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Hexa- and Octanuclear Gold Complexes of *p*-Phenylenediphosphine

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p-Phenylenediphosphine 1,4-$C_6H_4(PH_2)_2$, synthesized according to a published procedure, has been fully characterized by its analytical and spectroscopic data. This diprimary phosphine was reacted with 2 equiv of $(LAu)_3O^+BF_4^-$ (L = *t*-Bu_3P or Ph_3P) to yield products of the type $[1,4\text{-}(LAu)_3P\text{–}C_6H_4\text{–}P(AuL)_3]^{2+}(BF_4^-)_2$ with two trigold moieties in the dications. The reaction of 2 equiv of an equimolar mixture of $(Ph_3PAu)_3O^+BF_4^-$ and $Ph_3PAu^+BF_4^-$ with 1,4-$C_6H_4(PH_2)_2$ leads to the product $[1,4\text{-}(Ph_3PAu)_4P\text{–}C_6H_4\text{–}P(AuPPh_3)_4]^{4+}(BF_4^-)_4$ in quantitative yield, which features two tetranuclear units in trans positions. The compounds were obtained as polycrystalline solids, which were readily identified by means of a detailed NMR and mass spectrometric analysis.

Introduction

In previous studies,[1] carried out independently in two different laboratories,[2,3] it could be demonstrated that primary amines,[4–8] phosphines,[9,10] and arsines[11] can be triply aurated on treatment with a stoichiometric amount of the oxonium reagent $(Ph_3PAu)_3O^+BF_4^-$ to give species of the type $RE(AuPPh_3)_3^+$, where E = N, P, and As, and R = alkyl and aryl. In the case of the phosphorus compounds further auration could be accomplished by reaction with the more powerful electrophile $Ph_3PAu^+BF_4^-$, which even leads to hypercoordinate dications $RP(AuPPh_3)_4^{2+}$.[11] This chemistry has now been extended to include the diprimary aromatic phosphine 1,4-$C_6H_4(PH_2)_2$.

Experimental Section

General Data. All reactions were carried out in oven-dried glassware using standard inert-atmosphere techniques. All solvents were dried and distilled before use. Exposure to direct sunlight was avoided. NMR spectra were recorded on JEOL GX 270 and JEOL GX 400 NMR spectrometers (for ^1H and ^{13}C, deuterated solvents as internal standards, converted to TMS; for ^{31}P, external 85% aqueous H_3PO_4); mass spectra were recorded on an MAT 90 mass spectrometer (FAB, CI and FD ionization). Elemental analyses were performed in the microanalytical laboratory of this Institute.

Starting Materials. $(Ph_3PAu)_3O^+BF_4^-$ (**2**),[12] $(t\text{-}Bu_3PAu)_3O^+BF_4^-$ (**3**),[13] and $Ph_3PAu^+BF_4^-$ [12] were prepared according to reported methods.

1,4-$C_6H_4(PH_2)_2$ (1), prepared according to ref 14, has the following spectroscopic data. ^1H NMR (270 MHz, $CDCl_3$, 25 °C): δ 7.40 (4H, ψ-t, $^3J(HP) = {}^4J(HP) = 4.2$ Hz, C_6H_4), 3.97 (4H, d, $^1J(HP) = 202.5$ Hz, PH_2). $^{13}C\{^1H\}$ NMR (68 MHz, $CDCl_3$, 25 °C): δ 134.52 (dd, $^2J(CP) = 9.9$ Hz, $^3J(CP) = 5.5$ Hz, C2/C3/C5/C6), 128.65 (d, $^1J(CP) = 8.3$ Hz, C1/C4). $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$, 25 °C): δ −123.9 (s, PH_2). MS (CI): *m*/*e* = 141.9 [M^+, 100%].

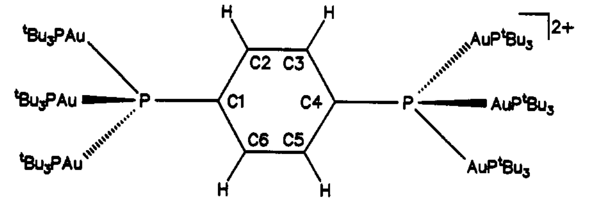

Figure 1. Proposed structure and atomic numbering for the dication $[1,4\text{-}C_6H_4\{P(AuP\text{-}t\text{-}Bu_3)_3\}_2]^{2+}$ in **4**.

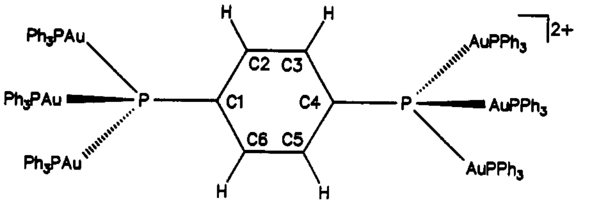

Figure 2. Proposed structure and atomic numbering for the dication $[1,4\text{-}C_6H_4\{P(AuPPh_3)_3\}_2]^{2+}$ in **5**.

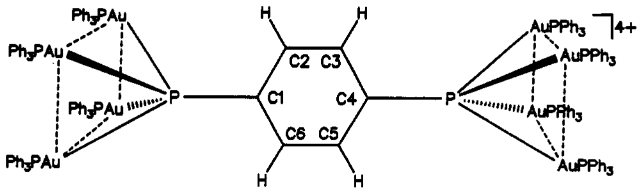

Figure 3. Proposed structure and atomic numbering for the tetracation $[1,4\text{-}C_6H_4\{P(AuPPh_3)_4\}_2]^{4+}$ in **6**.

Preparation of Compounds. $[1,4\text{-}C_6H_4\{P(AuP\text{-}t\text{-}Bu_3)_3\}_2]^{2+}(BF_4^-)_2$ (4). A sample of **3** (1.30 g, 1.0 mmol) was dissolved in CH_2Cl_2 (25 mL) and treated with a solution of **1** (71 mg, 0.5 mmol) in the same solvent (10 mL) at −78 °C. The colorless reaction mixture was warmed to ambient temperature after ca. 3 h, and pentane (100 mL) was added. A colorless oil separated, which was dried in a vacuum to yield **4** as a polycrystalline solid: yield 1.29 g (95%). Anal. Calcd for $C_{78}H_{166}Au_6B_2F_8P_8$ (M_r 2707.38): C, 34.60; H, 6.18; Au, 43.65. Found: C, 34.32; H, 6.22; Au, 43.97. ^{13}H NMR (270 MHz, $CDCl_3$, 25 °C); δ 7.40 ($A_2A'_2XX'$, 4H, C_6H_4), 1.44 (d, $^3J(PH) = 13.8$ Hz, 162 H, *t*-Bu). $^{13}C\{^1H\}$ NMR (68 MHz, $CDCl_3$, 25 °C): δ 139.45 (AXX', Cl), 134.56 (AXX', C2), 39.41 (d, $^1J(CP) = 14.32$ Hz, CP), 32.28 (s, br, CH_3). $^{31}P\{^1H\}$ NMR (109 MHz, $CDCl_3$, 25 °C): δ 106.2 (d of $(AX_3)_2$, br, $^2J(PP) = 233.8$ Hz, *t*-Bu_3P), 13.2 (q of $(AX_3)_2$, $^2J(PP) = 233.8$ Hz, $^5J(PP) = 3.8$ Hz, PAu_3). MS (FD, CH_2Cl_2 solution): *m*/*e* = 1265.9 [M^{2+}, 100%].

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$[1,4\text{-}C_6H_4\{P(AuPPh_3)_3\}_2]^{2+}(BF_4^-)_2$ (5). The preparation followed the procedure outlined for compound **4** using reagent **2** (1.48 g, 1.0 mmol). The product separated as a red oil, which was dried to give a red polycrystalline solid: yield 1.38 g (90%). Anal. Calcd for $C_{114}H_{94}Au_6B_2F_8P_8$ (M_r 3067.20): C, 44.64; H, 3.09; Au, 38.53. Found: C, 44.18; H, 3.17; Au, 39.04. ^1H NMR (400 MHz, CD_2Cl_2, 25 °C): δ 6.65–7.60 (m, $PPh_3 + C_6H_4$). $^{13}C\{^1H\}$ NMR (100 MHz, CD_2Cl_2, 25 °C): δ 135.79 (*A*XX′, br, C2), (C1 resonance obscured), 134.52 (d, $^2J(CP)$ = 12.97 Hz, C2′/6′), 132.35 (s, C4′), 129.79 (d, $^3J(CP)$ = 10.3 Hz, C3′/5′), 129.75 (d, $^1J(CP)$ = 52.64 Hz, C1′). $^{31}P\{^1H\}$ NMR (161 MHz, CD_2Cl_2, −80 °C): δ 45.81 (d, br, $^2J(PP)$ = 245 Hz, Ph_3P), −5.59 (q, br, PAu_3). MS (FAB, matrix material 4-nitrobenzyl alcohol): *m/e* = 1445.9 [M^{2+}, 100%].

$[1,4\text{-}C_6H_4\{P(AuPPh_3)_4\}_2]^{4+}(BF_4^-)_4$ (6). Freshly prepared $Ph_3PAu^+BF_4^-$ (546 mg, 1.0 mmol) in THF (10 mL) was added dropwise to a solution of **2** (1.48 g, 1.0 mmol) in CH_2Cl_2 (20 mL) at −78 °C. Stirring was maintained for ca. 30 min, and a solution of **1** (71 mg, 0.5 mmol) in THF (10 mL) was slowly added. After 3 h cold pentane (100 mL) was added, and **6** separated as a yellow oil; drying in a vacuum gave a polycrystalline solid: yield 2.08 g (100%). Anal. Calcd for $C_{150}H_{124}Au_8B_4F_{16}P_{10}$ (M_r 4159.33): C, 43.31; H, 3.00; Au, 37.88. Found: C, 42.92; H, 3.12; Au, 38.09. ^1H NMR (270 MHz, CD_2Cl_2, 25 °C), δ: 8.17 ($A_2A'_2XX'$, 4H, C_6H_4), 7.65–7.05 (m, 120H, PPh_3). $^{13}C\{^1H\}$ NMR: (68 MHz, CD_2Cl_2, 25 °C), δ: 132.4 (br, C2′/C6′), 131.0 (br, C4′), 128.2 (br, C3′/C5′), 126.0 (d, br, $^1J(CP) \approx 60$ Hz, C1′), (C1, C2 resonances not detected). $^{31}P\{^1H\}$ NMR (109 MHz, CD_2Cl_2, 25 °C), δ: 39.58 (X-part of an $(AX_4)_2$ spin system, Ph_3P, $^2J(PP)$ = 195.0 Hz), −38.94 (A-part of an $(AX_4)_2$ spin system, PAu_4, $^2J(PP)$ = 195.0 Hz, $^5J(PP)$ = 6.8 Hz). MS (FAB, matrix material 4-nitrobenzylic alcohol): m/e = 720.6 [$(Ph_3P)_2Au^+$, 100%], 458.8 [Ph_3PAu^+, 63.6%].

Results

Synthesis and Characterization of $[1,4\text{-}C_6H_4\{P(AuP\text{-}t\text{-}Bu_3)_3\}_2]^{2+}(BF_4^-)_2$ (4) and $[1,4\text{-}C_6H_4\{P(AuPPh_3)_3\}_2]^{2+}(BF_4^-)_2$ (5). *p*-Phenylenediphosphine (1,4-diphosphinylbenzene) $1,4\text{-}C_6H_4(PH_2)_2$ (**1**) was found to react with 2 equiv of the trinuclear gold(I) oxonium compounds $(LAu)_3O^+BF_4^-$ (**2**, L = *t*-Bu_3P) and (**3**, L = Ph_3P) in CH_2Cl_2 to give products in which both phosphinyl groups are triply aurated in high yields of 95% (**4**) and 90% (**5**), respectively (eq 1).

$$\underset{\textbf{1}}{1,4\text{-}C_6H_4(PH_2)_2} + 2\,\underset{\begin{array}{c}\textbf{2}\ (L = Ph_3P)\\ \textbf{3}\ (L = t\text{-}Bu_3P)\end{array}}{(LAu)_3O^+BF_4^-} \xrightarrow[-2H_2O]{CH_2Cl_2} \underset{\begin{array}{c}\textbf{4}\ (L = t\text{-}Bu_3P)\\ \textbf{5}\ (L = Ph_3P)\end{array}}{[1,4\text{-}C_6H_4\{P(AuL)_3\}_2]^{2+}(BF_4^-)_2} \quad (1)$$

Compounds **4** and **5** separate from CH_2Cl_2 solutions on addition of pentane as colorless and red oils, respectively, which solidify to give polycrystalline products on drying in a vacuum. The compounds are insensitive to air and moisture and dissolve readily in polar solvents. While solutions of **4** are stable, **5** slowly undergoes decomposition in solution with precipitation of metallic gold. No single crystals could be grown from such solutions. The compounds have therefore been characterized by ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectroscopy, elemental analyses, and mass spectrometry.

Proton, carbon and phosphorus NMR spectra of compounds **4** and **5** in $CDCl_3$ and CD_2Cl_2 solutions show only one set of resonances for the tertiary phosphine ligands. These data suggest equivalent bonding of all six AuL units in the dications.

According to the $^{31}P\{^1H\}$ spectrum of compound **4** the phenylene-bound phosphorus atoms are magnetically inequivalent; the quartet pattern for these atoms is further split by $^5J(PP)$ coupling to give an $(AX_3)_2$ spin system. The ^{31}P chemical shift values of the $C_6H_4(PH_2)_2$ resonance (δ = −123.8 ppm for **1**) is increased by 137 ppm to +13.2 ppm for **4**. For compound **5** only a broad doublet and a multiplet in the intensity ratio of about 3:1 are discernible at a temperature as low as −80 °C, indicating some site exchange of the bulky $[LAu]^+$ units in CD_2Cl_2.

The ^1H and $^{13}C\{^1H\}$ resonances of the phenylene groups are of high diagnostic value for establishing the structures of **4** and **5**. The ^1H NMR signals are $A_2A'_2XX'$ spin systems, while the carbon spectra exhibit *A*XX′ patterns for the two distinguishable groups of phenylene carbon atoms C1/C4 and C2/C3/C5/C6 (Fig 1). The *di*cations of **4** and **5** can be detected directly by means of field desorption or fast atom bombardment mass spectrometry with the base peaks at *m/e* = 1265.9 and 1445.9, respectively, representing *half* of the masses of the parent ions.

Synthesis and Characterization of $[1,4\text{-}C_6H_4\{P(AuPPh_3)_4\}_2]^{4+}(BF_4^-)_4$ (6). The conversion of **1** into the doubly tetraaurated phosphonium salt **6** was achieved in quantitative yield by reaction with 2 equiv of an equimolar mixture of the trifunctional oxonium compound **2** and the monofunctional reagent $Ph_3PAu^+BF_4^-$ at −78 °C in THF/CH_2Cl_2 (eq 2). The

$$\underset{\textbf{1}}{1,4\text{-}C_6H_4(PH_2)_2} + 2\,\underset{\textbf{2}}{(Ph_3PAu)_3O^+BF_4^-} + 2\,Ph_3PAu^+BF_4^- \xrightarrow[-2H_2O]{THF/CH_2Cl_2} \underset{\textbf{6}}{[1,4\text{-}C_6H_4\{P(AuPPh_3)_4\}_2]^{4+}(BF_4^-)_4} \quad (2)$$

product (**6**) separates as a yellowish oil upon addition of pentane to the reaction mixture and is converted into a polycrystalline solid when dried in a vacuum. The dry material is air-stable, but solutions in CH_2Cl_2 or CH_3CN decompose slowly at ambient temperature. Unfortunately, no single crystals of **6** could be obtained as yet.

The tetracations of **6** have not been observed by mass spectrometry owing to the high formal +4 charge. FAB ionization leads to a base peak at *m/e* = 720.6 for the very stable fragment $(Ph_3P)_2Au^+$. Peaks with low intensity found at higher *m/e* ratios could not be assigned to plausible degradation products.

The $^{31}P\{^1H\}$ NMR spectra of CD_2Cl_2 solutions of compound **6** indicate that all PPh_3 groups are equivalent at room temperature. They show a sharp doublet/quintet pattern with $^2J(PP)$ = 195.0 Hz, with some additional splitting caused by long-range coupling of $^5J(PP)$ = 6.8 Hz. In the spectra no evidence was obtained for impurities such as compound **5** or other byproducts with a lower degree of auration.

The proton and ^{13}C resonances are slightly broadened probably owing to restricted rotation of the congested PPh_3 groups. The $A_2A'_2XX'$ pattern of the phenylene protons (δ_A = 8.17 ppm) is clearly separated from the PPh_3 proton resonances, and the intensity ratio of 4:120 (1 × C_6H_4/24 × C_6H_5) is in agreement with the proposed stoichiometry.

Discussion

This study has shown that a diprimary aromatic phosphine, $1,4\text{-}C_6H_4(PH_2)_2$, can be aurated on reaction with 2 equiv of the oxonium reagent $(LAu)_3O^+BF_4^-$ (L = *t*–Bu_3P or Ph_3P) to yield hexanuclear products of the type $[1,4\text{-}(LAu)_3P\text{–}C_6H_4\text{–}P\text{-}(AuL)_3]^{2+}(BF_4^-)_2$ with two η^3-PAu_3 units in the para positions. These results complement previous studies concerning the auration of primary amines, phosphines, and arsines which gave triply aurated cations of the type $RE(AuL)_3^+$, where E = N, P, and As and R = alkyl and aryl, with a pseudotetrahedral pnicogenium coordination.[3,9,11]

While with difunctional *amines* only the corresponding *hexa*nuclear aurated species could be isolated,[6] it has now been found that the reaction of 2 equiv of an equimolar mixture of $(Ph_3PAu)_3O^+BF_4^-$ and $Ph_3PAu^+BF_4^-$ with $1,4\text{-}C_6H_4(PH_2)_2$ leads to an *octa*nuclear product, $[1,4\text{-}(Ph_3PAu)_4P\text{–}C_6H_4\text{–}P\text{-}(AuPPh_3)_4]^{4+}(BF_4^-)_4$, in quantitative yield, which features two tetranuclear η^4-PAu$_4$ units in the trans positions of the central arene ring. Each of these two η^4-PAu$_4$ units resembles those detected in RP(AuL)$_4^{2+}$ species, which are known to have a square pyramidal structure.[11]

It is noteworthy that the octanuclear complex cation is stable in spite of the exceedingly high positive charge (+4). The two η^4-P(AuL)$_4^{2+}$ units are well separated owing to the transpositioning at the central arene ring, with the 2+ charges delocalized over the two PAu$_4$ pyramids, which are known to be stabilized by significant Au···Au bonding.[1,11]

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