Organometallics 1985, *4*, 154–157

Molecular Structures of $[Au(CH_2)_2PPh_2]_2(CN)_2$ and $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2(CN)_2$. The First Ylide Dimer Possessing Gold(III) Centers Bonded Only to Carbon[†]

H. H. Murray, Anthony M. Mazany, and John P. Fackler, Jr.*

Department of Chemistry, Laboratory for Molecular Structure and Bonding, Texas A&M University,
College Station, Texas 77843

Received July 3, 1984

The addition of $Hg(CN)_2$ to $[Au(CH_2)_2PPh_2]_2$ in THF gives the gold(II) dicyanide adduct $[Au(CH_2)_2PPh_2]_2(CN)_2$, **1**. The addition of AgCN to the gold(III)-bridging methylene product of the reaction between $[Au(CH_2)_2PPh_2]_2$ and CH_2ClBr (2:1 ratio) gives $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2(CN)_2$, **2**. This is the first "A-frame" gold dimer containing metal centers bonded only to carbon. Complex **1**, $[Au(CH_2)_2PPh_2]_2(CN)_2$, is formally a Au(II) d^9 (diamagnetic) system and has a Au–Au distance of 2.637 (2) Å, indicative of a bonding interaction. Complex **2**, $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2(CN)_2$, formally a Au(III) d^8 complex has a Au$\cdots$Au distance of 3.167 (5) Å. The Au$\cdots$Au distance in **2** is 0.18 Å greater than in the starting material $[Au(CH_2)_2PPh_2]_2$, a Au(I), d^{10} diamagnetic complex with no formal Au–Au bonding interaction. Structural similarities between **1** and **2** are discussed. For **1**, $C_{30}H_{28}N_2Au_2P_2$: monoclinic space group $C2/c$; $a = 13.481$ (6) Å, $b = 12.089$ (5) Å, $c = 17.645$ (8) Å, $\beta = 101.98$ (4)°, and $Z = 4$. The structure was refined to $R = 0.0614$ and $R_w = 0.0619$. For **2**, $C_{31}H_{30}N_2Au_2P_2$: tetragonal space group $I4_1/a$; $a = 28.979$ (6) Å, $c = 33.135$ (5) Å, and $Z = 32$. The structure was refined to $R = 0.0780$ and $R_w = 0.0716$.

Recent work in our laboratory has demonstrated the C–H bond activating[1] nature of the Au–Au bond in $[Au(CH_2)_2PPh_2]_2(OOCPh)_2$. Since the benzoate ligand in this system can be considered a pseudohalogen, the chemistry of other Au(II) pseudohalogenated ylide dimer systems are also of interest. Also, as we have demonstrated[2] that CH_2N_2 addition to $[Au(CH_2)_2PPh_2]_2Br_2$ yields the bridging methylenegold(III) ylide dimer, microscopic reversibility suggests that gold(III) ylide dimers containing bridging CH_2 groups may be useful under some conditions as methylene-transfer agents.

Continuing our studies of the potential of the Au(II) pseudohalogenated dimers to activate C–H bonds, we undertook a single-crystal X-ray structural investigation of the gold ylide dimer $[Au(CH_2)_2PPh_2]_2(CN)_2$, **1**. At the same time we prepared and studied the structure of the closely related methylene-bridged complex $(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2(CN)_2$, **2**. We report here these structures. The Au(III)-bridging methylene complex **2** is the first neutral ylide dimer to contain Au(III) metal centers bonded to only carbon atoms.

Experimental Section

All reactions were carried out in oven-dried Schlenk glassware using standard inert-atmosphere techniques. All solvents were dried before use. Tetrahydrofuran was distilled from sodium and benzophenone, and acetonitrile was distilled from P_4O_{10} before use. Mercury(II) cyanide was purchased from Aldrich, silver cyanide was purchased from Mallinckrodt, and bromochloromethane was purchased from Alfa and used without further purification. All ^1H NMR spectra were obtained in $CDCl_3$ at 90 MHz with a Varian EM-390 at 35 °C using internal Me_4Si as a standard. All infrared spectra were obtained in CH_2Cl_2 or as Nujol mulls on a Perkins-Elmer 783 at 20 °C using NaCl cells. The gold(I) ylide dimer $[Au(CH_2)_2PPh_2]_2$ was prepared in a manner similar to Schmidbaur's method[3] for the dimethyl analogue. The ylide $Ph_2CH_3PCH_2$ was obtained from deprotonation of the phosphonium salt $[Ph_2PMe_2]Br$ with KH in THF.[4] The gold(I) ylide dimer was separated from $[Ph_2PMe_2]Cl$ by washing the precipitate with methanol and then THF followed by recrystallization from hot benzene.

$[Au(CH_2)_2PPh_2]_2(CN)_2$. To 15 mg (0.02 mmol) of $[Au(CH_2)_2PPh_2]_2$ in 5 mL of THF at 22 °C was added 9 mg (0.04 mmol) of $Hg(CN)_2$. The solution was stirred for 24 h at room temperature, the solvent was removed in vacuo, and the product was isolated by extracting it from the precipitate with chloroform in about 35% yield: IR (Nujol) $\nu(C{\equiv}N)$ 2145 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz, 35 °C) δ 1.95 (d, $^2J_{PH}$ = 9.7 Hz, PCH_2Au), 7.6–7.3 (m, PPh). Crystals (light yellow in color) suitable for X-ray crystallographic analysis were obtained from a dichloromethane–hexane mixture at 0 °C.

$(\mu\text{-}CH_2)[Au(CH_2)_2PPh_2]_2(CN)_2$. To 50 mg (0.06 mmol) of $[Au(CH_2)_2PPh_2]_2$ was added 5 mL of CH_2ClBr. The solution was stirred for 18 h at room temperature. The solvent was removed in vacuo, leaving a light yellow to white powder. To this bridging methylenegold(III) ylide dimer was added 10 mL of CH_3CN followed by 16.3 mg (0.12 mmol) of AgCN. This mixture was stirred for 18 h at room temperature. The product was isolated in approximately 50% (26.5 mg) yield by filtering off the silver halide precipitate and taking the acetonitrile solution to dryness in vacuo: IR (Nujol) $\nu(C{\equiv}N)$ 2140 cm^{-1}; ^1H NMR of this product (90 MHz, $CDCl_3$, 35 °C) δ 1.74 (s, $\mu\text{-}CH_2$), 1.74, 2.55 (dd, $J_{PH} \simeq J_{HH} \simeq 12.3$, $AuCH_2P$), 7.83–7.35 (m, PPh). Colorless crystals suitable for X-ray crystallographic analysis were obtained by layering a CH_2Cl_2 solution of **2** with hexane. A ^1H NMR spectrum of these crystals was not obtained.

X-ray Diffraction Data Collection. Crystal data for **1** and **2** are provided in Table I. Intensity data were collected at ambient temperature on a Nicolet P3F four-circle diffractometer controlled by a Data General Nova 4 minicomputer. All crystallographic computations were performed by using the SHELXTL (Revision 4.1) crystallographic computational package installed on a Data General Eclipse S/140 minicomputer. All data were corrected for Lorentz, polarization, linear decay, (every 100 reflections, **1**, 3% decay, **2**, 60% decay). An empirical absorption correction was applied to **1** and **2**.

Structure Determinations and Refinements. The initial positional parameters for the gold atom in **1** and **2** were determined from the Au–Au vector obtained from the Patterson function listing. The space group for **1** was determined to be $C2/c$ or Cc from the systematic absences. The correct space group

---

[†] This paper is dedicated to the memory of Prof. E. L. Muetterties, a man of vision and action who very early influenced the career of J.P.F.

(1) Knachel, H. C.; Dudis, D. S.; Fackler, J. P., Jr. *Organometallics* **1984**, *3*, 1312–1314.

(2) Murray, H. H.; Fackler, J. P., Jr.; Mazany, A. M. *Organometallics* **1984**, *3*, 1310–1311.

(3) (a) Schmidbaur, H.; Franke, R. *Inorg. Chem.* **1975**, *13*, 79. (b) *Ibid.* **1975**, *13*, 85.

(4) Basil, J. D. Ph.D. Thesis, Case Western Reserve University, 1982.

0276-7333/85/2304-0154$01.50/0

Table I

	Au(II)	Au(III)
formula	$C_{30}H_{28}N_2Au_2P_2$	$C_{31}H_{30}N_2Au_2P_2$
fw	872.18	886.19
space group	$C2/c$ (C_{2h}^6, No. 15)	$I4_1/a$ (C_{4h}^6, No. 88)
systematic absences	$h + k = 2n; l = 2n$	$h + k + l = 2n; h = 2n; l = 4n$
a, Å	13.481 (6)	28.979 (6)
b, Å	12.089 (5)	28.979 (6)
c, Å	17.645 (8)	33.135 (5)
α, deg	90.000	90.000
β, deg	101.98 (4)	90.000
γ, deg	90.000	90.000
V, Å^3	2813 (2)	27 828 (3)
Z	4	32
d_{calcd}, g/cm^3	1.99	2.06
cryst size, mm	0.4 × 0.2 × 0.5	0.35 × 0.2 × 0.4
$F(000)$, e	1575.52	14 044.03
μ(Mo Kα), cm^{-1}	105.30	86.00
radiatn (monochromated in Mo Kα (λ_α = 0.710 73 Å) incident beam)		
orientatn reflctns, no., range (2θ)	25, 16-27	25, 15-24
temp, °C	22	22
scan method	ω scan	ω scan
data col range, 2θ, deg	$3 < 2\theta < 45, +h,+k,\pm l$	$3 < 2\theta < 30, +h,+k,+l$
total reflctns measd	3584	14 180
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1979, 1561	5766, 2323
check reflctns	3	3
no. of parameters refined	139	257
tran. factors, max, min	0.415, 0.237	0.435, 0.231
R^a	0.0614	0.0780
$R_w{}^b$	0.0619	0.0716
goodness-of-fit indicator^c	0.950	1.98
largest shift/esd, final cycle	0.000	0.013
largest peak, e/Å^3	2.7	1.8
g^b	0.003 71	0.0004

[a] $R = \Sigma ||F_o| - |F_c||/\Sigma |F_o|$. [b] $R_w = [\Sigma (w)^{1/2}(|F_o| - |F_c|)]/\Sigma (w)^{1/2}|F_o|; w^{-1} = [\sigma^2(|F_o|) + g|F_o|^2]$. [c] Goodness-of-fit = $[\Sigma w(|F_o| - |F_c|)^2/N_o - N_p]^{1/2}$.

proved to be $C2/c$ by virtue of successful refinement. All remaining non-hydrogen atoms were located by using different Fourier techniques. All phenyl rings were refined as rigid groups with C-C fixed at 1.395 Å and C-C-C angles of 120.0°. All non-hydrogen atoms in the structure of 1 were refined anisotropically. All non-hydrogen and non-carbon atom positions in 2 were refined with anisotropic thermal parameters. Structure 2 contained a CH_2Cl_2 molecule of crystallization that partially appeared in two sites with an occupancy of 0.65 and 0.35, respectively. The former refined well; however, the latter was highly disordered. Substantial degradation of the crystal occurred during data collection. Structure 1 refined to $R = 0.0614$ and $R_w = 0.0619$ for 1561 reflections with $I \geq 3.0\sigma(I)$. Structure 2 refined to $R = 0.0788$ and $R_w = 0.0780$ for 2323 reflections with $I \geq 3.0\sigma(I)$.

Results and Discussion

There are few well-characterized mononuclear[5] and apparently no dinuclear gold complexes coordinated to four carbon atoms.[6] In 1933 Gibson[7-9] claimed to have prepared the first complex containing four gold-carbon bonds. Further investigation[7b,10] showed "$AuR_2(CN)_2$" to be a tetrameric Au(I) complex with Au–N bonding.[11]

Table II. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for $[Au(CH_2)_2PPh_2]_2(CN)_2$

atom	x	y	z	U^a
Au	3347 (1)	1939 (1)	5231 (1)	33 (1)
P	1532 (4)	564 (5)	4187 (3)	33 (2)
N	5348 (19)	655 (22)	5972 (15)	85 (11)
C(1)	2694 (18)	397 (16)	4920 (10)	39 (8)
C(2)	808 (18)	1612 (20)	4512 (18)	56 (10)
C	4648 (18)	1081 (18)	5670 (15)	46 (8)
C(11)	5120 (11)	5732 (11)	6529 (8)	43 (8)
C(12)	5661 (11)	6718 (11)	6693 (8)	75 (13)
C(13)	5260 (11)	7702 (11)	6346 (8)	57 (11)
C(14)	4319 (11)	7702 (11)	5836 (8)	63 (11)
C(15)	3778 (11)	6716 (11)	5672 (8)	49 (9)
C(16)	4179 (11)	5732 (11)	6019 (8)	41 (8)
C(21)	2505 (11)	4701 (11)	7025 (8)	50 (9)
C(22)	2277 (11)	4421 (11)	7737 (8)	82 (15)
C(23)	2715 (11)	3486 (11)	8134 (8)	69 (12)
C(24)	3379 (11)	2830 (11)	7820 (8)	73 (12)
C(25)	3607 (11)	3110 (11)	7108 (8)	47 (8)
C(26)	3170 (11)	4045 (11)	6711 (8)	38 (8)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

In 1975, Tobias and Rice reported[12] the synthesis of tetramethylaurate(III) anion; ^{1}H NMR and Raman data suggested a four-coordinate tetramethyl anion $[AuMe_4]^-$. Sulfoxonium,[13] sulfonium,[14] and phosphonium[15] ylides have

---

(5) Schmidbaur, H. In "Gmelin Handbuch der Anorganischen Chemie, Au Organic Compounds"; Slawisch, A., Ed.; Springer-Verlag: Berlin, Bundesrepublik Deutschand: 1980; p 98.

(6) The dinuclear gold ylide complex $[Au(CH_2)_2PMe_2]_2(Me)_2$ first reported by Schmidbaur[3b] *may be* the only other dimer containing a gold center bonded to four carbon atoms. However, due to the lack of definitive characterization of this complex and the contradictory reports regarding the nature of the formal oxidation state of the gold centers (Au(I)–Au(III))[3,5,7] vs. Au(II)–Au(II[8]), this complex cannot be considered well characterized.

(7) (a) Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62. (b) Anderson, G. K. *Adv. Organomet. Chem.* **1982**, *20*, 39.

(8) (a) Kaska, W. C. *Coord. Chem. Rev.* **1983**, *48*, 1. (b) Jandik, P. Ph.D. Thesis, Technischen Universitat, Munchen, 1982.

(9) Gibson, C. S. *Nature (London)* **1933**, *130*, 130.

(10) Burawoy, A.; Gibson, C. S. *J. Chem. Soc.* **1936**, *324*.

(11) Phillips, R. F.; Powell, H. M. *Proc. R. Soc. London, Ser. A* **1939**, *173*, 147.

(12) (a) Rise, G. W.; Tobias, R. S. *Inorg. Chem.* **1975**, *14*, 2402. (b) *Ibid.* **1975**, *15*, 489.

(13) Fackler, J. P., Jr.; Paparizos, C. *J. Am. Chem. Soc.* **1977**, *99*, 2363.

Table III. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$) for (μ-CH_2)[$Au(CH_2)_2PPh_2$]$_2$(CN)$_2$ (A-Frame)

atom	x	y	z	U	atom	x	y	z	U
Au(1)	8062 (1)	5295 (1)	−426 (1)	75 (1)[a]	C(32)	9542 (9)	4230 (12)	869 (9)	79 (19)
Au(2)	7720 (1)	5610 (1)	443 (1)	69 (1)[a]	C(33)	9961 (9)	4450 (12)	947 (9)	60 (17)
Au(3)	6599 (1)	5276 (1)	901 (1)	74 (1)[a]	C(34)	10029 (9)	4906 (12)	825 (9)	94 (21)
Au(4)	6679 (1)	4794 (1)	1751 (1)	74 (1)[a]	C(35)	9677 (9)	5142 (12)	625 (9)	100 (22)
P(1)	7328 (6)	6134 (5)	−338 (5)	82 (8)[a]	C(36)	9258 (9)	4922 (12)	547 (9)	45 (16)
P(2)	8755 (6)	5208 (5)	326 (5)	80 (8)[a]	C(51)	6821 (15)	6622 (17)	2014 (12)	199 (36)
P(3)	6334 (6)	5881 (5)	1679 (5)	85 (8)[a]	C(52)	6862 (15)	7048 (16)	2207 (12)	186 (34)
P(4)	6484 (5)	4156 (6)	974 (5)	80 (8)[a]	C(53)	6468 (15)	7291 (16)	2320 (12)	184 (34)
C(1)	8604 (15)	4952 (16)	−126 (13)	66 (18)	C(54)	6032 (15)	7109 (16)	2241 (12)	218 (40)
C(2)	7488 (17)	5672 (17)	−656 (15)	84 (20)	C(55)	5990 (15)	6683 (16)	2048 (12)	162 (31)
C(3)	7176 (15)	5930 (16)	159 (13)	67 (18)	C(56)	6384 (15)	6440 (16)	1935 (12)	99 (22)
C(4)	8265 (14)	5260 (14)	667 (12)	45 (15)	C(41)	8873 (10)	6119 (14)	496 (8)	67 (17)
C(5)	7637 (16)	5082 (15)	45 (14)	64 (17)	C(42)	9051 (10)	6558 (14)	424 (8)	120 (24)
C(6)	6627 (15)	5913 (14)	1209 (13)	61 (17)	C(43)	9314 (10)	6641 (14)	79 (8)	104 (22)
C(7)	6674 (15)	4617 (13)	641 (12)	45 (15)	C(44)	9399 (10)	6285 (14)	−194 (8)	115 (24)
C(8)	6736 (15)	4148 (14)	1458 (12)	47 (15)	C(45)	9221 (10)	5845 (14)	−122 (8)	75 (19)
C(9)	6618 (16)	5462 (14)	2019 (13)	67 (17)	C(46)	8957 (10)	5762 (14)	223 (8)	64 (17)
C(10)	7090 (17)	5086 (18)	1312 (15)	97 (21)	C(61)	5525 (15)	5361 (13)	1790 (9)	119 (24)
C(1a)	8504 (20)	5494 (19)	−908 (18)	87 (22)	C(62)	5070 (15)	5247 (13)	1693 (9)	128 (25)
N(1a)	8704 (19)	5595 (19)	−1164 (18)	144 (24)	C(63)	4818 (15)	5528 (13)	1432 (9)	162 (31)
C(4b)	6286 (18)	4528 (18)	2152 (16)	75 (19)	C(64)	5020 (15)	5922 (13)	1268 (9)	158 (29)
N(4b)	6089 (15)	4309 (14)	2404 (13)	80 (16)	C(65)	5475 (15)	6036 (13)	1365 (9)	144 (28)
C(2a)	7815 (20)	6157 (20)	846 (19)	96 (22)	C(66)	5727 (15)	5755 (13)	1626 (9)	58 (17)
N(2a)	7829 (18)	6385 (18)	1114 (16)	126 (21)	C(71)	6267 (11)	3309 (15)	543 (11)	122 (25)
C(3b)	6109 (20)	5448 (19)	547 (17)	96 (22)	C(72)	6400 (11)	2902 (15)	350 (11)	161 (30)
N(3b)	5859 (16)	5567 (16)	249 (14)	103 (18)	C(73)	6865 (11)	2781 (15)	332 (11)	113 (23)
C(11)	6379 (17)	6306 (12)	−469 (10)	146 (28)	C(74)	7198 (11)	3066 (15)	506 (11)	159 (30)
C(12)	6005 (17)	6512 (12)	−664 (10)	123 (25)	C(75)	7065 (11)	3473 (15)	699 (11)	115 (23)
C(13)	6081 (17)	6839 (12)	−965 (10)	140 (27)	C(76)	6599 (11)	3594 (15)	717 (11)	80 (19)
C(14)	6530 (17)	6961 (12)	−1072 (10)	157 (30)	C(81)	5606 (16)	4448 (12)	831 (10)	96 (21)
C(15)	6904 (17)	6756 (12)	−878 (10)	119 (24)	C(82)	5127 (16)	4459 (12)	876 (10)	166 (31)
C(16)	6829 (17)	6428 (12)	−576 (10)	87 (20)	C(83)	4916 (16)	4194 (12)	1174 (10)	133 (26)
C(21)	7748 (10)	6893 (13)	2 (9)	78 (19)	C(84)	5183 (16)	3917 (12)	1428 (10)	162 (30)
C(22)	8073 (10)	7249 (13)	5 (9)	83 (19)	C(85)	5662 (16)	3906 (12)	1383 (10)	103 (22)
C(23)	8412 (10)	7269 (13)	−293 (9)	89 (20)	C(86)	5873 (16)	4172 (12)	1084 (10)	89 (21)
C(24)	8426 (10)	6934 (13)	−595 (9)	120 (24)	Cl(1)	479 (9)	6099 (9)	530 (8)	110 (10)
C(25)	8101 (10)	6578 (13)	−599 (9)	83 (20)	Cl(2)	524 (10)	7005 (10)	269 (9)	142 (11)
C(26)	7762 (10)	6558 (13)	−300 (9)	95 (21)	C(91)	592 (31)	6352 (31)	173 (26)	114 (36)
C(31)	9191 (9)	4467 (12)	669 (9)	103 (22)	Cl(3)	8570 (12)	3384 (12)	728 (11)	58 (12)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

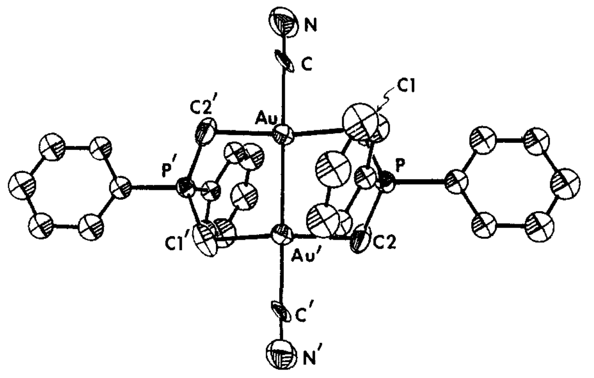

Figure 1. Molecular structure of 1, [$Au(CH_2)_2PPh_2$]$_2$(CN)$_2$ (hydrogen atoms omitted for clarity). Selected bond lengths: Au–Au = 2.637 (2) Å, Au–C = 2.046 (22) Å, Au–C(1) = 2.086 (20) Å, C(1)–P = 1.823 (20) Å, C–N = 1.109 (33) Å. Selected bond angles: C(1)–Au–C = 8.6 (1)°, Au′–Au–C = 176 (1)°, C(1)–Au–C(2)′ = 171.4 (10)°, C(1)–Au–Au′ = 95.0 (6)°.

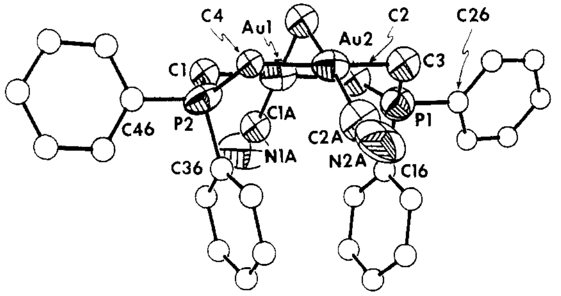

Figure 2. Molecular (representative[17]) structure of 2, (μ-CH_2)[$Au(CH_2)_2PPh_2$]$_2$(CN)$_2$ (hydrogen atoms omitted for clarity). Selected (mean[17]) distances: Au(1)···Au(2) = 3.167 [3] Å, Au(1)–C(5) = 2.056 [11] Å, Au(1)–C = 2.009 [33] Å, C–N = 1.160 [44] Å, Au(1)–C(2) = 2.098 [16] Å. Selected (average) bond angles: C(1)–Au(1)–C(2) = 173.7 [9]°, Au–C–N = 169.4 [2.9]°, C(5)–Au(1)–C(1) = 87.3 [7]°, Au(1)–C(5)–Au(2) = 100.7 [20]°.

been used to stabilize the $Au^{III}R_3$ moiety, by delocalization of the positive charge of the metal center, yet possess four gold–carbon bonds. Consequently, a number of mononuclear neutral, coordinatively saturated gold(III) complexes have been isolated. Mononuclear[16] and dinuclear[16] Au(III) complexes with CN ligands are known. To the best of our knowledge none are dimeric neutral species containing four carbon–gold bonds. Molecular diagrams of the structures of [$Au(CH_2)_2PPh_2$]$_2$(CN)$_2$, 1, and (μ-CH_2)[Au-

---

(14) Stein, J.; Fackler, J. P., Jr.; Paparizos, C.; Chen, H.-W. *J. Am. Chem. Soc.* **1981**, *103*, 2192.

(15) (a) Facker, J. P., Jr.; Basil, J. D. *Organometallics* **1982**, *1*, 871. (b) Fackler, J. P., Jr.; Mazany, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 801. (c) Schmidbaur, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 907 and references within.

(16) (a) Foss, M. E.; Gibson, C. S. *J. Chem. Soc.* **1949**, 3063. (b) Burawoy, A.; Gibson, C. S.; Holt, S. *J. Chem. Soc.* **1935**, 1024. (c) Vson, R.; Laguna, A.; Buil, J. *J. Organomet. Chem.* **1975**, *85*, 403. (d) Stocco, F.; Stocco, G. C.; Scovell, W. M.; Tobias, R. S. *Inorg. Chem.* **1971**, *10*, 2639. (e) Stocco, G. C.; Tobias, R. S. *J. Am. Chem. Soc.* **1971**, *93*, 5057. (f) Komiya, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 7599.

$(CH_2)_2PPh_2]_2(CN)_2$, **2**, are given in Figures 1 and 2 along with the atomic labeling scheme and selected bond distances and angles. Atom coordinates and temperature factors for complexes **1** and **2** are given in Tables II and III, respectively.

The bridging methylene of **2** and the perturbation therefore imposed on the geometry appears to give rise to the structural differences between **1** and **2**. The most dramatic difference is the Au···Au distance. In **1**, the two Au(II) centers are only 2.637 (2) Å apart. This is considered a bonding interaction consistent with the two d^9 metal centers and the diamagnetism observed for these and other Au(II) ylide dimers. In **2**, the two d^8 Au(III) centers are in the range[17] of 3.152 (3) to 3.180 (3) Å apart. The longer (0.54–0.51 Å) Au···Au distance in **2** compared with **1** is consistent with the absence of a Au–Au bond. A comparison of Au···Au distance in **2** with the Au···Au distance in the precursor $[Au(CH_2)_2PPh_2]_2$ shows the Au(III) centers in **2** to be significantly (by 0.20–0.17 Å) further apart than in the Au(I) dimer of the starting material. Presumably, the methylene bridge causes[17b] the two gold centers to move further apart. The only other structured[18] Au(III)-bridging methylene complex $(\mu\text{-}CH_2)[Au(CH_2)_2PMe_2]Cl_2$ also shows a significantly longer 0.047 Å Au···Au distance when compared with its Au(I) precursor.[19]

Structurally, the other obvious perturbation due to the steric constraint of the bridging methylene is the configuration of the eight-membered ring. The bridging methylenegold(III) dicyanide complex **2** in the solid state can be described as being in a boat configuration, while the Au(II) dicyanide was observed to be in the chair configuration.[20] Schmidbaur[18] has made the same observation in the bridging methylenegold(III) complex $(\mu\text{-}CH_2)[Au(CH_2)_2PMe_2]_2Cl_2$.

No significant difference is observed in the Au–CN distances in **1** and **2** that are approximately 2.04 Å. The Au–CN distance in the gold(III) tetramer $[(\eta\text{-}C_3H_7)_2AuCN]_4$ is given[11] as approximately[21] 2.1 Å and found to not be significantly different than the Au–CN distances observed in **1** and **2**.

In both complexes **1** and **2** the gold atoms may be described as four coordinated square-planar centers. In **1** there is a Au–Au bond. The two gold centers of complex **1** are coplanar. In **2**, the dihedral angle between planes associated with gold centers is 100.7°. The two cyano groups of **1** are colinear. In complex **2** the two cyano groups are coplanar but *not* colinear. These considerations, taken together with the different formal charges of the gold centers (**1**, Au(II); **2**, Au(III)),p suggested that the infrared stretching frequencies of the cyano groups in **1** and **2** could be informative. Complex **2** was of particular interest as the stretching frequencies of the cyano groups may, in principle, be coupled with both the symmetric and asymmetric stretches being active[22] in the infrared.

The solution (CH_2Cl_2) IR spectrum of the C≡N stretching region in complex **2** consists of only one absorbance at 2143 cm^{-1} with a width at half-height of about 10 cm^{-1}. Consistent with the first law of well-regulated discourse[23] we offer the following brief explanation as to the nature of our observation. The observation of a single absorbance in the IR spectrum indicates that the extent of coupling between the two cyano groups in **2** may be quite small. A comparison of an estimation of the force constants[24] (using the harmonic oscillator approximation) for the C≡N bond (ν 2135 cm^{-1}; $k \simeq 17.2$ mdyn/Å) and the Au-CH_2 bond (ν 200–350 cm^{-1}; $k \simeq 1$ mdyn/Å) suggests that the two cyano groups are only very weakly coupled. Acting as independent oscillators, they give either unresolved symmetric and antisymmetric stretching frequencies or only the antisymmetric C≡N stretch. The small difference between the C≡N stretching frequencies in **1** and **2** (as observed in Nujol, 2145 and 2140 cm^{-1}, respectively) may be associated with the presence of different trans influences of Au and CH_2.

Acknowledgment. The National Science Foundation (CHE 83-05046) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, are thanked for supporting this work. The Robert A. Welch Foundation is acknowledged for supporting some chemical purchases.

Registry No. 1, 93110-57-7; 2, 90914-55-9; $[Au(CH_2)_2PPh_2]_2$, 81457-56-9; CH_2ClBr, 74-97-5; Au, 7440-57-5.

Supplementary Material Available: For structures **1** and **2**, respectively, tables of anisotropic temperature factors, observed and calculated structure factor amplitudes, and bond lengths and angles (31 pages). Ordering information is given on any current masthead page.

---

[17] (a) Complex **2** has two independent molecules per asymmetric unit; therefore, average rather than specific distances and angles are reported here for **2**. The two independent molecules per asymmetric unit arise from the different orientations of the phenyl rings. The estimated deviation for the mean values reported here are given in square brackets and are calculated as follows: $[\ ] = [\sum_n \sigma / n(n-1)]^{1/2}$ where σ are the esd's of the n values. (b) Hoffmann, R.; Hoffman, D. *Inorg. Chem.* **1981**, *20*, 3543 has discussed factors influencing the A-frame geometry.

[18] Jandik, P.; Schubert, V.; Schmidbaur, H. *Angew. Chem.* **1982**, *94*, 74; *Angew. Chem. Suppl.* **1982**, 1–12; *Angew Chem., Int. Ed. Engl.* **1982**, *21*, 73.

[19] Schmidbaur, H.; Mandl, J. R.; Richter, W.; Bejenke, V.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 2236.

[20] As there appears to be no specific geometric constraints in the gold(II) dicyanide complex **1**, the chair to boat interconversion is assumed to be occurring in solution.

[21] The atomic coordinates of this structure were determined from film data prior to the advent of modern computers.

[22] Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd Ed.; Wiley-Interscience: New York, 1972, p 697.

[23] Cotton, F. A.; Hunter, D. L. *J. Am. Chem. Soc.* **1976**, *98*, 1413. (b) See also: Baral, S.; Cotton, F. A.; Illsey, W. H. *Inorg. Chem.* **1981**, *20*, 2692. (c) Cotton, F. A.; Roth, W. J. *Inorg. Chem.* **1983**, *22*, 3654.

[24] Drago, R. S. "Physical Methods in Chemistry", 1st ed.; W. B. Saunders: Philadelphia, PA, 1977; p 135.