



# Electronic interactions in gold(I) complexes of 2,5-diferrocenyl-1-phenyl-1*H*-phosphole



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## ABSTRACT

The synthesis of gold(I) complexes of 2,5-diferrocenyl-1-phenyl-1*H*-phosphole (**1**) is presented. Chloro(2,5-diferrocenyl-1-phenyl-1*H*-phosphole)gold (**3**) has successfully been prepared by the reaction of **1** with AuCl(SMe<sub>2</sub>) (**2**). Treatment of **2** with aryethyne (aryl = ferrocenyl, phenyl) using catalytical amounts of [CuI] and 1 equiv. of **1** gave aryethynyl-(2,5-diferrocenyl-1-phenyl-1*H*-phosphole)gold **4a** and **4b** (aryl: **a** = ferrocenyl; **b** = phenyl). Compound [ $\mu$ -(1,4-phenylenedi-2,1-ethynediyl)]bis(2,5-diferrocenyl-1-phenyl-1*H*-phosphole)digold (**5**) could be synthesized by a similar procedure using 0.5 equiv. of 1,4-diethynylbenzene. The electrochemical properties of **3**, **4a,b** and **5** were investigated by cyclic and square wave voltammetry. In **3**, **4a** and **4b** each ferrocenyl unit shows one reversible redox event with redox separations of the ferrocenyl moieties in 2,5 position of approximately 260 mV. In **5** two redox events for the four ferrocenyl groups were observed. Spectroelectrochemical measurements of **3**, **4a** and **4b** reveal IVCT absorptions with intensities of 1100–1300 L mol<sup>-1</sup> cm<sup>-1</sup> and a full-width-at-half-height of  $\approx$ 3650 cm<sup>-1</sup>. In **5** two mixed-valent units are present per molecule and therefore, the intensity of the IVCT band is increased to 2700 L mol<sup>-1</sup> cm<sup>-1</sup>. Compounds **3**, **4a,b** and **5** can be classified as moderately coupled class II systems according to Robin and Day. The complexation of the gold(I) fragment by the phosphorus atom leads to a decreased metal–metal interaction when compared to **1**.

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## 1. Introduction

In recent years, molecules bearing two or more redox-active metal fragments connected *via* a  $\pi$ -conjugated bridging unit were intensively studied as they can be applied in electron transfer studies and therefore, can be regarded as models for molecular wires [1–6]. Ferrocenyl units are well suited as redox-active termini due to the stability of the Fc/Fc<sup>+</sup> redox couple and their straightforward modification possibilities [2]. Heterocycles have been amongst the earliest bridging units explored in mixed-valence chemistry and the role that variation of the bridging moiety can play on the properties of these systems is well established [7,8]. Whilst *N*-containing heterocycles (particularly pyridine and pyrazine) are commonly used, heterocycles containing other hetero elements have also been explored, notably thiophene [9–13]. Recently, we have shown that metallacycles, five- and six-membered heterocycles as  $\pi$ -conjugated connecting units are well suited to facilitate electron transfer between mixed-valent

redox-active termini, while also granting the possibility to modify their electronic properties [4,9,10,14–23]. In this respect, modifications of the heteroatom, the backbone of the heterocycle, and/or the ferrocenyl unit can influence the metal–metal interactions of the ferrocenyl moieties bonded to the heterocycle [10,24].

In contrast to analogous heterocycles such as furan, thiophene and pyrrole, the chemistry of phospholes is not as intensively studied. However, in recent years phospholes have attracted more interest especially due to the straightforward modification possibilities at the phosphorus' lone pair, and it could be shown that the electronic nature of the  $\pi$  system could easily be modified [25–39]. Chemical functionalization of the phosphorus atom, such as oxidation from P<sup>III</sup> to P<sup>V</sup> or complexations, make these molecules suitable for fine-tuning of electronic properties in the design of new materials [34,38,40–44]. Gold phosphole complexes, for example, have shown to exhibit interesting photophysical properties [45–50].

In earlier studies we have shown that the strength of the electronic interaction of the Fc/Fc<sup>+</sup> termini *via* the heterocyclic core in 2,5-diferrocenyl-1-phenyl-1*H*-phosphole is decreased when compared to the pyrrole analogues [51]. Furthermore, an increase

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of the steric demand of the substituent bonded to phosphorus led to an increased delocalization within the heterocyclic ring, which in turn increases the metal–metal interaction *via* the phosphole motif [52].

In addition, the complexation of the phosphorus atom to a M(0) fragment in 2,5-diferrocenyl-1-phenyl-1*H*-phosphole metal carbonyl complexes barely influences the metal–metal interactions [53]. In contrast, cationic metal fragments such as Au(I) are expected to have a greater influence on the electronics of the phosphole unit as a result of their greater net-electronegativity.

Herein, we report on the synthesis of gold(I) complexes of 2,5-diferrocenyl-1-phenyl-1*H*-phosphole. UV-VIS/NIR spectroelectrochemistry was carried out to examine the influence of the metal(I) center on the electronic interaction of the Fc/Fc<sup>+</sup> groups.

## 2. Results and discussion

### 2.1. Synthesis and characterization

Chloro(2,5-diferrocenyl-1-phenyl-1*H*-phosphole)gold (**3**) was synthesized by the reaction of 2,5-diferrocenyl-1-phenyl-1*H*-phosphole (**1**) [51] with chloro(thiobis[methane])gold (**2**). The reaction of **2** with ethynylferrocene or phenylacetylene using catalytical amounts of [CuI] and one equiv. of **1** resulted in the formation of arylethynyl-(2,5-diferrocenyl-1-phenyl-1*H*-phosphole)gold **4a,b** (aryl: **a** = ferrocenyl; **b** = phenyl) (Scheme 1). Thereby, the alkynes were added to **2** dissolved in a mixture of tetrahydrofuran/diisopropylamine of ratio 1:1 (v/v), followed by the addition of catalytical amounts of CuI. During this reaction procedure it is not necessary to isolate potentially explosive intermediates [54]. Using the same reaction procedure but applying 0.5 equiv. of 1,4-diethynylbenzene produced [ $\mu$ -(1,4-phenylenedi-2,1-ethynediyl)]bis(2,5-diferrocenyl-1-phenyl-1*H*-phosphole)digold (**5**).

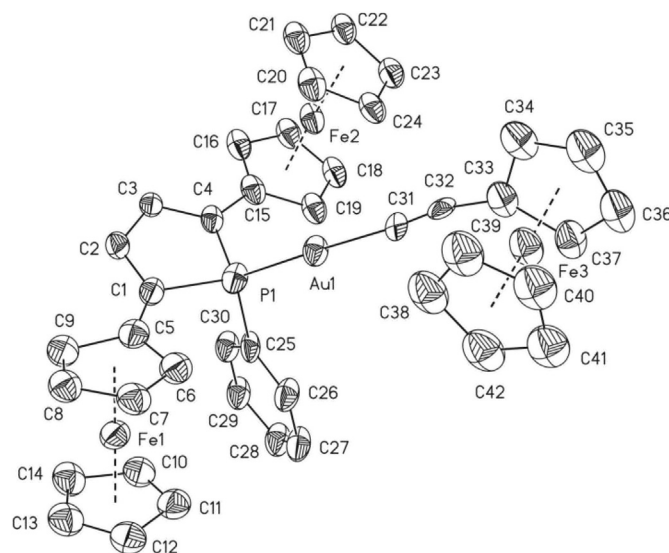
Compounds **3**, **4a,b** and **5** are stable towards air and moisture in the solid state and in solution. They were characterized by elemental analysis, IR and NMR (<sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H}, <sup>31</sup>P{<sup>1</sup>H}) spectroscopy, and ESI-TOF mass spectrometry. The redox behavior was investigated by cyclic (CV) and square wave voltammetry (SWV) and the spectroelectrochemical behavior was studied by *in situ* UV–Vis/NIR

measurements. In addition, the structure of **4a** in the solid state was determined by single-crystal X-ray diffraction analysis.

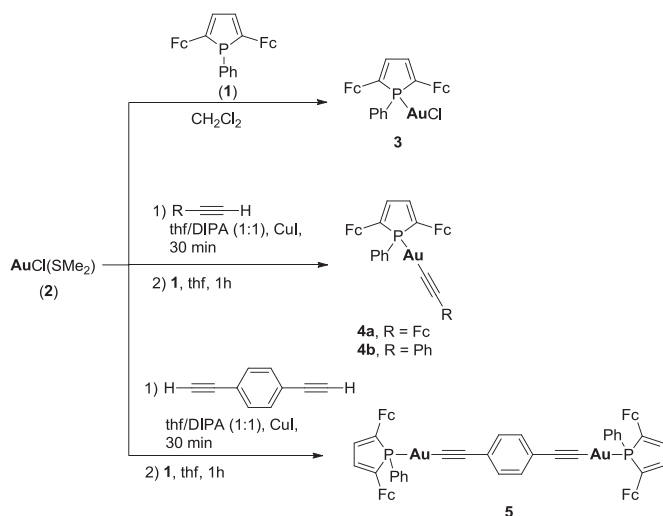
In the <sup>1</sup>H NMR spectra of **3**, **4a**, **4b** and **5** one singlet for the C<sub>5</sub>H<sub>5</sub> protons and four multiplets between 4.1 ppm and 4.6 ppm for the C<sub>5</sub>H<sub>4</sub> protons of the ferrocenyl units were observed. In **4a**, one additional singlet and two multiplets were found for the Fc/Fc≡C group (Experimental Section). The signals for the ferrocenyl moieties in **3**, **4a**, **4b** and **5** are slightly shifted to lower field when compared to **1** [51]. For the phosphole protons a doublet at approximately 6.9 ppm with a <sup>3</sup>J<sub>PH</sub> coupling constant of 27 Hz is characteristic. The complexation of the phosphorus atom to the gold fragment leads to an increase of the coupling constant (*i. e.*; **1**, <sup>3</sup>J<sub>PH</sub> = 11.4 Hz [51]; **3**, <sup>3</sup>J<sub>PH</sub> = 29.5 Hz). The signals for the C<sub>6</sub>H<sub>5</sub> groups appear as multiplets between 7.4 ppm and 7.9 ppm and the C<sub>6</sub>H<sub>4</sub> protons in **5** as singlet at 7.4 ppm.

The resonances of the C≡C carbon atoms are found between 101 and 103 ppm in the <sup>13</sup>C{<sup>1</sup>H} NMR spectra [54–56]. Due to the low solubility of **5** no <sup>13</sup>C{<sup>1</sup>H} NMR spectrum could be obtained. The coordination of the phosphorus atom in **3**, **4a** and **4b** to the gold moiety leads to a shift of the <sup>13</sup>C<sub>4</sub>H<sub>2</sub>P *ipso*-carbon atom to higher field ( $\approx$  140 ppm), which is accompanied by a significant increase of <sup>1</sup>J<sub>CP</sub> ( $\approx$  50 Hz) (Experimental Section). Phosphorus coordination to Au(I) results in a shift of the phosphorus signal from 5.1 ppm [51] in **1** to lower field (**3**, 30.4 ppm; **4a**, 43.2 ppm; **4b**, 43.1 ppm; **5**, 43.1 ppm) in the <sup>31</sup>P{<sup>1</sup>H} spectra. The IR spectra of **4a,b** and **5** are characterized by  $\nu_{C\equiv C}$  absorptions at 2107 cm<sup>-1</sup> (**4a,b**) and 2117 cm<sup>-1</sup> (**5**), respectively.

The molecular structure of **4a** in the solid state was determined by single-crystal X-ray diffraction analysis. The ORTEP diagram of this compound with selected bond lengths (Å), bond angles (°) and torsion angles (°) is shown in Fig. 1.



**Fig. 1.** ORTEP diagram (30% probability level) of the molecular structure of **4a** with the atom numbering scheme. All hydrogen atoms have been omitted for clarity. Selected bond distances (Å), angles (°), and torsion angles (°): P1–C1 = 1.86(2), C1–C2 = 1.36(3), C2–C3 = 1.47(3), C3–C4 = 1.35(3), C4–P1 = 1.76(2), P1–C25 = 1.84(2), P1–Au1 = 2.262(6), Au1–C31 = 2.091(18), C31–C32 = 1.12(16), D1–Fe1 = 1.636(4), D2–Fe1 = 1.645(4), D3–Fe2 = 1.635(4), D4–Fe2 = 1.642(4), D5–Fe3 = 1.653(4), D6–Fe3 = 1.620(4), D1–Fe1–D2 = 177.8(3), D3–Fe2–D4 = 176.9(3), D5–Fe3–D6 = 179.0(3), C1–P1–C4 = 94.7(10), P1–Au1–C31 = 178.4(5), Au1–C31–C32 = 175(2), Au1–P1–C1 = 117.4(7), Au1–P1–C4 = 115.7(8), C1–P1–C25 = 105.1(10), C4–P1–C25 = 105.5(11), C5–D1–D2–C10 = 5.6(17), C15–D3–D4–C20 = 1.1(17), C33–D5–D6–C38 = –22.1(19), D1 = centroid of C5–C9; D2 = centroid of C10–C14, D3 = centroid of C15–C19; D4 = centroid of C20–C24, D5 = centroid of C33–C37, D6 = centroid of C38–C42.



<sup>a</sup> Fc = Fe( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>); thf = tetrahydrofuran, DIPA = diisopropylamine.

**Scheme 1.** Synthesis of gold complexes **3**, **4a,b** and **5**.

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