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Heterometallic Assemblies with Bridging Cyano Ligands

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The Au(I) cyanides $(Ph_3P)AuCN$ (**2**) and $Na[Au(CN)_2]$ (**5**) react with $\{[Ti](C{\equiv}CSiMe_3)_2\}Cu(NCMe)[BF_4]$ (**1**) or $\{[Ti](C{\equiv}CSiMe_3)_2\}CuOTf$ (**4**) ($[Ti] = (\eta^5\text{-}C_5H_4SiMe_3)Ti$) to give cationic heterotrimetallic $\{[Ti](C{\equiv}CSiMe_3)_2\}Cu[NCAu(PPh_3)][BF_4]$ (**3**) or pentanuclear $\{[Ti](C{\equiv}CSiMe_3)_2Cu\}_2[N,N'\text{-}\mu\text{-}Au(CN)_2][OTf]$ (**6**). In contrast, the reaction of $\{[Ti](C{\equiv}CSiMe_3)_2\}Ag[BF_4]$ (**7**) with **2** produces neutral $\{[Ti](C{\equiv}CSiMe_3)_2\}Ag[NCAu(PPh_3)][FBF_3]$ (**8**), while the reaction of $\{[Ti](C{\equiv}CSiMe_3)_2\}CuCN$ (**9**) with $Cr(CO)_5(THF)$ affords $\{[Ti](C{\equiv}CSiMe_3)_2\}CuCN{\rightarrow}[Cr(CO)_5]$ (**11**).

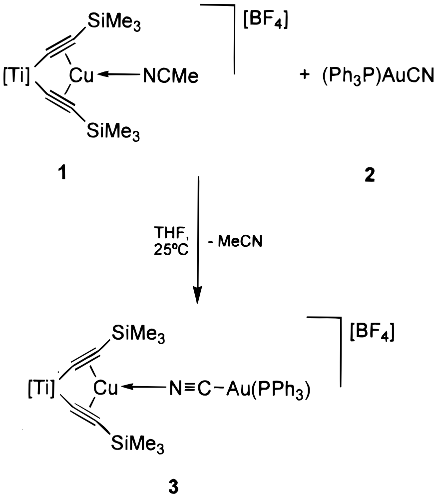
Introduction

Complexes of the general type $\{[Ti](C{\equiv}CR)_2\}MX$ (Chart 1, type **A** molecule;[1] M = Cu, Ag; X = OTf, BF_4, ClO_4, ...) react with Lewis bases L (L = PhCN, MeCN, THF, ...) to produce either cationic type **B**[2] or neutral type **C** molecules.[3] In the formation of type **B** molecules the trigonal-planar environment at the Cu(I) center as well as its 16-electron count is maintained when compared to **A**.[2] However, in the reaction of the isostructural silver complexes with L the coordination sphere of the metal center expands to adopt an 18-valence-electron count, with silver in a tetrahedral configuration.[3]

This reaction behavior with organic N-donor ligands prompted us to extend our studies toward transition-metal (TM) complexes incorporating a donor-active site, e.g., a cyanide ligand, since it is well-established that TM cyanide complexes can possess magnetically and/or electronically interesting properties.[4] In this context, we here describe the introduction of group 11 cyanide complexes as linking components for the preparation of oligometallic cyano-bridged TM complexes.

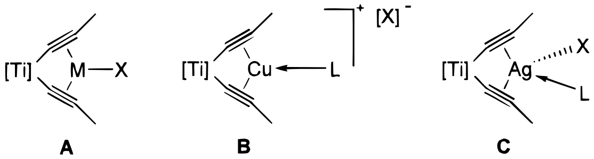
Results and Discussion

Treatment of $\{[Ti](C{\equiv}CSiMe_3)_2\}Cu(NCMe)[BF_4]$ (**1**)[3] with 1 equiv of $(Ph_3P)AuCN$ (**2**)[4a] affords heterometallic cationic $\{[Ti](C{\equiv}CSiMe_3)_2\}Cu[NCAu(PPh_3)][BF_4]$ (**3**; eq 1).

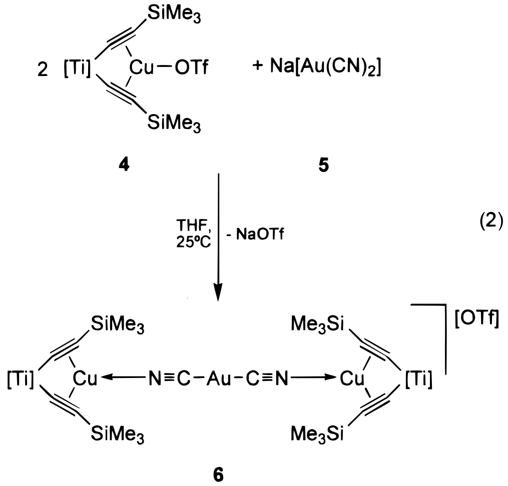


(1)

Chart 1



A pentametallic cationic complex, $\{[Ti](C{\equiv}CSiMe_3)_2Cu\}_2[N,N'\text{-}\mu\text{-}Au(CN)_2][OTf]$ (**6**), can be obtained when $\{[Ti](C{\equiv}CSiMe_3)_2\}CuOTf$ (**4**)[6] is reacted with $Na[Au(CN)_2]$ (**5**)[5a] in a 2:1 ratio (eq 2).



(2)

A common feature in both reactions is the replacement of the Cu(I) η^1-bonded ligands (**1**, NCMe; **4**, OTf) by the cyanide moieties, leading to the formation of linear Ti−Cu←N≡C−Au arrays. Within these building blocks, Cu(I) maintains its trigonal-planar environment.

To synthesize neutral oligometallic TM complexes, rather than cationic ones, stoichiometric amounts of $\{[Ti](C{\equiv}CSiMe_3)_2\}Ag[BF_4]$ (**7**)[3] were reacted with $(Ph_3P)AuCN$ (**2**)[4a] to yield $\{[Ti](C{\equiv}CSiMe_3)_2\}Ag\,[NCAu(PPh_3)][FBF_3]$ (**8**; eq 3).

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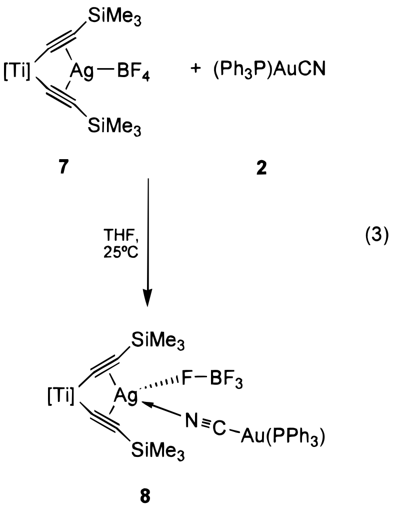
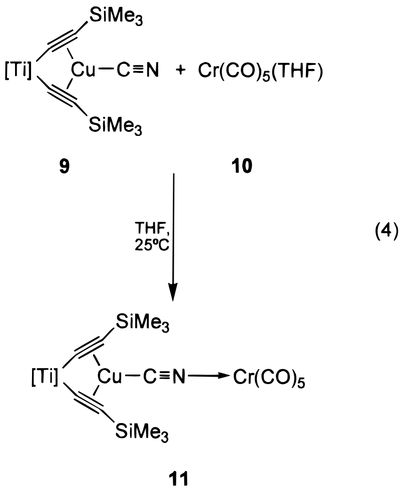
10.1021/om9905299 CCC: $19.00



(3)



(4)

In contrast to **3** and **6**, compound **8** displays a nonlinear Ti−Ag←N≡C−Au sequence with the Ag(I) ion in a tetrahedral environment. A similar structural motif has been demonstrated by $\{[Ti](C{\equiv}CSiMe_3)_2\}Ag(THF)[FBF_3]$.[3] The retention of the coordinated fluoroborate group is shown by IR studies, displaying three ν_{BF} stretching modes, characteristic for an η^1-coordinated $F{-}BF_3$ unit (IR: 720−1170 cm^{-1}).[8]

This kind of different coordination behavior of Cu(I) versus Ag(I) toward Lewis bases can be explained by the different sizes of the corresponding group 11 metal ions (Cu, 77 pm; Ag, 115 pm).[9]

A modified approach to structural type **C** assemblies is given by the reaction of $\{[Ti](C{\equiv}CSiMe_3)_2\}CuCN$ (**9**)[10] with $\{[Ti](C{\equiv}CSiMe_3)_2\}Ag[BF_4]$ (**7**).[3] Surprisingly, no reaction between these two components seems to take place, not even under the various reaction conditions applied. This is probably due to the fact that the addition of the Cu(I) cyanide **9** is hindered either by the bulkiness of the bis(alkynyl)titanocene groups or by the different coordination mode imposed by Ag(I), i.e., the bent Ti−Ag←N≡C−Cu unit. Nevertheless, compound **9** reacts with $Cr(CO)_5(THF)$ (**10**)[11] to form heterotrinuclear $\{[Ti](C{\equiv}CSiMe_3)_2\}CuCN{\rightarrow}[Cr(CO)_5]$ (**11**; eq 4).

However, due to its high instability **11** could only be characterized spectroscopically. While ^{1}H NMR studies gave no characteristic changes with respect to the chemical shifts of the organic groups present, when changing from **9** to **11**, IR and EI mass spectroscopy (MS) were shown to be suitable methods to prove the formation of heterometallic **11**. In the IR spectrum, four distinct $\nu_{C\equiv O}$ absorption bands are found in the region 1870−2080 cm^{-1}, which is typical for $M(CO)_5$ fragments (M = Cr, Mo, W).[12] The CN stretching frequency appears at 2132 cm^{-1}.[13] Representative in the EI-MS is the appearance of $[M]^+$, $[M - 5\ CO]^+$, $[M - Cr(CO)_5]^+$, and $(C_5H_4SiMe_3)_2Ti^+$ with $[C_3H_9Si]^+$ as the base peak.

In contrast, all other complexes could be fully characterized by elemental analysis and spectroscopic studies (IR, ^{1}H NMR, $^{13}C\{^1H\}$ NMR, $^{31}P\{^1H\}$ NMR).

The IR spectra of **3**, **6**, and **8** display $\nu_{C\equiv C}$ absorption bands at 1914 (**6**), 1921 (**3**), and 1952 cm^{-1} (**8**), respectively, which are typical values for copper- and silver-containing titanium tweezer complexes of this sort.[1] For the last two, these frequencies remain nearly unchanged from the starting materials **1** and **7**.[2,3] The ν_{CN} absorption is found between 2170 and 2190 cm^{-1}, a representative region for N-coordinated group-11 cyanide species.[13]

As already outlined for **11**, the ^{1}H NMR spectra of **3**, **6**, and **8** also do not exhibit characteristic changes as compared to those of the corresponding starting materials: characteristic is a AA′XX′ pattern for the protons of the cyclopentadienyl ligands and two distinct resonance signals for the cyclopentadienyl- as well as alkynyl-bound $SiMe_3$ groups. In the case of **3** and **8**, a multiplet between 7.2 and 7.7 ppm for the phenyl protons of the Ph_3P group is found.

Likewise, $^{13}C\{^1H\}$ NMR studies reveal the characteristic resonance signals for the bridging CN groups at 102.7 (**8**), 163.8 (**3**), and 164.5 ppm (**6**). This difference in the chemical shifts can best be explained by the altered coordination environment around the group 11 metal atom (**3** and **6**, trigonal-planar; **8**, tetrahedral). All other $^{13}C\{^1H\}$ NMR resonances are typical for these types of molecules.[1]

Furthermore, $^{31}P\{^1H\}$ NMR spectroscopic studies carried out on complexes **3** and **8** show that the ^{31}P

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resonance signals appear virtually unchanged compared to that of $(Ph_3P)AuCN$ (**2**).[4a]

Experimental Section

General Methods. All reactions were carried out under an atmosphere of nitrogen using standard Schlenk techniques. THF and Et_2O were purified by distillation from sodium/benzophenone ketyl; *n*-pentane was purified by distillation from calcium hydride. Infrared spectra were obtained with a Perkin-Elmer FT-IR Spectrum 1000 spectrometer. ^1H NMR were recorded on a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier transform mode; $^{13}C\{^1H\}$ NMR spectra were recorded at 62.895 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the reference signal ($CDCl_3$: ^1H NMR δ 7.27; $^{13}C\{^1H\}$ NMR δ 77.0). $^{31}P\{^1H\}$ NMR were recorded at 101.255 MHz in $CDCl_3$ with $P(OMe)_3$ as external standard (δ 139.0, relative to 85% H_3PO_4). Melting points were determined on a Gallenkamp MFB 595 010 M melting point apparatus. Microanalyses were performed by the Department of Organic Chemistry, Technical University of Chemnitz.

General Remarks. $\{[Ti](C\equiv CSiMe_3)_2\}Cu(NCMe)[BF_4]$ (**1**),[2] $\{[Ti](C\equiv CSiMe_3)_2\}CuOTf$ (**4**),[6] $\{[Ti](C\equiv CSiMe_3)_2\}AgBF_4$ (**7**),[3] $\{[Ti](C\equiv CSiMe_3)_2\}CuCN$ (**9**),[10] $Na[Au(CN)_2]$ (**5**),[7] $(Ph_3P)AuCN$ (**2**),[5] and $Cr(CO)_5(THF)$ (**10**)[11] were prepared according to published procedures. All other chemicals were purchased by commercial providers and were used as received.

Synthesis of $\{[Ti](C\equiv CSiMe_3)_2\}Cu[NCAu(PPh_3)][BF_4]$ (3). To 100 mg of **1** (0.14 mmol) in 20 mL of THF was added 70 mg of $(Ph_3P)AuCN$ (**2**; 0.14 mmol) at 25 °C in one portion. After the mixture was stirred for 3 h, all volatiles were removed in vacuo and the residue was extracted with Et_2O (5 × 10 mL) and then with CH_2Cl_2 (3 × 10 mL). Evaporation of the combined CH_2Cl_2 extracts in vacuo gave **3** (140 mg, 0.12 mmol; 85% yield based on **1**) as an orange solid.

Mp (°C): 135. IR (KBr; cm^{-1}): 2186 ($\nu_{C\equiv N}$), 1921 ($\nu_{C\equiv C}$). ^1H NMR ($CDCl_3$; δ): 0.21 (s, 18 H, Si*Me*$_3$), 0.34 (s, 18 H, Si*Me*$_3$), 6.19 (pt, J_{HH} = 2.1 Hz, 4 H, C_5H_4), 6.27 (pt, J_{HH} = 2.1 Hz, 4 H, C_5H_4), 7.5−7.7 (m, 15 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 0.0 (Si*Me*$_3$), 0.4 (Si*Me*$_3$), 115.5 (*CH*/C_5H_4), 118.3 (*CH*/C_5H_4), 125.6 (^{i}**C**/C_5H_4), 129.8 (^{i}**C**/C_6H_5), 130.1 (*CH*/C_6H_5), 132.9 (*CH*/C_6H_5), 134.1 (*CH*/C_6H_5), 135.7 (TiC≡*C*), 159.7 (Ti*C*≡C), 163.8 (*C*N). $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ): 40.4 (PPh_3). Anal. Calcd for $C_{45}H_{67}AuBCuF_4NPSi_4Ti$ (1152.55): C, 46.90; H, 5.16, N, 1.22; Si, 9.75. Found: C, 46.38; H, 5.49; N, 1.41; Si, 9.98.

Synthesis of $\{[Ti](C\equiv CSiMe_3)_2Cu\}_2[N,N'\text{-}\mu\text{-}Au(CN)_2][OTf]$ (6). To 110 mg of **4** (0.15 mmol) dissolved in 30 mL of THF was added 20 mg of $Na[Au(CN)_2]$ (**5**; 0.07 mmol) at 25 °C in one portion. The reaction mixture was stirred for 6 h, whereupon a yellow precipitate formed. Then, all volatiles were removed in vacuo and, subsequently, the residue was extracted with Et_2O (2 × 10 mL) and THF (2 × 5 mL) and then with CH_2Cl_2 (3 × 10 mL). The combined CH_2Cl_2 extracts were concentrated to 5 mL. Then 20 mL of *n*-pentane was added and the supernatant solution was decanted from the yellow solid. Yellow **6** was dried in vacuo (yield: 80 mg, 0.05 mmol; 70% yield based on **5**).

Mp (°C): 105 (dec). IR (KBr; cm^{-1}): 2180 ($\nu_{C\equiv N}$), 1914 ($\nu_{C\equiv C}$). ^1H NMR ($CDCl_3$; δ): 0.20 (s, 18 H, Si*Me*$_3$), 0.31 (s, 18 H, Si*Me*$_3$), 6.10 (pt, J_{HH} = 1.6 Hz, 4 H, C_5H_4), 6.20 (pt, J_{HH} = 1.6 Hz, 4 H, C_5H_4). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): −0.3 (Si*Me*$_3$), 0.2 (Si*Me*$_3$), 114.8 (*CH*/C_5H_4), 117.6 (*CH*/C_5H_4), 124.7 (^{i}*C*/C_5H_4), 135.2 (TiC≡*C*), 157.8 (Ti*C*≡C), 164.5 (*C*N). FAB-MS (*m/z* (relative intensity)): 1409 (40) [M − OTf]$^+$, 578 (100) $[C_{26}H_{44}CuSi_4Ti]^+$, 322 (80) $[C_{16}H_{26}Si_2Ti]^+$. Anal. Calcd for $C_{55}H_{88}AuCu_2F_3N_2O_3SSi_8Ti$ (1558.87): C, 42.38; H, 5.69; N, 1.80. Found: C, 42.41; H, 5.79; N, 2.09.

Synthesis of $\{[Ti](C\equiv CSiMe_3)_2\}Ag[NCAu(PPh_3)][BF_4]$ (8). Reaction conditions and workup were identical with those described for **3**. Experimental details: **7** (80 mg, 0.11 mmol), **2** (55 mg, 0.11 mmol), THF (30 mL). Yield: 105 mg, 0.08 mmol; 80% based on **7**.

Mp (°C): 126 (dec). IR (KBr; cm^{-1}): 2171 ($\nu_{C\equiv N}$), 1952 ($\nu_{C\equiv C}$). ^1H NMR ($CDCl_3$; δ): 0.24 (s, 18 H, Si*Me*$_3$), 0.31 (s, 18 H, Si*Me*$_3$), 6.37 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 6.40 (pt, J_{HH} = 1.8 Hz, 4 H, C_5H_4), 7.2−7.7 (m, 15 H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$; δ): 0.0 (Si*Me*$_3$), 0.0 (Si*Me*$_3$), 102.7 (CN), 116.8 (*CH*/C_5H_4), 119.9 (*CH*/C_5H_4), 127.0 (^{i}*C*/C_5H_4), 128.4 (TiC≡*C*), 129.6 (d, J_{CP} = 7.0 Hz, *CH*/C_6H_5), 132.3 (*CH*/C_6H_5), 134.2 (d, J_{CP} = 13.0 Hz, *CH*/C_6H_5), 132.2 (d, J_{CP} = 62.0 Hz, ^{i}*C*/C_6H_5), 149.7 (Ti*C*≡C). $^{31}P\{^1H\}$ NMR ($CDCl_3$; δ): 40.8 (PPh_3). Anal. Calcd for $C_{45}H_{59}AgAuBF_4NPSi_4Ti$ (1196.88): C, 45.16; H, 4.97; N, 1.17; Si, 9.39. Found: C, 45.25; H, 4.87; N, 1.22; Si, 9.43.

Synthesis of $\{[Ti](C\equiv CSiMe_3)_2\}CuCN\rightarrow[Cr(CO)_5]$ (11). At 0 °C, a solution of 50 mg of $Cr(CO)_5(THF)$ (**10**; 0.17 mmol) in 30 mL of THF was added to a solution of **9** (100 mg, 0.17 mmol) in 20 mL of THF. After the mixture was stirred for 5 h, all volatiles were removed in vacuo. The brown residue was extracted with a 2:1 Et_2O/THF mixture (2 × 10 mL) and then with CH_2Cl_2 (3 × 10 mL). The combined CH_2Cl_2 extracts were concentrated to 5 mL, and then Et_2O (20 mL) was added. The supernatant solution was decanted, and the residue was dried in vacuo to yield **11** as a brown solid (70 mg, 0.09 mmol, 50% based on **9**).

Mp (°C): dec. IR (KBr; cm^{-1}): 2132 ($\nu_{C\equiv N}$), 2057 (w), 1973 (sh), 1926 (s), 1881 (m) (ν_{CO}). ^1H NMR ($CDCl_3$; δ): 0.24 (s, 18 H, Si*Me*$_3$), 0.40 (s, 18 H, Si*Me*$_3$), 5.83 (pt, J_{HH} = 2.1 Hz, 4 H, C_5H_4), 6.07 (pt, J_{HH} = 2.1 Hz, 4 H, C_5H_4). EI-MS (*m/z* (relative intensity)): 797 (5) [M]$^+$, 657 (35) [M − 5 CO]$^+$, 482 (30) $[C_{21}H_{35}CuSi_3Ti]^+$, 322 (80) $[C_{16}H_{26}Si_2Ti]^+$, 73 (100) $[C_3H_9Si]^+$. Anal. Calcd for $C_{32}H_{44}CrCuNO_5Si_4Ti$ (797.05): C, 48.18; H, 5.56; Si, 14.04. Because of the high instability of **11**, a $^{13}C\{^1H\}$ NMR measurement and satisfactory elemental analysis could not be obtained.

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