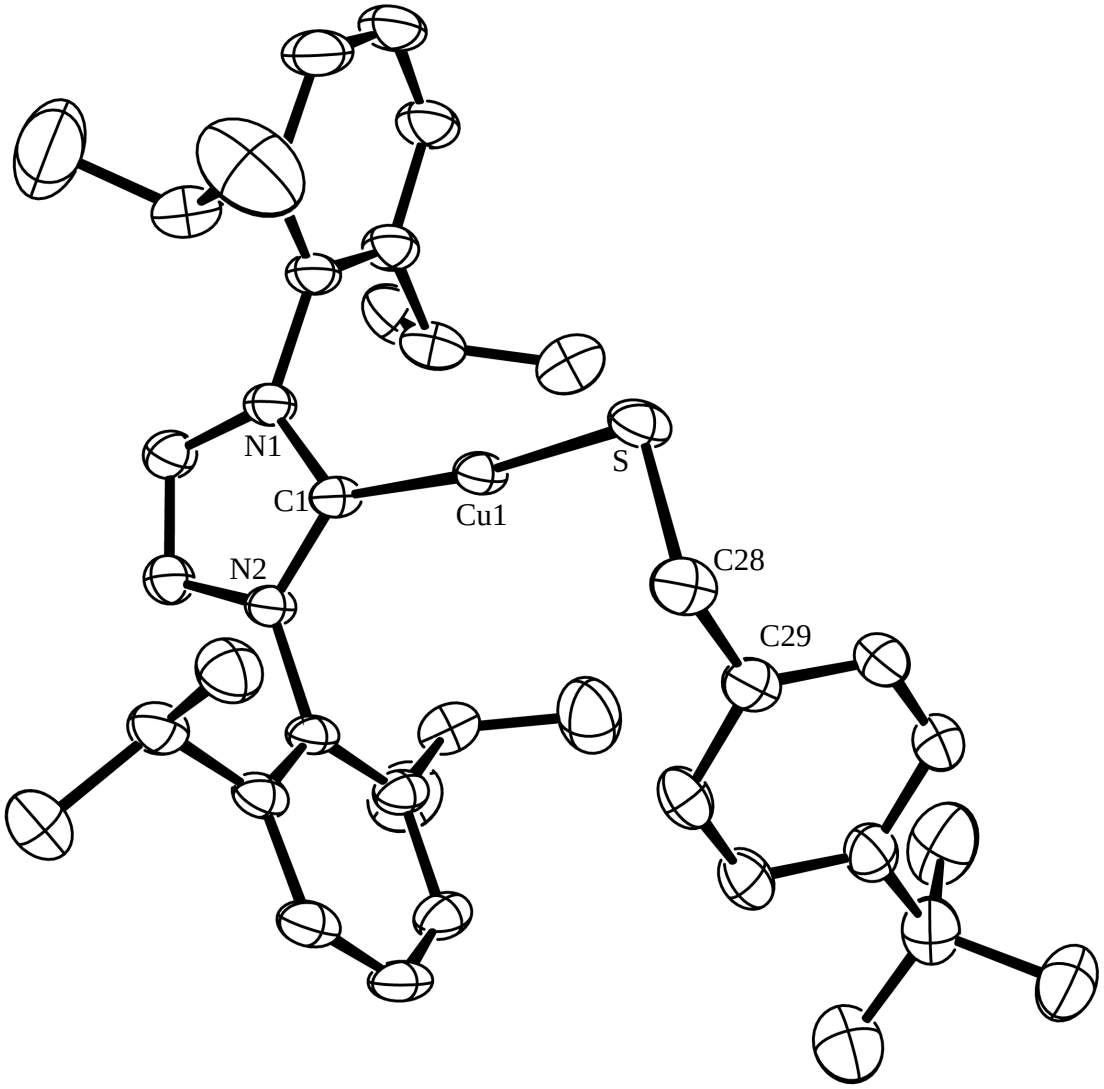

Figure S8. ORTEP diagram of IPrCu-SCH_2Ar^{tBu} (**3**) (all H atoms omitted; thermal ellipsoids represented at the 50% probability level). Selected bond distances (Å) and angles (deg): Cu–C1 1.884(2), Cu–S 2.1304(7), S–C28 1.840(2), C1–Cu–S 172.90(6), C28–S–Cu 105.80(7), N2–C1–Cu 129.34(15), N1–C1–Cu 126.59(15), C29–C28–S 111.92(15).

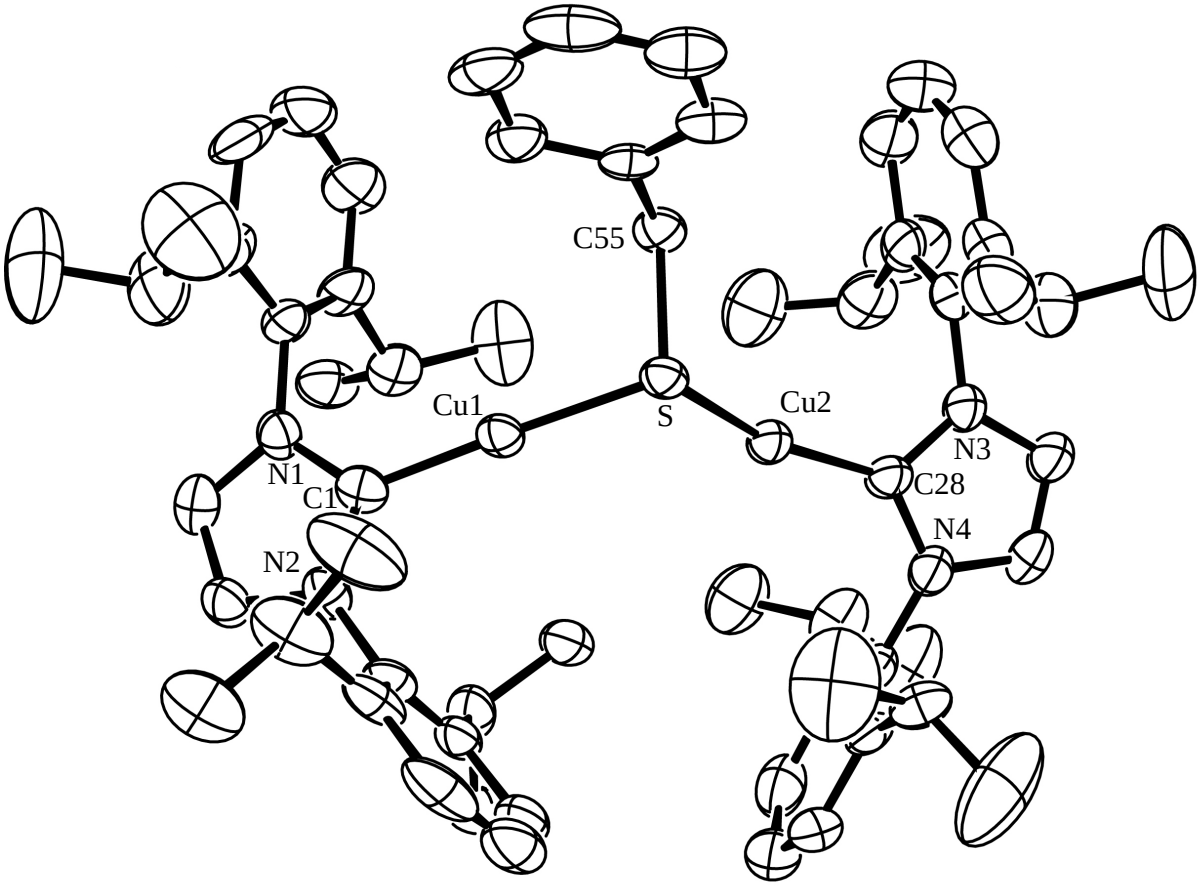

Figure S9. X-ray structure of the $[\{IPrCu\}_2(\mu\text{-}SBn)]^+$ cation in **4** (all H atoms and BF_4 anion omitted; thermal ellipsoids represented at the 50% probability level). Selected bond distances (Å) and angles (deg): Cu–C1 1.882(6), Cu1–S 2.1570(16), Cu2-C28 1.874(6), Cu2-S 2.1462(16), Cu1···Cu2 3.575(1), S-C55 1.858(5), C55–S–Cu1 103.70(18), C55-S-Cu2 105.89(19), C1-Cu1-S 162.41(18), C28-Cu2-S 176.01(17), N2–C1–Cu1 131.8(4), N1–C1–Cu 123.5(4), N3–C28–Cu2 127.5(4), N4–C28–Cu2 128.2(4), Cu1-S-Cu2 112.34(7).

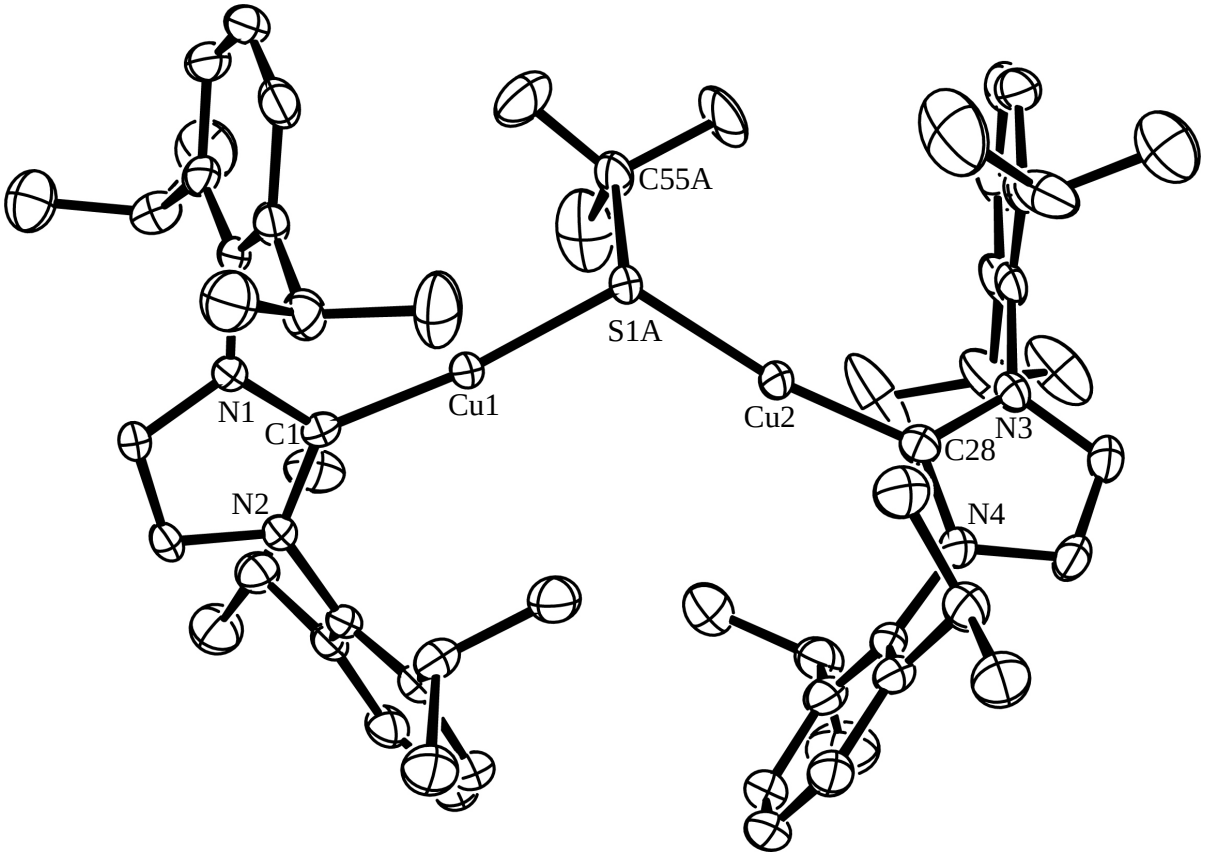

Figure S10. X-ray structure of the $[\{IPrCu\}_2(\mu\text{-}S^tBu)]^+$ cation in **5** (all H atoms, 2 THFs of solvation and BF_4 anion omitted; thermal ellipsoids represented at the 50% probability level). Two similar conformations of the S^tBu group are present in a 53:47 ratio. Only the major occupancy is shown for clarity. Selected bond distances (Å) and angles (deg): Cu–C1 1.894(3), Cu1–S1A 2.185(4), Cu2-C28 1.891(3), Cu2-S1A 2.164(4), Cu1···Cu2 3.732(1), S1A–C55A 1.845(9), C1–Cu1–S1A 166.63(14), Cu1-S1A-Cu2 118.19(18), C28-Cu2-S1A 167.02(14), C55A–S1A–Cu1 108.2(3), C55A-S1A-Cu2 104.8(3), N1–C1–Cu1 125.5(2), N2–C1–Cu1 130.4(2), N3–C28–Cu2 125.6(2), N4–C28–Cu2 130.9(2).