## Inorganic Chemistry

# Early–Late Heterometallic Complexes of Gold and Zirconium: Photoluminescence and Reactivity

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Abstract: OH functionalized triarylphosphines were used to assemble zirconocene-based metalloligands with phosphine donor sites in varying positions. These complexes were subsequently treated with different gold precursors to obtain early-late heterometallic compounds in which the metal atoms exhibit different intermetallic distances. All compounds were fully investigated by spectroscopic techniques, photoluminescence measurements and single crystal X-ray

## Introduction

The combination of early and late transition metals within one organometallic compound to afford early-late heterobimetallic complexes (ELHBs) has been extensively investigated over the past few decades.<sup>[1]</sup> Interest in these complexes is driven by their potential use in heterobimetallic catalysis. Central aims include the development of more active catalysts, the investigation of novel catalytic transformations, and the catalysis of two different reactions in one system.<sup>[2,3]</sup> Moreover, the investigation of ELHBs contributes to a better understanding of intermetallic interactions, as can be found in bioinorganic systems,<sup>[4]</sup> and solid-state compounds, including luminescent materials and heterogeneous catalysts.<sup>[5,6]</sup> In these materials, a late precious metal (e.g., Pd or Pt) is attached to an oxide surface (support) like MgO or Al<sub>2</sub>O<sub>3</sub>. Higher catalytic activity is often achieved compared to the bulk metal, and this can be attributed to interactions between the precious metal and the support. This can be understood as electronic communication between the early and late transition metals and/or cooperative activation of the substrates.<sup>[7]</sup> In addition to potential ap-

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Supporting information for this article can be found under http:// dx.doi.org/10.1002/chem.201600476. diffraction. Quantum chemical calculations were also performed. Some compounds show bright emission even at room temperature with quantum yields of up to 19% (excitation at 350 nm). Furthermore, the reactivity of dimethyl zirconocene derivatives towards gold complexes was investigated, revealing simultaneous ligand exchange and transmetallation reactions.

plications in catalysis, oxide materials like TiO<sub>2</sub> or ZrO<sub>2</sub> are suitable support materials for the anchoring of organic molecules. Besides bulk samples, the supports can consist of thin layers or nanoparticles. Biologically relevant molecules or organometallic compounds can then be bound to the surface-attached anchoring groups, leading to surface-functionalized materials that can be used as phosphors or catalysts.<sup>[8-10]</sup> Hence, the assembly of two electronically different metals within one complex can act as a model system to investigate intermetallic communication or cooperative behaviour with respect to their luminescent or catalytic properties.<sup>[2]</sup>

The synthesis of heterometallic ELHBs usually requires ligand systems which take the different affinities of the metals for certain donor atoms into account. Typically, soft donor centres (phosphines, NHCs or thiolates) are combined with hard donor centres (alkoxides, amidinates) on a common backbone.[11-14] Another possibility is the synthesis of a mono- or polynuclear complex which can function as a metalloligand for the coordination of other metals.<sup>[6, 15-20]</sup> This approach could also be used to synthesize ELHBs of gold and zirconium and this particular combination of metals is attractive with regard to the photophysical properties of the resulting complexes. Gold(I) compounds often display interesting photoluminescence (PL) behaviour,<sup>[21-25]</sup> which can be significantly influenced by intermetallic interactions<sup>[12]</sup> in polynuclear gold compounds.<sup>[26]</sup> Zirconium complexes, in particular zirconocene-based ones, also often show intense PL in the visible range.[27-29] It can be expected that the electronic communication between the metal sites would directly influence the photophysical properties of the Au-Zr compounds. Furthermore, structurally characterized ELHBs of gold and zirconium are scarce. A search of the Cambridge Structural Database revealed that only six heterometallic compounds of these metals are known.<sup>[5,6,30]</sup> Herein, we present the synthesis of zirconocene-based metalloligands as

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model compounds for zirconium-oxide-anchored ligands and give a full account of their Au<sup>1</sup> chemistry. The reactivity of methyl-substituted zirconocenes with gold substrates, as well as their photoluminescence properties are discussed. The role of metal-metal bonding is discussed by means of quantum-chemical calculations. Investigation of polynuclear Au–Zr based ELHBs, with respect to their photophysical properties, has not been described in the literature to date.

## **Results and Discussion**

As starting materials for the synthesis of zirconium-based metalloligands, we chose OH-functionalized triarylphosphines and dimethyl zirconocene.<sup>[31]</sup> In previous investigations, Erker et al. showed that phosphines linked to a Zr<sup>IV</sup> centre via an alkoxide bridge are suitable candidates for frustrated Lewis pairs (FLPs), which can react with nitrobenzene or activate small molecules.<sup>[32]</sup> The synthesis of OH-functionalized phosphines is described in the literature and can be easily conducted on multigram scale through palladium-catalysed P–C coupling of iodophenols and diphenylphosphine in dimethylacetamide (Scheme 1).<sup>[33–35]</sup>



**Scheme 1.** Synthesis of X-(diphenylphosphino)phenols I, II and III (X = 2, 3, 4).

The synthesis of the metalloligands was achieved by the treatment of dimethyl zirconocene with [*X*-(diphenylphosphine)phenol] (X = 2, 3, 4) I, II, and III in toluene at room temperature. The reaction of I with [Cp<sub>2</sub>ZrMe<sub>2</sub>] (Cp =  $\eta^{5}$ -C<sub>5</sub>H<sub>5</sub>) yielded the desired metalloligand [Cp<sub>2</sub>Zr(p-O-C<sub>6</sub>H<sub>4</sub>-PPh<sub>2</sub>)<sub>2</sub>] (1) within a few minutes, as indicated by rapid gas evolution (CH<sub>4</sub>) upon addition of the solvent (Scheme 2).



Scheme 2. Synthesis of the bidentate metalloligand 1.

Compound 1 can be obtained as single crystals by slow diffusion of pentane into the reaction mixture. The metalloligand was fully characterized by standard analytic and spectroscopic techniques. In the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra, a symmetric set of resonances is observed, indicating the formation of the bis(phenolate) complex. Both cyclopentadienyl units are chemically equivalent, showing a singlet at 5.89 ppm in the <sup>1</sup>H NMR spectrum. In the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, the phenolic C-atom is shifted downfield to 166.9 ppm. Both phosphorus atoms exhibit a chemical shift of -6.6 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, and this is in the usual region for unsaturated triaryl-phosphines. The metalloligand **1** was also characterized by single-crystal X-ray diffraction. It crystallizes in the orthorhombic space group *Pnma* with half a molecule in the asymmetric unit. The solid-state structure is shown in Figure 1. The zirconium atom is located at the symmetry centre of the molecule (a mirror plane passes through the middle of the molecule).



**Figure 1.** Solid-state structure of 1. Hydrogen atoms are not displayed for clarity. Cp-atoms: C19-C24. Selected bond lengths [Å] and angles [°]: Zr1-O1 1.998(2), Zr1-O1 1.998(2), Zr1-C19 2.522(3), Zr1-C20 2.521(4), Zr1-C21 2.543(4), Zr1-C22 2.480(3), Zr1-C23 2.505(4), Zr1-C24 2.513(5); O1-Zr1-O1' 96.71(13).

The zirconium-oxygen bond lengths are both 1.998(2) Å, and are similar in length to other zirconocene alkoxides.<sup>[16,36]</sup> The O1-Zr1-O1' bond angle (96.71(13)°) differs slightly from an ideal tetrahedral angle, so the coordination geometry of the zirconium centre can be best described as distorted tetrahedral. The cyclopentadienyl rings coordinate to the metal in a staggered conformation, with carbon–zirconium bond lengths from 2.480(3) to 2.543(4) Å. Because of the large distance between both donor sites, **1** cannot be used as a chelating ligand. However, it was used to synthesize the heterometallic complex,  $[Cp_2Zr(p-O-C_6H_4-PPh_2-AuCl)_2]$  (**2**), by a ligand exchange reaction with two equivalents of [AuCl(tht)] (tht = tetrahydrothiophene) in dichloromethane (Scheme 3).

Compound **2** can be obtained in very good yield by precipitating the product with diethyl ether or by crystallization from



Scheme 3. Synthesis of the heterometallic complex 2.

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CH<sub>2</sub>Cl<sub>2</sub>/pentane. In the <sup>1</sup>H NMR spectrum, the resonance corresponding to the Cp ligands (6.38 ppm) is shifted downfield relative to that of the metalloligand 1. Upon coordination of both AuCl units, the absolute values of the P-C coupling constants in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum are significantly increased and range from  ${}^{4}J_{PC} = 2.3$  Hz up to  ${}^{1}J_{PC} = 69.0$  Hz. In the  ${}^{31}P{}^{1}H{}$ NMR spectrum, a single resonance at 31.8 ppm is observed, indicating symmetric coordination of both gold atoms, and this is shifted considerably downfield relative to that of 1 (+ 38.4 ppm). The composition of the compound was confirmed by elemental analysis and single crystal X-ray diffraction. By slow diffusion of pentane into a saturated solution of 2 in CH<sub>2</sub>Cl<sub>2</sub>, single crystals suitable for structural analysis were obtained. The heterometallic complex crystallizes in the monoclinic space group  $P2_1/n$  with one molecule and 1.5 molecules of CH<sub>2</sub>Cl<sub>2</sub> in the asymmetric unit (Figure 2).

The Zr–O bond lengths (2.021(10) and 2.004(10) Å) are slightly elongated compared with those of **1**. For the PAuCl units, bond lengths of 2.270(4) and 2.288(4) Å (Au-Cl), and 2.228(4) and 2.242(4) Å (P–Au), are displayed. Both gold atoms



Figure 2. Solid-state structure of 2. Hydrogen atoms are not displayed for clarity. Selected bond lengths [Å] and angles [°]: Au1-Cl1 2.270(4), Au1-P1 2.228(4), Au2-Cl2 2.288(4), Au2-P2 2.242(4), Zr1-O1 2.021(10), Zr1-O2 2.004(10), P1-Au1-Cl1 179.4(2), P2-Au2-Cl2 175.92(2), O2-Zr1-O1 98.8(4).

are ligated in an almost linear fashion, as indicated by P-Au-Cl bond angles of 175.92(2)° and 179.4(2)°. Upon coordination of the gold atoms, the O1-Zr1-O2 angle widens slightly to 98.8(4)°. Inter- or intramolecular aurophilic interactions are not observed in the solid state.

Based on these results, we felt challenged to bring both gold atoms into closer proximity by modifying the metalloligand. Hence, dimethyl zirconocene was treated with phosphine II to obtain the metalloligand  $[Cp_2Zr(m-O-C_6H_4-PPh_2)_2]$ (3), which is a structural isomer of 1, and features a smaller distance between both phosphine units (Scheme 4).

Complex **3** was obtained in good yield and it was fully characterized by analytic and spectroscopic techniques. Resonances observed in the NMR spectra show similar shifts and coupling constants to those of **1**, for example, a singlet at -5.2 ppm is observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum. Subsequent reaction with two equivalents of [AuCl(tht)] led to the formation of the heterometallic complex, [Cp<sub>2</sub>Zr(*m*-*O*-C<sub>6</sub>H<sub>4</sub>-PPh<sub>2</sub>-AuCl)<sub>2</sub>] (**4**) (Scheme 4). During the reaction, minor decomposition was indicated by the formation of purple gold particles. However, compound **4** can be obtained analytically pure by crystallization from CH<sub>2</sub>Cl<sub>2</sub>/pentane. It crystallizes as small colourless rods in the triclinic space group *P*1 with one molecule of **4** and two molecules of CH<sub>2</sub>Cl<sub>2</sub> in the asymmetric unit (Figure 3).

Again, an almost linear coordination mode of both gold atoms is observed (P1-Au1-Cl1 = 177.29(11)° and P2-Au2-Cl = 171.96(11)°). The O1-Zr1-O2 bond angle (94.7(4)°) is slightly more acute than the corresponding angles in 1 and 2. As expected, the Au-Cl bond lengths (Au1-Cl1 2.285(3) Å and Au2-Cl2 2.292(3) Å) and the Au-P bond lengths (Au1-P1 2.231(3) Å and Au2-P2 2.229(4) Å) do not differ significantly from those of 2. The complex was further analysed by elemental analysis and NMR spectroscopy. A single resonance is observed at 33.1 ppm in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum.



Scheme 4. a) Synthesis of the metalloligand 3 with both phosphine groups in the *meta*-position and subsequent transformation to the heterometallic complex 4. b) Synthesis of the metalloligand 5 with both phosphine groups in the *ortho*-position and subsequent transformation to the heterometallic complex 6.

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**Figure 3.** Solid-state structure of **4.** Hydrogen atoms and solvent molecules  $(CH_2Cl_2)$  are not displayed for clarity. Selected bond lengths [Å] and angles [°]: Au1-Cl1 2.285(3), Au1-P1 2.231(3), Au2-Cl2 2.292(3), Au2-P2 2.229(4), Zr1-O1 1.987(8), Zr1-O2 2.014(9), P1-Au1-Cl1 177.29(11), P2-Au2-Cl2 171.96(11), O1-Zr1-O2 94.7(4).

In order to bring the phosphorus atoms into even closer proximity, we synthesized the metalloligand  $[Cp_2Zr(o-O-C_6H_4-PPh_2)_2]$  (5) by the same reaction procedure described above but this time we used phosphine III, which bears the OH group in the *ortho*-position. The zirconocene complex 5 can be obtained in good yield as colourless crystals from toluene. In contrast to the other metalloligands, the resonance in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum is observed at higher frequency (-16.7 ppm), and this corresponds with the upfield resonance of III.

Metalloligand **5** was reacted with [AuCl(tht)] and [AuC<sub>6</sub>F<sub>5</sub>(tht)] in CH<sub>2</sub>Cl<sub>2</sub> to obtain the heterometallic complexes, [Cp<sub>2</sub>Zr(o-O-C<sub>6</sub>H<sub>4</sub>-PPh<sub>2</sub>-AuCl)<sub>2</sub>] (**6**) and [Cp<sub>2</sub>Zr(o-O-C<sub>6</sub>H<sub>4</sub>-PPh<sub>2</sub>-AuCl)<sub>2</sub>] (**7**), respectively (Scheme 4). Both compounds were fully characterized by analytic methods, and in both cases, the molecular structures were determined by single crystal X-ray diffraction. Complexes **6** and **7** crystallize in the triclinic space group  $P\bar{1}$  with one molecule of CH<sub>2</sub>Cl<sub>2</sub> in the asymmetric unit. The solid-state structures are depicted in Figures 4 and 5.



**Figure 4.** Solid-state structure of **6**. Hydrogen atoms and solvent molecules  $(CH_2Cl_2)$  are not displayed for clarity. Selected bond lengths [Å] and angles [°]: Au1-Cl1 2.296(2), Au1-P1 2.237(2), Au2-Cl2 2.289(2), Au2-P2 2.241(3), Zr1-O1 2.043(6), Zr1-O2 2.034(6), O1-C1 1.322(10), O2-C19 1.340(9). P1-Au1-Cl1 175.55(10), P2-Au2-Cl2 176.00(9), O2-Zr1-O1 94.9(2).

Both compounds have similar structures, and the gold atoms feature a linear coordination geometry in both complexes. Whilst the Au–Cl, Au–P and Zr–O bond lengths of **6** are similar to those of its structural isomers **2** and **4**, the metal atoms are located on an almost straight line through the molecule. As indicated by an Au1-Zr1-Au2 angle of  $170.730(1)^{\circ}$ , and

a Cl1-Au1-Au2-Cl2 torsion angle of 26.36(2)°, both PAuCl units are nearly co-planar. The intermetallic distances are 4.4131(11) Å (Au1-Zr1) and 4.4116(12) Å (Au2-Zr1). An identical arrangement of the heavy atoms is observed in the solid-state structure of the pentafluorophenyl derivative 7 (Figure 5). Hence, the assembly of these heterometallic complexes is not significantly influenced by the nature of the anionic gold ligand. The intermetallic distances in 7 are 4.309(2) Å (Au1-Zr1) and 4.512(2) Å (Au2-Zr1). The angle between the heavy atoms is 161.28(2)°, illustrating a modest deviation from linearity. This can be explained by longer P-Au bond lengths (2.2859(14) and 2.2894(13) Å) than in 6. The Au–C<sub>6</sub>F<sub>5</sub> units are again arranged in a co-planar fashion, as indicated by the C19-Au1-Au2-C43 torsion angle (4.48(3)°). The intermetallic distances between gold and zirconium are longer than in systems with attributed metallic bonding, for example, a Zr-Ru system  $[Cp_2Zr(CO)(\mu-\eta^1(Zr),\eta^5-C_5H_4)Ru(CO)_2]$ ,<sup>[37]</sup> a phenomenon found in other distal ELHB complexes as well.  $\ensuremath{^{[1]}}$  In some cases, close intermetallic distances in ELHB complexes can be described as dative  $d^{10} \rightarrow d^0$  interactions. The gold-zirconium distances of the compounds described above are in a similar range as Zr-Ni distances, for example, in {[Cp<sub>2</sub>Zr(CH<sub>2</sub>PMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>Ni} with Zr-Ni gaps of 4.367(1)-4.416(1) Å.[38] Although there are no significant interactions between the gold and zirconium atoms, the arrangement of the metal atoms might be caused by weak electrostatic interactions between the electron-rich gold atom and the electron-poor zirconium centre (see below for guantum chemical investigations). This is supported by the fact that the arrangement of the atoms is independent of the nature and steric bulk of the anionic gold ligands. This is further supported by a third structure, described below, which was obtained from a totally different reaction.

Both compounds **6** and **7** were further investigated by elemental analysis, IR and NMR spectroscopy. In the  ${}^{31}P{}^{1}H{}$  NMR spectra, a singlet at 23.3 ppm is observed for **6**, whereas a pseudo-quintet is seen at 34.4 ppm (with a coupling constant of 8.8 Hz) for **7**. The signal splitting is caused by long-range coupling to the fluorine atoms of the C<sub>6</sub>F<sub>5</sub> ligands, and



**Figure 5.** Solid-state structure of **7.** Hydrogen atoms and solvent molecules (CH<sub>2</sub>Cl<sub>2</sub>) are not displayed for clarity. Selected bond lengths [Å] and angles [°]: Au1-P1 2.2859(14), Au1-C19 2.056(5), Au2-P2 2.2894(13), Au2-C43 2.055(4), Zr1-O1 2.042(3), Zr1-O2 2.028(3). C19-Au1-P1 173.89(15), C43-Au2-P2 175.57(14), O2-Zr1-O1 94.38(13), C1-O1-Zr1 134.2(3), C25-O2-Zr1 135.0(3).



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this can also be observed in comparable compounds.<sup>[26, 39]</sup> In the <sup>19</sup>F{<sup>1</sup>H} NMR spectrum, a characteristic set of signals, with an integration ratio of 2:1:2 for the C<sub>6</sub>F<sub>5</sub> groups, is observed at –116.1 ppm (*ortho-F*), –158.8 ppm (<sup>3</sup>J<sub>FF</sub> = 20.4 Hz, *para-F*) and –162.3 ppm (*meta-F*), respectively. Upon metal coordination, the resonances in the <sup>31</sup>P{<sup>1</sup>H} NMR spectra are shifted significantly downfield (+40 ppm for **6** and +51.1 ppm for **7**) from that of the free ligand **5**.

Because of the close proximity of the phosphine groups in **5**, and the flexibility of the ligand, we investigated whether **5** could be used as a bidentate chelating ligand. Hence, we used  $[Au(tht)_2][ClO_4]$  as the gold source since both tht ligands are easily replaced by stronger phosphine donors. The reaction between **5** and  $[Au(tht)_2][ClO_4]$  was conducted in CH<sub>2</sub>Cl<sub>2</sub>, and after simple workup, the cationic heterobimetalic complex  $[Cp_2Zr(o-O-C_6H_4-PPh_2)_2Au][ClO_4]$  (**8**) was obtained in good yield (Scheme 5).



Scheme 5. Synthesis of the ELHB complex 8.

Analysis by NMR spectroscopy revealed symmetric sets of signals in both the <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra. The formation of macrocyclic structures or polymeric chains via Au<sup>+</sup>-bridged metalloligands 5 is not observed in solution. Instead, signal splitting into pseudo-triplets ( $J_{PC} = 2.2-32.3$  Hz) is observed for the carbon atoms of the phenolate substituent. This is typically observed for metal atoms symmetrically coordinated by two phosphine ligands. In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, the chemical shift of the phosphorus atom is 29.9 ppm (a + 46.6 ppm downfield shift relative to 5). ESI-MS experiments were conducted and they confirm the proposed composition. The spectrum shows a major signal at 971.11 Da, and it also displays the correct isotopic distribution. Single crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a CH<sub>2</sub>Cl<sub>2</sub> solution of 8. The compound crystallizes in the triclinic space group P1 with one molecule in the asymmetric unit (Figure 6).

The gold cation is coordinated in a linear fashion by both phosphines (P1-Au1-P2=179.53(4)°), and the Au–P bond lengths are almost identical at 2.2999(14) Å (P1–Au1) and 2.2981(14) Å (P2–Au2), respectively. Due to the chelating metal complexation, the O1-Zr1-O2 angle (99.32(13)°) is wider than the corresponding angles in the other complexes, and this demonstrates a certain flexibility of the ligand. The distance between the gold atom and the zirconium atom is 4.094(2) Å. Although the metalloligand **5** exhibits a certain degree of flexibility, the formation of macrocyclic or oligomeric products could not be observed.



Figure 6. Solid-state structure of 8. Hydrogen atoms are not displayed for clarity. Selected bond lengths [Å] and angles [°]: Au1-P1 2.2999(14), Au1-P2 2.2981(14), Zr1-O1 1.989(3), Zr1-O2 2.018(3), P2-Au1-P1 179.53(4), O1-Zr1-O2 99.32(13).

All compounds described above are based on bifunctionalized and coordinatively saturated zirconocene units which act as bidentate ligands. On the other hand, a methyl zirconocene derivative would offer the possibility of further modification of the zirconium centre or it could be used as a precatalyst for hydroamination or polymerization.<sup>[40,41]</sup> With this is mind, we reacted dimethyl zirconocene with only one equivalent of **III** to obtain the monofunctionalized methylzirconocene phosphine,  $[Cp_2ZrMe(o-O-C_6H_4-PPh_2)]$  (**9**), as colourless single crystals from a toluene/pentane mixture (Scheme 6).



Scheme 6. Synthesis of the monofunctionalized zirconocene 9.

In the <sup>1</sup>H NMR spectrum, a singlet corresponding to the metal-bound CH<sub>3</sub> group is observed at 0.48 ppm. The chemical shift of the phosphorus atom is found at -16.8 ppm. Complex **9** is very sensitive to air and moisture, and decomposes with evolution of methane within short periods of time. Single crystal X-ray diffraction revealed the successful formation of the methyl zirconocene derivative. The compound crystallizes in the triclinic space group  $P\bar{1}$  with one molecule in the asymmetric unit (Figure 7).

The Zr1–O1 bond length of 1.996(2) Å is significantly shorter than the Zr1–C1 bond length of 2.270(3) Å. Although it is known that zirconocene alkyl complexes can lead to the reduction of metal compounds (e.g.,  $PbCI_2$ ),<sup>[42]</sup> we treated the monodentate ligand **9** with one equivalent of [AuCl(tht)] at low temperature (Scheme 7).

At -78 °C, no decomposition (as would be evidenced by the reaction mixture developing a pink colour) was observed, and after letting the reaction mixture reach room temperature,

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**Figure 7.** Solid-state structure of **9.** Hydrogen atoms are not displayed for clarity. Selected bond lengths [Å] and angles [°]: Zr1-O1 1.996(2), Zr1-C1 2.270(3); O1-Zr1-C1 96.85(10).



Scheme 7. Reaction of 9 with [AuCl(tht)] yielding the heterometallic bismethylgold complex 10.

a colourless solution was obtained. By crystallization from  $CH_2Cl_2$ /pentane, colourless crystals suitable for X-ray diffraction were obtained. Surprisingly, no heterobimetallic complex in the form of an expected AuCl phosphine complex was obtained. Instead, transmetallation and double ligand exchange took place to give the heterometallic bis(methylgold) complex,  $[Cp_2Zr(o-O-C_6H_4-PPh_2-AuCH_3)_2]$  (10). The complex crystallizes in the monoclinic space group  $P2_1/c$  (Figure 8).



Figure 8. Solid-state structure of 10. Most hydrogen atoms are not displayed for clarity. Selected bond lengths [Å] and angles [°]: Au1-P1 2.287(3), Au1-C1 2.057(13), Au2-P2 2.302(4), Au2-C2B 2.03(4), Zr1-O1 2.040(9), Zr1-O2 2.032(9), C1-Au1-P1 176.3(4), C2B-Au2-P2 174.0(2), O2-Zr1-O1 92.8(4).

The solid-state structure of **10** features the same structural arrangement observed for **6** and **7**. Two phosphine-phenolate ligands are bound to the zirconium atom. Each phosphine coordinates to a AuCH<sub>3</sub> moiety and the gold atoms are coordinated in a linear fashion with bond angles of  $176.3(4)^{\circ}$  and  $174.0(2)^{\circ}$ . As one methyl group is disordered, only the structural parameters of Au1–C1 are discussed. The Au–C1 distance of 2.057(13) Å (Au–C1) is considerably shorter than the corresponding bond length in [AuMe(PPh<sub>3</sub>)],<sup>[43]</sup> and more similar in length to Au–C bonds in Au NHC complexes.<sup>[44]</sup> Again, a near

linear arrangement of the heavy atoms is seen (Au1-Zr1-Au2 = 169.54(5)°). The intermetallic distances of Au–Zr (Au1–Zr1 = 4.4105(1) Å and Au2–Zr1 = 4.4814(12) Å) are slightly longer than in its structural analogues. The solid-state structure was supported by elemental analysis and NMR spectroscopy. In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, a singlet is observed at 41.9 ppm, corresponding to a distinctive downfield shift of +58.6 ppm relative to the starting material. In the <sup>1</sup>H NMR spectrum, a doublet is seen at 0.56 ppm with a <sup>3</sup>J<sub>PH</sub> coupling constant of 8.0 Hz, similar to that of [AuMe(PPh<sub>3</sub>)].<sup>[45]</sup> The presence of the AuMe moiety is further confirmed by the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, in which a doublet (<sup>2</sup>J<sub>PC</sub>=98.0 Hz) is observed.

According to these results, full transmetallation and ligand exchange took place in the reaction of a methylzirconocene with [AuCl(tht)], and this has not been observed before. Presumably, zirconocene dichloride is formed during the reaction and the ligand exchange reactions are in good agreement with the HSAB principle.<sup>[46,47]</sup> It is noteworthy that since [LAu]<sup>+</sup> species are considered isolobal with H<sup>+</sup>,<sup>[48]</sup> LAuMe complexes can be considered isolobal with CH<sub>4</sub>.

#### Quantum chemical investigation

The nature of the Au-Zr bonding in 2, 4 and 6 was investigated by quantum chemical RI-DFT calculations (functional BP86)<sup>[49-53]</sup> that were dispersion corrected by the D3 method of Grimme.<sup>[54]</sup> The basis set of each atom was of def-SV(P) quality,<sup>[55,56]</sup> calculations were performed using the program system TURBOMOLE.<sup>[57]</sup> The theoretical investigation clearly confirmed the non-bonding situation in 2 and 4. In 6 the situation is less obvious despite the promising concatenation of the Zr and the two Au atoms. From an Ahlrichs-Heinzmann-Roby-Davidson population analysis<sup>[58]</sup> the atomic charges Q were calculated to be +1.53 (Zr) and -0.07 (Au). The shared electron number (SEN(Au-Zr) = 0.0) indicates that there is no covalent bonding between the metal atoms. This interpretation is supported by comparison of the Zr-Au distance (exptl 4.41 Å, calcd 4.07 Å) with the sum of the metallic radii (about 3 Å). Presumably, the deviation of the calculated from the experimental Au-Zr distance in 6 (4.413 Å (exptl), 4.066 Å (calcd)) results from a metalloligand-guided crystal packing influence that exceeds the metal-metal interaction.

To obtain a deeper understanding of the Zr–Au bonding we applied the strategy which was pursued when analysing the questionable metal–metal interaction in a bimetallic Lu–Pd complex.<sup>[11]</sup> We investigated a model compound  $[Cp_2ZrF_2\cdot2[P(CH_3)_3AuCI]]$ , in which Zr and Au are not connected to each other through the ligand (Figure 9). The calculated Zr–Au distances in the model and **6** (4.133 and 4.066 Å) match each other very well. Similar results were observed for the population analysis (model compound: Q(Zr) = +1.59, Q(Au) = -0.09, SEN(Zr–Au) = 0.0). At large distances, the model complex dissociates into the expected units composing of highly ionic  $Cp_2ZrF_2$  and two [(PMe<sub>3</sub>)AuCI] molecules (the potential energy curve is given in Figure S1 of the Supporting Information). Comparable to the Lu/Pd system reported before,<sup>[11]</sup> the long-range interaction shows  $R^{-2}$  behaviour, which is typical



Figure 9. Model system  $[Cp_2ZrF_2 2P(CH_3)_3AuCI]$  investigated to interpret metal-metal bonding in 6.

for a charge–dipole interaction. Due to our understanding of the Lu/Pd system, we interpret the bonding between Zr and Au in **6** to be comparably weak.

#### Photophysical investigations

Figure 10 combines solid-state PL excitation (PLE) and emission (PL) spectra of the metalloligand 1 and Au-Zr complexes 2, 4 and 6–8, measured at cryogenic (20 K) and ambient (295 K) temperatures. The PLE spectra are rather similar, reflecting the similar organic framework of the complexes. The onset of absorption (more steep at low temperatures) is observed at about 350 nm for 1, 2, 4 and 8. In complexes 6 and 7 (likely exhibiting weak Au–Zr interactions) the onset is shifted to about 370 nm (dashed line).

At ambient temperature, the above complexes show weakto-moderate phosphorescence within a spectral range of approximately 400–650 nm, with the exception of the bright



**Figure 10.** Photoluminescence excitation (PLE) and emission (PL) spectra of solid complexes **1**, **2**, **4**, **6**–**8** at low (20 K) and ambient temperature. PL/PLE spectra were excited/recorded at 320 nm/emission maximum. The intensities of the spectra are scaled for clarity.

emitter 6 (see below). The PL maximum and efficiency apparently significantly depend on the specific molecular structure. The metalloligand 1 emits at approximately 550 nm with a PL quantum yield of 0.24%, as determined using an integrating sphere and excitation at 330 nm (see the Experimental Section). The PL intensity increases by a factor of approximately 10 by decreasing the temperature to 20 K (Figure 10). The Au-Zr compound **2** demonstrates analogous spectra and  $\Phi_{PL}$  = 0.68% (295 K). Despite the same composition and rather similar structure of 2 and 4 (cf. Figures 2, 3), the latter complex shows distinct PL with bright emission at about 430 nm at cryogenic temperatures. This shifts to about 500 nm at ambient temperature and strongly decreases in intensity. Also characteristic are different PL lifetimes (extracted from biexponential fits): the emission of 1 and 2 decays at 20 K on a time scale of tens to hundreds of µs, whereas the 430 nm band of 4 slowly decays within tens of milliseconds (contributed to components of roughly equal amplitude with  $\tau_1 = 0.71$  ms and  $\tau_2 =$ 6.9 ms). At ambient temperature, both 1, 2 and 4 (the band at 500 nm) demonstrate fast PL decay within a few (sub)microseconds.

The above observations likely indicate that the different metal (Zr, Au) sites may contribute to the PL, depending on the molecular (crystal) structure and temperature. We tentatively ascribe the low-temperature band of 4 at 430 nm to a ligand-to-metal charge-transfer (LMCT) excited state "localized" on the gold atom and phosphine ligand. On the other hand, the emission at approximately 500-530 nm observed for 2 and 4 (at ambient temperature) may be related to the zirconocene site, that is, to the emission of 1. The low-temperature PL of bimetallic Zr-Au complex 8 at about 470 nm is particularly broad and likely contributed by both metal sites (perhaps weakly interacting due to the relatively short Zr-Au distance; see quantum chemical investigation above). This picture seems to be in accordance with the complex emission-wavelengthdependent PL kinetics which were only observed for 8: the PL at the short-wavelength edge (e.g., at 440 nm) decays within hundreds of µs, whereas decay at longer emission wavelengths (e.g., at 600 nm) proceeds much faster, within tens of us.

As discussed above, trinuclear Au-Zr-Au complexes 6 and 7 exhibit a nearly identical, linear arrangement of the metal cations, which beneficially affects their photoluminescent behaviour, although no strong metal-metal interactions are present in the electronic ground states based on experimental findings and calculation (for 6). However, in our investigations the arrangement of the metals presumably contributes to the particular PL properties of 6 and 7 since these complexes were found to be the brightest emitters among the compounds studied at cryogenic temperatures. In fact, 6 remains an efficient emitter at ambient temperature, demonstrating  $\Phi_{\mathsf{PL}} =$ 19% (excitation at 350 nm). The PL efficiency of 6 becomes even larger upon cooling and approaches approximately 100% at low temperatures (Figure 10). The PL of 6 and 7 is also distinguished by characteristic emission decay parameters: the decay is monoexponential with  $\tau = 1.05$  and 0.97 ms at 20 K and  $\tau = 1.2$  and 0.20 µs at ambient temperature, respectively. Interestingly, such strongly reduced PL lifetimes at ambient



temperature—in relation to only moderately decreased PL intensities—indicate a significant increase of the radiative decay rate in **7** and particularly **6** by increasing the temperature.

## Conclusions

By using OH-funtionalized triarylphosphines, dimethyl zirconocene was converted to three different metalloligands in which the phosphine donor sites exhibit different spatial proximity to each other. The metalloligands were treated with [AuCl(tht)] and [AuC<sub>6</sub>F<sub>5</sub>(tht)] to obtain heterometallic complexes with varying intermetallic distances. Complex 5 could also successfully be used as a chelating ligand to obtain the heterobimetallic complex 8. By synthesizing the methylzirconocene derivative 9 and its subsequent reaction with [AuCl(tht)], full transmetallation as well as ligand exchange from the early to the late transition metal was observed leading to the heterometallic bis(methylgold) complex 10. The Zr-metalloligand 1, trimetallic and bimetallic Zr-Au complexes 2, 4, and 6-8 were investigated with respect to their photoluminescent properties. Our results suggest that weak cooperative Zr-Au intermetallic interactions, which are expected to be present in 6-8, may significantly affect the PL properties. Quantum chemical calculations on the Au-Zr interaction were conducted and reveal a weak interaction between the two metals. However, a detailed description of those interactions and their possible effects on the excited states will require more dedicated theoretical studies. An important aspect of our present work is that it provides a structurally related set of well-characterized reference compounds for such future studies.

## **Experimental Section**

#### **General procedures**

All manipulations were performed under rigorous exclusion of moisture and oxygen in flame-dried Schlenk-type glassware or in an argon-filled MBraun glovebox. For the most part gold compounds were handled with the exclusion of light by wrapping the compound-containing flasks in aluminium foil. Prior to use, CH<sub>2</sub>Cl<sub>2</sub> was distilled under nitrogen from CaH<sub>2</sub>. Hydrocarbon solvents (THF, diethyl ether, n-pentane) were dried using an MBraun solvent purification system (SPS-800). Deuterated solvents were obtained from Carl Roth GmbH (99.5 atom % D). NMR spectra were recorded on a Bruker Avance II 300 MHz or Avance 400 MHz. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} chemical shifts were referenced to the residual <sup>1</sup>H and <sup>13</sup>C resonances of the deuterated solvents and are reported relative to tetramethylsilane, <sup>31</sup>P{<sup>1</sup>H} and <sup>19</sup>F{<sup>1</sup>H} resonances were referenced to external 85% phosphoric acid and CFCl<sub>3</sub>, respectively. IR spectra were obtained on a Bruker Tensor 37. El-mass spectra were recorded at 70 eV on a Thermo Scientific DFS. ESI mass spectra were obtained using a FT-ICR (Fourier transform ion cyclotron resonance) lonSpec Ultima mass spectrometer equipped with a 7 T magnet (Cryomagnetics). FAB-Mass spectra were recorded with a Finnigan MAT90 spectrometer. Elemental analyses were carried out with an Elementar Vario EL or Micro Cube. [AuCl(tht)],<sup>[59]</sup> [Au(tht)<sub>2</sub>][ClO<sub>4</sub>],<sup>[60]</sup>  $[AuC_6F_5(tht)]^{[61]}$  as well as the employed phosphines  $I_7^{[34]}$   $II^{[35]}$  and  $III^{[33]}$  were prepared according to literature procedures.  $Cp_2ZrMe_2$ was purchased from Sigma-Aldrich (97%) and used as received.

#### X-ray crystallographic studies

A suitable crystal was covered in mineral oil (Aldrich) and mounted on a glass fibre. The crystal was transferred directly to the cold stream of a STOE IPDS 2 or a STOE StadiVari diffractometer. All structures were solved by direct methods or by the Patterson method (SHELXS-2013).<sup>[62]</sup> The remaining non-hydrogen atoms were located from difference in Fourier map calculations. The refinements were carried out by using full-matrix least-squares techniques on F, minimizing the function  $(F_0 - F_c)^2$ , where the weight is defined as  $4F_0^2/2(F_0^2)$  and  $F_0$  and  $F_c$  are the observed and calculated structure factor amplitudes using the program SHELXL-2013.<sup>[62]</sup> Carbon-bound hydrogen atom positions were calculated. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance. Positional parameters, hydrogen atom parameters thermal parameters, bond lengths and angles have been provided as Supporting Information.

### Synthesis

Synthesis of [(Cp<sub>2</sub>Zr(p-OC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (1): Dimethyl zirconocene (200 mg, 0.79 mmol, 1.00 equiv) and 4-(hydroxyphenyl)diphenylphosphine I (443 mg, 1.59 mmol, 2.00 equiv) were dissolved in toluene (10 mL) and stirred at 50  $^\circ\text{C}$  for 1 h. The colourless solution was concentrated to approximately 5 mL volume. The desired product crystallized, overnight, by vapour diffusion of pentane into the toluene phase. The mother liquor was decanted off and the product was dried under vacuum. Yield: 360 mg (59%, single crystals). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz):  $\delta$  = 5.89 (s, 10 H, Cp-H), 6.61–6.66 (m, 4H, CH), 7.03-7.12 (m, 12H, CH), 7.46-7.55 ppm (m, 12H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz):  $\delta = 113.4$  (Cp-C), 119.1 (d, <sup>3</sup>J=8.2 Hz,  $m-C_{\rm P}h$ ), 126.5 (d,  ${}^{3}J=8.6$  Hz,  $m-C_{\rm P}h$ ), 128.6 (s,  $p-C_{\rm P}h$ ), 128.8 (d,  ${}^{3}J=$ 6.6 Hz, o-C<sub>P</sub>h), 134.0 (d,  ${}^{2}J=19.2$  Hz, o-C<sub>P</sub>h), 136.4 (d,  ${}^{1}J=21.7$  Hz, PC), 139.4 (d, <sup>1</sup>J=12.3 Hz, PC), 166.9 ppm (s, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 121 MHz):  $\delta = -6.6$  ppm. IR (ATR):  $\tilde{\nu} = 3113$  (vw), 3050 (w), 3001 (m), 2923 (w), 1574 (m), 1541 (w), 1457 (vs.), 1431 (vs.), 1282 (vs.), 1268 (vs.), 1245 (vs.), 1180 (w), 1156 (w), 1120 (w), 1093 (w), 1067 (w), 1017 (m), 870 (s), 801 (s), 748 (vs.), 694 (s), 611 (m), 499 (m), 461 (m), 431 cm<sup>-1</sup> (w). Elemental analysis calcd (%) for  $[{\rm C}_{46}{\rm H}_{38}{\rm O}_2{\rm P}_2{\rm Zr}]$  (775.98): C 71.20, H 4.94; found C 69.81, H 4.63.

Synthesis of [(Cp<sub>2</sub>Zr(p-OC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>)(AuCl)<sub>2</sub>] (2): The phosphinefunctionalized metalloligand 1 (60 mg, 0.07 mmol, 1.00 equiv) and [AuCl(tht)] (50 mg, 0.15 mmol, 2.00 equiv) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and stirred for 3 h at room temperature. The colourless solution was concentrated to 2 mL and diethyl ether (25 mL) was added to precipitate a colourless solid. The residue was washed with diethyl ether (2×5 mL) and dried under vacuum. Single crystals suitable for X-ray analysis were obtained from slow diffusion of pentane into a solution of 2 in CH<sub>2</sub>Cl<sub>2</sub>. Yield: 75 mg (79%). <sup>1</sup>H NMR  $(CD_2CI_2, 400 \text{ MHz}): \delta = 6.38 \text{ (s, 10 H, Cp-H), 6.67-6.75 (m, 4H, CH),}$ 7.40–7.57 ppm (m, 24 H, CH).  ${}^{13}C{}^{1}H{}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz):  $\delta =$ 114.3 (Cp-C), 117.1 (d, <sup>1</sup>J=69.0 Hz, CP), 119.1 (d, <sup>3</sup>J=13.4 Hz, m-CH), 129.7 (d,  ${}^{3}J=11.8$  Hz, m-CH), 130.5 (d,  ${}^{1}J=62.5$  Hz, PC), 132.2 (d, <sup>4</sup>J=2.6 Hz, p-CH), 134.5 (d, <sup>2</sup>J=13.6 Hz, o-CH), 136.7 (d, <sup>2</sup>J=15.5 Hz, o-CH), 169.3 ppm (d, <sup>4</sup>J=2.3 Hz, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz):  $\delta = 31.8$  ppm. IR (ATR):  $\tilde{\nu} = 3050$  (w), 1582 (vs.), 1491 (vs.), 1435 (m), 1286 (vs.), 1169 (m), 1102 (vs.), 1016 (w), 998 (w), 870 (m), 834 (m), 805 (m), 746 (m), 691 (m), 636 (vw), 617 (vw), 545 (m), 531 (w), 504 (m), 477 (w), 449 cm<sup>-1</sup> (w). Elemental analysis calcd (%) for [C<sub>46</sub>H<sub>38</sub>Au<sub>2</sub>Cl<sub>2</sub>O<sub>2</sub>P<sub>2</sub>Zr] (1240.81): C 44.53, H 3.09; found C 44.18, H 3.16.

Synthesis of  $[Cp_2Zr(m-OC_6H_4PPh_2)_2]$  (3): Dimethyl zirconocene (182 mg, 0.72 mmol, 1.00 equiv) and 3-(hydroxyphenyl)diphenyl-

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phosphine II (402 mg, 1.44 mmol, 2.00 equiv) were dissolved in toluene (5 mL) and stirred for 2 h at ambient temperature. By slow diffusion of pentane into the reaction mixture, colourless crystals were obtained. They were separated from the mother liquor by decantation and dried under vacuum. Yield: 402 mg (71%, single crystals). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 400 MHz):  $\delta = 5.81$  (s, 10 H, Cp-H), 6.66–6.70 (m, 2H, CH), 6.80-6.85 (m, 2H, CH), 7.03-7.14 (m, 16H, CH), 7.47-7.56 ppm (m, 8H, CH).  $^{13}\text{C}\{^{1}\text{H}\}$  NMR (C\_6D\_6, 100 MHz):  $\delta\!=\!113.3$  (Cp-C), 119.2 (CH), 123.8 (d, <sup>2</sup>J=18.1 Hz, CH), 125.3 (d, <sup>2</sup>J=21.1 Hz, CH), 128.8 (s, p-CH), 128.8 (d, <sup>3</sup>J=6.7 Hz, m-CH) 130.0 (d, <sup>3</sup>J=8.6 Hz, CH), 134.3 (d,  ${}^{2}J = 19.5$  Hz, o-CH), 138.5 (d,  ${}^{1}J = 12.6$  Hz, PC), 139.0 (d,  ${}^{1}J =$ 12.0 Hz, PC), 166.1 ppm (d,  ${}^{3}J = 7.9$  Hz, CO).  ${}^{31}P{}^{1}H{}$  NMR (C<sub>6</sub>D<sub>6</sub>, 162 MHz):  $\delta = -5.2$  ppm. IR (ATR):  $\tilde{\nu} = 3049$  (vw), 1572 (s), 1473 (s), 1433 (m), 1401 (s), 1271 (vs.), 1243 (s), 1156 (vw), 1090 (vw), 1068 (vw), 1015 (w), 993 (w), 915 (m), 804 (m), 784 (m), 743 (m), 693 (vs.), 620 (w), 606 (w), 539 (vw), 496 (w), 462 (vw), 417 cm<sup>-1</sup> (vw).

Synthesis of [(Cp<sub>2</sub>Zr(m-OC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>)(AuCl)<sub>2</sub>] (4): The phosphinefunctionalized metalloligand 3 (150 mg, 0.19 mmol, 1.00 equiv) and [AuCl(tht)] (124 mg, 0.38 mmol, 2.00 equiv) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and stirred for 3 h at room temperature. After filtration, the colourless solution was concentrated to 2 mL and diethyl ether (25 mL) is added to precipitate a colourless solid. The residue is washed with diethyl ether  $(2 \times 5 \text{ mL})$  and dried under vacuum. Single crystals suitable for X-ray analysis were obtained from slow diffusion of pentane into a solution of 2 in CH<sub>2</sub>Cl<sub>2</sub>. Yield: 212 mg (89%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta = 6.22$  (s, 10 H, Cp-H), 6.65–6.72 (m, 4 H, CH), 6.95 (dd,  ${}^{3}J = 13.1$  Hz,  ${}^{3}J = 7.5$  Hz, 2 H, CH), 7.26–7.33 (m, 2H, CH), 7.46–7.61 ppm (m, 20H, CH).  $^{13}\text{C}\{^1\text{H}\}$  NMR (CD\_2Cl\_2, 100 MHz):  $\delta =$  114.1 (s, Cp-C), 122.5 (d,  ${}^{4}J =$  2.2 Hz, CH), 124.1 (d,  $^{2}J = 14.4$  Hz, CH), 125.1 (d,  $^{2}J = 12.9$  Hz, CH), 129.7 (d,  $^{3}J = 11.8$  Hz, CH), 129.7 (d,  ${}^{1}J = 62.0$  Hz,  $C_{a}$ ), 130.0 (d,  ${}^{1}J = 54.4$  Hz,  $C_{a}$ ), 131.0 (d,  ${}^{3}J = 14.3$  Hz, CH), 132.5 (d,  ${}^{4}J = 2.5$  Hz, CH), 134.7 (d,  ${}^{2}J = 13.6$  Hz, CH), 166.2 ppm (d,  ${}^{3}J = 15 \text{ Hz}$ ,  $C_{q}O$ ).  ${}^{31}P{}^{1}H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz):  $\delta \!=\!$  33.1 ppm. IR (ATR):  $\tilde{\nu} \!=\!$  3050 (w), 2953 (w), 2924 (w), 1575 (S9, 1561 (s), 1543 (w), 1474 (vs.), 1461 (s), 1435 (s), 1403 (s), 1307 (s), 1275 (cs), 1250 (s), 1183 (w), 1160 (w), 1099 (s), 1014 (w), 992 (m), 924 (m), 805 (m), 785 (m), 734 (m), 710 (m), 689 (s), 618 (w), 605 (w), 588 (w), 543 (m), 504 (m), 479 (w), 432 cm<sup>-1</sup> (w). Elemental analysis calcd (%) for  $[C_{46}H_{38}Au_2Cl_2O_2P_2Zr \cdot 2CH_2Cl_2]$  (1240.81): C 40.87, H 3.00; found C 40.76, H 2.997.

Synthesis of [Cp<sub>2</sub>Zr(o-OC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>] (5): Dimethyl zirconocene (91 mg, 0.36 mmol, 1.00 equiv) and 2-(hydroxyphenyl)diphenylphosphine III (200 mg, 0.72 mmol, 2.00 equiv) were dissolved in toluene (4 mL) and stirred at 50 °C for 1 h. By slow diffusion of pentane into the reaction mixture, colourless crystals can be obtained which are separated from the mother liquor by decantation and dried under vacuum. Yield: 194 mg (70%, single crystals). <sup>1</sup>H NMR  $(C_6 D_{67} 300 \text{ MHz}): \delta = 5.95 \text{ (s, 10 H, Cp-H), 6.68-6.73 (m, 2 H, CH), 6.94}$ (ddd, <sup>3</sup>*J*=7.8 Hz, <sup>3</sup>*J*=4.7 Hz, <sup>4</sup>*J*=1.5 Hz, 2 H, CH), 7.03–7.13 (m, 14 H, CH), 7.41–7.49 ppm (m, 8H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz):  $\delta =$ 114.0 (Cp-C), 119.3 (CH), 120.2 (CH), 125.3 (d, <sup>3</sup>J=6.9 Hz, PC<sub>a</sub>), 128.8 (d, <sup>3</sup>*J*=6.8 Hz, *m*-C<sub>P</sub>*h*), 128.8 (s, *p*-C<sub>P</sub>*h*), 131.0 (s, *C*H), 133.6 (s, *C*H), 134.5 (d,  ${}^{2}J = 19.8$  Hz,  $o-C_{P}h$ ), 138.2 (d,  ${}^{1}J = 11.7$  Hz, PC<sub>o</sub>), 168.5 ppm (d,  ${}^{2}J = 18.2 \text{ Hz}$ , CO).  ${}^{31}P{}^{1}H$  NMR (C<sub>6</sub>D<sub>6</sub>, 121 MHz):  $\delta = -16.7 \text{ ppm}$ . IR (ATR):  $\tilde{v} = 3049$  (vw), 2999 (m), 1574 (m), 1560 (m), 1476 (w), 1458 (vs.), 1431 (vs.), 1285 (vs.), 1277 (vs.), 1266 (vs.), 1245 (vs.), 1180 (w), 1156 (w), 1120 (w), 1089 (w), 1067 (w), 1022 (w), 1013 (w), 875 (m), 866 (m), 829 (vw), 811 (s), 799 (vs.), 745 (vs.), 729 (w), 694 (s), 677 (w), 612 (m), 500 (m), 461 (m), 431 cm<sup>-1</sup> (w). FAB-MS: m/z [*M*-C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>]<sup>+</sup>: 513.1, 514.1, 515.1. Elemental analysis calcd (%) for [C<sub>46</sub>H<sub>38</sub>O<sub>2</sub>P<sub>2</sub>Zr] (775.98): C 71.20, H 4.94; found C 70.71, H 4.91.

Synthesis of  $[(Cp_2Zr(o-OC_6H_4PPh_2)_2)(AuCI)_2]$  (6): The phosphine-functionalized metalloligand 5 (81 mg, 0.10 mmol, 1.00 equiv) and

[AuCl(tht)] (67 mg, 0.21 mmol, 2.00 equiv) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and stirred for 3 h at room temperature. The colourless solution was concentrated to 2 mL and diethyl ether (25 mL) was added to precipitate a colourless solid. The residue was washed with diethyl ether (2×5 mL) and dried under vacuum. Single crystals suitable for X-ray analysis were obtained from slow diffusion of pentane into a solution of **6** in  $CH_2CI_2$ . Yield: 108 mg (84%).  $^{1}\text{H}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta\!=\!6.15$  (s, 10 H, Cp-H), 6.49–6.57 (m, 4H, CH), 6.79-6.87 (m, 2H, CH), 7.36-7.42 (m, 2H, CH), 7.53-7.64 ppm (m, 20 H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz):  $\delta = 115.2$ (Cp-C), 115.9 (d,  ${}^{1}J = 67.7$  Hz,  $C_{q}$ ), 120.2 (d,  ${}^{3}J = 18.0$  Hz, CH), 120.3 (d,  ${}^{3}J = 13.1$  Hz, CH), 129.5 (d,  ${}^{1}J = 64.2$  Hz, C<sub>q</sub>), 129.7 (d,  ${}^{3}J = 12.0$  Hz, CH), 132.5 (d, <sup>4</sup>J=2.5 Hz, CH), 133.3 (d, <sup>2</sup>J=6.4 Hz, CH), 134.0 (d,  $^{4}J$  = 1.5 Hz, CH), 135.0 (d,  $^{2}J$  = 13.9 Hz), 167.2 ppm (d,  $^{2}J$  = 6.0 Hz, CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz):  $\delta = 23.3$  ppm. IR (ATR):  $\tilde{\nu} =$ 3072 (w), 3053 (w), 1579 (m), 1480 (w), 1459 (m), 1433 (vs.), 1284 (m), 1266 (bs), 1246 (s), 1184 (w), 1154 (w), 1128 (m), 1101 (m), 1069 (w), 1023 (w), 1011 (w), 998 (w), 864 (w), 838 (w), 825 (w), 810 (s), 774 (m), 750 (s), 691 (s), 636 (vw), 598 (w), 557 (w), 528 (m), 483 (m), 445 cm<sup>-1</sup> (vw). Elemental analysis calcd (%) for  $[C_{46}H_{38}Au_2Cl_2O_2P_2Zr]$  (1240.81): C 44.53, H 3.09; found C 43.74, H 3.16.

Synthesis of  $[(Cp_2Zr(o-OC_6H_4PPh_2)_2)(AuC_6F_5)_2]$  (7): The phosphinefunctionalized metalloligand 5 (75 mg, 0.09 mmol, 1.00 equiv) and [AuC<sub>6</sub>F<sub>5</sub>(tht)] (87 mg, 0.19 mmol, 2.00 equiv) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and stirred for 3 h at room temperature. The colourless solution was concentrated to 2 mL and pentane (25 mL) was added to precipitate a colourless solid. The residue was washed with pentane (2×5 mL) and dried under vacuum. Single crystals suitable for X-ray analysis were obtained from slow diffusion of pentane into a solution of 7 in CH<sub>2</sub>Cl<sub>2</sub>. Yield: 130 mg (88%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta = 5.88$  (s, 10 H, Cp-H), 6.50–6.54 (m, 2H, CH), 6.59 (ddd, <sup>3</sup>J=11.7 Hz, <sup>3</sup>J=7.7 Hz, <sup>4</sup>J=1.6 Hz, 2H, CH), 6.80-6.90 (m, 2H, CH), 7.33-7.43 (m, 2H, CH), 7.53-7.63 (m, 12H, CH), 7.64–7.77 ppm (m, 8H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz):  $\delta = 114.8$  (Cp-C), 116.9 (d, <sup>1</sup>J = 60.2 Hz, C<sub>q</sub>), 120.2 (d, <sup>3</sup>J = 4.9 Hz, CH), 120.4 (d,  ${}^{3}J=9.3$  Hz, CH), 129.8 (d,  ${}^{3}J=11.3$  Hz, CH), 130.8 (d,  ${}^{1}J=$ 56.6 Hz,  $C_q$ ), 132.2 (d,  ${}^4J=2.3$  Hz, CH), 133.7 (d,  ${}^2J=5.5$  Hz, CH), 134.0 (d,  ${}^{4}J = 1.5$  Hz, CH), 135.1 (d,  ${}^{2}J = 13.8$  Hz), 167.1 ppm (d,  ${}^{2}J =$ 6.9 Hz, CO). Carbon atoms of the  $C_6F_5$  ligands cannot be observed.  $^{31}\text{P}\{^{1}\text{H}\}$  NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz):  $\delta\!=\!34.4~\text{ppm}$  (pseudo-quintet).<sup>19</sup>F{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 376 MHz):  $\delta = -116.1$  (m, o-F), -158.8 (t,  ${}^{3}J = 20.4$  Hz, *p-F*), -162.3 ppm (m, *m-F*). IR (ATR):  $\tilde{\nu} = 3054$  (w), 1635 (vw), 1581 (w), 1561 (vw), 1501 (m), 1482 (w), 1453 (s), 1434 (vs.), 1353 (w), 1287 (m), 1267 (m), 1244 (m), 1183 (vw), 1159 (w), 1130 (w), 1100 (w), 1072 (w), 1059 (m), 1011 (w), 952 (s), 866 (m), 810 (s), 790 (w), 751 (m), 693 (s), 637 (vw), 603 (w), 555 (w), 524 (m), 483 (m), 442 cm<sup>-1</sup> (vw). Elemental analysis calcd (%) for [C<sub>58</sub>H<sub>38</sub>Au<sub>2</sub>F<sub>10</sub>O<sub>2</sub>P<sub>2</sub>Zr·CH<sub>2</sub>Cl<sub>2</sub>] (1504.03): C 44.60, H 2.54; found C 44.33, H 2.53.

Synthesis of [(Cp<sub>2</sub>Zr(o-OC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>)Au][ClO<sub>4</sub>] (8): The phosphinefunctionalized metalloligand 5 (50 mg, 0.06 mmol, 1.00 equiv) and [Au(tht)<sub>2</sub>][ClO<sub>4</sub>] (30 mg, 0.06 mmol, 1.00 equiv) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL) and stirred for 3 h at room temperature under exclusion of light. The colourless solution was dried under vacuum and the residue was washed with diethyl ether. The product was obtained as a colourless powder after drying again under high vacuum. Single crystals suitable for X-ray analysis were obtained from slow diffusion of diethyl ether into a solution of 7 in CH<sub>2</sub>Cl<sub>2</sub>/ acetonitrile. Yield: 62 mg (90%). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  = 5.98 (s, 10H, Cp-H), 6.58–6.66 (m, 2H, CH), 6.79–6.84 (m, 2H, CH), 6.92– 6.97 (m, 2H, CH), 7.52–7.64 ppm (m, 22H, CH). <sup>13</sup>C[<sup>1</sup>H] NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz):  $\delta$  = 114.5 (s, Cp), 115.0 (t, J=32.3 Hz, C<sub>q</sub>), 120.3 (t, J=



2.2 Hz, CH), 120.7 (t, J=4.6 Hz, CH), 129.3 (t, J=30.0 Hz,  $C_q$ ), 130.4 (t, J=5.8 Hz, CH), 133.0 (s, 2xCH, overlapping), 134.8 (d, J=7.6 Hz, CH), 135.4 (s, CH), 167.3 ppm (t, J=4.3 Hz,  $C_q$ O). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz):  $\delta$ =29.9 ppm. IR (ATR):  $\tilde{\nu}$ =3013 (vw), 2966 (w), 2873 (w), 1508 (w), 1457 (s), 1435 (s), 1396 (vs.), 1295 (m), 1264 (w), 1092 (vs.), 873 (w), 809 (w), 748 (w), 691 (w), 619 (w), 519 (w), 486 (w), 458 (vw), 415 cm<sup>-1</sup> (vw). ESI-MS: m/z [M]<sup>+</sup>: calcd 971.1060; found 971.11, 972.11, 973.11, 974.11, 975.11, 976.11, 977.11, 978.11, 979.11 (isotopic pattern). Elemental analysis calcd (%) for [C<sub>46</sub>H<sub>38</sub>AuClO<sub>6</sub>P<sub>2</sub>Zr] (1072.39): C 51.52, H 3.57; found C 50.96, H 3.70.

Synthesis of [Cp<sub>2</sub>Zr(Me)(o-OC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)] (9): Dimethyl zirconocene (200 mg, 0.79 mmol, 1.00 equiv) and 2-(hydroxyphenyl)diphenylphosphine (221 mg, 0.79 mmol, 1.00 equiv) were suspended in toluene (3 mL). The suspension was warmed until a clear solution was obtained. By slow diffusion of pentane into the reaction mixture, colourless crystals were obtained. They were separated from the mother liquor by decantation and dried under vacuum. Yield: 286 mg (70%, single crystals). <sup>1</sup>H NMR ( $C_6D_{6r}$  300 MHz):  $\delta = 0.48$  (s, 3 H, CH<sub>3</sub>), 5.75 (s, 10 H, Cp-H), 6.59 (ddd,  ${}^{3}J = 8.0$  Hz,  ${}^{3}J = 5.0$  Hz,  ${}^{4}J =$ 0.9 Hz, 1 H, CH), 6.67–6.72 (m, 1 H, CH), 6.88 (ddd,  ${}^{3}J=7.6$  Hz,  ${}^{3}J=$ 4.3 Hz, <sup>4</sup>J=1.6 Hz, 1 H, CH), 7.04-7.14 (m, 7 H, CH), 7.38-7.45 ppm (m, 4H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (C<sub>6</sub>D<sub>6</sub>, 75 MHz):  $\delta = 24.3$  (CH<sub>3</sub>), 111.6 (Cp-C), 118.4 (d,  ${}^{3}J = 1.7$  Hz), 120.1 (CH), 125.1 (d,  ${}^{3}J = 7.6$  Hz, PC<sub>a</sub>), 128.7 (d,  ${}^{3}J = 4.7$  Hz,  $m - C_{p}h$ ), 128.8 (s,  $p - C_{p}h$ ), 130.7 (s, CH), 133.7 (s, CH), 134.5 (d,  ${}^{2}J = 19.9$  Hz, o-C<sub>P</sub>h), 138.1 (d,  ${}^{1}J = 11.9$  Hz, PC<sub>a</sub>), 167.9 ppm (d,  $^2J\!=\!18.3~\text{Hz},~\text{CO})\!.$   $^{31}\text{P}\{^1\text{H}\}$  NMR (C\_6D\_6, 121 MHz):  $\delta\!=\!-16.8~\text{ppm}.$ IR (ATR):  $\tilde{\nu} = 3066$  (w), 3052 (w), 2999 (w), 2922 (w), 2868 (w), 1576 (m), 1475 (w), 1458 (vs.), 1431 (vs.), 1408 (w), 1306 (w), 1289 (vs.), 1272 (m), 1252 (m), 1180 (w), 1159 8w), 1139 (w), 1121 (w), 1097 (w), 1067 (w), 1035 (w), 1014 (m), 881 (m), 803 (s), 758 (s), 748 (s), 730 (s), 696 (s), 622 (w), 503 (w), 493 (w), 473 (w), 458 (w), 429 cm<sup>-1</sup> (w). FAB-MS: *m*/*z* [*M*-CH<sub>3</sub>]<sup>+</sup>: 497.0, 498.1, 499.0, 500.0, 501.0 (isotopic pattern). EI-MS: *m/z* [*M*-CH<sub>3</sub>]<sup>+</sup>: 497.192, 498.194, 499.193, 500.193. Elemental analysis calcd (%) for  $[C_{29}H_{27}OPZr]$ (513.73): C 67.80, H 5.30; found C 65.41, H 4.88. The compound was found to be repeatedly low in carbon in the microanalysis.

Synthesis of  $[(Cp_2Zr(o-OC_6H_4PPh_2)_2)(AuCH_3)_2]$  (10): The monofunctionalized metalloligand 9 (50 mg, 0.10 mmol, 1.00 equiv) and [AuCl(tht)] (33 mg, 0.10 mmol, 1.00 equiv) were cooled to -78 °C in a Schlenk tube.  $CH_2CI_2$  (3 mL) was slowly added and the colourless solution was stirred at low temperature for one hour. After warming to room temperature, the clear solution was carefully layered with diethyl ether. After a few days, colourless crystals were observed on the glass wall. They were separated from the mother liquor by decantation and finally dried under high vacuum. Yield: 28 mg (50%, single crystals). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 400 MHz):  $\delta$  = 0.56 (d, <sup>3</sup>J=8.0 Hz, 6 H, AuCH<sub>3</sub>), 6.06 (s, 10 H, Cp-H), 6.47–6.55 (m, 4 H, CH), 6.75–6.82 (m, 2H, CH), 7.32 (dt, <sup>3</sup>J=7.9 Hz, <sup>4</sup>J=1.1 Hz, 2H, CH), 7.43–7.70 ppm (m, 20 H, CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 100 MHz):  $\delta$  = 7.1 (d, <sup>2</sup>J=98 Hz, CH<sub>3</sub>), 114.8 (Cp-C), 120.0 (d, <sup>3</sup>J=7.3 Hz, CH), 120.1 (d, <sup>3</sup>J=4.4 Hz, CH), 129.4 (d, <sup>3</sup>J=10.6 Hz, *m*-CH), 131.4 (d, <sup>4</sup>J=2.0 Hz, *p*-CH), 132.6 (d,  ${}^{1}J = 43.0$  Hz, PC<sub>q</sub>), 132.9 (d,  ${}^{3}J = 4.2$  Hz), 133.5 (d,  ${}^{3}J =$ 5.0 Hz), 135.2 ppm (d,  ${}^{2}J$ =13.9 Hz, o-CH). Due to poor solubility, two quaternary carbon atoms could not be detected. <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 162 MHz):  $\delta = 41.9$  ppm. IR (ATR):  $\tilde{v} = 3049$  (w), 3007 (w), 2964 (w), 2907 (vw), 1494 (w), 1476 (w), 1459 (s), 1434 (vs.), 1396 (m), 1363 (w), 1301 (m), 1284 (m), 1268 (m), 1248 (s), 1182 (vw), 1156 (w), 1126 (w), 1100 (m), 1068 (m), 1015 (m), 866 (m), 812 (s), 752 (m), 695 (m), 636 (vw), 600 (w), 555 (w), 521 (m), 484 (m), 446 cm  $^{-1}$  (vw). Elemental analysis calcd (%) for  $[\mathsf{C}_{48}\mathsf{H}_{44}\mathsf{Au}_2\mathsf{O}_2\mathsf{P}_2\mathsf{Zr}]$ (1199.98): C 48.04, H 3.70; found C 47.41, H 3.60.

## **Crystal data**

Crystal data for C<sub>46</sub>H<sub>38</sub>O<sub>2</sub>P<sub>2</sub>Zr (1) (M=775.92 g mol<sup>-1</sup>): orthorhombic, space group *Pnma* (no. 62), *a*=12.490(3) Å, *b*=39.145(8) Å, *c*=7.8589(16) Å, *V*=3842.3(13) Å<sup>3</sup>, *Z*=4, *T*=120.15 K,  $\mu$ (Mo<sub>Kα</sub>)=0.407 mm<sup>-1</sup>, *D*<sub>calcd</sub>=1.341 g cm<sup>-3</sup>, 10324 reflections measured (4.162°  $\leq 2\Theta \leq 50.764^{\circ}$ ), 3568 unique ( $R_{int}$ =0.0658,  $R_{sigma}$ =0.1052) which were used in all calculations. The final  $R_1$  was 0.0358 ( $l > 2\sigma$ (l)) and  $wR_2$  was 0.0645 (all data).

Crystal data for  $C_{47.5}H_{41}Au_2CI_5O_2P_2Zr$  (**2**) ( $M = 1368.14 \text{ gmol}^{-1}$ ): monoclinic, space group  $P2_1/n$  (no. 14), a = 12.307(3) Å, b = 21.800(4) Å, c = 21.063(4) Å,  $\beta = 105.07(3)^{\circ}$ , V = 5457(2) Å<sup>3</sup>, Z = 4, T = 200.15 K,  $\mu(Mo_{K\alpha}) = 5.888 \text{ mm}^{-1}$ ,  $D_{calcd} = 1.665 \text{ g cm}^{-3}$ , 24274 reflections measured ( $3.736^{\circ} \le 2\Theta \le 52.03^{\circ}$ ), 10644 unique ( $R_{int} = 0.1204$ ,  $R_{sigma} = 0.1255$ ) which were used in all calculations. The final  $R_1$  was 0.0739 ( $l > 2\sigma(l)$ ) and  $wR_2$  was 0.2033 (all data).

Crystal data for  $C_{48}H_{42}Au_2Cl_6O_2P_2Zr$  (4)  $(M = 1410.61 \text{ g mol}^{-1})$ : triclinic, space group P1 (no. 2), a = 8.5826(17) Å, b = 14.031(3) Å, c = 21.075(4) Å,  $\alpha = 98.45(3)^{\circ}$ ,  $\beta = 96.69(3)^{\circ}$ ,  $\gamma = 107.05(3)^{\circ}$ , V = 2365.8(9) Å<sup>3</sup>, Z = 2, T = 103.15 K,  $\mu(Mo_{Ka}) = 6.848 \text{ mm}^{-1}$ ,  $D_{calcd} = 1.980 \text{ g cm}^{-3}$ , 21779 reflections measured ( $3.34^{\circ} \le 2\Theta \le 52.23^{\circ}$ ), 9210 unique ( $R_{int} = 0.1180$ ,  $R_{sigma} = 0.1700$ ) which were used in all calculations. The final  $R_1$  was 0.0541 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.1118 (all data).

Crystal data for  $C_{47}H_{40}Au_2Cl_4O_2P_2Zr$  (6)  $(M = 1325.68 \text{ g mol}^{-1})$ : triclinic, space group  $P\bar{1}$  (no. 2), a = 10.729(2) Å, b = 15.006(3) Å, c = 15.187(3) Å,  $\alpha = 70.21(3)^{\circ}$ ,  $\beta = 75.39(3)^{\circ}$ ,  $\gamma = 82.24(3)^{\circ}$ , V = 2222.9(9) Å<sup>3</sup>, Z = 2, T = 100.15 K,  $\mu(Mo_{K\alpha}) = 7.165 \text{ mm}^{-1}$ ,  $D_{calcd} = 1.981 \text{ g cm}^{-3}$ , 20445 reflections measured ( $2.888^{\circ} \le 2\Theta \le 52.084^{\circ}$ ), 8690 unique ( $R_{int} = 0.0690$ ,  $R_{sigma} = 0.1126$ ) which were used in all calculations. The final  $R_1$  was 0.0416 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0913 (all data).

Crystal data for  $C_{59}H_{40}Au_2Cl_2F_{10}O_2P_2Zr$  (7) ( $M = 1588.90 \text{ gmol}^{-1}$ ): triclinic, space group  $P\bar{1}$  (no. 2), a = 13.880(3) Å, b = 13.924(3) Å, c = 17.149(3) Å,  $\alpha = 104.51(3)^{\circ}$ ,  $\beta = 93.44(3)^{\circ}$ ,  $\gamma = 119.42(3)^{\circ}$ , V = 2728.2(12) Å<sup>3</sup>, Z = 2, T = 100.15 K,  $\mu(MO_{K\alpha}) = 5.786$  mm<sup>-1</sup>,  $D_{calcd} = 1.934$  g cm<sup>-3</sup>, 23.885 reflections measured ( $3.416^{\circ} \le 2\Theta \le 52.108^{\circ}$ ), 10644 unique ( $R_{int} = 0.0511$ ,  $R_{sigma} = 0.0611$ ) which were used in all calculations. The final  $R_1$  was 0.0291 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0612 (all data).

Crystal data for C<sub>46</sub>H<sub>38</sub>AuClO<sub>6</sub>P<sub>2</sub>Zr (**8**) (M=1072.34 g mol<sup>-1</sup>): triclinic, space group  $P\bar{1}$  (no. 2), a=11.839(2) Å, b=12.774(3) Å, c=15.225(3) Å,  $\alpha$ =75.87(3)°,  $\beta$ =79.14(3)°,  $\gamma$ =69.33(3)°, V=2075.9(9) Å<sup>3</sup>, Z=2, T=100.15 K,  $\mu$ (Mo<sub>Ka</sub>)=3.971 mm<sup>-1</sup>,  $D_{calcd}$ =1.716 g cm<sup>-3</sup>, 27424 reflections measured (3.474°  $\leq 2\Theta \leq 52°$ ), 8155 unique ( $R_{int}$ =0.0772,  $R_{sigma}$ =0.0682) which were used in all calculations. The final  $R_1$  was 0.0336 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0750 (all data).

Crystal data for  $C_{29}H_{27}$ OPZr (**9**) (M=513.69 gmol<sup>-1</sup>): triclinic, space group  $P\bar{1}$  (no. 2), a=10.363(2) Å, b=10.797(2) Å, c=12.432(3) Å,  $\alpha$ =85.34(3)°,  $\beta$ =74.50(3)°,  $\gamma$ =61.54(3)°, V=1176.6(5) Å<sup>3</sup>, Z=2, T= 110.15 K,  $\mu$ (Mo<sub>K $\alpha$ </sub>)=0.552 mm<sup>-1</sup>,  $D_{calcd}$ =1.450 g cm<sup>-3</sup>, 10368 reflections measured (4.59°  $\leq 2\Theta \leq 52.818°$ ), 4592 unique ( $R_{int}$ =0.0462,  $R_{sigma}$ =0.0712) which were used in all calculations. The final  $R_1$  was 0.0332 ( $I > 2\sigma(I)$ ) and  $wR_2$  was 0.0693 (all data).

Crystal data for  $C_{48}H_{44}Au_2O_2P_2Zr$  (**10**)  $(M = 1199.92 \text{ gmol}^{-1})$ : monoclinic, space group  $P_2_1/c$  (no. 14), a = 16.916(3) Å, b = 14.338(3) Å, c = 17.689(4) Å,  $\beta = 101.84(3)^\circ$ , V = 4199.0(15) Å<sup>3</sup>, Z = 4, T = 100.15 K,  $\mu(MO_{k\alpha}) = 7.329 \text{ mm}^{-1}$ ,  $D_{calcd} = 1.898 \text{ g cm}^{-3}$ , 20.285 reflections measured ( $3.688^\circ \le 2\Theta \le 52.214^\circ$ ), 8208 unique ( $R_{int} = 0.0819$ ,  $R_{sigma} = 0.0891$ ) which were used in all calculations. The final  $R_1$  was 0.0736 ( $l > 2\sigma(l)$ ) and  $wR_2$  was 0.2115 (all data).

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CCDC 1450770, 1450771, 1450772, 1450773, 1450774, 1450775, 1450776, and 1450777 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

#### Photophysical measurements

The PL measurements were performed on a Horiba Jobin-Yvon Fluorolog-322 spectrometer equipped with a closed-cycle optical cryostat (Leybold) operating at approximately 20-300 K. Solid samples (crystalline powders) were dispersed in a thin layer of polyfluoroester oil (ABCR GmbH), layered between two quartz plates and mounted on a cold finger of the cryostat. All emission spectra were corrected for the wavelength-dependent response of the spectrometer and detector (in relative photon flux units). Emission decay traces were recorded by connecting a photomultiplier to an oscilloscope (typically via a 500 Ohm load) and using a N<sub>2</sub>-laser for pulsed excitation at 337 nm ( $\approx$ 2 ns,  $\approx$ 5  $\mu$ J per pulse). PL quantum yields of solid complexes 1, 2 and 6 at ambient temperature were determined according to the method of Mello et al.,<sup>[63]</sup> using a 10 cm integrating sphere made out of optical PTFE with low auto-luminescence (Berghof GmbH), which was installed in the sample chamber of the Fluorolog-322. The accuracy of determination of the quantum yields was estimated to be  $\pm 10$  %.

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