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## Bi- and Tetrametallic Complexes of the Noble Metals with PNP-

## Ligands

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<sup>d</sup>Lehn Institute of Functional Materials (LIFM), Sun Yat-Sen University (SYSU), Xingang Road West, Guangzhou 510275, China. Two new ligands with  $\{(Ph_2P)_2N\}$  functions have been synthesized and introduced into the chemistry of gold(I). The first ligand N, N,-bis(diphenylphosphanyl)-4-(phenyldiazenyl)aniline (DPPPA) is a derivative of an azo dye. Reaction of DPPPA with [(tht)AuCl] (tht = tetrahydrothiophene) in CH<sub>2</sub>Cl<sub>2</sub> gave the dye functionalized bimetallic gold(I) complex The m-N.N.N'.N'- $[DPPPA(AuCl)_2]$ (1). second ligand, tetrakis(diphenylphosphanyl)xylylenediamine, (DPPXA), has two  $\{(Ph_2P)_2N\}$  functional groups in a xylylenediamine backbone. DPPXA was reacted with [(tht)AuCl] to give the tetrametallic gold complex [DPPXA(AuCl)<sub>4</sub>] (2). Reaction of DPPXA with [(COD)MCl<sub>2</sub>] (M = Pd, Pt) (COD = 1,5-cyclooctadiene) in DMSO resulted in the bimetallic palladium and platinum complexes  $[DPPXA(MCl_2)_2]$  (M = Pd (3), Pt (4)). DPPPA and all metal complexes were characterized by single crystal X-ray diffraction. The complexes demonstrate quite different photophysical properties. Whereas no photoluminescence (PL) was detected for 1 and 4, complex 2 shows red PL in methylene chloride solution as well as in the solid state. Near-infrared emission at ~800 nm was observed for complex 3 at temperatures below ~50 K.

Keywords: Chelates, Gold, Luminescence, Multimetallic compounds, Palladium,

Photoluminescence, Platinum, P-N-P Ligands

### Introduction

Gold chemistry is currently one of the rapidly growing fields of chemistry [1-6]. The number of publications dealing with the application of gold and gold compounds in material and surface sciences, in heterogeneous and especially in homogenous catalysis has recently increased dramatically. This is mirrored by a significant number of reviews dealing with various topics of gold chemistry [1, 7-34]. Molecular gold(I) compounds with a closed shell d<sup>10</sup> electronic configuration show a significant attractive interaction between the gold atoms which are in most cases linearly two-fold coordinated. This fascinating phenomenon has been described as "aurophilicity" and "aurophilic bonding" [1]. The Au-Au distance of these intraand intermolecular aurophilic contacts, which are a result of strong relativistic contractions and low coordination numbers [27, 35], usually range in the area of 2.70 Å - 3.50 Å [1]. The energies of such Au-Au interactions lie in the range of those of hydrogen bonds [36]. Besides their influence on structural properties, aurophilic interactions also have an influence on the photophysical properties of gold complexes [32]. Intramolecular aurophilic bonding is often observed when phosphorus atoms are in close proximity in the ligand scaffold, enabling intramolecular Au-Au interactions. In this context, bis(diphenylphosphino)methane (dppm) and its derivatives play a vital role as bridging ligands (semi-supporting according to the classification of Schmidbaur and Schier) [34] between two gold atoms enabling intramolecular aurophilic bonds [34, 37]. Closely related to dppm is the isoelectronic bis(diphenylphosphino)amine, [(Ph<sub>2</sub>P)<sub>2</sub>NH]. Derivatives of this compound [(Ph<sub>2</sub>P)<sub>2</sub>NR] can be obtained in relatively facile approach by reacting a primary amine RNH<sub>2</sub> with Ph<sub>2</sub>PCl in the presence of a base [38]. Nevertheless, in comparison to dppm and its derivatives only few gold(I) compounds with bis(diphenylphosphino)amine ligands are known [38-51]. Among these compounds only one is known with two  $\{(Ph_2P)_2N\}$  functional groups in the ligand [50]. Specifically, coordinated 2,6four gold atoms were to

bis(bis(diphenylphosphino)amino)pyridine forming [{( $ClAuPh_2P$ )\_2N}<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N] which is stable in the solid state only, but decomposes slowly in solution on exposure to air/moisture [50]. To our knowledge, no other metal complexes with this ligand have been reported.

In this contribution we report on two new bi- and tetrametallic gold(I) complexes in which the ligands bear one or two  $\{(Ph_2P)_2N\}$  functions in the backbone, respectively. Furthermore, the new ligand with two  $\{(Ph_2P)_2N\}$  functions was also used for the synthesis of the related palladium and platinum compounds.

### **Results and Discussion**

Synthesis and Characterization: For our studies we envisaged to synthesize two new ligands with  $\{(Ph_2P)_2N\}$  functions. The first ligand has one  $\{(Ph_2P)_2N\}$  function and a 4-(phenyldiazenyl)aniline backbone. 4-(phenyldiazenyl)aniline is a yellow azo dye also known "aniline yellow". This ligand was also envisaged as it may introduce the as photoisomerisation functionality of the azobenzene group [52] to optical properties of a metal The synthesis functionalized complex. of the  $\{(Ph_2P)_2N\}$ azo dye N.N.bis(diphenylphosphanyl)-4-(phenyldiazenyl)aniline (DPPPA) was achieved by reaction of 4-(phenyldiazenyl)aniline with chlorodiphenylphosphane in a 1: 2 ratio in the presence of NEt<sub>3</sub> which acts as a base (Scheme 1). To the best of our knowledge no similarly functionalized dye is known. DPPPA has been characterized by standard analytical / spectroscopic techniques and the solid-state structure was established by single crystal X-ray diffraction.



Scheme 1. Synthesis of the ligand DPPPA.

The resonances of the 29 aromatic protons in the <sup>1</sup>H NMR spectrum were detected in the range between  $\delta$  6.89 and 7.89 ppm. One signal is seen in the <sup>31</sup>P{<sup>1</sup>H} NMR at  $\delta$  69.0 ppm which is nearly identical with the one reported for [(Ph<sub>2</sub>P)<sub>2</sub>NPh] (68.6 ppm) [53]. DPPPA crystallizes in the triclinic space group *P*-1. The diazo function has *E* configuration. The bonding parameters are in the expected range. Thus, the P-N bond distances of P1-N1 1.737(2) Å and P2-N1 1.732(2) Å are in the range of the corresponding distances in [(Ph<sub>2</sub>P)<sub>2</sub>NPh] (P-N 1.7315(15) Å) [54].

Further reaction of DPPPA with [(tht)AuCl] (tht = tetrahydrothiophene) in CH<sub>2</sub>Cl<sub>2</sub> gave the dye functionalized bimetallic gold(I) complex [DPPPA(AuCl)<sub>2</sub>] (1) as orange crystals (Scheme 2). Once crystallized, 1 is surprisingly poorly soluble in common organic solvents (e.g. THF, CH<sub>2</sub>Cl<sub>2</sub>, chloroform, acetonitrile, DMSO). The signals of the 29 aromatic protons were observed in the range between  $\delta$  7.84 and 6.46 ppm in the <sup>1</sup>H NMR spectrum. The signal of the lattice bound methylene chloride was detected at  $\delta$  5.33 ppm. In the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum one signal at  $\delta$  88.3 ppm was seen which is 19.3 ppm down field with respect to the free ligand.



Scheme 2. Synthesis of 1.

Compound **1** crystallizes in the monoclinic space group  $P2_1/n$  with four molecules of **1** and two molecules of CH<sub>2</sub>Cl<sub>2</sub> in the unit cell (Figure 2). As observed for DPPPA the azo function adopts *E* configuration. The gold atoms are in a typically linear coordination mode with bond angles of P1-Au1-Cl1 175.04(9)° and P2-Au2-Cl2 176.15(9)°. Moreover a close Au-Au contact of 3.0095(7) Å which is characteristic for an aurophilic interaction is observed [1]. The observed Au-Au distance is slightly shorter than in the compounds [(ClAuPh<sub>2</sub>P)<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-4-Br] (3.0402(5) Å) [40] and 5-[*N*,*N*-bis(diphenylphosphanyl- $\kappa P$ : $\kappa P$ ')-amino]isophthalate}bis[chlorogold(I)] (3.0593(7) Å) [38].

To obtain a ligand with two { $(Ph_2P)_2N$ } functional groups in the scaffold we chose xylylenediamine as rigid backbone. Using a benzyl functionalized ligand in which the { $(Ph_2P)_2N$ } functional groups are not directly attached to the benzene ring gives a system with a better solubility. This has a significant advantages in comparison to e.g. bis(bis(diphenylphosphino)amino)pyridine [50]. The synthesis of the new ligand *m*-*N*,*N*,*N*',*N*'-tetrakis(diphenylphosphanyl)xylylenediamine (DPPXA) was achieved by reacting xylylenediamine with chlorodiphenylphosphane in a 1: 4 ratio in the presence of a base (Scheme 3). DPPXA was characterized by <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR, IR and Raman spectroscopy. A characteristic triplet is observed for the benzyl protons in the <sup>1</sup>H NMR

spectrum at  $\delta$  4.30 ppm. Moreover, the signals of the xylylene ring form a characteristic pattern which consists of triplet (6.87 ppm,  ${}^{3}J_{\rm HH} = 7.6$  Hz), a double doublet (6.63 ppm;  ${}^{3}J_{\rm HH} = 7.7$  Hz), and a singlet (6.44 ppm). One signal was detected in the  ${}^{31}P{}^{1}H$  NMR at  $\delta$  59.5 ppm which is in the range of [{(Ph\_2P)\_2N}\_2C\_5H\_3N] (59.0 ppm) [55] but differs by about 10 ppm from the value of the corresponding phenyldiamine derivative 1,3-{(Ph\_2P)\_2N}\_2C\_6H\_4 [56].



Scheme 3. Synthesis of the ligand DPPXA.

DPPXA was further reacted with suitable gold(1), palladium(II), and platinum(II) complexes. Reaction of DPPXA with [(tht)AuCl] in CH<sub>2</sub>Cl<sub>2</sub> resulted in the desired tetrametallic gold complex [DPPXA(AuCl)<sub>4</sub>] (**2**) (Scheme 4). The new complex has been characterized by standard analytical/spectroscopic techniques. The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} spectra show the expected set of signals. Only broadened signals were seen in the <sup>1</sup>H NMR spectrum but a sharp signal at  $\delta$  78.8 ppm is observed in the <sup>31</sup>P{<sup>1</sup>H} NMR which is about 20 ppm downfield shifted in comparison to the free ligand DPPXA. In comparison to the diamino pyridine based gold complex [{(ClAuPh<sub>2</sub>P)<sub>2</sub>N}<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N] **2** seems to be significantly more stable in solution [50]. In contrast to [{(ClAuPh<sub>2</sub>P)<sub>2</sub>N}<sub>2</sub>C<sub>5</sub>H<sub>3</sub>N] single crystals of **2** suitable for X-ray diffraction could be obtained. Compound **2** crystallizes in the monoclinic space group *C*2/*c* with four molecules of **2** and eight molecules of chloroform in the unit cell. A crystallographic *C*2-axis is observed in the center of the xylylene ring along C1 and C4. As seen in the unsubstituted P-N-P gold compound [(ClAuPh<sub>2</sub>P)<sub>2</sub>N-C<sub>6</sub>H<sub>4</sub>-4-Br] [40] the gold atoms in **2** are almost linearly coordinated exhibiting a twofold coordination mode typical for Au(I) (e.g. P1-

Au1-Cl1 176.98(8)°). Moreover, an intramolecular aurophilic interaction is indicated with a Au1-Au2 distance of 3.5257(6) Å. This distance which falls into the upper limit of an aurophilic interaction [1] is about 0.5 Å longer than in compound **1**. The chlorine atom Cl2 is disordered. The Au-P distances are in the expected range of Au1-P1 2.225(2) Å and Au2-P2 2.230(2) Å.



Reacting DPPXA with [(COD)PdCl<sub>2</sub>] (COD = 1,5-cyclooctadiene) in DMSO resulted in the bimetallic palladium complex [DPPXA(PdCl<sub>2</sub>)<sub>2</sub>] (**3**) (Scheme 5). As expected each {(Ph<sub>2</sub>P)<sub>2</sub>N} function coordinates in a chelating fashion to one metal atom. Although numerous palladium complexes which are coordinated to {(Ph<sub>2</sub>P)<sub>2</sub>N} function are known there are to the best of our knowledge only one bimetallic {(Ph<sub>2</sub>P)<sub>2</sub>N} palladium complexes known in which the two metal atoms are bound to one rigid backbone. In this complex, [1,3-*{cis*-PdCl<sub>2</sub>(PPh<sub>2</sub>)<sub>2</sub>N*/*<sub>2</sub>C<sub>6</sub>H<sub>4</sub>], the metal atoms are ligated by *N*,*N*,*N'*,*N'*-tetrakis-(diphenylphosphanyl)-1,3-diaminobenzene [57]. In the <sup>1</sup>H NMR spectrum of compound **3** a well resolved triplet was observed for the benzyl group at  $\delta$  4.13 ppm (<sup>3</sup>*J*<sub>HP</sub> = 13.0 Hz). In comparison to the free ligand this signal is slightly upfield shifted. In the <sup>31</sup>P{<sup>1</sup>H} NMR one signal is observed at  $\delta$  30.9 ppm. In contrast to **2** which shows a downfield shift of this signal in comparison to DPPXA an upfield shift was seen in **3**.



Scheme 5. Synthesis of 3 and 4.

Compound **3** crystallizes in the monoclinic space group  $P2_1/n$  (Figure 6). In the bimetallic compound each metal center is four-fold coordinated. Two phosphorus atoms from one  $\{(Ph_2P)_2N\}$  function and two chlorine atoms form a square planar arrangement. This kind of coordination mode is typically observed in comparable compounds such as  $[Cl_2Pd\{(Ph_2P)_2N_2C_6H_4-4-Br\}]$ , [40]  $[Cl_2Pd\{(Ph_2P)_2N-C_6H_4-2-Et\}]$  [58], and  $[Cl_2Pd\{(Ph_2P)_2N-benzyl\}]$  [59]. The observed Pd-P bond length of Pd1-P1 2.1996(9) Å, Pd1-P2 2.2214(9) Å, Pd2-P3 2.2191(9) Å, and Pd2-P4 2.2032(9) Å are in the expected range [40, 57-59].

By applying similar conditions as used for the reaction of **3**, treatment of DPPXA with  $[(COD)PtCl_2]$  in DMSO resulted in the bimetallic platinum complex  $[DPPXA(PtCl_2)_2]$  (**4**) (Scheme 5). Compound **4** was fully characterized by standard analytical /spectroscopic techniques. In the <sup>1</sup>H NMR spectrum the expected signals are well resolved. Most characteristic are the singlet of the central phenyl ring at  $\delta$  5.56 and the triplet of the benzyl group at  $\delta$  4.05 ( ${}^{3}J_{HP} = 13.4$  Hz). The chemical shifts are in a comparable range to compound **4**. As a result of the <sup>195</sup>Pt nucleus, characteristic platinum satellites were observed in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum at  $\delta$  16.7 ppm ( ${}^{1}J_{PtP} = 3282$  Hz). The corresponding triplet in the <sup>195</sup>Pt NMR was detected at  $\delta$  4032 ppm. Single crystals of compound **4** could be obtained from the mother liquor (Figure 5). In the solid state compound **3**. Thus, one square planar coordinated metal atom is bound to each of the two {(Ph<sub>2</sub>P)<sub>2</sub>N} functions. Unfortunately, only crystals of low

quality were obtained. Although, the X-ray data collected from **4** was poor the connectivity of **4** and its composition were deduced. However, further bonding parameters cannot be discussed.

### **Figure 5 here**

Photophysical Properties: The solid-state absorption spectrum of deeply colored complex 1 is closely related to those of the aniline yellow azo dye and its DPPPA derivative (Figure 6). The onset of absorption at ~550 nm is apparently determined by the phenyldiazenyl moiety in these complexes moderate-to-intense compounds. In general, gold(I)show photoluminescence (PL) in particular at low (cryogenic) temperatures. In contrast, no emission was detected for solid complex 1 at temperatures varying between 18 and 293 K. We roughly estimate the upper limit of PL quantum yield of 1 to be less than  $\sim 10^{-6}$ . The absence of PL can be attributed to very efficient (fast) non-radiative electronic relaxation via the phenyldiazenyl moiety. Such relaxation is well documented for azobenzene and its derivatives and has been related to rotational motions along the azo bond [60-63]. The photophysical properties of 1 in solution, including its possible photoisomerisation, were not investigated because of the very poor solubility of **1** in the solvents probed (see above).

In difference to 1, complex 2 absorbs light below ~400 nm and shows PL in a methylene chloride solution as well as in the solid state (Figure 7). The emission band A at ~470 nm is especially prominent at temperatures below ~150 K. It decays on the time scale of nanoseconds (upper bound estimate) and can tentatively be attributed to fluorescence of the xylylenediamine, i.e. ligand backbone, moiety. The blue fluorescence has also been observed for xylylenediamine polymer derivatives [64]. The red-near-infrared emission *B* at ~700 nm is

relatively weak but dominates at ambient temperature. The width of band *B* indicates that several emissive excited states/configurations may be involved. The emission *B* decays within a few microseconds at ambient temperature and tens of microseconds at T = 18 K (biexponential fits were used) and can be assigned to phosphorescence of the {(ClAuPh<sub>2</sub>P)<sub>2</sub>N} core. A similar weak emission band at 650 nm is also observed for dissolved complex **2** (Figure 7). The low energy of the emission *B* is likely related to Au-Au intramolecular interaction in photoexcited **2** [65, 66].

### Figures 6 and 7 here

Similar to 1, no luminescence was detected from solid Pt-complex 4 at temperatures varying between 18 and 293 K. The photophysical properties of homologous Pd and Pt complexes typically correlate well [67, 68]. However, in contrast to non-luminescent 4, Pd-complex 3 shows near-infrared PL centered at ~800 nm at temperatures below ~50 K (Figure 8). The emission lifetime is about 20  $\mu$ sec at T = 18K. The PL intensity is relatively weak in comparison to complex 2 and decreases quickly by increasing the temperature above ~50 K. Such low-energy emission might be contributed by collective (excimeric) excitations in the solid state of 3. Its assignment requires further investigations.

Figure 8 here

### Summary

In summary, three bimetallic complexes of gold, palladium, and platinum as well as a tetrametallic gold complex have been synthesized and structurally characterized. The photophysical properties of all metal complexes were determined. Reaction of DPPPA, a derivative of an azo dye, with [(tht)AuCl] gave the dye functionalized bimetallic gold(I) complex  $[DPPPA(AuCl)_2]$ (1). The ligand, m-N,N,N',N'second tetrakis(diphenylphosphanyl)xylylenediamine, has two  $\{(Ph_2P)_2N\}$  functional groups in the scaffold of a xylylenediamine backbone. Reaction of DPPXA with [(tht)AuCl] gave the tetrametallic gold complex [DPPXA(AuCl)<sub>4</sub>] (2). Treatment of DPPXA with [(COD)MCl<sub>2</sub>] (M = Pd, Pt) (COD = 1,5-cyclooctadiene) in DMSO resulted in the bimetallic palladium and platinum complexes  $[DPPXA(MCl_2)_2]$  (M = Pd (3), Pt (4)]. In difference to 1 and 4, which show no detectable PL, complex 2 is luminescent in solution and especially in the solid state. Its red emission at ~650-700 nm may indicate the effect of Au-Au intramolecular interaction. In difference to the homologous Pt-complex 4, Pd-complex 3 shows near-infrared PL at ~800 nm in the solid state at temperatures below ~50 K.

### **Experimental Section**

Although all products are not very air sensitive all manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenktype glassware either or in an argon-filled *MBraun* glove box. THF was distilled under nitrogen from potassium benzophenone ketyl prior to use. Hydrocarbon solvents (toluene and *n*-pentane) were dried using an *MBraun* solvent purification system (SPS-800). All solvents for vacuum line manipulations were stored *in vacuo* over LiAlH<sub>4</sub> in resealable flasks. Deuterated solvents were obtained from *Aldrich* (99 atom % D) and were degassed, dried, and stored *in vacuo* over Na/K alloy in resealable flasks. NMR spectra were recorded on a *Bruker* Avance II 300 MHz and a *Bruker* Avance 500 MHz FT-NMR spectrometer. Chemical shifts

are referenced to internal solvent resonances and are reported relative to tetramethylsilane. IR spectra were obtained on a Bruker Tensor 34 or a Perkin Elmer Spectrum GX. Raman spectra were carried out with a Bruker MultiRAM. Mass spectra were recorded at 70 eV on a Finnigan MAT 8200 and a Thermo Scientific DFS. Elemental analyses were carried out with an *Elementar* Vario EL. [(tht)AuCl] [69, 70] (tht = tetrahydrothiophene) was prepared according to modified standard procedures. UV-Vis spectra were obtained on a Varian Cary 50 Spectrophotometer. Solid state absorption spectra were measured using a Labsphere integrating sphere. Photoluminescence (PL) spectra were recorded on a Horiba JobinYvon Fluorolog-322 spectrometer equipped with Hamamatsu R9910 and R5509 photomultipliers (PMT) as detectors for the spectral range of ~250-800 nm and ~450-1400 nm, respectively. Solid samples were placed into a closed-cycle optical cryostat (Leybold) and measured at temperatures varying between 293 K and 18 K. The emission spectra were corrected for the wavelength-dependent response of the spectrometer and detector (in relative photon flux units). PL decay traces were recorded by connecting a PMT to an oscilloscope and using a nitrogen laser for a pulsed excitation at 337 nm (with pulses of ~2 nsec duration and ~5 µJ energy).

### Synthesis of *N*,*N*,-Bis(diphenylphosphanyl)-4-(phenyldiazenyl)aniline (DPPPA).

3.94 g (20 mmol) of 4-Aminoazobenzene were dissolved in 100 mL of toluene. Then, 5.6 mL (40 mmol) NEt<sub>3</sub> are added to the mixture. At 0 °C 7.2 mL (40 mmol) of freshly distilled Ph<sub>2</sub>PCl were added dropwise. After stirring for 14 h at room temperature the resulting colorless precipitate (HNEt<sub>4</sub>Cl) was filtered off and washed twice with 10 mL of toluene. The filtrate was brought under reduced pressure to dryness yielding a yellow powder which was recrystallized from toluene/-hexane (1:3). Yield 8.5 g (15 mmol, 75 %) Suitable crystals for

X-ray structure analysis were best grown by layering a toluene solution with *n*-hexane. Anal. Calcd  $C_{36}H_{29}N_3P_2$  - C 76.45, H 5.17, N 7.43, found C 76.29, H 5.30, N 7.44.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.88 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.6, 2H), 7.59 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.7, 2H), 7.54-7.49 (m, 2H), 7.44-7.49 (m, 9H), 7.40-7.29 (m, 12H), 6.89 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.6, 2H). - <sup>31</sup>P{<sup>1</sup>H} NMR (202.47 MHz, CDCl<sub>3</sub>):  $\delta$  69.0. - IR (FT, KBr, cm<sup>-1</sup>): 3049 (w), 2926 (w), 2854 (w), 2499 (w), 2354 (w), 1960 (w), 1890 (w), 1635 (w), 1592 (m), 1492 (m), 1479 (m), 1435 (m), 1430 (m), 1385 (w), 1306 (w), 1281 (w), 1224 (m), 1215 (s), 1183 (w), 1152 (w), 1121 (w), 1092 (m), 1070 (w), 1026 (w), 996 (w), 951 (w), 918 (w), 896 (s), 827 (w), 770 (m), 751 (m), 741 (s), 726 (m), 694 (vs), 686 (s), 668 (w), 639 (w), 569 (w), 556 (m), 521 (w), 507 (m), 483 (w), 466 (m), 421 (w).

# Synthesis of [N,N,-Bis(diphenylphosphanyl) $\kappa P:\kappa P'-4-(phenyldiazenyl)aniline$ $bischlorogold(I)] ([DPPPA(AuCl)_2], 1)$

A solution of 0.42 g (0.75 mmol) of DPPPA in 15 mL of  $CH_2Cl_2$  was added to a solution of 0.48 g (1.50 mmol) of [(tht)AuCl] in 10 mL  $CH_2Cl_2$ . After stirring for 1 hour the reaction mixture was stored at +4 °C for 14 hours leading to the crystallization of orange blocks of  $1 \cdot \frac{1}{2}CH_2Cl_2$ . Reduction of the volume of the mother solution led to further crystals. After filtration and washing with small amounts of dichloromethane and diethylether the product was dried in vacuum. Single crystals were obtained from CDCl<sub>3</sub> in a NMR tube. Yield: 0.61 g (0.57 mmol, 76 %). Anal. Calcd  $C_{36.5}H_{30}Au_2Cl_3N_3P_2 - C 40.86$ , H 2.82, N 3.92, found C 40.29, H 2.73, N 3.89.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  7.84-7.80 (m, 2H), 7.74-7.67 (m, 7H), 7.60-7.55 (m, 2H), 7.52-7.44 (m, 12H), 7.36 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.6 Hz, 2H), 6.46 (d, <sup>3</sup>*J*<sub>HH</sub> = 8.2, 2H), 5.33 (s, 1H, <sup>1</sup>/<sub>2</sub> CH<sub>2</sub>Cl<sub>2</sub>) - <sup>31</sup>P{<sup>1</sup>H} NMR (202.47 MHz, CDCl<sub>3</sub>):  $\delta$  88.3 ppm. - IR (FT, KBr, cm<sup>-1</sup>): 3052 (w),

3015 (w), 2976 (w), 2865 (w), 2199 (w), 1967 (w), 1894 (w), 1813 (w), 1774 (w), 1584 (w), 1481 (m), 1435 (m), 1334 (w), 1305 (w), 1221 (w), 1283 (w), 1263 (w), 1220 (w), 1190 (m), 1155 (m), 1101 (s), 1071 (m), 998 (m), 961 (m), 940 (s), 899 (s), 772 (m), 747 (s), 690 (w), 586 (m), 568 (m), 541 (m), 512 (m), 480 (m).

### Synthesis of *m*-*N*,*N*,*N*',*N*'-Tetrakis(diphenylphosphanyl)xylylenediamine (DPPXA)

0.66 ml (0.681 g, 5 mmol) of *m*-xylylenediamine and 2.8 ml (2.02 g, 20 mmol) of triethylamine were dissolved in 50 ml of CH<sub>2</sub>Cl<sub>2</sub>. To this solution 3.6 mL (4.41 g, 20 mmol) of chlorodiphenylphosphane in 10 mL CH<sub>2</sub>Cl<sub>2</sub> were added dropwise under stirring at 0 °C over a period of 30 min. A colorless precipitate was formed. After warming to ambient temperature the reaction mixture was stirred for 16 hours. The solution was evaporated and the remaining residue was extracted with THF (3 × 10 ml). The solvent of the extract was evaporated and the remaining residue was subsequently dried *in vacuo* for 3 hours. The product was obtained as a colorless powder. Yield: 4.06 g (93%). Anal. Calcd C<sub>56</sub>H<sub>48</sub>N<sub>2</sub>P<sub>4</sub> - C 77.05, H 5.54, N 3.21, found C 76.82, H 5.80, N 3.28.

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  7.41-7.33 (m, 16H, PPh), 7.33-7.25 (m, 24H, PPh), 6.87 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 1H, CH), 6.63 (dd, <sup>3</sup>J<sub>HH</sub> = 7.7, 1.3 Hz, 2H, CH), 6.44 (s, 1H, CH), 4.30 (t, <sup>3</sup>J<sub>HP</sub> = 10.5 Hz, 4H, CH<sub>2</sub>). - <sup>31</sup>P{<sup>1</sup>H} NMR (121.48 MHz, CDCl<sub>3</sub>):  $\delta$  59.5. - IR (ATR, cm<sup>-1</sup>): 3047 (w), 2898 (w), 2864 (w), 1586 (w), 1478 (m), 1432 (m), 1347 (w), 1308 (w), 1181 (w), 1162 (w), 1090 (m), 1034 (m), 1013 (w), 982 (m), 894 (w), 875 (m), 822 (s), 795 (m), 740 (vs), 693 (vs), 624 (w), 613 (w), 571 (w), 558 (w), 519 (m). - Raman (solid state, cm<sup>-1</sup>): 3051 (m), 1586 (m), 1180 (w), 1156 (w), 1093 (m), 1027 (m), 1000 (s), 671 (w), 618 (w), 266 (w), 218 (m), 210 (m). - EI-MS (70 eV): m/z (%) = 872 ([M]<sup>+</sup>, <1), 688 ([M - PPh<sub>2</sub>]<sup>+</sup>, <1), 386 ([N(PPh<sub>2</sub>)<sub>2</sub>]<sup>+</sup>, 75), 504 ([M - N(PPh<sub>2</sub>)<sub>2</sub>]<sup>+</sup>, 1), 183 ([M - 2(N(PPh<sub>2</sub>)<sub>2</sub>)]<sup>+</sup>, 91), 106 ([C<sub>8</sub>H<sub>9</sub>]<sup>+</sup>, 48), 77 ([Ph]<sup>+</sup>, 64).

# Synthesisof[m-N,N,N',N'-Tetrakis(diphenylphosphanyl)-κP:κP':κP'':κP'''-xylylenediaminetetrakischlorogold(I)] ([DPPXA(AuCl)<sub>4</sub>], 2)

0.32 g (1.00 mmol) of chloro(tetrahydrothiophene)gold(I) were dissolved in 25 ml of CH<sub>2</sub>Cl<sub>2</sub>. 0.22 g (0.25 mmol) of *m-N,N,N',N'*-tetrakis(diphenylphosphanyl)xylylendiamine were added under stirring. The mixture was stirred for 1 hour at ambient temperature. The solution was then evaporated. The remaining residue was washed with diethylether (3 × 10 ml) and subsequently dried *in vacuo*. The product was obtained as a colorless powder. Yield: 0.41 g (90 %). Anal. Calcd  $C_{56}H_{48}Au_4Cl_4N_2P_4 \cdot 2CH_2Cl_2 - C 35.32$ , H, 2.66, N, 1.42, found C 34.93, H 3.44, N 1.08.

<sup>1</sup>H NMR (300.13 MHz, CDCl<sub>3</sub>):  $\delta$  7.84-7.64 (br, m, 16H, Ph), 7.64-7.40 (br, m, 20H, Ph), 6.46-6.39 (br, m, 1H, Ph), 6.28-6.18 (br, m, 1H, Ph), 6.07-5.94 (br, m, 2H, Ph), 4.78-4.54 (br, m, 4H, CH<sub>2</sub>). - <sup>31</sup>P{<sup>1</sup>H} NMR (121.49 MHz, CDCl<sub>3</sub>):  $\delta$  78.8. - IR (ATR, cm<sup>-1</sup>): 2963 (m), 1480 (w), 1435 (m), 1310 (w), 1260 (s), 1154 (w), 1097 (vs), 1015 (vs), 878 (w), 797 (vs), 746 (m), 689 (s), 580 (w), 535 (m). - Raman (solid state, cm<sup>-1</sup>): 3056 (m), 2910 (m), 1586 (m), 1186 (w), 1161 (w), 1101 (w), 1027 (m), 1000 (s), 705 (w), 618 (w), 331 (m), 264 (m), 193 (w). - FAB-MS: *m/z* (%) = 1767 ([M - Cl]<sup>+</sup>, 100), 1534 ([M - (AuCl<sub>2</sub>)]<sup>+</sup>, 24), 1117 ([M - (PPh<sub>2</sub>AuCl<sub>2</sub>)]<sup>+</sup>, 28).

# Synthesis of [m-N,N,N',N'-Tetrakis(diphenylphosphanyl)- $\kappa^2 P,P'$ : $\kappa^2 P'',P'''$ xylylenediaminetetrakisdichloropaladium(II)] ([DPPXA(PdCl\_2)\_2], 3)

0.14 g (0.5 mmol) of dichloro(1,5-cyclooctadiene)palladium(II) were dissolved in 5 ml of DMSO. 0.22 g (0.25 mmol) of m-N,N,N',N'-tetrakis(diphenylphosphanyl)xylylendiamine were added under stirring. The mixture was heated to 100 °C and stirred for 1 hour. After

cooling down to ambient temperature the product was obtained as yellow crystals. Yield: 0.23 g (75 %). Anal. Calcd  $C_{56}H_{48}Cl_4N_2P_4Pd_2$ · 1.5 $C_2H_6OS$  - C 52.70, H 4.27, N 2.08, S 3.58, found C 52.40, H 4.18, N 2.07, S 2.97.

<sup>1</sup>H NMR (300.13 MHz, DMSO): δ 7.77-7.62 (m, 24H, Ph), 7.61-7.51 (m, 16H, Ph), 6.00 (t, <sup>3</sup> $J_{HH} = 7.6$  Hz, 1H, CH), 5.78 (d, <sup>3</sup> $J_{HH} = 9.2$  Hz, 2H, CH), 5.58 (s, 1H, CH), 4.13 (t, <sup>3</sup> $J_{HP} = 13.0$ Hz, 4H, CH<sub>2</sub>). - <sup>31</sup>P{<sup>1</sup>H} NMR (121.49 MHz, DMSO): δ (ppm) = 30.9. - IR (ATR, cm<sup>-1</sup>): 3057 (w), 3001 (w), 2913 (w), 1480 (m), 1434 (s), 1306 (m), 1184 (w), 1162 (m), 1098 (vs), 1053 (s), 1023 (m), 991 (s), 894 (m), 842 (m), 801 (s), 749 (s), 720 (m), 690 (vs), 659 (m), 567 (m), 509 (s). - FAB-MS: m/z (%) = 1193 ([M - Cl]<sup>+</sup>, 100), 1156 ([M - 2Cl]<sup>+</sup>, 62), 1120 ([M - 3Cl]<sup>+</sup>, 50).

# Synthesis of [m-N,N,N',N'-Tetrakis(diphenylphosphanyl)- $\kappa^2 P,P'$ : $\kappa^2 P'',P'''$ xylylenediaminetetrakisdichloroplatinum(II)] ([DPPXA(PtCl\_2)\_2], 4)

0.11g (0.3 mmol) of dichloro(1,5-cyclooctadiene)platinum(II) were dissolved in 3 ml of DMSO. 0.13 g (0.15 mmol) of *m-N,N,N',N'*-tetrakis(diphenylphosphanyl)xylylendiamine were added under stirring. The mixture was heated to 100 °C and stirred for 1 hour. After cooling down to ambient temperature the product was obtained as pale yellow crystals. Yield: 0.15 g (70 %). Anal. Calcd  $C_{56}H_{48}Cl_4N_2P_4Pt_2 \cdot 1.5C_2H_6OS - C$  46.56, H 3.77, N 1.84, S 3.16, found C 46.54, H 3.68, N 1.84, S 2.61.

<sup>1</sup>H NMR (300.13 MHz, DMSO): δ 7.74-7.59 (m, 24H, Ph), 7.58-7.51 (m, 16H, Ph), 5.97 (t, <sup>3</sup> $J_{HH} = 7.6$  Hz, 1H, CH), 5.76 (d, <sup>3</sup> $J_{HH} = 7.6$  Hz, 2H, CH), 5.56 (s, 1H, CH), 4.05 (t, <sup>3</sup> $J_{HP} = 13.4$ Hz, 4H, CH<sub>2</sub>) - <sup>31</sup>P{<sup>1</sup>H} NMR (121.49 MHz, DMSO): δ (ppm) = 16.7 (s and d, <sup>1</sup> $J_{PtP} = 3282$ Hz). - <sup>195</sup>Pt NMR (86.02 MHz, DMSO): δ (ppm) = 4032 (t, <sup>1</sup> $J_{PtP} = 3282$  Hz). - IR (ATR, cm<sup>-1</sup>): 3058 (w), 2921 (m), 2852 (m), 1480 (w), 1457 (w), 1434 (s), 1306 (m), 1264 (w), 1183

(w), 1162 (m), 1100 (vs), 1053 (s), 1024 (m), 990 (s), 950 (w), 893 (m), 839 (s), 798 (s), 748
(s), 721 (s), 691 (vs), 661 (s), 574 (s), 518 (s). - Raman (solid state, cm<sup>-1</sup>): 3060 (s), 3006 (w), 2909 (m), 1587 (s), 1186 (w), 1161 (w), 1101 (m), 1027 (m), 1000 (vs), 617 (w), 580 (w), 331 (w) 302 (m), 270 (w), 232 (w), 217 (m), 193 (m). - FAB-MS: *m/z* (%) = 1405 ([M]<sup>+</sup>, 5), 1370 ([M - Cl]<sup>+</sup>, 100).

**X-ray Crystallographic studies of DPPPA and 1-3:** Single crystals were grown as described in the synthetic procedures of each compound. Suitable crystals were covered in mineral oil (Aldrich) and mounted onto a glass fiber. Data were collected on diffractometer equipped with a STOE imaging plate detector system IPDS2 using MoK $\alpha$  radiation with graphite monochromatization ( $\lambda = 0.71073$  Å) at low temperatures. Subsequent computations were carried out on an Intel Core2Quad. Structure solution was performed by direct methods; full-matrix-least squares refinement against  $F^2$  using SHELXS-97 and SHELXL-97 software [71]. Figures 1-5 were generated using the program Diamond3.2 [72].

Crystal data for DPPPA:  $C_{36}H_{29}N_3P_2$ , M = 565.56, triclinic, a = 11.1761(6) Å, b = 11.1965(6)Å, c = 14.1318(7) Å,  $\alpha = 99.258(4)^\circ$ ,  $\beta = 103.902(4)^\circ$ ,  $\gamma = 115.270(4)^\circ$ , V = 1480.74(13) Å<sup>3</sup>, T = 180(2) K, space group P-1, Z = 2,  $\mu$ (MoK $\alpha$ ) = 0.177 mm<sup>-1</sup>, 10061 reflections measured, 5216 independent reflections ( $R_{int} = 0.1397$ ). The final  $R_I$  values were 0.0575 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.2036 (all data). The goodness of fit on  $F^2$  was 1.168.

Crystal data for 1:  $C_{36\cdot50}H_{30}Au_2Cl_3N_3P_2$ , M = 1072.86, monoclinic, a = 10.177(2) Å, b = 26.446(5) Å, c = 13.202(3) Å,  $\beta = 96.31(3)^\circ$ , V = 3531.7(12) Å<sup>3</sup>, T = 120(2) K, space group  $P2_1/n$ , Z = 4,  $\mu(MoK\alpha) = 8.647$  mm<sup>-1</sup>, 16400 reflections measured, 6522 independent reflections ( $R_{int} = 0.0701$ ). The final  $R_1$  values were 0.0470 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.0768 (all data). The goodness of fit on  $F^2$  was 0.989.

Crystal data for 2:  $C_{58}H_{50}Au_4Cl_{10}N_2P_4$ , M = 2041.25, monoclinic, a = 19.742(4) Å, b = 18.125(4) Å, c = 20.570(4) Å,  $\beta = 112.74(3)^\circ$ , V = 6788(2) Å<sup>3</sup>, T = 200(2) K, space group C2/c, Z = 4,  $\mu$ (MoK $\alpha$ ) = 9.143 mm<sup>-1</sup>, 21679 reflections measured, 6243 independent reflections ( $R_{int} = 0.0673$ ). The final  $R_1$  values were 0.0416 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.1092 (all data). The goodness of fit on  $F^2$  was 1.044.

Crystal data for **3**: C<sub>58</sub>H<sub>54</sub>Cl<sub>4</sub>N<sub>2</sub>OP<sub>4</sub>Pd<sub>2</sub>S, M = 1305.57, monoclinic, a = 17.1159(7) Å, b = 16.2598(5) Å, c = 20.7904(8) Å,  $\beta = 96.553(3)^{\circ}$ , V = 5748.2(4) Å<sup>3</sup>, T = 150(2) K, space group  $P2_1/n$ , Z = 4,  $\mu$ (MoK $\alpha$ ) = 1.000 mm<sup>-1</sup>, 65134 reflections measured, 12547 independent reflections ( $R_{int} = 0.0831$ ). The final  $R_1$  values were 0.0447 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.0978 (all data). The goodness of fit on  $F^2$  was 1.037.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no. CCDC-927333 (DPPPA), 927334 (1), 927335 (2), 927336 (3). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+(44)1223-336-033; email: <u>deposit@ccdc.cam.ac.uk</u>).

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### **Figure Captions**

Figure 1. Solid-state structure of DPPPA, omitting hydrogen atoms [72]. Selected bond lengths [Å] and angles [°]: P1-N1 1.737(2), P2-N1 1.732(2), N2-N3 1.247(3); P1-N1-P1 120.72(11).

**Figure 2.** Solid-state structure of **1**, omitting hydrogen atoms [72]. Selected bond lengths [Å] and angles [°]: Au1-P1 2.236(3), Au1-Cl1 2.290(2), Au1-Au2 3.0095(7), Au2-P2 2.235(2), Au2-Cl2 2.285(2), P1-N1 1.696(8), P2-N1 1.712(7), N2-N3 1.270(11); P1-Au1-Cl1 175.04(9), P1-Au1-Au2 85.60(6), Cl1-Au1-Au2 99.12(7), P2-Au2-Cl2 176.15(9), P2-Au2-Au1 85.58(6), Cl2-Au2-Au1 98.09(7), P1-N1-P2 123.4(4).

Figure 3. Solid-state structure of 2, omitting hydrogen atoms [72]. Selected bond lengths [Å], angles [°] or torsion angles [°]: Au1-Cl1 2.288(2), Au2-Cl2B 2.323(6), Au1-P1 2.225(2), Au2-P2 2.230(2), N-P1 1.703(6), N-P2 1.717(6), Au1-Au2 3.5257(6); P1-Au1-Cl1 176.98(8), N-P1-Au1 109.0(2), N-P2-Au2 112.4(2), P1-N-P2 115.7(3), Cl1-Au1-Au2 106.68(6), P1-Au1-Au2 75.69(6), P2-Au2-Au1 65.70(4); P1-Au1-Au2-P2 58.08(2).

**Figure 4.** Solid-state structure of **3**, omitting hydrogen atoms [72]. Selected bond lengths [Å], angles [°] or torsion angles [°]: Pd1-Cl1 2.3627(11), Pd1-Cl2 2.3464(9), Pd2-Cl3 2.3610(9), Pd2-Cl4 2.3706(9), Pd1-P1 2.1996(9), Pd1-P2 2.2214(9), Pd2-P3 2.2191(9), Pd2-P4

2.2032(9), N1-P1 1.699(3), N1-P2 1.696(3), N2-P3 1.698(3), N2-P4 1.692(3); C11-Pd1-Cl2 96.33(4), Cl3-Pd2-Cl4 96.57(3), P1-Pd1-P2 71.92(3), P3-Pd2-P4 71.43(3), Cl1-Pd1-P1 94.77(3), Cl2-Pd1-P2 97.24(4), Cl3-Pd2-P3 96.01(3), Cl4-Pd2-P4 96.38(3), Cl1-Pd1-P2 166.09(3), Cl2-Pd1-P1 168.29(4), Cl3-Pd2-P4 166.78(3), Cl4-Pd2-P3 166.05(3), Pd1-P1-N1 94.40(10), Pd1-P2-N1 93.70(10), Pd2-P3-N2 94.29(10), Pd2-P4-N2 95.02(10), P1-N1-P2 99.74(15), P3-N2-P4 99.19(14).

**Figure 5.** Solid-state structure of **4**, omitting hydrogen atoms. As result of the low quality of the collected data no bond lengths and angles are given.

**Figure 6.** UV-Vis solid state absorption spectra of aniline yellow, DPPPA and complex **1**. The spectra are vertically shifted for clarity.

**Figure 7**. Photoluminescence excitation (PLE) and emission (PL) spectra of **2** in the (a) methylene chloride solution and (b) solid (polycrystalline) state. The PL and PLE spectra were excited and recorded at 300 and 650 nm and 300 and 800 nm in (a) and (b), respectively. The low-temperature PL of solid **2** is relatively bright and was recorded with the excitation and emission monochromator slits set to 2 nm spectral width.

**Figure 8**. Photoluminescence excitation (PLE) and emission (PL) spectra of solid complex **3** cooled to 18 K. The PL and PLE spectra were excited and recorded at 350 and 750 nm, respectively



Synthesis of ligands with one or two  $\{(Ph_2P)_2N\}$  functions in the backbone

Synthesis of bi- and tetrametallic gold complexes

Synthesis of bimetallic palladium and platinum complexes

















wavelength (nm)