Chiral Phosphine Ligands Derived from Sugars. 3. Syntheses, Structures, and Spectroscopic Properties of Gold(I) Complexes with Chiral Phosphines from Glucose. X-ray Structures of [Au(2-MBPA)Cl] and [Au(3-MBPA)(2-pyS)]

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A series of gold(I) complexes of the type [AuP′X] (P′ = 2-MBPA: X = Cl, **1**; X = 2-pyS, **2**; X = 2-bimS, **3**. P′ = 3-MBPA: X = Cl, 4; X = 2-pyS, **5**; X = 2-bimS, **6**. 2-pySH = pyridine-2-thiol; 2-bimSH = 2-mercaptobenzimidazole) containing phosphine ligands (methyl 4,6-*O*-benzylidene-2-deoxy-2-(diphenylphosphino)-α-D-altropyranoside, 2-MBPA; methyl 4,6-*O*-benzylidene-3-deoxy-3-(diphenylphosphino)-α-D-altropyranoside, 3-MBPA) derived from glucose have been prepared and characterized by ^{1}H, ^{13}C, and ^{31}P NMR and infrared spectra in which the assignments of the gold−ligand vibrations have been carried out. The structures of [Au(2-MBPA)Cl] (**1**) and Au(3-MBPA)(2-pyS)] (**5**) have been determined by X-ray crystallographic techniques. Compound **1** crystallizes in the monoclinic space group $P2_1$ with unit-cell dimensions a = 9.907(4) Å, b = 10.394(4) Å, c = 13.542(7) Å, β = 110.70(4)°, V = 1304(2) Å^3, and Z = 2. Compound **5** crystallizes in orthorhombic space group $P2_12_12_1$ with unit-cell dimensions a = 9.857(3) Å, b = 14.466(2) Å, c = 20.263(6) Å, V = 2889(1) Å^3 and Z = 4. The structures were refined to final R = 5.6% and R = 4.1% for **1** and **5**, respectively. Complex **5** features a nearly linear gold atom geometry defined by phosphorus and sulfur atoms with Au−P = 2.256(3) Å, Au−S = 2.303(4) Å and P−Au−S = 177.6(1)°, in which 2-pyS adopts a complete monodentate coordination mode involving only the S-donor atom ligated to the Au(I) ion, and complex **1** is also linear with larger deviation (P−Au−Cl angle = 174.5(3)°) with distances Au−P = 2.232(6) Å and Au−Cl = 2.275(7) Å.

Interest in complexes containing chromophore P−Au−S arises from their potential use in medicine. Auranofin [(2,3,4,6-tetra-*O*-acetyl-1-thio-*β*-D-glucopyranosato-*S*)(triethylphosphine)]gold(I) is efficacious and well tolerated, and exibits therapeutic properties superior to the traditional chrysotherapeutic agents for the treatment of rheumatoid arthritis[1−3] and has also been found to be highly cytotoxic to tumor cells[4] and active against interperitoneal P388 leukaemia.[5] For the above mentioned medicinal applications, the chemistry of gold(I) has attracted renewed attention.[6−9] But, problems concerning the toxicity of this type of compounds have precluded some of them from further development as practical drugs.[10]

It is very attractive to synthesize chiral phosphine ligands from cheap sugars for asymmetric catalysis. After we found an effective method to incorporate phosphorus atoms into the carbons of pyrano rings and prepared some new chiral phosphines,[11,12] it is our belief that, the use of those phosphines derived from glucose instead of ordinary organophosphines may provide less toxic derivatives retaining or enhancing the efficacy of the gold(I) complexes.

We have engaged for many years in the investigation of the structural chemistry of transition metal complexes with mixed phosphine and thiolate ligands.[13,14] This contribution reports the syntheses and characterization of a series of gold(I) complexes with the general formula [Au(P′)X] (P′ = methyl 4,6-*O*-benzylidene-2-deoxy-2-(diphenylphosphino)-α-D-altropyranoside, 2-MBPA, or methyl 4,6-*O*-benzylidene-3-deoxy-3-(diphenylphosphino)-α-D-altropyranoside, 3-MBPA; X = Cl, pyridine-2-thiol (2-pySH), or 2-mercaptobenzimidazole (2-bimSH)).

Experimental Section

Elemental analyses were performed by the Chemical Analysis Division of this Institute. Infrared spectra were measured on a Nicolet

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[⊗] Abstract published in *Advance ACS Abstracts,* March 15, 1996.

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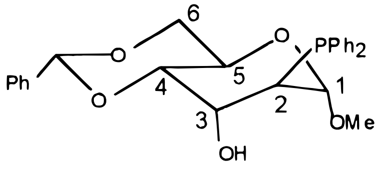
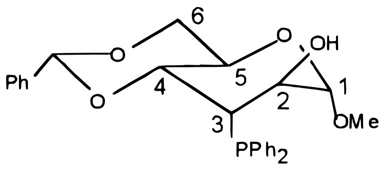


2-MBPA



3-MBPA

Magna-750 FT spectrometer (in KBr disks, 4000−400 cm^{-1}) and a Digilab FTS-20 E/D-V spectrometer (in CsI disks, 550−120 cm^{-1}). NMR spectra were measured in $CDCl_3$ (for **1** and **4**) or $(CD_3)_2SO$ (for **2**, **3**, **5**, and **6**) on a Varian Unity-500 spectrometer operating at 499.98 MHz for ^1H, 125.71 MHz for ^{13}C, and 202.36 MHz for ^{31}P. Chemical shifts are expressed in parts per million (ppm) downfield from internal TMS (^1H and ^{13}C) or external 85% H_3PO_4 (^{31}P) standards as positive values.

The reagents 2-pySH, 2-bimSH, ethyl sulfide, and $HAuCl_4{\cdot}4H_2O$ were used as received. Sodium methoxide was prepared by dissolving sodium metal in dry methanol and then evaporating the solvent and drying under reduced pressure. Methyl 4,6-*O*-benzylidene-2-deoxy-2-(diphenylphosphino)-α-D-altropyranoside (2-MBPA) and methyl 4,6-*O*-benzylidene-3-deoxy-3-(diphenylphosphino)-α-D-altropyranoside (3-MBPA) were prepared as reported.[11,12] Analytical grade solvents were used without further purification.

Preparation of Compounds. [Au(SEt$_2$)Cl]. A modified procedure[15] was used to prepare the compound. To a stirred H_2O:EtOH solution (5:25 cm^3) of 3.0 g (7.5 mmol) of $HAuCl_4{\cdot}4H_2O$ was added dropwise 1.8 cm^3 (17 mmol) of Et_2S. After being stirred at room temperature for 30 min, the colorless solution was filtered and the filtrate was chilled overnight. White needle crystals of the product were collected by filtration and washed twice with cold EtOH (5 cm^3). Similar to [Au(tht)Cl] (tht = tetrahydrothiophene),[16] [Au(SEt$_2$)Cl] decomposes slowly at room temperature, but is stable at 0 °C for a few weeks.

[Au(P′)Cl]: P′ = 2-MBPA, 1; P′ = 3-MBPA, 4. To a CH_2Cl_2 solution (5 cm^3) of 0.32 g (1.0 mmol) of [Au(SEt$_2$)Cl] was added 0.45 g (1.0 mmol) of 2-MBPA or 3-MBPA. After being stirred at room temperature under N_2 atmosphere for 15 min, the solution was evaporated to dryness. Recrystallization of the residue from CH_2Cl_2/EtOH gave the products.

[Au(P′)X]: P′ = 2-MBPA: X = 2-pyS, 2; X = 2-bimS, 3. P′ = 3-MBPA: X = 2-pyS, 5; X = 2-bimS, 6. General Procedure: An CH_2Cl_2 solution (2 cm^3) of [Au(P′)Cl] (0.023 g, 0.033 mmol) was mixed with an EtOH solution (2 cm^3) of RSH (0.035 mmol) containing MeONa (0.0019 g, 0.035 mmol). The mixture was stirred for 2 h at room temperature and left to stand overnight. The solution was filtered and the filtrate was left to evaporate slowly to obtain the desired products.

Crystallographic Measurements. Single crystals of **1** and **5** were obtained directly from the respective reactions and mounted on glass fibers. Data collections were performed at 296 K on an Enraf-Nonius CAD 4 diffractometer with Mo Kα radiation (λ = 0.710 69 Å) and a graphite monochromator. The unit cell parameters were obtained by least-squares refinements of the θ range of 25 reflections. Crystal and instrument stabilities were monitored with a set of three standard reflections measured every 300 reflections; in all cases no significant variations were found. The intensity data collected were corrected for *Lp* factors and empirical absorptions. The structures were solved by heavy atom methods and difference Fourier syntheses and refined by full-matrix least-squares techniques with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were not refined, but added to the structure factor calculations. The crystallographic data for complexes **1** and **5** are listed in Table 1 together with the data collection parameters. All calculations were performed on a MICROVAX 3100 computer using RIGAKU/MSC TEXSAN V2.1 program package. Final atomic coordinates for **1** and **5** are given in Tables 2 and 3, respectively.

Table 1. Crystallographic Data for Complexes **1** and **5**

	1	**5**
empirical formula	$C_{26}H_{27}AuClO_5P$	$C_{31}H_{31}AuNO_5PS$
fw	682.89	757.59
crystal dimensions, mm^3	0.22 × 0.22 × 0.30	0.45 × 0.32 × 0.15
space group	$P2_1$ (No. 4)	$P2_12_12_1$ (No. 19)
a, Å	9.907(4)	9.857(3)
b, Å	10.394(4)	14.466(2)
c, Å	13.542(7)	20.263(6)
β, deg	110.70	
V, $Å^3$	1304(2)	2889(1)
Z	2	4
D_{calcd}, g cm^{-1}	1.74	1.74
F(000)	668	1496
θ range for lattice param, deg	12.01−12.93	13.02−13.81
scan mode	ω−2θ	ω−2θ
2θ range, deg	2−50	2−50
$T_{min} - T_{max}$	0.6895−1.000	0.6186−1.000
no. of reflcns collcd	2591	2900
no. of obsd reflcns with I ≥ 3σ(I)	2157	2587
no. of reflcns used	2025	2585
no. of variables	307	361
S	1.37	1.38
Δ/σ	0.32	0.00
R^a	0.056	0.041
$R_w{}^b$	0.061	0.050

[a] $R = (\sum||F_o| - |F_c||)/\sum|F_o|$. [b] $R_w = \{[\sum w(|F_o| - |F_c|)^2]/\sum w|F_o|^2\}^{1/2}$. $w = 1/\sigma^2(F_i)$.

Results and Discussion

Syntheses and Spectroscopic Studies. The reduction of $HAuCl_4{\cdot}4H_2O$ with 2 equiv of SEt_2 reducing reagent in ethanol−water, which is a general procedure[16,17] to obtain gold(I) starting materials, yielded [Au(SEt$_2$)Cl].[15] The latter reacts easily with the chiral phosphine P′ (P′ = 2-MBPA or 3-MBPA) to give [Au(P′)Cl] in high yields. Equimolar reactions of [Au(P′)Cl], base and 2-pySH or 2-bimSH in ethanol-dichloromethane solution yielded solid complexes of the general formula [Au(P′)(SR)] (R = 2-py or 2-bim) according to eq 1. Table 4 summarizes the elementary analyses and the yields.

$$[Au(P')Cl] \quad + \quad NaSR \xrightarrow{\quad} [Au(P')(SR)] \quad + \quad NaCl \qquad (1)$$

P′ = 2-MBPA, **1**
P′ = 3-MBPA, **4**

P′	R	
2-MBPA	2-py	**2**
2-MBPA	2-bim	**3**
3-MBPA	2-py	**5**
3-MBPA	2-bim	**6**

The important features of the infrared spectra recorded in KBr for near-IR and in CsI for far-IR are also listed in Table 4. The far-IR spectra of **1** and **4** show intense Au−Cl stretching vibrations at 334 and 316 cm^{-1}, respectively, in which the isotopic splitting for ν(Au^{35}−Cl) and ν(Au^{37}−Cl) (sh) is observed, in agreements with those reported.[18−24] According to our knowledge, the assignment of Au−S vibrations in complexes of the type of [Au(PR$_3$)(SR′)] (R′ = aryl or alkyl)

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Table 2. Positional Parameters and Their Estimated Standard Deviations for Compound **1**

atom	*x*	*y*	*z*	B(eq)[a]
Au	0.75629(7)	0.9308	0.81313(6)	3.25(3)
Cl	0.6552(7)	1.0866(8)	0.8826(6)	6.0(3)
P	0.8490(5)	0.7646(6)	0.7543(4)	2.7(2)
O(1)	0.674(1)	0.455(1)	0.829(1)	3.2(6)
O(3)	0.955(1)	0.478(1)	0.977(1)	3.7(6)
O(4)	0.945(1)	0.690(2)	1.111(1)	3.5(6)
O(5)	0.628(1)	0.662(1)	0.871(1)	2.9(5)
O(6)	0.739(1)	0.745(2)	1.149(1)	3.6(6)
C(1)	0.680(2)	0.585(2)	0.808(2)	3.2(9)
C(2)	0.843(2)	0.614(2)	0.825(1)	2.8(8)
C(3)	0.937(2)	0.607(2)	0.942(1)	2.9(8)
C(4)	0.867(2)	0.693(2)	1.002(2)	2.9(8)
C(5)	0.712(2)	0.655(2)	0.983(2)	2.4(7)
C(6)	0.651(2)	0.746(2)	1.041(2)	4.0(10)
C(7)	0.883(2)	0.778(2)	1.160(2)	3.0(8)
C(8)	0.532(2)	0.411(3)	0.817(2)	5.0(10)
C(11)	0.970(2)	0.780(2)	1.281(2)	4.0(10)
C(12)	1.107(3)	0.730(3)	1.317(2)	5.0(10)
C(13)	1.170(4)	0.740(5)	1.430(4)	8.0(20)
C(14)	1.112(4)	0.781(5)	1.492(3)	8.0(20)
C(15)	0.978(4)	0.826(4)	1.454(2)	8.0(20)
C(16)	0.908(3)	0.830(4)	1.346(2)	7.0(20)
C(21)	0.751(2)	0.723(3)	0.617(2)	4.0(10)
C(22)	0.641(3)	0.808(3)	0.558(2)	6.0(10)
C(23)	0.564(4)	0.785(4)	0.453(2)	9.0(20)
C(24)	0.589(4)	0.677(5)	0.407(2)	9.0(20)
C(25)	0.704(4)	0.586(3)	0.464(2)	8.0(20)
C(26)	0.783(4)	0.628(4)	0.571(3)	6.0(20)
C(31)	1.037(2)	0.781(2)	0.770(2)	2.9(8)
C(32)	1.127(3)	0.683(3)	0.778(2)	5.0(10)
C(33)	1.269(2)	0.704(3)	0.785(2)	5.0(10)
C(34)	1.323(2)	0.822(2)	0.793(2)	4.0(10)
C(35)	1.232(2)	0.919(4)	0.782(2)	4.0(10)
C(36)	1.088(2)	0.908(3)	0.768(2)	5.0(10)

[a] $B(\mathrm{eq}) = (8\pi^2/3)\sum_i\sum_j \mathbf{U}_{ij} a_i^* b_j^* a_i a_j$.

has not been seen very often. The Au−S absorptions appearing in the range 322−326 cm^{-1} for **2**, **3**, **5**, and **6**, are higher than those in the region 291−306 cm^{-1} reported for complexes Au(SCN)(PR_3).[20,23,24] The ν(Au−P) values for **1**−**6** appear in the range 368−399 cm^{-1} according to the literature.[20,24] The ν(P−C) modes are strong in the range 1416−1439 cm^{-1}, which are nearly identical to their free ligands.[12]

The ^1H, ^{13}C and ^{31}P NMR data recorded in $CDCl_3$ or $(CD_3)_2SO$ for the ligands and the complexes are listed in Tables 5 and 6, respectively. The integrations for ^1H NMR spectra are consistent with the formulations of the complexes. Even at 500 MHz, the ^1H NMR spectra can not be analyzed easily, mainly owing to long-range coupling.[12,25] The assignments were aided by the comparison with the spectra of their individual free ligands and with those of the complex *trans*-[Rh(CO)(P′)$_2$Cl] (P′ = 2-MBPA, 3-MBPA)[26] which have been ascertained by ^1H−^1H COSY and ^1H−^{13}C HMQC (heteronuclear multiple-quantum coherence) spectra. In addition, the spectra of **5** and **6** have been interpreted unambiguously also by HMQC and ^1H−^1H COSY spectra.

Table 3. Positional Parameters and Their Estimated Standard Deviations for Compound **5**

atom	*x*	*y*	*z*	*B*(eq)[a]
Au	0.23012(4)	0.41925(3)	0.11190(3)	2.59(2)
S	0.4575(3)	0.4104(3)	0.1375(2)	3.9(2)
P	0.0056(3)	0.4234(2)	0.0902(1)	2.2(1)
O(1)	0.0951(9)	0.4044(6)	0.2496(5)	3.2(4)
O(2)	−0.255(1)	0.4601(6)	0.2436(5)	3.4(4)
O(4)	−0.0336(8)	0.6352(5)	0.1117(5)	2.5(3)
O(5)	−0.002(1)	0.5456(6)	0.2788(4)	3.2(4)
O(6)	0.085(1)	0.7394(6)	0.1764(4)	3.3(4)
N	0.571(1)	0.3136(8)	0.2315(6)	3.2(5)
C(1)	−0.022(1)	0.4485(8)	0.2685(6)	2.6(5)
C(2)	−0.131(1)	0.4307(8)	0.2169(6)	2.6(5)
C(3)	−0.107(1)	0.4804(8)	0.1511(6)	2.0(5)
C(4)	−0.073(1)	0.5836(8)	0.1680(6)	2.2(4)
C(5)	0.036(1)	0.5898(9)	0.2187(6)	2.6(5)
C(6)	0.055(2)	0.693(1)	0.2359(7)	3.7(7)
C(7)	−0.017(1)	0.7310(7)	0.1297(6)	2.5(5)
C(8)	0.205(2)	0.420(1)	0.2938(7)	4.7(7)
C(11)	0.015(1)	0.7846(8)	0.0693(7)	2.8(6)
C(12)	0.149(2)	0.792(1)	0.0468(9)	4.6(8)
C(13)	0.182(2)	0.842(1)	−0.0094(8)	4.7(8)
C(14)	0.079(2)	0.886(1)	−0.043(1)	5.0(10)
C(15)	−0.052(2)	0.882(1)	−0.021(1)	6.0(10)
C(16)	−0.081(2)	0.831(1)	0.0357(9)	4.4(8)
C(21)	−0.066(1)	0.3068(8)	0.0844(6)	2.4(5)
C(22)	0.023(1)	0.237(1)	0.0669(8)	3.5(7)
C(23)	−0.029(2)	0.147(1)	0.058(1)	4.9(9)
C(24)	−0.166(2)	0.130(1)	0.068(1)	4.5(8)
C(25)	−0.251(1)	0.199(1)	0.0853(8)	4.1(7)
C(26)	−0.203(1)	0.2880(8)	0.0942(6)	2.7(6)
C(31)	−0.033(1)	0.4749(9)	0.0106(7)	2.7(6)
C(32)	0.051(1)	0.543(1)	−0.0140(7)	3.4(6)
C(33)	0.023(2)	0.582(1)	−0.0747(7)	4.6(7)
C(34)	−0.084(2)	0.555(1)	−0.1113(8)	4.8(8)
C(35)	−0.163(2)	0.486(1)	−0.0890(8)	4.8(8)
C(36)	−0.144(2)	0.448(1)	−0.0283(8)	4.3(8)
C(41)	0.471(1)	0.3113(9)	0.1878(7)	2.9(6)
C(43)	0.589(2)	0.241(1)	0.2720(8)	4.3(8)
C(44)	0.506(2)	0.164(1)	0.268(1)	5.0(10)
C(45)	0.402(2)	0.162(1)	0.224(1)	4.9(9)
C(46)	0.383(2)	0.235(1)	0.1836(9)	4.8(8)

[a] *B*(eq): see Table 2.

It is found that **1** is stable in $CDCl_3$ solution for only a few hours. The appearance of a −CHO signal at 10.02 ppm in the ^1H NMR indicates hydrolysis, with the 2-MBPA losing a PhCHO molecule. However, **4** is stable for several days in $CDCl_3$. This phenomenon was also observed in the compounds *trans*-[Pd(P′)$_2$Cl$_2$] and [Rh(CO)(P′)$_2$Cl].[26] Considering the structures of 2-MBPA and 3-MBPA, the P−C(pyrano ring) of 2-MBPA can rotate freely but not that of 3-MBPA.[11,12] This suggests that [Au(2-MBPA)Cl] (**1**) in $CDCl_3$ possesses a chelate structure in which the hydroxyl oxygen O(3) will be bonded to the metal and thus releases HCl, resulting in hydrolysis of the molecule.

The proton-decoupled ^{13}C NMR spectra of **1**−**6** have been measured and assigned first by DEPT spectra. The resonances in the highest field are from the pyrano ring carbons attached to the phosphorus atoms for all complexes synthesized. Compared with the values for the free ligands, the differences of the resonances of the pyrano ring carbons, including those attached to the phosphorus atoms are not obvious (see Table 6), consistent with the fact that gold(I) has little effect on the conformation or the electronic structure of the pyrano ring.[27]

Crystal Structures. The molecular structures of [Au(2-MBPA)Cl] (**1**) and [Au(3-MBPA)(2-pyS)] (**5**) are illustrated in Figures 1 and 2, respectively. Selected interatomic distances and bond angles are listed in Tables 7 and 8, respectively. The

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Table 4. Analytical, Physical, and Infrared (cm^{-1}) Data for Complexes **1**−**6**

compound		yield		anal[a]			selected IR data		
no.	formula	(%)	color	C	H	N	ν(PC)	ν(AuP)	ν(AuX)[b]
1	[Au(2-MBPA)Cl]	94	white	45.59 (45.73)	3.88 (4.00)		1437 s 1420 s	399 m	334 s
2	[Au(2-MBPA)(2-pyS)]	87	pale yellow	49.36 (49.15)	4.07 (4.12)	1.53 (1.85)	1438 s	392 m	326 s 301 m
3	[Au(2-MPBA)(2-bimS)]	75	white	49.73 (49.69)	4.1 (4.04)	3.27 (3.51)	1437 s 1423 s	368 m	324 m
4	[Au(3-MBPA)Cl]	92	white	45.61	4.06 (45.73)	(4.00)	1439 s	392 m	316 s (sh)
5	[Au(3-MBPA)(2-pyS)]	80	pale yellow	48.87 (49.15)	4.09 (4.12)	1.65 (1.85)	1438 s 1416 s	395 m	326 s
6	[Au(3-MBPA)(2-bimS)]	83	white	49.54 (49.69)	4.17 (4.04)	3.41 (3.51)	1435 s 1423 s	390 w	322 m

[a] Values in parentheses are the calculated values. [b] X = Cl for **1** and **4**; X = S for **2, 3, 5,** and **6**.

Table 5. ^{1}H NMR Chemical Shifts (ppm) (Alkyl Parts) for Complexes **1**−**6** and the Free Ligands[a]

	H1	H2	H3	H4	H5	H6	H6′	CH3	PhCH
2-MBPA	4.46 (d)	3.24 (m)	4.30 (m)	4.17 (q)	4.00 (m)	4.35 (m)	3.90 (t)	3.30 (s)	5.64 (s)
1	4.61 (d)	3.60 (m)	4.35 (m)	4.83 (q)	4.06 (m)	4.39 (m)	4.00 (t)	3.33 (s)	5.71 (s)
2	4.54 (d)	3.66 (m)	4.12 (m)	4.21 (q)	4.01 (m)	4.14 (m)	3.39 (d)	3.27 (s)	5.64 (s)
3	4.47 (d)	3.75 (m)	4.15 (m)	4.82 (m)	3.97 (m)	4.24 (m)	3.89 (m)	3.16 (s)	5.41 (s)
3-MBPA	4.48 (s)	3.52 (m)	3.49 (m)	4.43 (m)	4.57 (m)	4.25 (dd)	3.78 (dt)	3.43 (s)	5.45 (s)
4	4.60 (s)	3.73 (d)	3.77 (m)	4.67 (m)	5.06 (m)	4.31 (q)	3.89 (dd)	3.44 (s)	5.41 (s)
5	4.54 (s)	3.53 (d)	4.10 (m)	4.74 (m)	5.08 (m)	4.24 (m)	3.82 (t)	3.27 (s)	5.55 (s)
6	4.51 (s)	3.51 (d)	4.14 (m)	4.70 (m)	5.27 (m)	4.23 (m)	3.81 (m)	3.20 (s)	5.58 (s)

[a] *n*(1−6′) indicates the proton on the *n* carbon atom of the pyrano ring.

Table 6. ^{31}P and ^{13}C NMR Data[a] (ppm) for Compounds **1**−**6** and the Free Ligands

	P	C1	C2	C3	C4	C5	C6	CH$_3$	PhCH
2-MBPA	−16.9	101.1	44.8	67.2	77.3	58.6	69.4	55.6	102.2
1	30.3	97.2	44.1	65.1	77.0	58.2	68.9	55.9	102.2
2	29.6	96.5	46.4	63.4	77.3	57.1	68.5	54.9	101.0
3	32.0	96.9	*b*	63.7	76.9	57.7	68.1	52.2	101.0
3-MBPA	−21.7	101.1	69.7	41.2	76.9	60.8	69.1	54.7	101.3
4	28.3	99.9	69.2	41.0	75.1	60.6	69.1	54.1	101.9
5	29.3	100.4	68.4	*b*	75.6	61.9	69.6	54.4	101.5
6	39.3	100.2	68.3	40.8	75.3	61.6	69.3	54.2	101.5
7	26.9	100.2	68.1	29.5	75.1	61.0	69.2	54.8	100.8

[a] Compounds **1** and **4** and free ligands in CDCl$_3$; **2**, **3**, **5**, and **6** in DMSO-d_6. [b] Immersed in the signals of DMSO.

Au atom in **1** exists in the expected linear geometry defined by P of the 2-MBPA ligand (Au−P = 2.232(6) Å) and Cl atom (Au−Cl = 2.275(7) Å), and the angle P−Au−Cl is 174.5(3)°. The Au−P bond length in **1** is comparable to that in [Au(PPh$_3$)-Cl][28] (2.235 Å) but shorter than that in [Au(PCy$_3$)Cl] (2.242 Å)[29] and longer than those[20] observed for [Au(DMPP)Cl] (2.227 Å) and [Au(DBP)Cl] (2.221 Å) (DMPP = 1-phenyl-3,4-dimethylphosphole, DBP = 1-phenyldibenzophosphole). This shows that for the phosphine ligands in these five complexes, the donor ability toward gold(I) decreases in the order DBP > DMPP > 2-MBPA > Ph$_3$P > Cy$_3$P even though the differences are small. The Au−Cl bond lengths show similar small changes but in the reverse order, consistent with the observation that the differential *trans*-influences[30−32] of these phosphorus donors do exist although they are small.[20,33] There is no significant intermolecular contact in the lattice of **1** and the closest Au- - -Au contact is longer than 3.60 Å.

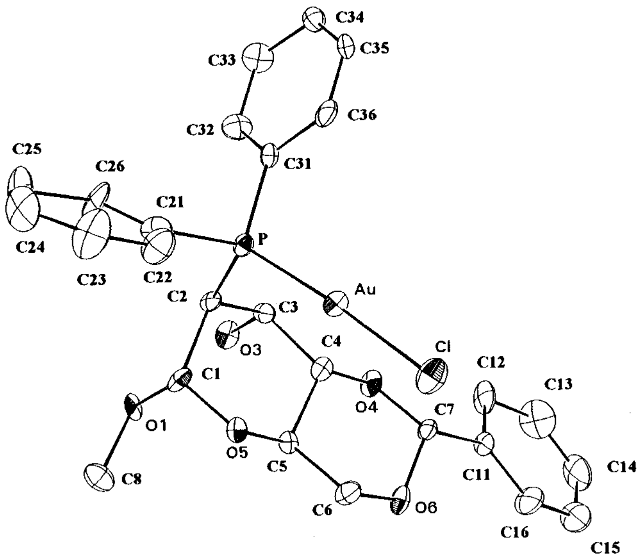

Figure 1. Molecular structure of [Au(2-MBPA)Cl] (**1**) showing the atom-labeling scheme.

As can be seen from Figure 1, the pyrano ring and the 4,6-*O*-benzylidene ring adopt a distorted chair conformation. Similar to the structure of the oxide of its free ligand,[12] the average torsion angles are ±56° (pyrano ring) and ±60° (4,6-*O*-benzylidene ring) for **1**, and ±57° (pyrano ring) and ±60° (4,6-*O*-benzylidene ring) for the oxide. The torsion angles P−C(2)−C(1)−O(1) and P−C(2)−C(3)−O(3) for **1** are 162° and 160°, respectively, indicating that these groups PPh$_2$, OH, and OMe are in *pseudo* axial positions.

The Au atom in [Au(3-MBPA)(2-pyS)] **5** has also a near-linear[8,34−37] geometry (P−Au−S = 177.6(1)°) with Au−P and Au−S bond lengths of 2.256(3) and 2.303(4) Å, respectively,

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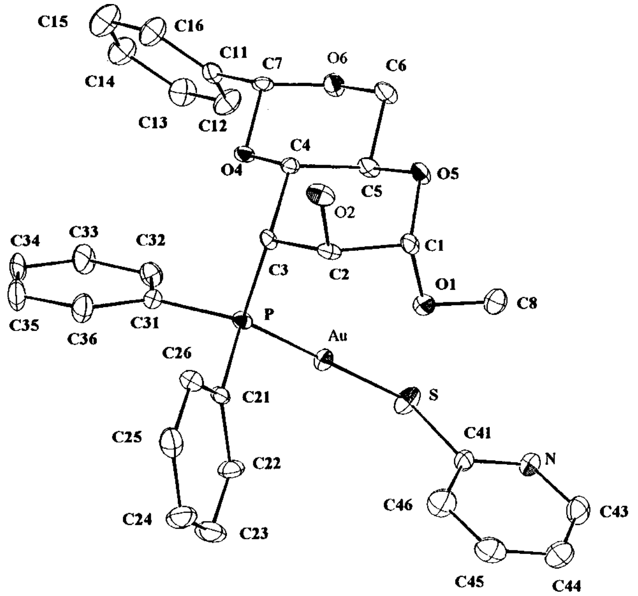

Figure 2. Molecular structure of [Au(3-MBPA)(2-pyS)] (**5**) showing the atom-labeling scheme.

Table 7. Selected Atomic Distances (Å) and Bond Angles (deg) for Compound **1**

Au−P	2.232(6)	Au−Cl	2.275(7)
P−C(31)	1.81(2)	P−C(21)	1.82(2)
P−C(2)	1.85(2)	O(5)−C(1)	1.40(2)
O(5)−C(5)	1.45(2)	O(6)−C(6)	1.42(3)
O(6)−C(7)	1.42(2)	O(4)−C(7)	1.40(2)
O(4)−C(4)	1.40(2)	O(1)−C(1)	1.38(3)
O(1)−C(8)	1.43(2)	O(3)−C(3)	1.42(3)
C(1)−C(2)	1.58(2)	C(2)−C(3)	1.52(2)
C(3)−C(4)	1.53(3)	C(4)−C(5)	1.51(2)
C(5)−C(6)	1.49(3)	C(7)−C(11)	1.56(3)
P−Au−Cl	174.5(3)	C(31)−P−C(21)	107.0(10)
C(31)−P−C(2)	104.0(9)	C(31)−P−Au	114.9(7)
C(21)−P−C(2)	103.0(10)	C(21)−P−Au	114.4(8)
C(2)−P−Au	112.1(6)	C(1)−O(5)−C(5)	114.0(10)
C(6)−O(6)−C(7)	110.0(20)	C(7)−O(4)−C(4)	108.0(10)
C(1)−O(1)−C(8)	113.0(20)	O(1)−C(1)−O(5)	113.0(20)
O(1)−C(1)−C(2)	106.0(20)	O(5)−C(1)−C(2)	112.0(20)
C(3)−C(2)−C(1)	111.0(10)	C(3)−C(2)−P	118.0(20)
C(1)−C(2)−P	108.0(10)	O(3)−C(3)−C(2)	111.0(20)
O(3)−C(3)−C(4)	107.0(20)	O(4)−C(4)−C(5)	109.0(20)
O(4)−C(4)−C(3)	111.0(20)	C(5)−C(4)−C(3)	112.0(20)
O(5)−C(5)−C(6)	109.0(20)	O(5)−C(5)−C(4)	110.0(20)
C(6)−C(5)−C(4)	109.0(20)	O(6)−C(6)−C(5)	109.0(20)
O(4)−C(7)−O(6)	113.0(20)	O(4)−C(7)−C(11)	110.0(20)
O(6)−C(7)−C(11)	106.0(20)		

Table 8. Selected Atomic Distances (Å) and Bond Angles (deg) for the Compound **5**

Au−P	2.256(3)	Au−S	2.303(4)
S−C(41)	1.76(1)	P−C(31)	1.82(1)
P−C(21)	1.83(1)	P−C(3)	1.85(1)
O(5)−C(5)	1.43(1)	O(5)−C(1)	1.43(1)
O(5)−C(7)	1.39(1)	O(6)−C(6)	1.41(2)
O(4)−C(4)	1.42(1)	O(4)−C(7)	1.44(1)
O(1)−C(1)	1.38(2)	O(1)−C(8)	1.42(2)
O(2)−C(2)	1.40(1)	C(1)−C(2)	1.52(2)
C(2)−C(3)	1.53(2)	C(3)−C(4)	1.57(2)
C(4)−C(5)	1.48(2)	C(5)−C(6)	1.55(2)
P−Au−S	177.6(1)	C(41)−S−Au	104.3(5)
C(31)−P−C(21)	103.9(6)	C(31)−P−C(3)	106.6(6)
C(31)−P−Au	112.8(4)	C(21)−P−C(3)	102.9(5)
C(21)−P−Au	111.4(4)	C(3)−P−Au	118.0(4)
C(5)−O(5)−C(1)	110.0(10)	C(7)−O(6)−C(6)	113.0(10)
C(4)−O(4)−C(7)	109.0(10)	C(1)−O(1)−C(8)	113.0(10)
O(1)−C(1)−O(5)	112.0(10)	O(4)−C(1)−C(2)	109.0(10)
O(5)−C(1)−C(2)	111.0(10)	O(2)−C(2)−C(1)	107.0(10)
O(2)−C(2)−C(3)	109.0(10)	C(1)−C(2)−C(3)	114.0(10)
C(2)−C(3)−C(4)	107.0(10)	C(2)−C(3)−P	117.7(9)
C(4)−C(3)−P	116.2(8)	O(4)−C(4)−C(5)	109.0(10)
O(4)−C(4)−C(5)	112.5(9)	C(5)−C(4)−C(3)	111.0(10)
O(5)−C(5)−C(4)	112.0(10)	O(5)−C(5)−C(6)	106.0(10)
C(4)−C(5)−C(6)	108.0(10)	O(6)−C(6)−C(5)	107.0(10)
O(6)−C(7)−O(4)	110.0(10)	O(6)−C(7)−C(11)	111.0(10)
O(4)−C(7)−C(11)	109.0(10)		

which are quite close to the distances in [Au(Ph_3P)(2-pyS)] (2.258 and 2.297 Å).[7] The *trans*-influence of the phosphorus donors exists also, although still small. The C−S bond distance of 1.76(1) Å is comparable to that in [Au(Ph_3P)(2-pyS)] (1.750 Å)[7] but longer than the C═S bond (1.692 Å) found in the free ligand 2-pySH,[38] which exists as the thione form in the solid state. This observation indicates that the 2-pyS anion is functioning as a thiolate in complex **5**. The 2-pyS ligand (including the S atom) is planar with a maximum deviation of ±0.01 Å, and the Au atom lies out of the plane by −1.0774 Å as manifested in the torsion angle of −151° for Au−S−C(41)−N. The Au- - -N separation (>3.60 Å) is longer than the sum of the van der Waals radii (3.25 Å) for those atoms.[39] In contrast to that in [Au(Ph_3P)(2-pyS)], the absence of this weak intramolecular interaction is consistent with the conclusion deduced from the EI-MS spectrum of its free ligand that the space around the P atom is congested.[11]

The deprotonated anion 2-pyS may coordinate to the metal center in a variety of structural modes[40] of which the most commonly observed is bidentate using the N- and S-donor atoms. Though monodentate coordination through the S-donor atom has been reported earlier,[7] a weak intramolecular interaction between the N-donor atom and the metal center was still observed. Complex **5** is the first example of "complete" monodentate coordination involving only the S atom.

Similar to those in the free phosphine ligand[11,12] and in **1**, the pyrano ring and the 4,6-*O*-benzyllidene ring in **5** again have distorted chair conformation. The average torsion angles are ±56° (pyrano ring) and ±60° (4,6-*O*-benzylidene ring) for **5**, and ±55° (pyrano ring) and ±60° (4,6-*O*-benzylidene ring) for the free ligand. The torsion angles P−C(3)−C(2)−O(2) and O(2)−C(2)−C(1)−O(1) for **5** are 164 and 164°, respectively, and the substituents PPh_2, OH, and OMe are in *pseudo*axial positions. The small changes of the torsion angles C(31)−P−C(3)−C(2) and C(21)−P−C(3)−C(4) of **5** (180 and 160°) compared to those of its free ligand (173 and 152°) support the prediction from $^1H-^1H$ COSY and ^{13}C NMR spectra of the latter that the rigidity of the ligand will maintain the coordination position relative to the metal centers.[12]

Studies on the biological activity of these compounds are in progress.

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Supporting Information Available: Tables listing anisotropic thermal factors, complete positional parameters, bond distances and angles, and torsion angles for the complexes [Au(2-MBPA)Cl] (**1**) (Tables S1−S5) and [Au(3-MBPA)(2-pyS)] (**5**) (Tables S5−S10) (11 pages). Ordering information is given on any current masthead page.

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