Supporting Information

For

Nitrosoarene-Cu(I) Complexes are Intermediates in Copper-Catalyzed Allylic Amination

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Experimental Section

All reactions were performed under nitrogen or argon. Solvents were dried, distilled and stored under nitrogen/argon before use. All chemicals used were obtained commercially except for phenyl hydroxylamine which was prepared by the reduction of nitrobenzene with zinc (Kamm, O. *Org. Syn.* **1925**, *4, 57*). ^{1}H-NMR spectra were obtained at 300 MHz. GC/MS and MS spectra were obtained at 70 eV(EI) or (the latter) by ESI. GC analyses utilized a 3m column packed with OV 101. In all cases, the percent yields are calculated based on the limiting reagent.

$[Cu(PhNO)_3]PF_6$, 1

$[Cu(CH_3CN)_4]PF_6$ (0.58 mmol) was dissolved in chloroform (15 mL) and solid nitrosobenzene (2.46 mmol) was added; the color changed immediately to dark red. After stirring at room temperature for 4 days, the dark red solution was filtered and the solvent removed under vacuum. The dark red solid was triturated with diethyl ether (2 x 10 mL) and then dried under vacuum. ^{1}H NMR (CD_2Cl_2, δ) 8.0 (d, J= 8 Hz, 2H), 7.8 (t, J= 8 Hz, 1H), 7.6 (t, J= 8 Hz, 2H); IR (KBr, cm^{-1}) 1600, 1437, 1398, 1326; Visible spectrum (CH_2Cl_2) 420 nm. Attempts to obtain mass spectra of **1** (EI, ESI, FAB) failed to provide interpretable fragments; attempts to crystallize **1** for X-ray diffraction led to decomposition.

ICP analysis of a sample of **1** digested in 1 mL of concentrated HCl showed a Cu content of 11.7%; %Cu calcd. for $Cu(PhNO)_3PF_6$ = 12.0%. When the above synthetic procedure was employed with $[Cu(CH_3CN)_4]PF_6$ (0.238g, 0.638 mmol) and PhNO (0.296g, 2.77 mmol), trituration of the reaction residue with Et_2O recovered 0.083 g (0.776 mmol) of unreacted PhNO (containing a small amount of azoxybenzene detected by GC). Assuming complete conversion of the $[Cu(CH_3CN)_4]PF_6$ the Cu/PhNO ratio in the product complex is calculated to be 1/3.1.

$[Cu(Et_2NPhNO)_3]PF_6$, 2

To a solution of $[Cu(CH_3CN)_4]PF_6$ (0.59 mmol) in dichloromethane (50 mL) was added solid N, N'-diethyl-4-nitrosoaniline (2.5 mmol). The initially colorless solution changed to dark red-green immediately. Stirring was continued for 24 h to ensure complete reaction. The dark red-green solution was filtered and the solvent was removed from the filtrate under vacuum. The solid residue was triturated with diethyl ether (30 mL x 3) and vacuum dried to obtain a dark red-green solid (70% based on $[Cu(CH_3CN)_4]PF_6$). On recrystallization from CH_2Cl_2/diethyl ether at -20°C, greenish crystals suitable for X-ray diffraction were obtained (*vide infra*). IR (KBr, cm^{-1}) 1600, 1420, 1375, 1330; MS (FAB) 419 $[(Et_2NPhNO)_2{}^{63}Cu]^+$, 421$[(Et_2NPhNO)_2{}^{65}Cu]^+$; UV-Vis (nm, CH_2Cl_2) 421. ^{1}H-NMR (CD_2Cl_2) 8.6 (bs, 1H), 7.2 (bs, 1H), 6.8 (bs, 2H), 3.55 (q, 4H), 1.28 (t, 6H).

Detection of 1 in the reaction of AMS with phenyl hydroxylamine in the presence of $[Cu(CH_3CN)_4]PF_6$.

PhNHOH (1.6 mmol) in dioxane (4 mL) was added slowly over a period of 2.5 h to a solution of $[Cu(CH_3CN)_4]PF_6$ (0.40 mmol) and AMS (3.8 mmol) in dioxane (10 mL) at 90°C and allowed to stir for an additional 0.5 h at the same temperature. After cooling the solution was evaporated under reduced pressure while warming with a water bath. The dark-red residual mass (0.19 mmol, 47%) was recrystallized from CH_2Cl_2/diethyl ether. The IR spectrum (KBr) of the product was identical to that of **1**.

Reaction of 1 with α-methylstyrene (AMS).

A dioxane solution (4 mL) containing 0.10 mL (0.77 mmol) of AMS, 6.2 mg of naphthalene (GC standard), and 27 mg (0.051 mmol) of **1** was heated at 90-100 °C for 20 h. GC and GC-MS analysis indicated that 40 % (0.0102 mmol) of the allylamine **3** had formed. The

calculated yield is based on the requirement that 2Cu(I) are needed to reduce one molecule of the allyl hydroxylamine to the allyl amine.

Catalytic amination of AMS by phenylhydroxylamine and 1

To a dioxane solution (2 mL) of **1** (0.11 mmol), naphthalene (0.23 mmol) as GC internal standard, and AMS (4.6 mmol) heated at 90-95°C was added phenyl hydroxylamine (1.37 mmol, dissolved in 8 mL of dioxane) over a period of 5-6 h with a syringe pump. Aniline (0.07 mmol, 5%), azobenzene (0.04 mmol, 3%), azoxybenzene (0.15 mmol, 11%) and the N-phenyl allylamine **3** (0.49 mmol, 36%) were detected by GC and GC-MS after 24 h.

A second run at lower loading of **1** gave the following results. To a dioxane solution (2 mL) of **1** (0.043 mmol), naphthalene (0.15 mmol) as GC internal standard, and AMS (3.1 mmol) at 100°C was added phenyl hydroxylamine (0.75 mmol in 8 mL of dioxane) over a period of 5 h with a syringe pump. The N-phenyl allylamine **3** (0.26 mmol, 34%) was detected by GC and GC/MS after 24h.

Catalytic amination of AMS by phenylhydroxylamine and 2

To a dioxane solution (2 mL) of **2** (0.029 mmol), naphthalene (0.15 mmol) as GC internal standard, and AMS (3.1 mmol) at 100°C was added phenyl hydroxylamine (0.30 mmol in 5 mL of dioxane) over a period of 4-5 h with a syringe pump. The N-phenyl allylamine **3** (0.042 mmol, 15%) and N, N'-diethyl-4-nitrosoaniline were detected by GC and GC/MS after 24h.

Reaction of 2 with 2-methyl-2-pentene

Complex **2** (0.0134 mmol) and 2-methyl-2-pentene (0.82 mmol) were dissolved in dioxane (5 mL) and then heated for 24 h at 100°C. Only free 4-diethylamino-nitrosobenzene, but no product derived from reaction of **2** and the olefin, was detected by GC.

Reaction of 1 and $[Cu(CH_3CN)_4]PF_6$ with AMS

Complex **1** (0.036 mmol) was dissolved in 8 mL dioxane. To this solution $[Cu(CH_3CN)_4]PF_6$ (0.215 mmol) and AMS (0.50 mL) were added and the mixture was heated for 20 h at 100°C. N-phenyl allyl amine **3** (0.0058 mmol, 16% based on **1**) and trace amounts of azobenzene and azoxybenzene were detected by GC.

Reaction of 1 and Cu-powder with AMS

Complex **1** (0.102 mmol) was dissolved in 8 mL dioxane. To this solution, Cu-powder (0.612 mmol) and AMS (0.5 mL) were added and the stirred mixture was heated for 20 h at 100°C. Allyl amine **3** (0.014, 14% based on **2**) and a trace amount of azobenzene and azoxybenzene were detected by GC.

Reaction of 1 with mixture of 2-methyl-2-pentene and 2,3-dimethyl-1,3-butadiene.

A dioxane solution (5 mL) containing 0.1 mL of 2-methyl-2-pentene (0.081 mmol), 0.085 mL of 2,3-dimethylbutadiene (0.0.081 mmol), and 32 mg (0.06 mmol) of **1** was heated at 80-90 °C for 24 h. An aliquot was analyzed by GC and GC-MS and found to contain allyl amines from the alkene (**4**, m/e 175; 0.005 mmol, 8%) and diene (**5**, m/e 173; 0.011 mmol, 18%), respectively. None of the hetero-Diels-Alder adduct **6** was detected.

Synthesis of adduct of 1 with styrene.

To a solution of **1** (0.24 mmol) dissolved in dry dichloromethane (20 mL) styrene (0.26 mmol) was added and the mixture was stirred at room temperature for 25 h. The solvent was removed in vacuum and the residue was triturated with hexane (3 x 5 mL); the resulting dark red solid was dried in vacuum for 2 days. The visible spectrum of the material (CH_2Cl_2) exhibited peaks at 348 and 455 nm (different from **1**). The ^1H NMR spectrum of the adduct (CD_2Cl_2) had peaks at 7.20-8.30 (br complex m, 20H), 6.45 (dd, J= 15,10 Hz, 0.8H), 5.35 (d, J= 15 Hz, 0.8H,

overlapped w/$CHDCl_2$), 4.85 (d, J= 10 Hz, 0.8H). The solid adduct was thermolyzed in an evacuated, sealed flask for 1h at > 250°C. After cooling, the residue was dissolved in CH_2Cl_2; GC-MS analysis of the solution showed the presence of styrene, azobenzene and azoxybenzene.

X-ray structure determination of 2.

The data were collected at 120(2) K on a Bruker Apex (CCD) diffractometer[21] using MoKα (λ = 0.71073 A) radiation. Intensity data, which approximately covered the full sphere of the reciprocal space, were measured as a series of ω oscillation frames each 0.3 for 25° sec/frame. The detector was operated in 512 x 512 mode and was positioned 6.12 cm from the crystal. Coverage of unique data was 97.1% complete to 55.4°(2θ). Cell parameters were determined from a nonlinear least squares fit of 3322 reflections in the range of $2.6<\theta<26.7°$. A total of 31514 reflections were measured.

The structure was solved by the direct method using SHELXTL system[22], and refined by full-matrix least squares on F2 using all reflections. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were included with idealized parameters. Crystals were twined and required SHELXTL twin refinement with HKLF 5 type data containing 2 components of 70% and 30% ratio.

Table S1. Crystal data and structure refinement for **2**

Identification code	kn4115t
Empirical formula	$C_{31}H_{44}Cl_2Cu\ F_6N_6O_3P$
Molecular formula	828.13
Temperature	120(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 8.396(7) Å α = 68.477(7)°
	b =14.281(11)Å β = 84.072(7)°
	c = 16.138(13)Å γ = 86.267(7)°
vol, Z	1790(2)Å^3, 2
Density (calculated)	1.537 Mg/m^3
Absorption coefficient	0.878 mm^{-1}
F(000)	856
Crystal size	0.28 x 0.12 x 0.10mm^3
θ range for data collection	2.39 to 27.69°
Index ranges	-10 <=h<=10, -17<k<=18, -20<=1<=20
Reflection collected	31514
Independent reflections	31518 [R(int) = 0.0000]
Completeness of θ = 25.00°	99.4%
Absorption correction	semi-empirical from equivalents
Max. and min. transmission	0.9174 and 0.7912
Refinement method	Full-matrix least-squares on F^2
Data/ restraints/parameters	31518 / 0/ 460
Goodness-of-fit on F^2	1.027
Final R indices [I>2sigma(I)]	R1 = 0.0531, wR2= 0.1369
R indices (all data)	R1 = 0.0701, wR2 = 0.1445
Largest diff. Peak and hole	0.906 and –0.978 e. Å^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Cu(1)	-1128(1)	-869(1)	6965(1)	24(1)
O(1)	-232(1)	-2430(1)	8441(1)	30(1)
O(2)	1093(1)	-1156(1)	5733(1)	27(1)
O(3)	-4176(1)	-64(1)	6916(1)	30(1)
N(1)	-2432(1)	47(1)	10850(1)	21(1)
N(2)	-683(1)	-1516(1)	8229(1)	22(1)
N(3)	4009(1)	2903(1)	5336(1)	23(1)
N(4)	565(1)	-500(1)	6042(1)	21(1)
N(5)	-6821(1)	-4245(1)	7495(1)	23(1)
N(6)	-3428(1)	-876(1)	6976(1)	23(1)
C(1)	-4691(2)	1307(1)	10528(1)	38(1)
C(2)	-2919(2)	1111(1)	10644(1)	23(1)
C(3)	-4048(2)	-1286(1)	12040(1)	31(1)
C(4)	-2609(2)	-615(1)	11799(1)	27(1)
C(5)	-1969(1)	-323(1)	10215(1)	20(1)
C(6)	-1963(1)	277(1)	9289(1)	21(1)
C(7)	-1528(1)	-131(1)	8662(1)	21(1)
C(8)	-1064(1)	-1152(1)	8895(1)	20(1)
C(9)	-1020(2)	-1748(1)	9809(1)	23(1)
C(10)	-1445(2)	-1356(1)	10443(1)	23(1)
C(11)	2471(2)	4501(1)	4980(1)	37(1)
C(12)	3415(2)	3699(1)	5658(1)	28(1)
C(13)	6884(2)	2444(1)	5535(1)	33(1)
C(14)	5646(2)	3013(1)	4895(1)	26(1)
C(15)	3136(2)	2101(1)	5451(1)	20(1)
C(16)	3733(2)	1336(1)	5121(1)	22(1)
C(17)	2891(2)	507(1)	5277(1)	21(1)
C(18)	1404(1)	373(1)	5790(1)	20(1)
C(19)	773(2)	1131(1)	6084(1)	21(1)
C(20)	1580(2)	1986(1)	5911(1)	22(1)
C(21)	-5818(2)	-5902(1)	8494(1)	40(1)

C(22)	-6059(2)	-5215(1)	7545(1)	28(1)
C(23)	-9307(2)	-3849(1)	6712(1)	33(1)
C(24)	-8579(2)	-4234(1)	7597(1)	28(1)
C(25)	-5992(2)	-3435(1)	7384(1)	21(1)
C(26)	-6805(2)	-2495(1)	7290(1)	22(1)
C(27)	-5995(2)	-1665(1)	7157(1)	21(1)
C(28)	-4304(1)	-1703(1)	7119(1)	20(1)
C(29)	-3492(2)	-2621(1)	7219(1)	24(1)
C(30)	-4291(2)	-3468(1)	7351(1)	23(1)
P(1)	1336(1)	6681(1)	2453(1)	25(1)
F(5)	901(1)	7769(1)	2492(1)	36(1)
F(6)	1800(1)	5600(1)	2403(1)	36(1)
F(4)	2026(1)	7196(1)	1438(1)	42(1)
F(3)	636(1)	6172(1)	3463(1)	44(1)
F(2)	-384(1)	6650(1)	2131(1)	52(1)
F(1)	3056(1)	6704(1)	2770(1)	43(1)
Cl(2)	8161(1)	5535(1)	-650(1)	48(1)
Cl(1)	6368(1)	3793(1)	485(1)	58(1)
C(31)	8083(2)	4215(1)	-221(1)	48(1)

Table S3. Bond lengths [Å] and angles [°] for **2**.

Cu(1)-N(4)	1.8983(15)
Cu(1)-N(6)	1.9296(19)
Cu(1)-N(2)	1.9701(18)
O(1)-N(2)	1.2646(16)
O(2)-N(4)	1.2517(16)
O(3)-N(6)	1.2582(16)
N(1)-C(5)	1.3297(19)
N(1)-C(2)	1.471(2)
N(1)-C(4)	1.4730(18)
N(2)-C(8)	1.358(2)
N(3)-C(15)	1.3455(18)
N(3)-C(12)	1.455(2)
N(3)-C(14)	1.4703(19)
N(4)-C(18)	1.3784(18)
N(5)-C(25)	1.3347(18)
N(5)-C(22)	1.465(2)
N(5)-C(24)	1.468(2)
N(6)-C(28)	1.3671(18)
C(1)-C(2)	1.513(2)
C(3)-C(4)	1.520(2)
C(5)-C(6)	1.4236(19)
C(5)-C(10)	1.434(2)
C(6)-C(7)	1.351(2)
C(7)-C(8)	1.404(2)
C(8)-C(9)	1.411(2)
C(9)-C(10)	1.343(2)
C(11)-C(12)	1.509(2)
C(13)-C(14)	1.518(2)
C(15)-C(20)	1.422(2)
C(15)-C(16)	1.424(2)
C(16)-C(17)	1.349(2)
C(17)-C(18)	1.4081(19)
C(18)-C(19)	1.388(2)
C(19)-C(20)	1.359(2)

C(21)-C(22)	1.511(2)
C(23)-C(24)	1.509(2)
C(25)-C(30)	1.422(2)
C(25)-C(26)	1.430(2)
C(26)-C(27)	1.342(2)
C(27)-C(28)	1.414(2)
C(28)-C(29)	1.400(2)
C(29)-C(30)	1.359(2)
P(1)-F(3)	1.5872(14)
P(1)-F(1)	1.5876(14)
P(1)-F(4)	1.5918(14)
P(1)-F(2)	1.5929(14)
P(1)-F(5)	1.5951(15)
P(1)-F(6)	1.5959(15)
Cl(2)-C(31)	1.756(2)
Cl(1)-C(31)	1.734(2)

N(4)-Cu(1)-N(6)	133.81(6)
N(4)-Cu(1)-N(2)	120.96(6)
N(6)-Cu(1)-N(2)	104.96(4)
C(5)-N(1)-C(2)	122.30(11)
C(5)-N(1)-C(4)	121.13(12)
C(2)-N(1)-C(4)	116.39(11)
O(1)-N(2)-C(8)	118.11(11)
O(1)-N(2)-Cu(1)	113.50(9)
C(8)-N(2)-Cu(1)	127.30(10)
C(15)-N(3)-C(12)	122.28(12)
C(15)-N(3)-C(14)	121.68(12)
C(12)-N(3)-C(14)	116.02(11)
O(2)-N(4)-C(18)	117.80(12)
O(2)-N(4)-Cu(1)	117.11(9)
C(18)-N(4)-Cu(1)	124.31(10)
C(25)-N(5)-C(22)	123.07(12)
C(25)-N(5)-C(24)	122.04(12)
C(22)-N(5)-C(24)	114.88(11)
O(3)-N(6)-C(28)	117.92(12)

O(3)-N(6)-Cu(1)	116.40(9)
C(28)-N(6)-Cu(1)	125.43(9)
N(1)-C(2)-C(1)	112.82(11)
N(1)-C(4)-C(3)	113.56(11)
N(1)-C(5)-C(6)	122.26(13)
N(1)-C(5)-C(10)	120.61(12)
C(6)-C(5)-C(10)	117.13(12)
C(7)-C(6)-C(5)	120.65(13)
C(6)-C(7)-C(8)	121.65(12)
N(2)-C(8)-C(7)	118.40(12)
N(2)-C(8)-C(9)	123.31(13)
C(7)-C(8)-C(9)	118.29(13)
C(10)-C(9)-C(8)	120.96(13)
C(9)-C(10)-C(5)	121.27(12)
N(3)-C(12)-C(11)	111.60(13)
N(3)-C(14)-C(13)	112.29(12)
N(3)-C(15)-C(20)	121.00(13)
N(3)-C(15)-C(16)	121.40(12)
C(20)-C(15)-C(16)	117.61(12)
C(17)-C(16)-C(15)	121.33(13)
C(16)-C(17)-C(18)	120.10(13)
N(4)-C(18)-C(19)	118.15(12)
N(4)-C(18)-C(17)	122.57(13)
C(19)-C(18)-C(17)	119.25(12)
C(20)-C(19)-C(18)	121.48(13)
C(19)-C(20)-C(15)	119.98(13)
N(5)-C(22)-C(21)	112.56(13)
N(5)-C(24)-C(23)	112.74(12)
N(5)-C(25)-C(30)	121.94(12)
N(5)-C(25)-C(26)	120.36(13)
C(30)-C(25)-C(26)	117.70(12)
C(27)-C(26)-C(25)	121.38(13)
C(26)-C(27)-C(28)	120.54(13)
N(6)-C(28)-C(29)	118.66(12)
N(6)-C(28)-C(27)	122.59(12)
C(29)-C(28)-C(27)	118.75(12)

C(30)-C(29)-C(28)	121.56(13)
C(29)-C(30)-C(25)	120.06(13)
F(3)-P(1)-F(1)	90.26(7)
F(3)-P(1)-F(4)	179.57(6)
F(1)-P(1)-F(4)	90.09(7)
F(3)-P(1)-F(2)	89.91(7)
F(1)-P(1)-F(2)	179.50(6)
F(4)-P(1)-F(2)	89.74(7)
F(3)-P(1)-F(5)	90.15(6)
F(1)-P(1)-F(5)	90.32(6)
F(4)-P(1)-F(5)	89.60(6)
F(2)-P(1)-F(5)	90.15(6)
F(3)-P(1)-F(6)	90.62(6)
F(1)-P(1)-F(6)	89.05(5)
F(4)-P(1)-F(6)	89.63(6)
F(2)-P(1)-F(6)	90.47(6)
F(5)-P(1)-F(6)	179.01(5)
Cl(1)-C(31)-Cl(2)	112.11(10)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Cu(1)	19(1)	25(1)	29(1)	-12(1)	-1(1)	-5(1)
O(1)	30(1)	26(1)	35(1)	-13(1)	1(1)	3(1)
O(2)	28(1)	28(1)	31(1)	-16(1)	-4(1)	0(1)
O(3)	28(1)	22(1)	41(1)	-13(1)	-4(1)	0(1)
N(1)	16(1)	25(1)	22(1)	-10(1)	-2(1)	1(1)
N(2)	13(1)	25(1)	29(1)	-12(1)	-1(1)	-2(1)
N(3)	20(1)	24(1)	25(1)	-9(1)	-1(1)	-3(1)
N(4)	20(1)	24(1)	21(1)	-8(1)	-7(1)	-1(1)
N(5)	18(1)	23(1)	31(1)	-14(1)	2(1)	-2(1)
N(6)	23(1)	24(1)	23(1)	-9(1)	-3(1)	-2(1)
C(1)	19(1)	30(1)	63(1)	-15(1)	-6(1)	2(1)
C(2)	20(1)	25(1)	29(1)	-13(1)	-2(1)	-2(1)
C(3)	26(1)	34(1)	28(1)	-8(1)	3(1)	-2(1)
C(4)	27(1)	32(1)	22(1)	-12(1)	-5(1)	3(1)
C(5)	10(1)	24(1)	27(1)	-11(1)	-2(1)	-2(1)
C(6)	17(1)	20(1)	26(1)	-7(1)	-4(1)	-2(1)
C(7)	15(1)	24(1)	22(1)	-5(1)	-3(1)	-4(1)
C(8)	10(1)	25(1)	27(1)	-10(1)	0(1)	-3(1)
C(9)	14(1)	21(1)	32(1)	-8(1)	-1(1)	1(1)
C(10)	18(1)	25(1)	23(1)	-6(1)	-2(1)	1(1)
C(11)	37(1)	29(1)	43(1)	-13(1)	2(1)	0(1)
C(12)	26(1)	28(1)	35(1)	-16(1)	1(1)	-6(1)
C(13)	19(1)	44(1)	35(1)	-14(1)	-3(1)	-2(1)
C(14)	20(1)	31(1)	26(1)	-10(1)	1(1)	-6(1)
C(15)	18(1)	24(1)	19(1)	-6(1)	-5(1)	0(1)
C(16)	16(1)	27(1)	22(1)	-10(1)	1(1)	1(1)
C(17)	19(1)	25(1)	21(1)	-11(1)	-1(1)	3(1)
C(18)	18(1)	24(1)	18(1)	-7(1)	-6(1)	-1(1)
C(19)	12(1)	26(1)	22(1)	-6(1)	-1(1)	1(1)
C(20)	21(1)	24(1)	23(1)	-11(1)	-1(1)	3(1)
C(21)	42(1)	30(1)	44(1)	-10(1)	2(1)	4(1)

C(22)	25(1)	26(1)	37(1)	-19(1)	4(1)	-2(1)
C(23)	21(1)	35(1)	47(1)	-19(1)	-3(1)	-5(1)
C(24)	20(1)	27(1)	41(1)	-18(1)	9(1)	-6(1)
C(25)	20(1)	23(1)	20(1)	-10(1)	-1(1)	0(1)
C(26)	16(1)	26(1)	26(1)	-12(1)	-1(1)	1(1)
C(27)	18(1)	23(1)	23(1)	-10(1)	-1(1)	3(1)
C(28)	18(1)	25(1)	18(1)	-9(1)	-2(1)	-2(1)
C(29)	16(1)	28(1)	29(1)	-13(1)	-2(1)	0(1)
C(30)	20(1)	23(1)	29(1)	-12(1)	-4(1)	3(1)
P(1)	25(1)	22(1)	27(1)	-7(1)	-1(1)	0(1)
F(5)	42(1)	26(1)	40(1)	-14(1)	7(1)	2(1)
F(6)	43(1)	22(1)	42(1)	-11(1)	-4(1)	2(1)
F(4)	68(1)	27(1)	28(1)	-10(1)	8(1)	-2(1)
F(3)	48(1)	35(1)	36(1)	-1(1)	12(1)	8(1)
F(2)	35(1)	39(1)	78(1)	-11(1)	-27(1)	0(1)
F(1)	28(1)	57(1)	58(1)	-35(1)	-8(1)	2(1)
Cl(2)	42(1)	47(1)	50(1)	-13(1)	3(1)	-5(1)
Cl(1)	86(1)	47(1)	39(1)	-14(1)	2(1)	-18(1)
C(31)	47(1)	48(1)	59(1)	-30(1)	-9(1)	7(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for **2**.

	x	y	z	U(eq)
H(1A)	-4933	2032	10341	57
H(1B)	-5307	954	11097	57
H(1C)	-4978	1063	10071	57
H(2A)	-2303	1528	10088	28
H(2B)	-2651	1319	11133	28
H(3A)	-4110	-1695	12680	46
H(3B)	-3935	-1728	11695	46
H(3C)	-5028	-867	11902	46
H(4A)	-2710	-193	12171	32
H(4B)	-1627	-1044	11944	32
H(6A)	-2268	970	9110	25
H(7A)	-1537	283	8048	25
H(9A)	-684	-2436	9980	27
H(10A)	-1398	-1772	11054	27
H(11A)	2097	5026	5216	55
H(11B)	1548	4199	4860	55
H(11C)	3156	4797	4425	55
H(12A)	4330	4008	5791	34
H(12B)	2723	3405	6220	34
H(13A)	7950	2524	5211	49
H(13B)	6634	1728	5795	49
H(13C)	6868	2714	6014	49
H(14A)	5900	3735	4637	31
H(14B)	5701	2759	4398	31
H(16A)	4745	1412	4785	26
H(17A)	3302	13	5040	25
H(19A)	-246	1050	6414	25
H(20A)	1104	2507	6096	27
H(21A)	-5307	-6538	8493	60
H(21B)	-6858	-6036	8845	60
H(21C)	-5133	-5578	8760	60

H(22A)	-5007	-5095	7191	33
H(22B)	-6733	-5553	7277	33
H(23A)	-10477	-3873	6817	49
H(23B)	-8924	-4271	6367	49
H(23C)	-8994	-3152	6377	49
H(24A)	-8967	-3802	7941	34
H(24B)	-8942	-4925	7944	34
H(26A)	-7942	-2457	7323	26
H(27A)	-6563	-1047	7088	25
H(29A)	-2355	-2652	7193	28
H(30B)	-3713	-4084	7422	28
H(31A)	8116	3971	-724	58
H(31B)	9037	3929	110	58

Table S6. Torsion angles [°] for **2**.

N(4)-Cu(1)-N(2)-O(1)	-74.76(9)
N(6)-Cu(1)-N(2)-O(1)	99.96(9)
N(4)-Cu(1)-N(2)-C(8)	117.49(10)
N(6)-Cu(1)-N(2)-C(8)	-67.79(11)
N(6)-Cu(1)-N(4)-O(2)	-85.51(10)
N(2)-Cu(1)-N(4)-O(2)	87.41(10)
N(6)-Cu(1)-N(4)-C(18)	104.87(11)
N(2)-Cu(1)-N(4)-C(18)	-82.20(11)
N(4)-Cu(1)-N(6)-O(3)	-85.86(11)
N(2)-Cu(1)-N(6)-O(3)	100.42(9)
N(4)-Cu(1)-N(6)-C(28)	100.06(11)
N(2)-Cu(1)-N(6)-C(28)	-73.66(11)
C(5)-N(1)-C(2)-C(1)	89.23(15)
C(4)-N(1)-C(2)-C(1)	-85.85(15)
C(5)-N(1)-C(4)-C(3)	-71.62(16)
C(2)-N(1)-C(4)-C(3)	103.52(14)
C(2)-N(1)-C(5)-C(6)	-2.18(18)
C(4)-N(1)-C(5)-C(6)	172.67(11)
C(2)-N(1)-C(5)-C(10)	177.64(11)
C(4)-N(1)-C(5)-C(10)	-7.51(17)
N(1)-C(5)-C(6)-C(7)	-178.10(11)
C(10)-C(5)-C(6)-C(7)	2.07(17)
C(5)-C(6)-C(7)-C(8)	-0.21(18)
O(1)-N(2)-C(8)-C(7)	178.49(10)
Cu(1)-N(2)-C(8)-C(7)	-14.26(16)
O(1)-N(2)-C(8)-C(9)	-1.59(17)
Cu(1)-N(2)-C(8)-C(9)	165.66(9)
C(6)-C(7)-C(8)-N(2)	178.32(11)
C(6)-C(7)-C(8)-C(9)	-1.61(18)
N(2)-C(8)-C(9)-C(10)	-178.43(12)
C(7)-C(8)-C(9)-C(10)	1.49(18)
C(8)-C(9)-C(10)-C(5)	0.43(19)
N(1)-C(5)-C(10)-C(9)	177.98(12)
C(6)-C(5)-C(10)-C(9)	-2.19(18)

C(15)-N(3)-C(12)-C(11)	-87.37(15)
C(14)-N(3)-C(12)-C(11)	94.25(14)
C(15)-N(3)-C(14)-C(13)	-83.57(16)
C(12)-N(3)-C(14)-C(13)	94.82(15)
C(12)-N(3)-C(15)-C(20)	-0.85(18)
C(14)-N(3)-C(15)-C(20)	177.44(11)
C(12)-N(3)-C(15)-C(16)	179.26(11)
C(14)-N(3)-C(15)-C(16)	-2.45(18)
N(3)-C(15)-C(16)-C(17)	176.60(12)
C(20)-C(15)-C(16)-C(17)	-3.30(18)
C(15)-C(16)-C(17)-C(18)	-1.32(19)
O(2)-N(4)-C(18)-C(19)	175.98(11)
Cu(1)-N(4)-C(18)-C(19)	-14.48(16)
O(2)-N(4)-C(18)-C(17)	-6.32(17)
Cu(1)-N(4)-C(18)-C(17)	163.22(9)
C(16)-C(17)-C(18)-N(4)	-173.64(11)
C(16)-C(17)-C(18)-C(19)	4.04(18)
N(4)-C(18)-C(19)-C(20)	175.80(11)
C(17)-C(18)-C(19)-C(20)	-1.98(18)
C(18)-C(19)-C(20)-C(15)	-2.75(19)
N(3)-C(15)-C(20)-C(19)	-174.58(11)
C(16)-C(15)-C(20)-C(19)	5.32(18)
C(25)-N(5)-C(22)-C(21)	92.07(15)
C(24)-N(5)-C(22)-C(21)	-86.64(15)
C(25)-N(5)-C(24)-C(23)	85.43(16)
C(22)-N(5)-C(24)-C(23)	-95.85(14)
C(22)-N(5)-C(25)-C(30)	-3.3(2)
C(24)-N(5)-C(25)-C(30)	175.28(12)
C(22)-N(5)-C(25)-C(26)	176.51(12)
C(24)-N(5)-C(25)-C(26)	-4.87(19)
N(5)-C(25)-C(26)-C(27)	-178.46(12)
C(30)-C(25)-C(26)-C(27)	1.39(19)
C(25)-C(26)-C(27)-C(28)	-1.0(2)
O(3)-N(6)-C(28)-C(29)	-177.75(11)
Cu(1)-N(6)-C(28)-C(29)	-3.76(17)
O(3)-N(6)-C(28)-C(27)	3.16(18)

Cu(1)-N(6)-C(28)-C(27)	177.15(9)
C(26)-C(27)-C(28)-N(6)	179.36(12)
C(26)-C(27)-C(28)-C(29)	0.27(19)
N(6)-C(28)-C(29)-C(30)	-179.19(12)
C(27)-C(28)-C(29)-C(30)	-0.1(2)
C(28)-C(29)-C(30)-C(25)	0.5(2)
N(5)-C(25)-C(30)-C(29)	178.68(13)
C(26)-C(25)-C(30)-C(29)	-1.17(19)

Symmetry transformations used to generate equivalent atoms:

Fig. S1. ORTEP of **2**

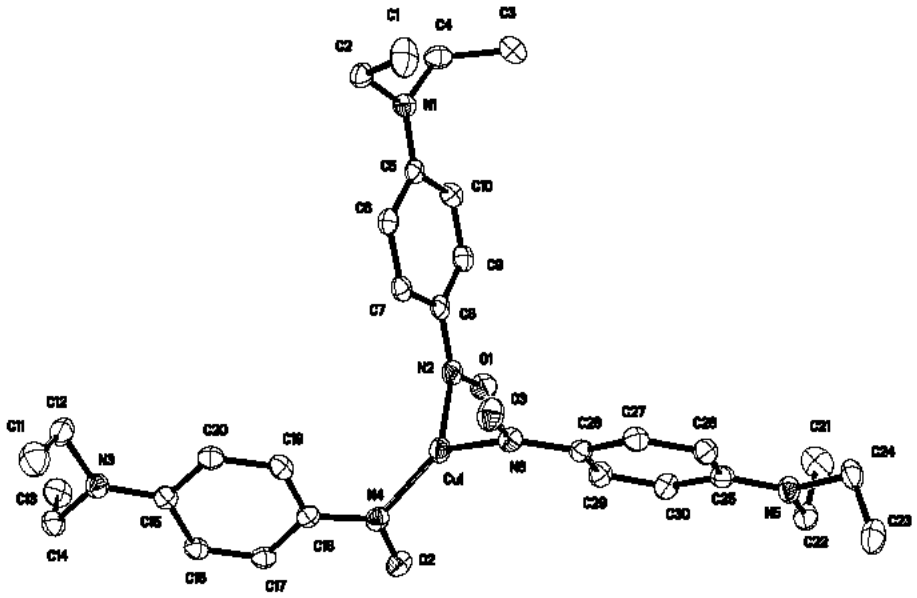
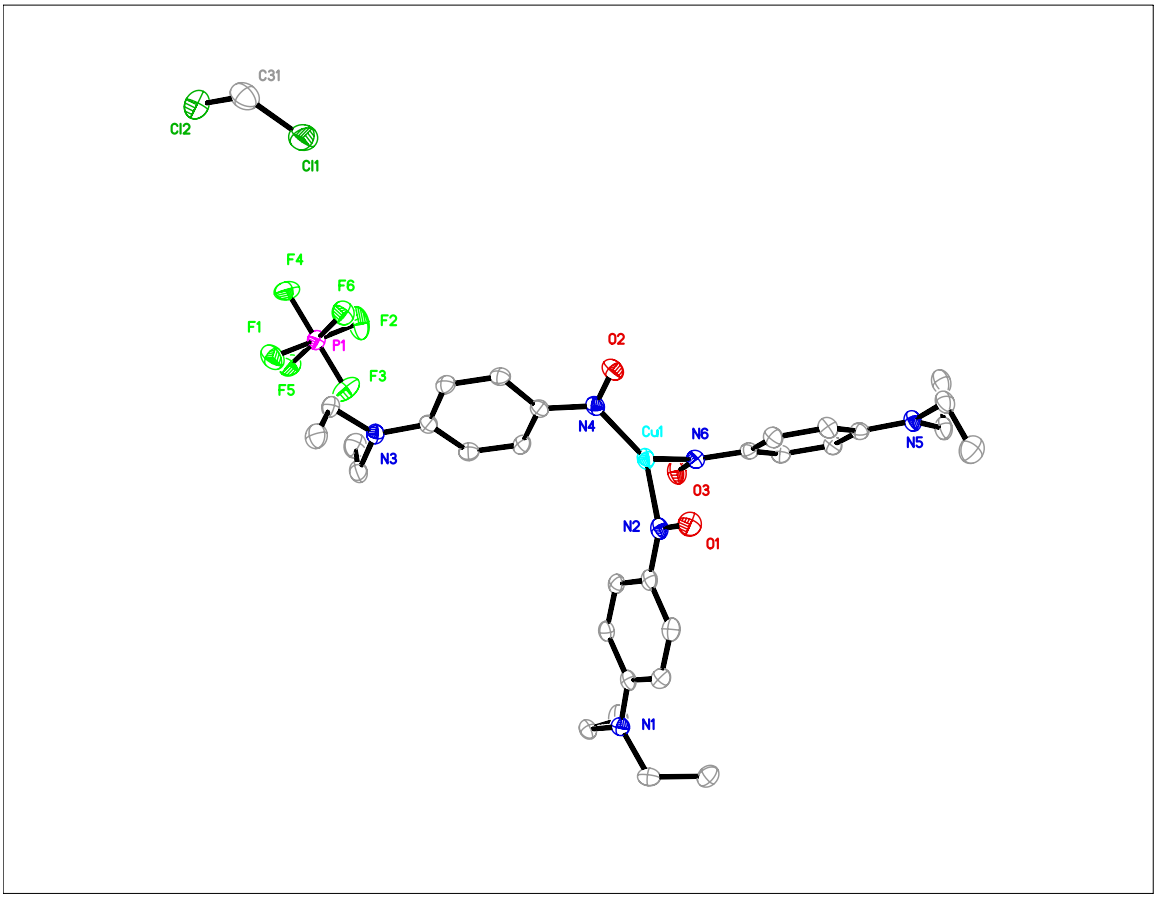


Fig. S3. ORTEP of **2** including anion and molecule of crystallization.



PLATON version of 12/07/2004; check.def file version of 12/07/2004

Datablock kn4115t - ellipsoid plot

M.O. Computations. PM3-level computations were carried out using the MacSpartan Plus program (Wavefunction, inc.). The output of frotier orbitals, energies and charges follows.

MacSpartan SEMIEMPIRICAL program: Release 1.1.7

```
CU(PHNO)3+ NON-PLAN
Geometry Optimization
PM3
H ... H repulsion correction added
Number of basis functions: 120
Number of electrons: 130
Total molecular charge:  1
Multiplicity: 1
Point group: C1
Number of independent degrees of freedom: 114
No useable symmetry or symmetry intentionally disabled
```

Cartesian Coordinates (Angstroms)

Atom		X	Y	Z
N	1	-1.3152940	0.6516204	-0.9289313
Cu	2	-0.2725219	-0.3844269	0.2250219
N	3	-1.0061576	-1.0645451	1.8035511
N	4	1.5011118	-0.7669072	-0.2162145
O	5	-1.4473565	-2.0691282	1.3034487
C	6	-1.1997825	-0.7765520	3.2231544
O	7	-1.7791665	-0.2806987	-1.5367739
C	8	-1.6934022	2.0270388	-1.2469854
O	9	2.0009471	0.1858850	0.3271493
C	10	2.3232463	-1.7447844	-0.9266890
C	11	-1.5311070	-0.1787175	5.9228744
C	12	-0.6073944	0.3765209	3.7643705
C	13	-1.9579488	-1.6278199	4.0424359
C	14	-2.1189545	-1.3216293	5.3871371
C	15	-0.7768504	0.6663062	5.1102513
H	16	-0.0064446	1.0536848	3.1420671
H	17	-2.4266368	-2.5341071	3.6333443
H	18	-2.7118967	-1.9852185	6.0288705
H	19	-0.3136924	1.5642009	5.5373977
H	20	-1.6608961	0.0572994	6.9864581
C	21	3.8440781	-3.6365207	-2.2939609
C	22	1.6940920	-2.8406562	-1.5412270
C	23	3.7186118	-1.6037689	-1.0018808
C	24	4.4687872	-2.5506461	-1.6850553
C	25	2.4597567	-3.7778961	-2.2200156
H	26	0.6039815	-2.9738934	-1.4966977
H	27	4.2255987	-0.7523783	-0.5263925
H	28	5.5587932	-2.4417110	-1.7447015
H	29	-3.7277691	3.8522401	-3.2840528
H	30	4.4426032	-4.3817539	-2.8325820
C	31	-2.3698708	4.6682845	-1.8146296
C	32	-2.6488406	2.3096987	-2.2359108
C	33	-1.0780980	3.0757837	-0.5434149

C	34	-1.4204270	4.3884362	-0.8330153
C	35	-2.9808305	3.6293596	-2.5119311
H	36	-3.1384094	1.4996737	-2.7950165
H	37	-0.3251439	2.8770855	0.2315286
H	38	-2.6353671	5.7091216	-2.0381332
H	39	1.9714550	-4.6346284	-2.7007901
H	40	-0.9403505	5.2103330	-0.2878287

Heat of Formation: 171.250 kcal/mol

Closed shell molecular orbital coefficients

mo:				61	62	63	64	65
eigenvalues:				-13.30590	-13.23877	-13.08053	-13.08010	-13.00023
				A	A	A	A	A
1	N	1	S	0.00516	0.03097	0.00080	0.00069	-0.00133
2	N	1	PX	-0.02274	0.03306	-0.00081	0.00108	-0.00151
3	N	1	PY	-0.00280	-0.01102	-0.00026	-0.00030	0.00038
4	N	1	PZ	0.02842	0.03955	0.00200	0.00048	-0.00131
5	Cu	2	S	0.03770	-0.00001	0.00057	0.00042	-0.00005
6	Cu	2	PX	0.04535	-0.00548	-0.00019	-0.00011	0.00008
7	Cu	2	PY	-0.01775	0.03175	0.00043	0.00028	-0.00065
8	Cu	2	PZ	-0.01594	-0.05104	0.00040	0.00017	0.00104
9	Cu	2	DZ**2	0.01306	0.04551	-0.00071	-0.00052	-0.00161
10	Cu	2	DYY-ZZ	-0.03060	0.01812	0.00009	-0.00014	-0.00066
11	Cu	2	DXY	0.05356	0.02651	-0.00012	0.00028	-0.00086
12	Cu	2	DXZ	0.04139	-0.03299	-0.00002	-0.00037	0.00091
13	Cu	2	DYZ	-0.00750	0.01864	0.00129	0.00065	-0.00073
14	N	3	S	0.00552	-0.03122	0.00105	0.00045	0.00131
15	N	3	PX	-0.02901	-0.02546	0.00018	-0.00136	0.00122
16	N	3	PY	0.02311	-0.03394	0.00126	0.00124	0.00114
17	N	3	PZ	-0.01213	0.03198	-0.00109	-0.00059	-0.00111
18	N	4	S	0.04422	0.00013	-0.00070	-0.00032	-0.00007
19	N	4	PX	-0.07453	0.00513	0.00098	0.00043	0.00021
20	N	4	PY	-0.00647	-0.02951	0.00004	0.00012	-0.00062
21	N	4	PZ	0.00450	0.04671	0.00002	-0.00016	0.00100
22	O	5	S	-0.00069	0.00365	0.00001	0.00004	-0.00006
23	O	5	PX	0.11003	0.04161	-0.00024	-0.00010	-0.00098
24	O	5	PY	-0.08007	0.02990	-0.00085	-0.00083	-0.00090
25	O	5	PZ	0.05868	-0.05946	0.00135	0.00139	0.00140
26	C	6	S	-0.00295	0.01533	-0.00054	-0.00029	-0.00047
27	C	6	PX	-0.34870	0.03125	-0.00118	-0.00301	-0.00090
28	C	6	PY	0.22269	-0.01863	0.00066	0.00266	0.00052
29	C	6	PZ	-0.08565	-0.02468	0.00061	-0.00033	0.00073
30	O	7	S	-0.00062	-0.00361	0.00004	-0.00002	0.00007
31	O	7	PX	0.08315	-0.05237	-0.00038	-0.00029	0.00133
32	O	7	PY	0.02459	0.03553	0.00096	0.00028	-0.00079
33	O	7	PZ	-0.10599	-0.04498	-0.00155	-0.00049	0.00126
34	C	8	S	-0.00261	-0.01520	-0.00043	-0.00033	0.00048
35	C	8	PX	-0.28760	-0.03413	-0.00279	0.00047	0.00099
36	C	8	PY	-0.00969	0.02703	0.00073	0.00034	-0.00082
37	C	8	PZ	0.27097	0.01258	0.00267	-0.00122	-0.00032
38	O	9	S	-0.00425	-0.00001	-0.00005	-0.00003	0.00000

39	O	9	PX	0.11084	-0.01902	0.00002	0.00008	-0.00003
40	O	9	PY	-0.01738	0.10547	-0.00029	0.00020	-0.00073
41	O	9	PZ	-0.02390	-0.16687	0.00016	-0.00054	0.00124
42	C	10	S	-0.02198	-0.00001	0.00015	0.00006	0.00005
43	C	10	PX	0.03084	0.05729	-0.00030	0.00005	-0.00030
44	C	10	PY	-0.02822	-0.30647	0.00060	-0.00066	0.00162
45	C	10	PZ	-0.02145	0.48786	-0.00058	0.00118	-0.00244
46	C	11	S	-0.00033	0.00136	0.00005	0.00005	-0.00003
47	C	11	PX	0.33176	-0.02441	-0.00257	-0.00879	0.00068
48	C	11	PY	-0.21139	0.01279	0.00189	0.00559	-0.00035
49	C	11	PZ	0.08732	-0.00474	-0.00083	-0.00210	0.00012
50	C	12	S	0.00053	0.00108	0.00018	-0.00060	-0.00004
51	C	12	PX	-0.10683	0.00645	0.12284	0.40107	-0.00025
52	C	12	PY	0.06687	-0.00430	-0.07796	-0.25725	0.00024
53	C	12	PZ	-0.02880	0.00408	0.03205	0.10687	-0.00014
54	C	13	S	-0.00036	-0.00288	0.00010	-0.00014	0.00013
55	C	13	PX	-0.10907	0.00091	-0.12167	-0.39983	0.00002
56	C	13	PY	0.07166	-0.01410	0.07782	0.25423	0.00039
57	C	13	PZ	-0.02977	0.01093	-0.03258	-0.10577	-0.00036
58	C	14	S	-0.00009	0.00131	-0.00005	-0.00011	-0.00005
59	C	14	PX	0.19602	-0.01004	-0.11884	-0.38931	0.00032
60	C	14	PY	-0.12552	0.00940	0.07566	0.24826	-0.00029
61	C	14	PZ	0.05296	-0.01061	-0.03121	-0.10297	0.00033
62	C	15	S	-0.00043	0.00090	-0.00013	-0.00002	-0.00003
63	C	15	PX	0.20021	-0.01318	0.11664	0.38295	0.00028
64	C	15	PY	-0.12805	0.00907	-0.07483	-0.24514	-0.00021
65	C	15	PZ	0.05410	-0.00889	0.03090	0.10027	0.00023
66	H	16	S	0.00073	-0.00499	0.00051	0.00047	0.00018
67	H	17	S	-0.00010	0.00024	-0.00003	0.00017	0.00000
68	H	18	S	0.00098	-0.00595	0.00017	-0.00014	0.00018
69	H	19	S	0.00061	-0.00102	-0.00005	0.00023	0.00001
70	H	20	S	-0.00027	0.00220	-0.00006	0.00030	-0.00007
71	C	21	S	-0.00223	-0.00001	0.00001	0.00000	0.00000
72	C	21	PX	-0.00349	-0.05461	0.00011	-0.00011	0.00065
73	C	21	PY	-0.00080	0.29182	-0.00041	0.00066	-0.00346
74	C	21	PZ	-0.00002	-0.46446	0.00065	-0.00106	0.00553
75	C	22	S	-0.00231	-0.00007	0.00004	0.00002	0.00000
76	C	22	PX	-0.00054	0.01718	0.00002	0.00006	-0.05063
77	C	22	PY	0.00247	-0.09175	0.00016	-0.00018	0.27036
78	C	22	PZ	0.00158	0.14595	-0.00018	0.00034	-0.43039
79	C	23	S	0.00389	0.00001	-0.00009	-0.00004	0.00001
80	C	23	PX	-0.02074	0.01805	0.00014	0.00012	0.05013
81	C	23	PY	-0.00178	-0.09706	0.00014	-0.00031	-0.26821
82	C	23	PZ	0.00132	0.15436	-0.00033	0.00044	0.42678
83	C	24	S	-0.00184	0.00002	0.00003	0.00001	0.00001
84	C	24	PX	0.00982	-0.03230	-0.00004	-0.00010	0.04891
85	C	24	PY	-0.00457	0.17276	-0.00016	0.00037	-0.26155
86	C	24	PZ	-0.00396	-0.27488	0.00038	-0.00053	0.41623
87	C	25	S	-0.00101	0.00002	0.00000	0.00000	0.00000
88	C	25	PX	0.00502	-0.03320	0.00001	-0.00010	-0.04838
89	C	25	PY	-0.00436	0.17724	-0.00025	0.00042	0.25844
90	C	25	PZ	-0.00329	-0.28208	0.00043	-0.00067	-0.41140
91	H	26	S	0.00644	-0.00002	-0.00007	-0.00003	-0.00001
92	H	27	S	-0.00027	-0.00004	-0.00001	-0.00001	-0.00001
93	H	28	S	0.00874	0.00002	-0.00006	-0.00003	0.00000
94	H	29	S	0.00089	0.00590	-0.00001	0.00022	-0.00018
95	H	30	S	-0.00318	0.00000	0.00003	0.00001	-0.00001

96	C	31	S	-0.00033	-0.00135	0.00007	0.00002	0.00003
97	C	31	PX	0.27296	0.02350	-0.00771	0.00251	-0.00065
98	C	31	PY	0.01388	0.00089	-0.00025	0.00000	-0.00002
99	C	31	PZ	-0.25950	-0.01869	0.00743	-0.00203	0.00050
100	C	32	S	-0.00040	0.00286	-0.00005	0.00016	-0.00013
101	C	32	PX	-0.08943	0.00145	-0.35136	0.10753	-0.00011
102	C	32	PY	-0.00442	-0.00359	-0.01861	0.00554	0.00014
103	C	32	PZ	0.08767	0.01790	0.33444	-0.10166	-0.00051
104	C	33	S	0.00036	-0.00108	-0.00039	0.00048	0.00004
105	C	33	PX	-0.08796	-0.00571	0.35291	-0.10701	0.00022
106	C	33	PY	-0.00544	-0.00233	0.01840	-0.00583	0.00004
107	C	33	PZ	0.08273	0.00696	-0.33706	0.10341	-0.00033
108	C	34	S	-0.00034	-0.00089	-0.00011	-0.00009	0.00003
109	C	34	PX	0.16461	0.01173	0.33674	-0.10293	-0.00023
110	C	34	PY	0.00930	0.00513	0.01639	-0.00475	-0.00014
111	C	34	PZ	-0.15754	-0.01487	-0.32106	0.09776	0.00034
112	C	35	S	-0.00002	-0.00130	-0.00009	0.00001	0.00005
113	C	35	PX	0.16097	0.00813	-0.34244	0.10430	-0.00025
114	C	35	PY	0.00896	0.00622	-0.01769	0.00554	-0.00020
115	C	35	PZ	-0.15433	-0.01518	0.32600	-0.09955	0.00047
116	H	36	S	-0.00018	-0.00024	0.00009	-0.00011	0.00000
117	H	37	S	0.00058	0.00494	0.00068	0.00017	-0.00018
118	H	38	S	-0.00022	-0.00219	0.00020	-0.00021	0.00007
119	H	39	S	0.00197	0.00000	0.00001	0.00001	-0.00001
120	H	40	S	0.00058	0.00102	0.00014	-0.00016	-0.00001

mo:				66	67	68	69	70
eigenvalues:				-4.47864	-4.31590	-4.26750	-2.84716	-2.84666
				A	A	A	A	A
1	N	1	S	-0.00178	0.03681	-0.06358	0.00095	0.00194
2	N	1	PX	0.27680	0.32014	0.12020	0.00560	-0.00156
3	N	1	PY	0.01937	0.02626	0.00401	0.00065	0.00042
4	N	1	PZ	-0.24425	-0.24842	-0.16254	-0.00443	0.00213
5	Cu	2	S	0.00026	-0.00455	0.00030	-0.00041	-0.00025
6	Cu	2	PX	0.00000	0.00079	0.00027	0.00216	0.00123
7	Cu	2	PY	-0.00243	0.00815	-0.00195	-0.00076	-0.00107
8	Cu	2	PZ	0.00334	0.00470	0.00266	-0.00133	0.00025
9	Cu	2	DZ**2	-0.00050	-0.07658	-0.05953	-0.00134	-0.00034
10	Cu	2	DYY-ZZ	0.00171	0.07266	-0.01069	0.00102	0.00050
11	Cu	2	DXY	-0.00603	-0.03542	-0.07331	-0.00094	0.00020
12	Cu	2	DXZ	0.00997	-0.04977	0.10758	-0.00043	-0.00126
13	Cu	2	DYZ	0.00172	0.07247	-0.01410	0.00130	0.00069
14	N	3	S	0.00145	0.03860	0.06264	0.00216	-0.00024
15	N	3	PX	-0.31467	0.35398	-0.15241	0.00214	0.00624
16	N	3	PY	0.17938	-0.17171	0.13343	-0.00020	-0.00358
17	N	3	PZ	-0.07889	0.07858	-0.05598	0.00070	0.00150
18	N	4	S	0.00020	-0.07284	0.00059	-0.00263	-0.00137
19	N	4	PX	0.03078	0.04679	-0.04786	0.00086	0.00025
20	N	4	PY	-0.17032	0.02136	0.26154	0.00029	0.00122
21	N	4	PZ	0.27015	0.00223	-0.41534	0.00103	-0.00116
22	O	5	S	-0.00008	0.00002	-0.00149	0.00002	0.00005
23	O	5	PX	0.24454	-0.25524	0.12569	-0.00162	-0.00532
24	O	5	PY	-0.13778	0.14182	-0.08107	0.00073	0.00293
25	O	5	PZ	0.06409	-0.07086	0.03246	-0.00081	-0.00096
26	C	6	S	-0.00163	-0.01728	-0.02748	-0.00114	0.00069

27	C	6	PX	-0.10947	0.14714	-0.08637	-0.00089	-0.00337
28	C	6	PY	0.06960	-0.08805	0.06341	0.00115	0.00329
29	C	6	PZ	-0.02642	0.06068	0.01347	0.00106	-0.00065
30	O	7	S	0.00002	0.00004	0.00146	0.00006	-0.00002
31	O	7	PX	-0.21516	-0.22737	-0.10541	-0.00464	0.00159
32	O	7	PY	-0.01781	-0.02321	-0.00367	-0.00033	-0.00042
33	O	7	PZ	0.18918	0.20061	0.10239	0.00392	-0.00123
34	C	8	S	0.00168	-0.01656	0.02787	-0.00005	-0.00135
35	C	8	PX	0.09642	0.12859	0.07771	-0.00284	0.00091
36	C	8	PY	0.00282	0.02793	-0.03273	0.00116	0.00082
37	C	8	PZ	-0.09029	-0.12905	-0.06141	0.00341	-0.00157
38	O	9	S	0.00002	0.00158	0.00000	0.00001	0.00001
39	O	9	PX	-0.02400	-0.00727	0.03535	0.00012	0.00013
40	O	9	PY	0.13188	-0.00941	-0.19456	-0.00035	-0.00064
41	O	9	PZ	-0.20916	-0.00062	0.30864	-0.00063	0.00040
42	C	10	S	-0.00007	0.03093	-0.00028	0.00125	0.00065
43	C	10	PX	0.01019	-0.02011	-0.02104	-0.00073	-0.00008
44	C	10	PY	-0.05448	0.03116	0.11360	0.00168	-0.00075
45	C	10	PZ	0.08655	0.01964	-0.18148	-0.00030	0.00242
46	C	11	S	0.00013	-0.00071	-0.00092	-0.00001	-0.00014
47	C	11	PX	-0.17905	0.22005	-0.11945	0.00187	0.00461
48	C	11	PY	0.11401	-0.13969	0.07658	-0.00132	-0.00377
49	C	11	PZ	-0.04724	0.05831	-0.03097	0.00056	0.00154
50	C	12	S	0.00221	-0.00122	0.00083	0.00018	-0.00219
51	C	12	PX	0.16387	-0.19724	0.10377	0.12219	0.38617
52	C	12	PY	-0.10695	0.12649	-0.07208	-0.07792	-0.24742
53	C	12	PZ	0.04201	-0.05073	0.02851	0.03182	0.10226
54	C	13	S	-0.00098	0.00775	0.00868	0.00055	0.00012
55	C	13	PX	0.16331	-0.19048	0.11170	-0.12117	-0.38362
56	C	13	PY	-0.10598	0.13165	-0.06025	0.07769	0.24406
57	C	13	PZ	0.04455	-0.05779	0.02208	-0.03232	-0.10109
58	C	14	S	0.00005	-0.00294	-0.00411	-0.00029	-0.00039
59	C	14	PX	0.03633	-0.05044	0.02767	0.12492	0.39545
60	C	14	PY	-0.02316	0.03311	-0.01634	-0.07959	-0.25227
61	C	14	PZ	0.00944	-0.00849	0.01382	0.03343	0.10500
62	C	15	S	-0.00068	-0.00067	-0.00214	0.00016	0.00121
63	C	15	PX	0.02924	-0.04126	0.02203	-0.12756	-0.40282
64	C	15	PY	-0.01846	0.02606	-0.01421	0.08169	0.25769
65	C	15	PZ	0.00852	-0.00886	0.00994	-0.03349	-0.10682
66	H	16	S	-0.00013	0.00307	0.00607	0.00008	0.00203
67	H	17	S	0.00063	0.00120	0.00327	-0.00003	-0.00022
68	H	18	S	-0.00032	0.00277	0.00333	0.00020	0.00009
69	H	19	S	0.00062	0.00025	0.00187	-0.00025	-0.00081
70	H	20	S	-0.00019	-0.00041	-0.00085	-0.00011	-0.00005
71	C	21	S	-0.00001	0.00118	0.00000	0.00004	0.00002
72	C	21	PX	0.01780	-0.00037	-0.03215	-0.00012	0.00023
73	C	21	PY	-0.09519	0.00232	0.17197	0.00065	-0.00121
74	C	21	PZ	0.15147	-0.00211	-0.27366	-0.00096	0.00197
75	C	22	S	-0.00011	0.00079	0.00010	-0.00019	-0.00010
76	C	22	PX	-0.01653	-0.00402	0.02909	-0.00007	-0.00023
77	C	22	PY	0.08827	-0.00303	-0.15466	-0.00055	0.00075
78	C	22	PZ	-0.14070	0.00185	0.24652	0.00058	-0.00135
79	C	23	S	0.00010	-0.01076	-0.00003	-0.00048	-0.00025
80	C	23	PX	-0.01669	0.01435	0.02889	0.00056	0.00016
81	C	23	PY	0.08835	0.00061	-0.15407	-0.00018	0.00062
82	C	23	PZ	-0.14064	0.00196	0.24521	0.00046	-0.00089
83	C	24	S	-0.00003	0.00479	-0.00003	0.00020	0.00010

84	C	24	PX	-0.00314	-0.00390	0.00680	-0.00007	-0.00019
85	C	24	PY	0.01687	0.00514	-0.03631	-0.00011	0.00078
86	C	24	PZ	-0.02692	0.00442	0.05773	0.00069	-0.00098
87	C	25	S	0.00003	0.00193	-0.00005	0.00013	0.00007
88	C	25	PX	-0.00299	-0.00272	0.00629	-0.00011	-0.00015
89	C	25	PY	0.01594	0.00207	-0.03343	-0.00007	0.00045
90	C	25	PZ	-0.02532	0.00230	0.05308	0.00040	-0.00056
91	H	26	S	0.00003	-0.00696	0.00006	-0.00020	-0.00010
92	H	27	S	-0.00002	-0.00340	0.00008	-0.00008	-0.00004
93	H	28	S	0.00003	-0.00409	0.00000	-0.00017	-0.00009
94	H	29	S	0.00025	0.00262	-0.00342	0.00019	0.00011
95	H	30	S	0.00001	0.00084	-0.00002	0.00004	0.00002
96	C	31	S	-0.00011	-0.00067	0.00094	-0.00014	0.00007
97	C	31	PX	0.15712	0.19620	0.10082	0.00420	-0.00093
98	C	31	PY	0.00808	0.01049	0.00446	0.00017	0.00000
99	C	31	PZ	-0.14940	-0.18628	-0.09606	-0.00487	0.00132
100	C	32	S	0.00070	0.00726	-0.00899	0.00039	0.00039
101	C	32	PX	-0.14313	-0.16817	-0.09694	-0.33725	0.10690
102	C	32	PY	-0.00776	-0.01080	-0.00304	-0.01746	0.00545
103	C	32	PZ	0.13836	0.17349	0.07666	0.32104	-0.10093
104	C	33	S	-0.00195	-0.00098	-0.00066	-0.00165	0.00140
105	C	33	PX	-0.14387	-0.17606	-0.08675	0.33963	-0.10724
106	C	33	PY	-0.00552	-0.00785	-0.00308	0.01719	-0.00575
107	C	33	PZ	0.13834	0.16733	0.08892	-0.32405	0.10299
108	C	34	S	0.00061	-0.00070	0.00211	0.00108	-0.00056
109	C	34	PX	-0.02558	-0.03711	-0.01790	-0.35431	0.11185
110	C	34	PY	-0.00202	-0.00018	-0.00454	-0.01818	0.00608
111	C	34	PZ	0.02460	0.03395	0.01957	0.33812	-0.10684
112	C	35	S	0.00000	-0.00279	0.00420	-0.00046	-0.00003
113	C	35	PX	-0.03188	-0.04556	-0.02245	0.34757	-0.11008
114	C	35	PY	-0.00159	0.00218	-0.00773	0.01845	-0.00556
115	C	35	PZ	0.03031	0.04164	0.02387	-0.33135	0.10489
116	H	36	S	-0.00054	0.00122	-0.00324	-0.00015	0.00008
117	H	37	S	0.00008	0.00289	-0.00617	0.00166	-0.00109
118	H	38	S	0.00018	-0.00040	0.00085	-0.00007	-0.00007
119	H	39	S	-0.00002	-0.00171	0.00007	-0.00009	-0.00005
120	H	40	S	-0.00053	0.00031	-0.00183	-0.00082	0.00027

Mulliken and electrostatic fit
charges (electrons)

atom	Mulliken	electro fit
N 1	0.911697	1.100232
Cu 2	-0.675465	-1.039876
N 3	0.911419	1.110561
N 4	0.928542	1.083585
O 5	-0.365094	-0.409371
C 6	-0.383527	-0.428668
O 7	-0.365405	-0.406934
C 8	-0.383630	-0.406780
O 9	-0.386271	-0.462307
C 10	-0.388781	-0.308351
C 11	-0.002889	0.064318
C 12	-0.006763	-0.030302

```
     C 13     0.003454      0.147078
     C 14    -0.111913     -0.141286
     C 15    -0.115790     -0.061760
     H 16     0.120199      0.109059
     H 17     0.131459      0.062381
     H 18     0.129684      0.103085
     H 19     0.126915      0.084617
     H 20     0.121800      0.076086
     C 21    -0.001727      0.028678
     C 22    -0.000669     -0.099141
     C 23     0.001454      0.061490
     C 24    -0.114279     -0.096300
     C 25    -0.115872     -0.033657
     H 26     0.127020      0.153427
     H 27     0.129595      0.085212
     H 28     0.128805      0.091657
     H 29     0.129683      0.105697
     H 30     0.121419      0.087489
     C 31    -0.002874      0.039471
     C 32     0.003440      0.150799
     C 33    -0.006718     -0.062695
     C 34    -0.115816     -0.037698
     C 35    -0.111937     -0.141870
     H 36     0.131471      0.057741
     H 37     0.120220      0.119258
     H 38     0.121802      0.087987
     H 39     0.128415      0.078003
     H 40     0.126926      0.079086

Graphics requests:

surface=homo resolution=med  pending
surface=lumo resolution=med  pending

Graphics files written:
surface=homo resolution=med  completed
surface=lumo resolution=med  completed


Time for Semi Empirical Engine     CPU: 000:00:56.58  Wall: 000:01:10.46
Time for Properties Engine         CPU: 000:01:10.59  Wall: 000:01:18.29
Time for Graphics Engine           CPU: 000:01:00.12  Wall: 000:01:06.40

Time for Cu(PhNO)3+ non-plan       CPU: 000:03:08.09  Wall: 000:03:35.55
Time for Graphics Engine           CPU: 000:01:25.50  Wall: 000:01:36.44

Time for Cu(PhNO)3+ non-plan       CPU: 000:01:25.50  Wall: 000:01:36.44
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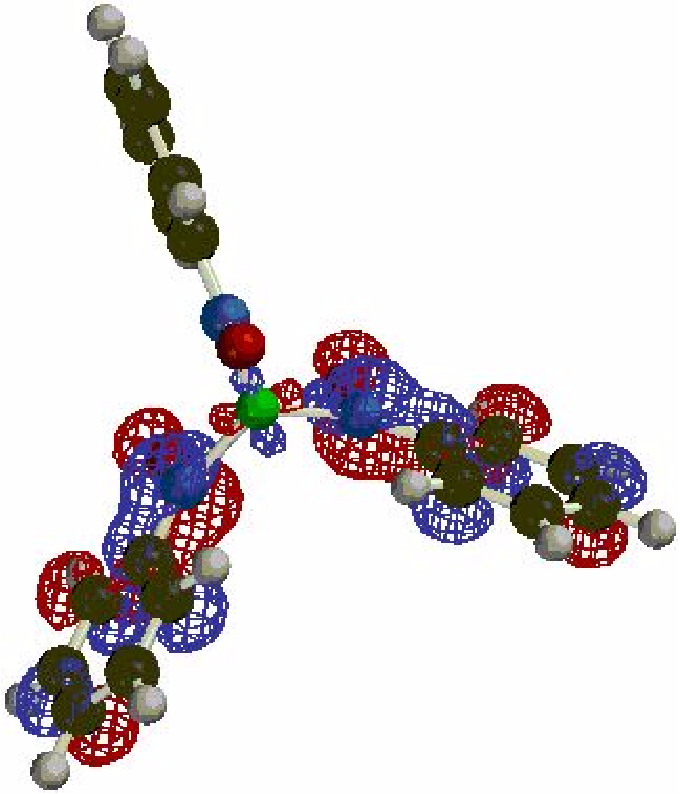

Fig. S4. One of three degenerate LUMOs of **1**.