

## Synthesis and $^{31}\text{P}$ NMR Spectroscopy of a Series of Gold(I) Amine Phosphine Cations

JEAN F. VOLLANO, DONALD H. PICKER and JOHN A. STATLER\*

Pharmaceutical Research Group, Johnson Matthey Inc., 1401 King Road, West Chester, PA 19380, U.S.A.

(Received March 10, 1988)

### Abstract

Several amine gold complexes of 1,2-bis(diphenylphosphino)ethane (dppe) and triphenylphosphine ( $\text{PPh}_3$ ), having the general formulae  $[(\text{AuNH}_2\text{R})_2(\text{dppe})](\text{NO}_3)_2$  and  $[\text{Au}(\text{NH}_2\text{R})(\text{PPh}_3)]\text{NO}_3$  ( $\text{R} =$  alkyl, hydrogen), have been prepared by the addition of an amine to  $(\text{AuNO}_3)_2(\text{dppe})$  or  $\text{Au}(\text{NO}_3)(\text{PPh}_3)$ . These gold(I) amine arylphosphine complexes represent a new class of coordination compounds. The complexes are dicationic in a chloroform/methanol solution used for  $^{31}\text{P}$  NMR spectroscopy. The dppe series displays a small downfield chemical shift as more hindered amines are coordinated. A similar range of chemical shifts was observed for two analogous triphenylphosphine complexes.

### Introduction

Gold(I) frequently exhibits a linear, two-coordinate geometry, and thus provides a useful system for studying  $^{31}\text{P}$  chemical shift effects from *trans* ligands uncomplicated by the presence of other ligands. Furthermore, few examples exist of gold complexes having both phosphine and amine ligands, the only examples being of triethylphosphine gold(I) [1]. Heretofore, there have been no examples of such arylphosphine complexes. Many investigators have correlated steric and electronic factors of phosphines to large changes in phosphorus chemical shift [2]. However, no reports have appeared concerning the relationship of  $^{31}\text{P}$  chemical shift to any property of a *trans* amine for gold phosphine complexes.

Several gold(I) complexes with 1,2-bis(diphenylphosphino)ethane (dppe) have now been prepared having varying amines bound *trans* to the phosphine. Phosphorus chemical shifts have been determined, as have the shifts of some related triphenylphosphine ( $\text{PPh}_3$ ) complexes.

### Experimental

$^{31}\text{P}$  NMR spectra were obtained on an IBM AF-80 spectrometer, using 85%  $\text{H}_3\text{PO}_4$  as an external reference. Melting points were determined in open capillaries using a Thomas-Hoover melting point apparatus and are uncorrected. CHN analyses were performed in-house using a Perkin-Elmer 240C Analyzer or were performed by Galbraith Laboratories. Melting point and microanalytical data may be found in Table 1.

All solvents were reagent grade and were used without further purification.  $\text{HAuCl}_4$  solution was obtained from Johnson Matthey Chemicals. The compounds  $(\text{AuCl})_2(\text{dppe})$  [3, 4] and  $\text{Au}(\text{NO}_3)(\text{PPh}_3)$  [5] were prepared by published procedures.  $[\text{Au}(\text{dppe})_2]\text{Cl}$  [3, 6],  $[\text{Pt}(\text{dppe})_2]\text{Cl}_2$  [7] and  $[\text{Ru}(\text{bipy})_3]\text{Cl}_2$  [8], which were used as standards for conductivity measurements, were also prepared by literature methods. All preparations reported here were performed under an atmosphere of dinitrogen in solvents purged with dinitrogen.

All NMR samples of dppe complexes were prepared at 0.04 M in 50/50 (*v/v*)  $\text{CDCl}_3/\text{CH}_3\text{OH}$ . The samples of  $\text{PPh}_3$  complexes were 0.08 M in the same solvent mixture. Conductivity measurements were of 0.001 M solutions in 50/50 (*v/v*)  $\text{CHCl}_3/\text{CH}_3\text{OH}$ , corrected for background conductance.

### Preparations of Complexes

#### *1,2-Bis(diphenylphosphino)ethanebis(nitrato-gold(I)), $(\text{AuNO}_3)_2\text{dppe}$ , (1)*

$(\text{AuCl})_2\text{dppe}$  (5.0 g, 5.5 mmol) was stirred in dichloromethane (200 ml).  $\text{AgNO}_3$  (1.8 g, 10 mmol) was added, dissolved in a minimum amount of 9/1 (*v/v*) ethanol/water. After stirring the mixture at ambient temperature for 30 min, shielded from light, the solution was filtered through diatomaceous earth to remove  $\text{AgCl}$  and excess starting gold complex. The product was precipitated by addition of diethyl ether, then purified by dissolving in dichloromethane and precipitating again with diethyl ether. Yield 1.2 g (26%).

\* Author to whom correspondence should be addressed. Present address: Dionex Corporation, 1228 Titan Way, Sunnyvale, CA 94088-3603, U.S.A.

TABLE 1. Melting Points and Microanalytical Data

Compound	Melting points <sup>a</sup>	Microanalysis: actual (theory)		
		C	H	N
1 [AuNO <sub>3</sub> ] <sub>2</sub> (dppe)	185–191	34.4 (34.1)	2.7 (2.6)	2.9 (3.1)
2 {[AuNH <sub>3</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	198–199	32.4 (32.8)	3.2 (3.2)	5.8 (5.9)
3 {[AuNH <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	163–164	34.3 (34.4)	3.6 (3.5)	5.6 (5.7)
4 {[AuNH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	166–167	35.4 (35.8)	3.8 (3.4)	5.4 (5.6)
5 {[AuNH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	184–185	36.9 (37.1)	4.1 (4.1)	5.2 (5.4)
6 {[AuNH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	169–171	38.5 (38.4)	4.5 (4.4)	5.2 (5.3)
7 {[AuNH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	203–205	36.9 (37.1)	4.1 (4.1)	5.2 (5.4)
8 {[AuNH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	199–200	38.9 (38.4)	4.4 (4.4)	5.3 (5.3)
9 {[AuNH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> ) <sub>2</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	193–194	39.7 (39.6)	4.6 (4.6)	5.2 (5.1)
10 {[AuNH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	179–180	39.6 (39.6)	4.6 (4.6)	5.2 (5.1)
11 {[AuNH <sub>2</sub> CH(CH <sub>2</sub> ) <sub>3</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub> <sup>b</sup>	191–193	37.6 (37.9)	4.2 (4.0)	4.9 (5.2)
12 {[AuNH <sub>2</sub> CH(CH <sub>2</sub> ) <sub>4</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	199–201	40.2 (39.8)	4.4 (4.2)	5.1 (5.2)
13 {[AuNH <sub>2</sub> CH(CH <sub>2</sub> ) <sub>5</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	214–216	40.9 (40.9)	4.6 (4.5)	5.0 (5.0)
14 {[AuNH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	208–209	39.7 (39.6)	4.6 (4.6)	5.2 (5.1)
15 {[AuNH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	207–208	38.1 (38.4)	4.4 (4.4)	5.2 (5.3)
16 {[AuNH <sub>2</sub> C(CH <sub>3</sub> ) <sub>3</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	236–237	38.3 (38.4)	4.6 (4.4)	5.1 (5.3)
17 {[AuNH(C <sub>2</sub> H <sub>4</sub> )] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	174–175	36.3 (35.9)	3.6 (3.4)	5.4 (5.6)
18 {Au[NH <sub>2</sub> CH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub> ](PPh <sub>3</sub> )}NO <sub>3</sub>	155–158	44.2 (44.5)	4.2 (4.4)	5.0 (4.7)
19 {Au(NH <sub>2</sub> CH <sub>3</sub> )(PPh <sub>3</sub> )}NO <sub>3</sub>	130–132	41.4 (41.3)	3.5 (3.7)	4.9 (5.0)
20 [Au(dppe) <sub>2</sub> ]NO <sub>3</sub>	89–92	59.3 (59.2)	4.5 (4.6)	1.2 (1.3)

<sup>a</sup>In degrees Celsius, darkens gradually before melting with decomposition. <sup>b</sup>Analyzed as the monohydrate.

*1,2-Bis(diphenylphosphino)ethanebis(ammine-gold(I)) nitrate, [(AuNH<sub>3</sub>)<sub>2</sub>(dppe)](NO<sub>3</sub>)<sub>2</sub>, (2)*

1 (3.0 g, 3.3 mmol) was dissolved in 150 ml of dichloromethane and filtered through diatomaceous earth. Gaseous NH<sub>3</sub> was slowly passed through the filtrate for 2 h. Dinitrogen was then passed through the solution to remove excess ammonia. The white precipitate was recovered by filtration and was washed with 50 ml of diethyl ether, then dried in air. Yield 2.8 g (89%).

*1,2-Bis(diphenylphosphino)ethanebis(methylaminegold(I)) nitrate, [(AuNH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>(dppe)](NO<sub>3</sub>)<sub>2</sub>, (3)*

1 (2.0 g, 2.2 mmol) was dissolved in 60 ml of dichloromethane and filtered through diatomaceous earth. Aqueous CH<sub>3</sub>NH<sub>2</sub> (4.8 mmol) was added to the stirred filtrate via syringe. Concentrating the solution under a stream of dinitrogen to ca. 20 ml produced a white precipitate, which was collected by filtration, followed by a diethyl ether wash. The solid was dried in air. Yield 0.50 g (23%). Similar procedures were used for ethylamine, n-propylamine, n-butylamine and isopropylamine, yielding the respective compounds 4 (43%), 5 (76%), 6 (25%) and 7 (44%). In these cases, the amines were added neat rather than as aqueous solutions.

*1,2-Bis(diphenylphosphino)ethanebis(2-methylpropylaminegold(I)) nitrate, {AuNH<sub>2</sub>CH<sub>2</sub>CH(CH<sub>3</sub>)<sub>2</sub>(dppe)}(NO<sub>3</sub>)<sub>2</sub>, (8)*

1 (1.7 g, 1.9 mmol) was dissolved in dichloromethane (25 ml) and filtered through diatomaceous earth. 2-Methylpropylamine (3.7 mmol) was added slowly by syringe to the stirred solution, forming a white precipitate. After stirring for 90 min, the white solid was filtered, washed with diethyl ether, and dried in air. Yield 1.2 g (61%). Similar procedures were used for 3-methylbutylamine, 2-methylbutylamine, cyclobutylamine, cyclopentylamine, cyclohexylamine, 1-methylbutylamine, 1-methylpropylamine, 1,1-dimethylethylamine and aziridine, yielding the respective compounds 9 (40%), 10 (66%), 11 (20%), 12 (57%), 13 (62%), 14 (46%), 15 (47%), 16 (55%) and 17(48%).

*1-Methylpropylaminetriphenylphosphinegold(I) nitrate, {Au[NH<sub>2</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>](PPh<sub>3</sub>)}NO<sub>3</sub>, (18)*

Au(NO<sub>3</sub>)(PPh<sub>3</sub>) (1.0 g, 1.9 mmol) was dissolved in 15 ml of dichloromethane. 1-Methylpropylamine (2.0 mmol) was added by syringe and the reaction stirred for 30 min with no change in appearance. The solution was concentrated to 5 ml, then diethyl ether (15 ml) was added to precipitate the product.

The white solid was recovered by filtration, followed by washing with 25 ml of diethyl ether. Yield 0.8 g (80%). A similar procedure, using aqueous  $\text{CH}_3\text{NH}_2$ , produced the corresponding methylamine product, **19** (66%).

*Bis[1,2-bis(diphenylphosphino)ethane]gold(I) nitrate, [Au(dppe)<sub>2</sub>]NO<sub>3</sub>, (20)*

**1** (1.0 g, 1.1 mmol) was added slowly as a solid to a stirred solution of dppe (1.4 g, 3.5 mmol) in acetone (70 ml). After stirring for 2 h, the mixture was filtered through diatomaceous earth. The filtrate was dried under vacuum, then recrystallized from acetone/diethyl ether at  $-20^\circ\text{C}$ . Yield 1.1 g (47%).

## Results and Discussion

### Synthesis

These arylphosphine alkylamine complexes represent a new class of gold complexes. The presence of chloride decomposes them to the free amine and insoluble  $(\text{AuCl})_2(\text{dppe})$ . The two methods of preparation of alkylamine complexes seem to be general, except that the more linear amines form complexes which are more soluble in dichloromethane; therefore, their preparations require concentration steps. Attempts at preparing the more soluble complexes in one step from  $(\text{AuCl})_2(\text{dppe})$ , silver nitrate, and an alkyl amine resulted in products contaminated with silver. The complexes are stable in most non-coordinating solvents. However, solutions of the less hindered amine complexes are rather light sensitive, turning dark after several hours. Even the isolated, white solids slowly darken in the light. The phosphine amine gold complexes could not be recrystallized, but could be adequately purified by precipitation from dichloromethane using diethyl ether.

### Spectroscopy

The  $^{31}\text{P}\{^1\text{H}\}$  NMR chemical shifts are listed in Table 2. Values are reproducible to within 0.1 ppm. All spectra are sharp singlets. Whereas proton-coupled spectra are also singlets, decoupling sharpens the signals slightly. Identical solvents and concentrations were used to eliminate chemical shift variations due to solvent effects. Single, non-coordinating solvents will not dissolve all compounds of the series. Very polar solvents, such as nitromethane, seem to decompose the compounds. The mixture of chloroform and methanol, however, dissolves all complexes listed in Table 2 without rapid decomposition when the solutions are stored protected from light.

The series of primary amine complexes display a small trend toward lower field with increasing

TABLE 2.  $^{31}\text{P}\{^1\text{H}\}$  NMR Chemical Shifts of Phosphine Amine Gold Complexes<sup>a</sup>

Phosphine	Amine	$\delta$ (ppm)
<b>1</b> dppe		20.9
<b>2</b> dppe	$\text{NH}_3$	25.9
<b>3</b> dppe	$\text{NH}_2\text{CH}_3$	26.3
<b>4</b> dppe	$\text{NH}_2\text{CH}_2\text{CH}_3$	26.7
<b>5</b> dppe	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	26.6
<b>6</b> dppe	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$	26.5
<b>7</b> dppe	$\text{NH}_2\text{CH}(\text{CH}_3)_2$	27.1
<b>8</b> dppe	$\text{NH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	27.0
<b>9</b> dppe	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_3)_2$	26.4
<b>10</b> dppe	$\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	26.9
<b>11</b> dppe	$\text{NH}_2\text{CH}(\text{CH}_2)_3$	26.8
<b>12</b> dppe	$\text{NH}_2\text{CH}(\text{CH}_2)_4$	26.7
<b>13</b> dppe	$\text{NH}_2\text{CH}(\text{CH}_2)_5$	26.9
<b>14</b> dppe	$\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{CH}_3$	27.1
<b>15</b> dppe	$\text{NH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	27.4
<b>16</b> dppe	$\text{NH}_2\text{C}(\text{CH}_3)_3$	27.3
<b>17</b> dppe	$\text{NH}(\text{C}_2\text{H}_4)$	25.4
<b>18</b> PPh <sub>3</sub>	$\text{NH}_2\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$	29.9
<b>19</b> PPh <sub>3</sub>	$\text{NH}_2\text{CH}_3$	28.9

<sup>a</sup>Determinations were made in 1/1 (v/v)  $\text{CDCl}_3/\text{CH}_3\text{OH}$  at 32.4 MHz.

amine steric bulk, varying over a little more than 1 ppm. A similar effect was seen with the two triphenylphosphine complexes. The effects can be interpreted as arising from the change in hybridization of the nitrogen. An increase in steric requirement enhances the s-character of the  $\text{sp}^3$  hybridization (toward sp) by forcing the Au–N–C bond angle to a more linear orientation. The lowering of Au–N bond polarization allows increased sigma electron donation from phosphorus, thereby deshielding it. Unfortunately, crystals suitable for X-ray diffraction studies could not be obtained, so the theorized variation in Au–N–C bond angle could not be verified crystallographically.

### Conductivity

In order to determine the nature of the solution structure of the amine complexes in the NMR solvent, conductivities of two of the complexes were measured. Well-characterized standards of roughly the same molecular mass were chosen in order to establish a range of conductivities for both 1:1 and 1:2 electrolytes. The nitrate complex **20**, although not as well characterized as the other three standards, was assumed to be a 1:1 electrolyte by structural analogy with the corresponding chloride complex, since they have identical NMR spectra. The two pairs of standards establish distinct regions of molar conductivity for the two classes of electrolytes.

It is clear from the conductivities of the compounds tested (Table 3) that the amine complexes

TABLE 3. Molar Conductivities of Gold(dppe) Amines in 50/50 (v/v) Chloroform/Methanol

Compound	Molar conductivity <sup>a</sup>
(AuNO <sub>3</sub> ) <sub>2</sub> (dppe)	26.8
{(AuNH <sub>3</sub> ) <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	59.6
{[AuNH <sub>2</sub> CH(CH <sub>3</sub> )CH <sub>2</sub> CH <sub>3</sub> ] <sub>2</sub> (dppe)}(NO <sub>3</sub> ) <sub>2</sub>	56.1
1:1 Electrolytes	
[Au(dppe) <sub>2</sub> ]Cl	36.3
[Au(dppe) <sub>2</sub> ]NO <sub>3</sub>	42.1
1:2 Electrolytes	
[Pt(dppe) <sub>2</sub> ]Cl <sub>2</sub>	59.7
[Ru(bipy) <sub>3</sub> ]Cl <sub>2</sub> <sup>b</sup>	63.6

<sup>a</sup>Values are expressed in cm<sup>2</sup> eq<sup>-1</sup> ohm<sup>-1</sup>. <sup>b</sup>bipy represents 2,2'-bipyridine.

are 2:1 electrolytes in the NMR solvent, whereas (AuNO<sub>3</sub>)<sub>2</sub>(dppe) is only partially dissociated, having a molar conductivity less than one would expect

for 1:1 electrolyte. Hence, the (AuNH<sub>2</sub>R)<sub>2</sub>(dppe)<sup>2+</sup> ions remain intact in solution.

### Acknowledgements

The authors wish to thank Drs Michael Abrams and Christen Giandomenico for helpful suggestions concerning conductivity measurements.

### References

- 1 E. M. Kinsch and D. W. Stephan, *Inorg. Chim. Acta*, **91** (1984) 263.
- 2 C. A. Tolman, *Chem. Rev.*, **17** (1977) 313.
- 3 F. Cariati, L. Naldini, G. Simonetta and L. Malatesta, *Inorg. Chim. Acta*, **1** (1967) 315.
- 4 S. J. Berners-Price, M. A. Mazid and P. J. Sadler, *J. Chem. Soc., Dalton Trans.*, (1984) 969.
- 5 L. Malatesta, L. Naldini, G. Simonetta and F. Cariati, *Coord. Chem. Rev.*, **1** (1966) 255.
- 6 P. A. Bates and J. M. Waters, *Inorg. Chim. Acta*, **81** (1984) 151.
- 7 A. D. Westland, *J. Chem. Soc.*, (1965) 3060.
- 8 J. A. Broomhead and C. G. Young, *Inorg. Synth.*, **21** (1982) 127.