Heteronuclear Complexes Containing {Au_2Rh}, {Au_2Ir} and {AuIr} Cores with a Dithiolate Ligand Bridging the Metal Centres − X-ray Structures of [$Au_2Ir(\mu\text{-}S_2C_6H_4)(cod)(PPh_3)_2]BF_4$ and [$AuIr(\mu\text{-}S_2C_6H_3CH_3)(cod)(PPh_3)$]

Inmaculada del Rio,[a] Raquel Terroba,[b] Elena Cerrada,[b] Michael B. Hursthouse,[c]
Mariano Laguna,*[b] Mark E. Light,[c] and Aurora Ruiz*[a]

Dedicated to Professor Rafael Usón on the occasion of his 75th birthday

Keywords: Gold / Rhodium / Iridium / S ligands / Hydrogenation

The use of dinuclear gold derivatives [$Au_2(\mu\text{-S-S})(PR_3)_2$] (S-S = benzenedithiolate, toluenedithiolate; PR_3 = PPh_3, PPh_2Me) as S-donor ligands, with rhodium and iridium complexes [$M(cod)_2]BF_4$ (M = Rh, Ir; cod = cyclooctadiene) affords new heteronuclear compounds containing the {Au_2M} core, with the general formulation [$Au_2M(\mu\text{-S-S})(cod)(PR_3)_2]BF_4$. One of these decomposes upon heating to give [$AuIr(\mu\text{-}S_2C_6H_4CH_3)(cod)(PPh_3)$]. The crystal structure of the former and [$Au_2Ir(\mu\text{-}S_2C_6H_4)(cod)(PPh_3)_2]BF_4$ have been established by X-ray diffraction. The sulfur atoms from the dithiolene ligands bridge two different metal centres.

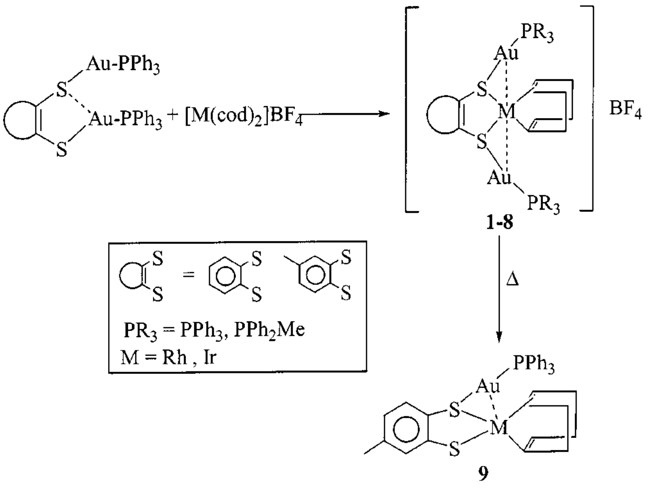
Introduction

Until recently, gold and its compounds were thought to be catalytically inactive.[1] In recent years, however, gold complexes have been used as homogeneous catalysts, mainly in the addition of water and alcohols to alkynes,[2] and in the use of luminescent compounds as photocatalysts.[3]

Heteropolynuclear complexes are particularly attractive because of their interesting structural and reactive features and their potential applications in catalysis.[4] In these complexes, two or more different metal atoms or ions are present in the same molecule and may cooperate in some reactions that could not be handled by a single metal centre. This leads to new types of reactions and affords new opportunities for catalytic processes.[5] Thus, heteropolynuclear complexes containing gold and other metal centres more commonly used in homogeneous catalysis, such as rhodium and iridium, can enhance the catalytic properties of the monometallic complexes.

Different approaches can be taken to the preparation of heterometallic derivatives. The tendency of thiolate ligands to act as bridges is a good starting point for the synthesis of polynuclear compounds, and several dinuclear thiolate complexes of rhodium and iridium are active in homogeneous catalytic hydrogenation reactions.[6] Some complexes containing gold and rhodium or iridium with thiolate ligands acting as a bridge between the metal centres have been reported, such as [$Cp^*M(\mu\text{-SR})_2AuCl_2]Cl$ (M = Rh, Ir), but their crystal structures are at present unknown.[7]

In this paper we present the synthesis of heterometallic complexes containing iridium or rhodium with dithiolene-gold compounds as ligands. The new derivatives have the general formula [$Au_2M(\mu\text{-S-S})(cod)(PR_3)_2]BF_4$ (M = Rh, Ir; S-S = benzenedithiolate, toluenedithiolate; cod = cyclooctadiene; PR_3 = PPh_3, PPh_2Me) and [$AuIr(\mu\text{-}S_2C_6H_4CH_3)(cod)(PPh_3)$]. The crystal structures of two gold-iridium complexes have been determined by X-ray diffraction and show short iridium−gold contacts ranging



Scheme 1. Synthesis of complexes **1−9**

---

[a] Departamento de Química Fisica i Inorgánica. Facultad de Química. Universitat Rovira i Virgili,
Pça. Imperial Tarraco 1, 43005 Tarragona, Spain
[b] Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C.,
50009 Zaragoza, Spain
E-mail mlaguna@posta.unizar.es
[c] Department of Chemistry, University of Southampton,
Highfield, Southampton SO17 1BJ, UK

from 2.8544(4) to 2.9120(8) Å. Their reactivity with H_2 and CO has been investigated.

Results and Discussion

Synthesis of Polynuclear Compounds $[Au_2M(\mu\text{-S-S})(cod)(PR_3)_2]BF_4$

The polynuclear compounds **1−8** were prepared by the reaction of $[Au_2(\mu\text{-S-S})(PR_3)_2]$ (S-S = benzenedithiolate or toluenedithiolate; PR_3 = PPh_3, PPh_2Me) with the corresponding $[M(cod)_2]BF_4$ (M = Rh, Ir) derivative (Scheme 1).

The compounds $[Au_2(\mu\text{-S-S})(PR_3)_2]$ have a dithiolate ligand bridging the two gold centres in a μ_2 fashion. The crystal structures of several of these complexes, with different dithiolenes and different phosphane ligands, have been determined by X-ray diffraction.[8,9] In these structures, in addition to the typical gold−gold interactions, there is also one weak interaction between S and Au. This interaction points to the possibility of further coordination to another metal centre through the sulfur atoms. We therefore tested the reactivity of these dinuclear gold compounds towards the incorporation of another gold atom giving rise to $[Au_3(\mu\text{-S-S})(PR_3)_3]ClO_4$.[8] This positive result and the recent reports regarding the activity of gold complexes as catalysts,[2] have encouraged us to synthesise complexes with these digold ligands and rhodium or iridium fragments. These two metals are well known in the homogeneous catalyst area, and, in particular, some dinuclear thiolate complexes of these metals have been shown to be active in catalytic hydrogenation reactions.[6]

$[M(cod)_2]^+$ (M = Rh, Ir) derivatives are used as starting materials, with the expectation that our gold-containing compounds could substitute one of the cyclooctadiene ligands, giving the corresponding heteronuclear products. The reactions were carried out in dichloromethane. Unknown yellow solids precipitated in this solvent and were filtered off. Little information about the yellow solids has at present been obtained, due to their insolubility in all the common solvents. Their elemental analyses indicate a low percentage of carbon, which would correspond to polynuclear species with high metallic content. From the remaining dichloromethane solutions, the new products **1−8** were obtained, together with $[Au(PR_3)_2]BF_4$, after addition of diethyl ether. Different solvents were tried to separate the complexes **1−8** from the bis(phosphane)gold(I) salts, with the best results being obtained by recrystallization from $CHCl_3$/diethyl ether. The final yields were quite poor (around 20%) due to the similar solubility of both compounds.

The IR spectra show an absorption corresponding to tetrahedral BF_4^-. From the two active vibration modes only the asymmetric tension vibration (ν_a) at ≈1050 cm^{-1} can be assigned. The asymmetric deformation vibration (∂_a) at ≈ 530 cm^{-1} is coincident with the phosphane vibration zone and it cannot be differentiated.

The $^{31}P\{^1H\}$ NMR spectra show a singlet due to the phosphanes for all the compounds (Table 1). In the new complexes **1−8**, after the metal coordination, the sulfur atoms become asymmetric centres. Therefore, the Au−PR_3 group can adopt an *anti* or a *syn* configuration. In both cases, only one singlet should appear in the ^{31}P NMR spectrum. NMR experiments at low temperature (193 K) still show the presence of only one singlet. This indicates that either there is only one diastereoisomer in solution or there is a very rapid interchange between the *anti* and the *syn* configuration. The singlets corresponding to the Rh complexes **1−4** appear at lower fields than those in the gold starting materials, whilst the singlets of the Ir complexes **5−8** are displaced to higher field, although in both cases the magnitude is about $\Delta\delta = 1$. It is worth noting that complexes with toluendithiolate (**2**, **4**, **6** and **8**) do not show the predicted two resonances for the phosphorous due to the asymmetric nature of the ligand: only one singlet is present in their spectra, even at low temperature, as in the gold starting materials $[Au_2(\mu\text{-}S_2C_6H_3CH_3)(PR_3)_2]$.[8] A fast interchange of $AuPPh_3$ fragments should be present in solution.

Crystal Structure of $[Au_2Ir(S_2C_6H_4)(cod)(PPh_3)_2]BF_4$ (5)

The molecular structure of the complex $[Au_2Ir(S_2C_6H_4)(cod)(PPh_3)_2]BF_4$ (**5**) has been established by X-ray diffraction and the cation is shown in Figure 1. General information is given in Table 2 and selected bond lengths and angles in Table 3. The cation of **5** consists of a benzenedithiolate ligand bridging two $AuPPh_3^+$ and one $Ir(cod)^+$ fragments, in a similar arrangement to $[Au_3(S_2C_6H_3CH_3)(PPh_3)_3]ClO_4$.[8] The dithiolene and cod ligands are chelated to the iridium centre. The average Ir−S distance is 2.32 Å and the average Ir−C distance 2.15 Å. These bond lengths are similar to the ones found in the Ir^I dimers $[Ir(\mu\text{-SR})(cod)]_2$.[10]

The iridium−gold distances are Ir−Au(1) = 2.9208(9) and Ir−Au(2) = 2.9120(8) Å. These distances are longer than the corresponding single Ir−Au bond, which are in the range 2.59−2.81 Å[11] and are similar to the reported metal−metal interactions in other iridium-gold complexes.[12] There is probably a considerable similarity be-

Table 1. ^{31}P{^{1} Rp NM^r in CDCl3 (δ in ppm)

S-S	PR_3	$[Au_2(\mu\text{-S-S})(PR_3)_2]$[8]	$[Au_2Rh(\mu\text{-S-S})(cod)(PR_3)_2]BF_4$	$[Au_2Ir(\mu\text{-S-S})(cod)(PR_3)_2]BF_4$
$S_2C_6H_4$	PPh_3	35.9	36.9 (**1**)	35.2 (**5**)
$S_2C_6H_4$	PPh_2Me	20.3	21.3 (**2**)	19.5 (**6**)
$S_2C_6H_3Me$	PPh_3	36.0	37.1 (**3**)	35.3 (**7**)
$S_2C_6H_3Me$	PPh_2Me	20.3	21.4 (**4**)	19.5 (**8**)

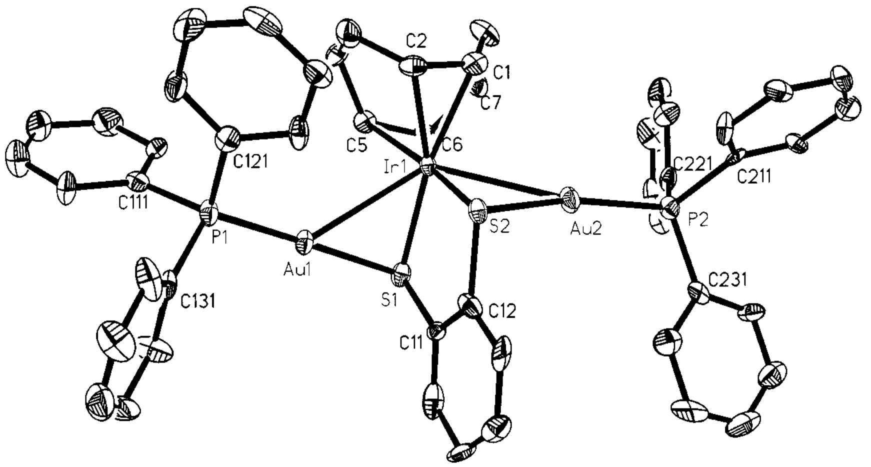


Figure 1. Molecular structure of **5** showing the cation; thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity

Table 2. Details of data collection and structure refinement for the complexes **5** and **9**

	5	**9**
Chemical formula	$C_{50}H_{46}Au_2BF_4IrP_2S_2$	$C_{33}H_{33}AuIrPS_2$
M	1443.87	913.85
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a [Å]	11.0590(10)	10.8676(2)
b [Å]	14.528(2)	18.7639(6)
c [Å]	15.634(2)	14.7198(4)
α [°]	93.78(2)	90
β [°]	102.210(10)	102.9159(18)
γ [°]	106.550(10)	90
V [Å^3]	2331.9(5)	2925.70(13)
Z	2	4
Dc (Mg m^{-3})	2.056	2.075
F(000)	1366	1736
Crystal size	0.20 × 0.16 × 0.14	0.25 × 0.18 × 0.1
T [K]	293(2)	293(2)
μ (Mo-K_α) [mm^{-1}]	9.101	9.772
θ range [°]	1.86 to 24.94	3.03 to 25.02
Reflections collected	10011	18537
Independent reflections	4526 [R(int) = 0.069]	5826 [R(int) = 0.0516]
Data/restraints/parameters	10011/6/559	5826/0/345
Quality of fit	0.999	1.161
$R1$[a]	0.0344	0.0385
$wR2$[b]	0.1010	0.0839
Residual ρ/eÅ^{-3}	1.290, −1.460	1.445, −2.011

[a] $R1\ (F) = \|F_o| - |F_c\|/|F_o|$. – [b] $wR2\ (F^2) = [\{w(F_o^2 - F_c^2)^2\}/\{w(F_o^2)^2\}]^{0.5}$.

tween the Au−Ir interaction in **5** and the numerous examples of short Au−Au contacts shown in Au^I complexes,[13] or in the case of $[Au_3(S_2C_6H_3CH_3)(PPh_3)_3]ClO_4$ [8] [2.9624(12) and 3.1966(14) Å]. The two $AuPPh_3$ units are in an up/down configuration either side of the Ir(S-S)(cod) square planar fragment. Therefore, taking into account these two gold−iridium interactions, the coordination around the iridium can be regarded as a heavily distorted octahedron.

Despite the presence of gold−iridium interactions, the gold atoms are almost linearly coordinated considering the P−Au−S arrangement, the most frequent type of configuration for gold(I) complexes, with angles P(1)−Au(1)−S(1) = 176.07(13)° and P(2)−Au(2)−S(2) = 161.33(12)°. These gold centres lie out of the plane formed by P−S−Ir by 0.079 Å for Au(1) and 0.042 Å for Au(2). The gold−sulfur bond lengths are Au(1)−S(1) = 2.372(3) and Au(2)−S(2) = 2.392(3) Å, and are a little longer than in the previously reported complex $[Au_3(S_2C_6H_3CH_3)(PPh_3)_3]ClO_4$ [8] [2.315(5) and 2.332(4) Å for the external gold atoms]. The gold−phosphorus distances are Au(1)−P(1) = 2.257(3) and Au(2)−P(2) = 2.248(3), and are similar to the values found in other Ir−Au phosphane complexes (2.199−2.292 Å).[14]

Table 3. Bond lengths [Å] and angles [°] for **5**

Au(1)−P(1)	2.257(3)
Au(1)−S(1)	2.372(3)
Au(1)−Ir(1)	2.9208(9)
Au(2)−P(2)	2.248(3)
Au(2)−S(2)	2.392(3)
Au(2)−Ir(1)	2.9120(8)
Ir(1)−C(2)	2.109(14)
Ir(1)−C(6)	2.144(14)
Ir(1)−C(5)	2.158(12)
Ir(1)−C(1)	2.201(14)
Ir(1)−S(2)	2.317(3)
Ir(1)−S(1)	2.318(4)
P(1)−Au(1)−S(1)	176.07(13)
P(1)−Au(1)−Ir(1)	129.21(10)
S(1)−Au(1)−Ir(1)	50.65(9)
P(2)−Au(2)−S(2)	161.33(12)
P(2)−Au(2)−Ir(1)	147.83(10)
S(2)−Au(2)−Ir(1)	50.66(8)
C(2)−Ir(1)−S(2)	93.6(4)
C(6)−Ir(1)−S(2)	155.4(4)
C(5)−Ir(1)−S(2)	165.9(4)
C(1)−Ir(1)−S(2)	94.7(4)
C(2)−Ir(1)−S(1)	157.0(4)
C(6)−Ir(1)−S(1)	91.2(4)
S(2)−Ir(1)−S(1)	87.89(12)
C(5)−Ir(1)−Au(2)	140.7(3)
S(2)−Ir(1)−Au(2)	52.96(8)
S(1)−Ir(1)−Au(2)	92.49(8)
S(2)−Ir(1)−Au(1)	88.05(8)
S(1)−Ir(1)−Au(1)	52.32(8)
Au(2)−Ir(1)−Au(1)	130.47(3)
C(11)−S(1)−Ir(1)	106.0(5)
C(11)−S(1)−Au(1)	97.1(4)
Ir(1)−S(1)−Au(1)	77.02(11)
C(12)−S(2)−Ir(1)	105.3(5)
C(12)−S(2)−Au(2)	94.4(4)
Ir(1)−S(2)−Au(2)	76.38(10)

The coordination plane for the Ir centre forms a dihedral angle of 176° with the dithiolene plane. The Au−PPh$_3$ groups are in an *anti* configuration, giving an *R*-configuration for both sulfur atoms.

Reactivity and Catalytic studies

We have studied the reactivity of the complexes [Au$_2$M(μ-S$_2$C$_6$H$_4$)(cod)(PPh$_3$)$_2$]BF$_4$ (M = Rh **1**, Ir **5**). Dichloromethane solutions of both products were treated with H$_2$ and CO at room temperature and pressure. While we did not observe any reaction with H$_2$, both compounds react with CO. The dichloromethane solutions change from yellow to green and two new absorptions are observed in the IR spectra at 1993 and 2019 cm^{-1}, corresponding to terminal ν$_{CO}$ vibrations due to the coordination of two CO molecules to the metal centres, replacing the cod ligand.[15] Evaporation of the solvent gives green solids that do not contain absorptions in the CO region, showing that the proposed dicarbonyl complex is not stable under these conditions.

Studies testing the catalytic activity of these complexes in the hydroformylation and hydrogenation of styrene were performed. The hydroformylation test was performed at 353 K and P_{CO/H_2} (1:1) = 5 atm., in dichloroethane, using complex **1** as the catalyst precursor. The catalytic test for the hydrogenation was performed at 298 K and P_{CO/H_2} = 5 atm., in dichloromethane. The catalyst precursor for the hydrogenation run was complex **5**. Both reactions were followed by gas chromatography, but neither hydroformylation nor hydrogenation were observed. The final reaction mixtures were green solutions with black solids in suspension. The black solids may correspond to the formation of reduced metals due to the presence of hydrogen pressure and/or higher temperatures.

Preparation and Crystal Structure of [AuIr(μ-S$_2$C$_6$H$_3$CH$_3$)(cod)(PPh$_3$)]

Since complex **1** decomposed in the hydroformylation and hydrogenation reactions, we studied the behaviour of complexes **1**−**8** at the temperature of refluxing acetone in order to test their thermal stability. All the complexes give insoluble black solids and [Au(PR$_3$)$_2$]BF$_4$, as confirmed by ^{31}P NMR spectroscopy. Only in the case of [Au$_2$Ir(μ-S$_2$C$_6$H$_3$CH$_3$)(cod)(PPh$_3$)$_2$]BF$_4$ (**7**) was one diethyl ether soluble complex isolated in quite good yield and characterized as [AuIr(μ-S$_2$C$_6$H$_3$CH$_3$)(cod)(PPh$_3$)] (**9**). It shows a similar ^{31}P NMR spectrum to that of **7** with only one signal at δ = 35.1, although with toluenedithiolate several isomers should be present. The ^{1}H NMR spectrum shows different resonances for the cod protons, pointing to the presence of a nonsymmetrical coordination for the diolefinic ligand. In addition, the integration of the phenyl protons suggests that only one AuPPh$_3$ group is present for each cod ligand. The elemental analysis and the IR spectrum, with the lack of absorptions corresponding to a BF$_4$ anion, confirm the proposed stoichiometry for **9**.

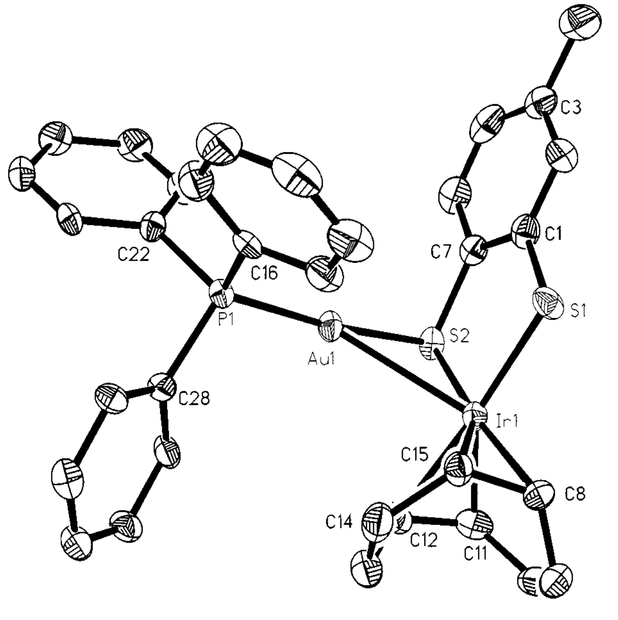


Figure 2. Molecular structure of **9**; thermal ellipsoids are drawn at the 50% probability level and H atoms have been omitted for clarity

The dinuclear structure of **9** was confirmed by X-ray analysis (Figure 2). General information is given in Table 2 and selected bond lengths and angles in Table 4. The molecule can be described as a toluenedithiolate ligand bridging one $AuPPh_3^+$ and one $Ir(cod)^+$ fragment, in a similar arrangement to that present in $[Au_2Ir(S_2C_6H_4)(cod)(PPh_3)_2]BF_4$ (**5**). In fact, the structure of **9** is very similar to **5** with the addition of a methyl group, the lack of the BF_4 anion and the presence of only one $AuPPh_3$ fragment. Complex **9** retains the planarity of the Ir(S-S)(cod) fragment and the pseudo linearity of $SAu(PPh_3)$ skeleton. The Ir−S, Au−S, Ir−C and Au−P distances are nearly identical in **5** and **9**. Only the Ir(1)−S(1) distance with the nonbridging sulfur is slightly shorter than either the Ir(1)−S(2) in complex **9** or any of the Ir−S distances in complex **5**. In addition only one iridium−gold distance in **9** [2.8544(4) Å] is shorter than the two Ir−Au contacts in **5**, showing that the interaction between the two metals is now stronger than in the trinuclear complex, although this value it is not short enough to be considered a real metal−metal bond.[11,12]

Table 4. Bond lengths [Å] and angles [°] for **9**

Au(1)−P(1)	2.2496(19)
Au(1)−S(2)	2.3829(18)
Au(1)−Ir(1)	2.8544(4)
Ir(1)−C(11)	2.133(8)
Ir(1)−C(15)	2.151(7)
Ir(1)−C(8)	2.151(7)
Ir(1)−C(12)	2.205(8)
Ir(1)−S(1)	2.2819(19)
Ir(1)−S(2)	2.3168(18)
P(1)−Au(1)−S(2)	171.82(7)
P(1)−Au(1)−Ir(1)	136.23(5)
S(2)−Au(1)−Ir(1)	51.56(4)
C(11)−Ir(1)−C(15)	98.0(3)
C(11)−Ir(1)−C(8)	81.0(3)
C(15)−Ir(1)−C(8)	39.1(3)
C(11)−Ir(1)−C(12)	38.6(3)
C(15)−Ir(1)−C(12)	80.7(3)
C(8)−Ir(1)−C(12)	88.8(3)
C(11)−Ir(1)−S(1)	147.7(2)
C(15)−Ir(1)−S(1)	95.2(2)
C(8)−Ir(1)−S(1)	91.1(2)
C(12)−Ir(1)−S(1)	173.5(2)
C(11)−Ir(1)−S(2)	94.3(2)
C(15)−Ir(1)−S(2)	151.2(2)
C(8)−Ir(1)−S(2)	169.7(2)
C(12)−Ir(1)−S(2)	93.2(2)
S(1)−Ir(1)−S(2)	88.05(7)
C(11)−Ir(1)−Au(1)	115.4(2)
C(15)−Ir(1)−Au(1)	97.6(2)
C(8)−Ir(1)−Au(1)	136.6(2)
C(12)−Ir(1)−Au(1)	83.9(2)
S(1)−Ir(1)−Au(1)	91.75(5)
S(2)−Ir(1)−Au(1)	53.66(5)
C(28)−P(1)−Au(1)	110.5(2)
C(16)−P(1)−Au(1)	112.5(2)
C(22)−P(1)−Au(1)	113.5(2)
C(7)−S(2)−Ir(1)	105.3(2)
C(7)−S(2)−Au(1)	96.5(2)
Ir(1)−S(2)−Au(1)	74.78(5)
C(1)−S(1)−Ir(1)	105.7(3)
C(15)−C(8)−Ir(1)	70.4(4)
C(9)−C(8)−Ir(1)	113.4(6)
C(12)−C(11)−Ir(1)	73.4(5)
C(10)−C(11)−Ir(1)	110.3(6)
C(8)−C(15)−Ir(1)	70.5(4)
C(14)−C(15)−Ir(1)	109.4(5)
C(11)−C(12)−Ir(1)	68.0(4)
C(13)−C(12)−Ir(1)	112.3(5)

In summary, we have prepared new polynuclear complexes with Au_2Rh, Au_2Ir, and AuIr cores using dithiolate ligands to bridge the metal centres. The crystal structures of $[Au_2Ir(\mu\text{-}S_2C_6H_4)(cod)(PPh_3)_2]BF_4$ (**5**) and $[AuIr(\mu\text{-}S_2C_6H_3CH_3)(cod)(PPh_3)]$ (**9**) show that there are gold−iridium interactions ranging from 2.9208(9) in the former to 2.8544(4) Å in the latter. The new complexes are not active precursors for either the hydroformylation or hydrogenation of styrene. This inactivity may be due to the instability of the complexes either at high P_{CO/H_2} or at high temperature.

Experimental Section

General: IR spectra were recorded on a Perkin−Elmer 883 spectrophotometer, over the range 4000−200 cm^{-1}, as Nujol mulls between polyethylene sheets. ^1H and ^{31}P NMR spectra were recorded on a Varian GEMINI 300 in $CDCl_3$ solution; chemical shifts are quoted relative to $SiMe_4$ (^1H) or H_3PO_4 (external ^{31}P). The C,H,N and S analyses were performed with a Perkin−Elmer 2400 microanalyser. Mass spectra were recorded on a VG Autospec, by liquid secondary ion mass spectrometry (LSIMS +) using nitrobenzyl alcohol as matrix and a caesium gun. Gas chromatography was performed on a Hewlett−Packard 5840A chromatograph with a flame ionisation detector using an Ultra-2 (5% diphenylsilicone/95% dimethylsilicone) capillary column (25 m × 0.2 mm Ø).

Materials: The starting materials $[Au_2(\mu\text{-}S_2C_6H_4)(PPh_3)_2]$,[8] $[Au_2(\mu\text{-}S_2C_6H_4)(PPh_2Me)_2]$,[8] $[Au_2(\mu\text{-}S_2C_6H_3Me)(PPh_3)_2]$,[8] $[Au_2(\mu\text{-}S_2C_6H_3Me)(PPh_2Me)_2]$,[8] $[Rh(cod)_2]BF_4$ [16] and $[Ir(cod)_2]BF_4$ [16] were prepared as previously described. All other reagents were commercially available, and all the reactions were carried out under an argon atmosphere. All the synthesised complexes were isolated as air-stable solids.

Preparation of Complexes 1−8: To a solution of $[Au_2(\mu\text{-}S\text{-}S)(PR_3)_2]$ [S-S = $S_2C_6H_4$, PR_3 = PPh_3 (0.106 g, 0.1 mmol), PPh_2Me (0.093 g, 0.1 mmol); S-S = $S_2C_6H_3Me$, PR_3 = PPh_3 (0.107 g, 0.1 mmol), PPh_2Me (0.095 g, 0.1 mmol)] in CH_2Cl_2 was added $[M(cod)_2]BF_4$ [M = Rh (0.041 g, 0.1 mmol), Ir (0.050 g, 0.1 mmol)]. After stirring for 1 h a yellow solid was filtered off. The solutions were concentrated in vacuum; addition of cold diethyl ether, resulted in the precipitation of yellow solids, which were filtered off, washed with cold diethyl ether and vacuum dried. These solids contained complexes **1−8** with $[Au(PR_3)_2]BF_4$. Recrystallization from chloroform/diethyl ether afforded the new compounds as yellow solids. Only the initial batch of crystals were collected as later fractions were found to be contaminated with bis(phosphane)gold(I) tetrafluoroborate.

1: Yield: 28 mg (20%). − $C_{50}H_{46}Au_2BF_4P_2RhS_2$: calcd. C 44.3, H 3.4, S 4.7; found C 44.7, H 3.4, S 4.4. − ^1H NMR: δ = 1.8 (m, 4 H, $-CH_2-_{endo}$, cod), 1.9 (m, 4 H, $-CH_2-_{exo}$, cod), 4.7 (m, 4 H, -CH=CH-, cod), 7.2−7.7 (m, 30 H, Ph + 2 H, C_6H_4), 7.9 (m, 2 H, C_6H_4). − IR (Nujol mull): ν_{BF} = 1056 cm^{-1}. − MS: *m*/*z* (%) = 1269 (10) $[M - BF_4]^+$.

2: Yield: 34 mg (27%). − $C_{40}H_{42}Au_2BF_4P_2RhS_2$: calcd. C 39.0, H 3.4, S 5.2; found C 39.3, H 3.7, S 4.9. − ^{1}H NMR: δ = 1.9 (m, 8 H, -CH_2-, cod), 2.2 (d, $^{2}J_{P-H}$ = 11.5 Hz, 6 H, PPh_2*Me*), 4.7 (m, 4 H, -CH=CH-, cod), 7.3−7.8 (m, 20 H, Ph + 2 H, C_6H_4), 7.9 (m, 2 H, C_6H_4). − IR (Nujol mull): ν_{BF} = 1057 cm^{-1}. − MS: *m*/*z* (%) = 1145 (5) $[M - BF_4]^+$.
3: Yield: 35 mg (25%). − $C_{51}H_{48}Au_2BF_4P_2RhS_2$: calcd. C 44.7, H 3.5, S 4.7; found C 44.3, H 3.6, S 4.2. − ^{1}H NMR: δ = 1.8 (m, 4 H, -CH_2-$_{endo}$, cod), 1.9 (m, 4 H, -CH_2-$_{exo}$, cod), 2.4 (s, 3 H, C_6H_3*Me*), 4.7 (m, 4 H, -CH=CH-, cod), 7.1 (dd, 1 H, C_6H_3Me), 7.3−7.7 (m, 30 H, Ph), 7.7 (m, 1 H, C_6H_3Me), 7.8 (d, $^{3}J_{H-H}$ = 7.7 Hz, 1 H, C_6H_3Me). − IR (Nujol mull): ν_{BF} = 1057 cm^{-1}. − MS: *m*/*z* (%) = 1283 (29) $[M - BF_4]^+$.
4: Yield: 33 mg (26%). −$C_{41}H_{44}Au_2BF_4P_2RhS_2$: calcd. C 39.5, H 3.5, S 5.1; found C 39.6, H 3.8, S 5.0. − ^{1}H NMR: δ = 1.9 (m, 8 H, -CH_2-, cod), 2.1 (d, $^{2}J_{P-H}$ = 11.8 Hz, 6 H, PPh_2*Me*), 2.4 (s, 3 H, C_6H_3*Me*), 4.7 (m, 4 H, -CH=CH-, cod), 7.1 (dd, 1 H, C_6H_3Me), 7.3−7.7 (m, 20 H, Ph), 7.7 (m, 1 H, C_6H_3Me), 7.8 (m, 1 H, C_6H_3Me). − IR (Nujol mull): ν_{BF} = 1060 cm^{-1}. − MS: *m*/*z* (%) = 1159 (18) $[M - BF_4]^+$.
5: Yield: 32 mg (22%). − $C_{50}H_{46}Au_2BF_4IrP_2S_2$: calcd. C 41.5, H 3.2, S 4.4; found C 41.0, H 3.2, S 4.3. − ^{1}H NMR: δ = 1.6 (m, 4 H, -CH_2-$_{endo}$, cod), 1.8 (m, 4 H, -CH_2-$_{exo}$, cod), 4.4 (m, 4 H, -CH=CH-, cod), 7.1−7.7 (m, 30 H, Ph + 2 H, C_6H_4), 8.1 (m, 2 H, C_6H_4). − IR (Nujol mull): ν_{BF} = 1055 cm^{-1}. − MS: *m*/*z* (%) = 1359 (12) $[M - BF_4]^+$
6: Yield: 40 mg (30%). − $C_{40}H_4Au_2BF_4Ir_2P_2S_2$: calcd. C 36.3, H 3.2, S 4.8; found C 36.8, H 3.5, S 4.9. − ^{1}H NMR: δ = 1.8 (m, 4 H, -CH_2-$_{endo}$, cod), 1.9 (m, 4 H, -CH_2-$_{exo}$, cod), 2.1 (m, 6 H, PPh_2*Me*), 4.4 (m, 4 H, -CH=CH-, cod), 7.8−7.2 (m, 20 H, Ph, 2 H, C_6H_4), 8.1 (m, 2 H, C_6H_4). − IR (Nujol mull): ν_{BF} = 1060 cm^{-1}. − MS: *m*/*z* (%) = 1235 (4) $[M - BF_4]^+$.
7: Yield: 34 mg (23%). − $C_{51}H_{48}Au_2BF_4IrP_2S_2$: calcd. C 41.9, H 3.3, S 4.4; found C 41.7, H 3.5, S 4.2. − ^{1}H NMR: δ = 1.6 (m, 4 H, -CH_2-$_{endo}$, cod), 1.8 (m, 4 H, -CH_2-$_{exo}$, cod), 2.5 (s, 3 H, C_6H_3*Me*), 4.4 (m, 4 H, -CH=CH-, cod), 7.1 (dd, 1 H, C_6H_3Me), 7.7−7.2 (m, 30 H, Ph), 7.7 (d, $^{4}J_{H-H}$ = 1.2 Hz, 1 H, C_6H_3Me), 7.9 (d, $^{3}J_{H-H}$ = 7.7 Hz, 1 H, C_6H_3Me). − IR (Nujol mull): ν_{BF} = 1056 cm^{-1}. − MS: *m*/*z* (%) = 1373(21) $[M - BF_4]^+$.
8: Yield: 27 mg (20%). $C_{41}H_{44}Au_2IrBF_4P_2S_2$: calcd. C 36.8, H 3.3, S 4.8; found C 36.9, H 3.7, S 4.5. − ^{1}H NMR: δ = 1.7 (m, 4 H, -CH_2-$_{endo}$, cod), 1.9 (m, 4 H, -CH_2-$_{exo}$, cod), 2.1 (d, $^{2}J_{P-H}$ = 10.2 Hz, 6 H, PPh_2*Me*), 2.5 (s, 3 H, C_6H_3*Me*), 4.4 (m, 4 H, -CH=CH-, cod), 7.1 (dd, 1 H, C_6H_3Me), 7.7−7.3 (m, 20 H, Ph), 7.8 (d, $^{4}J_{H-H}$ = 3.6 Hz, 1 H, C_6H_3Me), 7.9 (d, $^{3}J_{H-H}$ = 10.8 Hz, 1 H, C_6H_3Me). − IR (Nujol mull): ν_{BF} = 1059 cm^{-1}. − MS: *m*/*z* (%) = 1249 (16) $[M - BF_4]^+$.

[AuIr(μ-$S_2C_6H_3$Me)(cod)(PPh_3)$_2$] (9): A solution of **7** (0.073 g, 0.05 mmol) in acetone (20 mL) was refluxed for 3 h. After removal of the solvent to ca. 5 mL and addition of diethyl ether (20 mL) a white solid was formed, which was characterized as $[Au(PPh_3)_2]BF_4$. Partial evaporation of the solution and addition of hexane gave a yellow solid. Yield: 26 mg (57%). − $C_{33}H_{33}AuIrPS_2$: calcd. C 43.4, H 3.6, S 7.0; found C 43.8, H 3.7, S 6.6. − ^{1}H NMR: δ = 1.6 (m, 4 H, -CH_2-$_{endo}$, cod), 1.8 (m, 4 H, -CH_2-$_{exo}$, cod), 2.4 (s, 3 H, C_6H_3*Me*), 4.0 (m, 2 H, -CH=CH-, cod), 4.1 (m, 2 H, -CH=CH-, cod), 6.7 (d, 1 H, C_6H_3Me), 7.3−7.1 (m, 15 H, Ph), 7.4 (s, 1 H, C_6H_3Me), 7.5 (d, $^{3}J_{H-H}$ = 9.0 Hz, 1 H, C_6H_3Me) − $^{31}P\{^{1}H\}$ NMR: δ = 35.1 (s, PPh_3). − MS: *m*/*z* (%) = 913 (20) $[M]^+$.

Crystallography: Single crystals were grown by diffusing hexane into dichloromethane solutions of [Au_2Ir(μ-$S_2C_6H_4$)(cod)(PPh_3)$_2$]BF_4 (**5**) and [AuIr(μ-$S_2C_6H_3$Me)(cod)(PPh_3)] (**9**). They were mounted at low temperature in inert oil. Crystal data and data collection parameters are summarised in Table 4. Data were collected on a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator with graphite monochromated Mo-K_α radiation (λ = 0.71069 Å), following procedures described elsewhere.[17]
Structure Solution and Refinement: The structures were solved using SHELXS-86 and SHELXS-97,[18] and refined by full-matrix least-squares on F_o^2, using the programs SHELXL-93 and SHELXL-97.[19] In the case of **5** the data were corrected with the program DIFABS,[20] and for **9** with the program SORTAV.[21] The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in idealized positions.

Crystallographic data (excluding structure factors) for the structure(s) included in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-157923 (**5** and **9**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

Hydrogenation Procedure: The reaction was carried out in a small home-made autoclave. The styrene (0.92 cm^3, 8 mmol) and catalyst precursor **5** (57.8 mg, 0.04 mmol) were dissolved in dichloromethane (6 cm^3) and shaken under 5 atm. of H_2 at 298 K for 24 h. The conversion was measured by gas chromatography.

Hydroformylation Procedure: The catalyst precursor **1** (68.1 mg, 0.05 mmol) and styrene (1.15 cm^3, 10 mmol) were dissolved in 7.5 cm^3 of dichloromethane. This solution was transferred to the evacuated autoclave, which was then pressurised with *syn*-gas to about 80% of the reaction pressure (5 atm.). The preheated water circuit was connected to the autoclave jacket, and when thermal equilibrium was reached (5−10 minutes) more gas mixture was introduced until the required pressure was achieved. At the end of the reaction the autoclave was cooled to room temperature and depressurised. The sample was analysed by gas chromatography.

Acknowledgments

The Spanish authors thank the Dirección General de Enseñanza Superior (PB98- 0542 and PB97−0407-C05−01) for financial support, the Ministerio de Educación y Cultura for a grant (to R.T.), and the Generalitat de Catalunya (CIRIT) for a grant (to I del R.). M.B.H. thanks the Engineering and Physical Sciences Research Council for support of the X-ray facilities.

[1] [1a] R J. Puddephatt, *The Chemistry of Gold*, Elsevier, The Netherlands, **1978**.
[2] [2a] H. Schmidbaur, *Gold progress in Chemistry, Biochemistry and Technology*, John Wiley and Sons. New York, **1999**. − [2b] G. C. Bond, D. T. Thompson, *Gold Bull.* **2000**, *33*, 41−50. − [2c] J. H. Teles, S. Brode, M. Chabanas, *Angew. Chem. Int. Ed.* **1998**, *37*, 1415−1418; *Angew. Chem.* **1998**, *110*, 1475−1478. − [2d] Q. Xu, Y. Imamura, M. Fujiwara, Y. Souma, *J. Org. Chem.* **1997**, *62*, 1594−1598. − [2e] S. Komiya, Y. Sone, T. Usui, M. Hirano, A. Fukuoka, *Gold Bull.* **1996**, *29*, 131−136. − [2f] D. A. Krogstad, W. V. Konze, L. H. Pignolet, *Inorg. Chem.* **1996**, *35*, 6763−6771. − [2g] Y. Fukuda, K. Utimoto, *J Org. Chem.* **1991**, *56*, 3729−3731. − [2h] K. Fukuda, Y. Utimoto, *Bull. Chem. Soc. Jpn.* **1991**, *64*, 2013−2015. − [2i] K. Fukuda, Y. Utimoto, *Synthesis* **1991**, 975−978. − [2j] K. Fukuda, Y. Utimoto, K. Nozaki, *Heterocycles* **1987**, *25*, 297−301. − [2k] Y. Ito,

M. Sawamura, T. Hayashi, *J. Am. Chem. Soc.* **1986**, *108*, 6405−6406.

[3] [3a] A. Grohmann, H. Schmidbaur, *Comprehensive Organometallic Chemistry II* (Eds. G. Wilkinson, F. G. A. Stone, E. W. Abel), vol 3, Pergamon, **1995**. − [3b] F. Gaspassini, M. Giovannoli, D. Misiti, G. Natile, G. Palmieri, L. Maresca, *J. Am. Chem. Soc.* **1993**, *115*, 4401−4402. − [3c] A. W. Olsen, Z. H. Kafafi, *J. Am. Chem. Soc.* **1991**, *113*, 7758−7760. − [3d] Y. Hori, A. Musata, K. Kikuchi, *J. Chem. Soc., Chem. Commun.* **1987**, 728−729.

[4] B. Chaudret, B. Delavaux, R. Poilblanc, *Coord. Chem. Rev.* **1988**, *86*, 191−243.

[5] D. W. Stephan, *Coord. Chem. Rev.* **1989**, *95*, 41−107.

[6] [6a] H. Schumann, H. Hemling, N. Goren, J. Blum, *J. Organomet. Chem.* **1995**, *485*, 209−213. − [6b] H. Schumann, B. Gorella, M. Eisen, J. Blum, *J. Organomet. Chem.* **1991**, *412*, 251−258. − [6c] M. Eisen, P. Weitz, S. Shtelzer, J. Blum, H. Schumann, B. Gorella, F. H. Görlitz, *Inorg. Chim. Acta* **1991**, *188*, 167 176. − [6d] M. Eisen, J. Blum, H. Schumann, B. Gorella, *J. Mol. Cat.* **1989**, *56*, 329−337. − [6e] P. Kalck, R. Poilblanc, R. P. Martin, A. Lovera, A. Gaset, *J. Organomet. Chem.* **1980**, *195*, C9−C12.

[7] J. J. García, M. L. Hernández, H. Torrens, A. Gutierrez, F. del Río, *Inorg. Chim. Acta* **1995**, *230*, 173−176.

[8] M. C. Gimeno, P. G. Jones, A. Laguna, M. Laguna, R. Terroba, *Inorg. Chem.* **1994**, *33*, 3932−3938.

[9] [9a] R. M. Dávila, A. Elduque, T. Grant, R. J. Staples, J. P. Fackler Jr., *Inorg. Chem.* **1993**, *32*, 1749−1755. − [9b] M. Nakamoto, H. Koijman, M. Paul, W. Hiller, H. Schmidbaur, *Z. Anorg. Allg. Chem.* **1993**, *619*, 1341−1346. − [9c] M. Nakamoto, A. Schier, H. Schmidbaur, *J. Chem. Soc., Dalton Trans.* **1993**, 1347−1348

[10] [10a] E. Fernández, A. Ruiz, S. Castillón, C. Claver, J. F. Pinella, A. Alvarez-Larena, G. Germain, *J. Chem. Soc., Dalton Trans.* **1995**, 2137−2142. − [10b] F. A. Cotton, P. Lahuerta, J. LaTorre, M. Sanasí, I. Solana, W. Schwotzer, *Inorg. Chem.* **1988**, *27*, 2131−2135.

[11] A. L. Balch, V. J. Catalano, *Inorg. Chem.* **1991**, *30*, 1302−1308.

[12] [12a] A. L. Balch, V. J. Catalano, *Inorg. Chem.* **1992**, *31*, 2730−2734. − [12b] A. L. Balch, V. J. Catalano, B. C. Noll, M. M. Olmstead, *J. Am. Chem. Soc.* **1990**, *112*, 7558−75566. − [12c] A L. Balch, V. J. Catalano, M. M. Olmstead, *J. Am. Chem. Soc.* **1990**, *112*, 2010−2013. − [12d] A. L. Balch, V. J. Catalano, M. M. Olmstead, *Inorg Chem.* **1990**, *29*, 585−586. − [12e] B. D. Alexander, P. D. Boyle, B. J. Johnson, J. A. Casalnuovo, S. M. Johnson, A. M. Mueting, L. H. Pignolet, *Inorg. Chem.* **1987**, *26*, 2547−2551.

[13] P. G. Jones, *Gold Bull.* **1981**, *14*, 102−118; **1983**, *16*, 114−124; **1986**, *19*, 46−57.

[14] [14a] C. Bianchini, A. Meli, M. Peruzzini, A. Vacca, F. Vizza, A. Albinati, *Inorg. Chem.* **1992**, *31*, 3841−3850. − [14b] A. G. Sykes, K. R. Mann, *J. Am. Chem. Soc.* **1990**, *112*, 7247−7254. − [14c] A. Albinati, F. Demartin, P. Jansen, L. F. Rhodes, L. M. Venanzi, *J. Am. Chem. Soc.* **1989**, *111*, 2115−2125. − [14d] A. Albinati, C. Ankin, P. Jansen, H. Lehner, D. Matt, P. S. Pregosin, L. M. Venanzi, *Inorg. Chem.* **1989**, *28*, 1105−1111.

[15] [15a] A. Ruiz, C. Claver, J. C. Rodriguez, M. Aguiló, X. Solans, M. Font-Altaba, *J. Chem. Soc., Dalton Trans.* **1984**, 2665−2669. − [15b] R. Usón, L. A. Oro, C. Claver, M. A. Garralda, *J. Organomet. Chem.* **1976**, *105*, 365−370.

[16] [16a] J. L. Herde, J. C. Lambert, C. V. Senoff, M. A. Cushing, *Inorg. Synth.* **1974**, *15*, 18−21. − [16b] R. Usón, L. A. Oro, F. Ibañez, *Rev. Acad. Ciencias Zaragoza* **1975**, *31*, 169.

[17] J. A. Darr, S. R. Drake, M. B. Hursthouse, K. M. Abdulmalik, *Inorg. Chem.* **1994**, *32*, 5704−5708.

[18] G. M. Sheldrick, SHELXS-86 and SHELXS-97, *Acta Crystallogr., Sect. A* **1990**, *46*, 467.

[19] G. M. Sheldrick, SHELXL-93 and SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen, **1993**.

[20] N. P. C. Walker, D. Stuart, *Acta Crystallogr., Sect. A* **1983**, *39*, 158 (adapted for FAST geometry by A. Karaulov, University of Wales, Cardiff, **1991**).

[21] [21a] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33−37. − [21b] R. H. Blessing, *J. Appl. Cryst.* **1997**, *30*, 421−426.

Received February 12, 2001
[I01049]