Electronic Supplementary Material (ESI) for Dalton Transactions.

Carbonyl complexes of copper(I) stabilized by bridging fluorinated pyrazolates and halide ions

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Supporting Information

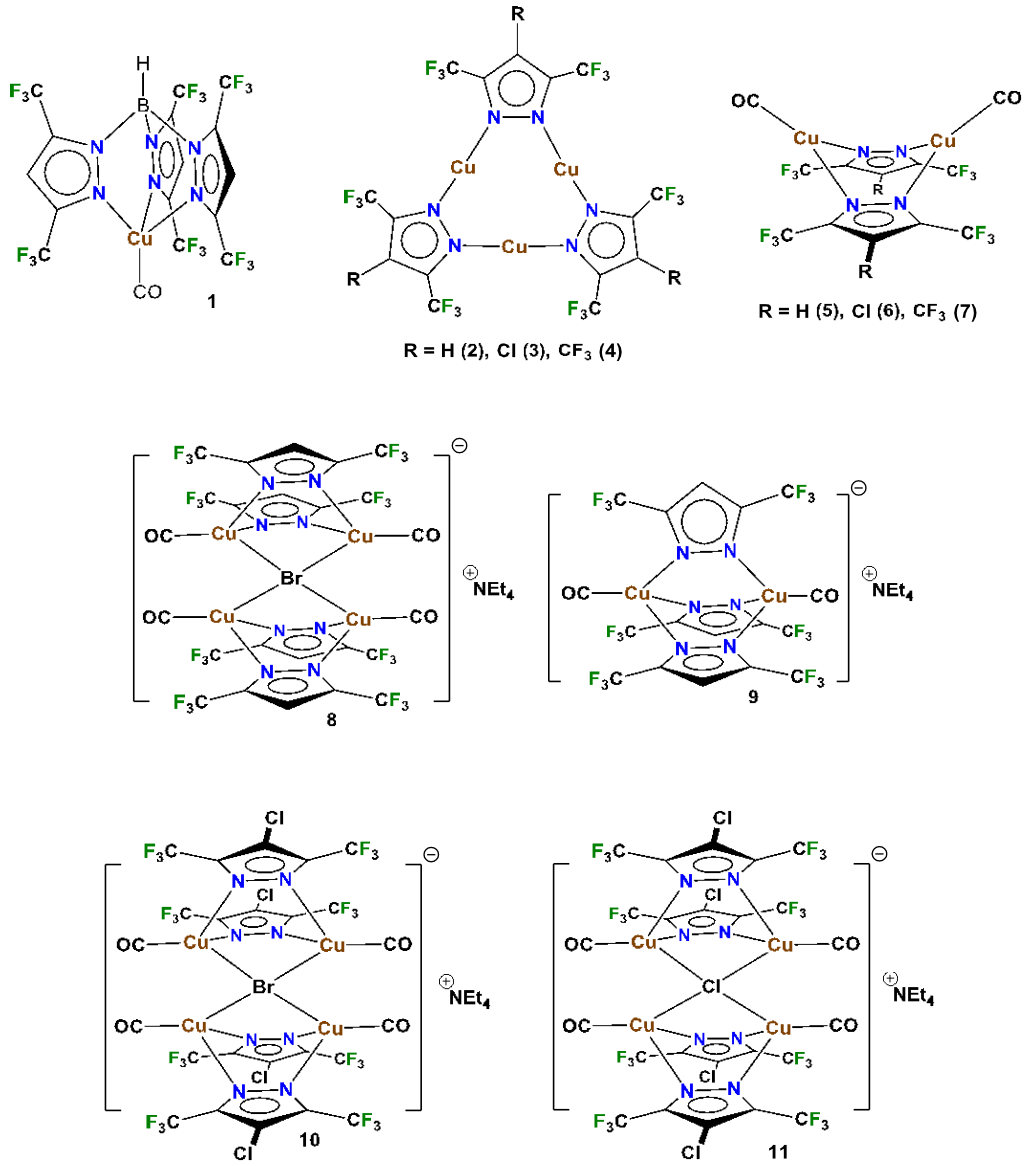
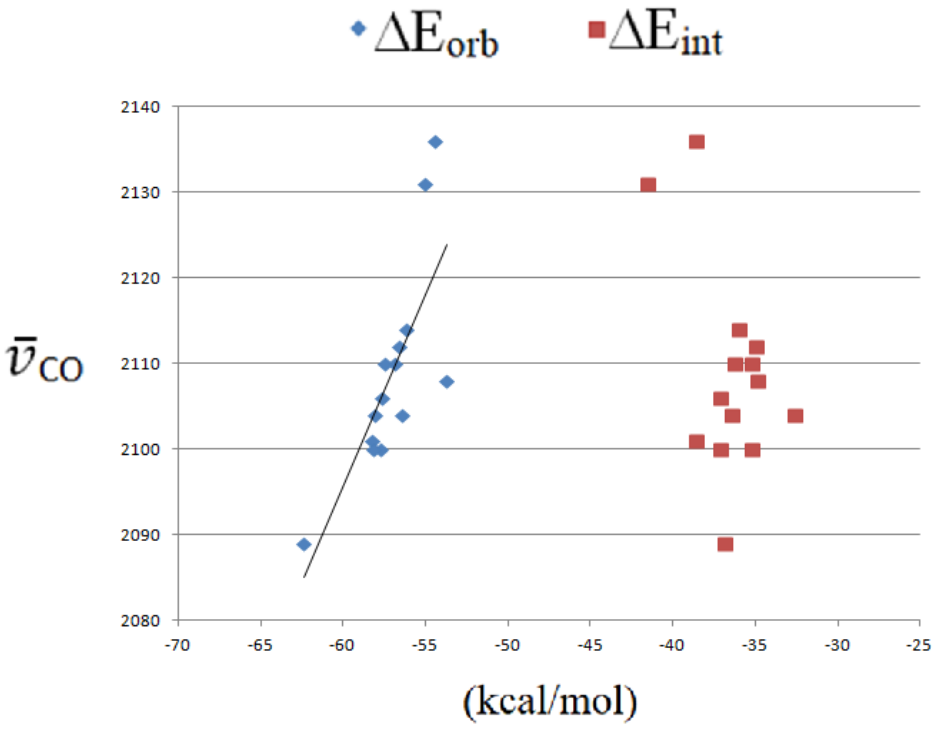


Figure S1. Structures of some of the molecules discussed in the manuscript.

Table S1. Vibrational and structural data for the calculated systems at the ZORA TZ2P/BP86-D3 level of theory. Distances in Angstrom, angles in degrees and ν_{CO} in cm^{-1}. Experimental results are given in parenthesis.

	ν_{CO}	Cu-N	Cu-X	Cu-CO	Cu-C-O
{[3,5-$(CF_3)_2$Pz]Cu(CO)}$_2$ (**5**)	2095/2101 (2099/2108)	2.064 (1.971)		1.830 (1.843)	172.2 (177.1)
{[4-Cl-3,5-$(CF_3)_2$Pz]Cu(CO)}$_2$ (**6**)	2099/2106 (2139)	2.078		1.835	168.4
{[3,4,5-$(CF_3)_3$Pz]Cu(CO)}$_2$ (**7**)	2102/2108 (2139)	2.042 (1.990)		1.853 (1.831)	178.9 (179.1)
{[3,5-$(CF_3)_2$Pz]$_3$Cu$_2$$(CO)_2$}$^-$ (**9**)	2089 (2087)	2.101 (2.043)		1.819 (1.813)	180.0 (179.1)
{[4-Cl-3,5-$(CF_3)_2$Pz]$_3$Cu$_2$$(CO)_2$}$^-$	2100	2.117		1.845	180.0
{[3,4,5-$(CF_3)_3$Pz]$_3$Cu$_2$$(CO)_2$}$^-$	2104	2.122		1.851	179.8
[{[3,5-$(CF_3)_2$Pz]Cu(CO)}$_4$(μ_4-Br)]$^-$ (**8**)	2104 (2098)	2.071 (2.002)	2.661 (2.740)	1.837 (1.817)	177.3 (177.2)
[{[4-Cl-3,5-$(CF_3)_2$Pz]Cu(CO)}$_4$(μ_4-Br)]$^-$ (**10**)	2110 (2106)	2.088 (2.019)	2.665 (2.595)	1.841 (1.817)	176.5 (174.9)
[{[3,4,5-$(CF_3)_3$Pz]Cu(CO)}$_4$(μ_4-Br)]$^-$	2112	2.073	2.678	1.843	173.9
[{[3,5-$(CF_3)_2$Pz]Cu(CO)}$_4$(μ_4-Cl)]$^-$	2100	2.069	2.537	1.835	176.3
[{[4-Cl-3,5-$(CF_3)_2$Pz]Cu(CO)}$_4$(μ_4-Cl)]$^-$ (**11**)	2110 (2105)	2.087 (2.023)	2.480 (2.465)	1.837 (1.823)	176.7 (175.8)
[{[3,4,5-$(CF_3)_3$Pz]Cu(CO)}$_4$(μ_4-Cl)]$^-$	2114	2.099	2.484	1.844	176.6
[H_2B(3,5-$(CF_3)_2$Pz)$_2$]CuCO	2136 (2127)	2.024		1.836	177.0
[HB(3,5-$(CF_3)_2$Pz)$_3$]CuCO (**1**)	2131 (2137)	2.108		1.833	180.0

Figure S2. Correlation between ν_{CO} vs ΔE_{orb} (blue), and ν_{CO} vs ΔE_{int} (red), along all the calculated series, denoting a better correlation in the former relationship.



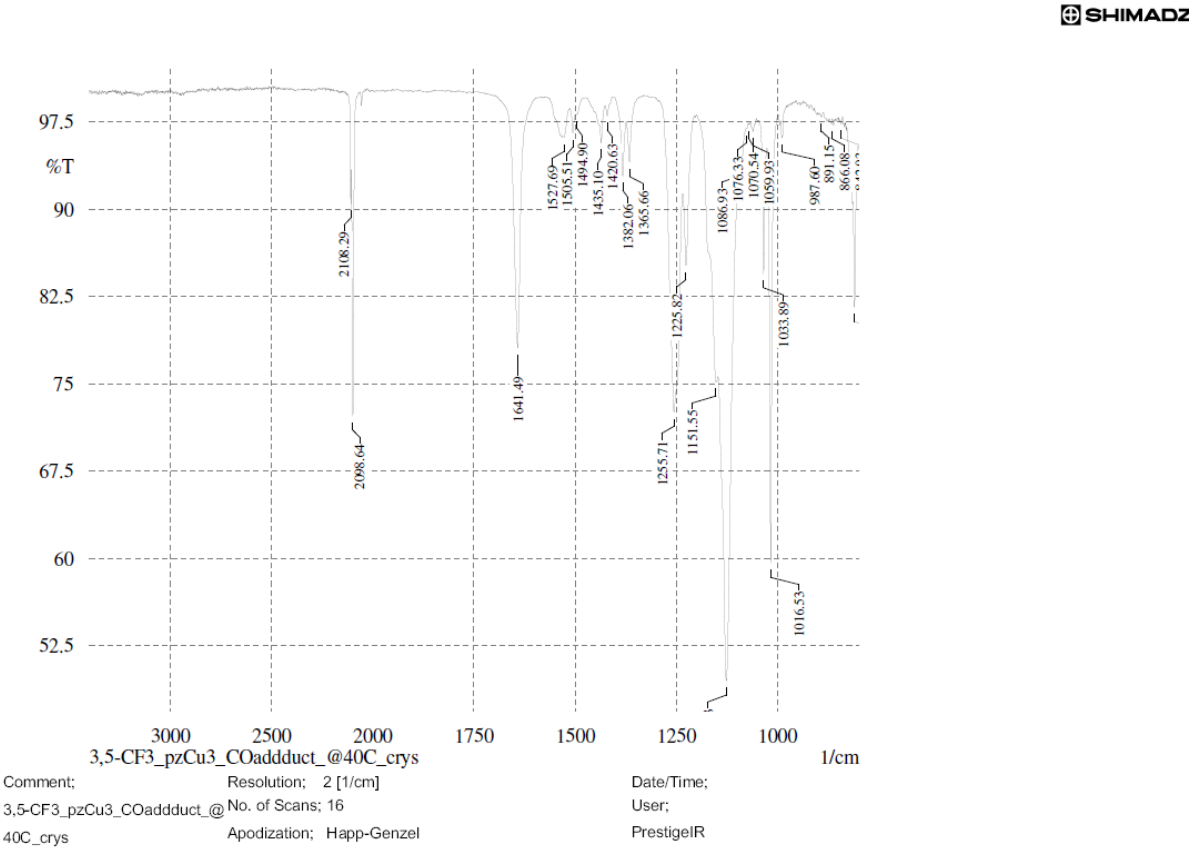


Figure S3. IR spectrum of {[3,5-$(CF_3)_2$Pz]Cu(CO)}$_2$ (**5**). ATR-IR spectrum of crystals (top) and CO stretch region in Nujol (bottom)

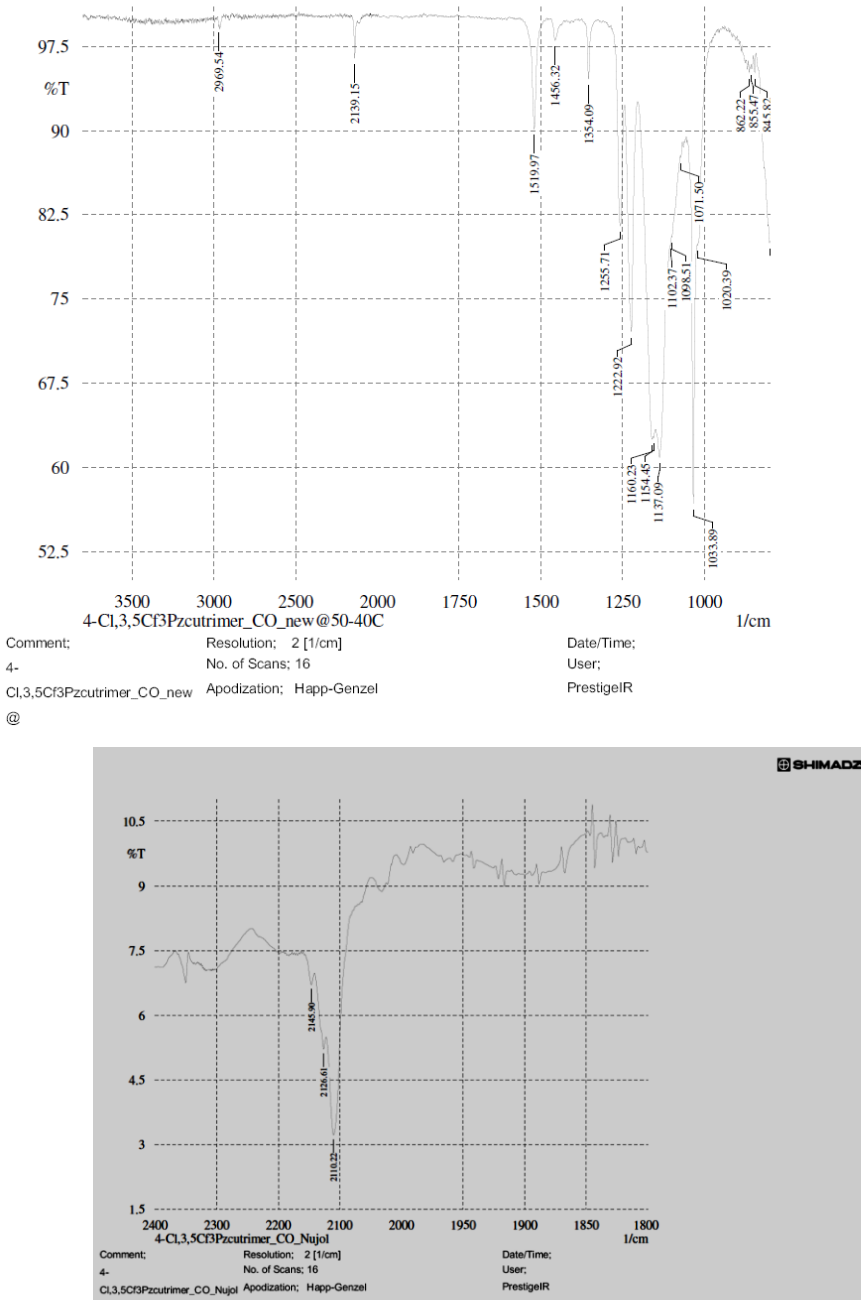
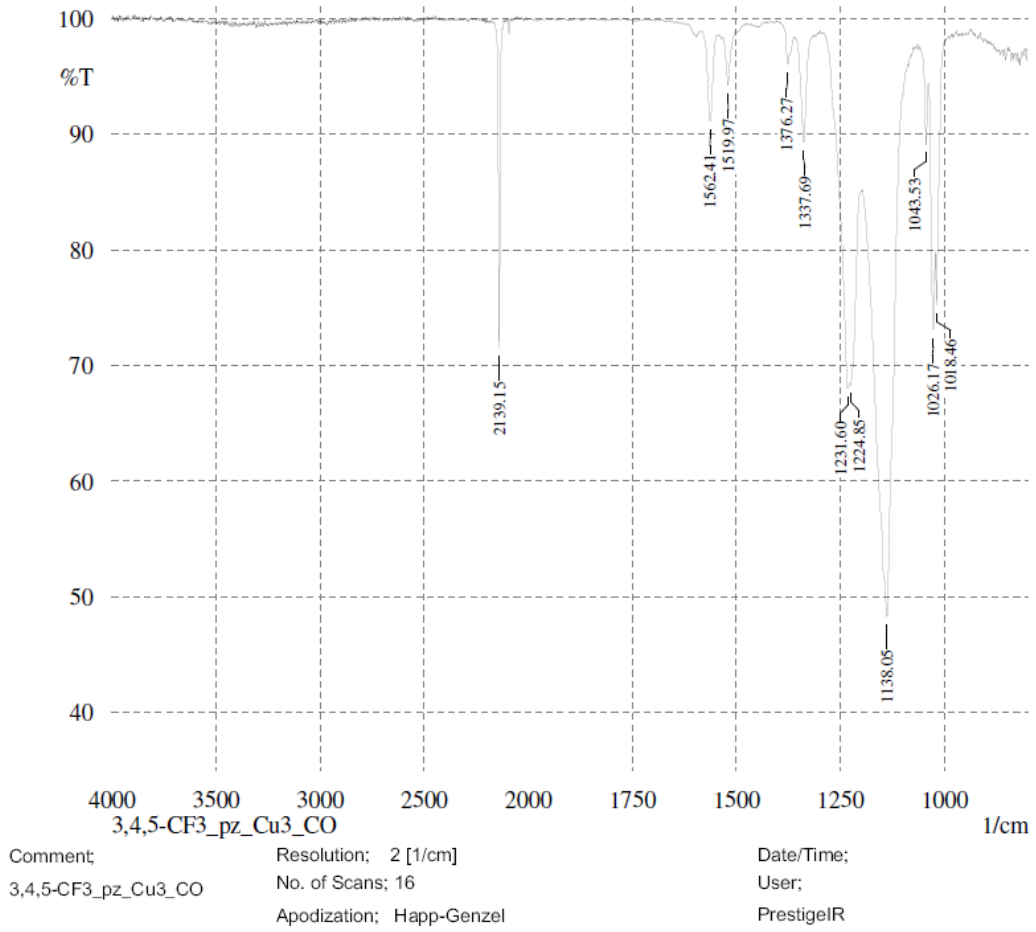


Figure S4. IR spectrum of {[4-Cl-3,5-$(CF_3)_2$Pz]Cu(CO)}$_2$ (**6**). ATR-IR spectrum of crystals (top) and CO stretch region in Nujol (bottom)



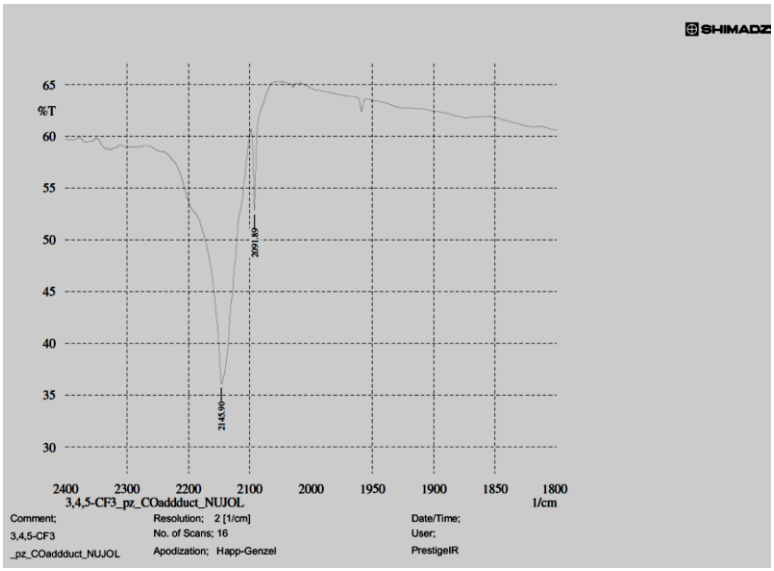


Figure S5. IR spectrum of {[3,4,5-$(CF_3)_3$Pz]Cu(CO)}$_2$ (**7**). ATR-IR spectrum of crystals (top) and CO stretch region in Nujol (bottom)

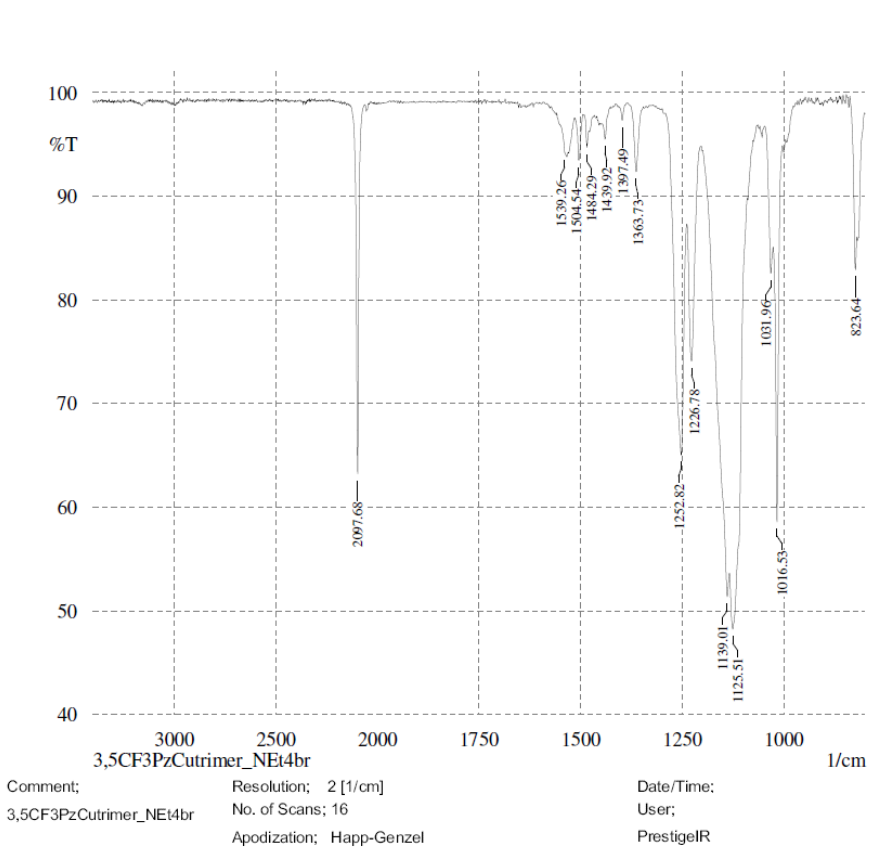


Figure S6. Infrared spectrum of [NEt_4][{[3,5-$(CF_3)_2$Pz]Cu(CO)}$_4$(μ_4-Br)] (**8**)

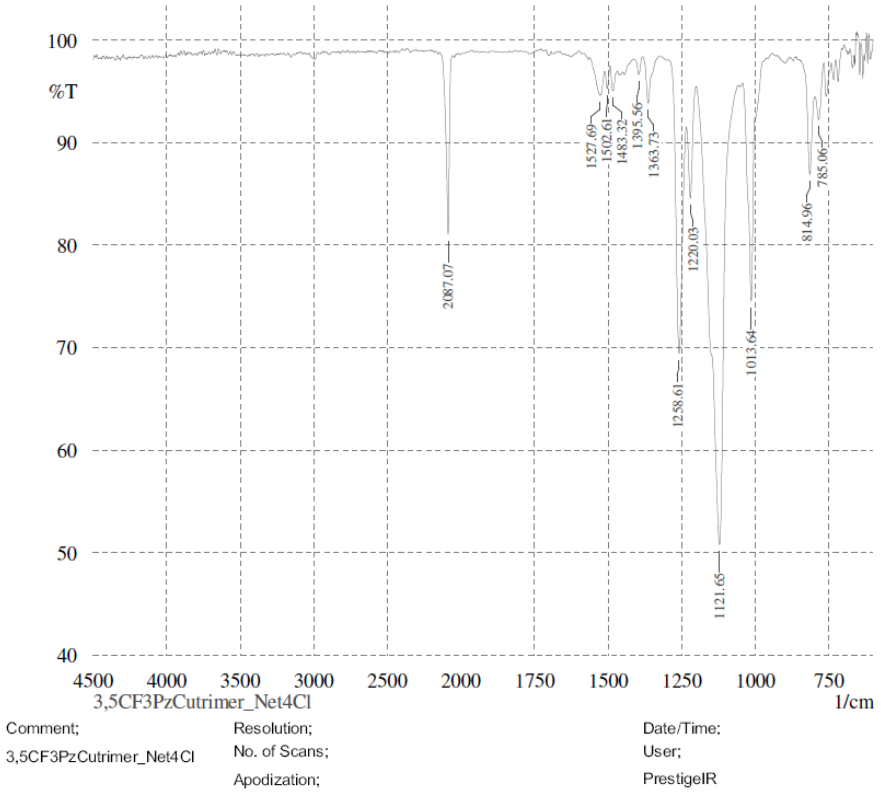


Figure S7. Infrared spectrum of $[NEt_4]\{[3,5\text{-}(CF_3)_2Pz]_3Cu_2(CO)_2\}$ (**9**)

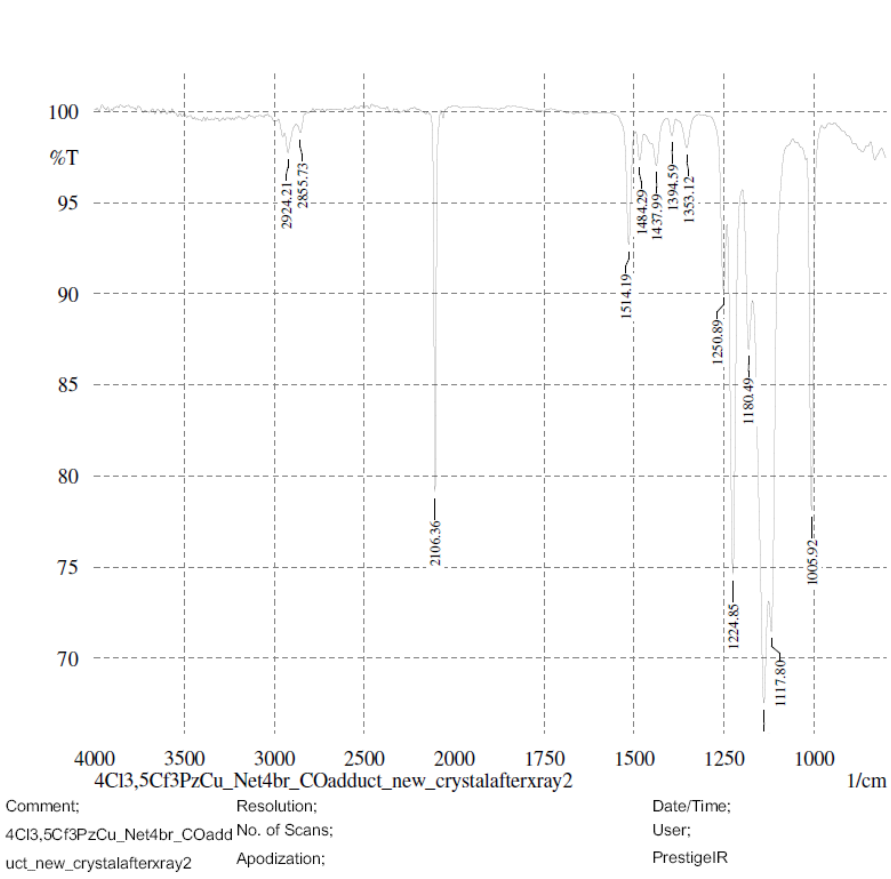


Figure S8. Infrared spectrum of $[NEt_4][\{[4\text{-Cl-3,5-}(CF_3)_2Pz]Cu(CO)\}_4(\mu_4\text{-Br})]$ (**10**)

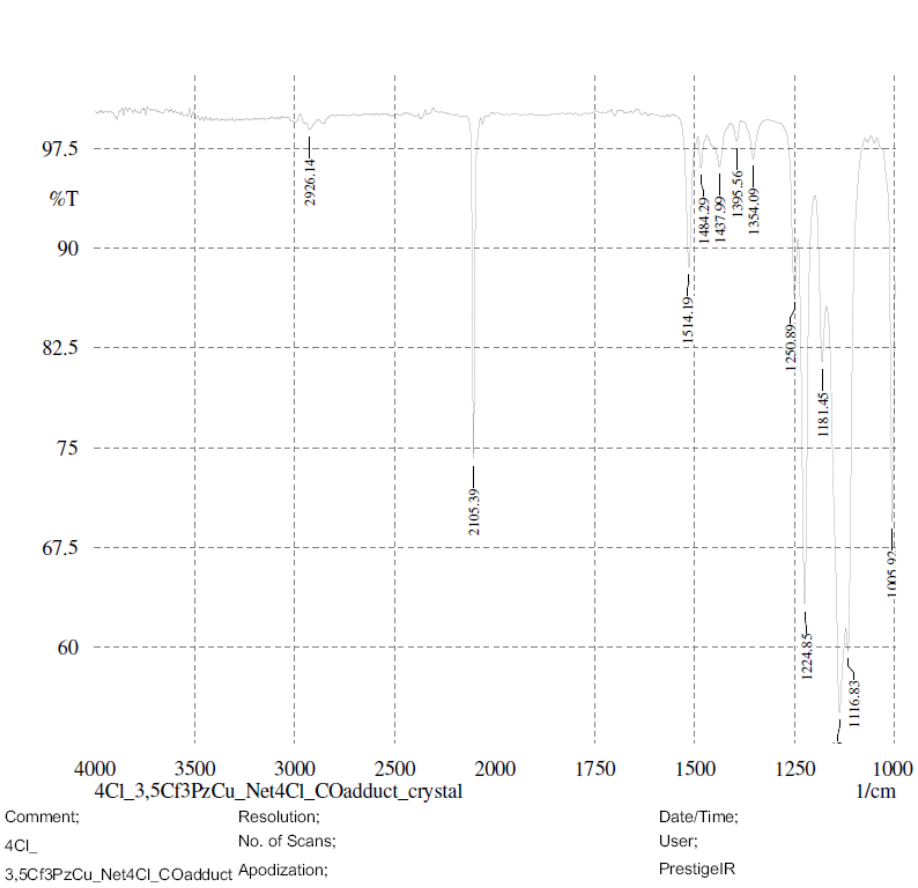


Figure S9. Infrared spectrum of $[NEt_4][\{[4\text{-Cl-3,5-}(CF_3)_2Pz]Cu(CO)\}_4(\mu_4\text{-Cl})]$ (**11**)

Table S2. Selected NMR spectroscopic (in $CDCl_3$ except for **1**, which was reported in C_6D_6) and IR data

Complexes	**^{1}H NMR (ppm)**	**^{19}F NMR (ppm)**	**IR** (cm^{-1})	**Ref**
$[HB(3,5\text{-}(CF_3)_2Pz)_3]CuCO$ **(1)**	6.06	-61.4 (s), -58.8 (d)	2137	[1]
$[H_2B(3,5\text{-}(CF_3)_2Pz)_2]CuCO$	-	-	2127	[2]
$\{[3,5\text{-}(CF_3)_2Pz]Cu\}_3$ **(2)**	7.07 (s)	-61.32 (s)	-	[3]
$\{[4\text{-}Cl\text{-}3,5\text{-}(CF_3)_2Pz]Cu\}_3$ **(3)**	-	-61.50 (s)	-	[4]
$\{[3,4,5\text{-}(CF_3)_3Pz]Cu\}_3$ **(4)**	-	-55.12 (s), -60.15 (s)	-	[5]
$\{[3,5\text{-}(CF_3)_2Pz]Cu(CO)\}_2$ **(5)**	7.06 (s)	-59.63 (br)	2099, 2108(sh)	
$\{[4\text{-}Cl\text{-}3,5\text{-}(CF_3)_2Pz]Cu(CO)\}_2$ **(6)**	-	-60.27 (s)	2139	
$\{[3,4,5\text{-}(CF_3)_3Pz]Cu(CO)\}_2$ **(7)**	-	-55.23 (s), -59.38 (s)	2139	
$[NEt_4][\{[3,5\text{-}(CF_3)_2Pz]Cu(CO)\}_4(\mu_4\text{-}Br)]$ **(8)**	1.21 (t), 3.03 (q), 6.84 (s)	-60.73 (br)	2098	
$[NEt_4]\{[3,5\text{-}(CF_3)_2Pz]_3Cu_2(CO)_2\}$ **(9)**	1.20 (t), 3.04 (q), 6.80 (s)	-60.63 (br)	2087	
$[NEt_4][\{[4\text{-}Cl\text{-}3,5\text{-}(CF_3)_2Pz]Cu(CO)\}_4(\mu_4\text{-}Br)]$ **(10)**	1.29 (t), 3.13 (q)	-60.25 (br)	2106	
$[NEt_4][\{[4\text{-}Cl\text{-}3,5\text{-}(CF_3)_2Pz]Cu(CO)\}_4(\mu_4\text{-}Cl)]$ **(11)**	1.30 (t), 3.14 (q)	-60.45 (br)	2105	
$[NEt_4][3,5\text{-}(CF_3)_2Pz]$	1.18 (t), 3.09 (q), 6.73 (s)	-60.33 (s)	-	
$[NEt_4][4\text{-}Cl\text{-}3,5\text{-}(CF_3)_2Pz]$	1.35 (br), 3.30 (br),	-60.96 (s)	-	

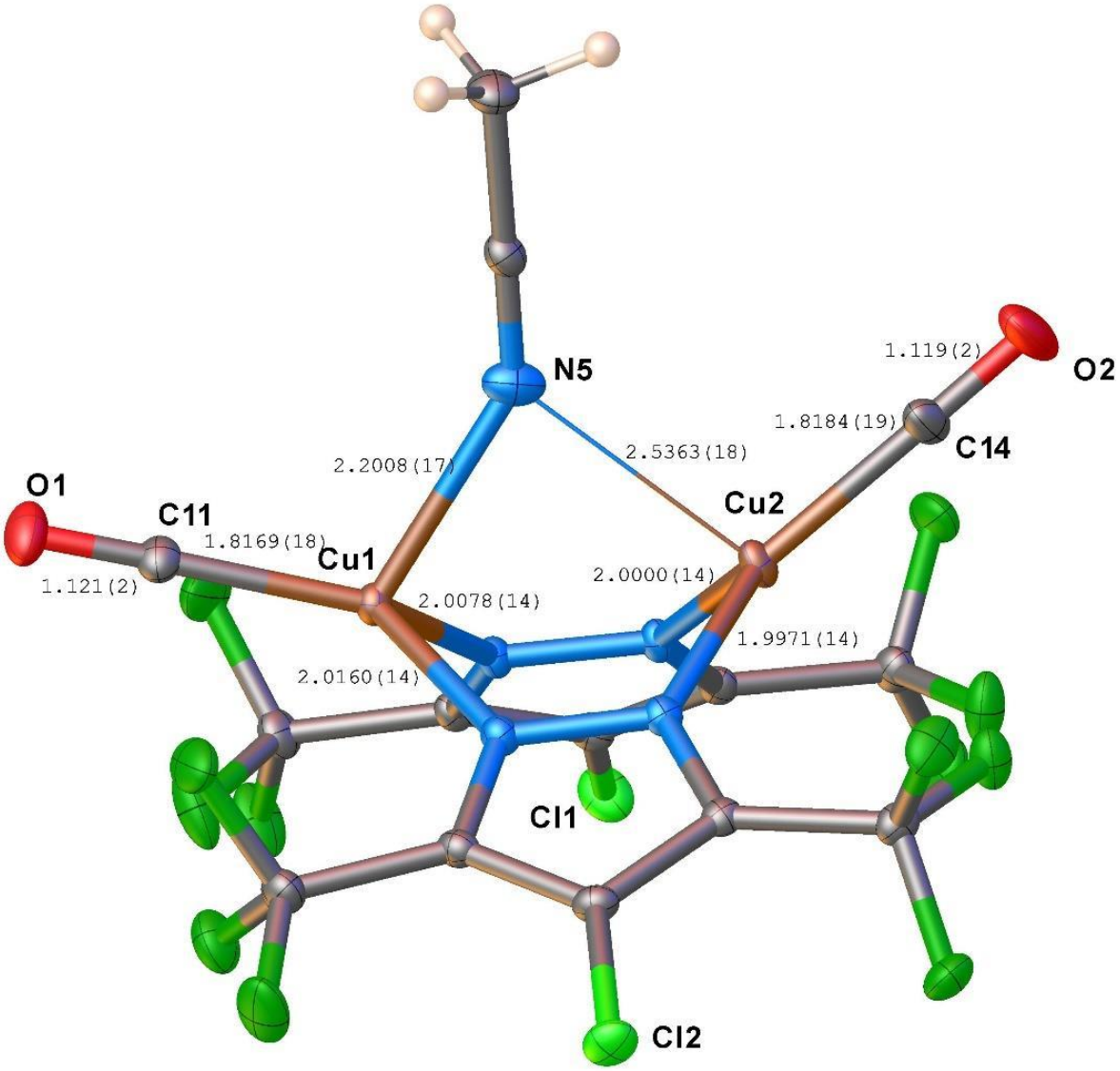


Figure S10. Selected bond distances of [{[4-Cl-3,5-$(CF_3)_2$Pz]Cu(CO)}$_2$(μ_2-CH_3CN)] showing the asymmetrically bound acetonitrile. Additional details are in the CIF.

References:

1. H. V. R. Dias and H.-L. Lu, *Inorg. Chem.*, 1995, **34**, 5380-5382.
2. G. Pampaloni, R. Peloso, D. Belletti, C. Graiff and A. Tiripicchio, *Organometallics*, 2007, **26**, 4278-4286.
3. H. V. R. Dias, H. V. K. Diyabalanage, M. G. Eldabaja, O. Elbjeirami, M. A. Rawashdeh-Omary and M. A. Omary, *J. Am. Chem. Soc.*, 2005, **127**, 7489-7501.
4. C. V. Hettiarachchi, M. A. Rawashdeh-Omary, D. Korir, J. Kohistani, M. Yousufuddin and H. V. R. Dias, *Inorg. Chem.*, 2013, **52**, 13576-13583.
5. N. B. Jayaratna, M. G. Cowan, D. Parasar, H. H. Funke, J. Reibenspies, P. K. Mykhailiuk, O. Artamonov, R. D. Noble and H. V. R. Dias, *Angew. Chem., Int. Ed.*, 2018, **57**, 16442-16446.