Synthesis and Characterization of a Novel Triangular Rh₂Au Cluster Compound Inspired by the Isolobality Concept

Hans-Christian Böttcher,*[a] Marion Graf,[a] Peter Mayer,[a] and Manfred Scheer[b]

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

The synthesis of [Rh₃{(η⁵-C₅)(μ-H)}(μ-PPh₃)]BF₄ (2) by protonation reaction of the metal basic complex [Rh₃{(η⁵-C₅)(μ-PPh₃)}] (1) with tetrfluoroboric 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 (PPh₃) as a synthetic strategy on the reaction of compound 2 with equivolamts of [Au(CH₃)₂(PPh₃)] in reflexing acetone resulted in the formation of the expected triangular cluster compound [Rh₃{μ-Au(PPh₃)}(η⁴-C₅)(μ-PPh₃)]BF₄ (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 Rh₂Au framework in 3 is in good accordance with the isolobal relation between H⁺ and Au⁻ because they share the respective same position in these closely related molecular structures.

1. Introduction

The isolobal relation between gold (I) cations [Au]⁺ and their complexes [AuL]⁻ on the one hand and protons [H]⁺ 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,[1] only a few years later Stone highlighted the importance of this concept in the field of the synthesis of bimetallic and multimetallic metal clusters also with particular consideration of the isolobal relationship between the fragments H and Au(PPh₃).[2] In this context Braunstein and Rose[3] reviewed the synthesis, the bonding situation as well as the chemical and catalytic activities of such bimetallic molecular clusters containing gold described at that time.[4] In 1985 the triangular Rh₂Au cluster [Rh₂{μ-Au(PPh₃)}(μ-CO)(η⁵-C₅)(μ-dpm)]BF₄ (PCH₃ = Ph₃CH₂PMe₂) 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.[5] Later, we also used this principle in our investigations and were successful in the preparation of [Fe₂M clusters (M = Cu, Ag, Au) using the complex [Fe₂{μ-CO}(CO)₃(μ-H)(μ-PR₃)] (R = Me) and the corresponding deprotonated species, respectively.[6] Even the synthesis of the metal cluster [Mo₂{μ-Au(PPh₃}{η⁴-C₅}(CO)₃(μ-PPh₃)] could be realized using this path-way. However the reaction principle was here successful only in the case of gold, not for the other coinage-metals copper and silver.[7] Moreover, Haupt and co-workers were successful in the preparation of dirhenium metal clusters containing two bridging M(PR₃) fragments (M = Au, Ag).[8] 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 Rauberheimer and Schmidbaur.[9] Sometime later Adams and co-workers described the isolobal relationship between the molecules [Re₂(CO)₃(μ-H)] and the cluster [Re₂{μ-Au(PPh₃)}(μ-CO)] [CO]₃. 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 [Rh₂{(η⁵-C₅)(μ-PPh₃)}].[10] Closely related complexes of that type were already reported by Werner and co-workers,[11] 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 phosphano-bridged species [Rh₂{(η⁵-C₅)(μ-PPh₃)}].[12] Now we have also studied the protonation reaction of the Rh–Rh bond in [Rh₂{(η⁵-C₅)(μ-PPh₃)}], affording the corresponding hydrogen-bridged cationic species which served as the precursor in the synthesis of the isolobal-analogous Rh₂Au cluster confirming the relationship between H and Au(PPh₃). On these findings we report in this paper.

2. Results and Discussion

The treatment of red solutions of [Rh₂{(η⁵-C₅)(μ-PPh₃)}] (1) in diethyl ether with tetrfluoroboric acid at ambient temperature resulted in a spontaneous reaction indicated by the quick
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 (1H and 31P), elemental analysis, and mass spectrometry afforded unambiguously hints at the formation of the expected salt \[\text{[Rh}_2(\eta^5\text{-Cp})_2(\mu-H)(\mu-PPh_3)_2]BF_4\] (2) in an analytically pure form and high yield. An indication that the corresponding hydrido species was formed resulted mainly from the 1H NMR spectrum of 2 showing a resonance signal in the high-field region as triplet of triplets at \(\delta = -15.4\) with the couplings \(J_{\text{HH}} = 20.0\) Hz and \(J_{\text{PH}} = 20.0\) Hz (CDCl3). These data correspond very well with the reported ones for \([\text{Rh}_2(\eta^5\text{-Cp})_2(\mu-H)(\mu-PMe_3)_2]BF_4\) \(\delta = -17.1\), \(J_{\text{HH}} = 34.0\) Hz and \(J_{\text{PH}} = 22.0\) Hz, CDNO31]. The 31P 1H NMR spectrum of 2 in CDCl3 exhibited a signal at \(\delta = 120.3\) as triplet \(J_{\text{PH}} = 98.3\) Hz, compare to the former compound11] \(J_{\text{PH}} = 98.2\) Hz. The starting compound 1 exhibited in its 31P 1H NMR spectrum a triplet at \(\delta = 137.5\) \(J_{\text{PH}} = 144.5\) Hz, CDCl3).11] 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(PPh3), we reacted equimolar amounts of 2 and \([\text{Au(CH}_3]_2(PPh_3)_2]\) in refluxing acetone. Successful preparations of gold-containing clusters using this principle, partially under mild reaction conditions, were already described in the literature.3 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 (1H and 31P), elemental analysis, and mass spectrometry. First indications for the successful preparation of the isolobal analogous RhAu cluster complex cation resulted from the 31P 1H NMR spectrum of the isolated product. The latter exhibited in its 31P 1H NMR spectrum a signal in the downfield region as doublet of triplets at \(\delta = 141.1\) \(J_{\text{PH}} = 112.1\) Hz, \(J_{\text{PH}} = 11.0\) Hz, CDCl3) 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 \(J_{\text{PH}} = 6.0\) Hz (P on Au) and \(J_{\text{PH}} = 11.0\) Hz. These values correspond well with reported literature data of the compound \([\text{Rh}_2(\mu-Au(PPh_3)_2)(\mu-\text{CO})(\eta^5\text{-Cp})_2(\mu-dppm)]BF_4\).4 Also, the other spectroscopic data of the product exhibited 3 as the triangular cluster compound \([\text{Rh}_2(\mu-Au(PPh_3)_2)(\eta^5\text{-Cp})_2(\mu-PPh_3)_2]BF_4\) (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(Rh–Rh) =...
2.7513(3)\(^{16}\) 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 Au(PPh\(_3\)). On the assumption that the isolobal relationship is valid for our pair of rhodium complexes, the replacement of H in 2 by Au(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 \(^{14}\):
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 Rh2Au cluster compound, \([\text{Rh}_2\{\mu\text{-Au}(\text{PPh}_3)_2\}\{\mu\text{-H}(\mu\text{-PPh}_3)_2\}]\text{BF}_4\) (2) for the latter compound the following parameters were reported: Rh1–Au, 2.690(2), Rh2–Au, 2.797(2) and Rh1–Rh2, 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 \([\text{Rh}_2\{\eta^5\text{-Cp}\}_2\{\mu\text{-PPh}_3\}_2]\) (1) and studied the reaction behavior of 1 towards the electrophile H⁺ using tetrafluoroboric acid as the proton source. Thus the protonation of the Rh–Rh bond in 1 resulted in the expected complex salt \([\text{Rh}_2\{\eta^5\text{-Cp}\}_2\{\mu\text{-H}(\mu\text{-PPh}_3)_2\}]\text{BF}_4\) (2) in nearly quantitative yield. Although such species were already described in the literature,\(^{19}\) 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⁺ and \([\text{Au}(\text{PPh}_3)_2]\)\(^{19}\), we undertook efforts to show the possibility of the substitution of H⁺ towards the corresponding coinage-metal fragment. Thus the preparation of the novel triangular cluster compound \([\text{Rh}_2\{\mu\text{-Au}(\text{PPh}_3)_2\}\{\eta^5\text{-Cp}\}_2\{\mu\text{-PPh}_3\}_2]\text{BF}_4\) (3) was realized in the reaction of 2 with \([\text{Au}(\text{CH}_3)(\text{PPh}_3)_2]\) 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 prepared before use. Reagents, including \([\text{Au}(\text{CH}_3)(\text{PPh}_3)_2]\), were purchased commercially from ABCR and used without further purification. NMR spectra were obtained using a Jeol Eclipse 400 instrument operating at 400 (1H) and 162 MHz (31P) respectively. Chemical shifts are given in ppm from SiMe₃ (1H) or 85% H₃PO₄ (31P). 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.

\([\text{Rh}_2\{\eta^5\text{-Cp}\}_2\{\mu\text{-H}(\mu\text{-PPh}_3)_2\}]\text{BF}_4\) (2)

Compound 1 (250 mg, 0.35 mmol) was dissolved in diethyl ether (50 mL) and to the stirred solution few drops of HBF₄Et₂O 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 recrystallized 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 %). \(^{1}H\) NMR (CDCl₃, 20 °C): δ = 120.3 8 (t, J_H = 98.3 Hz). \(^{13}C\) NMR (CDCl₃, 20 °C): δ = 7.12 (m, 20 H, C₆H₄), 5.59 (s, 10H, C₆H₄), -15.40 (tH, J_BF = 20.0 Hz, J_BF = 20.0 Hz 1 MS (ESI) m/z = 706 [M⁺ - H] (100 %). Anal. Calcd. for C₅₆H₃₄BF₄P₂Rh₂: C 47.82, H 3.78, found: C 47.38, H 3.82 %.

\([\text{Rh}_2\{\mu\text{-Au}(\text{PPh}_3)_2\}\{\eta^5\text{-Cp}\}_2\{\mu\text{-PPh}_3\}_2]\text{BF}_4\) (3)

The dichloromethane solvate of 2 (150 mg, 0.17 mmol) was dissolved in acetone (15 mL) and \([\text{Au}(\text{CH}_3)(\text{PPh}_3)_2]\) (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 %). \(^{31}P\) (1H) NMR (CDCl₃ 20 °C): δ = 141.13 (dt, J_H = 112.1 Hz, J_BF = 11.0 Hz, δ_H = 58.2 Hz, J_BF = 6.0 Hz (P on Au) and J_BF = 11.0 Hz, Au(PPC₃)). \(^{1}H\) NMR (CDCl₃, 20 °C): δ = 7.28 (m, 35H, P(C₆H₄)), and P(C₂H₄)), 5.38 (s, 10H, C₆H₄). MS (ESI): m/z = 1165 [M⁺] (55 %). Anal. Calcd. for C₉₁H₆₄BF₄P₂Rh₂: 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 TXS diffractometer using Mo-Kα radiation (λ = 0.7073 Å). The frames were integrated with the Bruker SAINT software package.\(^{15}\) Data were corrected for absorption effects using the Multi-scan method (SADABS).\(^{16}\) The structures were solved and refined using the Bruker SHELXTL Software package.\(^{16}\) 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

| Compound | 2 – CH₂Cl₂ | 3 – C₁₂H₁₂BF₄P₂Rh₂ |
|----------|------------|-----------------|
| M⁺ | 879.08 | 1252.38 |
| Crystal system | monoclinic | monoclinic |
| Space group | P2₁/n | |
| a (Å) | 16.7513(7) | 13.3869(7) |
| b (Å) | 10.1622(4) | 24.8082(12) |
| c (Å) | 20.0897(7) | 16.6749(8) |
| β [°] | 97.0460(10) | 94.502(10) |
| V [Å³] | 3392.6(2) | 5520.75(5) |
| Z | 4 | 4 |
| T [K] | 102(2) | 100(2) |
| μₐss [µg cm⁻³] | 1.721 | 1.507 |
| μ [mm⁻¹] | 1.772 | 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 |
| R₁ | 0.0346 | 0.0668 |
| R₁ [I > 2σ(I)] | 0.0250 | 0.0316 |
| wR₂ (all data) | 0.0569 | 0.0822 |
| Parameters | 439 | 614 |
| Goodness of fit on R² | 1.076 | 1.088 |
| Largest diff. peak/hole [e Å⁻³] | 0.465/0.634 | 1.024/0.868 |

© 2020 The Authors. Published by Wiley-VCH GmbH
case, the centrosymmetric space group C2/c could be excluded since even the metal complex does not show C2 or inversion symmetry. The disorder of CH₄Cl₂ as well as of BF₄⁻ has been described by split models. For CH₄Cl₂, 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[16] and in the figures the CH₄Cl₂ and the BF₄⁻ have been omitted. For the disorder of BF₄⁻ 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 BF₄⁻ 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[18] output there are two equivalent voids, each with a volume of 592 Å³ and 131 squeezed-out electrons. This would fit to 2 CH₄Cl₂ (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/).

Acknowledgments

The authors are grateful to the Department of Chemistry of the Ludwig-Maximilians Universität Munich for financial support of these investigations.

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. Böhland, J. Reinhold, J. Sieler, J. Ladrriere, 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. Schmidtaur, 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.