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Synthesis and Multinuclear NMR Investigation on Binuclear Gold(I)-Diphenylphosphinoammine (dppa)-Arylazoimidazole Complexes

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Abstract Reaction of $[Au_2(dppa)Cl_2]$ with AgOTf in dichloromethane medium followed ligand addition leads to $[Au_2(dppa)(RaaiR^{/})](OTf)$ [$RaaiR^{/}$ = *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 $N^{/}$, respectively; R = H (*a*), Me (*b*), Cl (*c*) and $R^{/}$ = Me (*1*), CH_2CH_3 (*2*), CH_2Ph (*3*), OSO_2CF_3 is the triflate anion, dppa is diphenylphosphinoammine ring]. 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 $cm^{-1.}$ The ^1H NMR spectral measurements suggest methylene, $–CH_2–$, in RaaiEt gives a complex AB type multiplet 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 different peaks in the ^{13}C NMR spectrum. In the ^1H-^1H COSY spectrum of the present complexes and contour peaks in the ^1H-^{13}C HMQC spectrum in the present complexes, assign the solution structure and stereoretentive transformation in each step.

Keywords Gold(I), Arylazoimidazole, COSY, HMQC NMR, ESI Mass, IR Spectra

1. Introduction

Interest in antimicrobial gold complexes originated from the work of Robert Koch at the end of 19th century, who demonstrated that potassium dicyanidoaurate(I), K[Au(CN)], showed activity against Myco- bacterium tuberculosis [1-12], a causative agent of tuberculosis. Subsequently, a large number of gold(I) and gold(III) complexes have been evaluated as possible antimicrobial agents against a broad spectrum of bacteria, fungi and parasites. The first part of the present review article summarizes the results) complexes. The represented gold(I) complexes have been divided into three distinct classes based on the type achieved in the field of antibacterial and antifungal activity of gold(I) and gold(III) of coordinated ligand: (i) complexes with phosphine-type ligands, (ii) complexes with N-heterocyclic carbene ligands and (iii) various other gold(I) complexes, while the results related to the antibacterial and antifungal gold(III) complexes have been mainly focused on the organometallic-type of complexes. The second section of this article rep- resents fi ndings obtained from the evaluation of antimalarial activity of gold complexes against chloroquine-sensitive and chloroquine-resistant strains of Plasmodium falciparum parasite. Antimalarial gold(I) and gold(III) complexes have been divided into the following classes, based on the nature of the coordinated ligand: (i) complexes with chloroquine and its derivatives, (ii) complexes with N-heterocyclic carbene ligands, (iii) complexes containing functionalised alkynes and (iv) thiosemicarbazonato ligands, as well as (v) other gold(I) and gold(III) complexes [3-44].

The chemistry of gold is very interesting and has some unique aspects, most likely as a consequence of the important elec tronic properties of the gold atom. The most important oxi- dation states of gold in its complexes are +1 and +3. As a soft Lewis acid, the Au(I) ion (d10 electronic configuration) favours complexation with ligands containing soft donor atoms. Thus, thiolates, thioethers, cyanide, phosphines and arsines form stable complexes with the Au(I) ion. X-ray crystallography has shown that gold(I) complexes can adopt linear, trigonal or tetrahedral geometries. Gold(I) complexes are stable in non-aqueous aprotic solvents such as acetonitrile. On the other hand, in aqueous solution, gold(I) complexes have a strong tendency to disproportionate as well as (v) other gold(I) and gold(III) complexes. Gold(I) and gold(III) complexes have been reported to be potential agents against parasites that cause amoebiasis, leishmaniasis and trypanosomiasis [5-6]. A systematic summary of these results could contribute to the future design of new gold(I)

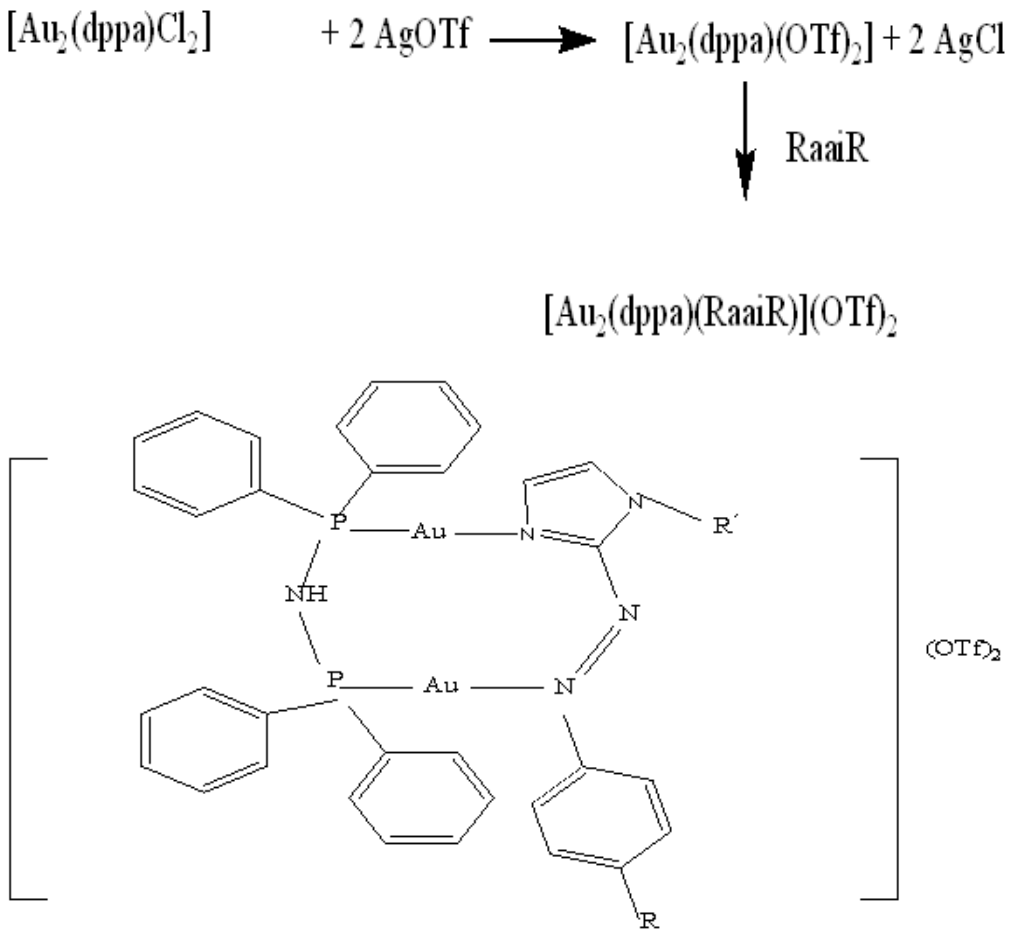
and gold(III) complexes as potential antimicrobial agents. The chemistry of gold is very interesting and has some unique aspects, most likely as a consequence of the important electronic properties of the gold atom. The most important oxidation states of gold in its complexes are +1 and +3. As a soft Lewis acid, the Au(I) ion (d10 electronic configuration) favours complexation with ligands containing soft donor atoms. Thus, thiolates, thioethers, cyanide, phosphines and arsines form stable complexes with the Au(I) ion. X-ray crystal- lography has shown that gold(I) complexes can adopt linear, trigonal or tetrahedral geometries. Gold(I) complexes are stable in non-aqueous aprotic solvents such as acetonitrile. On the other hand, in aqueous solution, gold(I) complexes have a strong tendency to disproportionate forming Au(III) and metallic Au(0) Consequently, the Au(III) ion has a preference for ligands containing nitrogen and oxygen donor atoms (hard Lewis bases). Other important ligands which form complexes with the Au(III) ion are chloride, bromide and cyanide. The dominant coordination geometry for gold(III) complexes is square planar, although trigonal bipyramidal and octahedral geometries are also observed. Trigonal bipyramidal and octa- hedral structures typically exhibit elongated axial bond lengths perpendicular to the square plane. Besides the many applications of gold in dentistry, mone- tary systems, jewellery and electronics, this metal and its com plexes have been used in medicine throughout the history of civilisation for the treatment of a wide range of diseases [7-88]. In the middle of 20th century gold(I) complexes found clinical use as antiarthritic agents for the treatment of rheumatoid arthritis and a variety of rheumatic diseases including psoria- tic arthritis, juvenile arthritis, palindromic rheumatism and discoid lupus erythematosus. Subsequently, a large number of gold(I) and gold(III) complexes have been evaluated for their potential use in the treatment of cancer, bronchial asthma, as anti-HIV and antimicrobial agents [9-98].

Transition metal complexes of diimine and related ligands have attracted much attention . Aurophilicity, the propensity for closed-shell d^{10} gold(I) centers to form weakly bonding interactions, leading to the fabrication of a large variety of supramolecular gold(I) compounds with novel structural and intriguing spectroscopic properties [13-33], has recently been an interesting and common phenomenon in gold(I) chemistry [11-18]. 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 [21-47]. In the present report we present new and noteworthy examples taken from the important class of gold phosphines-azoimidazole. Syntheses of hetero-*tris*-chelates, $[Ru(bpy)_n(RaaiR^{/})_{3-n}](ClO_4)_2$ are reported from Prof. Sinha´s laboratory [14-50]. Syntheses of molybdenum-bis-chelates with carbonyl, containing this ligand centres are reported from Prof. Ankermann´s laboratory. Prof. A Chakravorty has unfolded this ligands rhenium chemistry. But the gold chemistry and their organometallic chemistry with multinuclear NMR spectroscopy of this ligand system is totally unexplored. In this paper, we examine the reaction of $RaaiR^{/}$ on gold(I) diphenylphosphinoammine derivatives and the products are isolated. 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.

2. Results and Discussion

The complexes $[Au_2(dppa)(RaaiR^{/})](OTf)_2$, were prepared by removing weakly coordinating triflate ion, OSO_2CF_3 , from $[Au_2(dppa)(OSO_2CF_3)_2]$, 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 orange complexes are soluble in common organic solvents viz. acetone, acetonitrile, chloroform, dichloromethane but insoluble in H_2O, methanol, ethanol. In MeCN, the complexes, (*1-3)* behave as 1:2 electrolytes (Λ_M = 80-100 $\Omega^{-1}cm^{-1}mol^{-1}$).

I.r. spectra of the complexes, $[Au_2(dppa)(RaaiR^{/})](OTf)_2$ show a 1:1 correspondence to the spectra of the tetrahydrothiophene 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) appear at 1365-1380 and 1570-1600 cm^{-1}, respectively. Other important frequencies are ν(dppa) at 1510-1520, 950-960 and 790-810 cm^{-1} along with weak bands at 1070 and 1072 cm^{-1}.



R = H(a), Me(b), Cl(c), R′ = Me(1), Et(2), Bz(3)

Scheme 1. The synthetic route and composition with ISIS draw structure of the complexes.

The ESI mass spectrum of a MeCN solution in the positive ion mode is structurally enlightening, since it displays a series of characteristic 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. The maximum molecular peak of (**3c**) is observed at m/z 1375.5 (12 %), which corresponds to the molecular ion, where calculated molecular weight is 1375.03. A very careful examination of the fragmentation pattern of the ESI mass spectrum reveals the stepwise elimination of triflate ion (m/z at 1075.51, 40%). All the complexes show similar ESI mass spectra. The details are discussed in the experimental section.

The ^{1}H n.m.r. spectra of [Au_2(dppa)(RaaiR$^{/}$)] (1-3) complexes were unambiguously assigned (Figure 1, Figure 2 and Figure 4) on comparing with Au_2(dppa)$(Cl)_2$ and the free ligand (RaaiR$^{/}$) [17,19,21]. 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) 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. The aryl protons 7-(7$^{/}$-) and 11-(11$^{/}$-)H resonate asymmetrically indicative of a magnetically anisotropic environment even in the solution 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_2(dppa)(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_2(dppa)(RaaiCH$_2$CH$_3$)]$(OTf)_2$. 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_2(dppa)(RaaiCH$_2$Ph)]$(OTf)_2$. The aryl-Me (R = Me) appears as a single signal at 2.30 ppm.

The ^{13}C NMR spectrum (measured in $CDCl_3$) provides direct information about the carbon skeleton of the molecule. Assignment of different resonant peaks to respective carbon atoms are done on nine complexes and the datas are given on experimental section (Figure 2, Figure 4). Carbon atoms neighbouring the nitrogen atom shifted to downfield due to an increased electron density resulting from the presence of electronegative nitrigen atom and pi 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 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 pi electron delocalization on the =N-CC=N- and =N—CC=CC-. Similarly the carbon atom adjacent to the dppa molecule in the complex resonance at a lower field resulting of the conjugative effect of the phenyl ring with more electronegative pi-conjugate system. The methyl carbon atom of the imidazole ring resonate at 40 ppm, resonably compare to the other carbon atoms resonance.

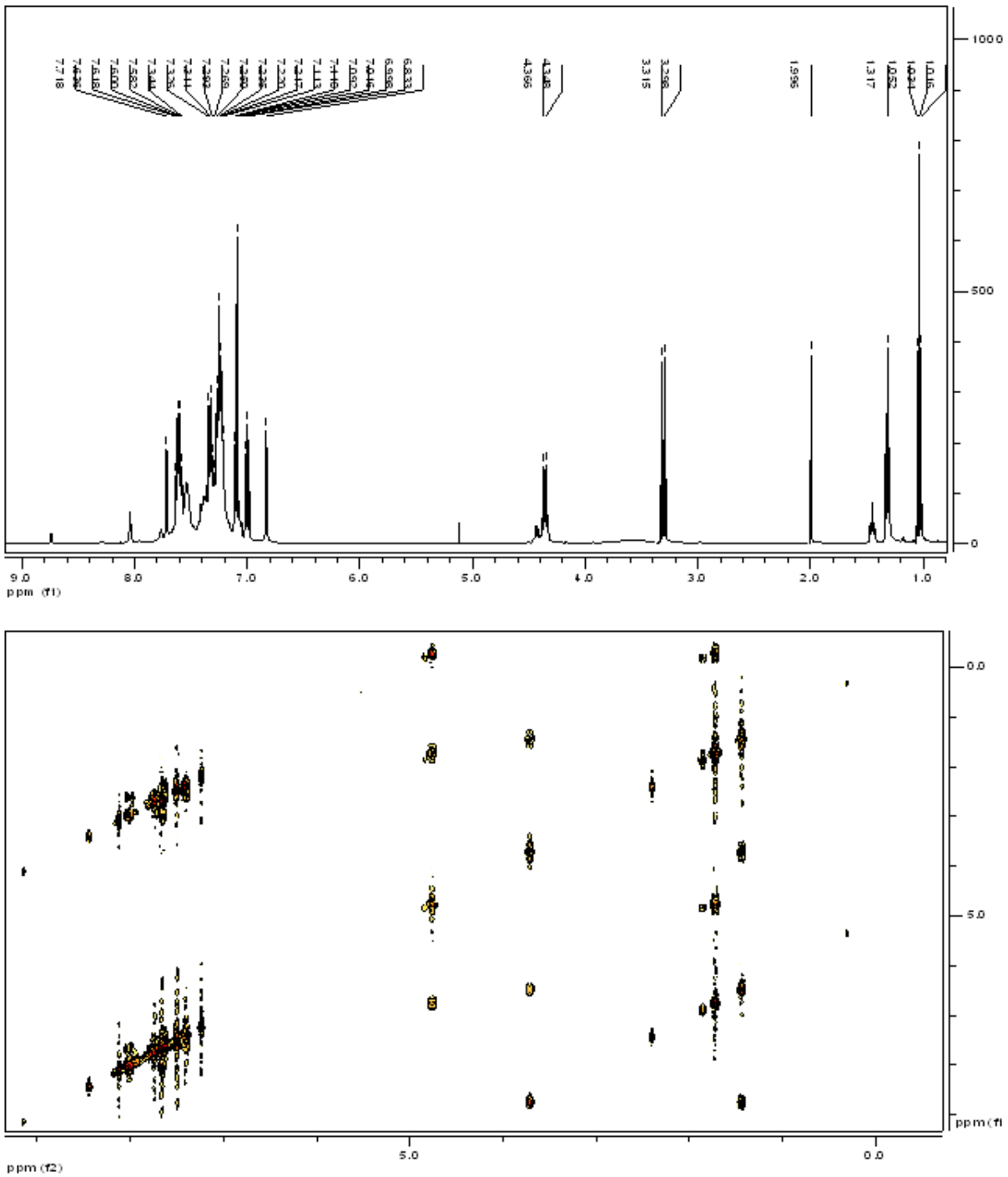


Figure 1. Complete ^{1}H NMR and ^{1}H ^{1}H COSY NMR of complex 2a

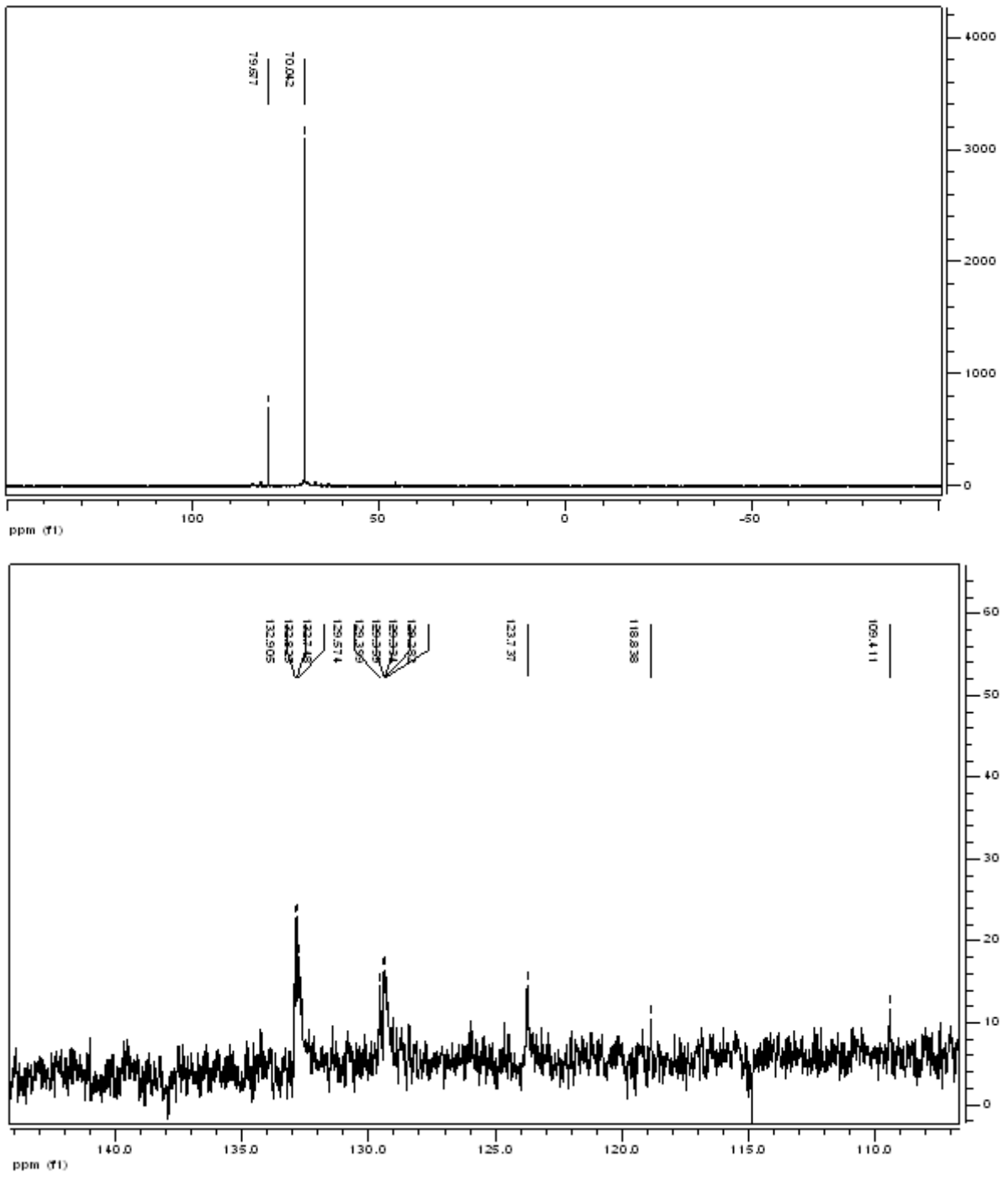


Figure 2. ^{31}P $\{^{1}H\}$ NMR and ^{13}C $\{^{1}H\}$ NMR the complex 2a

The COSY spectrum reveals (measured in $CDCl_3$) the ^{1}H-^{1}H coupling interections 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 (Figure 2 and Figure 3). 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 ppm 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 δ = 7.92 ppm of the RaaiR′ molecule and these protons interect with dppa moiety, ie, 20 protons. The doublet of the C(7)H and C(11)H protons show coupling interection with the doublet at δ = 7. 2 ppm and 7.8 ppm [C(8)H and C(10)H]. The ^{1}H-^{13}C heteronuclear multiple-quantum coherence (HMQC) spectrum provides information (measured in $CDCl_3$) 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 C2, C6, C-dppa, carbon atoms respectively. This is because, they belong to the non-protonated carbon atoms on the imidazole, phenyl and phosphine rings. So they unable to show any direct ^{1}H-^{13}C heteronuclear multiple-quantum coherence. The peaks observed at δ = 134.12,131.76,135.67 ppm 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 ppm 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 ^{1}H-^{13}C HMQC spectrum.

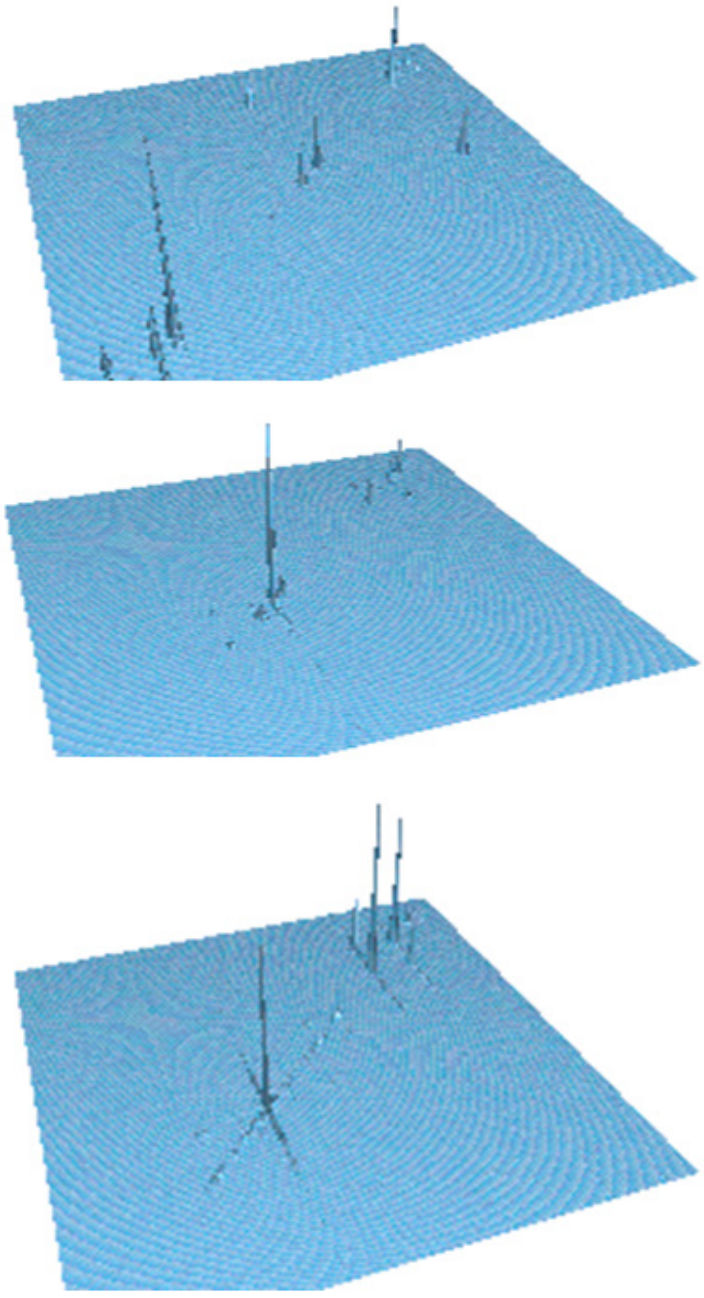


Figure 3. 3D view of the ^{1}H ^{1}H COSY spectrum of complex 1b, 1c, 2b(From above)

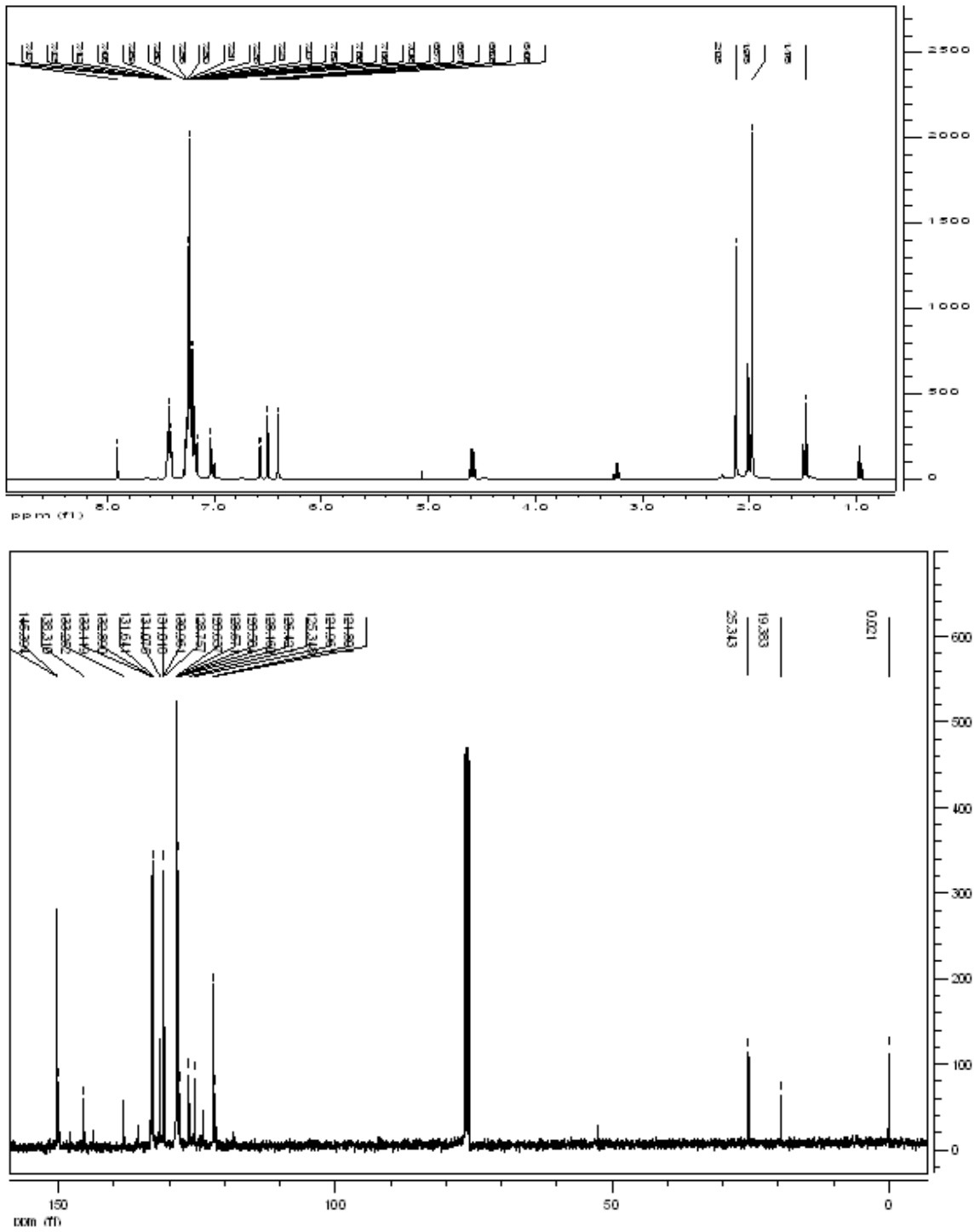


Figure 4. **^{1}H NMR of complex 1c and ^{13}C {^{1}H} NMR of complex 3a.**

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 not display gold oxidation couple at positive side but show the ligand reductions at the negative to SCE. In the potential range +2.0 to -2.0 V at the scan rate 50 mV s^{-1} two redox couples are observed prominent and all are at the negative side of the voltammogram. First one is quasireversible as is evident from peak-to-peak separation value, ΔE_p>110 mV. 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 -0.60 to –0.94 and -1.00 to -1.22. Two redox couples at negative to SCE are due to reductions of ligand. Arylazoimidazoles can accommodate two electrons at LUMO mostly characterised by azo group [11-20]. These two couples may be due to azo^{-}/azo redox reaction of coordinated RaaiR$^{/}$.

3. Conclusions

This work describes the isolation of a novel series of Gold(I) azo-imine complexes with a diphenylphosphinoammine link and their spectral and elemental characterisation. ^{1}H NMR study suggests quartet splitting of ethyl substitution. $^{31}P\{H\}$NMR is very much informative and they show the sharp signals near at 70.134 ppm which is lower than the parent complex. ^{13}C NMR gives the molecular skeleton in solution phase. ^{1}H-^{1}H COSY spectrum as well as the contour peaks in the ^{1}H-^{13}C HMQC spectrum of the present complexes, confirm their assignment of accurate structure and in solution proton proton interection, proton-carbon interection, respectively. Electrochemistry helps to assign ligand reduction.

4. Experimental

Published methods were used to prepare RaaiR/ [7-9], $Au_2(dppa)(Cl)_2$ [17-20]. 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 [8-14]. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. I.r. spectra were obtained using a Perkin Elmer spectrophotometer (using KBr disks, 4000-200 cm^{-1}). The ^{1}H nmr spectra in $CDCl_3$ were obtained on a Bruker 500 MHz FT n.m.r spectrometer using $SiMe_4$ as internal reference. Mass spectra were recorded on VG Autospec FAB and ESI usuing 3-nitrobenzyl as matrix.

I.r. spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000-200 cm). The H nmr spectra in $CDCl_3$ were obtained on a Bruker 500 MHz FT n.m.r spectrometer using $SiMe_4$ as internal reference. Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration 10 M in acetonitrile. Electrochemical work was carried out using an EG & G PARC Versastat computer controlled 250 electrochemical system. All experiments were performed under a N_2 atmosphere at 298K 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).

[(diphenylphosphinoammine*){1-ethyl-2-(p-tolylazo)imidazole}-bis-aurate(I)]triflate, [Au_2(dppa) (MeaaiEt)](OTf)$_2$,* ***2b***

To an dichloromethane colourless solution (15 cm^3) of $[Au_2(dppa)Cl_2]$ (0.945 g, 0.20 mmol) AgOTf was added (1:2) to produce de-chloro product, ie, $[Au_2(dppa)\ (OSO_2CF_3)_2]$ (0.20 mmol) into this, was added yellow dichloromethane solution of 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 (70%). All other complexes were prepared similarly as stated above.

Analysis for $[C_{36}H_{31}N_5P_2Au_2S_2O_6F_6]$, **1a**, Calc(found): C, 34.14(34.38), H, 2.46(2.44), N, 5.56(5.57); IR ν(N=N) 1370, ν(C=N), 1590, ESI mass, M(%abundance), 1265.3(09)[M^+], 965.8(34) [M-2OTf]; Proton n.m.r., ^{1}H, ppm, H(7,11), 8.07(d, J = 8Hz), H(8,10), 8.01(d, J=6.5Hz), H(9), 7.99(s,), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), 9.01, NH of dppa, CH_3 of Me, 1.5(t, J=6Hz); phosphoro n.m.r., $^{31}P\ \{H\}$, ppm in (dppa), 70.042, $^{13}C\ \{H\}$, ppm, 129-130(dppa, 24C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 42,50(Me Gr.); Analysis for $[C_{37}H_{33}N_5P_2Au_2S_2O_6F_6]$, **1b**, Calc(found): C, 33.74(33.78), H, 2.56(2.54), N, 5.46(5.47); IR ν(N=N) 1374, ν(C=N), 1595, ESI mass, M(%abundance), 1279.3(09)[M^+], 979.08(31) [M-2OTf]; Proton n.m.r., ^{1}H, ppm, H(7,11), 8.07(d, J = 8Hz), H(8,10), 8.01(d, J=7.5Hz), H(9), 7.99(s,), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), 9.00, NH of dppa, CH_3 of Me, 1.5(t, J=6Hz); phosphoro n.m.r., $^{31}P\{H\}$, ppm in (dppa), 70.002, $^{13}C\{H\}$, ppm, 129-131(dppa, 24C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 40,50(Me Gr.); Analysis for $[C_{36}H_{30}N_5P_2ClAu_2S_2O_6F_6]$, **1c**, Calc(found): C, 33.24(33.28), H, 2.31(2.34), N, 5.36(5.37); IR ν(N=N) 1374, ν(C=N), 1595, ESI mass, M(%abundance), 1299.3(09)[M^+], 999.08(31) [M-2OTf]; Proton n.m.r., ^{1}H, ppm, H(7,11), 7.97(d, J = 8Hz), H(8,10), 8.01(d, J=7.5Hz), H(9), 7.99(s,), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=6.5Hz), 9.01, NH of dppa, CH_3 of Me, 1.5(t, J=6Hz); phosphoro n.m.r., $^{31}P\{H\}$, ppm in (dppa), 70.992, $^{13}C\{H\}$, ppm, 129-133(dppa, 24C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 40,50(Me Gr.); Analysis for $[C_{37}H_{33}N_5P_2Au_2S_2O_6F_6]$, **2a**, Calc(found): C, 33.74(33.78), H, 2.56(2.54), N, 5.46(5.47); IR ν(N=N) 1378, ν(C=N), 1595, ESI mass, M(%abundance), 1279.3(09)[M^+], 979.08(31) [M-2OTf]; Proton n.m.r., ^{1}H, ppm, H(7,11), 8.07(d, J = 8.2Hz), H(8,10), 8.01(d, J=7.5Hz), H(9), 7.99(s,), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), 9.01, NH of dppa, CH_2 of Et, 4.5(quartet, J=6.2Hz); CH_3 of Et, 1.5(t, J=6Hz); phosphoro n.m.r., $^{31}P\{H\}$, ppm in (dppa), 70.002, $^{13}C\{H\}$, ppm, 129-131(dppa, 24C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 40.50, 45.0(Et Gr.); Analysis for $[C_{38}H_{35}N_5P_2Au_2S_2O_6F_6]$, **2b**, Calc(found): C, 35.24(33.28), H, 2.76(2.74), N, 5.46(5.47); IR ν(N=N) 1378, ν(C=N), 1599, ESI mass, M(%abundance), 1293.3(09)[M^+], 993.08(31) [M-2OTf]; Proton n.m.r., ^{1}H, ppm, H(7,11), 8.07(d, J = 8.2Hz), H(8,10), 8.01(d, J=7.5Hz), H(9), 7.99(s,), H(4), 7.26(d, J=6.2Hz), H(5), 7.34(d, J=5.4Hz), 1.98(s, 9-Me), 9.21, NH of dppa, CH_2 of Et, 4.1(quartet, J=6.2Hz); CH_3 of Et, 1.5(t, J=6Hz); phosphoro n.m.r., $^{31}P\{H\}$, ppm in (dppa), 70.332, $^{13}C\{H\}$, ppm,

129-131(dppa, 24C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 40.50, 45.0(Et Gr.); Analysis for $[C_{37}H_{32}N_5ClP_2Au_2S_2O_6F_6]$, **2c**, Calc(found): C, 33.74(33.8), H, 2.46(2.44), N, 5.36(5.37); IR ν(N=N) 1378, ν(C=N), 1595, ESI mass, M(%abundance), 1313.3(09)[M^+], 1013.08(31) [M-2OTf]; Proton n.m.r., ^{1}H, ppm, H(7,11), 8.07(d, J = 8.2Hz), H(8,10), 8.01(d, J=7.5Hz), H(9), 7.99(s,), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), 9.01, NH of dppa, CH_2 of Et, 4.5(quartet, J=6.2Hz); CH_3 of Et, 1.5(t, J=6Hz); phosphoro n.m.r., ^{31}P{H}, ppm in (dppa), 70.772, ^{13}C{H}, ppm, 129-131(dppa, 24C), 134.5(C2), 124.8(C4), 125.9(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 40.50, 45.0(Et Gr.); Analysis for $[C_{42}H_{34}N_5P_2Au_2S_2O_6F_6]$, **3a**, Calc(found): C, 37.54(37.58), H, 2.56(2.54), N, 5.26(5.27); IR ν(N=N) 1371, ν(C=N), 1595, ESI mass, M(%abundance), 1341.3(09)[M^+], 1041.0(21) [M-2OTf]; Proton n.m.r., ^{1}H, ppm, H(7,11), 8.07(d, J = 8.2Hz), H(8,10), 8.01(d, J=7.5Hz), H(9), 7.99(s,), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), 9.01, NH of dppa, CH_2 of Bz, 4.95(quartet, J=6.02Hz); Ph of Bz, 7.5-7.7(m, broad); phosphoro n.m.r., ^{31}P{H}, ppm in (dppa), 70.992; ^{13}C{H}, ppm, 129-131(dppa, 24C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 40.50, 45.0(Et Gr.); Analysis for $[C_{43}H_{36}N_5P_2Au_2S_2O_6F_6]$, **3b**, Calc(found): C, 38.04(38.08), H, 2.66(2.64), N, 5.16(5.17); IR ν(N=N) 1371, ν(C=N), 1590, ESI mass, M(%abundance), 1355.3(09)[M^+], 1055.0(21) [M-2OTf]; Proton n.m.r., ^{1}H, ppm, H(7,11), 8.07(d, J = 8.2Hz), H(8,10), 8.01(d, J=7.5Hz), H(9), 7.99(s,), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), 9.01, NH of dppa, CH_2 of Bz, 4.99(quartet, J=6.02Hz); Ph of Bz, 7.5-7.7(m, broad); phosphoro n.m.r., ^{31}P{H}, ppm in (dppa), 70.992; ^{13}C{H}, ppm, 129-131(dppa, 24C), 134.5(C2), 124(C4), 125(C5), 125.3(C7,11), 129.2(C8,10), 134(C6), 40.50, 44.0(Et Gr.); Analysis for $[C_{42}H_{33}ClN_5P_2Au_2S_2O_6F_6]$, **3c**, Calc(found): C, 36.64(36.58), H, 2.46(2.44), N, 5.06(5.07); IR ν(N=N) 1371, ν(C=N), 1595, ESI mass, M(%abundance), 1375.3(09)[M^+], 1075.5(21) [M-2OTf]; Proton n.m.r., ^{1}H, ppm, H(7,11), 8.07(d, J = 8.2Hz), H(8,10), 8.01(d, J=7.5Hz), H(9), 7.99(s,), H(4), 7.26(d, J=6Hz), H(5), 7.34(d, J=5Hz), 9.01, NH of dppa, CH_2 of Bz, 4.95(quartet, J=6.02Hz); Ph of Bz, 7.5-7.7(m, broad); phosphoro n.m.r., ^{31}P{H}, ppm in (dppa), 71.002; ^{13}C{H}, ppm, 129-131(dppa, 24C), 134.5(C2), 124.2(C4), 125.7(C5), 125.3(C7,11), 129.2(C8,10), 134.3(C6), 39.50, 43.0(Et Gr.).

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REFERENCES

[1] M. L. Williams, Inflammopharmacology, 2008, 16, 110–111.

[2] E. A. Pacheco, E. R. T. Tiekink and M. W. Whitehouse, Gold compounds and their applications in medicine, in Gold Chemistry: Applications and Future Directions in the Life Sciences, ed. F. Mohr, Wiley-VCH Verlag GmbH & Co. KGaA, Wienheim, 2009, pp. 283–319.

[3] S. F. Shaw III, Chem. Rev. , 1999, 99, 2589–2600.

[4] H. Schmidbaur, S. Cronje, B. Djordjevic and O. Schuster, Chem. Phys. , 2005, 311, 151–161.

[5] B. Đ. Gli š i ć, S. Rajkovi ć, Z. D. Stani ć and M. I. Djuran, Gold Bull. , 2011, 44,91–98.

[6] A. M. Bond ž i ć, T. D. Lazarevi ć-Pa š ti, B. P. Bond ž i ć, M. B. Č olovi ć, M. B. Jadranin andV. M. Vasi ć, New J. Chem. , 2013, 37, 901–908.

[7] B. Đ Gli š i ć, M. I. Djuran, Z. D. Stani ć and S. Rajkovi ć, Gold Bull. , 2013, DOI:

[8] S. P. Fricker, Gold Bull. , 1996, 10.1007/s13404-013-0108-7. 29,53–60.

[9] E. R. T. Tiekink, Gold Bull. , 2003, 36, 117–124.

[10] Uson R, Laguna A., Laguna M.. Jimenez J, and Durana E., lnorg,Chim. Acta, 1990, 168, 89.

[11] Puddephatt R.J.. In: G. Wilkinson, R.D. Gillard and J.A. McCleverty, Editors, Comprehensive Coordination Chemistry vol. 2, Pergamon, Oxford, 1987

[12] M. Contel, J. Garrido, M.C. Gimeno, P.G. Jones, A. Laguna and M. Laguna. Organometallics, 1996, 15, p. 4939. M.C. Gimeno and A. Laguna. Chem. Rev. 1997, 97, p. 511.

[13] Schmidbaur H., Editor, Gold: Progress in Chemistry, Biochemistry and Technology, John Wiley and Sons, Chichester, 1999;

[14] Deb A. K., and Goswami S., Polyhedron, 1991, 10, 1799; Misra T. K., Das D., Sinha C., Ghosh P. K. and Pal C. K., Inorg. Chem., 1998, 37, 1672;

[15] Byabartta P., Transition Met. Chem., 2005, 30, 902.

[16] Byabartta P., Transition Met. Chem., 2005, 30, 575.

[17] Byabartta P., Transition Met. Chem., 2005, 30, 672.

[18] Jemmis E. D., Subramanian G., Nowek A., Gora R. W., Sullivan R. H. and Leszczynski J., J. Mol. Struct., 2000, 556, 315.

[19] Chattopadhyay S., Ghosh K., Pattanayak S. and Chakravorty A., J. Chem. Soc., Dalton Trans., 2001, 1259.

[20] Greenwood N. N. andEarnshaw A., Chemistry of the Elements, Pergamon Press, Oxford, 1989, p-519.

[21] Chakravarty A. R. and Chakravorty A., J. Chem. Soc., Dalton Trans., 1983, 961.

[22] Murray H.H..,lwen W. l, Sherman S.E., Greaney M.A., Edksen KA., Carstense B,.A, Halhbert T R and Sliefel E.I,, Angrew. Chem,, 1995, 34, 841.

[23] Cerrada E., Fernandez EJ., Gimeno M.C., Laguna A., Laguna

M., Termba R. and Villacampa M,D., J. Organomet, Chem., 1995, 492, 105.

[24] Uson R, Laguna A. and Laguna M., Inorg. Synth..,1989, 26, 85.

[25] Uson R. and Laguna A., Organomet. Synth., 1985, 3, 325.

[26] Uson R., Laguna A., Laguna M., Jilnenez J., Gemez M.P., Slfinz A. and Jones P.G., J. Chem Soc., Dalton Trans., 1990, 3457,

[27] Contel M., Jimenez L, Jones P.G., Laguna A. and Laguna M. J. Chem. Soe., Dalton Trans.,1994, 2515.

[28] Assefa, Z.; Omary, M. A.; McBurnett, B. G.; Mohamed, A. A.; Patterson, H. H.; Staples, R. J.; Fackler, J. P., Jr. Inorg. Chem. 2002, 41, 6274-6280.

[29] Fackler, J. P., Jr.; Trzcinska-Bancroft, B. Organometallics 1985, 4, 1891-1893.

[30] Bennett, M. A.; Bhargava, S. K.; Hockless, D. C. R.; Welling, L. L.; Willis, A. C. J. Am. Chem. Soc. 1996, 118, 10469-10478.

[31] Gold. Progress in Chemistry, Biochemistry and Technology , ed. Schmidbaur H., John Wiley & Sons, Chichester, 1999.

[32] Gold chemistry. Applications and future directions in the life Sciences , ed. Mohr F., Wiley-VCH, Weinheim, 2009.

[33] Usón R., Vicente J. and Chicote M. T., Inorg. Chim. Acta,1979,35, L305–L306.

[34] Usón A., Vicente J. and Chicote M. T.,J. Organomet. Chem.,1980,198, 105–112.

[35] Usón R., Vicente J. and Chicote M. T.,J. Organomet. Chem.,1981,209, 271–279.

[36] Usón R., Vicente J., Chicote M. T., Jones P. G. and Sheldrick G. M.,J. Chem. Soc., Dalton Trans., 1983, 1131–1136.

[37] Meyer N., Sivanathan S. and Mohr F.,J. Organomet. Chem.,2011,696, 1244–1247.

[38] Meyer N., Lehmann C. W., Lee T. K. M., Rust J., Yam V. W. W. and Mohr F.,Organometallics, 2009,28,2931–2934.

[39] Partyka D. V., Zeller M., Hunter A. D. and Gray T. G.,Angew.Chem., Int. Ed., 2006,25, 8188–8191.

[40] Yam V. W. W. and Wong K. M. C.,Chem. Commun., 2011,47, 11579–11592.

[41] Bronner C. and Wenger O. S.,Dalton Trans., 2011,40,12409–12420.

[42] Yersin H., Rausch A. F., Czerwieniec R., Hofbeck T. and Fischer T.,Coord. Chem. Rev., 2011,255, 2622–2652.

[43] Kriechbaum M., List M., Berger R. J. F., Patzschke M. and Monkowius U.,Chem.–Eur. J., 2012,18, 5506–5509.

[44] Au V. K. M., Zhu N. and Yam V. W. W.,Inorg. Chem., 2013,52, 558–567.

[45] To W. P., Chan K. T., Tong G. S. M., Ma C., Kwok W. M., Guan X., Low K. H. and Che C. M.,Angew. Chem., Int. Ed.,2013,52, 6648–6652.

[46] Szentkuti A., Bachman M., Garg J. A., Blacque O. and Venkatesan K.,Chem.–Eur. J., 2014,20, 2585–2596.

[47] Tanaka Y., Wong K. M. C. and Yam V. W. W.,Chem. Sci.,2012,3, 1185–1191.

[48] To W. P., Tong G. S. M., Lu W., Ma C., Liu J., Chow A. L. F. and Che C. M.,Angew. Chem., Int. Ed., 2012,51, 2654–2657.

[49] Smith D. A., Roşca D. A. and Bochmann M.,Organometal-lics, 2012,31, 5998–6000.

[50] Muñoz-Rodríguez R., Buñuel E., Williams J. A. G. and Cárdenas D. J.,Chem. Commun., 2012,48, 5980–5982.

[51] Roşca D. A., Smith D. A. and Bochmann M., Chem.Commun., 2012,48, 7247–7249.

[52] Lu W., Chan K. T., Wu S. X., Chen Y. and Che C. M.,Chem.Sci., 2012,3, 752–755.

[53] Garg J. A., Blacque O., Fox T. and Venkatesan K.,Inorg.Chem., 2010,49, 11463–11472.

[54] Mohr F., Privér S. H., Bhargava S. K. and Bennett M. A.,Coord. Chem. Rev., 2006,250, 1851–1888.

[55] Schuh E., Valiahdi S. M., Jakupec M. A., Keppler B. K., Chiba P. and Mohr F.,Dalton Trans., 2009, 10841–10845.

[56] Schuh E., Pflüger C., Citta A., Folda A., Rigobello M. P., Bindoli A., Casini A. and Mohr F.,J. Med. Chem., 2012,55,5518–5528.

[57] Molter A., Rust J., Lehmann C. W. and Mohr F.,Tetra-hedron, 2012,68, 10586–10591.

[58] Citta A., Schuh E., Mohr F., Folda A., Massimino M. L., Bindoli A., Casini A. and Rigobello M. P.,Metallomics,2013,5, 1006–1015.

[59] Contel M., Edwards A. J., Garrido J., Hursthouse M. B., Laguna M. and Terroba R.,J. Organomet. Chem., 2000,607,129–136.

[60] Gaillard S., Slawin A. M. Z., Bonura A. T., Stevens E. D. and Nolan S. P.,Organometallics, 2010,29, 394–402.

[61] Chatt, J.; Leigh, G. J.; Slade, R. W. J. Chem. Soc., Dalton Trans. 1973, 2021.

[62] (a) Herrmann, W. A.; Kellner, J.; Riepl, H. J. Organomet. Chem. 1990, 389, 103. (b) Toth, Z.; Joo, F.; Beck, M. T. Inorg. Chem. Acta 1980, 42, 153.

[63] Mohr, B.; Lynn, D. M.; Grubbs, R. H. Organometallics 1996, 15, 4317.

[64] Hoots, J. E.; Rauchfuss, T. B.; Wrobleski, D. A. Inorg. Synth. 1982, 21, 175.

[65] Ellis, J. W.; Harrison, K. N.; Hoye, P. A. T.; Orpen, A. G.; Pringle, P. G.; Smith, M. B. Inorg. Chem. 1992, 31, 3026.

[66] Hoye, P. A. T.; Pringle, P. G.; Smith, M. B.; Worboys, K. J. Chem. Soc., Dalton Trans. 1993, 269.

[67] Darensbourg, D. J.; Beckford, F. A.; Reibenspies, J. H. J. Cluster Sci. 2000, 11, 95.

[68] Darensbourg, D. J.; Robertson, J. B.; Larkins, D. L.; Reibenspies, J. H. Inorg. Chem. 1999, 38, 2473.

[69] Darensbourg, D. J.; Stafford, N. W.; Joo, F.; Reibenspies, J. H.

Organomet. Chem. 1995, 488, 99.

[70] Joo, F., Nadasdi, L.; Benyei, A. C.; Darensbourg, D. J. J. Organomet. Chem. 1996, 512, 45.

[71] Darensbourg, D. J.; Decuir, T. J.; Stafford, N. W.; Robertson, J. B.; Draper, J. D.; Reibenspies, J. H. Inorg. Chem. 1997, 36, 4218.

[72] Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. H. Organometallics 1992, 11, 1990.

[73] Darensbourg, D. J.; Joo, F.; Kannisto, M.; Katho, A.; Reibenspies, J. H.; Daigle, D. J. Inorg. Chem. 1994, 33, 200.

[74] Forward, J. M.; Assefa, Z.; Fackler, J. P. J. Am. Chem. Soc. 1995, 117, 9103.

[75] Forward, J. M.; Fackler, J. P.; Staples, R. J. Organometallics 1995, 14, 4195.

[76] Forward, J. M.; Assefa, Z.; Staples, R. J.; Fackler, J. P. Inorg. Chem. 1996, 35, 16.

[77] Assefa, Z.; McBurnett, B. G.; Staples, R. J.; Fackler, J. P. Inorg. Chem. 1995, 34, 4965.

[78] Assefa, Z.; McBurnett, B. G.; Staples, R. J.; Fackler, J. P. Inorg. Chem. 1995, 34, 75.

[79] Alyea, E. C.; Ferguson, G.; Kannan, S. Chem. Commun. 1998, 345.

[80] Nadasdi, L. Joo, F. Inorg. Chem. Acta 1999, 293, 218.

[81] Assmann, B.; Angermaier, K.; Paul, M.; Reide, J.; Schmidbauer, H. Chem. Ber. 1995, 128, 891.

[82] Daigle, D. J.; Pepperman, A. B. J. Heterocycl. Chem. 1975, 12, 579.

[83] Daigle, D. J.; Boudreaux, G. J.; Vail, S. L. J. Chem. Eng. Data 1976, 21, 240.

[84] Shriver, D. F.; Drezdon, M. A. The Manipulation of Air-Sensitive Compounds; John Wiley & Sons: New York, 1986.

[85] Cornils, B. Org. Process Res. Dev. 1998, 2, 121-127.

[86] Cornils, B.; Herrmann, W. A. Aqueous-Phase Organometallic Catalysis Concepts and Applications; Wiley-VCH: Weinheim, 1998.

[87] Joó, F. Aqueous Organometallic Catalysis; Kluwer Academic Publishers: Dordrecht, 2001.

[88] Casado, R.; Contel, M.; Laguna, M.; Romero, P.; Sanz, S. J. Am. Chem. Soc. 2003, 125, 11925-11935

[89] Mohr, F.; Cerrada, E.; Laguna, M. Organometallics 2006, 25, 644-648.

[90] See for example: (a) Schmidbaur, H.; Grohmann, A.; Olmos, M. E. Organogold chemistry. In Gold Progress in Chemistry, Biochemistry and Technology, Schmidbaur, H., Ed.; John Wiley & Sons: Chichester, 1999; pp 647-746. (b) Fackler, J. P., Jr. Polyhedron 1997, 16, 1-17. (c) Mohr, F.; Privér, S. H.; Bhargava, S. K.; Bennett, M. A. Coord. Chem. Rev., in press.

[91] Laguna, A.; Laguna, M. Coord. Chem. Rev. 1999, 193-195, 837-856.

[92] Méndez, L. A.; Jiménez, J.; Cerrada, E.; Mohr, F.; Laguna, M. J. Am. Chem. Soc. 2005, 127, 852-853.

[93] Bhargava, S. K.; Mohr, F.; Bennett, M. A.; Welling, L. L.; Willis, A. C. Organometallics

[94] See for example: (a) Phillips, A. D.; Gonsalvi, L.; Romerosa, A.; Vizza, F.; Peruzzini, M. Coord. Chem. Rev. 2004, 248, 955-993. (b) Cornils, B.; Kuntz, E. G. J. Organomet. Chem. 1995, 502, 177-186. (c) Pinault, N.; Bruce, D. W. Coord. Chem. Rev. 2003, 241, 1-25. (d) Katti, K. V.; Hariprasad, G.; Smith, C. J.; Berning, D. E. Acc. Chem. Res. 1999, 32, 9-17, and references therein. (e) Assefa, Z.; Forward, J. M.; Grant, T. A.; Staples, R. J.; Hanson, B. E.; Mohamed, A. A.; Fackler, J. P., Jr. Inorg. Chim. Acta 2003, 352, 31.

[95] Darensbourg, D. J.; Ortiz, C. G.; Kamplain, J. W. Organometallics 2004, 23, 1747-1754.

[96] Murray, H. H.; Fackler, J. P., Jr.; Porter, L. C.; Mazany, A. M. J. Chem. Soc., Chem. Commun. 1986, 321-322.

[97] Usón, R.; Laguna, A.; Laguna, M.; Jiménez, J.; Jones, P. G. J. Chem. Soc., Dalton Trans. 1991, 1361-1365.

[98] Schmidbaur, H.; Grohmann, A.; Olmos, M. E. Gold, Progress in Chemistry, Biochemistry and Technology. In Gold, Progress in Chemistry, Biochemistry and Technology; Schmidbaur, H., Ed.; John Wiley & Sons: Chichester, 1999; p 747, and references therein