Electronic Supplementary Information

Dramatic Tuning of Ligand Donor Properties in (Ttz)CuCO through Remote Binding of H^+ (Ttz = Hydrotris(triazolyl)borate)

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Table of Contents

General Methods and Experimental Procedures

General Methods. All synthesis and experiments were performed under an atmosphere of dry nitrogen using standard Schlenk techniques and an M. Braun UNILAB glove-box. All chemicals were purchased from Aldrich and were used without further purification. Solvents were dried using a M. Braun solvent purification system with alumina columns or were freshly distilled from drying agents using standard methods. $KTtz^{tBu,Me}$ and $(Ttz^{tBu,Me})CuCO$ (**1**) were prepared according to the literature procedures.[1,2] IR spectra were recorded on a Perkin-Elmer Spectrum One Fourier-transform IR absorption spectrophotometer. ^{1}H-NMR spectra were recorded on a Varian 500 MHz spectrometer. Chemical shifts are reported relatively to the solvent's residual protons peak or hexamethylcyclotrisiloxane as an internal standard in ppm.

Synthesis of $KTtz^{iPr2}$. The procedure for synthesis of this ligand is identical to the procedure for synthesis of $KTtz^{tBu,Me}$, which is in the literature.[1,3] A mole ratio of 5.8 equiv. of 3,5-di-isopropyl-1,2,4-triazole[4] (5.01 g, 32.7 mmol) to 1 equiv. of KBH_4 (0.305 g, 5.64 mmol) was used, and a 80% yield of the product ($KTtz^{iPr2}$, 2.279 g, 4.490 mmol) was obtained. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 3.401 (m, 3 H), 2.99 (m, 3 H), 1.22 (d, 18 H), 1.18 (d, 18 H); ^{13}C-NMR: (300 MHz, $CDCl_3$): δ 21.586 (CH_3-iPr), 22.379 (CH_3-iPr), 26.636 (CH-iPr), 28.513 (CH-iPr), 166.272 (C-tz), 168.134 (C-tz); IR: 2479 cm^{-1} (B-H); CI-MS m/z = 508.3467 $[M+H]^+$ (calc = 508.344981). A suitable analysis was not obtained; in our experience (see Supporting Info. of this reference[1]) KTtz ligands are typically contaminated with 1-3% unreactive inorganic salts which are removed after transition metal complexation during recrystallization.

Synthesis of $(Ttz^{iPr2})CuCO$ ($\mathbf{1}^{iPr}$). The procedure for synthesis of $\mathbf{1}^{iPr}$ is very similar to the published procedure for synthesis of **1**.[2] The $KTtz^{iPr2}$ ligand, 0.150g (0.296 mmol), was dried under vacuum in a flask and then 10 mL of dry THF and 0.043g (0.44 mmol) $Cu^{I}Cl$ was added (in a glove-box). The reaction mixture was stirred for 30 min. The solutions was then removed from the glove-box and was purged with $CO_{(g)}$ for 4.5 hours, adding dry THF as necessary. The solution was filtered to remove KCl and the resulting solution was pale green in color. The solvent was then removed to yield 0.114 g (0.204 mmol, 69% yield) pale green solids. ^{1}H-NMR ($CDCl_3$): δ 3.43 (m, 3H, iPr), 3.13 (m, 3H, iPr), 1.35 (d, 18H, iPr), 1.31 (d, 18H, iPr); IR: ν 2969.55 (C-H), 2534.80 (B-H), 2067.04 (CO), 1494.35 (C-N); CI-MS *m/z:* 560.308171 $[M+H]^+$ (calc = 560.305787), error is 4.3 ppm and in the MS all peaks showed the expected isotopic distribution based upon isotopic modeling. This complex is very air and moisture sensitive.

Synthesis of $(Ttz^{tBu,Me})Cu(NCCH_3)$. A 10 mL CH_2Cl_2 solution of $Tl(Ttz^{tBu,Me})$ (0.131g, 0.208 mmol) was combined with a 2 mL CH_3CN solution of $[Cu(NCCH_3)_4]PF_6$ (0.123g, 0.331 mmol). The contents were then stirred for 6 h at room temperature. A white precipitate formed was filtered off and the solvent from the filtrate removed under vacuum. The crude product was purified by recrystallization from a mixture of dichloromethane and acetonitrile at room temperature to produce $(Ttz^{tBu,Me})Cu(NCCH_3)$ in 89% yield (0.098 g, 0.18 mmol). ^{1}H-NMR ($CDCl_3$): 1.42 (s, 27H, $(CH_3)_3$), 2.32 (s, 3H, CH_3CN), 2.52 (s, 9H, CH_3); ^{1}H-NMR (CD_3CN): 1.38 (s, 27H, $(CH_3)_3$), 2.50 (s, 9H, CH_3); ^{13}C-NMR ($CDCl_3$): 1.24 (CH_3 of CH_3CN)), 13.62 (CH_3), 30.13 (($CH_3)_3$), 32.16 ($C(CH_3)_3$), 115.83 (*C*N of CH_3CN), 157.88 (5-tz), 169.32 (3-tz);

^{13}C-NMR (CD_3CN): 13.08 (CH_3), 29.97((CH_3)$_3$), 33.35(C(CH_3)$_3$), 156.74 (5-tz), 165.09 (3-tz); IR (cm^{-1}): 2515.87 (νB-H); HRCI-MS: m/z = 490.263464 $[M\text{-}NCCH_3]^+$ (experimental), 490.263922 $[M\text{-}NCCH_3]^+$ (calculated), all peaks showed the expected isotopic pattern. Elemental analysis, found C 52.07, H 7.72**,** N 26.30, calcd. for **1** C 52.02, H 7.59, N 26.38.

General Sample Preparation for Vibrational Spectroscopy and Data Analysis. A Perkin-Elmer Spectrum One Fourier-Transform IR absorption spectrophotometer was used to record infrared (IR) spectra. The desired amount of 0.01 M acid in dichloromethane was added to 0.1 mL of a 0.019 M solution of $Ttz^{R1,R2}CuCO$ in dichloromethane. Dichloromethane was added to bring the total volume of the resulting solution to 0.3 mL. Multifit® was used to deconvolute the spectral CO bands of $Ttz^{tBu,Me}CuCO$ following the guidelines reported in the literature.[5] The acid studies and observed ν_{CO} are listed in Table-S1 and the Multifit parameter file is given in Table-S2. The stacked plot shows the change of peak position and profile of the band assigned to the CO stretching vibration of complex $\mathbf{1}^{iPr2}$ with increasing equivalents of HBF_4•Et_2O is given in Figure-S1.

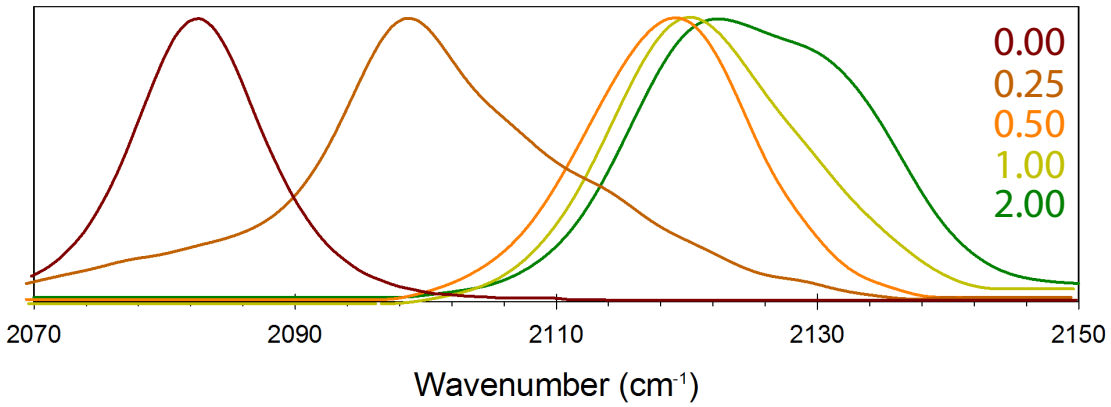


Figure-S1. The stacked plot shows the change of peak position and profile of the band assigned to the CO stretching vibration of complex $\mathbf{1}^{iPr}$ with increasing equivalents of HBF_4•Et_2O (legend in top right shows color code for how many equivalents of H^+ have been added). The spectra are unchanged between 2 and 3 equiv. of H^+.

Table-S1: ν_{CO} measured in the presence of several acids.

Acid equiv.	**HCl*** **pK_a= -7**	**HBF_4** **pK_a = -0.4**	**HCOOH** **pK_a= 7.1**	**4-NO_2-C_6H_5OH** **pK_a= 12.4**	**TFE** **pK_a=12.4**	**Ethanol** **pK_a= 15.9**	**Ether Control**
0.5	-	2098	2086	2084	2084	2084	2086
1	-	2105	2096	2085	2084	2084	2084
2	-	2116	2098	2085	2085	2084	2084
3	-	2116	2098	2086	2086	2085	2084

* HCl led to decomposition.

Table-S2: Wavenumbers and halfwidths obtained from the self-consistent decomposition of CO stretch band profiles into Voigtian sub-bands.

Sub-bands (cm^{-1})	Function	HWB	Function	HWB
2085.60	Lorentian	4.20	Gaussian	9.90
2097.83	Lorentian	2.56	Gaussian	12.32
2105.20	Lorentian	1.87	Gaussian	12.83
2114.79	Lorentian	2.47	Gaussian	10.59
2116.51	Lorentian	3.81	Gaussian	8.10

Titration curve of $Ttz^{tBu,Me}CuCO$, as evidence for formation of 2. The Multifit parameter file given in Table-S2 was used to determine the concentration of [$Ttz^{tBu,Me}CuCO$] and $(Ttz^{tBu,Me}CuCO)_2H$ at low concentrations of HBF_4•Et_2O. The early section of the titration plot is the region of interest, before a significant amount of $H(Ttz^{tBu,Me}CuCO)$ accumulates, and is given in Figure-S2. A K_c value of $8x10^8$ is determined from the slope and supports that $(Ttz^{tBu,Me}CuCO)_2H$ readily forms. The equilibrium expression and equation for $(Ttz^{tBu,Me}CuCO)_2H$ is given in eq. 1.

$$2\,[Ttz^{tBuMe}CuCO] + HBF_4 \bullet Et_2O \rightleftharpoons [(Ttz^{tBuMe}CuCO)]_2H + BF_4^- \bullet Et_2O$$

$$K_c = \frac{[(Ttz^{tBuMe}CuCO)_2H]}{[Ttz^{tBuMe}CuCO]^2[H^+]} \qquad (1)$$

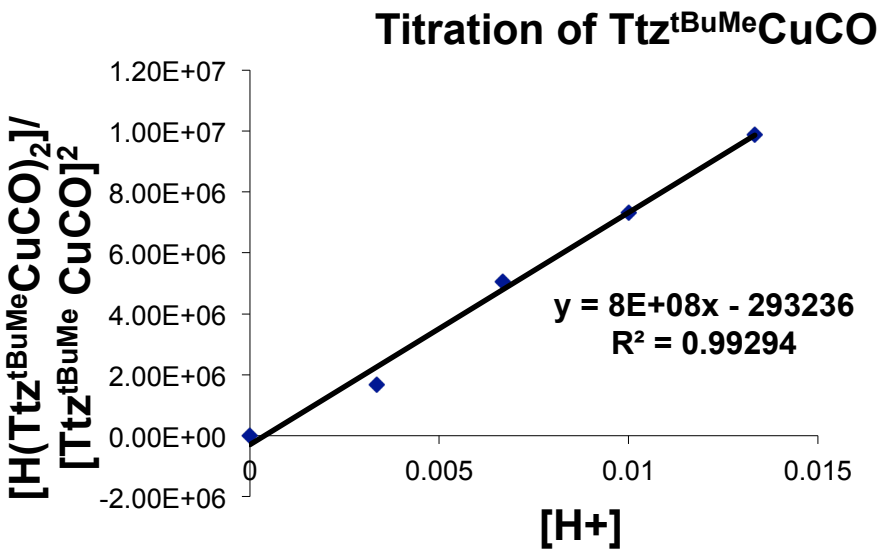


Figure-S2: Plot of $Ttz^{tBuMe}CuCO$ titration with [HBF_4•Et_2O] (region shown at low concentrations).

We also attempted to detect **2** by mass spectrometry analysis. Complex **2** appears to fragment before reaching the detector from both ESI and FAB-MS analysis.

Density Functional Theory (DFT) Calculations. For all calculations, the model complexes were optimized using the BP86 functional[6,7] and the TZVP basis set.[8,9] The crystal structure of the pseudo-tetrahedral complex $Ttz^{tBu,Me}CuCO$ (**1**) was used as a starting point for geometry optimizations of the protonated species.[2] Vibrational frequencies have been calculated for all structures showing no imaginary frequencies. B3LYP/TZVP single point calculations on the fully optimized BP86/TZVP structures were employed to determine relative energies (see **Table-S3**). All geometry optimizations and single point energy calculations were performed with the program package Gaussian 03.[10] In all Gaussian calculations, the convergence was reached when the relative change in the density matrix between subsequent iterations was less than $1x10^{-8}$. The optimized structures for **1•H_2O** and the alternative monoprotonated species are given in **Figure-S3**. The resulting data is given in **Table-S3** and the empirical correlation between theory and experiment is given in **Table-S4**. The cartesian coordinates for all optimized structures are given in **Tables S5-S13**.

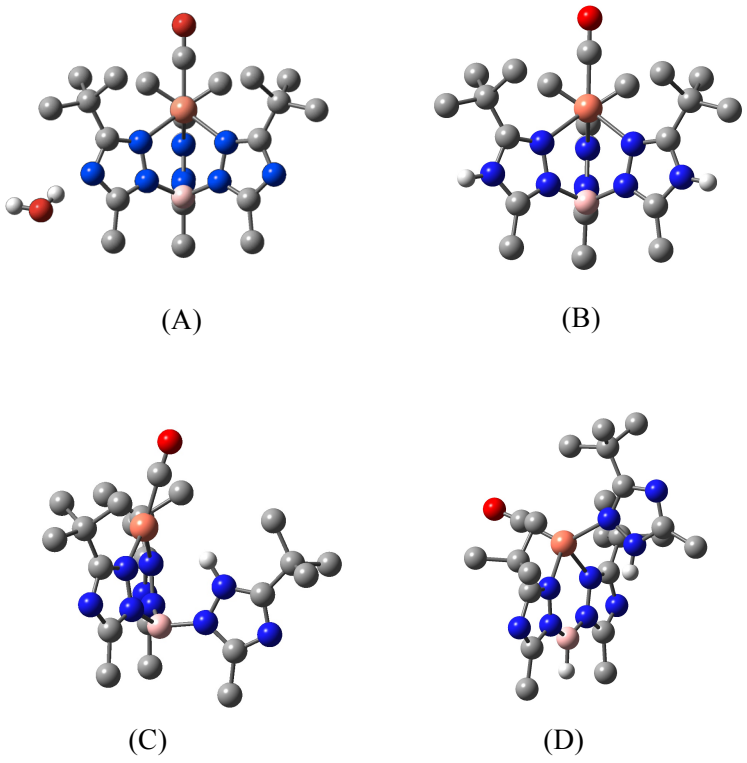


Figure S3: Optimized structures of the singlet states of $(Ttz^{tBu,Me})CuCO$ with a H_2O molecule H-bound to the 4-position nitrogen atom (N4) of one triazolyl ring (A), protonation of the N4 nitrogen atoms of all three triazole rings (B), alternative structures of the mono-protonated species, including: protonation of the Cu-bound nitrogen of the triazolyl ligand, leading to a broken Cu-N bond (C), and protonation of the borate atom, leading to a broken B-N bond of the triazole ligand (D). All structures were calculated at the BP86/TZVP level of theory.

Table-S3: Important structural and spectroscopic parameters for the singlet ground states of [Cu(L)(CO)] complexes (L = $Ttz^{tBu,Me}$).

Complex	ν(C-O) [cm^{-1}]	Int.	Geometric Parameters [Å]			Relative Energies [kcal/mol]	
			ΔCu-N1	ΔCu-N2	ΔCu-N3	BP86	B3LYP
[Cu(L)(CO)]	2051	525	2.090	2.093	2.085	0	0
$[Cu(L)(CO)](H_2O)$	2052	523	2.098	2.084	2.088	-	-
$[Cu(HL)(CO)]^+$	2077	467	2.290	2.042	2.042	-240.5	-242.7
$[Cu(H_2L)(CO)]^{2+}$	2103	403	2.175	2.023	2.170	-425.6	-429.5
$[Cu(H_3L)(CO)]^{3+}$	2126	334	2.127	2.127	2.127	-555.2	-561
$[(Cu(L)(CO))_2(H)]^+$	2065	530	2.162	2.070	2.071	-	-
	2073	497	2.290	2.053	2.051	-	-
Alternative Monoprotonated Species							
$[Cu(HL)(CO)]^+$	2077	467	2.290	2.042	2.041	-240.5 (0.0)	-242.7 (0.0)
$[Cu(CO)(L)]^+$, Cu-N bond broken	2097	468	3.375	2.010	1.990	-233.6 (+6.9)	-236.7 (+6.0)
$[Cu(CO)(L)]^+$, B-N bond broken	2086	422	2.093	2.146	2.135	-214.5 (+19.1)	-219.9 (+16.8)

Table-S4: Comparison of experimental and theoretically calculated values for ν_{CO}. All values are reported in cm^{-1}.

Species:	$\Delta\nu_{expt}$	$\Delta\nu_{expt}$	ν_{calc}	$\Delta\nu_{calc}$	Adj. $\Delta\nu_{calc}$ [c]
$(Ttz^{tBu,Me})CuCO$	2086	-	2051	-	-
$[(Ttz^{tBu,Me})CuCO]_2H^+$	2095	9	2065	14	9.1
	2100	14	2073	22	14.3
$[(Ttz^{tBu,Me})CuCO]H^+$	2105	19	2077	26	16.9
$[(Ttz^{tBu,Me}CuCO)H^+]_2H^+$ [a]	2115	29	-	-	-
$H_2[(Ttz^{tBu,Me})CuCO]^{2+}$	2117	31	2103	52	33.8
$H_3[(Ttz^{tBu,Me})CuCO]^{3+}$ [b]	-	-	2126	75	48.8

[a] DFT was not performed on this species, its proposed structure is described in the text.
[b] Not observed experimentally.
[c] [Adjusted value of $\Delta\nu_{calc}$] = 0.65 × $\Delta\nu_{calc}$; scaling factor of 0.65 was empirically determined from $\Sigma\,\Delta\nu_{expt} / \Sigma\,\Delta\nu_{calc}$.

Table-S5. Coordinates [Å] of [Cu(L)(CO)] for the singlet ground state optimized with BP86/TZVP (L = $Ttz^{tBu,Me}$)

Atom	x	y	z
Cu	0.00449500	-0.01239800	-0.93427400
B	0.00597800	0.01855500	2.10356300
H	0.00828400	0.03158400	3.30811000
N	-0.15956400	1.72672000	0.21255000
N	-0.12374000	1.47238400	1.56759300
N	-0.32404300	3.66826200	1.33878300
N	-1.41022800	-1.00915900	0.24236500
N	-1.19394900	-0.82746200	1.59268700
N	-3.01192400	-2.08221500	1.40355900
N	1.57725800	-0.72681800	0.23347000
N	1.33373700	-0.60209600	1.58533200
N	3.34392400	-1.51492900	1.38287300
O	-0.03109400	-0.05532200	-3.89781900
C	-0.01677000	-0.03383800	-2.74557500
C	-0.28192500	3.06293300	0.12077700
C	-0.22420500	2.66008800	2.21484500
C	-0.36694600	3.82510400	-1.19214700
C	-1.60732000	3.35135700	-1.98478100
H	-1.56457300	2.27298200	-2.19352500
H	-1.66878700	3.88639400	-2.94552000
H	-2.53176600	3.55052400	-1.42167000
C	0.91648500	3.57824300	-2.01833900
H	1.80703200	3.92668200	-1.47349500
H	0.86240700	4.12511600	-2.97284600
H	1.05308400	2.51051700	-2.24119200
C	-0.49865400	5.33356800	-0.90604400
H	0.36565200	5.71171800	-0.34235000
H	-1.39907600	5.55279600	-0.31544100
H	-0.56214500	5.88037500	-1.85982100
C	-0.22253300	2.83158200	3.69851200
H	-1.05226500	2.28807700	4.17423700
H	-0.32838700	3.89999000	3.92143600
H	0.71294600	2.46921000	4.15027300
C	2.79959200	-1.28214000	0.15754500
C	2.41542700	-1.08442800	2.24670400
C	3.50540000	-1.61998900	-1.14626500
C	2.65974700	-2.64032300	-1.94305200
H	2.53788200	-3.57574600	-1.37609600
H	3.15622300	-2.87925800	-2.89667600
H	1.65783600	-2.24708600	-2.16604000
C	3.70282300	-0.33101000	-1.97765600
H	4.21088600	-0.56756300	-2.92583000
H	4.31988100	0.39806100	-1.43075600
H	2.74198200	0.14836100	-2.21308900

C	4.88358300	-2.23809600	-0.84158500
H	4.78751600	-3.15715800	-0.24682800
H	5.51864000	-1.54319300	-0.27455800
H	5.38981900	-2.48349800	-1.78834200
C	2.56122100	-1.13471200	3.73226700
H	3.52758700	-1.59654000	3.96739800
H	1.76293400	-1.72833300	4.20165600
H	2.53415700	-0.12985400	4.17974000
C	-2.51586700	-1.77133900	0.17500100
C	-2.17406300	-1.48543700	2.26111000
C	-3.14734900	-2.24717100	-1.12363300
C	-2.12618300	-3.10002800	-1.91152500
H	-1.22070700	-2.52484600	-2.15151100
H	-2.57331600	-3.44903600	-2.85560400
H	-1.82095500	-3.98295100	-1.32953900
C	-4.38680300	-3.10741400	-0.80994000
H	-4.84142900	-3.44888700	-1.75307800
H	-5.13760100	-2.53752900	-0.24503200
H	-4.12207800	-3.98912700	-0.20960700
C	-3.58146900	-1.02571300	-1.96669600
H	-2.72722900	-0.37639400	-2.20518800
H	-4.32564700	-0.42101700	-1.42652000
H	-4.03368800	-1.36147300	-2.91308400
C	-2.31196800	-1.54078200	3.74722800
H	-3.14957300	-2.20540800	3.99045900
H	-2.51897900	-0.54780300	4.17445200
H	-1.40168300	-1.92586000	4.22915400

Table-S6. Coordinates [Å] of [Cu(L)(CO)](H_2O) for the singlet ground state optimized with BP86/TZVP (L = $Ttz^{tBu,Me}$)

Atom	x	y	z
Cu	0.46451900	0.01048800	-0.94385000
B	-0.27653700	-0.03732000	2.00448100
H	-0.56873800	-0.05921700	3.17145800
N	-1.49997200	-0.19211300	-0.23541100
N	-1.56629000	-0.18735800	1.14290200
N	-3.63839300	-0.39968700	0.40763300
N	1.17372100	-1.40662900	0.40949800
N	0.69076500	-1.21026300	1.68695600
N	2.01821600	-2.98318100	1.77523800
N	0.84642900	1.58005100	0.37865100
N	0.41191600	1.31161200	1.66059500
N	1.31448300	3.33573100	1.70630000
O	1.17549400	0.06509000	-3.82098800
C	0.89659600	0.04284700	-2.70313200
C	-2.77284900	-0.32089200	-0.64124200
C	-2.86483800	-0.31319000	1.50200900
C	-3.20823000	-0.35775000	-2.09729300
C	-2.51154500	-1.53552600	-2.81742400
H	-1.41731900	-1.44881600	-2.76612700
H	-2.80629600	-1.55500600	-3.87811500
H	-2.79648600	-2.49699500	-2.36399200
C	-2.82851700	0.97985900	-2.77588500
H	-3.34054100	1.82483100	-2.29148700
H	-3.12497500	0.96047500	-3.83622500
H	-1.74615200	1.16398200	-2.72298100
C	-4.73493300	-0.54967000	-2.18390100
H	-5.27741600	0.25490900	-1.66790800
H	-5.04335400	-1.50609600	-1.73685400
H	-5.03983700	-0.55105400	-3.24172300
C	-3.38082800	-0.35794200	2.90239500
H	-3.07126900	-1.28299300	3.41260400
H	-4.47789200	-0.32108000	2.87221200
H	-3.01110100	0.48930200	3.49666100
C	1.38431800	2.81038400	0.45303200
C	0.70851700	2.38762500	2.43205300
C	2.00367800	3.54436700	-0.72547000
C	3.19192800	2.72260800	-1.27734100
H	3.97142700	2.59649300	-0.51064300
H	3.64063200	3.23793300	-2.14107100
H	2.87170500	1.72211300	-1.60120600
C	0.93796200	3.74247800	-1.82852200
H	1.37794500	4.26982200	-2.68923400
H	0.09354600	4.34079500	-1.45427400

H	0.54083000	2.78000700	-2.18107100
C	2.51475200	4.92305200	-0.26432600
H	3.27409400	4.82603900	0.52416800
H	1.69859400	5.53898800	0.13829200
H	2.96323500	5.45044400	-1.12062400
C	0.40739500	2.50687200	3.89018900
H	0.70890500	3.50718100	4.22308900
H	0.95770400	1.76009000	4.48218000
H	-0.66398900	2.37261500	4.09869500
C	1.97017000	-2.48569300	0.50957100
C	1.21805300	-2.17475200	2.48191400
C	2.73725500	-3.09425700	-0.65357400
C	3.71177000	-2.04568500	-1.23880700
H	3.17749900	-1.15729600	-1.60404900
H	4.27154400	-2.48114900	-2.08122800
H	4.43595900	-1.71692400	-0.47828000
C	3.54597800	-4.30926000	-0.15852600
H	4.09661600	-4.74872000	-1.00493800
H	2.89109300	-5.07943300	0.27215800
H	4.26872400	-4.01983900	0.61710300
C	1.74267100	-3.55927700	-1.74310200
H	1.13160800	-2.72416400	-2.11388500
H	1.06152900	-4.32926500	-1.35009200
H	2.29217300	-3.98935000	-2.59512900
C	0.95237000	-2.32139000	3.94454800
H	1.50656500	-3.19468800	4.30863600
H	-0.11736700	-2.46993500	4.15344500
H	1.28077900	-1.43587000	4.50878300
O	-6.38467900	-0.05922600	1.11846400
H	-5.48393200	-0.23503900	0.74073800
H	-6.92708800	-0.80354200	0.81082600

Table-S7. Coordinates [Å] of [Cu(L)(CO)](BF_3) for the singlet ground state optimized with BP86/TZVP (L = $Ttz^{tBu,Me}$)

Atom	x	y	z
Cu	1.13545500	-0.00318500	-0.92636200
B	0.10351500	-0.03110600	1.93140900
H	-0.30393300	-0.04271900	3.06402900
N	-0.78307700	-0.63604300	-0.38635600
N	-1.00558000	-0.54844900	0.97180600
N	-2.88074200	-1.31223100	0.06910500
N	2.01415500	-1.09971800	0.61643900
N	1.35326900	-0.94837800	1.81779700
N	3.05239100	-2.32107200	2.19585000
N	0.98345700	1.70052200	0.27275400
N	0.49198200	1.41998500	1.53106000
N	0.89132900	3.59987100	1.47640800
O	2.12906000	0.02720200	-3.71863200
C	1.74373500	0.01326000	-2.63246500
C	-1.93893000	-1.10087300	-0.89168300
C	-2.27370800	-0.96359100	1.21201900
C	-2.17254300	-1.37089300	-2.36994700
C	-1.15029500	-2.41785300	-2.87086100
H	-0.11697300	-2.07181800	-2.72832300
H	-1.30449900	-2.61115100	-3.94399200
H	-1.26704500	-3.36921600	-2.33004800
C	-2.01802000	-0.05468100	-3.16763600
H	-2.75851500	0.69101800	-2.84067300
H	-2.17255500	-0.24309300	-4.24163400
H	-1.01817000	0.38244500	-3.03581100
C	-3.59590600	-1.92123100	-2.58064100
H	-4.35708900	-1.19936700	-2.25465300
H	-3.75516700	-2.85067600	-2.01640700
H	-3.75058200	-2.12892700	-3.65088600
C	-2.91016400	-1.02872100	2.56184200
H	-2.30992200	-1.62256100	3.26616200
H	-3.89640300	-1.49646800	2.45941500
H	-3.04176300	-0.02746700	2.99909300
C	1.21007000	3.02609500	0.28433700
C	0.45051700	2.58293700	2.22800700
C	1.75887800	3.80945700	-0.89749100
C	3.16559700	3.27855700	-1.26087100
H	3.86015100	3.39919400	-0.41571500
H	3.56975800	3.83718600	-2.11963700
H	3.13752100	2.21228200	-1.52649100
C	0.80580200	3.65954600	-2.10585700
H	1.20151600	4.21523500	-2.97040000
H	-0.19175000	4.05953800	-1.86861800
H	0.68721400	2.60661400	-2.39788300

C	1.86543000	5.30065500	-0.52324700
H	2.53444300	5.45125000	0.33537200
H	0.88446700	5.71707700	-0.25503600
H	2.26314900	5.86370400	-1.38206900
C	-0.01422700	2.72075000	3.64092500
H	0.01098100	3.78367300	3.90913300
H	0.63449400	2.16865800	4.33772300
H	-1.03948800	2.34582800	3.77373400
C	3.03201100	-1.93459500	0.89126000
C	2.00322200	-1.69548000	2.74477600
C	4.05739700	-2.39838000	-0.13101900
C	4.80334300	-1.17275800	-0.70747400
H	4.11013500	-0.47240800	-1.19466500
H	5.54478300	-1.49869300	-1.45381100
H	5.33302900	-0.62660000	0.08763100
C	5.07704400	-3.33316700	0.54934200
H	5.81931700	-3.66435300	-0.19365800
H	4.58708900	-4.22028700	0.97437000
H	5.60457000	-2.82358800	1.36779800
C	3.34652500	-3.16918100	-1.26764300
H	2.60711900	-2.53813600	-1.78058000
H	2.82325500	-4.05367100	-0.87390500
H	4.08425000	-3.50921700	-2.01113300
C	1.61099600	-1.81304300	4.18142700
H	2.32665500	-2.47793900	4.67958500
H	0.60107300	-2.23427700	4.29576600
H	1.62327500	-0.83757200	4.68974500
B	-7.02516600	0.02315800	0.40184400
F	-7.45496000	-0.27673400	-0.81746500
F	-6.45141500	1.19796000	0.63410100
F	-7.19115300	-0.84136800	1.39637700

Table-S8. Coordinates [Å] of $[Cu(HL)(CO)]^+$ for the singlet ground state optimized with BP86/TZVP (L = $Ttz^{tBu,Me}$)

Atom	x	y	z
Cu	-0.08747600	-0.23533800	-0.96462400
B	0.02084500	0.05849400	2.10670400
H	0.04950600	0.13418600	3.30481100
N	0.57061600	1.65686500	0.14292200
N	0.52789600	1.46343600	1.51372000
N	1.26637000	3.45724600	1.17344200
N	-1.70876200	-0.32100100	0.27398600
N	-1.41708400	-0.16443300	1.61887400
N	-3.59984000	-0.51364700	1.47461200
N	1.13825100	-1.30587100	0.26794700
N	0.98550100	-1.03017200	1.61642300
N	2.44051500	-2.69391700	1.46485300
O	-0.07477500	-0.18490700	-3.93101100
C	-0.07481500	-0.18595500	-2.78252500
C	1.02616500	2.88313800	-0.05621500
C	0.95097900	2.55764400	2.14669000
C	1.25509100	3.57530200	-1.38385300
C	-0.08393200	3.61215000	-2.15974500
H	-0.48237100	2.60165500	-2.32049900
H	0.07722700	4.07917500	-3.14188000
H	-0.84399600	4.19858800	-1.62241900
C	2.32042900	2.78052500	-2.17767500
H	3.28542500	2.76303400	-1.64963500
H	2.47486700	3.25656100	-3.15657200
H	2.00274200	1.74293600	-2.34521400
C	1.75633700	5.01670900	-1.15400100
H	2.72549500	5.04442200	-0.62942900
H	1.02342400	5.63281400	-0.60800900
H	1.91247000	5.50122200	-2.12751500
C	1.08800100	2.80132100	3.60560300
H	0.62247400	1.98822700	4.17161400
H	0.60689300	3.74957000	3.88700400
H	2.15033700	2.85917800	3.88983900
C	2.02466000	-2.31815700	0.22517200
C	1.78741100	-1.88938600	2.30614800
C	2.51226500	-2.97978200	-1.05290100
C	1.31120100	-3.61370300	-1.79471700
H	0.82429900	-4.37985900	-1.17329100
H	1.65618800	-4.09495400	-2.72209800
H	0.55333700	-2.86193200	-2.06126400
C	3.19872400	-1.92529600	-1.95233200
H	3.54639700	-2.39709400	-2.88365600
H	4.07185800	-1.48531400	-1.44707800
H	2.50976600	-1.11055600	-2.21968900

C	3.52980900	-4.08466500	-0.70558900
H	3.08146000	-4.85787200	-0.06705300
H	4.40056400	-3.67788200	-0.17304400
H	3.87955200	-4.55947000	-1.63455700
C	1.91126200	-1.94703400	3.79281400
H	2.67679100	-2.69030100	4.04399100
H	0.96550100	-2.25062400	4.26635100
H	2.20750900	-0.97927400	4.22321700
C	-3.03794500	-0.53123600	0.23571100
C	-2.58477700	-0.28714700	2.31076400
C	-3.83610000	-0.76549300	-1.03628100
C	-3.27509400	-1.99958700	-1.78119500
H	-2.21800200	-1.86576800	-2.05533300
H	-3.84783100	-2.17207800	-2.70480800
H	-3.35140800	-2.90356800	-1.15888000
C	-5.31286500	-1.02235000	-0.67643100
H	-5.88699600	-1.19049200	-1.59992000
H	-5.75209100	-0.16807600	-0.14328100
H	-5.42186300	-1.90666200	-0.03375300
C	-3.74728300	0.48945700	-1.93729700
H	-2.70788500	0.71258000	-2.21995000
H	-4.16099700	1.37131900	-1.42507000
H	-4.32524000	0.32966400	-2.85987600
C	-2.72098400	-0.19031000	3.79433600
H	-3.76707600	-0.38785100	4.05549400
H	-2.45570400	0.81093400	4.16671200
H	-2.08552400	-0.92260600	4.31313800
H	1.61821100	4.40134100	1.32390400

Table S-9. Coordinates [Å] of $[Cu(H_2L)(CO)]^{+2}$ for the singlet ground state optimized with BP86/TZVP (L = $Ttz^{tBu,Me}$)

Atom	x	y	z
Cu	-0.00303300	0.06109100	-0.98424000
B	0.00359100	-0.01077400	2.11754800
H	0.00496100	-0.03069200	3.31502500
N	1.50513900	-0.93072800	0.22854100
N	1.28205300	-0.78783300	1.59396800
N	3.19969400	-1.73156100	1.35234800
N	0.00392400	1.68077500	0.22773300
N	0.00516100	1.41298700	1.59132000
N	0.01092200	3.61580900	1.37157800
N	-1.50991700	-0.92241000	0.23327400
N	-1.27904200	-0.78389500	1.59784600
N	-3.20122200	-1.72039900	1.36383900
O	-0.00674600	-0.05787800	-3.95612500
C	-0.00521800	-0.03306100	-2.81191000
C	2.68901500	-1.51383500	0.09195000
C	2.32069900	-1.27477200	2.28240100
C	3.40523100	-1.89044600	-1.18883300
C	3.71140900	-0.59431300	-1.98142100
H	2.79245900	-0.04687300	-2.23151400
H	4.21928600	-0.85799000	-2.91989900
H	4.37132100	0.07980300	-1.41595600
C	2.49254100	-2.83190200	-2.01170600
H	2.28734200	-3.76820400	-1.47195300
H	2.99542600	-3.08741700	-2.95486000
H	1.53428000	-2.35348300	-2.25551700
C	4.72829600	-2.61590800	-0.86007900
H	4.56682800	-3.55241200	-0.30216500
H	5.43570700	-1.97300100	-0.31136300
H	5.22566300	-2.89234500	-1.79939700
C	2.54400500	-1.31815200	3.74965100
H	1.64204900	-1.01949300	4.29239100
H	3.35967600	-0.63374800	4.03225400
H	2.82948300	-2.33212300	4.06718200
C	-2.69661900	-1.50079600	0.10131000
C	-2.31569300	-1.26929700	2.29039900
C	-3.42124000	-1.87082900	-1.17668600
C	-3.72265600	-0.57151100	-1.96585400
H	-4.37524900	0.10612200	-1.39611600
H	-4.23689900	-0.83035600	-2.90220300
H	-2.80131900	-0.02984500	-2.21973100
C	-2.51867300	-2.81696800	-2.00536000
H	-3.02791400	-3.06784400	-2.94634600
H	-2.31683100	-3.75539500	-1.46803300
H	-1.55859700	-2.34433700	-2.25328600
C	-4.74748900	-2.58804700	-0.84270700

H	-5.44772400	-1.94151100	-0.28908500
H	-4.58948800	-3.52680700	-0.28758400
H	-5.25137000	-2.85923900	-1.78008300
C	-2.53175200	-1.31487100	3.75870500
H	-2.84421400	-2.32206700	4.07194400
H	-3.32589000	-0.60904200	4.05015000
H	-1.61851300	-1.04539100	4.29789300
C	0.00774100	3.02647000	0.14450900
C	0.00980000	2.61558400	2.24809100
C	0.00761700	3.81323100	-1.15490500
C	-1.26387700	3.46669900	-1.96629100
H	-1.31100500	2.39531600	-2.21569600
H	-1.26894300	4.03412900	-2.90820400
H	-2.17420000	3.73068400	-1.40778600
C	0.01104400	5.32371500	-0.84452800
H	0.01109600	5.88399500	-1.79072500
H	0.89937600	5.61683100	-0.26885400
H	-0.87481100	5.62040600	-0.26686600
C	1.27591300	3.46146300	-1.96910700
H	1.31836500	2.38976300	-2.21800700
H	2.18852900	3.72228700	-1.41285700
H	1.28095200	4.02839700	-2.91132200
C	0.01950600	2.78989500	3.72982900
H	-0.06075900	3.86105700	3.94803800
H	0.95336800	2.42001400	4.17998900
H	-0.82102300	2.27291900	4.21538800
H	4.10146700	-2.16698300	1.54821600
H	-4.10349100	-2.15318100	1.56328300

Table-S10. Coordinates [Å] of $[Cu(H_3L)(CO)]^{+3}$ for the singlet ground state optimized with BP86/TZVP (L = $Ttz^{tBu,Me}$)

Atom	x	y	z
Cu	-0.00419500	0.00044800	-0.99488300
B	0.00207300	-0.00787100	2.11944600
H	0.00281900	-0.01050200	3.31402900
N	1.24994000	-1.21176700	0.21991700
N	1.05733500	-1.03985500	1.59165600
N	2.57829000	-2.53734200	1.33867300
N	0.42160700	1.68600400	0.23035900
N	0.36920500	1.42470700	1.60009500
N	0.91144500	3.49025200	1.36031600
N	-1.67669000	-0.47797800	0.22851700
N	-1.42126100	-0.40422400	1.59855400
N	-3.48010000	-0.97281800	1.35829500
O	-0.01020600	0.01377400	-3.97883600
C	-0.00775200	0.00878000	-2.83786500
C	2.19167300	-2.13967700	0.07770300
C	1.87556500	-1.85595100	2.27665100
C	2.78362000	-2.70233400	-1.19855800
C	3.42288000	-1.54150500	-2.00224100
H	2.68230600	-0.77450500	-2.26974400
H	3.84501000	-1.94325000	-2.93379700
H	4.23900400	-1.06119000	-1.44284300
C	1.65191600	-3.37870700	-2.01425800
H	1.20177700	-4.21865500	-1.46514300
H	2.07354500	-3.77531000	-2.94841900
H	0.85783500	-2.66580100	-2.27704400
C	3.86730100	-3.74960900	-0.85833500
H	3.46041900	-4.61802500	-0.31508900
H	4.71177000	-3.31717200	-0.29762200
H	4.28719900	-4.14147100	-1.79444500
C	2.02608900	-2.03961600	3.74168000
H	1.46660900	-1.28396700	4.30148100
H	3.08673300	-1.97327400	4.02889100
H	1.66413200	-3.03658000	4.04166100
C	-2.95235300	-0.82850500	0.09408400
C	-2.53200000	-0.70874000	2.29037000
C	-3.74680800	-1.04590800	-1.17723900
C	-3.77797600	0.28468400	-1.97258400
H	-4.27277000	1.08611000	-1.40462200
H	-4.34517700	0.13132300	-2.90106000
H	-2.76728200	0.62047300	-2.24403300
C	-3.06537900	-2.16504600	-2.00494200
H	-3.62592700	-2.31010400	-2.93891600
H	-3.05823100	-3.12300000	-1.46464400

H	-2.03081400	-1.90386900	-2.26854500
C	-5.19163700	-1.47028700	-0.83012700
H	-5.73920900	-0.69325000	-0.27225500
H	-5.23141400	-2.42552400	-0.28191700
H	-5.74783100	-1.62763000	-1.76399300
C	-2.75856500	-0.73922600	3.75690600
H	-3.33251400	-1.63458200	4.03799800
H	-3.34421400	0.14134700	4.07038500
H	-1.81474000	-0.74244200	4.31079200
C	0.75733100	2.96556200	0.09594500
C	0.67204400	2.53562700	2.29216000
C	0.95334300	3.76448200	-1.17605400
C	-0.36902600	3.74355600	-1.98440100
H	-0.66783500	2.71938400	-2.24891100
H	-0.22583100	4.30594200	-2.91758300
H	-1.19205500	4.21694400	-1.42922200
C	1.32054300	5.22456500	-0.82916900
H	1.46128800	5.78590900	-1.76245100
H	2.27097500	5.30330700	-0.27656600
H	0.51976800	5.74067100	-0.27514900
C	2.10585100	3.12189500	-1.98963900
H	1.88376200	2.07884800	-2.25631200
H	3.05636000	3.14704600	-1.43672900
H	2.24357700	3.68770600	-2.92142700
C	0.77998500	2.74024700	3.75829200
H	0.33316700	3.70348700	4.04492200
H	1.84002900	2.76440200	4.06274600
H	0.27765500	1.94389900	4.31584200
H	3.29419200	-3.24325400	1.52549700
H	-4.44756100	-1.24265500	1.55052000
H	1.16813600	4.46081600	1.55384100

Table-S11. Coordinates [Å] of $[Cu(L)(CO)]^+$ where the Cu-N bond of the triazolyl ligand is broken, and the corresponding nitrogen atom is protonated. Obtained for the singlet ground state with BP86/TZVP (L = $Ttz^{tBu,Me}$)

Atom	x	y	z
Cu	-0.69806300	0.69687900	-0.95441600
B	0.02607600	-0.83304100	1.79511900
H	0.10421800	-1.27343800	2.91148800
N	2.05770000	-0.92197000	0.12930100
N	1.13061000	-1.57374300	0.90266000
N	2.53371000	-3.06113800	-0.00532900
N	0.24742500	1.45917700	0.65206700
N	0.35333700	0.67358600	1.79930700
N	0.86287000	2.75258300	2.38571600
N	-1.79703600	-0.65811800	-0.00461300
N	-1.38509300	-1.10864500	1.24088900
N	-3.48468300	-1.77553000	0.96737800
O	-0.21230600	1.12581700	-3.85365300
C	-0.41369500	0.98316900	-2.73510100
C	2.89690300	-1.83445000	-0.41101600
C	1.46221400	-2.88294100	0.79378000
C	4.06766100	-1.51354700	-1.30787900
C	4.16424400	0.00137200	-1.56860800
H	3.26992800	0.39164600	-2.08100400
H	5.02172700	0.20384000	-2.22507200
H	4.32840700	0.57323600	-0.64108400
C	3.87425600	-2.27620100	-2.64160100
H	3.78586700	-3.35661400	-2.46605700
H	4.74367900	-2.09773100	-3.29084400
H	2.97419100	-1.93464900	-3.17499600
C	5.35417100	-2.01443800	-0.60359000
H	5.29597300	-3.09196700	-0.39950800
H	5.52535500	-1.48743700	0.34726400
H	6.21925500	-1.82918800	-1.25688900
C	0.73322900	-3.98442700	1.47606800
H	0.56892000	-3.75402800	2.53850500
H	1.32467300	-4.90316300	1.39245300
H	-0.24794500	-4.15792300	1.00799800
C	-3.07204500	-1.08615000	-0.12442800
C	-2.43591200	-1.77503600	1.79694600
C	-3.95228700	-0.83171400	-1.33669800
C	-4.05790200	0.68969200	-1.59610500
H	-4.48727300	1.21418400	-0.72972900
H	-4.70470700	0.87838400	-2.46579400
H	-3.07246800	1.13673600	-1.81272200
C	-3.34279500	-1.54341500	-2.56869300
H	-3.97302000	-1.36473500	-3.45256300
H	-3.28527100	-2.63006500	-2.40721400

H	-2.32972200	-1.17750200	-2.79243300
C	-5.36383600	-1.39257300	-1.07290400
H	-5.83201000	-0.91307000	-0.20225500
H	-5.33689400	-2.47389700	-0.88271200
H	-5.99602700	-1.20886000	-1.95423800
C	-2.44867900	-2.40500900	3.14985100
H	-3.47156900	-2.73926500	3.35854300
H	-2.13904600	-1.69930400	3.93315400
H	-1.78454400	-3.28032200	3.20559500
C	0.55880000	2.71028900	1.06720400
C	0.73236400	1.49181000	2.81742800
C	0.55470800	3.93429600	0.16728800
C	-0.85436700	4.11534900	-0.44706100
H	-1.14305500	3.25124600	-1.06964100
H	-0.87125700	5.00819900	-1.08942500
H	-1.61741100	4.24178800	0.33490600
C	0.90609900	5.18396400	0.99862000
H	0.90270500	6.06700600	0.34279400
H	1.89982000	5.09523200	1.45830900
H	0.17945300	5.34726900	1.80604800
C	1.60502200	3.75578700	-0.95481100
H	1.38751600	2.87725600	-1.58068100
H	2.61602200	3.64413500	-0.53485100
H	1.60790900	4.64060400	-1.60836900
C	0.96889400	1.05625900	4.22389800
H	1.36369700	1.90914400	4.78770000
H	1.68708600	0.22611000	4.28130400
H	0.03525500	0.72499100	4.70276200
H	2.00830500	0.09538400	0.03380800

Table-S12. Coordinates [Å] of $[Cu(L)(CO)]^+$ where the B-N bond of the triazolyl ligand is broken, and the corresponding nitrogen atom is protonated. Obtained for the singlet ground state with BP86/TZVP (L = $Ttz^{tBu,Me}$)

Atom	x	y	z
Cu	0.07655300	-0.02968400	-0.82025200
B	1.82287600	2.64042500	0.40061900
H	2.45495500	3.59862300	0.70853400
N	-0.94469600	-1.18122300	0.59901300
N	-0.74389700	-0.71679800	1.87809600
N	-2.03746700	-2.45768100	2.11375400
N	2.06216600	0.12768100	-0.02049900
N	2.56018500	1.41429400	0.25575400
N	4.31473900	0.05334700	0.25983600
N	-0.55153700	1.91992900	-0.21681300
N	0.40515800	2.83992600	0.24209800
N	-1.53695900	3.91582100	0.22166500
O	0.22985300	-0.32665300	-3.79211900
C	0.14542200	-0.24861700	-2.65158100
C	-1.74500700	-2.25314200	0.79440200
C	-1.40324400	-1.49277900	2.77217200
C	-2.32215500	-3.19088200	-0.25195000
C	-1.89439500	-4.63355400	0.11893300
H	-0.80168100	-4.75317100	0.06391900
H	-2.34996900	-5.34293200	-0.58802000
H	-2.22127500	-4.89235200	1.13457000
C	-1.85991300	-2.87965900	-1.68281100
H	-2.17913500	-1.88151500	-2.01410500
H	-2.30887700	-3.61095400	-2.37107000
H	-0.76850900	-2.95779900	-1.78688400
C	-3.86685200	-3.08733500	-0.17500400
H	-4.21445500	-2.07771300	-0.44225300
H	-4.22571600	-3.32257400	0.83595500
H	-4.31752600	-3.80080500	-0.88101800
C	-1.39033700	-1.27748900	4.24633400
H	-0.83889600	-0.36859300	4.52266000
H	-0.92369700	-2.13660300	4.75020800
H	-2.41923100	-1.19409200	4.62298900
C	-1.69285600	2.61935000	-0.22363900
C	-0.26011100	4.04527700	0.49119000
C	-3.07206200	2.12614200	-0.61641400
C	-3.85978900	3.29806500	-1.24829200
H	-3.96441600	4.13784600	-0.55057000
H	-4.86313900	2.94371400	-1.52667900
H	-3.36494900	3.66792900	-2.15859800
C	-3.01404900	0.96476400	-1.61913900
H	-4.03758000	0.64315000	-1.86168100
H	-2.47870900	0.09797600	-1.20800600

H	-2.52828200	1.26927200	-2.55824500
C	-3.78876700	1.67522900	0.68431000
H	-3.83537900	2.49628200	1.41428800
H	-3.27880500	0.81762200	1.14822200
H	-4.81925100	1.37239500	0.44571200
C	0.38226300	5.29408400	0.99045100
H	-0.39809000	6.05680000	1.09167300
H	1.14709400	5.66419500	0.29193500
H	0.86228400	5.14732500	1.96890100
C	3.15345400	-0.64573800	-0.00605900
C	3.94664600	1.30020900	0.41846700
C	3.25390800	-2.13428900	-0.26208100
C	4.07793900	-2.31797900	-1.56469200
H	3.55780300	-1.88775700	-2.43410300
H	4.22285600	-3.39234600	-1.75216300
H	5.06531200	-1.84460900	-1.47857700
C	4.02540100	-2.77055300	0.92245600
H	4.16073800	-3.84483800	0.72829100
H	3.46729200	-2.66354200	1.86522700
H	5.01389200	-2.31033100	1.04734200
C	1.89153300	-2.81876900	-0.40651700
H	1.30727400	-2.39656400	-1.23684800
H	1.29329600	-2.73681400	0.51104300
H	2.04567800	-3.88701400	-0.61790800
C	4.87167200	2.42980200	0.71821700
H	5.88835600	2.02529300	0.77846200
H	4.62841200	2.91568500	1.67448100
H	4.84375500	3.19858700	-0.06764400
H	-0.16070300	0.10226100	2.02828200

Table-S13. Coordinates [Å] of $[Cu(L)(CO)]_2H^+$ for the singlet ground state optimized with BP86/TZVP (L = $Ttz^{tBu,Me}$)

Atom	x	y	z
Cu	5.68750400	-0.89460000	-0.02071500
B	4.51916200	1.92398900	0.13088600
H	4.06108900	3.03468800	0.19226500
N	3.57019600	-0.46577500	0.07453100
N	3.33019800	0.88791900	0.11312900
N	1.35778100	-0.10499100	0.08938300
N	6.03634700	0.42960500	1.53110600
N	5.40128200	1.64582900	1.36834400
N	6.54923500	1.77464200	3.25916700
N	5.93675900	0.55330300	-1.48067600
N	5.33278000	1.75679100	-1.17170900
N	6.37688700	2.04662400	-3.10408900
O	6.75571600	-3.65517100	-0.18881900
C	6.33097500	-2.58820300	-0.12240000
C	2.36428000	-1.04224900	0.06595400
C	2.00003700	1.08522900	0.12413800
C	2.16740100	-2.55083000	0.05547100
C	2.91296800	-3.16655100	1.26352400
H	3.98449600	-2.92918300	1.23798900
H	2.80077300	-4.26111200	1.25278100
H	2.50732600	-2.78932600	2.21462600
C	2.73061800	-3.12802500	-1.26564600
H	2.18705000	-2.73244500	-2.13703500
H	2.63079000	-4.22389800	-1.26869300
H	3.79306200	-2.87816800	-1.38852400
C	0.67565000	-2.91302800	0.16518100
H	0.09757000	-2.53116800	-0.68753900
H	0.23326900	-2.52818500	1.09611600
H	0.56931300	-4.00764600	0.17510200
C	1.34021800	2.42441700	0.18262600
H	1.71428800	3.01434600	1.03066700
H	0.25595600	2.30606900	0.29679200
H	1.53047600	3.00858500	-0.72971100
C	6.55564900	0.77448700	-2.65519000
C	5.62092300	2.63269400	-2.17006500
C	7.37640400	-0.26348600	-3.40308000
C	8.58379300	-0.68581100	-2.53237600
H	9.23479000	0.17531600	-2.31973600
H	9.18153300	-1.44386200	-3.06121400
H	8.26162200	-1.11149700	-1.57100800
C	6.49638600	-1.49377000	-3.72456500
H	7.09263900	-2.25374500	-4.25211700
H	5.65038900	-1.21375900	-4.37045500
H	6.09125800	-1.95180600	-2.81083600

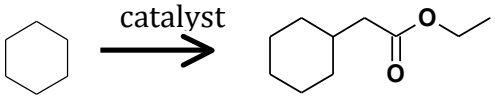
C	7.89483300	0.34100500	-4.72262700
H	8.52691400	1.22084300	-4.54126300
H	7.06702700	0.65657900	-5.37306500
H	8.49122000	-0.41375400	-5.25756400
C	5.17790700	4.05810400	-2.21940500
H	5.52809300	4.49368400	-3.16251400
H	5.59981600	4.64291900	-1.38837800
H	4.08318800	4.15356000	-2.17215500
C	6.71757500	0.55235300	2.68511700
C	5.73414300	2.43072700	2.42717600
C	7.58719600	-0.53796300	3.29000100
C	8.72981900	-0.89077100	2.30904300
H	8.34045500	-1.24693200	1.34443900
H	9.36258900	-1.68305000	2.73728400
H	9.36502800	-0.01371600	2.11495500
C	8.19723500	-0.03611400	4.61344400
H	8.82692200	-0.82836300	5.04614900
H	7.41793400	0.22823400	5.34161400
H	8.81839700	0.85622000	4.45576500
C	6.72491900	-1.79013400	3.57461500
H	6.26912500	-2.18474100	2.65499800
H	5.91617700	-1.55767700	4.28416100
H	7.34788700	-2.58335000	4.01543000
C	5.27064900	3.83477900	2.63778200
H	5.70907900	4.20368300	3.57241000
H	4.17507400	3.89942700	2.71618000
H	5.58645100	4.49668700	1.81804200
Cu	-5.80611600	0.11247000	-0.88105200
B	-4.58558600	-0.14657100	1.92540800
H	-4.12924900	-0.24714700	3.03312500
N	-6.05506800	-1.50616200	0.35738900
N	-5.45093400	-1.37393000	1.59385500
N	-6.55643700	-3.29248900	1.62804900
N	-3.55686900	0.02424200	-0.46255900
N	-3.36660800	-0.10291700	0.90418100
N	-1.39864800	-0.09099800	-0.00617200
N	-5.97177100	1.52409000	0.59796000
N	-5.37351600	1.16862800	1.79264200
N	-6.37086300	3.11639300	2.13485900
O	-6.94801500	0.33273200	-3.61039200
C	-6.47861700	0.25094100	-2.56479400
C	-6.71202700	-2.68010600	0.42328500
C	-5.77557200	-2.46931100	2.33290500
C	-7.54765100	-3.26567900	-0.70330600
C	-6.67248500	-3.43713700	-1.96661800
H	-6.25384300	-2.47804600	-2.30409900

H	-7.27570900	-3.85403000	-2.78714000
H	-5.83672800	-4.12700800	-1.77397700
C	-8.73899000	-2.32344100	-0.99906800
H	-9.38380800	-2.21685500	-0.11404900
H	-9.34895800	-2.73342900	-1.81823600
H	-8.40010000	-1.31950900	-1.29353800
C	-8.09151000	-4.64406500	-0.27839900
H	-8.72165600	-4.56816200	0.61796300
H	-7.27678600	-5.34618300	-0.05303300
H	-8.69653100	-5.06261100	-1.09680300
C	-5.34054900	-2.72146700	3.73889600
H	-4.24593200	-2.78930900	3.82699700
H	-5.77423900	-3.67385100	4.06519300
H	-5.68322600	-1.92938000	4.42068900
C	-6.56250400	2.70739800	0.85150300
C	-5.63640900	2.15173300	2.69574700
C	-7.36783900	3.50336000	-0.16225400
C	-6.48793700	3.82518900	-1.39278000
H	-5.61617500	4.43208200	-1.10449500
H	-7.07155100	4.39558600	-2.13100700
H	-6.12228000	2.91013100	-1.88084200
C	-8.60539000	2.67954800	-0.59206400
H	-9.19498900	3.24497100	-1.32951900
H	-9.25359300	2.46428500	0.27042200
H	-8.31703200	1.72017800	-1.04580300
C	-7.84009900	4.82410200	0.47660800
H	-6.99035800	5.44135700	0.80025000
H	-8.47146500	4.64218800	1.35675100
H	-8.42482600	5.39453500	-0.26082300
C	-5.18904400	2.15597600	4.12035900
H	-5.55367400	3.07647100	4.59082600
H	-4.09290900	2.12877900	4.21063600
H	-5.59215300	1.29657300	4.67613500
C	-2.34399500	0.03157500	-1.00566700
C	-2.05984900	-0.17191800	1.17169800
C	-1.98895300	0.20683800	-2.46946700
C	-1.38844700	1.62403500	-2.65697400
H	-2.10131500	2.40430300	-2.35253400
H	-1.14533600	1.77826600	-3.71856700
H	-0.46206600	1.74959000	-2.07863600
C	-0.94477600	-0.85659500	-2.88090300
H	-0.70104700	-0.72930500	-3.94562700
H	-1.33525200	-1.87598000	-2.74412800
H	-0.00826200	-0.75574000	-2.31296900
C	-3.23507900	0.06398700	-3.35681500
H	-3.96950900	0.85101900	-3.14169400

H	-3.71767500	-0.91502700	-3.22674600
H	-2.93756400	0.16095300	-4.41083800
C	-1.41239700	-0.31244100	2.50501800
H	-0.32189300	-0.28775400	2.39087000
H	-1.69736900	-1.26123600	2.98089100
H	-1.71944500	0.50107200	3.17628000
H	-0.30632200	-0.14297200	-0.06393500

General Procedure for C-H Activation of Cyclohexane Catalyzed by (Ttz^{tBuMe})Cu($NCCH_3$) (5). The procedure used for C-H activation is very similar to that reported in the literature.[10] The C-H activation reactions were performed in a 25 mL round bottomed flask equipped with a nitrogen inlet, rubber septum, and a magnetic stir bar. In a typical experiment, 0.01 mmol of (Ttz^{tBuMe})Cu($NCCH_3$) (**5**) was mixed with 5 mL of cyclohexane and 1 mL of dichloromethane. In a separate flask, 0.5 mmol of ethyl diazoacetate (EDA) was mixed with 3.5 mL of dichloromethane and 5 mL of cyclohexane. The EDA solution was slowly added over 6 hours at 50°C under N_2 via a syringe pump. For studies under acidic conditions, all conditions were identical to those listed above, except 0.01 mmol or 0.02 mmol of HBF_4 in dichloromethane was added to the solution of **5** prior to starting the reaction. This presumably forms monoprotonated or doubly-protonated **5**.

For both acidic and non-acidic conditions, at the end of 6 hours, the volatiles were removed and the % yield of product was determined by ^{1}H-NMR, with an exact mass of hexamethylcyclotrisiloxane added to the NMR tube as an internal standard. The reaction that occured is shown in eq. 2, and the yield of product was determined by the integration of the italicized hydrogens in cyclohexyl-C*H*$_2$CO$_2$Et, which have δ = 2.16 ppm (doublet). The results are shown in **Table-S5**.



(2)

Table-S5. Product yields for C-H activation of cyclohexane with EDA in the presence of **5** and **[5•H]**$^+$ and **[5•2H]**$^{2+}$. In each case, **5** or protonated **5** is present at 2 mol % relative to EDA.

Catalyst	Yield of product[a]	TON[b]	TOF[c] (h^{-1})
5	10%	5	0.83
[5•H]$^+$	20%	10	1.7
[5•2H]$^{2+}$	40%	20	3.3

[a]Percent yields are determined by ^{1}H-NMR. Diethyl fumarate and diethyl maleate side-products account for the remainder. [b]TON = turnover numbers. [c]TOF = turnover frequency.

Control Experiment: Reactivity of Cyclohexane with HBF_4•$(CH_3CH_2)_2O$. The procedure used is nearly identical to the one described above; however, 0.01 mmol of HBF_4•$(CH_3CH_2)_2O$ was mixed with 5 mL of cyclohexane and 1 mL of dichloromethane with no catalyst present. In a separate flask, 0.5 mmol of ethyl diazoacetate (EDA) was mixed with 3.5 mL of dichloromethane and 5 mL of cyclohexane. The EDA solution was slowly added over 6 hours at room temperature under N_2 via a syringe pump.

At the end of 6 hours, the volatiles were removed and the product was analyzed by ^{1}H-NMR, with an exact mass of hexamethylcyclotrisiloxane added to the NMR tube as an internal standard. No product was detected by ^{1}H-NMR, this confirms that the acid does not activate the C-H bond in cyclohexanes. However, diethyl fumarate and diethyl maleate were detected, suggesting that H^+ lead to decomposition of the ethyl diazoacetate.

Titration of ($Ttz^{tBu,Me}$)CuCO (1) to determine apparent pK_a in mixed media. Complex **1**

(0.016g, 0.031 mmol) was dissolved in 90% CH_3CN / 10% H_2O and first protonated with excess HCl (more than 2 equiv.) in the same solvent mixture. The titration curve for protonation of **1** did not show readily discernible equivalence points, so deprotonation of the complex prepared above from **1** and HCl, which is presumably **1•2H**$^+$, was used to measure apparent acidity. **1•2H**$^+$ was treated with a standardized solution of KOH (0.0042M) in 90% CH_3CN /10% H_2O, and the apparent pH was monitored by a pH meter. The volume of KOH solution added was recorded from the buret reading at each pH measurement, to produce the titration curve shown in Fig. S3. From an analysis of the first and second derivatives of the curve in Fig. S3, there are two equivalence points, one at 2.07 mL of KOH solution is assigned to neutralization of excess HCl, and a second equivalence point at 20.00 mL of KOH solution is assigned to deprotonation of **1•2H**$^+$ to form **1**. This second equivalence point corresponds to a ratio of 2.43 equiv. of base to 1 equiv. of **1•2H**$^+$ [2.43 to 1 ratio calculated as (17.93 mL × 0.0042M / 0.031 mmol)]. Given the experimental error of these measurements, we assign this to removal of 2 protons from **1•2H**$^+$. The apparent pK_a for this process is approximately 3.6.

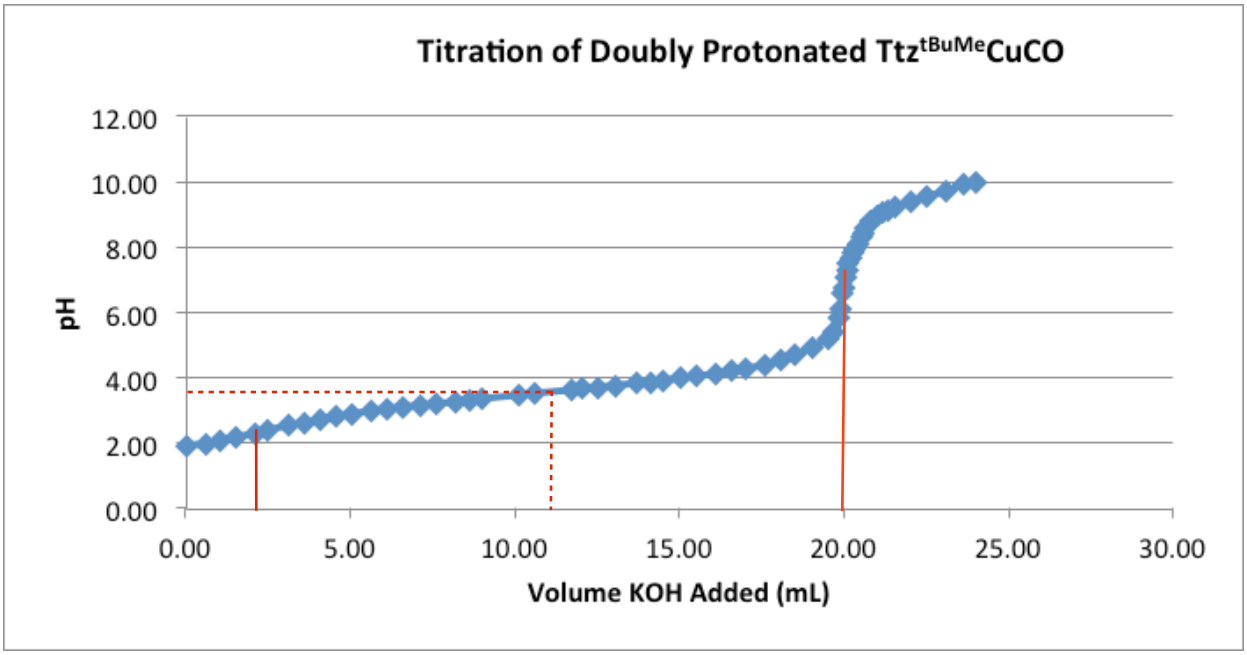


Figure S3. Titration curve for deprotonation of **1•2H**$^+$ with KOH in 90% CH_3CN /10% H_2O. Solid lines (in red) show the approximate locations of equivalence points (at 2.07 mL and 20.00 mL) for neutralization of excess HCl and **1•2H**$^+$, respectively. The dotted lines show the location of the half equivalence point for **1•2H**$^+$ at 11.04 mL of KOH and pH ~ 3.6 = pK_a.

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