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

Rico Packheiser, Bernhard Walfort, Heinrich Lang*

Technische Universität Chemnitz, Fakultät für Naturwissenschaften, Institut für Chemie, Lehrstuhl für Anorganische Chemie, Straße der Nationen 62, 09111 Chemnitz, Germany.

Received on July 2, 2006 Accepted on Aug. 28, 2006

Abstract

Heterotetrametallic \(\text{[Ti(μ-σ,π-C≡CSiMe_3)_2]}\text{Cu-bipy-C≡C-AuPh_2PFc]}\text{PF_6}\) (5) ([Ti] = \(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3\)\text{2Ti}; Fc = \(\eta^5\text{-C}_5\text{H}_4\)\(\eta^5\text{-C}_5\text{H}_5\)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-AuC≡C-bipy (3) which further reacts with \(\text{[Ti(μ-σ,π-C≡CSiMe_3)_2]}\text{Cu(N≡CMe)}\text{]}\text{PF_6}\) (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 \(\text{[Ti(μ-σ,π-C≡CSiMe_3)_2]}\text{Cu-bipy-C≡C-AuPh_2PFc]}\text{PF_6}\) (5) ([Ti] = \(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3\)\text{2Ti}; Fc = \(\eta^5\text{-C}_5\text{H}_4\)\(\eta^5\text{-C}_5\text{H}_5\)Fe; bipy = 2,2′-bipyridine) by using FcPPh_2Au-C≡Cbipy and \(\text{[Ti(μ-σ,π-C≡CSiMe_3)_2]}\text{Cu(N≡CMe)}\text{]}\text{PF_6}\) 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\(_2\)O 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

* Corresponding Author: E-mail: heinrich.lang@chemie.tu-chemnitz.de
transform mode. $^{1}$H NMR spectra were recorded at 250.130 MHz (internal standard, relative to CDCl$_3$, $\delta$ 7.26). $^{13}$C($^1$H) NMR spectra were recorded at 62.902 MHz (internal standard, relative to CDCl$_3$, $\delta$ 77.16). $^{31}$P($^1$H) NMR spectra were recorded at 101.249 MHz in CDCl$_3$, external standard P(OMe)$_3$, $\delta$ = 139.0 ppm relative to H$_3$PO$_4$, $\delta$ = 0.0 ppm. Chemical shifts are reported in $\delta$ 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.

Elemental analysis: Found: C, 48.70; H, 4.68; N, 2.18. C$_{60}$H$_{70}$AuCuF$_6$FeN$_2$P$_2$Si$_4$Ti requires C, 48.97; H, 4.79; N, 1.90 %. Mp 172 °C (decomp.). IR: $\nu_{\text{max}}/\text{cm}^{-1}$ 2118w (AuC≡C), 1924w (TiC≡C), 841s (P-F). $^1$H NMR ($\delta$H (CDCl$_3$): -0.49 (18 H, s, SiMe$_3$), 0.27 (9 H, s, SiMe$_3$), 4.21 (5H, s, C$_5$H$_5$), 4.39 (2 H, dpt, $J_{\text{HH}}$ = 1.9 Hz, $J_{\text{HP}}$ = 2.5 Hz, $^1$H/C$_5$H$_4$, Fc), 4.58 (2 H, br s, $^1$H/C$_5$H$_4$, Fc), 6.26 – 6.30 (8 H, m, C$_5$H$_4$), 7.41 – 7.64 (10 H, m, Ph) 7.69 (1 H, dd, $^3$J$_{\text{H5}}$H$_4$ = 7.8 Hz, $^3$J$_{\text{H5}}$H$_9$ = 5 Hz, H5'), 8.18 (1 H, dd, $^3$J$_{\text{H4H3}}$ = 8.5 Hz, $^3$J$_{\text{H4H5}}$ = 2 Hz, H4), 8.22 (1 H, ddd, $^3$J$_{\text{H4H3}}$H$_5$ = $^3$J$_{\text{H4H5}}$H$_9$ = 7.8 Hz, $^4$J$_{\text{H4H6}}$ = 1.8 Hz, H4'), 8.39 (1 H, d, $^3$J$_{\text{H3}}$H$_4$ = 7.8 Hz, H3'), 8.50 (1 H, d, $^3$J$_{\text{H3H4}}$ = 8.5 Hz, H3), 8.53 (1 H, d, $^3$J$_{\text{H6}}$H$_{15}$ = 4.4 Hz, H6'), 8.56 (1 H, d, $^4$J$_{\text{H6H4}}$ = 2 Hz, H6). $^{13}$C($^1$H) NMR ($\delta$C (CDCl$_3$): -0.61 (SiMe$_3$), 0.17 (SiMe$_3$), 0.23 (SiMe$_3$), 69.2 (d, $^1$CP = 68.2 Hz, $^1$C/C$_5$H$_4$, Fc), 70.1 (C$_3$H$_5$, Fc), 72.7 (d, $^3$J$_{\text{CP}}$ = 8.6 Hz, $^1$C/C$_5$H$_4$, Fc), 73.7 (d, $^2$J$_{\text{CP}}$ = 13.8 Hz, $^3$C/C$_3$H$_4$, Fc), 98.7 (AuC≡C), 115.2 (CH/C$_5$H$_4$), 115.3 (CH/C$_5$H$_4$), 117.2 (CH/C$_5$H$_4$), 117.3 (CH/C$_5$H$_4$), 122.0 (bipy), 122.9 (bipy), 122.9 (C/C$_5$H$_4$), 123.3 (C/C$_5$H$_4$), 125.8 (bipy), 126.8 (bipy), 129.1 (d, $^3$J$_{\text{CP}}$ = 11.3 Hz, $^1$C/Ph), 131.6 (d, $^1$CP = 2.4 Hz, $^3$C/Ph), 131.7 (d, $^1$CP = 58.3 Hz, $^3$C/Ph), 133.7 (C=C(Si)), 133.8 (d, $^2$J$_{\text{CP}}$ = 13.7 Hz, $^3$C/Ph), 140.5 (bipy), 142.7 (bipy), 147.8 (bipy), 149.2 (bipy), 150.7 (bipy), 151.8 (bipy), 165.9 (TiC≡C) (the signal for the Au≡C carbon atom (C$_{\alpha}$) could not be assigned). $^{31}$P($^1$H) NMR ($\delta$P (CDCl$_3$): 36.2 (s, PPh$_2$), -145.1 (septet, $^1$J$_{\text{PF}}$ = 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 Kα radiation (λ = 0.71073 Å). Reflections were collected in the omega scan mode in 0.4° steps and a exposition time of 30 seconds per frame. The structure was solved by direct methods using SHELXS-97. The structure was refined by full-matrix least-square on F² using SHELXL-97. 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: C₆₀.₂₅H₇₀.₇₅AuCl₀.₇₅CuF₆FeN₂P₂Si₄Ti, M = 1501.33, triclinic, a = 16.9879(8), b = 21.3635(11), c = 22.9555(11) Å, α = 98.8570(10), β = 95.7660(10), γ = 105.0720(10)°, V = 7861.9(7) Å³, space group P-1, Z = 4, 69529 reflections measured, 32186 unique (Rint = 0.0819) which were used in all calculations. The final wR(F²) was 0.2472 (all data).

Results and Discussion

The reaction of heterobimetallic FcPPh₂-Au-C≡C-bipy (3) (Fc = (η⁵-C₅H₅)(η⁵-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)₂}Cu(N≡CMe)]PF₆ (4) (Ti] = (η⁵-C₅H₅SiMe₃)₂Ti) gives heterotetrametallic [[{[Ti](µ-σ,π-C≡CSiMe₃)₂}Cu-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, [CuI], 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). Besides the vC≡C frequency for
the Au-C≡C-bipy unit a characteristic νC≡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 3¹P{¹H} 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 J₉₆ = 713 Hz is found.

¹H and ¹³C{¹H} 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 C₅H₅SiMe₃ ligands two singlets at 6.26 ppm (C₅H₅) 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 ¹³C{¹H} NMR spectra of 5 also two signal patterns are observed for the C₅H₅SiMe₃ moieties.

The chelate-binding of the bipy entity in 5 to the heterobimetallic organometallic π-tweezer fragment [{[Ti(µ-σ,π-C≡CSiMe₃)₂]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 ¹³C{¹H} 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.
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. 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 $\left\{[[\text{Ti}](\mu-\sigma,\pi-C\equiv\text{CSiMe}_3)_2]\text{Cu}\right\}^+$ are in accordance with this type of molecules.

In the cyclic voltammogram of 1, 3 and 5 a redox wave at $E_0 = 0.28 \text{ V} \ (\Delta E_p = 135 \text{ mV})$ (3) and 0.27 V ($\Delta E_p = 155 \text{ mV}$) (5) is found for the ferrocenyl group in the cathodic region similar to 1 ($E_0 = 0.29 \text{ V}, \Delta E_p = 160 \text{ mV}$). This indicates a decreased electron density at the Fe(II) ion in 1, 3 and 5, when compared with FcPPh$_2$, 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. 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 $E_0 = -2.69 \text{ V} \ (\Delta E_p = 230 \text{ mV})$ (3) and -2.70 V ($\Delta E_p = 390 \text{ mV}$) (5) are observed.

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 ($E_0 = -1.42 \text{ V}, \Delta E_p = 120 \text{ mV}$).
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 [Ti](C≡CSiMe3)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.\[^{[15]}\]

![Cyclic voltammogram of 5 in tetrahydrofuran at 25 °C, \([nBAuN]PF_6\) supporting electrolyte (0.1 M), scan rate = 100 mV. All potentials are referenced to the FcH/FcH+ redox couple (FcH = \(\eta^5\)-C5H5)2Fe, \(E_0 = 0.00 \, V\).\[^{[16, 17]}\)](image)

**Figure 2.**

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 \([\{[Ti](\mu-\sigma, \pi=C\equivCSiMe3)2Cu-bipy-C≡C-AuPh2PFC\}PF_6, ([Ti] = (\eta^5\)-C5H4)(\eta^5\)-C5H5)2Ti, Fc = (\eta^5\)-C5H4)(\eta^5\)-C5H5)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.

**Acknowledgement**

This work was supported in part by the Deutsche Forschungsgemeinschaft (DFG).
References


