

Articles

Dinuclear Gold(II) Complexes Containing Two Different Bridging Ligands. Crystal Structure of $[\text{Au}_2\{\mu\text{-(CH}_2\text{)}_2\text{PPh}_2\}\{\mu\text{-S}_2\text{CN(CH}_2\text{Ph)}_2\}\text{Br}_2]$

Manuel Bardají,[†] M. Concepción Gimeno,[†] Peter G. Jones,[‡]
Antonio Laguna,^{*,†} and Mariano Laguna[†]

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain, and Institut für Anorganische und Analytische Chemie, Technische Universität Braunschweig, Postfach 3329, D-38023 Braunschweig, Germany

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The oxidative addition of halogens to $[\text{Au}_2\{\mu\text{-(CH}_2\text{)}_2\text{PPh}_2\}\{\mu\text{-(PPh}_2\text{)}_2\text{Y}\}]\text{ClO}_4$ ($\text{Y} = \text{CH}_2$ or NH) or $[\text{Au}_2\{\mu\text{-(CH}_2\text{)}_2\text{PPh}_2\}\{\mu\text{-S}_2\text{CNR}_2\}]\text{ClO}_4$ ($\text{R} = \text{Me, Et}$ or CH_2Ph) leads to the gold(II) derivatives $[\text{Au}_2\{\mu\text{-(CH}_2\text{)}_2\text{PPh}_2\}\{\mu\text{-(PPh}_2\text{)}_2\text{Y}\}\text{X}_2]\text{ClO}_4$ or $[\text{Au}_2\{\mu\text{-(CH}_2\text{)}_2\text{PPh}_2\}\{\mu\text{-S}_2\text{CNR}_2\}\text{X}_2]$ ($\text{X} = \text{Cl, Br}$, or I), respectively. The reaction of $[\text{Au}_2\{\mu\text{-(CH}_2\text{)}_2\text{PPh}_2\}\{\mu\text{-S}_2\text{CNR}_2\}\text{X}_2]$ with $\text{Ag}(\text{OCIO}_3)(\text{PPh}_3)$ or $\text{Ag}(\text{C}_6\text{F}_5)$ gives the mixed-valence gold(I)–gold(III) complexes $[\text{Au}_2\{\mu\text{-(CH}_2\text{)}_2\text{PPh}_2\}\{\mu\text{-S}_2\text{CNR}_2\}(\text{PPh}_3)_2](\text{ClO}_4)_2$ ($\text{R} = \text{Me, CH}_2\text{Ph}$) or $[\text{Au}_2\{\mu\text{-(CH}_2\text{)}_2\text{PPh}_2\}\{\mu\text{-S}_2\text{CNMe}_2\}(\text{C}_6\text{F}_5)_2]$, respectively. The structure of $[\text{Au}_2\{\mu\text{-(CH}_2\text{)}_2\text{PPh}_2\}\{\mu\text{-S}_2\text{CN(CH}_2\text{Ph)}_2\}\text{Br}_2]$ has been determined by a single-crystal X-ray diffraction study. It crystallizes in the space group $P\bar{1}$ with $a = 11.937(3)$ Å, $b = 12.105(2)$ Å, $c = 12.568(2)$ Å, $\alpha = 80.04(2)^\circ$, $\beta = 81.77(2)^\circ$, $\gamma = 71.58(2)^\circ$, and $Z = 2$. The two gold atoms are part of an eight-membered ring with a twisted conformation; both exhibit a square-planar geometry with a short gold–gold bond of 2.5653(10) Å.

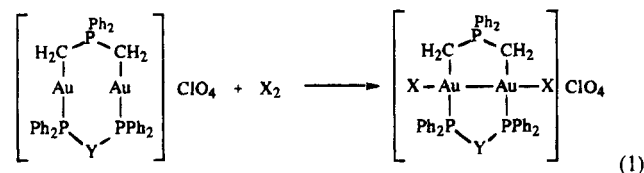
Introduction

In recent years, syntheses of dinuclear gold(II) complexes have been investigated extensively. Most of these dinuclear derivatives contain two identical bridging ligands, one on each side of the metal–metal bond,^{1–9} and to the best of our knowledge, no hetero-bridged complexes have been reported so far.

In the present paper we describe the preparation of several hetero-bridged dinuclear gold(II) complexes containing neutral (diphosphine) or anionic [dithiocarbamate or bis(ylide)] bridging ligands, by oxidative addition of halogens to the corresponding hetero-bridged gold(I) compounds. The molecular structure of $[\text{Au}_2\{\mu\text{-(CH}_2\text{)}_2\text{PPh}_2\}\{\mu\text{-S}_2\text{CN(CH}_2\text{Ph)}_2\}\text{Br}_2]$ has been established by X-ray studies.

Results and Discussion

The reaction of the cationic complexes $[\text{Au}\{\mu\text{-(CH}_2\text{)}_2\text{PPh}_2\}\{\mu\text{-(PPh}_2\text{)}_2\text{Y}\}]\text{ClO}_4$ [$\text{Y} = \text{CH}_2$ (dppm) or NH (dppa)], previously described by us,¹⁰ with a slight excess of halogen gives the corresponding gold(II) derivatives, according to eq 1. The oxidation of the dppm derivative



$\text{Y} = \text{CH}_2$, $\text{X} = \text{Cl}$ (1), Br (2), I (3); $\text{Y} = \text{NH}$, $\text{X} = \text{Cl}$ (4), Br (5), I (6)

with the stoichiometric amount of halogen leads to a mixture of the starting gold(I) and the gold(II) complex; it requires an excess of the halogen to be complete.

Complexes 1–6 are air- and moisture-stable solids at room temperature, but they decompose slowly in solution, and are yellow (1, 4), orange (2, 5), or garnet (3, 6). They behave as 1:1 electrolytes in acetone solution (Λ_M ca. $120 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ for $5 \times 10^{-4} \text{M}$ solutions), and their IR spectra show bands at 1100 (s, br) and 620 (m) cm^{-1} which are characteristic of the ClO_4^- anion; bands at ca. 580 (m) and 278 (m) cm^{-1} are due to $\nu(\text{Au-C}_{\text{ylide}})$ ¹¹ and $\nu(\text{Au-Cl})$,¹² respectively. The FAB⁺ mass spectra show the peaks corresponding to the

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[‡] Technische Universität Braunschweig.

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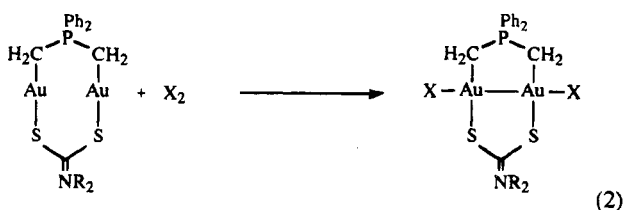
Table 1. Analytical and NMR Data for the Complexes

complex	yield (%)	analyses (%) ^a			³¹ P{ ¹ H} NMR ^b		¹ H NMR ^c δ(CH ₂ -Au)
		C	H	N	δ _{ylide}	δ _{phos}	
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }(μ-dppm)Cl ₂](ClO ₄) (1)	65	40.05(40.3)	2.85(3.1)		40.9 (br)	19.6 (br)	2.75 (br)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }(μ-dppm)Br ₂](ClO ₄) (2)	71	37.8(37.45)	3.0(2.9)		44.7 (t)(18.4)	15.4 (d)	2.85 (br)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }(μ-dppm)I ₂](ClO ₄) (3)	75	34.4(34.85)	2.55(2.7)		53.8 (br)	9.3 (br)	3.07 (br)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }(μ-dppa)Cl ₂](ClO ₄) (4)	68	39.4(39.25)	3.6(3.05)	1.15(1.2)	41.3 (t)(18.7)	62.7 (d)	2.61 (m)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }(μ-dppa)Br ₂](ClO ₄) (5)	67	36.4(36.45)	2.7(2.8)	1.15(1.1)	45.0 (t)(18.1)	59.1 (d)	2.70 (m)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }(μ-dppa)I ₂](ClO ₄) (6)	62	33.6(33.9)	2.6(2.6)	1.05(1.05)	54.0 (t)(18.4)	52.9 (d)	2.88 (m)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }(μ-S ₂ CNMe ₂)Cl ₂] (7)	76	25.7(25.55)	2.4(2.5)	1.4(1.75)	42.0 (s)		2.66 (d)(8.8)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }(μ-S ₂ CNMe ₂)Br ₂] (8)	64	22.8(23.0)	2.35(2.25)	1.65(1.6)	45.2 (s)		2.75 (d)(8.8)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }(μ-S ₂ CNMe ₂)I ₂] (9)	83	20.35(20.8)	2.2(2.05)	1.2(1.45)	52.2 (s)		2.82 (d)(9.1)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }(μ-S ₂ CNEt ₂)Cl ₂] (10)	67	27.4(27.6)	2.75(2.95)	1.45(1.7)	41.8 (s)		2.60 (s)(8.8)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }(μ-S ₂ CNEt ₂)Br ₂] (11)	63	24.95(24.95)	2.6(2.65)	1.5(1.55)	44.9 (s)		2.67 (d)(8.8)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }(μ-S ₂ CNEt ₂)I ₂] (12)	67	22.8(22.6)	2.25(2.4)	1.2(1.4)	51.9 (s)		2.73 (d)(8.8)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }{μ-S ₂ CN(CH ₂ Ph) ₂ }Cl ₂] (13)	77	36.4(36.65)	3.15(2.95)	1.0(1.45)	42.0 (s)		2.62 (d)(8.5)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }{μ-S ₂ CN(CH ₂ Ph) ₂ }Br ₂] (14)	77	33.45(33.5)	2.6(2.7)	1.1(1.35)	45.5 (s)		2.67 (d)(8.8)
[Au ₂ {μ-(CH ₂) ₂ PPh ₂ }{μ-S ₂ CN(CH ₂ Ph) ₂ }I ₂] (15)	66	30.45(30.75)	2.3(2.5)	1.1(1.25)	52.5 (s)		2.79 (d)(8.8)
[Au ₂ {(CH ₂) ₂ PPh ₂ }(S ₂ CNMe ₂)(PPh ₃) ₂](ClO ₄) ₂ (16)	68	44.2(43.9)	3.45(3.45)	1.0(0.95)	<i>d</i>	<i>d</i>	2.79 (dd) (9.7, 7.2), 1.83 (dd) (13.3, 9.7)
[Au ₂ {(CH ₂) ₂ PPh ₂ }{S ₂ CN(CH ₂ Ph) ₂ }(PPh ₃) ₂](ClO ₄) ₂ (17)	73	48.65(48.7)	3.7(3.65)	0.75(0.85)	<i>d</i>	<i>d</i>	2.87 (dd) (10.4, 6.2), 1.87 (dd) (12.7, 8.3)
[Au ₂ {(CH ₂) ₂ PPh ₂ }(S ₂ CNMe ₂)(C ₆ F ₅) ₂] (18)	64	33.0(32.8)	1.95(1.9)	1.05(1.3)	35.3		2.87 (d) (10.9), 1.57 (d) (13.0)

^a Calculated values in parentheses. ^b Recorded in CDCl₃, referenced to external H₃PO₄. ^c Recorded in CDCl₃ at 300 MHz, referenced to external SiMe₄. Coupling constants in hertz are given in parentheses; s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, br = broad. ^d See text.

cations [M - ClO₄]⁺ at *m/z* = 1061 (13%, 1), 1151 (0.5%, 2), 1062 (9%, 4), 1152 (14%, 5), and 1246 (30%, 6), except for complex 3. The strongest peaks at *m/z* = 991 (1–3) and 992 (4–6) correspond to [M - 2X - ClO₄]⁺. The NMR spectra are as expected (Table 1 and Experimental Section). The ³¹P{¹H} spectra show a triplet at *ca.* δ 41 (4), 45 (2, 5), or 54 (5) for the ylide phosphorus and a doublet for the two phosphorus atoms of the diphosphine. The spectra of complexes 1 and 3 are not well resolved. The ¹H NMR spectra show the resonance of the ylide methylene protons as multiplets (Table 1).

Complexes 2 and 5 react with Ag(OClO₃)(PPh₃) (molar ratio 1:2) in dichloromethane with precipitation of AgBr, but from the solution only the gold(I) derivative [Au{μ-(CH₂)₂PPh₂}{μ-(PPh₂)₂Y}] (Y = CH₂ or NH) can be isolated. The reaction of the nine-membered ring complex [Au{μ-(CH₂)₂PPh₂}(μ-dppe)] (dppe = PPh₂CH₂-CH₂PPh₂) with chlorine or iodine gives a mixture of products, but no formation of the corresponding gold(II) complex was observed. The oxidative addition of halogen to the hetero-bridged neutral gold(I) complexes [Au{μ-(CH₂)₂PPh₂}(μ-S₂CNR₂)]¹⁰ leads to the corresponding gold(II) derivatives (eq 2).



R = Me, X = Cl (7), Br (8), I (9); R = Et, X = Cl (10), Br (11), I (12); R = CH₂Ph, X = Cl (13), Br (14), I (15)

Complexes 7–15 are orange (X = Cl or Br) or garnet (X = I) solids, air- and moisture-stable at room temperature, both in the solid state and in solution. Their acetone solutions are nonconducting. The IR spectra

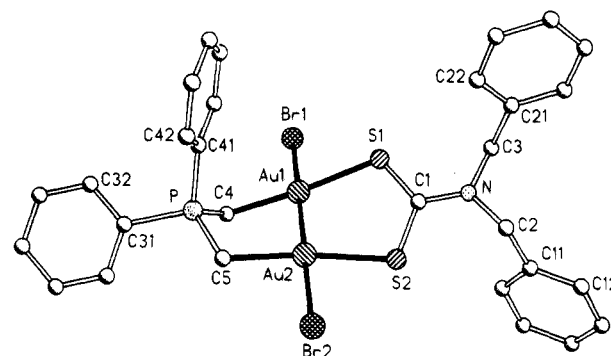


Figure 1. Molecular structure of complex 14, with the atom-numbering scheme. Radii are arbitrary.

show bands at 258 (m) (7), 267 (m) (10), or 272 (m) (13) cm⁻¹ that are assignable to ν(Au-Cl) and at *ca.* 570 (m) cm⁻¹ due to ν(Au-C_{ylide}). The FAB⁺ mass spectra show the molecular cation peak (M), except for complexes 8, 12, or 15, at *m/z* = 798 (3%, 7), 981 (7%, 9), 826 (10%, 10), 915 (5%, 11), 950 (3%, 13), and 1039 (12%, 14). Other peaks at *m/z* = 762 (39%, 7), 808 (45%, 8), 854 (55%, 9), 790 (55%, 10), 836 (35%, 11), 882 (65%, 12), 914 (36%, 13), 960 (55%, 14), and 1006 (45%, 15) are due to [M - X]⁺ and at *m/z* = 727 (17%, 7; 25%, 8; 20% 9), 755 (15%, 10; 20%, 11; 22% 12), and 879 (20%, 13; 25%, 14; 12%, 15) are due to [M - 2X]⁺.

The ³¹P{¹H} NMR spectra show a singlet at *ca.* δ 42 (7, 10, 13), 45 (8, 11, 14), or 52 (9, 12, 15) for the phosphorus atom (Table 1), and the ¹H NMR spectra show a doublet at *ca.* δ 2.7 for the ylide methylene protons. The cyclic voltammograms of complexes 7–9 (in CH₂Cl₂, scan rate 200 mV s⁻¹) show irreversible oxidation waves with peak potentials at 0.72 (9) and 1.36 (8), and we do not observe any peak down to 1.5 V for 7. They also show irreversible reduction peaks at -0.35 (9), -0.37 (8), and -0.44 (7) V.

The crystal structure of complex 14 (as a 1:1 dichloromethane solvate) has been determined by X-ray crystallography (Figure 1). It possesses the general features of dinuclear gold(II) complexes: an eight-membered ring, which here has a twisted conformation

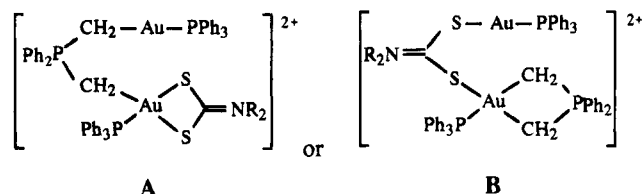
(the angle between the vectors C(4)—S(1) and C(5)—S(2) is 24°), and a transannular metal—metal bond. The Au(1)—Au(2) distance is 2.5653(10) Å, which is shorter than the 2.614(1) Å in the symmetrical [Au₂{μ-(CH₂)₂-PPh₂}Br₂]⁶ or the 2.570(5) Å in (Bu₄N)₂[Au₂{μ-MNT}₂Br₂]⁷ (MNT = 1,1-dicyanoethylene-2,2-dithiolate). Ylide gold(II) complexes usually present gold—gold bonds that follow the trend Cl < Br < I ([Au₂{μ-(CH₂)₂PR₂}X₂]: R = Ph, X = Cl, 2.600(1),¹³ X = Br, 2.614(1) Å⁶; R = Me, X = I, 2.654(1)¹⁴ Å). The Au—Au distance in our complex is one of the shortest known; cf. the complex (Bu₄N)₂[Au₂{μ-MNT}₂Cl₂]⁷ with 2.550(1) and [Au₂{μ-SPPPh₂CH₂}₂Cl₂]¹⁵ with 2.553(1) Å, in both cases involving sulfur donor centers at gold (as in complex 14). As far as we are aware, no crystal structures have previously been reported for dinuclear dithiocarbamate gold(II) complexes. The two Au—Br distances differ significantly, Au(1)—Br(1) 2.5022(14) and Au(2)—Br(2) 2.5253(14) Å, whereas intermediate values are found in [Au₂{μ-(CH₂)₂PPh₂}Br₂] [2.516(1) Å]⁶ and (Bu₄N)₂[Au₂{μ-MNT}₂Br₂] [2.510(8) Å];⁷ Au^{III}—Br bond lengths are usually ca. 2.41 Å.¹⁶ There are no obvious reasons for the asymmetry; the shortest relevant intermolecular contact is Au(2)—Br(2; 1 - x, 1 - y, -z) 4.10 Å. The Au—S bond lengths 2.337(3) and 2.338(3) Å are slightly longer than in the gold(I) dimer [Au₂{μ-(CH₂)₂-PPh₂}₂(μ-S₂CNET₂)] [2.293(6)—2.326(6) Å, two independent molecules]¹⁰ and the gold(II) complexes (Bu₄N)₂[Au₂{μ-MNT}₂Br₂] [2.294(13) and 2.303(13) Å]. The Au—C lengths 2.075(10) and 2.076(10) Å are similar to those in other ylide gold(II) complexes.

The two gold atoms exhibit essentially square-planar geometry, with minor distortions. The five atoms Au(2) and its immediate neighbors are coplanar to within 0.008 Å (mean deviation), whereas at Au(1), S(1) lies 0.17 Å out of the best plane of the other four atoms (mean deviation 0.007 Å). The C—Au—S angles are 174.8(3) and 172.8(3)°; cf. values from 174.7(5) to 178.3(6)° in the related gold(I) derivative [Au₂{μ-(CH₂)₂-PPh₂}₂(μ-S₂CNET₂)], where there are short gold—gold contacts (rather than formal bonds) of 2.8679(15) and 2.8665(15) Å. The chain Br—Au—Au—Br is almost linear (angles 178.6, 178.7°).

The gold(II) complexes 9 and 14 react with Ag-(OCIO₃)(PPh₃)¹⁷ in a manner different from that of complexes 2 and 5. The precipitation of AgI and AgBr, respectively, is also observed, but from the solution complexes of the stoichiometry [Au{(CH₂)₂PPh₂}(S₂CNR₂)(PPh₃)₂] (R = Me (16) or CH₂Ph (17)) are obtained. Complexes 16 and 17 are air- and moisture-stable light yellow solids. They behave as 1:2 electrolytes in acetone solution (Λ_M ca. 215 Ω⁻¹ cm² mol⁻¹). The IR spectra show bands at 1100 (s, br) and 620 (m) cm⁻¹ which are characteristic of the ClO₄⁻ anion, but it is not possible to assign the vibration ν(Au—C_{ylide}), probably because it is masked by bands due to the PPh₃ and dithiocarbamate ligands. The highest peak of the FAB⁺

mass spectrum for 16 appears at *m/z* = 1350 (2%) and corresponds to the cation [M - ClO₄]⁺.

The NMR spectra of these complexes are different from those expected for gold(II) derivatives, and an isomerization to the corresponding mixed-valence gold(I)—gold(III) complexes, similar to that reported by Fackler,¹⁸ has occurred. The decision however, is not straightforward as to which isomer (A or B) has been



formed. The ³¹P{¹H} NMR spectra show two doublets [δ 42.51 and 35.99, *J*(PP) = 8.7 Hz (16), and 42.53 and 35.92, *J*(PP) = 8.8 Hz (17)] and a singlet [δ 29.91 (16) and 29.83 (17)]. The two doublets are very similar to that found for other Au^I—CH₂—PPh₂—CH₂—Au^I—PPh₃ systems¹⁹ and can be assigned to the ylide phosphorus and the PPh₃ bonded to gold(I) (isomer A), respectively. The resonance at higher field (singlet) should correspond to the PPh₃ bonded to gold(III), which favors structure A (for B it should be a doublet).

The ¹H NMR spectra show the presence of two different ylide CH₂ groups, which appear as a doublet of doublets (Table 1). Also two resonances are observed for the methyl (16) or methylene (17) groups of the dithiocarbamate ligands (see Experimental Section), which should be compatible with both structures A and B.

The reaction of complex 9 with Ag(C₆F₅)₂²⁰ leads to the precipitation of AgI, and the mixed-valence gold(I)—gold(III) complex (18) is obtained from the solution as a yellow solid. It is air- and moisture-stable at room temperature and nonconducting in acetone solutions.

The IR spectra show two bands at 838 (m) and 801 (m) cm⁻¹, implying the presence of two different C₆F₅ groups.²¹ This is also confirmed by the ¹⁹F NMR spectrum (see Experimental Section). The ¹H NMR spectrum shows two doublets corresponding to two different ylide CH₂ groups (Table 1) and two singlets for the CH₃ groups (see Experimental Section). Only a singlet is observed in the ³¹P NMR spectrum (Table 1). These data confirm the formation of a mixed-valence complex (as for 16 and 17), instead of the gold(II) derivative.

The chemical shifts for the ylide groups in 16–18 suggest that the three complexes have the same structure and point to isomer A, with a CH₂ bonded to gold(III) (2.79–2.89 ppm) and the other to gold(I) (1.83 ppm when trans to the phosphine and 1.57 ppm when trans to the aryl ligand).

Experimental Section

IR spectra were recorded on a Perkin-Elmer 559 or 883 spectrophotometer, over the range 4000–200 cm⁻¹, by using

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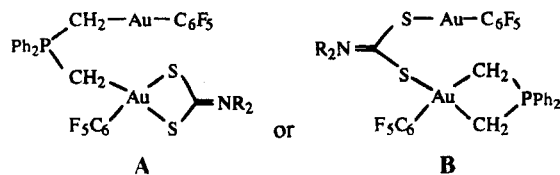
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Nujol mulls between polyethylene sheets. ^1H , ^{19}F , and ^{31}P NMR spectra were recorded on a Varian UNITY 300 in CDCl_3 solutions; chemical shifts are quoted relative to SiMe_4 (external, ^1H), CFCl_3 (external, ^{19}F), and H_3PO_4 (external, ^{31}P). C, H, and N analyses were performed with a Perkin-Elmer 2400 microanalyzer. Conductivities were measured in acetone solution with a Philips PW 9509 apparatus. Melting points were measured on a Büchi apparatus and are uncorrected. Mass spectra were recorded on a VG Autospec using FAB⁺ techniques.

Electrochemical studies were carried out using an EG and G Model 273 potentiostat, in conjunction with a three-electrode cell. The auxiliary electrode was a platinum wire, and the working electrode was a platinum bead. The reference was an aqueous saturated calomel electrode (SCE) separated from the test solution by a fine-porosity frit and an agar bridge saturated with KCl. CH_2Cl_2 solutions were 5×10^{-4} M in complex and 0.1 M in $[\text{NBu}_4][\text{PF}_6]$ as the supporting electrolyte. All potentials are standardized against the $[\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]^+ - [\text{Fe}(\eta\text{-C}_5\text{H}_5)_2]$ and $[\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2]^+ - [\text{Fe}(\eta\text{-C}_5\text{Me}_5)_2]$ couples as internal standards ($E^\circ = +0.47$ and -0.09 V, respectively).

The yields, C, H and N analyses, and $^{31}\text{P}\{^1\text{H}\}$ and some ^1H NMR data are listed in Table 1.

Syntheses. $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}\{\mu\text{-dppm}\}_2]\text{X}_2$ [$\text{X} = \text{Cl}$ (1), Br (2), I (3)]. To a solution of $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}\{\mu\text{-dppm}\}_2]\text{ClO}_4^{10}$ (0.082 g, 0.075 mmol) in dichloromethane (20 mL) at 0°C was added a slight excess of halogen (0.09 mmol; Cl_2 , Br_2 in CCl_4 solution; I_2 0.024 g). The mixture was stirred for 90 min and then was concentrated to ca. 5 mL. Addition of diethyl ether (20 mL) afforded complexes 1–3. **1:** mp 160°C dec; ^1H NMR δ 7.95–7.26 (m, 30H, Ph), 4.78 (br, 2H, PCH_2P), 2.75 (br, 4H, $\text{CH}_2\text{-Au}$). **2:** mp 150°C dec; ^1H NMR δ 7.93–7.24 (m, 30H, Ph), 4.96 [t, 2H, $J(\text{PH}) = 12.6$ Hz, PCH_2P], 2.85 (br, 4H, $\text{CH}_2\text{-Au}$). **3:** mp 104°C dec; ^1H NMR δ 7.84–7.26 (m, 30H), 5.26 [t, 2H, $J(\text{PH}) = 10.6$ Hz, PCH_2P], 3.07 (br, 4H, $\text{CH}_2\text{-Au}$).

$[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}\{\mu\text{-dppa}\}_2]\text{X}_2$ [$\text{X} = \text{Cl}$ (4), Br (5), I (6)]. To a solution of $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}\{\mu\text{-dppa}\}_2]\text{ClO}_4^{10}$ (0.082 g, 0.075 mmol) in dichloromethane (20 mL) at 0°C was added a slight excess of halogen (0.08 mmol; Cl_2 , Br_2 in CCl_4 solution; I_2 0.021 g). The mixture was stirred for 60 min and then was concentrated to ca. 5 mL. Addition of diethyl ether (20 mL) led to complexes 4–6. **4:** mp 130°C dec; ^1H NMR δ 8.84 (s, 1H, H–N), 7.80–7.41 (m, 30H, Ph), 2.61 (m, 4H, $\text{CH}_2\text{-Au}$). **5:** mp 147°C ; ^1H NMR δ 8.92 (s, 1H, H–N), 7.83–7.41 (m, 30H, Ph), 2.70 (m, 4H, $\text{CH}_2\text{-Au}$). **6:** mp 135°C ; ^1H NMR δ 9.22 (s, 1H, H–N), 7.80–7.40 (m, 30H, Ph), 2.88 (m, 4H, $\text{CH}_2\text{-Au}$).

$[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}\{\mu\text{-S}_2\text{CNR}_2\}_2]\text{X}_2$ [$\text{R} = \text{Me}$, $\text{X} = \text{Cl}$ (7), Br (8), I (9); $\text{R} = \text{Et}$, $\text{X} = \text{Cl}$ (10), Br (11), I (12); $\text{R} = \text{CH}_2\text{-Ph}$, $\text{X} = \text{Cl}$ (13), Br (14), I (15)]. To a solution of $[\text{Au}_2\{\mu\text{-(CH}_2)_2\text{PPh}_2\}\{\mu\text{-S}_2\text{CNR}_2\}_2]^{10}$ (0.1 mmol; $\text{R} = \text{Me}$, 0.073 g; Et , 0.075 g; or CH_2Ph , 0.088 g) in dichloromethane (20 mL) was added the stoichiometric amount of halogen (0.1 mmol; Cl_2 , Br_2 , in CCl_4 solution; I_2 , 0.025g). After stirring for about 15 min at room temperature, the solution was concentrated to ca. 5 mL. Addition of diethyl ether (20 mL) led to complexes 7–15. **7:** mp 140°C dec; ^1H NMR δ 7.76–7.56 (m, 10H, Ph), 3.45 (s, 6H, Me), 2.66 [d, 4H, $J(\text{PH}) = 8.8$ Hz, $\text{CH}_2\text{-P}$]. **8:** mp 163°C ; ^1H NMR δ 7.80–7.52 (m, 10H, Ph), 3.44 (s, 6H, Me), 2.75 [d, 4H, $J(\text{PH}) = 8.8$ Hz, $\text{CH}_2\text{-P}$]. **9:** mp 109°C ; ^1H NMR δ 7.90–7.40 (m, 10H, Ph), 3.41 (s, 6H, Me), 2.82 [d, 4H, $J(\text{PH}) = 9.1$ Hz, $\text{CH}_2\text{-P}$]. **10:** mp 102°C dec; ^1H NMR δ 7.80–7.43 (m, 10H, Ph), 3.84 [q, 4H, $J(\text{HH}) = 7.0$ Hz, $\text{CH}_2\text{-N}$], 2.60 [d,

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex 14

Au(1)–C(4)	2.075(10)	Au(1)–S(1)	2.337(3)
Au(1)–Br(1)	2.5022(14)	Au(1)–Au(2)	2.5653(10)
Au(2)–C(5)	2.076(10)	Au(2)–S(2)	2.338(3)
Au(2)–Br(2)	2.5253(14)	S(1)–C(1)	1.729(11)
S(2)–C(1)	1.717(11)	P–C(5)	1.777(10)
P–C(4)	1.785(11)	P–C(41)	1.816(9)
P–C(31)	1.817(11)	C(1)–N	1.335(13)
C(2)–N	1.455(12)	C(2)–C(11)	1.534(14)
C(3)–N	1.477(13)	C(3)–C(21)	1.513(13)
C(4)–Au(1)–S(1)	174.8(3)	C(4)–Au(1)–Br(1)	88.9(3)
S(1)–Au(1)–Br(1)	87.17(8)	C(4)–Au(1)–Au(2)	90.0(3)
S(1)–Au(1)–Au(2)	93.97(7)	Br(1)–Au(1)–Au(2)	178.55(3)
C(5)–Au(2)–S(2)	172.8(3)	C(5)–Au(2)–Br(2)	86.5(3)
S(2)–Au(2)–Br(2)	86.30(8)	C(5)–Au(2)–Au(1)	94.2(3)
S(2)–Au(2)–Au(1)	92.98(7)	Br(2)–Au(2)–Au(1)	178.74(3)
C(1)–S(1)–Au(1)	110.1(4)	C(1)–S(2)–Au(2)	110.3(4)
C(5)–P–C(4)	105.0(5)	C(5)–P–C(41)	108.8(4)
C(4)–P–C(41)	111.4(4)	C(5)–P–C(31)	112.2(4)
C(4)–P–C(31)	111.0(5)	C(41)–P–C(31)	108.4(4)
N–C(1)–S(2)	118.3(8)	N–C(1)–S(1)	118.5(8)
S(2)–C(1)–S(1)	123.1(6)	N–C(2)–C(11)	114.3(8)
N–C(3)–C(21)	111.5(9)	P–C(4)–Au(1)	105.5(5)
P–C(5)–Au(2)	111.8(5)	C(1)–N–C(2)	121.8(9)
C(1)–N–C(3)	123.0(9)	C(2)–N–C(3)	115.1(8)

Table 3. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{Å}^2 \times 10^3$) for Complex 14

	x	y	z	U(eq)
Au(1)	2186.8(4)	5536.4(3)	2580.0(3)	20.7(3)
Au(2)	4172.1(4)	5778.0(3)	1657.2(3)	21.0(3)
Br(1)	248.6(10)	5272.2(10)	3443.0(8)	30.6(6)
Br(2)	6104.1(10)	6039.8(10)	712.1(8)	30.2(6)
S(1)	1507(3)	7428(2)	3074(2)	31(2)
S(2)	3400(3)	7822(2)	1296(2)	33(2)
P	4177(3)	3180(3)	2717(2)	26(2)
C(1)	2231(10)	8330(9)	2234(8)	30(4)
C(2)	2446(10)	10290(9)	1658(8)	30(4)
C(3)	817(9)	10024(10)	3037(8)	31(4)
C(4)	2724(10)	3804(9)	2278(8)	28(2)
C(5)	5054(10)	3988(9)	1868(8)	28(3)
N	1853(8)	9480(8)	2304(7)	29(4)
C(11)	1885(10)	10916(8)	608(8)	33(5)
C(12)	1999(10)	12002(9)	198(7)	35(6)
C(13)	1574(11)	12582(9)	–785(8)	42(6)
C(14)	1059(11)	12055(9)	–1361(9)	40(6)
C(15)	959(10)	10962(9)	–980(7)	37(6)
C(16)	1364(10)	10399(9)	12(7)	36(5)
C(21)	1187(9)	10392(7)	3990(8)	36(5)
C(22)	1943(10)	9573(9)	4693(8)	40(6)
C(23)	2277(10)	9910(10)	5575(8)	43(7)
C(24)	1859(10)	11057(8)	5745(8)	42(7)
C(25)	1132(11)	11887(10)	5068(8)	43(7)
C(26)	800(10)	11562(9)	4178(8)	37(6)
C(31)	4735(9)	1619(9)	2605(6)	29(5)
C(32)	4548(10)	797(8)	3482(8)	37(7)
C(33)	4956(11)	–376(8)	3366(8)	45(8)
C(34)	5534(10)	–729(10)	2407(6)	37(7)
C(35)	5696(11)	68(8)	1538(8)	39(7)
C(36)	5309(11)	1248(8)	1622(8)	39(7)
C(41)	4193(7)	3368(9)	4117(7)	33(3)
C(42)	5271(9)	3267(9)	4471(7)	31(3)
C(43)	5293(9)	3445(10)	5535(7)	34(4)
C(44)	4259(7)	3697(10)	6217(8)	35(4)
C(45)	3191(10)	3801(11)	5850(7)	41(4)
C(46)	3150(9)	3625(9)	4789(7)	33(3)
Cl(1)	9250(5)	3877(4)	1646(4)	93(4)
Cl(2)	8120(4)	2089(4)	1566(4)	85(3)
C(6)	8664(15)	3193(15)	828(12)	83(12)

4H, $J(\text{PH}) = 8.8$ Hz, $\text{CH}_2\text{-P}$], 1.33 [t, 6H, CH_3]. **11:** mp 160°C dec; ^1H NMR δ 7.79–7.45 (m, 10H, Ph), 3.83 [q, 4H, $J(\text{HH}) = 7.2$ Hz, $\text{CH}_2\text{-N}$], 2.67 [d, 4H, $J(\text{PH}) = 8.8$ Hz, $\text{CH}_2\text{-P}$], 1.27 [t, 6H, CH_3]. **12:** mp 90°C ; ^1H NMR δ 7.82–7.34 (m, 10H, Ph), 3.81 [q, 4H, $J(\text{HH}) = 7.1$ Hz, $\text{CH}_2\text{-N}$], 2.73 [d, 4H, $J(\text{PH}) = 9.1$ Hz, $\text{CH}_2\text{-P}$], 1.25 (t, 6H, CH_3). **13:** mp 130°C ; ^1H NMR

δ 7.77–7.19 (m, 20H, Ph), 5.04 (s, 4H, CH₂-N), 2.62 [d, 4H, $J(\text{PH}) = 8.5$ Hz, CH₂-P]. **14**: mp 132 °C dec; ¹H NMR δ 7.71–7.17 (m, 20H, Ph), 5.00 (s, 4H, CH₂-N), 2.67 [d, 4H, $J(\text{PH}) = 8.8$ Hz, CH₂-P]. **15**: mp 120 °C dec; ¹H NMR δ 7.90–7.10 (m, 20H, Ph), 5.01 (s, 4H, CH₂-N), 2.79 [d, 4H, $J(\text{PH}) = 8.8$ Hz, CH₂-P].

[Au₂{(CH₂)₂PPh₂}(S₂CNR₂)(PPh₃)₂](ClO₄)₂ [R = Me (**16**), CH₂Ph (**17**)]. To a solution of complex **9** (0.049 g, 0.05 mmol) or **14** (0.052 g, 0.05 mmol) in dichloromethane (30 mL) was added Ag(OClO₃)(PPh₃)¹⁷ (0.047 g, 0.1 mmol). After 1 h of stirring at room temperature in the dark, AgX was removed and the solution evaporated to ca. 5 mL. Addition of diethyl ether (20 mL) led to precipitation of complexes **16** or **17**. **16**: mp 148 °C; ¹H NMR δ 7.64–7.18 (m, 40H, Ph), 3.15 (s, 3H, Me-N), 3.10 (s, 3H, Me-N), 2.79 [dd, 2H, $J(\text{PH}) = 9.7$ and 7.2 Hz, CH₂-Au], 1.83 [dd, 2H, $J(\text{PH}) = 13.3$ and 9.7 Hz, CH₂-Au]. **17**: 128 °C dec; ¹H NMR δ 7.78–6.83 (m, 50H, Ph), 4.52 (s, 2H, CH₂-N), 4.33 (s, 2H, CH₂-N), 2.87 [dd, 2H, $J(\text{PH}) = 10.4$ and 6.2 Hz, CH₂-Au], 1.87 [dd, 2H, $J(\text{PH}) = 12.7$ and 8.3 Hz, CH₂-Au].

[Au₂{(CH₂)₂PPh₂}(S₂CNMe₂)(C₆F₅)₂] (**18**). To a freshly prepared solution of AgC₆F₅²⁰ (0.22 mmol) in anhydrous diethyl ether (40 mL) was added an anhydrous dichloromethane solution (20 mL) of complex **9** (0.098 g, 0.1 mmol). After stirring the mixture for 35 min at room temperature in the dark, AgI was removed and the solution evaporated to ca. 5 mL. Addition of hexane (20 mL) led to precipitation of complex **18**. **18**: mp 92 °C dec; ¹H NMR δ 7.70–7.36 (m, 10H, Ph), 3.26 (s, 3H, Me), 3.17 (s, 3H, Me), 2.87 [d, 2H, $J(\text{PH}) = 10.9$ Hz, CH₂-P], 1.57 [d, 2H, $J(\text{PH}) = 13.0$ Hz, CH₂-Au]; ¹⁹F NMR –116.80 (“d”, 2 F_o), –120.25 (“d”, 2 F_o), –157.47 (m, 1 F_p), –161.48 (m, 2 F_m), –162.54 (m, 1 F_p), –164.08 (m, 2 F_m).

X-ray Structure Determination of Compound 14. Crystal data: 14·CH₂Cl₂, C₃₀H₃₀Au₂Br₂Cl₂NPS₂, $M_r = 1124.29$, triclinic, space group $P\bar{1}$, $a = 11.937(3)$ Å, $b = 12.105(2)$ Å, $c = 12.568(2)$ Å, $\alpha = 80.04(2)^\circ$, $\beta = 81.77(2)^\circ$, $\gamma = 71.58(2)^\circ$, $V = 1689.4(6)$ Å³, $Z = 2$, $D_c = 2.210$ Mg m⁻³, $F(000) = 1052$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 11.4$ mm⁻¹, $T = -100$ °C.

Data Collection and Reduction. Single crystals of compound **14** in the form of yellow plates were obtained by

slow diffusion of diethyl ether into a dichloromethane solution. A crystal of size 0.30 × 0.20 × 0.04 mm was mounted in inert oil (Type RS 3000, donated by Riedel-de-Haën), transferred to the cold gas stream of a Siemens R3 diffractometer, and used to collect 6866 intensities to $2\theta_{\text{max}} 50^\circ$ (monochromated Mo K α radiation). An absorption correction based on ψ -scans was applied, with transmission factors 0.33–1.0. Merging equivalents gave 5960 independent reflections ($R_{\text{int}} 0.031$). Cell constants were refined from setting angles of 50 reflections in the range $2\theta 20$ – 23° . **Structure Solution and Refinement.** The structure was solved by the heavy-atom method and subjected to anisotropic full-matrix least-squares refinement on F^2 (program system SHELXL-93).²² Hydrogen atoms were included using a riding model. The weighting scheme was $w^{-1} = [\sigma^2(F^2) + (aP)^2 + bP]$, where $3P = F_o^2 + 2F_c^2$. Refinement proceeded to $wR(F^2) 0.115$ for 5958 reflections, conventional $R(F) 0.037$ for 361 parameters and 287 restraints ($S = 1.02$; maximum $\Delta\rho 1.8$ e Å⁻³).

Selected bond and angles are collected in Table 2; atomic coordinates in Table 3.

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Supplementary Material Available: Description of the crystal structure determinations, including tables of crystal data, data collection, and solution and refinement parameters, atomic coordinates, bond distances and angles, and thermal parameters (5 pages). Ordering information is given on any current masthead page.

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