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Gold(III)pentafluorophenylarylazoimidazole: Synthesis and spectral (H, C, COSY, HMQC NMR) characterisation

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Abstract. Reaction of $[Au^{III}(C_6F_5)_3(tht)]$ with RaaiR′ in dichloromethane medium leads to $[Au^{III}(C_6F_5)_3(RaaiR')]$ [RaaiR′ = *p*-R-C_6H_4-N=N-C_3H_2-NN-1-R′, (**1–3**), R = H (**a**), Me (**b**), Cl (**c**) and R′ = Me (**1**), CH_2CH_3 (**2**), CH_2Ph (**3**), tht is tetrahydrothiophen]. The nine new complexes are characterised by ES/MS as well as FAB, IR and multinuclear NMR (^1H, ^{13}C, ^{19}F) spectroscopic studies. In addition to dimensional NMR studies as ^1H, ^1H COSY and ^1H ^{13}C HMQC permit complete assignment of the complexes in the solution phase.

Keywords. Gold(I); 1-alkyl-2-(arylazo)imidazole; ^1H, ^{13}C, ^{19}F; COSY; HMQC NMR.

1. Introduction

Transition metal complexes of diimine and related ligands have attracted much attention.[1–10] The recent years have witnessed a great deal of interest in the synthesis of the complexes of gold with *a*-diimine type of ligands because of their photochemical and catalytic properties, energy conversion and ability to serve as building blocks in supramolecular arrays.[11–17] Researchers have engaged in modifying the properties of Au-pyridine complexes by replacing the ligands at other donor centres, altering the steric and electronic properties of the ligands, and obtaining differently substituted polypyridine mixed-donor heterocycles. The search for suitable precursors to synthesize azoimine-complexes is a challenging task and the compounds are found to be useful in this context.[6] Recently, we have developed the arylazoimidazole chemistry of ruthenium and have synthesised dichloro componds $RuCl_2(RaaiR')_2$ (**4–6**) and diaquo species $[Ru(OH_2)_2(RaaiR')_2]^{2+}$ [RaaiR′ = *p*-R-C_6H_4-N=N-C_3H_2-NN-1-R′, (**1–3**), R = H, Me, Cl and R′ = Me, CH_2CH_3, CH_2Ph, abbreviated as N,N′-chelators where N and N′ represent N(imidazole) and N(azo) respectively]. Syntheses of hetero-*tris*-chelates, $[Ru(bpy)_n(RaaiR')_{3-n}](ClO_4)_2$ [bpy = 2,2′-bipyridine; n = 1, 2) from the solvento complexes $[Ru(OH_2)_2(bpy)_2]^{2+}$/$[Ru(OH_2)_2(RaaiR')_2]^{2+}$ containing labile reaction centres are reported from Sinha's laboratory.[4–10] Rhenium chemistry of this ligand system has been explored by A Chakravorty's group. Syntheses of molybdenum-bis-chelates with carbonyl, containing these ligand centres are reported from Ankermann's laboratory. However, gold and its 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) pentafluorophenyl derivatives and the products are isolated. The complexes are well characterised by IR, ^1H NMR, ^{13}C NMR, ^1H–^1H COSY NMR, ^1H–^{13}C HMQC and mass spectrometry.

2. Experimental

2.1 *Materials and physical measurements*

Published methods were used to prepare RaaiR′,[7–9] $[Au(C_6F_5)_3(tht)]$.[17–20] All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, Sigma Aldrich). The purification of MeCN used as solvent and other solvents was done following the literature method.[8–14] Microanalytical data (C, H, N) were collected using a Perkin–Elmer 2400 CHN instrument (table 1). IR spectra were obtained using a Perkin–Elmer spectrophotometer (KBr disks, 4000–350 cm^{-1}). The ^1H NMR spectra in

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Table 1. Microanalytical [found (calc.)] and IR spectral data

Compound	C	H	N	IR		
				n (N=N)	*n* (C=N)	*n* (C_6F_5)
[Au(C_6F_5)$_3$(HaaiMe)], $C_{28}H_{10}F_{15}N_4Au$, **1a**	37·59 (37·58)	1·12 (1·13)	6·28 (6·25)	1370	1590	1510, 960, 800
[Au(C_6F_5)$_3$(MeaaiMe)], $C_{29}H_{12}F_{15}N_4Au$, **1b**	38·32 (38·38)	1·31 (1·31)	6·10 (6·17)	1377	1597	1512, 964, 806
[Au(C_6F_5)$_3$(ClaaiMe)], $C_{28}H_9F_{15}N_4AuCl$, **1c**	36·12 (36·38)	0·93 (0·98)	6·00 (6·01)	1377	1597	1512, 964, 806
[Au(C_6F_5)$_3$(HaaiEt)], $C_{29}H_{12}F_{15}N_4Au$, **2a**	38·32 (38·38)	1·31 (1·31)	6·10 (6·17)	1377	1597	1512, 964, 806
[Au(C_6F_5)$_3$(MeaaiEt)], $C_{29}H_{12}F_{15}N_4Au$, **2b**	39·03 (39·08)	1·53 (1·51)	6·05 (6·10)	1377	1597	1512, 964, 806
[Au(C_6F_5)$_3$(ClaaiEt)], $C_{29}H_{11}F_{15}N_4AuCl$, **2c**	36·92 (38·38)	1·17 (1·11)	5·91 (5·91)	1377	1597	1512, 964, 806
[Au(C_6F_5)$_3$(HaaiBz)], $C_{34}H_{14}F_{15}N_4Au$, **3a**	42·02 (42·03)	1·39 (1·38)	5·71 (5·717)	1377	1597	1512, 964, 806
[Au(C_6F_5)$_3$(MeaaiBz)], $C_{35}H_{16}F_{15}N_4Au$, **3b**	42·68 (42·66)	1·63 (1·63)	5·61 (5·71)	1377	1597	1512, 964, 806
[Au(C_6F_5)$_3$(ClaaiBz)], $C_{34}H_{13}F_{15}N_4AuCl$, **3c**	40·63 (40·68)	1·29 (1·31)	5·59 (5·6)	1377	1597	1512, 964, 806

$CDCl_3$ were obtained on a Bruker 500 MHz FT NMR spectrometer using $SiMe_4$ as internal reference, $CFCl_3$ (external ^{19}F). Mass spectra were recorded on VG Autospec FAB technique using 3-nitrobenzyl (NBA) as matrix.

2.2 *Preparation of the complexes tris-(pentafluorophenyl){1-methyl-2-(p-tolylazo)imidazole} aurate(III), [Au(C_6F_5)$_3$(MeaaiMe)]*

Yellow dichloromethane solution of 1-methyl-2-(*p*-tolylazo)imidazole, 0·039 g (0·20 < mmol) was added to a colourless dichloromethane solution (15 cm^3) of [Au(C_6F_5)$_3$(tht)] (0·0941 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 refrigerated overnight. The addition of hexane to the above red solution gave a precipitate which was collected by filtration, washed thoroughly with hexane to remove excess ligand and tht, 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%). Fluorine NMR, ^{19}F {^1H}, ppm of **1a**, –121·76 (*m*, F_{ortho}, 4F), –121·01 (*m*, F_{ortho}, 2F), –157·11 (*t*, F_{para}, 2F), –157·01 (*t*, F_{para}, 1F), –161·21 (*m*, F_{meta}, 4F), –161·52 (*m*, F_{meta}, 2F); FAB mass, *M* (% abundance), 894 (10), ES/MS 578 (50%); Fluorine NMR, ^{19}F {^1H}, ppm of **1b**, –122·76 (*m*, F_{ortho}, 4F), –121·81 (*m*, F_{ortho}, 2F), –157·81 (*t*, F_{para}, 2F), –157·91 (*t*, F_{para}, 1F), –161·61 (*m*, F_{meta}, 4F), –161·59 (*m*, F_{meta}, 2F); FAB mass, *M* (% abundance), 908 (10), ES/MS 578·7 (40%); Fluorine NMR, ^{19}F {^1H}, ppm of **1c**, –121·96 (*m*, F_{ortho}, 4F), –121·81 (*m*, F_{ortho}, 2F), –157·91 (*t*, F_{para}, 2F), –157·01 (*t*, F_{para}, 1F), –161·91 (*m*, F_{meta}, 4F), –161·59 (*m*, F_{meta}, 2F); FAB mass, *M* (% abundance), 928·5 (10), ES/MS 578 (50%); Fluorine NMR, ^{19}F {^1H}, ppm of **2a**, –121·66 (*m*, F_{ortho}, 4F), –121·41 (*m*, F_{ortho}, 2F), –157·61 (*t*, F_{para}, 2F), –157·91 (*t*, F_{para}, 1F), –161·81 (*m*, F_{meta}, 4F), –161·92 (*m*, F_{meta}, 2F); FAB mass, *M* (% abundance), 908 (10), ES/MS 578·01 (20%); Fluorine NMR, ^{19}F {^1H}, ppm of **2b**, –121·76 (*m*, F_{ortho}, 4F), –121·51 (*m*, F_{ortho}, 2F), –157·81 (*t*, F_{para}, 2F), –157·61 (*t*, F_{para}, 1F), –161·91 (*m*, F_{meta}, 4F), –161·72 (*m*, F_{meta}, 2F); FAB mass, *M* (% abundance), 922 (9), ES/MS 578 (40%); Fluorine NMR, ^{19}F {^1H}, ppm of **2c**, –121·46 (*m*, F_{ortho}, 4F), –121·61 (*m*, F_{ortho}, 2F), –157·81 (*t*, F_{para}, 2F), –157·91 (*t*, F_{para}, 1F), –161·01 (*m*, F_{meta}, 4F), –161·92 (*m*, F_{meta}, 2F); FAB mass, *M* (% abundance), 942·5 (17), ES/MS 578 (30%); Fluorine NMR, ^{19}F {^1H}, ppm of **3a**, –121·46 (*m*,

F_{ortho}, 4F), –121·51 (*m*, F_{ortho}, 2F), –157·81 (*t*, F_{para}, 2F), –157·91 (*t*, F_{para}, 1F), –161·88 (*m*, F_{meta}, 4F), –161·32 (*m*, F_{meta}, 2F); FAB mass, *M* (% abundance), 970 (13), ES/MS 578 (30%); Fluorine NMR, ^{19}F {^{1}H}, ppm of **3b**, –121·76 (*m*, F_{ortho}, 4F), –121·71 (*m*, F_{ortho}, 2F), –157·81 (*t*, F_{para}, 2F), –157·71 (*t*, F_{para}, 1F), –161·31 (*m*, F_{meta}, 4F), –161·72 (*m*, F_{meta}, 2F); FAB mass, *M* (% abundance), 984 (16), ES/MS 578 (60%); Fluorine NMR, ^{19}F {^{1}H}, ppm of **3c**, –121·46 (*m*, F_{ortho}, 4F), –121·31 (*m*, F_{ortho}, 2F), –157·21 (*t*, F_{para}, 2F), –157·61 (*t*, F_{para}, 1F), –161·91 (*m*, F_{meta}, 4F), –161·62 (*m*, F_{meta}, 2F); FAB mass, *M* (% abundance), 1004·5 (17), ES/MS 578 (30%).

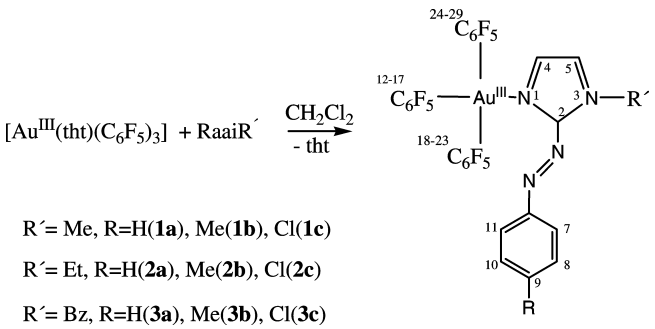
3. Results and discussion

3.1 *Synthesis and formulation*

The complexes $[Au(C_6F_5)_3(RaaiR')]$, were prepared in good yield (65–85%) by removing tht from $[Au(C_6F_5)_3(tht)]$ (tht = tetrahydrothiophen), with RaaiR′ under stirring at 343–353 K in dichloromethane solution. The synthetic routes are shown in scheme 1. The compositions of the complexes are supported by microanalytical results. The orange complexes are soluble in common organic solvents viz. acetone, acetonitrile, chloroform and dichloromethane but insoluble in H_2O, methanol and ethanol.

3.2 *Spectral studies*

Fast atom bombartment (FAB) mass spectra of the complexes were recorded in dichloromethane medium. In the mass spectra the best technique for these complexes is FAB using NBA as matrix. In all cases, the parent peak appears with abundance in the range of 10–15%. Other spectroscopically soft techniques such as ES/MS show the [M-L] fragment (i.e., $[Au(C_6F_5)_3]^+$) and once again the fragmentation



Scheme 1.

unit (i.e., $[Au(C_6F_5)_2]^+$) as the base peak of the spectra.

IR spectra of the complexes $[Au(C_6F_5)_3(RaaiR')]$ show correspondence to the spectra of the parent tetrahydrothiophene analogue $[Au(C_6F_5)_3(tht)]$,[18,19] except for the appearance of intense stretching at 1365–1370 and 1570–1580 cm^{-1} with concomitant loss of *n*(Au-S(tht)) at 320–340 cm^{-1}. They are assigned to *n*(N=N) and *n*(C=N) respectively. Other important frequencies are *n*(C_6F_5) at 1510–1520, 950–960 and 790–810 cm^{-1} along with weak bands at about 1070 and 1072 cm^{-1} due to the *n*(C–F) and *n*(C=C) bond stretching of the pentafluorophenyl ring.

Fluorine NMR, ^{19}F {^{1}H}, (measured in $CDCl_3$) provides a great deal of information about the present series of complexes. The fluorine atoms in each complex show six sharp signals corresponding to ortho, meta and para fluorine atoms, respectively, of the pentafluorophenyl ring of the complexes. Due to the *trans/cis* orientation, there are four ortho, two para, four meta fluorine atom (in the *trans*), whereas in the *cis* form the number is just half. Thus the spectra shows 2 : 1 intensity ratio, as *trans* (fluorine): *cis* (fluorine). This is the AA′BB′C type spin system, i.e. second-order spin system. On changing the substitution at R, R′ on the ligand, there is a slight change in chemical shift values of these complexes.[14,18]

The ^{1}H NMR spectra of $[Au(C_6F_5)_3(RaaiR')]$ (**1–3**) complexes were unambiguously assigned (table 2, figure 1) compared with the free ligand (RaaiR′)[7,9,11]. The aryl protons (7-H–11-H) are shifted downfield by 0·1–0·7 ppm as compared to those of the parent derivatives.[7–9] 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. The aryl protons 7-(7′-) and 11-(11′-)H resonate asymmetrically, indicative of a magnetically anisotropic environment,[7,8] even in the solution phase. The proton movement upon substitution (9-R) is corroborated with the electromeric effect of R. The 1-R′ [R′ = Me, CH_2CH_3, CH_2(Ph)] exhibit the usual spin–spin interaction. 1-Me appears as a singlet at 4·2 ppm for $[Au(C_6F_5)_3(RaaiMe)]$; the methylene protons, 1-CH_2-(CH_3) show AB type sextet (≈ 4·4, 4·6 ppm, *J* = 7–9 Hz) and (1-CH_2)-CH_3 gives a triplet at 1.5 ppm (coupling constant = 8·0 Hz) for $[Au(C_6F_5)_3(RaaiCH_2CH_3)]$; 1-$CH_2$(Ph) protons appear at AB type quartets (≈ 5·5, 5·7 ppm) with geminal coupling constant avg. 8·58 Hz in $[Au(C_6F_5)_3$

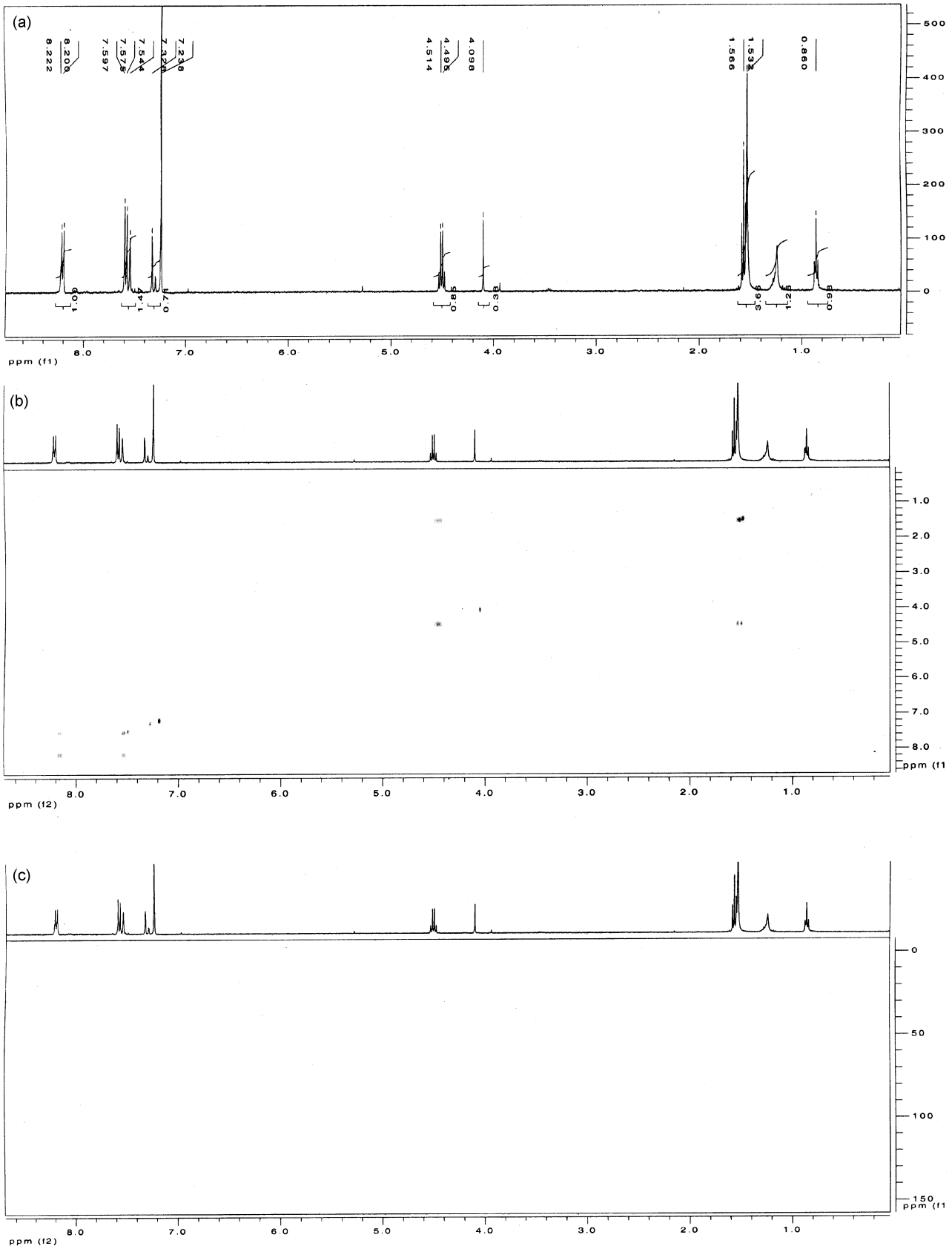


Figure 1. (**a**) H NMR, (**b**) H–H COSY NMR and (**c**) H–C HMQC NMR of complex **2c**.

Table 2. ^{1}H-NMR spectral data, *d* (J/Hz), ppm of the complexes in $CDCl_3$.

Compound	4-H[c]	5-H[c]	11-H[c]	7-H[c]	8,10-H	N-CH_3	N-CH_2
(**1a**)[a]	7·15 (7·5)	7·06 (7·5)	8·03 (8·1)	7·99 (8·1)	7·45 (8·1)[d]	2·09[f]	
(**1b**)	6·98 (7·5)	6·86 (7·5)	8·17 (8·1)	8·04 (8·1)	7·34 (8·1)[c]	2·17[f]	
(**1c**)	7·13 (8·1)	7·02 (8·1)	8·15 (7·8)	7·95 (7·8)	7·55 (7·8)[c]	2·16[f]	
(**2a**)[a]	7·14 (7·5)	7·00 (7·5)	8·01 (7·8)	7·85 (7·8)	7·45 (8·1)[d]	1·52 (8·1)[d]	4·42, 4·55 (10·0)[e]
(**2b**)	7·33 (8·1)	7·24 (8·1)	8·11 (7·5)	8·04 (7·5)	7·52 (7·5)[c]	1·58 (8·1)[d]	4·54, 4·56 (10·0)[e]
(**2c**)	7·34 (8·1)	7·36 (8·1)	8·04 (7·5)	7·54 (7·5)	7·46 (7·5)[c]	1·55 (8·1)[d]	4·54, 4·53 (11·0)[e]
(**3a**)[a]	7·06 (7·8)	6·98 (7·8)	8·08 (8·1)	8·00 (8·1)	7·48 (8·1)[d]		5·48, 5·73 (11·0)[g]
(**3b**)	6·97 (8·1)	6·99 (8·1)	8·21 (8·1)	8·10 (8·1)	7·10 (8·1)[c]		5·46, 5·73 (12·0)[g]
(**3c**)	7·11 (7·8)	7·02 (7·8)	8·15 (8·1)	8·05 (8·1)	7·58 (8·1)[c]		5·44, 5·70 (13·0)[g]

[a]*d*(9-H) 7·60 ppm (m); [b]*d* (9-Me); [c]doublet; [d]triplet; [e]AB type quartet, geminal coupling constant; [f]1-Me, singlet; [g]AB type quartet, geminal coupling constant; [h]phenyl-H

Table 3. ^{13}C-NMR spectral data of $[Au(C_6F_5)_3(RaaiR')]$ in $CDCl_3$.

	2-C	6-C	4-C	5-C	7,11-C	8,10.-C	9-C	12, 18, 24-C	13, 17, 19, 23, 25, 29-C	14, 16, 20, 22, 26, 28-C	15, 21, 27-C	9-R′-C	N-Me, Et, Bz
1a	140·87	139·89	120·21	122·76	130·98	128·98	127·56	148·87	150·98	145·66	144·99		30·98
1b	141·87	139·89	122·21	122·76	131·98	127·98	126·56	149·87	152·98	145·66	144·99	24·45	31·98
1c	140·87	139·89	120·21	122·76	130·98	128·98	137·56	148·87	150·98	145·66	144·99		30·08
2a	141·87	139·89	121·21	123·76	131·98	127·98	127·56	147·87	151·98	144·66	144·99		30·98, 41·12
2b	140·87	139·89	120·21	122·76	130·98	128·98	127·56	148·87	150·98	145·66	144·99	23·33	31·98, 42·09
2c	141·87	139·89	122·21	122·76	131·98	128·98	126·56	148·87	151·98	145·66	144·99		30·98, 42·65
3a	140·87	139·89	120·21	122·76	130·98	128·98	127·56	148·87	150·98	145·66	144·99		31·98, 128–132
3b	141·87	138·89	121·21	122·76	131·98	128·98	125·56	148·87	151·98	145·66	145·99	22·33	30·98, 128–137
3c	140·87	139·89	120·21	122·76	130·98	128·98	127·56	148·87	150·98	145·66	144·99		30·98, 129–138

(RaaiCH_2Ph)]. 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-Me (R = Me) in $[Au(C_6F_5)_3(MeaaiR')]$ appears as a single signal at 1·55 ppm.

The ^{13}C NMR spectrum provides direct information about the carbon skeleton of the molecule. Assignments of different resonant peaks to respective carbon atoms are done for nine complexes (figure 2) and the data are given in table 3. Considering two arylazoimidazole moieties there are twenty-eight different carbon atoms in the molecule, which show different peaks in the ^{13}C NMR spectrum. Carbon atoms neighbouring the nitrogen atom shift downfield due to an increased electron density resulting from the presence of electronegative nitrogen atoms and *p*-electron delocalization in the magnetic environment. The non-protonated carbon atoms at C(2) and C(6) of the arylazoimidazole moiety is shifted farthest downfield in the spectrum (d = 170·12 ppm and 168 ppm) effected by the magnetic interaction of two bulky phenyl rings environment and the methyl, ethyl, benzyl substituted imidazole rings and the *p*-electron delocalization on the =N–CC=N– and =N–C–C=C–C–. Similarly, carbon atoms at 12, 18, 24 positions on the C_6F_5 molecule in the complex, resonant at lower fields of $\approx$ 165 ppm, resulting from the conjugative effect of the phenyl rings with the more electronegative fluorine atoms.

COSY spectra reveal the ^{1}H–^{1}H coupling interactions in the molecule. They are usually plotted as three-dimensional contours, where the conventional spectrum is represented along the diagonal (figure 1). The cross peaks along both the sides of the diagonal identify the nuclei that are coupled to one another. On the contrary, the protons that are

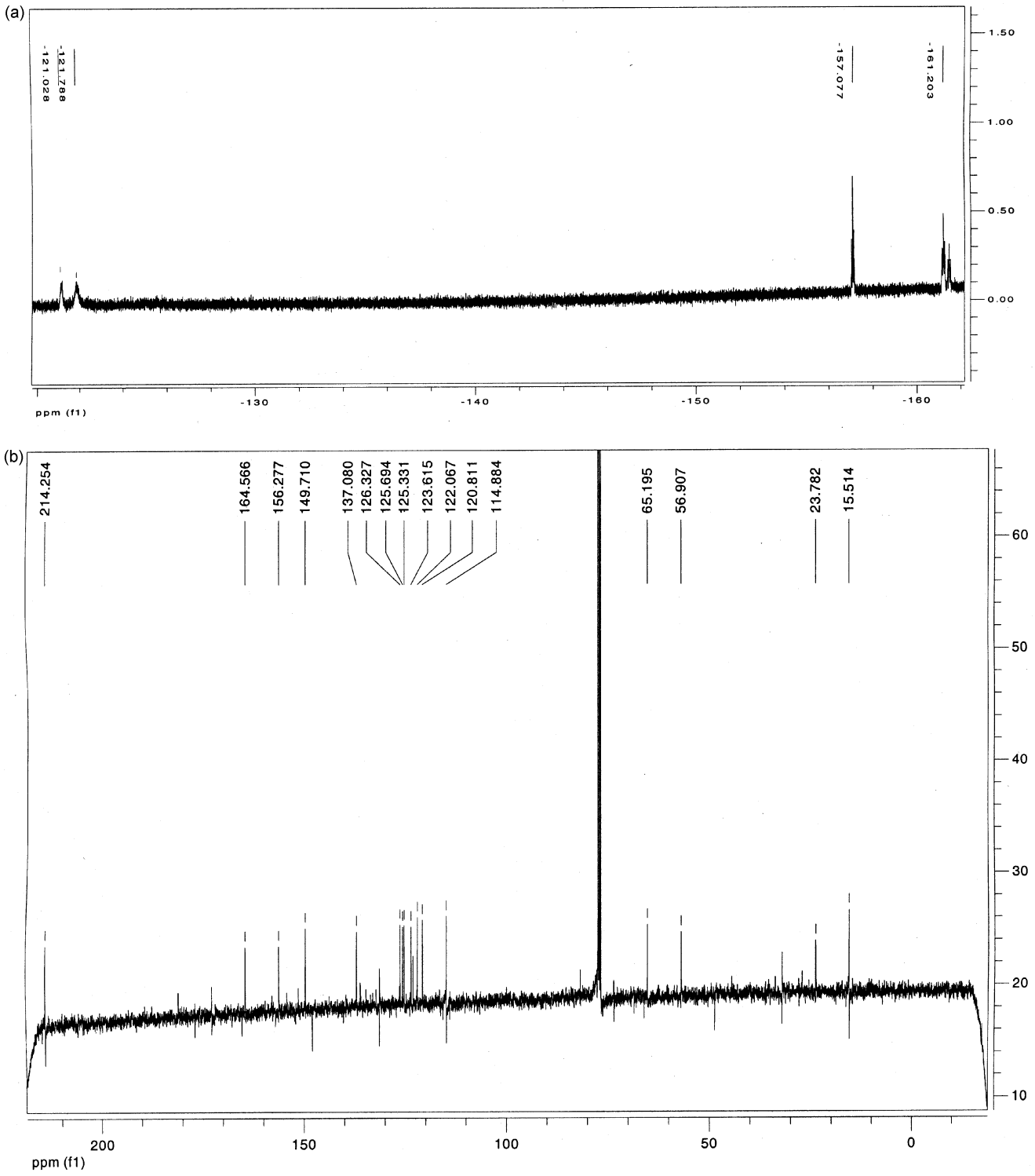


Figure 2. (**a**) F NMR of complex **2c**, (**b**) C NMR of **3b**.

decoupled from the adjacent ones due to the lack of *a*-protons show no correlation in the spectrum. For instance, in the COSY spectrum of the present complexes, absence of any off-diagonal peaks extending from d = 14·12 ppm and 9·55 ppm confirm their assignment of no protons on N(1) and N(3) respectively. However, extending horizontal and vertical lines from d = 8·32 ppm [C(a)H] and 868 ppm

[C(b)H] encounter cross peaks at d = 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 comparatively weaker coupling interactions of C(8)H and C(10)H with the C(4)H and C(5)H protons of the imidazole moiety positioned far apart are shown by the poorly resolved cross peaks at d = 7·32 ppm and 7·83 ppm. This also helps to assign phenyl and imidazole moiety protons to their respective values accurately, which is contrary to the expected greater downfield shift of C(11)H d = 7·92 ppm of the RaaiR′ molecule. COSY spectrum also turns out to be 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 interaction with the doublet at d = 7·12 ppm and 7·68 ppm [C(8)H and C(10)H].

^{1}H–^{13}C heteronuclear multiple-quantum coherence (HMQC) spectra provide information regarding the interactions between the protons and the carbon atoms to which they are directly attached. Contrary to COSY, only the resultant interactions are plotted as contour peaks in the HMQC spectrum (figure 1). In the present complexes, the absence of any contours at d = 147·12, 160·76, 155·67 ppm and 157.68 ppm assign them to the C(2), C(6), C(12,18,24) and C(13–17, 19–23 and 25–29) carbon atoms respectively. This is because they belong to the non-protonated carbon atoms on the imidazole, phenyl and pentafluorophenyl rings. Thus they are unable to show any direct ^{1}H–^{13}C heteronuclear multiple-quantum coherence. The peaks observed at d = 144·12, 151·76, 155·67 ppm and 147·68 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 d = 7·42, 7·55, 7·82, 7·80 ppm and 7·38 ppm. The evidence for the presence of protons attached to the different types of carbon atoms in the spectra is obtained from the ^{1}H–^{13}C HMQC spectra. The doublets at d = 7·92, 7·45, 7·82 ppm and 7.68 ppm [H(7), H(11), H(8) and H(10)] show contours at d = 148.42, 147·55, 144·82 ppm and 140·68 ppm [C(7), C(11), C(8), and C(10)] which help to distinguish these carbon resonances, which are close to one another.

4. Conclusions

This work describes the isolation of [Au(C_6F_5)$_3$ (RaaiR′)] and their spectral and elemental characterisation. ^{19}F {^{1}H} NMR is very informative and they show six sharp signals which correspond to ortho, meta, para fluorine atom from the *trans* and *cis* pentafluorophenyl group. In the ^{1}H–^{1}H COSY spectra of the present complexes, absence of any off-diagonal peaks extending from d = 14·12 ppm and 9·55 ppm confirm their assignment of no proton on N(1) and N(3) respectively. Contour peaks in the ^{1}H–^{13}C HMQC spectrum in the present complexes, the absence of any contours at d = 147·12, 160·76, 155·67 ppm and 157·68 ppm assign them to the C(2), C(6), C(12) and C(13, 14, 15, 16 and 17) carbon atoms respectively.

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