# Accepted Manuscript

New Cationic Organometallic Phosphane Ligands and their Coordination to Gold(I)

Tobias R. Eger, Isabel Munstein, Annika Steiner, Yu Sun, Gereon Niedner-Schatteburg, Werner R. Thiel

PII: S0022-328X(16)30070-5

DOI: 10.1016/j.jorganchem.2016.02.037

Reference: JOM 19421

To appear in: Journal of Organometallic Chemistry

Received Date: 22 December 2015

Revised Date: 24 February 2016

Accepted Date: 25 February 2016

Please cite this article as: T.R. Eger, I. Munstein, A. Steiner, Y. Sun, G. Niedner-Schatteburg, W.R. Thiel, New Cationic Organometallic Phosphane Ligands and their Coordination to Gold(I), *Journal of Organometallic Chemistry* (2016), doi: 10.1016/j.jorganchem.2016.02.037.

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.



Cationic arylphosphines bearing a  $\eta^6$ -coordinated ( $\eta^5$ -Cp)Fe<sup>+</sup> moiety were synthesized via a nucleophilic aromatic substitution reaction. Such ligands open up the access to bimetallic complexes, and allow studying cooperative effects between the metal sites.

Graphics for contents



# New Cationic Organometallic Phosphane Ligands and their Coordination to Gold(I)

Tobias R. Eger, Isabel Munstein, Annika Steiner, Yu Sun, Gereon Niedner-Schatteburg, Werner R. Thiel\*

Dedicated to Professor Heinrich Lang on the occasion of his 60<sup>th</sup> birthday

\* Technische Universität Kaiserslautern, Fachbereich Chemie, Erwin-Schrödinger-Straße 54, D-67663 Kaiserslautern, Germany. E-mail: thiel@chemie.uni-kl.de

## Abstract

Two novel metallated phosphino ligands  $[(\eta^5-Cp)Fe(\eta^6-C_6H_5PPh_2)](PF_6)$  and  $[(\eta^5-Cp)Fe(\eta^6-1,2-C_6H_4(PPh_2)_2)](PF_6)$  have successfully been synthesized. Therein, the phosphane moieties are directly bound to the cationic  $(\eta^5-Cp)Fe$  fragment. By reaction of  $[(\eta^5-Cp)Fe(\eta^6-C_6H_5PPh_2)](PF_6)$  with (thiophene)AuCl, the heterobimetallic complex  $[(\eta^5-Cp)Fe(\eta^6-C_6H_5PPh_2)](PF_6)$  was obtained in good yields. It was characterized spectroscopically as well as by X-ray structure analysis.

Keywords: Iron, Gold, Phosphine, Solid state structure, Synthesis

#### Introduction

Tuning the activity and selectivity of transition metal compounds by slight variations of the ligand structure is a strategy frequently used in homogeneous catalysis to optimize the performance of the catalyst. In this context, the substitution of classical aromatic sites in the ligand backbone against organometallic substituents allows further variations of the steric and electronic impact of a given ligand system. Since solely stable compounds can be used for this purpose, ferrocene based systems [1,2], including chiral ones [3,4,5,6,7], became the most prominent representatives for this strategy during the last two decades. Furthermore, ferrocene chemistry is closely related to well-established arene chemistry allowing to introduce a broad variety of substituents into the ligand backbone. Even the effects of a reversible switching between the Fe<sup>II</sup> and the Fe<sup>III</sup> redox states on the properties of a series of transition metal catalysts have been investigated [8,9,10,11].

In contrast to the well-known chemistry of ferrocene-based ligands in transition metal chemistry, the coordinative behavior of ligands bearing a  $[(\eta^5-Cp)Fe(\eta^6-arene)]^+$  fragment instead of the ferrocenyl moiety is much less established. The starting materials for the synthesis of such systems have been known for long, since the first  $[(\eta^5-Cp)Fe(\eta^6-arene)]^+(X^-)$ compounds have already been reported in the 1960ies [12,13]. Due to the electronwithdrawing feature of the  $[(\eta^5-Cp)Fe]^+$  fragment, the  $\eta^6$ -coordinated arene site becomes accessible towards nucleophilic aromatic substitution reactions [14,15,16,17]. For applying this type of reactivity to obtain more complex systems, a chloro arene ligand has to be introduced, as it is the case for compounds such as  $[(\eta^5-Cp)Fe(\eta^6-C_6H_5Cl)]^{\dagger}(PF_6)$  and ortho-, *meta*-, resp. *para*-substituted  $[(\eta^5-Cp)Fe(\eta^6-C_6H_4Cl_2)]^+(PF_6^-)$ . These compounds can be synthesized from a mixture of ferrocene, AICl<sub>3</sub> and the corresponding chloro benzene in quite reasonable yields [13]. We recently were able to prove this concept by synthesizing the cationic *N*,N'-chelating ligand  $[(\eta^5-Cp)Fe(\eta^6-C_6H_5NHCH_2CH_2NH_2)]^+$ . This compound can e.g. be coordinated in a chelating manner to palladium dichloride giving the first transition metal complex bearing a  $[(\eta^{5}-Cp)Fe(\eta^{6}-arene)]^{+}$  based donor site [18]. Furthermore, the palladium complex shows an unexpected fragmentation behavior under CID ESI-MS conditions by splitting FeCl<sub>2</sub>, being in the electronic quintet state .

In 1995, Roberts et al. described the synthesis of  $[(\eta^5-Cp)Fe(\eta^6-arene)]^+$  cations by reacting ferrocene, aluminum chloride and aluminum with a variety of arenes under microwave

conditions [19]. By applying this method on triphenyl phosphine, they were able to obtain mixtures of the mono-cationic compound  $[(\eta^5-Cp)Fe(\eta^6-C_6H_5PPh_2)](PF_6)$  and the di-cationic species  $[((\eta^5-Cp)Fe(\eta^6-C_6H_5))_2PPh][PF_6]_2$  with medium to good yields. However, the authors gave no description on the separation of these mixtures and there is no hint in the literature that these compounds have ever been used for coordination to transition metal sites. In 2008 Danjo et al. reported the synthesis of a series of (tricarbonyl)chromium compounds containing  $\eta^6$ -coordinating arylphosphine ligands by introducing the phosphine site using BH<sub>3</sub> protected lithium phosphides [20]. They took the fluorine substituted derivatives  $[Cr(CO)_3(\eta^6-C_6H_{6-x}F_x)]$  (x = 1,2) as the starting materials, since fluoro substituents are wellknown to be perfect leaving groups in nucleophilic aromatic substitution reactions. Aubert, Fensterbank, and H. Amouri could obtain  $[(\eta^5-Cp)Ru(\eta^6-C_6H_5PPh_2)](OTf)$  (OTf = triflate) by nucleophilic aromatic substitution of the chloro substituent in  $[(\eta^5-Cp^*)Ru(\eta^6-C_6H_5CI)](OTf)$ against a diphenylphosphino substituent [21,22,23]. The corresponding complex with AuCl coordinated to the phosphine site catalyzes the cyclisation of  $\beta$ -hydroxyallenynes with much higher activity than its counterpart (PPh<sub>3</sub>)AuCl. This clearly speaks for a collaborative interaction between the gold site and the  $[(\eta^5-Cp)Ru(\eta^6-arene)]^+$  cation. It should be mentioned at this point, that Salzer et al. have published cationic phosphine ligands based on the cobaltocinium structure by using  $Li(C_5H_4-PPh_2)$  as the transfer reagent [<sup>24</sup>].

We here report the first access to triaryl phosphane ligands bearing a ( $\eta^5$ -Cp)Fe<sup>+</sup> fragment being  $\eta^6$ -coordinated to one of the aryl moieties by applying a nucleophilic aromatic substitution reaction. Furthermore, the first transition metal complex of such a type of ligand could be obtained by coordinating the phosphorus donor site to gold(I).

## **Results and discussion**

Treatment of ferrocene with chlorobenzene or 1,2-dichlorobenzene in the presence of aluminum chloride according to a published procedure gave the halogenated cationic  $\eta^5$ -cyclopentadienyliron(II)arene complexes **1a** and **1b** in good yields (Scheme 1) [13]. These intermediates were converted into the cationic organometallic phosphine ligands **2a** and **2b** by means of a nucleophilic aromatic substitution reaction with lithium diphenylphosphide (LiPPh<sub>2</sub>) in THF. Lithium diphenylphosphide was freshly prepared from freshly distillated diphenylphosphine and butyllithium. Alternatively, a commercially available solution of

potassium diphenylphosphide (KPPh<sub>2</sub>, 0.5 M in THF) can be applied, giving slightly lower yields. **1a** was obtained from one equivalent of LiPPh<sub>2</sub>,  $[(\eta^5-Cp)Fe(\eta^6-C_6H_5PPh_2)](PF_6)$  (**2a**) after 12 h of reaction as an orange microcrystalline solid in 71% yield.



Scheme 1. Synthesis of the cyclopentadienyl iron(II) arene complexes 1a,b and 2a,b.

The <sup>1</sup>H NMR spectrum recorded from a solution of **2a** in aceton-d<sup>6</sup> proved the synthesis of the compound (for spectra see the Supporting Information): A singlet 5.23 ppm can be assigned to the protons of the cyclopentadienyl ring. It is found shifted slightly to higher field compared to compound 1a. The resonances of the protons in the meta- and the paraposition of the  $\eta^6$ -coordinating arene ring are observed as two triplets at 6.21 and 6.57 ppm. A doublet at 6.60 ppm can be assigned to the protons in the *ortho*-position of this ring, which implies a quite small coupling of these two protons to the phosphorous atom in the close neighborhood. The resonances of the other aromatic protons of the diphenylphosphinyl moiety are identified as a multiplet at around 7.52 ppm. Aside to the typical septet resonance of the hexafluorophosphate anion, there is a singlet at -5.9 ppm in the <sup>31</sup>P NMR spectrum of **2a** which is assigned to the central phosphorus atom of the cation  $[(\eta^5-Cp)Fe(\eta^6-C_6H_5PPh_2)]^+$ . This chemical shift is quite typical for triaryl phosphines. It is only slightly deshielded compared to triphenylphosphine [25] and in good agreement with the data published by Roberts et al. for a mixture of **2a** and the dicationic species  $[((\eta^5-Cp)Fe(\eta^6 C_6H_5)_2PPh](PF_6)_2$  [19]. There is no hint for the formation of a phosphine oxide in the <sup>31</sup>P NMR spectrum. ESI mass spectrometry further confirms the synthesis of 2a: a molecular mass of m/z = 383.1 amu (calcd: 383.1) was found. The infrared spectrum of **2a** mainly shows weak aromatic C-H stretching vibrations (3121, 2963, 2874 cm<sup>-1</sup>) and a very strong peak for the hexafluorophosphate anion at 827 cm<sup>-1</sup>.

By gas diffusion of diethyl ether into a saturated solution of **2a** in dichloromethane, crystals being suitable for a single-crystal X-ray analysis could be obtained. Compound **2a** crystallizes

in the monoclinic space group  $P2_1/c$  with four cations and four hexafluorophosphate anions in the unit cell. Figure 1 shows the structure of **2a** in the solid state.



**Figure 1.** Molecular structure of **2a** in the solid state; characteristic bond lengths [Å] and bond angles [°]: Fe1-C1 2.052(4), Fe1-C2 2.055(3), Fe1-C3 2.053(4), Fe1-C4 2.060(3), Fe1-C5 2.055(3), Fe1-C6 2.068(3), Fe1-C7 2.078(3), Fe1-C8 2.091(3), Fe1-C9 2.083(3), Fe1-C10 2.082(3), Fe1-C11 2.104(3), P1-C11 1.847(3), P1-C12 1.826(3), P1-C18 1.840(3), P2-F4 1.596(2), P2-F5 1.562(3), P2-F6 1.609(2), P2-F2 1.586(2), P2-F3 1.580(2), P2-F1 1.605(3), C11-P1-C12 100.75(13), C11-P1-C18 100.76(14), C12-P1-C18 103.73(14).

Compound **2a** adopts the structure of a typical sandwich-type complex. The two planes of the five- and the six-membered ring are oriented almost parallel to each other ( $\angle$ : 0.61°). The distances between the iron site and the carbon atoms of the coordinating aromatic moieties are typical for  $[(\eta^5-Cp)Fe(\eta^6-arene)]^+$  derivatives. Among all distances between the iron site and the carbon atoms of the six- membered ring, the distance Fe1-C11 is clearly the longest, implying a slight steric or electronic perturbation in this position caused by the neighboring phosphorus atom. This is confirmed by a bending of the C11-P1 bond towards

the iron center by approx. 10° with respect to the plane of the six-membered ring. The lengths of the P-C bonds are comparable to the values observed for diphenylphosphino ferrocene (1.843 Å, 1.840 Å, 1.810 Å) [26]. The same is true for the C-P-C angles which are smaller than the ideal tetrahedral angle (mean values: **2a**, 101.74°; diphenylphosphino ferrocene, 101.1° [26],  $[(\eta^5-Cp^*)Ru(\eta^6-C_6H_5PPh_2)AuCl, 105.02°$  [21]). Therefore, sum of the C-P-C angles in **2a** (305.23°) is also smaller than the sum of the C-P-C angles in triphenyl phosphine (308.57°) which can be explained by the presence of the electron-withdrawing  $[(\eta^5-Cp)Fe]^+$  fragment [27].

Treatment of the compound  $[(\eta^5-Cp)Fe(\eta^6-1,2-C_6H_4Cl_2)](PF_6)$  (1b) with two equivalents of lithium diphenylphosphide in THF resulted in the formation of  $[(\eta^5-Cp)Fe(\eta^6-1,2-1)]$  $C_6H_4(PPh_2)_2](PF_6)$  (2b) as a reddish brown microcrystalline solid in 42% yield (Scheme 1). The <sup>1</sup>H NMR spectrum recorded from a solution of **2b** in acetonitrile-d<sup>3</sup> proved the presence of a pure compound. A singlet at 5.16 ppm can be assigned to the resonances of the cyclopentadienyl protons. It is found at almost the same chemical shift as the Cp resonance of 2a. Two multiplets at 6.30 and 6.75 ppm are due to the presence of the four protons of the  $\eta^6$ -coordinating six-membered ring. A set of multiplets at around 7.38 ppm can be assigned to the protons of the phenyl moieties not coordinating to the iron site. In the <sup>31</sup>P NMR spectrum of **2b**, there is a resonance at -144.6 ppm (hexafluorophosphate) and only one further signal at 9.41 ppm. The presence of solely one signal for the two phosphorus centers in 2b speaks for either a rapid rotation (with respect to the NMR time-scale) around the P-C bonds connecting the phosphorus atoms and the central  $\eta^{6}$ -1,2-C<sub>6</sub>H<sub>4</sub> unit, or the presence of one symmetric and frozen rotamer. In comparison to 2a the resonance at 9.41 ppm is strongly shifted towards lower field! The same is true for comparison of this value with the data of free 1,2-bis(diphenylphosphino)benzene ( $\delta$  = -14.3 ppm) [28]. This speaks for a pronounced deshielding of the phosphorus centers in compound 2b. Since 1,2bis(diphenylphosphino)benzene is well-known to form stable chelating and binuclear complexes with a whole series of transition metal fragments, the successful synthesis of 2a shall open up an access to a broad range of novel heterobi- and -trimetallic complexes.

To synthesize the heterobimetallic iron(II)-gold(I) complex **3**, the cationic phosphine ligand **2a** was reacted in dichlormethane with one equivalent of tetrahydrothiophene gold(I)

chloride. The reaction, which was performed under exclusion of light, was finished in between 30 min. After work-up, **2a** was obtained as a yellow solid in yields of 71%.



Scheme 2. Synthesis of the iron(II)-gold(I) complex 3.

ESI mass spectrometry (m/z = 614.9; calcd.: 615.0) as well as elemental analysis confirm the synthesis of  $[(\eta^{5}-Cp)Fe(\eta^{6}-C_{6}H_{5}PPh_{2}(AuCI))](PF_{6})$  (**3**). In the <sup>1</sup>H NMR spectrum, there is a singlet at 4.95 ppm, being assigned to the resonance of the  $\eta^{5}$ -Cp protons. This resonance is slightly shifted to higher field compared to the data of **2a**, which can be interpreted as the result of an enhanced steric shielding of these protons due to the presence of the AuCI moiety. The resonances of the coordinating six-membered ring are found in the region between 6.25 and 6.40 ppm, those of the two non-coordinating phenyl rings are observed at 7.49 to7.70 ppm. The coordination of the phosphorus atom to the gold(I) site is most clearly visible in the <sup>31</sup>P NMR spectrum: The according resonance appears as a singlet at 32.2 ppm, thus as expected strongly shifted to lower field compared to **2a** due to the coordination of the gold(I) center. The resonance of the analogue ruthenium complex  $[(\eta^{5}-Cp)Ru(\eta^{6}-C_{6}H_{5}PPh_{2}(AuCI))](PF_{6})$  was observed at 35.6 ppm as documented in the literature [21].

By slow diffusion of diethyl ether into a saturated solution of **3** in dichloromethane, yellow crystals suitable for a single crystal X-ray structure analysis could be obtained. The heterobimetallic complex **3** crystallizes as a dimer in the monoclinic space group P2<sub>1</sub>. Figure 2 shows the structure of the cation **3** in the solid state and Figure 3 shows its dimeric structure.



**Figure 2.** Molecular structure of one of the two crystallographically independent cations of compound **3** in the solid state; characteristic bond lengths [Å], bond angles [°], and dihedral angles [°].The bond parameters for the second cation are almost identical: Au1-Cl1 2.282(2), Au1-P1 2.227(2), Fe1-C1 2.072(9), Fe1-C2 2.061(10), Fe1-C3 2.078(12), Fe1-C4 2.056(14), Fe1-C5 2.041(14), Fe1-C6 2.064(12), Fe1-C19 1.996(13), Fe1-C20 2.032(15), Fe1-C21 2.045(12), Fe1-C22 2.029(14), Fe1-C23 2.033(15), P1-C1 1.827(8), P1-C7 1.814(8), P1-C13 1.804(8), Cl1-Au1-P1 170.59(7), Au1-P1-C1 109.9(3), Au1-P1-C7 119.0(3), Au1-P1-C13 112.0(3), Au1-P1-C1-C2 45.4(8).



**Figure 3.** Molecular structure of the Au-Au bound dimer of compound **3** in the solid state; characteristic bond lengths [Å] and dihedral angles [°]: Au1-Au2 3.179(6), Cl1-Au1-Au2-Cl2 107.93(7), P1-Au1-Au2-P2 113.48(7), Cl1-Au1-Au2-P2 69.21(7), Cl2-Au2-Au1-P1 69.38(8).

In the dimeric structure, two cationic subunits are connected via a typical gold(I)-gold(I) (d<sup>10</sup>d<sup>10</sup>) interaction [29,30,31]. The bond length (d<sub>AuAu</sub>: 3.179 Å) is shorter than the sum of the van-der-Waals radii of gold(I) (3.32 Å). The Au-Cl vectors of the two subunits are opening up a dihedral angle (Cl1-Au1-Au2-Cl2) of 107.9°. The structural parameters of both subunits are almost identical: In contrast to chlorido(triphenylphosphine)gold(I), which comprises an almost linear P-Au-Cl arrangement [32], P-Au-Cl angles of 170.9° and 170.6° are found for **3**. This is not due to a steric repulsion between the P-Au-Cl fragment and the ( $\eta^6$ -Cp)Fe( $\eta^6$ -C<sub>6</sub>H<sub>5</sub>) site, since the bending of the P-Au-Cl angle brings this fragment closer to the iron center. In contrast there might be a weak attraction between the cationic center and the electron rich gold(I) ion or weak hydrogen bonds between the chlorido ligand and the protons of the neighboring cyclopentadienyl protons. The P-Au distances (2.238(2) and 2.227(2) Å) are close to the value found for chlorido(triphenylphosphine)gold(I) [33]. The distances between the iron(II) center and the carbon atoms of the coordinating sixmembered ring are in sum shorter than those found for the precursor compound (**2a**).

#### Conclusion

We were able to show, that nucleophilic aromatic substitution opens up an efficient route for the synthesis of triaryl phosphine ligands containing the  $\eta^5$ -CpFe<sup>+</sup> fragment being coordinated to one of the phosphine's aryl units. Hereby mono- as well as diphosphine ligands can be obtained. By coordination of the AuCl fragment, the first transition metal complex of such a cationic phosphine could be obtained. In the near future, other transition metal containing fragments will be reacted with the novel phosphine ligands described herein. The electronic impact of the cationic aryl substituent on spectroscopic features as well as on the reactivity of the desired multimetallic complexes will be investigated.

#### **Experimental section**

**General Remarks:** All reactions were carried out under an argon atmosphere using Schlenk techniques. The solvents were dried and degassed before use according to standard techniques. Other reagents were obtained from commercial suppliers and used as received. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on BRUKER Spectrospin Avance 200, 400 and 600 spectrometers. The chemical shifts are referenced to internal solvent resonances. Infra-red spectra were recorded on a Perkin Elmer FT-ATR-IR spectrometer Spectrum 100 equipped with a diamond coated ZnSe window. ESI-mass measurements were performed on a BRUKER Esquire 6000plus device by introducing solutions of the compounds in acetonitrile. Elemental analyses were carried out with a vario MICRO cube elemental analyzer at the Analytical Department of the Technische Universität Kaiserslautern. Compounds **1a** and **1b** were obtained according to procedures published in the literature [13]. The NMR spectra of the iron complexes generally show slightly broadened resonances. This might be due to some paramagnetic impurities and hinders the assignment of P,C-coupling constants.

( $\eta^6$ -Diphenylphosphinobenzene)( $\eta^5$ -cyclopentadienyl)iron(II) hexafluorophosphate (2a): 0.8 mL (688 mg, 2.00 mmol) of *n*-butyllithium were added drop-wise to a solution of 250 mg (1.34 mmol) of diphenylphosphine in 10 mL of diethyl ether kept at -30 °C. The reaction mixture was stirred for 4 h while slowly warming up to room temperature. The solvent was removed under vacuum and the crude product was washed two times with 15 mL of *n*pentane. The resulting yellow solid was dissolved in 20 mL of THF. 521 mg (1.38 mmol) of  $\eta^6$ -

chlorobenzene- $\eta^5$ -cyclopentadienyliron(II) hexafluorophosphate **(1a)** were added and the solution was stirred for further 18 h. The solvent was removed under vacuum and the crude product was redissolved in 20 mL of dichloromethane. The organic solution was filtered, the solvent was removed under vacuum and the crude product was washed two times with 15 mL of diethyl ether. Crystallization from dichloromethane/diethyl ether gave orange crystals. Yield: 502 mg (0.94 mmol, 71%). Elemental analysis calcd. for C<sub>23</sub>H<sub>20</sub>F<sub>6</sub>FeP<sub>2</sub>: C 52.30, H 3.82, found: C 51.98, H 3.77%. <sup>1</sup>H NMR (600.13 MHz, acetone-d<sup>6</sup>):  $\delta$  7.53–7.51 (m, 10 H, H<sub>Ph</sub>), 6.60 (d, <sup>3</sup>J<sub>HH</sub> = 4.3 Hz, 2 H, H-2), 6.57 (t, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 1 H, H-4), 6.21 (t, <sup>3</sup>J<sub>HH</sub> = 5.4 Hz, 2 H, H-3), 5.23 (s, 5 H, H<sub>Cp</sub>) ppm. <sup>13</sup>C(<sup>1</sup>H} NMR (150.92 MHz, acetone-d<sup>6</sup>):  $\delta$  135.2 (C-9), 135.0 (C-10), 131.3 (C-7), 130.2 (C-8), 103.0 (C-1), 91.2 (C-3), 89.4 (C-2), 88.8 (s, C-4), 78.6 (C<sub>Cp</sub>) ppm. <sup>31</sup>P(<sup>1</sup>H} NMR (376.46 MHz, acetone-d<sup>6</sup>):  $\delta$  -5.9 (s), -144.2 (sept, <sup>1</sup>J<sub>PF</sub> = 707.9 Hz, PF<sub>6</sub><sup>-</sup>) ppm. <sup>19</sup>F(<sup>1</sup>H} NMR (376.46 MHz, acetone-d<sup>6</sup>):  $\delta$  -72.5 (d, <sup>1</sup>J<sub>PF</sub> = 707.7 Hz, PF<sub>6</sub><sup>-</sup>) ppm. ESI MS (acetonitrile): m/z = 383.1 [CpFeC<sub>6</sub>H<sub>5</sub>PPh<sub>2</sub>]<sup>+</sup>. IR (ATR): v = 3121w, 2963w, 2874w, 1588w, 1572w, 1506w, 1479w, 1436m, 1421m, 1403w, 1318w, 1287w, 1160w, 1122w, 1097w cm<sup>-1</sup>.

 $(\eta^{6}-1,2-Bis(diphenylphosphino)benzene)(\eta^{5}-cyclopentadienyl)iron(II) hexafluorophosphate$ (2b): 1.6 mL (1.38 mg, 4.00 mmol) of n-butyllithium were added drop-wise to a solution of 500 mg (2.68 mmol) of diphenylphosphine in 10 mL of diethyl ether at -30 °C. The reaction mixture was stirred for 4 h while slowly warming up to room temperature. The solvent was removed under vacuum and the crude product was washed twice with 15 mL of *n*-pentane. The obtained yellow solid was dissolved in 20 mL of THF. 553 mg (1.34 mmol) of  $\eta^6$ -1,2dichlorobenzene- $\eta^5$ -cyclopentadienyliron(II) hexafluorophosphate were added and the solution was stirred for further 18 h, while the color of the solution turned from green to dark red. The solvent was removed under vacuum and the crude product was redissolved in 20 mL of dichloromethane. The organic solution was filtered and the solvent was removed under vacuum. The crude product was washed twice with 15 mL of diethyl ether yielding 400 mg (0.56 mmol, 42%) of a reddish brown solid. Elemental analysis calcd. for C<sub>35</sub>H<sub>29</sub>F<sub>6</sub>FeP<sub>3</sub>: C 59.01, H 4.10, found: C 59.31, H 4.21%. <sup>1</sup>H NMR (400 MHz, acetonitrile- $d^3$ ):  $\delta$  7.30-7.45 (m, 20 H, H<sub>Ph</sub>), 6.75 (m, 2 H, H-4), 6.30 (m, 2 H, H-3), 5.16 (s, 5 H, H<sub>Cp</sub>) ppm. <sup>13</sup>C{<sup>1</sup>H} NMR (101 MHz, acetonitrile-d<sup>3</sup>): δ 134.4 (C-9), 130.9 (C-10), 129.2 (C-7), 127.7 (C-8), 107.8 (C-1), 89.7 (C-4), 88.6 (C-3), 82.1 ( $H_{Cp}$ ) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, acetonitrile- $d^3$ ):  $\delta$  9.41 (s), -144.6

(sept,  ${}^{1}J_{PF}$  = 706.2 Hz, PF<sub>6</sub>) ppm.  ${}^{19}F{}^{1}H$  NMR (376 MHz, acetonitrile- $d^{3}$ ):  $\delta$  -72.9 (d,  ${}^{1}J_{PF}$  = 707.7 Hz, PF<sub>6</sub>) ppm. ESI MS (acetonitrile): m/z = 567.1 [CpFeC<sub>6</sub>H<sub>4</sub>-(PPh<sub>2</sub>)<sub>2</sub>]<sup>+</sup>.

# $(\eta^{6}-Diphenylphosphinobenzene)(\eta^{5}-cyclopentadienyl)iron(II)gold(I)chloride$

hexafluorophosphate (3): 112 mg (0.36 mmol) of chloro(tetrahydrothiophene)gold(I) were added to a solution of 173 mg (0.34 mmol) of **1** in 15 mL of dichloromethane. The mixture was stirred for 30 min at room temperature in the absence of light. The solvent was removed under vacuum and the crude product was washed twice with 5 mL of diethyl ether. Crystallization from dichloromethane/diethyl ether gave 176 mg (0.24 mmol, 71%) of prismatic yellow crystals. Elemental analysis calcd. for C<sub>23</sub>H<sub>20</sub>AuClF<sub>6</sub>FeP<sub>2</sub>: C 36.32, H 2.65, found: C 36.22, H 2.44%. <sup>1</sup>H NMR (400 MHz, acetonitrile-*d*<sup>3</sup>): δ 7.80-7.25 (m, 10 H, H<sub>Ph</sub>), 6.33 (m, 5 H, H<sub>Ar</sub>), 4.95 (s, 5 H, H<sub>Cp</sub>) ppm. <sup>31</sup>P{<sup>1</sup>H} NMR (162 MHz, acetonitrile-*d*<sup>3</sup>): δ 32.20 (s), -144.6 (sept, <sup>1</sup>J<sub>PF</sub> = 706.2 Hz, PF<sub>6</sub><sup>-</sup>) ppm. <sup>19</sup>F{<sup>1</sup>H} NMR (376 MHz, acetonitrile-*d*<sup>3</sup>): δ -72.9 (d, <sup>1</sup>J<sub>PF</sub> = 707.7 Hz, PF<sub>6</sub><sup>-</sup>) ppm. ESI MS (acetonitrile): *m/z* = 615.0 [CpFeC<sub>6</sub>H<sub>5</sub>-PPh<sub>2</sub>(AuCl)]<sup>+</sup>.

**X-ray structure determinations:** Crystal data and refinement parameters are collected in Table 1. The structures were solved using a direct method (SIR92 [34]), completed by subsequent difference Fourier syntheses, and refined by full-matrix least-square procedures [35]. Semi-empirical absorption correction from equivalents (Multiscan) was carried out for compound **2a**, while analytical numeric absorption correction was performed on complex **3** [36]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in calculated positions and refined using a riding model.

|  | 2a                         | 3                          |
|--|----------------------------|----------------------------|
| empirical formula                                  | $C_{23}H_{20}F_{6}FeP_{2}$ | $C_{23}H_{20}AuClF_6FeP_2$ |
| formula weight                                     | 528.18                     | 760.60                     |
| temperature / K                                    | 150(2)                     | 150(2)                     |
| wavelength / Å                                     | 1.54184                    | 0.71073                    |
| crystal system                                     | monoclinic                 | monoclinic                 |
| space group  | P 2 <sub>1</sub> / c       | P 2 <sub>1</sub>           |
| a /Å   | 10.4305(2)                 | 9.2349(2)                  |
| <i>b</i> /Å  | 20.9065(4)                 | 24.0489(4)                 |
| c /Å   | 10.1661(2)                 | 10.9736(2)                 |
| lpha /°  | 90                         | 90                         |
| $oldsymbol{eta}$ /°                                | 97.910(2)                  | 96.965(2)                  |
| $\gamma/^{\circ}$                                  | 90                         | 90                         |
| $V/Å^3$  | 2195.78(7)                 | 2419.13(8)                 |
| Z  | 4                          | 4                          |
| D <sub>calcd.</sub> /Mg/m <sup>3</sup>             | 1.598                      | 2.088                      |
| absorption coefficient /mm <sup>-1</sup>           | 7.438                      | 6.957                      |
| F(000)   | 1072                       | 1456                       |
| $\theta$ range for data collection/°               | 4.23 to 62.64              | 2.794 to 32.489            |
| index ranges                                       | -11<=h<=11                 | -11<=h<=13                 |
|  | -16<=k<=24                 | -36<=k<=19                 |
|  | -10<=l<=11                 | -16<=l<=16                 |
| reflections collected                              | 15075                      | 16220                      |
| R <sub>int</sub>                                   | 0.0382                     | 0.0308                     |
| data/restraints/parameters                         | 3511/0/289                 | 10082/121/613              |
| goodness-of-fit on F <sup>2 a</sup>                | 1.038                      | 1.023                      |
| final $R_{int} [I > 2\sigma (I)]^{b}$              | R1 = 0.0420                | R1 = 0.0381                |
|  | wR2 = 0.1156               | wR2 = 0.0652               |
| R <sub>int</sub> (all data)                        | R1 = 0.0474                | R1 = 0.0459                |
|  | wR2 = 0.1176               | wR2 = 0.0678               |
| absolute structure parameter                       | -                          | 0.004(5)                   |
|  | 0.822 and -                | 1.021 and -1.166           |
| largest difference peak and hole/e-A <sup>-3</sup> | 0.301                      |                            |

<sup>a</sup> GooF =  $[\Sigma\omega(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ ; <sup>b</sup>  $R_1 = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$ ,  $\omega R_2 = [\Sigma\omega(F_o^2 - F_c^2)^2/\Sigma\omega Fo2]^{1/2}$ 

# Acknowledgement

We gratefully thank the DFG-funded transregional collaborative research center SFB/TRR 88 "Cooperative effects in homo- and heterometallic complexes (3MET)" for the financial support.

#### Scheme, Figure and Table captions

Scheme 1. Synthesis of the cyclopentadienyl iron(II) arene complexes 1a,b and 2a,b.

**Figure 1.** Molecular structure of **2a** in the solid state; characteristic bond lengths [Å] and bond angles [°]: Fe1-C1 2.052(4), Fe1-C2 2.055(3), Fe1-C3 2.053(4), Fe1-C4 2.060(3), Fe1-C5 2.055(3), Fe1-C6 2.068(3), Fe1-C7 2.078(3), Fe1-C8 2.091(3), Fe1-C9 2.083(3), Fe1-C10 2.082(3), Fe1-C11 2.104(3), P1-C11 1.847(3), P1-C12 1.826(3), P1-C18 1.840(3), P2-F4 1.596(2), P2-F5 1.562(3), P2-F6 1.609(2), P2-F2 1.586(2), P2-F3 1.580(2), P2-F1 1.605(3), C11-P1-C12 100.75(13), C11-P1-C18 100.76(14), C12-P1-C18 103.73(14).

Scheme 2. Synthesis of the iron(II)-gold(I) complex 3.

**Figure 2.** Molecular structure of one of the two crystallographically independent cations of compound **3** in the solid state; characteristic bond lengths [Å], bond angles [°], and dihedral angles [°].The bond parameters for the second cation are almost identical: Au1-Cl1 2.282(2), Au1-P1 2.227(2), Fe1-C1 2.072(9), Fe1-C2 2.061(10), Fe1-C3 2.078(12), Fe1-C4 2.056(14), Fe1-C5 2.041(14), Fe1-C6 2.064(12), Fe1-C19 1.996(13), Fe1-C20 2.032(15), Fe1-C21 2.045(12), Fe1-C22 2.029(14), Fe1-C23 2.033(15), P1-C1 1.827(8), P1-C7 1.814(8), P1-C13 1.804(8), Cl1-Au1-P1 170.59(7), Au1-P1-C1 109.9(3), Au1-P1-C7 119.0(3), Au1-P1-C13 112.0(3), Au1-P1-C1-C2 45.4(8).

**Figure 3.** Molecular structure of the Au-Au bound dimer of compound **3** in the solid state; characteristic bond lengths [Å] and dihedral angles [°]: Au1-Au2 3.179(6), Cl1-Au1-Au2-Cl2 107.93(7), P1-Au1-Au2-P2 113.48(7), Cl1-Au1-Au2-P2 69.21(7), Cl2-Au2-Au1-P1 69.38(8).

**Table 1.** Crystallographic data, data collection and refinement.

## References

- [1] P. Stepnicka (Ed.), Ferrocenes: Ligands, Materials and Biomolecules, John Wiley & Sons, Hoboken, 2008.
- [2] H. Togni, Ferrocenes: Homogeneous Catalysis, Organic Synthesis, Materials Science, John Wiley & Sons, Hoboken, 1995.
- [3] D. Schaarschmidt, H. Lang, Organometallics 2013 (32) 5668.
- [4] R. Gomez Arrayas, J. Adrio, J. C. Carretero, Angew. Chem. Int. Ed. 45 (2006) 7674.
- [5] H. U. Blaser, B. Pugin, F. Spindler, M. Thommen, Acc. Chem. Res. 40 (2007) 1240.
- [6] H. Dai, Chiral Ferrocenes in Asymmetric Catalysis, John Wiley & Sons, Hoboken, 2010.
- [7] N. A. Butt, D. L. Liu, W. B. Zhang, Synlett 25 (2014) 615.
- [8] C. S. Slone, C. A. Mirkin, G. P. A. Yap, I. A. Guzei, A. L. Rheingold, J. Am. Chem. Soc. 119 (1997) 10743.
- [9] P. Neumann, H. Dib, A. M. Caminade, E. Hey-Hawkins, Angew. Chem. Int. Ed. 54 (2015) 311.
- [10] C. K. A. Gregson, V. C. Gibson, N. J. Long, E. L. Marshall, P. J. Oxford, A. J. P. White, J. Am. Chem. Soc. 128 (2006) 7410.
- [11] R. Savka, S. Foro, M. Gallei, M. Rehahn, H.Plenio, Chem. Eur. J. 19 (2013) 10655.
- [12] A. N. Nesmeyanov, N. A. Vol'kenau, I. N. Bolesova, Tetrahedron Lett. 1963, 4, 1725.
- [13] I. U. Khand, P. L. Pauson, W. E. Watts, J. Chem. Soc. C 17 (1968) 2261.
- [14] A. S. Abdelaziz, Y. Lei, C. R. Dedenus, Polyhedron 14 (1995) 1585.
- [15] N. Raouafi, N. Belhadj, K. Boujlel, Ourari, C.Amatore, E. Maisonhaute, B. Schollhorn, Tetrahedron Lett. 50 (2009) 1720.
- [16] A. S. Abdelaziz, E. K. Todd, T. H. Afifi, Macromol. Rapid Commun. 23 (2002) 113.
- [17] A. S. Abdelaziz, C. R. de Denus, H. M. Hutton, Can. J. Chem. 73 (1995) 289.
- [18] M. Gaffga, I. Munstein, P. Müller, J. Lang, W. R. Thiel, G. Niedner-Schatteburg, J. Phys. Chem., DOI: 10.1021/acs.jpca.5b06952.
- [19] Q. Dabirmanesh, S. I. S. Fernando, R. M. G. Roberts, J. Chem. Soc., Perkin Trans. 1 7 (1995) 743.
- [20] Y. Yamamoto, H. Danjo, K. Yamaguchi, T. Imamoto, J. Organometal. Chem. 693 (2008) 3546.
- [21] M. R. Axet, M. Barbazanges, M. Augé, C. Desmarets, J. Moussa, C. Ollivier, C. Aubert, L. Fensterbank, V. Gandon, M. Malacria, L. M. Chamoreau, H. Amouri, Organometallics 29 (2010) 6636
- [22] L. T. Ball, M. Green, G. C. Lloyd-Jones, C. A. Russell, Org. Lett. 12 (2010) 4724.
- [23] J. Dubarle-Offner, M. Barbazanges, M. Augé, C. Desmarets, J. Moussa, M. R. Axet, C. Ollivier, C. Aubert, L. Fensterbank, V. Gandon, M. Malacria, G. Gontard, H. Amouri, Organometallics 32 (2013) 1665.
- [24] C. C. Brasse, U. Englert, A. Salzer, H. Waffenschmidt, P. Wasserscheid, Organometallics 19 (2000) 3818.
- [25] S. O. Grim, A. W. Yankowsky, J. Org. Chem. 42 (1977) 1236.
- [26] J. A. Adeleke, Acta Cryst. C49 (1993) 680.
- [27] H. A. Bent, Chem. Rev. 61 (1961) 275.
- [28] G. A. Bowmaker, Chem. Ber. 116 (1983) 3567.
- [29] H. Schmidbaur, A. Schier, Chem. Soc. Rev. 37 (2008) 1931.
- [30] H. Schmidbaur, A. Schier, Chem. Soc. Rev. 41 (2012) 370.
- [31] P. Pyykko, W. Schneider, A. Bauer, A. Bayler, H. Schmidbaur, Chem. Commun. (1997) 1111.

- [32] N. C. Baenziger, W. E. Bennett, D. M. Soborofe, Acta Crystal. B 32 (1976) 962.
- [33] A. O. Borissova, A. A. Korlyukov, M. Yu. Antipin, K. A. Lyssenko, J. Phys. Chem. A 112 (2008) 11521.
- [34] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camilli, J. Appl. Crystallogr. 27 (1994) 435.
- [35] G. M. Sheldrick, Acta Crystallogr. A, 64 (2008) 112.
- [36] CrysAlisPro, Agilent Technologies, Version 1.171.36.32, 2013 and Version 1.171.37.31, 2014.

CHR MAR

# Highlights

- two novel cationic phosphines bearing a  $\eta^6$ -coordinated ( $\eta^5$ -Cp)Fe<sup>+</sup> moiety synthesized
- one of these ligands was structurally characterized by X-ray structure analysis
- a transition metal complex (gold) of such a ligand synthesized
- structural characterization of the gold complex by X-ray structure analysis

CER MAN