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Digold Phosphinine Complexes Are Stable with a Bis(Phosphinine) Ligand but Not with a 2-Phosphinophosphinine

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Abstract: The reaction of [bis{3-methyl-6-(trimethylsilyl)phosphinine-2-yl}dimethylsilane] (**19**) with one and two equivalents of [AuCl(tht)] was attempted in order to selectively form the mono and digold species, respectively. The digold species [$(AuCl)_2$(**19**)] (**21**) was synthesized in 32% yield and comprehensibly characterized (multinuclear NMR spectroscopy, elemental analysis, mass spectrometry and single-crystal X-ray diffraction). The monogold species showed no ^{31}P nuclear magnetic resonance at 25 °C but two resonances at −70 °C due to rapid exchange of AuCl between the phosphinine donors at 25 °C and was also susceptible to redistribution reactions to form the digold species. Analogous reactions of [AuCl(tht)] with 2-diphenylphosphino-3-methyl-6-trimethylsilylphosphinine (**22**) revealed preferential coordination of the AuCl unit to the PPh_2 donor first, with coordination to the phosphinine achieved upon reaction with the second equivalent of [AuCl(tht)]. Unexpectedly, the digold complex was not stable, undergoing decomposition to give an unidentified black precipitate. Structural information could only be obtained on the digold hydrolysis product [$(AuCl)_2$(1-OH-2-PPh_2-3-MePC_5H_4)], which showed an aurophilic interaction.

Keywords: phosphinine; phosphorus ligands; gold complexes; ligand properties

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1. Introduction

Phosphinines are aromatic six-membered phosphorus heterocycles, and their properties are often contrasted with their nitrogen analogue, pyridine. First synthesized in 1966 by Märkl [1], the parent unsubstituted phosphinine was later synthesized by Ashe in 1971 [2]. Phosphinines feature low-coordinate phosphorus and P-C multiple bonding, so have been historically important in the development of main group chemistry [3]. More recently, their coordination chemistry and applications in homogeneous catalysis have reinvigorated this area of research [4–11]. The ability of phosphinines to act as π-accepting ligands gives them the ability to interact in a dynamic fashion with transition metal (TM) centres, opening up the possibility of synergy between the main group element and TM.

While metallic gold has had a significant impact on humanity, gold complexes have attracted less attention. Exceptions include Au(I) and Au(III) compounds used in medicine [12,13] and the discovery of gold's unique catalytic ability in the 1980s [14]. The subsequent decades following this discovery saw a rapid growth in interest into gold catalysis [15,16]. Gold(I) complexes have a linear structure and commonly feature one chloride ligand in addition to a neutral ligand. These complexes are usually activated for catalysis using a silver salt to perform halide abstraction forming silver chloride and the catalytically active coordinatively unsaturated cation $[AuL]^+$. This cationic species can then coordinate to π-systems, which activates the π-system towards nucleophilic attack [17].

The first example of a gold phosphinine complex was published in 1973 when Schmidbaur and coworkers combined 2,4,6-triphenylphosphinine with [AuCl(CO)], forming the gold phosphinine **1** (Figure 1) [18]. **1** was subsequently synthesized using [AuCl(tht)]

(tht = tetrahydrothiophene) and crystallographically characterized [19]. This complex remained the only example of a gold phosphinine for more than 25 years until Mathey, Le Floch and coworkers reported the next examples of gold phosphinine complexes when studying the coordination chemistry and reactivity of bis(silyl)phosphinine gold complexes (**2**–**5**). They found that coordination to gold activated the phosphinine towards [4 + 2] cycloaddition reactions with alkynes to form phosphabarrelenes [20].

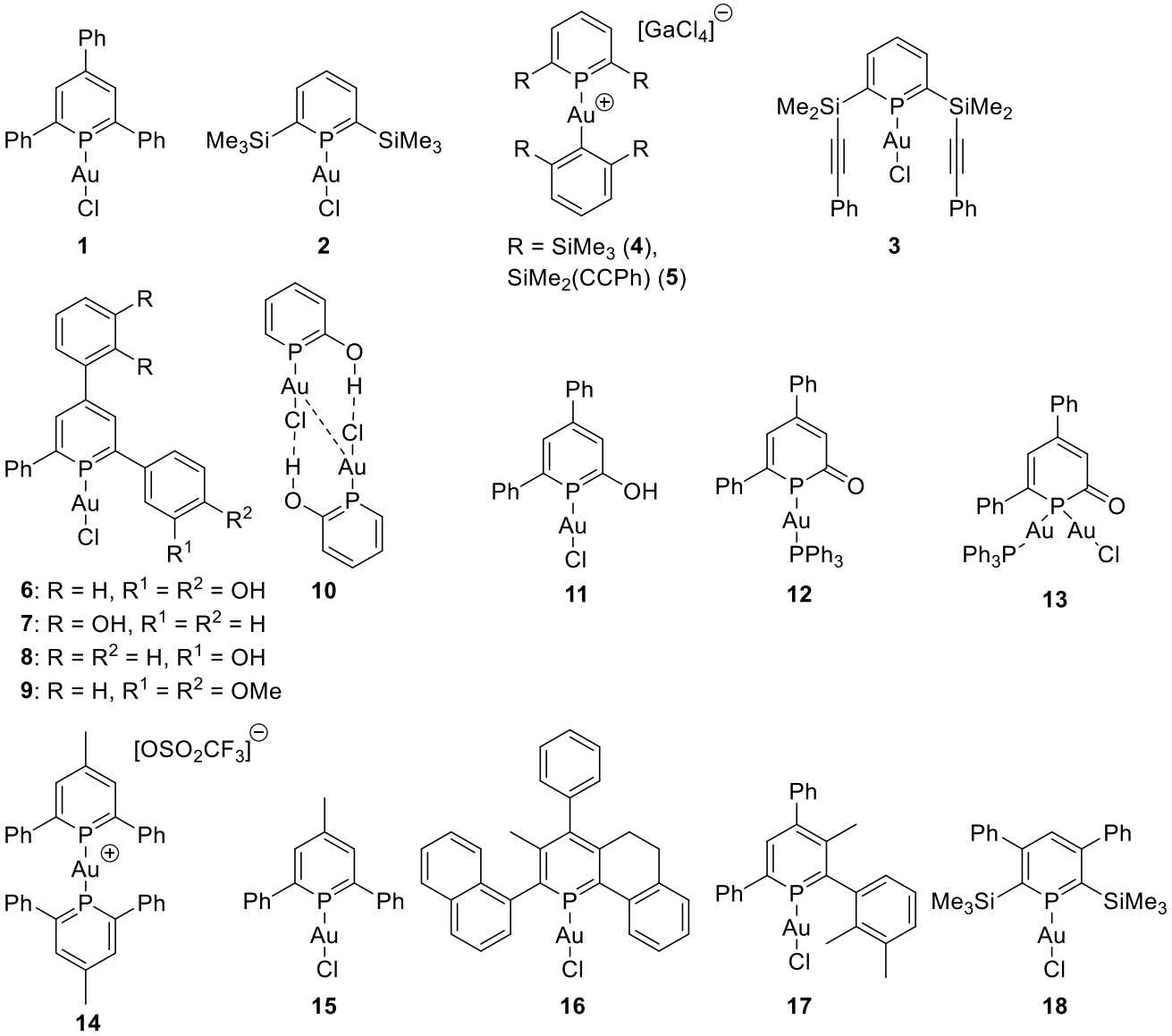


Figure 1. Gold phosphinine complexes.

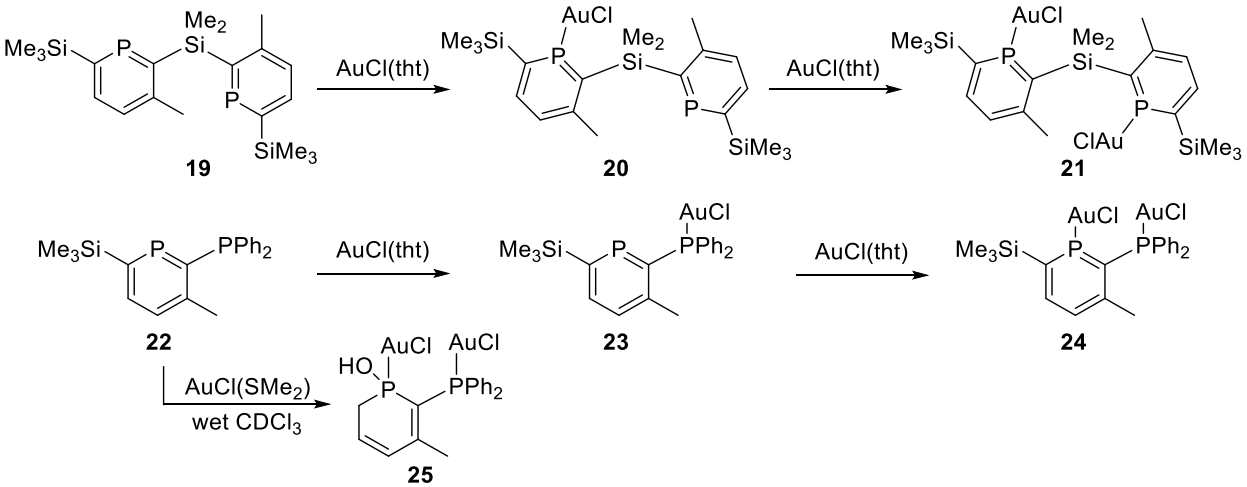
Phosphinine macrocycles were also developed [21] from a diazaphosphinine intermediate [22,23] which led to the formation of Au(I) complexes and a rare example of a Au(0) complex [24,25]. Mezailles and coworkers investigated gold complexes of an SPS pincer ligand derived from nucleophilic attack at the phosphinine P atom (e.g., with Li^{n}Bu or LiMe) [26]. [AuCl(2,4,6-^{t}Bu$_3$-PC$_5$H$_2$)], the tertiary butyl analogue of **1**, was synthesized [27], whereas the analogous complex with the 1,3,5-triphosphabenzene 2,4,6-^{t}Bu$_3$P$_3$C$_3$ [28] could not be made. Triphosphabenzene was, however, shown to coordinate to Au in an η^1 mode in [Au(2,4,6-^{t}Bu$_3$P$_3$C$_3$)(L)][SbF$_6$] (L = NHC or bulky phosphine) [29]. Phosphinine gold complexes with pendent phenol and catechol moieties (Figure 1, **6**–**9**) were synthesized to probe the immobilization of phosphinines on TiO_2 and surface-modified SiO_2. Coordination to gold showed a decrease in the ^{31}P NMR chemical shift ($\Delta\delta$ = −30–−33 ppm), but

reactions with TiO_2 or SiO_2 of either the gold complex or phosphinine precursor showed a loss of the aromatic phosphinine moiety [30]. Other gold phosphinine complexes bearing hydroxyl substituents have since been described (**10** and **11**), as well as some unusual 2-oxy-phosphinines (**12** and **13**) [31,32]. The phosphinine gold complexes **14** and **15** were synthesized to investigate the photoluminescence of Au phosphinine complexes. Photoluminescence was detected in the solid state but not in solution [33]. Gold phosphinine complexes have also been studied for their application in homogeneous catalysis, including **16,** which was characterized to investigate the properties of very bulky phosphinine ligands for applications in asymmetric Rh catalysis [34]. The gold phosphinine complexes **1**, **17** and **18** were used by the Müller group in two studies to investigate the use of gold phosphinines in gold-catalysed cyclization reactions [35,36].

As well as phosphinines, other low-coordinate phosphorus species are known that are not part of an aromatic system. They are kinetically stabilized using sterically bulky groups such as Mes* (2,4,6-tri-*t*-butylphenyl) [37]. Phosphaalkenes with Mes* substituents have been applied in gold catalysis, and we became interested in this work because a digold bis(phosphaalkene) complex was shown to be effective without the use of a silver salt [38]. The removal of silver salts is a desirable feature for gold catalysis in order to eliminate any effects from the silver atoms that are present, which have been known to interfere with the catalytic cycle through the formation of off-cycle intermediates [39]. Phosphaalkenes are, like phosphinines, weak σ-donor ligands but strong π-accepting ligands [40]. Their π-accepting ability is thought to increase the Lewis acidity of a coordinated gold center and hence promote catalytic activity despite the bound chloride [39]. Additionally, a digold bis(phosphaalkene)complex featuring an aurophilic interaction was effective as a catalyst for the cyclization of a 1,6-enyne, whereas an isomer without an aurophilic interaction showed almost no catalytic activity under the same conditions [38]. This prompted us to investigate phosphinine gold complexes that could coordinate two gold atoms to see if and when aurophilic interactions were present and whether silver-free catalysis would result. Our results show that the formation of stable digold complexes was not always straightforward, being highly dependent on the ligand used.

2. Results

Two ligands were utilized in this research: a bis(phosphinine) (**19**) [41,42] and a phosphinophosphinine (**22**, Scheme 1) [43,44].



Scheme 1. Synthesis of gold phosphinine complexes.

These two ligands feature different separations between the two phosphorus donors, with the phosphinophosphinine often functioning as a small bite-angle ligand [45], which has proven useful in homogeneous catalysis [43,46–48]. The bis(phosphinine) forms a six-membered chelate ring, and consequently has a larger separation between the two

donor atoms. For gold complexes, chelation was not anticipated, but the distance between the two gold atoms would be controlled based on the ligand framework. Due to the potential moisture sensitivity of phosphinines deriving from the P-C multiple bonding, experiments were conducted under anaerobic conditions with dry solvents. **19** featured one ^{31}P nuclear magnetic resonance at 261 ppm. The addition of one equivalent of [AuCl(tht)] led to the complete loss of this resonance, with no new resonance appearing. The addition of a second equivalent of [AuCl(tht)] gave a new complex with a ^{31}P nuclear magnetic resonance at 209 ppm, revealing a decrease in chemical shift upon coordination to gold of 52 ppm. Multinuclear NMR spectroscopic analysis is in agreement with a symmetrical structure, with only one set of resonances for the phosphinine rings and one ^{13}C and ^{1}H resonance for the $SiMe_2$ linker. The digold complex **21** precipitated out of the reaction in pure form, as determined by elemental analysis, and single crystals suitable for X-ray diffraction were grown from a CH_2Cl_2 solution layered with hexane at 5 °C (Figure 2; see Supplementary information for additional crystallographic details).

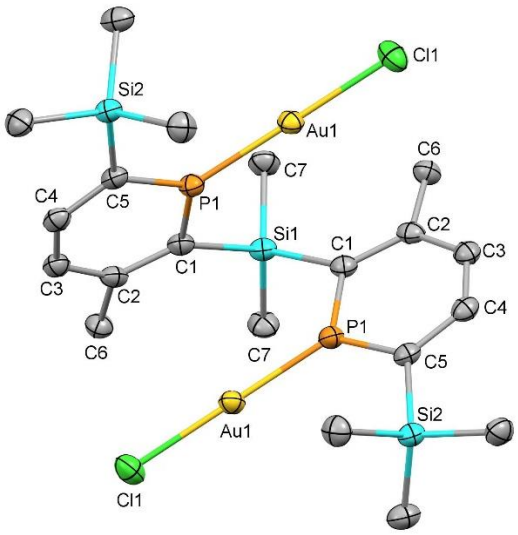


Figure 2. Molecular structure of **21** (thermal ellipsoids at 50%; all H atoms have been omitted for clarity). Selected bond lengths (Å) and angles (°): Au1-Cl1 2.2742(12), Au1-P1 2.2078(12), P1-C1 1.721(4), P1-C5 1.709(4), C1-C2 1.396(6), C2-C3 1.398(6), C2-C6 1.524(6), C3-C4 1.396(6), C4-C5 1.388(6), P1-Au1-Cl1 178.13(4), η^2 interaction: Au1-C1′ 3.287, Au1-C2′ 3.460.

The structure determined by X-ray diffraction showed a bis(phosphinine) with Au-Cl units bound to each phosphorus atom, as expected. The Au-Cl bonds are orientated in opposite directions, with the phosphinine rings situated in almost perpendicular planes at an angle of 80.3°. The molecule is situated on a twofold rotation axis passing through Si1 of the $SiMe_2$ group. As expected, the P-Au-Cl motif is almost linear, with a bond angle of 178.13(4)°. This bond angle is in line with what has been observed previously in known gold phosphinine complexes where the P-Au-Cl bond angle typically falls in the range of 176–178° with some exceptions, such as when affected by a second gold center in the range of an aurophilic attraction [19,27,30,33,35,36]. The P-Au bond length is 2.208(1) Å, which is within the error of reported values for phosphinine gold complexes ranging from 2.20–2.23 Å. The Au-Cl bond has a length of 2.274(1) Å, again within the range of known phosphinine gold complexes in the literature, which are mostly within 2.27–2.28 Å and are all within the range of 2.27–2.31 Å [19,27,30,33,35,36]. The P-C bonds within the aromatic ring are 1.721(4) Å and 1.709(4) Å, and the four C-C bonds are between 1.388(6)–1.398(6) Å, clearly in agreement with its aromatic nature. The shortest Au-Au distance in the crystal structure is 5.35 Å, which is significantly greater than usual the range of aurophilic interactions, both intermolecular and intramolecular, which is normally between 2.50–3.50 Å [49]. Comparisons can be made with the structure of [AuCl(2,6-Me_2-4-Ph-PC_5H_2], which displayed an Au . . . Au distance of 3.60 Å [19]. However, the Au-arene

distances of 3.29 Å and 3.46 Å (from Au1 to the C atoms in the C1-C2 bond) are in the range of known Au ... π(arene) interactions [50]. In fact, the solid-state structure of **1** displayed two different Au ... arene interactions (two independent molecules in the asymmetric unit cell), 3.32(3) Å for an η^1 interaction to the meta carbon, and with Au ... C distances of 3.39(3) and 3.44(3) Å in an η^2 interaction [19]. It is possible that the π-accepting ability of the phosphinine increases the Lewis acidity of the gold center, giving it a greater propensity to coordinate to π-systems such as the C=C bond of an adjacent phosphinine ring.

Further attempts were made to characterize and isolate the monogold intermediate, but, unfortunately, crystallization of solutions of **20** only led to the digold product **21**. Reinvestigation of the $^{31}P\{^1H\}$ NMR spectra of **20** at low temperature showed the appearance of two resonances at 259 and 207 ppm at −70 °C, similar to the free phosphinine and bound phosphinine signals seen in **19** and **21,** respectively. Thus, the lack of a phosphorus resonance for **20** at 25 °C is a consequence of rapid exchange of the AuCl unit between P donor sites, causing a broadening of the signal to the extent that it could not be observed. ^1H NMR spectra of solutions of **20** and **21** at 25 °C were very similar, with the major difference being the amount of free tht present from the [AuCl(tht)] precursor (see Supplementary information). The addition of another equivalent of [AuCl(tht)] to a solution of **20,** which exhibited no ^{31}P NMR signal, resulted in the ^{31}P nuclear magnetic resonance of **21** being observed.

The addition of one equivalent of [AuCl(tht)] to the phosphinophosphinine **22** demonstrated coordination of the AuCl unit to the phosphine donor (**23**), as anticipated from previous studies that identified selenation of the phosphine donor in preference to the phosphinine moiety [42]. The phosphinine doublet resonance (252 ppm, 86 Hz) was at an almost identical chemical shift to that observed in the free ligand (250 ppm, 32 Hz) [43], but the coupling had increased greatly. In contrast, the $ClAuPPh_2$ unit was identified as a doublet at 29.5 ppm (c.f. −7.5 ppm in **22**). The addition of a second equivalent of [AuCl(tht)] led to coordination of the phosphinine donor, as revealed by ^{31}P NMR spectroscopy by the broad resonance at 207 ppm, at a very similar chemical shift to **21** (209 ppm). However, this digold species turned out to be unexpectedly unstable at room temperature, particularly when concentrations were increased in many attempts to scale up and isolate this compound. The addition of two equivalents of [AuCl(tht)] to **22** caused the precipitation of a black solid almost immediately, with more black precipitate forming over time. This severely hampered any attempts to acquire further data on this complex, as even carefully filtering and storing solutions of this compound at −20 °C led to the formation of a purple-black precipitate covering the walls of the Schlenk vessel used to exclude air and moisture.

The reaction of **22** with $[AuCl(SMe_2)]$ was attempted using non-dry chloroform as the solvent in order to see what effect moisture had on the reaction. As anticipated, ^{31}P NMR spectroscopy revealed the loss of all resonances in the aromatic region, with a mixture of products now evident. ^{31}P nuclear magnetic resonances ranged between 99.5 and 3 ppm, with the major product identified by two doublet resonances at 66.6 and 27.1 ppm (115 Hz). The reaction of complexes featuring the phosphinophosphinine ligand with water was observed previously [44]. Out of this reaction mixture, a crystal suitable for X-ray diffraction experiments was grown and the molecular structure of **25** was obtained (Figure 3). An AuCl unit was bound to each phosphorus atom with similar Au-P distances of 2.2180(10) (Au1-P1) and 2.2401(10) Å (Au2-P2). There was a short Au ... Au distance of 3.0576(2) Å well within the range of normal aurophilic interactions [50]. The phosphinine moiety was no longer present, as water had added over the P1=C5 bond to generate a phosphacyclohexadiene with C1=C2 (1.370(5) Å) and C3=C4 (1.340(6) Å) double bonds now present. The H atom on the P-OH moiety was located in the Fourier difference map and refined corroborating the assignment of this species. Also notable is that the $SiMe_3$ group has been removed and replaced with an H atom. This outcome has been noted in a $[Ru(C_6Me_6)]^+$ complex [44]; however, here the additional H atom was located bound to the ortho-$CPPh_2$ carbon rather than the C5 position, as was noted in **25**. Cleavage of

phosphinine-$SiMe_3$ groups can be achieved readily using HCl [47,51], and it is possible that HCl as an impurity in the chloroform solvent led to this outcome.

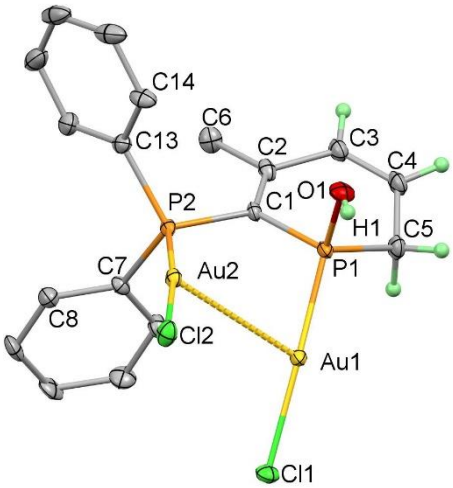


Figure 3. Molecular structure of **25** (thermal ellipsoids at 50%; H atoms on the Ph and Me groups have been omitted for clarity). A chloroform solvate molecule has also been omitted for clarity. Selected bond lengths (Å) and angles (°): Au1-Au2 3.0576(2), Au1-Cl1 2.3047(9), Au1-P1 2.2180(10), Au2-Cl2 2.2919(10), Au2-P2 2.2401(10), P1-O1 1.596(3), P1-C1-1.787(4), P1-C5 1.800(4), P2-C1 1.818(3), C1-C2 1.370(5), C2-C3 1.462(5), C3-C4 1.340(6), C4-C5 1.490(6), P1-Au1-Cl1 169.29(4), P2-Au2-Cl2 173.94(3), P1-C1-P2 114.4(2).

3. Discussion

The aim at the beginning of this work was to compare monogold species with digold analogues using the ditopic ligands **19** and **22**. For the symmetrical bis(phosphinine) ligand **19**, this was not possible, as **20** could not be isolated without ligand redistribution occurring to form the digold species. However, the formation of the symmetrical digold species **21** was achieved, and this species showed evidence of additional Au ... π(arene) interactions rather than an aurophilic interaction, as was initially anticipated. The ditopic phosphinophosphinine ligand showed preferential binding of AuCl to the phosphine donor, with a second equivalent of AuCl binding to the phosphinine donor. However, this complex showed very poor stability, an unexpected outcome, which meant we could not determine its molecular structure in order to establish whether or not aurophilic interactions were present. Instead, a hydrolysis product was characterized by X-ray crystallography and revealed that, as anticipated, this small bite-angle ligand enforces close proximity of two AuCl units, leading to an aurophilic interaction. However, the phosphinine unit was no longer present, having reacted with water, and the $SiMe_3$ substituent was also no longer present.

4. Materials and Methods

All reactions requiring inert conditions were performed under an oxygen-free nitrogen atmosphere using standard Schlenk-line techniques or using an MBRUAN UNILab Plus glovebox, unless otherwise noted. Dry toluene was obtained from a solvent purification system (MBraun SP-300) and stored over 4 Å molecular sieves prior to use. When required to be dry, C_6D_6 and $CDCl_3$ were dried over activated 4 Å molecular sieves prior to use. Non-dry solvents were used as received from Fisher Scientific or Goss Scientific (deuterated solvents). The phosphinines **19** [41] and **22** [43] were synthesized as previously described. NMR spectra were obtained using either a Bruker AVIII400 (400 MHz) or AVIIHD (400 MHz) spectrometer. ^{1}H NMR spectra were recorded at 400 MHz and referenced to the residual solvent peak (7.26 for $CDCl_3$ and 7.16 for C_6D_6). $^{13}C\{^1H\}$ NMR spectra were recorded at 101 MHz and referenced to the residual solvent peak (77.16 for $CDCl_3$ and 128.06 for C_6D_6). $^{31}P\{^1H\}$ NMR spectra were recorded at 162 MHz and referenced to an external standard.

Mass spectrometry was conducted at the National Mass Spectrometry Facility at Swansea University using the techniques stated. Elemental analyses were performed by Dr Brian Hutton (Heriot-Watt University, Edinburgh, UK).

Single crystals suitable for X-ray diffraction were covered in inert oil and placed under the cold stream of a Bruker D8 Venture four-circle diffractometer cooled to 100 K. Exposures were collected using Mo or Cu K_α radiation. Indexing, data collection and absorption corrections were performed. The structures were then solved using SHELXT [52] and refined by full-matrix least-squares refinement (SHELXL) [53] interfaced with the programme OLEX2 [54].

4.1. Attempted preparation of **20**

Under nitrogen, **19** (228 mg, 0.54 mmol), [AuCl(tht)] (169 mg, 0.313 mmol) and toluene were sealed in a Schlenk flask. The solution was stirred for 18 h at room temperature, forming a precipitate. The solvent was removed under reduced pressure and the resultant solid was dried. Recrystallization using CH_2Cl_2 solutions layered with hexane at 5 °C led to the formation of **21**.

$^{31}P\{^1H\}$ (162 MHz, C_6D_6, 298 K): No signal. **$^{31}P\{^1H\}$ (162 MHz, C_6D_6, 203 K):** 258.7 and 207.0 ppm.

4.2. Preparation of **21**

Under nitrogen, **19** (219 mg, 0.521 mmol), [AuCl(tht)] (340 mg, 1.059 mmol) and toluene (30 cm^3) were combined in a Schlenk flask, and the reaction was stirred at room temperature for 18 h forming a white precipitate. The supernatant solvent was removed by filtration and the solid was dried under reduced pressure, yielding **21** as a white powder (145.6 mg, 0.164 mmol, 32%).

$^{31}P\{^1H\}$ (162 MHz, $CDCl_3$, 298 K) δ = 209.3 (s, phosphinine-P); **^1H NMR (400 MHz, $CDCl_3$, 298 K)** δ = 8.19 (dd, 2 H, $^3J_{P\text{-}H}$ = 31.7 Hz, and $^3J_{H\text{-}H}$ = 8.5 Hz, *meta*-phosphinine-H), 7.42 (dd, 2 H, $^3J_{H\text{-}H}$ = 8.5 Hz, $^4J_{P\text{-}H}$ = 4.9 Hz, *para*-phosphinine-H), 2.70 (d, 6 H, $^4J_{P\text{-}H}$ = 1.3 Hz, phosphinine-Me), 1.05 (s, 6 H, $SiMe_2$), 0.46 (s, 18 H, $SiMe_3$); $^{13}C\{^1H\}$(100.6 MHz, $CDCl_3$, 298 K) δ = 156.2 (br. s, *ortho*-*C*$SiMe_2$), δ = 156.1 (d, 4.8 Hz, *meta*-*C*Me), δ = 155.7 (m, *ortho*-*C*$SiMe_3$), 143.7 (m, CH, *meta*-Ar-H), 130.9 (d, $^3J_{P\text{-}C}$ = 46.6 Hz CH, *para*-Ar-H), δ = 28.6 (m, *meta*-Me), 6.7 (t, 4.8 Hz, $SiMe_2$), 0.7 (m, $SiMe_3$); **$^{29}Si\{^1H\}$ NMR (79.5 MHz, $CDCl_3$, 298 K)** δ = 0.00 (d, $^2J_{P\text{-}Si}$ = 18.5 Hz, $SiMe_3$), −3.97 (d, $^2J_{P\text{-}Si}$ = 20.6 Hz, $SiMe_2$); **HRMS (ASAP/QTof):** *m/z*: calcd. for $C_{20}H_{34}P_2Cl^{197}Au_2Si_3$: 849.0463 $[M\text{-}Cl]^+$, found: 849.0474; **elemental analysis:** anal. calcd. for $C_{20}H_{34}P_2Cl_2Au_2Si_3$: C 27.13, H 3.87, N 0, found: C 27.31, H 3.92, N 0.

4.3. Reactions of **22** *with [AuCl(L)]*

NMR-scale reactions were attempted for one equivalent of phosphinophosphinine **22** (7–10 mg) with either one or two equivalents of gold reagent [AuCl(L)] (L = tht, SMe_2; 6.4–18.3 mg). When L = SMe_2, the reaction was performed in non-dry (wet) $CDCl_3$, under air, and when L = tht (tetrahydrothiophene), the reaction was prepared in the glovebox under N_2 using dry C_6D_6. In all cases, reagents were charged to separate vials; the solvent was added first to **22** to give a very pale-yellow solution, then this was added to the gold reagent. On mixing at room temperature, this afforded a bright yellow solution. At this point, the sample was sealed in an NMR tube equipped with a J. Young cap, and $^{31}P\{^1H\}$ NMR spectra were taken.

Larger-scale reactions were performed similar to the following: **22** (106 mg, 0.29 mmol), [AuCl(tht)] (100 mg, 0.31 mmol) and toluene were sealed in a Schlenk flask. The solution was stirred for 18 h at room temperature, forming a precipitate. The solvent was removed under vacuum and the solid was dried under reduced pressure.

Using two equivalents of [AuCl(tht)] (202 mg, 0.630 mmol), 101 mg **22** was used (0.274 mmol). The formation of purple-black ppt. was noticed from decomposition.

4.4. Data for **23***:*

$^{31}P\{^{1}H\}$ (162 MHz, $CDCl_3$, 298 K) δ = 252 (d, $^{2}J_{P\text{-}P}$ = 86 Hz) and 29.5 ppm (d, $^{2}J_{P\text{-}P}$ = 86 Hz).

4.5. Data for **24***:*

$^{31}P\{^{1}H\}$ (162 MHz, $CDCl_3$, 298 K) δ = 206.7 ppm (bs) and 27.8 ppm (d, $^{2}J_{P\text{-}P}$ = 48.6 Hz).

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/inorganics10110203/s1, NMR and mass spectra, table of additional crystallographic information. CIF and check CIF output files for the solid-state structures of **21** and **25**.

Author Contributions: Conceptualization, P.A.C. and S.M.M.; methodology, P.A.C., B.G. and S.M.M.; validation, M.M., B.G., D.J.W. and S.M.M.; formal analysis, all authors.; investigation, all authors.; data curation, S.M.M.; writing—original draft preparation, S.M.M.; writing—review and editing, all authors; visualization, S.M.M.; supervision, S.M.M.; project administration, S.M.M.; funding acquisition, S.M.M. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The crystallographic data in this study are available in the Cambridge Structural Database, deposition numbers CCDC 2212070 (**21**) and 2212069 (**25**).

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Conflicts of Interest: The authors declare no conflict of interest.

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