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1,1′-Bis(diphenylphosphino)ferrocene (dppf) Complexes of Gold(I) and Gold(III). Crystal Structures of [(dppf)AuPPh$_3$]ClO$_4$·CHCl$_3$ and [(dppf)Au(μ-dppf)Au(dppf)](ClO$_4$)$_2$·2CH$_2$Cl$_2$

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Displacement of tetrahydrothiophene in gold(I) complexes such as [AuX(tht)] or [Au(tht)L]ClO$_4$ by the 1,1′-bis(diphenylphosphino)ferrocene ligand leads to the neutral [(dppf)(AuX)$_2$] [X = C$_6$F$_5$ (**1**), Cl (**2**)] or cationic dinuclear complexes [(dppf)(AuL)$_2$](ClO$_4$)$_2$ [L = CH$_2$PPh$_3$ (**3**), CH$_2$PPh$_2$Me (**4**), CH$_2$PPhMe$_2$ (**5**)]. Other dinuclear complexes have been prepared by substitution reactions of compound **2**, namely [(dppf)(AuL)$_2$]$^{n+}$ [L = SCN, n = 0 (**6**); L = tht, n = 2 (**7**)]. Three- and four-coordinated derivatives of the types [(dppf)AuCl] (**8**), [(dppf)(AuPR$_3$)]ClO$_4$[PR$_3$ = PPh$_3$ (**9**), PPh$_2$Me (**10**)], [Au(dppf)$_2$]ClO$_4$ (**11**), and [(dppf)Au(μ-dppf)Au(dppf)](ClO$_4$)$_2$ (**12**) are obtained by reaction of the gold(I) precursor and the diphosphine. The reaction of equimolecular amounts of dppf and [Au(tht)$_2$]ClO$_4$ affords a mixture of the dinuclear linear complexes [Au(dppf)]$_2$(ClO$_4$)$_2$ (**13**) and the mononuclear three-coordinated complex [(dppf)Autht]ClO$_4$ (**14**). Similarly, by displacement of tht in [AuR$_3$tht] or [AuR$_2$(tht)$_2$]ClO$_4$ (R = C$_6$F$_5$) by the dppf ligand, the gold(III) derivatives [(dppf)AuR$_3$] (**15**), [(dppf)(AuR$_3$)$_2$] (**16**), and [(dppf)AuR$_2$]ClO$_4$ (**17**) can be synthesized. Cyclic voltammetry of some of the compounds reveals one chemically reversible phosphinoferrocene-based oxidation. Single-crystal X-ray structure determinations were performed for complexes **9** and **12**. [(dppf)(AuPPh$_3$)]ClO$_4$ (**9**) crystallizes in space group $P2_1/c$, monoclinic, with a = 14.239(6) Å, b = 16.889(4) Å, c = 20.866(8) Å, β = 95.81(3)°, and Z = 4. [(dppf)Au(μ-dppf)Au(dppf)](ClO$_4$)$_2$ (**12**) crystallizes in space group $C2/c$, monoclinic, with a = 32.858(6) Å, b = 14.821(3) Å, c = 26.399(5) Å, β = 128.48(2)°, and Z = 4. The cation of **12** is exactly centrosymmetric. Both complexes show trigonal planar coordination at gold. The ferrocene rings are staggered by 18–36°.

Introduction

The synthesis and reactivity of transition metal complexes with ferrocene-bridged bis(tertiary phosphine) ligands such as 1,1′-bis(diphenylphosphino)ferrocene (dppf) have been a topic of interest in the last few years, mainly because of the catalytic properties displayed by some of them.[1,2] These include rhodium(I) in hydrogenation of olefins,[3,4] palladium(II)- and nickel(II)-catalyzed Grignard cross-coupling reactions,[2,5–7] platinum(II)-catalyzed hydrosilation of ketones,[8] and also gold(I)-catalyzed aldol reactions of enolates with aldehydes to give optically active β-hydroxycarbonyl compounds.[9,10]

Moreover, the antitumor activity of bis(diphenylphosphines) and their bis(gold(I)) complexes has been of recent interest.[11,12] Although some of the ligands themselves have significant antitumor activity, the coordination of the diphosphine to gold(I) enhances its cytotoxic and antitumor activity, and complexes such as [Au(dppe)$_2$]$^+$ [dppe = bis(diphenylphosphino)ethane] are active against a wide spectrum of tumors *in vivo*.[13,14] Apart from that, ferrocenium salts have been reported to inhibit several solid tumors.[15]

These considerations and the fact that very few gold(I)[16] and no gold(III) complexes with the 1,1′-bis(diphenylphosphino)ferrocene ligand have been reported led us to synthesize them.

Here we have studied the coordination of the ferrocenylphosphine as a bridging or chelating ligand in two-, three-, or four-coordinated gold(I) complexes or in gold(III) derivatives. The redox behavior of some of these complexes has also been studied by cyclic voltammetry.

After submission of this work, we learned about a parallel study in the chemistry of gold–dppf complexes arising as an independent synthesis and structure determination of the compound [(dppf)(AuCl)]$_n$ (**8**) and the [NO$_3^-$] salt of [(dppf)Au(μ-dppf)Au(dppf)]$^{2+}$ (**12**).[17]

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Table I. Analytical Data and Other Properties for the Complexes

no.	complex	yield/%	anal./% C	H	Λ_M[a]	Mp (°C)
1	$[(dppf)(AuC_6F_5)_2]$	93	42.66[b] (43.06)[c]	2.16 (2.20)	1	245(d)
3	$[(dppf)(AuCH_2PPh_3)_2](ClO_4)_2$	84	52.03 (51.68)	3.41 (3.79)	171[d]	130
4	$[(dppf)(AuCH_2PPh_2Me)_2](ClO_4)_2$	90	47.25 (47.62)	3.71 (3.71)	166[d]	110
5	$[(dppf)(AuCH_2PPhMe_2)_2](ClO_4)_2$	89	43.85 (43.85)	3.96 (3.89)	158[d]	100
6	$[(dppf)(AuSCN)_2]$	61	40.38 (40.63)	2.40 (2.65)	19	190
7	$[(dppf)(Au(tht))_2](ClO_4)_2$	65	38.07 (38.20)	3.34 (3.21)	198	125
8	$[(dppf)AuCl]$	67	51.46 (51.9)	4.22 (3.86)	23	227
9	$[(dppf)AuPPh_3]ClO_4$	70	56.44 (56.11)	3.82 (3.89)	143	90
10	$[(dppf)AuPPh_2Me]ClO_4$	98	53.34 (53.71)	3.83 (3.93)	125	180
12	$[(dppf)Au(\mu\text{-}dppf)Au(dppf)](ClO_4)_2$	40	54.12 (54.25)	3.73 (3.74)	160[d]	130
15	$[(dppf)Au(C_6F_5)_3]$	68	48.27 (47.61)	2.16 (2.11)	4	227
16	$[(dppf)\{Au(C_6F_5)_3\}_2]$	63	43.45 (43.10)	1.57 (1.44)	11	260
17	$[(dppf)Au(C_6F_5)_2]ClO_4$	77	46.49 (46.62)	2.40 (2.38)	180	90

[a] Ω^{-1} cm^2 mol^{-1}. [b] Found. [c] Calculated. [d] Measured in CH_3NO_2.

Table II. ^1H and $^{31}P\{^1H\}$ NMR Data for the Complexes[a]

		$^1H/\delta$			$^{31}P\{^1H\}/\delta$	
			L			
no.	complex	C_5H_4	CH_2	Me	dppf	L
1	$[(dppf)(AuC_6F_5)_2]$	4.41 (m), 4.75 (m)			37.2 (m)	
3	$[(dppf)(AuCH_2PPh_3)_2](ClO_4)_2$	4.02 (m), 4.39 (m)	2.32 (dd) (13.6, 8.31)		36.8 (d) (7.2)	31.9 (d) (7.2)
4	$[(dppf)(AuCH_2PPh_2Me)_2](ClO_4)_2$	4.10 (m), 4.37 (m)	2.09 (dd) (13.67, 8.30)	2.34 (d) (13.1)	36.7 (s)	28.7 (s)
5	$[(dppf)(AuCH_2PPhMe)_2](ClO_4)_2$	4.16 (m), 4.39 (m)	1.78 (s, br)	2.02 (d) (13.06)	37.4 (d) (9.9)	29.2 (d) (9.9)
6	$[(dppf)(AuSCN)_2]$	4.34 (m), 4.69 (m)			31.7 (s)	
7	$[(dppf)(Au(tht))_2](ClO_4)_2$	4.54 (m), 4.58 (m)	2.24 (m), 3.57 (m)		31.1 (s)	
8	$[(dppf)AuCl]$	4.15 (m), 4.39 (m)			31.4 (s)	
9	$[(dppf)AuPPh_3]ClO_4$	4.25 (m), 4.50 (m)			38.2[b] (161.7)	46.8
10	$[(dppf)AuPPh_2Me]ClO_4$	4.26 (m), 4.48 (m)			36.7[b] (166.4)	27.1
11	$[Au(dppf)_2]ClO_4$	4.11 (m), 4.28 (m)			22.8 (s)	
12	$[(dppf)Au(\mu\text{-}dppf)Au(dppf)](ClO_4)_2$	4.01 (m), 4.11 (m), 4.28 (m), 4.51 (m)			36.7[b] (174.3)	40.6
13	$[Au(dppf)]_2(ClO_4)_2$	4.36 (m), 4.61 (m)			42.4 (s)	
14	$[(dppf)Au(tht)]ClO_4$	4,50 (m), 4.75 (m)	2.19 (m), 3.50 (m)		40.3 (s, br)	
15	$[(dppf)Au(C_6F_5)_3]$	3.88 (m), 4.02 (m), 4.22 (m)			16.7 (m), −18.9 (s)	
16	$[(dppf)\{Au(C_6F_5)_3\}_2]$	4.11 (m), 4.21 (m)			16.9 (m)	
17	$[(dppf)Au(C_6F_5)_2]ClO_4$	4.56 (m), 4.80 (m)			26.5 (m)	

[a] Coupling constants in hertz are shown in parentheses; s = singlet, d = doublet, m = multiplet, dd = doublet of doublets. [b] Part B_2 of an AB_2 system; the spectra of **12** were measured in CD_2Cl_2.

Results and Discusion

Linear Dinuclear Gold(I) Complexes. The reaction of the gold(I) complexes $[AuX(tht)]$ ($X = C_6F_5$, Cl) with dppf in a molar ratio of 2:1 leads to the dinuclear derivatives $[(dppf)(AuX)_2]$ [$X = C_6F_5$ (**1**), Cl (**2**)], where the ferrocenylphosphine bridges the two gold fragments (see Scheme I).

Complex **2** has been previously reported,[16] although synthesized by another procedure. The $^{31}P\{^1H\}$ NMR spectrum of complex **1** shows a multiplet because of the coupling between the phosphorus and fluorine nuclei. In the ^1H NMR spectrum, three multiplets with a ratio of 1:1:5 appear, corresponding to the cyclopentadienyl protons (two different enviroments in each ring) and the phenyl groups, respectively. The ^{19}F NMR spectrum agrees with the presence of equivalent C_6F_5 groups.

The FAB$^+$ mass spectra for complexes **1** and **2** show in both cases the molecular cation peaks at m/z = 1282 (12%, **1**) and m/z = 1018 (7%, **2**). These derivatives easily lose one anionic ligand to give the fragments $[(dppf)Au_2X]^+$ (40%, **1**; 100%, **2**). In both spectra, the fragment $[Au(dppf)]^+$ appears; it is also present in the spectra of all subsequent gold(I) complexes, always with high intensity.

The reaction of dppf with $[Au(tht)L]ClO_4$ in a molar ratio of 1:2 leads to the cationic dinuclear complexes $[(dppf)(AuL)_2](ClO_4)_2$ [$L = CH_2PPh_3$ (**3**), CH_2PPh_2Me (**4**), CH_2PPhMe_2 (**5**)]. The NMR data are consistent with structures similar to those of the neutral complexes **1** and **2**. The $^{31}P\{^1H\}$ NMR spectra in every case show two different phosphorus enviroments, and two doublets appear in the spectra of three complexes. The ^1H NMR spectra show resonances for the C_5H_4 rings (two multiplets) and the ylide ligand (doublet of doublets for the methylene group and a doublet for the methyl group). The $^{13}C\{^1H\}$ NMR spectra provide additional evidence for the assigned structure. With the exception of the phenyl carbons, all appear coupled with the nearest phosphorus nuclei, and thus a doublet (Me), a doublet of doublets

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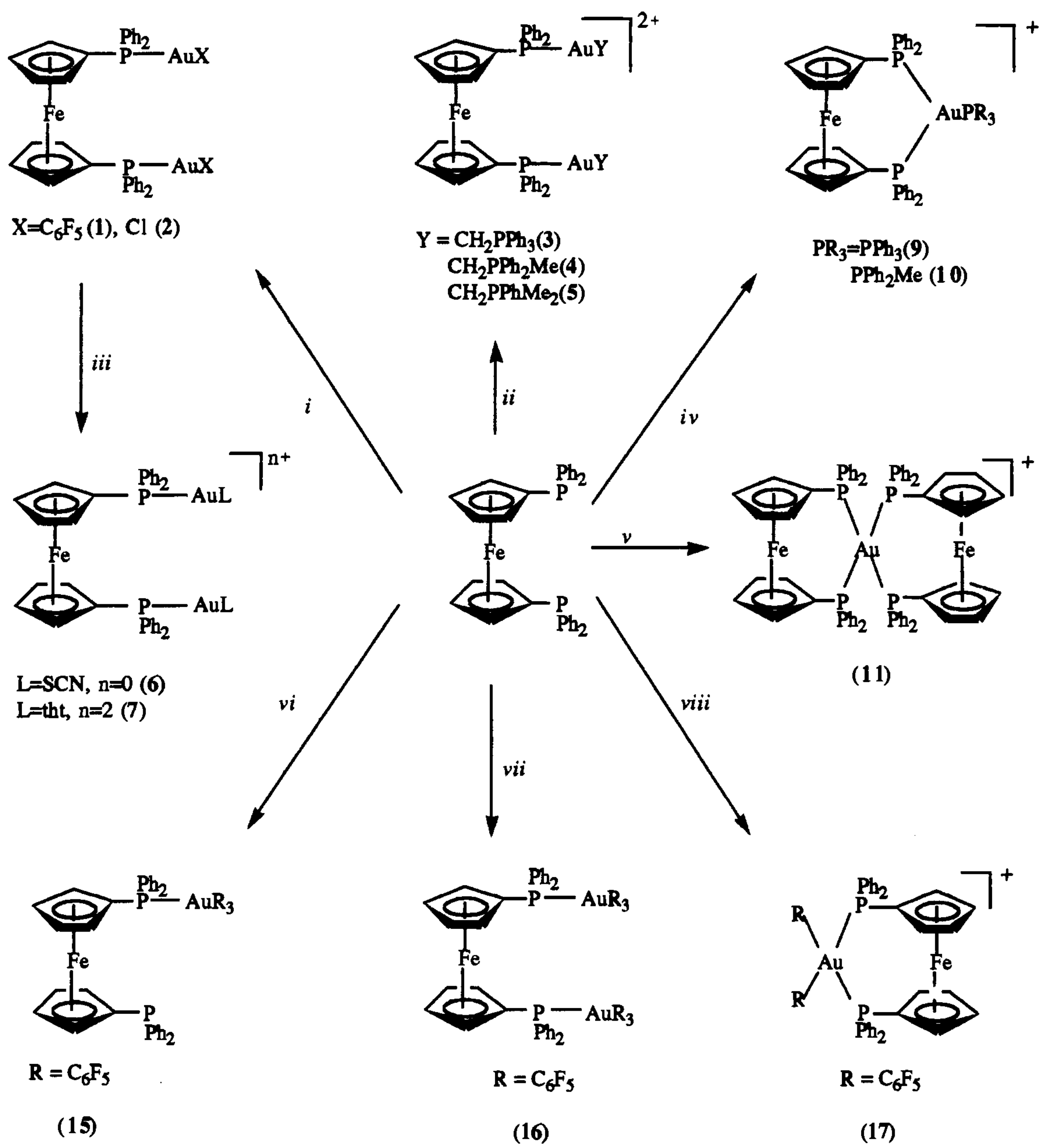
Scheme I



i) 2 [AuX(tht)], *ii)* 2 [Au(tht)Y]$^+$, *iii)* 2 KSCN or [AgOClO$_3$(tht)], *iv)* [Au(tht)PR$_3$]$^+$, *v)* 1/2 [Au(tht)$_2$]$^+$, *vi)* [AuR$_3$(tht)], *vii)* 2 [AuR$_3$(tht)], *viii)* [AuR$_2$(tht)$_2$]$^+$

(CH$_2$, coupled to both phosphorus), and three doublets for the C$_5$H$_4$ carbons which are equivalent 2:2:1, the last being linked to phosphorus, are observed.

Other dinuclear complexes with the diphosphine bridging both gold atoms can be prepared by substitution reactions of compound **2**. Thus the reaction of **2** with KSCN causes the substitution of the chlorine by the thiocyanate ligand; in a similar manner, **2** reacts with 2 equiv of [Ag(OClO$_3$)tht] with precipitation of AgCl, the free coordination site being occupied by the tht ligand.

The ^{1}H NMR spectrum of [(dppf)(AuSCN)$_2$] (**6**) shows three multiplets, one for the phenyl protons and two for the cyclopentadienyl groups. In the ^{1}H NMR spectrum of [(dppf)(Au(tht))$_2$](ClO$_4$)$_2$ (**7**), there are also two multiplets for the tetrahydrothiophene protons. For both complexes, only one resonance appears in the ^{31}P{^{1}H} NMR spectra.

The IR spectra of both complexes show the absence of the vibration ν(Au–Cl). Compound **7** shows characteristic bands for tht at 1270 and 1257 cm^{-1}, and for complex **6** the vibration ν(C–N) appears at 2118 cm^{-1}.

In the FAB$^+$ mass spectrum of compound **6**, the molecular cation peak does not appear, although the peak corresponding to loss of one SCN$^-$ ligand does appear at m/z = 1006 (45%). The loss of one anionic ligand in neutral complexes in the FAB$^+$ has been previously observed by us for other gold complexes.

Three- and Four-Coordinated Gold(I) Species. The most commonly observed geometry for gold(I) is linear two-coordination. Three- and four-coordinated complexes are appreciably less common. The flexibility of the 1,1′-bis(diphenylphosphino)ferrocene system, as shown in the preparation of other square planar or tetrahedral transition metal complexes, prompted us to synthesize three- and four-coordinated gold(I) complexes by using the appropiate molar ratio between reactants.

The reaction of [AuCl(tht)] with dppf in a molar ratio of 1:1 leads to the three-coordinated derivative [(dppf)AuCl] (**8**). The structure was assigned on the basis of NMR spectroscopy and analytical data. Its ^{1}H NMR spectrum shows two multiplets for the C$_5$H$_4$ rings, and the ^{31}P{^{1}H} NMR spectrum shows a broad singlet at δ 31.4.

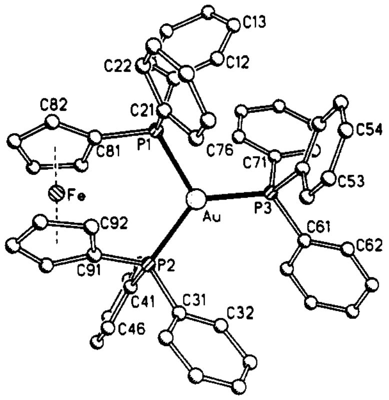


Figure 1. Structure of the cation of complex **9**, with the atom-numbering scheme. Hydrogen atoms are omitted for clarity; atomic radii are arbitrary.

Although $^{31}P\{^1H\}$ NMR chemical shifts alone do not appear to be a reliable guide to gold(I) coordination numbers, some studies of other linear and three-coordinated complexes show a displacement to lower frequencies with increasing coordination number.[18,19] However, the chemical shift for the related linear complex [(dppf)(AuCl)$_2$] (δ 28.2) is not consistent with these observations. The reason for this inconsistency could be that compound **8** is a dimer or polymer. In the above-mentioned paper by Hor *et al.*, the crystal structure of this complex has been established and exists as a polymer of [(dppf)(AuCl)] units.[17]

The reaction of dppf with equimolecular amounts of [Au(tht)PR$_3$]ClO$_4$ gives the cationic trigonal planar complexes [(dppf)AuPR$_3$]ClO$_4$ [PR$_3$ = PPh$_3$ (**9**), PPh$_2$Me (**10**)].

The ^1H NMR spectra of complexes **9** and **10** show two multiplets for the C_5H_4 groups, and complex **10** also shows a doublet for the methyl group of the phosphine (at −55 °C). The $^{31}P\{^1H\}$ NMR spectra of complexes **9** and **10** show two broad resonances at room temperature, but when the samples are cooled to −55 °C typical AB_2 systems appear. Eight out of the maximum nine transitions are observed.

In the FAB$^+$ mass spectra of these complexes, the molecular cation peaks appear at m/z = 1013 (5%, **9**) and m/z = 951 (12%, **10**). In both spectra the maximum-intensity peak corresponds to m/z = 751 [Au(dppf)]$^+$ (100%).

The crystal structure of complex **9** has been established by X-ray diffraction. The cation is shown in Figure 1. The coordination at the gold atom is to a reasonable approximation trigonal planar, the "bite" of the diphosphine ligand [109.5(1)°] being the major deviation from ideal geometry. The gold atom lies 0.066 Å out of the plane of the three phosphorus atoms. The shortest Au–P bond corresponds to the monodentate phosphine; however, the difference is less significant than that in [{$B_{10}H_{10}C_2$(PPh$_2$)$_2$}AuPPh$_3$]ClO$_4$, in which this distance is appreciably shorter than those to the diphosphine: Au–PPh$_3$ = 2.318(1) Å; Au–P = 2.405(1) and 2.417(1) Å.[19] The Au–P bond lengths 2.343(2)–2.409(2) Å are similar to those found in the [Au(PPh$_3$)$_3$]$^+$ cation.[20,21]

The five-membered rings do not deviate significantly from planarity and deviate only slightly from being parallel (the angle between the best planes of atoms C(81)–C(85) and C(91)–C(95) is 1°). P(1) and P(2) are 0.099 and 0.162 Å out of the cyclopentadienyl rings, respectively, both displaced toward Fe. The cyclopentadienyl rings are staggered by 18° around the Cp···Cp axis defined by the torsion angle C(81)–center–center–C(92); the corresponding angle C(81)–center–center–C(91) is 55°. The distances of the iron atom from the planes of the cyclopentadienyl rings (1.644 and 1.656 Å) compare well with the values reported for other ferrocene moieties, as do the Fe–C distances, 2.019(8)–2.068(9) Å, and P–C distances, P(2)–C(91) = 1.799(8) and P(1)–C(81) = 1.804(8) Å.

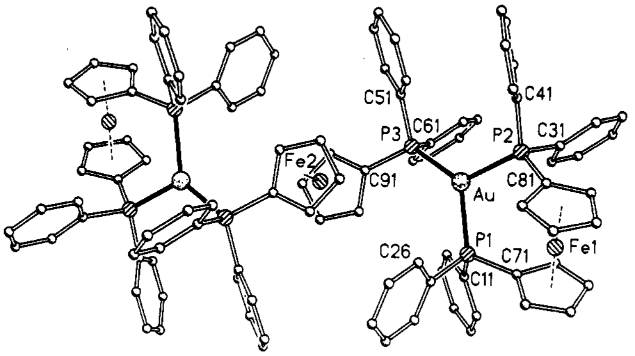
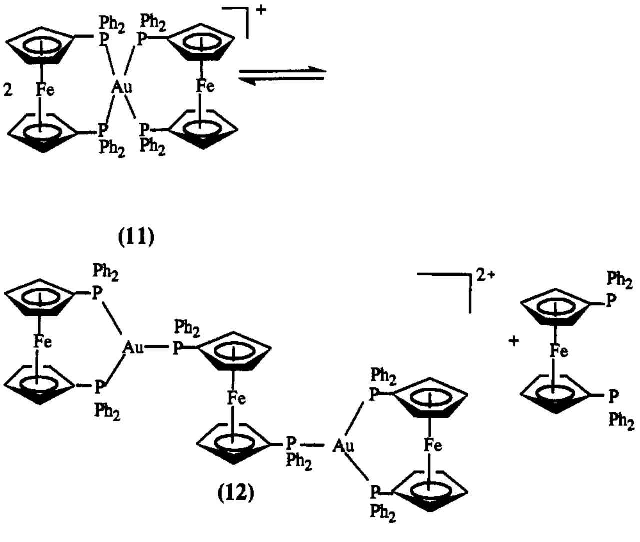


Figure 2. Structure of the cation of complex **12** showing the labeling scheme. Hydrogen atoms are omitted for clarity; atomic radii are arbitrary.

The reaction of 2 equiv of dppf with [Au(tht)$_2$]ClO$_4$ leads to an orange solid. The $^{31}P\{^1H\}$ NMR spectra of this complex display a temperature-dependent behavior, which is indicative of a chemical-exchange process. Thus a single resonance at δ 22.8 and a broad resonance at δ 36 appear at room temperature. Upon cooling, the broad resonance gives rise to an AB_2 system, but the integral ratio between signals does not remain constant. The most abundant species at room temperature is that at δ 22.8; on cooling, the species with the AB_2 pattern increases. The low-temperature pattern is consistent with the presence of one species with all the phosphorus atoms equivalent, as in the four-coordinated [Au(dppf)$_2$]ClO$_4$ (**11**), and the species with an AB_2 system must be in a chemical enviroment similar to that of the three-coordinated complex **9**.

We therefore suggest that the four-coordinated complex [Au(dppf)$_2$]ClO$_4$ (**11**) undergoes a dimerization process via formation of complex **12** which involves bridging and chelating coordination modes and free dppf. The three species have been detected by $^{31}P\{^1H\}$ NMR spectroscopy.



(11)

(12)

In the ^1H NMR spectra, the same temperature dependence is observed for the cyclopentadienyl protons.

The FAB$^+$ mass spectrum shows the molecular cation peak at m/z = 1305 ([Au(dppf)$_2$]$^+$, (7%), and other fragmentations peaks arise from loss of dppf (m/z = 705, Au(dppf)$^+$, 100%) and gold (m/z = 554, dppf, 6%).

The structure of complex **12** was confirmed by X-ray diffraction analysis (Figure 2). Fe(2) lies on a crystallographic inversion center; thus, the asymmetric unit is only half of the formula unit. The compound crystallizes as a 1:2 dichloromethane solvate. The geometry around the gold atom is three-coordinate, with slight deviations from the ideal 120° because of the P(1)–Au–P(2)

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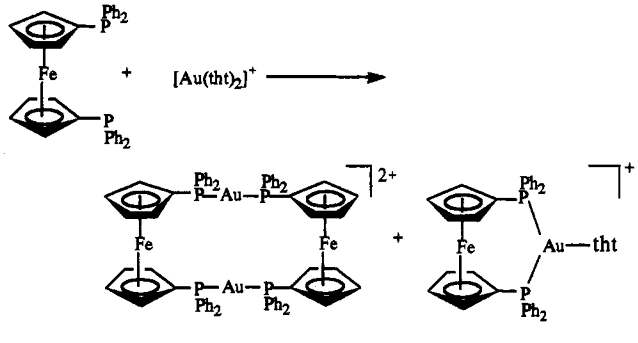
angle of 108.8(1)° imposed by the ligand bite. The gold atom lies 0.073 Å out of the plane of the three phosphorus atoms. The Au–P bond distances are more equal than in complex **9**; Au–P(1) = 2.377(3), Au–P(2) = 2.385(3), and Au–P(3) = 2.332(4) Å, the shortest being to the phosphorus of the bridging diphosphine.

The cyclopentadienyl rings are parallel (exact for Fe(2); dihedral angle 1° for Fe(1)). The rings are staggered by 30° at Fe(1) (torsion angle C(71)–center–center–C(82); cf. C(71)···C(81) = –43°) and the ideal 36° at Fe(2) (C(91)···C(94)′). Other bond distances are similar to thôse found in compound **9** and in other dppf complexes.

When the reaction of dppf and $[Au(tht)_2]ClO_4$ is carried out with equimolecular amounts, the expected dinuclear complex $[Au(dppf)]_2(ClO_4)_2$ (**13**) is obtained, but as a mixture with the three-coordinated compound $[(dppf)Au(tht)]ClO_4$ (**14**).



(**13**) (**14**)

Both complexes can be assigned in the ^1H NMR spectrum which shows two pairs of multiplets in a ratio of 60:40 for the C_5H_4 protons and two further multiplets for the tetrahydrothiophene protons. Proton integration indicates that complex **13** is the major component. In the $^{31}P\{^1H\}$ NMR spectrum, two resonances appear: δ 41.5 assigned to complex **13** and δ 40.3 assigned to complex **14**, according to the accepted change in the chemical shift with coordination number.

However, in the FAB^+ mass spectrum only compound **13** is detected. A low-intensity peak at $m/z = 1602$ corresponds to the species $[Au(dppf)]_2ClO_4^+$ (5%), and other fragments are $[Au(dppf)]_2^+$ ($m/z = 1502$, 5%) and $[Au(dppf)]^+$ ($m/z = 751$, 100%).

Gold(III) Complexes. 1,1′-Bis(diphenylphosphino)ferrocene can also displace the tht ligand in gold(III) complexes to give derivatives with the diphosphine acting as a monodentate, bidentate bridging, or bidentate chelating ligand.

The reaction of $[AuR_3(tht)]$ ($R = C_6F_5$) with 1 or 0.5 equiv of dppf affords the complex $[(dppf)AuR_3]$ (**15**) or $[(dppf)(AuR_3)_2]$ (**16**), respectively.

The ^{19}F NMR spectra for both complexes have a similar pattern since two different C_6F_5 enviroments are observed in general for $[Au(C_6F_5)_3L]$ complexes. The ^1H NMR spectrum of **16** shows two multiplets for the C_5H_4 rings while that of complex **15** shows two multiplets for the $C_5H_4PPh_2$ moiety linked to the gold(III) center and only one resonance for the free $C_5H_4PPh_2$ unit. In the $^{31}P\{^1H\}$ NMR spectra of these compounds, it is easy to distinguish between both coordination modes: complex **15** shows two signals, one of them very close to the free dppf ligand, and for complex **16** only one resonance is observed.

In the FAB^+ mass spectra of compounds **15** and **16**, the molecular cation peaks appear at $m/z = 1252$ (16%, **15**) and $m/z = 1950$ (11%, **16**). The fragment at $m/z = 1252$ for complex **16** corresponds to loss of the AuR_3 fragment.

The reaction of $[AuR_2(tht)_2]ClO_4$ with dppf affords the square planar derivative $[(dppf)AuR_2]ClO_4$ (**17**). The ^1H, ^{19}F, and $^{31}P\{^1H\}$ NMR spectra display the expected resonances: two multiplets for the C_5H_4 rings (^1H), equivalent C_6F_5 groups (^{19}F), indicating the mutual cis disposition, and a multiplet (^{31}P) from coupling with fluorine. The molecular cation peak at $m/z = 1085$ (13%) is observed in the FAB^+ mass spectrum.

Table III. Cyclic Voltammetric Data for the Oxidation of Ferrocenylgold(I) Complexes

complex	E_{pa}/V	E_{pc}/V	$E_{1/2}$/V	i_{pc}/i_{pa}	ΔE_p/mV
$[(dppf)(AuC_6F_5)_2]$	1.02[a,b]	0.942	0.981	1.15	78
$[(dppf)(AuCH_2PPh_2Me)_2](ClO_4)_2$	1.07[a,b]	0.986	1.028	1.13	84
$[(dppf)(AuSCN)_2]$	1.13[a,b]	1.07	1.11	1.19	60
$[(dppf)AuPPh_3]ClO_4$	0.970[a,b]	0.888	0.929	1.25	82
ferrocene			0.47[a,b]		
dppf		0.68[a,b]			
$[ClAu(\mu\text{-dppf})Cr(CO)_5]$	0.810[c,d]	0.729	0.769		81
$[ClAu(\mu\text{-dppf})Mo(CO)_5]$	0.809[c,d]	0.721	0.765		88
$[(dppf)Re(CO)_3Cl]$			0.67[b,c]		

[a] Vs SCE. [b] Scan rate 100 mV s^{-1}. [c] Vs Ag/Ag^+. [d] Scan rate 50 mV s^{-1}.

Table IV. Details of Data Collection and Structure Refinement for Complexes **9** and **12**

chem formula	$C_{53}H_{44}AuCl_4FeO_4P_3$	$C_{104}H_{88}Au_2Cl_6Fe_3O_8P_6$
space group	$P2_1/c$	$C2/c$
a/Å	14.239(6)	32.858(6)
b/Å	16.889(4)	14.821(3)
c/Å	20.866(8)	26.399(5)
β/deg	95.81(3)	128.48(2)
V/Å^3	4992(3)	10063(3)
Z	4	4
D_c/Mg m^{-3}	1.64	1.6
M	1232.4	2425.7
$F(000)$	2448	4816
λ(Mo Kα)/Å	0.710 73	0.710 73
T/°C	–95	–100
μ(Mo Kα)/mm^{-1}	3.6	3.6
transm factor	0.81–0.92	0.26–0.85
R[a]	0.046	0.053
R_w[b]	0.051	0.067

[a] $R = \sum||F_o| - |F_c||\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

Electrochemistry. Although ferrocene undergoes a higly reversible oxidation process, the presence of a diphenylphosphino group on each cyclopentadienyl ring in dppf makes the oxidation of Fe(II) to Fe(III) much more difficult. In fact, the redox pattern for free dppf is much more complicated and the ligand undergoes an essentially reversible one-electron oxidation followed by a fast chemical reaction, involving the phosphorus substituent on the cyclopentadienyl rings, to give dppfO, $dppfO_2$, $dppfH^+$, and $dppfH_2^+$.[22,23]

We have investigated the redox behavior of a selection of each type of complex. All the gold(I) complexes studied showed reversible oxidations at higher potential values than the ferrocene or the free dppf ligand (see Table III; other dppf complexes are included for comparison). This peak is phosphinoferrocene-based, as evidenced from the electrochemistry of dppf-substituted complexes, which give a one-electron transfer with potential values considerably more anodic than that displayed by the uncoordinated ligand.[22-24] The reason that the cathodic to anodic current ratio, i_{pc}/i_{pa}, is higher than 1 could be that the waves are close to the solvent breakdown limit or/and the limited solubility of this type of complexes. The gold(III) derivatives were also studied, but they showed no reversible oxidation waves.

Experimental Section

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} solutions

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Table V. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^4$) for Complex **9**

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Au	2313.7(2)	1756.5(2)	4994.8(1)	232(1)	C(55)	3815(7)	3676(6)	6786(5)	451(24)
Fe	2417.9(8)	−662.3(6)	4980.5(6)	235(3)	C(56)	3014(6)	3591(5)	6334(4)	337(20)
P(1)	2267.4(15)	929.7(13)	5931.7(9)	229(7)	C(61)	2252(6)	3835(5)	4467(4)	277(19)
P(2)	2665.0(15)	975.4(13)	4113.9(9)	226(7)	C(62)	2833(7)	4481(5)	4528(4)	429(23)
P(3)	2146.0(16)	3126.7(12)	5117.0(10)	256(7)	C(63)	2872(7)	5019(6)	4035(5)	520(27)
C(11)	1480(6)	1273(4)	6513(4)	240(18)	C(64)	2326(7)	4905(6)	3463(5)	470(25)
C(12)	1777(6)	1933(5)	6891(4)	308(20)	C(65)	1722(7)	4269(6)	3387(5)	462(25)
C(13)	1156(6)	2284(5)	7271(4)	364(21)	C(66)	1698(6)	3729(5)	3885(4)	370(22)
C(14)	253(7)	1979(5)	7293(4)	404(23)	C(71)	1046(6)	3400(5)	5424(4)	286(19)
C(15)	−35(7)	1310(5)	6929(4)	387(23)	C(72)	809(6)	4198(5)	5514(4)	345(21)
C(16)	595(6)	971(5)	6541(4)	321(20)	C(73)	−52(7)	4376(6)	5739(4)	422(23)
C(21)	3392(5)	821(5)	6420(4)	246(18)	C(74)	−664(7)	3790(5)	5860(4)	431(24)
C(22)	3466(6)	382(5)	6986(4)	314(20)	C(75)	−442(7)	3003(5)	5776(4)	399(24)
C(23)	4317(7)	373(6)	7375(5)	456(25)	C(76)	414(6)	2820(5)	5555(4)	323(20)
C(24)	5083(7)	793(6)	7204(4)	450(25)	C(81)	1852(5)	−43(5)	5684(4)	237(18)
C(25)	5016(7)	1233(5)	6650(4)	411(23)	C(82)	2109(6)	−815(5)	5908(4)	309(20)
C(26)	4167(6)	1252(5)	6250(4)	347(21)	C(83)	1586(6)	−1368(6)	5501(4)	382(22)
C(31)	3603(6)	1425(5)	3708(4)	256(18)	C(84)	1039(6)	−952(5)	5017(4)	320(20)
C(32)	3456(7)	2202(6)	3511(4)	464(25)	C(85)	1183(6)	−137(5)	5127(4)	283(19)
C(33)	4132(7)	2624(6)	3221(5)	530(27)	C(91)	3046(5)	−19(5)	4312(4)	241(18)
C(34)	4994(7)	2263(6)	3164(4)	470(25)	C(92)	3713(6)	−208(5)	4865(4)	271(19)
C(35)	5145(7)	1496(5)	3351(4)	383(23)	C(93)	3773(6)	−1037(5)	4906(4)	307(20)
C(36)	4453(6)	1072(5)	3625(4)	302(20)	C(94)	3165(6)	−1384(5)	4413(4)	323(20)
C(41)	1682(6)	875(5)	3495(4)	282(19)	C(95)	2728(5)	−757(5)	4044(4)	260(19)
C(42)	797(6)	1160(5)	3602(4)	320(21)	Cl(1)	7425(2)	2837(2)	7226(1)	521(9)
C(43)	37(7)	1109(5)	3132(4)	383(22)	O(1)	6980(8)	3492(7)	7511(5)	1265(39)
C(44)	162(7)	777(6)	2557(5)	488(26)	O(2)	6960(8)	2155(8)	7340(6)	1316(41)
C(45)	1035(7)	479(6)	2431(4)	435(24)	O(3)	8301(14)	2923(11)	7209(9)	2274(79)
C(46)	1793(6)	534(5)	2896(4)	346(21)	O(4)	7154(12)	3023(9)	6537(8)	1934(65)
C(51)	3127(5)	3377(5)	5715(4)	279(18)	C(100)	7511(10)	1429(9)	8814(7)	936(45)
C(52)	4035(6)	3262(5)	5530(4)	400(21)	Cl(2)	7073(3)	510(2)	8606(2)	1130(18)
C(53)	4823(7)	3356(6)	5974(4)	456(23)	Cl(3)	8759(3)	1416(3)	8982(2)	1274(22)
C(54)	4701(7)	3564(6)	6601(5)	492(26)	Cl(4)	6973(4)	1807(3)	9479(3)	1637(30)

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for Complex **9**

Au–P(1)	2.409(2)	Au–P(2)	2.357(2)
Au–P(3)	2.343(2)	P(1)–C(11)	1.828(8)
P(1)–C(21)	1.818(8)	P(1)–C(81)	1.804(8)
P(2)–C(31)	1.818(9)	P(2)–C(41)	1.813(8)
P(2)–C(91)	1.799(8)	P(3)–C(51)	1.826(8)
P(3)–C(61)	1.827(8)	P(3)–C(71)	1.811(9)
Fe–C	2.019(8)–2.068(9)		
Fe–cent.	1.645 and 1.656		

P(1)–Au–P(2)	109.5(1)	P(1)–Au–P(3)	118.2(1)
P(2)–Au–P(3)	132.0(1)	Au–P(1)–C(11)	115.1(3)
Au–P(1)–C(21)	114.7(3)	Au–P(1)–C(81)	109.3(3)
Au–P(2)–C(31)	110.7(3)	Au–P(2)–C(41)	113.5(3)
Au–P(2)–C(91)	115.2(3)	Au–P(3)–C(51)	102.9(3)
Au–P(3)–C(61)	123.3(3)	Au–P(3)–C(71)	113.1(3)

with a Philips 9509 conductimeter, and Λ_M is given in Ω^{-1} cm^2 mol^{-1}. C and H analyses were carried out with a Perkin-Elmer 240C microanalyzer. NMR spectra were recorded on Varian XL200 and Varian 300 Unity spectrometers in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^1H), 85% H_3PO_4 (external, ^{31}P), and $CFCl_3$ (external, ^{19}F). Mass spectra were recorded on a VG Autospec, with the FAB technique, using nitrobenzyl alcohol as matrix. 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 supporting electrolyte. Under the present experimental conditions, the ferrocenium/ferrocene couple was located at 0.47 V. The yields, analysis, and conductivities for the new complexes are listed in Table I. All reactions were carried out at room temperature.

Safety Note! 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. [(dppf)(AuX)$_2$] [X = C_6F_5 (1), Cl (2)]. A solution of [Au(C_6F_5)(tht)][25] (0.090 g, 0.2 mmol) or [AuCl(tht)][25] (0.064 g, 0.2 mmol) in dichloromethane (20 mL) was treated with dppf (0.055 g, 0.1 mmol), and the mixture was stirred for 30 min. Solvent was concentrated to ca. 5 mL, and addition of diethyl ether (15 mL) gave complex **1** or **2** as an orange solid. ^{19}F NMR of **1**: δ −116.4 (*o*-F, m), −158.7 [*p*-F, t, *J*(FF) = 19.8 Hz], −162.5 (*m*-F, m).

[(dppf)(AuL)$_2$](ClO$_4$)$_2$ [L = CH_2PPh_3 (3), CH_2PPh_2Me (4), CH_2PPhMe_2 (5)]. To a dichloromethane solution (30 mL) of [Au(tht)(CH_2PPh_3)]ClO_4[26] (0.132 g, 0.2 mmol), [Au(tht)(CH_2PPh_2Me)]ClO_4[26] (0.119 g, 0.2 mmol), or [Au(tht)(CH_2PPhMe_2)]ClO_4[26] (0.107 g, 0.2 mmol) was added dppf (0.055 g, 0.1 mmol). The mixture was stirred for 1 h, and then the solution was concentrated to ca. 5 mL. Addition of diethyl ether (15 mL) gave complex **3** or **4** or **5** as a yellow solid.

[(dppf)(AuSCN)$_2$] (6). A solution of complex **2** (0.204 g, 0.2 mmol) in CH_2Cl_2 (15 mL)–acetone (10 mL) was treated with KSCN (0.039, 0.4 mmol), the mixture was stirred for 1 h. The solution was filtered through Celite and the solvent evaporated to ca. 5 mL. Addition of diethyl ether afforded a yellow solid of complex **6**.

[(dppf)(Au(tht))$_2$](ClO$_4$)$_2$ (7). To a dichloromethane (20 mL) solution of complex **2** (0.204 g, 0.2 mmol) was added O_3ClOAg(tht)[27] (0.118 g, 0.4 mmol), and the suspension was stirred for 2 h. The suspension was filtered through Celite to remove precipitated AgCl, and the yellow filtrate was concentrated to ca. 10 mL. Addition of diethyl ether (25 mL) led to complex **7** as a yellow solid.

[(dppf)AuCl] (8). To a solution of [AuCl(tht)] (0.064 g, 0.2 mmol) in dichloromethane (20 mL) was added dppf (0.111 g, 0.2 mmol), and the mixture was stirred for 30 min. The solution was evaporated to ca. 10 mL, and addition of diethyl ether (15 mL) led to compound **8** as a yellow solid

[(dppf)AuPR$_3$]ClO$_4$ [PR$_3$ = PPh$_3$ (9), PPh$_2$Me (10)]. To a dichloromethane (20 mL), solution of [Au(tht)PPh_3]ClO_4[28] (0.130 g, 0.2 mmol) or [Au(tht)PPh_2Me]ClO_4[28] (0.117 g, 0.2 mmol) was added dppf (0.111 g, 0.2 mmol), and the mixture was stirred for 2 h. The solvent was evaporated to ca. 5 mL, and addition of diethyl ether (15 mL) gave complex **9** or **10** as a yellow solid.

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Table VII. Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Coefficients (Å² × 10⁴) for Complex **12**

	x	*y*	*z*	*U*(eq)[a]		*x*	*y*	*z*	*U*(eq)[a]
Au	6688.3(1)	5393.6(3)	5425.0(2)	278(2)	C(55)	8438	4379	6006	571(33)
Fe(1)	6265.7(5)	5398(1)	6621.9(6)	272(7)	C(56)	7960	4763	5764	409(25)
Fe(2)	7500	7500	5000	405(14)	C(51)	7566	4822	5097	349(23)
P(1)	6097(1)	6434(2)	5339(1)	271(14)	C(62)	6395(3)	3857(4)	4139(2)	384(24)
P(2)	6859(1)	4215(2)	6150(1)	284(15)	C(63)	6009	3353	3599	514(30)
P(3)	6970(1)	5390(2)	4804(1)	306(14)	C(64)	5692	3756	2990	495(29)
C(12)	5064(2)	7037(4)	4407(2)	338(23)	C(65)	5761	4664	2920	510(28)
C(13)	4623	7219	3775	369(24)	C(66)	6146	5168	3460	450(28)
C(14)	4613	6986	3255	414(26)	C(61)	6464	4764	4069	319(22)
C(15)	5044	6570	3367	444(27)	C(72)	5903(3)	6620(3)	6271(3)	339(22)
C(16)	5484	6388	3999	295(21)	C(73)	5663	6109	6476	317(22)
C(11)	5494	6622	4519	244(19)	C(74)	5472	5298	6111	337(23)
C(22)	6085(2)	8337(5)	5392(3)	702(39)	C(75)	5593	5307	5681	299(21)
C(23)	6318	9168	5673	835(46)	C(71)	5860	6124	5780	264(20)
C(24)	6840	9205	6220	524(30)	C(82)	7046(3)	5438(4)	7107(3)	337(21)
C(25)	7128	8412	6487	511(30)	C(83)	6942	5534	7553	389(24)
C(26)	6895	7581	6205	419(26)	C(84)	6670	4753	7505	369(23)
C(21)	6374	7544	5658	303(22)	C(85)	6605	4175	7031	319(22)
C(32)	6448(2)	2501(4)	6035(2)	367(24)	C(81)	6838	4598	6785	288(20)
C(33)	6089	1806	5691	459(28)	C(92)	7242(3)	6676(5)	4235(4)	516(30)
C(34)	5663	1929	5041	536(31)	C(93)	7116	7582	4012	683(38)
C(35)	5598	2745	4735	494(29)	C(94)	6796	7933	4156	596(34)
C(36)	5957	3440	5079	393(25)	C(95)	6724	7245	4468	507(30)
C(31)	6383	3318	5729	301(22)	C(91)	7000	6468	4516	397(25)
C(42)	7520(2)	2986(4)	6198(2)	380(24)	Cl(1)	1648(1)	3810(2)	2560(1)	533(18)
C(43)	7999	2572	6481	456(27)	O(1)	1253(4)	3976(10)	2623(6)	1224(96)
C(44)	8425	2783	7116	493(29)	O(2)	2135(3)	4096(5)	3149(3)	523(51)
C(45)	8372	3407	7468	512(30)	O(3)	1685(5)	2884(6)	2482(5)	1245(101)
C(46)	7893	3820	7185	394(25)	O(4)	1536(4)	4306(6)	2026(4)	805(67)
C(41)	7467	3610	6550	292(21)	Cl(2)	−151(4)	4791(7)	4251(5)	1121(31)
C(52)	7650(3)	4497(5)	4673(2)	476(28)	Cl(3)	−195(5)	6135(9)	3306(6)	1397(40)
C(53)	8128	4114	4915	577(33)	Cl(4)	265(4)	3641(8)	2741(6)	1375(41)
C(54)	8522	4054	5582	658(37)	Cl(5)	627(6)	3890(10)	3717(7)	1543(46)

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

Table VIII. Selected Bond Lengths (Å) and Angles (deg) for Complex **12**

Au–P(1)	2.377(3)	Au–P(2)	2.385(3)
Au–P(3)	2.332(4)	P(1)–C(11)	1.831(5)
P(1)–C(21)	1.813(8)	P(1)–C(71)	1.819(11)
P(2)–C(31)	1.814(6)	P(2)–C(41)	1.812(7)
P(2)–C(81)	1.813(10)	P(3)–C(51)	1.805(8)
P(3)–C(61)	1.838(5)	P(3)–C(91)	1.797(9)
Fe–C	2.015(7)–2.076(7)		
Fe(1)–cent.	1.662 and 1.651		
Fe(2)–cent.	1.655		
P(1)–Au–P(2)	108.8(1)	P(1)–Au–P(3)	126.3(1)
P(2)–Au–P(3)	124.3(1)	Au–P(1)–C(21)	113.6(3)
Au–P(1)–C(11)	115.5(3)	Au–P(1)–C(71)	115.1(2)
Au–P(2)–C(31)	111.3(2)	Au–P(2)–C(41)	117.0(3)
Au–P(3)–C(51)	120.0(3)	Au–P(3)–C(61)	104.4(3)

[Au(dppf)$_2$]ClO$_4$ (11) and [(dppf)Au(μ-dppf)Au(dppf)](ClO$_4$)$_2$ (12). A mixture of [Au(tht)$_2$]ClO$_4$[28] (0.094 g, 0.2 mmol) and dppf (0.222 g, 0.4 mmol) in dichloromethane (20 mL) was stirred for 2 h. The solvent was evaporated in vacuo to ca. 5 mL, and addition of diethyl ether gave complex **11** as a yellow solid. Compound **12** was obtained by slow diffusion of diethyl ether into a dichloromethane solution of **11**.

Crystal Structure Determinations of Compounds 9 and 12. The following conditions were common to the structure determinations of both complexes: Siemens R3 diffractometer with an LT-2 low-temperature attachment, monochromated Mo Kα radiation, absorption correction based on ψ-scans, cell constants refined from setting angles of 50 reflections in the range 2θ = 20–23°; solutions by the heavy-atom method, full-matrix least-squares refinement on *F* (program system Siemens SHELXTL-PLUS).[29] Au, Fe, P, and Cl atoms were refined anisotropically. H atoms were included using a riding model. Further details are given in Table IV. Atomic positional parameters for **9** are listed in Table V and Table VI contains selected bond lengths and angles. Final atomic coordinates for complex **12** are given in Table VII, with selected bond lengths and angles in Table VIII.

Further Syntheses. [Au(dppf)]$_2$(ClO$_4$)$_2$ (13) and [(dppf)Au(tht)]ClO$_4$ (14). A mixture of [Au(tht)$_2$]ClO$_4$ (0.094 g, 0.2 mmol) and dppf (0.111 g, 0.2 mmol) in dichloromethane (20 mL) was stirred for 30 min. The solvent was evaporated in vacuo to ca. 5 mL, and addition of diethyl ether (15 mL) gave a mixture of complexes **13** and **14** as yellow-orange solids.

[(dppf)Au(C$_6$F$_5$)$_3$] (15). To a solution of [Au(C$_6$F$_5$)$_3$tht][30] (0.157 g, 0.2 mmol) in dichloromethane (20 mL) was added dppf (0.111 g, 0.2 mmol), and the mixture was stirred for 30 min. The solution was evaporated to ca. 5 mL, and addition of *n*-hexane (15 mL) gave a yellow solid of complex **15**. ^{19}F NMR: δ −119.9 and −121.9 (*o*-F, m), −158.2 (*J*(FF) = 19.2 Hz) and −157.8 (*J*(FF) = 19.9 Hz) (*p*-F, t), −161.5 and -161.7 (*m*-F, m).

[(dppf){Au(C$_6$F$_5$)$_3$}$_2$] (16). A dichloromethane solution (20 mL) containing [Au(C$_6$F$_5$)$_3$tht] (0.157 g, 0.2 mmol) and dppf (0.055 g, 0.1 mmol) was stirred for 1 h. The solution was evaporated to ca. 5 mL, and addition of diethyl ether (15 mL) gave compound **16** as a yellow powder. ^{19}F NMR: δ −119.0 and −122.1 (*o*-F, m), −154.2 (*J*(FF) = 19.6 Hz) and −153.5 (*J*(FF) = 19.3 Hz) (*p*-F, t), −161.5 and −162.0 (*m*-F, m).

[(dppf)Au(C$_6$F$_5$)$_2$]ClO$_4$ (17). A mixture of [Au(C$_6$F$_5$)$_2$(tht)$_2$]ClO$_4$[31] (0.161 g, 0.2 mmol) and dppf (0.111 g, 0.2 mmol) in dichloromethane (20 mL) was stirred for 1 h. The solvent was evaporated to ca. 5 mL, and addition of diethyl ether afforded complex **17** as an orange-red solid. ^{19}F NMR: δ −122.5 (*o*-F, m), −154.1 (*J*(FF) = 20.0 Hz) (*p*-F, t), −158.3 (*m*-F, m).

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Supplementary Material Available: Addition ORTEP diagrams and tables of crystal data, data collection, and solution and refinement parameters, hydrogen atomic coordinates, bond distances and angles, and thermal parameters (15 pages). Ordering information is given on any current masthead page.

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