

# Monomeric Bis( $\eta^2$ -alkyne) Complexes of ( $\eta^1$ -Mesityl)copper(I) and ( $\eta^1$ -Mesityl)silver(I) Obtained from a Bis(alkynyl)titanocene; X-Ray Structure of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]\text{Cu}(\eta^1\text{-Mes})$ (Mes = $\text{C}_6\text{H}_2\text{Me}_3\text{-2,4,6}$ )

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Polynuclear mesitylcopper and mesitylsilver react with  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]$  **1** to afford the monomeric complexes  $[\mathbf{1}\cdot\text{Cu}(\eta^1\text{-Mes})]$  **2**, and  $[\mathbf{1}\cdot\text{Ag}(\eta^1\text{-Mes})]$  **3**, in which both alkyne moieties of the 3-titanopenta-1,4-diyne unit are  $\eta^2$ -coordinated to a MesCu(Ag) unit.

Organo-copper(I) and -silver(I) complexes, CuR and AgR, are generally encountered as polynuclear species which exist either as discrete aggregates or as polymers.<sup>1</sup> The aggregation state of organocoppers has a crucial effect on their reactivity as reagents in organic synthesis, and an understanding of this reactivity is hampered by the presence of complex equilibria between aggregated species. Complexes with a low nuclearity have been obtained by using either R groups with steric constraints or coordinating ligands,<sup>2</sup> while N, P, O, or S donors and alkynes have been used to stabilize cationic copper(I) and silver(I) monomers.<sup>3</sup> However, up to now little has been known about the nature of monomeric,  $\eta^1$ -bonded, organocopper(I) and organosilver(I) complexes.

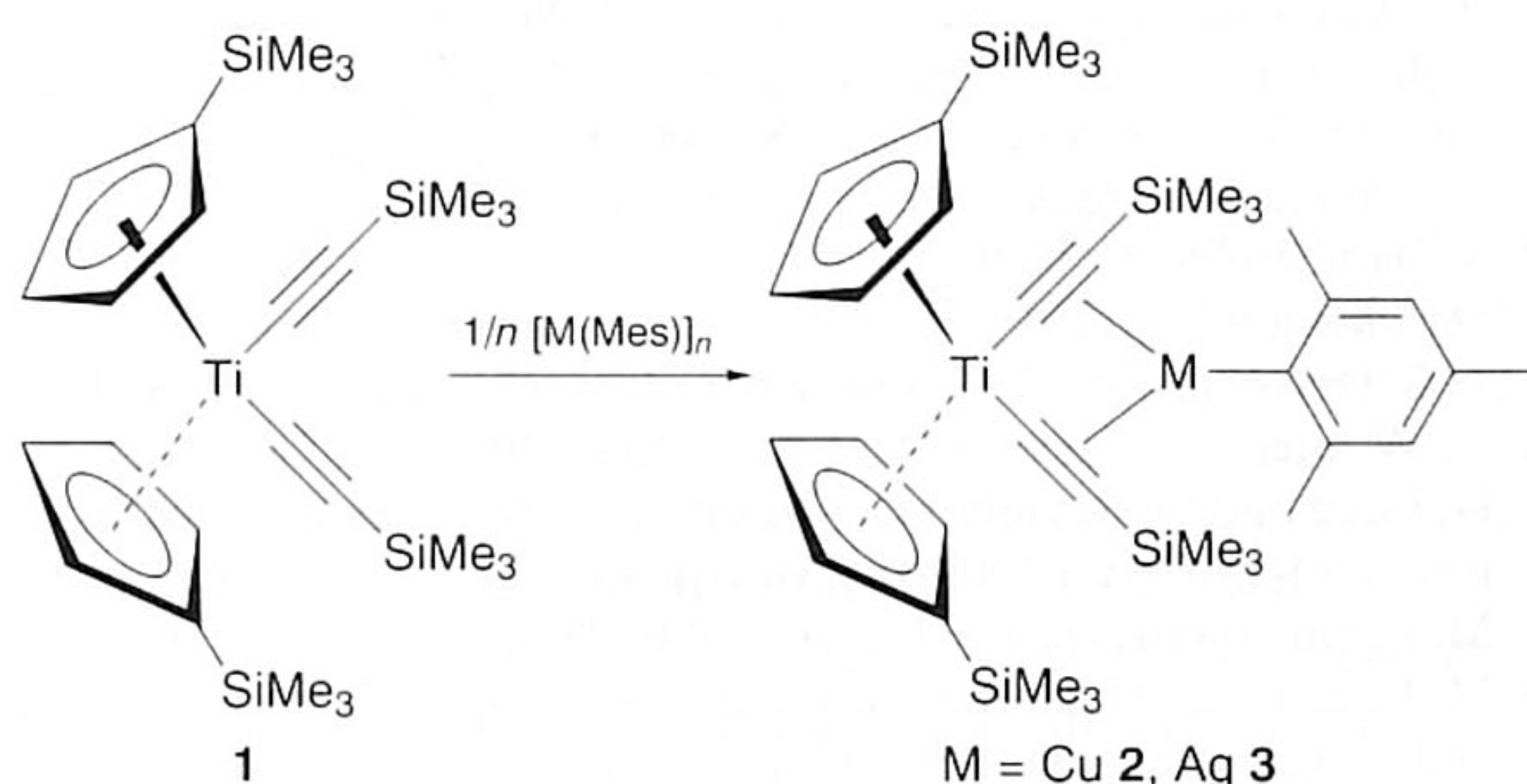
Here we report the first examples of monomeric bis( $\eta^2$ -alkyne)( $\eta^1$ -aryl)-copper and -silver complexes that result from the use of a correctly designed organometallic species containing two alkyne functions of the type Ti-C $\equiv$ C-SiMe<sub>3</sub>.

The reaction of the bis(alkynyl)titanocene  $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\text{C}\equiv\text{CSiMe}_3)_2]$  **1**<sup>4</sup> with an equimolar amount (based on Cu) of  $[\text{Cu}(\text{Mes})]_5$  in THF, Et<sub>2</sub>O or toluene at ambient temperature affords in high yield the corresponding monomeric copper complex  $[\mathbf{1}\cdot\text{Cu}(\text{Mes})]$  **2** [eqn. (1)].<sup>†</sup> The analogous silver complex  $[\mathbf{1}\cdot\text{Ag}(\text{Mes})]$  **3**<sup>5</sup> is obtained similarly from the reaction of **1** with an equimolar amount (based on Ag) of  $[\text{Ag}(\text{Mes})]_4$ .

bonded mesityl group and a chelate bonded bis(alkynyl)-titanocene **1**. Both structures contain a crystallographic two-fold rotation axis that runs through Ti(1), the Group 11 metal, and the *ipso* (C14), *para* (C17) and *para*-Me (C19) carbon atoms of the mesityl group.

Complexes **2** and **3** are the first examples of neutral arylcopper or arylsilver units complexed by a neutral bidentate bis(alkyne) ligand. The copper and silver atoms in **2** and **3** have a formal 16 electron count and this implies that the Ti...Cu and Ti...Ag distances [2.9418(5) and 3.104(7) Å] represent non-bonding situations.<sup>5,6</sup>

The structural data of complexes  $[\mathbf{1}\cdot\text{MR}]$  (M = Cu, Ag) provide an excellent possibility for evaluation of the nature of the alkyne to copper (silver) interaction since the structure of the free organometallic ligand, *i.e.* bis(alkynyl)titanocene **1**, is known. The alkyne C atoms (C1, C2, C1' and C2'), the copper (silver) atom and the mesityl C<sub>*ipso*</sub> atom (C14) are all in one plane and this is consistent with  $\eta^2$ -alkyne to Group 11 metal bonding. Important observations with respect to the latter interaction are: (a) a C $\equiv$ C bond lengthening from 1.203(9) and 1.214(6) Å (the uncoordinated C $\equiv$ C bond lengths in **1**)<sup>7</sup> to 1.250(2) Å in **2** and 1.24(1) Å in **3**, and (b) bending of the Ti-C $\equiv$ C-Si units from the linear arrangement in the free ligand **1** (Ti-C-C 177° and C-C-Si 176.5°) to 163.7(1) and 155.5(2)°, respectively, in **2** and 166.6(6) and 162.9(7)°, respectively, in **3**.



Complexes **2** and **3** are orange to deep red crystalline solids which are soluble in most common organic solvents. Remarkably, solid arylcopper complex **2** and its silver analogue **3** do not decompose significantly on being exposed to air for several days; solutions of **3** are slightly photosensitive. Cryoscopic molecular mass determinations of **2** and **3** in C<sub>6</sub>H<sub>6</sub> show these complexes to be monomeric and the <sup>1</sup>H and <sup>13</sup>C NMR spectra of these species in C<sub>6</sub>D<sub>5</sub>CD<sub>3</sub> (temperature independent) are consistent with the schematic structure shown in Fig. 1.

The molecular structures of **2** (Fig. 1)<sup>‡</sup> and **3**<sup>‡</sup> in the solid state as determined by X-ray diffraction analysis show these complexes to be isostructural, monomeric species that contain a Group 11 metal which is trigonally coordinated by an  $\eta^1$ -

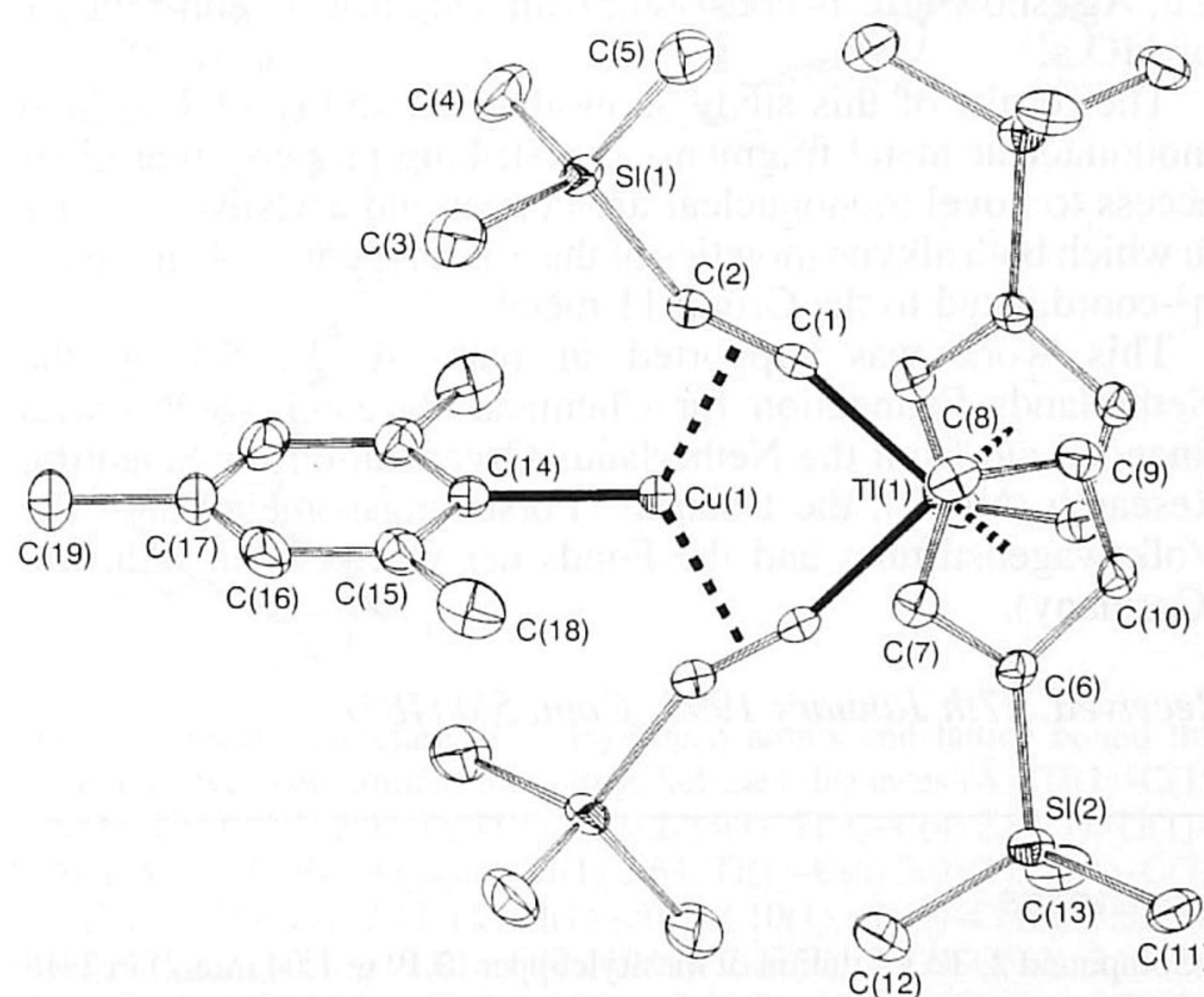


Fig. 1 ORTEP drawing (50% probability level) of  $[\mathbf{1}\cdot\text{Cu}(\text{Mes})]$  **2**. Selected distances (Å) and bond angles (°): Cu(1)-C(1) 2.064(2), Cu(1)-C(2) 2.082(2), Cu(1)-C(14) 1.947(2), Ti(1)-C(1) 2.078(2), C(1)-C(2) 1.250(2), Cu(1)-Ti(1) 2.9418(5); Ti(1)-C(1)-C(2) 163.7(1), C(1)-C(2)-Si(1) 155.5(2), C(1)-Ti(1)-C(1') 89.11(6).



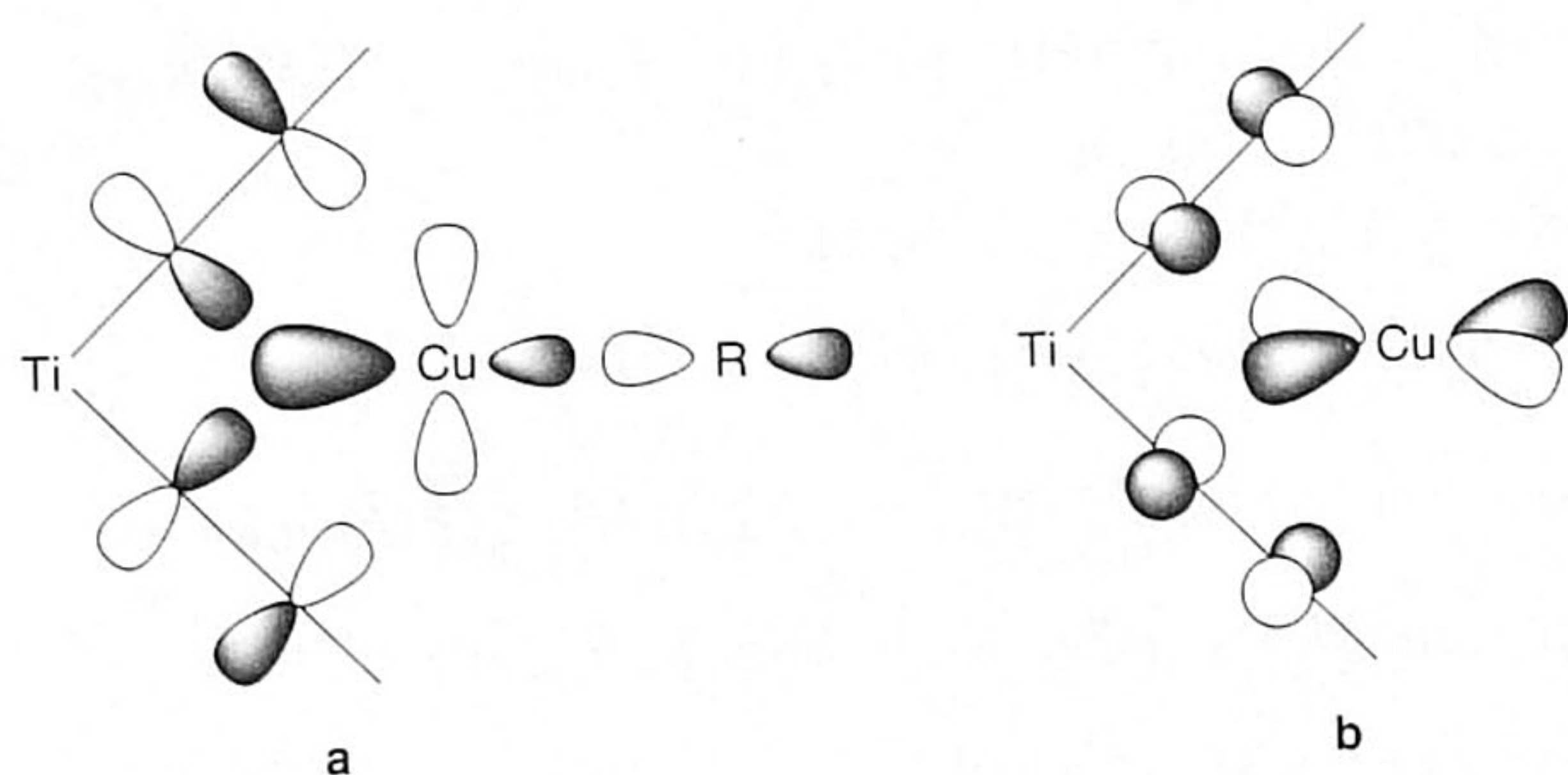


Fig. 2 Molecular orbitals for back-donation from copper to alkyne: **a** major contributing MO (in-plane), **b** minor contributing MO (out-of-plane)

The metal to  $\eta^2$ -alkyne distances and the metal to  $C_{ipso}$  (mesityl) distances in silver complex **3** are longer by 0.21 and 0.15 Å, respectively, than those in **2**, reflecting the difference in metal ion radii (Cu: 0.96; Ag: 1.26 Å). The two-electron two-centre ( $2e-2c$ ) metal- $C_{ipso}$ (mesityl) bond lengths [1.947(2) in **2** and 2.099(5) Å in **3**] fit perfectly in the ranges expected for this type of bond with  $Cu^I$  and  $Ag^I$  centres.<sup>§</sup>

In the  $^{13}C$  NMR spectrum of **3** there is coupling to  $^{107,109}Ag$  found on a number of signals including that of  $C_{ipso}$  mesityl at  $\delta$  168.3 with  $^1J_{^{107}Ag^{13}C}$  and  $^1J_{^{109}Ag^{13}C}$  of 142 and 164 Hz, respectively, and those of  $C_\alpha$  and  $C_\beta$  of the alkyne units, *i.e.* both alkyne carbon atoms are bonded to the silver centre.<sup>¶</sup> These data are the first  $^{107,109}Ag$  coupling constant values for an  $\eta^1$ , two-electron two-centre, silver-carbon(aryl) bond, and as expected they are larger (due to the higher degree of s-orbital participation in **3**) than those reported for the two-electron three-centre bond in  $[Ag_2Li_2(C_6H_4CH_2NMe_2)_2]_4$  (118.3 and 136.0 Hz, respectively) and  $[Ag_2Li_2(C_6H_5)_4]$  (115 and 132 Hz, respectively).<sup>§</sup>

Alkyne to copper (silver) bonding has been described as arising from two components, namely  $\sigma$ -donation of electron density from a filled  $\pi$ -orbital on the alkyne to a suitable empty orbital on Cu (Ag) and a component involving the back-donation of electron density from a filled d-orbital on the metal to an empty  $\pi^*$  orbital on the alkyne (Fig. 2). Preliminary (Extended Hückel) calculations<sup>9</sup> on bis( $\eta^2$ -alkyne)- $CuR$  and  $-AgR$  complexes indicate that the latter component is more important and its major contribution is to be found in the in-plane interaction. This means that back-donation should be influenced by the  $\sigma$ -donating capacity of R and preliminary spectroscopic results from a series of complexes  $[1-MR]$  ( $M = Cu, Ag$ ) show effects consistent with a significant contribution of MO **a**.<sup>§</sup>

The results of this study show that the ability of **1** to bind mononuclear metal fragments is a striking property that gives access to novel mononuclear arylcopper and arylsilver species in which both alkyne moieties of the 3-titanopenta-1,4-diyne are  $\eta^2$ -coordinated to the Group 11 metal.

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## Footnotes

† Compound **2**: To a solution of mesitylcopper (0.19 g; 1.04 mmol) in THF (15 ml) was added **1** (0.54 g; 1.04 mmol). After stirring for 0.5 h, the solvent was removed *in vacuo*. X-Ray suitable crystals are obtained from  $Et_2O$  at  $-20^\circ C$ . Yield: 0.61 g (84%) of **2**, mp  $124^\circ C$  (decomp.); IR(KBr)  $\nu/cm^{-1}$

1856 ( $C\equiv C$ );  $^1H$  NMR (300.13 MHz,  $C_6D_6$ )  $\delta$  0.11 (s, 18H, SiMe<sub>3</sub>), 0.30 (s, 18H, SiMe<sub>3</sub>), 2.36 (s, 3H, *p*-Me), 2.37 (s, 6H, *o*-Me), 5.17 (t, 4H, C<sub>5</sub>H<sub>4</sub>,  $J$  2 Hz), 5.82 (t, 4H, C<sub>5</sub>H<sub>4</sub>,  $J$  2 Hz), 6.99 (s, 2H, ArH);  $^{13}C$  NMR (75.47 MHz,  $C_6D_6$ )  $\delta$  0.2 (SiMe<sub>3</sub>), 0.6 (SiMe<sub>3</sub>), 21.4 (*p*-Me), 28.0 (*o*-Me), 110.7 (C<sub>5</sub>H<sub>4</sub>), 113.0 (C<sub>5</sub>H<sub>4</sub>), 116.7 (*ipso*-C<sub>5</sub>H<sub>4</sub>), 125.0 ( $C\equiv C-Si$ ), 126.3 (Mes-3), 133.6 (Mes-4), 145.2 (Mes-2), 201.8 (Ti- $C\equiv C$ ); *ipso* of Mes is not observed; FD-MS  $m/z$  698 ( $M^+$ , Calc. 698).

‡ Crystal data for **2**:  $C_{35}H_{55}CuSi_4Ti$ , red crystal (0.3 × 0.5 × 0.5 mm), orthorhombic, space group *Pbcn*, with  $a = 12.429(1)$ ,  $b = 19.877(1)$ ,  $c = 15.532(1)$  Å,  $V = 3837.2(4)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_c = 1.2109(1)$  g cm<sup>-3</sup>,  $\mu(Mo-K\alpha) = 9.0$  cm<sup>-1</sup>.

Crystal data for **3**:  $C_{35}H_{55}AgSi_4Ti$ , red crystal (0.25 × 0.25 × 0.25 mm), orthorhombic, space group *Pbcn*, with  $a = 12.47(3)$ ,  $b = 20.00(3)$ ,  $c = 15.53(3)$  Å,  $V = 3873(13)$  Å<sup>3</sup>,  $Z = 4$ ,  $d_c = 1.276(4)$  g cm<sup>-3</sup>,  $\mu(Mo-K\alpha) = 8.5$  cm<sup>-1</sup>.

3699 (**2**) and 3393 (**3**) unique reflections ( $1.9 < \theta < 26.48^\circ$  for **2**;  $1.02 < \theta < 25.00^\circ$  for **3**;  $\omega/2\theta$  scan;  $T = 150$  K) were measured on an Enraf-Nonius CAD-4T rotating anode diffractometer using graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Data were corrected for Lp effects and absorption (DIFABS). The structures were solved by Patterson (**2**: SHELXS86; **3**: DIRDIF92) techniques and refined by full-matrix least squares methods (SHELX76) to an  $R_1 = 0.026$ ,  $wR = 0.031$ ,  $S = 1.14$ ,  $w^{-1} = \sigma^2(F)$  for 3082 reflections with  $I > 2.5 \sigma(I)$  for **2** and to an  $R_1 = 0.055$ ,  $wR = 0.063$ ,  $S = 3.95$ ,  $w^{-1} = [\sigma^2(F) + 0.00085F^2]$  for 2068 reflections with  $I > 2.5 \sigma(I)$  for **3**. Hydrogen atoms were introduced on calculated positions and refined riding on their carrier atoms. All non-H atoms were refined with anisotropic thermal parameters. A final Fourier map showed no residual density outside  $-0.38$  and  $0.27$  e Å<sup>-3</sup> for **2** or outside  $-0.93$  and  $0.88$  e Å<sup>-3</sup> for **3** (near the  $\eta^5-C_5H_4SiMe_3$  ring). Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

§ Reported two-electron two-centre ( $2e-2c$ ) C-Cu bonds. For  $sp^3$ -carbon atoms:  $[(Ph_3P)_3CuMe]$  2.04(1) Å;<sup>2</sup>  $sp^2$ -carbon atoms:  $[MeC(CH_2PPh_2)_3CuPh]$  2.020(4) Å;<sup>2</sup>  $[Cu(C_6H_2Bu^t_3-2,4,6)(Me_2S)]$  1.916(3) Å;<sup>2</sup>  $sp$ -carbon atoms:  $[1-CuC\equiv CSiMe_3]$  1.898(3) Å.<sup>5</sup>

¶ Natural abundance  $^{107}Ag$  ( $I = 1/2$ ) 51.8%,  $^{109}Ag$  ( $I = 1/2$ ) 48.2%.

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