

GOLD(I) AND PLATINUM(II) AZOLATES AS LIGANDS IN CATIONIC RHODIUM(I) COMPLEXES

R. USON, L.A. ORO, M.A. CIRIANO, M.T. PINILLOS and J.A. CABEZA

Department of Inorganic Chemistry, University of Zaragoza, Zaragoza (Spain)

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Summary

Several cationic heterometallic rhodium complexes have been obtained by using the complexes ImAuPPh_3 or $(\text{az})_2\text{Pt}(\text{dpe})$ (az = imidazolate (Im) or pyrazolate (Pz) anions) as ligands. Attempts to prepare rhodium(I)–gold(I) derivatives containing pyrazolate-bridging ligands proved unsuccessful, rearrangements giving the complexes $[\text{Y}_2\text{Rh}(\mu\text{-Pz})]_2$ and $[\text{Ph}_3\text{PAu}(\mu\text{-Pz})\text{AuPPh}_3]\text{ClO}_4$, $[\text{Au}(\text{PPh}_3)_2]\text{ClO}_4$ or AuClPPh_3 as end-products.

Introduction

Azolato ligands (az) frequently make use of only one of their two nitrogen atoms and act as monodentate groups. This happens e.g. in the complexes $(\text{az})_2\text{M}(\text{L-L})$ ($\text{M} = \text{Pt}, \text{Pd}$) and $(\text{az})\text{AuPPh}_3$ [1,2]. Reactions in which complexes of this type behave as bi- or mono-dentate ligands towards other metal centres give rise to the formation of polymetallic azolato complexes [1,3] which may be of interest in relation to electrical or catalytic cooperative effects between adjacent metal centres [4].

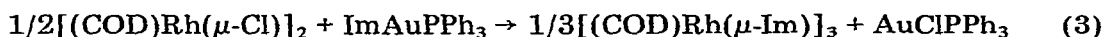
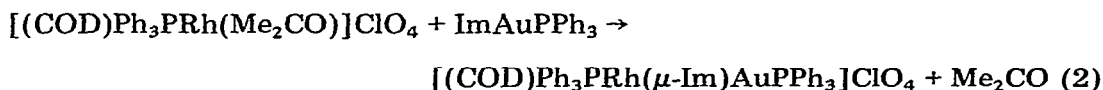
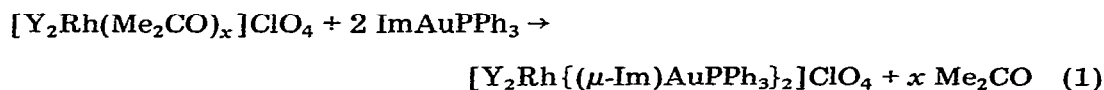
In the present paper we describe a study of the coordination properties of $(\text{az})\text{AuPPh}_3$ and $(\text{az})_2\text{Pt}(\text{dpe})$ (az = imidazolate (Im), pyrazolate (Pz) anions; dpe = 1,2-bis(diphenylphosphino)ethane) towards rhodium(I).

Results and discussion

(a) Reactions of rhodium(I) complexes with $(\text{az})\text{AuPPh}_3$

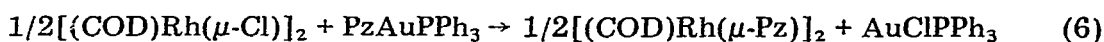
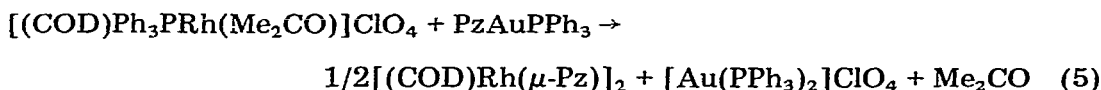
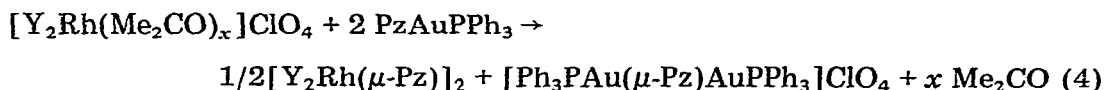
Three different types of complexes were used as precursors $[\text{Y}_2\text{Rh}(\text{Me}_2\text{CO})_x]\text{ClO}_4$ ($\text{Y}_2 = \text{COD}, (\text{CO})_2, (\text{CO})(\text{PPh}_3)$), $[(\text{COD})\text{Ph}_3\text{PRh}(\text{Me}_2\text{CO})]\text{ClO}_4$ and $[(\text{COD})\text{Rh}(\mu\text{-Cl})]_2$; the first two contain one or more Me_2CO groups which are readily displaced by other ligands, and the third contains a bridge which is readily cleaved. The course of the reaction between the precursors and (az) -

AuPPh₃ depends upon whether az is Im or Pz. For az = Im, the following reactions occur (eq. 1, 2 and 3):

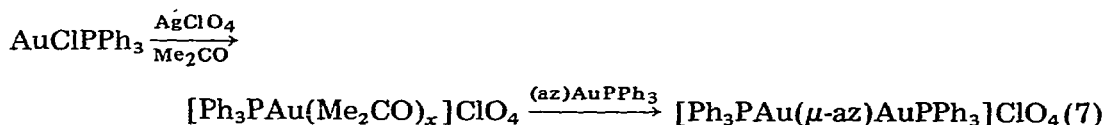


The resulting cationic complexes probably have a square-planar structure with the two ImAuPPh₃ groups *cis* to each other, as may be seen from the values of $\nu(CO)(CH_2Cl_2)$ for $[(CO)_2Rh\{(\mu-Im)AuPPh_3\}_2]ClO_4$ (II) (2083 and 2012 cm⁻¹) and $[(CO)Ph_3PRh\{(\mu-Im)AuPPh_3\}_2]ClO_4$ (III) (1986 cm⁻¹) [5,6]. Table 1 lists analytical and physical data for the new complexes. Their molar conductivities in acetone show them to be 1/1 electrolytes. Their ionic character is also supported by the presence of two strong bands at ca. 1095 and 623 cm⁻¹, which are characteristic of the ClO₄⁻ ion (*T_d*) [7].

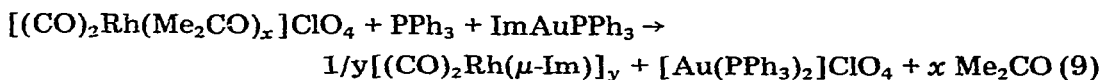
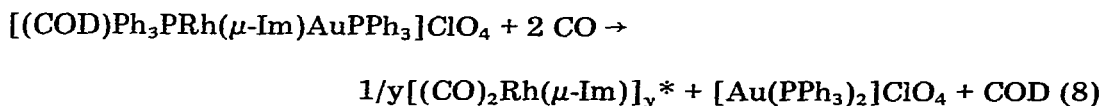
In contrast, reactions involving PzAuPPh₃ do not give heteronuclear complexes but instead give the results shown in eq. 4, 5 and 6:



The $[Ph_3PAu(\mu-Pz)AuPPh_3]ClO_4$ complex V, and the analogous az = Im derivative (VI) can also be obtained directly (eq. 7).



Finally, reactions of $[(COD)Ph_3PRh(\mu-Im)AuPPh_3]ClO_4$ with carbon monoxide (eq. 8) or of $[(CO)_2Rh(Me_2CO)_x]ClO_4$ with PPh₃ and ImAuPPh₃ (1/1/1) (eq. 9) give rise to rearrangement of the ligands:



* *y* was between 3 and 4 by molecular weight measurements [8].

TABLE 1
ANALYTICAL DATA FOR THE CATIONIC RHODIUM(I) AND/OR GOLD(I) COMPLEXES

Complex	Analysis (Found (calcd.)) (%)			ΔM (ohm ⁻¹ cm ² mol ⁻¹)	Colour	Yield (%)
	C	H	N			
[(COD)Rh{(μ -Im)AuPPh ₃] ₂]ClO ₄ (I)	42.49 (44.05)	3.56 (3.55)	4.02 (4.11)	129	yellow	87
[(CO) ₂ Rh{(μ -Im)AuPPh ₃] ₂]ClO ₄ (II)	39.09 (40.31)	2.77 (3.02)	3.81 (4.27)	139	pale brown	74
[(CO)Ph ₃ PRh{(μ -Im)AuPPh ₃] ₂]ClO ₄ (III)	46.99 (47.41)	3.83 (3.33)	3.53 (3.62)	141	pale yellow	79
[(COD)Ph ₂ PRh(μ -Im)AuPPh ₃]ClO ₄ (IV)	50.72 (51.36)	3.99 (4.13)	2.24 (2.55)	124	pale yellow	90
[Ph ₃ PAu(μ -Pz)AuPPh ₃]ClO ₄ (V)	43.36 (43.18)	3.39 (3.04)	2.92 (2.58)	139	white	75
[Ph ₃ PAu(μ -Im)AuPPh ₃]ClO ₄ (VI)	43.31 (43.18)	3.39 (3.04)	2.80 (2.58)	130	white	84

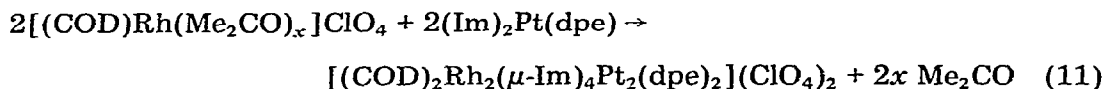
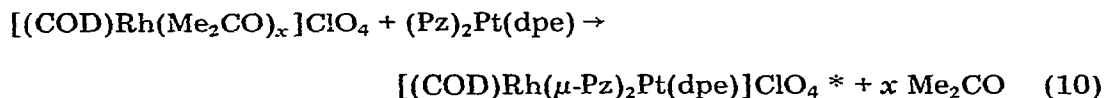
TABLE 2
ANALYTICAL DATA FOR THE CATIONIC HETEROBIMETALLIC COMPLEXES OF PLATINUM(II) WITH RHODIUM(I) OR IRIIDIUM(I)

Complex	Analysis (Found (calcd.)) (%)			ΔM (ohm ⁻¹ cm ² mol ⁻¹)	Colour	Yield (%)	$\nu(\text{CO})(\text{CH}_2\text{Cl}_2)$ (cm ⁻¹)
	C	H	N				
[(COD)Rh(μ -Pz) ₂ Pt(dpe)]ClO ₄ (VII)	45.31 (46.28)	4.11 (4.08)	5.38 (5.40)	144 ^a	yellow	92	—
[(COD)Ir(μ -Pz) ₂ Pt(dpe)]ClO ₄ (VIII)	42.14 (42.61)	3.88 (3.75)	5.12 (4.97)	125 ^a	yellow	60	—
[(COD) ₂ Rh ₂ (μ -Im) ₄ Pt ₂ (dpe) ₂]ClO ₄ (IX)	45.24 (46.28)	4.03 (4.08)	5.33 (5.40)	178 ^b	yellow	88	—
[(CO) ₂ Rh(μ -Pz) ₂ Pt(dpe)]ClO ₄ (X)	41.88 (41.42)	3.36 (3.07)	5.33 (5.68)	138 ^a	pale yellow	80	2090 2030
[(CO) ₄ Rh ₂ (μ -Im) ₄ Pt ₂ (dpe) ₂]ClO ₄ (XI)	40.06 (41.42)	3.14 (3.07)	5.77 (5.68)	182 ^b	pale-yellow	70	2082 2015
[(CO)Ph ₃ PRh(μ -Pz) ₂ Pt(dpe)]ClO ₄ (XII)	49.60 (50.20)	3.75 (3.72)	4.48 (4.59)	131 ^a	pale yellow	86	1990
[(CO)(PhO) ₃ PRh(μ -Pz) ₂ Pt(dpe)]ClO ₄ (XIII)	48.15 (48.30)	4.00 (3.58)	4.04 (4.42)	139 ^a	pale yellow	80	2010

^a Acetone solution. ^b Nitromethane solution.

(b) Reactions of rhodium(I) complexes with (az)₂Pt(dpe)

The compounds (Pz)₂Pt(dpe) [1] and (Im)₂Pt(dpe) can act as bidentate ligands to give heteronuclear platinum–rhodium complexes (eq. 10 and 11):



Bubbling carbon monoxide through solutions of these complexes leads to the displacement of the coordinated diolefin and formation of [(CO)₂Rh(μ-Pz)₂Pt(dpe)]ClO₄ (X) or [(CO)₄Rh₂(μ-Im)₄Pt₂(dpe)₂](ClO₄)₂ (XI).

The formulation of complexes IX and XI as 1/2 electrolytes is based on conductivity studies in nitromethane at various concentrations, which gives a slope of 548 and 532, respectively (Onsager's equation) [9].

Addition of stoichiometric amounts of PPh₃ or P(OPh)₃ to complex X gives [(CO)LRh(μ-Pz)₂Pt(dpe)]ClO₄ (L = PPh₃ (XII) or P(OPh)₃ (XIII)).

The analytical and physical data for the cationic heterobimetallic complexes are listed in Table 2.

Experimental

C, H and N analyses were carried out with a Perkin–Elmer 240B micro-analyzer. IR spectra were recorded on a Perkin–Elmer 577 spectrophotometer (over the range 4000–200 cm⁻¹) using Nujol mulls between polyethylene sheets or potassium bromide discs. Conductivities were measured in ca. 5 × 10⁻⁴ M acetone solutions using a Philips 9501/01 conductimeter.

The reactions were generally carried out at room temperature with 0.1–0.2 mmol of the reagents.

Preparation of ImAuPPh₃ and PzAuPPh₃

Addition of a stoichiometric amount of AuClPPh₃ [10] in dichloromethane to a solution of K(az) in methanol (prepared by treating H(az) with potassium hydroxide in methanol) followed by 30 min stirring led to precipitation of KCl. After evaporation to dryness and extraction with dichloromethane the KCl was filtered off. The colourless filtrate was concentrated to ca. 2 ml and ether was added to precipitate the off-white complexes, which were filtered off. ImAuPPh₃: m.p. 183°C. Analysis: Found: C, 46.64; H, 3.38; N, 5.01. C₂₁H₁₈AuN₂P calcd.: C, 47.94; H, 3.42; N, 5.32%. PzAuPPh₃: m.p. 164°C. Analysis: Found: C, 47.80; H, 3.35; N, 5.07. C₂₁H₁₈AuN₂P calcd.: C, 47.94; H, 3.42; N, 5.32%.

Preparation of [Y₂Rh{(μ-Im)AuPPh₃}]₂ClO₄ complexes

Addition of ImAuPPh₃ to acetone solutions of [Y₂Rh(Me₂CO)_x]ClO₄ (Y₂ =

* The analogous platinum–iridium complex [(COD)Ir(μ-Pz)₂Pt(dpe)]ClO₄ (VIII) was obtained by the same method.

COD; (CO)₂; (CO)(PPh₃) [11,12] in 2/1 molar ratio led to a darkening of the solution (for [(CO)₂Rh(Me₂CO)_x]ClO₄ the reaction must be carried out under argon and in the absence of daylight). After 1 h stirring followed by addition of ether the yellow (Y₂ = COD; (CO)(PPh₃)) or pale-brown (Y = CO) complexes precipitated out and were filtered off.

Preparation of [(COD)Ph₃PRh(μ-Im)AuPPh₃]ClO₄

Stirring for 10 min of (COD)Ph₃PRhCl in acetone with the stoichiometric amount (1/1) of AgClO₄ (in the absence of light) led to precipitation of AgCl which was filtered off. The filtrate [13] was added to a stoichiometric amount (1/1) of ImAuPPh₃ in the same solvent (which caused the solid to dissolve within a few minutes), and the solution stirred for 2 h. Concentration to ca. 2 ml and addition of ether gave a pale-yellow precipitate which was filtered off.

Reaction of [Y₂Rh(Me₂CO)_x]ClO₄ with PzAuPPh₃

Addition of PzAuPPh₃ to acetone solutions of [Y₂Rh(Me₂CO)_x]ClO₄ (Y₂ = COD or TFB; Y = CO) [11] in 2/1 molar ratio led to a darkening of the yellow solutions. After 1 h stirring and concentration to ca. 2 ml, ether was added to precipitate the off-white [Ph₃PAu(μ-Pz)AuPPh₃]ClO₄. This was filtered off and recrystallized from dichloromethane/ether to give a white solid. The filtrate was evaporated to dryness, the residue was stirred with methanol/water (1/2), and the yellow solids, having the formula [Y₂Rh(μ-Pz)]₂, were filtered off.

The products were identified by elemental analyses and by comparison of their IR spectra with those of authentic samples [14].

Reaction of [(COD)Ph₃PRh(Me₂CO)]ClO₄ with PzAuPPh₃

To an acetone solution of [(COD)Ph₃PRh(Me₂CO)]ClO₄ was added the stoichiometric amount (1/1) of PzAuPPh₃. After 2 h stirring the solution was concentrated to ca. 2 ml. Addition of ether gave an off-white precipitate which was recrystallized from chloroform/ether. The resulting white complex of the formula [Au(PPh₃)₂]ClO₄ [15] was characterized by its IR spectrum and elemental analysis. The filtrate was evaporated to dryness and the yellow-residue was treated with methanol/water (1/2) to give a precipitate of [(COD)Rh(μ-Pz)]₂ which was also characterized by elemental analysis and IR spectroscopy. It was identical with an authentic sample [14].

Reactions of [(COD)Rh(μ-Cl)]₂ with (az)AuPPh₃ (az = Pz or Im)

The reactions were carried out with stoichiometric amounts of the reagents in dichloromethane. After 2 h stirring vacuum-concentration gave a solid. This was treated with ether filtered off, and identified as AuClPPh₃ [10]. The filtrate was evaporated to dryness; the residue was treated with methanol/water to give a yellow solid, which was recrystallized from methanol/water and shown to be [(COD)Rh(μ-Pz)]₂ or [(COD)Rh(μ-Im)]₃ [16].

The three products were identified by elemental analysis and IR spectroscopy.

Preparation of [Ph₃PAu(μ-az)AuPPh₃]ClO₄ (az = Pz or Im)

The stoichiometric amount (1/1) of (az)AuPPh₃ was stirred for 30 min with an acetone solution of [Ph₃PAu(Me₂CO)_x]ClO₄ (prepared by reacting AuClPPh₃

with AgClO_4). The solution was concentrated to ca. 2 ml and ether was added to precipitate the white complexes, which were filtered off, washed with ether, and air-dried.

Reaction of $[(\text{COD})\text{Ph}_3\text{PRh}(\mu\text{-Im})\text{AuPPh}_3]\text{ClO}_4$ with CO

Anhydrous CO was bubbled for 20 min through a dichloromethane solution of $[(\text{COD})\text{Ph}_3\text{PRh}(\mu\text{-Im})\text{AuPPh}_3]\text{ClO}_4$. The products $[\text{Au}(\text{PPh}_3)_2]\text{ClO}_4$ and $[(\text{CO})_2\text{Rh}(\mu\text{-Im})]_y$ were isolated by the work-up procedure described for the next experiment.

Reaction of $[(\text{CO})_2\text{Rh}(\text{Me}_2\text{CO})_x]\text{ClO}_4$ with ImAuPPh_3 and PPh_3

In the absence of light and under argon ImAuPPh_3 and PPh_3 were added to an acetone solution of $[(\text{CO})_2\text{Rh}(\text{Me}_2\text{CO})_x]\text{ClO}_4$ (1/1/1 molar ratio). After 2 h stirring and concentration to ca. 2 ml, ether was added to precipitate a pale-yellow solid, which was recrystallized from chloroform/ether to give a white solid, which was shown to be $[\text{Au}(\text{PPh}_3)_2]\text{ClO}_4$. Evaporation of the filtrate to dryness and addition of methanol/water (1/2) gave a yellow compound, which was identified as $[(\text{CO})_2\text{Rh}(\mu\text{-Im})]_y$.

The same results were obtained from reactions at room temperature or -78°C .

Preparation of $[(\text{COD})\text{M}(\mu\text{-Pz})_2\text{Pt}(\text{dpe})]\text{ClO}_4$ ($\text{M} = \text{Rh}$ or Ir)

A suspension of $[(\text{COD})\text{M}(\mu\text{-Cl})]_2$ in acetone and AgClO_4 (1/2 molar ratio) was stirred for 30 min in an inert atmosphere and with exclusion of daylight. The suspension was filtered through kieselguhr to remove AgCl and the filtrate was added to a stoichiometric amount of $(\text{Pz})_2\text{Pt}(\text{dpe})$ in dichloromethane. Vacuum-concentration and addition of ether led to the precipitation of a yellow solid which was isolated by filtration.

Preparation of $[\text{Y}_2\text{Rh}_2(\mu\text{-Im})_4\text{Pt}_2(\text{dpe})_2](\text{ClO}_4)_2$ ($\text{Y}_2 = \text{COD}$ or $(\text{CO})_2$)

An acetone solution of $[(\text{COD})\text{Rh}(\text{Me}_2\text{CO})_x]\text{ClO}_4$ (0.162 mmol) was stirred with an acetone suspension of $(\text{Im})_2\text{Pt}(\text{dpe})$ (0.128 g, 0.176 mmol) (prepared by treating $\text{PtCl}_2(\text{dpe})$ with imidazol and potassium hydroxide in refluxing methanol). The insoluble residues were filtered off and the yellow filtrate was evaporated to dryness. The yellow solid was recrystallized from dichloromethane/ether, filtered off, washed with ether and air-dried. It was identified as $[(\text{COD})_2\text{Rh}_2(\mu\text{-Im})_4\text{Pt}_2(\text{dpe})_2](\text{ClO}_4)_2$.

Bubbling of CO through a dichloromethane solution of this complex and addition of ether led to precipitation of $[(\text{CO})_4\text{Rh}_2(\mu\text{-Im})_4\text{Pt}_2(\text{dpe})_2](\text{ClO}_4)_2$. The pale-yellow solid was filtered off, washed with ether, and air-dried.

Preparation of $[(\text{CO})_2\text{Rh}(\mu\text{-Pz})_2\text{Pt}(\text{dpe})]\text{ClO}_4$

CO was bubbled for 10 min through a dichloromethane solution of $[(\text{COD})\text{-Rh}(\mu\text{-Pz})_2\text{Pt}(\text{dpe})]\text{ClO}_4$. Evaporation of the solution and addition of ether gave a pale-yellow solid, which was isolated by filtration.

Preparation of $[(\text{CO})\text{LRh}(\mu\text{-Pz})_2\text{Pt}(\text{dpe})]\text{ClO}_4$ ($\text{L} = \text{PPh}_3$ or $\text{P}(\text{OPh})_3$)

CO was bubbled for 10 min through a dichloromethane solution of $[(\text{COD})\text{-}$

$\text{Rh}(\mu\text{-Pz})_2\text{Pt}(\text{dpe})\text{ClO}_4$, and the appropriate phosphorus donor ligand was then added (1/1 molar ratio). After 15 min stirring the solution was vacuum-concentrated. Addition of ether gave a pale-yellow solid, which was filtered off, washed with ether, and air-dried.

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