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Gold(I)-Clustering at a Primary Arylphosphine with Bulky Substituents: $[2,4,6\text{-}(Me_3C)_3C_6H_2P(AuPR_3)_n]^{(n-2)+}$ (R = *t*-Bu, Ph; *n* = 2–4) Complexes and Crystal Structure of the Species with *n* = 3 and R = Ph

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Reaction of the primary phosphine $ArPH_2$ (Ar = $2,4,6\text{-}(Me_3C)_3C_6H_2$) with $[O(AuL)_3]^+BF_4^-$ reagents yields the trinuclear gold complexes $[ArP(AuL)_3]^+BF_4^-$ (**1**, L = PPh_3; **2**, L = P-*t*-Bu_3). A further equivalent of $Ph_3PAu^+BF_4^-$ can be added to **1** to give $[ArP(AuPPh_3)_4]^{2+}(BF_4^-)_2$ (**3**), whereas for **2** the analogous reaction leads to decomposition and formation of $[(t\text{-}Bu_3P)_2Au]^+BF_4^-$. The neutral intermediate $[ArP(AuP\text{-}t\text{-}Bu_3)_2]$ (**4**) can be obtained in a mixture with **2** upon treatment of $ArPH_2$ with the corresponding oxonium reagent in a molar ratio of 3:2. All products are colorless air-stable solids, which have been characterized by analytical and spectroscopic data, including an X-ray crystal structure analysis for complex **1**. Crystals of **1**·$2CH_2Cl_2$ from CH_2Cl_2/diethyl ether are triclinic, $P\bar{1}$, with a = 13.520(1) Å, b = 13.901(1) Å, c = 20.346(2) Å, α = 85.57(1)°, β = 87.23(1)°, γ = 87.23(1)°, V = 3678.2 Å^3, d_{calc} = 1.73 g/cm^3, and Z = 2. In the cations of **1**, the phosphorus atom is attached to a single gold atom on one side of the ArP plane and to a pair of gold atoms on the other. Clearly, the two ortho *t*-Bu groups separate the gold atom triad, which is known to form a triangle in the absence of steric hindrance. In solution, rapid site exchange renders the LAu units NMR-equivalent. A symmetrical structure with two Au_2 pairs at the pentacoordinate phosphorus atom is assigned to complex **3**, while for **4** the digold(I) arylphosphide stoichiometry indicates a three-coordinate phosphorus atom.

Introduction

Novel polynuclear gold complexes of the general type $[E(Au^IL)_n]$[1] have been discovered in recent years, where attractive interactions between closed-shell gold(I) atoms ([Xe]$4f^{14}5d^{10}$) contribute to the ease of formation and the stability of these complexes. These compounds contain an interstitial main group element E between two to six AuL units (L = tertiary phosphine ligand). The binding forces between the gold atoms act perpendicular to the principal axis of the linear EAuL units. This peripheral bonding is unexpected for the electronic configuration of gold but could be explained and even predicted by theoretical studies, based on relativistic effects.[2] Thus even hypercoordinated species of the types $[C(AuL)_6]^{2+}$,[3] $[C(AuL)_5]^+$,[4] and $[RC(AuL)_4]^{2+}$ [5] with interstitial carbon and $[N(AuL)_5]^{2+}$ [6] with interstitial nitrogen are now well established. Chalcogens and halogens form related onium species like $[E(AuL)_3]^+$ (E = O, S, Se) and $[Cl(AuL)_2]^+$.[7] With phosphorus, highly charged clusters like $[P(AuL)_6]^{3+}$ (together with the species $[P(AuL)_5]^{2+}$ and $[P(AuL)_4]^+$)[8,9] could be detected, and for arsenic most unusual square-pyramidal cations $[As(AuL)_4]^+$,[10] whose structure is at variance with the Le Bel/van't Hoff rule for sp^3 hybrids, are formed in favor of short Au–Au contacts, whereas the analogous ammonium compound has a classical tetrahedral configuration at nitrogen.[11]

Strangely enough, considering this background, aryltriauriophosphonium cations $[RP(AuPPh_3)_3]^+$ (R = C_6H_5, 2-$CH_3C_6H_5$)[9] have a tetrahedral coordination at phosphorus with long intermetallic distances. However, electrophilic addition of a further Ph_3PAu^+ unit produces novel tetraaurated species $[RP(AuPPh_3)_4]^{2+}$ with a square-pyramidal Au_4P core and short Au–Au distances.[12] In this type of compound, the apical organic group at phosphorus plays an important role. If small and electronegative, it makes the PAu_4 core more susceptible to nucleophilic degradation. If large and electropositive, it not only is sterically and electronically protective but also helps to bring the gold atoms close together and thus assists in building the metal cluster. In the present study, therefore, one of the most bulky organic groups was chosen in order to probe these effects.

Experimental Section

All reactions were performed under an atmosphere of purified nitrogen by using standard Schlenk and vacuum-line techniques. Methylene chloride was distilled from P_2O_5 prior to use. Tetrahydrofuran (THF) and diethyl ether were dried over a sodium/potassium alloy and distilled. (2,4,6-Tri-*tert*-butylphenyl)phosphine[13] and $[O(AuPPh_3)_3]^+BF_4^-$ [14] were prepared according to reported methods. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on JEOL GX 270 and JEOL GX 400 NMR spectrometers. ^1H chemical shift data refer to deuterated solvents as internal standards, and ^{31}P shift data are referenced to external 85% aqueous H_3PO_4. Mass spectra were obtained using a Varian Mat 90 spectrometer (positive FAB source; matrix material 4-nitrobenzyl alcohol). In elemental analyses, the carbon content is generally somewhat unreliable owing to carbide formation.

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(1) For a review see: Schmidbaur, H. *Gold. Bull.* **1990**, *23*, 11–21.
(2) Pyykkö, P.; Desclaux, J. P. *Acc. Chem. Res.* **1979**, *12*, 276–281.
(3) Scherbaum, F.; Grohmann, A.; Müller, G.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 463–465.
(4) Scherbaum, F.; Grohmann, A.; Huber, B.; Krüger, C.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1544–1546.
(5) Scherbaum, F.; Huber, B.; Müller, G.; Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1542–1544.
(6) Grohmann, A.; Riede, J.; Schmidbaur, H. *Nature* **1990**, *345*, 140–142.
(7) Jones, P. G.; Sheldrick, G. M.; Hädicke, E. *Acta Crystallogr., Sect. B* **1980**, *36*, 2777–2780. Lensch, C.; Jones, P. G.; Sheldrick, G. M. *Z. Naturforsch., B* **1982**, *37*, 944–947. Jones, P. G.; Sheldrick, G. M.; Uson, R.; Laguna, A. *Acta Crystallogr., Sect. B* **1980**, *36*, 1486–1488.
(8) Zeller, E.; Schmidbaur, H. *J. Chem. Soc., Chem. Commun.* **1993**, 69–70.
(9) Schmidbaur, H.; Weidenhiller, G.; Steigelmann, O. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 433–435.
(10) Zeller, E.; Beruda, H.; Kolb, A.; Bissinger, P.; Riede, J.; Schmidbaur, H. *Nature* **1991**, *352*, 141–143.
(11) Slovokhotov, Yu. L.; Struchkov, Yu. T. *J. Organomet. Chem.* **1984**, *277*, 143–146.
(12) Schmidbaur, H.; Zeller, E.; Weidenhiller, G.; Steigelmann, O.; Beruda, H. *Inorg. Chem.* **1992**, *31*, 2370–2372.
(13) Issleib, K.; Schmidt, H.; Wirkner, C. *Z. Anorg. Allg. Chem.* **1982**, *488*, 75–79.
(14) Nesmeyanov, A. N.; Perevalova, E. G.; Struchkov, Y. T.; Antipin, M. Y.; Grandberg, K. I.; Dyadchenko, V. P. *J. Organomet. Chem.* **1980**, *201*, 343–349.

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Table I. Crystallographic Data for **1**

formula	$C_{74}H_{78}Au_3BCl_4F_4Cl_4$
fw	1910.84
space group	$P\bar{1}$
a, Å	13.520(1)
b, Å	13.901(1)
c, Å	20.346(1)
α, deg	85.57(1)
β, deg	87.23(1)
γ, deg	87.23(1)
V, Å^3	3678.2
Z	2
d_{calc}, g/cm^3	1.725
μ(Mo Kα), cm^{-1}	62.39
radiation λ(Mo Kα), Å	0.701 69

Preparation of [2,4,6-$(Me_3C)_3C_6H_2P(AuPPh_3)_3]^+BF_4^-$ (1). A solution of 2,4,6-$(Me_3C)_3C_6H_2PH_2$ (78 mg, 0.28 mmol) in CH_2Cl_2 (10 mL) was added dropwise to a stirred solution of $[O(AuPPh_3)_3]^+BF_4^-$ (414 mg, 0.28 mmol) in CH_2Cl_2 (20 mL) at −78 °C. After 2 h of stirring, the yellowish solution was allowed to warm to ambient temperature, and the volatiles were removed in vacuo. The residue was washed with diethyl ether, recrystallized from a CH_2Cl_2/diethyl ether mixture (1:1), and dried in vacuo to give a colorless microcrystalline product. Yield: 480 mg (98.5%). Anal. Calcd (found) for $C_{72}H_{74}Au_3BF_4P_4$ (M_r = 1740.98): C, 49.67 (47.44); H, 4.28 (4.20); Au, 33.94 (32.30). ^1H NMR (270 MHz, CD_2Cl_2), δ: 7.22–7.54 (m, 47H, Ph + C_6H_2), 1.95 (s, 18H, *t*-Bu), 1.58 (s, 9H, *t*-Bu). $^{31}P\{^1H\}$ NMR (109 MHz, CD_2Cl_2), δ: 42.6 (B part of an AB_3 spin system, $^2J_{PP}$ = 250 Hz, PPh_3), −10.8 (A part of an AB_3 spin system, $^2J_{PP}$ = 250 Hz, PAu_3). MS, *m/e*: 1652.4 (M^+, 57.6%), 1192.4 ($M^+ - AuPPh_3$, 13.7%), 720.7 ($(Ph_3P)_2Au^+$, 89.1%), 458.9 (Ph_3PAu^+, 100%).

Preparation of [2,4,6-$(Me_3C)_3C_6H_2P(AuPPh_3)_4]^{2+}(BF_4^-)_2$ (3). Compound **1** was prepared as described above, except that **1** was left in solution and cooled again to −78 °C. Freshly prepared $Ph_3PAu^+BF_4^-$ (152 mg, 0.28 mmol) in THF (20 mL) was added to the vigorously stirred solution of **1**, and the mixture was kept at low temperature for about 2 h, then allowed to warm to ambient temperature, and added to ether (60 mL). The precipitate was crystallized from CH_2Cl_2/pentane (1:2). Yellow crystals formed in nearly quantitative yield. Anal. Calcd (found) for $C_{90}H_{89}Au_4B_2F_8P_5$ (M_r = 2287.05): C, 47.26 (46.03); H, 3.92 (3.99); Au, 34.45 (34.30). ^1H NMR (270 MHz, CD_2Cl_2), δ: 0.89 (s, 9H, *t*-Bu), 1.89 (s, 18H, *t*-Bu), 7.10–7.56 (m, 62H, Ph + C_6H_2). $^{31}P\{^1H\}$ NMR (147 MHz, CD_2Cl_2), δ: 37.67 (d, $^2J_{PP}$ = 195.2 Hz, PPh_3), −47.69 (quint, $^2J_{PP}$ = 195.3 Hz, PAu_4). MS, *m/e*: 1653.6 ($M^{2+} - AuPPh_3$, 19.2%), 1193.2 ($M^{2+} - 2AuPPh_3$, 4.8%), 721.0 ($(Ph_3P)_2Au^+$, 59.2%), 459.1 (PPh_3Au^+, 100%).

Preparation of [2,4,6-$(Me_3C)_3C_6H_2P(AuP$-*t*-$Bu_3)_3]^+BF_4^-$ (2) and [2,4,6-$(Me_3C)_3C_6H_2P(AuP$-*t*-$Bu_3)_2$] (4). A solution of $[O(AuP$-*t*-$Bu_3)_3]^+BF_4^-$ (364 mg, 0.28 mmol) in THF (15 mL) was treated with a solution of 2,4,6-$(Me_3C)_3C_6H_2PH_2$ (117 mg, 0.42 mmol) in the same solvent (5 mL) at −78 °C. Stirring was continued while the colorless mixture was warmed to ambient temperature after 3 h and then allowed to react for another 2 h at 20 °C. Addition of pentane (60 mL) gave a mixture of **2**, **4** and unreacted 2,4,6-$(Me_3C)_3C_6H_2PH_2$. Separation of **2** and **4** was impossible owing to very similar solubility properties. The reaction of $[O(AuP$-*t*-$Bu_3)_3]^+BF_4^-$ with 2,4,6-$(Me_3C)_3C_6H_2PH_2$ in equimolar quantities yields pure **2** in quantitative yield. Anal. Calcd (found) for $C_{54}H_{110}Au_3BF_4P_4$ (**2**) (M_r = 1561.07): C, 41.54 (40.32); H, 7.10 (7.19); Au, 37.85 (37.70). ^1H NMR (270 MHz, $CDCl_3$), δ: 7.04 (s, 2H, C_6H_2), 1.73 (s, 18H, *t*-Bu), 1.51 (s, 9H, *t*-Bu), 1.42 (d, 81H, $^3J_{PH}$ = 13.5 Hz, P-*t*-Bu_3). $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$), δ: 98.00 (d, $^2J_{PP}$ = 237.4 Hz, P-*t*-Bu_3), 2.56 (q, $^2J_{PP}$ = 237.6 Hz, PAu_3). MS, *m/e*: 1473.2 (M^+, 100%), 1074.0 (M^+ − AuP-*t*-Bu_3, 9.3%). $^{31}P\{^1H\}$ NMR data for **4** (109 MHz, $CDCl_3$), δ: 95.39 (d, $^2J_{PP}$ = 257.9 Hz, P-*t*-Bu_3), −33.19 (t, $^2J_{PP}$ = 257.9 Hz, PAu_2).

X-ray Structure Determination of 1. White crystals of **1** were prepared by slow crystallization from CH_2Cl_2/diethyl ether. X-ray data were collected with Mo Kα radiation on an Enraf-Nonius CAD 4 diffractometer at −50 °C from a crystal of dimensions 0.25 × 0.25 × 0.40 mm. Unit cell parameters were obtained by least-squares refinement of 25 reflections ($21.00 \leq 2\theta \leq 27°$). Data were collected in the (*hkl*) range from (−17,−17,0) to (17,17,25) with 5 reflections monitored every 100. A total of 16 000 reflections were collected, of which 15 998 were unique and 12 375 were confirmed as observed ($F_o \geq 3.00\sigma(F_o)$). Lorentz, polarization, and absorption corrections (DIFABS)[15] were applied, and the structure was solved under $P\bar{1}$ symmetry by Patterson methods using SHELXS-86.[16] Missing non-hydrogen atoms were located by successive difference Fourier syntheses using CRYSTALS.[17] Final refinement by diagonal-matrix approximation was carried out with anisotropic parameters for all non-hydrogen atoms and the use of the structure factors of calculated hydrogen atoms in fixed positions. Refinement of 812 parameters in 92 blocks converged to R = 0.049 and R_w = 0.064 using the weighting scheme of Prince.[18] Further crystallographic data are given in Table I.

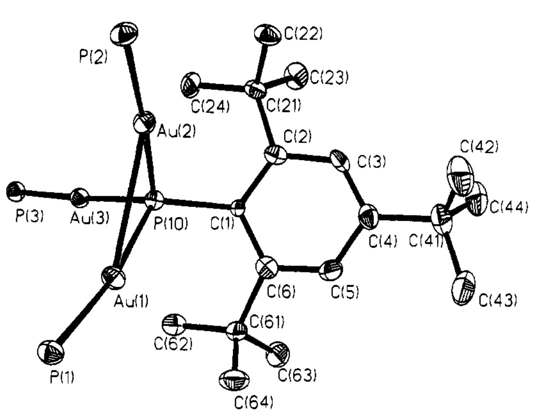

Figure 1. ORTEP plot (PPh_3 phenyl rings omitted) of the cation [2,4,6-$(Me_3C)_3C_6H_2P(AuPPh_3)_3]^+$ in **1**.

Results and Discussion

Synthesis, Properties, and Structure of [2,4,6-$(Me_3C)_3C_6H_2P(AuPPh_3)_3]^+BF_4^-$ (1). The reaction of the oxonium compound $[O(AuPPh_3)_3]^+BF_4^-$ with 2,4,6-$(Me_3C)_3C_6H_2PH_2$ ($ArPH_2$) in CH_2Cl_2 or THF affords complex **1** in high yield as a stable, pale cream-colored crystalline solid (eq 1). The pale solutions of **1** in CH_2Cl_2, $CHCl_3$, or CH_3CN show no decomposition even after several days of storage. Analogous compounds with smaller aryl substituents at the central phosphorus atom (C_6H_5 or 2-$CH_3C_6H_5$) proved far less stable and were found to decompose quickly in solution at ambient temperature.

$$[O(AuL)_3]^+BF_4^- + ArPH_2 \rightarrow [ArP(AuL)_3]^+BF_4^- + H_2O \quad (1)$$
$$\mathbf{1}\ (L = PPh_3)$$

^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra of **1** recorded in CH_2Cl_2 show only one set of resonances for the $AuPPh_3$ units, indicating their equivalence in solution both at 25 °C and at −80 °C. The ^1H NMR spectrum exhibits two *t*-Bu resonances for the 2,6- and the 4-*t*-Bu groups, respectively, in the expected intensity ratio of 2:1. The proton-decoupled ^{31}P NMR spectrum shows an AB_3 spin system, which can be reproduced by parameters with a ratio $J/\delta\nu = 0.043$ (J = 250 Hz, ν = 109 MHz, δ = 53.4 ppm). From the spectra, there is no evidence for paramagnetism. Compound **1** was also identified by elemental analysis and mass spectrometry (FAB source), revealing the parent peak at *m/e* 1652.4 with a relative intensity of 57.6%.

Compound **1** could be crystallized from CH_2Cl_2/diethyl ether to give single crystals of the composition [2,4,6-$(Me_3C)_3C_6H_2P(AuPPh_3)_3]^+BF_4^-\cdot 2CH_2Cl_2$ (triclinic, space group $P\bar{1}$). The lattice is built from a trinuclear gold(I) arylphosphonium cation, a tetrafluoroborate anion, and two solvent molecules, which have no specific intermolecular or interionic contacts. In the cation the three gold atoms are attached to the primary phosphorus center, but they do not form the equilateral triangle commonly

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(15) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158–166.
(16) Sheldrick, G. M. SHELXS-86, Universität Göttingen, 1986.
(17) Watkin, D. J.; Betteridge, P. W.; Carruthers, J. R. *CRYSTALS User Manual*; Oxford University Computing Laboratory: Oxford, U.K., 1986.
(18) Prince, E. *Mathematical Techniques in Crystallography*; Springer Verlag: Berlin, 1982.

Table II. Selected Bond Distances (Å) and Angles (deg) for Compound **1**[a]

	Distances		
Au(1)–P(10)	2.319(1)	Au(1)–P(1)	2.293(1)
Au(2)–P(10)	2.328(1)	Au(2)–P(2)	2.303(1)
Au(3)–P(10)	2.316(1)	Au(3)–P(3)	2.292(1)
Au(1)–Au(2)	3.1546(3)	P(10)–C(1)	1.866(5)
Au(2)–Au(3)	3.9443(3)	Au(1)–Au(3)	3.6571(3)
	Angles		
C(1)–P(10)–Au(1)	116.5(2)	Au(2)–P(10)–Au(3)	116.27(5)
C(1)–P(10)–Au(2)	110.1(2)	Au(1)–P(10)–Au(3)	104.19(5)
C(1)–P(10)–Au(3)	119.4(2)	P(1)–Au(1)–P(10)	170.04(5)
Au(1)–P(10)–Au(2)	85.51(4)	P(2)–Au(2)–P(10)	175.52(5)
P(3)–Au(3)–P(10)	176.58(5)		

[a] For atomic numbering, see Figure 1.

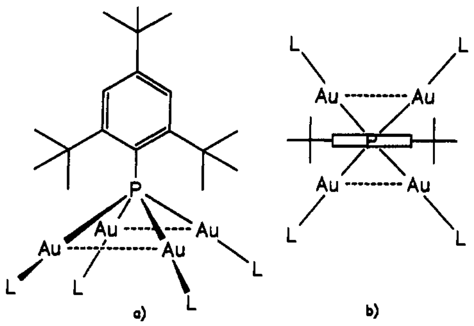
Table III. Atomic Positional and Equivalent Isotropic Displacement U_{eq} (pm^2 × 10^4) Parameters for Compound **1**[a]

atom	*x/a*	*y/b*	*z/c*	*U*(eq)
Au(1)	0.48889(1)	0.45022(1)	0.196664(1)	0.0206
Au(2)	0.27669(1)	0.44250(1)	0.27377(1)	0.0201
Au(3)	0.50126(1)	0.29567(1)	0.37162(1)	0.0190
P(1)	0.5672(1)	0.5887(1)	0.13061(7)	0.0230
P(2)	0.1571(1)	0.5670(1)	0.27061(8)	0.0232
P(3)	0.5879(1)	0.2596(1)	0.46800(7)	0.0211
P(10)	0.40666(9)	0.3254(1)	0.27779(7)	0.0172
Cl(1)	0.8792(2)	0.2942(2)	0.2280(2)	0.0739
Cl(2)	0.7428(2)	0.4201(3)	0.2851(2)	0.0755
Cl(3)	0.8431(2)	0.1686(3)	0.1016(2)	0.0845
Cl(4)	0.9026(4)	–0.0130(4)	0.0666(3)	0.1162
C(1)	0.3668(3)	0.2180(4)	0.2482(2)	0.0153
C(2)	0.2682(4)	0.1835(4)	0.2679(3)	0.0213
C(3)	0.2213(4)	0.1459(4)	0.2210(3)	0.0209
C(4)	0.2669(4)	0.1382(4)	0.1588(3)	0.0249
C(5)	0.3681(4)	0.1532(5)	0.1495(3)	0.0263
C(6)	0.4216(4)	0.1878(4)	0.1941(3)	0.0199
C(7)	0.8513(7)	0.3478(8)	0.2952(5)	0.0606
C(8)	0.8779(8)	0.039(1)	0.1361(6)	0.0772
C(21)	0.2085(4)	0.1740(4)	0.3370(3)	0.0195
C(22)	0.1134(4)	0.2394(4)	0.3270(3)	0.0248
C(23)	0.1774(5)	0.0647(4)	0.3632(3)	0.0257
C(24)	0.2639(5)	0.1955(5)	0.3944(3)	0.0271
C(41)	0.2064(5)	0.1100(5)	0.1059(3)	0.0311
C(42)	0.1173(6)	0.1812(7)	0.0911(5)	0.0446
C(43)	0.2654(6)	0.1181(7)	0.0394(4)	0.0431
C(44)	0.1711(6)	0.0033(6)	0.1327(4)	0.0404
C(61)	0.5367(4)	0.1867(4)	0.1786(3)	0.0229
C(62)	0.5966(4)	0.2008(4)	0.2358(3)	0.0240
C(63)	0.5662(5)	0.0800(5)	0.1709(4)	0.0332
C(64)	0.5658(5)	0.2644(5)	0.1122(3)	0.0321
C(111)	0.4807(4)	0.6872(5)	0.0917(3)	0.0254
C(112)	0.3887(5)	0.6602(5)	0.0765(3)	0.0338
C(113)	0.3196(5)	0.7364(6)	0.0495(4)	0.0402
C(114)	0.3424(6)	0.8343(6)	0.0355(4)	0.0415
C(115)	0.4330(7)	0.8591(5)	0.0520(4)	0.0417
C(116)	0.5030(5)	0.7873(5)	0.0780(4)	0.0370
C(121)	0.6513(4)	0.5632(4)	0.0630(3)	0.0231
C(122)	0.7229(5)	0.4862(6)	0.0806(4)	0.0341
C(123)	0.7844(5)	0.4645(7)	0.0276(5)	0.0422
F(2)	0.0104(5)	0.0054(6)	0.7198(4)	0.0913
F(3)	0.0461(4)	0.1478(5)	0.7402(4)	0.0755
F(4)	0.0514(8)	0.1315(8)	0.6352(5)	0.1368

[a] U_{eq} is one-third the trace of the orthogonalized U matrix.

formed by this type of compound. Instead the Au_3 unit is split into a single gold atom on one side of the aryl plane and a twin set on the other. The Au–Au distance in the pair of gold atoms is found to have a standard distance of 3.1546(3) Å, whereas the distances to the third gold atom are well beyond the limit for efficient gold–gold interactions (3.6571(3) and 3.9443(3) Å). Correspondingly, the Au–P–Au angle for the gold pair is acute (85.51(4)°), while the two others are much larger (104.19(5) and 116.27(5)°). The P–Au–P angles deviate significantly from linearity, but this is not unexpected in molecules with serious congestion of ligands.

Chart I. Proposed Structure for the Dication $ArP(AuL)_4^{2+}$ in **3**: (a) Perspective view; (b) Projection down the ArP Axis



Synthesis and Properties of $[2,4,6-(Me_3C)_3C_6H_2P(AuPPh_3)_4]^{2+}(BF_4^-)_2$ (3). The two-step reaction of $ArPH_2$ with the oxonium reagent $[O(AuPPh_3)_3]^+BF_4^-$, followed by electrophilic addition of a further equivalent of $Ph_3PAu^+BF_4^-$ in CH_2Cl_2/THF without isolation of the intermediate **1**, affords **3** in quantitative yield (eq 2). The compound is a very stable white

$$\mathbf{1} + LAuBF_4 \rightarrow \underset{\mathbf{3}\ (L = PPh_3)}{[ArP(AuL)_4]^{2+}(BF_4^-)_2} \qquad (2)$$

solid which shows no sign of decomposition in solution. Single crystals obtained from CH_2Cl_2/pentane were twinned, and therefore no X-ray diffraction study could be carried out. However, the compound has been fully characterized by NMR spectroscopy and by elemental analysis. The existence of a $P(AuP)_4$ unit of local C_{2v} symmetry is confirmed by a doublet/quintet pattern in the $^{31}P\{^1H\}$ NMR spectrum (δ = 36.67 and –47.69 ppm, $^2J_{PP}$ = 195.3 Hz). The ^1H NMR spectrum shows three signals for the substituted aryl group in the intensity ratio of 2:9:18. The *t*-Bu groups in 2,6-positions and the aryl hydrogen atoms in 3,5-positions are thus equivalent. Even at a temperature of –80 °C, no line broadening or further splitting of the signals is observed. These data suggest a cationic structure, where two pairs of gold atoms, one on each side of the aryl plane, form a rectangle which is capped by the phosphorus atom of the primary phosphine. This phosphorus atom is thus pentacoordinate and bears a formal 2+ charge. The aryl plane should bisect the two longer edges of the rectangle. This model accounts for the symmetry relationship derived from NMR spectroscopy and is in good agreement with the structure determined by X-ray diffraction for an analogous species with less bulky substituents[12].

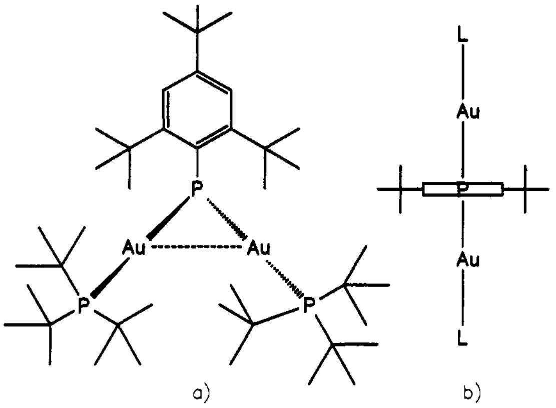
Upon FAB ionization, the cations of compound **3** lose one $AuPPh_3$ group, and therefore the FAB mass spectra resemble those obtained for **1**. No parent peak was observed for the dicationic species.

Synthesis and Properties of $[2,4,6-(Me_3C)_3C_6H_2P(AuP\text{-}t\text{-}Bu_3)_3]^+BF_4^-$ (2) and $[2,4,6-(Me_3C)_3C_6H_2P(AuP\text{-}t\text{-}Bu_3)_2]$ (4). Attempted Synthesis of $[2,4,6-(Me_3C)_3C_6H_2P(AuP\text{-}t\text{-}Bu_3)_4]^{2+}(BF_4^-)_2$. In the reaction of the oxonium reagent $[O(AuP\text{-}t\text{-}Bu_3)_3]^+BF_4^-$ with $ArPH_2$ in the molar ratio 1:1, compound **2** is formed exclusively (eq 3). All spectroscopic data

$$[O(AuL)_3]^+BF_4^- + ArPH_2 \rightarrow \underset{\mathbf{2}\ (L = P\text{-}t\text{-}Bu_3)}{[ArP(AuL)_3]^+BF_4^-} + H_2O \qquad (3)$$

for **2** are within the expected range and are comparable with those for **1**. The NMR data for the product give no evidence for an inequivalence of the AuP-*t*-Bu_3 units in solution even at temperatures as low as –80 °C. Performance of the reaction using a 3:2 molar ratio of phosphine vs oxonium salt produces a mixture of the neutral digold arylphosphide **4** together with a small amount of unreacted $ArPH_2$ and the trinuclear complex **2**

Chart II. Proposed Structure for the Neutral Compound $ArP(AuP\text{-}t\text{-}Bu_3)_2$ (**4**): (a) Perspective View; (b) Projection down the ArP Axis



(eq 4). Unfortunately, **4** could not be separated quantitatively

$$2[O(AuL)_3]^+BF_4^- + 3ArPH_2 \rightarrow 3[ArP(AuL)_2] + 2H_3O^+BF_4^- \quad (4)$$

$$\mathbf{4}\ (L = P\text{-}t\text{-}Bu_3)$$

from **2** owing to very similar solubility properties of these compounds. The reaction carried out with an excess of $ArPH_2$ leads to partial substitution of tertiary phosphine ligands at gold, and the relative yield of diaurated species is not increased. **4** can be easily identified even in a mixture with **2** by its characteristic doublet/triplet pattern (δ = 95.39 and −33.19 ppm, $^2J_{PP}$ = 258 Hz) for the $P\text{-}t\text{-}Bu_3$ and ArP groups, respectively, in the $^{31}P\{^1H\}$ NMR spectrum. A protonated phosphonium species can be ruled out by the absence of a $^1J_{PH}$ splitting in a proton-coupled ^{31}P NMR spectrum recorded for this purpose.

4 is the first neutral digold(I) arylphosphide $RP(AuL)_2$ that could be isolated in the studies on polyaurated main group elements. There is only one further example in the literature for a compound with more than one metal atom attached at the 2,4,6-$(Me_3C)_3C_6H_2P$ unit. The cobalt compound $[ArPCo_2(CO)_2(C_5H_5)_2]$[19] with its "open" phosphinidene structure has a planar coordination at phosphorus. A similar strain-free geometry is also proposed for compound **4**. As expected for this combination of very bulky ligands, all attempts to add a further 1 equiv of $t\text{-}Bu_3PAu^+BF_4^-$ to the trinuclear complex **2** result in decomposition. The only product that can be isolated is $[(t\text{-}Bu_3P)_2Au]^+BF_4^-$, which results from degradation of the cluster by excess phosphine.

Conclusions

In this study oxonium reagents of the type $[O(AuL)_3]^+BF_4^-$ have been reacted with the very bulky primary arylphosphine 2,4,6-$(Me_3C)_3C_6H_2PH_2$. Two tertiary phosphine ligands L (L = Ph_3P, $t\text{-}Bu_3P$) of different sterical demands have been employed as ligands for gold(I). In both cases, the expected triply aurated phosphonium compounds (**1** and **2**) could be isolated in high yields as crystalline products of high thermal stability. The stability in solution as compared with the stability of complexes of this kind bearing smaller aryl groups is particularly noteworthy. As ascertained by an X-ray analysis, the $RPAu_3$ core in **1** deviates significantly from the classical tetrahedral geometry, owing to the steric hindrance of the Au–Au interaction by the 2,6-*t*-Bu groups of the phosphinidene group. Only one pair of gold atoms is able to retain short Au–Au contacts in the crystalline ground-state geometry. In solution, fast aryl rotation about the P–C bond leads to NMR-equivalent AuL groups.

Only complex **1** with its smaller PPh_3 groups can add a further 1 equiv of $Ph_3PAu^+BF_4^-$ to give the dicationic hypercoordinate species $[ArP(AuPPh_3)_4]^{2+}$ in the form of its tetrafluoroborate salt **3**, whereas for **2** no such addition is possible. The reaction leads to decomposition with concomitant formation of $[(t\text{-}Bu_3P)_2Au]^+BF_4^-$. Compound **3** is assigned a square-pyramidal structure of the $RPAu_4$ core, with the four gold atoms forming a rectangle capped by the phosphorus atom and with the aryl group in the apical position. With L = $t\text{-}Bu_3P$, the neutral diaurioarylphosphine $[ArP(AuP\text{-}t\text{-}Bu_3)_2]$ (**4**) can be identified in the reaction mixture if the reagents are used in a higher RPH_2:$O(AuL)_3^+$ molar ratio. Compound **4**, which is assigned a trigonal-planar structure at the phosphinidene phosphorus atom, could not be separated from **2**, which is a byproduct in the process.

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Supplementary Material Available: For complex **1**, tables of atomic coordinates and complete thermal parameters (2 pages). Ordering information is given on any current masthead page.

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[19] Arif, A. M.; Cowley, A. H.; Pakulski, M.; Pearsall, M. A.; Clegg, W.; Norman, N. C.; Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1988**, 2713–2721.