Nat. Volatiles & Essent. Oils, 2020;07 (4):139-165

NVEO
Natural Volatiles & Essential Oils

Cytotoxicity (Reactivity With BSA) Of Newly Synthesised Di-Tertiary-Butyl-Catecholato (Dtbcat)- Gold-Phosphine-Complexes.

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Ag+- assisted dechlorination of Gold(I) and Gold(III) phosphine complexes followed by the reaction with 5-t-But-Catecholato (DTBCat)- (H2CA) in presence of Et3N gives a neutral violet complexes whereas **1-9,8a**, **14-16** are Gold(I) two coordinate linear complexes and **10-13** are Gold(III) square planar four coordinate complexes. The seventeen new complexes are charecterised by ESIMS, IR and multinuclear NMR (1H, 13C, 19F; 31P) spectroscopic studies. In addition by dimentional NMR studies as 1H 1H COSY permit a complete assignment of the complexes in the solution phase.

Keywords. Gold(I), Gold(III), catechol, phosphine, 1H, 13C, 19F, 31P, COSY, NMR, ESIMS.

Gold-based probe development and drug discovery remain a burgeoning area of biological research and treatment for disease indications such as cancer [1–5], arthritis [6–9], and microbial infection [10,11] following the FDA approval of tetra-O-acetylglucose-1-thiolgold(I) triethylphosphine complex (auranofin). Exploring the Au(I) and Au(III) chemical space has given rise to enormous diversity of gold compounds of biological relevance, infuenced by creative ligand design [12–16]. Despite effective clinical and preclinical treatment of cancer and rheumatoid arthritis by gold complexes such as auranofn, the molecular basis of drug action remains unclear for gold(III) phos- phine compounds present in this report. Years of research implicates a number of disease targets including: (i)proteasome-associated deubiquitinases [6–99]; (ii) thiol-rich enzymes such as thioredoxin and glutathione reductase [17–20]; (iii) thiol-dependent proteases [21]; iv) autophagy induction [22]; and superoxide/oxyradical ion generation [23].Auranofn, which is under clinical and preclinical investigation for the treatment of a variety of cancers including leukemia [24,25] and ovarian malignancies [26–28] as well as microbial infections [29–81] is a phosphinogold complex. Tis has accelerated the development and discovery of several gold-phosphine complexes for therapeutic applications. Gold(I)-phosphine anti-cancer complexes have been identifed to trigger apoptosis by targeting the mitochondria and inhibiting thioredoxin reductase [32–64]. Structural diversity of gold complexes bearing phosphine ligands have important implications for anticancer activity and probe development [20,35]. Work by Berners-Price et al. demonstrated the anticancer efect of gold-phosphine complexes and have also tried to improve the in vitro and in vivo efcacy of this class of compounds [2,5,36–42]. Gold complexes bearing dithiocarbamate [43–45] and triorganophosphine ligands [33,46] of the type [(R3P) Au(S2CNR2)] display anticancer activity across a panel of cancer cells including ovarian cancer cells [47]. Recently, Darkwa and co-workers synthesized dinuclear phosphinogold(I) complexes bearing varied phosphine ligandsincluding triphenyl phosphine, and diphenylphosphino-alkanes and dithiocarbamates of the type [Au2Cl2(dppe)] and evaluated their anticancer activity [47]. Te complexes displayed broad spectrum of activity in a number of cancer cell lines. Additionally, the anticancer activity of phosphinogold(I) complexes bearing thioglucose ligands as in the case of auranofn show higher potency than their thiolate counterparts even in cisplatin resistant cells. For example, the P – Au – S structural motif is prevalent in a number of gold-phosphine complexes such as the lupinylsulfde (OmS) or

sulfanylpropenoate (sppa) [48] containing phosphinogold(I), [AuOmS)2(Ph2P(CH2)2PPh2] or[Au(PPh3)(sppa)], respectively and they exhibit good anticancer activity [49]. Improving the biological activity of gold-phosphine complexes require ligand tuning that expand diversity, lipophilicity, physiological stability, and high selective cytotoxicity in cancer cells over normal cells [50,51].Whereas a lot of work has been conducted with linear phosphinogold(I), its high oxidation state counterpart gold(III) needs further exploration. Recent advancement of cyclometalated gold(III) in anticancer development show promising results [1,52–55]. These ligands impart strong σ- donating character to the gold center for stability and offer the possibility of diferent ligands around the metal center, given its square-planar geometry [56]. Che and co-workers showed that dinuclear cyclometalated gold(III) phosphine, [(C^N^C)2Au2(μ-dppp)]CF3SO3)2 inhibit hepatocellular carcinoma in vivo by inducing ER stress [57]. Tere still remains the need to expand the structural diversity of gold-phosphine complexes by designing new gold(III)-phosphine complexes. Another important feature of ligands in the context of biological effecacy is chirality, since they possess the property to tune substrates to respective biological targets for improved target engagement that may be elusive for non-chiral ones. The use of chiral ligands in gold drug discovery remain largely unexplored. Incorporating chiral ligands into gold(I) or gold(III) complexes will expand the chemical space to further opportunities in medicinal inorganic chemistry. Here I synthesized gold(III) complexes bearing chiral or achiral phosphine ligands and in addition mononuclear (C^N)-cyclometalated gold(III) bearing chiral or achiral phosphine ligands. Te complexes displaypotent cytotoxic activity in diferent cancer cell lines by triggering apoptosis through ROS induction. Te study establishes the need for a broader scope of gold complexes for cancer therapy. The coordination chemistry of quinonoid systems are important because of their existence in various redox state (catechole (CQ)/semiquinone (SQ)/quinone (RQ)), optoelectronic communication, biological model study, DNA intercalation etc [1-15]. A common feature of the metal-RQ chemistry is delocalization of active electrons beween the metal and the quinonoid ligand. This is mainly due to closer energy of quinonoid based ligands to those of metal based d□-orbitals and recently much effort has been devoted to the study of the electrochemical and spectroscopic properties of ruthenium complexes. The presence of □-acidic co-ligands like CO, [4] pyridines (R-Py), □-diimines (bpy, phen, tpy), [5-15] PPh3, [2,3,6] and 2-(arylazo)pyridines [7] efficiently control the energy of metal d□ levels. Various approaches have been chosen to establish the participation of metal, coligand and RQ orbitals in the spectroscopic and redox states [9-13]. Because of the presence of equivalent O,O- donor centers on either side of the aromatic backbone of L2- the isolation of monomeric complexes are difficult. In continuation of comprehensive studies on chemistry of catecholato system in this article I describe some Gold(I) and Gold(III) phosphine complexes of catecholates. The complexes are well charecterized by IR, 1H NMR, 19F (1H)NMR, 31P (1H)NMR,13C (1H)NMR, 1H-1H COSY NMR and mass spectrometry. Gold(I) complexes have recently emerged as a potential chemotherapeutic alternative to conventional medical cancer treatments based on platinum(II) agents, such as cisplatin (CDDP) or oxaliplatin (OXP). [1,2] Wiping out side-effects and improving biological activity have become the main purposes of new antitumor compounds research, which eventually led to the development of several innovative therapeutic strategies. In fact, numerous gold complexes with antitumor activity have been previously reported, [3−10] and even the established antiarthritic gold(I) thiolate drug auranofin is currently undergoing evaluation in different US clinical trials because of its antineoplastic properties. [11] In the current context, N-heterocyclic carbene (NHC) gold derivatives have garnered greater and greater attention as anticancer agents, lately, because of their stability under physiological conditions and biological activity, [12−18] mainly due to their excellent σ-donating capacity and easy modulation of both the steric and electronic properties. Moreover, gold(I) phosphine complexes display remarkable anticancer properties since their lipophilicity facilitates transport across cell membranes. [19−21] On the other hand, keeping in mind that half of the current treatments in human neoplasms therapy are dependent on the functional p53-protein, the use of chalcones as auxiliary ligands is a particularly promising aspect in the design of novel anticancer agents. Evidence is growing that chalcones are effective inhibitors of the p53-MDM2 interaction, as, for instance, recently reported for the platinum(IV) derivative prodrugs chalcoplatin and monochalcoplatin. [22,23] Chalcoplatin arrests the cell cycle at G2/M phase, significantly induces p53 activation, and triggers downstream apoptotic pathways, which is a mechanism of action that indicates the role of the p53 agonist. The p53- dependent anticancer activity of the Au(I) NHC complex MC3 has been recently reported, [24] whereas During the past decade polynuclear gold(I) complexes, and in particular their photophysics, has attracted a considerable attention because of their potential applications to the field of photonic devices and nanomaterials.1 The strong

relativistic effects displayed by gold atoms, that is, the phenomenon associated to high-speed electrons moving close to the heavy atomic nucleus, confer them distinct properties.2 An increase in the effective nuclear charge causes a contraction of the less-diffuse orbitals, whereas the more-diffuse orbitals expand due to the enhanced shielding effect by the contracted orbitals. Gold exhibits the maximum relativistic effect among their neighbors in the periodic table, which means that the extent of contraction in the 6s and 6p orbitals, and at the same time the expansion of 5d orbitals is the most significant.3 These effects are in the basis of the observation of aurophilic interactions between gold centers, which have attracted a growing attention and accelerated the development of gold(I) chemistry. This phenomenon (aurophilicity4) even became a model for the description of relativistic effects in closed-shell metals, of which gold(I) is the best example. [5−7] Because of a similarity in energy and directionality between aurophilic interactions and hydrogen bonds, aurophilicity plays a key role in molecular aggregation in both solid state and solution. The luminescence studies of gold(I) complexes are of particular interest due to the possibility offered of a straightforward way to study Au···Au interactions, which in some cases are reported to be the origin of the luminescence behavior. Several examples found in the literature of structural and spectroscopic evidence of the effect of the aurophilic interactions on the observed luminescence induced scientists to carry out theoretical studies which intend to give the scientific community an explanation of the luminescence of gold compounds and its relation to aurophilicity through the Au···Au distance dependence of the luminescence features. [8−10] Yet, its nature has not been rationalized in a consensual and general view and continuous efforts in the assignment of the states responsible for the observed emissions are still needed.11 The difficulties result in part of the extensive state mixing that occurs in metal complexes, which turns difficult to find simple assignments to the states, such as the presence of a low energy molecular orbital centered at Au···Au, which would be one of the orbitals involved in the lowest energy electronic transition observed in emission. This would constitute the ideal and straightforward assignment of an “aurophilic” emissive state. In addition, gold complexes without aurophilic interactions, as measured by X-ray crystallographic distances, sometimes show identical luminescence to the ones claimed to be unequivocal proof of aurophilic interactions. In fact, the luminescence is affected by the nature of the ligands, by the geometry around the metal center or by the presence of metal−metal interactions in the complexes, which in principle permits the rational design of complexes for specific applications. The coordination chemistry of gold is currently of interest due to the luminescent behavior [1−3] and catalytic activity [4−6] of these complexes. Complexes of gold(I) generally have coordination numbers of two, three, or four.7,8 The properties and reactivities of these complexes are intimately connected with their coordination geometry. Linear, two-coordinate gold(I) complexes are usually colorless and are frequently nonluminescent in the absence of aurophilic interactions.9 Such two-coordinate complexes can become luminescent through aggregation that results from the formation of aurophillic interactions that induce close Au···Au contacts. For example, the two- coordinate gold(I) salts [(C6H11NC)2Au](PF6) and [(C6H11NC)2Au](AsF6) are colorless, monomeric, and nonluminescent in solution, but upon crystallization they form two luminescent polymorphs with extended Au···Au interactions between cations,

EXPERIMENTAL

Materials and Physical Measurements: Gold phosphine complexes were synthesized from literature method [2]. Commercially available silica gel (60–120 mesh) from SRL was used for chromatographic separations. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN elemental analyzer. Infrared spectra were obtained using a JASCO 420 spectrophotometer (KBr disks, 4000–200 cm–1). The 1H NMR spectra in CDCl3 were obtained on a Bruker 500 MHz FT-NMR spectrometer using SiMe4 as internal reference. Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ?10–3 mol/l in acetonitrile. All experiments were performed under a N2 atmosphere at 298 K.

Preparation & analysis of complexes: To a series of methanolic suspension of Gold-phosphine complexes, [Au(Cl)(PPh3)2], 1, (0.990 g, 2.00 mmol), [Au(Cl)(P(Ph-oMe)3)2], 2, (1.074 g, 2.00 mmol), [Au(Cl)(P(Ph- mMe)3)2], 3, (1.074 g, 2.00 mmol), [Au(Cl)(P(Ph-pMe)3)2], 4, (1.074g, 2.00mmol), [Au(Cl)(P(Ph2Me)2], 5,

(0.866g, 2.00mmol), [Au(Cl)(P (PhMe2)2], 6, (0.741 g, 2.00 mmol), [Au(Cl)(P(Cy-hx)3)2], 7, (1.020g, 2.00mmol),

[Au(Cl)(P(NEt2)3)2], 8, (0.955 g, 2.00 mmol), [Au(Cl)(P(NMe2)3)2], 8a, (0.791 g, 2.00 mmol), [Au(Cl)(AsPh3)2], 9,

(1.076 g, 2.00 mmol), separately added AgOTf solution (0.514 g, 2.00 mmol) in 2 :2 stoichimetric ratio was added and refluxed for 15 min, AgCl so precipitated was filtered off over a G4 crucible. This solution was kept in Ar- atmosphere. To a methanolic solution of DTBcatechol (0.230 g, 1.00 mmol) two drops of NEt3 added and the colour changes to pale violet in most cases. This solution was then added to the above solution and the resulting mixture was stirred for 1h under argon. The solution was then evaporated to half its original volume, cooled to room temperature, filtered and then washed thoroughly with diethyl ether and dried in *vacuo*. The yield was 60%. In case of 10-13 complexes the stoichiometric ration are [Au(Br)2(C6F5)2]NBu4, 10, (0.933 g, 1.00 mmol), [Au(Br)2(C6F5)(PPh3)], 11, (0.786 g, 1.00 mmol), [Au(Br)2(PPh3)2]ClO4, 12, (0.981 g, 1.00 mmol),

[Au(Br)3(PPh3)], 13, (0.699 g, 1.00 mmol), separately added AgOTf solution (0.514 g, 2.00 mmol) in 1:2 ratio, then DTBcatechol(0.230g, 1.00mmol) followed by NEt3, Whereas in [Au2(Cl)2(dppa)], 14, (0.850g, 1.00 mmol), [Au2(Cl)2(dppm)], 15, (0.849g, 1.00 mmol), [Au2(Cl)2(dppe)], 16, (0.863g, 1.00 mmol), separately added AgOTf solution (0.514 g, 2.00 mmol) in 1:2 ratio and then DTBcatechol(0.230g, 1.00mmol) followed by NEt3. All other complexes were prepared similarly; yield, 55-60%. Analysis for [Au(PPh3)2(5-t-But-Catecholato DTBCA)], **1**, Found: C, 49.17 , H, 3.2, Calcd. for [C48H50P2AuO2], C, 49.2, H, 3.3, IR(nujol, cm-1) (PPh3) 1100, 755, 695, 545,

(C=C) 1630 (C=O) 1525,1360,1297, ESIMS, 721(Au(PPh3)2), 31P (1H)NMR(CDCl3), ppm, 27.12; Analysis for [Au(P(Ph(o-Me))3)2(5-t-But-Catecholato DTBCA)], **2**, Found: C, 50.7, H, 3.6, Calcd. for [C50H54P2AuO2], C, 50.8, H, 3.7, IR(nujol, cm-1) (PPh3) 1100, 759, 699, 555, (C=C) 1620 (C=O) 1528,1365,1297, ESIMS,

721(Au(PPh3)2), 31P (1H)NMR(CDCl3), ppm, 25.03,; Analysis for [Au(P(Ph(m-Me))3)2(5-t-But-Catecholato DTBCA)], **3**, Found C, 50.7 (50.5), H, 3.6 (3.5) Calcd for [C50H54P2AuO2], C, 51.0, H, 3.7, IR(nujol, cm-1)

(PPh3) 1100, 759, 699, (C=C) 1620 (C=O) 1528,1365, ESIMS, 721(Au(PPh3)2), 31P (1H)NMR (CDCl3), ppm,

25.23,; Analysis for [Au(P(Ph(p-Me))3)2(DTBCA)], **4**, Found: C, 50.7, H, 3.6 Calcd for [C50H54P2AuO2], C, 50.9,

H, 3.8, IR(nujol, cm-1) (PPh3) 1100, 759, 699, (C=C) 1620 (C=O) 1528,1297, ESIMS, 721(Au(PPh3)2), 31P

(1H)NMR(CDCl3), ppm, 25.16; Analysis for [Au(P(Ph2Me))2(5-t-But-Catecholato DTBCA)], **5,** Found: C, 42.7, H, 3.3, Calcd for [C38H46P2AuO2], C, 43.0, H, 3.2, IR(nujol, cm-1) (PPh2) 1100, 759, 699, 555, (C=C) 1620 (C=O) 1528,1365,1297, 31P (1H)NMR(CDCl3), ppm, 13.03; Analysis for [Au(P(PhMe2))2 (DTBCA)], **6**, Found: C, 33.7, H, 3.3, Calcd for [C28H42P2AuO2], C, 33.8, H, 3.4; IR(nujol, cm-1) (PPh) 1100, 759, (C=C) 1620 (C=O) 1528,1365,1297, 31P (1H)NMR(CDCl3), ppm, -1.03; Analysis for [Au(P(cyclohexane)3)2(5-t-But- Catecholato DTBCA)], **7,** Found: C, 49.17, H, Calcd for [C48H48P2AuO2], C, 49.2, H, 3.4, IR(nujol, cm-1) (C=C) 1650 (C=O) 1525, 1369,1291, 31P (1H)NMR(CDCl3), ppm, 64.614;

Analysis for [Au(P(NEt2)3)2(5-t- But-Catecholato DTBCA)], **8,** Found: C, 26.27, H, 4.3, Calcd for [C36H80P2AuN6O2], C, 26.3, H, 4.4, IR(nujol, cm-1) (C=C) 1630 (C=O) 1525,1369,1291, 31P (1H)NMR(CDCl3), ppm, 134.14(singlet); Analysis for [Au(P(NMe2)3)2(5-t-But-Catecholato DTBCA)], **8a**, Found: C, 26.1, H, 4.8, Calcd for [C24H56P2AuN6O2],C, 26.0, H, 4.9, IR(nujol, cm-1) (C=C) 1630 (C=O) 1525,1369, 1291, 31P (1H)NMR(CDCl3), ppm,

104.74(singlet); Analysis for [Au(AsPh3)2(5-t-But-Catecholato DTBCA)], **9**, Found: C, 45.27, H, 3.3 Calcd for [C48H50As2AuO2], C, 45.3, H, 3.4; IR(nujol, cm-1) (C=C) 1630 (C=O) 1525,1369,1291, Analysis for NBu4[AuIII(C6F5)2(DTBCA)], **10**, Found: C, 46.3, H, 4.19, Calcd for [C40H52NF10AuO2], C, 46.2, H, 4.2, IR(nujol,

cm-1) (C6F5) 1500, 955, 800, (C=C) 1620 (C=O) 1525,1369, 19F (1H)NMR(CDCl3), ppm, 115.2(o-F), 156.2(p- F), 160.2(m-F); Analysis for [AuIII(C6F5)(PPh3)(DTBCA)], **11**, Found: C, 51.3, H, 2.9, Calcd for [C36H35F5AuO2], C, 51.4, H, 3.0; IR(nujol, cm-1) (C6F5) 1530, 955, 800, (C=C) 1620 (C=O) 1525,1369, 19F (1H)NMR(CDCl3),

ppm, 115(o-F), 156(p-F), 160(m-F); Analysis for NBu4[AuIII(PPh3)2(5-t-But-Catecholato DTBCA)], **12,** Found: C, 54.3, H, 3.9, Calcd for C48H50P2AuO2]ClO4, C, 54.2, H, 4.0; IR(nujol, cm-1) (C=C) 1620 (C=O) 1525,1369,

31P (1H)NMR(CDCl3), ppm, 46.1(major), 35(minor); Analysis for [AuIIIBr(PPh3)(5-t-But-Catecholato DTBCA)],

13, Found: C, 44.7, H, 2.9, Calcd. for [C40H35PBrAuO2], C, 44.6, H, 2.8, IR(nujol, cm-1) (PPh3) 1100, 755, 695,

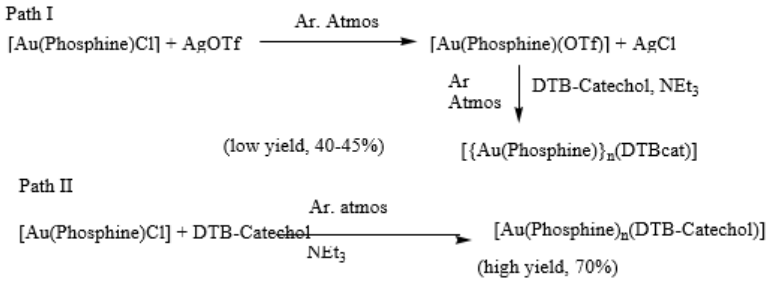
545, (C=C) 1620 (C=O) 1525,1369, 31P (1H)NMR(CDCl3), ppm, 35.24(singlet); Analysis for [AuI (dppa)(DTBCA)], **14,** Found: C, 40.3, H, 2.9, Calcd for [C H P NAu O], C, 40.4, H, 2.8, IR(nujol, cm-1) (dppa) 1100, 755, 545, (C=C) 1629 (C=O) 1525,1379, $^{31}P_2$(1H)NMR(CDCl3), ppm, 82.27(singlet); Analysis

for [AuI (dppm)(5-t-But-Catecholato DTBCA)], **15,** Found: C, 41.9, H, 2.9, Calcd for [C H P NAu O], C, 42.0, H, 3.0; IR(nujol, cm-1) (dppm) 1100, 755, (C=C) 1629, (C=O) 1525,1379, Analysis for [AuI2(dppe)(5-t-

But-Catecholato DTBCA)], **16,** Found: C, 42.7, H, 3.1, Calcd for [C38H44P2Au2O2], C, 42.8, H, 3.2; IR(nujol,

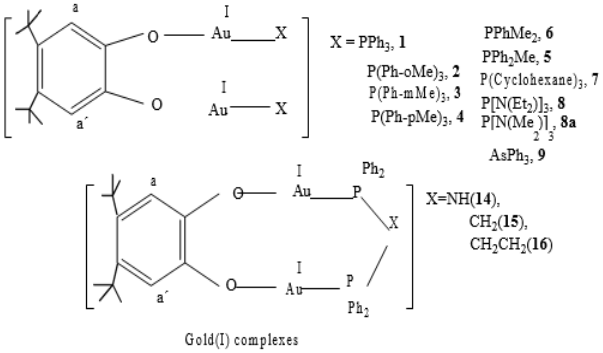
cm-1) (dppe) 1120, 755, 540, (C=C) 1620 (C=O) 1525,1369.

RESULTS & DISCUSSION



Scheme-I

Silver+- assisted dechlorination of Gold(I) and Gold(III) complexes (**1-16)** in methanol has prepared a solvated species and then addition of DTB-catechol (H2CA) (one equivalent) to this solution followed by Et3N (2.5 equivalent) under stirring condition has synthesized the title compound **1-9,10-13,14-16** (*Scheme 1*). Reaction temperature should be strictly maintained to optimize the yield of the product. At higher temperature (>1000C) the reaction gives some unidentified products. The composition of **1-9,10-13,14-16** were formulated by elemental analyses. Complexes **1-9**, **10-13** are soluble in D2O, CHCl3, MeOH which permit to measure all NMR, ES/MS Exp. But complexes **14-16** are poorly soluble in D2O, CHCl3, MeOH **(Scheme**-I, II, III).

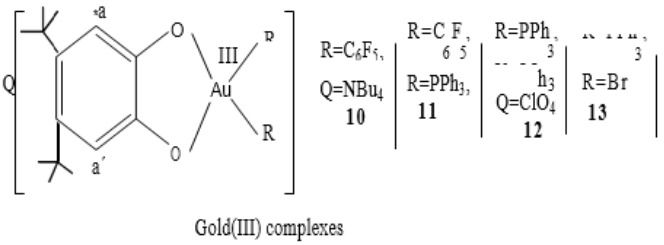


Scheme-II

Spectral study:

The infrared spectra of **1-9,10-13,14-16** complexes have been assigned on comparing with the spectra of the precursor chloro complexes and catechol. Important part of IR spectra (KBr disc, nujol) of the complexes, **1-9,10- 13,14-16** are the disappearance of stretching at 325-330 and 310-320 cm-1 correspond to AuCl configuration of the precursors. The characteristics stretchings at 1000-1200 and 1620-1630 cm-1 are assigned to □ (PPh3) and □ (C=N) + □ (C=O), respectively. A broad weak stretch at 3170-3180 cm-1 may be assigned to the stretching of water of crystallization in the solid state. The □ (C-O) appears at 1525, 1360, 1297 cm-1 in the complexes and the free catechol values are 1664, 1630, 1360, 1265 cm-1. Phosphorous n.m.r., 31 P(1H), (Fig. 1,2, measured in CDCl3) gives a concrete idea on the present series of complexes. A sharp peak assigned at 27.12 for [(Au(P(Ph3)2(5-t-But- Catecholato DTBCA)], 25.12 for [(Au(P(Ph-oMe)3)2(5-t-But-Catecholato DTBCA)], 25 for [(Au(P(Ph- mMe)3)2(5-t-But-Catecholato DTBCA)], 25.1 for [(Au(P(Ph-pMe)3)2(5-t-But-Catecholato DTBCA)], 13.12 for [(Au(P(Ph2Me)2(5-t-But-Catecholato DTBCA)], -1.1 for [(Au(PPhMe2)2 (5-t-But-Catecholato DTBCA)], 64.62 for [(Au(P(Cy3))2(5-t-But-Catecholato DTBCA)], 134.12 for [(Au(P(NEt2)3)2(5-t-But-Catecholato DTBCA)],

104.72 for [(Au (P(NMe2)3)2(5-t-But-Catecholato DTBCA)], 46.12 for [(AuIII(PPh3)2(5-t-But-Catecholato DTBCA)], 35.12 for [(AuIII(PPh3)Br(5-t-But-Catecholato DTBCA)], 82.27 for [(Au2(dppa)(5-t-But-Catecholato DTBCA)], whereas the parent chloro complex arises at 33.3 for [Au(Cl)(PPh3)], 31.29 for [(Au(Cl)(P(Ph-oMe)3], 31 for [(Au(Cl)(P(Ph-mMe)3], 17.23 for [(Au(Cl)(P(Ph2Me)], 4.23 for [(Au(Cl)(P(PhMe2)], 54.55 for [(Cl)(Au(P(Cy)3],

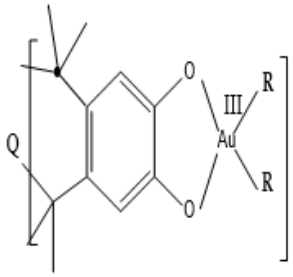


Scheme III

45.03 for [(Au(PPh3)2](ClO4), 31.31 for [(Au(Br)3(PPh3)], 41.93 (major, trans), 31.83 (minor,cis) for [(Au(Br)2(PPh3)2](ClO4), 67.27 for [(Au2(Cl)2(dppa)], respectively. These data establish the catecholato adduct linear and square planar gold phosphine product. Fluorine n.m.r., 19 F {1H}, (Fig. 1, measured in CDCl3) is much informative of the present series of complexes(**10,11)**. The fluorine atoms in each complex show three sharp signals corresponding to *ortho*, *meta* and *para* fluorine atom, respectively, of the pentafluorophenyl ring of the complexes. There are four *ortho*,

two *para,* four *meta* fluorine atom (in complex **10**) whereas in complex **11** the number is just half. The 1H n.m.r. data for the complexes and proton numbering pattern (measured in CDCl3) is shown in *Scheme 1.* Protons are assigned on the basis of spin-spin interaction, effect of substitution on PPh3 and on comparing with the spectra of precursor chloro complexes. They are broad singlet in spin interaction pattern. It may

be due to charge delocalization from coordinated catecholato ion to □-acidic phosphine. Aryl-H are affected by substituent Me; electron donating substituent –Me shifts the protons to lower □ compared with phenyl group. Catechol protons give two sharp peak near at 6.6 and 6.7 charecteristic of the product with broad multiplet at the aromatic region due to the presence of a lot of phenyl rings.



$R=C_6F_5$, $R=PPh_3$, 11

$R=PPh_3$, $R=Br$, 13

Two isomer possible for diff. conformation

Scheme-IV

The 13C (1H)NMR spectrum provides direct information about the carbon skeleton of the molecule(Fig. 1,2, measured in CDCl3). The non-protonated carbon atoms at C(PPX3, X=Ph,Cy, NEt2,NMe2,Ph2Me,PhMe2) and C(dppa) of the phosphine moiety is shifted farthest downfield in the spectrum (□ = 140.12 ppm and 138 ppm) effected by the magnetic interaction of two bulky phenyl rings environment and the methyl substituted phenyl rings and the pi electron delocalization on the aromatic ring system. Similarly the carbon atom at pentafluorophenyl ring on **10,11** molecule in the complexes resonance at a lower field of 135 ppm resulting of the conjugative effect. The methyl carbon atom of the substituted phenyl ring resonate at 20 ppm, resonably compare to the other carbon atoms resonance. The COSY spectrum reveals the 1H-1H coupling interactions in the molecule(Fig.2, measured in CDCl3). Extending horizontal and vertical lines from □ = 6.32 ppm [C(a)H] and 6.68 ppm [C(b)H] encounter cross peaks at □ = 7.12 ppm and 7.23 ppm, where the C(Ph)H and C(PhMe2)H resonances are merged into multiplets along with the phenyl ring proton resonances. The doublet of the C(a)H and C(b)H protons show coupling interaction with the multiplets at □ = 7.12 ppm and 7.68 ppm [C(Ph)H and C(Ph-Me)H].

Reactivity with BSA. In a reaction with bovine serum albumin (BSA) was performed under physiological conditions. Taking advantage of the intense absorption bands of the gold complexes and BSA, I monitored the progress of the reaction using 1:1 ratio of BSA and bufered solutions of each gold complex over 24h. Serum albumin is a major soluble protein component present in the circulatory system and has many physiological functions. Importantly, BSA acts as a carrier for various pharmacological agents. It must be noted that BSA has been extensively studied, and shares homology with human serum albumin (HSA). Ofen, gold compounds bind methionine and cysteine residues in BSA via the sulfur atoms. Te inherent absorption peaks for complexes 2–6 were minimally affected by the addition of the BSA solution over a 24h period. It is also worth pointing out that the peak corresponding to the absorption of BSA at 280nm was unafected under the experimental conditions. The ability for compound 1 to aggregate in aqueous solution limited the ability to evaluate it under the experimental conditions. However, a solution of compound 1 with BSA did not afect the peak attributed to BSA. For compound 2, while a decrease in the absorption band corresponding to MLCT at ~250nm was observed, no changes in the band at 325nm was observed in the course of the experiment. Te observed decrease is consistent with the time-dependent study of 2 in PBS. Also, the peak corresponding to BSA remained unchanged through-out the 24 h period. Complexes 3 and 6 are gold(III) compounds with cyclometalated ligands but diferent bis-phosphine ligands. Interestingly, none of the peaks associated with the complexes or BSA changed, indicative of stability in the presence of BSA over 24h. While the shoulder peak at 300nm disappeared in the case of complex 4 (LMCT), the BSA peak at 250nm was unmodifed. Complex 5 on the other hand did not display any alteration in its peak. In general, there was no indication of the formation of metallic gold as no brown precipitate formed in any of the reaction over the duration of the experiments. Using HPLC we characterized the extent of interaction of the test compounds and BSA. This approach can be used to quantify potential binding of gold compounds with BSA by evaluating the retention times and area of peaks associated with individual agents as well as reaction solutions of test compounds and BSA. Following the UV-vis studies, we used compounds 2 and 3 for the HPLC study based on the common chiral ligands but diferent oxidation states. There were

no changes in the peaks, indicative of no covalent modifcation of BSA or changes to the gold compounds. Tese compounds by virtue of their coordinated ligands and cyclometalation demonstrate high stability even towards proteins like BSA. Detailed studies by Minghetti and co- workers99-118 on the reactivity of selected gold(III) complexes with serum albumin under similar experimental conditions showed varied stability of the gold complexes in the presence of BSA. This result has important implications for the pharmacological activity of these gold complexes, in that they can avoid premature deactivation until they reach their target and also reduce of-target efects.

Cellular toxicity studies.

The antiproliferative properties of these gold complexes were evaluated in a panel of cancerous cell lines using crystal violet assay. We used an ATP-dependent luminescence cell assay, cell titre glo, cells. To extend the therapeutic utility of these novel drug candidates, we performed cytotoxicity studies with normal retinal pigment epithelium, RPE-NEO. Auranofn and cisplatin were used as controls. We obtained dose-response curves from the cell viability experiments and subsequently derived IC50 values (concentration required to kill 50% of cells). Complexes 1–6 displayed high nanomolar to low micromolar cell killing which are 2–10 folds better than cisplatin. None of the gold-phosphine complexes display cross-resistance evidenced by indiferent toxicities in cis-platin resistant cells, including the well- characterized high grade-serous ovarian cancer cell line, which demonstrate the example of high potency of these novel Au complexes in clinically relevant tumor cells. Generally, the gold compounds studied are slightly less potent toward RPE-Neo cells, indicative of selective toxicity for cancerous cells compared.

In conclusion, in this work we have synthesised and characterized seventeen gold-phosphine mixed ligand complexes using 5-t-But-Catecholato DTBcatecholate ion (CA2-). The CA2- is a well known chelating as well as bridging ligand. In this case it forms Gold(I) two coordinate linear complexes and Gold(III) square planar four coordinate complexes with quinonoid end. The complexes are fully charecterised by IR, 1H NMR, 19F (1H)NMR, 31P (1H)NMR, 13C (1H)NMR, 1H-1H COSY NMR and ESIMS mass spectrometry. 31P (1H)NMR technique helps to get the correct assignment regarding new the complex nature.

I thank the Ministerio de Ciencia y Technologia (Spain) for financial support (CTQ2005-08099-CO3-01, Grant no. SB2004-0060) and Prof. M Laguna, C Sinha for constant help. Department of Science and Technology (DST) is thanked for financial support. (FAST TRACK Grand No. **SERB/F/4888/2012-13 Dated 30.11.2012,** Project Title:GOLD(I) & GOLD(III) ARYLAZOIMIDAZOLE (N, N DONAR) & OXO COMPLEXES: SYNTHESIS, STRUCTURE, SPECTRAL STUDY, ELECTROCHEMISTRY AND CHEMICAL REACTIVITY).

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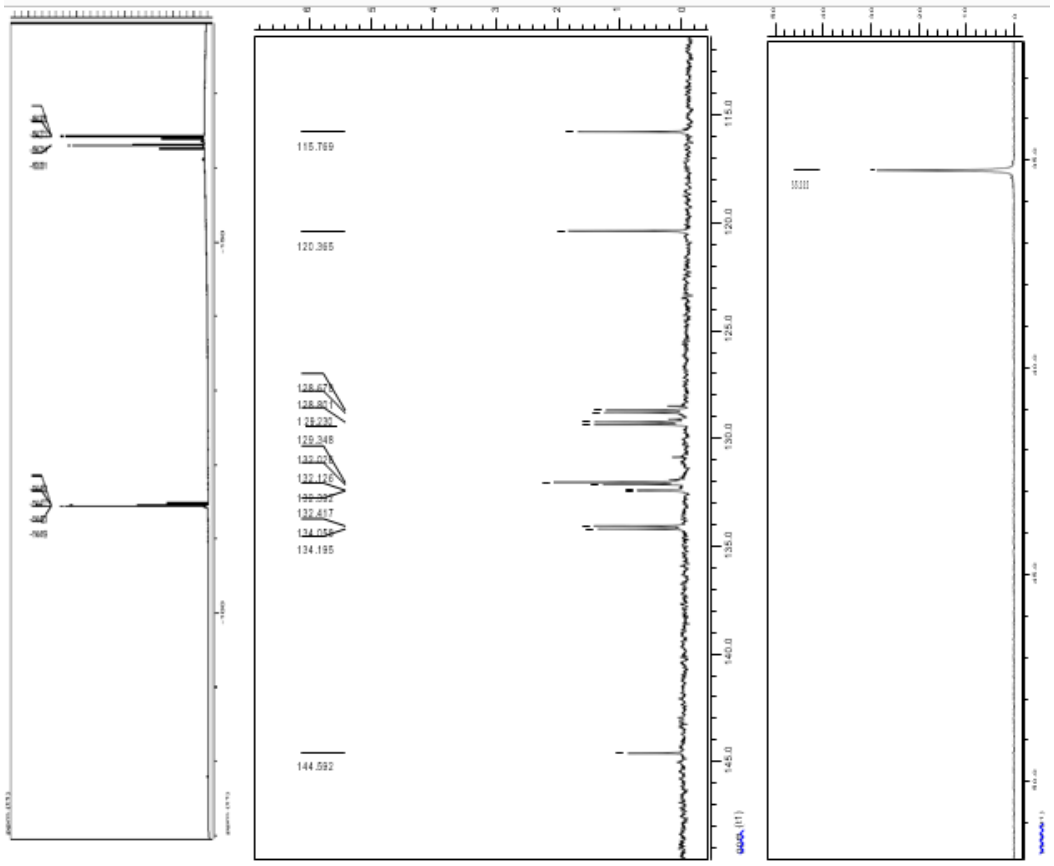
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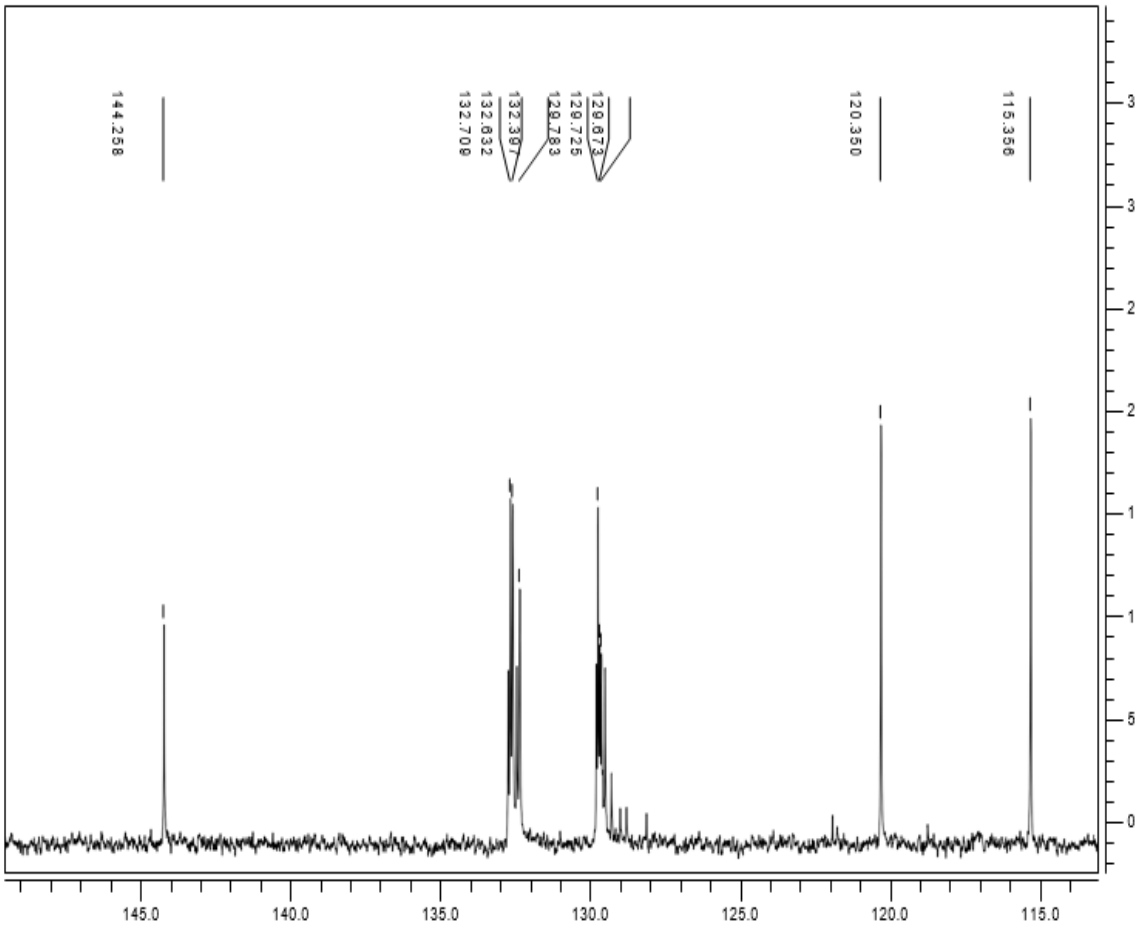
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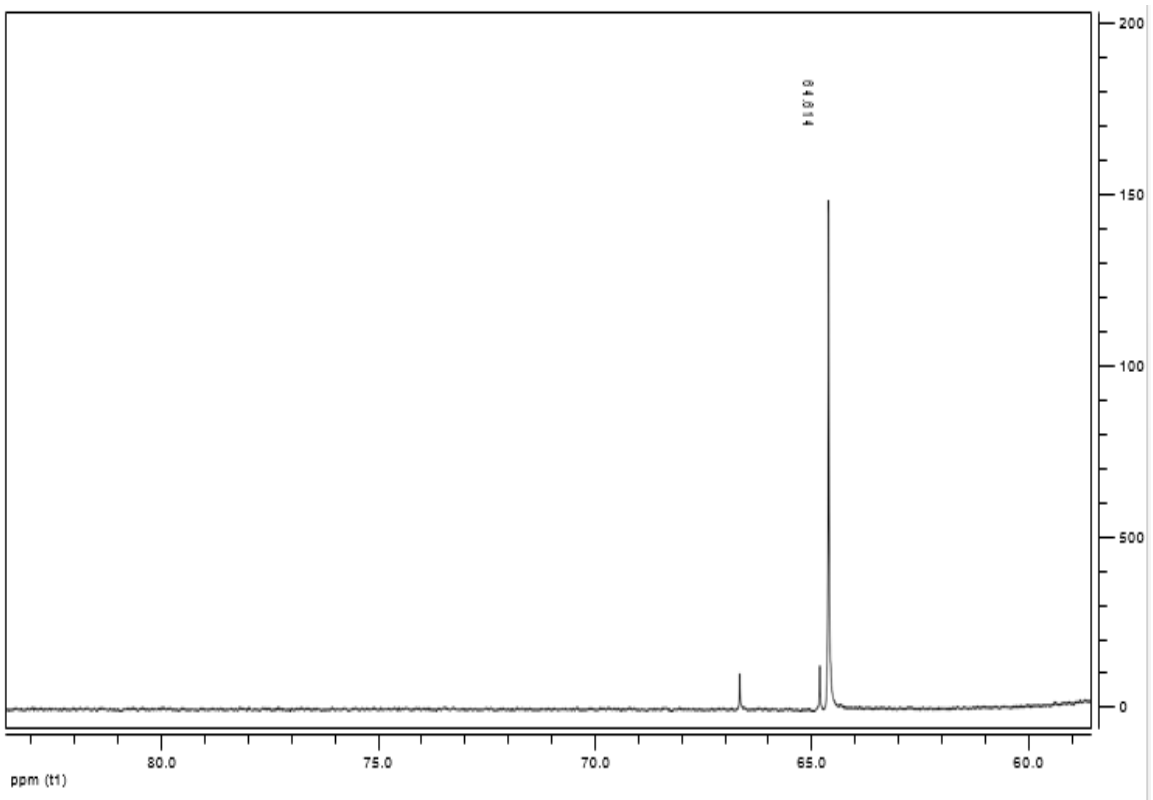

Fig1. ^{19}F of **10,**, ^{13}C&^{31}P (H)NMR of **13**,^{31}P(H)NMR of **5** ^{13}C of **5**, ^{31}P (H)NMR of **7**