A Non-Classical Copper Carbonyl on a Tri-alkene Hydrocarbon Support

Mauro Fianchini, Nathan J. DeYonker, Thomas R. Cundari, H. V. Rasika Dias

Supporting Information

Experimental:

All manipulations were carried out under an atmosphere of dry purified argon using standard Schlenk techniques. Solvents were purchased from commercial sources, distilled and degassed by the freeze-pump-thaw method twice prior to use. Glassware was dried in the oven at 150°C overnight. The deuterated solvent (CD_2Cl_2) was dried over activated molecular sieves overnight and degassed with argon for 15 minutes prior to use. NMR spectra were recorded at 298 K on JEOL Eclipse 500 spectrometer (^1H, 500.16 MHz, ^{13}C, 125.77 MHz). IR spectra were recorded at 298 K on JASCO FT/IR-410 instrument. Raman spectra were recorded at 298 K on JORIBA JOBIN YVON instrument using a 633 nm laser source. Crystals of the samples were tightly sealed under argon in a quartz cuvette by the mean of a greased Teflon cap for the Raman study. Different experimental settings (laser intensity, level of magnification, time of exposure, number of cycles) were used for each compound in order to obtain the best signal-to-noise ratio. *Trans,trans,trans*-1,5,9-cyclododecatriene (*ttt*-cdt), $AgSbF_6$, CuCl and CO were purchased from commercial sources.

[Ag(*ttt*-cdt)(SbF_6)]$_n$: 2.161 g of $AgSbF_6$ (98% purity, 6.16 mmol) and 1.000 g of (E,E,E)-1,5,9-cyclododecatriene (6.16 mmol) were placed in a 25 mL flask with a magnetic stir bar. Dichloromethane (20 mL) was added to this mixture at room temperature. A white solid was precipitated immediately. The mixture was stirred overnight and then the supernatant liquid was removed. The precipitate was washed with 2 x 10 mL of dichloromethane to give [Ag(*ttt*-cdt)(SbF_6)]$_n$ as a white powder in quantitative yield. It is not soluble in chlorinated solvents (perhaps has a polymeric structure), but dissolves well in acetone. It is not overly sensitive to

light either. ^{1}H NMR (C_3D_6O, 298 K, ppm): δ 2.04, 2.05 (d, 12 H, overlapping with deuterated solvent), 5.03 (s, C*H*=C*H*). ^{13}C {^{1}H} NMR (C_3D_6O, 298 K, ppm): δ 33.0 (s, CH_2), 36.5 (s, CH_2), 131.2 (s, *C*H=*C*H). Elemental analysis: calc., C, 28.49 %, H, 3.59 %; found, C, 27.89 %, H, 3.71 %. M.P.: dec > 160 °C.

[Cu(*ttt*-cdt)(FSbF$_5$)]: 0.500 g of [Ag(*ttt*-cdt)(SbF$_6$)]$_n$ (0.99 mmol) and 0.163 g of CuCl (90%, 1.48 mmol) were placed in a 50 mL flask with a magnetic stir bar. Dichloromethane (40 mL) was added to the mixture at room temperature. The mixture was stirred for about 24 hours and filtered over a bed of Celite. The filtrate was collected and the solvent was removed under vacuum to give [Cu(*ttt*-cdt)(FSbF$_5$)] in essentially quantitative yield. X-ray quality colorless crystals can be obtained from a CH_2Cl_2/hexafluorobenzene (1:1) solution at -20°C. This compound does not show any decomposition when exposed to air at room temperature. It can be stored in a vial without any precautions. However, solutions of [Cu(*ttt*-cdt)(FSbF$_5$)] in chlorinated solvents, wet acetone and THF tend to decompose over time giving a deep green-bluish solution. ^{1}H NMR (CD_2Cl_2, 298 K, ppm): δ 2.42 (m, 6H), 2.60 (d, 6H), 5.87 (s, C*H*=C*H*). ^{13}C {^{1}H} NMR (CD_2Cl_2, 298 K, ppm): δ 36.4 (s, CH_2), 131.1 (s, *C*H=). Raman (solid, 298K, notable bands, cm^{-1}): 1581 (s, C=C). IR (Nujol, 298K, cm^{-1}): 1582 (vw, C=C). Elemental analysis: calc., C, 31.23 %, H, 3.93 %; found, C, 31.27 %, H, 3.84 %. Mp.: dec > 220 °C.

[Cu(*ttt*-cdt)(CO)][SbF$_6$]: 0.500 g of [Cu(*ttt*-cdt)(FSbF$_5$)] (1.08 mol) were dissolved in 5 mL of dichloromethane at room temperature. Carbon monoxide was gently bubbled into the solution for about 15 mins. The solution was concentrated under reduced pressure to a point where about 1 mL of solvent was left in the flask. Then the remaining solvent was evaporated under a carbon monoxide stream to give the carbonyl compound [Cu(*ttt*-cdt)(CO)][SbF$_6$] in >90% yield. ^{1}H NMR (CD_2Cl_2, 298 K, ppm): δ 2.38 (m, 6H), 2.57 (d, 6H), 5.86 (s, C*H*=C*H*). ^{13}C {^{1}H} NMR (CD_2Cl_2, 298 K, ppm): δ 36.2 (s, CH_2), 130.4, *C*H=). Raman (solid, 298K, notable bands, cm^{-1}): 2160 (s, C≡O), 1601 (s, C=C). IR (Nujol, 298K, cm^{-1}): 2160 (s, CO), 1602 (vw, C=C). Mp: dec > 220 °C, Solid material under Ar shows no appreciable change such as the loss of the coordinated CO. Solid samples of this adduct can be handled in air for a short period or placed under reduced pressure for about an hour without noticeable decomposition. Solid samples can also be stored in a sealed container for 30 days under an inter atmosphere without decomposition, but CH_2Cl_2 solutions of [Cu(*ttt*-cdt)(CO)][SbF$_6$] lose CO upon concentration under vacuum.

Table S1. Summary of key NMR and Raman spectroscopic data

Compound	^{1}H NMR (CD_2Cl_2, ***CH***, C**H**$_2$)	$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, ***CH***, CH_2)	$\bar{\upsilon}$ (C=C) (cm^{-1})	$\bar{\upsilon}$ (CO) (cm^{-1})
(E,E,E)-1,5,9-cyclododecatriene **(*ttt*-cdt)**	***5.00***, 2.03	***132.0***, 32.9	1671 (Raman)	-
[Cu(*ttt*-cdt)($FSbF_5$)]	***5.87***, 2.60 and 2.42	***131.1***, 36.4	1581 (Raman)	-
[Cu(*ttt*-cdt)(CO)][SbF_6]	***5.86***, 2.57 and 2.38	***130.4***, 36.2	1601 (Raman)	2160 (Raman)

X-ray crystallographic data:

A suitable crystal covered with a layer of cold hydrocarbon oil was selected and mounted with paratone-N oil in a cryo-loop and immediately placed in the low-temperature nitrogen stream. The X-ray intensity data were measured at 100(2) K on a Bruker SMART APEX CCD area detector system equipped with a Oxford Cryosystems 700 Series cooler, a graphite monochromator, and a Mo Kα fine-focus sealed tube (λ= 0.710 73 Å). The data frames were integrated with the Bruker SAINT-Plus software package. Data were corrected for absorption effects using the multi-scan technique (SADABS). Structures were solved and refined using Bruker SHELXTL (Version 6.14) software package.

[Cu(*ttt*-cdt)($FSbF_5$)] crystallizes in the Monoclinic *P*2_1/m space group (No. 11). The Cu, Sb, F2 and F3 of [Cu(*ttt*-cdt)($FSbF_5$)] sits on a mirror plane. The *trans,trans,trans*-1,5,9-cyclododecatriene (*ttt*-cdt) ligand in the $[Cu(C_{12}H_{18})]^+$ cation has D_3 structure (propeller shape) but disordered over two positions (the two *ttt*-cdt components are present in equal amounts and are related by a mirror plane and are enantiomers). The angles involving copper and the centroids of the three olefins in $[Cu(ttt\text{-cdt})]^+$ are 118.8°, 118.2° and 117.7° (sum of Cu-alkene angles = 354.7° and Cu-olefin$_{cent}$ distances = 2.010, 2.023, 2.024 Å) while the displacement of copper from the three olefin-centroid plane is 0.2723 Å.

[Cu(*ttt*-cdt)(CO)][SbF_6] crystallizes in the Cubic *P*$2_1$3 space group. (No. 198) Cu, Sb and the CO moiety sits on a three fold rotation axis. The *trans,trans,trans*-1,5,9-cyclododecatriene (*ttt*-cdt) ligand in the $[Cu(ttt\text{-cdt})]^+$ cation has D_3 structure but disordered over two position. The two *ttt*-cdt components are present in equal amounts. The angles involving copper and the three olefin centroids of *ttt*-cdt component one (Cu-olefin$_{cent}$ distance 2.146 Å) and two (Cu-olefin$_{cent}$ distance 2.162 Å) in $[Cu(C_{12}H_{18})CO]^+$ are 106.9°, 106.9° and 106.9° (sum of Cu-alkene angles = 320.7°) and 105.0°, 105.0°, and 105.0° (sum of Cu-alkene angles =

315.0°), respectively while the displacement of copper from the three olefin-centroid planes are 0.8022 Å and 0.8676 Å, respectively (for the disordered components one and two).

Overall, the disorder in [Cu(*ttt*-cdt)($FSbF_5$)] and [Cu(*ttt*-cdt)(CO)][SbF_6] were resolved satisfactorily. All the non hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and refined riding on the corresponding carbons. The CCDC 712593 and 712594 contain the supplementary crystallographic data. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge, CB2 1EZ, UK).

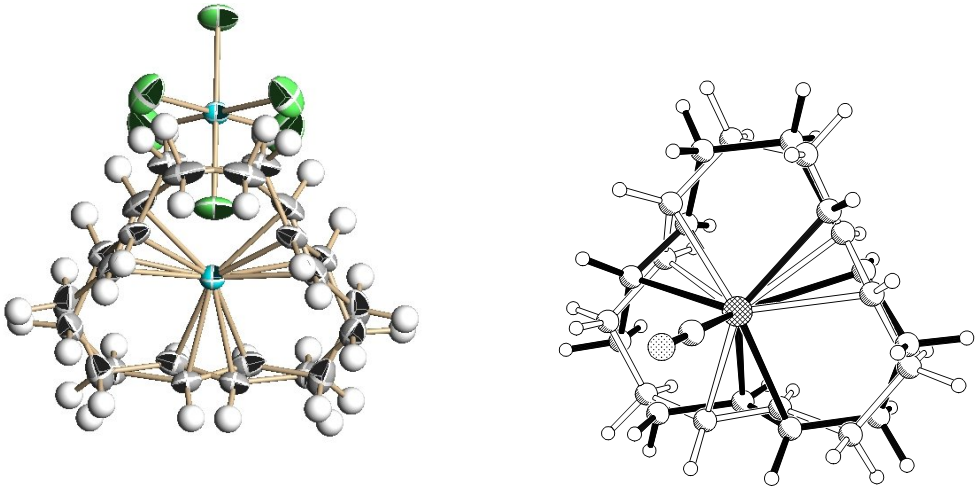


Figure S1. A view showing the *trans,trans,trans*-1,5,9-cyclododecatriene (*t,t,t*-cdt) ligand disorder in [Cu(*ttt*-cdt)($FSbF_5$)] (left) and [Cu(*ttt*-cdt)(CO)]$^+$ (right)

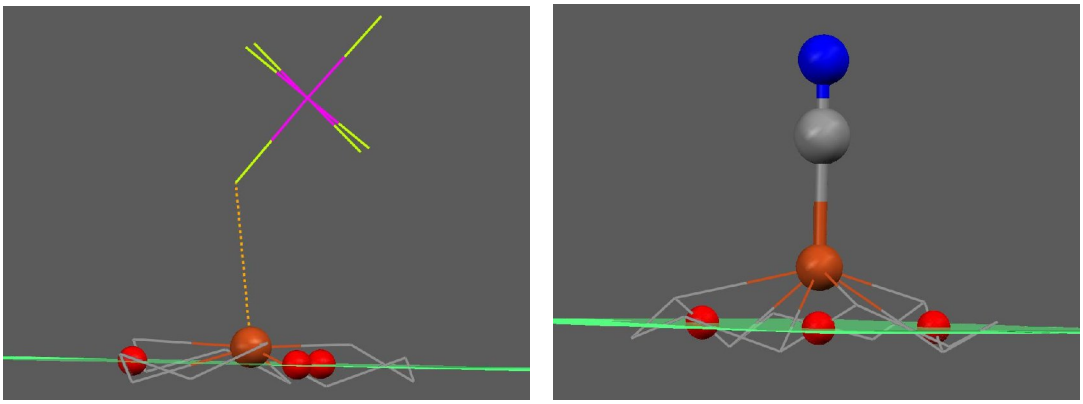


Figure S2. A view showing the displacement of copper atoms out of the three olefin plane in [Cu(*ttt*-cdt)($FSbF_5$)] (left) and [Cu(*ttt*-cdt)(CO)]$^+$ (right); *red spheres indicate alkene centroid positions*.

Table S2. Crystal data and structure refinement for [Cu(*ttt*-cdt)($FSbF_5$)].

Identification code	dias586s	
Empirical formula	C12 H18 Cu F6 Sb	
Formula weight	461.55	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/m	
Unit cell dimensions	a = 7.6618(4) Å	α= 90°.
	b = 11.4769(6) Å	β= 113.717(1)°.
	c = 9.0706(5) Å	γ = 90°.
Volume	730.25(7) $Å^3$	
Z	2	
Density (calculated)	2.099 Mg/m^3	
Absorption coefficient	3.357 mm^{-1}	
F(000)	448	
Crystal size	0.20 x 0.15 x 0.13 mm^3	
Theta range for data collection	2.45 to 28.31°.	
Index ranges	-10<=h<=10, -15<=k<=15, -12<=l<=12	
Reflections collected	7159	
Independent reflections	1903 [R(int) = 0.0195]	
Completeness to theta = 28.31°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6694 and 0.5532	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1903 / 0 / 152	
Goodness-of-fit on F^2	1.034	
Final R indices [I>2sigma(I)]	R1 = 0.0194, wR2 = 0.0527	
R indices (all data)	R1 = 0.0198, wR2 = 0.0532	
Largest diff. peak and hole	0.590 and -0.608 $e.Å^{-3}$	

Table S3. Bond lengths [Å] and angles [°] for [Cu(*ttt*-cdt)($FSbF_5$)].

Cu-C(1)#1	2.110(4)	C(2)-H(2A)	1.0000
Cu-C(1)	2.110(4)	C(3)-C(4)	1.542(10)
Cu-C(5)	2.117(3)	C(3)-H(3A)	0.9900
Cu-C(5)#1	2.117(3)	C(3)-H(3B)	0.9900
Cu-C(9)	2.128(4)	C(4)-C(5)	1.501(8)
Cu-C(9)#1	2.128(4)	C(4)-H(4A)	0.9900
Cu-C(2)	2.133(4)	C(4)-H(4B)	0.9900
Cu-C(2)#1	2.133(4)	C(5)-C(6)	1.354(5)
Cu-C(10)#1	2.141(4)	C(5)-H(5A)	1.0000
Cu-C(10)	2.141(4)	C(6)-C(7)	1.524(8)
Cu-C(6)	2.149(4)	C(6)-H(6A)	1.0000
Cu-C(6)#1	2.149(4)	C(7)-C(8)	1.507(12)
Sb-F(4)#1	1.8633(14)	C(7)-H(7A)	0.9900
Sb-F(4)	1.8633(14)	C(7)-H(7B)	0.9900
Sb-F(3)	1.8640(17)	C(8)-C(9)	1.504(12)
Sb-F(1)	1.8640(13)	C(8)-H(8A)	0.9900
Sb-F(1)#1	1.8640(13)	C(8)-H(8B)	0.9900
Sb-F(2)	1.8789(18)	C(9)-C(10)	1.353(7)
C(1)-C(2)	1.355(6)	C(9)-H(9A)	1.0000
C(1)-C(12)	1.519(9)	C(10)-C(11)	1.512(9)
C(1)-H(1A)	1.0000	C(10)-H(10A)	1.0000
C(2)-C(3)	1.522(8)	C(11)-C(12)	1.532(7)

C(11)-H(11A)	0.9900	C(12)-H(12A)	0.9900
C(11)-H(11B)	0.9900	C(12)-H(12B)	0.9900
C(1)#1-Cu-C(1)	90.0(3)	C(10)#1-Cu-C(6)	157.84(19)
C(1)#1-Cu-C(5)	132.0(2)	C(10)-Cu-C(6)	119.75(19)
C(1)-Cu-C(5)	111.54(19)	C(1)#1-Cu-C(6)#1	148.5(2)
C(1)#1-Cu-C(5)#1	111.54(19)	C(1)-Cu-C(6)#1	112.93(19)
C(1)-Cu-C(5)#1	132.0(2)	C(5)-Cu-C(6)#1	20.21(13)
C(5)-Cu-C(5)#1	24.7(2)	C(5)#1-Cu-C(6)#1	37.00(14)
C(1)#1-Cu-C(9)	24.61(17)	C(9)-Cu-C(6)#1	124.6(2)
C(1)-Cu-C(9)	112.3(2)	C(9)#1-Cu-C(6)#1	88.3(2)
C(5)-Cu-C(9)	110.99(18)	C(2)-Cu-C(6)#1	81.47(16)
C(5)#1-Cu-C(9)	88.22(18)	C(2)#1-Cu-C(6)#1	119.58(16)
C(1)#1-Cu-C(9)#1	112.3(2)	C(10)#1-Cu-C(6)#1	119.75(19)
C(1)-Cu-C(9)#1	24.61(17)	C(10)-Cu-C(6)#1	157.84(19)
C(5)-Cu-C(9)#1	88.22(18)	C(6)-Cu-C(6)#1	38.2(2)
C(5)#1-Cu-C(9)#1	110.99(18)	F(4)#1-Sb-F(4)	89.89(12)
C(9)-Cu-C(9)#1	131.4(3)	F(4)#1-Sb-F(3)	89.58(8)
C(1)#1-Cu-C(2)	126.26(19)	F(4)-Sb-F(3)	89.58(8)
C(1)-Cu-C(2)	37.25(16)	F(4)#1-Sb-F(1)	179.68(6)
C(5)-Cu-C(2)	88.92(14)	F(4)-Sb-F(1)	89.82(9)
C(5)#1-Cu-C(2)	113.59(14)	F(3)-Sb-F(1)	90.26(7)
C(9)-Cu-C(2)	149.6(2)	F(4)#1-Sb-F(1)#1	89.82(9)
C(9)#1-Cu-C(2)	22.26(15)	F(4)-Sb-F(1)#1	179.68(7)
C(1)#1-Cu-C(2)#1	37.25(16)	F(3)-Sb-F(1)#1	90.26(7)
C(1)-Cu-C(2)#1	126.26(19)	F(1)-Sb-F(1)#1	90.46(11)
C(5)-Cu-C(2)#1	113.59(14)	F(4)#1-Sb-F(2)	91.69(8)
C(5)#1-Cu-C(2)#1	88.92(14)	F(4)-Sb-F(2)	91.69(8)
C(9)-Cu-C(2)#1	22.26(15)	F(3)-Sb-F(2)	178.20(9)
C(9)#1-Cu-C(2)#1	149.6(2)	F(1)-Sb-F(2)	88.47(7)
C(2)-Cu-C(2)#1	157.5(2)	F(1)#1-Sb-F(2)	88.47(7)
C(1)#1-Cu-C(10)#1	89.0(2)	C(2)-C(1)-C(12)	127.7(5)
C(1)-Cu-C(10)#1	18.71(13)	C(2)-C(1)-Cu	72.3(2)
C(5)-Cu-C(10)#1	124.54(18)	C(12)-C(1)-Cu	100.3(4)
C(5)#1-Cu-C(10)#1	147.94(19)	C(2)-C(1)-H(1A)	114.9
C(9)-Cu-C(10)#1	113.5(2)	C(12)-C(1)-H(1A)	114.9
C(9)#1-Cu-C(10)#1	36.96(18)	Cu-C(1)-H(1A)	114.9
C(2)-Cu-C(10)#1	38.29(17)	C(1)-C(2)-C(3)	122.9(5)
C(2)#1-Cu-C(10)#1	120.22(18)	C(1)-C(2)-Cu	70.4(2)
C(1)#1-Cu-C(10)	18.71(13)	C(3)-C(2)-Cu	101.5(4)
C(1)-Cu-C(10)	89.0(2)	C(1)-C(2)-H(2A)	116.8
C(5)-Cu-C(10)	147.94(19)	C(3)-C(2)-H(2A)	116.8
C(5)#1-Cu-C(10)	124.54(18)	Cu-C(2)-H(2A)	116.8
C(9)-Cu-C(10)	36.96(18)	C(2)-C(3)-C(4)	111.3(6)
C(9)#1-Cu-C(10)	113.5(2)	C(2)-C(3)-H(3A)	109.4
C(2)-Cu-C(10)	120.22(18)	C(4)-C(3)-H(3A)	109.4
C(2)#1-Cu-C(10)	38.29(17)	C(2)-C(3)-H(3B)	109.4
C(10)#1-Cu-C(10)	82.1(3)	C(4)-C(3)-H(3B)	109.4
C(1)#1-Cu-C(6)	112.93(19)	H(3A)-C(3)-H(3B)	108.0
C(1)-Cu-C(6)	148.5(2)	C(5)-C(4)-C(3)	109.8(5)
C(5)-Cu-C(6)	37.00(14)	C(5)-C(4)-H(4A)	109.7
C(5)#1-Cu-C(6)	20.21(13)	C(3)-C(4)-H(4A)	109.7
C(9)-Cu-C(6)	88.3(2)	C(5)-C(4)-H(4B)	109.7
C(9)#1-Cu-C(6)	124.6(2)	C(3)-C(4)-H(4B)	109.7
C(2)-Cu-C(6)	119.58(16)	H(4A)-C(4)-H(4B)	108.2
C(2)#1-Cu-C(6)	81.47(16)	C(6)-C(5)-C(4)	127.9(4)

C(6)-C(5)-Cu	72.8(2)	C(10)-C(9)-Cu	72.1(2)
C(4)-C(5)-Cu	100.7(3)	C(8)-C(9)-Cu	99.7(4)
C(6)-C(5)-H(5A)	114.7	C(10)-C(9)-H(9A)	114.9
C(4)-C(5)-H(5A)	114.7	C(8)-C(9)-H(9A)	114.9
Cu-C(5)-H(5A)	114.7	Cu-C(9)-H(9A)	114.9
C(5)-C(6)-C(7)	125.4(4)	C(9)-C(10)-C(11)	125.7(6)
C(5)-C(6)-Cu	70.2(2)	C(9)-C(10)-Cu	71.0(2)
C(7)-C(6)-Cu	101.2(4)	C(11)-C(10)-Cu	101.0(3)
C(5)-C(6)-H(6A)	115.9	C(9)-C(10)-H(10A)	115.7
C(7)-C(6)-H(6A)	115.9	C(11)-C(10)-H(10A)	115.7
Cu-C(6)-H(6A)	115.9	Cu-C(10)-H(10A)	115.7
C(8)-C(7)-C(6)	112.2(6)	C(10)-C(11)-C(12)	112.3(6)
C(8)-C(7)-H(7A)	109.2	C(10)-C(11)-H(11A)	109.1
C(6)-C(7)-H(7A)	109.2	C(12)-C(11)-H(11A)	109.1
C(8)-C(7)-H(7B)	109.2	C(10)-C(11)-H(11B)	109.1
C(6)-C(7)-H(7B)	109.2	C(12)-C(11)-H(11B)	109.1
H(7A)-C(7)-H(7B)	107.9	H(11A)-C(11)-H(11B)	107.9
C(9)-C(8)-C(7)	110.2(6)	C(1)-C(12)-C(11)	108.8(5)
C(9)-C(8)-H(8A)	109.6	C(1)-C(12)-H(12A)	109.9
C(7)-C(8)-H(8A)	109.6	C(11)-C(12)-H(12A)	109.9
C(9)-C(8)-H(8B)	109.6	C(1)-C(12)-H(12B)	109.9
C(7)-C(8)-H(8B)	109.6	C(11)-C(12)-H(12B)	109.9
H(8A)-C(8)-H(8B)	108.1	H(12A)-C(12)-H(12B)	108.3
C(10)-C(9)-C(8)	127.9(5)		

Symmetry transformations used to generate equivalent atoms:
#1 x,-y+1/2,z

Figure S3. Several views of [Cu(*ttt*-cdt)($FSbF_5$)] (left) and [Cu(*ttt*-cdt)]$^+$ moiety (right). H-atoms have been removed for clarity in some views

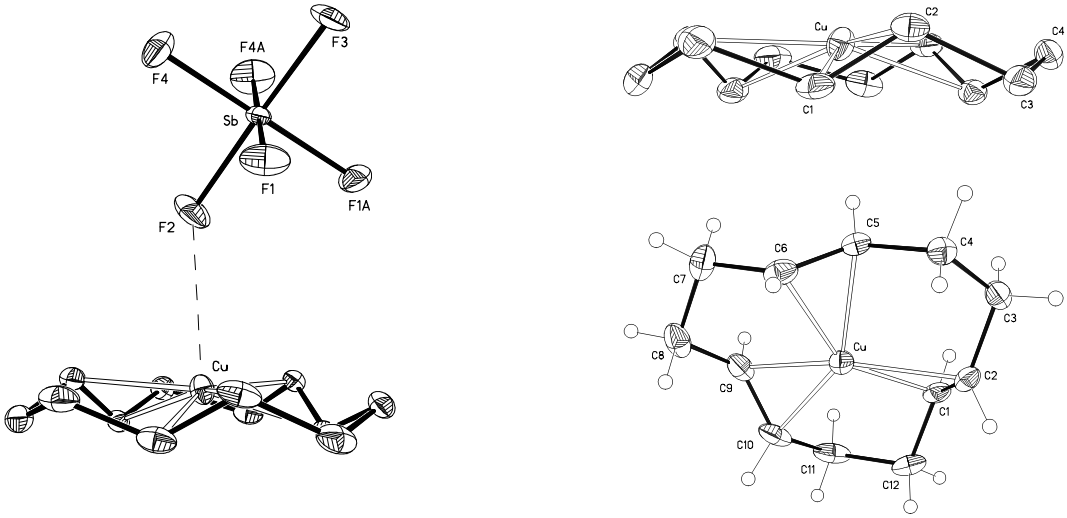


Table S4. Crystal data and structure refinement for [Cu(*ttt*-cdt)(CO)][SbF_6].

Identification code	dias587s	
Empirical formula	C13 H18 Cu F6 O Sb	
Formula weight	489.56	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Cubic	
Space group	P2(1)3	
Unit cell dimensions	a = 11.7046(12) Å	α= 90°.
	b = 11.7046(12) Å	β= 90°.
	c = 11.7046(12) Å	γ = 90°.
Volume	1603.5(3) $Å^3$	
Z	4	
Density (calculated)	2.028 Mg/m^3	
Absorption coefficient	3.069 mm^{-1}	
F(000)	952	
Crystal size	0.22 x 0.20 x 0.18 mm^3	
Theta range for data collection	2.46 to 28.31°.	
Index ranges	-15<=h<=15, -15<=k<=15, -15<=l<=15	
Reflections collected	15645	
Independent reflections	1340 [R(int) = 0.0217]	
Completeness to theta = 28.31°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.6081 and 0.5517	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1340 / 7 / 103	
Goodness-of-fit on F^2	1.111	
Final R indices [I>2sigma(I)]	R1 = 0.0168, wR2 = 0.0428	
R indices (all data)	R1 = 0.0168, wR2 = 0.0428	
Absolute structure parameter	0.03(2)	
Largest diff. peak and hole	0.537 and -0.229 e.$Å^{-3}$	

Table S5. Bond lengths [Å] and angles [°] for [Cu(*ttt*-cdt)(CO)][SbF_6].

Cu-C(5)	1.942(4)	C(1A)-C(2A)	1.517(6)
Cu-C(4B)#1	2.238(5)	C(1A)-H(1AA)	1.0000
Cu-C(4B)	2.238(5)	C(2A)-C(3A)	1.528(7)
Cu-C(4B)#2	2.238(5)	C(2A)-H(2AA)	0.9900
Cu-C(1B)#2	2.254(5)	C(2A)-H(2AB)	0.9900
Cu-C(1B)	2.254(5)	C(3A)-C(4A)	1.510(6)
Cu-C(1B)#1	2.254(5)	C(3A)-H(3AA)	0.9900
Cu-C(4A)#1	2.266(4)	C(3A)-H(3AB)	0.9900
Cu-C(4A)	2.266(4)	C(4A)-C(1A)#1	1.361(7)
Cu-C(4A)#2	2.266(4)	C(4A)-H(4AA)	1.0000
Cu-C(1A)#2	2.267(5)	C(1B)-C(4B)#2	1.328(8)
Cu-C(1A)	2.267(5)	C(1B)-C(2B)	1.514(6)
Sb-F(2)	1.8590(17)	C(1B)-H(1BA)	1.0000
Sb-F(2)#3	1.8590(17)	C(2B)-C(3B)	1.522(8)
Sb-F(2)#4	1.8590(17)	C(2B)-H(2BA)	0.9900
Sb-F(1)	1.8754(16)	C(2B)-H(2BB)	0.9900
Sb-F(1)#3	1.8754(16)	C(3B)-C(4B)	1.515(7)
Sb-F(1)#4	1.8754(16)	C(3B)-H(3BA)	0.9900
O-C(5)	1.126(5)	C(3B)-H(3BB)	0.9900
C(1A)-C(4A)#2	1.361(7)	C(4B)-C(1B)#1	1.328(8)

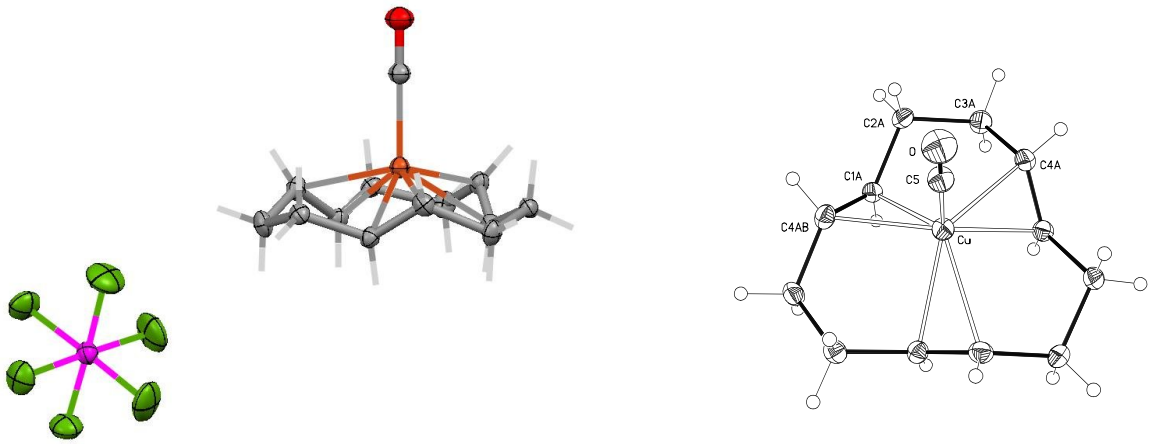
C(4B)-H(4BA)	1.0000

C(5)-Cu-C(4B)#1	120.59(15)
C(5)-Cu-C(4B)	120.59(15)
C(4B)#1-Cu-C(4B)	96.4(2)
C(5)-Cu-C(4B)#2	120.59(15)
C(4B)#1-Cu-C(4B)#2	96.4(2)
C(4B)-Cu-C(4B)#2	96.4(2)
C(5)-Cu-C(1B)#2	101.92(14)
C(4B)#1-Cu-C(1B)#2	34.4(2)
C(4B)-Cu-C(1B)#2	129.3(2)
C(4B)#2-Cu-C(1B)#2	82.9(2)
C(5)-Cu-C(1B)	101.92(14)
C(4B)#1-Cu-C(1B)	129.3(2)
C(4B)-Cu-C(1B)	82.9(2)
C(4B)#2-Cu-C(1B)	34.4(2)
C(1B)#2-Cu-C(1B)	115.85(10)
C(5)-Cu-C(1B)#1	101.92(14)
C(4B)#1-Cu-C(1B)#1	82.9(2)
C(4B)-Cu-C(1B)#1	34.4(2)
C(4B)#2-Cu-C(1B)#1	129.3(2)
C(1B)#2-Cu-C(1B)#1	115.85(10)
C(1B)-Cu-C(1B)#1	115.85(10)
C(5)-Cu-C(4A)#1	102.96(15)
C(4B)#1-Cu-C(4A)#1	19.72(16)
C(4B)-Cu-C(4A)#1	100.3(2)
C(4B)#2-Cu-C(4A)#1	114.9(2)
C(1B)#2-Cu-C(4A)#1	39.83(19)
C(1B)-Cu-C(4A)#1	148.7(2)
C(1B)#1-Cu-C(4A)#1	76.98(18)
C(5)-Cu-C(4A)	102.96(15)
C(4B)#1-Cu-C(4A)	114.9(2)
C(4B)-Cu-C(4A)	19.72(16)
C(4B)#2-Cu-C(4A)	100.3(2)
C(1B)#2-Cu-C(4A)	148.7(2)
C(1B)-Cu-C(4A)	76.98(18)
C(1B)#1-Cu-C(4A)	39.83(19)
C(4A)#1-Cu-C(4A)	115.12(11)
C(5)-Cu-C(4A)#2	102.96(15)
C(4B)#1-Cu-C(4A)#2	100.3(2)
C(4B)-Cu-C(4A)#2	114.9(2)
C(4B)#2-Cu-C(4A)#2	19.72(16)
C(1B)#2-Cu-C(4A)#2	76.98(18)
C(1B)-Cu-C(4A)#2	39.83(19)
C(1B)#1-Cu-C(4A)#2	148.7(2)
C(4A)#1-Cu-C(4A)#2	115.12(11)
C(4A)-Cu-C(4A)#2	115.12(11)
C(5)-Cu-C(1A)#2	122.77(12)
C(4B)#1-Cu-C(1A)#2	18.79(15)
C(4B)-Cu-C(1A)#2	107.15(19)
C(4B)#2-Cu-C(1A)#2	79.96(16)
C(1B)#2-Cu-C(1A)#2	22.51(16)
C(1B)-Cu-C(1A)#2	114.1(2)
C(1B)#1-Cu-C(1A)#2	100.34(19)
C(4A)#1-Cu-C(1A)#2	34.95(18)
C(4A)-Cu-C(1A)#2	126.8(2)
C(4A)#2-Cu-C(1A)#2	81.74(17)
C(5)-Cu-C(1A)	122.77(12)
C(4B)#1-Cu-C(1A)	107.15(19)
C(4B)-Cu-C(1A)	79.96(16)
C(4B)#2-Cu-C(1A)	18.79(15)
C(1B)#2-Cu-C(1A)	100.34(19)
C(1B)-Cu-C(1A)	22.51(16)
C(1B)#1-Cu-C(1A)	114.1(2)
C(4A)#1-Cu-C(1A)	126.8(2)
C(4A)-Cu-C(1A)	81.74(16)
C(4A)#2-Cu-C(1A)	34.95(18)
C(1A)#2-Cu-C(1A)	93.47(16)
F(2)-Sb-F(2)#3	91.19(11)
F(2)-Sb-F(2)#4	91.19(11)
F(2)#3-Sb-F(2)#4	91.19(11)
F(2)-Sb-F(1)	177.40(10)
F(2)#3-Sb-F(1)	91.41(10)
F(2)#4-Sb-F(1)	88.73(10)
F(2)-Sb-F(1)#3	88.73(10)
F(2)#3-Sb-F(1)#3	177.40(10)
F(2)#4-Sb-F(1)#3	91.41(10)
F(1)-Sb-F(1)#3	88.67(8)
F(2)-Sb-F(1)#4	91.41(10)
F(2)#3-Sb-F(1)#4	88.73(10)
F(2)#4-Sb-F(1)#4	177.40(10)
F(1)-Sb-F(1)#4	88.67(8)
F(1)#3-Sb-F(1)#4	88.67(8)
O-C(5)-Cu	180.0(5)
C(4A)#2-C(1A)-C(2A)	126.0(5)
C(4A)#2-C(1A)-Cu	72.5(3)
C(2A)-C(1A)-Cu	96.1(3)
C(4A)#2-C(1A)-H(1AA)	116.1
C(2A)-C(1A)-H(1AA)	116.1
Cu-C(1A)-H(1AA)	116.1
C(1A)-C(2A)-C(3A)	110.7(5)
C(1A)-C(2A)-H(2AA)	109.5
C(3A)-C(2A)-H(2AA)	109.5
C(1A)-C(2A)-H(2AB)	109.5
C(3A)-C(2A)-H(2AB)	109.5
H(2AA)-C(2A)-H(2AB)	108.1
C(4A)-C(3A)-C(2A)	111.9(5)
C(4A)-C(3A)-H(3AA)	109.2
C(2A)-C(3A)-H(3AA)	109.2
C(4A)-C(3A)-H(3AB)	109.2
C(2A)-C(3A)-H(3AB)	109.2
H(3AA)-C(3A)-H(3AB)	107.9
C(1A)#1-C(4A)-C(3A)	122.4(5)
C(1A)#1-C(4A)-Cu	72.6(3)
C(3A)-C(4A)-Cu	105.8(3)
C(1A)#1-C(4A)-H(4AA)	115.7
C(3A)-C(4A)-H(4AA)	115.7
Cu-C(4A)-H(4AA)	115.7
C(4B)#2-C(1B)-C(2B)	124.2(6)
C(4B)#2-C(1B)-Cu	72.1(3)

C(2B)-C(1B)-Cu	105.2(4)	C(4B)-C(3B)-H(3BA)	109.3
C(4B)#2-C(1B)-H(1BA)	115.3	C(2B)-C(3B)-H(3BA)	109.3
C(2B)-C(1B)-H(1BA)	115.3	C(4B)-C(3B)-H(3BB)	109.3
Cu-C(1B)-H(1BA)	115.3	C(2B)-C(3B)-H(3BB)	109.3
C(1B)-C(2B)-C(3B)	112.0(5)	H(3BA)-C(3B)-H(3BB)	108.0
C(1B)-C(2B)-H(2BA)	109.2	C(1B)#1-C(4B)-C(3B)	129.0(6)
C(3B)-C(2B)-H(2BA)	109.2	C(1B)#1-C(4B)-Cu	73.5(3)
C(1B)-C(2B)-H(2BB)	109.2	C(3B)-C(4B)-Cu	96.8(4)
C(3B)-C(2B)-H(2BB)	109.2	C(1B)#1-C(4B)-H(4BA)	114.7
H(2BA)-C(2B)-H(2BB)	107.9	C(3B)-C(4B)-H(4BA)	114.7
C(4B)-C(3B)-C(2B)	111.5(5)	Cu-C(4B)-H(4BA)	114.7

Symmetry transformations used to generate equivalent atoms:
#1 -z+1,x-1/2,-y+1/2 #2 y+1/2,-z+1/2,-x+1 #3 -z+3/2,-x+1,y+1/2
#4 -y+1,z-1/2,-x+3/2

Figure S4. A view of [Cu(*ttt*-cdt)(CO)][SbF_6] (left) and the [Cu(*ttt*-cdt)(CO)]$^+$ (right)



Computational Methods

All quantum calculations employed the Gaussian03 package.[i] The BP86 functional was employed in conjunction with the Stevens (SBK[ii]) valence basis sets and effective core potentials for the coinage metals. The SBK scheme utilizes a semi-core approximation for transition metals. The standard SBK valence basis set is triplet-zeta for transition metals. The valence basis sets of the transition metals were augmented with the Couty-Hall p functions[iii] (fully uncontracted) and the f polarization functions published by Frenking and coworkers.[iv] The 6-311++G(d,p) basis sets was utilized to model carbon and hydrogen atoms.

All complexes modeled were closed-shell (diamagnetic) species and were modeled within the restricted Kohn-Sham formalism. All systems were fully optimized and analytic calculations of the energy Hessian were performed to confirm species as minima to obtain calculated enthalpies and free energies (determined using unscaled vibrational frequencies) in the gas phase at 1 atm and 298.15 K. The calculated NMR properties employed the GIAO approximation.

---

[i] Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A.; Gaussian, Inc., Wallingford CT, 2004.

[ii] Stevens, W. J.; Krauss, M.; Basch, H.; Jasien, P. G. *Can. J. Chem.* **1992**, *70*, 612 - 630.

[iii] Couty, M.; Hall, M. B. *J. Comp. Chem.* **1996**, *17*, 1359-1370.

[iv] Frenking, G.; Ehlers, A. W.; Boehme, M.; Dapprich, S.; Gobbi, A.; Hoellwarth, A.; Jonas, V.; Koehler, K. F.; Stegmann, R.; Veldkamp, A. *Chem. Phys. Lett.* **1993**, *208*, 111-114.

Table S5. Cartesian coordinates (Å) of computed structures.

CO

	x	y	z
O	0.000000	0.000000	0.488494
C	0.000000	0.000000	-0.651325

$CuCO^+$

Cu	0.000000	0.000000	0.806667
C	0.000000	0.000000	-1.024513
O	0.000000	0.000000	-2.155782

SbF_6^-

Sb	0.000000	0.000000	0.000115
F	0.000000	1.939767	0.000038
F	1.939767	0.000000	0.000038
F	0.000000	0.000000	-1.939296
F	-1.939767	0.000000	0.000038
F	0.000000	-1.939767	0.000038
F	0.000000	0.000000	1.938490

ttt-cdt **free ligand**

C	1.765299	1.213234	-0.358900
H	1.711352	1.272275	-1.456118
C	2.795722	0.268607	0.199374
H	2.823846	0.354239	1.300425
C	2.527486	-1.214992	-0.198246
H	2.521978	-1.304536	-1.299274
H	3.375513	-1.824941	0.166133
C	1.232770	-1.740630	0.361046
H	1.157503	-1.766267	1.458309
C	0.167746	-2.118279	-0.363898
C	-1.162402	-2.548818	0.193777
H	-1.100159	-2.622386	1.294257
H	-1.422237	-3.557917	-0.178028
C	-2.319417	-1.579831	-0.195943
H	-2.402122	-1.530377	-1.296411
H	-3.267589	-2.012685	0.174936
C	-2.127957	-0.195089	0.362399
H	-2.104403	-0.117188	1.459477
C	-1.929224	0.916887	-0.363288

H	-1.931925	0.835091	-1.460327
C	-1.630136	2.282912	0.194403
H	-1.725360	2.265857	1.294872
H	-2.369724	3.016875	-0.177360
C	-0.209405	2.790552	-0.195007
H	0.124117	2.834673	-1.295534
H	-0.103544	3.828276	0.173961
C	0.888341	1.926661	0.365300
H	0.928427	1.850425	1.462049
H	3.802842	0.543553	-0.166557
H	0.236781	-2.072259	-1.460924

Cu(*ttt*-cdt)$^{+}$

Cu	0.00000000	0.00000000	0.00348800
C	-0.99678500	1.84469400	-0.36382900
H	-1.09685700	1.83046700	-1.46134900
C	0.00000000	2.85374000	0.19043700
H	-0.09516700	2.91775500	1.28769600
C	1.45832900	2.45234300	-0.19433800
H	1.56991100	2.45293300	-1.29190500
H	2.16339100	3.20248800	0.20287200
C	1.80134800	1.07815800	0.36430300
H	1.88442700	1.01772800	1.46154200
C	2.09594400	-0.05910600	-0.36382900
C	2.47141100	-1.42687000	0.19043700
H	2.57443300	-1.37646100	1.28769600
H	3.45172200	-1.73470500	-0.21201600
C	1.39462700	-2.48912200	-0.19433800
H	1.33934600	-2.58604900	-1.29190500
H	1.69174000	-3.47479500	0.20287200
C	0.03303900	-2.09909200	0.36430300
H	-0.06083500	-2.14082600	1.46154200
C	-1.09916000	-1.78558800	-0.36382900
H	-1.03680300	-1.86513900	-1.46134900
C	-2.47141100	-1.42687000	0.19043700
H	-2.47926700	-1.54129400	1.28769600
H	-3.22816000	-2.12192600	-0.21201600
C	-2.85295600	0.03677900	-0.19433800
H	-2.90925800	0.13311700	-1.29190500
H	-3.85513100	0.27230700	0.20287200
C	-1.83438600	1.02093400	0.36430300
H	-1.82359200	1.12309800	1.46154200
H	-0.22356200	3.85663200	-0.21201600
H	2.13365900	0.03467200	-1.46134900

Cu(*ttt*-cdt)CO^+

Cu	0.00101400	0.00424200	-0.33910700
O	-0.00221700	-0.00153100	-3.36553400
C	-0.00081400	0.00027900	-2.22262800
C	1.48263100	1.21981600	0.84937100
H	1.27771200	0.99003000	1.90504100
C	1.04433700	2.59487300	0.39333200
H	1.23637900	2.72799400	-0.68461400
C	-0.45793300	2.83675600	0.72283500
H	-0.58173000	2.85444600	1.81908600
H	-0.75695900	3.82907700	0.35049500
C	-1.37081800	1.76982800	0.13821400
H	-1.78273300	1.94775400	-0.86400800
C	-1.79693000	0.67493700	0.84736200
C	-2.76849200	-0.39289800	0.39258800
H	-2.97954200	-0.29417400	-0.68552800
H	-3.73056000	-0.25136800	0.91862900
C	-2.22625000	-1.81393800	0.72331800
H	-2.17888900	-1.92879600	1.81960800
H	-2.93592200	-2.56989900	0.35221200
C	-0.84612200	-2.07063800	0.13815900
H	-0.79464900	-2.51148500	-0.86626300
C	0.31478500	-1.89789000	0.84844000
H	0.21799300	-1.60438400	1.90409300
C	1.72556700	-2.20346100	0.39340800
H	1.74578100	-2.43660800	-0.68451700
H	2.08551900	-3.10627100	0.92029300
C	2.68343400	-1.02209800	0.72377800
H	2.76071400	-0.92399700	1.82004400
H	3.69289800	-1.25703300	0.35152700
C	2.21403600	0.30125100	0.13919400
H	2.57156500	0.56741700	-0.86430600
H	1.64713200	3.35770000	0.91966100
H	-1.49093600	0.61007000	1.90168400

Cu(*ttt*-cdt)SbF_6

Cu	0.19970100	0.33593500	-0.11617200
C	2.31925600	-0.08814500	-0.02883800
H	2.79235000	0.89626600	0.11521700
C	2.50915100	-0.69832300	-1.40766800
H	2.03417400	-1.69190100	-1.45204400
C	1.90266200	0.23682400	-2.49735500
H	2.42963900	1.20739800	-2.47945300

H	2.06971000	-0.20416300	-3.49507900
C	0.41399600	0.45576100	-2.27346800
H	-0.24766700	-0.38160300	-2.53173600
C	-0.15195900	1.62718200	-1.82225600
C	-1.63010400	1.91003900	-1.60909100
H	-2.22411900	1.00671300	-1.82432600
H	-1.96496200	2.69811300	-2.30877900
C	-1.88595400	2.38072200	-0.14512000
H	-1.34223800	3.32562400	0.03333700
H	-2.96008700	2.59471300	-0.01244300
C	-1.44033400	1.33432800	0.86735100
H	-2.09880800	0.46817800	1.02106800
C	-0.31820500	1.44763300	1.66025100
H	0.26787500	2.37722300	1.58183900
C	0.14809600	0.46685100	2.72353200
H	-0.52956500	-0.40145800	2.75520000
H	0.11475900	0.95220100	3.71652900
C	1.60712100	0.00447400	2.43026500
H	2.28472000	0.87629500	2.47143300
H	1.93069300	-0.70025700	3.21481300
C	1.71506500	-0.66429000	1.06712700
H	1.32598900	-1.69059600	0.99715300
H	3.58689200	-0.84048000	-1.60968900
H	0.51853100	2.48603000	-1.66202400
Sb	-1.86230200	-2.98231600	0.39476500
F	-2.26371100	-1.68910500	1.78419900
F	-3.46526800	-2.46564000	-0.52775800
F	-2.72114100	-4.40268400	1.33862700
F	-0.16410200	-3.30472000	1.26700900
F	-1.32917000	-4.10445400	-1.06643100
F	-0.94459500	-1.46976400	-0.52742900

Cu(*ttt*-cdt)CO(SbF_6)

Cu	0.68454000	-0.77968400	-2.88861900
O	1.86752900	-0.50996100	-5.65120400
C	1.41774100	-0.61030300	-4.60019000
C	1.81367800	-0.14996100	-1.04350700
H	1.14795400	-0.40450200	-0.20741900
C	1.92870800	1.32658800	-1.35351400
H	2.56198000	1.49527800	-2.24260600
H	2.42724900	1.82691600	-0.50229200
C	0.51926700	1.96049400	-1.53663000
H	-0.01220000	1.89485200	-0.57431000

H	0.62875100	3.02654700	-1.79415400
C	-0.31184500	1.25626700	-2.59975600
H	-0.24882000	1.63247100	-3.63086100
C	-1.22433000	0.27457200	-2.30247300
H	-1.37256300	0.02048000	-1.24372800
C	-2.15620300	-0.41575800	-3.27437200
H	-1.90457200	-0.15139700	-4.31694500
H	-3.18591900	-0.05705700	-3.08951400
C	-2.13037400	-1.95781900	-3.06268300
H	-2.53305400	-2.17227500	-2.06041600
H	-2.78838100	-2.43857700	-3.80475700
C	-0.72974200	-2.54606500	-3.15881100
H	-0.39088500	-2.90210700	-4.14217900
C	0.05815500	-2.77269100	-2.05715600
H	-0.36884700	-2.54423100	-1.07117000
C	1.41827900	-3.43564800	-2.03915700
H	1.80314700	-3.57431400	-3.06517000
H	1.31306900	-4.44287000	-1.59449200
C	2.41620000	-2.61790800	-1.16913900
H	2.05683300	-2.63651900	-0.12836900
H	3.40648600	-3.10094200	-1.19748300
C	2.53733100	-1.16729300	-1.61510900
H	3.31644900	-0.92108400	-2.35063800
Sb	-1.36797500	-1.25570400	1.87254300
F	-1.88370500	-2.93142400	2.64663000
F	-0.79959100	0.37360100	0.95545700
F	-2.99986900	-0.40404500	2.40646600
F	0.27544400	-2.05790400	1.18539800
F	-0.45010500	-0.69842800	3.46018600
F	-2.17304900	-1.77350900	0.16975500

Table S6. Olefin tilt of the calculated structures, defined as angle (°) between C=C vector and three-fold rotational axis.

Free *ttt*-cdt	32.6
Cu(*ttt*-cdt)$^+$	23.5
CuCO(*ttt*-cdt)$^+$	26.6

Table S7. Olefin bond distances (Å)

ttt-cdt	Cu(*ttt*-cdt)$^+$	CuCO(*ttt*-cdt)$^+$
1.3501	1.3822	1.3723
1.3501	1.3822	1.3723
1.3501	1.3822	1.3719
average		
1.3501	1.3822	1.3722

C_2H_4	$Cu(C_2H_4)_3^+$
1.338	1.374

Table S8. Cu-C=C(centroid) bond distances (Å)

Cu(*ttt*-cdt)$^+$ complex

$r_{CuC_centroid}$
2.12871
2.13013
2.12871
2.13013
2.12871
2.13013
average
2.12942

$Cu(C_2H_4)_3^+$ complex

2.063

Cu(*ttt*-cdt)CO$^+$ complex

$r_{CuC_centroid}$
2.28627
2.25613
2.29141
2.26425
2.25506
2.28352
average
2.272773

Table S9. C=C frequencies (in cm^{-1})

	$\nu_{C=C}$
Cu(*ttt*-cdt)$^+$	1548 – 1550
Cu(*ttt*-cdt)CO$^+$	1573 – 1576
Free *ttt*-cdt	1816 – 1818
$Cu(C_2H_4)_3^+$	1543 – 1544
Free C_2H_4	1632

Table S10. NBO Population analysis

	π population per olefin	π* pop per olefin	C=C Bond order	BO change (free vs. complex)
Free *ttt*-cdt	1.98	0.06	1.93	-
Cu(*ttt*-cdt)$^+$	1.85	0.15	1.84	*0.09*
Cu(*ttt*-cdt)CO$^+$	1.87	0.14	1.85	*0.08*
Free C_2H_4	2.00	0.00	2.00	-
$Cu(C_2H_4)_3^+$	1.81	0.16	1.82	*0.18*

The bond order is defined as the sum of the NBO calculated σ_{CC} plus π_{CC} populations minus the populations of both antibonding counterparts, all divided by 2, *i.e.*, $BO_{CC} = (Pop_\sigma + Pop_\pi - Pop_{\pi*} - Pop_{\sigma*}) / 2$. Note that for all cases the NBO-calculated populations of σ_{CC} and σ^*_{CC} are close to ideal values of 2.00 and 0.00 e^-, respectively.

Table S11. Calculated ^{13}C chemical shifts (relative to TMS) in ppm**.**

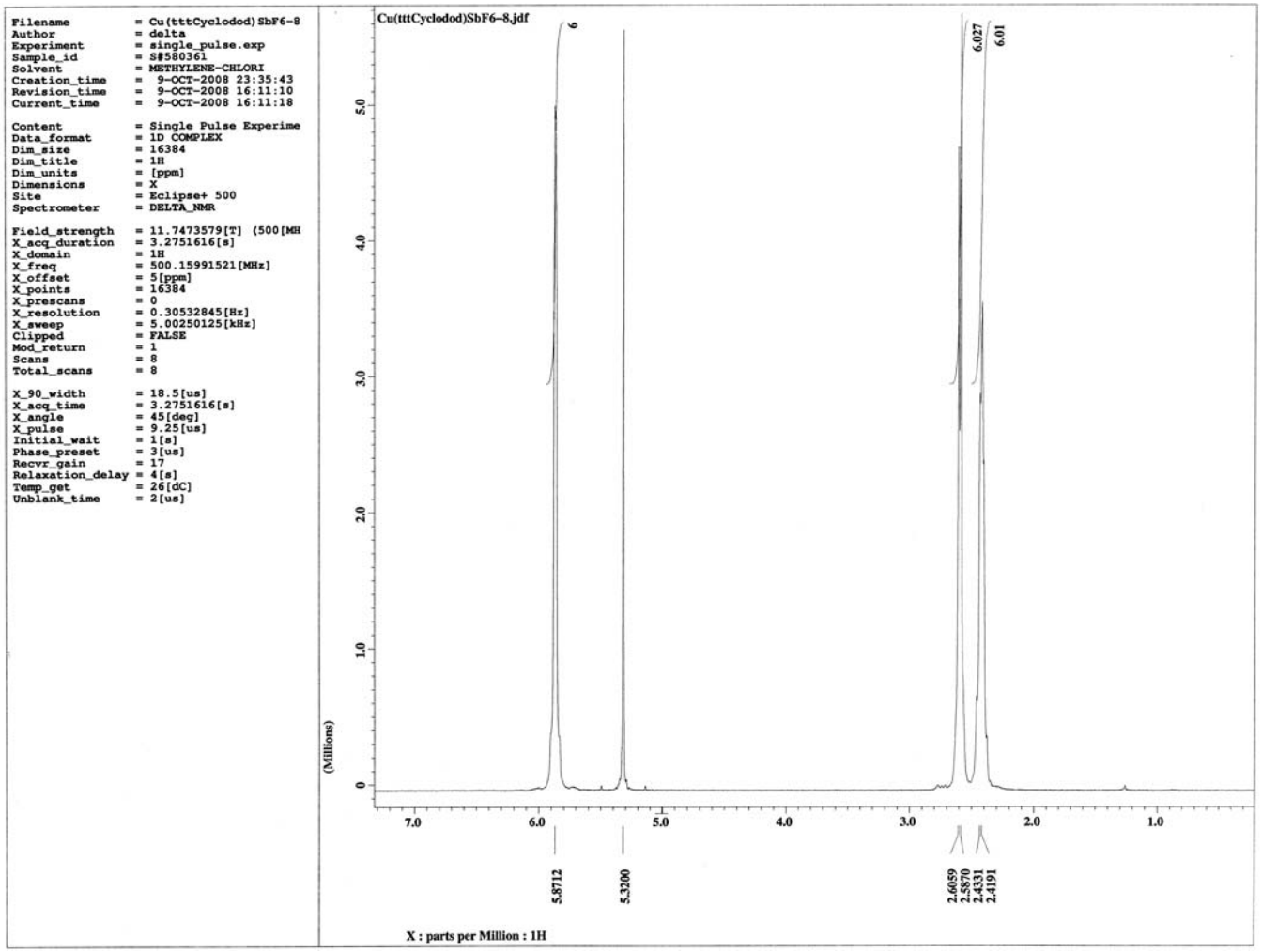
Free ttt-cdt	*139 – 140*
Cu(*ttt*-cdt)$^+$	141
Cu(*ttt*-cdt)CO$^+$	132 – 135
Free C_2H_4	*128.5*
$Cu(C_2H_4)_3^+$	100.0

Table S12. Copper NBO partial charge

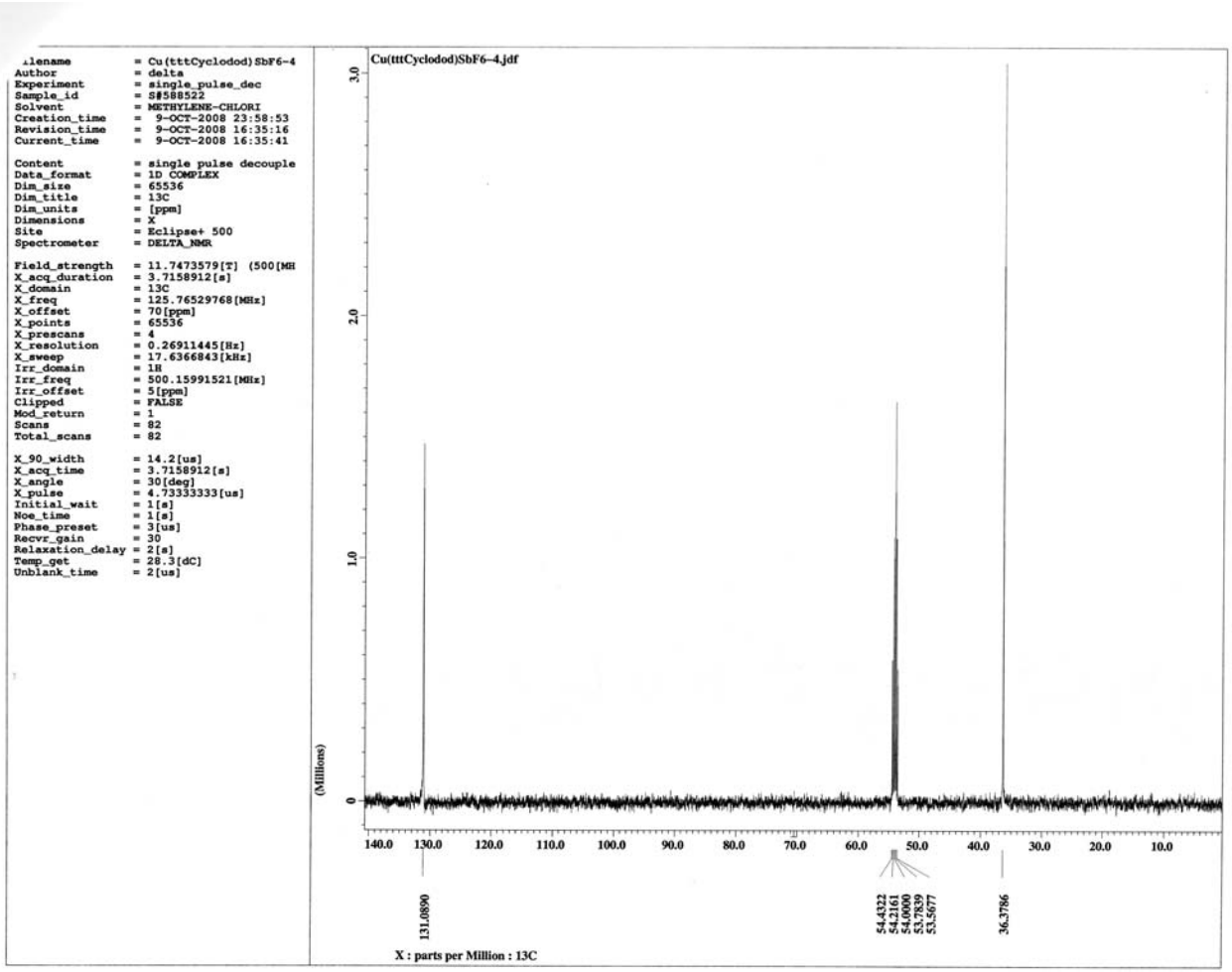
	Cu(*ttt*-cdt)$^+$	CuCO(*ttt*-cdt)$^+$	Cu(C_2H_4)$_3^+$
Free cation (i.e., w/o SbF_6^-)	0.881	0.865	0.894

Calculated data for ethylene and $[Cu(C_2H_4)_3]^+$ are shown for comparison and is obtained at the same level of theory utilized here for *ttt*-cdt and its complexes. See "Synthesis and characterization of the first gold(I)-tris(ethylene) complex: $[Au(C_2H_4)_3][SbF_6]$;" H. V. R. Dias, M. Fianchini, T. R. Cundari, C. F. Campana *Angew. Chem., Int. Ed.* **2008**, *47*, 556 - 559.

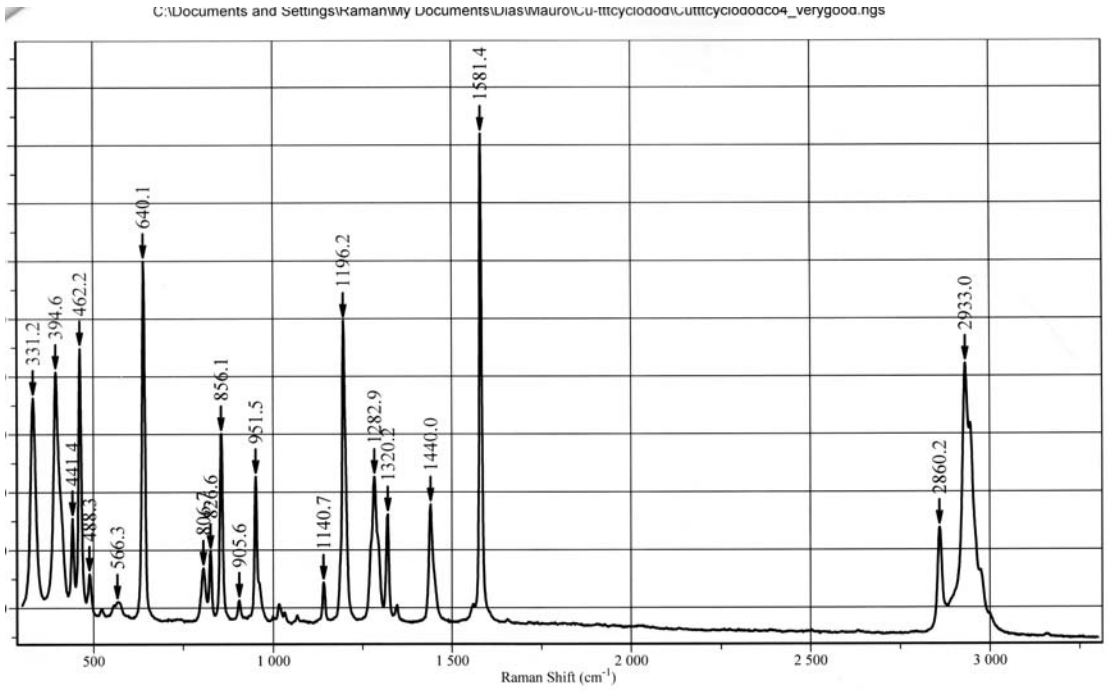
^{1}H NMR spectrum of [Cu(*ttt*-cdt)($FSbF_5$)] (in CD_2Cl_2)



$^{13}C\{^{1}H\}$ NMR spectrum of [Cu(*ttt*-cdt)($FSbF_5$)] (in CD_2Cl_2)



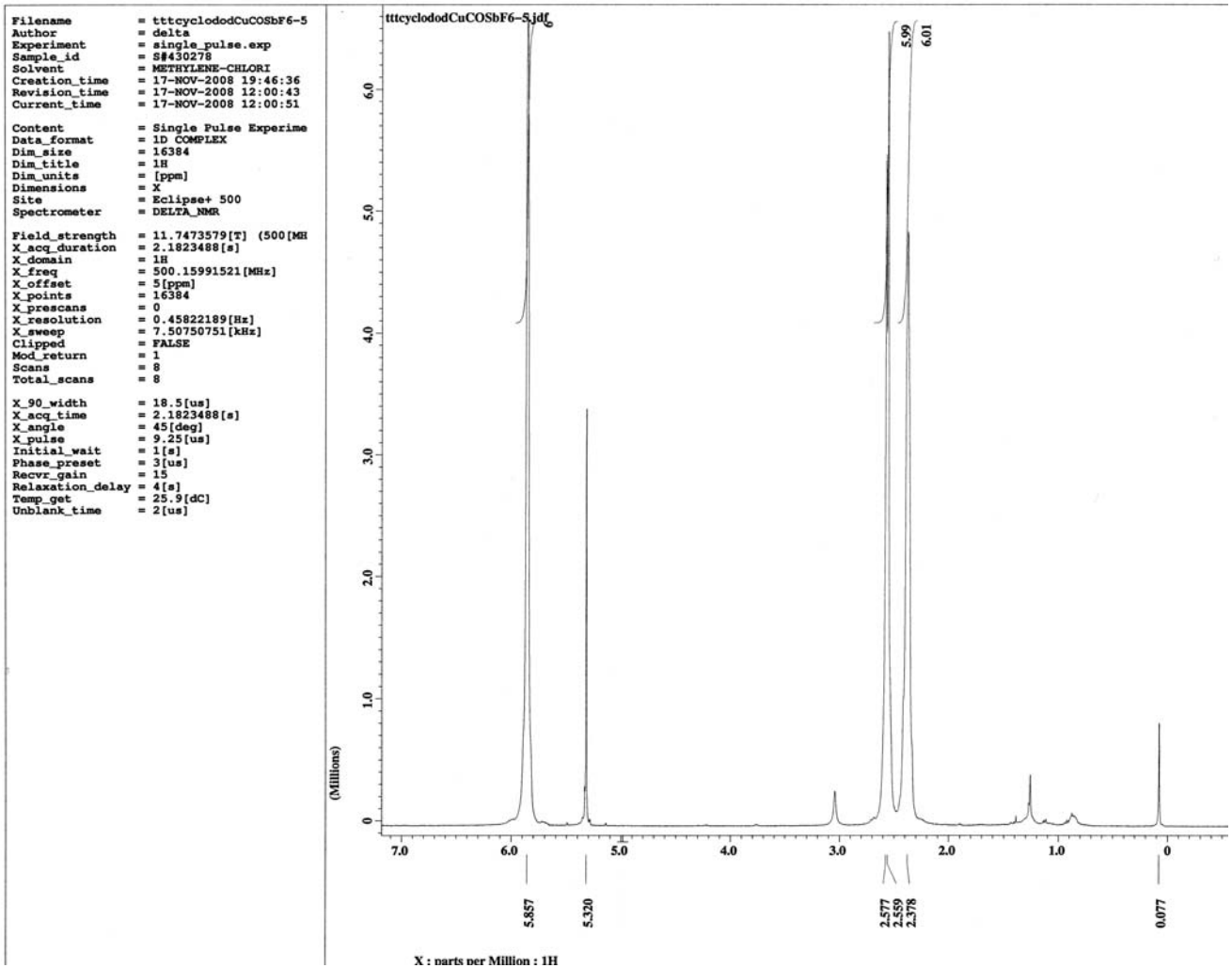
Raman spectrum of [Cu(*ttt*-cdt)($FSbF_5$)] (crystals)



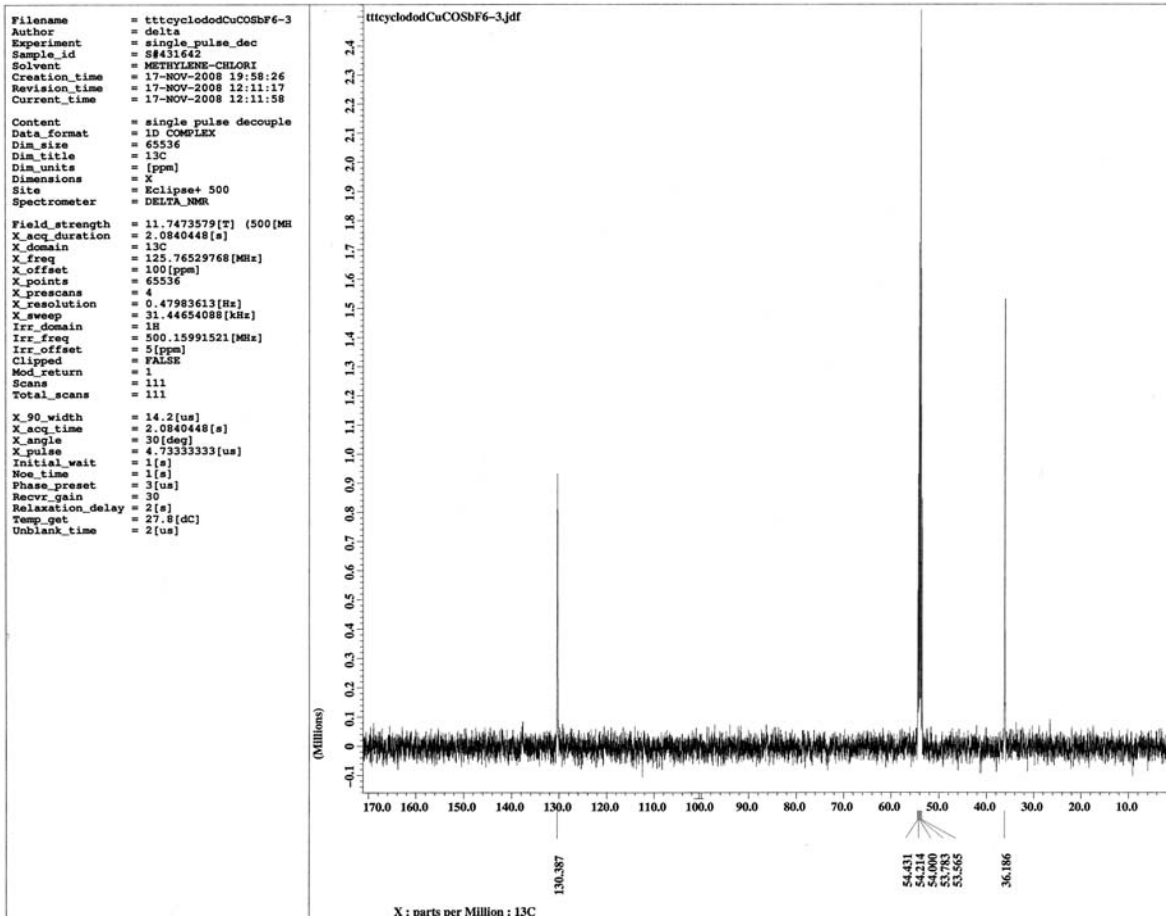
on	1	Slit	100
lation	20	Operator	Mauro
	632.81	Sample	[Cu(C12H18)]SbF6
	Multi	Remark	20 accum.
	200	Power	laser633 D0.6

HORIBA JOBIN YVON

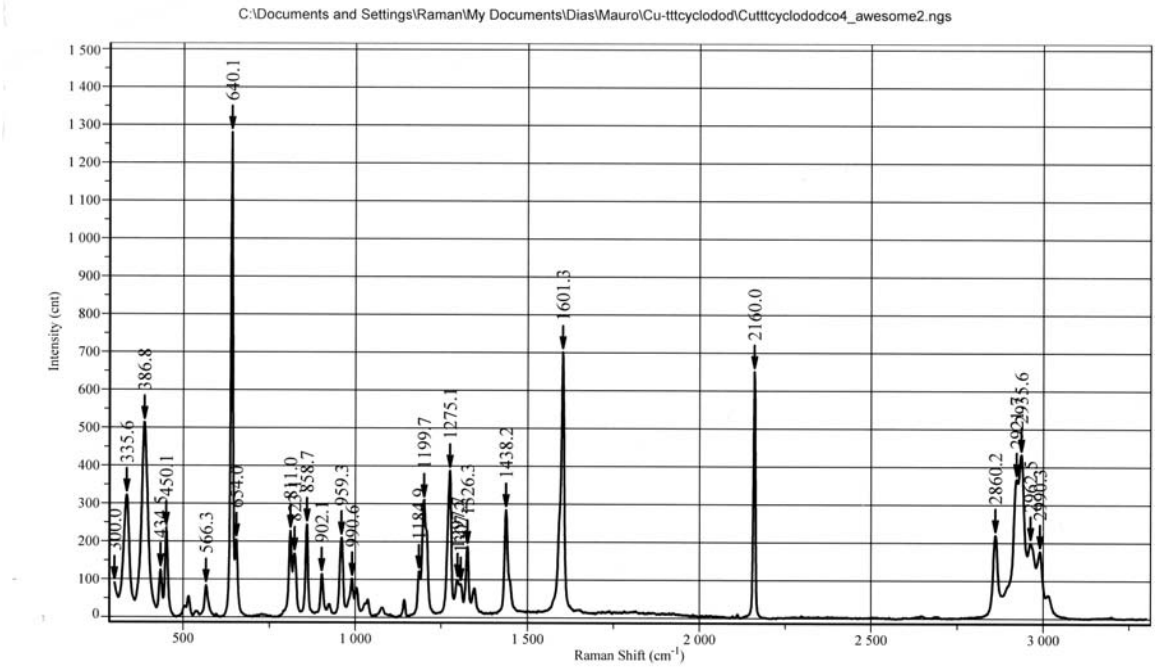
^{1}H NMR spectrum of [Cu(*ttt*-cdt)(CO)][SbF_6] (in CD_2Cl_2)



$^{13}C\{^{1}H\}$ NMR spectrum of [Cu(*ttt*-cdt)(CO)][SbF_6] (in CD_2Cl_2)



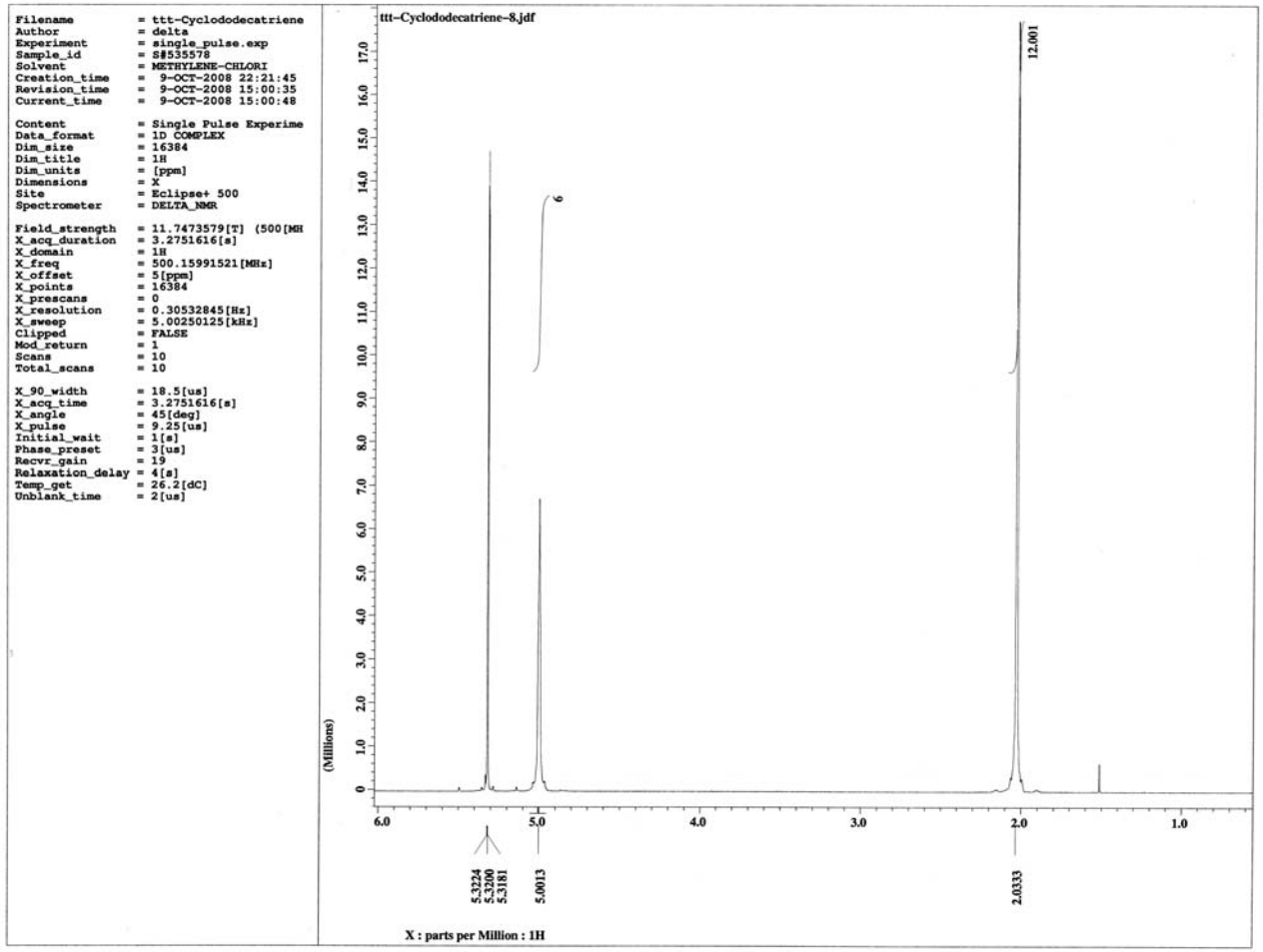
Raman spectrum of [Cu(*ttt*-cdt)(CO)][SbF_6] (crystals)



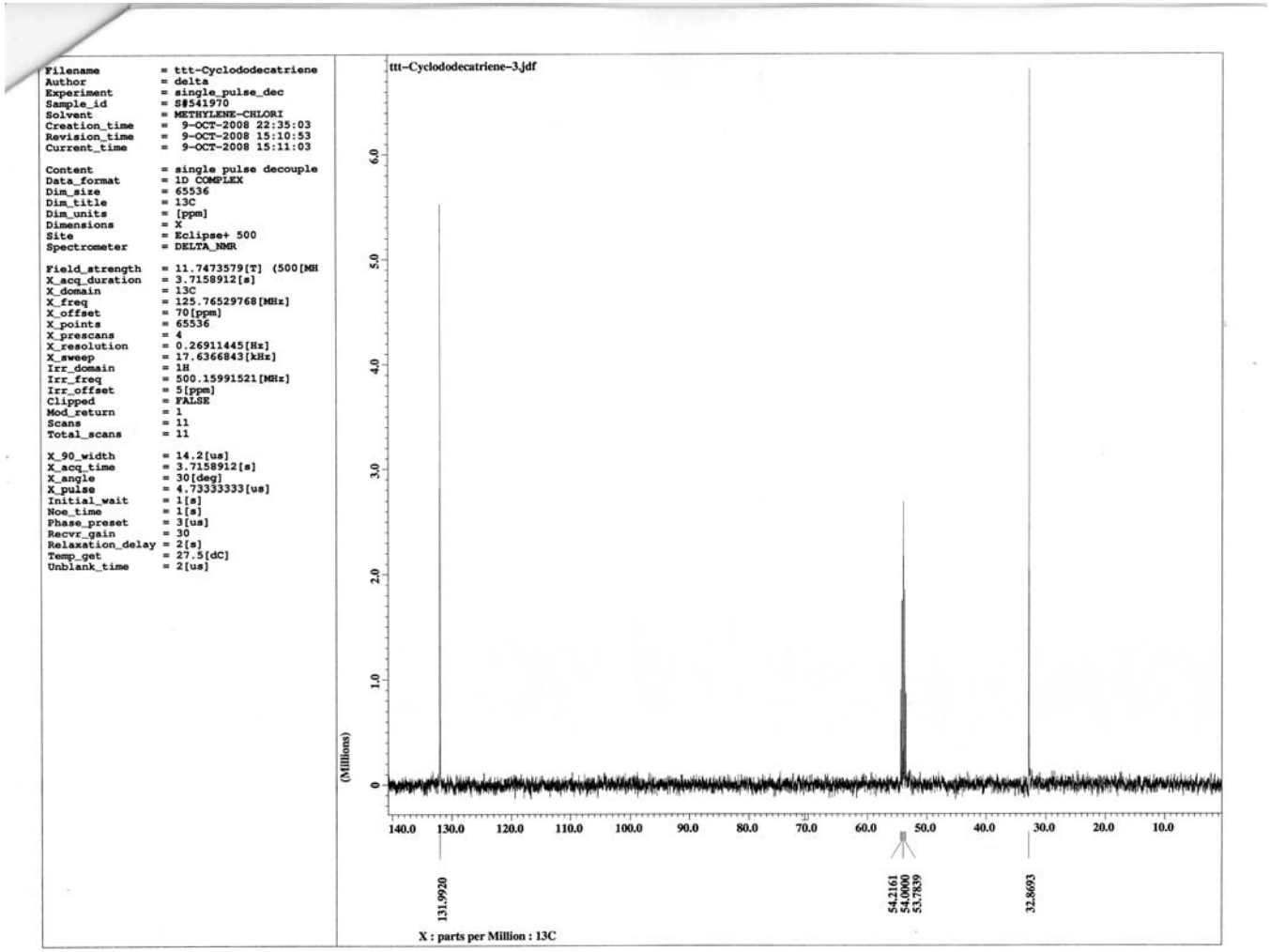
Exposition	1	Slit	100
Accumulation	100	Operator	Mauro
Laser	632.81	Sample	[Cu(C12H18)(CO)]SbF6
Spectro	Multi	Remark	100 accum.
Hole	200	Power	laser633 full

HORIBA JOBIN YVON

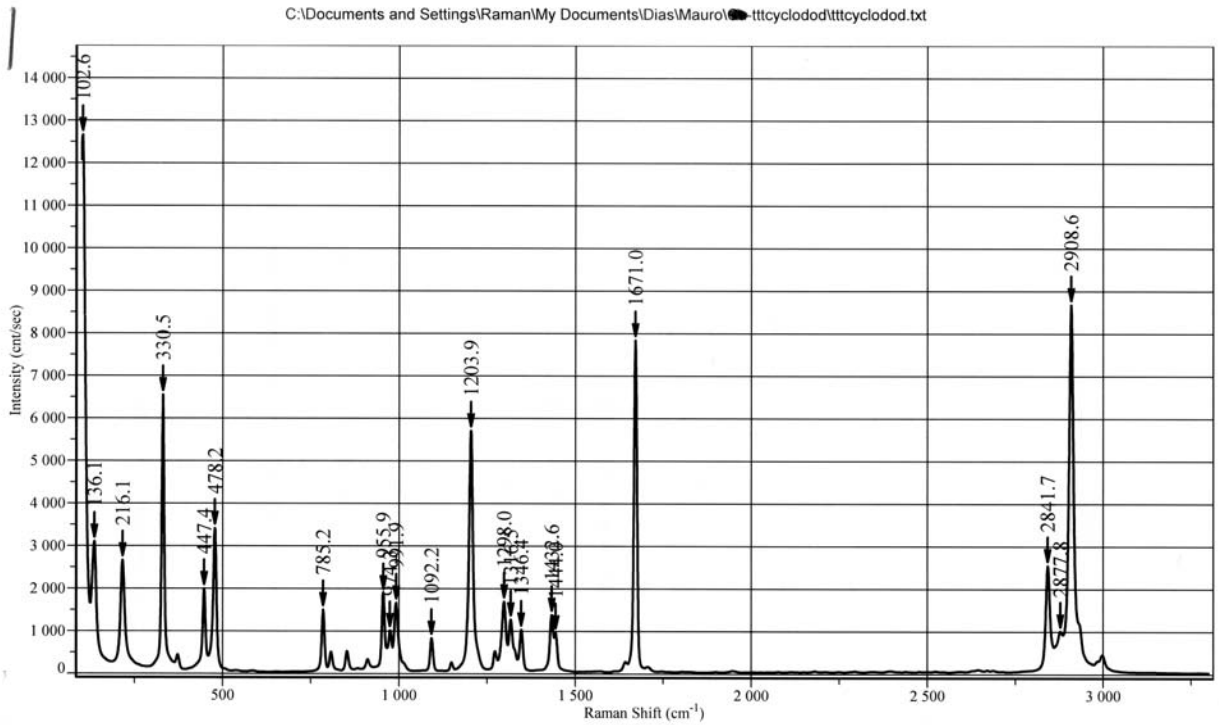
^{1}H NMR spectrum of free *ttt*-cdt (in CD_2Cl_2)



$^{13}C\{^{1}H\}$ NMR spectrum of free *ttt*-cdt (in CD_2Cl_2)



Raman spectrum of free *ttt*-cdt (solid)



Exposition	1	Slit	100
Accumulation	30	Operator	Mauro
Laser	632.81	Sample	[redacted](t,t,t-cyclodod)[redacted]
Spectro	Multi	Remark	30 accum.
Hole	200	Power	laser633nm D2

HORIBA JOBIN YVON