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Bibenizimidazolate as Bridging Ligand in Bi-, Tri- and Tetranuclear Gold(I) or Gold(I) and Palladium(II) Complexes

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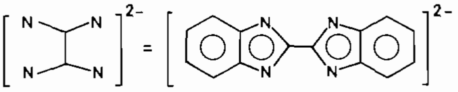
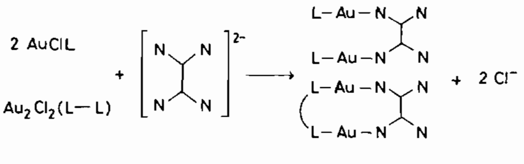
Recently we have described the synthesis of binuclear palladium(II) amidocomplexes [1] and of a gold(III) complex [2] containing the ligand 2,2'-bibenzimidazolate: BiBzIm^{2-} or



Only a few gold(I) amidocomplexes of the types $[Au(\mu\text{-}az)]_n$, $Au(az)PPh_3$ and $[AuPPh_3]_2(\mu\text{-}az)$ (az = pyrazol, triazol and tetrazol derivatives) have hitherto been reported [3–5]. In the present paper we describe the preparation of binuclear amido gold(I) complexes, in which the anion BiBzIm^{2-} acts as a bridging ligand. These complexes are used as precursors for the synthesis of tri- and tetranuclear gold(I) complexes or heteronuclear gold(I) and palladium(II) derivatives.

Potassium or thallium salts of 2,2'-bibenzimidazole in CH_2Cl_2/MeOH suspension (or solution) react at room temperature with the gold(I) halocomplexes AuClL or $Au_2Cl_2(L\text{–}L)$ to give binuclear amidocomplexes (eqn. 1)



(1)

L = PPh$_3$ (I); L–L = dpm (II)

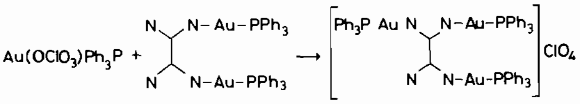
If L is a nitrogen (pyridine) or sulfur ligand (tht = tetrahydrothiophene) the reaction leads to the formation of insoluble solids and the strong smell of the free ligand can be appreciated, which is doubtlessly due to the displacement by BiBzIm^{2-}, according to eqn. (2)

$$2AuClL + BiBzIm^{2-} \rightarrow 1/x[Au_2(\mu\text{-}BiBzIm)]_x + 2Cl^- + 2L \qquad (2)$$

Complex (I) can be isolated by concentrating the solution *in vacuo* and subsequent addition of diethyl ether. Its molecular weight (osmometrically in $CHCl_3$) proves it to be binuclear.

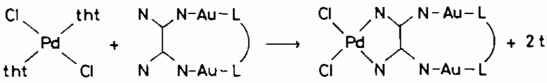
Complex (II) is little soluble and precipitates spontaneously, therefore its molecular weight could not be determinated, though the complex is possibly also binuclear. Both compounds are pale-yellow, light- and moisture-stable solids.

Both amidocomplexes are Lewis bases, containing two N atoms which are potentially donors. It is therefore possible to use one of them or both for forming bonds to one or two metal centres giving rise to neutral or cationic tri- or tetranuclear complexes. Thus, the reaction (1:1) of (I) with $Au(OClO_3)PPh_3$ leads (eqn. 3) to the cationic trinuclear complex $[Au_3(\mu\text{-}BiBzIm)(PPh_3)_3]ClO_4$ (III)



(3)

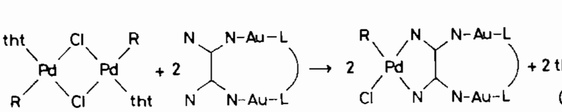
whilst the reaction of (II) with *trans*-$PdCl_2(tht)_2$ renders the neutral trinuclear complex (IV) (eqn. 4)



(4)

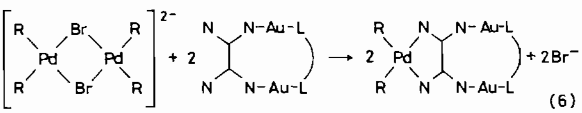
(IV)

Similar trimetallic neutral complexes can be obtained if (II) is used for cleaving the bridges of binuclear neutral or anionic palladium(II) complexes, *e.g.*, the reaction (2:1) of (II) with $[Pd(\mu\text{-}Cl)R(tht)]_2$ yields (V) and that with $[Bu_4N]_2[Pd(\mu\text{-}Br)R_2]_2$ ($R = C_6F_5$) leads to (VI) (eqns. 5 and 6)



(5)

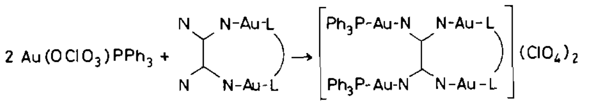
(V)



(6)

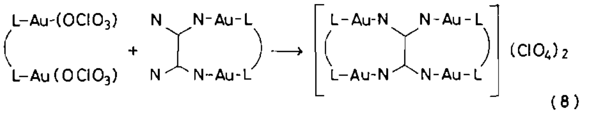
(VI)

Finally, tetranuclear cationic complexes in which each of the nitrogen atoms of BiBzIm^{2-} is attached to a metal atom can be obtained on reacting (1:2) complex (II) with $Au(OClO_3)PPh_3$ (eqn. 7) or on reacting (1:1) complex (II) with $Au(OClO_3)_2(\mu\text{-L-L})$ (eqn. 8).



(7)

(VII)



(8)

(VIII)

All the above-described complexes (I–VIII) were obtained in 60–80% yields. Their elemental analyses are consistent with the proposed formulae and their conductance is that expected for (1:1) or, respectively, (2:1) electrolytes. Their IR spectra show the bands which are characteristic for the ligand $BiBzIm^{2-}$ along with those of the respective ligands. The molecular weights (osmometric) for the soluble neutral complexes (I, V and VI) in chloroform solution are those expected for the proposed formulae.

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