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Phosphole Complexes of Gold(I) Halides: Comparison of Solution and Solid-State Structures by a Combination of Solution and CP/MAS ^{31}P NMR Spectroscopy and X-ray Crystallography

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A series of complexes of 1-phenyldibenzophosphole (DBP), 1-phenyl-3,4-dimethylphosphole (DMPP), and triphenylphosphine of the type L_nAuX ($n = 1$, L = DBP, DMPP, Ph$_3$P, X = Cl, Br, I; $n = 3$, L = DBP, X = Cl, Br, I; $n = 3$, L = Ph$_3$P, X = Cl; $n = 4$, L = DBP, DMPP, X = PF$_6$) have been prepared and characterized. The structures of (DBP)AuCl (**1**), (DBP)$_3$AuCl (**2**), and (DMPP)AuCl (**3**) have been determined from three-dimensional X-ray data collected by counter methods. Compound **1** crystallized in space group $P\bar{1}$ with $a = 10.257$ (1) Å, $b = 10.992$ (2) Å, $c = 17.131$ (3) Å, $\alpha = 83.04$ (1)°, $\beta = 81.62$ (1)°, $\gamma = 66.96$ (1)°, and $Z = 4$. Compound **2** crystallized in space group $P\bar{1}$ with $a = 11.152$ (2) Å, $b = 10.729$ (2) Å, $c = 19.168$ (5) Å, $\alpha = 84.92$ (2)°, $\beta = 87.22$ (2)°, $\gamma = 76.08$ (2)°, and $Z = 2$. Compound **3** crystallized in space group $C2/c$ with $a = 10.281$ (2) Å, $b = 14.812$ (4) Å, $c = 16.867$ (4) Å, $\alpha = 89.96$ (2)°, $\beta = 91.71$ (2)°, $\gamma = 90.00$ (2)°, and $Z = 8$. The three structures were refined by least-squares methods with $R_F = 0.0286$ for **1**, $R_F = 0.0364$ for **2**, and $R_F = 0.0265$ for **3** for 4715, 6086, and 1787 unique reflections with $I/\sigma(I) \geq 3.0$ for **1–3** respectively. A moderately strong relativistic interaction occurs between the two independent molecules of **1** with an Au–Au distance of 3.116 (2) Å. One of these molecules is nearly linearly coordinated ($\angle$PAuCl = 178.8 (1)°) while the other is slightly bent ($\angle$PAuCl = 172.4 (1)°). The CP/MAS ^{31}P{^{1}H} NMR spectrum of this complex shows two resonances in a 1:1 intensity ratio. Complex **3** is nearly linear in the solid state ($\angle$PAuCl = 176.1 (1)°), and its CP/MAS ^{31}P{^{1}H} NMR spectrum shows three resonances in a 1:1:1 intensity ratio for reasons that are not yet understood. Complex **2** is a distorted tetrahedral molecule that exhibits an attractive interaction between two adjacent dibenzophosphole planes. Though the three phospholes are crystallographically inequivalent (d(AuP) = 2.359 (1), 2.382 (1), and 2.374 (2) Å) the molecule has effective C_s symmetry as evidenced by the observation of two ^{31}P resonances in a 2:1 intensity ratio in its CP/MAS ^{31}P{^{1}H} NMR spectrum. Variable-temperature ^{31}P{^{1}H} NMR spectra obtained on solutions of LAuCl + L in various ratios were analyzed to determine the nature of the species present in solution and to gain information regarding their relative stabilities as a function of the nature of the phosphine.

Introduction

Tertiary phosphine complexes of gold(I) have long been known[2] and have in recent years received considerable attention[3–33] due in part to their biomedical applications as antiarthritics and antitumor drugs.[23,27,34–38] Several reviews on both their solution and solid-state properties have appeared.[39–46] Phospholes, such as 1-phenyl-3,4-dimethylphosphole (DMPP)[47–51] and 1-phenyl-

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dibenzophosphole (DBP),[52,53] are phosphorus donors with unusual donor properties, and no phosphole complexes of gold have previously been reported. Because of our continued interest in the donor properties of phospholes and the reactions of their coordination compounds,[54-59] we have prepared and characterized a series of phosphole complexes of gold(I). We were particularly interested in comparing their structures in solution and in the solid state since for the previously investigated phosphine complexes it has been noted[29] that, though several species are capable of existence in solution, the species which crystallize do not necessarily correspond to the major species present in solution. In the solid state, gold(I) phosphine complexes with coordination numbers greater than 2 are relatively uncommon.[11,18-20,22] Since the phospholes are sterically small, we hoped that they might provide additional examples of higher coordination numbers in the solid state. We wished also to further extend our studies of the utility of CP/MAS $^{31}P\{^{1}H\}$ NMR spectroscopy for solid-state structural determination.[60-62]

Experimental Section

(A) Reagents and Physical Measurements. All chemicals were reagent grade and were used as received or synthesized as described below. All solvents, when necessary, were dried by standard procedures and stored over Linde 4-Å molecular sieves. All reactions involving phospholes were conducted under an N_2 atmosphere. Chloroauric acid was obtained from Strem Chemicals. 1-Phenyl-3,4-dimethylphosphole[63] (DMPP) and 1-phenyldibenzophosphole[64] (DBP) were prepared by literature methods.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Melting points were determined on a Meltemp apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1800 FT-IR instrument as polyethylene pellets. The solution $^{31}P\{^{1}H\}$ NMR spectra were recorded at 40.26 MHz on a JEOL FX-100 spectrometer in the FT mode. Chemical shifts were referenced to an external sample of Ph$_3$P in CDCl$_3$ (δ = −6.0 ppm) and converted to an 85% H$_3$PO$_4$ reference with a positive value being downfield of the respective reference. Cross-polarization magic-angle-spinning (CP/MAS) $^{31}P\{^{1}H\}$ NMR spectra were obtained on a JEOL GX-270 wide-bore spectrometer operating at 6.43 T (^{31}P at 109.25 MHz) using a 40-kHz sweep width, recycle delay time of 6 s, and a proton-decoupling field of 10 G. Between 200 and 300 mg of the compound was spun at 4 kHz in Delrin or Kel-F rotors. All the CP/MAS chemical shifts were referenced to an external sample of Ph$_3$P (δ = −6.0 ppm). The uncertainties in chemical shifts are estimated to be ±0.5 ppm.

(B) Syntheses. (DBP)AuCl. To a solution of chloroauric acid (HAuCl$_4$·H$_2$O, 0.58 g, 1.62 mmol) in 20 mL of absolute ethanol was added 0.89 g (3.42 mmol) of DBP at 25 °C. The color of the solution changed from yellow to colorless within a few minutes as a colorless precipitate formed. The solution was heated at reflux for 3 h and cooled to room temperature; the precipitate was isolated by filtration, washed with anhydrous diethyl ether, and vacuum-dried to yield 0.64 g (76.2%) of colorless microcrystals, mp 227–228 °C. Anal. Calcd for C$_{18}$H$_{13}$AuClP: C, 43.88; H, 2.66. Found: C, 43.22; H, 2.74.

(DBP)AuBr. To a solution containing 0.31 g (0.63 mmol) of (DBP)AuCl in 10 mL of CHCl$_3$ was added 20 mL of a saturated 1:1 ethanol/H$_2$O solution of NaBr. After this mixture was stirred magnetically for 1 h at ambient temperature, the solvents were removed on a rotary evaporator at 50 °C. The resulting colorless solid was extracted with six 10-mL portions of CH$_2$Cl$_2$. The extracts were combined, filtered through a layer of anhydrous K$_2$CO$_3$, and reduced in volume to about 10 mL on a rotary evaporator. n-Hexane (10 mL) was added, and the mixture was placed in a freezer at −20 °C. The colorless rods that separated were isolated by filtration, washed with n-hexane, and vacuum-dried to yield 0.21 g (62.7%) of product, mp 214–215 °C. Anal. Calcd for C$_{18}$H$_{13}$AuBrP: C, 40.25; H, 2.44. Found: C, 40.23; H, 2.60.

(DBP)AuI. A solution containing 0.46 g (0.97 mmol) of (DBP)AuCl and 0.5 mL of 57% aqueous HI in 15 mL of CHCl$_3$ was heated at reflux for 5 h. The solution was then cooled to room temperature and filtered through a layer of anhydrous K$_2$CO$_3$. The filtrate was reduced in volume to 5 mL on a rotary evaporator, and n-hexane was added dropwise until the mixture just became cloudy. The mixture was then placed in a freezer at −20 °C. The colorless needles that formed were isolated by filtration, washed with n-hexane, and vacuum-dried to yield 0.41 g (74.6%) of product, mp 227–229 °C. Anal. Calcd for C$_{18}$H$_{13}$AuIP: C, 37.01; H, 2.25. Found: C, 36.83; H, 2.36.

(DMPP)AuCl. By the same method used for (DBP)AuCl, from 0.97 g (2.71 mmol) of HAuCl$_4$·H$_2$O and 1.2 g (6.4 mmol) of DMPP was obtained 0.88 g (77.3%) of off-white needles, mp 201–203 °C dec. Anal. Calcd for C$_{12}$H$_{13}$AuClP: C, 34.26; H, 3.12. Found: C, 34.44; H, 3.23.

(DMPP)AuBr. By the same method used for (DBP)AuBr, from 0.42 g (1.0 mmol) of (DMPP)AuCl was obtained 0.35 g (75.3%) of colorless needles, mp 174–175 °C dec. Anal. Calcd for C$_{12}$H$_{13}$AuBrP: C, 30.99; H, 2.82. Found: C, 30.72; H, 3.02.

(DMPP)AuI. To a solution containing 0.64 g (1.52 mmol) of (DMPP)AuCl in 20 mL of CHCl$_3$ was added 10 mL of a saturated 1:1 ethanol/water solution of NaI. This mixture was stirred magnetically at ambient temperature for 4 h, and then the solvents were removed on a rotary evaporator. The solid residue was extracted with six 10-mL portions of CH$_2$Cl$_2$. The extracts were combined, filtered through a layer of anhydrous K$_2$CO$_3$, and reduced in volume to about 10 mL. n-Hexane was added dropwise until the solution just became cloudy, and the mixture was placed in a freezer at −20 °C. The colorless needles that resulted were isolated by filtration, washed with hexane, and vacuum-dried to yield 0.67 g (86%) of product, mp 182–184 °C dec. Anal. Calcd for C$_{12}$H$_{13}$AuIP: C, 28.14; H, 2.56. Found: C, 27.79; H, 2.53.

(DBP)$_3$AuCl. A solution containing 1.00 g (2.03 mmol) of (DBP)AuCl and 1.08 g (4.15 mmol) of DBP in 10 mL of CH$_2$Cl$_2$ was stirred magnetically at ambient temperature for 15 min. The volume of the transparent colorless solution was reduced to a minimum on a rotary evaporator, anhydrous diethyl ether was added dropwise to incipient cloudiness, and the mixture was placed in a freezer at −20 °C. The resultant pale yellow crystals were isolated by filtration, washed with anhydrous diethyl ether, and air-dried to yield 1.83 g (89.3%) of product, mp 203–205 °C. Anal. Calcd for C$_{54}$H$_{39}$AuClP·1.1CH$_2$Cl$_2$: C, 59.79; H, 3.76. Found: C, 59.72; H, 3.86. The presence of CH$_2$Cl$_2$ was confirmed by ^{1}H NMR (CDCl$_3$): δ = 5.27.

(DBP)$_3$AuBr. Similarly, from 0.462 g (0.86 mmol) of (DBP)AuBr and 0.675 g (2.59 mmol) of DBP was obtained 0.627 g (68.9%) of off-white crystals, mp 203–205 °C. Anal. Calcd for C$_{54}$H$_{39}$AuBrP$_3$·3H$_2$O: C, 58.87; H, 4.08. Found: C, 58.23; H, 3.66. The presence of H$_2$O was confirmed by infrared spectroscopy, ν_{OH} (Nujol mull) = 3604 cm^{-1}, and by mass loss after the product was heated in a vacuum oven at 100 °C for several hours.

(DBP)$_3$AuI. Similarly, from 0.546 g (0.935 mmol) of (DBP)AuI and 0.729 g (2.80 mmol) of DBP was obtained 0.997 g (96.5%) of pale yellow-green needles, mp 208–210 °C. Anal. Calcd for C$_{54}$H$_{39}$AuIP$_3$·5H$_2$O: C, 54.30; H, 4.10. Found: C, 53.87; H, 3.50. The presence of water was confirmed by infrared spectroscopy, ν_{OH} (Nujol mull) = 3604 cm^{-1}, and by mass loss after the product was heated in a vacuum oven at 100 °C for several hours.

[(DBP)$_4$Au]$^+$PF$_6$$^-$. To a solution containing 1.02 g (2.08 mmol) of (DBP)AuCl and 1.82 g (7.01 mmol) of DBP in 50 mL of CH$_2$Cl$_2$ was added 20 mL of a saturated aqueous solution of KPF$_6$. The mixture was stirred magnetically at ambient temperature for 1 h, and the solvents were removed on a rotary evaporator. The resulting colorless solid was extracted with six 10-mL portions of CH$_2$Cl$_2$; the extracts were combined, washed with water, dried over anhydrous potassium carbonate, and reduced in volume to about 10 mL on a rotary evaporator. Anhydrous diethyl ether was added dropwise to incipient cloudiness, and the mixture was placed in a freezer at −20 °C. The resultant colorless microcrystals were isolated by filtration, washed with anhydrous diethyl ether, and vacuum-dried to yield 2.52 g (87.7%) of product, mp 300–302 °C. Anal. Calcd for C$_{72}$H$_{52}$AuF$_6$P$_5$: C, 62.52; H, 3.80. Found: C, 62.28; H, 3.84.

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Table I. Crystallographic Data for 1–3

	(DBP)AuCl·0.25C$_4$H$_{10}$O (1)	(DBP)$_3$AuCl (2)	(DMPP)AuCl (3)
formula	C$_{19}$H$_{15.5}$AuClO$_{0.25}$P	C$_{54}$H$_{39}$AuClP$_3$	C$_{12}$H$_{13}$AuClP
space group	P$\bar{1}$	P$\bar{1}$	C2/c
fw	511.10	1012.5	420.5
a, Å	10.257 (1)	11.152 (2)	10.281 (2)
b, Å	10.992 (2)	10.729 (2)	14.812 (4)
c, Å	17.131 (3)	19.168 (5)	16.867 (4)
α, deg	83.04 (1)	84.92 (2)	89.96 (2)
β, deg	81.62 (1)	87.22 (2)	91.71 (2)
γ, deg	66.96 (1)	76.08 (2)	90.00 (2)
V, Å^3	1754.1 (5)	2216.7 (8)	2567.5 (1)
Z	4	2	8
T, K	290	290	293
λ, Å	0.716 09	0.716 09	0.716 09
ρ_{calc}, g cm^{-3}	1.87	1.517	1.57
μ, cm^{-1}	86.1	34.05	117.40
transm coeff	0.28–0.50	0.18–0.83	0.075–0.339
R$_F$	0.0286	0.0364	0.0265
R$_{wF}$	0.0295	0.0374	0.0275
g (wt param)	0.002	0.001	0.005
no. of params	395	532	143

[(DMPP)$_4$Au]$^+$PF$_6^-$. In a similar manner, from 1.00 g (2.39 mmol) of (DMPP)AuCl and 1.80 g (9.55 mmol) of DMPP was obtained 2.58 g (98.6%) of a pale yellow oil. Anal. Calcd for C$_{48}$H$_{52}$AuF$_6$P$_5$: C, 52.68; H, 4.76. Found: C, 52.45; H, 4.59.

(Ph$_3$P)AuCl,[65] (Ph$_3$P)AuBr,[9] (Ph$_3$P)AuI,[9] and (Ph$_3$P)$_3$AuCl[24] were prepared by literature methods.

(C) ^{31}P{^{1}H} NMR Ligand-Addition Studies. Approximately 100-mg quantities of (R$_3$P)AuCl and the appropriate quanitites of R$_3$P were accurately weighed into 10-mm NMR tubes, and 3 mL of dried CH$_2$Cl$_2$ were added under a nitrogen blanket. The tubes were capped and sealed with Teflon tape. The ^{31}P{^{1}H} NMR spectra were recorded at 40.26 MHz on a JEOL FX-100 spectrometer using a ^{7}Li external lock or on a Bruker AM-250 spectrometer[53] at 101.26 MHz at various temperatures. Chemical shifts were referenced to an external sample of Ph$_3$P in CDCl$_3$ set to −6.0 ppm. Relative resonance intensities were determined by machine integration and/or cutting and weighing.

(D) Crystal Structure Analyses. Colorless plates of (DBP)AuCl (1) were isolated from CH$_2$Cl$_2$/Et$_2$O, pale yellow plates of (DBP)$_3$AuCl (2) from CH$_2$Cl$_2$/Et$_2$O, and pale yellow plates of (DMPP)AuCl (3) from CH$_2$Cl$_2$/n-C$_6$H$_{14}$ solutions. Crystal data and additional details of data collection and refinement are given in Table I. Intensity data were taken with a Syntex P2$_1$ diffractometer in the θ–2θ mode and were corrected for Lorentz, polarization, and absorption effects, the last by the Gaussian method. Systematic absences (hkl, h + k ≠ 2n; h0l, l ≠ 2n) indicated space group C2/c for 2 and no systematic absences were found for 1 or 3. The heavy atoms were located by Patterson techniques, and the light atoms were then found on successive Fourier syntheses. For 1 the Fourier syntheses included a solvent (presumably Et$_2$O) molecule disordered across a center of symmetry, which was described approximately by three carbon and one oxygen atoms all with 0.5 occupancy. Anisotropic temperature factors were used for all non-H atoms except for the solvent molecule in 1. Hydrogen atoms were given fixed isotropic temperature factors, U = 0.07 Å^2, and were inserted at calculated positions and not refined. For 3, the methyl groups were treated as rigid CH$_3$ units. Final refinement was by cascaded least-squares methods (minimizing $\sum w(F_o - F_c)^2$). The largest positive and negative peaks on final difference Fourier syntheses were of height (e/Å^3) +1.1 and −0.5 for 1, +0.8 and −0.7 for 3, and ±0.9 for 2. For 1, these were in the vicinity of the disordered solvent. Weighting schemes of the form $1/(\sigma^2(F) + gF^2)$ were shown to be satisfactory by weight analyses. Three standard reflections monitored every 200 reflections showed no change for 3 and slight decreases during data collection for 1 and 2. The data for 1 and 2 were rescaled to correct for this. Computing was done with the SHEXTL system[66] on a Data General DG 30 computer. Scattering factors were taken from ref 67. For 1, some of the carbon atoms of phosphole 1 (DBP 1) show relatively large and highly anisotropic thermal parameters. The principal axes of the thermal ellipsoids are oriented in the ring plane, indicating that this group is librating about P(1). Final atom coordinates for 1–3 are given in Tables II–IV and selected bond lengths and angles in Tables V–VII, respectively.

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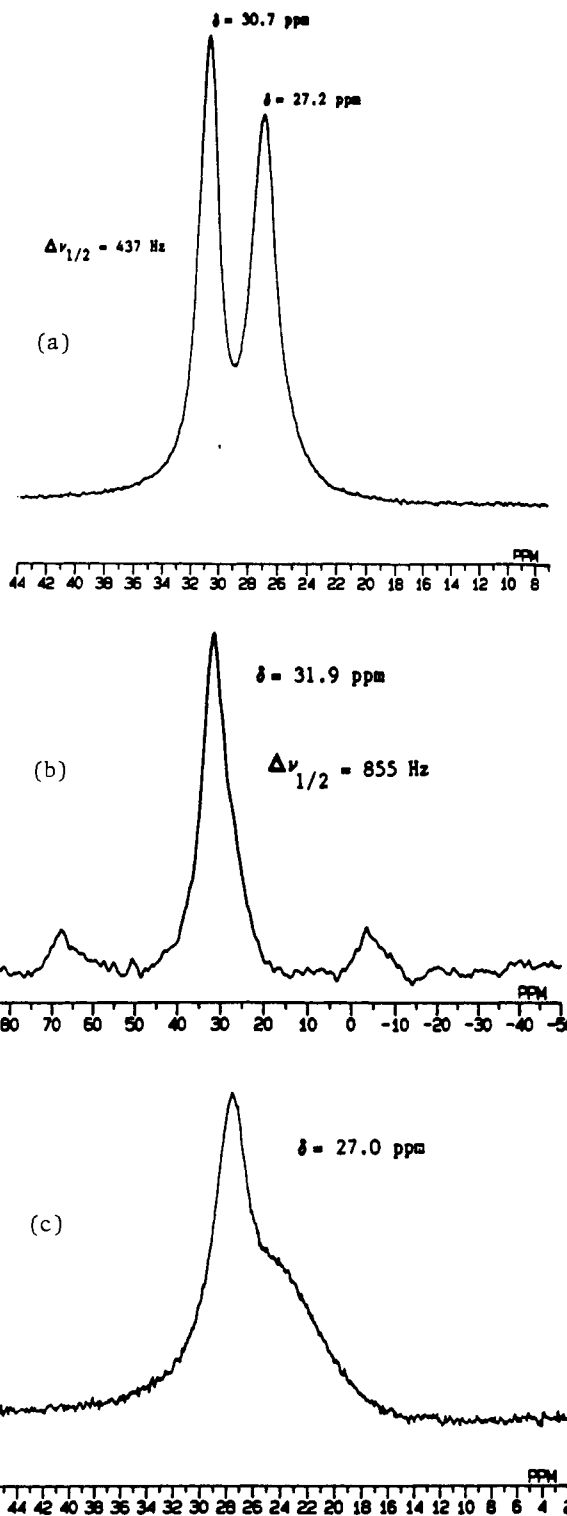

Figure 1. 109.25-MHz CP/MAS ^{31}P{^{1}H} NMR spectra of (a) (DBP)AuCl, (b) (DBP)AuBr, and (c) (DBP)AuI. In spectrum b the weak outer resonances are spinning sidebands.
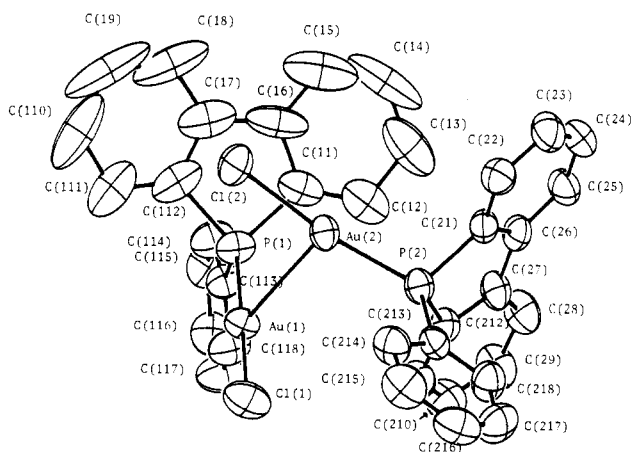
Results and Discussion

I. Solid-State Structures. (a) (R$_3$P)AuX Complexes. The reduction of HAuCl$_4$ with 2 equiv of R$_3$P in ethanol, a general reaction whose kinetics and mechanism have been studied by Roulet et al.,[68] yields the (R$_3$P)AuCl complex with the concomitant formation of the dichlorophosphorane R$_3$PCl$_2$, which is converted to R$_3$P=O (the ligand oxide). The bromide and iodide analogues were then prepared by simple metathesis reactions.

(68) Roulet, R.; Lan, N. Q.; Mason, W. R.; Fenske, G. P., Jr. *Helv. Chim. Acta* **1973**, *56*, 2405.

Table II. Atomic Coordinates ($\times 10^4$) for (DBP)AuCl (**1**)

	x	y	z
Au(1)	969.7 (3)	75.6 (3)	1446.2 (2)
Au(2)	-790.5 (3)	2220.1 (3)	2632.4 (2)
O(1)	285 (22)	4893 (22)	5490 (11)
C(001)	1401 (16)	4637 (15)	6200 (10)
C(002)	-949 (27)	4607 (24)	4241 (15)
C(004)	-40 (18)	4741 (14)	5081 (11)
Cl(1)	817 (3)	1803 (2)	535 (1)
Cl(2)	1216 (2)	1419 (2)	3271 (1)
P(1)	1156 (2)	-1634 (2)	2316 (1)
P(2)	-2902 (2)	3074 (2)	2166 (1)
C(11)	-241 (9)	-1351 (6)	3111 (4)
C(12)	-1674 (10)	-975 (7)	3058 (5)
C(13)	-2597 (13)	-726 (9)	3757 (6)
C(14)	-2034 (15)	-855 (10)	4470 (6)
C(15)	-606 (15)	-1211 (10)	4491 (6)
C(16)	320 (12)	-1467 (7)	3837 (5)
C(17)	1868 (12)	-1842 (7)	3753 (5)
C(18)	2697 (15)	-1948 (9)	4347 (7)
C(19)	4098 (20)	-2206 (12)	4167 (9)
C(110)	4718 (14)	-2346 (10)	3410 (10)
C(111)	3921 (11)	-2251 (8)	2799 (7)
C(112)	2494 (10)	-1990 (7)	2985 (5)
C(113)	1396 (7)	-3150 (6)	1905 (4)
C(114)	1679 (9)	-4323 (7)	2374 (5)
C(115)	1780 (9)	-5451 (7)	2062 (5)
C(116)	1644 (9)	-5427 (8)	1272 (5)
C(117)	1386 (11)	-4304 (8)	803 (5)
C(118)	1237 (9)	-3142 (7)	1132 (5)
C(21)	-4313 (7)	3365 (6)	2965 (4)
C(22)	-4622 (8)	4206 (7)	3564 (4)
C(23)	-5719 (8)	4229 (8)	4154 (5)
C(24)	-6433 (8)	3410 (8)	4130 (5)
C(25)	-6111 (7)	2556 (7)	3545 (4)
C(26)	-5071 (7)	2547 (7)	2941 (4)
C(27)	-4617 (7)	1789 (7)	2244 (4)
C(28)	-5230 (8)	983 (7)	2028 (5)
C(29)	-4684 (9)	325 (8)	1330 (5)
C(210)	-3547 (9)	487 (8)	861 (5)
C(211)	-2940 (8)	1298 (7)	1062 (4)
C(212)	-3489 (7)	1967 (7)	1748 (4)
C(213)	-3270 (7)	4582 (7)	1519 (4)
C(214)	-2333 (8)	5217 (7)	1420 (5)
C(215)	-2631 (10)	6370 (8)	949 (5)
C(216)	-3833 (11)	6901 (8)	563 (5)
C(217)	-4744 (10)	6243 (8)	661 (5)
C(218)	-4508 (8)	5102 (7)	1145 (5)

Table III. Atomic Coordinates ($\times 10^4$) for (DBP)$_3$AuCl (**2**)

	x	y	z
Au(1)	3309.0 (2)	3951.3 (2)	2247.8 (1)
Cl(1)	5287.5 (14)	4953.4 (16)	2170.3 (10)
P(1)	1518.0 (12)	5362.7 (13)	1852.9 (8)
P(2)	4145.9 (14)	2085.8 (13)	1638.9 (8)
P(3)	3353.8 (17)	3257.2 (15)	3459.3 (9)
C(11)	288 (5)	5816 (5)	2506 (3)
C(12)	329 (6)	6435 (6)	3106 (3)
C(13)	-712 (7)	6643 (7)	3357 (4)
C(14)	-1733 (7)	6230 (7)	3407 (4)
C(15)	-1776 (6)	5582 (7)	2821 (4)
C(16)	-756 (5)	5377 (6)	2361 (3)
C(17)	-616 (5)	4697 (6)	1722 (3)
C(18)	-1465 (6)	4161 (7)	1434 (4)
C(19)	-1187 (7)	3541 (8)	834 (4)
C(110)	-33 (7)	3452 (7)	500 (4)
C(111)	832 (6)	4013 (6)	769 (3)
C(112)	538 (5)	4627 (5)	1378 (3)
C(113)	1589 (5)	6839 (5)	1328 (3)
C(114)	2731 (5)	7003 (5)	1051 (3)
C(115)	2774 (6)	8107 (6)	625 (4)
C(116)	1707 (7)	9047 (6)	495 (4)
C(117)	603 (6)	8898 (6)	759 (4)
C(118)	524 (5)	7796 (5)	1172 (3)
C(21)	3515 (6)	723 (6)	1961 (3)
C(22)	2292 (7)	689 (8)	2028 (4)
C(23)	2025 (9)	-451 (9)	2328 (4)
C(24)	2974 (12)	-1496 (9)	2533 (4)
C(25)	4149 (10)	-1440 (7)	2470 (4)
C(26)	4456 (7)	-321 (6)	2184 (3)
C(27)	5697 (6)	-86 (5)	2095 (3)
C(28)	6831 (8)	-930 (7)	2288 (4)
C(29)	7899 (8)	-508 (8)	2161 (4)
C(210)	7881 (7)	703 (11)	1879 (5)
C(211)	6779 (6)	1546 (7)	1696 (4)
C(212)	5692 (6)	1157 (5)	1795 (3)
C(213)	4026 (5)	2295 (5)	690 (3)
C(214)	4141 (5)	3454 (6)	344 (4)
C(215)	4009 (6)	3678 (7)	-366 (4)
C(216)	3754 (7)	2733 (7)	-747 (4)
C(217)	3635 (7)	1589 (7)	-408 (4)
C(218)	3782 (7)	1356 (7)	308 (4)
C(31)	4632 (7)	1947 (6)	3711 (4)
C(32)	5882 (7)	1904 (8)	3625 (4)
C(33)	6734 (9)	744 (9)	3822 (5)
C(34)	6311 (10)	-310 (8)	4093 (5)
C(35)	5090 (11)	-284 (8)	4160 (5)
C(36)	4229 (8)	854 (6)	3975 (4)
C(37)	2840 (9)	1078 (7)	3994 (4)
C(38)	2160 (12)	199 (9)	4206 (5)
C(39)	883 (14)	529 (12)	4183 (6)
C(310)	332 (11)	1753 (12)	3959 (6)
C(311)	975 (9)	2670 (9)	3734 (5)
C(312)	2249 (8)	2335 (7)	3770 (4)
C(313)	3265 (8)	4495 (6)	4069 (4)
C(314)	4023 (10)	5318 (8)	3943 (5)
C(315)	3967 (13)	6284 (10)	4376 (7)
C(316)	3112 (16)	6463 (9)	4918 (6)
C(317)	2322 (16)	5663 (11)	5026 (6)
C(318)	2401 (11)	4658 (9)	4612 (5)

Figure 2. ORTEP plot of the structure of chloro(1-phenyldibenzo-phosphole)gold(I) (**1**), showing the atom-labeling scheme and 50% probability ellipsoids, with hydrogens omitted.

The two resonances observed in the CP/MAS ^{31}P{^{1}H} NMR spectrum of (DBP)AuCl (Figure 1) are at first glance puzzling since the crystal structure of the analogous (Ph$_3$P)AuCl complex[12] shows that it is a linear molecule with four symmetry-related molecules in an orthorhombic unit cell. Thus, for (DBP)AuCl, only one ^{31}P chemical shift was anticipated. Gold-197 is 100%

abundant, with $I = {}^3/_2$ and a quadrupole moment[69] $Q = 0.59 \times 10^{-28}$ m^2. Because of the large value of the quadrupole moment, the gold relaxation time is short and no spin coupling of gold with other nuclei has ever been observed, even in high-symmetry species such as [AuF$_6$]$^-$.[39] Chlorine-35 (75.53% abundant, $I = {}^3/_2$) has a smaller quadrupole moment, $Q = -7.89 \times 10^{-30}$ m^2, than gold but again no coupling of phosphorus to ^{35}Cl has been observed.[69] Thus, the presence of two resonances in Figure 1 is not likely to be the result of spin-spin coupling.

The two phosphorus chemical shifts may however be explained simply by the X-ray crystal structure of (DBP)AuCl (Figure 2; dimensions given in Table V). This structure is unique in two

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(69) Harris, R. K.; Mann, B. E. *NMR and the Periodic Table*; Academic Press: London, 1978.

Table IV. Atomic Coordinates (×10⁴) for (DMPP)AuCl (3)

atom	x	y	z
Au	1317.9 (2)	5865.4 (2)	9850.2 (2)
P(1)	2614.2 (17)	5624.9 (12)	8837.1 (11)
Cl(1)	39.2 (19)	6212.2 (12)	10894.8 (12)
C(1)	3850 (6)	4774 (4)	9000 (4)
C(2)	5014 (7)	4793 (6)	8622 (5)
C(3)	5920 (8)	4106 (5)	8737 (7)
C(4)	5646 (9)	3386 (6)	9212 (6)
C(5)	4514 (8)	3364 (5)	9597 (5)
C(6)	3600 (8)	4058 (4)	9502 (5)
C(7)	3316 (6)	6635 (5)	8473 (4)
C(8)	2877 (6)	6806 (4)	7748 (4)
C(9)	2041 (6)	6084 (5)	7393 (4)
C(10)	1827 (6)	5399 (4)	7891 (4)
C(11)	3133 (9)	7653 (5)	7293 (5)
C(12)	1486 (9)	6131 (7)	6572 (5)

Table V. Selected Bond Lengths (Å) and Angles (deg) for the Two Independent Molecules of (DBP)AuCl (1)

Bond Lengths			
Au(1)–Au(2)	3.116 (2)	P(1)–C(112)	1.838 (47)
Au(1)–Cl(1)	2.282 (9)	P(1)–C(113)	1.774 (40)
Au(1)–P(1)	2.221 (8)	P(2)–C(21)	1.816 (28)
Au(2)–Cl(2)	2.285 (10)	P(2)–C(212)	1.769 (41)
Au(2)–P(2)	2.220 (9)	P(2)–C(213)	1.848 (31)
P(1)–C(11)	1.821 (35)		

Bond Angles			
Au(2)–Au(1)–Cl(1)	86.1 (1)	Au(2)–Au(1)–P(1)	95.1 (1)
Cl(1)–Au(1)–P(1)	178.8 (1)	Au(1)–Au(2)–Cl(2)	84.9 (1)
Au(1)–Au(2)–P(2)	107.7 (1)	Cl(2)–Au(2)–P(2)	172.4 (1)
Au(1)–P(1)–C(112)	114.5 (3)	Au(1)–P(1)–C(11)	115.8 (2)
Au(1)–P(1)–C(113)	115.5 (2)	C(11)–P(1)–C(112)	92.3 (4)
C(112)–P(1)–C(113)	108.7 (3)	C(11)–P(1)–C(113)	107.5 (4)
Au(2)–P(2)–C(212)	117.8 (2)	Au(2)–P(2)–C(21)	110.4 (2)
Au(2)–P(2)–C(213)	116.8 (3)	C(21)–P(2)–C(212)	91.5 (3)
C(212)–P(2)–C(213)	108.7 (4)	C(21)–P(2)–C(213)	108.5 (3)
P(1)–C(11)–C(16)	109.6 (7)	C(11)–C(16)–C(17)	113.7 (7)
P(1)–C(112)–C(17)	110.3 (8)	C(21)–C(26)–C(27)	112.8 (6)
P(2)–C(21)–C(26)	110.7 (5)	P(2)–C(212)–C(27)	110.0 (6)

Table VI. Selected Bond Lengths (Å) and Angles (deg) for (DBP)₃AuCl (2)

Bond Lengths			
Au(1)–Cl(1)	2.735 (2)	Au(1)–P(1)	2.359 (1)
Au(1)–P(2)	2.382 (1)	Au(1)–P(3)	2.374 (2)
P(1)–C(11)	1.848 (6)	P(1)–C(112)	1.838 (6)
P(1)–C(113)	1.816 (6)	P(2)–C(21)	1.832 (7)
P(2)–C(212)	1.843 (6)	P(2)–C(213)	1.821 (6)
P(3)–C(31)	1.824 (7)	P(3)–C(312)	1.838 (9)
P(3)–C(313)	1.827 (7)		

Bond Angles			
Cl(1)–Au(1)–P(1)	115.9 (1)	Cl(1)–Au(1)–P(2)	97.5 (1)
P(1)–Au(1)–P(2)	119.1 (1)	Cl(1)–Au(1)–P(3)	98.3 (1)
P(1)–Au(1)–P(3)	116.2 (1)	P(2)–Au(1)–P(3)	106.4 (1)
Au(1)–P(1)–C(11)	117.5 (2)	Au(1)–P(1)–C(112)	115.5 (2)
C(11)–P(1)–C(112)	88.7 (3)	Au(1)–P(1)–C(113)	119.2 (2)
C(11)–P(2)–C(113)	106.1 (2)	C(112)–P(1)–C(113)	105.3 (3)
Au(1)–P(2)–C(21)	111.9 (2)	Au(1)–P(2)–C(212)	120.6 (2)
C(21)–P(2)–C(212)	92.6 (3)	Au(1)–P(2)–C(213)	115.7 (2)
C(21)–P(2)–C(213)	108.1 (3)	C(212)–P(2)–C(213)	105.1 (3)
Au(1)–P(3)–C(31)	114.7 (2)	Au(1)–P(3)–C(312)	115.6 (2)
C(31)–P(3)–C(312)	93.7 (3)	Au(1)–P(3)–C(313)	116.6 (2)
C(31)–P(3)–C(313)	106.7 (3)	C(312)–P(3)–C(313)	106.9 (4)
P(1)–C(11)–C(16)	112.7 (4)	P(2)–C(21)–C(26)	108.7 (5)
C(11)–C(16)–C(17)	113.0 (5)	C(21)–C(26)–C(27)	115.6 (6)
C(17)–C(112)–P(1)	113.1 (4)	C(27)–C(212)–P(2)	110.4 (5)
P(3)–C(31)–C(36)	109.7 (6)	C(37)–C(312)–P(3)	109.6 (7)
C(31)–C(36)–C(37)	113.4 (6)		

respects. First, it contains two structurally different (DBP)AuCl molecules. One of them is nearly linear (∠PAuCl = 178.8 (1)°) and the other is bent (∠PAuCl = 172.4 (1)°). Second, there is an attractive Au–Au relativistic[70] interaction with a Au–Au

(70) Pyykkö, P., *Chem. Rev.* **1988,** *88,* 563.

Table VII. Selected Bond Lengths (Å) and Angles (deg) for (DMPP)AuCl (3)

Bond Lengths			
Au–P(1)	2.227 (2)	Au–Cl(1)	2.288 (2)
P(1)–C(1)	1.805 (7)	P(1)–C(7)	1.778 (7)
P(1)–C(10)	1.798 (7)	C(7)–C(8)	1.316 (10)
C(8)–C(9)	1.488 (9)	C(8)–C(11)	1.498 (11)
C(9)–C(10)	1.338 (9)	C(9)–C(12)	1.484 (11)

Bond Angles			
P(1)–Au–Cl(1)	176.1 (1)	Au–P(1)–C(1)	115.5 (2)
Au–P(1)–C(7)	112.9 (2)	C(1)–P(1)–C(7)	110.4 (3)
Au–P(1)–C(10)	116.5 (2)	C(1)–P(1)–C(10)	107.5 (3)
P(1)–C(1)–C(6)	118.9 (5)		
C(7)–P(1)–C(10)	91.5 (3)	P(1)–C(1)–C(2)	122.3 (6)
C(7)–C(8)–C(9)	114.5 (6)	P(1)–C(7)–C(8)	110.6 (5)
C(9)–C(8)–C(11)	120.3 (6)	C(7)–C(8)–C(11)	125.3 (7)
C(8)–C(9)–C(12)	122.9 (6)	C(8)–C(9)–C(10)	113.3 (6)
P(1)–C(10)–C(9)	109.8 (5)	C(10)–C(9)–C(12)	123.8 (7)

separation of 3.116 (2) Å. Although, this Au–Au distance is short by Jones' classification,[45] whereby any such distance less than about 3.5 Å is considered unexpected and that of about 3.00 Å or less ranks as very short, it is greater than the distance normally attributed to a Au–Au bond (3.00 Å or less).[45,46] The two Au–P bond lengths are identical (2.221 (8), 2.220 (9) Å) as are the two AuCl bond lengths (2.282 (9), 2.285 (10) Å).

The CP/MAS ³¹P{¹H} NMR spectra of the analogous (DBP)AuBr and (DBP)AuI complexes are quite different. For the former, only one chemical shift is observed but the line width of the resonance is approximately twice those of the (DBP)AuCl complex. This suggests that (DBP)AuCl and (DBP)AuBr are isostructural but the two phosphorus environments in (DBP)AuBr are more similar than they are in (DBP)AuCl, giving rise to a smaller chemical shift difference. The spectrum of the (DBP)AuI complex shows overlapping narrow and broad resonances, again indicating the presence of phospholes in two different environments and suggesting that they have different relaxation rates. It appears then that for these three compounds crystal packing forces due to intermolecular interactions increase as the halide size decreases, which in turn leads to reduced molecular mobility in the crystal.

Similar arguments may not be used to explain the anomalous appearance of the CP/MAS ³¹P{¹H} NMR spectrum of (Ph₃P)-AuCl (Figure 3). Its X-ray crystal structure shows that there is only one phosphorus environment in the solid state, yet three and two closely spaced ³¹P{¹H} chemical shifts are observed at 109.25 and 121.47 MHz, respectively. It has been argued that the different chemical shifts result from different fixed conformations of the phenyl rings on Ph₃P in the solid state.[71] The postulation of "conformational effects" as a dominant factor in the appearance of the CP/MAS ³¹P{¹H} NMR spectra of transition-metal phosphine complexes in general,[60–62] and of (R₃P)AuX complexes in particular, has been further advanced by Healy and co-workers in their study[71] of a series of (Ph₃P)AuX complexes. These authors suggest that the (Ph₃P)AuCl molecules may, in fact, crystallize in each enantiomeric $P2_12_12_1$ cell in either of two forms with the phenyl rings of the Ph₃P ligand twisted about the P–C bonds in opposite senses such that the molecules are virtually enantiomeric. This would lead to diastereomeric phosphorus environments.

The 109.25-MHz CP/MAS ³¹P{¹H} NMR spectra of (DMPP)AuX (X = Cl, Br, I) (Figure 4) show similar anomalies. The chloride complex shows three field-independent chemical shifts, while the bromide shows two resonances and the iodide complex only one broad resonance. The X-ray crystal structure of chloro(1-phenyl-3,4-dimethylphosphole)gold(I) (Figure 5) shows that the eight molecules in the monoclinic unit cell, which is centrosymmetric, are all symmetry related with only one phosphorus environment. Thus, the observations of more than one phosphorus resonance for some of these solids are not yet understood, and the previous explanations are not likely to be correct.

(71) Barron, P. F.; Engelhardt, L. M.; Healy, P. C.; Oddy, J.; White, A. H. *Aust. J. Chem.* **1987,** *40,* 1545.
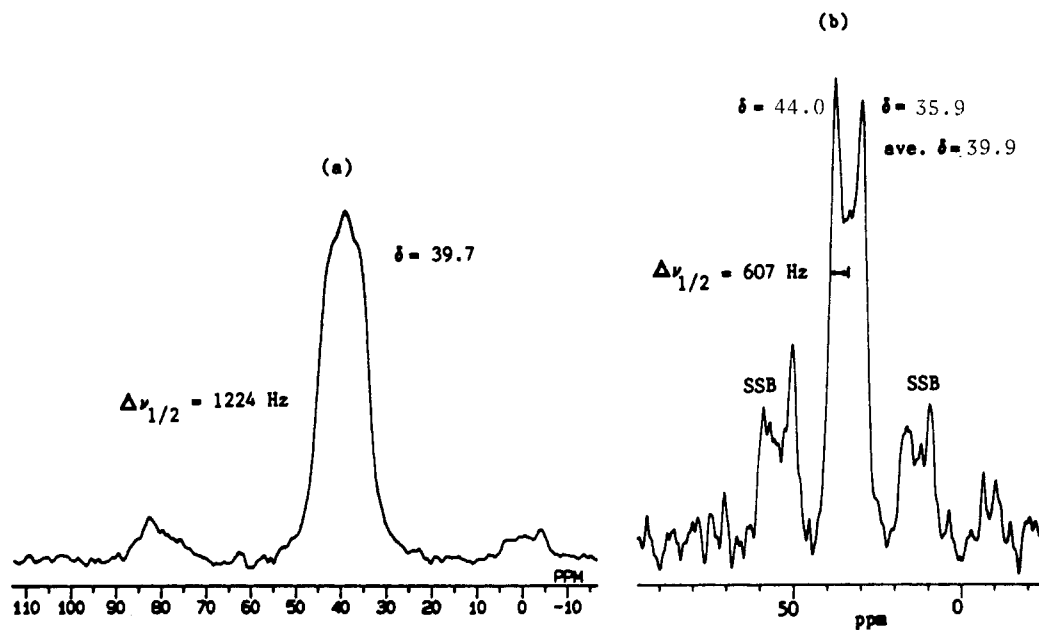
Figure 3. 109.25- (a) and 120.61-MHz[71] (b) CP/MAS ^{31}P{^{1}H} NMR spectra of (Ph$_3$P)AuCl.
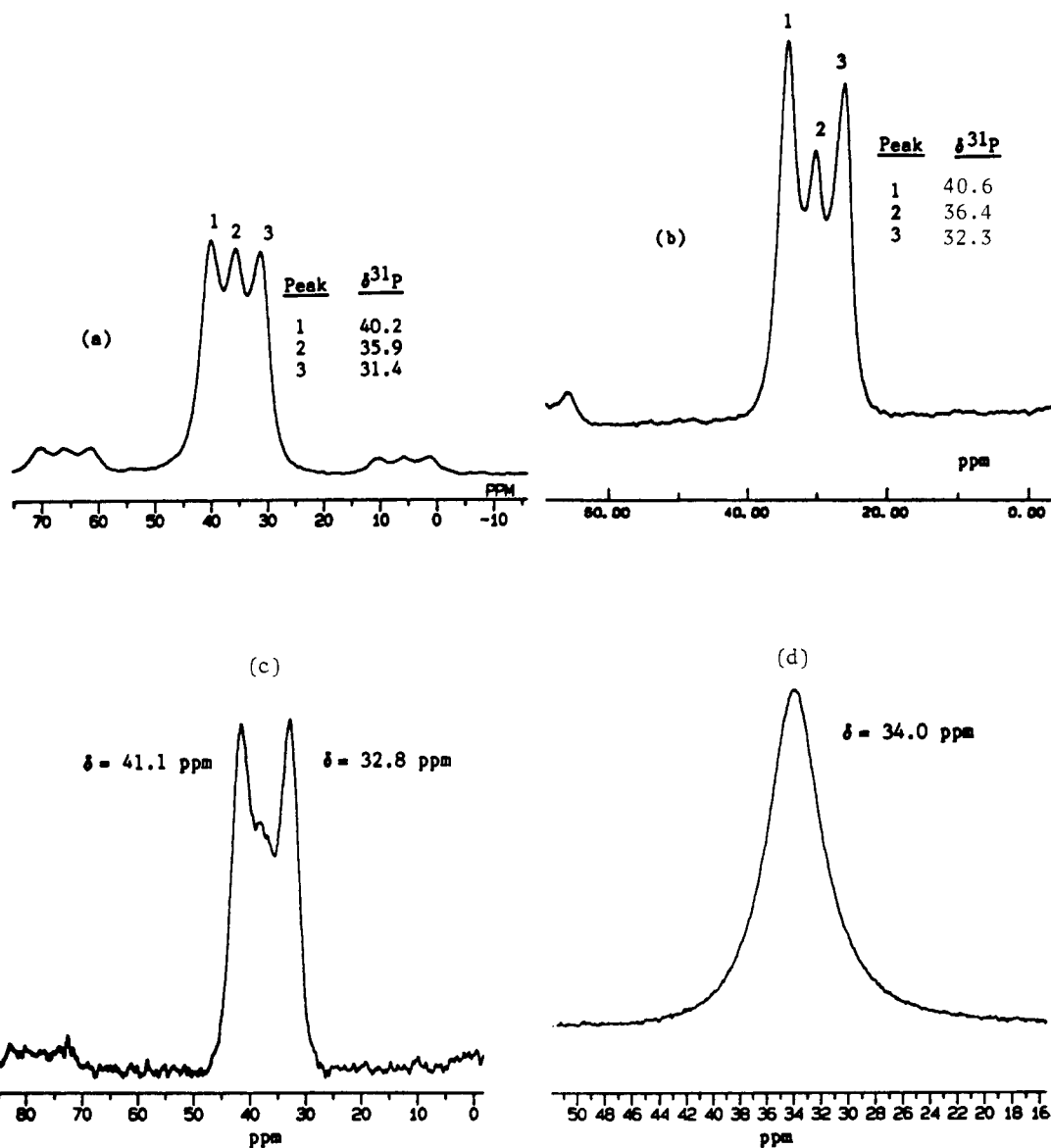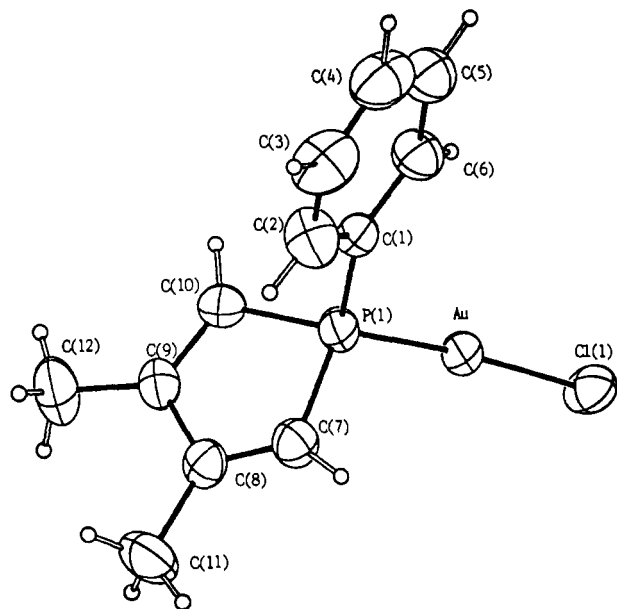

Figure 4. 109.25- (a) and 120.61-MHz (b) CP/MAS ^{31}P{^{1}H} NMR spectra of (DMPP)AuCl. 109.25-MHz CP/MAS ^{31}P{^{1}H} NMR spectra of (c) (DMPP)AuBr and (d) (DMPP)AuI.

Figure 5. ORTEP plot of the structure of chloro(1-phenyl-3,4–dimethylphosphole)gold(I) (3), showing the atom-labeling scheme and 50% probability ellipsoids, with hydrogen atom radii arbitrary.

Table VIII. Gold(I)–Halogen Stretching Frequencies $(\nu_{AuX})^a$ for L_nAuX Complexes

L	LAuX $(\nu_1)^b$			L_3AuX $(\nu_1)^b$		
	X = Cl	X = Br	X = I	X = Cl	X = Br	X = I
DBP^c	338	234	185	170	87*	76*
	(331, 324 sh)					
DMPP^c	(329, 320 sh)^c	229	207	NI	NI	NI
Ph$_3$P	(330, 323, sh)^c	234^c	189^c	167^c	NI	NI
	(329, 323, sh)^d	233,^{d} 229^e	187^e	163^i		
	333^e	226^g				
MePh$_2$P	(323, 315, sh)^e	220^e				
Me$_2$PhP	314^e	221^e				
Me$_3$P	(311, 305 sh)^d	205^h	164^h			
EtPh$_2$P	323^f					
Et$_3$P	(312, 305 sh)^d	210^d				
n-Bu$_3$P	310–330^f					

$^a\nu_{AuX}$ in cm^{-1}. Key: NI = not isolated; sh = shoulder [the two ν_{AuX} values written in parentheses represent the main (higher energy) absorption due to ^{35}Cl and a lower-energy shoulder due to ^{37}Cl]; * = ambiguous assignment. $^b\nu_1$ corresponds to the stretching frequency due to terminal halide. ^{c}From this work (recorded as polyethylene pellets). ^{d}Reference 65; recorded as Nujol mulls between CsI plates. ^{e}Reference 9; recorded as Nujol mulls between polyethylene plates. ^{f}Reference 7; recorded as Nujol mulls (the ν_{AuCl} band for L = n-Bu$_3$P is very broad). ^{g}Reference 5; recorded as CsI pellets. ^{h}Reference 8; recorded as Nujol mulls between CsI-supported thin polyethylene plates. ^{i}Reference 24; recorded as petroleum jelly (Nujol) mulls between polyethylene plates.

The (DMPP)AuCl complex is a typical near-linear (∠PAuCl = 176.1 (1)°) complex with Au–P and Au–Cl bond lengths (Table VII) of 2.227 (2) and 2.288 (2), respectively. The Au–P bond lengths in (DMPP)AuCl and (DBP)AuCl are very similar and are somewhat shorter than those observed for (Ph$_3$P)AuCl[12] (2.235 Å) and (Cy$_3$P)AuCl[26] (2.242 Å) respectively. This suggests that for these four phosphorus ligands the donor ability toward gold(I) decreases in the order DBP > DMPP > Ph$_3$P > Cy$_3$P though the differences are small. The AuCl bond lengths show similar small changes in the reverse order, suggesting that the differential trans influences[72–74] of these phosphorus donors are small.[13]

(b) (R$_3$P)$_3$AuX Complexes. While the reactions of (DBP)AuX with DBP in CH$_2$Cl$_2$ led to crystalline (DBP)$_3$AuX complexes, in similar reactions of (DMPP)AuX with DMPP only (DMPP)AuX could be isolated as solids. The CP/MAS ^{31}P{^{1}H} NMR spectra of (DBP)$_3$AuX (X = Cl, Br, I) and (Ph$_3$P)$_3$AuCl[24] are shown in Figure 6. It is evident from the spectra in Figure 6 that (DBP)$_3$AuCl and (Ph$_3$P)$_3$AuCl have different solid-state structures. The X-ray crystal structure of (DBP)$_3$AuCl is shown in Figure 7. Two of the dibenzophospholes in this molecule have attractive interactions between them that stabilize a face-to-face arrangement as has been observed in other complexes containing two or more dibenzophospholes.[52] It is interesting to note that both (Ph$_3$P)$_3$AuCl[22] and (DBP)$_3$AuCl are only slightly distorted tetrahedral complexes, but each complex contains three crystallographically independent phosphorus atoms (d(AuP) = 2.431 (2), 2.404 (2), and 2.395 (2) Å for (Ph$_3$P)$_3$AuCl and d(AuP) = 2.359 (1), 2.382 (1), and 2.374 (2) for (DBP)$_3$AuCl). The smaller average Au–P bond lengths for (DBP)$_3$AuCl (2.372 Å) compared to (Ph$_3$P)AuCl (2.410 Å) are consistent with the previous conclusion that DBP is a better donor toward gold(I). The longer Au–P bonds in the (R$_3$P)$_3$AuCl complexes than in the (R$_3$P)AuCl complexes are a result of a combination of increased intramolecular steric effects and increased interelectronic repulsions as the gold coordination number increases. The bond angles listed in Table VI reveal that the coordination geometry for (DBP)$_3$AuCl is only slightly distorted from a regular tetrahedron (average of the three P–Au–P angles is 113.9°). The same is true for the (Ph$_3$P)$_3$AuCl complex with the above-mentioned average bond angle being 117.4°. The change in the symmetry of the gold environment affects the CP/MAS ^{31}P{^{1}H} NMR line width as expected. For

the (R$_3$P)AuCl complexes $\Delta\nu_{1/2}$ = 437 Hz (DBP) and 607 Hz (Ph$_3$P) compared with 298 and 336 Hz for (R$_3$P)$_3$AuCl (R$_3$P = DBP and Ph$_3$P, respectively). This is a result of a reduction in the quadrupole line-broadening effect of ^{197}Au with an increase in the symmetry of the gold environment.

Comparing the crystal structures of (Ph$_3$P)$_3$AuCl and (DBP)$_3$AuCl makes it clear that the three Ph$_3$P ligands can attain similar environments by way of low-energy librations of the phenyl groups whereas two of the DBP ligands are held in a parallel arrangement in (DBP)$_3$AuCl. Hence, (DBP)$_3$AuCl has effective mirror symmetry as perceived by ^{31}P{^{1}H} CP/MAS spectroscopy, and two resonances in a 2:1 relative intensity ratio are observed. (Ph$_3$P)$_3$AuCl has effective C_3 symmetry, and only one ^{31}P{^{1}H} CP/MAS resonance is observed for it. A similar ^{31}P{^{1}H} CP/MAS spectrum is observed for (DBP)$_3$AuBr, but for (DBP)$_3$AuI, three resonances are present. Presumably, therefore, in (DBP)$_3$AuI the phosphole rings do not possess approximate mirror symmetry.

(c) [(R$_3$P)$_4$Au]$^+$X$^-$ Complexes. Only two complexes of this type have been crystallographically characterized: [(Ph$_3$P)$_4$Au]$^+$BPh$_4^-$ (three different solvates: CHCl$_3$, EtOH, and CH$_3$CN)[18] and [(MePh$_2$P)$_4$Au]$^+$PF$_6^-$.[20,75] The high tendency of Au(I) for lower coordination numbers is demonstrated by the observation that none of the three modifications of [(Ph$_3$P)$_4$Au]$^+$BPh$_4^-$ show a simple tetrahedral geometry. All three complexes show either trigonal coordination with an additional very distant PPh$_3$ (d(AuP) = 3.95 Å) or a disorder between trigonal and tetrahedral geometries. The [(MePh$_2$P)$_4$Au]$^+$PF$_6^-$ complex is the only "true" tetrahedral (R$_3$P)$_4$Au$^+$ complex thus far structurally characterized. In addition, the [(Me$_3$P)$_4$Au]$^+$X$^-$ (X = Cl, Br, I) complexes have been shown[75] to liberate Me$_3$P readily. Though crystalline [(DBP)$_4$Au]$^+$PF$_6^-$ precipitates from a CH$_2$Cl$_2$/H$_2$O mixture containing KPF$_6$ and a DBP:Au ratio of 4.5, [(DMPP)$_4$Au]$^+$PF$_6^-$ formed as an oil under similar conditions and could not be induced to crystallize. The CP/MAS ^{31}P{^{1}H} NMR spectrum of [(DBP)$_4$Au]$^+$PF$_6^-$ is compared with its ^{31}P{^{1}H} spectrum obtained in dimethyl sulfoxide solution in Figure 8. In both cases, a narrow resonance for the cation is observed, suggesting that both structures in both states are tetrahedral. The stoichiometry is supported by the relative integrated intensities of the [(DBP)$_4$Au]$^+$ and PF$_6^-$ resonances.

II. Far-Infrared Spectroscopy. The gold–halogen stretching frequencies for the (R$_3$P)$_n$AuX complexes are listed in Table VIII. The frequency of ν_{AuX} decreases as n increases, consistent with

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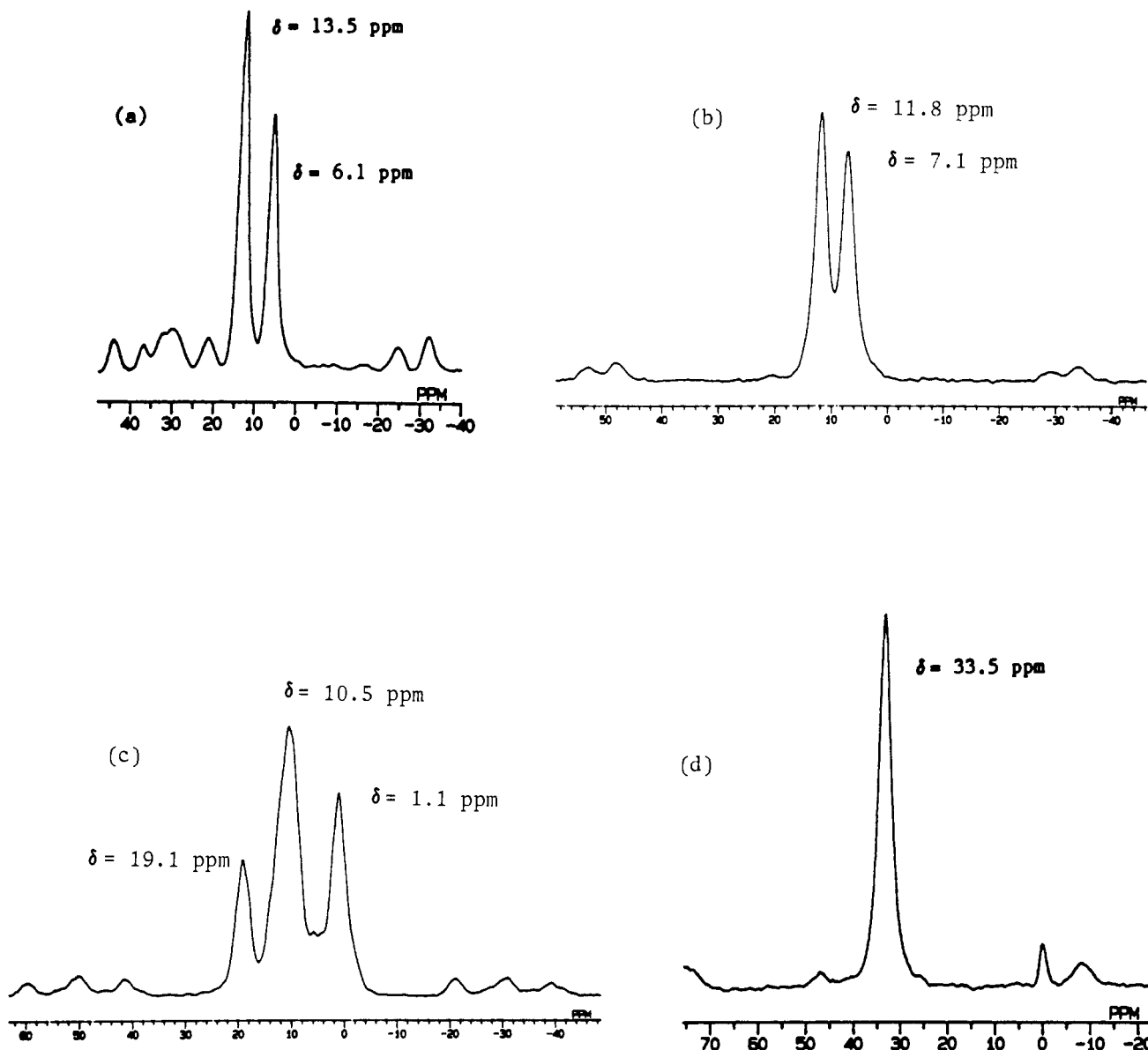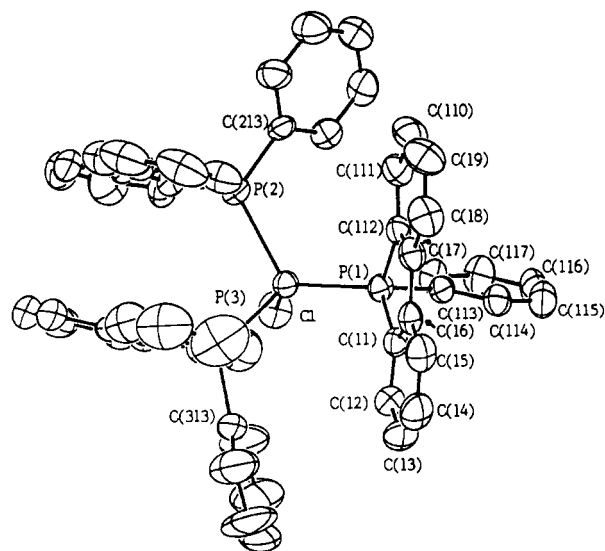(76) Schmidbaur, H.; Franke, R. *Chem. Ber.* **1972**, *105*, 2985.

δ = 13.5 ppm

(a)

δ = 6.1 ppm

PPM

40 30 20 10 0 -10 -20 -30 -40

(b)

δ = 11.8 ppm

δ = 7.1 ppm

PPM

50 40 30 20 10 0 -10 -20 -30 -40

δ = 10.5 ppm

(c)

δ = 1.1 ppm

δ = 19.1 ppm

PPM

60 50 40 30 20 10 0 -10 -20 -30 -40

(d)

δ = 33.5 ppm

PPM

70 60 50 40 30 20 10 0 -10 -20

Figure 6. 109.25-MHz CP/MAS $^{31}P\{^1H\}$ NMR spectra of (a) (DBP)$_3$AuCl, (b) (DBP)$_3$AuBr, (c) (DBP)$_3$AuI, and (d) (Ph$_3$P)$_3$AuCl.

Figure 7. ORTEP plot of the structure of chlorotris(1-phenyldibenzophosphole)gold(I) (**2**), showing the atom labeling scheme and 50% probability ellipsoids, with hydrogens omitted.

a weakening of the Au–X bond with increasing coordination number.[24] There are two sharp ν_{AuCl} vibrations observed for

(DBP)AuCl (338 and 331 cm^{-1}) whereas for all other (R$_3$P)AuCl compounds only one ν_{AuCl} is observed. This is consistent with the x-ray crystal structure (Figure 2) in which there are two structurally different molecules. For all the (R$_3$P)AuCl compounds the Au–Cl stretch shows a low-frequency shoulder due to the ^{37}Cl isotope,[9] which aids in the assignment of this vibration. Williamson and Baird[8] have ranked the relative trans influence[72–74] of neutral ligands on the basis of the frequency of ν_{AuCl}, with a decrease in ν_{AuCl} indicating an increase in the trans influence of the neutral ligand. On this basis, the trans influence of the phosphorus donors decreases in the order Bu$_3$P > Me$_3$P > Et$_3$P > Me$_2$PhP > MePh$_2$P ≈ EtPh$_2$P > DMPP > Ph$_3$P > DBP though the range is small and there is believed[39] to be strong coupling of the AuCl and AuP stretching modes.

III. Solution Behavior. The complex solution behavior of gold(I) phosphine complexes has long been realized. For example, Westland[5] studied equilibria (eq 1) in nitrobenzene solutions by

$$(Ph_3P)AuX + (n - 1)Ph_3P \rightleftharpoons (Ph_3P)_nAu^+ + X^- \quad (1)$$
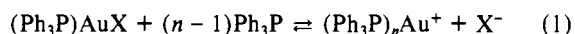
conductivity measurements. The results of this study showed that the equilibrium constants decreased (X = Cl$^-$ > Br$^-$ > I$^-$) as expected as the coordinating ability of the halide increased. He suggested that for weakly coordinating anions (NO$_3^-$, ClO$_4^-$, and BF$_4^-$) the ionic complexes [(Ph$_3$P)$_2$Au]$^+$ and [(Ph$_3$P)$_3$Au]$^+$ are probably formed extensively. Earlier, via infrared, conductivity, and molecular weight measurements, Meyer and Allred[4] concluded
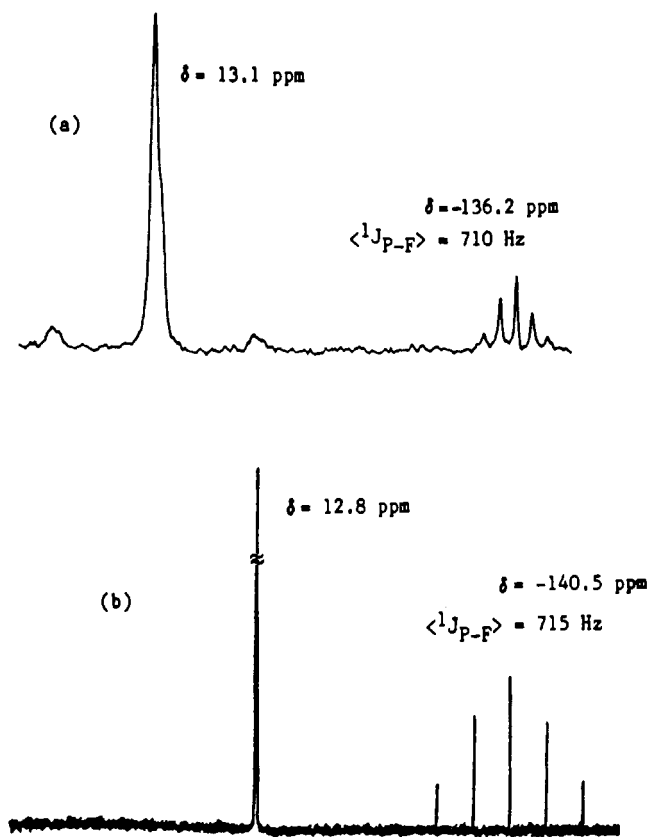
Figure 8. Comparison of (a) 109.25-MHz CP/MAS $^{31}P\{^1H\}$ and (b) 40.26-MHz (DMSO solution) $^{31}P\{^1H\}$ NMR spectra of [(DBP)$_4$Au]$^+$-PF$_6^-$.

that only the ionic, linear [(Ph$_3$P)$_2$Au]$^+$X$^-$ (X = Cl, Br, I) complexes existed in both the solution and the solid state. Muetterties and Alegranti[6] concluded from low-temperature $^{31}P\{^1H\}$ NMR and conductivity studies that LAuX (X = Cl, Br, I), [L$_2$Au]$^+$, [L$_3$Au]$^+$, and possibly [L$_4$Au]$^+$ (L = (p-CH$_3$C$_6$H$_4$)$_3$P) existed in CH$_2$Cl$_2$ solution. Furthermore, they found that L$_2$AuCl partially disproportionates according to equilibrium 2, with K_{eq}

$$2L_2AuCl \rightleftharpoons [L_3Au]^+Cl^- + LAuCl \qquad (2)$$
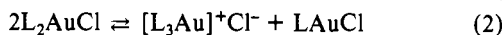
= 10^{-1} at -80 °C. Mays and Vergnano[16] found that the addition of L = Et$_3$P to CH$_2$Cl$_2$ solutions of [L$_2$Au]$^+$PF$_6^-$ or LAuCl at -90 °C led to the formation of [L$_3$Au]$^+$ and [L$_4$Au]$^+$. Moreover, addition of (EtO)$_3$P to solutions of [L$_2$Au]$^+$PF$_6^-$ or LAuCl gave mixed species of the type [(Et$_3$P)$_n$Au{P(OEt)$_3$}$_{4-n}$]$^+$ (n = 1-3).

A series of similar $^{31}P\{^1H\}$ NMR studies by McAuliffe and co-workers[15,17,21,25,29] on the solution behavior of a variety of L$_n$AuX complexes showed that more species are capable of existence in solution than can be crystallized from that same solution. Moreover, the isolated solids do not necessarily correspond to the major species present in solution. Finally, these same workers[29] followed the exchange kinetics of a variety of systems by variable-temperature $^{31}P\{^1H\}$ NMR and showed them to be associative in nature.

The ^{31}P NMR data for the isolated complexes are given in Table IX. The ^{31}P chemical shifts for the linear (R$_3$P)AuX complexes of each ligand increase in the order X = Cl < Br < I in contrast to expectations based upon the relative trans influence of the halides. This trend is probably due to an increase in the contribution of the paramagnetic term (σ_P) to the ^{31}P chemical shift[77] caused by the an increase in the atomic mass of the halide. This may be an example of the so-called "heavy-atom effect" as explained by Webb[78] where the nuclear shielding of a lighter atom (^{31}P) is influenced by a change in its electronic energy levels

Table IX. $^{31}P\{^1H\}$ NMR Chemical Shifts (δ)^a and Coordination Chemical Shifts ($\Delta\delta$)^b for L$_n$AuX Complexes^c

		$\delta(^{31}P)$, ppm ($\Delta\delta$, ppm)		
L	X	[LAuX]	[L$_3$AuX]	[L$_4$Au]$^+$PF$_6^-$
DBP	Cl	23.9 (34.4)	12.2 (22.7)	NA
	Br	26.4 (36.9)	10.5 (21.0)	NA
	I	31.8 (42.3)	8.01 (18.5)	NA
	PF$_6$	NA	NA	12.8^d (23.3)
DMPP	Cl	24.9 (27.4)	NI	NA
	Br	28.2 (30.7)	NI	NA
	I	33.8 (36.3)	NI	NA
	PF$_6$	NA	NA	44.0^d (46.5)
Ph$_3$P	Cl	32.7 (38.7)	20.0 (26.9)	NA
	Br	34.4 (40.4)	NA, e	NA
	I	38.4 (44.4)	NA, e	NA

^{a} Measured at 40.26 MHz in CDCl$_3$ at 30 °C. $\delta(^{31}P)$ relative to 85% H$_3$PO$_4$ (positive values indicate lower fields). ^{b} Coordination chemical shift ($\Delta\delta$) = $\delta_{complex} - \delta_{ligand}$. The following δ_{ligand} values were used: -10.5 ppm (DBP), -2.5 ppm (DMPP), and -6.0 ppm (Ph$_3$P), all measured at 30 °C. ^{c} Key: NI = not isolated; NA = not available. ^{d} Measured in DMSO-d_6. ^{e} The syntheses of the two [(Ph$_3$P)$_3$AuX] (X = Br, I) complexes were not attempted in this work since Bowmaker and Rogers[24] reported that their attempted preparation of the latter two compounds met with failure.

because of spin-orbit coupling with a neighboring heavy nucleus (^{79}Br or ^{127}I).

The coordination chemical shifts decrease with increasing coordination number and in the sequence Ph$_3$P > DMPP > DBP for the chloride complexes but Ph$_3$P > DBP > DMPP for the bromide and iodide complexes and probably reflect relative strengths of the R$_3$P–Au interactions. These complexes all have the same structures in solution and in the solid state for the (R$_3$P)AuX and [(R$_3$P)$_4$Au]$^+$PF$_6^-$ species, but the exact nature of the (R$_3$P)$_3$AuX species in solution is not established by the observation of a single phosphorus resonance. In order to gain more information with respect to the nature of the species present in solution, ligand-addition studies were performed in CH$_2$Cl$_2$ solutions at -80 °C. For mixtures of (DBP)AuCl and DBP up to a DBP:Au ratio of 4:1, only two resonances were observed at δ 23.9 and 2.9. These are assignable to (DBP)AuCl and [(DBP)$_4$Au]$^+$Cl$^-$, respectively.[79] When the DBP:Au ratio exceeded 4:1, the resonance of free DBP was observed at -11.5 ppm. A similar experiment with (DMPP)AuCl and DMPP in various ratios showed the existence of (DMPP)AuCl (25.1 ppm), (DMPP)$_2$AuCl (49.8 ppm), (DMPP)$_3$AuCl (41.4 ppm), and [(DMPP)$_4$Au]$^+$Cl$^-$ (9.2 ppm) for all ratios up to 3:1. Above a 3:1 ratio, the (DMPP)AuCl species was no longer present, and at a 4:1 ratio, free DMPP (-2.4 ppm) was present. For (Ph$_3$P)AuCl, addition of small amounts of Ph$_3$P produced (Ph$_3$P)AuCl (30.7 ppm), (Ph$_3$P)$_2$AuCl (38.0 ppm) and (Ph$_3$P)$_3$AuCl (39.2 ppm). In each case, exchange equilibria are occurring.

The observations that [(DBP)$_4$Au]$^+$Cl$^-$ is the thermodynamically most stable of the DBP complexes in solution (its relative concentration increases with decreasing temperature), that [(Ph$_3$P)$_4$Au]$^+$Cl$^-$ was never observed, and that [(DMPP)$_4$Au]$^+$Cl$^-$ is the dominant species in solutions containing at least a 2:1 DMPP:Au ratio are all consistent with the higher coordination number complexes gaining stability as the ligand bulk decreases.

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