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Secondary Phosphine Oxide–Gold(I) Complexes and Their First Application in Catalysis

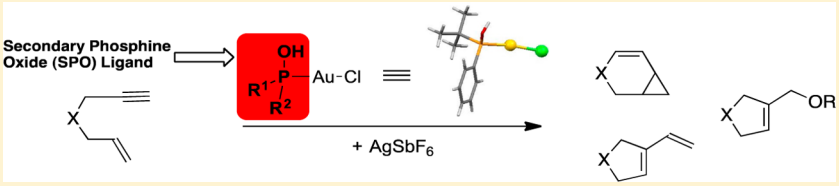
Felix Schröder,[†] Coralie Tugny,[†] Elise Salanouve,[†] Hervé Clavier,[‡] Laurent Giordano,[‡] Delphine Moraleda,[‡] Yves Gimbert,[§] Virginie Mouriès-Mansuy,[†] Jean-Philippe Goddard,[†,⊥] and Louis Fensterbank*[,†]

[†]Institut Parisien de Chimie Moléculaire (UMR CNRS 8232), UPMC Univ Paris 06, Sorbonne Universités, 4 place Jussieu, C. 229, 75005 Paris, France

[‡]Aix Marseille Université, Centrale Marseille, CNRS, iSm2 UMR 7313, 13397, Marseille, France

[§]Univ Grenoble Alpes and CNRS, DCM UMR 5250, F-38000 Grenoble, France

Supporting Information



ABSTRACT: A series of new secondary phosphine oxide (SPO)–gold(I) complexes have been synthesized and characterized by X-ray crystallography. Complexes exhibited dimeric structures interconnected by O–H···Cl hydrogen bonds. Their first use in homogeneous catalysis is reported and suggests a broad field of application in prototypical enyne cycloisomerization and hydroxy- and methoxycyclization reactions.

INTRODUCTION

After sporadic reports in the 1980s and 1990s featuring landmarks such as Hayashi's asymmetric aldol reaction,[1] Teles' addition of alcohol to alkyne,[2] and Hashmi's phenol synthesis,[3] homogeneous gold catalysis has emerged over the past decade as a highly versatile synthetic methodology providing unique opportunities in the construction of carbon–carbon or carbon–heteroatom bonds.[4] Indeed, in 2004, Echavarren,[5] Fürstner,[6] and Toste[7] disclosed enyne cycloisomerizations in the presence of gold(I) cationic complexes. It is also now well established and consistent with Xu's[8] recent report that the nature of the ligand coordinated to the gold center plays a major role in the reactivity and selectivity of gold-catalyzed reactions, as well as in the sustainability of the catalytic cycle. While initially the ancillary ligands were phosphorus-based ligands such as phosphites and phosphines (triphenylphosphine, JohnPhos, etc.), subsequently stronger σ-donor NHC ligands and related structures have been widely used, for instance in cycloisomerization reactions, allowing new reactivity.[9] Thus, there is still an important need to provide new gold complexes, based on original ligands, to give access to unprecedented reactivities and optimal catalytic cycles.[10]

As part of our ongoing efforts to develop new gold-catalyzed cyclizations of enynes, we were interested in studying the reactivity of secondary phosphine oxide (SPO)–gold complexes. These ligands are very attractive for metal catalysis under homogeneous conditions because they are air and moisture stable. Moreover, a tautomeric equilibrium exists in solution which can be displaced in favor of the phosphinous acid (PA) form by preferred coordination of the phosphorus atom to a transition metal (Figure 1).[11]

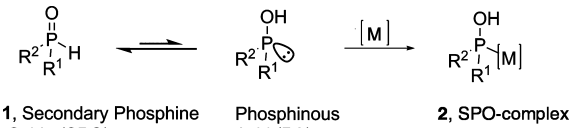


Figure 1. Coordination of an SPO ligand to a metal.

Thus, SPO catalysts have enjoyed great interest since the first report by Li, who used these preligands in very efficient palladium-catalyzed cross-coupling reactions for the formation of C–C, C–N, and C–S bonds using unactivated aryl chlorides.[12] Since this breakthrough, novel SPO–transition-metal complexes have been used in various other cross-coupling[13] and hydrogenation reactions.[14] Furthermore, some of us reported a formal palladium-catalyzed [2 + 1] cycloaddition[15] and more recently an unprecedented intermolecular tandem [2 + 1]/[3 + 2] cycloaddition sequence catalyzed by SPO–platinum complexes.[16] Note also that for a dissymmetric SPO ($R^1 \neq R^2$), the phosphorus atom becomes stereogenic, thereby giving access to asymmetric catalysis.[17]

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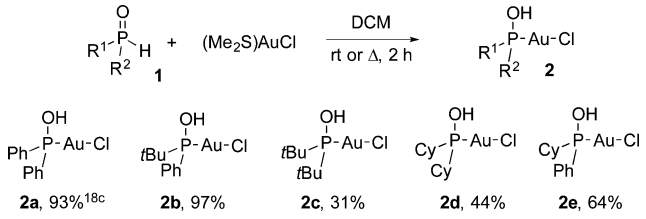
Particularly worthy of note, to the best of our knowledge, is the absence of applications of SPO−gold complexes in homogeneous catalysis. In a few publications, the Schmidbaur group examined the coordination chemistry of SPO−gold complexes.[18] Notably, the structure of the complex $[Ph_2P(OH)AuCl]_2$ (**2a**) was confirmed by X-ray analysis.[18c,d] However, no catalytic activity was reported in any of these studies. This year, van Leeuwen used the complex $[t\text{-}Bu(naphthalen\text{-}1\text{-}yl)P(OH)AuCl]_2$ as a precursor for gold nanoparticles that proved to be highly active catalysts for the hydrogenation of substituted aldehydes.[19]

RESULTS AND DISCUSSION

SPO-Au(I) Complexes. In this context, we prepared a library of SPO−gold(I) complexes following Schmidbaur's procedure by treatment of the corresponding SPOs $(R^1R^2P(O)H$, **1a−e**$)$[20] with (dimethyl sulfide)gold(I) chloride in CH_2Cl_2 (Scheme 1). After partial evaporation of CH_2Cl_2, gold

Scheme 1. Preparation of SPO−Gold(I) Complexes



complexes were isolated by precipitation from pentane in moderate yields of 31% for the sterically demanding bis-*tert*-butyl SPO ligand **2c** to excellent yields of 97% for **2b** and were fully characterized (see the Supporting Information).

Suitable crystals were obtained in order to determine the structures of **2b−e** by XRD.[21] Except for **2e**, which exhibited distinct features,[22] all structures **2b−d** share common features with **2a** (Table 1). They are dimeric, interconnected by two peripheral O−H···Cl hydrogen bonds, the bond lengths being in the typical range of 2.03−2.37 Å. Interestingly, they all show rather unusual bent P−Au−Cl angles, from 170° (**2b**) to 175° (**2c**). As is the case for **2a**, they do exhibit Au−Au interactions, but to a weaker extent, since the Au···Au distance in **2a** is 3.11 Å while it is between 3.35 and 3.75 Å in **2b−d**.[23] The structure of complex **2b**, shown in Figure 2, is chosen as a representative example. In this case, crystals are triclinic with a $P\bar{1}$ space group ($Z = 1$ molecular unit in the unit cell). Therefore, the O−H···Cl length (2.207 Å) and the P−Au−Cl angle (170.68°) are identical in the two units of the dimer. Similar P−Au−Cl angles deviating from linearity have been found in gold complexes bearing very bulky biarylphosphines.[24] In our case, we ascribed the values of the P−Au−Cl angles to the dimeric assembly which would generate constraints favoring the nonlinearity. To probe this hypothesis, we prepared cationic complex **2f** (Scheme 2) by treatment of **2b** with 1 equiv of $AgSbF_6$ in

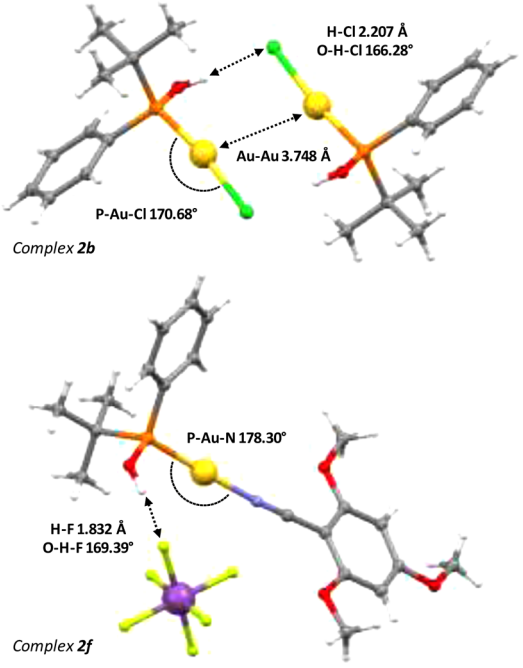
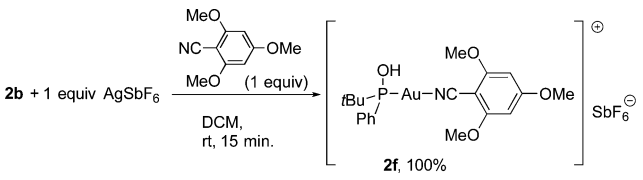


Figure 2. X-ray structures of complexes **2b,f**.

Scheme 2. Preparation of Cationic Complex 2f



the presence of 1 equiv of 2,4,6-trimethoxybenzonitrile in CH_2Cl_2. A quantitative yield of **2f** was obtained, and a single-crystal X-ray diffraction analysis revealed a monomeric structure featuring a P−Au−N angle of 178.30°. This confirmed our assumption that the dimeric arrangement was responsible for the angle deviation.

Whereas currently buried volumes are commonly used to quantify the steric properties of phosphine and NHC ligands, no metric for SPO ligands has been reported to date.[25] Having in hand a set of X-ray structures for the gold−SPO complexes **2a−e**, we assessed the steric bulk of these ligands by calculating the percent buried volume ($\%V_{bur}$).[26,27] A comparison of V_{bur} values revealed a narrow range for SPO ligands **1a−e** (Table 2). As expected, $tBu_2P(OH)$ (**1c**; entry 5) is significantly more sterically demanding than the other SPOs (entries 1, 3, 7, and 8). A comparison with their phosphine parents showed a moderate difference between $Ph_2P(OH)$ and PPh_3 (entry 1 vs 2), but this gap gradually increases with congeners exhibiting greater steric hindrance around phosphorus (entry 3 vs 4 and entry 5 vs 6).

Table 1. Characteristic Bond Lengths and Bond Angles of SPO−Au^{I}Cl

gold complex	OH(1)···Cl(2) (Å)	OH(2)···Cl(1) (Å)	Au(1)···Au(2) (Å)	P(1)−Au(1)−Cl(1) (deg)	P(2)−Au(2)−Cl(2) (deg)
$Ph_2(OH)PAuCl$ (**2a**)	2.029	2.105	3.111	169.18	170.85
$tBuPh(OH)PAuCl$ (**2b**)	2.207	2.207	3.748	170.68	170.68
$tBu_2(OH)PAuCl$, (**2c**)	2.374	2.223	3.349	175.59(9)	173.3(1)
$Cy_2(OH)PAuCl$ (**2d**)	2.177	2.224	3.390	174.58	175.15

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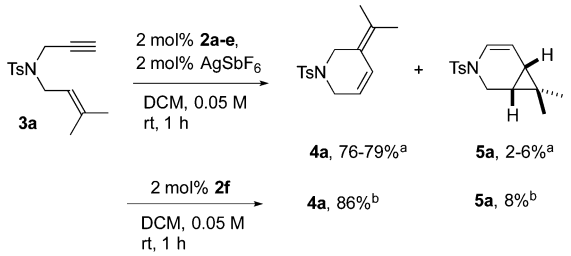
Table 2. Au−P Bond Lengths and Percent Buried Volumes (%V_{bur}) of SPO Ligands 1a−e

entry	ligand	d(Au−P) (Å)	V_{bur} (%)
1	$Ph_2P(OH)$ (**1a**)	2.220	27.3
2	PPh_3	2.232	30.7
3	$Cy_2P(OH)$ (**1d**)	2.230	28.9
4	PCy_3	2.242	34.1
5	$tBu_2P(OH)$ (**1c**)	2.232	32.6
6	$PtBu_3$	2.252	38.6
7	PhCyP(OH) (**1e**)	2.238	27.1
8	Ph*t*BuP(OH) (**1b**)	2.225	29.2

We investigated the catalytic potential of complexes **2** in the context of enyne cycloisomerization, focusing initially on substrate **3a** (Scheme 3).[28] Typical conditions involved 1

Scheme 3. Preliminary Catalytic Tests



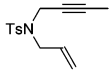
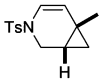
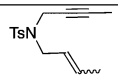
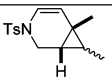
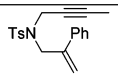
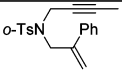
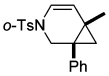
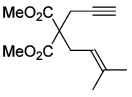
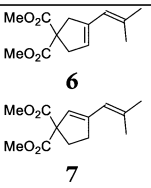
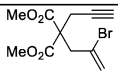
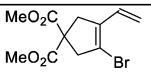
[a]NMR yield. [b]Isolated yield.

equiv of $AgSbF_6$, with respect to the gold complex, in CH_2Cl_2 for less than 1 h at room temperature. Full conversion of **3a** was observed with all salts **2a−e** to give uniformly good yields of **4a** as a very major product (yields: 76−79%), accompanied by minor amounts of **5a** (yields: 2−6%).[29] No effect of the ligand structure was noticed in this series of reactions. Interestingly, cationic complex **2f** proved to be competent for this reaction and gave in slightly optimized yields a mixture of **4a** (86%) and **5a** (8%).

We also examined the more demanding substrate **3b**, which has so far proven to be rather reluctant to cycloisomerization under various metal-catalyzed conditions.[30,31] Initial testing under conditions similar to those before with complexes **2b−e** proved however to be much less rewarding, since moderate yields of the corresponding product **5b** were generally obtained (see Table 3, entries 1−4).

We then decided to run the following experiment. To a solution of **2b** (0.036 mmol) in 0.6 mL of CH_2Cl_2 was added 1 equiv of $AgSbF_6$ at room temperature. Some AgCl precipitated instantaneously. After filtration over a Teflon filter, a limpid yellow solution was obtained, to which 1 equiv of **3b** was added. This led to a new production of AgCl. ^{1}H NMR analysis of the crude product showed full conversion of the starting material **3b**. Thus, enyne **3b** presumably intervened in the formation of the cationic gold catalytic species. This finding was highly reminiscent of Echavarren's recent report dealing with the detrimental formation of chloride-bridged digold complexes,[32] the latter being potentially cleaved by the addition of more coordinating substrates.[33] We thus further investigated the possible implication of such a phenomenon in our reactions by running the following NMR-MS coupled analyses (see the Supporting Information). We first mixed in CD_2Cl_2 1 equiv of **2b** with 0.25 equiv of $AgSbF_6$. Some AgCl precipitated

Table 3. Enyne Cycloisomerization

Entry	Substrate	[Au]	Cond.	Products	Yields (%)
1		**2b**	A[a]		30
2		**2c**	A		38
3		**2d**	A		35
4	**3b**	**2e**	A	**5b**	33
5		**2a**	B[b]		69
6		**2b**	B		61
7	 **3c**, ds 7 : 1	**2b**	A	 **5c**, ds 7 : 1	74
8	 **3d**	**2b**	A	 **5d**	72
9	 **3e**	**2b**	A	 **5e**	82
10	 **3f**	**2b**	A	 **6** **7**	**6** : 88, **7** : 7
11	 **3g**	**2b**	B[c]	 **8**	73

[a]Conditions A: 2 mol % of complex **2** and 2 mol % of $AgSbF_6$ in CH_2Cl_2 at room temperature for 0.5−2 h. [b]Conditions B: 2 mol % of complex **2** and 4 mol % of $AgSbF_6$ in CH_2Cl_2 at room temperature for 4−15 h. [c]Reaction in refluxing toluene for 40 h.

instantaneously, and ^{31}P NMR showed a broad resonance at 111 ppm, presumably corresponding to **2b** (δ(^{31}P) 111 ppm) and other cationic entities, accompanied by a minor and sharper peak at 85 ppm (most likely a hydrate cationic Au(I) complex[34]). The ESI MS spectrum at 60 V revealed a peak at m/z 379 ascribed to the [*t*-BuPhP(OH)Au]$^+$ fragment and a peak at m/z 793 corresponding to the expected bridged complex [*t*-BuPhP(OH)AuClAu(OH)P-*t*-BuPh]$^+$. Charging 0.5 equiv of $AgSbF_6$ gave no observable change in the aspect of the ^{31}P NMR and mass spectra. However, in the presence of 2 equiv of $AgSbF_6$, while the ^{31}P NMR spectrum was globally identical, the MS spectrum showed the disappearance of the peak at m/z 793 in favor of the peak at m/z 379, suggesting strongly, and as observed by Echavarren,[32a] that an excess of silver is needed to fully obtain the active cationic complex (Scheme 4).

These findings drove us to try another set of conditions with 2 equiv of $AgSbF_6$ (conditions B, see Table 1) when the reaction was sluggish with only 1 equiv (conditions A). This proved to be beneficial, as illustrated by yields superior to 60%

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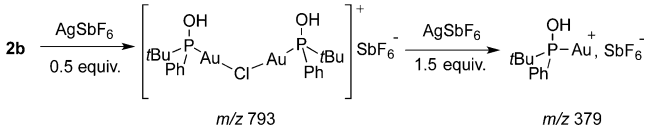
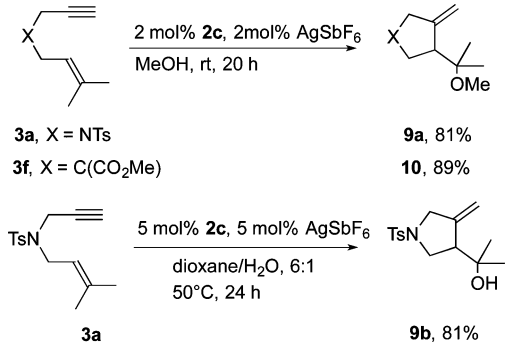
Scheme 4. Monitoring by MS of the Formation of a Cationic SPO−Au^{I} Complex



recorded with precatalysts **2a,b** (entries 5 and 6). Interestingly, these yields were better than that recorded with PPh_3AuSbF_6 (**5b**; 55%).[30d] A series of substrates (**3c−f**, **6**, and **7**) could also be smoothly engaged in catalytic reactions, giving satisfactory yields of the corresponding products (**5c−f**, **6**, and **7**) by using the simple conditions A. Interestingly, substrate **3g**, which has to the best of our knowledge never been engaged in gold-catalyzed reactions, provided additional information about a putative silver salt effect. Preliminary testing under conditions A (CH_2Cl_2, room temperature for 2 h) showed very little conversion (**3g**:**8** 80:20). In contrast, in refluxing toluene for 40 h, in the presence of an equimolar mixture of **2b** and $AgSbF_6$, significant formation of product **8** was observed (**3g**:**8** 40:60). Strikingly, as observed with precursor **3b**, conditions B, based on a 2-fold excess of $AgSbF_6$, resulted in the ratio 20:80 for **3g** and **8** and 73% isolated yield of **8** as the sole product.[35] Thus, the use of an SPO ligand proved particularly beneficial for the cycloisomerization of this substrate since, in comparison, the use of the 2 mol % $PPh_3AuCl−AgSbF_6$ mixture was poorly productive, as demonstrated by little conversion, giving a 90:10 mixture of **3g** and **8** in CH_2Cl_2 for 2 h at room temperature and a 70:30 mixture of **3g** and **8** in refluxing toluene for 40 h accompanied by byproducts.

We also looked at methoxy- and hydroxycylization reactions[36] from precursors **3a,f**. The latter smoothly transformed into the corresponding adducts **9a**, **10**, and **9b** (Scheme 5).

Scheme 5. Methoxy- and Hydroxycyclization Reactions



CONCLUSION

In summary, SPO ligands have been successfully coordinated to gold(I) chloride, providing good yields of the corresponding new complexes, which have been fully characterized. Dimeric structures, interconnected by O−H···Cl hydrogen bonds and featuring Au−Au interactions, have been recorded in the solid state. Using X-ray crystallographic data, percent buried volumes ($\%V_{bur}$) have been calculated to provide the previously undetermined steric parameter value of SPO ligands. Their first uses in gold(I) homogeneous catalysis have been described, suggesting a broad versatility. They have proven to be high-performing precatalysts for difficult cycloisomerization reactions, which now ranks them in the short list of valuable ligands for gold homogeneous catalysis. This study also provided some confirming elements about the detrimental intervention of chloride-bridged digold complexes, as recently reported by Echavarren. Finally, an opportunity for asymmetric gold catalysis is at hand with chiral SPO ligands.

EXPERIMENTAL SECTION

General Information. All reactions were performed under an argon atmosphere. All solvents were freshly distilled prior to use: tetrahydrofuran over sodium and benzophenone and dichloromethane over calcium hydride. Silica gel (35−70 mm) was used for column chromatography. Thin-layer chromatography (TLC) was performed on silica gel and visualized with a UV lamp (254 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature unless otherwise required on 300 and 400 MHz spectrometers with the solvent resonance as the internal standard (^{1}H NMR, $CDCl_3$ at 7.26 ppm; ^{13}C NMR, $CDCl_3$ at 77.16 ppm; ^{31}P NMR, H_3PO_4 at 0 ppm). Chemical shifts (δ) are given in parts per million (ppm), and coupling constants (J) are given in hertz (Hz). The letters m, s, d, t, and q stand for multiplet, singlet, doublet, triplet, and quartet, respectively. The letter b indicates that the signal is broad. Referenced high-resolution mass spectra were obtained at UPMC using a mass spectrometer with an electron spray ion source (ESI) and a TOF detector. Melting points (mp) were recorded with a melting point apparatus. IR data are reported as characteristic bands (cm^{-1}).

General Procedure for the Synthesis of SPO−AuCl Complexes 2. To a solution of secondary phosphine oxide **1** (5.5 mmol, 1.0 equiv) in dry dichloromethane (70 mL) was added chloro(dimethyl sulfide)gold(I) (5.5 mmol, 1.0 equiv). The mixture was stirred at room temperature or at reflux for 2 h in the absence of light under an argon atmosphere. The crude mixture was concentrated under vacuum. The resulting brown solid was dissolved in dichloromethane (3 mL), and pentane (30 mL) was added to precipitate the expected complex as a white solid, which was isolated by filtration. The latter was dissolved in dichloromethane (3 mL), and pentane was added slowly in order to obtain a biphasic solution. Overnight crystallization occurred to give crystals of the expected complex.

*Chloro(diphenylphosphinous acid)gold(I) (**2a**).* According to the general procedure, using commercially available diphenylphosphine oxide (1.11 g, 5.5 mmol) and chloro(dimethyl sulfide)gold(I) complex (1.62 g, 5.5 mmol) at room temperature, **2a** was isolated after filtration (2.22 g, 93%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69−7.51 (m, 4H), 7.50−7.47 (m, 2H), 7.46−7.37 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.4 (d, J = 74.7 Hz), 132.4 (d, J = 2.0 Hz), 131.6 (d, J = 15.1 Hz), 129.1 (d, J = 12.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 89.9; mp 132−133 °C; IR (neat, cm^{-1}) 3055, 1588, 1481, 1436. The spectral data for this compound correspond to the previously reported data.[37]

*(±)-Chloro(tert-butylphenylphosphinous acid)gold(I) (**2b**).* According to the general procedure, using (±)-*tert*-butylphenylphosphine oxide (**1b**;[38] 1.0 g, 5.5 mmol) and chloro(dimethyl sulfide)gold(I) complex (1.62 g, 5.5 mmol) at room temperature, **2b** was isolated as a white solid (2.23 g, 97%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.61 (m, 2H), 7.47−7.43 (m, 1H), 7.39−7.34 (m, 2H), 1.07 (d, J = 16.0 Hz, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.1 (d, J = 2.0 Hz), 131.9 (d, J = 14.1 Hz), 131.4 (d, J = 61.6 Hz), 128.4 (d, J = 12.1 Hz), 35.3 (d, J = 46.5 Hz), 24.6 (d, J = 6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 110.5; mp 178−179 °C; IR (neat, cm^{-1}) 3124, 2961, 2866, 1474, 1459, 1393, 1364; HRMS (ESI+) calcd for $[C_{10}H_{15}AuClOP + Na]^+$ m/z 437.0107, found 437.0124.

*Chloro(dicyclohexylphosphinous acid)gold(I) (**2d**).* According to the general procedure, using dicyclohexylphosphine oxide (**1d**;[38] (0.103 g, 0.48 mmol) and chloro(dimethylsulfide)gold(I) complex (0.142 g, 0.48 mmol) at reflux, **2d** was isolated as a white solid (0.095 g, 44%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (bs, 1H), 1.98−1.71 (m, 10H), 1.50−1.48 (m, 2H), 1.35−1.22 (m, 10H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 38.0 (d, J = 43.4 Hz), 27.7 (d, J = (5.1 Hz), 26.7 (d, J

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= 2.0 Hz), 26.4 (d, J = 9.1 Hz), 26.2 (d, J = 6.1 Hz), 25.9 (d, J = 1.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 118.48; mp 224−225 °C; IR (neat, cm^{-1}) 3135, 2927, 2852; HRMS (ESI−) calcd for $[C_{12}H_{23}AuClOP - H]^-$ m/z 445.7678, found 445.7670.

*(±)-Chloro(cyclohexylphenylphosphinous acid)gold(I) (**2e**).* According to the general procedure, using (±)-cyclohexylphenylphosphine oxide (**1e**;[38] 0.69 g, 0.33 mmol) and chloro(dimethyl sulfide)gold(I) (0.98 g, 0.33 mol) at room temperature, **2e** was isolated as a white solid (0.93 g, 64%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71−7.66 (m, 2H), 7.51−7.47 (m, 1H), 7.44−7.39 (m, 2H), 2.75 (bs, 1H), 1.97−1.82 (m, 2H), 1.79−1.59 (m, 4H), 1.31−1.08 (m, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6 (d, J = 66.6 Hz), 132.2 (d, J = 3.0 Hz), 131.3 (d, J = 15.1 Hz), 128.8 (d, J = 12.1 Hz), 42.8 (d, J = 48.5 Hz), 26.6 (d, J = 4.0 Hz), 26.5 (d, J = 55.5 Hz), 26.0 (d, J = 2;0 Hz), 25.8 (d, J = 2.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 103.5; HRMS (ESI+) calcd for $[C_{12}H_{21}NOPAuCl + NH_4]^+$ m/z 458.0709, found 458.0713.

*Chloro(di-tert-butylphosphinous acid)gold(I) (**2c**).* To a solution of di-*tert*-butylphosphine oxide (**1c**;[38] 0.14 g, 0.86 mmol, 1.0 equiv) in dry dichloromethane (25 mL) was added chloro(dimethyl sulfide)-gold(I) (0.255 g, 0.86 mmol, 1.0 equiv). The mixture was stirred at reflux for 2 h in the absence of light under an argon atmosphere. The crude product was concentrated under vacuum. The resulting solid was dissolved in dichloromethane (3 mL), and pentane (30 mL) was added to precipitate the nonreactive $ClAuSMe_2$. After removal of the solvent, the expected complex **2c** was obtained as a white solid which could be crystallized in a cyclohexane/CH_2Cl_2 mixture (20/1). **2c** was isolated after filtration (0.106 g, 31%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (s, 9H), 1.35 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 37.9 (d, J = 35.5 Hz), 27.5 (d, J = 7.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 133.1; IR (neat, cm^{-1}) 3133, 2954, 2868, 1472, 1393, 1370; low-resolution MS (ESI 30 V, CH_2Cl_2) m/z 395.1 (36), 393.1 (100).

*(±)(tert-Butylphenylphosphinous acid)(2,4,6-trimethoxybenzonitrile)gold(I) Hexafluoroantimonate (**2f**).* To a solution of **2b** (0.415 g, 1.0 mmol, 1.0 equiv) and 2,4,6-trimethoxybenzonitrile (0.197 g, 1.0 mmol, 1.0 equiv) in dry dichloromethane (11 mL) was added $AgSbF_6$ (0.351 g, 1.0 mmol, 1.0 equiv) under an argon atmosphere. A white precipitate of AgCl appeared instantly. The mixture was stirred in the dark for 15 min, and then it was filtered through a Teflon filter to afford a yellow solution which was concentrated under vacuum. The crude solid was dissolved in dichloromethane (3 mL), and pentane (3 mL) was added slowly in order to obtain a biphasic solution. Overnight crystallization gave gray crystals of complex **2f** (0.808 g, 1.0 mmol, quantitative): ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.75−7.69 (m, 2H), 7.60−7.53 (m, 3H), 6.13 (s, 2H), 3.91 (s, 6H), 3.89 (s, 3H), 1.16 (d, J = 16.0 Hz, 9H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.7, 166.6, 133.6 (d, J = 3.0 Hz), 132.3 (d, J = 15.2 Hz), 129.9 (d, J = 66.7 Hz), 129.4 (d, J = 12.1 Hz), 119.8, 91.7, 57.2, 56.9, 35.7 (d, J = 48.5 Hz), 24.5 (d, J = 7.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 113.6; mp 170−171 °C; IR (neat, cm^{-1}) 3608, 2956, 2249, 1603, 1576, 1477, 1460, 1437, 1421.02; HRMS (ESI+) calcd for $[C_{20}H_{26}AuNO_4P]^+$ m/z 572.1259, found 572.1272.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, and CIF files giving experimental procedures and characterization data for all new compounds and crystallographic data for all X-ray structures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for L.F.: louis.fensterbank@upmc.fr.

Present Address

⊥Laboratoire de Chimie Organique et Bioorganique EA4566, Université de Haute-Alsace, Ecole Nationale Supérieure de Chimie de Mulhouse, 3 rue Alfred Werner, F-68093 Mulhouse Cedex, France.

Author Contributions

The experiments described were performed by F.S., C.T., E.S., H.C., L.G., D.M., Y.G., V.M.-M., and J.-P.G. Buried volumes were determined by H.C.. The manuscript was written by V.M.-M. and L.F.

Notes

The authors declare no competing financial interest.

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