

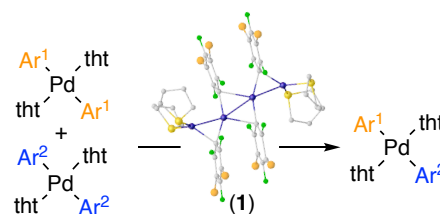
# [Cu(C<sub>6</sub>Cl<sub>2</sub>F<sub>3</sub>)(tht)]<sub>4</sub>: An Extremely Efficient Catalyst for the Aryl Scrambling Between Palladium Complexes

María Pérez-Iglesias, Olmo Lozano-Lavilla, Juan A. Casares\*

IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47011 Valladolid (Spain)

Supporting Information Placeholder

**ABSTRACT:** The copper compound [Cu(C<sub>6</sub>Cl<sub>2</sub>F<sub>3</sub>)(tht)]<sub>4</sub> (**1**) (tht: tetrahydrothiophene) is an excellent catalysts for the *trans*- to *cis*- isomerization of complexes [PdAr<sub>2</sub>(tht)<sub>2</sub>](Ar: fluoroaryl) and also for the exchange of aryls between those palladium complexes. Herein, we also communicate the synthesis and characterization of **1**, and some of its derivatives. The x-ray structure of **1** shows a linear chain of copper atoms, supported by fluoroaryl rings. The NMR <sup>19</sup>F-DOSY study indicates that this structure is preserved in solution although in equilibrium with other species.



Multimetallic systems are receiving ongoing attention from the organometallic community, due to their role in catalyzed processes.<sup>1-3</sup> Unfortunately, the understanding of systems composed by two or more metals is far from complete and the rational design of bimetallic catalytic systems is nowadays an almost unachievable task. Most of the difficulties come from the fact that catalytic cycles are formed by highly reactive organometallic intermediates which can react with complexes containing the second metal as well as with organic substrates, producing unwanted interferences in the reaction pathway. In addition, the exchange of “spectator ligands” or of electrons between the metals may also spoil a “well designed” catalytic cycle.<sup>4</sup> Considering the difficulties, it is remarkable the large number of multimetallic co-catalyzed processes. Particularly important are bimetallic systems involving copper and palladium. In addition to the Wacker reaction, an historic landmark in catalysis, copper accelerates the Stille cross-coupling, the copper/palladium pair catalyzes many other C-C and C-E coupling reactions including the Sonogashira reaction.<sup>1-3</sup> Leaving aside the copper mediated electron-transfer reactions, the role attributed to organocopper in these reactions is to act as transmetalating reagent towards complexes of the type [PdRXL<sub>2</sub>] or as ligand scavenger in the “copper effect”,<sup>5</sup> but there are no reports of the role of copper complexes as catalysts for other reaction steps.<sup>3</sup> The hypothetical intervention of organocopper complexes in other steps of the cross-coupling reactions has not been addressed so far.

Here we report new organometallic copper complexes, the study of their ability to catalyze the isomerization

reaction of palladium(II) complexes and also the very fast aryl scrambling that copper(I) produces between aryl palladium complexes.<sup>5</sup>

We have synthesized the complex “CuRf(tht)” (Rf = 3,5-dichloro2,4,6-trifluorophenyl, C<sub>6</sub>Cl<sub>2</sub>F<sub>3</sub>) with the purpose of studying the copper-catalyzed *trans*- to *cis*- isomerization of complexes [PdRf<sub>2</sub>(tht)<sub>2</sub>], by analogy with related studies with gold complexes.<sup>6a</sup> In “CuRf(tht)” the Rf group provides extra stability to the C-Cu bond when compared with non-fluorinated aryls,<sup>7,8</sup> and allows a straightforward <sup>19</sup>F NMR monitoring.<sup>9</sup> The distinctive feature for organometallic copper(I) compounds is the variability in stoichiometries and the structural diversity of its complexes.<sup>10,11</sup> Homoleptic compounds “CuR” are usually cyclic oligomers but copper complexes of stoichiometry [CuRL] show typically linear geometry, similar to gold(I) derivatives.<sup>12-20</sup> The only report of linear complexes with tht [CuR(tht)] includes the very encumbered group R = 2,6-bis(2,4,6-triisopropylphenyl)phenyl.<sup>20</sup> Trigonal-planar complexes CuRL<sub>2</sub>, and oligomers with several other stoichiometries such as [CuRL<sub>0.5</sub>]<sub>n</sub>, are also known.<sup>21</sup>

The synthesis of a complex of formula [CuRf(tht)] was achieved by reacting RfLi with CuBr in the presence of an excess of tht. The <sup>19</sup>F NMR signals of the product are very broad and are not resolved at low temperature, thus

an X-Ray structure study was undertaken. The molecular structure is shown in Figure 1 and consists of a chain-copper aggregate of formula  $[\text{CuRf}(\text{tht})_4]$  (**1**) where Rf aryls act as the bridges between copper centers, and the four tht ligands are at the ends of the chain. This is a quite unusual structure, the only known linear copper structure similar to that corresponds to the stoichiometry  $[\text{CuRL}_{0.5}]_4$ , (R:  $\text{C}_6\text{F}_5$ ; L: N-heterocyclic germylene NHGes).<sup>22</sup> In complex **1** the fluoroaryls seems to form relatively strong three-center two electron bonds, preferring this structure to the use of tht to form four-electron sulfur-bridges.<sup>23</sup> Several complexes of formula  $[\text{Cu}(\text{C}_6\text{F}_5)\text{L}]$  have been reported, but their structures are linear monomers with the exception of the dimer  $[\text{Cu}(\text{C}_6\text{F}_5)(\text{NHGes})]_2$ .<sup>22,24,25</sup>

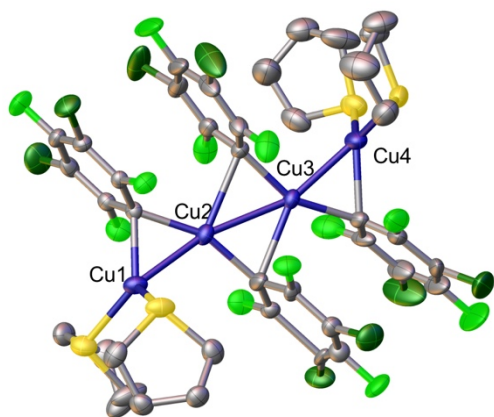


Figure 1. Molecular structure obtained from X-Ray diffraction of complex **1** showing 50% probability ellipsoids. Some selected distances: Cu1-Cu2: 2.4443(9) Å, Cu2-Cu3: 2.5603(8) Å, Cu3-Cu4: 2.4249(9) Å.

As stated above the NMR spectra of **1** are indicative of an equilibrium between complexes. In fact, the addition of tht to solutions of **1** produces a change in the chemical shift and the shape of the  $^{19}\text{F}$  NMR, eventually leading to the formation of  $[\text{CuRf}(\text{tht})_2]$  (**3**) (Scheme 1). This complex has not been isolated, since the equilibrium is shifted to form **1** during the crystallization, but calculated by DFT calculations predict a planar-trigonal geometry (See SI). The behavior in solution of **1** has been further examined by analyzing the chemical shift and diffusion properties of solutions of **1** with different amounts of tht added. We assumed that the broad NMR signals may contain not only the signals from the inequivalent fluoroaryls in the tetramer **1**, but also signals from homoleptic species  $[\text{CuRf}]_n$ , the trigonal monomer  $[\text{CuRf}(\text{tht})_2]$  (**3**), and other possible oligomers  $[\text{CuRf}(\text{tht})]_n$ .<sup>26</sup> Since the  $^{19}\text{F}$  NMR signals are not resolved at  $-70^\circ\text{C}$  the complete speciation of the sample is not possible. Nonetheless, the study of the diffusion properties and chemical shift is quite informative.

#### Scheme 1

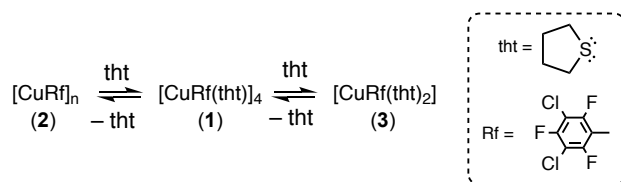


Figure 2a represents the drift of the chemical shift with the amount of added tht, showing that the chemical shift does not change after the addition of four (or more) tht per  $[\text{CuRf}(\text{tht})_4]$ , thus  $[\text{CuRf}(\text{tht})_2]$  is the limiting composition and no tetrahedral complexes are formed in relevant concentration. Also, the average diffusion coefficient ( $D$ ) of the sample has been measured by DOSY experiments at 298 K, leading to the same conclusion (Figure 2b). The diffusion coefficient and the molecular weight are related by the empirical law  $D = \text{KM}_w^\alpha$  (where  $K$  is a constant and  $\alpha$  is a coefficient that depends on the size and shape of the particles).<sup>27,28</sup> By measuring  $D$  for various known fluorinated organometallic complexes, we have found a value of  $\alpha = -0.39$  (Figure 2, see also SI).

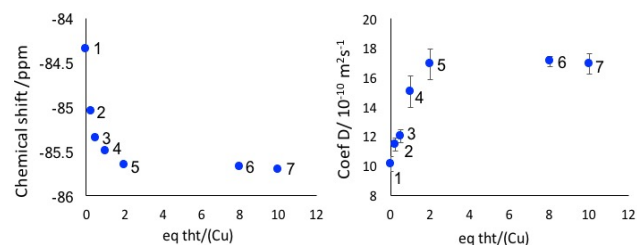


Figure 2. (a) Graphic representation of chemical shift versus equivalents of tht added in THF. (b) Graphic representation of experimental  $D$  ( $D$  = Diffusion coefficient) obtained from DOSY experiments versus equivalents of tht added THF

The experimental value of  $\ln D$  for the mixtures of **1** with different amounts of tht (orange dots in Figure S1) have been interpolated on the line obtaining a “observed molecular weight” ( $M_{\text{Wobs}}$ ) for the samples. The  $M_{\text{Wobs}}$  value at very high concentrations of tht is  $317 \pm 125$ , that agree with the formation of **3** which has a  $M_w$  of 440. The solution without added tht, gives a  $M_{\text{Wobs}}$  of  $1174 \pm 184$ , being the  $M_w$  of **1** 1407. Thus, data suggest that solutions of complex **1** consist of an equilibrium in which the tetramer **1** is the major species, with small amounts of  $[\text{CuRf}(\text{tht})_2]$  and  $[\text{CuRf}]_n$  formed by disproportionation. From complex **1** the monomeric complex  $[\text{CuRf}(4,4'\text{-bipy})]$  (used for diffusion experiments) was easily obtained by substitution of the tht (see x-ray structure and experimental details in SI).

Complexes **1** and **3** (made from complex **1** in the presence of a large excess of tht) have been used to test the copper-catalyzed *trans*- to *cis*- isomerization of palladium complexes  $[\text{PdRf}_2(\text{tht})_2]$  (complexes **4** and **5**) (eq. 2, Figure 3). The use of these complexes is quite convenient to avoid the exchange of neutral ligands between copper and

palladium systems similar to that found in gold(I)/palladium(II) systems.<sup>4b</sup>

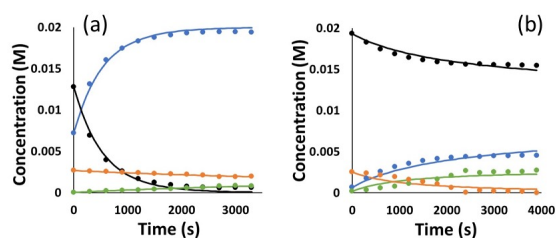
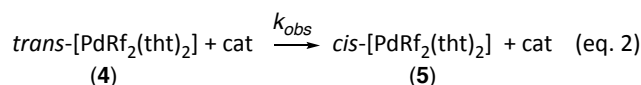
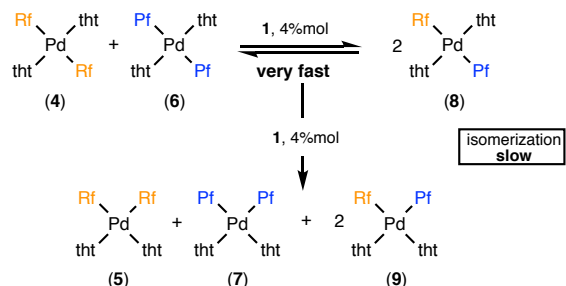


Figure 3. Concentration/time plot of the copper catalyzed isomerization reaction of *trans*-[PdRf<sub>2</sub>(tht)<sub>2</sub>] (4) (black spots) to *cis*-[PdRf<sub>2</sub>(tht)<sub>2</sub>] (5) (blue spots) in THF at 25 °C. Starting concentrations a) [4]<sub>0</sub> = 0.02 M, [CuRf(tht)<sub>4</sub>] = 7.5 · 10<sup>-4</sup> M, (no tht added); b) [4]<sub>0</sub> = 0.02 M, [1]<sub>0</sub> = 7.5 · 10<sup>-4</sup> M, and [tht] = 0.063 M.

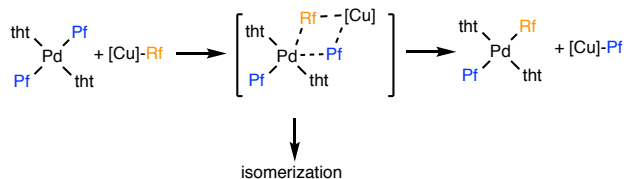
The catalyzed reaction takes place at 25 °C and the observed reaction rate using **1** as catalyst (4% mol) is  $k_{\text{obs}} = 3 \text{ s}^{-1}\text{Lmol}^{-1}$ . For [AuRf(tht)] as catalyst at 31 °C  $k_{\text{obs}}$  is about  $5 \text{ s}^{-1}\text{Lmol}^{-1}$ , that is of the same order of magnitude than **1**.<sup>6a</sup> Note, however, that since  $k_{\text{obs}}$  has been calculated assuming that the tetramer **1** is the catalyst, it is plausible that the true catalyst is some fragment of the type ‘‘CuRf(tht)’’ present in low concentration in the solution, meaning that the activity of the copper would be much higher. When **3**, prepared by addition of tht to **1**, was used as catalyst a  $k_{\text{obs}}$  value of  $7 \cdot 10^{-2} \text{ s}^{-1}\text{Lmol}^{-1}$  was obtained (Figure 3b).<sup>29</sup> For this concentration of tht, the reaction is much slower and the hydrolysis of the copper complex with the residual water competes with the aryl exchange, so it has to be considered in the kinetics to obtain meaningful values.

With the aim of establishing whether the isomerization takes place with or without copper/palladium transmetalation of the aryl group, we tried the isomerization reaction of a mixture of fluoroaryl complexes *trans*-[PdRf<sub>2</sub>(tht)<sub>2</sub>] (**4**) and *trans*-[PdPf<sub>2</sub>(tht)<sub>2</sub>] (**6**) (Pf = C<sub>6</sub>F<sub>5</sub>). In this experiment the formation of the mixed isomer *cis*-[PdRfPf(tht)<sub>2</sub>] (**9**) would demonstrate the transmetalation during the isomerization. To our surprise the first spectrum of the series showed the equilibrium of the complexes **4** and **6** with *trans*-[PdRfPf(tht)<sub>2</sub>] (**8**) (Scheme 2). The non-catalyzed aryl exchange between **4** and **6** to produce **8** has been studied and is very slow at 25 °C.<sup>30</sup> Thus, the transmetalation takes place, but it is a much faster process than the isomerization. This does not exclude a transmetalation during the isomerization but excludes the transmetalation as the rate determining step. Once the equilibrium between **4**, **6** and **8** has been established, all of them evolve to the *cis* isomers **5**, **7** and **9** (Scheme 2).



Scheme 2.

In view of these results, the catalyzed aryl exchange between complexes *cis*- complexes **5** and **7** was tested with a similar result: *cis*-[PdRfPf(tht)<sub>2</sub>] (**9**) is formed in a very fast process. The reaction takes place even at –65 °C, with an observed reaction rate of  $3 \cdot 10^{-4} \text{ s}^{-1}\text{Lmol}^{-1}$ . This corresponds to a  $\Delta G^{\ddagger}_{208} = 15.4 \text{ kcal mol}^{-1}$ , what makes of this an extremely fast reaction for the organo-palladium isomerization or transmetalation standards. A plausible reaction pathway is depicted in scheme 3. The substitution reaction could involve a fluoroarylcopper unsaturated species, capable to form three-center two electron bonds involving also the Pf-Pd bond. This scheme allow a substitution conserving the stereochemistry at the palladium and should be retarded by the addition of ligand by decreasing the concentration of unsaturated copper(I) complexes.



Scheme 3.

In conclusion, fluoroaryl-copper(I) complexes have shown to be very active catalyst for the isomerization and for the scrambling of organic groups between palladium complexes, showing a very small activation energy. Detailed mechanistic studies are ongoing including kinetic and DFT studies.

## ASSOCIATED CONTENT

**Supporting Information.** The supporting information contains: Experimental and computational methods (11 pages). This material is available free of charge via the Internet at <http://pubs.acs.org>

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [casares@qi.uva.es](mailto:casares@qi.uva.es)

### Funding Sources

No competing financial interests have been declared.

## ACKNOWLEDGMENT

Financial support is gratefully acknowledged to the Spanish MINECO (Project CTQ2016-80913-P) and the Junta de Castilla y León (Project JCyL VA 051P17 and VA062G18). María Pérez-Iglesias thanks the Junta de Castilla y León for a contract as predoctoral researcher.

## REFERENCES

- Shibasaki, M.; Yamamoto, Y. John Wiley & Sons., *Multimetallic Catalysts in Organic Synthesis*, Wiley-VCH, **2004**.
- Pye, D. R.; Mankad, N. P. Bimetallic Catalysis for C–C and C–X Coupling Reactions. *Chem. Sci.* **2017**, *8*, 1705–1718.
- (a) Pérez-Temprano, M. H.; Casares, J. A.; Espinet, P. Bimetallic Catalysis Using Transition and Group 11 Metals: An Emerging Tool for C–C Coupling and Other Reactions. *Chem. - A Eur. J.* **2012**, *18*, 1864–1884. (b) delPozo, J.; Casares, J. A.; Espinet, P. In Situ Generation of ArCu from CuF<sub>2</sub> Makes Coupling of Bulky Aryl Silanes Feasible and Highly Efficient. *Chem. Eur. J.* **2016**, *22*, 4274–4284 and references therein. (c) Semba, K.; Nakao, Y. Cross-Coupling Reactions by Cooperative Metal Catalysis. *J. Synth. Org. Chem., Jpn.* **2017**, *75*, 1133–1140.
- (a) For a case of redox-incompatibility see: D. Weber and M. R. Gagné. Pd(0)/Au(I) Redox Incompatibilities as Revealed by Pd-Catalyzed Homo-Coupling of Arylgold(I)-Complexes. *Chem. Commun.*, **2011**, *47*, 5172–5174. (b) As an example of the ligand exchange processes associated to catalytic systems: delPozo, J.; Casares, J. A.; Espinet, P. The Decisive Role of Ligand Metathesis in Au/Pd Bimetallic Catalysis. *Chem. Commun.* **2013**, *49*, 7246–7248.
- Casado, A. L.; Espinet, P. Quantitative Evaluation of the Factors Contributing to the “Copper Effect” in the Stille Reaction. *Organometallics*, **2003**, *22*, 1305–1309.
- The *cis-trans* isomerization of complexes [PdR<sub>1</sub>R<sub>2</sub>L<sub>2</sub>] associated to transmetalation processes has been previously observed for different organometallics, such organogold, organozinc and organotin derivatives. See: a) Casado, A. L.; Espinet, P. A Novel Reversible Aryl Exchange Involving Two Organometallics: Mechanism of the Gold(I)-Catalyzed Isomerization of Trans-[PdR<sub>2</sub>L<sub>2</sub>] Complexes (R = Aryl, L = SC<sub>4</sub>H<sub>8</sub>). *Organometallics* **1998**, *17*, 3677–3683. b) delPozo, J.; Gioria, E.; Casares, J. A.; Álvarez, R.; Espinet, P. Organometallic Nucleophiles and Pd: What Makes ZnMe<sub>2</sub> Different? Is Au Like Zn?. *Organometallics* **2015**, *34*, 3120–3128. c) Pérez-Temprano, M. H.; Gallego, A. M.; Casares, J. A.; Espinet, P. Stille Coupling of Alkynyl Stannane and Aryl Iodide, a Many-Pathways Reaction: The Importance of Isomerization. *Organometallics* **2011**, *30*, 611–617.
- Clot, E.; Mégret, C.; Eisenstein, O.; Perutz, R. N. Exceptional Sensitivity of Metal-Aryl Bond Energies to Ortho-Fluorine Substituents: Influence of the Metal, the Coordination Sphere, and the Spectator Ligands on M–C/H–C Bond Energy Correlations. *J. Am. Chem. Soc.* **2009**, *131*, 7817–27.
- Pérez-Iglesias, M.; Espinet, P.; Casares, J. A. Comparing Protonolysis and Transmetalation Reactions: Microcalorimetric Studies of C–Au<sup>I</sup> Bonds in [AuRL] Complexes. *Inorg. Chem.* **2018**, *57*, 11193–11200.
- Espinet, P.; Albéniz, A. C.; Casares, J. A.; Martínez-Illarduya, J. M. <sup>19</sup>F NMR in Organometallic Chemistry. Applications of Fluorinated Aryls. *Coord. Chem. Rev.* **2008**, *252*, 2180–2208.
- Breit, B.; Demel, P. Modern Organocopper Chemistry. *Cheminform* **2002**, *34*, 188–223.
- van Koten, G. Organocopper Compounds: From Elusive to Isolable Species, from Early Supramolecular Chemistry with RCu<sup>I</sup> Building Blocks to Mononuclear R<sub>2–n</sub>Cu<sup>II</sup> and R<sub>3–m</sub>Cu<sup>III</sup> Compounds. A Personal View. *Organometallics* **2012**, *31*, 7634–7646.
- Xie, W.; Yoon, J. H.; Chang, S. (NHC)Cu-Catalyzed Mild C–H Amidation of (Hetero)Arenes with Deprotectable Carbamates: Scope and Mechanistic Studies. *J. Am. Chem. Soc.* **2016**, *138*, 12605–12614.
- Bour, J. R.; Kariofillis, S. K.; Sanford, M. S. Synthesis, Reactivity, and Catalytic Applications of Isolable (NHC)Cu(CHF<sub>2</sub>) Complexes. *Organometallics* **2017**, *36*, 1220–1223.
- Dubinina, G. G.; Furutachi, H.; Vivic, D. A. Active Trifluoromethylating Agents from Well-Defined Copper(I)-CF<sub>3</sub> Complexes. *J. Am. Chem. Soc.* **2008**, *130*, 8600–8601.
- Nolte, C.; Mayer, P.; Straub, B. F. Isolation of a Copper(I) Triazolide: A “Click” Intermediate. *Angew. Chemie - Int. Ed.* **2007**, *46*, 2101–2103.
- Mankad, N. P.; Gray, T. G.; Laitar, D. S.; Sadighi, J. P. Synthesis, Structure, and CO<sub>2</sub> Reactivity of a Two-Coordinate (Carbene)Copper(I) Methyl Complex. *Organometallics* **2004**, *23*, 1191–1193.
- Schaper, F.; Foley, S. R.; Jordan, R. F. Acrylonitrile Polymerization by Cy<sub>3</sub>PCuMe and (Bipy)<sub>2</sub>FeEt<sub>2</sub>. *J. Am. Chem. Soc.* **2004**, *126*, 2114–2124.
- Rungthanaphatsophon, P.; Barnes, C. L.; Walensky, J. R. Copper(I) Clusters with Bulky Dithiocarboxylate, Thiolate, and Selenolate Ligands. *Dalton Trans.* **2016**, *45*, 14265–14276.
- Sundararaman, A.; Zakharov, L. N.; Rheingold, A. L.; Jäkle, F. Cuprophilic and π-Stacking Interactions in the Formation of Supramolecular Stacks from Dicoordinate Organocopper Complexes. *Chem. Commun.* **2005**, 1708–1710.
- Groysman, S.; Holm, R. H. A Series of Mononuclear Quasi-Two-Coordinate Copper(I) Complexes Employing a Sterically Demanding Thiolate Ligand. *Inorg. Chem.* **2009**, *48*, 621–627.
- Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. Synthesis and Structure of a Mononuclear Copper(I) Complex Containing the Copper(I)-Sigma-Phenyl Functionality. *J. Chem. Soc. Chem. Commun.* **1983**, 1156–1158.
- Zhao, N.; Zhang, J.; Yang, Y.; Zhu, H.; Li, Y.; Fu, G. β-Diketiminato Germylene-Supported Pentafluorophenylcopper(I) and -Silver(I) Complexes [LGe(Me)(Cu<sub>6</sub>F<sub>5</sub>)<sub>n</sub>]<sub>2</sub> (n = 1, 2), LGe[C(SiMe<sub>3</sub>)N<sub>2</sub>]<sub>2</sub>AgC<sub>6</sub>F<sub>5</sub>, and {LGe[C(SiMe<sub>3</sub>)N<sub>2</sub>](AgC<sub>6</sub>F<sub>5</sub>)<sub>2</sub>}<sub>2</sub> (L = HC[C(Me)N-2,6-Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]<sub>2</sub>): Synthesis and Structural Characterization. *Inorg. Chem.* **2012**, *51*, 8710–8718.
- The behavior of tht as bridging ligand between copper(I) centers has been reported, see: Henline, K. M.; Wang, C.; Pike, R. D.; Ahern, J. C.; Sousa, B.; Patterson, H. H.; Kerr, A. T.; Cahill, C. L. Structure, Dynamics, and Photophysics in the Copper(I) Iodide–Tetrahydrothiophene System. *Cryst. Growth Des.* **2014**, *14*, 1449–1458.
- Xie, W.; Yoon, J. H.; Chang, S. (NHC)Cu-Catalyzed Mild C–H Amidation of (Hetero)Arenes with Deprotectable Carbamates: Scope and Mechanistic Studies. *J. Am. Chem. Soc.* **2016**, *138*, 12605–12614.
- Doshi, A.; Sundararaman, A.; Venkatasubbaiah, K.; Zakharov, L. N.; Rheingold, A. L.; Myahkostupov, M.; Piotrowiak, P.; Jäkle, F.; Ja, F. Pentafluorophenyl Copper-Pyridine Complexes: Synthesis, Supramolecular Structures via Cuprophilic and π-Stacking Interactions, and Solid-State Luminescence. *Organometallics* **2012**, *31*, 1546–1558.
- When **1** is dissolved in dichloromethane, a powder of [Cu(C<sub>6</sub>F<sub>5</sub>Cl<sub>2</sub>)<sub>n</sub>] (2) is slowly separated evidencing the extrusion of tht. That solid is not formed in THF, where complex **2** is soluble.
- Auge, S.; Schmit, P. O.; Crutchfield, C. A.; Islam, M. T.; Harris, D. J.; Durand, E.; Clemancey M.; Quoineaud, A. A.; Lancelin, J. M.; Prigent, Y. et al., NMR Measure of Translational Diffusion and Fractal Dimension. Application to Molecular Mass Measurement. *J. Phys. Chem. B* **2009**, *113*, 1914–1918.
- Neufeld, R.; Stalke, D. Accurate Molecular Weight Determination of Small Molecules via DOSY-NMR by Using External Calibration Curves with Normalized Diffusion Coefficients. *Chem. Sci.* **2015**, *6*, 3354–3364.
- Note that the excess of tht has two effects: i) the formation of **2** as main species in solution and ii) a retardation effect if the reaction mechanism is similar to that found for [AuRf(tht)]. See reference 6a.
- Casado, A. L.; Casares, J. A.; Espinet, P. An Aryl Exchange Reaction with Full Retention of Configuration of the Complexes: Mechanism of the Aryl Exchange between [PdR<sub>2</sub>L<sub>2</sub>] Complexes in Chloroform (R = Pentahalophenyl, L = Thioether). *Organometallics* **1997**, *16*, 5730.