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New Iron(II)- and Gold(I)-Containing Metallocenes. X-ray Structure of a Three-Coordinate Gold(I) Ferrocenophane-Type Representative

Manuella Viotte,[†] Bernard Gautheron,[*,†] Marek M. Kubicki,[†] Yves Mugnier,[†] and Richard V. Parish[‡]

Laboratoire de Synthèse et d'Electrosynthèse Organométalliques, URA CNRS No. 1685, Université de Bourgogne, BP 138, 21004 Dijon Cèdex, France, and Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD, U.K.

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The metallophosphines 1,1′-bis(diphenylphosphino)octamethylferrocene (dppomf) (**5**) and (1,1′-octamethylferrocenediyl)phenylphosphane (**4**) have been synthesized by reacting $FeCl_2$ with lithium (diphenylphosphino)tetramethylcyclopentadienide and bis(tetramethylcyclopentadienyl)phenylphosphine dilithium salt, respectively. When **5** was reacted with ClAu(tht) (tht = tetrahydrothiophene) in a 1:2 ratio, **6** was obtained in which one AuCl unit is coordinated to each phosphine group. The proportion 1:1 led to the three-coordinate gold(I) monomer complex **7**, of which the X-ray structure has been established. It crystallizes in space group $P2_1/c$, monoclinic, with $a = 23.153(4)$ Å, $b = 9.070(4)$ Å, $c = 20.414(3)$ Å, $\beta = 114.2(1)°$, and $Z = 4$. The gold atom is trigonal planar, the Au−P and Au−Cl bond lengths are greater than those in linear P−Au−Cl complexes. The cyclopentadienyl rings are planar, parallel, and staggered by 17°, and the methyl substituents deviate slightly both sides from the plane. The pseudotriplets observed in ^{13}C NMR for the cyclopentadienyl part are the result of long-range coupling with the two phosphorus atoms through gold. The stability of **7** in solution is shown by finding the same spectrum again after several hours. Electrochemistry showed the formation of Fe(III) derivatives of the metallophosphine gold(I) complexes, which can also be obtained by direct reaction of the precursors with electrochemically generated $[Cp_2Fe]^+$. The ^{197}Au Mössbauer parameters for **6** and **8** are typical for linear two-coordination of gold(I), and the particularly small IS value for **7** can be explained by the strained P−Au−P angle which decreases the s-character of the P−Au bond. The reactivity of **6** and **7** was shown by the substitution of the chlorine atoms by the nucleophile $C_6F_5^-$ affording the fluorine-containing complexes **8** and **9**, respectively. Compound **9** represents the first example of a P−Au(−P)−C tricoordinate gold(I). Complexes **5**−**8** have been tested *in vitro* against various human cancer cells. The cytotoxicity, although improved by the presence of gold, is not better than that of drugs already known.

Introduction

The metallophosphine 1,1′-bis(diphenylphosphino)ferrocene (dppf) has been widely used as a mono- and diphosphine ligand in the synthesis of heteropolymetallic complexes.[1−6] A large range of metals has been employed but relatively few studies have been devoted to gold(I) metallocene derivatives[7−11] in spite of their potential interest. For example, some of them have been used as catalysts for enantioselective aldol reactions[9,12] and both gold(I) complexes and ferrocene compounds show *in vitro* and *in vivo* therapeutic activity as antiarthritic and antitumoral agents,[11,13−19] although one article[11] has discussed the relatively poor effect of [dppf(AuCl)$_2$] against the specific experimental tumors tested.

Two recent publications on [(dppf)Au(I)] complexes[20a,b] deal with results closely related to our preliminary communication.[21] We report now the full results we have obtained on gold(I)-containing ferrocene.

Our contribution in this area deals with gold(I) complexes of the crowded metallocenobiphosphine 1,1′-bis(diphenylphos-

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[*] To whom correspondence should be addressed.

[†] Université de Bourgogne.

[‡] University of Manchester Institute of Science and Technology.

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phino)octamethylferrocene (dppomf), a bifunctional ligand published few years ago.[22,23] Compared to the dppf analogs, a different behavior is expected in this case regarding the ligand properties (and hopefully the biological activity) due to the electronic releasing effect of the methyl groups. In addition, the NMR signals of these substituents represent a convenient reference which can be used to follow reactions and to establish the purity of the complexes prepared. The solubility of the complexes is also increased by substitution which is of interest for therapeutic applications. Besides dppomf, we have also prepared the hitherto unknown (1,1′-octamethylferrocenediyl)-phenylphosphane (**4**) and studied the capability of its phosphorus atom to coordinate gold(I).

Experimental Section

Materials. $Na[AuCl_4]\cdot 2H_2O$ was a generous gift from Johnson Matthey Technology Centre, Blount's Court, Reading RG4 9NH, U.K. The reagents [(tht)AuCl],[24] $[C_6F_5Li]$,[25] and $[(tht)AuC_6F_5]$[26] were prepared as reported in the literature.

The compounds synthesized are shown in Schemes 1 and 2.

General Procedures. All reactions were conducted under an atmosphere of pure dry argon. Solvents were dried and deoxygenated over sodium/benzophenone ketyl and distilled immediately before use. Transfers were carried out via syringes or cannulas.

Microanalyses were performed by the Microanalysis Centre in UMIST (Manchester, U.K.). Melting points were determined with a Kofler apparatus without correction. ^1H, $^{13}C\{^1H\}$, ^{19}F, and ^{31}P nuclear magnetic resonance spectra were recorded in $CDCl_3$ with a Bruker AC 200 spectrometer operating at 200.0, 50.3, 187.8, and 81.0 MHz, respectively. Chemical shifts are reported in δ units, parts per million downfield from internal tetramethylsilane for ^1H and $^{13}C\{^1H\}$, from external $CFCl_3$ for ^{19}F, and from external H_3PO_4 for ^{31}P. The EPR spectra were obtained with a Bruker ESP 300 apparatus coupled to a Microware computer (calibration with *N,N′*-diphenylpycrylhydrazyl radical: $g = 2.0036$). Complexes reported are air- and moisture-stable after being isolated.

^{197}Au Mössbauer Spectroscopy. The Mössbauer spectra were obtained in the Technische Universität München (Garching, Germany). The ^{197}Pt activity feeding the 77.3 keV Mössbauer transition was produced by neutron irradiation of enriched ^{196}Pt metal. Both source and absorber were kept at 4.2 K, and a sinusoidal velocity wave form and an intrinsic Ge detector were used. A sample of the absorber with ca. 50 mg of Au/cm^{-2} was used, and spectra were fitted to Lorentzian lines.

Electrochemistry. All manipulations were performed in an atmosphere of dry nitrogen or argon. Tetrahydrofuran was distilled under argon from sodium/benzophenone. CH_2Cl_2 was purified by simply passing the solvent through a column packed with alumina previously dried at 120 °C; it was deoxygenated by bubbling argon immediately before use. Tetrabutylammonium hexafluorophosphate was purchased from Fluka and degassed before use.

In cyclic voltammetry experiments the concentration of **4**−**7** was about 10^{-3} M. Voltammetric analyses were carried out in a standard three-electrode cell with a Tacussel UAP4 unit cell. The reference electrode was a saturated calomel electrode separated from the solution by a sintered glass disk. The auxiliary electrode was a platinum wire, and for all voltammetric measurements the working electrode was a vitreous carbon electrode. The controlled potential electrolyses were performed with an Amel 552 potentiostat coupled to an Amel 721 electronic integrator. Large scale electrolyses were performed in a cell with three compartments separated with a fritted glass of medium porosity. A carbon gauze was used as the cathode, a platinum plate as the anode, and a saturated calomel electrode as the reference electrode. The electrolyte was either tetrahydrofuran or methylene chloride 0.2 M in tetrabutylammonium hexafluorophosphate.

Crystal Structure Analysis of 7. Crystals of **7** were grown from toluene solution. A yellow irregularly shaped crystal of approximate dimensions 0.20 × 0.15 × 0.10 mm was mounted on an Enraf-Nonius CAD 4 diffractometer. The pertinent crystal data and data collection parameters are given in Table 1.

Table 1. Crystallographic Data for (dppomf)AuCl·$^1/_2$toluene (**7**)

formula $C_{45.5}H_{48}AuClFeP_2$	fw 945.10
$a = 23.153(4)$ Å	space group $P2_1/c$ (No. 14)
$b = 9.070(4)$ Å	$\varrho_{calc} = 1.527$ g mL^{-1}
$c = 20.414(3)$ Å	$\lambda = 0.710\,73$ Å
$\beta = 114.2(1)°$	μ(Mo Kα) = 42.5 cm^{-1}
$V = 3909.7$ Å^3	$R(F) = 0.036^a$
$Z = 4$	$R_w(F) = 0.041^b$
$T = 20$ °C	GOF = 1.226^c

[a] $R(F) = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w(F) = \{\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2\}^{1/2}$, where $w = 1/[\sigma^2(F) + gF^2]$ ($g = 0.00139$). [c] $GOF = [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

The unit cell was determined and refined from 25 randomly selected reflections ($8 < \theta < 17°$) obtained by use of the CAD4 routines. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction (ψ scan) was made. The Enraf-Nonius SDP library was used for data reductions, and the solution and refinement of the structure were performed with SHELX76 programs (G. M. Sheldrick, University of Cambridge, Cambridge, U.K., 1976). The structure was solved and refined by conventional three-dimensional Patterson, difference Fourier, and full-matrix least-squares methods. All non-hydrogen atoms in the organometallic molecule were refined with anisotropic temperature factors to $R = 0.046$. A difference Fourier synthesis revealed the presence of five peaks near a symmetry center ($^1/_2$, 0, $^1/_2$). They correspond to a highly disordered molecule of toluene. Because the multiplicity of this special position is two, there are two molecules of toluene in the unit cell per four organometallic molecules. The carbon atoms of toluene were introduced in final refinements with isotropic temperature factors. The final difference Fourier synthesis shows the highest peak (1.02 e/Å^3) close to the Au atom (0.84 Å). Other peaks (0.40−0.55 e/Å^3) are found near the carbon atoms of the disordered molecule of toluene. No significant peak could be assigned to the hydrogen atom. Thus, because we are not able to calculate the positions of 24 hydrogens of the groups present on the Cp rings (CH_3 bound to sp^2 carbon atoms) from a total of 44 in the organometallic molecule, no attempt was made to introduce the hydrogens in the model. Final atomic coordinates are given in Table 2.

Antitumor Testing. Antitumor activity was assessed on an *in vitro* panel of seven human tumor cell lines: colon carcinoma (SW620 and SW1116), breast carcinoma (ZR-75-1), bladder carcinoma (HT1376), ovarian carcinoma (SK-OV-3 and PA-1), and colon carcinoma (LS174T). Cell cultures were grown in suitable medium as monolayers at 37 °C in a 5% CO_2 atmosphere and seeded with a suspension of the tumor cells. After a 72 h culture, the total cell protein was determined using sulforhodamine B.[27]

The IC_{50}, the concentration of test compound giving 50% survival with respect to controls, was calculated from the dose/response curves.

(1,1′-Octamethylferrocenediyl)phenylphosphane (4). A solution of Cl_2PPh (1.76 mL, 12.95 mmol) in diethyl ether (20 mL) was added to a stirred suspension of **1** (3.32 g, 25.91 mmol) in diethyl ether (150 mL). Stirring was maintained at room temperature for 1 night. The solid (LiCl) was filtered off, and BuLi in hexane (1.65 M, 15.71 mL, 25.91 mmol) was added to the yellow filtrate at −40 °C. The mixture was stirred overnight at room temperature, and the white solid formed (3.50 g) was dissolved in THF (80 mL). This solution was added

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Table 2. Atomic Coordinates ($\times 10^4$) and B_{eq}[a] Values for (dppomf)AuCl·$^1/_2$toluene (**7**)

atom	*x*	*y*	*z*	B_{eq} (Å^2)
Au	7636(0)	13(0)	3125(0)	3.16(1)
Fe	7674(1)	854(1)	1169(1)	2.47(3)
Cl	7629(2)	−1044(3)	4219(1)	6.29(11)
P1	6811(1)	1244(2)	2233(1)	2.77(6)
P2	8568(1)	−251(2)	2943(1)	2.69(6)
C1	6893(3)	1155(8)	1386(4)	2.63(22)
C2	6924(3)	2307(8)	902(4)	2.99(23)
C3	6901(3)	1582(9)	273(4)	3.12(23)
C4	6866(3)	34(9)	358(4)	3.37(22)
C5	6861(3)	−253(8)	1036(4)	2.91(23)
C21	6962(4)	3957(9)	1011(5)	3.99(29)
C31	6900(4)	2367(11)	−392(4)	4.69(32)
C41	6805(4)	−1107(11)	−211(4)	4.34(29)
C51	6797(4)	−1741(9)	1335(4)	3.64(28)
C6	8488(3)	311(7)	2055(3)	2.47(21)
C7	8511(3)	1814(8)	1852(4)	2.81(22)
C8	8472(3)	1803(9)	1137(4)	3.02(24)
C9	8414(3)	348(10)	897(4)	3.43(25)
C10	8414(3)	−604(9)	1454(4)	2.84(22)
C71	8594(4)	3170(9)	2311(4)	4.08(29)
C81	8527(4)	3181(10)	737(4)	4.67(31)
C91	8393(5)	−152(11)	175(4)	4.93(32)
C101	8334(4)	−2258(10)	1395(5)	4.47(31)
C111	6732(3)	3167(9)	2439(4)	3.07(24)
C112	7249(4)	3823(9)	3002(4)	3.49(26)
C113	7195(5)	5298(10)	3183(5)	4.64(36)
C114	6652(5)	6080(10)	2800(5)	4.30(32)
C115	6144(5)	5443(11)	2243(6)	5.18(40)
C116	6188(4)	3968(10)	2071(5)	4.27(30)
C121	6013(4)	529(9)	1995(5)	3.53(27)
C122	5886(5)	−64(11)	2555(6)	5.30(36)
C123	5288(6)	−645(15)	2404(8)	7.60(55)
C124	4820(6)	−610(15)	1701(8)	7.14(49)
C125	4955(4)	−46(12)	1178(6)	5.63(36)
C126	5554(4)	512(11)	1303(5)	4.48(29)
C211	8964(4)	−2050(9)	3107(4)	3.38(25)
C212	8763(5)	−3062(10)	3479(4)	4.54(31)
C213	9122(7)	−4400(11)	3717(5)	5.86(41)
C214	9667(6)	−4614(12)	3604(6)	5.91(40)
C215	9846(5)	−3608(11)	3234(5)	5.00(33)
C216	9504(4)	−2331(10)	2984(4)	4.09(28)
C221	9220(3)	825(8)	3592(3)	2.84(23)
C222	9173(4)	1248(9)	4216(4)	4.05(28)
C223	9698(6)	1862(12)	4771(5)	5.71(38)
C224	10270(5)	2007(11)	4728(5)	5.29(35)
C225	10312(4)	1636(11)	4082(5)	5.12(34)
C226	9789(4)	1039(10)	3516(5)	4.17(29)
CT1[b]	4423(11)	693(26)	5522(12)	11.03(56)
CT2	5037(7)	−1236(18)	5228(8)	6.55(32)
CT3	4742(13)	−872(33)	5528(14)	5.94(57)
CT4	5317(13)	−1564(30)	4943(14)	5.56(56)
CT5	4756(13)	236(30)	5268(15)	5.37(55)

[a] *B* values for anisotropically refined atoms are given in the form of the isotropic equivalent parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$. [b] CT indicates the carbon atoms of the disordered toluene molecule.

dropwise to a brown suspension of $FeCl_2$ (1.25 g, 9.86 mmol) in THF (100 mL) at room temperature. The mixture was stirred for 12 h and then hydrolyzed and extracted with diethyl ether. The solvent was taken off, giving 1.55 g (40%) of a brown solid, which was recrystallized from heptane. Anal. Calcd for $C_{24}H_{29}FeP$: C, 71.3; H, 7.2. Found: C, 71.0; H, 7.1. Mp: 206 °C.

[dppomf(AuCl)$_2$] (6). A solution of dppomf (**5**) (0.121 g, 0.182 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of [(tht)AuCl] (0.116 g, 0.363 mmol) in CH_2Cl_2 (20 mL) at 0°C. Stirring was maintained a few hours while the solution warmed slowly to room temperature. The orange solution was then concentrated to 5 mL, and MeOH (10 mL) was added. The orange microcrystalline solid formed was isolated, washed with 3 × 5 mL MeOH, and crystallized from toluene yielding 0.127 g (0.033 mmol, 62%) of orange crystals. Anal. Calcd for $C_{42}H_{44}Au_2Cl_2FeP_2$: C, 44.6; H, 3.9. Found: C, 44.3; H, 3.8. Mp: >260 °C.

Compound **6** can also be prepared by adding **7** (0.009 g, 0.010 mmol) in CH_2Cl_2 (10 mL) to [(tht)AuCl] (0.003 g, 0.010 mmol) in CH_2Cl_2 (10 mL) at room temperature. The product was isolated as above.

[dppomf(AuCl)] (7). A solution of dppomf (**5**) (0.107 g, 0.161 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of [(tht)AuCl] (0.052 g; 0.161 mmol) in CH_2Cl_2 (20 mL) at 0 °C. The orange solution was allowed to warm slowly to room temperature and was concentrated under reduced pressure. MeOH (5 mL) was added to precipitate the small amount of **6** formed together with **7**. The solution was separated from the solid. The solvent was removed, and the solid residue was crystallized from toluene yielding 0.107 g (0.119 mmol, 73.7%) of orange crystals containing included toluene. Anal. Calcd for $C_{42}H_{44}AuClFeP_2{\cdot}0.5C_6H_5CH_3$: C, 57.8; H, 5.1. Found: C, 58.2; H, 5.4. Mp: 256 °C, followed by decomposition.

[dppomf(AuC$_6$F$_5$)$_2$] (8). A solution of dppomf (**5**) (0.102 g, 0.152 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a solution of [(tht)AuC$_6$F$_5$] (0.138 g, 0.305 mmol) in CH_2Cl_2 (20 mL) at 0 °C. Stirring was maintained for a few hours during which the solution came slowly to room temperature, and the solution was then evaporated to dryness. The solid residue was crystallized from CH_2Cl_2/CH_3CN yielding 0.091 g (0.065 mmol, 43%) of orange crystals. Anal. Calcd for $C_{54}H_{44}Au_2F_{10}FeP_2$: C, 46.5; H, 3.2. Found: C, 46.5; H, 3.0. ^{19}F NMR: δ −115.8 to −115.5 (m, 4F, *o*-F), −158.4 (t, 2F, *p*-F, $^3J_{F-F}$ = 20.1 Hz), −162.5 to −162.1 (m, 4F, *m*-F). Mp: 266 °C.

Compound **8** can also be prepared by addition of **6** (0.100 g, 0.088 mmol) in CH_2Cl_2 (40 mL) to a suspension of a slight excess of [C_6F_5-Li] in diethyl ether at −78 °C. The solution was then allowed to warm to room temperature. The solvent was evaporated to dryness, and the residue was crystallized from toluene.

[dppomf(AuC$_6$F$_5$)] (9). A solution of [(tht)AuC$_6$F$_5$] (0.029 g, 0.064 mmol) in CH_2Cl_2 (10 mL) was added to a solution of dppomf (**5**) (0.043 g, 0.064 mmol) in CH_2Cl_2 (10 mL) at 0°C. Stirring was maintained for a few hours during which the solution warmed slowly to room temperature, and the solution was then evaporated to dryness, affording orange crystals. ^1H, ^{31}P, and ^{19}F NMR of this orange solid show a mixture of compounds **9**, **8**, and **5**. ^{19}F NMR of **9**: δ −114.7 to −114.4 (m, 4F, *o*-F), −159.8 (t, 2F, *p*-F, $^3J_{F-F}$ = 20.3 Hz), −162.5 to −162.1 (m, 4F, *m*-F).

Results

Preparation of the Compounds. The anion **1**[22] is the common starting reagent for preparing the two tertiary phosphines **2** and **3** (Scheme 1) by reaction with $ClPPh_2$ and Cl_2PPh, respectively, at room temperature. As is commonly observed for tertiary phosphines, **2** and **3** show a great tendency to oxidize. They were converted, without isolation, into their lithium salts at low temperature, and the metallocenophosphines **4** and **5** were finally obtained by reaction with $FeCl_2$.

Compound **4** is a new member of the ferrocenophane family; previous examples have bridging atoms drawn from groups 14 (Si, Ge) or 15 (P, As)[28−31] or group 4 (Zr).[32] Although very strained by the short bridge and sterically congested by the methyl groups, **4** was obtained in a reasonable yield (40%).

In contrast to the unsubstituted series,[30] the direct reaction of Cl_2PPh on the octamethylferrocene dilithium/TMEDA salt did not lead to complex **4**. Instead, a viscous mixture was formed from which no definite compound could be characterized. The preparation and characterization of compound **5** are described elsewhere.[33]

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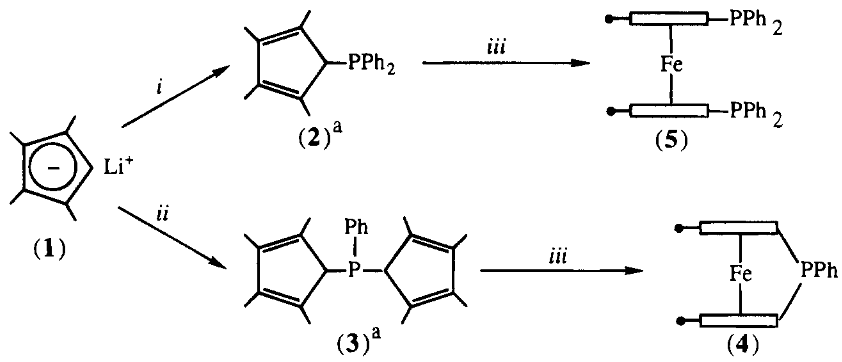
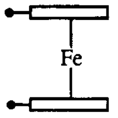
Scheme 1

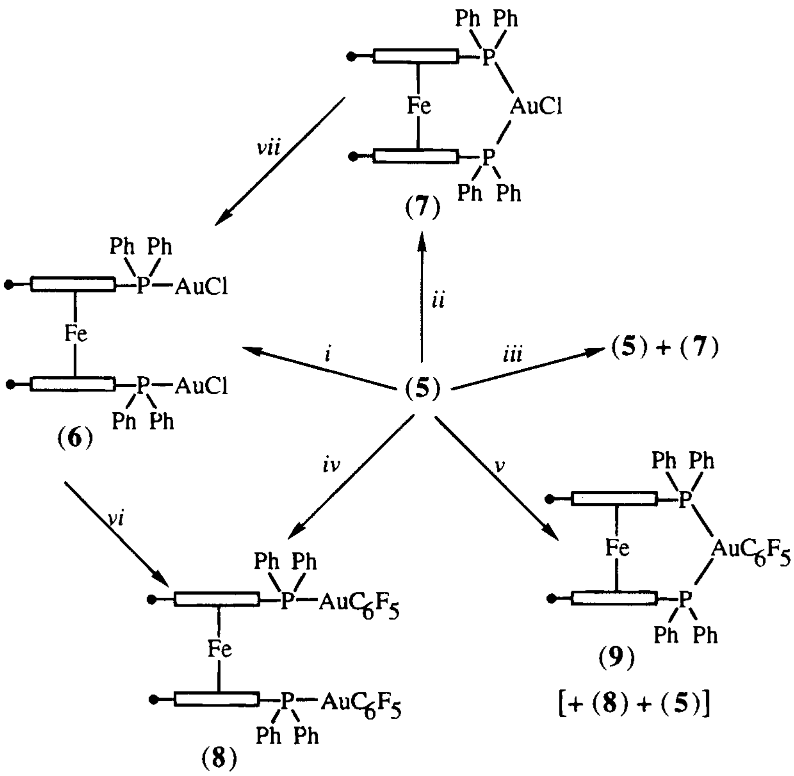


i) $ClPPh_2$; *ii*) Cl_2PPh ; *iii*) 1) BuLi, 2) $FeCl_2$
a) mixture of isomers



= $(\eta^5\text{-}C_5Me_4)_2Fe$

Scheme 2



i) ClAu(tht) [Fe/Au = 1:2], *ii*) ClAu(tht) [Fe/Au = 1:1]
iii) ClAu(tht) [Fe/Au = 2:1], *iv*) C_6F_5Au(tht) [Fe/Au = 1:2]
v) C_6F_5Au(tht) [Fe/Au = 1:1], *vi*) C_6F_5Li, *vii*) ClAu(tht)

When the gold salt [ClAu(tht)] (tht: tetrahydrothiophene)[26] was reacted with dppomf, two types of complexe were obtained depending on the Fe/Au ratio used (Scheme 2).

At a ratio of 1:2, the trimetallic species [dppomf$(AuCl)_2$] (**6**) was formed by the replacement of tht by the metallophosphine ligand. The presence of two gold atoms is shown by the unique ^{31}P NMR signal and, above all, by the microanalysis and the conversion **7** → **6**.

A 1:1 stoichiometry afforded the bimetallic species **7** instead of a simple substitution of the tht by only one phosphorus atom leaving gold bicoordinated. The gold atom in complex **7** appeared three-coordinate from the single crystal X-ray analysis and ^{197}Au Mössbauer spectroscopy (see below). This situation contrasts strongly with that for the nonmethylated metallocenophosphine which is reported to give rise to a polymeric structure.[15,20a,b]

The substitution of the chlorine atoms in **6** was achieved by reacting (pentafluorophenyl)lithium (Scheme 2). The trimetallic perfluorophenyl derivative **8** was also directly isolated from ligand exchange between **5** and [C_6F_5Au(tht)] (1:2 ratio). Other substitution reactions of the chlorine atoms in **6** are currently being pursued for comparison with those described very recently for [dppf$(AuCl)_2$].[34]

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Table 3. ^{1}H, ^{31}P, and ^{13}C{^{1}H} NMR Data (ppm) for the Complexes (*J* Values in Hz)[a]

	^{1}H NMR			^{13}C{^{1}H} NMR		
compds	methyl	phenyl	^{31}P NMR	methyl	cyclopentadienyl	phenyl
4	1.26 (s, 6H) 1.68 (s, 6H) 1.74 (s, 6H) 2.05 (s, 6H)	7.44–7.64 (m, 3H, *m*-H, *p*-H) 7.92–8.06 (m, 2H, *o*-H)	+42.0	9.8 (s) 9.9 (s) 10.2 (s) 11.6 (s)	19.4 (d, C–P), $^1J_{C-P} = 87.8$ 85.9 (d), $J = 13.9$ 90.9 (d), $J = 10.2$ 91.7 (d), $J = 10.2$ 92.6 (d), $J = 9.2$	127.8 (d), $J = 12.9$ 130.3 (d), $J = 12.9$ 131.9 (s, *p*-C) 137.4 (d, C–P), $^1J_{C-P} = 97.1$
6	1.64 (s, 12 H, β-Me) 2.00 (s, 12H, α-Me)	7.22–7.38 (m, 12H, *m*-H, *p*-H) 7.40–7.49 (m, 8H, *o*-H)	+22.1	10.7 (s) 13.3 (s)	68.4 (d, C–P), $^1J_{C-P} = 68.1$ 85.0 (d, α-C), $^2J_{C-P} = 9.8$ 86.5 (d, β-C), $^3J_{C-P} = 7.2$	128.3 (s, *p*-C) 129.1 (d, *m*-C), $^3J_{C-P} = 11.8$ 131.0 (d, C–P), $^1J_{C-P} = 68.5$ 134.6 (d, *o*-C), $^2J_{C-P} = 14.2$
7	1.37 (s, 12 H, β-Me) 1.65 (s, 12 H, α-Me)	7.27–7.38 (m, 12H, *m*-H, *p*-H) 7.66–7.80 (m, 8H, *o*-H)	+25.5	8.9 (s) 12.3 (s)	77.5 (t, C–P), $^1J_{C-P} = 24.6$ 83.1 (t, β-C), $^3J_{C-P} = 2.8$ 84.1 (t, α-C), $^2J_{C-P} = 4.4$	128.7 (t, *m*-C), $^3J_{C-P} = 5.2$ 130.4 (s, *p*-C) 133.6 (t, C–P), $^1J_{C-P} = 20.9$ 135.1 (t, *o*-C), $^2J_{C-P} = 9.5$
8	1.67 (s, 12 H, β-Me) 2.01 (s, 12 H, α-Me)	7.25–7.44 (m, 20H)	+30.6	10.9 (s) 13.2 (s)	69.4 (d, C–P), $^1J_{C-P} = 59.4$ 85.0 (d, α-C), $^2J_{C-P} = 9.0$ 86.3 (d, β-C), $^3J_{C-P} = 6.3$	129.0 (d, *m*-C), $^3J_{C-P} = 11.3$ 131.0 (d, C–P), $^1J_{C-P} = 54.7$ 131.2 (s, *p*-C) 134.8 (d, *o*-C), $^2J_{C-P} = 14.1$
9 (non-isolated)	1.44 (s, 12 H, β-Me) 1.84 (s, 12 H, α-Me)	7.22–7.44 (m, 20H)	+8.0			

[a] s = singlet; d = doublet; t = triplet; m = multiplet.

Curiously, when **5** was reacted with [C_6F_5Au(tht)] in 1:1 proportion, an equilibrium mixture of **9** (≈64%) with smaller but equivalent amounts of **5** and **8** (≈18% each) was detected by ^{1}H, ^{31}P, and ^{19}F NMR. ^{197}Au Mössbauer spectroscopy showed that the isolated solid also contained **9** and **8** in approximately 3:1 ratio. In contrast to the reported behavior of dppf,[10] reaction of **5** and [ClAu(tht)] in 2:1 ratio afforded only a mixture of the starting reagent **5** and compound **7**.

All our attempts in preparing gold complexes from the metallophosphine **4** have so far systematically failed. Instead of the expected bimetallic species, decomposition of the starting molecules takes place with the concomitant formation of bright yellow microscopic flakes of gold metal. At the same time, the supernatant solvent showed a light blue reflection as the result, we believe, of the oxidation of the ferrocene moiety into the ferrocenium ion. An oxidation–reduction reaction Fe(II)/Au(I) → Fe(III)/Au(0) could proceed between the starting reagents because the value of the electrochemical potential of gold is the greatest of any metal.

NMR Spectroscopy. The ^{1}H NMR spectrum of **4** (Table 3) strongly supports a static ferrocenophane structure, and four methyl signals are detected for each equivalent cyclopentadienyl ligand. The phenyl group attached to the distorted tetrahedral phosphorus atom makes the four substituents on each Cp ring magnetically nonequivalent. The phenyl part classically appears as two multiplets, the *ortho*-protons being the more deshielded. The ^{31}P resonance of **4** is shifted considerably to low field of that of **5** (δ +42.0 and −18.2 ppm, respectively). A similar, but less dramatic, shift occurs in the nonmethylated system (δ +11.5 and −11.2 ppm).[30]

The proton-decoupled ^{13}C NMR of **4** also reflects the diastereotopy of the methyl substituents (four singlets) and that for the cyclopentadienyl carbon atoms (five doublets by coupling with the phosphorus atom) (Table 3). The C *ipso* is shifted to particularly high field (δ 19.4) and has an increased coupling constant ($^1J_{C-P} = 87.6$ Hz).

In contrast to **4**, the proton NMR spectrum of **6** exhibits only two sets of methyl groups, the more deshielded being probably in the α position to the phosphorus as usually found. The coordination of two gold atoms is reflected by the unique ^{31}P NMR signal typically strongly deshielded by complexation at +22.1 ppm compared to that of the free phosphine ligand (δ −18.2). The NMR spectra of complex **7** are consistent with the proposed conformationally static [3]metalloferrocenophane structure, in which the P–Au–P bridge defines a plane of symmetry. The not exceptional presence, for ferrocenophanes,[34] of solvate molecules is readily detectable by NMR (and also microanalysis).

The ^{13}C{^{1}H} NMR signals for compounds **6**–**8** (Table 3) are easily assignable to the different carbon atoms by a careful examination of the coupling constants with phosphorus. All the carbon atoms, those of the methyl substituents excepted, exhibit split signals. For the "open" complexes **6** and **8** the cyclopentadienyl resonance displays a set of three doublets due to normal C–P coupling. The correct assignment of the different signals to C-*ipso*, α-C, and β-C follows the assumption that a longer P–C distance causes the coupling constant to be dramatically decreased. For example, compound **6** displays the three assignable doublets C-*ipso* (δ 68.4; ^1J = 68.1 Hz), α-C (δ 85.0; ^2J = 9.8 Hz), β-C (δ 86.5; ^3J = 7.2 Hz) for the cyclopentadienyl part. On the contrary and curiously, all the aromatic carbon atoms in the ferrocenophane **7** resonate as pseudotriplets (apart from the phenyl *para*-carbon, the most distant from the phosphorus).

By contrast to [dppf(AuC_6F_5)$_2$],[20a] **8** shows no P–F coupling, and the complicated pattern of the C_6F_5 carbons caused by fluorine couplings is only barely detectable. Compounds **8** and **9** display ^{19}F NMR consisting of two poorly resolved multiplets and one triplet (δ −158.4 ppm and $^3J_{F-F}$ = 20.1 Hz for **8**; δ −159.8 ppm and $^3J_{F-F}$ = 20.3 Hz for **9**) assignable to the *para* fluorine atom.

Electrochemistry. Each of the derivatives **4**–**7** undergoes a one-electron oxidation resulting in the corresponding Fe(III) complexes (Figure 1). Both reduction and oxidation processes for **5**–**7** were detectable in tetrahydrofuran (THF) owing to the relatively large potential window of this solvent, but only the oxidation was displayed in CH_2Cl_2. Bulk electrolytic oxidations were performed in CH_2Cl_2, because the Fe(III) electrode products are generally more stable in this solvent.

Table 4 summarizes the most important cyclic voltammetry data for complexes **4**–**7**.

In the case of the electro-oxidation of **4** and **5**, and for sweep rates (v) lying in the range 0.01–0.20 V s^{-1}, the ratio ip/$v^{1/2}$ is constant and in agreement with diffusion control. The values ΔE_p are in the range expected for fast one-electron couples in resistive solvents and are always close to those observed for the [Cp_2Fe]$^{0/+}$ reference in the same solvent. Coulometric

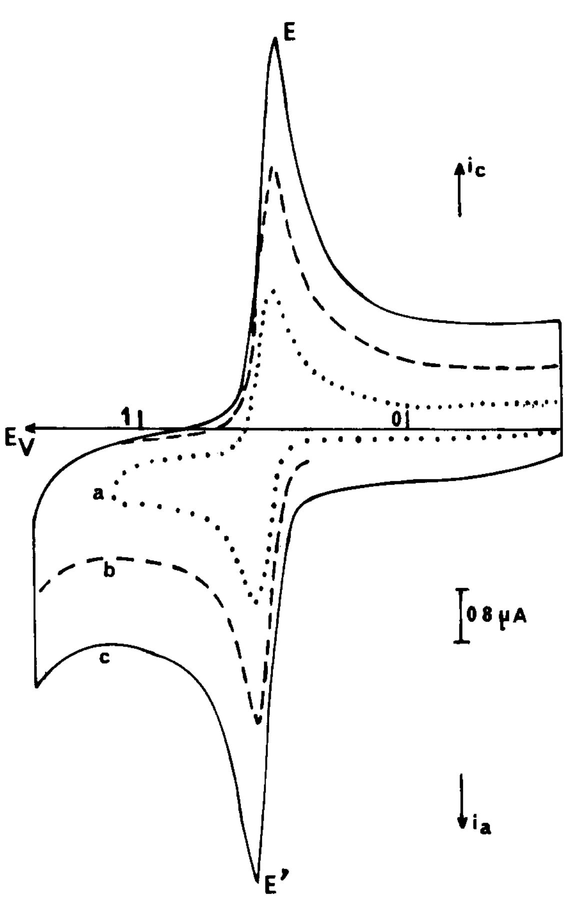

Figure 1. Cyclic voltammograms of **6** in CH_2Cl_2/Bu_4NPF_6 solution on a vitreous carbon electrode. Starting potential: −0.6 V. Sweep rate (mV s^{-1}): (a) 20; (b) 50; (c) 100.

Table 4. Cyclic Voltammetry Data for the Oxidation of Complexes in CH_2Cl_2 (or in THF in parentheses)/0.2 M Bu_4NPF_6 (Potentials versus SCE Electrode, Scan Rate 50 mV s^{-1})[a]

complex	E_{p_a}/V	E_{p_c}/V	$E_{1/2}$/V	ip_a/ip_c	ΔE_p/mV
4	0.41 (0.53)	0.33 (0.46)	0.37 (0.50)	1.14 (1.04)	80 (70)
5	0.08 (0.32)	0.02 (0.25)	0.05 (0.29)	0.99 (1.00)	60 (70)
6	0.57 (0.68)	0.51 (0.60)	0.54 (0.64)	1.02 (1.12)	60 (80)
7	0.36 (0.45)	0.29 (0.39)	0.33 (0.42)	1.08 (1.08)	70 (60)

[a] For derivatives **4** and **7** in CH_2Cl_2, a second oxidation step appears at 1.3 and 1.1 V, respectively. In THF, derivatives **4**−**7** exhibit irreversible reduction peaks at −2.60, − 2.66, − 2.25, and 2.13 V, respectively.

Table 5. Preparative Oxidation of Iron Complexes Studied in CH_2Cl_2/0.2 M Bu_4NPF_6

complex	*E* applied (V)[a]	*Q* (F/mol)	color
4	0.7	1.0	green
5	0.5	0.96	green
6	0.8	1.16	yellow
7	0.5	0.92	yellow

[a] Electrolyses were carried out under an argon atmosphere at room temperature on a carbon gauze electrode.

experiments (Table 5) also have established the redox processes to be one-electron reactions.

As previously reported,[10] the presence of a diphenylphosphino group on the cyclopentadienyl rings in the ferrocene derivatives makes the oxidation of Fe(II) to Fe(III) much more difficult. In addition, the oxidation wave for the metallophosphine **4** appears at higher anodic potential than that of **5**. The influence of the peralkylated Cp ligand is also expressed by a drastic shift to less positive oxidation potential compared to the unsubstituted analog (1,1′-bis (diphenylphosphino)ferrocene is oxidized at 0.68 V).[20] It should be noted that the electrochemical oxidation process for this latter derivative is complicated by the oxidation of the phosphorus atoms on the cyclopentadienyl rings.[6,35] On the contrary, when the electrolysis of **5** is performed at a carbon gauze electrode at 0.5 V, a green solution of the cationic derivative **5′** (Table 5) is obtained after consumption of about one electron. This solution displays an EPR signal at 100 K in dichloromethane ($H_{\parallel}$ = 1632.1 Hz, $g_{\parallel}$ = 4.2, $H_{\perp}$ = 3413.5 Hz, $g_{\perp}$ = 2.0). The rde (rotating disk electrode) voltammogram of the electrolyzed solution exhibits a reduction wave approximately located at the same potential. Reduction of this resulting solution regenerates the rde voltammogram of the initial product. The species **5′** is reasonably stable in CH_2Cl_2 solution even in the presence of water or air. Similar results are obtained from compound **4**.

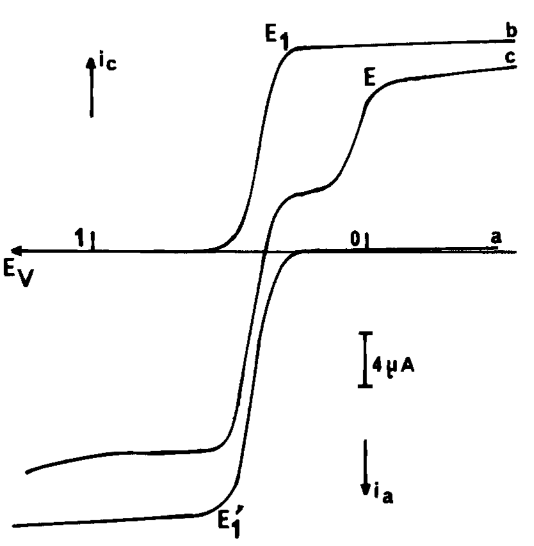

Figure 2. Rde voltammogram of Cp_2Fe in CH_2Cl_2/Bu_4NPF_6 solution: (a) before electrolysis; (b) after one-electron oxidation at +0.5 V; (c) after addition of 0.7 equiv of **5**.

We have also investigated the redox behavior of the gold complexes **6** and **7**. All show a reversible oxidation at higher potential value than that of the parent diphosphine **5**. This effect of complexing has been already reported.[20a] Figure 2 shows the cyclic voltammogram (CV) of a CH_2Cl_2 solution of complex **6** at a vitreous carbon electrode. Analysis of the CV response with the scan rate indicates that the peak system E′/E corresponds to an electrochemically reversible process (at 50 mV s^{-1} the value of ΔE_p is 60 mV and the ip_a/ip_c ratio of the system remains unitary). Exhaustive electrolysis carried out at carbon gauze electrode at +0.8 V consumes 1 faraday/mol of complex **6**, and the cation **6′** was quantitatively formed.

The above results lead to the conclusion that the one-electron oxidation of complexes **4**−**7** afford to the corresponding Fe(III) cationic derivatives **4′**−**7′**, which are remarkably stable compared to their unsubstituted congeners.

In the course of our investigations in the chemical synthesis of the cationic compounds we were interested in the reaction of $[Cp_2Fe]^+$ with the neutral starting complexes. The rde voltammogram (in CH_2Cl_2 solution) on a vitreous carbon electrode of ferrocene, Cp_2Fe, itself displays the oxidation wave E'_1 (Figure 2a). When electrolysis is performed at the potential of the wave E'_1, the current drops to zero after the consumption of one electron and the solution turns blue due to the formation of $[Cp_2Fe]^+$ reducible at the potential of wave E_1 ($E_{1/2}$ = +0.39 V) (Figure 2b). By addition of less than 1 (0.7) equiv of derivative **5**, the oxidation E'_1 and reduction E waves immediately appear (Figure 2c), the color of the solution turning

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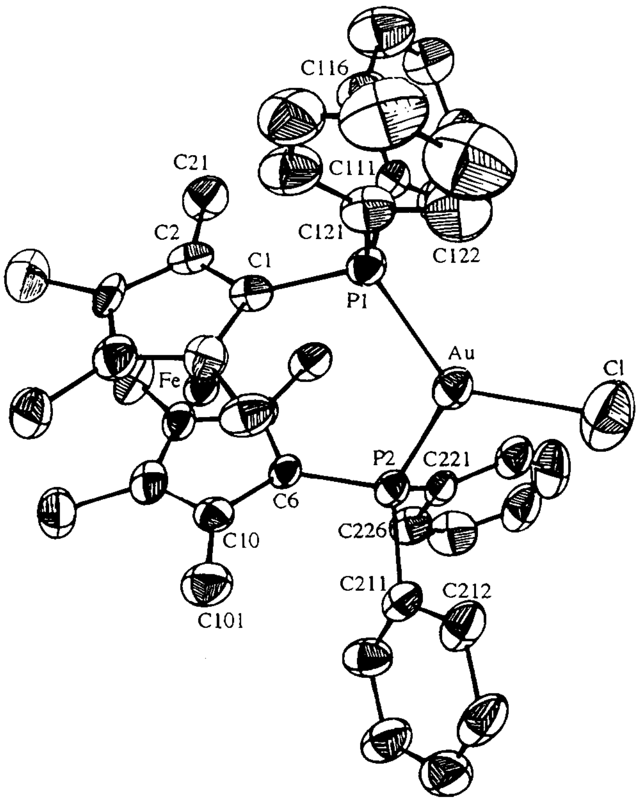

Figure 3. ORTEP drawing of [dppomf(AuCl)] (**7**).

Table 6. Selected Interatomic Distances (Å) and Angles (deg) for (dppomf)AuCl·$^1/_2$toluene (**7**)

Au··Fe	4.103(2)	P1–C1	1.82(2)
Au–Cl	2.436(5)	P1–C111	1.82(2)
Au–P1	2.316(3)	P1–C121	1.83(2)
Au–P2	2.348(4)	P2–C6	1.82(2)
Fe–Cp1*	1.663	P2–C211	1.83(2)
Fe–Cp2*	1.667	P2–C221	1.83(1)
Cl–Au–P1	126.7(2)	Au–P1–C121	117.1(6)
Cl–Au–P2	117.2(2)	Au–P2–C6	114.0(4)
P1–Au–P2	116.1(1)	Au–P2–C211	119.0(6)
Au–P1–C1	110.7(4)	Au–P2–C221	111.7(5)
Au–P1–C111	114.1(4)		

[a] Cp1* and Cp2* are the best least-squares planes of the C1–C5 and C6–C10 atoms, respectively.

from blue to green-yellow. E corresponds to the reduction of the cationic species **5′**.

These results are in agreement with the following reaction:

$$Cp_2Fe^+ + \mathbf{5} \rightarrow Cp_2Fe + \mathbf{5'}$$

We have also obtained quantitatively the cationic species **4′**, **6′**, and **7′** in solution after addition of **4**, **6**, and **7**, respectively, to the electrogenerated cation $[Cp_2Fe]^+$. Nevertheless this reaction is much slower in the case of **6**. These experiments represent a suitable and clean access to Fe(III) complexes. As we have not so far been successful in properly synthesizing the Fe(III) species by using classical oxidizing reagents, we are currently trying their preparation through the chemically obtained oxidizing reagent $[Cp_2Fe]PF_6$.

Molecular Structure of (dppomf)AuCl·$^1/_2C_7H_8$. The molecular structure of **7** is shown in Figure 3, and the selected bond lengths and angles are given in Table 6. The coordination about the gold is trigonal planar. The gold atom is displaced by only 0.003 Å from the best plane of the P_2AuCl unit, and the sum of the three angles in this unit is equal to 360.0°. The Au–P distances of 2.316(3) and 2.348(4) Å are longer than the Au–P distances reported for two-coordinate linear gold(I) complexes (2.21–2.27 Å),[36,37] but fall in the range observed for trigonal compounds (2.31–2.41 Å).[20b,38–40] In particular, they are essentially the same as in $[ClAu(PPh_3)_2]$ (2.323(4) and 2.339(4) Å).[40] As expected, the Au–Cl bond length of 2.436(5) Å in **7** is greater than in linear P–Au–Cl complexes (2.27–2.30 Å)[36,41,42] but considerably shorter than in $[ClAu(PPh_3)_2]$ (2.500(4) Å)[40] or in the chain polymer Au–P structure of [dppfAuCl] (2.624(9) and 2.550(3) Å).[20b] The comparison of the P–Au–P angle and Au–Cl distance observed in **7** with the corresponding values reported for $[ClAu(PPh_3)_2]$ indicates the influence of steric effects on geometrical parameters. The P–Au–P angle in $[ClAu(PPh_3)_2]$ is largely opened (132.1(1)°) because of repulsions between the phosphino ligands; the change in hybridization results in greater p-character for the Au–Cl bond, which is lengthened. The bite angle in **7** is smaller (116.1(1)°) leading to a decrease in the steric repulsions between phenyl groups and the chlorine atom and to a shorter Au–Cl bond.

The cyclopentadienyl rings are planar and parallel. Three methyl substituents on each ring deviate slightly (0.02–0.10 Å) from the C_5 plane away from the iron atom, while the fourth one (C21 or C101) exhibits a comparable magnitude of deviation but toward Fe. Similar displacements have been observed in the structure of parent complex **5**.[23] The P1 and P2 atoms are slightly out the C1–C5 (0.178(4) Å) and C6–C10 (0.095(4) Å) planes to the other side with respect to Fe. A smaller deviation (0.018 Å) in the same direction was found in the parent centrosymmetric complex. In the structure of $[dppf(AuPPh_3)]^+$, displacements of the phosphorus atoms (0.162 and 0.099 Å) toward Fe have been observed.[20a] The cyclopentadienyl rings in **7** are staggered by 17° (FeC1P1/FeC6P2 dihedral angle). The distances of the iron atom from the planes of C_5 rings (1.663(2) and 1.667(2) Å) are nearly the same as in other substituted or unsubstituted ferrocenes[20a,43a–d] indicating that steric effects of substituents have little influence on Fe–Cp π-bonding. The distance (4.1 Å) between gold and iron precludes any direct electronic interaction.

^{197}Au Mössbauer Spectroscopy. In spite of the short half-life of the ^{197}Pt source needed for ^{197}Au Mössbauer spectroscopy, this technique is an excellent means of obtaining information about the bonding and structures of gold complexes, and has been extensively reviewed.[44,45a] Data for **6**–**9** are given in Table 7 and agree well with the proposed structures. The parameters for **6** are in good agreement with those for $[dppf(AuCl)_2]$[11] and $[Ph_3PAuCl]$.[45a,b] The IS and QS for **8** are similar

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Table 7. Mössbauer Data

compds	QS (mm·s^{-1})	IS[a] (mm·s^{-1})	half-width (mm·s^{-1})	ref
6	7.54	4.25	1.96	
7	8.89	3.18	2.06	
8	9.65	5.25	1.89	
9[b]	9.96	3.03	1.99	
[dppf(AuCl)$_2$]	7.52	3.81		11
[dppf(Aucl)]$_2$	7.99	2.62		10
[(PPh$_3$)AuCl]	7.45	4.07		45b
	7.43	4.08		45a
[(PPh$_3$)$_2$AuCl]	8.19	2.36		53
	8.22	2.35		45a
[Ph$_3$PAuC≡CPh]	10.21	5.36		44

[a] Relative to gold metal. [b] From the mixture shown in Figure 1.

Table 8. Cytotoxicity Data (IC$_{50}$, μg mL^{-1})

	cell line						
compd	SW620	SW1116	ZR75−1	HT1376	SKOV-3	PA-1	LS174T
5	In.[a]	In.	In.	In.	In.	>200	In.
6	15.9	15.8	24.4	9.3	13.5	9.4	14.5
7	61.5	48.9	155.7	57.6	66.4	129.0	124.6
8	In.	101	In.	In.	In.	In.	In.
dppe[48]	7	8	<1	11	13		
cis-Pt[48]	19.2	28.2	8.8	5.5	6.3	1.6	1.9

[a] In. = inactive.

to values for other compounds containing linear two-coordinate P−Au−C systems[44] but are greater than those for linear P−Au−Cl complexes, as expected from the greater covalency of the Au−C bond. The parameters for the two three-coordinate compounds, **7** and **9**, are significantly lower than for their two-coordinate analogues (**6**, **8**); this is the normal trend.

The spectrum of **9** also contains a doublet due to **8**, showing that the mixture detected by NMR is present also in the solid state; from the relative intensities, **9** and **8** are in about a 3:1 ratio (it is not possible to be precise, because the recoil-free fractions will differ).

***In Vitro* Cytotoxicity.** In the light of the reported cytotoxic activity of gold phosphines,[17] ferrocenium salts,[46] and mono- and binuclear metallocene-type complexes,[13,18,47] compounds **6**−**8** were examined as potential drugs. They were tested *in vitro* at the Johnson Matthey Technology Centre (Reading, U.K.) for antitumor activity against the seven cell lines reported in Table 8. For comparison, the results for free dppe,[48] cis-platin,[48] and the ligand **5**[48] are also reported. The IC$_{50}$ values (concentration of test compound required to preserve 50% of the cells) were determined. The data reveal the metallophosphine **5** and the trimetallic perfluorophenyl derivative **8** not to be toxic for the tumor cells tested, whereas the aliphatic biphosphine dppe exhibits high toxicity. After complexation to gold, **5** affords the bisgold complex **6** which is substantially more cytotoxic than the monogold congener **7**. In addition, **6** exhibits a slight selectivity for the cell lines HT 1376 (bladder carcinoma line) and PA-1 (ovarian carcinoma line).

Increase in cytotoxic potency of the Au complex over the free ligand has been observed previously. The reason for this better efficiency is not known, but it has been suggested that Au(I) could protect the phosphine ligand from oxidation.[19,49] The very poor solubility of **8** in the medium could explain its inactivity. The cytotoxicity of the ferrocene−gold complexes appears to be connected to the $E^{1/2}$ oxidation potential for iron: the more anodic the potential, the better the antitumor activity. This could mean that any factor able to delay the oxidation process would be profitable to the cytostatic efficiency of a phosphinoferrocene−gold drug. This conclusion needs to be proved by the synthesis and oxidation study of a larger range of ferrocene derivatives, and we are currently working in this area.

Discussion

At first glance, the results reported above clearly indicate a difference of behavior between dppomf and the unsubstituted congener dppf in complexation to gold. The bimetallic **7** is unique in being monomeric and having a three-coordinate gold atom in a ferrocenophane bridge. It is obtained at both 1:1 and 2:1 ratios of the phosphine and gold reagent. This differs strongly from what it is observed with (diphenylphosphino)-ferrocene.[10] In this case, the 1:1 ratio leads to a "dimer" tetranuclear species incorporating two dppf and two Au−Cl moieties and the 2:1 ratio affords a P$_3$Au coordination: one dppf is bound in a strained bidentate manner and a second acts as monodentate ligand (this structure is supported by the observation of two types of phosphorus atoms in ^{31}P NMR). The formation of **7** probably results from our experimental procedure consisting of a slow addition at low temperature of the phosphine to the gold salt in a noncomplexing (CH$_2$Cl$_2$) solvent. The three-coordinate **7** can be readily transformed into the two-coordinate **6** by treatment with [ClAu(tht)] (Scheme 2), and this transformation is presumably made easy by the weakening of the Au−P bonds resulting from the relatively long distance between the two atoms displayed by X-ray diffraction. But also what could be invoked is the gold−gold interaction undoubtedly prevalent in **6** which contributes to the stabilization of the product. The mixture obtained (Scheme 2) when the parent metallophosphine **5** is reacted with [C$_6$F$_5$Au(tht)] (1:1 ratio) suggests a disproportionation equilibrium: 2 **9** $\rightleftharpoons$ **8** + **5** with a constant calculated from the concentration of the reagents detected by NMR, $K = \{[\mathbf{5}][\mathbf{8}]/[\mathbf{9}]^2\} \approx 0.8$. This value remains unchanged by addition of **5** to the solution. In the solid state the mixture is also characterized by the ^{197}Au Mössbauer spectrum which displays two doublets corresponding to compounds **8** and **9** (Figure 4).

Complex **9** appears to be the first established three-coordinate (phosphorus−carbon−phosphorus) gold(I) complex yet reported. Its instability to disproportionation, relative to **7**, is presumably due to the softer nature of the C$_6$F$_5$ ligand, displayed also by the Mössbauer parameters for **9**.

The ferrocenophane **4** (Scheme 1) exhibits a nonfluxional structure which is characterized by four methyl signals in ^{1}H NMR. The two cyclopentadienyl ligands are magnetically equivalent as the result of a mirror plane in the molecule through Fe and P. The high positive value observed at the ^{31}P chemical shift ($\delta = +42.0$) could be interpreted in terms of a direct Fe−P electronic interaction weakening the electronic density at the phosphorus atom but also in terms of a modification in the orbital geometry of the probably highly distorted phosphorus atom. Distortions in the molecule are also reflected by the ^{13}C{H} NMR spectrum. The C-*ipso* signal appears at high field (δ 19.4) with a large coupling constant $^1J_{\mathrm{C-P}} = 87.6$ Hz. The difference from values found for the "open" biphosphine **5** (δ 72.8; $^1J_{\mathrm{C-P}} = 12.3$ Hz)[33] is probably the consequence of the strained bridge and could be indicative of a change from sp^2 hybridization of the C-*ipso* to one approaching sp^3.[29,30] X-ray analysis could give the answer, but we have been unsuccessful so far in preparing suitable crystals.

The proton NMR spectrum pattern of the trimetallic **6** (Scheme 2) largely differs from that of **4**. Only two sets of

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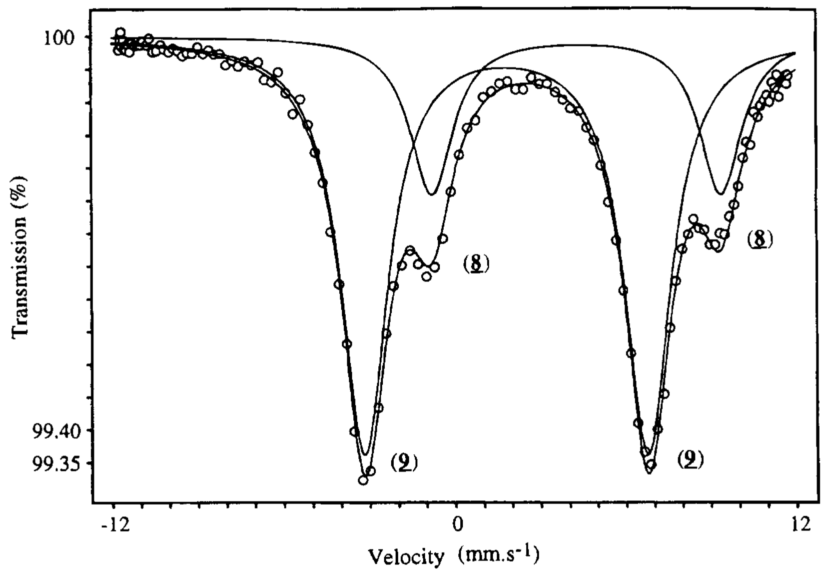

Figure 4. ^{197}Au Mössbauer spectrum of the compounds from the equilibrium 2 **9** $\rightleftharpoons$ **8** + **5**.

methyl groups are displayed, and this is in agreement with a modification in the symmetry. In fact two symmetry species could produce two signals for methyls: a C_{2h} symmetry giving rise to the iron atom as a centre of symmetry and a C_{2v} symmetry as displayed in the Scheme 2. The latter could prevail if the two gold atoms are held together as dinuclear Au_2, but only, this time also, a structural investigation could allow a final answer.

A C_{2v}-type symmetry is observed for the trinuclear **7**, and the ^{1}H NMR only exhibits two methyl signals. In fact, the X-ray crystal measurements show a slightly distorted structure (see molecular structure), the two cyclopentadienyl ligands being staggered by 17° and the two phosphorus, gold, and chlorine atoms remaining coplanar.

Additionally, the consequent differentiation in the ^{13}C{^{1}H} NMR when comparing spectra of **6**–**8** (Table 3) can also be discussed. While most of the carbon atoms of **6** and **8** display doublets due to a normal C–P coupling, those for the ferrocenophane structure **7** resonate as a pseudotriplet. Such unexpected changed in the NMR features are not unprecedented in metal-complexed ferrocene biphosphines[50] and are discussed in detail for a range of transition metals in the literature.[33] The suggested explanation for the uncommon splitting observed is a long-range coupling of the carbon atoms with both phosphorus nuclei.[50] We have never observed any modification in the NMR pattern of **7** when samples were allowed to stand for several hours in solution at room temperature. This observation confirms the suggestion that **7** maintains the three-coordinate structure; the structure with one two-coordinate gold and a free phosphine group would probably be fluxional, showing apparent equivalence of the two rings, but could show coupling to one phosphorus only.

It is well documented that, for P_nAu systems, a change from two- to three-coordination results in a marked shift in the ^{31}P resonance to higher frequency (lower δ).[45b,51] For the PAuX and P_2AuX systems, the situation is less clear. The carborane–diphosphine $B_{10}H_{10}C(PPh_2)_2$ is the most similar to the present one and shows a strong decrease in chemical shift with increasing coordination number (50.2 to 36.2 ppm, X = Cl; 56.4 to 31.8 ppm, X = C_6F_5).[38] A very small decrease (*ca.* 1 ppm) is recorded for the depe–AuCl complexes (depe = $Ph_2P(CH_2)_2PPh_2$).[52] We find different behavior for X = Cl or C_6F_5. There is a large decrease in chemical shift from **8** to **9** (X = C_6F_5; 30.6 to 8.0 ppm), fully consistent with an increase in coordination number. On the other hand, the chemical shift of **7** (X = Cl) is slightly greater than that of **6** (25.5 and 22.1 ppm, respectively). This may indicate that **7** dissociates ionically in solution to give [dppomf(Au)]Cl.

Concerning the ^{197}Au Mössbauer data, the greater values of IS and QS measured in **8** with P–Au–C bonds compared to P–Au–Cl systems (Table 5) is due to the increase in electron donation from the carbon ligand toward the Au atom compared to that for the chlorine one. Also three-coordinate gold(I) complexes usually show considerably lower IS and greater QS values than the corresponding two-coordinate complex as a result of the change in hybridization of the gold atom.[45a] This is well shown by [dppfAuCl]$_2$,[10] [(Ph$_3$P)$_2$AuCl],[53] **7**, and **9**. That **7** has an IS even lower than [(Ph$_3$P)$_2$AuCl] is probably related to the smaller P–Au–P angle in the former (116° vs 132°), which decreases the s-character of the P–Au bonds. These bonds, being the most covalent in the system, have the greatest influence on the s-character and the IS. The slightly greater QS value for **7** is consistent with the greater covalency indicated by the short Au–Cl bond.

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Supplementary Material Available: Tables of crystallographic data, anisotropic temperature factors, bond distances, bond angles, and least-squares planes and a drawing of the disordered molecule of toluene in the structure (7 pages). Ordering information is given on any current masthead page.

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