Indian Journal of Chemistry
Vol. 63, April 2024, pp. 413-421
DOI: 10.56042/ijc.v63i4.4657

Phosphine-aryldiethynyls (–C≡C(Ar)C≡C–)-gold(I)-gold(III) complexes: Synthesis and spectral study

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Received 7 August 2023; accepted (*revised*) *25 January 2024*

[Au_2(dppm/dppe/dppa)$(Cl)_2$], which on reaction with aryldiethynyls, -C≡C(Ar)C≡C-, and gold(I) phosphines in MeOH, CH_2Cl_2 medium, by the self assembly technique leads to [(PPh_3)Au(1,4-B)Au(PPh_3/PPh-oMe/PPh_2Me/$PPhMe_2$/PCy_3/$PNEt_2$/$PNMe_2$/$AsPh_3$/DAPTA)], (**1a-1j**, **2**), [{Au_2(dppm/dppe/dppa)}{(1,4B)Au(PPh_3/PPh-oMe/PPh_2Me/$PPhMe_2$/PCy_3/$PNEt_2$/$PNMe_2$/$AsPh_3$)}$_2$], (**3**, **6**, **7**, **8**, **9**, **10**, **11**), [{Au_4(dppm/dppe/dppa)$_2$(1,4B)$_2$}], **4**, [$(AuPPh_3)_2Au^{III}$(14B)(Mes/$C_6F_5)_2$, **5a**, **5b** [dppm/dppe/dppa = diphenyl phosphino-methane(*a*), -ethane(*b*), ammine(*c*), C_6F_5/Mes pentafluorophenyl/mesitylene, 14B = arylethynyl benzene, DAPTA=diacetyl 1,3,5-triaza-7-phosphaadamantane]. The maximum molecular peak of the corresponding molecule is observed in the ESI mass spectrum. IR spectra of the complexes show -C=C- , -C=N-, as well as phosphine, mesitylene and pentafluorophenyl stretching. The ^{1}H NMR spectra as well as ^{31}P (^{1}H)NMR suggest solution stereochemistry, proton movement and phosphorus proton interaction. ^{13}C (H)NMR spectrum reflects the molecular skeleton. In the ^{1}H-^{1}H COSY spectrum of the present complexes assign the solution structure. Complex 2 is water soluble and the spectra measured in D_2O.

Keywords: Gold(I), Gold(III), 14B, NMR, ESI-MS, IR

Aryldiethynyls, -C≡C(Ar)C≡C-, together with other unsaturated carbon ligands such as alkynyls, arylethynyls, arylethenyls, and cumulenes[1-10] are of great interest in the organometallic chemistry of transition metals. This is due to their electronically unsaturated nature, which confers to such compounds a number of interesting properties and applications such as (i) reversible redox chemistry[2a,b,g,l,m,3,6i], (ii) easily accessible mixed-valent states in binuclear complexes[2c,g,k,m], (iii) liquid crystalline behaviour[11] (iv) luminescence[3,5a,c,d,f,6b,c,f,i], (v) third-order nonlinear optical materials[1,2e,4f,12] and molecular electronics[2c,5b,6h,7,13]. The prevailing use of the aryldiethynyl group lies in bridging two or more transition metals to form binuclear or oligonuclear complexes which extend to the interesting field of organometallic polymers[4e,5a,b,e,f,6]. If the chosen metals exhibit reversible redox couples such as, for example, M(II)/M(III), iron or ruthenium binuclear complexes with arylethynyl bridging ligands usually allow the generation of mixed-valence species and the study of intramolecular electron transfer (ET) in such mixed-valence systems. The study of ET through mixed-valence compounds is a very active field of research. A large number of compounds have been synthesized, allowing the study of various factors such as the distance of the redox centers, solvent effects, and the nature of the bridging ligand. Aryldiethynyl bridging ligands are ideally suited to learn how the ET depends on the (electronic) structure of such bridges. The aryl core can be varied to a great extent by replacing the common 1,4-phenylene, for example, by 1,3-phenylene[2a,f,j,4f], 2,5-pyridine[2b,k], 2,5-thiophene[2a-c,k,4e,5f,6i], 9,10-anthracene[2a-c,4e,5f], or 4,4'-biphenylene[2b,e,5c,f]. Further promising variations are the prolongation of the chain length to bis(aryldiethynyl), tris(aryldiethynyl), *etc*. or the incorporation of metals into such extended systems. The extension of the unsaturated carbon chain which is very common for cummulenes[2a,8f,9a,b], for example, has been so far restricted for aryldiethynyl complexes to only a few cases of mononuclear ruthenium systems[5a-c], a binuclear gold system[5c], and some polymeric platinum systems[5f,6b-f]. A study on the ET properties of such extended ligands has not been reported so far. Studies on the incorporation of metals into the chain to form trinuclear [M]-C≡C(Ar)C≡C-[M']-C≡C(Ar)C≡C-[M][4g] or oligonuclear systems[6j] have so far been restricted to synthetic details. ET studies on related acetylide-bridged heterotrinuclear systems with ferrocene end

groups have been reported recently. In this paper, we examine the reaction by self assemble method and isolated the product, [(PPh_3)Au(1,4-B)Au(PPh_3/PPh-oMe/PPh_2Me/$PPhMe_2$/PCy_3/$PNEt_2$/$PNMe_2$/$AsPh_3$/DA PTA)], (**1a-j**, **2**), [{Au_2(dppm/dppe/dppa)}{(1,4B) Au(PPh_3/PPh-oMe/PPh_2Me/$PPhMe_2$/PCy_3/$PNEt_2$/ $PNMe_2$/$AsPh_3$)}$_2$], (**3**, **6**, **7**, **8**, **9**, **10** ,**11**), [{Au_4(dppm/ dppe/dppa)$_2$(1,4B)$_2$}], (**4**), [($AuPPh_3$)$_2$$Au^{III}$(14B) (Mes/$C_6F_5$)$_2$, (**5a**, **5b**) [dppm/dppe/dppa = diphenyl phosphino-methane (a), -ethane (b), ammine (c), C_6F_5/Mes pentafluorophenyl/mesitylene, 14B = arylethynyl benzene, DAPTA=diacetyl 1,3,5-Triaza-7-phosphaadamantane]. The complexes are well charecterised by IR, ^{1}H NMR, ^{31}P (^{1}H) NMR, ^{19}F (^{1}H) NMR, ^{13}C (^{1}H) NMR, ^{1}H-^{1}H COSY NMR, ^{1}H-^{13}C HMQC and ESI-MS mass spectrometry.

Experimental Section

Preparation of [{Au((PPh_3)}{(1,4B)Au(PPh_3)}$_2$], 1a-j, 2,

To a CH_2Cl_2 solution (15 cm^3) of [Au(PPh_3)Cl] (0.990 g, 0.20 mmol the appropriate 1,4 B (0.126g,0.10mmol)], excess base NaOH, was then added slowly, drop-wise, and the mixture was stirred at 343-353 K for 12 h. The solution that resulted was concentrated to (4 cm^3) and kept in a refrigerator overnight (1 h). The addition of ether to the above solution gave a precipitate which was collected by filtration, washed thoroughly with ether to remove the excess of ligand and then dried *in vacuo* over a pump overnight. The yield was 0.088 g (80%). All other complexes were prepared similarly as stated above, for (**1b**), [Au(PPh-oMe)$_3$)Cl] (1.040 g, 0.20 mmol), 1,4-B (0.126g,0.10mmol)], and for (**1c**) [Au(PPh-mMe)$_3$)Cl] (1.040 g, 0.20 mmol), 1,4-B (0.126g,0.10mmol)], for (**1d**), [Au(PPh-pMe)$_3$)Cl] (1.040 g, 0.20 mmol), 1,4-B(0.126g,0.10mmol)], for (**1e**), [Au(PPh_2Me))Cl] (0.860 g, 0.20 mmol), 1,4-B(0.126g,0.10mmol)], for (**1f**), [Au($PPhMe_2$)Cl] (0.740 g, 0.20 mmol), 1,4-B(0.126g,0.10mmol)], for (**1g**), [Au(PCy_3)Cl] (1.120 g, 0.20 mmol), 1,4-B(0.126g,0.10mmol)], for (**1h**), [Au($PNEt_2$)$_3$)Cl] (1.114 g, 0.20 mmol), 1,4-B(0.126g,0.10mmol)], for (**1i**), [Au($PNMe_2$)$_3$)Cl] (0.800 g, 0.20 mmol), 1,4-B(0.126g,0.10mmol)], for (**1j**), [Au($AsPh_3$)Cl] (0.860 g, 0.20 mmol), 1,4-B(0.126g,0.10mmol)], for (**2**), [Au(DAPTA)(Cl)] (0.462 g, 0.10 mmol), [Au(PPh_3)Cl] (0.495 g, 0.10 mmol), 1,4-B(0.126g, 0.10mmol)], Analysis for [{Au(PPh_3)(14B)Au(PPh_3)], (**1a**), Found: C, 52.8, H, 3.3, Calcd. for $C_{46}H_{34}Au_2P_2$, C, 52.97, H, 3.3, IR(nujol) ν(C=C), 1610, ν(PPh_3) 1100,750,690,550,505 cm^{-1} ESI-MS, 1042[M$^+$]; ^{1}H NMR($CDCl_3$), ppm, 9.01(H(a,a′-H), d, J = 6.6Hz), 8.37(H(b,b′-H), d, J = 6.9Hz), 7.3-7.48(broad, PPh_3), 7.1-7.3(broad); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 29.25; ^{13}C ^{1}H NMR, ppm, 131.2,133.5,133.6,132.7,130.9 (PPh_3, 36C), 123,121,129 (6C, 14B); Analysis for [{Au(PPh-oMe)$_3$)(14B)Au(PPh-oMe)$_3$], (**1b**), Found: C, 55.1, H, 4.6; Calcd for $C_{52}H_{52}Au_2P_2$, C, 55.2, H, 4.6; IR(nujol) ν(C=C), 1610, ν(PPh_3) 1100,750,692, 552,503 cm^{-1} ESI-MS, 1132[M$^+$]; ^{1}H NMR($CDCl_3$), ppm, 8.41(H(a,a′-H), d, J = 6Hz), 7.99(H(b,b′-H), d, J = 6Hz), 8.3-81(broad, PPh_3), 2.1(Ph-oMe); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 32.62; ^{13}C ^{1}H NMR, ppm,118,118,3, 133,133.6, 138.7,139.9 (PPh_3, 36C), Analysis for [{Au(PPh-mMe)$_3$)(14B)Au(PPh-mMe)$_3$], (**1c**), Found C, 55.1, H, 4.1; Calcd for $C_{52}H_{52}Au_2P_2$, C, 55.2, H, 4.7; IR (nujol) ν(C=C), 1610, ν(PPh_3) 1102,753,692,554,503 cm^{-1} ESI-MS, 1132[M$^+$]; ^{1}H NMR($CDCl_3$), ppm, 9.02 (H(a,a′-H), d, J = 6Hz), 8.32 (H(b,b′-H), d, J = 6Hz), 7.3-7.7 (broad, PPh_3), 2.1 (Ph-mMe); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 27.92; ^{13}C ^{1}H NMR, ppm, 131,133,133.6, 132.7,130.9 (PPh_3, 36C), Analysis for [{Au(PPh-pMe)$_3$)(4,4bpy) Au(PPh-pMe)$_3$], (**1d**), Found C, 55.1, H, 4.1; Calcd for $C_{52}H_{52}Au_2P_2$, C, 55.2, H, 4.6; IR(nujol) ν(C=C), 1610, ν(PPh_3) 1103,753,692,552,503 cm^{-1} ESI-MS, 1132[M$^+$]; ^{1}H NMR($CDCl_3$),,ppm, 9.0 (H(a,a′-H), d, J = 6Hz), 8.33 (H(b,b′-H), d, J = 6Hz), 7.6-7.7 (broad, PPh_3), 2.1 (Ph-pMe); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 32.32; ^{13}C ^{1}H NMR, ppm, 131,133,133.6, 132.7,130.9 (PPh_3, 36C), Analysis for [{Au(PPh_2Me)$_3$)(14B)Au (PPh_2Me)$_3$], (**1e**), Found C, 47.1, H, 3.1; Calcd for $C_{36}H_{30}Au_2P_2$, C, 47.2, H, 3.6; IR(nujol) ν(C=C), 1610, ν(PPh) 1103,753,692,552,503 cm^{-1} ESI-MS, 918[M$^+$]; ^{1}H NMR($CDCl_3$),ppm, 7.17 (H(a,a′-H), d, J = 6Hz), 7.33 (H(b,b′-H), d, J = 6Hz), 7.46-7.40,7.24-7.36 (broad, PPh), 2.1 (Me); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 30.52; ^{13}C ^{1}H NMR, ppm, 131,133,133.6, 132.7, 130.9 (PPh_2), Analysis for [{Au($PPhMe_2$)$_3$)(14B)Au ($PPhMe_2$)$_3$], (**1f**), Found C, 39.1, H, 3.1; Calcd for $C_{26}H_{26}Au_2P_2$, C, 39.2, H, 3.3; IR(nujol) ν(C=C), 1610, ν(PPh) 1103,753,692, cm^{-1} ESI-MS, 794 [M$^+$]; ^{1}H NMR($CDCl_3$),ppm, 7.1 (H(a,a′-H), d, J = 6Hz), 7.3 (H(b,b′-H), d, J = 6Hz), 7.46-7.40,7.24-7.36 (broad, PPh), 2.1 (Me); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 20.52; ^{13}C ^{1}H NMR, ppm, 131,133,133.6, (PPh), Analysis for [{Au(PCy_3)$_3$)(14B)Au(PCy_3)$_3$], (**1g**), Found C, 51.1, H, 6.1; Calcd for $C_{46}H_{64}Au_2P_2$, C, 51.2, H, 5.9; IR(nujol) ν(C=C), 1610, ν(PCy) 1103,753, cm^{-1} ESI-MS,

1072[M^+]; ^{1}H NMR($CDCl_3$),ppm, 7.33 (H(a,a′-H), d, J = 6Hz), 7.26 (H(b,b′-H), d, J = 6Hz), 1.2,1.4,1.6,1.66,1.8,1.88,1.99,2.16 (broad, PCy); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 54, 56.52; ^{13}C ^{1}H NMR, ppm, 25.8,25.9,26,27,27.3,27.8,30,8,122.7, Analysis for [{Au($PNEt_2$)$_3$)(14B)Au($PNEt_2$)$_3$], (**1h**), Found C, 40.1, H, 6.1; N,8.3, Calcd for $C_{34}H_{64}N_6Au_2P_2$, C, 40.2, H, 6.6; N,8.4, IR(nujol) ν(C=C), 1610, cm^{-1} ESI-MS, 1012[M^+]; ^{1}H NMR($CDCl_3$),ppm, 7.37 (H(a,a′-H), d, J = 6Hz), 7.33 (H(b,b′-H), d, J = 6Hz), 3.06(dd, J = 8Hz, Et),1.06(t, J = 6Hz, Et), ^{31}P ^{1}H NMR($CDCl_3$, ppm), 104.2; ^{13}C ^{1}H NMR, ppm, 131,131.9,39.6, 39.7,13.9, 13.7, Analysis for [{Au($PNMe_2$)$_3$)(14B) Au($PNMe_2$)$_3$], (**1i**), Found C, 31.1, H, 4.71; N,9.9, P, 7.3, Calcd for $C_{22}H_{40}N_6Au_2P_2$, C, 31.2, H, 4.6; N, 9.9, P, 7.6; IR(nujol) ν(C=C), 1610, cm^{-1} ESI-MS, 844[M^+]; ^{1}H NMR($CDCl_3$),ppm, 7.43 (H(a,a′-H), d, J = 6Hz), 7.33 (H(b,b′-H), d, J = 6Hz), 2.66, 2.64(Me), ^{31}P ^{1}H NMR($CDCl_3$, ppm), 110.65; ^{13}C ^{1}H NMR, ppm, 131,131.9,37.6, 124, 37.7, Analysis for [{Au($AsPh_3$)(14B)Au($AsPh_3$)$_3$], (**1j**), Found C, 50.1, H, 3.1; Calcd for $C_{46}H_{34}Au_2As_2$, C, 50.2, H, 3.6; IR(nujol) ν(C=C), 1610, cm^{-1} ESI-MS, 1086[M^+]; ^{1}H NMR($CDCl_3$),ppm, 7.46(H(a,a′-H), d, J = 8.6Hz), 7.39 (H(b,b′-H), d, J = 6Hz), 7.43-7.36(m, broad,Ph), ^{13}C ^{1}H NMR, ppm, 131,131.9,133.6, 132.7,129.9, 122.7, Analysis for [{Au(DAPTA)(14B)Au(PPh_3)], (*2*}, Found: C, 44.6, H, 3.61, N, 4.18; Calcd for $C_{38}H_{37}Au_2P_2N_3$, C, 44.6, H, 3.6, N, 4.11, P, 6.1; IR(nujol) ν(C=C), 1610, ν(DAPTA) 1510, 955, 800, ν(PPh_3) 1100,750,692,552,503 cm^{-1} ESI-MS, 1023[M^+];.^{1}H NMR(D_2O),ppm, 7.80 (H(a,a′-H, d, J = 4Hz), 7.19(H(b,b′-H, d, J = 3Hz), 4.2,4.4, 2.1,(DAPTA), 7.12-7.29(broad, PPh_3); Phosphoro NMR, ^{31}P ^{1}H NMR(D_2O, ppm), 42.42; Carbon, ^{13}C ^{1}H NMR(D_2O), ppm, 131,133,133.6.

Preparation of [{Au_2(dppm/dppe/dppa)}{(14B)Au-(PPh_3/PPh-oMe/PCy/$PNEt_2$/$PNMe_2$/AsPh)}$_2$], 3a-c, 6a-c, 7a-c, 8a-c, 9a-c, 10a-c, 11a-11

The procedure are the same as stated above but the stoichiometric ratio are as follows, for complex (**3a**), [Au_2(dppm)Cl_2], (0.849g, 0.10mmol), + [Au(PPh_3)Cl] (0.990 g, 0.20 mmol), + 14B(0.249g,0.20mmol)], for complex (**3b**), [Au_2(dppe)Cl_2], (0.963g, 0.10mmol), + [Au(PPh_3)Cl] (0.990 g, 0.20 mmol), + 14B(0.249g, 0.20mmol)], for complex (**3c**), [Au_2(dppa)Cl_2], (0.8509g, 0.10mmol), + [Au(PPh_3)Cl] (0.990 g, 0.20 mmol), + 14B(0.249g,0.20mmol)]; for complex (*6a*), [Au_2(dppm)Cl_2], (0.849g, 0.10mmol), + [Au(PPh-oMe_3)Cl] (1.090 g, 0.20 mmol), + 14B(0.249g, 0.20mmol)], for complex (**6b**), [Au_2(dppe)Cl_2], (0.963g, 0.10mmol), + [Au(PPh-oMe_3)Cl] (1.090 g, 0.20 mmol), + 14B(0.249g,0.20mmol)], for complex (*6c*), [Au_2(dppa)Cl_2], (0.850g, 0.10mmol), + [Au(PPh-oMe_3)Cl] (1.090 g, 0.20 mmol), + 14B(0.249g, 0.20mmol)]; for complex (**8a**), [Au_2(dppm)Cl_2], (0.849g, 0.10mmol), + [Au(PCy_3)Cl] (1.20 g, 0.20 mmol), + 14B(0.249g,0.20mmol)], for complex (**8b**), [Au_2(dppe)Cl_2], (0.963g, 0.10mmol), + [Au(PCy_3)Cl] (1.20 g, 0.20 mmol), + 14B(0.249g,0.20mmol)], for complex (**8c**), [Au_2(dppa)Cl_2], (0.850g, 0.10mmol), + [Au(PCy_3)Cl] (1.20 g, 0.20 mmol), + 14B(0.249g, 0.20mmol)]; for complex (**9a**), [Au_2(dppm)Cl_2], (0.849g, 0.10mmol), + [Au($PNEt_3$)Cl] (1.140 g, 0.20 mmol), + 14B(0.249g,0.20mmol)], for complex (**9b**), [Au_2(dppe)Cl_2], (0.963g, 0.10mmol), + [Au($PNEt_3$)Cl] (1.140 g, 0.20 mmol), + 14B(0.249g,0.20mmol)], for complex (**9c**), [Au_2(dppa)Cl_2], (0.850g, 0.10mmol), + [Au($PNEt_3$)Cl] (1.140 g, 0.20 mmol), + 14B(0.249g, 0.20mmol)]; for complex (**10a**), [Au_2(dppm)Cl_2], (0.849g, 0.10mmol), + [Au($PNMe_3$)Cl] (0.790 g, 0.20 mmol), + 14B(0.249g,0.20mmol)], for complex (**10b**), [Au_2(dppe)Cl_2], (0.963g, 0.10mmol), + [Au($PNMe_3$)Cl] (0.790 g, 0.20 mmol), + 14B(0.249g,0.20mmol)], for complex (**10c**), [Au_2(dppa)Cl_2], (0.8509g, 0.10mmol), + [Au($PNMe_3$)Cl] (0.790 g, 0.20 mmol), + 14B(0.249g, 0.20mmol)]; for complex (**11a**), [Au_2(dppm)Cl_2], (0.849g, 0.10mmol), + [Au($AsPh_3$)Cl] (0.80 g, 0.20 mmol), + 14B(0.249g,0.20mmol)], for complex (**11b**), [Au_2(dppe)Cl_2], (0.963g, 0.10mmol), + [Au($AsPh_3$)Cl] (0.806 g, 0.20 mmol), + 14B(0.249g,0.20mmol)], for complex (**11c**), [Au_2(dppa)Cl_2], (0.850g, 0.10mmol), + [Au($AsPh_3$)Cl] (0.80 g, 0.20 mmol), + 14B(0.249g, 0.20mmol)]; Analysis for [{Au_2(dppm){(14B)Au (PPh_3)}$_2$] (**3a**), Found C, 50.1, H, 3.1; Calcd for $C_{81}H_{60}Au_4P_4$, C, 50.2, H, 3.1, IR(nujol) ν(C=C), 1610, ν(PPh_3) 1103,753,692,552,503 cm^{-1} ESI-MS, 1942[M^+]; ^{1}H NMR, (MeOD, $CDCl_3$), ppm, 7.8 (H(a,a′-H), d, J = 6Hz), 7.33 (H(b,b′-H), d, J = 5Hz), 7.6-7.7(broad, PPh_3), 7.1-7.5(dppm); ^{31}P ^{1}H NMR(MeOD, $CDCl_3$, ppm), 46,30; ^{13}C ^{1}H NMR(MeOD), ppm, 131,133,133.6, 132.7,130.9 (PPh_3, dppm); Analysis for [{Au_2(dppe){(14B)Au(PPh_3)}$_2$] (**3b**), Found C, 50.3, H, 3.2; Calcd for $C_{82}H_{62}Au_4P_4$, C, 50.2, H, 3.1, IR(nujol) ν(C=C), 1610, ν(dppe,PPh_3) 1103,753,692, 552,503 cm^{-1} ESI-MS, 1956[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.4 (H(a,a′-H), d, J = 6Hz), 7.33 (H(b,b′-H), d, J = 5Hz), 7.6-7.7, 7.1-7.3(dppm, PPh); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 30; ^{13}C ^{1}H NMR (MeOD), ppm, 133,133.6, 132.7,130.9 (PPh_3, dppm);

Analysis for [{Au_2(dppa){(14B)Au(PPh_3)}$_2$] (**3c**), Found C, 49.1, H, 3.1, N, 0.7; Calcd for $C_{80}H_{59}Au_4P_4N$, C, 50.2, H, 3.1, N, 0.7; IR(nujol) ν(C=C), 1610, ν(dppa,PPh_3) 1103,753,692,552,503 cm^{-1} ESI-MS, 1943[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.8 (H(a,a′-H), d, *J* = 6Hz), 7.33 (H(b,b′-H), d, *J* = 5Hz), 7.1-7.5(dppm); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 46,37; ^{13}C ^{1}H NMR(MeOD), ppm, 125,126.6,123.6,133.6, 132.7,138.9 (PPh_3, dppm); Analysis for [{Au_2(dppm){(14B)Au(PPh-o-me_3)}$_2$] (**6a**), Found C, 50.1, H, 3.1; Calcd for $C_{82}H_{63}Au_4P_4$, C, 50.2, IR(nujol) ν(C=C), 1610, ν(PPh_3) 1103,753,692,552,503 cm^{-1} ESI-MS, 1984[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.8 (H(a,a′-H), d, *J* = 6Hz), 7.33 (H(b,b′-H), d, *J* = 5Hz), 7.6-7.7(broad, PPh_3), ^{31}P ^{1}H NMR($CDCl_3$, ppm), 33; ^{13}C ^{1}H NMR(MeOD, CDCl3), ppm, 131,133,133.6, 132.7,130.9 (PPh_3, dppm); Analysis for [{Au_2(dppe){(14B)Au(PPh-o-me_3)}$_2$] (**6b**), Found C, 50.1, H, 3.1; Calcd for $C_{82}H_{63}Au_4P_4$, C, 50.2, IR(nujol) ν(C=C), 1610, ν(PPh_3) 1103,753,692,552,503 cm^{-1} ESI-MS, 1984[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.8 (H(a,a′-H), d, *J* = 6Hz), 7.3 (H(b,b′-H), d, *J* = 5Hz), 7.6-7.7(broad, PPh_3), ^{31}P ^{1}H NMR($CDCl_3$, ppm), 33; ^{13}C ^{1}H NMR(MeOD), ppm, 131,133,133.6, 132.7,130.9 (PPh_3, dppe); Analysis for [{Au_2(dppa){(14B)Au(PPh-o-me_3)}$_2$] (**6c**), Found C, 50.1, Calcd for $C_{82}H_{63}Au_4P_4$, C, 50.2, IR(nujol) ν(C=C), 1610, ν(PPh_3) 1103,753,692,552,503 cm^{-1} ESI-MS, 1984[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.8 (H(a,a′-H), d, *J* = 6Hz), 7.6-7.7(broad, PPh_3), ^{31}P ^{1}H NMR($CDCl_3$, ppm), 33; ^{13}C ^{1}H NMR(MeOD), ppm, 131,133,133.6, 132.7, 130.9 (PPh_3, dppa); Analysis for [{Au_2(dppm){(14B)Au(PPh-p-me_3)}$_2$] (**7a**), Found C, 50.1, H, 3.1; Calcd for $C_{82}H_{63}Au_4P_4$, C, 50.2, IR(nujol) ν(C=C), 1610, ν(PPh_3) 1103,753,692,552,503 cm^{-1} ESI-MS, 1984[M^+]; Analysis for [{Au_2(dppe){(14B)Au(PPh-p-me_3)}$_2$] (**7b**), Found C, 50.1, H, 3.1; Calcd for $C_{82}H_{63}Au_4P_4$, C, 50.2, IR(nujol) ν(C=C), 1610, ν(PPh_3) 1103,753,692,552,503 cm^{-1} ESI-MS, 1984[M^+]; Analysis for [{Au_2(dppa){(14B)Au(PPh-p-me_3)}$_2$] (**7c**), Found C, 50.1, H, 3.1; Calcd for $C_{82}H_{63}Au_4P_4$, C, 50.2, IR(nujol) ν(C=C), 1610, ν(PPh_3) 1103,753,692,552,503 cm^{-1} ESI-MS, 1984[M^+]; Analysis for [{Au_2(dppm){(14B)Au(PCy_3)}$_2$] (**8a**), Found C, 49.1, H, 4.6, P, 6.3; Calcd for $C_{81}H_{90}Au_4P_4$, C, 50.2, H, 4.6, P, 6.3, IR(nujol) ν(C=C), 1610, ν(dppm,PPh_3) 1103,753,692,552,503 cm^{-1} ESI-MS, 1974[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.2 (H(a,a′-H), d, *J* = 6Hz), 7.33 (H(b,b′-H), d, *J* = 5Hz), 1.6-2.4(broad, PCy_3), ^{31}P ^{1}H NMR($CDCl_3$, ppm), 56,33; ^{13}C ^{1}H NMR, ppm, 32.7, 30.9,131,133,133.6, (PCy, dppm); Analysis for [{Au_2(dppe){(14B)Au(PCy_3)}$_2$] (**8b**), Found C, 49.5, H, 4.6, P, 6.3; Calcd for $C_{82}H_{92}Au_4P_4$, C, 50.2, H, 4.6, P, 6.5, IR(nujol) ν(C=C), 1610, ν(dppe,PPh_3) 1103,753,692, 552,503 cm^{-1} ESI-MS, 1988[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.2 (H(a,a′-H), d, *J* = 6Hz), 7.33 (H(b,b′-H), d, *J* = 5Hz), 1.6-2.4(broad, PCy_3), ^{31}P ^{1}H NMR($CDCl_3$, ppm), 56,37; ^{13}C ^{1}H NMR, ppm, 32.7, 30.9,131,133,133.6, (PCy, dppe); Analysis for [{Au_2(dppa){(14B)Au(PCy_3)}$_2$] (**8c**), Found C, 48.6, H, 4.6, N, 0.7, P, 6.3; Calcd for $C_{80}H_{89}Au_4P_4$, C, 48.2, H, 4.6, N, 0.7, P, 6.3, IR(nujol) ν(C=C), 1610, ν(dppa,PPh_3) 1103,753,692,552,503 cm^{-1} ESI-MS, 1975[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.2 (H(a,a′-H), d, *J* = 6Hz), 7.33 (H(b,b′-H), d, *J* = 5Hz), 1.6-2.4(broad, PCy_3), ^{31}P ^{1}H NMR($CDCl_3$, ppm), 54, 56.4,65.74; ^{13}C ^{1}H NMR, ppm, 32.7, 30.9,131,133,133.6, (PCy, dppa); Analysis for [{Au_2(dppm){(14B)Au($PNEt_3$)}$_2$] (**9a**), Found C, 43.9, H, 4.9, P, 6.8; Calcd for $C_{69}H_{90}Au_4P_4$, C, 43.2, H, 4.6, P, 6.3, IR(nujol) ν(C=C), 1610, ν(dppm,PPh_3) 1103,753,692,503 cm^{-1} ESI-MS, 1830[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.2 (H(a,a′-H), d, *J* = 6Hz), 7.33 (H(b,b′-H), d, *J* = 5Hz), 1.06(t,*J* = 6Hz), 3.18(dd,*J* = 7Hz); ^{13}C ^{1}H NMR, ppm, 32.7, 30.9,13,13.9, 131,133,133.6, (PNEt, dppm); Analysis for [{Au_2(dppe){(14B)Au($PNEt_3$)}$_2$] (**9b**), Found C, 45.9, H, 4.9, P, 6.8; Calcd for $C_{70}H_{92}Au_4P_4$, C, 45.2, H, 4.9, P, 6.3, IR(nujol) ν(C=C), 1610, ν(dppe,PPh_3) 1103,753,692,503 cm^{-1} ESI-MS, 1844[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.2 (H(a,a′-H), d, *J* = 6Hz), 7.33 (H(b,b′-H), d, *J* = 5Hz), 1.06(t,*J* = 6Hz), 3.18(dd,*J* = 7Hz); ^{13}C ^{1}H NMR, ppm, 32.7, 30.9,13,13.9, 131,133,133.6, (PNEt, dppe); Analysis for [{Au_2(dppa){(14B)Au($PNEt_3$)}$_2$] (**9c**), Found C, 44.9, H, 4.9, N, 0.76, P, 6.8; Calcd for $C_{69}H_{90}Au_4P_4$, C, 43.2, H, 4.6,N, 0.77, P, 6.3, IR(nujol) ν(C=C), 1610, ν(dppm,PPh_3) 1103,753,692,503 cm^{-1} ESI-MS, 1831[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.2 (H(a,a′-H), d, *J* = 6Hz), 7.33 (H(b,b′-H), d, *J* = 5Hz), 1.06(t,*J* = 6Hz), 3.18(dd,*J* = 7Hz); ^{13}C ^{1}H NMR, ppm, 32.7, 30.9,13,13.9, 131,133,133.6, (PNEt, dppa); Analysis for [{Au_2(dppm){(14B)Au($PNMe_3$)}$_2$] (**10a**), Found C, 41.9, H, 3.9, P, 7.8; Calcd for $C_{57}H_{66}Au_4P_4$, C, 41.2, H, 3.6, P, 7.3, IR(nujol) ν(C=C), 1610, ν(dppm) 1103,753,692,503 cm^{-1} ESI-MS, 1662[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.2 (H(a,a′-H), d, *J* = 6Hz), 7.33 (H(b,b′-H), d, *J* = 5Hz), 1.96; ^{13}C ^{1}H NMR, ppm, 23,23.9, 131,133,133.6, (PNMe, dppm); Analysis for [{Au_2(dppe){(14B)Au($PNMe_3$)}$_2$] (**10b**), Found C, 41.9, H, 4.19, P, 7.8; Calcd for $C_{58}H_{68}Au_4P_4$, C, 41.2, H, 4.6, P, 7.3, IR(nujol)

ν(C=C), 1610, ν(dppe) 1103,753,692,503 cm^{-1} ESI-MS, 1676[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.0 (H(a,a′-H), d, J = 6Hz), 7.33 (H(b,b′-H), d, J = 5Hz), 1.96; ^{13}C ^{1}H NMR, ppm, 23,23.9, 131,133,133.6, (PNMe, dppe); Analysis for [{Au_2(dppa){(14B)Au($PNMe_3$)}$_2$] (**10c**), Found C, 40.9, H, 3.9, N, 0.8, P, 7.8; Calcd for $C_{56}H_{65}NAu_4P_4$, C, 40.2, H, 3.6, N, 0.8, P, 7.3, IR(nujol) ν(C=C), 1610, ν(dppa) 1103,753,692,503 cm^{-1} ESI-MS, 1663[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.2 (H(a,a′-H), d, J = 6Hz), 7.33 (H(b,b′-H), d, J = 5Hz), 1.96; ^{13}C ^{1}H NMR, ppm, 23,23.3, 131,133,133.6, (PNMe, dppa); Analysis for [{Au_2(dppm){(14B)Au-($AsPh_3$)}$_2$] (**11a**), Found C, 47.9, H, 2.9, P, 3.8; Calcd for $C_{81}H_{60}Au_4P_2As_2$, C, 47.2, H, 2.6, P, 3.3, IR(nujol) ν(C=C), 1610, ν(dppm) 1103,753,692,503 cm^{-1} ESI-MS, 2032[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.2 (H(a,a′-H), d, J = 6Hz), 7.33 (H(b,b′-H), d, J = 5Hz), 7.06-7.2(Ph); ^{13}C ^{1}H NMR, ppm, 131,133, 133.6, (dppm); Analysis for [{Au_2(dppe){(14B)Au ($AsPh_3$)}$_2$] (**11b**), Found C, 47.9, H, 3.0, P, 3.8; Calcd for $C_{82}H_{62}Au_4P_2As_2$, C, 48.2, H, 2.6, P, 3.3, IR(nujol) ν(C=C), 1610, ν(dppe) 1103,753,692,503 cm^{-1} ESI-MS, 2046[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.2 (H(a,a′-H), d, J = 6Hz), 7.33 (H(b,b′-H), d, J = 5Hz), 7.06-7.2(Ph); ^{13}C ^{1}H NMR, ppm, 131,133,133.6, (dppe); Analysis for [{Au_2(dppa){(14B)Au($AsPh_3$)}$_2$] (**11c**), Found C, 47.2, H, 2.9, N, 0.7, P, 3.8; Calcd for $C_{80}H_{59}Au_4P_2As_2$, C, 47.2, H, 2.9, N, 0.7, P, 3.3, IR(nujol) ν(C=C), 1610, ν(dppa) 1103,753,692,503 cm^{-1} ESI-MS, 2033[M^+]; ^{1}H NMR, ($CDCl_3$),ppm, 7.2 (H(a,a′-H), d, J = 6Hz), 7.33 (H(b,b′-H), d, J = 5Hz), 7.06-7.2(Ph); ^{13}C ^{1}H NMR, ppm, 131,133,133.6, (dppa).

Preparation of [{Au_4(dppm/dppe/dppa)$_2$(14B)$_2$], 4a-4c

The procedure are siamilar as stated above but the stoichiometric ratios are as follows, for complex (**4a**), [Au_2(dppm)Cl_2], (0.849g, 0.10mmol), + 14B(0.126g,0.10mmol)], for complex (**4b**), [Au_2(dppe)Cl_2], (0.963g, 0.10mmol), + 14B(0.126g, 0.10mmol)], for complex (**4c**), [Au_2(dppa)Cl_2], (0.850g, 0.10mmol), + 14B(0.126g,0.10mmol)]. Analysis for [{Au_4(dppm)$_2$(14B)$_2$] (**4a**), Found: C, 46.61, H, 2.9, Calcd for $C_{70}H_{52}Au_4P_4$; C, 46.6, H, 3.0, IR(nujol) ν(C=C), 1610, ν(dppm) 1103,753,692,552, 503 cm^{-1} ESI-MS, 1804[M^+]; ^{1}H-NMR($CDCl_3$), ppm, 7.5 (a,a′-H, d, J = 6Hz), 7.36 (b,b′-H, d, J = 5Hz), 7.1-7.3 (broad, dppm), 1.5(dppm); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 31.86; ^{13}C ^{1}H NMR, ppm, 133,133.6,133.9, 132.7,130.9, 129 (dppm); Analysis for [{Au_4(dppe)$_2$ (14B)$_2$] (**4b**), Found: C, 47.61, H, 3.1, Calcd for $C_{72}H_{56}Au_4P_4$; C, 47.2, H, 3.1, IR(nujol) ν(C=C), 1610, ν(dppe) 1103,753,692,552,503 cm^{-1} ESI-MS, 1830[M^+]; ^{1}H-NMR($CDCl_3$), ppm, 7.64 (a,a′-H, d, J = 6Hz), 7.63 (b,b′-H, d, J = 5Hz), 7.1-7.3 (broad, dppe), 1.5(dppe); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 40.16; ^{13}C ^{1}H NMR, ppm, 133, 133.6, 133.9, 132.7, 132.9, 129.3, 129.4, 129.8 (dppe); Analysis for [{Au_4(dppa)$_2$(14B)$_2$] (**4c**), Found: C, 45.21, H, 2.81,N, 1.55, Calcd for $C_{68}H_{50}N_2Au_4P_4$; C, 45.2, H, 2.81, N, 1.6; IR(nujol) ν(C=C), 1610, ν(dppa) 1103,753,692,552,503 cm^{-1} ESI-MS, 1806[M^+]; ^{1}H-NMR($CDCl_3$), ppm, 7.9(NH), 7.84 (a,a′-H, d, J = 6Hz), 7.49 (b,b′-H, d, J = 5Hz), 7.1-7.3 (broad, dppa); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 79.6, 76.6; ^{13}C ^{1}H NMR, ppm, 133,133.6,133.9, 132.7,132.9, 129.3, 129.4, 129.8, 128.9, 128.4 (dppa).

Preparation of [{Au^{III}(C_6F_5/Mes)$_2$}{(14B)Au(PPh_3)}$_2$], 5

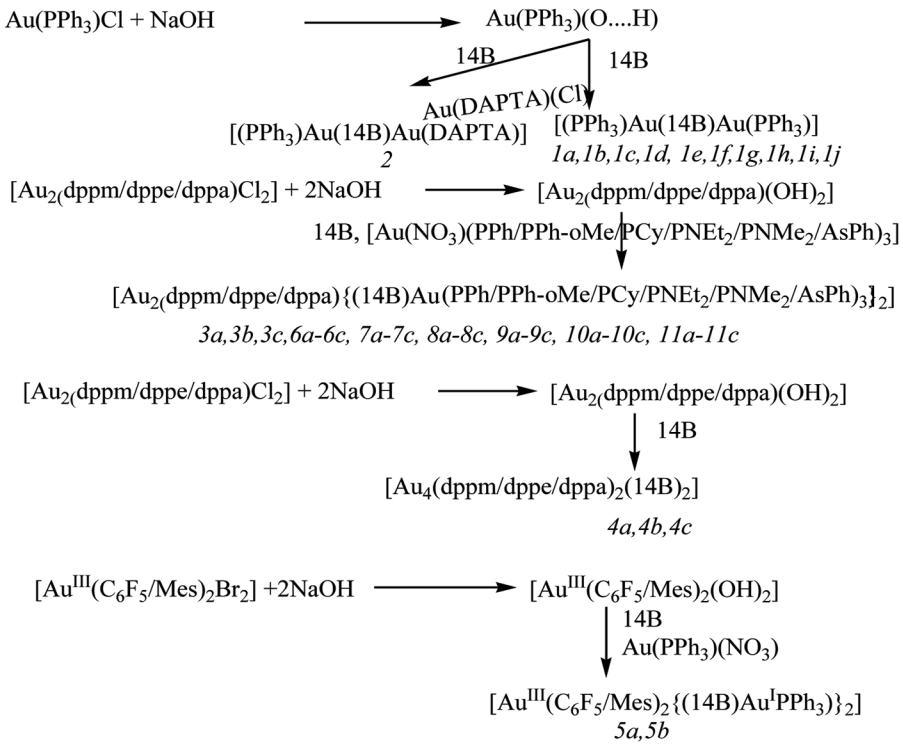
The procedure are same as stated above but the stoichiometric ratio are as follows, for complex (**5a**), NBu_4[Au(C_6F_5)$_2Br_2$], (0.933g, 0.10mmol), + 14By (0.242g,0.20mmol)], + Au(PPh_3)Cl(0.990g, 0.20mmol), for complex (**5b**), PPN[Au(Mes)$_2Cl_2$], (1.047g, 0.10mmol), + 14B(0.242g,0.20mmol)], + Au(PPh_3)Cl (0.990g, 0.20mmol), Analysis for [{Au^{III}(C_6F_5)$_2$ (14B)$_2$ {Au(PPh_3)}], (**5a**), Found: C, 48.61, H, 2.21; Calcd for $C_{68}H_{38}Au^{III}Au^{I}{}_2P_2F_{10}$, C, 48.1, H, 2.24; IR(nujol) ν(C=C), 1610, ν(PPh_3) 1103,753,692,552, 503 cm^{-1} ν(C_6F_5) 1510, 955, 800, ESI-MS, 1697[M^+]; Fluoro NMR, ^{19}F {H}NMR($CDCl_3$), ppm, -115.03(F_{ortho}), -158.03(F_{para}), -160.12(F_{meta}); ^{1}H NMR ($CDCl_3$), ^{1}H,ppm, 7.3 (a,a′-H, d, J = 6Hz), 8.0 (b,b′-H, d, J = 5Hz), 7.1-7.5 (broad, PPh_3); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 32.812; ^{13}C ^{1}H NMR, ppm, 131,133,133.6, 132.7,130.9 (PPh_3), 133,134(C_6F_5); Analysis for [{Au^{III}(Mes)$_2$(4,4bpy)$_2$}{Au(PPh_3)}](NO_3)$_3$, (*5b*), Found: C, 46.1, H, 2.6; Calcd for $C_{74}H_{68}Au^{III}Au^{I}{}_2P_2$, C, 46.9, H, 2.9, IR(nujol) ν(C=C), 1610, ν(PPh_3) 1103,753,692,552,503 cm^{-1} ν(Mes) 1510, 955; ^{1}H NMR ($CDCl_3$), ^{1}H,ppm, 6.99 (H,Mes), 8.0 (a,a′-H, d, J = 6Hz), 7.3 (b,b′-H, d, J = 5Hz), 7.1-7.5(broad, PPh_3); ^{31}P ^{1}H NMR($CDCl_3$, ppm), 32.912; ^{13}C ^{1}H NMR, ppm, 131,133,133.6, 132.7,130.9 (PPh_3), 43,134(Mes).

Results and Discussion

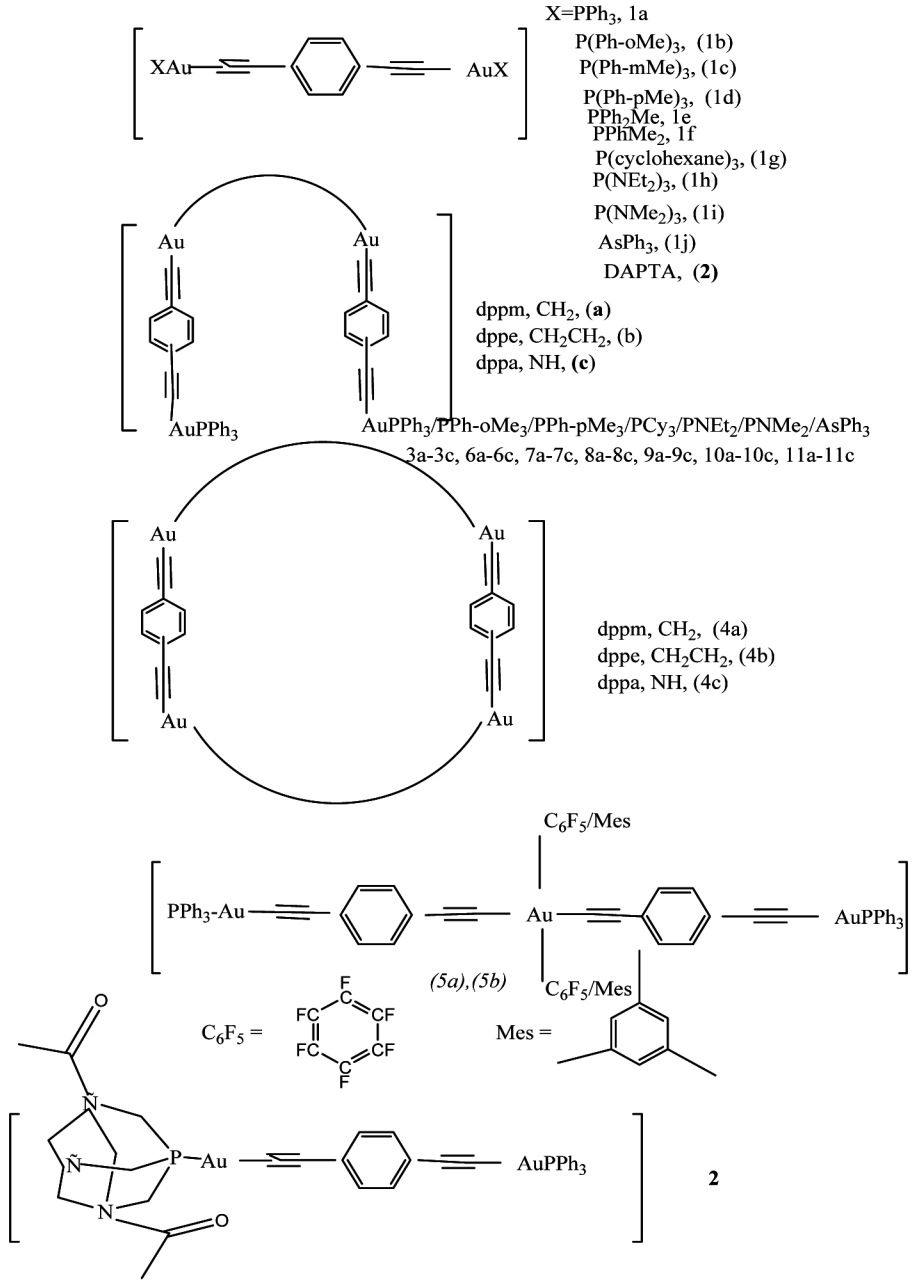
The complexes [(PPh_3)Au(1,4-B)Au(PPh_3/PPh-oMe/ PPh_2Me/$PPhMe_2$/PCy_3/$PNEt_2$/$PNMe_2$/ $AsPh_3$/DAPTA)],

(*1a-1j*,*2*), [{Au_2(dppm/dppe/dppa)}{(1,4B)Au(PPh_3/PPh-oMe/PPh_2Me/$PPhMe_2$/PCy_3/ $PNEt_2$/$PNMe_2$/$AsPh_{33}$)}$_2$], (**3**, **6**, **7**, **8**, **9**, **10**, **11**), [{Au_4(dppm/dppe/dppa)$_2$ (1,4B)$_2$}], (**4**), [$(AuPPh_3)_2Au^{III}$(14B)(Mes/C_6F_5)$_2$, (**5a**, **5b**) [dppm/dppe/dppa = diphenyl phosphino-methane (a), -ethane (b), ammine (c), C_6F_5/Mes pentafluorophenyl/ mesitylene, 14B = arylethynyl benzene, DAPTA=diacetyl 1,3,5-Triaza-7-phosphaadamantane], were prepared by removing weakly coordinating halogen, 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 complexes are partly soluble in common organic solvents *viz*. acetone, acetonitrile, chloroform, dichloromethane but insoluble in H_2O, methanol, ethanol (Scheme 2) whereas the complex **2** is soluble in water, D_2O.

IR spectra of the complexes, show a 1:1 correspondence with the spectra of the parent analogue, except the appearance of intense stretching at 1600-1660 cm^{-1} with concomitant loss of ν(Au-Cl) at 320-340 cm^{-1}. They are assigned as ν(C=C) 1600-1660 cm^{-1}. Other important frequencies are ν(phosphines)/ν(PPh_3) 1109,750,690,559, 790, 509 cm^{-1} along with weak bands at 570 and 692 cm^{-1}. Due to the presence of the pi-conjugated 14B system the values are shifted by low energy portions. The ESI mass spectrum of a MeCN solution are discussed in the Experimental Section. Phosphorous NMR, ^{31}P ^{1}H NMR, is very much important to characterize the complexes, (Fig. S2,3-10, measured in D_2O, MeOD, $CDCl_3$). In each complex environment the peak shifted to downfield region from the parent dibromo complex due to presence of more pi-conjugated diimine 14B self-assembled electron rich system. Hence the values are 29.25 for [(PPh_3)Au(14B)Au(PPh_3)], 32.25 for [(PPh_3)Au(14B) Au(PPh-oMe)$_3$)], 32,31 for [{Au_2(dppm}{(14B) Au(PPh_3)}$_2$], (*3a*), 32.812 for [{(PPh_3)Au^{I}(4,4′-bpy)}$_2$ Au^{III}(C_6F_5)] (NO_3)$_3$, (*5a*) whereas the parent chloro/bromo complexes arise at 33.3 for [(Au(PPh_3) (Cl)], 45.03 for [(Au(PPh_3)$_2$](ClO_4), 31.31 (major, trans), 31.83 (minor,cis) for [(Au(PPh_3)$_2$(Br_2)] (ClO_4), respectively[6-14]. The ^{1}H NMR spectra of complexes, [(PPh_3)Au(1,4-B)Au(PPh_3/PPh-oMe/PPh_2Me/$PPhMe_2$/ PCy_3/$PNEt_2$/$PNMe_2$/$AsPh_3$/DAPTA)], (**1a-j**, **2**), [{Au_2(dppm/dppe/dppa)} {(1,4B)Au(PPh_3/PPh-oMe/PPh_2Me/$PPhMe_2$/PCy_3/$PNEt_2$/$PNMe_2$/$AsPh_{33}$)}$_2$] (**3**, **6**, **7**, **8**, **9**, **10**, **11**), [{Au_4(dppm/dppe/dppa)$_2$(1,4B)$_2$}], (**4**), were



Scheme 1



Scheme 2

unambiguously assigned (measured in D_2O, MeOD, $CDCl_3$, Fig. S1-10) on comparing with parent complexes and the free ligand[7,9,11-14] and the aromatic portion is broad due to lot of phenyl protons. Due to the presence of pi-conjugated 14B system the values are shifted to downfield portion then the parent complexes. 14B protons (a,a′,b,b′) resonance at high frequency due to electron rich moiety and a,a′greater value than b,b′as they are nearer to nitrogen atom. Fluorine NMR, ^{19}F ^{1}H NMR, is important for the complexes, $[\{(PPh_3)Au^{I}(14B)\}_2Au^{III}(C_6F_5/Mes)]$, (*5a*). as they show three sharp resonances at -116, -156, -160 ppm due to the presence of two *ortho*, two *meta* and one *para* fluorine atom which are supported by the integration value. In the complex environment the values are shifted to more ppm value than the parent one as here extended pi-conjugation and electron delocalisation over a long self assembled chain. Assignment of different resonant peaks in the ^{13}C (^{1}H)NMR spectrum (Fig. S1-10, in D_2O, MeOD,

$CDCl_3$) to respective carbon atoms of are done on all complexes and the data are given in the experimental section. The non-protonated carbon atoms of the phosphine and 14B moiety are shifted farthest downfield in the spectrum effected by the magnetic interaction of two bulky phenyl rings environment and the pi electron delocalization. 14B carbons (a,a′,b,b′) resonance at high frequency due to electron rich moiety and again, a,a′greater value than b,b′as they are nearer to more electronegative, nitrogen atom. The methyl carbon atom of the phosphine ring resonate at 33 ppm, resonably compare with the other carbon atoms resonance. The cross peaks in the ^1H ^1H COSY spectrum along both the sides of the diagonal identify the nuclei that are coupled with each other of on the contrary, the protons that are decoupled from the adjacent ones due to the lack of α-protons will show no correlation in the spectrum. Here, 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 14B portion. The phenyl protons of the phosphines are broad, show coupling interaction with the singlet of methyl near δ = 2 ppm (Fig. S1,2, measured in D_2O, MeOD, $CDCl_3$). In conclusions, this work describes the isolation of a novel series of organometallic Gold(I)-Gold(III) complexes, [(PPh_3)Au(1,4-B)Au(PPh_3/PPh-oMe/PPh_2Me/$PPhMe_2$/ PCy_3/ $PNEt_2$/$PNMe_2$/$AsPh_3$/DAPTA)], (*1a-1j*,*2*), [{Au_2(dppm/dppe/dppa)}{(1,4B)Au(PPh_3/PPh-oMe/ PPh_2Me/$PPhMe_2$/PCy_3/ $PNEt_2$/$PNMe_2$/$AsPh_3$)}$_2$], (*3*,*6*,*7*,*8*,*9*,*10*,*11*), [{Au_4(dppm/dppe/dppa)$_2$(1,4B)$_2$}], (*4*), [($AuPPh_3$)$_2$$Au^{III}$(14B)(Mes/$C_6F_5$)$_2$, (5a,5b) and their spectral and elemental characterisation. Phosphoro NMR, ^{31}P ^1H NMR, directly cherecterize the complexes. ^1H NMR study suggests aromatic protons as well as aliphatic protons. ^{13}C ^1H NMR gives the idea of the carbon skeleton. ^1H-^1H COSY spectrum of the present complexes, confirm their assignment of accurate structure and in solution proton-proton interaction, respectively. Water soluble complex is also reported with spectral data.

Supplementary Information

Supplementary information is available in the website http://nopr.niscpr.res.in/handle/123456789/58776.

Acknowledgement

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 donor) and oxo complexes: Synthesis, structure, spectral study, electrochemistry and chemical reactivity.

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