

# Synthesis and Characterization of a Novel Triangular Rh<sub>2</sub>Au Cluster Compound Inspired by the Isolobality Concept

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Dedicated to Professor *Paul Knochel* on the occasion of his 65th birthday

The synthesis of [Rh<sub>2</sub>(η<sup>5</sup>-Cp)<sub>2</sub>(μ-H)(μ-PPh<sub>2</sub>)<sub>2</sub>]BF<sub>4</sub> (**2**) by protonation reaction of the metal basic complex [Rh<sub>2</sub>(η<sup>5</sup>-Cp)<sub>2</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>] (**1**) with tetrafluoroboric acid in diethyl ether is described. Complex salt **2** was obtained in high yield and fully characterized by spectroscopic means and X-ray crystal diffraction. Applying the isolobal analogy between H and the fragment Au(PPh<sub>3</sub>) as a synthetic strategy on the reaction of compound **2** with equimolar amounts of [Au(CH<sub>3</sub>)(PPh<sub>3</sub>)] in refluxing acetone resulted in the formation of the expected triangular cluster

compound [Rh<sub>2</sub>{μ-Au(PPh<sub>3</sub>)}(η<sup>5</sup>-Cp)<sub>2</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>]BF<sub>4</sub> (**3**) in good yield. Metal cluster salt **3** was fully characterized by spectroscopic data and its molecular structure in the crystal was determined by X-ray diffraction. The structural comparison of the protonated dirhodium core in the cationic complex of **2** with the Rh<sub>2</sub>Au framework in **3** is in good accordance with the isolobal relation between H<sup>+</sup> and Au<sup>+</sup> because they share the respective same position in these closely related molecular structures.

## 1. Introduction

The isolobal relation between gold (I) cations [Au]<sup>+</sup> and their complexes [AuL]<sup>+</sup> on the one hand and protons [H]<sup>+</sup> on the other hand is well established in the literature. After the first general introduction of the isolobal analogy as a bridge between inorganic, organometallic, and organic chemistry by *Hoffmann*,<sup>[1]</sup> only a few years later *Stone* highlighted the importance of this concept in the field of the synthesis of bi- and multimetallic metal clusters also with particular consideration of the isolobal relationship between the fragments H and Au(PPh<sub>3</sub>).<sup>[2]</sup> In this context *Braunstein* and *Rose*<sup>[3]</sup> reviewed the synthesis, the bonding situation as well as the chemical and catalytic reactivities of such bimetallic molecular clusters containing gold described at that time.<sup>[3]</sup> In 1985 the triangular Rh<sub>2</sub>Au cluster [Rh<sub>2</sub>{μ-Au(PPh<sub>3</sub>)}(μ-CO)(η<sup>5</sup>-Cp)<sub>2</sub>(μ-dppm)]BF<sub>4</sub> (dppm = Ph<sub>2</sub>PCH<sub>2</sub>PPh<sub>2</sub>)<sup>[4]</sup> was reported even by the use of the isolobal relationship between the groups μ-H and μ-Au(L) as synthetic tool operating also in the case of a related silver fragment.<sup>[5]</sup> Later, we also used this principle in our investigations and were successful in the preparation of Fe<sub>2</sub>M clusters (M = Cu, Ag, Au) using the complex [Fe<sub>2</sub>(μ-CO)(CO)<sub>6</sub>(μ-H)(μ-PR<sub>2</sub>)] (R = *t*Bu) and the corresponding deprotonated species, respectively.<sup>[6]</sup> Even the synthesis of the metal cluster [Mo<sub>2</sub>{μ-Au

(PPh<sub>3</sub>)}(η<sup>5</sup>-Cp)(CO)<sub>4</sub>(μ-PPh<sub>2</sub>)] could be realized using this pathway. However the reaction principle was here successful only in the case of gold, not for the other coinage-metals copper and silver.<sup>[7]</sup> Moreover, *Haupt* and co-workers were successful in the preparation of dirhenium metal clusters containing two bridging M(PR<sub>3</sub>) fragments (M = Au, Ag).<sup>[8]</sup> In this context, in 2012, the chemistry of gold under the special consideration of the isolobality concept as a guide in the synthesis of metal clusters was reviewed by *Raubenheimer* and *Schmidbauer*.<sup>[9]</sup> Sometime later *Adams* and co-workers described the isolobal relationship between the molecules [Re<sub>2</sub>(CO)<sub>8</sub>(μ-H)<sub>2</sub>] and the cluster [Re<sub>2</sub>{μ-Au(PPh<sub>3</sub>)}<sub>2</sub>(CO)<sub>8</sub>].<sup>[10]</sup> Both complexes can be regarded as 32-valence electron species and are formally unsaturated species.

Recently we have reported the synthesis and structural characterization of new, doubly phosphanyl-bridged rhodium(II) complexes of the formula [(Rh(η<sup>5</sup>-Cp)(μ-PPh<sub>2</sub>))<sub>2</sub>].<sup>[11]</sup> Closely related complexes of that type were already reported by *Werner* and co-workers,<sup>[12]</sup> and they were described as electron-rich species exhibiting strong metal basic properties which allow a protonation of the Rh–Rh bond. The molecular structure of this type of complex was confirmed at that time by the crystal-structure determination of the mixed phosphanido-bridged species [Rh<sub>2</sub>(η<sup>5</sup>-C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(μ-PMe<sub>2</sub>)(μ-PPh<sub>2</sub>)].<sup>[13]</sup> Now we have also studied the protonation reaction of the Rh–Rh bond in [(Rh(η<sup>5</sup>-Cp)(μ-PPh<sub>2</sub>))<sub>2</sub>], affording the corresponding hydrido-bridged cationic species which served as the precursor in the synthesis of the isolobal-analogous Rh<sub>2</sub>Au cluster confirming the relationship between H and Au(PPh<sub>3</sub>). On these findings we report in this paper.

## 2. Results and Discussion

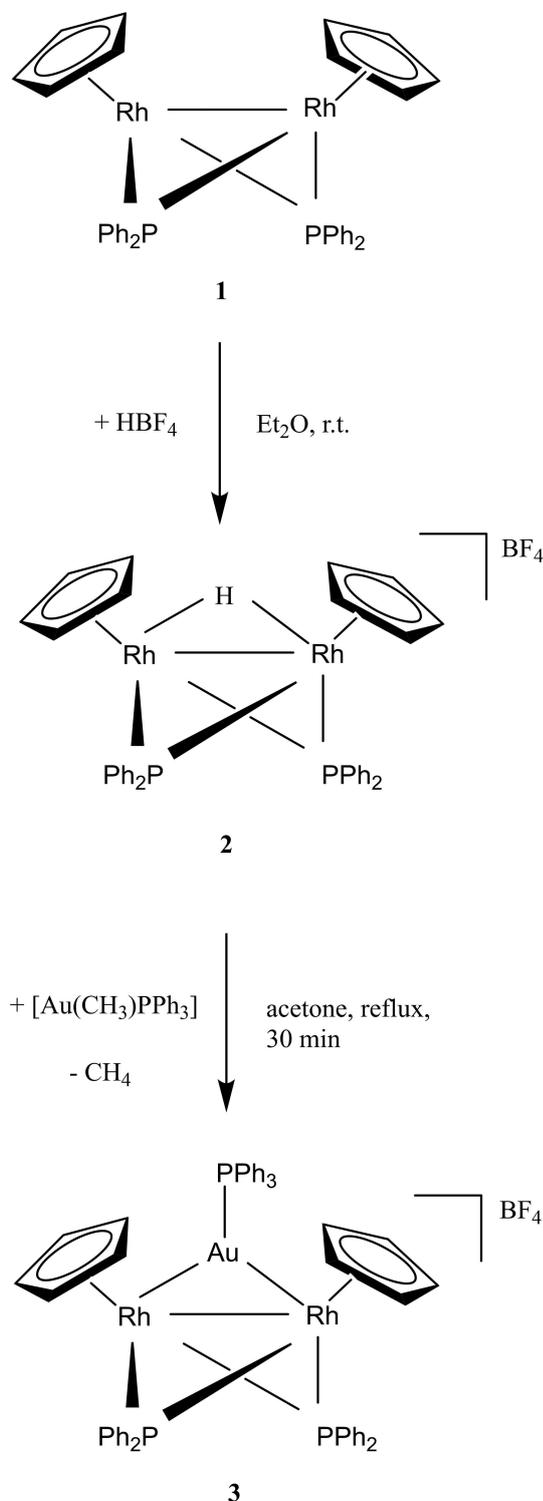
The treatment of red solutions of [Rh<sub>2</sub>(η<sup>5</sup>-Cp)<sub>2</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>] (**1**) in diethyl ether with tetrafluoroboric acid at ambient temperature resulted in a spontaneous reaction indicated by the quick

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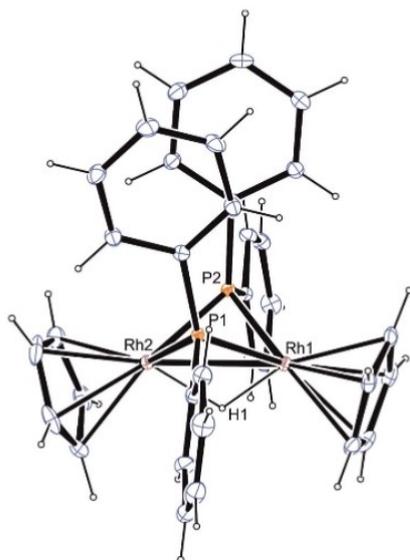
appearance of a dark red-brown precipitate (Scheme 1). After being stirred for a short time, the product was separated by filtration. The spectroscopic characterization by NMR methods ( $^1\text{H}$  and  $^{31}\text{P}$ ), elemental analysis, and mass spectrometry afforded unambiguously hints at the formation of the expected salt  $[\text{Rh}_2(\eta^5\text{-Cp})_2(\mu\text{-H})(\mu\text{-PPh}_2)_2]\text{BF}_4$  (**2**) in an analytically pure form



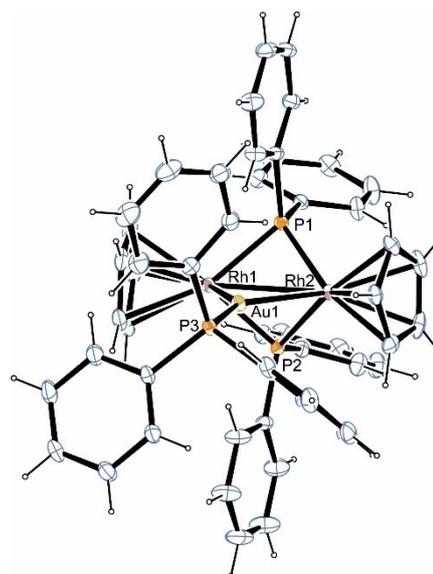
**Scheme 1.** Synthesis of  $[\text{Rh}_2(\eta^5\text{-Cp})_2(\mu\text{-H})(\mu\text{-PPh}_2)_2]\text{BF}_4$  (**2**) and transformation into compound  $[\text{Rh}_2(\mu\text{-Au}(\text{PPh}_3))(\eta^5\text{-Cp})_2(\mu\text{-PPh}_2)_2]\text{BF}_4$  (**3**).

and high yield. An indication that the corresponding hydrido species was formed resulted mainly from the  $^1\text{H}$  NMR spectrum of **2** showing a resonance signal in the high-field region as triplet of triplets at  $\delta = -15.4$  with the couplings  $^2J_{\text{PH}} = 20.0$  Hz and  $J_{\text{RHH}} = 20.0$  Hz ( $\text{CD}_2\text{Cl}_2$ ). These data correspond very well with the reported ones for  $[\text{Rh}_2(\eta^5\text{-Cp}^*)_2(\mu\text{-H})(\mu\text{-PMe}_2)_2]\text{PF}_6$  ( $\delta = -17.1$ , tt,  $^2J_{\text{PH}} = 34.0$  Hz and  $J_{\text{RHH}} = 22.0$  Hz,  $\text{CD}_3\text{NO}_2$ ).<sup>[12]</sup> The  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{CD}_2\text{Cl}_2$  exhibited a signal at  $\delta = 120.3$  as triplet ( $J_{\text{RHP}} = 98.3$  Hz, compare to the former compound:<sup>[12]</sup>  $J_{\text{RHP}} = 98.2$  Hz). The starting compound **1** exhibited in its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum a triplet at  $\delta = 137.5$  ( $J_{\text{RHP}} = 144.5$  Hz,  $\text{CD}_2\text{Cl}_2$ ).<sup>[11]</sup> Finally, single crystals of **2** suitable for X-ray diffraction were obtained and its molecular structure could be confirmed (see below). To proof the isolobal principle between H and Au( $\text{PPh}_3$ ), we reacted equimolar amounts of **2** and  $[\text{Au}(\text{CH}_3)(\text{PPh}_3)]$  in refluxing acetone. Successful preparations of gold-containing clusters using this principle, partially under mild reaction conditions, were already described in the literature.<sup>[3]</sup> During a reaction period of 30 min, a color change of the solution containing **2** and the gold component from red to red-brown was observed. After removal of the solvent, crystals of a red-brown product (**3**) were obtained from dichloromethane/dioxane, which were characterized by NMR spectroscopy ( $^1\text{H}$  and  $^{31}\text{P}$ ), elemental analysis, and mass spectrometry. First indications for the successful preparation of the isolobal analogous  $\text{Rh}_2\text{Au}$  cluster complex cation resulted from the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of the isolated product. The latter exhibited in its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum a signal in the downfield region as doublet of triplets at  $\delta = 141.1$  ( $J_{\text{RHP}} = 112.1$  Hz,  $^3J_{\text{PP}} = 11.0$  Hz,  $\text{CD}_2\text{Cl}_2$ ) unambiguously indicating a coupling with a second phosphorus atom. The signal of that nucleus was registered as triplet of triplets at  $\delta = 58.2$  with  $^2J_{\text{RHP}} = 6.0$  Hz (P on Au) and  $^3J_{\text{PP}} = 11.0$  Hz. These values correspond well with reported literature data of the compound  $[\text{Rh}_2\{\mu\text{-Au}(\text{PPh}_3)\}(\mu\text{-CO})(\eta^5\text{-Cp})_2(\mu\text{-dppm})]\text{BF}_4$ .<sup>[4]</sup> Also, the other spectroscopic data of the product exhibited **3** as the triangular cluster compound  $[\text{Rh}_2\{\mu\text{-Au}(\text{PPh}_3)\}(\eta^5\text{-Cp})_2(\mu\text{-PPh}_2)_2]\text{BF}_4$  (see Experimental Section). Moreover, single crystals of **3** suitable for X-ray diffraction were obtained and the molecular structure could be confirmed (see below). The described reaction sequence on the way from **1** to **3** is illustrated in the Scheme 1.

Single crystals of **2** suitable for X-ray diffraction were grown by the diffusion method from dichloromethane/diethyl ether at room temperature overnight. The compound **2** crystallized as red-brown crystals in the monoclinic space group *Cc* with four molecules in the unit cell. A view of the cationic complex of compound **2** in the crystal is depicted in Figure 1, selected bond lengths and angles are given in the caption. The protonation reaction of **1** resulting in its corresponding oxidative addition product **2** is connected with a change in the oxidation number of the central rhodium atoms from +II in compound **1** to +III in the product **2**. The cationic complex of **2** counts 34 valence electrons and should exhibit a Rh–Rh bond. This is in agreement with its observed diamagnetic property and the found Rh–Rh distance of 2.7640(3) Å. During the change from **1** to **2**, a lengthening of the Rh–Rh bond was expected and was indeed observed, compare to **1**:  $d(\text{Rh}–\text{Rh}) =$



**Figure 1.** Selected view of the molecular structure of the cationic complex of compound **2** in the crystal (dichloromethane and tetrafluoroborate omitted). Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Rh1–Rh2, 2.7640(3); Rh1–P1, 2.2519(9); Rh1–P2, 2.2543(9); Rh2–P1, 2.2584(10); Rh2–P2, 2.2613(9); Rh1–H1, 1.68(6); Rh2–H1, 1.74(6). P1–Rh1–P2, 80.16(4); P1–Rh2–P2, 79.88(4); P1–Rh1–H1, 81(2); P1–Rh2–H1, 80(2); Rh1–P1–Rh2, 75.59(3); Rh1–P2–Rh2, 75.49(3).



**Figure 2.** Selected view of the molecular structure of the cationic complex of compound **3** in the crystal. Displacement ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Rh1–Rh2, 2.8887(3); Rh1–Au1, 2.6987(3); Rh2–Au1, 2.7114(3); Rh1–P1, 2.2313(9); Rh2–P1, 2.2334(9); Rh1–P2, 2.2408(9); Rh2–P2, 2.2488(8); Au1–P3, 2.2680(9). Rh1–Au1–Rh2, 64.545(8); Au1–Rh1–Rh2, 57.941(8); Au1–Rh2–Rh1, 57.514(8); Rh1–Au1–P3, 147.56(2); Rh2–Au1–P3, 147.11(2); Rh2–Rh1–P1, 49.71(2); Rh2–Rh1–P2, 50.07(2); Au1–Rh1–P1, 91.19(2); Au1–Rh1–P2, 88.54(2); P1–Rh1–P2, 81.26(3); P1–Rh2–P2, 81.04(3).

2.7513(3).<sup>[11]</sup> The lengthening of a M–M bond upon protonation is expected due to the conversion of a 2c–2e bond to a 3c–2e bond, and the Rh–Rh distance is lengthened with respect to **1** as a consequence of the interaction of the electrophilic agent with the rhodium-to-rhodium bond. Moreover, the overall bonding parameters of compound **1** and the cationic complex in **2** were found in very good agreement. The position of the bridging hydrido ligand in complex **2** could be unambiguously determined during the structure refinement.

Single crystals of **3** suitable for X-ray diffraction were obtained by the diffusion method from dichloromethane/dioxane at room temperature overnight. Compound **3** crystallized as red-brown crystals in the monoclinic space group  $P2_1/n$  with four molecules in the asymmetric unit. A selected view of the cationic complex of **3** in the crystal is shown in Figure 2, selected bond lengths and angles are given in the caption. Shining light on the isolobality relationship of the cationic complex species of **2** and **3**, a comparison of their molecular structures seemed to be useful. Since the position of the bridging hydrido ligand in **2** could be unambiguously determined, the question was of interest whether its position is occupied after the substitution by gold from the incoming fragment  $\text{Au}(\text{PPh}_3)$ . On the assumption that the isolobal relationship is valid for our pair of rhodium complexes, the replacement of H in **2** by  $\text{Au}(\text{PPh}_3)$  in **3** should not be connected with major changes in their molecular structures. Thus, an inspection of the dihedral angles between the individual triangular planes building the three “butterfly”-arrangements in the ground core of these two complexes seemed to be of interest. The following dihedral angles between the corresponding planes were found for the hydrido complex in **2** [°]:

Rh1–Rh2–P1 / Rh1–Rh2–P2 = 71.16(5), Rh1–Rh2–H1 / Rh1–Rh2–P1 = 44.0(4), and Rh1–Rh2–H1 / Rh1–Rh2–P2 = 65.0(4). In comparison with the  $\text{Rh}_2\text{Au}$  cluster complex in **3**, the corresponding dihedral angles [°] were found: Rh1–Rh2–P1 / Rh1–Rh2–P2 = 63.28(4), Rh1–Rh2–Au1 / Rh1–Rh2–P1 = 55.73(4), and Rh1–Rh2–Au1 / Rh1–Rh2–P2 = 60.99(4). Despite the higher steric demand of the  $\text{Au}(\text{PPh}_3)$  fragment no significant changes in the ground core geometry of the two molecules were observed. This was mainly manifested by the good agreement of the dihedral angles between the planes Rh1–Rh2–H1 / Rh1–Rh2–P2 in **2** and Rh1–Rh2–Au1 / Rh1–Rh2–P2 in **3**. The main structural differences may be rationalized by the greater steric demand of the  $\text{Au}(\text{PPh}_3)$  fragment compared with that of the hydrido ligand.

As mentioned above, the X-ray crystal structure of the triangular  $\text{Rh}_2\text{Au}$  compound  $[\text{Rh}_2\{\mu\text{-Au}(\text{PPh}_3)\}\{\mu\text{-CO}\}(\eta^5\text{-Cp})_2(\mu\text{-dppm})]\text{BF}_4$ <sup>[4]</sup> was reported as the first example of a  $\text{Rh}_2\text{Au}$  species structurally characterized in the literature. The Rh–Rh distance in the latter compound of 2.760(2) Å falls within the range reported for similar Rh–Rh bonded species. However in these molecules the rhodium-to-rhodium bond is generally bridged by the dppm ligand. The Rh1–Rh2 bond with 2.8886(5) Å in our compound **3** is presumably elongated because of the introduction of the bigger  $\text{Au}(\text{PPh}_3)$  fragment. In the aforementioned  $\text{Rh}_2\text{Au}$  species,<sup>[4]</sup> however, an almost equilateral triangle was found [Rh1–Au, 2.718(1) and Rh2–Au, 2.732(1) Å] which is in some disagreement with our observations. Presumably, the both rhodium atoms in the metal cluster compound<sup>[4]</sup> were held closer together by the bridging dppm ligand which is

not comparable to the situation in our compound **3**. However, the discussed distances in **3** are in a better accordance with the observed ones in a second structurally characterized Rh<sub>2</sub>Au cluster compound, [Rh<sub>2</sub>{μ-Au(PPh<sub>3</sub>)}{μ-1,8-(NH)<sub>2</sub>C<sub>10</sub>H<sub>6</sub>}(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>ClO<sub>4</sub>]<sup>[14]</sup>. For the latter compound the following parameters were reported: Rh–Au, 2.690(2), Rh<sub>2</sub>–Au, 2.797(2) and Rh–Rh<sub>2</sub>, 2.815(2) Å which lie in between the corresponding bond lengths of the three characterized compounds of interest.

### 3. Conclusions

In summary, we confirmed herein the strong metal basic properties of [Rh<sub>2</sub>(η<sup>5</sup>-Cp)<sub>2</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>] (**1**) and studied the reaction behavior of **1** towards the electrophile H<sup>+</sup> using tetrafluoroboric acid as the proton source. Thus the protonation of the Rh–Rh bond in **1** resulted in the expected complex salt [Rh<sub>2</sub>(η<sup>5</sup>-Cp)<sub>2</sub>(μ-H)(μ-PPh<sub>2</sub>)<sub>2</sub>]BF<sub>4</sub> (**2**) in nearly quantitative yield. Although such species were already described in the literature,<sup>[12]</sup> no results on X-ray crystal-structure data of such species were reported to date. During our investigations it was possible to determine the molecular structure of **2** in the crystal. Inspired by the well-established isolobal relationship between H<sup>+</sup> and [Au(PPh<sub>3</sub>)]<sup>+</sup>, we undertook efforts to show the possibility of the substitution of H<sup>+</sup> towards the corresponding coinage-metal fragment. Thus the preparation of the novel triangular cluster compound [Rh<sub>2</sub>{μ-Au(PPh<sub>3</sub>)}(η<sup>5</sup>-Cp)<sub>2</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>]BF<sub>4</sub> (**3**) was realized in the reaction of **2** with [Au(CH<sub>3</sub>)(PPh<sub>3</sub>)] in refluxing acetone. That result is a further contribution using the isolobality concept, which can serve as a good guide to develop synthetic routes with the aim of preparing heteronuclear metal clusters containing coinage-metal ligand fragments.

## Experimental Section

### General

All reactions were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. Diethyl ether was dried over sodium-benzophenone ketyl and freshly distilled prior to use. Reagents, including [Au(CH<sub>3</sub>)(PPh<sub>3</sub>)], were purchased commercially from ABCR and used without further purification. NMR spectra were obtained using a Jeol Eclipse 400 instrument operating at 400 (<sup>1</sup>H) and 162 MHz (<sup>31</sup>P) respectively. Chemical shifts are given in ppm from SiMe<sub>4</sub> (<sup>1</sup>H), or 85% H<sub>3</sub>PO<sub>4</sub> (<sup>31</sup>P). Mass spectra were recorded using a Thermo Finnigan MAT 95 spectrometer. Microanalyses were performed by the Microanalytical Laboratory of the Department of Chemistry, LMU Munich, using a Heraeus Elementar Vario EL instrument.

### [Rh<sub>2</sub>(η<sup>5</sup>-Cp)<sub>2</sub>(μ-H)(μ-PPh<sub>2</sub>)<sub>2</sub>]BF<sub>4</sub> (**2**)

Compound **1** (250 mg, 0.35 mmol) was dissolved in diethyl ether (50 mL) and to the stirred solution few drops of HBF<sub>4</sub>·Et<sub>2</sub>O were added until a red-brown precipitate was obtained. The solution was stirred at room temperature for additional 10 min. The solid was removed by filtration and washed twice with 20-mL-portions of diethyl ether. The crude product was dried in vacuo and recrystal-

lized by the diffusion method overnight from dichloromethane/diethyl ether affording **2** as dichloromethane solvate as dark red crystal plates suitable for X-ray diffraction. Yield: 283 mg (92%). <sup>31</sup>P {<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): δ = 120.3 8 (t, J<sub>RhP</sub> = 98.3 Hz). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): δ = 7.12 (m, 20 H, C<sub>6</sub>H<sub>5</sub>), 5.59 (s, 10H, C<sub>5</sub>H<sub>5</sub>), –15.40 (tt, 1H, <sup>2</sup>J<sub>PH</sub> = 20.0 Hz, J<sub>RhH</sub> = 20.0 Hz). MS (ESI<sup>+</sup>): m/z = 706 [M<sup>+</sup> – H] (100%). Anal. Calcd. for C<sub>35</sub>H<sub>33</sub>BCl<sub>2</sub>F<sub>4</sub>P<sub>2</sub>Rh<sub>2</sub> (879.12): C 47.82, H 3.78, found: C 47.38, H 3.82%.

### [Rh<sub>2</sub>{μ-Au(PPh<sub>3</sub>)}(η<sup>5</sup>-Cp)<sub>2</sub>(μ-PPh<sub>2</sub>)<sub>2</sub>]BF<sub>4</sub> (**3**)

The dichloromethane solvate of **2** (150 mg, 0.17 mmol) was dissolved in acetone (15 mL) and [Au(CH<sub>3</sub>)(PPh<sub>3</sub>)] (81 mg, 0.17 mmol) was added. Then the mixture was refluxed for 30 min resulting in a dark red-brown solution. After cooling to room temperature, the solvent was removed in vacuo to dryness. The remaining residue was dissolved in dichloromethane (2 mL) and the solution carefully layered with dioxane (30 mL). Red-brown crystals of **3** suitable for X-ray diffraction were obtained overnight. Yield: 183 mg (86%). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): δ = 141.1 (dt, J<sub>RhP</sub> = 112.1 Hz, <sup>3</sup>J<sub>PP</sub> = 11.0 Hz, μ-P), 58.2 [tt, <sup>2</sup>J<sub>RhP</sub> = 6.0 Hz (P on Au) and <sup>3</sup>J<sub>PP</sub> = 11.0 Hz, Au(PPh<sub>3</sub>)]. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>, 20 °C): δ = 7.28 (m, 35H, P (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub> and P(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>), 5.38 (s, 10H, C<sub>5</sub>H<sub>5</sub>). MS (ESI<sup>+</sup>): m/z = 1165 [M<sup>+</sup>] (55%). Anal. Calcd. for C<sub>52</sub>H<sub>45</sub>AuBF<sub>4</sub>P<sub>3</sub>Rh<sub>2</sub> (1252.43): C 49.87, H 3.62, found: C 49.84, H 3.93%.

### Crystal-Structure Determination and Refinement

Crystals suitable for X-ray crystallography of **2** and **3**, respectively, were obtained as described in the Experimental section. Crystals were selected by means of a polarization microscope, mounted on a MiTeGen MicroLoop, and investigated with a Bruker D8 Venture XTS diffractometer using Mo-Kα radiation (λ = 0.71073 Å). The frames were integrated with the Bruker SAINT software package.<sup>[15]</sup> Data were corrected for absorption effects using the Multi-scan method (SADABS).<sup>[16]</sup> The structures were solved and refined using the Bruker SHELXTL Software package.<sup>[16]</sup> All hydrogen atoms have been calculated in ideal geometry riding on their parent atoms. The structure of **2** has been refined as a 2-component inversion twin. The volume ratio of twin domains was refined to 0.52/0.48. In that

**Table 1.** Details of the X-ray crystal data collection and structure refinement for compounds **2** and **3**.

Compound	<b>2</b> – CH <sub>2</sub> Cl <sub>2</sub>	<b>3</b>
Empirical formula	C <sub>35</sub> H <sub>33</sub> BCl <sub>2</sub> F <sub>4</sub> P <sub>2</sub> Rh <sub>2</sub>	C <sub>52</sub> H <sub>45</sub> AuBF <sub>4</sub> P <sub>3</sub> Rh <sub>2</sub>
M <sub>r</sub>	879.08	1252.38
Crystal system	monoclinic	monoclinic
Space group	Cc	P2 <sub>1</sub> /n
a [Å]	16.7513(7)	13.3869(7)
b [Å]	10.1622(4)	24.8082(12)
c [Å]	20.0809(7)	16.6749(8)
β [°]	97.0460(10)	94.502(10)
V [Å <sup>3</sup> ]	3392.6(2)	5520.7(5)
Z	4	4
T [K]	102(2)	100(2)
ρ <sub>calcd.</sub> [g cm <sup>-3</sup> ]	1.721	1.507
μ [mm <sup>-1</sup> ]	1.272	3.373
θ range for data collection [°]	3.379 to 30.497	2.902 to 30.508
Reflections collected	20385	100307
Independent reflections	8899	16826
R <sub>int</sub>	0.0346	0.0668
R <sub>1</sub> [I > 2σ(I)]	0.0250	0.0316
wR <sub>2</sub> (all data)	0.0569	0.0822
Parameters	439	614
Goodness of fit on F <sup>2</sup>	1.078	1.088
Largest diff. peak/hole [e Å <sup>-3</sup> ]	0.465/-0.634	1.024/-0.868

case, the centrosymmetric space group  $C2/c$  could be excluded since even the metal complex does not show  $C_2$  or inversion symmetry. The disorder of  $\text{CH}_2\text{Cl}_2$  as well as of  $\text{BF}_4^-$  has been described by split models. For  $\text{CH}_2\text{Cl}_2$ , the ratio of site occupation factors was refined to 0.52/0.48 (refined anisotropically). The figures have been drawn at the 50% probability level,<sup>[18]</sup> and in the figures the  $\text{CH}_2\text{Cl}_2$  and the  $\text{BF}_4^-$  have been omitted. For **3** the disorder of  $\text{BF}_4^-$  has been described by a split model. The ratio of site occupation factors of the two disordered parts was refined to 0.76/0.24. Within a  $\text{BF}_4^-$  ion, all B–F bonds have been restrained to be equal within a standard deviation of 0.01 Å while all F–F distances have been restrained to be equal within a standard deviation of 0.02 Å. The solvent could not be modeled properly and has been squeezed out. According to the PLATON SQUEEZE<sup>[19]</sup> output there are two equivalent voids, each with a volume of 592 Å<sup>3</sup> and 131 squeezed-out electrons. This would fit to 2  $\text{CH}_2\text{Cl}_2$  (84 electrons) and 1 dioxane (48 electrons) with a total count of 132 electrons. Details of the crystal data, data collection and structure refinement parameters of compounds **2** and **3** are summarized in Table 1. Crystallographic data for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-2013907 (**2**) and CCDC-2013908 (**3**) (<https://www.ccdc.cam.ac.uk/structures/>).

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** cyclopentadienyl compounds · crystal structures · gold · isolobality concept · rhodium

- [1] R. Hoffmann, *Angew. Chem. Int. Ed.* **1982**, *21*, 711; *Angew. Chem.* **1982**, *94*, 725.
- [2] F. G. A. Stone, *Angew. Chem. Int. Ed.* **1984**, *23*, 89; *Angew. Chem.* **1984**, *96*, 85.
- [3] P. Braunstein, J. Rose, *Gold Bull.* **1985**, *18*, 17 and references cited therein.
- [4] S. Lo Schiavo, G. Bruno, F. Nicolò, P. Piraino, F. Faraone, *Organometallics* **1985**, *4*, 2091.
- [5] G. Bruno, S. Lo Schiavo, P. Piraino, F. Faraone, *Organometallics* **1985**, *4*, 1098.
- [6] a) B. Walther, H. Hartung, H.-C. Böttcher, U. Baumeister, U. Böhlend, J. Reinhold, J. Sieler, J. Ladriere, H.-M. Schiebel, *Polyhedron* **1991**, *10*, 2423; b) H.-C. Böttcher, H. Hartung, A. Krug, B. Walther, *Polyhedron* **1994**, *13*, 2893.
- [7] H. Hartung, B. Walther, U. Baumeister, H.-C. Böttcher, A. Krug, F. Rosche, P. G. Jones, *Polyhedron* **1992**, *11*, 1563.
- [8] H.-J. Haupt, D. Petters, U. Flörke, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1652.
- [9] H. G. Raubenheimer, H. Schmidbaur, *Organometallics* **2012**, *31*, 2507.
- [10] R. D. Adams, Y. O. Wong, Q. Zhang, *Organometallics* **2013**, *32*, 7540.
- [11] H.-C. Böttcher, M. Graf, P. Mayer, M. Scheer, *Eur. J. Inorg. Chem.* **2019**, 2648.
- [12] B. Klingert, H. Werner, *J. Organomet. Chem.* **1987**, *333*, 119.
- [13] H. Werner, B. Klingert, *Organometallics* **1988**, *7*, 911.
- [14] M. J. Fernández, J. Modrego, L. A. Oro, M.-C. Apreda, F. H. Cano, C. Foces-Foces, *J. Chem. Soc. Dalton Trans.* **1989**, 1249.
- [15] Bruker (2012), SAINT, Bruker AXS Inc., Madison, Wisconsin, USA.
- [16] G. M. Sheldrick (1996), SADABS, University of Göttingen, Germany.
- [17] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3.
- [18] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849.
- [19] A. L. Spek, *Acta Crystallogr. Sect. C* **2015**, *71*, 9.

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