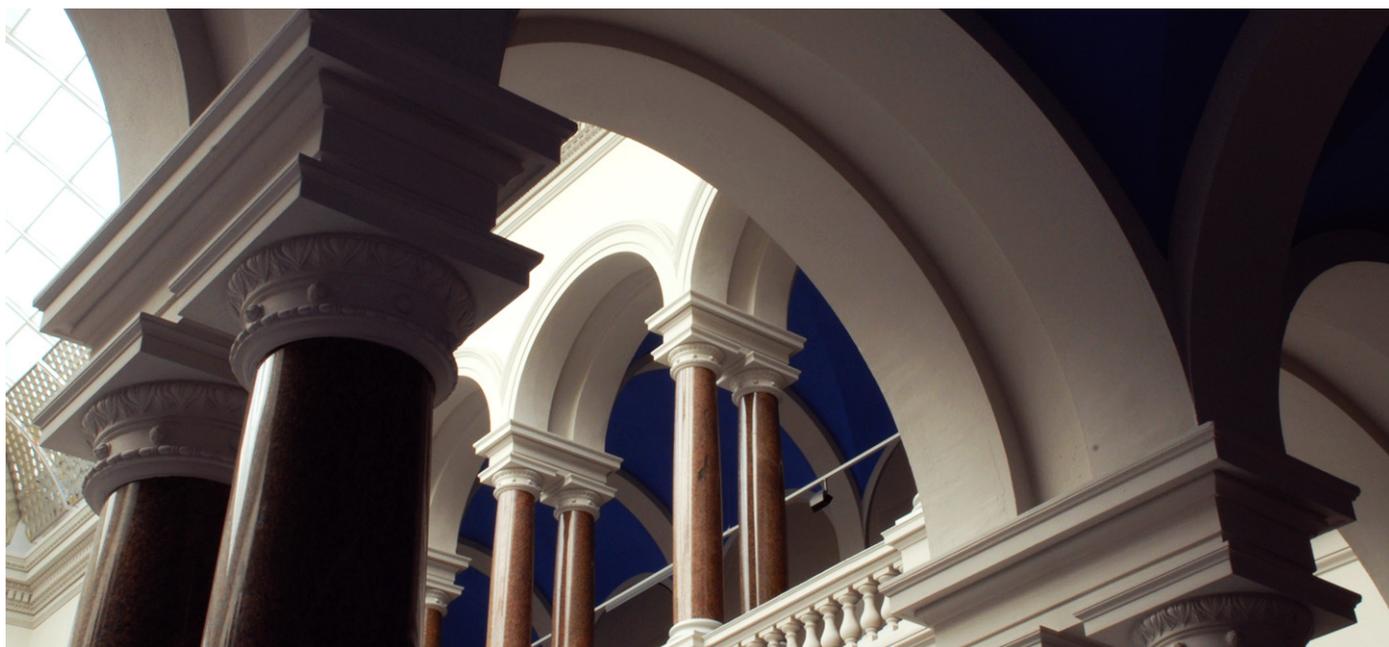


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Substituted Bisphosphanilamines as Ligands in Gold(I) Chemistry – Synthesis and Structures

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Abstract.

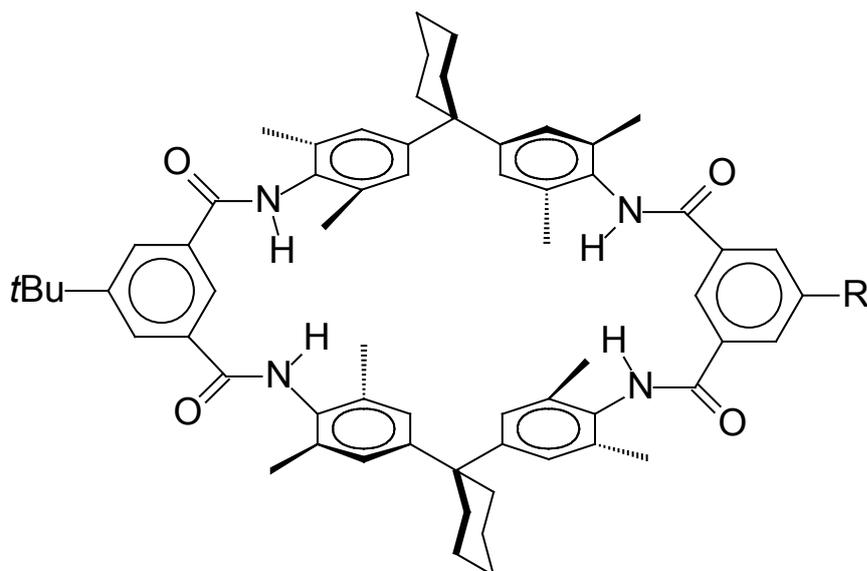
Dimethyl 5-aminoisophthalate, which is a building block of amino-substituted tetralactam macrocycles, was used as ligand in gold(I) chemistry to form model complexes for macrocyclic gold compounds. Reaction of dimethyl 5-aminoisophthalate with chlorodiphenylphosphine gave the diphosphine compound dimethyl 5-[*N,N*-bis(diphenylphosphanyl)amino]isophthalate (dmbpaip). This compound can further be reacted with [AuCl(tht)] (tht = tetrahydrothiophene) to give the dinuclear complex [Au₂Cl₂(dmbpaip)]. In contrast, treatment of dmbpaip with [Au(tht)₂]ClO₄ resulted in the ionic compound [Au₂(dmbpaip)₂](ClO₄)₂ in which the cation forms an eight-membered ring. In both gold(I) compounds Au···Au interactions are observed. All new compounds were characterized by single-crystal X-ray diffraction.

.Keywords: Chelates, Gold, N-P Ligands, P Ligands

Introduction

Besides the challenges in synthetic chemistry, gold(I) compounds [1] were recently intensively studied for catalytic applications [2, 3]. Moreover, gold(I) compounds are also of interest for photophysical [4, 5, 6] and pharmaceutical [7] applications. Most solid-state structures and many molecular configurations of di- or multinuclear two-coordinated gold(I) complexes are influenced by aurophilic interactions [8]. These contacts, which were subject of many experimental [1] and theoretical studies [9], have an energy gain of about 5–10 kcal per contact [10]. This energy is in the range of a conventional hydrogen bond.

Since Au(I) tends to have a coordination number of two with linear stereochemistry, it is well-suited to form linear rigid-rod structures including large rings and polymers [11]. Based on these considerations, we are exploring the possibility to couple a macrocyclic organic ring with two Au(I) atoms and the possibility to build larger structures with this motif. In organic chemistry, tetralactam macrocycles are known to be obtained in a straightforward synthesis. Besides their stability, the major advantage is the broad variety of functional groups which can be attached to the macrocycle (Scheme 1) [12]. Thus, transition metals such as copper and ruthenium could be coordinated to tetralactam macrocycles. As a result, larger setups, in which the macrocycles are bridged by a transition-metal atom, were obtained [13].

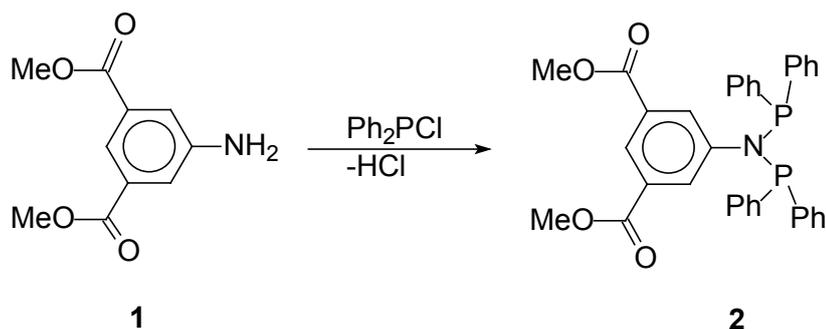


(Scheme 1)

Herein, we report our first results of this long-term project. In a first attempt to attach Au(I) ions to such a cycle, we planned to incorporate an aniline function ($R = NH_2$; Scheme 1). As a model compound for the macrocycle, we used dimethyl 5-aminoisophthalate (**1**) which is a building block in the synthesis of the tetralactam macrocycle [12, 13].

Results and Discussion

To attach suitable bonding sites for the Au(I) atoms to the model compound, dimethyl 5-aminoisophthalate (**1**) was reacted with chlorodiphenylphosphine in the presence of triethylamine in a straightforward synthesis to give the desired compound dimethyl 5-*N,N*-bis(diphenylphosphanyl)amino]isophthalate (dmbpaip) (**2**) in almost quantitative yield (Scheme 2).



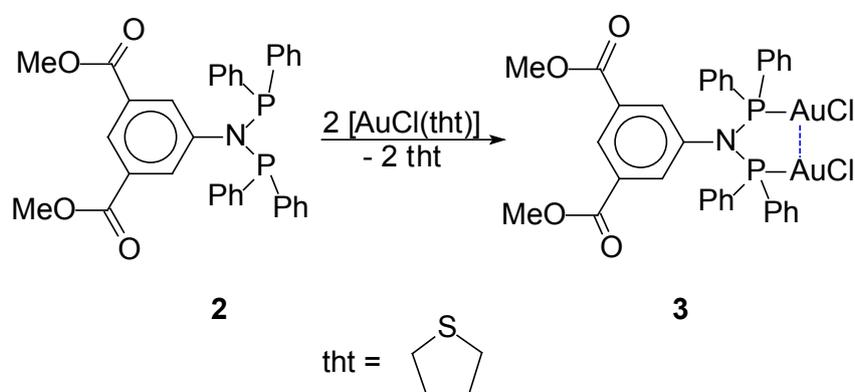
(Scheme 2)

The new diphosphine compound has been characterized by standard analytical/spectroscopic techniques and the solid-state structure was established by single-crystal X-ray diffraction. The most characteristic features of the $^1\text{H-NMR}$ spectrum are the singlets of the hydrogen atoms of the aminoisophthalate ring at $\delta = 8.86$ and 8.10 ppm. Moreover, the expected signal of the phosphorus atoms is observed at $\delta = 69.1$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum. Compound **2** crystallizes in the monoclinic space group $C2/c$ having eight molecules of compound **2** in the unit cell (Figure 1). The solid-state structure is in agreement with the data obtained in solution. The bond lengths and angles are in the expected range of N-P1 $1.7319(13)$ Å, N-P2 $1.7280(13)$ Å, and P1-N-P2 $115.63(7)^\circ$.

Figure 1 here

Further reaction of compound **2** with chloro(tetrahydrothiophene)gold(I) in CH_2Cl_2 resulted in the dinuclear compound μ -{dimethyl 5-[*N,N*-bis(diphenylphosphanyl- $\kappa P:\kappa P$)amino]isophthalate}bis[chlorogold(I)] (**3**) (Scheme 3). The analog compound bis(diphenylphosphanyl)amine (dppa) and its gold derivatives $[\text{RAu}(\text{dppa})\text{AuR}]$ ($\text{R} = \text{Cl}, \text{C}_6\text{F}_5,$ and C_6Cl_5) were reported earlier [14, 15, 16]. As a result of the coordination of the gold atoms, a high-field shift of the phosphorus

resonance from $\delta = 69.1$ ppm in **2** to $\delta = 87.8$ ppm in **3** is observed in the $^{31}\text{P}\{^1\text{H}\}$ -NMR spectrum. Single crystals of compound **3** could be obtained by slow diffusion of *n*-pentane into a saturated solution of complex **3** in CH_2Cl_2 . Compound **3** crystallizes in the monoclinic space group $C2/c$ having four per unit cell (Figure 2). The solid-state structure of compound **3** clearly confirms the dinuclear setup. The distance between the gold(I) ions ($3.0593(7)$ Å) is significantly shorter than the one observed in the analog bis(diphenylphosphanyl)amine complex $[\text{ClAu}(\text{dppa})\text{AuCl}]$ ($3.121(1)$ Å) [16]. The P-Au-Cl1 angle of $174.07(10)^\circ$ indicates the expected almost linear coordination of the ligands around the gold atoms. A crystallographic $C2$ -axis along N1 and C1 is observed. As a result of this $C2$ -symmetry, the *P*-phenyl rings adopt a staggered conformation along the P-P' axis. The N-P bonding distance of $1.711(5)$ Å is in the same range as observed in compound **2**, whereas the P-N-P' angle of $118.6(5)^\circ$ is a bit wider compared to compound **2** ($115.63(7)^\circ$).

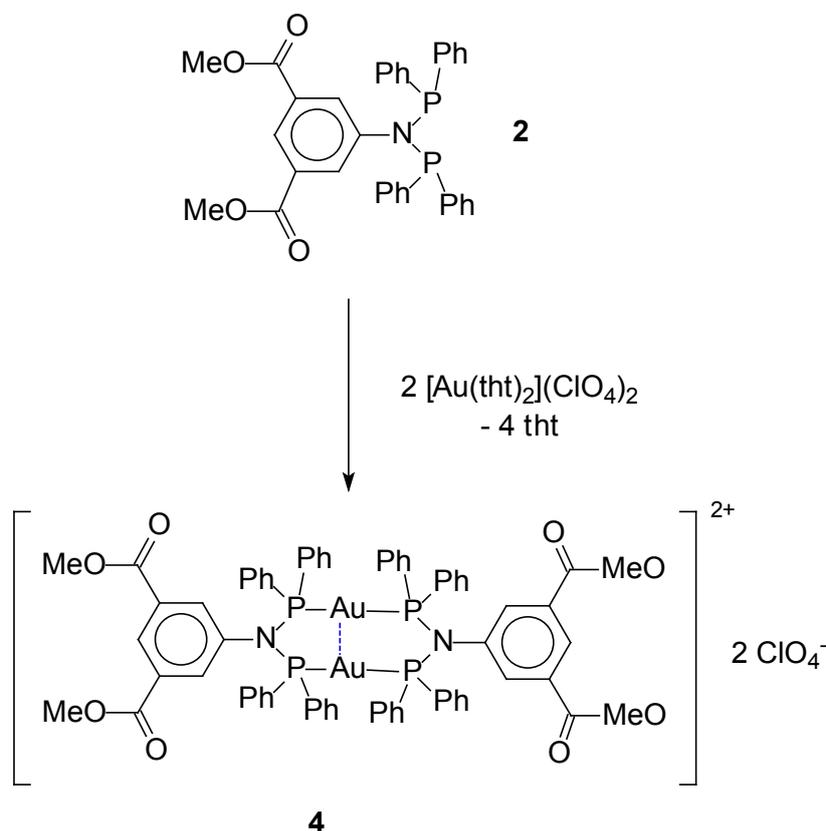


(Scheme 3)

Figure 2 here

To assemble two equivalents of compound **2** at the dinuclear gold(I) backbone, we first tried to further react complex **3** with compound **2**. During our investigations, it turned out that the reaction of compound **2** with bis(tetrahydrothiophene)gold(I)

perchlorate resulted in a one step protocol to give the desired ionic complex bis- μ -{dimethyl 5-[*N,N*-bis(diphenylphosphanyl)- $\kappa P:\kappa P'$]isophthalate} digold(I) perchlorate (**4**) (Scheme 4). The new complex has been characterized by standard analytical/spectroscopic techniques and the solid-state structure was established by single-crystal X-ray diffraction. In the $^3\text{P}\{^1\text{H}\}$ -NMR spectra ($\delta = 97.9$ ppm), a significant high-field shift of approximately 10 ppm compared to compound **3** can be detected. In the ESI-MS spectra of **4** dissolved in acetone, the molecular peaks of the dipositive cation $[\text{Au}_2(\text{dmbpaip})_2]^{2+}$ and the perchlorate anions could clearly be detected.



(Scheme 4)

Compound **4** crystallizes in the triclinic space group $P\bar{1}$. The $[\text{Au}_2(\text{dmbpaip})_2]^{2+}$ cation consists of an almost planar eight-membered ring in the solid state. In the center

of this eight-membered ring, a crystallographic inversion center is observed. The Au \cdots Au distance of 2.798(2) Å is significantly shorter than in other digold(I) ring systems such as [Au₂(dcpm)₂](ClO₄)₂ (dcpm = bis(dicyclohexylphosphanyl)methane, 3.0132(6) Å) [17] and [Au₂(dppm)₂][BH₃CN]₂ (dppm = bis(diphenylphosphanyl)methane, 2.982(2) Å) [18]. As a result of the aurophilic interaction, the P1-Au-P2 angle of 169.0(2)° shows a significant deviation from the expected linear setup. The ring strain gives rise to a P1-N-P2 angle of 130.1(10)° that is about 11.5° larger compared to the corresponding angle in compound **2**.

Figure 3 here

Conclusions

We have prepared some new dinuclear gold(I) compounds forming Au \cdots Au interactions. These are the five-membered ring complex [Au₂Cl₂(dmbpaip)] and the eight-membered ring compound [Au₂(dmbpaip)₂](ClO₄)₂. In both compounds, the gold(I) atoms are ligated by dimethyl 5-aminoisophthalate which is a building block in the synthesis of the tetralactam macrocycle. In the future, we plan to extend our research from the presented model compounds to real tetralactam macrocycles to couple the latter via Au \cdots Au interactions.

Acknowledgement

This work was supported by the *Evangelische Studienwerk e. V. Villigst* (D. W.) and the *Fonds der Chemischen Industrie*. We thank Prof. C. A. Schalley (Freie Universität Berlin) for helpful discussions.

Experimental Section

General Considerations: All manipulations of air-sensitive materials were performed with the rigorous exclusion of oxygen and moisture in flame-dried Schlenk-type glassware either on a dual-manifold Schlenk-line interfaced to a high-vacuum (10^{-4} torr) line or in an argon-filled MBraun glove-box. Tetrahydrofuran was pre-dried over Na wire and distilled from Na/K benzophenone-ketyl prior under nitrogen to use. Hydrocarbon solvents (toluene and *n*-pentane) were distilled from LiAlH_4 under nitrogen. All solvents for vacuum-line manipulations were stored *in vacuo* over LiAlH_4 in resealable flasks. Deuterated solvents were obtained from *Chemotrade Chemiehandelsgesellschaft mbH* or *Euriso-Top GmbH* and were dried, degassed, and stored *in vacuo* over Na/K alloy in resealable flasks. NMR spectra were recorded on a Jeol JNM-LA 400 FT-NMR spectrometer. Chemical shifts were referenced to internal solvent resonances and are reported relative to tetramethylsilane in case of ^1H and $^{13}\text{C}\{^1\text{H}\}$ spectra. $^{31}\text{P}\{^1\text{H}\}$ spectra were referenced to the electronically stored frequency of phosphoric acid (85 %). Mass spectra were recorded at 4000 V on an ESI-TOF-spectrometer Agilent 6210. Elemental analyses were carried out with an Elementar vario EL III. Dimethyl 5-aminoisophthalate (**1**) was purchased from *Sigma-Aldrich Co.* $[\text{AuCl}(\text{tht})]$ [19] and $[\text{Au}(\text{tht})_2]\text{ClO}_4$ [20] (tht = tetrahydrothiophene) were prepared according to modified standard procedures.

Dimethyl 5-[*N,N*-bis(diphenylphosphanyl)amino]isophthalate (dmbpaip) (2).

1.08 ml (6.0 mmol) of chlorodiphenylphosphine and 0.84 ml (6.0 mmol) of triethylamine dissolved in 25 ml of CH_2Cl_2 were slowly added (30 min) to a solution of 0.63 g (3.0 mmol) of dimethyl 5-aminoisophthalate (**1**) at $0\text{ }^\circ\text{C}$. The mixture was stirred

for 30 min at ambient temperature. The solution was evaporated and the remaining residue was extracted with diethylether (3 × 20 mL). The solvent of the extracts was then evaporated *in vacuo*. The product was obtained as colorless powder.

Yield: 1.68 g (97 %). - ^1H NMR (399.65 MHz, C_6D_6 , 21 °C): δ = 8.86 (s, 1H; Ph), 8.10 (s, 2H; Ph), 7.56–7.54 (m, 8H; Ph), 7.05–7.01 (m, 12H; Ph), 3.25 ppm (s, 6H; Me). - $^{31}\text{P}\{^1\text{H}\}$ NMR (161.70 MHz, C_6D_6 , 24 °C): δ = 69.1 ppm. - IR (KBr): 3065, 3051 (m; $\nu[\text{ArH}]$), 2950 (m; $\nu[\text{CH}_3]$), 1727 (vs; $\nu[\text{CO}]$), 1585 (m; $\nu[\text{CC}]$), 1478 (m), 1444, 1431 (vs; $\nu[\text{PPh}]$), 1320 (vs), 1244 (vs; $\nu[\text{PN}]$), 1121, 1091 (m; $\nu[\text{COMe}]$), 1021 (s), 1000 (s), 940 (vs), 859 (vs; $\nu[\text{NPN}]$), 741, 699, 682 (vs; $\gamma[\text{CCH}]$), 552 (m), 513 (s), 496 (s), 456 cm^{-1} (m). - Anal. Calcd for $\text{C}_{34}\text{H}_{29}\text{NO}_4\text{P}_2$ (577.56): C 70.71, H 5.07, N 2.43 %, found C 70.70, H 4.80, N 2.15 %.

μ -{Dimethyl 5-[*N,N*-bis(diphenylphosphanyl- $\kappa\text{P}:\kappa\text{P}$)amino]isophthalate}-bis[chlorogold(I)] (3).

0.58 g (1.0 mmol) of **2** were slowly added (30 min) to a solution of 0.64 g (2.0 mmol) of chloro(tetrahydrothiophene)gold(I) dissolved in 30 ml of CH_2Cl_2 at 0 °C. The mixture was stirred for 30 min at ambient temperature. The solution was then evaporated. The remaining residue was washed with diethylether (3 × 20 mL) and subsequently dried *in vacuo*. The product was obtained as colorless powder.

Yield: 1.02 g (98 %). - ^1H NMR (399.65 MHz, CDCl_3 , 22 °C): δ = 8.20 (s, 8H; Ph), 7.65–7.60 (m, 8H; Ph), 7.56–7.52 (m, 4H; Ph), 7.45–7.41 (m, 8H; Ph), 7.10 (s, 2H; Ph), 3.77 ppm (s, 6H; Me). - $^{13}\text{C}\{^1\text{H}\}$ NMR (100.40 MHz, CDCl_3 , 25 °C): δ = 164.2 (s; COOMe), 137.0 (s), 133.9 (t, $J_{\text{CP}} = 8$ Hz), 133.3 (s), 131.1 (s), 129.7 (s), 129.3 (t, $J_{\text{CP}} = 6$ Hz), 128.6 (t, $J_{\text{CP}} = 33$ Hz), 127.6 (s), 52.2 ppm (s; CH_3). - $^{31}\text{P}\{^1\text{H}\}$ NMR (161.70

MHz, CDCl₃, 25 °C): δ = 87.8 ppm. - IR (KBr): 3072, 3054 (w; ν [ArH]), 2978 (w; ν [CH₃]), 1725 (vs; ν [CO]), 1585 (m; ν [CC]), 1476 (m), 1434 (vs; ν [PPh]), 1318 (s), 1250 (vs; ν [PN]), 1102 (s; ν [COMe]), 1016 (s), 997 (s), 952 (m), 932 (m), 877, 869 (m; ν [NPN]), 811 (s), 721 (s), 702 (s), 690 (s; γ [CCH]), 551 (m), 503 (m), 479 cm⁻¹ (m). - Anal. Calcd for C₃₄H₂₉Au₂Cl₂NO₄P₂ (1042.40): C 39.18, H 2.80, N 1.34 %, found C 38.90, H 2.36, N 1.30 %.

Bis- μ -{dimethyl 5-[*N,N*-bis(diphenylphosphanyl- κ P: κ P')amino]isophthalate}digold(I) perchlorate (4).

0.32 g (0.6 mmol) of **2** were slowly added (60 min) to a solution of 0.26 g (0.6 mmol) bis(tetrahydrothiophene)gold(I) perchlorate dissolved in 35 ml of CH₂Cl₂ at 0 °C. The mixture was stirred for 30 min at ambient temperature. The solution was then evaporated. The remaining residue was washed with THF (3 \times 20 mL) and subsequently dried *in vacuo*. The product was obtained as colorless powder.

Yield: 0.24 g (50 %). - ¹H NMR (399.65 MHz, CDCl₃, 23 °C): δ = 8.28 (s, 2H; Ph), 7.71 (m, 16H; Ph), 7.52 (m, 24H; Ph), 6.93 (s, 4H; Ph), 3.71 ppm (s, 12H; Me). - ¹³C{¹H} NMR (100.40 MHz, CDCl₃, 26 °C): δ = 164.2 (s; COOMe), 137.0 (s), 136.8 (s), 134.2 (m), 134.0 (s), 131.3 (s), 130.6 (s), 130.1 (m), 126.2 (d, J_{CP} = 8 Hz), 52.6 ppm (s; CH₃). - ³¹P{¹H} NMR (161.70 MHz, CDCl₃, 26 °C): δ = 97.9 ppm. - IR (ATR): 3529, 3170, 3057 (w; ν [ArH]), 2955, 2847 (w; ν [CH₃]), 1725 (vs; ν [CO]), 1586 (m; ν [CC]), 1481 (w), 1434 (s; ν [PPh]), 1315 (s), 1253 (vs; ν [PN]), 1085 (vs; ν [COMe]), 1011 (s), 995 (s), 960 (s), 932 (s), 889, 877 (m; ν [NPN]), 805 (s), 748 (s), 721 (s), 699, 670 (vs; γ [CCH]), 622 (vs), 569 cm⁻¹ (m). - Anal. Calcd for C₆₈H₅₈Au₂Cl₂N₂O₁₆P₄

(1747.95): C 46.73, H 3.34, N 1.60 %, found C 45.99, H 2.87, N 1.57 %. - MS (ESI[+], acetone): $m/z = 792$ ($[M]^{2+}$). - MS (ESI[-], acetone): 99 ($[\text{ClO}_4]^-$), 83 ($[\text{ClO}_3]^-$).

X-ray Crystallographic Studies of 2–4. Crystals of 2–4 were coated in mineral oil (Sigma-Aldrich) and mounted on glass fibers. The crystal was transferred directly to the -73 °C cold stream of a STOE IPDS 2T or a Bruker SMART 1000 diffractometer with Mo- K_α radiation. Structures were solved using SHELXS-97 [21] and refined against F^2 using SHELXL-97 [21].

2: $\text{C}_{34}\text{H}_{29}\text{NO}_4\text{P}_2$, Monoclinic, $C2/c$ (Nr. 15); lattice constants $a = 24.6396(12)$, $b = 10.2524(4)$, $c = 23.1932(11)$ Å, $\beta = 91.689(4)^\circ$, $V = 5856.4(5)$ Å³, $Z = 8$, $\mu(\text{Mo-}K_\alpha) = 0.188$ mm⁻¹; $\theta_{max} = 25.0$; 5137 [$R_{int} = 0.0370$] independent reflections measured of which 4445 were considered observed with $I > 2\sigma(I)$; max. residual electron density 0.497 and -0.264 e/Å⁻³; 372 parameters, R_1 ($I > 2\sigma(I)$) = 0.0338; wR_2 (all data) = 0.0882.

3: $\text{C}_{35}\text{H}_{31}\text{Au}_2\text{Cl}_4\text{NO}_4\text{P}_2$, Monoclinic, $C2/c$ (Nr. 15); lattice constants $a = 20.9608(14)$, $b = 17.1209(9)$, $c = 14.2942(9)$ Å, $\beta = 129.399(4)^\circ$, $V = 3964.0(4)$ Å³, $Z = 4$; $\mu(\text{Mo-}K_\alpha) = 7.780$ mm⁻¹; $\theta_{max} = 25.0$; 3495 [$R_{int} = 0.0623$] independent reflections measured of which 3169 were considered observed with $I > 2\sigma(I)$; max. residual electron density 3.514 and -1.328 e/Å⁻³; 218 parameters, R_1 ($I > 2\sigma(I)$) = 0.0442; wR_2 (all data) = 0.1247.

4: C₆₈H₅₈Au₂Cl₂N₂O₁₆P₄, Triclinic, *P*-1 (No. 2); lattice constants $a = 11.243(2)$, $b = 13.620(3)$, $c = 14.170(3)$ Å, $\alpha = 98.71(3)$, $\beta = 111.69(3)$, $\gamma = 108.44(3)^\circ$, $V = 1822.0(6)\text{Å}^3$, $Z = 2$; $\mu(\text{Mo-}K_\alpha) = 4.247 \text{ mm}^{-1}$; $\theta_{max} = 23.87$; 5283 [$R_{int} = 0.0910$] independent reflections measured of which 3674 were considered observed with $I > 2\sigma(I)$; max. residual electron density 5.258 and -3.972 e/Å^{-3} ; 401 parameters, $R_1 (I > 2\sigma(I)) = 0.1007$; $wR_2 (\text{all data}) = 0.2924$.

Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 697734 - 697736. Copies of this information may be obtained free of charge from the Director, CCDC, 12, Union Road, Cambridge CB2 1EZ [FAX +44(1223)336-033] or e-mail deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>.

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Figure Caption:

Figure 1. Solid-state structure of **2** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] and angles [°]: N-P2 1.7280(13), N-P1 1.7319(13); P1-N-P2 115.63(7).

Figure 2. Solid-state structure of **3** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] and angles [°]: N-P 1.711(5), Au-P 2.227(2), Au-Cl1 2.274(2), Au-Au' 3.0593(7); P-Au-Cl1 174.07(10), P-Au-Au' 80.35(5), Cl1-Au-Au' 105.54(8), P-N-P' 118.6(5).

Figure 3. Solid-state structure of **4** showing the atom labeling scheme, omitting hydrogen atoms. Selected bond lengths [Å] and angles [°]: Au-Au' 2.798(2). P1-Au' 2.236(5), P2-Au 2.232(5), N1-P1 1.65(2), P2-N1 1.70(2); P1-Au'-Au 92.6(2), P2-Au-Au' 92.9(2); P1-Au-P2 169.0(2), P1-N-P2' 130.1(10).

Figure 1.

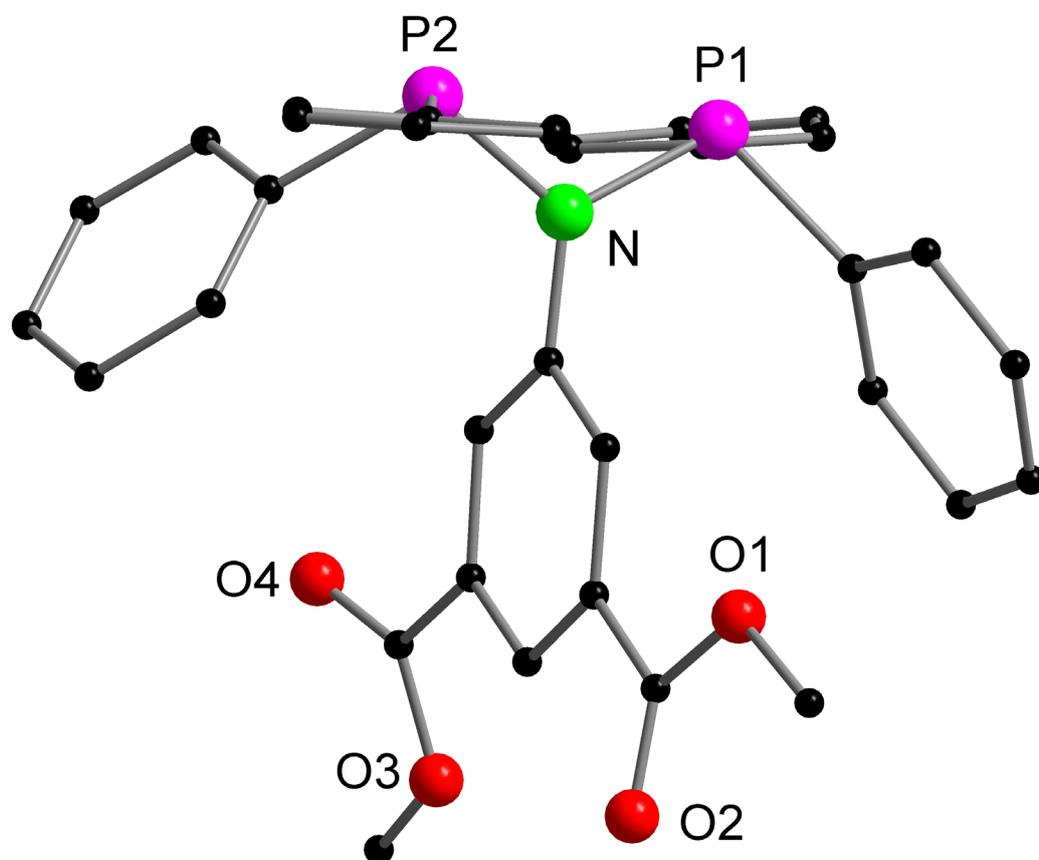


Figure 2.

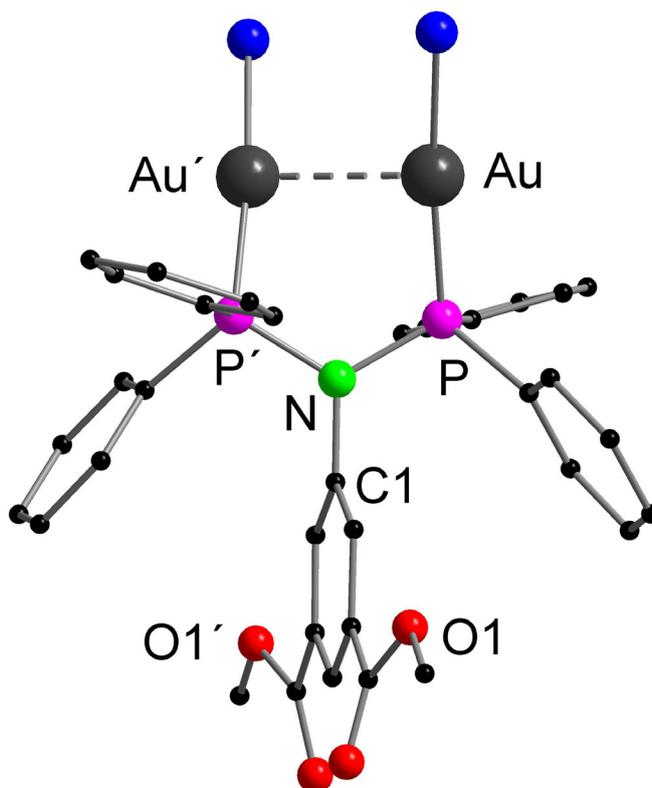


Figure 3.

