

Gold and Silver Complexes with the Ferrocenyl Phosphine $\text{FcCH}_2\text{PPh}_2$ [Fc = $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$]

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Received May 17, 1999

Linear gold(I) and silver(I) complexes with the ferrocenyl phosphine $\text{FcCH}_2\text{PPh}_2$ [Fc = $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4)$] of the types $[\text{AuR}(\text{PPh}_2\text{CH}_2\text{Fc})]$, $[\text{M}(\text{PPh}_3)(\text{PPh}_2\text{CH}_2\text{Fc})]\text{OTf}$, and $[\text{M}(\text{PPh}_2\text{CH}_2\text{Fc})_2]\text{OTf}$ (M = Au, Ag) have been obtained. Three-coordinate gold(I) and silver(I) derivatives of the types $[\text{AuCl}(\text{PPh}_2\text{CH}_2\text{Fc})_2]$ and $[\text{M}(\text{PPh}_2\text{CH}_2\text{Fc})_3]\text{X}$ (M = Au, X = ClO_4 ; M = Ag, X = OTf) have been obtained from the corresponding gold and silver precursors in the appropriate molar ratio, although some of them are involved in equilibria in solution. The crystal structures of $[\text{AuR}(\text{PPh}_2\text{CH}_2\text{Fc})]$ (R = Cl, C_6F_5), $[\text{AuL}(\text{PPh}_2\text{CH}_2\text{Fc})]\text{OTf}$ (L = PPh_3 , $\text{FcCH}_2\text{PPh}_2$), $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2\text{Fc})]$, and $[\text{Ag}(\text{PPh}_2\text{CH}_2\text{Fc})_3]\text{OTf}$ have been determined by X-ray diffraction studies.

Introduction

Phosphine ligands containing ferrocene moieties currently attract a great deal of interest, as is shown by the large number of transition metal complexes described for the chelating ligand 1,1'-bis(diphenylphosphino)ferrocene (dppf).¹ Much attention has also been paid to chiral ferrocenyl phosphines in asymmetric catalysis.^{2,3} In all of these ligands the phosphine moiety is linked directly by a P–C bond to the cyclopentadienyl ring of the ferrocene. However, examples of ferrocenyl phosphines containing a carbon spacer between the cyclopentadienyl ring and the phosphorus atom are rare. Although the synthesis of the first (ferrocenylmethyl)phosphine was reported as early as 1963,^{4,5} only recently has the 1,1'-bis(diphenylphosphinomethyl)-ferrocene been synthesized⁶ or the reactivity of $\text{FcCH}_2\text{P}(\text{CH}_2\text{OH})_2$ (leading to various ferrocene-derived phosphines or metal complexes) studied.^{7–10}

As part of our studies in ferrocene derivatives as ligands in gold chemistry,¹¹ we report here the synthesis of several gold

and silver complexes with the (ferrocenylmethyl)phosphine $\text{FcCH}_2\text{PPh}_2$, whose coordination chemistry has not yet been studied. Two- and three-coordinate gold and silver complexes have been prepared. Cyclic voltammetry shows one-electron reversible oxidation based on the ferrocene moiety.

Results and Discussion

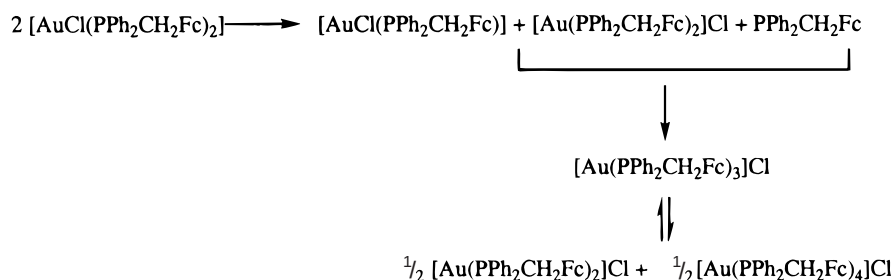
Synthesis. The reaction of $\text{FcCH}_2\text{PPh}_2$ with 1 equiv of $[\text{AuX}(\text{tht})]$ (tht = tetrahydrothiophene) in dichloromethane gives orange solids of the neutral complexes $[\text{AuR}(\text{PPh}_2\text{CH}_2\text{Fc})]$ (R = Cl, **1**; C_6F_5 , **2**) (see Scheme 1). These are air- and moisture-stable and are nonconducting in acetone solutions. Their IR spectra show the vibration $\nu(\text{Au}–\text{Cl})$ at $336 (\text{m}) \text{ cm}^{-1}$ (**1**) and the bands arising at the pentafluorophenyl group bonded to gold-(I) at $1505 (\text{vs})$, $954 (\text{s})$, and $790 (\text{m}) \text{ cm}^{-1}$ (**2**).

The ^1H NMR spectra show two multiplets for the α and β protons of the substituted cyclopentadienyl group, a singlet for the protons of the unsubstituted Cp, and a doublet for the protons of the methylene group, which are coupled with the phosphorus atom. The ^{19}F NMR spectrum of **2** presents three resonances for the three different fluorines of the pentafluorophenyl group.

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Scheme 2



The LSIMS mass spectrum shows the molecular peak at $m/z = 1082$ (100%) and other fragmentation peaks at $m/z = 748$ ($[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_2\text{CH}_2\text{Fc})]^+$), 581 ($[\text{Au}(\text{PPh}_2\text{CH}_2\text{Fc})]^+$), and 384 ($\text{PPh}_2\text{CH}_2\text{Fc}^+$).

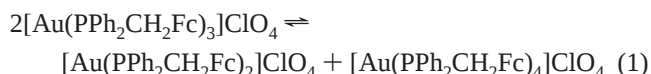
The three-coordinate gold complex $[\text{AuCl}(\text{PPh}_2\text{CH}_2\text{Fc})_2]$ (**8**) has been obtained by reaction of $[\text{AuCl}(\text{tht})]$ and 2 equiv of $\text{PPh}_2\text{CH}_2\text{Fc}$.

The ^1H NMR spectrum of complex **8** at room temperature in dichloromethane shows three multiplets in a 2:2:5 ratio for the ferrocene protons and a doublet for the methylene protons. In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum, a broad singlet at 33.8 appears because of the equivalence of the phosphorus atoms. The variable-temperature ^1H NMR spectra show broadening of the signals in the range -20 to -40 °C, and below -60 °C five signals appear in the ferrocene region. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum also shows broadening of the signal; at -20 °C two broad signals appear, from -40 to -60 °C two singlets are present at 32.4 and 42.3 ppm, and at -80 °C two more small resonances appear at 38.5 and 28.2 ppm. The two main resonances possess chemical shifts close to those in the complexes $[\text{Au}(\text{PPh}_2\text{CH}_2\text{Fc})_2]\text{ClO}_4$ and $[\text{AuCl}(\text{PPh}_2\text{CH}_2\text{Fc})]$. According to these data we propose that there is an equilibrium between three- and two-coordinate species such that at room temperature the three-coordinate complex is present and at low temperature a reorganization process takes place (Scheme 2). If this process takes place, the presence of free phosphine should be observed, but we do not see this in the NMR time scale; therefore, we propose that the free phosphine would react immediately with the $[\text{AuP}_2]^+$ complex to give the three-coordinate species. The latter, as we propose below, is in equilibrium with the linear and four-coordinate species. This explain the four resonances present that are only seen at -80 °C. To corroborate this we have also carried out variable-temperature studies of a sample prepared "in situ" from 1 equiv of $[\text{AuCl}(\text{tht})]$ and 2 equiv of the phosphine. The spectra at different temperatures are similar, but now below -60 °C the four signals can be observed and those at 28.2 (AuP_4^+) and 38.3 (AuP_3^+) ppm with more intensity.

The LSIMS mass spectrum shows the molecular peak at $m/z = 1001$, although with very low intensity (3%). The most intense peak appears at $m/z = 965$ and corresponds to the loss of the chlorine ligand.

We have also carried out the reactions of 3 equiv of the phosphine $\text{PPh}_2\text{CH}_2\text{Fc}$ with $[\text{Au}(\text{tht})_2]\text{ClO}_4$ or AgOTf , leading to the three-coordinate compounds $[\text{Au}(\text{PPh}_2\text{CH}_2\text{Fc})_3]\text{ClO}_4$ (**9**) and $[\text{Ag}(\text{PPh}_2\text{CH}_2\text{Fc})_3]\text{OTf}$ (**10**). The ^1H NMR spectra of both complexes show multiplets for the methylene, substituted and unsubstituted Cp, and phenyl protons, whereas the $^{31}\text{P}\{^1\text{H}\}$ spectra show broad signals at chemical shifts different from those observed for complexes **5** or **6**. In the LSIMS mass spectra the molecular peak appears only for complex **10** at $m/z = 1349$ (2%).

Low-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectral studies have been carried out for both complexes. For complex **9** the initial resonance at 41.7 splits into three with different intensities at 43.8, 38.3, and 28.2 ppm. We also propose an equilibrium between the different species, $[\text{Au}(\text{PPh}_2\text{CH}_2\text{Fc})_2]^+$, $[\text{Au}(\text{PPh}_2\text{CH}_2\text{Fc})_3]^+$, and $[\text{Au}(\text{PPh}_2\text{CH}_2\text{Fc})_4]^+$, respectively, in a manner similar to that reported for other tertiary phosphines (eq 1).¹² Complex **10** shows two doublets in the ^{31}P spectrum because of the coupling of the equivalent phosphorus with both silver nuclei.



Crystal Structure Determinations. Crystal Structures of $[\text{AuR}(\text{PPh}_2\text{CH}_2\text{Fc})]$ ($\text{R} = \text{Cl}$ (1**), C_6F_5 (**2**)).** The crystal structures of the neutral complexes $[\text{AuR}(\text{PPh}_2\text{CH}_2\text{Fc})]$ ($\text{R} = \text{Cl}$ (**1**), C_6F_5 (**2**)) have been determined by X-ray diffraction studies. Figures 1a and 2 show their molecular structures, and a selection of bond lengths and angles are presented in Tables 1 and 2. In these complexes the gold atoms exhibit a very regular linear geometry, with $\text{P}-\text{Au}-\text{Cl}$ and $\text{P}-\text{Au}-\text{C}$ angles of $176.01(7)^\circ$ and $174.3(2)^\circ$, respectively. For complex **1** the $\text{Au}-\text{Cl}$ distance, 2.3014(18) Å, is similar to those found in complexes with ferrocenyl phosphines such as $[\text{Au}_2\text{Cl}_2(\mu\text{-dppf})]$ ($\text{dppf} = 1,1'$ -bis(diphenylphosphino)ferrocene) (two independent determinations: 2.2815(13), 2.273–2.300 Å)^{13,14} or $[\text{AuCl}(\text{PFc}_6\text{Ph})]$ (2.289(2) Å).¹⁵ The shortest gold–gold distance in the lattice is 5.388 Å, which excludes the possibility of any bonding interaction between gold atoms. However, there are unusually short $\text{H}\cdots\text{Au}$ contacts: $\text{H}11\cdots\text{Au}$ ($1-x, -y, 1-z$) 2.73, $\text{H}33\cdots\text{Au}$ ($x, 0.5-y, -0.5+z$) 2.76 Å, and also three weak intermolecular $\text{C}-\text{H}\cdots\text{Cl}$ contacts ($\text{H}\cdots\text{Cl}$ 2.88–2.91 Å) of acceptable linearity that may correspond to weak hydrogen bonds. The secondary contacts are shown in Figure 1b.

The $\text{Au}-\text{C}(11)$ distance in **2**, 2.070(5) Å, compares well with those obtained for other gold(I) complexes, such as $[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)]$ (2.07(2) Å)¹⁶ or the ferrocene derivative $[\text{Au}_2(\mu\text{-dppf})(\text{C}_{16}\text{H}_9)_2]$ (2.061(8) Å).¹⁷ Again the complex does not display aurophilic interactions (the shortest gold–gold distance is 5.560 Å); but in the lattice there are contacts $\text{F}2\cdots\text{F}2$ of 2.858 Å and $\text{F}\cdots\text{H}34$ of 2.55 and 2.60 Å.

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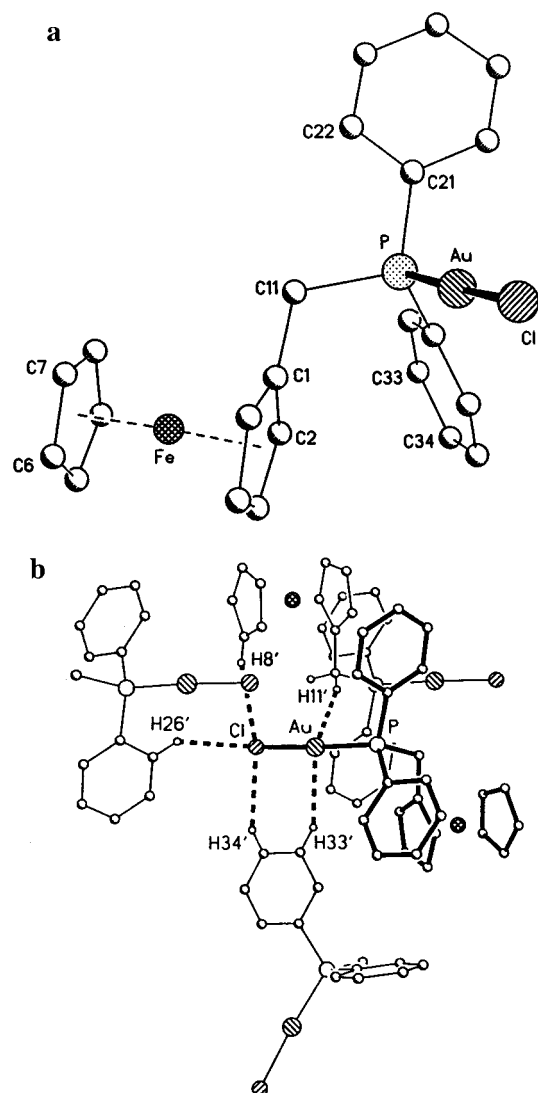


Figure 1. (a) Structure of complex **1** in the crystal with the atom-numbering scheme. The H atoms are omitted for clarity. (b) Environment of the molecule of **1**. The parent molecule is drawn with thick bonds, and secondary contacts (see text) are drawn as broken bonds. Only H atoms involved in secondary contacts are shown. Ferrocene moieties of peripheral molecules are omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complex **1**

Au–P	2.2366(18)	P–C(21)	1.821(7)
Au–Cl	2.3014(18)	P–C(11)	1.843(6)
P–C(31)	1.807(7)	C(1)–C(11)	1.508(9)
P–Au–Cl	176.01(7)	C(9)–C(10)–Fe	70.4(4)
C(31)–P–C(21)	108.5(3)	C(1)–C(11)–P	111.9(4)
C(31)–P–C(11)	100.4(3)	C(26)–C(21)–P	118.2(5)
C(21)–P–C(11)	106.6(3)	C(22)–C(21)–P	122.8(5)
C(31)–P–Au	116.2(2)	C(36)–C(31)–P	119.7(5)
C(21)–P–Au	110.3(2)	C(32)–C(31)–P	118.6(5)
C(11)–P–Au	114.2(2)		

The Au–P distances are 2.2366(18) Å in **1** and 2.284(2) Å in **2**; the difference may be attributable to the higher trans influence of the pentafluorophenyl group compared with the chloro ligand. They are of the same order as found in other similar complexes such as $[\text{AuCl}(\text{PFc}_2\text{Ph})]$ (2.234(2) Å)¹⁵ for **1** and $[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_3)]$ (2.265(2) Å)¹⁶ or $[\text{Au}_2(\mu\text{-dppf})(\text{C}_{16}\text{H}_9)_2]$ (2.295(2) Å)¹⁷ for **2**.

Crystal Structures of $[\text{AuL}(\text{PPh}_2\text{CH}_2\text{Fc})]\text{OTf}$ ($\text{L} = \text{PPh}_3$ (3**), $\text{FcCH}_2\text{PPh}_2$ (**5**)).** Figures 3 and 4 show the crystal structures

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

Au–C(11)	2.070(5)	Au–P	2.284(2)
P–C(21)	1.818(6)	P–C(31)	1.819(5)
P–C(1)	1.828(5)	C(1)–C(41)	1.498(7)
C(11)–Au–P	174.3(2)	C(21)–P–C(31)	105.3(2)
C(21)–P–C(1)	107.3(3)	C(31)–P–C(1)	104.0(2)
C(21)–P–Au	112.1(2)	C(31)–P–Au	116.8(2)
C(1)–P–Au	110.6(2)	C(41)–C(1)–P	111.4(3)

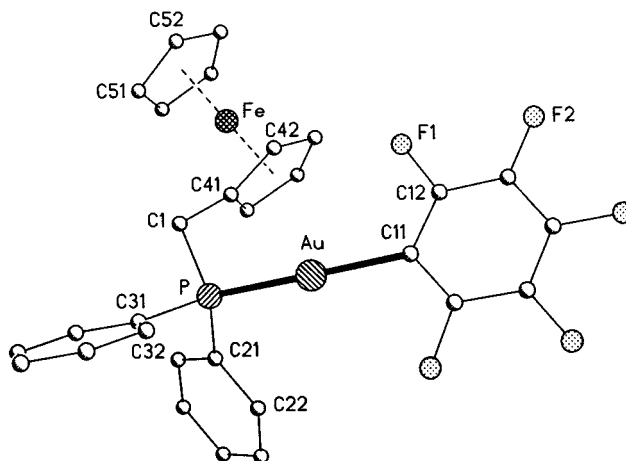


Figure 2. Molecular structure of complex **2** in the crystal. H atoms are omitted for clarity.

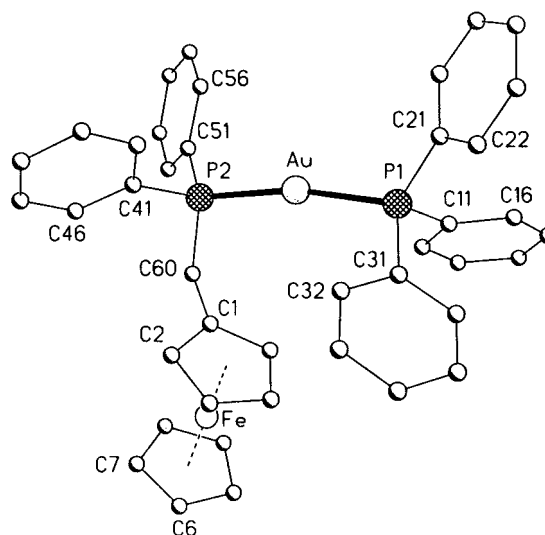


Figure 3. Structure of the cation of complex **3** in the crystal. H atoms are omitted for clarity.

of the cations of **3** and **5**, and Tables 3 and 4 show a selection of bond lengths and angles. The gold atom in complex **3** exhibits a distorted linear geometry with an angle P–Au–P of 168.74(4)°, whereas in **5**, with imposed symmetry, the gold center displays an ideal linear geometry. Deviation from ideal linearity, sometimes by more than 10°, seems to be common for these bis(phosphine) complexes; some examples are $[\text{Au}(\text{PFc}_2\text{Ph})_2]\text{X}$ (X = ClO_4 or PF_6) (169.41(6)°)^{18,19} and $[\text{Au}\{\text{Fc}(\text{CH}_2\text{P}(\text{CH}_2\text{OH})_2)\}]\text{Cl}$ (176.51(6)°).¹⁰ The Au–P distances are 2.3210(13) and 2.3259(13) Å in **3**, with different phosphine ligands, and 2.309(2) Å in **5**. The latter value is similar to those found in

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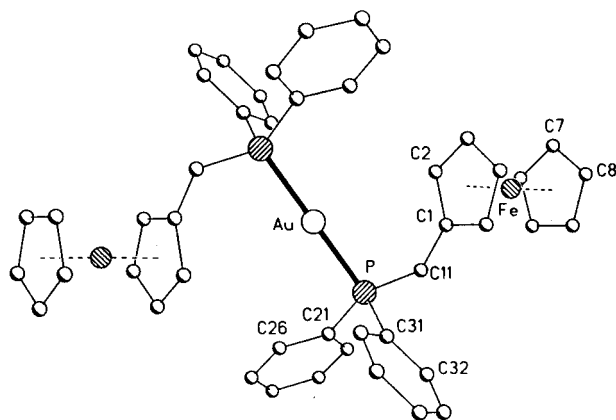


Figure 4. Perspective view of the cation of complex **5** in the crystal. H atoms are omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **3**

Au–P(2)	2.3210(13)	Au–P(1)	2.3259(13)
P(1)–C(21)	1.823(4)	P(1)–C(11)	1.824(4)
P(1)–C(31)	1.829(4)	P(2)–C(51)	1.827(4)
P(2)–C(41)	1.831(4)	P(2)–C(60)	1.842(4)
C(1)–C(60)	1.511(6)		
P(2)–Au–P(1)	168.74(4)	C(21)–P(1)–C(11)	104.5(2)
C(21)–P(1)–C(31)	106.2(2)	C(11)–P(1)–C(31)	106.3(2)
C(21)–P(1)–Au	119.66(14)	C(11)–P(1)–Au	110.64(14)
C(31)–P(1)–Au	108.75(14)	C(51)–P(2)–C(41)	106.0(2)
C(51)–P(2)–C(60)	105.4(2)	C(41)–P(2)–C(60)	107.1(2)
C(51)–P(2)–Au	116.42(14)	C(41)–P(2)–Au	113.2(2)
C(60)–P(2)–Au	108.2(2)	C(12)–C(11)–P(1)	118.9(3)
C(16)–C(11)–P(1)	121.3(3)	C(22)–C(21)–P(1)	121.3(3)
C(26)–C(21)–P(1)	119.7(3)	C(36)–C(31)–P(1)	121.7(3)
C(32)–C(31)–P(1)	118.4(3)	C(42)–C(41)–P(2)	120.5(3)
C(46)–C(41)–P(2)	120.7(3)	C(52)–C(51)–P(2)	122.1(3)
C(56)–C(51)–P(2)	118.6(3)	C(1)–C(60)–P(2)	111.3(3)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for Complex **5**

Au–P#1 ^a	2.309(2)	P–C(11)	1.825(8)
P–C(21)	1.819(8)	C(1)–C(11)	1.484(10)
P–C(31)	1.820(8)		
P#1–Au–P	180.00(5)	C(21)–P–Au	111.6(2)
C(21)–P–C(31)	105.6(3)	C(31)–P–Au	111.3(2)
C(21)–P–C(11)	107.9(3)	C(11)–P–Au	111.7(3)
C(31)–P–C(11)	108.5(3)		

^a Symmetry transformations used to generate equivalent atoms: (#1) $-x, -y + 1, -z$.

the complex $[\text{Au}(\text{PF}_2\text{Ph})_2]\text{ClO}_4$ (2.293(2) and 2.301(2) Å), whereas the former are more similar to those in alkyl or aryl phosphine complexes such as $[\text{Au}(\text{PR}_3)_2]^+$ ($\text{PR}_3 = \text{PPh}_2\text{Me}$, 2.316(4) Å; PCy_3 , 2.321(2) Å).^{20,21}

Crystal Structure of $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2\text{Fc})]$ (7**).** The molecular structure of complex **7** is shown in Figure 5, with selected bond lengths and angles in Table 5. The gold center exhibits the expected square planar coordination, lying 0.015-(1) Å out of the ligand plane. The Au–C distances are in the range 2.067(3)–2.080(4) Å and are similar to those found in other tris(pentafluorophenyl)gold(III) derivatives.²² The Au–P distance (2.3503(9) Å) compares well with the longest found in phosphinogold(III) complexes such as $\text{NBu}_4[\{\text{Au}(\text{C}_6\text{F}_5)_3\text{PPh}_2-$

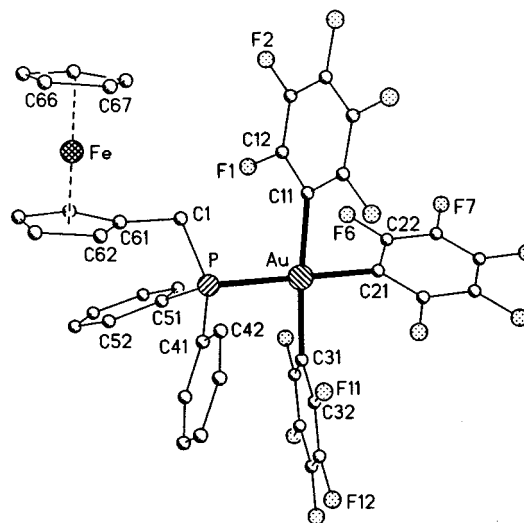


Figure 5. Molecular structure of complex **7** in the crystal. H atoms are omitted for clarity.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **7**

Au–C(21)	2.067(3)	Au–C(11)	2.068(4)
Au–C(31)	2.080(4)	Au–P	2.3503(9)
P–C(41)	1.804(4)	P–C(51)	1.809(4)
P–C(1)	1.835(4)	C(1)–C(61)	1.496(5)
C(21)–Au–C(11)	86.91(13)	C(21)–Au–C(31)	88.59(13)
C(11)–Au–C(31)	174.80(13)	C(21)–Au–P	179.43(11)
C(11)–Au–P	93.30(9)	C(31)–Au–P	91.23(9)
C(41)–P–C(51)	108.9(2)	C(41)–P–C(1)	107.1(2)
C(51)–P–C(1)	105.1(2)	C(41)–P–Au	109.89(12)
C(51)–P–Au	112.69(12)	C(1)–P–Au	112.99(11)
C(61)–C(1)–P	114.9(3)		

$\text{CH}_2\text{PPh}_2\}_2\text{Au}]^{23}$ (2.367(2) Å) and $[\text{AuMe}_3(\text{PPh}_3)]^{24}$ (2.350(6) Å and 2.347(6) Å, two independent molecules), but longer than in $[\text{AuCl}_3(\text{PPh}_3)]^{25}$ (2.335(4) Å) or $[\text{Au}(\text{C}_6\text{F}_5)(\text{S}_2\text{C}_6\text{H}_4)(\text{PPh}_3)]^{26}$ (2.340(1) Å), consistent with the higher trans influence of the pentafluorophenyl groups.

Crystal Structure of $[\text{Ag}(\text{PPh}_2\text{CH}_2\text{Fc})_3]\text{OTf}$ (10**).** The structure of the cation of complex **10** is shown in Figure 6, with a selection of bond lengths and angles in Table 6. The silver atom presents a slightly distorted trigonal geometry, lying 0.046 Å out of the plane of the three phosphorus atoms. The Ag–P distances (2.440(4)–2.483(4) Å) are similar to those obtained for three-coordinate silver complexes such as $[\text{AgX}(\text{L-L})]^{27}$ ($\text{L-L} = 2,11$ -bis(diphenylphosphino)methylbenzo[*c*]-phenanthrene, $\text{X} = \text{Cl}$, SnCl_3 , ClO_4 , or NO_3) (2.40(3)–2.455(1) Å), $[\text{Ag}(\text{dppf})(\text{PPh}_3)]\text{ClO}_4$ (2.4386(13)–2.4870(12) Å)^{11b} or to the highest values for $[\text{Ag}(7.8-(\text{PPh}_2)_2-7.8-\text{C}_2\text{B}_9\text{H}_{10})(\text{PPh}_3)]$ (2.3974(10)–2.4942(10) Å)²⁸ which correspond to the Ag–P(diphosphine) bonds.

Electrochemistry. The electrochemical behavior of these complexes has been studied by cyclic voltammetry at a platinum

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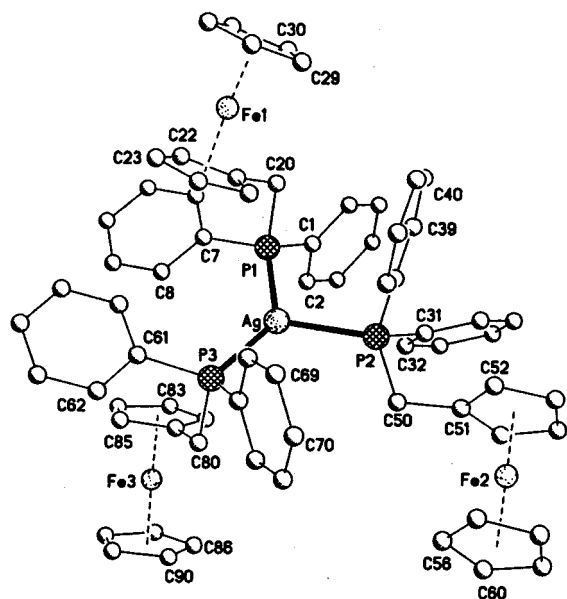


Figure 6. Structure of the cation of complex **10** in the crystal. H atoms are omitted for clarity.

Table 6. Selected Bond Lengths (Å) and Angles (deg) for Complex **10**

Ag–P(1)	2.440(4)	P(2)–C(38)	1.775(12)
Ag–P(3)	2.443(4)	P(2)–C(31)	1.811(9)
Ag–P(2)	2.483(4)	P(2)–C(50)	1.851(15)
P(1)–C(1)	1.822(8)	P(3)–C(67)	1.813(9)
P(1)–C(7)	1.821(8)	P(3)–C(61)	1.825(8)
P(1)–C(20)	1.832(13)	P(3)–C(80)	1.842(14)
P(1)–Ag–P(3)	135.11(14)	C(67)–P(3)–C(80)	106.8(6)
P(1)–Ag–P(2)	112.87(14)	C(61)–P(3)–C(80)	101.6(6)
P(3)–Ag–P(2)	111.32(14)	C(67)–P(3)–Ag	112.9(4)
C(1)–P(1)–C(7)	102.8(5)	C(61)–P(3)–Ag	122.5(3)
C(1)–P(1)–C(20)	104.8(6)	C(80)–P(3)–Ag	108.5(5)
C(7)–P(1)–C(20)	102.3(6)	C(2)–C(1)–P(1)	117.0(6)
C(1)–P(1)–Ag	120.0(4)	C(6)–C(1)–P(1)	123.0(6)
C(7)–P(1)–Ag	119.2(3)	C(8)–C(7)–P(1)	118.5(5)
C(20)–P(1)–Ag	105.6(5)	C(12)–C(7)–P(1)	121.3(5)
C(38)–P(2)–C(31)	105.3(6)	C(21)–C(20)–P(1)	110.6(8)
C(38)–P(2)–C(50)	105.9(7)	C(39)–C(38)–P(2)	121.2(9)
C(31)–P(2)–C(50)	103.8(6)	C(51)–C(50)–P(2)	115.2(10)
C(38)–P(2)–Ag	104.3(5)	C(66)–C(61)–P(3)	118.6(5)
C(31)–P(2)–Ag	117.2(4)	C(68)–C(67)–P(3)	119.3(7)
C(50)–P(2)–Ag	119.0(5)	C(72)–C(67)–P(3)	120.6(7)
C(67)–P(3)–C(61)	103.1(5)	C(81)–C(80)–P(3)	110.7(9)

electrode in CH_2Cl_2 . The redox pattern of the free phosphine ligand is complicated and resembles that of the 1,1'-bis-(diphenylphosphino)ferrocene ligand. Thus the phosphine undergoes a quasi-reversible one-electron oxidation process, based on the ferrocene unit, followed by a chemical reaction involving the phosphorus substituent. The cyclic voltammograms, at a scan rate of 100 mV s^{-1} , of the gold derivatives show an essentially reversible wave arising from the oxidation–reduction of the ferrocene moiety at slightly higher potentials than the phosphine–ferrocene ligand. The silver(I) compounds show, in addition to the wave due to the ferrocene oxidation, a more anodic irreversible wave that can be assigned to the one-electron oxidation of Ag^+ to Ag^{2+} . Table 7 summarizes the electrochemical data for these compounds.

Conclusions

We have reported on a series of new gold and silver complexes with ferrocenylmethylphosphine in different coordination numbers. Interesting equilibria or reorganization

Table 7. Electrochemical Data for Complexes **1–10**

compound	E_1 (V)	E_2 (V)
1 $[\text{AuCl}(\text{PPh}_2\text{CH}_2\text{Fc})]$	0.51	
2 $[\text{Au}(\text{C}_6\text{F}_5)(\text{PPh}_2\text{CH}_2\text{Fc})]$	0.48	
3 $[\text{Au}(\text{PPh}_3)(\text{PPh}_2\text{CH}_2\text{Fc})]\text{OTf}$	0.51	
4 $[\text{Ag}(\text{PPh}_3)(\text{PPh}_2\text{CH}_2\text{Fc})]\text{OTf}$	0.45	1.18
5 $[\text{Au}(\text{PPh}_2\text{CH}_2\text{Fc})_2]\text{ClO}_4$	0.53	
6 $[\text{Ag}(\text{PPh}_2\text{CH}_2\text{Fc})_2]\text{OTf}$	0.48	1.16
7 $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{PPh}_2\text{CH}_2\text{Fc})]$	0.56	
8 $[\text{AuCl}(\text{PPh}_2\text{CH}_2\text{Fc})_2]$	0.54	
9 $[\text{Au}(\text{PPh}_2\text{CH}_2\text{Fc})_3]\text{ClO}_4$	0.53	
10 $[\text{Ag}(\text{PPh}_2\text{CH}_2\text{Fc})_3]\text{OTf}$	0.49	1.1

processes take place in the three-coordinate gold(I) derivatives to give a mixture of the linear, three-coordinate, and four-coordinate species. Several complexes have been characterized by X-ray diffraction; one shows interesting C–H...Cl and H...Au intermolecular contacts that can be considered as weak hydrogen bonds. The electrochemical behavior consists of one reversible electron oxidation process for the gold compounds at slightly higher potential than the ferrocene itself; the silver complexes also show one irreversible wave corresponding to the oxidation to Ag^{2+} .

Experimental Section

Instrumentation. Infrared spectra were recorded in the range $4000\text{--}200 \text{ cm}^{-1}$ on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. $5 \times 10^{-4} \text{ mol dm}^{-3}$ solutions with a Philips 9509 conductimeter. C, H, and S analyses were carried out with a Perkin-Elmer 2400 microanalyzer. Mass spectra were recorded on a VG Autospec, with the liquid secondary-ion mass spectra (LSIMS) technique, using nitrobenzyl alcohol as matrix. NMR spectra were recorded on a Varian Unity 300 spectrometer and a Bruker ARX 300 spectrometer in CDCl_3 (otherwise stated). Chemical shifts are cited relative to SiMe_4 (^1H , external) and 85% H_3PO_4 (^{31}P , external). Cyclic voltammetric experiments were performed by employing an EG&G PARC model 273 potentiostat. A three-electrode system was used, which consists of a platinum disk working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode. The measurements were carried out in CH_2Cl_2 solutions with 0.1 M Bu_4NPF_6 as a supporting electrolyte. Under the present experimental conditions, the ferrocenium/ferrocene couple was located at 0.47 V vs SCE.

Materials. The starting materials $\text{FcCH}_2\text{PPh}_2$,⁵ $[\text{AuCl}(\text{tht})]$,²⁹ $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$,³⁰ and $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt})_2]$ ³¹ were prepared by published procedures. $[\text{Au}(\text{OTf})(\text{PPh}_3)]$ was prepared from $[\text{AuCl}(\text{PPh}_3)]$ ³² by reaction with AgOTf in dichloromethane and $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$ by reaction of AgOTf and PPh_3 in diethyl ether.

Safety Note. CAUTION! Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and these should be handled with great caution.

Syntheses. $[\text{AuR}(\text{PPh}_2\text{CH}_2\text{Fc})]$ [$\text{R} = \text{Cl}$ (**1**), C_6F_5 (**2**)]. To a solution of $[\text{AuCl}(\text{tht})]$ (0.032 g, 0.1 mmol) or $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$ (0.045 g, 0.1 mmol) in 20 mL of dichloromethane was added $\text{PPh}_2\text{CH}_2\text{Fc}$ (0.038 g, 0.1 mmol), and the mixture was stirred for 1 h. Concentration of the solution to ca. 5 mL and addition of hexane (10 mL) gave complexes **1** or **2** as orange solids. Complex **1**: yield 79%. $\Lambda_M = 0.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental anal. Found: C, 44.87; H, 3.11. Calcd for $\text{C}_{23}\text{H}_{21}\text{AuClFeP}$: C, 44.80; H, 3.43. ^1H NMR, δ : 3.56 (d, 2H, CH_2 , $J(\text{PH})$ 10.16 Hz), 4.01 (m, 2H, C_5H_4), 4.04 (m, 2H, C_5H_4), 4.10 (m, 5H, C_5H_5), 7.2–7.6 (m, 10H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : 30.9 (s). Complex **2**: yield

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Table 8. Details of Data Collection and Structure Refinement for the Complexes 1–3

	1	2	3
chem formula	C ₂₃ H ₂₁ AuClFeP	C ₂₉ H ₂₁ AuF ₅ FeP	C ₄₂ H ₃₆ AuF ₃ FeO ₃ P ₂ S
cryst habit	yellow block	yellow tablet	orange tablet
cryst size/mm	0.20 × 0.20 × 0.15	0.38 × 0.21 × 0.17	0.68 × 0.48 × 0.16
λ	0.710 73	0.710 73	0.710 73
cryst syst	monoclinic	triclinic	triclinic
space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 1	<i>P</i> 1
<i>a</i> /Å	9.886(3)	10.960(2)	10.859(3)
<i>b</i> /Å	17.539(4)	11.049(2)	11.463(4)
<i>c</i> /Å	11.867(3)	12.562(2)	16.517(5)
α /deg		115.374(14)	74.69(2)
β /deg	99.35(2)	109.135(12)	80.33(2)
γ /deg		94.918(14)	79.98(2)
<i>V</i> /Å ³	2030.3(9)	1252.1(4)	1919.1(10)
<i>Z</i>	4	2	2
<i>D_c</i> /g cm ^{−3}	2.017	1.985	1.718
<i>M</i>	616.63	748.24	992.52
<i>F</i> (000)	1184	720	980
<i>T</i> /°C	−100	−100	−100
2 $\theta_{\max}$ /deg	50	50	48
μ (Mo <i>K</i> α)/cm ^{−1}	81.48	65.50	43.87
transmission	0.595–0.801	0.705–0.922	0.610–0.958
no. of reflns meas	5922	4199	6993
no. of unique reflns	3564	4158	5931
<i>R</i> _{int}	0.0393	0.0145	0.014
<i>R</i> ^a (<i>F</i> > 4 σ (<i>F</i>))	0.0328	0.03	0.029
<i>R</i> _w ^b (<i>F</i> ² , all reflns)	0.0723	0.052	0.072
no. of reflns used	3564	4158	5927
no. of params	244	355	478
no. of restraints	213	93	365
<i>S</i> ^c	0.898	0.888	0.996
max $\Delta\rho$ /e Å ^{−3}	1.271	0.908	2.72

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w(F^2) = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program. ^c $S = [\sum \{w(F_o^2 - F_c^2)^2\} / (n - p)]^{0.5}$, where *n* is the number of data and *p* the number of parameters.

Table 9. Details of Data Collection and Structure Refinement for the Complexes 5, 7, and 10

	5	7	10
chem formula	C ₄₇ H ₄₄ AuCl ₃ Fe ₂ O ₄ P ₂	C ₄₁ H ₂₁ AuF ₁₅ FeP	C ₇₁ H ₆₅ AgCl ₂ F ₃ Fe ₃ O ₃ P ₃ S
cryst habit	orange plate	orange prism	dull orange tablet
cryst size/mm	0.20 × 0.20 × 0.05	0.50 × 0.40 × 0.20	0.35 × 0.30 × 0.15
cryst system	triclinic	monoclinic	monoclinic
space group	<i>P</i> 1	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> /Å	9.0828(18)	13.6515(14)	12.692(3)
<i>b</i> /Å	9.5568(16)	17.101(2)	18.467(4)
<i>c</i> /Å	13.501(2)	16.274(2)	28.693(6)
α /deg	86.587(12)		
β /deg	89.573(14)	91.566(7)	93.08(2)
γ /deg	77.154(14)		
<i>V</i> /Å ³	1140.6(4)	3797.7(6)	6716(3)
<i>Z</i>	1	4	4
<i>D_c</i> /g cm ^{−3}	1.674	1.893	1.478
<i>M</i>	1149.18	1082.36	1494.52
<i>F</i> (000)	570	2088	3048
<i>T</i> /°C	−100	−100	−100
2 $\theta_{\max}$ /deg	50	50	46
μ (Mo <i>K</i> α)/cm ^{−1}	41.24	43.88	11.59
transmission	0.789–0.991	0.608–0.966	
no. of reflns meas	4031	6694	9408
no. of unique reflns	4003	6676	8750
<i>R</i> _{int}	0.038	0.016	0.058
<i>R</i> ^a (<i>F</i> > 4 σ (<i>F</i>))	0.049	0.025	0.095
<i>R</i> _w ^b (<i>F</i> ² , all reflns)	0.1254	0.044	0.278
no. of reflns used	4003	6676	8750
no. of params	290	532	258
no. of restraints	281	507	19
<i>S</i> ^c	0.973	0.886	0.878
max $\Delta\rho$ /e Å ^{−3}	1.723	0.368	1.252

^a $R(F) = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $R_w(F^2) = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program. ^c $S = [\sum \{w(F_o^2 - F_c^2)^2\} / (n - p)]^{0.5}$, where *n* is the number of data and *p* the number of parameters.

85%. $\Lambda_M = 1.7 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental anal. Found: C, 46.73; H, 3.22. Calcd for C₂₉H₂₁AuF₅FeP: C, 46.55; H, 2.83. ¹H NMR, δ : 3.58

(d, 2H, CH₂, *J*(PH) 9.43 Hz), 4.05 (m, 2H, C₅H₄), 4.08 (m, 2H, C₅H₄), 4.10 (m, 5H, C₅H₅), 7.2–7.7 (m, 10H, Ph). ³¹P{¹H} NMR, δ : 30.1 (m).

^{19}F NMR, δ : -116.3 (m, 2F, o-F), -158.8 (t, 1F, p-F, $J(\text{FF})$ 20.0 Hz), -162.7 (m, 2F, m-F).

[M(PPh₂CH₂Fc)(PPh₃)OTf] [M = Au (3), Ag (4)]. To a solution of $[\text{Au}(\text{OTf})(\text{PPh}_3)]$ (0.061 g, 0.1 mmol) or $[\text{Ag}(\text{OTf})(\text{PPh}_3)]$ (0.052 g, 0.1 mmol) in 20 mL of dichloromethane was added $\text{PPh}_2\text{CH}_2\text{Fc}$ (0.038 g, 0.1 mmol), and the mixture was stirred for 1 h. Concentration of the solution to ca. 5 mL and addition of hexane (10 mL) gave **3** or **4** as yellow solids. Complex **3**: yield 95%. $\Lambda_{\text{M}} = 105 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental anal. Found: C, 50.39; H, 3.31; S, 3.31. Calcd for $\text{C}_{42}\text{H}_{36}\text{AuF}_3\text{FeO}_3\text{P}_2\text{S}$: C, 50.82; H, 3.65; S, 3.23. ^1H NMR, δ : 3.82 (m, 1H, CH₂), 3.90 (m, 1H, CH₂), 3.93 (m, 2H, C₅H₄), 3.95 (m, 2H, C₅H₄), 4.12 (m, 5H, C₅H₅), 4.14 (s, 5H, C₅H₅), 7.2–7.7 (m, 25H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : 44.4 (s), 45.3 (s). Complex **4**: yield 65%. $\Lambda_{\text{M}} = 104.2 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental anal. Found: C, 55.95; H, 3.79; S, 3.33. Calcd for $\text{C}_{42}\text{H}_{36}\text{AgF}_3\text{FeO}_3\text{P}_2\text{S}$: C, 55.78; H, 4.01; S, 3.54. ^1H NMR, δ : -80°C , (CDCl₃)₂CO, δ : 3.55 (m, 2H, CH₂), 3.80 (m, 2H, C₅H₄), 3.94 (m, 2H, C₅H₄), 4.06 (m, 5H, C₅H₅), 7.2–7.7 (m, 25H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : P_A 12.4, P_B 15.8, $J(\text{P}_\text{A}\text{P}_\text{B})$ 45 Hz, $J(\text{P}_\text{A}^{107}\text{Ag})$ 375 Hz, $J(\text{P}_\text{A}^{109}\text{Ag})$ 427.5 Hz, $J(\text{P}_\text{B}^{107}\text{Ag})$ 500 Hz, $J(\text{P}_\text{B}^{109}\text{Ag})$ 570 Hz.

[M(PPh₂CH₂Fc)₂]X [M = Au, X = ClO₄ (5); Ag, X = OTf (6)]. To a solution of $[\text{Au}(\text{tht})_2\text{ClO}_4]$ (0.047 g, 0.1 mmol) or AgOTf (0.021 g, 0.1 mmol) in 20 mL of dichloromethane was added $\text{PPh}_2\text{CH}_2\text{Fc}$ (0.076 g, 0.2 mmol), and the mixture was stirred for 1 h. Concentration of the solution to ca. 5 mL and addition of hexane (10 mL) gave **5** or **6** as yellow solids. Complex **5**: yield 93%. $\Lambda_{\text{M}} = 100 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental anal. Found: C, 51.61; H, 3.73. Calcd for $\text{C}_{46}\text{H}_{42}\text{AuClFe}_2\text{O}_4\text{P}_2$: C, 51.88; H, 3.97. ^1H NMR, δ : 3.86 (m, 2H, CH₂), 3.94 (m, 2H, C₅H₄), 3.98 (m, 2H, C₅H₄), 4.17 (m, 5H, C₅H₅), 7.4–7.8 (m, 20H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : 44.2 (s). Complex **6**: yield 65%. $\Lambda_{\text{M}} = 115 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental anal. Found: C, 55.62; H, 4.39; S, 2.74. Calcd for $\text{C}_{47}\text{H}_{42}\text{AgF}_3\text{Fe}_2\text{O}_3\text{P}_2\text{S}$: C, 55.05; H, 4.13; S, 3.12. ^1H NMR, δ : 3.26 (m, 2H, CH₂), 3.72 (m, 2H, C₅H₄), 3.84 (m, 2H, C₅H₄), 4.03 (m, 5H, C₅H₅), 7.1–7.5 (m, 20H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : -60°C CDCl₃, δ : 8.6 ppm (2d, $J(\text{P}^{107}\text{Ag})$ 320 Hz, $J(\text{P}^{109}\text{Ag})$ 367.8 Hz).

[Au(C₆F₅)₃(PPh₂CH₂Fc)] (7). To a solution of $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt})_2]$ (0.077 g, 0.1 mmol) in 20 mL of dichloromethane was added $\text{PPh}_2\text{CH}_2\text{Fc}$ (0.038 g, 0.1 mmol), and the mixture was stirred for 1 h. Concentration of the solution to ca. 5 mL and addition of hexane (10 mL) gave complex **7** as an orange solid. Yield: 91%. $\Lambda_{\text{M}} = 0.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental anal. Found: C, 45.68; H, 1.72. Calcd for $\text{C}_{41}\text{H}_{21}\text{AuF}_{15}\text{FeP}$: C, 45.49; H, 1.95. ^1H NMR, δ : 3.47 (d, 2H, CH₂, $J(\text{PH})$ 7.87 Hz), 3.74 (m, 2H, C₅H₄), 3.99 (m, 2H, C₅H₄), 4.04 (m, 5H, C₅H₅), 7.2–7.7 (m, 10H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : 13.9 (m). ^{19}F NMR, δ : -120.1 (m, 4F, o-F), -121.8 (m, 2F, o-F), -156.9 (t, 2F, p-F, $J(\text{FF})$ 19.75 Hz), -157.4 (t, 1F, p-F, $J(\text{FF})$ 19.88 Hz), -160.7 (m, 4F, m-F), -161.4 (m, 2F, m-F).

[AuCl(PPh₂CH₂Fc)₂] (8). To a solution of $[\text{AuCl}(\text{tht})]$ (0.032 g, 0.1 mmol) in 20 mL of dichloromethane was added $\text{PPh}_2\text{CH}_2\text{Fc}$ (0.076 g, 0.2 mmol), and the mixture was stirred for 1 h. Concentration of the solution to ca. 5 mL and addition of hexane (10 mL) gave **8** as an

orange solid. Complex **8**: yield 50%. $\Lambda_{\text{M}} = 14 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental anal. Found: C, 55.73; H, 3.71. Calcd for $\text{C}_{46}\text{H}_{42}\text{AuClFe}_2\text{P}_2$: C, 55.31; H, 4.03. ^1H NMR, CD₂Cl₂, room temperature, δ : 3.69 (d, 2H, CH₂, $J(\text{PH})$ 9.6 Hz), 4.04 (m, 2H, C₅H₄), 4.05 (m, 2H, C₅H₄), 4.14 (m, 5H, C₅H₅), 7.4–7.7 (m, 20H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : 33.8 (s, br), -80°C , 3.60 (d, 2H, CH₂, $J(\text{PH})$ 10.5 Hz), 3.79 (m, C₅H₄), 3.95 (m, C₅H₄), 3.99 (m, C₅H₄), 4.01 (m, C₅H₄), 4.08 (m, C₅H₅), 7.4–7.7 (m, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : 28.2 (s), 32.4 (s), 38.5(s), 42.3 (s).

[M(PPh₂CH₂Fc)₃]X [M = Au, X = ClO₄ (9); M = Ag, X = OTf (10)]. To a solution of $[\text{Au}(\text{tht})_2\text{ClO}_4]$ (0.047 g, 0.1 mmol) or AgOTf (0.021 g, 0.1 mmol) in 20 mL of dichloromethane was added $\text{PPh}_2\text{CH}_2\text{Fc}$ (0.114 g, 0.3 mmol), and the mixture was stirred for 1 h. Concentration of the solution to ca. 5 mL and addition of hexane (10 mL) gave **9** or **10** as yellow solids. Complex **9**: yield 80%. $\Lambda_{\text{M}} = 90.5 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental anal. Found: C, 57.42; H, 3.92. Calcd for $\text{C}_{69}\text{H}_{63}\text{AuClFe}_3\text{O}_4\text{P}_3$: C, 57.19; H, 4.38. ^1H NMR, room temperature, δ : 3.77 (m, 6H, CH₂), 3.94 (m, 12H, C₅H₄), 4.15 (m, 15H, C₅H₅), 7.2–7.8 (m, 30H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : 41.7 (s, br), -60°C , 3.77 (m), 3.84 (m), 3.97 (m), 4.10 (m), 7–7.8 (m, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : 28.2 (s), 38.3 (s), 43.8 (s). Complex **10**: yield 85%. $\Lambda_{\text{M}} = 107 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$. Elemental anal. Found: C, 59.7; H, 3.91; S, 2.82. Calcd for $\text{C}_{70}\text{H}_{63}\text{AgF}_3\text{Fe}_3\text{O}_3\text{P}_3\text{S}$: C, 59.38; H, 4.40; S, 2.29. ^1H NMR, δ : 3.37 (m, 2H, CH₂), 3.81 (m, 2H, C₅H₄), 3.83 (m, 2H, C₅H₄), 4.05 (m, 5H, C₅H₅), 7.3–7.5 (m, 30H, Ph). $^{31}\text{P}\{^1\text{H}\}$ NMR, δ : -60°C , δ : 14.8 ppm (2d, $J(\text{P}^{107}\text{Ag})$ 509 Hz, $J(\text{P}^{109}\text{Ag})$ 586.3 Hz).

Crystallography. The crystals were mounted in inert oil on a glass fiber and transferred to the cold gas stream of a Siemens P4 diffractometer equipped with an LT-2 or Oxford low-temperature attachment. Data were collected using monochromated Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Scan type: ω or $\theta-2\theta$ (**3**). Cell constants were refined from setting angles of ca. 60 reflections in the range 2θ 7–25°. Psi scans were applied for all of the complexes with the exception of compound **10**, for which no absorption correction was applied. The structures were solved by direct methods for **3** and **10**, otherwise by the heavy-atom method, and refined on F^2 using the programs SHELXL-93 or SHELXL-97.³³ All non-hydrogen atoms were refined anisotropically (except for complex **10**). Hydrogen atoms were included using a riding model. Special refinement details: A system of restraints to light-atom displacement-factor components and local ring symmetry was used. Compounds **3** and **10** contain badly disordered solvent (dichloromethane). Further details of the data collection are given in Tables 8 and 9.

Acknowledgment. We thank the Dirección General de Investigación Científica y Técnica (No. PB97-1010-C02-01), the Caja de Ahorros de la Inmaculada (No. CB4/98), and the Fonds der Chemischen Industrie for financial support.

Supporting Information Available: Six X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC9905446

(33) Sheldrick, G. M. *SHELXL-93 and SHELXL-97, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1993/1997.