

## Mononuclear Gold(I) and Heteronuclear Gold(I)–Palladium(II) Bibenzimidazolate Complexes with New Coordination Modes of the Ligand

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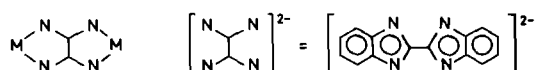
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Metathetic reactions of gold(I) halide complexes and the potassium salt of 2,2'-bibenzimidazole afford binuclear bibenzimidazolate gold(I) complexes with the general formula  $\{Au_2L_2\}(\mu-BiBzIm)$   $L = PPh_3$ ,  $PBu_3^+$ ,  $P(OMe)_3$ ;  $L_2 = 1,1$ -bis(diphenylphosphine)methane (dppm), 1,2-bis(diphenylphosphine)ethane (dppe). These complexes are Lewis bases and can be used as precursors for the synthesis of tri and tetranuclear cationic gold(I) complexes, or trinuclear gold(I) and palladium(II) complexes where the bibenzimidazolate anion is acting as bridging tetranuclear ligand. An hexanuclear gold(I)–palladium(II) complex is also described.

### Introduction

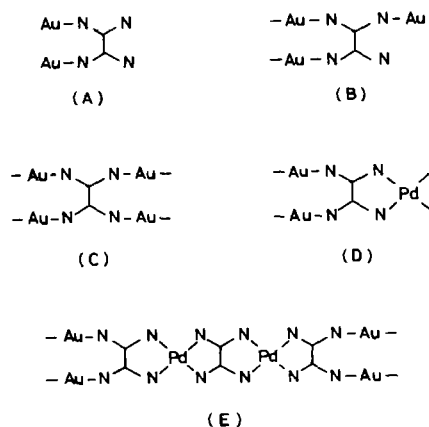
Recently we have shown that the bibenzimidazolate anion,  $BiBzIm^{2-}$ , can act as tetradentate bridging ligand between two metal centres



thus giving rise to the formation of stable binuclear Au(III), Mn(I) and Pd(II) complexes [1–3]. Moreover, owing to its very nature a higher versatility may be expected for this ligand. In consequence we endeavoured to study new coordination modes of the  $BiBzIm^{2-}$  group.

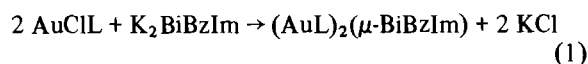
In the present paper we describe the synthesis and properties of novel binuclear Au(I) complexes (A), which, behaving as potential mono or bidentate ligands, allow the preparation of different types of tri- and tetranuclear Au(I) complexes (B), (C), trinuclear hetero-atomic Au(I)–Pd(II) complexes (D), as well as an hexanuclear Au(I)–Pd(II) complex (E). All of them exhibit new types of coordination of the  $BiBzIm^{2-}$  ligand.

Some of these results have been the subject of a preliminary communication [4].



### Results and Discussion

Metathetic reactions at room temperature between dichloromethane solutions of gold(I) halide complexes and the potassium salt of 2,2'-bibenzimidazole ( $H_2BiBzIm$ ), according to eqn. 1



$L = PPh_3$ (I),  $PBu_3^+$ (II),  $P(OMe)_3$ (III)

lead to solutions, from which can be isolated binuclear gold(I) complexes with the bibenzimidazolate anion acting as a bidentate ligand bridging the two Au atoms. The analogous complexes  $[(L-L)Au_2](\mu-BiBzIm)$  ( $L-L = dppm$ (IV),  $dppe$ (V)) are similarly obtained as insoluble precipitates.

These complexes, which still contain two potential nitrogen donor atoms, behave as Lewis bases and can be used as precursors for the preparation of tri- and tetranuclear complexes.

#### Trinuclear Complexes

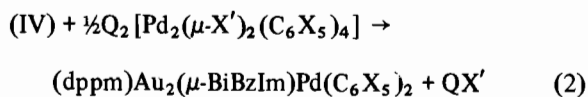
The addition of  $[(dppm)Au_2](\mu-BiBzIm)$  (IV) to dichloromethane solutions of binuclear palladium-

TABLE I. Analytical, Conductance and Molecular Weight Data for the New Complexes.<sup>a</sup>

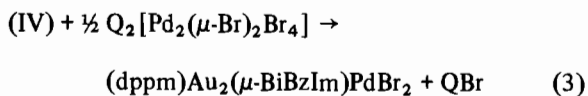
Complexes	%C	%H	%N	%Au	M.W.	$\Lambda_M^b$	M.P. °C
I [(Ph <sub>3</sub> P) <sub>2</sub> Au <sub>2</sub> ]( $\mu$ -BiBzIm)	51.77 (52.19)	3.31 (3.33)	4.75 (4.87)	33.77 (34.23)	1149 (1150.8)		300
II [(Bu <sup>n</sup> <sub>3</sub> P) <sub>2</sub> Au <sub>2</sub> ]( $\mu$ -BiBzIm)	45.36 (44.29)	6.20 (6.06)	5.56 (5.43)	37.40 (38.23)	998 (1030.8)		210 <sup>d</sup>
III {[(OMeO) <sub>3</sub> P] <sub>2</sub> Au <sub>2</sub> }( $\mu$ -BiBzIm)	27.97 (27.45)	3.09 (2.99)	6.45 (6.40)	44.37 (45.07)	840 (874.3)		165
IV [(dppm)Au <sub>2</sub> ]( $\mu$ -BiBzIm)	47.20 (46.37)	3.11 (2.99)	5.69 (5.54)	39.41 (38.99)	<sup>c</sup>		265 <sup>d</sup>
V [(dppe)Au <sub>2</sub> ]( $\mu$ -BiBzIm)	45.64 (46.90)	3.16 (3.14)	5.65 (5.47)	36.95 (38.46)	<sup>c</sup>		230 <sup>d</sup>
VI {[(Ph <sub>3</sub> P) <sub>3</sub> Au <sub>3</sub> ]( $\mu$ -BiBzIm)}ClO <sub>4</sub>	47.12 (47.77)	3.14 (3.12)	3.36 (3.27)	22.52 (23.04)		149	248
VII (dppm)Au <sub>2</sub> ( $\mu$ -BiBzIm)PdCl <sub>2</sub>	39.71 (39.42)	2.75 (2.52)	4.97 (4.71)		<sup>c</sup>		270 <sup>d</sup>
VIII (dppm)Au <sub>2</sub> ( $\mu$ -BiBzIm)Pd(C <sub>6</sub> F <sub>5</sub> )Cl	40.62 (40.95)	2.50 (2.27)	4.30 (4.24)		1529 (1319.5)		268 <sup>d</sup>
IX (dppm)Au <sub>2</sub> ( $\mu$ -BiBzIm)PdBr <sub>2</sub>	37.65 (36.68)	2.55 (2.35)	5.43 (4.38)		<sup>c</sup>		280 <sup>d</sup>
X (dppm)Au <sub>2</sub> ( $\mu$ -BiBzIm)Pd(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub>	42.89 (42.18)	3.52 (2.06)	3.62 (3.86)		1461 (1451.1)		225 <sup>d</sup>
XI (dppm)Au <sub>2</sub> ( $\mu$ -BiBzIm)Pd(C <sub>6</sub> Cl <sub>5</sub> ) <sub>2</sub>	38.55 (37.89)	2.57 (1.85)	3.13 (3.46)		<sup>c</sup>		254 <sup>d</sup>
XII [(dppm)Au <sub>2</sub> ( $\mu$ -BiBzIm)Pd(acac)]ClO <sub>4</sub>	40.47 (40.16)	3.07 (3.42)	4.09 (4.26)			91	228 <sup>d</sup>
XIII [(dppm)Au <sub>2</sub> ( $\mu$ -BiBzIm)Pd(C <sub>6</sub> F <sub>5</sub> )(PPh <sub>3</sub> )]ClO <sub>4</sub>	44.83 (45.97)	2.78 (2.73)	3.09 (3.40)			83	300 <sup>d</sup>
XIV {[(Ph <sub>3</sub> P) <sub>4</sub> Au <sub>4</sub> ]( $\mu$ -BiBzIm)}(ClO <sub>4</sub> ) <sub>2</sub>	44.68 (45.54)	3.31 (3.02)	2.44 (2.47)			189	285
XV {[(dppm) <sub>2</sub> Au <sub>4</sub> ]( $\mu$ -BiBzIm)}(ClO <sub>4</sub> ) <sub>2</sub>	39.51 (38.68)	2.77 (2.63)	2.69 (2.81)	16.78 (17.37)		204	300
XVI [(dppm)Au <sub>2</sub> ( $\mu$ -BiBzIm)Au <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	42.90 (42.43)	2.77 (2.84)	3.12 (2.63)	37.23 (37.03)		185	225 <sup>d</sup>
XVII [(dppm)Au <sub>2</sub> ( $\mu$ -BiBzIm)Au <sub>2</sub> (PBu <sup>n</sup> <sub>3</sub> ) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	37.20 (37.69)	3.68 (4.21)	3.47 (2.79)	39.05 (39.24)		190	175
XVIII [(dppm)Au <sub>2</sub> ( $\mu$ -BiBzIm)Au <sub>2</sub> {P(OMe) <sub>3</sub> }] <sub>2</sub> (ClO <sub>4</sub> ) <sub>2</sub>	36.36 (36.98)	2.85 (2.61)	3.61 (3.02)	42.81 (42.56)		177	210 <sup>d</sup>
XIX {[(dppm)Au <sub>2</sub> ( $\mu$ -BiBzIm)Pd]} <sub>2</sub> ( $\mu$ -BiBzIm)}(ClO <sub>4</sub> ) <sub>2</sub>	42.41 (41.45)	2.74 (2.54)	6.35 (6.30)			153	265 <sup>d</sup>

<sup>a</sup>Calculated values are given in parenthesis. <sup>b</sup> $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , acetone solutions. <sup>c</sup>Not soluble enough for determination. <sup>d</sup>Decomposes.

(II) halide complexes gives rise to the cleavage of the halide bridges (eqns. 2, 3)

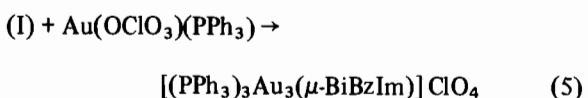
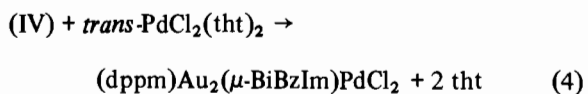


X = F; X' = Br(X); X = X' = Cl(XI); Q = NBu<sub>4</sub><sup>+</sup>

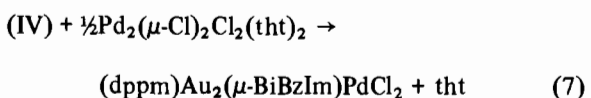
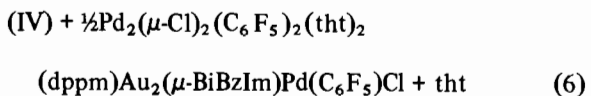


and to the formation of the corresponding heteronuclear gold(I)–palladium(II) derivatives (complexes IX–XI; Table I).

The basicity of the binuclear amido gold(I) complexes allows the displacement of poorly coordinating ligands in processes such as the following (eqns. 4, 5)

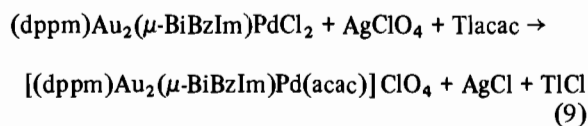
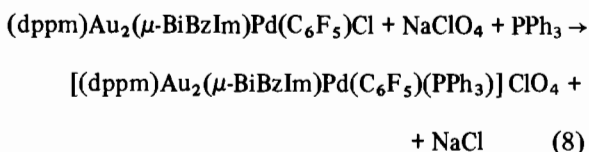


or in processes in which the displacement proceeds with simultaneous cleavage of the halide bridge (eqns. 6, 7)



Both types lead to the formation of trinuclear complexes (complex VI–VIII, Table I). Attempts to prepare complex X by displacing the tht group from Pd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(tht)<sub>2</sub> proved unsuccessful, and the unchanged reactants were recovered even after 28 h stirring at room temperature.

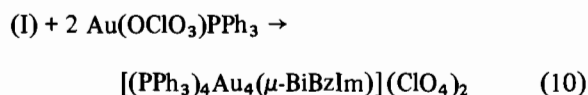
Addition of NaClO<sub>4</sub> and PPh<sub>3</sub> or AgClO<sub>4</sub> and Tl(acac) allows the synthesis of cationic derivatives (eqns. 8, 9)



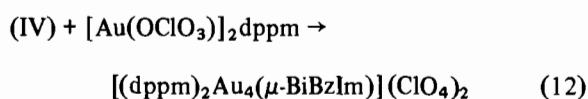
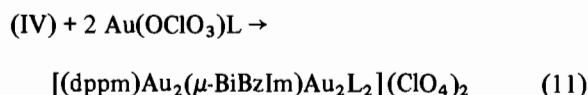
The reactions take place smoothly at room temperature, giving rise to the precipitation of MCl (M = Na or, respectively Ag and Tl) and to the formation of complexes (XII and XIII, Table I) which can be isolated from the filtrate.

#### Tetranuclear Complexes

Displacement of the perchlorate group as in (5) (at room temperature in dichloromethane solution, but using a 1:2 ratio of the reactants) according to eqn. (10)

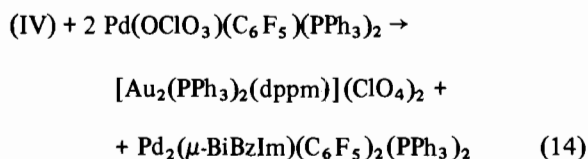
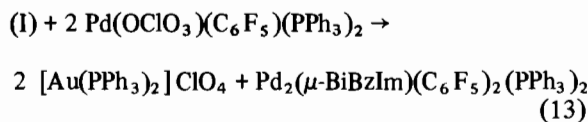


or to eqns. (11) and (12)



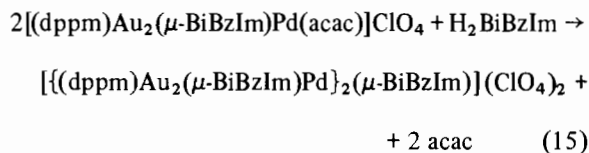
leads to solutions, which, after partial concentration and addition of ether, render the corresponding tetranuclear complexes (XIV–XVIII, Table I).

Attempts to prepare tetranuclear mixed gold(I)–palladium(II) complexes proved unsuccessful, since the displacement of the perchlorate group proceeds with simultaneous rearrangements (eqns. 13 and 14) leading to the formation of homonuclear compounds.



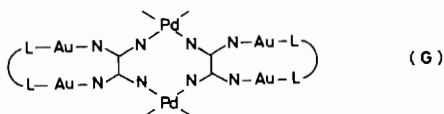
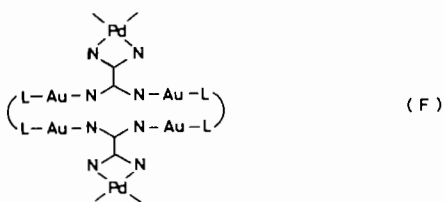
The synthesis of complexes of higher nuclearity is generally hindered by similar rearrangements, which lead to mixtures whose resolution could not be accomplished. Nevertheless, one hexanuclear complex, resulting from the reaction of the acac deriva-

tive (XII) with  $\text{H}_2\text{BiBzIm}$  in 2:1 ratio, (eqn. 15), could be isolated



All the complexes are air-stable. Their analytical data, melting points and conductivities, along with the molecular weights of the soluble neutral complexes, are listed in Table I. These data point to three different coordination modes of the  $\text{BiBzIm}^{2-}$  anion: as bidentate (complexes I–V) (A), as tridentate (complex VI) (B) or as tetradentate ligand (complexes VII–XI) (D) and (complexes XIV–XVIII) (C).

Coordination as tetradentate ligand bridging a larger number of metal atoms, as in F or G, can be ruled out, since a) the molecular weights of the



neutral complexes VIII and X (very low solubility prevents the determination for complexes VII, IX and XI) show they are trinuclear; b) the value of  $\Lambda$  in Onsager's equation\* for complex XII in acetone solutions of different concentrations is 353. This confirms the structure as trinuclear (1:1 electrolyte), since 2:1 electrolytes should give  $\Lambda$  values of ca. 600–700 [3].

The IR spectra of the tri- and tetranuclear complexes show absorption bands due to the tetradentate anion  $\text{BiBzIm}^{2-}$  identical to those described for this ligand in binuclear palladium(II) complexes [3]. The only observed differences are located in the 1300–1200  $\text{cm}^{-1}$  region (in plane C–H bending) where the spectra of complexes I–V and XII–XVIII exhibit a group of four or respectively, two absorption bands.

The pentafluoro and pentachlorophenyl derivatives show absorptions characteristic of these groups

\* $\Lambda_e = \Lambda_0 - \Lambda\sqrt{c}$ .

[5–7], whereas for complexes VII–IX the bands expected for the metal-halogen vibration (at 350–200  $\text{cm}^{-1}$ ) are masked by another band, probably arising from the  $\text{BiBzIm}^{2-}$  anion.

All the cationic complexes exhibit the two absorption bands which are characteristic of the perchlorate anion (Td), at ca. 1095(s,br) and 623(s)  $\text{cm}^{-1}$ .

## Experimental

The IR spectra were recorded on a Perkin-Elmer 577 spectrophotometer (over the range 4000–200  $\text{cm}^{-1}$ ) using Nujol between polyethylene or NaCl sheets. The conductivities were measured in acetone solution with a Philips PW 9501/01 conductimeter. C, H and N analyses were carried out with a Perkin-Elmer 240 microanalyzer. The molecular weights were determined in chloroform solutions with a Hitachi-Perkin-Elmer mod. 115 osmometer. The analytical data, molecular weights and conductivities for the novel compounds are listed in Table I. Au was determined by ashing the samples together with an aqueous solution of hydrazine.

The binuclear palladium compounds were prepared as described elsewhere:  $(\text{NBu}_4)_2[\text{Pd}_2(\mu\text{-Br})_2(\text{C}_6\text{F}_5)_4]$  [5],  $(\text{NBu}_4)_2[\text{Pd}_2(\mu\text{-Cl})_2(\text{C}_6\text{Cl}_5)_4]$  [7],  $(\text{NBu}_4)_2[\text{Pd}_2\text{Br}_6]$  [8],  $\text{Pd}_2(\mu\text{-Cl})_2(\text{C}_6\text{F}_5)_2(\text{tbt})_2$  [9] and  $\text{Pd}_2\text{Cl}_4(\text{tbt})_2$  by treating  $\text{PdCl}_2(\text{tbt})_2$  with  $\text{PdCl}_2$  in refluxing acetone.

The synthesis of  $\text{H}_2\text{BiBzIm}$  was carried out as described in [10].

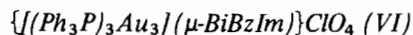
### Preparation of the Complexes

All the reactions were carried out at room temperature.

#### Binuclear Compounds $[\text{L}_2\text{Au}_2](\mu\text{-BiBzIm})$

A solution of  $\text{AuClL}$  or  $\text{AuCl}_2(\text{L-L})$  (0.3 mmol) in 20 ml of  $\text{H}_2\text{CCl}_2$  was stirred with  $\text{K}_2\text{BiBzIm}$  (obtained by treating 0.3 mmol of  $\text{H}_2\text{BiBzIm}$  with 0.6 mmol of  $\text{KOH}$  in 50 ml of  $\text{H}_2\text{CCl}_2/\text{MeOH}$  (1:1) for 0.5 h) for 1–2 h (II, III, V) or, respectively, 24 h (I, IV). The white complexes (IV) and (V) which precipitated spontaneously, were repeatedly washed with  $\text{H}_2\text{O}$  and vacuum-dried (60–80% yield). The white complexes (I) and (II) and the yellow complex (III) were isolated after evaporating the solution to dryness, re-crystallization from dichloromethane and addition of ether to the filtrate (50–70% yield).

#### Trinuclear Compounds



An equimolecular mixture (0.25 mmol) of (I) and  $\text{Au}(\text{OCIO}_3)\text{PPh}_3$  (obtained *in situ* by reacting  $\text{AuClPPh}_3$  with  $\text{AgClO}_4$  and subsequent removal of

AgCl) in 30 ml of  $\text{H}_2\text{CCl}_2$  was stirred for 2 h. Partial evaporation of the solvent and addition of ether led to the precipitation of the white complex (VI) (75% yield).

$(\text{dppm})\text{Au}_2(\mu\text{-BiBzIm})\text{PdX}_2$  ( $X = \text{Cl}$  (VII) or  $\text{Br}$  (IX))

Complex (IV) (0.28 mmol) was stirred with  $\text{PdCl}_2(\text{tht})_2$  (0.28 mmol) or  $\text{Pd}_2(\mu\text{-Cl})_2\text{Cl}_2(\text{tht})_2$  (0.14 mmol) in 30 ml of  $\text{H}_2\text{CCl}_2$  for 16 or, respectively, 3.5 h. The precipitated yellow complex (VII) was filtered off and washed repeatedly with  $\text{H}_2\text{CCl}_2$  (73% yield).

(IX) was obtained similarly by reacting (IV) with  $(\text{Bu}_4\text{N})_2[\text{Pd}_2(\mu\text{-Br}_2\text{Br}_4)]$ . It was washed with methanol (80% yield).

$(\text{dppm})\text{Au}_2(\mu\text{-BiBzIm})\text{Pd}(\text{C}_6\text{F}_5)\text{Cl}$  (VIII)

A mixture of (IV) (0.101 g, 0.10 mmol) and  $\text{Pd}_2(\mu\text{-Cl})_2(\text{C}_6\text{F}_5)_2(\text{tht})_2$  (0.04 g, 0.05 mmol) in 50 ml of  $\text{H}_2\text{CCl}_2$  was stirred for 3.5 h. Partial evaporation of the solvent and addition of methanol led to the precipitation of the white complex (VIII), which was washed with hexane (45% yield).

$(\text{dppm})\text{Au}_2(\mu\text{-BiBzIm})\text{Pd}(\text{C}_6\text{X}_5)_2$  ( $X = \text{F}$  (X) or  $\text{Cl}$  (XI))

To a  $\text{H}_2\text{CCl}_2$  solution (30 ml) of  $(\text{Bu}_4\text{N})_2[\text{Pd}_2(\mu\text{-X}')_2(\text{C}_6\text{X}_5)_4]$  ( $X = \text{F}$ ;  $X' = \text{Br}$ ) (0.08 g, 0.052 mmol) or  $X = X' = \text{Cl}$  (0.080 g, 0.04 mmol) was added 0.105 g (0.104 mmol) or, respectively, 0.091 g (0.08 mmol) of complex (IV). After 20 h stirring the solution was filtered.

For the pale yellow complex (X) the filtrate was evaporated to dryness and the oily residue was extracted with *n*-butanol/hexane. For the yellow complex (XI) the filtrate was partially evaporated and butanol was added ( $X = 56\%$  and  $XI = 59\%$  yields).

$[(\text{dppm})\text{Au}_2(\mu\text{-BiBzIm})\text{Pd}(\text{acac})]\text{ClO}_4$  (XII)

An equimolecular (0.08 mmol) mixture of VII, Tlacac and  $\text{AgClO}_4$  in 40 ml of  $\text{H}_2\text{CCl}_2$  was stirred for 3.5 h in the absence of light. The formed TlCl and AgCl were removed by filtration and the solvent was partially evaporated. Addition of isopropanol led to the precipitation of the orange-yellow complex XII (46% yield).

$[(\text{dppm})\text{Au}_2(\mu\text{-BiBzIm})\text{Pd}(\text{C}_6\text{F}_5)\text{PPh}_3]\text{ClO}_4$  (XIII)

An equimolecular mixture of (VIII) (0.09 mmol)  $\text{NaClO}_4$  and  $\text{PPh}_3$  in 30 ml of acetone was stirred for 5 h. The formed NaCl was filtered off and the filtrate was concentrated to dryness. The resulting yellow solid was successively washed with  $\text{H}_2\text{O}$ , isopropanol and ether, filtered, and air-dried (44% yield).

**Tetranuclear Compounds:**  $\{[(\text{Ph}_3\text{P})_4\text{Au}_4](\mu\text{-BiBzIm})\}(\text{ClO}_4)_2$  (XIV) and  $[(\text{dppm})_2\text{Au}_2(\mu\text{-BiBzIm})\text{-Au}_2\text{L}_2](\text{ClO}_4)_2$  ( $\text{L}_2 = \text{dppm}$  (XV);  $\text{L} = \text{PPh}_3$  (XVI),  $\text{PBu}_3^n$  (XVII) or  $\text{P}(\text{OMe})_3$  (XVIII))

To a solution of  $\text{Au}(\text{OClO}_3)\text{L}$  or  $[\text{Au}(\text{OClO}_3)]_2\text{-dppm}$  (0.1 mmol) (obtained *in situ* by reacting  $\text{AuClL}$  or, respectively,  $(\text{AuCl})_2\text{dppm}$  with  $\text{AgClO}_4$  and removing the formed AgCl) in 50 ml of  $\text{H}_2\text{CCl}_2$  was added 0.05 mmol of complex (IV). After 15 h stirring, the solution was concentrated to ca. 5 ml and ether was added to precipitate complexes XV–XVIII (60–70% yield). (XIV) was similarly obtained by reacting  $\text{Au}(\text{OClO}_3)\text{PPh}_3$  with complex (I) (2:1 ratio) (80% yield).

**Preparation of  $[(\text{dppm})\text{Au}_2(\mu\text{-BiBzIm})\text{Pd}]_2(\mu\text{-BiBzIm})$  ( $\text{ClO}_4$ )<sub>2</sub> (XIX)**

A mixture of complex (XII) (0.144 g, 0.1 mmol) and  $\text{H}_2\text{BiBzIm}$  (0.012 g, 0.05 mmol) in 60 ml of acetone was stirred for 86 h. The filtered solution was concentrated to ca. 5 ml, and ether was added to precipitate the yellow complex (XIX) (40% yield).

**Reaction of  $(\text{Ph}_3\text{P})_2\text{Au}_2(\mu\text{-BiBzIm})$  with  $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$**

To a solution of  $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$  (0.34 mmol) in 40 ml of benzene (obtained *in situ* by treating  $\text{PdCl}(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$  with  $\text{AgClO}_4$  and filtering off the formed AgCl) was added  $[(\text{Ph}_3\text{P})_2\text{Au}_2](\mu\text{-BiBzIm})$  (0.2 g, 0.17 mmol). Stirring for 16 h rendered an insoluble solid which was filtered off and extracted with refluxing acetone. The residue was identified by its elemental analysis and IR spectrum as  $\text{Pd}_2(\mu\text{-BiBzIm})(\text{C}_6\text{F}_5)_2(\text{PPh}_3)_2$  [3]. Partial evaporation of the filtrate and addition of ether yielded a white solid which was identified by IR spectroscopy and elemental analysis as  $[\text{Au}(\text{PPh}_3)_2]\text{-ClO}_4$ . (Found %: C, 53.5; H, 3.85. Calcd.: C, 52.7; H, 3.65).

**Reaction of  $(\text{dppm})\text{Au}_2(\mu\text{-BiBzIm})$  with  $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$**

To a solution of  $\text{Pd}(\text{OClO}_3)(\text{C}_6\text{F}_5)(\text{PPh}_3)_2$  (0.2 mmol) (obtained as described before) was added  $[(\text{dppm})\text{Au}_2](\mu\text{-BiBzIm})$  (0.1 g, 0.1 mmol) in 60 ml of  $\text{H}_2\text{CCl}_2$  and stirred for 20 h. The formed precipitate was identified (elemental analysis, IR spectroscopy) as a mixture of  $[\text{Au}_2(\text{PPh}_3)_2(\text{dppm})](\text{ClO}_4)_2$  and  $\text{Pd}_2(\mu\text{-BiBzIm})(\text{C}_6\text{F}_5)_2(\text{PPh}_3)_2$ , which could not be separated.

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