

in which the metal-metal separation more closely approaches that of the bis-(dipyromethene) macrocycles at 5.145 (1) Å, the copper(II) ions are reduced to copper(I) via one dielectronic step.

The variability of the nature of the two one-electron reductions of the dicopper(II) sites suggests the utility of these complexes as catalysts for the activation of small molecules via concurrent two-electron reductions. Of considerable interest, in view of the simultaneous one-electron reduction steps in the  $\text{Cl}^-$ ,  $\text{N}_3^-$ , and  $\text{NCS}^-$  salts, is the potential of these complexes to catalyze the oxidation of organic substrates. Preliminary results in this direction indicate that the azido complex catalyzes the oxidation of 3,5-di-*tert*-butylcatechol in the presence of molecular oxygen. These studies will be reported in detail elsewhere.

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**Registry No.** 1 ( $n = 3$ ), 98737-20-3; 3,3'-diethyl-5,5'-diformyl-4,4'-dimethyldipyromethane, 967-68-0; 1,3-propanediamine, 109-76-2;  $\text{Pb}_2(\text{bi-dptmd})(\text{SCN})_2$ , 98759-99-0;  $\text{Zn}_2(\text{bi-dptmd})(\text{Cl})_2$ , 98760-00-0;  $\text{Cu}_2(\text{bi-dptmd})(\text{Cl})_2$ , 98760-01-1;  $\text{Cu}_2(\text{bi-dptmd})(\text{ClO}_4)_2$ , 98760-02-2;  $\text{Cu}_2(\text{bi-dptmd})(\text{BF}_4)_2$ , 93081-48-2;  $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2 \cdot \frac{1}{2}\text{CH}_3\text{OH}$ , 98760-04-4;  $\text{Cu}_2(\text{bi-dptmd})(\text{SCN})_2$ , 98760-05-5;  $\text{Zn}_2(\text{bi-dpen})(\text{Cl})_2$ , 98760-06-6;  $\text{Cu}_2(\text{bi-dpen})(\text{ClO}_4)_2$ , 98777-04-9;  $\text{Cu}_2(\text{bi-dptmd})(\text{N}_3)_2$ , 98760-03-3; ethylenediamine, 107-15-3.

**Supplementary Material Available:** Tables of elemental analyses, solution conductivities, structure factors, thermal parameters, hydrogen atom parameters, and torsional angles (41 pages). Ordering information is given on any current masthead page.

## Experimental and Theoretical Studies of Dinuclear Gold(I) and Gold(II) Phosphorus Ylide Complexes. Oxidative Addition, Halide Exchange, and Structural Properties Including the Crystal and Molecular Structures of $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2$ and $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2(\text{CH}_3)\text{Br}^\dagger$

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Contribution from the Laboratory for Molecular Structure and Bonding, Department of Chemistry, Texas A&M University, College Station, Texas 77843, the Department of Chemistry, University of Dayton, Dayton, Ohio 45469, and the Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106. Received January 29, 1985

**Abstract:** The reactions of the dinuclear phosphorus ylide gold(I) complexes  $[\text{Au}(\text{CH}_2)_2\text{P}(\text{Me})_2]_2$ , **1**, and  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2$ , **2**, with the alkyl halides MeI,  $(\text{Me})_3\text{SiCH}_2\text{I}$ , and  $\text{PhCH}_2\text{Br}$  have been studied. It is observed by  $^1\text{H}$  NMR spectroscopy that equilibrium is rapidly achieved between the Au(I) dimer (**1** or **2**), the free alkyl halide, and the Au(II) alkyl halide adduct. This appears to be the first example of a reversible two-center two-electron oxidative addition of an alkyl halide to a dinuclear complex. The MeI adduct reductively eliminates alkyl halide when the solid is heated. When  $\text{CDCl}_3$  solutions of the Au(II) alkyl halide adducts are heated or exposed to light, the Au(II) dihalide dimers, along with other products, are formed. Catalytic halogen exchange between  $\text{CH}_3\text{Br}$  and  $\text{CD}_3\text{I}$  is observed in solution in the presence of **2**. This process is thought to involve an  $\text{S}_{\text{N}}2$  reaction between the free alkyl halide and the postulated intermediate  $\{[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2(\text{Me})\}$  [**1**]. Halogen exchange between  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{Br}_2$  and MeI is observed only when **2** is present. One-electron transfer from **2** to the alkyl halide is suggested as the initial step in the overall two-center two-electron oxidative addition reaction. Cyclic voltammetry of **2** and the dihalide adducts suggests consecutive one-electron steps are involved in the electrochemical oxidations and reductions. Although the alkyl halides show resolved oxidation and reduction waves, the processes are irreversible. No free halide is observed in the presence of excess  $\text{CH}_3\text{Br}$  or  $\text{CH}_3\text{I}$ . The ready ionization of the Au-halide bonds in the alkyl halide adducts appears related to the exceptional structural *trans* effect observed in these compounds. In general the Au-halide bond lengths observed in the dinuclear C-Au-Au-halide species are 5-10% longer than the *trans* Au-halide bonds in mononuclear C-Au-halide compounds. Molecular orbital calculations (Atom Superposition and Electron Delocalization) have been used to indicate the character of the bonding in the alkyl halide and dihalide Au(II) complexes. The trends observed in the energy levels correlate well with electrochemical reduction potentials for the dihalides. The structures of  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2$ , **2**, and  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2(\text{Me})\text{Br}$ , **2-MeBr**, have been determined by a single-crystal X-ray diffraction study. Crystal data for **2**:  $\text{C}_{28}\text{H}_{28}\text{Au}_2\text{P}_2$ , crystallizes in the monoclinic space group  $P2_1/n$  with  $a = 8.576$  (1) Å,  $b = 9.378$  (2) Å,  $c = 15.915$  (3) Å,  $\beta = 96.48$  (1)°, and  $Z = 2$ . Refinement with 2039 reflections with  $F_o^2 > 3\sigma(F_o^2)$  yielded  $R = 0.028$  and  $R_w = 0.027$ . Crystal data for **2-MeBr**:  $\text{C}_{29}\text{H}_{31}\text{P}_2\text{Au}_2\text{Br}$ , crystallizes in the monoclinic space group  $Cc$  with  $a = 13.385$  (2) Å,  $b = 12.340$  (1) Å,  $c = 17.360$  (3) Å,  $\beta = 103.65$  (1)°, and  $Z = 4$ . Refinement with 2629 reflections with  $F_o^2 > 3\sigma(F_o^2)$  yielded  $R = 0.061$  and  $R_w = 0.059$ .

Organogold chemistry<sup>1</sup> and the study of dinuclear transition-metal complexes<sup>2</sup> are both among the rapidly developing areas of organometallic and metal cluster chemistry. While many mechanistic studies have been reported on mononuclear metal

systems which undergo oxidative addition-reductive elimination steps,<sup>3</sup> only recently have reports appeared of oxidative addition

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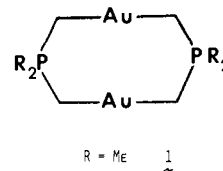
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involving more than one transition-metal center.<sup>4</sup> Mechanistic investigations with dinuclear transition-metal complexes can clarify and define the role of a second metal atom in the process. Such studies also provide insight into general problems relating to the reactivity of multi- and heterometallic systems.

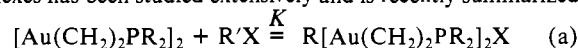
Several recent reports have demonstrated the synthesis of  $\mu$ -alkylidene complexes<sup>4a-d</sup> from *gem*-dihalides. These reactions involve a four-electron oxidation of dinuclear transition-metal complexes. The reaction of diazo alkanes with dimetallic M-M bonded complexes<sup>4e-g</sup> further indicates the synthetic potential of the oxidative addition chemistry of dinuclear complexes. The following additions of alkyl monohalides to dimetallic complexes have been reported: MeI to  $\text{Rh}_2(\text{dcp})_4^{2+}$  (dcp = 1,3-diisocyanopropane),<sup>5</sup>  $[(\text{CO})_2\text{Rh}(\text{CH}_2)_2\text{PMe}_2]_2$ ,<sup>6</sup>  $[\text{Ir}(\text{CO})(\text{PPh}_3)(\mu\text{-pyrazolyl})]_2$ ,<sup>7</sup>  $\text{Pt}_2(\text{P}_2\text{O}_5\text{H}_2)_4$ ,<sup>8</sup>  $[\text{Ir}(\text{COD})(\mu\text{-pyrazolyl})]_2$ ,<sup>9</sup>  $[\text{Au}(\text{CH}_2)_2\text{PMe}_2]_2$ ,<sup>10</sup> and  $(\text{C}_5\text{Me}_5)\text{Rh}(\mu\text{-PMe}_2)_2\text{Mo}(\text{CO})_4$ .<sup>11</sup> *n*-BuI to  $\text{Rh}_2(\text{dcp})_4^{2+}$ ; 2-MeBuI to  $[\text{Ir}(\text{CO})(\text{PPh}_3)(\mu\text{-pyrazolyl})]_2$ .<sup>7</sup> In each case the resulting product involves a one-electron oxidation of each metal center with bonding of both the alkyl and the halide. Other dimetallic methyl halide complexes have been prepared, but these involve either reaction at only one metal center or protonation of a methylene bridge.<sup>4d,12</sup>

The thermodynamically stable dinuclear gold(I) phosphorus ylide complex **1**, first reported<sup>1e</sup> by Schmidbaur in 1973, has been shown to be a reactive, coordinatively unsaturated dimetal system. While several dinuclear gold(I) complexes can be oxidized chemically to gold(III),<sup>4c,14</sup> the existence of authentic  $\text{d}^9\text{-d}^9$ , Au(II)-Au(II) metal-metal single bonded compounds has been established only recently by X-ray crystallography,<sup>15</sup> ESCA,<sup>16</sup>

Raman,<sup>17</sup> and Mössbauer spectroscopy.<sup>16b-d,17</sup> The addition of halogens to the digold(I) complexes is a general route to these gold(II) complexes.<sup>15,16,18</sup>

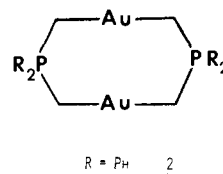


The addition of alkyl halides, reaction a, to mononuclear gold(I) complexes has been studied extensively and is recently summarized



X = halide; R' = alkyl

in a general review of the oxidative addition chemistry of Au(I).<sup>19</sup> Because the gold ylide dimers **1** and **2** have a potentially rich redox chemistry and are suitable for study by <sup>1</sup>H NMR spectroscopy, we have undertaken a study of the reactions of **1** and **2** with MeI, MeBr, Me<sub>3</sub>SiCH<sub>2</sub>I, and PhCH<sub>2</sub>Br. Preliminary results of the X-ray crystal structure of **1**-MeI and a brief description of its properties have been reported.<sup>20</sup>



## Experimental Section

All reactions and measurements were performed in dry, degassed glassware in an atmosphere of dry nitrogen. Unless otherwise specified, all reactions take place at room temperature. Precautions were taken to protect solutions of the Au(II) alkyl compounds from exposure to light.

Solvents were purified under nitrogen by standard techniques.<sup>21</sup> (Iodomethyl)trimethylsilane and benzyl bromide (Aldrich) were used as received. Methyl iodide was purified prior to use and stored<sup>21</sup> over a drop of Hg. The dinuclear ylide complex **1** was prepared according to Schmidbaur's method.<sup>14d</sup> The new complex **2**, the diphenyl analogue of **1**, was prepared in a similar manner starting with  $[\text{Ph}_2\text{PMe}_2]\text{Br}$ . Deprotonation of the phosphonium salt to the ylide was carried out in THF with KH. The desired complex, **2**, was separated by washing the precipitate with THF then methanol followed by recrystallization from hot benzene. Since crystals of **2** suitable for X-ray crystallographic analysis were obtained by recrystallization of **2** from hot toluene.

**Electrochemical Studies.** Voltammetric studies in  $\text{CH}_2\text{Cl}_2$ - $[\text{n-Bu}_4\text{N}][\text{BF}_4]$  (0.5 M) and THF- $[\text{n-Bu}_4\text{N}][\text{BF}_4]$  (0.1 M) employed a BAS 100 Electrochemical Analyzer, interfaced with a Houston Instrument HIPLLOT DMP-40 Plotter. Voltammograms were recorded with use of a three electrode cell configuration, with a Pt or Au micro disk as working electrode, Ag/AgCl reference electrode (-35 mV relative to SCE), and a Pt wire counter electrode. Routine scan rates were 100 mV

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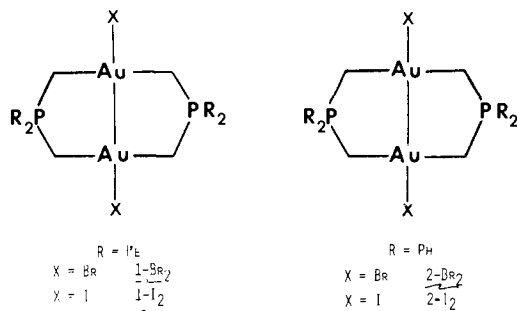
Table I. Crystallographic Data.

	<b>2</b> , [Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ] <sub>2</sub>	<b>2-MeBr</b> , [Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ] <sub>2</sub> - (CH <sub>3</sub> )Br
formula	C <sub>28</sub> H <sub>28</sub> P <sub>2</sub> Au <sub>2</sub>	C <sub>29</sub> H <sub>31</sub> P <sub>2</sub> Au <sub>2</sub> Br
formula wt	820.16	915.08
space group	<i>P2</i> <sub>1</sub> / <i>n</i> (No. 14)	<i>Cc</i> (No. 9)
systematic absences	<i>h0l</i> , <i>h + l = 2n</i> <i>0k0</i> , <i>k = 2n</i>	<i>hkl</i> , <i>h + k = 2n</i> <i>h0l</i> , <i>l = 2n</i>
<i>a</i> , Å	8.576 (1)	13.385 (2)
<i>b</i> , Å	9.378 (2)	12.340 (1)
<i>c</i> , Å	15.915 (3)	17.360 (3)
$\beta$ , deg	96.48 (1)	103.65 (1)
<i>V</i> , Å <sup>3</sup>	1274.9	2789.1
<i>Z</i>	2	4
<i>d</i> <sub>calcd</sub> , g/cm <sup>3</sup>	2.14	2.18
crystal size, mm	0.30 × 0.25 × 0.30	0.20 × 0.15 × 0.20
<i>u</i> (Mo K $\alpha$ ), cm <sup>-1</sup>	116.4	120.4
data collection instrument	Nicolet P3F	Nicolet P3F
radiation (monochromated in incident beam)	Mo K $\alpha$	Mo K $\alpha$
orientation reflect: no. and range (2 $\theta$ ), deg	25, 20–29	25, 25–35
temp, °C	22	22
scan method	2 $\theta$	$\omega$
data col. range, 2 $\theta$ , deg	4–50	3–55
no. unique data, total with <i>F</i> <sub>o</sub> <sup>2</sup> > 3 $\sigma$ ( <i>F</i> <sub>o</sub> <sup>2</sup> )	2339, 2039	3491, 2629
no. of parameters refined	121	151
<i>R</i> <sup>a</sup>	0.028	0.061
<i>R</i> <sub>w</sub> <sup>b</sup>	0.027	0.059
goodness-of-fit indicator <sup>c</sup>	1.269	1.112
largest shift/esd, final cycle	0.01	0.02
largest peak, e/Å <sup>3</sup>	1.35	1.00

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

s<sup>-1</sup> in cyclic voltammetry and 10 mV s<sup>-1</sup> in other modes. Coulometric studies employed an Ag/AgCl reference electrode and a Pt basket working electrode with a Pt wire counter electrode separated by a salt-bridge (with a frit) from the working compartments. Cell solutions, approximately 5 × 10<sup>-4</sup> M in complex, were degassed with solvent-saturated argon prior to all measurements.

**Nuclear Magnetic Resonance Measurements.** All alkyl halide adducts were stored in the dark. The Au(II) dihalide dimers [Au(CH<sub>2</sub>)<sub>2</sub>PMe<sub>2</sub>]<sub>2</sub>X<sub>2</sub> (X = Br, 1-Br<sub>2</sub>; X = I, 1-I<sub>2</sub>) and [Au(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>]<sub>2</sub>X<sub>2</sub> (X = Br, 2-Br<sub>2</sub>; X = I, 2-I<sub>2</sub>) were identified as the major photolytic decomposition products (vide infra) of the Au(II) alkyl halide adducts by independently preparing authentic samples of these materials and comparing their <sup>1</sup>H NMR and visible absorption spectra. The preparation and characterization of these dihalides (1-Br<sub>2</sub>, 1-I<sub>2</sub>, 2-Cl<sub>2</sub>, 2-Br<sub>2</sub>, 2-I<sub>2</sub>) are similar as described below.

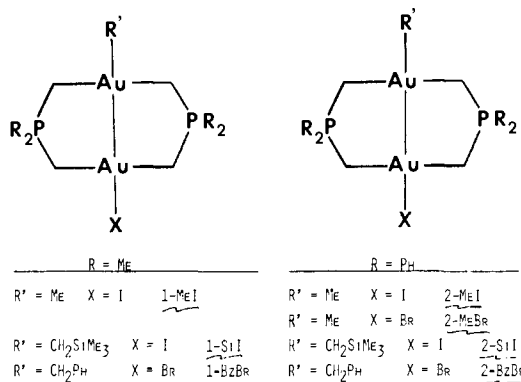


<sup>1</sup>H NMR spectra were recorded on Varian EM-390(CW), XL-100, and XL-200 (FT) spectrometers; chemical shifts are reported in parts per million (ppm) downfield from internal Me<sub>4</sub>Si. All splittings are given in hertz as the absolute value; no sign determinations were made. The <sup>31</sup>P NMR spectra were recorded on Varian XL-100-IS and XL-200 spectrometers at 40 and 80 MHz, respectively. Chemical shifts are reported in ppm downfield of 85% H<sub>3</sub>PO<sub>4</sub> (external). When dry, O<sub>2</sub>-free CDCl<sub>3</sub> is specified; this solvent was refluxed and distilled from P<sub>4</sub>O<sub>10</sub>, freeze-pump-thaw degassed. Samples were prepared and maintained in an atmosphere of dry N<sub>2</sub>.

**Molecular Orbital Calculations.** The molecular orbital calculations were done by using the ASED theory described elsewhere.<sup>22-24</sup> The bond lengths and angles were derived from X-ray structural data. The skeletal eight-member ring was kept constant whenever possible. The ASED theory uses  $\zeta$  and double- $\zeta$  Slater-type orbitals. The  $\zeta$  exponents were calculated by Clementi.<sup>25</sup> The diagonal elements of the secular determinant, *H*<sub>ii</sub>, are expressed as ionization potentials<sup>26</sup> which were appropriately adapted for the ionic species. The parameters used in this calculation are listed in Table II.

**Collection and Reduction of X-ray Diffraction Data.** Crystal data for **2** and **2-MeBr** are provided in Table I. 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 with use of the SHELXTL (Versions 4.0 and 4.1) crystallographic computational package installed on a Data General Eclipse S140 minicomputer. All data were corrected for Lorentz, polarization, decay, and absorption.

**Solutions and Refinements of Structures.** The initial positional parameters for the gold atoms in **2** and **2-MeBr** were determined from the Au-Au vector obtained from the Patterson function listing. The space group for **2-MeBr** was chosen as *Cc* and not *C2/c* by virtue of successful refinement. The apparent 10% Br/Me disorder (as determined by



refinement of site occupation factors) introduces a pseudocentric nature to the structure by approximating a mirror in the plane of the two P atoms normal to the Au-Au vector (bond). Thus, the following restrictions were imposed on refinement: the Au-Br, Au-Me, and Br-Me distances were tied together (respectively) and refined as separate, single variables; the isotropic temperature factor of C(5) was arbitrarily set at 3 times that of C(6). Structure **2-MeBr** refined to *R* = 0.061, *R*<sub>w</sub> = 0.059 for 2629 reflections with *F*<sub>o</sub><sup>2</sup> > 3.0 $\sigma$ (*F*<sub>o</sub><sup>2</sup>). Refinement with negative phasing produced no significant improvement in results.

The space group *P2*<sub>1</sub>/*n* was uniquely determined for **2** by systematic absences. All remaining non-hydrogen atoms were located by using difference Fourier techniques. All phenyl rings were refined as rigid groups with C-C fixed at 1.395 Å and C-C-C = 120°. All non-hydrogen atoms were refined anisotropically. Structure **2** refined to *R* = 0.028 and *R*<sub>w</sub> = 0.027 for 2039 reflections with *F*<sub>o</sub><sup>2</sup> > 3 $\sigma$ (*F*<sub>o</sub><sup>2</sup>).

**Syntheses:** Bis[ $\mu$ -(dimethyldimethylenephosphoranyl-*C,C*)]iodomethylidigold(II) (*Au-Au*) [1-MeI], Bis[ $\mu$ -(diphenyldimethylenephosphoranyl-*C,C*)]iodomethylidigold(II) (*Au-Au*) [2-MeI], and Bis[ $\mu$ -(diphenyldimethylenephosphoranyl-*C,C*)]bromomethylidigold(II) (*Au-Au*) [2-MeBr]. The methylhalogold(II) complexes were synthesized in a similar manner and exhibited similar properties. For 1-MeI: To a flask containing 285 mg (0.49 mmol) of **1**, 20 mL of Et<sub>2</sub>O, and a magnetic stirring bar, 0.5 mL (8.0 mmol) of MeI was added, and the mixture was stirred for 3 h at 25 °C. The yellow precipitate was removed by filtration, washed with Et<sub>2</sub>O, and dried in vacuo; yield 315 mg, 90%. Melting point: turned white at 140–145 °C and then gradually darkened, melting to a black tar at 216–220 °C (lit.<sup>10</sup> mp 143 °C; mp for **1** 216–218 °C<sup>10</sup>). The <sup>1</sup>H NMR spectrum after heating to above 145 °C but less than 200 °C is that of **1**. (The color change at 140–145 °C is due to a thermally induced solid-state reductive elimination reaction liberating MeI (bp

(22) Anderson, A. B. *J. Chem. Phys.* **1974**, *60*, 2477.(23) Anderson, A. B. *J. Chem. Phys.* **1975**, *62*, 1187.(24) Trzcinska, B. M.; Fackler, J. P., Jr.; Anderson, A. B. *Organometallics* **1984**, *3*, 319.

(25) Clementi, E.; Roetti, C. "Atomic Tables and Nuclear Data Tables," Academic Press: New York, 1974; Vol. 14, p 177.

(26) (a) Lot, W. *J. Opt. Soc. Am.* **1970**, *60*, 206. (b) Moore, C. E. "Atomic Energy Levels"; National Bureau of Standards: Washington, D.C., 1949; Vol. I-IV.

Table II. Parameters Used in the ASED Calculation

element	s			p			d					
	n	exp <sup>b</sup>	IP <sup>a</sup>	n <sup>c</sup>	exp <sup>b</sup>	IP <sup>a</sup>	n <sup>c</sup>	exp <sup>b</sup>	IP <sup>a</sup>	exp <sup>b</sup>	c <sub>1</sub> <sup>d</sup>	c <sub>2</sub> <sup>d</sup>
Au	6	2.4	9.23	6	2.1	4.51	5	6.163	11.1	2.794	0.64418	0.53558
C	2	1.7	20.00	2	1.6	11.26						
H	1	1.2	13.6									
I	5	2.8	20.61	5	2.5	10.45	5	2.4	2.0	3.939	0.55190	0.52767
Br	4	2.75	23.7	4	2.45	11.7	4	2.4	1.0	4.874	0.38965	0.72376
Cl	3	2.36	24.54	3	2.04	13.01						
P	3	1.88	16.15	3	1.63	10.55						

<sup>a</sup>IP = ionization potentials in eV.<sup>26</sup> <sup>b</sup>exp = Slater  $\zeta$  exponents.<sup>25</sup> <sup>c</sup>n = principal quantum number. <sup>d</sup>c<sub>1</sub>, c<sub>2</sub> = double- $\zeta$  coefficients.

41–43 °C) and regenerating **1** (vide infra). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 90 MHz, 35 °C)  $\delta$  1.63 (d, <sup>2</sup>J<sub>PH</sub> = 10.3 Hz, P–Me), 1.51 (s, Au–Me), 1.44 and 0.93 (d, <sup>2</sup>J<sub>PH</sub> = 9.5 and 10.2 Hz, respectively, Au–CH<sub>2</sub>–P). <sup>31</sup>P NMR {<sup>1</sup>H} 31.08.

**Synthesis of 2-MeI:** To a flask containing 54 mg (0.07 mmol) of **2** and 1.5 mL of toluene was added 0.07 mL (1.1 mmol) of MeI, and the mixture was stirred for 1–2 h at 25 °C. The product **2-MeI** (40 mg, 64%) was isolated by filtration; an additional 12 mg was obtained as well-formed light yellow crystals by adding 2 mL of hexane to the toluene solution giving an overall yield of 84%. Melting point 172 °C, color change from yellow to white, melting with decomposition to a black tar at 230–231 °C. MeI is thermally eliminated at 172 °C generating **2**. Anal. Calcd for C<sub>29</sub>H<sub>31</sub>P<sub>2</sub>Au<sub>2</sub>I (fw 962.35): C, 36.19; H, 3.25. Found: C, 35.97; H, 3.28. <sup>1</sup>H NMR of **2-MeI** (CDCl<sub>3</sub>)  $\delta$  1.94 and 1.37 (d, <sup>2</sup>J<sub>PH</sub> = 11.3 Hz and 10.2 Hz), 1.23 (s, Au–Me), 7.8–7.0 (m, P–Ph). <sup>31</sup>P NMR {<sup>1</sup>H} 38.85.

**Synthesis of 2-MeBr:** To a Schlenk tube containing 170 mg (0.21 mmol) of **2** in 10 mL of benzene was added an excess of MeBr. The solution was stirred overnight at 25 °C. The product (155 mg, 0.17 mmol) was isolated in 81% yield as a yellow powder by taking the solution to dryness in vacuo. Melting point 205–210 °C, color change from yellow to white, melting with decomposition to a black tar at 230–231 °C. (Methyl bromide is thermally eliminated between 205 and 210 °C, giving **2**.) <sup>1</sup>H NMR spectrum (22 °C, 200 MHz, CDCl<sub>3</sub>)  $\delta$  1.753 and 1.393 (d, <sup>2</sup>J<sub>PH</sub> = 11.8 Hz, and <sup>2</sup>J<sub>PH</sub> = 10.5 Hz, P–CH<sub>2</sub>–Au), 1.094 (s, Au–Me), 7.37 and 7.63 (m, P–Ph). Single crystals of **2-MeBr** suitable for X-ray crystallographic analysis were obtained by recrystallization of **2-MeBr** from a dichloromethane/hexane solution at 0 °C. Crystal data information is given in Table I.

**Bis[ $\mu$ -(dimethyldimethylenephosphoranyl-C,C)]iodo(trimethylsilyl)methylene]digold(II)(Au–Au) [1-SiI] and Bis[ $\mu$ -(diphenyldimethylenephosphoranyl-C,C)]iodo(trimethylsilyl)methylene]digold(II)(Au–Au) [2-SiI]. Both (trimethylsilyldimethylene)gold(II) complexes were synthesized in a similar manner and exhibited similar properties. For **1-SiI**: To 10.6 mg (0.02 mmol) of **1** in 0.50 mL of dry, O<sub>2</sub>-free CDCl<sub>3</sub>/C<sub>6</sub>H<sub>6</sub> (9:1 v/v) in a 5-mm <sup>1</sup>H NMR tube was added 12.4  $\mu$ L (0.08 mmol) of Me<sub>3</sub>SiCH<sub>2</sub>I. After 15 h, the <sup>1</sup>H NMR was mainly that of **1-SiI** (CDCl<sub>3</sub>/C<sub>6</sub>H<sub>6</sub> (9:1)  $\delta$  1.49 (d, <sup>2</sup>J<sub>PH</sub> = 11 Hz, P–CH<sub>3</sub>), 1.15 and 0.92 (d, <sup>2</sup>J<sub>PH</sub> = 9 and 11 Hz, P–CH<sub>2</sub>–Au), 1.34 (s, Au–CH<sub>2</sub>–Si), –0.01 (s, Si–(Me)<sub>3</sub>).**

For **2-SiI**: To 10.6 mg (0.013 mmol) of **2** in 0.45 mL of dry, O<sub>2</sub>-free CDCl<sub>3</sub> in a 5-mm NMR tube was added a 4-fold excess of (Me)<sub>3</sub>SiCH<sub>2</sub>I. After 15 h of reaction at ambient temperature, the <sup>1</sup>H NMR spectra showed only the presence of **2-SiI**. <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.98 (d, <sup>2</sup>J<sub>PH</sub> = 10 Hz, Au–CH<sub>2</sub>–P), 1.44 (s, Si–CH<sub>2</sub>–Au), 1.27 (d, <sup>2</sup>J<sub>PH</sub> = 9 Hz, Au–CH<sub>2</sub>–P), –0.06 (s, (Me)<sub>3</sub>Si), 7.8–7.0 (m, Ph). <sup>31</sup>P{<sup>1</sup>H} NMR 36.32.

**Bis[ $\mu$ -(dimethyldimethylenephosphoranyl-C,C)]benzylbromodigold(II)(Au–Au) [1-BzBr] and Bis[ $\mu$ -(diphenyldimethylenephosphoranyl-C,C)]benzylbromodigold(II)(Au–Au) [2-BzBr]. Both benzylbromide gold(II) complexes were synthesized similarly. For **1-BzBr**: PhCH<sub>2</sub>Br (0.035 mL) was added to a stirred suspension of 49 mg (0.085 mmol) of **1** in 30 mL of Et<sub>2</sub>O. After 12 h, 39 mg (0.05 mmol, yield 58%) of **1-BzBr** was obtained as a brown precipitate. The product melted between 127–130 °C. <sup>1</sup>H NMR of **1-BzBr** (CDCl<sub>3</sub>)  $\delta$  3.58 (t, <sup>2</sup>J<sub>PH</sub> = 2 Hz, Au–CH<sub>2</sub>–Ph), 1.61 (d, <sup>2</sup>J<sub>PH</sub> = 12 Hz, P–CH<sub>3</sub>), 1.41 and 1.01 (d, <sup>2</sup>J<sub>PH</sub> = 12, Au–CH<sub>2</sub>–P), 7.8–7.0 (m, Ph). Complex **1** and free PhCH<sub>2</sub>Br were observed in equilibrium with **1-BzBr** in the <sup>1</sup>H NMR spectrum.**

For **2-BzBr**, 141 mg (0.17 mmol) of **2** was dissolved in a minimal amount of 1,2-dichloroethane. The solution was gravity filtered through a coarse frit (under N<sub>2</sub>) into a flask containing a magnetic stirring bar. Benzyl bromide (0.20 mL, 1.7 mmol) was added to the stirred solution. After 2 h the solution was concentrated by evaporation in vacuo to 1/4 of its original volume, cooled to –18 °C for 20 h, and filtered. The resulting peach-colored powdery precipitate was rinsed with Et<sub>2</sub>O and triturated with four 5-mL portions of Et<sub>2</sub>O to remove excess PhCH<sub>2</sub>Br. After drying, 108 mg (65% yield) was obtained: melting point, yellow

at 110 °C, melted to a brown liquid between 174 and 177 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.52 (t, <sup>2</sup>J<sub>PH</sub> = 2 Hz, Au–CH<sub>2</sub>–Ph), 1.83 and 1.38 (d, <sup>2</sup>J<sub>PH</sub> = 11 Hz, Au–CH<sub>2</sub>–P), 7.8–7.0 (m, Ph). Complex **2** and free PhCH<sub>2</sub>Br were observed in equilibrium with **2-BzBr** in the <sup>1</sup>H NMR spectrum.

**Bis[ $\mu$ -(dialkyl- and diaryldimethylenephosphoranyl-C,C)]dihalodigold(II)(Au–Au) Complexes.** All dinuclear gold(II) dihalide complexes may be synthesized in a similar manner. Stoichiometric amounts of **1** or **2** were combined with halogens in 4 mL of CH<sub>2</sub>Cl<sub>2</sub> at 25 °C and stirred for 2 h. The orange to red precipitate was filtered, washed with hexane, and dried in vacuo. **1-Br<sub>2</sub>**: 88 mg (0.15 mmol) of **1** reacted with 7.7  $\mu$ L of Br<sub>2</sub> to give 105 mg, 96% yield, mp 222 °C (lit.<sup>10</sup> mp 224 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.60 (d, <sup>2</sup>J<sub>PH</sub> = 12.2 Hz, P–Me), 1.41 (d, <sup>2</sup>J<sub>PH</sub> = 9.8 Hz, Au–CH<sub>2</sub>–P). [Au(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>]<sub>2</sub>Br<sub>2</sub> (**2-Br<sub>2</sub>**): 98.6 mg (0.12 mmol) of **2** reacted with 6.15  $\mu$ L (0.12 mmol) of Br<sub>2</sub> to give 97.2 mg, 83% yield; mp 229–235 °C dec; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.90 (d, <sup>2</sup>J<sub>PH</sub> = 9.8 Hz, Au–CH<sub>2</sub>–P), 7.61–7.36 (m, Ph). **1-I<sub>2</sub>**: 205 mg (0.35 mmol) of **1** reacted with 89 mg (0.35 mmol) of I<sub>2</sub> to give 266 mg, 92% yield; mp 215 °C (lit.<sup>11</sup> mp 216 °C); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.57 (d, <sup>2</sup>J<sub>PH</sub> = 9.8 Hz, P–Me), 1.51 (d, <sup>2</sup>J<sub>PH</sub> = 12.3 Hz, Au–CH<sub>2</sub>–P). **2-I<sub>2</sub>**: 54 mg (0.066 mmol) of **2** reacted with 17 mg of I<sub>2</sub> (0.067 mmol) to give 55 mg, 77.6% yield; mp 190–196 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.97 (d, <sup>2</sup>J<sub>PH</sub> = 10.0 Hz, Au–CH<sub>2</sub>–P) 6.11, 7.56–7.36 (m, P–Ph).

An alternative synthesis using carbon tetrahalides is available. For **2-Cl<sub>2</sub>**: 25 mg (0.03 mmol) of **2** was added to approximately 5 mL of CCl<sub>4</sub> and the solution was stirred for 1 h at 25 °C. The bright yellow precipitate, **2-Cl<sub>2</sub>**, which formed was washed with ether and dried in vacuo to give 26.3 mg 98% yield; mp 237–239 °C dec; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  1.85 (d, <sup>2</sup>J<sub>PH</sub> = 9.8 Hz, Au–CH<sub>2</sub>–P), 7.63–7.37 (m, Ph).

## Results

The dinuclear Au(I) complexes **1** and **2** react with MeI, Me<sub>3</sub>SiCH<sub>2</sub>I, and PhCH<sub>2</sub>Br to give Au(II) alkyl halide adducts. In solution (CDCl<sub>3</sub>, by <sup>1</sup>H NMR) the Au(II) alkyl halide adducts are in equilibrium<sup>27,28</sup> with the Au(I) complex and the halocarbon. In the solid state, **2-MeI** and **2-MeBr** undergo a thermally induced<sup>29</sup> reductive elimination giving **2** and MeI or MeBr, respectively. (<sup>1</sup>H NMR and gas-phase IR spectroscopic identification of products and reactants was made by comparison with authentic samples.)

Facile (within 3 min of mixing) halogen exchange was observed via <sup>2</sup>H NMR spectroscopy by the appearance<sup>30</sup> of CD<sub>3</sub>Br when **2-MeBr** and<sup>31</sup> **2-CD<sub>3</sub>I** were combined in CHCl<sub>3</sub> at 22 °C. (There was no indication from the <sup>2</sup>H NMR that deuterated or partially deuterated ethane was generated in this reaction.) Upon further reaction (>24 h at 22 °C) halogen exchange with the solvent also was observed by detection of CD<sub>3</sub>Cl in the <sup>2</sup>H NMR spectrum.

(27) Fackler, J. P., Jr.; Basil, J. D.; Murray, H. H. *Organometallics* **1984**, *3*, 821.

(28) In Schmidbauer's original report of the oxidative addition of CH<sub>3</sub>I to **1** there is no mention that the <sup>1</sup>H NMR spectrum of this gold(II) dinuclear methyl iodide adduct shows it to be in equilibrium with the gold(I) dinuclear ylide and MeI. See ref 10 and 8c.

(29) Schmidbauer<sup>10</sup> reported the melting point (dec) of **1-MeI** to be 143 °C; we have now correctly identified this observation as a solid state reductive elimination process giving MeI and **1**.

(30) The chemical shifts of CD<sub>3</sub>Br and CD<sub>3</sub>I are  $\delta$  = 2.61 and 2.12, respectively.

(31) Complex **2-CD<sub>3</sub>I** is synthesized as for **2-MeI**; however, CD<sub>3</sub>I (Aldrich) is used rather than CH<sub>3</sub>I.

(32) Basil, John D. Ph.D. Thesis, 1983, Case Western Reserve University.

(33) P. Kalck and J. J. Bonnet have reported that the addition of CH<sub>3</sub>I to some dinuclear iridium(I) complexes ([Ir( $\mu$ -t-BuS)(CO)(PR<sub>3</sub>)<sub>2</sub>]<sub>2</sub>) gives the corresponding Ir(II) diiodo complex. Kalck, P.; Bonnet, J.-J. G. *Organometallics* **1982**, *1*, 1211.

**Table III.** Selected Lengths and Angles for [Au(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>]<sub>2</sub> (**2**) and [Au(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>]<sub>2</sub>(CH<sub>3</sub>)Br (**2-MeBr**)

lengths, Å		angles, deg	
<b>2</b>			
Au-Au'	2.977 (1)	C(1)-Au-C(2)'	179.0 (3)
Au-C(1)	2.091 (7)	Au'-Au-C(2)'	89.7 (2)
Au'-C(2)	2.085 (7)	C(1)-P-C(2)	113.0 (3)
P-C(1)	1.766 (7)		
P-C(2)	1.760 (7)		
<b>2-MeBr</b>			
Au(1)-Au(2)	2.674 (1)	Au(1)-Au(2)-Br	170.8 (1)
Au(2)-C(6)	2.159 (2)	Au(1)-Au(2)-C(6)	177.6 (7)
Au(1)-Br	2.698 (3)	C(1)-Au(2)-Au(1)	95.4 (6)
Au(2)-C(1)	2.118 (2)	C(4)-Au(1)-Au(2)	89.8 (5)
Au(1)-C(2)	2.007 (2)	C(1)-P(1)-C(2)	113.5 (1)
Au(2)-C(3)	2.116 (2)	C(3)-P(2)-C(4)	104.2 (1)
Au(1)-C(4)	2.107 (2)		

Complex **2** catalytically effects halogen exchange between CD<sub>3</sub>I and MeBr when an excess of the MeBr is combined in CDCl<sub>3</sub> with CD<sub>3</sub>I and **2**. After 20 h at 25 °C, ca. 18 CD<sub>3</sub>Br molecules were generated per molecule of **2** ( $7.3 \times 10^{-3}$  M).

In other observations of halogen exchange (monitored by <sup>1</sup>H NMR spectroscopy), **2-Br<sub>2</sub>** and excess MeI in CDCl<sub>3</sub> at 25 °C gave **2-I<sub>2</sub>** and MeBr within minutes of mixing in the presence of **2**. When **2-Br<sub>2</sub>** and MeI were combined in CDCl<sub>3</sub> in the absence of **2**, no halogen exchange was observed after 20 h of mixing. The <sup>1</sup>H NMR spectrum of the methylene protons of **2-Br<sub>2</sub>** in CDCl<sub>3</sub> is a doublet ( $\delta$  1.90, <sup>2</sup>J<sub>HP</sub> = 9.9 Hz,  $W_{1/2}$  = 3.0 Hz). Upon the addition of a small amount of **2**, significant broadening and a slight shift of the major resonance (original doublet) is observed.

The stabilities of the gold(II) alkyl halide adducts under the exchange reaction conditions were examined because of this halogen exchange. It was found that **2-MeI** in CDCl<sub>3</sub> gives **2-I<sub>2</sub>** when heated (<62 °C, bp of CHCl<sub>3</sub>) or irradiated (Hg,  $\lambda$  > 300 nm, glass filter). The nature of this transformation or the fate of the methyl group is not yet clear. The interaction of **2-MeI** with the chlorinated solvent is apparent as MeCl is observed (<sup>1</sup>H NMR) as a product from this reaction in the absence of O<sub>2</sub>. Ethane is not observed as a product in this transformation.

Qualitative observations (<sup>1</sup>H NMR spectroscopy) of the rate of formation of **2-BzBr**, **2-MeI**, and **2-SiI**, respectively, were made by monitoring changes in the ratio of **2** to product with time. Equivalent amounts of halocarbon and **2** were mixed in CDCl<sub>3</sub>. The rate constants for reaction **a** of **2** with PhCH<sub>2</sub>Br, MeI, and Me<sub>3</sub>SiCH<sub>2</sub>I were obtained at 31, -24, and 22 °C, respectively, the temperature being selected to give rates compatible with the technique. Rate constants of 0.12 (6), 0.025 (3), and 0.0010 (3) M<sup>-1</sup> s<sup>-1</sup>, respectively, were obtained. The data fit a second-order forward reaction opposed by a first-order back reaction.<sup>34</sup> Although no species other than **2**, the alkyl halide, and the gold(II) alkyl halide adducts were observed, the formation of the **2-I<sub>2</sub>** in heated or irradiated CDCl<sub>3</sub> solutions of **2-MeI** indicates that other reactions also occur (presumably at slower rates) in these solutions.<sup>35</sup>

For the reaction of **2** with MeI in CDCl<sub>3</sub> and Me<sub>3</sub>SiCH<sub>2</sub>I in Me<sub>2</sub>SO the formation constant,  $K = [\text{Au}^{\text{I}}\text{RI}]/[\text{RI}][\text{Au}^{\text{II}}]$ , was observed as a function of temperature, 50 to -55 °C for MeI and 98 to 21 °C for Me<sub>3</sub>SiCH<sub>2</sub>I. A least-squares fit of  $\ln K$  vs.  $1/T$  gave  $\Delta H^\circ = -3.65$  kcal/mol,  $\Delta S^\circ = 1.3$  cal/(mol deg), and  $\Delta G^\circ_{298} = -3.3$  kcal/mol for the reaction of **2** with MeI in CDCl<sub>3</sub>. For the reaction of **2** with Me<sub>3</sub>SiCH<sub>2</sub>I in Me<sub>2</sub>SO,  $\Delta H^\circ = -8.3$  kcal/mol,  $\Delta S^\circ = -18.2$  cal/(mol deg), and  $\Delta G^\circ_{298} = -2.9$

(34) Linear plots of  $\ln(X_e(a^2 - XX_e)/a^2(X_e - X))$  vs.  $t$  where  $a$  = initial concentration of the Au(I) dimer = initial concentration of RX,  $X_e$  = concentration of Au(II) dimer at equilibrium, and  $X$  = concentration of Au(II) dimer at time  $t$ . See: Frost, A.; Pearson, R. G. "Kinetics and Mechanism"; John Wiley and Sons, Inc.: New York, 1962.

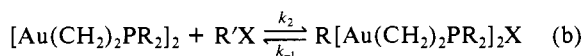
(35) Other integrated forms of rate equations (second-order forward and reverse as well as first-order forward and second-order back reaction) were found to give similarly good fits for the <sup>1</sup>H NMR data; therefore, no single overall reaction order was accurately determined.

**Table IV.** Redox Potentials for the Series [Au(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>]<sub>2</sub>X<sub>2</sub> (where X = Cl, Br, I) [Au(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>]<sub>2</sub>(CH<sub>3</sub>)Br, and [Au(CH<sub>2</sub>)<sub>2</sub>PPh<sub>2</sub>]<sub>2</sub>(CH<sub>3</sub>)I<sup>a</sup>

complex	reduction	oxidation
[Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ] <sub>2</sub>		+0.11, 0.235
[Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ] <sub>2</sub> Cl <sub>2</sub>	-0.92	+1.5
[Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ] <sub>2</sub> Br <sub>2</sub>	-0.69	+1.22
[Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ] <sub>2</sub> I <sub>2</sub>	-0.58	+0.88, <sup>b</sup> 1.115 <sup>b</sup>
[Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ] <sub>2</sub> (CH <sub>3</sub> )Br	-0.75, -1.18	+0.38 <sup>c</sup>
[Au(CH <sub>2</sub> ) <sub>2</sub> PPh <sub>2</sub> ] <sub>2</sub> (CH <sub>3</sub> )I	-0.68, -1.14	+0.42 <sup>c</sup>

<sup>a</sup> Potentials are quoted as Ag/AgCl reference electrode measured as the forward peak current potential in the cyclic voltammetric mode ( $\nu$  = 50 mV/s<sup>-1</sup>). The solvent is THF with 0.1 M [*n*-Bu<sub>4</sub>N][BF<sub>4</sub>] electrolyte. <sup>b</sup> From differential pulse voltammetry where the two processes are more clearly resolved. <sup>c</sup> A second anodic peak sometimes can be observed greater than +0.97 V.

kcal/mol. Note that the data are for different solvents. At the temperature used to measure the rate of reaction **b**, assuming  $(k_2/k_{-1}) = K$ , the following results were obtained. For **2-MeI** (-24 °C),  $K = 3000$  M<sup>-1</sup>,  $k_{-1} = 8 \times 10^{-6}$  s<sup>-1</sup>. For **2-SiI** (22 °C),  $K = 150$  M<sup>-1</sup>,  $k_{-1} = 7 \times 10^{-6}$  s<sup>-1</sup>.



Electrochemical studies show that complex **2** in 0.1 M [*n*-Bu<sub>4</sub>N][BF<sub>4</sub>]-THF undergoes two quasi-reversible, stepwise (presumably one electron) oxidations at 0.11 and 0.235 V vs. Ag/AgCl with  $\Delta E_p$  values of ~250 mV and  $i_p/i_{p1} = 0.6$  at  $\nu = 100$  mV s<sup>-1</sup>. The situation, however, is complicated by the precipitation of a yellow material of unknown composition, in the immediate vicinity of the working electrode (Pt or Au), effectively isolating the working electrode from the bulk solution.

The electrochemistry of the Au(II) halogen adducts were routinely studied in 0.5 M [*n*-Bu<sub>4</sub>N][BF<sub>4</sub>]-CH<sub>2</sub>Cl<sub>2</sub> with either Pt or Au working electrodes. The same results were also obtained with THF as a solvent. With use of cyclic voltammetry, an irreversible reduction is observed, the potential of which is dependent on halogen (Table IV). A chemical reaction following the charge-transfer step yields **2** (together with some unidentified species) which can be clearly detected electrochemically. Coulometry gave an  $n$  value of 2 electrons per mole.

Each gold(II) dimer also exhibits an oxidation step, the potential (Table IV) and character of which depends on halogen. Cyclic voltammetric studies of **2-I<sub>2</sub>** show two oxidation waves, both quasi-reversible in nature with peak potential separations of the order of 150 mV (at  $\nu = 20$  mV s<sup>-1</sup>) and  $i_{p1}/i_{p2} = 0.75$ . Both **2-Br<sub>2</sub>** and **2-Cl<sub>2</sub>** show only one ill-defined irreversible oxidation process. In each case, the free halide ion can be identified. *The presence of the halide ion, however, is dependent on a small quantity of Au(I) dimer being present in the electrochemical solution.* (Apparently the quantity produced by the chemical reaction following the reduction step is sufficient to initiate the reaction.)

The electrochemistry of the Au(II) alkyl halides **2-MeBr** and **2-MeI** is complicated by the equilibrium in solution between the Au(II) alkyl halides and the "parent" gold(I) dimer. This results in a very poorly resolved voltammetry which after 15 min is completely lost. The addition of excess alkyl halide results in the electrochemistry returning to its initial character, with greater resolution. The following observations, therefore, were recorded with excess alkyl halide present.

Each complex shows two irreversible reduction waves with cathodic peak potentials of  $E_{p1} = -0.75$ ,  $-1.18$  and  $E_{p2} = -0.68$  and  $-1.14$  V for **2-MeBr** and **2-MeI**, respectively. An associated oxidation wave is seen at +0.2 V, which can be assigned to the presence of gold(I) dimer formed as a product of a chemical reaction following the reduction step.

Both complexes exhibit two oxidations, the ones at less positive potentials being quasi-reversible in nature, with  $\Delta E_p$  values of 360 and 260 mV for **2-MeBr** and **2-MeI**, respectively.

**Crystal Structure of 2.** In the solid state, **2** exists as discrete dinuclear molecules with no significant intermolecular interaction.

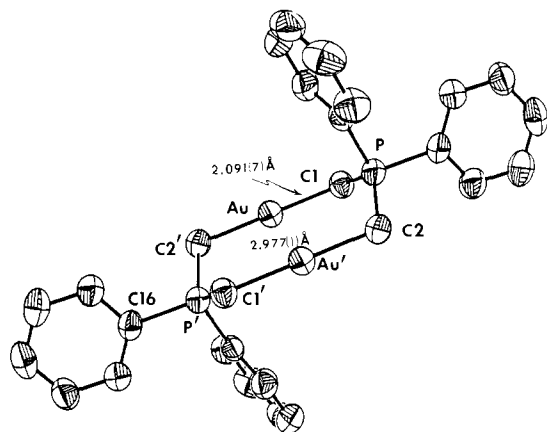


Figure 1. Molecular structure of  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2$ , **2** (hydrogen atoms eliminated for clarity, 50% probability thermal ellipsoids).

(Crystal data and collection parameters for both **2** and **2-MeBr** are given in Table I.) The general structure of **2** is shown in Figure 1.

The eight-membered ring of **2**, is described as having a chair conformation with two phenyl rings in axial and two in equatorial positions. The four methylene carbon atoms and two gold atoms are coplanar. The plane defined by the phosphorus atom and two adjacent ring methylene centers intersects the plane of the gold atoms at  $145.1^\circ$ . The Au...Au distance is 2.977 (1) Å, a non-bonding distance. The gold centers are formally described as Au(I). Some important distances and angles are given in Table III.

**Crystal Structure of 2-MeBr.** In the solid state, **2-MeBr** is found to crystallize with 10% disorder (see solution and refinement of structure). Each gold atom contains square-planar coordination with a twist of  $6.4^\circ$  between the two planes. The complex is in a chair configuration. The Au-Au distance is 2.674 (1) Å, slightly shorter than the Au-Au distance (2.695(4) Å) of the methyl iodide adduct, **2-MeI**, previously reported,<sup>20</sup> and only somewhat longer than the Au-Au bond (2.61 Å) of **2-Br<sub>2</sub>**, the dibromide gold(II) complex.<sup>36</sup> However, the Au-Br distance of 2.698 (3) Å is found to be significantly longer (longer by 0.20 Å) than the Au-Br distance of 2.51 Å found in **2-Br<sub>2</sub>**. This *structural trans effect*, as previously seen in the structure of the methyl iodide adduct, **2-MeI**, is transmitted through the Au-Au bond. Some important bond distances and angles are given in Table III.

### Discussion

The oxidative addition of the alkyl halides to gold(I) complexes **1** and **2** generate gold(II) alkyl halide adducts. The R-Au-Au-X segment of the gold(II) product has  $\sigma$  bonds polarized due to the differences in the electron-donating electron-withdrawing properties of the alkyl and halide substituents. The  $d^9$ - $d^9$ , Au(II)-Au(II), system (16 valence electrons at each Au center) has a nearly filled  $\sigma$  framework.

The chemistry of these gold dimers may be understood by examining the HOMO which is metal-metal bonding and metal-halide antibonding and the LUMO which is totally  $\sigma$  antibonding (Figure 3). The polarization of the HOMO is significantly associated with the electronic properties of the methyl halide, the methyl iodide adduct being the most polarized, the bromide showing less polarization and the chloride only a small polarization.

The HOMO has vastly different orbital coefficients for the various halides. However, in all cases the electron distribution is concentrated on the halide. This is true particularly for the

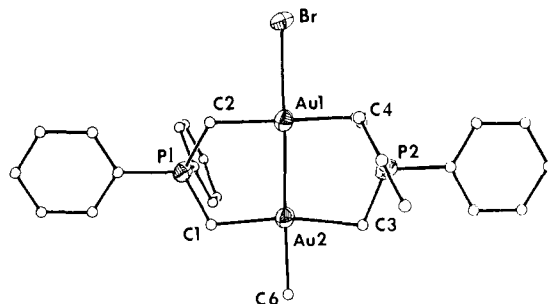


Figure 2. Molecular structure of  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2](\text{CH}_3)\text{Br}$ , **2-MeBr** (hydrogen atoms eliminated for clarity, 50% probability thermal ellipsoids for all non-carbon atoms).

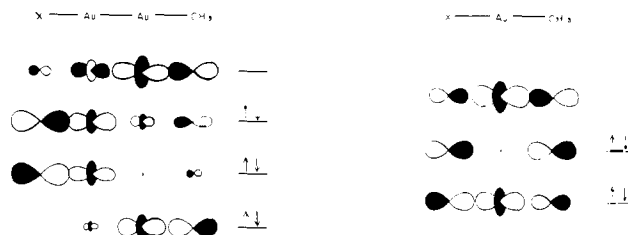


Figure 3. Schematic comparison of the  $\sigma$  framework of the orbitals in the dimeric X-M-M-R and monomeric X-M-R units. For simplicity the monomer represents a system of any three orbitals, not necessarily  $d_{z^2}$  since for gold(I) participation of the  $p_z$  orbital must be considered.

iodide dimer where the coefficient for the halide contribution to the HOMO is 0.77.

Consistent with the bonding model both **1-MeI** and **2-MeI** are light sensitive. Two possible mechanisms result. One is promotion of an electron from the HOMO to the LUMO followed by free radical homolytic cleavage of the Au-Me bond (gold-alkyl, not Au-ylide). The other is a charge-transfer excitation of the electrons of the M-X bond resulting in a heterolytic cleavage (ionization) or weakening of this bond. This latter process appears to be most consistent with both experimental observations and theoretical results since: (1) no radical species have been detected by magnetic resonance measurements, although their transient presence cannot be ruled out; (2) radical inhibitors added to solutions of the complex appear to have little if any effect on the decomposition reaction (this observation has been confirmed by reactions of *N*-thiophenolphthalimide and  $(\text{Me})_2\text{SnBr}_2$  with **2** in the presence and absence of radical inhibitors) (3) the LUMO has similar coefficients for all three halides, Cl, Br, and I (this would predict no differences in reactivity for the homolytic radical decomposition, contrary to observation); and (4) the HOMO-LUMO separation of the gold(II) alkyl halides are of the same order as in the dihalides, yet the latter compounds do not appear to be light sensitive.

The chemistry of the Au-Me and Au-X bonds in these dimers is largely associated with the  $\sigma$  bond framework along the Au-Au axis. The bonding itself is dominating by the interactions with the terminal atoms. The gold atoms magnify the effect. This clearly was observed<sup>20</sup> in the X-ray structure of **1-MeI** where the Au-I bond is elongated by 0.2 Å as compared with the Au-I bond in **1-I<sub>2</sub>** (structural trans effect).

An important observation to be made from this bonding picture is that enhancement of the structural trans effect is expected (and found experimentally) in the dinuclear compounds compared with the mononuclear species. This enhancement arises since the HOMO is antibonding with respect to the metal halide bond in the dinuclear complex (Figure 3). In mononuclear  $d^8$  (16 valence electron) species the orbital which is antibonding with respect to the metal and the halide is unoccupied (LUMO). Here the structural trans effect occurs largely through polarization of the  $\sigma$  bonding orbital. This polarization also exists in the dinuclear species, but the effect is amplified by the metal-halide antibonding character of the HOMO.

(36) Two X-ray structural determinations of **2-Br<sub>2</sub>** have been performed in our laboratory. (One of these is given in the Ph.D. Thesis of D. Dudis, Case Western Reserve University, 1984.) The two structures are slightly different (2% cell volume difference) but both show monoclinic  $C2/c$  symmetry with  $a = 13.3$  Å,  $b = 12.4$  Å,  $c = 17.6$  Å,  $\beta = 103^\circ$ . Refinement at  $R = 0.055$  in each case gives the distances listed to  $\pm 0.01$  Å.

Experimental evidence for this amplified structural trans effect in dinuclear gold(II) species (and similar M–M bonded dinuclear species generally) is rapidly developing.<sup>37</sup> Data exist on one complex which is especially useful. In the compound  $\text{Br}_2\text{AuBr}_2\text{Au}(\text{Me})_2$  studied by Komiya et al.<sup>38</sup> there are Au–Br bonds trans to  $\text{CH}_3$  and Au–Br bonds trans to Au–Br. Comparing Au–Br bridging bonds lengths only, a 6.4% increase in the Au–Br bond is observed. We find, however, that there is a 11.8% increase in the Au–Br bond length (2.698 Å) trans to Me in the dinuclear complex, **2-MeBr**, over the Au–Br bond length (2.518 Å) in the dinuclear gold(II) dibromide, **2-Br**.

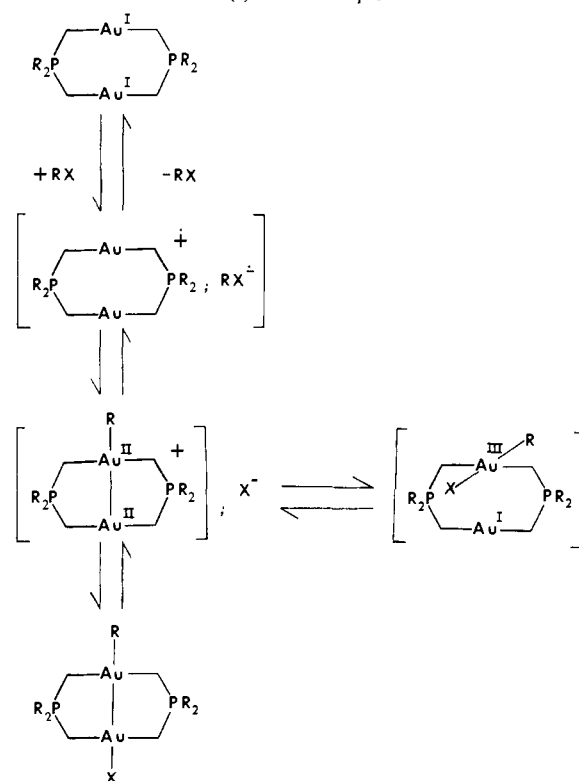
The bonding in the symmetrical dihalide complexes also is governed by the Au–X interactions. The most electronegative halide, chloride, has the ability to push the antibonding LUMO to high energies, making reduction more difficult. Once electrons are placed in the LUMO a bond-breaking process appears likely which makes the electrochemical reduction irreversible. The **2-I** has a lower lying LUMO making reduction easier. Of the halides examined, iodide has an ionization potential closest to that of gold. Combining this with its polarizability, substantial delocalization of the electrons over all four atoms is expected. The reversible oxidation of **2-I** indicates that the iodide is sufficiently different from other halides to alter the electrochemistry of the whole molecule, possibly because of delocalization of charge.

From these theoretical studies we conclude the following: (1) the more electronegative the halide, the further it raises the LUMO making reduction more difficult; (2) the more polarizable the halide, the greater the effect of the methyl group trans to it, consequently the greater the reactivity of the complex for Au–X ionization.

The reactions of MeI,  $\text{PhCH}_2\text{Br}$ , and  $(\text{Me})_3\text{Si}(\text{CH}_2)\text{I}$  with **1** and **2** give Au(II) alkyl halide 2-center 2-electron oxidative addition products. These dinuclear Au(II) alkyl halides are in equilibrium with the Au(I) dinuclear ylide and the alkyl halide. These reactions are the first examples of reversible oxidative addition–reduction elimination reactions involving a dinuclear gold complex. If an excess of the alkyl halide is present, the only gold complex observed (via  $^1\text{H}$  NMR) is the Au(II) alkyl halide adduct.<sup>39</sup> *The reversibility of this reaction is further demonstrated by the solid-state reductive elimination<sup>29</sup> reaction observed by heating 2-MeI or 2-MeBr.*

The complexity and significance of the oxidative addition–reductive elimination equilibria involving the complexes **1** and **2** was realized when we observed halogen exchange between **2-MeBr** and **2-CD<sub>3</sub>I** in  $\text{CHCl}_3$  by  $^2\text{H}$  NMR spectroscopy. Detection of  $\text{CD}_3\text{Br}$  upon mixing indicates that the process involves more than the interaction of **1** or **2** and the alkyl halide, otherwise only  $\text{CD}_3\text{I}$  would have been observed.<sup>27</sup> Furthermore, we have demonstrated that this halogen exchange process is catalytic, not stoichiometric. The importance of the presence of the gold(I) complex **2** in these halogen exchange processes<sup>27</sup> was demonstrated conclusively when  $\text{CH}_3\text{I}$  and **2-Br** were observed to undergo halogen exchange but only in the presence of **2**. From the  $^1\text{H}$  NMR spectra of **2-Br** in the absence and presence of **2**, it is clear that there is significant labilization of the Au–Br bond when **2** is present. This result is not surprising in view of the observation<sup>41</sup> that when combined in solution  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{Br}_4$  and **2** give **2-Br** quantitatively. Our observations regarding the oxidative addition–reductive elimination equilibrium, halogen exchange between the dinuclear gold(II) dihalides and alkyl halides, and the dynamic  $^1\text{H}$  NMR spectra of the dinuclear gold(II) dihalides all appear to be in-

Scheme I. Proposed Reaction Scheme for Addition of Alkyl Halides to Dinuclear Gold(I) Ylide Complexes<sup>a</sup>



<sup>a</sup> Species in brackets are plausible, but to date unidentified components.

fluenced by the gold(I) dimers and their labeling effect on some R–X or Au–X bonds.

Electrochemical studies raise a number of points.

The two-step oxidation of **2** at relatively mild potentials is in accord with the ready ability of the complex to undergo oxidative–addition chemistry.

The  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{X}_2$  complexes show a trend in reduction potential which follows the same ordering as determined by theoretical calculations ( $\text{Cl} > \text{Br} > \text{I}$ ). The irreversible nature of the reduction step is not surprising as the LUMO is entirely antibonding with respect to both Au–X and Au–Au bonds. Thus the overall two-electron reduction leads to an unfavorable bonding situation relieved by a further chemical reaction. The formation of the gold(I) dimer **2** as one of the products seems reasonable. The appreciable chemical reversibility of the oxidation of **2-I** may be associated with the somewhat different chemical behavior of this complex compared with the Cl and Br species.

The identification of free halide ion in the voltammetry, but only in the presence of Au(I) dimer, is of considerable importance. This further confirms the labilizing effect of the Au(I) dimers **1** and **2** on Au–X bonds, as is suggested by the  $^1\text{H}$  NMR exchange experiments.

The kinetic rate data of the oxidative addition of  $\text{PhCH}_2\text{Br}$ , MeI, and  $(\text{Me})_3\text{SiCH}_2\text{I}$  with **2** has revealed a trend which parallels the stability of the analogous alkyl radical. The first step in the process parallels the ease of electron transfer from the gold dimer. This suggests the initial formation of caged radical species (not detectable) followed by the rapid alkylation of a gold center as depicted in the reaction scheme. Ionic exchange of coordinated halide has been observed previously.<sup>27</sup> Further work is in progress related to the mechanism(s) involved in the oxidative addition steps ultimately taking both gold centers to Au(III).

This work has demonstrated relationships between the dinuclear gold(I) ylide complex, the dihalogold(II) complex, and the alkyl halide adducts  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2(\text{Me})\text{X}$  ( $\text{X} = \text{I}; \text{Br}$ ). Interconversion and interaction must be taken into account if the system is to be understood. The halogen exchange observed between

(37) Additional structures such as for the "A-frame"  $(\mu\text{-CH}_2)[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2\text{Br}_2$  and the tetrabromide,<sup>40</sup> **2-Br<sub>4</sub>**, and the  $[\text{Au}(\text{CH}_2)_2\text{PPh}_2]_2(\text{CH}_2\text{CN})\text{Br}$  corroborate these observations. A 10.3% increase is observed<sup>41</sup> in the Au–Br distance of the latter compound.

(38) Komiya, S.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1977**, *1253*. Here the Au–Br lengths are 2.402 Å (terminal), 2.450 Å (bridging), and 2.450 Å (bridging trans to  $\text{CH}_3$ ).

(39) This appears to be the reason that this significant observation was not reported by Schmidbauer and Franke<sup>10</sup> in their original manuscripts.

(40) Dudis, D.; Fackler, J. P., Jr. *Inorg. Chem.*, in press.

(41) Murray, H. H.; Fackler, J. P., Jr. *Organometallics*, in press.

**2-MeBr** and **2-MeI** is consistent with the observation of the exceptionally long Au-Br bond of **2-MeBr**. Halogen exchange may also involve a mixed valence Au(I)/Au(III) complex<sup>42</sup> or oligomeric pairs of complexes. Further studies specifically addressing these possibilities are being pursued.

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(42) Fackler, J. P., Jr.; Trzcinska-Bancroft, B. *Organometallics* 1985, 4, 1633-1637.

Chemical Society, and The Welch Foundation.

**Registry No.** 1, 50449-81-5; 1-MeI, 55927-69-0; 1-Br<sub>2</sub>, 55873-02-4; 1-I<sub>2</sub>, 55744-31-5; 1-SiI, 98678-29-6; 1-BzBr, 98678-30-9; 2, 81457-56-9; 2-MeI, 81457-57-0; 2-MeBr, 89462-48-6; 2-I<sub>2</sub>, 81457-58-1; 2-SiI, 98678-28-5; 2-BzBr, 98687-67-3; 2-Br<sub>2</sub>, 89462-50-0; 2-CD<sub>3</sub>I, 89462-49-7; 2-Cl<sub>2</sub>, 97571-09-0; MeI, 74-88-4; MeBr, 74-83-9; Me<sub>3</sub>SiCH<sub>2</sub>I, 4206-67-1; PhCH<sub>2</sub>Br, 100-39-0; Br<sub>2</sub>, 7726-95-6; I<sub>2</sub>, 7553-56-2; CCl<sub>4</sub>, 56-23-5; CD<sub>3</sub>Br, 1111-88-2; CD<sub>3</sub>I, 865-50-9; MeCl, 74-87-3; CD<sub>3</sub>Cl, 1111-89-3.

**Supplementary Material Available:** Tables of thermal parameters, calculated hydrogen atom coordinates, bond lengths and bond angles, and structure factors (62 pages). Ordering information is given on any current masthead page.

## Metal-Spine Conductivity in a Partially Oxidized Metallomacrocycle: (Phthalocyaninato)cobalt Iodide

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**Abstract:** Oxidation by iodine of (phthalocyaninato)cobalt(II), Co(pc), affords the title compound, Co(pc)I, which is comprised of metal-over-metal columnar stacks of partially (<sup>1</sup>/<sub>3</sub>) oxidized Co(pc) groups that are surrounded by chains of I<sub>3</sub><sup>-</sup> ions. Co(pc)I crystallizes in space group *D*<sub>2h</sub><sup>2</sup>-*P4/mcc* of the tetragonal system with *a* = 13.927 (1) Å, *c* = 6.247 (1) Å, *V* = 1212 Å<sup>3</sup>, and *Z* = 2. The value of *R* on *F*<sub>o</sub><sup>2</sup> for 66 variables and 540 observations is 0.055. Results of physical measurements, in particular the sign of the thermoelectric power, show the metal centers to be the site of oxidation. Charge transport thus proceeds along one-dimensional chains of metal atoms, as in the linear-chain platinum compounds. Strong interactions among the partially oxidized metal centers of the cobalt spine force the Co(pc) subunits to adopt an anomalously small interplanar spacing (3.12 Å). They lead to an approximately temperature-independent susceptibility that is associated with strong Coulomb correlations in a one-dimensional cobalt d<sub>z<sup>2</sup></sub> band. The room-temperature conductivity of Co(pc)I is  $\sigma \sim 50 \Omega^{-1} \text{cm}^{-1}$ , which is comparable with that of the best Pt-spine conductors despite the fact that cobalt is a first transition series element at a much greater Co-Co spacing (3.12 Å) than that (~2.95 Å) for the conductors based on the third transition series element, Pt. Although the reflectivity shows a sharp edge at  $6 \times 10^3 \text{cm}^{-1}$ , it provides evidence for a small band gap. The temperature response of the conductivity of Co(pc)I is nonmetallic ( $d\sigma/dT > 0$ ), whereas that of the isostructural Ni(pc)I is metallic. These differences can be understood by considering the effects of potentials from the I<sub>3</sub><sup>-</sup> chains on conduction bands with different occupancies, <sup>1</sup>/<sub>3</sub> filling for Co(pc)I but <sup>5</sup>/<sub>6</sub> filling for Ni(pc)I.

We discuss the structural, optical, charge transport, and magnetic properties of the molecular conductor (phthalocyaninato)cobalt iodide, Co(pc)I. This material, prepared by partial oxidation of Co(pc) with iodine,<sup>1,2</sup> is isostructural with the low-temperature molecular metal Ni(pc)I,<sup>2,3</sup> both compounds being comprised of metal-over-metal columnar stacks of partially (<sup>1</sup>/<sub>3</sub>) oxidized M(pc) units that are surrounded by chains of I<sub>3</sub><sup>-</sup> ions. However, the change of incorporated metal introduces qualitative modifications in the electronic structure of the M-(L)-based molecular conductors *without* associated changes in the crystal structure. The Ni(L) compounds incorporate a d<sup>8</sup> Ni<sup>2+</sup> ion. Oxidation of Ni(pc) occurs at the ring, and the charge carriers of Ni(pc)I are associated with the highest-occupied delocalized  $\pi$  molecular orbital of pc.<sup>3b</sup> For Ni(tbp)I<sup>4</sup> the charge carriers are predominantly associated with the ring, but the compound exhibits a "doubly mixed valence" state, in which the hole-carriers also can hop from ring to metal. In contrast, Co(pc) incorporates a d<sup>7</sup> Co<sup>2+</sup> ion, and we now report that physical measurements, in particular the sign of the thermoelectric power, indicate that iodination proceeds by <sup>1</sup>/<sub>3</sub> oxidation of the metal from "Co<sup>2+</sup>" to

"Co<sup>2.33+</sup>". Thus charge transport in Co(pc)I proceeds along a one-dimensional chain of metal centers, as in the Krogmann salts.<sup>5</sup>

Co(pc)I represents the first metal-spine conductor prepared from a metallomacrocycle, and to our knowledge it is the only one in which the metal ion in the parent complex is not Pt<sup>2+</sup>, a

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