Scholarly Research Exchange

SRX Chemistry • Volume 2010 • Article ID 424392 • doi:10.3814/2010/424392

Research Article

Gold-dppm-Arylazoimidazole Complexes: Synthesis, Spectra, and Redox Study

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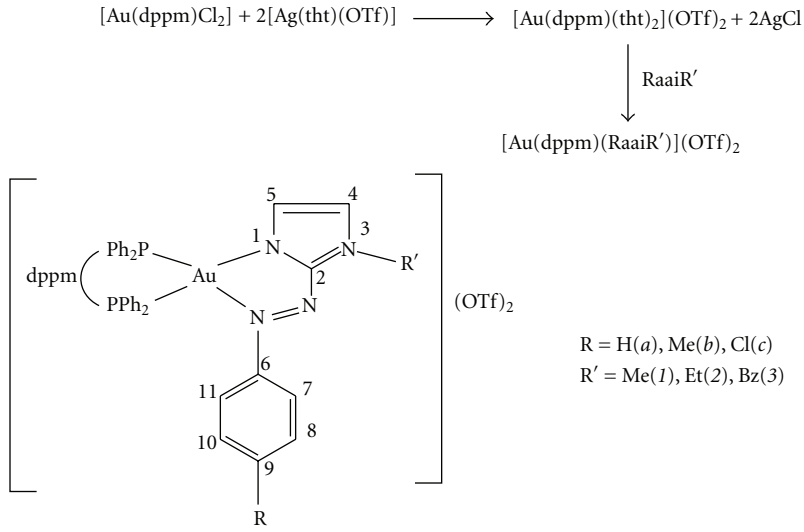
Received 31 July 2009; Accepted 23 September 2009

[Ag(tht)(OTf)]-assisted reaction produces $[Au^{III}(dppm)(tht)_2](OSO_2CF_3)_2$, reacts with RaaiR′ in dichloromethane medium followed by ligand addition, and leads to $[Au^{III}(dppm)(RaaiR')](OTf)_2$(RaaiR′=*p*–R–$C_6H_4$–N = N–$C_3H_2$–NN–1–R′, (*1–3*), abbreviated as N,N′-chelator, where N(imidazole) and N(azo) represent N and N′, resp.; R = H (*a*), Me (*b*), Cl (*c*) and R′= Me (*1*), CH_2CH_3(*2*), CH_2Ph (*3*), dppm is diphenylphosphinomethane, OSO_2CF_3 is the triflate anion, and tht is tetrahydrothiophen). Ir spectra of the complexes show –C=N– and –N=N– stretching near at 1590 and 1370 cm^{-1} and near at 1100, 755, 695, 545, and 505 cm^{-1} due to the presence of dppm. The ^{1}H NMR spectral measurements suggest that methylene, –CH_2–, in RaaiEt gives a complex AB type multiplet while in RaaiCH_2Ph it shows AB type quartets. Electrochemistry assigns ligand reduction.

1. Introduction

The biochemistry of gold with D-penicillamine, gluthadione, thiomalic acid, 2,3-dimercaptopropanol, [1, 2], and albumin has been studied. The reactivity of gold occurs through the thiolate function of these biological molecules and leads to the formation of gold(I) thiolates, also called chrysotherapy agents. Other types of gold complexes used in medicinal chemistry are gold(I) mono- or bis-phosphines. They can bind to DNA via the guanine and cytosine bases [3, 4] and act as antitumor agents against L1210 leukemia and M5076 reticulum cell sarcoma. In 1972, Sutton synthesized a gold complex with a thiolate and a phosphine ligand: the 2, 3, 4, 6-tetra-*O*-acetyl-1-thio-D-pyranosato-*S*-(triethylphosphine) gold(I) compound also known by the trade name Auranofin. It became one of the most promising gold complexes in medicinal chemistry, with a great potency against rheumatoid arthritis and cancer cells such as P388 leukemia and B16. A small number of scattered observations in the early structural chemistry of gold(I) complexes [5] have grown into a wealth of reports on related phenomena in the last two decades, which finally provided a clear pattern of the conditions under which direct interactions between closed-shell gold(I) centers can contribute significantly to the stability of molecular and multidimensional structures. The underlying "aurophilic" bonding has been analyzed in theoretical studies [6, 7]. Syntheses of hetero-*tris*-chelates, $[Ru(bpy)_n(RaaiR')_{3-n}](ClO_4)_2$[bpy = 2,2′-bipyridine; n = 1, n = 2) containing labile reaction centres are reported from Professor Sinha's laboratory. Professor A. Chakravorty has unfolded this ligands rhenium chemistry. But the gold chemistry with multinuclear NMR spectroscopy of this ligand system is totally unexplored. In this paper, I examine the reaction of RaaiR′ on gold(III) dppm derivatives and the products are isolated, $[Au(dppm)(RaaiR')](OTf)_3$ (RaaiR′ = *p*–R–C_6H_4–N=N–C_3H_2–NN–1–R′, (*1–3*), abbreviated as N,N′-chelator, where N(imidazole) and N(azo) represent N and N′, resp.; R = H (*a*), Me (*b*), Cl (*c*) and R′ = Me (*1*), CH_2CH_3(*2*), CH_2Ph (*3*), dppm is diphenylphosphinomethane, OSO_2CF_3 is the triflate anion, and tht is tetrahydrothiophen). The complexes are well charecterised by i.r., ^{1}H n.m.r., ^{13}C nmr, ^{1}H–^{1}H COSY nmr, ^{1}H–^{13}C HMQC, and mass spectrometry.



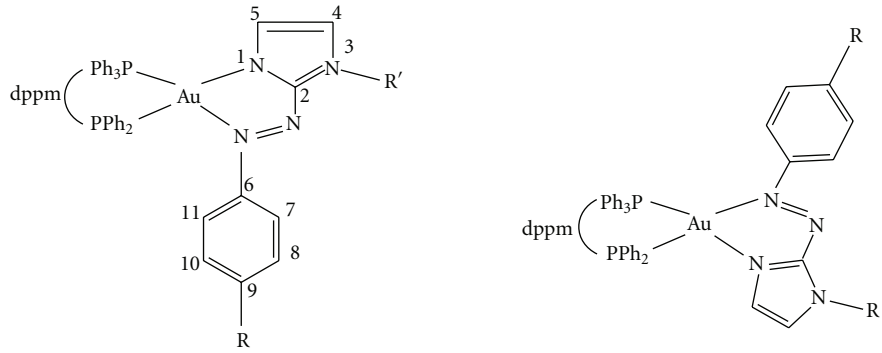
Scheme 1

2. Results and Discussion

The complexes, $[Au^{III}(dppm)(\ RaaiR')](OTf)_2$ (RaaiR′ = *p*–R–C_6H_4–N=N–C_3H_2–NN–1–R′, (*1–3*), abbreviated as N,N′-chelator, where N(imidazole) and N(azo) represent N and N′, resp.; R = H (*a*), Me (*b*), Cl (*c*) and R′ = Me (*1*), CH_2CH_3 (*2*), CH_2Ph (*3*), dppm is diphenylphosphinomethane, OSO_2CF_3 is the triflate anion, and that is tetrahydrothiophen), were prepared by removing tht from $[Au^{III}(dppm)(tht)_2](OSO_2CF_3)_2$, with RaaiR′ under stirring at 343–353 K in dichloromethane solution in good yield (75%–80%). The synthetic routes are shown in Scheme 1. The composition of the complexes is supported by microanalytical results. The red orange complexes are soluble in common organic solvents, namely. acetone, acetonitrile, chloroform, and dichloromethane but insoluble in H_2O, methanol, and ethanol. In MeCN, the complexes, (*1–3)* behave as 1 : 2 electrolytes (Λ_M = 60–90 $\Omega^{-1}cm^{-1}mol^{-1}$).

I.r. spectra of the complexes show a 1 : 1 correspondence to the spectra of the bromo analogue, except for the appearance of intense stretching at 1365–1370 and 1570–1580 cm^{-1} with concomitant loss of ν(Au–Cl) at 320–340 cm^{-1}. They are assigned to ν(N=N) and ν(C=N) appear at 1365–1380 and 1570–1600 cm^{-1}, respectively (Figure 1). Other important frequencies are ν(dppm) at 1110–1120, 1200–1210, 1250–1260, 750–760, 695–700, and 500–510 cm^{-1} along with weak bands at 545–550 cm^{-1}. Phosphorous n.m.r., $^{31}P\ \{^1H\}$nmr, gives a concrete idea on the nature of complexes and is very much informative of the present series of complexes. Due to the presence of azo-imine function, which is pi acidic in nature, stabilises the gold (III) oxidation state giving the value of 36.3. Fluorine n.m.r., $^{19}F\ \{H\}$NMR, of the present series of complexes shows a sharp peak at −78 for the presence of triflate ion. The ^1H n.m.r. spectra of (*1–3*) complexes were unambiguously assigned (Figures 1 and 2) on comparing with parent complex and the free ligand (RaaiR′). The proton movement upon substitution (9-R) is corroborated with the electromeric effect of R. The aryl protons (7-H-11-H) of (*7–9)* are downfield shifted by 0.1–0.7 ppm as compared to those of the parent derivatives. They are affected by substitution; 8- and 10-H are severely perturbed due to changes in the electronic properties of the substituents in the C(9)-position. Imidazole 4- and 5-H appear as doublet at the lower-frequency side of the spectra (7.0–7.2 ppm for 4-H; 6.9–7.1 ppm for 5-H). The aryl protons 7-(7′-) and 11-(11′-)H resonate asymmetrically indicating a magnetically anisotropic environment even in the solution phase. The 1-R′ [R′ = Me, CH_2CH_3, CH_2(Ph)] exhibits usual spin-spin interaction. 1-Me appears as a singlet at 2.0 ppm for $[Au(dppm)(RaaiMe)]^{2+}$; the methylene protons 1-CH_2-(CH_3) show AB type quartet (*ca.* 4.4, 4.6 ppm) and (1-CH_2)CH_3 gives a triplet at 1.5 ppm (7.0–8.0 Hz) for $[Au(dppm)(RaaiCH_2CH_3)]^{2+}$. 1-$CH_2$(Ph) protons appear at AB type quartets (ca. 5.5, 5.7 ppm) with geminal coupling constant avgerage 8.8 Hz in $[Au(dppm)(RaaiCH_2Ph)]^{2+}$ (Scheme 2).

The ^{13}C (H)NMR spectrum provides direct information about the carbon skeleton of the molecule. Assignment of different resonant peaks to respective carbon atoms is done on nine complexes and the data are given on experimental section (Figures 1 and 2). The carbon atom is adjacent to the PPh_3 molecule in the complex resonance at a lower field resulting in the conjugative effect of the phenyl ring with more electronegative pi-conjugate system. The methyl carbon atom of the imidazole ring resonates at 30 ppm, reasonably comparing to the other carbon atoms resonance. In the COSY spectrum, absence of any off-diagonal peaks extending from δ = 14.1 ppm and 9.5 ppm confirms their assignment of no proton on N(1) and N(3), respectively. However, extending horizontal and vertical lines from δ = 8.3 ppm [C(8)H] and 8.6 ppm [C(10)H] encounter cross peaks at δ = 7.1 ppm and 7.2 ppm, where the C(7)H and C(11)H resonances are merged into multiplets along with the phenyl ring proton resonances. The ^1H–^{13}C heteronuclear



Isomer A Isomer B

Scheme 2

multiple-quantum coherence (HMQC) spectrum provides information regarding the interaction between the protons and the carbon atoms to which they are directly attached. The peaks observed at δ = 134, 131, 135 ppm, and 137 ppm assign them to the C(9), C(8), C(7), C(11), and C(10) carbon atoms, respectively, due to their interaction with H resonance at δ = 7.4, 7.5, 7.8, 7.80 ppm, and 7.3 ppm. The electrochemical properties of the complexes were examined cyclic voltammetrically at a glassy carbon-working electrode in MeCN and the potentials are referred to SCE. The voltammogram shows the ligand reductions at the negative to SCE. In the potential range +2.0 to −2.0 V at the scan rate 50 mVs^{-1} two redox couples are observed prominent and all are at the negative side of the voltammogram. One electron nature of the redox process is supported by the i_{pa}/i_{pc} ratio (i_{pa} = anodic peak current and i_{pc} = cathodic peak current) which varies from −0.60 to −0.79 and from −0.90 to −1.05. Two redox couples at negative to SCE are due to reductions of ligand.

3. Conclusion

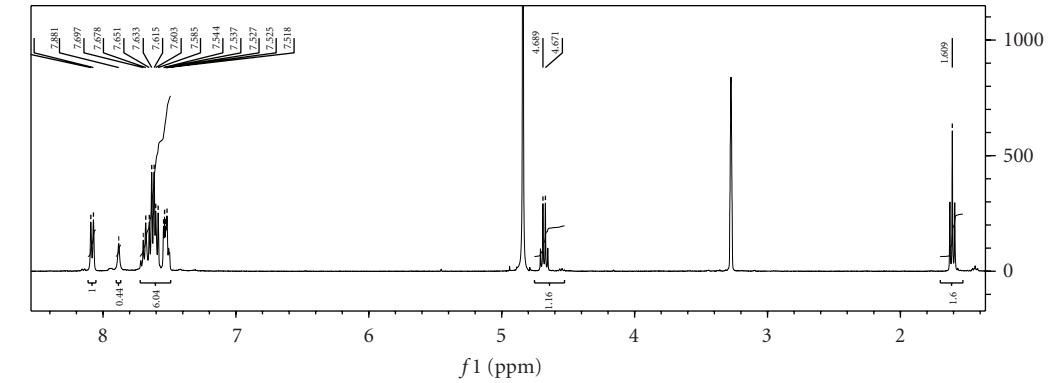
This work describes the isolation of a novel series of Gold(III) azo-imine complexes, $[Au^{III}(dppm)(RaaiR')](OTf)_2$, and their spectral and elemental characterisation. ^1H NMR study suggests quartet splitting of ethyl substitution. $^{31}P\{^1H\}$NMR is very much informative and they show that the sharp signals at 36.13 ppm ^{13}C (^1H)NMR study suggests molecular skeleton. ^1H–^1H COSY spectrum as well as contour peaks in the ^1H–^{13}C HMQC spectrum assigns them to the carbon hydrogen atoms interaction. Electrochemistry assigns ligand reduction part rather than metal oxidation.

4. Experimental

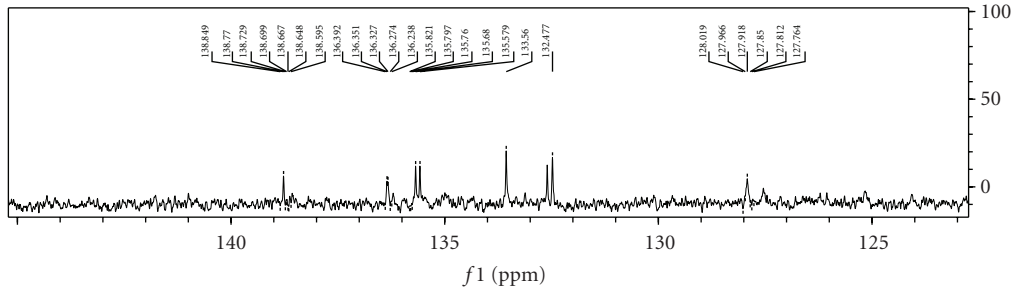
Published methods were used to prepare RaaiR′, $[Au^{III}(dppm)(Cl)_2]$. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, Sigma Alhrich). The purification of MeCN used as solvent and other solvents was done following literature method. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. I.r. spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000–200 cm^{-1}). The ^1H nmr spectra in $CDCl_3$ were obtained on a Bruker 500 MHz FT n.m.r spectrometer using $SiMe_4$ as internal reference, $CFCl_3$ (external ^{19}F). Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration $\sim 10^{-3}$ M in acetonitrile. Mass spectra were recorded on VG Autospec ESI-mass spectrometry. Electrochemical work was carried out using an EG & G PARC Versastat computer-controlled 250 electrochemical system. All experiments were performed under an N_2 atmosphere at 298 K using a Pt-disk milli working electrode at a scan rate of 50 mVs^{-1}. All results were referenced to a saturated calomel electrode (SCE).

*4.1. Preparation of the Complexes $[Au^{III}(dppm)(HaaiEt)](OTf)_3$, **2b**.* To a dichloromethane slight yellow colour solution (15 cm^3) of $[Au^{III}(dppm)Cl_2]$ (0.665 g, 0.10 mmol) [Ag(tht)(OTf)] was added (1 : 2) to produce $[Au^{III}(dppm)(tht)_2](OSO_2CF_3)_2$ (0.945 g, 0.20 mmol) into this, yellow dichloromethane solution of 1-ethyl-2-(p-tolylazo)imidazole was added slowly, dropwise, and the mixture was stirred at 343–353 K for 12 hours, where, respectively, added the other ligands, HeaaiMe (0.0186 g, 0.1 mmol, **1a**), MeaaiMe (0.020 g, 0.1 mmol, **1b**), ClaaiMe (0.0220 g, 0.1 mmol, **1c**), HaaiEt (0.020 g, 0.1 mmol, **2a**), MeaaiEt (0.0214 g, 0.1 mmol, **2b**), ClaaiEt (0.0235 g, 0.1 mmol, **2c**), HaaiBz (0.0262 g, 0.1 mmol, **3a**), MeaaiBz (0.0276 g, 0.1 mmol, **3b**), and ClaaiBz (0.0297 g, 0.1 mmol, **3c**). The orange solution that resulted was concentrated (4 cm^3) and kept in a refrigerator overnight (1 hour). The addition of hexane to the above red solution gives precipitate which was collected by filtration, washed thoroughly with hexane to remove excess ligand, and then dried *in vacuo* over pump overnight. The yield was 0.088 g (80%). All other complexes were prepared similarly as stated above.

Analysis for $[Au^{III}(dppm)(HaaiMe)](OTf)_2$, **1a**, Found, C, 54.83, H, 4.16, N, 7.36, Calcd. For $[C_{35}H_{32}N_4P_2Au](OSO_2CF_3)_2$, C, 54.8, H, 4.2, N, 7.4; IR ν(N=N) 1370 ν(C=N) 1590 ν(dppm) 1100, 750, 690, 550, 505; $^{31}P\{^1H\}$NMR, ppm, 36.13; ^1H NMR, ppm, 8.2(d, H(7,11), J = 8 Hz), 8.02(d,



(a)



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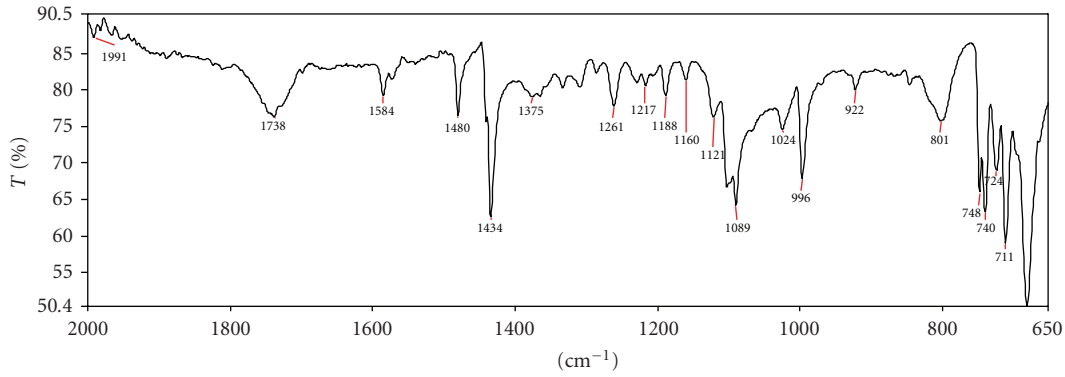
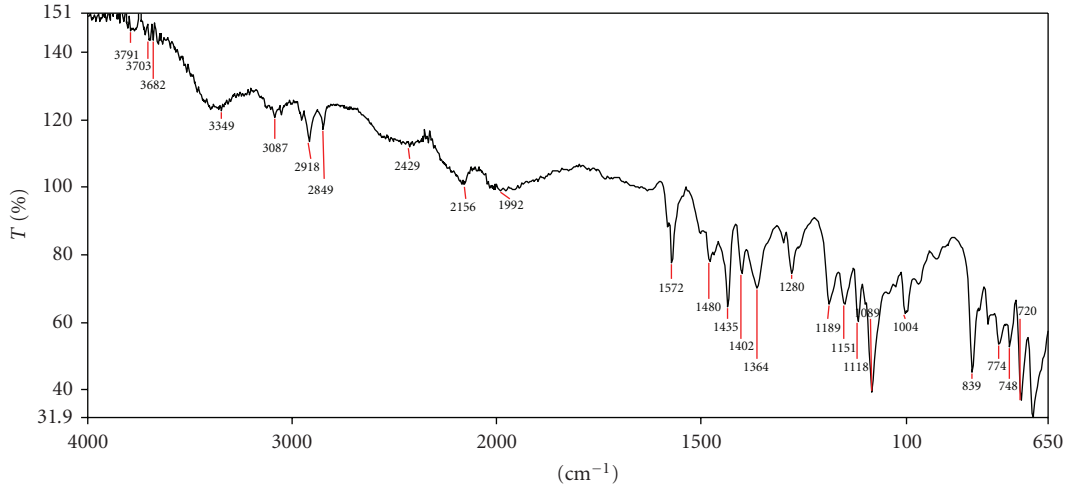


(c)



(d)

Figure 1: From above, H NMR, ^{13}C (H)NMR of complex **2a** and below, IR spectra of complex **2a** and **2b**.

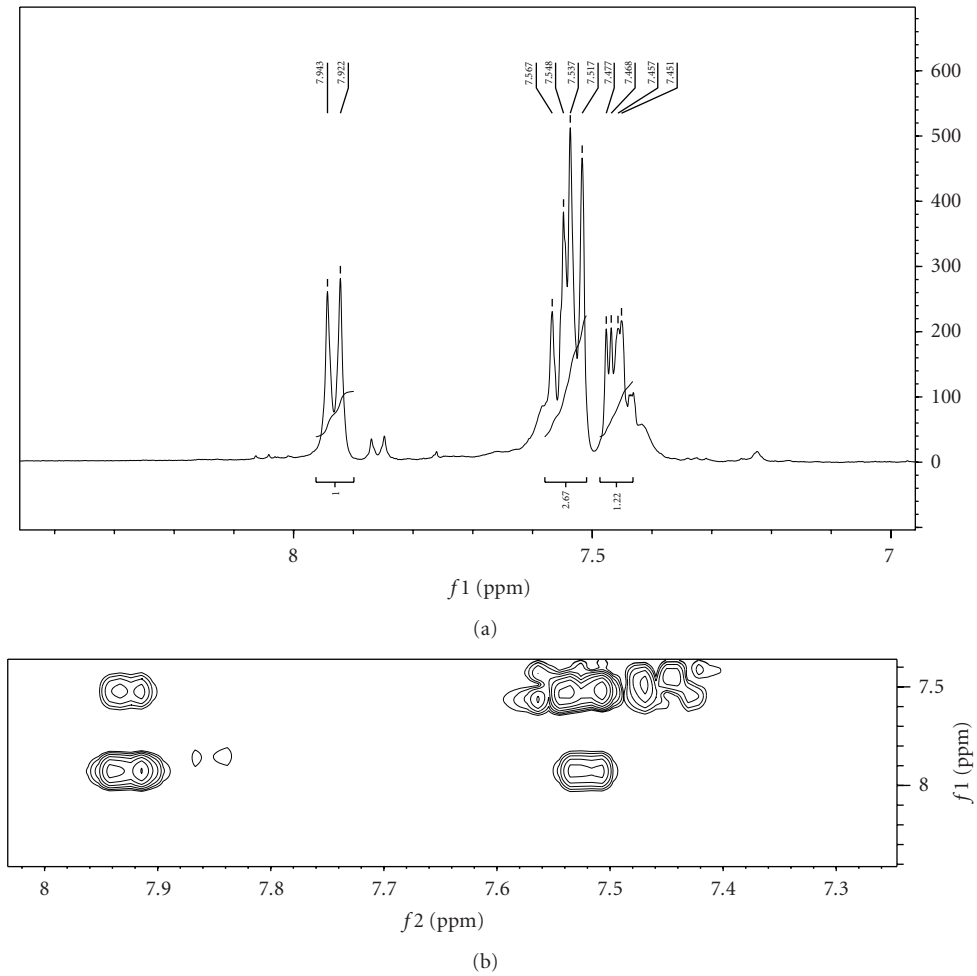


Figure 2: H NMR of complex **2c** and H H COSY NMR of complex **2c** and its extended portion.

H(8,10), J = 6.5 Hz), 7.26(d, H(4), J = 6 Hz), 7.34(d, H(5), J = 5 Hz), 7.1-7.2 (m, dppm); ^{19}F {^{1}H}NMR, ppm, −78.02(OTf), ^{13}C {^{1}H}NMR, ppm, 129.1, 129.3–130.4 (dppm, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42(Me Gr.); ESIMS, 767(M–OTf); Analysis for [Au^{III}(dppm)(MeaaiMe)](OTf)$_2$, **1b**, Found, C, 55.3, H, 4.6, N, 7.3, Calcd. For [$C_{36}H_{34}N_4P_2Au$](OSO$_2$CF$_3$)$_2$, C, 55.8, H, 4.5, N, 7.2; IR ν(N=N) 1370 ν(C=N) 1590 ν(dppm) 1100, 750, 690, 550, 505; ^{31}P {^{1}H}NMR, ppm, 36.1; ^{1}H NMR, ppm, 8.0(d, H(7,11), J = 8 Hz), 8.12(d, H(8,10), J = 6 Hz), 1.9(s, H(CH$_3$),), 7.2(d, H(4), J = 6 Hz), 7.44(d, H(5), J = 7 Hz), 7.01–7.2(m, dppm); ^{19}F {^{1}H}NMR, ppm, −78.02(OTf), ^{13}C {^{1}H}NMR, ppm, 129.1, 129.3–130.4 (dppm, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), ESIMS, 781(M–OTf); Analysis for [Au^{III}(dppm)(ClaaiMe)](OTf)$_2$, **1c**, Found, C, 52.43, H, 3.86, N, 6.96, Calcd. For [$C_{35}H_{31}N_4P_2AuCl$](OSO$_2$CF$_3$)$_2$, C, 52.8, H, 3.82, N, 7.0; IR ν(N=N) 1370 ν(C=N) 1590 ν(dppm) 1105, 755, 690, 555, 505; ^{31}P {^{1}H}NMR, ppm, 36.23; ^{1}H NMR, ppm, 8.2(d, H(7,11), J = 4Hz), 8.12(d, H(8,10), J = 6.5 Hz), 1.9(s, N–(CH$_3$),), 7.26(d, H(4), J = 6 Hz), 7.34(d, H(5), J = 5 Hz), 7.1-7.2(m, dppm); ^{19}F {^{1}H}NMR, ppm, −78.02(OTf), ^{13}C {^{1}H}NMR, ppm, 129, 129.3–130.4(dppm, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129(C8,10), 134(C6), not obs.(Me Gr.); ESIMS, 801(M–OTf); Analysis for [Au^{III}(dppm)(HaaiEt)](OTf)$_2$, **2a**, Found, C, 55.3, H, 4.46, N, 7.26, Calcd. For [$C_{36}H_{34}N_4P_2Au$](OSO$_2$CF$_3$)$_2$, C, 55.38, H, 4.2, N, 7.24; IR ν(N=N) 1370 ν(C=N) 1590 ν(dppm) 1100,750, 690,555,505; ^{31}P {^{1}H}NMR, ppm, 36.33; ^{1}H NMR, ppm, 8.12(d, H(7,11), J = 8 Hz), 8.02(d, H(8,10), J = 6.5 Hz), 7.26(d, H(4), J = 6 Hz), 7.3(d, H(5), J = 4 Hz), 4,1.88(N–Et), 7.01–7.2(m, dppm); ^{19}F {^{1}H}NMR, ppm, −78.02(OTf), ^{13}C {^{1}H}NMR, ppm, 129.1, 129.3–130(dppm, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), not obs. (Et Gr.); ESIMS, 781(M–OTf); Analysis for [Au^{III}(dppm)(MeaaiEt)](OTf)$_2$, **2b**, Found, C, 55.83, H, 4.56, N, 7.06, Calcd. For [$C_{37}H_{36}N_4P_2Au$](OSO$_2$CF$_3$)$_2$, C, 55.8, H, 4.52, N, 7.04; IR ν(N=N) 1370 ν(C=N) 1590 ν(dppm) 1100,750, 690, 550, 505; ^{31}P {^{1}H}NMR, ppm, 36.03; ^{1}H NMR, ppm, 8.0(d, H(7,11), J = 8 Hz), 8.02(d, H(8,10), J = 6.5 Hz), 1.9(s, H(CH$_3$), 4.0,2.0(N–Et), 7.26(d, H(4), J = 6 Hz), 7.34(d, H(5), J = 5 Hz), 7.1-7.2(m, dppm); ^{19}F {^{1}H}NMR, ppm, −78.02(OTf), ^{13}C {^{1}H}NMR, ppm, 129.1, 129–130.4(dppm, 18C),

134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 30,42(Et Gr.); ESIMS, 795(M–OTf); Analysis for $[Au^{III}(dppm)(ClaaiEt)](OTf)_2$, **2c**, Found, C, 51.53, H, 4.06, N, 6.86, Calcd. For $[C_{36}H_{33}N_4P_2AuCl](OSO_2CF_3)_2$, C, 51.58, H, 4.02, N, 6.84; IR ν(N=N) 1370 ν(C=N) 1590 ν(dppm) 1105, 755, 695, 555, 505; ^{31}P $\{^1$H$\}$NMR, ppm, 36.13; ^{1}H NMR, ppm, 8.2(d, H(7,11), J = 8 Hz), 8.02(d, H(8,10), J = 6.5 Hz), 4.0, 1.9(s, N–(Et),), 7.26(d, H(4), J = 6 Hz), 7.34(d, H(5), J = 5 Hz), 7.1-7.2(m, dppm); ^{19}F $\{^1$H$\}$NMR, ppm, −78.02(OTf), ^{13}C $\{^1$H$\}$NMR, ppm, 129.1, 129.3–130.4(dppm, 18C), 134(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 30, 42(Et Gr.); ESIMS, 815(M–OTf); Analysis for $[Au^{III}(dppm)(HaaiBz)](OTf)_2$, **3a**, Found, C, 58.33, H, 4.26, N, 6.6, Calcd. For $[C_{41}H_{36}N_4P_2Au](OSO_2CF_3)_2$, C, 58.8, H, 4.2, N, 6.4; IR ν(N=N) 1370 ν(C=N) 1590 ν(dppm) 1100, 750, 690, 550, 505; ^{31}P $\{^1$H$\}$NMR, ppm, 36.13; ^{1}H NMR, ppm, 8.2(d, H(7,11), J = 8 Hz), 8.02(d, H(8,10), J = 6.5 Hz), 5.29(s, N(Bz), 7.26(d, H(4), J = 6 Hz), 7.34(d, H(5), J = 5 Hz), 7.1-7.2(m, dppm); ^{19}F $\{^1$H$\}$NMR, ppm, −78.02(OTf), ^{13}C $\{^1$H$\}$NMR, ppm, 129.1, 129.3–130.4(dppm, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42(Me Gr.); ESIMS, 843(M–OTf); Analysis for $[Au^{III}(dppm)(MeaaiBz)](OTf)_2$, **3b**, Found, C, 58.83, H, 4.46, N, 6.36, Calcd. For $[C_{42}H_{38}N_4P_2Au](OSO_2CF_3)_2$, C, 58.8, H, 4.42, N, 6.4; IR ν(N=N) 1370 ν(C=N) 1590 ν(dppm) 1100, 750, 690, 550, 505; ^{31}P $\{^1$H$\}$NMR, ppm, 36.3; ^{1}H NMR, ppm, 8.2(d, H(7,11), J = 8 Hz), 8.12(d, H(8,10), J = 6.5 Hz), 1.9(s, $H(CH_3)$,), 7.26(d, H(4), J = 6 Hz), 7.34(d, H(5), J = 5 Hz), 7.1-7.2(m, dppm); ^{19}F $\{^1$H$\}$NMR, ppm, −78.02(OTf), ^{13}C $\{^1$H$\}$NMR, ppm, 129.1, 129.3–130.4(dppm, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), ESIMS, 857(M–OTf); Analysis for $[Au^{III}(dppm)(ClaaiBz)](OTf)_2$, **1a**, Found, C, 56.83, H, 4.06, N, 6.36, Calcd. For $[C_{41}H_{35}N_4P_2AuCl](OSO_2CF_3)_2$, C, 56.8, H, 4.02, N, 6.4; IR ν(N=N) 1370 ν(C=N) 1595 ν(dppm) 1105, 750, 695, 555, 505; ^{31}P $\{^1$H$\}$NMR, ppm, 36.3; ^{1}H NMR, ppm, 8.2(d, H(7,11), J = 8 Hz), 8.02(d, H(8,10), J = 6.5 Hz), 4.9(s, H(Bz), 7.26(d, H(4), J = 6 Hz), 7.34(d, H(5), J = 5 Hz), 7.1-7.2(m, dppm); ^{19}F $\{^1$H$\}$NMR, ppm, −78.02(OTf), ^{13}C $\{^1$H$\}$NMR, ppm, 129.1, 129.3–130.4(dppm, 18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), ESIMS, 877(M–OTf).

Acknowledgment

The Ministerio De Education Y Ciencia (Grant no. SB2004-0060), Madrid, is thanked for financial support.

References

[1] C. M. Che, H. L. Kwong, W. W. Yam, T. F. Lai, and C. M. Che, "A novel series of gold(III)-bis-triphenylphosphine-arylazoimidazole complexes: synthesis and spectroscopic and redox study," *Journal of the Chemical Society, Dalton Transactions*, p. 3747, 1990.

[2] H. Schmidbaur, Ed., *Gold: Progress in Chemistry, Biochemistry and Technology*, John Wiley & Sons, Chichester, UK, 1999.

[3] A. J. Lewis, J. Cottney, D. D. White, et al., "Action of gold salts in some inflammatory and immunological models," *Agents and Actions*, vol. 10, no. 1-2, pp. 63–77, 1980.

[4] C. K. Mirabelli, C.-M. Sung, J. P. Zimmerman, D. T. Hill, S. Mong, and S. T. Crooke, "Interactions of gold coordination complexes with DNA," *Biochemical Pharmacology*, vol. 35, no. 9, pp. 1427–1433, 1986.

[5] C. K. Mirabelli, R. K. Johnson, C. M. Sung, L. Faucette, K. Muirhead, and S. T. Crooke, "Evaluation of the in vivo anti-tumor activity and in vitro cytotoxic properties of auranofin, a coordinated gold compound, in murine tumor models," *Cancer Research*, vol. 45, no. 1, pp. 32–39, 1985.

[6] P. Byabartta, "A novel series of sulphur-bridged ruthenium-molybdenum complexes: $[(RaaiR')_2Ru(\mu\text{-}S)_2Mo(OH)_2]$. Synthesis, spectroscopic and electrochemical characterization. RaaiR′=1-alkyl-2-(arylazo) imidazole," *Transition Metal Chemistry*, vol. 30, no. 5, pp. 575–581, 2005.

[7] P. Byabartta, "Synthesis, spectra and electrochemistry of dinitro-bis-{1-alkyl-2-(arylazo) imidazole} ruthenium(II). Nitro-nitroso derivatives and reactivity of the electrophilic $\{Ru\text{-}NO\}^6$system," *Transition Metal Chemistry*, vol. 30, no. 7, pp. 804–813, 2005.