Supplementary Material (ESI) for Dalton Transactions

Synthesis and Catalytic Activity of an Electron-Deficient Copper-Ethylene Triazapentadienyl Complex

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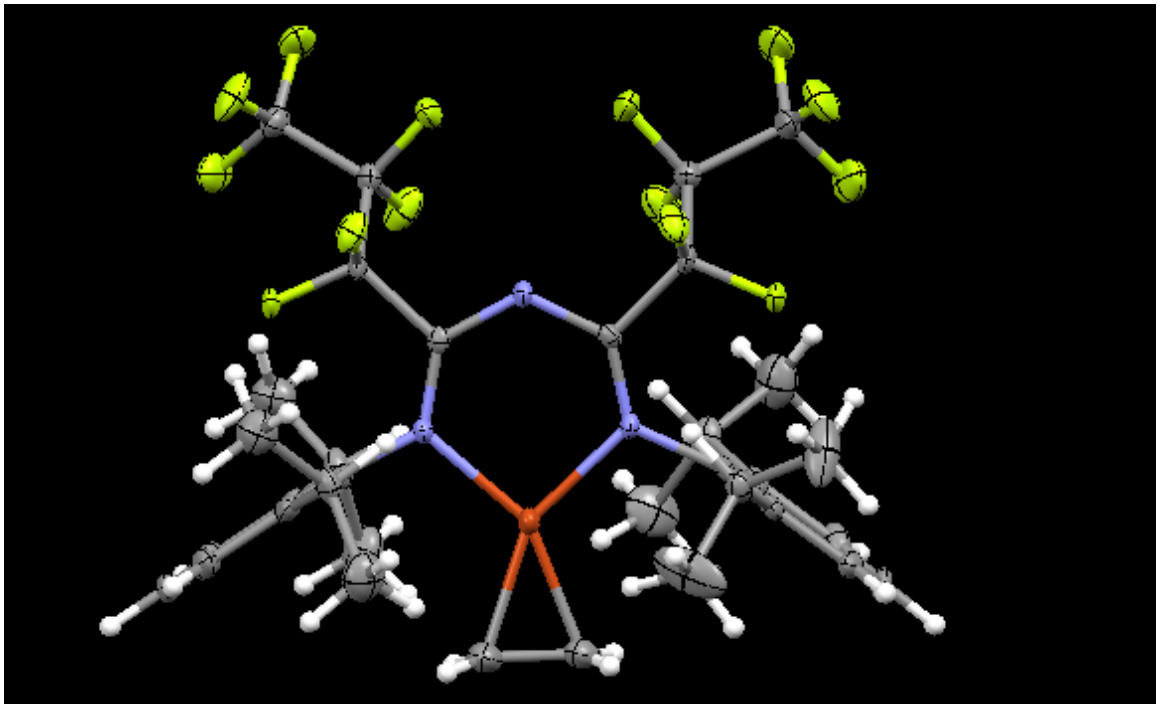
Supporting Information

Table S1. Crystal data and structure refinement for $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$, dias174t.

Identification code	dias174t	
Empirical formula	C34 H38 Cu F14 N3	
Formula weight	818.21	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/n	
Unit cell dimensions	a = 10.4857(4) Å	α= 90°.
	b = 23.4593(9) Å	β= 97.622(1)°.
	c = 14.9020(6) Å	γ = 90°.
Volume	3633.3(2) $Å^3$	
Z	4	
Density (calculated)	1.496 Mg/m^3	
Absorption coefficient	0.702 mm^{-1}	
F(000)	1672	
Crystal size	0.31 x 0.21 x 0.05 mm^3	
Theta range for data collection	1.63 to 27.52°.	
Index ranges	-13<=h<=13, -30<=k<=30, -19<=l<=19	
Reflections collected	50026	
Independent reflections	50113 [R(int) = 0.0338]	
Completeness to theta = 27.52°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9664 and 0.8144	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	50113 / 0 / 516	
Goodness-of-fit on F^2	1.031	
Final R indices [I>2sigma(I)]	R1 = 0.0431, wR2 = 0.0643	
R indices (all data)	R1 = 0.0685, wR2 = 0.0679	
Largest diff. peak and hole	1.380 and -0.922 e.$Å^{-3}$	



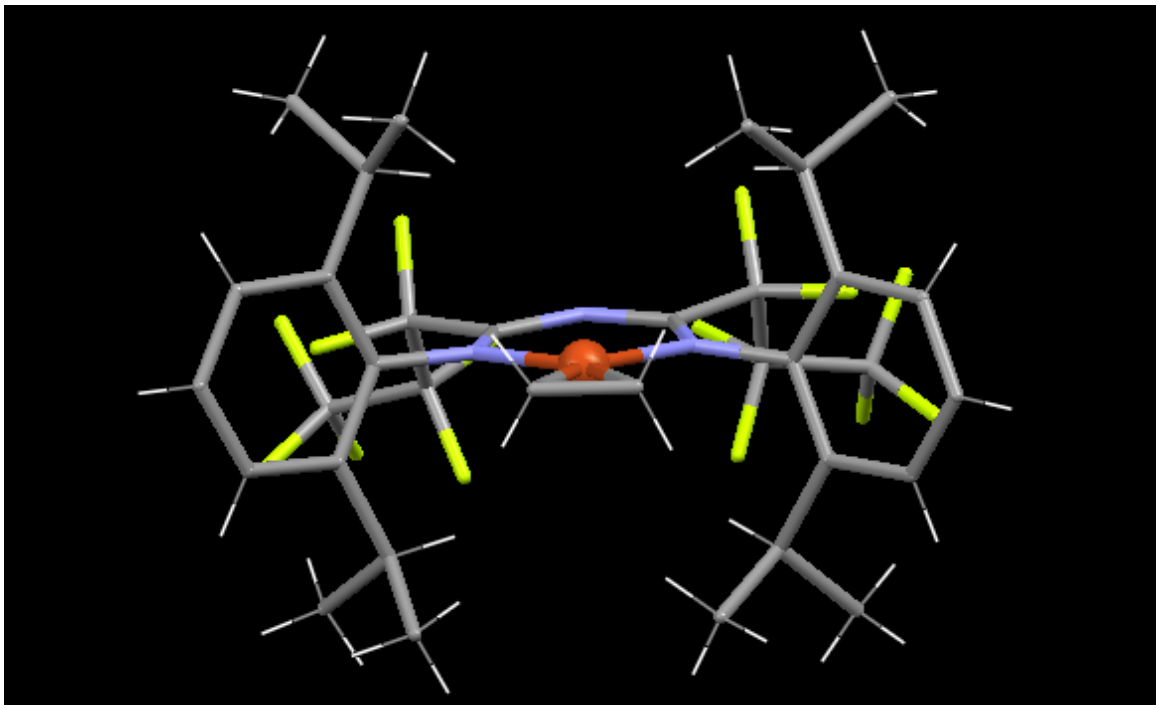
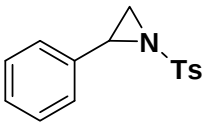


Figure S1. Two views of $[N\{(C_3F_7)C(Dipp)N\}_2]Cu(C_2H_4)$ based on X-ray data

Starting material: $[N\{(C_3F_7)C(Dipp)N\}_2]H$ (Dipp = 2,6-diisopropylphenyl)[1], $[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$[1] and *N*-(p-toluenesulfonyl)phenyliodinane[2] were synthesized using published procedures. $(CuOTf)_2$·benzene, n-butyllithium, ethylene, ethyl diazoacetate and Silica gel, 200 - 400 mesh, 60 Å were purchased from commercial sources. Experimental details are in the manuscript.

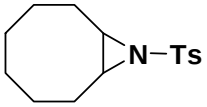
<u>Products from catalytic processes and the ^{1}H NMR data</u>

N-(*p*-Toluenesulfonyl)-2-phenylaziridine.[3-5]



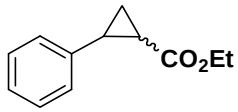
^{1}H NMR ($CDCl_3$) δ = 7.85 (d, 2H, *J* = 8.3 Hz), 7.32 to 7.19 (m, 7H), 3.76 (dd, 1H, *J* = 7.3 Hz, *J* = 4.4 Hz, 1H), 2.97 (d, 1H, *J* = 6.8 Hz), 2.42 (s, 3H, C*H*$_3$), 2.37 (d, 1H, *J* = 4.9 Hz)

N-(*p*-Toluenesulfonyl)-9-azabicyclo[6.1.0]nonane.[5-8]



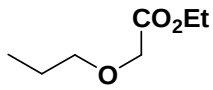
^{1}H NMR ($CDCl_3$) δ = 7.78 (d, 2H, *J* = 7.3 Hz, *m*-Ar), 7.29 (d, 2H, *J* = 7.3 Hz, *o*-Ar), 2.78-2.74 (m, 1H), 2.42 (s, 3H, C*H*$_3$), 2.20-1.97 (m, 1H), 1.55 to 1.25 (m, 12H, C*H*$_2$)

Ethyl 2-phenylcyclopropane-1-carboxylate.[9-11]



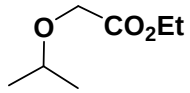
^{1}H NMR ($CDCl_3$) δ = Cis: 7.27 to 7.14 (m, 5H, *o*,*m*,*p*-Ar), 3.86 (q, 2H, *J* = 7.2 Hz, C*H*$_2$), 2.57 (q, 1H, *J* = 8.1 Hz), 2,10 to 2.01 (m, *J* = 6.0 Hz, 1H), 1.73 to 1.66 (m, *J* = 5.3 Hz 1H), 1.35 to 1.26 (m, 1H), 0.95 (t, 3H, *J* = 7.1 Hz, C*H*$_3$); trans: 7.29 to 7.60 (m, 5H, *o*,*m*,*p*-Ar), 4.15 (q, 2H, *J* = 7.0 Hz, C*H*$_2$), 2.53-2.47 (m, 1H, *J* = 5.0 Hz), 1.92 to 1.85 (m, 1H, *J* = 4.5 Hz), 1.63 to 1.55 (m, 1H, *J* = 4.8 Hz), 1.33 to 1.27 (m, 1H), 1.26 (t, 3H, *J* = 7.3 Hz, C*H*$_3$)

Ethyl propoxyacetate.[12]



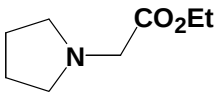
^{1}H NMR ($CDCl_3$) δ = 4.19 (q, 2H, *J* = 7.2 Hz, CO_2C*H*$_2$), 4.04 (s, 2H, C*H*$_2CO_2$), 3.46 (t, 2H, *J* = 6.7 Hz, C*H*$_2$O), 1.62 (sextet, 2H, *J* = 7.2 Hz, C*H*$_2$), 1.26 (t, 3H, *J* = 7.3 Hz, CH_2C*H*$_3$), 0.91 (t, 3H, *J* = 7.6 Hz, C*H*$_3$)

Ethyl isopropoxyacetate.[12]



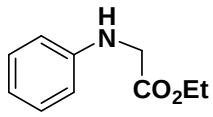
^{1}H NMR ($CDCl_3$) δ = 4.19 (q, 2H, *J* = 7.0 Hz, CO_2C*H*$_2CH_3$), 4.04 (s, 2H, C*H*$_2CO_2$), 3.65 (heptet, 1H, *J* = 6.3 Hz, C*H*$(CH_3)_2$), 1.26 (t, 3H, *J* = 7.1 Hz, C*H*$_3$), 1.18 (d, 6H, *J* = 6.4 Hz, $CH(CH_3)_2$)

Ethyl N-pyrrolidinylacetate.[13]



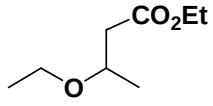
^{1}H NMR ($CDCl_3$), selected: δ = 3.30 (s, 2H, NC*H*$_2$CO$_2$C$_2$H$_5$).

Ethyl 2-(phenylamino)acetate.[13-14]



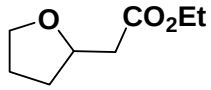
^{1}H NMR ($CDCl_3$) δ = 7.19 (t, 2H, *J* = 7.8 Hz, *m*-Ar), 6.74 (t, 1H, *J* = 7.3 Hz, *p*-Ar), 6.60 (d, 2H, *J* = 7.8 Hz, *o*-Ar), 4.23 (q, 2H, *J* = 7.3 Hz, C*H*$_2$), 3.89 (s, 2H, C*H*$_2$), 1.28 (t, 3H, *J* = 7.1 Hz, C*H*$_3$)

Ethyl 3-ethoxybutanoate.[15]



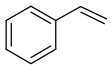
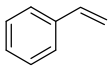
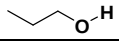
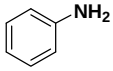
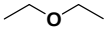
^{1}H NMR ($CDCl_3$) δ = 4.12 (q, 2H, *J* = 7.2 Hz, CO$_2$C*H*$_2$CH$_3$), 3.84 (sextet, 1H, *J* = 6.4 Hz, C*H*), 3.48 (m, 2H, *J* = 7.1 Hz, C*H*$_2$O), 2.55 (dd, 1H, *J* = 14.7 Hz, *J* = 7.3 Hz, C*H*$_2$CO$_2$), 2.33 (dd, 1H, *J* = 14.7 Hz, *J* = 6.0 Hz, C*H*$_2$CO$_2$), 1.23 (t, 3H, *J* = 7.1 Hz, C*H*$_3$), 1.17 (d, 3H, *J* = 6.0 Hz, CHC*H*$_3$), 1.14 (t, 3H, *J* = 6.9 Hz, C*H*$_3$)

Ethyl (tetrahydrofuran-2-yl)acetate.[15]



^{1}H NMR ($CDCl_3$) δ = 4.22 (quintet, 1H, *J* = 6.8 Hz, C*H*), 4.13 (q, 2H, *J* = 7.1 Hz, $CO_2CH_2CH_3$), 3.89 to 3.68 (m, 2H, *J* = 7.0 Hz, CH_2O), 2.56 (dd, 1H, *J* = 15.1 Hz, *J* = 7.2 Hz, CH_2CO_2), 2.43 (dd, 1H, *J* = 15.1 Hz, *J* = 6.2 Hz, CH_2CO_2), 2.05 (m, 1H, CH_2), 1.88 (m, 2H, CH_2), 1.53 (m, 1H, CH_2), 1.24 (t, 3H, *J* = 6.9 Hz, CH_3)

Table S2. Catalysis by nitrene and carbene transfer with $[N\{(C_3F_7)C(Dipp)N\}_2]CuL$, L = $NCCH_3$, C_2H_4.

Entry	**Catalyst →** **Substrate**	$[N\{(C_3F_7)C(Dipp)N\}_2]CuNCCH_3$ **Yield (%)**	$[N\{(C_3F_7)C(Dipp)N\}_2]CuC_2H_4$ **Yield (%)**	**Catalyst Loading (mol%)**
Aziridination of alkenes				
1		98	96	5
2		76	76	5
Cyclopropanation of styrene				
3		97 (1.6)*	93 (1.6)*	5
O-H activation of alcohols				
4		85	90	2
5		85	91	2
N-H activation of amines				
6		80	93	2
7		85	~100	2
C-H Activation of ethers				
8		94	92	5
9		98	98	5

*cis/trans

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