Gold-dppm-Arylazoimidazole Complexes: Synthesis, Spectra, and Redox Study

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[Ag(ths)(OTf)]-assisted reaction produces [Au III(dppm)(ths)2](OSO2CF3)2, reacts with RaaiR′ in dichloromethane medium followed by ligand addition, and leads to [Au III(dppm)(RaaiR′)](OTf)2(RaaiR′=p–R–C6H4–N=N–C3H2–NN=1–R′, (1–3), abbreviated as N,N′-chelator, where N(imidazole) and N(azo) represent N and N′, resp.; R = H (a), Me (b), Cl (c) and R′ = Me (1), CH2CH3(2), CH2Ph (3), dppm is diphenylphosphinomethane, OSO2CF3 is the triflate anion, and tht is tetrahydrothiophen). Infrared spectra of the complexes show –C=N– and –N=N– stretching near at 1590 and 1370 cm\(^{-1}\) and near at 1100, 755, 695, 545, and 505 cm\(^{-1}\) due to the presence of dppm. The \(^1\)H NMR spectral measurements suggest that methylene, –CH 2–, in RaaiEt gives a complex AB type multiplet while in RaaiCH2Ph it shows AB type quartets. Electrochemistry assigns ligand reduction.

1. Introduction

The biochemistry of gold with D-penicillamine, glutathione, thiomalic acid, 2,3-dimercaptopropanol, [1, 2], and albumin has been studied. The reactivity of gold occurs through the thiolate function of these biological molecules and leads to the formation of gold(I) thiolates, also called chrysotherapy agents. Other types of gold complexes used in medicinal chemistry are gold(I) mono- or bis-phosphines. They can bind to DNA via the guanine and cytosine bases [3, 4] and act as antitumor agents against L1210 leukemia and M5076 reticulum cell sarcoma. In 1972, Sutton synthesized a gold complex with a thiolate and a phosphine ligand: the 2, 3, 4, 6-tetra-O-acetyl-1-thio-D-pyranosato-S-(triethylphosphine) gold(I) compound also known by the trade name Auranofin. It became one of the most promising gold complexes in medicinal chemistry, with a great potency against rheumatoid arthritis and cancer cells such as P388 leukemia and B16. A small number of scattered observations in the early structural chemistry of gold(I) complexes [5] have grown into a wealth of reports on related phenomena in the last two decades, which finally provided a clear pattern of the conditions under which direct interactions between closed-shell gold(I) centers can contribute significantly to the stability of molecular and multidimensional structures. The underlying “aurophilic” bonding has been analyzed in theoretical studies [6, 7]. Syntheses of hetero-tris-chelates, [Ru(bpy)n(RaaiR′)3–n](ClO4)2 [bpy = 2,2′-bipyridine; n = 1, n = 2] containing labile reaction centres are reported from Professor Sinha’s laboratory. Professor A. Chakravorty has unfolded this ligands rhenium chemistry. But the gold chemistry with multinuclear NMR spectroscopy of this ligand system is totally unexplored. In this paper, I examine the reaction of RaaiR′ on gold(III) dppm derivatives and the products are isolated, [Au(dppm)(RaaiR′)](OTF)3 (RaaiR′ = p–R–C6H4–N=N–C3H2–NN=1–R′, (1–3), abbreviated as N,N′-chelator, where N(imidazole) and N(azo) represent N and N′, resp.; R = H (a), Me (b), Cl (c) and R′ = Me (1), CH2CH3(2), CH2Ph (3), dppm is diphenylphosphinomethane, OSO2CF3 is the triflate anion, and tht is tetrahydrothiophen). The complexes are well characterised by i.r., \(^1\)H n.m.r., \(^1\)C n.m.r, \(^1\)H–\(^1\)H COSY nmr, \(^1\)H–\(^13\)C HMQC, and mass spectrometry.
2. Results and Discussion

The complexes, [AuIII(dppm)(RaaiR′)](OTf)2 (RaaiR′ = p-R-C6H4-N=N-C6H3-NH−1-R′, (1−3), abbreviated as N,N′-chelator, where N(imidazole) and N(azo) represent N and N′, resp; R = H (a), Me (b), Cl (c) and R′ = Me (1), CH2CH3 (2), CH2Ph (3), dppm is diphenylphosphinomethane, OSO2CF3 is the triflate anion, and that is π acidic in nature, stabilises the gold (III) oxidation state giving the value of 36.3. Fluorine n.m.r., 19F n.m.r., gives a concrete idea on the nature of the substituents in the C(9)-position. Imidazole 4- and 5-H appear as doublet at the lower-frequency side of the spectra (7.0–7.2 ppm for 4-H; 6.9–7.1 ppm for 5-H). The aryl protons 7-(7′-H) and 11-(11′-H) resonate asymmetrically indicating a magnetically anisotropic environment even in the solution phase. The 1-R′ (R′ = Me, CH2CH3, CH2(Ph)) exhibits usual spin-spin interaction. 1-Me appears as a singlet at 2.0 ppm for [Au(dppm)(RaaiMe)]2+. The methylene protons 1-CH2-, (CH3) show AB type quartet (5.5, 5.7 ppm) with geminal coupling constant average 8.8 Hz in [Au(dppm)(RaaiCH2Ph)]2+. 1-CH2(Ph) protons appear at AB type quartets (5.5, 5.7 ppm) with geminal coupling constant average 8.8 Hz in [Au(dppm)(RaaiCH2Ph)]2+ (Scheme 2).

The 13C (H)NMR spectrum provides direct information about the carbon skeleton of the molecule. Assignment of different resonant peaks to respective carbon atoms is done on nine complexes and the data are given on experimental section (Figures 1 and 2). The carbon atom is adjacent to the PPh3 molecule in the complex resonance at a lower field resulting in the conjugative effect of the phenyl ring with more electronegative pi-conjugate system. The methyl carbon atom of the imidazole ring resonates at 30 ppm, reasonably comparing to the other carbon atoms resonance. In the COSY spectrum, absence of any off-diagonal peaks extending from δ = 14.1 ppm and 9.5 ppm confirms their assignment of no proton on N(1) and N(3), respectively. However, extending horizontal and vertical lines from δ = 8.3 ppm [C(8)H] and 8.6 ppm [C(10)H] encounter cross peaks at δ = 7.1 ppm and 7.2 ppm, where the C(7)H and C(11)H resonances are merged into multiplets along with the phenyl ring proton resonances. The 1H−13C heteronuclear...
Published methods were used to prepare RaaiR′, [AuIII(dppm)(RaaiR′)](OTf)2. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, Sigma Aldrich). The purification of MeCN used as solvent and other solvents was done following literature method. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. I.r. spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000–200 cm−1). The 1H nmr spectra in CDCl3 were obtained on a Bruker 500 MHz FT n.m.r spectrometer using SiMe4 as internal reference, CFCl3 (external 19F). Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ~10−3 M in acetonitrile. Mass spectra were recorded on VG Autospec ESI-mass spectrometry. Electrochemical work was carried out using an EG & G PARC Versastat computer-controlled 250 electrochemical system. All experiments were performed under an N2 atmosphere at 298 K 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).

4.1. Preparation of the Complexes [AuIII(dppm)(HaaiEt)](OTf)2, 2b. To a dichloromethane slight yellow colour solution (15 cm3) of [AuIII(dppm)Cl2] (0.665 g, 0.10 mmol) [Ag(tht)(OTf)] was added (1 : 2) to produce [AuIII(dppm)(tht)2]([OSO2CF3]2, (0.945 g, 0.20 mmol) into this, yellow dichloromethane solution of 1-ethyl-2-(p-tolylazo)imidazole was added slowly, dropwise, and the mixture was stirred at 343–353 K for 12 hours, where, respectively, added the other ligands, HeaaiMe (0.0276 g, 0.1 mmol, 3b). The 1H nmr spectra in CDCl3 were very much informative and they show that the sharp signals at 36.13 ppm 13C (1H)NMR study suggests molecular skeleton. 1H–13C HMQC spectrum as well as contour peaks in the 1H–13C HMQC spectrum assigns them to the carbon hydrogen atoms interaction. Electrochemistry assigns ligand reduction part rather than metal oxidation.

3. Conclusion

This work describes the isolation of a novel series of Gold(III) azo-imine complexes, [AuIII(dppm)(RaaiR′)](OTf)2, and their spectral and elemental characterisation. 1H NMR study suggests quartet splitting of ethyl substitution. 31P 1H NMR study suggests molecular skeleton. 1H–13C COSY spectrum as well as contour peaks in the 1H–13C HMQC spectrum assigns them to the carbon hydrogen atoms interaction. Electrochemistry assigns ligand reduction part rather than metal oxidation.

4. Experimental

Published methods were used to prepare RaaiR′, [AuIII(dppm)(Cl)]2. All other chemicals and organic solvents used for preparative work were of reagent grade (SRL, Sigma Aldrich). The purification of MeCN used as solvent and other solvents was done following literature method. Microanalytical data (C, H, N) were collected using a Perkin Elmer 2400 CHN instrument. I.r. spectra were obtained using a JASCO 420 spectrophotometer (using KBr disks, 4000–200 cm−1). The 1H nmr spectra in CDCl3 were obtained on a Bruker 500 MHz FT n.m.r spectrometer using SiMe4 as internal reference, CFCl3 (external 19F). Solution electrical conductivities were measured using a Systronics 304 conductivity meter with solute concentration ~10−3 M in acetonitrile. Mass spectra were recorded on VG Autospec ESI-mass spectrometry. Electrochemical work was carried out using an EG & G PARC Versastat computer-controlled 250 electrochemical system. All experiments were performed under an N2 atmosphere at 298 K 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).
Figure 1: From above, H NMR, $^{13}$C (H)NMR of complex 2a and below, IR spectra of complex 2a and 2b.
Figure 2: H NMR of complex 2c and H H COSY NMR of complex 2c and its extended portion.
References


