by combining $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+$ and $P(OEt_3)$ in the dark under otherwise similar conditions. Thus, the isomerization of the pentaphenylcyclopentadienyl ligand to the skeleton of II requires both the metal complex and triethyl phosphite and probably involves photoisomerization of $[C_5Ph_5]^-$ or the radical at the metal center.

Photolytic ligand-exchange reactions of $[Fe(\eta^5\text{-}C_5H_5)(\text{arene})]^+$ complexes are well-known,[40,44,47,48,50,52] and photoinduced loss of arene from $[Fe(\eta^5\text{-}C_5H_5)(\eta^6\text{-arene})]^+$ cations appears to be important in the generation of catalysts for photoimaging systems.[58,59] It was demonstrated recently that the nature of the cyclopentadienyl substituents is important in determining the rates of arene exchange, with electron-withdrawing substituents facilitating the photoreaction but destabilizing the solvated intermediates.[51,54] Thus, for example, sunlight is sufficient to initiate arene exchange of $[Fe(\eta^5\text{-}C_5H_5)(\text{arene})]^+$ cations in CH_2Cl_2.[39,40,41,43] Likewise, irradiation of the acyl-substituted derivative $[Fe(\eta^5\text{-}C_5H_4COR)(\eta^6\text{-}C_6H_6)]^+PF_6^-$ with 24 equiv of trimethyl phosphite in CH_2Cl_2 at 0 °C (conditions similar to those of the present experiment) produces $[Fe(\eta^5\text{-}C_5H_4COR)\{P(OMe)_3\}_3]^+PF_6^-$ in 73% (R = Me) or 77% (R = Ph) yield in 1 h.[54] By contrast, $[Fe(\eta^5\text{-}C_5Me_5)(\text{arene})]^+$ cations are photolabile only in the presence of a sensitizer, such as acetone or anthracene.[51] The compounds $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-arene})]^+[BPh_4]^-$ are, however, recrystallized from acetone. Additionally, $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+[BPh_4]^-$ was stirred in acetone in the presence of 20 equiv of triethyl phosphite. No reaction was observed in the dark. Irradiation of the solution with visible light yielded unchanged $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+[BPh_4]^-$ (ca. 80%) and C_5Ph_5H (ca. 20%).

Pentaphenylcyclopentadiene was not detected as a coproduct of II from the irradiation of $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+[BPh_4]^-$ in the presence of $P(OEt)_3$ in CH_2Cl_2. Pentaphenylcyclopentadiene has only limited solubility in CH_2Cl_2 but is unchanged on irradiation in CH_2Cl_2 in the presence of 20 equiv of triethyl phosphite, and thus it is unlikely that II is generated from free pentaphenylcyclopentadiene.

Because of the low yield of II, we are unable to speculate on the course of the reaction. However, the generation of $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_5C_5Ph_4)]$ by photolysis of $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+$ in CH_2Cl_2 demonstrates that photoinduced arene exchange can occur in this system. Moreover, several crystal structure determinations have established that, at least in the solid state, the phenyl groups of the $[C_5Ph_5]^-$ ligand are sterically constrained from assuming coplanarity with the C_5 ring and appear to act as electron-donating substituents.[64] The low yield of II is then consistent with the low photolability of complexes with electron-donating substituents on the C_5 ring.

Thermal or acid-induced rearrangements of 1,2,3,4,5-pentaphenyl-2,4-cyclopentadien-1-ol have been reported.[65–67] However, we have not detected any of the products of these reactions following the $[Fe(\eta^5\text{-}C_5Ph_5)(\eta^6\text{-}C_6H_6)]^+[BPh_4]^-/P(OEt)_3/CH_2Cl_2$ photolysis.

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Supplementary Material Available: Listings of atom coordinates, anisotropic thermal parameters, details of least-squares planes calculations, and torsion angles (20 pages); tables of observed and calculated structure factor amplitudes (30 pages). Ordering information is given on any current masthead page.

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Auration of an Aryltris[(triarylphosphine)aurio(I)]phosphonium(+) Cation To Give a Hypercoordinate Aryltetrakis[(triarylphosphine)aurio(I)]phosphonium(2+) Dication

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Treatment of (2-methylphenyl)phosphine with tris[(triphenylphosphine)aurio(I)]oxonium(+) tetrafluoroborate(−) affords colorless, air-stable (2-methylphenyl)tris[(triphenylphosphine)aurio(I)] phosphonium(+) tetrafluoroborate(−): $(2\text{-}MeC_6H_4)[Ph_3PAu]_3P^+BF_4^-$ (**1**); Me = methyl, Ph = phenyl. The crystal structure features tetrahedral cations with a central phosphorus atom surrounded by three gold atoms and one carbon atom. With the Au–P–Au angles showing only slight deviations from the tetrahedral value and the P–Au–P angles close to linear, the Au···Au distances are too long to allow bonding metal–metal interactions. An analogous arsenic compound $(2\text{-}MeC_6H_4)[(Ph_3PAu]_3As^+BF_4^-$ (**3**) is available from (2-methylphenyl)arsine and shows similar properties. Reaction of **1** with $[Ph_3PAu]^+BF_4^-$ gives high yields of the colorless, crystalline, air-stable species $(2\text{-}MeC_6H_4)[Ph_3PAu]_4P^{2+}(BF_4^-)_2$ (**2**). The dications have a square-pyramidal structure with phosphorus at the center, the *o*-tolyl group at the apex, and the four gold atoms forming the base with short Au···Au contacts (ca. 3.0 Å). These short distances are held responsible for the ease of formation and stability of this novel hypercoordinate unit. An analogous arsenic compound could not be prepared. Crystal data for **1**: $a = 13.341$ (3) Å, $b = 15.363$ (3) Å, $c = 16.369$ (3) Å, $\alpha = 107.88$ (1)°, $\beta = 98.17$ (1)°, $\gamma = 103.09$ (1)°, triclinic, space group $P\bar{1}$, $Z = 2$. Crystal data for $\mathbf{2}\cdot 4C_6H_6$: $a = 13.712$ (2) Å, $b = 17.873$ (3) Å, $c = 20.748$ (2) Å, $\alpha = 95.04$ (1)°, $\beta = 104.58$ (1)°, $\gamma = 96.08$ (1)°, triclinic, space group $P\bar{1}$, $Z = 2$.

Introduction

Recent work has demonstrated that a pair, trio, or quartet of gold(I) atoms clustered at or around a main group element like carbon, nitrogen, phosphorus, arsenic, oxygen, sulfur, and selenium shows a pronounced tendency to attract additional units LAu^+ to form novel hypercoordinate species.[1] For carbon,[2] the trigonal-bipyramidal cations $C(AuL)_5^+$ and octahedral dications $C(AuL)_6^{2+}$ are the prototypes for this new type of clustering phenomenon for closed-shell atoms [d^{10} for Au(I), L = tertiary

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phosphine]. For nitrogen,[3] in addition to the $N(AuL)_4^+$ cation with a distorted tetrahedral structure, the unprecedented trigonal-bipyramidal species $N(AuL)_5^{2+}$ has been discovered, and for phosphorus,[4] an analogous dication $P(AuL)_5^{2+}$ is known, though its structure has not yet been determined. Arsenic[5] has been found to form only $As(AuL)_4^+$ cations, but these have a nonclassical square-pyramidal structure, one of the extremely rare violations of the Le Bel/van't Hoff rule. Finally, for oxygen,[6] sulfur,[7] and selenium,[8] the oxonium, sulfonium, and selenonium cations $E(AuL)_3^+$ have been described (E = O, S, Se). And even (phosphine)gold(I) chlorides form the corresponding bis[(phosphine)aurio(I)]chloronium salts.[9]

It appears that in all of these species short bonding Au···Au contacts[10] of ca. 3.0 Å are responsible for the ease of formation and the unexpected stability of the element-centered clusters, and relativistic effects are likely to play a decisive role in the energy characteristics.[11-13] Since such relativistic effects are known to be particularly strong for gold,[14,15] it does not come as a surprise that it is with this element that most of the novel hypercoordinate species have been discovered. However, even without considering relativity, at least the $C(AuL)_6^{2+}$ dication had been predicted very early on the ground of molecular orbital theory.[16,17]

The above examples are all homoleptic species, and only in one case[18] has a cation been found where a non-gold substituent is part of the "hyper"-coordination sphere around the central element. This (dimeric) unit $RC(AuL)_4^+$ has a square-pyramidal structure with a carbon atom in the center, the R = oxazolinyl substituent at the apex, and the four gold atoms at the base. We now report a similar compound containing *phosphorus* as the hypercoordinate center in a dication $[RP(AuL)_4]^{2+}$. The tetrahedral four-coordinate precursor $[RP(AuL)_3]^+$ was described in a preliminary communication.[4]

Analogous nitrogen cations $[RN(AuL)_4]^+$ are not stable for nonfunctional substituents R. Attempts to add cations LAu^+ to cations $[RN(AuL)_3]^+$, with R = aryl or alkyl, have not been successful.[19] However, with R bearing a donor atom in a stereochemically acceptable position, like 8-quinolinyl, the clustering of four gold atoms at nitrogen becomes also possible through the assistance of the extra donor center. Species of the type $[RN(AuL)_4]^{2+}$ can thus be isolated as stable tetrafluoroborate salts.[20]

Experimental Section

General Data. All reactions were carried out in oven-dried glassware using standard inert-atmosphere techniques. All solvents were dried, saturated with nitrogen, and distilled before use. Exposure to direct daylight was avoided if possible.

Table I. Crystallographic Data for Complexes **1** and **2**·$4C_6H_6$

	1	**2**·$4C_6H_6$
chem formula	$C_{61}H_{52}Au_3BF_4P_4$	$C_{103}H_{91}Au_4B_2F_8P_5$
fw	1586.70	2445.21
T, °C	24	−44
λ, Å	0.710 69	0.710 69
space group	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a, Å	13.341 (3)	13.712 (2)
b, Å	15.363 (3)	17.873 (3)
c, Å	16.369 (3)	20.748 (2)
α, deg	107.88 (2)	95.04 (1)
β, deg	98.17 (2)	104.58 (1)
γ, deg	103.09 (2)	96.08 (1)
V, Å^3	3027.8	4856.6
Z,	2	2
ρ_{calc}, g cm^{-3}	1.740	1.671
μ, cm^{-1}	73.79	61.41
R^a	0.075	0.043
R_w^b	0.083	0.044

[a] $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $[\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$; $w = 1/\sigma^2(F_o)$.

Equipment. A JEOL GX 400 NMR spectrometer (deuterated solvents as internal standards, converted to TMS, for ^1H; external aqueous H_3PO_4 for ^{31}P) and a MAT 90 mass spectrometer (FAB source) were used. Melting points (sealed capillaries in a Büchi apparatus) are uncorrected. Elemental analyses were performed in the microanalytical laboratory of this institute.

Reagents. 2-Methylphenylphosphine[21] and -arsine[22] and tris[(triphenylphosphine)aurio(I)]oxonium tetrafluoroborate[6] and (triphenylphosphine)gold(I) tetrafluoroborate[6] were prepared by following the literature procedures.

(2-Methylphenyl)tris[(triphenylphosphine)aurio(I)]phosphonium(+) Tetrafluoroborate (1). $[(C_6H_5)_3PAu]_3O^+BF_4^-$ (0.90 g, 0.61 mmol) was suspended in tetrahydrofuran (90 mL) and treated with a solution of *o*-$TolPH_2$ (0.08 g, 0.61 mmol) in the same solvent (10 mL) with stirring. The color of the initially colorless reaction mixture changed via yellow to orange-brown. After 20 min the brown precipitate was filtered, dried in a vacuum, and recrystallized from a mixture of dichloromethane and diethylether (1:1): yield 0.28 g (29%) of colorless crystals; mp 183–186 °C dec; soluble in CH_2Cl_2 and $CHCl_3$.

^1H NMR (CD_2Cl_2, 25 °C): δ = 2.91 (s, 3 H, CH_3), 7.11–7.25 (m, 4 H, C_6H_4), 7.37–7.56 (m, 45 H, C_6H_5). $\{^1H\}^{31}P$ NMR (CD_2Cl_2): at 20 °C, δ = 46.0 (s, br, 3 P, *P*Ph_3), −19.1 (s, br, 1 P, *o*-Tol*P*); at −70 °C, δ = 45.4 (d, $^2J(PP)$ = 249 Hz, *P*Ph_3), −19.0 (quart., $^2J(PP)$ = 249 Hz, *o*-TolP). Anal. Calcd for $C_{61}H_{52}Au_3BF_4P_4$ (M_r 1586.68): C, 46.18; H, 3.30; P, 7.80. Found: C, 45.52; H, 3.52; P, 8.05.

Phenyltris[(triphenylphosphine)aurio(I)]phosphonium(+) Tetrafluoroborate. The oxonium reagent (1.06 g, 0.72 mmol) was suspended in tetrahydrofuran (10 mL) and treated with a solution of phenylphosphine (0.08 g, 0.72 mmol) in the same solvent (5 mL). The color of the reaction mixture changed from colorless via yellow and orange to brown. After 20 min pentane was added (100 mL) to generate an orange-red precipitate. Repeated reprecipitation from dichloromethane with pentane gave a dark oil and an orange solid in low yield. The $\{^1H\}^{31}P$ NMR spectrum of the solid dissolved in dichloromethane-d_2 showed two broad signals at δ = 46.1 (3 P, PPh_3) and −4.6 ppm (1 P, PPh), at both +20 and −70 °C. The compound is unstable at ambient temperature and decomposes rapidly both in the solid state and in solution, turning black and depositing dark precipitates, respectively. Owing to the small quantities available and the low stability of the compound, no further analytical studies were possible.

(2-Methylphenyl)tetrakis[(triphenylphosphine)aurio(I)]phosphonium(2+) Bis(tetrafluoroborate) (2). A brown reaction mixture containing **1** was prepared as described above, but instead of the workup the suspension was cooled to −70 °C and treated with a freshly prepared solution of $[Ph_3PAu]^+[BF_4]^-$ (0.33 g, 0.61 mmol) in tetrahydrofuran (40 mL) with vigorous stirring. When the mixture was warmed up to ambient temperature (after ca. 1 h), a small amount of dark precipitate was filtered and pentane (20 mL) added to the filtrate. A yellow oil was precipitated which could be crystallized from a dichloromethane/diethyl ether mixture (1:2): yield 0.72 g (55%) of colourless crystals; dec pt

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Table II. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **1**

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å^2	atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å^2
Au1	0.04004 (9)	0.8780 (1)	0.64204 (7)	0.057	C220	0.282 (2)	1.276 (1)	0.981 (1)	0.064
Au2	0.2341 (1)	1.0385 (1)	0.84915 (7)	0.056	C221	0.352 (2)	1.297 (1)	0.930 (1)	0.063
Au3	0.2081 (1)	0.7840 (1)	0.77232 (8)	0.069	C222	0.387 (2)	1.390 (1)	0.931 (1)	0.089
P1	−0.1335 (6)	0.8454 (6)	0.5691 (5)	0.054	C223	0.353 (2)	1.462 (1)	0.983 (1)	0.106
P2	0.2441 (7)	1.1530 (7)	0.9807 (5)	0.072	C224	0.282 (2)	1.441 (1)	1.035 (1)	0.096
P3	0.2202 (7)	0.6656 (7)	0.8264 (5)	0.082	C225	0.247 (2)	1.348 (1)	1.034 (1)	0.103
P4	0.2069 (6)	0.9091 (6)	0.7213 (5)	0.054	C230	0.117 (1)	1.141 (2)	1.012 (1)	0.053
C40	0.311 (2)	0.923 (2)	0.659 (1)	0.053	C231	0.031 (1)	1.136 (2)	0.950 (1)	0.107
C41	0.327 (2)	0.842 (2)	0.600 (1)	0.076	C232	−0.068 (1)	1.129 (2)	0.971 (1)	0.114
C42	0.411 (2)	0.852 (2)	0.558 (1)	0.107	C233	−0.080 (1)	1.128 (2)	1.054 (1)	0.091
C43	0.479 (2)	0.942 (2)	0.576 (1)	0.112	C234	0.007 (1)	1.132 (2)	1.116 (1)	0.087
C44	0.464 (2)	1.023 (2)	0.635 (1)	0.154	C235	0.105 (1)	1.139 (2)	1.095 (1)	0.079
C45	0.380 (2)	1.013 (2)	0.677 (1)	0.111	C310	0.296 (2)	0.598 (2)	0.772 (1)	0.041
C110	−0.224 (2)	0.748 (1)	0.585 (1)	0.054	C311	0.377 (2)	0.571 (2)	0.815 (1)	0.073
C111	−0.333 (2)	0.733 (1)	0.562 (1)	0.068	C312	0.431 (2)	0.515 (2)	0.765 (1)	0.083
C112	−0.402 (2)	0.654 (1)	0.570 (1)	0.111	C313	0.405 (2)	0.485 (2)	0.673 (1)	0.089
C113	−0.362 (2)	0.590 (1)	0.600 (1)	0.082	C314	0.324 (2)	0.512 (2)	0.631 (1)	0.094
C114	−0.253 (2)	0.605 (1)	0.623 (1)	0.111	C315	0.270 (2)	0.568 (2)	0.681 (1)	0.077
C115	−0.184 (2)	0.684 (1)	0.615 (1)	0.083	C320	0.096 (2)	0.577 (2)	0.814 (1)	0.075
C120	−0.183 (2)	0.945 (1)	0.606 (1)	0.039	C321	0.002 (2)	0.602 (2)	0.808 (1)	0.067
C121	−0.207 (2)	0.997 (1)	0.553 (1)	0.072	C322	−0.094 (2)	0.534 (2)	0.795 (1)	0.114
C122	−0.239 (2)	1.079 (1)	0.588 (1)	0.084	C323	−0.096 (2)	0.442 (2)	0.789 (1)	0.113
C123	−0.248 (2)	1.108 (1)	0.675 (1)	0.094	C324	−0.002 (2)	0.416 (2)	0.796 (1)	0.173
C124	−0.224 (2)	1.056 (1)	0.728 (1)	0.104	C325	0.094 (2)	0.484 (2)	0.809 (1)	0.128
C125	−0.192 (2)	0.975 (1)	0.693 (1)	0.070	C330	0.280 (2)	0.708 (2)	0.9418 (9)	0.060
C130	−0.151 (2)	0.814 (2)	0.451 (1)	0.061	C331	0.376 (2)	0.780 (2)	0.9691 (9)	0.071
C131	−0.059 (2)	0.849 (2)	0.425 (1)	0.061	C332	0.430 (2)	0.816 (2)	1.0574 (9)	0.088
C132	−0.061 (2)	0.831 (2)	0.336 (1)	0.079	C333	0.389 (2)	0.782 (2)	1.1183 (9)	0.078
C133	−0.154 (2)	0.777 (2)	0.272 (1)	0.072	C334	0.293 (2)	0.710 (2)	1.0910 (9)	0.080
C134	−0.246 (2)	0.742 (2)	0.298 (1)	0.106	C335	0.239 (2)	0.673 (2)	1.0028 (9)	0.065
C135	−0.244 (2)	0.761 (2)	0.387 (1)	0.090	C410	0.267 (5)	0.764 (5)	0.571 (3)	0.051
C210	0.334 (1)	1.147 (2)	1.072 (1)	0.048	C450	0.352 (6)	1.085 (6)	0.701 (4)	0.090
C211	0.380 (1)	1.228 (2)	1.148 (1)	0.050	B	0.589 (2)	0.336 (2)	0.695 (2)	0.200
C212	0.449 (1)	1.222 (2)	1.218 (1)	0.095	F1	0.657 (2)	0.277 (2)	0.692 (1)	0.132
C213	0.471 (1)	1.136 (2)	1.212 (1)	0.073	F2	0.518 (2)	0.320 (3)	0.749 (2)	0.287
C214	0.424 (1)	1.056 (2)	1.137 (1)	0.147	F3	0.649 (2)	0.433 (2)	0.730 (2)	0.219
C215	0.356 (1)	1.061 (2)	1.067 (1)	0.094	F4	0.531 (2)	0.314 (2)	0.609 (2)	0.223

175–180 °C. ^{1}H NMR (dimethyl-d_6 sulfoxide, 25 °C): $\delta = 3.32$ (s, 3 H, CH_3), 6.70–7.05, 8.30–8.40 (m, 4 H, C_6H_4), 7.17–7.73 (m, 60 H, C_6H_5). $\{^1H\}^{31}P$ NMR (CD_2Cl_2): $\delta = 38.4$ (d, $^2J(PP) = 196$ Hz, *P*Ph$_3$), −54.6 (quint, $^2J(PP) = 196$ Hz, *o*-Tol*P*). MS (FAB, matrix nitrobenzyl alcohol): $m/z = 1501.0$ [$M^+ - AuPPh_3$] (11.0%), 980.2 [M^{2+}] (38.6%), 721.8 [$(Ph_3P)_2Au^+$] (100%). Anal. Calcd for $C_{79}H_{67}Au_4B_2F_8P_5$ (M_r 2132.74): C, 44.49; H, 3.17; Au, 36.94. Found: C, 45.0; H, 3.25; Au, 37.0.

(2-Methylphenyl)tris[(triphenylphosphine)aurio(I)]arsonium(+) Tetrafluoroborate (3). A solution of the oxonium reagent (0.600 mg, 0.4 mmol) in dichloromethane (20 mL) was treated with a solution of (2-methylphenyl)arsine (60 mg, 0.36 mmol) in the same solvent (3 mL) at −50 °C. An orange solution formed, which was warmed to −25 °C after 30 min and layered with pentane (8 mL). An orange oil separated, which left a red solid when dried in a vacuum. Precipitation from dichloromethane solution with diethyl ether gave a pure yellow microcrystalline product: yield 520 mg (87%); mp 140 °C dec. ^{1}H NMR ($CDCl_3$, 25 °C): $\delta = 2.80$ (s, 3 H, CH_3), 7.35–7.65 (m, 47 H, C_6H_5 + *m*-C_6H_4), 8.20–8.40 (m, 2 H, *o,p*-C_6H_4). $\{^1H\}^{31}P$ NMR (CD_2Cl_2): $\delta = 44.95$ (s). ^{197}Au Mössbauer spectrum (4 K): IS = 3.11 mm/s; QS = 7.73 mm/s. MS (FAB, matrix nitrobenzyl alcohol): $m/z = 1542.3$ [M^+] (100%), 1280.3 [$M^+ - PPh_3$] (13%), 1084.5 [$M^+ - AuPPh_3$] (10%). Anal. Calcd for $C_{61}H_{52}AsAu_3BF_4P_3$ (M_r 1630.63): C, 44.93; H, 3.21; Au, 36.24. Found: C, 44.02; H, 3.21; Au, 36.20.

Crystal Structure Determinations. Suitable crystals of **1** and **2** were mounted in glass capillaries under argon and examined directly on the diffractometer. Crystal data and important numbers pertinent to data collection and refinement are compiled in Table I. Unit cell dimensions and their standard deviations were derived from the setting angles of 25 automatically centered reflections. Data were corrected for Lorentz and polarization factors and empirically for the absorption (transmission coefficient: for **1**, $T = 0.33$–1.00; for **2**, $T = 0.71$–1.00). Structure **1** was solved by direct methods, and structure **2**, by automated Patterson methods. Both solutions were completed by difference Fourier syntheses and refined by full-matrix least-squares techniques. Hydrogen atoms were neglected. All heavy atoms (Au, P) were refined anisotropically. For **1** the phenyl rings were refined isotropically in idealized geometry, employing a split model (SOF 0.5:0.5) for the two possible positions of the *o*-tolyl group. The anion was refined as an idealized tetrahedron in the region of highest electron density. For **2** all non-hydrogen atoms of the cation and the anion were refined anisotropically; those of the crystal benzene molecules were included with isotropic temperature factors into the refinement. The fractional atomic coordinates and equivalent isotropic displacement parameters are presented in Tables II and III. Programs used were DELOS, LEPAGE (cell reduction), SHELXS-86 (structure solution), SHELX-76 (structure refinement), and local routines.

Results

In recent work tris[(triphenylphosphine)aurio(I)]oxonium tetrafluoroborate was found to be an efficient aurating agent for many main group element nucleophiles. Among the most straightforward reactions ranks the auration of primary amines RNH_2, with R = alkyl or aryl, to give the quaternary organotris[(triorganophosphine)aurio(I)]ammonium salts of the type $RN(AuPR'_3)_3^+X^-$, with X^- as a noncoordinating counterion.[23-25] These "gilded" primary amines feature short Au···Au contacts, comparable to those in the homoleptic species[5] $N(AuPR_3)_4^+X^-$, which strongly support the aggregation of the three metal atoms at nitrogen. In contrast, the analogous auration of primary phosphines had not been reported in the literature.

Synthesis and Structure of the (2-Methylphenyl)tris[(triphenylphosphine)aurio(I)]phosphonium Cation. In the present study it could be shown that arylphosphines can also be aurated by $(Ph_3PAu)_3O^+BF_4^-$, but the products were found to be much less stable than their nitrogen analogues. The *P*-phenyl compound was too unstable to be isolated in a pure state and was only identified in solution through its $\{^1H\}^{31}P$ NMR spectrum (see Experimental Section). The *P*-(*o*-tolyl) compound **1** (eq 1) could

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(23) Perevalova, E. G.; Grandberg, K. I.; Smyslova, E. I.; Kuz'mina, L. G.; Korsunskii, V. I.; Kravtsov, D. N. *Organomet. Chem. USSR* **1989**, *2*, 523–526.

(24) Ramamoorthy, V.; Sharp, P. R. *Inorg. Chem.* **1990**, *29*, 3336–3341.

(25) Grohmann, A.; Riede, J.; Schmidbaur, H. *J. Chem. Soc., Dalton Trans.* **1991**, 783–787.

Table III. Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters for **2**$\cdot 4C_6H_6$ ($U(\mathrm{eq}) = (U(1)U(2)U(3))^{1/3}$, Where $U(1)$, $U(2)$, and $U(3)$ are the Eigenvalues of the $U(ij)$ Matrix and Esd's are in Parentheses)

atom	*x/a*	*y/b*	*z/c*	*U*(eq), Å^2
Au1	0.48257 (3)	0.24954 (2)	0.19104 (2)	0.029
Au2	0.53298 (3)	0.25620 (2)	0.34015 (2)	0.030
Au3	0.41148 (3)	0.10429 (2)	0.32313 (2)	0.026
Au4	0.37928 (3)	0.09656 (2)	0.17353 (2)	0.028
P	0.5224 (2)	0.1517 (1)	0.2601 (1)	0.025
C11	0.6367 (8)	0.1080 (6)	0.2666 (4)	0.024
C12	0.6256 (9)	0.0301 (7)	0.2517 (6)	0.038
C13	0.711 (1)	−0.0096 (9)	0.2577 (7)	0.053
C14	0.806 (1)	0.031 (1)	0.2787 (8)	0.061
C15	0.819 (1)	0.109 (1)	0.2948 (7)	0.054
C16	0.7340 (9)	0.1505 (9)	0.2871 (6)	0.046
C17	0.753 (1)	0.2353 (9)	0.301 (1)	0.064
P1	0.4278 (2)	0.3422 (2)	0.1261 (1)	0.031
C111	0.457 (1)	0.3351 (6)	0.0464 (5)	0.039
C112	0.484 (1)	0.2670 (7)	0.0216 (6)	0.048
C113	0.502 (1)	0.2588 (9)	−0.0418 (7)	0.060
C114	0.495 (1)	0.3191 (8)	−0.0796 (7)	0.057
C115	0.466 (1)	0.3877 (8)	−0.0552 (7)	0.058
C116	0.451 (1)	0.3964 (7)	0.0087 (6)	0.049
C121	0.485 (1)	0.4364 (6)	0.1693 (5)	0.037
C122	0.428 (1)	0.4956 (7)	0.1735 (6)	0.047
C123	0.483 (2)	0.5663 (7)	0.2110 (8)	0.053
C124	0.585 (2)	0.574 (1)	0.2393 (7)	0.060
C125	0.638 (1)	0.514 (1)	0.2335 (9)	0.072
C126	0.589 (1)	0.4446 (8)	0.1989 (8)	0.061
C131	0.2921 (9)	0.3413 (6)	0.1060 (6)	0.041
C132	0.2475 (9)	0.3589 (7)	0.1602 (7)	0.045
C133	0.143 (1)	0.3612 (8)	0.1455 (7)	0.055
C134	0.082 (1)	0.3463 (8)	0.080 (1)	0.068
C135	0.126 (1)	0.326 (1)	0.0281 (9)	0.074
C136	0.232 (1)	0.3247 (8)	0.0406 (7)	0.059
P2	0.5341 (2)	0.3598 (2)	0.4133 (1)	0.030
C211	0.5207 (9)	0.3349 (6)	0.4943 (5)	0.033
C212	0.437 (1)	0.3502 (7)	0.5169 (6)	0.041
C213	0.429 (1)	0.3270 (8)	0.5788 (7)	0.054
C214	0.503 (1)	0.2887 (8)	0.6163 (7)	0.057
C215	0.586 (1)	0.2755 (8)	0.5932 (7)	0.061
C216	0.596 (1)	0.2977 (7)	0.5312 (6)	0.049
C221	0.4256 (9)	0.4070 (6)	0.3758 (5)	0.032
C222	0.4400 (9)	0.4830 (6)	0.3628 (5)	0.037
C223	0.354 (1)	0.5162 (7)	0.3329 (6)	0.043
C224	0.257 (1)	0.4746 (8)	0.3160 (6)	0.051
C225	0.244 (1)	0.3993 (8)	0.3291 (6)	0.048
C226	0.3294 (9)	0.3649 (7)	0.3585 (6)	0.041
C231	0.6477 (8)	0.4293 (6)	0.4317 (5)	0.035
C232	0.703 (1)	0.4337 (7)	0.3841 (6)	0.046
C233	0.788 (1)	0.4891 (8)	0.3960 (7)	0.052
C234	0.817 (1)	0.5368 (7)	0.4547 (7)	0.050
C235	0.7641 (9)	0.5308 (7)	0.5035 (6)	0.047
C236	0.6788 (9)	0.4764 (6)	0.4919 (6)	0.039
P3	0.2966 (2)	0.0675 (1)	0.3820 (1)	0.027
C311	0.2231 (8)	0.1428 (6)	0.3948 (5)	0.030
C312	0.1566 (9)	0.1642 (7)	0.3380 (7)	0.046
C313	0.1000 (9)	0.2244 (7)	0.3454 (7)	0.045
C314	0.111 (1)	0.2630 (7)	0.4098 (7)	0.048
C315	0.179 (1)	0.2412 (7)	0.4651 (7)	0.049
C316	0.235 (1)	0.1815 (7)	0.4583 (6)	0.043
C321	0.3536 (8)	0.0442 (6)	0.4654 (5)	0.029
C322	0.4422 (9)	0.0893 (7)	0.5028 (6)	0.040
C323	0.483 (1)	0.0794 (7)	0.5710 (6)	0.046
C324	0.436 (1)	0.0232 (8)	0.5984 (6)	0.044
C325	0.348 (1)	−0.0237 (8)	0.5597 (6)	0.046
C326	0.3077 (9)	−0.0133 (7)	0.4927 (6)	0.043
C331	0.2035 (8)	−0.0131 (6)	0.3393 (5)	0.031
C332	0.1072 (8)	−0.0249 (7)	0.3498 (6)	0.040
C333	0.039 (1)	−0.0889 (7)	0.3180 (7)	0.050
C334	0.068 (1)	−0.1414 (8)	0.2761 (7)	0.053
C335	0.166 (1)	−0.1313 (7)	0.2659 (7)	0.055
C336	0.234 (1)	−0.0662 (7)	0.2966 (6)	0.045
P4	0.2300 (2)	0.0533 (2)	0.0942 (1)	0.031
C411	0.1265 (8)	0.0788 (6)	0.1286 (5)	0.034
C412	0.1222 (9)	0.1560 (7)	0.1439 (6)	0.042
C413	0.041 (1)	0.1780 (8)	0.1684 (6)	0.049
C414	−0.032 (1)	0.1219 (9)	0.1789 (7)	0.053
C415	−0.0249 (9)	0.0456 (9)	0.1652 (6)	0.048
C416	0.0548 (9)	0.0227 (7)	0.1397 (6)	0.042
C421	0.2105 (8)	−0.0484 (6)	0.0728 (5)	0.034
C422	0.263 (1)	−0.0913 (7)	0.1199 (6)	0.047
C423	0.249 (1)	−0.1714 (7)	0.1048 (7)	0.053
C424	0.184 (1)	−0.2051 (8)	0.0447 (8)	0.063
C425	0.134 (1)	−0.1612 (8)	−0.0022 (7)	0.059
C426	0.1476 (9)	−0.0822 (7)	0.0108 (6)	0.046
C431	0.2111 (8)	0.0940 (6)	0.0155 (5)	0.034
C432	0.1186 (9)	0.1189 (6)	−0.0142 (6)	0.040
C433	0.107 (1)	0.1462 (7)	−0.0771 (6)	0.049
C434	0.185 (1)	0.1473 (8)	−0.1092 (7)	0.058
C435	0.276 (1)	0.123 (1)	−0.0793 (7)	0.064
C436	0.290 (1)	0.0967 (9)	−0.0160 (7)	0.053
F1	0.4269 (7)	0.1634 (5)	0.7102 (4)	0.072
F2	0.4879 (9)	0.1477 (6)	0.8188 (4)	0.076
F3	0.5739 (8)	0.1197 (7)	0.7471 (5)	0.084
F4	0.558 (1)	0.2414 (6)	0.7770 (5)	0.093
B1	0.513 (1)	0.1681 (9)	0.7623 (7)	0.048
F5	0.8493 (8)	0.4109 (8)	0.2682 (5)	0.093
F6	0.9804 (9)	0.3527 (8)	0.2519 (7)	0.108
F7	0.986 (1)	0.402 (1)	0.3509 (7)	0.134
F8	0.998 (1)	0.4739 (9)	0.271 (1)	0.168
B2	0.953 (2)	0.411 (1)	0.287 (1)	0.069
C1	0.567 (1)	0.0654 (9)	0.0007 (8)	0.069
C2	0.510 (1)	0.0285 (9)	−0.0578 (8)	0.065
C3	0.558 (1)	0.0354 (9)	0.0616 (8)	0.070
C4	0.089 (1)	0.036 (1)	0.5459 (9)	0.079
C5	−0.066 (1)	0.042 (1)	0.4602 (9)	0.077
C6	0.022 (1)	0.078 (1)	0.5052 (9)	0.081
C7	0.256 (1)	0.248 (1)	0.760 (1)	0.091
C8	0.231 (2)	0.302 (1)	0.801 (1)	0.103
C9	0.157 (2)	0.350 (1)	0.772 (1)	0.110
C10	0.117 (2)	0.343 (1)	0.707 (1)	0.110
C11	0.137 (2)	0.292 (1)	0.664 (1)	0.112
C12	0.212 (2)	0.240 (1)	0.692 (1)	0.111
C13	0.871 (2)	0.253 (1)	0.490 (1)	0.113
C14	0.898 (2)	0.330 (1)	0.489 (1)	0.111
C15	0.901 (2)	0.378 (1)	0.541 (1)	0.102
C16	0.884 (2)	0.358 (1)	0.598 (1)	0.112
C17	0.858 (2)	0.279 (1)	0.603 (1)	0.109
C18	0.856 (2)	0.227 (1)	0.549 (1)	0.106
C19	0.784 (2)	0.347 (1)	0.791 (1)	0.116
C20	0.767 (3)	0.368 (2)	0.854 (2)	0.183
C21	0.835 (2)	0.425 (2)	0.916 (2)	0.152
C22	0.932 (3)	0.447 (2)	0.909 (2)	0.183
C23	0.939 (4)	0.420 (3)	0.835 (3)	0.242
C24	0.871 (3)	0.368 (2)	0.797 (2)	0.193

be obtained in 30% yield in crystalline form, however, and its crystal structure determined by single-crystal X-ray diffraction.

$$2\text{-}MeC_6H_4PH_2 + (Ph_3PAu)_3O^+BF_4^- \rightarrow H_2O + \underset{\mathbf{1}}{2\text{-}MeC_6H_4P(AuPPh_3)_3^+BF_4^-} \quad (1)$$

Compound **1** is a colorless crystalline solid, soluble in polar solvents like halomethanes, dimethyl sulfoxide, dimethylformamide, and hexamethyl phosphoric triamide and stable in air. When heated in a sealed capillary, it melts with decomposition at 183–186 °C. It is readily identified by elemental analysis and NMR spectroscopy. The proton spectrum (in CD_2Cl_2) exhibits the methyl singlet and the aryl multiplets in the correct overall intensity ratios (3:4:45). In the proton-decoupled ^{31}P spectrum (same solvent, room temperature) only two broad resonances are obtained in the intensity ratio 3:1, but these are split into the expected doublet/*quartet* patterns at −70 °C, with a $^2J(PP)$ coupling constant of 249 Hz. This temperature dependence of the signal patterns is indicative of intermolecular exchange processes in solution, probably involving the transfer of Ph_3PAu^+ groups between phosphine centers.

Crystals of compound **1** are triclinic, space group $P\bar{1}$, with two formula units in the unit cell related by a center of inversion. The structure is composed of independent phosphonium cations and tetrafluoroborate anions. Some disorder of the latter together with a rotational disorder of the 2-methylphenyl group are mainly

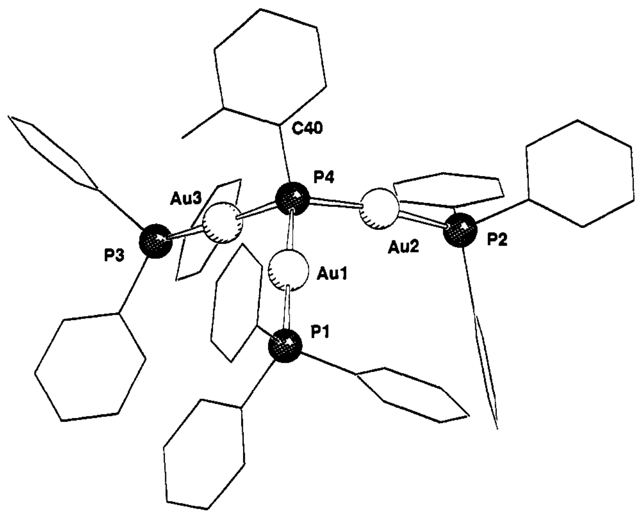

Figure 1. Structure of the cation $[(o\text{-Tol})P(AuPPh_3)_3]^+$ in crystals of the tetrafluoroborate salt **1**, with atomic numbering. (SCHAKAL; for clarity, phenyl and tolyl groups are shown as hexagons only.)

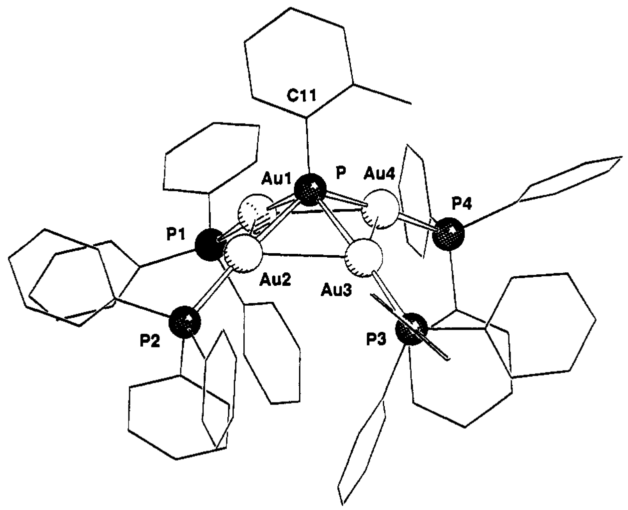

Figure 2. Structure of the dication $[(o\text{-Tol})P(AuPPh_3)_4]^{2+}$ in crystals of the tetrafluoroborate salt $\mathbf{2}\cdot 4C_6H_6$, with atomic numbering. (SCHAKAL; for clarity, phenyl and tolyl groups are shown as hexagons only.)

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

	Distances		
Au1–P4	2.277 (7)	Au3–P3	2.280 (9)
Au2–P4	2.317 (8)	P4–C40	1.85 (2)
Au3–P4	2.321 (8)	Au1$\cdots$Au2	3.709 (1)
Au1–P1	2.315 (8)	Au1$\cdots$Au3	3.696 (1)
Au2–P2	2.288 (8)	Au2$\cdots$Au3	3.639 (1)
	Angles		
P1–Au1–P4	176.4 (3)	C40–P4–Au3	109.6 (9)
P2–Au2–P4	172.3 (3)	Au1–P4–Au2	107.7 (3)
P3–Au3–P4	176.4 (3)	Au1–P4–Au3	107.0 (3)
C40–P4–Au1	114.7 (7)	Au2–P4–Au3	103.3 (3)
C40–P4–Au2	113.7 (9)		

[a] For atomic numbering, see Figure 1.

responsible for the not fully satisfactory quality of the final solution ($R = 0.091$; $R_w = 0.0754$).

The cations of compound **1** have the expected tetrahedral structure (Figure 1) with the P–Au–P angles close to linearity and the Au–P–Au and Au–P–C angles close to 109°. Only the angle Au2–P4–Au3 is significantly smaller [103.3 (3)°] than the standard value (Table I). As a consequence of these tetrahedral angles the intramolecular Au$\cdots$Au contacts are all larger than 3.6 Å, in fact close to the van der Waals distances, and therefore do not suggest any metal–metal bonding. This is in contrast to the short Au$\cdots$Au contacts in the corresponding ammonium salts[20,24,25] (above), where distances of ca. 3.0 Å prevail owing to the smaller atomic radius of nitrogen as compared to phosphorus. The high stability of these ammonium species with almost any given substituent R has been attributed to appreciable Au$\cdots$Au bonding.[20,25] The limited stability of the phosphonium species with common *P*-alkyl or *P*-aryl substituents can therefore now be ascribed to the absence of such *sub* van der Waals metal–metal interactions.

It appeared likely, however, that the metal trio in **1** should be "auriophilic" for just this reason[1] and should act as an acceptor for an additional Ph_3PAu^+ unit which could secure close metal–metal contacts. The compound was therefore reacted with 1 equiv of $Ph_3PAu^+BF_4^-$.

Synthesis and Structure of the (2-Methylphenyl)tetrakis[(triphenylphosphine)aurio(I)]phosphonium Dication. The reaction of **1** with (triphenylphosphine)gold(I) tetrafluoroborate in tetrahydrofuran at −70 °C was found to afford an overall 55% yield of the expected product (**2**, eq 2), which first appeared as a yellow oil, but could be crystallized from dichloromethane/benzene (2:1) as colorless air-stable crystals (decomposition temperature 175–180 °C).

$$\underset{\mathbf{1}}{[2\text{-}MeC_6H_4P(AuPPh_3)_3]^+BF_4^-} + (Ph_3PAu)^+BF_4^- \rightarrow \underset{\mathbf{2}}{[2\text{-}MeC_6H_4P(AuPPh_3)_4]^{2+}[BF_4^-]_2} \quad (2)$$

The identity of the product (**2**) is readily confirmed by elemental analysis, mass spectrometry, and NMR spectroscopy. Fast atom bombardment mass spectra produced the *dication* of the salt (m/z = 980.2) in high relative intensity (38.6%), together with the cation of **1** (11.0% relative intensity), and $[(Ph_3P)_2Au]^+$ as the basis peak (100%).

Proton NMR spectra (in dimethyl-d_6 sulfoxide) show the signals of the methyl and aryl groups in the correct overall intensity ratios (3:4:60). Proton-decoupled ^{31}P NMR spectra (in dichloromethane-d_2) show two resonances with the expected intensity ratio and the expected doublet/*quintet* patterns, even at ambient temperature. The value of the coupling constant $^2J(PP)$ = 196 Hz is much lower than for the starting material in eq 1 (**1**). Though no relative signs have been determined, this reduction of J by more than 20% means a strongly reduced s-character of the orbitals engaged in the bonding of the central phosphorus atom, as expected for tetra- and pentacoordination, respectively. As with **1**, there is no NMR evidence for paramagnetism with compound **2**.

Crystals of $\mathbf{2}\cdot 4C_6H_6$ are triclinic, space group $P\bar{1}$, with $Z = 2$ formula units in the unit cell. The structure is composed of independent pentacoordinate phosphonium(2+) dications and two tetrafluoroborate counterions. The structure of the dication can be described as slightly distorted square-pyramidal with a phosphorus atom in the center, the 2-methylphenyl group at the apex, and the four gold atoms at the base (Figure 2). The apical 2-methylphenyl ring is staggered relative to the Au_4 square (with the phenyl ring thus bisecting two Au–Au edges: Au1–Au2, Au3–Au4) and tilted toward one of these edges (Au3–Au4) to give the *o*-methyl group more space. All four P–Au–P angles are close to linearity, and (as for **1**) the geometries of the triphenylphosphine groups show no anomalies.

The four Au–P–Au angles range from 75.3 to 79.0°. These small angles give rise to four short Au$\cdots$Au contacts along the edges of the Au_4 square with values between 2.891 (1) and 3.012 (1) Å, exactly as expected from previous work on hypercoordinate element-centered gold clusters (Introduction). There can be no doubt that the short Au$\cdots$Au contacts established through the addition of an extra Ph_3PAu^+ unit to the structure of the cation in **1** must be held responsible for the ease of formation and stability of the dication in **2**.

The Au–P(center) distances range from 2.354 (2) to 2.379 (2) Å and are therefore longer than the terminal Au–P(Ph_3) bonds with distances between 2.286 (3) and 2.301 (2) Å. They are also longer than the reference distances in the cation of **1** with a tetracoordinate phosphorus atom [2.277 (7)–2.321 (8) Å, (Table IV)]. The bonds to the hypercoordinate phosphorus atom P are

Table V. Selected Bond Distances (Å) and Angles (deg) for Compound 2[a]

	Distances		
Au1-P	2.379 (2)	Au4-P4	2.289 (3)
Au2-P	2.354 (2)	P-C11	1.81 (1)
Au3-P	2.379 (2)	Au1···Au2	2.984 (1)
Au4-P	2.357 (2)	Au2···Au3	2.975 (1)
Au1-P1	2.295 (3)	Au3···Au4	3.012 (1)
Au2-P2	2.286 (3)	Au4···Au1	2.891 (1)
Au3-P3	2.301 (2)		
	Angles		
P-Au1-P1	174.1 (1)	C11-P-Au4	116.2 (3)
P-Au2-P2	176.3 (1)		
P-Au3-P3	174.9 (1)	Au1-P-Au2	78.2 (1)
P-Au4-P4	173.2 (1)	Au2-P-Au3	77.9 (1)
C11-P-Au1	122.1 (3)	Au3-P-Au4	79.0 (1)
C11-P-Au2	116.2 (3)	Au4-P-Au1	75.3 (1)
C11-P-Au3	116.2 (3)		

[a] For atomic numbering, see Figure 2.

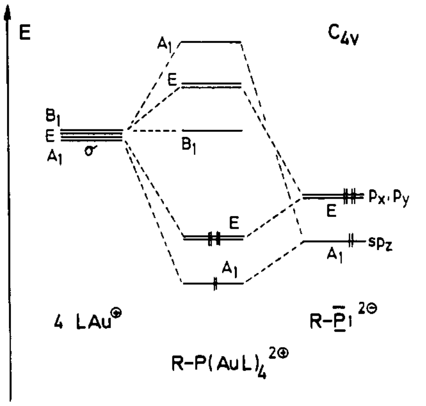

Figure 3. Qualitative molecular orbital diagram for the bonding in the square pyramid of the cations $(o\text{-Tol})P[AuPPh_3]_4^{2+}$ in 2 (idealized C_{4v} symmetry).

therefore weaker than the standard $Ph_3P\text{-}Au$ donor bonds, and in fact they have to be described as electron-deficient. The P-C(o-Tol) distance appears to be "normal", however, within the experimental error (Table V), in agreement with a qualitative molecular orbital scheme (Figure 3).

Investigations of Arsenic Analogues of 1 and 2. The studies on the (2-methylphenyl)tris- and (2-methylphenyl)tetrakis[triphenylphosphine)aurio(I)]phosphonium tetrafluoroborates (1, 2) were extended to include the corresponding arsenic analogues. The conversion of (2-methylphenyl)arsine into the triaurated arsonium salt 3 (eq 3) through the reaction with the oxonium reagent in dichloromethane at −50 °C was achieved in 87% yield. The colorless, air-stable crystalline product, mp 140 °C with decomposition, is readily soluble in standard polar solvents.

$$2\text{-}MeC_6H_4AsH_2 + [Ph_3PAu]_3O^+BF_4^- \rightarrow H_2O + \underset{\mathbf{3}}{2\text{-}MeC_6H_4As[AuPPh_3]_3^+BF_4^-} \quad (3)$$

Compound 3 was identified by its elemental analysis, by mass spectrometry, and by NMR and Mössbauer spectroscopy. FAB-MS produced the parent peak of the arsonium cation at m/z = 1542.3 (100%), accompanied by m/z = 1280.3 for $M^+ - PPh_3$ (13%), and m/z = 1084.5 for $M^+ - AuPPh_3$ (10%). The proton NMR spectrum (in $CDCl_3$) contains the methyl and aryl signals in the appropriate intensity ratio (3:2:2:45). The proton-decoupled ^{31}P NMR spectrum shows only one line at $\delta = 44.95$ (in CD_2Cl_2). The ^{197}Au Mössbauer spectrum (at 4 K) features a slightly asymmetric quadrupole doublet (quadrupole splitting 7.73 mm/s) with an isomeric shift value IS = 3.11 mm/s, indicating the presence of three equivalent gold atoms in oxidation state +I.[26,27] No single crystals of compound 3 could be grown, and hence its crystal structure could not be determined. The structure of the cation is not expected to be very different, however, from that of the phosphonium analogue 1.

Very surprisingly, compound 3 could not be aurated further using $[Ph_3PAu]^+BF_4^-$ under conditions successfully applied for the auration of 1 to give 2. There is a parallel in the reaction behavior observed here as related to the studies with the homoleptically aurated phosphonium salts. While $[Ph_3PAu]_4P^+$ is known[4] to accept $[Ph_3PAu]^+$ to give $[Ph_3PAu]_5P^{2+}$, $[Ph_3PAu]_4As^+$ could not be aurated[5] to give $[Ph_3PAu]_5As^{2+}$. The longer atomic radius of As as compared to P, which renders intramolecular Au···Au contacts too long in the pentacoordinate complex, is the only plausible reason to be invoked for these differences.

Discussion

The present study has shown that both (2-methylphenyl)-phosphine and -arsine can be converted into triply aurated phosphonium (1) and arsonium salts (3), respectively, using tris[(triphenylphosphine)aurio(I)]oxonium fluoroborate. These salts are robust products, easily characterized by standard analytical and spectroscopic techniques. According to an X-ray analysis, the cations of 1 feature a standard tetrahedral geometry at the central phosphorus atom with linear coordination at the three gold atoms (Figure 1), in keeping with the classical picture of bonding in phosphonium and arsonium salts. The large atomic radius of phosphorus (as compared to nitrogen) and the tetrahedral angles preclude significant metal-metal bonding, which is an important stabilizing factor for the corresponding ammonium compounds.[24,25]

The phosphonium cation in compound 1 has been found to accept a fourth $[Ph_3PAu]^+$ unit to form a novel pentacoordinate dicationic species $o\text{-}TolP[AuPPh_3]_4^{2+}$. As again determined by an X-ray analysis of the fluoroborate salt (2), the dication features a square-pyramidal geometry with four gold atoms at the base, the 2-methylphenyl group at the apex, and the phosphorus atom in the center (Figure 2). The gold atoms form a slightly distorted square with short Au···Au contacts along the edges. These contacts with distances at ca. 3.0 Å must be taken as bonding interactions, as already suggested for related element-centered gold(I) aggregates, and are an important factor in stabilizing the system.[1]

With the *Au···Au bonding neglected*, the pentagonal-pyramidal skeleton is electron-deficient with only eight valence electrons available for five bonds: [P-C(Tol)] and 4[P-Au]. In a simplified molecular orbital diagram under idealized C_{4v} symmetry, the $RP(AuL)_4^{2+}$ pyramid can be composed of the (2-methylphenyl)phosphide dianion $R\text{-}P^{2-}$ with three pairs of electrons available for bonding and four $[LAu]^+$ acceptor units each directing an empty σ orbital (an sp hybrid) toward the phosphide center. The $R\text{-}P^{2-}$ orbitals obey A_1 and E symmetry, while the four gold σ orbitals transform into A_1, E, and B_1 (Figure 3). Symmetry-allowed linear combination of orbitals leads to three bonding states, which can be filled by the six electrons available to give a diamagnetic ground state. (Note that 2 is diamagnetic.) The bond orders are thus 1 for the apical P-tolyl bond, and $^3/_4$ for each of the four Au-P(center) bonds. Calculations *including Au···Au interactions* are a much more formidable task,[12,13] since relativistic effects have to be taken into account.[11] Results of work in this direction, which follows current studies of the carbon-, nitrogen-, and arsenic-centered aggregates,[12,13] will be reported in due course.

Regarding structure and bonding in 2 there remains also the question of the role of the *P-aryl* substituent and its geometrical orientation (bisecting two Au···Au edges). This point is important since analogous *P-alkyl* compounds appear to be inherently unstable. (All experiments to synthesize such compounds have failed.) It is tempting to assume a delocalization of electrons from the aromatic ring into the electron-deficient square pyramid, as borne out by a treatment of the skeleton under reduced (C_{2v})

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symmetry (neglecting the *o*-methyl substitutent of the tolyl group). This effect should also be operative for an arsenic analogue, but preparative experiments have so far been unsuccessful, probably owing to a further increase of the radius of the central element, which renders Au···Au contacts more difficult.

Arylphosphinidene groups RP bridging four metal atoms are not completely unknown in the structural chemistry of metal clusters. A very good example in case is the tetranuclear rhodium(I) complex $\{Rh_4(CO)_4[\mu\text{-}P(C_6H_{11})_2]_4(\mu_4\text{-}PC_6H_{11})\}$ with 4-fold symmetry.[28] It should be noted, however, that the open-shell configuration of electrons of the Rh(I) centers ($4d^8$) suggests metal–metal bonding in classical terms for these clusters, while for gold(I) with its formally closed-shell configuration ($5d^{10}$) such bonding interactions are ruled out, unless a mixing with empty 6s states[29] through relativistic contraction of the latter provides a new basis for such bonding contacts. It is this point which makes the title compounds interesting novel species in cluster chemistry, and the almost complete absence of similar phenomena with the neighboring elements platinum and mercury once more distinguishes gold as a unique element.

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Registry No. 1, 132157-62-1; 2, 141088-89-3; 2·4C_6H_6, 141088-92-8; 3, 141088-91-7; $[(C_6H_5)_3PAu]_3O^+BF_4^-$, 53317-87-6; $[Ph_3PAu]^+[BF_4]^-$, 67215-70-7; phenyltris[(triphenylphosphine)aurio(I)]phosphonium(+) tetrafluoroborate, 132157-66-5.

Supplementary Material Available: For complexes 1 and 2, tables of crystallographic data and anisotropic thermal parameters (12 pages); tables of observed and calculated structure factor amplitudes (122 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Reactivity of Ruthenium Carbonyl Complexes Containing a Chelating Triphosphine Ligand and Two Weakly Coordinated Anions

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Protonation of *cis-mer*-$RuH_2(CO)(Cyttp)$ (Cyttp = $PhP(CH_2CH_2CH_2PCy_2)_2$) with excess HX (X = BF_4, O_3SCF_3) in benzene/diethyl ether produces air-stable complexes with two weakly coordinated anions, viz., *cis-mer*-$RuX_2(CO)(Cyttp)$ (X = BF_4 (**2**), O_3SCF_3 (**3**)). A single-crystal X-ray diffraction analysis at 223 K shows that **3** crystallizes in the space group $P2_1/c$ with cell parameters $a = 11.712$ (2) Å, $b = 15.338$ (2) Å, $c = 27.072$ (3) Å, $\beta = 98.58$ (1)°, $Z = 4$, $V = 4809$ (1) Å^3, $R = 0.041$, and $R_w = 0.046$ for the 7036 intensities with $F_o^2 > 3\sigma(F_o^2)$ and the 539 variables. The molecules contain two cis-oriented monodentate $O_3SCF_3^-$ ligands. The structural behavior of **2** and **3** in both CD_2Cl_2 and acetone-d_6 was investigated by variable-temperature $^{31}P\{^1H\}$ and $^{19}F\{^1H\}$ NMR spectroscopies in the range 178–303 K; a complex behavior involving species with coordinated and free BF_4^- and $O_3SCF_3^-$ ions was observed. **2** and **3** are useful synthons for a variety of coordination and organometallic complexes. **2** undergoes substitution reactions with acetonitrile and organic isocyanides to afford disubstituted complexes *cis-mer*-$[Ru(CO)L_2(Cyttp)][BF_4]_2$ (L = MeCN, CNBu-*t*, CNCy). New Ru–F complexes $[Ru(F)(CO)(L)(Cyttp)][BF_4]$ (L = H_2O, CO, CNBu-*t*) have also been synthesized from **2**. The absence of fluoride abstraction from triflate and the solubility of **3** in THF render this a more versatile starting material than **2**. Substitution reactions with acetonitrile and ammonia produce disubstituted complexes *cis-mer*-$[Ru(CO)L_2(Cyttp)][O_3SCF_3]_2$ (L = MeCN, NH_3). The reaction of **3** with an excess of trimethyl phosphite leads only to the monosubstituted phosphite products $[Ru(CO)(P(OMe)_3)(Cyttp)][O_3SCF_3]_2$ (**11a**, **11b**), which probably differ by the orientation of the Ph group of Cyttp. Complexes with the cations $[Ru(X)(CO)(P(OMe)_3)(Cyttp)]^+$ (X = Cl, OMe) are generated from reactions of mixtures of **11a** and **11b** with the appropriate anion. **3** also reacts with selected anions (X^- = Me^-, I^-, and H^-) to afford complexes *cis-mer*-$RuX_2(CO)(Cyttp)$.

Introduction

In recent years, transition-metal complexes with weakly coordinated anions have been the focus of many studies and several reviews.[1] These complexes have been recognized for their utility as starting materials that readily undergo substitution reactions even with weakly nucleophilic ligands under mild conditions.[2] Although some ruthenium complexes with multiple phosphine ligands and weakly coordinated anions have been isolated,[3,4] we found no examples that contain a chelated triphosphine ligand. The advantages of using chelated triphosphine ligands over monodentate phosphine ligands in the synthesis of transition-metal complexes have been enumerated.[5] One advantage in particular, viz., the added control on the coordination number and geometry of products, was utilized in this study to prepare complexes with weakly coordinated anions that do not lose phosphine ligands.

A variety of reactions of ruthenium dihydridophosphine complexes with hydride abstracting reagents[6] or with strong acids containing poorly coordinating anions[7,8] have failed to produce ruthenium phosphine complexes with weakly ligated anions. In particular, the reaction of *cis-mer*-$RuH_2(CO)(PPh_3)_3$ with HBF_4 (aq) gives *mer*-$[RuH(CO)(H_2O)(PPh_3)_3][BF_4]$, which upon carbonylation loses phosphine to yield $[RuH(CO)_2(H_2O)(PPh_3)_2][BF_4]$.[8] However, the reactions of *cis-mer*-$RuH_2(CO)(PPh_3)_3$ with sulfonic acids, HO_3SR (R = Me, CF_3, and

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