$(S_2CPEt_3)_2(OAc)_2(THF)_2]^{2+}$. When 4 equiv of S_2CPEt_3 was reacted with $Mo_2(O_2CCH_3)_4$ in the presence of 4 equiv of acid, the same purple-red solution was produced. After several days of reaction, a layer of hexane was floated on top, immediately resulting in the precipitation of the excess ligand.

The compound $[Mo_2(S_2CPEt_3)(OAc)_3OPEt_3](BF_4)$ crystallized in a monoclinic cell with four molecules per cell. The cation is situated at a general position and contains no crystallographically imposed symmetry. The positional parameters and their errors are given in Table IV, and the bond distances and angles, in Table V. Figure 2 is an ORTEP drawing of the cation.

The general features of the cation are quite similar to those of $[Mo_2(pdc)_2(OAc)_2OPPh_3]$. The Mo–Mo distance is 2.1384 (8) Å. Again one molybdenum is tightly bound to the oxygen of the phosphine oxide. This Mo–O distance of 2.348 (5) Å is the shortest bond length observed for any axially coordinated, quadruply bonded molybdenum dimer. The other molybdenum is again coordinated to an oxygen of an acetate on a neighboring dimer related by an inversion center. In this case the Mo–O axial bond is much shorter than in the pdc dimer. In addition, the Mo–Mo–O′ angle is 159.6 (1)°, in agreement with the 163.0 (1)° for the pdc dimer. It appears that the net positive charge on the dimer results in these shorter distances because all the Mo–S bonds are also shorter than in $[Mo_2(pdc)_2(OAc)_2OPPh_3]$.

The dithiocarboxylato group in S_2CPEt_3 is required to exist in the dithio acid resonance form. The C–S distances are typical for this form and agree with those observed in the pdc dimer. In general, the two ligands pdc and S_2CPEt_3 seem to behave in a very similar fashion toward dimolybdenum dimers. The inability of S_2CPEt_2 to completely replace the acetates may have to do with trying to form a 4+ cation in an organic solvent.

Registry No. $[Mo_2(pdc)_2(OAc)_2OPPh_3]\cdot 1^1/_2C_6H_6$, 98244-72-5; $[Mo_2(S_2CPEt_3)(OAc)_3OPEt_3](BF_4)$, 98218-58-7; $[Mo_2(pdc)_2(OAc)_2]$, 98218-59-8; $[Mo_2(S_2CPEt_3)_2(OAc)_2(THF)_2]^{2+}$, 98218-60-1; Mo, 7439-98-7.

Supplementary Material Available: Tables of least-squares planes, thermal parameters, rigid-group parameters, and observed and calculated structure factors for *cis*-$[Mo_2(pdc)_2(OAc)_2OPPh_3]\cdot 1^1/_2C_6H_6$ and tables of thermal parameters and observed and calculated structure factors for $[Mo_2(S_2CPEt_3)(OAc)_3OPEt_3](BF_4)$ (48 pages). Ordering information is given on any current masthead page.

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

Geometrical Isomers of $[Ph_2P(CH_2)_2AuX_2]_2$. Crystal and Molecular Structures of *trans,trans*-$[Ph_2P(CH_2)_2AuBr_2]_2$ and *cis,trans*-$[Ph_2P(CH_2)_2AuCl_2]_2$

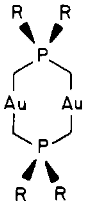
DOUGLAS S. DUDIS and JOHN P. FACKLER, JR.*

Received November 26, 1984

The X-ray structure of the dinuclear gold(III) ylide complex *trans,trans*-$[Ph_2P(CH_2)_2AuBr_2]_2$ has been determined. This is the first completely characterized dimer of this type. While no metal–metal bond is suggested for the compound in its eclipsed configuration, there is an unusual "semibridging" halide. When the same compound stands in $CDCl_3$ for prolonged periods, the geometrical isomer with a cis,trans configuration is formed. The chloride analogue of this cis,trans compound, formed by reaction of the gold(II) dimer with $SnCl_2\cdot 2H_2O$ in $CDCl_3$, has been characterized structurally and is reported here. For *trans,trans*-$[Ph_2P(CH_2)_2AuBr_2]_2\cdot CDCl_3$, $a = 11.657$ (2) Å, $b = 13.244$ (3) Å, $c = 26.374$ (5) Å, $\beta = 120.299$ (13)°, $Z = 4$, and $V = 3515.4$ (1.1) Å^3 for the yellow crystals which conform to a monoclinic $C2/c$ space group. The *cis,trans*-$[PhP_2(CH_2)_2AuCl_2]_2\cdot 2CDCl_3$ product crystallizes in $P2_1/c$ with $a = 12.695$ (2) Å, $b = 24.198$ (5) Å, $c = 13.2279$ (2), $\beta = 108.523$ (11)°, $V = 3852.8$ (1.0) Å^3, and $Z = 4$.

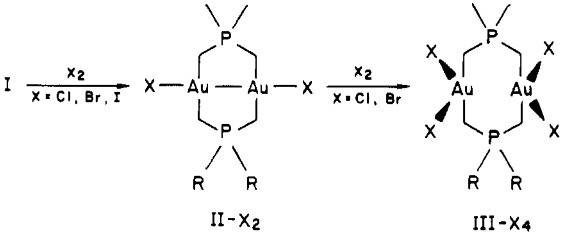
Introduction

The oxidation of the dinuclear gold(I) ylide complexes I with



I, R=alkyl or aryl

X_2 (X = Cl, Br) occurs[1] stepwise to give gold(II) and gold(III) products (eq 1). The structures of I and II-X_2 have been confirmed for a variety of alkyl substituents and halogens.[2-6] Upon oxidation from I to II-X_2, the Au–Au distance decreases from 3.0 to 2.6 Å. No crystallographic studies for the gold(III) derivatives, III-X_4, have been reported. Thus, the Au···Au separation (and presumably any experimental data regarding the Au···Au interaction) was, heretofore, unknown. These III-X_4 compounds are known to contain gold(III) on the basis of ^{197}Au Mössbauer and photoelectron spectra,[7] but the suggested structures are described as "tentative". Metathesis of I and III-X_4 gives[8] II-X_2, which supports the formulation of III-X_4. This reaction of a M(I) and M(III) compound to yield a stable M(II) species is unprecedented in mononuclear gold chemistry. Recently, we were able to obtain single crystals of III-Br_4 (R = Ph for all gold compounds described hereafter) and an isomeric form of the chloro derivative,[9]



II-X_2 III-X_4 (1)

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(1) Schmidbaur, H.; Franke, R. *Inorg. Chim. Acta* **1975**, *13*, 85–89.

(2) Basil, J. D.; Murray, H. H.; Fackler, J. P., Jr.; Toucher, J.; Mazany, A. M.; DeLord, T. T.; Trzcinska-Bancroft, B. M.; Knachel, H.; Dudis, D. S.; Marler, D. O. *J. Am. Chem. Soc.*, in press.

(3) Schmidbaur, H.; Mandl, J. E.; Richter, W.; Bejenke, V.; Frank, A.; Huttner, G. *Chem. Ber.* **1977**, *110*, 2236–2241.

(4) Schmidbaur, H.; Mandl, J. R.; Frank, A.; Huttner, G. *Chem. Ber.* **1976**, *109*, 466–472.

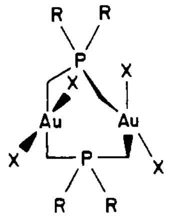
(5) Paparizos, C. Ph.D. Dissertation, Case Western Reserve University, 1977.

(6) Schmidbaur, H.; Scherm, H.; Subert, U. *Chem. Ber.* **1978**, *111*, 764–769.

(7) Schmidbaur, H. "Gmelin Handbuch der Anorganischen Chemie", 8th ed.; Springer-Verlag: Berlin, 1980; Au-Organic Compounds, p 263.

(8) Basil, J. D. Ph.D. Dissertation, Case Western Reserve University, 1983.

III′-Cl_4. The results of the X-ray structural analyses are reported herein.



III′-Cl_4, R = C_6H_5, X = Cl

Experimental Section

^1H NMR spectra were recorded with a Varian EM-390 (90-MHz) spectrometer. Deuteriotrichloromethane was dried over molecular sieves prior to use. Chemical shifts (downfield positive) are reported relative to Me_4Si. Commercial reagents were used as received. Bis(μ-diphenyldimethylenephosphoranyl-*C,C*)digold(I) (I), was prepared according to literature methods[8] from methyldiphenylmethylenephosphorane and (triphenylphosphine)gold chloride in toluene. Bis(μ-diphenyldimethylenephosphoranyl-*C,C*)dichlorodigold(*Au–Au*) (II-Cl_2) was prepared[8] by mixing I with CCl_4.

Bis(μ-diphenyldimethylenephosphoranyl-*C,C*)tetrabromodigold(III) (III-Br_4). An NMR tube was charged with 24.2 mg of I (29.5 μmol) dissolved in approximately 1 mL of $CDCl_3$. After a preliminary spectrum was recorded, 5 μL of bromine (98 μmol of Br_2) was added. The NMR spectrum was immediately recorded and showed only III-Br_4. A large number of yellow crystals (parallelepipeds) had formed by the time the sample was removed from the spectrometer.

The solution was decanted into a small beaker, then pipetted into another NMR tube. The crystals were briefly air-dried and weighed (31 mg, 97% yield of the $CDCl_3$ solvate).

1-*cis*,2-*trans*-Tetrachloro-1κ^2*Cl*,2κ^2*Cl*-bis[μ-(methylene-1κ*C*-diphenylphosphoranyl)methyl-2κ*C*]digold (III′-Cl_4). An NMR tube was charged with 10.3 mg (11.6 μ mol) of II-Cl_2 dissolved in 1 mL of $CDCl_3$ (no Me_4Si; internal CH_2Cl_2 served as a standard). After an initial spectrum was recorded, two crystals (2.4 mg, 11 μmol) of $SnCl_2{\cdot}2H_2O$ were added. A dark (black-brown-green) material coated the $SnCl_2{\cdot}2H_2O$ crystals and was occasionally separated from them by agitation. In less than 24 h, clumps of yellow needles/plates appeared in the bottom of the tube. No color change occurred in the solution throughout the course of the experiment. After 1 week the NMR spectrum showed only the doublet due to II-Cl_2 and a small singlet at 1.44 ppm (not H_2O, which was a small singlet at 1.5 ppm). Integration of the signals relative to CH_2Cl_2 indicated 80% of the II-Cl_2 remained unreacted after more than 1 week. The solution was evaporated in a petri dish, keeping the crystals separated from the evaporating solvent. Yellow crystals were removed mechanically (1.0 mg, 7% yield based on II-Cl_2). They were shown by X-ray analysis (vide infra) to be III′-Cl_4.

Crystallography

Intensity data were collected at ambient temperature on a Nicolet R3m/E diffractometer (equipped with a graphite monochromator) by using standard procedures (ω scans). The data were corrected for Lorentz, polarization, decay, and absorption (azimuthal scans) effects. Normalized transmission factors for III-Br_4 ranged between 0.2 and 1.0, while those for III′-Cl_4 were between 0.1 and 1.0. The crystal of III-Br_4 was sealed in a Lindeman capillary since crystals exposed to the atmosphere turned opaque and crumbled (apparently due to solvent loss) within 24 h. The data crystal of III′-Cl_2 showed a 20% decrease in the intensity of three check reflections (monitored every 100 reflections) during the course of data collection.

The coordinates of the gold atoms were determined from three-dimensional Patterson functions, and the coordinates of all remaining non-hydrogen atoms were determined from successive least squares-difference Fourier cycles (for both structures). Refinement proceeded uneventfully, although the temperature factors of some atoms in III′-Cl_4 went nonpositive definite when refined with the nonabsorption corrected data. All calculations employed the SHELXTL[11] package of programs.

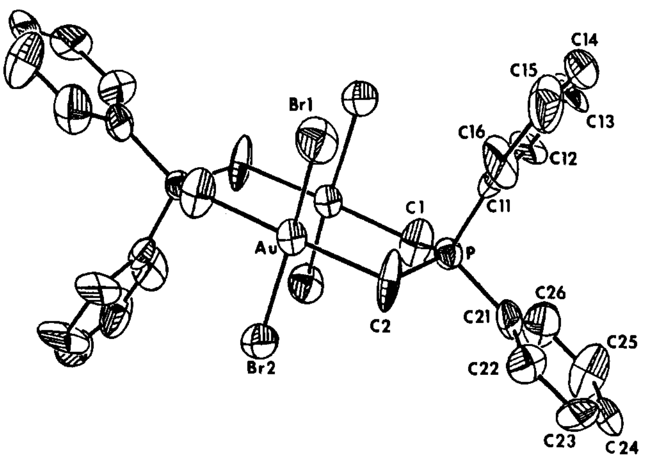


Figure 1. Thermal ellipsoid plot (50% probability) for *trans,trans*-$[Ph_2P(CH_2)_2AuBr_2]_2$. The molecule resides on a crystallographic inversion center.

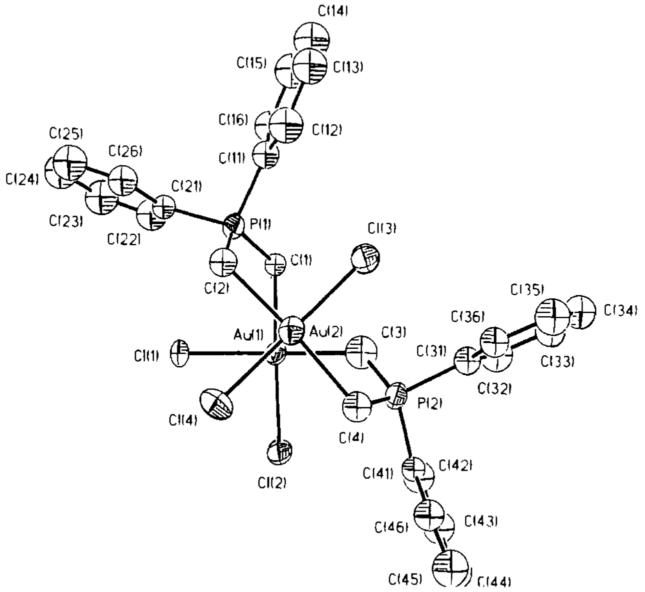


Figure 2. Thermal ellipsoid plot (50% probability) for *cis,trans*-$[Ph_2P(CH_2)_2AuCl_2]_2$.

Phenyl rings were refined as regular hexagons (C–C = 1.395 Å), and hydrogen atoms (phenyl and methylene) were fixed at idealized locations 0.96 Å from the carbon atoms to which they are bound. No corrections were made for secondary extinction. The function minimized was $\sum w[|F_o| - |F_c|]^{1/2}/\sum wF^2$, where $w = 1/\sigma^2(F)$. Crystallographic data are summarized in Table I while Tables II and III give atomic coordinates. Single-molecule thermal ellipsoid drawings of III-Br_4 and III′-Cl_4 are given in Figures 1 and 2, respectively. Important bond lengths and angles are given in Table IV for both III-Br_4 and III′-Cl_4.

Prolonged standing with very slow evaporation of a $CDCl_3$ solution of III-Br_4 resulted in long yellow needles $P2_1/c$ with a = 12.473 (4) Å, b = 23.916 (9) Å, c = 13.586 (4) Å, β = 106.11 (2)°, and V = 3893.7 (17) Å^3, isomorphous with III′-Cl_4. However, the crystals were small and diffracted weakly. They decomposed rapidly in the X-ray beam necessitating rapid data collection and preventing an absorption correction. Consequently, only the coordinates of the heavy atoms could be determined/refined.

Results and Discussion

Various attempts were made to prepare crystals of III-Br_4 suitable for X-ray diffraction.[10] Several solvents were employed coupled with slow evaporation, cooling, and vapor diffusion. The sensitivity of the solvated crystals to the atmosphere rationalizes, in retrospect, the previous failures. The crystals, from which the

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(9) In addition to the Au(III)/Au(III) compounds reported here,[10] a *trans,trans*-$[Ph_2P(CH)_2AuCl_2]_2$ isomer has been prepared and studied structurally. Furthermore, a *trans,trans*-$[Ph_2P(CH_2)_2AuBr_2]_2$ isomer with no lattice solvent has been synthesized and structured.[10] This compound shows a shorter Au···Au interaction (3.067 Å) and no semibridging Br.

(10) Porter, L.; Raptis, R.; Murray, H. H.; Fackler, Jr., J. P., to be submitted for publication. The *trans,trans*-$[Ph_2P(CH_2)_2AuBr_2]_2$ isomer can be formed readily by reacting Br_2 with $[Ph_2P(CH_2)_2AuBr]_2(\mu\text{-}CH_2)$.

(11) Sheldrick, G. M. "SHELXTL Program for Crystal Structure Determination (Version 4.0)"; Nicolet: Fremont, CA, 1983.

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

Table I. Crystallographic Data for III-Br_4 and III′-Cl_4

formula	$Au_2Br_4P_2C_{28}H_{28}\cdot CDCl_3$	$Au_2Cl_4P_2C_{28}H_{28}\cdot 2CDCl_3$
fw	1260.42	1203.00
space group	$C2/c$	$P2_1/c$
systematic absences	hkl, $h + k = 2n + 1$ $h0l$, $l = 2n + 1$	$h0l$, $l = 2n + 1$ $0k0$, $k = 2n + 1$
a, Å	11.657 (2)	12.695 (2)
b, Å	13.244 (3)	24.198 (5)
c, Å	26.374 (5)	13.227 (2)
α, deg	90	90
β, deg	120.299 (13)	108.523 (11)
γ, deg	90	90
V, Å^3	3515.4 (11)	3852.8 (10)
Z	4	4
d_{calcd}, g/cm^3	2.38	2.07
crystal size, mm	0.30 × 0.40 × 0.50	0.10 × 0.14 × 0.48
$F(000)$, e	2328	2272
μ(Mo, Kα), cm^{-1}	131.68	83.99
radiation (monochromated in Mo Kα ($\lambda\alpha$ = 0.71073 Å) incident beam)	0.71069	0.71069
Orientation reflections: no.; range (2θ), deg	25; $20 \geq 2\theta \geq 25$	25; $20 \geq 2\theta \geq 26$
temp, °C	22	22
scan method	ω	ω
data collected; range (2θ), deg	$h,k,\pm l$; $2.0 < 2\theta < 50.0$	$h,k,\pm l$; $2.0 < 2\theta < 45.0$
total reflcns measd	3800	6600
no. of unique data, total with $F_o^2 > 3\sigma(F_o^2)$	1348	2259
no. of check reflections	3	3
no. of parameters refined	158	199
transmissn factors: max, min	1.0, 0.2	1.0, 0.1
R^a	0.0653	0.0636
$R_w{}^b$	0.0726	0.0748
goodness-of-fit indicator^c	1.538	1.042
largest shift/esd, final cycle	0.07	0.01
largest peak, e/Å^3	3.69	2.5

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w^{1/2}(|F_o| - |F_c|)]/\sum w^{1/2}|F_o|$; $w^{-1} = [\sigma^2(|F_o|) + g|F_o|^2]$, $g = 0.0016$. [c] Goodness-of-fit $= [\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$.

specimen used in this study was selected, were prepared directly in the synthesis of III-Br_4. The gold(I) precursor, I, is very soluble in $CHCl_3$. Upon addition of bromine to a concentrated solution of the gold(I) dimer, the less soluble gold(III) product crystallizes.

The X-ray analysis confirms the proposed[1] structure for III-Br_4. This completes a series, $Au_2(\mu\text{-ylide})_2X_n$ (n = 0, 2, 4; X = halide), of gold products. Two successive 2-electron oxidations of I with halogens leads first to the M–M-bonded product II-X_2, followed by formation of III-X_4 and rupture of the M–M bond.

The Au_2Br_4 plane, Figure 3, reveals a distortion from the idealized D_{2h} conformation. The difference in the nonbonded Au–Br distances (3.690 (3) Å vs. 4.588 (4) Å) is substantial. Though the observed structure may suggest an incipient ionizable bromine atom, attempts[13] to prepare cationic species from III-Br_4 and $AgBF_4$ have resulted in II-Br_2 and a small amount of an undentified product.

Table II. Atomic Coordinates for *trans*,*trans*-$[Ph_2P(CH_2)_2AuBr_2]_2$

atom	x	y	z
Au	0.53365 (15)	0.60908 (8)	0.02281 (6)
Br(2)	0.7346 (4)	0.6183 (3)	0.11909 (16)
Br(2)	0.3349 (4)	0.6489 (3)	−0.0685 (2)
P	0.3786 (8)	0.4708 (5)	0.0751 (4)
Cl(1)	0.495 (2)	−0.2148 (16)	0.1940 (9)
Cl(2)	0.5000	−0.050 (2)	0.2500
C(1)	0.346 (4)	0.380 (2)	0.167 (15)
C(2)	0.417 (4)	0.597 (2)	0.0644 (14)
C(3)	0.5000	−0.169 (4)	0.2500
C(11)	0.499 (2)	0.4249 (15)	0.1449 (10)
C(12)	0.502 (2)	0.3220 (15)	0.1570 (10)
C(13)	0.586 (2)	0.2864 (15)	0.2138 (10)
C(14)	0.666 (2)	0.3536 (15)	0.2587 (10)
C(15)	0.662 (2)	0.4564 (15)	0.2466 (10)
C(16)	0.579 (2)	0.4921 (15)	0.1898 (10)
C(21)	0.226 (2)	0.4765 (13)	0.0781 (9)
C(22)	0.195 (2)	0.5645 (13)	0.0978 (9)
C(23)	0.082 (2)	0.5681 (13)	0.1031 (9)
C(24)	0.000 (2)	0.4836 (13)	0.0888 (9)
C(25)	0.031 (2)	0.3956 (13)	0.0691 (9)
C(26)	0.144 (2)	0.3921 (13)	0.0638 (9)

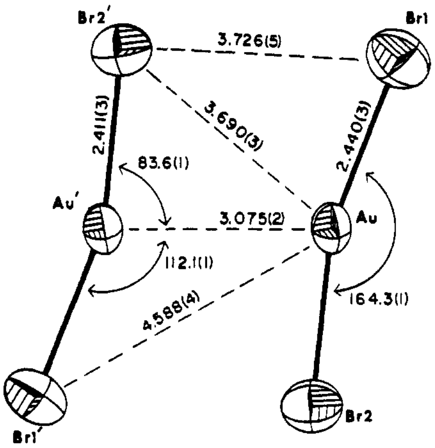

Figure 3. View normal to the Au_2Br_4 plane in *trans*,*trans*-$[Ph_2P(CH_2)_2AuBr_2]_2$. Ylide ligands omitted for clarity.

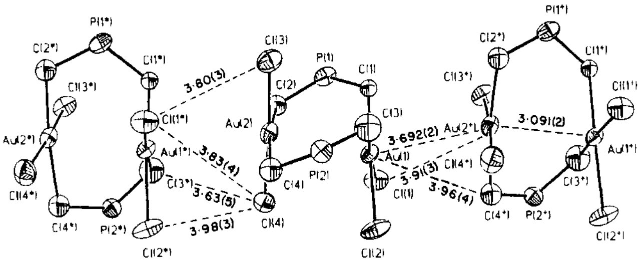

Figure 4. Stacking of *cis*,*trans*-$[Ph_2P(CH_2)_2AuCl_2]_2$ along the z axis. Phenyl rings omitted for clarity.

The formation of III′-Cl_4 was unexpected. Normally gold(I) and gold(III) chlorides are reduced by stannous chloride.[14] The dinuclear palladium(I) complex (a d^9 system) $[Pd(dppm)Cl]_2$ and stannous chloride[15] react with insertion into the Pd–Cl bond to give $Pd_2(dppm)_2ClSnCl_3$. Diazomethane reacts with II-Br_2 by inserting into the Au–Au bond to give a methylene-bridged product.[12] Thus, this novel oxidation/rearrangement observed with II-Cl_2 and $SnCl_2$ is distinct from established Au or Pd chemistry.

With prolonged standing in halocarbon solvents, halogen abstraction by I to give II-X_2 occurs.[8] The formation of III-X_4 and related Au(III)/Au(III) species also can be observed but only with

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(13) Dudis, D. S. Ph.D. Dissertation, Case Western Reserve University, 1984.

(14) Puddephatt, Richard J. "The Chemistry of Gold"; Elsevier: New York, 1978.

(15) Olmstead, M. M.; Benner, L. S.; Hope, H.; Balch, A. L. *Inorg. Chim. Acta* **1979**, *32*, 193–198.

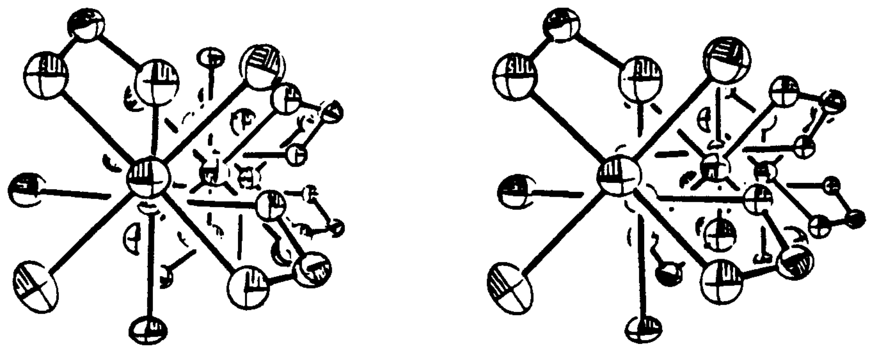

Figure 5. Stereoscopic view of contents in Figure 4, rotated by ~80°.

Table III. Atomic Coordinates for *cis,trans*-$[Ph_2P(CH_2)_2AuCl_2]_2$

atom	*x*	*y*	*z*
Au(1)	0.07326 (12)	0.73020 (5)	0.62342 (10)
Au(2)	0.02517 (12)	0.74746 (5)	0.83611 (10)
P(1)	−0.1687 (8)	0.6888 (3)	0.6459 (7)
P(2)	0.1457 (8)	0.8477 (3)	0.7554 (7)
Cl(1)	0.0778 (8)	0.6333 (3)	0.6041 (7)
Cl(2)	0.2670 (7)	0.7357 (3)	0.6763 (7)
Cl(3)	−0.1077 (8)	0.8140 (3)	0.7880 (7)
Cl(4)	0.1580 (8)	0.6802 (3)	0.8953 (7)
Cl(a)	−0.3164 (14)	0.9035 (7)	0.6181 (14)
Cl(b)	−0.211 (2)	0.8789 (8)	0.4682 (14)
Cl(c)	−0.298 (2)	0.9845 (7)	0.469 (2)
Cl(d)	−0.4500 (16)	0.3978 (7)	0.3340 (15)
Cl(e)	−0.3257 (16)	0.4586 (6)	0.2294 (14)
Cl(f)	−0.4522 (2)	0.3661 (7)	0.1297 (15)
C(1)	−0.101 (2)	0.7285 (11)	0.567 (2)
C(2)	−0.097 (3)	0.6832 (12)	0.785 (2)
C(3)	0.069 (3)	0.8152 (13)	0.630 (3)
C(4)	0.160 (3)	0.8085 (12)	0.870 (2)
C(12)	−0.349 (2)	0.7389 (9)	0.6962 (12)
C(13)	−0.457 (2)	0.7599 (9)	0.6660 (12)
C(14)	−0.521 (2)	0.7612 (9)	0.5585 (12)
C(15)	−0.477 (2)	0.7415 (9)	0.4813 (12)
C(16)	−0.369 (2)	0.7205 (9)	0.5115 (12)
C(11)	−0.305 (2)	0.7192 (9)	0.6190 (12)
C(22)	−0.198 (2)	0.6018 (8)	0.4988 (16)
C(23)	−0.232 (2)	0.5489 (8)	0.4607 (16)
C(24)	−0.276 (2)	0.5133 (8)	0.5203 (16)
C(25)	−0.285 (2)	0.5306 (8)	0.6180 (16)
C(26)	−0.250 (2)	0.5835 (8)	0.6561 (16)
C(21)	−0.206 (2)	0.6191 (8)	0.5964 (16)
C(32)	0.067 (2)	0.9471 (9)	0.6653 (15)
C(33)	0.019 (2)	0.9996 (9)	0.6578 (15)
C(34)	−0.018 (2)	1.0192 (9)	0.7395 (15)
C(35)	−0.008 (2)	0.9864 (9)	0.8288 (15)
C(36)	0.039 (2)	0.9339 (9)	0.8363 (15)
C(31)	0.077 (2)	0.9142 (9)	0.7545 (15)
C(42)	0.313 (2)	0.8757 (9)	0.6718 (13)
C(43)	0.416 (2)	0.8981 (9)	0.6776 (13)
C(44)	0.493 (2)	0.9110 (9)	0.7766 (13)
C(45)	0.466 (2)	0.9015 (9)	0.8697 (13)
C(46)	0.363 (2)	0.8791 (9)	0.8638 (13)
C(41)	0.286 (2)	0.8663 (9)	0.7649 (13)
C(y)	−0.367 (4)	0.3930 (16)	0.251 (3)
C(z)	−0.244 (5)	0.930 (2)	0.545 (4)

mixed solvents[16] such as CCl_4–THF. Since $CDCl_3$ solutions of II-Cl_2 do not give Au(III) species, the $SnCl_2{\cdot}2H_2O$ must play a vital role. Since stannous chloride is normally a reducing agent, it seems unlikely this is oxidizing the gold. A possible function of stannous chloride appears to be that of a Lewis acid. As such, the hydrated stannous chloride may catalyze ionization of a chloride from a gold center. If this is followed by isomerization of the gold moiety to a mixed-valent gold(I)/gold(III) species, the resultant gold(I) could abstract halogen from the solvent. It has been found[16] that THF allows CCl_4 to oxidize I to *trans,-trans*-$[(Ph_2P(CH_2)_2)_2Au_2Cl_3(CCl_3)]$ in high yield.

Table IV. Important Bond Lengths and Angles for III-Br_4 and III′-Cl_4

	III-Br_4		
	Lengths, Å		
Au–Au[a]	3.075 (2)	Au–C(1)	2.13 (5)
Au–Br(1)	2.440 (3)	Au–C(2)	2.14 (5)
Au–Br(2)	2.411 (3)	P–C(av)	1.81 (2)
	Angles, deg		
Au′–Au–Br(1)	112.1 (1)	Au′–Au–C(1)	88.4 (7)
Au′–Au–Br(2)	83.6 (1)	Au′–Au–C(2)	91.8 (8)
Br(1)–Au–Br(2)	164.3 (1)	Br(1)–Au–C(1)	89.0 (8)
Br(1)–Au–C(2)	89.6 (8)	Br(2)–Au–C(1)	92.0 (8)
Br(2)–Au–C(2)	89.4 (8)	C(1)–Au–C(2)	178.6 (11)
	III′-Cl_4		
	Lengths, Å		
Au(1)–Au(2)[a]	3.091 (2)	Au(1)–Cl(1)	2.360 (7)
Au(1)–Cl(2)	2.338 (9)	Au(1)–C(1)	2.10 (3)
Au(1)–C(3)	2.06 (3)	Au(2)–Cl(3)	2.272 (9)
Au(2)–Cl(4)	2.295 (9)	Au(2)–C(2)	2.14 (3)
Au(2)–C(4)	2.20 (3)	P–C(av)	1.81 (2)
	Angles, deg		
Cl(1)–Au(1)–Cl(2)	91.7 (3)	Cl(1)–Au(1)–C(1)	90.0 (8)
Cl(2)–Au(1)–C(1)	176.0 (8)	Cl(1)–Au(1)–C(3)	176.4 (11)
Cl(2)–Au(1)–C(3)	88.4 (12)	C(1)–Au(1)–C(3)	89.7 (14)
Cl(3)–Au(2)–Cl(4)	176.3 (4)	Cl(3)–Au(2)–C(2)	91.7 (9)
Cl(3)–Au(2)–C(4)	92.5 (9)	Cl(4)–Au(2)–C(2)	88.4 (8)
Cl(4)–Au(2)–C(4)	88.0 (8)	C(2)–Au(2)–C(4)	171.4 (14)

[a] Not bonded.

All bond lengths and angles appear normal in the cis,trans Au(III) complex III′-Cl_4. The Au···Au distance is nearly identical with this distance[17] (3.088 (10) Å) in the trans,trans isomer, III-Cl_4. The Au–C and Au–Cl distances show the expected trans influences. However, the most unusual feature of this compound is the stacking.

The short nonbonded interactions are shown in Figure 4, while Figure 5 gives a stereoscopic view almost normal to the orientation of Figure 4. This appears to be the first example to date of a stacked Au(III) complex. Numerous examples of stacked gold(I) compounds are known, while the only previous example[19] of a stacked compound containing gold(III) is a mixed-valent gold(I)/gold(III) species. The stacking in the present case is generated by the *c* glide. The coordination planes are virtually parallel, and the coordination planes adjacent to a given gold atom are staggered approximately 45° with respect to its plane. This stacking suggests

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(16) Murray, H. H.; Fackler, J. P., Jr., to be submitted for publication.

(17) Porter, L.; Murray, H. H.; Fackler, Jr., J. P., to be submitted for publication.

(18) The compound II-Cl_2 is found to isomerize (Fackler, J. P., Jr.; Trzcinska-Bancroft, B. *Organometallics*, in press) to a mixed-valence Au(III)/Au(I) species containing bridging and a terminal (chelating) ylide ligands. Oxidation of the Au(I) center followed by a terminal to bridge ylide rearrangement could lead to III′-Cl_4. It is apparent that various geometric isomers are going to be found with these dinuclear complexes.

(19) Mazany, A. M.; Fackler, J. P., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 801–802.

a substantial lattice energy and consequent low solubility, which accounts for our inability to observe a solution NMR spectrum for this product.

These results confirm a previous report of Schmidbaur[7] concerning gold(III) ylide dimers but also show the chemistry to be much more complicated than originally suggested. Though the source of the extra chlorine atoms in the formation of III′-Cl_4 is uncertain, its formation from II-Cl_2 in the presence of $SnCl_2{\cdot}2H_2O$ is unusual in that an oxidation takes place in the presence of a reducing agent. This reaction opens the path to isomeric gold(III) dimers[18] derived from I.

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Registry No. I (R = Ph), 81457-56-9; II-Cl_2 (R = Ph), 97571-09-0; II-Br_2 (R = Ph), 89462-50-0; III-Br_4 (R = Ph), 98268-94-1; III-$Br_4{\cdot}CDCl_3$ (R = Ph), 98391-74-3; III-Cl_4 (R = Ph), 98391-76-5; III′-Cl_4 (R = Ph), 98268-95-2; III′-$Cl_4{\cdot}2CDCl_3$ (R = Ph), 98391-75-4; *trans*,-*trans*-$[(Ph_2P(CH_2)_2)_2AuCl_3(CCl_3)]$, 98268-96-3; $[Ph_2P(CH_2)_2AuBr]_2(\mu\text{-}CH_2)$, 90742-64-6; $SnCl_2$, 7772-99-8.

Supplementary Material Available: Listings of thermal parameters, calculated hydrogen atom coordinates, bond lengths and bond angles, and structure factors (Tables V–XII) (28 pages).

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Covalent Bonding in *cis*-$[Fe(bpy)_2Cl_2][FeCl_4]$ Studied by X-ray Diffraction at 120 K

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A valence-orbital-based charge-density analysis of $[Fe(bpy)_2Cl_2][FeCl_4]$ using an extensive accurate X-ray data set collected at 120 K is reported. It complements an earlier spin-density study. Positional and thermal motion parameters agree well with results from neutron diffraction experiments. The crystals form rectangular prisms, with a = 1.4996 (7) nm, b = 1.2325 (7) nm, c = 1.3336 (7) nm, space group *Pccn*, and $Z = 8$. For the cation we observe for the octahedrally coordinated iron atom valence populations $t_{2g}{}^{3.42}e_g{}^{2.04}$, with no significant 4p-like contribution, and "overlap" populations in the Fe–ligand bond centers of 0.06–0.28 e. The chlorine atoms donate substantially to the iron atom (~0.7 e each) while the bipyridyl ligands are *net electron acceptors* (~0.8 e/bipyridyl). There appears to be strong "intermolecular" polarization of the charge distributions on the donor chlorine atoms so that it is not possible to distinguish between σ and π Fe–L bonding contributions with any confidence. The bipyridyl acceptor role is not unexpected since simple theories predict π-back-bonding to be greater than σ-donation. For the anion, the tetrahedrally coordinated iron atom populations are $t_2{}^{3.94}e^{1.74}$"$4p$"$^{1.6}$. The chlorine atoms donate substantially to the iron atom, as in the cation about 0.7 e each; again there seems to be strong "intermolecular" polarization of the Cl density, and that inhibits differentiation between σ- and π-bonding. If we compare the metal, donor atom, and bipyridyl charge and spin distributions, both show qualitative features of agreement with simple ligand field and MO treatments of the bonding. However, quantitative incompatibilities of spin and charge result from substantial spin-polarization effects. Thus any quantitative treatment of metal–ligand bonding must allow spin polarization, via for example configuration interaction, to be of more than minor success.

Introduction

The spin and charge distributions in a complex, when combined and compared, give a detailed description of the bonding, as we have shown for the fairly simple molecule, *trans*-tetraamminedinitronickel(II).[1] We have published a report of a polarized neutron diffraction (pnd) study of the spin distribution in a complex of moderate size, where the data, although lacking in completeness, are of good quality.[2] The complex is *cis*-bis(2,2′-bipyridyl)dichloroiron(III) tetrachloroferrate(III), $Fe(bpy)Cl_3$. We have now obtained an accurate and extensive X-ray data set at a moderately low temperature for $Fe(bpy)Cl_3$, which we present and discuss in this paper.

The compound $Fe(bpy)Cl_3$ can be crystallized in the space group *Pccn* with $Z = 8$.[3] The deuterated material has been studied by using conventional (unpolarized) neutrons to give structures at 4.2 and at 115 K.[4] Both this[3] and another polymorph[5] have been studied by X-ray diffraction at ca. 295 K. The *Pccn* polymorph is composed of *cis*-$[Fe(bpy)_2Cl_2]^+$ cations and $FeCl_4^-$ anions (Figure 1) each possessing a 2-fold axis, along c. The asymmetric unit consists of half of each of the ions, giving only 25 atoms. The presence of both octahedrally and tetrahedrally coordinated iron(III) in the same unit cell provides the possibilities of a valuable check on consistency and interesting comparisons between the two types of iron atom.

The pnd study[2] showed that over 15% of the spin resides on the donor atoms of the ligands. Surprisingly, little spin appears beyond the nitrogen atoms of the bipyridyl molecules in the ring system. The spin remaining on the two Fe(III) atoms is in each case 3d-like with little evidence of a diffuse (4s-like) component although the possibility of an aspherical 4p-like population could not be excluded. *Qualitatively*, the spin density conforms to simple ligand field theory. We may note that in $Ni(NH_3)_4(NO_2)_2$, also, the pnd experiment yielded results in qualitative agreement with simple ligand theory but that a comparison with the X-ray data showed substantial *quantitative* deviations.

First, using deformation density maps, we shall discuss the qualitative features observed in the charge-density distribution of $[Fe(bpy)_2Cl_2][FeCl_4]$. Quantitative comparison with the pnd results will then be examined by valence population refinements using least-squares methods.

Experimental Section

Partially deuterated (90 (2)%) amber crystals of $Fe(bpy)Cl_3$ were available.[2] Deuteration helps with the X-ray diffraction studies since at low temperatures the thermal motion is much reduced.[4]

A crystal was mounted on a Syntex $P2_1$ four-circle diffractometer equipped with a locally developed liquid-nitrogen gas-cooled attachment. The cell constants at 120 (3) K were determined by least-squares refinement of the setting angles of six reflections. Monochromatic Mo Kα radiation was employed. A complete sphere of data to $2\theta = 30°$ was collected, accompanied by a hemisphere to $2\theta = 80°$, with the zero layers $h0l$, $hk0$, and $0kl$, and a further octant to $2\theta = 60°$. Standard reflection collection, scan widths, and other experimental parameters and corrections were as described previously.[1b] Long-period intensity variations due to equipment instability were about 3%, and any crystal decomposition was undetectable.

Crystal data are given in Table I. After adjustment for variation in the standards, the data were corrected analytically for absorption by using the program ABSCOR of the X-RAY 76 system.[6] The agreement

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