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# Synthesis and characterization of alkynes β-diketonate copper(I) complexes

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#### Abstract

The reactions of 1,3,5-tris-(trimethylsilylethynyl)benzene (1) with Cu<sub>2</sub>O and 1,1,1,5,5,5,-hexafluoroacetylacetone in alkyne to Cu ratios 1:0.5, 1:1 and 1:3 in CH<sub>2</sub>Cl<sub>2</sub> at room temperature give copper complexes  $(\eta^2-1,3,5-\text{tris}(\text{trimethylsilylethynyl})$ benzene)(Cu(hfac)) (2),  $(\eta^2:\eta^2-1,3,5-\text{tris}(\text{trimethylsilylethynyl})$ benzene)(Cu(hfac))<sub>2</sub> (3) and  $(\eta^2:\eta^2:\eta^2-(1,3,5-\text{tris}(\text{trimethylsilylethynyl})$ benzene))<sub>2</sub>(Cu(hfac))<sub>3</sub>(4), respectively. In the same conditions, 2,5-bis-(trimethylsilylethynyl)thiophene (5) reacts with 0.5 or 1 equiv. of Cu<sub>2</sub>O to give  $(\eta^2:\eta^2-2,5-\text{bis}(\text{trimethylsilylethynyl})$ thiophene)(Cu(hfac))<sub>2</sub> (7), respectively, and 1,4-bis(trimethylsilyl)-1,3-butadiyne (8) with 0.5 equiv. of Cu<sub>2</sub>O give  $(\eta^2:\eta^2-1,4-\text{bis}(\text{trimethylsilyl})-1,3-\text{butadiyne})(Cu(hfac))_2$  (9). All the new compounds have been characterized by analytical and spectroscopic methods and their thermal properties were examined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). © 2004 Elsevier B.V. All rights reserved.

Keywords: Copper(I); β-Diketonate complexes; Polyynes

## 1. Introduction

Chemical vapor deposition (CVD) is a useful technique for depositing conformal films over substrates with varying topography [1]. Research geared toward the identification and synthesis of volatile metal precursors specifically for chemical vapor deposition (CVD) of high-purity films is actively being pursued. The utility of a specific precursor depends upon the precursor's chemical structure and its resulting chemical and physical properties. A wide variety of Cu(I) complexes have been synthesized and characterized to date with the intention to be used as copper precursor complexes in metal-organo chemical vapor deposition [2].

The reactive copper(I)  $\beta$ -diketonate moiety may be ligated with phosphines [3] or unsaturated organics, such as alkenes [4], dienes [5] and alkynes [6,7] to obtain an assortment of precursors with different physicochemical properties. In the mononuclear copper(I)-alkyne  $\beta$ -diketonate complexes, the alkyne is  $\eta^2$  bonded to the copper(I) center, parallel to the copper  $\beta$ -diketonate plane [8].

As a continuation on the preparation of polyynes transition metal complexes [9,10], we report in this work the synthesis and spectroscopic data of novel multicoordinated  $\beta$ -diketonate copper(I) polyyne ligand complexes. The alkynes employed are the 1,3-bis (trimethylsilyl) butadiyne, 2,5-bis(trimethylsilylethynyl) thiophene and 1,3,5-tris(trimethylsilylethynyl)benzene, which allow different coordination modes.

## 2. Experimental

# 2.1. Reagents and general techniques

All manipulations were carried out by using standard Schlenk vacuum-line and syringe techniques under an atmosphere of oxygen-free Ar. All solvents for synthetic use were reagent grade, dried as appropriate and distilled under Ar. All solvents were bubbled with Ar for 30 minutes after distillation and then stored under Ar, or degassed by means of at least three freeze-pump-thaw

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cycles after distillation and before use. 1,3,5-tribromobenzene, 1,4-bis (trimethylsilyl)-1,3-butadiyne, Me<sub>3</sub>Si-C=CH (TMSA), 2,5-dibromothiophene (Aldrich), and Cu<sub>2</sub>O, 1,1,1,5,5,5-hexafluoroacetylacetone (Fluka) were used as received. The 1,3,5-tris(trimethylsilyl)ethynylbenzene [10] and 2,5-bis(trimethylsilylethynyl)thiophene [11] were prepared according to literature procedures. The <sup>1</sup>H, <sup>13</sup>C and HMBC (Heteronuclear Multiple Bond Correlation) NMR spectra were recorded on a Bruker AMX-300 or 500 instrument. <sup>1</sup>H NMR spectra were referenced to tetramethylsilane. Infrared spectra were measured on a Perkin-Elmer 1650 infrared spectrometer. Elemental analysis were performed by the Microanalytical Laboratory of the University Autónoma of Madrid on a Perkin-Elmer 240 B microanalyzer. Mass spectra were measured on a VG-Autospec mass spectrometer for FAB by the Mass Laboratory of the University Autónoma of Madrid.

The thermal properties of all complexes were examined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC). The gravimetric data were obtained on a Seiko DTA/TG 320 U using an open pan which was purged with N<sub>2</sub> and a heating rate of 5 °C/min. The calorimetric data were obtained with a Perkin–Elmer Pyris 1DSC instrument using a sealed pan with a heating rate of 5 °C/min. The melting points were also obtained via a conventional melting point apparatus.

2.2. Preparation of  $(\eta^2-1,3,5-tris(trimethylsilylethynyl)$ benzene)(Cu(hfac)) (2),  $(\eta^2:\eta^2-1,3,5-tris(trimethylsily$ lethynyl)benzene) (Cu(hfac))<sub>2</sub> (3) and  $(\eta^2:\eta^2:\eta^2-(1,3,5-tris(trimethylsilylethynyl)benzene))<sub>2</sub>(Cu(hfac))<sub>3</sub> (4)$ 

A three-neck round-bottom flask was charged with 0.13 g (0.35 mmol) of 1,3,5-tris(trimethylsilylethynyl)benzene (1) and 0.5 equiv. (2), 1 equiv. (3) or 3 equiv. (4) of Cu<sub>2</sub>O, respectively, and stirred in 30 mL of spectroscopic grade methylene chloride. Hexafluoroacetylacetone (0.1 mL, 0.7 mmol) was added dropwise to the stirred suspension. After the mixture was stirred for 3 h at room temperature the solution becomes yellow. Isolation of the products was achieved by filtering off the excess cuprous oxide and washing several times with CH<sub>2</sub>Cl<sub>2</sub>. The filtrates and washes were combined and removed under vacuum. The compounds were isolated and purified as yellow (2, 3) or green (4) solids by recrystallization from hot hexane.

(2) Yield: 93%. IR (KBr pellet, cm<sup>-1</sup>): v(uncoordinated C=C) 2166 (s), v(coordinated C=C) 1976.8 (m); v(C=O) 1637.3 (s);  $\delta$ (C-F) 1471.4 (m). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): v(coordinated C=C) 1972 (m). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.67 (s, 3H, benzene); 6.17 (s, 1H, hfac); 0.28 (s, 27H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  178.29 (q, C<sub>7</sub>O, J<sub>CF</sub> = 34.8 Hz); 135.25 (s, C<sub>1</sub>); 123.77 (s, C<sub>2</sub>); 117.67 (q, C<sub>8</sub>F<sub>3</sub>, J<sub>CF</sub> = 285.3 Hz);

104.92 (s, C<sub>3</sub>); 95.92 (s, C<sub>4</sub>); 89.92 (s, C<sub>6</sub>); -0.41 (s,  $-CSiMe_3$ ). MS (FAB<sup>+</sup>, m/z): 636.0 (M<sup>+</sup>). PF 128.3 °C.

(3) Yield: 90%. IR (KBr, cm<sup>-1</sup>): v(uncoordinated C=C) 2168 (s); v(coordinated C=C) 1969.9 (m); v(C=O) 1642.1 (s);  $\delta$ (C-F) 1471.4 (m). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): v(coordinated C=C) 1965 (m). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.82 (s, 3H, benzene); 6.17 (s, 2H, hfac); 0.34 (s, 27H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.26 (q, C<sub>7</sub>O, J<sub>CF</sub> = 34.7 Hz); 135.47 (s, C<sub>1</sub>); 123.92 (s, C<sub>2</sub>); 117.66 (q, C<sub>8</sub>F<sub>3</sub>, J<sub>CF</sub> = 285.3 Hz); 106.60 (s, C<sub>3</sub>); 96.24 (s, C<sub>4</sub>); 89.95 (s, C<sub>6</sub>); -0.53 (s, -CSiMe<sub>3</sub>). MS (FAB<sup>+</sup>, m/z): 700.8 (M<sup>+</sup>-hfac). Anal. Calc. for C<sub>31</sub>H<sub>32</sub>O<sub>4</sub>F<sub>12</sub>Cu<sub>2</sub>Si<sub>3</sub>: C, 40.97; H, 3.52. Found: C, 40.65, H, 3.45%. PF 143 °C.

(4) Yield: 60%. IR (KBr, cm<sup>-1</sup>):  $v(C\equiv C)$  1974.2 (m); v(C=O) 1639.2 (s);  $\delta(C-F)$  1462.7 (m). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1970 (m). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.76 (s, 6H, benzene); 6.17 (s, 3H, hfac); 0.31 (s, 54H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.25 (q, C<sub>7</sub>O,  $J_{CF} = 37.0$  Hz); 135.39 (s, C<sub>1</sub>); 123.82 (s, C<sub>2</sub>); 117.65 (q, C<sub>8</sub>F<sub>3</sub>,  $J_{CF} = 284.82$  Hz); 105.84 (s, C<sub>3</sub>); 96.09 (s, C<sub>4</sub>); 89.95 (s, C<sub>6</sub>); -0.47 (s, -CSiMe<sub>3</sub>). *Anal.* Calc. for C<sub>57</sub>H<sub>63</sub>O<sub>6</sub>F<sub>18</sub>Cu<sub>3</sub>Si<sub>6</sub>: C, 44.30; H, 4.08. Found: C, 44.12, H, 3.98%. PF 115 °C.

2.3. Preparation of  $(\eta^2:\eta^2-2,5-bis(trimethylsilylethy$ nyl)thiophene)(Cu(hfac)) (6) and  $(\eta^2:\eta^2-2,5-bis(trim$  $ethylsilylethynyl)thiophene)(Cu(hfac))_2$  (7)

By a similar procedure, to a solution of 0.05 g (0.35 mmol) of 2,5-bis(trimethylsilylethynyl)thiophene (5) in  $CH_2Cl_2(40 \text{ mL})$  was added 0.5 equiv. (6) or one equivalent (7) of  $Cu_2O$ , respectively. Hexafluoroacetylacetone (0.22 mL, 1.4 mmol) was added dropwise. After similar working, 6 and 7 were separated as yellow solids.

(6) Yield: 63%. IR (KBr, cm<sup>-1</sup>): v(uncoordinated C=C) 2146; v(coordinated C=C) 1957.4 (m); v(C=O) 1639.2 (s); (C–F) 1473.3 (m). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): v(coordinated C=C) 1954 (m). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.31 (s, 2H, thiophene); 6.18 (s, 1H, hfac); 0.34 (s, 18H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.3 (q, C<sub>7</sub>O, J<sub>CF</sub> = 34.8 Hz); 133.03 (s, C<sub>1</sub>); 125.76 (s, C<sub>2</sub>); 117.65 (q, C<sub>8</sub>F<sub>3</sub>, J<sub>CF</sub> = 285.2 Hz); 100.92 (s, C<sub>3</sub>); 99.82 (s,C<sub>4</sub>); 90.02 (s, C<sub>6</sub>); -0.49 (s, -CSiMe<sub>3</sub>). MS (FAB<sup>+</sup>, m/z): 546.0(M<sup>+</sup>). PF 180 °C (dec.).

(7) Yield: 85%. IR (KBr, cm<sup>-1</sup>):  $v(C\equiv C)$  1945.8 (m); v(C=O) 1637.3 (s);  $\delta$  (C–F) 1469.5 (m). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1942.5 (m). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.40 (s, 2H, thiophene); 6.18 (s, 2H, hfac); 0.38 (s, 1,8H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ : 179.2 (q, C<sub>7</sub>O,  $J_{CF} = 34.8$  Hz); 134.13 (s, C<sub>1</sub>); 126.95 (s, C<sub>2</sub>); 118.8 (q,  $C_8F_3$ ,  $J_{CF} = 285.3$  Hz); 102.84 (s, C<sub>3</sub>); 100.64 (s,C<sub>4</sub>); 90.92 (s, C<sub>6</sub>); 0.35 (s, -CSiMe<sub>3</sub>). MS (FAB<sup>+</sup>, *m*/*z*): 610.9(M<sup>+</sup>-hfac). *Anal.* Calc. for C<sub>24</sub>H<sub>22</sub>O<sub>4</sub>F<sub>12</sub>SSi<sub>2</sub>Cu<sub>2</sub>: C, 35.22; H, 2.70. Found: C, 35.08; H, 2.52%. PF 180 °C (dec.). 2.4. Preparation of  $(\eta^2:\eta^2-1,4-bis(trimethylsilyl)-1,3-but$  $adiyne)(Cu(hfac))_2$  (9)

The same procedure was followed in the preparation of this compound using 1:0.5 ratio (1,4-bis(trimethylsilyl)-1,3-butadiyne (8): Cu<sub>2</sub>O). A yellow solid is isolated. (9) Yield: 67%. IR (KBr, cm-<sup>1</sup>):  $v(C\equiv C)$  1895.6 (s); v(C=O) 1644.0 (f);  $\delta(CF)$  1462.7 (m). IR (CH<sub>2</sub>Cl<sub>2</sub>, cm<sup>-1</sup>): 1893.5 (m). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 6.16 (s, 2H, hfac); 0.36 (s, 18H, SiMe<sub>3</sub>). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 178.36 (q, C<sub>5</sub>O,  $J_{CF} = 34.8$  Hz); 117.6 (q, C<sub>6</sub>F<sub>3</sub>,  $J_{CF} = 285.3$  Hz); 97.3 (s, C<sub>1</sub> and C<sub>2</sub>); 90.02 (s, C<sub>4</sub>); -0.95 (s, -CSiMe<sub>3</sub>). MS (FAB<sup>+</sup>, *m*/*z*): 528.9(M<sup>+</sup>-hfac). *Anal.* Calc. for C<sub>20</sub>H<sub>20</sub>O<sub>4</sub>F<sub>12</sub>Cu<sub>2</sub>Si<sub>2</sub>: C, 32.63; H, 2.72. Found: C, 32.45; H, 2.60%. PF 115 °C.

## 3. Results and discussion

Synthesis of the alkyne-copper complexes in this report was inspired by previously reported methods. Thus, the complexes have been obtained by reaction of Cu<sub>2</sub>O on the free acid  $\beta$ -diketone in the presence of alkyne [6a,12]. By changing the stoichiometry of reagents, we obtained complexes with different numbers of copper hfac groups bound to the alkyne.

So, 1,3,5-tris-(trimethylsilylethynyl)benzene (1) reacts with  $Cu_2O$  and 1,1,1,5,5,5,-hexafluoroacetylacetone in alkyne to Cu ratios 1:0.5, 1:1 and 1:3 in CH<sub>2</sub>Cl<sub>2</sub> at room temperature to give after workup copper complexes ( $\eta^2$ -1,3,5-tris(trimethylsilylethynyl)benzene) (Cu(hfac)) (2),  $(\eta^2:\eta^2-1,3,5-tris(trimethylsilylethynyl)$ benzene) (Cu(hfac))<sub>2</sub> (3) and  $(\eta^2:\eta^2:\eta^2-(1,3,5-\text{tris})$ (trimethylsilylethynyl)benzene)) $_2(Cu(hfac))_3(4)$ , respectively. In the same conditions, 2,5-bis-(trimethylsilylethynyl)thiophene (5) reacts with 0.5 or 1 equiv. of  $Cu_2O$  to  $(\eta^2:\eta^2-2,5-bis(trimethylsilylethynyl)thiophene)$ give (Cu(hfac)) (6) and  $(\eta^2:\eta^2-2,5-bis(trimethylsilylethy$ nyl)thiophene)(Cu(hfac))<sub>2</sub> (7), respectively, and 1,4bis(trimethylsilyl)-1,3-butadiyne (8) with 0.5 equiv. of Cu<sub>2</sub>O gives ( $\eta^2$ : $\eta^2$ -1,4-bis(trimethylsilyl)-1,3-butadiyne)  $(Cu(hfac))_2$  (9).

All these compounds have been characterized by analytical and spectroscopic data (IR, <sup>1</sup>H-, <sup>13</sup>C NMR, MS). Details are given in Section 2 (Scheme 1).

The dominant bonding mode in the alkyne-metal complexes may be evaluated by vibrational spectroscopy (IR) and NMR spectral shift. In Table 1 we compare the "free" alkyne stretch frequencies  $v(C\equiv C)$  to those in the copper(I)  $\beta$ -diketonato complexes. Alkyne-transition metal bonding usually decreases the bond order of the alkyne (from sp to sp<sup>2</sup>) and thereby lowers the frequency of the alkyne stretching vibration ( $\Delta v$ ) [8,13]. The magnitude of this change is directly related to the alkyne bond order and nuclearity of the complex. Relatively small frequency changes ( $\Delta v \approx 190$  cm<sup>-1</sup>) are observed

for all complexes reported herein as shown in Table 1. These values are indicative of  $\eta^2$ -coordination mode of the Me<sub>3</sub>SiC=C units to Cu(hfac) with predominant  $\sigma$ bonding contribution acting each triple bond as a twoelectron donor with poor back-donation from Cu(I) to the alkynes [14]. When the C<sub>2</sub> unit of the alkyne ligand is  $\eta^2$ -coordinated to two copper(I) centers acting as a fourelectron donor, larger vibrational changes are observed ( $\Delta v = 368 \text{ cm}^{-1}$ ) for BTSA (Cu(hfac))<sub>2</sub>[6a]. The enolized 1,3-dicarbonyl stretching frequencies are ca. 1640 cm<sup>-1</sup> and all complexes have sharp C–F deformation frequencies at ca. 1470 cm<sup>-1</sup>.

The <sup>1</sup>H and <sup>13</sup>C NMR spectra in CDCl<sub>3</sub> of all new synthesized compounds consist of sharp and well resolved signals for each of the organic ligands present. The <sup>1</sup>H chemical shifts ( $\Delta\delta$ ) of the "free" alkyne with the copper coordinated alkyne for the complexes are listed in Table 2. In all cases, deshielding of the hydrogens (protons) on the  $\alpha$  carbon atom ( $\alpha$  to the alkyne moiety) is observed. The  $\Delta\delta$  varies from +0.19 (2) to +0.36 (7); these NMR chemical shift changes are similar to other Cu(hfac) (alkyne) complexes [6c,15].

For  $(\eta^2-1,3,5-tris(trimethylsilylethynyl)benzene)$ (Cu(hfac)) (2),  $(\eta^2:\eta^2-1,3,5-tris(trimethylsilylethynyl))$ benzene) (Cu(hfac))<sub>2</sub> (3) and  $(\eta^2:\eta^2:\eta^2-(1,3,5-tris(tri$ methylsilylethynyl)benzene))<sub>2</sub>(Cu(hfac))<sub>3</sub> (4), also the integration of the methine protons (H<sup>6</sup>), SiMe<sub>3</sub> groups  $(H^5)$  and aromatic protons  $(H^1)$  of the ligand peaks confirms the 1:1, 1:2 and 2:3 (alkyne:hfac) ratio, respectively. The deshielding of the hydrogens on the SiMe<sub>3</sub> groups observed with respect to free ligand is proportional to the Cu(hfac) units coordinated to alkyne ( $\Delta \delta = +0.06$  ppm (2), +0.12 ppm (3) and +0.09 ppm (4)). All compounds show a single signal for the benzene ring and SiMe<sub>3</sub> groups and it is indicative of symmetric coordination mode wherein, according to alkyne:hfac ratio, one (2), two (3) or three (4) Cu(hfac) units are coordinated to one (2), two (3) or three (4) triple bonds of 1,3,5-tris(trimethylsilylethynyl)benzene ligands, respectively. For 2 and 3, each Cu(hfac) unit could be bonded to one or two triple bonds, respectively, and, in solution at room temperature, they exchange each other quickly. This is supported by the IR spectra (KBr) where two  $v(C \equiv C)$ (uncoordinated and coordinated) are observed and by the variable-temperature <sup>1</sup>H NMR experiments in  $CD_2Cl_2$  over the range  $-95^{\circ}$  to 25°. It is clearly seen that the signal due to aromatic protons is broader to lower temperature (-95 °C) although the split is not observed, while the methine protons signal is not affected. It could suggest a too quickly exchange process with an estimated activation energy lesser than 6 kcal/mol. These low values indicate that the exchange motion is easy according to a weak interaction Cu(hfac)-triple bond. Similar exchange is proposed by  $[Cu(hfac)O_2S(C \equiv C^tBu)_2]$  [16a] and analogous diynes compounds [16b]. For complex 4, a dimeric



Scheme 1.

structure is proposed where two 1,3,5-tris(trimethylsilylethynyl)benzene ligands are bridged by three Cu(hfac) building blocks (Scheme 1). This structural type is described on {[LnM(C $\equiv$ CR)<sub>2</sub>}M<sup>I</sup>X (M<sup>I</sup> = Cu, Ag) complexes [17]. No change is observed in the variabletemperature <sup>1</sup>H NMR experiment.

For  $(\eta^2:\eta^2-2,5-bis(trimethylsilylethynyl)thiophene)$ (Cu(hfac)) (6) and  $(\eta^2:\eta^2-2,5-bis(trimethylsilylethynyl)$ thiophene)(Cu(hfac))<sub>2</sub> (7), the integration of the methine protons (H<sup>6</sup>), SiMe<sub>3</sub> groups (H<sup>5</sup>) and aromatic protons (H<sup>1</sup>) of the thiophene ligands peaks confirms the 1:1 and 1:2 (alkyne:hfac) ratio, respectively. For **6** a single signal for the thiophene ring, methine and SiMe<sub>3</sub> groups is observed in the <sup>1</sup>H NMR spectrum at room temperature, but at variable-temperature, carried out on same conditions than for **2** and **3**, an analogous behavior is observed. It is also in agreement with the fact that Cu(hfac) unit is coordinated to only triple bond and, in solution at room

Table 1 Vibrational frequencies for the alkyne stretch ( $\nu$ (C=C)) for the 'free' alkynes and the alkyne–Cu(hfac) complexes

Compound	$v(C \equiv C) (cm^{-1})$	$\Delta v(C \equiv C) (cm^{-1})$		
1	2164.0			
2	1976.8	185.2		
3	1969.9	192.1		
4	1974.2	187.8		
5	2146.0			
6	1957.4	188.6		
7	1945.8	200.2		
8	2065.4			
9	1895.7	169.8		

temperature, they exchange each other quickly. The solidstate IR spectrum (KBr pellet) shows both  $v(C \equiv C)$  signals corresponding to uncoordinated (2146 cm<sup>-1</sup>) and coordinated alkyne (1957 cm<sup>-1</sup>). Finally, for ( $\eta^2$ : $\eta^2$ -1,4bis(trimethylsily)-1,3-butadiyne)(Cu(hfac)<sub>2</sub>) (9), the integration of the <sup>1</sup>H NMR peaks confirms the 1:2 (alkyne:hfac) ratio.

In general, <sup>13</sup>C NMR spectral changes are more useful for evaluating the dominant bonding mode in alkyne-metal complexes. In Table 2, the alkyne-carbon  $\Delta\delta(C\equiv C)$  are given for our complexes, where  $\Delta\delta$ represents the experimentally measured chemical shift and coordination chemical shift. For both  $\pi$  and  $\sigma$ bonding to copper(I) hfac, the  $\Delta\delta$  for the alkyne carbons will always result in shielding of the alkyne carbons. Therefore, in case of dominant  $\sigma$  bonding, deshielding of these carbons will be observed [18]. In Table 2 we can observe that the <sup>13</sup>C NMR signal for the carbon atoms of the  $C \equiv C$  triple bond is only slightly shifted on coordination to copper(I); a small downfield shift is observed. The same trend is observed for other alkyne-copper complexes [18,19] and is indicative of dominant  $\sigma$  bonding mode and weak interaction between the  $C \equiv C$  triple bond and copper center in the title compounds. If we compare complexes 2 and 3, where one or two Cu(hfac) are coordinated to 1,3,5-tris(trimethylsilylethynyl)benzene ligand, the small downfield shift observed increases on

going from 2 to 3. For complex 4, where three Cu(hfac) units are coordinated to two ligands, the downfield shift is intermediate between both. The same variation is observed for complexes 5 and 6. We have assigned the carbons of the triple bonds unambiguously by using HMBC experiments.

The thermal properties of all compounds were examined by thermal gravimetric analysis (TGA/DTA) and differential scanning calorimetry (DSC). 2 begins to sublime and loses mass, less than 1% residue, at about 98 °C and the maximum rate of weight loss occurs at 122.7 °C. The thermal behavior of compounds 3 and 4 is similar, with maximum rate at 141.5 and 93.3 °C, respectively. The decomposition temperature is higher for 2 and 4 than for 3, because at 165 °C 2 and 4 have lost about 30% and 40%, respectively, of the original mass and 3, at the same temperature, only about 4%. DSC analysis of a hermetically sealed sample of 2 displays a sharp endothermic at 122.63 °C, which corresponds to the melting point; in 3 an endothermic peak at 107 °C is observed, attributed to a phase change, and at 142.10 °C a sharp endothermic appears corresponding to the melting point. The same endothermic peak is observed at 109.8 °C for 4. The sublimation of 6 and 7 has an onset of 50 °C, with also less than 1% residue and maximum rate of weight loss occurring at 144.7 and 66.4 °C, respectively. At 165 °C, 6 has lost the 41.3% and 7 only the 15.9%. DSC of 6 has an endothermic peak at 175.37 °C attributed to melting and another endothermic peak at 199.13 °C, while 7 shows an exothermic peak at 84.77 °C. Finally, the sublimation of 9 has an onset at 85 °C and maximum rate of weight loss occurs at 137.3 °C with an endothermic peak at 136.8 °C in agreement with the melting point. These behaviors are also observed in copper  $\beta$ -diketonate compounds [20]. It is apparent from the TG/ DTA data that these compounds exhibit low volatility, although 4 and 6 have higher volatility and could be tested as precursors in copper chemical vapor deposition.

Table 2

Experimentally measured chemical shift and coordination chemical shift ( $\Delta\delta$ ) obtained from <sup>1</sup>H NMR and <sup>13</sup>C NMR of the 'free' alkyne and the alkyne Cu(I)hfac

Compound	$\mathrm{H}^{1}$	H <sup>3</sup>	$H^5$	$C^1$	$C^2$	$C^3$	$C^4$
1	7.48		0.22			103.1	95.50
2	7.67		0.28			104.92	95.92
3	7.82		0.34			106.60	96.24
4	7.76		0.31			105.84	96.09
5	7.04		0.24			97.02	99.72
6	7.31		0.34			100.92	99.82
7	7.40		0.38			102.84	100.64
8		0.18		87.95	85.81		
9		0.36		97.30	97.30		

# 4. Conclusions

The synthesis and spectroscopic characterization of novel multicoordinated  $\beta$ -diketonate copper(I) complexes with polyynes, which allow different coordination modes, are reported. IR and NMR spectral analyses suggest  $\eta^2$ -coordination mode of the Me<sub>3</sub>SiC $\equiv$ C units to Cu(hfac) with predominant  $\sigma$  bonding contribution acting each triple bond as a two-electron donor with poor back-donation from Cu(I) to the alkynes. The thermal stability and volatility grade have been evaluated. Complexes 2, 3, and 4, with the 1,3,5-tris(trimethylsilylethynyl)benzene ligand, show the stability sequence 3 > 2 > 4. Complexes with the 2,5-bis(trimethylsilylethynyl)thiophene ligand, 7, with only a Cu(hfac) unit, have greater stability than 6, which has two Cu(hfac) units.

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