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# Syntheses of Au(III) and Au(I) Complexes of 3,4,5,6-Tetraphenyl-2,2´-bipyridine

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## Abstract

Treatment of the ligand 3,4,5,6-tetraphenyl-2,2´-bipyridine (LH) **VIII** with $HAuCl_4$ in acetonitrile afforded the cyclometallated square-planar Au(III) complex $[LAuCl]ClO_4$ (**7**) containing the anionic tridentate (N^N^C) ligand, *via* orthometallation. Treatment of (**7**) with 4-dimetylaminopyridine (DMAP) and $AgClO_4$ in acetonitrile produced $[LAu(DMAP)][ClO_4]_2$ (**8**), showing the same coordination mode. Analogous complex $[LAu(PPh_3)][ClO_4]_2$ (**9**) was prepared by using $PPh_3$ instead of DMAP. Reaction of **VIII** with $HAuCl_4$ at room temperature in aqueous acetonitrile resulted the non-cyclometallated Au(III) complex $[(LH)AuCl_2]Cl$ (**10**), in which **VIII** is a bidentate (N^N) ligand. Treatment of **VIII** with the filtrate obtained by mixing $[AuCl(PPh_3)]$ and $AgO_2CCF_3$ in acetone resulted the non-cyclometallated Au(I) complex $[(LH)Au(PPh_3)]O_2CCF_3$ (**11**) having bidentate (N^N) ligand. Above complexes were adequately characterized by a combination of elemental analysis, IR, Mass and NMR spectroscopy. The X-ray crystal structures of (**7**) and (**8**) were determined.

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## Introduction

Although gold has been known for centuries, the past two decades have witnessed a renaissance of gold chemistry and it has become one of the most popular areas of research and technology (Raubenheimer & Schmidbaur, 2014). Both gold(I) and gold(III) complexes have found applications in catalysis (Raubenheimer & Schmidbaur, 2014; Rocchigiani & Bochmann, 2021; Nijamudheen & Datta, 2020; Collado, 2021; Casini & Thomas, 2021) and nanotechnology (Raubenheimer & Schmidbaur, 2014; Daniel & Astruc, 2004). Medicinal applications of gold complexes are well documented (Casini & Thomas, 2021; Casini et al, 2010; Palanichamy et al, 2012; Yeo et al, 2018; Abás et al, 2021; Galassi et al, 2021; Neu et al, 2018). For example, auranofin, myocrisin and solganol (Figure 1) are being used to treat arthritis (Abás et al, 2021).

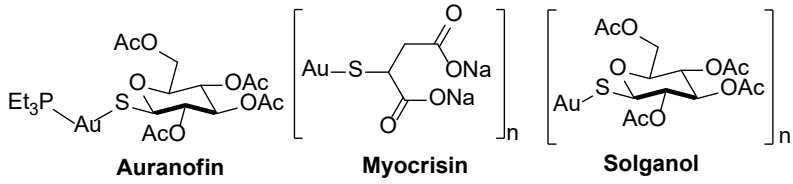



**Figure 1.** Molecular structures of gold(I)-based drugs

These antiarthritic gold(I) complexes have shown significant antitumor properties as both cancer and rheumatoid arthritis are associated with uncontrolled inflammatory processes. Au(III) complexes (**1**) – (**3**) (Figure 2), bearing bipyridyl-type ligands, have exhibited promising anti-cancer properties (Palanichamy et al, 2012; Casini et al, 2010; Yeo et al, 2018).

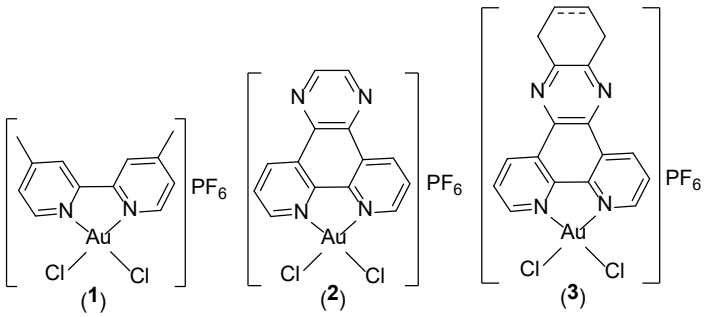



**Figure 2.** Molecular structures of Au(III) salts (**1**) - (**3**)

Recently, cyclometallated dithiocarbamate Au(III) complexes of the type (**4**) derived from 2-phenyl pyridine (Figure 3) were evaluated as potential antimicrobial drugs (Abás et al, 2021). Triphenylphosphine-Au(I) complexes (**5**) and (**6**) with the P-Au-N bonds around the metal centre (Figure 3) showed anticancer activity by inhibiting DHFR (dihydrofolate reductase) and TrxR (thioredoxin reductase) in breast cancer cells (Galassi et al, 2021).

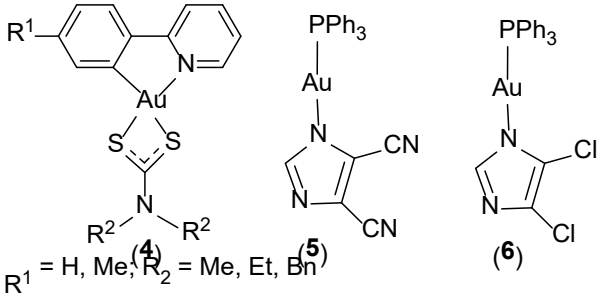



**Figure 3.** Molecular structures of complexes (**4**) - (**6**)

Cyclometallated Au(III) complexes containing pyridine and bipyridine ligands have shown interesting photophysical properties (Kumar & Nevado, 2017; Bronner & Wenger, 2011; Chan et al, 2021; Kumar et al, 2017).

Cyclometallated Au(III) complexes containing (i) a bidentate (C^N)Au unit, (ii) tridentate units such as (C^C^N)Au, (C^N^C)Au and (C^N^N)Au, and (iii) tridentate salts containing (N^N^N)Au unit derived from pyridine, bipyridine and terpyridine derivatives

were well reviewed (Bronner & Wenger, 2011; Kumar et al, 2017). Some of the basic ligand types (**I**-**VII**) are depicted in Figure 4.

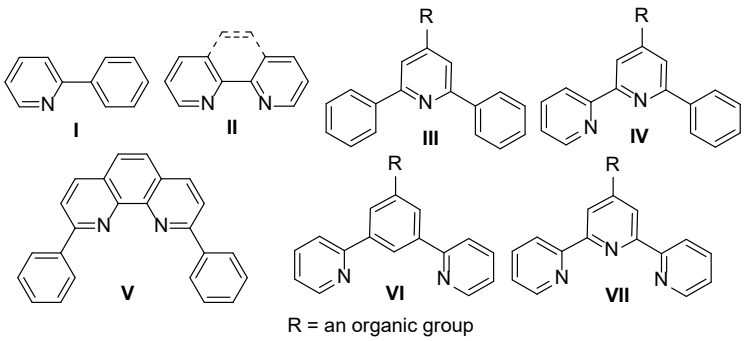
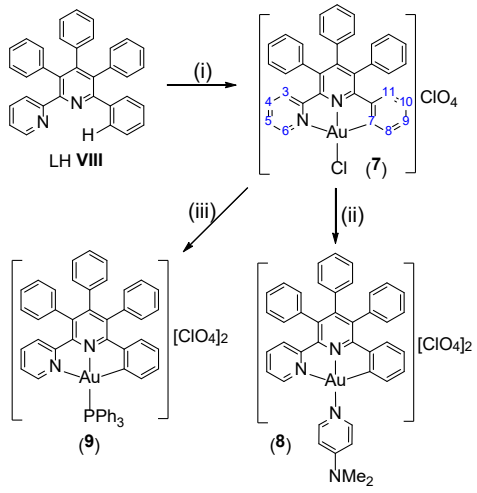



**Figure 4.** Molecular structures of ligands **I – VII**

Facile synthetic routes to cyclometallated Rh(III), Pd(II) and Pt(II) complexes (Ollangnier et al, 2008; Perera, 2018; 2020a) of 3,4,5,6-tetraphenyl-2,2´-bipyridine (LH) **VIII** and non-cyclometallated complexes of it with Cu(I), Ag(I) and Re(I) were reported (Perera, 2020b; 2021; 2022). Thus, it is interesting to explore the chemistry of gold with this bulky bipyridine ligand **VIII** (Scheme 1).




**Scheme 1.** Synthetic routes to salts (**7**)-(**9**). (i) $HAuCl_4.xH_2O$ & $AgClO_4$; (ii) DMAP & $AgClO_4$, (iii) $PPh_3$ & $AgClO_4$; and the atom labelling used for the assignment of NMR data

In this publication, synthetic routes to cyclometallated Au(III) complexes of the type $[LAuCl]ClO_4$ (**7**), $[LAu(DMAP)][ClO_4]_2$ (**8**), $[LAu(PPh_3)][ClO_4]_2$ (**9**), and the uncyclometallation Au(III) salt $[AuCl_2(LH)]Cl$ (**10**) and the Au(I) complex $[(LH)Au(PPh_3)]O_2CCF_3$ (**11**) are presented.

## Material and Methods

All the experiments were carried out once in an inert atmosphere (dinitrogen or argon). Elemental analyses were carried out on a Carlo Erba 1006 automatic analyser. IR spectra were recorded on a PerkinElmer Spectrum One FT-IR spectrometer fitted with a universal ATR sampling accessory. Mass spectral data were obtained using a micromass LCT electrospray mass spectrometer. Mass spectral data were obtained using a micromass LCT electrospray mass spectrometer. NMR spectra were recorded on a Bruker DPX 400 spectrometer (operating frequencies for $^1H$, $^{19}F$ and $^{13}C$ are 400.1, 376.5 and 100.6 MHz, respectively) or Bruker Avance$^{II}$ 600 spectrometer (operating frequencies for $^1H$ and $^{13}C$ are 600.13 and 150.9 MHz). $^1H$ and $^{13}C$ chemical shifts (δ) are in ppm with respect to TMS and coupling constants (J) are in Hz. $^{19}F$ chemical shifts (δ) are in ppm relative to $CFCl_3$. $^{31}P$ NMR spectra were recorded at 161.02 MHz and were standardized with respect to 85% phosphoric acid. Single-crystal analyses were performed on a Bruker SMART APEX CCD diffractometer using graphite monochromised Mo-Kα (λ = 0.71073 Å) radiation and refinements were obtained using SHELXS software. Figures 6 and 7 feature the images obtained by using Mercury software. $HAuCl_4.xH_2O$ was purchased from Aldrich. 3,4,5,6-Tetraphenyl-2,2´-bipyridine **VIII** (Ollangnier et al, 2008) and $[Au(PPh_3)Cl]$ (Cooke et al, 1997) were prepared according to literature procedures.

### *[LAuCl]ClO₄ (7)*

A solution containing the ligand **VIII** (140 mg, 0.30 mmol), $HAuCl_4.xH_2O$ (122 mg, 0.30 mmol) and $AgClO_4$ (126 mg, 0.60 mmol) in acetonitrile (50 mL) was refluxed for 4 days. The solution was concentrated to about 25 mL and AgCl precipitate was filtered off. The filtrate was concentrated to give a yellow solid (105 mg, 44%). Analytical sample was crystallised from dichloromethane/methanol. Found: C, 46.46; H, 2.67; N, 3.26, calcd. (%) for $C_{34}H_{23}Cl_2N_2O_4Au{\cdot}1.5CH_2Cl_2$: C, 46.47; H, 2.75; N,

3.05. IR (neat): 3059, 1627, 1549, 1474, 1443, 1410, 1228, 1083 and 766. ESI-MS (MeCN, m/z): Found: 691.1229, calcd. 691.1215 for $C_{34}H_{23}N_2ClAu$, $[M\text{-}ClO_4]^+$. $^1H$ NMR (400 MHz, $CDCl_3$): δ 9.07 (dd, 1H, $^3J(HH)$ 5.0 Hz, $^4J(HH)$ 1.5 Hz, $H^6$), 7.95 (dt, 1H, $^3J(HH)$ 8.0 Hz, $^4J(HH)$ 1.5 Hz, $H^4$), 7.88 (m, 1H, $^3J(HH)$ 5.0 Hz, $^4J(HH)$ 1.5 Hz, $H^5$), 7.78 (dd, 1H, $^3J(HH)$ 8.0 Hz, $^4J(HH)$ 1.0 Hz, $H^8$), 7.45-7.35 (m, 6H, Ph), 7.29-7.20 (m, 5H, $^3J(HH)$ 8.0 Hz, $^4J(HH)$ 1.5 Hz, Ph & $H^9$), 7.06-6.95 (m, 4H, $^3J(HH)$ 8.0 Hz, $^4J(HH)$ 1.5 Hz, Ph & $H^{10}$), 6.95-6.88 (m, 2H, Ph), 6.82 (d, 1H, $^3J(HH)$ 8.0 Hz, $H^3$), and 6.06 (dd, 1H, $^3J(HH)$ 8.5 Hz, $^4J(HH)$ 1.5 Hz, $H^{11}$). $^{13}C$ NMR: δ 149.8 ($C^6$), 144.1 ($C^4$), 133.7 ($C^9$), 133.5 ($C^8$), 132.8 ($C^{11}$), 130.4 ($C^{10}$), 130.1 ($C^3$) and 130.0 ($C^5$).

### *[LAu(DMAP)][ClO$_4$]$_2$ (8)*

A solution containing [LAuCl]$ClO_4$ (**7**) (15 mg, 0.0189 mmol), 4-dimetylaminopyridine (DMAP) (5 mg, 0.04 mmol) and $AgClO_4$ (5 mg, 0.024 mmol) in acetonitrile (3 mL) was refluxed for 1 h. The solution was allowed to cool and AgCl precipitate was filtered off. The filtrate was concentrated to a low volume and ethanol was added to give the required product as a yellow solid, (15 mg, 81%). Analytical sample was crystallised from dichloromethane/methanol. Found: C, 49.40; H, 3.27; N, 5.41, calcd. (%) for $C_{41}H_{33}Cl_2N_4O_8Au{\cdot}0.5CH_2Cl_2$: C, 48.9; H, 3.36; N, 5.49. IR (neat): 3059, 1628, 1561, 1411, 1229, 1079, 771 and 699. ESI-MS (MeCN, m/z): Found: 389.1172, calcd. 389.1185 for $C_{41}H_{33}N_4Au$, $[M\text{-}2ClO_4]^{2+}$. $^1H$-NMR (400 MHz, $CDCl_3$, δ in ppm): 8.84 (d, 2H, $^3J(HH)$ 7.0 Hz, Ar), 8.08 (d, br, 1H, $^3J(HH)$ 4.5 Hz, $H^6$), 7.70 (dt, 1H, $^3J(HH)$ 7.5 Hz, $^4J(HH)$ 1.5 Hz, $H^4$), 7.57 (m, 1H, $H^5$), 7.37-7.27 (m, 6H, Ph), 7.26-7.22 (m, 2H, Ph), 7.02-6.95 (m, 4H, Ph & $H^9$), 6.92 (d, 2H, $^3J(HH)$ 7.0 Hz, Ar), 6.89-6.83 (m, 2H, $^3J(HH)$ 7.5 Hz, $H^3$ & $H^{10}$), 6.83-6.78 (m, 2H, Ph), 6.34 (d, 1H, $^3J(HH)$ 8.0 Hz, $H^8$), 6.10 (d, 1H, $^3J(HH)$ 8.0 Hz, $H^{11}$) and 3.29 (s, 6H, Me). $^{13}C$ NMR: δ 160.1, 155.6, 150.7 (Ar), 148.5($C^6$), 147.9, 147.3, 141.5 ($C^4$), 133.6, 133.5, 131.8 ($C^{11}$), 131.7 ($C^9$), 129.8 ($C^{Ph}$), 129.5 ($C^{Ph}$), 129.3($C^{Ph}$), 129.3, 129.2 ($C^8$), 128.9, 129.1 ($C^{Ph}$), 128.9 ($C^{Ph}$), 128.8 ($C^{Ph}$), 127.7 ($C^{Ph}$), 127.4 ($C^5$), 126.8 ($C^{Ph}$), 126.6 ($C^3$), 124.7 ($C^{10}$), 109.7 (Ar) and 39.7 (Me).

***[LAu(PPh$_3$)][ClO$_4$]$_2$ (9)***

A degassed solution containing [LAuCl]$ClO_4$ (**7**) (15 mg, 0.0189 mmol), triphenylphosphine (7 mg, 0.026 mmol) and $AgClO_4$ (5 mg, 0.024 mmol) in acetonitrile (3 mL) was refluxed under dinitrogen for 1 h. The solution was allowed to cool and AgCl precipitate was filtered off. The filtrate was concentrated to a low volume and ethanol was added to give the required product as a yellow solid, (19 mg, 90%). Analytical sample was crystallised from dichloromethane/methanol. Found: C, 53.19; H, 3.37; N, 2.00, calcd. (%) for $C_{52}H_{38}Cl_2N_2O_8PAu{\cdot}0.75CH_2Cl_2$: C, 53.65; H, 3.37; N, 2.37. IR (neat): 3058, 1601, 1479, 1437, 1069, 753 and 691. ESI-MS (MeCN, m/z): Found: 919.2473, calcd. 919.2516 for $C_{52}H_{39}N_2PAu$, $[M\text{-}2ClO_4+H]^+$. $^{31}$P NMR (100 MHz, $CDCl_3$): 41.2 ppm. $^1$H NMR (600 MHz, $CDCl_3$): δ 8.20-8.11 (m, 6H, Ph), 7.80-7.68 (m, 6H, Ph), 7.53 (m, 1H, H$^4$), 7.60-7.23 (m, 14H, Ph), 7.03-6.88 (m, 6H, Ph, H$^3$ & H$^5$), 6.75 (t 1H, $^3$J(HH) = $^4$J(PH) 7.2 Hz, H$^8$), 6.72 (d, 1H, $^3$J(HH) 5.6 Hz, H$^6$), 6.63 (app. t, 1H, $^3$J(HH) 6.8 Hz, H$^9$), 6.53 (t, 1H, $^3$J(HH) 7.5 Hz, H$^{10}$) and 6.37 (d, 1H, $^3$J(HH) 7.4 Hz, H$^{11}$).

***[(LH)AuCl$_2$]Cl (10)***

To a solution containing the ligand **VIII** (46 mg, 0.10 mmol) in acetonitrile (2.5 mL), was added a solution of $HAuCl_4.xH_2O$ (40 mg, 0.10 mmol) in water (2 mL). The reaction mixture was stirred at room temperature for 40 h. The resulting yellow precipitate was filtered off and washed with methanol (62 mg, 82%). Analytical sample was crystallised from chloroform and methanol. Found: C, 50.44; H, 2.91; N, 3.29, calcd. (%) for $C_{34}H_{24}Cl_3N_2PAu{\cdot}0.5CHCl_3$: C, 50.31; H, 2.99; N, 3.40. IR (neat): 3058, 1600, 1541, 1485, 1443, 1394, 1073, 835, 755 and 695. ESI-MS (MeCN, m/z): Found: 727.0989, calcd. 727.0982, for $C_{34}H_{24}N_2Cl_2Au$, $[M\text{-}Cl]^+$. $^1$H NMR (400 MHz, $CDCl_3$): δ 9.00 (dd, 1H, $^3$J(HH) 6.0 Hz, $^4$J(HH) 1.0 Hz, H$^6$), 7.66 (dt, 1H, $^3$J(HH) 7.5 Hz, $^4$J(HH) 1.5 Hz, H$^4$), 7.59-7.55 (m, 2H, Ph), 7.50 (m, 1H, $^3$J(HH) 6.0 Hz, $^4$J(HH) 1.5 Hz, H$^5$), 7.31-6.93 (m, 17H, Ph & H$^3$) and 6.79-6.76 (m, 2H, Ph). $^{13}$C NMR (100.6 MHz, $CDCl_3$): δ 157.9, 156.1, 152.1, 151.0 (C$^6$), 150.2, 139.3 (C$^4$), 138.1, 137.4, 137.2, 136.7, 136.5, 135.3, 131.1 (C$^3$), 130.9, 130.7, 130.5, 128.4, 128.3, 127.8, 127.7, 127.6,127.3, 127.0, 126.9 and 125.7 (C$^5$).

***[(LH)Au(PPh$_3$)](O$_2$CCF$_3$) (11)***

Mixing of $AgO_2CCF_3$ (8.9 mg, 0.04 mmol) and [Au($PPh_3$)Cl] (20 mg, 0.04 mmol) in acetone (4 mL) gave a white precipitate of AgCl. After 2 h, AgCl was filtered off and the ligand **VIII** (19 mg, 0.041 mmol) was added to the filtrate to give a colourless solution. After 3 h, it was concentrated to a low volume and diethyl ether was added to give an oily residue, which was cooled in the freezer to give a white solid (21 mg, 51%). Found: C, 63.15; H, 3.95; N, 2.75, calcd. (%) for $C_{54}H_{39}F_3N_2O_2PAu$: C, 62.80; H, 3.80; N, 2.71. IR (neat, $cm^{-1}$): 1683, 1604, 1480, 1437, 1400, 1199, 1160, 1103, 1076, 819, 782, 754, 701, 692 and 654. Maldi (DCM, m/z): found: 919.2489; calcd. 919.2516 for $C_{52}H_{39}N_2PAu$ [M-$O_2CCF_3$]. $^1$H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, 1H, $^3$J(HH) 4.5 Hz, $H^6$), 7.60-7.53 (m, 3H, Ph & $H^4$), 7.53-7.43 (m, 4H, Ph), 7.43-7.38 (m, 5H, Ph & $H^3$/$H^5$), 7.34-7.32 (m, 2H, $H^{Ph}$), 7.23 (m, 1H, $H^3$/$H^5$), 7.19-7.09 (m, 2H, $H^{Ph}$), 7.05-6.98 (m, 4H, $H^{Ph}$), 6.98-6.92 (m, 4H, $H^{Ph}$), 6.92-6.84 (m, 2H, $H^{Ph}$) and 6.82-6.77 (m, 2H, $H^{Ph}$). $^{31}$P NMR (161 MHz, $CDCl_3$): δ 27.8 ppm. $^{19}$F NMR (376.5 MHz, $CDCl_3$): δ -75.0 (s) ppm.

## Results and Discussion

Treatment of the ligand **VIII** with $HAuCl_4.xH_2O$ in the presence of $AgClO_4$ in boiling acetonitrile for 4 days afforded the cyclometallated square-planar Au(III) complex [LAuCl]$ClO_4$ (**7**) containing an anionic tridentate (N^N^C) ligand as a yellow solid (Scheme 1). The complex (**7**) and other complexes were adequately characterized by a combination of IR, Mass and NMR spectroscopy. The aromatic region of the proton NMR spectrum of (**7**) is shown in Figure 5; the proton ($H^6$) was the most deshielded proton and the resonance appeared as a doublet of doublets at 9.07 ppm with $^3$J(HH) = 5.0 Hz and $^4$J(HH) = 1.5 Hz. $H^3$ and $H^{11}$ are the most shielded protons.

The $^1$H and $^{13}$C NMR chemical shifts were assigned by performing H–H and C–H COSY experiments and the $^{13}$C resonances at 149.8 ($C^6$), 144.1 ($C^4$), 130.1 ($C^3$) and 130.0 ($C^5$) ppm were assigned accordingly.

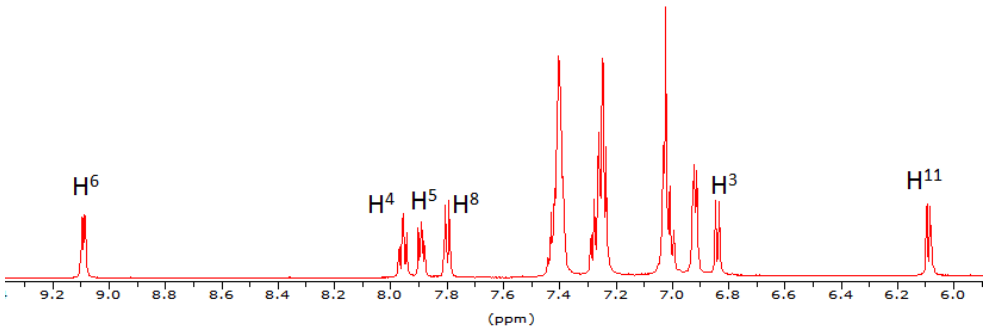



**Figure 5.** Aromatic region of the $^{1}H$ NMR spectrum of (**7**) with the atom labelling used for the assignment of NMR data

The X-ray crystallography of the complex (**7**) confirmed the orthometallation and slightly distorted square-planar geometry around the Au(III) centre (Figure 6).

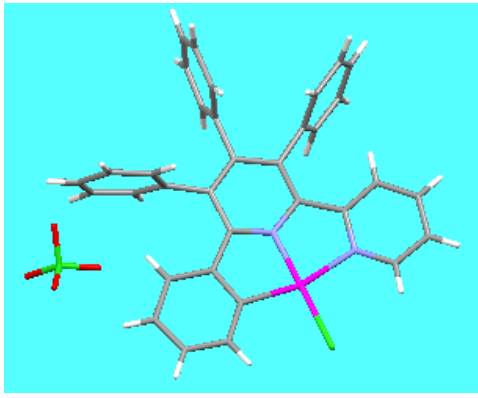


**Figure 6.** Molecular structure of $[LAuCl]ClO_4$ (**7**)

Substitution reactions of (**7**) with neutral ligands were studied (Scheme 1). Replacement of the labile chloride ligand in (**7**) with 4-dimetylaminopyridine (DMAP) in the presence of $AgClO_4$ resulted in the formation of the di-cationic salt $[LAu(DMAP)][ClO_4]_2$ (**8**) as a yellow solid in 81% yield. In its $^{1}H$-NMR spectrum, the methyl proton resonance of the $NMe_2$ group in DMAP appeared as a singlet at 3.29 ppm. The complex (**8**) was characterised by X-ray crystallography (Figure 7) and it showed orthometallation and slightly distorted square-planar geometry around the Au(III) centre; the DMAP ligand was placed perpendicular to the plane of the tridentate (N^N^C) ligand.

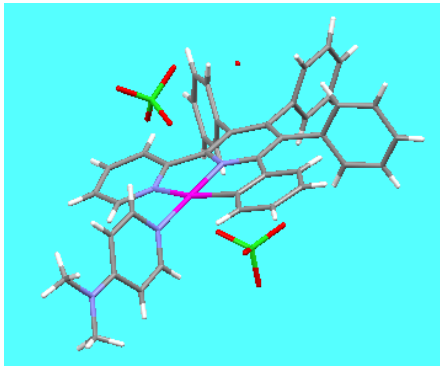
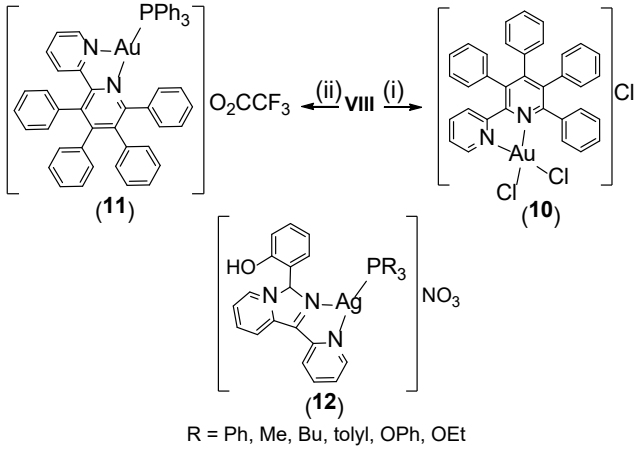


**Figure 7.** Molecular structure of $[LAu(DMAP)][ClO_4]_2$ (**8**)

Treatment of the complex (**7**) with $PPh_3$ in the presence of $AgClO_4$ formed the di-cationic salt $[LAu(PPh_3)][ClO_4]_2$ (**9**) as a yellow solid in 90% yield. The $^{31}P$-$\{^1H\}$ NMR spectrum of (**9**) showed a singlet at 41.2 ppm for the $PPh_3$ ligand.

The cyclometallated Au(III) complex (**7**) was prepared by carrying out the reaction in boiling acetonitrile for 4 days. In order to prepare the non-cyclometallated Au(III) complex the reaction was carried out at room temperature in aqueous acetonitrile. The Au(III) salt $[AuCl_2(LH)]Cl$ (**10**) was precipitated as a yellow solid in 82% yield, in which **VIII** is a bidentate (N^N) ligand (Scheme 2).




**Scheme 2.** Synthetic routes to complexes (**10**)-(**11**). (i) $HAuCl_4$ in $MeCN/H_2O$; (ii) $AgO_2CCF_3$ in MeCN, and the diagram of the Ag(I) complexes (**12**)

The proton resonance at 9.00 ppm {dd, 1H, $^{3}J(HH)$ = 6.0 Hz, $^{4}J(HH)$ =1.0 Hz} was assigned to $H^{6}$. $H^{6}$ was the most shielded proton. The elemental analysis and spectral data are in agreement with the proposed structure (**10**). The above-mentioned bipyridyl-based complexes (**1**) - (**3**) with the cation $[AuCl_2(N^N)]^+$ had shown a similar four coordinated *cis*-arrangement (Casini et al, 2010; Palanichamy et al, 2012).

The trigonal-planar white Au(I) complex $[(LH)Au(PPh_3)]O_2CCF_3$ (**11**) was isolated by treating $[AuCl(PPh_3)]$ with **VIII** in the presence of $AgO_2CCF_3$. The elemental and mass spectral analyses confirmed the proposed structure with the composition $C_{54}H_{39}F_3N_2O_2PAu$. $H^{6}$ was the most shielded proton. The $^{19}F$ NMR spectrum showed a singlet at -75.0 ppm for the fluorine nuclei in the $CF_3$ group and $^{31}P$ NMR spectrum showed a singlet at 27.8 ppm for the $PPh_3$ ligand. A series of similar trigonal-planar Ag(I) complexes (**12**) have been prepared and four of them were characterized by X-ray crystallography (Durini et al, 2017).

## Conclusions

Synthetic routes to cyclometallated Au(III) complexes with an anionic (N^N^C) ligand, $[LAuCl]ClO_4$ (**7**), $[LAu(DMAP)][ClO_4]_2$ (**8**), $[LAu(PPh_3)][ClO_4]_2$ (**9**) were developed. Non-cyclometallated Au(III) complex with a bidentate N^N ligand $[(LH)AuCl_2]Cl$ (**10**) and the Au(I) complex $[(LH)Au(PPh_3)]O_2CCF_3$ (**11**) were also devised.

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