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Structural and Spectroscopic Characterisation of Linearly Coordinated Gold(I) Tribenzylphosphane Complexes

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The 1:1 tribenzylphosphane (PBn_3) complexes of gold(I)-[$(Bn_3P)AuX$] (X = Cl and Br) have been synthesised, and their structures were determined by single-crystal X-ray crystallography. The compounds are isomorphous, neutral molecules with linearly coordinated P–Au–X arrays. Each structure contains three independent [$(Bn_3P)AuX$] entities lying on the three threefold axes of space group *P*3*c*1. The mean bond lengths are Au–Cl 2.302(8), Au–P 2.227(11) Å for the chloride and Au–Br 2.404(10), Au–P 2.229(4) Å for the bromide. These contrast with the 1:1 adducts previously reported for copper(I), which take the form [$Cu(PBn_3)_2$][CuX_2]. The 1:2 AuX:PBn_3 compounds that have been synthesised are formulated as [$Au(PBn_3)_2$]X·$n$$H_2O$ (X = Cl, n = 1 or 2; X = I and BF_4, n = 0). Single-crystal X-ray structures show that linearly two-coordinate centrosymmetric [$Au(PBn_3)_2$]$^+$ arrays are found in [$Au(PBn_3)_2$]Cl·H_2O and [$Au(PBn_3)_2$]BF_4 with Au–P bond lengths of 2.2988(7) and 2.3016(7) Å for the chloride and 2.2975(7) Å for the tetrafluoroborate. ν(AuX) bands in the far-IR spectra of [$(Bn_3P)AuX$] are assigned at 320 and 227 cm^{-1} for X = Cl and X = Br, respectively. The ^{31}P CP MAS NMR spectra of [$(Bn_3P)AuX$] (X = Cl, Br) and [$Au(PBn_3)_2$]X (X = Cl·H_2O, Cl·2H_2O, I, BF_4) are reported, and the observation of ^2J(PP) coupling in the spectrum of [$Au(PBn_3)_2$]Cl·2H_2O is consistent with the presence in this complex of noncentrosymmetric cations in which the two phosphorus atoms are inequivalent.

Introduction

By comparison with triphenylphosphane (PPh_3), less is known about the coordination chemistry of tribenzylphosphane (PBn_3). The insertion of methylene spacers between the phosphorus atom and the phenyl rings in PBn_3 alters its physical properties in that it becomes a more bulky ligand than PPh_3 with a Tolman cone angle of 165° compared to 145° for PPh_3, and it is also more basic, the pK_a's of the conjugate acids being 2.7 and 6.0 (estimate), respectively.[1] Further comparison of these properties with those of alkylphosphanes (PEt_3, cone angle, 137°, pK_a, 8.69; PCy_3, 170, 9.7, P*t*Bu_3, 182, 11.40) shows that the introduction of the phenyl ring results in a steric bulk comparable with secondary alkyl groups such as tricyclohexyl, but diminished basicity. Thus PBn_3 may be considered to be a bulky, relatively basic, alkylphosphane in which the presence of conformationally flexible phenyl groups would be expected to influence the coordination chemistry. This has been observed for complexes of both copper(I) and mercury(II). With 1:1 adducts of copper(I) chloride and bromide ligand disproportionation occurs, so that ionic compounds of the form [$Cu(PBn_3)_2$][CuX_2] are obtained in the solid state with linear [$Cu(PBn_3)_2$]$^+$ cations.[2,3] This contrasts with the situation for the corresponding adducts of copper(I) and silver(I) halides with other tertiary phosphanes, which usually yield neutral [$(R_3P)CuX$]$_n$ complexes which are either tetrameric, dimeric or [$(R_3P)CuX$] monomers depending on the steric bulk of the PR_3 ligands.[4] Similarly, with mercury(II) [$Hg(PBn_3)_2$]$(BF_4)_2$ contains [$Hg(PR_3)_2$]$^{2+}$ cations with linear P–Hg–P coordination, the first example of a truly two-coordinate [$Hg(PR_3)_2$]$^{2+}$ complex.[5] The driving force for the formation of ionic adducts with PBn_3 has been ascribed to interligand "embraces" within the linear two-coordinate cation,[2,3] such an embrace presumably preventing secondary coordination of the mercury to the BF_4^- counterions. Recently, the structure of the complex [$Au(PAd_2Bn)_2$][$AuCl_2$] (Ad = 1-adamantyl) has been reported as the first example of an ionic form of a

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1:1 chlorophosphanegold(I) complex.[6] However, no single-crystal X-ray structures have been reported for Au(I) complexes of Bn_3P itself.

A cursory study on the tribenzylphosphane complex, $[(Bn_3P)AuCl]$ has been reported[7a] as well as the conversion of $[(Bn_3P)AuX]$ (X = Cl, Br, I), upon reaction with $AgBF_4$, to cationic binuclear gold(I) complexes with formula $[\{(Bn_3P)Au\}_2X]^+BF_4^-$.[7b] The complex$[(Bn_3P)AuCl]$ (along with similar compounds) has been evaluated for in vitro cytotoxic potency against (e.g. B16 mouse melanoma cells) and was found more cytotoxic than the triphenylphosphane analogue due to its increased lipophilicity.[7c] In this context, we extend our work with PBn_3 to further study the nature of the complexes formed by this ligand with some gold(I) salts. The present report describes the synthesis and structural characterisation of 1:1 AuX:PBn_3 (X = Cl or Br) as monomeric complexes $[(Bn_3P)AuX]$ and the syntheses of 1:2 complexes for X = Cl, I or BF_4, all of which are ionic $[Au(PBn_3)_2]X$ and contain the linear coordinated $[Au(PBn_3)_2]^+$ cation with a noncoordinated anion, characterised crystallographically for its X = Cl(·H_2O), BF_4 salts. The far-IR and ^{31}P CP MAS NMR spectra of all of these new complexes are reported and discussed in relation to their structure and bonding.

Results and Discussion

Synthesis

The reaction of $[Bu_4N][AuX_2]$ (X = Cl, Br) with PBn_3 in a 1:1 molar ratio in warm *N*,*N*′-dimethylformamide yielded the 1:1 complexes $[(Bn_3P)AuX]$, whereas for X = I, gold metal was deposited with formation of the ligand oxide. The 1:1 complex is not thus far accessible for the iodo species and in this respect it parallels the chemistry of CuI with PBn_3.[3] When the molar ratio was 1:2 in thf $[Au(PBn_3)_2]Cl\cdot 2H_2O$ was isolated which, interestingly, converted into the monohydrate $[Au(PBn_3)_2]Cl\cdot H_2O$ upon crystallisation from dmf. In a similar way, $[Au(PBn_3)_2]I$ was obtained from thf and $[Au(PBn_3)_2]BF_4$ from $[Au(NCCH_3)_2]BF_4$ in acetonitrile. All the new compounds are moderately soluble in common solvents such as dichloromethane and acetonitrile.

Crystal Structures

The results of the single-crystal X-ray structure determinations on the AuX:PBn_3 (1:1) (X = Cl or Br) adducts are consistent with their formulation as neutral mononuclear $[(Bn_3P)AuX]$ species. The two structures are isomorphous. Although one molecule comprises the asymmetric unit of the structure [Figure 1, (a)], it is made up of three independent components, disposed with their linear PAuX arrays on the three distinct crystallographic 3-axes of space group *P*3*c*1. Bond lengths, along with those of related compounds, are presented in Table 1.

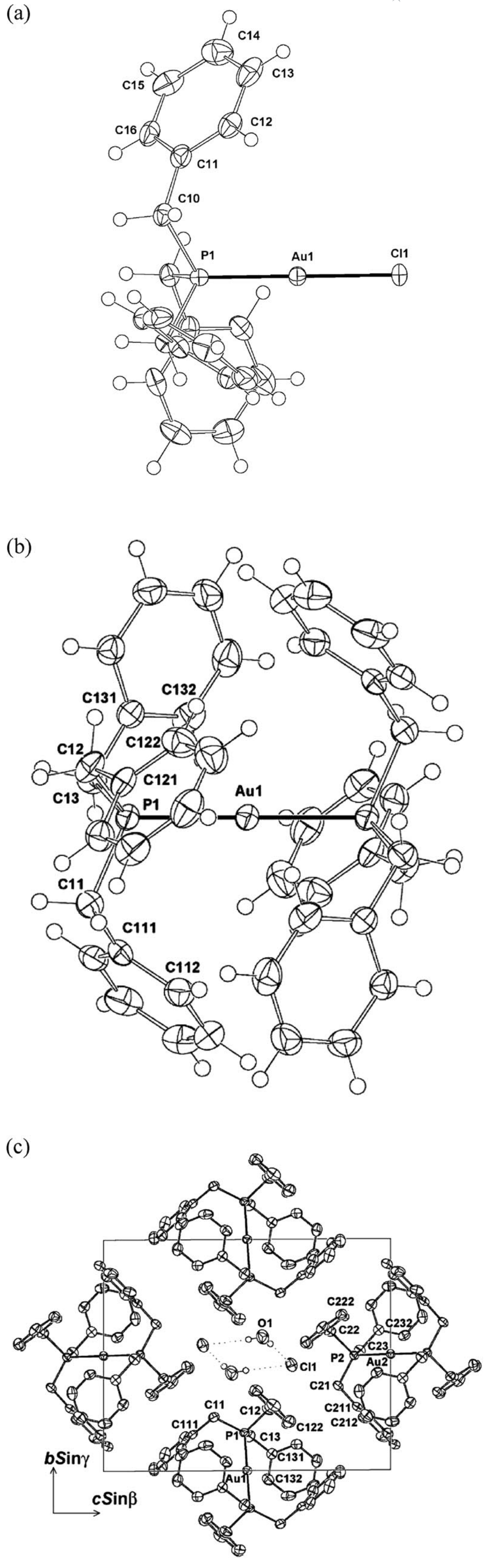

Figure 1. (a) Molecule 1 of $[(Bn_3P)AuCl]$ (the other two molecules and those of the isomorphous bromide analogue are similar); (b) Cation 1 of $[Au(PBn_3)_2]Cl\cdot H_2O$ (the other cation and that of the BF_4 salt are similar); (c) Unit cell contents of $[Au(PBn_3)_2]Cl\cdot H_2O$, projected down the *a* axis.

Table 1. Au–P and Au–X bond lengths [Å] for [(R_3P)AuX] (X = Cl, Br or I; R = alkyl or aryl substituent) complexes.

	Au–P			Au–X		
PR_3	X = Cl	X = Br	X = I	X = Cl	X = Br	X = I
PMe_3[a]	2.233(3)	2.242(7)	2.256(3)	2.306(4)	2.419(3)	2.583(1)
	2.234(4)	2.235(5)		2.310(4)	2.415(3)	
	2.233(3)	2.228(6)		2.310(4)	2.415(3)	
PEt_3[b]	2.232(9)			2.305(8)		
	2.231(8)			2.306(8)		
PBn_3[c]	2.226(3)	2.232(3)		2.309(3)	2.410(1)	
	2.216(3)	2.229(3)		2.305(3)	2.410(1)	
	2.239(3)	2.225(3)		2.293(3)	2.393(2)	
PCy_3[d]	2.242(4)	2.247(2)	2.263(3)	2.279(5)	2.395(1)	2.551(1)
			2.265(4)			2.555(1)
P*i*Pr_3[e]	2.239(2)			2.284(3)		
P*t*Bu_3[f]	2.253(6)			2.284(6)		
PPh_3[g]	2.235(3)	2.252(6)	2.254(5)	2.279(3)	2.407(2)	2.556(2)
P*o*tol_3[h]	2.240(4)	2.254(5)	2.265(4)	2.290(4)	2.411(2)	2.556(1)
	2.236(4)	2.243(5)	2.261(4)	2.270(4)	2.388(2)	2.538(2)
	2.243(2)			2.281(3)		
$Pmes_3$[i]	2.263(2)	2.279(3)	2.292(3)	2.272(2)	2.393(2)	2.544(1)
	2.260(2)	2.288(4)		2.272(3)	2.391(2)	
$Ptmpp_3$[j]	2.255(2)			2.294(2)		

[a] Ref.[39a–39c] [b] Ref.[39d] [c] Ref.[39e] [d] Ref.[39f,39g] [e] Ref.[39a] [f] Ref.[39h] [g] Ref.[39i,39j] [h] Ref.[39k,39l] [i] Ref.[39m,39n] [j] Ref.[39o]

The structure of AuCl:PBn_3 (1:2) is found to be ionic and a monohydrate, comprised of $[Au(PBn_3)_2]^+$ cations [Figure 1, (b)] and chloride counterions. Again one formula unit comprises the asymmetric unit of the structure, and again this is made up of component fragments disposed about crystallographic symmetry elements – in this case, a pair of gold atoms lying on inversion centres, so that the gold atom coordination environments are obligate linear [Au–P are 2.3016(7) and 2.2988(7) Å]. The water molecule and chloride ion, close to an inversion centre, form, with their images, a centrosymmetric dimer [Cl···Cl′ 5.217(1); O···O′ 3.744(4); O···Cl, Cl′ 3.216(4), 3.206(3) Å] [Figure 1, (c)]. The tetrafluoroborate is similarly ionic with one half of the $[Au(PBn_3)_2]BF_4$ formula unit comprising the asymmetric unit of the structure. The gold atom again lies on a crystallographic inversion centre with an obligate linear P–Au–P coordination environment [Au–P 2.2975(7) Å]. The anion is disposed with the boron atom lying on a crystallographic 2-axis (space group *C*2/*c*), the fluorine atoms being disordered over sites of occupancy 0.5.

For the purposes of comparison with potentially (linear) two-coordinate LML arrays, containing M–X (X = halide) and/or M–P bonds, it is useful to consider baseline distances for such species. For X = halide, X–M–X geometries, especially the M–X distance(s), vary greatly in the abundance with which they have been established, some such species having an innate tendency to oligomerise, so that for some there is a plethora, while others are accessible only within unusual crystal lattice forms. Even for the former, there is considerable divergence consequent on individual lattice circumstances (see, in particular, outliers for Ag/Cl, I), and there is some futility in attempting to define values to any precision better than 0.01 Å. For copper(I) and silver(I) the review of ref.[8] offers a compilation of structural data extant to that point, and, in the cases of the more abundant cohorts, there is little point in attempting improvement by further augmentation with consequent examples. The manner in which the values adopted below originate is summarised in the associated references/footnotes, for M,X = Cu,Cl;[9] Cu,Br;[10] Cu,I;[11] Ag,Cl;[12] Ag,Br;[13] Ag,I;[14] Au,Cl;[15] Au,Br;[16] Au,I.[17] From these, we take as baseline M–X bond length estimates (Å) in $[XMX]^-$ as:

Cu: Cl 2.09, Br 2.22, I 2.39

Ag: Cl 2.33, Br 2.44, I 2.92 (?) (see ref.[14])

Au: Cl 2.27, Br 2.36, I 2.54

noting the implication of a larger atomic radius for silver(I) than gold(I) as described previously.[18] With an initial focus on gold(I) as the metal atom in complexes of the form $[M(PR_3)_2]X$ and [(R_3P)MX], an array of established structural data is presented in Table 1 and 2, respectively; a datum value for the Au–P distance in $[Au(PPh_3)_2]^+$ is taken as 2.31 Å.[19]

Table 2. Bond lengths [Å] and angles [°] for $[M(PR_3)_2]X$ (M = Cu, Ag or Au) complexes.

PR_3	X	M–P	P–M–P
	M = Cu		
PBn_3[a]	PF_6	2.191(1)	180
PBn_3[b]	$[CuCl_2]$	2.205(3)	180
PBn_3[c]	$[CuBr_2]$	2.1955(14)	180
tmsp[d]	BF_4	2.242(2)	
	M = Ag		
PMe_3[e]	$[Au(C_2Ph)_2]$	2.368(5), 2.419(5)	175.8(2)
	$[Au(C_2Ph)_3]$	2.392(3)	177.1(1)
$P(CH_2CH_2CN)_3$[f]	NO_3	2.383(1)	
tmsp[g]	PF_6	2.461(6)	
tmsp[d]	BF_4	2.4409(9)	179.80(6)
tmpp[h]	$[Ag_5I_7]_{(\infty\vert\infty)}$	2.36(2)–2.40(2)	175.9(9), 179(1)
tmpp[i]	$[Ag_5I_7(py)_2]$	2.409(4), 2414(4)	177.9(2)
	$[Ag_5I_6(quin)]_{(\infty\vert\infty)}$	2.411(6), 2.426(6)	178.5(2)
tmpp[j]	$[(py)Ag(CN)_2]$	2.417(2)	177.38(7)
$[PPh_3]$[k]	BF_4	2.4177(12), 2.4219(13)	156.65(4)[k]
	M = Au		
PMe_3[l]	Cl	2.304(1) (×2)	175.4(1)
PBu_3[m]	BPh_4	2.310(3), 2.305(4)	176.1(1)
PCy_3[n]	Cl	2.318(1) (×2)	180
PCy_3[n]	Br	2.328(3), 2.305(3)	178.4(1)
PAd_2Bn[o]	$[AuCl_2]$	2.3348(9) (× 2)	180
PBn_3[p]	Cl	2.2988(7) (× 2)	180
		2.3016(7) (× 2)	180
PBn_3[p]	BF_4	2.2975(8) (× 2)	180
P*t*Bu_3[q]	Cl	2.323(1), 2.321(1)	180
PPh_3[r]	PF_6	2.314(2), 2.309(2)	177.4(1)
tmsp[d]	BF_4	2.3525(10)	179.72(7)

[a] Ref.[40a] [b] Ref.[40b] [c] Ref.[40c] [d] Ref.[40d] [e] Ref.[40e] [f] Ref.[40f] [g] Ref.[40g] [h] Ref.[40h] [i] Ref.[40i] [j] Ref.[40j] [k] Ref.[40k] [l] Ref.[40l] [m] Ref.[40m] [n] Ref.[40n] [o] Ref.[40o] [p] Ref.[40p] [q] Ref.[40q] [r] Ref.[40r]

Based on the above, the following trends in the bond lengths in [(Bn_3P)AuX] are apparent:

(1) Au–X are longer than the corresponding average values in $[AuX_2]^-$, the phosphane ligand being a stronger σ-donor than the halide ligand.[20] This holds for all of the

results in Table 3, except that for [(tmpp)CuBr] [tmpp = tris(2,4,6-trimethoxyphenyl)phosphane (2.177(1) < 2.22 Å); see below].

Table 3. M–P and M–X bond lengths [Å] in [$(R_3P)MX$] (M = Cu, Au or Ag; X = Cl, Br or I).

PR_3	Cu–P	Cu–Cl	Au–P	Au–Cl	Ag–P	Ag–Cl
tmsp			2.27	2.28[a,b]		
tmpp	2.177(1)	2.118(2)[c]	2.25	2.30[d,e]	2.379(1)	2.342(1)[f]
PBn_3			2.23(1)	2.302(8)[g]		
PPh_3			2.2280(10)	2.2882(10)[h]		
	Cu–P	Cu–Br	Au–P	Au–Br	Ag–P	Ag–Br
tmsp	2.193(2)	2.225(1)[i]	2.28	2.39[c]		
tmpp	2.197(3)	2.177(1)[c]	2.255(4)	2.413(2)[d]	2.374(2)	2.448(1)[f]
PBn_3			2.229(4)	2.404(10)[g]		
PPh_3			2.2366(8)	2.4059(4)[h]		
	Cu–P	Cu–I	Au–P	Au–I	Ag–P	Ag–I
tmsp			2.292(3)	2.544(1)[b]		
tmpp	2.188(4)	2.417(2)[j]	2.239(7)	2.586(2)[d]		
PBn_3						
PPh_3			2.2533(5)	2.5633(2)[h]		

[a] Ref.[41a] [b] Ref.[41b] [c] Ref.[41c] [d] Ref.[41d] [e] Ref.[41e] [f] Ref.[41f] [g] Ref.[41g] [h] Ref.[41h] [i] Ref.[41i] [j] Ref.[41j]

(2) Au–P are shorter than in [$Au(PBn_3)_2$]$^+$. The reason for this is the same as in (1). The corresponding relationship is true for all cases in Table 1.

(3) Au–P increases from X = Cl to Br (to I). This is sensible because AuBr is expected to be a weaker σ-acceptor than AuCl (etc.). This is true for all of the cases in Table 3 (except those for the adducts of tmpp: [(tmpp)CuX] [X = Br, I; [2.188(4) < 2.197(3) Å]] and [(tmpp)AgX] [X = Cl, Br; [2.374(2) < 2.379(1) Å]] – see below).

For those unidentate phosphane ligands, PR_3, which form 1:1 MX:PR_3 adducts across all of M = Cu, Ag or Au and X = Cl, Br or I, namely, tmpp, and trimesitylphosphane, (tmsp), M–P distances in the [$M(PR_3)_2$]$^+$ cations have been established for Cu, Au, Ag to the extent presented in the summary in Table 2.

These comparisons highlight the exceptional nature of the tmpp complexes, which is probably due to the fact that the methoxy oxygen atoms are involved to a small extent in coordination to the metal, particularly in the Cu and Ag cases. This, in turn, highlights a significant difference between the tmpp and PBn_3 ligands, both of which have been used to stabilise two-coordinate coinage metal complexes. In the case of PBn_3 this stabilisation is achieved by interaction of the R groups of the two ligands with each other, whereas in the case of tmpp it is through interaction of the R groups with the metal ion.

While isolation of the 1:2 $AuBF_4$:PBn_3 adduct in its ionic form is not surprising, the occurrence of the chloride in that form rather, than, e.g. mononuclear [$(Bn_3P)_2AuCl$], is unusual, given the precedents for [$(Ph_3P)_2AuX$] (X = Cl, Br, I)[21] and supports previous speculation concerning the bestowal of some stability via the embracing concept arising from the coordination of a pair of PBn_3 ligands, even if insufficient to result in ligand disproportionation of the 1:1 array; it may also be consequent on interference between the pair of ligands in the neutral complex. However, the structural definition of species such as [$(Bn_3P)_2Cu\{(btz)BH_2(btz)\}$] (btz = benzotriazolyl),[22] in which the smallest of the coinage metal(I) species is found to lie in a trigonal planar environment, with Cu–P only slightly increased over the [$Cu(PBn_3)_2$]$^+$ value [Cu–P 2.2380(5), 2.2463(6) Å, P–Cu–P 139.23(2)°; Cu–N 2.021(2), N–Cu–P 112.56(5), 108.09(5)° [Σ_{Cu} 359.9°] is indicative of considerable flexibility in the situation.

IR Spectra

The mid-IR spectra mainly contain bands due to the coordinated PBn_3 ligand, and they are very similar for all of the complexes. However, the spectra of the mono- and dihydrates of [$Au(PBn_3)_2$]Cl show some differences that confirm that these are distinct compounds. The spectra of these compounds in the 4000–2500 cm^{-1} region, where the ν(OH) and ν(CH) bands occur, are shown in Figure 2. While the ν(CH) bands (3100–2800 cm^{-1}) for the two complexes are almost identical, the ν(OH) bands (3500–3200 cm^{-1}) show differences that are consistent with the different number of water molecules present. The bands in the monohydrate [$Au(PBn_3)_2$]Cl·H_2O [Figure 2, (a)] are better resolved and occur at higher wavenumber than those in the dihydrate [$Au(PBn_3)_2$]Cl·$2H_2O$ [Figure 2, (b)]. These differences, suggest a lesser degree of hydrogen bonding between the water molecules in the monohydrate, in consequence of the greater degree of separation of the water molecules in this complex. The greater overall intensity of the ν(OH) bands in the dihydrate is consistent with the greater number of water molecules in this compound.

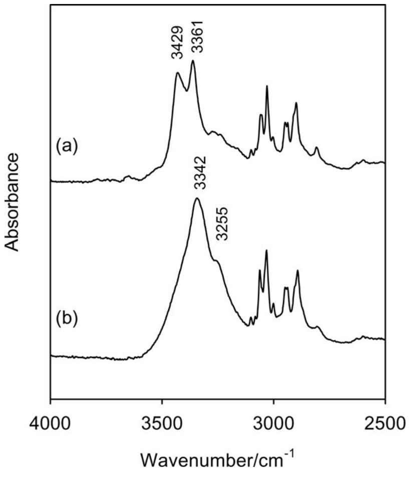

Figure 2. IR spectra of (a) [$Au(PBn_3)_2$]Cl·H_2O; (b) [$Au(PBn_3)_2$]Cl·$2H_2O$ in the 4000–2500 cm^{-1} region. The bands assigned to ν(OH) modes are labelled with their wavenumbers.

The far-IR spectra of [$(Bn_3P)AuX$] (X = Cl, Br) are shown in Figure 3. The ν(AuX) bands occur at 320 and 227 cm^{-1}, respectively. These assignments are based on the strong halogen dependence of the frequencies and on assignments for analogous [LAuX] complexes with aliphatic or aromatic phosphane ligands L.[23–26] In the case of the chloride complex the ν(AuCl) band overlaps with a ligand band at about 315 cm^{-1}, but the relatively high intensity of the ν(AuCl) peak allows unambiguous assignment of this band. The ν(AuX) wavenumbers are compared with those for a number of [(R_3P)AuX] complexes in Table 4. The values for [(Bn_3P)AuX] lie between those for the corresponding PMe_3 and PPh_3 complexes. This type of complex provides an opportunity to observe the *trans*-influence of the ligand L on the ν(AuX) vibrational frequency, without complications arising from the presence of other ligands in the metal atom coordination sphere,[26] and the order $PMe_3 > PBn_3 > PPh_3$ of *trans*-influence as reflected in the data in Table 2 seems reasonable in relation to the expected change in the inductive effect of the organic substituents in the phosphane ligands and the effect of this on the σ-donor basicity of the ligands. Although complicated by overlap with the ligand band at 315 cm^{-1}, the ν(AuCl) band in [(Bn_3P)AuCl] shows evidence of incompletely resolved splitting above 320 cm^{-1}, which is probably due to the presence of multiple inequivalent molecules in the crystal structure (see above).

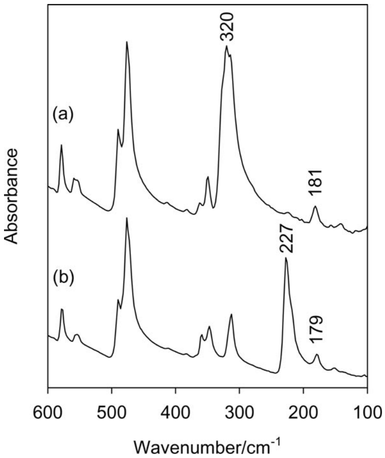

Figure 3. Far-IR spectra of [(Bn_3P)AuX]; (a) X = Cl; (b) X = Br.

Table 4. Wavenumbers [cm^{-1}] of the ν(AuX) modes in some [(R_3P)AuX] complexes.

Complex	ν(AuCl)	ν(AuBr)
[(Bn_3P)AuX][a]	320	227
[(Me_3P)AuX][b]	312	214
[(Ph_3P)AuX][c]	329	234
[(tmpp)AuX][d]	313	218

[a] This work. [b] Ref.[23] [c] Ref.[25] [d] Ref.[24]

The far-IR spectra of [Au(PBn_3)$_2$]X, (X = Cl·2H_2O, I, BF_4) are shown in Figure 4. The absence of any ν(AuX) bands is consistent with the ionic structures determined crystallographically for the X = Cl, BF_4 salts and supports the proposed ionic formulation for the X = I case. All of the bands observed in these spectra are due to the [Au(PBn_3)$_2$]$^+$ cation that each of them contains, with the possible exception of the band at 519 cm^{-1} in [Au(PBn_3)$_2$]BF_4, which is probably due to the $\nu_4(T_2)$ mode of BF_4^-. Most of the [Au(PBn_3)$_2$]$^+$ bands in this region are due to the coordinated PBn_3 ligand, but a ν(AuP) band might also occur in the region below 200 cm^{-1}.[26] Weak bands at about 180 cm^{-1} in the spectra of both [(Bn_3P)AuX] (Figure 3) and [Au(PBn_3)$_2$]X (Figure 4) are in the right region to be so assigned, but the multiplicity of such bands in the case of the [Au(PBn_3)$_2$]X complexes suggests that there is at least some contribution from vibrations of the coordinated PBn_3.

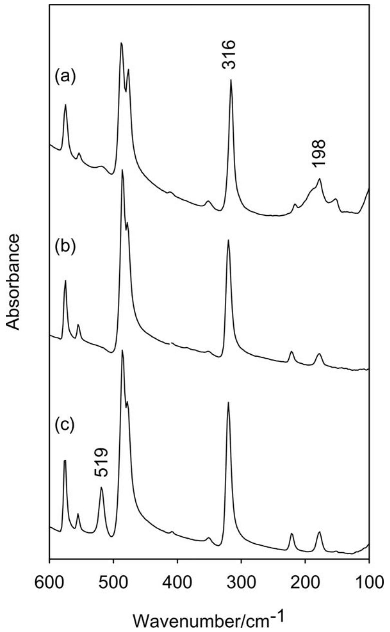

Figure 4. Far-IR spectra of [Au(PBn_3)$_2$]X, (a) X = Cl·2H_2O; (b) X = I, (c) X = BF_4.

NMR Spectra

The ^{31}P CP MAS spectra of [(Bn_3P)AuX] (X = Cl, Br) at 11.7 T are shown in Figure 5. The signals in both show partially resolved splittings that are most likely due to the presence of multiple inequivalent molecules in the crystal structure (see above). The mean chemical shifts of the multiplets are 41 and 42 ppm, respectively. The increase in chemical shift from the chloride to the bromide is consistent with, but rather lower than, those previously reported for the corresponding PPh_3 and PMe_3 compounds.[23,27]

The ^{31}P CP MAS spectra of [Au(PBn_3)$_2$]X (X = Cl·H_2O, Cl·2H_2O, I, BF_4) at 11.7 T are shown in Figure 6. The spectrum of the chloride monohydrate shows two well-resolved signals, consistent with the presence of two distinct cations in the asymmetric unit (see Crystal Structures above). The spectrum of the chloride dihydrate shows a well-resolved multiplet structure that will be discussed further below. The chemical shifts for the four compounds are 60.9 (av.), 63.8 (av.), 59.0, 58.2 ppm, respectively. These are about 20 ppm higher than for the 1:1 complexes [(Bn_3P)AuX], reflecting the change in coordination environment from P–Au–X in the 1:1 compounds to P–Au–P in the 1:2 compounds. The fact that the chemical shifts for [Au(PBn_3)$_2$]Cl·2H_2O and

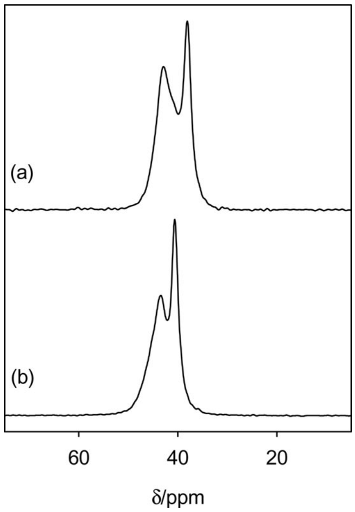

Figure 5. ^{31}P CP MAS spectra of $[(Bn_3P)AuX]$ at $B = 11.7$ T, (a) X = Cl, (b) X = Br.

$[Au(PBn_3)_2]I$ are very close to those of the corresponding BF_4 complex lends further support to the proposed ionic structure of these compounds.

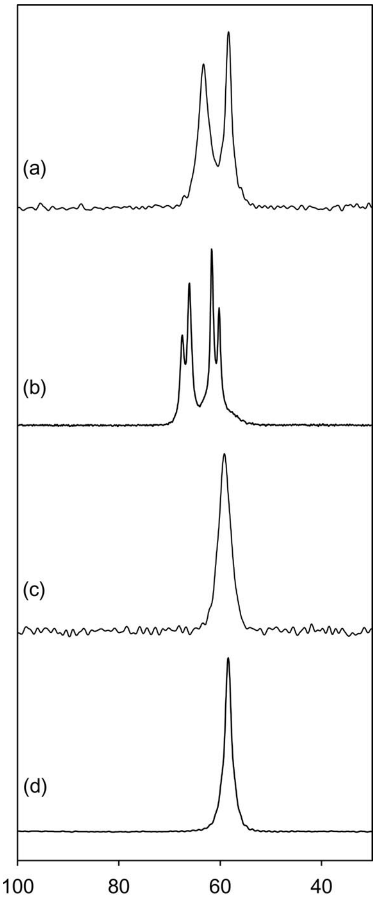

Figure 6. ^{31}P CP MAS spectra of $[Au(PBn_3)_2]X$ at $B = 11.7$ T; (a) X = $Cl{\cdot}H_2O$; (b) X = $Cl{\cdot}2H_2O$; (c) X = I; (d) X = BF_4.

In the case of $[Au(PBn_3)_2]Cl{\cdot}2H_2O$ a quartet signal is observed [Figure 6, (b)]. We have considered two possible explanations for this multiplet structure:

(a) Splitting due to $^1J(^{31}P\text{-}^{197}Au)$ coupling. In a number of cases in the past it has been shown that splitting due to $^1J(^{31}P\text{-}^{197}Au)$ coupling can be observed in the MAS ^{31}P NMR spectra of gold(I) complexes containing phosphane ligands.[23,27–29] The expected form of the MAS NMR spectrum of a spin $I = 1/2$ nucleus coupled to a quadrupolar ($I > 1/2$) nucleus has been discussed by Menger and Veeman,[30] who showed that the form of the spectrum depends on the parameters $R = D/J$ (where D is the dipolar coupling constant and J is the indirect or scalar coupling constant) and $K = -3\chi/4I(2I - 1)Z$ (where χ is the quadrupole coupling constant and Z the Zeeman interaction for the quadrupolar nucleus of spin I). In the case of ^{31}P coupled to ^{197}Au ($I = 3/2$), the parameter R is small, and an equally spaced four-line pattern [spacing = $^1J(^{31}P\text{-}^{197}Au)$] of the ^{31}P spectrum is predicted for small K. This has been observed in the ^{31}P MAS NMR spectra of the compounds $[Au(dppey)_2]X$ [dppey = *cis*-1,2-bis(diphenylphosphanyl)ethene; X = NO_3 or PF_6], where the near tetrahedral coordination of the Au is assumed to result in a ^{197}Au quadrupole coupling constant close to zero,[28] and hence corresponds to $K \approx 0$. For the opposite case of large K a doublet pattern is predicted with a spacing of about 1.65 times the $^1J(^{31}P\text{-}^{197}Au)$ coupling constant,[30,31] and this has been observed in the linear two-coordinate complexes $[(Ph_3P)AuX]$ (X = Cl, Br, I),[27] $[(Me_3P)AuX]$ (X = Cl, I)[23] and $[(Me_3P)_2Au]X$ (X = Cl, Br).[32] In these cases the linear coordination of the gold atom and the large quadrupole moment of the gold nucleus results in a large ^{197}Au quadrupole coupling constant and hence a large value of K (estimated to be ≈ 34).[23] However, this splitting is not found in all cases where it might appear. Thus, it is not observed in the case of [(tmpp)AuX],[24] despite the close similarity between these and the corresponding PPh_3 complexes or $[(Cy_3P)AuX]$. Also, it is not observed in $[(Me_3P)AuBr]$ despite the fact that the doublet splitting is clearly resolved in the corresponding Cl and I compounds.[23] In $[Au(PMe_3)_2]X$ the doublet splitting is observed for X = Cl, Br but not for X = I.[32] There are clearly very subtle structural effects that influence the ^{197}Au relaxation processes, which determine whether the coupling is observed or not. In the present study, the splitting observed in the spectrum of $[Au(PBn_3)_2]Cl{\cdot}2H_2O$ is of the right magnitude to be attributed to $^1J(^{31}P\text{-}^{197}Au)$ coupling. The unequally spaced quartet pattern is exactly what is expected in the transition from the equally spaced quartet corresponding to $K = 0$ to the doublet corresponding to large K.[30] The weighted average separation between the two outermost partially collapsed doublets is about 1100 Hz, corresponding to $^1J(^{31}P\text{-}^{197}Au) \approx 670$ Hz. This is similar in magnitude to the values obtained previously for $[(Ph_3P)AuX]$ (412–521 Hz),[27] $[(Me_3P)AuX]$ (553–648 Hz)[23] and $[Au(PMe_3)_2]X$ (ca. 340 Hz).[32]

(b) Splitting due to $^2J(^{31}P\text{-}^{31}P)$ coupling between two inequivalent phosphorus atoms. This would result in an AB quartet pattern, and spectra of this kind have previously been observed for $[(Cy_3P)_2AuX]$ (X = Br, I).[33] In the case of $[Au(PBn_3)_2]Cl\cdot 2H_2O$ this would imply the presence of noncentrosymmetric $[Au(PBn_3)_2]^+$ cations in the structure in which the two phosphorus atoms are inequivalent, in contrast to the case of $[Au(PBn_3)_2]Cl\cdot H_2O$, in which the two phosphorus atoms in each of the two $[Au(PBn_3)_2]^+$ ions in the structure are equivalent (see Crystal Structures, above).

In order to distinguish between the above two possibilities, the spectrum of $[Au(PBn_3)_2]Cl\cdot 2H_2O$ was run at two different field strengths, 9.4 and 7.0 T, and the results are shown as a frequency plot in Figure 7. The predicted changes in the frequency plot spectra with the decrease in field strength from 9.4 to 7.0 T (400 to 300 MHz proton NMR frequency) are as follows:

(a) ^1J(AuP) case: The K parameter will increase by a factor of 1.33, so the splitting between the outer doublets will decrease while the separation of the doublet centres will remain unchanged.

(b) ^2J(PP) case: The splitting of the outer doublets will remain unchanged while the separation of the doublet centres will decrease by a factor of 0.75. The intensity of the inner relative to the outer lines will change from 1.8 to 2.3.

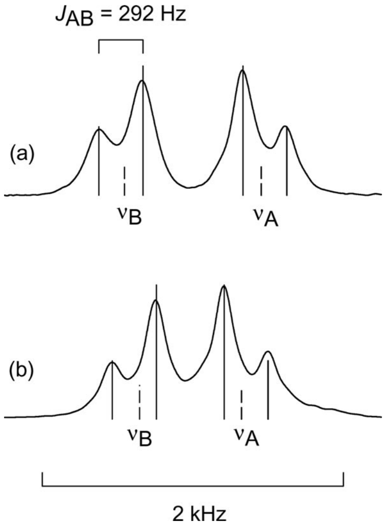

Figure 7. ^{31}P CP MAS spectra of $[Au(PBn_3)_2]Cl\cdot 2H_2O$, (a) B = 9.4 T; (b) B = 7.0 T. The superimposed stick plots are the calculated AB spectra for the two fields, with $\delta_A = 60.9$, $\delta_B = 66.6$, J_{AB} = 292 Hz.

It is clear from Figure 7 that the results fit case (b) very well, while the behaviour predicted for case (a) is not observed at all. The superimposed stick plots are the calculated AB spectra for the two fields, with $\delta_A = 60.9$, $\delta_B = 66.6$, J_{AB} = 292 Hz. The coupling constant is of a similar magnitude to ^2J(PP) values found in similar systems, e.g. 270 Hz in $[(PCy_3)_2AuBr]$,[33] and ca. 300 Hz in $[Au_2(Ph_2P(CH_2)_2PEt_2)_2]Cl_2$.[34] The observation of ^2J(PP) coupling in $[Au(PBn_3)_2]Cl\cdot 2H_2O$ indicates that the cations in this complex are noncentrosymmetric with two inequivalent phosphorus atoms.

Conclusions

Two-coordinate, tribenzylphosphane (PBn_3) complexes of gold(I), $[(Bn_3P)AuX]$ (X = Cl and Br), have been synthesised. The compounds contain linear P–Au–X arrays, each structure containing three independent $[(Bn_3P)AuX]$ entities lying on the three threefold axes of space group $P3c1$. ν(AuX) bands in the far-IR spectra of $[(Bn_3P)AuX]$ are assigned at 320 and 227 cm^{-1} for X = Cl and X = Br, respectively. In contrast, the 1:1 adducts previously characterised for copper(I) take the form $[Cu(PBn_3)_2][CuX_2]$ and contain linear P–M–P cationic and X–Cu–X anionic moieties.[2,3] In this study, similar linear cations are found in the compounds $[Au(PBn_3)_2]X\cdot nH_2O$ (X = Cl, n = 1 or 2; X = I and BF_4, n = 0). The ^{31}P CP MAS NMR spectra of all the new compounds are reported and discussed. The spectrum of the cationic monohydrate, $[Au(PBn_3)_2]Cl\cdot H_2O$, shows two well-resolved signals consistent with the presence of two distinct cations in the asymmetric unit, each with equivalent phosphorus atoms. In contrast, the dihydrate, $[Au(PBn_3)_2]Cl\cdot 2H_2O$, shows a well-resolved multiplet due to ^2J(PP) coupling, which indicates that the cations in this complex are noncentrosymmetric with two inequivalent phosphorus atoms.

Experimental Section

Synthesis: Tetrahydrofuran (thf) was distilled from sodium/benzophenone, dimethylformamide (dmf) was distilled from molecular sieves and other solvents were dried by standard procedures. Tribenzylphosphane (PBn_3) was prepared according to the method of ref.[35] or obtained from Sigma Aldrich Co. Bis(acetonitrile)gold tetrafluoroborate $[Au(NCCH_3)_2]BF_4$ was prepared from gold powder and $NOBF_4$ by an adaptation of the method described in the literature for the perchlorate salt[36a] while $[Bu_4N][AuX_2]$ (X = Cl, Br, I) were prepared according to literature methods.[36b] The 1:1 adducts with gold(I) chloride and bromide were prepared following the method of ref.[7a], by the dissolution of millimolar quantities of $[Bu_4N][AuX_2]$ (X = Cl, Br) and PBn_3 in 1:1 ratio in ca. 10 mL warm dmf as described in detail below, well-formed crystals depositing on standing. With the iodide, tribenzylphosphane oxide only was deposited and identified crystallographically, as described in a footnote.[37] All reactions were carried out under dinitrogen.

Chlorotribenzylphosphanegold(I) $[(Bn_3P)AuCl]$: A mixture of $[Bu_4N][AuCl_2]$ (0.255 g, (0.5 mmol) and tribenzylphosphane (0.152 g, 0.5 mmol) in 7.5 mL dimethylformamide was warmed to 60 °C under N_2 with stirring for 15 min. Colourless crystals deposited on cooling to room temperature and were filtered and dried under vacuum to give 0.12 g (45% yield). $C_{21}H_{21}AuClP$ (536.79): calcd. for C 46.99, H 3.94; found C 47.03, H 3.93.

Bromotribenzylphosphanegold(I) $[(Bn_3P)AuBr]$: A warmed solution of tribenzylphosphane (0.152 g, 0.5 mmol) in 3 mL of dmf was slowly added, under N_2, to a warmed (60 °C) solution of $[Bu_4N][AuBr_2]$ (0.30 g, 0.5 mmol) in 2 mL of dmf. After 5 min stirring at 60 °C the reaction mixture was cooled to room temperature. Colourless crystals deposited on cooling and were filtered and dried under vacuum to give 0.063 g (22% yield). $C_{21}H_{21}AuBrP$ (581.24): calcd. C 43.40, H 3.64; found C 43.45, H 3.70.

Bis(tribenzylphosphane)gold(I) Chloride Dihydrate $[Au(PBn_3)_2]Cl\cdot 2H_2O$: A mixture of $[Bu_4N][AuCl_2]$ (0.128 g, 0.25 mmol) and tribenzylphosphane (0.155 g, 0.51 mmol) in 5 mL tetrahydrofuran was warmed to 60 °C under N_2 with stirring for 5 min. The product precipitated on cooling to room temperature and was filtered and dried under vacuum to give 0.195 g of a colourless solid (93% yield). $C_{42}H_{46}AuClO_2P_2$ (877.19): calcd. C 57.51, H 5.29; found C 57.43, H 5.27. Mp 233–235 °C (decomp.).

Bis(tribenzylphosphane)gold(I) Chloride Monohydrate $[Au(PBn_3)_2]Cl\cdot H_2O$: Pentane was diffused into a solution containing 30 mg of $[Au(PBn_3)_2]Cl\cdot 2H_2O$ dissolved in 8 mL dimethylformamide to give X-ray quality crystals of a colourless product. $C_{42}H_{44}AuClOP_2$ (859.17): calcd. C 58.71, H 5.16; found C 58.63, H 5.14.

Bis(tribenzylphosphane)gold(I) Iodide $[Au(PBn_3)_2]I$: A mixture of $[Bu_4N][AuI_2]$ (0.173 g, 0.25 mmol) and tribenzylphosphane (0.155 g, 0.51 mmol) and 5 mL tetrahydrofuran was warmed to 60 °C under N_2 with stirring for 5 min. The product precipitated on cooling to room temperature and was filtered to give a colourless solid which was recrystallised from nitromethane and dried under vacuum to give 0.08 g of a white crystalline powder (34%). $C_{42}H_{42}AuIP_2$ (932.61): calcd. C 54.09, H 4.54: found C 54.06, H 4.64.

Bis(tribenzylphosphane)gold(I) Tetrafluoroborate $[Au(PBn_3)_2]BF_4$: A solution of bis(acetonitrile)gold tetrafluoroborate (0.12 g, 0.355 mmol) in 40 mL acetonitrile was added to tribenzylphosphane (0.216 g, 0.708 mmol) and the reaction mixture refluxed under N_2 for 1.5 h. The resulting white solid was recrystallised from dmf and dried under vacuum to give 0.20 g of off-white crystals (63%). $C_{42}H_{42}AuBF_4P_2$ (892.51): calcd. C 56.52, H 4.74; found C 56.48, H 4.69.

Structure Determinations: Full spheres of 'low'-temperature CCD area-detector diffractometer data were measured (monochromatic Mo-K_α radiation, λ = 0.71073 Å) yielding N_{total} reflections, these merging to N unique [R_{int} cited] after 'empirical'/multiscan absorption correction (proprietary software), N_o with $I > 4\sigma(I)$ being considered 'observed'; all data were used in the full-matrix least-squares refinements on F^2, refining anisotropic displacement parameter forms for the non-hydrogen atoms, hydrogen atom treatment following a 'riding' model. Neutral atom complex scattering factors were employed within the context of the SHELXL 97 program.[38] Friedel data were retained distinct and x_{abs} refined where appropriate. Pertinent results are given in the Tables and Figures, the latter showing 50% probability amplitude displacement ellipsoids for the non-hydrogen atoms, hydrogen atoms (where shown) having arbitrary radii of 0.1 Å. See Table 5. CCDC-617832, -617833, -696892 and -696893 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Infrared Spectroscopy: IR spectra were recorded at 4 cm^{-1} resolution on dry powders using a Perkin–Elmer Spectrum 400 FT-IR spectrometer equipped with a Universal ATR sampling accessory. Far-infrared spectra were recorded at 4 cm^{-1} resolution with a Nicolet 8700 FTIR spectrometer on samples suspended in Polythene disks.

NMR Spectroscopy: ^{31}P Cross-polarisation, magic-angle-spinning (CPMAS) NMR spectroscopic data were acquired at 7.0, 9.4 and 11.7 T on Varian Infinity Plus-300, Bruker DSX-400 and Bruker Avance III-500 spectrometers operating at ^{31}P frequencies of 121.47, 161.92 and 202.41 MHz, respectively. All spectra were obtained with conventional cross-polarisation (CP) methods and a MAS frequency of ca. 10 kHz using a Bruker 4 mm double-air-bearing probe. The typical pulse parameters employed were: a ^{1}H $\pi/2$ pulse time of 3.5 µs, a Hartmann–Hahn contact period of 10 ms, a recycle delay of 20 s and a ^{1}H decoupling field strength during acquisition of ca. 80 kHz. All data were referenced to 85% H_3PO_4 via an external reference of $(NH_4)(H_2PO_4)$ (δ = 1.0 ppm), which was also used to set the Hartmann–Hahn match condition.

Table 5. Crystal and refinement data for the complexes.

Compound	$[(Bn_3P)AuCl]$	$[(Bn_3P)AuBr]$	$[Au(PBn_3)_2]Cl\cdot H_2O$	$[Au(PBn_3)_2]BF_4$
Empirical formula	$C_{21}H_{21}AuClP$	$C_{21}H_{21}AuBrP$	$C_{42}H_{44}AuClOP_2$	$C_{42}H_{42}AuBF_4P_2$
M [Da]	536.76	581.22	859.13	892.47
T [K]	100(2)	170(2)	203(2)	200(2)
Crystal system	trigonal[a]	trigonal[a]	triclinic	monoclinic
Space group	$P3c1$ (No. 158)	$P3c1$ (No. 158)	$P\bar{1}$(No. 2)	$C2/c$ (No. 15)
a (Å)	13.926(1)	13.9414(4)	9.8244(1)	14.1316(2)
b [Å]	13.926(1)	13.9414(4)	12.9542(1)	13.4801(1)
c [Å]	17.239(3)	17.6558(5)	15.8826(2)	19.4918(1)
α [°]	90	90	84.133(1)	90
β [°]	90	90	72.441(1)	92.814(2)
γ [°]	120	120	71.549(1)	90
V [Å^3]	2895.3(6)	2971.9(1)	1828.04(4)	3708.62(6)
Z	6	6	2	4
μ [Mo-K_α] [mm^{-1}]	7.8	9.5	4.2	4.1
$\rho_{\text{calcd.}}$ [g cm^{-3}]	1.84_7	1.94_9	1.56_1	1.59_8
$2\theta_{\text{max.}}$ [°]	74	68	55	54
N_{total}	110703	66499	17359	10234
N [R_{int}]	9661 [0.056]	7245 [0.034]	7898 [0.022]	4004 [0.021]
N_o	4357	4961	6246	3301
$R1$	0.028	0.026	0.022	0.022
$wR2$	0.066	0.064	0.045	0.044
$x_{\text{abs.}}$	–0.045(8)	0.047(10)	n/a	n/a
S	0.96	1.00	1.05	1.10

[a] The cell dimensions are remarkably similar to those of the hexagonal setting of the 1:1 CuBr:PBn_3 adduct [a = 13.829(1), c = 17.429(2) Å, V = 2887 Å^3 at 298 K] which takes the form $[Cu(PBn_3)_2][CuBr_2]$ in space group $R\bar{3}$.[2]

Acknowledgments

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[9] (Cu,Cl) From those values of Table 1 of ref.[8] with s.u. values better than 0.003 Å, 2.09 Å would seem a reasonable value to adopt.

[10] (Cu,Br) cf. ref.[8], we adopt 2.22 Å.

[11] (Cu,I) a) N. P. Rath, E. M. Holt, *J. Chem. Soc., Chem. Commun.* **1986**, 311 [2.394(2), 2.383(1) Å]; b) C. Di Nicola, Effendy, F. Fazaroh, C. Pettinari, B. W. Skelton, N. Somers, A. H. White, *Inorg. Chim. Acta* **2005**, *358*, 720 [2.388(2), 2.380(2) Å]; c) M. Amirnasr, A. D. Khalaji, L. R. Falvello, *Inorg. Chim. Acta* **2006**, *359*, 713 [2.4178(5), 2.4340(6) Å]. We use 2.39 Å as an appropriate value.

[12] (Ag,Cl) a) G. Helgesson, S. Jagner, *Inorg. Chem.* **1991**, *30*, 2574 [2.328(2), 2.330(2) Å]; b) G. Exarchos, S. C. Nyburg, S. D. Robinson, *Polyhedron* **1998**, *17*, 1257 [2.304(1), 2.306(4) Å]; c) A. A. D. Tulloch, A. A. Danopoulos, G. J. Tizzard, S. J. Coles, M. B. Hursthouse, R. S. Hay-Motherwell, W. B. Motherwell, *Chem. Commun.* **2001**, 1270 [2.342(14), 2.372(12) Å; Cl–Ag–Cl 164.1(1)°]; d) the isolated species in P. de Frémont, N. M. Scott, E. D. Stevens, T. Ramnial, O. C. Lightbody, C. L. B. Macdonald, J. A. C. Clyburne, C. D. Abernethy, S. P. Nolan, *Organometallics* **2005**, *24*, 6301 gives 2.534(5) Å, which seem strangely high. We adopt 2.33 Å.

[13] (Ag,Br) a) J. A. Cras, J. H. Noordik, P. T. Beurskens, A. M. Verhoeven, *J. Cryst. Mol. Struct.* **1971**, *1*, 155 [2.450(5) Å]; b) S. K. Schneider, W. A. Herrmann, E. Herdtweck, *Z. Anorg. Allg. Chem.* **2003**, *629*, 2363 [2.4261(7) Å]. We adopt 2.44 Å.

[14] (Ag,I) A. D. Khalaji, R. Welter, *Inorg. Chim. Acta* **2006**, *359*, 4403 [2.9244(5) Å]. The value 2.9244(5) Å for Ag–I is for the single compound [Cu(Phca$_2$en)$_2$][AgI$_2$], seemingly the only one to date that has been shown to contain discrete [AgI$_2$]$^-$ species. However, the [AgI$_2$]$^-$ anions in the crystal structure are associated with some of the phenyl rings in the cations, producing a one-dimensional network of [Cu(Phca$_2$en)$_2$][AgI$_2$] components. This interaction possibly weakens and lengthens the Ag–I bonds. Extrapolation from data for the other [MX$_2$]$^-$ species suggests an Ag–I bond length of ca. 2.61 Å might be expected.

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