Supporting Information

Room Temperature Stable Organocuprate Cu(III) Complex

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Supporting Information

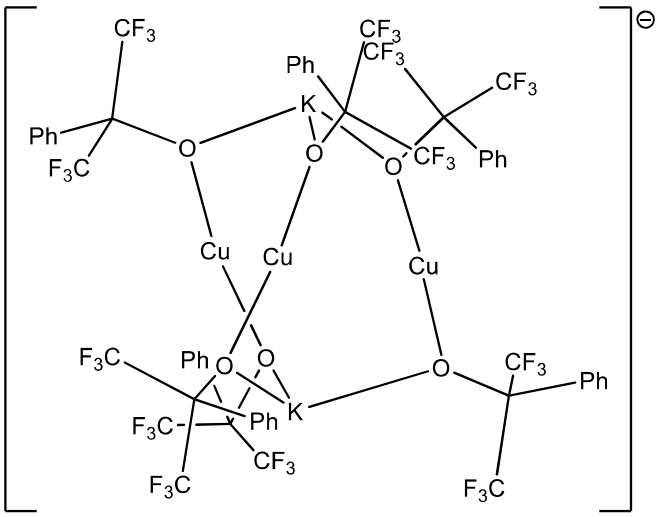

Figure S1: Molecular Structure of the anion of **4**, $[K_2\{Cu(OC(C_6H_5)(CF_3)_2)_2\}_3]^-$. Cation $\{K(18C6\}^+$ omitted for clarity.

Table S1: Summary of X-ray crystallographic data collection parameters for copper complexes.

Complex #	**2**	**3**	**4**	**5**
Formula	$C_{24}H_{33}CuF_{18}CuKO_9$	$C_{27}H_{15}CuF_{18}KO_3$	$C_{44}H_{36}Cu_2F_{24}K_2O_8$	$C_{30}H_{32}CuF_{12}KO_8$
Formula Weight	910.141	832.03	1354.01	851.20
Temp (K)	200(2)	173(2)	150(2)	100
Crystal System	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
***a* (Å)**	22.1068(11)	11.9365(6)	25.3378(15)	8.6969(2)
***b* (Å)**	8.5756(4)	22.8275(15)	15.1435(9)	19.4441(3)
***c* (Å)**	18.6294(9)	22.8784(11)	23.1089(13)	10.5153(2)
α (°)	90	90	90	90
β (°)	90	103.971(2)	118.6050(10)	105.309(1)
γ (°)	90	90	90	90
***V* (Å^3)**	3531.7(3)	6049.5(6)	7784.7(8)	1715.08(6)
Z	4	8	6	2
ρ, calc. (g/cm^3)	1.712	1.827	1.733	-
μ(MoKα) (mm^{-1})	0.877	1.002	1.116	3.03 (CuKα)
Collected	14706	41886	69978	33125
Independent	5690	6234	7141	3005
***R*(int)**	0.0280	0.0241	0.0340	0.038
***R*(*F*), %[a]**	2.90	3.47	3.11	2.80
***R*(ωF^2), %[b]**	7.29	6.54	5.99	7.20

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$ [b] $R(\omega F^2)=\{\Sigma[\omega(F_o^2-F_c^2)^2]/\Sigma[\omega(F_o^2)^2]\}^{1/2}$;

[b] $\omega=1/[\sigma^s(F_o^2)+(aP)^2+bP]$, $P=[2F_c^2+\max(F_o,0)]/3$

Table S2: Selected distances (Å) and angles (deg) for complexes **2** – **5**.

Complex #		**Distance (Å)**		**Angle (°)**
2	Cu(1)-O(7)	1.8283(18)	O(7)-Cu(1)-O(9)	113.88(9)
	Cu(1)-O(9)	1.8349(19)	O(7)-Cu(1)-O(8)	136.69(9)
	K(1)-O(5)	2.8141(19)	O(9)-Cu(1)-O(8)	109.42(10)
	K(1)-O(8)	2.8456(16)		
	K(1)-O(4)	2.860(2)		
	K(1)-O(3)	2.864(2)		
	K(1)-O(1)	2.872(2)		
	K(1)-F(11)	2.891(2)		
	K(1)-F(8)	2.8957(19)		
	K(1)-O(6)	2.904(2)		
	K(1)-O(2)	2.914(2)		
	O(1)-C(12)	1.419(4)		
	O(1)-C(1)	1.425(3)		
	O(2)-C(3)	1.404(4)		
	O(2)-C(2)	1.425(4)		
	O(3)-C(4)	1.414(4)		
	O(3)-C(5)	1.426(4)		
	O(4)-C(6)	1.413(4)		
	O(4)-C(7)	1.435(4)		
	O(5)-C(8)	1.422(4)		
	O(5)-C(9)	1.427(4)		
	O(6)-C(10)	1.419(3)		

Complex #		Distance (Å)		Angle (°)
	O(6)-C(11)	1.429(4)		
	O(7)-C(14)	1.381(3)		
	O(8)-C(18)	1.379(3)		
	O(9)-C(22)	1.377(3)		
3	Cu(1)-O(3)	1.8336(11)	O(3)-Cu(1)-O(1)	154.24(5)
	Cu(1)-O(1)	1.8429(11)	O(3)-Cu(1)-O(2)	114.93(5)
	Cu(1)-O(2)	1.8850(11)	O(1)-Cu(1)-O(2)	90.73(5)
	K(1)-O(1)	2.6852(11)		
	K(1)-O(2)	2.9187(11)		
	K(1)-F(3)	3.1484(15)		
	K(1)-F(5)	3.0645(13)		
	K(1)-F(11)	2.8687(14)		
	K(1)-F(3)	3.1484(15)		
	K(2)-O(3)	2.7021(11)		
	K(2)-F(9)	2.7145(10)		
	K(2)-F(16)	2.8212(11)		
	K(2)-F(14)	2.9463(11)		
	O(1)-C(2)	1.3821(19)		
	O(2)-C(11)	1.374(2)		
	O(3)-C(20)	1.3869(19)		
4	Cu(1)-O(1)	1.8312(12)	O(1)-Cu(1)-O(2)	173.22(5)
	Cu(1)-O(2)	1.8373(12)	O(3)-Cu(2)-O(3)	171.09(8)
	Cu(2)-O(3)	1.8366(12)		

Complex #		Distance (Å)		Angle (°)
	K(1)-O(1)	2.6623(13)		
	K(1)-O(2)	2.6699(13)		
	K(1)-O(3)	2.6283(13)		
	K(1)-F(21)	2.7709(11)		
	K(1)-F(23)	3.1487(13)		
	K(1)-F(26)	2.8487(12)		
	K(1)-F(28)	2.9280(13)		
	K(1)-F(35)	3.0687(12)		
	K(1)-F(36)	3.0809(12)		
	C(10)-O(2)	1.370(2)		
	C(19)-O(3)	1.372(2)		
5	Cu(1)-O(1)	1.8173(12)	O(1)-Cu(1)-C(1)	86.59(6)
	Cu(1)-C(1)	1.9314(17)	O(1_i)-Cu(1)-C(1)	93.41(6)
	K(1)-O(2)	2.7412(12)	O(1)-Cu(1)-O(1_i)	180.0
	K(1)-O(3)	2.7734(12)		
	K(1)-O(4)	2.8324(12)		
	C(7)-O(1)	1.392(2)		
	C(12)-O(3)	1.425(2)		
	C(10)-O(2)	1.421(2)		
	C(13)-O(4)	1.424(2)		
	C(11)-O(3)	1.422(2)		
	C(14)-O(4)	1.424(2)		
	C(15)-O(2)	1.420(2)		

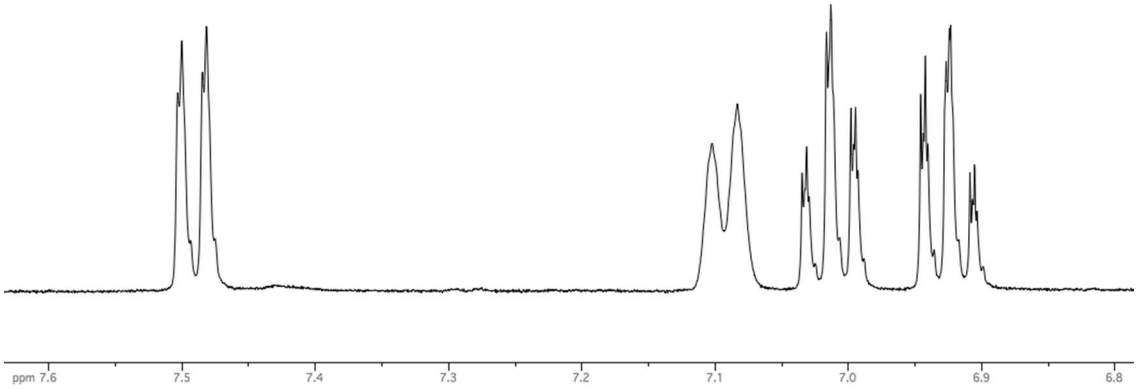

Figure S2: Phenyl region of the ^{1}H-NMR spectrum of **5** in d_8-THF**.**

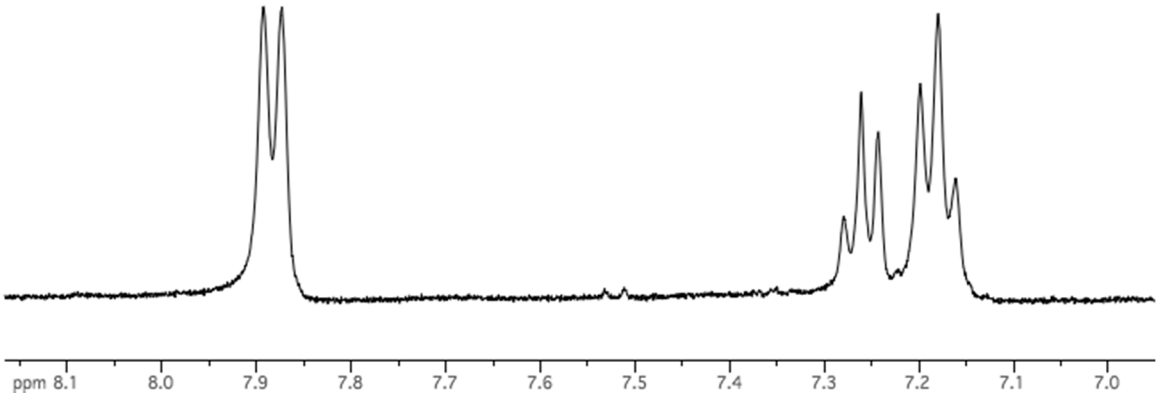

Figure S3: Phenyl region of the ^{1}H-NMR spectrum of **4** in CD_2Cl_2.

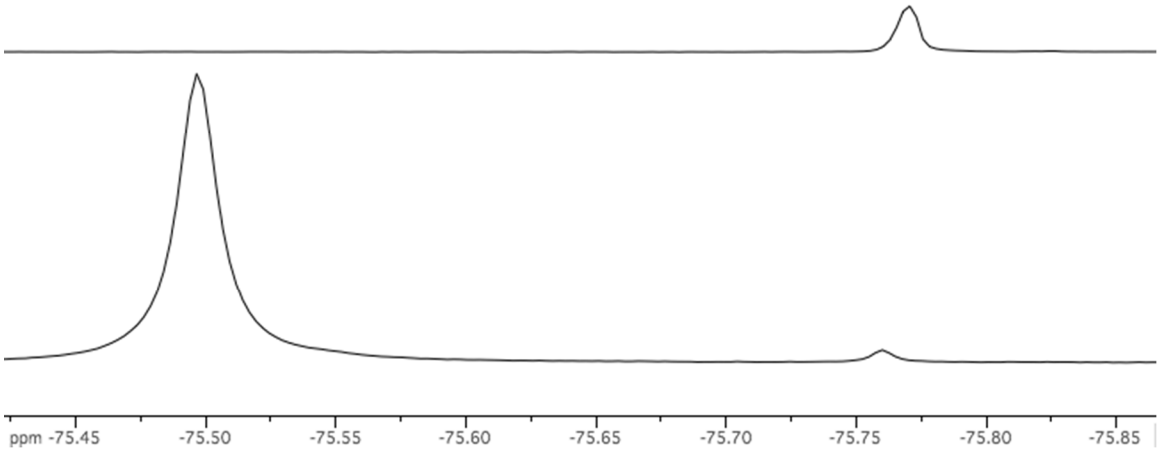

Figure S4: ^{19}F-NMR spectrum in d_8-THF of isolated product of synthetic procedure undertaken to obtain **5** (top). ^{19}F-NMR spectrum in CD_2Cl_2 of isolated product of synthetic procedure undertaken to obtain **4** and **5** (bottom).

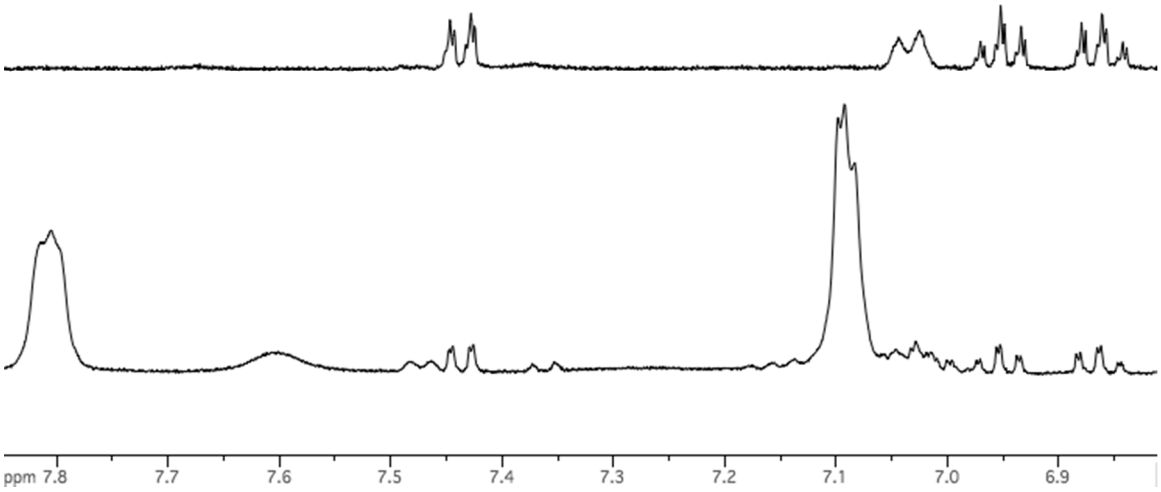

Figure S5: Phenyl region of ^{1}H-NMR spectrum in d_8-THF of crude mixture containing **5** (bottom) displaying same resonances as purified **5** (top). The top spectrum is identical to Figure S2 and was repeated for clarity.

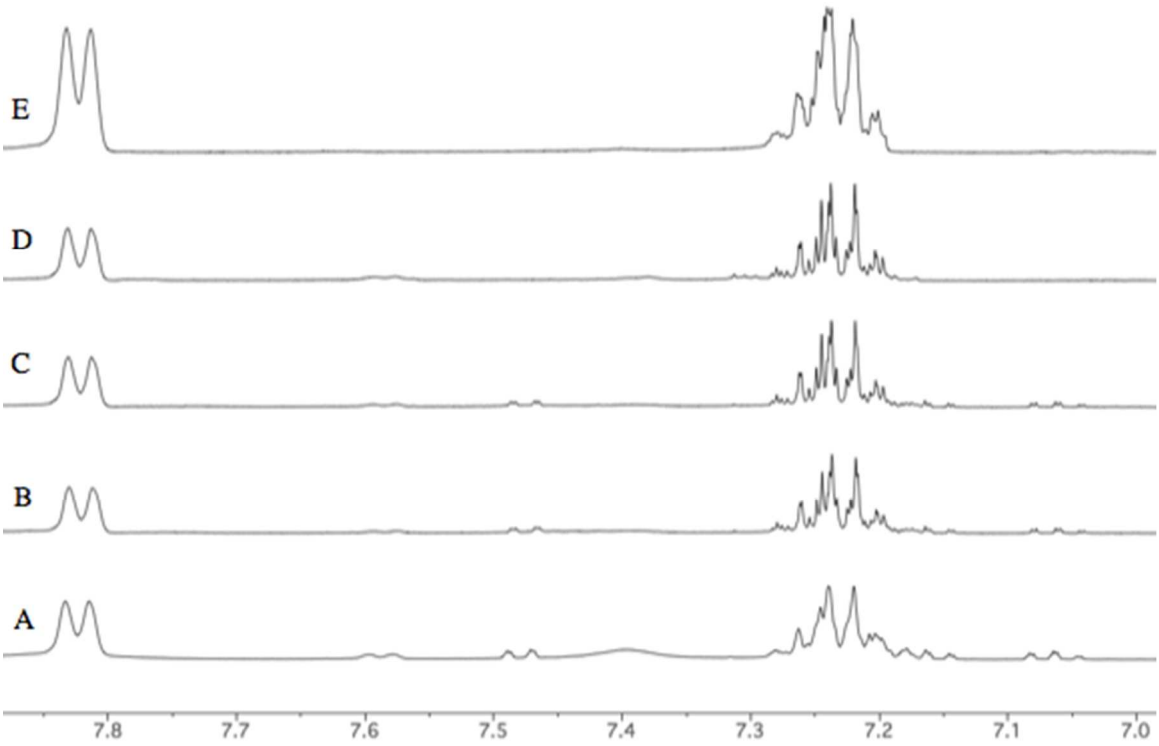

Figure S6:

A. Phenyl region of ^{1}H-NMR spectrum in CD_2Cl_2 of crude product of reaction undertaken to obtain **5**.

B. After stirring in a solution of CH_2Cl_2 for one hour in the dark.

C. After stirring in a solution of CH_2Cl_2 for ten hours in the dark.

D. After stirring in a solution of CH_2Cl_2 for ten hours in ambient light.

E. Phenyl region of ^{1}H-NMR spectrum of independently prepared $\{K(18C6)\}[Cu\{OC(C_6H_5)(CF_3)_2\}_2]$[1] in CD_2Cl_2.

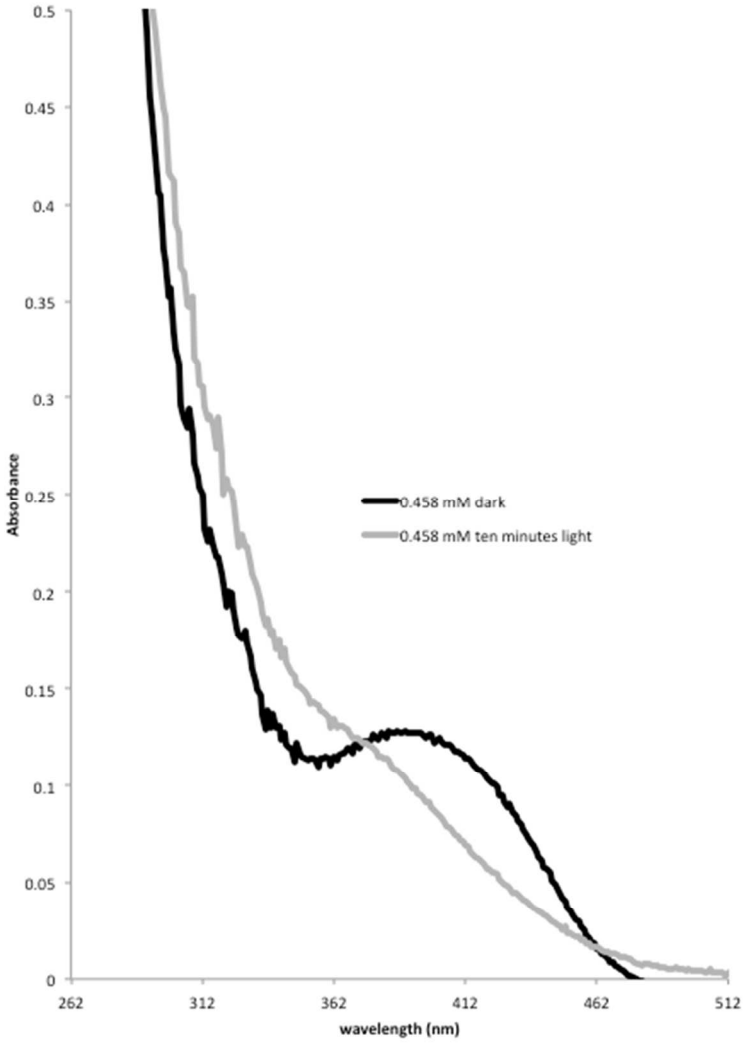

Figure S7: Ultraviolet-visible spectrum of 0.458 mM dark THF solution of **5** (black trace), and ultraviolet-visible spectrum of 0.458 mM THF solution of **5** after being exposed to light for ten minutes (grey trace).

Figure S8: Insolubility of **5** in H_2O.

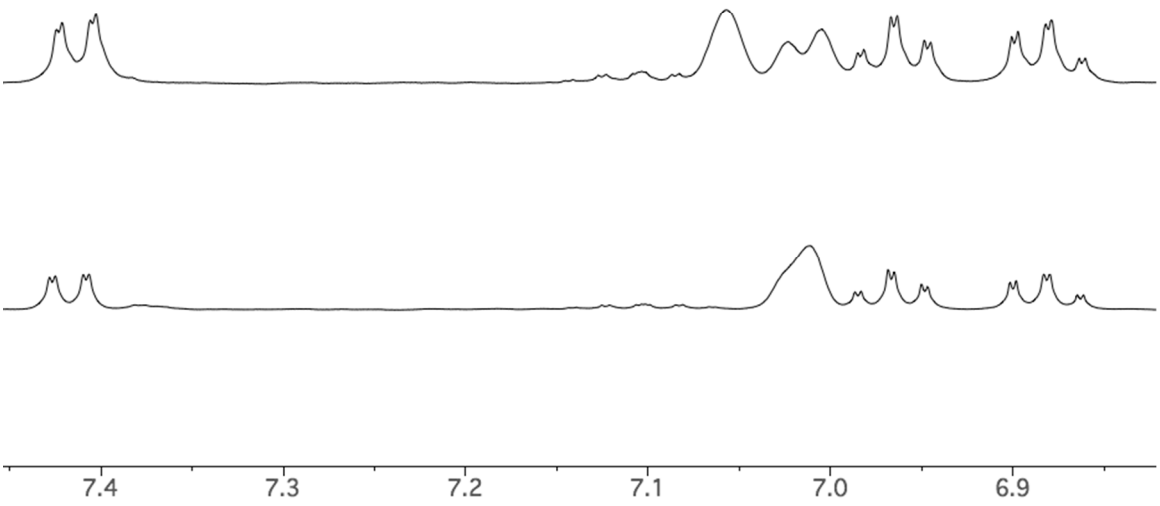

Figure S9: Phenyl region of the ^{1}H-NMR spectrum of **5** after to exposure to H_2O for one week, directly after dissolving in d_8-THF (bottom). Phenyl region of the ^{1}H-NMR of **5** after to exposure to H_2O for one week, twenty-four hours after dissolving in d_8-THF (top).

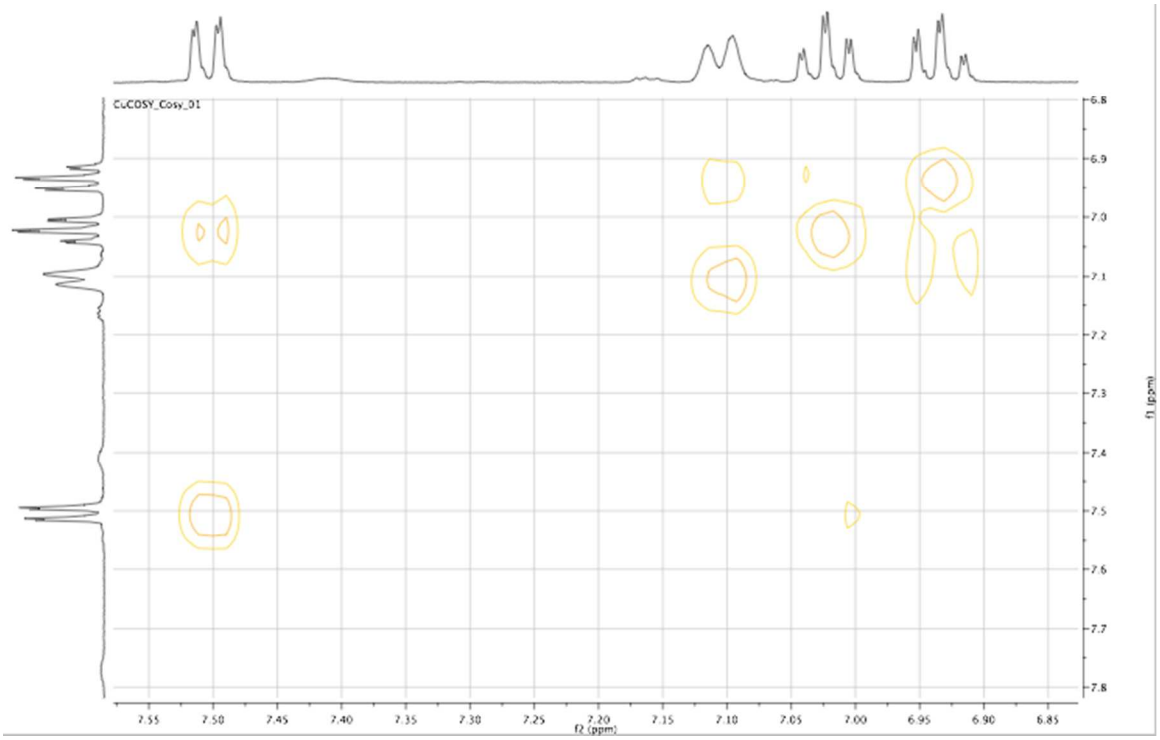

Figure S10: Phenyl region of the ^{1}H-^{1}H COSY spectrum of **5**. ^{1}H-NMR resonances occupy both the horizontal and vertical axes.

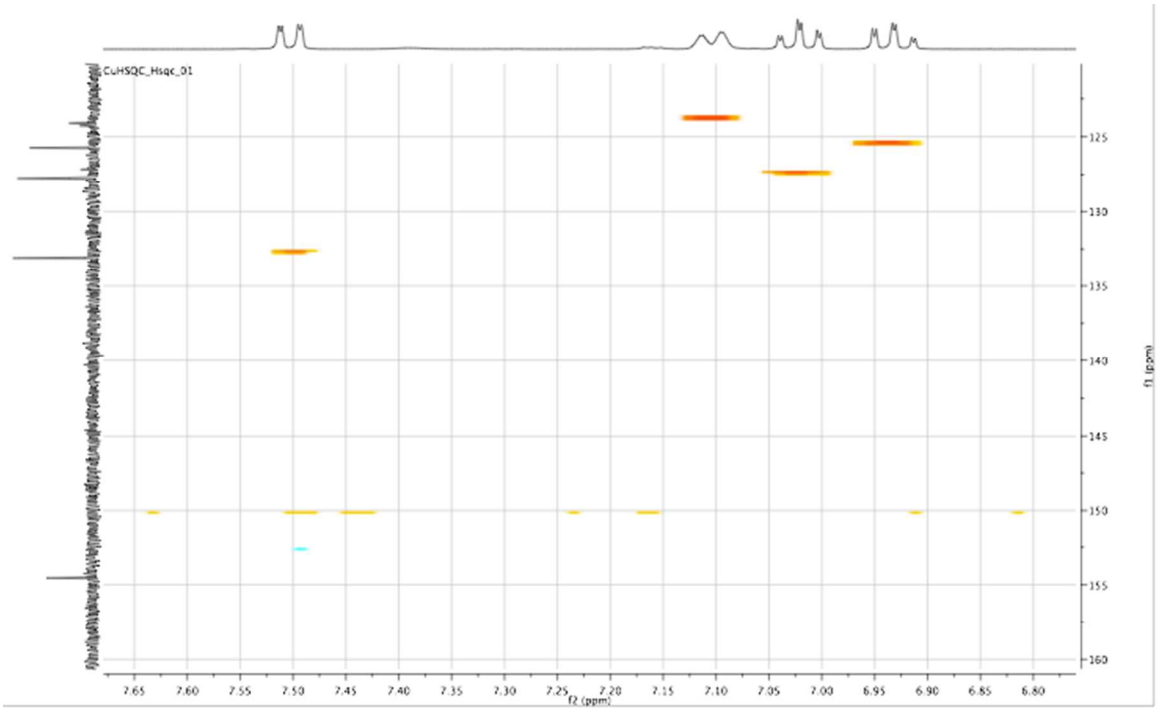

Figure S11: Phenyl region of the ^{1}H-^{13}C HSQC spectrum of **5**. ^{1}H-NMR resonances occupy the horizontal axis and ^{13}C-NMR resonances occupy the vertical axis.

Cambridge Structural Database Search.

A search of the Cambridge Structural Database (V. 5.33)[2] was performed, which included a four-coordinate metal bound in the "bow-tie" geometry displayed Figure S12. This search revealed eleven structures, four of which had two coordinate oxygen atoms in the five membered chelate ring surrounding the metal center. Those structures are listed below, and all include *p*-block elements and no *d*-block transition metals.

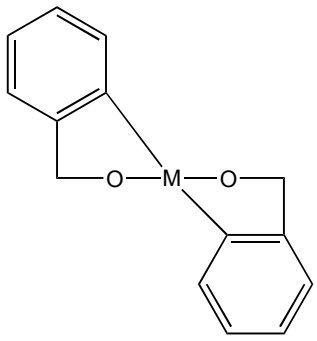

Figure S12: Motif used in Cambridge Structural Database search.

Table S3: List of search results from Cambridge Structural Database

CSD Code	**Compound**	**M-O Distances (Å)**	**M-C Distances (Å)**	**Reference**
KUWXEF	$[NEt_4][Sb(OC(C_6H_4)(CF_3)_2)_2]$	2.133 2.139	2.133 2.162	[3]
YAHYEL	$[NEt_4][Bi(OC(C_6H_4)(CF_3)_2)_2]$	2.273 2.306	2.237 2.249	[4]
YAHYEL10	$[NEt_4][Bi(OC(C_6H_4)(CF_3)_2)_2]$	2.273 2.306	2.237 2.249	[5]
SIRVIY	$[Ge(OC(C_6H_4)(CF_3)_2)_2]$	1.780 1.791	1.896 1.900	[6]
-	**5**	1.8173	1.9314	This work

References.

(1) Lum, J. S.; Tahsini, L.; Golen, J. A.; Moore, C.; Rheingold, A. L.; Doerrer, L. H. *Chem. Eur. J.* **2013**, *19*, 6374.

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