

Synthesis and Characterization of a Heterotetrametallic Fe-Au-Ti-Cu Transition Metal Complex

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Abstract

Heterotetrametallic $[[\{Ti(\mu-\sigma, \pi-C\equiv CSiMe_3)_2\}Cu-bipy-C\equiv C-AuPh_2PF_6]PF_6$ (**5**) ($[Ti] = (\eta^5-C_5H_4SiMe_3)_2Ti$; $Fc = (\eta^5-C_5H_4)(\eta^5-C_5H_5)Fe$; $bipy = 2,2'$ -bipyridine) is accessible by the consecutive reaction of $FcPPh_2-AuCl$ (**1**) with 5-ethynyl-2,2'-bipyridine (**2**) producing $FcPPh_2-Au-C\equiv C-bipy$ (**3**) which further reacts with $[[\{Ti(\mu-\sigma, \pi-C\equiv CSiMe_3)_2\}Cu(N\equiv CMe)]PF_6$ (**4**) to give the title complex in which four different transition metals are connected by carbon-rich π -conjugated organic units. The electrochemical behavior of **1**, **3** and **5** is reported as well.

Keywords: Heteromultimetallic; Transition metals; X-ray structure; Cyclic voltammetry.

Introduction

The synthesis of heteromultimetallic transition metal complexes in which different metals are linked by π -conjugated organic units is a challenge, because they may possess interesting chemical and physical properties. ^[1] Besides homobimetallic complexes, ^[2] also a number of heterobi- and -trimetallic species are known. ^[3] In contrast, only one example of a heterotetrametallic compound is reported in which the respective early and late transition metals are connected *via* carbon-rich organic bridging units. ^[4]

We describe here a straightforward synthesis procedure for the preparation of novel heterotetrametallic $[[\{Ti(\mu-\sigma, \pi-C\equiv CSiMe_3)_2\}Cu-bipy-C\equiv C-AuPh_2PF_6]PF_6$ ($[Ti] = (\eta^5-C_5H_4SiMe_3)_2Ti$; $Fc = (\eta^5-C_5H_4)(\eta^5-C_5H_5)Fe$; $bipy = 2,2'$ -bipyridine) by using $FcPPh_2Au-C\equiv Cbipy$ and $[[\{Ti(\mu-\sigma, \pi-C\equiv CSiMe_3)_2\}Cu(N\equiv CMe)]PF_6$ as molecular tinker toys.

Experimental Part

General Methods

All reactions were carried out in an atmosphere of purified nitrogen (O_2 traces: CuO catalyst, BASF AG, Ludwigshafen, Germany; H_2O traces: molecular sieve, 4 Å) using standard Schlenk techniques. Solvents were purified by distillation (n-hexane: calcium hydride; tetrahydrofuran: sodium / benzophenone ketyl). FT-IR spectra were recorded with a Perkin-Elmer FT-IR 1000 spectrometer (KBr pellets). NMR spectra were recorded with a Bruker Advance 250 spectrometer, operating in the Fourier

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transform mode. ^1H NMR spectra were recorded at 250.130 MHz (internal standard, relative to CDCl_3 , δ 7.26). $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were recorded at 62.902 MHz (internal standard, relative to CDCl_3 , δ 77.16). $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded at 101.249 MHz in CDCl_3 , external standard $\text{P}(\text{OMe})_3$, $\delta = 139.0$ ppm relative to H_3PO_4 , $\delta = 0.0$ ppm. Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane with the solvent signal as reference signal. Melting points were determined using analytically pure samples, sealed off in nitrogen-purged capillaries with a Gallenkamp MFB 595 010 melting point apparatus. Microanalyses were performed by the Institute of Organic Chemistry at the University of Heidelberg.

General remarks

Compounds **1**, ^[5] **2**, ^[6] **3**, ^[7] and **4** ^[8] were prepared as described elsewhere. All other chemicals were purchased from commercial suppliers and were used as received.

Synthesis of 5

Complex **4** (65 mg, 0.085 mmol) was dissolved in 40 mL of tetrahydrofuran and 65 mg (0.085 mmol) of **3** were added. Stirring was continued for 3 h at 25 °C. Afterward the reaction mixture was filtered through a pad of Celite. The solvent was reduced to 5 mL and the desired product was precipitated by addition of 20 mL of n-hexane and washed twice with 10 mL portions of n-hexane. The orange coloured solid was dried in *oil-pump vacuum*. Yield: 110 mg (0.075 mmol, 88 %).

Elemental analysis: Found: C, 48.70; H, 4.68; N, 2.18. $\text{C}_{60}\text{H}_{70}\text{AuCuF}_6\text{FeN}_2\text{P}_2\text{Si}_4\text{Ti}$ requires C, 48.97; H, 4.79; N, 1.90 %. Mp 172 °C (decomp.). IR: $\nu_{\text{max}}/\text{cm}^{-1}$ 2118w ($\text{AuC}\equiv\text{C}$), 1924w ($\text{TiC}\equiv\text{C}$), 841s (P-F). ^1H NMR δ_{H} (CDCl_3): -0.49 (18 H, s, SiMe_3), 0.27 (9 H, s, SiMe_3), 0.28 (9 H, s, SiMe_3), 4.21 (5H, s, C_5H_5), 4.39 (2 H, dpt, $J_{\text{HH}} = 1.9$ Hz, $J_{\text{HP}} = 2.5$ Hz, $^{\alpha}\text{H}/\text{C}_5\text{H}_4$, Fc), 4.58 (2 H, br s, $^{\beta}\text{H}/\text{C}_5\text{H}_4$, Fc), 6.26 – 6.30 (8 H, m, C_5H_4), 7.41 – 7.64 (10 H, m, Ph) 7.69 (1 H, dd, $^3J_{\text{H}_5'\text{H}_4'} = 7.8$ Hz, $^3J_{\text{H}_5'\text{H}_6'} = 5$ Hz, H_5'), 8.18 (1 H, dd, $^3J_{\text{H}_4\text{H}_3} = 8.5$ Hz, $^4J_{\text{H}_4\text{H}_6} = 2$ Hz, H_4), 8.22 (1 H, ddd, $^3J_{\text{H}_4'\text{H}_3'} = ^3J_{\text{H}_4'\text{H}_5'} = 7.8$ Hz, $^4J_{\text{H}_4'\text{H}_6'} = 1.8$ Hz, H_4'), 8.39 (1 H, d, $^3J_{\text{H}_3'\text{H}_4'} = 7.8$ Hz, H_3'), 8.50 (1 H, d, $^3J_{\text{H}_3\text{H}_4} = 8.5$ Hz, H_3), 8.53 (1 H, d, $^3J_{\text{H}_6'\text{H}_5'} = 4.4$ Hz, H_6'), 8.56 (1 H, d, $^4J_{\text{H}_6\text{H}_4} = 2$ Hz, H_6). $^{13}\text{C}\{^1\text{H}\}$ NMR δ_{C} (CDCl_3): -0.61 (SiMe_3), 0.17 (SiMe_3), 0.23 (SiMe_3), 69.2 (d, $^1J_{\text{CP}} = 68.2$ Hz, $^i\text{C}/\text{C}_5\text{H}_4$, Fc), 70.1 (C_5H_5 , Fc), 72.7 (d, $^3J_{\text{CP}} = 8.6$ Hz, $^{\beta}\text{C}/\text{C}_5\text{H}_4$, Fc), 73.7 (d, $^2J_{\text{CP}} = 13.8$ Hz, $^{\alpha}\text{C}/\text{C}_5\text{H}_4$, Fc), 98.7 ($\text{AuC}\equiv\text{C}$), 115.2 ($\text{CH}/\text{C}_5\text{H}_4$), 115.3 ($\text{CH}/\text{C}_5\text{H}_4$), 117.2 ($\text{CH}/\text{C}_5\text{H}_4$), 117.3 ($\text{CH}/\text{C}_5\text{H}_4$), 122.0 (bipy), 122.9 (bipy), 122.9 ($^i\text{C}/\text{C}_5\text{H}_4$), 123.3 ($^i\text{C}/\text{C}_5\text{H}_4$), 125.8 (bipy), 126.8 (bipy), 129.1 (d, $^3J_{\text{CP}} = 11.3$ Hz, $^m\text{C}/\text{Ph}$), 131.6 (d, $^4J_{\text{CP}} = 2.4$ Hz, $^p\text{C}/\text{Ph}$), 131.7 (d, $^1J_{\text{CP}} = 58.3$ Hz, $^i\text{C}/\text{Ph}$), 133.7 ($\text{C}\equiv\text{CSi}$), 133.8 (d, $^2J_{\text{CP}} = 13.7$ Hz, $^o\text{C}/\text{Ph}$), 140.5 (bipy), 142.7 (bipy), 147.8 (bipy), 149.2 (bipy), 150.7 (bipy), 151.8 (bipy), 165.9 ($\text{TiC}\equiv\text{C}$) (the signal for the $\text{AuC}\equiv\text{C}$ carbon atom (C_{α}) could not be assigned). $^{31}\text{P}\{^1\text{H}\}$ NMR δ_{P} (CDCl_3): 36.2 (s, PPh_2), -145.1 (septet, $^1J_{\text{PF}} = 713$ Hz, PF_6).

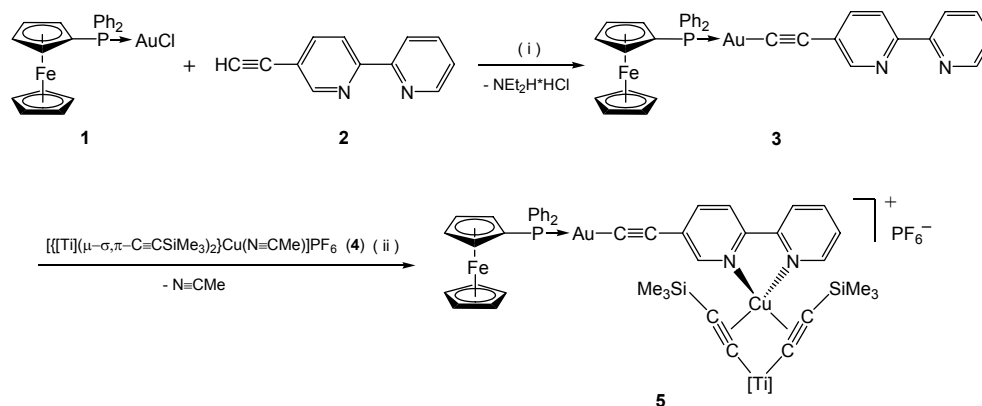
Crystal structure determination and refinement data of **5**

Single crystals of **5** were obtained by vapour diffusion of n-hexane into a chloroform solution of **5**. The preparation of suitable crystals were done in perfluoroalkyl ether 216 (Riedel-de Haën) for protection against air and moisture. Data were collected with a Bruker axs Smart 1k CCD diffractometer at 183(2) K using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Reflections were collected in the omega scan mode in 0.4° steps and an exposure time of 30 seconds per frame. The structure was solved by direct methods using SHELXS-97.^[9] The structure was refined by full-matrix least-square on F^2 using SHELXL-97.^[10] All *non*-hydrogen atoms were refined anisotropically. All hydrogen atoms were refined using a riding model. The asymmetric unit contains two symmetrically independent complex molecules, two PF₆⁻ counter ions and one half occupied chloroform solvent molecule.

Crystal data: C_{60.25}H_{70.25}AuCl_{0.75}CuF₆FeN₂P₂Si₄Ti, $M = 1501.33$, triclinic, $a = 16.9879(8)$, $b = 21.3635(11)$, $c = 22.9555(11) \text{ \AA}$, $\alpha = 98.8570(10)$, $\beta = 95.7660(10)$, $\gamma = 105.0720(10)^\circ$, $V = 7861.9(7) \text{ \AA}^3$, space group $P-1$, $Z = 4$, 69529 reflections measured, 32186 unique ($R_{\text{int}} = 0.0819$) which were used in all calculations. The final $wR(F_2)$ was 0.2472 (all data).

Results and Discussion

The reaction of heterobimetallic FcPPh₂-Au-C≡C-bipy (**3**) (Fc = (η^5 -C₅H₄)(η^5 -C₅H₅)Fe; bipy = 2,2'-bipyridine), which is accessible by treatment of FcPPh₂-AuCl (**1**) with 5-ethynyl-2,2'-bipyridine (**2**) (route i, Scheme 1) with equimolar amounts of [[Ti](μ - σ , π -C≡CSiMe₃)₂Cu(N≡CMe)]PF₆ (**4**) ([Ti] = (η^5 -C₅H₄SiMe₃)₂Ti) gives heterotetrametallic [[Ti](μ - σ , π -C≡CSiMe₃)₂Cu-bipy-C≡C-AuPh₂PfC]PF₆ (**5**) (route ii, Scheme 1). After appropriate work-up, compound **5** could be isolated as an orange colored solid in 88 % yield.



Scheme 1. Synthesis of **3** and **5** ((i) NEt₂H, [Cu], 25 °C, 12 h; (ii) tetrahydrofuran, 25 °C, 3 h).

The formation of **3** and **5** has been inferred through IR spectroscopic studies. The C≡C stretching vibration of **3** (2115 cm⁻¹) is, as expected, shifted to higher wavenumbers as compared to that of **2** (2096 cm⁻¹).^[6] Besides the $\nu_{\text{C}=\text{C}}$ frequency for

the Au-C≡C-bipy unit a characteristic $\nu_{C=C}$ absorption is found at 1924 cm^{-1} for the Ti-C≡C-Si entity in **5**.^[12]

A downfield shift for the PPh₂ group is typical in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum by going from **1** (27.60 ppm) to **3** (35.95 ppm). Similar observations have been made for (PPh₃)AuC≡CR species.^[11] The appropriate resonance signal for **5** appears at almost the same chemical shift (36.20 ppm) as **3**. For the PF₆⁻ counter ion in **5** a septet at -145.1 ppm with $J_{\text{PF}} = 713\text{ Hz}$ is found.

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR studies of **3** and **5** show only minor changes for the protons and carbons of the ferrocenyl, bipy and the titanium-bonded cyclopentadienyl units. Complex **4** displays for the C₅H₄SiMe₃ ligands two singlets at 6.26 ppm (C₅H₄) and 0.30 ppm (SiMe₃),^[12] while in **5** the cyclopentadienyl ring protons appear as a multiplet between 6.2 – 6.3 ppm and the SiMe₃ protons give rise to two resonances at 0.27 and 0.28 ppm, respectively. This is attributed to the different chemical environment around the cyclopentadienyl building blocks (for comparison see X-ray structure analysis, Figure 1). In the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **5** also two signal patterns are observed for the C₅H₄SiMe₃ moieties.

The chelate-binding of the bipy entity in **5** to the heterobimetallic organometallic π -tweezer fragment $[\{\text{Ti}\}(\mu\text{-}\sigma,\pi\text{-C}\equiv\text{CSiMe}_3)_2\text{Cu}]^+$ influences the chemical shifts of the protons involved (**3**: H3, 8.31; H3', 8.37; H4, 7.92; H4', 7.79; H5', 7.26; H6, 8.83; H6', 8.66. **5**: H3, 8.50; H3', 8.39; H4, 8.18; H4', 8.22; H5', 7.69; H6, 8.56; H6', 8.53 ppm). Notable to mention is that in the ^1H NMR spectra of **5** a high field shift is observed for the Me₃SiC≡C protons, when compared with **4** (**4**: 0.25 ppm, **5**: -0.49 ppm), which can be explained by the ring current of the bipy ligand. A similar trend is found in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **5**.

The solid state structure of **5** was determined by single crystal X-ray structure analysis (Figure 1). Due to the needle-like habitus of the crystals, however, data did not refine very well. For this reason only main structural features are discussed. The drawing of **5** is presented in Figure 1.

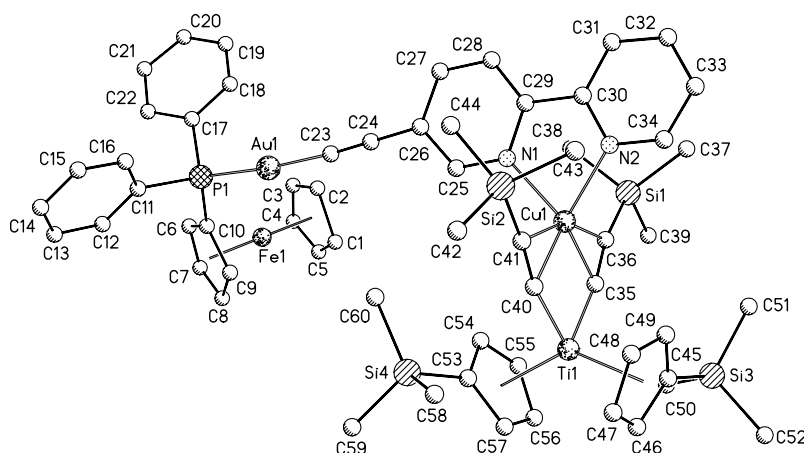


Figure 1. Crystal structure of **5**. All hydrogen atoms, the PF_6^- counter ion and a chloroform molecule are omitted for clarity. Selected bond distances (Å) and angles ($^\circ$): P(1)-Au(1), 2.267(3); Au(1)-C(23), 1.999(11); C(23)-C(24), 1.201(13); Cu(1)-N(1), 2.104(7); Cu(1)-N(2), 2.080(7); Ti(1)-C(35), 2.096(10); Ti(1)-C(40), 2.108(10); C(35)-C(36), 1.240(13); C(40)-C(41), 1.225(13); P(1)-Au(1)-C(23), 175.8(3); Au(1)-C(23)-C(24), 174.6(9); C(23)-C(24)-C(26), 177.1(11); Ti(1)-C(35)-C(36), 167.56(9); Ti(1)-C(40)-C(41), 166.62(8); C(35)-C(36)-Si(1), 161.5(9); C(40)-C(41)-Si(2), 162.3(9).

Heterotetranuclear **5** features the transition metals gold, copper, iron and titanium, whereby Au(1) is two-coordinated, Fe(1) is part of a sandwich structure and Cu(1) and Ti(1) possess a pseudo-tetrahedral environment (Figure 1). A linear 1-dimensional P(1)-Au(1)-C(23)-C(24)-C(26) arrangement is set-up (Figure 1) which is typical for phosphane-stabilized gold(I) acetylides.^[11] The bipy ligand is chelate-bonded *via* the nitrogen atoms N(1) and N(2) to Cu(1), thus resulting in a pseudo-tetrahedral coordination at Cu(1).

The structural features of the organometallic π -tweezer unit $[[\text{Ti}](\mu\text{-}\sigma,\pi\text{-C}\equiv\text{CSiMe}_3)_2\text{Cu}]^+$ are in accordance with this type of molecules.^[12]

In the cyclic voltammogram of **1**, **3** and **5** a redox wave at $E_0 = 0.28$ V ($\Delta E_p = 135$ mV) (**3**) and 0.27 V ($\Delta E_p = 155$ mV) (**5**) is found for the ferrocenyl group in the cathodic region similar to **1** ($E_0 = 0.29$ V, $\Delta E_p = 160$ mV).^[5] This indicates a decreased electron density at the Fe(II) ion in **1**, **3** and **5**, when compared with FcPPh_2 ,^[13] which can be explained by the electron-withdrawing effect of the gold(I) moiety. In the anodic region a irreversible reduction peak at -2.77 V (**1**) and -2.62 V (**3**) is observed for the Au(I) ion typical for phosphane gold(I) species.^[11] The cyclic voltammogram of **5** shows a irreversible reduction peak at -2.45 V due to the Au(I)/Au(0) process. For the bipy/bipy⁻ redox couple characteristic one-electron potentials at $E_0 = -2.69$ V ($\Delta E_p = 230$ mV) (**3**) and -2.70 V ($\Delta E_p = 390$ mV) (**5**) are observed.^[14]

Furthermore, in the cyclic voltammogram of **5** an irreversible reduction for copper(I) is found at -1.48 V. By measuring only the region around this potential the respective reduction process is changed ($E_0 = -1.42$ V, $\Delta E_p = 120$ mV). The

titanium(IV) centre of the organometallic π -tweezer part gives rise to two further redox processes attributed to the Ti(IV)/Ti(III) redox couple of intact **5** ($E_0 = -1.63$ V, $\Delta E_p = 190$ mV) and $[\text{Ti}](\text{C}\equiv\text{CSiMe}_3)_2$ ($E_0 = -1.76$ V, $\Delta E_p = 170$ mV), which most probably is formed by fragmentation as a result of the Cu(I) reduction. ^[15]

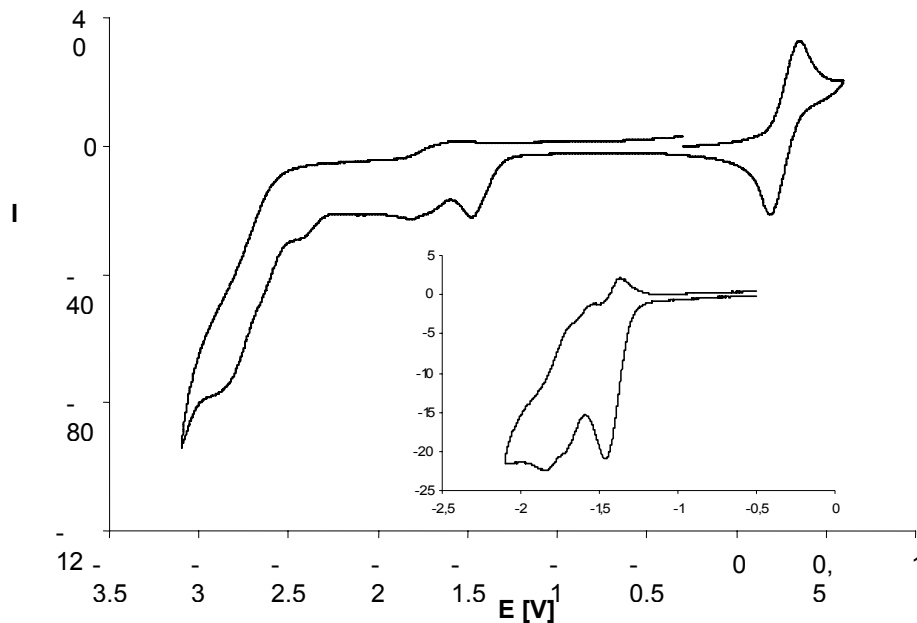


Figure 2. Cyclic voltammogram of **5** in tetrahydrofuran at 25 °C, $[\text{nBu}_4\text{N}]\text{PF}_6$ supporting electrolyte (0.1 M), scan rate = 100 mV. All potentials are referenced to the FcH/FcH^+ redox couple ($\text{FcH} = (\eta^5\text{-C}_5\text{H}_5)_2\text{Fe}$, $E_0 = 0.00$ V). ^[16, 17]

Within this work a straightforward method to prepare novel heterotetrametallic Ti-Fe-Au-Cu in which the respective transition metals are connected by π -conjugated organic carbon-rich units is discussed. Complex $\{[\text{Ti}](\mu\text{-}\sigma,\pi\text{-C}\equiv\text{CSiMe}_3)_2\text{Cu-bipy-C}\equiv\text{CAuPh}_2\text{PFC}\}\text{PF}_6$ ($[\text{Ti}] = (\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}$, $\text{Fc} = (\eta^5\text{-C}_5\text{H}_4)(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$) illustrates a transition metal complex in which alkynyl, cyclopentadienyl, bipyridine and diphenylphosphino units are linking four different metals, such as titanium, gold, iron and copper and hence, represents a new class of complexes.

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