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Synthesis, characterization and electrochemical behavior of unsymmetric transition metal-terminated biphenyl ethynyl thiols

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Abstract

The synthesis of the biphenyl alkynyl thiols and thioesters $R'-C \equiv C-C_6H_4-SR$ (3: $R' = SiMe_3$, R = C(O)Me; 4: $R' = SiMe_3$, R = H; 5: R' = H, R = C(O)Me) from I–C₆H₄–C₆H₄–SC(O)Me (1) is described. Molecules 1 and 5 have been used as starting materials in the synthesis of mono- and heterobimetallic transition metal complexes of type $L_nM'-C \equiv C-C_6H_4-C_6H_4-SR$ (7: $L_nM' = Fc$, R = C(O)Me; 8: $L_nM' = Fc$, R = H; 10: $L_nM' = (Ph_3P)Au$, R = C(O)Me; 14: $L_nM' = FcPPh_2-Au$, R = C(O)Me; $Fc = (\eta^5-C_5H_5)(\eta^5-C_5H_4)Pe$). While complex 7 is accessible by the Sonogashira cross-coupling of Fc–C $\equiv CH$ (6) with 1, molecules 10 and 14 can be prepared by treatment of the thioester 5 with (Ph_3P)AuCl (9) and FcPPh_2-AuCl (13), respectively.

The molecular solid state structures of **3**, **7**, **10** and **13–15** have been determined by single crystal X-ray crystallographic analysis. Typical features of these species are their linear M-C \equiv C-C₆H₄-C₆H₄-SR structure and the lack of coplanarity of the biphenyl arene rings. The overall length of these complexes are 13.345(2) Å for **3** (molecule A), 15.146(3) Å for **7**, 15.705(2) Å for **10** (molecule A) and 15.649(4) Å for **14**. The thioester groups are pointing away from the ferrocene building block. In **7** a linear 1D chain is set-up by π -interactions between two independent molecules of **7**. Characteristic for **15** is the formation of a Au₂I₂ ring, while **13** is monomeric.

All compounds were studied with cyclic voltammetry. Characteristic are the reversible ferrocene Fe(II)/Fe(III) redox wave, the irreversible reduction of Au(I) to Au(0), the oxidative cleavage of the S–C(O)Me sulfur–carbon (3, 5, 7, 10 and 14) and of the sulfur–hydrogen bond (4 and 8), respectively. Electronic effects extending from the –SH-end group to the ferrocene unit resulting in considerable shifts of the redox potential of the latter entity are found. Coordination of Au(I) at the FcPPh₂ moiety also results in a shift of the redox potential of the ferrocene group indicative of an electron withdrawing effect of the Au(I) species. © 2006 Elsevier B.V. All rights reserved.

Keywords: Ferrocene; Gold; Thiol; Thioester; Biphenyl; Alkyne; X-ray structure; Cyclic voltammetry

1. Introduction

The fabrication of electrochemically and catalytically active surfaces and 2D templates is an important challenge from both, scientific viewpoint and in view of possible practical applications [1]. A promising bottom-up approach for the preparation of the respective systems is molecular selfassembly, involving the functionalization of the relevant substrate by the so-called self-assembled monolayers (SAMs) [2,3,11], which are 2D polycrystalline films of semi-rigid molecules that are chemically anchored to the substrate. A large advantage of these systems is a flexible molecular architecture of the SAM constituents, which generally consist of three essential parts: a head group that binds strongly to the substrate, a tail group that constitutes

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the outer surface of the film, and a spacer that separates head and tail groups. Within this general framework, one can combine different moieties and functional groups to a simple rod-like molecule, a complex assembly, or even a molecular device, which carry an active element, connected to the substrate over the spacer and headgroup. As such active element, different functional groups can be used, including molecular switches, rectifying optically active moieties, redox complexes, etc. Among other possibilities, promising active elements are ferrocenes, which are very robust compounds and excellent organometallic one-electron reservoirs [4]. In the entire molecular device, the ferrocene unit should be electrically connected to the substrate by a suitable molecular spacer, which should possess a possibly high electric conductivity. In this regard, a oligophenyl or phenylene-ethenylene chain is the best choice, considering that these moieties have much lower resistance as compared to the aliphatic chain frequently used in the SAM design [5.6]. In addition, the headgroup is of importance. since the contact resistance of the molecule to the substrate depends strongly on its bonding [7,8]. In this regard, a thiol derivative headgroup is a good choice, since the respective anchor has a high affinity to many metal and semiconductor surfaces and is characterized by a quite low contact resistance [7,8]. Another argument in favor of the thiol derivatives is the fact that thiol-derived SAMs are the most frequently studied SAM systems at present, available results include analysis of their structure, thermodynamics and kinetics of their formation, and design of application-relevant systems [3,9–12]. Next to ω -functionalized alkanethiols, also organometallic thiols and thioesters based on ferrocene have been studied in detail [12,13].

Recently, we used functionalized ferrocenes in the synthesis of multi(hetero)metallic complexes in which the different transition metals are connected by π -conjugated organic and/or inorganic bridges [14]. Based on these studies, we focused recently our attention on the synthesis of unsymmetric biphenyl-thiol- and -thioester-functionalized ferrocenes, because this permits systematic modification and, hence, studies of the nature of interfacial barriers to gain a more universal structure-relationship how structural effects can mediate electron transfer [15].

Herein, we report on an efficient synthesis of biphenyl ethynyl terminated thioesters. A general synthetic scheme for the preparation of mono- and heterobimetallic ferrocene and/or triphenylphosphine gold biphenyl ethynyl thioesters and their transformation to the appropriate thiols is discussed as well. In addition, the electrochemical redox and solid state properties of the latter molecules will be presented.

2. Results and discussion

As shown in Scheme 1, the thio-acetyl molecule $Me_3Si-C \equiv C-C_6H_4-C_6H_4-SC(O)Me$ (3) can be synthesized in a straightforward manner through the palladium–copper catalyzed Sonogashira cross-coupling of $I-C_6H_4-C_6H_4-SC(O)Me$ (1) with $Me_3SiC \equiv CH$ (2). Compound 3 can be converted to $Me_3Si-C \equiv C-C_6H_4-C_6H_4-SH$ (4) by its consecutive reaction with NH_4OH and HCl in tetrahydrofuran as solvent at room temperature (Scheme 1). When 3 is treated with ["Bu₄N]F in a ratio of 1:2.5 and a proton source is added, then $HC \equiv C-C_6H_4-C_6H_4-SC(O)Me$ (5) is accessible (Scheme 1).

Compounds 3–5 were characterized by elemental analysis, NMR (${}^{1}H$, ${}^{13}C{}^{1}H$ }, ${}^{29}Si{}^{1}H$) and IR spectroscopy. The exchange of the Me₃Si and the C(O)Me groups in 3 with hydrogen to give 4 and 5 is indicated by very prominent resonance signals and vibrations, which allow to monitor the



Scheme 1. Synthesis of 3-5 (Ac = C(O)Me).



Fig. 1. ORTEP plot (50% probability level) of the three crystallographically independent molecules of 3(3A-3C) with the atom numbering scheme. The orientations shown for 3A-3C are related to their arrangement in the asymmetric unit.

progress of the appropriate reaction by NMR and IR spectroscopy (Section 3).

Single crystals of **3** suitable for X-ray diffraction studies could be grown from a saturated dichloromethane solution at 25 °C. The molecular structure of **3** is shown in Fig. 1. Compound **3** crystallizes in the triclinic space group $P\overline{1}$ with the three crystallographically independent molecules **3A–3C** within the asymmetric unit. Selected bond distances (Å) and bond angles (°) are summarized in Table 1. Crystallographic and refinement data are given in Section 3 (Table 6).

Related bond lengths of 3A-3C are equivalent within their standard deviations, while bond angles of 3A-3Cshow some differences (Table 1). The major difference between 3A and 3C are the dihedral angles of the biphenyl units being 26.8(2)° for 3A (C6–C11 vs. C12–C17), 22.8(2)° for 3B (C25–C30 vs. C31–C36) and 36.2(1)° for 3C (C44– C49 vs. C50–C55). This indicates that no favorable rotamere of 3A-3C exists in the solid state. The difference of the dihedral angles in 3A-3C can most likely be explained by packing effects (see Table 2).

Table 2 Selected bond distances $({\rm \mathring{A}})$ and bond angles (°) for $7^{\rm a}$

Bond distances					
C6C11	1.430(3)	C11-C12	1.193(3)	C12C13	1.440(3)
C16-C19	1.484(3)	C22-S1	1.776(2)	S1-C25	1.795(3)
C25–O1	1.196(3)	C25-C26	1.500(3)	Fe1–D1 ^b	1.648(1)
Fe1–D2 ^b	1.645(1)				
Bond angles					
C6-C11-C12	178.2(3)		C11-C12-	-C13	179.6(3)
C22-S1-C25	100.43(11)				

^a Standard uncertainties of the last significant digit(s) are shown in parenthesis.

^b D_1 = centroid of C_5H_5 , D_2 = centroid of C_5H_4 .

Table 1

Selected bond distances (Å) and bond angles (°) for the three independent molecules of 3^a

3A		3B		3C	
Bond distances					
Sil-C4	1.846(4)	Si2–C23	1.843 (4)	Si3-C42	1.840 (4)
C4–C5	1.204(5)	C23–C24	1.203(5)	C42–C43	1.197 (5)
C5-C6	1.437(5)	C24–C25	1.438(5)	C43–C44	1.440(5)
C9-C12	1.490(5)	C28–C31	1.497(4)	C47–C50	1.489(5)
C15-S1	1.771(4)	C34–S2	1.770(3)	C53–S3	1.772(3)
S1-C18	1.771(5)	S2-C37	1.789(4)	S3-C56	1.785(4)
C18-O1	1.194(6)	C37–O2	1.197(5)	C56–O3	1.198(4)
C18-C19	1.515(6)	C37–C38	1.502(5)	C56–C57	1.503(5)
Si1-S1	13.345(2)	Si2–S2	13.347(2)	Si3–S3	13.310(2)
Bond angles					
Si1-C4-C5	176.8(4)	Si2-C23-C24	175.5(4)	Si3-C42-C43	175.2(3)
C4-C5-C6	179.4(4)	C23-C24-C25	178.8(4)	C42-C43-C44	178.0 (4)
C15-S1-C18	104.01(19)	C34–S2–C37	104.10(17)	C53-S3-C56	102.33(16)

^a Standard uncertainties of the last significant digit(s) are shown in parenthesis.



Fig. 2. Graphical representation of the π - π -interaction (C7–C7A) between pairs of **3A** (d(C7–C7A) = 3.313 Å).

Within the asymmetric unit no π - π -interactions between molecules **3A**-**3C** exist. However, such a structural motif is found for a pair of two molecules of **3A** as given by the distance of 3.313 Å between C7 and C7A, respectively, which is remarkable short (Fig. 2) [16].

All other bond distances and angles of **3** agree well with those reported for similar molecules [17]. Finally, the overall length of a single molecule of **3** is 13.345(2) Å for **3A**, 13.347(2) Å for **3B** and 13.310(2) Å for **3C** as calculated between Si(1,2,3) and S(1,2,3) (Fig. 1).

The thio acetyl derivatives 1 and 5 are particularly well suited to prepare the ferrocene and triphenylphosphine gold complexes 7, 10 and 14 as shown in Eq. (1) and Schemes 2 and 3, respectively.

Carbon-carbon cross-coupling catalyzed by transition metals can successfully be used to prepare linear Fc-C= C-C₆H₄-C₆H₄-SC(O)Me (7) (Fc = $(\eta^5$ -C₅H₅)(\eta^5-C₅H₄)Fe) (Scheme 2). In this respect, I-C₆H₄-C₆H₄-SC(O)Me (1) was reacted with FcC=CH (6) in presence of catalytic amounts of [(Ph₃P)₂PdCl₂/CuI] in triethylamine as solvent



Scheme 3. Synthesis of 14 by reacting 13 with 5 (Ac = C(O)Me, tht = tetrahydrothiophene).

following the Sonogashira cross coupling protocol (Scheme 2) [18]. After appropriate work-up, complex 7 could be isolated as an orange solid in 83% yield. The *S*-acetyl group in 7 can successfully be converted to a SH moiety by the subsequent reaction of 7 with NH_4OH and HCl under similar reaction conditions as described for the synthesis of 4 (vide supra).

In order to obtain structural parameters that might be of interest in the investigation of SAMs derived from such complexes we carried out a single X-ray structure analysis of 7. Orange single crystals could be obtained by slow evaporation of a diethyl ether solution containing 7 at 5 °C. Geometric details are listed in Fig. 3 and experimental crystal data in Table 6 (Section 3).

Compound 7 is set-up by the sandwich unit (η^5) - C_5H_5)(η^5 - C_5H_4)Fe and the biphenyl ethynyl moiety $C \equiv C - C_6 H_4 - C_6 H_4 - SC(O) Me$ (Fig. 3). The carbon-carbon triple bond involved in connecting together the organometallic and organic entities is 1.193(3) Å (C11–C12) which is typical for this type of bonding [19]. The two cyclopentadienyl rings are nearly parallel oriented to each other $(1.9(2)^{\circ})$ with D₁-Fe-D₂ separations being 1.648(1) and 1.645(1) Å (D₁ = centroid of the cyclopentadienyl ring C_5H_5 , D_2 = centroid of the cyclopentadienyl ring C_5H_4). As shown in Fig. 3, the aromatic rings defined by C13-C18 and C19–C24 are rotated by 19.6(1)° and 14.0(1)°, respectively, into opposite directions of the cyclopentadienyl unit C6-C10. The dihedral angle of C13-C18 and C19–C24 is 33.0(1) ° assuming that in 7 the two biphenyl arene rings are free to rotate as already discussed for 3 (vide supra). The thio-acetyl group is pointing to the opposite site of the ferrocenyl sandwich entity. The overall length of 7 is with 15.146(3) Å and 15.149(3) Å, respectively, as calculated from C8 and C9 to the sulfur atom S1 by 1.81 Å longer as found for 3 (Fig. 1). Furthermore, 7 forms in the solid state a 1D-chain set-up by π -interactions (Fig. 4). Significant π -contacts are observed between C6A-C23B (3.587 Å), C7A-C23B (3.468 Å), C7A-C24B (3.467 Å), C8A–C24B (3.369 Å) and C9A–C19B (3.603 Å), whereby the suffixes A and B correspond to

two independent molecules of 7. Respecting this structural mode it finally leads to the 1D chain formation of 7.

A further possibility to introduce a thio-acetyl or thiolcontaining group in organometallic chemistry is outlined in Eq. (1) and Scheme 3 and involves the reaction of a phosphino gold(I) chloride entity with the alkyne $HC\equiv C-C_6H_4-C_6H_4-SC(O)Me$ (5). The gold acetylide (Ph₃P)Au-C $\equiv C-C_6H_4-C_6H_4-SC(O)Me$ (10) was prepared basically in accordance with the method reported by Vicente et al., i.e., treatment of 5 with (Ph₃P)AuCl (9) in triethylamine as solvent [20]. It should be mentioned that this reaction requires the addition of catalytic amounts of [CuI] to obtain colorless 10 in high yield [21].



A similar synthesis procedure can be used for the preparation of heterobimetallic $FcPh_2P-Au-C \equiv C-C_6H_4-C_6H_4-SC(O)Me$ (14) by reacting $FcPh_2P-AuCl$ (13) with 5 in a 1:1 molar ratio as depicted in Scheme 3. After appropriate work-up, complex 14 could be isolated in 53% yield.

Within the reaction of 5 with 13 heterobimetallic $FcPh_2P-AuI$ (15) is formed as side product in 3% yield. It could be separated from 14 by column chromatography (Section 3). An explanation for the formation of 15 is given by the halide exchange reaction between [CuI] and $FcPh_2P-AuCl$ (13), respectively.

All synthesized compounds are colorless (3–5 and 10), yellow (13, 14 and 15) or orange (7 and 8) crystalline materials that could be purified by conventional column chromatography (Section 3). They nicely dissolve in common organic polar solvents such as dichloromethane and tetrahydrofuran. All compounds are stable toward moisture



Fig. 3. ORTEP plot (50% probability level) of 7 with the atom numbering scheme.



Fig. 4. Schematic view of the 1D chain function of 7.

and air, except the SH-terminated species **4** and **8**. These compounds, both in the solid state and in solution, are all prone to oxidation (in solution more rapidly) to the corresponding disulfides. However, in deoxygenated and dried solvents they are stable and can be kept for months without decomposition.

Analytic and spectroscopic (IR, ¹H, ¹³C{¹H}, ³¹P{¹H}, ²⁹Si{¹H} NMR, ESI-TOF MS) analyses of **3–5**, **7**, **8**, **10** and **13–15** support their structural formulation as biphenyl ethynyl thiols and unsymmetric transition metal-terminated biphenyl ethynyl thiols (vide supra).

Structural information concerning the presence of the thioesters and thiol moieties in 3–5, 7, 8, 10 and 14 was obtained from the IR spectra (Section 3). Most informative are the C=C, C=O and SH vibrations. For the HC=C unit an absorption band is found at 2103 cm⁻¹, while the Me₃Si–C=C and L_nM–C=C building blocks show their C=C stretching frequencies between 2100 and 2200 cm⁻¹. The acetyl group in 3, 5, 7, 10 and 14 gives rise to a very characteristic band at ca. 1700 cm⁻¹, while the SH vibration in 4 and 8 is found at ca. 2560 cm⁻¹.

The ³¹P{¹H} NMR spectra are most informative in terms of the coordination mode of the phosphine groups or the exchange of the gold-bonded chloride in 9 and 13 by an acetylide moiety. A deshielding of the phosphorus atom in 11 is observed, when this unit is datively-bonded to a AuCl and Au–C=C–C₆H₄–C₆H₄–SC(O)Me moiety, respectively, i.e., 11: -17.52 ppm, 13: 27.6 ppm, 14: 36.4 ppm.

The ¹H and ¹³C{¹H} NMR spectra of the newly synthesized compounds are also conclusive, especially the C \equiv C, C(O)Me, C₅H₅ and C₅H₄ groups (Section 3).

Additionally, the molecular structures of **10**, **13**, **14** and **15** were determined by single X-ray diffraction. The solid

state structures of these species are shown in Figs. 5-9, the crystallographic data are summarized in Tables 6 and 7 (Section 3). From Figs. 5 to 9 it can be seen that the structures of **10** and **14** as well as **13** and **15** are essentially similar as far as the molecule backbone is concerned.

Mononuclear 10 crystallizes in the triclinic space group $P\bar{1}$ with two molecules in the asymmetric unit (10A, 10B), while heterobimetallic 14 crystallizes in the monoclinic space group P2(1)/c (Fig. 5: 10, Fig. 6: 14). In addition complex 14 exhibits a disorder of its terminal C₆H₄–SC(O)Me groups with occupation factors of 0.58 and 0.42. Selected bond lengths (Å) and bond angles (°) are given in Table 3 (10) and Table 4 (14).

Compounds 10 and 14 represent the first synthesized and structurally characterized transition metal complexes of type M–C \equiv C–C₆H₄–C₆H₄–SR (R = H, alkyl, aryl, C(O)Me, etc.), while complexes of structural type M– C \equiv C–C₆H₄–SR [22] and M–C₆H₄–C₆H₄–SR [23] are already described.

Most characteristic for **10** and **14** is their almost linear P–Au–C=C–C arrangement (**10A**: P1–Au1–C1 (177.0 (3)°), Au1–C1–C2 (177.0(3)°), C1–C2–C3 (176.3(4)°); **10B**: P2–Au2–C35 (177.69(10)°), Au2-C35-C36 (177.4 (3)°), C35–C36–C37 (178.3(4)°); **14**: P1–Au1–C23 (177.9 (2)°), Au1–C23–C24 (170.9(7)°), C23–C24–C25 (175.2 (8)°)) (Tables 3 and 4) and the lack of coplanarity of the biphenyl arene rings (Figs. 5 and 6). These structural features are similar to related species, i.e. $M-C=C-C_6H_4$ –SR [22] and $M-C_6H_4-C_6H_4$ –SR [23].

The ferrocenyl group in **14** with Fe1–D1 and Fe1–D2 separations of 1.640(3) and 1.634(3) Å, respectively, exhibits a nearly coplanar conformation of the cyclopentadienyl rings. The dihedral angle of the calculated mean plans of the cyclopentadienyl rings is $3.5(6)^{\circ}$.



Fig. 5. The molecular structures (ORTEP plot, 50% probability level) of the two crystallographically independent molecules of 10 (10A: above, 10B: below) with the atom numbering scheme. Hydrogen atoms are omitted for clarity. The orientation of 10A and 10B does not reflect their orientation within the asymmetric unit.



Fig. 6. The molecular structure of 14 (ORTEP plot, 50% probability level) with the atom numbering scheme. Only one position of the disordered terminal C_6H_4 -SC(O)Me group is shown.

For 14 unusual short intermolecular contacts between C29–C30A, C30–C30A, C30–C29A, C26A–C34B, C27A–C35B and C27A–C34B are observed in the solid state (Fig. 7). For 10 a similar trend is recognized, which most probably is originated from packing effects. Additionally, significant π -interactions are found for 14 as shown in Fig. 7. A 1D chain is formed by repeating sets of three molecules of 14. The overall length of 10 and 14 is 15.705(2) Å (P1–S1) for 10A, 15.750(2) Å (P2–S2) for 10B, 15.649(4) Å (P1–S1) and 15.751(5) Å (P1–S1') for 14.

The molecular solid state structures of FcPPh₂-AuX (13: X = Cl, 15: X = I) are shown in Fig. 8, selected bond

lengths (Å) and angles (°) are given in Table 5. Although the molecular structures of 13 and 15 are very similar, both complexes are not iso-structural. The reason therefore is the formation of Au···I contacts between two molecules of 15 (d(Au···I) = 3.817 Å) (Fig. 9). A similar behavior was found in (η^5 -C₅H₄PPh₂-AuI)₂Fe (d(Au···I) = 3.909 Å) as well as in its chloride derivative [24] (see Table 7).

The Au·I interactions in **15** are very weak, as the sum of the van der Waals radii of Au and I amounts to 3.65-3.82 Å [25]. In the case of $(\eta^5-C_5H_4PPh_2-AuI)_2Fe$ it is questionable, whether an interaction can be discussed or not, however, the *non*-isostructurality of $(\eta^5-C_5H_4PPh_2-AuI)_2Fe$



Fig. 7. π -Interactions between a set of three molecules of 14. Only the PhSAc unit with the major occupation is considered. d(C29-C30A) = 3.435 Å, d(C30-C30A) = 3.590 Å, d(C30-C29A) = 3.435 Å, d(C26A-C34B) = 3.578 Å, d(C27A-C35B) = 3.584 Å, d(C27A-C34B) = 3.594 Å.



Fig. 8. ORTEP plot (50% probability level) of the asymmetric unit of 13 (left) and 15 (right) with the atom numbering scheme.

vs. $(\eta^5-C_5H_4PPh_2-AuCl)_2Fe$ indicates a very weak Au···I contact, too. Further ((RR'R")P)AuI compounds which show intermolecular Au···I contacts are not described so far. Complexes of this type were either found to be monomeric (e.g. R = R' = R'' = Ph [26], 2,4,6-Me₃C₆H₂ [27]) or exhibiting Au–Au contacts (e.g. R = R' = Me, R'' = Ph [28]).

Due to the formation of a Au₂I₂ 4-membered ring in 15 the P1–Au1–I1 angle with 171.19(2)° deviates significantly from linearity, when compared with the P1–Au1–Cl1 angle (177.12(10)°) in 13. As observed for (η^5 -C₅H₄PPh₂– AuCl)₂Fe (d(P–Au) = 2.2262(13) Å) and (η^5 -C₅H₄PPh₂– AuI)₂Fe (d(P–Au) = 2.248(9)/2.240(8) Å) [24], the P–Au distances in 13 are significantly shorter, when compared with 15 (13: d(Au1–Pl) = 2.228(2) Å vs. 15: d(Au1– P1) = 2.2542(9) Å), which most probably can be explained by the higher *trans* influence of the iodide vs. the chloride ligand. A further structural feature of 13 vs. 15 is the different conformation of the cyclopentadienyl rings. For 13 a nearly ecliptic conformation is observed, whereas the respective rings in **15** adopt a staggered conformation. In both cases the cyclopentadienyl rings are nearly parallel oriented to each other, as expressed by their interplanar angles of the calculated mean planes (**13**: $1.4(8)^{\circ}$ and **15**: $2.4(3)^{\circ}$).

The gold-halide distances are 2.280(2) Å for 13 and 2.5758(3) Å for 15. These values are in close agreement with other phosphane–gold complexes featuring Au–Cl or Au–I bonds [24,28,29].

All compounds were studied with cyclic voltammetry. In positive going potential scans of 3 and 5 a current shoulder in the onset of electrolyte solution oxidation is observed at $E_{\text{FeC}} = 1.38$ V for 3 and at $E_{\text{FeC}} = 1.35$ V for 5 (Fig. 10); it is assigned to removal of an electron from the sulfur atom and subsequent cleavage of the S–C(O)Me sulfur–carbon bond with formation of an acylium cation and a sulfonium radical. Recombination of the latter species to a disulfide is conceivable, a weak cathodic current wave in the negative



Fig. 9. Intermolecular Au₂I₂ ring formation in 15 (d(Au···I) = 3.817 Å).

Table 3 Selected bond distances (Å) and bond angles (°) for 10^{a}

10A		10B	
Bond distances			
P1-C17	1.819(4)	P2-C51	1.816(4)
P1-C23	1.819(4)	P2-C57	1.822(3)
P1-C29	1.813(3)	P2-C63	1.821(4)
P1–Au1	2.2758(9)	P2–Au2	2.2733(9)
Au1–C1	2.009(4)	Au2–C35	2.001(4)
C1-C2	1.192(5)	C35–C36	1.199(5)
C2–C3	1.445(5)	C36–C37	1.434(5)
C6–C9	1.486(5)	C40–C43	1.485(5)
C12-S1	1.776(4)	C46–S2	1.774(4)
S1-C15	1.791(4)	S2-C49	1.686(7)
C15-C16	1.515(5)	C49–C50	1.524(7)
C15–O1	1.202(5)	C49–O2	1.235(6)
Bond angles			
C17-P1-C23	105.91(18)	C51-P2-C57	106.31(16)
C17-P1-C29	103.94(17)	C51-P2-C63	106.63(17)
C17–P1–Au1	115.96(13)	C51-P2-Au2	110.40(12)
C23-P1-C29	104.74(16)	C57-P2-C63	104.20(16)
C23–P1–Au1	110.71(12)	C57–P2–Au2	115.05(12)
C29-P1-Au1	114.60(12)	C63–P2–Au2	113.60(12)
P1-Au1-C1	177.12(10)	P2-Au2-C35	177.69(10)
Au1–C1–C2	177.0(3)	Au2-C35-C36	177.4(3)
C1C2C3	176.3(4)	C35-C36-C37	178.3(4)
C12-S1-C15	101.67(18)	C46-S2-C49	107.7(2)

^a Standard uncertainties of the last significant digit(s) are shown in parenthesis.

going scan observed with related molecules showing the same oxidation behavior supports this assumption [15].

Respective oxidation potentials for the other compounds are $E_{\text{FeC}} = 1.42 \text{ V}$ (7), $E_{\text{FeC}} = 1.45 \text{ V}$ (8), $E_{\text{FeC}} = 1.42 \text{ V}$ (10), $E_{\text{FeC}} = 1.45 \text{ V}$ (14). Because in all cases no well-defined peaks but only current shoulders are observed and the assigned potentials show only a small scattering it is not justified to speculate about electronic effects of the molecules and the involved substituents on the oxidation potential.

In case of -SH-terminated groups oxidation of the sulfur again resulting in the formation of a sulfonium radical is observed at $E_{\text{FeC}} = 1.1 \text{ V}$ (4) and $E_{\text{FeC}} = 1.24 \text{ V}$ (8) (Fig. 11).

Despite the rather similar inductive effects of the molecules attached to the -SH-group oxidation is more difficult (*i.e.* electron density at the -SH group is smaller) in the case of **8**.

A further building block shared by 7, 8, 13, 14 and 15 is the ferrocene unit. This moiety can be employed to probe electron density shifts in molecules caused by substituents and intramolecular electronic communication. In a direct comparison of 7 and 8 differing only in the sulfur-containing end-group the former shows a redox potential $E_{\rm FeC} =$ 0.18 V, the latter (8) $E_{\text{FeC}} = 0.04$ V. Obviously oxidation of 8 is easier, i.e. charge density at the ferrocene moiety is higher. As already observed in Fig. 11, oxidation of the ferrocene unit in 8 and subsequent oxidation of the -SH group results in a practically complete disappearance of the reduction wave of the ferrocene entity. This could only be observed (with the result stated above) in narrow potential scans around $E_{\text{FeC}} = 0.04 \text{ V}$. In case of 13 $E_{\text{FeC}} = 0.32 \text{ V}$, 14 $E_{\text{FeC}} = 0.29$ V, and 15 $E_0 = 0.30$ V were observed for the ferrocene unit. The redox potentials of 14 and 15 are very similar implying a dominant electron withdrawing influence of the Au(I) species coordinated to the PPh₂ unit and an only slightly larger electron withdrawing effect of the halides in 13 and 15. Reduction of this Au(I) species is always irreversible, i.e., no reoxidation is observed. The reduction appears as a wave on the cathodic decomposition of the electrolyte system. The respective current waves are observed at E = -2.59 V (10), E = -2.72 V (13), E =-2.66 V (14, very weak) and E = -2.78 V (15). In case of 10 a Ph_3P unit is coordinated to Au(I), in all other remaining molecules a PPh₂Fc unit is in this position. The potential difference of about 70 mV between the 10 and 14 (the molecules differ only in this unit) implies, that only the properties of the PX substituents have an effect on the gold reduction potential. The halide substituents in 13 and 15 affect a further electron drag resulting in a negative shift of the reduction potential, the shifts do not reflect the electronegativities of the halide elements.

In this work, new linear biphenyl ethynyl thiol and thio acetyl molecules were synthesized and characterized. Based on these studies we used these molecules as starting materials for the preparation of mono- and heterobimetallic complexes containing the C=C-C₆H₄-C₆H₄-SR (R = H, C(O)Me) ligand by applying different synthesis strategies. Complexes L_nM -C=C-C₆H₄-C₆H₄-SR (L_nM = Fc, (Ph₃P)Au, FcPPh₂-Au); Fc = ((η⁵-C₅H₅)(η⁵-C₅H₄)Fe) are rigid-rod structured. The electrochemical behavior of these compounds, in particular the oxidation of the sulfur-containing end-group, the irreversible reduction of the Au(I) species and the redox behavior of the ferrocene unit can

Table 4 Selected bond distances (Å) and bond angles (°) for 14^{a}

Bond distances					
P1-C6	1.784(7)	P1-C11	1.813(7)	P1-C17	1.819(6)
P1-Au1	2.2737(15)	Au1–C23	2.017(6)	C23–C24	1.172(9)
C24–C25	1.463(9)	C28–C31	1.512(9)	C34–S1	1.757(7)
S1-C37	1.707(15)	C37–C38	1.858(17)	C37–O1	1.244(17)
Fel–D1 ^b	1.640(3)	Fe1–D2	1.634(3) ^b		
Bond angles					
C6-P1-C11	105.7(3)		C6-P1-C17		103.9(3)
C11-P1-C17	105.8(3)		P1-Au1-C23		177.9(2)
Au1-C23-C24	170.9(7)		C23-C24-C25		175.2(8)
C34-S1-C37	105.6(7)		C34'-S1'-C37' °		104.4(8)

^a Standard uncertainties of the last significant digit(s) are shown in parenthesis.

^b $D_1 =$ centroid of C_5H_5 , $D_2 =$ centroid of C_5H_4 .

^c ' = disordered atoms.

Table 5 Selected bond distances (Å) and bond angles (°) for 13~(X=Cl) and $15~(X=I)^a$

	Bond distances			Bond angles	
	13	15		13	15
P1–Au1	2.228(2)	2.2542(9)	P1-Au1-X1	177.12(10)	171.19(2)
P1-C6	1.781(8)	1.782(3)	C6–P1–Au1	112.6(3)	118.93(11)
P1-C11	1.812(4)	1.820(4)	C11–P1–Au1	112.46(18)	113.00(11)
P1-C17	1.823(5)	1.824(4)	C17–P1–Au1	115.3(2)	109.69(11)
Fe1–D1 ^b	1.372(4)	1.656(2)	C6-P1-C11	106.6(3)	105.67(16)
Fe1–D2 ^b	1.630(4)	1.649(2)	C6-P1-C17	104.1(3)	104.62(16)
Au1–X1	2.280(2)	2.5758(3)	C11–P1–C17	105.0(3)	103.57(16)

^a Standard uncertainties of the last significant digit(s) are shown in parenthesis.

^b D_1 = centroid of C_5H_5 , D_2 = centroid of C_5H_4 .

be rationalized in terms of electron-donating and -withdrawing properties of the various building blocks of the investigated molecules. Preparation of self-assembled monolayers by applying the bottom-up approach of the synthesized species is in progress [30].

3. Experimental

3.1. General methods

All reactions were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. n-Hexane and tetrahydrofuran were purified by distillation from sodium/benzophenone ketyl; dichloromethane was purified by distillation from phosphorus pentoxide. Triethylamine was dried by distillation from KOH. Infrared spectra were recorded with a Perkin-Elmer FT-IR 1000 spectrometer. NMR spectra were recorded with a Bruker Avance 250 spectrometer. ¹H NMR spectra were recorded at 250.130 MHz (internal standard, relative to CDCl₃, δ 7.26) and ¹³C{¹H}NMR spectra at 62.902 MHz (internal standard, relative to CDCl₃, δ 77.16). Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane with the solvent as the reference signal. ³¹P{¹H}NMR spectra were recorded at 101.254 MHz with $P(OMe_3)$ as external standard (δ 139 ppm, relative to 85%) H₃PO₄, δ 0.00) and ²⁹Si{¹H} NMR spectra at 49.693 MHz as external standard (relative to SiMe₄, δ 0.00) in CDCl₃. Cyclic voltammograms were recorded in a dried singlecompartment cell purged with purified argon at 25 °C. Platinum wires served as working and as counter electrodes. A non-aqueous saturated calomel electrode served as reference electrode. For ease of comparison, all potentials are converted to the ferrocene-ferrocenium couple Cp_2Fe/Cp_2Fe^+ ($Cp_2Fe = (\eta^5 - C_5H_5)_2Fe$) as the reference $(E_0 = 0.00 \text{ V}, \Delta E = 125 \text{ mV})$ [31,32]. Electrolyte solutions were prepared from freshly distilled dichloromethane or tetrahydrofuran solutions and $[^{n}Bu_{4}N]PF_{6}$ (dried in oilpump vacuum at 120 °C, c = 0.1 M). The organometallic complexes were added at c = 1 mM. Cyclic voltammograms were recorded at a scan rate of 100 mV s^{-1} using a Radiometer Copenhagen DEA 101 Digital Electrochemical analyzer with an IMT 102 Electrochemical Interface. Elemental analyses were performed with a Vario EL, Elementar Analysensysteme GmbH (Hanau). Melting points were determined using sealed nitrogen purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus.

3.2. General remarks

I-C₆H₄-C₆H₄-SC(O)Me (1) [33] Me₃Si-C \equiv CH (2) [34] FcC \equiv CH (6) [35] (η^{5} -C₅H₅)(η^{5} -C₅H₄PPh₂)Fe (11) [36]

Table 6 Crystal and intensity collection data for **3**, **7** and **10**

	3	7	10
Formula	C ₁₉ H ₂₀ OSiS	C ₂₆ H ₂₀ FeOS	C34H26AuOPS
Formula weight	324.50	436.33	710.54
Crystal color	Colorless	Orange	Colorless
Crystal dimensions (mm)	$0.4 \times 0.3 \times 0.1$	$0.3 \times 0.2 \times 0.2$	$0.4 \times 0.2 \times 0.2$
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	$P\overline{1}$	Pbca	$P\bar{1}$
a (Å)	10.2299(16)	12.7684(9)	10.7472(8)
$b(\mathbf{A})$	16.263(3)	11.3473(8)	12.3863(9)
$c(\dot{A})$	17.485(3)	27.789(2)	21.9950(11)
α (°)	72.296(2)	_	89.994(5)
β (°)	79.084(2)	_	93.363(5)
γ (°)	85.944(2)	_	101.255(6)
$V(Å^3)$	2720.9(7)	4026.3(5)	2866.5(3)
Ζ	6	8	4
$\rho_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.188	1.440	1.646
F(000)	1032	1808	1392
Absorption coefficient (mm^{-1})	0.244	0.868	5.286
Scan range Θ (°)	1.31-26.46	1.47-26.41	2.91-26.06
Index ranges	$-12 \leqslant h \leqslant 12$,	$0 \leqslant h \leqslant 29$,	$-13 \leq h \leq 13$,
-	$-19 \leqslant k \leqslant 20,$	$0 \leqslant k \leqslant 14$,	$-15 \leq k \leq 15$,
	$0 \leqslant l \leqslant 21$	$0 \leqslant l \leqslant 34$	$-27 \leqslant l \leqslant 27$
Temperature (K)	298(2)	183(2)	100(2)
Total reflections	30792	46440	28510
Unique reflections	11132	4643	11250
Data	11106	4129	11250
Restraints	0	0	0
Parameter	607	263	680
$R_1, wR_2 [I \ge 2\sigma(I)]^{a,b}$	0.0609, 0.1759	0.0321, 0.0691	0.0234, 0.0515
R_1 , wR_2 (all data) ^{a,b}	0.0798, 0.1852	0.0545, 0.0790	0.0376, 0.0537
$R_{\rm int}$, Goodness-of-fit on F^2 ^c	0.0315, 1.097	0.0706, 1.027	0.0238, 0.977
Maximum and minimum peak in final Fourier map $(e \mathring{A}^{-3})$	0.637, -0.342	0.280, -0.314	1.566, -1.491

^a
$$R_1 = \sum (|F_o - |F_c||) / \sum |F_o|; wR_2 = \left[\sum (w(F_o^2 - F_c^2)^2) / \sum (wF_o^4) \right]^{1/2}$$

^b $W = 1/[\sigma^2(F_o^2) + (0.0612P)^2], P = (F_o^2 + 2F_c^2)/3.$
^c $S = \left[\sum w(F_o^2 - F_c^2)^2 \right] / (n - p)^{1/2}.$

and (tht)AuCl (12) [37] were prepared following published procedures. All other chemicals are commercially available and were used as received.

4. Synthesis of 3

Compound I–C₆H₄–C₆H₄–SAc (1) (1.00 g, 2.82 mmol) was dissolved in 5 mL of tetrahydrofuran and Me₃SiC= CH (2) (0.41 g, 4.17 mmol), NEt(${}^{i}C_{3}H_{7}$)₂ (0.65 g, 4.54 mmol), (PPh₃)₂PdCl₂ (99.3 mg, 0.14 mmol, 5 mol%) and [CuI] (26.9 mg, 0.14 mmol, 5 mol%) were added. After 36 h of stirring at 25 °C all volatiles were removed in oilpump vacuum and the residue was purified by column chromatography (column size: 20 × 3 cm, Silica gel, *n*-hexane:dichloromethane = 1:1). Evaporation of the solvents in oil-pump vacuum gave a colorless solid. Yield: 0.67 g (2.08 mmol, 74% based on 1).

Elemental analysis: Anal. Calc. for $C_{19}H_{20}OSSi$ (324.10): C, 70.32; H, 6.21. Found: C, 70.22; H, 6.21%. M.p: 100 °C. IR (KBr): $v \text{ [cm}^{-1}\text{]}$ 3393 (m), 3030 (w), 2958 (s), 2153 (s) ($v_{C=C}$), 1914 (w), 1707 (vs) ($v_{C=O}$), 1509 (w), 1478 (s), 1388 (s), 1352 (s), 1250 (vs), 1191 (w), 1120 (vs), 1090 (vs), 1001 (s), 952 (s), 846 (vs), 814 (vs), 758 (vs),

660 (s), 622 (s), 564 (m), 537 (s), 502 (m). ¹H NMR (CDCl₃): δ 0.27 (s, 9H, SiMe₃), 2.45 (s, 3H, CH₃), 7.47 ((AB)₂-system, ⁴J_{HH} = 2.3 Hz, ³J_{HH} = 8.1 Hz, ⁵J_{HH} = 0.3 Hz, 2 H, ⁶H/C₆H₄-SC(O)Me), 7.53 ((AB)₂-system, ⁴J_{HH} = 2.0 Hz, ³J_{HH} = 8.9 Hz, ⁵J_{HH} = 0.5 Hz, 4H, C=C-C₆H₄), 7.61 ((AB)₂-system, ⁴J_{HH} = 1.7 Hz, ³J_{HH} = 8.1 Hz, ⁵J_{HH} = 0.3 Hz, 2H, ^mH/C₆H₄-SC(O)Me). ¹³C{¹H}NMR (CDCl₃): δ 0.1 (SiMe₃); 30.4 (CH₃), 95.5 (C=C-C₆H₄), 104.9 (C=C-C₆H₄), 122.7 (C=C-ⁱC/ C₆H₄), 127.0 (C=C-C₆H₄), 127.4 (C-S), 127.9 (^mC/ C₆H₄-SC(O)Me), 132.6 (C=C-C₆H₄), 134.9 (^oC/C₆H₄-SC(O)Me), 140.2 (C=C). ²⁹Si{¹H} NMR (CDCl₃): δ -17.63. ESI-MS [m/z (rel int)]: 325.11 [(M+H)⁺] (100).

5. Synthesis of 4

Thioacetate **3** (80 mg, 0.24 mmol) was dissolved in 2 mL of tetrahydrofuran at 25 °C and 25% $NH_4OH_{(aq)}$ (83.7 mg, 2.46 mmol) was added in one portion. After 20 min of stirring at this temperature the reaction mixture was acidified with 3 M HCl and was then extracted three times with 15 mL of dichloromethane. After evaporation of the

Table 7 Crystal and intensity collection data for 13–15

	13	14	15
Formula	C22H19AuClFeP	C ₃₈ H ₃₀ AuFeOPS	C ₂₂ H ₁₉ AuFeIP
Formula weight	603.62	818.47	694.06
Crystal color	Yellow	Yellow	Yellow
Crystal dimensions (mm)	$0.3 \times 0.2 \times 0.2$	$0.3 \times 0.2 \times 0.2$	$0.4 \times 0.25 \times 0.15$
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P2(1)/c	P2(1)/c	P2(1)/n
<i>a</i> (Å)	8.3428(8)	9.1179(6)	10.6915(8)
b (Å)	18.8982(17)	24.2458(16)	15.2519(11)
<i>c</i> (Å)	12.9700(12)	15.1348(10)	12.3902(9)
β (°)	94.594(2)	102.7040(10)	100.801(6)
$V(\text{\AA}^3)$	2038.3(3)	3264.0(4)	1984.6(3)
Ζ	4	4	4
$ \rho_{\rm calc} ({\rm g} {\rm cm}^{-3}) $	1.967	1.666	2.323
<i>F</i> (000)	1156	1608	1296
Absorption coefficient (mm ⁻¹)	8.113	5.076	9.754
Scan range Θ (°)	1.91-26.42	1.61-26.41	3.09-26.05
Index ranges	$-10 \leqslant h \leqslant 10$,	$-11 \leqslant h \leqslant 11$,	$-13 \leqslant h \leqslant 13$,
	$0 \leqslant k \leqslant 23,$	$0 \leqslant k \leqslant 30$,	$-18 \leqslant k \leqslant 18$,
	$0 \leqslant l \leqslant 16$	$0 \leqslant l \leqslant 18$	$-12 \leqslant l \leqslant 15$
Temperature (K)	293(2)	298(2)	100(2)
Total reflections	15457	37670	11 348
Unique reflections	4312	6878	3877
Data	4166	6702	3877
Restraints	40	282	0
Parameter	211	457	235
$R_1, wR_2 [I \ge 2\sigma(I)]^{a,b}$	0.0457, 0.1021	0.0410, 0.0909	0.0199, 0.0468
R_1 , wR_2 (all data) ^{a,b}	0.0814, 0.1165	0.0722, 0.1027	0.0237, 0.0478
$R_{\rm int}$, Goodness-of-fit on F^2 ^c	0.0755, 1.012	0.0521, 1.082	0.0266, 1.059
Maximum and minimum peak in final Fourier map (e $Å^{-3}$)	1.726, -1.476	1.300, -1.066	1.326, -1.647

^a
$$R_1 = \sum (|F_o - |F_c||) / \sum |F_o|; wR_2 = \left[\sum (w(F_o^2 - F_c^2)^2) / \sum (wF_o^4) \right]^{1/2}.$$

^b $W = 1/[\sigma^2(F_o^2) + (0.0612P)^2], P = (F_o^2 + 2F_c^2)/3.$
^c $S = \left[\sum w(F_o^2 - F_c^2)^2 \right] / (n - p)^{1/2}.$



Fig. 10. Cyclic voltammogram of **3** and **5** in dichloromethane at 25 °C, [^{*n*}Bu₄N]PF₆ supporting electrolyte (0.1 M), scan rate = 100 mV s⁻⁴, positive going scan.

solvent of the combined organic fractions in oil-pump vacuum a colorless solid was obtained. Yield: 66.0 mg (0.23 mmol, 95% based on 3).



Fig. 11. Cyclic voltammogram of **4** and **8** in dichloromethane at 25 °C, [^{*n*}Bu₄N]PF₆ supporting electrolyte (0.1 M), scan rate = 100 mV s^{-4} , positive going scan.

Elemental analysis: Anal. Calc. for $C_{17}H_{18}SSi$ (282.48): C, 72.28; H, 6.42. Found: C, 71.28; H, 6.63%. mp: 134 °C. IR (KBr): $v[cm^{-1}]$ 3447 (w), 3078 (w), 3028 (w), 2955 (m) (v_{CH3}), 2896 (w), 2567 (w) (v_{S-H}), 2156 (s) ($v_{C=C}$), 1654 (w), 1593 (m), 1484 (s), 1396 (m), 1253 (s), 1244 (s), 1134 (w), 1103 (m), 1002 (w), 867 (vs), 843 (vs), 811 (vs), 759 (s), 698 (w), 658 (m), 553 (w), 512 (m). ¹H NMR (CDCl₃): δ 0.26 (s, 9H, SiMe₃), 3.49 (s, 1 H, SH), 7.33 ((AB)₂-system, ⁴J_{HH} = 2.2 Hz, ³J_{HH} = 8.1 Hz, ⁵J_{HH} = 0.4 Hz, 2H, ^oH/C₆H₄-SH), 7.45 ((AB)₂-system, ⁴J_{HH} = 2.0 Hz, ³J_{HH} = 8.1 Hz, ⁵J_{HH} = 0.4 Hz, 2 H, ^mH/C₆H₄-SH), 7.49, 7.51 ((AB)₂-system, ⁴J_{HH} = 1.9 Hz, ³J_{HH} = 8.1 Hz, ⁵J_{HH} = 0.5 Hz, ⁴J_{HH} = 1.8 Hz, 4H, C=C-C₆H₄). ¹³C{¹H}NMR (CDCl₃): δ 0.1 (SiMe₃), 126.6 (C=C-<u>C₆H₄), 127.7 (^mC/C₆H₄-SH), 129.9 (C=C-<u>C₆H₄), 132.6</u> (^oC/C₆H₄-SH).²⁹Si{¹H} NMR (CDCl₃): δ -17.69. ESI-MS [m/z (rel int)]: 282.9 [M⁺] (5).</u>

6. Synthesis of 5

To **3** (0.34 g, 1.04 mmol) dissolved in 20 mL of tetrahydrofuran, acetic acid (0.27 g, 4.50 mmol) and acetic anhydride (0.42 g, 4.09 mmol) was added. Afterward tetrabutylammonium fluoride hydrate (0.67 g, 2.58 mmol) dissolved in 30 mL tetrahydrofuran was dropwise added. After stirring over night at 25 °C the solvents were removed in oil-pump vacuum and the residue was purified by column chromatography (column size: $20 \times$ 3 cm, Silica gel, *n*-hexane:dichloromethane = 1:2). The solvents were removed from the eluate in oil-pump vacuum to leave a colorless solid. Yield: 0.26 g (1.01 mmol, 97% based on **3**).

Elemental analysis: Anal. Calc. for C₁₆H₁₂OS (252.06): C, 76.16; H, 4.79. Found: C, 75.88; H, 4.90%. M.p: 113 °C. IR (KBr): $v \text{ [cm}^{-1}\text{]}$ 3272 (s) ($v \equiv C-H$), 3025 (w), 2922 (w), 2103 (w) ($v_{C=C}$), 1915 (w), 1693 (vs) ($v_{C=O}$), 1481 (s), 1387 (m), 1352 (m), 1255 (w), 1125 (s),1112 (s), 1097 (m), 1003 (m), 943 (m), 854 (m), 818 (vs), 676 (m), 660 (m), 627 (s), 579 (w), 560 (w), 537 (m), 517 (w), 449 (w). ¹H NMR (CDCl₃): δ 2.45 (s, 3 H, CH₃), 3.15 (s, 1H, HC \equiv C), 7.48 ((AB)₂-system, ${}^{4}J_{HH} = 1.9$ Hz, ${}^{3}J_{HH} =$ 8.1 Hz, ${}^{5}J_{HH} = 0.4$ Hz, ${}^{2}H$, ${}^{o}H/C_{6}H_{4}$ -SC(O)Me), 7.55, 7.57 ((AB)₂-system, ${}^{4}J_{HH} = 2.0$ Hz, ${}^{3}J_{HH} = 8.0$ Hz, ${}^{5}J_{HH} = 0.6 \text{ Hz}, {}^{2}J_{HH} = 1.8 \text{ Hz}, 4\text{H}, C = C - C_{6}H_{4}), 7.62$ ((AB)₂-system, ${}^{4}J_{HH} = 2.1 \text{ Hz}, {}^{3}J_{HH} = 8.1 \text{ Hz}, {}^{5}J_{HH} =$ $0.4 \text{ Hz}, 2\text{H}, {}^{m}\text{H/C}_{6}\text{H}_{4}\text{-SC}(\text{O})\text{Me}). {}^{13}\text{C}{}^{1}\text{H}\text{NMR} (\text{CDCl}_{3}):$ δ 30.4 (CH₃), 78.3 (C=C-C₆H₄), 83.5 (C=C-C₆H₄), 121.7 (C \equiv C $^{-i}$ C/C₆H₄), 127.2 (C \equiv C $^{-}$ C₆H₄), 127.5 (C $^{-}$ S), 127.9 (${}^{m}C/C_{6}H_{4}-SC(O)Me$), 132.8 (C=C- $C_{6}H_{4}$), 135.0 $({}^{o}C/C_{6}H_{4}-SC(O)Me), 140.6 (C \equiv C_{-}{}^{p}C/C_{6}H_{4}), 141.5 ({}^{p}C/$ C₆H₄-SC(O)Me), 194.0 (C=O).

7. Synthesis of 7

To FcC=CH (6) (0.72 g, 3.41 mmol) and $I-C_6H_4-C_6H_4-SAc$ (1) (1.00 g, 2.84 mmol) in 80 mL of triethylamine, (PPh₃)₂PdCl₂ (99.8 mg, 0.14 mmol, 5 mol%) and [CuI] (54.2 mg, 0.28 mmol, 10 mol%) were added at 25 °C. After 24 h of stirring at 50 °C all volatiles were removed in oil-pump vacuum and the title compound

was purified by column chromatography (column size: 25×2 cm, Silica gel, *n*-hexane:dichloromethane = 3:2). Evaporation of the solvents in oil-pump vacuum gave a orange-brown solid. Yield: 1.03 g (2.35 mmol, 83% based on **1**).

Elemental analysis: Anal. Calc. for C₂₆H₂₀FeOS (436.09): C, 71.57; H, 4.62. Found: C, 70.97; H, 4.72%. M.p: 147 °C. IR (KBr): v [cm⁻¹] 3099 (w) (v_{Arvl-H}), 2962 (m), 2200 (m) ($v_{C=C}$), 1698 (vs) ($v_{C=O}$), 1653 (m) ($v_{C=C}$), 1484 (m), 1413 (m), 1387 (m), 1354 (m), 1261 (s), 1106 (s), 1033 (s), 961 (m), 923 (m), 857 (m), 814 (vs) (δ_{Arvl-H}), 612 (s), 564 (m), 538 (m), 504 (s), 473 (m). ¹H NMR (CDCl₃): δ 2.46 (s, 3H, CH₃), 4.28 (pt, ³J_{HH} = 1.8 Hz, 2H, ${}^{\beta}$ H/C₅H₄), 4.28 (s, 5H, C₅H₅), 4.55 (pt, ${}^{3}J_{HH} = 1.8$ Hz, 2H, ${}^{\alpha}$ H/C₅H₄), 7.50 ((AB)₂-system, ${}^{4}J_{HH} = 2.1$ Hz, ${}^{3}J_{\rm HH} = 8.1 \text{ Hz}, {}^{5}J_{\rm HH} = 0.4 \text{ Hz}, 2 \text{ H}, {}^{\rho}\text{H/C_{6}H_{4}-SC(O)Me)},$ 7.58 ((AB)₂-system, ${}^{4}J_{HH} = 0.1 \text{ Hz}, {}^{3}J_{HH} = 8.9 \text{ Hz},$ ${}^{5}J_{HH} = 0.4 \text{ Hz}, {}^{4}J_{HH} = 3.7 \text{ Hz}, 4\text{H}, C \equiv C - C_{6}H_{4}), 7.65$ ((AB)₂-system, ${}^{4}J_{HH} = 2.0 \text{ Hz}, {}^{3}J_{HH} = 8.1 \text{ Hz}, {}^{5}J_{HH} =$ $0.4 \text{ Hz}, 2 \text{ H}, {}^{m}\text{H/C_{6}H_{4}-SC(O)Me}.{}^{13}\text{C}{}^{1}\text{H}\text{NMR} (CDCl_{3}):$ δ 30.3 (CH₃), 65.2 (^{*i*}C/C₅H₄), 69.0 (^βC/C₅H₄), 70.1 (C₅H₅), 71.5 ($^{\alpha}C/C_5H_4$), 85.6 (C=C-C₆H₄), 89.7 (C=C-C₆H₄), 123.6 (C \equiv C $-^{i}$ C/C₆H₄), 127.1 (C \equiv C-C₆H₄), 127.2 (C-S), 127.7 (${}^{m}C/C_{6}H_{4}$ -SC(O)Me), 131.9 (C=C- $C_{6}H_{4}$), 134.9 $({}^{o}C/C_{6}H_{4}-SC(O)Me)$, 139.2 (C=C- ${}^{p}C/C_{6}H_{4}$), 141.6 (${}^{p}C/$ C_6H_4 -SC(O)Me), 194.0 (C=O). ESI-MS [m/z (rel. int.)]: $436.09 [M^+] (10).$

8. Synthesis of 8

The same procedure as used in the synthesis of **4** was applied in the preparation of **8**. Fc–C \equiv C–C₆H₄–C₆H₄– SAc (7) (100.0 mg, 0.23 mmol) and 25% NH₄OH_(aq) (78.0 mg, 2.29 mmol) were reacted. After appropriate work-up, complex **8** was obtained as a orange-brown solid. Yield: 85.9 mg (0.21 mmol, 95% based on 7).

Elemental analysis: Anal. Calc. for C₂₄H₁₈FeS (394.05): C, 73.10; H, 4.60. Found: C, 72.80; H, 4.75%. M.p: 158 °C. IR (KBr): $v [cm^{-1}] 3080$ (w) (v_{Arvl-H}), 2959 (w), 2922 (w), 2848 (w), 2553 (w) (v_{S-H}), 2369 (w), 2199 (w) (v_{C=C}), 1654 (m) $(v_{C=C})$, 1557 (w), 1488 (m), 1395 (w), 1260 (m), 1103 (m), 1023 (m), 919 (w), 812 (vs) $(\delta_{\text{Arvl-H}})$, 500 (m).¹H NMR (CDCl₃): δ 3.59 (s, 1H, SH), 4.17 (pt, ${}^{3}J_{\text{HH}} = 1.7$ Hz, 2H, ${}^{\beta}H/C_{5}H_{4}$), 4.17 (s, 5H, C₅H₅), 4.44 (pt, ${}^{3}J_{HH} = 1.7 \text{ Hz}, 2H, {}^{\alpha}H/C_{5}H_{4}), 7.35 \text{ ((AB)}_{2}\text{-system}, {}^{4}J_{HH} = 2.1 \text{ Hz}, {}^{3}J_{HH} = 8.1 \text{ Hz}, {}^{5}J_{HH} = 0.4 \text{ Hz}, 2H, {}^{\rho}H/C_{6}H_{4}\text{-SH}), 7.48 \text{ ((AB)}_{2}\text{-system}, {}^{4}J_{HH} = 2.2 \text{ Hz}, {}^{3}J_{HH} = 2.2 \text{ Hz}, {}^{3}J_{H} = 2.2 \text{ Hz}, {}$ 8.1 Hz, ${}^{5}J_{\rm HH} = 0.4$ Hz, 2H, ${}^{m}H/C_{6}H_{4}$ -SH), 7.51, 7.54 $((AB)_2$ -system, ${}^4J_{HH} = 1.7 \text{ Hz}, {}^3J_{HH} = 8.0 \text{ Hz}, {}^5J_{HH} =$ 0.5 Hz, ${}^{4}J_{\rm HH} = 2.2$ Hz, 4H, C \equiv C-C₆H₄). 13 C{ 1 H}NMR (CDCl₃): δ 65.3 (^{*i*}C/C₅H₄), 69.0 (^{β}C/C₅H₄), 70.1 (C₅H₅), 71.5 ($^{\alpha}C/C_5H_4$), 85.7 (C $\equiv C-C_6H_4$), 89.4 (C $\equiv C-C_6H_4$), 123.1 (C \equiv C $^{-i}$ C/C₆H₄), 126.7 (C \equiv C $^{-}$ C₆H₄), 127.6 (^mC/ C_6H_4 -SH), 129.9 (°C/C₆H₄-SH), 130.4 (^{*i*}C/C₆H₄-SH), 131.9 (C \equiv C–<u>C</u>₆H₄), 138.0 (^{*p*}C/C₆H₄–SH), 139.5 $(C \equiv C_{-p}C/C_{6}H_{4})$. ESI-MS [m/z (rel int)]: 394.03 [M⁺] (100).

9. Synthesis of 10

To (Ph₃P)AuCl (9) (149.1 mg, 0.30 mmol) and HC=C-C₆H₄-C₆H₄-SAc (5) (83.6 mg, 0.33 mmol) in 5 mL of tetrahydrofuran were added 10 mL of triethylamine. After 1 h of stirring at 25 °C all volatiles were removed in oilpump vacuum and the residue was purified by column chromatography (column size: 25×2 cm, Silica gel, *n*-hexane:dichloromethane = 1:2). After evaporation of the solvents in oil-pump vacuum, **10** could be isolated as a colorless solid. Yield: 124.0 mg (0.17 mmol, 58% based on **9**).

Elemental analysis: Anal. Calc. for C₃₄H₂₆AuOPS (710.11): C, 57.47; H, 3.69. Found: C, 58.23; H, 4.31%. M.p: 151 °C. IR (KBr): v [cm⁻¹] 3049 (m), 2922 (s), 2852 (m), 2106 (w) ($v_{C=C}$), 1701 (vs) ($v_{C=O}$), 1595 (w), 1478 (s), 1434 (s) (v_{P-Ph}), 1387 (w), 1350 (w), 1261 (w), 1180 (w), 1099 (vs), 1025 (w), 1000 (w), 948 (w), 817 (vs), 746 (m), 692 (vs), 610 (m), 536 (vs). ¹H NMR (CDCl₃): δ 2.43 (s, 3H, CH₃), 7.41–7.63 (m, 23H, C₆H₄,C₆H₅). ¹³C{¹H}NMR (CDCl₃): δ 30.4 (CH₃), 124.7 (C=C^{-*i*}C/C₆H₄), 126.8 (C=C-C₆H₄), 127.8 (^mC/C₆H₄-SC(O)Me), 129.3 (d, ³J_{CP} = 11.0 Hz, ^mC/C₆H₅), 130.3 (C–S), 131.7 (d, ⁴J_{CP} = 2.4 Hz, ^{*p*}C/C₆H₅), 133.0 Hz (C=C-C₆H₄), 134.4 (d, ²J_{CP} = 13.4 Hz, ^oC/C₆H₄), 142.0 (^{*p*}C/C₆H₄-SC(O)Me), 138.4 (C=C-^{*p*}C/C₆H₄), 142.0 (^{*p*}C/C₆H₄-SC(O)Me), 194.3 (C=O). ³¹P{¹H}NMR (CDCl₃): δ 41.29 (s).

10. Synthesis of 13

To 220 mg (0.686 mmol) of (tht)AuCl (2) dissolved in 10 mL of tetrahydrofuran were added 260 mg (0.703 mmol) of FcPPh₂ (1) dissolved in 20 mL of tetrahydrofuran during 1 h. After 1 h of stirring at 25 °C all volatiles were removed in oil-pump vacuum. The remaining orange solid was purified by column chromatography (column size: 25×2 cm, Silica gel, diethyl ether). The product was obtained as a yellow solid. Yield: 295 mg (0.49 mmol, 71% based on 12).

Elemental analysis: Anal. Calc. for C₂₂H₁₉AuClFeP (602.63): C, 43.85; H, 3.18. Found: C, 44.12; H, 3.20%. M.p: 151 °C.¹H NMR (CDCl₃): δ 4.20 (s, 5H, C₅H₅), 4.36 (dt, 2H, C₅H₄), 4.57 (m, 2H, C₅H₄), 7.41–7.62 (m, 10H, C₆H₅). ¹³C{¹H}NMR (CDCl₃): δ 69.0 (d, ¹*J*_{CP} = 75.1 Hz, ^{*i*}C/C₅H₄), 70.2 (C₅H₅), 72.6 (d, ³*J*_{CP} = 8.9 Hz, ^{*β*}C/C₅H₄), 73.5 (d, ²*J*_{CP} = 14.1 Hz, ^{*α*}C/C₅H₄), 129.0 (d, ³*J*_{CP} = 11.8 Hz, ^{*m*}C/C₆H₅), 131.0 (d, ¹*J*_{CP} = 62.2 Hz, ^{*i*}C/C₆H₅), 131.7 (d, ⁴*J*_{CP} = 1.9 Hz, ^{*p*}C/C₆H₅), 133.6 (d, ²*J*_{CP} = 13.7 Hz, ^{*o*}C/C₆H₅). ³¹P{¹H}NMR (CDCl₃): δ 27.6 (s).

11. Synthesis of 14 and 15

FcPPh₂-AuCl (13) (200 mg, 0.33 mmol) and HC \equiv C–C₆H₄-C₆H₄-SAc (5) (100 mg, 0.39 mmol) were dissolved in 5 mL of tetrahydrofuran. Triethylamine (10 mL) and [CuI] (2 mol%) were added. After 2 h of stirring at 25 °C

the solvents were removed in oil-pump vacuum and the residue was purified by column chromatography (column size: 25×2 cm, Silica gel, *n*-hexane:tetrahydrofuran = 7:1). Evaporation of the solvents in oil-pump vacuum gave a yellow solid. Yield: 140.0 mg (0.17 mmol, 53% based on 13) of 14 and 6.87 mg (0.009 mmol, 3% based on 13) of 15.

14: Elemental analysis: Anal. Calc. for C₃₈H₃₀AuFeOPS (818.08): C, 55.76; H, 3.69. Found: C, 56.03; H, 4.01%. IR (KBr): $v [cm^{-1}] 3072$ (m), 2956 (m), 2113 (w) ($v_{C=C}$), 1909 (w), 1704 (vs) ($v_{C=0}$), 1598 (m), 1544 (w), 1510 (w), 1479 (s), 1435 (s) (v_{P-Ph}), 1387 (m), 1353 (m), 1307 (m), 1218 (m), 1172 (m), 1103 (vs), 1027 (m), 1001 (m), 950 (m), 816 (vs), 747 (m), 687 (s), 611 (m), 553 (m), 526 (m), 496 (m), 471 (m), 449 (m). ¹H NMR (CDCl₃): δ 2.43 (s, 3H, CH₃), 4.20 (s, 5H, C₅H₅), 4.39 (bs, 2H, ^αH/C₅H₄), 4.55 (bs, 2H, ${}^{\beta}H/C_5H_4$), 7.38–7.65 (m, 18H, C₆H₄, C_6H_5).¹³C{¹H}NMR (CDCl₃): δ 30.4 (CH₃), 68.0 (^{*i*}C/ C_5H_4), 70.1 (C_5H_5), 72.4 (d, ${}^{3}J_{CP} = 9.6$ Hz, C^{19}), 73.6 (d, ${}^{2}J_{CP} = 13.9 \text{ Hz}, \quad {}^{\alpha}C/C_{5}H_{4}), \quad 126.8 \quad (C \equiv C - C_{6}H_{4}), \quad 127.7$ $\binom{mC}{C_6H_4-SC(O)Me}$, 128.9 (d, ${}^{3}J_{CP} = 11.5$ Hz, ${}^{mC}/C_6H_5$), 132.9 (C=C- C_6H_4), 133.8 (d, ${}^{2}J_{CP} = 13.9$ Hz, ${}^{o}C/$ $({}^{o}C/C_{6}H_{4}-SC(O)Me)$. ${}^{31}P{}^{1}H{}NMR$ C_6H_5), 134.8 (CDCl₃): δ 36.40 (s). ESI-MS [m/z (rel int)]: 818.07 [M⁺] (38).

15: Elemental analysis: Anal. Calc. for C₂₂H₁₉AuFeIP (693.93): C, 38.07; H, 2.76. Found: C, 38.88; H, 2.72%. M.p: 193 °C. IR (KBr): v [cm⁻¹] 2920 (m), 1654 (m), 1480 (m), 1433 (vs), 1385 (m), 1309 (m), 1195 (m), 1175 (s), 1100 (vs), 1071 (m), 1027 (s), 999 (m), 908 (w), 825 (vs), 748 (vs), 695 (vs), 627 (m), 555 (vs), 521 (vs).¹H NMR (CDCl₃): δ 4.21 (s, 5H, C₅H₅), 4.37 (bs, 2 H, ^αH/C₅H₄), 4.56 (bs, 2H, ^βH/C₅H₄), 7.39-7.65 (m, 10 H, C₆H₅). ¹³C{¹H}NMR (CDCl₃): δ 68.9 (^{*i*}C/C₅H₄), 70.2 (C₅H₅), 72.5 (d, ³J_{CP} = 9.1 Hz, ^βC/C₅H₄), 73.5 (d, ²J_{CP} = 14.3 Hz, ^αC/C₅H₄), 128.9 (d, ³J_{CP} = 11.5 Hz, ^{*m*}C/C₆H₅), 131.5 (d, ¹J_{CP} = 59.5 Hz, ^{*i*}C/C₆H₅), 131.6 (d, ⁴J_{CP} = 2.8 Hz, ^{*p*}C/C₆H₅), 133.5 (d, ²J_{CP} = 13.9 Hz, ^{*α*}C/C₆H₅). ³¹P{¹H}NMR (CDCl₃): δ 34.65 (s). ESI-MS [*m*/z (rel int)]: 694.00 [M⁺] (53).

12. X-ray structure determination

For data collection of **3**, **7**, **10** and **13–15** a Bruker Smart 1K CCD diffractometer with graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) was used. For protection against oxygen and moisture, the preparation of single crystals was preformed in perfluoro alkyl ether (ABCR GmbH&Co KG; viscosity 1600 cSt). Data collection and cell determination has been done with the program SMART [38,39]. For data integration and refinement of the unit cell the program SAINT was used [39]. The space group was determined using the program XPREP [39] and the absorption has been corrected semi-empirically with SADABS [40]. The structures were solved by direct methods with the program SHELXS-97 [41] and refined by full-matrix least-squares procedures on F^2 , using SHELXL-97 [42]. All *non*-hydrogen atoms were fully refined anisotropically in their local positions. The hydrogen atom positions have been refined with a riding model.

13. Supplementary material

CCDC 624420, 624419, 624417, 624418, 624421 and 624416 contain the supplementary crystallographic data for **3**, **7**, **10**, **13**, **14** and **15**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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