ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2009, Vol. 35, No. 4, pp. 253–258. © Pleiades Publishing, Ltd., 2009.

Synthesis and Multinuclear NMR Investigation on Gold(III)-Triphenylphosphine-Pentafluorophenyl-Arylazoimidazole[1]

P. Byabartta[a,b]

[a] *Departmento de Quimica Inorganica-ICMA, The Universidad de Zaragaza-CSIC, Zaragaza 50009, Spain*
[b] *GIST, ICARE Complex Haldia Institute Technology, Hatiberia, Haldia 721657, India*
e-mail: prithwis33@yahoo.com, pribatta@rediffmail.com

Received April 10, 2008

Abstract—Reaction of $[Au(C_6F_5)(PPh_3)(OSO_2CF_3)_2]$ with RaaiR' in dichloromethane medium followed ligand addition leads to $[Au(PPh_3)(C_6F_5)(RaaiR')](OSO_2CF_3)_2$ where RaaiR' = p-R–C_6H_4–N=N–C_3H_2–NN-1-R' (I–III), abbreviated as N,N'-chelator, where N(imidazole) and N(azo) represent N and N', respectively; R = H (a), Me (b), Cl (c) and R' = Me (I), CH_2CH_3 (II), CH_2Ph (III), PPh_3 is triphenylphosphine, OSO_2CF_3 is the triflate anion. The maximum molecular peak of the corresponding molecule is observed in the ESI mass spectrum. IR spectra of the complexes show –C=N– and –N=N– stretching near at ~1590 and 1370 cm^{-1} and at ~1100, 755, 695, 545, and 505 cm^{-1} due to the presence of triphenylphosphine and pentafluoropheny ring. The ^{1}H NMR spectral measurements suggest methylene (–CH_2–) in RaaiEt that gives a complex AB type multiplet with coupling constant of av. 6.6 Hz while in $RaaiCH_2Ph$ it shows AB type quartets with coupling constant of av. 6.2 Hz. Considering all the moitie there are a lot of different carbon atoms in the molecule which gives a lot of eleven different peaks in the $^{13}C\{^1H\}$NMR spectrum. In the ^{1}H–^{1}H COSY NMR spectrum of the present complexes and contour peaks in the ^{1}H–^{13}C HMQC NMR spectrum in the present complexes, assign the solution structure and stereo-retentive transformation in each step.

DOI: 10.1134/S1070328409040046

INTRODUCTION

Transition metal complexes of diimine and related ligands have attracted much attention [1–4]. Running years have witnessed a great deal of interest in the synthesis of the complexes of gold with α-diimine type of ligands because of their photochemical, catalytic properties [5–7], energy conversion and ability to serve as building blocks in supramolecular arrays [8–10]. Researchers have engaged in modifying the properties of Au-pyridine complexes by replacing the ligands of other donor centres, altering the steric and electronic properties of the ligands, differently substituted polypyridine mixed donor heterocycles. The search for a suitable precursor to synthesize azoimine- complexes is a challenging domain and the compounds are found to be useful in this context [6]. A small number of scattered observations in the early structural chemistry of gold(I) complexes [11–14] has 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 [15–17]. The underlying "aurophilic" bonding has been analyzed in theoretical studies which have confirmed the experimental results and gave an explanation for the finding that the "metallophilic" bonding is strongest and therefore most obvious for heavy metals in general, and for gold complexes in particular [1–3].

In the present report we present new and noteworthy examples taken from the important class of gold pentafluorophenyl-triphenylphosphines. These compounds have interesting photophysical properties [2] and are relevant to homogeneous gold catalysis [1] and to gold/silver thin film technology [3]. Syntheses of hetero-*tris*-chelates, $[Ru(Bipy)_n(RaaiR')_{3-n}](ClO_4)_2$, where Bipy = 2,2'-bipyridine; n = 1, 2 from the solvento complexes $[Ru(OH_2)_2(Bipy)_2]^{2+}/[Ru(OH_2)_2(RaaiR')_2]^{2+}$ containing labile reaction centres are reported [4–6, 8, 9]. Syntheses of molybdenum-*bis*-chelates with carbonyl, containing this ligand centres are reported [18]. Prof. A. Chakravorty has unfolded this ligand in rhenium chemistry [7, 19]. But the gold chemistry and organometallic chemistry with multinuclear NMR spectroscopy of this ligand system is totally unexplored. In this paper, we examine the reaction of RaaiR' on gold(III) triphenylphosphine pentafluorophenyl derivatives and the products, $[Au(PPh_3)(C_6F_5)(RaaiR')](OTf)_2$ are isolated. The complexes are well charecterised by IR, ^{1}H NMR, $^{13}C\{^1H\}$NMR, $^{31}P\{^1H\}$NMR, $^{19}F\{^1H\}$NMR ^{1}H–^{1}H COSY NMR, ^{1}H–^{13}C HMQC and mass spectrometry.

---

[1] The article is published in the original.

EXPERIMENTAL

Published methods were used to prepare RaaiR' [8–10], $Au(PPh_3)(Cl)$ [12–14]. 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 were done following the literature method [7, 9, 10, 15, 16, 18, 19].

Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. IR 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 NMR 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 ~10^{-3} mol/l in acetonitrile. Mass spectra were recorded on VG Autospec FAB and ESI usuing 3-nitrobenzyl as matrix.

Synthesis of the complexes [(triphenylphosphine)(pentafluorophenyl){1-ethyl-2-(*p*-tolylazo)imidazole}aurate(III)]triflate, $[Au(PPh_3)(C_6F_5)(p\text{-}MeaaiEt)](OTf)_2$ (IIb). To an dichloromethane slight yellow color solution (15 cm^3) of $[Au(PPh_3)(C_6F_5)Br_2]$ (0.945 g, 0.20 mmol) AgOTf (OTf = OSO_2CF_3) was added (1 : 2) to produce de-bromo product, i.e., $Au(PPh_3)(C_6F_5)(OTf)_2$ into this was added yellow dichloromethane solution of the ligand, 1-ethyl-2-(*p*-tolylazo)imidazole (0.039 g, 0.20 mmol) slowly, dropwise, and the mixture was stirred at 343–353 K for 12 h. The red solution that resulted was concentrated (4 cm^3) and kept in a refrigerator overnight (1 h). 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. Analytically pure complexes were obtained after chromatography over an alumina (neutral) column on eluting the red band with toluene–acetonitrile (4 : 1, v/v) and evaporating slowly in air. The yield was 0.088 g (80%). All other complexes were prepared similarly as stated above.

RESULTS AND DISCUSSION

Complexes $[Au(PPh_3)(C_6F_5)(RaaiR')](OSO_2CF_3)_2$ (**Ia–IIIc**) were carried out at 343–353 K in dichloromethane solution in good yield (75–80%) according to the following sheme:

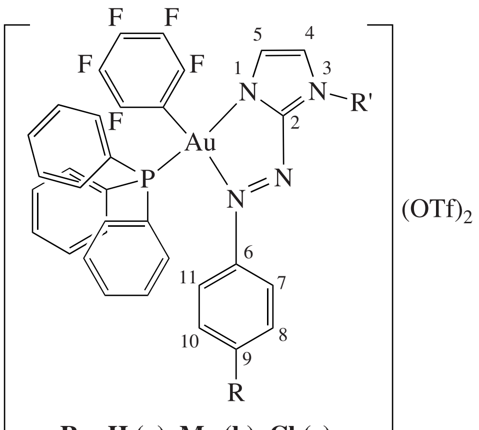
$$[Au(C_6F_5)(PPh_3)Br_2] + 2AgOTf$$

$$\longrightarrow [Au(C_6F_5)(PPh_3)(OTf)_2] + 2AgCl$$

$$\Big\downarrow \text{RaaiR'}$$

$$[Au(C_6F_5)(PPh_3)(RaaiR)(OTf)_2]$$

The composition of the complexes is supported by microanalytical results. The red orange complexes are soluble in common organic solvents, *viz*. acetone, acetonitrile, chloroform, dichloromethane but insoluble in H_2O, methanol, ethanol. In MeCN, the complexes **I–III** behave as 1 : 2 electrolytes (Λ_M = 60–90 Ohm^{-1} cm^2 mol^{-1}).



R = H (a), Me (b), Cl (c)
R' = Me (I), Et (II), Bz (III)

IR spectra of the complexes, $[Au(PPh_3)(C_6F_5)(RaaiR')](OTf)_2$ show a 1 : 1 correspondence to the spectra of the parent analogue, except 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) appearing at 1365–1380 and 1570–1600 cm^{-1}, respectively. Other important frequencies are $\nu(PPh_3)$ and (C_6F_5) 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} (table).

The ESI mass spectrum of a MeCN solution in the positive ion mode is structurally enlightening, since it displays a series of characteristics singly. Population of gas phase ions generated by ESI often closely reflects that in solution. Hence, we used ESI-MS to verify the solution and gas phase stability of the complexes, and to structurally characterize such isomeric thermally labile complexes via ESI-MS and collision-induced dissociation (CID) in tandem mass spectrometry (ESI-MS/MS) experiments. The maximum molecular peak of IIIc is observed at *m*/*z* 1210.5 (12%), which corresponds to the molecular ion, where calculated molecular weight is 1210.03. A very careful examination of the fragmentation pattern of the ESI mass spectrum reveals the stepwise elimination of two triflate ion (*m*/*z* at 910.51, 40%). All the complexes show similar ESI mass spectra (table).

The ^1H NMR spectra of $[Au(PPh_3)(C_6F_5)(RaaiR')](OTf)_2$ complexes were unambiguously assigned on comparing with $Au(PPh_3)(C_6F_5)(Cl)_2$ and the free ligand (RaaiR') [8, 10, 18]. 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 proton movement upon substitution (9-R) is corroborated with the electromeric effect of R. The aryl protons (7-H–11-H) are downfield shifted by 0.1–0.7 ppm as compared to those of the parent derivatives [8–10]. They are affected by substitution; 8- and 10-H are severely perturbed due to changes

Element analysis, IR, ESI-mass, and NMR spectral data of the complexes

Compound	Contents calcd(found), %	IR, cm^{-1}	ESI mass, M (% abundance)	^{31}P{^{1}H} NMR, ppm	^{1}H NMR, ppm	^{19}F{^{1}H} NMR, ppm	^{13}C{^{1}H} NMR, ppm
[Au(PPh$_3$)(C$_6$F$_5$)(HaaiMe)] (**Ia**), [$C_{36}H_{25}N_4F_5PAu$](OSO$_2$CF$_3$)$_2$	C, 39.24(40.8), H, 2.26(2.4), N, 5.096(4.97)	ν(N=N) 1374; ν(C=N) 1599; ν(PPh$_3$) 1105, 756, 690, 550, 505	1100.3(09)[M$^+$], 800.8(34) [M–2OTf]	45.574	H(7.11), 8.27(d., $J = 8$Hz), H(8.10), 8.21(d., $J = 7.5$Hz), H(9-H), 7.99(d.d., $J = 7.86$Hz), H(4), 7.26(d., $J = 6$Hz), H(5), 7.34(d., $J = 5$Hz), PPh$_3$, 7.5–7.8(m., 15H), CH$_3$, 1.56(t., $J = 6$Hz)	–78.02(OTf), –118.03(F$_{ortho}$), –156.03(F$_{para}$), –159.12(F$_{meta}$)	134.2, 134.5, 134.6, 134.7, 134.9(6C), 129.1, 129.3–130.4(18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6)
[Au(PPh$_3$)(C$_6$F$_5$)(MeaaiMe)] (**Ib**), [$C_{37}H_{27}N_4F_5PAu$](OSO$_2$CF$_3$)$_2$	C, 39.8(39.8), H, 2.4(2.4), N, 5.06(4.97)	ν(N=N) 1370; ν(C=N) 1590; ν(PPh$_3$) 1100, 750, 690, 550, 505	1114.3(09)[M$^+$], 814.8(34) [M–2OTf]	45.104	H(7.11), 8.2 (d., $J = 8$Hz), H(8.10), 8.29(d., $J = 6.5$Hz), H(9), 7.99(d.d., $J = 7.2$Hz), H(4), 7.21(d., $J = 6$Hz), H(5), 7.34(d., $J = 5$Hz), PPh$_3$, 7.5–7.7(m., 15H), CH$_3$, 1.5(t., $J = 7$Hz)	–78.02(OTf), –118.63(F$_{ortho}$), –156.83(F$_{para}$), –159.92(F$_{meta}$)	134.2, 134.5, 134.6, 134.7, 134.9(6C), 129.1, 129.3–130.4(18C), 134.6(C2), 124(C4), 124(C5), 124.3(C7,11), 128.2(C8,10), 134(C6)
[Au(PPh$_3$)(C$_6$F$_5$)(ClaaiMe)] (**Ic**), [$C_{36}H_{24}N_4F_5PAuCl$](OSO$_2$CF$_3$)$_2$	C, 38.14(38.8), H, 2.11(2.14), N, 4.93(4.97)	ν(N=N) 1370; ν(C=N) 1595; ν(PPh$_3$) 1106, 750, 696, 550, 505	1134.3(09)[M$^+$], 834.8(34) [M–2OTf]	45.834	H(7.11), 8.27(d., $J = 8$Hz), H(8.10), 8.21(d., $J = 6.5$Hz), H(4), 7.26(d., $J = 6$Hz), H(5), 7.34(d., $J = 5$Hz), PPh$_3$, 7.5–7.7(m., 15H), CH$_3$, 1.5(t., $J = 6$Hz)	–78.02(OTf), –118.93(F$_{ortho}$), –156.43(F$_{para}$), –159.10(F$_{meta}$)	134.2, 134.5, 134.6, 134.7, 134.9(6C), 129.1, 129.3–130.4 (18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6)
[Au(PPh$_3$)(C$_6$F$_5$)(HaaiEt)] (**IIa**), [$C_{37}H_{27}N_4F_5$ PAu](OSO$_2$CF$_3$)$_2$	C, 39.8(39.8), H, 2.4(2.4), N, 5.06(4.97)	ν(N=N) 1370; ν(C=N) 1590; ν(PPh$_3$) 1100, 750, 690, 550, 505	1114.3(09)[M$^+$], 814.8(34) [M–2OTf]	45.104	H(7.11), 8.2 (d, $J = 8$Hz), H(8.10), 8.29(d., $J = 6.5$Hz), H(9), 7.99(d.d., $J = 7.2$Hz), H(4), 7.21(d., $J = 6$Hz), H(5), 7.34(d., $J = 5$Hz), PPh$_3$, 7.5–7.7(m., 15H), CH$_2$ of Et, 4.57(q., $J = 5.9$, 6.5Hz), CH$_3$ of Et, 1.5(t., $J = 7$Hz)	–78.02(OTf), –118.63(F$_{ortho}$), –156.83(F$_{para}$), –159.92(F$_{meta}$)	134.2, 134.5, 134.6, 134.7, 134.9(C$_6$F$_5$), 129.1, 129.3–130.4(18C), 134.6(C2), 124(C4),124(C5) 124.3(C7,11), 28.2(C8, 10), 134(C6), 42, 50(Et Gr.)
[Au(PPh$_3$)(C$_6$F$_5$)(MeaaiEt)] (**IIb**), [$C_{38}H_{29}N_4F_5$ PAu](OSO$_2$CF$_3$)$_2$	C, 40.4(40.8), H, 2.6(2.4), N, 4.96(4.97)	ν(N=N) 1370; ν(C=N) 1590; ν(PPh$_3$) 1100, 750, 690, 550, 505	1128.3(09)[M$^+$], 828.8(34) [M–2OTf]	45.134	H(7.11), 8.27(d., $J = 8$Hz), H(8.10), 8.21(d., $J = 6.5$Hz), H(CH$_3$), 1.99(s.,), H(4), 7.26(d., $J = 6$Hz), H(5), 7.34(d., $J = 5$Hz), PPh$_3$, 7.5–7.7(m., 15H), CH$_2$ of Et, 4.57(q., $J = 5.9$, 6.1Hz), CH$_3$ of Et, 1.5(t., $J = 6$Hz)	–78.02(OTf), –18.03(F$_{ortho}$), –56.03(F$_{para}$), –59.12(F$_{meta}$)	134.2, 134.5, 134.6, 134.7, 134.9 (C$_6$F$_5$), 129.1, 129.3–130.4(18C), 134.5(C2), 124(C4), 125(C5) 125.3(C7,11), 129.2(C8,10), 134(C6), 42, 50(Et Gr.)

Table. (Contd.)

Compound	Contents calcd(found), %	IR, cm^{-1}	ESI mass, M (% abundance)	$^{31}P\{^1H\}$ NMR, ppm	^1H NMR, ppm	$^{19}F\{^1H\}$ NMR, ppm	$^{13}C\{^1H\}$ NMR, ppm
$[Au(PPh_3)(C_6F_5)(ClaaiEt)]$ (**IIc**), $[C_{37}H_{26}N_4F_5PAu](OSO_2CF_3)_2$	C, 38.65(38.8), H, 2.26(2.4), N, 4.86(4.97)	ν(N=N) 1370; ν(C=N) 1590; $ν(PPh_3)$ 1100, 750, 690, 550, 505	$1148.3(25)[M^+]$, 848.8(30) [M–2OTf]	45.194	H(7.11), 8.27(d., $J = 8Hz$), H(8.10), 8.21(d., $J = 6.5Hz$), H(4), 7.26(d., $J = 6Hz$), H(5), 7.34(d., $J = 5Hz$), PPh_3, 7.5–7.7(m., 15H), CH_2 of Et, 4.57(q., $J = 5.9$, 6.1Hz), CH_3 of Et, 1.5(t., $J = 6Hz$)	–78.02(OTf), $–118.03(F_{ortho})$, $–156.03(F_{para})$, $–159.12(F_{meta})$	134.2, 134.5, 134.6, 134.7.134.9 (C_6F_5), 129, 129.3–130.4(18C), 134.5(C2), 124(C4),125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42, 50(Et Gr.)
$[Au(PPh_3)(C_6F_5)(HaaiBz)]$ (**IIIa**), $[C_{42}H_{31}N_4F_5PAu](OSO_2CF_3)_2$	C, 42.84(42.8), H, 2.6(2.54), N, 4.796(4.97)	ν(N=N) 1376; ν(C=N) 1590; $ν(PPh_3)$ 1107, 750, 699, 550, 505	$1176.3(09)[M^+]$, 876.8(34) [M–2OTf]	45.934	H(7.11), 8.27(d., $J = 8Hz$), H(8.10), 8.21(d., $J = 7.5Hz$), $H(CH_3)$, 1.99(s.,), H(4), 7.26(d., $J = 6Hz$), H(5), 7.34(d., $J = 5Hz$), PPh_3, 7.5–7.7(m., 15H), CH_2 of Bz, 4.57(q., $J = 5.9$, 6.1Hz), Ph of Bz, 7.5–7.6	–78.02(OTf), $–118.93(F_{ortho})$, $–156.93(F_{para})$, $–159.92(F_{meta})$	134.2, 134.5, 134.6, 134.7, 134.9(6C), 129.1, 129.3–130.4 (18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6)
$[Au(PPh_3)(C_6F_5)(MeaaiBz)]$ (**IIIb**), $[C_{43}H_{32}N_4F_5PAu](OSO_2CF_3)_2$	C, 43.4(43.8), H, 2.6(2.4), N, 4.76(4.87)	ν(N=N) 1370; ν(C=N) 1590; $ν(PPh_3)$ 1100, 755, 695, 550, 505	$1190.3(09)[M^+]$, 890(34) [M–2OTf]	45.834	H(7.11), 8.27(d., $J = 8Hz$), H(8.10), 8.21(d., $J = 6.5Hz$), $H(CH_3)$, 1.99(s.,), H(4), 7.26(d., $J = 6Hz$), H(5), 7.34(d., $J = 5Hz$), PPh_3, 7.5–7.7(m., 15H), CH_2 of Bz, 4.66(q, $J = 5.9$, 6.1Hz), Ph of Bz, 7.5–7.9	–78.02(OTf), $–118.03(F_{ortho})$, $–156.03(F_{para})$, $–159.12(F_{meta})$	134.2, 134.5, 134.6, 134.7, 134.9 (6C), 129.1, 129.3–130.4(18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6)
$[Au(PPh_3)(C_6F_5)(ClaaiBz)]$ (**IIIc**), $[C_{42}H_{29}N_4F_5PAuCl](OSO_2CF_3)_2$	C, 41.64(40.8), H, 2.6(2.4), N, 4.6(4.7)	ν(N=N) 1377; ν(C=N) 1590; $ν(PPh_3)$ 1100, 750, 690, 505	$1210.3(09)[M^+]$, 910.8(34) [M–2OTf]	45.874	H(7.11), 8.27(d., $J = 8Hz$), H(8.10), 8.21(d., $J = 6.5Hz$), $H(CH_3)$, 1.99(s.,), H(4), 7.26(d., $J = 6Hz$), H(5), 7.34(d., $J = 5Hz$), PPh_3, 7.5–7.7(m., 15H), CH_2 of Bz, 5.057(q., $J = 5.9$, 6.1Hz), Ph of Bz, 7.5–7.9	–78.02(OTf), $–118.93(F_{ortho})$, $–156.93(F_{para})$, $–159.12(F_{meta})$	134.2, 134.5, 134.6, 134.7, 134.9 (6C), 129.1, 129.3–130.4(18C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6)

in the electronic properties of the substituents in the C(9)-position. The aryl protons 7(7')- and 11(11')-H resonate asymmetrically indicative of a magnetically anisotropic environment [8, 9] even in the solution (liquid phase). The 1-R' (R' = Me, CH_2CH_3, $CH_2(Ph)$) exhibit usual spin-spin interaction. 1-Me appears as a singlet at 4.2 ppm for $[Au(PPh_3)(C_6F_5)(RaaiMe)](OTf)_2$; the methylene protons, 1-CH_2–(CH_3) show AB type sextet (ca. 4.4, 4.6 ppm, *J* = 6–7 Hz) and (1-CH_2)CH_3 gives a triplet at 1.5 ppm (7.0–8.0 Hz) for $[Au(PPh_3)(C_6F_5)(RaaiCH_2CH_3)]$. 1-$CH_2$(Ph) protons appear at AB type quartets (ca. 5.5, 5.7 ppm) with geminal coupling constant avg. 8.8 Hz in $[Au(PPh_3)(C_6F_5)(RaaiCH_2Ph)]$. The aryl-Me (R = Me) in $[Au(PPh_3)(C_6F_5)(MeaaiR')](OTf)_2$ appears as a single signal at 2.30 ppm (table).

Phosphorous NMR, $^{31}P\{^1H\}$, is very much informative of the present series of complexes. Due to the presence of azo-imine function, which is π-acidic in nature, stabilises the gold(III) oxidation state giving the value of 45.123 where the parent complex shows the peak at 36.78. Changing the substitution at R, R' on the ligand there is a slight chemical shift of value changes of these complexes [13, 16] (table).

Fluorine NMR, $^{19}F\{^1H\}$, is very much important of the present series of complexes. Among five fluorine atoms in each complexes, they show three sharp signals which are corresponds to two *ortho*, two *meta* and one *para* fluorine atom, respectively, of the pentafluorophenyl ring of the complexes with the addition of a peak for the triflate ion (table).

The $^{13}C\{^1H\}$NMR spectrum provides direct information about the carbon skeleton of the molecule. Assignment of different resonant peaks to respective carbon atom are done on nine complexes and the data are given on experimental section. Carbon atoms neighbouring the nitrogen atom shifted to downfield due to an increased electron density resulting from the presence of electronegative nitrigen atom and π electron delocalisation in the magnetic environment. Considering one arylazoimidazole moities there are different carbon atoms in the molecule which gives different peaks in the $^{13}C\{^1H\}$NMR spectrum. The non-protonated carbon atoms at C(2) and C(6) of the arylazoimidazole moiety is shifted farthest downfield in the spectrum effected by the magnetic interection of two bulky phenyl rings environment and the methyl, ethyl, benzyl substituted imidazole rings and the π-electron delocalization on the =N–C–C=N– and =N–C–C=C–C–. Similarly the carbon atom adjacent to the PPh_3 molecule and in the pentafluorophenyl ring in the complex resonance at a lower field resulting of the conjugative effect of the phenyl ring with more electronegative π-conjugate system. The methyl carbon atom of the imidazole ring resonate at 40 ppm, resonably compare to the other carbon atoms resonance (table).

The COSY spectrum reveals the ^1H–^1H coupling interactions in the molecule. The cross peaks along both the sides of the diagonal identify the nuclei that are coupled to each other. On the contrary, the protons that are decoupled from the adjacent ones due to the lack of α-protons will show no coorelation in the spectrum. It is usually plotted as three dimentional contours, where the conventional spectrum is represented along the diagonal. For instance, in the COSY spectrum of the present complexes, absence of any off-diagonal peaks extending from δ = 14.12 ppm and 9.55 ppm confirm their assignment of no proton on N(1) and N(3, respectively. However, extending horizontal and vertical lines from δ = 8.32 ppm (C(8)H) and 8.68 ppm (C(10)H) encounter cross peaks at δ = 7.12 ppm and 7.23 ppm, where the C(7)H and C(11)H resonances are merged into multiplets along with the phenyl ring proton resonances. The comperatively weaker coupling interections of C(8)H and C(10)H with the far apart positioned C(4)H and C(5)H protons of the imidazole moity are shown by the poorly resolved cross peaks at δ = 7.32 and 7.33 ppm. This also helps to accurately assign phenyl and imidazole moity protons to their respective values, which is contrary to the expected more downfield shift of C(11)H at δ = 7.92 ppm of the RaaiR' molecule and these protons interect with PPh_3 moiety, i.e., 15 protons. COSY spectrum also turns out very helpful in the accurate assignment of proton resonance in the aromatic region. The doublet of the C(7)H and C(11)H protons show coupling interection with the doublet at δ = 7. 2 and 7. 8 ppm (C(8)H and C(10)H).

The ^1H–^{13}C heteronuclear multiple-quantum coherence (**HMQC**) spectrum provides information regarding the interection between the protons and the carbon atoms to which they are directly attached. In the present complexes, the absence of any contours at higher frequency region assign them to the C(2), C(6), C-pentafluorophenyl, carbon atoms, respectively. This is because, they belong to the non-protonated carbon atoms on the imidazole, phenyl and aryl rings. So they unable to show any direct ^1H–^{13}C heteronuclear multiple-quantum coherence. The peaks observed at δ = 134.12, 131.76, 135.67, and 137.68 ppm assign them to the C(9), C(8), C(7), C(11), and C(10) carbon atoms, respectively, due to their interection with H resonance at δ = 7.42, 7.55, 7.82, 7.80, and 7.38 ppm. The evidence for the presence of protons attached to the different types of carbon atoms in the spectrum is obtained from the ^1H–^{13}C HMQC spectrum.

This work describes the isolation of a novel series of gold(III) azo-imine complexes with a organometallic link with pentafluorophenyl ring, $[Au(PPh_3)(C_6F_5)(RaaiR')]$ and their spectral and elemental characterization. ^1H NMR study suggests quartet splitting of ethyl substitution. $^{31}P\{^1H\}$ NMR is very much informative and they show the sharp signals at 45.134 ppm which is lower than the parent complex. ^1H–^1H COSY spectrum of the present complexes, confirm their assignment of accurate structure and in solution proton interection, respectively. Contour peaks in the ^1H–^{13}C HMQC spectrum in the present complexes, assign them to the carbon hydrogen atoms interection and contour respectively.

ACKNOWLEDGMENTS

The Ministerio De Education Y Ciencia (Grant no. SB2004–0060), Madrid is thanked for financial support and Prof. C. Sinha, M. Laguna, B. Guchait, Pravas, Latika Byabartta for constant help and valuable comments on this work.

REFERENCES

1. Puddephatt, R.J. In: *Comprehensive Coordination Chemistry*, vol. 2, Wilkinson, G., Gillard, R.D., and McCleverty, J.A., Eds, Oxford: Pergamon, 1987.
2. *Gold: Progress in Chemistry, Biochemistry and Technology*, Schmidbaur, H., Ed., Chichester: John Wiley and Sons, 1999.
3. Dryden, N.H., Shapter, J.G., Coatsworth, L.L., et al., *Chem. Mater.,* 1992, vol. 4, p. 979.
4. Deb, A.K. and Goswami, S., *Polyhedron*, 1991, vol. 10, p. 1799.
5. Sinha, S., Das, P.K., and Ghosh, B.K., *Polyhedron*, 1994, vol. 13, p. 2665.
6. Byabartta, P., *Transition Met. Chem.*, 2005, vol. 30, p. 575.
7. Chattopadhyay, S., Sinha, C., Chakravorty, et al., *Dalton Trans.*, 2001, p. 1259.
8. Byabartta, P. and Laguna, M., *Transition Met. Chem.*, 2007, vol. 32, p. 180.
9. Byabartta, P. and Laguna, M., *Transition Met. Chem.*, 2007, vol. 32, p. 186.
10. Jemmis, E.D., Subramanian, G., Nowek A., et al., *J. Mol. Struct.,* 2000, vol. 556, p. 315.
11. Uson, R. and Laguna, A., *Organomet. Synth.*, 1985, vol. 3, p. 325.
12. Uson, R., Laguna, M., and Laguna, A., *Dalton Trans.*, 1990, p. 3457.
13. Uson, R., Laguna, M., and Cerrada, E., *Inorg. Chim. Acta*, 1990, vol. 168, p. 89.
14. Contel, M., Laguna, A., and Oro, L., *Dalton Trans.*, 1994, p. 2515.
15. Murray, H.H., Hur, G., and Ellena, G., *Ang. Chem., Int. Ed.*, 1995, vol. 34, p. 841.
16. Cerrada, E., Fernandez, E.J., Cimeno, M.C., et al., *J. Organomet. Chem.*, 1995, vol. 492, p. 105.
17. Uson, R., Laguna, A., and Laguna, M., *Inorg. Synth.*, 1989, vol. 26, p. 85.
18. Greenwood, N.N. and Earnshaw, A., *Chemistry of the Elements*, Oxford: Pergamon Press, 1989, p. 519.
19. Chakravarty, A.R., Chakravorty, A., Das, S., et al., *Dalton Trans.*, 1983, p. 961.