between the two closest distances to the nickel atom, and it can be seen that the charge (+1.5) is consistent with the Mulliken population analysis on the nickel atom found in the present EHMO calculations.

Certainly this method involves the appearance of two new parameters that could be avoided if we apply a charge iteration scheme using the results of a Kohn–Sham calculation instead of the usual iteration parameters. Work on this line is in progress and will be presented elsewhere.

Supplementary Material Available: Atom coordinates (Tables S1–S3), anisotropic temperature factors (Tables S4–S6), equations for least-squares planes (Table S7), atomic deviations from least-squares planes (Table S8), hydrogen coordinates (Tables S9–S11), and packing diagrams (Figures S1–S3) (15 pages); tables of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, Texas 77843, and Department of Chemistry, University of Texas at Austin, Austin, Texas 78712

Synthesis and X-ray Crystal Structures of $[Au(CH_2)_2PPh_2]_2(CF_3)_2$, $[Au(CH_2)_2PPh_2]_2(C_6F_5)_2$, and $[PPN][Au(C_6F_5)_4]$: Two Dinuclear Gold(II) Ylide Complexes Containing Alkyl and Aryl Ligands and a Tetrakis(pentafluorophenyl)aurate(III) Anion Complex

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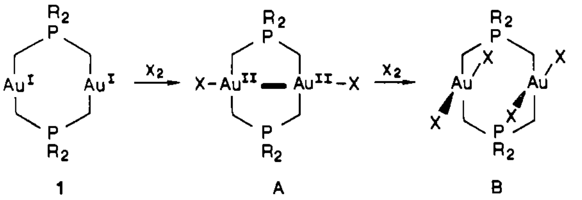
The reaction of $[Au(CH_2)_2PPh_2]_2Br_2$ with $Cd(CF_3)_2(glyme)$ in CH_2Cl_2 produces $[Au(CH_2)_2PPh_2]_2(CF_3)_2$, the first dialkyl Au(II) phosphorus ylide dimer to be structurally characterized. In both the solid state (X-ray) and solution (via ^1H NMR) the complex is symmetrically substituted along the Au(II)–Au(II) axis. The reaction of $Tl(C_6F_5)_2Cl$ with $[Au(CH_2)_2PPh_2]_2$ gives the diaryl Au(II) phosphorus ylide dimer $[Au(CH_2)_2PPh_2]_2(C_6F_5)_2$, which also has been structurally characterized by single-crystal X-ray diffraction. In solution (via ^1H NMR) as well as in the solid state (X-ray) this complex is also symmetrically substituted along the Au(II)–Au(II) axis. The preparation and X-ray crystal structure of the Au(III) anion $[Au(C_6F_5)_4]^-$ as the PPN salt is described. For $[Au(CH_2)_2PPh_2]_2(CF_3)_2$: monoclinic, $C2/c$ (No. 15), $a = 13.194$ (6) Å, $b = 12.882$ (7) Å, $c = 17.609$ (8) Å, $\beta = 103.62$ (4)°, $Z = 4$, $R = 0.0231$, $R_w = 0.0233$ for 1492 reflections with $F_o > 3\sigma(F_o^2)$ and 221 refined parameters. For $[Au(CH_2)_2PPh_2]_2(C_6F_5)_2$: triclinic, $P\bar{1}$ (No. 2), $a = 11.822$ (4) Å, $b = 12.450$ (4) Å, $c = 20.232$ (6) Å, $\alpha = 90.42$ (3)°, $\beta = 105.67$ (3)°, $\gamma = 103.18$ (3)°, $Z = 3$, $R = 0.0422$, $R_w = 0.0416$ for 4532 reflections with $F_o > 3\sigma(F_o^2)$ and 322 refined parameters. For $[(Ph_3P)_2N][Au(C_6F_5)_4]$: orthorhombic, $Pbca$ (No. 61), $a = 19.130$ (5) Å, $b = 29.733$ (6) Å, $c = 19.296$ (5) Å, $Z = 8$, $R = 0.0552$, $R_w = 0.0580$ for 3024 reflections with $F_o > 3\sigma(F_o^2)$ and 332 refined parameters.

Introduction

The gold(I) phosphorus ylide dimer $[Au(CH_2)_2PPh_2]_2$ (**1**) has several properties that make it a good model for physical[1] and theoretical[2] studies of bimetallic organometallic systems. It has proved to be a system that displays interesting features of structure[3] and reactivity.[4,5] Complex **1** contains a pair of two-coordinate Au(I) metal centers constrained in an eight-membered heterocyclic ring. The metal centers are electronically and sterically unsaturated, yet are held closely enough together to allow for a Au···Au interaction.[6] Complex **1** undergoes a facile two-center two-electron oxidative addition with halogens (for example Br_2) and pseudohalogens (for example benzoyl peroxide) acquiring two ligands and a Au(II)–Au(II) bond with each four-coordinate metal center in a fused five-membered heterocyclic ring, $[Au(CH_2)_2PPh_2]_2Br_2$ (**2**). These diamagnetic Au(II) centers remain electronically and sterically unsaturated and can undergo further oxidative addition, giving a dimer containing two Au(III) four-coordinate metal centers, $[Au(CH_2)_2PPh_2]_2Br_4$ (**3**).



R = Ph; X = halide

Complex **1** also shows facile oxidative addition with alkyl halides, RX, to give an asymmetrically substituted Au(II) dimeric species $[Au(CH_2)_2PPh_2]_2RX$ (**4**) that is in equilibrium[1] with **1**. These alkyl halide complexes give a Au–X bond length significantly longer than observed in the Au(II) symmetrically sub-

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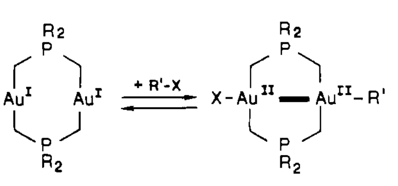

1 4

R = Ph; R' = alkyl; X = halide

stituted dihalide.[2] This *amplified structural trans effect*[7] appears to influence the reaction chemistry (trans effect[8] or trans influence) of these compounds.

Although there is evidence[9,10] that bis(alkylgold(II)) dimer complexes of type A, X = alkyl, can be formed, ambiguity exists and no structural studies have appeared. Here we report the first X-ray crystal structure of a bis(alkylgold(II) ylide) complex, $[Au(CH_2)_2PPh_2]_2(CF_3)_2$ (**5**). The single-crystal X-ray structural investigations of the first bis(arylgold(II) phosphorus ylide) dimer $[Au(CH_2)_2PPh_2]_2(C_6F_5)_2$ (**6**) and the mononuclear tetraarylaurate(III) anion $[Au(C_6F_5)_4]^-$ (**7**), synthesized as the $[PPN]^+$ salt in the course of this study, are also presented.

Experimental Section

Materials and NMR Spectroscopy. All solvents were distilled and dried according to standard methods[11] and stored over molecular sieves before use. All reactions were carried out with the rigorous exclusion of oxygen and water by using standard[12] Schlenk techniques or a drybox. The complexes $[Au(CH_2)_2PPh_2]_2$, $[Au(CH_2)_2PPh_2]_2Br_2$, and $Au(S(CH_2)_4)Cl$ were prepared according to previously published[2,13] procedures. The reagent $Tl(C_6F_5)_2Cl$ was prepared according to the method of Uson.[14] The synthesis and general description of the $Cd(CF_3)_2(gly)$ (gly = glyme) reagent is described by Lagow et al.[15] All ^1H NMR spectra were obtained in $CDCl_3$ at 35 °C at 90 MHz with a Varian EM-390 instrument using Me_4Si as an internal standard or at 200 MHz at 20 °C in CD_2Cl_2 with a Varian XL-200 instrument using $CHDCl_2$ as an internal standard. All ^{19}F NMR spectra were obtained in $CDCl_3$ at 35 °C at 84.6 MHz on a Varian 390 instrument with $CFCl_3$ as a standard. No attempt was made to determine the sign of the coupling constants.

$[Au(CH_2)_2PPh_2]_2(CF_3)_2$. To 138 mg (0.14 mmol) of $[Au(CH_2)_2PPh_2]_2Br_2$ in 10 mL of CH_2Cl_2 at 25 °C was added dropwise 48 mg (0.14 mmol) of $Cd(CF_3)_2(gly)$ in 10 mL of CH_2Cl_2 over 5 min (drybox, argon atmosphere). An immediate reaction occurred, precipitating $CdBr_2$. After 15 min the solution was filtered and taken to dryness in vacuo. The solid that remained was triturated with ether to remove a $Hg(CF_3)_2$ impurity (Hg in $Cd(CF_3)_2(gly)$ reagent) and excess glyme. The yellow solid product was triturated twice with CH_2Cl_2, giving a total of 67 mg (0.07 mmol) of crude $[Au(CH_2)_2PPh_2]_2(CF_3)_2$ (~50% yield). Single crystals, light yellow in color, suitable for an X-ray diffraction study were obtained by dissolving the product in CH_2Cl_2 and allowing diethyl ether to slowly diffuse into the CH_2Cl_2 solution of the product in a closed system at 25 °C. ^1H NMR, 200 MHz: δ 7.60–7.28 (m, Ph), 1.725 (d, J_{HP} = 10.0 Hz, $AuCH_2P$). Mass spectra: no parent peak observed; *m/e* 889, loss of CF_3; *m/e* 820, loss of second CF_3.

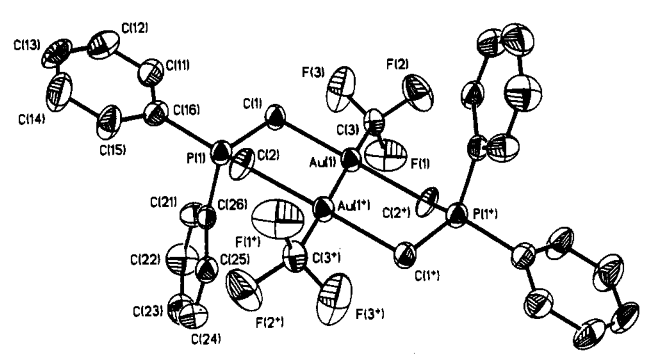

Figure 1. Perspective drawing of $[Au(CH_2)_2PPh_2]_2(CF_3)_2$ (**5**), showing the crystallographic numbering scheme, with hydrogen atoms omitted for clarity (50% probability thermal ellipsoids).

$[Au(CH_2)_2PPh_2]_2(C_6F_5)_2$. To 22 mg (0.027 mmol) of $[Au(CH_2)_2PPh_2]_2$ in 2 mL of dry benzene at 25 °C was added approximately 22 mg (0.054 mmol) of $Tl(C_6F_5)_2Cl$. Immediately upon the addition of $Tl(C_6F_5)_2Cl$ the turbid white benzene mixture went through a number of color changes (yellow, orange, dark orange) with formation of a precipitate. After 20 min the solvent was removed in vacuo and the solid residue taken up in CH_2Cl_2 and filtered. The product, 20 mg (0.016 mmol, 62% yield), is obtained as clear light yellow crystals via diffusion of diethyl ether into a CH_2Cl_2 solution in a closed system. ^1H NMR, 90 MHz, $CDCl_3$: δ 7.66–7.23 (m, Ph), 1.66 (d, J_{HP} = 9.7 Hz, $AuCH_2P$). Mp: 230 °C.

$[PPN][Au(C_6F_5)_4]$. To 176 mg (0.22 mmol) of $Au(C_6F_5)_3(S(CH_2)_4)$ dissolved in 20 mL of CH_2Cl_2 at 25 °C was added a solution of 159 mg (0.22 mmol) of $[PPN][Co(CO)_4]$ (Strem, used as received) in 20 mL of CH_2Cl_2, and the mixture was stirred for 5 min. The solution immediately became deep purple in color. Evaporation of the solvent in air gave a purple solid, which was extracted with diethyl ether. Upon standing, the purple solution changed to yellow and a brown solid precipitated when the solution was cooled to 5 °C. Additional product was obtained upon the addition of hexane: yield 0.165 g (53%); mp 210 °C dec. Single crystals, yellow brown in color, suitable for X-ray diffraction were obtained from a 5:1 ether:hexane mixture. **Note Added in Proof:** R. Uson reports mp 218–219 °C for colorless crystals obtained in the absence of $Co(CO)_4^-$ (private communication).

Crystallographic Experimental Procedures. The structures of all of the complexes described here were determined from intensity data collected at room temperature by using a Nicolet R3m/E diffractometer. Data collection was carried out on suitably formed single crystals mounted in random orientations on the ends of glass fibers by using the ω scanning technique in bisecting geometry (graphite-monochromated Mo $K\alpha$ radiation). In each case refined cell parameters were obtained from the setting angles of 20–25 high-angle reflections. Data was collected in the $+h,+k,\pm l$ octant for **5**, $+h,\pm k,\pm l$ for **6**, and $+h,+k,+l$ for **7**. The data were corrected for standard decay, absorption, Lorentz, and polarization effects. None of the structures described here had reflections with intensities outside the range for valid coincidence correction. Absorption corrections for **5** and **6** were estimated empirically on the basis of azimuthal scans of eight medium-intensity reflections spanning a range of 2θ values. For **7**, absorption corrections were applied by using the Gaussian quadrature method following accurate measurement of the crystal dimensions and assignment of indices to the crystal faces.

Structure Solution and Refinement. The structures of all three complexes were determined by using the SHELXTL collection of crystallographic software. In each case the gold atom coordinates were determined from sharpened Patterson maps and used as an initial phasing model for a difference Fourier synthesis. Neutral-atom scattering factors, including terms for anomalous dispersion, were taken from ref 16. Refinement was based on F with weights of the form $w^{-1} = \sigma^2|F_o| + g(F_o^2)$. Details of the crystallographic experimental procedures for all three complexes are summarized in Table I.

Compound **5** crystallized in the centrosymmetric $C2/c$ space group with half of a single centrosymmetric Au(II) dimer in the asymmetric unit. All non-hydrogen atoms were refined anisotropically, and during later stages of refinement, peaks of residual electron density of approximately 1 e/Å^3 began appearing in chemically reasonable positions within 1 Å of the phenyl ring carbon atoms. These were assigned as hydrogen

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Table I. Crystallographic Data

	5	**6**	**7**
formula	$C_{30}H_{28}Au_2P_2F_6$	$C_{40}H_{28}Au_2P_2F_{10}$	$C_{36}H_{10}AuP_2F_{20}N$
fw	958.12	1154.18	1403.82
space group	*C*2/*c*	$P\bar{1}$	*Pbca*
syst abs	*hkl* (*h* + *k* = 2*n* + 1), *h*0*l* (*l* = 2*n* + 1)		0*kl* (*k* = 2*n* + 1), *h*0*l* (*l* = 2*n* + 1), *hk*0 (*h* = 2*n* + 1)
a, Å	13.169 (3)	11.822 (4)	19.131 (5)
b, Å	12.871 (3)	12.450 (4)	29.733 (6)
c, Å	17.601 (4)	20.232 (6)	19.296 (5)
α, deg	90.000	90.42 (3)	90.00 (2)
β, deg	103.74 (2)	105.67 (3)	90.00 (2)
γ, deg	90.000	103.18 (3)	90.00 (2)
V, $Å^3$	2897 (1)	2788 (2)	10975.92
Z	4	3	8
d_{calcd}, g/cm^3	2.16	2.05	1.69
cryst size, mm	0.2 × 0.8 × 0.10	0.3 × 0.4 × 0.4	0.33 × 0.40 × 0.32
F(000), e	1776	1638	5487
μ(Mo Kα), cm^{-1}	102.23	82.3	28.38
radiation	*d*	*d*	*d*
orientation reflcns: no.; range (2θ), deg	20; $30 \le 2\theta \le 35$	25; $25 \le 2\theta \le 30$	25; $30 \le 2\theta \le 35$
temp, °C	22	22	22
scan method	ω	ω	ω
data collection range (2θ), deg	$0 \le 2\theta \le 45.0$	$0 \le 2\theta < 45.0$	$0 < 2\theta \le 45.0$
total no. of reflcns measd	1891	5050	5584
total no. with $F_o^2 > 3\sigma(F_o^2)$	1492	4532	3024
check reflcns	3 every 100	3 every 100	3 every 100
no. of params refined	221	322	332
trans factors: max; min	0.351; 0.298	0.963; 0.486	0.462; 0.411
R^a	0.0231	0.0422	0.0552
$R_w{}^b$	0.0233	0.0416	0.0580
goodness-of-fit indicator	1.113	1.635	1.532
largest shift/esd, final cycle	0.009	0.51	0.064
largest, peak, e/$Å^3$	0.66	0.86	1.82
g	0.00018	0.00015	0.00077

[a] $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)]^2 / \sum w|F_o|^2$; $w^{-1} = [\sigma^2(|F_o|) + g|F_o|^2]$. [c] Goodness-of-fit $= [w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$. [d] Monochromated in Mo Kα (λ = 0.71073 Å) incident beam.

Table II. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Parameters ($Å^2 \times 10^3$) for $[Au(CH_2)_2PPh_2]_2(CF_3)_2$

atom	*x*	*y*	*z*	U^a
Au(1)	−1648 (1)	−1954 (1)	333 (1)	30 (1)
P(1)	3465 (2)	−651 (2)	5802 (1)	32 (1)
F(1)	−562 (4)	−1297 (5)	4333 (3)	79 (3)
F(2)	−19 (4)	−1359 (4)	3311 (3)	72 (2)
F(3)	350 (4)	−71 (4)	4057 (4)	94 (3)
C(1)	2408 (6)	−502 (5)	4957 (4)	40 (3)
C(2)	4258 (7)	−1681 (5)	5628 (5)	41 (3)
C(3)	295 (6)	−1111 (6)	4072 (4)	36 (3)
C(11)	3772 (8)	1498 (7)	5697 (6)	49 (4)
C(12)	4313 (7)	2395 (7)	5859 (6)	52 (4)
C(13)	5279 (8)	2402 (7)	6339 (6)	65 (4)
C(14)	5721 (8)	1483 (8)	6637 (6)	77 (5)
C(15)	5184 (7)	577 (6)	6477 (5)	59 (4)
C(16)	4194 (6)	556 (6)	6012 (4)	37 (3)
C(21)	2313 (7)	−175 (7)	6865 (5)	44 (3)
C(22)	1950 (9)	−309 (9)	7530 (7)	62 (5)
C(23)	2253 (8)	−1143 (9)	8011 (6)	61 (4)
C(24)	2927 (10)	−1858 (10)	7816 (7)	59 (5)
C(25)	3309 (6)	−1751 (6)	7143 (5)	41 (3)
C(26)	2995 (5)	−888 (6)	6662 (4)	31 (3)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table III. $[Au(CH_2)_2PPh_2]_2(CF_3)_2$ Bond Parameters

Bond Lengths (Å)			
Au(1)–Au(1A)	2.679 (1)	Au(1)–C(1A)	2.127 (7)
Au(1)–C(2A)	2.121 (7)	Au(1)–C(3A)	2.140 (7)
P(1)–C(1)	1.793 (7)	P(1)–C(2)	1.760 (8)
P(1)–C(16)	1.821 (8)	P(1)–C(26)	1.794 (8)
Bond Angles (deg)			
Au(1A)–Au(1)–C(1A)	93.2 (2)	Au(1A)–Au(1)–C(2A)	92.2 (2)
C(1A)–Au(1)–C(2A)	174.1 (3)	Au(1A)–Au(1)–C(3A)	176.8 (2)
C(1A)–Au(1)–C(3A)	87.9 (3)	C(2A)–Au(1)–C(3A)	86.8 (3)
C(1)–P(1)–C(2)	108.3 (4)	C(1)–P(1)–C(16)	110.3 (3)
C(2)–P(1)–C(16)	111.9 (4)	C(1)–P(1)–C(26)	111.3 (4)
C(2)–P(1)–C(26)	110.9 (4)	C(16)–P(1)–C(26)	104.2 (4)
		P(1)–C(2)–Au(1C)	110.1 (4)

atoms and included during the refinement process. Convergence to conventional *R* values of *R* = 0.0221 and R_w = 0.0232 was obtained by using 221 variable parameters and 1492 reflections with $F_o > 3\sigma(F_o^2)$.

Compound **6** crystallized in the centrosymmetric triclinic space group $P\bar{1}$ with three molecules in the unit cell. A sharpened Patterson map showed clearly the presence of three heavy atoms that were subsequently used as an initial phasing model. All non-hydrogen atoms were located by using difference Fourier techniques. All atoms except carbon and hydrogen were refined anisotropically; phenyl rings were refined as idealized polygons using hydrogen atoms placed in idealized positions with fixed isotropic thermal parameters (*U*(H) = 0.08 $Å^2$). One intense, low-angle reflection (100) was severely affected by extinction and was therefore omitted during the refinement process. Convergence to final *R* values of *R* = 0.0422 and R_w = 0.0416 was obtained by using 322 variable parameters and 4532 reflections with $F_o \ge 3\sigma(F_o^2)$.

Compound **7** crystallized in the orthorhombic space group *Pbca* with $[N(PPh_3)_2]$, PPN, as the counterion in the lattice. Because of the large number of phenyl groups in this structure, phenyl rings were refined as rigid polygons using individual isotropic carbon atom thermal parameters and hydrogen atoms placed in idealized positions with fixed thermal parameters. Two intense low-angle reflections (011 and 010) suffered from severe extinction and were therefore omitted during refinement process. Refinement was uneventful and convergence to final *R* values of *R* = 0.0552 and R_w = 0.0580 was obtained by using 3024 reflections with $F_o \ge 3\sigma(F_o^2)$.

Description of the Structures

Perspective drawings of structures **5**–**7** are shown in Figures 1–3, respectively. Atomic positional parameters, bond distances, and angles for all three complexes are presented in Tables II–VII. A drawing of the PPN counterion associated with **7** has not been included.

The structure of the bis(trifluoromethyl)gold(II) product (**5**) consists of discrete dinuclear gold(II) ylide dimers. The asymmetric unit consists of half of a centrosymmetric dimer. The overall geometry of this complex is that of an eight-membered

Table IV. Atom Coordinates (×10^4) and Temperature Factors (Å × 10^3) for $[Au(CH_2)_2PPh_2]_2(C_6F_5)_2$

atom	*x*	*y*	*z*	U^a	atom	*x*	*y*	*z*	U^a
Au(1)	−1327 (1)	−2069 (1)	497 (1)	32 (1)*	C(33)	3818 (11)	−1595 (7)	−1137 (5)	66 (5)
Au(2)	429 (1)	−547 (1)	1351 (1)	32 (1)*	C(34)	3086 (11)	−2612 (7)	−1065 (5)	69 (5)
Au(3)	1102 (1)	4802 (1)	−4788 (1)	33 (1)*	C(35)	2290 (11)	−2672 (7)	−661 (5)	59 (5)
P(1)	1236 (4)	−1774 (3)	229 (2)	37 (2)*	C(36)	2225 (11)	−1714 (7)	−327 (5)	38 (4)
P(2)	8367 (4)	8250 (3)	2003 (2)	37 (2)*	C(41)	−3812 (10)	−1750 (8)	2311 (4)	68 (5)
P(3)	1112 (4)	7298 (3)	−5016 (2)	37 (2)*	C(42)	−4491 (10)	−1620 (8)	2760 (4)	75 (6)
F(11)	−3177 (8)	−1911 (6)	−975 (4)	56 (4)*	C(43)	−3932 (10)	−1403 (8)	3462 (4)	62 (5)
F(12)	−4994 (8)	−3407 (7)	−1829 (4)	63 (4)*	C(44)	−2694 (10)	−1317 (8)	3714 (4)	77 (6)
F(13)	−5613 (8)	−5529 (7)	−1517 (5)	69 (4)*	C(45)	−2015 (10)	−1447 (8)	3265 (4)	71 (6)
F(14)	−4331 (9)	−6181 (6)	−322 (5)	70 (5)*	C(46)	−2574 (10)	−1664 (8)	2564 (4)	38 (4)
F(15)	−2478 (9)	−4708 (7)	550 (5)	67 (4)*	C(51)	−3404 (9)	−2942 (5)	−809 (5)	37 (4)
F(21)	773 (8)	2045 (6)	1869 (4)	52 (4)*	C(52)	−4363 (9)	−3693 (5)	−1257 (5)	45 (4)
F(22)	2586 (10)	3487 (7)	2756 (5)	76 (5)*	C(53)	−4689 (9)	−4784 (5)	−1090 (5)	50 (5)
F(23)	4634 (10)	2904 (8)	3410 (5)	96 (5)*	C(54)	−4055 (9)	−5124 (5)	−476 (5)	44 (4)
F(24)	4854 (9)	798 (9)	3195 (6)	93 (5)*	C(55)	−3095 (9)	−4373 (5)	−28 (5)	45 (4)
F(25)	3037 (8)	−666 (7)	2324 (5)	73 (5)*	C(56)	−2769 (9)	−3282 (5)	−195 (5)	44 (4)
F(31)	2793 (9)	3723 (9)	−5532 (5)	82 (5)*	C(61)	1735 (8)	1709 (8)	2176 (5)	40 (4)
F(32)	4964 (10)	3251 (9)	−5041 (6)	94 (6)*	C(62)	2676 (8)	2461 (8)	2635 (5)	44 (4)
F(33)	6196 (9)	3734 (9)	−3702 (6)	93 (6)*	C(63)	3727 (8)	2143 (8)	2974 (5)	59 (5)
F(34)	5226 (9)	4691 (9)	−2839 (5)	86 (5)*	C(64)	3836 (8)	1073 (8)	2852 (5)	63 (5)
F(35)	3063 (9)	5167 (8)	−3315 (5)	74 (5)*	C(65)	2895 (8)	321 (8)	2392 (5)	47 (4)
C(1)	−321 (14)	−2043 (11)	−214 (7)	42 (4)	C(66)	1845 (8)	640 (8)	2055 (5)	49 (4)
C(2)	1612 (13)	−507 (11)	725 (7)	35 (4)	C(71)	2288 (9)	8109 (9)	−3687 (6)	88 (7)
C(3)	−2480 (14)	−2163 (11)	1143 (7)	39 (4)	C(72)	2381 (9)	8324 (9)	−2996 (6)	106 (8)
C(4)	−706 (14)	−383 (11)	1983 (8)	44 (4)	C(73)	1369 (9)	7994 (9)	−2751 (6)	68 (5)
C(5)	1988 (14)	6321 (11)	−5074 (7)	43 (4)	C(74)	263 (9)	7449 (9)	−3197 (6)	75 (6)
C(6)	−386 (14)	6759 (11)	−5514 (7)	44 (4)	C(75)	171 (9)	7234 (9)	−3888 (6)	58 (5)
C(11)	2700 (8)	−2804 (7)	1188 (5)	56 (5)	C(76)	1183 (9)	7564 (9)	−4133 (6)	34 (4)
C(12)	2945 (8)	−3656 (7)	1606 (5)	58 (5)	C(81)	1015 (9)	9396 (9)	−5443 (6)	68 (5)
C(13)	2034 (8)	−4600 (7)	1587 (5)	57 (5)	C(82)	1482 (9)	10428 (9)	−5653 (6)	71 (6)
C(14)	879 (8)	−4693 (7)	1150 (5)	74 (6)	C(83)	2660 (9)	10692 (9)	−5713 (6)	89 (7)
C(15)	635 (8)	−3841 (7)	733 (5)	51 (5)	C(84)	3370 (9)	9924 (9)	−5564 (6)	109 (8)
C(16)	1546 (8)	−2897 (7)	752 (5)	42 (4)	C(85)	2902 (9)	8892 (9)	−5354 (6)	80 (6)
C(21)	500 (9)	−2401 (6)	2629 (5)	51 (5)	C(86)	1724 (9)	8629 (9)	−5294 (6)	43 (4)
C(22)	1150 (9)	−3176 (6)	2900 (5)	77 (6)	C(91)	3351 (9)	3963 (8)	−4877 (4)	51 (5)
C(23)	548 (9)	−4274 (6)	2912 (5)	69 (5)	C(92)	4479 (9)	3726 (8)	−4624 (4)	60 (5)
C(24)	−705 (9)	−4598 (6)	2652 (5)	68 (5)	C(93)	5108 (9)	3982 (8)	−3934 (4)	50 (4)
C(25)	−1356 (9)	−3824 (6)	2380 (5)	64 (5)	C(94)	4611 (9)	4476 (8)	−3497 (4)	58 (5)
C(26)	−753 (9)	−2725 (6)	2368 (5)	41 (4)	C(95)	3484 (9)	4713 (8)	−3750 (4)	40 (4)
C(31)	2957 (11)	−697 (7)	−399 (5)	66 (5)	C(96)	2854 (9)	4457 (8)	−4440 (4)	36 (4)
C(32)	3753 (11)	−637 (7)	−803 (5)	80 (6)					

[a] An asterisk denotes equivalent isotropic *U* values defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

chair. The coordination geometry of the gold atoms in this complex is best described as square planar, with each gold center bonded to a second gold atom, two methylene carbons, and one trifluoromethyl ligand. The metal–metal distance is this complex, 2.679 (1) Å, is consistent with the presence of a Au(II)–Au(II) single bond. The bond to C(3) of the trifluoromethyl group measures 2.140 (7) Å; those to C(1) and C(2) of the ylide methylene carbons are 2.127 (7) and 2.121 (7) Å, respectively. Interaxial angles around the metal center in this complex range from 88.1 (7) to 90.1 (7)° with the C–Au–Au–C atoms forming an essentially linear array. Within the trifluoromethyl groups, the bonds to fluorine atoms show little variation and range from 1.339 (10) to 1.345 (9) Å. The average F–C–F bond angle measures 103.0 (6)° with no evidence of the semibridging behavior that has been observed in some dinuclear gold(II) complexes containing alkyl halide groups. In the bridging ylide ligands, the phosphorus centers have tetrahedral geometries and form bonds to both methylene and phenyl carbon atoms. The phosphorus–carbon bond lengths in this structure range from 1.760 (8) to 1.821 (8) Å, with bonds to methylene carbon atoms that are, on the average, shorter by 0.031 (8) Å compared with bonds to phenyl carbons.

The asymmetric unit of the related bis(perfluorophenyl)gold(II) compound (**6**) consists of one entire Au(II) dimer in a boat configuration and half of a centrosymmetric Au(II) dimer in a chair configuration. Since there are a total of three dimers in a centrosymmetric triclinic cell, two molecules are in general positions, with a third in a special position. Despite differences in the overall configuration of the two complexes, the gold–gold distances show little variation and have an average length of 2.677 (1) Å (Au(1)–Au(2) = 2.675 (1) Å; Au(3)–Au(3a) = 2.679 (1) Å). Bonds to the perfluorophenyl groups in the two conformers range from 2.145 (8) to 2.164 (7) Å. For all three gold centers the coordination geometry is square planar, with each gold center forming a bond to a second gold atom, two methylene carbon atoms, and one carbon atom of a perfluorophenyl ligand. As with the bis(trifluoromethyl)gold(II) structure (**5**), the phosphorus atom centers in both adducts maintain a tetrahedral coordination geometry, with bonds to phenyl rings that are, on the average, slightly longer than those to methylene carbon atoms.

The crystal structure of the tetrakis(pentafluorophenyl)aurate(III) anion complex shown in Figure 3 consists of an anionic gold(III) center with [PPN] as a counterion in the lattice. All molecules in this cell occupy general positions with no crystallographically imposed elements of symmetry. The gold center in this molecule forms bonds only to carbon atoms of the pentafluorophenyl groups with no close interactions with other gold centers in different parts of the lattice. The torsion angles associated with the planar pentafluorophenyl groups give this molecule a propeller-like appearance and prohibit any close approach between the gold centers of different molecules in adjacent sites in the lattice. Gold–carbon bond distances range from 2.075 (11) to 2.084 (11) Å, with interaxial angles ranging from 88.2 (6) to 90.1 (7)°. The gold atom coordination geometry is square planar and has an overall geometry which is best described as having D_4 symmetry. The closest Au···F distance, 3.17 Å for Au(1)···F(31), is to the *o*-fluorine atoms of the ring but is longer than expected for any Au···F interaction. The [PPN] counterion displays no unusual features, and features of the structure are unexceptional.

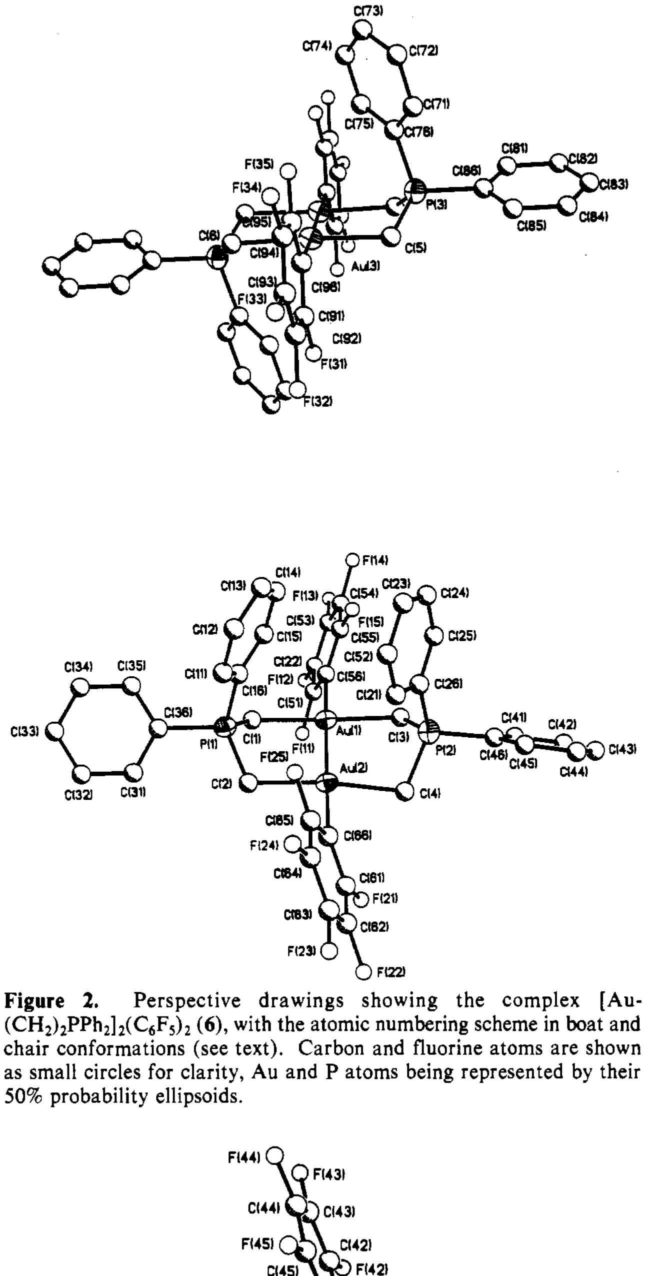

Figure 2. Perspective drawings showing the complex [Au$(CH_2)_2PPh_2]_2(C_6F_5)_2$ (**6**), with the atomic numbering scheme in boat and chair conformations (see text). Carbon and fluorine atoms are shown as small circles for clarity, Au and P atoms being represented by their 50% probability ellipsoids.

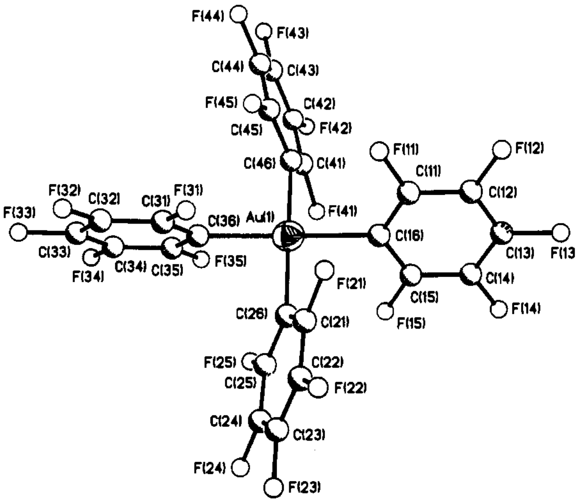

Figure 3. Perspective drawing showing the coordination about the Au(III) anion $[N(PPh_3)_2][Au(C_6F_5)_4]$ (7) with the atomic numbering scheme. The [PPN] cation is not shown, and carbon and fluoride atoms are shown as small circles for clarity, the Au atom being represented by its 50% probability ellipsoids.

Discussion

The ability of phosphorus ylide ligands to stabilize gold(II) dimers and form strong metal–carbon bonds has made the dinuclear gold ylide complexes[17] $[Au(CH_2)_2PR_2]_2$ quite interesting.

Table V. $[Au(CH_2)_2PPh_2]_2(C_6F_5)_2$ Bond Parameters

Bond Lengths (Å)			
Au(1)–Au(2)	2.675 (1)	Au(1)–C(1)	2.094 (18)
Au(1)–C(3)	2.113 (7)	Au(1)–C(56)	2.164 (7)
Au(2)–C(2)	2.117 (17)	Au(2)–C(4)	2.127 (18)
Au(2)–C(66)	2.145 (8)	Au(3)–C(5)	2.110 (14)
Au(3)–C(96)	2.147 (11)	Au(3)–Au(3A)	2.679 (1)
Au(3)–C(6A)	2.101 (14)	P(1)–C(1)	1.774 (15)
P(1)–C(2)	1.768 (14)	P(1)–C(16)	1.805 (10)
P(1)–C(36)	1.819 (14)	P(2)–C(3A)	1.770 (14)
P(2)–C(4A)	1.810 (14)	P(2)–C(26A)	1.813 (11)
P(2)–C(46A)	1.808 (13)	P(3)–C(5)	1.791 (18)
P(3)–C(6)	1.763 (14)	P(3)–C(76)	1.794 (14)

Bond Angles (deg)			
Au(2)–Au(1)–C(1)	92.3 (3)	Au(2)–Au(1)–C(3)	92.6 (3)
C(1)–Au(1)–C(3)	174.9 (5)	Au(2)–Au(1)–C(56)	179.0 (3)
C(1)–Au(1)–C(56)	88.3 (5)	C(3)–Au(1)–C(56)	86.9 (4)
Au(1)–Au(2)–C(2)	92.5 (3)	Au(1)–Au(2)–C(4)	92.0 (3)
C(2)–Au(2)–C(4)	173.3 (5)	Au(1)–Au(2)–C(66)	178.5 (3)
C(2)–Au(2)–C(66)	87.9 (4)	C(4)–Au(2)–C(66)	87.7 (4)
C(5)–Au(3)–C(96)	86.6 (5)	C(5)–Au(3)–Au(3A)	94.5 (4)
C(96)–Au(3)–Au(3A)	179.0 (3)	C(5)–Au(3)–C(6A)	174.2 (7)
C(96)–Au(3)–C(6A)	87.7 (5)	Au(3A)–Au(3)–C(6A)	91.2 (5)
C(1)–P(1)–C(2)	107.5 (8)	C(1)–P(1)–C(16)	110.4 (6)
C(2)–P(1)–C(16)	112.0 (6)	C(1)–P(1)–C(36)	114.2 (7)
C(2)–P(1)–C(36)	109.9 (6)	C(16)–P(1)–C(36)	102.9 (5)
C(3A)–P(2)–C(4A)	105.8 (7)	C(3A)–P(2)–C(26A)	111.8 (6)
C(4A)–P(2)–C(26A)	112.8 (6)	C(3A)–P(2)–C(46A)	112.8 (7)
C(4A)–P(2)–C(46A)	108.4 (7)	C(26A)–P(2)–C(46A)	105.3 (5)
C(5)–P(3)–C(6)	108.8 (7)	C(5)–P(3)–C(76)	109.3 (6)

When the role of one metal center on another in the oxidative addition of alkyl halides to gold(I) dimers is assessed, the possibility of initial formation of mixed-valent gold centers must be considered. In a related system, Fackler and Mazany[18] were able to completely characterize valence isomers of $[Au(CH_2(S)PPh_2)]_2I_2$, both the symmetric Au(II)/Au(II) species and the mixed-valent Au(I)/Au(III) isomer. More recently[19] the spontaneous isomerization of the digold(II) phosphorus ylide dichloride dimer to a mixed-valence Au(III)/Au(I) isomer has been reported. In both cases the homovalent digold(II) ylide dimers are diamagnetic with a formal Au–Au bond[20] of approximately 2.6 Å. However the heterovalent Au(I)/Au(III) isomers have no metal–metal bond with Au···Au distances greater than 3.00 Å.

In 1975, Schmidbaur and Franke[17] reported that the reaction of LiMe with the digold(III) tetrabromide ylide dimer, $[Au(CH_2)_2PMe_2]_2Br_4$, forms a mixed valent dimethyldigold(I,III) ylide dimer. Thermolysis of this product is reported to give ethane and the gold(I) ylide dimer. From both the kinetic studies of Kochi et al.[21,22] and theoretical considerations,[23] reductive coupling of methyl components from a Au(III) center in solution (Me_2SO) to give ethane (a) is intramolecular and (b) involves three-coordinate electron deficient 14-electron species having "T" and "Y" geometries. For the mixed-valent dimethyldigold(I,III) product (trans at Au(III)) reported by Schmidbaur and co-workers, symmetry considerations would seem to preclude intramolecular reductive coupling to give the reported products. Unfortunately, however, the crystal structure of a heterovalent dimethylgold-

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(17) (a) Schmidbaur, H.; Franke, R. *Inorg. Chim. Acta* **1975**, *13*, 79. (b) *Ibid.* **1975**, *13*, 85.

(18) Mazany, A. M.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1985**, *106*, 801.

(19) Fackler, J. P., Jr.; Trzcinska-Bancroft, B. *Organometallics* **1985**, *4*, 1891.

(20) The following symmetrically substituted Au(II)–Au(II) phosphorus ylide dimers have been investigated by single-crystal X-ray diffraction techniques in our laboratory, Au–Au bond lengths are given in parentheses in angstroms for $[Au(CH_2)_2PPh_2]_2X_2$ for X = SePh (2.654), Cl (2.600), Br (2.611), I (2.693), S_2CNEt_2 (2.647), NO_2 (2.596), O_2CPh (2.587), O_2CCH_3 (2.592), and CN (2.637).

(21) Tamaki, A.; Magennis, S. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6140.

(22) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic: New York, 1978; p 266.

(23) (a) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K.; *J. Am. Chem. Soc.* **1976**, *98*, 7255. (b) Komiya, S.; Albright, T. A.; Hoffmann, R.; Kochi, J. K. *J. Am. Chem. Soc.* **1977**, *99*, 8440.

Table VI. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3) for [PPN][Au(C$_6$F$_5$)$_4$]

atom	*x*	*y*	*z*	*U*[a]	atom	*x*	*y*	*z*	*U*[a]
Au(1)	141 (1)	1555 (1)	1770 (1)	52 (1)*	C(41)	−890 (7)	1337 (3)	607 (6)	87 (6)
P(1)	278 (2)	979 (1)	6398 (2)	48 (2)*	C(42)	−1451 (7)	1430 (3)	167 (6)	98 (7)
P(2)	−953 (2)	818 (1)	7275 (2)	51 (2)*	C(43)	−1673 (7)	1872 (3)	72 (6)	84 (6)
F(11)	1011 (6)	2183 (3)	752 (5)	107 (5)*	C(44)	−1334 (7)	2222 (3)	417 (6)	109 (7)
F(12)	2025 (5)	2004 (4)	−163 (5)	116 (6)*	C(45)	−773 (7)	2130 (3)	857 (6)	79 (6)
F(13)	2486 (6)	1153 (4)	−348 (5)	130 (6)*	C(46)	−551 (7)	1687 (3)	952 (6)	63 (5)
F(14)	1887 (6)	458 (4)	368 (6)	136 (6)*	C(51)	−1837 (5)	309 (3)	6459 (5)	64 (5)
F(15)	884 (5)	636 (3)	1305 (6)	105 (5)*	C(52)	−2377 (5)	3 (3)	6341 (5)	80 (6)
F(21)	1539 (5)	2041 (3)	2299 (5)	92 (5)*	C(53)	−2673 (5)	−231 (3)	6895 (5)	87 (6)
F(22)	2405 (6)	1860 (4)	3392 (5)	114 (6)*	C(54)	−2428 (5)	−159 (3)	7567 (5)	97 (7)
F(23)	2134 (5)	1163 (4)	4228 (5)	112 (5)*	C(55)	−1887 (5)	146 (3)	7685 (5)	84 (6)
F(24)	1003 (5)	628 (4)	4006 (5)	107 (5)*	C(56)	−1592 (5)	380 (3)	7131 (5)	60 (5)
F(25)	159 (5)	787 (3)	2912 (5)	87 (4)*	C(61)	−1898 (6)	1338 (3)	7993 (5)	68 (5)
F(31)	−41 (5)	2393 (3)	2770 (5)	79 (4)*	C(62)	−2314 (6)	1718 (3)	8091 (5)	93 (7)
F(32)	−1021 (5)	2622 (3)	3688 (5)	87 (4)*	C(63)	−2276 (6)	2076 (3)	7625 (5)	96 (7)
F(33)	−2139 (5)	2081 (4)	3905 (5)	101 (5)*	C(64)	−1823 (6)	2053 (3)	7060 (5)	96 (7)
F(34)	−2253 (5)	1290 (4)	3199 (6)	105 (5)*	C(65)	−1407 (6)	1673 (3)	6961 (5)	73 (6)
F(35)	−1268 (5)	1057 (3)	2275 (5)	90 (5)*	C(66)	−1445 (6)	1315 (3)	7428 (5)	55 (5)
F(41)	−723 (6)	910 (3)	753 (5)	103 (5)*	C(71)	−192 (7)	254 (4)	8085 (6)	99 (7)
F(42)	−1736 (6)	1071 (5)	−172 (6)	153 (7)*	C(72)	215 (7)	141 (4)	8659 (6)	128 (8)
F(43)	−2201 (6)	1955 (5)	−331 (6)	167 (8)*	C(73)	337 (7)	459 (4)	9177 (6)	104 (7)
F(44)	−1554 (7)	2641 (5)	327 (7)	180 (8)*	C(74)	52 (7)	889 (4)	9122 (6)	115 (7)
F(45)	−489 (6)	2475 (3)	1211 (5)	104 (5)*	C(75)	−355 (7)	1002 (4)	8548 (6)	88 (6)
N(1)	−500 (6)	862 (4)	6586 (6)	49 (4)	C(76)	−477 (7)	685 (4)	8029 (6)	74 (6)
C(11)	1202 (6)	1755 (3)	664 (5)	45 (4)	C(81)	885 (5)	1638 (3)	5556 (5)	60 (5)
C(12)	1729 (6)	1666 (3)	184 (5)	72 (6)	C(82)	892 (5)	1913 (3)	4971 (5)	61 (5)
C(13)	1969 (6)	1227 (3)	91 (5)	70 (5)	C(83)	314 (5)	1925 (3)	4530 (5)	77 (6)
C(14)	1681 (6)	877 (3)	479 (5)	85 (6)	C(84)	−271 (5)	1661 (3)	4675 (5)	106 (7)
C(15)	1154 (6)	966 (3)	959 (5)	64 (5)	C(85)	−278 (5)	1386 (3)	5261 (5)	74 (5)
C(16)	914 (6)	1405 (3)	1052 (5)	54 (5)	C(86)	300 (5)	1374 (3)	5701 (5)	41 (4)
C(21)	1416 (6)	1691 (3)	2697 (5)	62 (5)	C(91)	685 (5)	1643 (3)	7288 (5)	51 (5)
C(22)	1851 (6)	1605 (3)	3263 (5)	71 (5)	C(92)	1024 (5)	1817 (3)	7869 (5)	74 (6)
C(23)	1706 (6)	1246 (3)	3705 (5)	61 (5)	C(93)	1474 (5)	1545 (3)	8254 (5)	73 (5)
C(24)	1127 (6)	972 (3)	3581 (5)	68 (5)	C(94)	1585 (5)	1099 (3)	8059 (5)	69 (5)
C(25)	692 (6)	1058 (3)	3016 (5)	59 (5)	C(95)	1245 (5)	925 (3)	7478 (5)	65 (5)
C(26)	837 (6)	1418 (3)	2574 (5)	59 (5)	C(96)	795 (5)	1197 (3)	7093 (5)	45 (4)
C(31)	−572 (5)	2124 (3)	2848 (5)	56 (5)	C(101)	385 (5)	80 (4)	6079 (5)	80 (6)
C(32)	−1086 (5)	2245 (3)	3326 (5)	56 (5)	C(102)	719 (5)	−303 (4)	5825 (5)	119 (8)
C(33)	−1654 (5)	1961 (3)	3443 (5)	75 (6)	C(103)	1401 (5)	−274 (4)	5575 (5)	88 (6)
C(34)	−1709 (5)	1556 (3)	3084 (5)	65 (5)	C(104)	1750 (5)	138 (4)	5578 (5)	95 (7)
C(35)	−1195 (5)	1434 (3)	2606 (5)	54 (5)	C(105)	1416 (5)	521 (4)	5832 (5)	78 (6)
C(36)	−627 (5)	1718 (3)	2488 (5)	57 (5)	C(106)	733 (5)	492 (4)	6083 (5)	56 (5)

[a] Asterisks denote equivalent isotropic *U* values defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table VII. [PPN][Au(C$_6$F$_5$)$_4$] Bond Parameters

	Bond Lengths (Å)		
Au(1)–C(16)	2.075 (11)	Au(1)–C(26)	2.084 (11)
Au(1)–C(36)	2.077 (10)	Au(1)–C(46)	2.098 (13)
P(1)–N(1)	1.571 (12)	P(1)–C(86)	1.787 (10)
P(1)–C(96)	1.788 (10)	P(1)–C(106)	1.796 (12)
P(2)–N(1)	1.593 (12)	P(2)–C(56)	1.807 (11)
P(2)–C(66)	1.776 (11)	P(2)–C(76)	1.763 (12)
	Bond Angles (deg)		
C(16)–Au(1)–C(26)	90.0 (4)	C(16)–Au(1)–C(36)	178.9 (3)
C(26)–Au(1)–C(36)	90.1 (4)	C(16)–Au(1)–C(46)	89.3 (4)
C(26)–Au(1)–C(46)	179.2 (4)	C(36)–Au(1)–C(46)	90.7 (4)

(I)gold(III) product has not been determined. Since the first description of this mixed-valent dialkyl product[17b] reports have appeared suggesting that the dialkyl complex is not a mixed-valent Au(I)/Au(III) complex but is, instead, the homovalent dimethyldigold(II) species.[10] None of the data are supported by any crystallographic studies.

In our work[24] with this dimeric gold ylide system and from the pioneering work of Stone et al.[25] with perfluoroalkyls it was clear that electron-withdrawing groups stabilize the metal–carbon bond. Via an exchange reaction with Cd(CF$_3$)$_2$(gly) and [Au(CH$_2$)$_2$PPh$_2$]$_2$Br$_2$ we have synthesized and subsequently fully characterized the first dialkyl complex of this system, a digold(II) product possessing a metal–metal bond. Furthermore, we have been able to synthesize and determine the X-ray crystal structure of the first diaryl complex of this same system. From a comparison of the ^{1}H NMR spectrum of this product with numerous[2,4] other systems, we conclude that in solution [Au(CH$_2$)$_2$PPh$_2$]$_2$(C$_6$F$_5$)$_2$ is a homovalent Au(II)/Au(II) dimer as observed in the solid state (Figure 2).

[PPN][Au(C$_6$F$_5$)$_4$] (7). The tetrakis(pentafluorophenyl)aurate(III) anion has been previously prepared by Uson et al.[13] from Li(C$_6$F$_5$) and a gold(III) halide. The synthesis (see Experimental Section) employed in this study, resulting in the Au(III) anion, probably occurs via a disproportionation. In the case of gold(I) complexes, Uson and coworkers[26] have found a similar reaction that leads to an increase in the number of coordinated pentafluorophenyl groups. Nevertheless, until this report, the homoleptic carbon-bound tetrakis(pentafluorophenyl)aurate(III) anion had not been structurally characterized.

The homoleptic anionic complex [Au(CH$_3$)$_4$]$^-$ has been reported by Tobias[27] and studied theoretically.[23] This relatively unstable anion (pyrophoric in air) has been crystalized as the lithium

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tetramethylethylenediamine salt but has not been characterized structurally. Related $(CH_3)_3AuY$ (Y = ylides, e.g. CH_2PR_3 and $CH_2S(O)R_2$) complexes also have been prepared[7a] that show considerably decreased reactivity to air and moisture. The increased stability has been attributed to the polar nature of the ylide ligand. The stability of $[Au(C_6F_5)_4]^-$ presumably arises from the electron-withdrawing properties of C_6F_5.

Two additional structural features in **7** require further discussion, (a) the relative orientation of the pentafluorophenyl rings (along with the Au-C bond distance) and (b) the Au···F distance compared with interactions seen in other group 11 polynuclear complexes.

Fehlhammer and Dahl[28] have described a Au(III) homoleptic carbon-bound ring system that is in many ways quite similar to **7**. In this tetrakis(1-isopropyltetrazol-5-ato)aurate(III) anion, $[Au(CN_4R)_4]^-$ (R = i-C_3H_7), Dahl argues that the Au–carbon bonds primarily reflect single-bond character. This is due to the lack of any significant metal to ligand or ligand to metal π-bonding as the delocalized tetrazolato ring is (a) nearly parallel with the filled d_{xy} gold orbitals and (b) is nearly orthogonal to the empty p_z gold orbital, precluding any orbital overlap. It seems that this same argument could be applied to the tetrakis(pentafluorophenyl)aurate(III) anion (**7**) described here. In both the tetrakis(tetrazolato)aurate(III) anion and the tetrakis(pentafluorophenyl)aurate(III) anion, the plane of the coordinated ligand ring and the plane of the four atoms coordinated to the Au(III) center from a dihedral angle between 76 and 71°. In **7** the gold–carbon bond distances range from 2.075 (11) to 2.084 (11) Å, with interaxial angles ranging from 88.2 (6) to 90.1 (7)°. Note that these distances are ~0.08 Å longer than in the Dahl structure.

Uson et al.[29] report a Ag···F interaction (2.60 and 2.69 Å) in a Pt/Ag tetranuclear complex containing the pentafluorophenyl moiety. This arises from favorable electronic and steric relationships. In complex **7** the steric relationships observed do not show any interaction (Au···F range 3.17–3.22 Å) between the o-fluorine of the pentafluorophenyl group and the Au center.

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Supplementary Material Available: Full listings of anisotropic displacement parameters and H atom positions for **5**–**7** (6 pages); tables of observed and calculated structure factors for **5**–**7** (80 pages). Ordering information is given on any current masthead page.

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Synthesis, Characterization, and Structural Studies of Thiolato-Bridged Titanium(IV)-Copper(I) Species: Heterobimetallic Complexes Containing $d^{10} \rightarrow d^0$ Dative Bonds

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Heterobimetallic complexes of the form $[(C_5H_5)_2Ti(\mu\text{-}SCH_2CH_3)_2CuL]PF_6$, where L = $P(C_6H_5)_3$ (**4**), $P(C_6H_{11})_3$ (**5**), $P(CH_2CH_3)_3$ (**6**), $P(CH_2C_6H_5)_3$ (**7**), NC_5H_5 (**8**), and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ (**9**), have been prepared and spectroscopically characterized. In solution at low temperature, the bridging ethanethiolato groups are cisoid (syn). At higher temperatures, a dynamic process that allows the averaging of the cyclopentadienyl ring environments takes place. Possible mechanisms of this averaging process involve either Cu–S bond cleavage or pyramidal inversion of the bridging S atoms. **4** crystallizes as the 1.62 THF solvate in the monoclinic space group $P2_1/c$, with a = 15.157 (4) Å, b = 15.809 (6) Å, c = 18.527 (7) Å, β = 100.86 (3)°, and Z = 4. Compound **5** crystallizes in the monoclinic space group $P2_1/n$, with a = 9.389 (2) Å, b = 36.333 (6) Å, c = 11.584 (3) Å, β = 107.81 (3)°, and Z = 4. In each case, the TiS_2Cu core is not planar; the angle between the TiS_2 and the CuS_2 planes is 13.02° for **4** and 17.92° for **5**. The Cu–Ti distances are 2.803 (3) and 2.840 (2) Å for **4** and **5**, respectively. The crystallographic and spectroscopic data are consistent with $d^{10} \rightarrow d^0$ dative bonds.

Introduction

The synthesis and study of heterobimetallic complexes have been the subject of active research over the past few years. Initial studies focused on species containing two different metal atoms usually from the same or neighboring groups.[1-4] More recently, interest has developed in complexes that contain widely divergent transition metals.[5-54] Interest in such compounds arises for several reasons. The combination of an electron-deficient and an electron-rich metal in a single complex presents the possibility of Lewis acid activation of a substrate molecule bound to the electron-rich metal center. This type of cooperative heterobimetallic activation holds potential for applications in catalysis.

A second reason for interest in heterobimetallic complexes stems from studies of heterogeneous catalysts in which electron-rich metals (e.g., Pt, Rh, Co, Ru, Fe) are supported on Lewis acidic supports (e.g., TiO_2, Al_2O_3).[55-59] Activity and surface studies of these catalysts imply that the support not only serves to maintain a dispersion of the electron-rich metal centers but also may play

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