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A cross-shaped Ag_5Ti_4 molecule based on a $[Ag(C\equiv N)_4]^{3-}$ core

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$K_3[Ag(C\equiv N)_4]$ (2) reacts with $\{[Ti](C\equiv CR)_2\}AgOClO_3$ {R = $SiMe_3$, 1a; R = Ph, 1b; [Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$} in a 1:4 molar ratio to produce the nonametallic Ag_5Ti_4 species $[Ag(C\equiv N\rightarrow Ag\{(RC\equiv C)_2[Ti]\})_4](ClO_4)$ (R = $SiMe_3$, 3a; R = Ph, 3b) in which four heterobimetallic titanium(IV)–silver(I) tweezer units, $[\{[Ti](C\equiv CR)_2\}Ag]^+$, are bridged by a $[Ag(C\equiv N)_4]^{3-}$ core; the reaction chemistry of 3 is reported.

Recently, oligonuclear cyanide bridged transition metal complexes have attracted much attention, since they possess interesting chemical as well as physical properties.[1,2]

In this context, we here describe a straightforward method for the preparation of, *e.g.* the cross-shaped structured Ag_5Ti_4 species $[Ag(C\equiv N\rightarrow Ag\{(RC\equiv C)_2[Ti]\})_4](ClO_4)$ by introduction of a group-11 metal cyanide core, $[Ag(C\equiv N)_4]^{3-}$, as linking component for heterobimetallic early–late organometallic building blocks, *e.g.* $[\{[Ti](C\equiv CR)_2\}Ag]^+$.

Treatment of orange $\{[Ti](C\equiv CR)_2\}AgOClO_3$ {R = $SiMe_3$, **1a**;[3] R = Ph, **1b**;[4] [Ti] = $(\eta^5\text{-}C_5H_4SiMe_3)_2Ti$} with $K_3[Ag(C\equiv N)_4]$[5] in a 4:1 molar ratio in tetrahydrofuran as solvent affords nonametallic orange-brown (**3a**) or red (**3b**) $[Ag(C\equiv N\rightarrow Ag\{(RC\equiv C)_2[Ti]\})_4](ClO_4)$ (R = $SiMe_3$, **3a**; R = Ph, **3b**) in excellent yields (Scheme 1).†

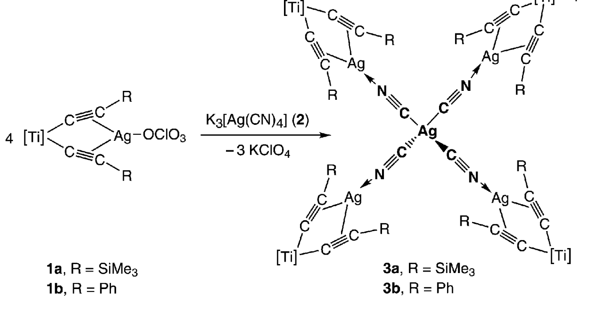
The most striking feature of **3a** and **3b** is the bridging cyano–argentate core $[Ag(C\equiv N)_4]^{3-}$, which links the four heterobimetallic early–late transition metal units $[\{[Ti](C\equiv CR)_2\}Ag]^+$, giving rise to the formation of the novel nonametallic Ag_5Ti_4 species **3a** or **3b**, respectively.

In **3** each cyano ligand of the $[Ag(C\equiv N)_4]^{3-}$ core is datively bonded to the silver(I) center of the respective end-grafted titanium–silver tweezer fragment $[\{[Ti](C\equiv CR)_2\}Ag]^+$. While, the core silver(I) center possesses a tetrahedral environment, the silver atoms of the corresponding tweezer moieties are trigonal-planar coordinated.[6]

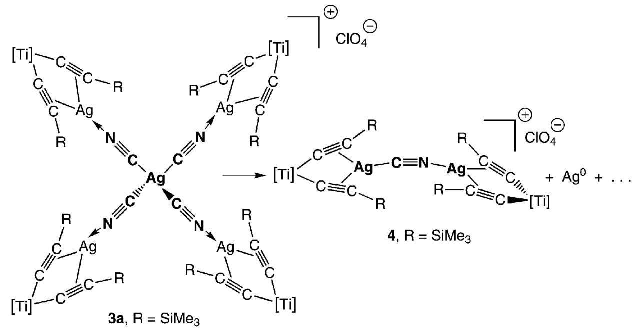
Although $[Fe(C\equiv N)_6]^{4-}$ can successfully be used for the preparation of, *e.g.* heptametallic cationic $\{Fe[C\equiv N\rightarrow Cu(tpa)]_6\}^{8+}$ [tpa = tris(2-pyridylmethyl)amine],[7] surprisingly no reaction seems to take place when $K_4[Fe(C\equiv N)_6]$ is reacted with **1a** or **1b**, even though various reaction conditions were applied.

Complexes **3a** and **3b** are readily soluble in polar organic solvents, such as acetone and tetrahydrofuran.

However, **3a** and **3b** decompose, even in the dark, in solution within several days. Besides the formation of elemental silver, the tetranuclear Ag_2Ti_2 complex **4** along with other undefined products is produced (Scheme 2).



Scheme 1



Scheme 2

A further possibility for the preparation of **4** is *via* reacting equimolar amounts of $\{[Ti](C\equiv CSiMe_3)_2\}AgOClO_3$ **1a** and $\{[Ti](C\equiv CSiMe_3)_2\}AgC\equiv N$ **6**.[4] In this reaction the cyano moiety in the latter molecule replaces the $OClO_3$ group in **1a**, thus yielding **4**.[4]

Tetranuclear **4** features a bent Ag–C≡N→Ag array as was demonstrated by single X-ray structure analysis (Fig. 1).‡

The molecular structure of **4** in the solid state shows that each of the two silver(I) centers possesses a trigonal-planar surrounding, caused by two η^2-coordinated alkynyl moieties [Ag(1): Ti(1)–C(1)–C(2)–Si(1), Ti(1)–C(6)–C(7)–Si(2); Ag(2): Ti(2)–C(27)–C(28)–Si(5); Ti(2)–C(32)–C(33)–Si(6)] and the μ-bridging C≡N unit C(53)–N(1) (Fig. 1). A *cis*-bending of the central Ag(1)–N(1)–C(53)–Ag(2) assembly is observed [Ag(1)–N(1)–

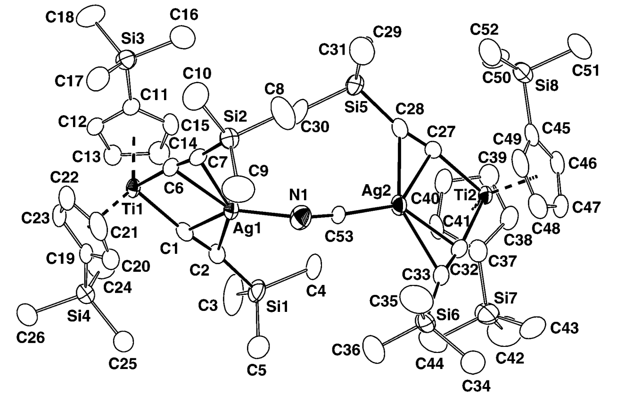


Fig. 1 ZORTEP drawing (50% probability level) of **4**. Selected interatomic bond distances (Å) and angles (°): Ti(1)···Ag(1) 3.1585(10), Ti(2)···Ag(2) 3.1705(9), Ag(1)–N(1) 2.152(5), Ag(1)–C(1) 2.279(5), Ag(1)–C(2) 2.445(5), Ag(1)–C(6) 2.313(5), Ag(1)–C(7) 2.442(5), Ag(2)–C(53) 2.106(5), Ag(2)–C(27) 2.290(5), Ag(2)–C(28) 2.443(5), Ag(2)–C(32) 2.309(5), Ag(2)–C(33) 2.434(5), Ti(1)–C(1) 2.133(5), Ti(1)–C(6) 2.112(5), Ti(2)–C(27) 2.135(5), Ti(2)–C(32) 2.124(5), C(1)–C(2) 1.216(6), C(6)–C(7) 1.248(6), C(27)–C(28) 1.223(7), C(32)–C(33) 1.236(6); Ag(1)–N(1)–C(53) 156.3(4), Ag(2)–C(53)–N(1) 158.5(5), C(1)–Ti(1)–C(6) 93.14(18), C(27)–Ti(2)–C(32) 92.85(18), Ti(1)–C(1)–C(2) 173.6(4), Ti(1)–C(6)–C(7) 171.3(4), Ti(2)–C(27)–C(28) 171.9(4), Ti(2)–C(32)–C(33) 171.2(4), C(1)–C(2)–Si(1) 164.9(4), C(6)–C(7)–Si(2) 169.5(4), C(27)–C(28)–Si(5) 163.3(5), C(32)–C(33)–Si(6) 167.4(5).

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C(53) 156.3(4)°, Ag(2)–C(53)–N(1) 158.5(5)°; Fig. 1]. The planes, comprised of the atoms Ti(1), C(1), C(2), Si(1), C(6), C(7), Si(2) and Ag(1) (rms deviation of fitted atoms 0.02 Å) as well as Ti(2), C(27), C(28), Si(5), C(32), C(33), Si(6) and Ag(2) (rms deviation of fitted atoms 0.04 Å), respectively, are at 87.3°, almost perpendicularly orientated to each other.

The structural features of the organometallic π-tweezer part $\{[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2\}\mathrm{Ag}$ are in accordance with this type of molecule: (i) the lengthening of the C≡C triple bonds, (ii) *trans*-bending of the Ti–C≡C–Si units and (iii) decreasing of the bite angle $_{\mathrm{C\equiv C}}\mathrm{C{-}Ti{-}C}_{\mathrm{C\equiv C}}$, as a result of the η^2-coordination of both C≡C triple bonds of the $[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2$ moieties to the corresponding silver centers.[6]

IR spectroscopy is a suitable method to prove the formation of **3a** and **3b**. While, in the starting material $\mathrm{K_3[Ag(C{\equiv}N)_4]}$ **2**, the $\nu_{\mathrm{C\equiv N}}$ frequency is found at 2097 cm^{-1}, it is shifted to 2152 cm^{-1} in **3a** and **3b**. This behaviour is common for cyanide complexes in which the C≡N moiety bridges two transition metal atoms.[8,9b] The counter-ion $\mathrm{ClO_4^-}$ in **3a** and **3b** is non-coordinated, since only one absorption band is found for the $\nu_{\mathrm{Cl{-}O}}$ stretching vibrations at 1097 cm^{-1} (**3a**) or 1100 cm^{-1} (**3b**) which differs from the starting materials **1a** and **1b** in which the perchlorate entities $\mathrm{OClO_3}$ are σ-bonded *via* the formation of a Ag–O bond to the corresponding silver(I) center, giving rise to two (**1a**: 1122, 1032 cm^{-1})[4] or three (**1b**: 1120, 1107, 1067 cm^{-1})[4] bands.[9]

$^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR studies on **3a** and **3b** show only minor changes with respect to the chemical shifts of **1a** and **1b**, however, ^{1}H NMR measurements reveal conspicious differences for the protons of the cyclopentadienyl ligands. While **1a** and **1b** display the characteristic AA′XX′ pattern with two pseudo-triplets at δ 6.38 and 6.68 for **1a**[3,4] or δ 6.49 and 6.63 for **1b**,[4] in **3b** two singlets at δ 6.77 and 6.87 and in **3a** only one singlet at δ 6.56 are observed, probably due to the fact that dynamic processes are involved. However, variable temperature ^{1}H NMR measurements could not be carried out, since **3a** and **3b** start to precipitate on cooling during the measurements.

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Notes and references

† *Experimental details*: as an example, the synthesis of **3a** is presented: to a tetrahydrofuran solution (80 mL) containing 500 mg (0.69 mmol) of $\{[\mathrm{Ti}](\mathrm{C{\equiv}CSiMe_3})_2\}\mathrm{AgOClO_3}$ **1a**,[3] 57 mg (0.17 mmol) of $\mathrm{K_3[Ag(C{\equiv}N)_4]}$[5] was added in one portion at 25 °C. The reaction mixture was stirred in the dark for 8 h. After filtration through a pad of Celite all volatiles were removed *in vacuo* (oil-pump) and the orange–brown residue washed twice with 20 mL of *n*-pentane (yield: 435 mg, 91%). **CAUTION**: Perchlorates of silver(I) can be explosive. Care has to be taken with all safety precautions followed.

Anal. Calc. for $\mathrm{C_{108}H_{176}Ag_5ClN_4O_4Si_{16}Ti_4}$ (2810.28): C, 46.16; H, 6.31; N, 1.99. Found: C, 45.78; H, 6.44; N, 1.69%. Mp: 147 °C (decomp.). IR (KBr, cm^{-1}): [$\nu_{\mathrm{C\equiv N}}$] 2152w; [$\nu_{\mathrm{C\equiv C}}$] 1949w; [$\nu_{\mathrm{Cl{-}O}}$] 1099s. ^{1}H NMR (d_6-acetone), 250.130 MHz, δ 0.29 (s, 72 H, SiMe$_3$), 0.37 (s, 72 H, SiMe$_3$), 6.56 (br s, 32 H, $\mathrm{C_5H_4}$). $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR (d_6-acetone, 62.902 MHz), δ 0.4 (SiMe$_3$), 1.1 (SiMe$_3$), 118.0 (CH/$\mathrm{C_5H_4}$), 120.6 (CH/$\mathrm{C_5H_4}$), 128.0 (^{i}C/$\mathrm{C_5H_4}$), 138.8 (C≡*C*Si), 156.3 (Ti*C*≡C); owing to the low solubility of **3a** in acetone the $^{13}\mathrm{C}\{^1\mathrm{H}\}$ NMR signals for the C≡N units could not be assigned.

‡ *Crystal data* for **4**: $\mathrm{C_{57}H_{96}Ag_2ClNO_5Si_8Ti_2}$, orange rods, 0.60 × 0.15 × 0.10 mm, $M_r = 1446.06$, triclinic, space group $P\bar{1}$, $a = 12.6070(2)$, $b = 16.9396(2)$, $c = 18.5179(3)$ Å, $V = 3695.49(9)$ Å^3, $\alpha = 99.1690(10)$, $\beta = 100.4600(10)$, $\gamma = 103.5460(10)$, $Z = 2$, $D_c = 1.300$ g cm^{-3}, $F(000) = 1504$, $T = 173$ K, Bruker Smart CCD, Mo-Kα radiation ($\lambda = 0.71073$ Å), $\mu = 0.936$ mm^{-1}, min., max. transmission 0.821695, 0.481409, ω-scans, $\theta_{\max} = 30.27°$, 18810 unique data, final $R1 = 0.0562$ and $wR2 = 0.0881$ [$I \geqslant 2\sigma(I)$], 709 refined parameters, structure solution by least square methods.

CCDC reference number 165761. See http://www.rsc.org/suppdata/cc/b1/b104841b/ for crystallographic data in CIF or other electronic format.

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