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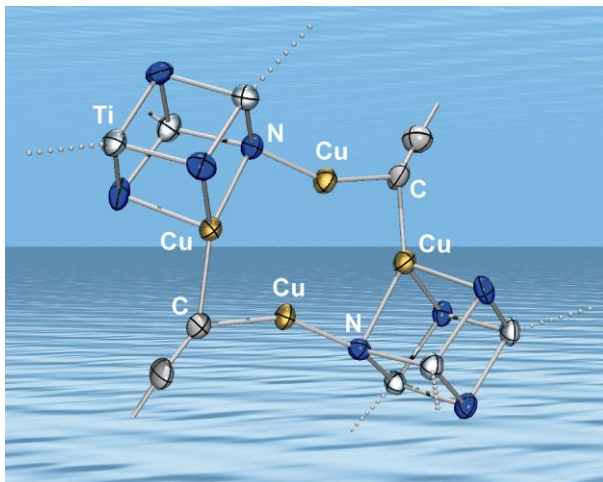
# Cyclopentadienyl and Alkynyl Copper(I) Derivatives with the $\{[\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})_3(\mu_3\text{-N})]\}$ Metalloligand

Noelia Martínez-Espada, Miguel Mena, Marta E. G. Mosquera, Adrián Pérez-Redondo, and  
Carlos Yélamos\*

Departamento de Química Inorgánica, Universidad de Alcalá. 28871 Alcalá de Henares-  
Madrid (Spain). FAX: (+34) 91-8854683. E-mail: carlos.yelamos@uah.es

## Summary:

The reaction of  $[\text{ClCu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  with organolithium reagents  $[\text{LiR}]$  ( $\text{R} = \text{C}_5\text{H}_5$ ,  $\text{C}\equiv\text{CR}$ ) affords the cyclopentadienyl  $[(\eta^2\text{-C}_5\text{H}_5)\text{Cu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  or alkynyl  $[(\text{RC}\equiv\text{C})\text{Cu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  copper(I) derivatives. Those complexes decompose in solution to give double-cube nitrido compounds  $[\{\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$  or  $[\{\text{Cu}(\mu\text{-}1\kappa\text{C}^1:2\kappa\text{C}^1\text{-C}\equiv\text{CR})\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$  (see picture) via elimination of RH organic fragments.



**Abstract:**

The treatment of  $[\text{ClCu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  (**2**) with lithium cyclopentadienide in toluene at room temperature affords  $[(\text{C}_5\text{H}_5)\text{Cu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  (**4**), where the cyclopentadienyl ligand is bound to copper(I) in an  $\eta^2$  fashion. The analogous reaction of **2** with lithium acetylides  $[\text{Li}(\text{C}\equiv\text{CR})]$  gives complexes  $[(\text{RC}\equiv\text{C})\text{Cu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  ( $\text{R} = \text{SiMe}_3$  (**5**), Ph (**6**)) with terminal alkynyl ligands bound to copper. Compound **6** is prepared in higher yield by the treatment of  $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$  (**1**) with  $[\text{Cu}(\text{C}\equiv\text{CPh})]$  in toluene at room temperature. The cyclopentadienyl derivative **4** decomposes in solution to generate the edge-linked double-cube nitrido complex  $[\{\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$  (**3**) via  $\text{C}_5\text{H}_6$  elimination. However, solutions of the alkynyl derivatives **5** and **6** lead to copper(I) acetylide-bridged double-cube complexes  $[\{\text{Cu}(\mu\text{-}1\kappa\text{C}^1:2\kappa\text{C}^1\text{-C}\equiv\text{CR})\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$  ( $\text{R} = \text{SiMe}_3$  (**7**), Ph (**8**)) along with **1** and  $\text{RC}\equiv\text{CH}$ . The X-ray crystal structures of **4**, **5**, **7**, and **8** have been determined.

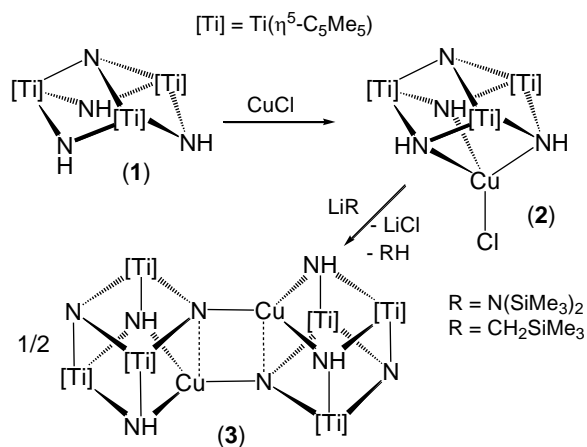
## Introduction

Organocopper(I) compounds CuR are generally encountered as polynuclear species with the organic ligands acting as bridging groups between the copper centers to give discrete aggregates or polymers.<sup>1,2</sup> However, neutral mononuclear CuR entities can be stabilized either by using R groups with steric constraints or by the additional coordination of appropriate ligands.<sup>3</sup> In particular, Lang and co-workers have successfully used  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]$  to isolate copper(I) compounds with alkyl, aryl or alkynyl terminal ligands.<sup>2,4,5</sup> The  $\eta^2$ -coordination of the alkynyl units of the titanocene molecule to the copper atom produces the rupture of  $(\text{CuR})_n$  species rendering a distorted trigonal planar environment of the group 11 metal center. Alternatively, preformed derivatives  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]\text{CuX}$  ( $\text{X} = \text{Cl}, \text{OTf}, \text{SC}_6\text{H}_4\text{CH}_2\text{NMe}_2$ ) react with organometallic reagents ( $\text{LiR}, \text{MgBrR}, \text{ZnR}_2$ ) to give complexes with monomeric CuR entities.

As part of a program related to the synthesis of polynuclear nitrido complexes,<sup>6</sup> we have been studying the coordination chemistry of the trinuclear titanium imido-nitrido complex  $[\{\text{Ti}(\eta^5\text{-C}_5\text{Me}_5)(\mu\text{-NH})\}_3(\mu_3\text{-N})]$ <sup>7,8</sup> (**1**) with a variety of main-group and transition metals. The structure of complex **1** reveals a six-membered  $[\text{Ti}_3(\mu\text{-NH})_3]$  ring with three NH electron-donor imido groups, and we have noted that **1** is prone to act as neutral tridentate chelate to a single metal through those imido groups.<sup>9</sup> In this bonding mode, the metalloligand **1** resembles other well-known facially coordinating six-electron donor ligands such as tris(pyrazolyl)methanes,<sup>10</sup> 1,4,7-triazacyclononanes,<sup>11</sup> and especially 1,3,5-triazacyclohexanes,<sup>12</sup> whose extensive coordination chemistry is known. However, once the adducts  $[(\mathbf{1})\text{ML}_n]$  are formed, the NH groups can be deprotonated if the coordination sphere

of the metal M contains imido, amido, or alkyl ligands, to give monoanionic, dianionic, and even trianionic forms of **1**, via elimination of the corresponding amine or alkane.<sup>13</sup>

In particular, we have recently reported that complex **1** entraps one equivalent of copper(I) halide or copper(I) trifluoromethanesulfonate to give  $[\text{XCu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  cube-type molecular compounds.<sup>14,15</sup> Subsequent treatment of the copper(I) chloride derivative  $[\text{ClCu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  (**2**) with lithium bis(trimethylsilyl)amido or lithium trimethylsilylmethyl (LiR) reagents leads to the edge-linked double-cube  $[\{\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$  (**3**) along with lithium chloride and amine or alkane molecules (Scheme 1).<sup>14</sup>



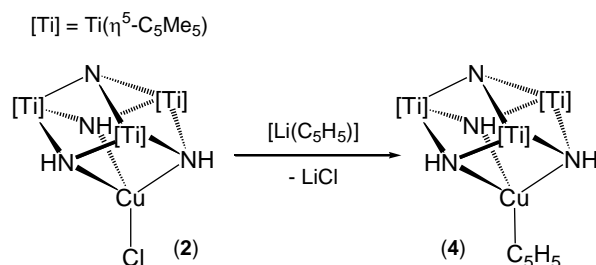
**Scheme 1.** Synthesis of copper(I) azaheterometallocubane complexes.

No intermediates were detected in the metathesis reactions, although formation of  $[\text{RCu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  ( $\text{R} = \text{N}(\text{SiMe}_3)_2, \text{CH}_2\text{SiMe}_3$ ) derivatives could be the first step. It appears that these copper amido or alkyl complexes immediately decompose at room temperature to give complex **3** through elimination of  $\text{NH}(\text{SiMe}_3)_2$  or  $\text{SiMe}_4$ . We envisaged that less basic R groups bonded to the copper center could confer a higher thermal stability to complexes containing monomeric CuR entities, and herein we

report the results obtained in the treatment of **2** with lithium cyclopentadienide and lithium acetylide reagents.

## Results and Discussion

The treatment of  $[\text{ClCu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  (**2**) with one equivalent of lithium cyclopentadienide in toluene affords the cyclopentadienyl copper(I) derivative  $[(\text{C}_5\text{H}_5)\text{Cu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  (**4**) (Scheme 2). Complex **4** decomposes slowly in solution at room temperature to give the double-cube compound  $[\{\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$  (**3**) and cyclopentadiene. Therefore, the preparative reaction was performed within 30 min at room temperature and complex **4** could be obtained after crystallization in a mixture of toluene/hexane at  $-20\text{ }^\circ\text{C}$ .



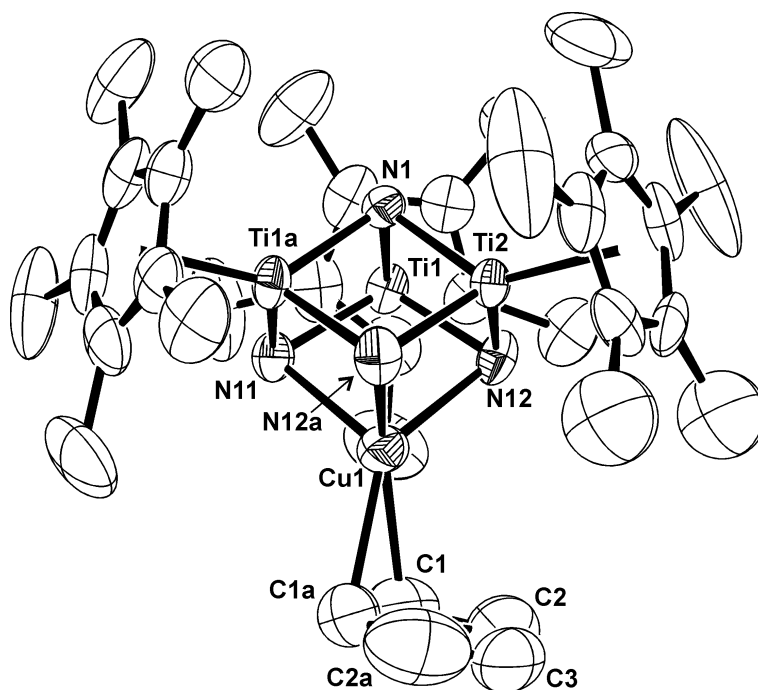
**Scheme 2.** Synthesis of the cyclopentadienyl complex **4**.

Compound **4** was isolated as air sensitive dark red crystals in a low yield (22%), and was characterized by spectroscopic and analytical methods, as well as by an X-ray crystal structure determination. The IR spectrum (KBr) reveals two  $\nu_{\text{NH}}$  vibrations at 3357 and  $3310\text{ cm}^{-1}$ , which are similar to the values determined for compounds **1** ( $3352\text{ cm}^{-1}$ )<sup>8</sup> and **2** ( $3362$  and  $3219\text{ cm}^{-1}$ )<sup>14</sup>.  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra in benzene- $d_6$  at room temperature show resonance signals for equivalent NH and  $\eta^5\text{-C}_5\text{Me}_5$  ligands. The NH resonance signal ( $\delta = 11.14$ ) is shifted to a higher field than that found for **1** ( $\delta = 13.80$ ), whereas the

resonance for the *ipso* carbon of the  $C_5Me_5$  groups ( $\delta = 119.1$ ) in the  $^{13}C$  NMR spectrum is slightly shifted downfield with respect to that found for **1** ( $\delta = 117.1$ ). We have noted an analogous shift in other adducts of **1**, and used those data to propose the tridentate chelate coordination of the NH groups to the metal centers.<sup>9,14</sup> The  $C_5H_5$  group of **4** shows a singlet resonance at  $\delta = 6.40$  in the  $^1H$  NMR spectrum and one resonance at  $\delta = 103.1$  in the  $^{13}C\{^1H\}$  NMR spectrum. The NMR data are consistent with an  $\eta^5$ -cyclopentadienyl ligand bound to copper,<sup>16</sup> or a coordination mode of lower hapticity (e.g.,  $\sigma$  or  $\eta^2$ ) if the ligand undergoes a dynamic exchange process with a low-energy barrier in solution.

The solid-state structure of complex **4** is presented in Figure 1, while selected distances and angles are given in Table 1. The molecular structure shows a  $[CuTi_3N_4]$  cube-type core with a mirror plane through the atoms Cu(1), Ti(2), N(1) and N(11), and the C(3) atom of the cyclopentadienyl ligand. Copper is bonded to three NH imido groups of the  $\{(\mu_3-NH)_3Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}$  metalloligand and two carbon atoms, C(1) and C(1)a, of the cyclopentadienyl ligand. Thus, if a centroid (Cm) between the C(1) and C(1)a atoms is considered, the coordination sphere about the copper atom may be described as distorted tetrahedral. In this geometry, the neutral ligand  $\{(\mu_3-NH)_3Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}$  coordinates in a tripodal fashion with nitrogen-copper-nitrogen angles of  $90.5(2)^\circ$ , whereas the nitrogen-copper-centroid angles are  $122.0^\circ$  and  $126.4^\circ$ . The Cu-N bond lengths of  $2.156(5)$  and  $2.137(4)$  Å are similar to those found in other copper(I) derivatives with the titanium metalloligand acting in a tridentate mode.<sup>15</sup> The Cu-C(1) bond length of  $2.263(6)$  Å and the dihedral angle of  $101^\circ$  between the Cu(1)-C(1)-C(1)a and the  $C_5H_5$  planes are consistent with an  $\eta^2$ -coordination of the cyclopentadienyl ligand. Indications of this type of coordination are the clearly longer distances between copper and the carbon atoms C(2) ( $2.953(9)$  Å) and C(3) ( $3.299(11)$  Å), which can be considered nonbonding, while the

deviation of the dihedral angle from the ideal  $90^\circ$  value may respond to the minimization of the steric repulsion of the cyclopentadienyl ring with the bulky pentamethylcyclopentadienyl ligand bonded to the Ti(2) atom. Further indication of this repulsion is the nonparallel distribution of the  $C_5H_5$  and N(11)-N(12)-N(12)a planes (dihedral angle of  $14^\circ$ ).



**Figure 1.** Perspective view of **4** with thermal ellipsoids at the 50% probability level.

Hydrogen atoms are omitted for clarity. The disorder of the pentamethylcyclopentadienyl ligand linked to Ti(2) is not shown.



**Table 1.** Selected Lengths (Å) and Angles (deg) for Complex **4**

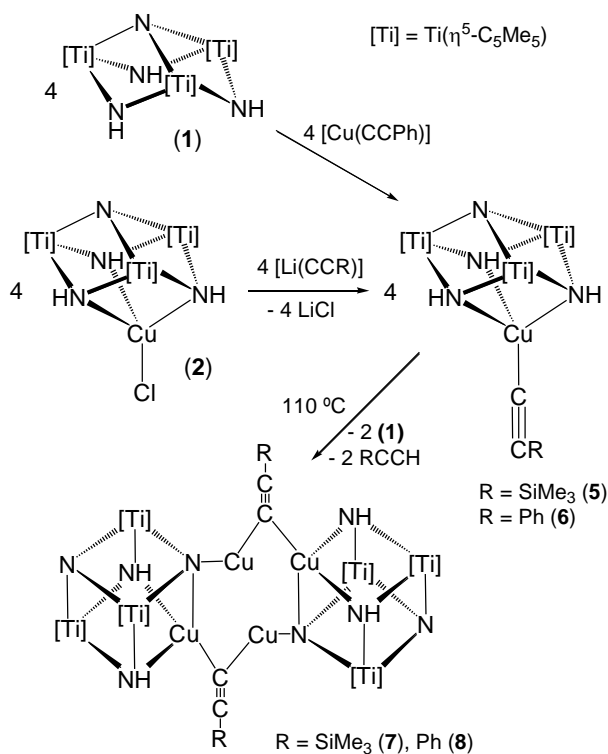
Cu(1)-N(11)	2.156(5)	Cu(1)-N(12)	2.137(4)
Cu(1)-C(1)	2.263(6)	Cu(1)···C(2)	2.953(9)
Cu(1)···C(3)	3.299(11)	C(1)-C(1)a	1.317(14)
C(1)-C(2)	1.410(11)	C(2)-C(3)	1.317(11)
Ti-N(1) <sup>a</sup>	1.941(2)	Ti-N <sup>a</sup>	1.954(4)
Ti···Ti <sup>a</sup>	2.840(1)	Cu-Cm <sup>b</sup>	2.166
N(11)-Cu(1)-N(12)	90.5(1)	N(12)-Cu(1)-N(12)a	90.5(2)
N(11)-Cu(1)-C(1)	120.5(2)	N(12)-Cu(1)-C(1)	111.1(2)
N(12)a-Cu(1)-C(1)	140.7(2)	C(1)-Cu(1)-C(1)a	33.8(4)
N(11)-Cu(1)-Cm <sup>b</sup>	122.0	N(12)-Cu(1)-Cm <sup>b</sup>	126.4
Cu(1)-C(1)-C(2)	104.6(5)	Cu(1)-C(1)-C(1)a	73.1(2)
C(2)-C(1)-C(1)a	107.6(6)	C(1)-C(2)-C(3)	106.7(9)
C(2)-C(3)-C(2)a	111.1(11)	Cu(1)-N-Ti <sup>a</sup>	83.6(2)
Ti-N-Ti <sup>a</sup>	93.2(1)	N-Ti-N <sup>a</sup>	102.3(1)
N-Ti-N(1) <sup>a</sup>	86.2(2)	Ti-N(1)-Ti <sup>a</sup>	94.1(1)

<sup>a</sup> Averaged values. <sup>b</sup> Cm = Centroid between C(1) and C(1)a carbon atoms.

While several copper(I) complexes with  $\eta^5$ -cyclopentadienyl ligands have been structurally characterized,<sup>16</sup> coordination modes of lower hapticity for these ligands are rare in the literature. Crystallographically documented copper(I) complexes with cyclopentadienyl rings bonded by only one  $\sigma$ -bond to a single copper atom are limited to two examples containing fluorenyl ligands, [Li(thf)<sub>4</sub>][Cu(fluorenyl)<sub>2</sub>(PPh<sub>3</sub>)]<sup>17</sup> and [Li(thf)<sub>4</sub>][Cu<sub>2</sub>(fluorenyl)<sub>3</sub>(S-Alkyne)] (S-Alkyne = 3,3,6,6-tetramethyl-1-thiacyclohept-4-yne).<sup>18</sup> In those examples, the Cu-C bond length (2.05-2.17 Å) is clearly shorter than the distances between copper and the remaining carbon atoms (2.78-3.91 Å). On the other hand, the  $\eta^2$  coordination mode of the cyclopentadienyl ligand has been only reported by Jutzi and co-workers in the anionic fragments of complexes [PPh<sub>4</sub>][Cu(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] and [Li(12-

crown-4)<sub>2</sub>][Cu<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>]·2THF.<sup>19</sup> The Cu-C bond lengths in those complexes are in the range 2.05-2.27 Å (cf. 2.263(6) in **4**), whereas the Cu-C distances with the other carbon atoms of the rings span 2.48-3.35 Å. Interestingly, the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of [PPh<sub>4</sub>][Cu(C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>] at -80 °C showed three resonance signals for the C<sub>5</sub>H<sub>5</sub> groups, which are consistent with the X-ray crystal structure, while the spectra at -5 °C revealed one singlet resonance according with a dynamic exchange process in solution.<sup>19</sup> The <sup>1</sup>H NMR spectrum in a 500 MHz spectrometer of a solution of **4** in dichloromethane-d<sub>2</sub> at -100 °C revealed sharp resonances for the C<sub>5</sub>Me<sub>5</sub> and C<sub>5</sub>H<sub>5</sub> ligands, indicating a smaller energy barrier for the fluxional process occurring on complex **4**. Although still rare, the η<sup>2</sup> binding mode is best represented in the solid-state structures of bis(cyclopentadienyl) derivatives of other metals, such as zinc<sup>20</sup> or cadmium.<sup>21</sup>

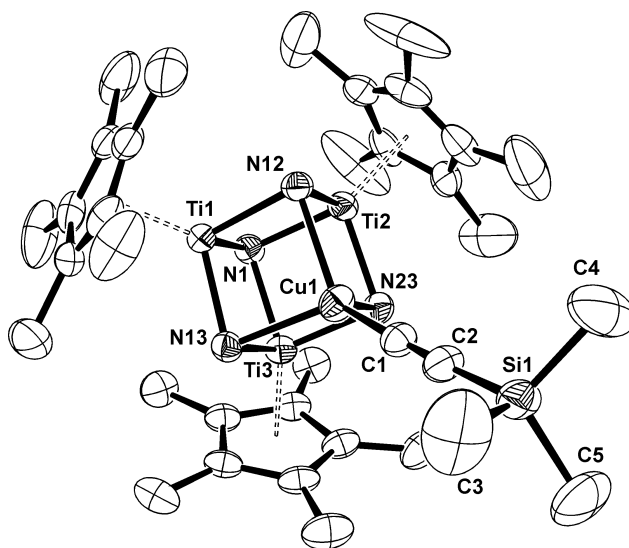
In a similar procedure to the preparation of complex **4**, the reaction of **2** with one equivalent of lithium acetylides [Li(C≡CR)] in toluene at room temperature afforded red solutions. Analysis by NMR spectroscopy of the solution components revealed a mixture of compounds where the expected copper(I) alkynyl derivatives [(RC≡C)Cu{(μ<sub>3</sub>-NH)<sub>3</sub>Ti<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>(μ<sub>3</sub>-N)}] (R = SiMe<sub>3</sub> (**5**), Ph (**6**)) were the major products (Scheme 3). After many attempts, a few red crystals of compound **5**·C<sub>7</sub>H<sub>8</sub> could be obtained in a pure form by crystallization in hexane at -30 °C. Thus, the trimethylsilylethynyl complex **5** was only characterized by <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectroscopy as well as by an X-ray crystal structure determination. The analogous phenylethynyl derivative **6** can be isolated in a better yield (68%) from the reaction of complex **1** with one equiv of [Cu(C≡CPh)] in toluene for 0.5 h, and was characterized by spectral and analytical methods.



**Scheme 3.** Synthesis of the alkynyl complexes **5-8**.

The IR spectrum (KBr) of complex **6** shows one strong absorption at 2072 cm<sup>-1</sup> for the  $\nu_{C\equiv C}$  vibration, which is typical of terminal alkynyl ligands bound to a single metal center.<sup>5,22</sup> The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra of complexes **5** and **6** in benzene-d<sub>6</sub> at room temperature are consistent with a C<sub>3v</sub> symmetry in solution and reveal signals for equivalent  $\eta^5$ -C<sub>5</sub>Me<sub>5</sub> and NH groups, along with the expected resonance signals for one alkynyl ligand. The solid-state structure of **5** is showed in Figure 2, while selected lengths and angles for this compound are given in Table 2. Crystals of **5** bear one toluene solvent molecule per cube-type complex. The molecular structure contains a [CuTi<sub>3</sub>N<sub>4</sub>] core with the copper atom bound to the three NH imido groups and one alkynyl carbon atom. The coordination sphere about the copper center is best described as distorted tetrahedral with N-Cu-N angles ranging 88.4(1)-89.3(1)° and N-Cu-C(1) spanning 123.6(1)-127.4(1)°. The copper-nitrogen bond lengths (av. 2.17(2) Å) are very similar to those found for compound

**4**, while the Cu-C(1) bond distance of 1.917(3) Å is in the normal range for other terminal alkynyl copper(I) complexes.<sup>5</sup> The alkynyl group is linear at C(1) (177.6(3)°) and C(2) (177.7(3)°) and has a C(1)≡C(2) bond length of 1.215(4) Å, all of which are typical for these ligands.<sup>22</sup>



**Figure 2.** Perspective view of **5** with thermal ellipsoids at the 50% probability level.

Hydrogen atoms and the C<sub>7</sub>H<sub>8</sub> solvent molecule are omitted for clarity. The disorder of the pentamethylcyclopentadienyl ligand linked to Ti(2) is not shown.

**Table 2.** Selected Lengths (Å) and Angles (deg) for Complex **5**

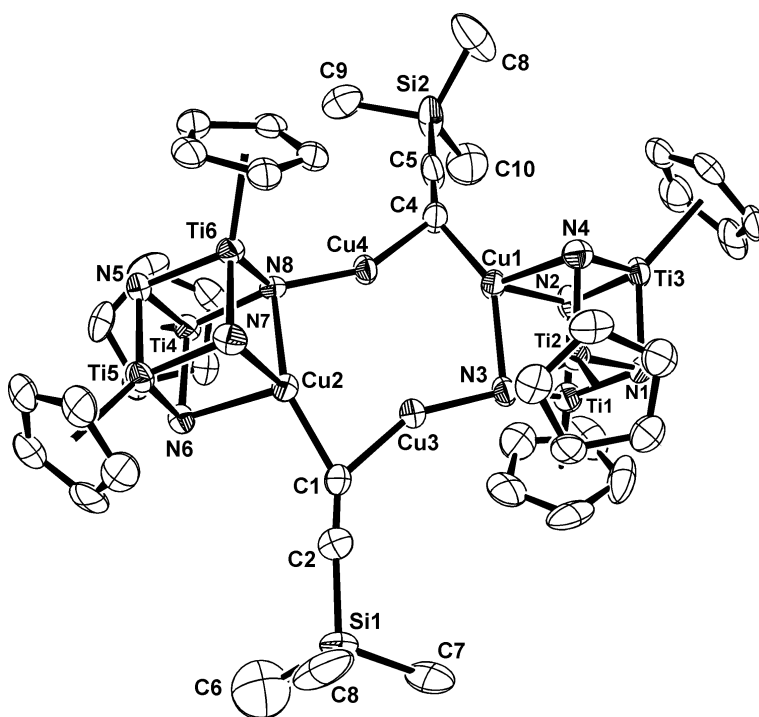
Cu(1)-N(12)	2.163(2)	Cu(1)-N(13)	2.167(2)
Cu(1)-N(23)	2.193(2)	Cu(1)-C(1)	1.917(3)
C(1)-C(2)	1.215(4)	Ti-N(1) <sup>a</sup>	1.940(2)
Ti-N <sup>a</sup>	1.962(6)	Ti...Ti <sup>a</sup>	2.846(1)
N(12)-Cu(1)-N(13)	89.3(1)	N(12)-Cu(1)-N(23)	88.4(1)
N(13)-Cu(1)-N(23)	89.0(1)	N(12)-Cu(1)-C(1)	127.0(1)
N(13)-Cu(1)-C(1)	127.4(1)	N(23)-Cu(1)-C(1)	123.6(1)
Cu(1)-C(1)-C(2)	177.6(3)	C(1)-C(2)-Si(1)	177.7(3)
Cu(1)-N-Ti <sup>a</sup>	84.6(4)	Ti-N(1)-Ti <sup>a</sup>	94.3(1)
Ti-N-Ti <sup>a</sup>	93.0(3)	N(1)-Ti-N <sup>a</sup>	86.2(2)
N-Ti-N <sup>a</sup>	101.9(4)	Ti-Ti-Ti <sup>a</sup>	60.0(1)

<sup>a</sup> Averaged values.

Compounds **5** and **6** decompose in toluene or benzene solutions, slowly at room temperature and rapidly at higher temperatures, to give the double-cube complexes [ $\{\text{Cu}(\mu\text{-}1\kappa\text{C}^1:2\kappa\text{C}^1\text{-C}\equiv\text{CR})\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2$ ] ( $\text{R} = \text{SiMe}_3$  (**7**), Ph (**8**)) (Scheme 3). The thermal decomposition of **6** in benzene- $\text{d}_6$  was monitored by  $^1\text{H}$  NMR spectroscopy. Spectra taken after leaving the solution at room temperature for 16 h revealed resonance signals for complex **6** along with minor resonances for other compounds (ca. 15%). After heating at 110 °C for 7 days, the spectra revealed signals due to **6** (ca. 40%) and resonances assigned to compounds **8**, **1** and  $\text{PhC}\equiv\text{CH}$ . Upon standing at room temperature, red crystals of **8** precipitated at the bottom of the NMR tube.

Complex  $\mathbf{8}\cdot 2\text{C}_7\text{H}_8$  was obtained in 65% yield after heating **6** at 110 °C in toluene for 3 days and subsequent cooling at -25 °C. In a similar fashion, the toluene solution resulting from the reaction of **2** with  $[\text{Li}(\text{C}\equiv\text{CSiMe}_3)]$  was heated at 110 °C to afford red crystals of **7** (17% yield). Compounds **7** and **8** were characterized by spectroscopic and analytical methods, as well as by X-ray crystal structure determinations. The IR spectra (KBr) of **7** and **8** show one strong or medium absorption for the  $\nu_{\text{C}\equiv\text{C}}$  vibration at 1971 and 2038  $\text{cm}^{-1}$ , respectively. The wavenumber value for this vibration in **8** is 34  $\text{cm}^{-1}$  lower than that found for the terminal phenylethynyl ligand in **6** (2072  $\text{cm}^{-1}$ ) and could be consistent with the alkynyl groups acting as bridging ligands.<sup>23</sup> Once isolated in the solid-state, the trimethylsilylethynyl derivative **7** exhibits a good solubility in toluene or benzene but compound **8** is poorly soluble in benzene- $\text{d}_6$  and decomposes within minutes in chloroform- $\text{d}_1$ . The  $^1\text{H}$  NMR spectra of complexes **7** and **8** in benzene- $\text{d}_6$  at room temperature reveal resonance signals for two  $\eta^5\text{-C}_5\text{Me}_5$  groups in a 2:1 ratio, one CCR ligand and a broad signal for the NH groups. The NMR data for these compounds are consistent with a  $C_s$  symmetry in solution as depicted in Scheme 3.

The solid-state structures of **7** and **8** are presented in Figures 3 and 4, and selected distances and angles for both compounds are given in Table 3. Complex **8** crystallizes with two toluene molecules per double-cube complex, whereas crystals of **7** do not contain solvent molecules. The crystal structures consist of two [CuTi<sub>3</sub>N<sub>4</sub>] cube-type cores held together by two [Cu(CCR)] fragments linking Cu-N edges of the cubes. Each copper atom of the cubes [Cu(1) and Cu(2)] is bonded to three nitrogen atoms and one carbon atom of the alkynyl ligand. The N-Cu-N angles (87.6(2)-89.5(3)°) around these copper atoms and their Cu-N bond lengths (2.120(3)-2.193(3) Å) are similar to those found in complexes **4** and **5**. However, the C-Cu(1)/Cu(2)-N angles (98.6(2)-150.2(2)°) and their Cu-C bond lengths (1.945(4)-1.982(8) Å) are clearly different from those of **5** (123.6(1)-127.4(1)° and 1.917(3) Å) due to the coordination of the acetylide ligands through the C(1) and C(4) atoms to Cu(3) and Cu(4), respectively. If Cu(1)···Cu(4) and Cu(2)···Cu(3) interactions are considered, the coordination sphere about Cu(1) and Cu(2) may be described as distorted trigonal bipyramidal. In this geometry, two nitrogen and one copper atoms [N(2), N(4) and Cu(4) for Cu(1); N(6), N(7) and Cu(3) for Cu(2)] occupy the equatorial positions (sum of angles subtended at the Cu(1) and Cu(2) centers in the equatorial plane spans 357.4-358.4°), and one nitrogen and one carbon atoms [N(3) and C(4) for Cu(1); N(8) and C(1) for Cu(2)] are in the axial coordination sites.



**Figure 3.** Simplified view of **7** with thermal ellipsoids at the 50% probability level. The methyl groups of the pentamethylcyclopentadienyl ligands and hydrogen atoms are omitted for clarity. The disorder of the trimethylsilyl groups is not shown.

**Table 3.** Selected Lengths (Å) and Angles (deg) for Complexes  $[\{\text{Cu}(\mu\text{-}1\kappa\text{C}^1:2\kappa\text{C}^1\text{-C}\equiv\text{CR})\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$  (**7** and **8**)

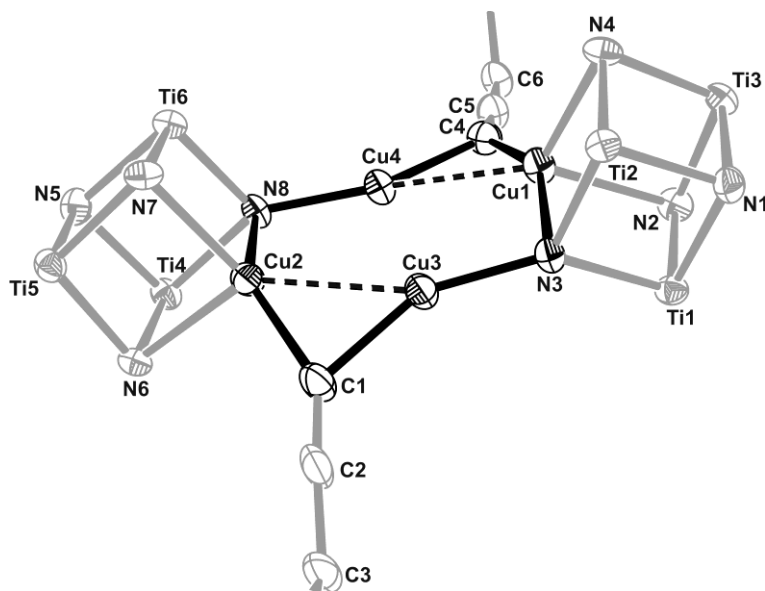
	<b>7</b> (R = SiMe <sub>3</sub> )	<b>8</b> (R = Ph)
Cu(1)-N	2.148(7)-2.161(6)	2.120(3)-2.193(3)
Cu(1)-C(4)	1.949(8)	1.945(4)
Cu(1)···Cu(4)	2.477(1)	2.493(2)
Cu(2)-C(1)	1.982(8)	1.959(5)
Cu(2)-N	2.161(6)-2.167(6)	2.128(4)-2.182(3)
Cu(2)···Cu(3)	2.475(2)	2.513(2)
Cu(3)-C(1)	1.961(8)	1.937(4)
Cu(3)-N(3)	1.854(6)	1.858(3)
Cu(4)-C(4)	1.954(8)	1.942(4)
Cu(4)-N(8)	1.864(6)	1.865(3)
C(1)-C(2)	1.193(12)	1.200(6)

C(4)-C(5)	1.233(11)	1.224(6)
N-Cu(1)-N	88.4(2)-89.5(3)	87.8(1)-89.5(1)
C(4)-Cu(1)-N	101.9(3)-146.5(3)	102.5(2)-150.2(2)
C(4)-Cu(1)-Cu(4)	50.7(2)	50.1(1)
N-Cu(2)-N	88.2(2)-89.1(2)	87.6(1)-88.6(1)
C(1)-Cu(2)-N	104.1(3)-148.9(3)	98.6(2)-136.7(2)
C(1)-Cu(2)-Cu(3)	50.7(2)	49.5(1)
C(1)-Cu(3)-Cu(2)	51.5(2)	50.2(1)
C(1)-Cu(3)-N(3)	153.2(3)	150.8(2)
N(3)-Cu(3)-Cu(2)	155.3(2)	158.9(1)
C(4)-Cu(4)-Cu(1)	50.5(2)	50.2(1)
C(4)-Cu(4)-N(8)	153.7(3)	149.1(2)
N(8)-Cu(4)-Cu(1)	155.6(2)	160.3(1)
Cu(2)-C(1)-Cu(3)	77.8(3)	80.4(2)
Cu(2)-C(1)-C(2)	148.0(7)	146.2(4)
Cu(3)-C(1)-C(2)	134.0(7)	132.3(4)
C(1)-C(2)-Si(1)/C(3)	173.5(9)	175.4(6)
Cu(1)-C(4)-Cu(4)	78.8(3)	79.8(2)
Cu(1)-C(4)-C(5)	147.0(7)	149.5(4)
Cu(4)-C(4)-C(5)	134.1(7)	130.7(4)
C(4)-C(5)-Si(2)/C(6)	168.6(11)	175.8(5)

Each copper atom between the cubes [Cu(3) and Cu(4)] is bonded to one alkynyl carbon atom and one nitrogen atom of a cube with bond distances of 1.937(4)-1.961(8) Å and 1.854(6)-1.865(3) Å, respectively. The C-Cu(3)/Cu(4)-N angles range 149.1(2)-153.7(3)°, and therefore the geometry about these two-coordinate copper atoms is not linear. However, if the Cu...Cu interactions are considered, the coordination sphere about Cu(3) and Cu(4) may be described as distorted trigonal planar (sum of angles spans 359.6-360.0°). Because a similar geometry is also present around the C(1) and C(4) acetylenic carbon atoms (sum of angles spanning 358.9-360.0°), we can consider one plane bearing the N(3), Cu(3), Cu(2), C(1) and C(2) atoms and a second plane containing the N(8), Cu(4), Cu(1), C(4) and C(5) atoms. The dihedral angles (27° in **7** and 45° in **8**) may respond to the



minimization of the steric repulsion between the CCR groups and the bulky pentamethylcyclopentadienyl ligands, and explain the nonplanarity of the central eight-membered  $\text{Cu}_4\text{C}_2\text{N}_2$  rings of the molecules. Further indication of this repulsion is the perpendicular distribution of the  $\text{C}_6\text{H}_5$  and the  $\text{Cu}_2\text{C}_2\text{N}$  planes (dihedral angles of  $89^\circ$  and  $85^\circ$ ) in the structure of **8**.



**Figure 4.** Simplified view of **8** with thermal ellipsoids at the 50% probability level. The pentamethylcyclopentadienyl ligands, phenyl groups, hydrogen atoms and the  $\text{C}_7\text{H}_8$  solvent molecules are omitted for clarity.

An additional interesting feature in the structures of **7** and **8** concerns the coordination mode of the bridging alkynyl ligands. The organic ligands bridge two copper centers with all  $\text{Cu}-\text{C}(1)/(\text{C}(4))$  bond lengths in the range  $1.937(4)$ - $1.982(8)$  Å, which are only slightly longer than the  $\text{Cu}-\text{C}$  bond distance in the terminal alkynyl ligand of complex **5** ( $1.917(3)$  Å). The distances between the copper atoms and the remaining carbons ( $\text{C}(2)$  and  $\text{C}(5)$ ) of the acetylenic groups are clearly longer ( $2.885$ - $3.063$  Å) and suggest little or no metal-alkynyl  $\pi$  interaction, supporting a  $\mu\text{-}1\kappa\text{C}^1:2\kappa\text{C}^1$  coordination mode of the alkynyl

ligands.<sup>17,24</sup> Further indications of the absence of  $\pi$  interactions are the acetylenic  $\text{C}\equiv\text{C}$  bond lengths (1.193(12)-1.233(11) Å) and the almost linear  $\text{C}\equiv\text{C}-\text{Si}/\text{C}$  angles (168.6(11)-175.8(5)°).

Although the Cu-C bond distances are almost identical, the bridging acetylide ligands are asymmetric showing a bending toward the two-coordinate copper centers with Cu(3)/Cu(4)- $\text{C}\equiv\text{C}$  angles spanning 130.7(4)-134.1(7)° while the Cu(1)/Cu(2)- $\text{C}\equiv\text{C}$  angles are ranging 146.2(4)-149.5(4)°. This tilting may be a consequence of the lower steric crowding about the two-coordinate Cu(3) and Cu(4) atoms. The Cu...Cu distances, 2.475(2)-2.513(2) Å, in compounds **7** and **8** are shorter than the interatomic separation found in metallic copper (2.56 Å) but are not uncommon in organocopper systems.<sup>1</sup> Similar or even shorter Cu...Cu distances have been observed in several structurally documented acetylide-bridged copper complexes.<sup>24</sup> The bonding and stereochemical trends in doubly bridged dinuclear copper(I) complexes has been examined in detail by means of DFT studies,<sup>25</sup> with a particular emphasis devoted to complexes containing  $\text{Cu}_2(\mu\text{-}1\kappa\text{C}^1:2\kappa\text{C}^1)_2$  frameworks. The theoretical calculations confirm the idea that the  $\sigma$  lone pairs of the bridges contribute most to the annular bonding as well as to the direct M-M linkage characterized by  $\sigma$  and  $\pi$  bonding combinations of empty Cu *s* and *p* $\pi$  orbitals.

## Conclusion

The reactions of the azaheterometallocubane complex  $[\text{ClCu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  with lithium cyclopentadienide or lithium acetylides afford organometallic derivatives  $[\text{RCu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  containing rare examples of  $\eta^2$ -cyclopentadienyl or terminal alkynyl ligands bound to the copper(I) centers. These compounds with single-cube structures decompose in solution to give edge-linked

$[\{\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$  or copper(I) acetylide-bridged  $[\{\text{Cu}(\mu\text{-}1\kappa\text{C}^1:2\kappa\text{C}^1\text{-C}\equiv\text{CR})\text{Cu}(\mu_4\text{-N})(\mu_3\text{-NH})_2\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}_2]$  double-cube nitrido compounds via elimination of RH organic fragments.

## Experimental Section

**General Comments.** All manipulations were carried out under argon atmosphere using Schlenk line or glovebox techniques. Hexane was distilled from Na/K alloy just before use. Toluene was freshly distilled from sodium. NMR solvents were dried with Na/K alloy ( $C_6D_6$ ) or calcium hydride ( $CDCl_3$ ,  $CD_2Cl_2$ ) and vacuum-distilled. Oven-dried glassware was repeatedly evacuated with a pumping system (ca.  $1 \times 10^{-3}$  Torr) and subsequently filled with inert gas.  $[Cu(CCPH)]$  was purchased from Strem and used as received. Lithium salts  $[LiR]$  ( $R = C_5H_5$ ,<sup>26</sup>  $C\equiv CSiMe_3$ ,<sup>27</sup>  $C\equiv CPh$ ) were prepared by treatment of freshly distilled  $C_5H_6$  or  $RC\equiv CH$  (Aldrich) with  $[Li*n*Bu]$  (Aldrich, 1.6 M in hexane).  $[Ti(\eta^5-C_5Me_5)(\mu-NH)]_3(\mu_3-N)$  (**1**),<sup>7,8</sup> and  $[ClCu\{(\mu_3-NH)_3Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$  (**2**)<sup>14a</sup> were prepared according to published procedures.

Samples for infrared spectroscopy were prepared as KBr pellets.  $^1H$  and  $^{13}C$  NMR spectra were recorded on a Varian Unity-300 and/or Unity-500 Plus spectrometer. Chemical shifts ( $\delta$ ) are given relative to residual protons or to carbon of the solvent,  $C_6D_6$  ( $^1H$ :  $\delta = 7.15$ ;  $^{13}C$ :  $\delta = 128.0$ ) or  $CDCl_3$  ( $^1H$ :  $\delta = 7.24$ ;  $^{13}C$ :  $\delta = 77.0$ ). Microanalyses (C, H, N) were performed in a Leco CHNS-932 microanalyzer.

**Synthesis of  $[(C_5H_5)Cu\{(\mu_3-NH)_3Ti_3(\eta^5-C_5Me_5)_3(\mu_3-N)\}]$  (**4**).** A 100 mL Schlenk flask was charged with **2** (0.50 g, 0.71 mmol),  $[Li(C_5H_5)]$  (0.050 g, 0.69 mmol) and toluene (20 mL). After stirring at room temperature for 0.5 h, the volatile components were removed under reduced pressure and the resultant brown solid was extracted with toluene (10 mL). Filtration of the toluene extract through a coarse glass frit gave a brown solution. The volume of this solution was concentrated to about 5 mL under reduced pressure and hexane (15 mL) was added to the solution. After 5 days at  $-20$  °C, dark red crystals of **4** (0.11 g, 22%) were isolated by decanting the solution. IR (KBr,  $cm^{-1}$ ): 3357 (m), 3310 (m), 3051

(m), 2910 (s), 2856 (s), 1489 (m), 1428 (s), 1376 (s), 1065 (w), 1023 (m), 991 (m), 892 (w), 789 (m), 740 (vs), 695 (s), 683 (s), 643 (vs), 518 (m), 475 (w), 429 (s), 399 (m).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 20 °C,  $\delta$ ): 11.14 (s br, 3H; NH), 6.40 (s, 5H;  $\text{C}_5\text{H}_5$ ), 1.88 (s, 45H;  $\text{C}_5\text{Me}_5$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 20 °C,  $\delta$ ): 119.1 ( $\text{C}_5\text{Me}_5$ ), 103.1 ( $\text{C}_5\text{H}_5$ ), 11.6 ( $\text{C}_5\text{Me}_5$ ). Anal. Calcd. for  $\text{C}_{35}\text{H}_{53}\text{CuN}_4\text{Ti}_3$  ( $M_r = 736.98$ ): C 57.04, H 7.25, N 7.60. Found: C 56.69, H 7.09, N 6.72.

**Synthesis of  $[(\text{Me}_3\text{SiC}\equiv\text{C})\text{Cu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  (5).** A 100 mL Schlenk flask was charged with **2** (0.30 g, 0.42 mmol),  $[\text{Li}(\text{C}\equiv\text{CSiMe}_3)]$  (0.044 g, 0.42 mmol) and toluene (15 mL). The reaction mixture was stirred for 0.5 h at room temperature to give a red solution. After filtration, the volatile components were removed under reduced pressure and the resultant red solid was extracted with hexane (5 mL). Filtration of the hexane extract through a coarse glass frit gave a red solution. After cooling at -30 °C for 5 days, a few single crystals of **5**· $\text{C}_7\text{H}_8$  were isolated by decanting the solution.  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 20 °C,  $\delta$ ): 11.77 (s br, 3H; NH), 1.85 (s, 45H;  $\text{C}_5\text{Me}_5$ ), 0.34 (s, 9H;  $\text{SiMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{C}_6\text{D}_6$ , 20 °C,  $\delta$ ): 119.0 ( $\text{C}_5\text{Me}_5$ ) 11.6 ( $\text{C}_5\text{Me}_5$ ), 2.5 ( $\text{SiMe}_3$ ), the  $\text{CCSiMe}_3$  resonance signals were not determined.

**Synthesis of  $[(\text{PhC}\equiv\text{C})\text{Cu}\{(\mu_3\text{-NH})_3\text{Ti}_3(\eta^5\text{-C}_5\text{Me}_5)_3(\mu_3\text{-N})\}]$  (6).** A 100 mL Schlenk flask was charged with **1** (0.30 g, 0.49 mmol),  $[\text{Cu}(\text{C}\equiv\text{CPh})]$  (0.081 g, 0.49 mmol) and toluene (20 mL). The reaction mixture was stirred at room temperature for 0.5 h to give a dark red solution. After filtration, the volatile components were removed under reduced pressure to give a red solid. The solid was washed with hexane (5 mL) and vacuum-dried to give **6** as a red powder (0.26 g, 68%). IR (KBr,  $\text{cm}^{-1}$ ): 3364 (m), 3295 (w), 2909 (s), 2857 (s), 2072 (s), 1593 (m), 1482 (s), 1429 (s), 1377 (s), 1205 (w), 1171 (w), 1067 (w), 1024 (m), 908 (w), 754 (s), 742 (s), 693 (s), 673 (s), 651 (vs), 641 (vs), 525 (m), 478 (w), 432 (m), 404 (m).  $^1\text{H}$  NMR ( $\text{C}_6\text{D}_6$ , 20 °C,  $\delta$ ): 11.94 (s br, 3H; NH), 7.70 (m, 2H; *o*- $\text{C}_6\text{H}_5$ ), 6.97 (m, 2H; *m*- $\text{C}_6\text{H}_5$ ),

6.85 (m, 1H; *p*-C<sub>6</sub>H<sub>5</sub>), 1.91 (s, 45H; C<sub>5</sub>Me<sub>5</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 20 °C, δ): 137.8, 131.9, 124.2 (CCC<sub>6</sub>H<sub>5</sub>), 119.2 (C<sub>5</sub>Me<sub>5</sub>) 11.7 (C<sub>5</sub>Me<sub>5</sub>), one C<sub>6</sub>H<sub>5</sub> and the CCC<sub>6</sub>H<sub>5</sub> resonance signals were not determined. Anal. Calcd for C<sub>38</sub>H<sub>53</sub>CuN<sub>4</sub>Ti<sub>3</sub> (M<sub>r</sub> = 773.01): C 59.04, H 6.91, N 7.25. Found: C 59.57, H 6.45, N 6.77.

**Synthesis of [{Cu(μ-1κC<sup>1</sup>:2κC<sup>1</sup>-C≡CSiMe<sub>3</sub>)Cu(μ<sub>4</sub>-N)(μ<sub>3</sub>-NH)<sub>2</sub>Ti<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>(μ<sub>3</sub>-N)}<sub>2</sub>]**

**(7).** A 25 mL ampule (Teflon stopcock) was charged with **2** (0.30 g, 0.42 mmol), [Li(C≡CSiMe<sub>3</sub>)] (0.044 g, 0.42 mmol) and toluene (20 mL). The reaction mixture was stirred at 110 °C for 2 days to give a dark red solution. The solution was filtered and its volume was concentrated under reduced pressure to ca. 5 mL. After 7 days at room temperature, dark red crystals of **7** (0.060 g, 17%) were isolated by decanting the solution. IR (KBr, cm<sup>-1</sup>): 3366 (m), 2906 (vs), 2855 (s), 1971 (vs), 1492 (w), 1431 (m), 1375 (s), 1243 (vs), 1129 (w), 1024 (w), 984 (w), 851 (vs), 836 (vs), 778 (s), 756 (s), 733 (s), 710 (s), 665 (vs), 623 (vs), 519 (m), 469 (w), 421 (m), 397 (m). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 20 °C, δ): 11.40 (s br, 4H; NH), 2.23 (s, 60H; C<sub>5</sub>Me<sub>5</sub>), 2.03 (s, 30H; C<sub>5</sub>Me<sub>5</sub>), 0.48 (s, 18H; SiMe<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 20 °C, δ): 117.8, 117.7 (C<sub>5</sub>Me<sub>5</sub>), 12.8, 12.0 (C<sub>5</sub>Me<sub>5</sub>), 1.7 (SiMe<sub>3</sub>), the CCSiMe<sub>3</sub> resonance signals were not determined. Anal. Calcd for C<sub>70</sub>H<sub>112</sub>Cu<sub>4</sub>N<sub>8</sub>Si<sub>2</sub>Ti<sub>6</sub> (M<sub>r</sub> = 1663.27): C 50.55, H 6.79, N 6.74. Found: C 50.57, H 6.93, N 6.72.

**Synthesis of [{Cu(μ-1κC<sup>1</sup>:2κC<sup>1</sup>-C≡CPh)Cu(μ<sub>4</sub>-N)(μ<sub>3</sub>-NH)<sub>2</sub>Ti<sub>3</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>(μ<sub>3</sub>-N)}<sub>2</sub>]** (**8**).

A 100 mL Schlenk flask was charged with **1** (0.30 g, 0.49 mmol), [Cu(C≡CPh)] (0.081 g, 0.49 mmol) and toluene (20 mL). The reaction mixture was stirred at room temperature for 3 h to give a dark red solution. The solution was filtered and its volume was concentrated under reduced pressure to ca. 10 mL. The solution was transferred to a 25 mL ampule (Teflon stopcock) and heated at 110 °C for 3 days. After that time, the solution was cooled at -25 °C to give dark red crystals of **8**·2C<sub>7</sub>H<sub>8</sub> (0.15 g, 65%). IR (KBr, cm<sup>-1</sup>): 3359 (w),

3023 (w), 2905 (vs), 2854 (s), 2721 (w), 2038 (m), 1591 (m), 1494 (w), 1482 (m), 1431 (s), 1375 (s), 1203 (w), 1067 (w), 1024 (m), 905 (w), 784 (m), 754 (s), 729 (s), 714 (m), 691 (m), 665 (vs), 629 (s), 592 (w), 519 (m), 465 (w), 445 (m), 420 (m), 398 (m). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 20 °C, δ): 11.65 (s broad, 4H; NH), 7.72 (m, 4H; *o*-C<sub>6</sub>H<sub>5</sub>), 7.22 (m, 4H; *m*-C<sub>6</sub>H<sub>5</sub>), 7.02 (m, 2H; *p*-C<sub>6</sub>H<sub>5</sub>), 2.22 (s, 60H; C<sub>5</sub>Me<sub>5</sub>), 1.97 (s, 30H; C<sub>5</sub>Me<sub>5</sub>). Anal. Calcd for C<sub>90</sub>H<sub>120</sub>Cu<sub>4</sub>N<sub>8</sub>Ti<sub>6</sub> (*M*<sub>r</sub> = 1855.38): C 58.26, H 6.52, N 6.04. Found: C 58.33, H 6.68, N 6.32.

**X-ray structure determination of 4, 5, 7, and 8.** Crystals of complexes **4**, **5**·C<sub>7</sub>H<sub>8</sub>, **7**, and **8**·2C<sub>7</sub>H<sub>8</sub> were grown as described in the Experimental Section, removed from the Schlenk flasks or ampules, and covered with a layer of a viscous perfluoropolyether (FomblinY). A suitable crystal was selected with the aid of a microscope, attached to a glass fiber, and immediately placed in the low temperature nitrogen stream of the diffractometer. The intensity data sets were collected on a Bruker-Nonius KappaCCD diffractometer equipped with an Oxford Cryostream 700 unit. The molybdenum K $\alpha$  radiation was used in all cases, graphite monochromated, and enhanced with a MIRACOL collimator. Crystallographic data for all the complexes are presented in the Supporting Information Available.

The structures were solved, using the WINGX package,<sup>28</sup> by direct methods (SHELXS-97) and refined by least-squares against F<sup>2</sup> (SHELXL-97).<sup>29</sup> Crystals of compounds **4**, **5** and **7** presented disorders, which were treated by using the PART tool and allowing free refinement of the occupancy factors with the FVAR command of the SHELXL-97 program. The crystal structure of compound **4** was studied with the *C2/m* and *C2* space groups, but only *C2/m* led to a sensible chemical model. These crystals showed disorder for the carbon atoms C(21)-C(26) of the pentamethylcyclopentadienyl group linked to Ti(2). The final values for the occupancy factors were 76 and 24% for each position. All non-hydrogen atoms were anisotropically refined, except carbon atoms C(26),

C(21)', C(22)', C(23)', C(24)', C(25)' and C(26)' for the disordered C<sub>5</sub>Me<sub>5</sub> group, which were refined isotropically. The hydrogen atoms were positioned geometrically and refined using a riding model, except for those of the imido groups, H(11)' and H(12)', which were located in the difference Fourier map and refined isotropically. Additionally the highest peak found in the difference Fourier map of 1.23 e·Å<sup>3</sup> were located close to C(26) of the disordered pentamethylcyclopentadienyl ligand (0.82 Å).

Complex **5** crystallized with one molecule of toluene, and presented disorder for the carbon atoms C(21)-C(30) of the pentamethylcyclopentadienyl ligand linked to Ti(2). After the described treatment, the occupancy factors were 75.9 and 24.1% for each disordered C<sub>5</sub>Me<sub>5</sub>. All non-hydrogen atoms were refined anisotropically, except C(22)', C(24)', and C(26)', which were refined isotropically. All the hydrogen atoms were positioned geometrically and refined using a riding model.

Crystals of **7** showed disorder for the atoms Si(1), C(3), C(6), C(7), Si(2), C(8), C(9), and C(10) of the trimethylsilyl groups. The final values for the occupancy factors were 52 and 48% for one SiMe<sub>3</sub> moiety, and 61 and 39% for the other. All non-hydrogen atoms were refined anisotropically, except C(6), C(10), C(3)', C(6)', C(7)', C(9)', and C(10)', which were refined isotropically. All the hydrogen atoms were positioned geometrically and refined using a riding model.

For compound **8** all non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms, except for the hydrogen atoms on N(2), N(6) and N(7) that were found in the Fourier map and refined freely. SIMU and DELU restrains were applied for all the carbon atoms. One of the two toluene molecules showed some disorder and DFIX and FLAT restrains were applied. Compound **8** was refined as a racemic twin using the TWIN and BASF instructions, the final value of the BASF parameter was 0.52723.



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**Supporting Information Available:** X-ray crystallographic files in CIF format for complexes **4**, **5**, **7**, and **8**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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