Indian Journal of Chemistry
Vol. 63, April 2024, pp. 407-412
DOI: 10.56042/ijc.v63i4.4655

5-*t*-But-catecholato (DTBcat)-gold-phosphine-complexes: Synthesis and spectral study

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Received 7 April 2023; accepted (revised) 19 January 2024

Ag^+- assisted dechlorination of Gold(I) and Gold(III) phosphine complexes followed by the reaction with 5-*t*-but-catecholato (DTBcat)- (H_2CA) in presence of Et_3N gives 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 ESI-MS, IR and multinuclear NMR (^1H, ^{13}C, ^{19}F; ^{31}P) spectroscopic studies. In addition, bi-dimensional NMR studies such as ^1H ^1H COSY permit a complete assignment of the complexes in the solution phase.

Keywords: Gold(I), Gold(III), catechol, phosphine, ^1H, ^{13}C, ^{19}F, ^{31}P, COSY, NMR, ESI-MS

The coordination chemistry of quinonoid systems are important because of their existence in various redox state (catechole (CQ)/semiquinone (SQ)/quinone (RQ)), their application in optoelectronic communication, biological model study, DNA intercalation *etc*[1-15]. A common feature of the metal-RQ chemistry is delocalization of active electrons between the metal and the quinonoid ligand. This is mainly due to closer energy of quinonoid based ligands to those of metal based dπ-orbitals and recently much effort has been devoted to the study of the electrochemical and spectroscopic properties of ruthenium complexes. The presence of π-acidic co-ligands like CO[4], pyridines (R-Py), α-diimines (bpy, phen, tpy)[5-15], PPh_3[2,3,6], and 2-(arylazo) pyridines[7] efficiently control the energy of metal dπ levels. Various approaches have been chosen to establish the participation of metal, co-ligand 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 L^{2-} the isolation of monomeric complexes are difficult. In continuation of comprehensive studies on chemistry of catecholato system in this article, some Gold(I) and Gold(III) phosphine complexes of catecholates are described. The complexes are well characterized by IR, ^1H NMR, ^{19}F (^1H) NMR, ^{31}P (^1H) NMR, ^{13}C (^1H) NMR, ^1H-^1H COSY NMR and mass spectrometry.

Experimental Section

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 $CDCl_3$ were obtained on a Bruker 500 MHz FT-NMR spectrometer using $SiMe_4$ 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 N_2 atmosphere at 298 K.

Preparation and analysis of complexes

To a series of methanolic suspension of Gold-phosphine complexes, $[Au(Cl)(PPh_3)_2]$, **1**, (0.990 g, 2.00 mmol), $[Au(Cl)(P(Ph\text{-}oMe)_3)_2]$, **2**, (1.074 g, 2.00 mmol), $[Au(Cl)(P(Ph\text{-}mMe)_3)_2]$, **3**, (1.074 g, 2.00 mmol), $[Au(Cl)(P(Ph\text{-}pMe)_3)_2]$, **4**, (1.074g, 2.00mmol), $[Au(Cl)(P(Ph_2Me)_2]$, **5**, (0.866g, 2.00mmol), $[Au(Cl)(P(PhMe_2)_2]$, **6**, (0.741 g, 2.00 mmol), $[Au(Cl)(P(Cy\text{-}hx)_3)_2]$, **7**, (1.020g, 2.00mmol), $[Au(Cl)(P(NEt_2)_3)_2]$, **8**, (0.955 g, 2.00 mmol), $[Au(Cl)(P(NMe_2)_3)_2]$, **8a**, (0.791 g, 2.00 mmol), $[Au(Cl)(AsPh_3)_2]$, **9**, (1.076 g, 2.00 mmol), separately added AgOTf solution (0.514 g,

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2.00 mmol) in 2:2 stoichiometric 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 DTB catechol (0.230 g, 1.00 mmol) two drops of NEt_3 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 1 h 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 ratio are $[Au(Br)_2(C_6F_5)_2]NBu_4$, **10**, (0.933 g, 1.00 mmol), $[Au(Br)_2(C_6F_5)(PPh_3)]$, **11**, (0.786 g, 1.00 mmol), $[Au(Br)_2(PPh_3)_2]ClO_4$, **12**, (0.981 g, 1.00 mmol), $[Au(Br)_3(PPh_3)]$, **13**, (0.699 g, 1.00 mmol), separately added AgOTf solution (0.514 g, 2.00 mmol) in 1:2 ratio, then DTB catechol (0.230g, 1.00mmol) followed by NEt_3, Whereas in $[Au_2(Cl)_2$ (dppa)], **14**, (0.850g, 1.00 mmol), $[Au_2(Cl)_2$(dppm)], **15**, (0.849g, 1.00 mmol), $[Au_2(Cl)_2$(dppe)], **16**, (0.863g, 1.00 mmol), separately added AgOTf solution (0.514 g, 2.00 mmol) in 1:2 ratio and then DTB catechol(0.230g, 1.00mmol) followed by NEt_3. All other complexes were prepared similarly; yield, 55-60%. Analysis for $[Au(PPh_3)_2$(5-*t*-But-Catecholato DTBCA)], **1**, Found: C, 49.17 , H, 3.2, Calcd. for $[C_{48}H_{50}P_2AuO_2]$, C, 49.2, H, 3.3, IR(nujol, cm^{-1}) ν(PPh_3) 1100, 755, 695, 545, ν(C=C) 1630 ν(C=O) 1525,1360,1297, ESI-MS, 721 ($Au(PPh_3)_2$), ^{31}P (^{1}H) NMR($CDCl_3$), 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 $[C_{50}H_{54}P_2AuO_2]$, C, 50.8, H, 3.7, IR(nujol, cm^{-1}) ν(PPh_3) 1100, 759, 699, 555, ν(C=C) 1620 ν(C=O) 1528,1365,1297, ESI-MS, 721($Au(PPh_3)_2$), ^{31}P (^{1}H) NMR($CDCl_3$), 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 $[C_{50}H_{54}P_2AuO_2]$, C, 51.0, H, 3.7, IR(nujol, cm^{-1}) ν(PPh_3) 1100, 759, 699, ν(C=C) 1620 ν(C=O) 1528,1365, ESI-MS, 721($Au(PPh_3)_2$), ^{31}P (^{1}H) NMR ($CDCl_3$), ppm, 25.23,; Analysis for [Au(P(Ph(p-Me))$_3$)$_2$(DTBCA)], **4**, Found: C, 50.7, H, 3.6 Calcd for $[C_{50}H_{54}P_2AuO_2]$, C, 50.9, H, 3.8, IR(nujol, cm^{-1}) ν(PPh_3) 1100, 759, 699, ν(C=C) 1620, ν(C=O) 1528,1297, ESI-MS, 721($Au(PPh_3)_2$), ^{31}P (^{1}H) NMR ($CDCl_3$), ppm, 25.16; Analysis for [Au(P(Ph$_2$Me))$_2$(5-*t*-But-Catecholato DTBCA)], **5,** Found: C, 42.7, H, 3.3, Calcd. for $[C_{38}H_{46}P_2AuO_2]$, C, 43.0, H, 3.2, IR(nujol, cm^{-1}) ν(PPh_2) 1100, 759, 699, 555, ν(C=C) 1620 ν(C=O) 1528,1365,1297, ^{31}P (^{1}H) NMR($CDCl_3$), ppm, 13.03; Analysis for [Au(P(PhMe$_2$))$_2$ (DTBCA)], **6**, Found: C, 33.7, H, 3.3, Calcd. for $[C_{28}H_{42}P_2AuO_2]$, C, 33.8, H, 3.4; IR(nujol, cm^{-1}) ν(PPh) 1100, 759, ν(C=C) 1620 ν(C=O) 1528,1365,1297, ^{31}P (^{1}H) NMR($CDCl_3$), ppm, –1.03; Analysis for [Au(P(cyclohexane)$_3$)$_2$(5-*t*-But-Catecholato DTBCA)], **7,** Found: C, 49.17, H, Calcd. for $[C_{48}H_{48}P_2AuO_2]$, C, 49.2, H, 3.4, IR(nujol, cm^{-1}) ν(C=C) 1650 ν(C=O) 1525, 1369,1291, ^{31}P (^{1}H) NMR($CDCl_3$), ppm, 64.614; Analysis for [Au(P(NEt$_2$)$_3$)$_2$(5-*t*-But-Catecholato DTBCA)], **8,** Found: C, 26.27, H, 4.3, Calcd. for $[C_{36}H_{80}P_2AuN_6O_2]$, C, 26.3, H, 4.4, IR(nujol, cm^{-1}) ν(C=C) 1630 ν(C=O) 1525,1369,1291, ^{31}P (^{1}H) NMR($CDCl_3$), ppm, 134.14(singlet); Analysis for [Au(P(NMe$_2$)$_3$)$_2$(5-*t*-But-Catecholato DTBCA)], **8a**, Found: C, 26.1, H, 4.8, Calcd. for $[C_{24}H_{56}P_2AuN_6O_2]$,C, 26.0, H, 4.9, IR(nujol, cm^{-1}) ν(C=C) 1630 ν(C=O) 1525,1369, 1291, ^{31}P (^{1}H) NMR($CDCl_3$), ppm, 104.74(singlet); Analysis for [Au(AsPh$_3$)$_2$(5-*t*-But-Catecholato DTBCA)], **9**, Found: C, 45.27, H, 3.3 Calcd. for $[C_{48}H_{50}As_2AuO_2]$, C, 45.3, H, 3.4; IR(nujol, cm^{-1}) ν(C=C) 1630 ν(C=O) 1525, 1369,1291, Analysis for NBu$_4$[Au^{III}(C$_6$F$_5$)$_2$ (DTBCA)], **10**, Found: C, 46.3, H, 4.19, Calcd. for $[C_{40}H_{52}NF_{10}AuO_2]$, C, 46.2, H, 4.2, IR(nujol, cm^{-1}) ν(C_6F_5) 1500, 955, 800, ν(C=C) 1620 ν(C=O) 1525,1369, ^{19}F (^{1}H) NMR($CDCl_3$), ppm, 115.2(o-F), 156.2(p-F), 160.2(m-F); Analysis for [Au^{III}(C$_6$F$_5$)(PPh$_3$)(DTBCA)], **11**, Found: C, 51.3, H, 2.9, Calcd. for $[C_{36}H_{35}F_5AuO_2]$, C, 51.4, H, 3.0; IR(nujol, cm^{-1}) ν(C_6F_5) 1530, 955, 800, ν(C=C) 1620 ν(C=O) 1525,1369, ^{19}F (^{1}H) NMR ($CDCl_3$), ppm, 115(o-F), 156(p-F), 160(m-F); Analysis for NBu$_4$[Au^{III}(PPh$_3$)$_2$(5-*t*-But-Catecholato DTBCA)], **12,** Found: C, 54.3, H, 3.9, Calcd. for $C_{48}H_{50}P_2AuO_2]$ ClO_4, C, 54.2, H, 4.0; IR(nujol, cm^{-1}) ν(C=C) 1620 ν(C=O) 1525,1369, ^{31}P (^{1}H) NMR($CDCl_3$), ppm, 46.1(major), 35(minor); Analysis for [Au^{III}Br(PPh$_3$)(5-*t*-But-Catecholato DTBCA)], **13,** Found: C, 44.7, H, 2.9, Calcd. for $[C_{40}H_{35}PBrAuO_2]$, C, 44.6, H, 2.8, IR(nujol, cm^{-1}) ν(PPh_3) 1100, 755, 695, 545, ν(C=C) 1620 ν(C=O) 1525,1369, ^{31}P (^{1}H) NMR($CDCl_3$), ppm, 35.24(singlet); Analysis for [Au$^{I}_2$(dppa)(DTBCA)], **14,** Found: C, 40.3, H, 2.9, Calcd. for $[C_{36}H_{41}P_2NAu_2O_2]$, C, 40.4, H, 2.8, IR(nujol, cm^{-1}) ν(dppa) 1100, 755, 545, ν(C=C) 1629 ν(C=O) 1525,1379, ^{31}P (^{1}H) NMR($CDCl_3$), ppm, 82.27(singlet); Analysis for [Au$^{I}_2$(dppm)(5-*t*-But-Catecholato DTBCA)], **15,** Found: C, 41.9, H, 2.9, Calcd. for $[C_{37}H_{42}P_2NAu_2O_2]$, C, 42.0, H, 3.0; IR(nujol, cm^{-1}) ν(dppm) 1100, 755, ν(C=C) 1629, ν(C=O) 1525,1379, Analysis for $[Au^{I}_2(dppe)($ 5-*t*-But-Catecholato DTBCA)], **16,** Found: C, 42.7, H, 3.1, Calcd. for $[C_{38}H_{44}P_2Au_2O_2]$, C, 42.8, H, 3.2; IR(nujol, cm^{-1}) ν(dppe) 1120, 755, 540, ν(C=C) 1620 ν(C=O) 1525,1369.

Results and Discussion

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 (H_2CA) (one equivalent) to this solution followed by Et_3N (2.5 equivalent) under stirring condition leads to the synthesis of 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 (>100°C), 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 D_2O, $CHCl_3$, MeOH which permit to measure all NMR, ES/MS Exp. But complexes **14-16** are poorly soluble in D_2O, $CHCl_3$, MeOH (Scheme — 1, 2, 3).

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

Path I

$$[\mathrm{Au(Phosphine)Cl}] + \mathrm{AgOTf} \xrightarrow{\text{Ar. Atmos}} [\mathrm{Au(Phosphine)(OTf)}] + \mathrm{AgCl}$$

$$\Big\downarrow \overset{\text{Ar}}{\text{Atmos}} \;\; \text{DTB-Catechol, NEt}_3$$

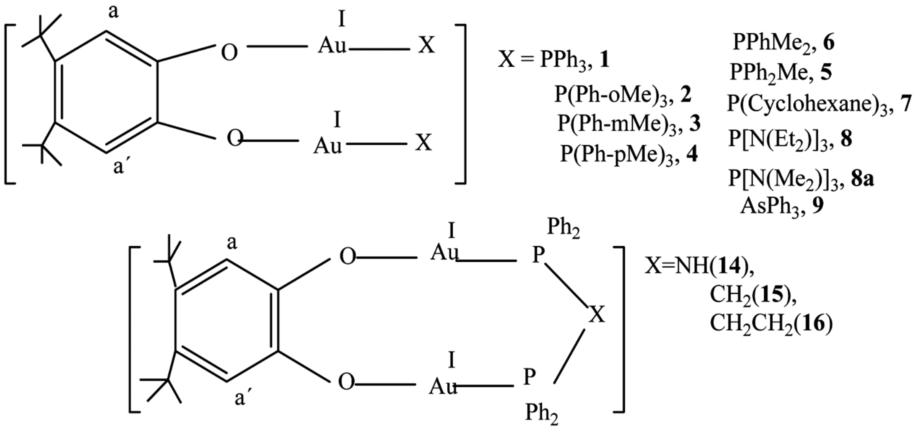
(low yield, 40-45%) $[\{\mathrm{Au(Phosphine)}\}_n(\mathrm{DTBcat})]$

Path II

$$[\mathrm{Au(Phosphine)Cl}] + \text{DTB-Catechol} \xrightarrow[\mathrm{NEt_3}]{\text{Ar. atmos}} [\mathrm{Au(Phosphine)}_n(\text{DTB-Catechol})]$$

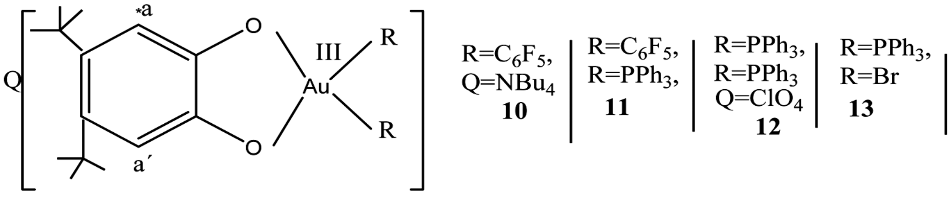
(high yield, 70%)

Scheme 1 — Scheme for synthesis of title compound



Gold(I) complexes

Scheme 2 — Scheme for synthesis of Gold(I) complexes



Gold(III) complexes

Scheme 3 — Scheme for synthesis of Gold(III) complexes 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} that correspond to AuCl configuration of the precursors. The characteristics stretchings at 1000-1200 and 1620-1630 cm^{-1} are assigned to ν (PPh$_3$) and ν (C=N) + ν (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 ν (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(^{1}H), (Fig. 1 and 2, measured in CDCl$_3$) gives a concrete idea on the present series of complexes. A sharp peak assigned at 27.12 for [(Au(P(Ph$_3$)$_2$(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(Ph$_2$Me)$_2$(5-*t*-But-Catecholato DTBCA)], -1.1 for [(Au(PPhMe$_2$)$_2$ (5-*t*-But-Catecholato DTBCA)], 64.62 for [(Au(P(Cy$_3$))$_2$(5-*t*-But-Catecholato DTBCA)], 134.12 for [(Au(P(NEt$_2$)$_3$)$_2$ (5-*t*-But-Catecholato DTBCA)], 104.72 for [(Au (P(NMe$_2$)$_3$)$_2$(5-*t*-But-Catecholato DTBCA)], 46.12 for [(Au^{III}(PPh$_3$)$_2$(5-*t*-But-Catecholato DTBCA)], 35.12 for [(Au^{III}(PPh$_3$)Br(5-*t*-But-Catecholato DTBCA)], 82.27 for [(Au$_2$(dppa)(5-*t*-But-Catecholato DTBCA)], whereas the parent chloro complex arises at 33.3 for [Au(Cl)(PPh$_3$)], 31.29 for [(Au(Cl)(P(Ph-oMe)$_3$], 31 for [(Au(Cl)(P(Ph-mMe)$_3$], 17.23 for [(Au(Cl) (P(Ph$_2$Me)], 4.23 for [(Au(Cl)(P(PhMe$_2$)], 54.55 for [(Cl)(Au(P(Cy)$_3$], 45.03 for [(Au(PPh$_3$)$_2$](ClO$_4$), 31.31 for [(Au(Br)$_3$(PPh$_3$)], 41.93 (major, trans), 31.83 (minor,cis) for [(Au(Br)$_2$(PPh$_3$)$_2$](ClO$_4$), 67.27 for [(Au$_2$(Cl)$_2$(dppa)], respectively. These data establish the catecholato adduct linear and square planar gold phosphine product.

Fluorine NMR, ^{19} F {^{1}H}, (Fig. 1, measured in CDCl$_3$) 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 ^{1}H NMR data for the complexes and proton numbering pattern (measured in CDCl$_3$) is shown in Scheme 1. Protons are assigned on the basis of spin-spin interaction, effect of substitution on PPh$_3$ 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 π-acidic phosphine. Aryl-H are affected by substituent Me; electron

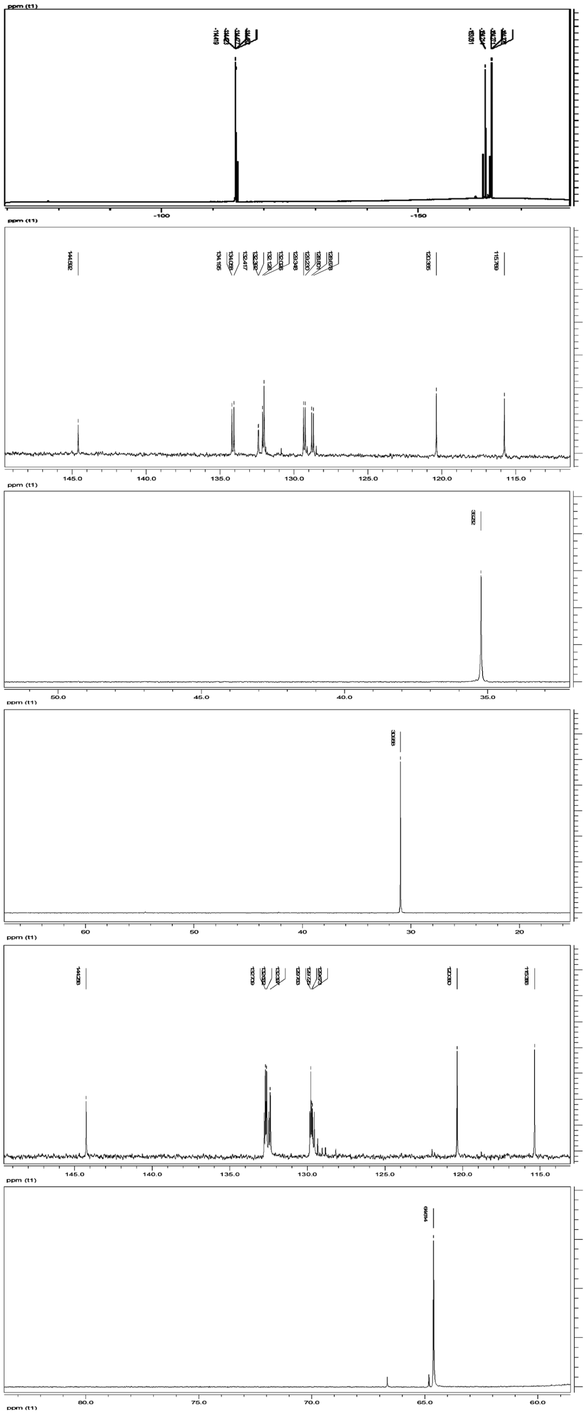


Fig. 1 — ^{19}F of **10**,, ^{13}C and ^{31}P (H) NMR of **13**,^{31}P(H) NMR of **5** ^{13}C of **5**, ^{31}P (H) NMR of **7**

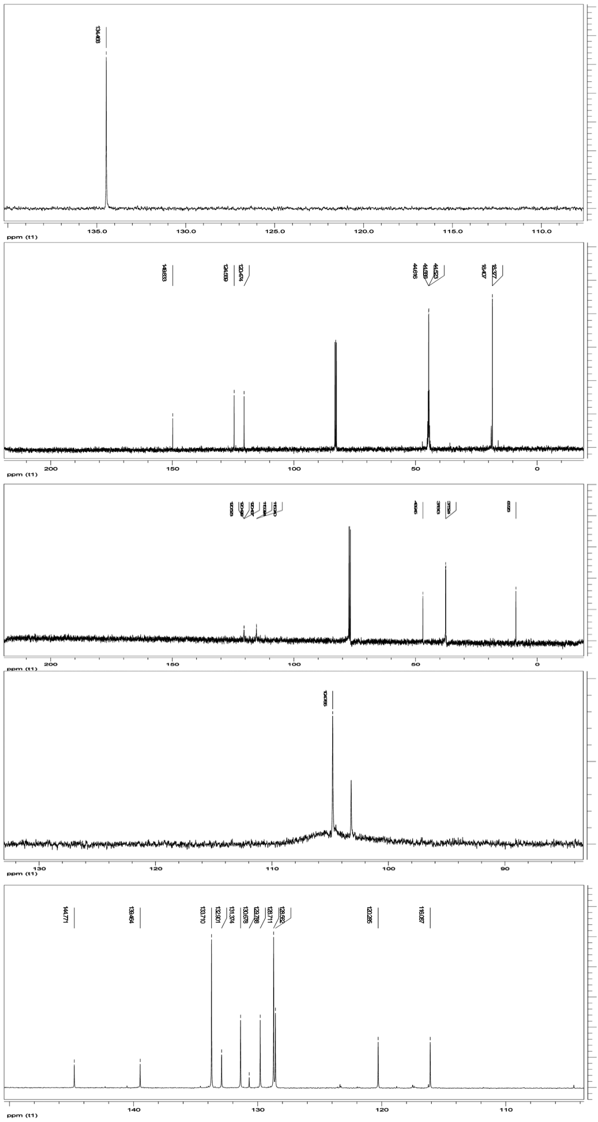
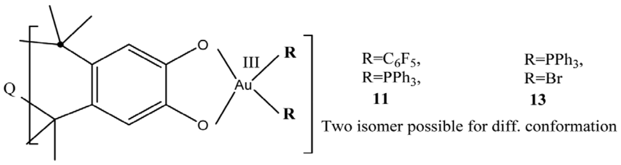


Fig. 2 — ^{31}P and ^{13}C NMR of **8**, ^{13}C and ^{31}P (H) NMR of **8a** ^{13}C (^{1}H) NMR of **9.**

donating substituent –Me shifts the protons to lower δ compared with phenyl group. Catechol protons give two sharp peak near at 6.6 and 6.7 characteristic of the product with broad multiplet at the aromatic region due to the presence of a lot of phenyl rings.

The ^{13}C (^{1}H) NMR spectrum provides direct information about the carbon skeleton of the molecule (Fig. 1, 2 measured in CDCl$_3$). The non-protonated carbon atoms at C(PPX$_3$, X=Ph,Cy, NEt$_2$,NMe$_2$, Ph$_2$Me,PhMe$_2$) and C(dppa) of the phosphine moiety is shifted farthest downfield in the spectrum (δ = 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, reasonably compared to the other carbon atoms resonance. The possible isomers from two different conformations of the complex are shown in Scheme 4. The COSY spectrum reveals the ^{1}H-^{1}H coupling interactions in the molecule (Fig. 2, measured in CDCl$_3$). Extending horizontal and vertical lines from δ = 6.32 ppm [C(a)H] and 6.68 ppm [C(b)H] encounter cross peaks at δ = 7.12 ppm and 7.23 ppm, where the C(Ph)H and C(PhMe$_2$)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 δ = 7.12 ppm and 7.68 ppm [C(Ph)H and C(Ph-Me)H].



Scheme 4 — Possible isomers for different conformations

Conclusions

In conclusion, in this work we have synthesised and characterized seventeen gold-phosphine mixed ligand complexes using 5-*t*-But-Catecholato DTBcatecholate ion (CA^{2-}). The CA^{2-} 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 characterised by IR, ^{1}H NMR, ^{19}F (^{1}H) NMR, ^{31}P (^{1}H) NMR, ^{13}C (^{1}H) NMR, ^{1}H-^{1}H COSY NMR and ESI-MS mass spectrometry. ^{31}P (^{1}H) NMR technique helps to get the correct assignment regarding new the complex nature.

Acknowledgements

The author thanks the Ministerio de Ciencia y Technologia (Spain) for financial support (CTQ2005-08099-CO3-01, Grant no. SB2004-0060) and Prof. M Laguna and C Sinha for constant help. Department of Science and Technology (DST) is thanked for financial support (Fast Track Grant No. SERB/F/4888/2012-13 Dated 30.11.2012, Project Title: Gold(I) and Gold(III)

Arylazoimidazole (N, N Donar) and Oxo Complexes: Synthesis, Structure, Spectral Study, Electrochemistry and Chemical Reactivity).

References

1 (a) Pierpont C G, Buchanan R M, *Coord Chem Rev*, 38 (1981) 45; (b) Kuzmina *et al* Metalloorg. Khim, 2 (1989) 1179

2 Churchill M R, Keil K M,.Bright F V, Pandey S, Baker G A, Keister J B*, Inorg Chem*, 39 (2000) 5807.

3 Churchill M R, Keil K M, Gilmartin B P, Schuster J T, Keister J B & Janik T S, *Inorg Chem*, 40 (2001) 4361.

4 Lever A B P, Auburn P R, Dodsworth E S, Liu W, Melnik M & Nevin W A*, J Am Chem Soc*, 110 (1988) 8076.

5 Stufkens D J, Snoeck T L & Lever A B P, *Inorg Chem,* 27 (1988) 953.

6 Masui H, Lever A B P & Auburn P R, *Inorg Chem,* 30 (1991) 2402.

7 Bag N, Pramanik A, Lahiri G K & Chakravorty A, *Inorg Chem*, 31(1992) 40.

8 Kitagawa S & Kawata S, *Coord Chem Rev*, 224 (2002) 11.

9 Armentano D, Munno G D, Lloret F, Palli A V, Julve M*, Inorg Chem*, 41 (2002) 2007.

10 Kabir M K, Kawahara M, Kumagai H, Adachi K, Kawata S, Ishii T, Kitagawa S, *Polyhedron,* 20 (2001) 1417.

11 Kawata S, Kitagawa S, Kumagai H, Kudo C, Kamesaki H, Ishiyama T, Suzuki R, Kando M & Katada M, *Inorg Chem*, 35 (1996) 4449.

12 Uson R & Laguna A, *Organomet Synth,* 3 (1985) 325.

13 Uson R, Laguna A, Laguna M, Jimenez J & Durana E, *lnorg Chim Acta,* 168 (1990) 89.

14 Contel M, Jimenez L, Jones P.G, Laguna A & Laguna M, *J Chem Soc Dalton Trans,* (1994) 2515.

15 Uson R, Laguna A, Laguna M, Jinenez J, Gomez M P, Silfinz A & Jones P G, *J Chem Soc Dalton Trans,* (1990) 3457.